Supporting Information

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Rigid Oligoperylenediimide Rods:
Anion-π Slides with Photosynthetic Activity

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Table of Content

1. Materials and Methods S2
2. Abbreviations S3
3. Synthesis S4
4. Ion Transport S19
5. Photosynthesis S26
6. References S30
1. Materials and methods. Reagents for synthesis were purchased from Fluka, amino acid derivatives from Novabiochem and Bachem, egg yolk phosphatidylcholine (EYPC) from Avanti polar lipids, HBTU from Applied Biosystems, HPTS from Molecular Probes, gramicidin A, buffers, and salts from Sigma or Fluka-Aldrich. All reactions were performed under argon atmosphere. Unless stated otherwise, column chromatography was carried out on silica gel 60 (Fluka, 40-63 μm). Analytical (TLC) and preparative thin layer chromatography (PTLC) was performed in silica gel 60 (Fluka, 0.2 mm) and silica gel GF (Analtech, 1000 μm), respectively. HPLC was performed using either Jasco HPLC system (PU-980, UV-970, FP-920) or an Agilent 1100 series apparatus with a photo diode array detector. [α]_D values were recorded on a Jasco P-1030 Polarimeter, melting points (m.p.) on a heating table from Reichert (Austria), IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate, unless stated) and are reported as wavenumbers ν in cm⁻¹ with band intensities indicated as s (strong), m (medium), w (weak). ESI-MS were performed on a Finnigan MAT SSQ 7000 instrument or a ESI API 150EX and are given in m/z (peak intensity in %). ¹H and ¹³C spectra were recorded (as indicated) either on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and are reported as chemical shifts (δ) in ppm relative to TMS (δ = 0). Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t), quartet (q) and quintet (quint) with coupling constants (J) given in Hz, or multiplet (m). ¹H and ¹³C resonances were assigned with the aid of additional information from 2D NMR spectra (H,H-COSY, DEPT 135, HSQC and HMBC). UV-Vis spectra were measured on a Varian Cary 1 Bio spectrophotometer equipped with a stirrer and a temperature controller (25 ºC) and are reported as maximal absorption wavelength λ in nm (extinction coefficient ε in mM⁻¹cm⁻¹). CD spectra were measured using a Jasco J-715 spectropolarimeter with a thermostated
cell holder (25 °C or as indicated) and are reported as wavelength \( \lambda \) of the extremum in nm (\( \Delta \varepsilon \) in M\(^{-1}\)cm\(^{-1}\)). Fluorescence measurements were preformed either on a FluoroMax-2 or a FluoroMax-3, Horiba Jobin Yvon, both equipped with an injector port, a stirrer and a temperature controller (25 °C). Fluorescence spectra are not corrected. The Mini-Extruder with a polycarbonate membrane, pore size 100 nm, used for LUV preparation was from Avanti polar lipids.

2. Abbreviations

Boc: \( t \)-Butoxycarbonyl; calcd: Calculated; DMA: \( N,N \)-Dimethylacetamide; DMAP: 4-Di(methylamino)pyridine; DMF: \( N,N \)-Dimethylformamide; \( en \): Ethylenediamine; EDTA: Ethylenediaminetetraacetic acid; EYPC LUVs: Egg yolk phosphatidylcholine large unilamellar vesicles; HBTU: 2-(1H-Benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate; HEPES: 4-(2-Hydroxyethyl)-1-piperazine-ethanesulfonic acid; HPTS: 8-Hydroxy-1,3,6-pyrenetrisulfonate; HRMS: High resolution mass spectrometry; NMP: 1-methyl-2-pyrrolidinone; PDI: Perylenediimide; Q: 1,4-Naphthoquinone-2-sulfonate, RPHPLC: Reverse phase high performance liquid chromatography; rt: Room temperature; sh: Shoulder; TEA: Triethylamine; TFA: Trifluoroacetic acid; Z: (Benzylxoy)carbonyl.
3. Synthesis

Scheme S1. Synthesis of O-PDI 1. a) 1. Br₂, I₂, H₂SO₄, 65 - 85 °C, 16 h; 2. NMP, 4, AcOH, 85 °C, 6 h, 52%;[S1] b) 6, 65 °C, 48 h, 93%;[S1] c) 1. KOH, iPrOH, H₂O, 80 °C, 3 h; 2. AcOH, rt, 15 min, 11 (42%), 8 (16%);[S1] d) 9, imidazole, toluene, DMF, 110 °C, 16 h, 42%; e) imidazole, toluene, 110 °C, 16 h, 23%; f) 13, DMAP, toluene, 110 °C, 5 h, 76%; g) HBTU, TEA, CH₂Cl₂, rt, 3 h, 88%; h) piperidine, DMF, rt, 20 min. 85%; i) 19, HBTU, TEA, CH₂Cl₂, rt, 3 h, 84%; j) piperidine, DMF, rt, 20 min 70%; k) HBTU, TEA, CH₂Cl₂, 6 h, 67%; l) CH₂Cl₂, TFA, 1 h, quantitative.
Compounds 5, 7, 8 and 11 were prepared from commercially available 3,4,9,10-perylenetetracarboxylic dianhydride (3) following literature procedures.[S1]

**Compound 10.** To a solution of 8 (210 mg, 0.04 mmol) and imidazole (500 mg) in toluene (25 ml), p-phenylenediamine (9) (430 mg, 0.4 mmol) in DMF (5 ml) was added. The resulting mixture was refluxed for 5 hours. The reaction was allowed to cool down to rt, then chloroform (30 ml) was added. The organic solution was washed successively with 1% HCl, saturated aqueous K₂CO₃ and water and dried over anhydrous Na₂SO₄. Concentration *in vacuo* followed by column chromatography (CH₂Cl₂/MeOH 98:2, *R*<sub>f</sub> = 0.3) yielded 10 (120 mg, 42%) as a green solid. Mp > 230 °C; UV/Vis (CHCl₃): 705 (36.4), 434 (12.6); IR (neat): 3347 (w), 2859 (w), 1688 (s), 1647 (s), 1588 (s), 1409 (s), 1342 (s), 1199 (m);<sup>1</sup>H NMR (400 MHz, CDCl₃): 8.52 (s, 2H), 8.46 (d, <sup>3</sup>J (H,H) = 8.1 Hz, 2H), 7.70 (d, <sup>3</sup>J (H,H) = 8.1 Hz, 2H), 7.12 (d, <sup>3</sup>J (H,H) = 8.6 Hz, 4H), 6.85 (d, <sup>3</sup>J (H,H) = 8.6 Hz, 4H), 3.93 - 3.64 (m, 4H), 2.93 - 2.76 (m, 4H), 2.16 - 1.91 (m, 8H);<sup>13</sup>C NMR (100 MHz, CDCl₃/MeOD 9:1): 164.7 (s), 164.6 (s), 146.7 (s), 146.6 (s), 130.6 (s), 130.3 (s), 129.3 (d), 127.1 (d), 126.2 (s), 124.1 (d), 122.6 (s), 122.1 (s), 121.2 (d), 119.3 (s), 115.8 (d), 52.3 (t), 25.9 (t); MS (ESI, CH₂Cl₂): 712 (100, [M + H]<sup>+</sup>).

**Compound 12.** A solution of 10 (240 mg, 0.34 mmol), 11 (32 mg, 0.05 mmol) and imidazole (1.0 g) in a toluene (6 ml)/DMF (6 ml) mixture was refluxed for 16 hours. The reaction was allowed to cool down and CH₂Cl₂ (20 ml) was added. The resulting solution was successively washed with 1% HCl, saturated aqueous K₂CO₃ and water and dried over anhydrous Na₂SO₄. After evaporating the solvent, compound 12 was purified by
column chromatography (CH$_2$Cl$_2$/MeOH 97:3, $R_f = 0.2$) to yield a green solid (16 mg, 23%). Mp > 230 °C; UV/Vis (CHCl$_3$/MeOH 9:1): 710 (73.0), 435 (25.0); IR (neat): 3364 (w), 2924 (w), 1690 (s), 1655 (s), 1590 (s), 1411 (s), 1337 (s), 1256 (m), 1124 (m); $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 9:1): 8.54 (d, $^3$J (H,H) = 3.8 Hz, 2H), 8.48 - 8.39 (m, 6H), 7.70 (d, $^3$J (H,H) = 6.8 Hz, 2H), 7.65 (d, $^3$J (H,H) = 7.8 Hz, 2H), 7.58 (s, 4H), 7.19 (d, $^3$J (H,H) = 8.0 Hz, 2H), 7.04 (d, $^3$J (H,H) = 7.9 Hz, 2H), 5.09 - 5.03 (m, 1H), 3.92 - 3.65 (m, 8H), 3.00 - 2.74 (m, 8H), 2.63 - 2.55 (m, 2H), 2.10 - 1.91 (m, 18H), 1.78 - 1.65 (m, 2H), 1.50 - 1.32 (m, 4H); MS (ESI, CH$_2$Cl$_2$, MeOH 9:1): 1305 (100, [M + H]$^+$).

**Compound 14.** A solution of 12 (19 mg, 0.014 mmol), succinic anhydride (13) (14 mg, 0.14 mmol) and DMAP (1 mg, 0.008 mmol) in toluene (4.5 ml) and DMF (0.5 ml) was refluxed for 3 hours. The reaction was allowed to cool down to rt, then CH$_2$Cl$_2$ (20 ml) was added and washed with HCl (1 M) and water. The solvent was evaporated under reduced pressure and the crude product was purified by silica gel flash column chromatography (CH$_2$Cl$_2$/MeOH, 92:8, $R_f = 0.03$) to yield 14 (15.5 mg, 76%) a green solid. Mp > 230 °C; UV/Vis (CHCl$_3$/MeOH 9:1): 711 (73.0), 435 (25.0); IR (neat): 3346 (m), 2926 (w), 1686 (s), 1655 (s), 1578 (s), 1412 (s), 1342 (s), 1259 (m), 1124 (m); $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 9:1): 8.51 (d, $^3$J (H,H) = 4.6 Hz, 2H), 8.47 (s, 1H), 8.45 - 8.35 (m, 5H), 7.74 - 7.62 (m, 6H), 7.52 (s, 4H), 7.22 (d, $^3$J (H,H) = 8.6 Hz, 2H), 5.05 - 4.99 (m, 1H), 3.82 - 3.66 (m, 8H), 2.90 - 2.73 (m, 8H), 2.70 - 2.65 (m, 4H), 2.59 - 2.49 (m, 2H), 2.16 - 2.02 (m, 8H), 2.00 - 1.89 (m, 8H), 1.86 - 1.82 (m, 2H), 1.75 - 1.63 (m, 2H), 1.48 - 1.31 (m, 4H); MS (ESI, CH$_2$Cl$_2$, +ve): m/z (%) 1405 (100, [M+H]$^+$), 703 (100, [M+2H]$^{2+}$); MS (ESI, CH$_2$Cl$_2$, -ve): 1403 (100, [M-H]).
**Compound 17.** To a suspension of Fmoc-Glu(OtBu)-OH (15) (1.58 g, 3.7 mmol), H-Glu(OtBu)-OtBu·HCl (16) (1.00 g, 3.4 mmol), HBTU (1.54 g, 4.1 mmol) in 50 ml of CH₂Cl₂ at 0°C, TEA (1.4 ml, 10.2 mmol) was added. The resulting mixture was stirred in dark at room temperature for 3 hours. The solution was washed successively with saturated aqueous NaHCO₃, water, KHSO₄ (1 M) and water. The organic layer was dried over anhydrous Na₂SO₄. Most of the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (CH₂Cl₂/MeOH 98.5:1.5, Rᵣ = 0.45) to give 17 (1.98 g, 88%) a colorless waxy solid. [α]²⁰D = -88.8 (c = 1, DMSO); IR (neat): 3301 (w), 2978 (m), 1727 (s), 1615 (m), 1519 (m), 1369 (m), 1154 (s), 842 (s); ¹H NMR (400 MHz, DMSO-d₆): 8.24 (d, J (H,H) = 7.6 Hz, 1H), 7.90 (d, J (H,H) = 7.3 Hz, 2H), 7.56 (d, J (H,H) = 8.1 Hz, 1H), 7.42 (t, J (H,H) = 7.2 Hz, 2H), 7.33 (t, J (H,H) = 7.3 Hz, 2H), 4.27 - 4.19 (m, 3H), 4.16 - 4.10 (m, 1H), 4.08 - 4.01 (m, 1H); ¹³C NMR (100 MHz, DMSO-d₆): 172.1 (s), 172.0 (s), 171.9 (s), 171.2 (s), 156.3 (s), 144.3 (s), 144.1 (s), 141.2 (s), 128.1 (d), 127.5 (d), 125.8 (d), 120.6 (d), 81.2 (s), 80.3 (s), 80.2 (s), 66.1 (t), 55.3 (d), 52.3 (d), 47.1 (d), 31.8 (t), 31.3 (t), 28.2 (q), 28.1 (q), 28.0 (q); MS (ESI, 1. 2 M NH₄AcO, 2. sample in DMSO): 685 (70, [M+NH₄]⁺), 668 (70, [M+H]⁺), 612 (30, [MH⁻Bu]⁺), 555 (30, [MH⁻2Bu]⁺), 499 (50, [MH⁻3Bu]⁺), 445 (100, [MH-Fmoc]⁺).

**Compound 18.** To a solution of 17 (700 mg, 1.0 mmol) in DMF (30 ml), piperidine (1.5 ml, 5% v/v) was added. The resulting mixture was stirred at room temperature for 1 hour. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (CH₂Cl₂/MeOH, from 99:1 to 91:9, Rᵣ = 0.6) to yield 18 (396 mg,
85%) as a colorless oil.  \([\alpha]^{20}_D = -49.0 \ (c = 1, \text{DMSO})\); IR (neat): 3320 (w), 2977 (m), 1729 (s), 1677 (m), 1509 (w), 1368 (m), 1154 (s), 847 (w); \(^1\text{H} \text{NMR} (400 \text{ MHz, DMSO-}d_6): 8.04 \ (s, 1H), 7.91 \ (s, 1H), 4.14 - 4.02 \ (m, 1H), 3.15 - 3.05 \ (m, 1H), 2.20 \ (s, 4H), 1.90 - 1.84 \ (m, 1H), 1.76 - 1.70 \ (m, 2H), 1.56 - 1.49 \ (m, 1H), 1.34 \ (s, 27H); \(^1^3\text{C} \text{NMR} (100 \text{ MHz, DMSO-}d_6): 174.9 \ (s), 172.2 \ (s), 171.5 \ (s), 170.9 \ (s), 80.7 \ (s), 79.8 \ (s), 79.4 \ (s), 53.7 \ (d), 51.6 \ (d), 31.4 \ (t), 31.0 \ (t), 30.6 \ (t), 27.8 \ (q), 27.6 \ (q), 26.4 \ (t); \text{MS (ESI, DMSO):} 445 \ (100, [M+H]^+), 389 \ (10, [MH-tBu]^+), 333 \ (10, [MH-2tBu]^+), 277 \ (10, [MH-3tBu]^+).

**Compound 20.** To a solution of 18 (380 mg, 0.86 mmol), Fmoc-Glu(OtBu)-OH (19) (440 mg, 1.0 mmol) and HBTU (450 mg, 1.2 mmol) in CH\(_2\)Cl\(_2\) (40 ml) at 0°C, TEA (0.52 ml, 3.4 mmol) was added. The resulting mixture was stirred in dark at room temperature for 2 hours. The solution was washed successively with saturated aqueous NaHCO\(_3\), water, (1 M) KHSO\(_4\) and water. The organic layer was dried over anhydrous Na\(_2\)SO\(_4\). The solvent was then evaporated under reduced pressure and the crude product was purified by column chromatography (CH\(_2\)Cl\(_2\)/MeOH, 98.5:1.5, \(R_f = 0.4\)) to yield 20 (610 mg, 84%) as a colorless solid.  \([\alpha]^{20}_D = -122.3 \ (c = 1, \text{DMSO})\); Mp = 86-87 °C; IR (neat): 3301 (w), 2978 (m), 1725 (s), 1644 (m), 1520 (m), 1366 (m), 1147 (s), 846 (w); \(^1\text{H} \text{NMR} (400 \text{ MHz, DMSO-}d_6): 8.24 \ (d, ^3J (H,H) = 7.3 \text{ Hz, 1H}), 8.00 \ (d, ^3J (H,H) = 7.8 \text{ Hz, 1H}), 7.90 \ (d, ^3J (H,H) = 7.3 \text{ Hz, 2H}), 7.72 \ (t, ^3J (H,H) = 6.3 \text{ Hz, 2H}), 7.57 \ (d, ^3J (H,H) = 8.1 \text{ Hz, 1H}), 7.42 \ (t, ^3J (H,H) = 7.3 \text{ Hz, 2H}), 7.33 \ (t, ^3J (H,H) = 7.3 \text{ Hz, 2H}), 4.33 - 4.20 \ (m, 4H), 4.14 - 4.09 \ (m, 1H), 4.05 - 3.99 \ (m, 1H), 2.25 - 2.22 \ (m, 6H), 1.95 - 1.83 \ (m, 3H), 1.79 - 1.68 \ (m, 3H), 1.38 \ (s, 27H), 1.36 \ (s, 9H); \(^1^3\text{C} \text{NMR} (100 \text{ MHz, DMSO-}d_6): 172.2 \ (s), 172.1 \ (s), 171.9 \ (s), 171.6 \ (s), 171.5 \ (s), 171.1 \ (s), 156.4 \ (s), 144.3 \ (s), 144.1 \ (s), 141.2 \ (s), 128.1 \ (d), 127.5 \ (d), 125.8 \ (d), 120.6 \ (d), 81.2 \ (s), 81.1 \ (s), 80.3 \ (s), 80.1 \ (s), 66.1 \ (t),
54.2 (d), 52.4 (d), 51.8 (d), 47.1 (d), 31.9 (t), 31.5 (t), 31.4 (t), 31.3 (t), 28.2 (q), 28.2 (q),
28.1 (q), 28.0 (q); MS (ESI, DMSO): 876 (20, [M+Na]+), 853 (100, [M+H]+).

**Compound 21.** To a solution of **20** (100 mg, 0.12 mmol) in DMF (15 ml), piperidine
(0.75 ml, 5% v/v) was added. The resulting mixture was stirred in dark at room
temperature for 1 hour. The solvent was evaporated under reduced pressure and the crude
product was purified by PTLC (CH₂Cl₂/MeOH 90:10, \( R_f = 0.5 \)) to yield **21** (52 mg, 70%)
as a colorless oil. \([\alpha]_{D}^{20} = -56.5 (c=1, DMSO); \text{IR (neat): } 3321 \text{ (w), 2975 \text{ (m), 1729 \text{ (s),}
1669 \text{ (m), 1509 \text{ (w), 1370 \text{ (m), 1153 \text{ (s), 845 } \text{(w); } ^1H \text{ NMR (400 MHz, DMSO-d₆): 8.28 \text{ (s, 1H}, 8.26 \text{ (s, 1H}, 8.00 \text{ (s, 1H), 4.29 - 4.24 \text{ (m, 1H), 4.10 - 4.05 \text{ (m, 1H), 3.15 - 3.11 \text{ (m,}
1H), 2.24 - 2.16 \text{ (m, 6H), 1.90 - 1.80 \text{ (m, 2H), 1.77 - 1.64 \text{ (m, 2H), 1.58 - 1.49 \text{ (m, 2H),}
1.35 \text{ (s, 36H); } ^{13}C \text{ NMR (100 MHz, DMSO-d₆): 174.9 \text{ (s, 172.7 \text{ (s, 172.1 \text{ (s, 171.9 \text{ (s,}
171.6 \text{ (s, 171.1 \text{ (s, 81.2 \text{ (s, 80.3 \text{ (s, 80.2 \text{ (s, 79.9 \text{ (s, 54.3 \text{ (d, 52.3 \text{ (d, 51.4 \text{ (d, 31.9}
(t), 31.5 (t), 31.4 (t), 30.7 (t), 28.3 (q), 28.2 (q), 28.0 (q), 26.5 (t); MS (ESI, DMSO): 630 \text{(100, [M+H]+), 575 \text{(20, [MH-tBu]+), 518 (10, [MH-2'Bu]+).}

**Compound 22.** To a solution of **14** (12 mg, 0.008 mmol) and **21** (35 mg, 0.06 mmol) in
DMF (5 ml) was added HBTU (10 mg, 0.015 mmol) and TEA (10 µl, 0.07 mmol). The
resulting mixture was stirred at room temperature for 2.5 hours. The solvent was
evaporated under reduced pressure. Purification by PTLC (CH₂Cl₂/MeOH 96:4, \( R_t = 0.4 \))
yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, CH₂Cl₂/MeOH 98:2, 1
ml/min, \( R_t = 7.48 \text{ min, Fig. S1A) 22 (11.8 mg, 67%) as a green solid. Mp > 230 °C;}
UV/Vis (CHCl₃/MeOH 9:1): 711 (73.0), 435 (25.0). IR (neat): 3385 (w), 2922 (s), 1736
(s), 1687 (s), 1655 (s), 1590 (s), 1509 (m), 1416 (s), 1341 (s), 1199 (m), 1126 (m); \(^1H
NMR (400 MHz, CDCl₃/CD₃OD 9:1): 8.51 (d, $^3J$ (H,H) = 6.1 Hz, 2H), 8.47 - 8.41 (m, 5H), 8.35 (d, $^3J$ (H,H) = 8.3 Hz, 1H), 7.76 - 7.66 (m, 7H), 7.57 (d, $^3J$ (H,H) = 7.1 Hz, 1H), 7.48 (s, 4H), 7.19 (d, $^3J$ (H,H) = 8.3 Hz, 2H), 5.04 - 4.95 (m, 1H), 4.32 - 4.24 (m, 3H), 3.80 - 3.67 (m, 5H), 2.88 - 2.75 (m, 6H), 2.69 - 2.64 (m, 2H), 2.32 - 2.19 (m, 10H), 2.12 - 1.76 (m, 34H), 1.73 - 1.66 (m, 2H), 1.38 (s, 9H), 1.36 (s, 27H); MS (ESI, 1.2 M NH₄AcO, sample in DMSO): 2034 (100, [M+NH₄]⁺), 1026 (20, [M+2NH₄]²⁺), 690 (80, [M+3NH₄]³⁺) (Fig. S3).

**Compound 1.** A solution of 22 (3 mg, 1.5 µmol) in TFA (1.5 ml) was stirred for 1 hour at rt. TFA was evaporated under reduced pressure. This procedure was repeated a second time. Removal of nonpolar impurities by solid-liquid extraction (hexane, 3x) afforded analytically pure (RP-HPLC, YMC-Pack ODS-A, 250 X 10 mm, H₂O/(CH₃CN, 1% TFA), 5:95, 2ml/min, $t_R = 7.08$ min, Fig. S1B) 2 (2.6 mg, quant) as a green solid. UV/Vis (DMSO): 715 (73.0), 431 (25.0), Fig. S3; $^1$H NMR (400 MHz, DMSO-d₆): 8.65 - 8.55 (m, 2H), 8.36 - 7.95 (several m, 6H), 7.74 - 7.64 (m, 6H), 7.50 (s, 4H), 7.14 - 7.07 (m, 2H), 5.06 - 4.97 (m, 1H), 4.30 - 4.26 (m, 3H), 3.80 - 3.40 (several m, 10H), 2.90 - 2.60 (m, 8H), 2.40 - 1.70 (several m, 40H).
Figure S1. (A) HPLC of 22 (detection at 254 nm, YMC-Pack SIL 250 X 4.6 mm, CH₂Cl₂/MeOH 98:2, 1 ml/min, Rᵣ = 7.48 min) and (B) RP HPLC of 1 (detection at 254 nm, YMC-Pack ODS-A, 250 X 10 mm, H₂O/(CH₃CN, 1% TFA), 5:95, 2 ml/min, tᵣ = 7.08 min).

Figure S2. ESI-MS of 22 (1. 2 M NH₄AcO, 2. sample in DMSO).
Figure S3. Emission (dotted, $\lambda_{ex} = 700$ nm), excitation (solid, $\lambda_{em} = 765$ nm) and absorption spectra of 1 (dashed) in DMSO.
Scheme S2. Synthesis of O-PDI 2. a) 1. Br₂, I₂, H₂SO₄, 65°C-85°C, 16 h; 2. NMP, 5, AcOH, 85 °C, 6 h, 52%;[S1] b) 6, 65 °C, 48 h, 93%;[S1] c) 1. KOH, iPrOH, 80 °C, 3 h; 2. AcOH, rt, 15 min, 48%;[S1] d) 9, imidazole, toluene, DMF, 110 °C, 16 h, 42%; e) 23, Cs₂CO₃, CuI, toluene/EtOAc, 110 °C, 5 h, 52%;[S2] f) 1. tPrOH, KOH, 80 °C, 15 min; 2. AcOH, rt, 15 min, 99%;[S2] g) DMA, 4, 160 °C, 5 h, 36%;[S2] h) imidazole, toluene, 110 °C, 16 h, 16%; i) 13, DMAP, toluene, 110 °C, 5 h, 52%; j) HBTU, TEA, CH₂Cl₂, rt, 3 h, 88%; k) piperidine, DMF, rt, 20 min, 85%; l) 19, HBTU, TEA, CH₂Cl₂, rt, 3 h, 84%; m)
piperidine, DMF, rt, 20 min, 70%; n) HBTU, TEA, CH$_2$Cl$_2$, 6 h, 50%; o) CH$_2$Cl$_2$, TFA, 1 h, quantitative.

Compounds 5, 7, 8 and 24, 25, 26 were prepared from commercially available 3,4,9,10-perylenetetracarboxylic dianhydride (3) following literature procedures.$^{[S1, S2]}$

**Compound 27.** A solution of 10 (230 mg, 0.3 mmol), 26 (26 mg, 0.03 mmol) and imidazole (400 mg) in a DMF (6 ml) / toluene (12 ml) mixture was refluxed for 5 hours. The reaction was allowed to cool down to rt, then CH$_2$Cl$_2$ (20 ml) was added. The resulting solution was washed with HCl (1 M) and saturated aqueous K$_2$CO$_3$ and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated and the crude product was purified by column chromatography (CH$_2$Cl$_2$/MeOH 99:1, $R_f$ = 0.2) to yield pure 27 (9.6 mg, 16%) as a dark red powder. Mp > 230 °C; UV/Vis (CHCl$_3$/MeOH 9:1): 706 (36.4), 552 (40.1), 434 (12.4), 411 (11.8); IR (neat): 2924 (s), 1697 (m), 1658 (m), 1590 (m), 1407 (m), 1335 (m), 784 (s); $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 9:1): 9.63 (dd, $^3J$ (H,H) = 7.8, Hz, $^3J$ (H,H) = 6.9 Hz, 2H), 8.59 (d, $^3J$ (H,H) = 8.3 Hz, 1H), 8.50 (d, $^3J$ (H,H) = 8.3 Hz, 1H), 8.46 (s, 1H), 8.42 (s, 1H), 8.36 (dd, $^3J$ (H,H) = 4.8 Hz, $^3J$ (H,H) = 7.5 Hz, 2H), 8.30 (s, 1H), 8.20 (s, 1H), 7.61 (t, $^3J$ (H,H) = 8.1 Hz, 2H), 7.45 (s, 4H), 7.29 (s, 2H), 7.08 (d, $^3J$ (H,H) = 8.5 Hz, 2H), 6.96 (d, $^3J$ (H,H) = 3.8 Hz, 4H), 6.93 (d, $^3J$ (H,H) = 8.6 Hz, 2H), 4.94 - 4.84 (m, 1H), 3.80 - 3.53 (m, 4H), 2.88 - 2.64 (m, 4H), 2.49 - 2.35 (m, 2H), 2.10 - 2.00 (m, 6H), 1.97 - 1.86 (m, 6H), 1.84 - 1.76 (m, 2H), 1.73 - 1.65 (m, 2H), 1.26 (s, 36H); MS (ESI, CH$_2$Cl$_2$): 1575 (100, [M + H]$^+$).

**Compound 28.** A solution of 26 (7.0 mg, 0.004 mmol), succinic anhydride (13) (5.0 mg,
0.05 mmol) and DMAP (1.0 mg, 0.008 mmol) in toluene (4.5 ml) and DMF (0.5 ml) was refluxed for 3 h. The reaction was allowed to cool down to rt, then CH₂Cl₂ (10 ml) was added and washed with HCl (1 M) and water. The solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography (CH₂Cl₂/MeOH 92:8, \( R_f = 0.03 \)) to yield 28 (3.9 mg, 52%) as a red solid. Mp > 230 °C; UV/Vis (CHCl₃/MeOH 9:1): 706 (36.4), 552 (40.1), 435 (12.6), 411 (11.8); IR (neat): 3368 (m), 2921 (s), 1698 (m), 1659 (m), 1590 (m), 1408 (m), 1335 (m), 779 (s); \(^1\)H NMR (400 MHz, CDCl₃/CD₃OD 9:1): 9.74 (d, \(^3\)J (H,H) = 3.3 Hz, 1H), 9.72 (d, \(^3\)J (H,H) = 3.5 Hz, 1H), 8.71 (d, \(^3\)J (H,H) = 8.3 Hz, 1H), 8.62 (d, \(^3\)J (H,H) = 8.6 Hz, 1H), 8.54 (d, \(^3\)J (H,H) = 11.4 Hz, 2H), 8.50 - 8.44 (m, 2H), 8.41 (s, 1H), 8.32 (s, 1H), 7.78 - 7.66 (m, 2H), 7.57 (d, \(^3\)J (H,H) = 8.1 Hz, 4H), 7.54 (s, 2H), 7.47 (d, \(^3\)J (H,H) = 8.1 Hz, 2H), 7.37 (s, 2H), 7.05 (d, \(^3\)J (H,H) = 6.8 Hz, 4H), 5.06 - 4.95 (m, 1H), 3.88 - 3.64 (m, 4H), 2.94 - 2.75 (m, 2H), 2.59 - 2.46 (m, 2H), 2.39 - 2.28 (m, 2H), 2.18 - 2.07 (m, 6H), 2.05 - 1.93 (m, 4H), 1.92 - 1.84 (m, 4H), 1.81 - 1.65 (m, 4H), 1.36 (s, 36H); MS (ESI, CH₂Cl₂): 1675 (100, [M + H]⁺).

**Compound 29.** To a solution of 28 (5 mg, 0.003 mmol), 21 (10 mg, 0.04 mmol) and HBTU (2 mg, 0.003 mmol) in CH₂Cl₂ (5 ml) at 0 °C, TEA (10 µl, 0.07 mmol) was added. The resulting mixture was stirred at rt for 16 hours. The reaction mixture was diluted with 20 ml of CH₂Cl₂ and extracted with water. The organic layer was dried on MgSO₄ and the solvent evaporated. Purification by PTLC (CH₂Cl₂/MeOH, 96:4, \( R_t = 0.5 \)) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, CH₂Cl₂/MeOH 98:2, 1 ml/min, \( R_t = 7.98 \) min, Fig. S4A) 29 (3.4 mg, 50%) as a dark red solid. Mp > 230 °C; UV/Vis (CHCl₃/MeOH 9:1): 705 (36.4), 553 (41.0), 434 (12.6), 411 (11.8); IR (neat): 2923 (s),
1710 (s), 1698 (s), 1660 (m), 1407 (m), 1336 (m), 1260 (s), 1154 (m), 805 (m), 758 (s); $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 9:1): 9.71 (t, $^3$J (H,H) = 7.3 Hz, 2H), 8.68 (d, $^3$J (H,H) = 8.3 Hz, 1H), 8.59 (d, $^3$J (H,H) = 9.1 Hz, 1H), 8.52 (d, $^3$J (H,H) = 7.6 Hz, 2H), 8.47 (dd, $^3$J (H,H) = 5.3 Hz, $^3$J (H,H) = 8.9 Hz, 2H), 8.37 (s, 1H), 8.30 (s, 1H), 7.73 (t, $^3$J (H,H) = 6.1 Hz, 2H), 7.53 - 7.51 (m, 2H), 7.41 (s, 4H), 7.43 (d, $^3$J (H,H) = 8.8 Hz, 2H), 7.33 (s, 2H), 7.02 (d, $^3$J (H,H) = 4.3 Hz , 4H), 6.98 (s, 2H), 4.99 - 4.91 (m, 1H), 4.39 - 4.30 (m, 3H), 3.83 - 3.71 (m, 2H), 3.67 - 3.61 (m, 2H), 3.12 - 3.06 (m, 10H), 2.90 - 2.80 (m, 2H), 2.32 - 2.23 (m, 2H), 2.10 - 1.97 (m, 5H), 1.88 - 1.82 (m, 4H), 1.77 - 1.69 (m, 2H), 1.61 - 1.52 (m, 4H), 1.40 (s, 20H), 1.31 (s, 36H), 1.21 (s, 30H); MS (ESI, 1. 2 M NH$_4$AcO, 2. sample in DMSO): 2305 (100, [M+NH$_4$]$^+$), 1543 (35, [2M+3NH$_4$]$^{3+}$), 1144 (45, [2M+2H]$^{2+}$) (Fig. S5).

**Compound 2.** A solution of 29 (3.0 mg, 1.3 µmol) in TFA (1.5 ml) was stirred for 1 hour at rt. TFA was evaporated under reduced pressure. This procedure was repeated a second time. Removal of nonpolar impurities by solid-liquid extraction (hexane, 3x) afforded analytically pure (YMC-Pack ODS-A, 250 X 10 mm, H$_2$O/(CH$_3$CN, 1% TFA), 5:95, 2 ml/min, $t_R$ = 7.36 min, Fig. S4B) 1 (2.7 mg, quant) as a red solid. UV/Vis (DMSO): 710 (36.4), 551 (41.0), 431 (12.6), 406 (11.8), Fig. S6; $^1$H NMR (400 MHz, DMSO-$d_6$): 10.22 - 10.18 (m, 2H), 8.45 - 7.52 (several m, 14H), 7.34 (s, 4H), 6.91 (s, 4H), 6.80 (s, 2H), 4.97 - 4.90 (m, 1H), 4.30 - 4.16 (m, 3H), 3.80 - 3.10 (several m, 14H), 2.76 - 2.10 (several m, 20H), 2.00 - 1.55 (m, 8H), 1.38 (s, 36H).
Figure S4. (A) HPLC of 29 (detection at 254 nm, YMC-Pack SIL 250 X 4.6 mm, CH₂Cl₂/MeOH 98:2, 1 ml/min, $R_t = 7.98$ min) and (B) RP HPLC of 2 (detection at 254 nm, YMC-Pack ODS-A, 250 X 10 mm, H₂O/(CH₃CN, 1% TFA), 5:95, 2 ml/min, $t_R = 7.36$ min).

Figure S5. ESI-MS of 29 (1. 2 M NH₄AcO, 2. sample in DMSO).
Figure S6. Emission (dotted, $\lambda_{ex} = 551$ nm), excitation (solid, $\lambda_{em} = 765$ nm) and absorption spectra of 2 (dashed) in DMSO.
4. Ion Transport

Ion transport experiments essentially adapt the methods described in ref. [S3]. A brief summary follows:

**Stock Solutions.** The following stock solutions were prepared: O-PDI monomer 1 (in DMSO), O-PDI monomer 2 (in DMSO). Final pH was adjusted spectroscopically following a previously described method,[S4] final concentrations were confirmed by UV-vis spectroscopy.

**EYPC-LUVs ⊕ HPTS.** Stock solutions of large unilamellar vesicles composed of egg yolk phosphatidylcholine loaded with HPTS were prepared by the previously described freeze-thaw-extrusion method.[S5] Final conditions: ~2.5 mM EYPC; inside: 1 mM HPTS, 10 mM HEPES, 100 mM NaCl or NaBr, pH 7.0, outside: 10 mM HEPES, 100 mM NaCl or NaBr, pH 7.0.

**HPTS Assay for Ion Selectivity.** EYPC-LUVs ⊕ HPTS (25 μl) in NaX (X = Cl, Br) were added to gently stirred, thermostated buffer (1980 μl, 10 mM HEPES, 100 mM MCl (M = Na, K, Rb, Cs) or 100 mM NaX (X = F, Cl, Br, I, AcO, NO₃, SCN, ClO₄) or 67 mM Na₂SO₄, pH = 7.0) in a fluorescence cuvette (t = 0 sec). The time course of HPTS fluorescence emission intensity, $F_t$, was monitored at $\lambda_{em} = 510$ nm ($\lambda_{ex}^1 = 450$ nm, pH-control: $\lambda_{ex}^2 = 405$ nm) during the addition of rods 1 (20 μl DMSO stock solution, 1.0 μM final concentration) or 2 (1.2 μM final) at $t = 100$ s, NaOH (20 μl, a) 0 or b) 0.5 M; a) without base pulse, b) with base pulse) at $t = 200$ s, and excess gramicidin A or triton X-
100 at the end of every experiment. For each situation, control experiments included and
background curves without rods 1 and 2 and reversal of addition. Fluorescence time
courses were normalized to fractional emission intensity $I^n$ using equation (S1)

$$I^n = \frac{(F_t - F_0)}{(F_\infty - F_0)} \quad \text{(S1)}$$

where $F_0 = F_t$ at slide or base addition, $F_\infty = F_t$ at saturation after complete leakage. The
baseline (DMSO only, no rod) $I^n_0$ was then subtracted from $I^n$ to give the fractional
emission intensity $I$ (S2),

$$I = I^n - I^n_0 \quad \text{(S2)}.$$

Pertinent results with or without base pulse are shown in Figs. 2 and S7-S10.

**Hill Plots.** Fractional activity $Y$ was introduced to compare fractional HPTS emissions $I$
at a given time. Usually, we defined $Y = I$ observed 200 s after the start of the experiment
just before termination of the transport experiment. $Y$ was then plotted against
concentration of O-PDIs 1 and 2 and fitted to the Hill equation (S3) to give effective
concentration $EC_{50}$ and the Hill coefficient $n$.

$$Y = Y_\infty + (Y_0 - Y_\infty) / \{1 + ([\text{O-PDI}] / EC_{50})^n\} \quad \text{(S3)}$$

$Y_0$ is $Y$ without O-PDI, $Y_\infty$ is $Y$ with excess O-PDI (Fig. S11).
**Fig. S7.** Change in relative HPTS emission $Y$ ($\lambda_{em} = 510$ nm; $\lambda_{ex}^1 = 450$ nm, pH-control: $\lambda_{ex}^2 = 405$ nm) during addition of 1 (A, 1.0 μM, 20 μl of 0.1 mM 1 in DMSO to 1980 μl) or 2 (B, 1.2 μM, 20 μl of 0.12 mM 2 in DMSO to 1980 μl) to EYPC-LUVs (inside: 10 mM HEPES, pH 7, 100 mM NaX, (A) X = Cl, (B) X = Br; outside: 10 mM HEPES, pH 7, 50 mM (Na$_2$SO$_4$ only) or 100 mM NaX, X as indicated).
Fig. S8. Change in relative HPTS emission $Y$ ($\lambda_{em} = 510$ nm; $\lambda_{ex}^1 = 450$ nm, pH-control: $\lambda_{ex}^2 = 405$ nm) during addition of base (20 μl of 0.5 M NaOH) to EYPC-LUVs (inside: 10 mM HEPES, pH 7, 100 mM NaBr; outside: 10 mM HEPES, pH 7, 100 mM NaX, X as indicated) with 1 (A, 1.0 μM) or 2 (B, 1.2 μM), and formal “lysis” at the end of each experiment for calibration only (excess gramicidin or Triton X-100). Background curves were subtracted after calibration.
**Fig. S9.** Change in relative HPTS emission $Y$ ($\lambda_{em} = 510$ nm; $\lambda_{ex}^1 = 450$ nm, pH-control: $\lambda_{ex}^2 = 405$ nm) during addition of base (20 µl of 0.5 M NaOH) to EYPC-LUVs (inside: 10 mM HEPES, pH 7, 100 mM NaCl; outside: 10 mM HEPES, pH 7, 100 mM NaX, X as indicated) with 1 (A, 1.0 µM) or 2 (B, 1.2 µM), and formal “lysis” at the end of each experiment for calibration only (excess gramicidin or Triton X-100). Background curves were subtracted after calibration.
Fig. S10. Change in relative HPTS emission $Y$ ($\lambda_{em} = 510$ nm; $\lambda_{ex}^1 = 450$ nm, pH-control: $\lambda_{ex}^2 = 405$ nm) during addition of base (20 µl of 0.5 M NaOH) to EYPC-LUVs (inside: 10 mM HEPES, pH 7, 100 mM NaCl; outside: 10 mM HEPES, pH 7, 100 mM MCl, M as indicated) with 1 (A, 1.0 µM) or 2 (B, 1.2 µM), and formal “lysis” at the end of each experiment for calibration only (excess gramicidin or Triton X-100). Background curves were subtracted after calibration.
Fig. S11. (A) Hill plots for the ion transport activity of O-PDI 1 (□, dashed, $EC_{50} = 1.4 \pm 0.2 \mu M$) and O-PDI 2 (〇, solid, $EC_{50} = 0.9 \pm 0.07 \mu M$). (B) Qualitative comparison of Hill plots for the ion transport activity of O-PDI 1 (□, dashed) and the photosynthetic activity of O-PDI 1 (■, solid, from Fig. 3B, $EC_{50} = 2.8 \pm 0.1 \mu M$). Additional comments (compare manuscript, particularly footnote [11]): 1. Reduced maximal activity of O-PDI 2 (but not 1) is in excellent agreement with the onset of competing precipitation around 5 μM found in photosynthesis assays (Fig. 3C). 2. The comparison in B is only partially valid because of the modestly different conditions needed in the two different assays.
5. Photosynthesis

**EYPC-LUVs$$\oplus$$[Co(bpy)$_3$]$^{3+}$.** A solution of EYPC (25 mg) in CHCl$_3$ was dried under vacuum (> 2 h) to form a thin film. Hydration for > 30 min (1 ml of 10 mM Co(Bpy)$_3$(ClO$_4$)$_3$, 10 mM HEPES, 90 mM NaCl, pH 7.1), freeze-thaw cycles (> 10x), extrusion (> 15x, 50 nm polycarbonate membranes), external buffer exchange (Sephadex G-50 column, 10 mM HEPES, 100 mM NaCl, pH 7.1) and dilution to 6 ml gave EYPC-LUVs$$\oplus$$[Co(bpy)$_3$]$^{3+}$: ~2 mM EYPC; inside: 10 mM Co(Bpy)$_3$(ClO$_4$)$_3$, 10 mM HEPES, 90 mM NaCl, pH 7.1, outside: 10 mM HEPES, 100 mM NaCl, pH 7.0.

**Photosynthesis (Hurst Assay).**$^{[56]}$ EYPC-LUVs$$\oplus$$[Co(bpy)$_3$]$^{3+}$ (400 µl), EDTA (200 µl; 0.1 M, 10 mM HEPES, 100 mM NaCl, pH 7.1) and external buffer (1400 µl; 10 mM HEPES, 100 mM NaCl, pH 7.1) were added to a fluorescence cuvette giving vesicles suspended in a stirred solution (10 mM EDTA, 9 mM HEPES, 90 mM NaCl, pH 7.1). To this solution, 1 or 2 were added as solutions in DMSO (< 25 µl) at varying concentrations. The solutions were degassed with nitrogen before the cuvette was sealed with parafilm. Immediately the cuvettes were irradiated using 200 W Xe lamp (cut off filter at 480 nm (2) or 580 nm (1)) for periods of 10 min. After each 10 min, the conversion of Co$^{3+}$ to Co$^{2+}$ was measured by following the UV-vis absorption spectrum at 320 nm. The obtained spectra were subtracted from the initial spectrum to eliminate constant contributions including PDI absorption (Fig. 3A). At the end of each experiment, triton X-100 was added and irradiation was continued for calibration. In all cases, a dark control was measured (same without irradiation). At completion of the experiment, this dark
control was irradiated and finally exposed to triton X-100, and the obtained kinetics were compared to the original ones. Identical values found in all cases demonstrated independence of photoactivity on dark incubation, i.e., excluded the occurrence of [Co(bpy)$_3$]$^{3+}$ efflux or more catastrophic events such as lysis (Fig. S12).

**Data analysis.** The obtained Co$^{2+}$ concentration was plotted as a function of irradiation time and the initial points were fitted to a linear function to estimate the velocity ± error (Fig. S12). The obtained initial velocity ($v$) was plotted against concentration of 1 or 2 and fitted to the Hill equation (S4) to give effective concentration $EC_{50}$ and the Hill coefficient $n$.

$$
 v = v_\infty + (v_0 - v_\infty) / \{ 1 + ([O-PDI] / EC_{50})^n \} \quad (S4)
$$

$v_0$ is $v$ without O-PDI, $v_\infty$ is $v$ with excess O-PDI (Fig. 3B and 3C). For recent discussions of the application of Hill analysis to self-assembly and supramolecular function, particularly the relation to thermodynamic stability and compatibility with structural studies, please see refs [S7] and [S8].

**Photosynthesis Mechanism (FCCP Assay).** EYPC-LUVs$\supset[Co(bpy)_3]^{3+}$ (400 µl), EDTA (200 µl; 0.1 M, pH 7.1) and external buffer (1400 µl, 10 mM HEPES, 100 mM NaCl, pH 7.1) were added to a fluorescence cuvette giving vesicles suspended in a stirred solution (10 mM EDTA, 9 mM HEPES, 90 mM NaCl, pH 7.1). To this solution, added 1 or 2 were added as a solution in DMSO ($< 25$ µl). Then, FCCP (20 µl stock solution, 5 µM final) was added, and the resultant solution was degassed with nitrogen and sealed.
with parafilm. Immediately the cuvettes were irradiated using 200 W Xe lamp (cut off filter at 480 nm (2) or 580 nm (1)) for periods of 10 min. After each 10 min, the conversion of Co\(^{3+}\) to Co\(^{2+}\) was measured by following the UV-vis absorption spectrum at 320 nm. The obtained spectra were subtracted from the initial spectrum to eliminate constant contributions including PDI absorption (Fig. 3A). At the end of each experiment, triton X-100 was added and irradiation was continued for calibration. In all cases, a dark control was measured (same without irradiation). At completion of the experiment, this dark control was irradiated and finally exposed to triton X-100, and the obtained kinetics were compared to the original ones. Identical values found in all cases demonstrated independence of photoactivity on dark incubation, i.e., excluded the occurrence of [Co(bpy)\(_3\)]\(^{3+}\) efflux or more catastrophic events such as lysis (Fig. S12). Data was analyzed as described above.
Fig. S12. Representative plot with all essential controls for photosynthetic activity of O-PDI 1 (1 µM) in EYPC-LUVs $\geq [\text{Co(bpy)}_3]^{3+}$ with externally added EDTA when irradiated using 200 W Xe lamp (cut off 580 nm) with (○) or without FCCP (●, ■, 5 µM; note: In this assay, highest activity is observed without membranes because EDTA oxidation is irreversible. This convenient characteristic is of use to calibrate after lysis and to identify passive leakage as dependence of photoactivity on incubation in the dark). For original samples (○, ●), change in absorption at 320 nm is shown as a function of time of irradiation time in the absence (0-50 min) and presence (50-70 min) of excess triton X-100 (40 µl 1.2% aqueous solution added). For dark controls (▲, ■), change in absorption at 320 nm is shown first as a function of incubation time in the dark (▲, 0-50 min, parallel to irradiation of original sample, ●) and then as a function of irradiation time in the absence (50-100 min, ■) and presence (100-120 min, ■) of excess triton X-100 (40 µl 1.2% aqueous solution added). Independence of photoactivity on dark incubation (●, 0-50 min vs ■, 50-100 min) relative to maximal activity after lysis (●, 50-70 min vs ■, 100-120 min).
min) excludes passive leaks or worse. Independence of photoactivity on FCCP (●, 0-50 min vs ○, 0-50 min) demonstrates the occurrence of electroneutral photosynthesis.

6. References


