

Supporting Information

Kinetic Model for Photoluminescence Quenching by Selective Excitation of D/A Blends: Implications for Charge Separation in Fullerene and Non-Fullerene Organic Solar Cells

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1. Kinetic model for quenching efficiency calculation

Let us assume the excitation of the donor near the D/A interface for the formation of the singlet exciton $S_{1,D}$. This exciton can then form the CT state by an electron transfer to the acceptor. Following the processes detailed in the main text, the time variation of the singlet state concentration in the donor material, $[S_{1,D}]$, is given by:

$$\frac{d[S_{1,D}]}{dt} = I - k_{D,SR}[S_{1,D}] - k_{ET}[S_{1,D}] + k_{EB}[CT], \quad (1)$$

where, I is the rate of exciton generation in the donor at the D/A interface, $k_{D,SR}$ is the donor singlet exciton recombination rate (the inverse of singlet exciton recombination lifetime), $[CT]$ is the concentration of CT state, k_{ET} is the electron transfer rate from $S_{1,D}$ to CT and k_{EB} is the electron back rate from CT to $S_{1,D}$ (see the main text). I in Eq. (1) involves excitons that are locally produced by direct photon absorption or excitons are produced in the vicinities and are able to diffuse to the interface. Under the steady state approximation Eq. (1) gives:

$$I = k_{D,SR}[S_{1,D}] + k_{ET}[S_{1,D}] - k_{EB}[CT]. \quad (2)$$

On the other hand, the time-dependent concentration of CT state at the D/A heterojunction is related to $[S_{1,D}]$ by

$$\frac{d[CT]}{dt} = k_{ET}[S_{1,D}] - k_{EB}[CT] - k_{ER}[CT] - k_{ES}[CT], \quad (3)$$

where k_{ER} is the electron recombination rate from CT to the ground state and k_{ES} is the rate of CT dissociation by electron separation. Due to small oscillation strength generally associated to the CT state, here we are neglecting the contribution to $[CT]$ of states formed by direct light absorption. Again invoking the steady state approximation, Eq. (3) is:

$$k_{ET}[S_{1,D}] = k_{EB}[CT] + k_{ER}[CT] + k_{ES}[CT], \quad (4)$$

or

$$[CT] = \frac{k_{ET}[S_{1,D}]}{k_{EB} + k_{ER} + k_{ES}} \quad (5)$$

Inserting Eq. (5) in Eq. (2) we find

$$I = k_{D,SR}[S_{1,D}] + k_{ET}[S_{1,D}] - k_{EB} \frac{k_{ET}[S_{1,D}]}{k_{EB} + k_{ER} + k_{ES}}, \quad (6)$$

which can be rewritten as follows

$$\frac{I}{[S_{1,D}]} = k_{D,SR} + k_{ET} - \frac{k_{EB}k_{ET}}{k_{EB} + k_{ER} + k_{ES}} = \frac{(k_{D,SR} + k_{ET})(k_{EB} + k_{ER} + k_{ES}) - k_{EB}k_{ET}}{k_{EB} + k_{ER} + k_{ES}} \quad (7)$$

or

$$[S_{1,D}] = \frac{I(k_{EB} + k_{ER} + k_{ES})}{(k_{D,SR} + k_{ET})(k_{EB} + k_{ER} + k_{ES}) - k_{EB}k_{ET}}. \quad (8)$$

In the absence of the acceptor (hence considering only an isolated donor), the time variation of the singlet state concentration $[S_{1,D}']$ at same position of the concentration given by Eq. (8), would be given by:

$$\frac{d[S_{1,D}']}{dt} = I' - k_{D,SR}[S_{1,D}'], \quad (9)$$

where I' is the rate of exciton generation in the absence of the acceptor.

From Eq. (9) assuming steady state conditions,

$$I' = k_{D,SR}[S_{1,D}'] \quad (10)$$

or

$$[S_{1,D}'] = \frac{I'}{k_{D,SR}}. \quad (11)$$

We define the exciton quenching as

$$Q_D = 1 - \frac{[S_{1,D}]}{[S_{1,D}']}. \quad (12)$$

Note that if the acceptor is not efficient to dissociate the excitons, then $[S_{1,D}'] \sim [S_{1,D}]$ and $Q_D \sim 0$ from Eq. (12). On the other hand, if the acceptor is very efficient to dissociate the excitons then $[S_{1,D}] \sim 0$ and $Q_D \sim 1$ from (12). Using the definition (12) and considering $I' = I$, after a few manipulations of the equations above one gets

$$Q_D = 1 - \frac{k_{D,SR}(k_{ES} + k_{EB} + k_{ER})}{(k_{D,SR} + k_{ET})(k_{ES} + k_{EB} + k_{ER}) - k_{ET}k_{EB}}. \quad (13)$$

Using Eq. (13) it is to show that $Q_D \rightarrow 0$ if $k_{D,SR} \rightarrow \infty$ or that $Q_D \sim 1$ if $k_{ES} \sim k_{ET} \gg k_{EB}$.

We can repeat the same reasoning above by assuming now the excitation of the acceptor and the formation of the CT by a hole transfer to the donor. In this case the quenching is

$$Q_A = 1 - \frac{[S_{1,A}]}{[S_{1,A}']} = 1 - \frac{k_{A,SR}(k_{HS} + k_{HB} + k_{HR})}{(k_{A,SR} + k_{HT})(k_{HS} + k_{HB} + k_{HR}) - k_{HT}k_{HB}}, \quad (14)$$

where $k_{A,SR}$ is the recombination rate of singlet exciton in the acceptor.

2. Expression for the charge generation yield

Our photoluminescence measurements were performed with the blend deposited over quartz. In an OPV structure, this would correspond to a measurement under open circuit (OC) conditions. This means that the internal electric field is zero. Under OC condition, there is not a long range charge transport. Under this simplification, the exciton quenching is then necessarily equal to the charge generation yield at the donor/acceptor interface. The further development of this analysis considering the influence of an electric field will be the subject of a new work that is now under preparation. We even tested the soundness of our mathematical model by writing down the expression for the charge generation yield. Starting from Eq. (5) and Eq. (6) we have to

$$[CT] = \frac{I k_{ET}}{(k_{D,SR} + k_{ET})(k_{EB} + k_{ER} + k_{ES}) - k_{EB} k_{ET}}. \quad (15)$$

Assuming that the flow (current) of generated charges is $J = k_{ES} [CT]$

$$J = \frac{I k_{ET} k_{ES}}{(k_{D,SR} + k_{ET})(k_{EB} + k_{ER} + k_{ES}) - k_{EB} k_{ET}}. \quad (16)$$

Therefore, the electron generation yield is

$$EGY = \frac{J}{I} = \frac{k_{ET} k_{ES}}{(k_{D,SR} + k_{ET})(k_{EB} + k_{ER} + k_{ES}) - k_{EB} k_{ET}}. \quad (17)$$

We can repeat the same reasoning above by assuming now the excitation of the acceptor and the formation of the CT by a hole transfer to the donor. In this case the hole generation yield is

$$HGY = \frac{k_{HT} k_{HS}}{(k_{A,SR} + k_{HT})(k_{HB} + k_{HR} + k_{HS}) - k_{HB} k_{HT}}. \quad (18)$$

When calculating this expression using the numerical values of the rates it gives the same value of the exciton quenching efficiency, as expected.

3. Potential energy surfaces for reorganization energy

The inner reorganization energy consists of two sections (see Figure S2). For electron transfer is given by^{1,2}:

$$\lambda_e = \lambda_1(A) + \lambda_2(D) \quad (5)$$

$$\lambda_1(A) = E_-^0(A) - E_0(A) \quad (6)$$

$$\lambda_2(D) = E_0^+(D) - E_+(D) \quad (7)$$

where $E_-^0(A)$ and $E_0(A)$ are the energies of the neutral acceptor at the anion geometry and the optimal ground-state geometry, respectively, and $E_0^+(D)$ and $E_+(D)$ are the energies of the cation donor at the neutral geometry and optimal cation geometry. As an approximation, we will use the same λ_e obtained for the electron transfer process also for the back and recombination processes.

Based on Eqs. 5-7, the inner reorganization energy for hole transfer was structured as follows:

$$\lambda_h = \lambda_3(A) + \lambda_4(D) \quad (4)$$

$$\lambda_3(A) = E_0^-(A) - E_-(A) \quad (5)$$

$$\lambda_4(D) = E_+^0(D) - E_0(D) \quad (6)$$

where $E_0^-(A)$ and $E_-(A)$ are the energies of the anion acceptor at the optimal ground-state geometry and optimal anion geometry, respectively, and $E_+^0(D)$ and $E_0(D)$ are the energies of the neutral donor at the cation geometry and optimal neutral geometry. Again as an approximation, we will use the same λ_h for the hole transfer, back and recombination processes. All these calculations were done with the B3LYP³ functional and 6-31G(d,p) basis set,⁴ in accordance with previously works.⁵⁻⁷

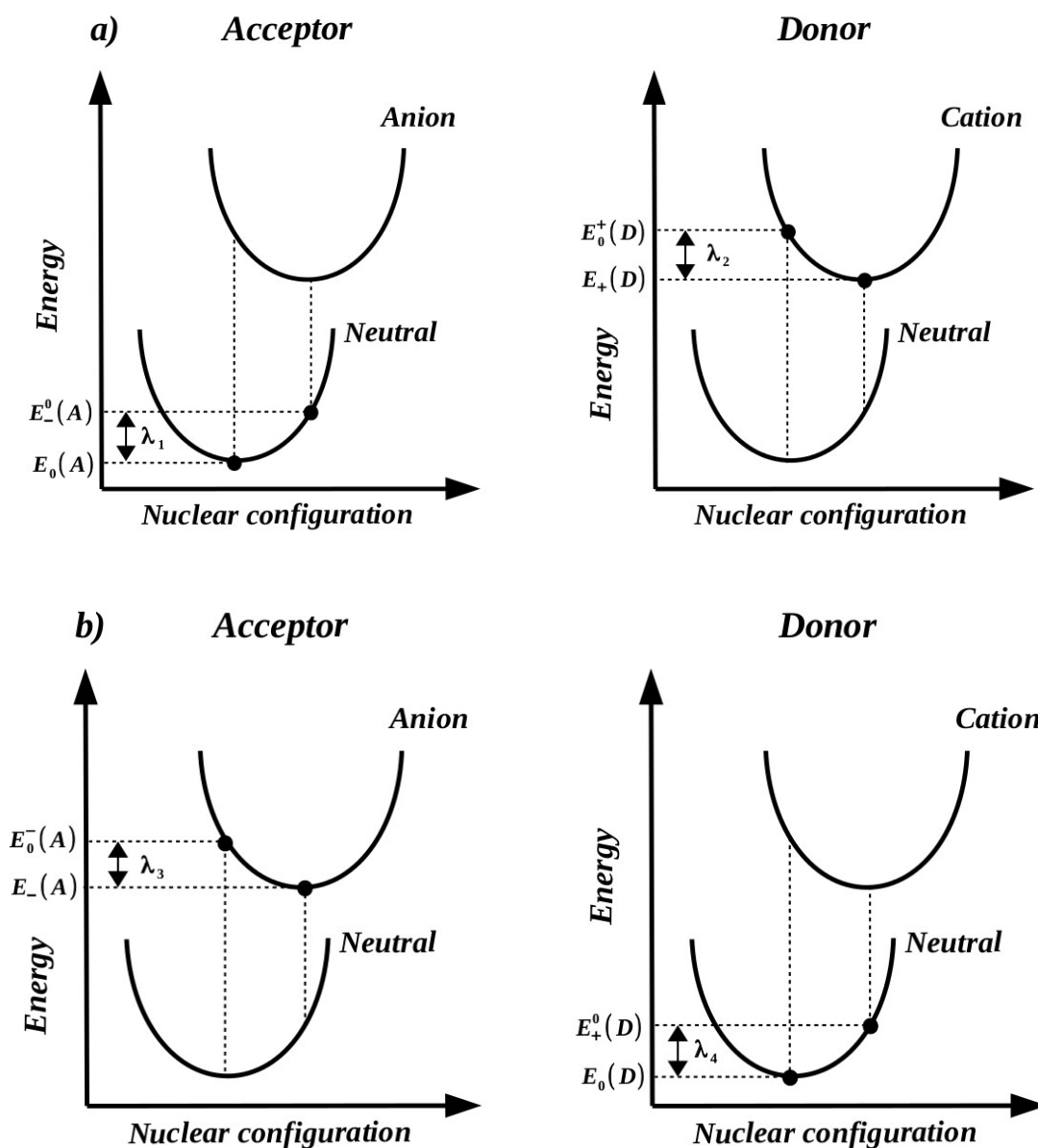


Figure S2 - Potential energy surfaces. (a) For electron transfer the inner reorganization energy consists of $\lambda_e = \lambda_1(A) + \lambda_2(D)$. (b) For hole transfer the inner reorganization energy consists of $\lambda_h = \lambda_3(A) + \lambda_4(D)$.

4. Absorption spectrum

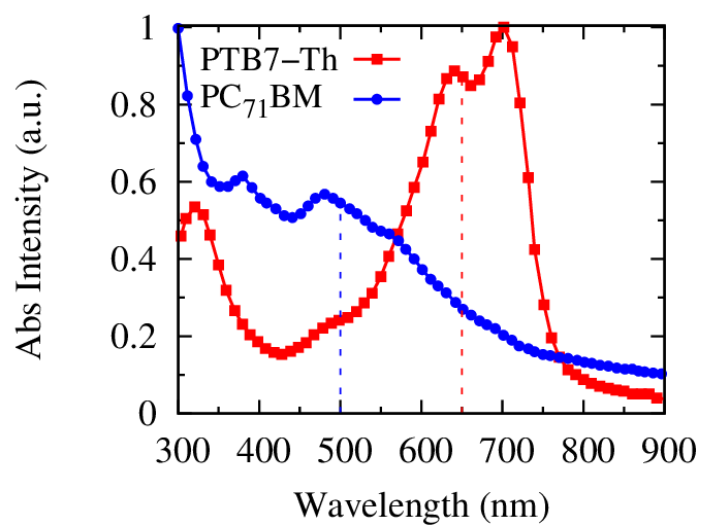


Figure S3 - Absorption spectrum of the films composed by pristine **PTB7-Th** and **PC₇₁BM**. The vertically dashed red and blue lines specify the excitation wavelengths for PL measurements.

5. References

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