Electronic Supplementary Information (ESI) for

Water-Dispersible Donor–Acceptor–Donor π-Conjugated Bolaamphiphiles Enabling Humidity-Responding Luminescence Color Change

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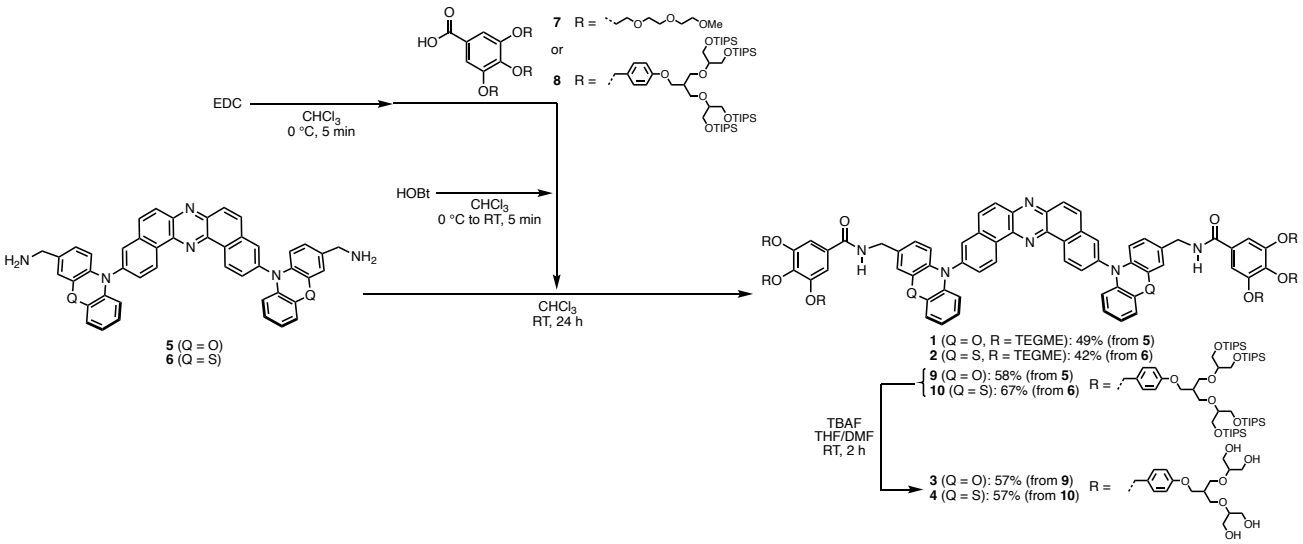
General Remarks. All reactions were carried out under an atmosphere of nitrogen unless otherwise noted. Products were purified by chromatography on silica gel BW-300 or Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Wako silicagel 70 FM TLC plate or Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp. Recycling preparative gel permeation chromatography (GPC) was conducted with a Japan Analytical Industry LaboACE. Lyophilization was performed with a TAITEC Freeze Dryer VD-800R. High performance liquid chromatography (HPLC) analysis was carried out on a system composed of SHIMADZU HPLC system with a GL Sciences Inc. InertSustain AQ-C18 column (ID = 20 mm, L = 250 mm). Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System or Yanaco Micro Melting Point Apparatus. All ^{1}H and ^{13}C NMR were recorded on a JEOL JMTC-400/54/SS Spectrometer (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) or Bruker AVANCE III 600 Spectrometer (^{13}C NMR, 150 MHz) using tetramethylsilane as an internal standard. Infrared spectra were acquired on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. Mass spectra and High-resolution mass spectra were obtained on a Shimadzu GCMS-QP 5000, JEOL JMS-700, and JEOL JMS-S3000 Mass Spectrometer. The elemental analysis (CHN) was carried out with JM10 (J-SCIENCE LAB CO., Ltd). UV-vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Steady-state emission spectra were recorded on a HAMAMATSU C11347-01 spectrometer with an integrating sphere or JASCO Spectrofluorometer FP-8300. Excitation spectra were recorded on JASCO Spectrofluorometer FP-8650. Thermogravimetric analysis (TGA) was performed on a SII Nano Technology Inc. TG/DTA-7200 system. Dynamic Light Scattering (DLS) and Electrophoretic Light Scattering (ELS) experiments were performed with Malvern-Panalytical Zetasizer Lab. TEM image was acquired with HITACHI H-7650. Ultra Small and small angle X-ray scattering（USAXS and SAXS）measurements were carried out using the BL19B2 beamline at Spring-8 at an incident X-ray beam wavelength of 0.068 nm.[S1] The camera lengths for USAXS and SAXS were set to 40.77 m and 3.04 m, respectively. The 2D SAXS profiles were obtained using a PILATUS-2M two-dimensional detector (Dectris Ltd., Baden, Switzerland). The scattering vector, q ($= 4\pi\sin\theta/\lambda$: 2θ and λ are the scattering angle and wavelength) was recorded between 5×10^{-3} nm^{-1} and 3.5 nm^{-1}.

Materials. Dehydrated chloroform and DMF for organic synthesis were used as received. Dehydrated 1,4-dioxane, THF, and toluene for organic synthesis were purified by passing through a solvent purification system. Potassium *N*-Boc-aminomethyltrifuluoroborate (**S2**) [CAS No. 1314538-55-0] and 3-bromo-10*H*-phenothiazine (**S4**) were purchased from chemical company. 3-Bromo-10*H*-phenoxazine (**S1**) [CAS No. 832734-15-3],[S2] 3,11-Dibromo-dibenzo[*a*,*j*]phenazine (**2**) [CAS No.

1620543-64-7],[S3] carboxylic acid **7** [CAS No. 1008460-19-2],[S4] and carboxylic acid **8** [CAS No. 1577258-66-2][S5] were synthesized according to the reported procedure.[S2–S5] Solvents of fluorescence spectroscopic grade for measurement of UV-vis and emission spectra were purchased from Nacalai Tesque Inc.

Synthetic Procedures and Spectroscopic Data of New Compounds

To install amphiphilic units at the edge of the D–A–D unit, aminomethyl-incorporated compounds **5** and **6** were synthesized [Eq. (S1)–(S6)]. Two amphiphilic units having three TEGME tails were readily installed into the D-A-D unit through the condensation of **5** and **6** with **7** to give **1** and **2** as an orange and reddish brown viscous solid, respectively (Scheme 1). More hydrophilic units were installed into the D–A–D compounds **5** and **6** through condensation with **8** that have dendric polyol silyl ethers to provide **9** and **10**, respectively. The silyl groups of **9** and **10** were readily removed by the action of fluoride to give compounds **3** and **4**. Lyophilization of **3** and **4** gave scarlet and orange fluffy solids, respectively.

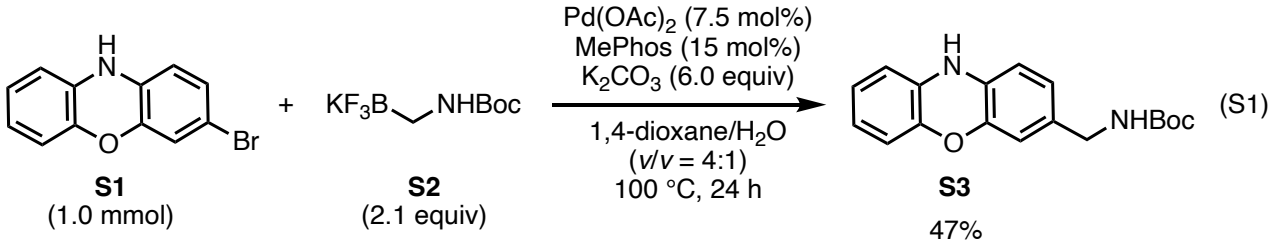


Scheme S1 Synthetic route to **1**–**4**.

*Preparation of 3-bromo-10H-phenothiazine (**S1**) [CAS No. 832734-15-3]*[S2]

The title compound was synthesized according to the procedure in literature,[S2] and ^{1}H and ^{13}C NMR spectra were in good agreement with those previously reported.[S5] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.35 (s, 1H), 6.87 (dd, J = 2.4, 8.4 Hz, 1H), 6.77 (d, J = 2.8 Hz, 1H), 6.75–6.71 (m, 1H), 6.61–6.55 (m, 2H), 6.43 (dd, J = 1.2, 7.6 Hz, 1H), 6.36 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.7, 142.3, 132.0, 131.7, 126.5, 124.4, 120.7, 117.7, 115.2, 114.5, 113.5, 110.2.

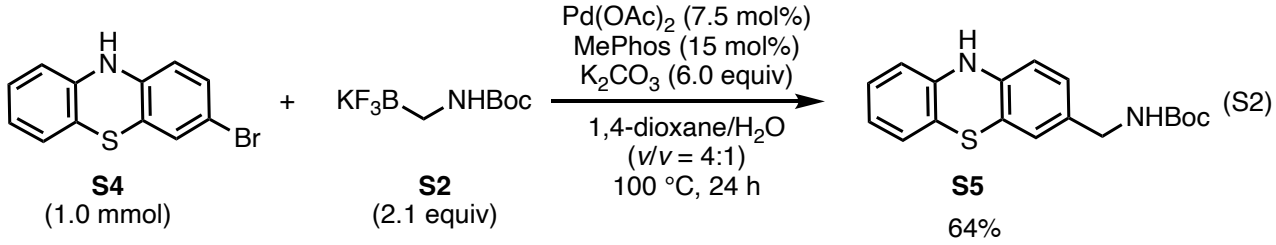
*Preparation of tert-butyl((10H-phenoxazin-3-yl)methyl)carbamate (**S3**)*



To a two-necked reaction tube (*tube A*) (3 mL) equipped with a stirring bar, were added $Pd(Oac)_2$ (16.9 mg, 0.075 mmol, 7.5 mol%) and MePhos (54.9 mg, 0.15 mmol, 15 mol%). The reaction vessel was sealed with a septum and a three-way stopcock, evacuated, and purged with N_2 gas for 3 times. 1,4-Dioxane was degassed through the freeze-pump-thaw cycling for 3 times, and the degassed solvent (0.8 mL) was injected to the *tube A* through the septum. The resulting reaction mixture was stirred at room temperature for 10 min (*solution A*). To another two-necked reaction tube (10 mL) (*tube B*) equipped with a stirring bar and a three-way-stopcock, were added 3-bromo-10*H*-phenoxazine (**S1**) (262.1 mg, 1.0 mmol, 1.0 equiv), potassium *N*-Boc-aminomethyltrifluoroborate (**S2**) (497.7 mg, 2.1 mmol, 2.1 equiv), and K_2CO_3 (829.7 mg, 6.0 mmol, 6.0 equiv), and the reaction vessel was sealed with a septum, evacuated, and purged with N_2 gas for 3 times. 1,4-Dioxane (2.4 mL) and de-ionized water (0.8 mL) degassed through the freeze-pump-thaw cycling for 3 times were added to the *tube B* through the septum. The reaction mixture was stirred at room temperature for 3 min, then *solution A* was added to the *tube B* through the septum under the flow of N_2 gas. The reaction mixture was stirred in a Personal Organic Synthesizer (EYELA, *Chemi-Station*) equipped with a cooling system under a reflux condition (aluminum block temperature: 100 °C) for 24 h. The reaction mixture was allowed for cooling to room temperature. Saturated $NaHCO_3$ (4 mL) was added to the reaction mixture, and the organic layer was extracted with $CHCl_3$ (15 mL×3). The combined organic extracts were washed with water (30 mL), dried over Na_2SO_4, and filtered. Solvents were evaporated from the filtrate in vacuo to give the crude product (374.3 mg) as brown solid, which was purified by flash column chromatography on NH silica gel (eluent: *n*-hexane/EtOAc = 9 : 1 to 8 : 2) to give pale yellow solid (170.4 mg) containing **S3**. The obtained solid was further purified by reprecipitation from a biphasic solution of *n*-hexane/EtOAc (*v*/*v* = 9:1) to give pure product **S3** as white solid (145.1 mg, 0.47 mmol, 47%). Mp 158 °C (dec.); T_d (5 wt%) 215 °C (under N_2 gas); 211 °C (under air); R_f 0.25 (*n*-hexane/EtOAc = 1 : 1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (s, 1H), 7.23 (t, J = 5.6 Hz, 1H), 6.72–6.68 (m, 1H), 6.59–6.52 (m, 3H), 6.47 (s, 1H), 6.42 (dd, J = 1.6, 8.0 Hz, 1H), 6.36 (d, J = 7.6 Hz, 1H), 3.88 (d, J = 6.0 Hz, 2H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.7, 142.7, 142.6, 132.52, 132.46, 131.0, 123.9, 122.4, 120.2, 115.1, 114.1, 113.3, 112.9, 77.7, 42.7, 28.3; IR (ATR): ν 3368, 3308, 3065, 3040, 3011, 2984, 2972, 2922, 2868, 2847, 1684, 1605, 1514, 1501, 1456, 1445, 1429,

1410, 1395, 1366, 1319, 1304, 1289, 1277, 1265, 1244, 1196, 1163, 1125, 1101, 1045, 1030, 968, 936, 926, 916, 885, 870, 853, 847, 816, 789, 768, 748, 718 cm^{-1}; MS (FAB^+, NBA): *m*/*z* (relative intensity, %): 313 ($[M+1]^+$, 6), 312 ($[M]^+$, 17), 256 ($[M–^tBu+1]^+$, 5), 255 ($[M–^tBu]^+$, 4), 196 ([M–NHBoc]$^+$, 5); HRMS (FAB^+, NBA): *m/z* calcd for $C_{18}H_{20}N_2O_3$ (M) 312.1474, found 312.1472; Elemental analysis (%) calcd. For $C_{18}H_{20}N_2O_3$: C 69.21, H 6.45, N 8.97, found: C 69.04, H 6.50, N 8.89.

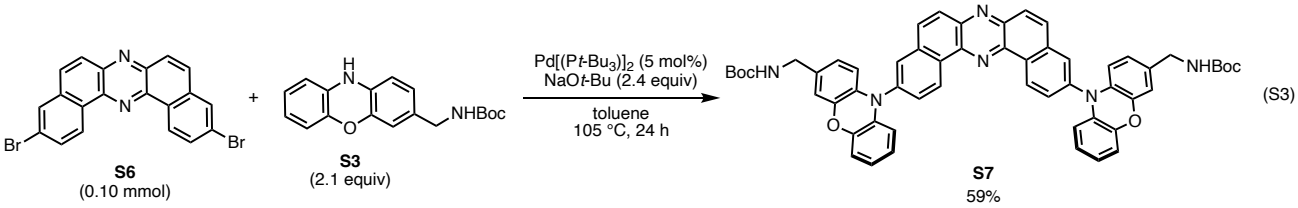
*Preparation of tert-butyl((10H-phenothiazin-3-yl)methyl)carbamate (**S5**)*



To a two-necked reaction tube (*tube A*) (3 mL) equipped with a stirring bar, were added $Pd(Oac)_2$ (16.8 mg, 0.075 mmol, 7.5 mol%) and MePhos (54.7 mg, 0.15 mmol, 15 mol%). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. 1,4-Dioxane was degassed through the freeze-pump-thaw cycling for 3 times, and the degassed solvent (0.8 mL) was injected to the *tube A* through the septum. The resulting reaction mixture was stirred at room temperature for 10 min (*solution A*). To another two-necked reaction tube (10 mL) (*tube B*) equipped with a stirring bar and a three-way-stopcock, were added 3-bromo-10*H*-phenothiazine (**S4**) (278.2 mg, 1.0 mmol, 1.0 equiv), potassium *N*-Boc-aminomethyltrifluoroborate (**S2**) (497.8 mg, 2.1 mmol, 2.1 equiv), and K_2CO_3 (829.2 mg, 6.0 mmol, 6.0 equiv), and the reaction vessel was sealed with a septum and evacuated and purged with N_2 gas for 3 times. 1,4-Dioxane (2.4 mL) and de-ionized water (0.8 mL) degassed through the freeze-pump-thaw cycling for 3 times were added to the *tube B* through the septum. The reaction mixture was stirred at room temperature for 3 min, then *solution A* was added to the *tube B* through the septum under the flow of N_2 gas. The reaction mixture was stirred in a Personal Organic Synthesizer (EYELA, *Chemi-Station*) equipped with a cooling system under a reflux condition (aluminum block temperature: 100 °C) for 24 h. The reaction mixture was allowed for cooling to room temperature. Saturated $NaHCO_3$ (4 mL) was added to the reaction mixture, and the organic layer was extracted with $CHCl_3$ (15 mL×3). The combined organic extracts were dried over Na_2SO_4 and filtered. Solvents were evaporated from the filtrate in vacuo to give the crude product as dark green solid, which was purified by flash column chromatography on NH silica gel (eluent: *n*-hexane/ethyl acetate = 7:3) to give white solid (256.3 mg) containing **S5**. The obtained solid was further purified by reprecipitation from a biphasic solution of *n*-hexane/EtOAc (*v*/*v*

= 9:1) to give pure **S5** as white solid (211.6 mg, 0.64 mmol, 64%). Mp 163 °C (dec.); T_d (5 wt%) 217 °C (under N_2 gas); 217 °C (under air); R_f 0.08 (*n*-hexane/EtOAc = 8:2); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (s, 1H), 7.27 (t, J = 6.0 Hz, 1H), 6.96 (dd, J = 7.2, 7.6 Hz, 1H), 6.90 (d, J = 7.2 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.75 (s, 1H), 6.72 (dd, J = 7.2, 7.6 Hz, 1H), 6.65 (d, J = 7.6 Hz, 1H), 6.60 (d, J = 7.6 Hz, 1H), 3.91 (d, J = 6.0 Hz, 2H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.7, 142.1, 140.7, 133.7, 127.6, 126.4, 126.2, 124.96, 124.90, 121.6, 116.1, 114.4, 114.2, 77.7, 42.6, 28.2; IR (ATR): ν 3387, 3289, 2999, 2978, 1682, 1607, 1580, 1520, 1464, 1429, 1391, 1368, 1300, 1283, 1256, 1236, 1209, 1171, 1128, 1080, 1045, 1031, 972, 933, 879, 856, 841, 810, 748 cm^{-1}; MS (EI$^+$): *m*/*z* (relative intensity, %): 330 ([M+2]$^+$, 6), 329 ([M+1]$^+$, 18), 328 ([M]$^+$, 81), 273 ([M–^{t}Bu+2]$^+$, 19), 272 ([M–^{t}Bu+1]$^+$, 100), 271 ([M–^{t}Bu]$^+$, 28), 254 ([M–^{t}BuO–H]$^+$, 59), 228 ([M–Boc+1]$^+$, 34), 227 ([M–Boc]$^+$, 23), 212 ([M–NHBoc]$^+$, 94), 200 ([M–BocNHCH$_2$+2]$^+$, 6), 199 ([M–BocNHCH$_2$+1]$^+$, 14), 198 ([M–BocNHCH$_2$]$^+$, 12); HRMS (FAB$^+$, NBA:PFK): *m/z* calcd for $C_{18}H_{20}N_2O_2S$ (M) 328.1245, found 328.1247; Elemental analysis (%) calcd. For $C_{18}H_{20}N_2O_2S$: C 65.83, H 6.14, N 8.53; found: C 65.74, H 6.08, N 8.43.

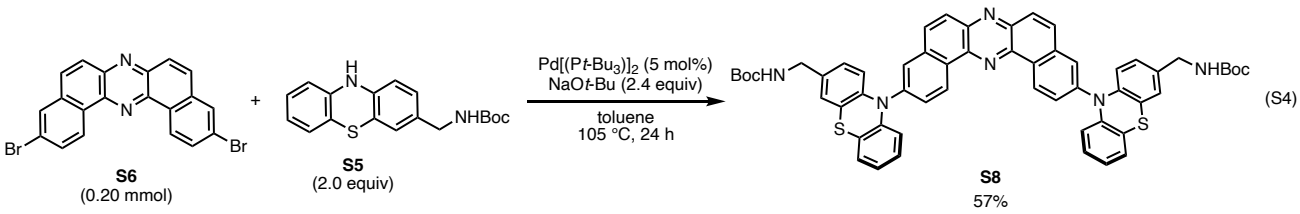
*Preparation of di-tert-butyl ((dibenzo[a,j]phenazine-3,11-diylbis(10H-phenoxazine-10,2-diyl))bis(methylene))dicarbamate (**S7**)*



A two-necked reaction tube (10 mL) equipped with a stirring bar was flame-dried. To the tube, were added dibromodibenzophenazine **S6** (43.8 mg, 0.10 mmol, 1.0 eq.) and phenoxazine **S6** (68.6 mg, 0.21 mmol, 2.1 equiv). The tube was transferred into a glovebox, where Pd[P(*t*-Bu)$_3$]$_2$ (2.6 mg, 5.0 μmol, 5 mol%) and NaO*t*-Bu (23.2 mg, 0.24 mmol, 2.4 equiv) were added to the vessel. The reaction tube was sealed with two rubber septum and taken from the glovebox. Toluene (2.0 mL) was added to the vessel. The mixture was stirred in a Personal Organic Synthesizer (EYELA, *Chemi-Station*) equipped with a cooling system under a reflux condition (aluminum block temperature: 105 °C) for 24 h. The reaction mixture was allowed to cool down to room temperature. $NaHCO_3$ aq. (2 mL) was added to the reaction mixture, and the organic layer was extracted with $CHCl_3$ (15 mL×3). The combined organic extracts were washed with water (30 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated under vacuum to give crude product (105.3 mg) as dark red solid, which was purified by flash column chromatography on NH silica gel (eluent: *n*-hexane/EtOAc = 8 : 2 to 7 : 3, and to EtOAc only) to give product **S7** (80.9 mg), which were then further purified by reprecipitation

from *n*-hexane/$CHCl_3$ (*v*/*v* = 9:1) to afford pure **S7** as orange solid (52.9 mg, 58.7 μmol, 59%). Mp 157 °C (dec.); T_d (5 wt%) 232 °C (under N_2 gas); 231 °C (under air); R_f 0.38 (*n*-hexane/EtOAc 5:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 9.2 Hz, 2H), 8.02 (d, J = 2.0 Hz, 2H), 7.84 (dd, J = 2.0, 8.8 Hz, 2H), 6.77–6.75 (m, 2H), 6.72–6.70 (m, 4H), 6.63–6.59 (m, 2H), 6.51 (dd, J = 1.8, 8.6 Hz, 2H), 6.04 (dd, J = 1.4, 8.2 Hz, 2H), 5.98 (d, J = 8.4 Hz, 2H), 4.76 (br, 2H), 4.13 (d, J = 6.0 Hz, 4H), 1.45 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 144.1, 143.9, 143.2, 140.4, 140.1, 135.5, 134.1, 133.4, 132.6, 132.2, 131.0, 130.3, 130.1, 128.6, 128.0, 123.4, 122.2, 121.8, 115.7, 114.9, 113.38, 113.32, 79.5, 43.9, 28.4; IR (ATR): ν 3422, 3345, 3063, 2974, 2930, 1699, 1607, 1597, 1489, 1476, 1460, 1431, 1391, 1356, 1329, 1314, 1275, 1248, 1233, 1206, 1159, 1119, 1101, 1042, 1020, 997, 976, 928, 885, 868, 855, 799, 787, 741, 727 cm^{-1}; MS (FAB^+, NBA): *m*/*z* (relative intensity, %): 901 ($[M+1]^+$, 3), 900 (M^+, 4); HRMS (FAB^+, NBA: PFK): *m*/*z* calcd for $C_{56}H_{48}N_6O_6$ (M) 900.3635, found 900.3637.

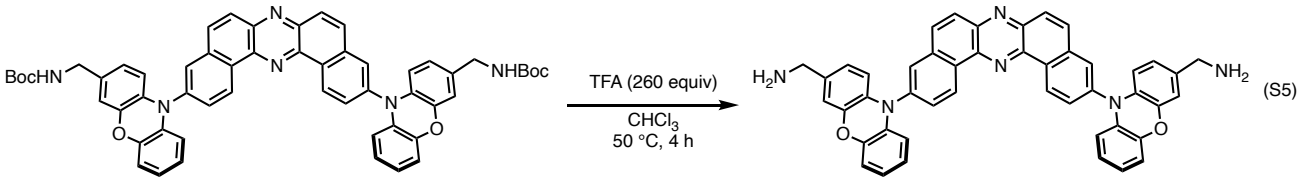
*Preparation of di-tert-butyl ((dibenzo[a,j]phenazine-3,11-diylbis(10H-phenothiazine-10,2-diyl))bis(methylene))dicarbamate (**S8**)*



A two-necked reaction tube (10 mL) equipped with a stirring bar was flame-dried. To the tube, were added dibromodibenzophenazine **S6** (87.3 mg, 0.20 mmol, 1.0 equiv) and phenothiazine **S5** (155.6 mg, 0.40 mmol, 2.2 equiv). The tube was transferred into a glovebox, where $Pd[P(t\text{-}Bu)_3]_2$ (5.9 mg, 10.0 μmol, 5 mol%) and NaO*t*-Bu (48.6 mg, 0.49 mmol, 2.4 equiv) were added to the vessel. The tube was sealed with two rubber septum and taken from the glovebox. Toluene (4.0 mL) was added to the vessel. The mixture was stirred in a Personal Organic Synthesizer (EYELA, *Chemi-Station*) equipped with a cooling system under a reflux condition (aluminum block temperature: 105 °C) for 24 h. Water (8.0 mL) was added to the reaction mixture, and the organic layer was extracted with $CHCl_3$ (25 mL×3). The combined organic extracts were dried over Na_2SO_4 and filtered, and the filtrate was concentrated under vacuum to give crude product (200.6 mg) as dark red solid, which was purified by flash column chromatography on NH silica gel (eluent: *n*-hexane/EtOAc = 7:3) to give orange solid containing product **S8** (145.5 mg). The obtained solid was then further purified by recrystallization from *n*-hexane/$CHCl_3$ (*v*/*v* = 9:1) to afford pure **S8** as orange solid (105.3 mg, 0.11 mmol, 57%). Mp 161 °C (dec.); T_d (5 wt%) 232 °C (under N_2 gas); 232 °C (under air); R_f 0.53 (*n*-hexane/EtOAc 5 : 5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H),

8.08 (d, J = 9.2 Hz, 2H), 7.94 (d, J = 1.6 Hz, 2H), 7.82 (dd, J = 1.6, 8.4 Hz, 2H), 7.16 (dd, J = 2.2, 7.0 Hz, 2H), 7.09 (d, J = 1.6 Hz, 2H), 6.98–6.85 (m, 6H), 6.53 (dd, J = 1.4, 7.4 Hz, 2H), 6.48 (d, J = 8.4 Hz, 2H), 4.80 (br, 2H), 4.20 (d, J = 5.2 Hz, 4H), 1.45 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 143.6, 142.9, 142.8, 140.5, 135.3, 134.2, 132.2, 129.7, 127.9, 127.8, 127.3, 127.1, 126.3, 126.2, 123.4, 123.3, 122.7, 122.6, 118.3, 118.2, 114.4, 79.6, 43.7, 28.4 (1C was not detected in the aromatic region, probably due to the overlap of signals); IR (ATR): ν 3420, 3345, 3057, 2974, 2930, 2868, 1699, 1614, 1599, 1578, 1543, 1495, 1466, 1439, 1410, 1391, 1354, 1321, 1304, 1242, 1163, 1146, 1109, 1076, 1044, 1026, 1020, 997, 972, 932, 855, 814, 797, 783, 745, 720 cm^{-1}; MS (FAB$^+$, NBA): m/z (relative intensity, %): 934 ([M+2]$^+$, 13), 933 ([M+1]$^+$, 23), 932 (M$^+$, 24), 818 ([M–2^{t}Bu]$^+$, 7), 702 ([M–2NHBoc]$^+$, 8), 328 (26); HRMS (FAB$^+$, TG+NBA): m/z calcd for $C_{56}H_{48}N_6O_4S_2$ (M) 932.3178, found 932.3187; Elemental analysis (%) calcd. For $C_{56}H_{48}N_6O_4S_2$: C 72.08, H 5.18, N 9.01, found: C 71.87, H 5.14, N 8.75.

*Preparation of di-tert-butyl (dibenzo[a,j]phenazine-3,11-diylbis(10H-phenoxazine-10,2-diyl))dimethanamine (**5**)*

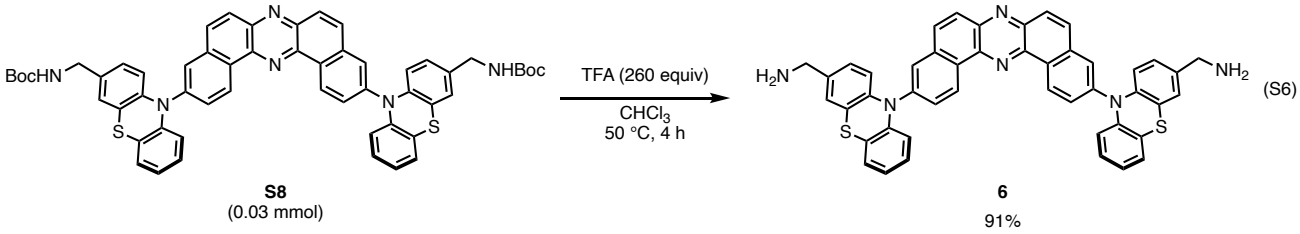


S7 (0.03 mmol) → **5** 63% (S5)

To a two-necked flask (100 mL) equipped with a magnetic stir bar, was added **S7** (26.9 mg, 0.030 mmol). The flask was sealed with a three-way-stopcock and a septum, evacuated, and refilled with N_2 gas for three times. $CHCl_3$ (6 mL, super dehydrated grade) was added to the flask. To the solution, trifluoroacetic acid (0.60 mL, 7.8 mmol, 260 equiv) was added dropwise. The resulting mixture was stirred at 50 °C (aluminum block temperature) for 4 h. 2 M NaOH aq. (10 mL) was added to the reaction mixture. The organic layer was extracted with $CHCl_3$ (15 mL×3) and washed with water (30 mL). The combined organic extracts were dried over Na_2SO_4 and filtered, and the filtrate was concentrated under vacuum to give crude product (19.9 mg) as red solid. The obtained crude product was purified by reprecipitation from n-hexane/$CHCl_3$ (v/v = 9:1) to afford pure **5** as orange solid (13.1 mg, 0.019 mmol, 63%). Mp 183 °C (dec.); T_d (5 wt%) 376 °C (under N_2 gas); 394 °C (under air); R_f 0.75 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 9.2 Hz, 2H), 8.15 (d, J = 9.2 Hz, 2H), 8.04 (d, J = 2.0 Hz, 2H), 7.85 (dd, J = 2.0, 8.0 Hz, 2H), 6.78–6.75 (m, 4H), 6.72–6.68 (m, 2H), 6.64–6.59 (m, 2H), 6.55 (dd, J = 1.4, 8.2 Hz, 2H), 6.05 (d, J = 8.0 Hz, 2H), 6.00 (d, J = 8.0 Hz, 2H), 3.69 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.9, 143.2, 140.4, 140.2,

137.3, 135.5, 134.2, 133.0, 132.2, 131.0, 130.3, 130.2, 128.6, 128.0, 123.4, 121.7, 121.6, 115.7, 114.6, 113.4, 45.7 (1C was not detected in the aromatic region, probably due to the overlap of signals); IR (ATR): ν 3374, 3057, 2914, 2851, 1611, 1595, 1545, 1508, 1489, 1476, 1460, 1429, 1383, 1354, 1327, 1312, 1273, 1231, 1204, 1144, 1121, 1101, 1042, 1018, 995, 976, 922, 885, 868, 853, 799, 779, 741, 727 cm^{-1}; MS (FAB^+, NBA): *m/z* (relative intensity, %): 701 ($[M+1]^+$, 1), 700 (M^+, 1), 685 ($[M–NH_2+1]^+$, 1), 684 ($[M–NH_2]^+$, 1); HRMS (MALDI): *m/z* calcd for $C_{46}H_{32}N_6O_2$ (M) 700.2587, found 700.25813.

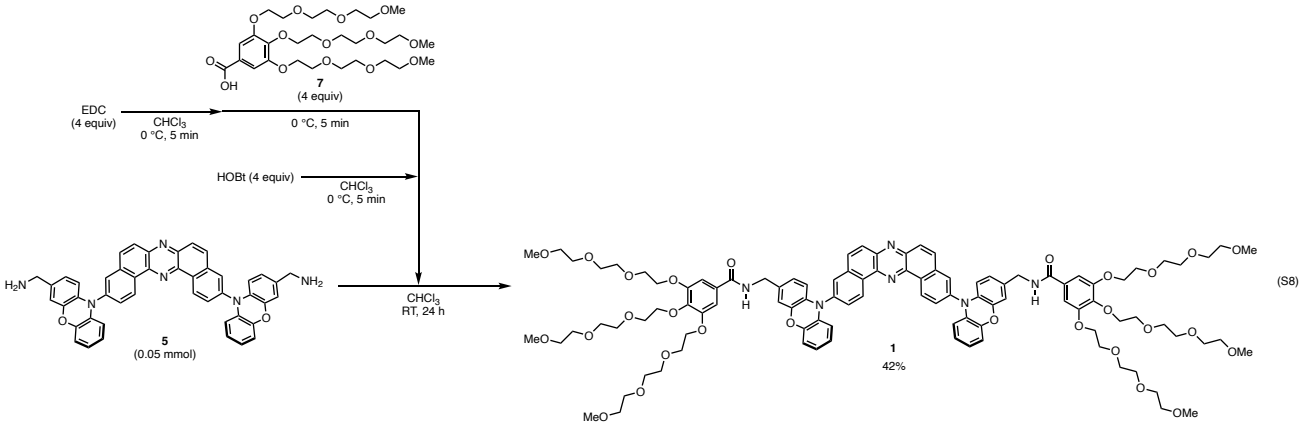
*Preparation of di-tert-butyl (dibenzo[a,j]phenazine-3,11-diylbis(10H-phenothiazine-10,2-diyl))dimethanamine (**6**)*



To a two-necked flask (50 mL) equipped with a magnetic stir bar, was added **S8** (28.0 mg, 0.030 mmol). The flask was sealed with a three-way-stopcock and a septum, evacuated, and refilled with N_2 gas for three times. $CHCl_3$ (6.0 mL, super dehydrated grade) was added to the flask. To the solution, trifluoroacetic acid (0.60 mL, 7.8 mmol, 260 equiv) was added dropwise, and the resulting mixture was stirred at 50 °C (aluminum block temperature) for 4 h. 2 M NaOH aq. (10 mL) was added to the reaction mixture, and the organic layer was extracted with $CHCl_3$ (15 mL×6) and washed with water (30 mL×2). The combined organic extracts were dried over Na_2SO_4 and filtered, and the filtrate was concentrated under vacuum to give crude product (20.7 mg) as dark brown solid, which was purified by recrystallization from *n*-hexane/$CHCl_3$ (*v*/*v* = 9:1) to afford pure **6** as orange solid (19.9 mg, 0.027 mmol, 91%). Mp 177 °C (dec.); T_d (5 wt%) 307 °C (under N_2 gas); 323 °C (under air); R_f 0.75 ($CHCl_3$/MeOH 9:1); ^1H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 9.2 Hz, 2H), 8.07 (d, *J* = 9.2 Hz, 2H), 7.93 (d, *J* = 2.0 Hz, 2H), 7.82 (dd, *J* = 2.0, 8.8 Hz, 2H), 7.18 (dd, *J* = 2.0, 7.2 Hz, 2H), 7.15 (d, *J* = 1.6 Hz, 2H), 7.01–6.90 (m, 6H), 6.58 (dd, *J* = 1.4, 7.8 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.3, 142.8, 142.4, 140.5, 138.8, 135.3, 132.1, 129.5, 127.9, 127.7, 127.4, 127.0, 126.1, 126.0, 125.8, 123.8, 123.49, 123.46, 118.8, 118.7, 45.6 (1C was not detected in the aromatic region, probably due to the overlap of signals); IR (ATR): ν 3368, 3055, 2916, 2853, 1614, 1595, 1576, 1545, 1489, 1466, 1439, 1410, 1379, 1354, 1304, 1256, 1244, 1146, 1130, 1107, 1076, 1063, 1044, 1018, 997, 972, 932, 885, 855, 814, 797, 745, 720, 704 cm^{-1}; MS (FAB^+, NBA): *m/z* (relative intensity, %): 733 ($[M+1]^+$, 1),

732 (M^+, 1), 716 ([M–NH_2]$^+$, 1); HRMS (FAB$^+$, TG: PEG+NaI): *m/z* calcd for $C_{46}H_{32}N_6S_2$ (M) 732.2130, found 732.2143.

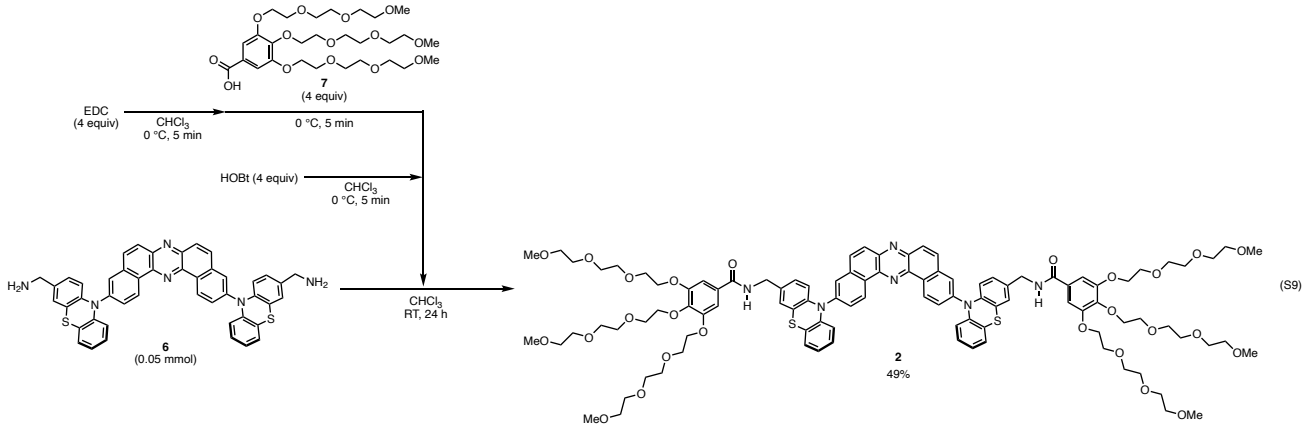
*Synthesis of N,N'-((dibenzo[a,j]phenazine-3,11-diylbis(10H-phenoxazine-10,2-diyl))bis(methylene))bis(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzamide) (**1**)*



To a two-necked reaction tube (*tube A*) (3 mL) equipped with a stirring bar, was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (31.1 mg, 0.20 mmol, 4.0 equiv). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. The vessel was cooled at 0 °C, and carboxylic acid **7** (122.3 mg, 0.20 mmol, 4.0 equiv) and $CHCl_3$ (2.8 mL, super dehydrated grade) were added, and the resulting solution was stirred at 0 °C for 5 min (*solution A*). To another two-necked reaction tube (3 mL) (*tube B*) equipped with a stirring bar, was added 1-hydroxybenzotriazole (HOBt) (27.0 mg, 0.20 mmol, 4.0 equiv). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. The vessel was cooled at 0 °C, and $CHCl_3$ (2.0 mL, super dehydrated grade) was added to the tube. *Solution A* was added to *tube B* at 0 °C, and the resulting solution was stirred at room temperature for 5 min (*solution B*). To a two-necked reaction tube (10 mL) (*tube C*) equipped with a stirring bar, was added compound **5** (35.0 mg, 0.050 mmol). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. To *tube C*, $CHCl_3$ (3.0 mL, super dehydrated grade) was added to dissolve compound **5**. *Solution B* was injected to *tube C* through septum, and the resulting solution was stirred at room temperature for 24 h. Water (4.0 mL) was added to the reaction mixture, and the organic layer was washed with 1 M HCl aq. (50 mL), 1 M NaOH aq. (100 mL), brine (100 mL), and water (100 mL×2). The combined organic extracts were dried over Na_2SO_4 and filtered. Solvents were evaporated from the filtrate in vacuo to give the crude product (94.7 mg) as red solid, which was purified by flash column chromatography on NH silica gel (eluent: EtOAc only to EtOAc/MeOH = 95:5 to 9:1) to give red solid (70.9 mg) containing **1**. The obtained solid was further purified with GPC ($CHCl_3$) to give product (43.2 mg), which was then further purified by reprecipitation from a biphasic solution of *n*-hexane/$CHCl_3$ (*v*/*v* = 9:1). Supernatant was removed, and

the residue solid was dried in a vacuum oven at 80 °C to give product **1** as orange solid (39.6 mg, 0.021 mmol, 42%). Mp 194 °C (dec.); T_d (5 wt%)； 368 °C (under N_2 gas); 335 °C (under air); R_f 0.93 (chloroform : MeOH = 9 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (d, J = 8.0 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 9.2 Hz, 2H), 8.03 (d, J = 2.0 Hz, 2H), 7.84 (dd, J = 1.6, 8.8 Hz, 2H), 7.11 (s, 4H), 6.78–6.74 (m, 4H), 6.71–6.67 (m, 2H), 6.63–6.58 (m, 4H), 6.03 (dd, J = 1.2, 8.0 Hz, 2H), 6.00 (d, J = 8.4 Hz, 2H), 4.42 (d, J = 5.2 Hz, 4H), 4.21–4.18 (m, 12H), 3.84–3.77 (m, 12H), 3.72–3.69 (m, 12H), 3.65–3.61 (m, 24H), 3.53–3.51 (m, 12H), 3.37 (s, 6H), 3.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 152.4, 144.1, 143.9, 143.3, 141.6, 140.4, 140.0, 135.5, 134.1, 133.6, 132.2, 132.1, 131.0, 130.3, 130.1, 129.6, 128.6, 128.0, 123.4, 122.8, 121.8, 115.7, 115.3, 113.4, 107.5, 72.3, 71.9, 70.67, 70.65, 70.62, 70.5, 70.4, 69.7, 69.1, 59.01, 59.00, 43.4 (3C of TEG groups in the aliphatic region and 1C in the aromatic region were not detected, probably due to the overlap of signals); IR (ATR): ν 3526, 3308, 3063, 2916, 2874, 2818, 1628, 1614, 1578, 1541, 1512, 1489, 1476, 1460, 1425, 1352, 1327, 1294, 1277, 1236, 1223, 1120, 1098, 1040, 1018, 997, 976, 885, 855, 818, 804, 785, 745, 729, 712 cm^{-1}; HRMS (MALDI): *m/z* calcd for $C_{102}H_{124}N_6O_{28}Na$ (M+Na) 1903.8361, found 1903.83558 (M+Na).

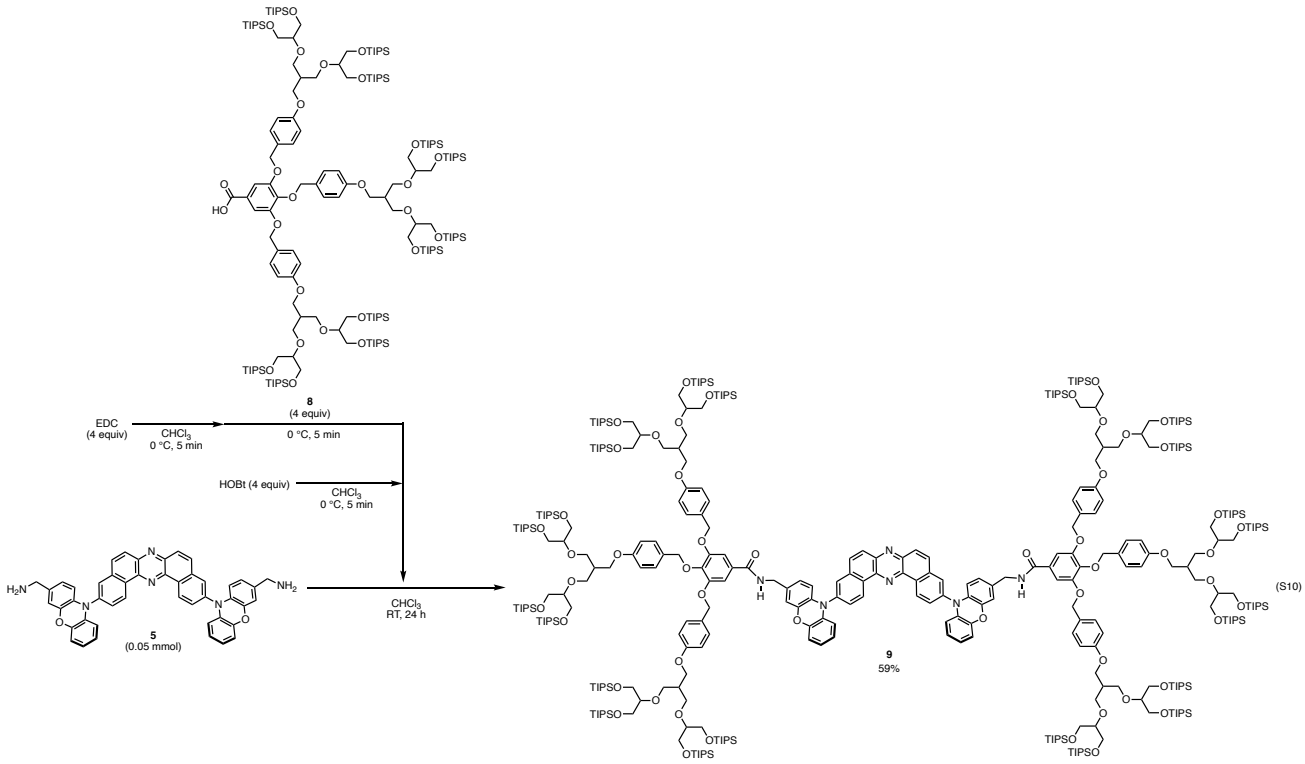
*Synthesis of N,N'-((dibenzo[a,j]phenazine-3,11-diylbis(10H-phenoxazine-10,2-diyl))bis(methylene))bis(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzamide) (**2**)*



To a two-necked reaction tube (*tube A*) (3 mL) equipped with a stirring bar, was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (32.0 mg, 0.20 mmol, 4.0 equiv). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. The vessel was cooled at 0 °C, and carboxylic acid **7** (123.8 mg, 0.20 mmol, 4.0 equiv) and $CHCl_3$ (2.8 mL, super dehydrated grade) were added, and the resulting solution was stirred at 0 °C for 5 min (*solution A*). To another two-necked reaction tube (3 mL) (*tube B*) equipped with a stirring bar, was added 1-hydroxybenzotriazole (HOBt) (27.0 mg, 0.20 mmol, 4.0 equiv). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. The

vessel was cooled at 0 °C, and $CHCl_3$ (2.0 mL, super dehydrated grade) was added to the tube. *Solution A* was added to *tube B* at 0 °C, and the resulting solution was stirred at room temperature for 5 min (*solution B*). To a two-necked reaction tube (10 mL) (*tube C*) equipped with a stirring bar, was added compound **6** (36.7 mg, 0.050 mmol). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. To *tube C*, $CHCl_3$ (3.0 mL, super dehydrated grade) was added to dissolve compound **6**. *Solution B* was injected to *tube C* through septum, and the resulting solution was stirred at room temperature for 24 h. Water (4.0 mL) was added to the reaction mixture, and the organic layer was washed with 1 M HCl aq. (50 mL), 1 M NaOH aq. (100 mL), brine (100 mL), and water (100 mL×2). The combined organic extracts were dried over Na_2SO_4 and filtered. Solvents were evaporated from the filtrate in vacuo to give the crude product (105.9 mg) as reddish brown viscous solid, which was purified by flash column chromatography on NH silica gel (eluent: EtOAc/MeOH = 99:1 to 9:1) to give reddish brown viscous solid (95.4 mg) containing **2**. The obtained solid was further purified with GPC ($CHCl_3$) to give product (52.1 mg), which was then further purified by reprecipitation from a biphasic solution of *n*-hexane/$CHCl_3$ (*v*/*v* = 9:1). Supernatant was removed, and the residue solid was dried in a vacuum oven at 80 °C to give product **2** as reddish brown viscous solid (46.8 mg, 0.025 mmol, 49%). Mp 127 °C (dec.); T_d (5 wt%)； 380 °C (under N_2 gas); 356 °C (under air); R_f 0.93 (chloroform : MeOH = 9 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 9.2 Hz, 2H), 8.08 (d, J = 9.6 Hz, 2H), 7.95 (d, J = 2.0 Hz, 2H), 7.82 (dd, J = 1.2, 8.8 Hz, 2H), 7.16–7.13 (m, 4H), 7.11 (s, 4H), 6.97–6.90 (m, 6H), 6.72 (br, 2H), 6.52–6.48 (m, 4H), 4.48 (d, J = 4.0 Hz, 4H), 4.20–4.18 (m, 12H), 3.82–3.77 (m, 12H), 3.70–3.68 (m, 12H), 3.65–3.60 (m, 24H), 3.53–3.50 (m, 12H), 3.36 (s, 6H), 3.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 152.4, 143.6, 143.0, 142.89, 142.85, 141.6, 140.5, 135.3, 133.8, 132.1, 129.7, 129.4, 127.9, 127.8, 127.3, 127.1, 126.78, 126.75, 126.6, 123.5, 122.8, 118.34, 118.28, 107.6, 72.3, 71.92, 71.89, 70.7, 70.6, 70.53, 70.50, 70.4, 69.7, 69.1, 59.00, 58.95, 43.2 (2C of TEG groups in the aliphatic region and 2C in the aromatic region were not detected, probably due to the overlap of signals); IR (ATR): ν 3340, 3323, 3304, 3057, 2870, 2823, 2631, 2604, 2587, 1653, 1638, 1578, 1541, 1491, 1466, 1439, 1423, 1352, 1329, 1300, 1240, 1200, 1094, 1042, 1026, 997, 974, 932, 851, 818, 799, 748 cm^{-1}; HRMS (MALDI): *m/z* calcd for $C_{102}H_{124}N_6O_{26}S_2$ (M) 1912.8007, found 1912.8001; Elemental analysis (%) calcd. For $C_{102}H_{124}N_6O_{26}S_2$: C 64.00, H 6.53, N 4.31, found: C 63.63, H 6.62, N 4.31.

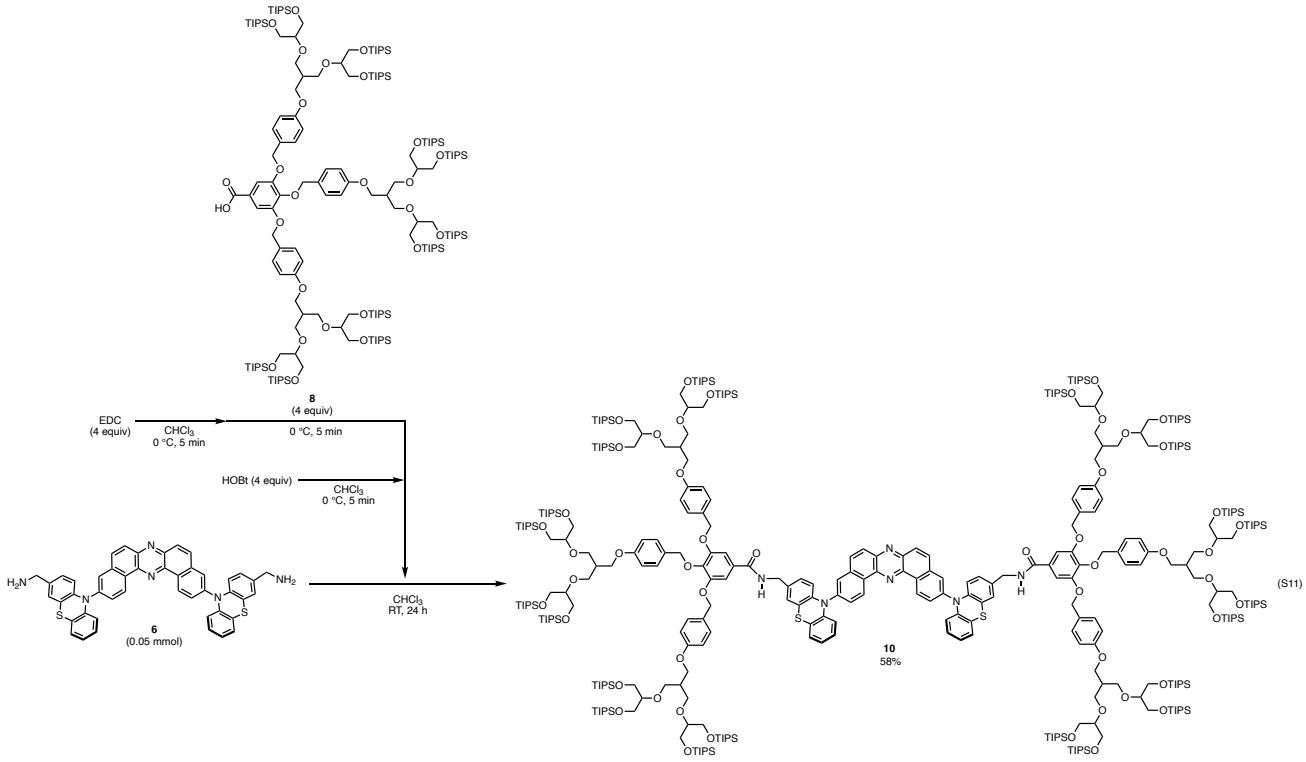
Preparation of ***9***



To a two-necked reaction tube (*tube A*) (3 mL) equipped with a stirring bar, was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (31.1 mg, 0.20 mmol, 4.0 equiv). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. The vessel was cooled at 0 °C, and carboxylic acid **8** (615.1 mg, 0.20 mmol, 4.0 equiv) and $CHCl_3$ (2.0 mL, super dehydrated grade) were added, and the resulting solution was stirred at 0 °C for 5 min (*solution A*). To another two-necked reaction tube (3 mL) (*tube B*) equipped with a stirring bar, was added 1-hydroxybenzotriazole (HOBt) (27.0 mg, 0.20 mmol, 4.0 equiv). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. The vessel was cooled at 0 °C, and $CHCl_3$ (2.0 mL, super dehydrated grade) was added to the tube. *Solution A* was added to *tube B* at 0 °C, and the resulting solution was stirred at room temperature for 5 min (*solution B*). To a two-necked reaction tube (10 mL) (*tube C*) equipped with a stirring bar, was added compound **5** (35.0 mg, 0.050 mmol). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. To *tube C*, $CHCl_3$ (1.8 mL, super dehydrated grade) was added to dissolve compound **5**. *Solution B* was injected to *tube C* through septum, and the resulting solution was stirred at room temperature for 24 h. Water (4.0 mL) was added to the reaction mixture, and the organic layer was washed with 1 M NaOH aq. (50 mL), brine (50 mL), and water (50 mL×2). The combined organic extracts were dried over Na_2SO_4 and filtered. Solvents were evaporated from the filtrate in vacuo to give the crude product (618.4 mg) as reddish brown viscous solid, which

was purified by flash column chromatography on NH silica gel (eluent: *n*-hexane/EtOAc = 9:1 to 8:2, and to 7:3) to give red viscous solid (304.0 mg) containing **9**. The obtained solid was further purified with GPC ($CHCl_3$) to give product **9** as orange viscous solid (202.1 mg, 0.030 mmol, 59%). Mp 84 °C; T_d (5 wt%)； 337 °C (under N_2 gas); 328 °C (under air); R_f 0.95 (*n*-hexane : AcOEt = 5 : 5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 9.6 Hz, 2H), 8.03 (d, J = 1.2 Hz, 2H), 7.85 (dd, J = 1.8, 8.6 Hz, 2H), 7.33 (d, J = 8.8 Hz, 8H), 7.28 (d, J = 8.8 Hz, 4H), 7.07 (s, 4H), 6.88 (d, J = 8.4 Hz, 8H), 6.79–6.75 (m, 8H), 6.71–6.68 (m, 2H), 6.62–6.58 (m, 4H), 6.14 (t, J = 5.4 Hz, 2H), 6.04–6.01 (m, 4H), 5.03–5.02 (m, 12H), 4.41 (d, J = 4.8 Hz, 4H), 4.05 (d, J = 6.0 Hz, 8H), 4.00 (d, J = 6.0 Hz, 4H), 3.77–3.67 (m, 72H), 3.44–3.39 (m, 12H), 2.36–2.31 (m, 6H), 1.11–1.01 (m, 504H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 159.2, 153.0, 144.3, 144.3, 143.8, 143.3, 141.5, 140.4, 140.0, 135.5, 134.0, 133.8, 132.1, 131.8, 131.0, 130.2, 130.0, 129.4, 129.2, 129.0, 128.6, 128.5, 128.1, 123.4, 122.9, 121.9, 115.8, 115.3, 114.5, 114.1, 113.4, 113.3, 107.4, 82.1, 82.0, 74.5, 71.5, 69.0, 66.2, 66.1, 63.4, 43.5, 40.87, 40.85, 18.0, 11.9 (2C in the aliphatic region and 2C in the aromatic region were not detected, probably due to the overlap of signals); IR (ATR): ν 3343, 2941, 2889, 2864, 2756, 2725, 1651, 1613, 1586, 1549, 1514, 1493, 1462, 1431, 1383, 1366, 1360, 1329, 1292, 1277, 1246, 1173, 1098, 1067, 1013, 995, 918, 882, 855, 793, 743, 729 cm^{-1}; HRMS (MALDI): *m/z* calcd for $C_{378}H_{676}N_6O_{52}Si_{24}Na$ (M+Na) 6827.4797, found 6827.4482 (M+Na)； Elemental analysis (%) calcd. For $C_{378}H_{676}N_6O_{52}Si_{24}$: C 66.65, H 10.00, N 1.23, found: C 66.34, H 10.20, N 1.32.

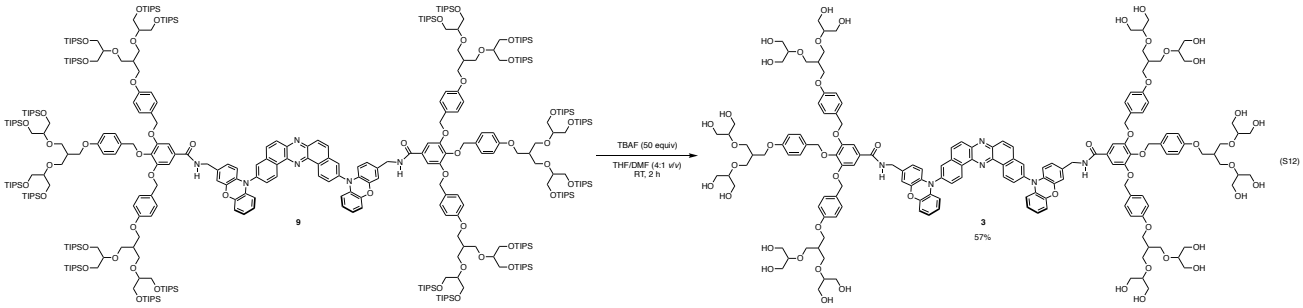
*Preparation of **10***



To a two-necked reaction tube (*tube A*) (3 mL) equipped with a stirring bar, was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (30.8 mg, 0.20 mmol, 4.0 equiv). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. The vessel was cooled at 0 °C, and carboxylic acid **8** (612.5 mg, 0.20 mmol, 4.0 equiv) and $CHCl_3$ (2.0 mL, super dehydrated grade) were added, and the resulting solution was stirred at 0 °C for 5 min (*solution A*). To another two-necked reaction tube (3 mL) (*tube B*) equipped with a stirring bar, was added 1-hydroxybenzotriazole (HOBt) (26.9 mg, 0.20 mmol, 4.0 equiv). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. The vessel was cooled at 0 °C, and $CHCl_3$ (2.0 mL, super dehydrated grade) was added to the tube. *Solution A* was added to *tube B* at 0 °C, and the resulting solution was stirred at room temperature for 5 min (*solution B*). To a two-necked reaction tube (10 mL) (*tube C*) equipped with a stirring bar, was added compound **6** (36.7 mg, 0.050 mmol). The reaction vessel was sealed with a septum and a three-way-stopcock, evacuated, and purged with N_2 gas for 3 times. To *tube C*, $CHCl_3$ (1.8 mL, super dehydrated grade) was added to dissolve compound **6**. *Solution B* was injected to *tube C* through septum, and the resulting solution was stirred at room temperature for 24 h. Water (4.0 mL) was added to the reaction mixture, and the organic layer was washed with 1 M NaOH aq. (30 mL), brine (30 mL), and water (50 mL×2). The combined organic extracts were dried over Na_2SO_4 and filtered. Solvents were evaporated from the filtrate in vacuo to give the crude product (555.1 mg) as reddish brown viscous solid, which

was purified by flash column chromatography on NH silica gel (eluent: *n*-hexane/EtOAc = 7:3 to EtOAc, and EtOAc : MeOH = to 99 : 1) to give orange viscous solid (261.1 mg) containing **10**. The obtained solid was further purified with GPC ($CHCl_3$) to give product **10** as red viscous solid (200.1 mg, 0.029 mmol, 58%). Mp 82 °C; T_d (5 wt%)； 330 °C (under N_2 gas); 328 °C (under air); R_f 0.95 (*n*-hexane : AcOEt = 5 : 5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 9.2 Hz, 2H), 8.09 (d, J = 9.2 Hz, 2H), 7.96 (d, J = 1.6 Hz, 2H), 7.84 (dd, J = 2.0, 8.8 Hz, 2H), 7.33 (d, J = 8.0 Hz, 8H), 7.28 (d, J = 8.0 Hz, 4H), 7.17–7.14 (m, 4H), 7.07 (s, 4H), 6.95–6.92 (m, 6H), 6.88 (d, J = 8.8 Hz, 8H), 6.78 (d, J = 8.4 Hz, 4H), 6.52–6.49 (m, 4H), 6.16 (t, J = 5.4 Hz, 2H), 5.03–5.02 (m, 12H), 4.48 (d, J = 4.8 Hz, 4H), 4.04 (d, J = 6.0 Hz, 8H), 4.00 (d, J = 6.0 Hz, 4H), 3.77–3.71 (m, 48H), 3.71–3.67 (m, 24H), 3.44–3.39 (m, 12H), 2.37–2.32 (m, 6H), 1.08–0.96 (m, 504H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 159.2, 153.0, 143.6, 143.2, 143.0, 142.8, 141.6, 140.5, 135.4, 133.4, 132.1, 130.0, 129.9, 129.3, 129.2, 129.02, 128.97, 128.5, 128.0, 127.9, 127.3, 127.1, 126.9, 126.8, 126.7, 123.6, 123.5, 122.6, 118.2, 114.5, 114.1, 107.4, 82.1, 82.0, 74.5, 71.5, 69.0, 66.2, 66.1, 63.39, 63.37, 43.4, 40.87, 40.85, 18.0, 11.9 (1C in the aliphatic region and 2C in the aromatic region were not detected, probably due to the overlap of signals); IR (ATR): ν 3327, 2941, 2889, 2864, 2764, 2725, 1634, 1614, 1584, 1537, 1514, 1489, 1464, 1429, 1383, 1366, 1356, 1329, 1302, 1246, 1173, 1098, 1067, 1013, 995, 918, 882, 793, 745, 721 cm^{-1}; HRMS (MALDI): *m/z* calcd for $C_{378}H_{676}N_6O_{50}S_2Si_{24}Na$ (M+Na) 6859.4340, found 6859.4023 (M+Na)； Elemental analysis (%) calcd. For $C_{378}H_{676}N_6O_{50}S_2Si_{24}$: C 66.34, H 9.96, N 1.23, found: C 66.44, H 10.17, N 1.22.

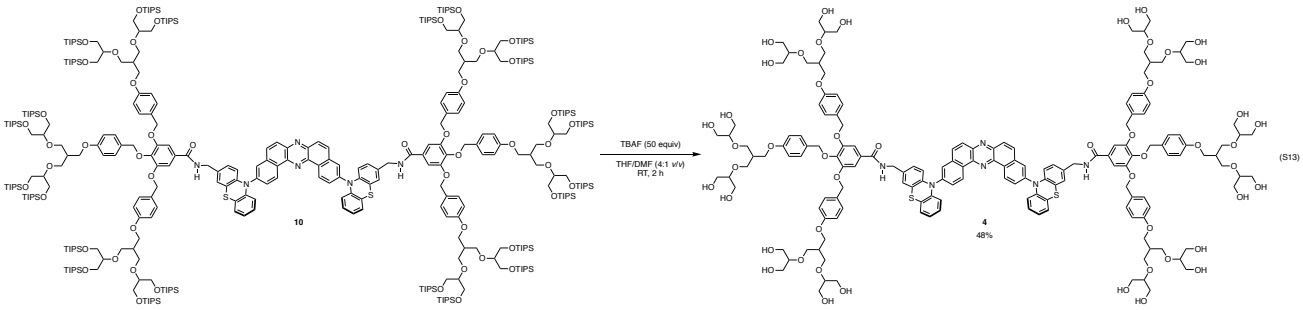
*Synthesis of **3***



A 1.0 M solution of tetrabutylammonium fluoride (TBAF) in THF (1.45 mL, 1.45 mmol, 50 equiv) was added dropwise to a solution of **9** (202.1 mg, 0.030 mmol) in a mixture of THF/DMF (*v*/*v* = 4:1, 10 mL) at room temperature. The mixture was stirred for 2 h at room temperature, quenched by a mixture of H_2O (27.0 mg, 1.50 mmol) and acetic acid (45.0 mg, 0.75 mmol), and evaporated. The crude product was purified by GPC (eluent: THF/MeOH = 4:1 v/v) and by HPLC (eluent: gradient from MeOH/H_2O = 3:1 to MeOH only) to afford **3** (52.0 mg, 0.017 mmol, 57%) as a scarlet cottony solid after lyophilization of the aqueous solution. M.p. 125 °C (dec.); T_d (5 wt%)； 319 °C (under N_2

gas); 311 °C (under air); R_f 0.40 ($CHCl_3$/MeOH 1:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.78 (d, J = 8.8 Hz, 2H), 8.85 (br, 2H), 8.36 (d, J = 9.2 Hz, 2H), 8.29 (d, J = 1.6 Hz, 2H), 8.17 (d, J = 9.6 Hz, 2H), 7.91 (d, J = 9.6 Hz, 2H), 7.32 (d, J = 8.0 Hz, 8H), 7.28 (s, 4H), 7.16 (d, J = 8.4 Hz, 4H), 6.91 (d, J = 8.0 Hz, 8H), 6.80–6.73 (m, 8H), 6.68–6.59 (m, 6H), 5.97–5.94 (m, 4H), 4.99 (s, 8H), 4.82 (s, 4H), 4.47–4.40 (m, 24H), 4.23 (br, 4H), 3.96 (d, J = 5.6 Hz, 8H), 3.92 (d, J = 6.0 Hz, 4H), 3.56–3.55 (m, 24H), 3.38–3.28 (m, 48H), 3.17–3.15 (m, 12H), 2.17–2.12 (m, 6H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 165.4, 158.60, 158.55, 152.0, 143.13, 143.07, 142.9, 139.8, 139.6, 139.5, 139.2, 135.3, 133.7, 133.6, 132.6, 132.5, 130.4, 130.2, 130.1, 129.9, 129.4, 129.3, 129.2, 128.7, 128.3, 127.6, 124.9, 123.9, 122.7, 121.8, 114.4, 114.1, 106.5, 81.9, 81.8, 73.6, 70.1, 67.6, 66.13, 66.07, 60.8, 42.0, 40.3, 40.1 (2C in the aliphatic region and 2C in the aromatic region were not detected, probably due to the overlap of signals); IR (ATR): ν 3314, 3078, 2926, 2874, 1632, 1611, 1584, 1543, 1514, 1491, 1476, 1462, 1422, 1356, 1329, 1302, 1277, 1242, 1175, 1101, 1038, 997, 974, 928, 853, 822, 801, 743, 727 cm^{-1}; HRMS (MALDI): *m/z* calcd for $C_{162}H_{196}N_6O_{52}Na$ (M+Na) 3080.2775, found 3080.2769 (M+Na).

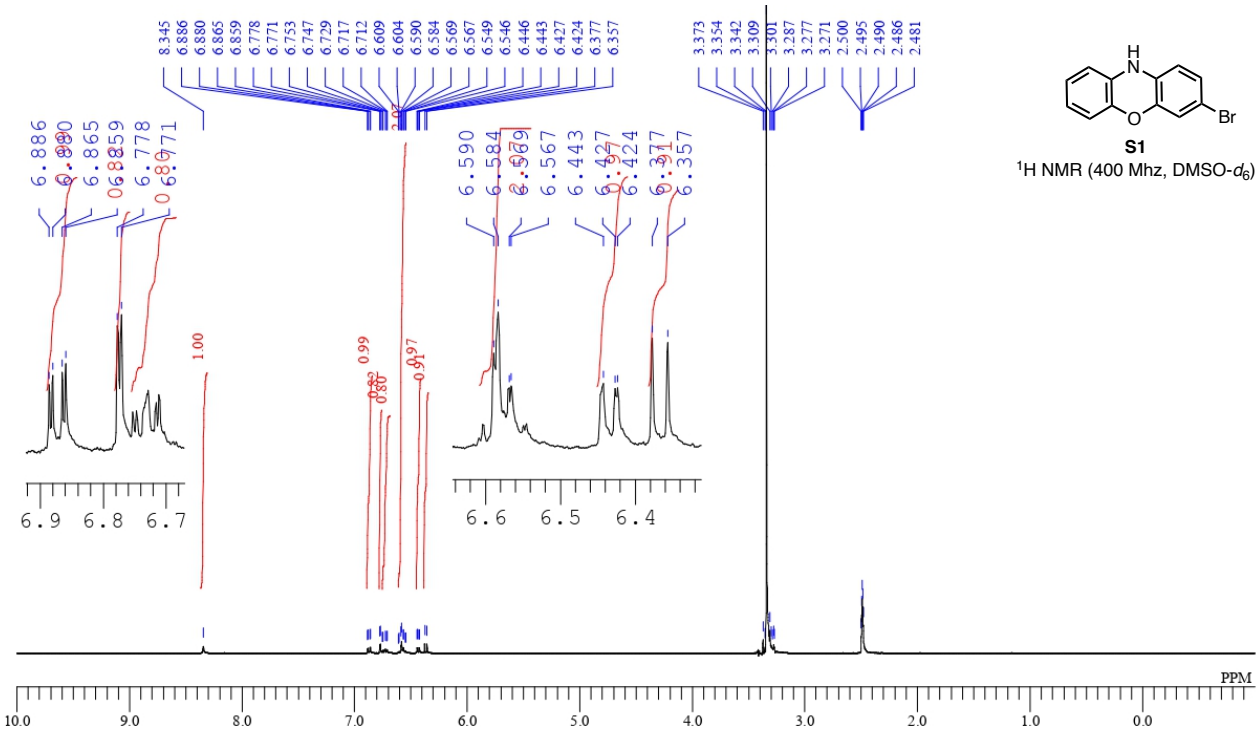
Synthesis of ***4***

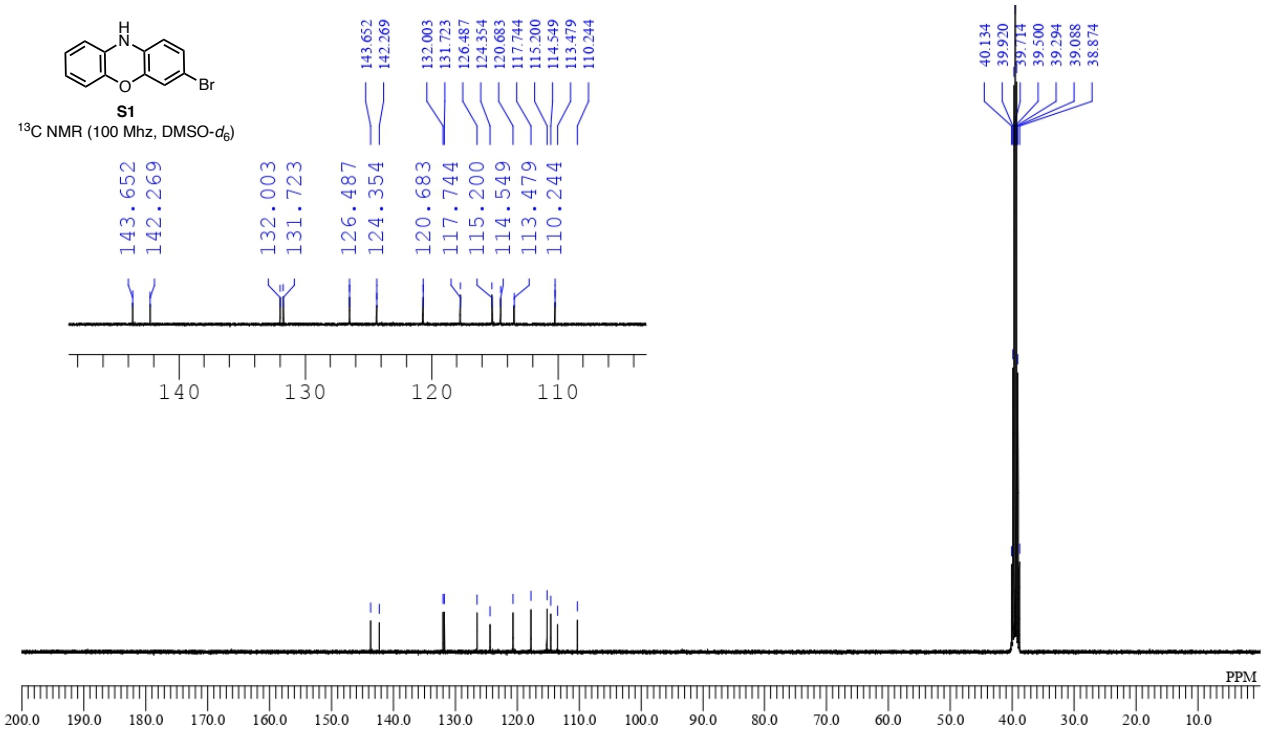


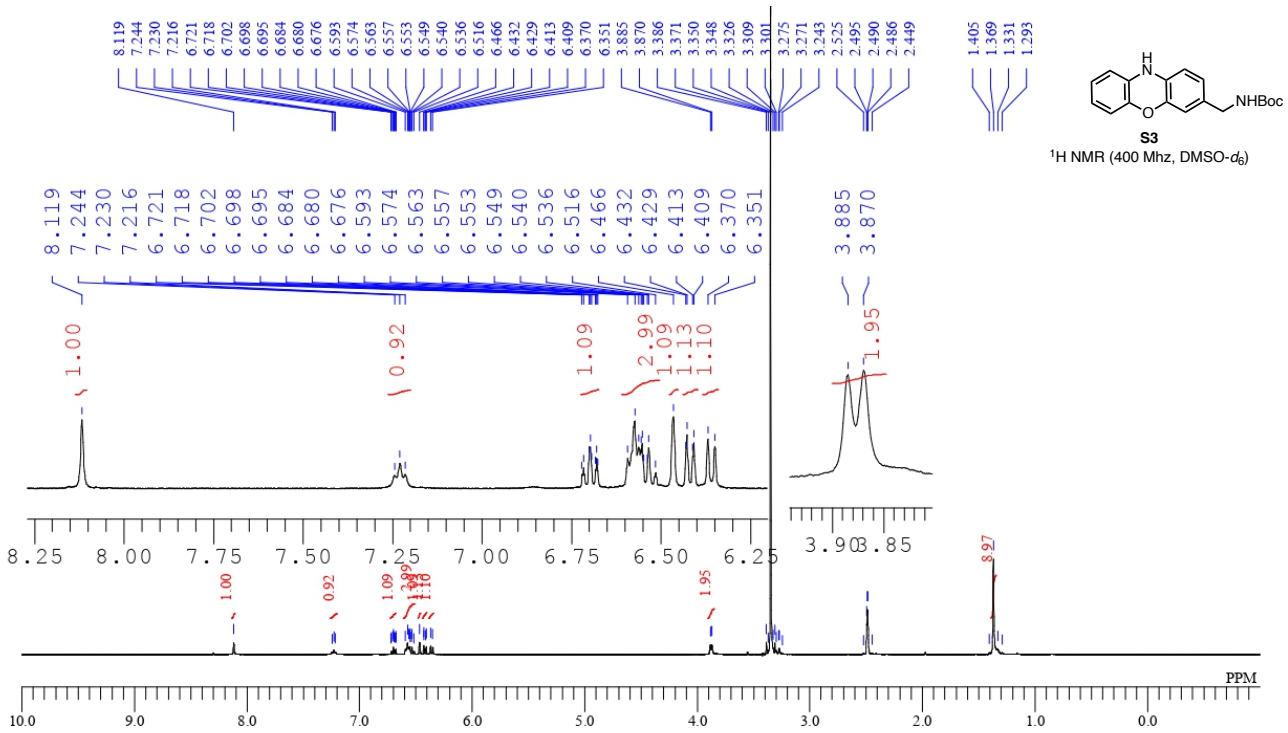
A 1.0 M solution of tetrabutylammonium fluoride (TBAF) in THF (1.45 mL, 1.45 mmol, 50 equiv) was added dropwise to a solution of **10** (200 mg, 0.029 mmol) in a mixture of THF/DMF (*v*/*v* = 4:1, 15 mL) at room temperature. The mixture was stirred for 2 h at room temperature, quenched by a mixture of H_2O (52 mg, 2.9 mmol) and acetic acid (87 mg, 1.5 mmol), and evaporated. The crude product was purified by GPC (eluent: THF/MeOH = 4:1) and by HPLC (eluent: gradient from MeOH/H_2O = 3:1 to MeOH only) to afford **4** (42.0 mg, 0.014 mmol, 48%) as an orange cottony solid after lyophilization of the aqueous solution. Mp 123 °C (dec.); T_d (5 wt%)； 307 °C (under N_2 gas); 272 °C (under air); R_f 0.30 ($CHCl_3$/MeOH 1:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (d, J = 8.8 Hz, 2H), 8.93 (br, 2H), 8.34 (d, J = 9.2 Hz, 2H), 8.18–8.15 (m, 4H), 7.88 (dd, J = 2.0, 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 8H), 7.33 (s, 4H), 7.25–7.19 (m, 8H), 7.07–7.01 (m, 6H), 6.97 (d, J = 8.4 Hz, 8H), 6.83 (d, J = 8.0 Hz, 4H), 6.60 (dd, J = 3.0, 8.0 Hz, 4H), 5.04 (s, 8H), 4.87 (s, 4H), 4.48 (br, 24H), 4.36 (br, 4H), 4.02 (d, J = 5.2 Hz, 8H), 3.98 (d, J = 5.6 Hz, 4H), 3.63–3.61 (m, 24H), 3.44–3.37 (m, 48H), 3.32–3.20 (m, 12H), 2.24–2.18 (m, 6H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 165.4, 158.59, 158.56,

152.1, 143.0, 142.6, 142.5, 141.8, 139.7, 139.5, 135.3, 135.1, 129.9, 129.4, 129.3, 129.2, 128.83, 128.78, 128.7, 127.6, 127,5, 127.2, 126.8, 126.3, 126.2, 123.7, 122.3, 122.2, 118.5, 114.4, 114.1, 106.5, 81.9, 81.8, 73.6, 70.1, 67.6, 66.13, 66.07, 60.8, 41.9, 40.3, 40.1 (2C in the aliphatic region and 3C in the aromatic region were not detected, probably due to the overlap of signals); IR (ATR): ν 3323 (br), 2928, 2874, 1632, 1613, 1582, 1543, 1514, 1489, 1466, 1439, 1420, 1354, 1329, 1302, 1240, 1177, 1101, 1032, 997, 972, 932, 905, 851, 820, 799, 745, 718 cm^{-1}; HRMS (MALDI): *m/z* calcd for $C_{162}H_{196}N_6O_{50}S_2Na$ (M+Na) 3112.2318, found 3112.2312 (M+Na).

NMR Charts of New Compounds






S3
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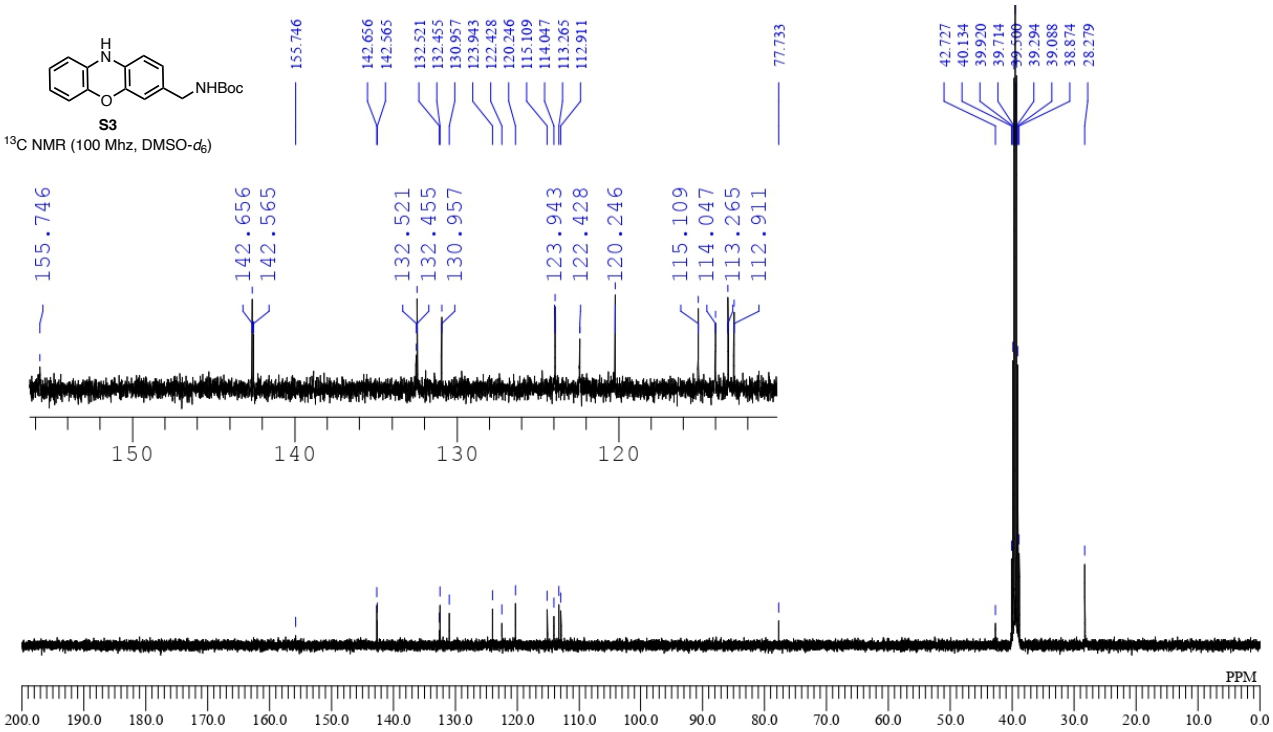
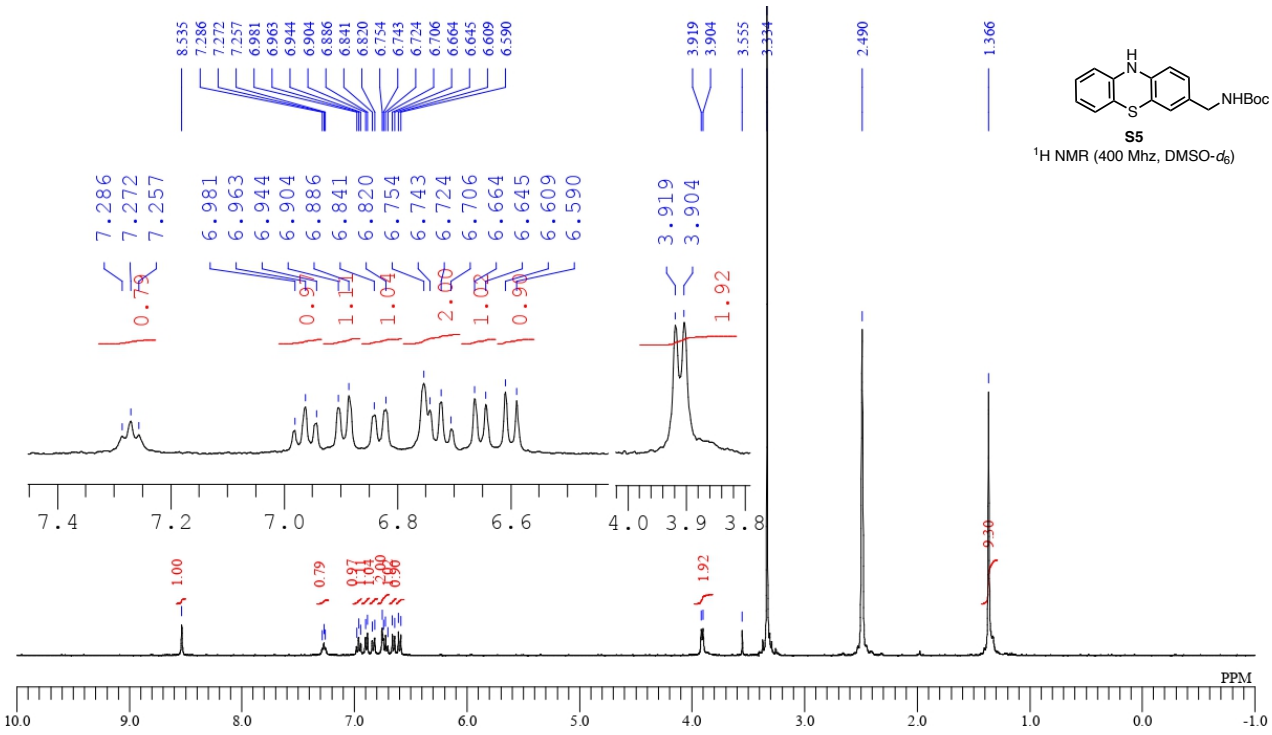
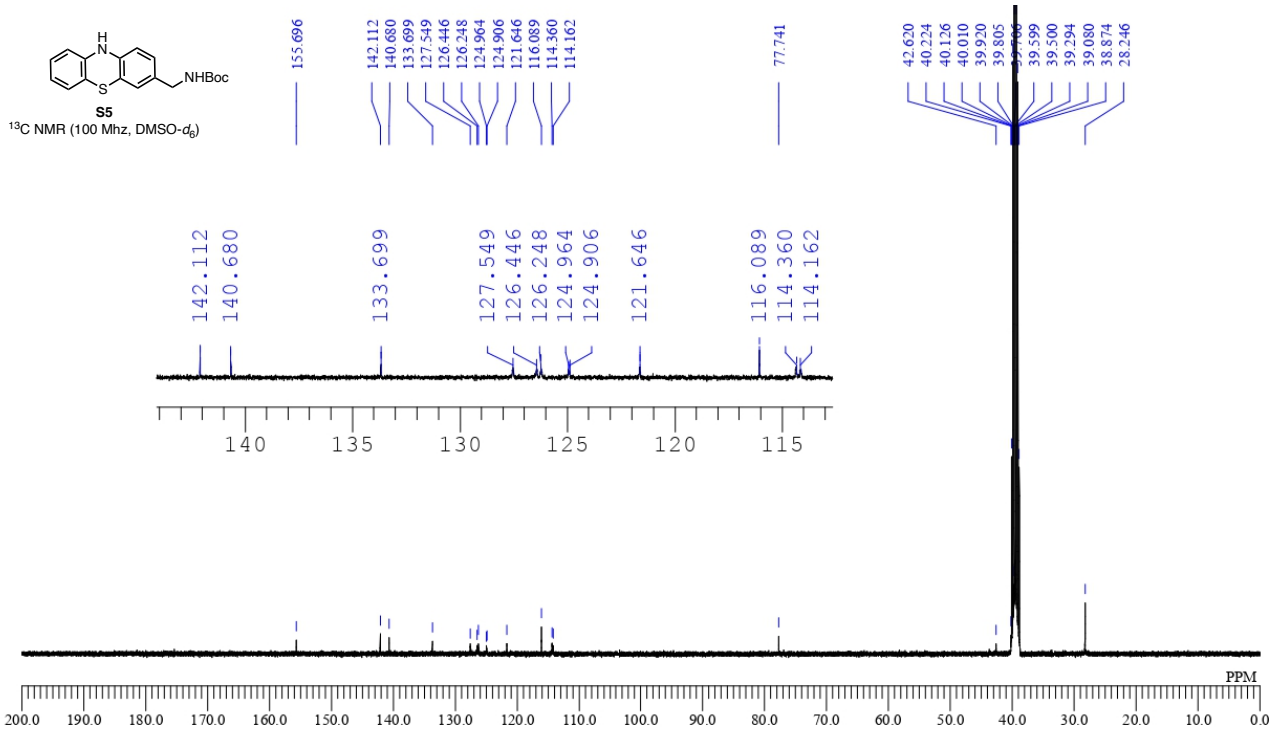
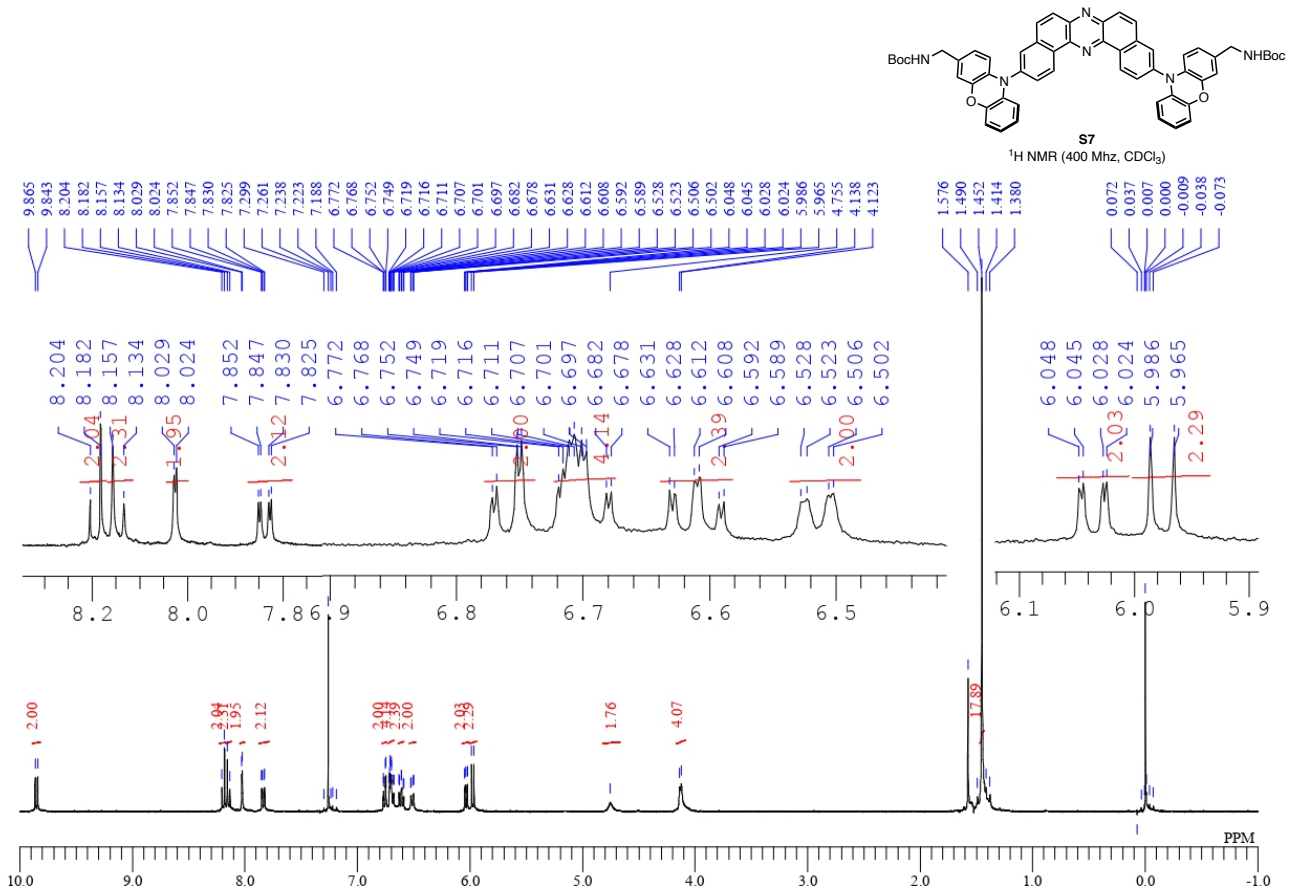
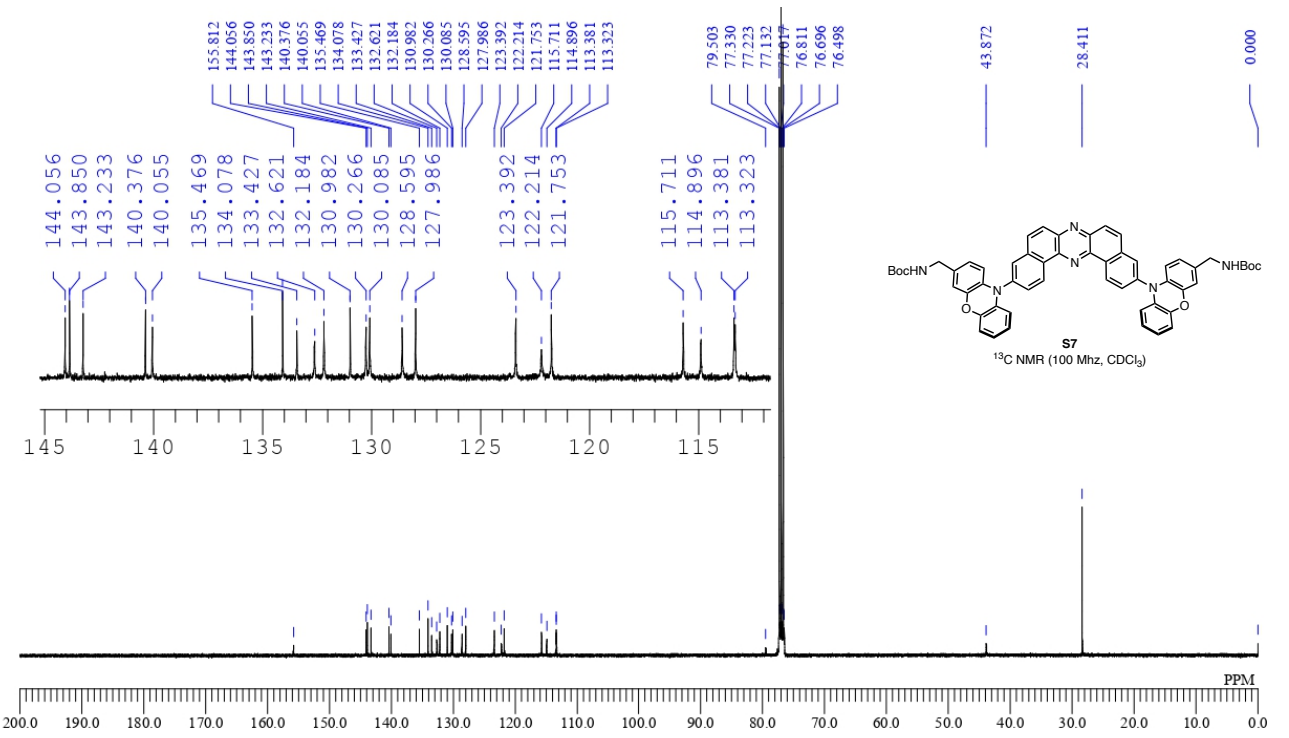
NHBoc
PPM

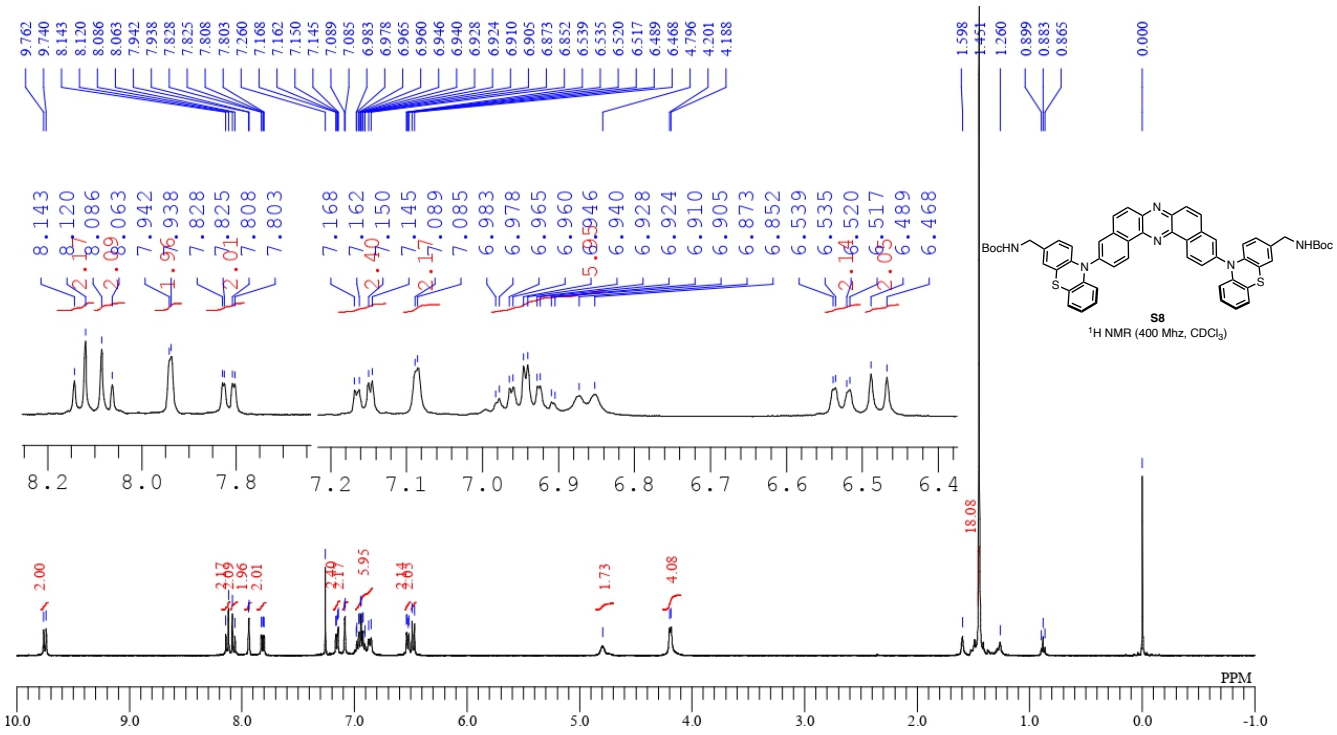

S3
^{13}C NMR (100 Mhz, DMSO-d_6)
NHBoc
PPM

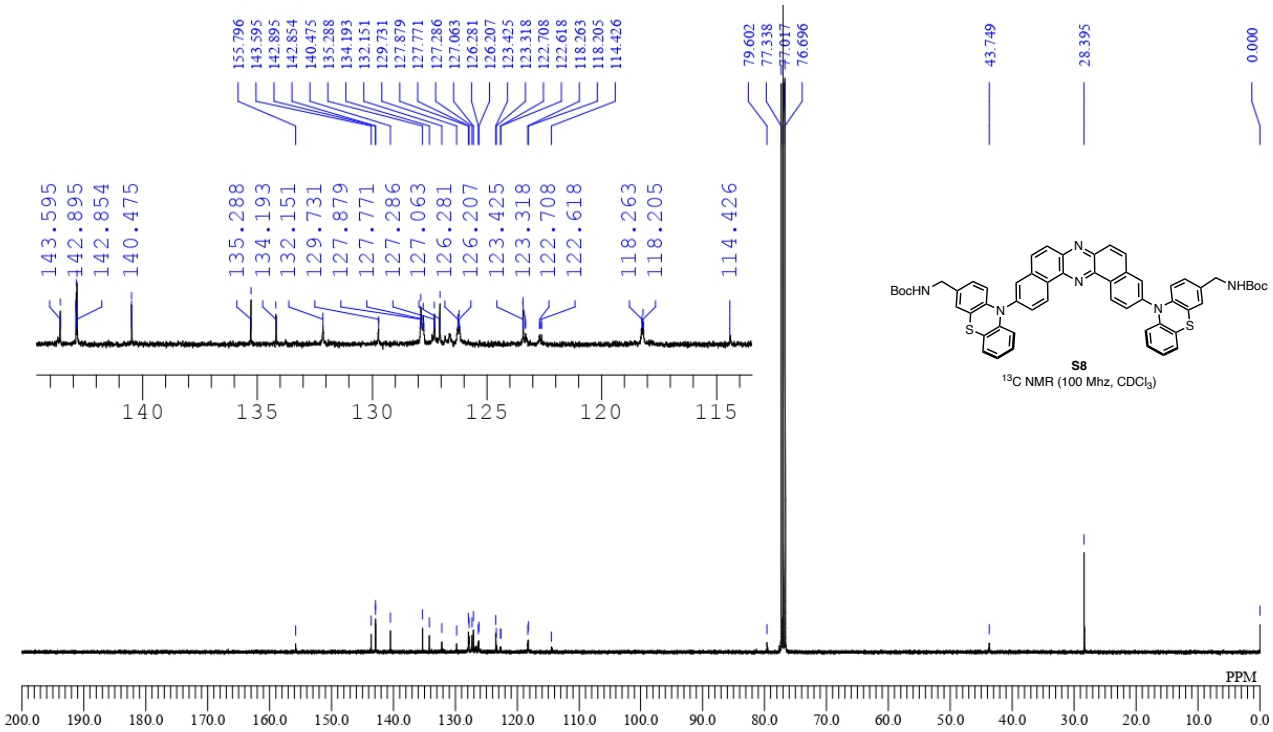

S5
^{1}H NMR (400 Mhz, DMSO-d_6)
NHBoc
PPM

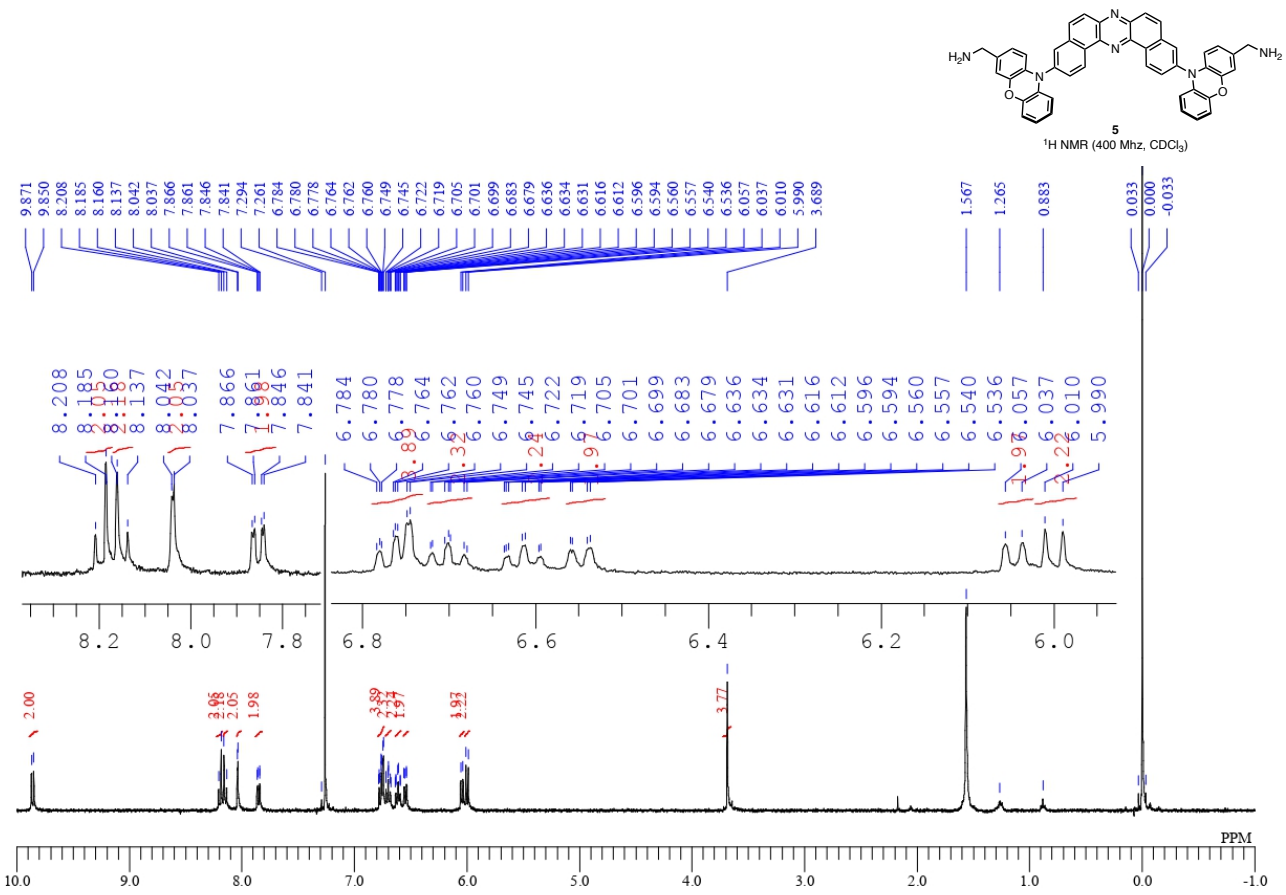

S5
^{13}C NMR (100 Mhz, DMSO-d_6)
NHBoc
PPM

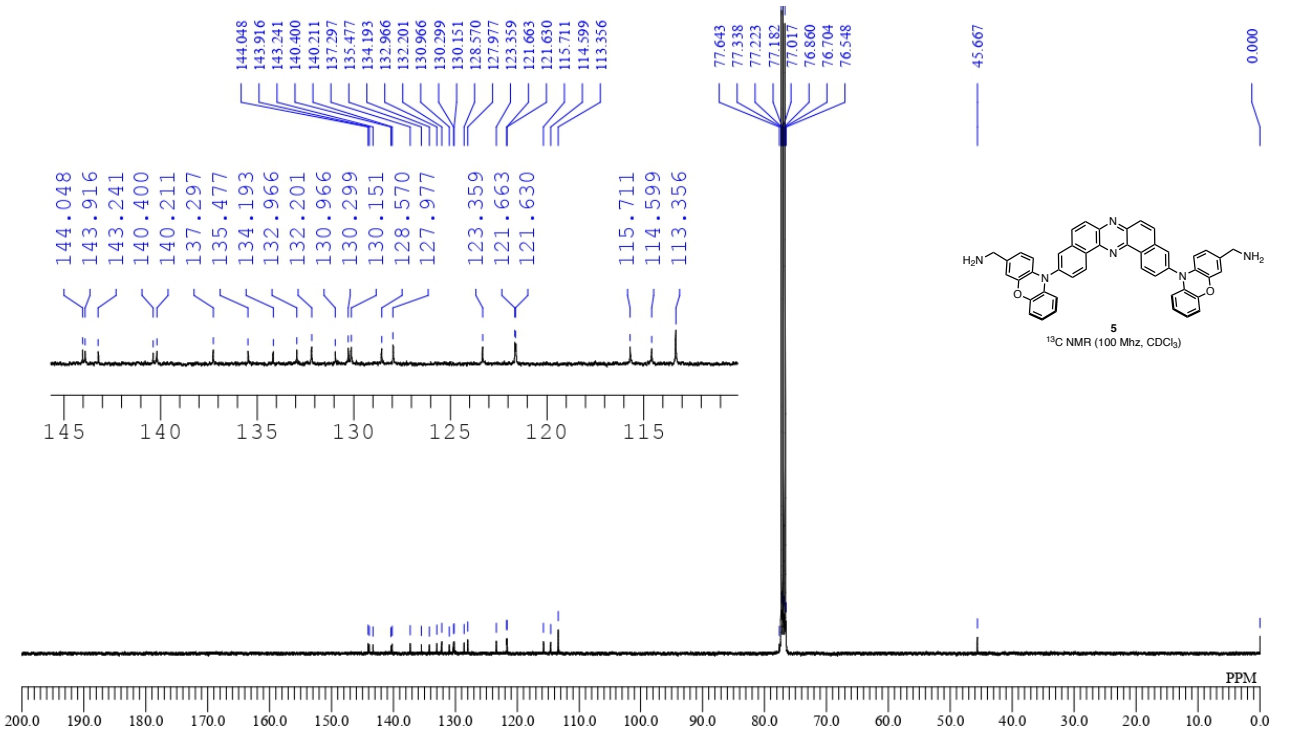

BocHN
NHBoc
S7
1H NMR (400 Mhz, CDCl3)
PPM


BocHN
NHBoc
S7
13C NMR (100 Mhz, CDCl3)
PPM


BocHN
NHBoc
S8
^{1}H NMR (400 Mhz, CDCl$_3$)


BocHN
NHBoc
S8
^{13}C NMR (100 Mhz, CDCl$_3$)


5
¹H NMR (400 Mhz, CDCl3)
PPM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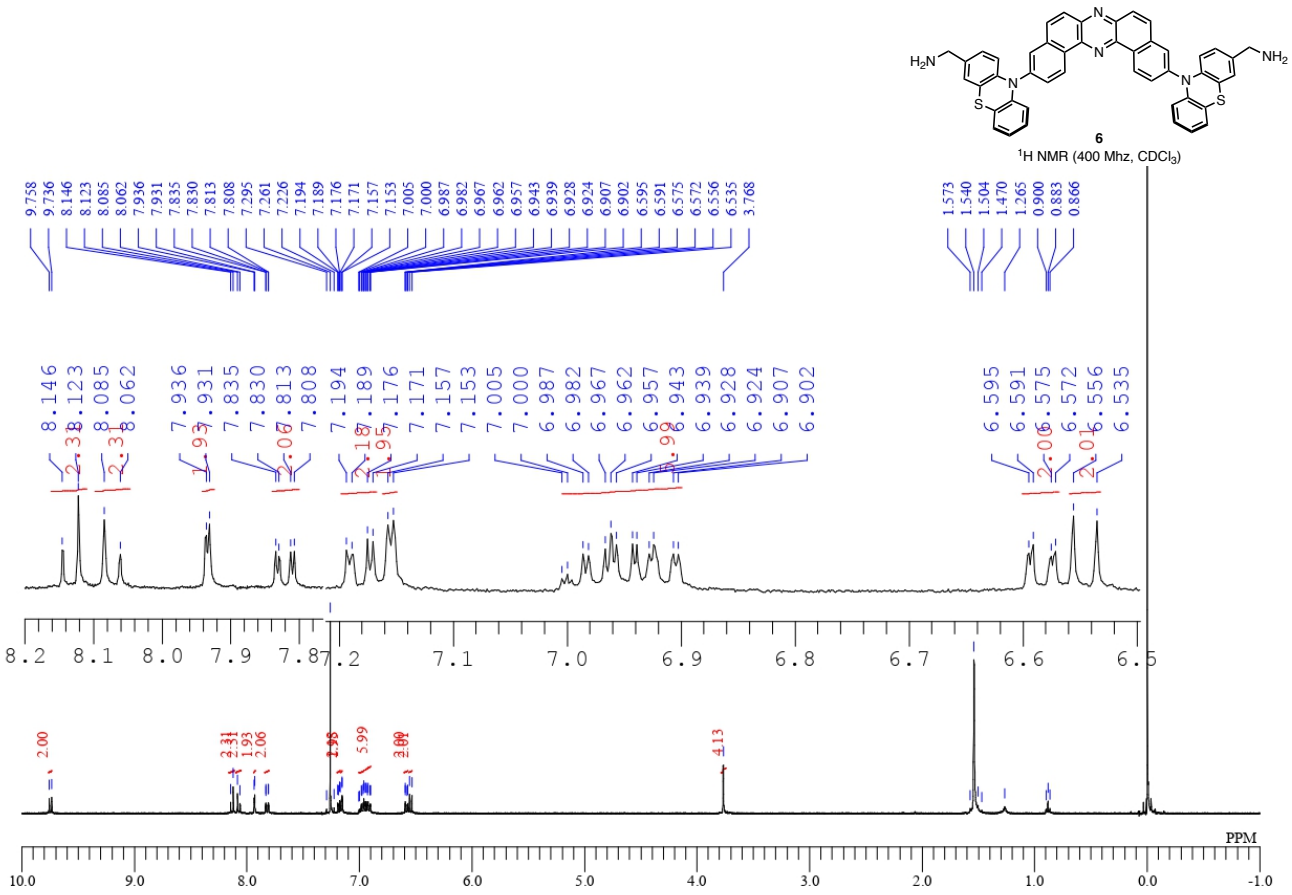
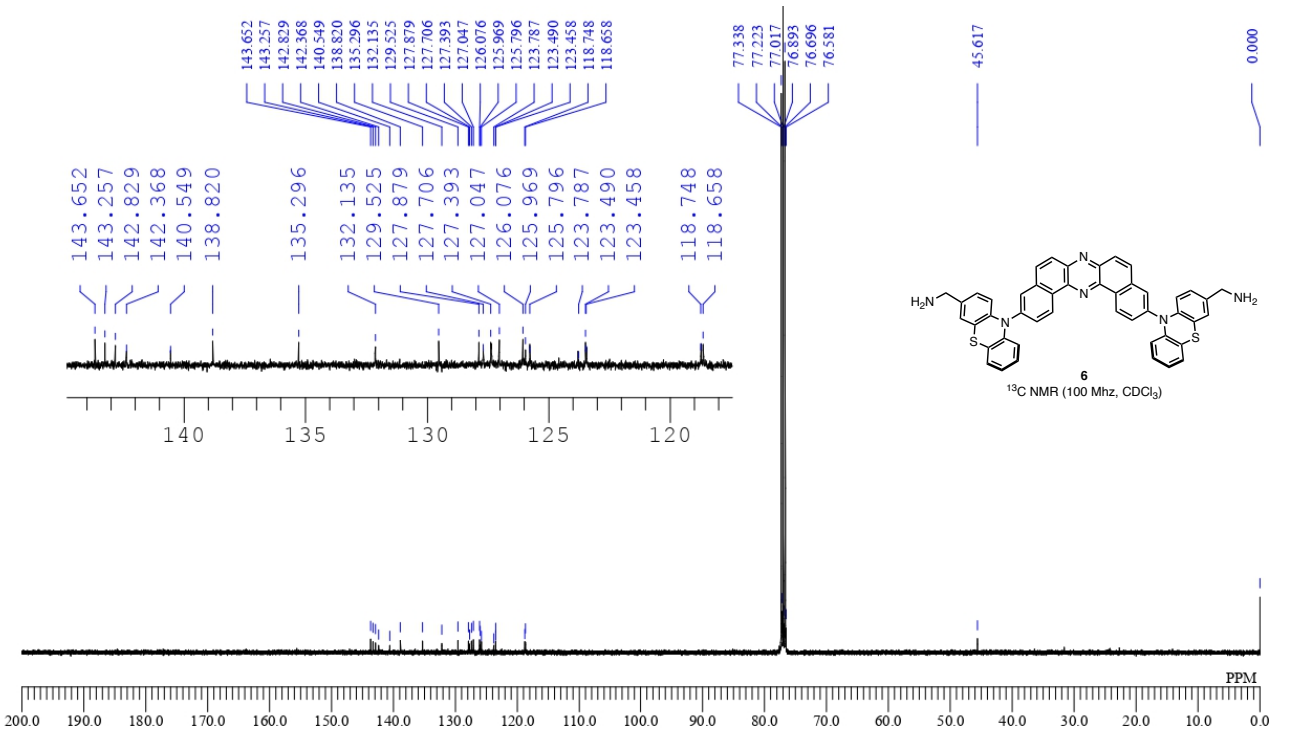
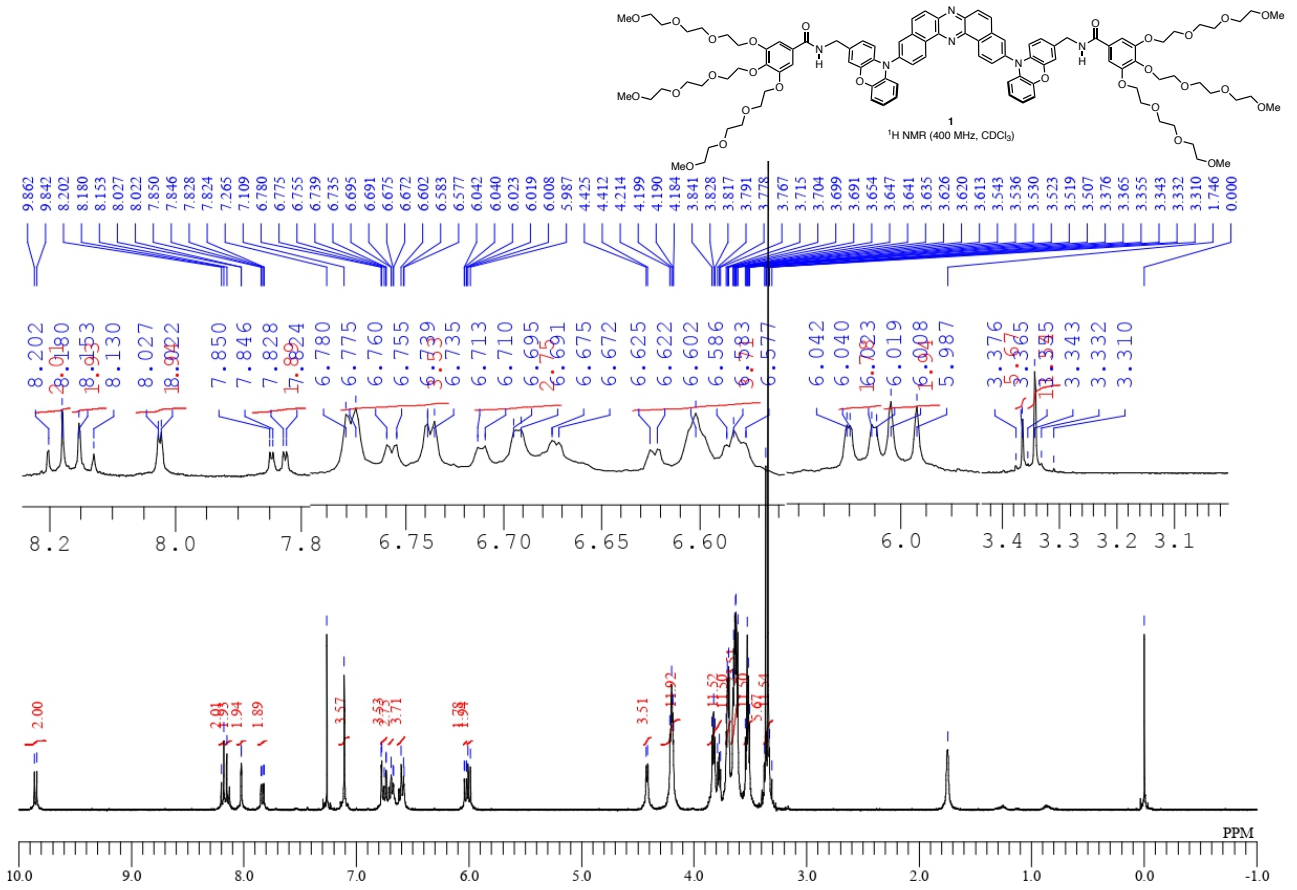
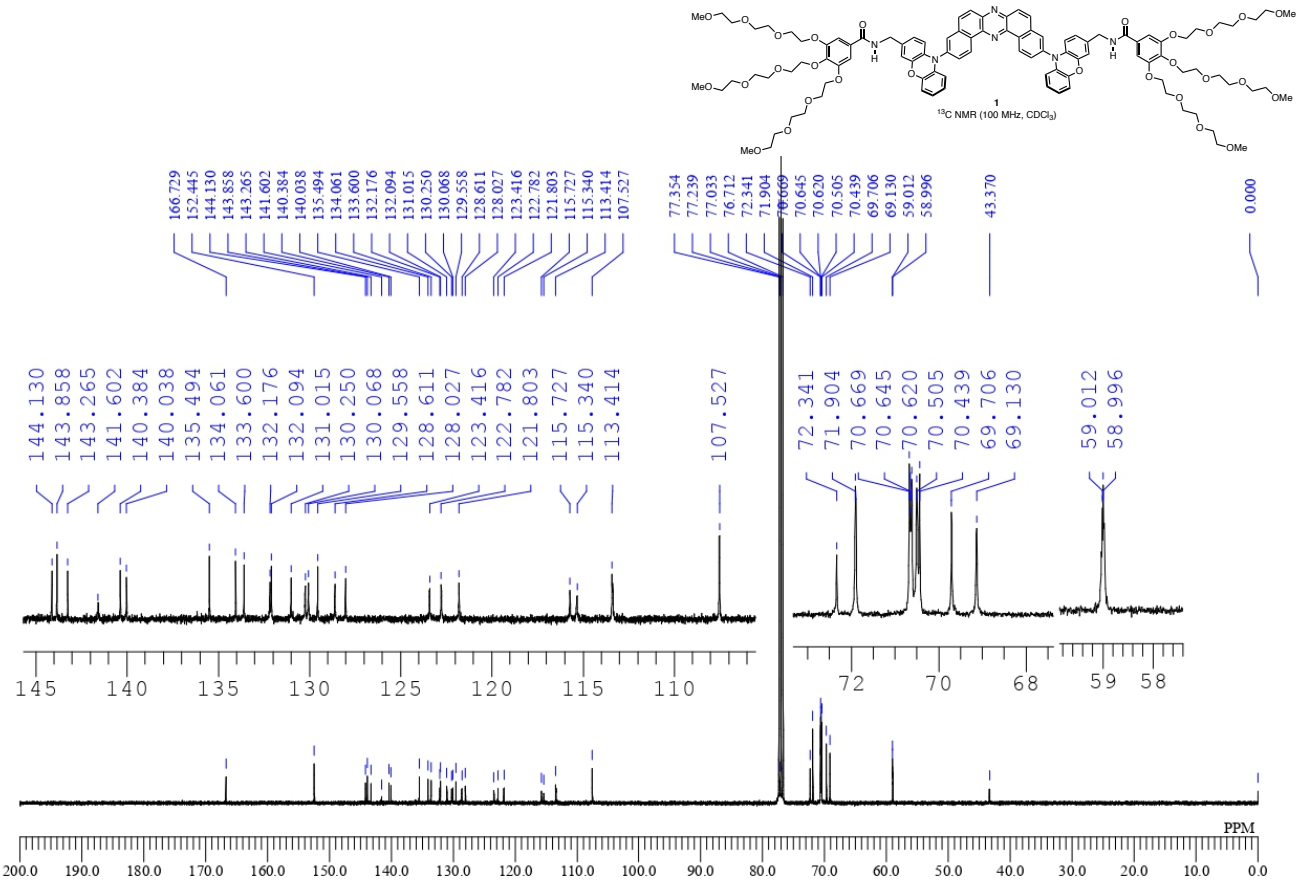
PPM


6
^{1}H NMR (400 Mhz, CDCl$_3$)
PPM


6
^{13}C NMR (100 Mhz, CDCl$_3$)
PPM


1
¹H NMR (400 MHz, CDCl3)
PPM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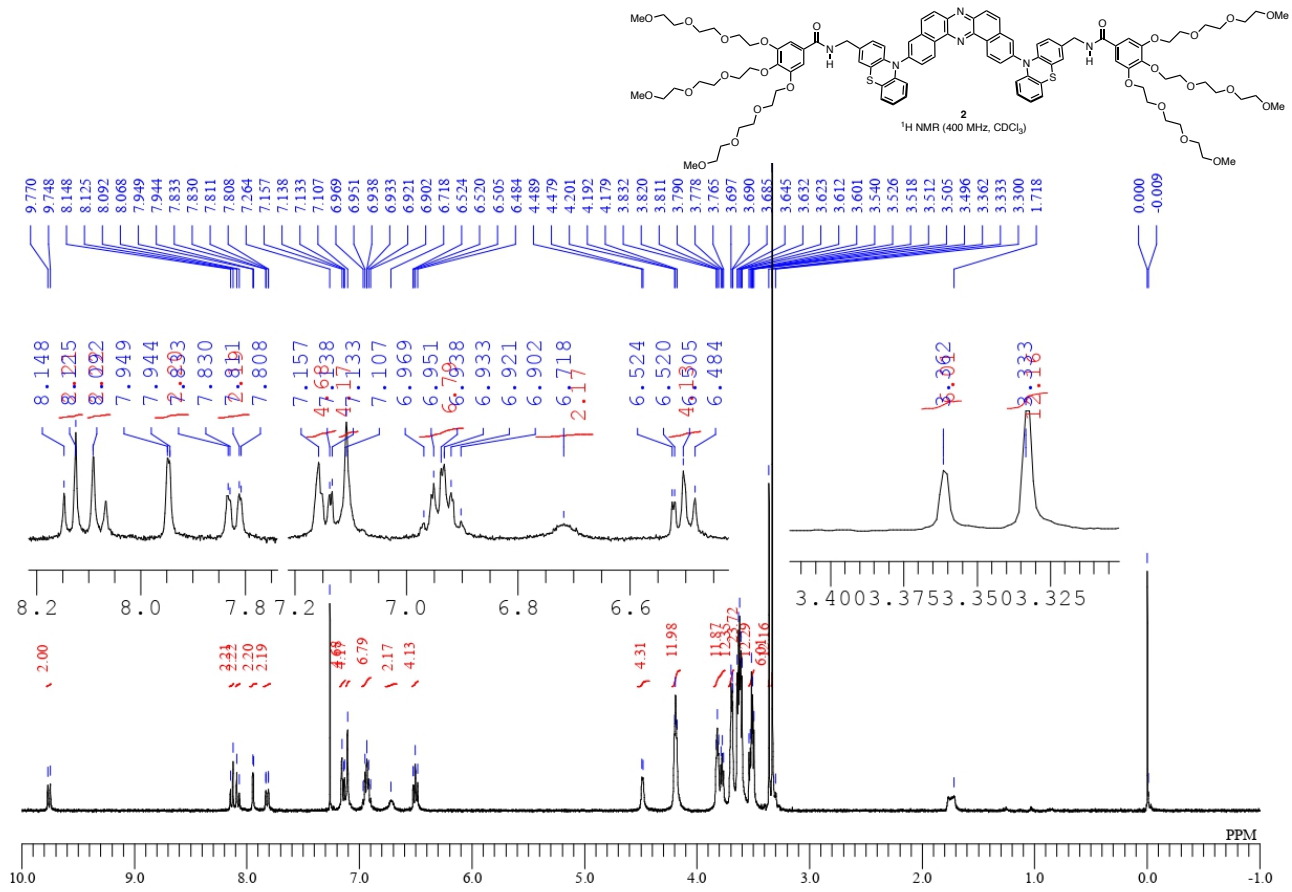
PPM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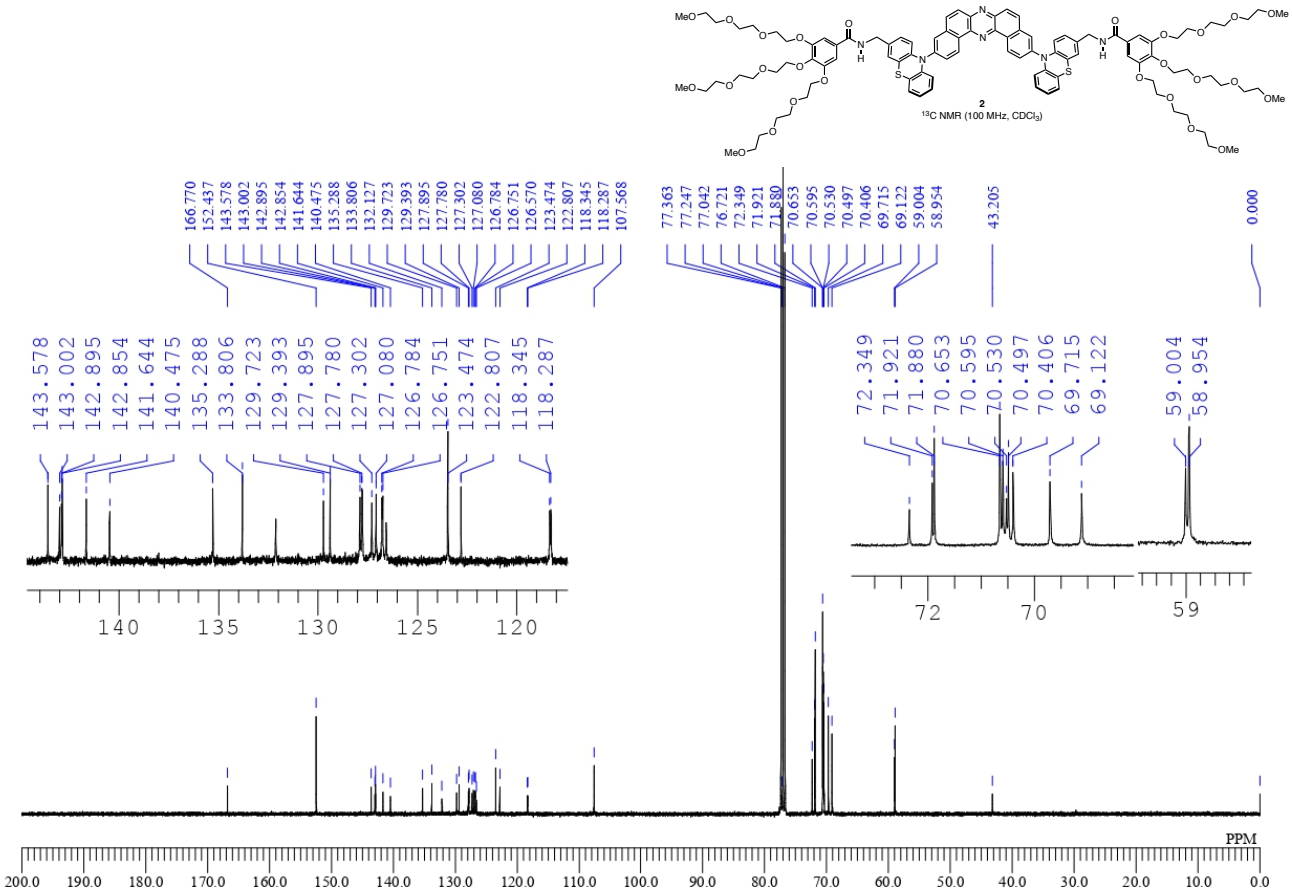
PPM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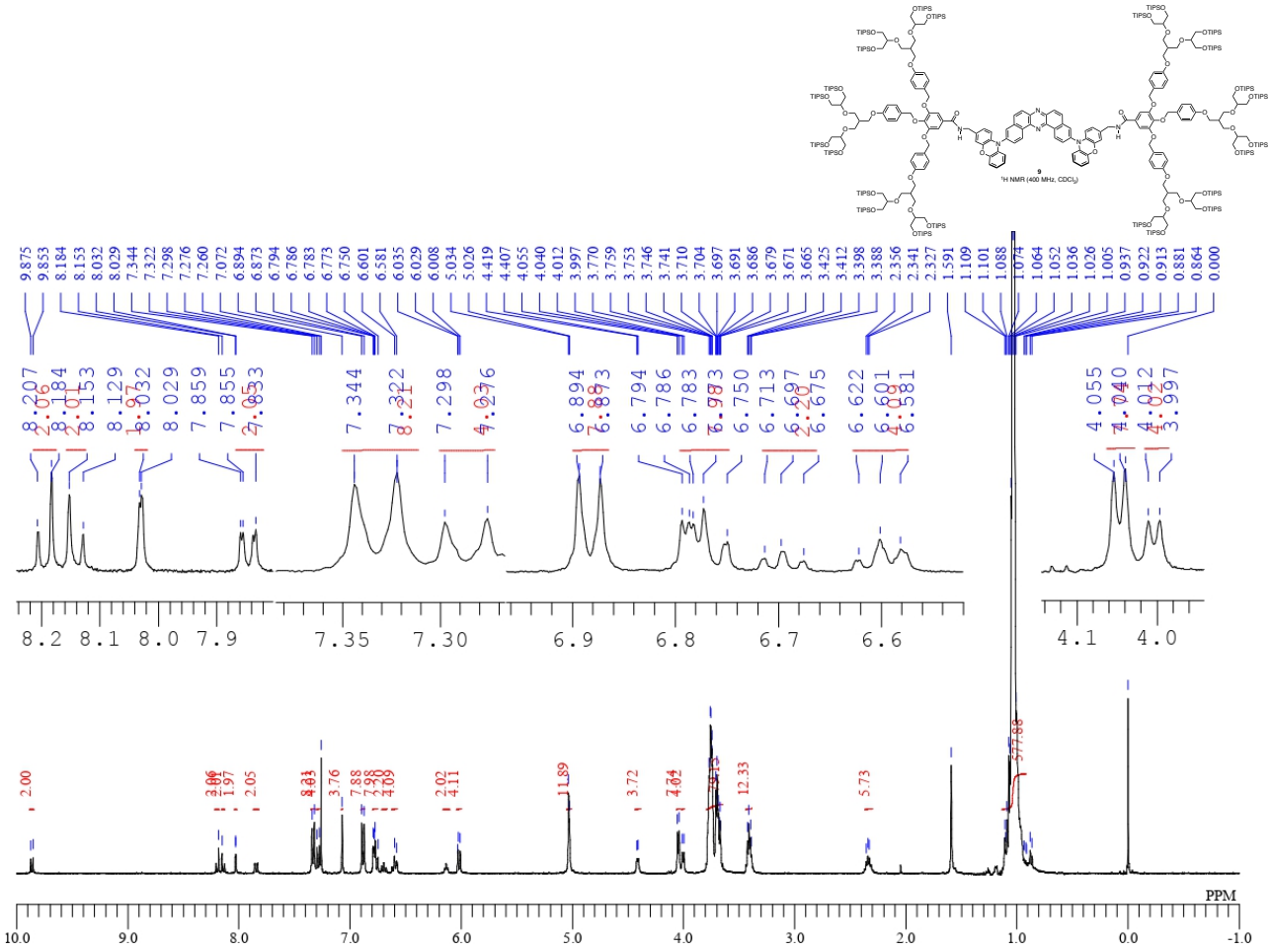
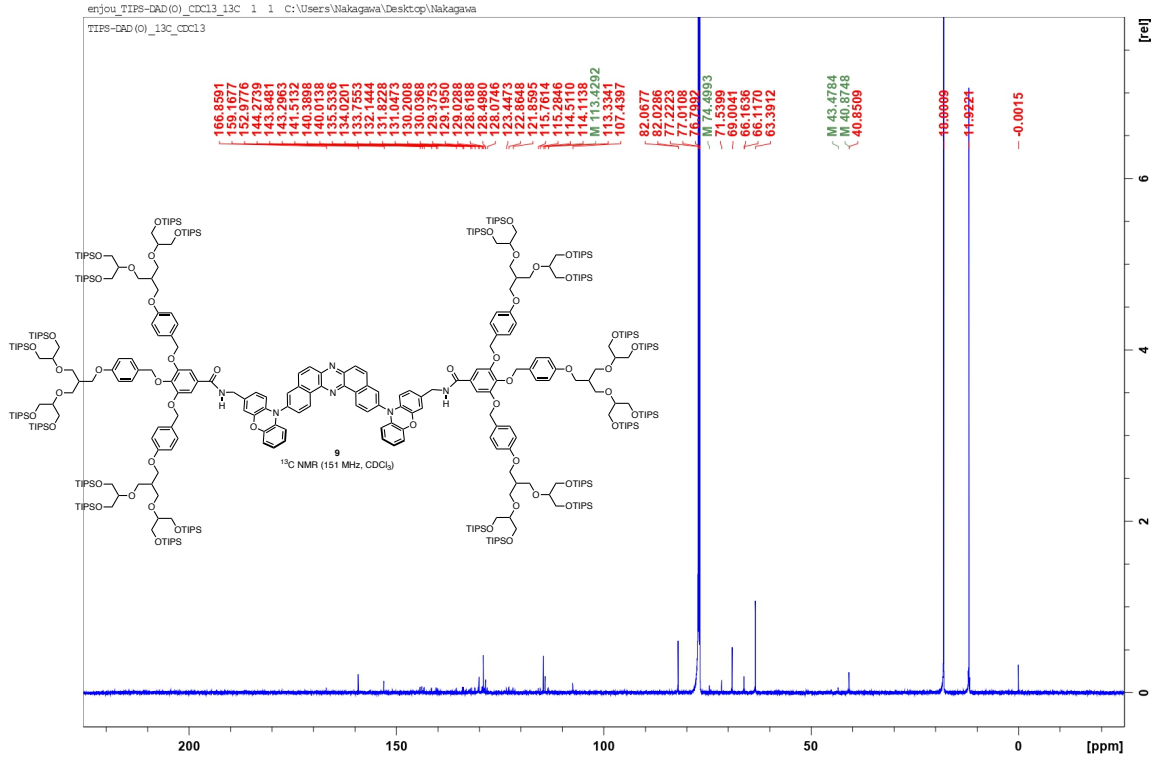
^{13}C NMR (100 MHz, CDCl$_3$)
PPM


9
^{1}H NMR (400 MHz, CDCl$_3$)
PPM


9
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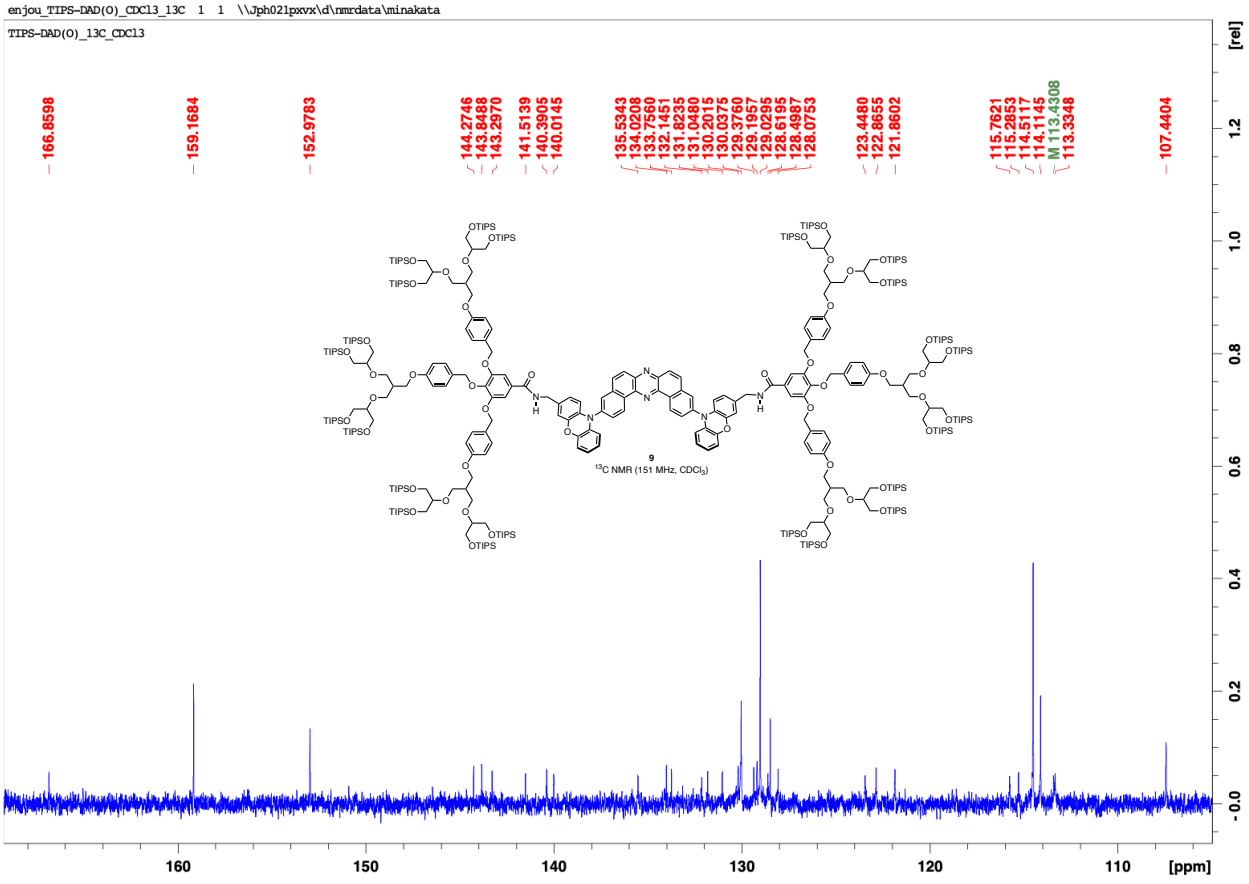
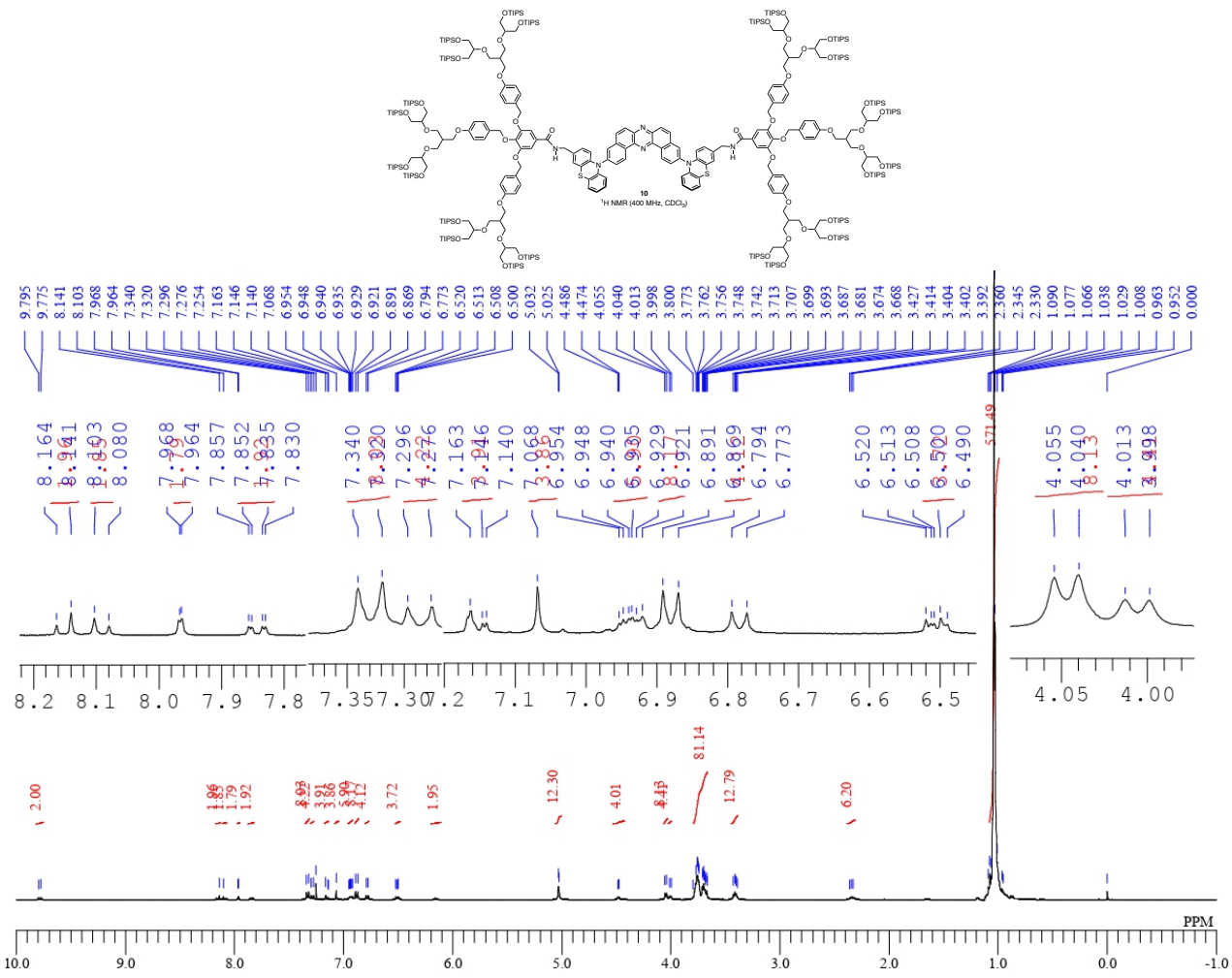
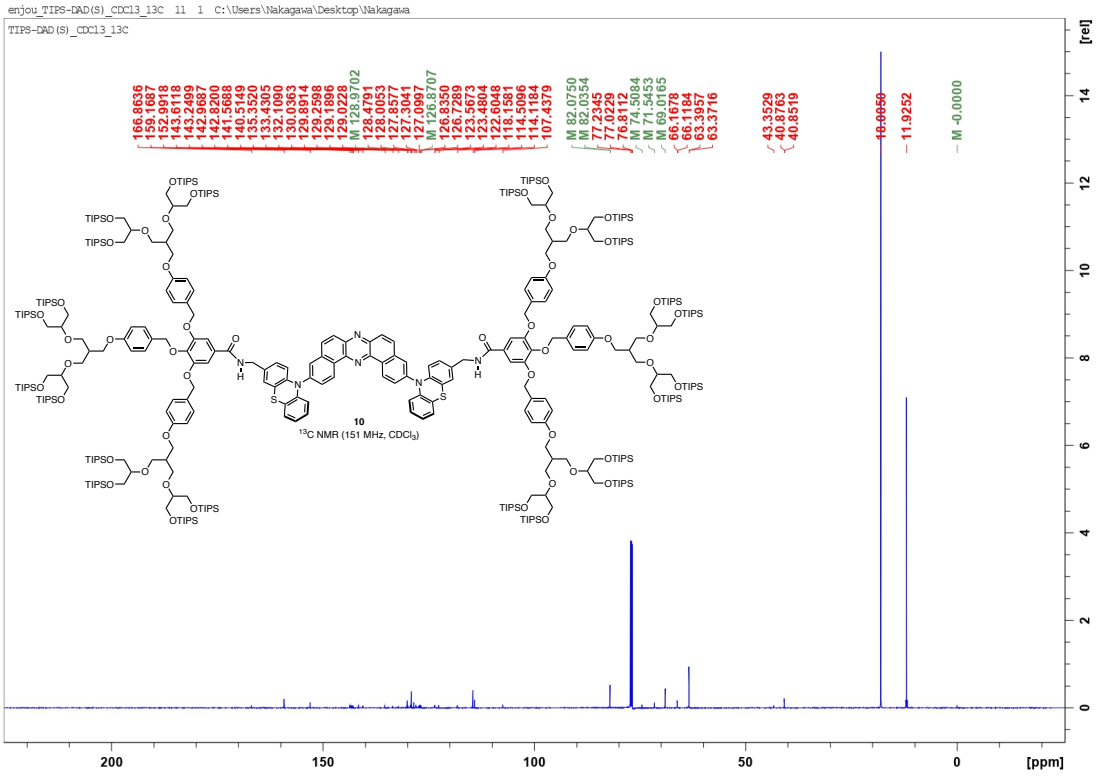
[ppm]
[rel]



9
^{13}C NMR (151 MHz, $CDCl_3$)

enlarged part of aromatic region of ^{13}C NMR of **9**


10
^{1}H NMR (400 MHz, CDCl$_3$)
PPM


10
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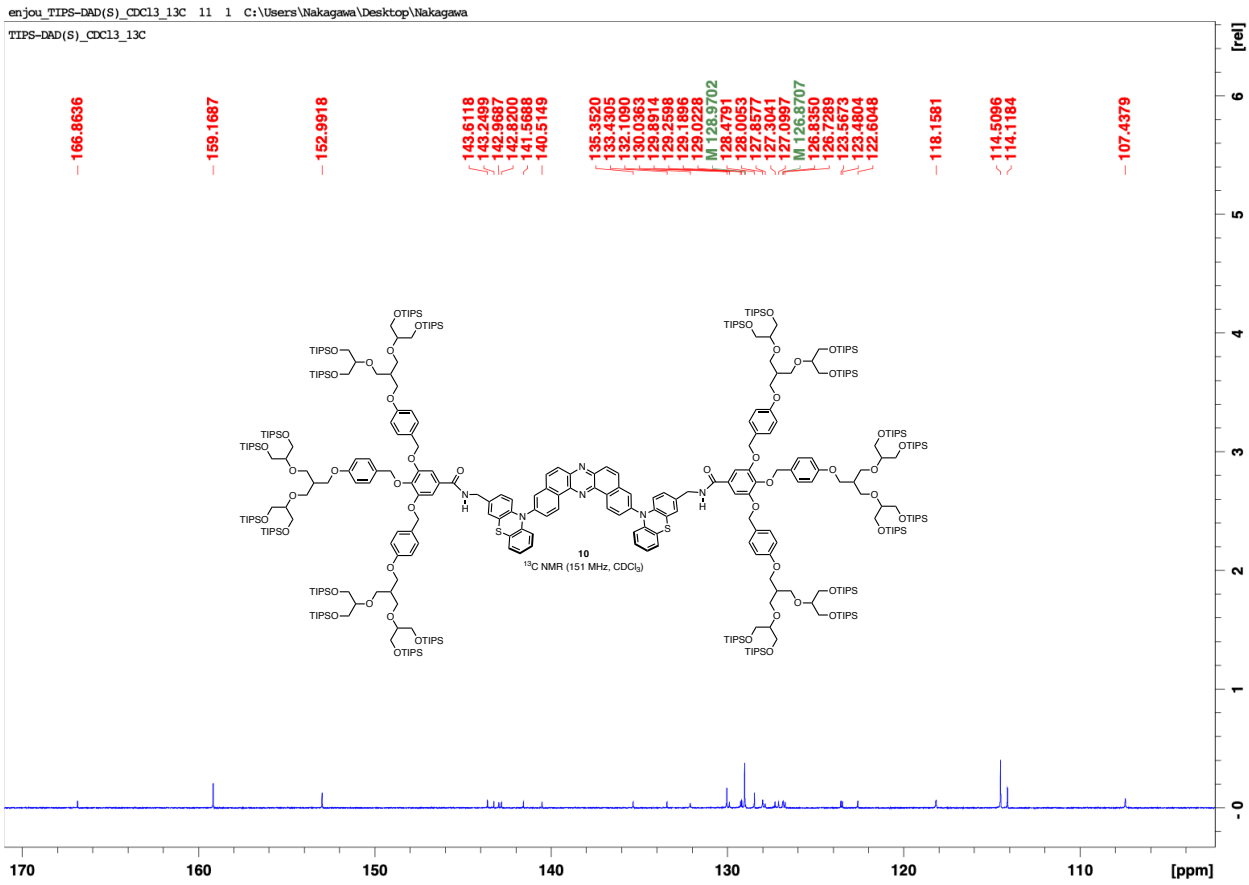
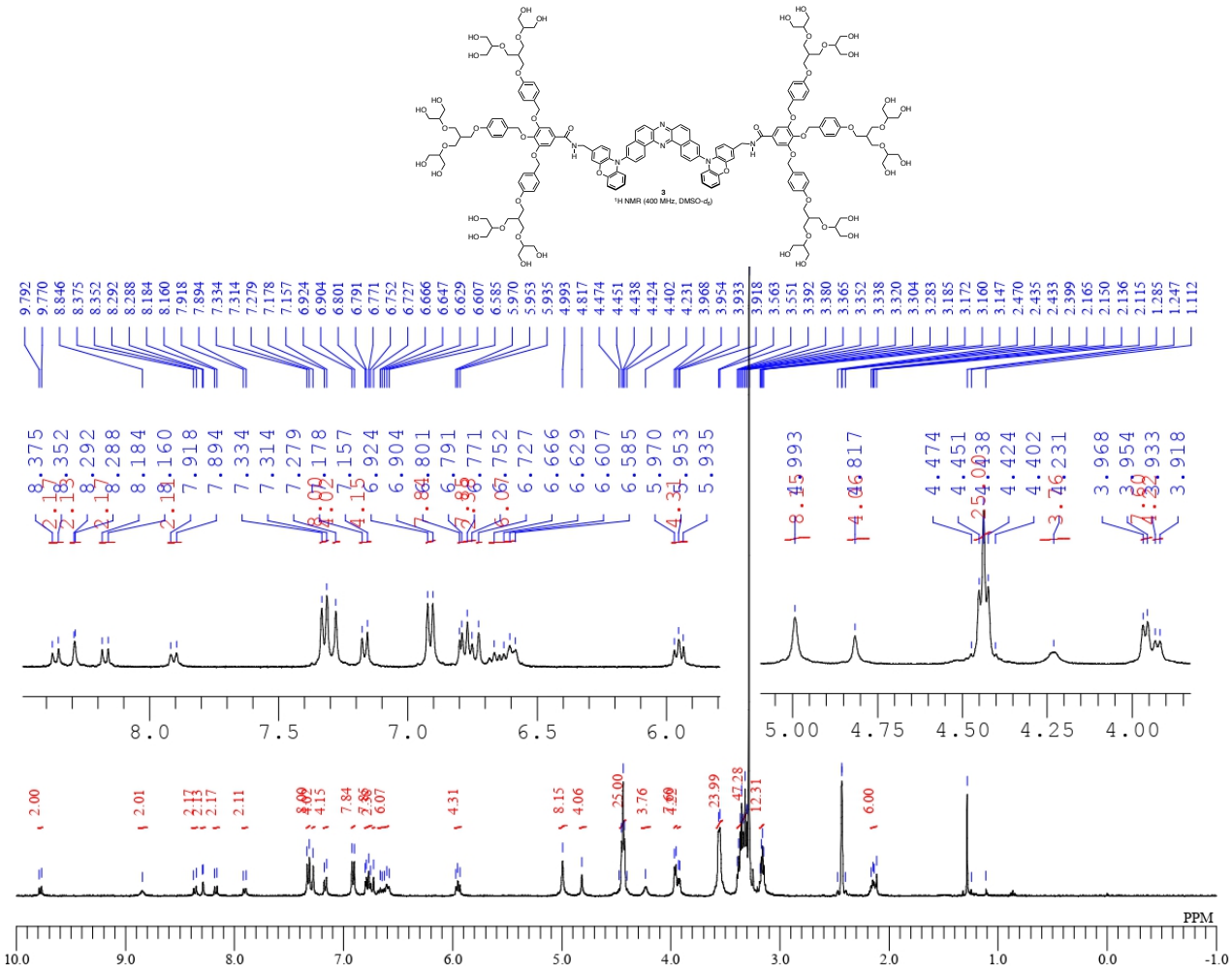
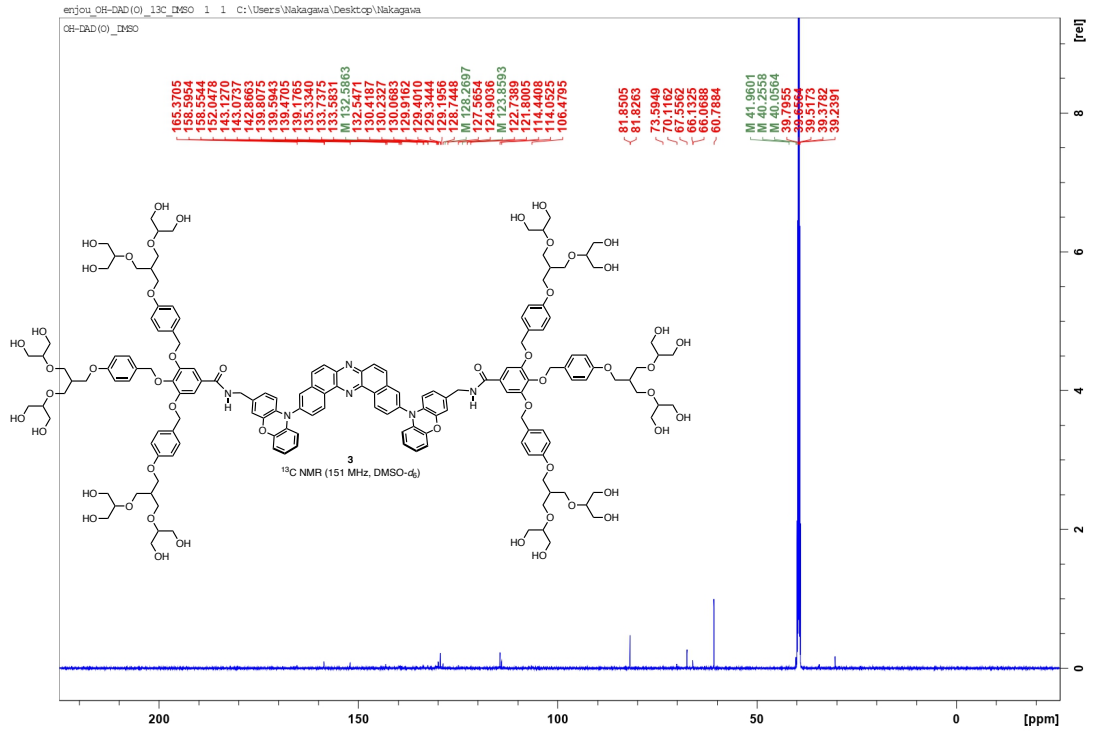


enlarged part of aromatic region of ^{13}C NMR of **10**


3
^{1}H NMR (400 MHz, DMSO-d_6)
PPM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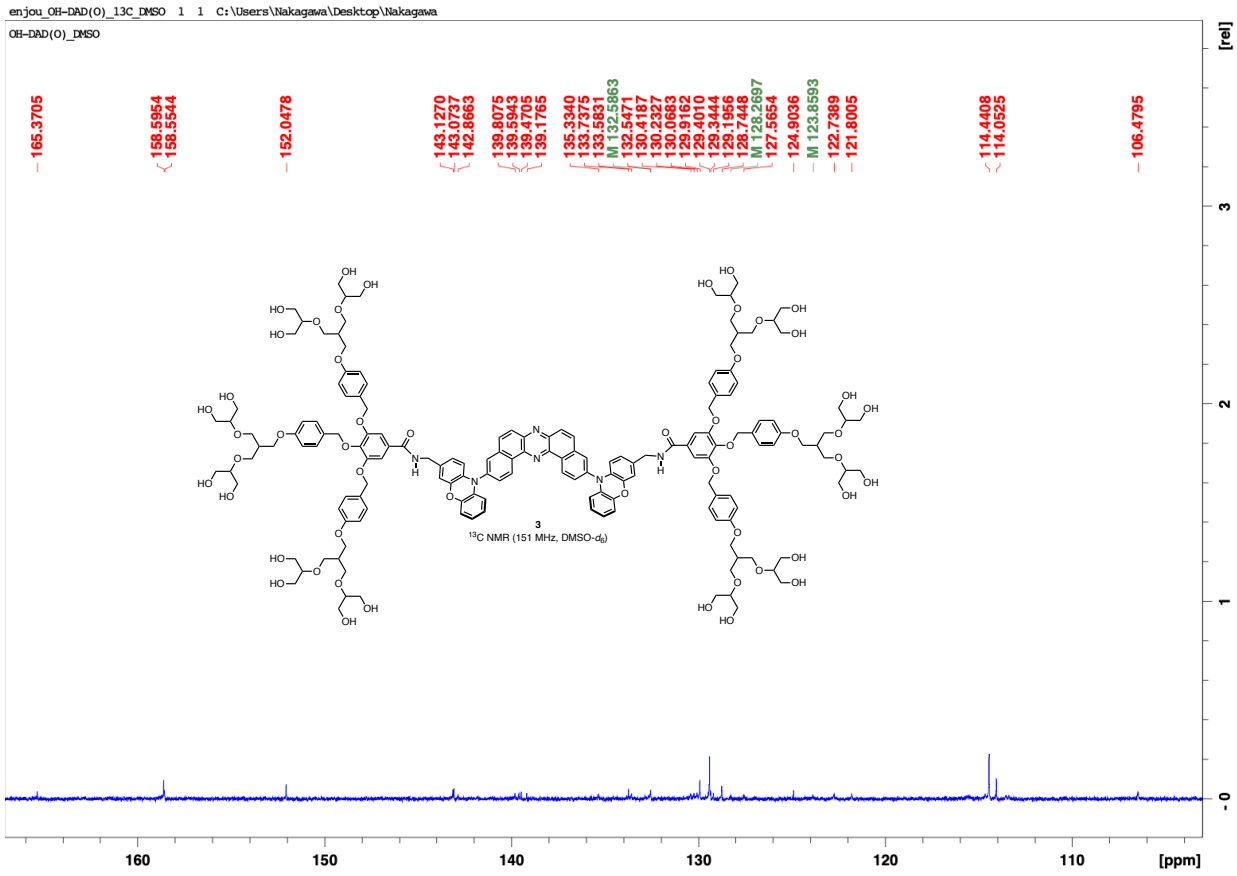
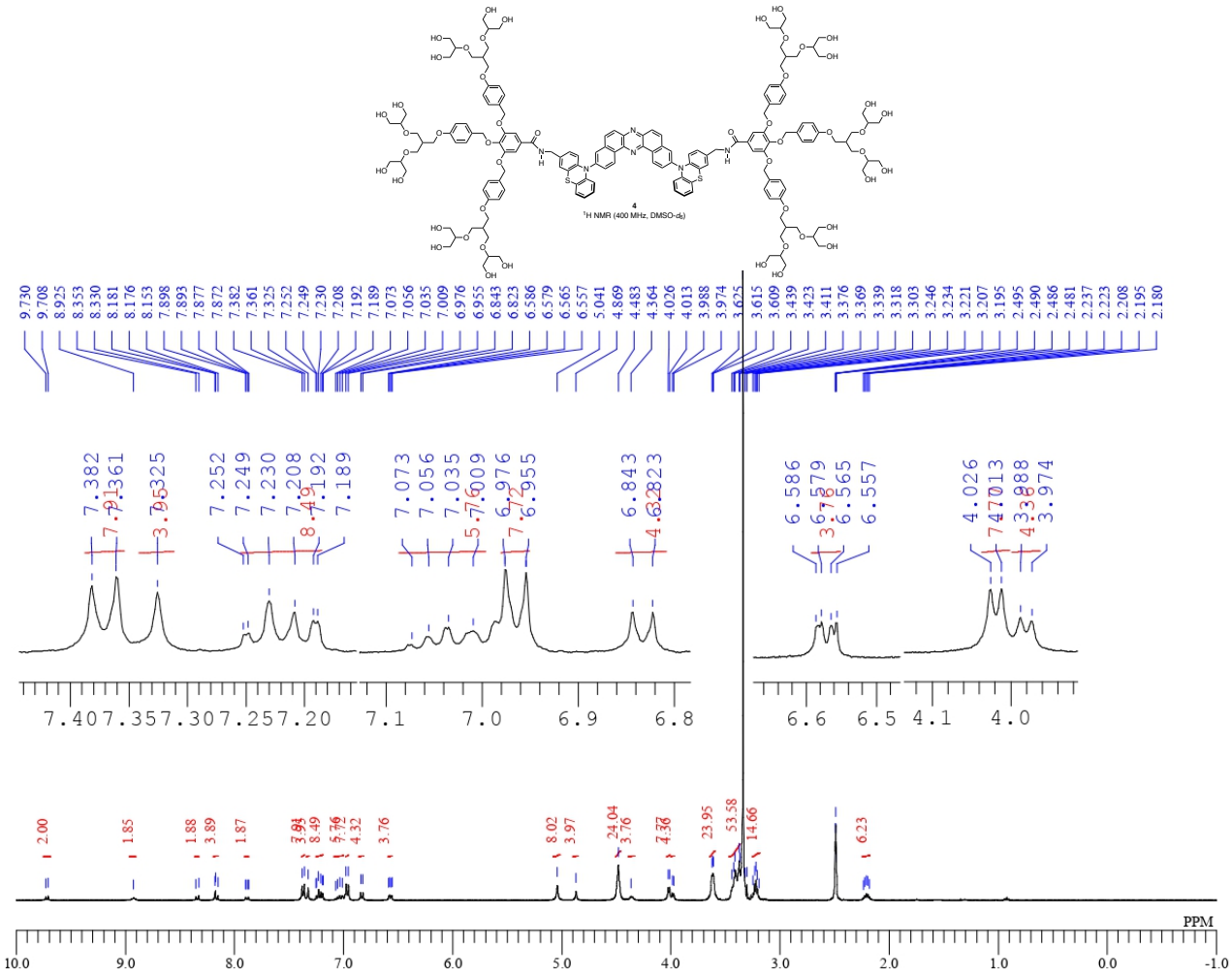
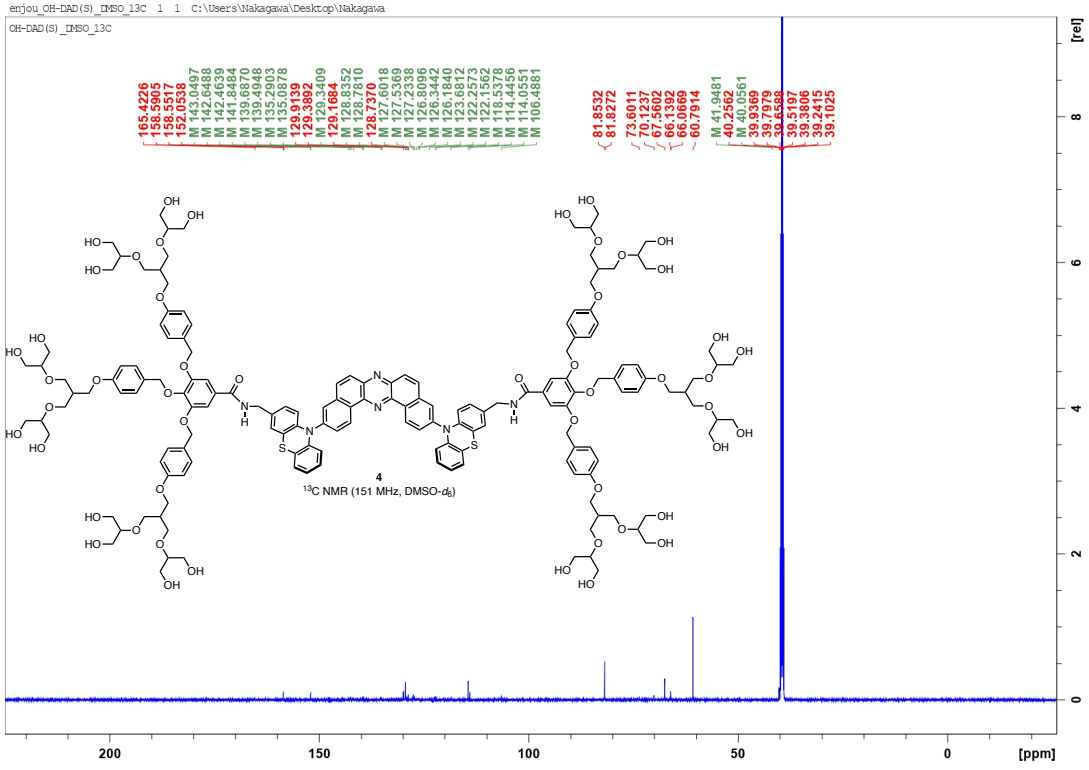
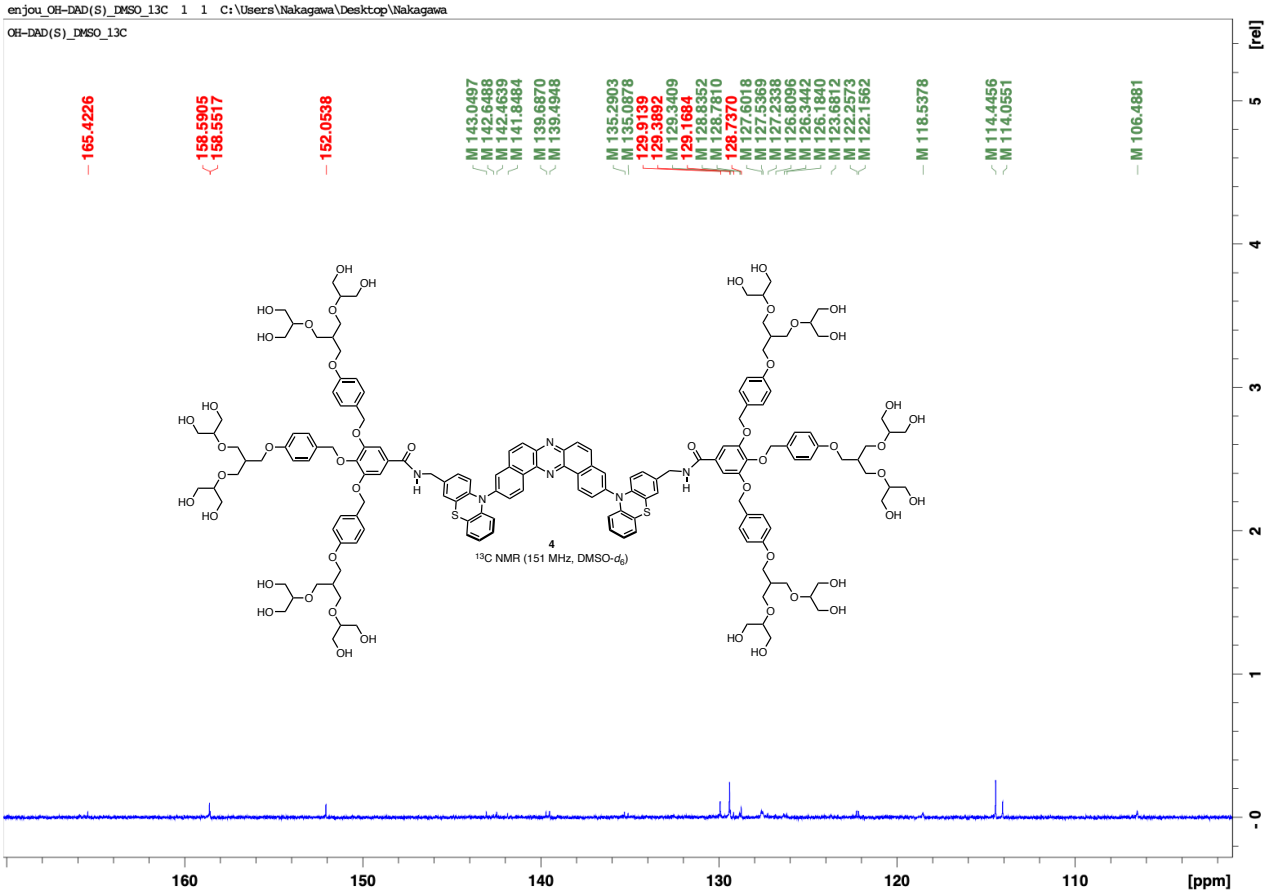
[ppm]
[rel]



enlarged part of aromatic region of ^{13}C NMR of **3**


4
^{1}H NMR (400 MHz, DMSO-d_6)
PPM


4
^{13}C NMR (151 MHz, DMSO-d_6)
[ppm]
[rel]



enlarged part of aromatic region of ^{13}C NMR of **4**

Appearance of Aqueous Solutions of 1–4

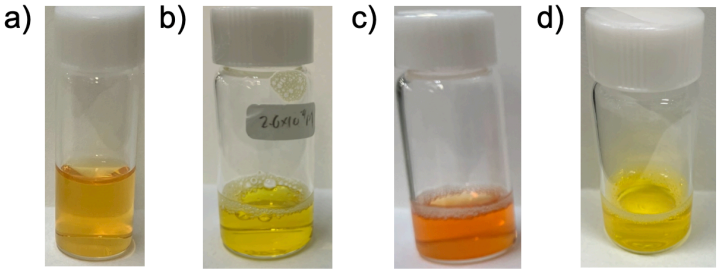


Fig. S1 Appearance of solutions of a) **1** ($c = 2.6 \times 10^{-4}$ M in THF/H_2O = 5/95), **2** ($c = 2.6 \times 10^{-4}$ M in THF/H_2O = 5/95), b) **3** ($c = 2.6 \times 10^{-4}$ M in H_2O), and c) **4** ($c = 2.6 \times 10^{-4}$ M in H_2O) after filtration.

Dynamic Light Scattering (DLS) and Electrophoretic Light Scattering (ELS) Experiments

Compound (1.04 μmol) was dissolved in deaerated THF (0.05 mL). To this solution, deaerated pure water (0.95 mL) was added, and the resulting mixture was sonicated over 3 h. This solution was filtered through a membrane filter (pore size: 50 μm). The filtrate was injected into a Zetasizer cell, and the Zeta potential was measured with a Zetasizer at 25 °C. DLS experiment was conducted with the same apparatus to acquire diffusion coefficient from the auto correlation function. The particle sizes were calculated from the Stokes-Einstein equation.

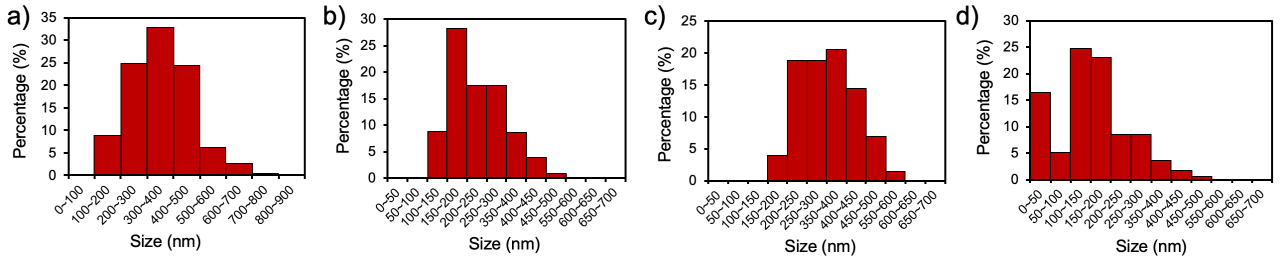


Fig. S2 Particle size distribution histograms of dynamic light scattering for a) **1** ($c = 2.6 \times 10^{-4}$ M in THF/H_2O = 5/95), b) **2** ($c = 2.6 \times 10^{-4}$ M in THF/H_2O = 5/95), c) **3** ($c = 2.6 \times 10^{-4}$ M in H_2O), and d) **4** ($c = 2.6 \times 10^{-4}$ M in H_2O).

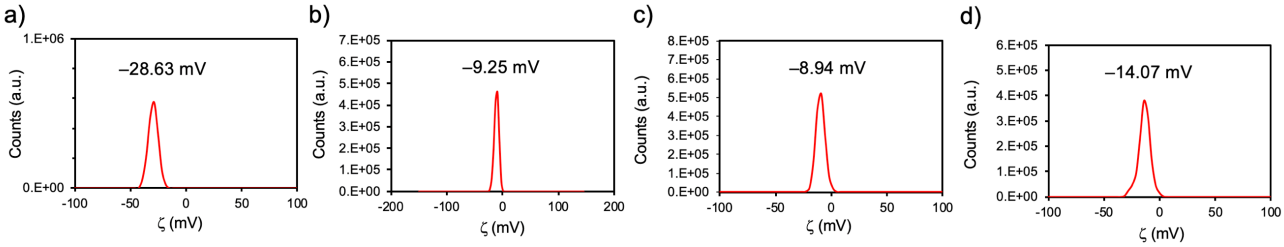


Fig. S3 Zeta potential of a) **1** ($c = 2.6 \times 10^{-4}$ M in THF/H_2O = 5/95), b) **2** ($c = 2.6 \times 10^{-4}$ M in THF/H_2O = 5/95), c) **3** ($c = 2.6 \times 10^{-4}$ M in H_2O), and d) **4** ($c = 2.6 \times 10^{-4}$ M in H_2O).

Transmission Electron Microscopy (TEM) Experiments

Each compound (1.04 μmol) was dissolved in deaerated THF (0.05 mL). To this solution, deaerated pure water (0.95 mL) was added, and the resulting mixture was sonicated over 3 h. This solution was filtered through a membrane filter (pore size: 50 μm). A 5 μL of the solution was dropped onto a carbon film grid (HRC-C10, Okenshoji Co., Ltd.) and left for 5 min. Eexcess solution was removed with a filter paper, and then an aqueous solution containing ammonium molybdate (0.5 wt%, 0.5 μL) was dropped for negative staining. The staining solution was left for 1 min before being removed with a filter paper. The grid substrate was observed with a TEM (Hitachi H-7650) operated at 100 kV.

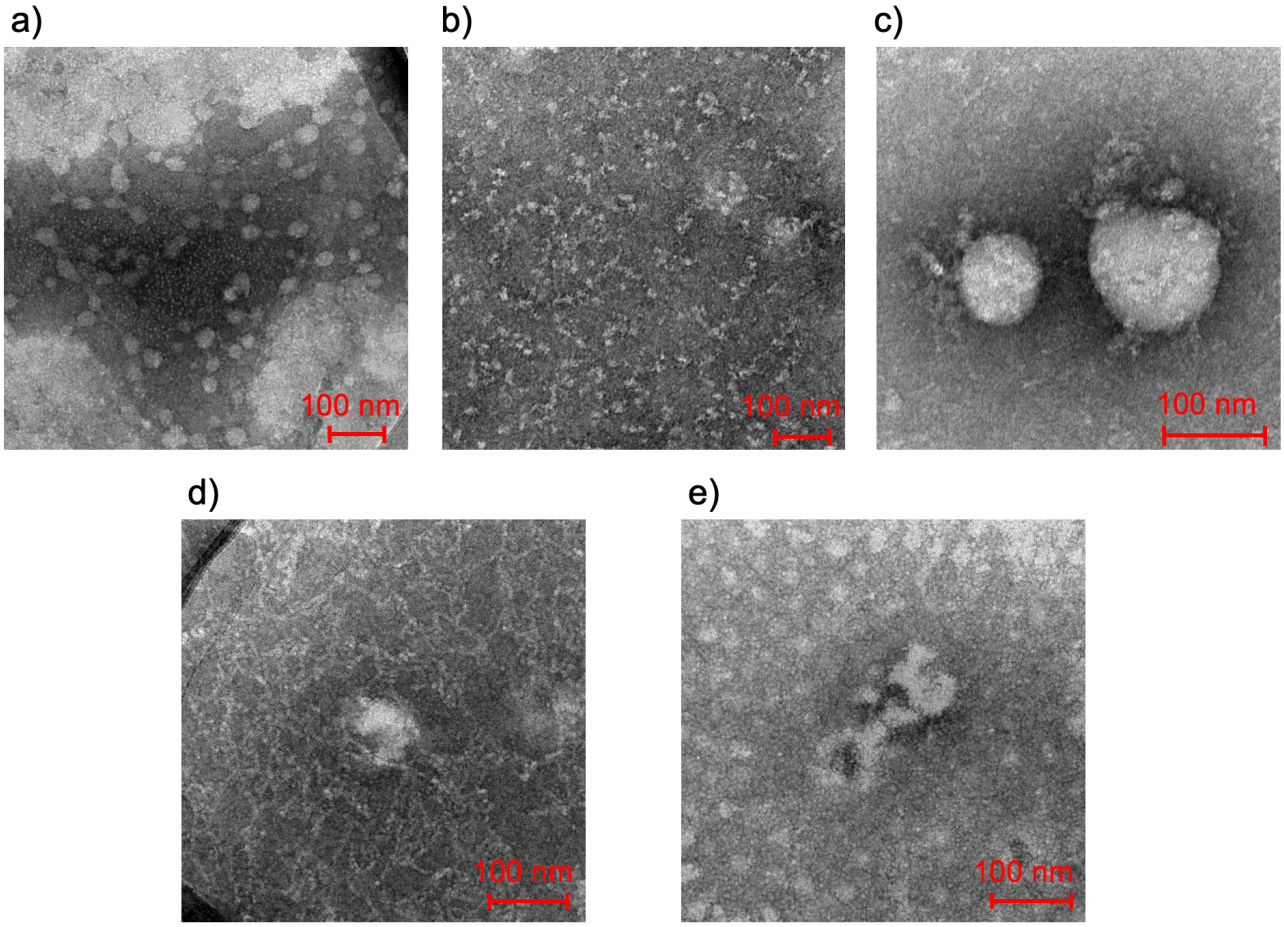


Fig. S4 TEM images of a) **1**, b) and c) **2**, d) **3**, and e) **4** on a carbon film grid. Compounds were negatively stained with ammonium molybdate.

Ultra Small and Small Angle X-ray Scattering (USAXS and SAXS) Measurements

The USAXS and SAXS profiles of **1**, **2**, **3**, and **4** were obtained in a 1.0-mm-thick sample cell sandwiched between poly(ether-ether-ketone) (0.025 mm-thick) films. We observed $q^{-2.4}$ in all samples in ultra-small angle region below q = 0.1 nm^{-1}. This is typical for mass fractal of highly branched objects with high surface-to-volume ratio of the very large structures above 100 nm with the DLS and TEM measurements.[S7] Furthermore, we focused on the nanometer-scale micelle structures formed by all samples in the region above q = 0.1 nm^{-1} (Fig. S5b): weak scattering due to weak micelle formation ability for **1** and **2**, but very distinct nanometer-scale structure origin for **3** and **4**. The radii of gyration, R_g, were derived using Guinier's formula: 10 nm for **1**, 3.5 nm for **2**, 5.0 nm for **3**, and 4.8 nm for **4**.

$$I(q) = I(0)\exp(-\frac{1}{3}R_g^2q^2)$$

We focused on micelles of **3** and **4**, which have strong micelle-forming ability. The micelles were assumed to be rod-shaped and each parameter was derived. In the lower concentration, the scattering from micelles becomes weaker.

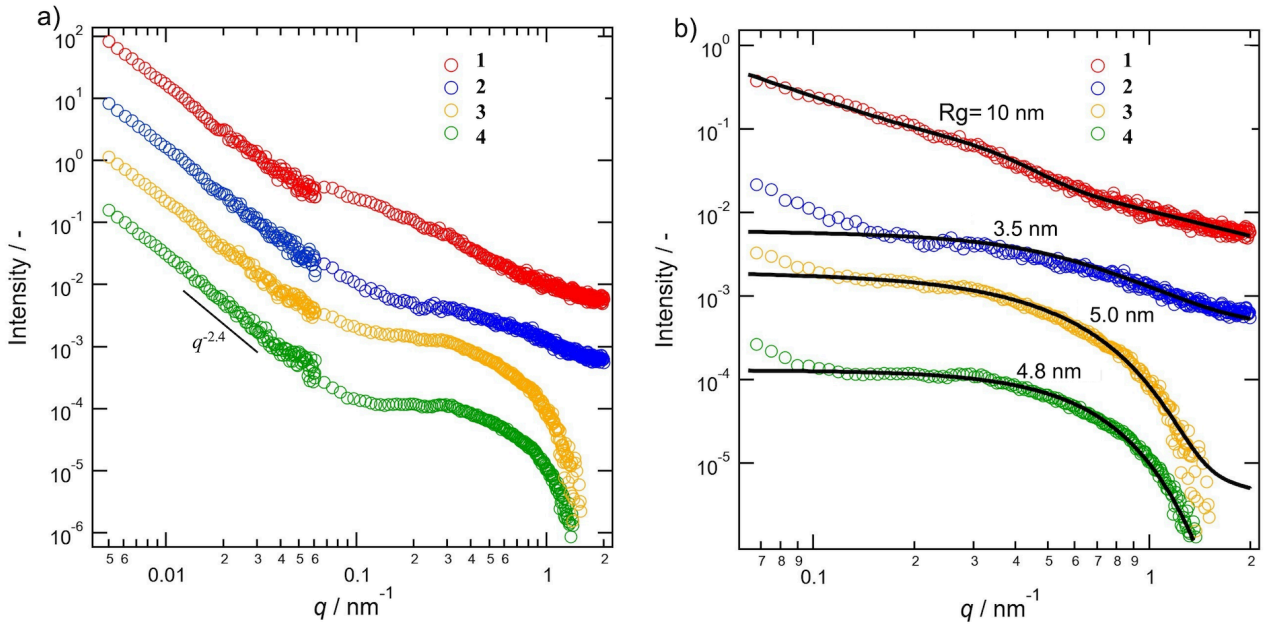


Fig. S5 a) Ultra-small and small angle X-ray scattering profiles for **1** (c = 2.6 × 10^{-4} M in THF/H_2O = 5/95), **2** (c = 2.6 × 10^{-4} M in THF/H_2O = 5/95), **3** (c = 5.0 × 10^{-4} M in H_2O), and **4** (c = 5.0 × 10^{-4} M in H_2O). b) Small angle X-ray scattering profiles for **1** (c = 2.6 × 10^{-4} M in THF/H_2O = 5/95), **2** (c = 2.6 × 10^{-4} M in THF/H_2O = 5/95), **3** (c = 5.0 × 10^{-4} M in H_2O), and **4** (c = 5.0 × 10^{-4} M in H_2O) and each fitting curve from Guinier formula.

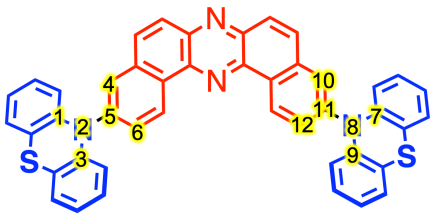
Theoretical Calculations (MD simulations)

All-atom MD simulations were performed by using MD program GROMACS 2016.3. In the initial structure, 12 molecules for each of axial-axial and equatorial-equatorial conformers of **2** were randomly placed in the MD cell and the rest of the space was filled with water molecules. The number of water molecules were 14491. The partial atomic charges of **2** were calculated using the restrained electrostatic potential (RESP)[S8] methodology based on DFT calculations (B3LYP/6-31G(d,p)) using the GAUSSIAN 16 revision C01 program package. The generalized Amber force field[S9] parameters were basically used for compound **2** and TIP4P-EW model was set for water molecules. To realize the axial and equatorial conformers, the force field parameters related to the proper dihedral angle interactions between atoms including the linkage of D and A (Fig. S6) were modified. The proper dihedral angle potential function is expressed as follows:

$$V_d(\phi_{ijkl}) = k_\phi(1 + \cos(n\phi - \phi_s))$$
$$(n = 2)$$

The values of k_ϕ set for the axial and equatorial conformers were 6.16788 and 125.520, respectively. Also, the values of ϕ_s set for the axial and equatorial conformers were 180° and 0°, respectively.

Before performing the equilibration run, the pre-equilibration run was carried out for 5 ns after the steepest descent energy minimization. The temperature and pressure were maintained at 300 K and 1 bar using the Berendsen thermostat and barostat[S10] with relaxation times of 0.2 ps and 2.0 ps, respectively. The equilibration run was performed for 200 ns at 300 K and 1 bar using the Nosé-Hoover thermostat[S11] and Parrinello-Rahman barostat[S12] with relaxation times of 1.0 and 5.0 ps, respectively. The time step was set to 2 fs since all bonds connected to hydrogen atoms were constrained with LINCS[S13] algorithm. The long-range Coulomb interactions were calculated with the smooth particle mesh Ewald[S14] method with a grid spacing of 0.30 nm. The real space cut-off for both the Coulomb and van der Waals interactions was 1.2 nm.



1-2-5-4	7-8-11-10
1-2-5-6	7-8-11-12
3-2-5-4	9-8-11-10
3-2-5-6	9-8-11-12

Fig. S6 Chemical structure of the core center part of **2** and eight combinations of proper dihedral angles consisting of four atoms including the linkage of D and A.

Plausible Explanation for the Formation of Large Hierarchical Assemblies of the Compounds: The molecules were simply designed with the combination of a twisted donor-acceptor-donor hydrophobic π-conjugated core and amphiphilic side chains at both ends, and a specific assembly structure was not intended. Therefore, the molecules did not form micelles and became a subunit consisting with spherical amorphous assembly with no anisotropy. In fact, MD simulations (Figure 3b) of the subunit suggests that the orientation of the molecules is almost random. Furthermore, the hydrophobic domains consisting of π-conjugated cores that happen to locate at the surface of the subunit cause further hydrophobic aggregation with the hydrophobic sites of other subunits, resulting in an assembly with a size of several hundred nm.

Excitation Spectra of 4 in water

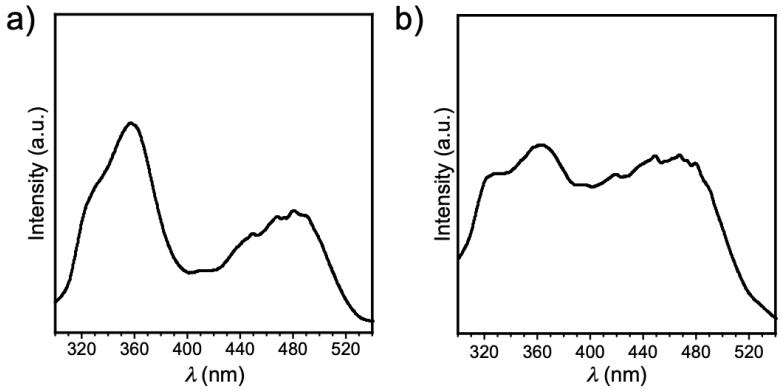


Fig. S7 Excitation spectra of **4** monitored at a) 553 nm and b) 647 nm in water ($c = 10^{-4}$ M, $\lambda_{ex} = 365$ nm).

PL Spectra of 3 and 4 in Polar Solvent

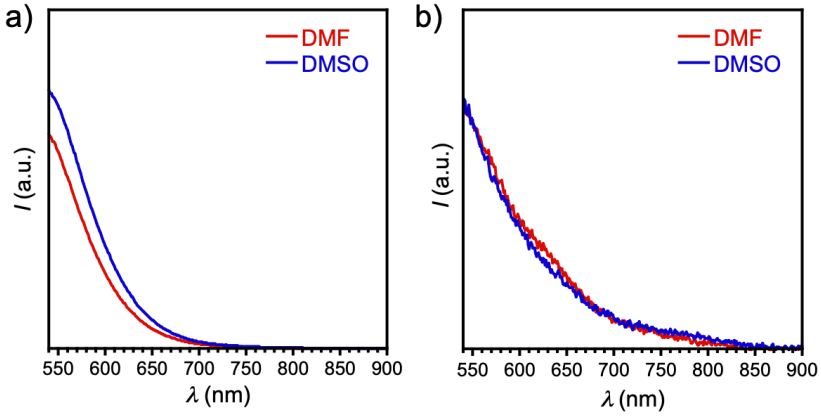


Fig. S8 PL spectra of a) **3** and b) **4** in DMF and DMSO ($c = 10^{-4}$ M, $\lambda_{ex} = 365$ nm). Under cut-off filter ($\lambda_{me} = 500$ nm) is applied to exclude the excitation light spectrum.

PLQY and Relative PL Intensity of 1@PVA and 2@PVA Against Humidity-Exposure Time

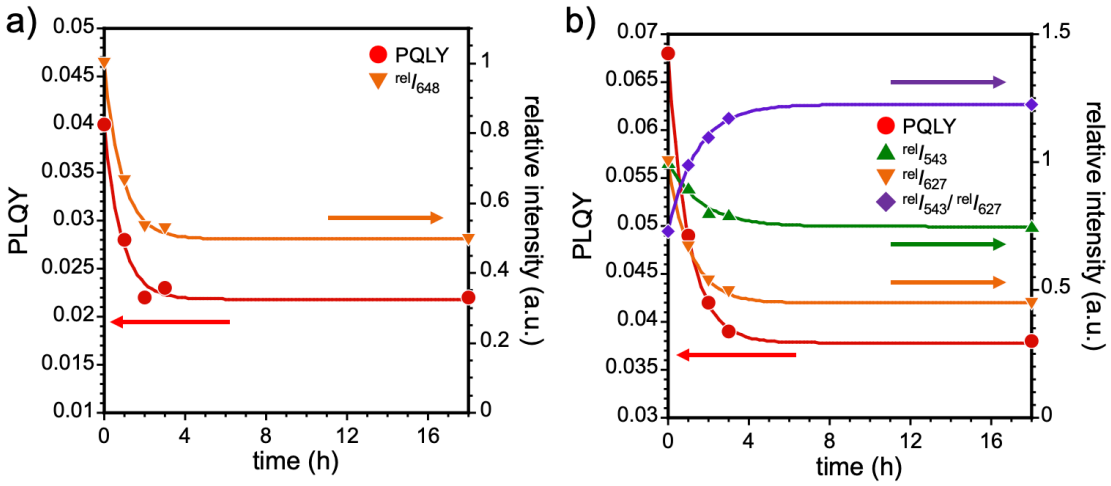


Fig. S9 Time-course profile of PLQY and PL relative intensity of a) **1**@PVA and b) **2**@PVA.

Humidity-Variable IR Spectroscopy.

Transmittance measurements were performed with a synchrotron FTIR at an infrared beamline BL43IR, SPring-8 synchrotron facility (Hyogo, Japan). At the beamline, an FTIR microspectrometer (BRUKER model HYPERION infrared microscope with model VERTEX70 FTIR spectrometer) was used with the infrared synchrotron radiation. The transmittance spectra in the range from 800 to 4000 cm^{-1} were collected at 25 °C with a resolution of 3 cm^{-1}. A few mg of powder D–A–D compound **2** in PVA (saponification degree 78–82 mol%, average molecular weight 2000, 1 wt%) and PVA was put on a BaF_2 substrate and inserted into the humidity control cell. The cell has a BaF_2 window to pass infrared light. The atmosphere in the cell was controlled by a mixing device (RIGAKU model HUM-1E), which mixes N_2 gas (99.99%, generated by a KOFLOC model MNT- 0.8SI nitrogen gas generator) and water vapor at the specified ratio. The water used in the mixing device was purified through a Millipore model Elix advantage-3 water purifier. The humidity in the cell was monitored by the humidity sensor (Sensirion model HYT271) that is put near the sample.

*Procedure for preparation of **2**@PVA*: PVA (99.6 mg) was dissolved in deaerated pure water (1.9 mL), and the solution was further dearerated by passing N_2 gas through the aqueous solution. To compound **2** (0.998 mg), deaerated THF (0.1 mL) was added, and the compound was dissolved. The THF solution was injected into PVA aqueous solution, and the resulting solution was sonicated over 3 h, which was then filtered through a membrane filter (pore size: 50 μm). A quartz substrate (20 mm × 20 mm) was washed with anhydrous acetone, and cleaned under UV/O_3 over 4 min. The filtered solution was dropped onto the substrate, and the solution was dried under ambient conditions to make film.

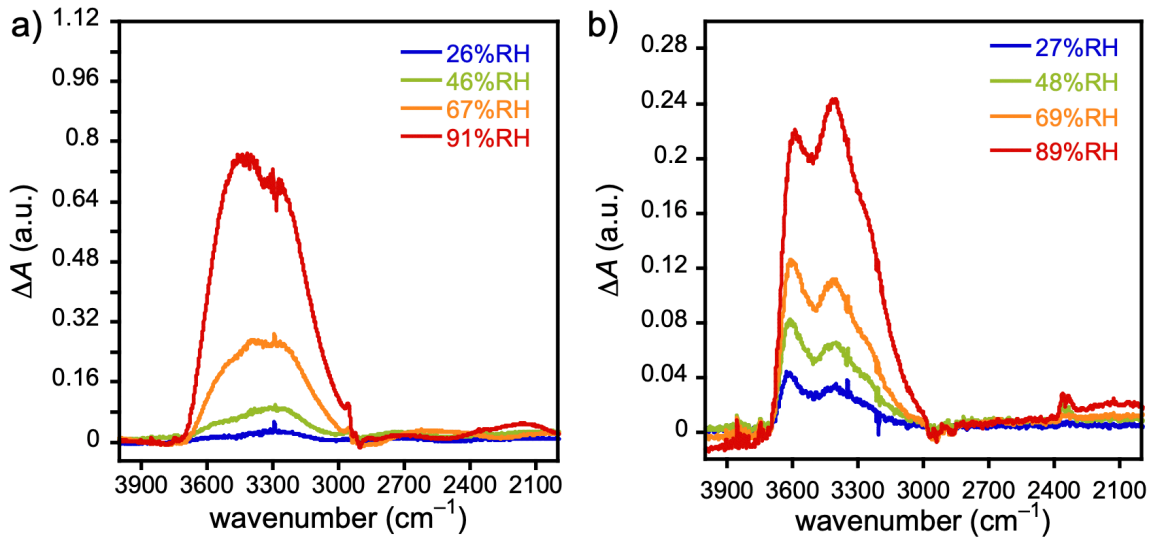


Fig. S10 Humidity-variable difference IR spectra of a) **2** in PVA (1 wt%) and b) PVA. The IR spectra were obtained by subtracting the IR spectrum at a 2% RH from the IR spectrum at each RH.

Thermogravimetric Analysis (TGA)

The TGA profiles of **1** were obtained using a Pt pan under the air or the N_2 gas flow (200 mL/min), starting from 40 °C to 1000 °C at the ramp rate of 10 °C/min.

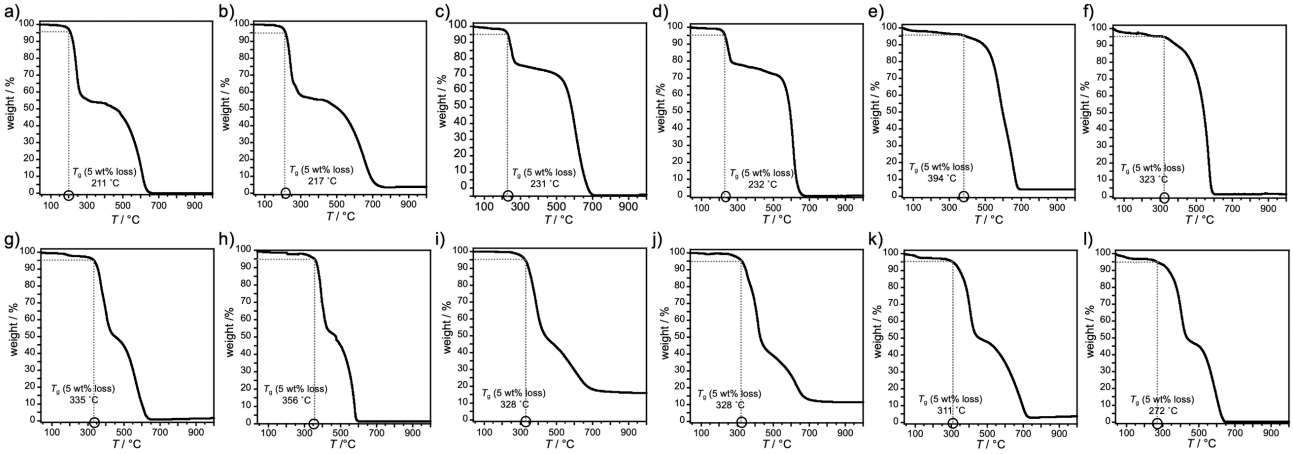


Figure S11. TGA profiles of a) **S3**, b) **S5**, c) **S7**, d) **S8**, e) **5**, f) **6**, g) **1**, h) **2**, i) **9**, j) **10**, k) **3**, and l) **4** under air.

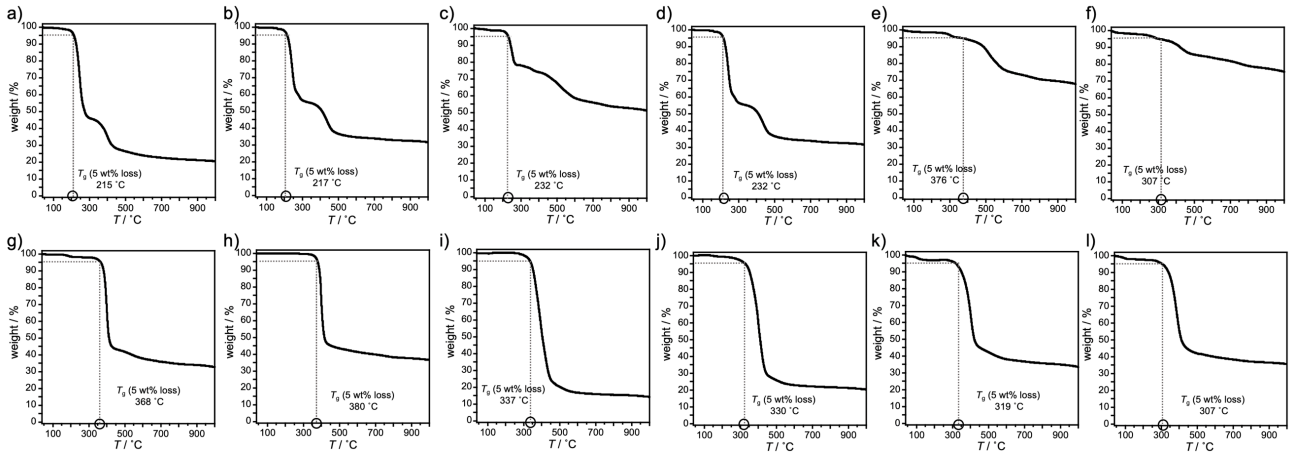


Figure S12. TGA profiles of a) **S3**, b) **S5**, c) **S7**, d) **S8**, e) **5**, f) **6**, g) **1**, h) **2**, i) **9**, j) **10**, k) **3**, and l) **4** under N_2 flow.

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