

Supporting information for:
Rapid Energy Transfer Enabling Control of
Emission Polarization in Perylene Bisimide
Donor–Acceptor Triads

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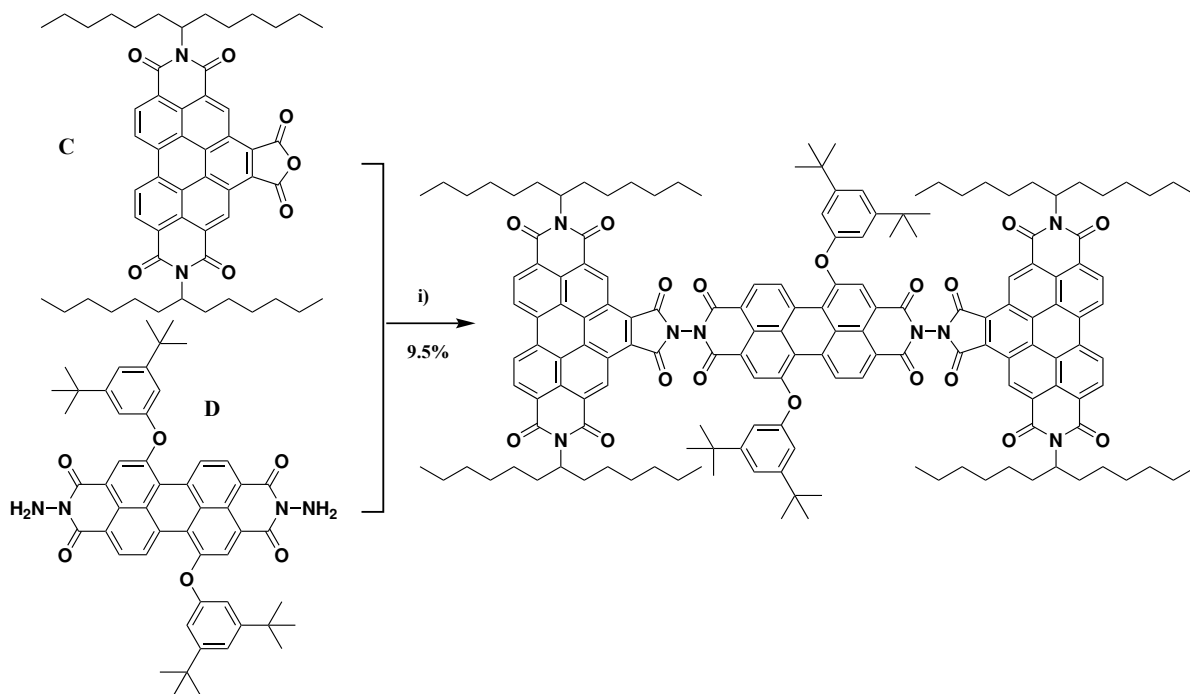
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1 Materials Synthesis and Characterization

Details of the synthesis, purification and characterization of all 5 dyes used in the study are described below. In characterising the dyes after synthesis and purification, a Shimadzu UV-3102 PC spectrophotometer was used for UV-Vis absorption spectroscopy. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using CDCl_3 as solvent and tetramethylsilane (TMS) as the internal standard. The matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectrometry (MS) was performed using a Biosystems Voyager-De Pro spectrometer With both trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyldene]malononitrile and α -cyano-4-hydroxycinnamic acid as a matrix. Gel permeation chromatography (GPC) measurements were performed in chloroform with a polystyrene based mixed-D (polymer laboratories) column (200-400.000 Da) equipped with a SPD-M20A photo diode array detector (190-800 nm, Shimadzu).

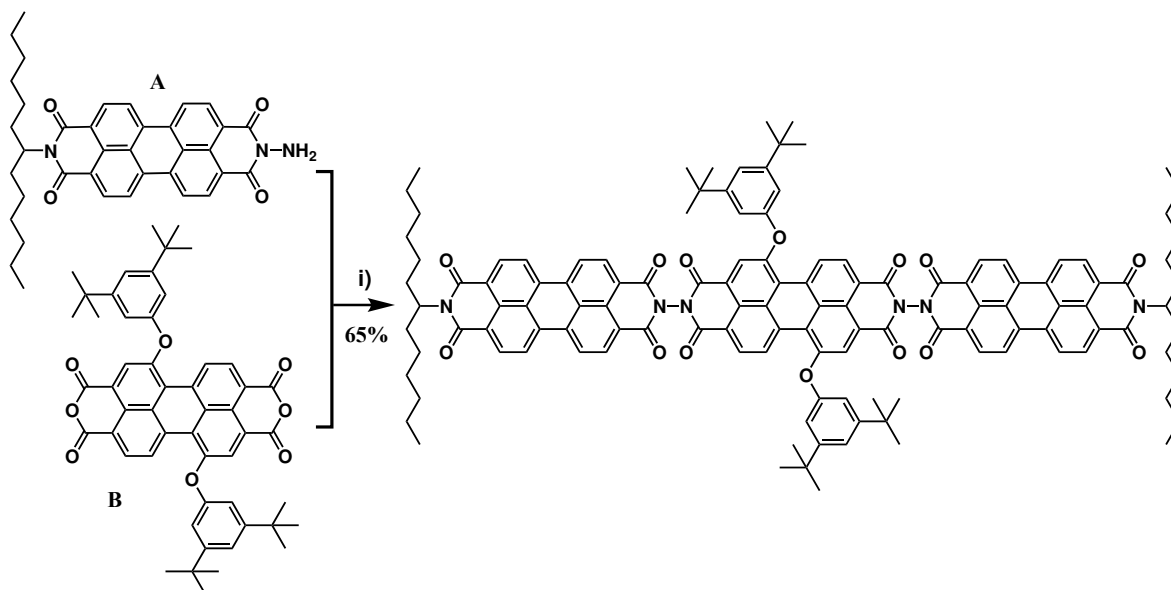
1.1 Synthesis of TH



Scheme S1: Synthesis of **TH**. (i) = DMA, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 185°C .

Compound C (94 mg, 0.111 mmol), Compound D (46 mg, 0.055 mmol) and zinc acetate (20 mg) are dissolved in dimethylacetamide (DMA, 12 ml) and refluxed for 16 hours. The reaction mixture was distilled to remove DMA and allowed to cool to room temperature before pouring into 2M aqueous HCl (40 ml) for 1 day. The precipitate was extracted with chloroform (3×80 ml) and purified by column chromatography (silica gel 40-63 μm, CHCl₃ followed by 1% EtOH in CHCl₃) and recycle GPC: Yield 13 mg (9.5%), R_f (Silica gel chloroform/ethanol 99:1) 0.8; ¹H NMR (400 MHz, CDCl₃) δ = 0.82 (t, 24H, CH₃), 1.24 (m, 32H, CH₂), 1.36 (s, 36H, t-butyl), 1.95 (m, 4H, α-CH₂), 2.34 (m, 4H, α-CH₂), 5.30 (m, 4H, NCH), 7.11 (s, 4H, ortho H-phenoxy), 7.37 (s, 2H, para H-phenoxy), 8.51 (s, 2H, perylene bisimide), 8.80 (d, 2H, perylene bisimide), 9.25 (s, 4H, perylene trisimide), 9.52 (d, 4H, perylene trisimide), 9.81 (s, 2H, perylene bisimide), 10.48 (s, 4H, perylene trisimide). UV/Vis (CHCl₃) λ_{max}(ε) = 377 (76500), 411 (35700), 436 (6900), 466 (101200), 524 (39400), 562 (60400); (MALDI-ToF MS) m/z: calculated for C₁₆₀H₁₆₈N₈O₁₈, 2489.24; found 2489.41([M]⁻).

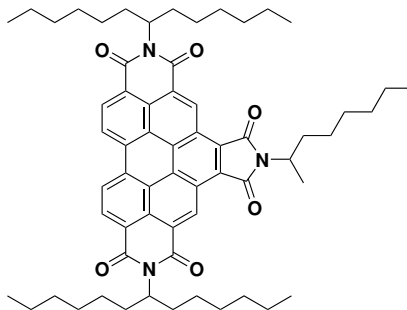
1.2 Synthesis of TL



Scheme S2: Synthesis of **TL**. (i) = DMA, Zn(OAc)₂·2H₂O, 185°C.

Compound **TL** was synthesized according to a procedure reported in the literature.^{S1} Yield 108 mg (65%), ¹H NMR (400 MHz, CDCl₃) δ = (0.83 (t, 12H, CH₃), 1.25 (m, 32H, CH₂), 1.34 (s, 36H, t-butyl), 1.89 (m, 4H, β -CH₂), 2.25 (m, 2H, β -CH₂), 5.2 (m, 2H, NCH), 7.08 (s, 4H, ortho-H-phenol), 7.36 (s, 2H, para-H-phenol), 8.46 (2H, s, H perylene bisimide), 8.6-8.8 (m, 18H, perylene), 9.77 (d, 2H, perylene bisimide); ¹³C NMR (100 MHz, CDCl₃) δ = 14.07, 22.61, 27.06, 29.25, 29.71, 31.4, 31.8, 32.39, 35.16, 54.91, 114.55, 119.82, 121.66, 122.34, 122.53, 123.21, 123.39, 125.08, 125.85, 126.28, 129.09, 129.63, 131.08, 132.39, 133.5, 134.12, 135.24, 153.85, 154.14, 156.26, 160.01, 160.12; UV/Vis (CHCl₃) $\lambda_{\max}(\epsilon)$ = 461.5 (34200), 494 (79800), 533 (152700), 556 (108800); (MALDI-ToF MS) m/z: calculated for C₁₂₆H₁₁₈N₆O₁₄, 1938.87; found 1938.95 ([M]⁻).

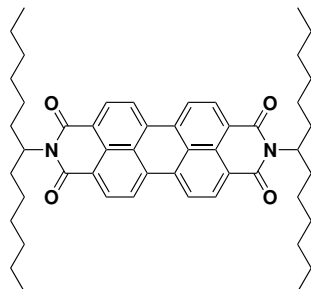
1.3 Synthesis of DH



Scheme S3: **DH**, the donor unit from dye **TH**.

Compound **DH** was synthesized according to a procedure reported by Langhals.^{S2} ¹H NMR (400 MHz, CDCl₃) δ = 0.83 (t, 15H, CH₃), 1.2-1.5 (m, 40H, CH₂), 1.73 (d, 3H, NCHCH₃), 1.96 (m, 5H, CH₂), 2.36 (m, 5H, α -CH₂), 4.66 (m, ¹H, NCH), 5.32 (m, 2H, NCH), 9.16 (s, 2H, perylene trisimide), 9.33 (s, 2H, perylene trisimide), 10.43 (s, 2H, perylene trisimide); UV/Vis (CHCl₃) $\lambda_{\max}(\epsilon)$ = 371.5 (36900), 411 (13000), 436 (34200), 466 (52900); (MALDI-ToF MS) m/z: calculated for C₆₂H₇₇N₃O₆, 959.58; found 959.57([M]⁻).

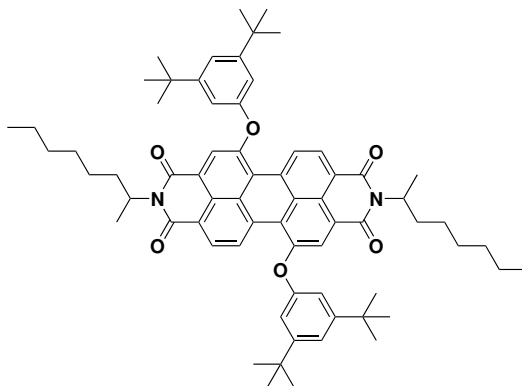
1.4 Synthesis of DL



Scheme S4: **DL**, the donor unit from dye **TL**.

Compound **DL** was synthesized according to procedure reported previously.^{S3} ^1H NMR (400 MHz, CDCl_3) $\delta = 0.83$ (d, 12H, CH_3), 1.12-1.31 (m, 24H, CH_2), 1.88 (m, 4H, $\beta\text{-CH}_2$), 2.26 (m, 4H, $\beta\text{-CH}_2$), 5,19 (m, 2H, NCH), 8.65 (m, 8H, perylene bisimide) UV/Vis (CHCl_3) $\lambda_{\text{max}}(\epsilon) = 459$ (16800), 490 (44300), 526.5 (71400); (MALDI-ToF MS) m/z: calculated for $\text{C}_{20}\text{H}_{62}\text{N}_2\text{O}_4$, 754.47; found 754.48($[\text{M}]^-$).

1.5 Synthesis of A



Scheme S5: **A**, the acceptor unit common to both **TH** and **TL**.

Compound **A** was synthesized according to a very similar procedure reported by Langhals.^{S2} ^1H NMR (400 MHz, CDCl_3) $\delta = 0.82$ (t, 6H, CH_3), 1.21 (m, 16H, CH_2), 1.35 (s, 36H, t-butyl), 1.54 (s, 6H, t-butyl, NCH CH_3), 1.87 (m, 2H, CH_2), 2.15 (m, 2H, $\beta\text{-CH}_2$), 5.22 (m, 2H, NCH), 7.03 (s, 4H, ortho-H-phenoxy), 7.36 (s, 2H, para-H-phenoxy), 8.35 (s, 2H, perylene

bisimide), 8.62 (d, 2H, perylene bisimide), 9.66 (d, 2H, perylene bisimide); UV/Vis (CHCl₃) $\lambda_{\max}(\epsilon) = 404$ (10800), 513 (33900), 550 (52100); (MALDI-ToF MS) m/z: calculated for C₆₈H₈₂N₂O₆, 1022.62; found 1022.63([M]⁻).

2 Experimental Details of Time-Resolved Photoluminescence Spectroscopy

Time and polarization resolved photoluminescence spectra and transients with sub-picosecond resolution of the triad dyes molecules were measured using the photoluminescence up-conversion technique. Solution phase samples were excited from the front face of a quartz glass cuvette with the frequency doubled output of a SpectraPhysics Mai-Tai Ti:sapphire oscillator with 80 MHz repetition rate and 100 fs pulse duration. The emitted photoluminescence was collected by a pair of off-axis parabolic mirrors and focused onto a β -barium borate (BBO) crystal mounted on a rotation stage to allow tuning of the phase matching angle. An intense vertically polarized gate beam arriving at the BBO crystal with adjustable time delay was used to up-convert the PL at given times after excitation. The resulting sum-frequency photons were collected, dispersed in a monochromator (Jobin-Yvon Triax 120) and detected by a liquid-nitrogen-cooled CCD (SpectraPhysics Symphony II). Only PL with the same polarization as the gate beam can be detected as required for type-I phase matching. PL polarized parallel (perpendicular) to the excitation pulse was detected by setting the polarization of the excitation beam vertical (horizontal) and measuring the sum-frequency generation intensity. Spectra at certain times after excitation were recorded by varying the relative delay between the pump and gate beams, and scanning the BBO crystal and monochromator grating synchronously to generate and measure up-converted photons from the whole of the PL spectrum. Spectra were corrected for the instrument response function through up-conversion of light from a W-filament lamp of known emissivity. *Time resolved photoluminescence decays (200 ps resolution)* of the individual donor and acceptor dyes were recorded using the time correlated single photon counting (TCSPC) technique on a PicoQuant Pico Harp 300 system. Samples were excited by the output from a 450 nm diode laser (LDH-P-C-450) powered by a picosecond pulsed diode laser driver (PDL 820) with pulse duration of 200 ps FWHM and a repetition rate of 16 MHz. These data were

primarily used for determination of PL lifetimes for use in FRET calculations, as described in the main text.

3 PL quantum efficiencies, PL lifetimes, transient PL intensities and PL anisotropy of reference dyes **DH**, **DL** and **A**

Time resolved photoluminescence transients of the 3 individual donor dyes **DH**, **DL** and **A** were measured with both the photoluminescence upconversion and TCSPC techniques as described in the previous section. Overall PL decay lifetimes were determined by fitting a monoexponential curve to the tail end of each trace, after any energy transfer has taken place. The *Photoluminescence Quantum Yield* of the triad dyes **TH** and **TL**, and the three reference dyes **DH**, **DL** and **A** was recorded using an integrating sphere (Newport 70682NS) with the technique described by Mello *et al.*^{S4} Solutions of each dye in chloroform were excited with the attenuated tunable output of an optical parametric oscillator (Inspire HF 100). PL emission and pump intensities were measured with a spectrally calibrated CCD and spectrometer which was fibre coupled to the exit port of the integrating sphere. Absolute quantum yield values of the 3 dyes were cross checked against a solution of known quantum efficiency, cresyl violet in ethanol.^{S5}

The extracted raw PL lifetimes and PL quantum efficiencies were used in the FRET calculations in the body and Figure 4 of the main text.

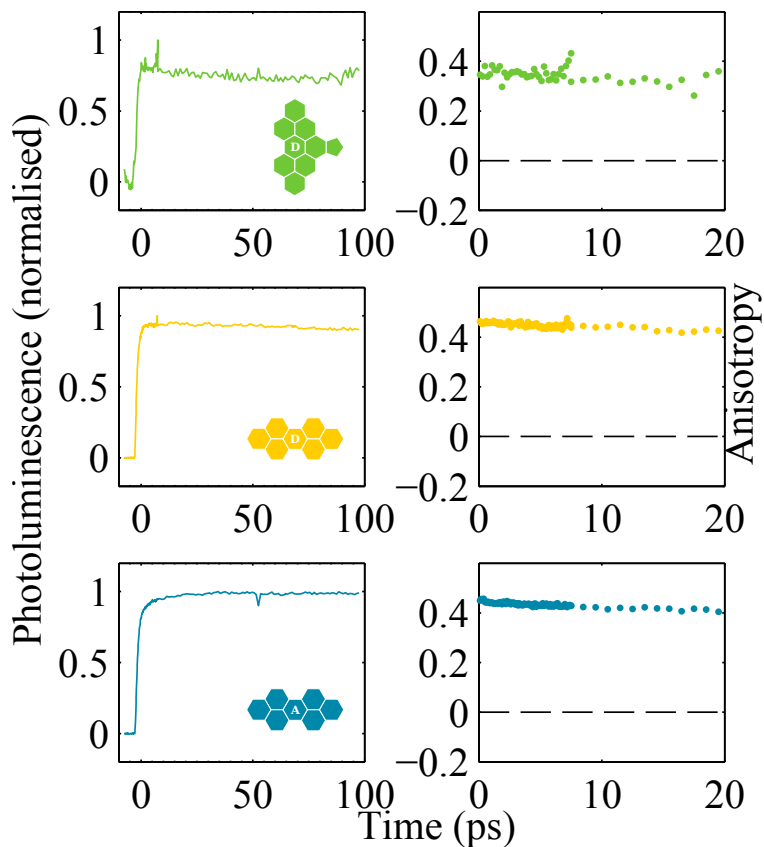


Figure S1: Time resolved photoluminescence measured by PL upconversion at 530 (DH and DL), and 620 nm (A), along with the calculated PL anisotropies for each of the 3 individual donor and acceptor units.

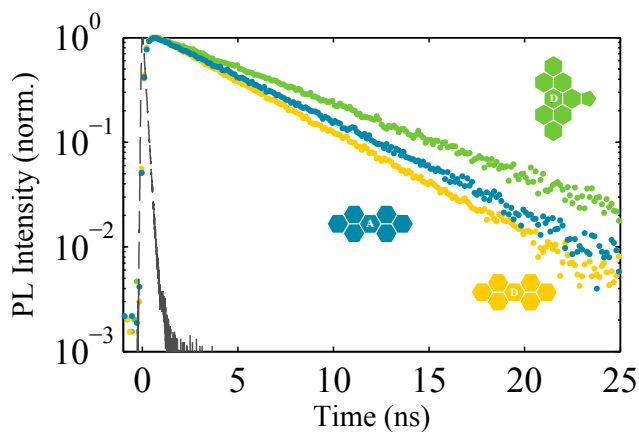


Figure S2: Time resolved photoluminescence transients measured by TCSPC for donor and acceptor reference dyes DH, DL, and A. The instrument response function is also included for reference (grey dashed line). All samples were measured in CHCl_3 solution. The pump beam was vertically polarized and the polarizer in the detection beam path was set to the magic angle (54.7°).

Table S1: Decay constants as determined by fitting a monoexponential decay to the tail of the PL spectra of each of the 5 dyes as measured by TCSPC. The short and long wavelengths correspond to emission detected from the donor and acceptor subunits respectively. Values in parentheses are the detection wavelengths in nm of the PL traces from which each of the lifetimes were extracted. ([†] - the approximate timescale of energy transfer from donor to acceptor as determined by fitting a bi-exponential decay model to the short lived PL with wavelength of 510 nm.)

Dye	τ_d (ps)	τ_a (ps)
TH	1.96 [†] (510)	4260 (590)
TL	1.05 [†] (510)	4220 (590)
DH	6300 (510)	–
DL	4400 (580)	–
A	–	5000 (580)

Table S2: Photoluminescence quantum yields for the triad dyes and monomers. Quantum yields are accurate to ± 0.05 . Excitation wavelength dependence of the quantum yield was found for the triad dyes **TH** and **TL**. The excitation wavelength for each of these dyes is given in the first column. No wavelength dependence was found for the reference dyes **DH**, **DL** and **A**.

Dye	λ_{ex}	PLQY
TH	460	0.66
	515	0.75
	525	0.80
TL	450	0.52
	490	0.62
	525	0.67
DH	410	0.20
DL	460	0.86
A	475	0.72

4 Time resolved PL spectrum of acceptor dye

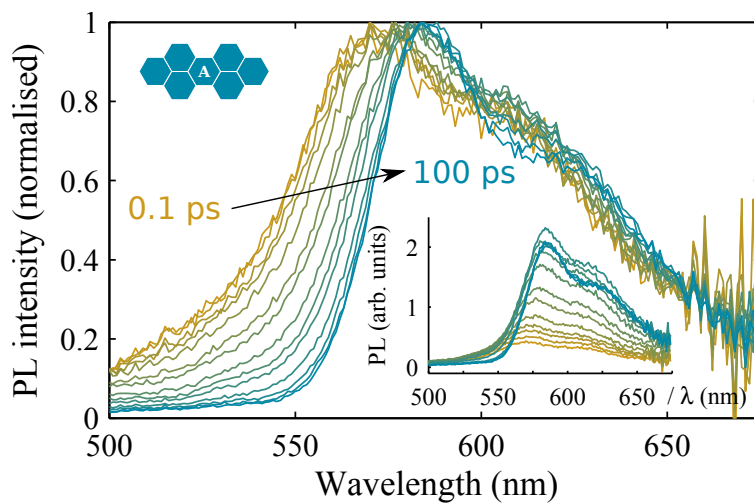


Figure S3: Time resolved PL spectra of dye 5 in solution at short times (0.1 to 100 ps) after excitation. The main plot shows the normalized time resolved PL, whereas the inset shows the raw data. Each spectrum was corrected for the spectral response of the system.

5 Steady State Photoluminescence

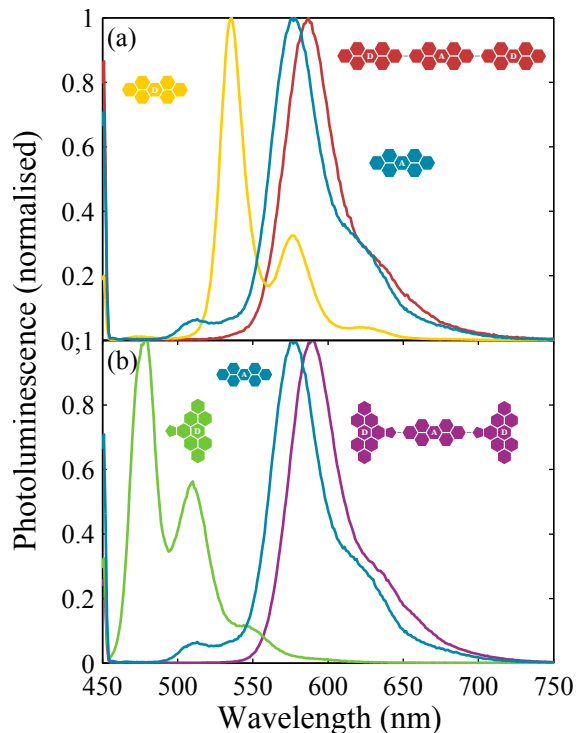


Figure S4: Time integrated photoluminescence spectra of dilute (peak absorbance ≤ 0.1 OD) solutions of a) dyes **TL**, **DL** and **A**; b) dyes **TH**, **DH** and **A** in CHCl_3 , recorded with a Horiba Fluorolog. In each case the dyes were excited with wavelength 450 nm. Dilute solutions were used in order to minimize fluorescence reabsorption effects. Light of 450 nm wavelength light preferentially excites the donor moiety. PL emission from the isolated donor molecules mirrors the donor absorption spectra. However, once they are coupled to an acceptor molecule in the triads, only PL from the acceptor is observed, indicating that efficient energy transfer has occurred.

6 Density Functional Theory

DFT calculations were performed with the NWChem 6.3 package^{S6} for Linux on a computer with an Intel Core i7-3770 CPU and 32 GB RAM. Ground state geometries were optimized at the B3LYP/6-31G* level. Calculations were carried out to assess the extent and energies of the frontier molecular orbitals. In order to reduce computation time we only include one donor and the central acceptor unit of the triad dye **TH** as we are primarily interested in the degree of direct electronic interaction between D/A units, and the donor units at either end of the triads are identical. The phenoxy groups at the bay positions of the acceptor unit were replaced with methoxy groups and the alkyl chains attached to the carboximide N atoms were replaced with methyl groups in order to further reduce computation time. The ground state geometry was optimized at the B3LYP/6-31G* level for the both the “flat” and “twisted” molecules and the extent and energy of the frontier molecular orbitals were then calculated.

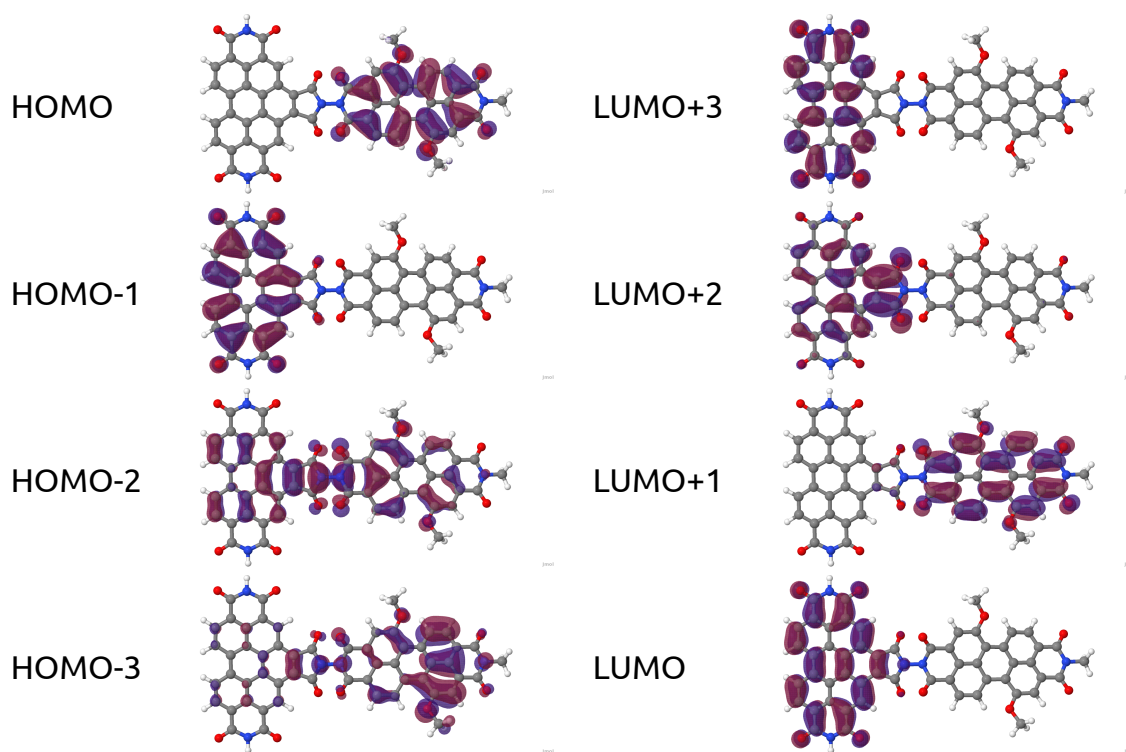


Figure S5: Isosurfaces and energies of the frontier molecular orbitals (HOMO-3 to LUMO+3) of a dimer consisting of one donor and the acceptor group of the dye **TH**. The isosurface value of each orbital is 0.2.

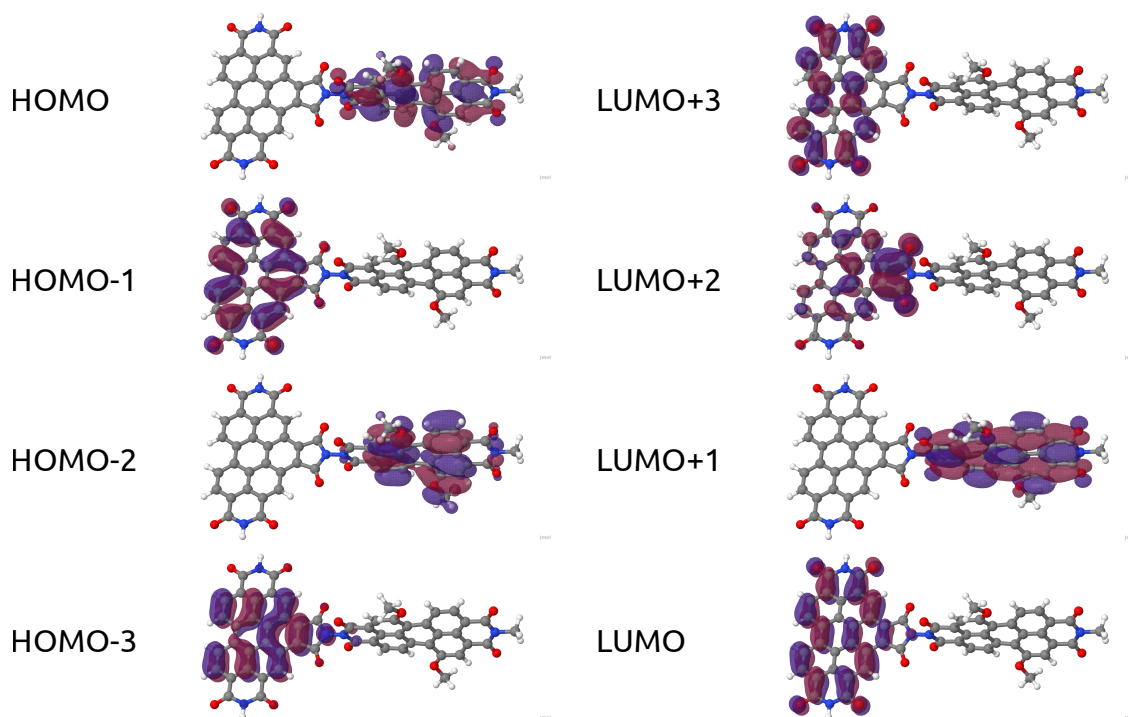


Figure S6: Isosurfaces and energies of the frontier molecular orbitals (HOMO-3 to LUMO+3) of a dimer consisting of one donor and the acceptor group of the dye **TH**. The donor is rotated by 90° about the N–N bond linking the donor and acceptor units relative to the twisted structure before ground state geometry optimization. The isosurface value of each orbital is 0.2.

References

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