Supplementary Information

The complexity of Classical Marcus analysis for charge transfer state in organic photovoltaics

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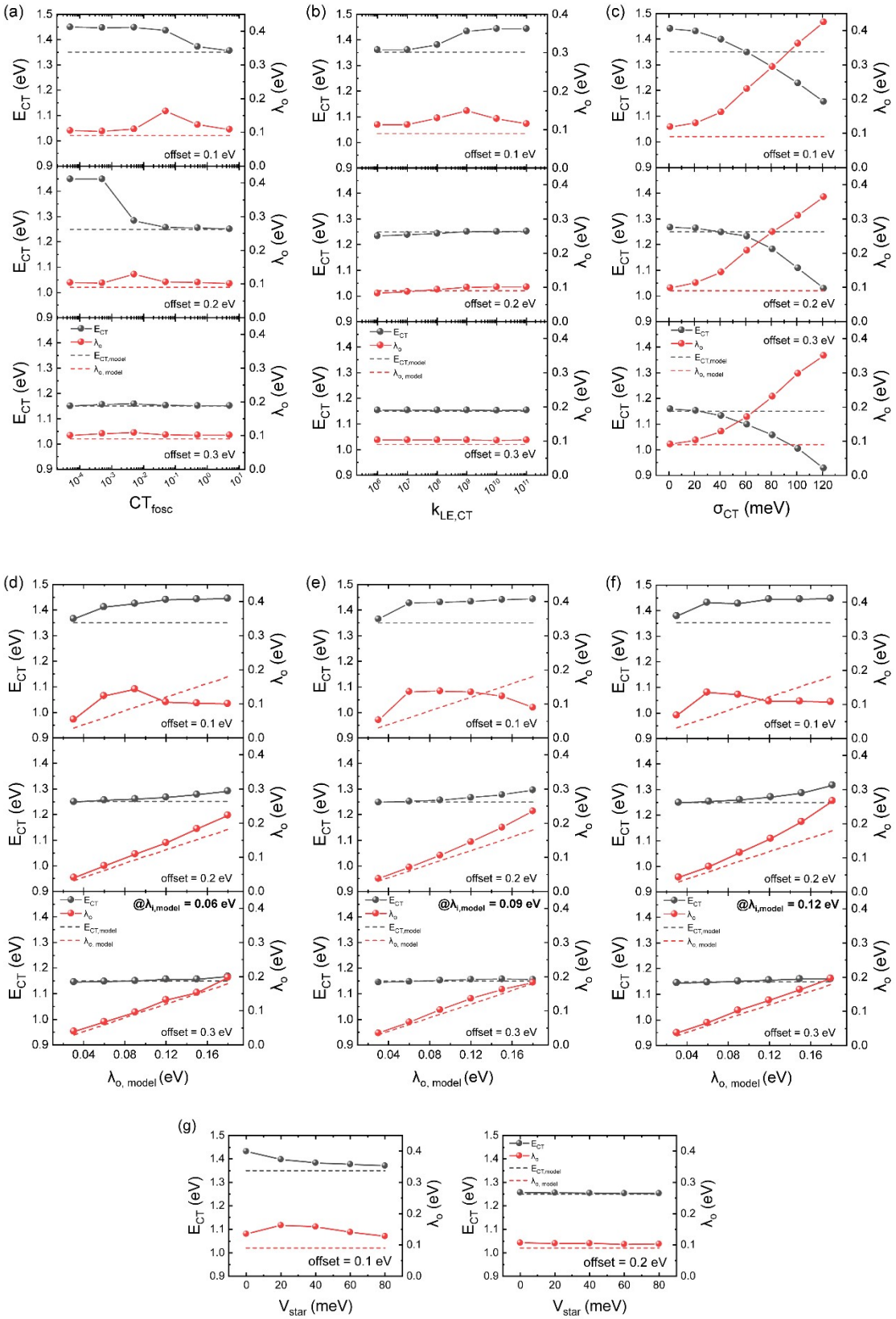

Fig. S1. Summary of comparing the physical parameters of the original model with Marcus theory fit results with different offset ($\Delta E_{LE,CT} = 0.1, 0.2, 0.3$ eV). The subplots depict the following control variables: (a)CT oscillator strength ($f_{osc,CT}$); (b) Rate constant of LE to CT

states ($k_{LE,CT}$); (c) CT sigma (σ_{CT}); (d-f) CT low frequency reorganization energy (λ_o) with CT high frequency reorganization energy (λ_i) as 60, 90, 120 meV; (g) Coupling between the LE and CT states (V_{star}). The dotted line represents the parameters set in the original model, and the solid line represents the result obtained by Marcus theory fitting. $\lambda_{o,model}$ corresponds to the low frequency reorganization energy of the CT state in the original model, and $E_{CT,model}$ corresponds to the free energy of the CT state. The parameter settings are the same as in **Supplementary Note 1**, but different offsets have been taken into account.

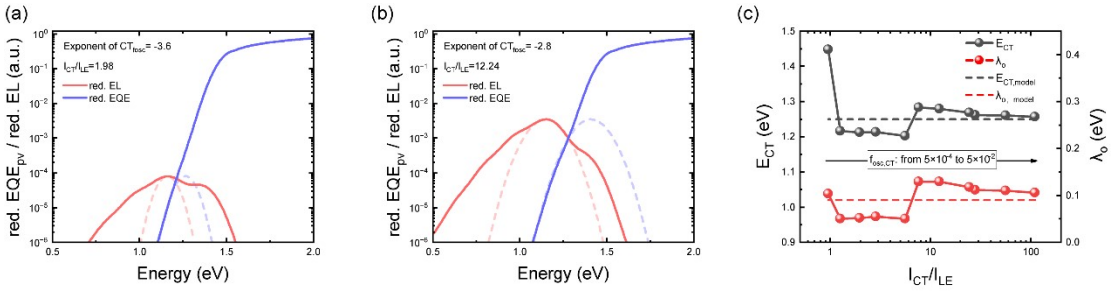

Fig. S2 Summary of the results for different CT oscillator strength ($f_{osc.CT}$) with $\Delta E_{LE,CT}$ = 0.2 eV via fitting EL and EQE spectra using the Classical Marcus theory. $f_{osc.CT}$ was systematically varied from 5×10^{-4} to 5×10^{-2} (11 data points, exponent step size = 0.2). (a-b) Fits obtained with $f_{osc.CT}$ exponents of -3.6 (approximately 2.5×10^{-4}) and -2.8 (approximately 1.6×10^{-3}), respectively. These conditions yield intensity ratio of CT to LE (I_{CT}/I_{LE}) of 1.98 and 12.24 for panels (a) and (b), respectively. (c) Comparison between the physical parameters of the original model and the Classical Marcus fit results across varying I_{CT}/I_{LE}. The previously developed model was used to generate EL and EQE data, with input parameters as shown in **Supplementary Note 1**. The dotted line represents the parameters set in the original model, and the solid line represents the result obtained by the Classical Marcus fitting. $\lambda_{o,model}$ corresponds to the low frequency reorganization energy of the CT state, and $E_{CT,model}$ corresponds to the free energy of the CT state in the original model.

Supplementary Notes

Supplementary Note 1: Generation of electroluminescence and external quantum efficiency data

We used the previously developed model mentioned in the main text as a tool for generating EL and EQE data. We set eight different combinations of physical parameters for qualitative analysis, with the values shown in **Supplementary Table 1** when other model parameters are fixed. The specific values of these fixed values are shown in **Supplementary Table 2**.

Supplementary Table 1. Different input physical model parameters for generating EL and EQE data

Set	Variable Parameter	Range	Unit
A	Offset between the LE and CT states ($\Delta E_{LE,CT}$)	[0, 0.1, 0.2, 0.3, 0.4, 0.5]	eV
B	CT oscillator strength ($f_{osc,CT}$)	[5e-5, 5e-4, 5e-3, 5e-2, 5e-1, 5e0]	/
C	Rate constant of LE to CT states ($k_{LE,CT}$)	[1e6, 1e7, 1e8, 1e9, 1e10, 1e11]	cm^3s^{-1}
D	CT sigma (σ_{CT})	[1, 21, 41, 61, 81, 101, 121]	meV
E	CT low frequency reorganization energy (λ_o)	[30, 60, 90, 120, 150, 180]	meV
F	Coupling between the LE and CT states (V_{star})	[0, 20, 40, 60, 80, 100, 120]	meV

***Note**: For all set, LE state energy is fixed at 1.45 eV, and CT state energy is derived from 1.45 minus $\Delta E_{LE,CT}$. For set E, we consider the low frequency reorganization energy (λ_o) under three conditions: CT high frequency reorganization energy (λ_i) are 60, 90 and 120 meV, respectively.*

Supplementary Table 2. Fixed Model Parameters

Parameter	Global Value	Unit
LE state energy	1.45	eV
LE oscillator strength	5	/
LE sigma	21	meV
LE low frequency reorganization energy	0.09	eV
LE high frequency reorganization energy	0.09	eV
LE vibronic mode energy	0.155	eV
LE number of states	20	/
CT state energy	1.25	eV
CT oscillator strength ($f_{osc,CT}$)	5e-2	/

CT sigma (σ_{CT})	21	meV
CT low frequency reorganization energy (λ_o)	0.09	eV
CT high frequency reorganization energy (λ_i)	0.09	eV
CT vibronic mode energy	0.155	eV
CT number of states	20	/
Offset between the LE and CT states ($\Delta E_{LE,CT}$)	0.2	eV
Ratio LE to CT states	1	/
Coupling between the LE and CT states (V_{star})	0	meV
Rate constant of LE to CT states ($k_{LE,CT}$)	1e9	s^{-1}
Temperature	300	K

***Note**: To control variables, when one of the set condition parameters in **Supplementary Table 1** varies within its range, the global values of the other parameters in the model are as shown in **Supplementary Table 2**.*

Supplementary Note 2: *Marcusfit*

The *Marcusfit* program quantitatively analyzes the EL and EQE spectra of organic optoelectronic devices based on the Marcus electron transfer theory. The program implements the Marcus theoretical framework and extracts key physical parameters of the charge transfer state through joint analysis of the EL and EQE spectra. The core of this approach is to exploit the different physical processes reflected by these two spectra: the EL spectrum describes the radiative recombination of the CT state, while the EQE spectrum reflects the photoexcited dissociation of the CT state.

Marcusfit provides a semi-automated fitting process through an intuitive graphical interface. The workflow begins by loading a CSV file with data columns for Energy (eV), EL (a.u.), Energy (eV), and EQE (a.u.). Users can fine-tune the fit by adjusting the offset, using the scroll wheel, or modifying key parameters such as f, E_{CT}, and λ. Results and plots can then be exported. The process is highly efficient, typically taking about 10 seconds to complete after minimal familiarization.

Theoretical formula

The theoretical model implemented in the program is based on Marcus theory expression at a temperature of 300 K. For the electroluminescence process, the normalized intensity function is defined as:

$$r_{EL}(E) = \frac{f}{\sqrt{4\pi\lambda k_B T}} exp\left(-\frac{\left(E_{CT} - \lambda - E\right)^2}{4\lambda k_B T}\right)$$

he external quantum efficiency process:

$$r_{EQE}(E) = \frac{f}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\left(E_{CT} + \lambda - E\right)^2}{4\lambda k_B T}\right)$$

Where E_{CT} is the charge transfer state energy, λ is the low frequency reorganization energy, f is the pre-factor, k_B is the Boltzmann constant, T is the temperature, which is 300 K here.

The code ensures the stability of the numerical calculation by setting $\lambda_{safe} = \max\left(\lambda, 1 \times 10^{-10}\right)$ to avoid division by zero errors. The key difference between these two expressions lies in the energy shift in the exponential term: $\left(E_{CT} - \lambda - E\right)^2$ in the EL process, while it is $\left(E_{CT} + \lambda - E\right)^2$ in the EQE process, reflecting the difference in the energy relationship between the excited state and the ground state.

Data processing

The program first normalizes the raw experimental data. For each set of data, the normalization process is defined as:

$$I_{norm}(E) = \frac{I_{raw}(E)}{\max\left(I_{raw}(E)\right)}$$

Where $I_{raw}(E)$ is the raw spectral intensity, and $I_{norm}(E)$ is the normalized intensity.

The program uses the *scipy.interpolate.interp1d* function to unify the different energy grids onto a standard grid. Values outside the bounds are set to zero to avoid extrapolation errors.

For EL data, the program also introduces a vertical offset adjustment mechanism:

$$I_{EL,adjusted}(E) = I_{EL,norm}(E) \times 10^{\Delta E_{LE,CT}}$$

where $\Delta E_{LE,CT}$ is a user-adjustable offset parameter ranging from -5.0 to 0.0, used to compensate for systematic intensity differences that may exist in the experiment.

Intersection recognition algorithm

The program uses numerical methods to automatically identify the intersection of the EL and EQE curves. Define the difference function:

$$\Delta(E) = I_{EL,norm}(E) - I_{EQE,norm}(E)$$

The intersection point corresponds to the position where $\Delta(E)$ = 0. The program identifies the intersection point by detecting the change in the sign of $\Delta(E)$:

$$cross_{indices} = i \mid sign\left(\Delta(E_i)\right) \neq sign\left(\Delta(E_{(i+1)})\right)$$

When there are multiple intersection points, the program selects the rightmost (high energy end) intersection point as the estimated value of E_{CT}. For the precise intersection point position, the program uses the linear interpolation method:

Assume that there is an intersection point in the interval $[E_i, E_{i+1}]$, then the energy position of the intersection point is calculated by the following formula:

$$t = \frac{I_{EQE}(E_i) - I_{EL}(E_i)}{\left[I_{EL}(E_{i+1}) - I_{EL}(E_i)\right] - \left[I_{EQE}(E_{i+1}) - I_{EQE}(E_i)\right]}$$

$$E_{intersection} = E_i + t(E_{i+1} - E_i)$$

$$I_{intersection} = I_{EL}(E_i) + t\left[I_{EL}(E_{i+1}) - I_{EL}(E_i)\right]$$

When a clear intersection point cannot be found, the program selects the position with the smallest $|\Delta(E)|$ as the approximate intersection point.

Initial parameter estimation

The charge transfer state energy is taken directly from the intersection position:

$$E_{CT,initial} = E_{intersection}$$

The reorganization energy is estimated by the relationship between the EL peak position and the intersection position. The program first finds the peak position of the EL spectrum:

$$E_{EL,peak} = \arg\max_E I_{EL,norm}(E)$$

According to Marcus theory, the relationship between the EL peak position and the CT state energy is:

$$E_{EL,peak} = E_{CT} - \lambda$$

Therefore, the initial value of the reorganization energy is:

$$\lambda_{initial} = E_{CT,initial} - E_{EL,peak}$$

Where $0.05\ \text{eV} \le \lambda \le 0.5\ \text{eV}$.

The prefactor is determined by requiring the theoretical EL curve to match the experimental value at the intersection point:

$$f_{initial} = \frac{I_{intersection}}{r_{EL}(E_{intersection}, 1.0, E_{CT,initial}, \lambda_{initial})}$$

Fine-tuning the algorithm

Define the objective function:

$$F(E_{CT}) = \left|r_{EL}(E_{intersection}, 1.0, E_{CT}, \lambda) - r_{EQE}(E_{intersection}, 1.0, E_{CT}, \lambda)\right|$$

his function characterizes the difference between the theoretical EL and EQE curves at the intersection point. The program performs a grid search with 100 equally spaced points in the range of $E_{CT,initial} \pm 0.2$ eV.

Choose the parameter value that minimize $F(E_{CT})$:

$$E_{CT,optimized} = \arg\min_{E_{CT,test}} F(E_{CT,test})$$

After adjustment, the pre-factor is recalculated as:

$$f_{final} = \frac{I_{intersection}}{r_{EL}(E_{intersection}, 1.0, E_{CT,optimized}, \lambda)}$$

Fitting result output

The program calculates and outputs the theoretical fitting curve at 300 energy points:

$$E_{range} = linspace(E_{min}, E_{max}, 300)$$

The corresponding theoretical strength is:

$$I_{EL,fit}(E) = r_{EL}(E, f_{final}, E_{CT,optimized}, \lambda)$$

$$I_{EQE,fit}(E) = r_{EQE}(E, f_{final}, E_{CT,optimized}, \lambda)$$

To ensure numerical stability, the program imposes lower bounds on the output results:

$$I_{fit}(E) = \max\left(I_{theoretical}(E), 1 \times 10^{-10}\right)$$

Numerical stability

In interpolation calculations, the program uses the *bounds_error=False* and *fill_value=0* settings to handle boundary conditions. In the parameter calculations, conditional judgment is used to avoid division by zero errors: when $\max(I_{raw}) = 0$, the normalized denominator is set to 1; when the theoretical function value is zero, the pre-factor is set to the default value of 1.0.