# Supplementary information for "Solvent-dependent Photoinduced Dynamics in a Non-rigidly Linked Perylene Diimide and Zinc Phthalocyanine Dyad Probed by Ultrafast Spectroscopy"

Bryan Kudisch<sup>1</sup>, Margherita Maiuri<sup>1</sup>, Vicente M. Blas-Ferrando<sup>2</sup>, Javier Ortiz<sup>2</sup>, Ángela Sastre-Santos<sup>2</sup>, Gregory D. Scholes<sup>1</sup>

<sup>1</sup>Department of Chemistry, Princeton University, Princeton, NJ, 08540, United States

<sup>2</sup>Área de Química Orgánica, Instituto de Bioingeniería, Universidad Miguel Hernández, Elche 03202, Spain

gscholes@princeton.edu, asastre@umh.es

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# Absorption and fluorescence spectra of PMAMI in THF, DCM, and PhCN



S1. Normalized absorption and fluorescence of PMAMI in DCM

S2. Normalized absorption and fluorescence of PMAMI in PhCN



S3. Normalized absorption and fluorescence of PMAMI in THF



#### Absorption spectra of ZnPc in THF, DCM, and PhCN

S4. Normalized absorption of ZnPc in DCM



S5. Normalized absorption of ZnPc in PhCN



S6. Normalized absorption of ZnPc in THF



# Absorption spectra of ZnPc-PDI in THF, DCM, and PhCN

S7. Normalized absorption of PDI-ZnPc in PhCN



S8. Normalized absorption of PDI-ZnPc in DCM



S9. Normalized absorption of PDI-ZnPc in THF



# Concentration dependent absorption spectra of PMAMI, ZnPc, and ZnPc-PDI in toluene, DCM, THF, and PhCN

Absorption spectra of all species were recorded with various concentrations of each species in a 1 mm cuvette, such that the optical density associated with those species spanned a range that includes the optical density of the transient absorption measurements. Little-to-no concentration dependence of the spectra were observed in all samples.

S10. Concentration dependence of PMAMI, ZnPc, and ZnPc-PDI in toluene at various concentrations in a 1 mm cuvette.



S11. Concentration dependence of PMAMI, ZnPc, and ZnPc-PDI in DCM at various concentrations in a 1 mm cuvette.



S12. Concentration dependence of PMAMI, ZnPc, and ZnPc-PDI in THF at various concentrations in a 1mm cuvette.



S13. Concentration dependence of PMAMI, ZnPc, and ZnPc-PDI in PhCN at various concentrations in a 1mm cuvette.



## Power-dependent transient absorption spectra of PMAMI, ZnPc, and ZnPc-PDI in toluene

Power-dependent transient absorption spectra of all species at 540 nm for PMAMI and ZnPc-PDI as well as at 685 nm for ZnPc and ZnPc-PDI in toluene are reported such that the experimental pump power spanned the 125 uW pump power reported in the manuscript. In all cases, there was no power dependence of the observed kinetics at 743 nm.

S14. Power dependent trace at 743 nm of PMAMI in toluene pumped at 540 nm





#### S15. Power dependent trace at 743 nm of ZnPc in toluene pumped at 685nm



### S16. Power dependent trace at 743 nm of ZnPc-PDI in toluene pumped at 540 nm

S17. Power dependent trace at 743 nm of ZnPc-PDI in toluene pumped at 685 nm



Raman excitation of low frequency DCM vibrational modes in ZnPc

S18. Solvent dependent oscillations are present in ZnPc in DCM but not in toluene, owing to the oscillations' origin in off-resonant Raman excitation of low frequency DCM vibrational modes.





S19. Pump-probe trace at 687 nm upon 540 nm photoexcitation of PDI-ZnPc

S20. Pump-probe trace at 480 nm upon 540 nm photoexcitation of PDI-ZnPc



S21. Pump-probe trace at 740 nm upon 540 nm photoexcitation of PDI-ZnPc



#### Modelling of orientation factor κ for energy transfer

The general equation for the orientation factor in three dimensions is:

$$\kappa = \hat{\mu}_D \cdot \hat{\mu}_A - 3(\hat{\mu}_D \cdot \hat{R})(\hat{\mu}_A \cdot \hat{R})$$

Where  $\hat{\mu}_D$  and  $\hat{\mu}_A$  are unit vectors describing the transition dipole moment orientation of the donor and acceptor chromophores, respectively and  $\hat{R}$  is the unit vector describing the direction from the center of the donor chromophore to the acceptor chromophore. By approximating that the transition dipole moments of the PDI and ZnPc moieties are coplanar, the dot products in the above equation can be replaced by cosine functions:

$$\kappa = \cos\left(\theta_{DA}\right) - 3(\cos\theta_{DR})(\cos\theta_{AR})$$

Where  $\theta_{DA}$ ,  $\theta_{DR}$ , and  $\theta_{AR}$  are the in plane angles between their respective unit vectors. In order to parametrize  $\theta_{DR}$  and  $\theta_{AR}$  in terms of  $\theta_{DA}$ , we model our system such that each molecular moiety is rigidly connected to a central pivot point on the molecular bridge according to the following picture:

S22. Schematic of orientation factor modeling for PDI-ZnPc arrangement of transition dipole moments



Where if we assume the moieties are rigidly connected to the pivot point and with equal length, we retrieve the relation:

$$\theta_{DA1} = 2\theta_{DR} = 2\theta_{AR}$$

Plugging into the equation for  $\kappa$ :

$$\kappa_1 = \cos\left(\theta_{DA}\right) - 3\left(\cos\left(\frac{\theta_{DA}}{2}\right)\right)\left(\cos\left(\frac{\theta_{DA}}{2}\right)\right)$$

We can write the orientation factor for the orthogonal transition dipole moment using the relation that:

$$\theta_{DA2} = \frac{\pi}{2} + \theta_{DA1}$$

Such that:

$$\kappa_2 = \sin(\theta_{DA}) - 3\left(\cos(\frac{\theta_{DA}}{2})\right)\left(\sin(\frac{\theta_{DA}}{2})\right)$$

Plotting  $\kappa_1^2 + \kappa_2^2$  for an expected range of values from 0 to  $\frac{\pi}{2}$  gives:

S13. Plot of  $\kappa_1^2 + \kappa_2^2$  using a model considering one donor transition dipole moment and one acceptor transition dipole moment with variable relative angle  $\theta_{DA}$ 



S23. Global analysis<sup>1</sup> after photoexcitation of PDI-ZnPc in DCM at 685 nm model with 5 evolution-associated decay spectra (EADS)



S24. Residual for above model at 687 nm



S25. Table of EADS with associated rate constants for above model

Spectrum	Decay rate (ps <sup>-1</sup> )
EADS1	2.07036 (0.007012)
EADS2	0.467947 (0.0007183)
EADS3	0.104808 (0.001707)
EADS4	0.0212738 (0.0001412)
EADS5	0.00273362 (5.833e-05)

S26. Global analysis after photoexcitation of PDI-ZnPc in toluene at 685 nm model with 5 EADS



S27. Residual for above model at 687 nm



S28. Table of EADS with associated rate constant for above model

Spectrum	Decay rate (ps <sup>-1</sup> )
EADS1	2.81437 (0.03756)
EADS2	0.402694 (0.004658)
EADS3	0.0974395 (0.002073)
EADS4	0.0169855 (0.0001571)
EADS5	0.000763885 (3.814e-06)

S29. Global analysis after photoexcitation of PDI-ZnPc in THF at 685 nm model with 5 EADS



S30. Residual for above model at 687 nm



S31. Table of EADS with associated rate constant for above model

Spectrum	Decay rate (ps <sup>-1</sup> )
EADS1	2.52500 (0.004709)
EADS2	0.182995 (0.007895)
EADS3	0.180985 (0.008134)
EADS4	0.00219742 (2.612e-05)
EADS5	0.000763885 (3.814e-06)

S32. Global analysis after photoexcitation of PDI-ZnPc in PhCN at 685 nm model with 5 EADS



S33. Residual for above model at 687 nm



S34. Table of EADS with associated rate constant for above model

Spectrum	Decay rate (ps <sup>-1</sup> )
EADS1	2.89022 (0.04410)
EADS2	0.232876 (0.009753)
EADS3	0.614688 (0.009506)
EADS4	0.0154456 (8.998e-05)
EADS5	0.00301086 (0.0002217)

S35. Residual at 687 nm for the 6 EADS model applied to photoexcitation of PDI-ZnPc in DCM at 685 nm



S36. Residual at 687 nm for the 6 EADS model applied to photoexcitation of PDI-ZnPc in toluene at 685 nm



S37. Global analysis after photoexcitation of PDI-ZnPc in THF at 685 nm model with 6 EADS



S38. Residual for above model at 687 nm



S39. Global analysis after photoexcitation of PDI-ZnPc in PhCN at 685 nm model with 6 EADS



S40. Residual for above model at 687 nm



S41. Rehm-Weller Calculations:

The Rehm-Weller equation<sup>1</sup> allows calculation of  $\Delta G_{CS}$  in any solvent from the reduction and oxidation potentials retrieved from cyclic voltammetry ( $E_{red}$  and  $E_{ox}$  respectively) and dielectric constant ( ${}^{\mathcal{E}}_{ref}$ ) in one solvent (in this case, THF), with the knowledge of the ionic radii of the molecular moieties ( $r_D$  and  $r_A$ ), the relative dielectric constants of the solvents ( ${}^{\mathcal{E}}_{S}$ ), the distance between the respective ions ( $r_{DA}$ ), and the absorption energy of the electron transfer donor ( $E_{00}$ ):

$$\Delta G_{CS}(eV) = E_{ox} - E_{red} - E_{00} - \frac{e^2}{4\pi r_{DA}\varepsilon_s\varepsilon_0} + \frac{e^2}{4\pi\varepsilon_0}(\frac{1}{2r_D} + \frac{1}{2r_A})(\frac{1}{\varepsilon_{ref}} - \frac{1}{\varepsilon_s})$$

For these calculations, both ionic radii and inter-ion distance were estimated to be 0.5 and 1.5 nm, respectively. Values of the relative dielectric constant for THF, DCM, PhCN, and toluene are 7.58, 8.93, 26.0, and 2.38, respectively. Values of  $\Delta G_{CR}$  were calculated by removing the E<sub>00</sub> term from the above equation.

#### S42. Reorganization energy calculations

The reorganization energy can be expressed in the Marcus representation<sup>2</sup> according to:

$$\lambda_{solvent}(eV) = \frac{e}{4\pi\varepsilon_0} (\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}})(\frac{1}{n^2} - \frac{1}{\varepsilon_s})$$

Where *n* is the refractive index of the solvent and  $n^2$  is an estimate for the optical dielectric constant. Values of index of refraction for THF, DCM, PHCN, and toluene are 1.41, 1.42, 1.53, and 1.50, respectively.

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