Excited-state dynamics of porphyrin-naphthalenediimide-porphyrin triads

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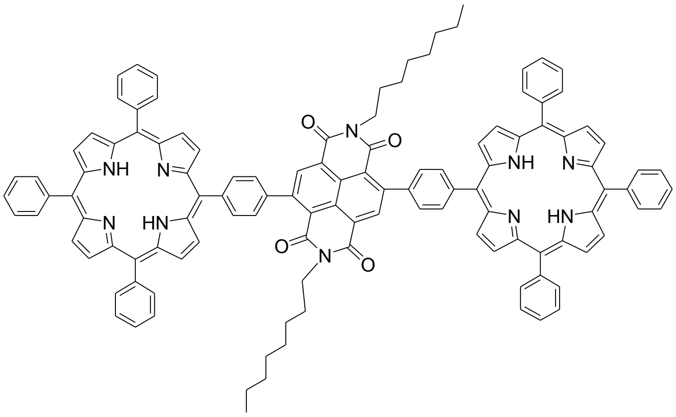
Synthesis of the triads 1 and 2

Naphthalenetetracarboxy dianhydride, octylamine, acetic acid (AcOH), pyrrole, benzaldehyde, 4-(tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde, boron trifluoride etherate ($BF_3{\cdot}O(Et)_2$), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), $Pd(PPh_3)_4$, sodium bicarbonate (Na_2CO_3), toluene, chloroform ($CHCl_3$), chloroform-d ($CDCl_3$), methanol (MeOH) and dichloromethane (DCM), zinc acetate ($Zn(OAc)_2.2H_2O$) were purchased from Aldrich and used without purification, unless otherwise specified. UV-vis absorption spectra were recorded on a Cary-50 spectrophotometer. ^{1}H NMR, ^{13}C-NMR spectra were recorded on a Bruker spectrometer using chloroform-d as solvent and tetramethylsilane as an internal standard. The solvents for spectroscopic studies were of spectroscopic grade and used as without further purification.

5,10,15-Triphenyl-20-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-porphyrin (boranic ester-porphyrin, **3***)*[S1] was prepared in one step following standard literature protocol. Condensation of 4-boronopinacolbenzaldehyde (1 equiv.) and benzaldehyde (3 equiv.) with pyrrole (4 equiv.) in the presence of catalytic amount of tetraphenylphosphonium chloride and trifluoroboron etherate, followed by DDQ oxidation, gives **3** in 5 % yield.[S1]

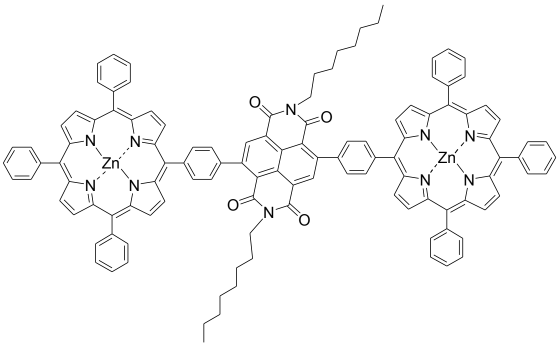
N,N'-di-(n-octyl)-2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic acid diimide (2,6-dibromo-substituted NDI, **4***)*[S2] was prepared in two steps following an earlier procedure: first, 2,6-dibromo-substituted 1,4,5,8-naphthalenetetracarboxylic acid (dibromo-NDA) was prepared in quantitative yield by reacting 1,4,5,8-naphthalene tetracarboxylic acid diimide with dibromoiso-cyanuric acid in hot sulfuric acid. Second, dibromo-NDA was reacted with n-octyl amine in hot acetic acid to afford NDI **4** in 30% yield after column chromatography.

2,7-Dioctyl-4,9-di-p-tolyl-benzo[lmn][3,8]phenanthroline-1,3,6,8-tetraone (cNDI) was prepared following our earlier protocol.[S2]

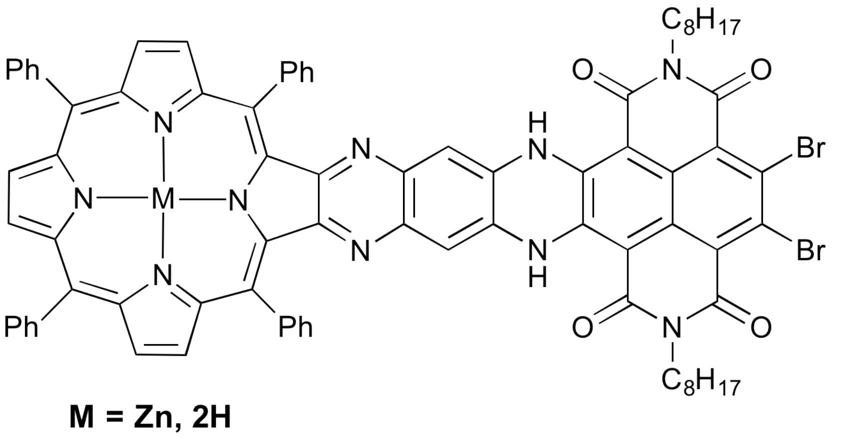


For the synthesis of the *free-base porphyrin core-substituted-NDI (***2***),* a mixture of aqueous 2 M Na_2CO_3 (2 mL) and toluene (15 mL) was repeatedly deoxygenated by purging with argon gas, and the boranic ester-porphyrin **3** (100 mg, 13.5 mmol), 2,6-dibromo-substituted NDI **4** (35 mg, 5.4 mmol) along with 2 mol% of $Pd(PPh_3)_4$ were added. The mixture was heated at 80 °C under argon atmosphere in the dark for 24 hrs, after which it was quenched with the addition of aqueous HCl (10 mL, 0.1 M). The organic layer was extracted with dichloromethane, washed consecutively with water and brine before being dried over sodium sulphate ($NaSO_4$) and concentrated. The crude product was then chromatographed over flash silica gel, with DCM-hexane (2:1) as eluent to afford the porphyrin-core-substituted NDI **2** (70 mg, 76 %) as a purple solid. Mp > 300 °C; Anal. Calcd. for $C_{118}H_{94}N_{10}O_4$: C 82.59, H 5.52, N 8.16; Found: C 82.44, H 5.16, N 8.21; Ms (MALDI-TOF, no matrix) *m/z*: calcd for $C_{118}H_{94}N_{10}O_4$ 1714.7460, found 1714.7442; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.64 (s, 2H), 8.38-8.18 (m 16H), 7.84 (d, J = 6.93 Hz, 4H), 7.50 (d, *J* = 6.83 Hz, 4H), 7.91-

7.36 (30H), 4.24 (t, *J* = 6.80 Hz, 4H), 1.89-1.79 (m, 4H),1.28-1.05 (br, m, 20H), 0.98 (t, *J* = 6.78 Hz, 6H), -2.81 (s, 4H); IR (cm^{-1}): 3309, 3064, 3051, 2969, 2918, 2869, 2214, 1717, 1676, 1594, 1560, 1418, 1352, 1331, 1216, 769, 732, 715, 689.



For the synthesis of *zinc-porphyrin-core-substituted NDI (ZnP-cNDI)* **1**, $Zn(OAc)_2 \cdot 2H_2O$ (50 mg, excess) dissolved in MeOH (1 mL) was added to a solution of FbP-cNDI 2 (30 mg) dissolved in $CHCl_3$ (10 mL), and the mixture was stirred for 14hrs at room temperature. The solution was then washed with water and dried over anhydrous sodium sulfate. The compound was purified over silica gel column using $CHCl_3$ as eluent giving purple solid in 90% yield. Mp > 300 °C; Anal. Calcd. for C118H90N10O4Zn2: C 76.91, H 4.92, N 7. 60; Found: C 76.84, H 4.56, N 7.21; Ms (MALDI-TOF, no matrix) m/z: calcd = 1838.5729, found 1838.5717.



Scheme S1: structure of the strongly coupled dyads investigated previously.[S3]

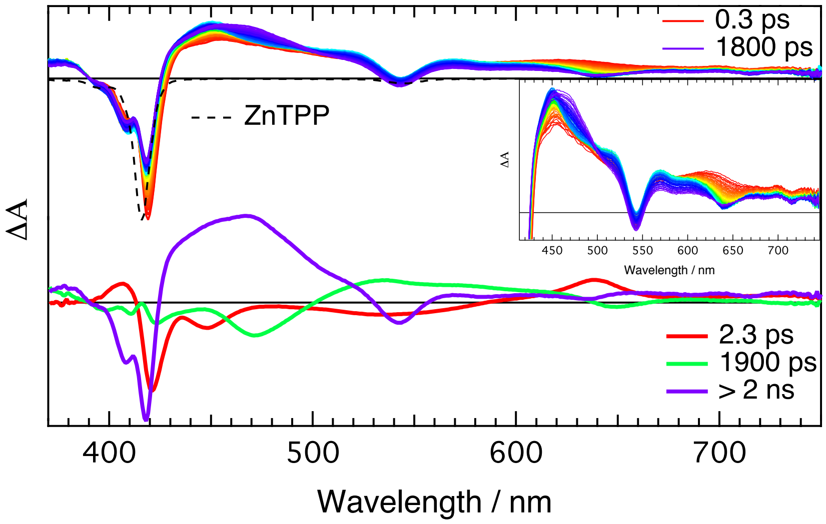


Figure S1: (Top and inset) Transient absorption spectra recorded with ZnP in CHX at different time delays upon 400 nm excitation, and (bottom) decay-associated difference spectra obtained from a global multiexponential analysis.

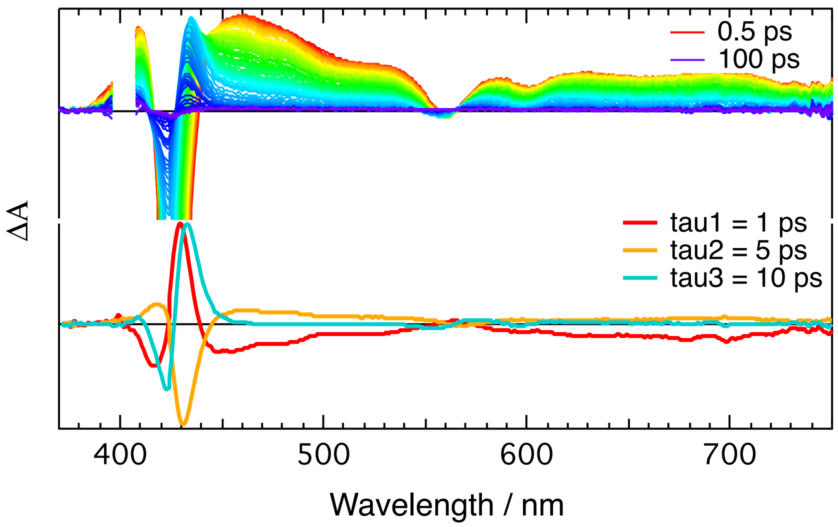


Figure S2: (Top) Transient absorption spectra recorded with triad **1** in THF at different time delays upon 400 nm excitation, and (bottom) decay-associated difference spectra obtained from a global multiexponential analysis.

Calculation of the EEH/T rate constants

According to Förster theory, the EEH/T rate constant, in ps^{-1}, can be expressed as:

$$k_{EEH(T)} = 1.18(\mathrm{ps}^{-1}\mathrm{cm}) \cdot |V_{dd}|^2 \, \Theta \qquad \text{(S1)}$$

where V_{dd} is the interaction energy between the transition dipole moment of the energy donor and that of the acceptor and Θ is the spectral overlap integral, obtained from the area-normalized emission and absorption bands of the donor and acceptor, respectively, represented on a wavenumber scale.

The dipole-dipole energy, V_{dd}, in cm^{-1} between two chromophores with a transition dipole, $\vec{\mu}_d$ and $\vec{\mu}_a$ (in D), where d and a are the energy donor and acceptor, respectively, at a distance $|\vec{r}_{da}| = r_{da}$ (in nm) can be calculated as:

$$V_{dd} = 5.04 \frac{|\vec{\mu}_d||\vec{\mu}_d| f_L^2}{\varepsilon_{op} r_{da}^3} \kappa \qquad \text{(S1)}$$

where $\varepsilon_{op} \simeq n^2$ is the dielectric constant at optical frequencies, n is the refractive index, $f_L = \left(\varepsilon_{op} + 2\right)/3$ the Lorentz local field correction factor, and κ the orientational factor:

$$\kappa = \cos\beta_{da} - 3\cos\beta_d \cos\beta_a \qquad \text{(S2)}$$

with β_{da}, the angle between $\vec{\mu}_d$ and $\vec{\mu}_a$, and β_d and β_d the angles between the dipoles and $\vec{r}_{da}$.

The B and Q states of ZnP are doubly degenerate with two perpendicular transition dipole moments ($\vec{\mu}_x$ and $\vec{\mu}_y$) located in the porphyrin plane (planar transition dipole). Therefore the excitation energy transfer rate constant between porphyrin 1 and 2 is the sum of four contributions:

$$k_{EEH/T} = k_{xx} + k_{yy} + k_{xy} + k_{yx} \qquad \text{(S3)}$$

In the triads, we place the x and y axes parallel and perpendicular to $\vec{r}_{da}$, respectively. If we assume free rotation of the porphyrins around the long axis of the triad, the angle between $\vec{\mu}_x(d)$ and $\vec{\mu}_y(a)$ is always 90 deg, that between $\vec{\mu}_x(d)$ and $\vec{\mu}_x(a)$ is 0 deg and that between $\vec{\mu}_y(d)$ and $\vec{\mu}_y(a)$ can vary between 0 and 90 deg.

As the average cosine in the 0-90 deg. interval is $2/\pi$, the reorientational factors are: $\kappa_{xx} = 2$, $\kappa_{yx,yx} = 0$, and $\kappa_{yy} = 2/\pi \approx 0.64$.

These values can be used to calculate V_{xx} and V_{yy}. For calculating $k_{EEH/T}$, the sum of the square values is used:

$$V_{dd}^2 = V_{xx}^2 + V_{yy}^2 \qquad \text{(S4)}$$

The $|V_{dd}|$ values listed in **Table 4** correspond to:

$$\left|V_{dd}\right| = \sqrt{V_{xx}^2 + V_{yy}^2} \qquad \text{(S5)}$$

In all cases, a refractive index of n=1.4 was used. The following parameters have been used for the calculation of the various EEH/T rate constants:

1) L_BS EEH between the ZnP units of triad **1**:

$\left|\vec{\mu}_x\right| = \left|\vec{\mu}_y\right| = 7.8$ D, r_{da}=2.3 nm

$|V_{xx}|$=44.8 cm^{-1}, $|V_{yy}|$=14.3 cm^{-1}, $|V_{dd}|$= 47 cm^{-1}.

2) L_QS EEH between the ZnP units of triad **1**:

$\left|\vec{\mu}_x\right| = \left|\vec{\mu}_y\right| = 2.25$ D, r_{da}=2.3 nm

$|V_{xx}|$=3.7 cm^{-1}, $|V_{yy}|$=1.2 cm^{-1}, $|V_{dd}|$= 3.8 cm^{-1}.

3) L_QS EEH between the FbP units of triad **2**:

$\left|\vec{\mu}_x\right| = \left|\vec{\mu}_y\right| = 2.2\text{ D}$ for FbP, r_{da}=2.3 nm

$|V_{xx}|$=3.7 cm^{-1}, $|V_{yy}|$=1.2 cm^{-1}, $|V_{dd}|$= 3.8 cm^{-1}.

4) EET from L_BS of ZnP to L_NS of cNDI of triad **1**:

For simplicity, we assumed that the $L_NS \leftarrow S_0$ transition dipole of cNDI is perpendicular to the long axis of the triad and thus interacts only with $\vec{\mu}_y$ of ZnP.

$\vec{\mu}$(NDI)= 2.4 D, $\vec{\mu}$(ZnP)= 7.8 D, $\kappa = 0.64$, r_{da}=1.15 nm

$|V_{yy}|$=$|V_{dd}|$= 35 cm^{-1}.

S1. A. E. Holmes, D. Das and J. W. Canary, *J. Am. Chem. Soc.*, 2007, **129**, 1506-1507.

S2. S. V. Bhosale, M. B. Kalyankar, S. V. Bhosale, S. J. Langford, E. F. Reid and C. F. Hogan, *New J. Chem.*, 2009, **33**, 2409-2413.

S3. Banerji, N.; Bhosale, S. V.; Petkova, I.; Langford, S. J.; Vauthey, E., *Phys. Chem. Chem. Phys.* 2011**, 13**, 1019-1029.