Double-channel photosystems with antiparallel redox gradient: Templated stack exchange with porphyrins and phthalocyanines

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Supplementary Information

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1. Materials and methods

As in ref. S1, Supporting Information. Briefly, reagents for synthesis were purchased from Fluka, Acros and Apollo scientific. MDESA was prepared according to ref. S2. Indium tin-oxide (ITO) coated glass substrates were obtained from Präzisions Glas & Optik GmbH (Iserlohn, Germany). Reactions were performed under N_2 or Ar atmosphere when specified. Unless stated otherwise, column chromatography was carried out on silica gel 60 (Fluka, 40-63 μm) and analytical thin layer chromatography (TLC) was performed on silica gel 60 (Fluka, 0.2 mm). Melting points were recorded with Büchi M-565. UV-Vis spectra were recorded on a JASCO V-650 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 $M^{-1}cm^{-1}$). 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). ^{1}H and ^{13}C NMR 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) and quartet (q) with coupling constants (*J*) given in Hz, or multiplet (m). Broad peaks are marked as br. ^{1}H and ^{13}C resonances were assigned with the aid of additional information from 1D & 2D NMR spectra (H,H-COSY, DEPT 135, HSQC and HMBC). Multiplicity of ^{13}C signals are assigned with the aid of DEPT 135, and reported as s (*C*), d (*CH*), t (CH_2) and q (CH_3). Multiplicity due to ^{13}C-^{31}P coupling is reported as ^{P}d, ^{P}t or ^{P}m. ESI-MS were performed on an ESI API 150EX with 2 mM ammonium acetate in methanol as a solvent and are reported as *m/z* (%). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Sciex QSTAR Pulsar or Bruker Daltonics maXis mass spectrometer, MALDI-TOF on a Axima CFR^{+} (Shimadzu).

Electrochemical measurements were done on an Electrochemical Analyzer with Picoamp booster and Faraday cage (CH Instruments 660C). Photocurrents were measured using a 150 W solar simulator (Newport) and an Electrochemical Analyzer (CH Instruments 660C). The irradiation power was measured using a radiant power energy meter (Newport model 70260). AFM images were acquired with a NanoScopeIIIa (Veeco/ Digital Instruments, Santa Barbara, CA) multimode atomic force microscope, in tapping mode using Si cantilevers (OMCL-AC160TS, Olympus) at scan rates of 1 Hz.

Abbreviations. AFM: Atomic force microscopy; Bn: Benzyl; CV: Cyclic voltammetry; DCM: Dichloromethane; DCTB: (*trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile); DMF: *N,N*-Dimethylformamide; DIPEA: *N*,*N*-Diisopropylethylamine; DTT: DL-Dithiothreitol; Fc: Ferrocene; HATU: (*O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*',*N*'-tetramethyluronium hexafluorophosphate); HABA: (2-(4'-Hydroxybenzeneazo) benzoic acid); IPCE: Incident photon to current conversion efficiency; ITO: Indium tin oxide; MDESA: *p*-Methoxy aniline di(2-ethylsulfonic acid); NDI: 1,4,5,8-Naphthalenediimide; Pc: Phthalocyanine; rt: Room temperature; SOSIP: Self-organizing surface-initiated polymerization; TFA: Trifluoroacetic acid; TMSBr: trimethylsilyl bromide.

2. Supporting text

2.1. Synthesis

2.1.1. Synthesis of phthalocyanine 7 and initiator 2a (Schemes S1 and S2)

Compound 10. This compound was synthesized adapting a reported procedure.[S3] Aminoacetaldehyde dimethyl acetal (**24**, 0.54 ml, 5.0 mmol) was slowly added to a solution of succinic anhydride (**25**, 0.5 g, 5.0 mmol) in dioxane (3 ml). The solution was stirred for 40 min at 80 °C. The reaction mixture was allowed to reach rt and solvent removed *in vacuo*, to give analytically pure **10** (1.04 g, 97%) as a pale yellow viscous oil. IR: 3333 (w), 2944 (w), 2836 (w), 1721 (s), 1635 (s), 1544 (s), 1390 (s), 1324 (w), 1244 (w), 1192 (s), 1163 (s), 1128 (s), 1059 (s), 972 (s), 894 (s), 870 (w), 826 (s); ^{1}H NMR (300 MHz, $CDCl_3$): 6.07 (br s, 1H), 4.40 (t, ^{3}J(H,H) = 5.3 Hz, 1H), 3.43 (t, ^{3}J(H,H) = 5.3 Hz, 2H), 3.40 (s, 6H), 2.70 (t, ^{3}J(H,H) = 6.4 Hz, 2H), 2.53 (t, ^{3}J(H,H) = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d6): 176.5 (s), 172.4 (s), 102.5 (d), 54.4 (q), 41.1 (t), 30.7 (t), 29.6 (t); MS (ESI, MeOH): 206 (62, $[M+H]^+$), 174 (100, $[M-OMe]^+$); HRMS (ESI, +ve) calcd for $C_8H_{16}NO_5$: 206.1022, found: 206.1022.

Compound 26. This compound was synthesized according to reported procedures.[S4]

Compound 27. A solution of **10** (0.10 g, 0.49 mmol) and HATU (0.185 g, 0.49 mmol) in DMF (13 ml) was added dropwise over the period of 1h to a solution of **26** (0.31 g, 0.49 mmol) and collidine (64 µl, 0.49 mmol) in DMF (18 ml). The mixture was stirred at rt under nitrogen for 16 h. The volume of the solvent was reduced to 5 ml, transferred into a centrifuge tube, precipitated from diethyl ether (45 ml x 3 times), centrifuged and supernatant removed. The

resulting green solid was taken into diethyl ether, transferred in a flask and concentrated *in vacuo*, to give 394 mg of **27**. The product was used for the next step without further purification.

Compound 28. A solution of 3,5-di-tert-butylbenzoic acid (**14**, 0.20 g, 0.87 mmol) and HATU (0.33 g, 0.87 mmol) in DMF (5 ml) was added to a solution of **27** (0.12 g, 0.15 mmol) and collidine (115 µl, 0.87 mmol) in DMF (7 ml). The mixture was stirred at rt under nitrogen for 2 h. The volume of the solvent was reduced to 2 ml, transferred into a centrifuge tube, precipitated from diethyl ether/hexane (1:9, 45 ml x 2 times) and diethyl ether (45 ml x 2 times), centrifuged and supernatant removed. The residue was purified by silica gel column chromatography (DCM/MeOH, 9.5:0.5; R_f 0.5 with DCM/MeOH, 9:1) to give pure **28** (70 mg, 32%) as a green-blue solid. Mp: > 400 ºC; IR: 3311 (w), 2956 (s), 2924 (s), 2855 (s), 1650 (s), 1595 (s), 1532 (s), 1491 (s), 1395 (s), 1340 (s), 1247 (s), 1134 (s), 1094 (s), 1053 (s), 888 (s), 823 (s), 744 (s), 721 (s); ^{1}H NMR (300 MHz, DMSO-d_6): 11.09-11.00 (m, 3H), 10.89-10.80 (m, 1H), 10.05-9.86 (m, 4H), 9.46-9.31 (m, 4H), 8.78-8.65 (m, 3H), 8.40-8.31 (m, 1H), 8.17-8.13 (m, 1H), 8.08 (s, 6H), 7.75 (s, 3H), 4.48-4.38 (m, 1H), 3.34 (s, 3H), 3.31 (s, 3H), 3.26 (d, ^3J(H,H) = 5.5 Hz, 2H), 2.87 (brt, 2H), 2.68 (brt, 2H), 1.48 (br s, 54H); ^{13}C NMR (125 MHz, DMSO-d_6): 171.6 (s), 171.2 (s), 166.6 (s), 152.9 (s), 150.7 (s), 141.0 (s), 138.8 (s), 134.4 (s), 133.2 (s), 132.6 (s), 125.6 (d), 122.8 (d), 122.4 (d), 122.0 (d), 120.7 (d), 114.0 (d), 113.7 (d), 112.3 (d), 112.1 (d), 102.2 (d), 53.2 (q), 40.5(t), 34.9 (s), 31.9 (t), 31.3 (q), 30.2 (t); MS (ESI, MeOH): 1443 (100, $[M\text{-}OMe]^+$), 1286 (50, $[M\text{-}(CO)_2(CH_2)_2NHCH_2CH(OMe)_2]^+$); HRMS (ESI, +ve) calcd for $C_{85}H_{93}N_{13}O_7Na_2Zn$: 1517.64 / 2 = 758.8198, found: 758.8177 ($[M+2Na]^{2+}$); MS (MALDI, HABA): 1472 (100, $[M+H]^+$).

Compound 7. TMSBr (2.5 mg, 16.2 μmol) was added to a solution of **28** (20 mg, 13.5 μmol) in DCM (2 ml). The mixture was stirred at rt for 1 h. The solvent was removed *in vacuo*, and the residue transferred into a centrifuge tube, precipitated from diethyl ether/hexane (1:9, 10 ml x 2 times) and diethyl ether (10 ml x 2 times), centrifuged and supernatant removed. The residue was concentrated *in vacuo* to give the desired **7** (16.5 mg, 86%) as green solid. Mp: > 400 ºC; IR: 3423 (s), 2956 (s), 1650 (s), 1596 (s), 1530 (s), 1491 (s), 1395 (s), 1341 (s), 1246 (s), 1137 (s), 1096 (s), 1052 (s), 950 (w), 891 (s), 825 (s), 744 (s), 719 (s); ^{1}H NMR (300 MHz, DMSO-d_6): 11.09-10.97 (br d, 3H), 10.90-10.79 (br s, 1H), 10.03-9.78 (m, 4H), 9.53-9.51 (brs, 1H) 9.44-9.26 (m, 4H), 8.79-8.62 (m, 4H), 8.56-8.49 (m, 1H), 8.40-8.31 (brd, 1H), 8.09 (s, 6H), 7.75 (s, 3H), 3.98 (t, ^{3}J(H,H) = 5 Hz, 2H), 2.90 (brt, 2H), 2.75 (brt, 2H), 1.48 (s, 54H);^{13}C NMR (125 MHz, DMSO-d_6): 200.2 (s), 200.1 (s), 166.7 (s), 153.1 (s), 150.7 (s), 141.0 (s), 139.1 (s), 138.8 (s), 134.3 (s), 133.1 (s), 132.6 (s), 125.9 (d), 122.8 (d), 122.4 (d), 122.0 (d), 120.7 (d), 114.0 (d), 113.7 (d), 112.4 (d), 112.1 (d), 34.9 (s), 30.4 (t); MS (ESI, MeOH): 1427 (100, $[M+H]^+$).

Compound 29. A solution of **30** (108 mg, 0.18 mmol) and HATU (69 mg, 0.18 mmol) in DMF (1 ml) was added to a solution of **27** (30 mg, 36.4 μmol) and collidine (24 μl, 0.18 mmol) in DMF (2 ml). The mixture was stirred at rt under nitrogen for 2 h. The volume of the solvent was reduced to 1 ml, transferred into a centrifuge tube, precipitated from diethyl ether/hexane (1:9, 45 ml x 2 times) and diethyl ether (45 ml x 2 times), centrifuged and supernatant removed. The residue was purified by silica gel column chromatography with (DCM/MeOH, 9.5:0.5; R_f 0.5 with DCM/MeOH, 9:1) to give pure **29** (39 mg, 41%) as a green solid. Mp: > 400 ºC; IR: 3380 (w), 3066 (w), 2926 (w), 1683 (s), 1599 (s), 1555 (s), 1492 (s), 1456 (s), 1398 (w), 1338 (s), 1230 (w), 1131 (s), 1093 (s), 996 (m), 823 (w), 733 (s), 696 (s); ^{1}H NMR (300 MHz, DMSO-d_6): 10.99 (brs, 3H), 10.82 (br s, 1H), 9.91-9.73 (m, 4H), 9.37-9.22 (m, 4H), 8.41-8.05 (m, 4H), 7.53-7.16 (m,

64H), 5.29-4.98 (m, 24H), 4.45-4.38 (m, 1H), 3.87-3.63 (tt, ^{3}J(H,H) = 5.5 Hz, ^{3}J(H,P) = 23.7 Hz, 3H), 3.34 (s, 3H), 3.30 (s, 3H), 3.27-3.14 (m, 8H), 2.89-2.79 (m, 2H), 2.71-2.61 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): 171.5 (s), 171.2 (s), 168.6(s), 168.2 (s), 153.5 (s), 153.1 (s), 153.0 (s), 152.8 (s), 152.5 (s), 141.1 (s), 140.7 (s), 139.1(s), 136.2 (s, ^{P}d, ^{3}J(C,P) = 6 Hz), 128.4 (d), 128.17 (d), 128.16 (d), 127.83 (d), 127.76 (d), 123.1 (d), 120.9 (d), 112.6 (d), 102.1 (d), 67.7 (t, ^{P}dd, ^{2}J (C,P) = 17 Hz, ^{4}J (C,P) = 6 Hz), 53.3 (d), 40.5 (t), 32.3 (t), 32.0 (t), 32.1 (d, ^{P}t, ^{3}J (C,P) = 134 Hz), 30.3 (t); MS (ESI, MeOH): 2522 (100, [M-OMe]$^{+}$); MS (MALDI, DCTB): 2554 (100, [M+H]$^{+}$).

Compound 31. TMSBr (12 µl, 92.1µmol) was added to a solution of **29** (10 mg, 3.8 µmol) in DCM (1 ml). The mixture was stirred at rt for 2 h. The solvent was removed *in vacuo*, and the residue transferred into a centrifuge tube, precipitated from diethyl ether/hexane (1:9, 10 ml x 2 times) and diethyl ether (10 ml x 2 times), centrifuged and supernatant removed. The residue was concentrated *in vacuo* to give the desired **31** (5.5 mg, 98%) as green solid. Mp: > 400 ºC; IR: 3054 (w), 2266 (w), 1766 (w), 1685 (s), 1604 (s), 1545 (s), 1487 (s), 1436 (s), 1339 (w), 1047 (s), 1021 (s), 957 (s), 908 (s), 825 (s), 744 (s), 643 (s); ^{1}H NMR (300 MHz, DMSO-d_6): 11.46-11.04 (m, 4H), 10.17 (brs, 1H), 9.89 (s, 1H), 9.59 (brs, 3H), 8.91 (s, 1H), 8.65 (brs, 4H), 3.76-3.12 (m, 15H).

Compound 32. This compound was synthesized according to reported procedures.[S1]

Compound 2a. This compound was prepared by stirring **32** (1.3 µmol) and **31** (4 mg, 2.7 µmol) in DMSO (0.24 ml) and AcOH (50 µl) for 1 day. The solution was diluted with DMSO and used for "initiation".

2.1.1. Synthesis of porphyrin 5 (Scheme S3)

Compound 33. This compound was synthesized according to reported procedures.[S5]

Compound 34. To a solution of **33** (50 mg, 74 μmol), HATU (28 mg, 74 μmol) and DIPEA (25 μl, 0.15 mmol) in dry DMF (2 ml), a solution of **10** (15 mg, 74 μmol) in 1 ml dry DMF was added dropwise for one hour under argon at room temperature. The stirring was continued for another four hours at room temperature. The reaction mixture was precipitated and washed with a mixture of diethyl ether: hexane (1:1) and the resulting dark purple precipitate **35** was used without any further purification. The resulting product was dissolved in 2 ml DMF and to this solution was added a mixture of **11** (73 μl, 0.46 mmol), HATU (0.18 g, 0.46 mmol), and DIPEA (0.16 ml, 0.93 mmol) and the reaction mixture was stirred at rt under Ar for 4 days. The reaction mixture was diluted with DCM and water. The layers were separated and the aqueous layer was extracted three times with small amounts of DCM. The combined organic layers were dried with anhydrous Na_2SO_4, then concentrated *in vacuo*. Silica gel column chromatography of the residue (DCM/MeOH 95:5; R_f 0.27) gave **34** (25 mg, 27%) as a purple solid. Mp: >230 ºC; IR: 3315 (w), 2919 (m), 2857 (w), 1659 (s), 1597 (m), 1522 (m), 1438 (w), 1388 (m), 1252 (m), 1182 (w), 735 (w); ^{1}H NMR (400 MHz, DMSO-d_6): 10.43 (s, 1H), 10.34 (s, 3H), 8.89-8.87 (br s, 8H), 8.15-8.03 (m, 16H), 4.39 (t, ^3J(H,H) = 8 Hz, 1H), 3.30 (m, 8H), 3.22 (t, ^3J(H,H) = 4 Hz, 3H), 2.73 (t, ^3J(H,H) = 4 Hz, 2 H), 2.59-2.50 (m, 3H), 1.72-1.67 (m, 6H), 1.59-1.50 (m, 6H), 1.42-1.37 (m, 12H), 1.00 (t, ^3J(H,H) = 8 Hz, 9H), 0.94 (t, ^3J(H,H) = 8 Hz, 9H), -2.91 (br s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): 174.6 (s), 171.5 (s), 170.9 (s), 139.3 (s), 139.2 (s), 135.8 (s), 135.7 (s), 134.4 (d), 119.8 (s), 117.4 (d), 117.0 (d), 101.9 (d), 64.6 (t), 53.0 (q), 48.2 (d), 40.3 (t), 31.8 (t), 31.6 (t), 30.0 (t),

29.2 (t), 25.5 (t), 22.1 (t), 14.9 (q), 13.7 (q), 11.7 (q); MS (ESI, MeOH): 1240 (100, $[M+H]^+$), 1263 (10, $[M+Na]^+$).

Compound 5. Compound **34** (10 mg, 8 μmol) was dissolved in 0.5 ml TFA; the solution immediately turned to green. After stirring for 40 min, the solvent was removed *in vacuo* and afterwards water and DCM was added to the residue. The organic layer was separated and the aqueous layer was extracted twice with small amounts of DCM. The combined organic layers were dried with Na_2SO_4, and concentrated *in vacuo*. Silica gel column chromatography of the residue (DCM/Acetone 3:1; R_f 0.17) gave **5** (5 mg, 51%) as a purple solid. IR: 3316 (w), 2923 (m), 2857 (w), 1704 (s), 1657 (m), 1597 (m), 1467 (w), 1305 (w), 1223 (m), 1177 (w), 851 (w); ^{1}H NMR (400 MHz, DMSO-d_6): 10.44 (s, 1H), 10.33 (s, 3H), 9.49 (s, 1H), 8.89 (br s, 8H), 8.15-8.05 (m, 16H), 3.94 (d, ^3J(H,H) = 8 Hz, 2H), 2.77-2.75 (m, 2H), 2.67-2.64 (m, 2H), 1.79-1.75 (m, 6H), 1.60-1.48 (m, 6H), 1.42-1.36 (m, 12H), 1.00 (t, ^3J(H,H) = 8 Hz, 9H), 0.94 (t, ^3J(H,H) = 8 Hz, 9H). MS (MALDI): 1195 (100, $[M+H]^+$).

2.2. Electrochemistry

Reduction potentials of **34** (1 mM in DMF) and **28** (0.25 mM in DMF) were determined using cyclic voltammetry and summarized in table S1. Scan rate: 100 mV/s, supporting electrolyte: 100 mM Bu_4NPF_6, working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: SCE. The potentials of **28** were further verified using square-wave voltammetry. The potentials were referenced to internal ferrocene.

2.3. Self-organizing surface-initiated polymerization

Initiation. Initiator **2** was deposited on ITO electrodes as reported.[S1] Initiation with **2a** was done similarly. Namely, ITO electrodes (1 x 2 cm^2) were cleaned in the RCA solution (boiling H_2O / 24% NH_4OH / 30% H_2O_2, 5 / 1 / 1, 15 min), rinsed with bidistilled water and EtOH, dried and immersed in the solution of **2a** (1 mM in DMSO). The coated electrode was tested for pin holes by measuring CV of potassium ferricyanide (0.5 mM $K_4Fe(CN)_6$, 0.1 M Na_2SO_4 in water) using the covered ITO as a working electrode (Fig. S15, Pt wire as a counter and Ag/AgCl as a reference). An anodic peak at ~0.4 V remained after more than 2 days of immersion in a solution of **2a**, and it was attributed to the presence of zinc-phthalocyanine on the electrode. The obtained ITO electrodes were heated in an oven for 1 h at 120 °C to achieve better bonding between phosphonic acids and ITO substrate. The electrodes were activated by a treatment with DTT (20 mM in 100 mM NH_4HCO_3aq) for 1 h at rt.

Propagation. ITO electrodes coated with activated initiator **2** or **2a** were placed in a deaerated solution of the propagator at c_{SOSIP} (**3**, 4 mM; **4**, 7 mM in $CHCl_3$/MeOH 1:1)[S1], with DIPEA (0.1 M) and shaken under argon atmosphere at rt. After 24 h, the electrodes were rinsed with DMSO and EtOH and dried under airflow.

Stack exchange. ITO electrodes after SOSIP (**16**) were shaken in an aqueous solution of NH_2OH HCl (1 M, pH 3) for 1 day at 40 °C to give **17**. The obtained electrodes were rinsed with water and EtOH, dried and then placed in solutions of aldehydes (**5** or **7**, 10 mM) in DMSO / AcOH (9/1) at 40 °C. Hydrazone formation was followed until no more changes in UV-vis spectra were observed.

Yields of stack exchanges were estimated after destroying the SOSIP film using 2-mercaptoethanol. Namely, the ITO electrode with SOSIP after stack exchange (**18** or **18a**) was placed in a solution of 2-mercaptoethanol (20 mM) and DIPEA (100 mM) in DMSO. Within about 5 min the film was complete dissolved. Yield was calculated from the molar ratio of NDI (as in **4**, 480 nm, $\varepsilon = 1.8 \times 10^4$) and Pc (as in **6**, 696 nm, $\varepsilon = 2 \times 10^5$) determined from the absorption spectrum of the resulting DMSO solution (Fig. S16b). The Pc/NDI ratio of 2 was assumed as 100%.

Metallation of porphyrin stacks. ITO electrodes after SOSIP with free base porphyrin stacks (**19**) were dipped and shaken in a solution of $Zn(OAc)_2$ (0.1 M in MeOH) at rt to give **20**. The course of the reaction was followed spectroscopically. Typically the reaction completed within ~10 min.

Formation of OMARG photosystems (Scheme S4, Fig. S17). ITO electrodes with activated initiator (**15**) were placed in a deaerated solution of **3** (4 mM in $CHCl_3$/MeOH 1:1) and DIPEA (0.1 M) and shaken under argon atmosphere at rt. After 6 h, the electrodes were rinsed with DMSO and EtOH and dried under flow of air. The resulting electrodes were briefly treated with DTT (20 mM in 100 mM NH_4HCO_3aq, 10 sec), rinsed with water and EtOH, dried, and dipped in a deaerated solution of **4** (7 mM in $CHCl_3$/MeOH 1:1) and DIPEA (0.1 M). After shaking for 16 h under argon atmosphere, the electrode was rinsed with DMSO and EtOH. Resulting electrode **38** was immersed in an aqueous solution of NH_2OH HCl (1 M) for 1 day at 40 °C, rinsed with water and EtOH, dried, and then immersed in a solution of **5** (10 mM) in DMSO/AcOH (10/1) for 1 day at 40 °C. The electrode was rinsed with DMSO and EtOH, and dried. Resulting electrode **21** was immersed in a solution of $Zn(OAc)_2$ (0.1 M in MeOH) for 0.5 min. The electrode was rinsed with

water and EtOH and dried to give **22**. The obtained electrode **22** was treated with NH_2OH HCl (1 M aqueous solution, rt, 5 min), rinsed with water and EtOH, dried, and then immersed in a solution of **7** (10 mM) in DMSO/AcOH (10/1) for 10 min. The resulting electrode was rinsed with DMSO and EtOH, and dried under flow of air to give **1**. The electrode **23** was obtained by the treatment of **21** with NH_2OH (1 min) followed by **7** (5 min).

2.4. Photocurrent measurements

Photocurrent measurements (Figs. 2 and 3). Coated ITO electrodes were used as a working electrode with a Pt wire as a counter electrode and Ag/AgCl as a reference electrode. The electrodes were immersed in a deaerated (by bubbling Ar gas through) aqueous solution of MDESA (50 mM) and Na_2SO_4 (0.1 M) and irradiated with a solar simulator (area of irradiation: a = ~0.7 cm^2). Changes in current upon on-off switching of irradiations were measured at 0 V *vs* Ag/AgCl unless stated. The power of irradiation was as indicated. Neutral density filters were used to reduce the light intensity to <42 mW/cm^2. Bimolecular recombination efficiencies η_{BR} were calculated from the dependence of photocurrent densities (J) to the irradiation power (I) using the equations S1 and S2.[S6]

$$J \propto I^{\alpha} \qquad \text{(S1)}$$

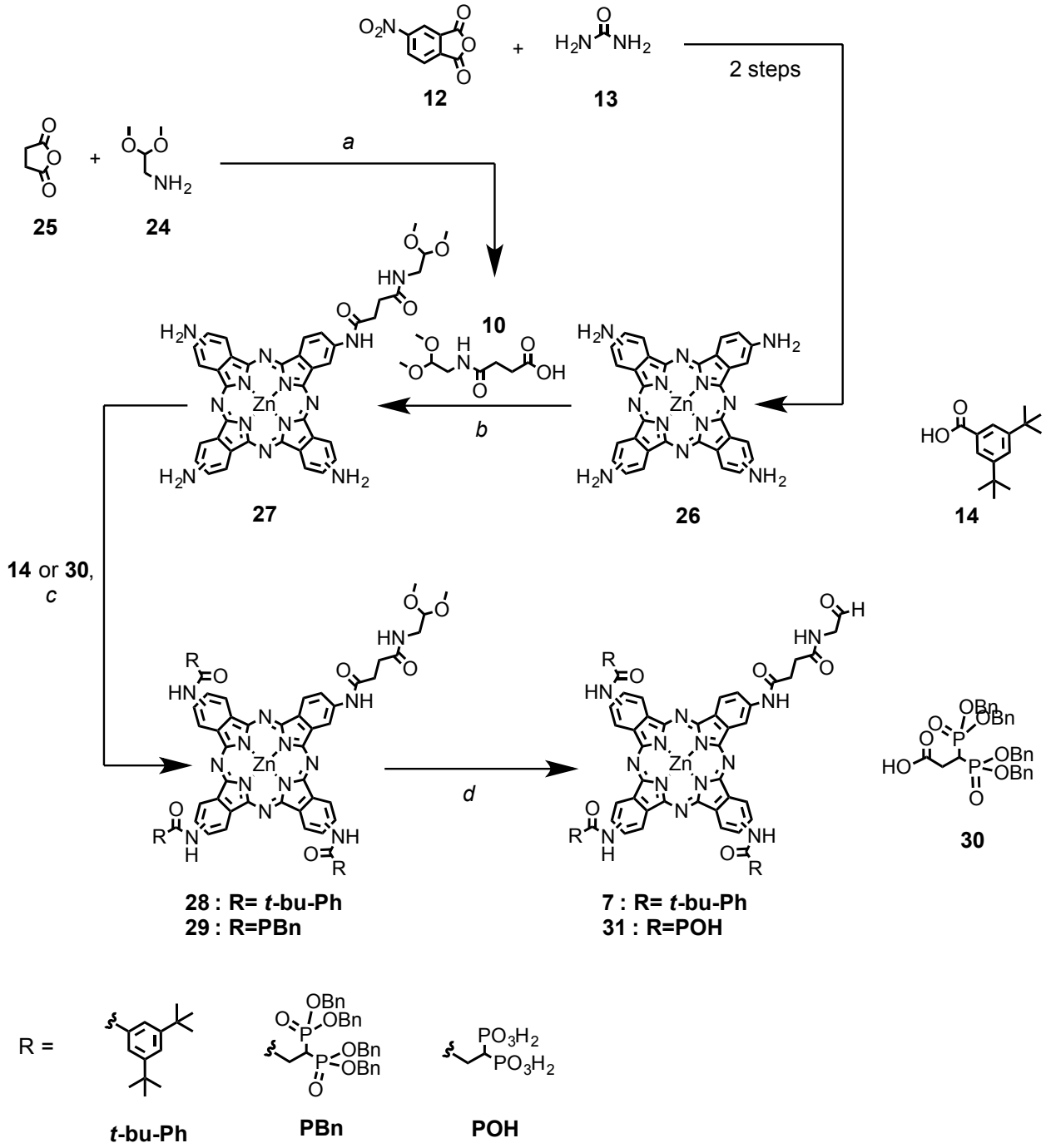
$$\eta_{BR} = \alpha^{-1} - 1 \qquad \text{(S2)}$$

Action Spectra (Fig. S16). Photocurrent densities were measured using MDESA (50 mM) and Na_2SO_4 (0.1 M) at 0 V *vs* Ag/AgCl upon excitation by monochromatic light (150 W Xe lamp with Oriel 1/8 m monochromator). The obtained current densities were converted into incident

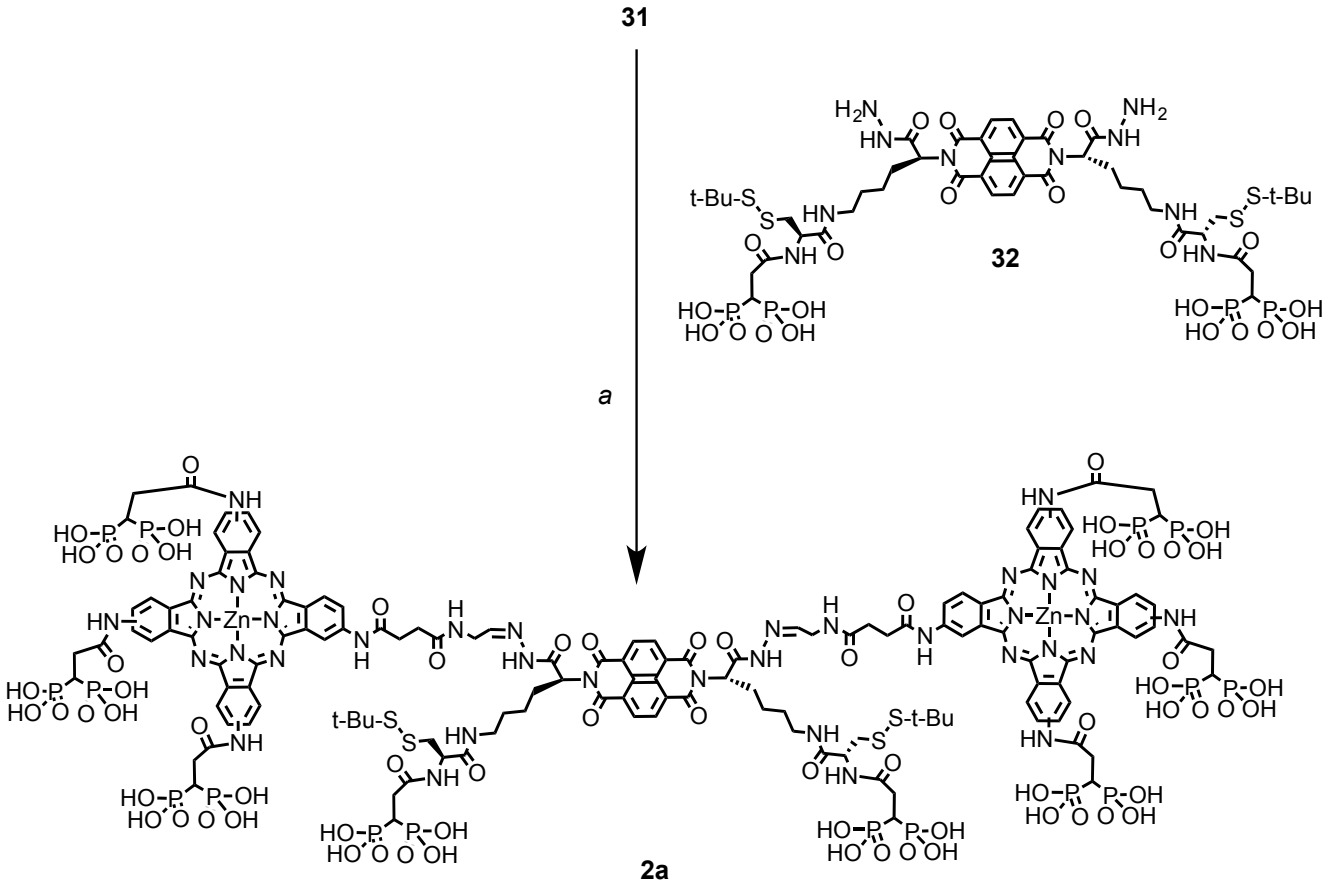
photon to current conversion efficiencies (IPCEs) by using the equation (S3).[S7] P_{in} is the irradiation power (W/cm^2).

$$IPCE = 1240 / \lambda\ (nm) \times J_{sc} / P_{in} \qquad (S3)$$

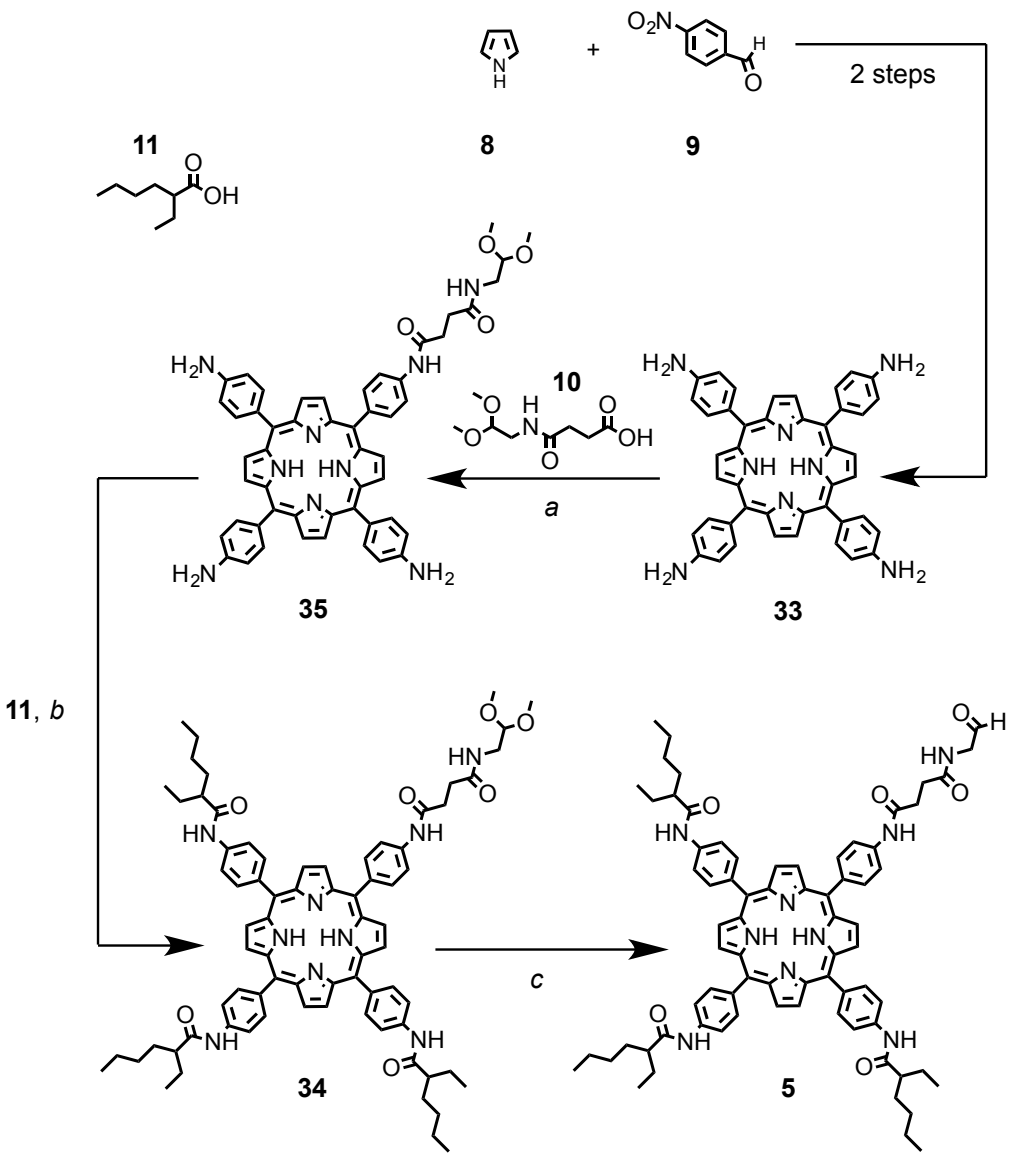
3. Supporting schemes and figures



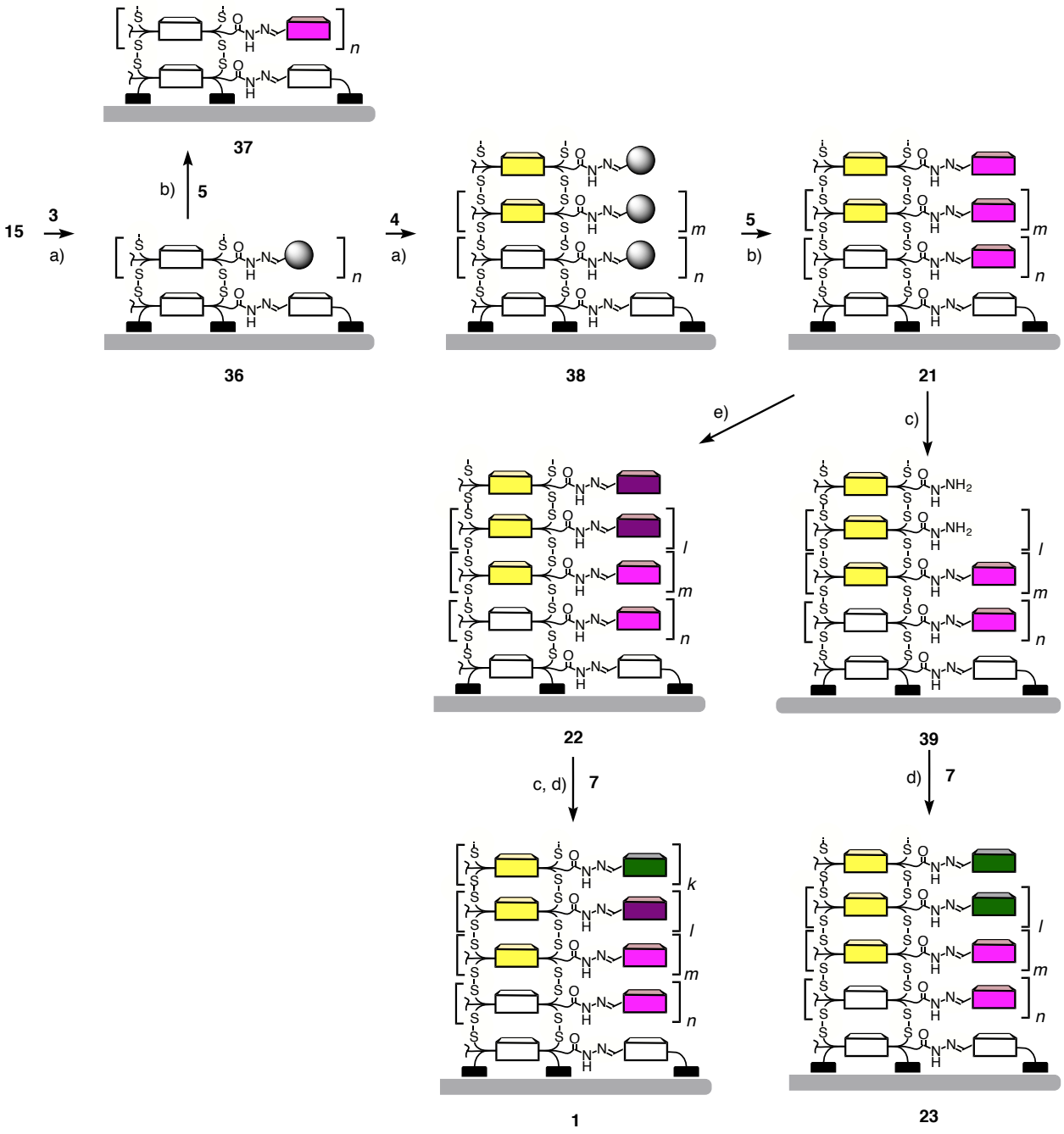
Scheme S1. a) 1,4-Dioxane, 80 ºC, 40 min (97%); b) **10**, HATU, 2,4,6-collidine, DMF, 16 h, r.t.; c) **14** or **30**, HATU, 2,4,6-collidine, DMF, 2 h, r.t. (**28**: 32%; **29**: 41%, over two steps); d) TMSBr, DCM, 1h (**7**: 86%; **31**: 98%).



Scheme S2. a) AcOH, DMSO, rt, 1 d.



Scheme S3. a) **10**, HATU, DIPEA, DMF, 5 h, r.t.; b) **11**, HATU, DIPEA, DMF, 4d, r.t. (2 steps 27%); c) TFA, DCM, 40 min (51%).



Scheme S4. a) **3** or **4**, DIPEA, $CHCl_3$, MeOH; b) 1. NH_2OH, 2. **5**, AcOH, DMSO; c) NH_2OH; d) **7**, AcOH, DMSO; e) $Zn(OAc)_2$.

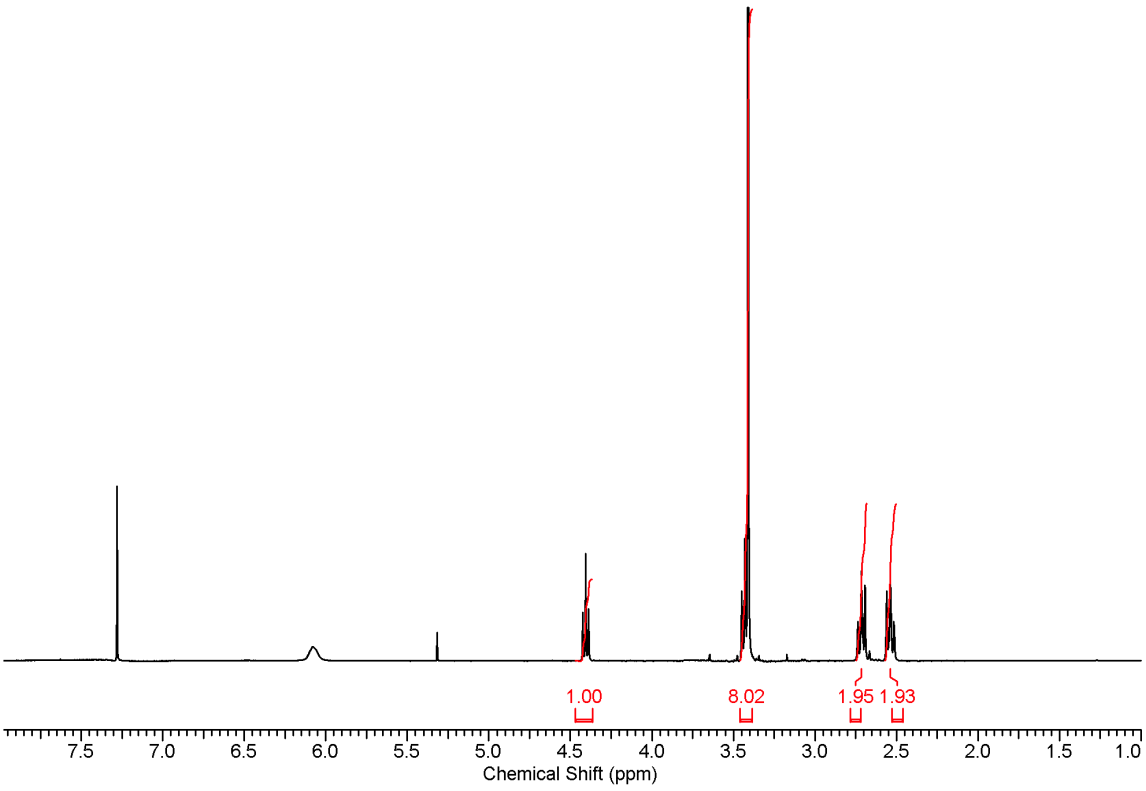


Figure S1. ^{1}H NMR spectrum of **10** in $CDCl_3$.

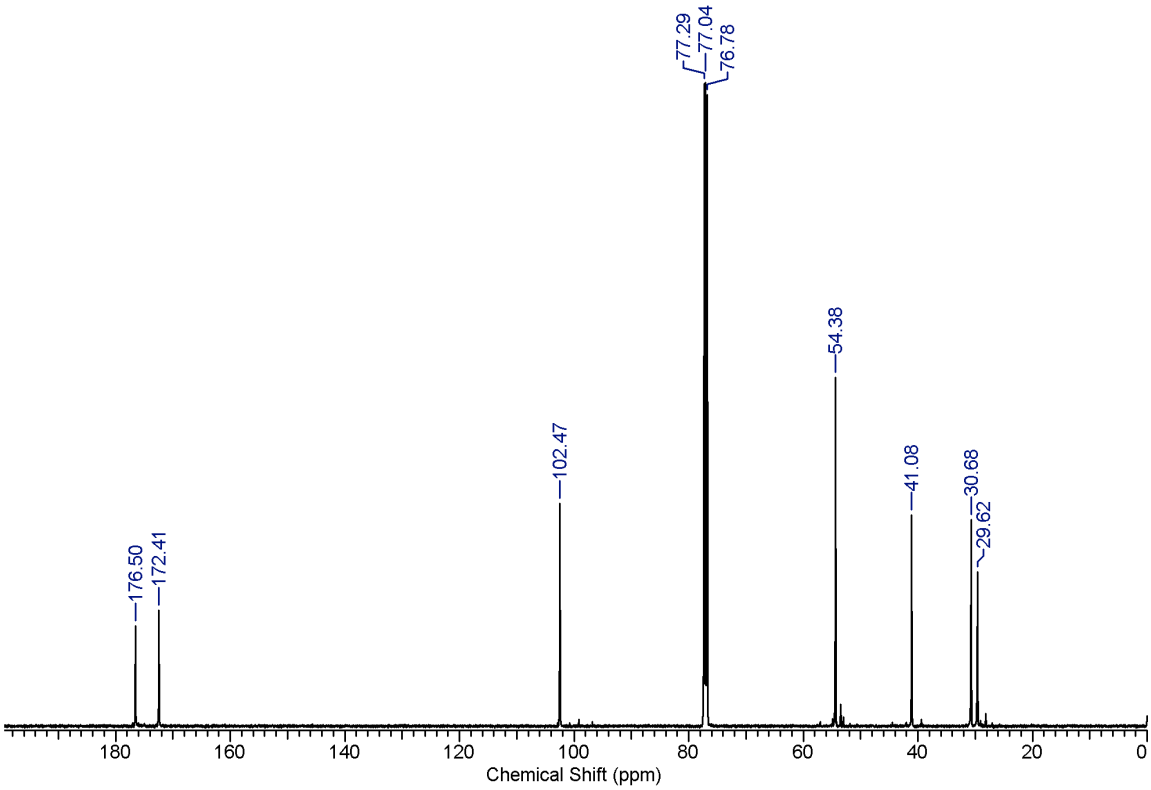


Figure S2. ^{13}C NMR spectrum of **10** in $CDCl_3$.

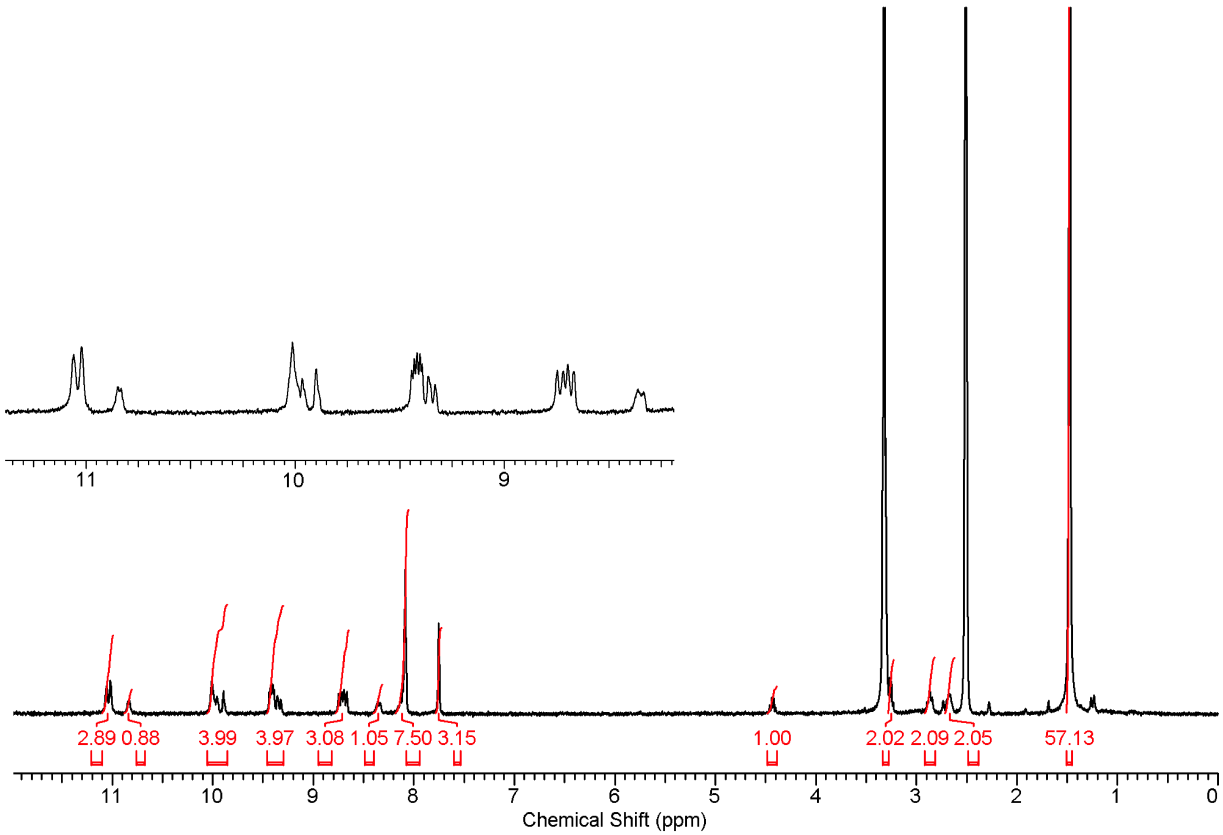


Figure S3. [1]H NMR spectrum of **28** in DMSO-d6. Inset: zoom of aromatic region.

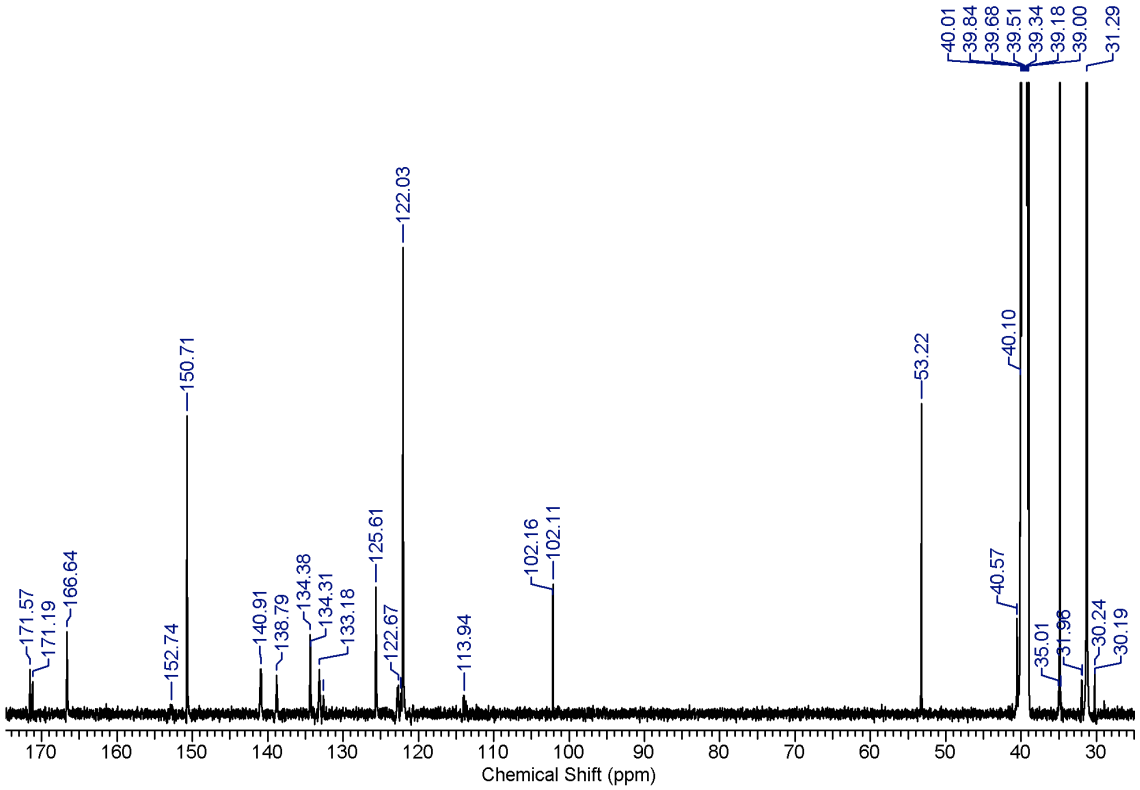


Figure S4. [13]C NMR spectrum of **28** in DMSO-d6.

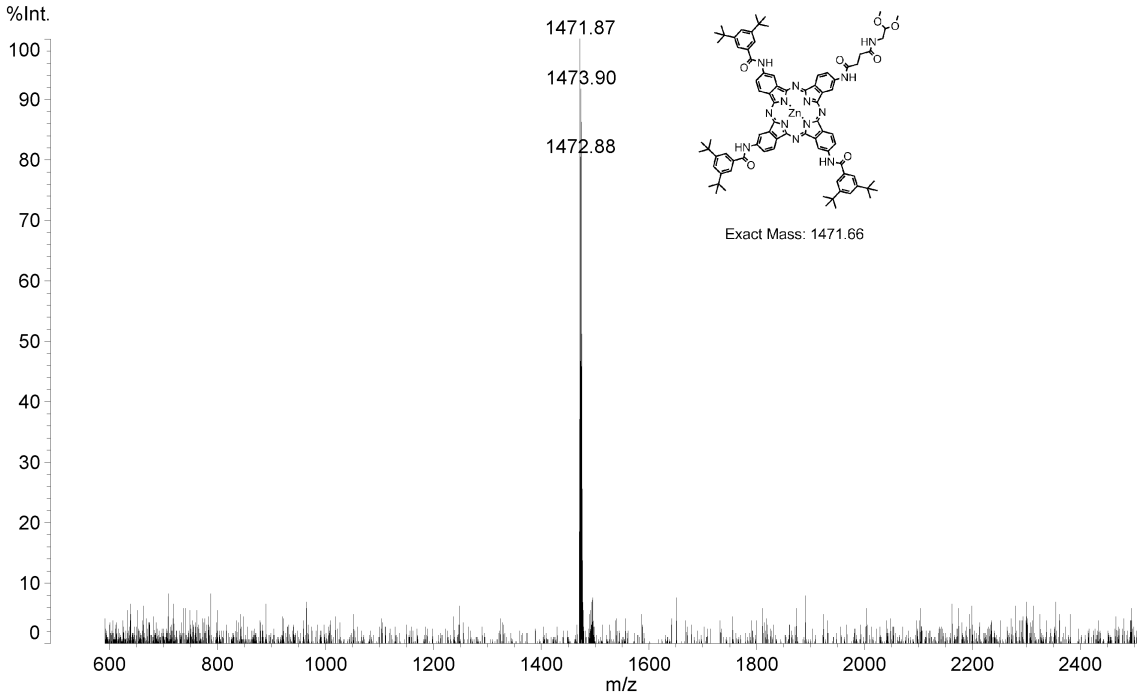


Figure S5. MALDI MS of **28** in HABA matrix.

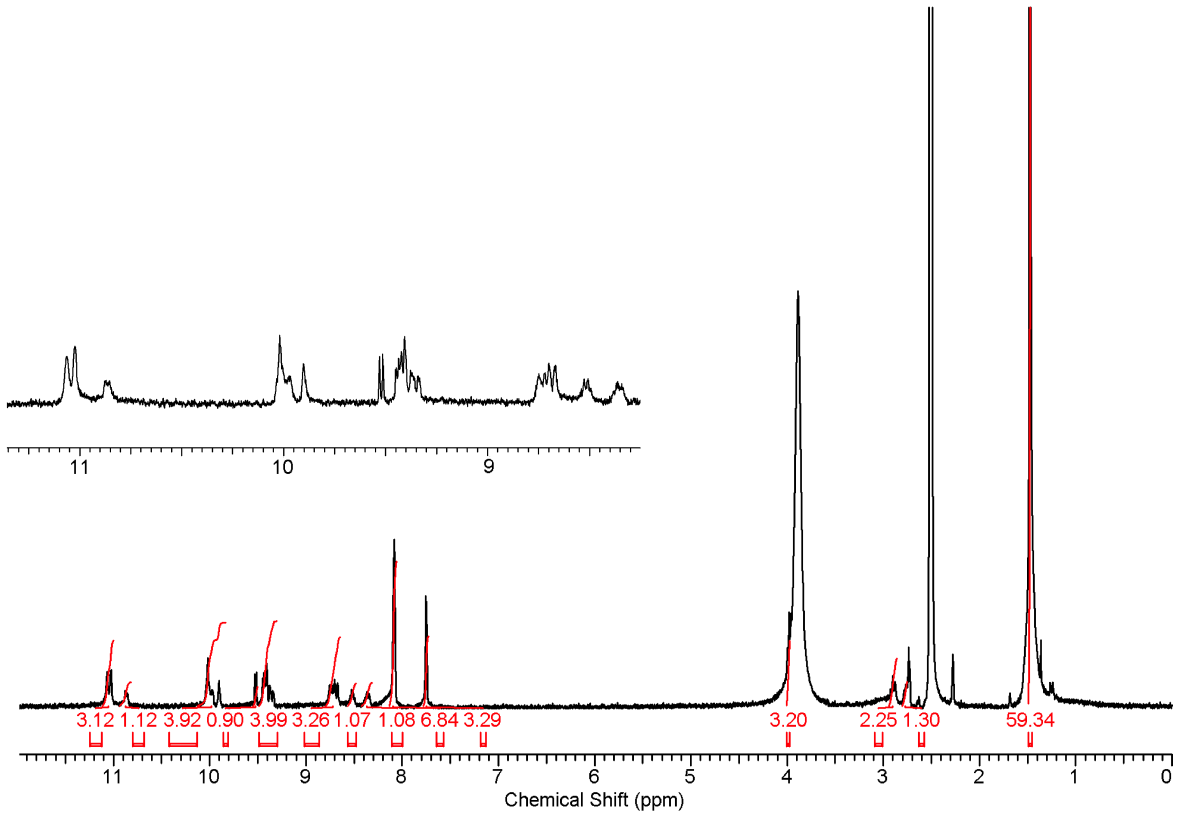


Figure S6. ^{1}H NMR spectrum of **7** in DMSO-d6. Inset: zoom of aromatic region.

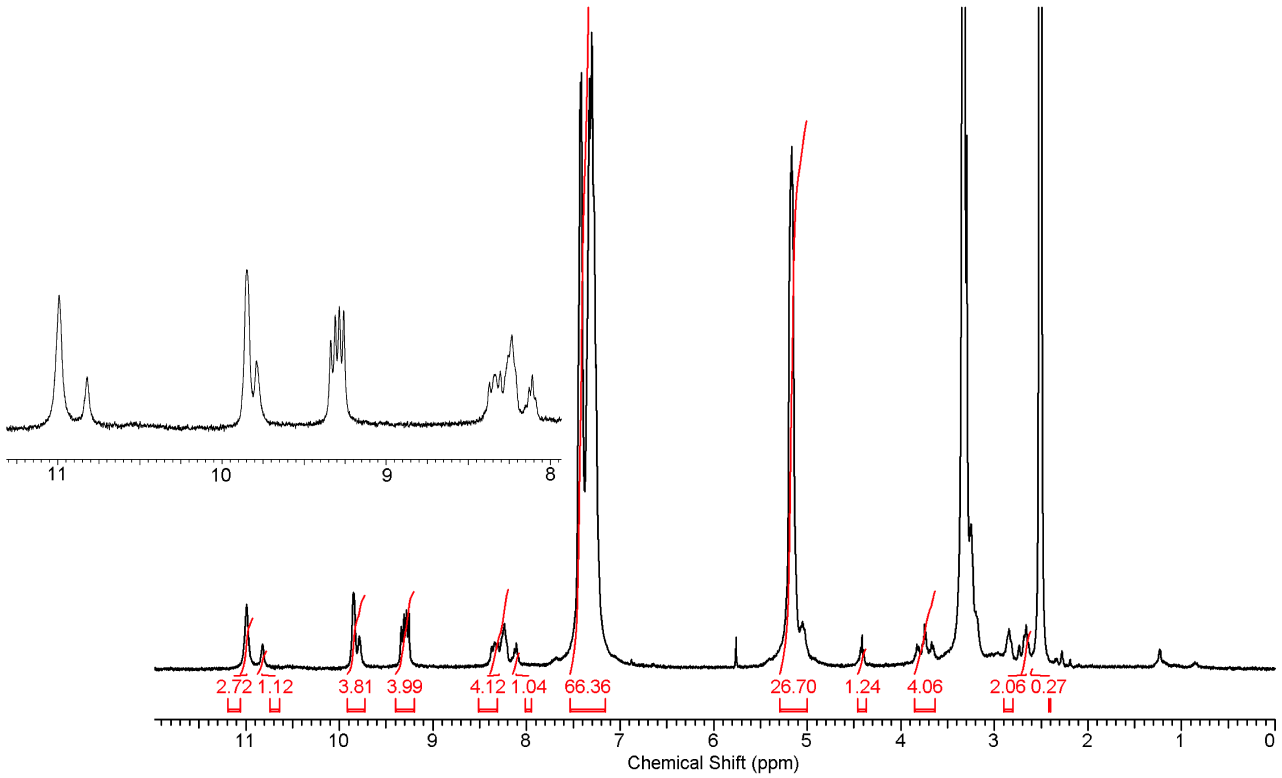


Figure S7. [1]H NMR spectrum of **29** in DMSO-d6. Inset: zoom of aromatic region.

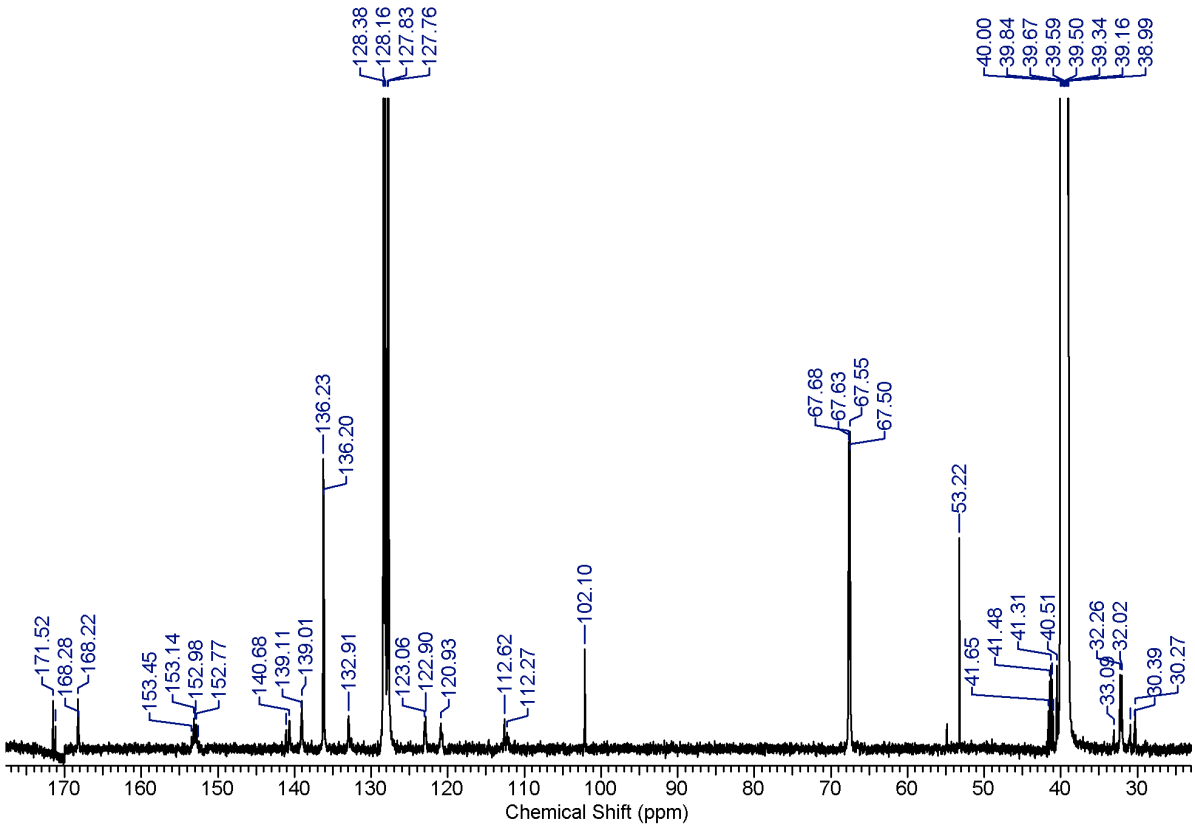


Figure S8. [13]C NMR spectrum of **29** in DMSO-d6.

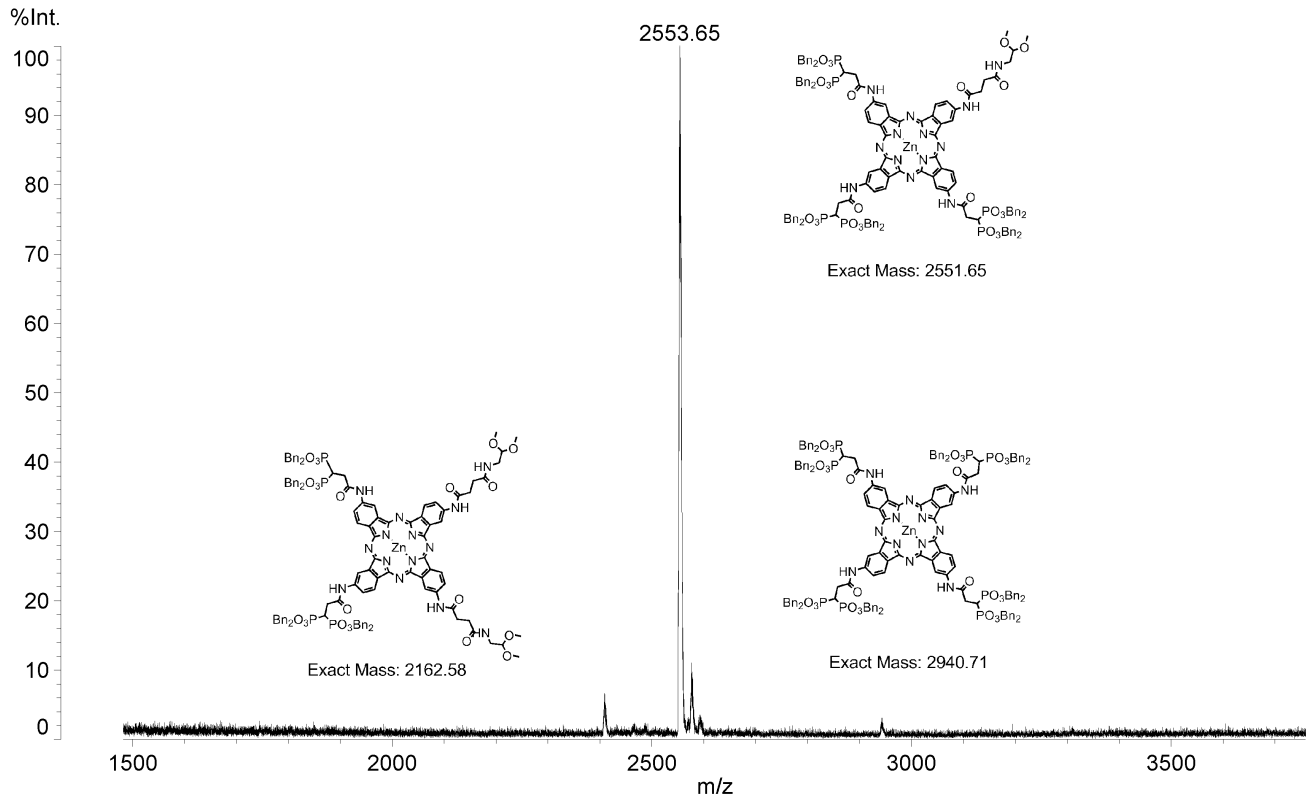


Figure S9. MALDI MS of **29** in DCTB matrix.

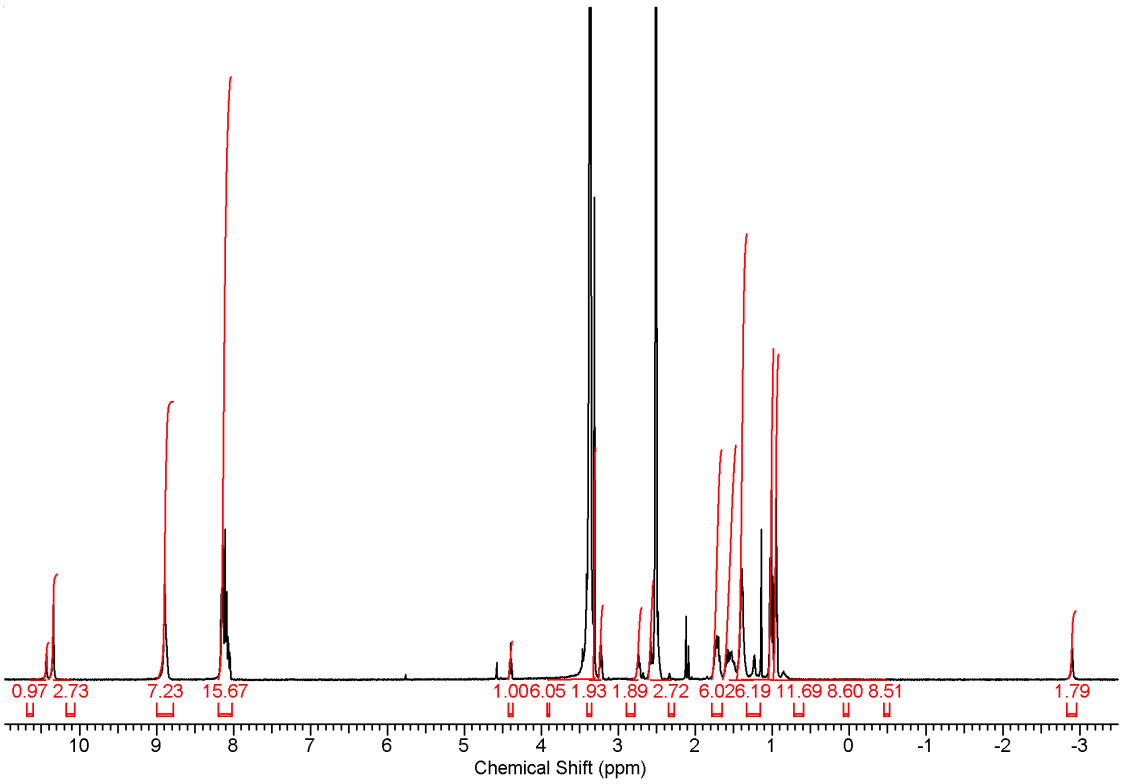


Figure S10. ^{1}H NMR spectrum of **34** in DMSO-d6.

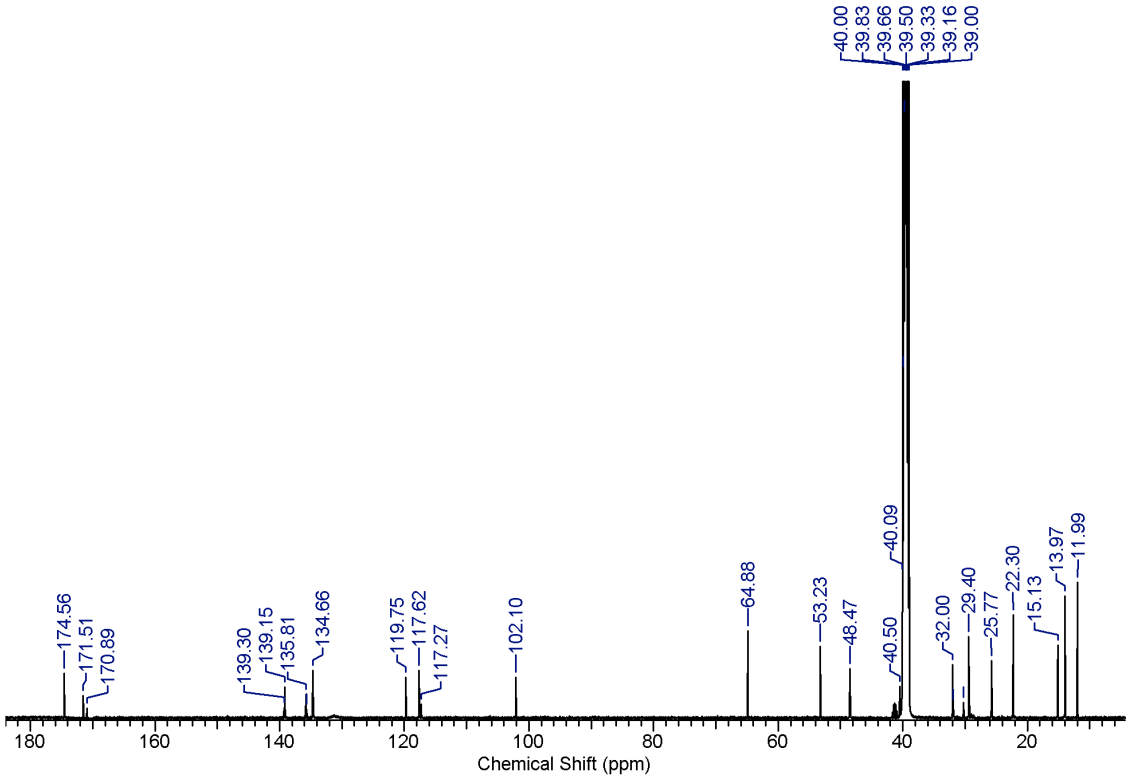


Figure S11. ^{13}C NMR spectrum of **34** in DMSO-d6.

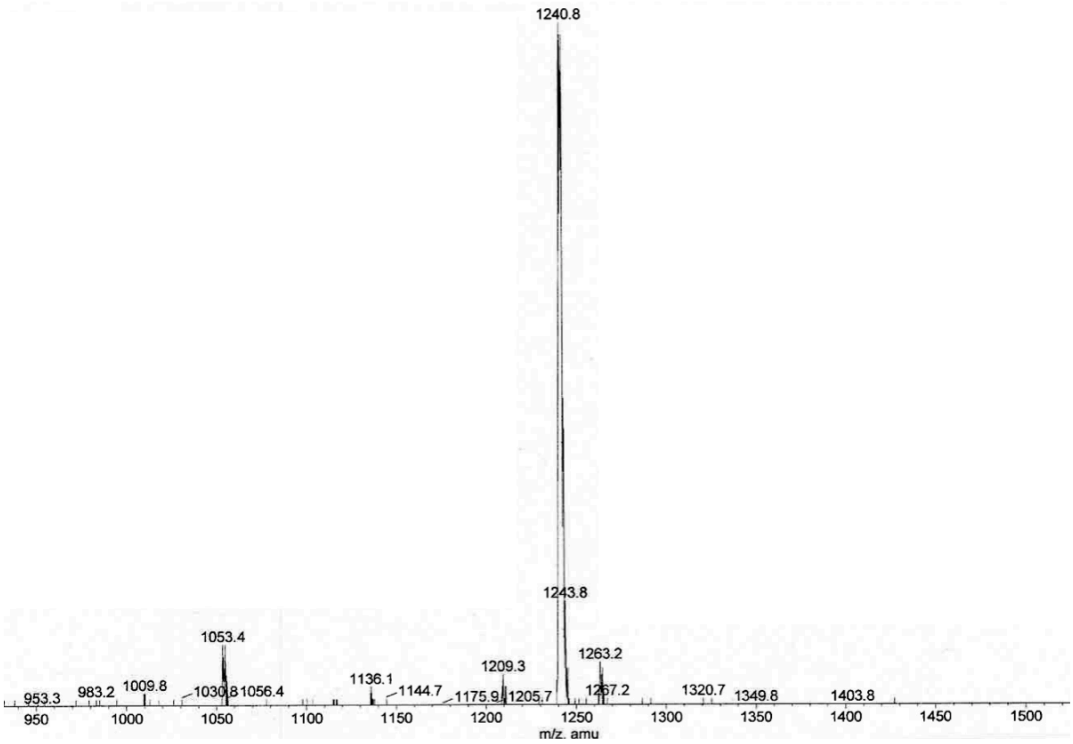


Figure S12. ESI-MS of **34**.

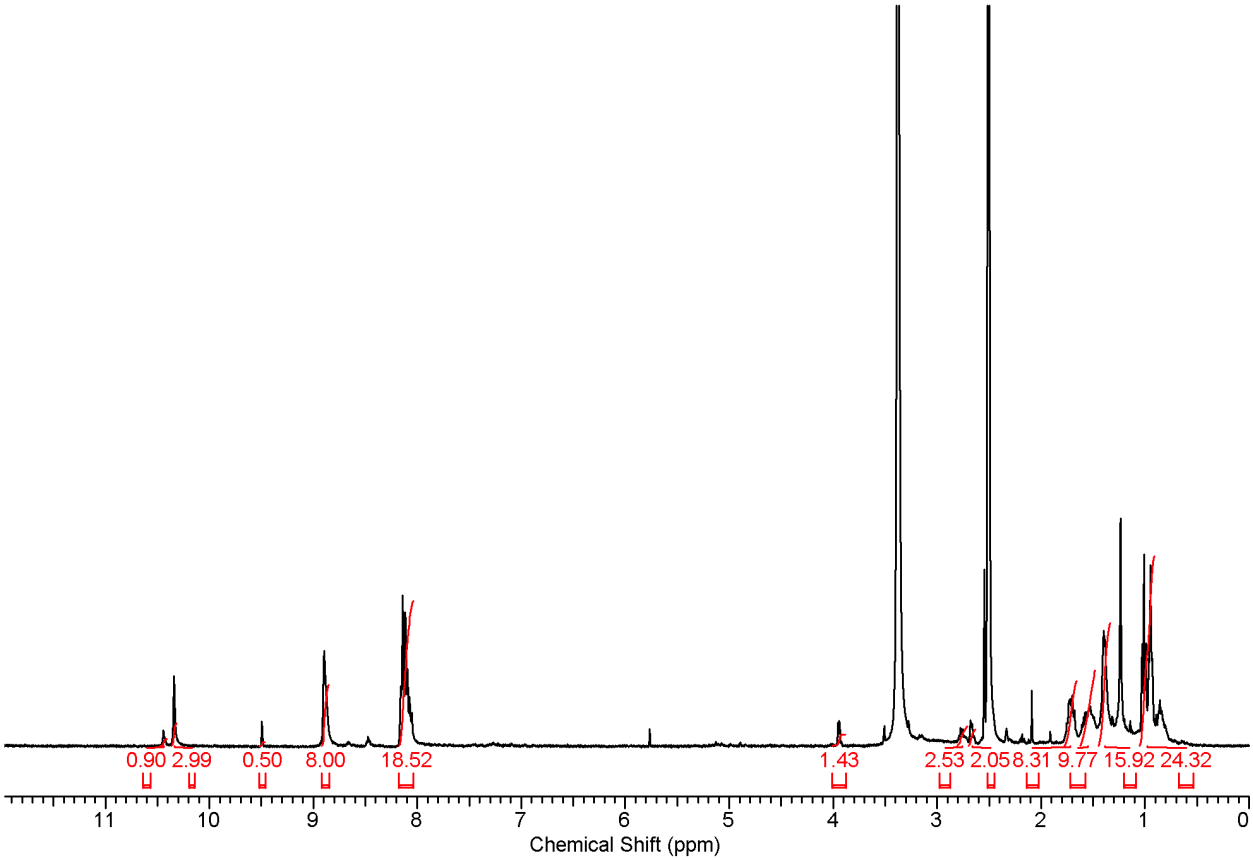


Figure S13. ^{1}H NMR spectrum of **5** in DMSO-d6.

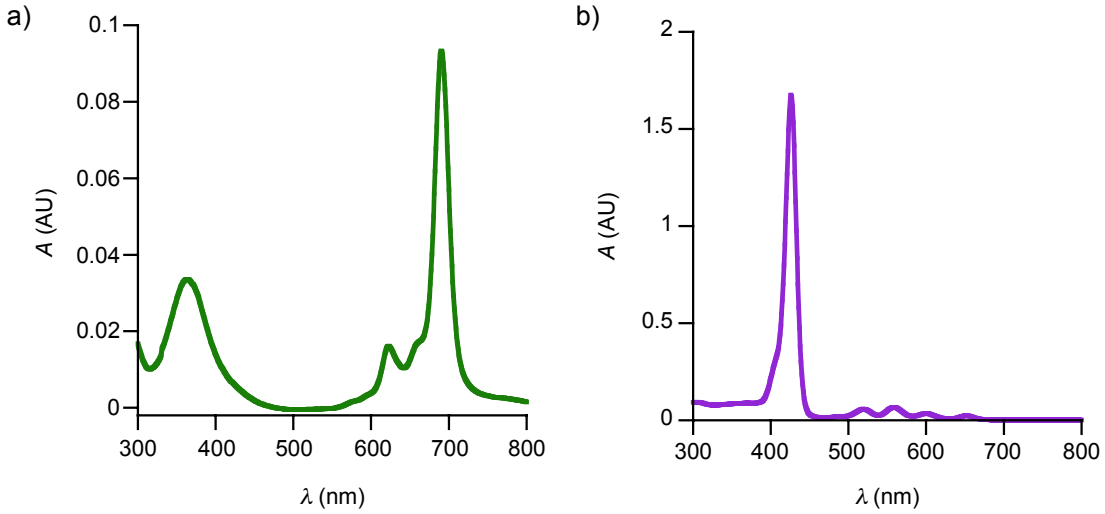


Figure S14. UV-vis absorption spectra of a) **28** and b) **34** in DMF.

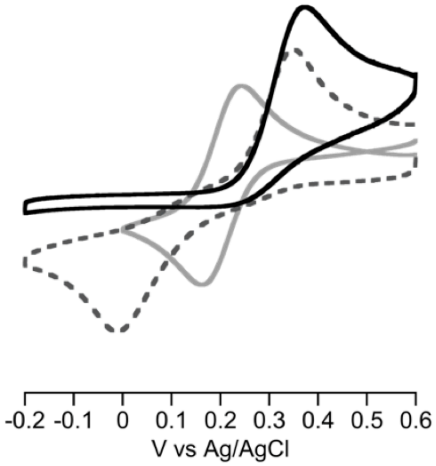


Figure S15. Cyclic voltammograms of aqueous ferricyanide measured using an ITO electrode as a working electrode before the deposition of the initiator (gray), after 1 (dashed) and >2 days (solid line) in the solution of the initiator **2a**.

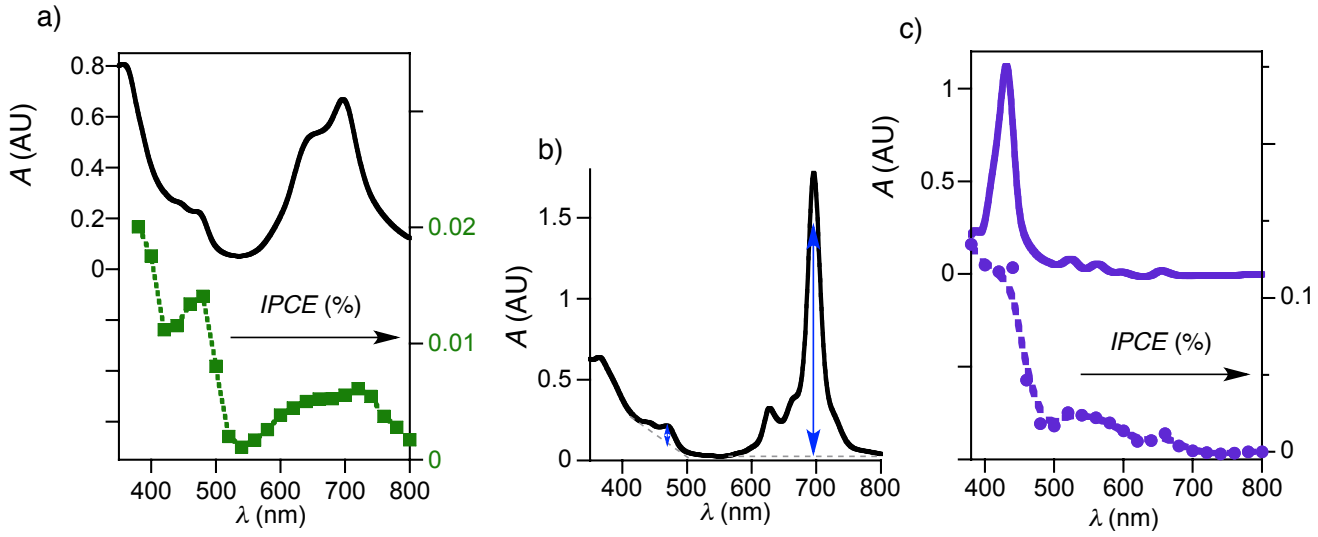


Figure S16. a) Absorption spectrum (top) of the film **18** formed using propagator **4** with an initiator **2** and phthalocyanine stack **7**, and its action spectrum (bottom); b) Absorption spectrum of the solution obtained by treating the same film **18** with 2-mercaptoethanol; c) Absorption spectrum (top) of the film **37** formed using propagator **3** with an initiator **2** and porphyrin stack **5**, and its action spectrum (bottom).

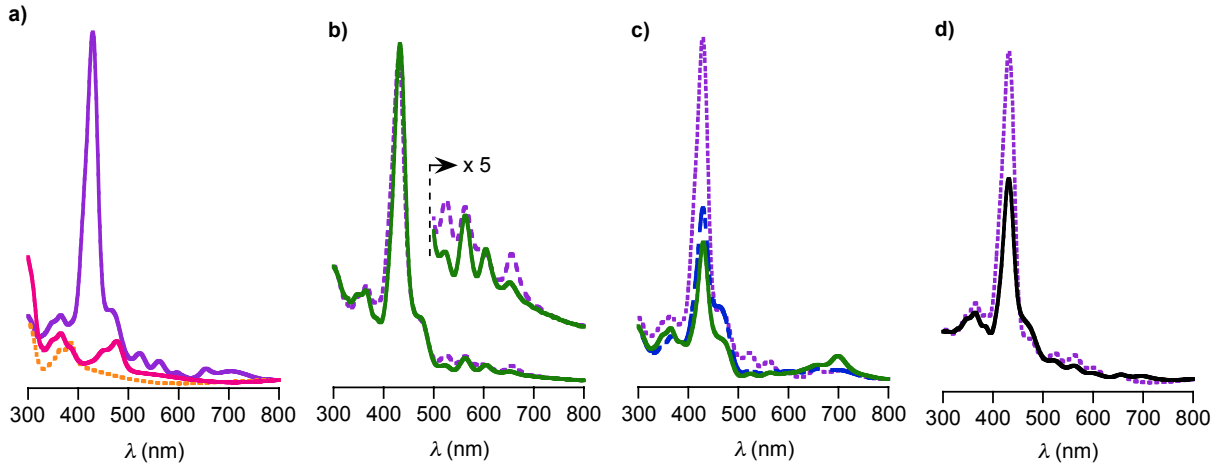


Figure S17. Build-up of multicomponent systems. a) **36** (orange dotted line), **38** (red solid line) and **21** (purple solid line); b) **21** (purple dotted line) and **22** (green solid line); c) **21** (purple dotted line), **39** (blue hatched line) and **23** (green solid line); d) **22** (purple dotted line) and **1** (black solid line).

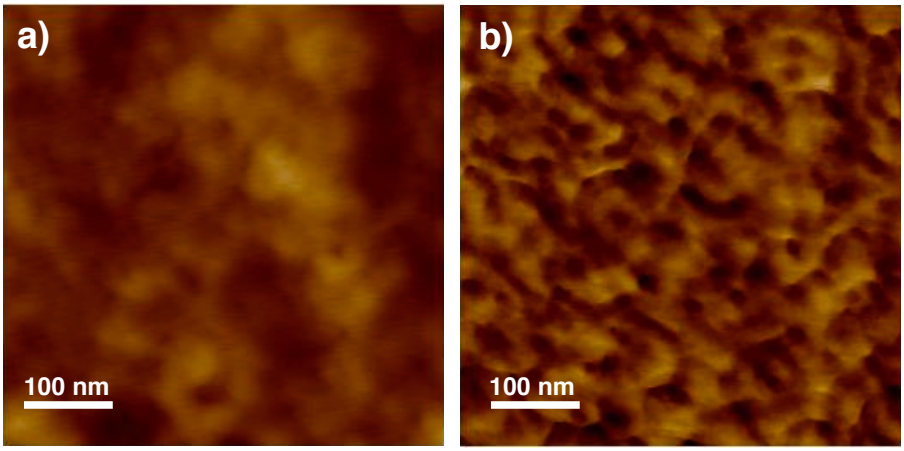


Figure S18. AFM images of a film **21**. a) Height image (0-30 nm); b) Phase contrast image (0-40°).

Comment: Despite the presence of large stacks, smooth surface (roughness R_a = 1.17 nm) and fine structures in phase contrast image, characteristic of SOSIP architectures were intact.

4. Supporting table

Table S1. Summary of optoelectronic data

Compound	E_{OX}[a] (V)	E_{RED}[a] (V)	E_{HOMO}[b] (eV)	E_{LUMO}[b] (eV)	$\Delta E_{HOMO/LUMO}^{opt}$[c] (eV)
28	0.21	-1.37	-5.31	-3.73	1.74
34	0.47	-1.57	-5.57	-3.53	1.80

[a]First oxidation and reduction potential in V against Fc/Fc^+, [b]HOMO and LUMO energies in eV against vacuum; from $E_{HOMO}/_{LUMO}$ = -5.1eV-$E_{red/ox}$(Fc), and [c]$\Delta E_{HOMO/LUMO}^{opt} = 1240/\lambda^{onset}$ (nm).

5. Supporting references

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