# Supporting information for:

# Short and Long-Range Electron Transfer Compete to Determine Free-Charge Yield in Organic Semiconductors

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## 1: Steady-state absorption and emission characterization:

**Figure S1.1** Normalized (at 500 nm) absorption spectra of all sensitizers in 1  $\mu$ M chlorobenzene solution (except Pc3 which is in pyridine), at 0.005 mol kg<sup>-1</sup> in polystyrene, 0.005 mol kg<sup>-1</sup> in PCBM films, and a neat PCBM film. In all our TRMC/TA experiments excitation is placed red of the neat PCBM absorption. Excitation wavelengths for each are shown inset on the absorption.



**Figure S1.2.** Normalized absorption and photoluminescence spectra of each sensitizer at 5 mmolal in a spray coated polystyrene host film. Samples are all excited at the same wavelength of 380 nm, away from the emission spectra. The wavelength at the intersection of the absorption and emission is then used to assign the exciton energy for the purposes of the driving force calculation.

**Table S1.1.** Table of relevant optical properties for each sensitizer used in the study. Exciton energies are the same values used in the manuscript to calculate driving force.  $\lambda_{max}$  is given for each spectrum for each sensitizer and the value in the parentheses are the relative shifts to the solution absorption max wavelength. The red-shift of the absorption max is consistent and small enough to say that we have sensitized all PCBM films successfully as there are also no new qualitative features in the resulting PS or PCBM host with reference to the solution.

Sensi	tizer	E <sub>ex</sub> (eV)	$\lambda_{_{max}}$ sol. (nm)	$\lambda_{_{max}}$ PS (nm)	$\lambda_{_{max}}$ PCBM (nm)
Sq1	2,4-bis[4-(N,N-diphenylamino)-2,6-dihydroxyphenyl] cyclobutene-diylium-1,3-bis(olate)	1.64	680	684 (+4)	714 (+34)
Sq2	2,4-bis(1-butyl-6,8-dimesitylbenzo[cd]indol-2(1H)-ylidene) methyl)cyclobutene-diylium-1,3-bis(olate)	1.24	937	943 (+6)	982 (+45)
Nc1	silicon 2,3-naphthalocyanine bis(trihexylsilyloxide)	1.58	776	777 (+1)	790 (+14)
Pc2	silicon 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine triethylsiloxide hydroxide	1.62	758	754 (-4)	770 (+12)
Nc2	5,9,14,18,23,27,32,36-octabutoxy-2,3-naphthalocyanine	1.39	866	871 (+5)	889 (+33)
Pc1	1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine	1.59	765	770 (+5)	780 (+15)
Pc3	zinc 1,4,8,11,15,18,22,25-octabutoxy phthalocyanine	1.60	741	742 (+1)	753 (+11)

#### Evidence of Sensitization via Absorption Spectroscopy

We note that for Pcs and Ncs, which also have a Soret absorption band in the 400-500 nm range, we focus specifically on the Q-band since these transitions absorb red of PCBM and are the ones excited for our pump-probe experiments. Relative to the solution state, red-shifting and broadening of absorption spectra for  $\pi$ -conjugated chromophores in the solid-state is well-documented and has been rationalized based on differences in dielectric environment and inhomogeneous broadening due to a distribution of microenvironments in which individual molecules reside.<sup>1</sup> In this regard, we believe even these trends in our two hosts, polystyrene (amorphous, low  $\varepsilon$ ) and PCBM (crystalline, higher  $\varepsilon$ ), are sensible given the difference in crystallinity and dielectric constant between them.<sup>2,3</sup> Based on the minor spectral shifts (<50 nm), moderate broadening, and lack of new spectral features relative to solution/polystyrene, we believe our crystalline PCBM films were successfully sensitized. We argue these films contain negligible sensitizer aggregation/crystallization and thus are suitable "solid-state solutions" for our optical and microwave measurements.



**Figure S1.3.** Representative photoluminescence quenching spectra for this study. **a.** Pc2 as a sensitizer in both PCBM and PS. **b.** Sq1 as a sensitizer in PCBM and PS. All spectra are normalized by the absorptance of the film at the excitation wavelength of 730nm as denoted by the FA values inset on each figure.



# 2: Electrochemical characterization of each compound

**3: Figure S2.1.** Triplicate cyclic voltammetry scans for each sensitizer, PCBM, and the ferrocene (Fc) standard measured at varying scan rates of 100, 150, and 200 mV/s as denoted by the increasing shades of color (lighter is slowest scan rate, darkest is fastest). Each set of colors is for a different independent solution at the same 2 mM

analyte concentration. All  $E_{1/2}$  values are given in the main text in Table 1 with error estimates, but the scans are shown here.

### 3: Detailed discussion of driving force tuning and calculation

Here we aim to describe the strategy for controllably varying driving force in our sensitized PCBM films in greater detail than was possible in the main text. This begins by discussing in detail the design principles of our sensitized films and underlying assumptions. The equation we use to calculate the Gibbs energy of the electron transfer reaction is given below (1) as discussed in the main text.

$$\Delta G_{CT} = E_{ox,D} - E_{red,A} - E_{ex} \tag{1}$$

where  $E_{ox,D}$  and  $E_{red,A}$  are the  $E_{\frac{1}{2}}$  oxidation and reduction potentials (vs. Fc/Fc<sup>+</sup>) of the donor sensitizer and accepting PCBM host CV respectively, and  $E_{ex}$  is the exciton energy - all in units of eV.<sup>4</sup> As we describe in the following paragraphs, the critical components to this calculation and achieving a sufficient range of driving force are (1) the sensitizer has smaller optical gap  $(E_{ex})$  than PCBM in the solid-state, (2) accurate and precise measurements of  $E_{ox,D}$  and  $E_{red,A}$  for all compounds under the same conditions in solution via CV, and (3) judiciously selecting sensitizers based on  $E_{ox,D}$  and  $E_{ex}$  to pair with  $E_{red,A}$  of PCBM such that driving forces between -0.01 and -0.69 eV are obtained.

Regarding point 1, in the **Results** section of the manuscript and also above we described successful sensitization of our PCBM host by sensitizers with smaller optical gaps. This was done to ensure that the sensitizer is the component in the solid-state solution with the lowest  $E_{ex}$  and can be selectively excited (i.e. no absorption from PCBM host). Selective excitation is an important factor in avoiding competing effects with PET, such as singlet energy transfer, which is possible in cases where sensitizer PL overlaps appreciably with PCBM absorption. Since neat and sensitized PCBM films were both fabricated via spray coating, we were able to track the absorption of the  $S_0 \rightarrow S_1$  transitions for each sensitizer relative to the spectrum of neat PCBM films to confirm spectral separation.  $E_{ex}$  for each sensitizer was estimated by the

photon energy at which the absorption and PL spectra overlap, normalized at  $S_0 \rightarrow S_1$  and  $S_1 \rightarrow S_0$ , respectively, in 0.005 mol kg<sup>-1</sup> polystyrene films (see **SI Figures 1.1-2.**). The small shifts (<50 nm) in sensitizer absorption between polystyrene and PCBM shows that PL measurements from polystyrene films provide a satisfactory approximation to PL that would come from sensitizers in PCBM in the absence of quenching. One exception can be found by comparing PL for Sq1 in both hosts, which had little PL quenching due to low driving force (**SI Figure 1.3**.). The same overlap measurements were done for PCBM in neat films and the  $E_{ex}$  value was compared to each sensitizer in PCBM. In this way,  $E_{ex}$  values could be reproducibly quantified for each sensitizer:PCBM combination.

The average  $E_{\frac{1}{2}}$  value for lowest oxidation couple vs. Fc/Fc<sup>+</sup> was taken for each sensitizer and set to  $E_{ox,D}$ . For PCBM the average  $E_{\frac{1}{2}}$  value of the lowest (reversible) reduction couple vs. Fc/Fc<sup>+</sup> was taken as  $E_{red,A}$ . With this approach we were able to quantify  $E_{ox,D}$  and  $E_{red,A}$  typically within ± 30 meV based on error propagation from CV measurements. At this precision, we were able to quantify  $\Delta G$  values ranging from -0.01 to -0.69 eV for seven sensitizer:PCBM combinations. As emphasized in point 2, accurate and precise measurements of  $E_{ox,D}$  and  $E_{red,A}$  are crucial to quantifying  $\Delta G$ . Although measured solid-state ionization potentials (IPs, for donors) and electron affinities (EAs, for acceptors) would be ideal for calculating driving force in these systems, the difficulties in obtaining reliable ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES) measurements on organic films is well-documented<sup>5</sup>. While EAs for fullerenes (including PCBM) have been measured by Yoshida using

low-energy inverse photoelectron spectroscopy (LEIPS) and some UPS has been done to measure IPs for vapor-deposited Pcs in the solid-state, neither of these measurements likely provide a reliable estimate of IP/EA for our current set of compounds due to differences in chemical structure of our sensitizers and the microstructure of our films.<sup>6,7</sup> Furthermore, numerous studies have showed that the calculation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies (correlated to gas phase IP and EA, respectively) from solution redox potentials is non-trivial and frequently misleading depending on the conversion factors used.<sup>8</sup> Based on the solution-like nature of our films, we argue that this issue can be circumvented by assuming that the IP of our isolated, donating sensitizers in our accepting PCBM host is proportional to  $E_{ox,D}$  for those molecules in solution.

If these solution measurements are performed under identical conditions via CV for our series of sensitizers and PCBM, we may obtain a self-consistent set of redox potentials and calculate  $\Delta G$  for each sensitizer:PCBM pair. In doing so we performed triplicate CV measurements on each sensitizer and PCBM in a 4:1 (v:v) o-dichlorobenzene: acetonitrile solution with TBAPF<sub>6</sub> electrolyte using Pt/Pt/Ag pseudo reference electrodes (see **Experimental** for more details, see **SI Figure S2.1.** for CV data)<sup>9</sup>.



# 4: Microwave conductivity data, fits, fit parameters, and trends

**Figure S4.1.** TRMC transients for 5 mmolal sensitized films of Sq1:PCBM including fits (black traces). All transients in the figure at varying fluences ranging from  $10^{11}$ - $10^{15}$  photons/cm<sup>2</sup> as shown in the fluence plot. Fits for the transients are all global biexponential fits. Fits to the fluence dependent data are modified Dicker fits from Ferguson et al.<sup>10,11</sup>



**Figure S4.2.** TRMC transients for 5 mmolal sensitized films of Sq2:PCBM including fits (black traces). All transients in the figure at varying fluences ranging from  $10^{11}$ - $10^{15}$  photons/cm<sup>2</sup> as shown in the fluence plot. Fits for the transients are all global biexponential fits. Fits to the fluence dependent data are modified Dicker fits from Ferguson et al.<sup>10,11</sup>



**Figure S4.3.** TRMC transients for 5 mmolal sensitized films of Nc1:PCBM including fits (black traces). All transients in the figure at varying fluences ranging from  $10^{11}$ - $10^{15}$  photons/cm<sup>2</sup> as shown in the fluence plot. Fits for the transients are all global biexponential fits. Fits to the fluence dependent data are modified Dicker fits from Ferguson et al.<sup>10,11</sup>



**Figure S4.4.** TRMC transients for 5 mmolal sensitized films of Pc2:PCBM including fits (black traces). All transients in the figure at varying fluences ranging from  $10^{11}$ - $10^{15}$  photons/cm<sup>2</sup> as shown in the fluence plot. Fits for the transients are all global biexponential fits. Fits to the fluence dependent data are modified Dicker fits from Ferguson et al.<sup>10,11</sup>



**Figure S4.5.** TRMC transients for 5 mmolal sensitized films of Nc2:PCBM including fits (black traces). All transients in the figure at varying fluences ranging from  $10^{11}$ - $10^{15}$  photons/cm<sup>2</sup> as shown in the fluence plot. Fits for the transients are all global biexponential fits. Fits to the fluence dependent data are modified Dicker fits from Ferguson et al.<sup>10,11</sup>



**Figure S4.6.** TRMC transients for 5 mmolal sensitized films of Pc1:PCBM including fits (black traces). All transients in the figure at varying fluences ranging from  $10^{11}$ - $10^{15}$  photons/cm<sup>2</sup> as shown in the fluence plot. Fits for the transients are all global biexponential fits. Fits to the fluence dependent data are modified Dicker fits from Ferguson et al.<sup>10,11</sup>



**Figure S4.7.** TRMC transients for 5 mmolal sensitized films of Pc3:PCBM including fits (black traces). All transients in the figure at varying fluences ranging from  $10^{11}$ - $10^{15}$  photons/cm<sup>2</sup> as shown in the fluence plot. Fits for the transients are individual biexponential fits as there is a small time dependence across fluence. Fits to the fluence dependent data are modified Dicker fits from Ferguson et al.<sup>10,11</sup>



**Figure S4.8.** TRMC transients for neat PCBM including fits (black traces). All transients in the figure at varying fluences ranging from  $10^{13}$ - $10^{15}$  photons/cm<sup>2</sup> as shown in the fluence plot. Fits for the transients are all global biexponential fits. Fits to the fluence dependent data are modified Dicker fits from Ferguson et al.<sup>10,11</sup>

**Table S4.1.** Table of all TRMC global fit parameters for each film for each sensitizer.  $\tau$  is the time constant while A is the amplitude for each exponential, indexed 0 and 1. \*Pc3 was not a global fit, each transient was fit individually as the global fit could not capture the time dependence as a function of the fluence. The fit parameters then are the averaged parameters over all individual fits for each transient.

Sensitizer	Sample	τ <sub>0</sub> (s <sup>-1</sup> )	τ <sub>1</sub> (s <sup>-1</sup> )	$A_{0}$	$A_{1}$
SqPhAm	T1	4.60E-09	3.90E-07	5.4E-05	4.9E-06
	T2	4.90E-09	3.40E-07	7.4E-05	6.4E-06
	Т3	5.10E-09	5.00E-07	6.8E-05	8.9E-06
SqId	T1	1.10E-08	3.60E-07	0.0014	0.0003
	T2	1.20E-08	3.50E-07	0.0006	0.0001
	Т3	1.10E-08	4.10E-07	0.0012	0.0003
SiNc	T1	4.40E-09	2.60E-07	0.0030	0.0002
	T2	5.20E-09	2.60E-07	0.0042	0.0003
	Т3	4.80E-09	2.30E-07	0.0044	0.0002
Pc2	T1	7.30E-09	6.40E-07	0.0032	0.0006
	T2	7.40E-09	6.20E-07	0.0031	0.0006
	Т3	8.70E-09	5.70E-07	0.0026	0.0005
ObNc	T1	5.70E-09	3.50E-07	0.0020	0.0002
	T2	7.60E-09	3.60E-07	0.0011	0.0002
	Т3	6.10E-09	3.60E-07	0.0019	0.0002
ObPc	T1	8.70E-09	5.70E-07	0.0028	0.0006
	T2	8.50E-09	5.40E-07	0.0025	0.0005
	Т3	8.80E-09	5.40E-07	0.0023	0.0005
ObZnPc <sup>*</sup>	T1	1.80E-08	2.20E-07	0.0053	0.0018
	T2	1.90E-08	2.50E-07	0.0033	0.0055
	Т3	1.60E-08	3.10E-07	0.0050	0.0032



**Figure S4.9.** Averaged individual time components for the 2 exponentials from the TRMC transient fits of the triplicate films,  $\tau_0$  and  $\tau_1$ , in **Table S4.1** as a function of driving force (average of T1-T3 for each sensitizer). We provide this plot alongside **Table S4.1** to demonstrate the minimal lifetime dependence for each sensitized PCBM sample as a function of driving force.



**Figure S4.10.** (a) Representative  $\phi \Sigma \mu$  transients at varying driving forces. The transients are normalized to one to demonstrate similarity of the transient shape across different driving forces. Fluence for these transients is shown inset on the plot. (b)  $\phi \Sigma \mu$  vs. fluence plots for extracting largest possible  $\phi \Sigma \mu$  from the lowest fluence.

#### **TRMC** Discussion

**Figure S4.10a.** shows a set of TRMC transients for Sq2:PCBM (normal), Pc2:PCBM (optimal), and Pc1:PCBM (inverted) at the same fluence (3.32E+12 photons/cm<sup>2</sup>). A key feature of all transients in this study is the biexponential shape, specifically a fast decay component (ca.  $10 \pm 5$  ns) most likely associated with a trapping process and a second slower decay component (ca.  $500 \pm 100$  ns) most likely due to recombination. However, those loss mechanisms occur on a timescale orders of magnitude longer than the charge generation step. This general trend is repeatable across all samples and has no  $\Delta G$  (i.e. sensitizer) dependence, which is consistent with our sensitized systems with only mobile electrons in the

PCBM host. **Table S4.1.** provides the relevant lifetime data for the discussed samples. All individual film transients with fits is given in the **SI Figures S4.1-7**.

**Figure S4.10b.** shows a series of  $\phi\Sigma\mu$  vs. fluence plots with fits for three samples from the three regions of the yield curve – Sq2:PCBM (small  $\Delta G_{CT}$ ), Pc2:PCBM (optimal  $\Delta G_{CT}$ ), and Pc1:PCBM (large  $\Delta G_{CT}$ ). Fits to these data are from a fluence-dependent exciton-charge quenching model described in detail by Ferguson et al.<sup>10,11</sup> The Sq2:PCBM sample shows little fluence dependence as difference in magnitude from the smallest to largest  $\phi\Sigma\mu$  is about a factor of two – observed over two orders of magnitude over a similar fluence range. Pc1:PCBM (optimal)  $\phi\Sigma\mu$  increases by nearly an order of magnitude over a similar fluence range. Pc1:PCBM (inverted) shift in driving force relative to the Pc2:PCBM (optimal) is about 0.2 eV while the Sq2:PCBM is about -0.4 eV, as such, it has a greater fluence dependence is consistent in that the greater dependence of charge recombination with fluence tracks with larger free electron yield. This explains why Sq2:PCBM (optimal) shows considerable fluence dependence.

# 5: Femtosecond transient absorption (TA) of both neat and sensitized films

TA measurements on sensitized polystyrene control samples were done to identify any processes competing with PET, such as triplet formation, for the sensitizers in the absence of a host capable of PET. Polystyrene serves as an inert host with sufficient hydrophobicity to mimic that of PCBM and allows us to deposit films in an identical manner to sensitized PCBM films.

For Pc and Nc samples, we excite the Q-band (750-800 nm) and model ground state bleach dynamics, singlet, and triplet exciton features. For samples measured with the visible probe (450-800 nm) bleach features typically appear as strong, negative signals >700 nm. At early times, singlet excited state absorption can be seen as broad positive features from ca. 450-700 nm. At later times, triplet excited state absorption (ESA) bands appear as broad positive features from 500-700 nm. For NIR-absorbing compounds, like Nc2, a NIR probe was used (825-1500 nm). For Nc2, bleach features appeared between 850 and 1000 nm, with broad singlet and triplet features (1000-1500 nm) at longer wavelengths. Pump scatter is removed from the TA images, in some samples.

Sq2 transients were measured using both the visible and NIR probe (800 nm pump) to due to weak singlet ESA in the NIR. The same model, only accounting for relaxation from the lowest-energy singlet excited state, was used to fit visible and NIR data with good agreement.

Sq1 transients (650 nm pump) showed a fast transient species at early times that appears to have a different absorption spectrum than the relaxed singlet excited state. This behavior was modeled successfully by including a higher-energy vibronic state, which is excited directly, and then relaxes to the lowest vibronic level of the singlet excited state. The relaxation from the lowest vibronic state then proceeds to the ground state without evidence of intersystem crossing to triplet states.

**Table S5.1**. Rate constants for radiative + nonradiative relaxation ( $k_{r+nr}$ ) and intersystem crossing ( $k_{ISC}$ ) determined from kinetic modeling of TA data.  $\phi_T$  is triplet yield calculated from  $k_{r+nr}$  and  $k_{ISC}$ . respectively, for the sensitizers. Transients, spectra, and equations for the modeling are given in **SI Figures S5.1-8**.

Sensitizer	Rate constant	Value (10 <sup>8</sup> s <sup>-1</sup> )	Lifetime (ns)	φ
Pc2	k <sub>r+nr</sub>	8.42	1.19	0.08
	k <sub>isc</sub>	0.707	14.1	
Pc3	k <sub>r+nr</sub>	25.2	0.397	0.14
	k <sub>isc</sub>	3.98	2.51	
Pc1	k <sub>r+nr</sub>	6.35	1.57	0.31
	k <sub>isc</sub>	2.85	3.51	
Nc1	k <sub>r+nr</sub>	17.3	0.578	0.05
	k <sub>isc</sub>	0.867	11.5	
Nc2	k <sub>r+nr</sub>	28	0.357	0.03
	k <sub>isc</sub>	0.736	13.6	
Sq2	k <sub>r+nr</sub>	637	0.0157	N/A
Sq1	k <sub>r+nr</sub>	8.03	1.25	N/A

Kinetic model and Jablonski diagram for triplet-forming sensitizers (all except SqId,SqPhAm). Note:  $k_{tr}$  (triplet relaxation to the ground state) is not included in actual fitting as it was not observed over the ~5 ns time window for these measurements.

Kinetic model and Jablonksi diagram describing kinetics of triplet-forming sensitizers.



**Figure S5.1**. 5 mmolal Pc2-sensitized polystyrene (a) TA image (450-800 nm, 5 ns window), (b) global fit of TA image, (c) image fit residuals, (d) spectra at different time delays, (e) normalized steady-state absorption and PL spectra, (f) transients (colored curves) and fits (black, dashed lines) from global kinetic model.



**Figure S5.2**. 5 mmolal Pc3-sensitized polystyrene (a) TA image (450-800 nm, 5 ns window), (b) global fit of TA image, (c) image fit residuals, (d) spectra at different time delays, (e) normalized steady-state absorption and PL spectra, (f) transients (colored curves) and fits (black, dashed lines) from global kinetic model.



**Figure S5.3**. 5 mmolal Pc1-sensitized polystyrene (a) TA image (450-800 nm, 5 ns window), (b) global fit of TA image, (c) image fit residuals, (d) spectra at different time delays, (e) normalized steady-state absorption and PL spectra, (f) transients (colored curves) and fits (black, dashed lines) from global kinetic model.



**Figure S5.4**. 5 mmolal Nc1-sensitized polystyrene (a) TA image (450-800 nm, 5 ns window), (b) global fit of TA image, (c) image fit residuals, (d) spectra at different time delays, (e) normalized steady-state absorption and PL spectra, (f) transients (colored curves) and fits (black, dashed lines) from global kinetic model.



**Figure S5.5**. 5 mmolal Nc2-sensitized polystyrene (a) TA image (825-1500nm, 5 ns window), (b) global fit of TA image, (c) image fit residuals, (d) spectra at different time delays, (e) normalized steady-state absorption and PL spectra, (f) transients (colored curves) and fits (black, dashed lines) from global kinetic model.

Kinetic scheme and for SqId with only singlet excitons, Jablonski diagram from above still applies.

$$\frac{dS_0}{dt} = -N_0 g(t) + k_r [S_1]$$
$$\frac{dS_1}{dt} = N_0 g(t) - k_r [S_1]$$



**Figure S5.6**. 5 mmolal Sq2-sensitized polystyrene (a) TA image (450-800 nm, 5 ns window), (b) global fit of TA image, (c) image fit residuals, (d) spectra at different time delays, (e) normalized steady-state absorption and PL spectra, (f) transients (colored curves) and fits (black, dashed lines) from global kinetic model.



**Figure S5.7**. 5 mmolal Sq2-sensitized polystyrene (a) TA image (825-1500nm, 5 ns window), (b) global fit of TA image, (c) image fit residuals, (d) spectra at different time delays, (e) normalized steady-state absorption and PL spectra, (f) transients (colored curves) and fits (black, dashed lines) from global kinetic model.

Kinetic scheme and Jablonski diagram for Sq1 accounting for fast internal conversions within the singlet excited state.  $S_{1v}$  is the higher-energy vibronic that subsequently relaxes to the bottom of the excited singlet state ( $S_1$ ).

$$\frac{dS_0}{dt} = -N_0 g(t) + (k_r + k_{nr}) [S_1]$$

$$\frac{dS_{1v}}{dt} = N_0 g(t) - k_v [S_{1v}]$$

$$\frac{dS_1}{dt} = k_v [S_{1v}] - (k_r + k_{nr}) [S_1]$$

$$S_1$$

$$S_1$$

$$K_r$$

$$S_0$$



**Figure S5.8**. 5 mmolal Sq1-sensitized polystyrene (a) TA image (450-800 nm, 5 ns window), (b) global fit of TA image, (c) image fit residuals, (d) spectra at different time delays, (e) normalized steady-state absorption and PL spectra, (f) transients (colored curves) and fits (black, dashed lines) from global kinetic model.



**Figure S5.9**. Comparison of sensitized PCBM TA and solution spectroelectrochemistry in chlorobenzene for (a) Sq2, (b) Nc2, (c) Nc1, and (d) Pc2

## 6: Time-resolved photoluminescence characterization of neat films

Modeled TRPL data (**SI Figure S6.1.**) shows that all sensitizers have exciton lifetimes of a few ns, successfully modeled with monoexponentials. The radiative rate constants shown in **Table S6.1.** were utilized in the TA modeling. Kinetic models of our TA data (**SI Figures S5.1-8.**) show that our Pcs/Ncs form triplets on a ~10+ ns timescale and in low yields (<30%). Furthermore, the squaraines studied here show no evidence of triplet formation nor other evidence of competing photophysical pathways with PET on a picosecond timescale. Based on this analysis, we conclude that all charges seen by our microwave conductivity measurements evolved from singlet excitons and that free electron yield is attainable. This argument, however, does not exclude the possibility of other species, like triplets, from facilitating charge recombination.



**Figure S6.1.** TRPL transients collected for 0.005 mol kg<sup>-1</sup> polystyrene films for five of the seven sensitizers that could be collected with the lifetimes included inset on in the plot. All fits are single exponentials convolved with the gaussian instrument response, fit shown in the last image. TRPL rate constants are used as the radiative recombination rate in the TA modeling to extract a real yield of fluorescence and triplets.

Sensitizer	IRF Position (s)	IRF Width (s)	τ <sub>0</sub> (s <sup>-1</sup> )	A <sub>0</sub>
Sq1	1.04E-09	1.50E-10	1.04E+09	101.9
Sq2	N/A	N/A	N/A	N/A
Nc1	1.04E-09	1.50E-10	8.31E+08	37.5
Pc2	1.04E-09	1.50E-10	5.57E+08	38.9
Nc2	N/A	N/A	N/A	N/A
Pc1	1.04E-09	1.50E-10	4.77E+08	56.1
Pc3	1.04E-09	1.50E-10	1.31E+09	85.9

**Table S6.1.** Table of all TRPL fitting parameters for five of seven sensitizers shown in the TRPL transients above. IRF is collected and kept the same for all samples which are collected under the same excitation wavelength of 700 nm. Sq2 and Nc2 have fluorescence outside of the detector window and therefore cannot be collected.

# 7: Description of the global fitting routine used to fit the model(s), and the resulting family of fit solutions

Global fits using the DRET and sequential CT-state models to PLQ and FC yield data were performed using a custom fit function through the Igor Pro 8 package. Orthogonal distance regression (ODR) was also applied as a functional argument for all fits allowing us to include weights for both x and y error estimates. Errors in both x and y for the ODR procedure are determined from standard errors as detailed in the **Experimental.** The global fit was accomplished by concatenating PLQ and FC yield data together into a single wave, and implementing a custom fit function that distinguished the two types of data based on the point number. This approach was required, as the GLobalFit routine available as a component of Igor Pro 8 does not support the orthogonal distance regression method.

Fits obtained from this procedure exhibited a family of equivalent solutions, where there exists a fairly long line through the  $\chi^2$  surface with roughly equivalent fit quality. This prevents us from obtaining a unique "best fit" solution, except when one of the complimentary fit parameters is held constant. **Figure S7.1** illustrates this family of solutions we chose to set  $H_{DA} = 2.5 \text{ meV}$ , as this choice keeps all the parameter values in a physically reasonable range. However, this also leads to misleadingly small error estimates on the reported parameters, and for this reason we do not report them in the main text.



**Figure S7.1.** The fitting figure of merit,  $\chi^2$ , for a family of best-fit parameters defining a minimum line through this 4-dimensional  $\chi^2$  surface for the DRET model fitting to the data in **Figure 2**. The  $\chi^2$  line becomes very flat and noisy for  $\lambda_{CT} > 1.2 \ eV$ , defining a family of fit solutions that are all equivalent. Larger values of  $\lambda_{CT}$  are accommodated in the model by correspondingly larger  $\lambda_{FC'} \beta$ , and  $H_{DA}$ . It is thus necessary to constrain one of these for parameters in order to determine the rest. We chose to set  $H_{DA} = 2.5 \ meV$ . Notably, the sequential CT-state model exhibits identical behavior.



## 8: Temperature-dependance and CT-state spectra predicted by the DRET model

**Figure S8.1.** Predicted temperature dependence of FC yield as a function of  $\Delta G_{CT}$  for both the sensitized (a) and blend (b) systems. Here, the model predicts that the peak FC yield in the sensitized regime has a sizable dependence on temperature, decreasing from ca. 80% to 30% between 350K to 200K. Meanwhile the peak FC yield in the blend has little temperature dependence as it decreases from 100% to 90% between 350K to 150K and only decreases significantly when approaching 100K. The prediction for the blend case here is consistent with temperature-dependent studies from Ebenhoch et al., Gao et al., and Hinrichsen et al. on common OPV device blends.<sup>12-14</sup>



**Figure S8.2.** Predicted CT-state spectra as a function of energy above the most localized CT state. This prediction assumes that the same exponential term which describes the electron transfer process can also describe the variation in oscillator-strength with increasing energy above the most localized CT state, or in other words, as the e-h separation distance, *r*, increases. In this case, the model predicts that the CT state has a much broader distribution and peaks at smaller excess energy than in the blend case, where the distribution is peaked at moderate separation distance and is sharper. These results are consistent with work from Vandewal.<sup>15</sup>



# 9: Comparison of fits using the DRET and a sequential CT-state models

**Figure S9.1.** (a), (b) FC and PLQ yield as a function of  $\Delta G_{CT}$ , reproduced from main text figure 2. The fit lines in (a) (dashed curves) are a global fit to this data using our DRET model, just as in the main text. The fit lines in (b) are a sequential version of the model, where localized CT states are intermediate between the exciton and free charges. These two different kinetic schemes are shown in (c) and (d). Manifestly, the sequential model in (b) and (d) cannot fit our data as well as the DRET model. In particular it cannot reproduce the divergence between  $\phi_{FC}$  and  $\phi_{PLQ}$  between 0 and -0.45 eV.

### **10: Description of the sequential CT-state model**

We implemented a different kinetic scheme that describes free-charge generation as a sequential process where the most localized CT states are intermediate between the exciton and FC states, which we refer to as the "sequential CT-state" model. This conceptual model, Illustrated in **Figure S9.1d**, is more common in the literature and thus serves as an important point of comparison with the DRET model. It uses all the same physical principles as the DRET model, described in the main text, but due to the difference in allowed kinetics the equations describing the yield of free charges and PL quenching are different. These are:

$$\varphi_{FC} = \frac{k_{FC}}{k_{FC} + k_G}$$
 S10.1

$$\varphi_{PLQ} = 1 - \frac{k_{r+nr}}{k_{r+nr} + k_{CT}}$$
 \$10.2

Where the new rate constant,  $k_{G'}$  is that for conversion of CT states to the ground state. In addition, the value of  $k_{FC}$  is different in this case, as it corresponds to CT states converting to FC states, not the excitons converting into FC states. Thus we have:

$$k_{CT} = \int_{r_0}^{r_c} k_{PET}(r)\Omega(r) P(r)dr$$
 S10.3

$$k_{FC} = \int_{r_c}^{\infty} k_{PET}(r)\Omega(r) P(r)dr$$
 S10.4

Just as in the DRET model, main text. Recall however that:

$$k_{PET}(r) = \frac{2\pi}{\hbar} \left| H_{DA} \right|^2 \frac{1}{\sqrt{4\pi\lambda k_B^T}} exp\left[ -\frac{\left(\lambda + \Delta G_{PET}(r)\right)^2}{4\lambda k_B^T} \right]$$
 S10.5

and

$$\Delta G_{PET}(r) = \Delta G_{CT} + \frac{q^2}{4\pi\varepsilon\varepsilon_0} \left(\frac{1}{r} - \frac{1}{r_0}\right)$$
 S10.6

Thus, in the calculation of  $k_{_{FC}}$  starting from the CT state we set  $\Delta G_{_{CT}}$ = 0, such that:

$$\Delta G_{FC}(r) = \frac{q^2}{4\pi\varepsilon\varepsilon_0} \left(\frac{1}{r} - \frac{1}{r_0}\right)$$
 S10.7

Note that because we still integrate over all the rate constants available for transfer to each microstate (equation S10.4),  $k_{FC}$  can be sizable, despite the fact that  $\Delta G_{FC}$  is always positive.

The new rate constant,  $k_{g}$ , is calculated from the Marcus equation but without a distance-dependence or any integration over microstates because there is only one final state:

$$k_{G} = \frac{2\pi}{\hbar} \left| H_{DA} \right|^{2} \frac{1}{\sqrt{4\pi\lambda k_{B}T}} exp\left[ -\frac{\left(\lambda + \Delta G_{CTG}\right)^{2}}{4\lambda k_{B}T} \right]$$
 S10.8

Where in this case  $\Delta G_{CTG}$  is calculated from the energy difference between the CT-state and the ground-state:

$$\Delta G_{CTG} = E_{ex} + \Delta G_{CT}$$
 S10.9

Examining the individual rate-constants that give rise to the fit in **S9.1b** illustrates how the sequential CT-state model differs from the DRET model, and the differing physical interpretation it provides. **Figure S10.1** shows  $k_{CT}$ ,  $k_{FC'}$  and  $k_{G}$  as a function of  $\Delta G_{CT}$ . Here it is the competition between  $k_{CT}$  and  $k_{r+nr}$  that accounts for PL quenching, and the competition between  $k_{FC}$  and  $k_{G}$  that accounts for free-charge yield.  $k_{CT}$  is nearly identical to that found for the DRET model, the only difference being due to the different fit parameters that were found in **Figure S9.1b**.  $k_{FC}$  on the other hand is very different from that found in the DRET model (**Figure 4a**, main text), being independent of  $\Delta G_{CT'}$  as one would expect from **equation S10.7**. Its magnitude is appreciable, but still small compared to  $k_{CT'}$  being ~ 1x10<sup>7</sup> s<sup>-1</sup> for the former vs. 8x10<sup>9</sup> s<sup>-1</sup> for the latter at  $\Delta G_{CT}$ =-300 meV. We see that the only way this model can account for an appreciable free-charge yield is because  $k_{G}$  is initially *very* small relative to  $k_{FC'}$  occasioned by the fact that recombination to the ground-state is actually in the Marcus-inverted regime, and that the "inverted yield" observed in our experimental data at high driving force is explained in this model by  $k_{G}$  growing in as  $\Delta G_{CT}$  becomes more negative and  $\Delta G_{CTG}$  becomes more positive as predicted by **equation S10.9**.



**Figure S10.1.** Individual rate-constants from the sequential CT-state model fits to our TRMC and PL quenching data in **Figure S9.1.** 

# 11: Benzoindole-squaraine synthesis and characterization

### **Materials & instrumentation**

All reagents and solvents were purchased from commercial sources and used without further purification. 1-Butylbenzo[cd]indol-2(1H)-one was synthesized as per the reported procedures.<sup>16</sup> <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were acquired on Varian Mercury 300 MHz. The spectra were calibrated using residual solvent as an internal reference (CDCl<sub>3</sub>: 7.26 ppm for <sup>1</sup>H NMR, 77.00 for <sup>13</sup>C{<sup>1</sup>H} NMR). High-resolution mass spectra were acquired on an Applied Biosystems 4700 Proteomics Analyzer using MALDI or a Micromass AutoSpec M using electron impact (EI) mode. Elemental analyses were performed by Atlantic Microlabs using a LECO 932 CHNS elemental analyzer.

## Synthesis



Scheme S11.1. Synthesis of benzoindole-squaraine, 4.

**Synthesis of 6,8-dibromo-1-butylbenzo[cd]indol-2(1H)-one, 1.** A solution of bromine (3.50 mL, 10.89 g, 68 mmol) in glacial acetic acid (5 mL) was added dropwise to a solution of 1-butylbenzo[cd]indol-2(1H)-one<sup>1</sup> (6.08 g, 27.00 mmol) in glacial acetic acid (15 mL) over one hour at 40 °C. The reaction mixture was stirred at 65 °C for 14 h, and the reaction mixture was added to a 10% solution of sodium thiosulfate (300 mL). The crude product was extracted with chloroform. The combined extracts were washed with 2% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, water, dried over sodium sulfate, and evaporated in vacuo. The crude product was purified by recrystallization from ethanol to give yellow solid as a product. Yield 8.58 g, 83 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.12 - 8.09 (m, 2H), 7.78 (dd, *J*<sub>HH</sub> = 7.2 Hz, *J* = 7.2 Hz, 1H), 7.73 (s, 1H), 4.18 (t, *J* = 7.5 Hz, 2H), 1.82 - 1.71 (m, 2H), 1.50 - 1.38 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz) δ 167.50, 136.72, 135.73, 130.41, 129.55, 127.76, 127.45, 125.92, 125.66, 114.69, 99.17, 40.40, 32.32, 19.91, 13.85. HRMS (MALDI) calcd for C<sub>15</sub>H<sub>13</sub>Br<sub>2</sub>NO (M<sup>+</sup>), 380.9358; found, 380.9373. Anal. Calcd. for C<sub>15</sub>H<sub>13</sub>Br<sub>2</sub>NO: C, 47.03; H, 3.42; N, 3.66. Found: C, 47.27; H, 3.41; N, 3.59.

**Synthesis of 1-butyl-6,8-dimesitylbenzo**[*cd*]**indol-2(1***H***)-one, 2**. A solution of 6,8-dibromo-1-butylbenzo[*cd*]**indol-2(1***H***)-one (5.75 g, 15.0 mmol) and 2,4,6-trimethylbenzeneboronic acid (5.4 g, 33 mmol) in toluene (200 mL) was degassed and then heated to 100 °C under N<sub>2</sub>.** 

Tetrakis(triphenylphosphine)palladium (3.47 g, 3.00 mmol) was added, and the reaction mixture was stirred at 100 °C for 30 min. The degassed solution of potassium carbonate (17.28 g, 125 mmol) in a mixture of methanol : water (1:2 v/v, 150 mL) was added, and the reaction mixture was stirred at 100 °C for 18 h. After allowing to cool to room temperature, water (50 mL) was added, and the product was extracted with toluene (100 mL). The combined extracts were washed with 5% HCl, water, brine, and dried over magnesium sulfate. The volatile solvents were evaporated in vacuo, and the residue was purified by column chromatography over silica gel with chloroform:methanol (99:1, v/v) as eluent. The fractions containing the product were collected, and the solvents were removed under reduced pressure to give a yellow oil. The target compound was obtained by recrystallization from acetonitrile as a yellow solid. Yield: 4.30 g, 62%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.08 (dd, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, J = 0.9 Hz, 1H), 7.63 - 7.53 (m, 2H), 6.98 (s, 2H), 6.96 (s, 2H), 6.91 (s, 1H), 3.43 (t, J = 7.8 Hz, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 2.09 (s, 6H), 1.97 (s, 6H), 1.31-1.21 (m, 2H), 0.99-0.87 (m, 2H), 0.66 (t, J = 7.3 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz) δ 168.61, 137.71, 137.04, 136.97, 136.52, 134.67, 133.91, 132.96, 132.39, 129.32, 128.15, 128.09, 127.79, 126.99, 126.04, 124.02, 120.21, 40.69, 31.29, 21.11, 21.09, 20.79, 20.65, 19.94, 13.46. HRMS (MALDI) calcd for C<sub>33</sub>H<sub>35</sub>NO (M<sup>+</sup>), 461.2713; found, 461.2720. Anal. Calcd. for C<sub>33</sub>H<sub>35</sub>NO: C, 85.86; H, 7.64; N, 3.03. Found: C, 85.69; H, 7.68; N, 3.16.

**Synthesis of 1-butyl-6,8-dimesityl-2-methylbenzo**[*cd*]indol-1-ium hexafluorophosphate, **3**. Under an inert atmosphere, a solution of 1-butyl-6,8-dimesitylbenzo[*cd*]indol-2(*1H*)-one (**2**) (0.7 g, 1.5 mmol) in anhydrous diethyl ether (15 mL) was heated to boiling, and a solution of methylmagnesium bromide (3 M in Et<sub>2</sub>O, 0.67 mL, 2.0 mmol) was added to the reaction mixture dropwise over 10 min. After boiling for 1 h, the mixture was allowed to cool to RT, and the solvent was evaporated *in vacuo* under an inert atmosphere. The resulting solids were treated with the mixture of distilled water (30 mL) and hexafluorophosphoric acid (2 mL, 55 wt%) and stirred for 10 min. The mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub>; the extracts were dried over magnesium sulfate, filtered, and evaporated to give a yellow-greenish oil. The crude residue was dissolved in dichloromethane (5 mL); the solution was filtered and hexane (45 mL) was added to precipitate the product. Yield: 0.76 g, 84%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.74 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 1H), 8.08 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz, 1H), 7.97 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, *J* = 7.8 Hz, 1H), 7.30 (s, 1H), 7.07 (s, 2H), 7.02 (s, 2H), 4.09 (t, *J* = 7.5 Hz, 2H), 3.22 (s, 3H), 2.37 (s, 6H), 2.08 (s, 6H), 1.93 (s, 6H), 1.55-1.44 (m, 2H), 1.03-0.92 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). HRMS (EI) calcd for C<sub>34</sub>H<sub>38</sub>N (M–PF<sub>6</sub><sup>+</sup>), 460.2999; found, 460.2966. Anal. Calcd. for C<sub>34</sub>H<sub>38</sub>F<sub>6</sub>NP: C, 67.43; H, 6.32; N, 2.31. Found: C, 67.16; H, 6.41; N, 2.33.

#### Synthesis

of

**2,4-bis(1-butyl-6,8-dimesitylbenzo**[*cd*]**indol-2(***1H***)-ylidene**)**methyl)cyclobutene-diylium-1,3-bis(olate)**, **4 (Sq2).** Squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) (0.017 g, 0.15 mmol) was dissolved in toluene/1-butanol (1:3, 4 mL) and heated at reflux under nitrogen for 20 min. Then solution of 1-butyl-6,8-dimesityl-2-methylbenzo[*cd*]**indol-1-i**um hexafluorophosphate (**3**) (0.18 g, 0.30 mmol) in toluene/1-butanol (3:1, 4 mL) with quinoline (0.039 g, 0.3 mmol) was added. The reaction mixture was refluxed for 12 h using the Dean-Stark trap. The solutions were then filtered and evaporated under reduced pressure, and the residue was purified by column chromatography over silica gel with CH<sub>2</sub>Cl<sub>2</sub> as an eluent. The fractions containing dye were collected, and the solvent was removed. The residue was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>; the solution was the filtered and evaporated under reduced pressure. The product was treated with diethyl ether, filtered, and dried. Yield: 0.068 g, 45%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  8.81 (d, <sup>3</sup><sub>JHH</sub> = 7.5 Hz, 2H), 7.76 (t, <sup>3</sup><sub>JHH</sub> = 7.8 Hz, 2H), 7.49 (d, <sup>3</sup><sub>JHH</sub> = 8.1 Hz, 2H), 7.04 (s, 4H), 7.02 (s, 4H), 6.95 (s, 2H), 6.31 (s, 2H), 3.80-3.71 (m, 4H), 2.37 (s, 12H), 2.12 (s, 12H), 1.99 (s, 12H), 1.57-1.47 (m, 4H), 1.00 - 0.88 (m, 4H), 0.72 (t, *J* = 7.2 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz)  $\delta$  150.89, 138.10, 137.16, 136.91, 136.49, 134.63, 134.55, 133.84, 132.65, 128.84, 128.28, 128.02, 126.48, 123.04, 91.56, 44.58, 30.87, 100 -

20.84, 20.81, 20.64, 20.38, 20.02, 13.15. HRMS (MALDI) calcd for  $C_{72}H_{72}N_2O_2$  (M<sup>+</sup>), 996.5588; found, 996.5573. Anal. Calcd. for  $C_{72}H_{72}N_2O_2$ : C, 86.71; H, 7.28; N, 2.81. Found: C, 86.63; H, 7.38; N, 2.84. UV-vis, toluene:  $\lambda_{max}$  = 936 nm,  $\varepsilon_{max}$  = 297000 M cm<sup>-1</sup>



Figure S11.1. <sup>1</sup>H NMR spectrum of 1 in CDCl<sub>3.</sub>







Figure S11.4.  $^{13}\text{C}\{^{1}\text{H}\}$  NMR spectrum of 2 in  $\text{CDCl}_{3.}$ 



**Figure S11.5**. <sup>1</sup>H NMR spectrum of **3** in CDCl<sub>3</sub>.







Figure S11.7.  ${}^{13}C{}^{1}H$  NMR spectrum of Sq2 in  $CD_2CI_2$ .

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