

Supporting Information

Photofunctional Self-assembled Nanostructures Formed by Perylene Diimide-Gold Nanoparticle Hybrids

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Materials and methods

Solvents and reagents were purchased from commercial sources and used as received, unless otherwise specified. Hydrogen tetrachloroaurate(III) and 1,9-nonanedithiol were purchased from ABCR. All the other chemicals and reagents were purchased from Aldrich chemical company. 1-Bromo-N,N'-Bis(ethylpropyl)perylene-3,4:9,10-tetracarboxylic Diimide was synthesized following literature procedure.¹

Organic solvents for spectroscopic and microscopic studies were of spectroscopic or HPLC grade and were dried over molecular sieves (3 Å), and filtered over 0.2 µm PTFE syringe filters prior to use. All procedures with air-sensitive intermediates were performed under inert gas atmosphere (dried N₂ or Argon) using a glovebox (MBRAUN, Labmaster) or standard Schlenk techniques. Organic solvents used for these procedures were degassed with Argon and stored over molecular sieves (3 Å) in the glovebox.

UV-vis absorption and steady-state fluorescence measurements were carried out using a Varian-cary-5000 spectrometer. and a Varian-cary eclipse fluorimeter respectively. Quantum yields of the PDI-thiols were determined following the standard procedure² and using *Sulforodamine 101* solution in ethanol ($\lambda_{\text{abs}} = 576 \text{ nm}$, $\lambda_{\text{em}} = 592 \text{ nm}$, $\phi = 0.9$) as reference.

MALDI-TOF mass spectrometry was carried out using a REFLEXTM reflector time-of-flight instrument with SCOUTTM multiprobe (384) inlet. ESI mass spectrometry was performed using a Miromass Platform instrument. The samples were introduced as a solution in chloroform.

TEM was performed using a Philips CM120 Super Twin (120kV, tungsten/LaB6) or FEI (Philips) T12 - Tecnai (120kV, tungsten / LaB6). For sample-preparation 4 µL of the sample was applied to a 300-mesh copper grid coated with nitrocellulose and lacey carbon (SPI supplies).

The images were analyzed using AnalySIS 5.0 (2004, Soft Imaging System GmbH). Presented lengths measurements include the arithmetic mean and standard deviation of at least 20 samples.

SEM images were taken using a Zeiss Ultra 55 scanning electron microscope operated at 1 kV with an aperture size set to 10 μm . The images were analyzed using AnalySIS 5.0 (2004, Soft Imaging System GmbH). Presented lengths measurements include the arithmetic mean and standard deviation of at least 20 samples.

Electrochemical studies on compound **1** and **2** were carried out using a CH Instruments electrochemical workstation (model 660C). The measurements were performed in methylene chloride containing 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆), and the ferrocene/ferrocenium redox couple (Fc/Fc^+ , 0.475 V vs. SCE in CH_2Cl_2) was used as an internal reference. Platinum disk electrode (3.0 mm diameter) was employed as a working electrode, and platinum wires as counter and auxiliary electrodes. Sample concentrations were 1 mM. All electrochemical measurements were performed in nitrogen filled glove-box.

Computations were carried out using Scigress Explorer Ultra (7.7.0.49). Geometry optimization of pi-stacks of **1** and **2** was performed in vacuum using the Augmented MM3 forcefield method. The alkyl substituent at the imide nitrogens were removed for simplicity.

Femtosecond transient absorption spectroscopy was performed using a system based on a modelocked Ti:sapphire oscillator (Spectra Physics Tsunami) pumped by a CW diode pumped Nd :YVO₄ laser (Millennia Pro X). The oscillator produces a train of <100-fs pulses (bandwidth ~ 10 nm FWHM), with a peak wavelength at around 785 nm, typically of 850 mW, corresponding to ~ 10 nJ per pulse. The weak oscillator pulses are amplified by a chirped pulse regenerative amplifier (CPA) (Spectra Physics Spitfire). The pulses are first stretched, then

regeneratively amplified in a Ti:sapphire cavity, pumped by a pulsed Nd :YLF laser (Spectra Physics Evolution-15) operating at 1 kHz. After the pulse has been amplified and recompressed, its energy is about 1.0 mJ in a train of 1-kHz pulses. An independent pump pulse is obtained by pumping an optical parametric amplifier (Spectra Physics OPA-800CF) that produces 120-fs pulses tunable from 300 nm to 3 microns.

The output power of the OPA is a few micro joules (depending on the chosen wavelength) at 1 kHz. The pump beam is mechanically chopped at half the amplifier repetition rate. The chopper (C-995 TTI) is synchronized with the Spitfire pulses. Normally a few thousand pulse pairs (pump on/pump off) are averaged to produce a transient absorption spectrum with a noise level below 0.3 mOD.

A small portion of the remaining amplified pulse is used to generate a white light continuum as a probe pulse. To this end, the Ti:sapphire beam is focused onto a 3-mm thick sapphire disk by a 10-cm focal length lens, and the numerical aperture of the beam is controlled by an iris placed in front of the lens to obtain a stable and smooth white light continuum. The resulting beam is passed through a short pass filter to remove the remains of the fundamental beam from the probe white light continuum.

The pump and probe pulses are crossed in the sample at a small angle, while maintaining a magic angle between the pump and probe polarizations. The remains of the pump pulse are removed by an iris, and the probe light is imaged onto an optical fiber that brings it into an imaging interface, which focuses the light onto the entrance slit of a Jobin Yvon Triax 180 spectrograph. The light is normally dispersed by a 300 gr/mm grating onto a fast CCD camera (Andor Newton DU-970N-UV, operating at 1,000 spectra per second using "crop mode"). The whole setup is controlled by National Instruments LabView software.

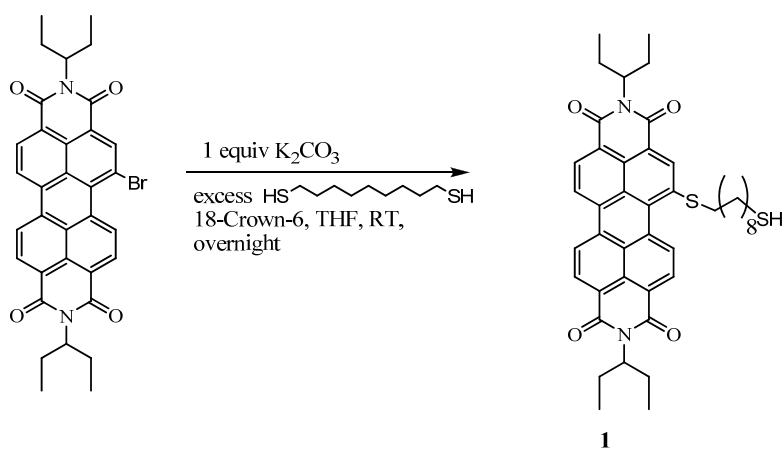
The pump power intensities were kept ~ 180 - 200 μW at 250 Hz as measured using Ophir thermal head powermeter in proximity to the sample. The laser spot of 300 micrometers diameter on the sample was measured by placing beamprofiler (Ophir Beamstar FX33) at the sample position and determining the 4-sigma (95% of the power) parameter. In the reported experiments the pump was turned to 575 nm and the optical densities of the samples (in 4 mm optical path length cuvettes) were kept between 0.2 and 0.5 at the excitation wavelength.

The instrument response function (300 fs) was recorded by repetition of the experiments with sample replaced by pure solvent and keeping all other parameters unchanged. Spectral corrections and analysis were performed using Surface Xplorer Pro (Ultrafast Systems) and Origin 7.5 (OriginLab) software.

Fluorescence lifetime measurements were performed by the time correlated single photon counting technique using FluoroCube (HORIBA Jobin Yvon) station equipped with TBX-04 detection module of less than 180 ps typical timing jitter and less than 100 ps overall time resolution. The instrument response function was obtained by measuring scattering from a standard sample (Ludox) with the monochromator set for detection at or close to the excitation source wavelength and remaining all other parameters unchanged. The excitation of samples was performed using a laser diode (NanoLED 470L) that generated 200 ps pulses of 466 nm light. The samples were excited with 1 MHz repetition rate and 10000 counts in the peak channel were collected. Lifetime decays were deconvoluted and fitted using Das6 decay analysis software. Fluorescence decays at different wavelengths were measured resulting in identical decay profiles. The representative graph for **1** corresponding to excitation at 466 nm and detection at 620 nm is provided (Figure S19).

Dynamic light scattering measurements were performed on a Viscotek 802 DLS instrument with detection at right angle using a laser wavelength of 830 nm. The data were analyzed by Omnisize 2.0 software with a correlator resolution 256 channel.

Synthesis of **1**



1-Bromo-*N,N'*-bis(ethylpropyl)perylene-3,4,9,10-tetracarboxylic diimide ¹ (20 mg, 0.033 mmol) was dissolved in THF in a glass vial which was purged continuously with N₂. K₂CO₃ (5.5 mg, 0.04 mmol) and 18-crown-6 (10.6 mg, 0.04 mmol) were also added to this mixture. Then 1,9-nonanedithiol (0.03 mL, 0.16 mmol) was added and the glass vial was closed under N₂ with the plastic lid equipped with a Teflon liner. The mixture was kept overnight under stirring at room temperature. It was then poured into dilute HCl and extracted with chloroform (3 X 50 mL), washed with brine and then with water, and dried with sodium sulfate. The solvents were removed and the solid was kept under high vacuum overnight. Then it was taken into the glove-box for purification by preparative-TLC. If purification is done on air, thiol oxidation to a mixture of products takes place.

The preparative-TLC was done by loading ~20mg of the crude compound on the TLC plate, and then eluted with 60:40 DCM/hexane mixtures. The predominant purple colored band was collected and extracted and the solvent was removed to give 15 mg (63% yield) of **1** as a red solid,. ^1H NMR (CDCl_3 , δ in ppm, 300MHz) : 8.98 (s, 1H, PDI), 8.95 (s, 1H, PDI), 8.64-8.77 (m, 5H, PDI), 5.02-5.14 (m, 2H, ethylpropyl-methyne), 3.23 (t, $J = 7.4\text{Hz}$, 2H, S-CH₂-CH₂-), , 2.20-2.34 (m, 4H, methylene of ethylpropyl), 1.87-2.02 (m, 4H, methylene of ethylpropyl), 1.70 (m, 2H, -CH₂SH), 1.25 – 1.55 (bm, 15H, nonyl+thiol), 0.90-0.94 (t, $J = 7.2\text{ Hz}$, 12H, Methyl of ethylpropyl); ^{13}C NMR(CDCl_3 , δ in ppm, 100MHz): 140, 134.5, 134.2, 133.6, 133, 129.5, 129.2, 128, 127.3, 126.8, 123.8, 122.7, 58, 57.8, 53.6, 39.3, 36.4, 34.2, 29.5, 29.4, 29.3, 29.2, 29, 28.7, 28.6, 28.5, 25.2, 24.8, 11.6.

HRMS-ESI: 720.3075 [M^+] (calculated for $\text{C}_{43}\text{H}_{48}\text{N}_2\text{O}_4\text{S}_2$: 720.3056).

UV/Vis (CHCl_3): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 545 (8778), 445 (4112).

Fluorescence (CHCl_3): $\lambda_{\text{max}}/\text{nm}$: 625, fluorescence quantum yield, $\Phi_{\text{f}} = 0.61$.

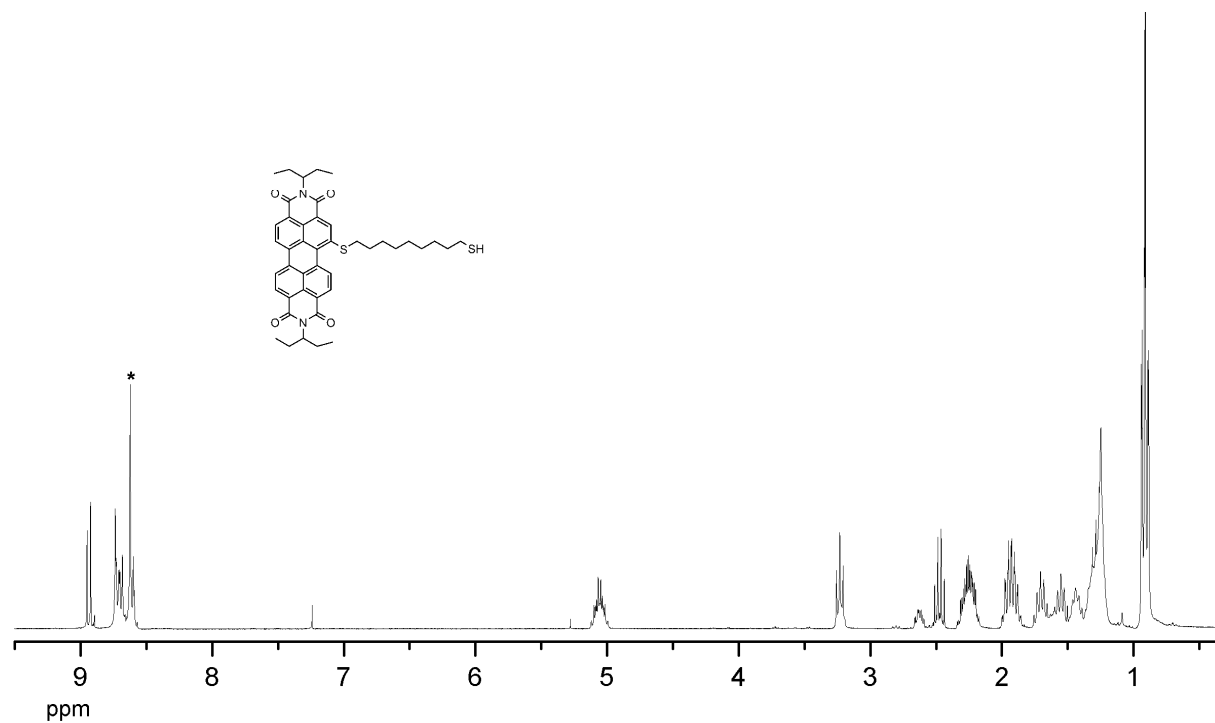


Figure S1: ¹H NMR spectrum of **1** in CDCl₃.

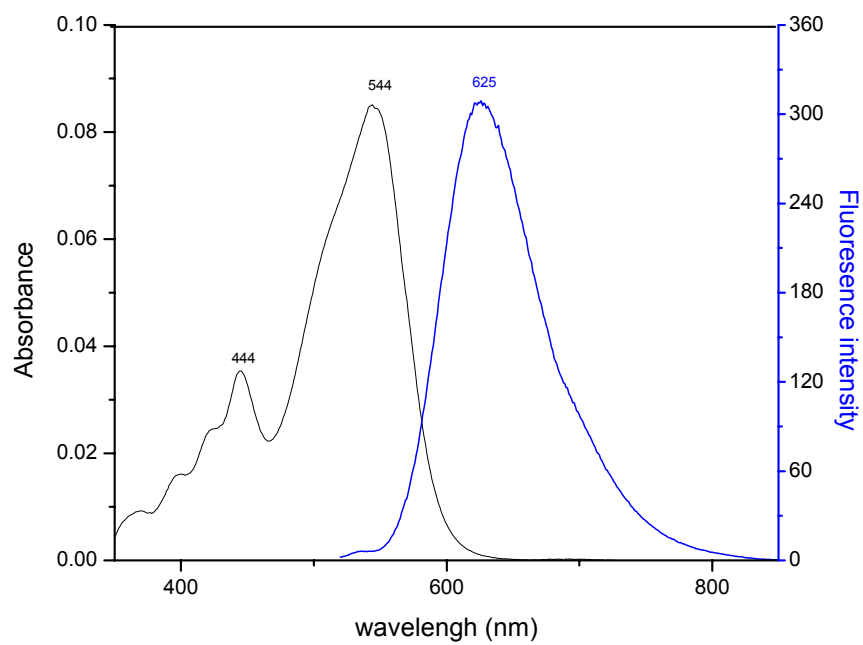
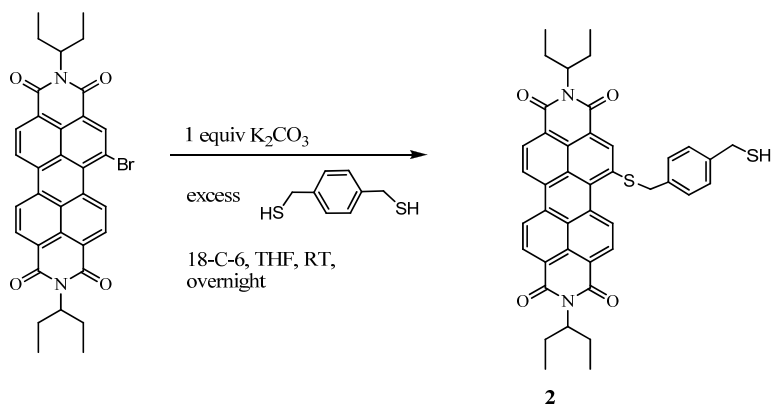


Figure S2: UV/Vis (black trace) and fluorescence (blue trace) spectra of **1** in CHCl₃.

Synthesis of 2.



1-Bromo-*N,N'*-bis(ethylpropyl)perylene-3,4:9,10-tetracarboxylic Diimide¹ (20 mg, 0.033 mmol), K₂CO₃ (5.5 mg, 0.04 mmol), 18-crown-6 (10.6 mg, 0.04 mmol) and 1,9-nonanedithiol (0.03 mL, 0.16 mmol) were reacted together and purified following the same procedure as **1** to give 15 mg (65% yield) of **2** as a red solid. ¹H NMR (CDCl₃, δ in ppm, 300MHz) : 8.88 (m, 2H, PDI), 8.63-8.72 (m, 5H, PDI), 7.20-7.31 (AA'BB', J = 8.1Hz 4H, phenyl), 5.08 (m, 2H, ethylpropyl-methylene), 4.44 (s, 2H, PDI-CH₂-S), 3.66 (d, J = 7.6 Hz, 2H, CH₂SH), 2.21-2.33 (m, 4H, methylene of ethylpropyl), 1.92-2.01 (m, 4H, methylene of ethylpropyl), 1.69 (t, J = 7.6Hz, 1H, SH), 0.90-0.95 (m, 12H, Methyl of ethylpropyl); ¹³C NMR(CDCl₃, δ in ppm, 100MHz): 141.1, 137.5, 134.2, 133.6, 133, 129.8, 129.7, 128.6, 128.2, 123.7, 122.7, 57.9, 57.8, 53.6, 43.0, 42.9, 41.0, 29.9, 28.7, 24.8, 11.6.

HRMS-ESI: 698.2284 [M⁺] (calculated for C₄₂H₃₈N₂O₄S₂: 698.2273).

UV/Vis (CHCl₃): λ_{max}/nm (ε/M⁻¹cm⁻¹): 545 (10400), 445 (5000).

Fluorescence (CHCl₃): λ_{max}/nm: 604.0, fluorescence quantum yield, Φ_f = 0.62.

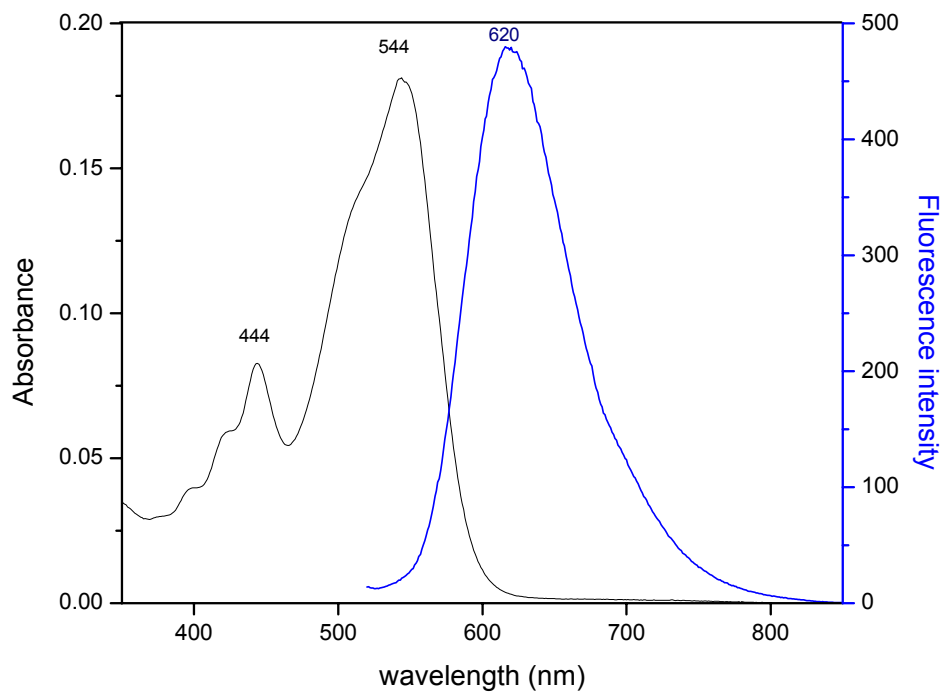


Figure S3: UV/Vis (black trace) and fluorescence (blue trace) spectra of **2** in CHCl_3 .

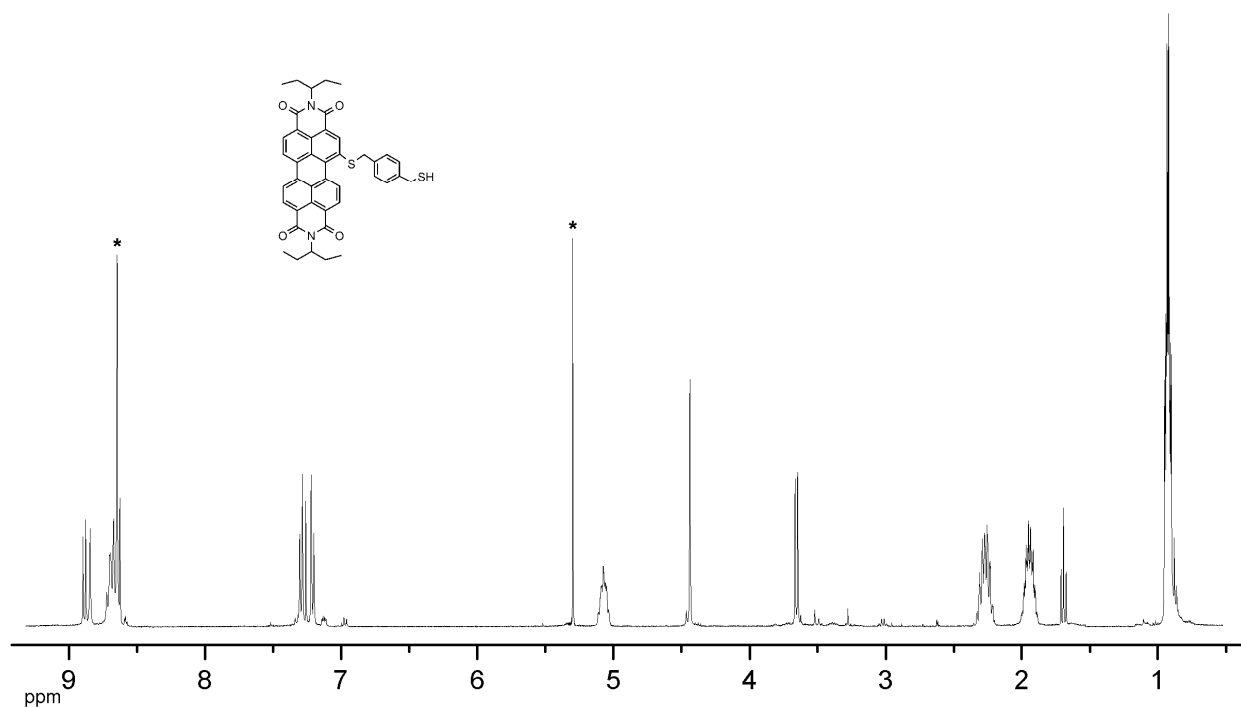


Figure S4: ^1H NMR spectrum of **2** in CDCl_3 . Stars indicate solvent peaks.

Synthesis of Triphenylphosphine stabilized gold nanoparticles

The triphenylphosphine stabilized Gold nanoparticles were synthesized following the reported procedure.³ Briefly, hydrogen tetrachloroaurate (50 mg, 0.13mmol) was added to nitrogen purged water/toluene mixture (20mL, 1:1 v/v) containing Tetra-n-octylammonium bromide (80 mg, 0.15mmol). After the Organic layer turns golden due to the transfer of the gold salt, tetraphenylphosphine (116 mg, 0.44mmol) was added. The layer lost coloration and after 10 min an aqueous solution of sodium borohydride (71 mg, 1.87mmol in 10 mL of water) was added with vigorous stirring. The resulting brown solution was stirred for three hours. The toluene layer was removed in vacuo and the resulting solid washed by a series of solvent mixtures.³ The sizes of the nanoparticles were evaluated by TEM and were found to show average particle size of 1.51 ± 0.3 nm

Preparation of the AuNP-PDI hybrids 3 and 4

In a 20 mL glass vial, gold nanoparticles and PDI thiols (~ 1:20 ratio) were mixed together in chloroform and kept with stirring under nitrogen atmosphere for 48 hours. The course of the ligand exchange reaction was monitored by the quenching of PDI fluorescence gradually over time. Hexane was added to this solution until the hybrid particles started to precipitate out. The mixture was centrifuged and the supernatant was discarded. The dried precipitate was then dissolved in chloroform and the solution was used for various experiments.

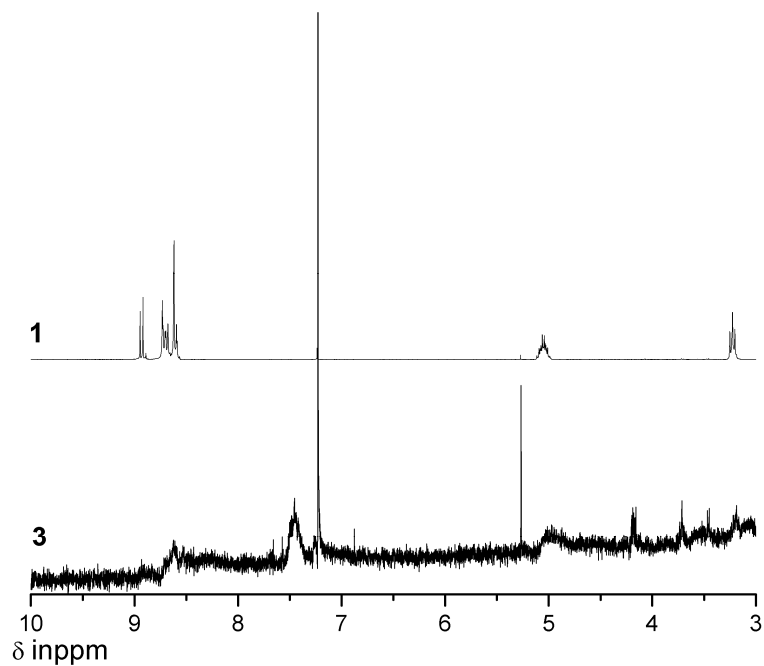


Figure S5: Comparison of ^1H NMR of **1** with the hybrid **3**, displaying the significant broadening of the peaks due to the binding of **1** to the nanoparticle surface.

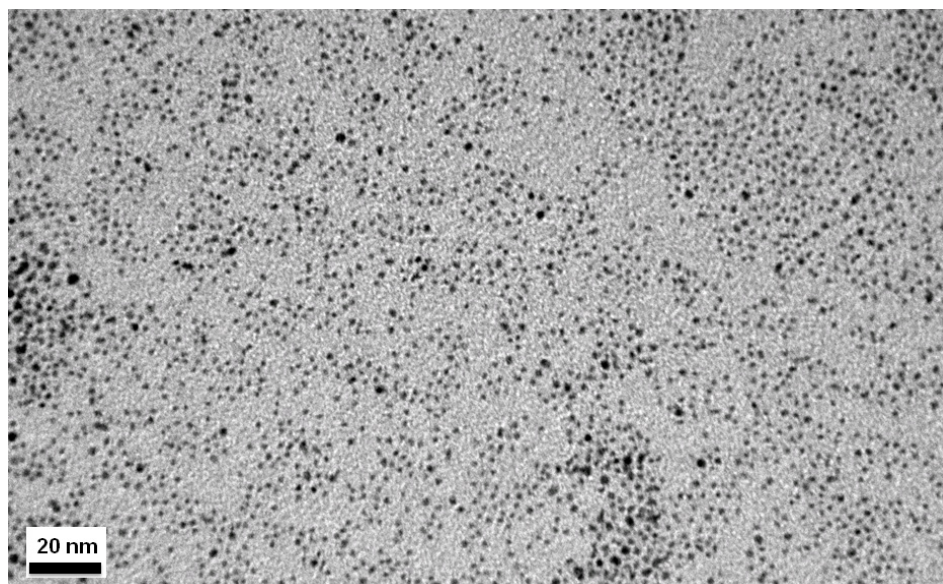


Figure S6: TEM image of tetraphenyl phosphine stabilized gold nanoparticles.

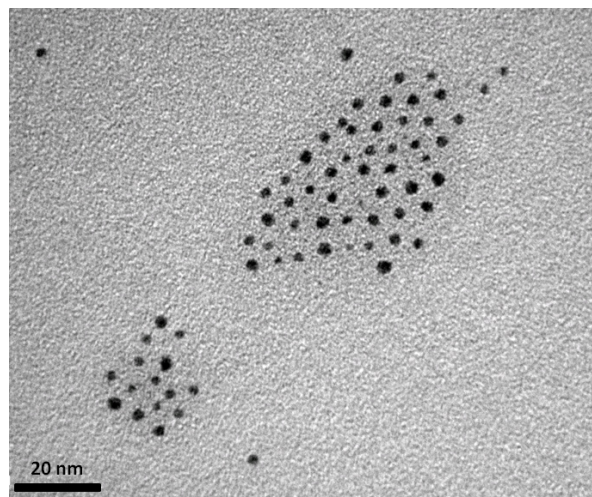


Figure S7: TEM image of small island-like aggregates of **3** deposited from 40% methanol/chloroform.

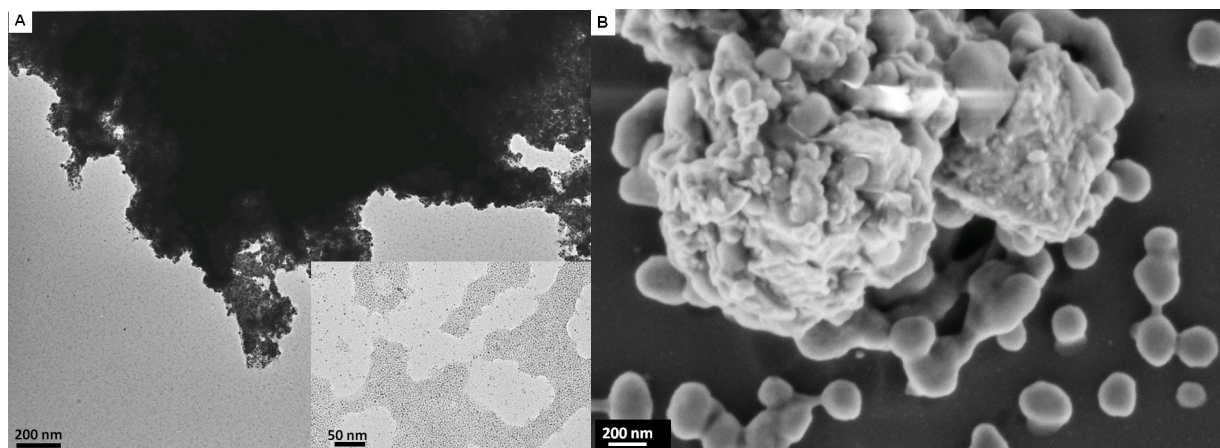


Figure S8: TEM image a) and SEM image b) of dense aggregates of **4** deposited from toluene. Inset in a) shows magnified image of a less-denser aggregate.

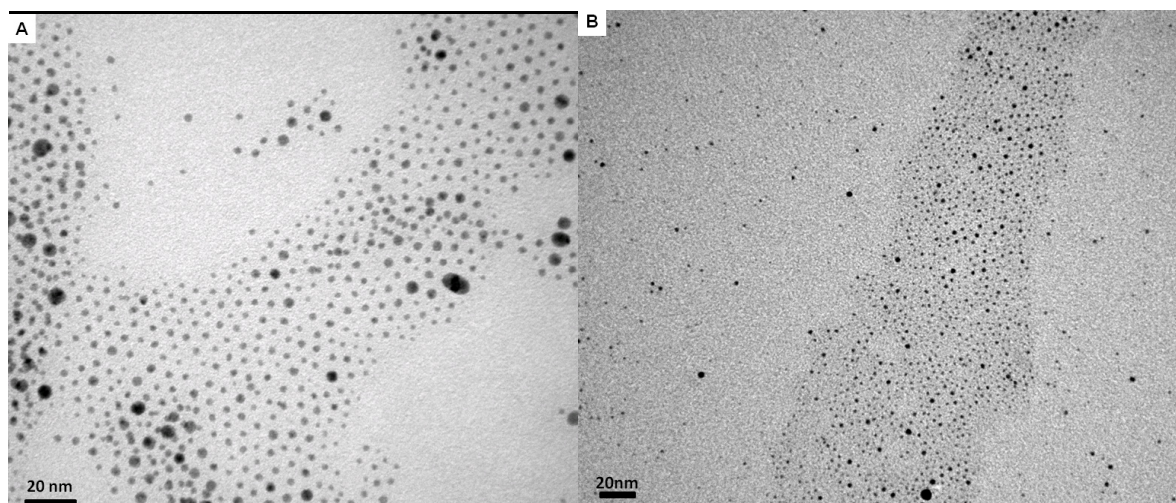


Figure S9: TEM images of a) **3** and b) **4** deposited from pure chloroform.

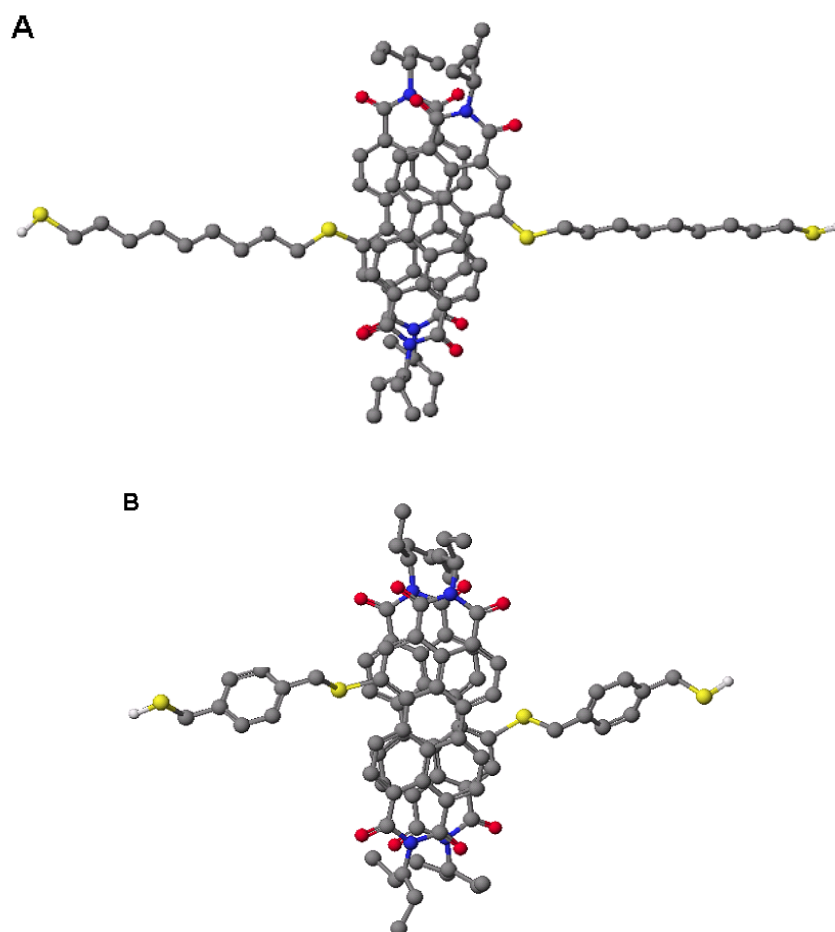


Figure S10: Molecular model of π -stack between two molecules of a) **1** and b) **2**. Hydrogens are omitted for clarity.

Photophysical studies.

Compound 1 in chloroform:

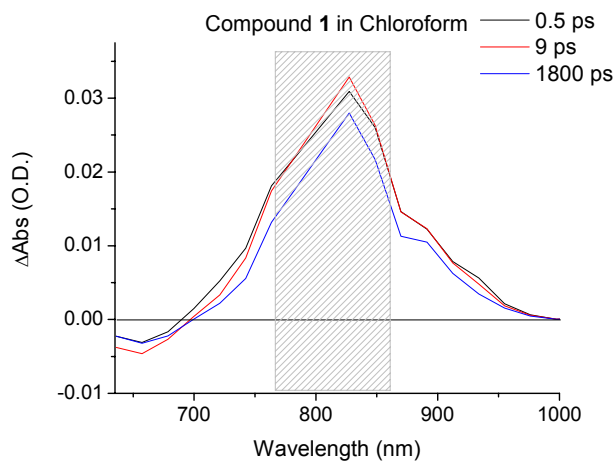


Figure S11: Representative spectra of compound **1** in chloroform. The sample was excited at 575 nm ($\sim 2 \text{ mJcm}^{-2}$).

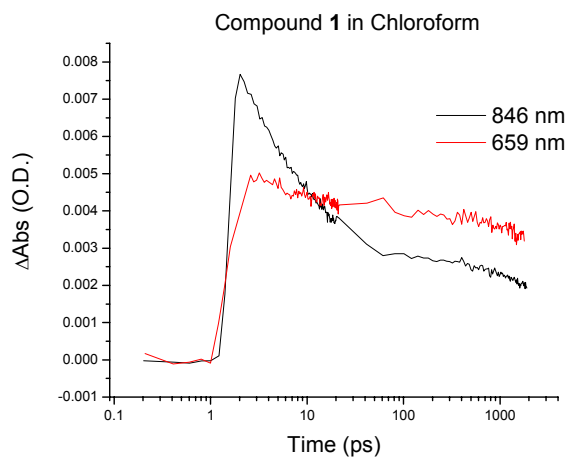


Figure S12. Decay kinetics of compound **1** in chloroform pumped at 575 nm ($\sim 2 \text{ mJcm}^{-2}$).

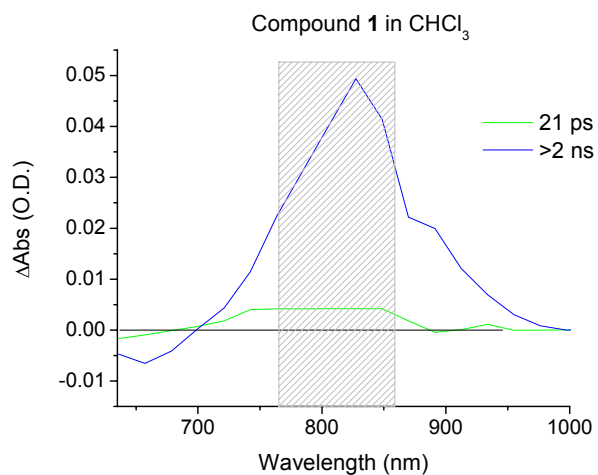


Figure S13. SADS obtained by global analysis of the transient absorption data for compound **1** in chloroform. The kinetic components associated with the SADS are mentioned in the legend.

Hybrid 3 in chloroform:

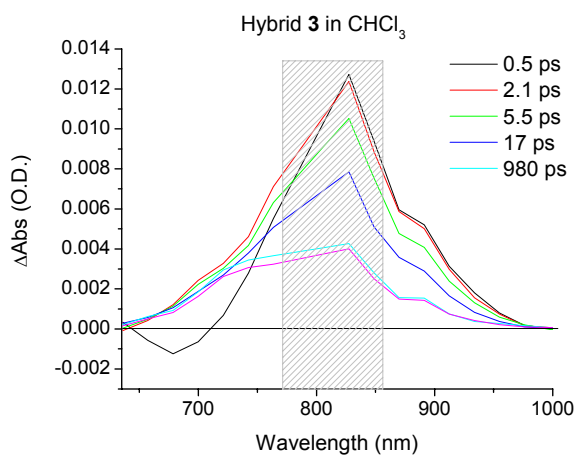


Figure S14. Representative spectra of hybrid **3** in chloroform. The sample was excited at 575 nm ($\sim 2 \text{ mJcm}^{-2}$).

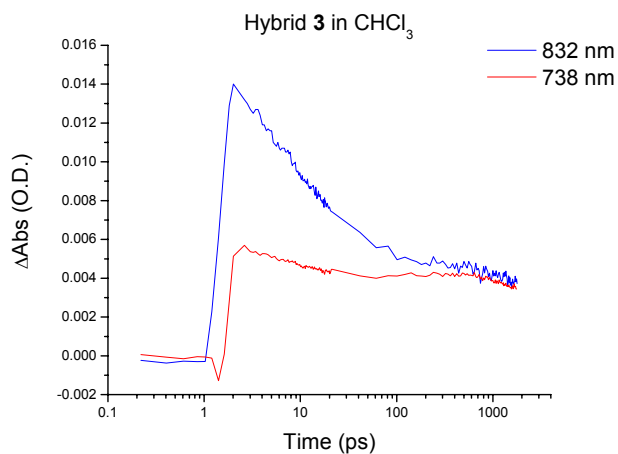


Figure S15. Decay kinetics of hybrid **3** in chloroform pumped at 575 nm ($\sim 2 \text{ mJcm}^{-2}$).

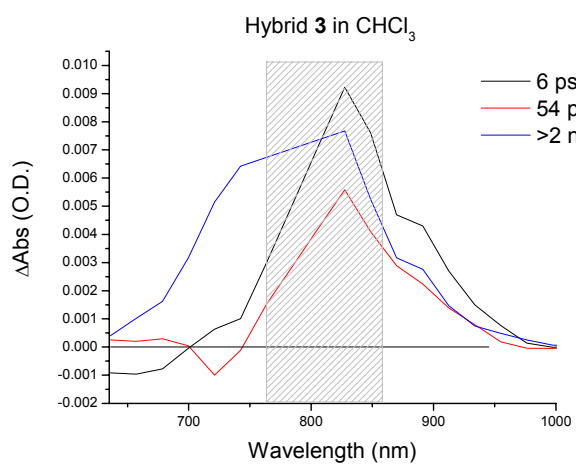


Figure S16. SADS obtained by global analysis of the transient absorption data for hybrid **3** in chloroform. The kinetic components associated with the SADS are mentioned in the legend.

Hybrid **3** in $\text{CHCl}_3/\text{MeOH}$:

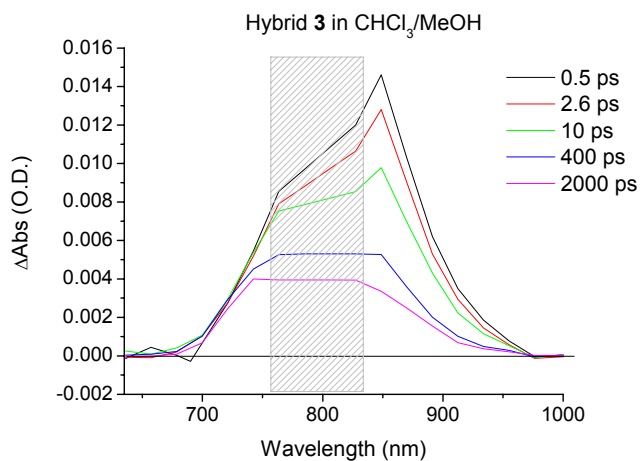


Figure S17. Representative spectra of hybrid **3** in $\text{CHCl}_3/\text{MeOH}$ mixture. The sample was excited at 575 nm ($\sim 2 \text{ mJcm}^{-2}$).

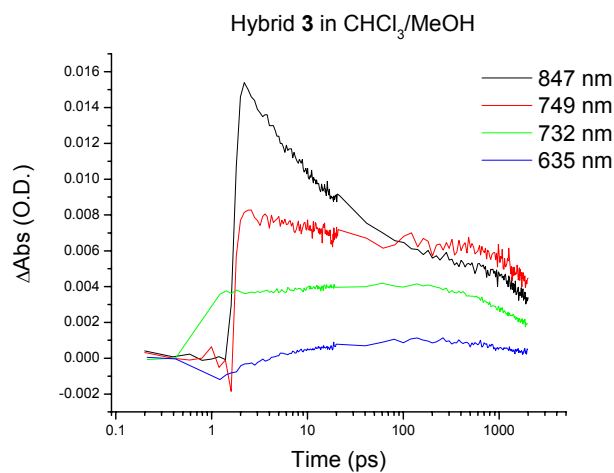


Figure S18. Decay kinetics of hybrid **3** in $\text{CHCl}_3/\text{MeOH}$ mixture pumped at 575 nm ($\sim 2 \text{ mJcm}^{-2}$).

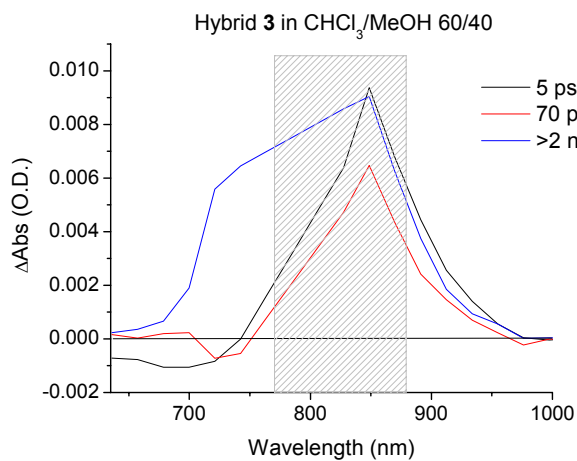


Figure S19. SADS obtained by global analysis of the transient absorption data for hybrid **3** in $\text{CHCl}_3/\text{MeOH}$ mixture. The kinetic components associated with the SADS are mentioned in the legend.

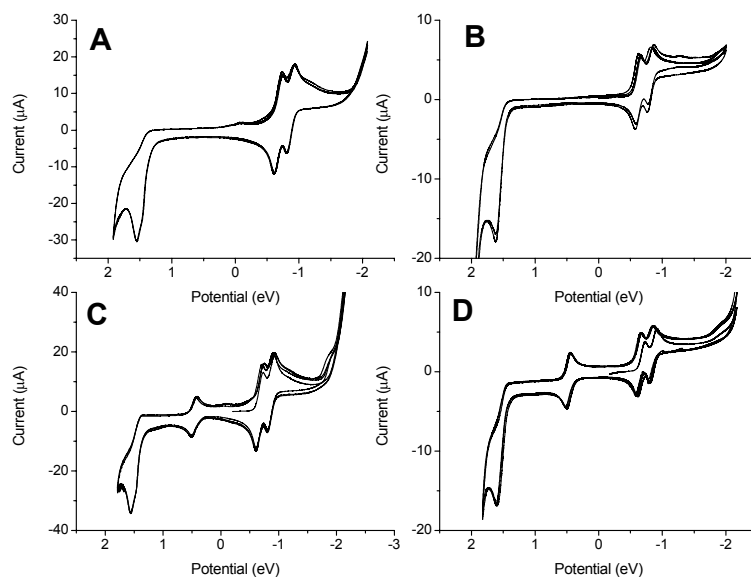


Figure S20. Cyclic voltammetry of **1** and **2** in methylene chloride (A and B) and with ferrocene added as internal standard (C and D).

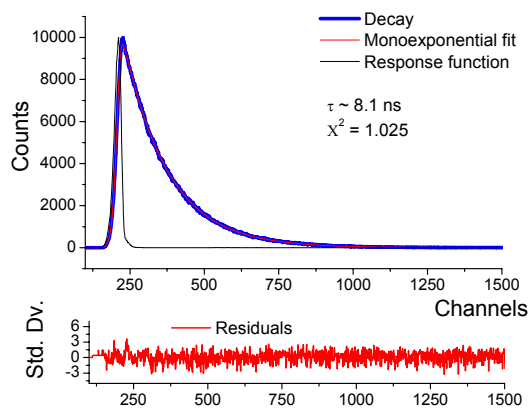


Figure S21. Emission lifetime measurement of compound **1** in chloroform. The sample presented was excited at 466 nm and the emission probed at 620 nm. Same profiles were obtained for **1** and **2** showing monoexponential decay with 8.1 ns time constant.

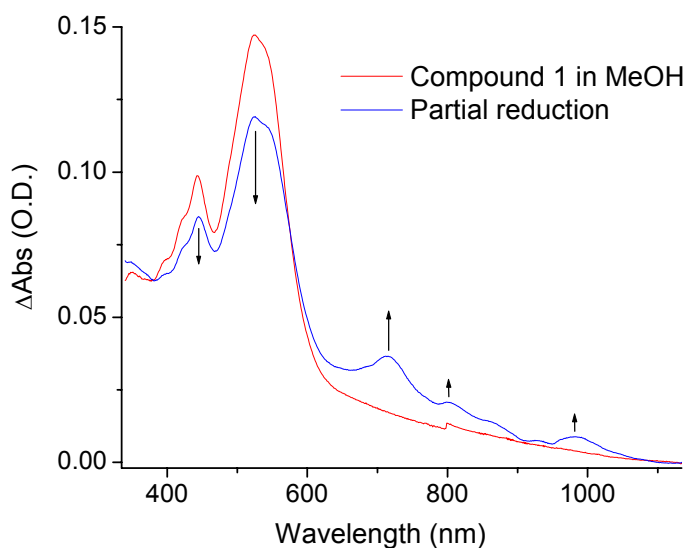


Figure S22. Chemical reduction of compound **1** in methanol using less than one equivalent of sodium dithionate (to avoid formation of dianions). The main feature of the PDI radical anion absorption spectrum at about 715 nm matches the absorption features of the SADS associated with the charge separation states.

References

1. Rajasingh, P.; Cohen, R.; Shirman, E.; Shimon, L. J. W.; Rybtchinski, B., *J. Org. Chem* **2007**, *72*, 5973-5979.
2. Lackowicz, J. R., *Principles of fluorescence spectroscopy*. 2nd ed.; Kluwer Academic/Plenum Publishers New York, 1999.
3. Weare, W. W.; Reed, S. M.; Warner, M. G.; Hutchison, J. E., *J. Am. Chem. Soc.* **2000**, *122*, 12890-12891.