A generalized Stark effect electromodulation model for extracting excitonic properties in organic semiconductors

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Electromodulation (EM) spectroscopy, a powerful technique to monitor the changes in polarizability $\Delta p$ and dipole moment $\Delta u$ of materials upon photo-excitation, can bring direct insight into the excitonic properties of materials. However, extracting $\Delta p$ and $\Delta u$ from the electromodulation spectrum relies on fitting with optical absorption of the materials where optical effect in different device geometries might introduce large variation in the extracted values. Here, we demonstrate a systematic electromodulation study with various fitting approaches in both commonly adopted reflection and transmission device architectures. Strikingly, we have found that the previously ascribed continuum state threshold from the deviation between the measured and fitting results is questionable. Such deviation is found to be caused by the overlooked optical interference and electrorefraction effect. A generalized electromodulation model is proposed to incorporate the two effects, and the extracted $\Delta p$ and $\Delta u$ have excellent consistency in both reflection and transmission modes in all organic film thicknesses.
A s the core of device physics, the properties of bound electron–hole pairs known as excitons are governing the charge dissociation and recombination efficiency in various low-dimensional materials, such as conjugated organic molecules and polymers, quantum dots, nano-wires, and organo-metal halide perovskites. Various techniques have been developed to probe the dynamics and energetics of the material excitonic properties including transient photoluminescence spectroscopy, transient absorption spectroscopy, time resolved Stark effect spectroscopy and steady state Stark effect electromodulation (EM) spectroscopy. Among these, the steady state EM spectroscopy has been regarded as a powerful technique with high sensitivity to monitor the energy level perturbation. According to the Stark effect, the Hamiltonian $H^{(1)}$ of a molecule interacting with an field strength $F$ along the $z$-direction can be expressed as

$$H^{(1)} = -D_z \cdot F,$$

where $D_z$ is the electric dipole moment operator along the direction of the electrical field. Thus, the energy level of material modulated by the electrical field will alter the absorption and therefore the light intensity transmitted or reflected by the samples. Such phenomenon can be expressed as

$$E(F) \approx E(0) - \mu_z \cdot F - \frac{1}{2} \rho \cdot F^2,$$

where $E(F)$ is the modulated energy level under electrical field and $E(0)$ refers to the energy level with the absence of electrical field. $\mu_z$ and $\rho$ stand for the permanent dipole moment and polarizability components along the electrical field direction, respectively.

EM was initially applied to determine the band structure of semiconductors such as Si, Ge, and GaAs. Particularly, electroabsorption (EA) spectroscopy has been widely applied to determine the electrical field distribution in stacked organic layers in organic-light-emitting diodes (OLEDs) and organic photovoltaics (OPVs), and electronic state symmetry. Another uniqueness of EA is its capability to extract two macroscopic material parameters, namely, polarizability change and dipole moment change which is correlated with various excitonic processes including exciton binding energy, delocalization of charge-transfer (CT) state, charge generation probability, and recombination processes. EM has also been recently applied to determine the exciton binding energy in 3D/2D organic-metal halide perovskite. The technique has also been used to probe the orientation of molecules, which have recently been found to be an excellent control of thermally activated delayed fluorescent (TADF) in OLEDs.

For EM measurement, there are generally three different device architectures have been used: (1) inter-digitized electrode configuration, due to a large spacing between electrodes (>5 μm), an applied voltage as high as hundreds of volt is required to achieve an electrical field ($10^4$–$10^5$ V/cm) with measurable EM signal; (2) sandwiched transmission configuration (T mode), where the organic layer is sandwiched by semi-transparent electrodes at both sides. The advantage of this mode is the optical interference effect is small which can be potentially ignored in the analysis, but it is limited by the choice of electrode materials; (3) sandwiched reflection configuration (R mode), where only the front electrode is required to be semi-transparent and it is most relevant to the practical OPV and OLED architectures. However, the reflective back electrode might induce strong optical interference effect which would complicate the EM spectrum analysis. Recently, the discrepancy issue of the fitting values obtained by reflection and transmission modes was raised by D. Ginger et al. on the analysis of CH$_3$NH$_3$PbI$_3$ perovskite. The authors found that the EA spectral line shape was thickness dependent in R mode. Whereas the line shape in T mode was mostly identical in different thicknesses. They regarded the different line shape obtained in R mode was due to both refractive index modulation known as electrorefraction (ER) and optical interference effects. However, it is still unclear on how such optical effects would affect the fitting values and how they could be resolved in both R and T modes. In several recent reports, by comparing EA spectra with corresponding thin film absorption derivatives, authors have found that enhanced delocalization of the excited state with increased polarizability in organic bulk heterojunction films. However, as will be demonstrated in this work, analyzing the EM spectrum using the thin film absorption is potentially risky, which will lead to a contradictory result.

Hence, more reliable analysis approach is crucial for giving a consensus conclusion on the understanding of the excitonic effect in organic semiconductor devices. By using EM, the nature of the excited state is whether Frenkcle or CT type can be quantitatively described by the extracted $\Delta p$ and $\Delta u$. $\Delta p$ can be interpreted as the polarizability gained in the excited state and $\Delta u$ can be regarded as the change of exciton radius including its dipole direction and length relative to its ground state. These two parameters not only draw attention in the area of semiconductor application but also in biological science as concerning the electron transfer in DNA and photosynthetic reactions. Particularly in OPV, it is still an open question whether free charge generation can be achieved in a single organic material system. Having such material can revolutionally change the viability of the technology and understanding of the materials science. Despite a record high quantum efficiency has been recently demonstrated in a homojunction OPV, it is still not clear how such superb exciton dissociation ability can be correlated with the fundamental material properties/structure.

Here, we report a systematic experimental and theoretical EM study for extracting the excitonic properties of organic materials in both reflection and transmission device architectures. A push–pull photovoltaic polymer poly[N-9′-hepta-decanyl-2,7-carbazolealt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) was used as a model material for this study. The amorphous nature of PCDTBT guarantees its thickness independent morphological and electronic properties. In order to elucidate the impact of optical interference and ER effects on the EM spectral line shape, the EM spectra were measured in both reflection and transmission configurations with different PCDTBT thicknesses. The measured results were first analyzed by fitting with the most commonly used thin film absorbance and device absorbance. Finally, for the first time, a generalized model incorporating both EA and ER contributions to the EM spectrum will be presented which demonstrates an excellent consistency of the extracted values in both R and T mode configurations.

**Results**

**Reflection and transmission mode EM.** Figure 1 shows the device structures used for reflection (R) mode and transmission (T) mode EM measurement, along with the molecular structure of PCDTBT. A thick 100 nm Al was used as a back reflective electrode in R mode, whereas a semi-transparent 15 nm Ag back electrode was used in T mode. During the EM measurement, an AC superimposed with a DC electrical field ($F = F_{AC} + F_{DC}$) applied on the device in reserve-biased condition. The electrical field for all the measurement was confined at a range of 10k–100 kV/cm. The measured data and fitting curve are represented in symbols and line, respectively. In addition, we confined the fitting to the first excitonic region of the measured EM data which is marked in red circle. The $Y$-axis in the EM spectra is
written as $\Delta R/R$ or $\Delta T/T$ for R mode or T mode, respectively. It is worth noting that the sign of the Y-axis has been confusing in the literature, and we have provided detailed analysis and discussion of this issue in Supplementary Figs. 1–4.

**Fitting with thin film absorbance.** In most reports, the absorption coefficient $\alpha$ that used to fit the measured EM spectrum in device were independently determined from the thin film optical absorbance\(^{51-53}\). However, due to optical interference effect, the absorption in thin film can be significantly different from the absorption of the active layer sandwiched in a multilayer structured device. In the case of neglecting both optical interference and multiple reflection, the light intensity after passing through the device in R mode and T mode can be expressed in Eqs. (3) and (4), respectively:

$$I_R = I_0 t_2 e^{-\alpha d},$$

(3)

$$I_T = I_0 t_2 e^{-\alpha d},$$

(4)

where $I_0$ is the incident light intensity, $t_2$ is the transmittance of metal cathode, $r_2$ is the reflectance of metal cathode, $\alpha$ is the active layer absorption coefficient, and $d$ is the thickness of the active layer. For small angle (<10°) reflection in R mode, the optical path can be approximated to two times of the active layer thickness, i.e. 2$d$, as shown in Eq. (3). While for T mode, the optical path is simply equal to $d$, as shown in Eq. (4). Hence, as demonstrated in Eqs. (5) and (6), $\Delta \alpha$ can be determined by measuring the change of reflectance $\Delta R$ or transmittance $\Delta T$ for R mode or T mode, respectively.

$$\frac{\Delta R}{R} = \frac{I_R - I_0 t_2 e^{-\alpha d}}{I_0 t_2 e^{-\alpha d}} = -2 \Delta \alpha d,$$

(5)

$$\frac{\Delta T}{T} = \frac{I_T - I_0 t_2 e^{-\alpha d}}{I_0 t_2 e^{-\alpha d}} = -\Delta \alpha d.$$  

(6)

A simple approach to determine the absorption coefficient is dividing the measured thin film absorbance $A$ by the film thickness $d$\(^{34}\). As described in Eqs. (7) and (8):

$$A = \log_10 \left( \frac{I_0}{I_{0e^{-\alpha d}}} \right) = \log_10(e^{\alpha d}) = \alpha d \cdot \log_{10} e \approx 0.434 d \alpha.$$  

(7)

$$\alpha \approx \frac{A}{0.434 d}.$$  

(8)

where $I$ is the light intensity after passing through the thin film measured by UV–vis spectroscopy. By combing the Stark effect in Eq. (2) and the change of absorption coefficient $\Delta \alpha$ approximated in the form of Taylor series truncated at the quadratic term, the overall equation can be expressed as

$$\Delta \alpha \approx \frac{1}{2} \frac{\Delta P}{E} \left( -\frac{\alpha d}{2} \right) + \frac{1}{6} \left( \frac{\Delta \mu}{F} \right)^2 \frac{\Delta \alpha}{E^2}.$$  

(9)

Details of the derivation of Eq. (9) is described in Supplementary Note 2. By combining Eqs. (5), (6) and (9), the measured EM data in R mode and T mode can be formulated with $\alpha$ determined by the thin film absorbance\(^{35}\), i.e.

$$\frac{\Delta R}{R} = -\alpha \cdot 2 d \approx -\frac{1}{0.434 d} \frac{\Delta \mu}{F} \frac{\Delta A}{E} = \frac{1}{1.29 d} \frac{1}{0.58 d} \left( \frac{\Delta \mu}{F} \right)^2 \frac{\Delta \alpha}{E^2},$$  

(10)

$$\frac{\Delta T}{T} = -\alpha \cdot d \approx -\frac{1}{0.86} \frac{\Delta P}{E} \frac{\Delta A}{E} = \frac{1}{2.58 d} \frac{1}{2.58 d} \left( \frac{\Delta \mu}{F} \right)^2 \frac{\Delta \alpha}{E^2}.$$  

(11)

with only $\Delta P$ and $\Delta \mu$ as the fitting parameters for both R mode and T mode.

In order to investigate the validity of this approach, we conducted both R mode and T mode measurement on PCDTBT with different thicknesses. We hypothesized that the approach could be justified by whether the fitting values of $\Delta P$ and $\Delta \mu$ were thickness independent and consistent between R mode and T mode. Figure 2 shows the measured and fitted EM results in R mode and T mode, whereas the thin film absorbance along with the calculated absorption coefficient and the corresponding 1st and 2nd derivatives are shown in Supplementary Fig. 5.

In the case of R mode, it can be clearly seen that, firstly, the measured EM spectral line shape is very sensitive to the film thickness indicating a strong influence of optical effect. Secondly, fitting with thin film absorbance generally results in poor fitting quality, the statistic coefficient of determination $R^2$ in fitting is ~0.88 when $d = 42$ nm as shown in Fig. 2a. Both $\Delta \mu$ and $\Delta P$ obtained in the 1st excitonic peak in different thicknesses span a wide range from 0D to 2D and 1.31 × 10⁻²² cm³ to 4.9 × 10⁻²³ cm³, respectively. Particularly, the EM spectra at higher energy >2.0 eV cannot be reproduced by the fitting. As in Fig. 2c, in the interval of 2.1–2.4 eV, the measured EM signal stays positive while both the 1st and 2nd derivatives of thin film absorbance are negative (Supplementary Fig. 5b). Therefore, it is impossible that the EM spectrum in this interval can be fitted with the combination of the 1st and 2nd derivatives.

In the case of T mode, the EM spectral line shape is less sensitive to the organic film thickness with smaller influence of optical interference effect. However, fitting with thin film absorbance in T mode also results in low fitting quality with $R^2$ value ~0.85. $\Delta \mu$ also spans a range from 0D to 2D, whereas $\Delta P$ spans a range from 3.64 × 10⁻²² cm³ to 9.50 × 10⁻²³ cm³. It is worth noting that there is no impact from the difference in electrical field strength on the observed variation of the EM spectral line shape. The fitting values of $\Delta \mu$ and $\Delta P$ are independent of the electric field strength.
In this case, Eq. (13) can be used for both R mode and T mode of a particular wavelength incident on the organic layer. In the case of R mode, large different thicknesses are shown in Supplementary Fig. 7 for R mode absorbance. The device absorbance and its derivatives spectra for being involved multiple reflections from multiple reflections. Moreover, various spectral features measured in R mode at higher energy >2.0 eV can be generally reproduced. It proves that R mode EM is indeed strongly influenced by the optical interference effect. Whereas such spectral variation is less in T mode where the contribution from multiple reflections is small.

As demonstrated above in both R and T modes, fitting the EM spectrum with thin film absorbance derivatives can neither guarantee good fitting quality nor consistent fitting value for different thicknesses. It is possibly due to the ignored optical interference effect in such multilayered devices.

**Fitting with device absorbance.** Bearing in mind that the optical absorption of the organic layer in a sandwiched device can be significantly different from that in thin film due to optical interference. Such effect in device can be incorporated by considering the device absorption, i.e.

$$ A_D = \log \frac{T_0}{T} = \log_{10} \left( \frac{T_0}{T_0 e^{-\alpha l}} \right) = \log_{10}(e^{\alpha l}) = \alpha l \log_{10} e \approx 0.43 \alpha l, $$

(12)

$$ \frac{\Delta T}{T} = -\Delta \alpha \cdot l \approx -\frac{1}{2} \frac{\Delta p E^2}{\partial E} \frac{\partial A_D}{\partial E} \cdot \frac{1}{0.43} - \frac{1}{6} \left( \frac{\Delta u \cdot F}{\partial E^2} \right) \frac{\partial^2 A_D}{\partial E^2} \cdot \frac{1}{0.43}, $$

(13)

where $A_D$ is the device absorbance, $T_0$ is the incident light intensity, and $T$ is the light intensity after passing through the device by reflection or transmission. $\frac{\partial A_D}{\partial E}$ is the 1st derivative of the device absorbance and $\frac{\partial^2 A_D}{\partial E^2}$ refers to the 2nd derivative. $\alpha$ is the active layer absorption coefficient. $l$ is the optical path of a particular wavelength incident on the organic layer. In this case, Eq. (13) can be used for both R mode and T mode fitting. Such approach has already considered the optical effect since the measured reflected or transmitted light intensity or transmitted light intensity $T$ involved multiple reflections.

Figure 3a–e shows the R mode and (f)–(j) T mode EM spectra being fitted with the 1st and 2nd derivatives of the device absorbance. The device absorbance and its derivatives spectra for different thicknesses are shown in Supplementary Fig. 7 for R mode and Supplementary Fig. 8 for T mode. In the case of R mode, large $r^2$ values around 0.90–0.98 can be obtained; for T mode, the $r^2$ values are all greater than 0.98. In general, good fitting quality at the 1st excitonic peak can be obtained in both R and T modes.

![Fig. 2 Thin film absorbance fitting.](image)

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distribution of the 1st excitonic peak is more intense at the front electrode ITO/PCDTBT for 25 nm PCDTBT and more intense at the back electrode PCDTBT/Ag for 110 nm PCDTBT. This unambiguously suggests that the thickness dependent fitting values obtained in R mode are neither caused by the interface dipole as previously proposed\textsuperscript{58,61}, nor the optical interference effect that has already been taken into account in device absorbance. It hints that there should be other mechanism that has not been considered in the EM model.

A generalized EM model. We sought to investigate the observed thickness dependent fitting results by considering the approach used to handle the device absorbance derivative. The light intensity \( I \) after passing through a multilayer structured device measured by a photodetector can be expressed as a function of the thickness \( (d_i) \), refractive index \( (n_i) \) and absorption coefficient \( (\alpha_i) \) of each layer, i.e. \( I(n_0, n_1, n_2, \ldots, \alpha_0, \alpha_1, \alpha_2, \ldots, d_0, d_1, d_2, \ldots) \). Thus, if the device absorbance is differentiated with respect to the excitation photon energy \( E \), the differentiations of all photon energy dependent elements, namely \( n \) and \( \alpha \) of each layer have to be considered. However, as both electrodes have much higher conductivity, most of the electrical field would only drop across the organic layer. Hence, a complete analytical model could simply consider the modulations of the refractive index \( n_1 \) and absorption coefficient \( \alpha_1 \) of the active layer under the electrical

Figure 3: Device absorbance fitting. a–e Reflectance mode electromodulation (EM) fitted with experimental device absorbance of five different thicknesses. The thickness refers to the thickness of active layer measured by profilometer. f–j Transmission mode EM fitted with experimental device absorbance of five different thicknesses. The thickness \( d \) of the active layer was measured by profilometer.

Figure 4: \( \Delta p \) and \( \Delta u \) values obtained by device absorbance fit vs. active layer thickness. The error bar in the x-axis represents the statistical standard deviation ±5 nm of the thickness determined by the profilometer. The error bar in the y-axis represents the statistical standard deviation of the possible fitting values. a Comparison of \( \Delta p \) extracted from device absorbance fit vs. thickness between reflection mode and transmission mode. b Comparison of \( \Delta u \) extracted from device absorbance fit vs. thickness between reflection mode and transmission mode.
field perturbation. Such correlation between \( n \) and \( \alpha \) can be found in Kramers–Kronig relation as shown below:\(^{62,63} \)

\[
n(E) = 1 + \frac{2\hbar}{e^2} P \int_0^\infty \frac{\alpha(E')}{E'^2 - E^2} dE'.
\]

where \( \hbar \) is Plank’s constant, \( c \) is the speed of light, \( e \) is the electron charge, \( E \) is the photon energy, and \( P \) indicates the principal value of the integral.

Equation (14) implies that the modulation of \( \Delta n \) will result in modulation of \( n \) simultaneously as

\[
\Delta n = \frac{2\hbar}{e^2} P \int_0^\infty \frac{\alpha(E')}{E'^2 - E^2} dE'.
\]

Since only \( n_1 \) and \( \alpha_1 \) are being modulated under the electrical field, the light intensity detected by the photodetector becomes \( I(n_0, n_1 + \Delta n_1, n_2, \ldots, \alpha_0, \alpha_1 + \Delta \alpha_1, \alpha_2, \ldots) \) and the Fourier component at a modulation frequency picked up by the lock-in amplifier is then

\[
\Delta I = I(n_0, n_1 + \Delta n_1, n_2, \ldots, \alpha_0, \alpha_1 + \Delta \alpha_1, \alpha_2, \ldots) - I(n_0, n_1, n_2, \ldots, \alpha_0, \alpha_1, \alpha_2, \ldots).
\]

It can be approximated by the two-variable Taylor expansion\(^{64} \) to the 1st order of \( n_1 \) and \( \alpha_1 \), i.e.

\[
\Delta I \approx \frac{\partial \Delta I}{\partial n_1} \Delta n_1 + \frac{\partial \Delta I}{\partial \alpha_1} \Delta \alpha_1.
\]

Using the Taylor series truncated at the quadratic term:

\[
\frac{\partial \Delta I}{\partial n_1} \approx \frac{\partial I}{\partial n_1} \left( \frac{\partial n_1}{\partial E} \Delta E + \frac{\partial \alpha_1}{\partial E} \Delta \alpha_1 \right), \quad \frac{\partial \Delta I}{\partial \alpha_1} \approx \frac{\partial I}{\partial \alpha_1} \left( \frac{\partial \alpha_1}{\partial E} \Delta E + \frac{\partial \alpha_1}{\partial \alpha_1} \Delta \alpha_1 \right)
\]

\[
\approx \frac{\partial I}{\partial n_1} \left( \frac{\partial n_1}{\partial E} \Delta \alpha_1 \cdot F^2 + \frac{1}{2} \frac{\partial \alpha_1}{\partial E} \Delta \alpha_1^2 \cdot F^2 \right), \quad \frac{\partial \Delta I}{\partial \alpha_1} \approx \frac{\partial I}{\partial \alpha_1} \left( \frac{\partial \alpha_1}{\partial E} \Delta \alpha_1 \cdot F^2 + \frac{1}{2} \frac{\partial \alpha_1}{\partial \alpha_1} \Delta \alpha_1^2 \cdot F^2 \right)
\]

\[
= \frac{\partial I}{\partial n_1} \left( \frac{\partial n_1}{\partial \alpha_1} \Delta \alpha_1 \cdot F^2 + \frac{1}{2} \frac{\partial \alpha_1}{\partial \alpha_1} \Delta \alpha_1^2 \cdot F^2 \right).
\]

In Eq. (19), since \( \alpha = \frac{\Delta \alpha_1}{\Delta k_1} \), we substitute \( \alpha \) with \( k \) so that all optical constants and the derivatives in the above equations are dimensionless which is convenient for further analysis. Dividing Eq. (19) by \( I \), a complete EM expression incorporating both absorption and refraction modulations can be written as

\[
\frac{\Delta I}{I} \approx \frac{\partial I}{\partial \alpha_1} \left( \frac{\partial k_1}{\partial E} \Delta \rho \cdot F^2 + \frac{1}{2} \frac{\partial \alpha_1}{\partial \alpha_1} \Delta \alpha_1^2 \cdot F^2 \right).
\]

The physical picture of Eq. (20) can be elaborated as (i) EM signal is a superposition of EA and ER signal which, respectively, refers to the first term and the second term; (ii) the optical effect is incorporated in \( \partial I/\partial \Delta k_1 \) and \( \partial I/\partial \Delta \alpha_1 \) which is determined by the device architecture. These two terms are constant if optical interference is ignored (See Supplementary Note 3). (iii) The terms inside the parentheses represent the contribution to the EA and ER signal by solely the intrinsic properties of active layer material, i.e. \( n_1 \) and \( \alpha_1 \), respectively. If only modulation of active layer \( \Delta k_1 \) is considered, in the case of negligible ER effect, Eq. (20) can be simplified to

\[
\frac{\Delta I}{I} \approx \frac{\partial I}{\partial \alpha_1} \left( \frac{\partial k_1}{\partial E} \Delta \rho \cdot F^2 + \frac{1}{2} \frac{\partial \alpha_1}{\partial \alpha_1} \Delta \alpha_1^2 \cdot F^2 \right).
\]
independent from different models. It suggests that the ER contribution is negligible in T mode. Previously, it has been mentioned that $\Delta n$ can be neglected for conducting polymer films\textsuperscript{41,65}, our study reveals that this may only be true for measurement conducted in T mode but not in R mode.

The improved consistency between the calculated and measured EM spectra considering both $\Delta k_1$ and $\Delta n_1$, using Eq. (20) can also be seen in Fig. 8. The $r^2$ values for both R and T modes are exceeding 0.97. Especially, in R mode, the spectral line shape at higher energy can be better reproduced with the analytical model compared with that using the device absorbance method. Although there is some mismatching in signal amplitude between the calculated and measured results in higher energy region (>2.7 eV), this work is mainly focusing on the 1st excitonic peak fitting, and the higher energy EM fitting will be discussed in future work. Briefly, the calculated EM signal at higher energy is smaller than the measured signal in both R and T mode. It suggests that the higher energy excited state should exhibit larger $\Delta p$ or $\Delta u$ which is in fact physically meaningful. Nevertheless, the overall fitting curve follows the trend well with the measured EM spectrum. Therefore, it is questionable in previous reports that the discrepancy between the measured and the calculated EA spectra at higher energy is ascribed to the forbidden transition from ground state to the continuum state\textsuperscript{41,66,67}. As demonstrated above, such discrepancy can be mostly resolved by incorporating the optical interference effect and ER modulation. Further analysis

**Fig. 6** Electromodulation spectra and optical field distribution. **a–c** Reflection (R) mode. **d–f** Transmission (T) mode. The optical field was calculated within the active layer. The scale bar on the right reflects the optical field intensity which is in the same scale for all cases. The thickness here refers to thickness of the active layer used in the optical simulation. Note: The 0 nm corresponds to the position at the ITO/active layer interface and the maximum thickness value in each graph refers to the position at the active layer/metal interface.
on the contribution from ER on the overall EM spectra is also demonstrated in the Supplementary Note 4, and we have found that the strong ER effect in R mode is originated from the modulated reflection at the active layer/electrode interface, which is schematically shown in Supplementary Fig. 12 and analyzed by simulation shown in Supplementary Fig. 13a. While for T mode, ER is small and such effect is decreasing with increasing the active layer thickness which is demonstrated in Supplementary Fig. 13b.

The viability of the proposed generalized model is further supported by the excellent fitting agreement and thickness independent results on other three archetypical materials (PTB7, PCE10, and PDTSTPD) as shown in Supplementary Fig. 14.

As discussed above, EM is a powerful technique which can be able to probe the excitonic characteristics in semiconducting...
materials. Consequently, an accurate determination of $\Delta p$ and $\Delta u$ is crucial to understand the degree of CT process in organic semiconducting materials\textsuperscript{68}, and bring insight into the correlation with material design. We have demonstrated that both the $\Delta p$ and $\Delta u$ extracted by the EM analysis are very sensitive to the optical effect inherent in sandwiched device architecture. Previous approaches using the thin film or device absorbance to analyze the EM results are not reliable which can lead to large variation of the extracted values. Particularly, even in a typical thickness of 50–100 nm of the organic film, the extracted $\Delta u$ can have two folds difference in extracted value. In this work, we have provided a detailed discussion on different measurement approaches and theoretical derivation to incorporate the perturbation theory and optical effect in EM analysis. We have demonstrated that a generalized model considering both optical interference and ER effects can achieve a high consistency of the extracted parameters in both reflection and transmission modes irrespective to the active layer thickness. Although there is added complexity in the analysis, given that such highly sensitive thickness dependence of the extracted parameters, it is still necessary to consider both EA and ER effect to ensure a reliable result.

Discussion
To conclude, the long-lasting issue of extracting the excitonic properties in organic thin films by EM has been systematically resolved by detailed experimental and theoretical approaches. Importantly, we have found that previously reported discrepancy between the measured and the calculated EM spectrum cannot be directly correlated with the different excitonic features from the spectral characteristics. We have shown that such discrepancy is associated with the strong optical interference and ER effects. A generalized model incorporating those effects shows excellent consistency in the extracted polarizability and dipole moment changes in both reflection and transmission modes. This work not only provides a more accurate access of the excitonic features in materials using EM technique, but also a deeper insight into the excitonic processes in organic electronic devices.

Methods

Fabrication of devices. PCDTBT was dissolved in chlorobenzene solution and stirred overnight at 70°C and then spin casted on commercially patterned ITO substrate. The ITO substrates were cleaned sequentially in a standard regimen of Decon®, acetone, alcohol and methanol in ultrasonic bath and dried with high purity nitrogen gun followed by ultraviolet (UV) ozone treatment for 15 min. The mg/mL) in solution and spin-speed (1000

EM spectroscopy. Home-made EM spectroscopy was used to measure EM signal. A monochromatic beam probed the sample through the ITO side with an incident angle of ~7° respect to the normal direction of sample surface for R mode EM spectrum and 0° for T mode EM. For T mode EM, the samples were encapsulated in nitrogen glovebox; For T mode EM, the samples were kept inside a vacuum cryostat without light source. The transmittance provided an additional data set that was simultaneously with the sets of $\Psi$ and $\Delta$ spectra using the CompleteEASE ellipsometry modeling software. For PCDTBT, especially, 10 samples of different thicknesses were simultaneously fitted in order to achieve accurate $n$ and $k$ values.

Optical absorbance. Absorbance was measured using Perkin-Elmer Lambda UV-Vis spectrometer and the corresponding organic film thickness was measured by Bruker OM-Dektak profilometer.

Data availability
All data that support the findings in this study are present in the paper and the Supplementary Information. Additional data related to this study are available from the corresponding author upon reasonable request.

Received: 15 May 2019; Accepted: 15 October 2019;
Published online: 08 November 2019

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Received: 15 May 2019; Accepted: 15 October 2019;
Published online: 08 November 2019

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