

CAVITY-MODIFIED FLUORESCENCE IN THE WEAK AND STRONG COUPLING REGIMES

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By
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We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

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Dedication

*To my mother, Zahida Perveen, with boundless love
and gratitude.*

ABSTRACT

CAVITY-MODIFIED FLUORESCENCE IN THE WEAK AND STRONG COUPLING REGIMES

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The modulation of fluorescence in optical microcavities provides a powerful route for engineering light-matter interactions, with applications in sensing, lasing, and photonic devices. Fabry-Pérot (FP) cavities, composed of planar metallic mirrors enclosing an active medium, enable controlled tuning of emission dynamics across weak and strong coupling regimes. In the weak coupling regimes, cavities reshape radiative decay rates via the Purcell effect. In contrast, in the strong coupling regime, coherent exciton-photon interactions produce vacuum Rabi splitting and exciton-polariton formation. While strong coupling has been extensively demonstrated using narrow-linewidth dyes such as rhodamines, the behavior of broadband emitters like fluorescein under cavity confinement remains poorly understood.

This thesis presents a systematic experimental investigation of fluorescein-doped poly(methyl methacrylate) (PMMA) thin films embedded in FP microcavities. Two concentrations of fluorescein were used, low (20 $\mu\text{g/mL}$) and high (60 mg/mL), across multiple film thicknesses defined by spin coating speeds (1000 - 5000 rpm). The low-concentration series comprised films with the thickness of 486, 349, 291, 253, and 240 nm, while the high-concentration series comprised cavities with the film thickness of 669, 476, 380, 334, and 307 nm. Optical properties were characterized by spectroscopic ellipsometry, UV-Vis spectroscopy, steady-state fluorescence, and angle-resolved reflectance. Transfer matrix method (TMM) simulations, incorporating measured refractive indices and extinction coefficients, validated experimental results.

At low dye concentrations, cavity confinement primarily induced significant spectral reshaping without mode splitting, consistent with the weak coupling regime. In contrast, high-concentration samples exhibited clear signatures of

strong exciton-photon coupling. Angle-resolved ellipsometry revealed secondary loops in the complex-plane ρ trajectories, while reflectance dispersion maps displayed anticrossing behavior when cavity modes overlapped with the fluorescein excitonic transition near 467 nm. Angle-resolved dispersion was fitted with a three-coupled-oscillator model, yielding vacuum Rabi splittings ranging from 34.8 nm to 48.5 nm, and the dispersion shows back-bending of the cavity mode near 467 nm, consistent with exciton-photon coupling.

These results demonstrate that, despite its broad linewidth, fluorescein can achieve strong coupling under optimized conditions of high concentration and tuned cavity thickness. The work provides a quantitative framework for extending cavity–emitter studies to broadband dyes and offers design principles for future cavity-enhanced light sources, lasers, and fluorescence-based sensors.

Keywords: Cavity-modified fluorescence, weak and strong coupling regimes, Fabry–Pérot microcavities, fluorescein-doped PMMA films, spectroscopic ellipsometry, transfer matrix method, vacuum Rabi splitting, exciton–polariton.

ÖZET

ZAYIF VE GÜÇLÜ KUPLAJ REJİMLERİNDE KAVİTE-MODİFİYE FLORESANS

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Optik mikrokavitelerde floresansın modülasyonu, algılama, lazer ve fotonik aygıtlar için ışık-madde etkileşimlerinin mühendisliğinde güçlü bir yol sunar. Düzlemsel metalik aynaların bir aktif ortamı çevrelemesiyle oluşan Fabry-Pérot (FP) kaviteleri, ışıma dinamiklerinin zayıf ve güçlü kuplaj rejimleri arasında dene-timli olarak ayarlanmasına imkân verir. Zayıf kuplaj rejiminde kaviteler Purcell etkisiyle ışıının hızlarını yeniden şekillendirirken, güçlü kuplajda koherent ek-siton-foton etkileşimleri vakum Rabi yarılması ve eksiton-polaritons oluşumuna yol açar. Rodaminler gibi dar çizgi genişlikli boyalarla güçlü kuplaj geniş ölçüde gösterilmiş olsa da, fluorescein gibi geniş bant yayıcıların kavite içinde sergilediği davranış yeterince anlaşılmış değildir.

Bu tez, FP mikrokavitelerine gömülü fluorescein katkılı poli(metil metakrilat) (PMMA) ince filmlerin sistematik bir deneysel incelenmesini sunar. Fluorescein iki derişimde kullanılmıştır: düşük (20 µg/mL) ve yüksek (60 mg/mL); film-ler 1000–5000 rpm döndürerek kaplama hızlarıyla elde edilen çoklu kalınlıklar üzerinde çalışılmıştır. Düşük derişimli seri 486, 349, 291, 253 ve 240 nm; yüksek derişimli seri ise 669, 476, 380, 334 ve 307 nm kalınlıklarından oluşur. Optik özellikler spektral elipsometri, UV-Vis spektroskopisi, durağan durum floresansı ve açısal çözünürlüklü yansıtma ile karakterize edilmiştir. Ölçülen kırılma indis-leri ve sönüm katsayıları dâhil edilerek yapılan Transfer Matris Yöntemi (TMM) benzetimleri, deneysel sonuçları doğrulamıştır.

Düşük boya derişiminde kavite kısıtlaması, mod yarılması olmaksızın belir-gin spektral yeniden şekillenme üreterek zayıf kuplaj rejimiyle tutarlı sonuçlar vermiştir. Buna karşılık, yüksek derişimli örnekler güçlü eksiton-foton ku-plajının açık imzalarını sergilemiştir. Açısal çözünürlüklü elipsometri, karmaşık

düzlemde yörüngelerinde ikincil döngüler ortaya koyarken, yansıma dağılım (dispersiyon) haritaları kavite kipleri 467 nm civarındaki fluorescein eksiton geçişiyle çakıştığında “anticrossing” davranışı göstermiştir. Açısal çözünürlüklü dispersiyon, üç osilatörlü (kavite + iki eksiton) bir modele uydurulmuş ve vakum Rabi yarılmaları 34,8 nm ile 48,5 nm aralığında bulunmuştur; ayrıca dispersiyonda 467 nm yakınında kavite-benzeri dalın “geri bükülme” (back-bending) gösterdiği gözlenmiştir.

Bu sonuçlar, geniş çizgi genişliğine rağmen fluorescein’in, yüksek derişim ve ayarlanmış kavite kalınlığı koşullarında güçlü kuplaja ulaşabildiğini göstermektedir. Çalışma, geniş bantlı boyalarla kavite-yayıcı etkileşimlerinin nicel incelenmesi için bir çerçeve sunar ve gelecekteki kaviteyle güçlendirilmiş ışık kaynakları, lazerleri ve floresansa dayalı algılama uygulamaları için tasarım ilkeleri sağlar.

Anahtar sözcükler: Kavite-modifiye floresans, zayıf ve güçlü kuplaj rejimleri, Fabry-Pérot mikrokaviteler, fluorescein katkılı PMMA ince filmleri, spektroskopik elipsometri, transfer matris yöntemi (TMM), vakum Rabi yarılması, eksiton-polaritonlar..

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Beyond results and figures, this thesis traces a quieter journey: learning to balance ambition with realism, effort with rest, and confidence with doubt. At the outset, I did not expect to come this far. Coming to Türkiye and living away from my family was, at the time, a significant step. From there, progress came through steady work, honest feedback, and the choice to continue when it would have been easier to stop. Reaching this point simply reminds me that persistence matters most.

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Abbreviations

FP Fabry–Pérot (optical cavity)

PMMA Poly(methyl methacrylate)

TMM Transfer Matrix Method

UV–Vis Ultraviolet–Visible Spectroscopy

PL Photoluminescence

SE Spectroscopic Ellipsometry

FSR Free Spectral Range

FRET Förster Resonance Energy Transfer

AR Angle-Resolved (e.g., AR reflectance)

CO Model Coupled-Oscillator Model

Q Quality factor

V Mode volume

UP / LP Upper / Lower polariton branch

Symbols and Notation

λ	Wavelength (nm)
θ	Incidence/measurement angle (degrees)
d	Film thickness (nm)
$n(\lambda), k(\lambda)$	Refractive index and extinction coefficient
$\varepsilon(\lambda)$	Dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$)
R, T, A	Reflectance, transmittance, absorbance ($A = 1 - R - T$)
I	Intensity (relative units unless noted)
Ψ, Δ	Ellipsometric amplitude and phase parameters
ρ	Complex ellipsometric ratio: $\rho = \tan(\Psi) e^{i\Delta}$
$E_c(k)$	Cavity-mode energy (angle/momentum dependent)
E_x	Exciton energy
$E_{\pm}$	Polariton eigenvalues in the coupled-oscillator model
Ω_R	Vacuum Rabi splitting
g	Light-matter coupling strength
κ	Cavity loss rate (photon decay)
γ	Exciton linewidth / dephasing rate
Q	Quality factor ($Q = \omega/\Delta\omega$)
V	Mode volume
c	Speed of light in vacuum

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Chapter 1

Introduction

The interaction between light and matter is a fundamental phenomenon that covers a broad spectrum of scientific disciplines, including photonics, laser physics, optical sensing, and quantum optics[8, 3, 9]. In recent years, engineered optical cavities have gained popularity for controlling emission properties and enhancing light-matter interactions. These optical resonators modify the local density of optical states, leading to a reshaping of the radiative decay active molecular layer[10, 11, 12].

A variety of optical cavity structures have been developed and used to study light-matter interactions, each providing unique benefits depending on the application. One of the simple but effective cavities, called the Fabry-Pérot cavity, contains two parallel mirrors[13, 14] and provides a platform for controlling the angular and spectral properties of the material under study[15]. When a molecule called an emitter, such as an organic dye molecule or J-aggregate, is placed inside the cavity, the emission and excitation of the dye molecule can be enhanced or suppressed depending on the positioning concerning the cavity modes. This interaction between the molecule and cavity mode can be of two types, depending on the strength of the interaction. In the weak coupling regime, only the emission properties are changed and can be described in terms of the Purcell effect[13].

However, in the strong coupling regime, new energy levels form, drastically changing the properties of the material[16].

Other kinds of cavities, such as whispering-gallery-mode (WGM) resonators[17], plasmonic nanocavities[18], and photonic crystal cavities[19], are also used to manipulate light at the nanoscale depending on the application. Organic dyes such as Rhodamine R6G and fluorescein offer high quantum yields with strong absorption, making them suitable candidates for optical modulation in various devices like lasers or sensors[20, 21]. However, a major drawback of fluorescein dye is its broad linewidth and fast dephasing, which present challenges for achieving the strong coupling regime. Nevertheless, through proper design of cavity parameters such as thickness and dye concentration, these limitations can be partially overcome, enabling exploration of both weak and strong coupling phenomena.

1.1 Motivation

The ability to engineer and manipulate the optical response of dye-doped thin films through cavity confinement holds significant promise for advanced light-emitting and sensing technologies. Although several studies have demonstrated strong coupling with dyes such as rhodamine 6G and cyanines, there remains limited experimental exploration of how fluorescein, in particular, behaves under cavity confinement. Moreover, few studies provide a systematic comparison of in-cavity and out-of-cavity emission and reflectance behaviors across varying dye concentrations and cavity geometries.

This research seeks to bridge that gap by investigating how the optical and fluorescence properties of fluorescein-doped PMMA thin films are modulated inside Fabry-Pérot cavities. Through a combination of angle-resolved reflectance, ellipsometry, and UV-Vis spectroscopy, we explore how cavity parameters influence excitation and emission behavior under both weak and strong coupling conditions.

1.2 Thesis Outline

This thesis is structured as follows:

Chapter 2 introduces the principles of light–matter interaction, including spontaneous emission, the Purcell effect, and cavity quantum electrodynamics. It covers the Fabry–Pérot cavity structure, distinguishes weak and strong coupling regimes, and discusses exciton–polariton formation. **Chapter 3** presents the use of the transfer matrix method to simulate the optical behavior of dye-doped PMMA cavity structures. Reflectance, transmittance, and absorbance spectra were modeled as functions of wavelength and angle for both low and high dye concentrations. **Chapter 4** describes the materials and experimental procedures used in the fabrication of dye-doped thin films and Fabry–Pérot cavities. It outlines the incorporation of fluorescein into a PMMA matrix at two concentrations, the preparation steps including substrate cleaning, solution formulation, spin-coating, silver mirror deposition, and the fabrication of reference films without mirrors for comparison. **Chapter 5** presents the thickness characterization of dye-doped PMMA films using spectroscopic ellipsometry and optical simulations. It explains how film thickness varies with spin speed for both low and high dye concentrations, and it describes how the thicknesses of cavity samples are determined by matching experimental and simulated transmission spectra using the TMM. **Chapter 6** examines the absorption and transmission properties of fluorescein-doped PMMA films using UV–Vis spectroscopy. It describes how Fabry–Pérot cavities introduce optical resonances and how these resonances vary with film thickness and dye concentration. **Chapter 7** investigates how Fabry–Pérot cavities affect the steady-state fluorescence of fluorescein-doped PMMA films across various thicknesses and dye concentrations. By comparing out-of-cavity emission and excitation spectra, the study reveals a transition from PMMA-dominated to fluorescein-dominated fluorescence with increasing excitation wavelength. Trends in Förster resonance energy transfer (FRET) and cavity-induced modifications are identified. High dye concentrations show strong fluorescein emission across all

conditions, while low concentrations reveal distinct spectral contributions from both PMMA and fluorescein depending on excitation wavelength and film thickness. **Chapter 8** applies angle-resolved spectroscopic ellipsometry to fluorescein-doped PMMA Fabry–Pérot microcavities to investigate how cavity thickness and dye concentration affect the ellipsometric parameters Ψ and Δ . Low-concentration samples serve as weak-coupling references, while certain high-concentration configurations display strong exciton–photon coupling. In the high-concentration samples, a secondary loop is observed in the complex ρ trajectory, serving as a clear signature of the strong coupling regime. **Chapter 9** applies angle-resolved reflectance spectroscopy to fluorescein-doped PMMA Fabry–Pérot microcavities. Low-concentration samples are used as weak-coupling references, while specific high-concentration and optimized thickness configurations exhibit strong exciton–photon coupling. These cases are analyzed using a three-coupled-oscillator model to determine the vacuum Rabi splitting and Hopfield coefficients, quantifying the relative photonic and excitonic contributions to the polariton states. **Chapter 10** summarises the main findings of the thesis, discusses their significance within light–matter interaction studies, and outlines future research directions.

Chapter 2

Theoretical Background

2.1 Fundamentals of Light-Matter Interaction

Light-matter interaction is one of the most fundamental phenomena governing a wide range of photonic devices. In the classical picture, light is treated as an electromagnetic wave, while matter responds as an oscillating system of dipoles. When light interacts with matter, it induces changes in the dipole moment of the material. As a result of this interaction, phenomena such as reflection, absorption, scattering, and emission occur.

In particular, light-matter interaction occurs at the subatomic level. When light interacts with a molecule, it transfers its energy to the electrons of that molecule. After absorbing this energy, the electron is excited to a higher energy level. After some time, it relaxes back to the ground state by emitting the excess energy, a process known as spontaneous emission[22].

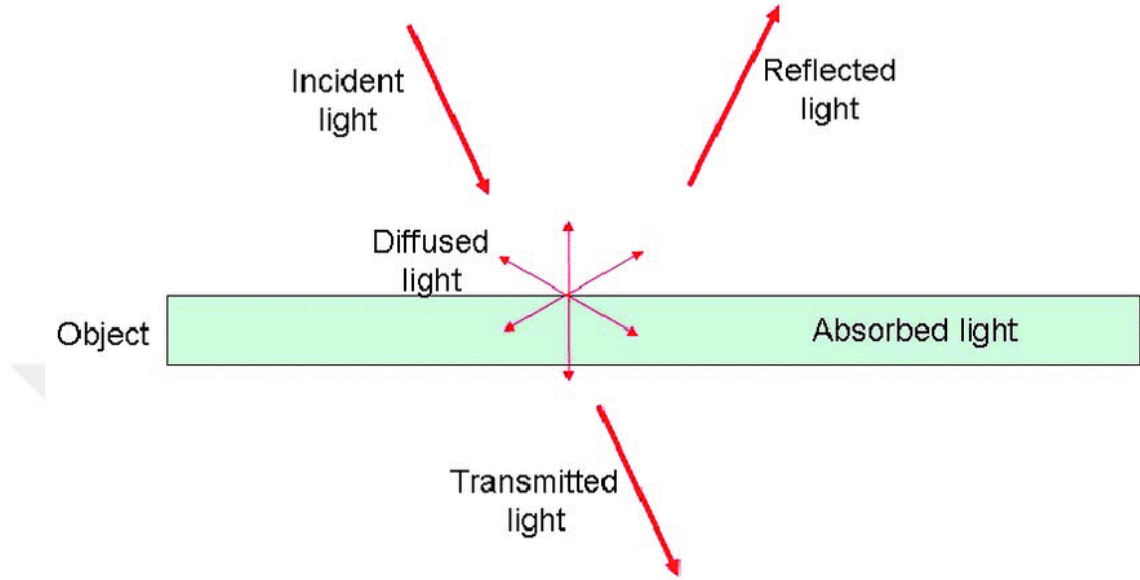


Figure 2.1: Light–matter interaction pathways at a planar sample: incident light is partitioned into reflected, transmitted, absorbed, and diffuse (scattered) components.[1]. Adapted from Maraloiu (2010), “A multiscale study of magnetic nanovectors”, Université Claude Bernard-Lyon I.

In the classical description, the power radiated by an oscillating dipole is given by the Larmor formula:

$$P = \frac{\mu_0 q^2 a^2}{6\pi c} \quad (2.1)$$

where q is the charge, a is the acceleration of the oscillating electron, and c is the speed of light.

2.2 The Purcell Effect and Emission Rate Modification

When a molecule is placed between two highly reflective mirrors, the cavity confinement can lead to either enhancement or suppression of its emission. The rate of this modification depends on the intrinsic free-space emission rate Γ_0 of the emitter as well as the properties of the surrounding medium. Inside optical cavities, the imposed boundary conditions alter the number and distribution of available optical modes. As a result, the molecule can only emit into specific modes defined by the local density of optical states (LDOS). This makes the emission of molecules fully controllable by tuning the cavity resonances.

The modified emission rate Γ is expressed as:

$$\Gamma = F_P \Gamma_0 \quad (2.2)$$

where Γ_0 is the free-space emission rate and F_P is the Purcell factor.

The Purcell factor quantifies the strength of cavity-induced modification and is given by:

$$F_P = \frac{3}{4\pi^2} \left(\frac{\lambda}{n} \right)^3 \cdot \frac{Q}{V} \quad (2.3)$$

where λ is the resonant wavelength, n is the refractive index of the medium, Q is the quality factor of the cavity, and V is the effective mode volume. A high Q ensures that photons remain confined for longer times, while a V concentrates the field intensity in a limited region of space. Together, these parameters determine the degree of enhanced light-matter interaction within the cavity. In dye-doped Fabry-Pérot cavities, these signatures are seen as angularly tunable fluorescence enhancement when the cavity modes overlap with the dye emission band[23].

2.3 Fabry-Pérot Optical Cavities

A Fabry-Pérot cavity consists of two parallel reflective mirrors separated by an active medium, forming a resonator that traps light inside in the form of optical modes. In this thesis, the cavities are constructed using a thin fluorescein-doped PMMA layer sandwiched between silver mirrors.

The resonance condition is given by:

$$2nL \cos \theta = m\lambda \quad (2.4)$$

where n is the refractive index of the medium, L is the cavity thickness, θ is the incident angle, m is an integer mode number, and λ is the wavelength.

The free spectral range (FSR) is defined as:

$$\Delta\lambda = \frac{\lambda^2}{2nL} \quad (2.5)$$

By controlling the cavity thickness and mirror reflectivity, the resonant modes can be aligned with the absorption or emission spectra of the embedded dye. This results in spectral confinement of optical modes and alters the emission properties of the molecules.

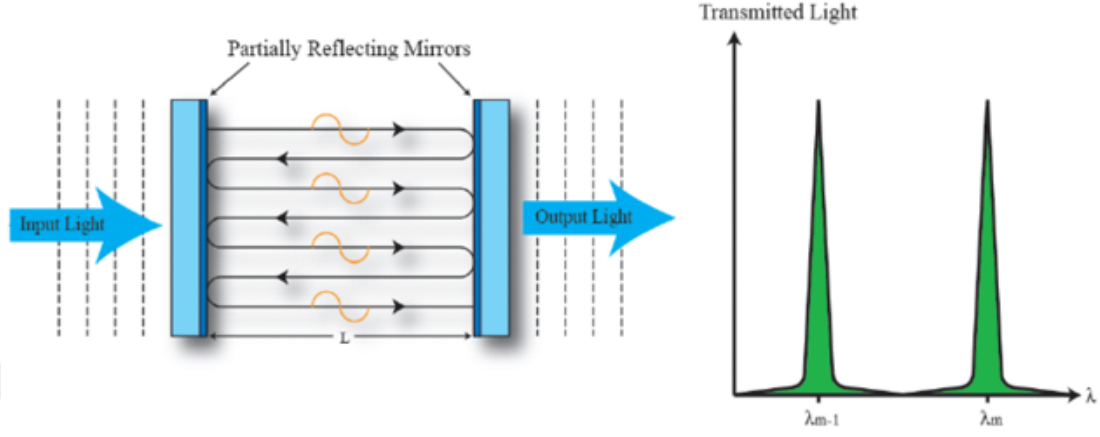


Figure 2.2: Fabry–Pérot cavity with partially reflecting mirrors (gap L). Multiple internal reflections produce narrow transmission resonances at wavelengths λ_m satisfying $2nL \cos \theta = m\lambda$. The mode spacing (FSR) is $\Delta\lambda \approx \lambda^2/(2nL)$; higher mirror reflectivity narrows the peaks (finesse $\mathcal{F} \approx \pi\sqrt{R}/(1-R)$). Resonances blue-shift with angle via the $\cos \theta$ factor[2]. Adapted from McMillen (2008), “Self-Powered Fiber Bragg Grating Sensors”, University of Pittsburgh.

One of the key features of Fabry-Pérot cavities is the angular dispersion of optical modes. This helps us to tune the cavity mode according to the excitonic peak position to get a strong light-matter interaction

$$\lambda(\theta) = \frac{2nL \cos \theta}{m} \quad (2.6)$$

This relation enables angle-resolved tuning of emission and reflectance spectra[24, 25, 26].

2.3.1 Angle-Dependent Cavity Modes (Dispersion)

Angle selects the in-plane wave-vector $k_{\parallel}$, so a fixed longitudinal mode of a Fabry–Pérot (FP) cavity disperses with angle. Parallel momentum is conserved at the interface, giving

$$k_{\parallel}(\lambda, \theta_{\text{out}}) = \frac{\omega}{c} n_{\text{out}} \sin \theta_{\text{out}} = \frac{\omega}{c} n \sin \theta_{\text{in}}, \quad (2.7)$$

with Snell's law $n_{\text{out}} \sin \theta_{\text{out}} = n \sin \theta_{\text{in}}$. For a planar FP of effective length L_{eff} , the longitudinal component is quantized as $k_z \approx q\pi/L_{\text{eff}}$ (mode index $q \in \mathbb{N}$), and the cavity dispersion follows

$$\omega_q(\theta) = \frac{c}{n_{\text{eff}}} \sqrt{k_z^2 + k_{\parallel}^2} \Rightarrow E_q(\theta) = \hbar\omega_q(\theta). \quad (2.8)$$

Equivalently, in a widely used effective-index form (air collection, $n_{\text{out}} = 1$),

$$E_q(\theta_{\text{out}}) = \frac{E_q(0)}{\sqrt{1 - (\sin \theta_{\text{out}}/n_{\text{eff}})^2}}, \quad (2.9)$$

which is the relation used to overlay bare cavity dispersions on angle-resolved maps.

2.4 Weak Coupling Regime

The interaction between light and matter can generally be divided into two regimes: weak coupling and strong coupling. In the weak coupling regime, the emitter interacts with the cavity, but the exchange of energy between the two systems is not coherent. Instead, the cavity primarily modifies the emission properties of the emitter by altering the local density of optical states. As a result, the emission can be either enhanced or suppressed depending on the spectral and spatial overlap between the emitter and the cavity mode.

One of the key signatures of weak coupling is the Purcell effect, where the spontaneous emission rate is modified according to the cavity parameters, as discussed in the previous section. In this regime, the emission spectrum of the emitter remains essentially unchanged, no new eigenstates are formed, but the lifetime, intensity, and directionality of the emission are strongly influenced by the cavity environment.

Physically, weak coupling occurs when the rate of spontaneous emission or absorption is faster than the rate of coherent energy exchange between the emitter and the cavity. Thus, while the cavity can decide how and where the emitter radiates, it does not fundamentally alter the energy levels of the system[27, 28, 29].

2.5 Strong Coupling Regime

When the interaction between the cavity and the molecular system is strong, a coherent energy exchange takes place between them. In the strong coupling (SC) regime, the original energy levels split into two distinct levels, forming new hybrid light-matter states that drastically alter the optical properties of the molecules. This phenomenon is known as Rabi splitting, denoted by Ω_R , and is illustrated in Fig. 2.3.

There is a criterion for the strong coupling. The coupling regime is determined by the relation between the coupling strength g , the emitter decay rate γ , and the cavity decay rate κ [30].

$$g < \gamma, \kappa \quad \Rightarrow \quad \text{Weak coupling} \quad (2.10)$$

$$g > \gamma, \kappa \quad \Rightarrow \quad \text{Strong coupling} \quad (2.11)$$

For resolvable Rabi splitting, a stricter condition must be satisfied:

$$2g > \frac{\kappa + \gamma}{2} \quad (2.12)$$

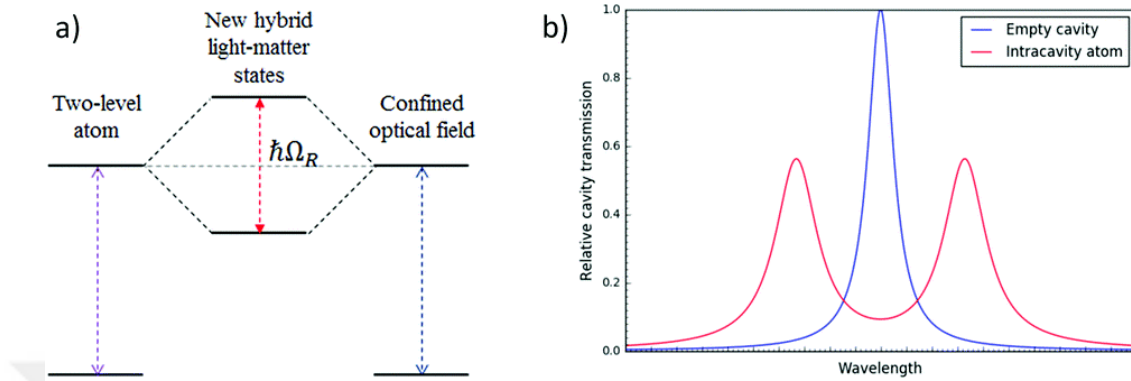


Figure 2.3: Illustration of strong light-matter coupling. (a) Schematic representation of a two-level atom interacting with a confined optical field inside a cavity. When the interaction strength exceeds the dissipative losses, the system no longer exhibits independent atomic and photonic modes, but instead forms new hybrid light-matter states separated by the vacuum Rabi splitting $\hbar\Omega_R$. (b) Transmission spectrum of the cavity. For the empty cavity (blue), a single resonance peak is observed, while in the presence of an intracavity atom (red), the resonance splits into two distinct polaritonic peaks, characteristic of strong coupling. [3]. Reproduced from Dovzhenko et al., *Nanoscale*, 10(8), 3589–3605 (2018), with permission from The Royal Society of Chemistry.

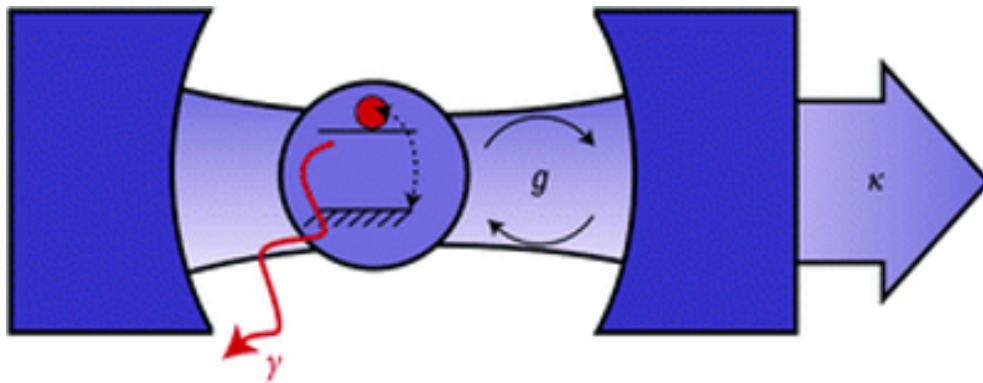


Figure 2.4: Schematic of light-matter interaction in a cavity. An emitter with decay rate γ couples to the cavity mode with strength g , while the cavity field decays at rate κ . Reprinted with permission from Khitrova et al., *Nature Physics* 2, 81–90 (2006). © 2006, Springer Nature

In this regime, the cavity photons and molecular excitations are no longer independent but coherently mix to form new quasiparticles known as exciton–polaritons, which inherit properties from both light and matter and serve as the hallmark of strong light–matter coupling[31, 32, 33].

2.6 Summary

This chapter has presented the theoretical framework necessary for understanding the interaction of light with fluorescein-doped optical cavities. Key concepts include light–matter interaction, emission modification via the Purcell effect, and the formation of hybrid polariton states. These principles form the basis for the experimental investigations in the following chapters.

Chapter 3

Transfer Matrix Method (TMM) Simulations

3.1 Fundamentals

The Transfer Matrix Method (TMM) is an analytical technique used to model the interaction of electromagnetic waves with layered media. It is a powerful and effective tool, particularly in optical thin-film analysis, where light encounters multiple interfaces between different materials with different refractive indices. In such systems, light is partially reflected and transmitted at each boundary, and interference effects arise because of the phase shifts that accumulate as light passes through each layer. TMM provides a reliable framework for calculating reflection, transmittance, and absorbance spectra as functions of wavelength, angle of incidence, and polarization [34].

The physical basis of the method is based on Maxwell's equations and boundary conditions. At each interface between two materials, the continuity of the tangential components of the electric and magnetic fields imposes constraints on how electromagnetic waves are transmitted and reflected. These conditions yield the well-known Fresnel equations, which express the reflection and transmission

coefficients in terms of the refractive indices and the angles of incidence and transmission [34, 35, 36].

To account for multilayer systems, the method uses a 2x2 matrix formalism. Each layer and interface are associated with a transmission matrix that relates the forward and backward propagating components of the electromagnetic wave through the layer. The overall system is then described by the sequential multiplication of all the individual matrices. For a given polarization state, the general transfer matrix M can be used to directly compute the complex reflection coefficients (r) and transmission (t) coefficients of the full stack [35, 37, 36]:

$$r = \frac{M_{21}}{M_{11}}, \quad t = \frac{1}{M_{11}} \quad (3.1)$$

At each interface, we use what are called Fresnel equations to calculate how much light is reflected and transmitted. Before applying these equations, we first determine how the angle of the light changes using Snell's law:

$$n_1 \sin(\theta_1) = n_2 \sin(\theta_2) \quad (3.2)$$

where n_1 and n_2 are the refractive indices of the two media, and θ_1 and θ_2 are the angles of incidence and refraction, respectively. This law tells us how much light bends when entering a new material [35, 37].

Reflectance R and transmittance T are obtained as the squared magnitudes of these coefficients, corrected by impedance matching factors to conserve energy:

$$R = |r|^2, \quad T = |t|^2 \cdot \frac{n_s \cos \theta_s}{n_0 \cos \theta_0} \quad (3.3)$$

Here, n_0 and θ_0 are the refractive index and angle of incidence in the initial medium (e.g. air), and n_s , θ_s are those in the substrate. The absorbance A is simply given by energy conservation:

$$A = 1 - R - T \quad (3.4)$$

In the implementation used in this study, a multilayer system consisting of air, a thin silver film, a PMMA layer containing fluorescent molecules, another silver film, and a quartz substrate was modeled. The input optical constants (complex refractive indices) for each material were interpolated based on the wavelength of the experimental data files. The system was simulated in the visible-light spectral range (250–800 nm) between an incident angle of 15° and 85°. Both TE (transverse electric or s-polarized) and TM (transverse magnetic or p-polarized) polarizations were considered.

In each layer, the electric field undergoes a phase shift that depends on the optical thickness of the layer. This phase accumulation is described by a propagation matrix:

$$P_j = \begin{bmatrix} e^{-i\delta_j} & 0 \\ 0 & e^{i\delta_j} \end{bmatrix}, \quad \delta_j = \frac{2\pi}{\lambda} n_j d_j \cos \theta_j \quad (3.5)$$

At each interface, an interface matrix based on the Fresnel reflection and transmission coefficients for the particular polarization is used. For TE (s) polarization, the interface matrix between the two media (i and j) is given by:

$$D_{ij}^{(s)} = \frac{1}{t_{ij}^{(s)}} \begin{bmatrix} 1 & r_{ij}^{(s)} \\ r_{ij}^{(s)} & 1 \end{bmatrix} \quad (3.6)$$

with

$$r_{ij}^{(s)} = \frac{n_i \cos \theta_i - n_j \cos \theta_j}{n_i \cos \theta_i + n_j \cos \theta_j}, \quad t_{ij}^{(s)} = \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + n_j \cos \theta_j} \quad (3.7)$$

For TM (p) polarization, the expressions are as follows [35, 37, 36]:

$$r_{ij}^{(p)} = \frac{n_j \cos \theta_i - n_i \cos \theta_j}{n_j \cos \theta_i + n_i \cos \theta_j}, \quad t_{ij}^{(p)} = \frac{2n_i \cos \theta_i}{n_j \cos \theta_i + n_i \cos \theta_j} \quad (3.8)$$

The total transfer matrix is obtained by sequentially multiplying the interface and propagation matrices of all layers in the order of their appearance, starting from the incident medium and ending at the substrate. This matrix comprises the entire optical behavior of the stack, and spectral properties can be extracted from it for both polarizations.

The final output of the simulation includes reflectance, transmittance, and absorbance spectra for TE, TM, and unpolarized light (assumed to be the average of TE and TM). These results are important for the design and optimization of optical coatings, filters, and photonic structures [34].

3.2 Low Dye Concentration Samples

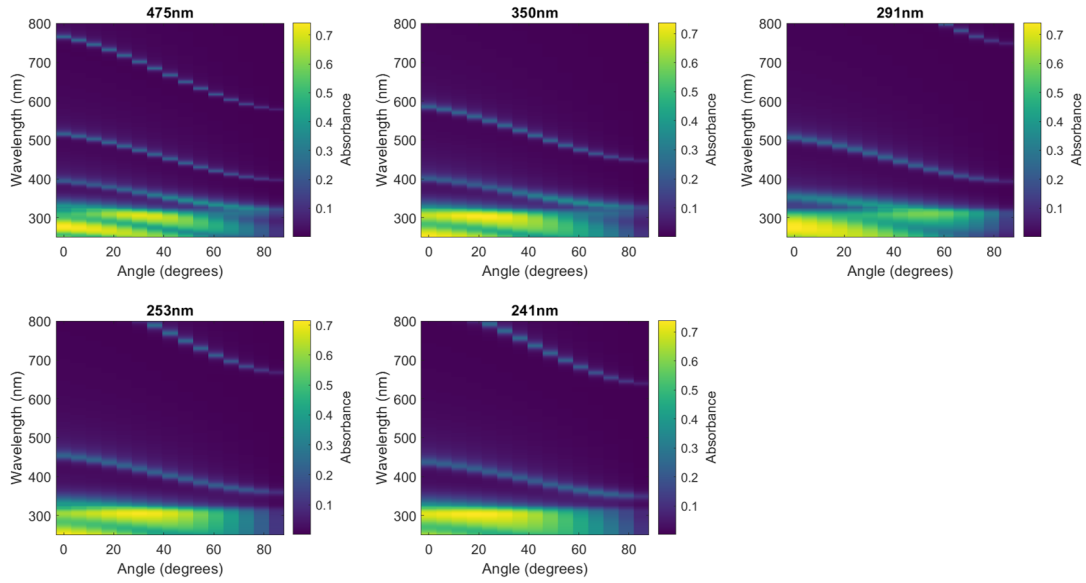


Figure 3.1: Simulated absorbance spectra for low dye concentration samples using (TMM), showing how light absorption varies with wavelength and incident angle.

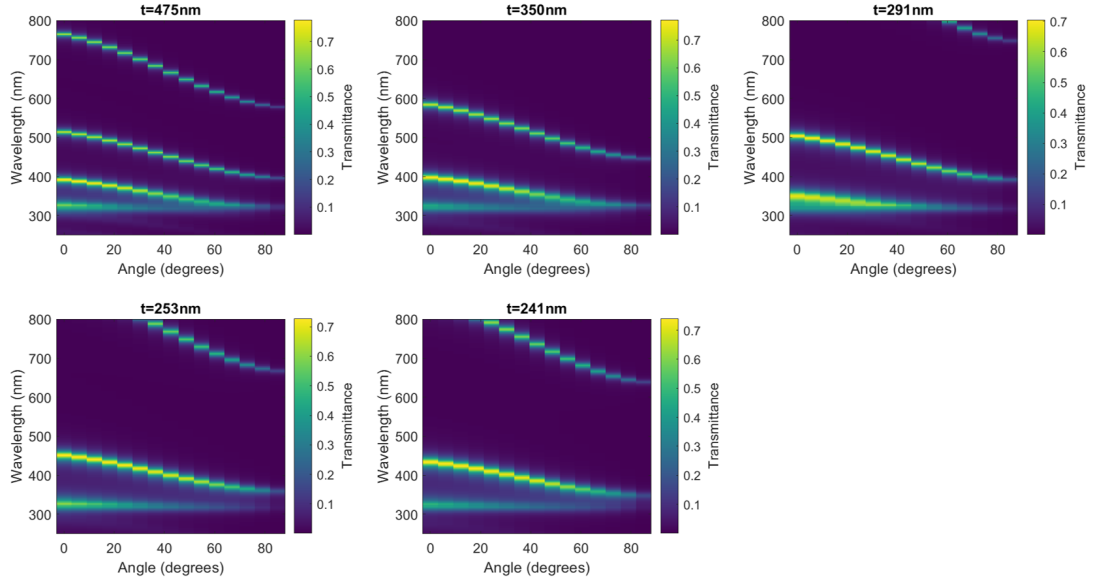


Figure 3.2: Simulated transmittance spectra for low dye concentration samples calculated using TMM, indicating the wavelength and angular dependence of transmitted light.

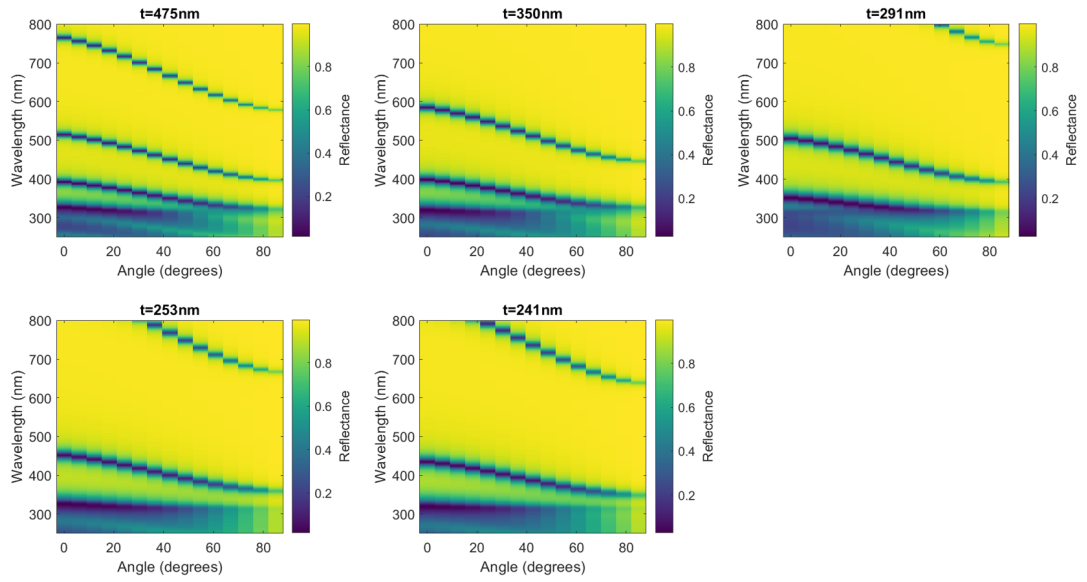


Figure 3.3: Simulated reflectance spectra for low dye concentration samples obtained using TMM, illustrating reflection changes with wavelength and angle of incidence.

3.3 High Dye Concentration Samples

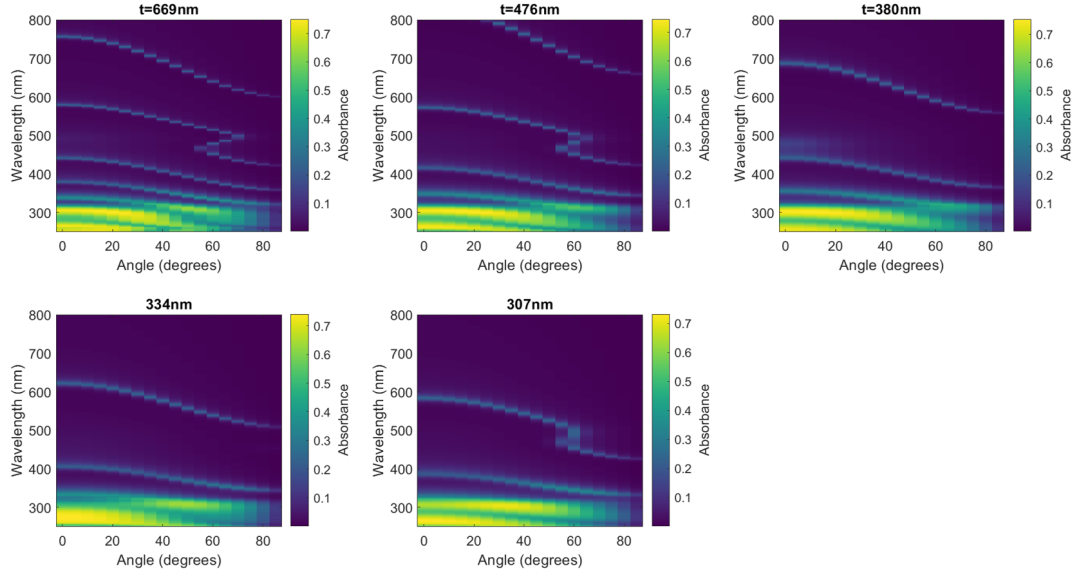


Figure 3.4: Simulated absorbance spectra for high dye concentration samples using (TMM), showing how light absorption varies with wavelength and incident angle.

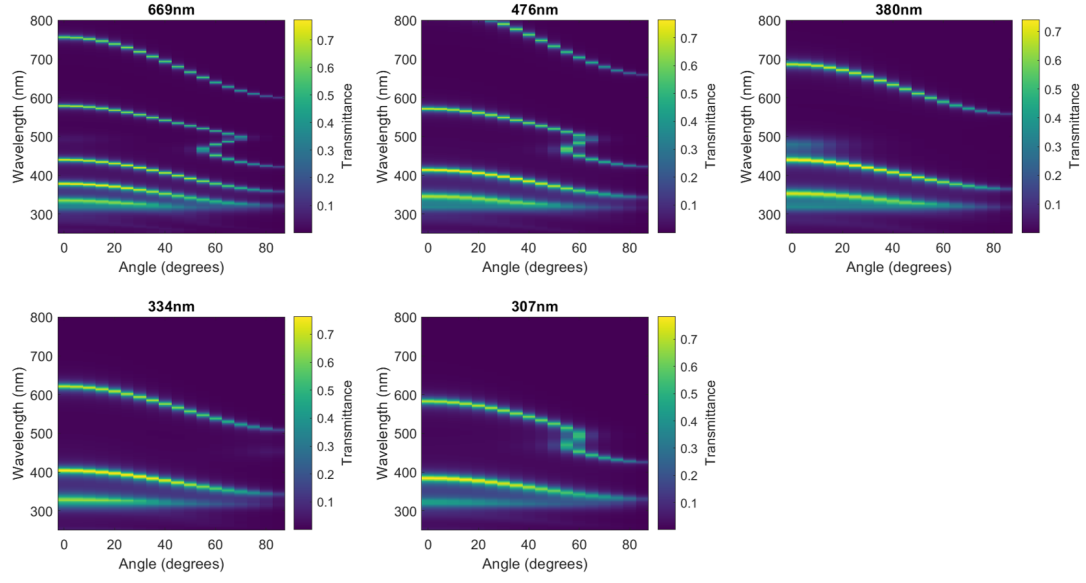


Figure 3.5: Simulated transmittance spectra for high dye concentration samples calculated using TMM, indicating the wavelength and angular dependence of transmitted light.

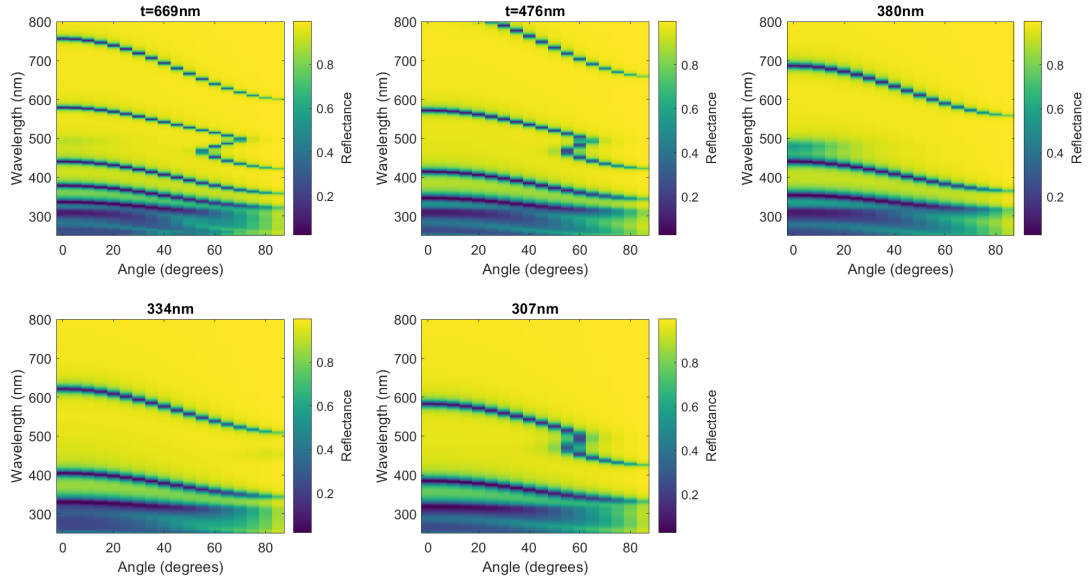


Figure 3.6: Simulated reflectance spectra for high dye concentration samples obtained using TMM, illustrating reflection changes with wavelength and angle of incidence.

For low dye concentration films, TMM reproduces purely photonic Fabry–Pérot behaviour: angle-dependent blue-shifting of cavity resonances, complementary extrema in R and T , and low A except near PMMA’s UV absorption. No avoided crossings appear when the cavity mode sweeps through ~ 467 nm, matching the experimental weak-coupling baseline.

For high dye concentration films, adding the dye’s dispersive/absorptive response (notably near ~ 467 nm) increases A and reshapes R and T , yielding stronger modulation and thickness–detuning dependent mode repulsion/back-bending in the simulated maps. The simulations clarify how film thickness controls free spectral range and mode overlap with the excitonic band, identify angle windows where splitting-like features are most pronounced, and explain the reduced transmittance contrast near resonance.

Finally, TMM served a practical role: (i) validating optical-constant models (n, k) used across the thesis; and (ii) estimating in-cavity thicknesses by peak matching when ellipsometry was not feasible (Ag/PMMA/Ag). Overall, the TMM results provide a consistent, quantitative foundation for the ellipsometry, reflectance/fluorescence, and three-oscillator analyses developed in subsequent chapters.

Chapter 4

Materials and Methods

4.1 Chapter Overview

In this chapter, we discuss the materials used in this research, their properties, and the reasons for selecting them. The main materials are poly(methyl methacrylate) (PMMA), which serves as the host polymer, and fluorescein dye, which is the active optical component. We describe the preparation of fluorescein dye solutions mixed with PMMA at two concentrations, low (20 $\mu\text{g/mL}$) and high (60 mg/mL), to study how dye concentration affects the optical behavior of the samples. We also explain the fabrication of two types of samples: cavity samples, where the dye-doped PMMA layer is placed between two 30 nm silver (Ag) layers forming a Fabry-Pérot resonator, and reference samples without silver layers, used as control samples for comparison. All fabrication steps were carried out under controlled conditions to ensure sample quality and consistency.

4.2 Overview of the Materials and their Properties

4.2.1 Poly(methyl methacrylate) (PMMA)

PMMA is a synthetic polymer produced by the polymerization of methyl methacrylate, which has the chemical name 1-(methoxycarbonyl) 1-methylethylene.

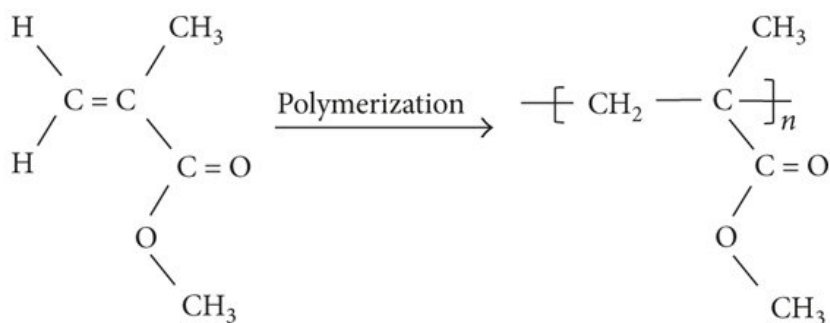


Figure 4.1: Polymerization of methyl methacrylate (MMA) to form poly(methyl methacrylate) (PMMA) by addition polymerization[4, 5]

PMMA has several properties that make it a suitable material for thin-film optical applications. Its refractive index typically ranges from 1.48 to 1.50 in undoped thin films, making it ideal for dielectric spacer layers in multilayer optical structures[38]. Due to its high transparency ($E_g = 4.273$ eV)[39] in the visible region, PMMA is commonly used as a host matrix for various dye molecules[40]. However, it shows absorption in the ultraviolet region due to electronic transitions associated with the carbonyl groups ($\text{C} = \text{O}$) present in its molecular structure[41, 42]. Additionally, PMMA forms smooth, uniform films and is easy to apply by spin-coating. Its flexibility helps prevent cracks or defects in thin films. PMMA is also chemically stable, has good thermal stability[43], and shows very low background fluorescence, making it suitable for fluorescence-based optical experiments. PMMA (Molecular weight = 950,000, CAS No. 9011-14-7) supplied by Kayaku Advanced Materials was used in this study. The PMMA

solutions, grades A3 and A8, were supplied pre-dissolved in anisole and used without further preparation. Here, “A” means anisole as the solvent, and the numbers indicate viscosity: A3 is thinner, producing thinner films, while A8 is thicker, producing thicker films.

4.2.2 Fluorescein Dye

Fluorescein is a widely used dye that belongs to the class of synthetic organic compounds and is a member of the xanthene dye family. It was first synthesized in 1871 by Adolf von Baeyer. It can be chemically modified by incorporating different functional groups, allowing its excitation and emission properties to be tuned[44].

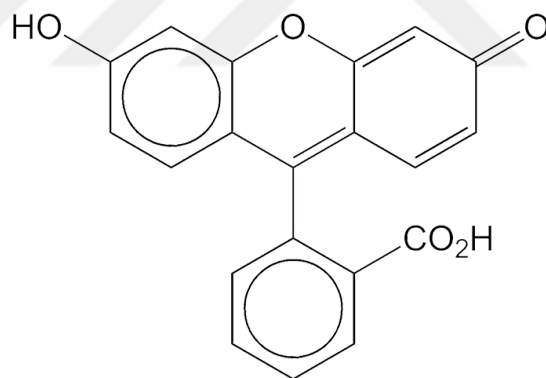


Figure 4.2: Chemical structure of protonated fluorescein dye

Fluorescein dye shows a strong response to the pH change in the environment. In acidic conditions (low pH), fluorescein is in a form that does not absorb much light, so its fluorescence is weak. When the pH becomes neutral or basic (higher pH), fluorescein changes into a form that shows strong fluorescence. This change usually happens around pH 6.4 to 6.8[45]. At pH values higher than this range, fluorescein shows its strongest and most stable fluorescence. Because of this pH sensitivity, fluorescein is often used as a pH indicator in biological and chemical experiments[46]. In solid films like PMMA, the pH effect is much smaller because protons do not move easily in the solid material. Still, knowing about this behavior is important when studying fluorescence, especially in cases where pH might

affect the results [47].

Fluorescein-doped PMMA thin film shows the strong excitation and emission wavelengths of 467 nm and 512 nm, respectively. The Stokes shift is the difference between the excitation (absorption) wavelength and the emission wavelength of a fluorescent molecule. This results in a Stokes shift of approximately 45 nm.

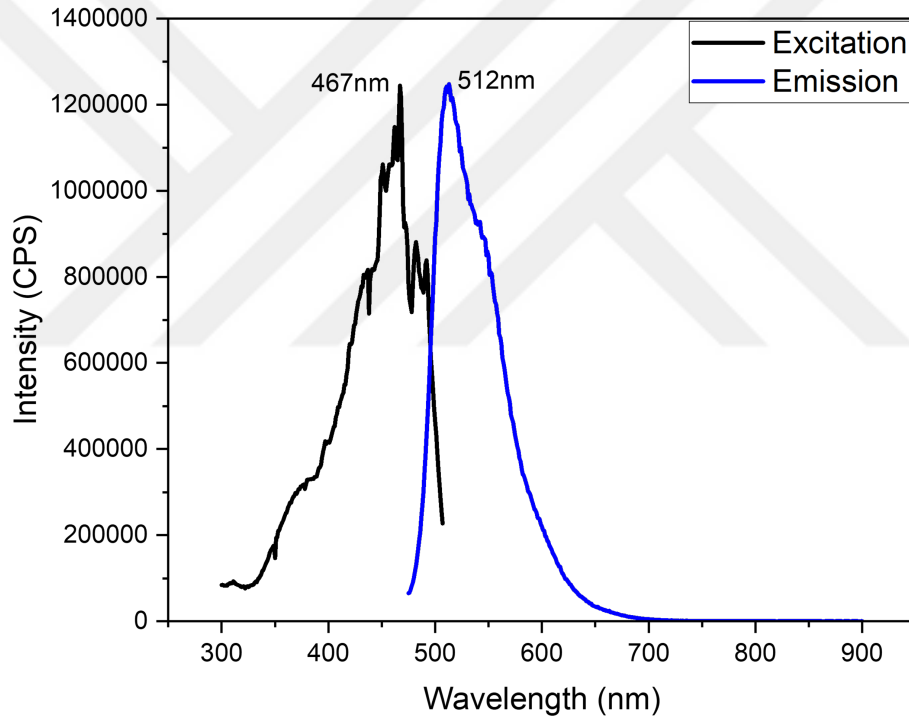


Figure 4.3: Measured excitation and emission spectra of fluorescein-doped PMMA thin film.

In this study, we use fluorescein as an active optical material to study weak and strong coupling regimes. One reason why it is difficult to study strong coupling with fluorescein is that it has a broad absorption and emission peak. For strong coupling to happen, the energy of the cavity mode needs to match closely with the energy of the excitonic transition of the dye. When the dye has a broad peak, it is difficult for the cavity to couple strongly because the overlap is not sharp and precise[48].

This broad peak also makes it difficult to see clear signs of strong coupling, such as splitting in the optical spectra. As a result, fluorescein usually shows weak coupling under normal conditions.

Even though this makes strong coupling challenging, it is still useful to study fluorescein because it helps us understand how light interacts with dyes that do not have sharp peaks. This knowledge can help in understanding the limitations faced by the material while developing new optical devices and sensors.

Material	Supplier	CAS Number	Molecular Weight (g/mol)
Fluorescein (Acid Yellow 73)	Sigma-Aldrich	2321-07-5	332.31
PMMA	Kayaku Advanced Materials	9011-14-7	950,000
DMF	Merck	68-12-2	73.09

Table 4.1: Chemicals used in this study with their suppliers, CAS numbers, and molecular weights.

Dimethylformamide (DMF) served as the solvent to effectively dissolve the fluorescein dye before it was mixed with the Poly(methyl methacrylate) (PMMA) matrix. Pure silver (99%) was utilized to create highly reflective mirrors for a Fabry-Pérot cavity, and quartz wafers were employed for the project.

4.3 Preparation of Fluorescein/PMMA Solutions

Two different concentrations of solutions were prepared to target weak and strong coupling regimes. In both solutions, PMMA A3 / PMMA A8 was used in a 3:1 volume ratio.

4.3.1 Low Concentration of Fluorescein in PMMA

A low-concentration fluorescein-doped PMMA solution was prepared by diluting a stock fluorescein solution of 2 mg/mL (in ethanol). Specifically, 10 μ L of the stock solution was mixed with 1 mL of PMMA solution, giving a total volume of 1.01 mL. The final dye concentration was calculated using the standard dilution relation:

$$C_f = \frac{C_i \times v_i}{v_f} \quad (4.1)$$

where C_i is the stock concentration, v_i is the volume of stock added, and v_f is the final solution volume. This yielded a final concentration of approximately 20 μ g/mL (19.8 μ g/mL), which was used to fabricate thin films for low-concentration optical measurements inside and outside the Fabry–Pérot cavity.

4.3.2 High Concentration of Fluorescein in PMMA

A high-concentration fluorescein/PMMA solution was prepared by dissolving 150 mg of fluorescein dye in 0.5 mL of DMF, followed by mixing with 1.5 mL of PMMA A3 and 0.5 mL of PMMA A8. The total solution volume was 2.5 mL, corresponding to a dye concentration of:

$$C_d = \frac{150 \text{ mg}}{2.5 \text{ mL}} = 60 \text{ mg/mL} \quad (4.2)$$

The mixture was magnetically stirred at 100 °C for 2.5 hours and subsequently left undisturbed for 1 hour to remove air bubbles. This high-concentration solution was used to prepare fluorescein-doped films for optical characterization.

4.3.3 Substrate Cleaning

Quartz substrates with dimensions of $2 \times 2 \text{ cm}^2$ were prepared by dicing quartz wafers using a dicing saw, followed by treatment with piranha solution to remove any tape residues from the cutting process. The substrates were then rinsed thoroughly with deionized (DI) water and subsequently sonicated for 10 minutes each in acetone, isopropanol, and DI water. Finally, the cleaned substrates were dried using a nitrogen gas.

4.4 Fabrication of Fabry-Pérot Cavities

4.4.1 Deposition of Bottom Ag Mirror

30 nm silver (Ag) mirrors were deposited on quartz wafers using an electron-beam evaporator. The process was carried out at a pressure below 5×10^{-6} Torr, with the deposition rate between 0.2 and 0.3 nm/s. A quartz crystal microbalance was used to monitor the thickness.

4.4.2 Spin-Coating of Fluorescein/PMMA Films

After the bottom mirrors were prepared, thin films of fluorescein-doped PMMA were spin-coated. Five of the samples were coated with a diluted dye solution, while the other five were coated with a concentrated solution to study the effect of dye concentration on the optical properties of the cavities.

The films were spin-coated for one minute at speeds ranging from 1000 to 5000 rpm, with an acceleration of 700 rpm, to achieve different film thicknesses. After coating, the samples were heated at 100°C for five minutes on a hot plate to remove any remaining solvent and to allow the films to stabilize.

4.4.3 Deposition of Top Ag Mirror

Finally, a top 30 nm silver mirror was deposited again using an e-beam evaporator under the same conditions to complete the fabrication process of the Fabry-Pérot cavities.

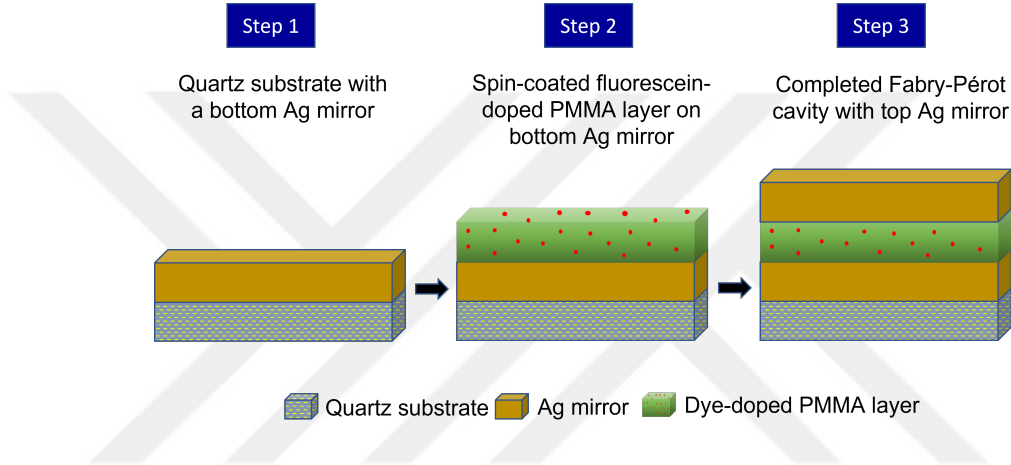


Figure 4.4: Fabrication of the Fabry-Pérot cavity with a bottom Ag mirror, spin-coated fluorescein-doped PMMA layer, and top Ag mirror.

4.5 Preparation of Out-of-Cavity Controls

Ten reference samples were made by spin-coating the diluted and concentrated fluorescein/PMMA solutions onto quartz ($2 \times 2 \text{ cm}^2$) wafers, without silver mirrors. The samples were spin-coated at speeds ranging from 1000 to 5000 rpm and baked under the same conditions as the cavity samples.

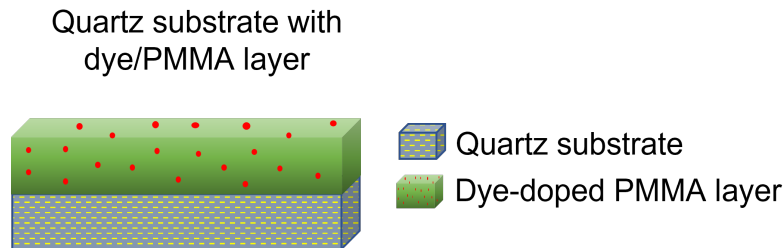


Figure 4.5: Fabrication of the out-of-cavity control samples

4.6 Summary

This chapter explained the materials used and the methods followed in this research. It covered the preparation of dye-doped PMMA solutions, the cleaning of quartz substrates, and the fabrication steps for both cavity and reference samples. The focus was on ensuring that the thin films were uniform and that the fabrication process could be repeated with consistent results.



Chapter 5

Thickness Characterization Fluorescein-Doped PMMA Films

5.1 Chapter Objectives

In this chapter, the primary objective is to present the thickness measurements of the fluorescein-doped PMMA films prepared during the experiments. These measurements help us understand how the film thickness changes with different spin speeds (1000 to 5000 rpm). We used ellipsometry (J.A. Woollam V-VASE with an HS-190 Monochromator) to measure the thickness of the reference samples. The results shared here will help explain the optical properties change of the samples as a function of thickness in the next chapters.

5.2 Measurement Procedure

In this study, spectroscopic ellipsometry was used to measure the thickness of dye-doped PMMA films. It is a non-destructive technique used to get the refractive index, extinction coefficient, thickness, surface roughness, and uniformity of the

thin film[49].

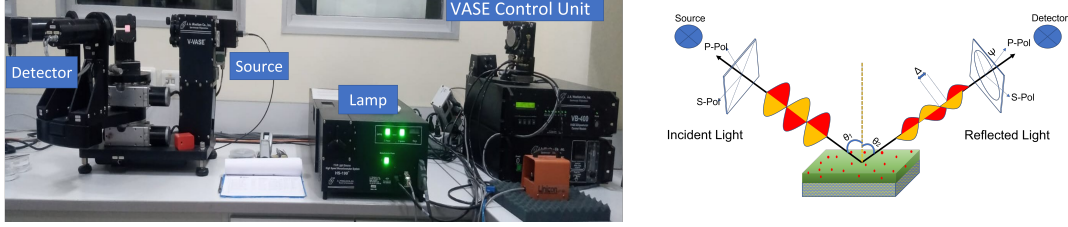


Figure 5.1: On the left: the J.A. Woollam VASE ellipsometer used for measurements in this study. On the right: schematic representation of the light beam interaction with the sample surface in ellipsometry.

The process began with the ignition of the xenon lamp, which was allowed to warm up for 30 minutes to stabilize. The first step before any sample measurement was the calibration of the system using a polished 4-inch silicon (Si) wafer. Calibration with a Si wafer is a standard procedure because silicon has well-known optical properties. This ensures the ellipsometer accurately reads the amplitude ratio (Ψ) and phase difference (Δ) values and corrects for any small instrumental errors.

After calibration, the actual film measurements were carried out. We selected a wavelength range from 250 nm to 1000 nm with a data point interval of 10 nm to study both the transparent and absorbing behavior of the films.

Data were collected at three angles of incidence, 55° , 60° , and 65° , which are near the Brewster angles for quartz. The Brewster angle θ_B is the angle of incidence at which p-polarized light experiences zero reflection at the interface of two materials with different refractive indices[50, 51, 52]. It is calculated using the following formula:

$$\theta_B = \arctan\left(\frac{n_2}{n_1}\right) \quad (5.1)$$

where n_1 is the refractive index of the incident medium (air, $n_1 = 1.00$) and

n_2 is the refractive index of the sample material (quartz, $n_2 = 1.46$). By putting the values, we can get the:

$$\theta_B = \arctan\left(\frac{1.46}{1.00}\right) = \arctan(1.46) = 55.4^\circ \quad (5.2)$$

Therefore, measurements were taken at 55° , 60° , and 65° angles to enhance the sensitivity of ellipsometry analysis and to avoid the reflection problem.

5.3 Thickness and Optical Constants Analysis of Samples with Low Dye Concentration

5.3.1 Model Fitting

Samples with low dye concentration contained PMMA as a major part of the active layer, and it does not absorb light in the visible region, so we simply used the Cauchy model to fit the Ψ and Δ values. This model is used for transparent material, like PMMA, and only provides the refractive index data. Here is the standard Cauchy dispersion equation used for transparent materials:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (5.3)$$

Where:

- $n(\lambda)$ is the refractive index at the wavelength λ .
- A , B , and C are fitting parameters, which are adjusted during the fitting process.
- λ is the wavelength of the light used in the measurement.

By fitting the measured Ψ and Δ values using the Cauchy model, the refractive index of the samples prepared at different spin speeds (from 1000 rpm to 5000 rpm) was determined. Since the dye concentration was low, no absorption features from the dye molecules were observed.

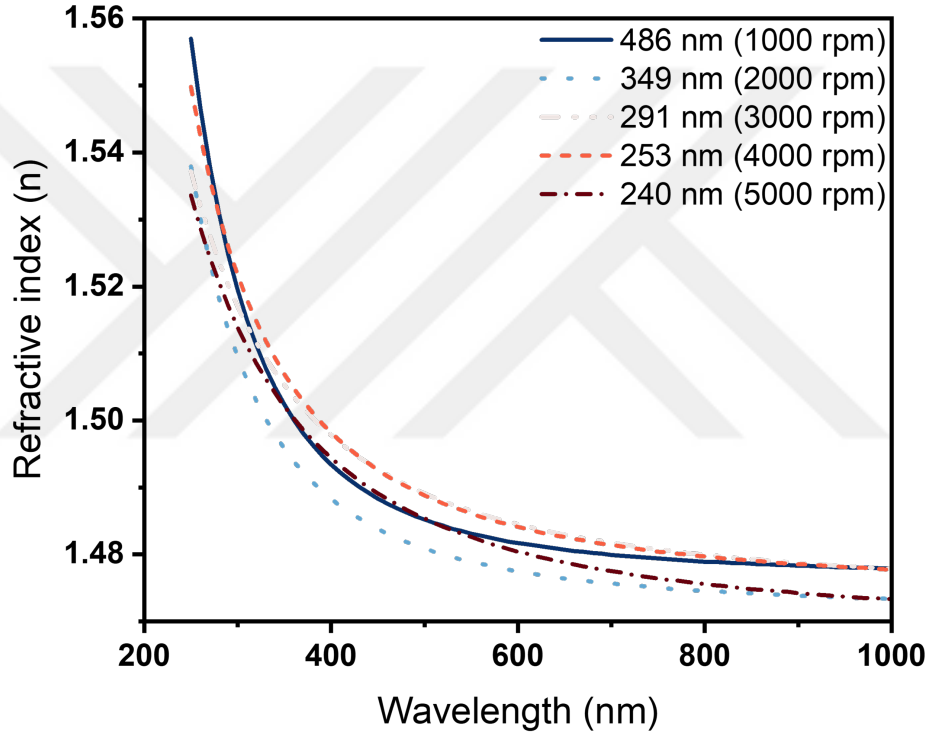


Figure 5.2: Wavelength-dependent refractive index (n) of low dye concentration samples ($20 \mu\text{g/mL}$) prepared at different spin-coating speeds ranging from 1000 to 5000 rpm.

The results mainly indicate the optical properties of PMMA, showing a trend similar to pure PMMA. For all samples, the refractive index remained almost constant in the wavelength range of 400 nm to 1000 nm. However, below 400 nm, a sharp increase in the refractive index was observed due to the inherent UV absorption of PMMA. We also checked the quality of our fitting using the Mean Square Error (MSE) values from the fitting software (CompleteEase). In the following section, the measured and fitted Ψ and Δ spectra for each low

dye concentration sample ($20 \mu\text{g/mL}$) prepared at spin speeds ranging from 1000 to 5000 rpm are presented. For each sample, the corresponding film thickness obtained from ellipsometry and the Mean Square Error (MSE) from the model fitting are reported, allowing for a direct comparison of fitting quality and thickness variation with spin speed.

5.3.2 Cavity Thickness of 486 nm

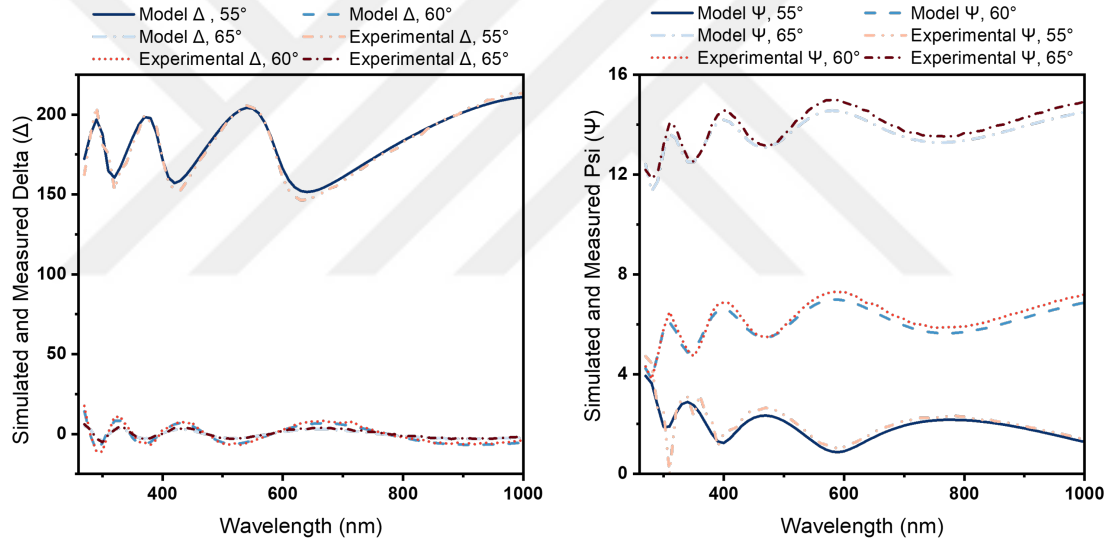


Figure 5.3: Measured and fitted Ψ and Δ spectra of dye-doped PMMA ($20 \mu\text{g/mL}$) thin film, obtained at 1000 rpm ($t = 486 \text{ nm}$).

At 1000 rpm, the measured thickness of the out-of-cavity low dye concentration sample was 486 nm, with a (MSE) of 1.946. The fitting parameters confirmed a good match between the experimental and simulated Ψ and Δ spectra.

5.3.3 Cavity Thickness of 349 nm

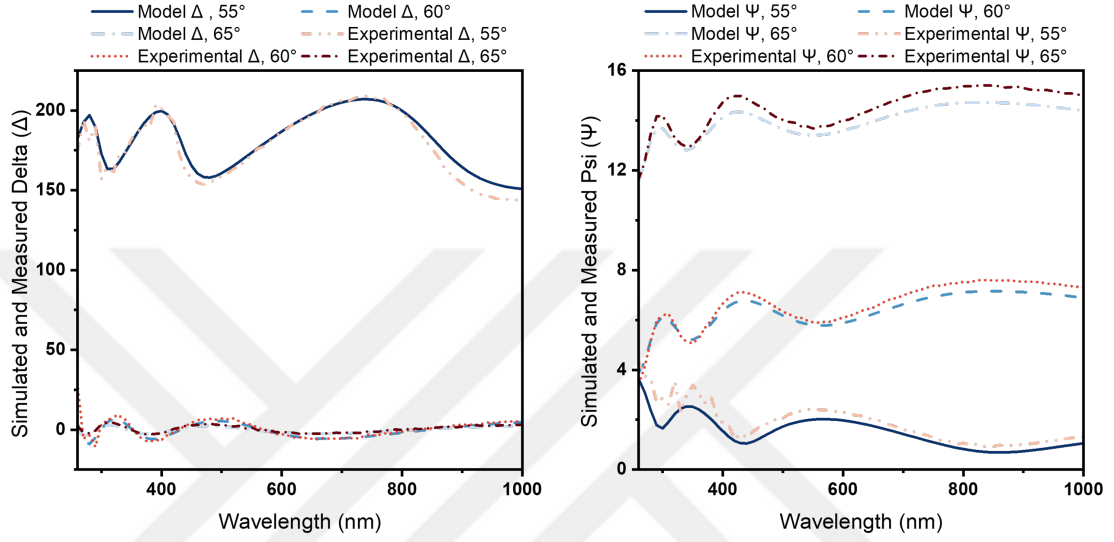


Figure 5.4: Measured and fitted Ψ and Δ spectra of dye-doped PMMA ($20 \mu\text{g/mL}$) thin film, obtained at 2000 rpm ($t = 349 \text{ nm}$).

For the sample spin-coated at 2000 rpm, the measured thickness was 349 nm, and the MSE was 3.259. Although the MSE was slightly higher than at lower speeds, the fitting still showed acceptable agreement with the experimental data.

5.3.4 Cavity Thickness of 291 nm

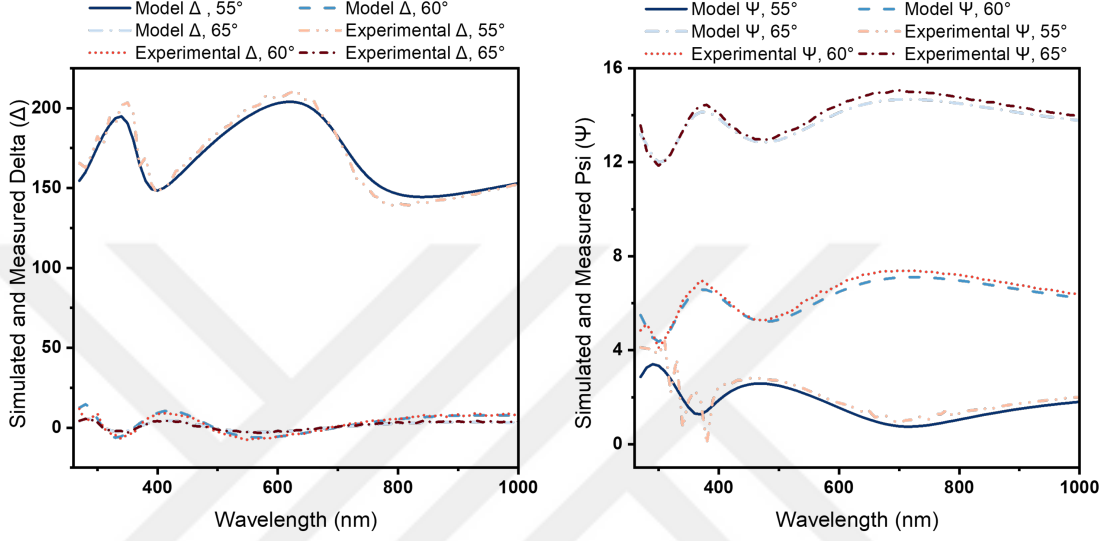


Figure 5.5: Measured and fitted Ψ and Δ spectra of dye-doped PMMA ($20 \mu\text{g/mL}$) thin film, obtained at 3000 rpm ($t = 291 \text{ nm}$).

At 3000 rpm, the measured thickness of the low dye concentration sample decreased to 291 nm, with an MSE of 2.312.

5.3.5 Cavity Thickness of 353 nm

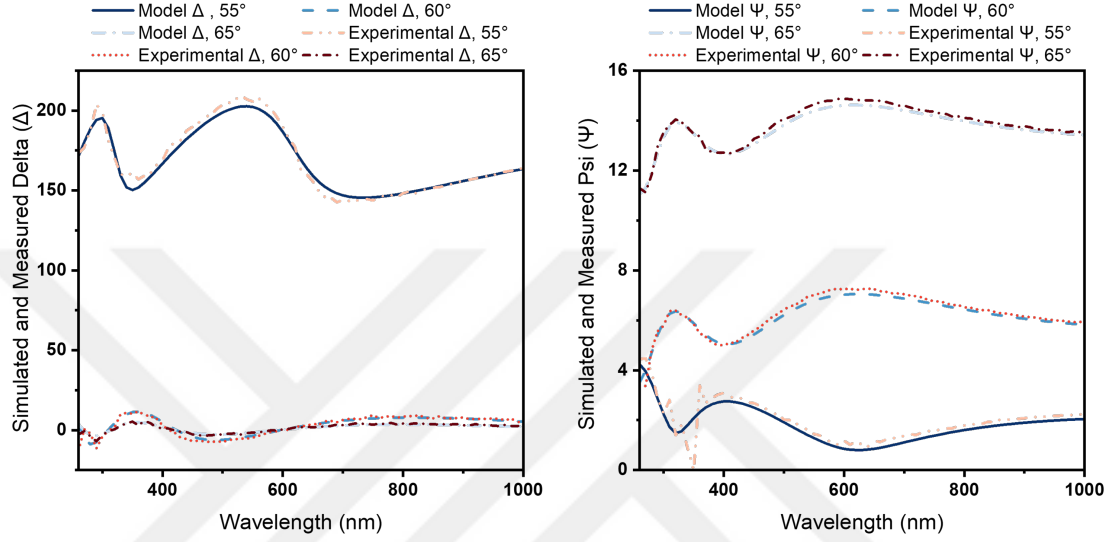


Figure 5.6: Measured and fitted Ψ and Δ spectra of dye-doped PMMA ($20 \mu\text{g/mL}$) thin film, obtained at 4000 rpm ($t = 253 \text{ nm}$).

The sample spin-coated at 4000 rpm showed a measured thickness of 253 nm, with a relatively low MSE of 1.859.

5.3.6 Cavity Thickness of 240 nm

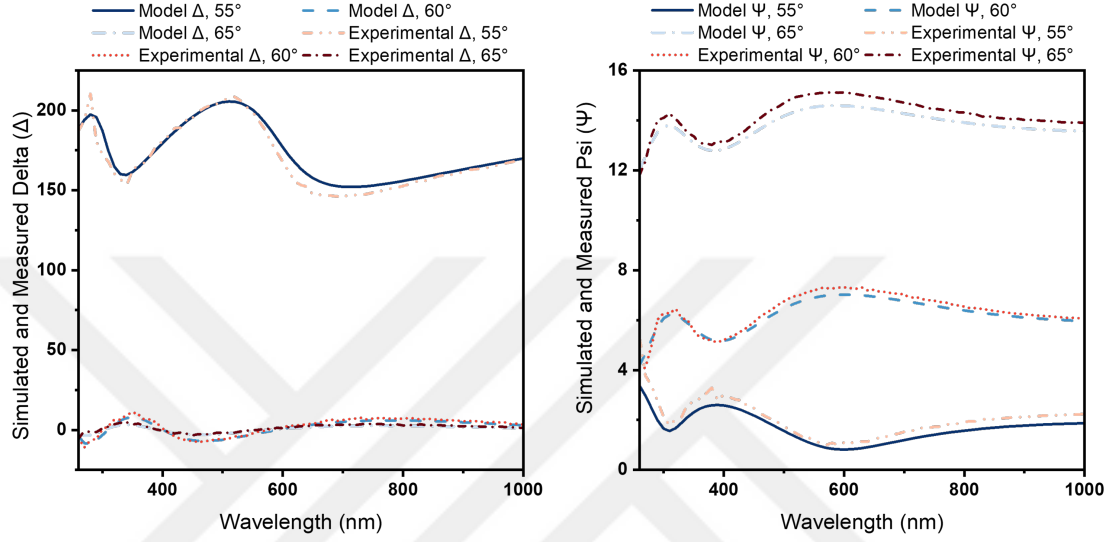


Figure 5.7: Measured and fitted Ψ and Δ spectra of dye-doped PMMA (20 $\mu\text{g/mL}$) thin film, obtained at 5000 rpm ($t = 240$ nm).

For the fastest spin speed of 5000 rpm, the measured film thickness was 240 nm, with an MSE of 2.342.

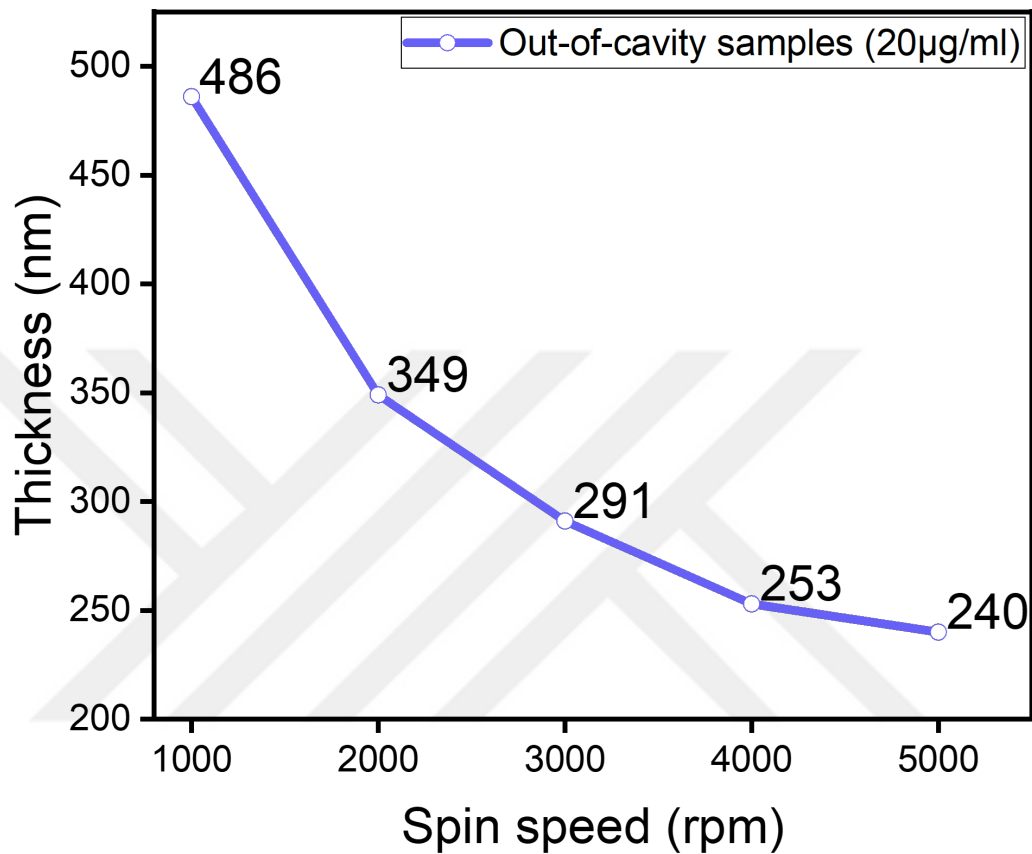


Figure 5.8: Thickness–rpm calibration for out-of-cavity fluorescein:PMMA films prepared from a ($20 \mu\text{g/mL}$) solution. Film thickness was tuned by varying the spin speed from 1000 to 5000 rpm and measured by spectroscopic ellipsometry. Thickness decreases monotonically with increasing rpm; the curve serves as the calibration used to select spacer thicknesses.

5.4 Thickness and Optical Constants Analysis of Samples with High Dye Concentration

5.4.1 Model Fitting

In the high dye concentration samples, the dye quantity was great enough to show its absorbance behavior in the spectra. The fitting was done in two steps. First, in the transparent region of the spectrum where the film hardly absorbed any light, we used the Cauchy dispersion model to find the refractive index and film thickness. However, in the regions where the dye absorbed more light, the Cauchy model alone did not give accurate results. To improve the fitting in these absorbing regions, we switched to a General Oscillator Model, which allowed us to include absorption features. Specifically, we used the Tauc-Lorentz oscillator model, which is commonly used for materials like amorphous semiconductors and organic films[53].

By combining these models, we were able to get both the refractive index and the extinction coefficient of the films across the full wavelength range. We again checked the quality of our fitting using the (MSE) values from the fitting software (CompleteEase). A low MSE indicated that the model provided a good fit to the experimental data, even in the presence of strong absorption features from the dye. The lowest MSE (2.243) was obtained for the sample spin-coated at 5000 rpm, corresponding to a film thickness of 307 nm.

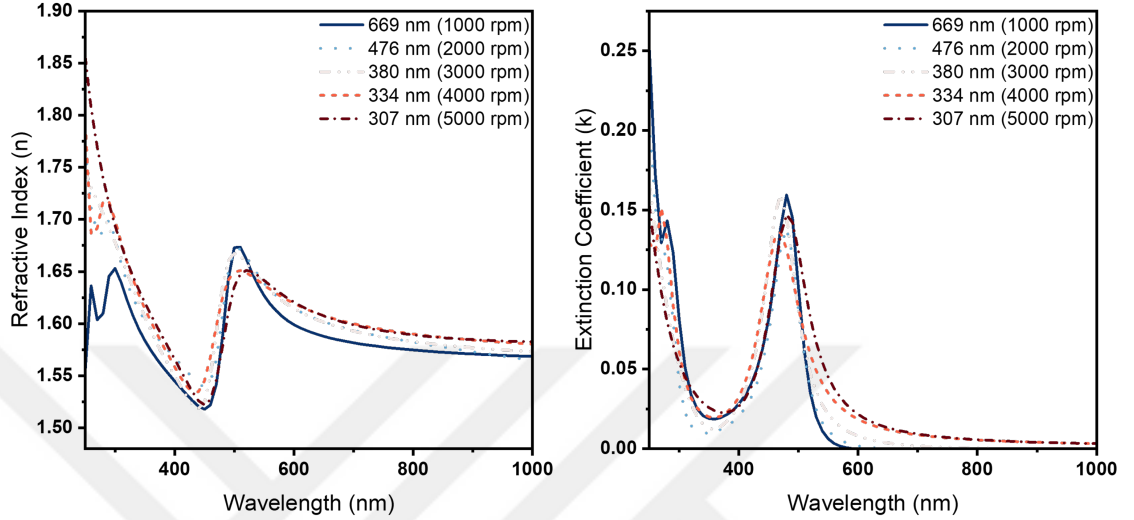


Figure 5.9: Wavelength-dependent refractive index (n) and extinction coefficient (k) of high dye concentration samples measured at different spin-coating speeds. The variation in n and k with spin speed shows the influence of film thickness on the optical properties of the films.

The refractive index (n) and extinction coefficient (k) of the high dye concentration samples were obtained by fitting the measured Ψ and Δ values using spectroscopic ellipsometry. Because of the higher dye concentration, absorption features appeared clearly in the ellipsometric spectra.

The k graph shows distinct absorption peaks, with the most noticeable peak at 467 nm, which corresponds to the characteristic absorption of the dye molecules. This confirms the successful incorporation of the dye into the PMMA films. In the n graph, a sharp decrease near 467 nm was observed. This drop in n occurs due to the absorption of light at this wavelength, which influences the dispersion behavior of the n .

Even though the spin-coating speed changes the thickness of the films, all samples showed similar intensity in both n and k across the measured wavelengths. This indicates that, for high dye concentration samples, the optical properties are dominated by the dye, and variations in film thickness have only a minor

influence on the n and k .

5.4.2 Cavity Thickness of 669 nm

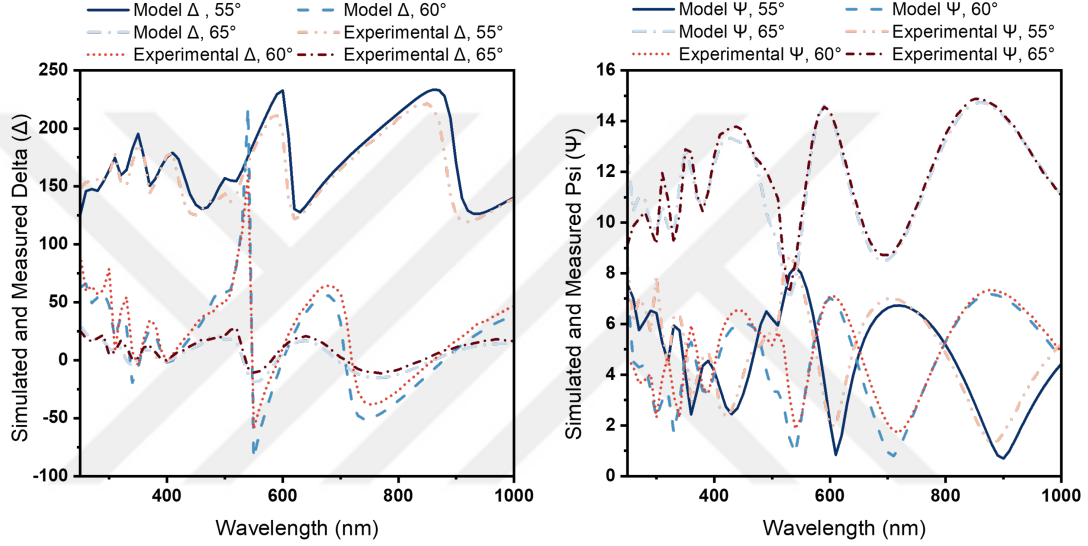


Figure 5.10: Measured and fitted Ψ and Δ spectra of dye-doped PMMA (60 mg/mL) thin film, obtained at 1000 rpm ($t = 669$ nm).

At 1000 rpm, the measured film thickness was 669 nm, and the fitting produced an MSE of 6.679. Although the simulated Ψ and Δ spectra followed the experimental data reasonably well, the higher (6.679) MSE suggests some mismatch. This may be due to the increased film thickness or slight non-uniformity of the film.

5.4.3 Cavity Thickness of 476 nm

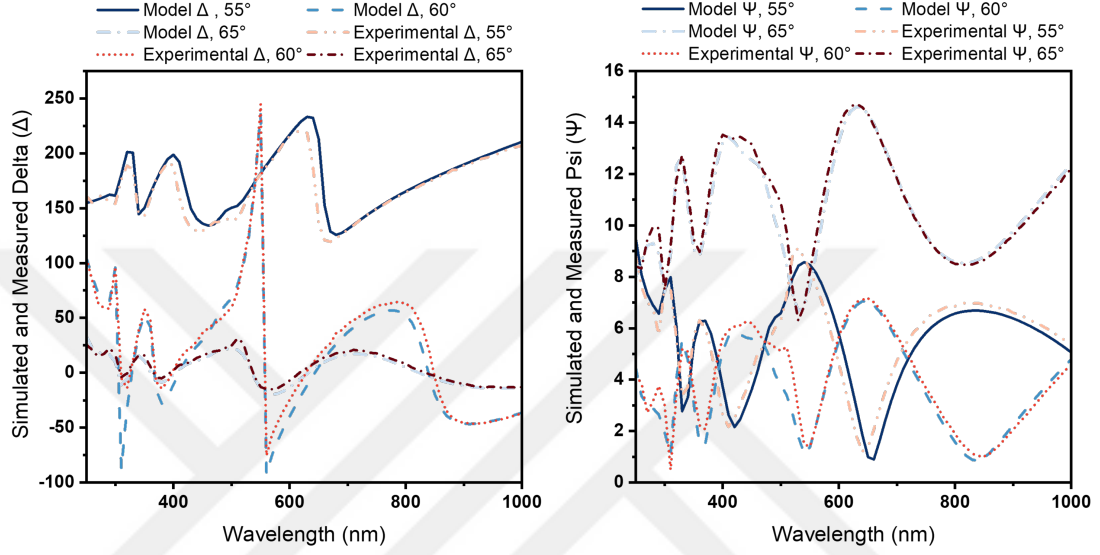


Figure 5.11: Measured and fitted Ψ and Δ spectra of dye-doped PMMA (60 mg/mL) thin film, obtained at 2000 rpm ($t = 476$ nm).

For the sample spin-coated at 2000 rpm, the thickness decreased to 476 nm, with an MSE of 5.295. The lower MSE compared to the 1000 rpm sample indicates an improvement in the fitting quality. The reduced thickness minimized optical losses, leading to better fitting results.

5.4.4 Cavity Thickness of 380 nm

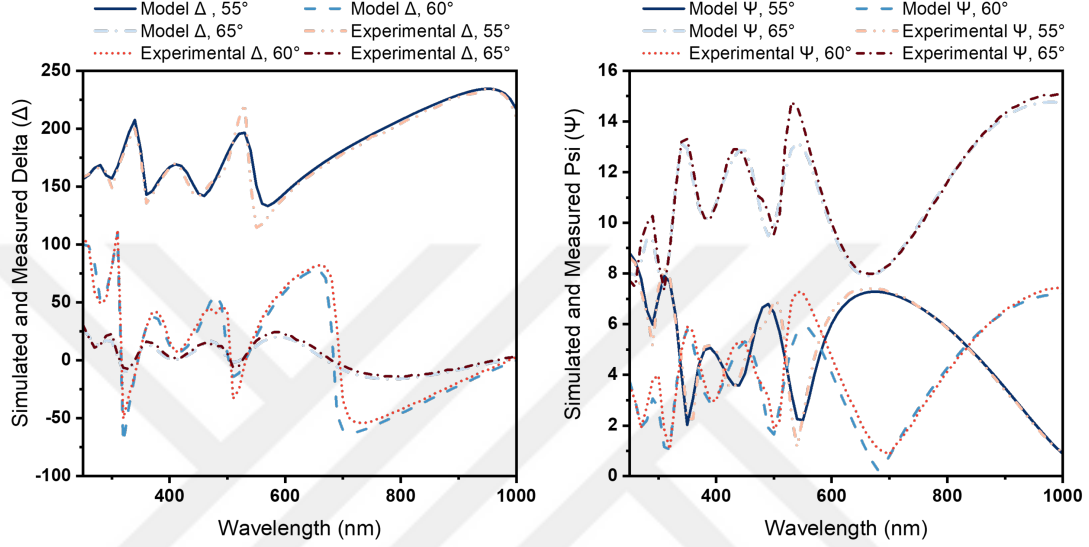


Figure 5.12: Measured and fitted Ψ and Δ spectra of dye-doped PMMA (60 mg/mL) thin film, obtained at 3000 rpm ($t = 380$ nm).

At 3000 rpm, the film showed a thickness of 380 nm, and the MSE further decreased to 4.868. The simulated data showed good agreement with the experimental Ψ and Δ curves.

5.4.5 Cavity Thickness of 334 nm

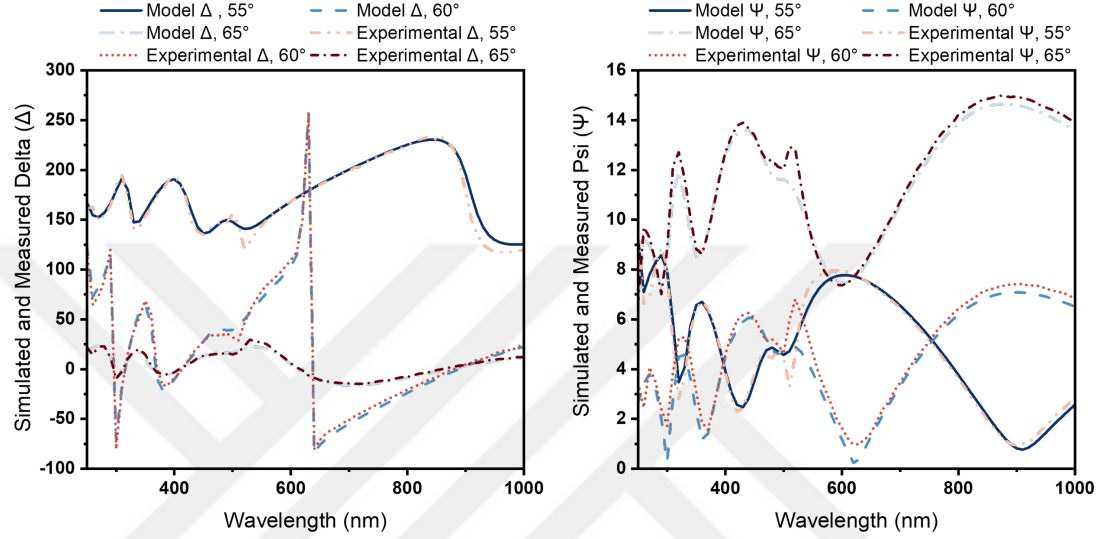


Figure 5.13: Measured and fitted Ψ and Δ spectra of dye-doped PMMA (60 mg/mL) thin film, obtained at 4000 rpm ($t = 334$ nm).

When the spin speed was increased to 4000 rpm, the film thickness reduced to 334 nm, with an MSE of 4.040. The good fitting quality shows the consistency between the experimental data and the simulation.

5.4.6 Cavity Thickness of 307 nm

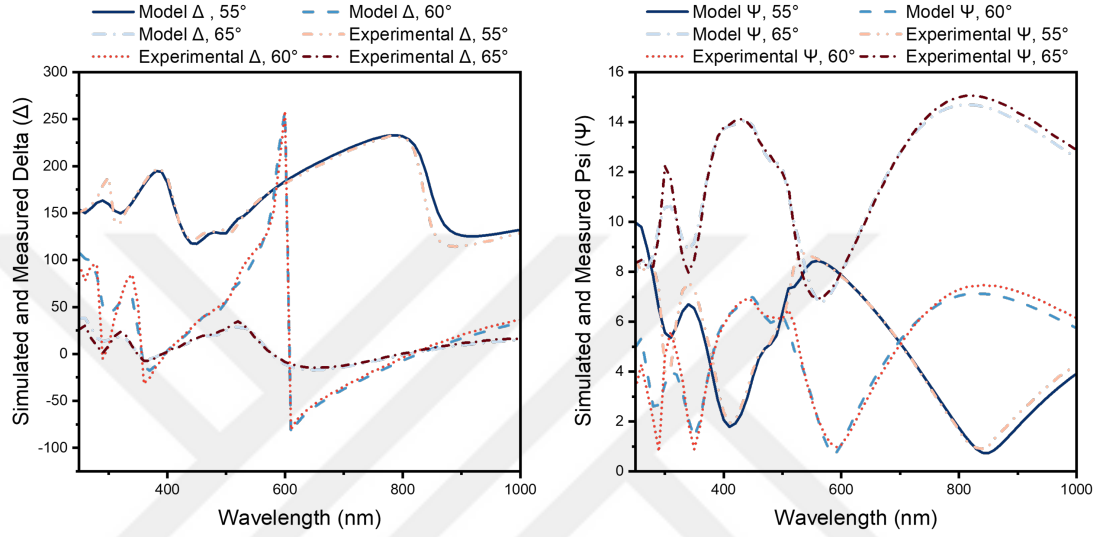


Figure 5.14: Measured and fitted Ψ and Δ spectra of dye-doped PMMA (60 mg/mL) thin film, obtained at 5000 rpm ($t = 307$ nm).

At the highest speed of 5000 rpm, the film reached a thickness of 307 nm, with a considerably low MSE of 2.243.

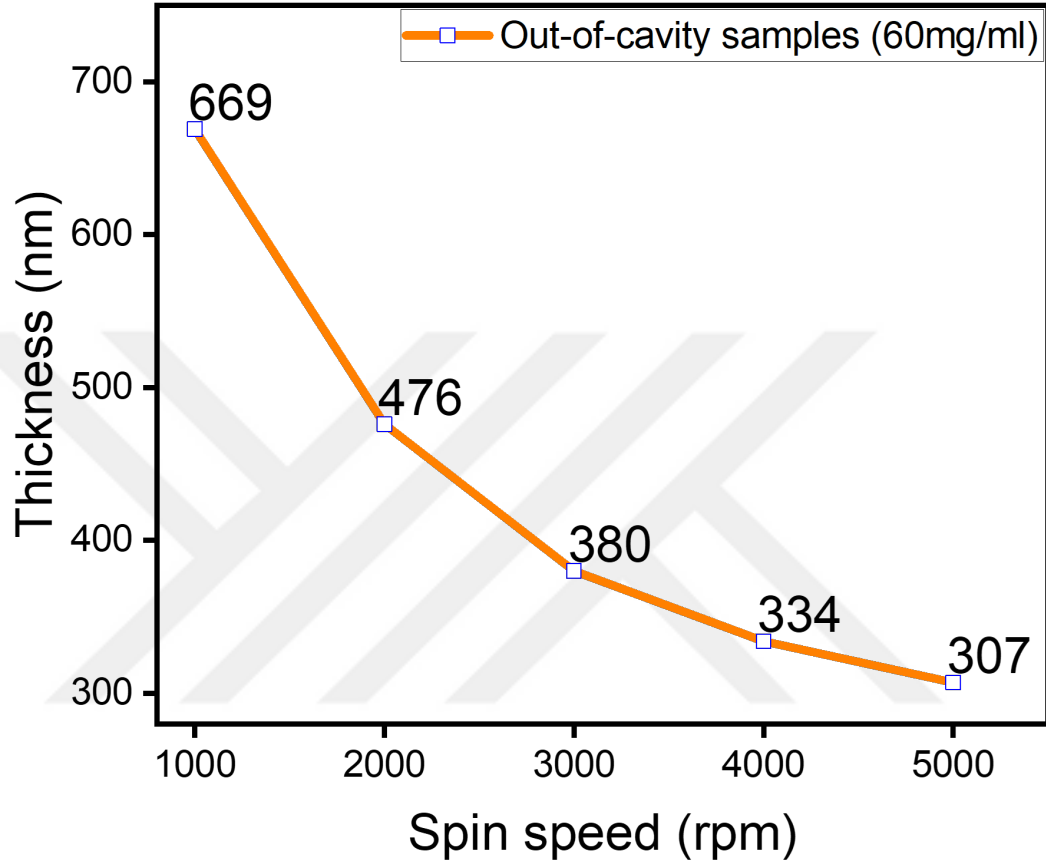


Figure 5.15: Thickness–rpm calibration for out-of-cavity fluorescein:PMMA films prepared from a (60 mg/mL) solution. Spin speed was swept from 1000 to 5000 rpm; ellipsometric thicknesses show the expected power-law decrease with rpm, and this higher-concentration batch yields thicker films at any given speed.

5.5 Validation by Transfer Matrix Method Simulation

For the out-of-cavity samples, we measured the film thickness directly using spectroscopic ellipsometry. However, it was not possible to measure the thickness of the in-cavity samples by ellipsometry because both the top and bottom surfaces were coated with Ag. These metal layers prevented light from passing through

the sample, making it impossible to perform ellipsometry measurements on the in-cavity films.

To estimate the thickness of the in-cavity samples, we used an indirect method. First, we measured the transmission spectra of the cavity samples using a Cary 5000 UV–Vis–NIR Spectrophotometer. These spectra revealed the positions of the transmission peaks of the cavities. Next, we simulated the transmission spectra using the Transfer Matrix Method (TMM). We adjusted the thickness of the dye-doped PMMA layer in the simulation and compared the results with the experimental spectra. By repeating this process and fine-tuning the thickness, we matched the simulated peaks with the experimental ones. This method allowed us to estimate the actual thickness of the in-cavity films with reasonable accuracy. The measured reference thicknesses, estimated in-cavity thicknesses, and Mean Square Error (MSE) values for both low dye concentration ($20\text{ }\mu\text{g/mL}$) and high dye concentration (60 mg/mL) samples at different spin-coating speeds are summarized in Tables 5.1 and 5.2.

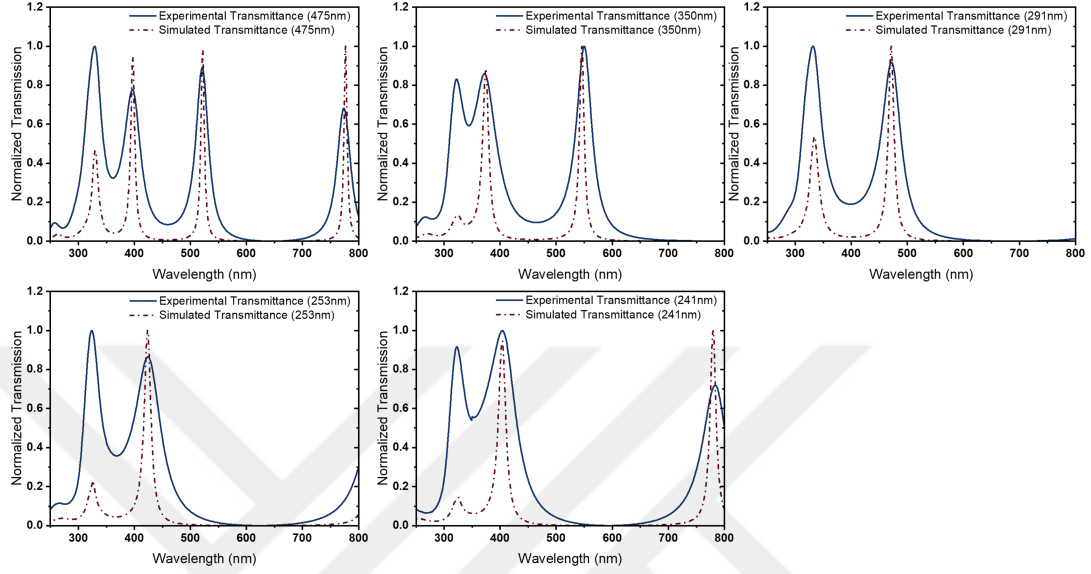


Figure 5.16: Measured and simulated transmittance spectra of dye-doped PMMA (low dye concentration, $20 \mu\text{g/mL}$) thin films prepared at five different spin-coating speeds, 1000 rpm (486 nm), 2000 rpm (349 nm), 3000 rpm (291 nm), 4000 rpm (253 nm), and 5000 rpm (240 nm). The comparison between experimental and simulated data shows good agreement, confirming the reliability of the optical model for low dye concentration samples.

Spin Speed(rpm)	In-Cavity thick.(nm)	Reference thick.(nm)	MSE
1000	475	486	1.946
2000	350	349	3.259
3000	291	291	2.312
4000	253	253	1.859
5000	241	240	2.342

Table 5.1: Measured film thickness of low dye concentration reference samples at various spin-coating speeds, obtained by ellipsometry. For cavity samples, thickness was estimated by matching experimental transmission spectra with simulated spectra using the (TMM).

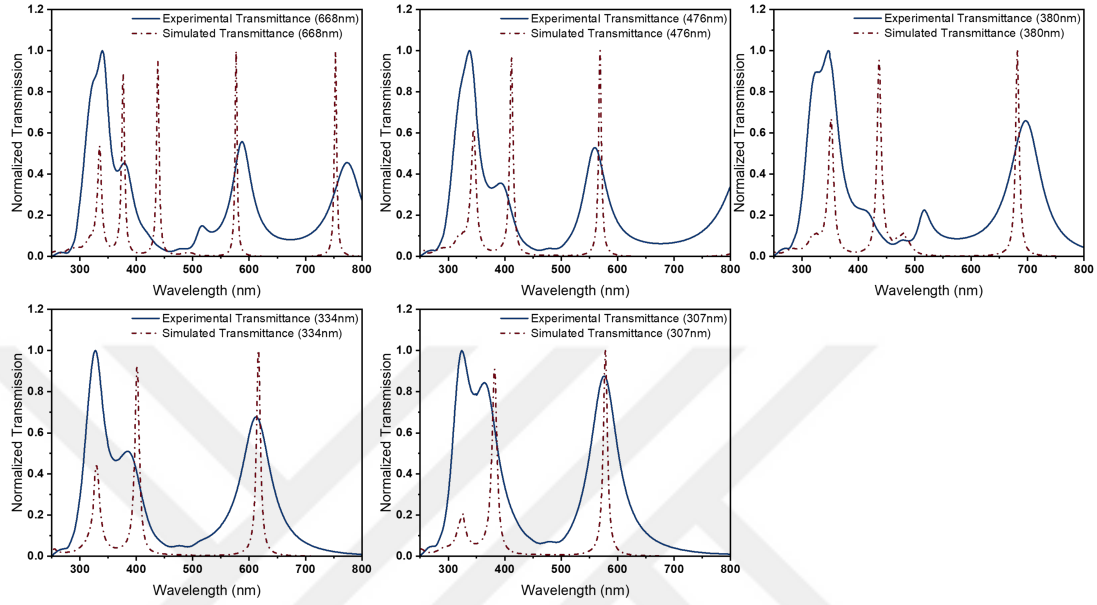


Figure 5.17: Measured and simulated transmittance spectra of dye-doped PMMA (high dye concentration, 60 mg/mL) thin films prepared at five different spin-coating speeds, 1000 rpm (669 nm), 2000 rpm (476 nm), 3000 rpm (380 nm), 4000 rpm (334 nm), and 5000 rpm (307 nm). The comparison between experimental and simulated data shows good agreement, confirming the reliability of the optical model for high dye concentration samples.

Spin Speed(rpm)	In-Cavity thick.(nm)	Reference thick.(nm)	MSE
1000	668	669	6.679
2000	476	476	5.295
3000	380	380	4.868
4000	334	334	4.040
5000	307	307	2.243

Table 5.2: Measured film thickness of high dye concentration reference samples (60 mg/mL) at various spin-coating speeds, obtained by ellipsometry. For cavity samples, thickness was estimated by matching experimental transmission spectra with simulated spectra using the TMM.

5.6 Summary

This chapter established the thickness and optical-constant baseline for fluorescein-doped PMMA films as a function of spin speed using spectroscopic ellipsometry (V-VASE). Reference (out-of-cavity) films were measured directly, while in-cavity films (Ag/PMMA/Ag) were thickness-estimated by matching experimental transmittance with transfer-matrix (TMM) simulations. Film thickness scales inversely with spin speed for both concentrations: low dye (20 $\mu\text{g/mL}$) gives {486, 349, 291, 253, 240} nm at {1000, 2000, 3000, 4000, 5000} rpm, and high dye (60 mg/mL) gives {669, 476, 380, 334, 307} nm at the same speeds.

For low dye concentration, a Cauchy model (transparent film) accurately fits Ψ, Δ with low MSE (1.86–3.26), yielding PMMA-like $n(\lambda)$, nearly flat across 400–1000 nm and rising below 400 nm. For high dye concentration, absorption requires a General Oscillator (Tauc–Lorentz) model to retrieve both $n(\lambda)$ and $k(\lambda)$, the spectra show a distinct k peak near 467 nm and the corresponding dispersive feature in n . Fit quality improves as thickness decreases (MSE 6.68–2.24 from 669 nm to 307 nm). TMM validation shows close agreement between simulated and measured spectra, supporting the inferred in-cavity thicknesses. These calibrated thicknesses and optical constants support the dispersion, reflectance, and coupling analyses developed in the following chapters.

Chapter 6

Optical Characterization: UV-Vis Spectroscopy

6.1 Chapter Overview

In this chapter, we present the optical characterization of the prepared fluorescein-doped PMMA films by analyzing their absorption and transmission spectra at both low and high dye concentrations. We measure samples placed inside the Fabry-Pérot cavity as well as out-of-cavity reference films, allowing a direct comparison of cavity-induced effects.

We begin with a pure PMMA film, which serves as a baseline reference. We then investigate a low-concentration sample ($20\text{ }\mu\text{g/mL}$), fabricated at various spin-coating speeds ranging from 1000 rpm (475 nm) to 5000 rpm (240 nm), and analyze its absorbance and transmission characteristics both inside and outside the cavity. Finally, we study the high-concentration samples (60 mg/mL) under the same conditions and compare their optical response to that of the low-concentration films, highlighting how to dye concentration and the presence of the optical cavity influence light absorption and transmission properties.

6.2 UV-Vis Spectroscopy

In UV-Vis spectroscopy, different molecules absorb specific amounts of energy that correspond directly to the energy gaps between their lower and upper electronic energy levels. The technique typically scans a wavelength range from 200 to 800 nm, producing spectra where the x-axis represents wavelength and the y-axis represents absorption, reflection, or transmission. At certain wavelengths, the sample absorbs a significant amount of light, producing a peak known as the maximum absorbance wavelength ($\lambda_{\max}$). The absorbance is directly dependent on the sample concentration; higher concentrations result in greater light absorption and increased peak intensity. This relationship is described by the Beer-Lambert law:

$$A = \varepsilon c l \quad (6.1)$$

where A is the absorbance, ε is the molar absorptivity ($\text{L mol}^{-1} \text{ cm}^{-1}$), c is the concentration of the solution (mol L^{-1}), and l is the path length of the cuvette (cm) or solid thin film sample[54, 55, 56].

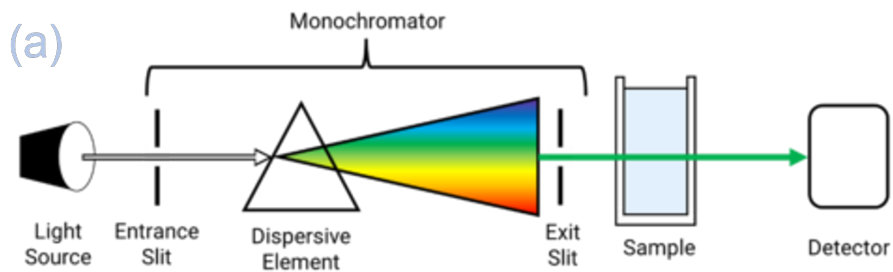


Figure 6.1: (a) Schematic diagram of a UV-Vis spectrophotometer showing the light source, monochromator, sample holder, and detector [6]. (b) Cary 5000 UV-Vis-NIR spectrophotometer used for absorbance and transmission measurements in this study (Cleanroom at Bilkent University, UNAM).

The UV-Vis spectrophotometer operates by passing light from a source through a monochromator, which separates the light into its component wavelengths. A selected wavelength beam then passes through the sample holder, where the sample absorbs part of the light. A photodetector detects the remaining transmitted light, and the absorbance is calculated based on the intensity difference between the incident and transmitted beams.

6.3 Bare PMMA Films

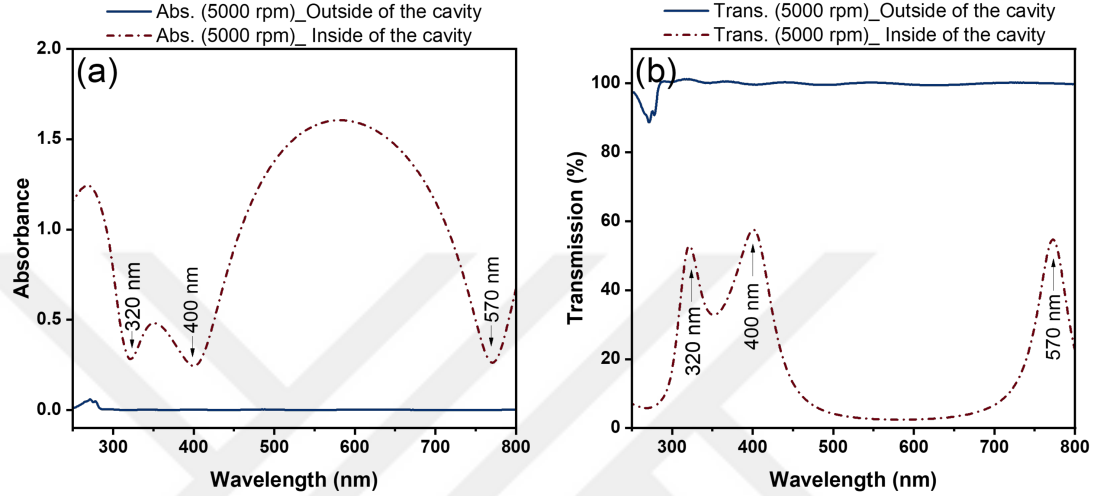


Figure 6.2: (a) Absorbance spectra and (b) transmission spectra of a pure PMMA thin film (5000 rpm) measured inside and outside the Fabry-Pérot cavity. This reference measurement characterizes the intrinsic optical response of the polymer layer without dye.

The pure PMMA film exhibits negligible absorption across the entire wavelength range of 300-800 nm, as shown in Figure 6.2(a). The solid blue line, corresponding to the out-of-cavity measurement, shows absorbance values close to zero, indicating that PMMA does not possess significant electronic transitions in this spectral region. Similarly, the transmission spectrum in Figure 6.2(b), also shown by the solid blue line, remains consistently near 100%, confirming the high optical transparency of PMMA when measured outside the Fabry-Pérot cavity.

When the same PMMA film is placed inside the Fabry-Pérot cavity, represented by the dashed red line, distinct optical resonances appear in both the absorbance and transmission spectra. Three cavity modes are observed, located approximately at 320 nm, 400 nm, and 570 nm. The peak near 320 nm is consistently present in all cavity measurements and is attributed to intrinsic optical features of the Ag mirrors rather than the PMMA film. The other peaks arise from cavity confinement effects. Importantly, no mode splitting or additional

spectral features are observed, indicating that there is no significant interaction between the PMMA matrix and the cavity modes.

6.4 Low-Concentration Fluorescein-Doped Films

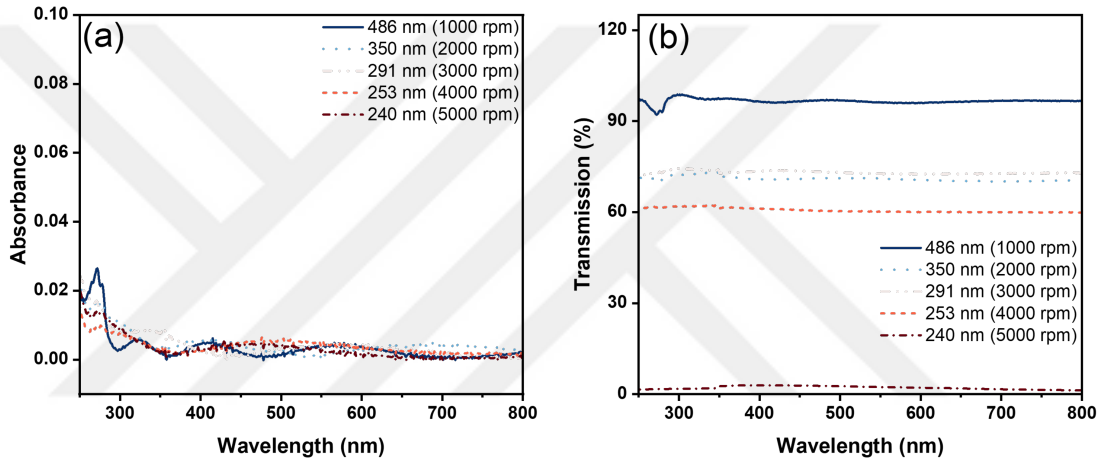


Figure 6.3: (a) Absorbance spectra and (b) transmission spectra of low-concentration fluorescein-doped PMMA films ($20 \mu\text{g/mL}$) measured outside the cavity at different spin-coating speeds, ranging from 1000 rpm (475 nm thickness) to 5000 rpm (240 nm thickness). Transmission decreases with increasing spin speed due to reduced film thickness.

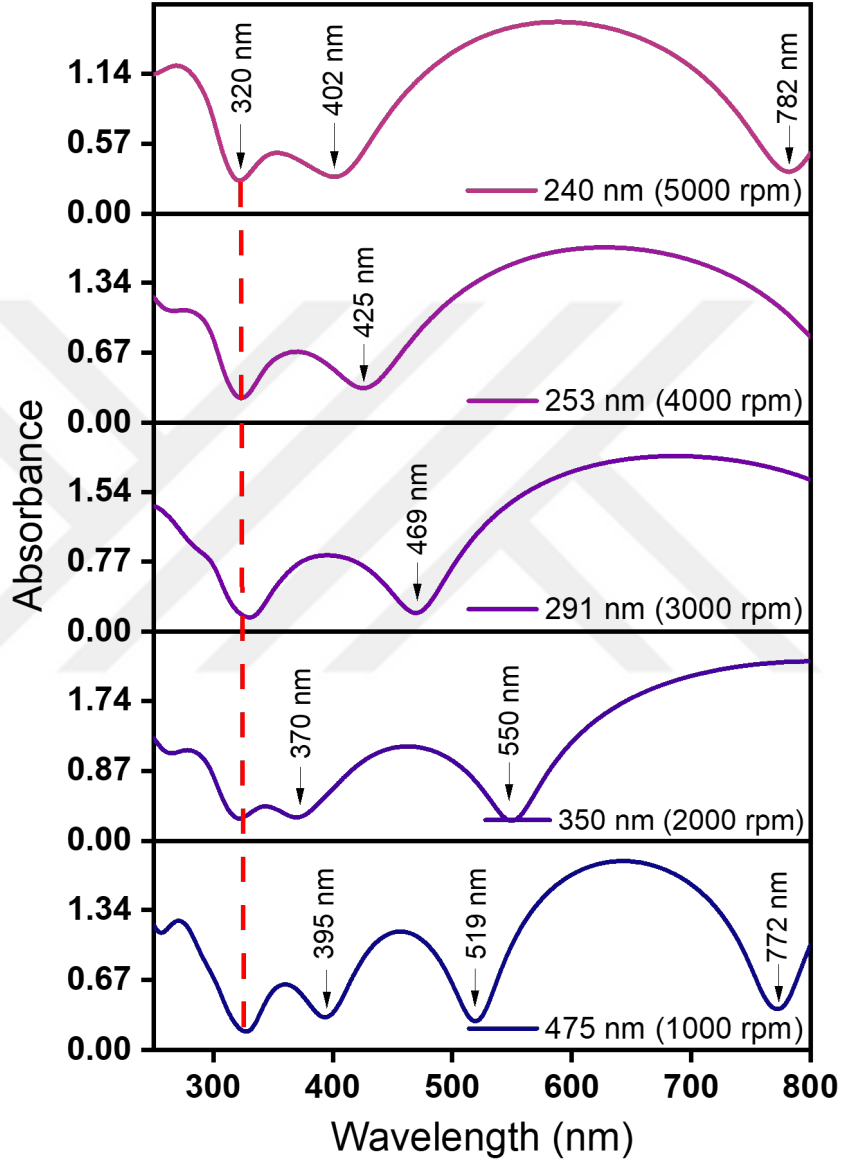


Figure 6.4: Absorbance spectra of low-concentration fluorescein-doped PMMA films ($20 \mu\text{g/mL}$) measured inside the Fabry-Pérot cavity. The cavity introduces slight modifications to the absorption profile due to internal reflections.

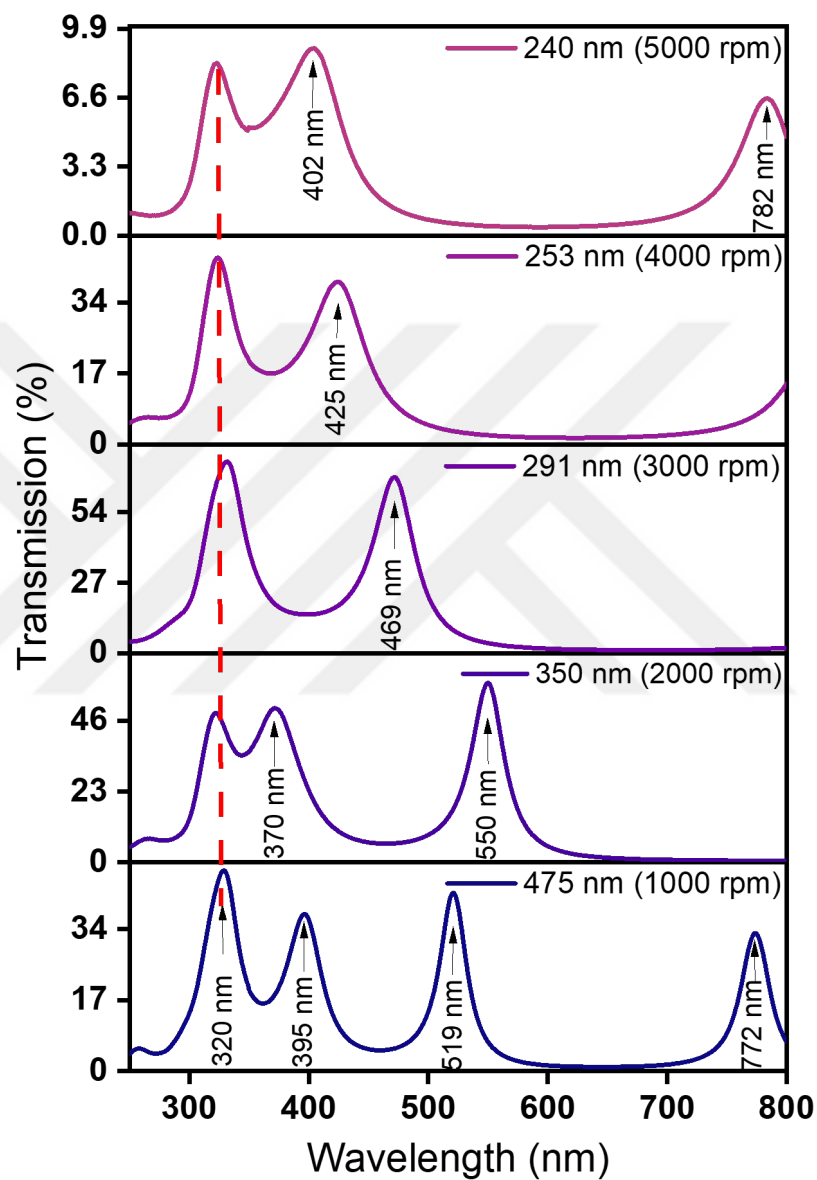


Figure 6.5: Transmission spectra of low-concentration fluorescein-doped PMMA films ($20 \mu\text{g/mL}$) measured inside the Fabry-Pérot cavity. Interference fringes are observed due to cavity resonance effects, altering the transmission behavior compared to the out-of-cavity samples.

The absorbance and transmission spectra of low-concentration fluorescein-doped PMMA films ($20 \mu\text{g/mL}$) measured outside the Fabry-Pérot cavity are shown in

Figure 6.3. At this very low dye loading, the absorbance remains close to zero across the measured wavelength range, and the small fluctuations observed are attributed to the presence of weak cavity modes, even without an optical cavity, rather than to true dye absorption. Transmission remains high (typically above 90%) and does not display any significant features, indicating that the films are effectively transparent at this concentration.

When measured inside the Fabry–Pérot cavity, shown in Figure 6.4 (absorbance) and Figure 6.5 (transmission), distinct cavity resonances become apparent. These resonances are not related to dye absorption but are instead optical modes created by multiple reflections inside the cavity. The number and wavelengths of these modes vary with film thickness, as summarized in Table 6.1.

A consistent resonance near 320 nm is observed across all measurements and originates from the intrinsic optical response of the Ag mirrors. Other cavity modes shift with film thickness due to changes in the optical path length of the cavity.

Table 6.1: Observed cavity mode positions for low-concentration (20 $\mu\text{g/mL}$) fluorescein-doped PMMA films at different spin speeds.

Spin Speed (rpm)	Number of Modes	Mode Wavelengths (nm)
1000	4	320, 395, 519, 772
2000	3	320, 370, 550
3000	2	320, 469
4000	2	320, 425
5000	3	320, 402, 782

6.5 High-Concentration Fluorescein-Doped Films

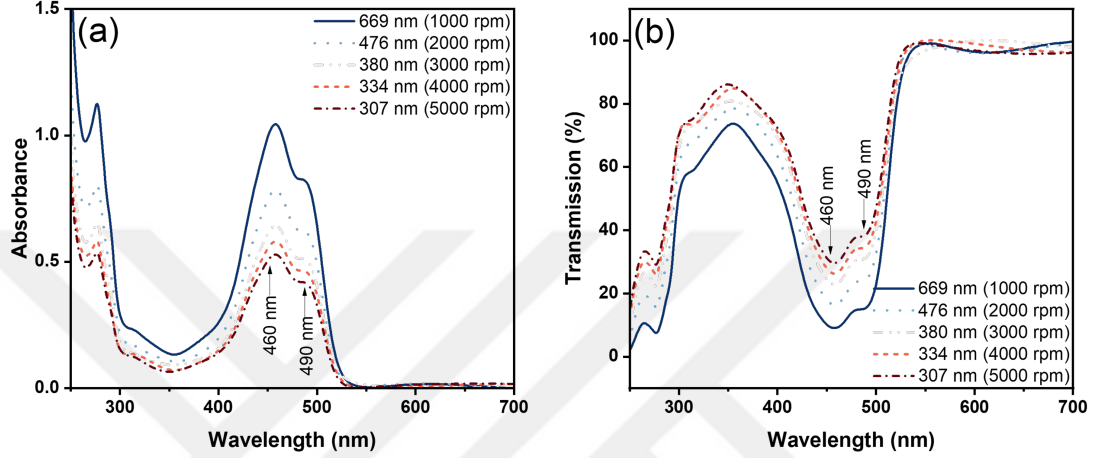


Figure 6.6: (a) Absorbance and (b) transmission spectra of high-concentration fluorescein-doped PMMA films (60 mg/mL) measured outside the cavity at different spin-coating speeds: 1000 rpm (669 nm), 2000 rpm (476 nm), 3000 rpm (380 nm), 4000 rpm (334 nm), and 5000 rpm (307 nm). Stronger absorption and lower transmission are observed compared to low-concentration samples due to the higher optical density at elevated dye loading.

All measurements for the high-concentration fluorescein-doped PMMA films (60 mg/mL) were also performed at a normal incidence angle of 0° . The absorbance and transmission spectra measured outside the Fabry-Pérot cavity are shown in Figure 6.6, where the solid blue line represents the 1000 rpm film and other colors correspond to progressively higher spin speeds (thinner films). Compared to low dye concentration films, these samples exhibit significantly stronger excitonic peak absorption in the visible region with one main peak at 460 nm and a shoulder at 490 nm. On the other hand, transmission is greatly reduced, dropping below 20% for thicker films (i.e., 1000 rpm), demonstrating that we now have enough molecules that can absorb light and are responsible for the reduction of transmission. When cavity samples with the same film thicknesses were measured (Figure 6.7), not only were optical cavity modes detected due to cavity confinement, but the strong spectral characteristics of the dye itself were also

observed.

The cavity introduces multiple optical resonances, represented by the dashed red lines, which partially overlap with the intrinsic dye absorption bands. Transmission spectra are also (Figure 6.8) exhibit pronounced Fabry–Pérot resonances with overall transmission significantly attenuated throughout the spectrum.

The number and spectral positions of the cavity modes at each spin speed are summarized in Table 6.2. A constant mode near 320 nm appears again for all films and is attributed to the Ag mirrors, while other modes shift with thickness and overlap with the dye’s absorption regions. At high dye loading, cavity modes are strongly damped, indicating intense photon absorption by the film. Despite the increased absorption, no distinct mode splitting is observed, meaning that at normal incidence (0°), even though the concentration is high, the system remains in the weak coupling regime.

Table 6.2: Observed cavity mode positions for high-concentration (60 mg/mL) fluorescein-doped PMMA films at different spin speeds.

Spin Speed (rpm)	Number of Modes	Mode Wavelengths (nm)
1000	4	320, 378, 586, 771
2000	3	320, 392, 558
3000	3	320, 347, 696
4000	3	320, 385, 612
5000	3	320, 365, 575,

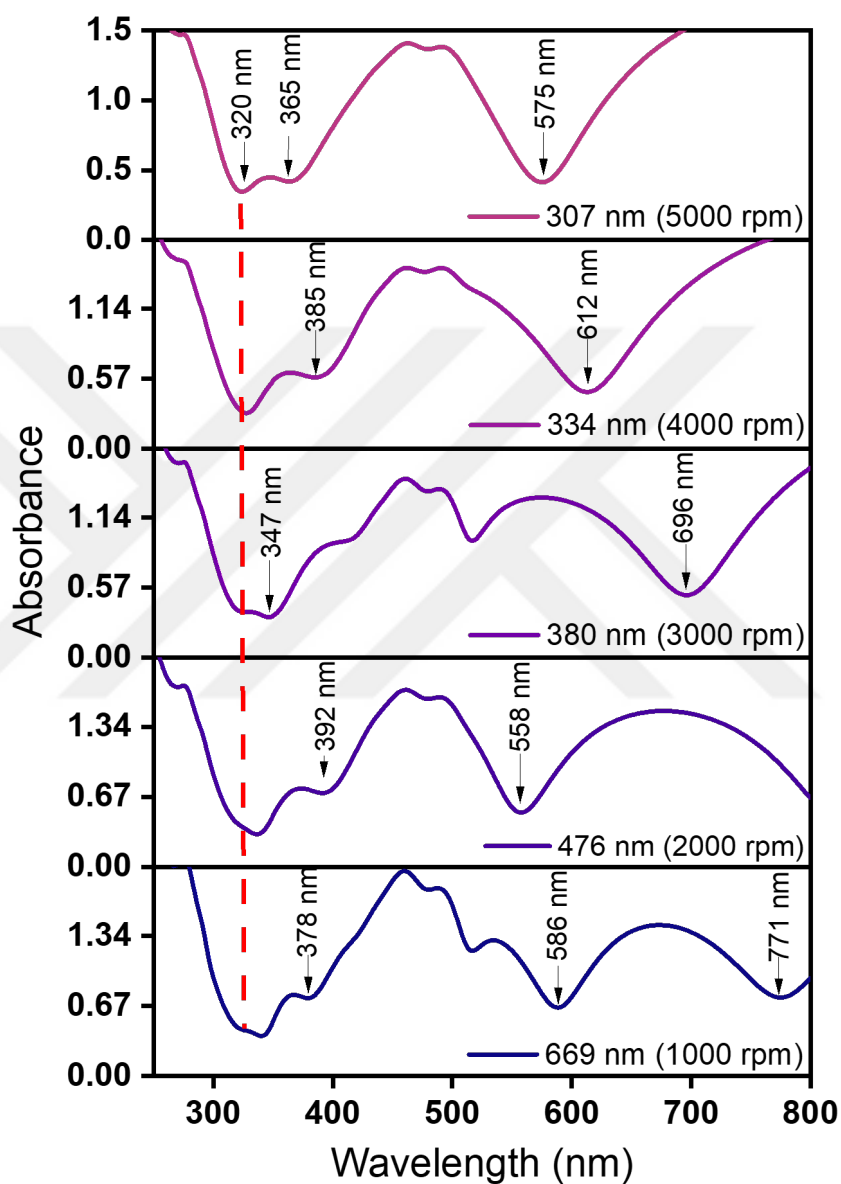


Figure 6.7: Absorbance spectra of high-concentration fluorescein-doped PMMA films (60 mg/mL) measured inside the Fabry-Pérot cavity. Enhanced absorption and slight spectral modifications occur due to higher dye loading and cavity-induced interference.

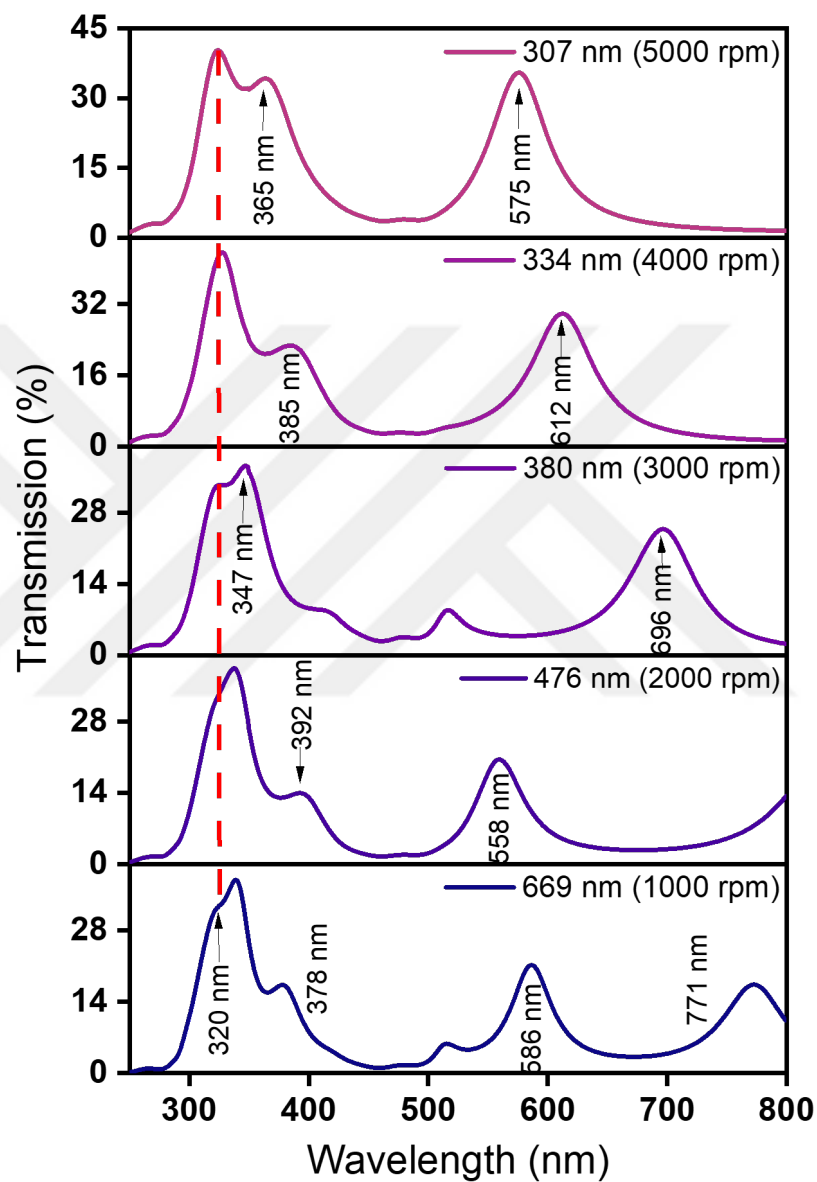


Figure 6.8: Transmission spectra of high-concentration fluorescein-doped PMMA films (60 mg/mL) measured inside the Fabry-Pérot cavity. Pronounced Fabry-Pérot fringes and significantly reduced transmission highlight strong light attenuation within the cavity.

6.6 Summary

This chapter presented an optical characterization of fluorescein-doped PMMA thin films using UV-Vis spectroscopy. Pure PMMA films exhibited negligible absorption, whereas low-concentration films remained largely transparent with only Fabry–Pérot interference effects. High-concentration films demonstrated pronounced absorption peaks and reduced transmission. When measured inside the Fabry–Pérot cavity, both concentrations exhibited optical resonances, which became weaker with increasing dye concentration. The findings indicate that dye loading and cavity confinement strongly influence the absorption and transmission characteristics of the thin films.

Chapter 7

Steady-State Fluorescence Response of Fluorescein-Doped PMMA in Fabry-Pérot Cavities

7.1 Chapter Overview

In this chapter, we study the effect of Fabry-Pérot cavities on the steady-state fluorescence of fluorescein-doped PMMA films. Our goal is to investigate how cavity confinement, dye concentration, and cavity thickness affect the fluorescence behavior of these thin films. In this study, we used the FL3-21. Horiba Jobin Yvon Fluorolog 3-21 fluorescence spectrophotometer. We begin by comparing the excitation and emission spectra of fluorescein recorded outside the cavity with those measured inside the cavity. This comparison enables us to examine changes in spectral peak positions, fluorescence intensity, and Stokes shift resulting from the optical environment created by the cavity.

7.2 Fluorescence

The process of radiative decay from the electronically excited singlet state $S_1 \rightarrow S_0$ with photon emission is called fluorescence. When a molecule absorbs light, it gains energy and is promoted to a higher electronic state. The excited molecule then relaxes back to the ground state, typically after undergoing vibrational relaxation and internal conversion[57]. Since part of the absorbed energy is dissipated non-radiatively during these processes, the emitted photon always has lower energy (longer wavelength) compared to the absorbed photon. This red shift in the emission spectrum relative to the absorption spectrum is known as the Stokes shift. Fluorescence typically occurs on the nanosecond timescale (10^{-9} - 10^{-8} s), which makes it distinct from the much slower process of phosphorescence (microseconds to seconds).

Once a molecule is promoted to a higher energy level, it may take several pathway to comeback to the ground state. Several deactivation pathways compete, such as radiative decay (k_r), quenching by the environment, internal conversion (k_{nr}), , intersystem crossing to the triplet state (T_1). There are two quantities we can measure to quantify the effectiveness of this decay[58].

The fluorescence quantum yield Φ_F and the lifetime τ , defined as

$$\Phi_F = \frac{k_r}{k_r + k_{nr}}, \quad \tau = \frac{1}{k_r + k_{nr}}, \quad (7.1)$$

which can be rearranged to give

$$k_r = \frac{\Phi_F}{\tau}, \quad k_{nr} = \frac{1 - \Phi_F}{\tau}. \quad (7.2)$$

Structural rigidity or reduced vibrational coupling suppresses non-radiative channels (k_{nr}), resulting in higher quantum yield Φ_F .

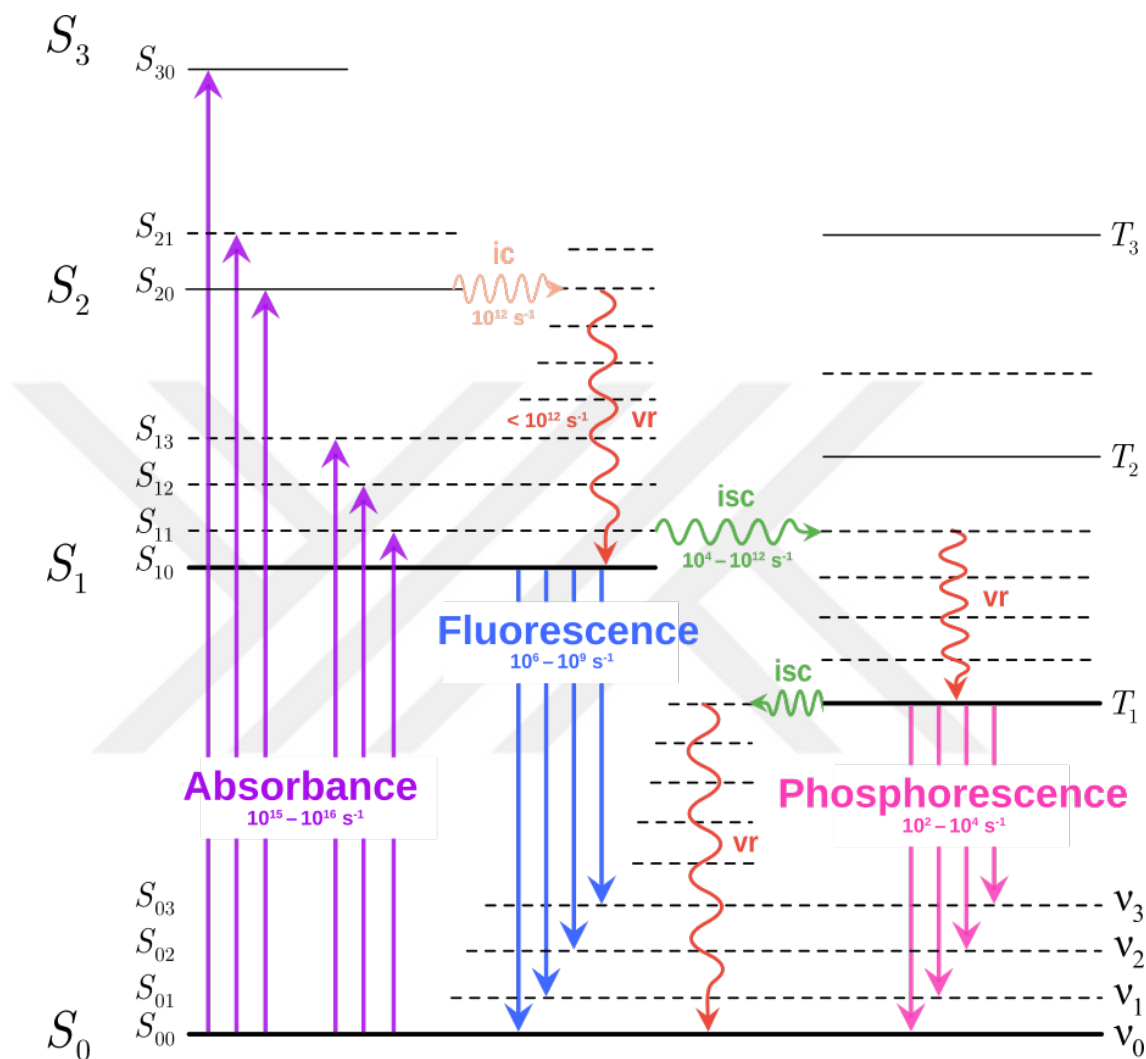


Figure 7.1: Jablonski diagram illustrating the main photophysical processes in organic molecules. Vertical arrows represent photon absorption ($S_0 \rightarrow S_n$) and radiative emission (fluorescence from $S_1 \rightarrow S_0$ and phosphorescence from $T_1 \rightarrow S_0$). Curved arrows indicate non-radiative processes: vibrational relaxation (vr), internal conversion (ic), and intersystem crossing (isc). Typical timescales for each process are shown, highlighting that fluorescence occurs on the nanosecond scale while phosphorescence is significantly slower[7].

7.3 Fluorescence of Bare PMMA Film and Fluorescein Dye Spectra

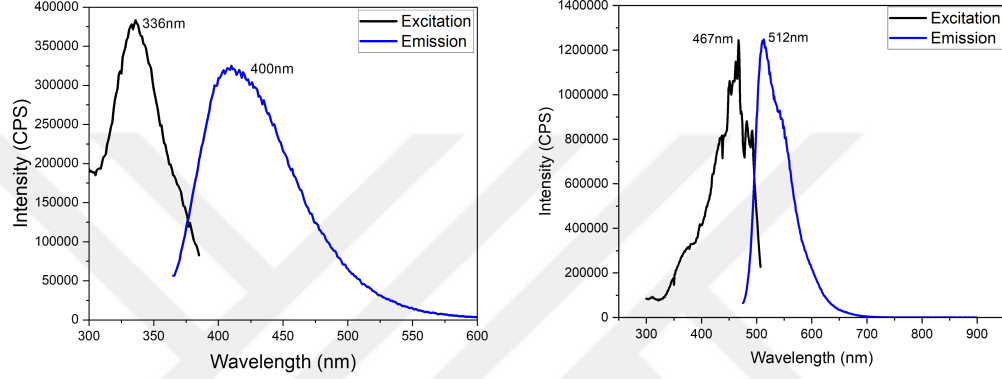


Figure 7.2: Excitation and emission spectra of pure PMMA (left) and fluorescein in solution (right). These measurements show the typical behavior of PMMA and fluorescein and are used as a reference for comparison with the doped films.

The reference spectra highlight three points relevant to the cavity data that follow. (i) Pure PMMA shows a weak UV excitation peak at ~ 336 nm with blue emission centered near ~ 400 nm; this band is far from the green emission window used later, so PMMA contributes only a small background to the 500 nm detection range. (ii) Fluorescein exhibits a strong excitation band near ~ 467 nm and green emission at ~ 512 nm, giving a Stokes shift of ~ 45 nm. These wavelengths are used throughout the chapter as fixed reference lines when comparing to angle-resolved reflectance/ellipsometry. (iii) The large intensity difference between the fluorescein emission and the PMMA background explains the high signal-to-background ratio observed for doped films in the emission window.

The peak positions and corresponding photon energies are summarized below (using $E = \frac{hc}{\lambda}$ with $hc = 1240$ eV nm).

Material	λ_{exc} (nm)	E_{exc} (eV)	λ_{em} (nm)	E_{em} (eV)
PMMA	336	≈ 3.69	400	≈ 3.10
Fluorescein	467	≈ 2.66	512	≈ 2.42

Stokes shift: PMMA ≈ 64 nm (~ 0.59 eV); Fluorescein ≈ 45 nm (~ 0.24 eV).

Because fluorescein's absorption band is broad, in later modeling we represent it with two excitonic oscillators to capture the vibronic envelope; the single peak at ~ 467 nm here provides the central reference for that treatment.

7.4 Fluorescence Behavior of Out-of-Cavity Control Samples

We studied the outside of the cavity spectra to obtain a reference for cavity samples of both low and high dye concentration. We measure the emission spectra by exciting the sample with various excitation wavelengths ranging from 300 nm to 450 nm, and also measure the excitation by providing different emission wavelengths starting from 400 to 550 nm.

7.4.1 Excitation and Emission Spectra at Low Dye Concentration

7.4.1.1 Control Sample with 475 nm Thickness

Excitation Spectra: The excitation spectra of the 475 nm thick fluorescein-doped PMMA film were recorded at several fixed emission wavelengths ranging from 400 nm to 550 nm. At an emission wavelength of 400 nm, a sharp and prominent excitation peak was observed at around 335 nm, corresponding to the intrinsic fluorescence of the PMMA matrix. This observation aligns well with

previous studies that reported UV-induced luminescence of PMMA(Ellingwood et al., 2022).

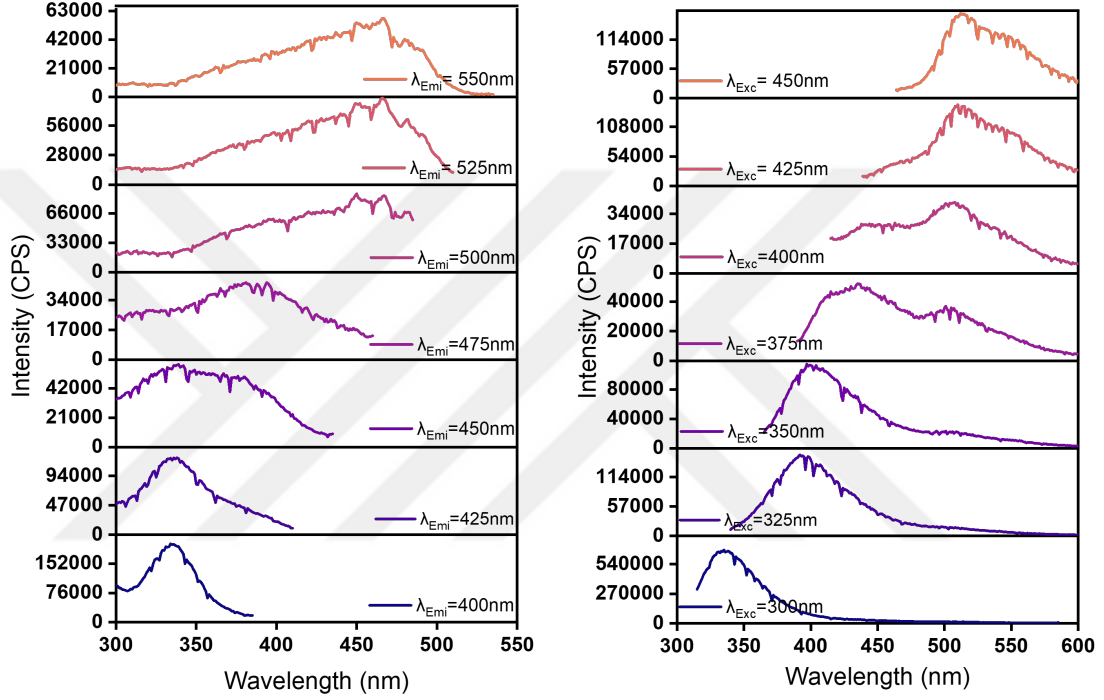


Figure 7.3: Excitation and emission spectra of 475 nm thick fluorescein-doped PMMA Film (low dye concentration, out-of-cavity). Excitation (left) and emission (right) spectra show a transition from PMMA-dominated fluorescence at lower wavelengths to fluorescein-dominated fluorescence at higher wavelengths.

As the emission wavelength increased to 425 nm and 450 nm, the 335 nm excitation peak began to broaden, and its intensity decreased slightly. Additionally, a new excitation feature began to emerge, corresponding to the known absorption of fluorescein. When the emission wavelength was further increased to 500 nm, 525 nm, and 550 nm, the excitation peak at 335 nm, attributed to PMMA, became almost negligible. Instead, the excitation spectra in this region were dominated by the fluorescein peak around 467 nm. These observations indicate a clear transition from PMMA-dominated excitation at lower emission wavelengths to fluorescein-dominated excitation at higher emission wavelengths.

This suggests that at lower excitation energies in the UV region, PMMA is primarily responsible for the fluorescence response observed around 400–450 nm, while at higher excitation energies in the visible region, fluorescein becomes the dominant fluorophore.

Emission Spectra: The emission spectra of the same sample were also analyzed by varying the excitation wavelength from 300 nm to 450 nm. At lower excitation wavelengths of 300 nm, 325 nm, and 350 nm, the emission spectra exhibited a strong PMMA emission peak around 400 nm, along with a minor contribution from fluorescein emission at longer wavelengths, though the intensity of the fluorescein peak was low. As the excitation wavelength increased to 375 nm and 400 nm, the emission spectra broadened and started showing a shoulder at 510 nm, indicating that the emission from fluorescein, along with PMMA emission. This suggests that some of the energy absorbed by PMMA is transferred to fluorescein, leading to its emission, a possible indication of Förster Resonance Energy Transfer (FRET). When excited at 425 nm and 450 nm, the emission spectra were dominated by fluorescein, with its characteristic emission band appearing between 500 nm and 550 nm, and PMMA's contribution became negligible. This emission behavior closely matches the trends observed in the excitation spectra, confirming a gradual transition from PMMA-dominated to fluorescein-dominated fluorescence as the excitation wavelength increased.

7.4.1.2 Control Sample with 350 nm Thickness

Excitation Spectra: The excitation spectra of the 350 nm thick fluorescein-doped PMMA film show a similar trend to thicker samples. The 335 nm PMMA excitation peak appears strongly at 400 nm emission, but becomes broader and weaker as the emission wavelength increases. The fluorescein excitation peak around 467 nm takes over at 500 nm emission and above. In this thinner sample, the fluorescein peak appears narrower, which may be due to reduced scattering or film effects.

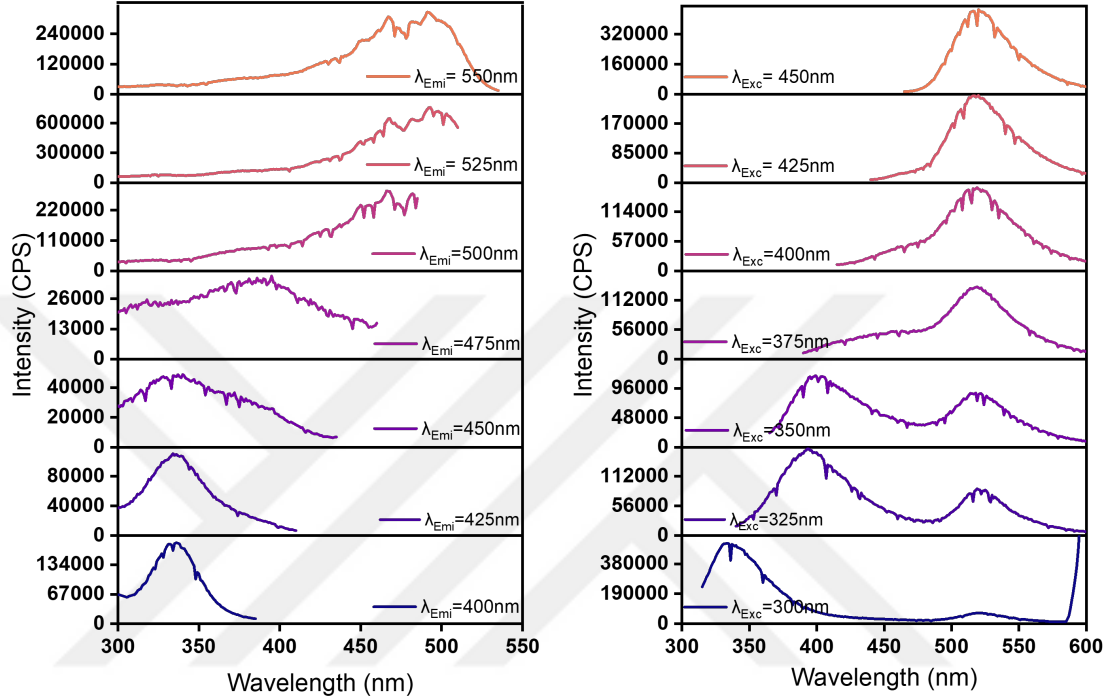


Figure 7.4: Excitation and emission spectra of 350 nm thick fluorescein-doped PMMA Film (low dye concentration, out-of-cavity). Excitation (left) and emission (right) spectra show a transition from PMMA-dominated fluorescence at lower wavelengths to fluorescein-dominated fluorescence at higher wavelengths.

Emission Spectra: The emission spectra also follow the same trend, but fluorescein emission is more pronounced at low excitation wavelengths (300–350 nm) compared to thicker samples. This suggests stronger interaction or possible energy transfer (FRET) between PMMA and fluorescein in the thinner film. As the excitation wavelength increases (375–400 nm), the fluorescein emission grows, and PMMA’s peak decreases. At 425 nm and 450 nm excitation, fluorescein dominates the emission spectrum.

7.4.1.3 Control Sample with 291 nm Thickness

Excitation Spectra: The excitation spectra of the 291 nm thick fluorescein-doped PMMA film inside the cavity show the same behavior as in thicker samples. The PMMA excitation peak at 335 nm appears clearly at 400 nm emission and weakens as the emission wavelength increases. The fluorescein excitation near 467 nm appears at higher emission wavelengths, following the same pattern as seen in the 475 nm and 350 nm cases. However, the excitation spectrum is broader just in the 475nm sample case and shows opposite results compared to the 350nm case. Here, the fluorescein excitation peak is narrow.

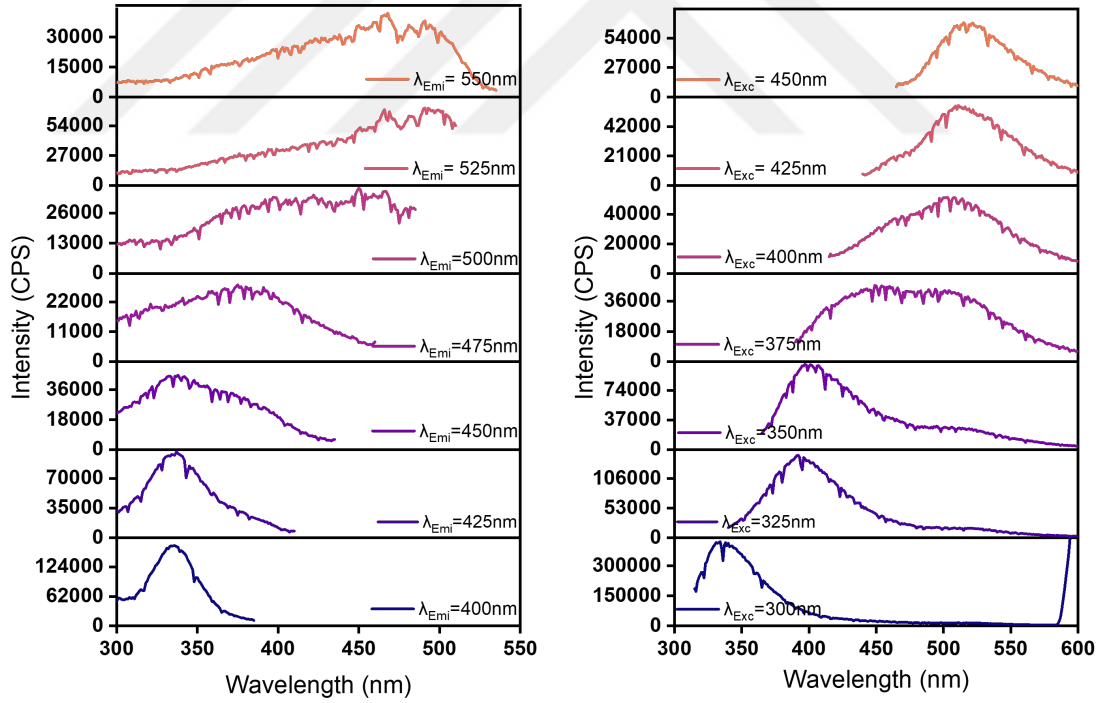


Figure 7.5: Excitation and emission spectra of 291 nm thick fluorescein-doped PMMA Film (low dye concentration, out-of-cavity). Excitation (left) and emission (right) spectra show a transition from PMMA-dominated fluorescence at lower wavelengths to fluorescein-dominated fluorescence at higher wavelengths.

Emission Spectra: The emission spectra also follow a similar trend. At

low excitation wavelengths (300–350 nm), PMMA emission remains dominant, and fluorescein emission stays weak, comparable to thicker films. This suggests that FRET is not enhanced in the 291 nm sample. As the excitation increases (375–400 nm), fluorescein emission grows while PMMA fades. At 425 nm and 450 nm excitation, the emission is dominated by fluorescein.

7.4.1.4 Control Sample with 253 nm Thickness

Excitation Spectra: The excitation and emission spectra of the 253 nm thick fluorescein-doped PMMA film inside the cavity show the same pattern as in the thicker samples. The PMMA excitation peak at 335 nm is strong at lower emission wavelengths and becomes weaker as the emission wavelength increases. At higher emission wavelengths, the fluorescein excitation peak around 467 nm takes over.

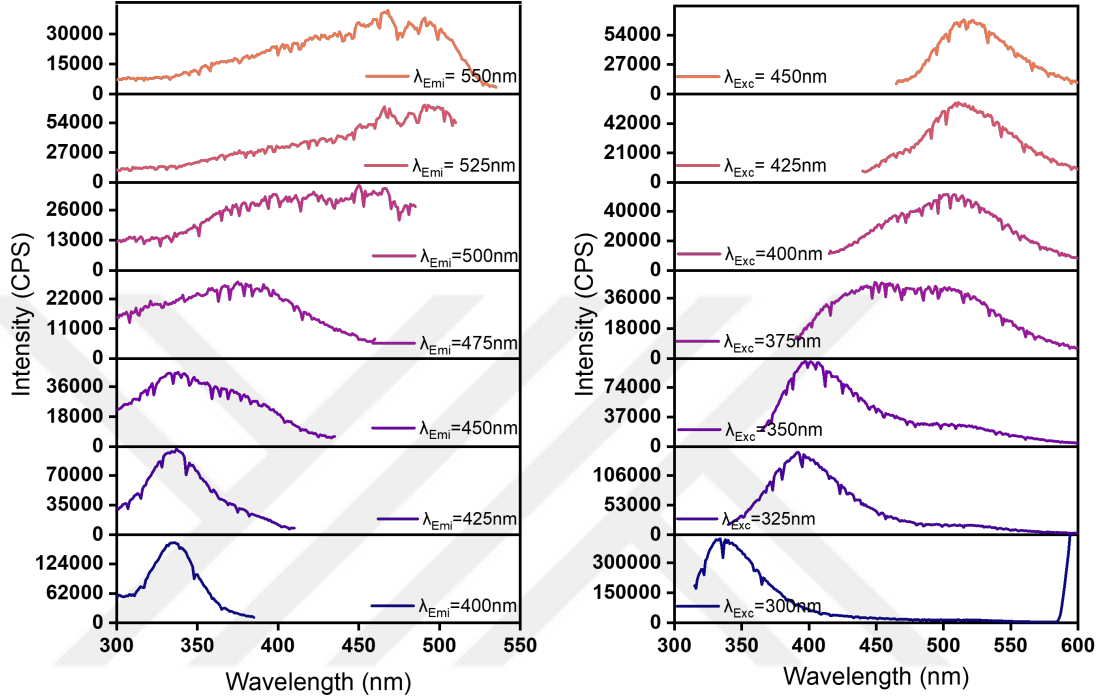


Figure 7.6: Excitation and emission spectra of 253 nm thick fluorescein-doped PMMA Film (low dye concentration, out-of-cavity). Excitation (left) and emission (right) spectra show a transition from PMMA-dominated fluorescence at lower wavelengths to fluorescein-dominated fluorescence at higher wavelengths.

Emission Spectra: In the emission spectra, PMMA gives the main emission at low excitation wavelengths (300–350 nm), while fluorescein also appears, but with lower intensity. This means there is some FRET happening, but it is less noticeable than in the 350 nm sample. As the excitation wavelength increases (375–450 nm), the emission shifts to fluorescein-dominated, just like in the thicker samples.

7.4.1.5 Control Sample with 240 nm Thickness

Excitation Spectra: The excitation and emission spectra of the 240 nm thick fluorescein-doped PMMA film outside the cavity show the same general trend

as the thicker out-of-cavity samples. The PMMA excitation peak at 335 nm is strong at lower emission wavelengths but weakens as the emission wavelength increases. At higher emission wavelengths, the fluorescein excitation around 467 nm becomes dominant.

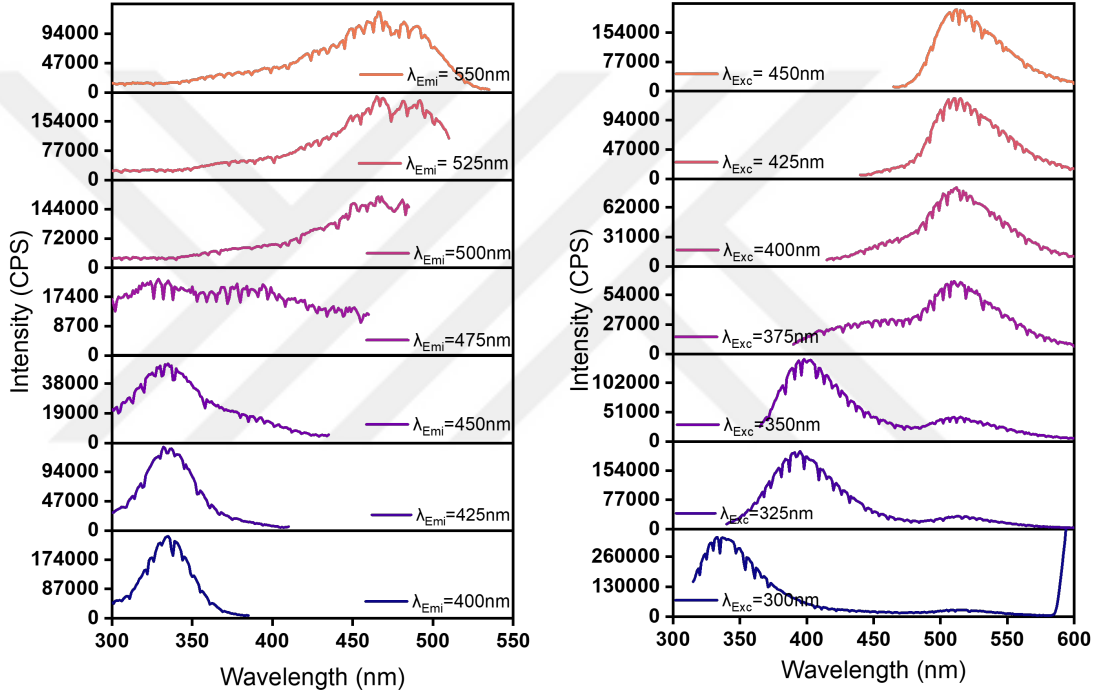


Figure 7.7: Excitation and emission spectra of 240 nm thick fluorescein-doped PMMA Film (low dye concentration, out-of-cavity). Excitation (left) and emission (right) spectra show a transition from PMMA-dominated fluorescence at lower wavelengths to fluorescein-dominated fluorescence at higher wavelengths.

Emission Spectra: In the emission spectra, PMMA fluorescence is dominant at low excitation wavelengths (300–350 nm), with fluorescein emission appearing but still weaker. This suggests that FRET is present but weak, similar to the other out-of-cavity films. As the excitation wavelength increases (375–450 nm), the emission shifts to being mostly fluorescein-dominated, following the same pattern seen in the other out-of-cavity cases.

7.4.2 Excitation and Emission Spectra at High Dye Concentration

7.4.2.1 Control Sample with 669 nm Thickness

Excitation Spectra: When we measured the excitation spectra of the 669 nm thick high-concentration sample, we still saw a PMMA peak at 335 nm when the emission was set at 400 nm. However, as we increased the emission wavelength, this PMMA peak faded, and the excitation became fully dominated by the fluorescein peak around 467 nm. This shows that at high dye concentration, fluorescein strongly controls the excitation, with only a small PMMA signal at low emission wavelengths.

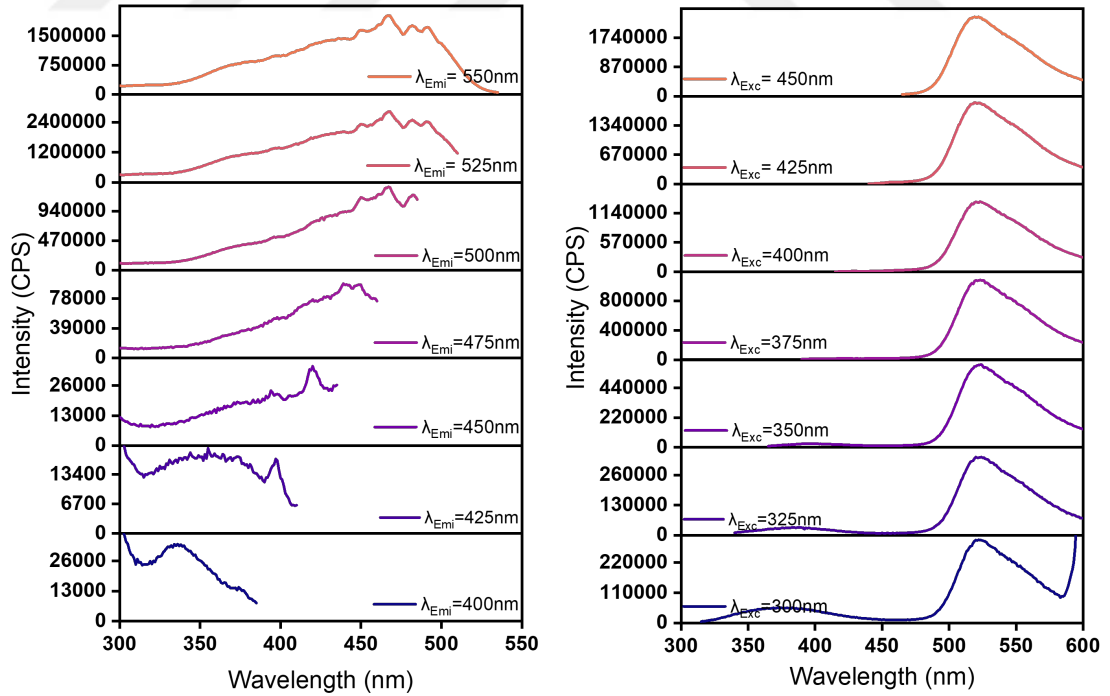


Figure 7.8: Excitation (left) and emission (right) spectra of the 669 nm thick fluorescein-doped PMMA film (high dye concentration, out-of-cavity). The spectra show that fluorescein dominates both excitation and emission, while PMMA contributes only at low emission or excitation wavelengths.

Emission Spectra: In the emission spectra, when we excited the sample at 300 nm, we saw a weak PMMA emission around 400 nm, but fluorescein was already the main contributor. As we moved to higher excitation wavelengths, the emission came almost entirely from fluorescein, with its peak between 500 nm and 550 nm, and the PMMA signal almost disappeared. Overall, this means that in the high-concentration case, fluorescein dominates both excitation and emission, and PMMA plays only a minor role.

7.4.2.2 Control Sample with 476 nm Thickness

Excitation Spectra: For the 476 nm sample, the excitation spectra are mainly dominated by the fluorescein peak around 470 nm. The PMMA peak at 335 nm appears only weakly when the emission wavelength is set at 400 nm. This behavior is consistent with the results observed for the 669 nm sample.

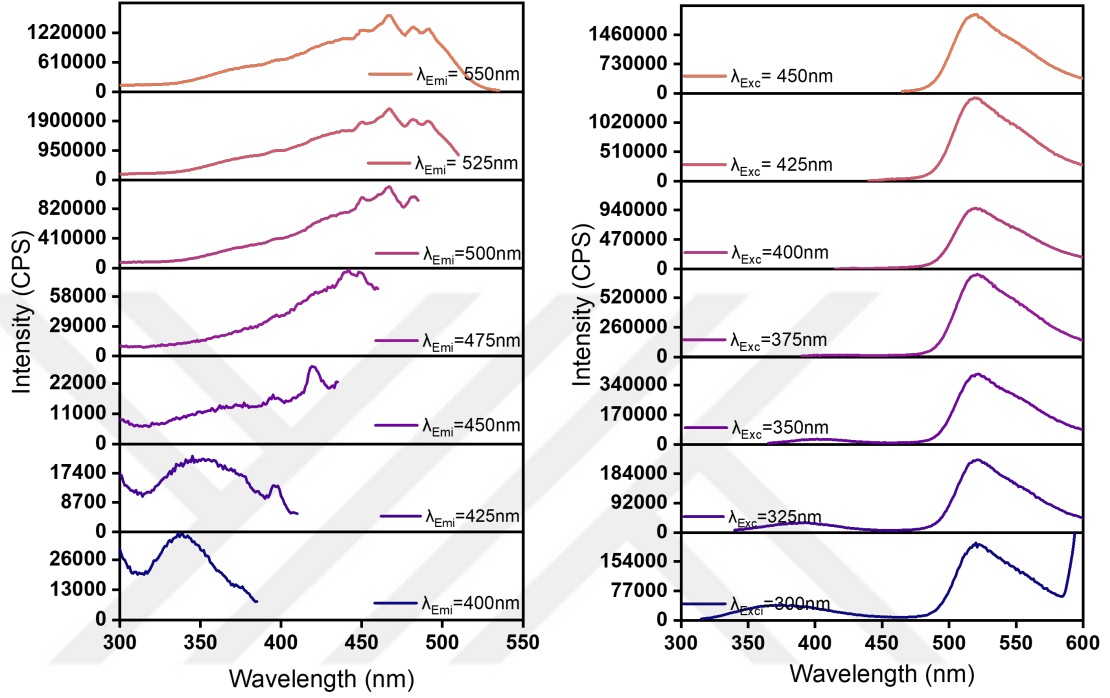


Figure 7.9: Excitation (left) and emission (right) spectra of the 476 nm thick fluorescein-doped PMMA film (high dye concentration, out-of-cavity). The spectra show that fluorescein dominates both excitation and emission, while PMMA contributes only at low emission or excitation wavelengths.

Emission Spectra: The emission spectra show strong fluorescein emission with a broad peak around 520–530 nm. PMMA emission is very weak and only appears at the lowest excitation wavelengths. This trend is in good agreement with the findings from the 669 nm sample.

7.4.2.3 Control Sample with 380 nm Thickness

Excitation Spectra: The excitation spectra still show a strong fluorescein peak at around 470 nm, while the PMMA peak at 335 nm is only visible when the emission is fixed at 400 nm. This trend is similar to the 669 nm and 476 nm samples.

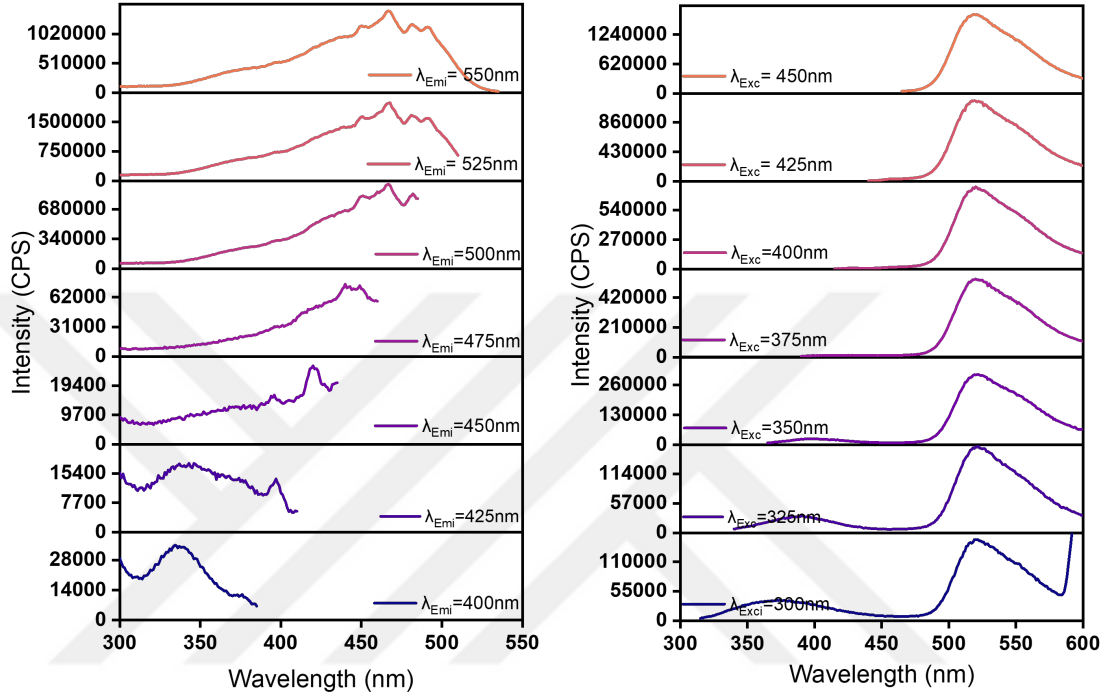


Figure 7.10: Excitation (left) and emission (right) spectra of the 380 nm thick fluorescein-doped PMMA film (high dye concentration, out-of-cavity). The spectra show that fluorescein dominates both excitation and emission, while PMMA contributes only at low emission or excitation wavelengths.

Emission Spectra: The emission spectra are again dominated by fluorescein emission with a clear peak around 520–530 nm. The PMMA emission is weak and only noticeable at the lowest excitation wavelengths, following the same pattern seen in the other samples.

7.4.2.4 Control Sample with 334 nm Thickness

Excitation Spectra: The excitation spectra continue to show the same trend, with a strong fluorescein peak around 470 nm becoming more dominant as the emission wavelength increases. A small PMMA-related peak at 335 nm appears only when emission is fixed at 400 nm, similar to previous thicknesses.

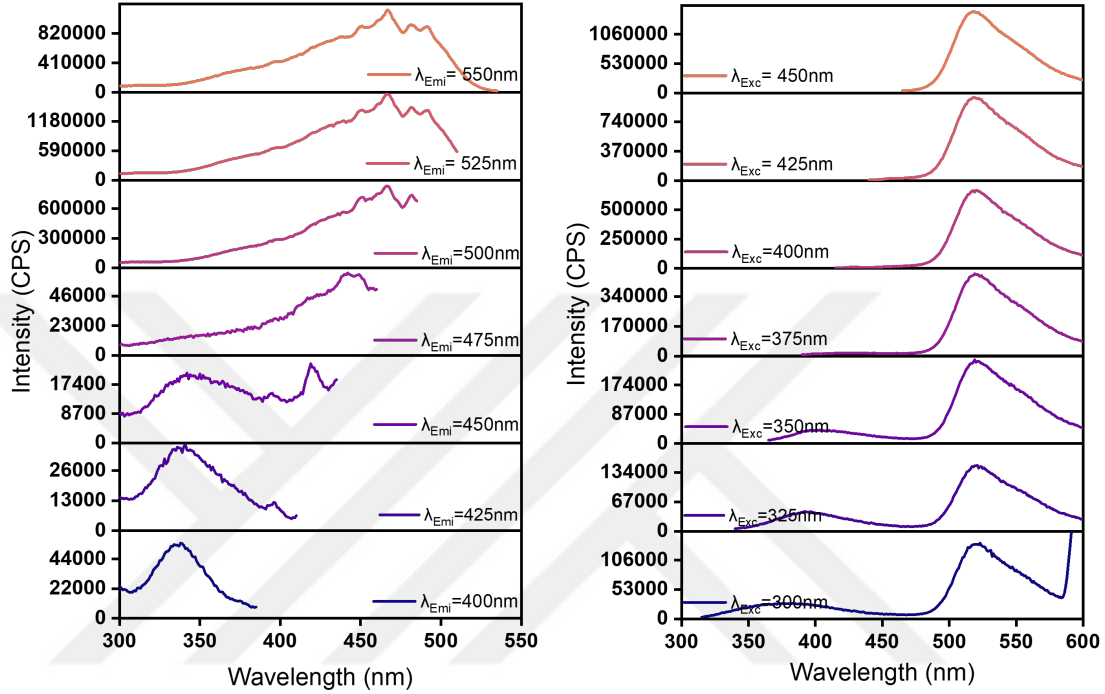


Figure 7.11: Excitation (left) and emission (right) spectra of the 334 nm thick fluorescein-doped PMMA film (high dye concentration, out-of-cavity). The spectra show that fluorescein dominates both excitation and emission, while PMMA contributes only at low emission or excitation wavelengths.

Emission Spectra: Fluorescein emission is dominant across all excitation wavelengths. A slight PMMA emission peak can be seen only when excited at the lowest wavelengths (e.g., 300 nm), but it is weak. The overall emission pattern is consistent with the 669 nm, 476 nm, and 380 nm samples.

7.4.2.5 Control Sample with 307 nm Thickness

Excitation Spectra: Same trend as before, the fluorescein peak near 470 nm dominates at higher emission wavelengths. The PMMA peak around 335 nm only appears when emission is fixed at 400 nm, and fades as emission shifts higher.

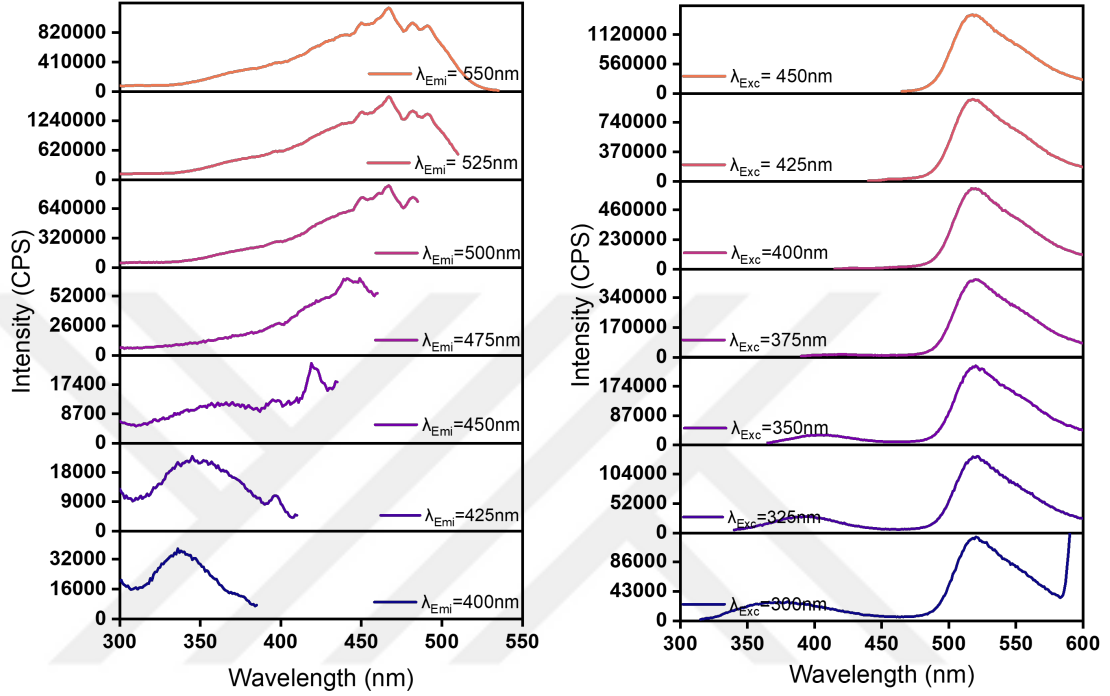


Figure 7.12: Excitation (left) and emission (right) spectra of the 307 nm thick fluorescein-doped PMMA film (high dye concentration, out-of-cavity). The spectra show that fluorescein dominates both excitation and emission, while PMMA contributes only at low emission or excitation wavelengths.

Emission Spectra: The emission spectra are also consistent with thicker samples. Fluorescein emission dominates under all excitation wavelengths, with a weak PMMA peak only at low excitation wavelengths (e.g., 300 nm). This confirms the same behavior across all thicknesses measured outside the cavity.

7.5 Fluorescence Behavior of In-Cavity Samples

We next examine the fluorescence response of the dye-doped PMMA films inside the Fabry–Pérot cavity. Unlike the out-of-cavity control spectra, which follow the broad intrinsic emission of fluorescein, the in-cavity measurements reveal

clear spectral reshaping due to the presence of cavity modes. To highlight these effects, we first present and interpret the results for the low dye concentration samples, followed by a discussion of the high concentration case, where cavity-induced modifications become more pronounced.

7.5.1 Excitation and Emission Spectra at Low Dye Concentration

7.5.1.1 Cavity Sample with 475 nm Thickness

Excitation spectra. Fixing the emission at $\lambda_{\text{emi}} = 400 \text{ nm}$ reveals a weakened, cavity-modulated PMMA feature near 335 nm. As λ_{emi} increases (425–550 nm), the fluorescein band around $\sim 470 \text{ nm}$ becomes dominant. Across all λ_{emi} , the excitation curves show fine modulations aligned with Fabry–Pérot resonances, indicating that excitation efficiency is shaped by the cavity modes rather than following a smooth dye absorption.

Emission spectra. Upon UV excitation (300–350 nm), a short-wavelength lobe ($\sim 400\text{--}420 \text{ nm}$) appears but is suppressed and narrowed by the cavity, while the fluorescein band (500–520 nm) emerges with a comb of narrow peaks at the cavity resonances. For higher λ_{exc} (375–450 nm), fluorescein dominates, yet the emission remains discretized into well-spaced resonant peaks, confirming cavity-controlled spontaneous emission.

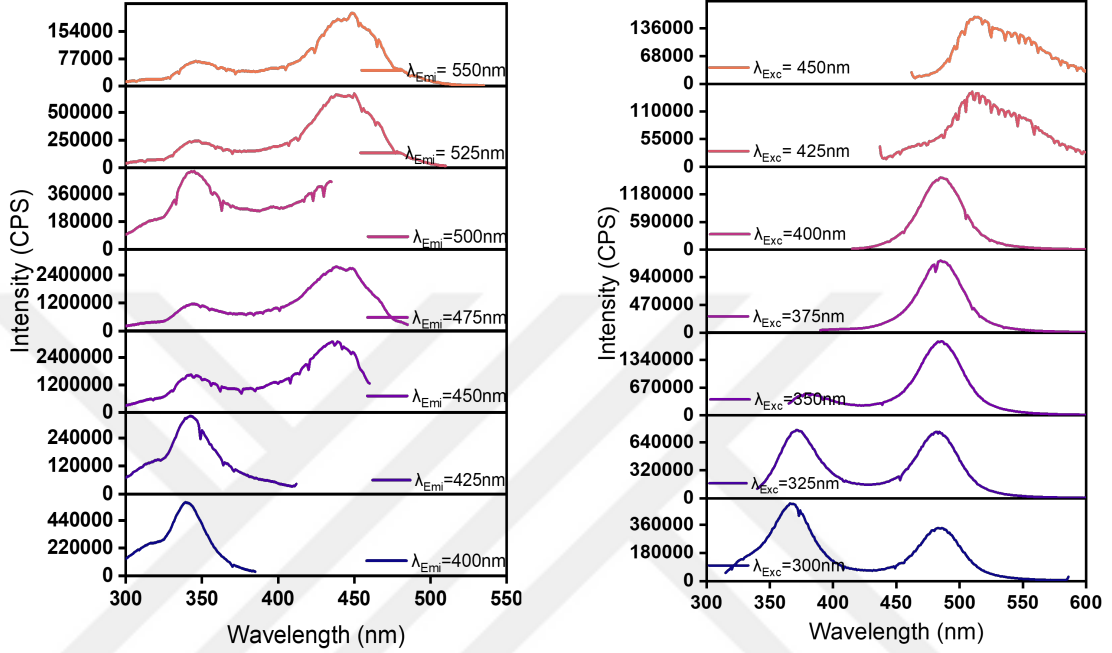


Figure 7.13: Excitation (left) and emission (right) spectra of the 475 nm fluorescein-doped PMMA film inside the Fabry-Pérot cavity (low dye concentration). Compared to the out-of-cavity reference, the PMMA signature at 335 nm is suppressed, and discrete cavity resonances reshape both excitation and emission; The broad fluorescein band is redistributed into narrow peaks with a constant free spectral range.

7.5.1.2 Cavity Sample with 350 nm Thickness

Both excitation and emission spectra follow the same trend as the 475 nm film: PMMA features are suppressed, while fluorescein dominates under cavity control. The main distinction is that the cavity resonances are sharper and more widely spaced, as expected from the reduced thickness.

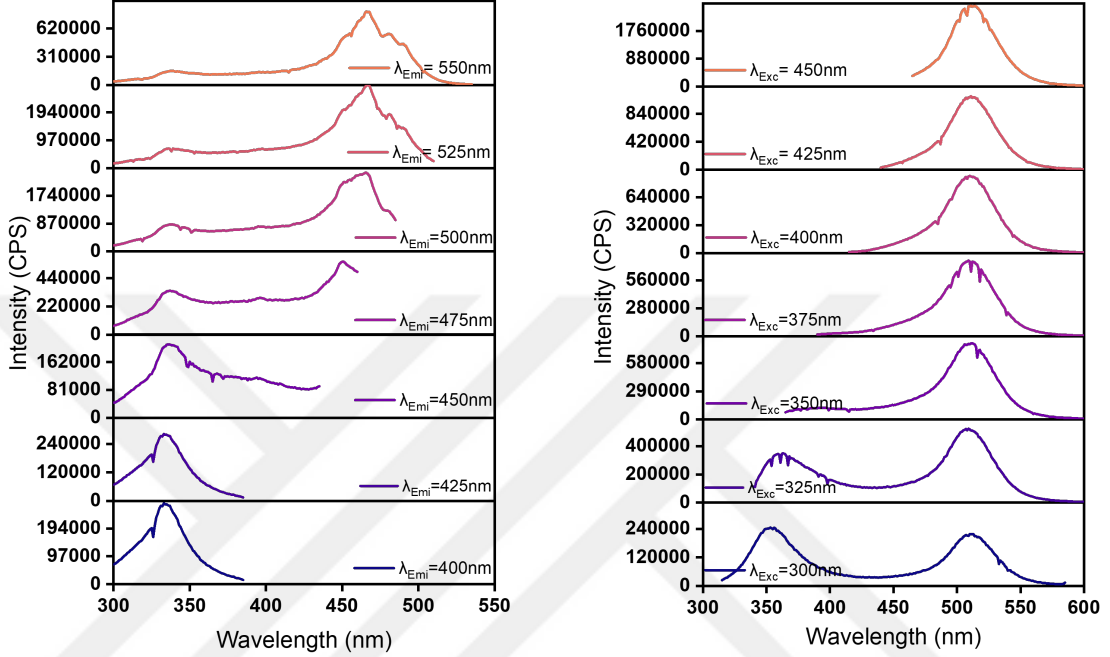


Figure 7.14: Excitation (left) and emission (right) spectra of the 350 nm fluorescein-doped PMMA film inside the cavity (low dye concentration). The spectra are similar to the 475 nm case, with sharper and more widely spaced cavity resonances due to reduced thickness.

7.5.1.3 Cavity Samples with 291 nm, 253 nm, and 240 nm Thickness

For the cavity samples with thicknesses of 291 nm, 253 nm, and 240 nm, the excitation and emission spectra exhibit a consistent trend dominated by a single cavity mode. In all three cases, this cavity mode strongly influences both the excitation and emission processes, leading to well-defined spectral peaks and suppressing broad background features. The natural fluorescence peak of fluorescein is still present, but it remains modulated by the cavity resonance, resulting in sharper, cavity-controlled emission. This uniform behavior across the three thicknesses highlights the stabilizing role of the cavity in dictating the optical response, regardless of small variations in film thickness.

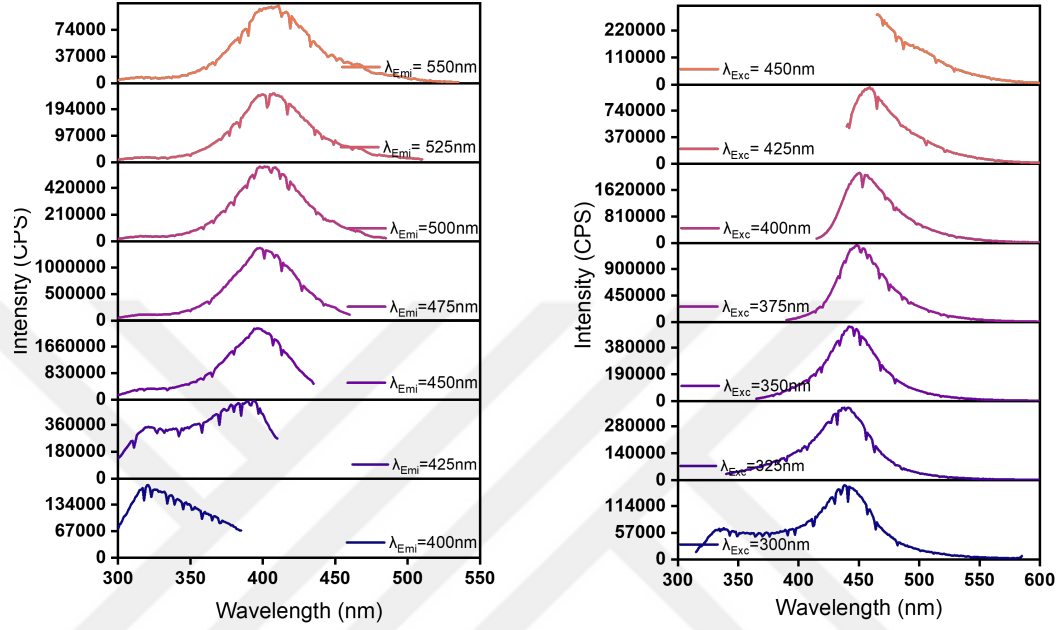


Figure 7.15: Excitation and emission spectra for the 291 nm cavity sample (low dye concentration). Behavior follows the general cavity-controlled trend.

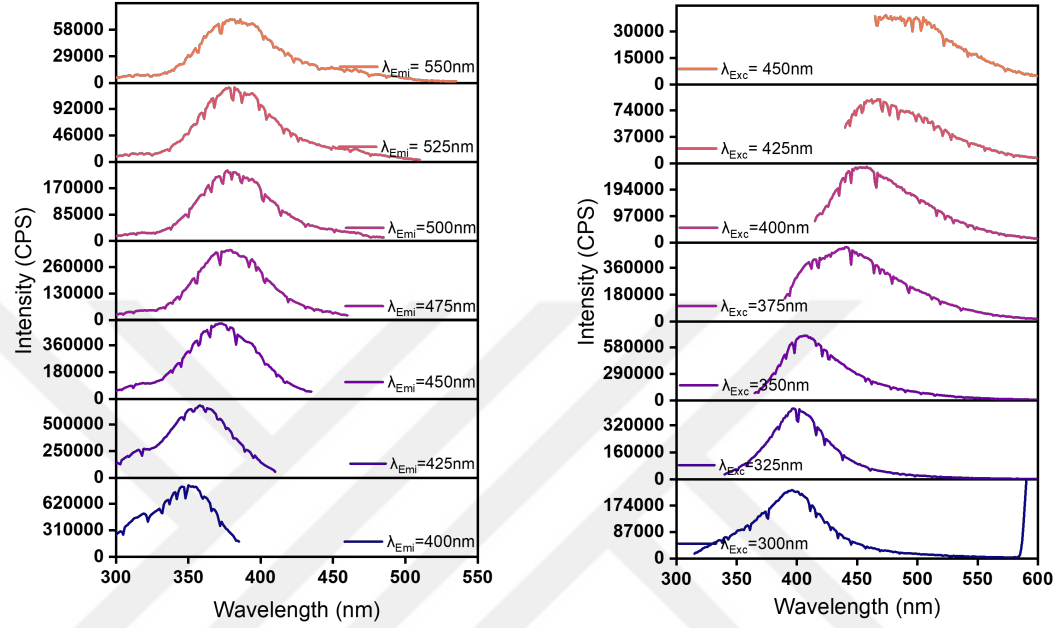


Figure 7.16: Excitation and emission spectra for the 253 nm cavity sample (low dye concentration). Spectral features remain cavity-mode dominated, consistent with the 291 nm and 240 nm cases.

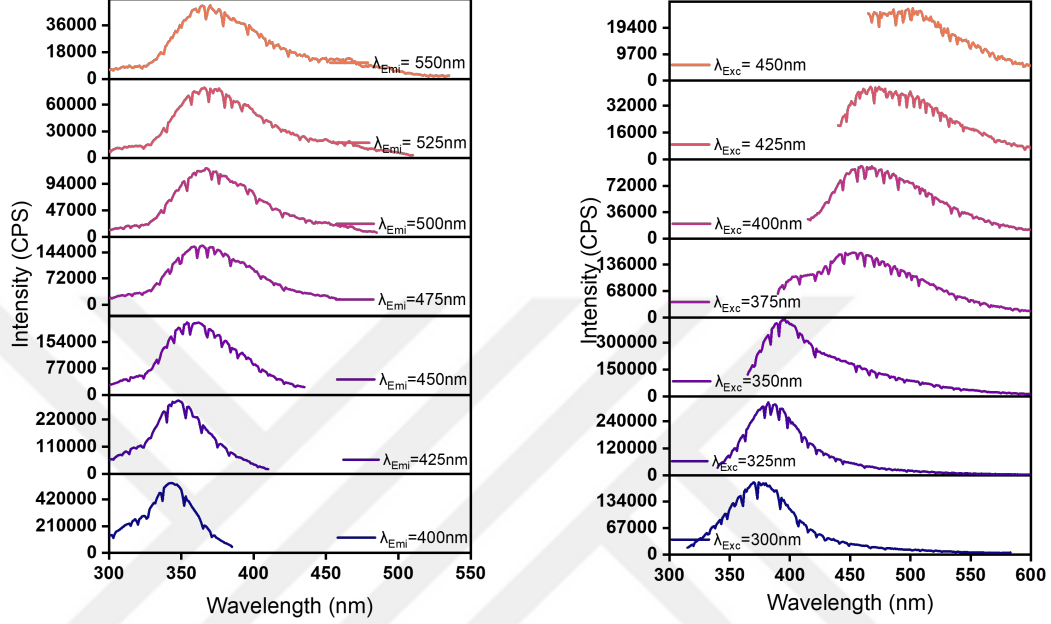


Figure 7.17: Excitation and emission spectra for the 240 nm cavity sample (low dye concentration). Again, the response is governed by a single cavity mode, in line with the 291 nm and 253 nm samples.

7.5.2 Excitation and Emission Spectra at High Dye Concentration

For the high dye concentration samples, all cavity thicknesses exhibit strong cavity–fluorescence coupling that dominates both excitation and emission spectra. At large cavity thicknesses (e.g., 669 nm), the intrinsic dye fluorescence band is significantly reshaped and broadened under cavity control. At 476 nm, the emission clearly shows dual contributions: a cavity-imposed lower-wavelength peak and the natural dye fluorescence peak, similar to lower concentration cases but with stronger cavity suppression of sidebands. As the cavity thickness decreases (380–334 nm), the excitation spectra develop cavity-induced shoulders and multiple modulations, while the emission transitions into a cavity-broadened envelope

rather than distinct dye-like peaks. At the shortest thickness (307 nm), cavity filtering becomes the dominant effect, with emission strongly reshaped and shifted compared to the free dye response. Collectively, these results confirm that at high dye concentrations, the cavity modes consistently dictate spectral redistribution, with the dye fluorescence being strongly modulated rather than freely expressed.

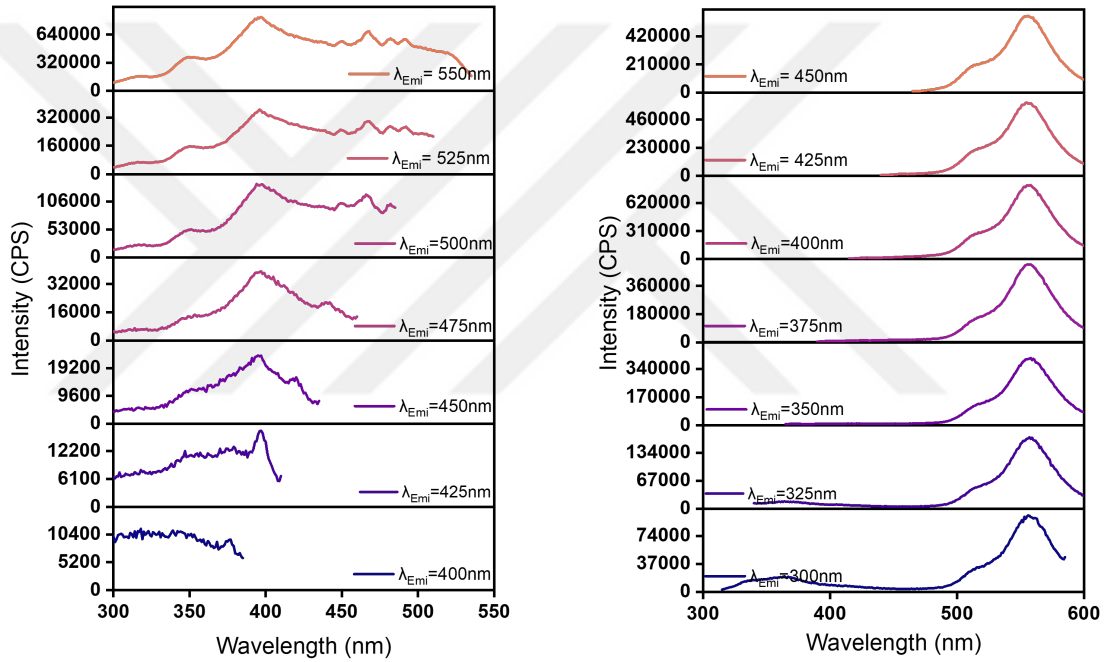


Figure 7.18: Excitation and emission spectra for cavity thickness of 669 nm (high dye concentration). Strong cavity-induced reshaping of the fluorescence profile is observed.

7.5.2.1 Control Sample with 476 nm Thickness

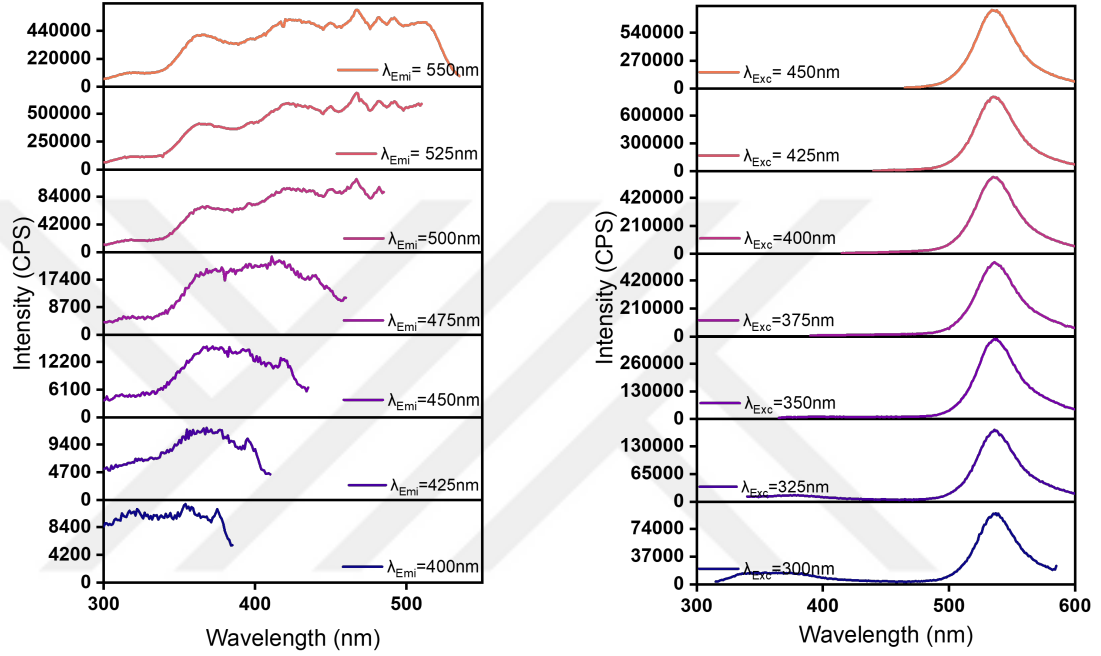


Figure 7.19: Spectra for 476 nm cavity (high dye concentration). Dual-peak emission arises from the interplay between intrinsic dye fluorescence and cavity resonances.

7.5.2.2 Control Sample with 380 nm Thickness

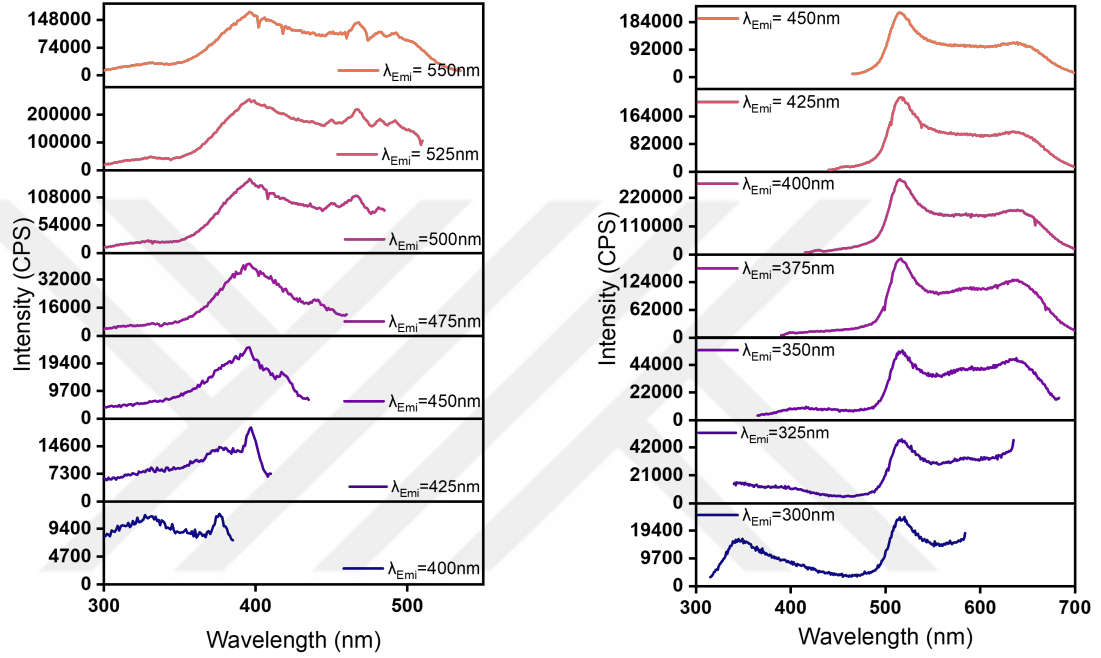


Figure 7.20: Spectra for 380 nm cavity (high dye concentration). Excitation shows cavity-induced shoulders, while emission remains cavity-controlled with a broadened response.

7.5.2.3 Control Sample with 334 nm Thickness

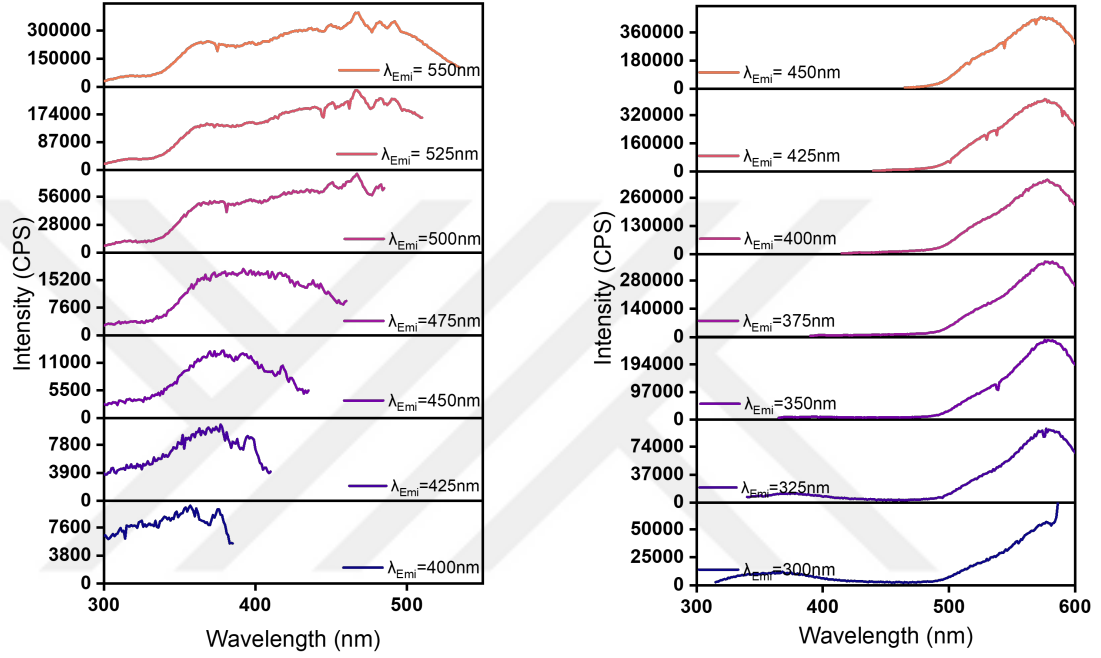


Figure 7.21: Spectra for 334 nm cavity (high dye concentration). Multiple cavity-induced modulations appear in excitation, and emission is redistributed under cavity feedback.

7.5.2.4 Control Sample with 307 nm Thickness

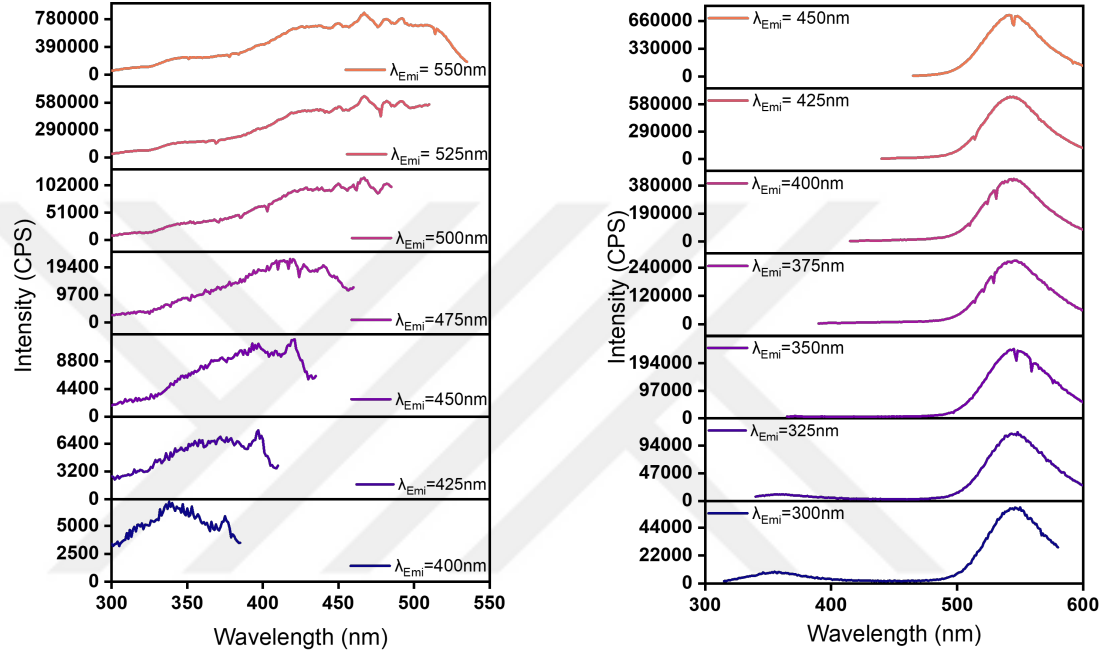


Figure 7.22: Spectra for 307 nm cavity (high dye concentration). Strong cavity filtering reshapes emission, highlighting persistent cavity dominance at high dye concentration.

7.6 Summary

In this chapter, the steady-state fluorescence of fluorescein-doped PMMA thin films was examined inside and outside Fabry–Pérot cavities to determine how confinement, thickness, and dye concentration affect emission. Control samples showed a transition from PMMA-dominated UV fluorescence to fluorescein-dominated green fluorescence, with weak energy transfer signatures at low dye concentrations and fluorescein dominance at high concentrations. Inside the cavity, the broad dye emission was reshaped into discrete resonant peaks, with thinner films producing sharper and more widely spaced modes. At higher dye concentrations, cavity effects became more pronounced, yielding dual-peak behavior

or strong cavity filtering where emission was entirely dictated by cavity modes.



Chapter 8

Angle-Resolved Ellipsometric (Psi (Ψ) and Delta (Δ)) and Reflectance Characterization

8.1 Chapter Overview

In this chapter, we present an optical analysis of fluorescein-doped PMMA thin films embedded in Fabry–Pérot microcavities using angle-resolved spectroscopic ellipsometry. The goal is to investigate how variations in film thickness and dye concentration affect the ellipsometric response of the cavity and the nature of exciton–photon interactions.

We begin with five low-dye concentration samples (20 $\mu\text{g/mL}$) prepared at different spin-coating speeds (1000 to 5000 rpm) and measure the ellipsometric parameters Ψ (amplitude ratio) and Δ (phase difference) as functions of angle (15° to 85°). For each sample, we first present the angle-resolved heatmaps of the ellipsometric parameters Ψ and Δ as functions of wavelength. These are followed by the corresponding angle-resolved line plots of $\tan(\Psi)$ and Δ . Finally, we plot the complex-plane trajectories of the reflectance ratio $\rho = \tan(\Psi) e^{i\Delta}$, derived

from the measured ellipsometric parameters. The same procedure is repeated for five high-dye concentration samples (60 mg/mL) prepared at different spin-coating speeds (1000 to 5000 rpm), to examine the influence of increased oscillator strength on light-matter coupling.

For the low dye concentration samples, strong coupling is not expected based on previous results. We therefore used these as reference cases and focused our analysis on identifying conditions under which strong exciton-photon coupling emerges. For those cases exhibiting characteristic signatures of strong coupling, we applied the coupled oscillator model to extract the Rabi splitting energy ($\hbar\Omega_R$). Furthermore, we calculated the Hopfield coefficients ($|\alpha_{\text{ex}}|^2$ and $|\alpha_c|^2$) for the upper and lower polariton branches to quantify the excitonic and photonic contributions, respectively.

These angle dependent Ψ and Δ tools are used to investigate how cavity resonances vary with angle, dye concentration, and thickness, as well as their interaction with excitonic absorption near 467 nm. Key features such as mode bending, phase shifts, and looping behavior in the ρ -trajectory serve as indicators of excitonic strong coupling. By comparing these optical signatures across different sample conditions, this chapter demonstrates how ellipsometry can effectively track the transition from the weak to the strong coupling regime.

8.2 Mathematical Description of Ellipsometric Response

As discussed in Chapter 5, ellipsometry is a non-destructive and contactless optical technique used to measure the optical constants, thickness, and surface roughness of thin films [59, 60, 61, 62]. The technique operates by analyzing the change in the polarization state of light upon reflection from a sample surface. It provides two primary parameters: Ψ (Psi) and Δ (Delta) [63], which are sensitive to interference within layered structures and material absorption such as

excitonic transitions. To fully capture both amplitude and phase evolution, it is common to define the complex reflectance ratio:

The complex reflectance ratio is defined as:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) e^{i\Delta} \quad (8.1)$$

where r_p and r_s are the Fresnel reflection coefficients for p- and s-polarized light, respectively. $\tan(\Psi)$ gives the magnitude ratio of the reflected electric field amplitudes, while Δ captures the phase difference. Together, these quantities provide rich information about thin-film optical behavior.

Cavity resonances are also evident in the behavior of $\tan(\Psi)$. A resonance appears as a distinct modulation, either a dip or a peak in $\tan(\Psi)$, depending on the relative magnitudes of r_p and r_s :

$$\tan(\Psi) = \left| \frac{r_p}{r_s} \right| \quad (8.2)$$

When $r_p < r_s$, $\tan(\Psi) < 1$ and a dip occurs; conversely, if $r_p > r_s$, $\tan(\Psi) > 1$ and a peak is observed. These features reflect polarization-sensitive interference and absorption effects within the microcavity. Monitoring the evolution of Ψ , Δ , and ρ under different experimental conditions thus provides a powerful framework to assess transitions between weak and strong coupling regimes[64].

8.2.1 Derivation and Interpretation of Real and Imaginary Components of ρ

To visualize the optical response more intuitively, ρ is often plotted in the complex plane as $\text{Re}(\rho)$ versus $\text{Im}(\rho)$, which simultaneously tracks amplitude and phase evolution across wavelengths. Using Euler's identity:

$$e^{i\Delta} = \cos(\Delta) + i \sin(\Delta) \quad (8.3)$$

Equation 8.1 becomes:

$$\rho = \tan(\Psi) \cdot [\cos(\Delta) + i \sin(\Delta)] \quad (8.4)$$

yielding:

$$\Re(\rho) = \tan(\Psi) \cdot \cos(\Delta), \quad \Im(\rho) = \tan(\Psi) \cdot \sin(\Delta) \quad (8.5)$$

These expressions form the basis for plotting ρ -trajectories, whose looping or distorted shapes can indicate the onset of light-matter interaction, particularly near excitonic absorption features (e.g., ~ 467 nm for fluorescein). Such trajectories are sensitive to the thickness of the film and cavity resonance.

8.3 Ellipsometric Analysis of Low-Concentration Samples

To investigate the development of cavity resonances in weakly coupled systems, we first examine the raw, angle-resolved spectra of ellipsometric parameters Ψ and Δ for low dye concentration samples. These measurements provide a baseline reference for understanding how cavity resonances manifest in polarization-dependent reflectance before transitioning to high-concentration and potentially strongly coupled regimes.

8.3.1 Raw Ψ and Δ Spectra

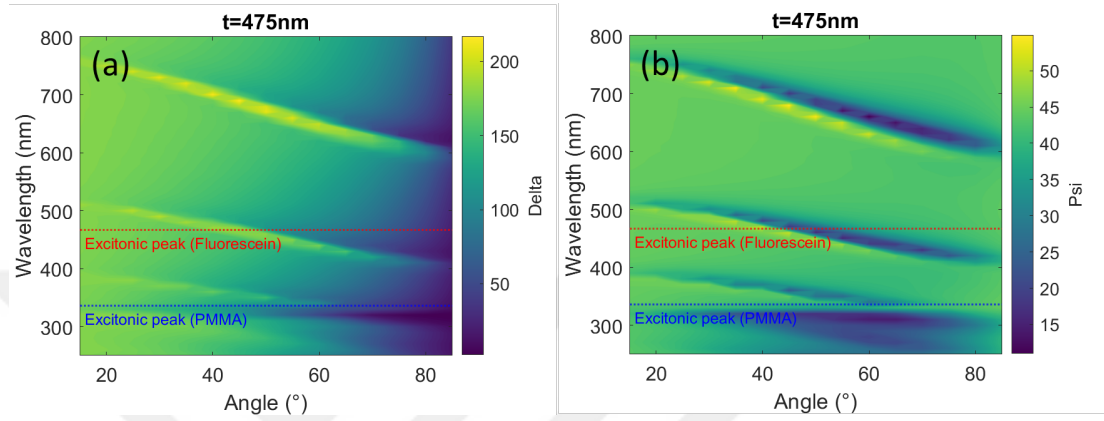


Figure 8.1: Angle-resolved contour plots of (a) Δ and (b) Ψ for the low dye concentration sample ($20\text{ }\mu\text{g/mL}$) prepared at 1000 rpm with a thickness of 475 nm.

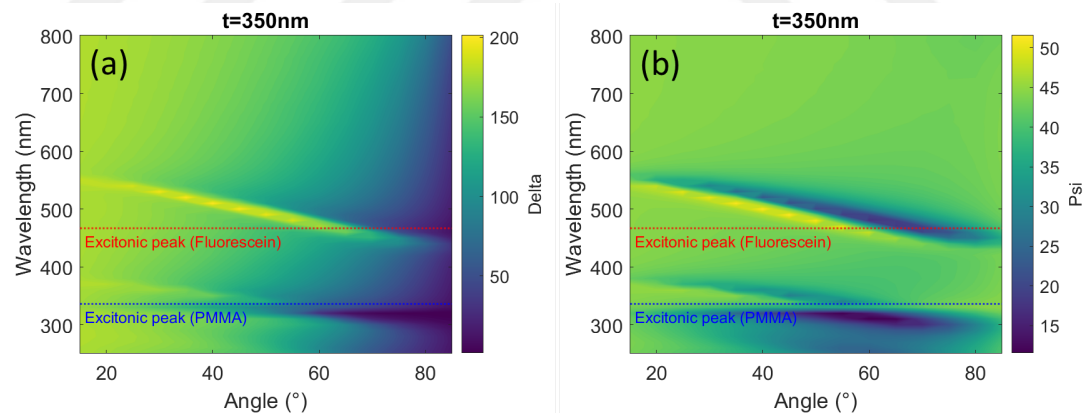


Figure 8.2: Angle-resolved contour plots of (a) Δ and (b) Ψ for the low dye concentration sample ($20\text{ }\mu\text{g/mL}$) prepared at 2000 rpm with a thickness of 350 nm.

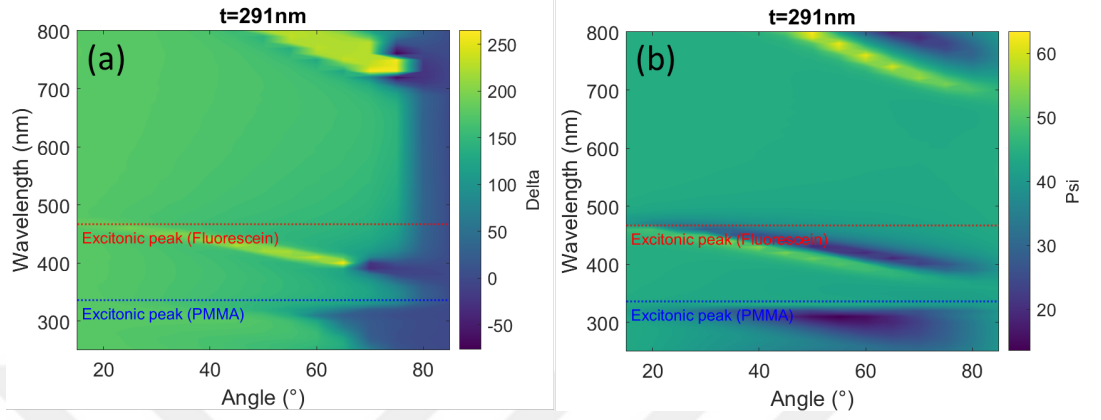


Figure 8.3: Angle-resolved contour plots of (a) Δ and (b) Ψ for the low dye concentration sample ($20\text{ }\mu\text{g/mL}$) prepared at 3000 rpm with a thickness of 291 nm.

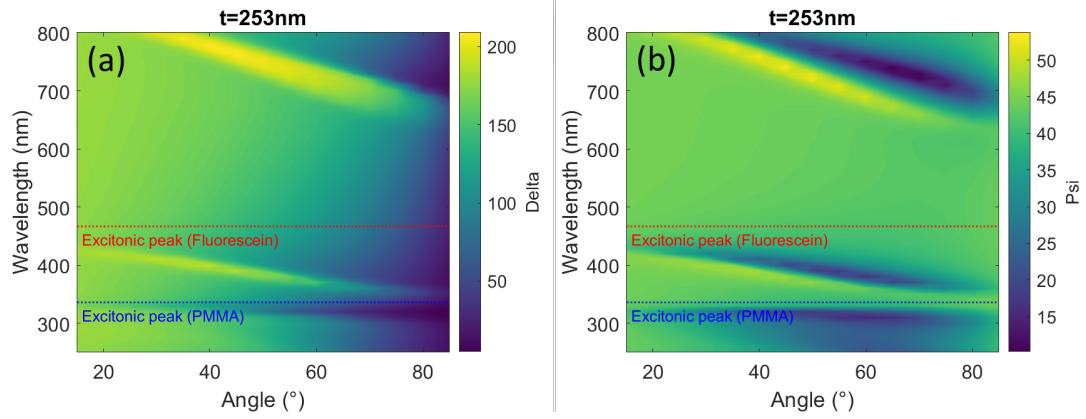


Figure 8.4: Angle-resolved contour plots of (a) Δ and (b) Ψ for the low dye concentration sample ($20\text{ }\mu\text{g/mL}$) prepared at 4000 rpm with a thickness of 253 nm.

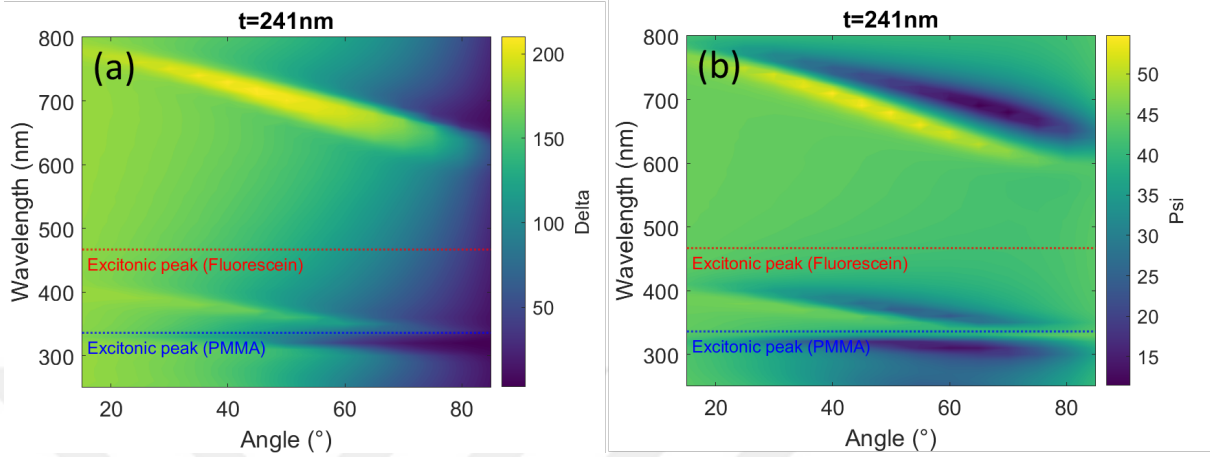


Figure 8.5: Angle-resolved contour plots of (a) Δ and (b) Ψ for the low dye concentration sample ($20 \mu\text{g/mL}$) prepared at 5000 rpm with a thickness of 241 nm.

Figures 8.1–8.5 display the angle-resolved ellipsometric spectra obtained from low-concentration ($20 \mu\text{g/mL}$) Fabry–Pérot microcavities with thicknesses varying between 475 nm and 241 nm. Each figure contains two heatmaps: the left panel (a) shows the measured phase difference (Δ), and the right panel (b) shows the amplitude ratio (Ψ). The horizontal axis represents the incidence angle (15° – 85°). The color scale encodes the magnitude of each parameter, with bright yellow representing high values of Ψ or Δ and dark blue corresponding to low values.

The interference fringes observed in both Δ and Ψ originate from multiple coherent reflections within the planar Fabry–Pérot cavity. Upon illumination, a fraction of the incident light reflects directly from the top mirror, while another fraction transmits into the dielectric spacer layer. The transmitted light undergoes multiple reflections between the top and bottom mirrors, accumulating additional optical path lengths and phase delays before leaking out of the cavity. The total reflected signal detected by the ellipsometer is therefore the coherent sum of (i) the immediate reflection at the air–mirror interface and (ii) the light that has propagated through multiple round trips inside the cavity.

At specific wavelengths and incidence angles that satisfy the Fabry–Pérot resonance condition:

$$m \frac{\lambda}{2} = n_{\text{eff}} t \cos(\theta_{\text{eff}}), \quad (8.6)$$

The delayed light from the cavity interferes with the directly reflected light. This interference can be constructive or destructive, producing strong changes in the reflected amplitude and phase. Switching between destructive and constructive interference involves a rapid phase shift of about π radians (180°). Because p- and s-polarized light have different Fresnel reflection coefficients and travel different optical paths, this phase shift happens differently for each polarization. The phase difference is given by:

$$\Delta = \phi_p - \phi_s, \quad (8.7)$$

where ϕ_p and ϕ_s represent the phases of the complex reflection coefficients r_p and r_s , respectively. This phase difference exhibits sharp variations at resonance. These appear as bright, curved fringes in the Δ spectra, corresponding to the abrupt 180° phase rotation experienced by one or both polarizations.

Similarly, the ellipsometric amplitude ratio Ψ oscillates as a function of wavelength and angle because Fabry–Pérot interference affects the reflected amplitudes of p and s polarized light unequally. At certain conditions, p-polarized reflection is strongly enhanced relative to s-polarization, producing bright yellow regions in the Ψ maps. Conversely, regions where s-polarized reflection dominates appear as dark fringes. So, the bright fringes observed in both Δ and Ψ plots directly show the Fabry–Pérot resonances of the microcavity. These fringes encode both the amplitude and phase response of the structure, revealing how the cavity thickness, incidence angle, and polarization jointly influence the optical interference and mode structure of the system.

In the 475 nm thick microcavity (Fig. 8.1a,b), the relatively large thickness allows multiple Fabry–Pérot modes to form within the cavity. This results in three distinct resonance modes that appear as bright curved fringes in both the phase difference (Δ , Fig. 8.1a) and amplitude ratio (Ψ , Fig. 8.1b) plots. The alternating bright yellow and blue regions indicate a sharp variation in the optical response:

as each resonance is approached, the reflected signal first increases (yellow), then decreases (blue), corresponding to constructive followed by destructive interference caused by a rapid 180° phase rotation. As the incidence angle increases, these resonances shift toward shorter wavelengths due to changes in the effective optical path length inside the cavity. Notably, the resonance starting around 500 nm approaches the molecular excitonic absorption peak of fluorescein (~ 467 nm), yet it passes through this region without showing any splitting or anti-crossing behavior. This smooth passage confirms that, at this low dye concentration, the number of molecules is insufficient to reach the strong coupling regime, and the cavity operates in the weak coupling limit.

As the cavity thickness is reduced from 350 nm to 241 nm (Figs. 8.2–8.5), the number of supported Fabry–Pérot modes systematically decreases. In the 350 nm cavity, two resonant modes are clearly visible as bright curved fringes in both Δ and Ψ spectra, showing similar angular dispersion and phase behavior as observed in the thickest cavity. Further thinning to 291 nm maintains two modes but with greater spectral separation, while the 253 nm cavity supports only a single dominant mode with a faint secondary feature that does not fully develop. The thinnest 241 nm cavity sustains only the fundamental longitudinal mode, producing a single interference fringe. In all these thinner cavities, the modes blue-shift more rapidly with angle due to shorter optical path lengths, and even when approaching the molecular excitonic resonance near 467 nm, they cross it smoothly without exhibiting mode splitting or avoided crossings. This consistent behavior across all reduced thicknesses confirms that the system remains in the weak coupling regime throughout.

8.3.2 Amplitude and Phase Interpretation via $\tan(\Psi)$ and Δ

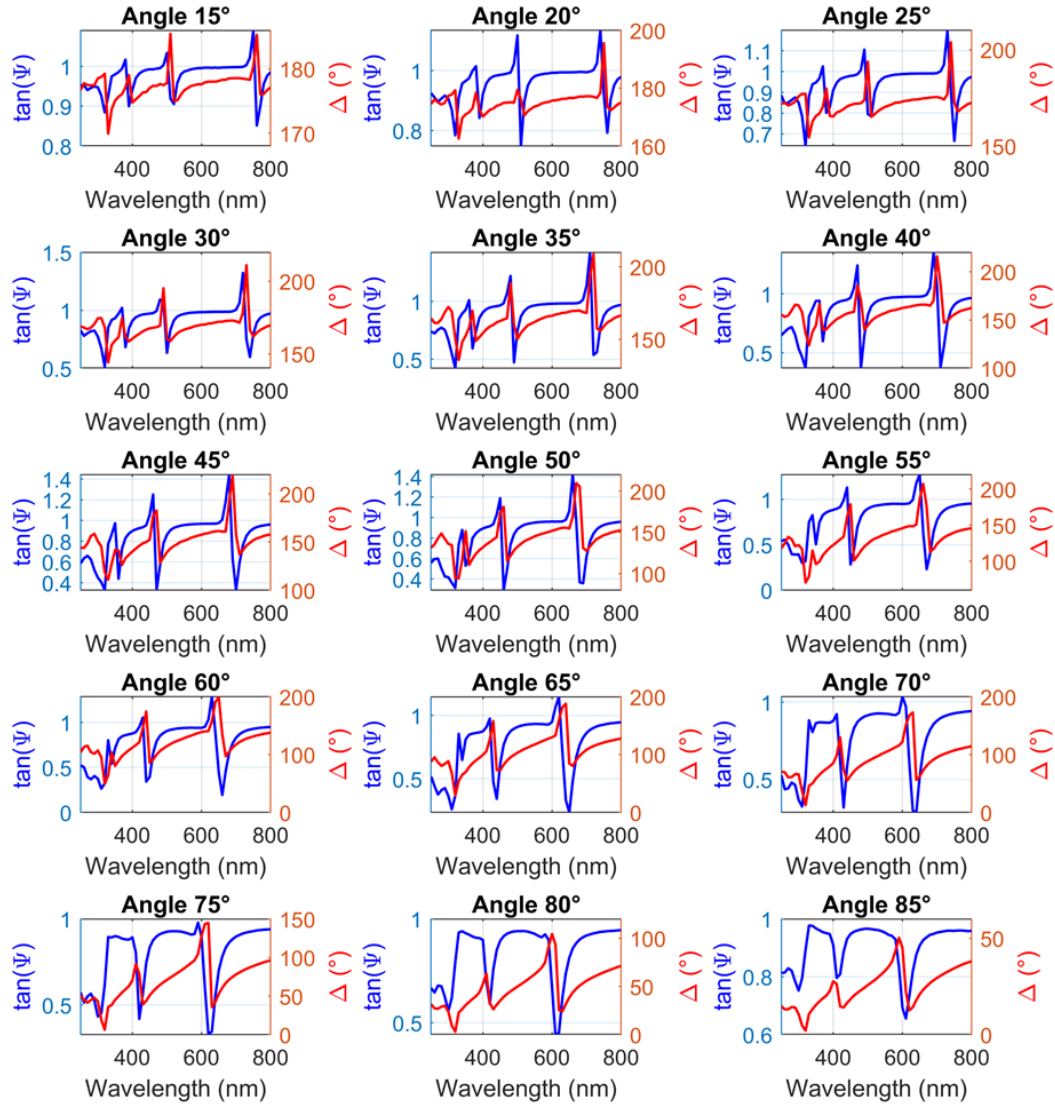


Figure 8.6: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 1000 rpm ($t = 475$ nm) low dye concentration sample.

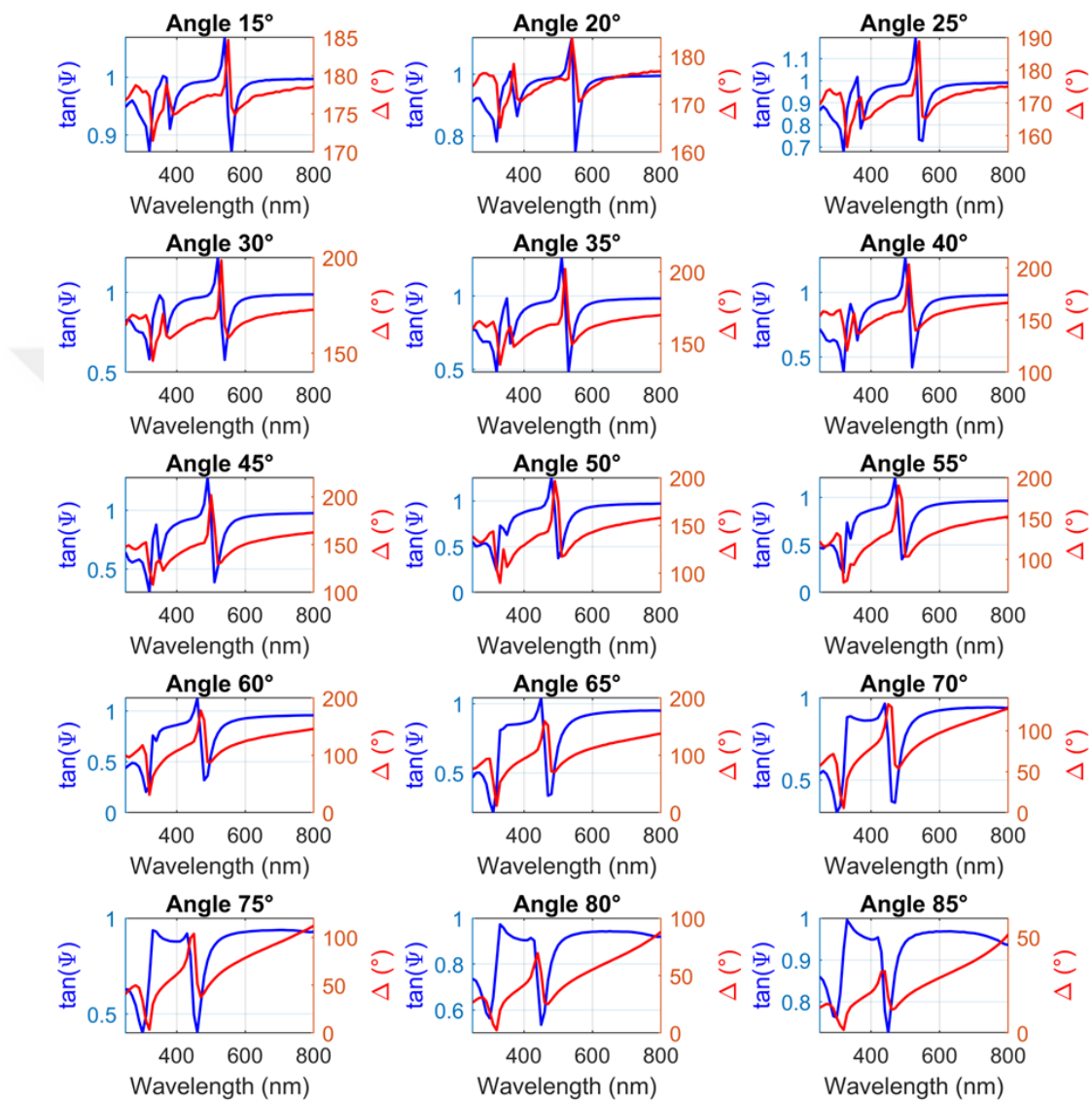


Figure 8.7: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 2000 rpm ($t = 350$ nm) low dye concentration sample.

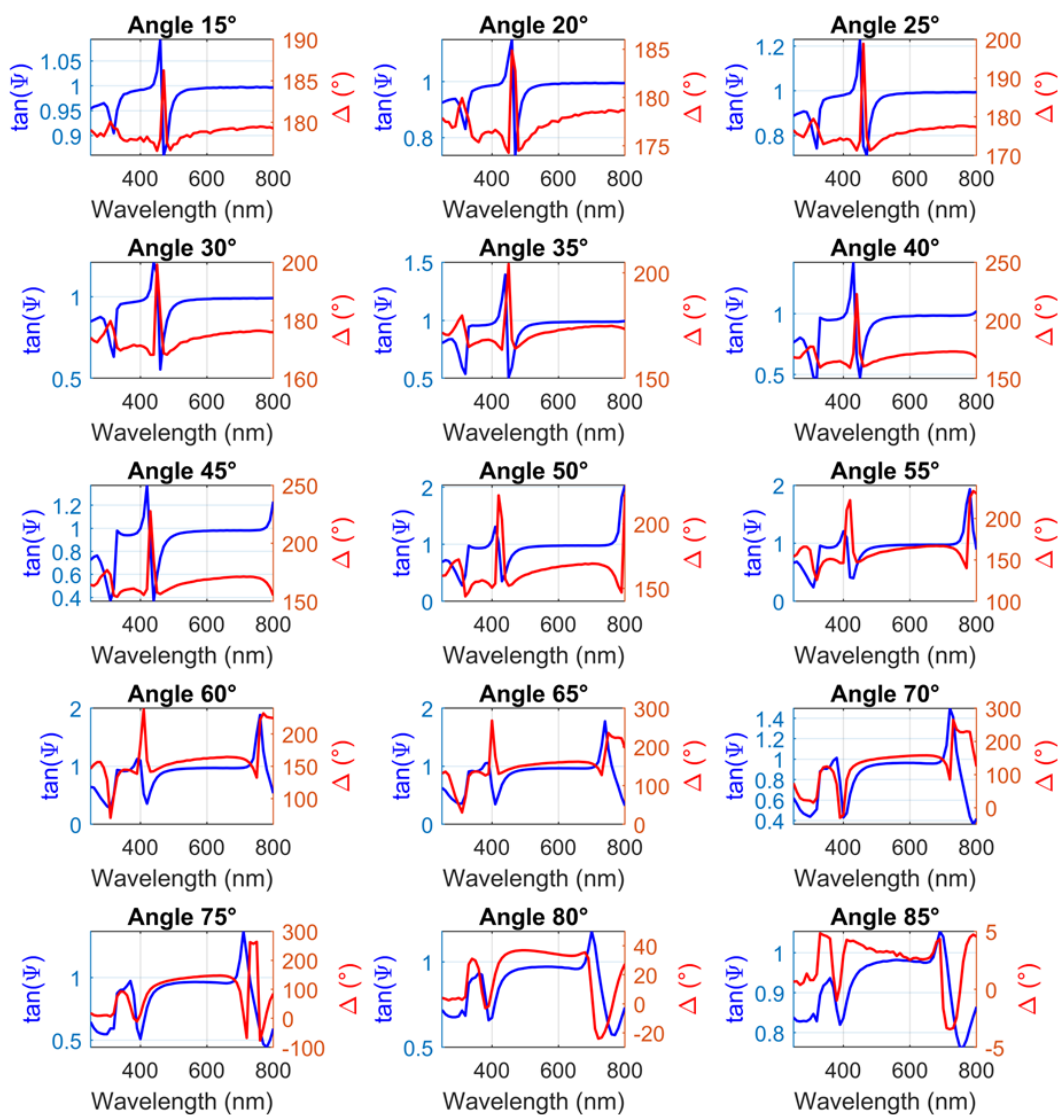


Figure 8.8: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 3000 rpm ($t = 291$ nm) low dye concentration sample.

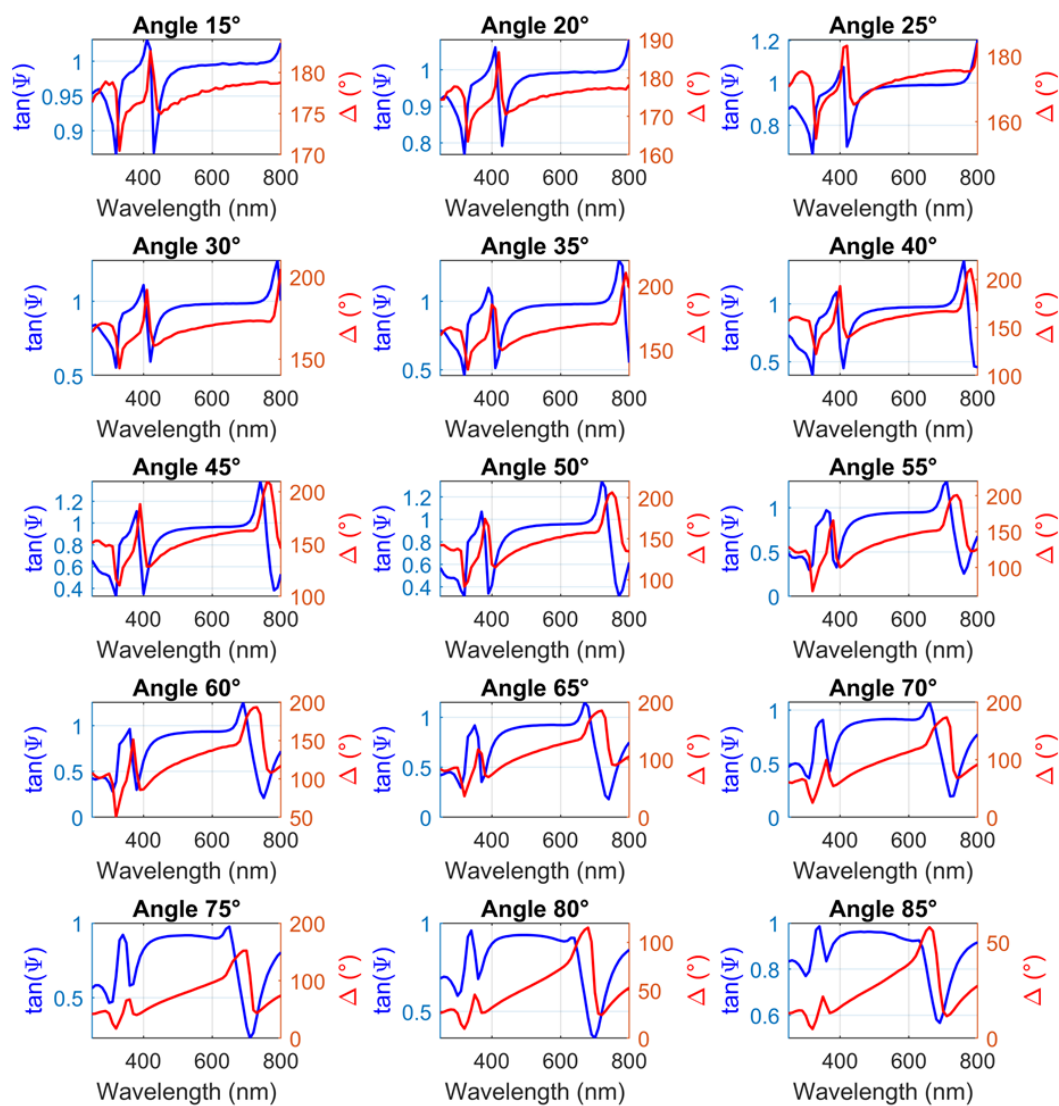


Figure 8.9: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 4000 rpm ($t = 253$ nm) low dye concentration sample.

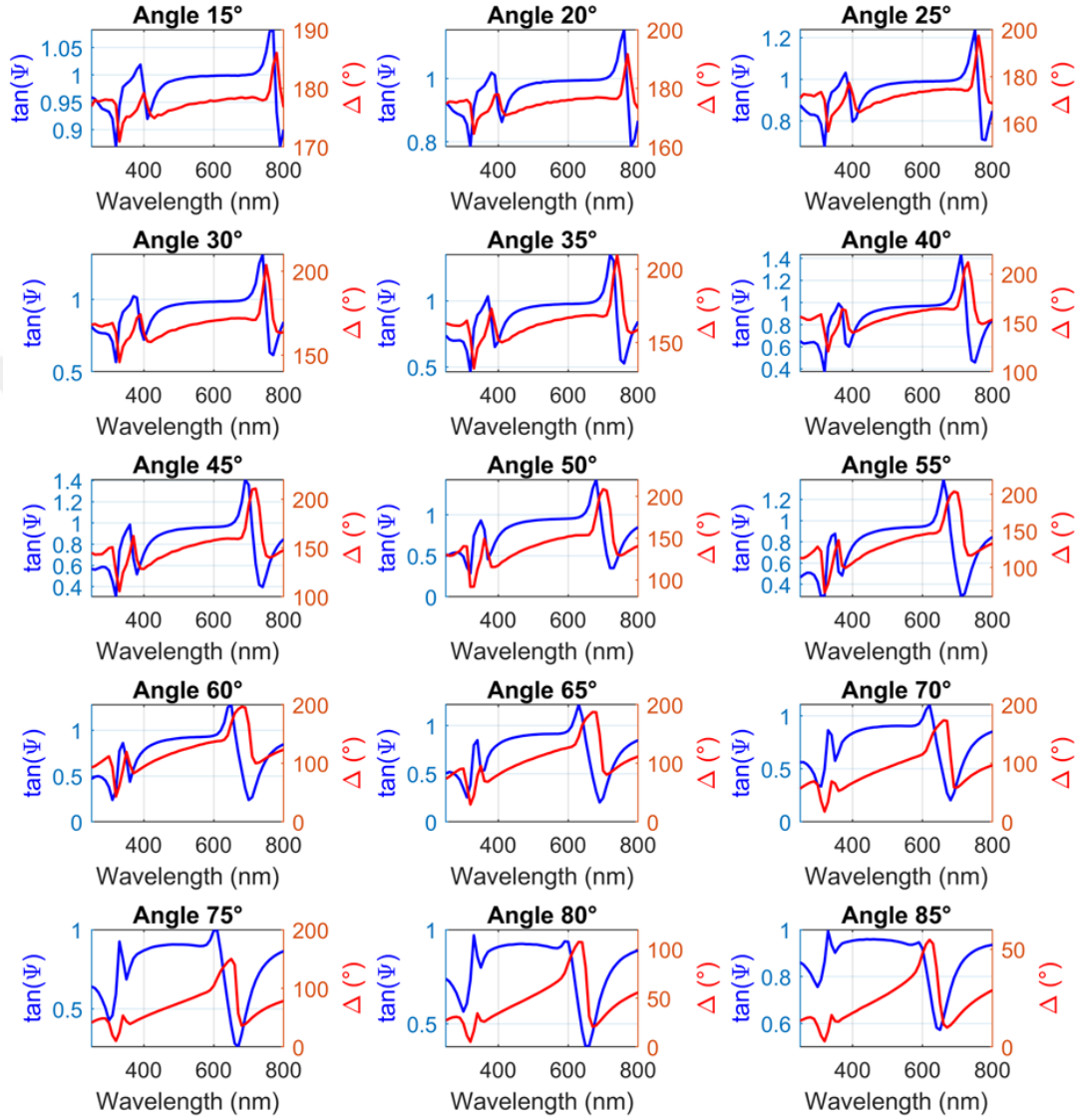


Figure 8.10: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 5000 rpm ($t = 241$ nm) low dye concentration sample.

These line spectra of $\tan(\Psi)$ and Δ , shown in Figures 8.6 to 8.10, correspond to the previously studied five Fabry–Pérot microcavities with decreasing cavity thicknesses. In the thickest cavity (475 nm, Fig. 8.6), multiple Fabry–Pérot modes are observed, producing several well-defined peaks in $\tan(\Psi)$ and sharp phase jumps in Δ . As the cavity becomes thinner (350 nm in Fig. 8.7 and 291 nm in Fig. 8.8), the number of resonant features reduces to two, and the peaks move

further apart due to the reduction in optical path length. In the thinnest samples (253 nm and 241 nm; Figures 8.9 and 8.10), only a single dominant resonance remains visible in both $\tan(\Psi)$ and Δ , indicating the presence of a single supported cavity mode. These spectral trends correspond directly to the patterns in the 2D heatmaps, as both representations are derived from the same dataset. In both cases, the number of bright interference fringes diminishes with decreasing cavity thickness, confirming the systematic transition to simpler mode structures while remaining in the weak coupling regime.

8.3.3 Complex-Plane Trajectories of ρ

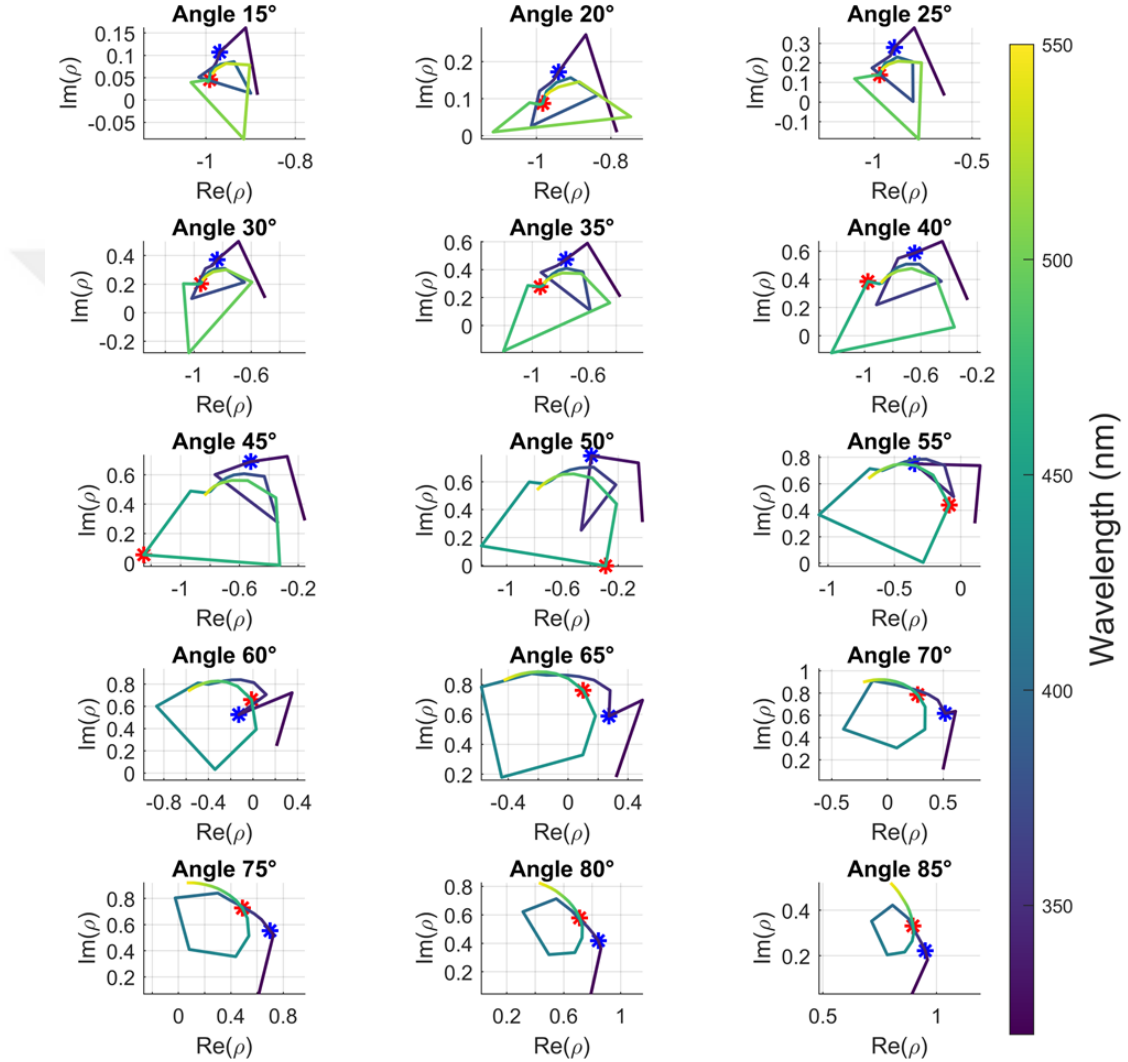


Figure 8.11: Complex-plane trajectory of $\rho = \tan(\Psi)e^{i\Delta}$ for the 1000 rpm ($t = 475$ nm) low dye concentration sample. The red marker indicates the excitonic peak position of fluorescein at 467 nm, while the blue marker indicates the PMMA peak at 336 nm.

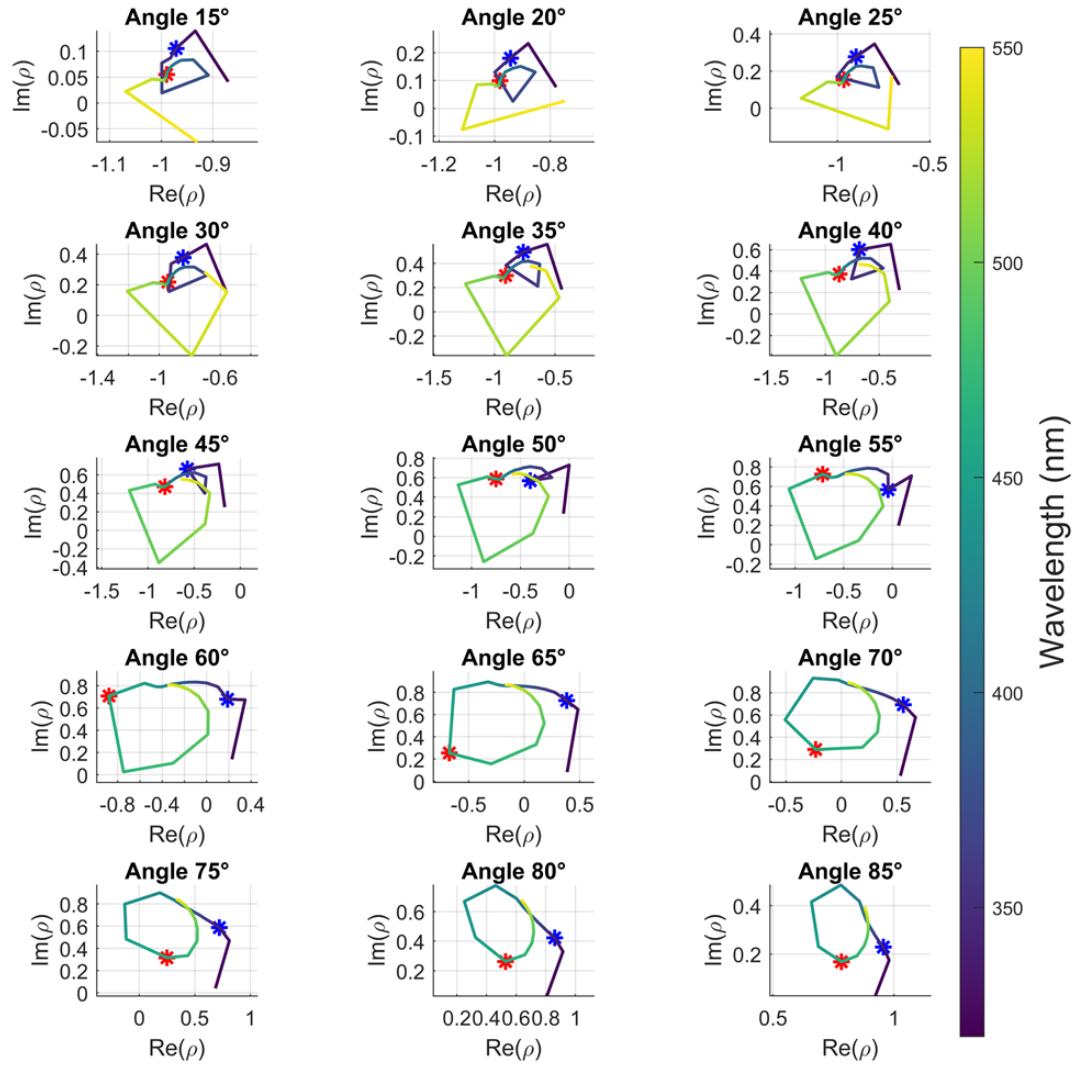


Figure 8.12: Complex-plane trajectory of $\rho = \tan(\Psi)e^{i\Delta}$ for the 2000 rpm ($t = 350$ nm) low dye concentration sample. The red marker indicates the excitonic peak position of fluorescein at 467 nm, while the blue marker indicates the PMMA peak at 336 nm.

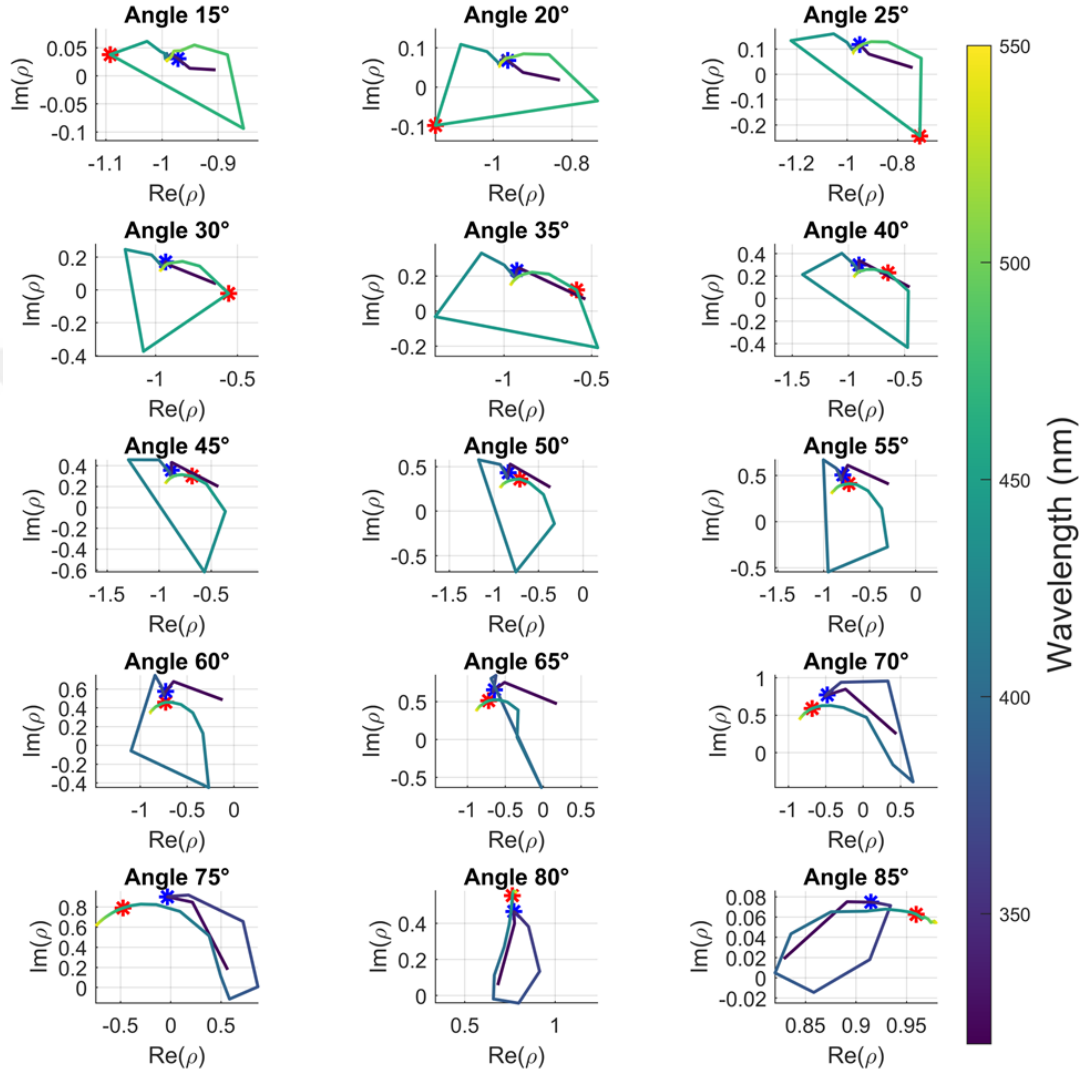


Figure 8.13: Complex-plane trajectory of $\rho = \tan(\Psi)e^{i\Delta}$ for the 3000 rpm ($t = 291$ nm) low dye concentration sample. The red marker indicates the excitonic peak position of fluorescein at 467 nm, while the blue marker indicates the PMMA peak at 336 nm.

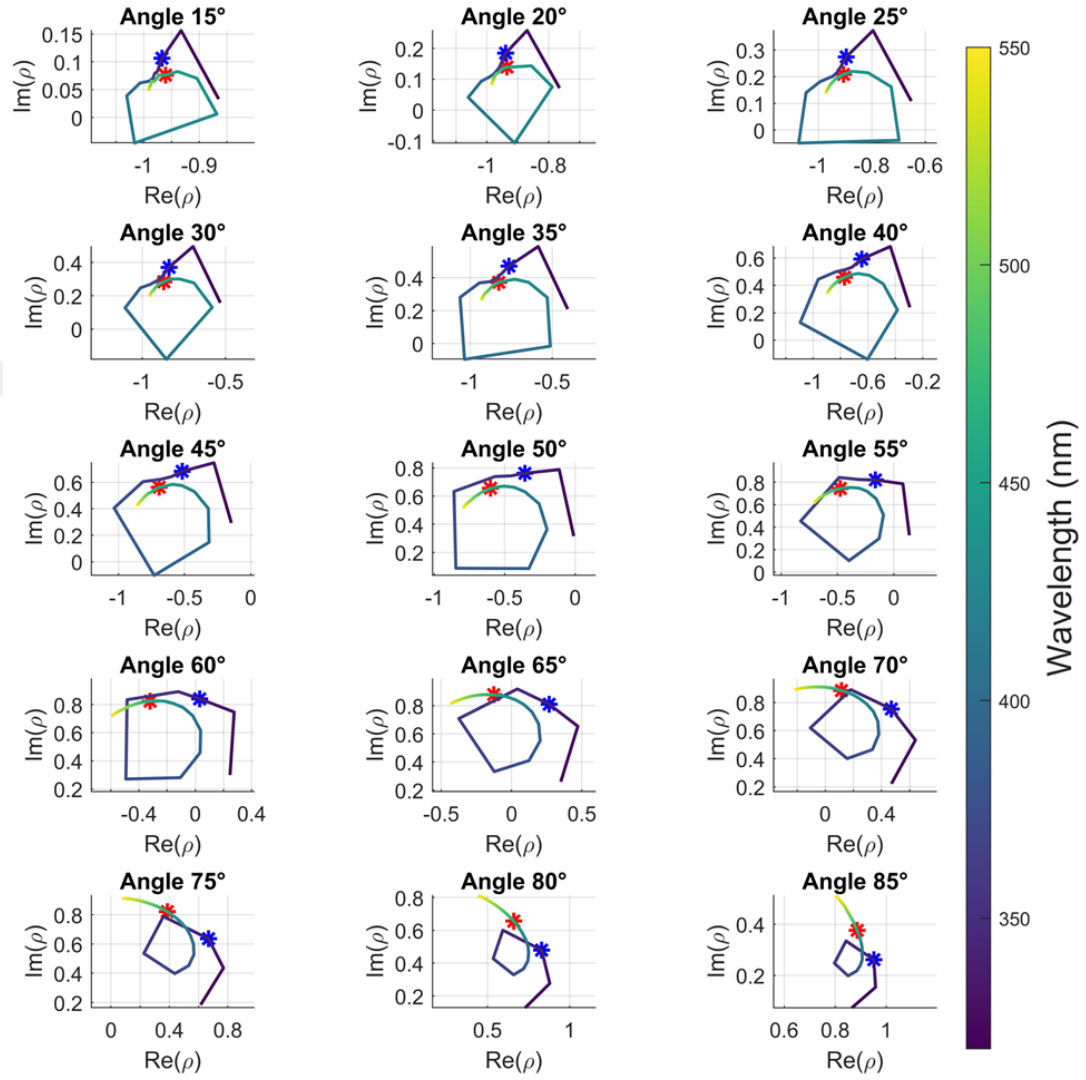


Figure 8.14: Complex-plane trajectory of $\rho = \tan(\Psi)e^{i\Delta}$ for the 4000 rpm ($t = 253$ nm) low dye concentration sample. The red marker indicates the excitonic peak position of fluorescein at 467 nm, while the blue marker indicates the PMMA peak at 336 nm.

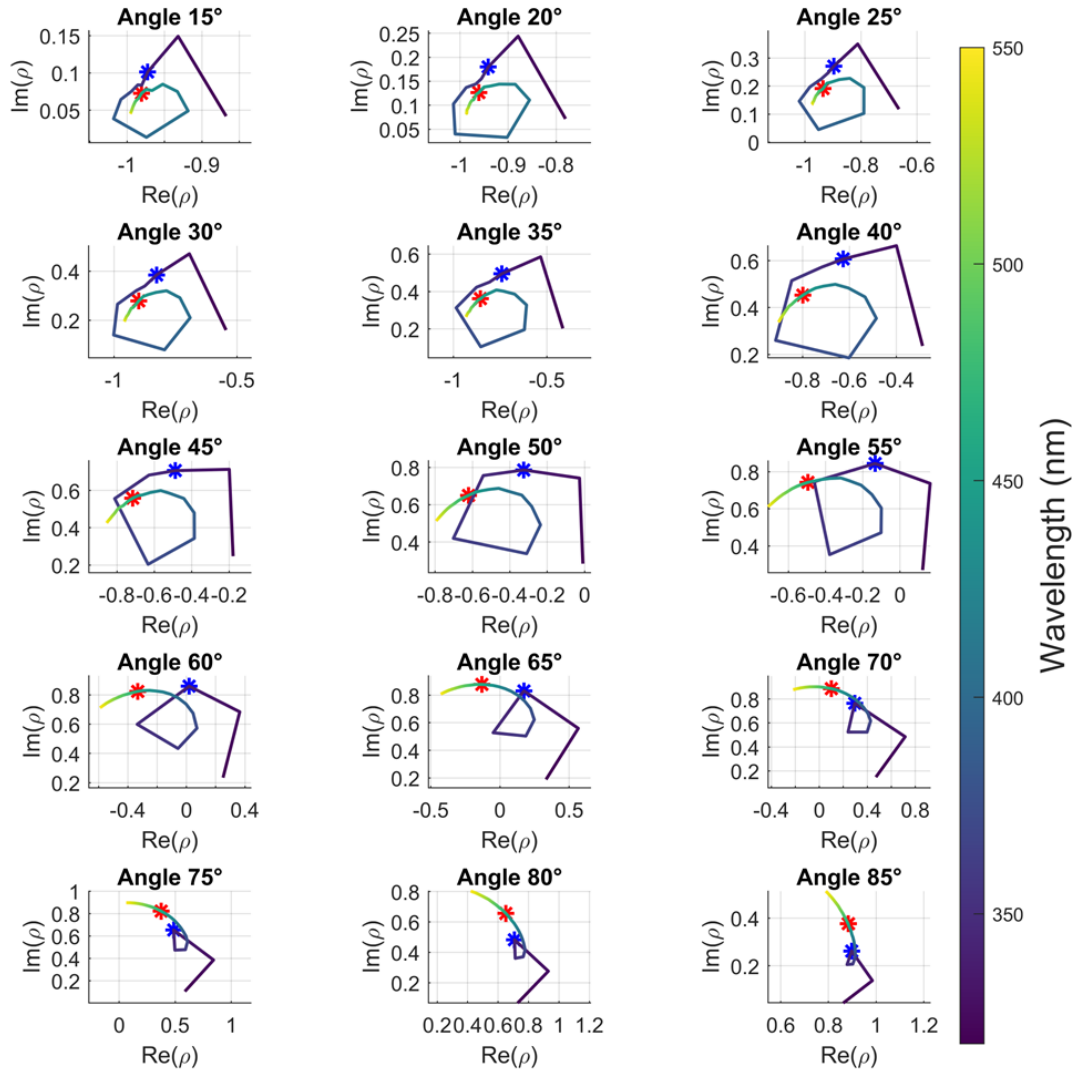


Figure 8.15: Complex-plane trajectory of $\rho = \tan(\Psi)e^{i\Delta}$ for the 5000 rpm ($t = 241$ nm) low dye concentration sample. The red marker indicates the excitonic peak position of fluorescein at 467 nm, while the blue marker indicates the PMMA peak at 336 nm.

Figures 8.11–8.15 show the trajectory plots of the complex reflection coefficient (ρ) for the same cavities studied in Figures 8.6 to 8.10. The red and blue markers indicate the known excitonic absorption peaks of fluorescein (467 nm, red star) and PMMA (336 nm, blue star), which are embedded within the cavity material. These plots illustrate how the reflection changes in the complex plane

with different angles and wavelengths. In thicker cavities, the trajectories are larger and more complex because multiple Fabry–Pérot modes are present. As the cavity becomes thinner, the trajectories become smaller and simpler, indicating fewer modes. The positions of these loops also change with angle, which matches the mode shifts observed in the heatmaps and line spectra. Near the excitonic resonance (red markers), the trajectories do not show strong splitting or major changes, confirming that the system operates in the weak coupling regime due to the low number of dye molecules. This analysis supports the earlier results from the heatmaps (Figures 8.1 - 8.5) and line spectra (Figures 8.6 - 8.10), demonstrating fewer cavity modes and weak exciton-photon interaction as the thickness decreases.

8.4 Strong Coupling Regime in High-Concentration Samples

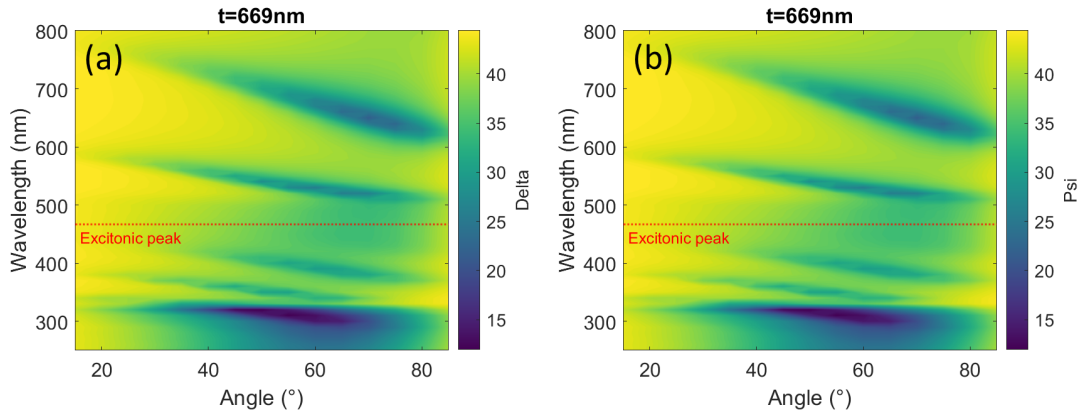


Figure 8.16: Angle-resolved contour plots of Ψ and Δ for the sample prepared at 1000 rpm with the thickness 669 nm (60 mg/mL).

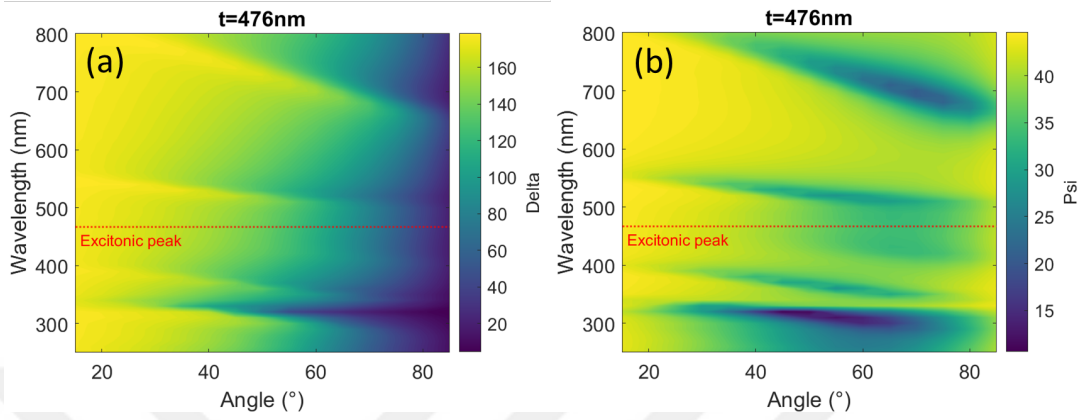


Figure 8.17: Angle-resolved contour plots of Ψ and Δ for the sample prepared at 2000 rpm with the thickness 476 nm (60 mg/mL).

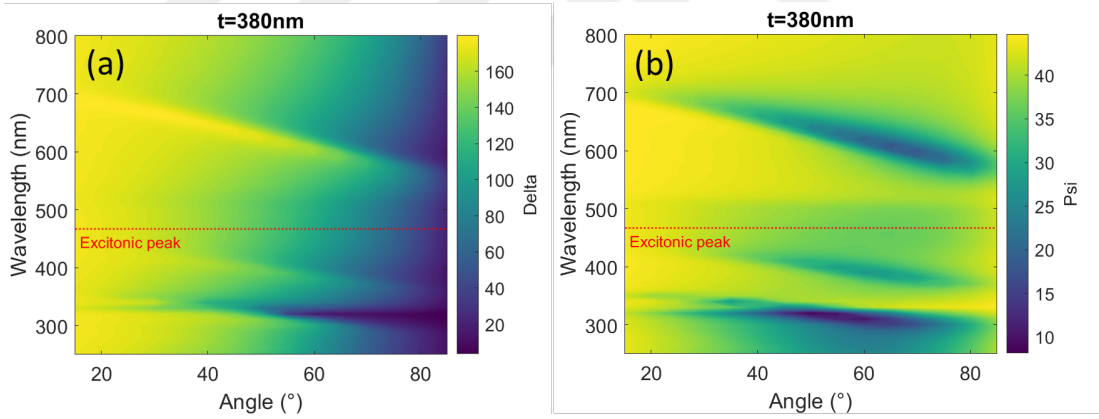


Figure 8.18: Angle-resolved contour plots of Ψ and Δ for the sample prepared at 3000 rpm with the thickness 380 nm (60 mg/mL).

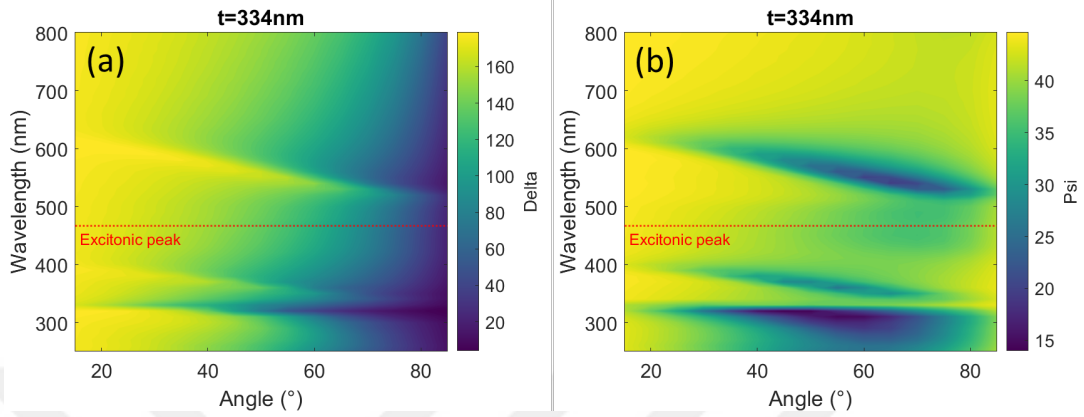


Figure 8.19: Angle-resolved contour plots of Ψ and Δ for the sample prepared at 4000 rpm with the thickness 334 nm (60 mg/mL).

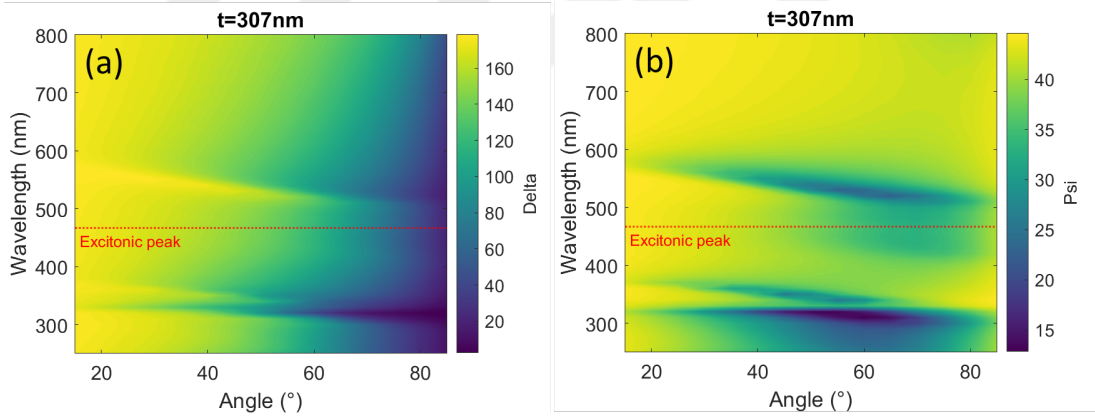


Figure 8.20: Angle-resolved contour plots of Ψ and Δ for the sample prepared at 5000 rpm with the thickness 307 nm (60 mg/mL).

For high dye concentration samples, a detailed examination of the angle-resolved ellipsometric measurements of Ψ and Δ reveals that only two specific cases 2000 rpm (thickness 476 nm) and 5000 rpm (thickness 307 nm) exhibit pronounced deviations from the typical cavity mode dispersion behavior (Figures 8.17 and 8.20).

In the 476 nm cavity (2000 rpm, Figure 8.17), as the incidence angle increases, the cavity mode moves closer to the excitonic absorption peak located at 467 nm.

Around an incidence angle of approximately 55° , the mode undergoes Rabi splitting, where the single photonic cavity mode hybridizes strongly with the excitonic transition of the dye molecules. This results in the formation of two separate energy branches: the upper polariton branch (UPB) and the lower polariton branch (LPB), which diverge as the coupling strength exceeds the combined losses of the system. The minimum energy separation (Rabi splitting) observed here is a signature of entering the strong light-matter coupling regime.

Similarly, in the 307 nm cavity (5000 rpm, Figure 8.20), a comparable phenomenon is observed, with the onset of mode hybridization occurring at a slightly larger angle of approximately 60° . Again, the cavity mode does not simply cross the excitonic resonance but instead exhibits a bending and splitting behavior, producing distinct UPB and LPB branches. This behavior highlights a resonant interaction between the confined cavity photons and excitons, leading to polariton formation.

In contrast, the other cavities (669 nm in Figure 8.16, 380 nm in Figure 8.18, and 334 nm in Figure 8.19) exhibit no pronounced Rabi splitting. Their cavity modes shift toward the excitonic peak at 467 as the angle increases, but they do so smoothly without evidence of avoided crossing or strong coupling. The absence of back-bending and splitting indicates that these cavities remain in the weak coupling regime, where exciton-photon interactions do not significantly modify the dispersion relation.

8.4.1 Resonance Features in $\tan(\Psi)$ and Δ

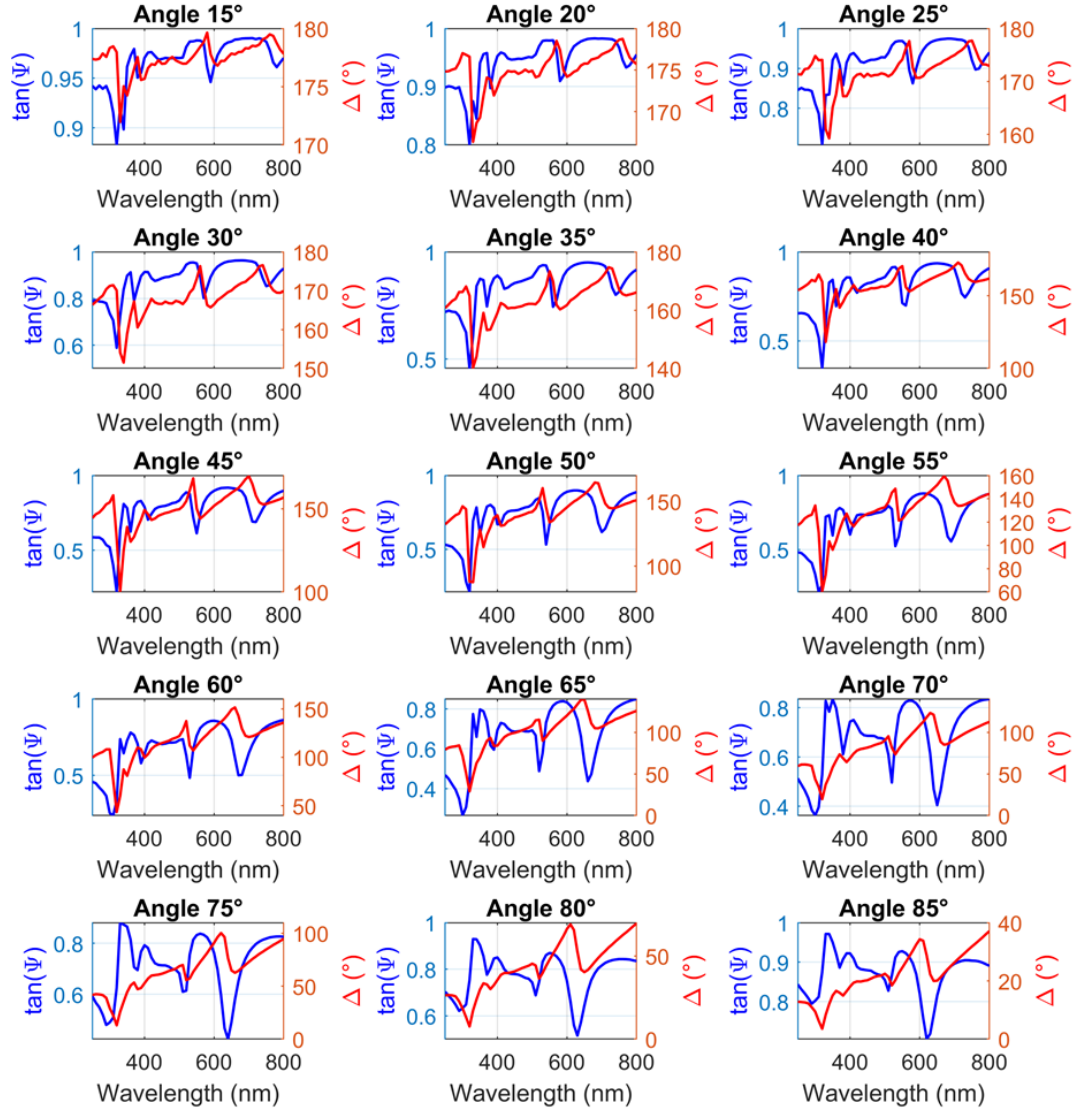


Figure 8.21: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 1000 rpm ($t = 669$ nm) high dye concentration sample.

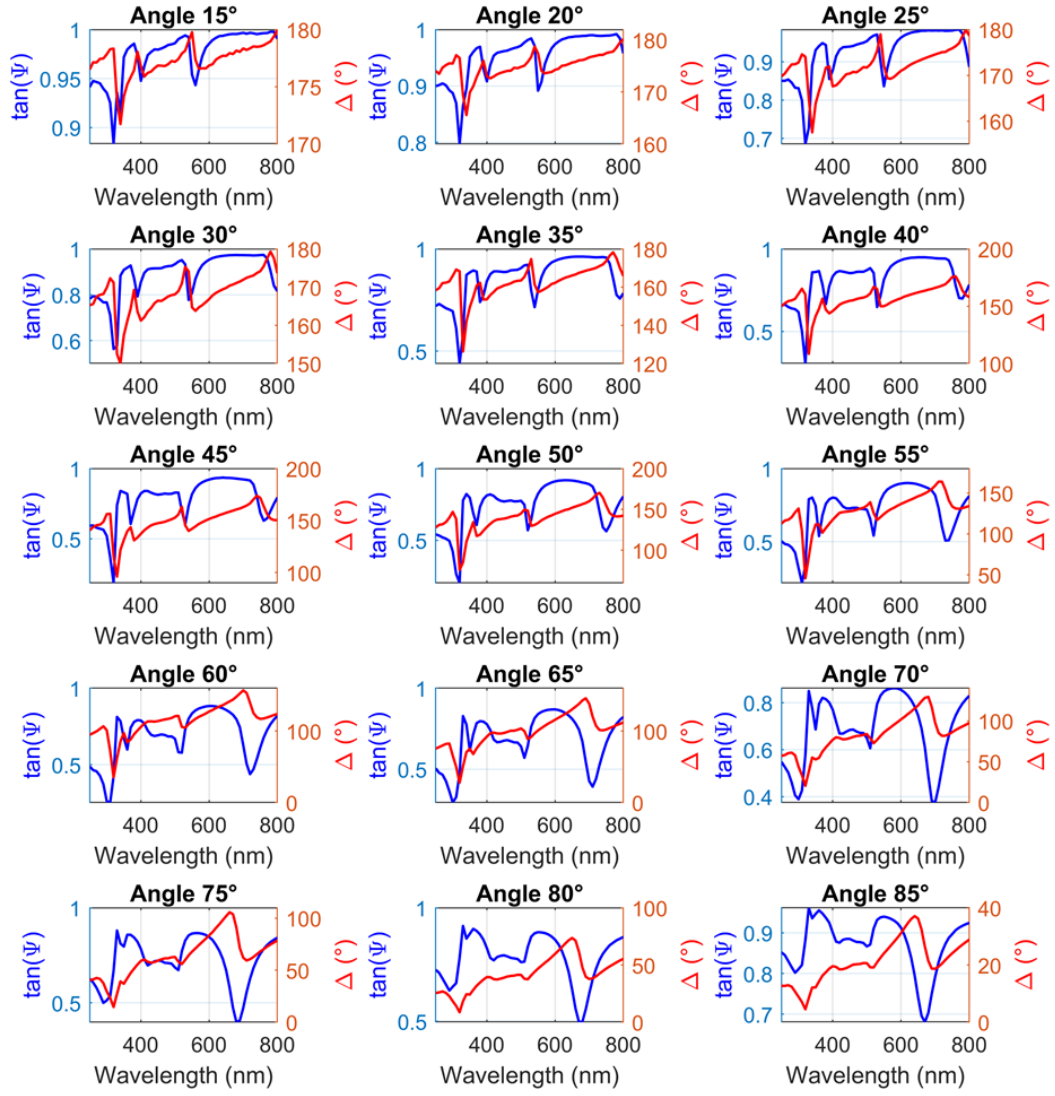


Figure 8.22: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 2000 rpm ($t = 476$ nm) high dye concentration sample.

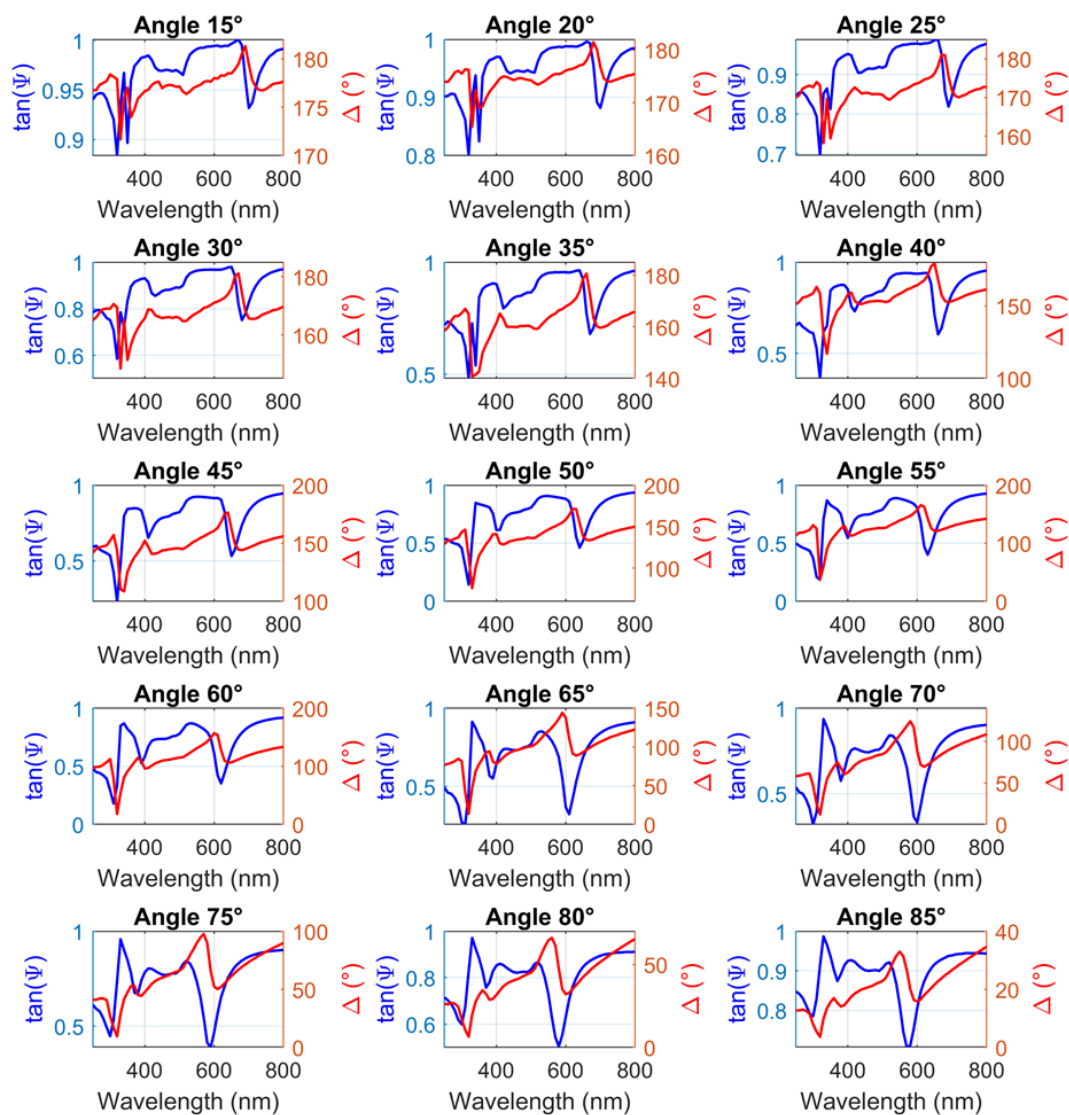


Figure 8.23: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 3000 rpm ($t = 380$ nm) high dye concentration sample.

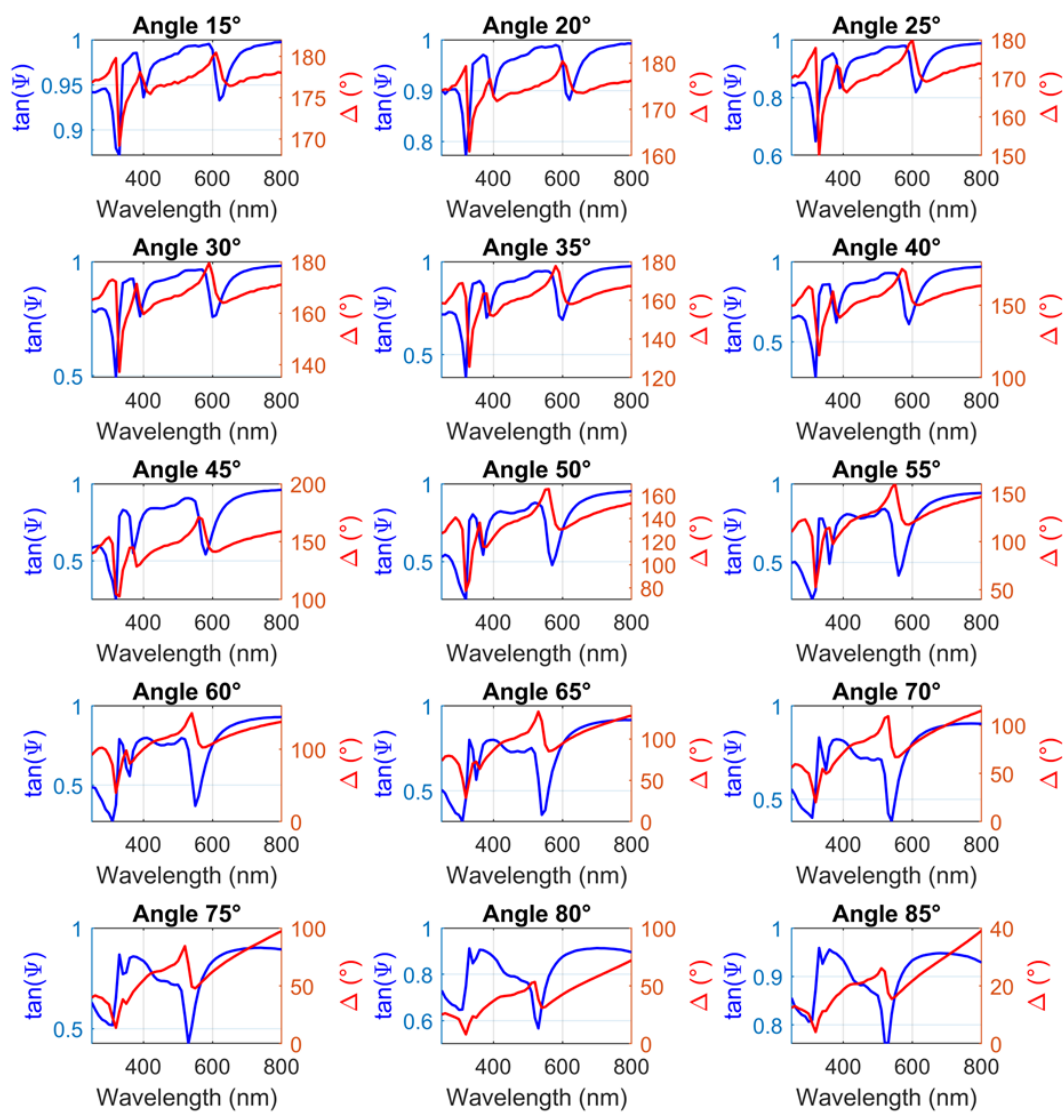


Figure 8.24: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 4000 rpm ($t = 334$ nm) high dye concentration sample.

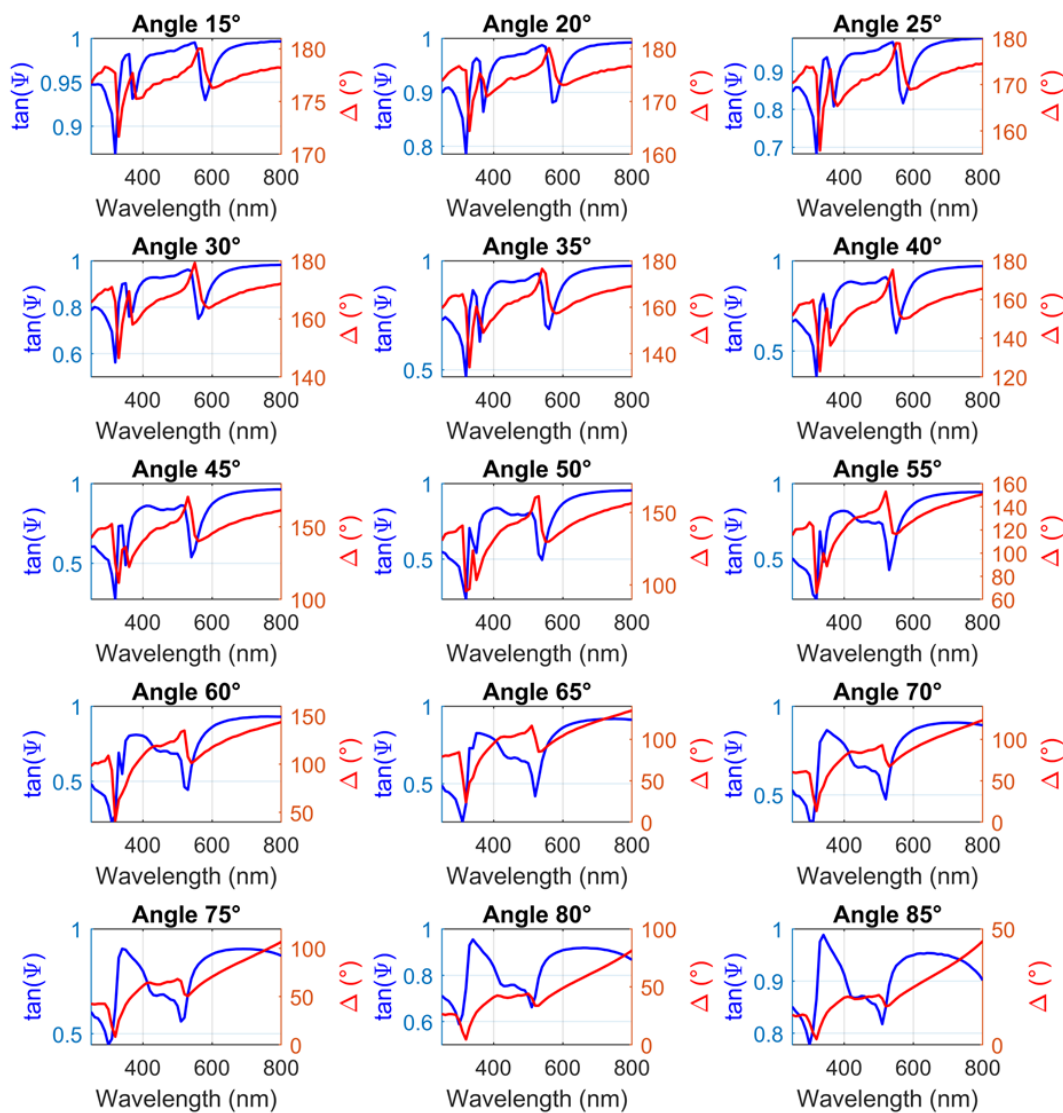


Figure 8.25: Angle-resolved spectra of $\tan(\Psi)$ and Δ for the 5000 rpm ($t = 307$ nm) high dye concentration sample.

Figures 8.21 – 8.25 show the angle-resolved $\tan(\psi)$ and Δ spectra for high dye concentration samples with varying film thicknesses. Compared to low dye concentration samples, these spectra appear smoother with fewer sharp resonances.

The samples prepared at 2000 rpm with a thickness of 476 nm (Figure 8.22) and 5000 rpm with a thickness of 307 nm (Figure 8.25) exhibit pronounced spectral

distortions which indicates strong exciton–photon coupling, leading to Rabi splitting. In these cases, the cavity mode strongly interacts with the excitonic peak near 467 nm, resulting in the formation of upper and lower polariton branches. The splitting is most evident around an incidence angle of approximately 55° for the 476 nm sample and 60° for the 307 nm sample.

Furthermore, the flattening of the line spectra, instead of displaying sharp features, provides additional evidence of strong coupling, specifically in the 476 nm and 307 nm cavities. In contrast, the other samples (1000 rpm, 3000 rpm, and 4000 rpm) show cavity modes that only gradually approach the excitonic resonance without distinct mode splitting, indicating a weaker coupling regime.

8.4.2 Complex ρ Trajectories

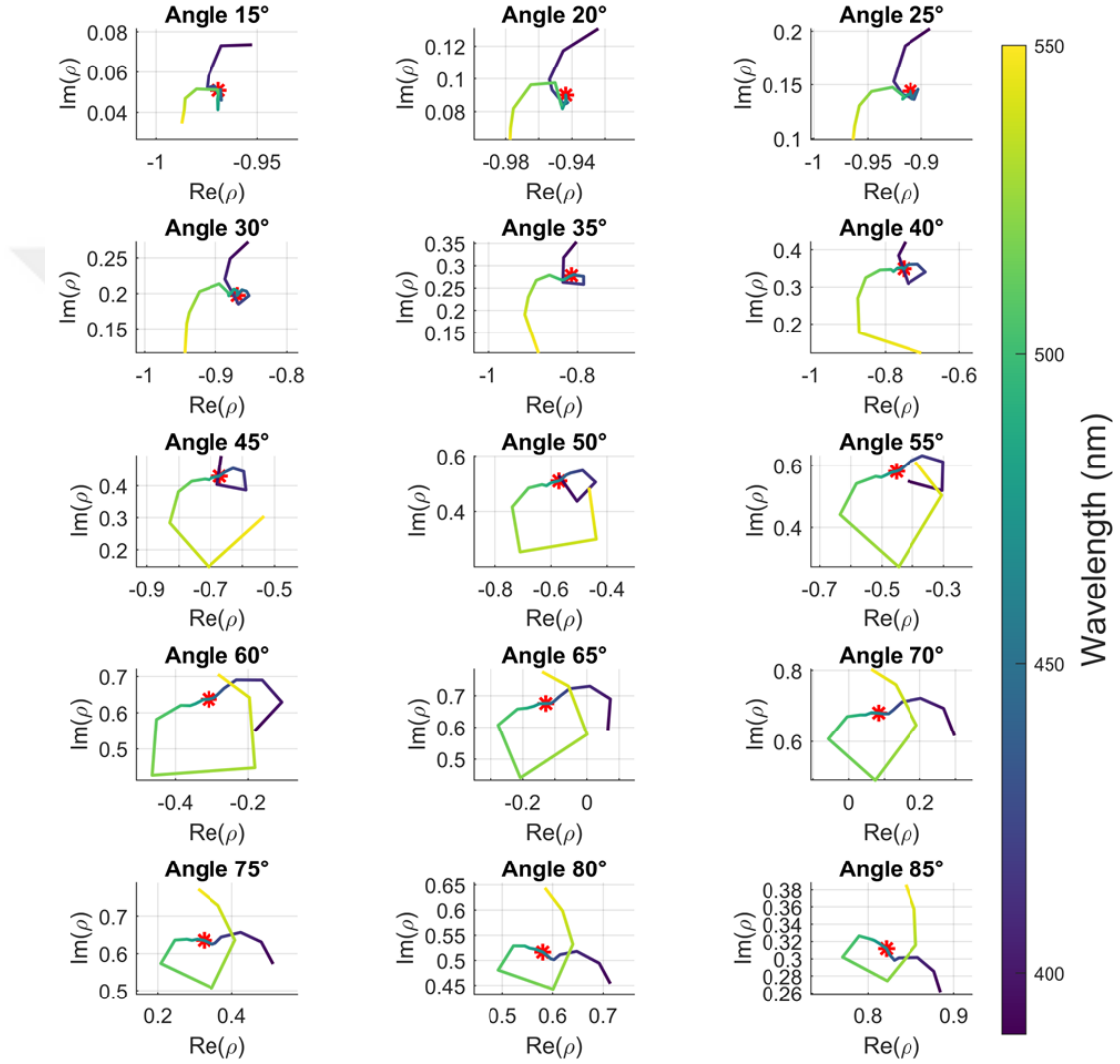


Figure 8.26: Complex-plane $\rho = \tan(\Psi) e^{i\Delta}$ trajectory for the high dye concentration sample prepared at 1000 rpm ($t = 669$ nm). The red marker indicates the excitonic peak position of fluorescein at 467 nm.

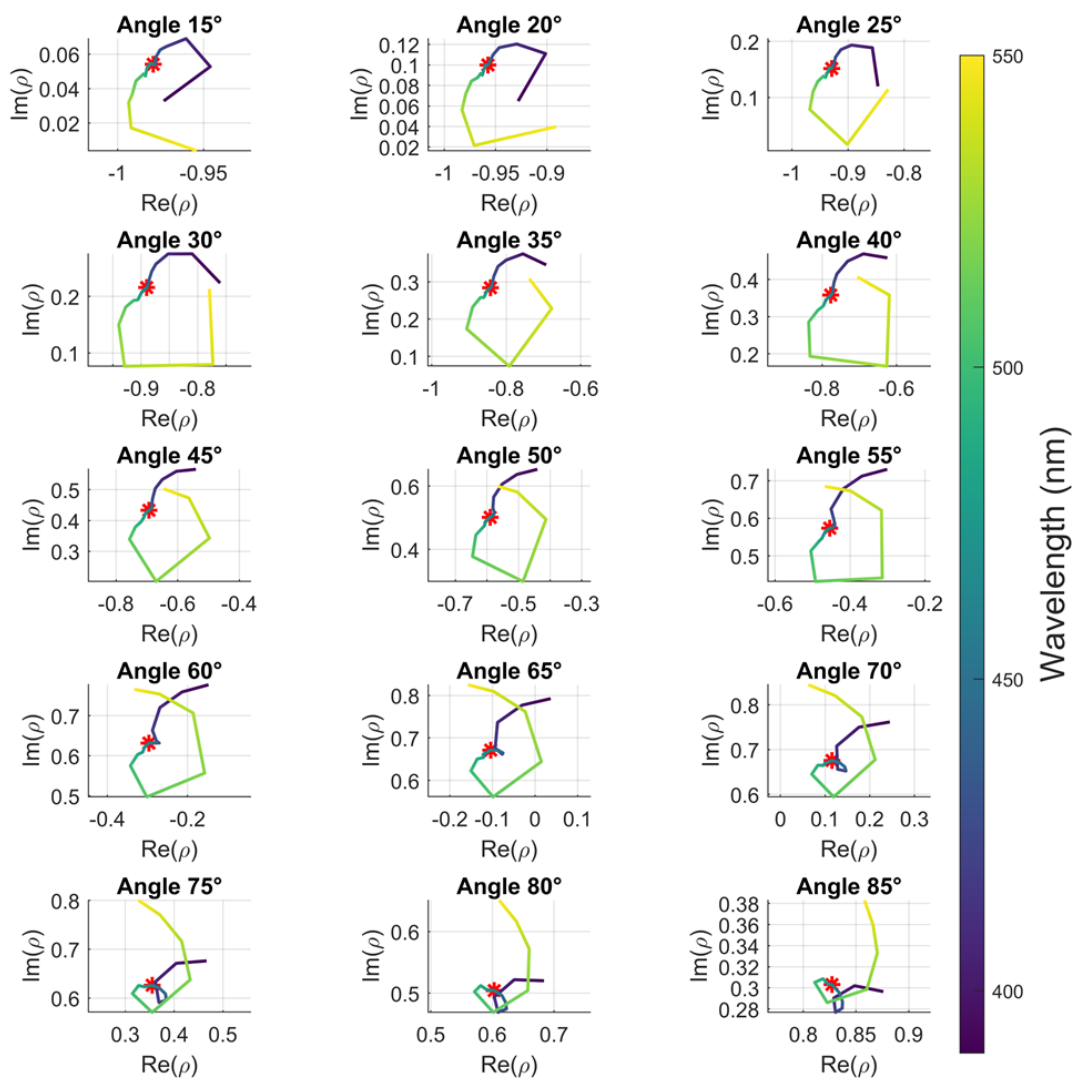


Figure 8.27: Complex-plane $\rho = \tan(\Psi)e^{i\Delta}$ trajectory for the high dye concentration sample prepared at 2000 rpm ($t = 476$ nm). The red marker indicates the excitonic peak position of fluorescein at 467 nm.

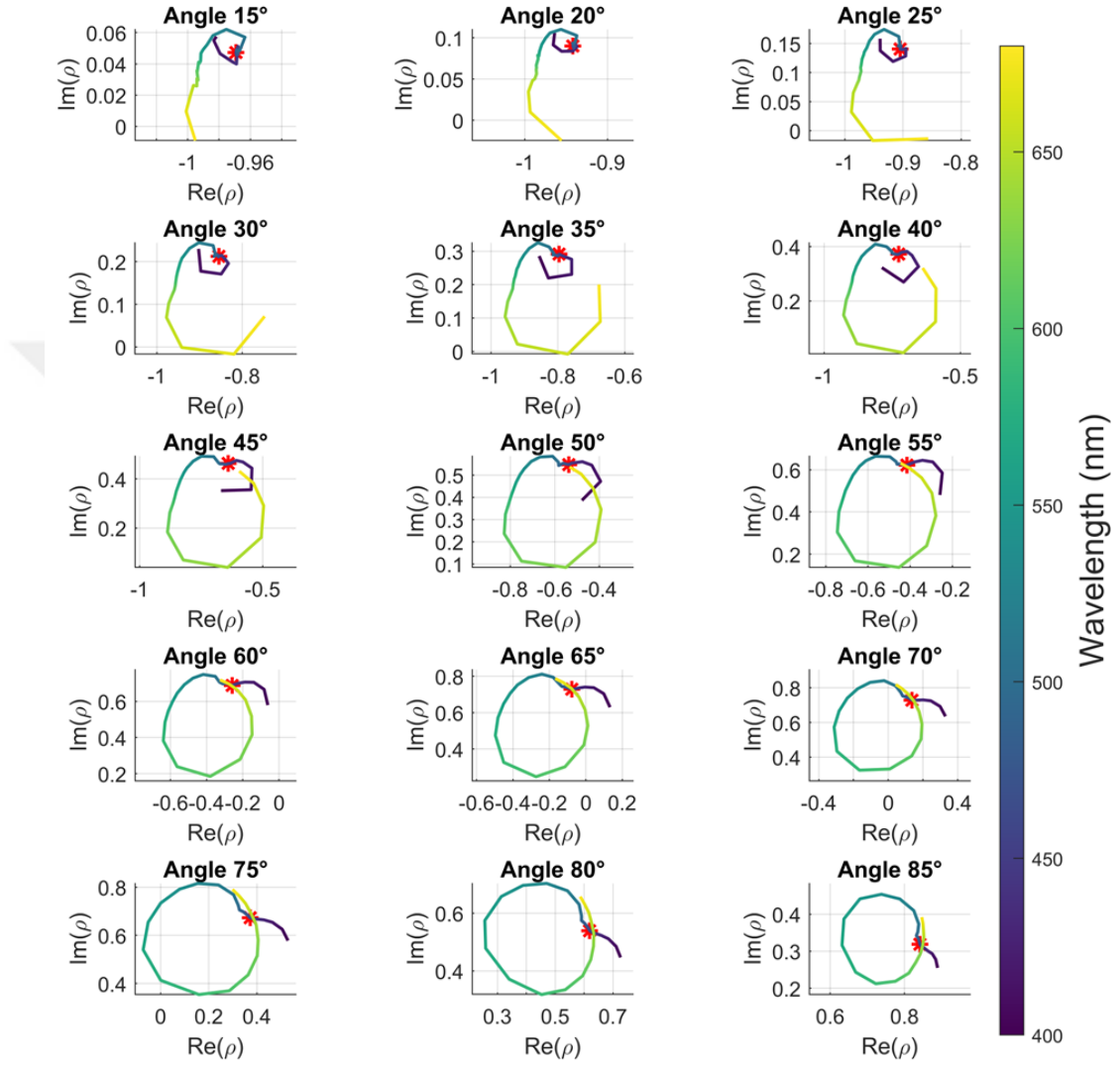


Figure 8.28: Complex-plane $\rho = \tan(\Psi) e^{i\Delta}$ trajectory for the high dye concentration sample prepared at 3000 rpm ($t = 380$ nm). The red marker indicates the excitonic peak position of fluorescein at 467 nm.

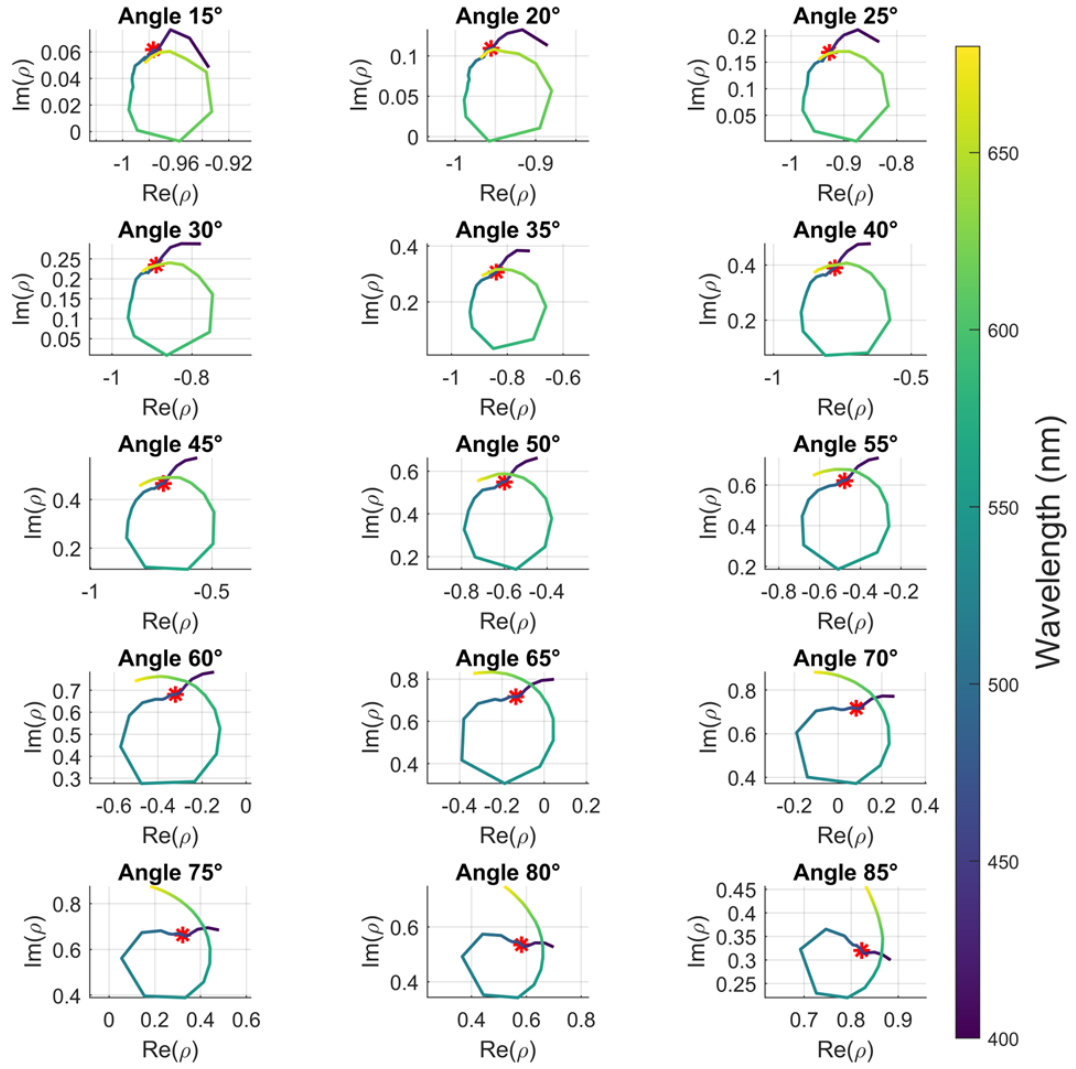


Figure 8.29: Complex-plane $\rho = \tan(\Psi) e^{i\Delta}$ trajectory for the high dye concentration sample prepared at 4000 rpm ($t = 334$ nm). The red marker indicates the excitonic peak position of fluorescein at 467 nm.

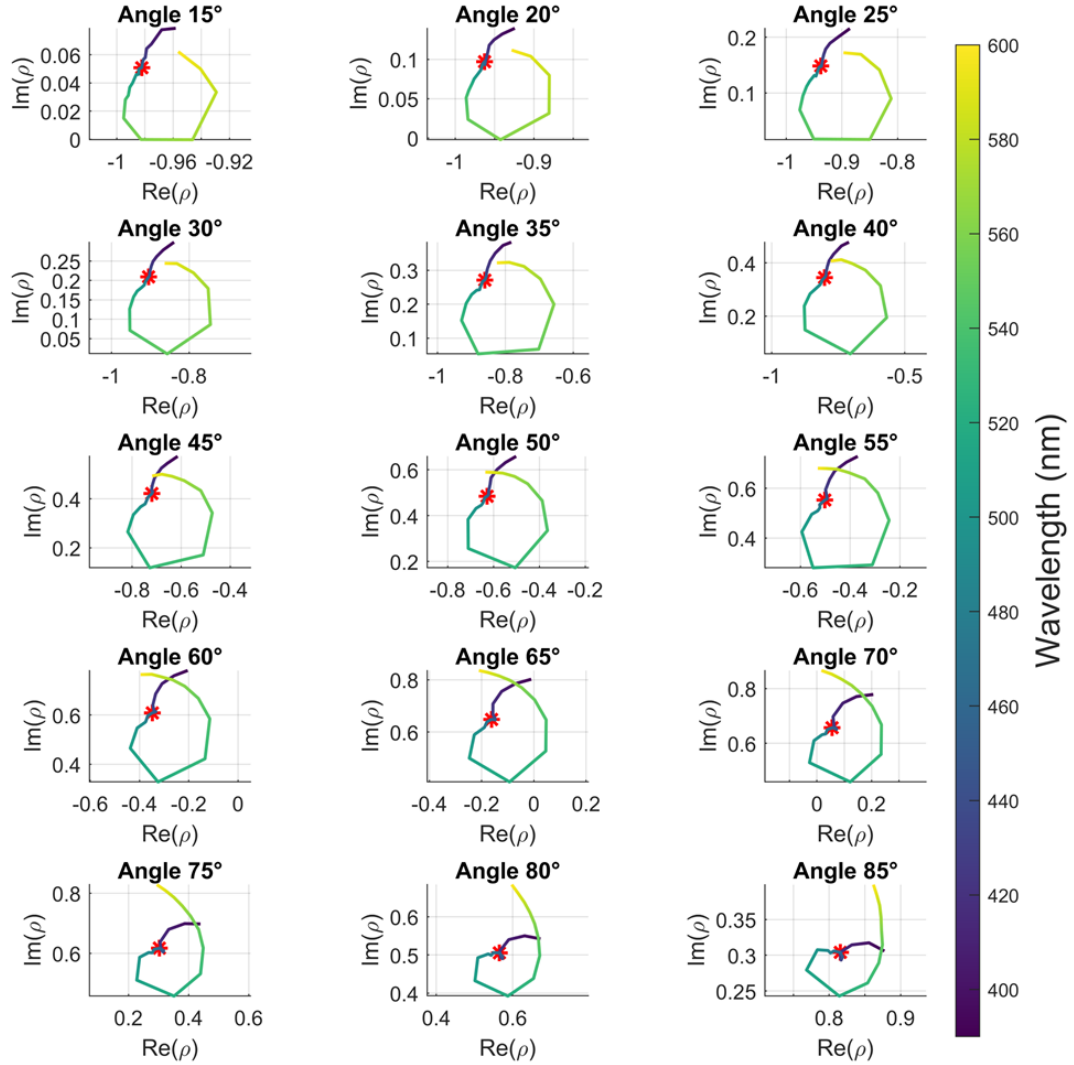


Figure 8.30: Complex-plane $\rho = \tan(\Psi) e^{i\Delta}$ trajectory for the high dye concentration sample prepared at 5000 rpm ($t = 307$ nm). The red marker indicates the excitonic peak position of fluorescein at 467 nm.

A more detailed analysis of the complex-plane $\rho = \tan(\Psi) e^{i\Delta}$ trajectories reveals notable distinctions between the samples with different thicknesses, as shown in Figures 8.27 and 8.30. For the sample prepared at 2000 rpm with a thickness of 476 nm, a secondary internal loop begins to emerge prominently at an incidence angle of approximately 55°. Similarly, for the sample fabricated at 5000 rpm with a thickness of 307 nm, a comparable secondary loop formation becomes visible

starting near 60° .

The presence of this secondary internal loop within the larger trajectory loop is a clear hallmark of strong exciton–photon coupling within the microcavity. Under normal weak coupling conditions, the trajectory forms a single smooth loop corresponding to the uncoupled cavity mode.

The emergence of these additional internal loops in the complex-plane representation directly corresponds to the anti-crossing behavior observed in the angle-resolved ellipsometric spectra for these samples. In the strong coupling regime, as seen here, the optical response of the system deviates from the sharp resonant features of weak coupling and instead exhibits a flatter, more distorted line shape. This flattened response, combined with the internal loop formation, signifies that the exciton and photon modes are no longer independent but instead strongly mixed, resulting in a new set of eigenmodes.

Therefore, Figures 8.27 and 8.30 provide compelling visual confirmation of the transition from weak to strong coupling in these high dye concentration microcavities. The interaction is strongest cavities 669 nm, 476 nm, and 307 nm, where the photonic mode energy closely matches the excitonic resonance, maximizing the coupling strength and leading to pronounced Rabi splitting effects. Still at 669 nm, the loop is not too obvious. In contrast, for the remaining samples with thicknesses of 380 nm (3000 rpm), and 334 nm (4000 rpm), as shown in Figures 8.28 and 8.29, respectively, no secondary internal loop formation is observed across the measured angular range. The complex-plane trajectories for these cases remain as single smooth loops, indicating that the interaction between the cavity photon mode and the excitonic resonance is not sufficiently strong to induce a Rabi splitting. These samples therefore, remain in the weak-coupling regime, where the cavity mode does not approach the excitonic peak.

8.5 Summary

This chapter used angle-resolved spectroscopic ellipsometry (maps of Ψ and Δ), line spectra of $\tan(\Psi)$ and Δ , and complex-plane $\rho = \tan(\Psi) e^{i\Delta}$ trajectories to diagnose cavity–exciton interactions in fluorescein–PMMA Fabry–Pérot microcavities. At low dye loading (20 $\mu\text{g/mL}$), all thicknesses (475–241 nm) show purely photonic dispersion: FP modes blue-shift with angle, cross the ~ 467 nm excitonic band without anticrossing, and yield single-loop ρ trajectories consistent with weak coupling. At high loading (60 mg/mL), the response depends on thickness: the 476 nm and 307 nm cavities exhibit clear back-bending/anticrossings and secondary internal loops in ρ near $\sim 55\text{--}60^\circ$, evidencing strong coupling and polariton formation. The 669 nm cavity represents an intermediate case: a minor back-bending is visible in the dispersion, but no secondary loop appears in ρ , indicating incipient coupling without fully developed polaritons. By contrast, the 380 nm and 334 nm cavities show no pronounced splitting and remain in the weak-coupling regime. Overall, ellipsometric amplitude/phase signatures and ρ -trajectory topology provide a consistent, angle-resolved picture of the progression from weak to strong coupling as concentration and detuning are optimized.

Chapter 9

Angle Dependent Reflectance

9.1 Chapter Overview

This chapter investigates angle-dependent reflectance and fluorescence in fluorescein-doped PMMA Fabry–Pérot microcavities, with cavity thickness controlled via spin-coating speed (1000–5000 rpm) and dye concentration varied to tune exciton oscillator strength. Dispersion mapping shows purely photonic dispersion in low-concentration samples (20 $\mu\text{g/mL}$) consistent with weak coupling, and pronounced backbending in high-concentration samples (60 mg/mL), indicative of strong coupling, where the degree of splitting is governed by cavity thickness and angular detuning. A three-coupled oscillator model is applied to extract coupling strengths.

9.2 Angle Dependent Reflectance and Fluorescence for Low Dye Concentration Samples

In the low dye concentration regime (20 $\mu\text{g/mL}$), the angle-resolved reflectance maps show one to three Fabry–Pérot cavity modes depending on optical thickness.

As the incidence angle increases, these resonances blue-shift and pass smoothly through the fluorescein absorption band with no avoided crossing. Changing the film thickness adjusts the free spectral range and the number of supported modes; thinner films display wider spacing and fewer modes. Angle-resolved fluorescence follows the cavity dispersion, giving directional out-coupling and intensity maxima where the emission band overlaps a cavity mode. These observations establish a clear weak-coupling baseline for comparison with high-concentration samples.



9.2.1 Reflectance and Fluorescence at 475 nm

$t=475\text{nm}$

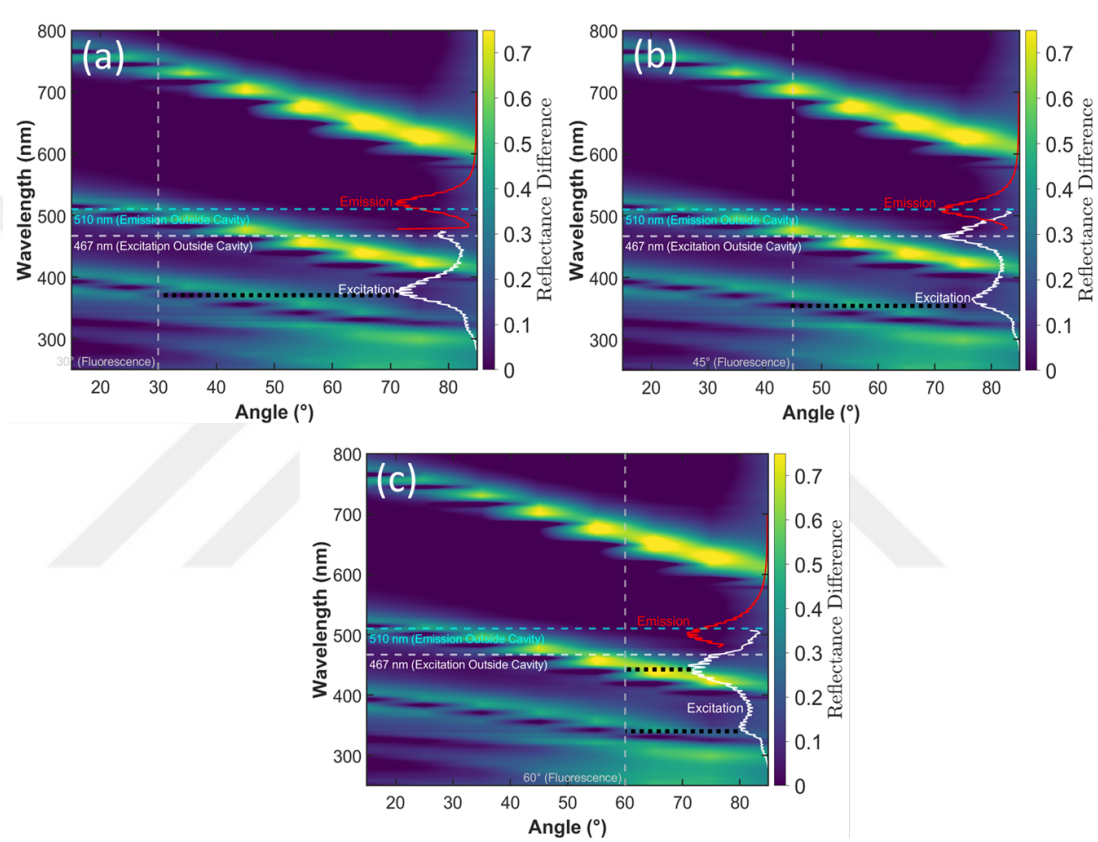


Figure 9.1: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the low dye concentration (20 $\mu\text{g/mL}$) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 1000 rpm ($t = 475\text{ nm}$). Reflectance was measured over incidence angles from 15° to 85° . The out-of-cavity excitation peak at 467 nm and emission peak at 510 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30° , 45° , and 60° , with respect to the excitation source. These angles were selected to obtain the strongest fluorescence signal.

9.2.2 Reflectance and Fluorescence at 350 nm

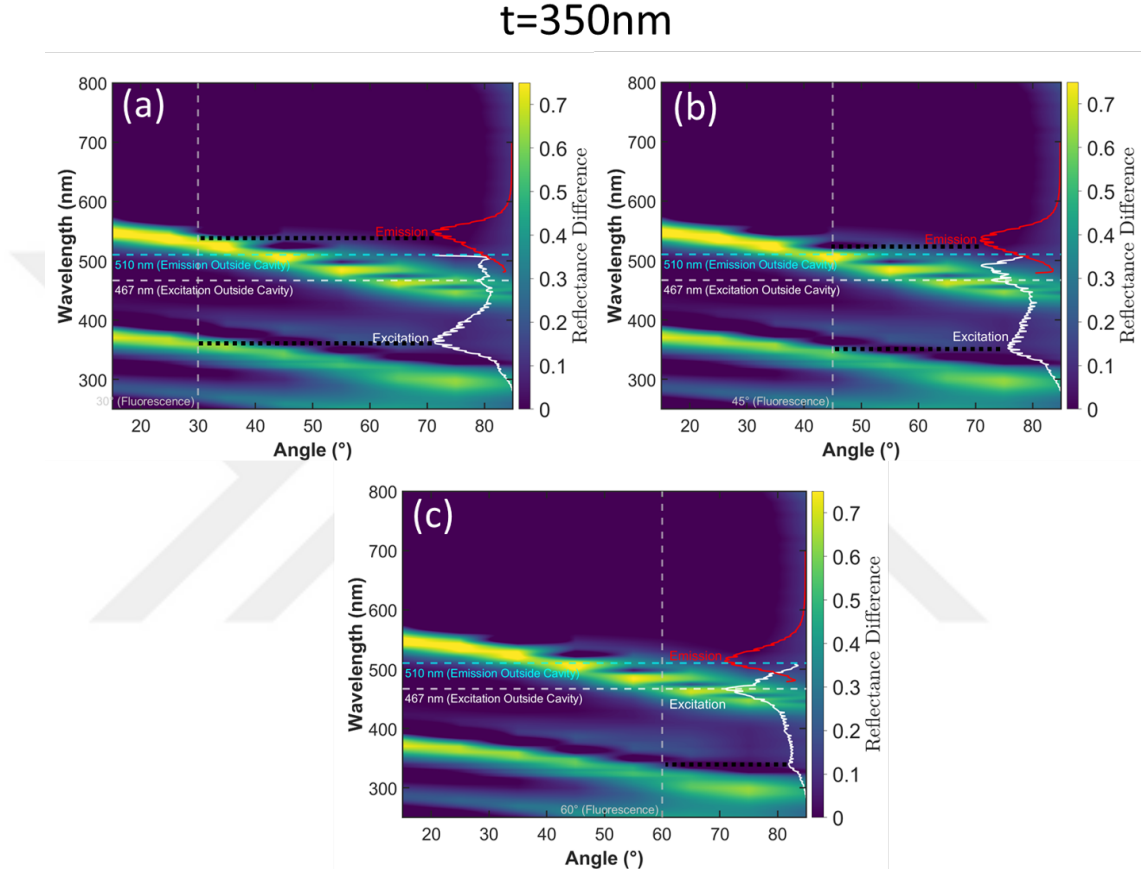


Figure 9.2: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the low dye concentration (20 $\mu\text{g/mL}$) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 2000 rpm ($t = 350\text{ nm}$). Reflectance was measured over incidence angles from 15° to 85° . The out-of-cavity excitation peak at 467 nm and emission peak at 510 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30° , 45° , and 60° , concerning the excitation source. These angles were selected to obtain the strongest fluorescence signal.

9.2.3 Reflectance and Fluorescence at 291 nm

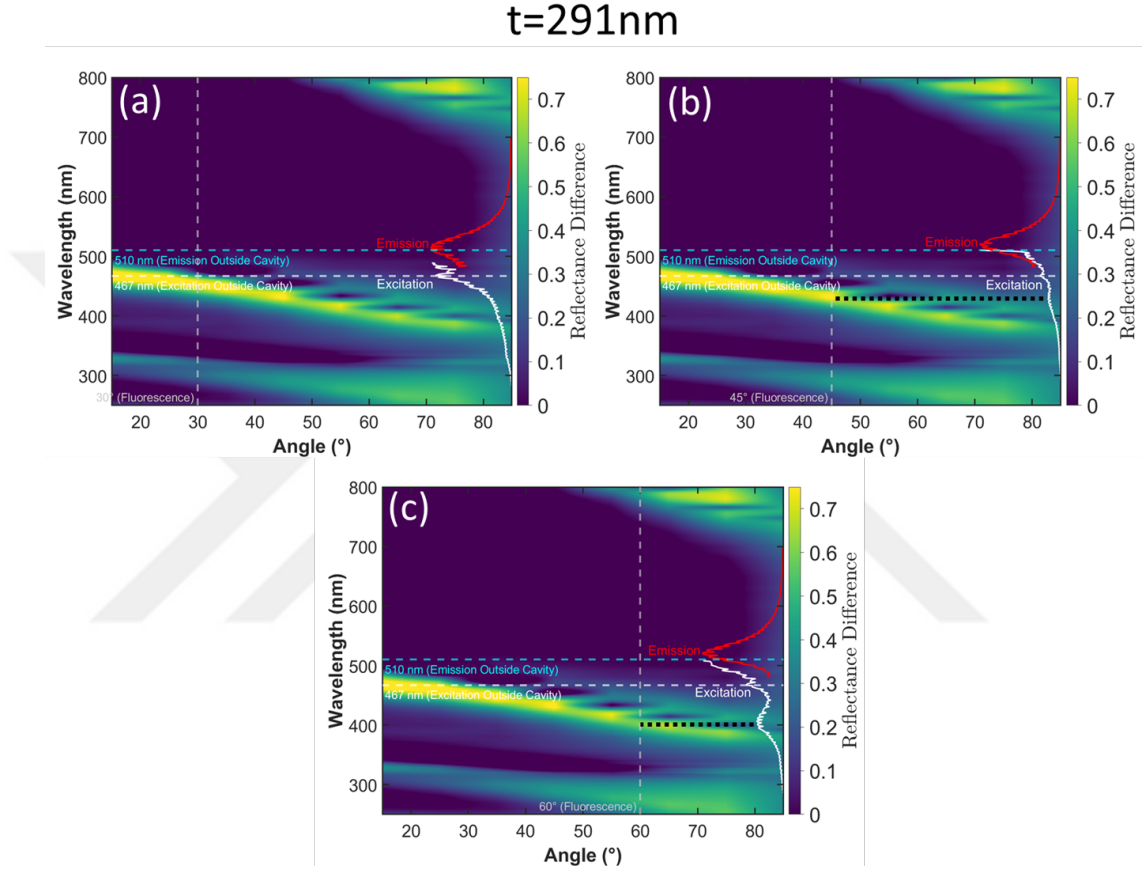


Figure 9.3: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the low dye concentration (20 µg/mL) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 3000 rpm ($t = 291$ nm). Reflectance was measured over incidence angles from 15° to 85°. The out-of-cavity excitation peak at 467 nm and emission peak at 510 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30°, 45°, and 60°, concerning the excitation source. These angles were selected to obtain the strongest fluorescence signal.

9.2.4 Reflectance and Fluorescence at 253 nm

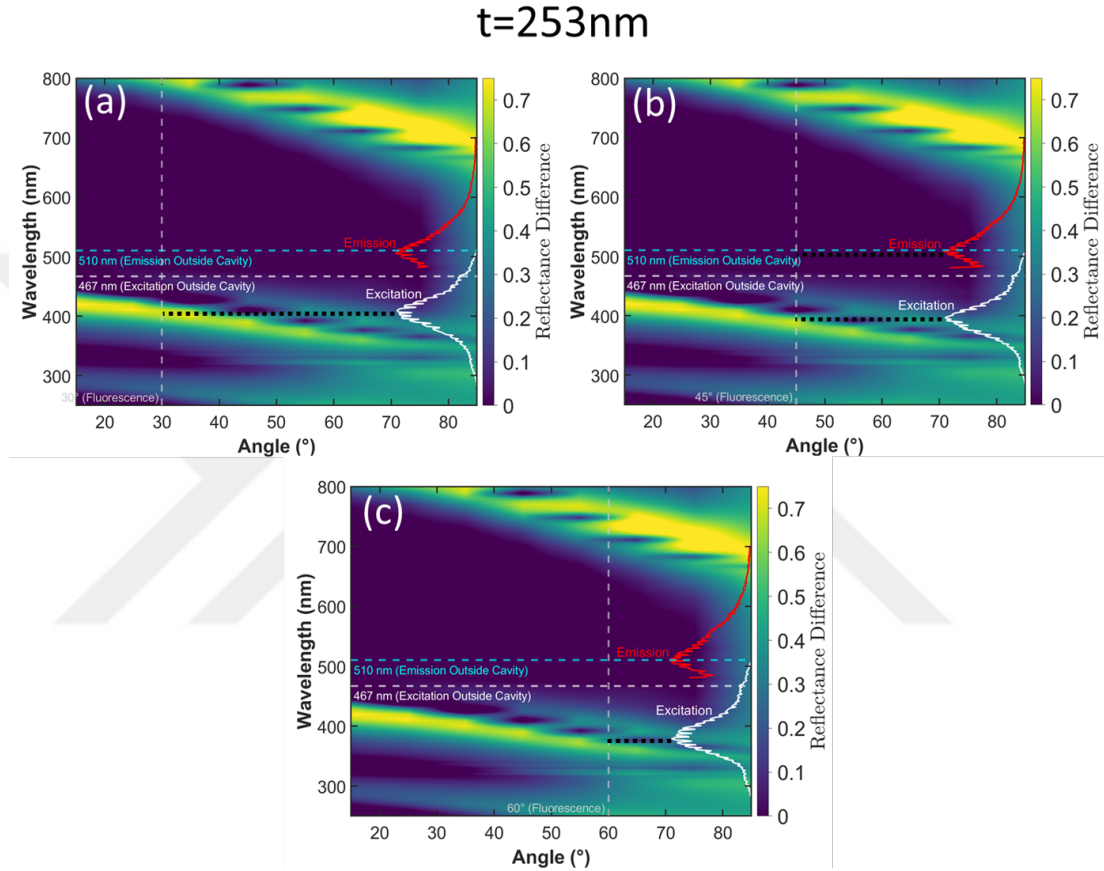


Figure 9.4: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the low dye concentration (20 $\mu\text{g/mL}$) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 4000 rpm ($t = 253\text{ nm}$). Reflectance was measured over incidence angles from 15° to 85° . The out-of-cavity excitation peak at 467 nm and emission peak at 510 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30° , 45° , and 60° , concerning the excitation source. These angles were selected to obtain the strongest fluorescence signal.

9.2.5 Reflectance and Fluorescence at 240 nm

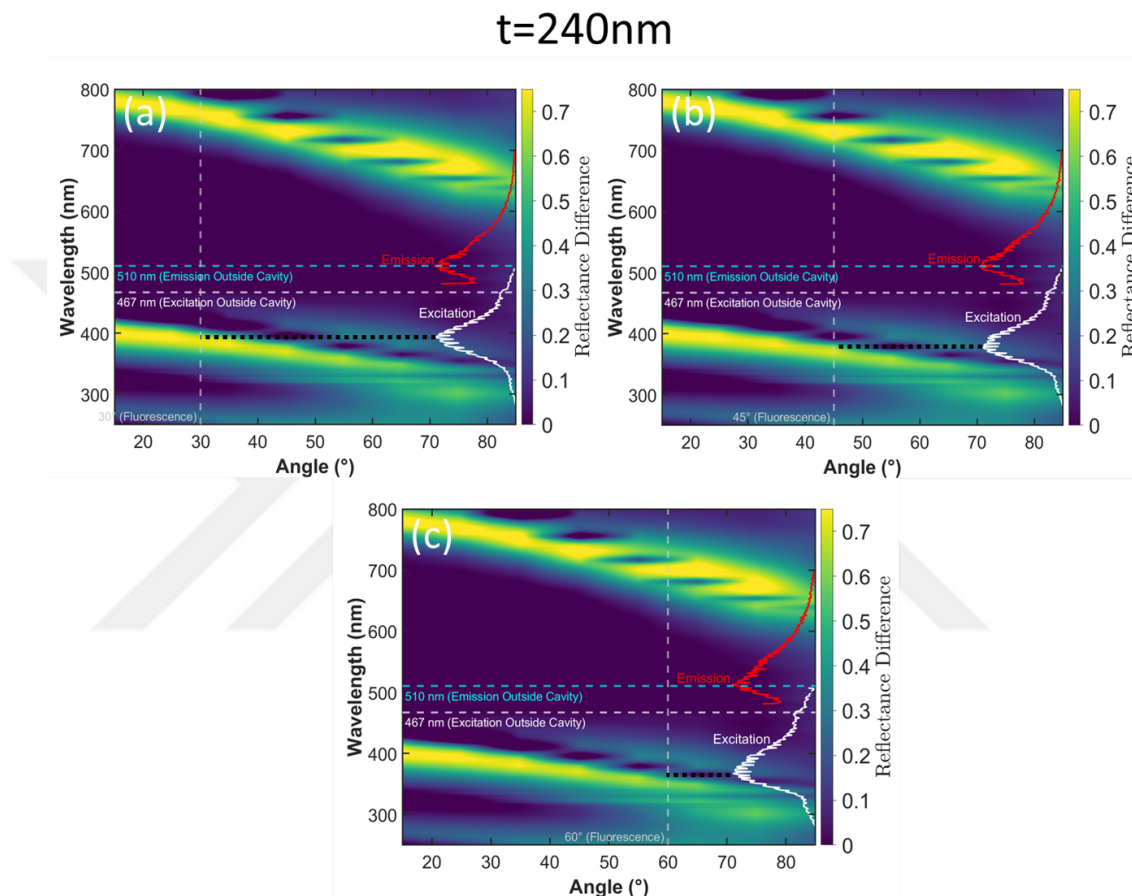


Figure 9.5: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the low dye concentration (20 $\mu\text{g/mL}$) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 5000 rpm ($t = 240\text{ nm}$). Reflectance was measured over incidence angles from 15° to 85° . The out-of-cavity excitation peak at 467 nm and emission peak at 510 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30° , 45° , and 60° , concerning the excitation source. These angles were selected to obtain the strongest fluorescence signal.

Figures 9.1–9.5 present the angle-resolved simulated and experimental reflectance maps for fluorescein-doped PMMA Fabry-Pérot cavities with a dye concentration

of 20 $\mu\text{g/mL}$, prepared at spin-coating speeds from 1000 rpm to 5000 rpm. In all cases, reflectance was measured from 15° to 85° , and the measured fluorescence (red) and excitation (white) spectra were overlaid for three selected angles (30° , 45° , and 60°) chosen for their strong fluorescence output. The dashed horizontal lines denote the out-of-cavity excitation and emission wavelengths at 467 nm and 510 nm, respectively.

For the 1000 rpm (Figure 9.1) and 2000 rpm (Figure 9.2) cavities, two distinct photonic modes are present within the spectral vicinity of the excitation peak at 467 nm. As the incidence angle changes, both modes approach and overlap different portions of the excitation band, producing modulation across the entire excitation spectrum. This dual-mode overlap significantly enhances the local photonic density of states over the whole excitation range, leading to well-defined shoulders and shaping in the measured excitation spectra.

In contrast, for the thinner cavities at 3000 rpm (Figure 9.3), 4000 rpm (Figure 9.4), and 5000 rpm (Figure 9.5), only one photonic mode intersects the excitation band. This mode sweeps across a limited spectral segment with angle, leading to more localized modulation and a less pronounced redistribution of the excitation intensity compared to the dual-mode cases.

In the emission band (510 nm), the degree of spectral modulation is determined by whether a cavity mode falls within this range at the measured angles. For the 1000 rpm sample (Fig. 9.1), the emission wavelength is only partially approached by a mode at low angles (e.g., 30°), so the profile remains largely unaltered at higher angles where the mode shifts away. In contrast, for the 2000 rpm sample (Fig. 9.2), a cavity mode remains within the emission band over the full angular range, producing continuous spectral modulation. For the 3000 rpm, 4000 rpm, and 5000 rpm samples (Figs. 9.3–9.5), no cavity mode intersects the emission wavelength at any measured angle, so the emission spectra remain unmodulated and match the natural out-of-cavity fluorescence profile. In all cases, only one cavity mode is present near the emission region when overlap occurs, consistent with the expected photonic mode spacing for the given cavity thicknesses.

9.3 Angle Dependent Reflectance and Fluorescence for High Dye Concentration Samples

In the high dye concentration regime (60 mg/mL), the angle-resolved reflectance maps show one to five Fabry–Pérot cavity modes depending on optical thickness. As the incidence angle increases, these resonances blue-shift and, on approaching the fluorescein absorption band, exhibit back-bending with a clear avoided crossing in both experimental and TMM-simulated reflectance.

9.3.1 Reflectance and Fluorescence at 669 nm

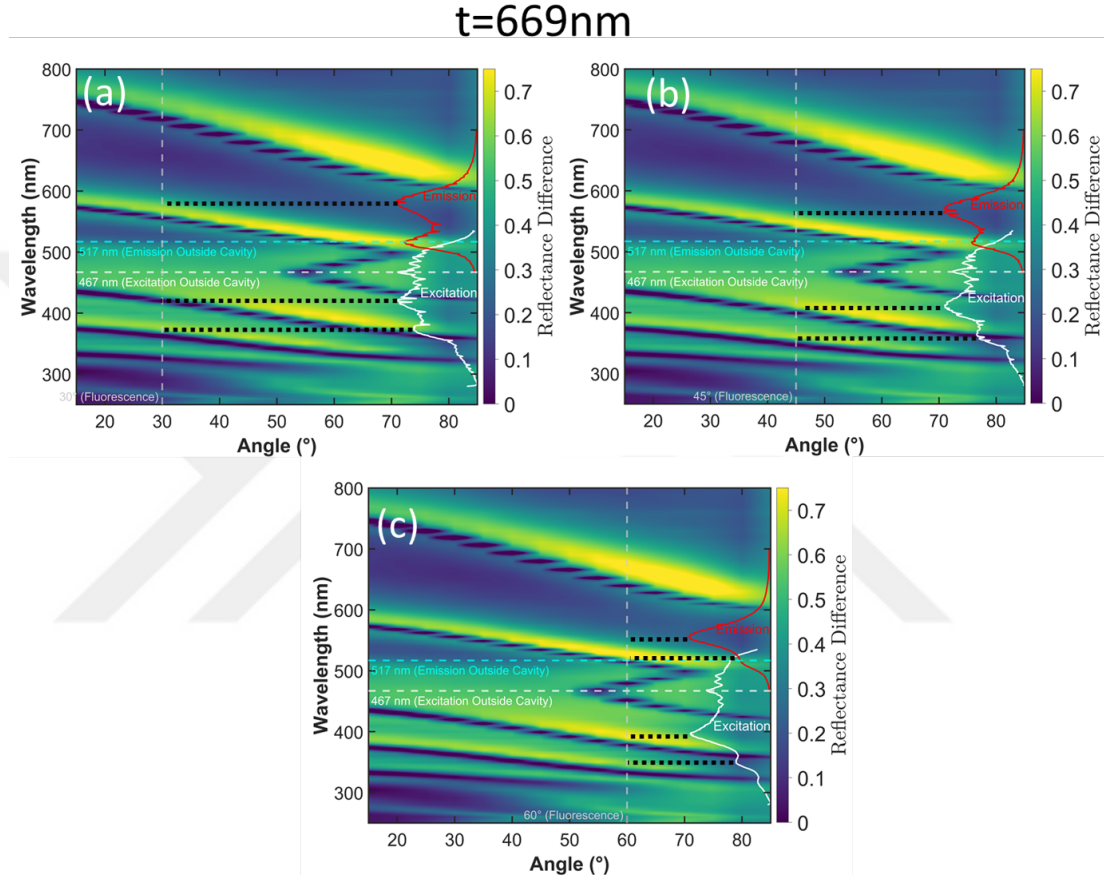


Figure 9.6: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the high dye concentration (60 mg/mL) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 1000 rpm ($t = 669\text{ nm}$). Reflectance was measured over incidence angles from 15° to 85° . The out-of-cavity excitation peak at 467 nm and emission peak at 517 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30° , 45° , and 60° , concerning the excitation source. These angles were selected to obtain the strongest fluorescence signal.

9.3.2 Reflectance and Fluorescence at 476 nm

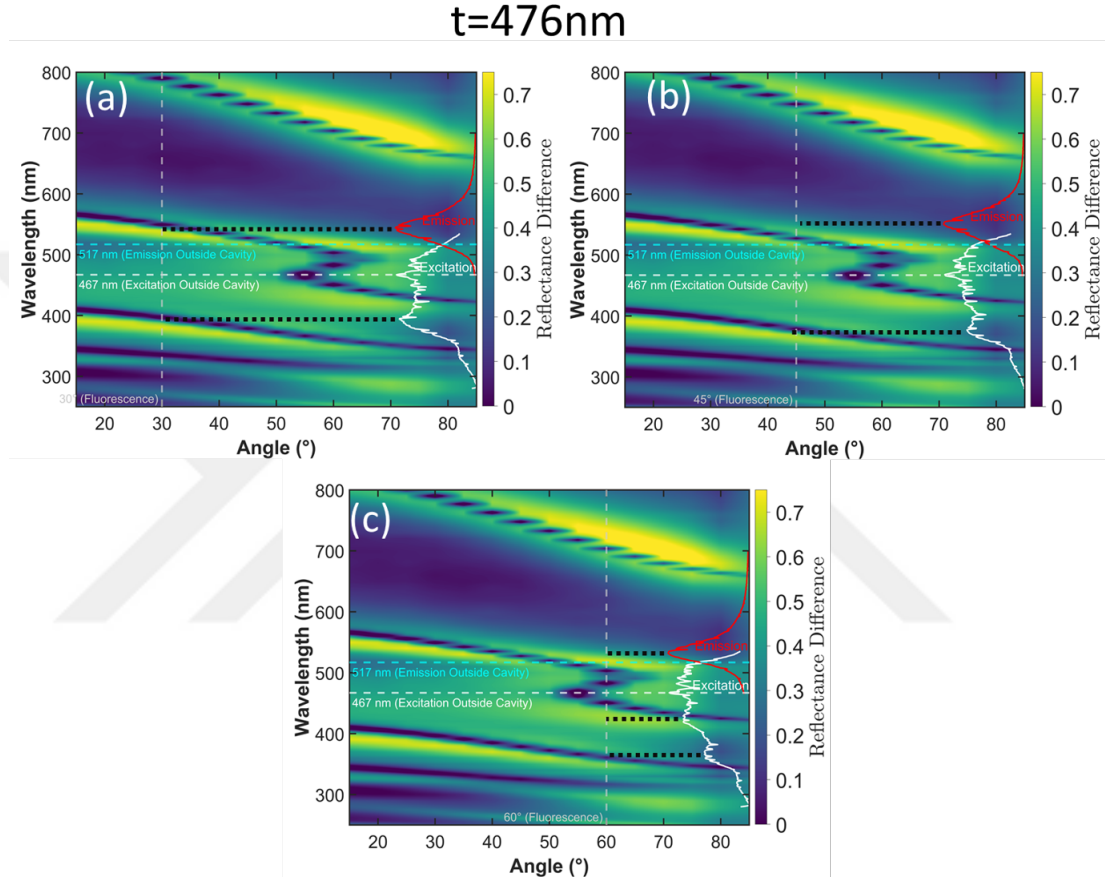


Figure 9.7: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the high dye concentration (60 mg/mL) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 2000 rpm ($t = 476$ nm). Reflectance was measured over incidence angles from 15° to 85° . The out-of-cavity excitation peak at 467 nm and emission peak at 517 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30° , 45° , and 60° , concerning the excitation source. These angles were selected to obtain the strongest fluorescence signal.

9.3.3 Reflectance and Fluorescence at 380 nm

$t=380\text{nm}$

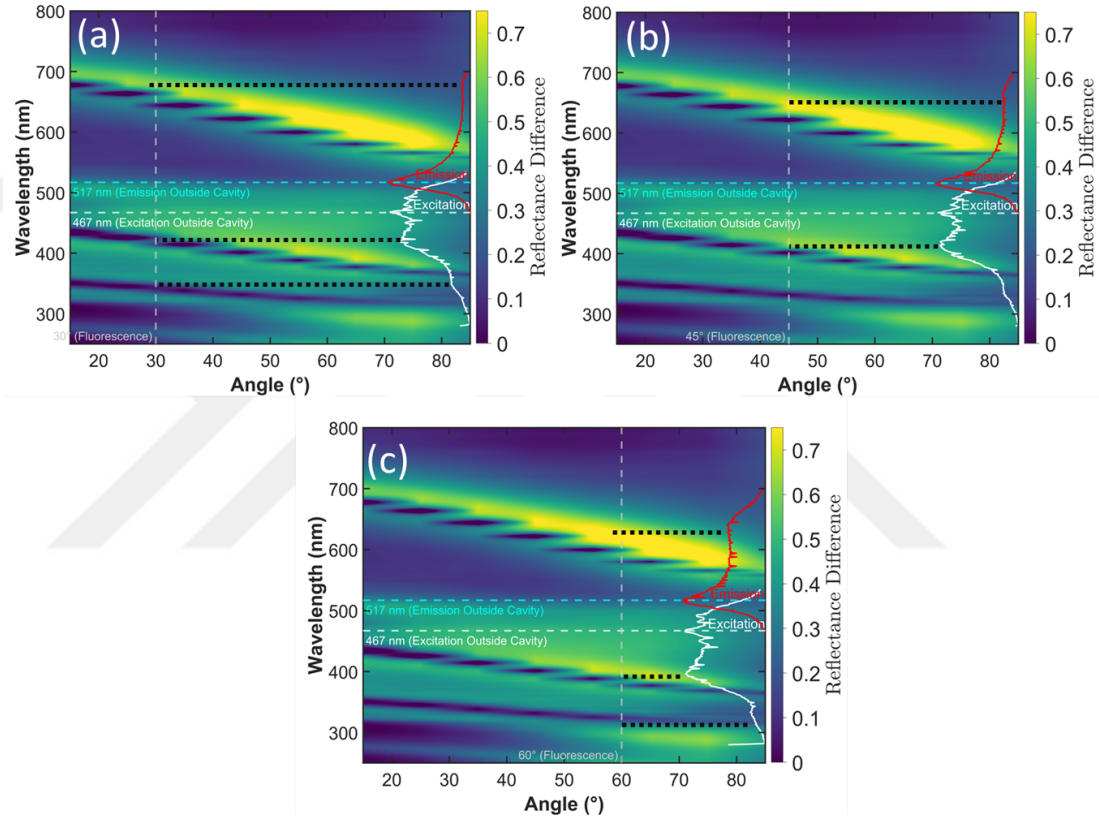


Figure 9.8: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the high dye concentration (60 mg/mL) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 3000 rpm ($t = 380$ nm). Reflectance was measured over incidence angles from 15° to 85° . The out-of-cavity excitation peak at 467 nm and emission peak at 517 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30° , 45° , and 60° , concerning the excitation source. These angles were selected to obtain the strongest fluorescence signal.

9.3.4 Reflectance and Fluorescence at 334 nm

$t=334\text{nm}$

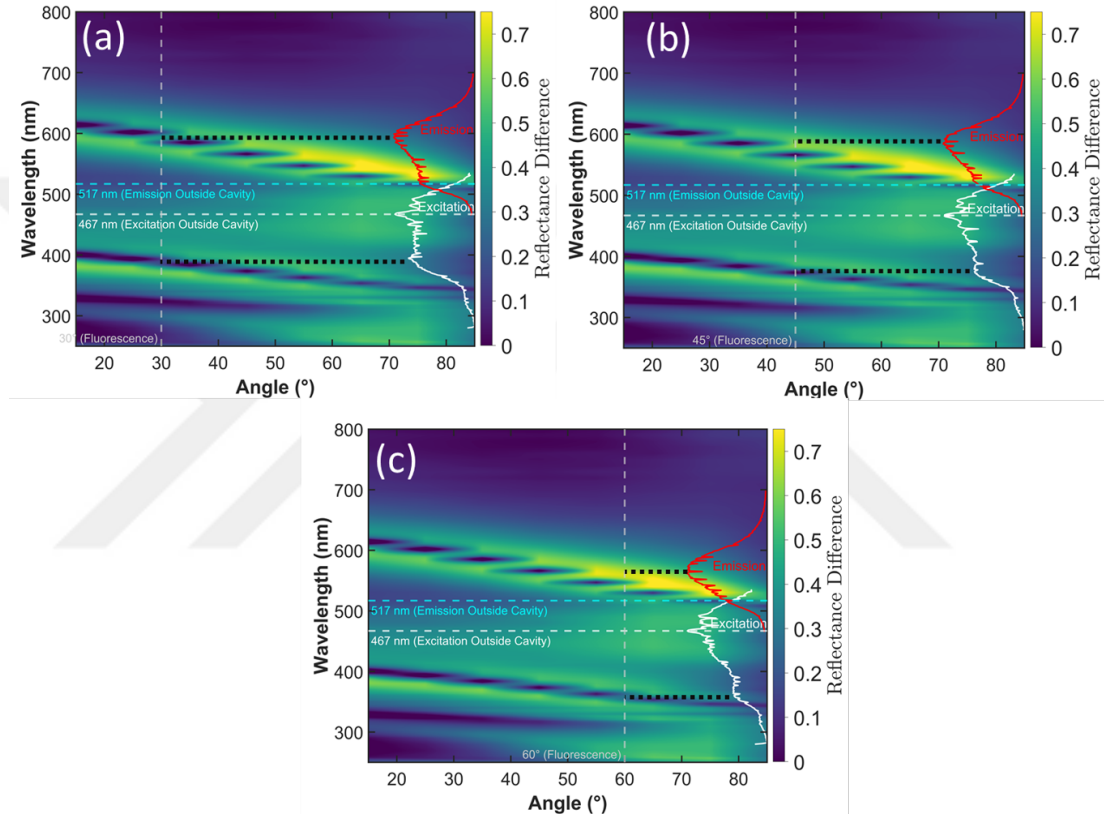


Figure 9.9: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the high dye concentration (60 mg/mL) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 4000 rpm ($t = 334$ nm). Reflectance was measured over incidence angles from 15° to 85° . The out-of-cavity excitation peak at 467 nm and emission peak at 517 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30° , 45° , and 60° , concerning the excitation source. These angles were selected to obtain the strongest fluorescence signal.

9.3.5 Reflectance and Fluorescence at 307 nm

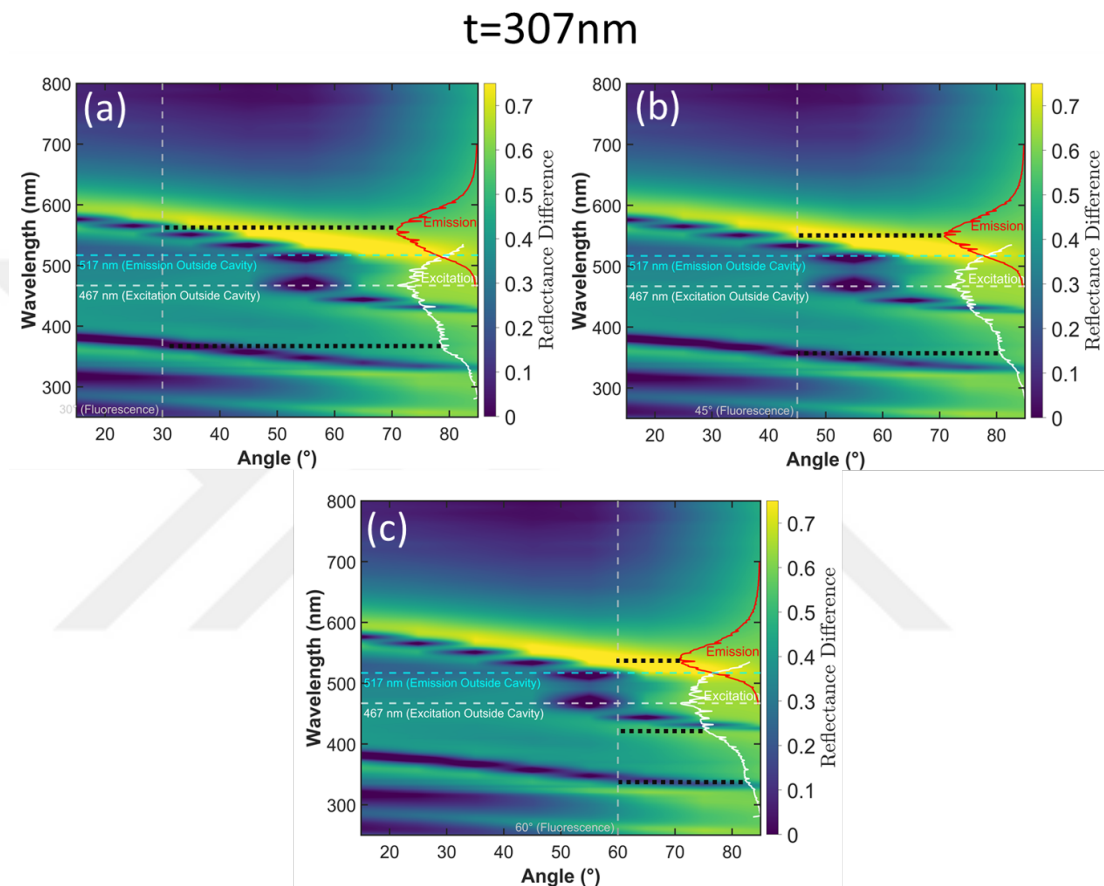


Figure 9.10: Angle-resolved simulated reflectance and corresponding experimental reflectance spectra for the high dye concentration (60 mg/mL) fluorescein-doped PMMA Fabry-Pérot cavity prepared at 5000 rpm ($t = 307$ nm). Reflectance was measured over incidence angles from 15° to 85° . The out-of-cavity excitation peak at 467 nm and emission peak at 517 nm are indicated by dashed horizontal lines. The measured excitation (white) and emission (red) spectra are overlaid on the reflectance maps, measured at three angles, 30° , 45° , and 60° , concerning the excitation source. These angles were selected to obtain the strongest fluorescence signal.

In the excitation region (467 nm), all high dye concentration (60 mg/mL) cavities exhibited angular modulation arising from the interaction between Fabry-Pérot

modes and the excitonic transitions of fluorescein. For the thickest films, 669 nm (1000 rpm, Figure 9.6) and 476 nm (2000 rpm, Figure 9.7), multiple photonic modes fell within the excitonic band, producing rich multi-feature modulation. In both cases, a dominant mode approached the exciton resonance and displayed pronounced back-bending, a hallmark of strong light–matter coupling, consistent with the large vacuum Rabi splittings extracted from the three-coupled-oscillator model. The 380 nm (3000 rpm, Figure 9.8) and 334 nm (4000 rpm, Figure 9.9) cavities also showed multi-feature modulation, but no clear back-bending was observed, suggesting reduced spectral overlap and weaker hybridization. In contrast, the thinnest cavity, 307 nm (5000 rpm, Figure 9.10), supported fewer modes but still exhibited back-bending at higher angles as a key mode intersected the excitonic peak, indicating that strong coupling persisted even with increased mode spacing.

In the emission region (517 nm), all cavities showed both natural fluorescence and cavity-coupled emission, with their relative intensities determined by how closely cavity modes matched the emission wavelength. The thicker cavities (669 nm, Figure 9.6, and 476 nm, Figure 9.7) had modes that overlapped the emission band over wide angle ranges, producing strong and continuous modulation that favored the cavity-coupled peak at higher angles. The intermediate-thickness cavities (380 nm, Figure 9.8, and 334 nm, Figure 9.9) also displayed two peaks, but modulation was limited to angles where a mode approached the emission wavelength. In the thinnest cavity (307 nm, Figure 9.10), modulation in the emission spectra is observed. So, cavity thickness controls the number and position of photonic modes, thereby shaping the strength and angular dependence of emission modulation.

9.4 Three-Coupled Oscillator Model

Strong light–matter coupling in the high–concentration cavities cannot be fully captured by a two-level exciton–photon model because two distinct fluorescein resonances lie close to the cavity mode. We therefore

adopt a *three-coupled-oscillator* (3CO) Hamiltonian in the uncoupled basis $\{|c\rangle, |x_1\rangle, |x_2\rangle\}$:

$$\mathbf{H}(\theta) = \begin{pmatrix} E_{\text{cav}}(\theta) & g_1 & g_2 \\ g_1 & E_{\text{exc},1} & 0 \\ g_2 & 0 & E_{\text{exc},2} \end{pmatrix}, \quad (9.1)$$

with the angle-dependent cavity energy

$$E_{\text{cav}}(\theta) = \frac{E_0}{\sqrt{1 - \left(\frac{\sin \theta}{n_{\text{eff}}}\right)^2}}, \quad (9.2)$$

where E_0 is the normal-incidence resonance and n_{eff} is the effective refractive index of the cavity medium. Diagonalization of Eqs. (9.1)–(9.2) yields three polariton branches—lower (LP), middle (MP), and upper (UP).

Figures 9.11–9.13 show the 3CO fits (solid curves) overlaid on the angle-resolved reflectance maps for the three representative thicknesses. The overlays include the bare exciton energies (near ~ 457 nm and ~ 490 nm) and the bare cavity dispersion for reference. Across all thicknesses, the cavity branch bends toward the dye resonances and exhibits clear back-bending (avoided crossings), producing LP/MP/UP branches that the 3CO model reproduces accurately[65].

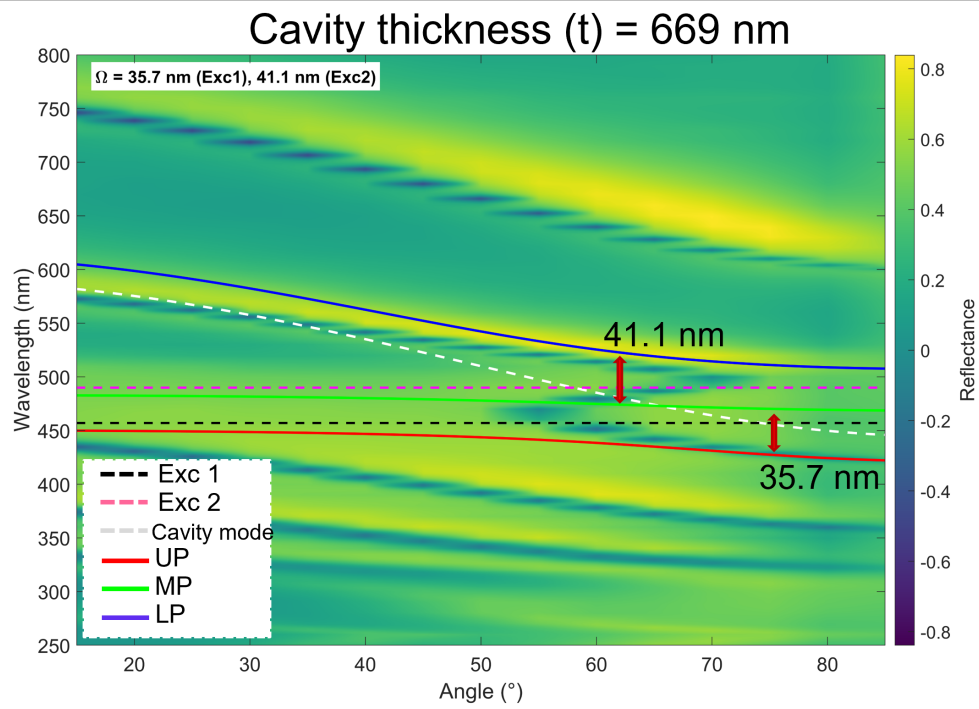


Figure 9.11: Three coupled oscillator model fit for high dye concentration sample prepared at 1000 rpm ($t = 669$ nm).

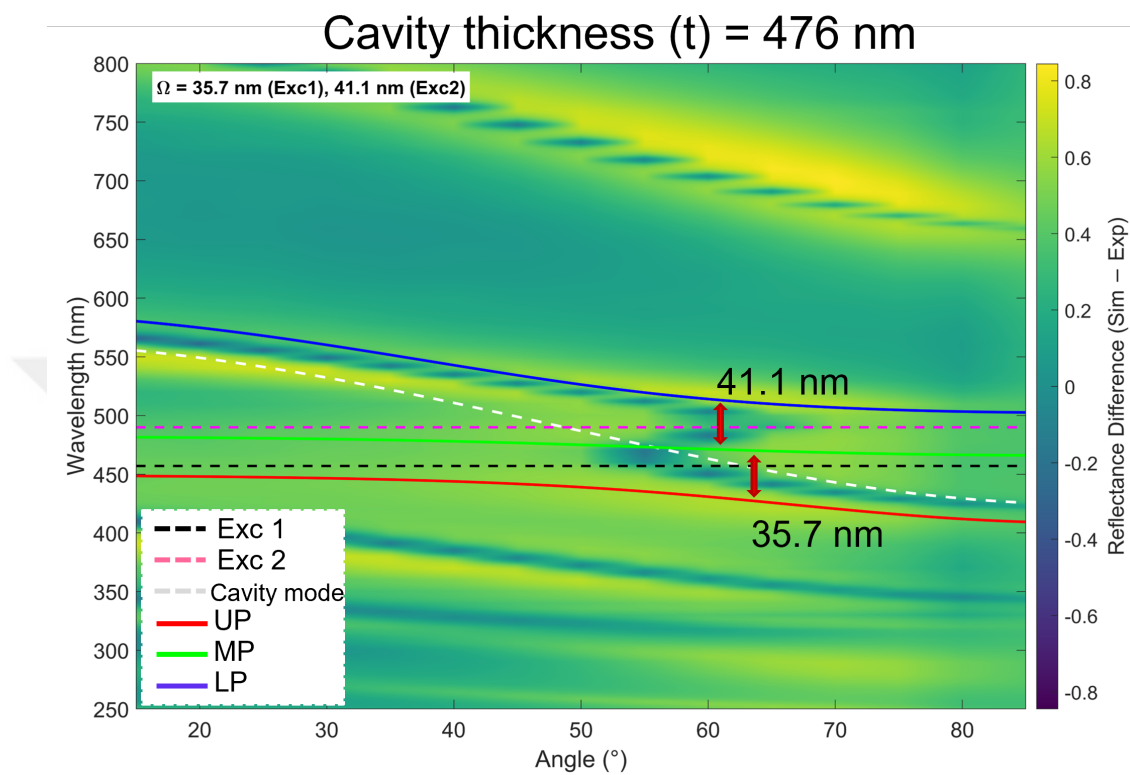


Figure 9.12: Three coupled oscillator model fit for high dye concentration sample prepared at 2000 rpm ($t = 476 \text{ nm}$).

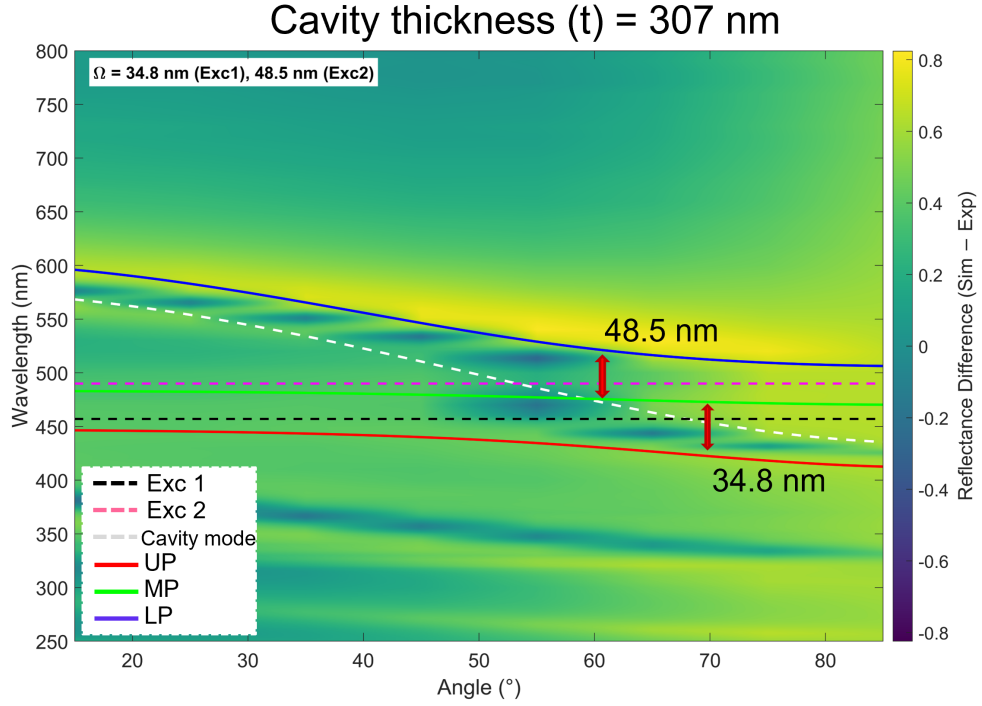


Figure 9.13: Three coupled oscillator model fit for high dye concentration sample prepared at 5000 rpm ($t = 307$ nm).

The extracted vacuum Rabi splittings (reported in wavelength units, as annotated on the overlays) are summarized in Table 9.1. The thinnest cavity ($t = 307$ nm) shows a noticeably larger coupling to the higher-energy exciton (Exciton 2), consistent with the stronger avoided crossing in Fig. 9.13.

Table 9.1: Summary of 3CO fits. $\Omega_{1,2}$ are the vacuum Rabi splittings to Exciton 1 (~ 457 nm) and Exciton 2 (~ 490 nm) read from the overlays.

Sample	t (nm)	Ω_1 (nm)	Ω_2 (nm)
1000 rpm	669	35.7	41.1
2000 rpm	476	35.7	41.1
5000 rpm	307	34.8	48.5

9.4.1 Hopfield Coefficients for 1000rpm Case

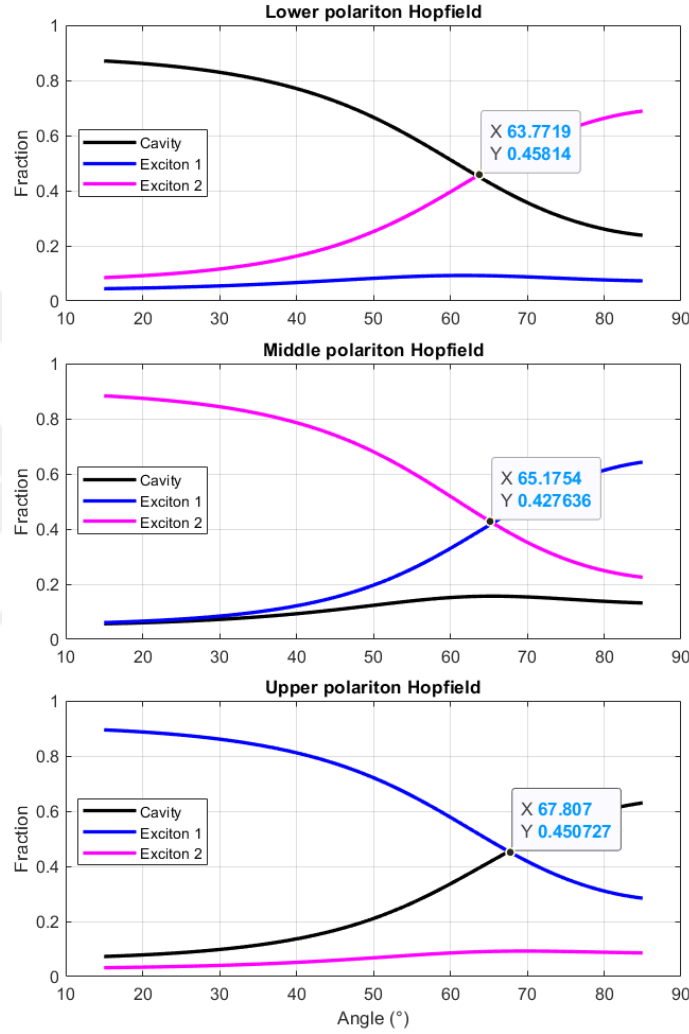


Figure 9.14: Hopfield coefficients for the lower, middle, and upper polariton branches at a spin speed of 1000 rpm. The curves represent the fractional contributions of the cavity mode (black), exciton 1 (blue), and exciton 2 (magenta) as functions of incidence angle. The lower polariton exhibits significant cavity character at low angles, gradually transitioning to an excitonic mix at higher angles. The middle polariton mode shows strong mixing between the two excitonic transitions, indicating a hybrid three-level coupling regime. The mixing angle for the lower polariton occurs around 63.8° , where cavity and exciton 2 contributions are comparable.

9.4.2 Hopfield Coefficients for 2000rpm Case

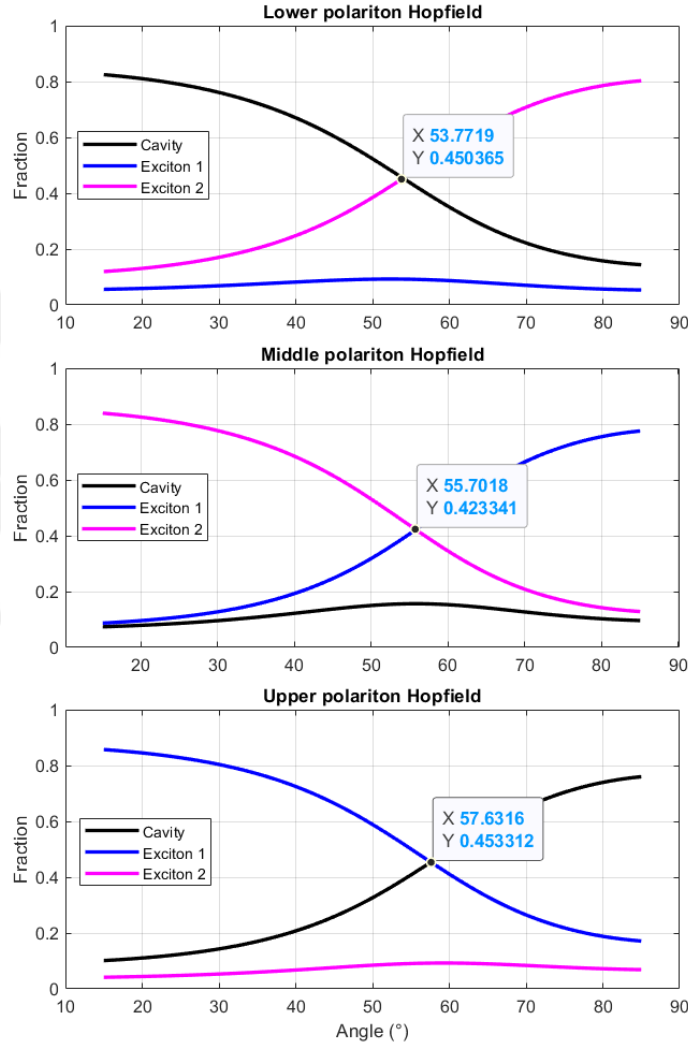


Figure 9.15: Hopfield coefficients for the lower, middle, and upper polariton branches at a spin speed of 2000 rpm. As the cavity resonance shifts due to reduced film thickness, the mixing angle moves to approximately 53.8° , indicating a redshift in the coupling regime. The lower polariton remains predominantly photonic at low angles and becomes excitonic at higher angles. The middle polariton continues to show significant hybridization, particularly between exciton 1 and exciton 2, reflecting the modified energetic landscape induced by the thinner cavity.

9.4.3 Hopfield Coefficients for 5000rpm Case

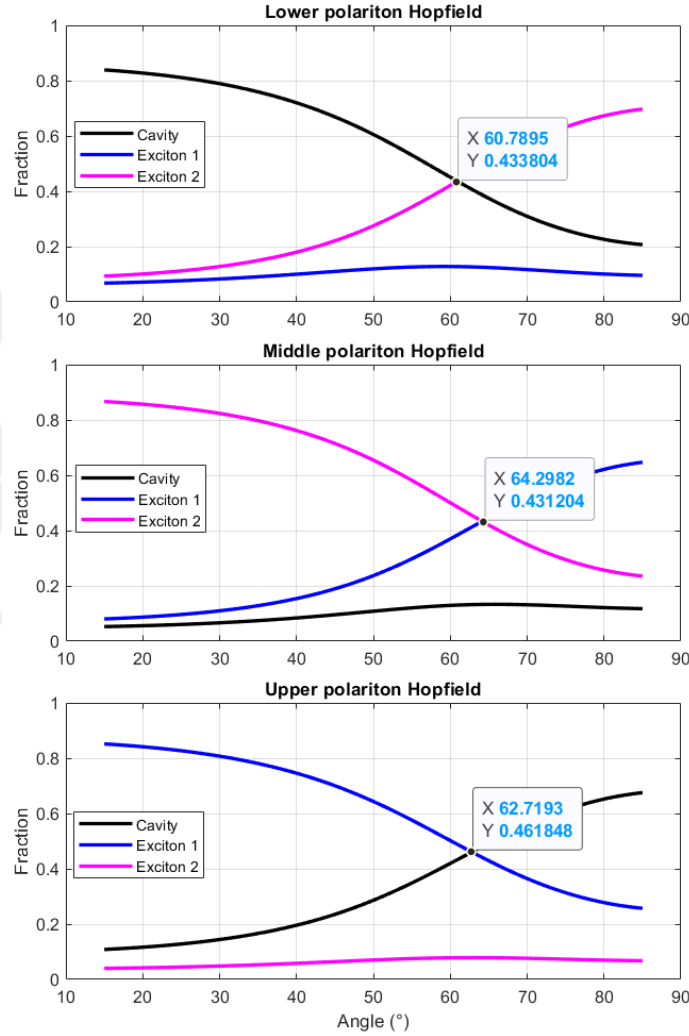


Figure 9.16: Hopfield coefficients for the polariton branches at a spin speed of 5000 rpm, corresponding to the thinnest active layer. The lower polariton's cavity-to-exciton transition occurs at a mixing angle of around 60.8° , reflecting a blue-shift in the cavity resonance. The increased energetic detuning at this thickness slightly reduces the overlap among modes, though strong coupling is still evident. The Hopfield fractions confirm that even with a thinner film, the system maintains strong hybridization between cavity and excitonic modes.

The Hopfield coefficients provide crucial insight into the nature and composition of polariton modes by quantifying the fractional contributions from the optical cavity mode and excitonic transitions. These coefficients are derived from the eigenvectors of the coupled oscillator model, allowing for a clear visualization of how the light–matter hybridization evolves with experimental parameters, such as the angle of incidence and film thickness.

As illustrated in Figures 9.14 through 9.16, the Hopfield coefficients are plotted for the three polariton branches—Lower Polariton (LP), Middle Polariton (MP), and Upper Polariton (UP)—under different film thickness conditions, controlled by varying the spin-coating speeds (1000, 2000, and 5000 rpm). These plots demonstrate that the character of each polariton branch changes gradually across the angular range, reflecting the dynamic interplay between photonic and excitonic components.

At lower incidence angles, the LP branch is predominantly photonic, characterized by a Hopfield coefficient near unity for the cavity mode. As the angle increases, this mode becomes increasingly excitonic, indicating enhanced coupling with the exciton transitions. In contrast, the UP branch displays the opposite behavior, it starts as predominantly excitonic and becomes more photonic with increasing angle. This smooth interchange of modal contributions is a signature of the strong coupling regime, where the interaction energy between light and matter is larger than the respective linewidths of the uncoupled modes, leading to energy-level splitting and hybrid state formation.

The MP branch, which arises due to the interaction with a second excitonic state, shows pronounced hybridization across all angles. It does not exhibit a simple transition from photonic to excitonic character but instead displays a well-mixed nature throughout. The significant involvement of both excitons in the MP branch is especially evident in the angular range of approximately 55° to 65° , where the Hopfield curves intersect. These intersections represent mixing angles where the contributions from cavity and excitons become comparable, emphasizing regions of maximal hybridization.

Importantly, the position of these mixing angles is not fixed but shifts with changes in the spin-coating speed. A slower spin speed (e.g., 1000 rpm) results in a thicker active layer, which lowers the cavity mode energy due to increased optical path length. Consequently, the energy detuning between the cavity and excitons decreases, shifting the mixing angle for the LP branch to approximately 63.8° . As the spin speed increases to 2000 rpm and 5000 rpm, the film becomes thinner, the cavity mode blue-shifts, and the mixing angles shift accordingly to 53.8° and 60.8° , respectively. This variation demonstrates that the light–matter interaction strength and the composition of polaritons can be finely tuned by simply adjusting the physical thickness of the cavity layer.

The Hopfield coefficient analysis confirms the presence of strong coupling between the cavity photon and two excitonic transitions in the system. Moreover, it highlights the role of cavity–exciton detuning in determining the polaritonic behavior and mode composition. This tunability opens up practical possibilities for modulating optical properties in polaritonic devices, such as polariton lasers, sensors, or light-harvesting systems, through straightforward adjustments in fabrication conditions.

9.5 Summary

This chapter mapped angle-dependent reflectance and fluorescence of fluorescein-doped PMMA Fabry–Pérot cavities across thickness and concentration. At low dye loading ($20\text{ }\mu\text{g/mL}$), the spectra show 1–3 photonic modes that blue-shift with angle and traverse the dye band without avoided crossing, establishing a weak-coupling baseline. At high loading (60 mg/mL), the maps exhibit 1–5 modes with clear back-bending in experiment and TMM, with position set by cavity thickness and detuning; emission modulation strengthens when a mode overlaps $\sim 517\text{ nm}$. A three-coupled-oscillator model reproduces the LP/MP/UP dispersions and yields vacuum Rabi splittings of $\sim 35\text{--}49\text{ nm}$ ($\approx 0.21\text{--}0.25\text{ eV}$). Together, these results show a controllable progression from purely photonic dispersion to polaritonic behaviour by tuning concentration, thickness, and observation angle.

Chapter 10

Conclusions and Future Directions

This thesis has explored the cavity-modified photophysical properties of fluorescein-doped PMMA thin films embedded in Fabry–Pérot resonators, with the unifying goal of understanding how optical cavities can reshape the light–matter interaction in broadband organic dyes. Through a combination of experimental techniques and theoretical modeling, the work has provided a systematic framework to link cavity design (thickness), dye concentration, and optical response.

The optical characterization using UV–Vis absorption and ellipsometry confirmed successful incorporation of fluorescein molecules into thin polymer(PMMA) layers and allowed precise determination of refractive indices and film thicknesses. These parameters were essential for accurately modeling cavity modes using the transfer matrix method (TMM), which in turn guided experimental angle-resolved reflectance and fluorescence measurements. The results revealed that even under weak to intermediate coupling conditions, the Fabry–Pérot cavities impose significant modifications on the excitation and emission properties of fluorescein. In particular, the shifting of excitation and emission spectra

according to the cavity mode peak position was consistently observed. The effect was tunable by varying cavity thickness, and dye concentration, highlighting the controllability of the system. Importantly, the experiments demonstrated signatures of hybridization between excitonic absorption and cavity resonances, pointing to the possibility of reaching the strong coupling regime under optimized conditions.

Future work could focus on time-resolved spectroscopy to study how exciton dynamics are modified inside the cavity. It will also be important to address the challenge of the not fully developed upper and lower polariton branches in fluorescence and UV-Vis spectra. Optimizing cavity design may allow clearer and direct observation of these polaritonic features in both fluorescence and UV-Vis spectra.

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