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Supporting Information for

Excited State Dynamics and Conformations of a Cu(II)-Phthalocyanine-Perylenebisimide Dyad

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1. Absorption and PL spectra of Copper-Phthalocyanine (CuPc) in solution

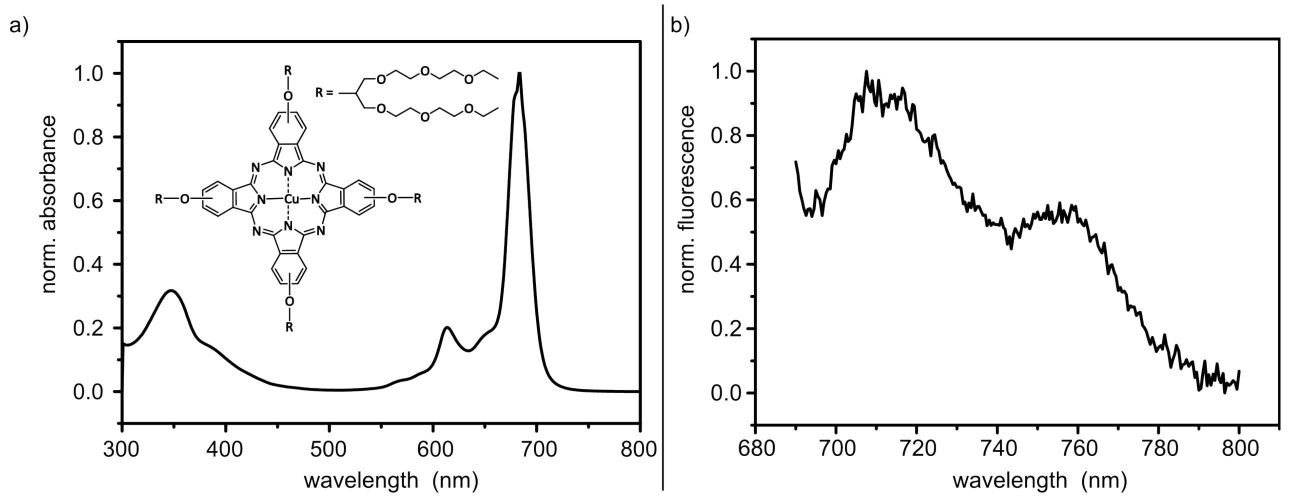

Fig. S1. Spectroscopy of the symmetric CuPc moiety dissolved in toluene. **a)** Absorption spectrum and the chemical structure. **b)** Photoluminescence of the Q-band of the CuPc moiety using an excitation wavelength of 683 nm.

2. Photophysics of Perylene Bisimide (PBI) in solution

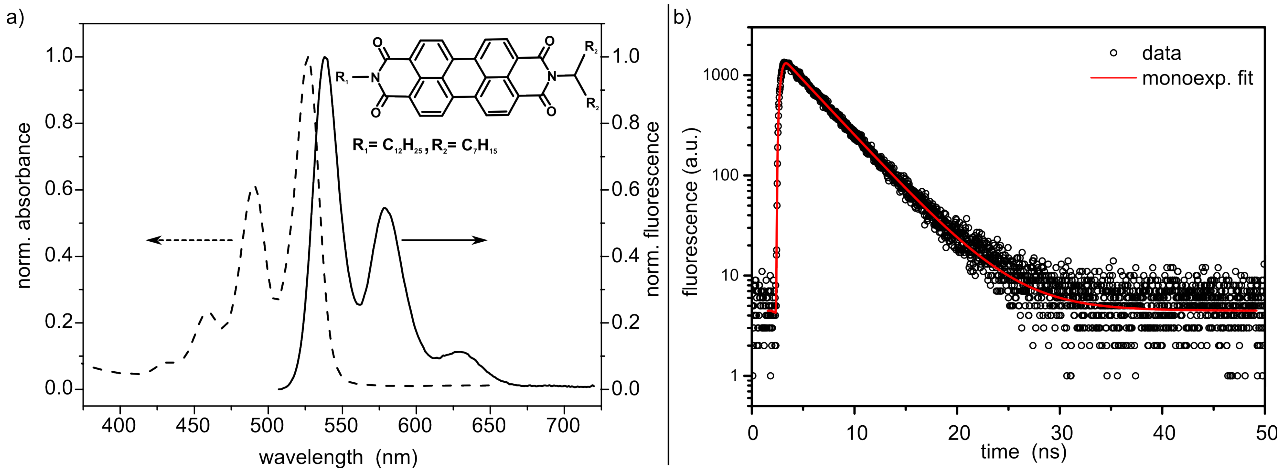

Fig. S2. a) Normalised absorption (dashed line) and PL spectrum (solid, excitation at 491 nm) of the PBI moiety. The chemical structure is shown in the inset. **b)** PL lifetime decay (black circles, excitation at 485 nm) of the PBI moiety with an exponential fit (red solid line) yielding a lifetime of 3.9 ns. Using the measured PL quantum yield of 0.88, we obtain a radiative lifetime of 4.43 ns. For all measurements PBI was dissolved in toluene.

3. Polarisation resolved picosecond lifetime measurements

Magic angle picosecond PL measurements allow to eliminate contributions due to rotational diffusion of the CuPc-PBI-dyads in solution; thus only the excited state decay is resolved. The magic angle intensity I_{ma} shown in Fig. 1c in the main text was calculated according to: [1]

$$I_{ma} = \frac{I_{\perp} + 2 \cdot I_{\parallel}}{3} . \tag{1}$$

The corresponding decay curves measured with parallel $I_{\parallel}$ and perpendicular $I_{\perp}$ polarisation with respect to the excitation polarisation using the Streak setup are shown in Fig. S3. The $I_{\parallel}$ curve can be fitted well with a bi-exponential function with lifetimes of 0.1 ns and 3.2 ns. For the $I_{\perp}$ curve three exponentials are required: two decaying components with time constants of 0.1 ns and 3.6 ns, respectively, as well as a rising component with a time constant of 0.1 ns (see table S1). This rising component is caused by rotational diffusion of the dyads.

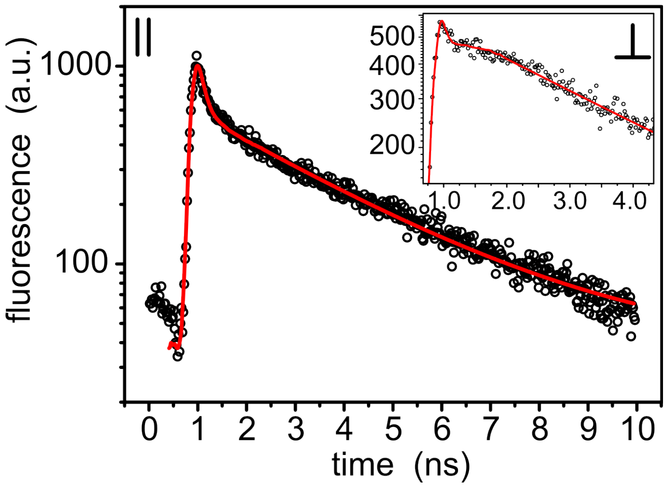

Fig. S3. Fluorescence decay curves (black circles) with polarisations parallel || and perpendicular ⊥ (inset) to the polarisation of the excitation light. The red lines are multi-exponential fits to the data, see table S1.

		decay		rise
		short	long	
∥	τ (ns)	0.1 ± 0.05	3.2 ± 0.05	-
	A (a.u.)	341 ± 20	127 ± 2	-
⊥	τ (ns)	0.1 ± 0.05	3.6 ± 0.05	0.1 ± 0.05
	A (a.u.)	1015 ± 44	171 ± 2	-518 ± 33

Table S1. Table with the fitted time constants τ and amplitudes *A* from the fits to the decay curves in Figure S3. Temporal errors represent the resolution of the setup.

4. Estimation of the fraction of FOLDED dyads

Based on the measured time constants for isolated PBI as well as for the dyads in the OPEN and FOLDED conformation, we can estimate the fraction of FOLDED dyads. To simplify the discussion we neglect the dyad's CuPc emission and consider only its PBI emission, which is justified by the data presented in Fig. 1 in the main text.

a) Isolated PBI:

For isolated PBI we measured a total decay rate of $k_{PBI} = k_{r,PBI} + k_{nr,PBI} = 1/(3.9\text{ ns})$, with $k_{r,PBI}$ and $k_{nr,PBI}$ being the radiative and non-radiative decay rates for PBI (Fig. S2). Together with the PL quantum yield $\Phi_{PBI} = 0.88$, measured with an integrating sphere, we obtain a radiative rate of $k_{r,PBI} = 1/(4.43\text{ ns})$.

b) OPEN dyad:

The measured decay rate of the PBI emission of the dyads in OPEN (or TRANS) conformation was $k_{OPEN} = 1/(3.2\text{ ns})$, see Fig. 1. Since in OPEN dyads energy transfer from the PBI to the CuPc unit with a rate constant $k_{T,O}$ also contributes, it follows $k_{OPEN} = k_{r,PBI} + k_{nr,PBI} + k_{T,O}$. Hence, $k_{T,O} = 1/(17.8\text{ ns})$, which translates into a transfer efficiency of $E_{T,O} = k_{T,O} / k_{OPEN} = 0.18$. The PL quantum yield of PBI in an OPEN dyad then is $\Phi_{OPEN} = k_{r,PBI} / k_{OPEN} = \Phi_{PBI} - E_{T,O} = 0.7$.

c) FOLDED dyad:

The picosecond data revealed a decay rate faster than 1/(0.1 ns) for the dyads in FOLDED conformation. As this rate is limited by the resolution of the Streak-setup, we start here with the transfer rate of $k_{T,F} = 1/(3\text{ ps})$ for the transfer from the PBI to the CuPc unit of the FOLDED dyads determined from the femtosecond pump-probe data (see Fig. 3b). Hence, the decay rate for PBI in a FOLDED dyad is $k_{FOLD} = k_{r,PBI} + k_{nr,PBI} + k_{T,F} = 1/(2.99\text{ ps})$. These numbers yield a transfer efficiency from PBI to

CuPc of $E_{T,F}$ = 0.997 and a calculated PL quantum yield of PBI of Φ_F = 0.0007 in a FOLDED dyad. The latter number is in good agreement with the measured PL quantum yield of ≤ 0.005.

From our picosecond data we obtained an amplitude for the short (FOLDED) component that is three times larger than that of the long (OPEN) component, or in other words, we measure three times more photons from FOLDED dyads than from OPEN ones. Based on the PL quantum yields of PBI in both conformations, as derived above, it is straightforward to show that more than 99.9 % of all dyads must exist in the FOLDED conformation to yield such amplitudes.

5. Additional nanosecond pump-probe data on the dyads

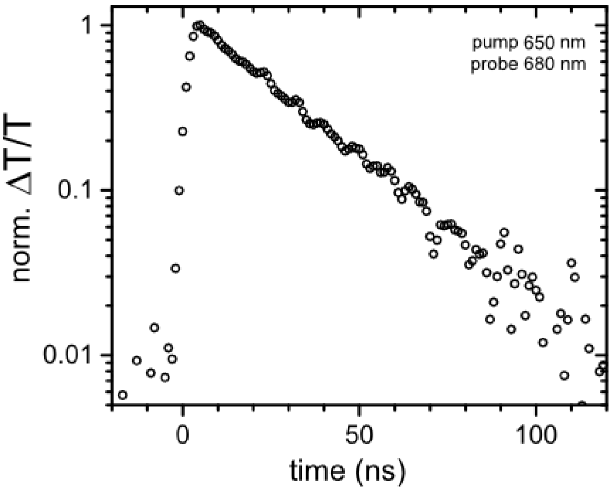

Fig. S4. Nanosecond pump-probe transient of the dyad dissolved in toluene using pump at 650 nm and probe at 680 nm.

6. Additional femtosecond pump-probe data on PBI

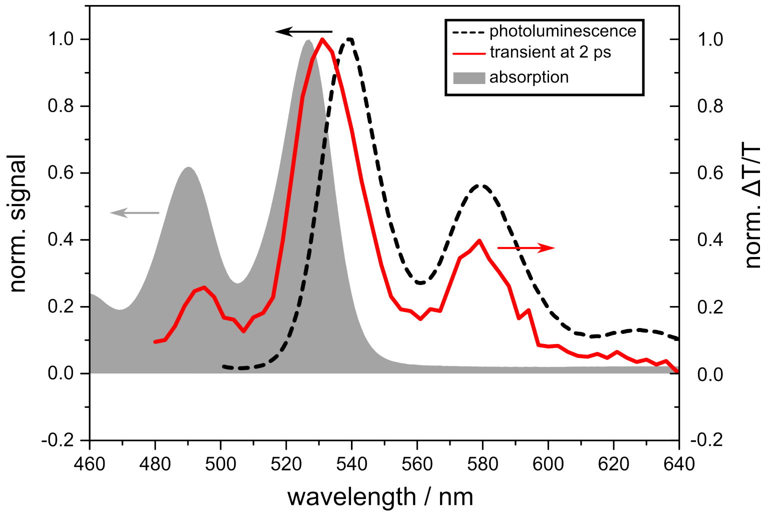

Fig. S5. Femtosecond pump-probe transient spectrum of the isolated PBI moiety at 2 ps delay with pump at 520 nm (solid red line). Comparing this transient with the absorption spectrum (grey filled area) and the PL spectrum of PBI (dashed line), the positive ΔT/T signals can be clearly attributed to ground state bleach (around 520 nm) and to stimulated emission (around 550 nm) of the PBI moiety.

7. Experimental section

A. Materials and Methods

4-{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-((2-ethoxyethoxy)-ethoxy)ethoxymethyl] ethyloxy}-1,2-dicyanobenzene (1) [2], 4-(6-hydroxyhexylsulfanyl)-1,2-dicyanobenzene (2) [3] and N-(1-Heptyloctyl),N'-(octyl-8'-azido)-perylene-3,4,9,10-tetracaboxylic acid bisimide (PBI-N3) [4] were synthesized and purified according to literature procedures. All reaction solvents were dried and purified as described by Perrin and Armarego [5]. The commercially available reagents were used without further purification. Silica gel (E. Merck) was used for column chromatography. Fourier transform infrared (FT-IR) spectra were recorded between 4000 and 650 cm^{-1} using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. The mass spectra were recorded on MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT using 2,5-dihydroxybenzoic acid as matrix.

For the spectroscopic measurements the molecules were dissolved in spectroscopic grade toluene (Sigma Aldrich, 99.8 %). The resulting concentration of all samples was 10^{-6} M. The steady-state absorption and emission spectra were recorded using commercial spectrometers (absorption: Perkin-Elmer Lambda-750, emission: Varian Cary Eclipse). The photoluminescence quantum yield was measured with a spectrofluorometer (JASCO, FP 8600) with an integrating sphere. The accuracy of these measurements is ± 0.005.

The fluorescence lifetime curves were measured using a Streak-camera setup. The solution was excited with a power of P = 0.58 mW at 450 nm using the frequency doubled and linearly polarized output of a pulsed titan:sapphire laser (Tsunami, Model 3980, both Spectra Physics; pulse width: 5 ps; repetition rate: 81 MHz). The emission of the dyad was collected under an angle of 90° to reduce scattered laser light and was directed to two broadband polarising beam splitters. To detect simultaneously the emission with parallel and perpendicular polarisation with respect to that of the excitation light, we slightly displaced the second beam splitter to combine both signals again with a spatial offset [6]. These two parallel beams are directed onto a spectrograph that is equipped with a mirror, and detected by a Streak-camera in photon counting mode (C5680, Hamamatsu). By reconvolution of the recorded picosecond transients with the instrument response function a time resolution of 100 ps is achieved. The instrument response function was measured using a scattering solution.

For the femtosecond pump-probe measurements we employed a RegA9000 regenerative amplifier system (pulse length 210 fs) at 100 kHz repetition rate from Coherent. 88 % of its output intensity was used to pump an OPA (Coherent), which provides the pump beam at a wavelength of 510 nm. The pump beam diameter was set to about 300 µm and the pump fluence was 10 – 30 µJ/cm². The remaining 12 % of the output intensity of the regenerative amplifier was used to create the probe light between 480 and 750 nm by means of a YAG-crystal. The DT/T spectra were recorded using a lock-in amplifier (SR830, Stanford Research) and a monochromator (spectral resolution 3 nm, $\lambda/\Delta\lambda = 200$) with a silicon diode.

Nanosecond pump-probe spectra were measured using a flash photolysis setup (Applied Photophysics). The sample solution was excited at 540 nm, 610 nm or 650 nm, respectively, by an optical parametric oscillator (Rainbow-Quantel) which was pumped with the 3rd harmonic output of a Nd:YAG laser (Brilliant-Quantel). The excitation energy flux was fixed to 360 µJ / cm². The probe was provided by a Xenon white light source. The $\Delta T/T$ spectra were recorded using a monochromator and a photomultiplier. The data were collected using a Keysight DSOS104A oscilloscope.

B. Synthesis

2(3),9(10),16(17)-Tri-({2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2- ethoxyethoxy)) ethoxymethyl] ethoxy}- 23- (6-hydroxyhexylsulfanyl) phthalocyaninato copper(II)(3)

A mixture of 4-{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-((2-ethoxyethoxy)-ethoxy) ethoxymethyl] ethyloxy}-1,2-dicyanobenzene (**1**) (783 mg, 1.740 mmol, 9 equiv.), 4-(6-hydroxyhexylsulfanyl)-1,2-dicyanobenzene (**2**) (51 mg, 0.194 mmol) and anhydrous $CuCl_2$ (174 mg, 1.305 mmol) were refluxed in anhydrous N,N-dimethylaminoethanol (1.8 ml) for 24 h under argon atmosphere. N,N-dimethylaminoethanol was removed by adding hexane to the reaction mixture, the crude product was precipitated. The solid was dissolved in dichloromethane, filtered to remove inorganic impurities, and then concentrated. The crude product was purified by column chromatography over silica gel using CH_2Cl_2:EtOH/25:1 as eluent to collect asymmetric **3** and symmetric Pc derivatives. Furthermore, the phthalocyanine **3** was purified by using preparative silica gel thin layer chromatography using CH_2Cl_2:EtOH/25:2 as eluent. Yield: 12% (40 mg). R_f 0.62 (CH_2Cl_2:EtOH/25:2). IR n_{max}/cm^{-1} (ATR): 3400 (OH), 3040 (ArCH), 2985-2860 (CH_2, CH_3), 1654 (C=N), 1608 (ArC=C), 1507, 1472, 1400, 1345, 1278, 1233, 1120-1085 (C–O–C). Calcd. for $C_{83}H_{118}N_8O_{22}SCu$: %C, 59.44; %H, 7.09; %N, 6.68. Found: %C, 59.25; %H, 7.05; %N, 6.70. MS (MALDI-TOF) *m/z*: Calc.: 1675.5; Found: 1676.9 $[M+H]^+$, 1838.4 $[M+7Na]^+$.

2(3),9(10),16(17)-Tri-({2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2- ethoxyethoxy)) ethoxymethyl] ethoxy} -23-[(prop-2-ynyloxy)hexylsulfanyl] phthalocyaninato copper(II) (4)

NaH (20 mg, 0.85 mmol) was added to solution of **3** (143 mg, 0.085 mmol) in anhydrous THF (6 ml) under argon atmosphere. After stirring for 10 min, propargyl bromide (1 ml, 7.2 mmol) was added. The reaction mixture was stirred under argon atmosphere at room temperature for 24 h. The greenish-blue mixture was filtered off and solvent was evaporated under reduced pressure. The oily crude product was purified by using preparative silica gel thin layer chromatography using CH_2Cl_2:EtOH/25:2 as eluent. Yield 85 mg (58 %). R_f 0.76 (CH_2Cl_2:EtOH/25:2). IR n_{max}/cm^{-1} (ATR): 3241 (CºC-H), 3040 (ArCH), 2972-2860 (CH_2, CH_3), 2105(CºC), 1605 (ArC=C), 1508, 1472, 1400, 1344, 1232, 1120-1080 (C–O–C). Calcd. for $C_{86}H_{120}N_8O_{22}SCu$: %C, 60.26; %H, 7.06; %N, 6.53. Found: %C, 60.12; %H, 7.05; %N, 6.45. MS (MALDI-TOF) *m*/*z*: Calc.: 1714.05; Found: 1789.6 $[M+2K]^+$, 1876.7$[M+7Na]^+$.

2(3),9(10),16(17)-Tri-({2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)) ethoxymethyl] ethoxy}- 23- [({N-(1-heptyloctyl), perylene-3,4,9,10-tetracaboxylic acid bisimide- N'-(octyl-)8'-1H-1,2,3-triazole-4-yl)}-methoxy) hexylsulfanyl)] phthalocyaninato copper(II)(CuPc-PBI Dyad)

Alkynylphthalocyanine **4** (75 mg, 0.044 mmol) and N-(1-heptyloctyl), N'-(octyl-8'-azido)-perylene-3,4,9,10-tetracaboxylic acid bisimide (**PBI-N3**) (54 mg, 0.072 mmol) were dissolved in degassed CH_2Cl_2 (10 mL) under argon atmosphere. N,N,N',N",N" pentamethyldiethylenetriamine (14 mg, 0.071 mmol) was added and the solution was purged 5 min with argon. Then copper (I) bromide (11 mg, 0.077 mmol) was added and the mixture was purged with argon 5 min more. The reaction mixture was stirred at room temperature for 24 h, then diluted with CH_2Cl_2 and washed with water (10 mL). The organic phase was dried on Na_2SO_4 and concentrated. CuPc-PBI Dyad was purified by silica gel column chromatography. Elution with ethylacetate removed most of the impurities, then the column was equilibrated with CH_2Cl_2 and eluted by a gradient ending with CH_2Cl_2: EtOH/25:2. CuPc-PBI Dyad was obtained pure in after a last purification by preparative silica gel thin layer chromatography using CH_2Cl_2: EtOH/100:9 as eluent. Yield: 63% (68 mg). R_f 0.62 (CH_2Cl_2: EtOH/100:9). IR n_{max}/cm^{-1} (ATR): 3040 (ArCH), 2922-2859 (CH_2, CH_3), 1692(C=N), 1654 (C=N), 1606 (ArC=C), 1508, 1466, 1403, 1341, 1233, 1120-1085 (C–O–C). Calcd. for $C_{133}H_{175}N_{13}O_{26}SCu$: %C, 64.72; %H, 7.16; %N, 7.37. Found: %C, 64.65; %H, 7.09; %N, 7.45. MS (MALDI-TOF) *m*/*z*: Calc.: 2468.02; Found: 2469.12 $[M+H]^+$, 2545.34$[M+2K]^+$, 2633.55$[M+7Na]^+$.

C. Molecular Dynamics, Forcefield Generation

MD simulations were carried out using Gromacs 5 1. [7]) In principle, an exact MD simulation would require the determination of force fields including partial charges from first-principles quantum-mechanical calculations, which would be a formidable task (for such a large molecule). We therefore take a more approximate route by using GROMOS 54A7 [8] compatible forcefield topologies which were created using automated topology builder (ATB)[9].

Copper atoms cannot be handled by the ATB server directly and the forcefield topology of the dyad thus had to be built in three steps. As a first step, a forcefield template (bonds, angles, dihedrals, etc.) without charges was calculated with ATB for the entire phthalocyanine-perylene dyad (Pc-PBI). The copper was omitted and replaced by two hydrogen atoms.

In the second step, the charge distribution was calculated. Here, the Pc-PBI dyad was split up along the aliphatic chain in two separate parts. Each part was submitted separately to the ATB server. From the two parts, the charge distribution was obtained and inserted into the Pc-PBI dyad template from the first step.

In the third step, the two hydrogen atoms were replaced by the copper atom (parameters from GROMOS 54A7 forcefield set) by hand and it was connected to the two nitrogen atoms by a metallic GROMOS bond manually. The partial charge of a copper atom in a similar CuPc molecule without the oxygen-substituted side-groups and the sulphur atom was calculated by Liao and Schreiner [10, 11]. Assuming that the side-groups do not change the main charge distribution significantly, we used their partial charges and modified them in order to be compatible with the additional side-groups of the dyad.

The toluene force field was taken directly from the ATB database [9].

Umbrella sampling was carried out using Gromacs and free energy curves were reconstructed using the WHAM algorithm as implemented by the Gromacs tool g_wham similar as in [12]). We pulled the PBI and CuPc units away from each other along two different paths: the umbrella sampling of the first path contains 19 simulation windows of 10 ns simulation time, and that of the second path comprises 23 windows of 10 ns simulation time. The curve shown in the main text is an average over both.

8. References

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