Optical Modeling of Organic Electronic Devices

by

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Abstract

Organic materials, with their superior photoluminescence and absorbance properties have revolutionized the technologies for displays and solar energy conversion. Due to the large transition dipoles, the localization of excited states or excitons in organic materials necessitates optical models that extend beyond classical far field methods. In this thesis we propose an extended near field calculation method using dyadic Green’s functions and demonstrate the applications of both our extended model and traditional far field models for different types of devices such as surface plasmon detectors, cavity organic light emitting devices and organic photovoltaics with external antennas.

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Chapter 1

Introduction

Optical modeling of multilayer thin film devices, in particular organic thin film devices that harness or emit light, is a useful tool in the optimize the device efficiencies. For organic light emitting devices (OLEDs) the lifetime problems and electronic injection problems have been largely solved by the recent advances in material chemistry and contact engineering (for a general review see Forrest). [1] Another major challenge with OLEDs, the ineffective triplet exciton emission has also been solved by introducing heavy metal spin-orbit coupling through the use of phosphorescent organic materials. [2] Thus the main challenge left with OLEDs is increasing the optical extraction efficiency, namely the outcoupling. Also for organic photovoltaics (OPVs), a strong light absorption is essential to increasing power conversion efficiency. In this work we concentrate on the optical modeling tools and applications related to these challenges. In this chapter a brief introduction to organic electronic devices is given and then the current optical challenges for efficiency improvements and models for optimizing designs are mentioned. Lastly the scope of this work is defined.

1.1. Organic Electronic Devices

The demand for solar energy conversion and better displays has encouraged the study of new materials and architectures. A particular set of non-traditional electronic materials,
namely organic semiconductors, offers efficient visible photoluminescence and light absorption along with mechanical flexibility and many possibilities for molecular design. Although these materials have low mobilities ($\mu \sim 10^{-6} - 10^6$ cm$^2$/Vs), they are suitable for optoelectronic applications that do not demand the optimum electronic transport materials. Two main applications of these materials are being widely researched and being commercialized. First one is the organic light emitting device (OLED) and the other is the organic photovoltaic device (OPV).

![Diagram of OLED and OPV structures](image)

Fig. 1.1. (a) The OLED structure of Tang and VanSlyke[3] (b) The OPV structure by Tang.[4]

The first realization of an OLED was demonstrated by Tang and VanSlyke in 1987 (see Fig. 1.1(a)).[3] Electrons are injected from the Mg:Ag contact into an electron transport material (8-hydroxyquinoline aluminum - Alq$_3$) and holes are injected from the optically transparent Indium Tin Oxide (ITO) into a hole transport material (a diamine variant) contact on the glass substrate. When the injected holes arrive the interface between the diamine variant and Alq$_3$ they combine with the electrons injected into the Alq$_3$ layer, forming excitons. These excitons can decay into photons and thus the light emission occurs. While this first OLED had an overall efficiency of 0.46% and a 100-hour lifetime, recent commercialized OLEDs have more than 10% efficiency and three
orders of magnitude longer lifetimes (see the website of Universal Display, http://www.universaldisplay.com).

OPVs possess a similar structure to OLEDs but operate in reverse, converting excitations to charge, rather than vice versa. Again the first realization of these devices was achieved by Tang in 1986 (See Fig. 1.1(b)). [4] Excitons are formed after the absorption in the hole transport layer (copper phthalocyanine (CuPc)) and the electron transport layer (a perylene tetracarboxylic derivative). When these photo-generated excitons diffuse to the organic-organic interface the electron of the exciton in CuPc hops to the other perylene tetracarboxylic layer with the hole remaining in CuPc, thus an electron and a hole is generated. If the exciton is originally formed in the electron transport layer, a hole is transferred. Consequently, the hole transport layer is known as the donor (of electrons), the hole transport layer is known as the acceptor (of the electrons). Charges are then collected by the contacts and electrical current is generated. While the power conversion efficiency of the original device was about 1%, the current efficiency record for OPVs is above 6%.[5] These improvements in device efficiencies have been obtained through the advances in the material chemistry, contact engineering, fabrication techniques and optimizations in device architecture. In the next section we explain the architectural challenges related to optical design, which offers potential for significant improvements.
1.2. Optical challenges and models

In this section we briefly explain the outcoupling and waveguiding problem in OLEDs and light absorption as well as interlayer energy transfer in OPVs. Methods for overcoming these problems are also summarized.

The outcoupling efficiency of an OLED is the percentage of the emitted photons emitted in the forward or viewing direction. Traditionally in OLEDs, devices we fabricated on a glass substrate and light emission occurs through this transparent substrate. The top contact is a thick metal contact that blocks all the light emission. Emission into the glass can be trapped by waveguiding due to total internal reflection. In addition to this, absorption and other energy losses such as waveguiding in organic layers and quenching in metal layers reduce the outcoupling efficiency. The outcoupling efficiencies of OLEDs are around 25%. [6] This is the most important remaining limit to the efficiency of OLEDs. Ways to remedy the outcoupling losses include cavity designs and even changing the bottom emission architecture (through glass substrate) to top emission.

For an OPV, on the other hand, to convert as much sunlight to electrical current, the OPV needs to absorb strongly and generate free charges efficiently. Since the free charge generation from excitons only occurs at the interface between the organic layers, the excitons need to diffuse to the interface; however, the diffusion lengths of organic materials are very small (less than 10nm for most materials like CuPc).[7] This necessitates using very thin films in order to get efficient current generation, which
reduces the absorption. One way to alleviate this trade-off is to design the layers for maximum field magnitude around the interface to concentrate the exciton generation in the vicinity of the interface. Another approach is to absorb the light in an external antenna layer and then transfer the absorbed energy into the photovoltaic layers in a near-field fashion[8] (such as using optical cavities and surface plasmons). There are also exciton loss pathways in OPVs that must be controlled, such as metal contact quenching due to surface plasmon modes in the metal. This can be reduced by using spacer materials between the metal and the photovoltaic or by using cavity designs. A common property of these solutions is the necessity of electromagnetic modeling.[8]

There are two main types of electromagnetic models that are widely used in organic electronic device research and development. These are far-field methods such as transfer matrix models[7] and near field methods such as dyadic Green’s functions theory.[9] Both models assume that the lateral dimensions of the films are much larger than their thickness. Far-field methods are useful for calculating reflection, transmission or absorption of any incident plane waves such as sunlight or laser light. Far field models are used to optimize layers and design optical cavities for absorption or emission of a particular frequency spectrum. Near field methods deal with the dipole fields of individual excitations and are used to calculate the dipole energy transfer and the angular distribution of light emission. Near field models are useful for optimizing the thicknesses of each layer or designing cavities for efficient outcoupling or interlayer energy transfer.
1.3. In this work

We develop a near field dipole energy transfer calculation method by extending the traditional dyadic Green’s functions model. The result is a computerized simulation package.[10] (published online, http://www.softsemi.mit.edu) We also develop another computerized simulation package using a traditional transfer matrix model. We used both packages to design organic electronic devices such as surface plasmon detectors,[11] OLEDs with metallic cavities[12] and OPVs with external antenna layers.[8] In this work we first begin with the far field method and its application in the detection of surface plasmons. Next we explain our theoretical extension [10] to the dyadic Green’s function method developed by Chance, Prock and Silbey in 1978 [9] and demonstrate cavity OLEDs[12] and OPVs with external antenna layers. [8]
Chapter 2

Far Field Modeling and Applications

Far field methods are used to predict the electric field distribution and resulting reflection, transmission and absorption of plane waves. In particular, we employ the transfer matrix method in this chapter. First a short introduction to transfer matrix theory is given and then its application to plasmonic detection using organic electronic devices is shown.[11]

2.1. Transfer Matrix Model

In the case of far fields such as sunlight or laser light, electromagnetic waves can be modeled as sinusoidal oscillations that move in one dimension. Transfer matrix theory considers these oscillations in multilayer thin film media. The field distribution is calculated from incoming and outgoing wave oscillations that are perpendicular to the surface of the media. Their amplitudes at any point inside the multilayer stack is calculated from the Fresnel coefficients at each interface. A detailed description of this method is given in Heavens [13] and a comprehensive application to photovoltaic cells is given Peumans.[7] We do not repeat the theory here and refer the reader to these sources. However, a technical difference in our numerical calculations is that we calculate the complex Poynting vector and its one dimensional derivative in order to calculate the
absorption. This is theoretically identical to using the field square method, as described in Peumans,[7] but we find our method numerically simpler.

2.2. Detecting surface plasmons using photovoltaics

Surface plasmon resonances (SPR) are commonly used in the real-time detection of chemical and biomolecular interactions at metal interfaces.[14] The main SPR detection methods are based on either the direct measurement of the amplitude or momentum of the reflected optical wave near resonance. Both techniques interrogate the reflected wave using an external photodiode element or array. In this section, we report on an integrated SPR detector using an organic photodetector whose upper electrode composes the active sensing element. Integration offers the benefits of miniaturization, and may have wide commercial applications, including industrial process control, environmental testing, point of care diagnostics, and food safety.

To realize SPP detection, we exploit the guided character of SPPs. The transduction element is a thin film organic photovoltaic cell.[7] Under conventional illumination, the cell is too thin to absorb much of the incoming radiation. But SPPs propagate parallel rather than perpendicular to device interfaces. The SPP propagation length at \( \lambda = 532 \text{ nm} \) is as much as \( \sim 30 \mu\text{m} \) for Ag films.[15] This compares to a typical organic photodetector thickness of 0.05 \( \mu\text{m} \). Thus, for absorption limited photodiodes, the propagation distance is a factor of \(< 600\) greater than the active device thickness, making absorption more likely.
Although typical external quantum efficiencies peaked at 0.05%, [16] photocurrent enhancements in organic Schottky photodiodes under surface plasmon polariton (SPP) excitation have been previously demonstrated. [17, 18] In this work, we detect the resonant change in total absorption within a thin film organic double heterojunction photodiode, illuminated with $\lambda = 532$ nm excitation in the Kretschmann geometry under attenuated total reflection. The detector is biased in the low-noise photovoltaic (PV) mode. We observe a doubling in external quantum efficiency at SPP resonance compared to the photonic illumination case. The peak external quantum efficiency of 12% represents a factor of 240 improvement in quantum efficiency over previous results. We also present a model of the SPP detector and characterize absorption losses in the metal electrode.

Fig. 2.1. Monochromatic $p$-polarized laser light of wavelength of 532 nm is incident on a prism coupled to the glass substrate through index matching fluid. As $\theta_i$ increases the onset of total internal reflection precedes an immediate dip in reflected light intensity and increase in monitored photocurrent at SPP resonance. The only interface that can support SPPs in this geometry is at the Ag cathode-air interface. The device structure investigated was glass/Ag (235 Å)/CuPc (190 Å)/C60 (200 Å)/BCP (75 Å)/Ag (285 Å).
To measure the efficiency of SPP detection, thin film double heterostructure organic photodiodes were fabricated on cleaned glass substrates. Commercially available organic layers were purified by thermal gradient sublimation. Films were deposited at room temperature at high vacuum (~10^-6 Torr) in the following order: 235Å silver, 190Å of the donor-like copper phthalocyanine (CuPC) and 200Å of the acceptor-like fullerene (C60).

Fig. 2.2 (a) Measured (dotted red line) and modeled (solid black line) reflectivity spectra sharply increase at $\theta_i=44^\circ$ corresponding to the onset of total internal reflection from the stack. As $\theta_i$ increases the reflectivity sharply drops, reaching a minimum at surface plasmon resonance when $\theta_i=52^\circ$. (b) The angular positions of maximum and minimum reflectivities align with the measured (dotted blue line) and modeled (solid black line) minimum and maximum external quantum efficiencies. At resonance, $\eta_{EQE}=12\%$, reaching twice the efficiency of off resonance excitation at $\theta_i=30^\circ$. The modeled internal quantum efficiency decreases slightly under plasmon illumination from 14% to 13%. (c) Modeled optical absorption in all device layers increases by a factor of 3 at resonance.
Next, a 85Å thick layer of bathocuproine (BCP) was grown; BCP has been previously shown to function as an exciton blocking, electron transport layer solar cells.[17] This layer was followed by a 285Å thick layer of silver shadow-masked to define cathodes of area $1.4 \times 10^{-2}$ cm$^2$.

Light was coupled to the diode via a hemicylindrical prism attached to the glass substrate with index matching fluid; see Fig. 2.1. The prism and photodiode were mounted on a computer controlled rotating stage and illuminated with p-polarized light of wavelength $\lambda = 532$ nm with an incident power intensity of 50 $\mu$W. The intensity of the reflected beam is monitored with a Si photodetector. The measured photocurrent in air at zero bias is measured with a Keithley sourcemeter. Spectral external quantum efficiency measurements were made by using a xenon lamp with monochromator, chopped at $\sim 90$ Hz and measured with a lock-in amplifier. Light intensity was measured with a calibrated silicon photodiode. The indices of refraction and extinction coefficients of all modeled thin films were derived from measurements using an Aquila reflection-transmission thin film spectrophotometer. Because Ag penetrates the thin BCP layer during deposition,[18, 19] the optical constants of the cathode were obtained from a BCP/Ag bilayer.

In Fig. 2.2(a) we plot the reflected light intensity (reflectivity, $R$) versus incident illumination angle, $\theta_i$, for p-polarized incident light. The mixed transversal and longitudinal electromagnetic field carried by SPPs can only be excited by p-polarized light and as such, only the p-polarized reflectivity exhibits a sudden decrease corresponding to SPP excitation at the condition of momentum conservation.[15] As $\theta_i$ increases, two features are observed: the increase at $44^\circ$, which corresponds to the onset
of total internal reflection; and a decrease at 52°, which corresponds to destructive interference of backscattered light given evanescent excitation of a SPP at the Ag cathode-air interface.

In Fig. 2.2(b), the external quantum efficiency, \( \eta_{\text{EQE}} \), is plotted versus \( \theta_i \). The resonance dip in reflectivity correlates to a peak in quantum efficiency of 12%, double that at plane wave illumination.

In Fig. 2.2(c), we plot the modeled absorption in each layer of the detector. To estimate the optical absorption within each layer of the SPP detector, we employ the plane wave matrix formulism to calculate the magnitude of the electromagnetic fields throughout the thickness of the device.[20] At low angles of incidence, \( \theta_i < \theta_{\text{SPR}} \), photocurrent is primarily limited by low light absorption. For instance, at \( \theta_i = 30^\circ \), the absorption within the active organic layers, CuPC and C\(_{60}\), \( \eta_{\text{ABS}}^{\text{org}} = 10\% \). At SPR, absorption in the complete stack, \( \eta_{\text{ABS}}^{\text{tot}} \), increases by more than a factor of three to 83%, and the absorption within the active layers is \( \eta_{\text{ABS}}^{\text{org}} = 30\% \). The increase in \( \eta_{\text{ABS}}^{\text{org}} \) by a factor of three at SPR mirrors the factor of three increase in \( \eta_{\text{EQE}} \), confirming that SPP detection is mediated by an increase in absorption. The ratio \( \eta_{\text{ABS}}^{\text{org}} / \eta_{\text{ABS}}^{\text{tot}} \) decreases by 2% in resonance, indicating that there is a negligible increase in the fraction of energy lost to joule heating and roughness induced scattering under SPP excitation.

To confirm the modeling results, \( \eta_{\text{EQE}} \) of this device is plotted in Fig. 2.3 as a function of wavelength at normal incidence. Below \( \lambda = 525 \) nm, photocurrent is primarily
generated in the C_{60} layer, while the CuPC layer primarily absorbs above \( \lambda = 525 \) nm. At \( \lambda = 532 \) nm, the extinction coefficients of C_{60} and CuPC are approximately equal at \( k \approx 0.10 \) and 0.08, respectively, as modeled from the reflectivity-transmission spectra; for derived \( n \) and \( k \). [11]

We modeled the BCP/Ag cathode bilayer as a single homogenous film. Seumori et al previously observed deep penetration of evaporation metal on amorphous organic films [21] and Rand et al examined solar cells where Ag penetration into very thin BCP yielded trap states and lowered the barrier to electron extraction.[18] These observations suggest that the BCP cannot be optically modeled as a uniform film; consistent with our findings. We evaporated a bilayer film of BCP and Ag with thicknesses identical to those in the solar cell and measured its absorption spectrum to derive its optical characteristics. The silver penetration into the BCP layer results in a film bilayer that is more absorptive [11] independent of whether excitation is via SPPs or photons, suggesting that the reduction of metal penetration by alternative electrode deposition methods may increase the internal quantum efficiency in organic PV.

To model the photocurrent spectrum of Fig. 2.3, we fit the exciton diffusion lengths by \( L_{D}^{CuPC} = 70 \) Å and \( L_{D}^{C_{60}} = 100 \) Å, similar to previously reported values of 100 \( \pm 30 \) Å for CuPC,[7] and 141 Å for C_{60}.[19] The fit is confirmed by comparison of the measured and modeled \( R(\theta) \) and \( \eta_{EQE}(\theta) \) spectra, as plotted in Figs. 2.2a and 2.2b. The modeling accurately predicts the angular location and intensity of SPR for both \( R(\theta) \) and \( \eta_{EQE}(\theta) \) to within 0.5° and 1%, respectively.
Fig. 2.3 Measured (dotted line) and modeled (solid line) external quantum efficiency vs wavelength for this device. The angular dependent quantum efficiency was interrogated at $\lambda = 532$ nm, where light absorption occurs nearly equally in CuPC and C60.

Finally, the performance limits of the SPP detector may be assessed from the modeled internal quantum efficiency of the device, defined by the relation $\eta_{EQE} = \eta_{ABS} \cdot \eta_{IQE}$ and shown in Fig. 2.2b. $\eta_{IQE}$ incorporates all losses that can occur in photocurrent generation subsequent to light absorption in the stack, including exciton losses during diffusion, and insufficient charge collection. Small deviations in $\eta_{IQE}$ are expected near total internal reflection due to spatial modulation of the optical field within the detector, which in turn varies the relative absorption of CuPC and C60. But the main conclusion is that the organic SPP detector is primarily limited by exciton diffusion losses which yield an internal quantum efficiency of only 13% near resonance. This may be due in part to photooxidation of C60.[17] To increase the sensitivity, the active absorbing layers can be made thinner, which has previously been shown to significantly increase $\eta_{IQE}$ by increasing the probability of exciton dissociation at the active interface.[22] In addition, the relative
enhancement in detection efficiency compared to the plane wave excitation will also increase. Thus, we expect that higher sensitivities are possible given device structure optimization.

In summary for this section, we have shown that organic photodiodes excited by surface waves can function as efficient surface plasmon polariton detectors. We have reported a photocurrent increase of ~200% under resonance, but further optimization is possible. Approaches include lowering exciton dissociation losses and positioning the active absorbing organic semiconductor closer to the interface supporting surface plasmons polaritons. Finally, we note that excitation by guided waves may offer a general method for enhancing the performance of organic solar cells and we return to this idea in the next chapter.
Chapter 3

Near Field Modeling and Applications

In this chapter the theory and applications of near field energy transfer from a dipole is discussed. First, the total near-field energy emission in a multilayer stack is determined using the Chance-Prock-Silbey (CPS) model.\cite{9} Next, the CPS model is extended by deriving an analytical expression for the surface-perpendicular component of the Poynting vector.\cite{10} This derivation enables the calculation of the modal and spatial distribution of the dipole energy transport. After this derivation, simulations of Förster energy transfer test and light emission in an organic light emitting device (OLED) are shown as applications of these calculations. These simulations respectively include the modal energy distribution, the spatial energy transfer and angular emission profile of a dipole in the multilayer stack. After the theoretical exposition we demonstrate cavity OLEDs\cite{12} and OPVs with external antenna layers.\cite{8}

3.1. Chance Prock Silbey theory for dipole lifetime

Spontaneous emission from a dipole depends on the local density of states at the position of the dipole. Following the formulation of Tai\cite{23} and the model of CPS,\cite{9} we calculate the interaction between the dipole and electromagnetic field using dyadic Green’s functions. Fig. 3.1 shows a general multilayer structure, where $\epsilon_j$ represents the complex dielectric function and $d_j$ the thickness of each layer. The first and last layers are
semi-infinite. The Green function coefficients $c_j$ and $f_j$ will be explained below. The randomly-oriented dipole resides in the $s^{th}$ layer, which is arbitrarily placed in the multilayer stack. Each layer is assumed to be isotropic and higher order multipole radiation is neglected.

$$E(R) = i \omega \mu_0 \int G(R | R') \cdot J(R') d^3 R'$$

where $\omega$ is the oscillation frequency, $\mu_0$ is the magnetic permeability, $J(R')$ is the current and $G(R | R')$ is the dyadic Green’s function, which incorporates the boundary conditions. For a two-dimensionally-symmetric multilayer stack the Green’s function can be described using two independent sets of eigenfunctions in cylindrical coordinates:[9]

$$M_{e,nc}(h) = e^{ih} \left[ \frac{n J_n(\kappa r) \sin n \phi \hat{r} - \partial J_n(\kappa r) \cos n \phi \hat{r}}{r \cos n \phi} \right]$$

$$N_{e,nc}(h) = \frac{e^{ih}}{k_j} \left[ \frac{\partial J_n(\kappa r) \cos n \phi \hat{r}}{r} \sin n \phi \hat{\theta} + \frac{J_n(\kappa r) \sin n \phi \hat{\theta}}{r} \cos n \phi \hat{r} + \kappa^2 J_n(\kappa r) \cos n \phi \hat{\phi} \right]$$
where \( j \) is the layer index, \( \kappa \) and \( h \) are the amplitudes of the parallel and perpendicular components of the propagation vector \( k \), and \( J_n \) refers to a Bessel function of the first type of order \( n \). Even and odd eigenfunctions are represented by \( e \) and \( o \). Using the eigenfunctions \( M \) and \( N \) we write the Green's functions for the source and scattering:

\[
G_{\text{sc}}(R|R') = \frac{i}{4\pi} \sum_{\ell \neq 0} \left[ \frac{2 - \delta_{\ell 0}}{kh_j} \right] \left[ M_{\text{me}}(h_j)M'_{\text{me}}(-h_j) + N_{\text{me}}(h_j)N'_{\text{me}}(-h_j) \right] z > 0 \\
G_{\text{src}}(R|R') = \frac{i}{4\pi} \sum_{\ell \neq 0} \left[ \frac{2 - \delta_{\ell 0}}{kh_j} \right] \left[ c_j M_{\text{me}}(h_j)M'_{\text{me}}(h_j) + f_j N_{\text{me}}(h_j)N'_{\text{me}}(h_j) \right]
\]

where primed eigenfunctions are functions of \( R' \), \( s \) denotes the source layer, \( j \) denotes the \( j^{th} \) layer, and the dipole position is taken as \( z = 0 \). In the convention we use, with the primed eigenfunctions in transpose form, \( G \) takes the form of a \( 3 \times 3 \) matrix to be multiplied by the \( 3 \times 1 \) \( J \) (current) vector, giving the integrand in Eq. (1).

The coefficients \( c, f \) and \( c', f' \) correspond to the left and right traveling eigenfunctions, respectively. Solving Maxwell's equations at the interfaces, the relations between these coefficients can be determined:

\[
c_j e^{i\kappa_j z_j} + c'_j e^{i\kappa'_j z_j} = c_{j+1} e^{-i\kappa_{j+1} z_{j+1}} + c'_{j+1} e^{i\kappa'_{j+1} z_{j+1}}
\]

\[
h_j k_j (f_j e^{-i\kappa_j z_j} + f'_j e^{i\kappa'_j z_j}) = h_{j+1} k_{j+1} (f_{j+1} e^{-i\kappa_{j+1} z_{j+1}} + f'_{j+1} e^{i\kappa'_{j+1} z_{j+1}})
\]

\[
-c_j h_j e^{-i\kappa_j z_j} + c'_j h_j e^{i\kappa'_j z_j} = -h_{j+1} c_{j+1} e^{-i\kappa_{j+1} z_{j+1}} + h_{j+1} c'_{j+1} e^{i\kappa'_{j+1} z_{j+1}}
\]

\[
k_j f_j e^{-i\kappa_j z_j} + k_j f'_j e^{i\kappa'_j z_j} = k_{j+1} f_{j+1} e^{-i\kappa_{j+1} z_{j+1}} + k_{j+1} f'_{j+1} e^{i\kappa'_{j+1} z_{j+1}}
\]

In the absence of external radiation sources, we begin the calculation of the coefficients of scattering Green's functions in each layer by setting \( c_1' = f_1' = 0 \) and \( c_N = f_N = 0 \). Next,
using the interface equations we numerically calculate the ratios of the coefficients starting at the outer layers. Arriving at the dipole layer, we determine the individual coefficients from the calculated ratios, noting the addition of the non-scattering Green's function \((G_0)\). Using these calculated coefficients and once again applying the interface equations, we calculate the coefficients for each layer from dipole layer to outermost layer. Once all the coefficients are determined, the value of the Green's function can be calculated at every point in the stack.

To calculate the dipole energy transfer efficiency, the real part of the time-averaged divergence of the complex Poynting vector must be normalized by the dipole decay rate. We begin with calculation of the dipole decay rate, \(b\). Following CPS, it is found by incorporating the effect of the reflected field on the dipole by the following equation:[25]

\[
b = \frac{e^3 k_s^3}{6\pi m_0 e} \left[ 1 + \frac{3q\varepsilon}{2p_0 k_s^2} \text{Im}(E_0) \right]
\]  

where the expression outside the brackets is the natural decay rate in vacuum, \(b_0\); \(E_0\) is the magnitude of the electric field at the dipole position, \(e\) is the electron charge, \(m\) is the reduced mass of the exciton, \(\varepsilon\) is the permittivity and \(q\) is the quantum yield of the emitting state. Due to the anisotropy of the electric field in Eq. (10), \(b\) is calculated for surface-parallel and perpendicular dipoles separately. Since there are two axes parallel to the layer plane and one axis in the perpendicular direction, the isotropic decay rate is \(b_{iso} = b^+/3 + 2b^/3\). Expanding the field in terms of the Green's functions we get the perpendicular and parallel components of \(b\):[9]

\[
\frac{b^+}{b_0} = 1 - q + q \left[ 1 + \frac{3}{2} \text{Re} \left[ \int_0^\infty \frac{k^3}{k_s} \left( f_s + f_{s'} \right) \right] \right]
\]  

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Next, we calculate the divergence of the Poynting vector. Because the structure is assumed to be infinite in the radial dimension, the presence of loss in any layer allows the divergence to be simplified as

$$
\int \nabla S \, dV = \oint S \, dA = \oint S_z \, dA.
$$

We start with the expression of $S_z$ in terms of general E field components in cylindrical coordinates [26]

$$
S_z = \frac{i}{2 \mu_0 \omega} \left[ E_\phi \left( \frac{\partial E_\phi}{\partial \tau} - \frac{\partial E_z}{\partial r} \right) + E_z \left( \frac{\partial E_\phi}{\partial \tau} - \frac{1}{r} \frac{\partial E_\phi}{\partial \phi} \right) \right]
$$

where * indicates the complex conjugate. Using Eq. (1), we restate the electric field components in terms of the spatial components of the eigenfunctions and the current. Assigning the dipole position to the origin we can define the current as

$$
J(R') = -i \omega p_0 \delta(R')
$$

where $p_0$ is the dipole vector.

As in the calculation of dipole decay rates, we consider surface-parallel and perpendicular dipole orientations separately. Using the fact that $M_{\tau}, J^\tau_{\tau,\phi},$ and $J^\phi_{\tau}$ are zero, we have two cases for the primed eigenfunctions at the origin: (1) when the Bessel function index $n = 1, M'_{\tau} = -M'_{\phi} = \kappa/2, N'_{\tau} = -N'_{\phi} = \kappa h_2^2 k_1,$ (2) when the Bessel...
function index \( n = 0 \), \( N' = \kappa^2 k_z \). For both cases, other components of the primed eigenfunctions are zero. Thus, \( E_{j\ell}^h \) is zero and we get the following expressions for the non-zero electric field components at each layer \( j \),

\[
E_{j\ell}^+ = \frac{\kappa h_j}{k_j k_z} \partial J_0 (\kappa r) \left( f_j e^{-ik_{j\ell} z} - f_j^* e^{ik_{j\ell} z} \right)
\]

\[
E_{j\ell}^h = \frac{\kappa^2}{2 k_j k_z} J_1 (\kappa r) \left( f_j e^{-ik_{j\ell} z} + f_j^* e^{ik_{j\ell} z} \right)
\]

where \( p_0 \) is the dipole moment in the absence of reflected field on the dipole.

Next, we calculate the final form of the Poynting vector perpendicular to the stack, \( S_z^* \), to determine the power flow. We insert the expressions, Eq. (15) through (19), for the electric field into the equation for \( S_z^* \) and integrate over the surface area. Products of Bessel functions of different indices are orthogonal. In the integration, the remaining Bessel functions add up to \( \kappa \) for \( J_0 \) terms, and \( \kappa^2 \) for \( J_1 \) terms. To simplify the wavevector components, we normalize the wavevector, \( \kappa = \kappa k_z \) and use two identities, \( \kappa^2 + \hbar^2 = k^2 \)
and \( k_j^2 = e_j k_j^2 \). Finally, we normalize with respect to the total energy of the free dipole \((b_0)\), given by \( mp_0^2 \omega^2 / 2e^2 \) (in Joules), and we obtain

\[
\text{Re} \left( \int \sigma_{ij}^l \left( \text{d} \alpha \right) \right) = \frac{3q}{4} \text{Re} \left[ \int \frac{u \left( \sqrt{E_j} \right)}{1-u^2} \left( E_j / E_i - u^2 \right)^{1/2} \left( f_j e^{i\theta_j} - f_i e^{-i\theta_i} \right) \left( f_j e^{i\theta_j} + f_i e^{-i\theta_i} \right) \right] \tag{20}
\]

\[
\text{Re} \left( \int \sigma_{ij}^r \left( \text{d} \alpha \right) \right) = \frac{3q}{8} \text{Re} \left[ \int \frac{u \left( \sqrt{E_j} \right)}{1-u^2} \left( E_j / E_i - u^2 \right)^{1/2} \left( f_j e^{i\theta_j} - f_i e^{-i\theta_i} \right) \left( f_j e^{i\theta_j} + f_i e^{-i\theta_i} \right) \right] \\
+ \int \frac{u \left( \sqrt{E_j} \right)}{1-u^2} \left( c_j e^{i\theta_j} + c_i e^{-i\theta_i} \right) \left( c_j e^{i\theta_j} - c_i e^{-i\theta_i} \right) \right] \tag{21}
\]

Equations (20) and (21) are the central result of this work. The dipole energy transfer efficiency to an individual layer as a unitless percentage of total power emitted is found by taking the difference of the magnitude of this flux found at both boundaries of the layer and then dividing it by \( b^4 / b_0 \) or \( b^4 / b_0 \); see Eq. (11)-(13).

### 3.3. Förster Energy Transfer

Förster energy transfer occurs when the evanescent near field of a donor dipole couples with the evanescent near field of an acceptor molecule.[27] Since the near fields of both dipoles fall off as \( 1/R^3 \), the overall rate of energy transfer falls off like \( 1/R^6 \). In addition, if the donor is to transfer energy \( E \), it is necessary that the acceptor possess an allowed transition to a state of energy \( E \) above the ground state. Although no real photon is emitted in Förster transfer, it is common to express this latter requirement in terms of
the overlap between the absorption spectrum of the acceptor and the emission spectrum of the donor.[27]

In Fig. 3.2(a), we show the energy transfer spectrum from an excited \( \text{Alq}_3 \) molecule at the origin. The excited molecule is embedded within an infinite film of 1\% copper phthalocyanine (CuPC) in \( \text{Alq}_3 \). Since the absorption of CuPC overlaps the \( \text{Alq}_3 \) fluorescent spectrum, we expect Förster energy transfer from \( \text{Alq}_3 \) to CuPC. The rate of energy transfer is plotted as a function of \( u \), which is the wavevector component parallel to the surface \( (k_\parallel) \) normalized by the wavevector magnitude in the dipole layer \( (k_0) \). As expected for evanescent coupling, the spectrum is dominated by short range energy transfer through modes with very large \( k_\parallel \). The \( z \) dependence of the normalized energy transfer rate is shown in Fig. 3.2(b). In cylindrical coordinates, the typical \( 1/R^6 \) dependence of the energy transfer rate, \( b_{ET} \), becomes

\[
\frac{1}{b_0} \int dr \text{Re} \left( \int dA \frac{dS_e^{\perp}}{dz} \right) = \frac{b_{ET}(z)}{b_0} = \int_0^\infty \int_0^{2\pi} dr \rho \frac{R_0^6}{r^2 + z^2} = \rho \frac{R_0^6}{2} \frac{\pi}{z^4}
\]

where \( R_0 \) is the Förster radius, a measure of the strength of the coupling,[9] and \( \rho \) is the density of acceptor molecules. Thus, we expect the rate of Förster transfer to decay as \( 1/z^4 \), consistent with the result in Fig. 3.2(b). The Förster radius is calculated to be \( R_0 = 38\text{Å} \).
Fig. 3.2. (a) Förster energy transfer as a function of z position and normalized to the surface-parallel wavevector. The excited molecule is embedded within an infinite film of 1% CuPC in Alq₃. The dipole is located at \( r = z = 0 \) and the emission wavelength is \( \lambda = 535 \text{ nm} \). Bright features correspond to a faster energy transfer. (b) The z dependence shows a \( 1/z^4 \) power law consistent with Eq. (22) and a Förster radius of \( R_0 = 38 \text{ Å} \). At \( \lambda = 535 \text{ nm} \), the dielectric constants for CuPC and Alq₃ are: \( \varepsilon = 1.908 + 0.265i \) and \( \varepsilon = 2.962 \), respectively.

This calculation demonstrates that Eqs (20) and (21) can be used to determine whether Förster transfer is enhanced in complex planar structures.[27] Clearly, however, the cavity must influence evanescent modes if near field energy transfer is to be enhanced.

### 3.4. Mode Distribution and Angular Emission Simulations

To test the model, we simulate the OLED of Segal et al.[6] This structure was chosen because its outcoupling fraction, \( \eta_o \), has been accurately measured using a reverse bias technique. In brief, the PL efficiency of the emissive layer is measured within the OLED by applying reverse bias. The applied field dissociates some excitons, and the decrease in PL is compared to the induced photocurrent. This yields the product of PL efficiency and
outcoupling efficiency, since the emissive layer is measured within the OLED structure. Then by normalizing to the free-space PL efficiency, the outcoupling fraction is found. Using this technique, Segal et al. obtained $\eta_c = (24\pm4)\%$. As with most OLEDs of this structure, the emission profile is approximately Lambertian.

The OLED has the following structure: the substrate is glass precoated with a 1600Å-thick layer of indium tin oxide (ITO) substrate. Next, a 300Å-thick layer of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulphonate) (PEDOT:PSS) is spun on. The organic layers are 500Å of $N,N'$-diphenyl-$N,N'$-bis(3-methylphenyl)-[1,1'-biphenyl]4,4'-diamine (TPD), 200Å of tris(8-hydroxyquinoline) aluminum (Alq₃), and 500Å of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP). The cathode is a 1000Å-thick Mg:Ag layer with 60:1 Mg:Ag ratio with a 200Å-thick Ag cap on top of everything. The device structure and the measurement setup are shown in Fig. 3.3.[6]

![Diagram](image)

Fig. 3.3. (a) The structure and experimental setup of the OLED from Segal et al. (b) The detailed measurement setup for the outcoupling measurement.[6]
To simulate the device, we obtain the optical constants of each layer using a spectrophotometer (Aquila Instruments® nkd8000). This measures the reflection and transmission (RT) from a thin film of the desired material on a glass substrate at a certain angle ($30^\circ$) under both $s$ and $p$ polarizations. The dielectric function is then determined iteratively by matching the RT calculation to the measurement. Then using Eqs (20) and (21) we calculate the angular dependence of power flow into a semi-infinite glass substrate. Subsequent energy transfer from glass to air is determined using classical ray optics.

![Diagram](image)

**Fig. 3.4.** (a) Absorption of the parallel dipole energy as a function of the position and normalized surface-parallel wavevector. The dipole is located at the middle of the Alq$_3$ layer and the emission wavelength is $\lambda = 535$ nm. Bright features correspond to a higher absorption. The green curve shows the outcoupled energy flux. (b) Same as part (a) but for perpendicular dipole. Perpendicular dashed lines divide this flux into air-outcoupled, glass-waveguided, organics-waveguided and surface plasmon polariton (SPP) portions. At $\lambda = 535$ nm, the dielectric constants for Mg, BCP, Alq$_3$, TPD, PEDOT, and ITO are: $\epsilon = 1.908 + 0.265i$, $\epsilon = 2.985 + (4.11 \times 10^{-5})i$, $\epsilon = 2.962$, $\epsilon = 2.985 + (4.11 \times 10^{-5})i$, $\epsilon = 2.304 + (3.33 \times 10^{-2})i$ and $\epsilon = 3.295 + (3.63 \times 10^{-2})i$, respectively. Note that the dielectric constant of TPD was assumed to be equal that of BCP.
The dipole energy outcoupling and absorption as a function of the distance from the dipole position and normalized surface-parallel wavevector ($u$) is shown in Fig. 3.4(a) and Fig. 3.4(b) for parallel and perpendicular dipoles, respectively. In the calculation, the emission wavelength is $\lambda = 535$nm and the dipole is placed at the center of the Alq$_3$ layer. Once again we normalize the surface-parallel wavevector ($k_\parallel$) using the magnitude of the wavevector in the dipole layer ($k_0$). The parallel dipole shows an absorption peak at $u \sim 1.07$ exponentially decaying in the metal layer, corresponding to a SPP mode, and two absorption peaks around $u \sim 0.90$ and $u \sim 0.96$ mainly in the ITO layer, corresponding to the waveguide modes in the ITO and organics. The perpendicular dipole also couples to an ITO/organic waveguide mode, but it displays almost ten times stronger SPP absorption. The green curves on top of Fig. 3.4(a) and Fig. 3.4(b) show the corresponding energy flux through the ITO-glass interface. These curves share the same $u$ axis with the main figure and they can be divided into three regions, shown by dashed gray lines on the figure. The first region extends from $u = 0$ to $u = 0.58$. This is the set of wavevectors that outcouple into air. The second region extends from $u = 0.58$ to $u = 0.87$. This region contains the wavevectors that are guided in the glass. Organic/ITO waveguide modes are found for $0.87 < u < 1$.

Integrating the function in Fig. 3.4, we obtain the energy transfer efficiencies, which are shown as a function of the distance from Alq$_3$-BCP interface in Fig. 3.5(a). A simplified model of the energy flow is shown in Fig. 3.5(b). The total losses in the organic and ITO layers are largely independent of the dipole position; however, the glass
Fig. 3.5. (a) The calculated distribution of the Alq$_3$ dipole energy versus the dipole distance from the BCP layer. (b) The basic structure and the emitting pathways of the OLED of Segal et al. [6]

waveguide coupling increases while energy transfer to the metal decreases with the increasing distance from the metal cathode. Averaged over the entire Alq$_3$ emissive layer we obtain $\eta_c = 22\%$, in agreement with the experimental result.[6]

Figure 3.6 shows our calculation for the angular emission profile for this OLED. Each red or blue curve corresponds to the angular emission profile into air and into the glass layer, respectively, for 10 different dipole positions spaced 20Å apart in the Alq$_3$ layer. The curves with maxima at larger angles correspond to the dipoles nearer to the metal cathode. Fig. 3.6(a) shows the angular profile of perpendicularly-oriented dipole emission. The strength at acute angles preferentially couples perpendicular dipoles to photonic and plasmonic waveguide modes. The parallel dipoles (Fig. 3.6(b)) dominate the radiated emission due to their strength around the normal. Hence the parallel and isotropic (Fig. 3.6(c)) angular distributions turn out to be very similar. The overall angular distribution of the emission of this OLED resembles a Lambertian emission profile as expected, which means the intensity is equal in all directions.
3.6. Organic Light Emitting Devices with Cavities

The development of a stable, efficient and saturated blue remains an important goal for phosphorescent organic light emitting devices (OLEDs). One important limitation is the broad photoluminescent (PL) spectrum characteristic of organic dyes. For example, greenish-blue or ‘sky-blue’ phosphors have strong emission in the blue. But optical transitions to higher vibrational modes of the electronic ground state extend their emission spectrum deep into the green. Because the eye responds strongly at green wavelengths, this broad emission spectrum yields an unsaturated color that is ill suited for most display applications. Unfortunately, increasing the energy of a sky-blue phosphor to
Fig. 3.7. (a) The structure of the strong microcavity OLED compared to that of a conventional, or weak microcavity OLED. In the strong microcavity the anode is a thin, semitransparent layer of Ag. The Al/LiF cathode is defined by a 1-mm-diameter shadow mask. The electron transport layer is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine or BCP). To aid hole injection from the silver anode, the first 60Å of the hole transport layer N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,10-phenanthroline (TPD) is doped with 3% by mass of the acceptor tetrafluorotetracyanoquinodimethane (F₄-TCNQ). The emissive layer consists of 6% by mass iridium(III)bisdipyridine-[1,1'-biphenyl]-4,4'-diamine (FIrpic) in N,N'-dicarbazolyl-3,5-benzene (mCP). Devices were grown directly on the smooth back surface of frosted glass and opal glass diffusers. The holographic diffuser was employed external to devices grown on regular glass. The weak microcavity OLED has an anode precoated with indium tin oxide (ITO) and poly(3,4-ethylenedioxythiophene): poly(4-styrenesulphonate) (PEDOT-PSS). All other layers were deposited by thermal evaporation at a base pressure of less than 3x10⁻⁶ Torr. Each layer is subject to 20% uncertainty in the interferometric measure of thickness. (b) The calculated distribution of energy dissipation within the OLEDs. In the strong microcavity OLED, energy lost to the cathode, anode and waveguide modes is labeled, Aluminum, Silver and Glass, respectively. The remaining energy is outcoupled to air. The modeled layers are Ag 250Å/ TPD 650Å/ mCP 135Å/ BCP 270Å/ Al 1000Å. In the conventional, or weak microcavity OLED, some energy is dissipated in the aluminum cathode, but most energy is lost to waveguided modes. Roughly 20% of the energy is coupled to waveguide modes in the organic films. These modes are absorbed by the PEDOT and ITO layers. Another ~ 30% is waveguided within the glass substrate. The modeled layers are ITO 1600Å/ PEDOT-PSS 200Å/ TPD 500Å/ mCP 200Å/ BCP 400Å/ Al 1000Å.

minimize its green emission requires strong confinement of excited states in the host and dye,[28] limiting the molecular design possibilities. In contrast, the triplet state of a sky-
blue phosphor is compatible with a broader range of host materials and sky-blue phosphors have achieved lifetimes exceeding 15,000 hours at an initial brightness of 200 cd/m².[29]

The color of a dye can be modified by inserting it within a microcavity.[30, 31] Indeed, a microcavity is formed within a conventional OLED by weak reflections from interfaces. But the effects of a weak microcavity on the electroluminescence (EL) are relatively minor. In a strong microcavity, the dye is positioned between two highly reflective films. A strong microcavity significantly modifies the photonic mode density within the OLED, suppressing EL at undesirable wavelengths, and enhancing EL from the homogeneously broadened phosphor at the microcavity resonance.

In this work, we demonstrate an efficient and saturated blue phosphorescent OLED using a strong microcavity. The usual disadvantages of a strong microcavity, namely the introduction of an angular dependence to the OLED’s color, and a non-Lambertian angular emission profile, are overcome by scattering the emitted radiation.

Strong and weak microcavity OLED structures are compared in Fig. 3.7(a). The sky-blue phosphor is FIrpic.[32, 33] The strong microcavity is formed by an aluminum cathode and a semitransparent silver anode with a doped [34] hole transport layer to aid hole injection. The weak microcavity OLED employs the conventional anode of indium tin oxide (ITO) and PEDOT:PSS rather than silver.

The strong microcavity was designed using analytical calculations of the Poynting vector.[10] This technique allows the exact determination of the spectral dependence of
energy dissipation in each layer within an OLED; see Fig. 3.7(b).[10] To optimize the color of the strong microcavity OLED, the resonant wavelength is blue-shifted by approximately 20nm relative to the peak of the intrinsic PL spectrum of FIrpic at \( \lambda = 470 \text{nm} \). At the microcavity resonance, the outcoupling fraction is calculated to be nearly 40%. The energy dissipation within the weak microcavity is also shown for comparison. Its outcoupling fraction to air is calculated to be \( \sim 30\% \) and only weakly dependent on wavelength. At the resonance, the strong microcavity enhances the photonic mode density for photons emitted in the forward hemisphere at the expense of the waveguide modes that dominate in a weak microcavity OLED.[31] The calculation also shows that most of the remaining energy in the strong microcavity is dissipated in the semitransparent silver layer, suggesting that replacing the silver with a dielectric mirror might further enhance the efficiency.[31]

The EL spectra as a function of angle from the surface normal are shown in Figs. 3.8(a) and b, for the strong microcavity OLED without and with the holographic diffuser, respectively. In Fig. 3.8(a) we compare the EL spectra of the strong microcavity OLED to the intrinsic PL spectrum of FIrpic. The strong microcavity is observed to strongly suppress the undesirable long wavelength emission. But there is a noticeable color shift with angle. Higher wavenumbers are enhanced for large emission angles, yielding a blue shift in the EL spectrum that is constrained only by the sharp high energy shoulder of the FIrpic PL spectrum. With the holographic diffuser, however, the color shift is barely perceptible and compares well to the expected EL spectrum after transmission through an ideal scattering medium. This prediction is obtained from the intrinsic PL spectrum of FIrpic and the calculated strong microcavity outcoupling spectrum from Fig. 3.7(b). The
color coordinates for all devices are shown in Fig. 3.8(c). The average color coordinates are deep blue \((x,y) = (0.116 \pm 0.004, 0.136 \pm 0.010)\), significantly shifted from the intrinsic PL spectrum of FIrpic: \((x,y) = (0.18, 0.34)\).

![Figure 3.8](image)

Fig. 3.8. Electroluminescent spectra of the strong microcavity FIrpic OLED as a function of angle from the surface normal (a) without and (b) with the holographic diffuser. With the holographic diffuser the color shift is barely perceptible. For comparison in (a) we plot the intrinsic photoluminescent spectrum of FIrpic and in (b) we plot the modeled electroluminescent spectrum of the strong microcavity after transmission through an ideal scattering filter. (c) The color coordinates of the strong microcavity devices with holographic diffusers are deep blue with \((x,y) = (0.116 \pm 0.004, 0.136 \pm 0.010)\). The intrinsic FIrpic photoluminescence spectrum is sky-blue with \((x,y) = (0.18, 0.34)\). **Inset:** the full CIE diagram identifying the expanded blue region.

To summarize the work in this section, we have coupled strong microcavity OLEDs with scattering filters. The scattering filter corrects the angular dependence of EL, and the strong microcavity gives a deep blue color with enhanced optical outcoupling. The demonstrated benefits to color and efficiency suggest that this architecture - strong microcavity OLEDs combined with a scattering filter - can be generally implemented to
the benefit of red, green and blue pixels in three color display applications. We also note that the maximum reported external quantum efficiency of a sky blue phosphor is nearly triple that of the control device reported here, [29] suggesting that stable, saturated blue OLEDs with external quantum efficiencies exceeding 10% are within reach.

3.6. Interlayer Energy Transfer

Next, as an example of layer-to-layer dipole energy transfer, we have calculated the emission spectra of the structure experimentally studied by Andrew and Barnes.[35] This structure is formed a glass substrate by first spin coating a 60-nm-thick donor film of polymethylmethacrylate (PMMA) doped with 4% Alq$_3$ by weight, then thermally evaporating a 60-nm-thick silver film, and finally spin coating a 60-nm-thick acceptor PMMA film doped with 1.6% rhodamine-6G (R6G) by weight. The samples are pumped by a laser on the donor side at a wavelength of $\lambda = 408$ nm. The excitation approximately corresponds to the Alq$_3$ absorption maximum and R6G absorption minimum. During photoexcitation the photoluminescent spectrum is recorded on the acceptor side of the sample. In the calculation, we integrated the contribution of dipoles throughout the donor and acceptor films. The result was found to be similar to the case where the dipoles are located at two thin strips at the middle of each PMMA film. The quantum yields ($q$) of the dipoles are taken to be [36,37] 25% and (95±1.5)% [38] for Alq$_3$ and R6G molecules, respectively.

Figure 3.9 shows the energy absorption in the silver and R6G-doped PMMA layers as a function of the normalized surface-parallel wavevector, $u$. Once again, the wavelength
used for this calculation is $\lambda = 535$ nm. The SPP peak at $u \sim 1.1$ dominates the absorption and is strongly evident in both the silver and the acceptor film. Thus, we conclude that the energy transfer to the R6G molecules occurs mainly via the SPP mode, although there is significant loss in the silver film. The coupling to SPP modes is best for perpendicular dipoles. As in the OLED simulation, parallel dipoles outcouple better to the air. The radiated modes have normalized surface-parallel wavevectors smaller than $u = 0.67$. Parallel wavevectors between $u = 0.67$ and $u = 1$ are guided in the glass and PMMA. (Note that the refractive index of PMMA is only slightly lower than that of glass). The amount of radiated power directly from Alq3, however, is small, due to the thick silver

Fig. 3.9. (a) Absorption of the parallel dipole energy as a function of the position and normalized surface-parallel wavevector. The dipole is located at the middle of the PMMA:Alq3 layer and the emission wavelength is $\lambda = 535$ nm. The green and blue curves show the outcoupled energy flux from the PMMA:R6G-air and PMMA:Alq3-glass interfaces, respectively. The blue curve is rescaled by 1/2000 to share the same y-axis with the green curve. (b) Same as part (a) but for perpendicular dipole. Perpendicular dashed lines divide the flux into air-outcoupled and glass-waveguided portions. Dielectric constants for PMMA and R6G were extracted from Ref. [35].
layer. Thus, the measured light emission from this structure is dominated by the R6G emission, which in turn, gains its energy predominantly from the SPP-assisted energy transfer from the Alq₃ dipoles. For completeness, we note that the Alq₃ dipoles also radiate into the glass substrate; see the blue curves in Fig. 3.9. The radiated power in the glass substrate is about 2000 times larger than the power radiated into the air on the acceptor side.

The spectral distribution of the outcoupled energy fraction with respect to the total dipole energy is shown in Fig. 3.10(a). It compares well with the experimental data of Andrew and Barnes; see Fig. 2b in Ref. [35]. Calculation of the emission spectra is done by multiplying the outcoupling fractions at each wavelength by the normalized intrinsic emission spectra extracted from Fig. 1d of Ref. [35]. We also calculate the total energy transfer efficiency by normalizing to the energy of an Alq₃ dipole. Fig. 3.10(b) shows an exponential decrease in the transfer efficiency as the silver thickness is increased. The maximum transfer efficiency is approximately 6%. Energy transfer can be enhanced by increasing the concentration of R6G molecules in the PMMA layer. Relative to Förster transfer between point dipoles, mediation by the SPP enables energy transfer over much longer distances.[35] The limitation for SPP-mediated energy transfer is typically the decay length of the evanescent SPP field in the donor and acceptor dielectrics. This may be on the order of 100nm, as compared to a typical Förster radius for point dipoles of < 5nm.
Fig. 3.10. (a) The calculated ratio of emitted power to the total dipole energy for the structure of Andrew and Barnes.[35] The data is shown for samples without the R6G acceptor (PMMA:Alq3/Ag/PMMA) (blue curve), samples without the Alq3 donor (PMMA/Ag/PMMA:R6G) (green curve) and samples containing both Alq3 and R6G (PMMA: Alq3/Ag/PMMA:R6G) (red curve). The silver layer thickness is 60 nm. The R6G absorption and PL spectra of R6G and Alq3 are extracted from Fig. 1(d) of Andrew and Barnes.[35] (b) The energy transfer efficiency, which is the ratio of the energy absorbed by the R6G-doped PMMA layer to the total Alq3 dipole energy, versus silver thickness.

3.6. Organic Photovoltaics with External antenna layers

With a theoretical efficiency similar to conventional inorganic photovoltaics (PV) and the potential to be manufactured inexpensively, organic semiconductor technology offers a promising route to ubiquitous solar energy generation.[39] Electronic localization in organic semiconductors yields structured optical absorption spectra with pronounced regions of weak absorption. This limits efficiency because the short exciton diffusion length within organic semiconductors demands uniformly strong absorption.[7]
Fig. 3.11. (a) Devices with resonant antenna cavities have the structure: glass/ indium tin oxide (ITO) (1100 Å)/ copper phthalocyanine (CuPc) (100Å)/ CuPc:fullerene (C60) (1:1) (100Å)/ C60 (200Å) / bathocuproine (BCP) (85Å)/ Ag (150Å)/ 30% Rubrene in CBP antenna (1250Å) / Ag (600Å). To quench or enhance the PL efficiency of the rubrene antenna we introduce either CuPC or DCJTB, respectively, at 2% weight ratio. Concentration quenching is minimized in the antenna by diluting rubrene with CBP. The devices are illuminated from the glass side. Organic materials were purified by vacuum thermal sublimation prior to use. All materials were deposited by thermal evaporation at \(-10^{-6}\) Torr. All active device areas are 0.01 cm². (b) For measurement of energy transfer efficiency, high internal quantum efficiency superlattice photodetectors are used with the structure: glass/ ITO (1100Å)/ 20 alternating layers of CuPc and 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI) (each layer 15Å)/ BCP(85Å)/ Ag (205Å)/ 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (H₂TFPP) (850Å). The photoluminescent (PL) efficiency of the H₂TFPP antenna is tuned by adding 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP) at varying concentrations. The devices are illuminated from the antenna side.

In this work, we enhance the optical absorption of organic PVs by fabricating a light-absorbing antenna on top of a conventional copper phthalocyanine (CuPC)-based PV; see the device structures in Fig. 3.11. Light absorbed in the antenna is coupled to the PV, using energy transfer via surface plasmon polaritons (SPPs) and radiation into waveguide...
modes.[35] SPPs are a particularly effective energy transfer mechanism as they propagate in the plane of the PV rather than parallel to the incident radiation, thereby providing a more efficient means of pumping thin charge generating structures.[11] In addition, the SPP mode extends deeply into both dielectric layers, extending the range of energy transfer up to \( \sim 100 \) nm. While this distance is much longer than the range of intermolecular Förster energy transfer, the 100 nm energy transfer limit demands antenna materials with absorption coefficients of at least \( \alpha = 10^5 \) cm\(^{-1}\) to capture sufficient light within the antenna.

![Absorption vs. Wavelength](image)

**Fig. 1.12.** Calculated absorption within the resonant cavity device given illumination from glass side. The tuned cavity results in significantly increased absorption in the antenna layer.

We couple resonant antennas to phthalocyanine-based PV cells, which exhibit a gap in their absorption spectra between the Q and Soret bands. To help fill this gap, we use rubrene, a common organic light emitting device material, which has an absorption
coefficient of $\alpha \sim 10^4 \text{ cm}^{-1}$ at $\lambda \sim 550\text{nm}$. Using rubrene as a Förster energy transfer donor for the laser dye 4-(dicyanomethylene)-2-\text{-}t\text{-}butyl-6-(1,1,7,7-tetramethyljulolidyl-9-\text{-}enyl)-4H-pyran (DCJTB), $\eta_{PL} = (90\pm10\%)$.

To tune the resonant antenna PV shown in Fig. 3.11(a), we calculate the expected optical absorption in each layer.[7] A 1250Å-thick film of 30% Rubrene and 2% DCJTB in transparent carbazole biphenyl (CBP) tunes the cavity close to the $\lambda \sim 500\text{ nm}$ absorption peak of rubrene; see Fig. 3.12. We model energy transfer within a multilayer organic PV stack by evaluating the Poynting vector, $\mathbf{P}$, using dyadic Green's functions.[10] The wavevector dependence of energy transfer from the antenna to the PV is shown in Fig 3.13a. The energy transfer rate is plotted against the component of the wavevector parallel to each interface normalized by the wavevector magnitude in the antenna, $u$. Normalized wavevectors with $u < 1$ correspond to radiative modes while those with $u > 1$ correspond to non-radiative energy transfer. The dipole was located in the middle of the antenna layer for these calculations. We find that energy transfer occurs predominantly via non-radiative coupling, mediated by SPP modes with $u > 1$. Loss in the silver layers is significant but is minimized by reducing the thickness of the silver cathode. We also model the dipole coupling efficiency to each layer in the PV stack as a function of the dipole distance from the antenna/cathode interface, see Fig. 3.13(b). Near the cathode $\eta_{ET} = 54\%$, but the efficiency decreases beyond $\sim 85\text{nm}$. Averaged over the antenna, $\eta_{ET} = 31\%$.

To demonstrate the potential improvement possible using an external resonant antenna in conventional C60/CuPC PV cells, we compare a control device without the antenna to
Fig. 3.13 (a) The normalized in-plane wavevector ($u$) dependence of energy transfer throughout the resonant cavity devices is shown for dipoles oriented perpendicular to the antenna/cathode interface. The free space quantum photoluminescent efficiency of excitons was assumed to be 90% at $\lambda = 650$ nm. Coupling is greatest for dipoles into modes with $u>1$, corresponding to surface plasmon polaritons (SPPs).

(b) The modeled dipole coupling fraction to each layer in the photovoltaic stack as a function of the dipole distance from the antenna/cathode interface. Coupling to the CuPC and C60 layers results in photocurrent.

devices with an antenna composed of 30% Rubrene and 2% DCJTB in CBP. Quenched antennas were also fabricated with the addition of 2% of the quenching material CuPC instead of DCJTB. External quantum efficiency measurements were made using a xenon lamp with monochromator, chopped at $f = 90$ Hz, and measured using a lock-in amplifier. Light intensity was measured with a calibrated silicon photodiode. The external quantum efficiencies of these devices as a function of wavelength are shown in Fig. 3.14 and compared to the reflectivity of the antenna cavity. The absorption of the antenna (from Fig. 3.12) and the internal quantum efficiency at the PL maximum of DCJTB, $\eta_{QE} = (30\pm10)\%$ at $\lambda = 640$nm, is used to determine $\eta_{ET}$. This yields $\eta_{ET} = (25\pm10)\%$, consistent with the calculated result of $\eta_{ET} = 31\%$ in Fig. 3.13b. As illustrated, with improved energy transfer, the efficiency in the spectral gap between absorption peaks could be
significantly improved. The absorption modeling also demonstrates that the improved quantum efficiency outside the region where the resonant cavity absorbs is due to reflectivity changes that modify the electric field profile within the device.

While the introduction of the antenna necessarily adds a step into the energy transduction process, it can be successfully employed in spectral regions where the absorption fraction of the PV cell drops below $\eta_{ET}$. To reduce the uncertainties in the measurement of $\eta_{ET}$, we fabricate an organic superlattice photodetector and antenna without the resonant cavity; see Fig. 3.11b. This structure should also enhance $\eta_{ET}$, since it contains more CuPC, increasing the absorption of SPPs in the charge generating layers.

![Fig. 3.14 External quantum efficiency (EQE) for resonant antenna devices. Devices with functional external rubrene-based antenna layers exhibit an increase in EQE over the wavelength range where rubrene absorption occurs and the cavity reflectivity decreases. Functional antennas (red squares) employ the laser dye, DCJTB, whereas nonfunctional antennas (green circles) employ the quencher CuPC. The functional antenna shows a significant performance enhancement versus both the quenched antenna and devices fabricated without any antenna (Δ). Comparison with modeling (—) indicates that the energy transfer efficiency is approximately 25%. We also show the expected EQE for energy transfer efficiencies of 0%, 50%, and 75%.](image)
Under an applied bias, the organic superlattice photodetector is expected to exhibit an internal quantum efficiency close to 100% for excitation by SPP-modes.\textsuperscript{[11]} We assume $\eta_{IQE} = 100\%$ which gives a lower bound for $\eta_{ET}$. The antenna material in this device is tetrakis(pentafluorophenyl)porphyrin ($\text{H}_2\text{TFPP}$). It is chosen for its combination of moderate PL efficiency $\eta_{PL} = 2\text{-}3\%$ and high absorption coefficient ($\alpha = 10^6 \text{ cm}^{-1}$ at $\lambda = 400\text{nm}$) that allows nearly 100% of incident radiation to be absorbed in the absence of a cavity within the ~100 nm range of SPP-mediated energy transfer.

![Fig. 3.15. Measurement of energy transfer efficiency using superlattice photodetectors. Top: Measurement of external quantum efficiency of devices with different antenna compositions: 3.5% CuPC in $\text{H}_2\text{TFPP}$ $\eta_{PL} = 0\%$ (solid), 100% $\text{H}_2\text{TFPP}$ $\eta_{PL} = (2.4\pm0.2)\%$ (long dashed), 90:10 $\text{H}_2\text{TFPP}$:CBP $\eta_{PL} = (2.5\pm0.3)\%$ (short dashed), 70:30 $\text{H}_2\text{TFPP}$:CBP $\eta_{PL} = (3.4\pm0.3)\%$ (dotted). Bottom: absorption spectra of different antenna layers on glass. Inset: Calculation of energy transfer efficiency normalized by the PL efficiencies of the various antennas yields $\eta_{ET} = (51\pm10)\%$.](image-url)
External quantum efficiency measurements were made at a reverse bias of 3.5V. The measured absorption and PL efficiency of the H₂TFPP antenna is used to determine \( \eta_{ET} \) from the increase in external quantum efficiency, \( \Delta \eta_{EQE} \), i.e. \( \eta_{ET} = \Delta \eta_{EQE}/ \eta_{ABS} \eta_{PL} \).

Four H₂TFPP antennas were fabricated with varying PL efficiencies by blending H₂TFPP with different concentrations of CBP. The addition of CBP reduces concentration quenching. To eliminate energy transfer altogether, additional devices were fabricated with non-functional antennas comprised of H₂TFPP codeposited with 3.5% of CuPC. Using the quenched antenna as the baseline, and noting that the absorption of H₂TFPP is \( \eta_{ABS} = 75\% \) for \( \lambda \leq 450 \text{ nm} \), we obtain \( \eta_{ET} = (51\pm10)\% \), substantially higher than the resonant antenna result; see the inset of Fig. 3.15. Note that the overall change in quantum efficiency is lower, however, due to the weak \( \eta_{PL} \) of H₂TFPP.

The peak efficiency of SPP-mediated energy transfer in previous studies[35] was approximately \( \eta_{ET} = 5\% \), too small for most applications.[10] The approximately order of magnitude improvement in this work is due to reductions in the thickness of the interfacial silver layer, and increasing the absorption of the acceptor, which must compete with SPP loss in the silver layer. It is possible to increase the quantum efficiency of an antenna further by optimizing the orientation and position of luminescent antenna excitons with respect to the thin Ag cathode.
4. Conclusions

An extension to the dyadic Green’s functions method of Chance, Prock, Silbey has been explained. This extension is made by analytically deriving a compact formula for the surface-perpendicular Poynting vector coefficient of a dipole in a multilayer thin film stack. Using this model we have designed cavity devices and photovoltaics with external antenna layers. We have shown increased outcoupling for deep-blue organic light emitting devices and broadening of the available sunlight absorption range in organic photovoltaics. Using traditional transfer matrix methods we have also designed an organic photovoltaic cell under Kretschmann configuration, as a novel example of integrated surface plasmon detection.
5. References


