

Electronic Supporting Information

A fully self-assembled asymmetric triad for
photoinduced charge separation

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Table of Contents

| | |
|--|----|
| Synthesis and Experimental Section | 6 |
| Fig SI1 ^1H NMR ($\text{DMSO-}d_6$) of NDI , with labelling scheme. Assignments have been made with a 2D H-H COSY experiment. | 9 |
| Fig SI2 ^1H NMR (CDCl_3) of NDI' , with labelling scheme. Assignments have been made with a 2D H-H COSY experiment. | 10 |
| Fig SI3 ^1H NMR (CDCl_3) of NDI'' , with labelling scheme. Assignments have been made with a 2D NMR experiments (H-H COSY, H-C HSQC and H-C HMBC). | 10 |
| Fig SI4 H-H COSY (CDCl_3) of NDI-AIP , see Figure 2 for peaks labelling. | 10 |
| Fig SI5 ^1H NMR (CDCl_3) of RuP-NDI''-RuP , with labelling scheme. Assignments have been made with 2D NMR experiments (H-H COSY, H-C HSQC and H-C HMBC). | 11 |
| Fig SI6 H-H COSY (CDCl_3) of RuP-NDI''-RuP , see Figure SI4 for peaks labelling. | 12 |
| Fig SI7 Selected region of the H-H COSY (pyridine- d_5) of AIMPyP , see Figure 3 for peaks labelling. | 12 |
| Scheme SI1 Schematic representation of the self-assembled oligomeric species (AIMPyP(ba))_n and of the formation of the monomeric species AIMPyP(ba) upon addition of an excess of pyridine. | 13 |
| Fig SI8 Selected region of the ^1H NMR of AIMPyP(ba) in CDCl_3 (top) and CDCl_3 +pyridine- d_5 (bottom), with labelling scheme. Assignments have been made with an H-H COSY experiment. Peaks of residual non-deuterated pyridine are indicated with an asterisk. | 14 |
| Fig SI9 H-H COSY (pyridine- d_5) of AIMPyP(ba) , see Figure SI6 for peaks labelling. | 15 |
| Fig SI10 H-H COSY (CDCl_3) of AIMPyP-RuP , see Figure 4 for peaks labelling. | 15 |
| Fig SI11 Selected region of the H-H COSY (CDCl_3) of NDI-AIMPyP-RuP , see Figure 5 for peaks labelling. | 16 |
| Fig SI12 Selected region of the H-H COSY (CDCl_3) of NDI-AIMPyP-RuP , see Figure 5 for peaks labelling. | 16 |
| Fig SI13 Absorption spectra of AIMPyP(ba) at different concentrations in dichloromethane. | 17 |
| Fig SI14 Transient absorption spectra obtained in the femtosecond spectroscopy of NDI-AIP in dichloromethane. Excitation wavelength = 550 nm. | 17 |
| Fig SI15 Transient absorption spectra obtained in the femtosecond spectroscopy of NDI-AIP in chloroform. Excitation wavelength = 550 nm. | 18 |
| Fig SI16 Transient absorption spectra obtained in the femtosecond spectroscopy of NDI-AIP in toluene. Excitation wavelength = 550 nm. | 18 |
| Fig SI17 Transient absorption spectrum obtained in the nanosecond laser flash photolysis of NDI-AIP in toluene. Excitation wavelength = 532 nm, delay time 50 ns. | 19 |
| Fig SI18 Transient absorption spectra obtained in the femtosecond spectroscopy of RuP-NDI''-RuP in dichloromethane. Excitation wavelength = 530 nm. | 19 |
| Fig SI19 Transient absorption spectra obtained in the nanosecond laser flash photolysis of NDI-AIMPyP-RuP in dichloromethane. Excitation wavelength = 590 nm. | 20 |
| Fig SI20 Energy level diagram and photophysical mechanisms for the NDI-AIMPyP-RuP triad in toluene. Shorthand notation: AIMPyP = Al, RuP = Ru. | 21 |

- Fig SI21** Transient absorption spectra obtained in the femtosecond spectroscopy of **NDI-AIMPyP-RuP** in toluene. Excitation wavelength = 590 nm. 21
- Fig SI22** X-ray structure of **NDI'**, single crystals obtained by slow diffusion of *n*-hexane into a chloroform solution of **NDI'**. 21
- Fig SI23** Crystal packing of **NDI'**. 22

General Experimental Section

Abbreviations: **MPyP** 5-(4'pyridyl)-10,15,20-(3,5-di-*tert*-butyl)-triphenylporphyrin, **P** *meso*-(4-*tert*-butyl)-tetraphenylporphyrin and *meso*-(3,5-di-*tert*-butyl)-tetraphenylporphyrin, **AIP** (*meso*-(3,5-di-*tert*-butyl)-tetraphenylporphyrinato-(hydroxo)aluminium (III), **AIMPyP** (5-(4'-pyridyl)-10,15,20-(3,5-di-*tert*-butyl)-triphenylporphyrinato-(hydroxo)aluminium(III), **RuP** b-(ethanol)[*meso*-(4-*tert*-butyl)- tetraphenylporphyrinato-a-(carbonyl)ruthenium(III), **ba** benzoic acid, **py** pyridine, **NDI** 2-(7-hexyl-1,3,6,8-tetraoxo-7,8-dihydrobenzo[*lmn*][3,8]phenanthroline-2(1*H*,3*H*,6*H*)-yl)acetic acid, **NDI'** 2,7-dihexylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone, **NDI''** (2*S*,2'*S*)-dimethyl 2,2'-(1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7(1*H*,3*H*,6*H*,8*H*)-diyl)bis(3-(1*H*-imidazol-2-yl)propanoate).

s = singlet, d = doublet, m = multiplet, br = broad. When proton multiplicity in the ¹H NMR assignments is not indicated, this is due to signal overlap with the resonance of residual water (at *ca.* δ = 1.54 in CDCl₃) or due to very broad resonances.

Solvents for spectroscopic and photophysical measurements were of spectroscopic grade, all the other solvents were of reagent grade quality, and used as received. CDCl₃, used in NMR experiments, was treated with basic alumina prior to use. Dichloromethane and chloroform used in time-resolved absorption experiments were treated with potassium carbonate, to remove traces of acidity that were found to promote photodecomposition under prolonged laser irradiation.^{1s}

The naphthalenediimide derivatives, **NDI**, **NDI'** and **NDI''** were synthesized via microwave one-pot and stepwise synthesis (for the symmetrical and the unsymmetrical systems, respectively) from 1,4,5,8-naphthalenetetracarboxylic dianhydride and the corresponding α-aminoacids (glycine and

O-methyl-L-histidine) and/or hexylamine, as previously reported^{2s} (see also Figure SI1, Figure SI2, and Figure SI3 for NMR solution characterizations with labelling schemes, and below for ¹H NMR assignments).

MPyP, and **P**, were synthesized and purified according to literature methods.^{3s} **AIP**,^{4s} **AIP(ba)**,^{4s} **RuP**,^{5s} and **RuP(py)**^{6s} were obtained following the experimental procedures reported earlier. **AIMPyP**, **AIMPyP(ba)**, were formed and purified following the same procedures described before for **AIP** and **AIP(ba)** by replacing **P**, with **MPyP** (see below for ¹H NMR assignments, Figure 3, Figure SI7, Figure SI8, and Figure SI9 for NMR solution characterizations with labelling scheme).^{4s}

¹H, ¹³C{¹H}, and 2D NMR spectra were recorded at 400MHz on a Bruker Avance 400 QNP and at 400 MHz on a Bruker Avance 500. All spectra were run at room temperature (298K) in CDCl₃, pyridine-*d*₅ or DMSO-*d*₆. Proton peak positions were referenced to the peak of residual non deuterated solvent (set at δ 7.26 for CDCl₃, 8.74 for pyridine-*d*₅, and 2.49 for DMSO-*d*₆, respectively). Carbon peak positions were referenced to the central peak of chloroform at δ 77.0.

All high-resolution (HR) electrospray ionization (ESI) mass spectra were recorded on a Waters LCT Premier XE instrument.

UV-vis absorption spectra were recorded with a Jasco V-570 UV/Vis/NIR spectrophotometer. Emission spectra were taken on a Spex-Jobin Ivon Fluoromax-2 spectrofluorimeter, equipped with Hamamatsu R3896 tubes.

Cyclic voltammetric measurements were carried out with a PC-interfaced Eco Chemie Autolab/Pgstat 30 Potentiostat. Argon-purged 10⁻⁴ M sample solutions in CH₂Cl₂ (Romil, Hi-dry), containing 0.1 M (TBA)PF₆ (Fluka, electrochemical grade, 99%; dried in an oven), were used. A conventional three-electrode cell assembly was used: a saturated calomel electrode (SCE Amel) and a platinum electrode, both separated from test solution by a frit, were used as reference and counter electrodes, respectively; a glassy carbon electrode was used as the working electrode.

The spectroelectrochemistry measurements were carried out on a Jasco V-570 UV/Vis/NIR spectrophotometer. For this purpose, sample solutions containing 0.1 M (TBA)PF₆ were transferred

into a thin-layer cell (optical path 1 mm) with a platinum mini-grid as the working electrode, a platinum wire as the counter electrode and a silver wire as quasi-reference electrode.

Nanosecond emission lifetimes were measured using a TCSPC apparatus (PicoQuant PicoHarp 300) equipped with subnanosecond LED sources (280, 380, 460, and 600 nm, 500-700 ps pulsewidth) powered with a PicoQuant PDL 800-B variable (2.5-40 MHz) pulsed power supply. The decays were analyzed by means of PicoQuant FluoFit Global Fluorescence Decay Analysis Software.

Nanosecond transient measurements were performed with an Applied Photophysics laser flash photolysis apparatus, with frequency doubled, (532 nm, 330 mJ) or tripled, (355 nm, 160 mJ) Surelite Continuum II Nd/YAG laser (halfwidth 6-8 ns). Photomultiplier (Hamamatsu R928) signals were processed by means of a LeCroy 9360 (600 MHz, 5 Gs/sec) digital oscilloscope.^{7s} Transient spectra were recorded by using as detection system a Princeton Instruments gated intensified CCD-Camera PI-MAX II equipped with an Acton SpectraPro 2300i triple grating flat field monochromator, an RB GenII intensifier, an ST133 controller and a PTG pulser.

Degassed samples were prepared by freeze-pump-thaw cycles. Triplet lifetimes were measured with reduced pulse power (1mJ/cm^2) to avoid triplet-triplet annihilation and to have good first-order kinetics.

Femtosecond time-resolved experiments were performed using a pump-probe setup based on the Spectra-Physics Hurricane Ti:sapphire laser source and the Ultrafast Systems Helios spectrometer.^{7s} The 560 nm pump pulses were generated with a Spectra Physics 800 OPA. Probe pulses were obtained by continuum generation on a sapphire plate (useful spectral range: 450-800 nm). Effective time resolution *ca.* 300 fs, temporal chirp over the white-light 450-750 nm range *ca.* 200 fs, temporal window of the optical delay stage 0-1000 ps. The time-resolved spectral data were analyzed with the Ultrafast Systems Surface Explorer Pro software.

The structure of the **NDI-AIP** dyad has been optimized at the DFT level of theory, with the Gaussian 98 software package,^{8s} using the B3LYP hybrid functional and 6-31G* basis set.

Synthesis and Experimental Section

NDI. A 8 ml microwave vial was charged with 200 mg (0.742 mmol) of 1,4,5,8-naphthalenetetracarboxylic dianhydride 0.098 ml of hexylamine (0.742 mmol), and 15ml of DMF. The mixture was sonicated until it became homogeneous (30min – 1h) and it was subsequently heated for 5 min at 140±5°C (direct vial measurement) in a dedicated microwave reactor. 0.056 g of glycine (0.742 mmol) and 0.1 ml of dry triethylamine were added to the mixture that was further heated for 5 min at 140±5°C in the microwave reactor. The solvent was removed under vacuum, the residue redissolved in the minimum amount of organic solvent (acetone, acetonitrile) and added dropwise to a dilute solution (1M) of HCl. The precipitate formed was collected under suction and dried under high vacuum. Several washing of the solid with hot chloroform yielded the pure product (isolated yield 60%). ¹H NMR (dms_o-d₆), δ_H: 13.19 (1H, br s, -COOH), 8.71 (4H, m, 1+2), 4.77 (2H, s, α), 4.06 (2H, m, 3), 1.66 (2H, m, 4), 1.31(4H, m 5+6), 0.87 (4H, m, 7+8). HRMS (ESI⁺): Calculated for [M+H]⁺: 409.1400, found: 408.1316.

General synthesis for symmetrical **NDI'** and **NDI''**:

A 8 ml microwave vial was charged with 200 mg (0.742 mmol) of 1,4,5,8-naphthalenetetracarboxylic dianhydride, the corresponding amount of amine or aminoacid (1.484 mmol), 0.2 ml dry triethylamine and 6 ml DMF. The mixture was sonicated until it became homogeneous (30min – 1h) and it was subsequently heated for 5 min at 140±5°C (direct vial measurement) in a dedicated microwave reactor. The solvent was removed under vacuum, the residue redissolved in the minimum amount of organic solvent (acetone, acetonitrile) and added dropwise to a dilute solution (1M) of HCl. The precipitate formed was collected under suction and dried under high vacuum (isolated yield 90%).

NDI'. ^1H NMR (CDCl_3), δ_{H} : 8.76 (4H, s 1), 4.19 (4H, m, 2), 1.74 (4H, m, 3), 1.44 (4H, m, 4), 1.35 (4H, m, 5), 0.90 (8H, m, 6+7). This compound was also characterized in the solid state, see X-ray structure details in Table SI1 and Figure SI20, Figure SI21.

NDI''. ^1H NMR (CDCl_3), δ_{H} : 10.4 (2H, br, s, -NH), 8.44 (4H, s, 1), 7.09 (2H, br, s, 2), 6.51 (2H, br, s 3), 5.81 (2H, m, α), 3.52 (6H, s, -CH₃), 3.35 (2H, m, B). HRMS (ESI+): Calculated for $[\text{M}+\text{H}]^+$: 571.1577, found: 571.1579.

AIMPyP. 300 mg of MPyP (2.82 mmol) were dissolved in 100 ml of dry toluene and 0.2 ml of trimethylaluminium (2.0M in toluene, 5.6 mmol) were added under N₂ atmosphere. The solution was stirred at room T, under N₂ atmosphere, for 4 hr, at which time 5ml of H₂O were added and stirring was continued overnight. The toluene was removed and the violet solid thus formed was redissolved in CH₂Cl₂. The solution was filtered dried over Na₂SO₄ and passed over a column of alumina to give 265 mg of product (85%). ^1H NMR (pyridine-*d*₅), δ_{H} : 9.28 (6H, m, $\beta_4 + \beta_3 + \beta_2$), 9.12 (4H, m, $\beta_1 + a$), 8.2 (6H, br d, oH+oH'), 8.15 (2H, d, b), 7.84 (3H, m, pH+pH'), 1.54 (s, *t*-Bu), 1.52 (s, *t*Bu).

AIMPyP(ba). ^1H NMR (CDCl_3 +pyridine-*d*₅), δ_{H} : 9.00 (6H, m, β), 8.81 (2H, br, m, α), 8.7 (2H, d, β), 8.15 (m, oH+oH'), 8.10 (br, m, b), 7.54 (3H, d, pH), 6.53 (1H, t, γ), 6.3 (2H, m, δ), 4.54 (2H, d, α), 1.54 (s, *t*-Bu).

NDI''-RuP- NDI''. ^1H NMR (CDCl_3), δ_{H} : 8.31 (16H, m, β), 8.10 (4H, s, 1), 8.01 (8H, d, oH), 7.83 (8H, d, oH'), 7.67 (8H, d, mH), 7.64 (8H, d, mH'), 7.44 (2H, br, s, -NH), 4.63 (2H, m α), 3.37 (6H, s, -CH₃), 2.03 (2H, m, B), 1.60 (72H, s, *t*-Bu), 1.43 (2H, br, s 2), 0.66 (2H, br, s 3).

NDI-AIP. 30 mg of AIP (2.72×10^{-2} mmol) and 11 mg of NDI (2.72×10^{-2} mmol) were partially dissolved in 30 ml of CHCl₃. The violet mixture was left stirring at room temperature for 30min. A violet solution formed. Concentration *in vacuo* to *ca.* half volume followed by addition of *n*-hexane induced the formation of the product as a violet powder, which was isolated by filtration, washed with *n*-hexane and vacuum dried (23 mg, 90%). ^1H NMR (CDCl_3), δ_{H} : 9.15 (8H, s, β), 8.47 (2H, d,

2), 8.25 (4H, br d, oH), 8.22 (2H, d, 1), 7.99 (2H, br d, oH'), 7.80 (4H, m, pH), 4.10 (2H, m, 3), 1.66 (2H, m, 4), 1.54 (s, *t*-Bu), 1.40 (α), 1.35 (m, 5+6), 0.86 (4H, m, 7+8).

AlMPyP-RuP. 30 mg of AlMPyP (1.43×10^{-2} mmol) and 14.5 mg of RuP (1.43×10^{-2} mmol) were partially dissolved in 30 ml of CHCl₃. The red mixture was left stirring at room temperature, a red solution formed in a few minutes. Concentration *in vacuo* to *ca.* half volume followed by addition of *n*-hexane induced the formation of the product as a red-violet powder, which was isolated by filtration, washed with *n*-hexane and vacuum dried (41.5 mg, 95%). ¹H NMR (CDCl₃), δ_{H} : 8.97 (2H, d β_4 -AlMPyP), 8.93 (2H, d, β_3 -AlMPyP), 8.79 (8H, s, β -RuP), 8.27 (4H, d, oH-RuP), 8.10 (4H, d, oH'-RuP), 7.97 (3H, br, s, oH-AlMPyP), 7.93 (3H, br s, oH'-AlMPyP), 7.78 (4H, d, mH-RuP), 7.69 (7H, m, mH'-RuP+pH-AlMPyP+pH'-AlMPyP), 7.49 (2H, d, β_1 -AlMPyP), 6.02 (2H, d, b), 1.93 (2H, d, a), 1.61 (36H, s, *t*-Bu-RuP), 1.59 (s, *t*-Bu-AlMPyP), 1.57 (s, *t*-Bu-AlMPyP).

NDI-AlMPyP-RuP. 30 mg of AlMPyP-RuP (9.8×10^{-3} mmol) and 4 mg of NDI (9.8×10^{-3} mmol) were partially dissolved in 30 ml of CHCl₃. The mixture was left stirring at room temperature, a red solution formed in a few minutes. Concentration *in vacuo* to *ca.* half volume followed by addition of *n*-hexane induced the formation of the product as a red-violet powder, which was isolated by filtration, washed with *n*-hexane and vacuum dried (32 mg, 95%). ¹H NMR (CDCl₃), δ_{H} : 8.77(8H, s, β -RuP), 8.69 (4H, m, β_4 -AlMPyP+ β_3 -AlMPyP), 8.62 (2H, d, β_2 -AlMPyP) 8.46 (2H, d, 2), 8.25 (4H, d, oH-RuP), 8.13 (4H, d, oH'-RuP), 7.93 (2H, d, 1), 7.77 (4H, d, mH-RuP), 7.77 (v br s oH+oH'-AlMPyP), 7.66 (4H, d, mH'-RuP), 7.62 (3H, m, pH-AlMPyP+pH'-AlMPyP), 7.48 (2H, d, β_1 -AlMPyP), 6.12 (2H, d, b), 4.18 (2H, m, 3), 1.92 (2H, d, a), 1.69 (2H, m, 4), 1.59 (s, *t*-Bu-RuP), 1.57 (s, *t*-Bu-AlMPyP), 1.55 (s, *t*-Bu-AlMPyP), 1.46 (m, 5), 1.41 (α), 1.36 (4H, m, 6+7), 0.91 (2H, m, 8).

