Supporting Information

The Effects of Heavy Atoms on the Exciton Diffusion Properties in Photoactive Thin Films of Tetrakis(4-carbomethoxyphenyl)porphyrins

Angy L. Ortiz, Graham C. Collier, Dawn M. Marin, Jennifer A. Kassel, Reynolds J. Ivins, Nicholas G. Grubich, and Michael G. Walter*

[*] Prof. M. G. Walter, Corresponding Author
Department of Chemistry
University of North Carolina at Charlotte
214-216 Burson Chemical Laboratory
Charlotte, NC 28223 (USA)

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S1. Electrochemistry of TCM_4PP, $TBCM_3PP$ and TCM_3IPP.

Cyclic voltammetry (CV) scans of TCM_4PP, $TBCM_3PP$, and TCM_3IPP show two reversible oxidations and reductions for each derivative (Figure S1b). The redox potentials of all three derivatives are similar, with a slight cathodic shift of E^1_{ox} and E^1_{red} for the $TBCM_3PP$/TCM_3IPP derivatives (10 – 20 mV). The HOMO/ LUMO energies in eV for each derivative were calculated by converting the redox potentials found using CV with a Ag/Ag^+ electrode to redox potential against a saturated calomel electrode (SCE) followed by the addition of 4.4 V to give the final energy in eV. The low-lying HOMO levels for the carboxyphenyl derivatives ($TBCM_3PP$ / TCM_3IPP) were calculated to be close to that of TCM_4PP (~ -5.6 eV). Table 1 shows the redox potentials for all the porphyrins characterized through CV studies and calculated energy levels. Altering one substituent on the phenyl portion of the porphyrin from a carbomethoxy to a halogen does not significantly affect the redox potentials of the porphyrin.

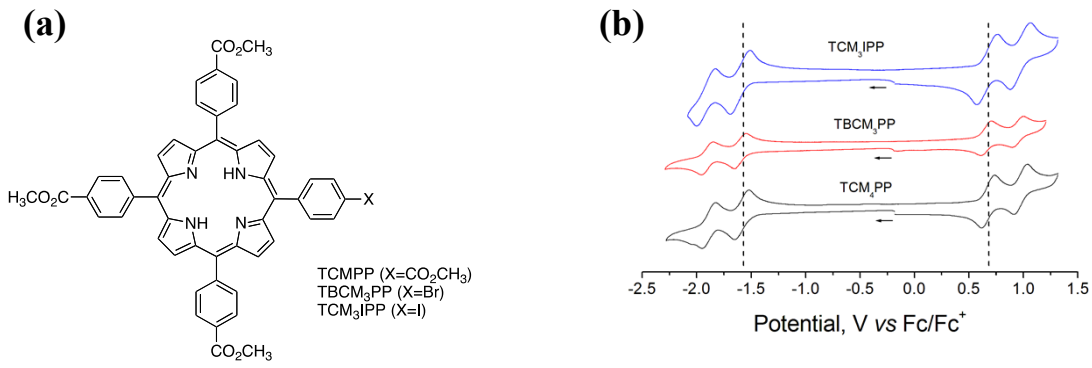


Figure S1. (a) Tetraphenylporphyrins synthesized. (b) CV scans of TCM_4PP, $TBCM_3PP$, and TCM_3IPP in dichloromethane. Scan rate was 100 mV s^{-1} with 0.1 M TBAH.

Table S1. CV[a] data of measured compounds and calculated HOMO/LUMO energy levels.

Compound	E^1_{ox} (V)	E^2_{ox} (V)	E^1_{red} (V)	E^2_{red} (V)	HOMO (eV)	LUMO (eV)	Energy Gap (eV)
TCM_4PP	0.69	0.98	-1.59	-1.89	-5.63	-3.35	2.3
$TBCM_3PP$	0.67	0.95	-1.61	-1.90	-5.61	-3.33	2.3
TCM_3IPP	0.67	0.96	-1.60	-1.90	-5.61	-3.34	2.3

[a]All the redox potentials were measured relative to Fc/Fc^+.

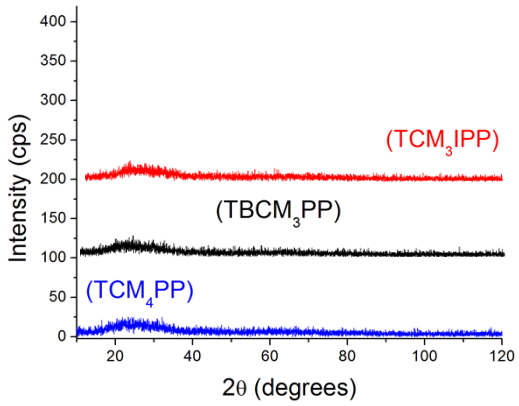


Figure S2. XRD patterns of TCM_4PP, $TBCM_3PP$, and TCM_3IPP thin films.

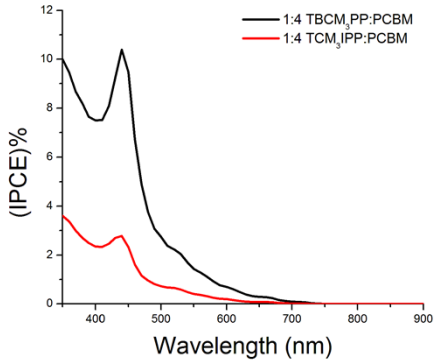


Figure S3. IPCE % spectrum of $TBCM_3PP$:PCBM and TCM_3IPP:PCBM devices.

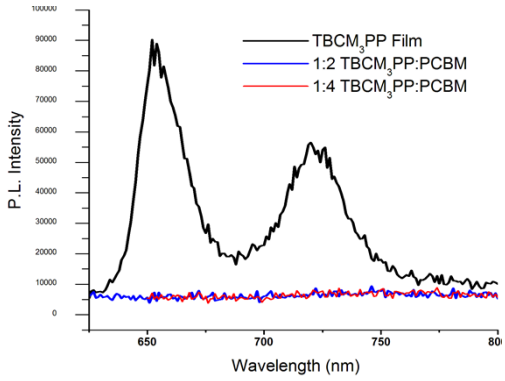
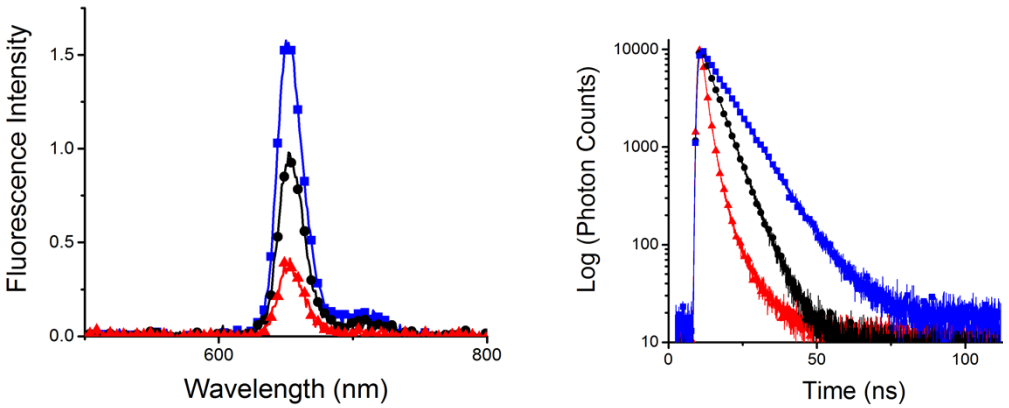


Figure S4. Steady-state PL quenching of $TBCM_3PP$ thin films with 1:2 and 1:4 PCBM by weight.



Porphyrin	τ_f, ns	ϕ_f	$k_r = \frac{\phi}{\tau}$, s^{-1}	ϕ_Δ
TCM_4PP	~ 8.52	0.10	1.17×10^7	0.54 ± .07
$TBCM_3PP$	~5.02	0.05	9.96×10^6	0.74 ± .02
TCM_3IPP	~2.34	0.02	8.55×10^6	0.91 ± .06

Figure S5. Fluorescent emission spectra, singlet lifetime decays (τ_f), quantum yields (ϕ_f), rate of radiative decay (k_r), and singlet oxygen quantum yield (ϕ_Δ) of the TCMPP derivatives in solution (TCM_4PP), ($TBCM_3PP$), and (TCM_3IPP).

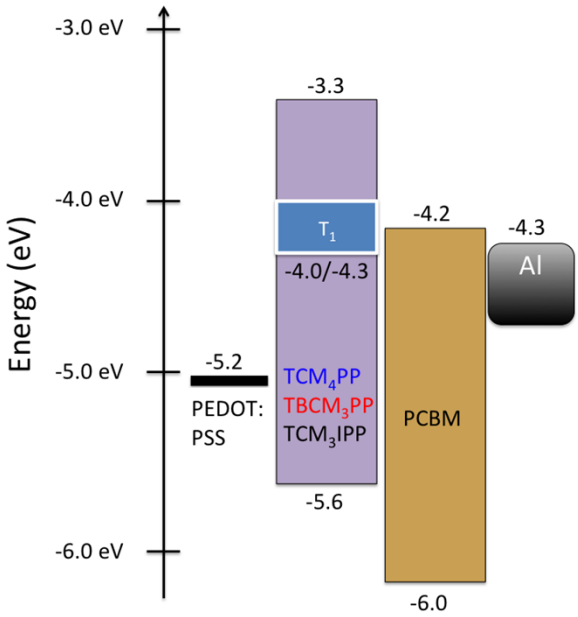


Figure S6. Energy level diagram of porphyrin (TCMPP derivatives) - PCBM organic photovoltaic devices with approximate porphyrin triplet state T_1 energies.