Self-organizing surface-initiated polymerization of perylenediimides on indium tin oxides

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Supplementary Information

Table of content

1. Materials and methods

As in ref. S1, Supporting Information. Briefly, reagents for synthesis were purchased from Fluka and Acros, amino acid derivatives from Novabiochem and Bachem. MDESA was prepared according to ref. S2. Indium tin-oxide (ITO) coated glass substrates were obtained from either Merck KGaA (Darmstadt, Germany) or 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 (TLC) were performed on silica gel 60 (Fluka, 0.2 mm). Melting points (m.p.) on a heating table from Reichert (Austria). 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 $mM^{-1}cm^{-1}$). Circular dichroism spectra were obtained using JASCO J-815 spectropolarimeter and are reported as extremum wavelength λ in nm (Δε 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 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. Proton signals with low deuterium exchange rates (half life ≥ 5 min) are marked "exchangeable". ^{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 NanoScope IIIa (Veeco/ Digital Instruments, Santa Barbara, CA) multimode atomic force microscope, in tapping mode using Si cantilevers (OMCL-AC160TS, Olympus) at scan rates of usually 1 Hz (0.25 Hz for scan area of 100 x 100 μm^2). Optical images were taken using a microscope equipped on AFM.

Abbreviations. AFM: Atomic force microscopy; Boc: *t*-Butoxycarbonyl; Cbz: (Benzyloxy)carbonyl; CV: Cyclic voltammetry; Cys: Cysteine; DCM: Dichloromethane; DMF: N,N-Dimethylformamide; DTT: DL-Dithiothreitol; Fc: Ferrocene; HOBt: 1-Hydroxybenzotriazole; IPCE: Incident photon to current conversion efficiency; ITO: Indium tin oxide; Lys: Lysine; MDESA: p-methoxy aniline di(2-ethylsulfonic acid); NDI: 1,4,5,8-Naphthalenediimide; PDA: 3,4,9,10-Perylenetetracarboxylicdianhydride; PDI: 3,4,9,10-Perylenetetracarboxylicdiimide; rt: Room temperature; SOSIP: Self-organizing surface-initiated polymerization; TBTU: *O*-(Benzotriazol-1-yl)-*N*,*N*,*N*',*N*'-tetramethyluronium tetrafluoroborate; TFE: 2,2,2-trifluoroethanol; TEA: Triethylamine; TEOA: Triethanolamine; TFA: Trifluoroacetic acid.

2. Supporting text

2.1. Synthesis

2.1.1. Synthesis of initiator 1 and 19 (Scheme S1)

Compound 4. This compound was synthesized according to reported procedures.[S3]

Compound 6. A solution of **4** (0.150 g, 0.28 mmol) and H-Lys(Cbz)-NH_2 (0.315 g, 1.1 mmol) in pyridine (6 ml) was refluxed (130 °C) for 18 h under argon. H-Lys(Cbz)-NH_2 (0.08 g, 0.28 mmol) was added and the mixture was further heated at reflux for 1 h. The reaction was then allowed to cool down and carefully poured on 80 ml of 1 M $KHSO_4$. The aqueous layer was extracted with AcOEt (4 x 50 ml) and the organic layer dried over anhydrous Na_2SO_4, then concentrated *in vacuo*. Silica gel column chromatography of the residue (DCM/MeOH 95:5; R_f 0.1) gave pure **6** (0.161 g, 55%) as a green solid. Mp: 154-155 ºC; CD (DCM/MeOH 1:1): 709 (+0.56), 432 (-0.91), 339 (+2.60), 283 (-1.59), 26 (-0.42); IR: 3347 (w), 2931 (w), 1685 (s), 1590 (m), 1512 (w), 1415 (m), 1343 (m), 1243 (m), 1126 (w), 735 (w); ^{1}H NMR (500 MHz, $CDCl_3$): 8.45-8.40 (m, 2H), 8.22 (s, 2H), 7.49-7.44 (m, 2H), 7.31-7.23 (m, 10H), 6.23-6.15 (m, 1H), 5.73-5.69 (m, 2H), 5.07-5.04 (m, 2H), 5.02-4.97 (m, 4 H), 3.85-3.75 (m, 2H), 3.45-3.31 (m, 2H), 3.15-3.00 (m, 4H), 2.38-2.30 (m, 2H), 2.14-2.01 (m, 8H), 1.72-1.64 (m, 2H), 1.60-1.45 (m, 4H), 1.41-1.31 (m, 2H), 1.23-1.15 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 172.4 (s), 164.8 (s), 163.1 (s), 156.4 (s), 146.5 (s), 136.6 (s), 133.3 (s), 129.1 (s), 128.5 (s), 128.0 (s), 126.5 (d), 125.1 (d), 121.7 (s), 121.5 (d), 120.8 (s), 118.5 (s), 117.7 (s), 66.5 (t), 54.48 (d), 53.5 (t), 50.73 (t), 40.8 (t), 29.7 (t), 28.3 (t), 25.8 (t), 23.7 (t); MS (ESI, DCM): 791 (100, $[M+H]^+$); HRMS (ESI, +ve) calcd for $C_{60}H_{61}N_8O_{10}$: 1053.4505, found: 1053.4493.

Compound 9. A solution of **6** (50 mg, 0.05 mmol), HBr (5.7 M in AcOH, 25 µl, 0.14 mmol), thioanisole (15 mg, 0.10 mmol) and pentamethylbenzene (7 mg, 0.05 mmol) in TFA (680 µl) was stirred for 3 h at rt. The mixture was concentrated *in vacuo*, and washed with diethylether (solid-liquid extraction). HCl (1 M in H_2O, 1 ml) was added to the residue and the mixture was concentrated *in vacuo*. To the residue was added the mixture of Boc-Cys(S-*t*-Bu)-OH (60 mg, 0.19 mmol), TBTU (60 mg, 0.19 mmol), HOBt (25 mg, 0.19 mmol) and 2,4,6-collidine (24 µl, 0.19 mmol) in DMF (600 µl). The pH of the solution was adjusted to about 8 by the addition of more collidine. The resulting mixture was stirred for 1.5 h at rt under argon, diluted with EtOAc, washed successively with 1 M HCl, brine, saturated $NaHCO_3$ aqueous solution, and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Silica gel column chromatography of the residue (DCM/MeOH 95:5; R_f 0.5 with DCM/MeOH 9:1) gave pure **9** (39 mg, 60%) as a green solid. Mp: 170-171 ºC; CD (DCM): 731 (-0.38), 676 (+0.33), 560 (-0.45), 445 (+0.68), 350 (-0.43), 320 (+0.55); IR: 3345 (w), 2959 (w), 2456 (w), 1688 (s), 1647 (s), 1591 (m), 1456 (w), 1416 (m), 1343 (m), 1244 (m), 1167 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 8.37 (d, ^3J (H,H) = 8.0 Hz, 2H), 8.17 (s, 2H), 7.44 (d, ^3J (H,H) = 8.0 Hz, 2H), 6.49 (s, 2H), 5.99 (br s, 2H), 5.69-5.63 (m, 2H), 5.42-5.37 (m, 2H), 4.32-4.26 (m, 2H), 3.79-3.73 (m, 2H), 3.49-3.39 (m, 2H), 3.18-3.06 (m, 4H), 3.02-2.94 (m, 4H), 2.37-2.25 (m, 2H), 2.17-1.95 (m, 8H), 1.67-1.57 (m, 4H), 1.41 (s, 18H), 1.28 (s, 18H), 1.20-1.10 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 172.3 (s), 170.4 (s), 164.7 (s), 163.3 (s), 155.5 (2), 146.6 (s), 133.5 (s), 129.3 (s), 126.6 (d), 125.0 (d), 121.8 (s), 121.5 (d), 120.9 (s), 118.5 (s), 117.8 (s), 80.5 (s), 54.5 (s), 53.3 (t), 51.1 (t), 48.4 (s), 42.6 (t), 39.4 (t), 29.9 (q), 29.3 (t), 28.5 (t), 28.4 (q), 25.9 (t), 23.8 (t); MS (ESI, DCM/MeOH 9:1): 1368 (50, $[M+H]^+$), 1268 (100, $[M+H-Boc]^+$), 1168 (50, $[M+H-2Boc]^+$), 684 (25, $[M+2H]^{2+}$), 584 (50, $[M+2H-2Boc]^{2+}$); HRMS (ESI, +ve) calcd for $C_{68}H_{91}N_{10}O_{12}S_4$: 1367.5695, found: 1367.5685.

Compound 10. This compound was prepared following the literature procedures.[S4]

Compound 11. A solution of **9** (47 mg, 34 μmol) in TFA (1 ml) and DCM (1 ml) was stirred for 2 h at rt under argon. The mixture was concentrated *in vacuo*, then redissolved in MeOH (1 ml) and HCl (1 M, 300 μl) and concentrated *in vacuo*. To the residue was added the mixture of **10** (80 mg, 0.14 mmol), TBTU (44 mg, 0.14 mmol) and 2,4,6-collidine (55 μl, 0.41 mmol) in DMF (0.33 ml) and DCM (0.33 ml). The resulting mixture was stirred for 1.5 h at rt, diluted with DCM, washed successively with 1 M aqueous $KHSO_4$, brine, saturated $NaHCO_3$ aqueous solution, and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Silica gel column chromatography of the residue (DCM/MeOH 95:5; R_f 0.41 with DCM/MeOH 9:1) afforded pure **11** (40 mg, 50%) as a green solid. Mp: 89-90 ºC; CD (DCM/MeOH 1:1): 707 (-0.37), 679 (-0.39), 554 (+0.24), 484 (-0.08), 444 (+0.36), 369 (+0.25), 345 (-0.01), 325 (+0.27); IR: 3310 (w), 2923 (m), 2853 (m), 1682 (s), 1655 (s), 1590 (m), 1455 (m), 1415 (m), 1341 (m), 1244 (s), 996 (s), 866 (w), 735 (m), 697 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 8.34 (d, ^3J(H,H) = 8.0 Hz, 2H), 8.25 (br s, 2H), 7.65-7.60 (m, NH), 7.51-7.44 (m, 2H), 7.27-7.2 (m, 40H), 6.55 (br s, NH), 5.70-5.60 (m, 2H), 5.04-4.89 (m, 16H), 4.70-4.60 (m, 2H), 3.68-3.53 (m, 8H), 3.36-3.34 (m, 2H), 3.20-3.10 (m, 4H), 3.10-3.00 (m, 4H), 2.80-2.62 (m, 4H), 2.40-2.25 (m, 2H), 2.22-2.07 (m, 2H), 2.05-1.70 (m, 8H), 1.60-1.45 (m, 4H), 1.42-1.32 (m, 2H), 1.28 (s, 20H); ^{13}C NMR (125 MHz, $CDCl_3$): 172.3 (s), 169.8 (s), 164.5 (s), 163.4 (s), 146.6 (s), 146.6 (s), 135.9 (s), 133.7 (s), 129.4 (s), 128.5 (d),126.7 (d), 124.6 (d), 121.9 (s), 121.4 (d), 121.0 (s), 118.5 (s), 117.8 (s), 68.7-68.2 (t, ^{P}m), 54.7 (d), 53.5 (d), 48.4 (s), 42.2 (t), 39.6 (t), 33.5 (d, ^{P}t, ^1J(C,P) = 134 Hz), 32.4 (t), 29.9 (q), 28.8 (t), 28.4 (t), 25.8 (t), 24.1 (t); MS (ESI, DCM): 2321 (24, $[M+H]^+$), 2302 (16, $[M+H-NH_3]^+$), 1183 (45, $[M+2Na]^{2+}$), 1171 (18, $[M+H+Na]^{2+}$), 1160 (100, $[M+2H]^{2+}$); HRMS (ESI, +ve) calcd for $C_{120}H_{135}N_8O_{22}P_4S_4$: 2319.7580, found: 2319.7570.

Compound 1. To a solution of **11** (17 mg, 7 μmol) in DCM (440 μl) was added TMSBr (15 μl, 0.11 mmol). The mixture was stirred for 2 h under argon at rt, and then concentrated in *vacuo*. To the residue was added MeOH (560 μl), and the resulting mixture was stirred for 0.5 h. The reaction mixture was concentrated in *vacuo*. The non-polar impurities were removed from the residue by solid-liquid extraction using diethylether (5 x 5 ml), petroleum ether (3 x 5 ml) and DCM (3 x 5 ml) to leave pure **1** as a green solid (12 mg, quant). Mp: >230 ºC; CD (DMSO/MeOH 1:1): 679 (+1.36), 478 (+0.31), 421 (-0.83), 342 (+3.68), 290 (-1.51); IR: 3233 (m), 2925 (w), 2857 (w), 1641 (s), 1587 (s), 1552 (s), 1416 (m), 1337 (m), 1233 (m), 1165 (m), 1122 (m), 998 (s), 910 (s), 803 (w), 749 (w); ^{1}H NMR (400 MHz, CD_3OD): 8.32-8.20 (m, 4H), 7.47 (br s, 2H), 5.71-5.65 (m, 2H), 4.54-4.49 (m, 2H), 3.73-3.64 (m, 8H), 3.17-2.81 (m, 14 H), 2.34-2.25 (m, 4H), 2.03-1.83 (m, 8H), 1.65-1.58 (m, 4H), 1.43-1.29 (m, 4H), 1.20 (s. 18 H); ^{13}C NMR (125 MHz, CD_3OD): 175.3 (s), 173.3 (s), 172.2 (s), 165.6 (s), 165.3 (s), 147.7 (s), 135.3(s), 130.8 (s), 127.9 (d), 125.2 (d), 123.2 (s), 122.4 (s), 122.1 (d), 119.7 (s), 118.8 (s), 55.5 (d), 54.7 (d), 42.6 (t), 40.3 (t), 35.7 (d, ^{P}t, ^{1}J(C,P) = 130 Hz), 32.9 (t), 30.2 (q), 29.9 (t), 29.4 (t), 26.7 (t), 25.0 (t); MS (MALDI) 1598 (60, $[M+H]^+$), 1582 (100, $[M-NH_2]^+$).

Compound 22. This compound was synthesized according to reported procedures.[S3]

Compound 23. A solution of **3** (25 mg, 0.064 mmol) and H-Lys(Cbz)-NH_2 (105 mg, 0.38 mmol) in pyridine (3.4 ml) was refluxed (120 °C) for 24 h. The reaction was then allowed to cool down and concentrated *in vacuo*. Silica gel column chromatography of the residue (DCM/MeOH 92:8; R_f 0.55 with DCM/MeOH 9:1) gave pure **23** (43 mg, 74%) as a red solid. Mp: >230 ºC; CD (DCM/MeOH 1:1): 542 (-0.75), 522 (-0.62), 496 (+0.07), 482 (-0.24), 350 (+0.27), 294 (-0.46), 265

(+0.44); IR: 2932 (w), 2849 (w), 2476 (w), 1674 (s), 1595 (w), 1437 (m), 1361 (w), 1258 (w), 1163 (w), 1044 (w), 743 (w); ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$ 1:1): 8.16 (d, ^{3}J (H,H) = 9.0 Hz, 4H), 7.85 (d, ^{3}J (H,H) = 9.0 Hz, 4H), 7.27-7.13 (m, 10H), 5.64-5.55 (m, 2H), 4.89 (s, 4H), 3.14 (t, ^{3}J (H,H) = 7.0 Hz, 4H), 2.34-2.22 (m, 4H), 1.67-1.57 (m, 4H), 1.50-1.35 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ 1:1): 173.5 (s), 163.7 (s), 157.9 (s), 137.2 (s), 134.2 (s), 131.7 (d), 129.0 (s), 128.8 (d), 128.3 (d), 128.1 (d), 125.5 (s), 123.6 (d), 122.7 (s), 66.8 (t), 55.2 (d), 41.0 (t), 29.9 (t), 28.7 (t), 24.5 (t); MS (ESI, DCM/MeOH 1:1): 938 (100, $[M+Na]^+$), 915 (10, $[M+H]^+$), 898 (20, $[M-NH_2]^+$); HRMS (ESI, +ve) calcd for $C_{52}H_{47}N_6NaO_{10}$: 937.3168, found: 937.3161.

Compound 24. A solution of **23** (50 mg, 0.05 mmol), HBr (5.7 M in AcOH, 30 µl, 0.05 mmol), thioanisole (7 mg, 0.05 mmol) and pentamethylbenzene (8 mg, 0.05 mmol) in TFA (820 µl) was stirred for 1 h at rt. The mixture was concentrated *in vacuo*, and washed with diethylether (solid-liquid extraction). HCl (1 M in H_2O, 1 ml) was added to the residue and the mixture was concentrated *in vacuo*. To the residue was added the mixture of Boc-Cys(S-*t*-Bu)-OH (67 mg, 0.22 mmol), TBTU (70 mg, 0.22 mmol), HOBt (34 mg, 0.22 mmol) and 2,4,6-collidine (28 µl, 0.22 mmol) in DMF (365 µl) and DCM (365 µl). The resulting mixture was stirred for 1 h at rt under argon, diluted with EtOAc, washed successively with 1 M HCl, brine, saturated $NaHCO_3$ aqueous solution, and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Silica gel column chromatography of the residue (DCM/MeOH 92:8; R_f 0.4 with DCM/MeOH 9:1) gave pure **24** (36 mg, 55%) as a red solid. Mp: 160-161 ºC; CD (DCM): 554 (-3.13), 492 (+4.36), 381 (-0.42), 354 (+0.72), 319 (-0.97), 290 (+0.52), 272 (-1.26); IR: 3378 (w), 2962 (w), 2924 (w), 2473 (w), 1696 (s), 1646 (s), 1592 (w), 1434 (m), 1401 (m), 1362 (s), 1341 (s), 1258 (s), 1164 (s), 1093 (s), 1019 (s), 861 (m), 746 (m); ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ 1:1): 8.13-8.07 (m, 4H), 7.85-7.75 (m, 4H), 5.59-5.53 (m, 2H), 4.30-4.26 (m, 2H), 3.26-3.20 (m, 4H), 3.05-2.98 (m, 2H), 2.93-2.86 (m,

2H), 2.39-2.29 (m, 2H), 2.25-2.15 (m, 2H), 1.70-1.60 (m, 4H), 1.40 (s, 22H), 1.26 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ 1:1): 172.5 (s), 170.8 (s), 162.6 (s), 155.6 (s), 133.2 (s), 130.7 (d), 128.0 (s), 124.5 (s), 122.6 (d), 121.8 (s), 79.7 (s), 54.2 (d), 47.5 (s), 42.2 (t), 38.9 (t), 29.0 (q), 28.5 (t), 27.9 (t), 27.6 (q), 23.69 (t); MS (ESI, DCM/MeOH 1:1): 1251 (100, $[M+Na]^+$), 1229 (10, $[M+H]^+$), 1211 (20, $[M-NH_2]^+$); HRMS (ESI, +ve) calcd for $C_{60}H_{78}N_8\ Na_2O_{12}S_4$: 637.2125, found: 637.2121.

Compound 25. A solution of **24** (32 mg, 26 μmol) in TFA (0.55 ml) and DCM (0.55 ml) was stirred for 2 h at rt under argon. The mixture was concentrated *in vacuo*, then redissolved in MeOH (1 ml) and HCl (1 M, 0.5 ml) and concentrated *in vacuo*. To the residue was added the mixture of **10** (62 mg, 0.10 mmol), TBTU (33 mg, 0.10 mmol) and 2,4,6-collidine (30 μl, 0.23 mmol) in DMF (0.65 ml). The resulting mixture was stirred for 1 h at rt, then 2,3,6-collidine (30 μl, 0.23 mmol) was added and the resulting mixture stirred for 1 h more. It was then diluted with EtOAc, washed successively with 1 M aqueous HCl, brine, saturated $NaHCO_3$ aqueous solution, and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Silica gel column chromatography of the residue (DCM/MeOH 93:7; R_f 0.37 with DCM/MeOH 93:7) afforded pure **25** (40 mg, 71%) as a red solid. Mp: 114-115 ºC; CD ($CHCl_3$): 554 (-11.14), 493 (+12.87), 382 (-2.03), 360 (+0.53), 322 (-2.22), 300 (+0.29), 271 (-7.2), 257 (-4.10); IR: 3391 (s), 1656 (m), 1591 (m), 1403 (w), 1343 (w), 1250 (w), 998 (w), 741 (w), 697 (w); ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ 1:1): 8.45 (d, ^3J(H,H) = 8.0 Hz, 4H), 8.31 (d, ^3J(H,H) = 8.0 Hz, 4H), 7.22-7.17 (m, 40H), 5.62-5.57 (m, 2H), 4.95-4.85 (m, 16H), 4.56-4.51 (m, 2H), 3.39-3.31 (m, 2H), 3.12-3.04 (m, 6H), 2.92-2.85 (m, 2H), 2.75-2.71 (m, 4H), 2.26-2.18 (m, 4H), 1.55-1.50 (m, 4H), 1.41-1.32 (m, 2H), 1.23 (s, 20H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ 1:1): 171.9 (s), 169.3 (s), 169.2 (s), 169.1 (s), 162.5 (s), 134.7 (s), 133.6 (s), 130.7 (d), 128.2 (s), 127.7 (d), 127.2 (d), 127.0 (d), 125.0 (s), 122.5 (d), 121.8 (s),

67.7-67.5 (t, ^{P}m), 53.7 (d), 52.4 (d), 40.9 (t), 38.3 (t), 31.9 (d, ^{P}t, ^{1}J(C,P) = 136 Hz), 30.5 (t), 28.8 (q), 27.7 (t), 27.2 (t), 22.9 (t); MS (ESI): 2199 (31, $[M+NH_4]^+$), 2182 (9, $[M+H]^+$), 1473 (69, $[2M+3NH_4]^{3+}$), 1466 (28, $[2M+H+2NH_4]^{3+}$), 1109 (84, $[M+2NH_4]^{2+}$), 1101 (31, $[M+H+Na]^{2+}$), 1092 (100, $[M+2H]^{2+}$); HRMS (ESI, +ve) calcd for $C_{112}H_{120}N_8\ Na_2O_{22}P_4S_4$: 1113.3067, found: 1113.3064.

Compound 19. To a solution of **25** (60 mg, 27 μmol) in DCM (1630 μl) was added TMSBr (54 μl, 0.41 mmol). The mixture was stirred for 2 h under argon at rt, and then concentrated in *vacuo*. To the residue was added MeOH (1080 μl), and the resulting mixture was stirred for 0.5 h. The reaction mixture was concentrated in *vacuo*. The non-polar impurities were removed from the residue by solid-liquid extraction using diethylether (3 x 5 ml) and DCM (3 x 5 ml) to leave pure **19** as a red solid (40 mg, quant). Mp: >230 ºC; CD (DMSO): 549 (-9.49), 492 (+10.04), 381 (-1.08.), 352 (+2.66), 276 (-3.66), 259 (-0.06); IR: 3295 (w), 2925 (w), 2865 (w), 1694 (m), 1648 (w), 1592 (w), 1436 (w), 1402 (w), 1342 (m), 1270 (m), 1129 (m), 998 (m), 911 (m), 808 (w), 746 (w); ^{1}H NMR (300 MHz, DMSO-d_6): 8.92 (d, ^{3}J(H,H) = 8.0 Hz, 4H), 8.56 (d, ^{3}J(H,H) = 8.0 Hz, 4H), 8.34-8.29 (m, 2H), 8.18 (s, 2H), 7.45 (s, 2H), 6.98 (s, 2H), 5.43-5.35 (m, 2H), 4.33-4.26 (m, 2H), 3.17-3.15 (m, 2H), 3.05-2.85 (m, 6H), 2.60-2.50 (m, 2H), 2.30-2.19 (m, 2H), 2.12-1.98 (m, 2H), 1.47-1.33 (m, 4H), 1.18 (s, 22 H) ; ^{13}C NMR (125 MHz, DMSO-d_6): 170.7 (s), 169.4 (s), 162.8 (s), 134.0 (s), 131.0 (d), 128.8 (s), 125.6 (s), 124.0 (d), 123.0 (s), 54.0 (d), 52.5 (d), 47.4 (s), 41.5 (t), 38.6 (t), 34.8 (d, ^{P}t, ^{1}J(C,P) = 127 Hz), 31.7 (t), 29.5 (q), 28.8 (t), 27.5 (t), 23.6 (t).

2.1.2. Synthesis of propagators 2, 17 and 20 (Schemes S2, S3)

Compound 7. This compound was prepared following the literature procedures.[S5] The product was recrystallized (EtOAc) before use.

Compound 2. To a solution of **6** (0.2 g, 0.19 mmol) in TFA (2.7 ml) were added pentamethylbenzene (28 mg, 0.19 mmol), thioanisole (24 mg, 0.19 mmol) and HBr (5.7 M in AcOH, 100 μl, 0.55 mmol). The mixture was stirred for 3 h at rt then HBr (5.7 M in AcOH, 100 μl, 0.55 mmol) was added again and the mixture stirred for 1.5 h more. After concentration, the residue was washed with diethylether (solid-liquid extraction), diluted with MeOH (1 ml) and 1 M HCl (0.5 ml), concentrated in *vacuo*, treated with TEA (0.2 ml) and concentrated in *vacuo*. The resulting product was dissolved in DCM (6.5 ml) and DMF (9.3 ml), and the pH of the solution was adjusted to ~8 by the addition of TEA. To this solution was added **7** (190 mg, 0.76 mmol), and the mixture was stirred for 40 min. TEA was added to the solution to maintain the pH at ~8. Saturated NH_4Cl aqueous solution was added to the solution, and the product was extracted with DCM, washed with brine, dried over Na_2SO_4 and concentrated in *vacuo* with small amount of silica gel (solid deposit). Column chromatography of the residue (DCM/MeOH 9:1; R_f 0.71 with DCM/MeOH 4:1) afforded pure **2** (130 mg, 65%) as a green solid. Disulfide **2** polymerized readily when dry and was therefore kept as a solution in $CHCl_3$/MeOH 1:1. Mp: >230 ºC; CD ($CHCl_3$/MeOH 1:1): 713 (+0.48), 446 (+0.54), 347 (-0.50), 322 (+0.80); IR: 3322 (w), 2931 (w), 1678 (s), 1643 (s), 1588 (s), 1574 (s), 1556 (s), 1414 (s), 1341 (s), 1234 (m), 1200 (w), 1120 (m), 954 (w), 865 (w), 804 (w), 754 (w), 730 (w); ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 2:1): 8.40 (s, 2H), 8.38 (d, ^3J (H,H) = 8.0 Hz, 2H), 7.63 (d, ^3J (H,H) = 8.0 Hz, 2H), 5.68 (t, ^3J (H,H) = 7.5 Hz, 2H), 3.74-3.68 (m, 4H), 3.15-2.95 (m, 14H), 2.69-2.55 (m, 4H), 2.30-2.20 (m, 4H), 2.15-1.85 (m, 8H), 1.65-1.45 (m, 4H), 1.40-1.25 (m, 2H), 1.25-1.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD 2:1): 174.9 (s), 173.6 (s), 166.0 (s), 165.5 (s), 148.2 (s), 136.0 (s), 131.3 (s), 128.4 (d), 125.9 (d), 123.6 (q), 122.8 (d), 122.6 (q), 119.9 (q), 119.6 (q), 55.7 (d), 53.7 (d), 43.7 (t), 40.5

(t), 30.1 (t), 29.3 (t), 27.3 (t), 24.9 (t); MS (ESI, DCM): 1071 (7, $[M+Na]^+$), 1049 (43, $[M+H]^+$), 1032 (100, $[M-NH_2]^+$); HRMS (ESI, +ve) calcd for $C_{52}H_{57}N_8O_8S_4$: 1049.3176, found: 1049.3178.

Compound 20. To a solution of **23** (185 mg, 0.2 mmol) in TFA (3.0 ml) were added pentamethylbenzene (30 mg, 0.2 mmol), thioanisole (25 mg, 0.2 mmol) and HBr (5.7 M in AcOH, 110 μl, 0.2 mmol). The mixture was stirred for 80 min. After concentration, the residue was washed with diethylether and petroleum ether (solid-liquid extraction), diluted with MeOH (1 ml) and 1 M HCl (0.5 ml), concentrated in *vacuo*, treated with TEA (2 ml) and concentrated in *vacuo*. The resulting product was dissolved in DCM (13 ml) and the pH of the solution was adjusted to ~8 by the addition of TEA. To this solution was added **7** (200 mg, 0.8 mmol), and the mixture was stirred for 30 min. Compound **7** (100 mg, 0.4 mmol) was added again and the mixture stirred for 1.5 h more. TEA was added to the solution to maintain the pH at ~8. The crude mixture was concentrated in *vacuo* with small amount of silica gel (solid deposit). Column chromatography of the residue (DCM/MeOH 91:9; R_f 0.47 with DCM/MeOH 17:3) afforded pure **20** (114 mg, 62%) as a red solid. Disulfide **20** polymerized readily when dry and was therefore kept as a solution in $CHCl_3$/TFE 1:1. Mp: 214-215 °C; CD ($CHCl_3$/TFE 1:1): 556 (-2.44), 492 (+2.78), 380 (-0.76), 313 (-1.59), 286 (+0.05); IR: 3289 (w), 3210 (w), 3082 (w), 2931 (w), 2867 (w), 2738 (w), 2677 (w), 1680 (s), 1632 (s), 1593 (w), 1536 (m), 1434 (w), 1332 (w), 1252 (w), 1207 (w), 1171 (w), 1035 (w), 980 (w), 807 (w); ^{1}H NMR (300 MHz, DMSO-d_6): 9.03-8.93 (m, 4H), 8.61-8.55 (m, 4H), 8.00-7.96 (m, 2H), 7.50-7.45 (m, 2H), 7.03-6.97 (m, 2H), 5.44-5.39 (m, 2H), 3.14-2.82 (m, 14H), 2.29-2.20 (m, 2H), 2.15-2.03 (m, 2H), 1.50-1.32 (m, 4H), 1.30-1.10 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6/$CDCl_3$ 9:1): 170.7 (s), 170.0 (s), 134.1 (s), 131.0 (d), 125.7 (s), 124.0 (d), 123.1 (s), 53.9 (d), 51.5 (d), 41.7 (t), 38.4 (t), 29.0 (t), 27.4 (t); MS (ESI, MeOH): 933 (51, $[M+Na]^+$), 911 (34, $[M+H]^+$), 894 (100, $[M-NH_2]^+$).

Compound 26. This compound was prepared following literature procedures.[S1]

Compound 17. To a solution of **26** (190 mg, 0.24 mmol) in TFA (4.4 ml) were added pentamethylbenzene (16 mg, 0.11 mmol), thioanisole (61 mg, 0.49 mmol) and HBr (5.7 M in AcOH, 102 μl, 0.2 mmol). The mixture was stirred overnight at rt. After concentration, the residue was washed with diethylether (solid-liquid extraction), diluted with 1 M HCl (1 ml), concentrated in *vacuo*, dissolved in MeOH (1 ml) and TEA (1 ml) and concentrated in *vacuo*. The resulting product was dissolved in DCM (1.6 ml) and DMF (3.2 ml), and the pH of the solution was adjusted to ~8 by the addition of TEA. To this solution was added **7** (237 mg, 0.96 mmol), and the mixture was stirred for 15 min. TEA was added to the solution to maintain the pH at ~8. The crude mixture was diluted with DCM and washed with saturated NH_4Cl aqueous solution. The product was extracted with DCM, washed with brine, dried over Na_2SO_4 and concentrated in *vacuo* with small amount of silica gel (solid deposit). Column chromatography of the residue (DCM/MeOH 9:1; R_f 0.62 with DCM/MeOH 4:1) afforded pure **17** (113 mg, 60%) as a brown solid. **17** polymerized readily when dry and was therefore kept as a solution in $CHCl_3$/MeOH 1:1. Mp: 159-160 ºC; CD ($CHCl_3$/MeOH 1:1): 377 (-0.38), 344 (+0.28), 307 (-0.37), 259 (+1.13); IR: 3315 (br , w), 2932 (w), 2414 (w), 1705 (m), 1659 (s), 1579 (m), 1451 (m), 1373 (m), 1331 (s), 1248 (s), 1199 (m), 1096 (w), 986 (w), 879 (w), 769 (m), 732 (s), 702 (m); ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 1:1): 8.75 (s, 4H), 5.64 (t, ^3J (H,H) = 7.5 Hz, 2H), 3.18-3.07 (m, 8H), 3.02-2.94 (m, 6H), 2.28 (q, ^3J (H,H) = 7.8 Hz, 4H), 1.65-1.43 (m, 4H), 1.40-1.27 (m, 2H), 1.27-1.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD 2:1): 174.5 (s), 173.8 (s), 1664.5 (s), 132.5 (d), 128.4 (s), 128.2 (s), 56.0 (d), 53.4 (d), 43.7 (t), 40.3 (t), 30.3 (t), 29.1 (t), 25.0 (t); MS (ESI, MeOH): 808 (100, $[M+Na]^+$); HRMS (ESI, +ve) calcd for $C_{34}H_{39}N_6O_8S_4$: 787.1706, found: 787.1684.

2.2. Electrochemistry

Cyclic voltammograms of **23** (1 mM in DMF) and **22** (0.25 mM in DCM) were determined using cyclic voltammetry (scan rate 100 mV/s) (Fig. S2, supporting electrolyte: 100 mM Bu_4NPF_6, working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/AgCl).

2.3. Self-organizing surface-initiated polymerization

Initiation. ITO electrodes were cut to give the area ~1 x 2 cm^2, cleaned in the RCA solution (boiling H_2O / 24% NH_4OH / 30% H_2O_2, 5:1:1, 5 min), rinsed with bidistilled water and MeOH, dried and immersed in the solution of **1** (1 mM in DMSO/MeOH 4:3) or **19** (0.5 mM in DMSO). The coated electrodes were tested for pin holes by measuring CV of potassium ferricyanide (0.5 mM $K_4Fe(CN)_6$, 0.2 M Na_2SO_4) using the covered ITO as a working electrode (Pt wire as a counter and Ag/AgCl as a reference; Fig. S1A and B).[S7] Nearly complete disappearance of the redox waves after 1 day of immersion confirmed the good coverage of the electrode by the initiator (Fig S1C and D). 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.[S7] The CVs of the bound initiator were obtained using the ITO electrode as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode in 0.1 M Bu_4NPF_6 in DMF (Fig. S2A and C). The observed linear dependence of the peak currents to the scan rate (Fig. S2B and D) confirmed the presence of redox active PDI on the electrode surface. Surface coverage $\wp$ was estimated from the charge Q ($\mu C/cm^2$) of the reduction waves using the equation (S1)[S8]

$$Q = nFA\wp \qquad \text{(S1)}$$

in which n is the number of electrons, F the Faraday constant and A the area of the electrode (the roughness factor: surface area / apparent area, was estimated from AFM to be 1.14). The obtained $\wp(\mathbf{1})$ = 0.12 nmol/cm^2 (0.7 molecule/nm^2) and $\wp(\mathbf{19})$ = 0.15 nmol/cm^2 (0.9 molecule/nm^2) is consistent with the nearly complete coverage of the surface by the initiator anchored with all four phosphonate groups to the surface.

The electrodes were activated by a treatment with DTT (20 mM in 10 mM NH_4HCO_3 aq) for 1 h at rt.

Propagation. Dependence on monomer concentration (Fig. 2a). ITO electrodes with or without activated initiator were placed in a deaerated solution of the corresponding propagator (**1** with **2**, 10-30 mM in $CHCl_3$/MeOH 1:1; **19** with **20**, 2-20 mM in $CHCl_3$/TFE 1:1), with *i*-Pr_2NEt (0.1 M) and shaken under argon atmosphere at rt. After 24 h (with **2**) or 2 h (with **20**), the electrodes were briefly sonicated in MeOH, then DMSO and dried under flow of N_2. Absorbance of the electrodes was recorded at 737 nm (**2**), or 508 nm (**20**).

Co-SOSIP. ITO electrodes were coated with **1** and activated with DTT as described in "Initiation". Then the electrodes were shaken in a solution of **2** (11 mM) and **17** (11 mM) in $CHCl_3$/MeOH 1:1 with 0.1 M *i*-Pr_2NEt for 24 h under argon atmosphere. The electrodes were briefly sonicated in MeOH, then DMSO and dried under flow of N_2.

2.4. Photocurrent measurements

Photocurrent measurements (Fig. 4). 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 N_2 gas) aqueous solution of TEOA (50 mM)

or MDESA (50 mM) and Na_2SO_4 (0.1 M) and irradiated with a solar simulator (area of irradiation: a = ~0.5 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 66 mW cm^{-2} unless stated otherwise. Currents were normalized using transmittance (T) of **15** and **18** at 737 nm and **21** at 508 nm.

Photocurrent measurements. Dependence on TEOA concentration (Fig. S5). Setup was as in "Photocurrent measurement" and TEOA concentration was varied between 30 mM and 1.0 M.

***J-V* measurements**. Short circuit current density (J_{sc}, A/cm^2) and open circuit voltage (V_{oc}, V) were determined by *J-V* measurements. Experimental conditions are as described in the above "photocurrent measurements", with 67 mW/cm^2 of irradiation. Fill factors (FF) were calculated from the maximum power (P_m, W/cm^2), J_{sc} and V_{oc} using equation (S2). [S9]

$$FF = P_m / J_{sc} V_{oc} \qquad \text{(S2)}$$

Action spectra (Fig. 3b and 5c). Photocurrent densities ($J_{sc} = I_{sc} / a$) were measured using TEOA (50 mM) or 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).[S10]

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

Estimation of film thickness. An estimate of the film thickness l was obtained by using the equation (S4).

$$l = n_{layer}\, d_{layer} \qquad \text{(S4)}$$

Where n_{layer} is the number of molecular layers in the film and d_{layer} is the intralayer distance which was assumed to be 3.5 Å. n_{layer} was calculated using the equation (S5).

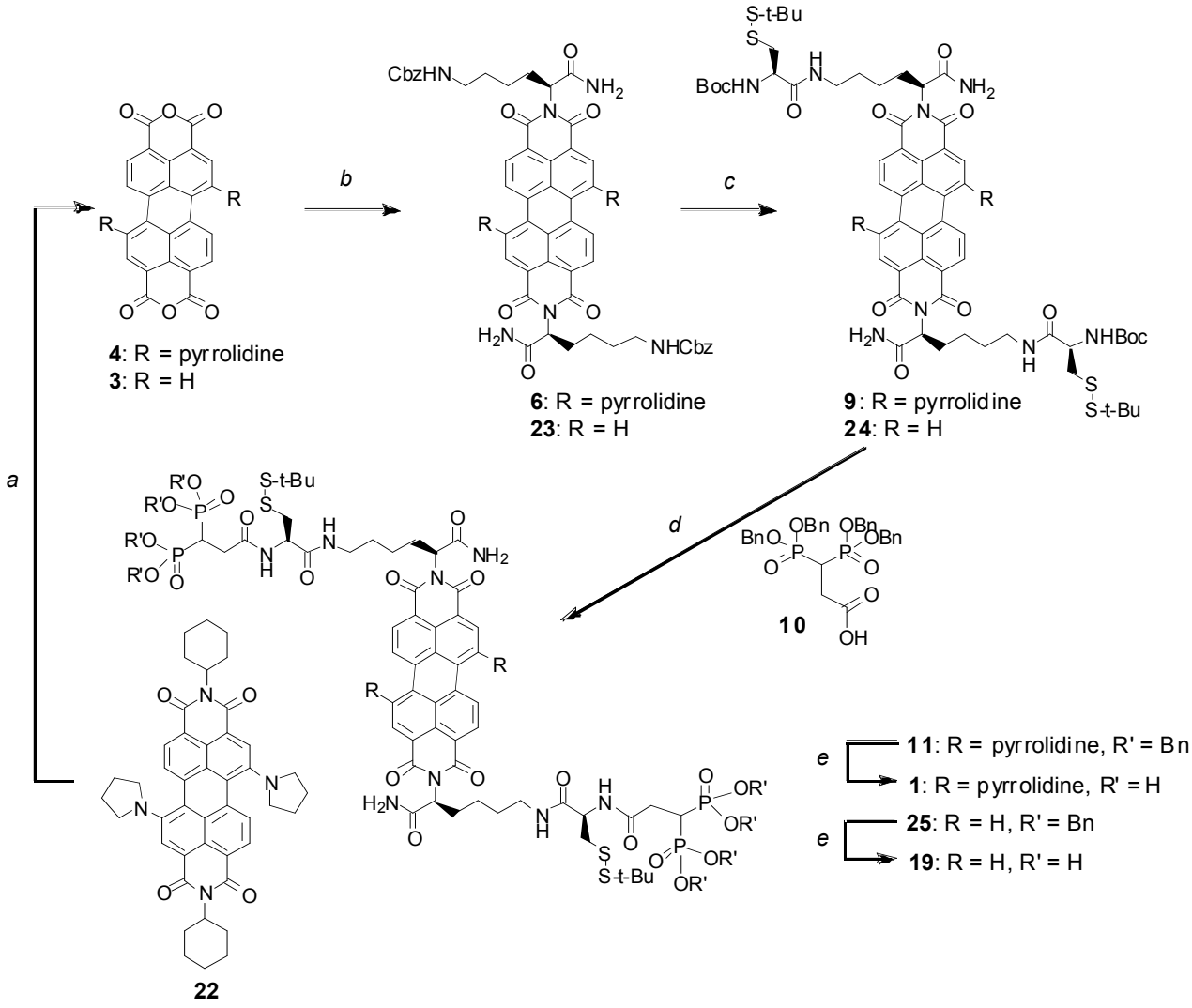
$$n_{layer} = x_{mol} / \wp\, A_e \qquad \text{(S5)}$$

Where $\wp$ is the surface coverage of the electrode and x_{mol} is the amount of molecules covering a certain area (A_e) of the electrode. x_{mol} was calculated using the equation (S6).

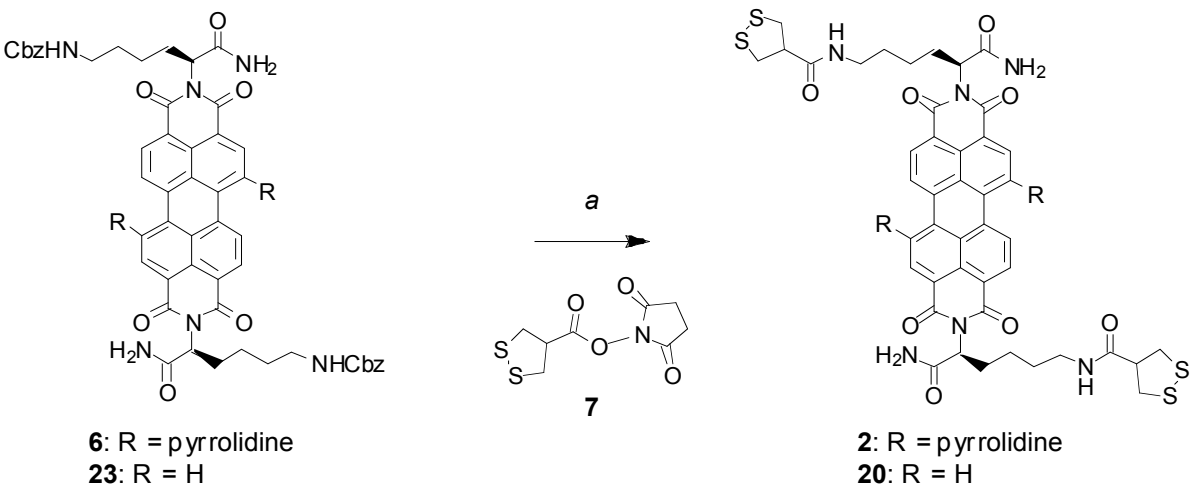
$$x_{mol} = (A_{MAX}\, A_e) / (\varepsilon_{MAX}\, 10^3) \qquad \text{(S6)}$$

Where A_{MAX} is the maximal absorbance of the polymer film and ε is the corresponding extinction coefficient. A_{MAX} = 0.1 a.u. corresponds to l = 7.4 nm for architecture **15** ($\wp$ (**15**) = 0.12 nmol/cm^2 and ε_{MAX} (**15**) = 39530 M^{-1} cm^{-1}); and to l = 3.4 nm for architecture **21** ($\wp$ (**21**) = 0.15 nmol/cm^2 and ε_{MAX} (**21**) = 67800 M^{-1} cm^{-1}).

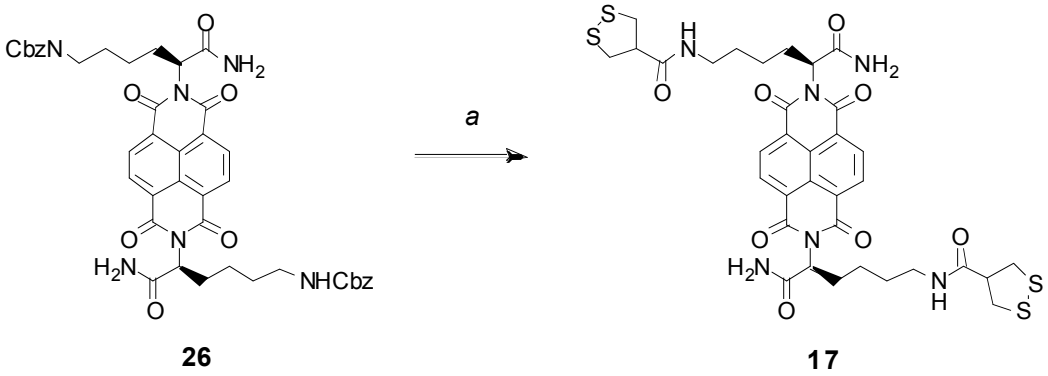
3. Supporting schemes and figures



Scheme S1. a) Ref S3; b) H-Lys(Cbz)-NH_2, pyridine, reflux (**6**: 55%; **23**: 74%); c) 1. HBr / AcOH, thioanisole, pentamethylbenzene, TFA. 2. Boc-Cys(S-*t*-Bu)-OH, TBTU, HOBt, 2,4,6-collidine, DMF (2 steps, **9**: 60%; **24**: 55%); d) 1. TFA, DCM. 2. **10**, TBTU, 2,4,6-collidine, DCM/ DMF (2 steps, **11**: 50%; **25**: 71%); e) 1. TMSBr. 2. MeOH (quant).



Scheme S2. a) 1. HBr / AcOH, thioanisole, pentamethylbenzene, TFA. 2. **7**, DCM/DMF, TEA, pH 8, 80 min (2 steps, **2**: 65%; **20**: 62%).



Scheme S3. a) 1. HBr / AcOH, thioanisole, pentamethylbenzene, TFA. 2. **7**, DCM/DMF, TEA, pH 8, 80 min (2 steps, 60%).

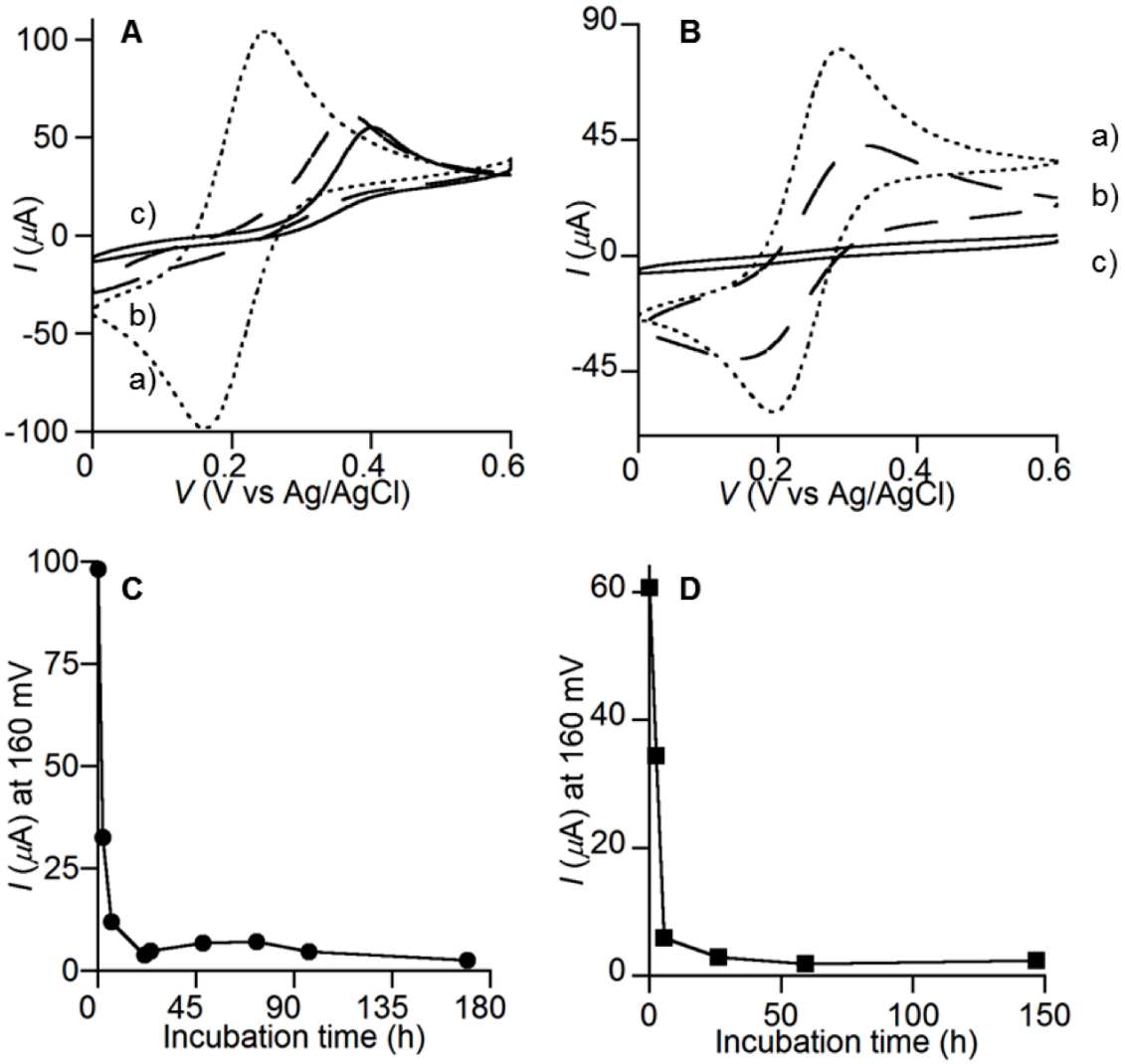


Figure S1. A. Cyclic voltammograms of aqueous ferricyanide measured with an ITO electrode (a) before the deposition of initiator **1**, (b) after 4 h, and (c) 24 h in the solution of the initiator as a working electrode. B. Same setup (a) before the deposition of initiator **19**, (b) after 2.5 h, and (c) 26 h. C. Initiator **1**: Peak current (absolute value) of the ferricyanide reduction wave as a function of the incubation time. D. Same with initiator **19**.

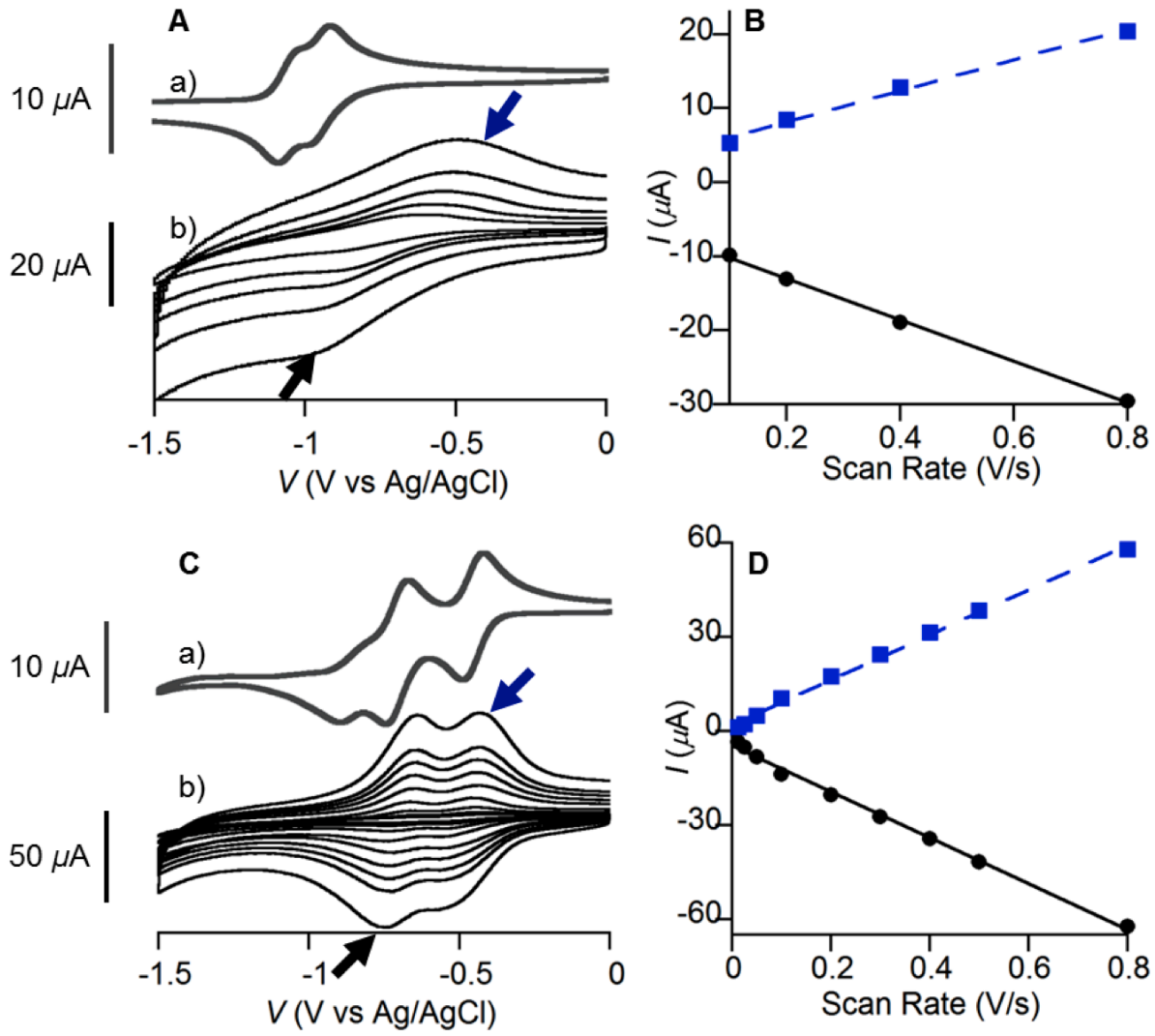


Figure S2. A. Cyclic voltammograms of (a) **22** (0.25 mM) in DCM, and (b) the initiator coated ITO electrode (**1** on ITO, scan rate = 0.05, 0.1, 0.2, 0.4, 0.8 V/s). B. Peak current of the second reduction (black arrow in Fig. S2A) and the second oxidation (blue arrow in Fig. S2A) as a function of Scan rates. C. Cyclic voltammograms of (a) **23** (1 mM) in DMF, and (b) the initiator coated ITO electrode (**19** on ITO, scan rate = 0.0125, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8 V/s). D. Peak current of the second reduction (black arrow in Fig. S2C) and the second oxidation (blue arrow in Fig. S2C) as a function of Scan rates.

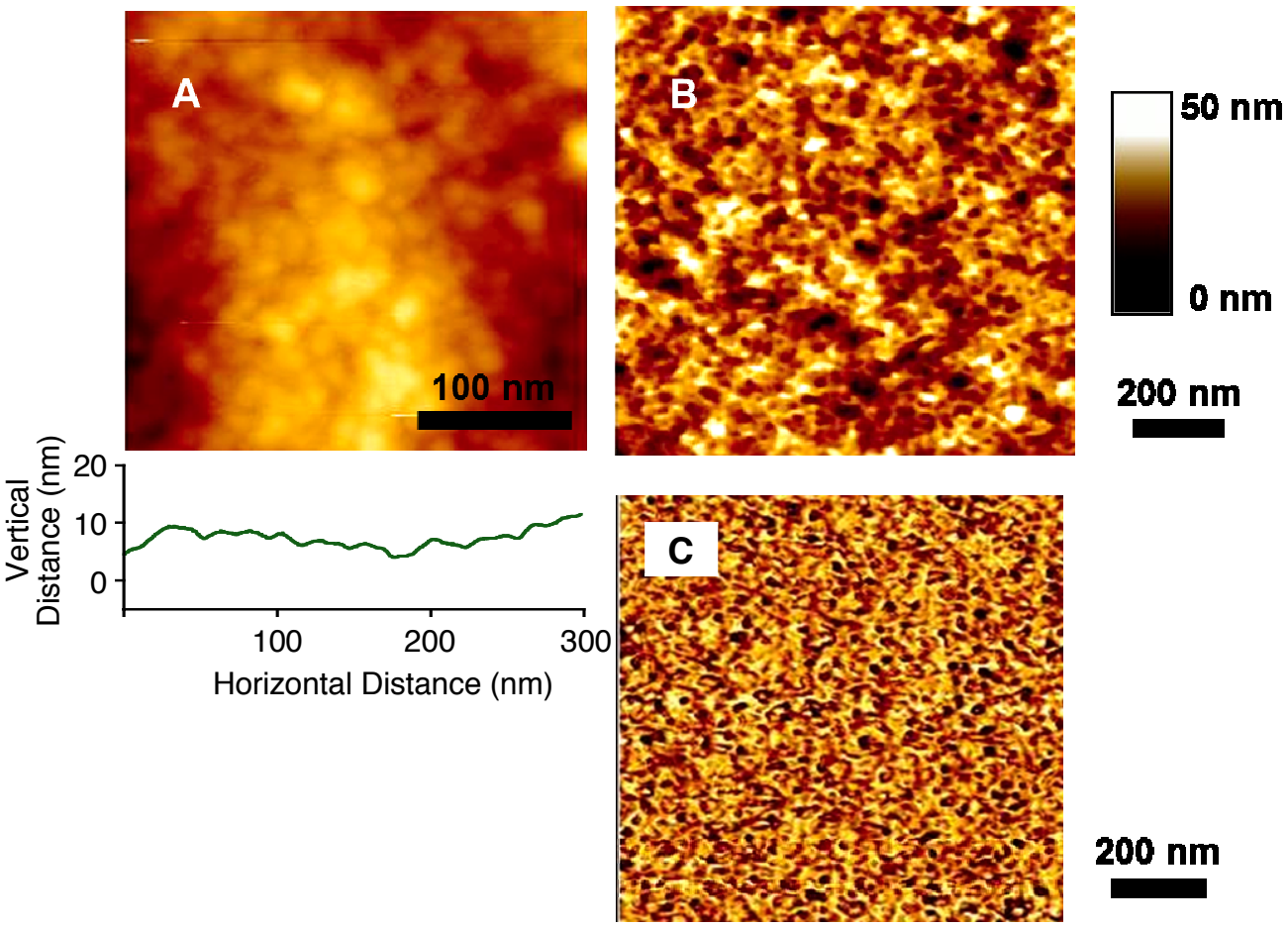


Figure S3. AFM height image and profile (A, below) of SOSIP architectures **15** (A), **21** (B) and AFM phase contrast image of SOSIP architecture **21** (C).

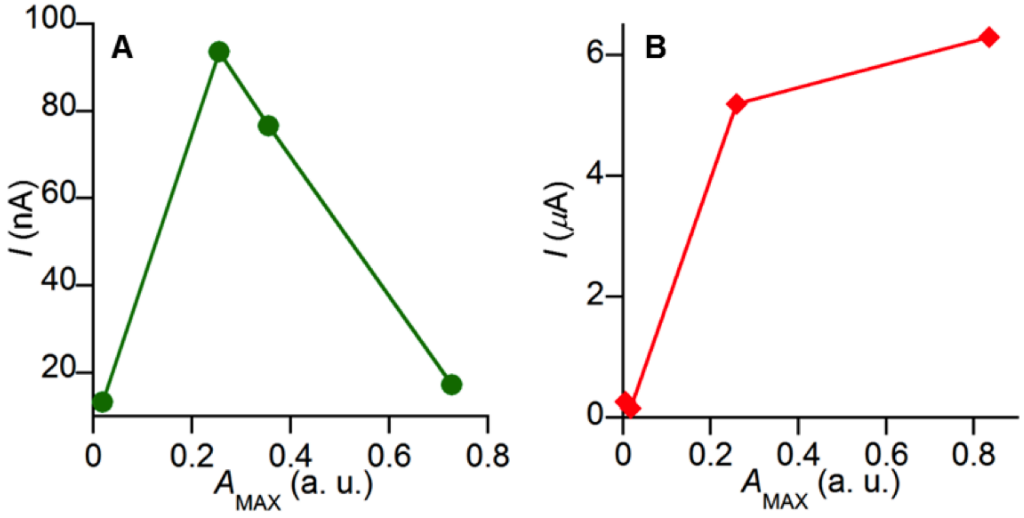


Figure S4. Photocurrent generated from (A) architecture **15** (TEOA concentration 1.0 M, power of irradiation 200 mW/cm^2) and (B) architecture **21** (TEOA concentration 50 mM, 67 mW/cm^2) as a function of the thickness of the film. A_{MAX} = 0.1 corresponds to a film thickness of ~7.4 nm for **15** and ~3.4 nm for **21**. These estimations are extremely qualitative despite because absorption depends strongly on variable extinction coefficients in self-assemblies, chromophore orientation vs incident light, and so on.

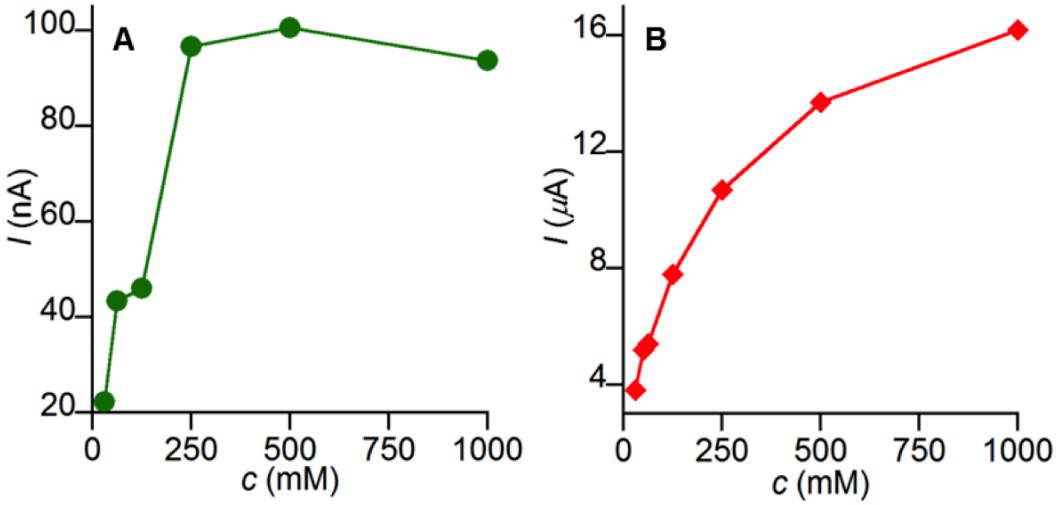


Figure S5. Photocurrent generated from (A) architecture **15** (power of irradiation 200 mW/cm^2) and (B) architecture **21** (67 mW/cm^2) as a function of the TEOA concentration.

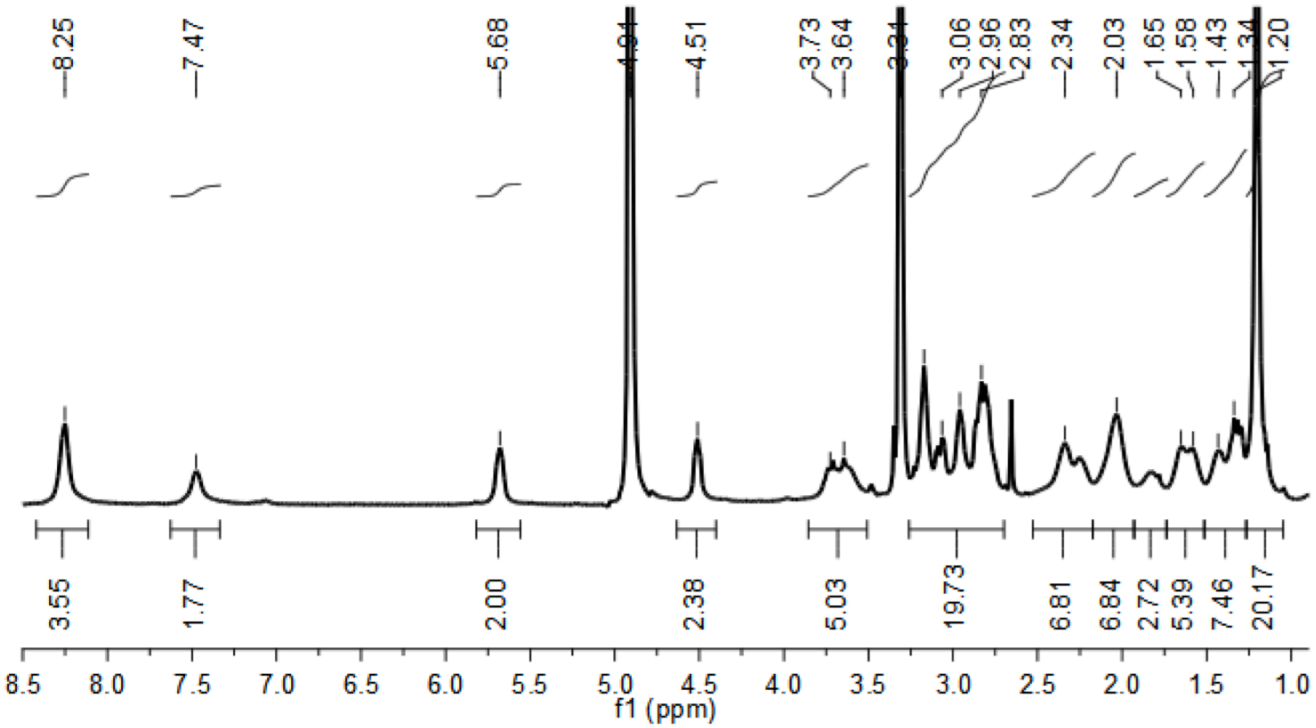


Figure S6. ^{1}H NMR spectrum of **1** in MeOD.

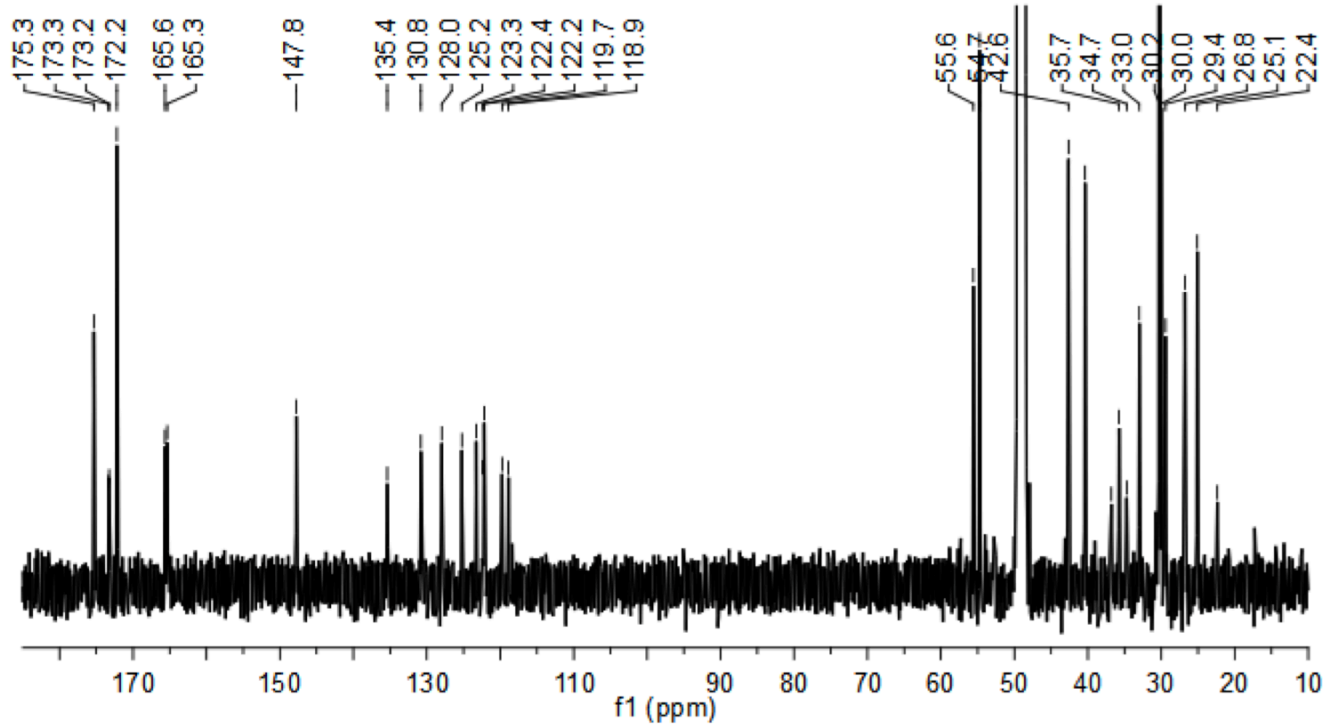


Figure S7. ^{13}C NMR spectrum of **1** in MeOD.

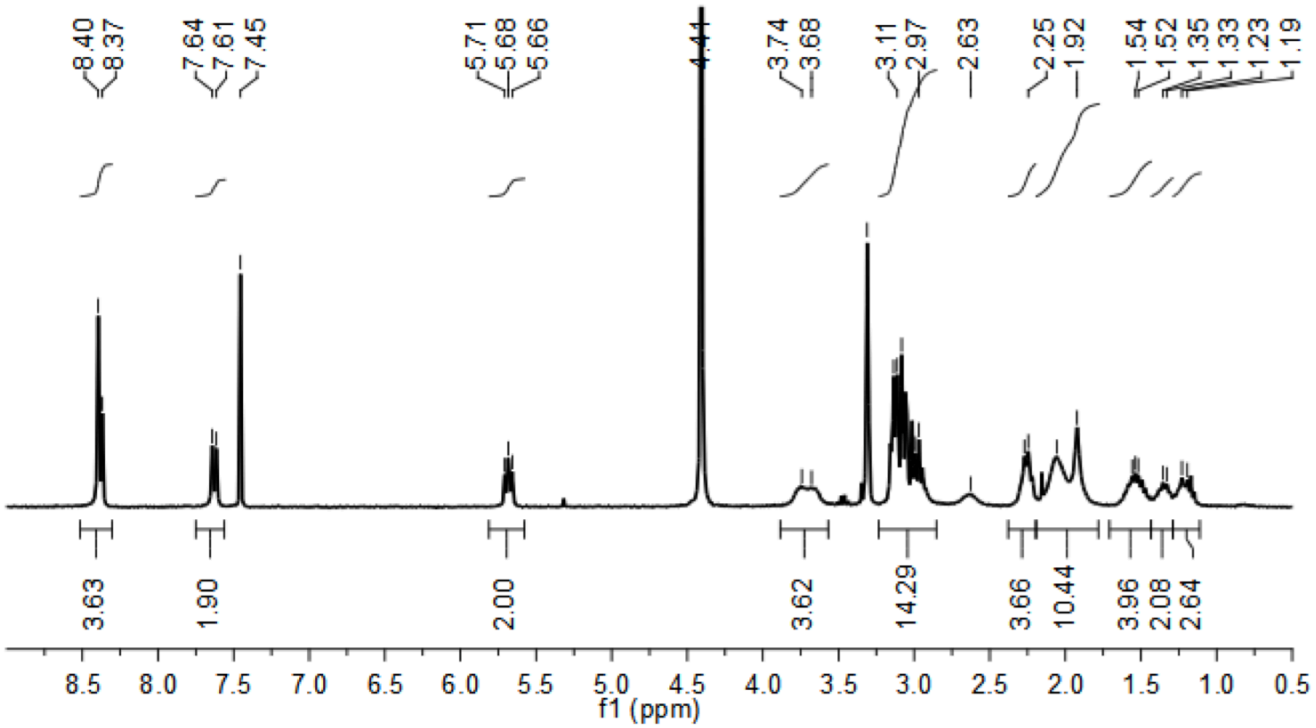


Figure S8. ^{1}H NMR spectrum of **2** in $CDCl_3$/MeOD 2:1.

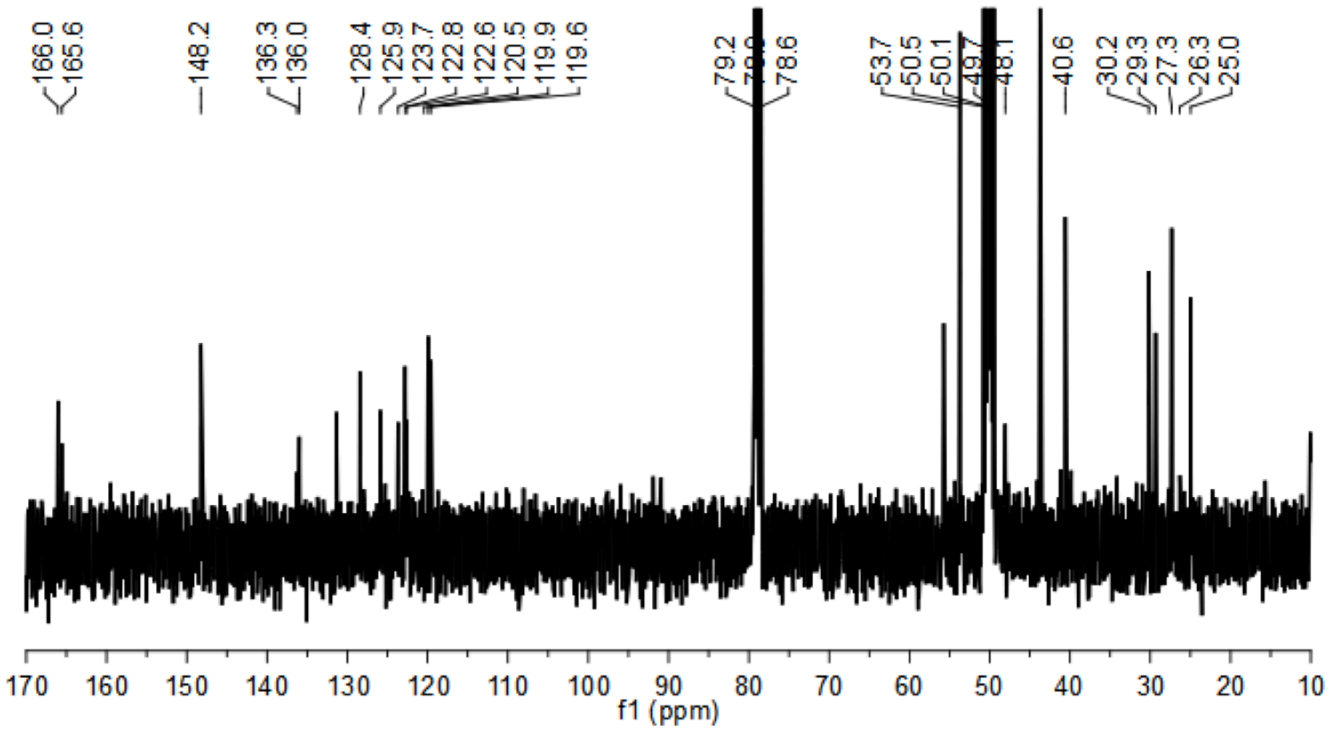


Figure S9. ^{13}C NMR spectrum of **2** in $CDCl_3$/MeOD 2:1.

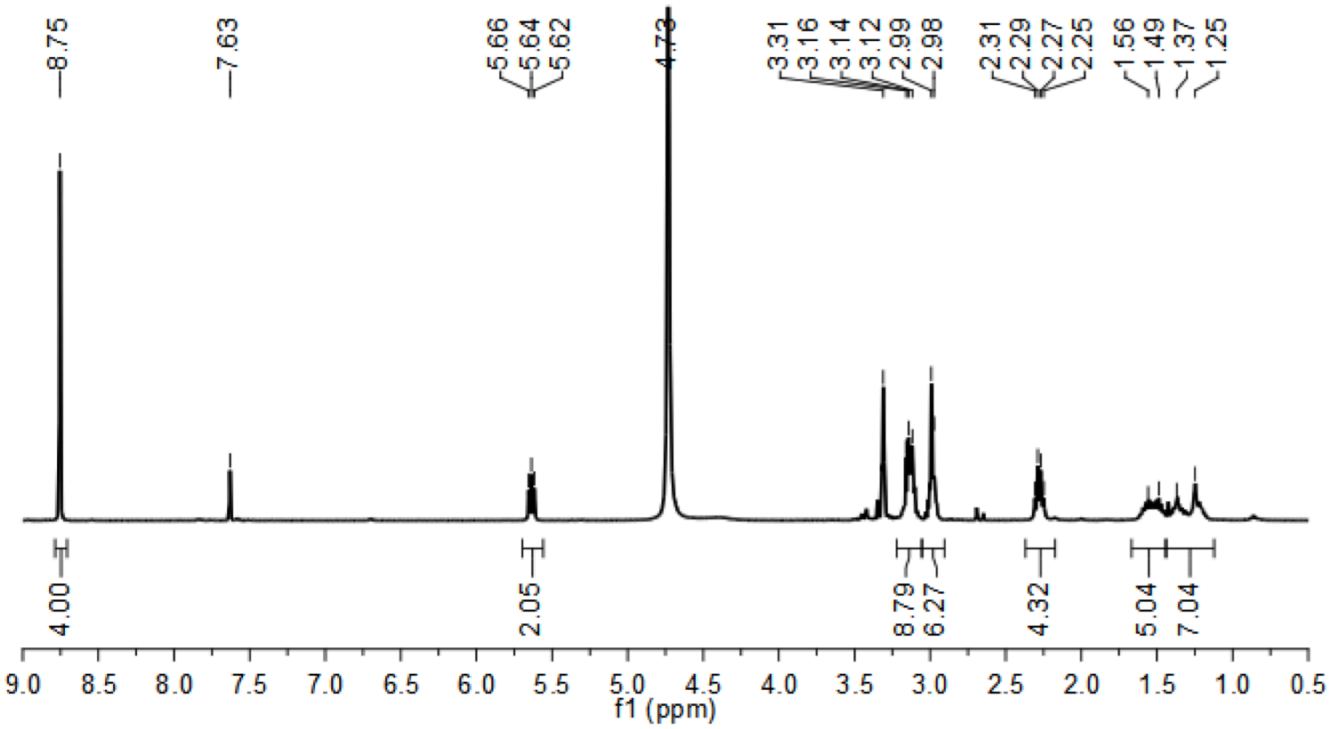


Figure S10. ^{1}H NMR spectrum of **17** in $CDCl_3$/MeOD 1:1.

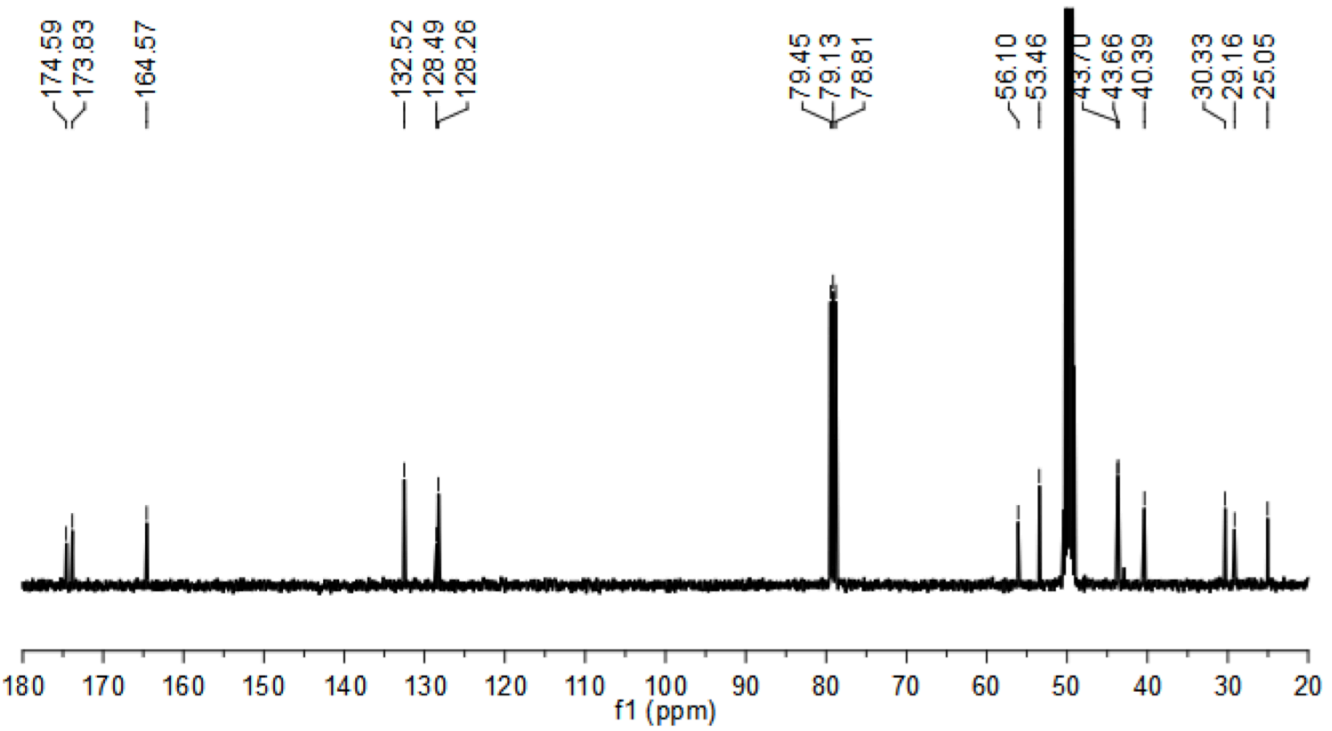


Figure S11. ^{1}H NMR spectrum of **17** in $CDCl_3$/MeOD 1:1.

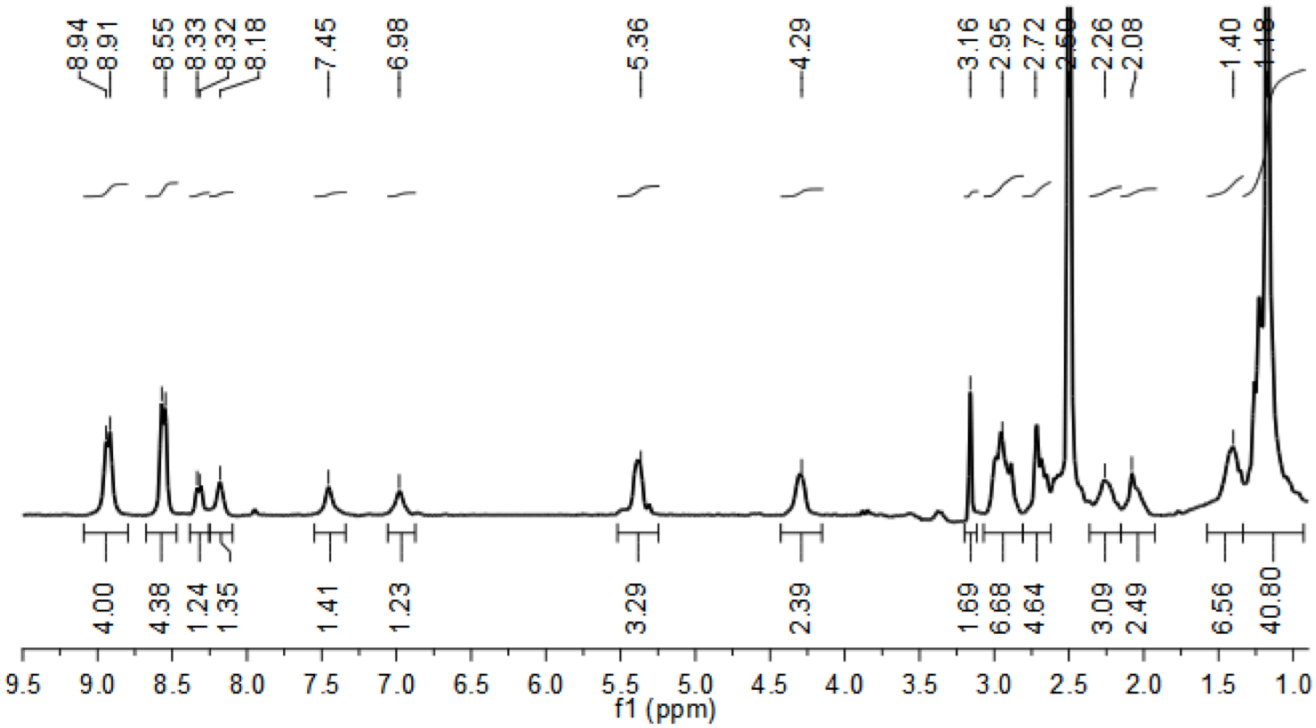


Figure S12. ^{1}H NMR spectrum of **19** in DMSO-d_6.

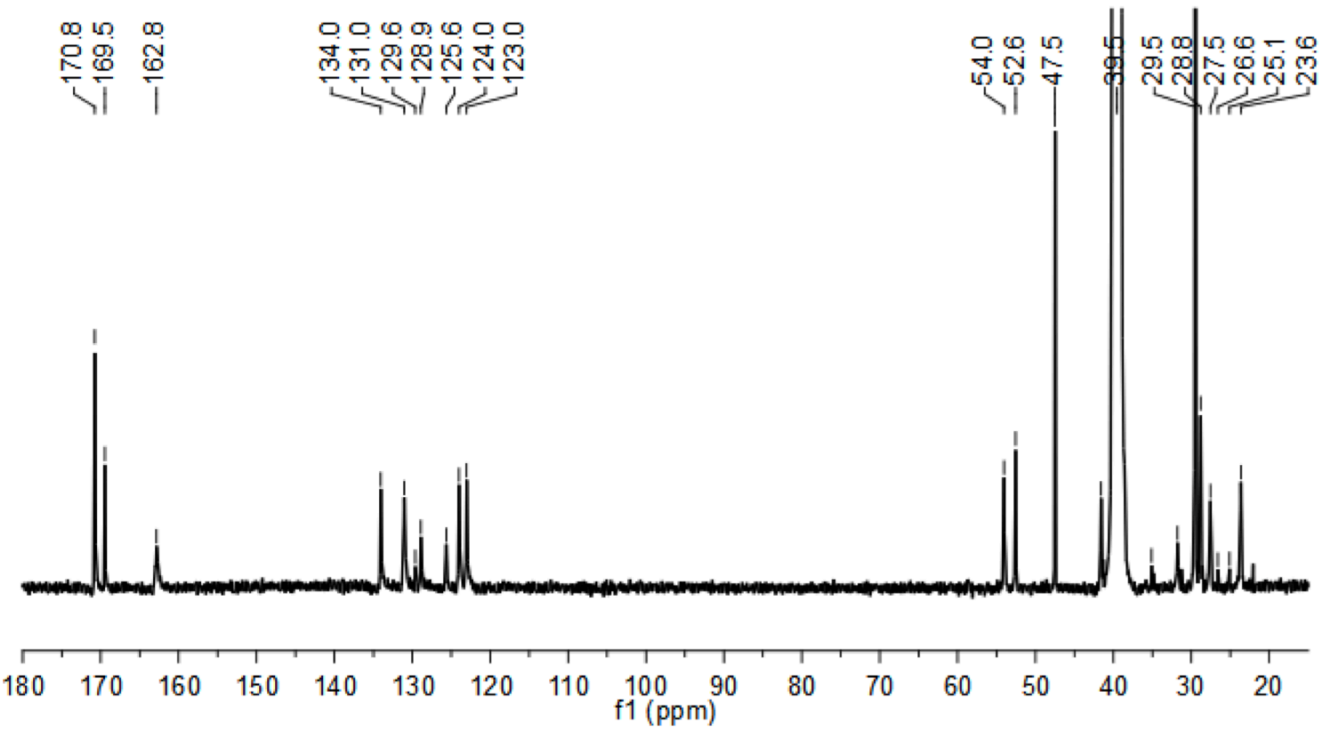


Figure S13. ^{13}C NMR spectrum of **19** in DMSO-d_6.

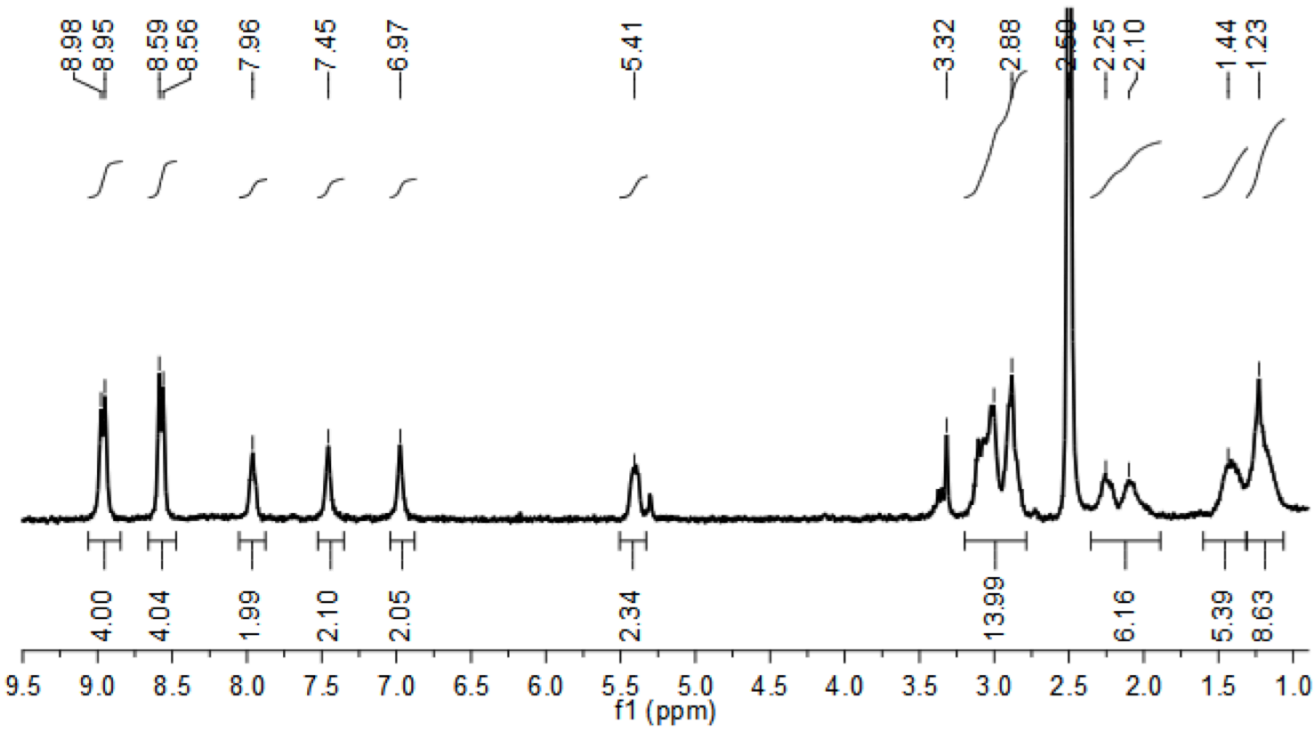


Figure S14. ^{1}H NMR spectrum of **20** in DMSO-d_6.

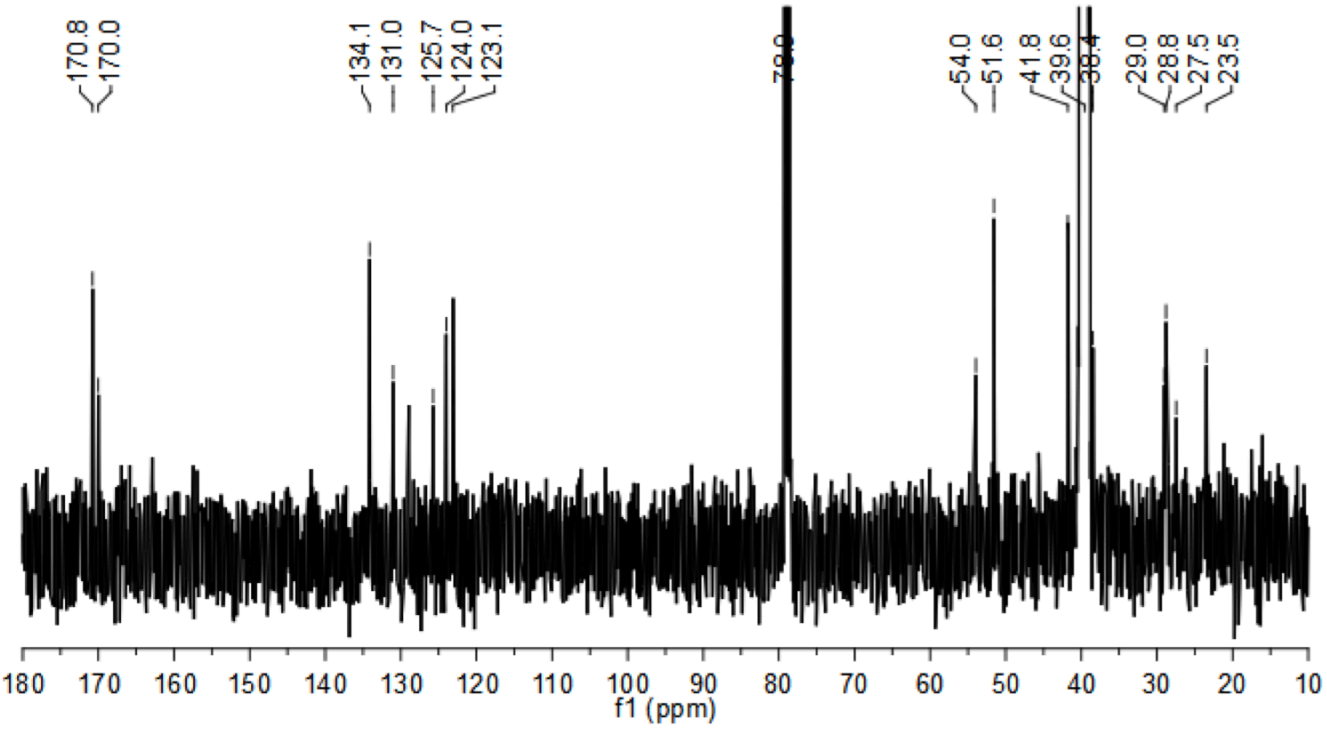


Figure S15. ^{13}C NMR spectrum of **20** in DMSO-d_6/$CDCl_3$ 9:1.

4. Supporting references

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