Supplementary Material

Selective Complexation of Di-*n*-hexylammonium Salts by Tailed Porphyrin Host

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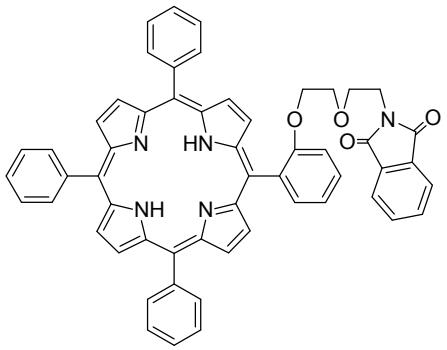
Experimental

Melting points are uncorrected. All reactions were performed under an atmosphere of dry nitrogen. The ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz spectrometers in the indicated solvents. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards. Elemental analysis was carried out at the analytical center. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification.

Determination of binding constants. Di-*n*-hexylammonium salts were added into the solution of tailed porphyrin. ^{1}H NMR titrations were carried out at the concentrations of 6.4 mM in $CDCl_3$ at 25°C. UV-Vis titrations were carried out at the concentration of 1×10^{-6} M in CH_2Cl_2 at 25°C. The 1:1 binding constants were calculated by using equation $K_{assoc} = \frac{[host]c}{[host]uc[guest]uc}$, in which the concentration of complexed and uncomplexed host was defined by Δ value of chemical shift or absorbance.[1,2]

Compound **OP-OH** and compound **3** was prepared according to the reference.[3,4]

General procedure for the synthesis of PN. To the solution of **OP-OH** in DMF was added compound **3** (1.5 equiv.), potassium carbonate (10 equiv.). The reaction mixture was stirred at 120 °C for 2h. After removing DMF in vacuo, dichloromethane was added to the residue and washed with water, dried over anhydrous Na_2SO_4. The solvent was evaporated, and the crude product was purified by column chromatography (DCM/MeOH, 100:1) to give the **PN** as a purple solid.



PN1

PN1: ^{1}H NMR ($CDCl_3$): δ -2.86 (s, 2H), 2.26 (t, 2H), 2.58 (t, 2H), 3.11 (t, 2H), 4.02 (t, 2H), 7.13 (t-d, 2H), 7.36 (m, 4H), 7.71-7.77 (m, 10H), 7.94 (d-d, 1H), 8.11 (d, 1H), 8.23 (d, 2H), 8.26 (m, 1H), 8.31 (m, 2H), 8.79-8.83 (m, 8H).

PN2: ^{1}H NMR ($CDCl_3$): δ -2.78 (s, 2H), 2.11 (t, 2H), 2.27 (t, 2H), 2.66 (t, 2H), 2.95 (t, 2H), 3.03 (t, 2H), 3.97 (t, 2H), 7.33 (d, 1H), 7.36 (t, 1H), 7.52 (m, 2H), 7.59 (m, 2H), 7.71-7.76 (m, 10H), 8.02 (d-d, 1H), 8.19 (m, 4H), 8.24 (d, 2H), 8.78-8.84 (m, 8H).

PN3: ^{1}H NMR ($CDCl_3$): δ -2.77 (s, 2H), 2.17 (t, 2H), 2.30 (t, 2H), 2.45 (t, 2H), 2.72 (t, 2H), 2.99 (t,

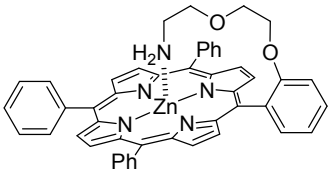
2H), 3.18 (t, 2H), 3.52 (t, 2H), 4.02 (t, 2H), 7.36 (m, 2H), 7.44 (m, 2H), 7.59 (m, 2H), 7.74-7.77 (m, 10H), 8.03 (d-d, 1H), 8.19 (d, 2H), 8.22 (d-d, 4H), 8.81-8.83 (m, 8H).

General procedure for the synthesis of OP. To the solution of **PN** in ethanol was added hydrazine hydrate (50 equiv.). The reaction mixture was stirred under reflux for 30 mins. After removing solvents by evaporation, dichloromethane was added to the residue and washed with diluted HCl, saturated $NaHCO_3$, brine, then dried over anhydrous $MgSO_4$. The solvent was evaporated to give the crude free base which was used without further purification. To the solution of free base in MeOH and $CHCl_3$ (v/v, 1:1) was added zinc acetate dihydrate (10 euqiv.). The reaction mixture was stirred at room temperature for 2h. After removing solvents by evaporation, the crude product was purified by column chromatography (CH_2Cl_2/MeOH, 20:1) to give the **OP** as a purple solid.

Freebase1: ^{1}H NMR ($CDCl_3$): δ -2.89 (s, 2H), 1.37 (t, 2H), 2.08 (t, 2H), 2.68 (t, 2H), 3.67 (t, 2H), 7.03 (m, 1H), 7.22 (m, 1H), 7.51 (m, 1H), 7.62 (m, 9H), 7.88 (m, 1H), 8.13 (m, 6H), 8.77-8.82 (m, 8H).

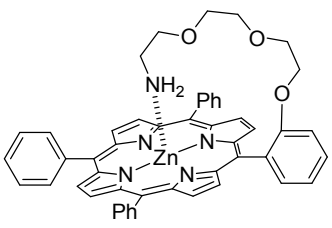
Freebase2: ^{1}H NMR ($CDCl_3$): δ -2.97 (s, 2H), 2.61 (t, 2H), 3.27 (t, 2H), 3.43 (t, 2H), 3.53 (t, 2H), 3.72 (t, 2H), 4.11 (t, 2H), 7.03 (m, 1H), 7.14 (m, 1H), 7.43 (m, 1H), 7.55 (m, 9H), 7.78 (m, 1H), 8.02 (m, 6H), 8.63-8.68 (m, 8H).

Freebase3: ^{1}H NMR ($CDCl_3$): δ -2.82 (s, 2H), 2.81 (t, 2H), 3.44 (t, 2H), 3.52 (t, 2H), 3.57 (t, 2H), 3.65 (t, 2H), 3.72 (t, 2H), 3.91 (t, 2H), 4.31 (t, 2H), 7.03 (m, 1H), 7.24 (m, 1H), 7.52 (m, 1H), 7.60 (m, 9H), 7.87 (m, 1H), 8.12 (m, 6H), 8.61-8.65 (m, 8H).



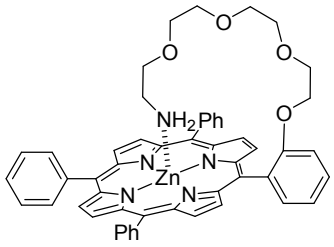
OP1

M.p. > 250 °C. ^{1}H NMR ($CDCl_3$): δ -4.13 (s, 2H), -1.60 (t, 2H), 0.56 (t, 2H), 2.48 (t, 2H), 3.61 (t, 2H), 7.14 (d-d, 1H), 7.60 (t-d, 1H), 7.72-7.84 (m, 10H), 8.25 (d-d, 2H), 8.37 (m, 2H), 8.43 (m, 2H), 8.65 (d-d, 1H), 8.96-8.99 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 35.8, 66.9, 68.3, 70.7, 115.5, 115.8, 120.6, 121.0, 126.4, 126.5, 126.7, 127.3, 127.4, 129.8, 131.5, 131.6, 131.7, 132.1, 133.2, 134.7, 134.9, 143.7, 143.8, 150.0, 150.1, 150.2, 150.3, 160.2. MS (MALDI): m/z 779.6 $[M]^+$. Anal. Calcd for $C_{48}H_{37}N_5O_2Zn$: C, 73.80; H, 4.77; N, 8.96. Found: C, 73.92; H, 4.98; N, 8.63.



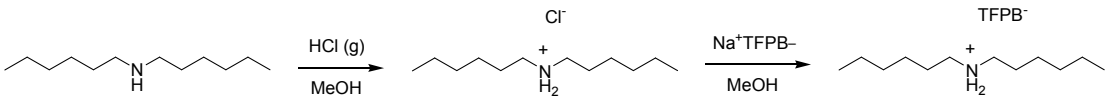
OP2

M.p. > 250 °C. ^{1}H NMR ($CDCl_3$): δ -4.10 (s, 2H), -1.78 (t, 2H), 0.48 (t, 2H), 2.13 (t, 2H), 2.71 (t, 2H), 3.06 (t, 2H), 4.04 (t, 2H), 7.27 (d-d, 1H), 7.41 (t-d, 1H), 7.74-7.76 (m, 10H), 8.16 (m, 3H), 8.25 (m, 2H), 8.32 (m, 2H), 8.85-8.88 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 36.6, 67.2, 69.0, 69.1, 69.5, 69.6, 112.6, 116.4, 120.0, 120.4, 120.7, 126.3, 126.4, 126.5, 126.7, 127.3, 127.4, 129.5, 131.5, 131.6, 131.8, 131.9, 133.2, 134.6, 134.7, 134.8, 135.0, 136.0, 143.8, 149.9, 150.0, 150.1, 150.2, 150.6, 159.3. MS (MALDI): m/z 823.6 $[M]^+$. Anal. Calcd for $C_{50}H_{41}N_5O_3Zn$: C, 72.77; H, 5.01; N, 8.49. Found: C, 73.03; H, 5.34; N, 8.08.



OP3

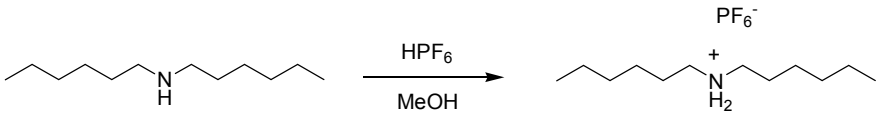
M.p. > 250 °C. ^{1}H NMR ($CDCl_3$): δ -3.87 (s, br, 2H), -1.97 (t, 2H), 0.73 (t, 2H), 2.14 (t, 2H), 2.68 (m, 4H), 2.75 (t, 2H), 3.18 (t, 2H), 4.07 (t, 2H), 7.31 (d-d, 1H), 7.35 (t-d, 1H), 7.70-7.77 (m, 10H), 7.99 (d-d, 1H), 8.17 (d-d, 2H), 8.21 (m, 2H), 8.31 (m, 2H), 8.81-8.85 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 36.8, 68.0, 68.9, 69.3, 69.4, 70.0, 70.2, 70.9, 112.3, 116.4, 120.0, 120.4, 120.7, 126.4, 126.5, 126.6, 127.3, 127.4, 129.5, 131.6, 131.8, 133.2, 134.6, 134.7, 134.8, 134.9, 135.0, 136.1, 143.9, 149.9, 150.0, 150.1, 150.6, 158.9. MS (MALDI): m/z 867.7 $[M]^+$. Anal. Calcd for $C_{52}H_{45}N_5O_4Zn$: C, 71.84; H, 5.22; N, 8.06. Found: C, 72.11; H, 5.36; N, 7.73.



4a **4c**

4a: To the solution of di-*n*-hexylamine (2 ml) in anhydrous methanol (15 ml) was bubbled dry HCl gas for 2.5 h. After removing methanol by evaporation, the residue was recrystallized from anhydrous $CHCl_3/Et_2O$ to give the **4a** as a white solid (3.46 g, 91%). ^{1}H NMR ($CDCl_3$): δ 0.85 (t, 6H), 1.32 (m, 12H), 1.85 (m, 4H), 2.88 (t, 4H), 9.44 (s, br, 2H).

4c: To the solution of **4a** (0.115 g, 0.52 mmol) in anhydrous methanol (3 ml) was added a solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (0.594 g, 0.67 mmol) in anhydrous methanol (2 ml). The reaction mixture was stirred overnight at room temperature. After removing methanol by evaporation, the brown residue was washed with deionized water and filtered off, then dried under vacuum to give the **4c** as a brown solid (0.485 g, 89%). ^{1}H NMR ($CDCl_3$): δ 0.85 (t, 6H), 1.26 (m, 12H), 1.59 (m, 4H), 2.97 (q, 4H), 6.41 (s, br, 2H), 7.55 (s, 4H), 7.70 (s, 8H).



4b

4b: To the solution of di-*n*-hexylamine (2ml) in anhydrous methanol (2 ml) was added a solution of hexafluorophosphoric acid (0.8 ml) in anhydrous methanol (2 ml). The reaction mixture was stirred at room temperature for 24h. After removing methanol by evaporation, the residue was recrystallized from anhydrous $CHCl_3/Et_2O$ to give the **4b** as a white solid (0.771 g, 22%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 6H), 1.32 (m, 12H), 1.74 (m, 4H), 3.02 (q, 4H), 6.79 (s, br, 2H).

Preparation of single crystal of OP1: By evaporation of methanol in the outside jar, it diffused into the dichloromethane solution of **OP1** in the inside vial, which facilitated the crystallization of **OP1**. The apparatus shown in Fig. S1 was used.

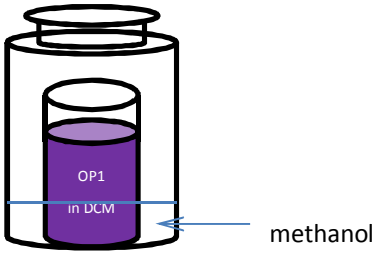


Fig. S1 The apparatus used for preparation of single crystal of **OP1**

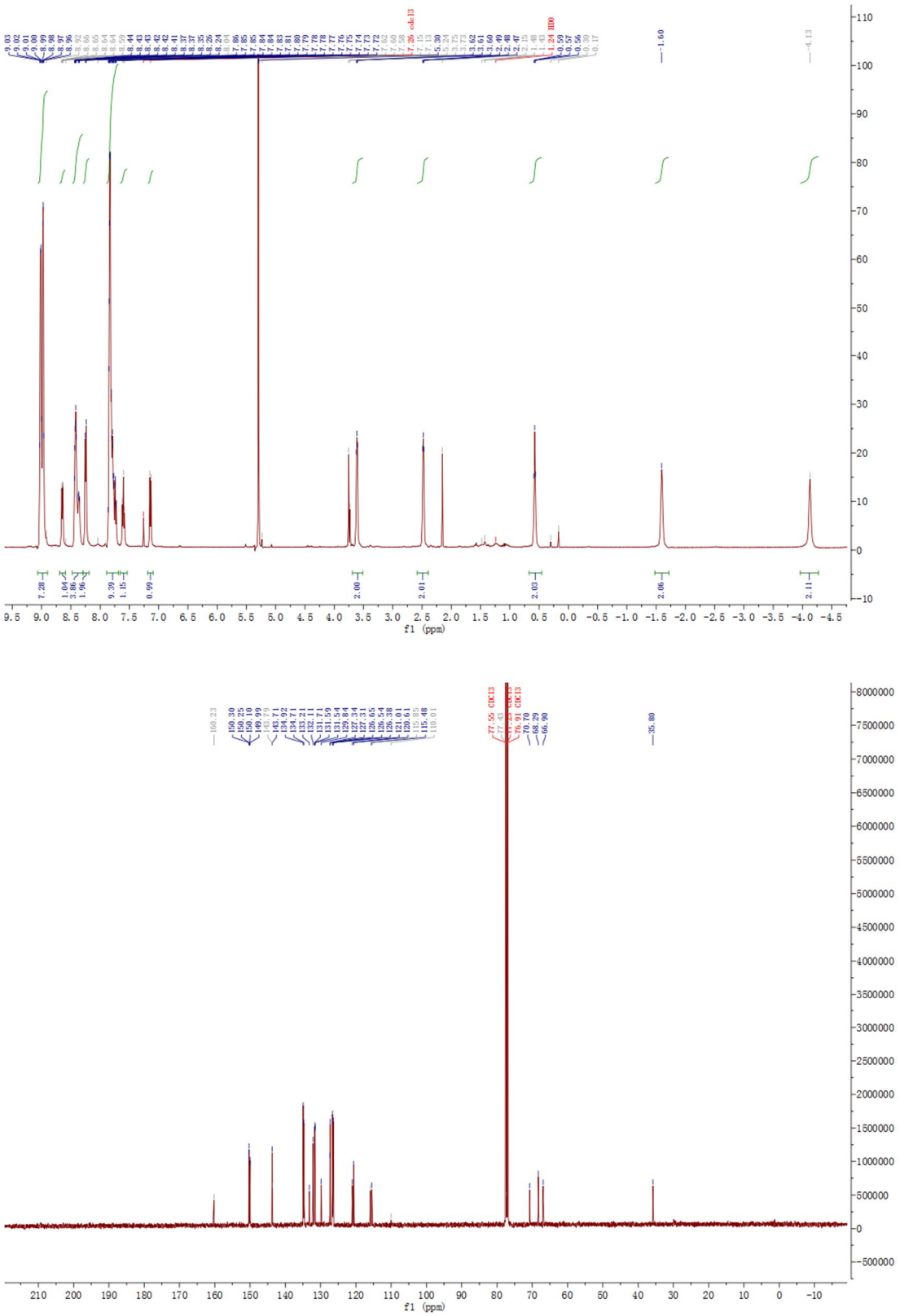


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of **OP1**.

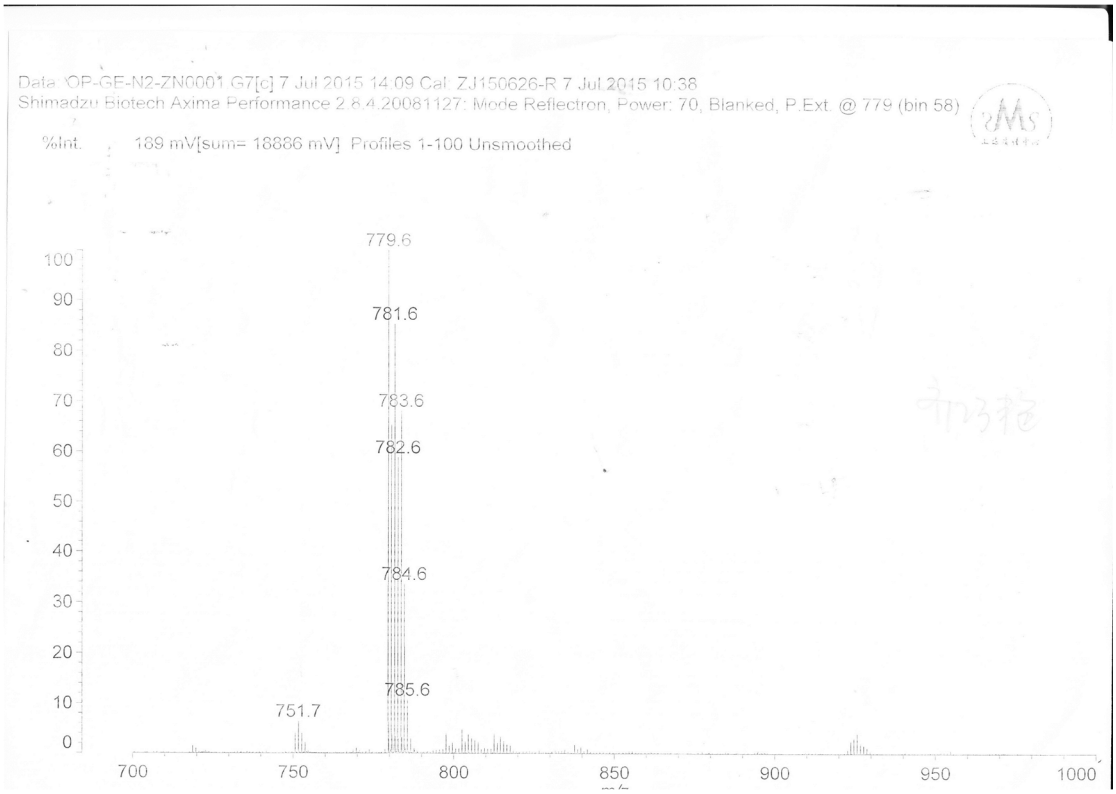


Figure S3. MALDI MS of **OP1**.

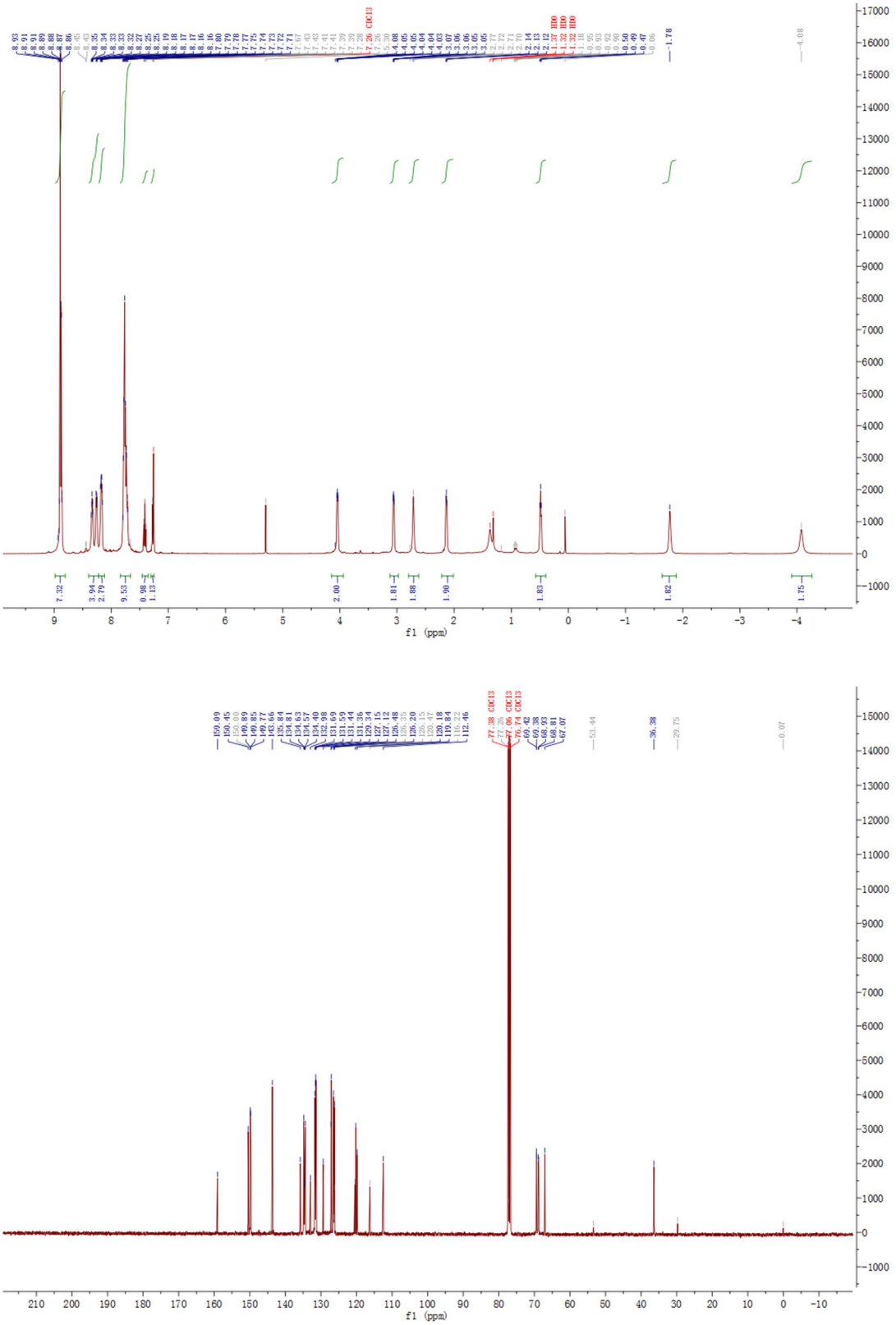


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of **OP2**.

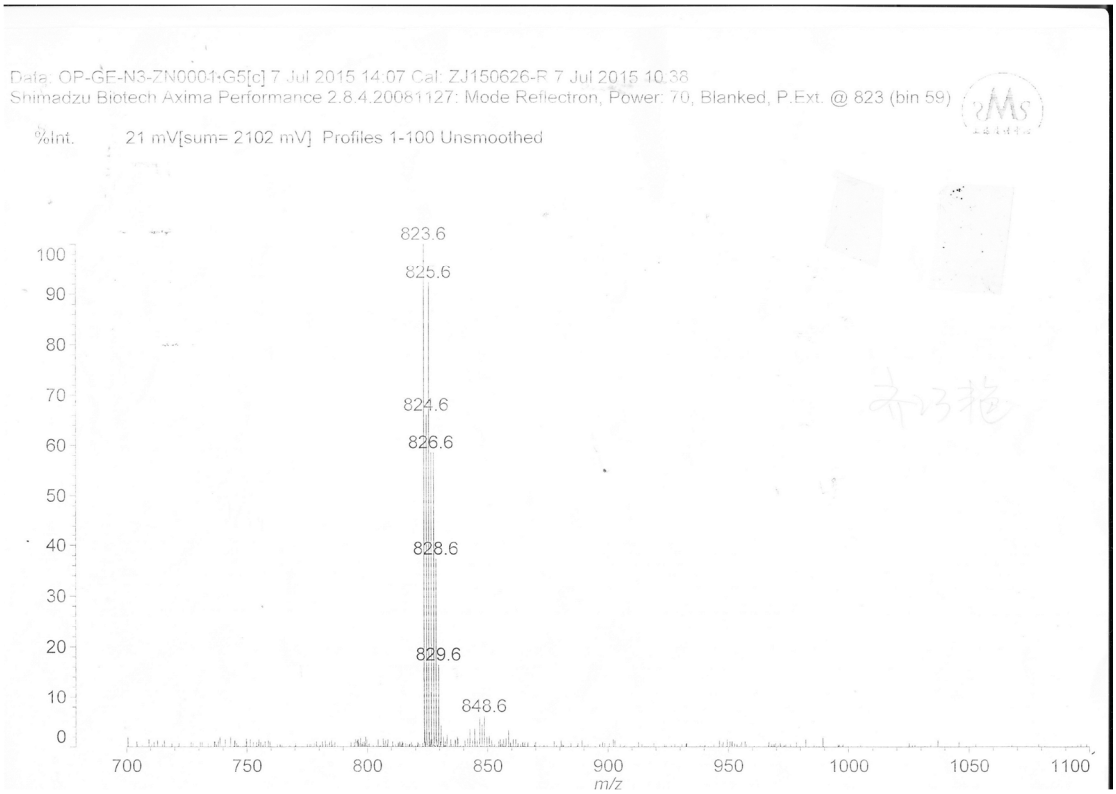


Figure S5. MALDI MS of **OP2**.

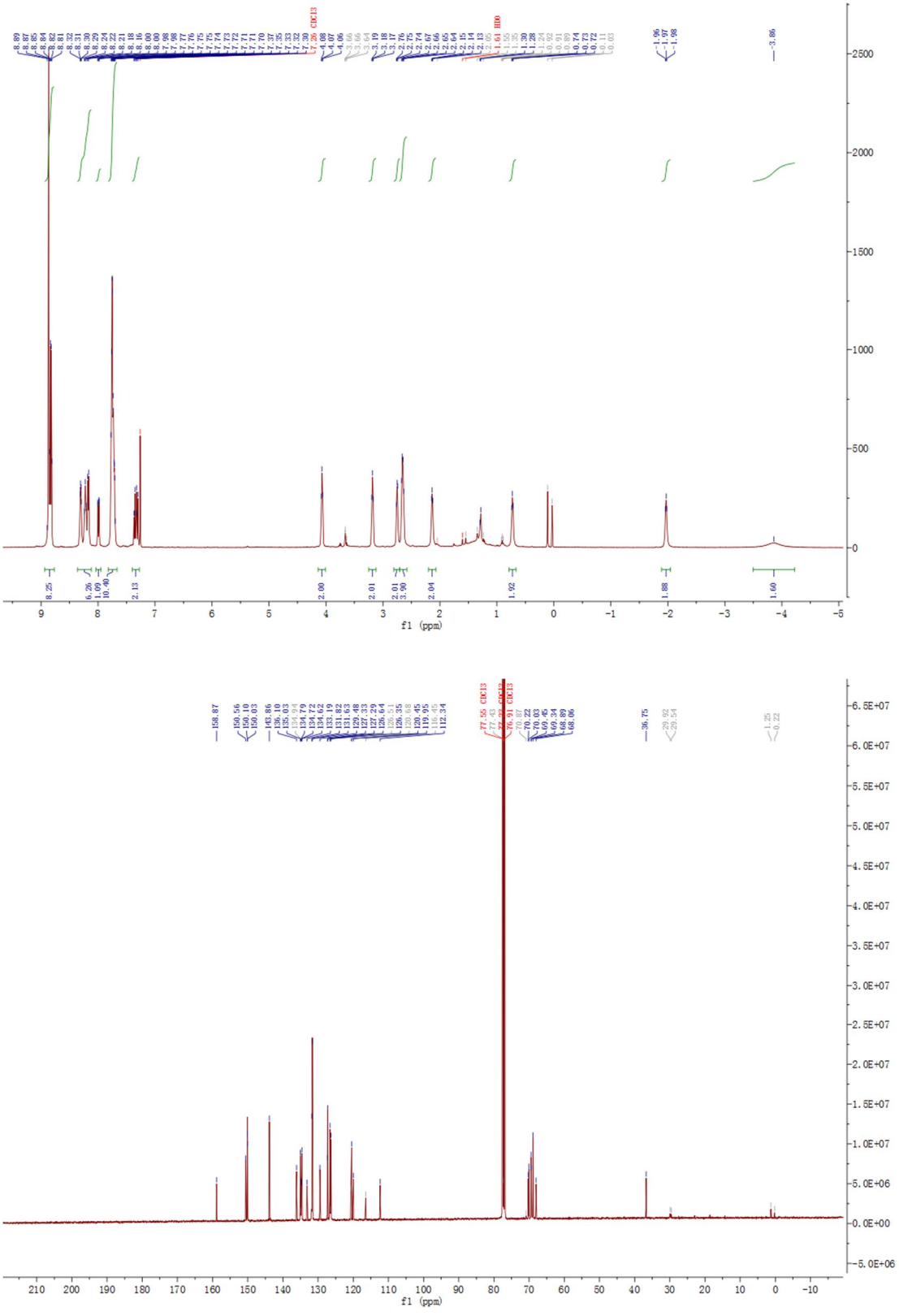


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of **OP3**.

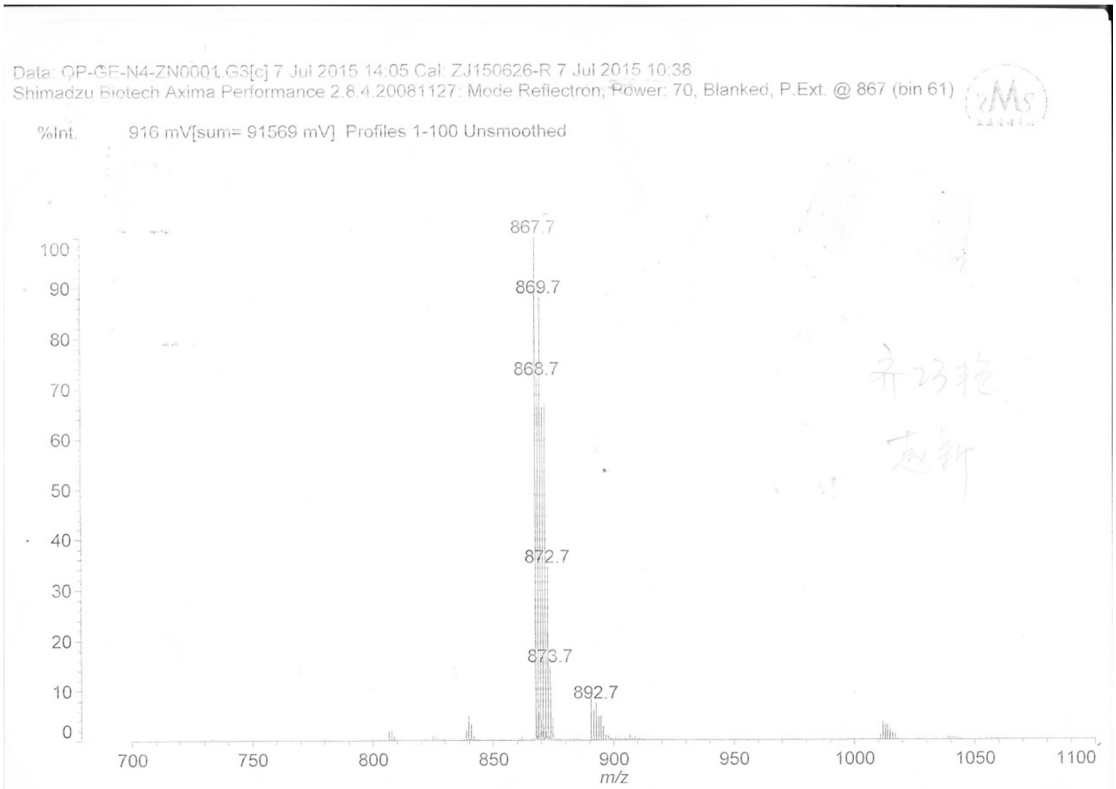


Figure S7. MALDI MS of **OP3**.

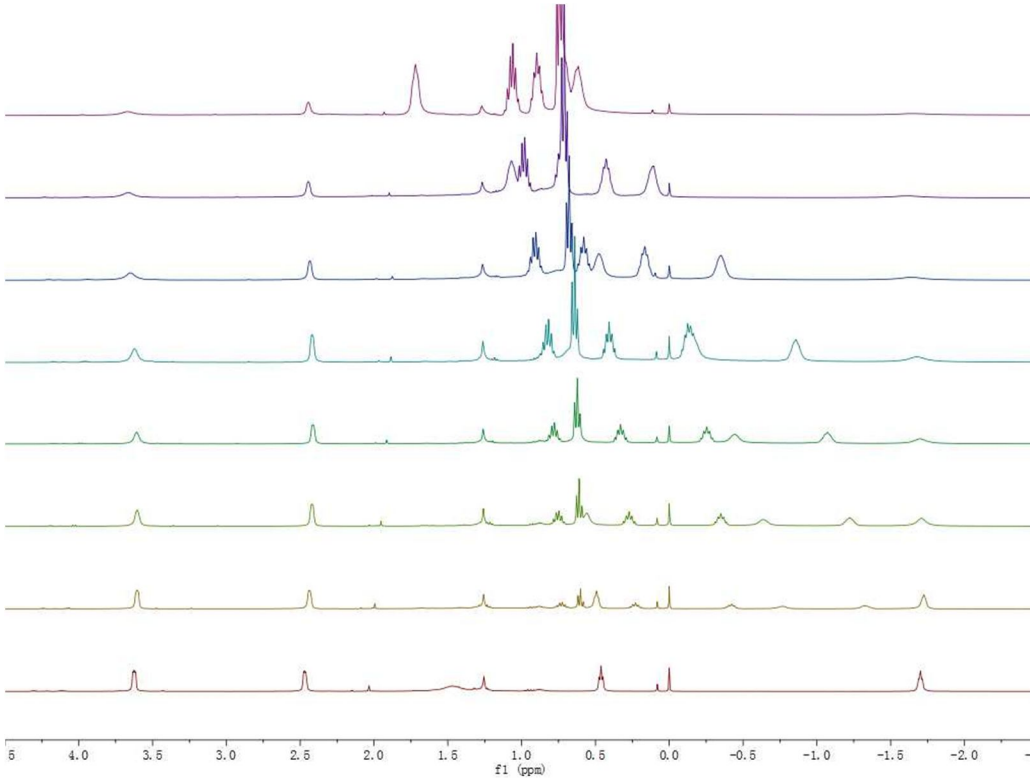


Figure S8. ^{1}H NMR titrations of host **OP1** (400 MHz, $CDCl_3$, 298 K) with the increment of **4c**: (a) 0.00 equiv., (b) 0.25 equiv., (c) 0.50 equiv., (d) 0.75 equiv., (e) 1.00 equiv., (f) 1.50 equiv., (g) 2.00 equiv., (h) 3.00 equiv.

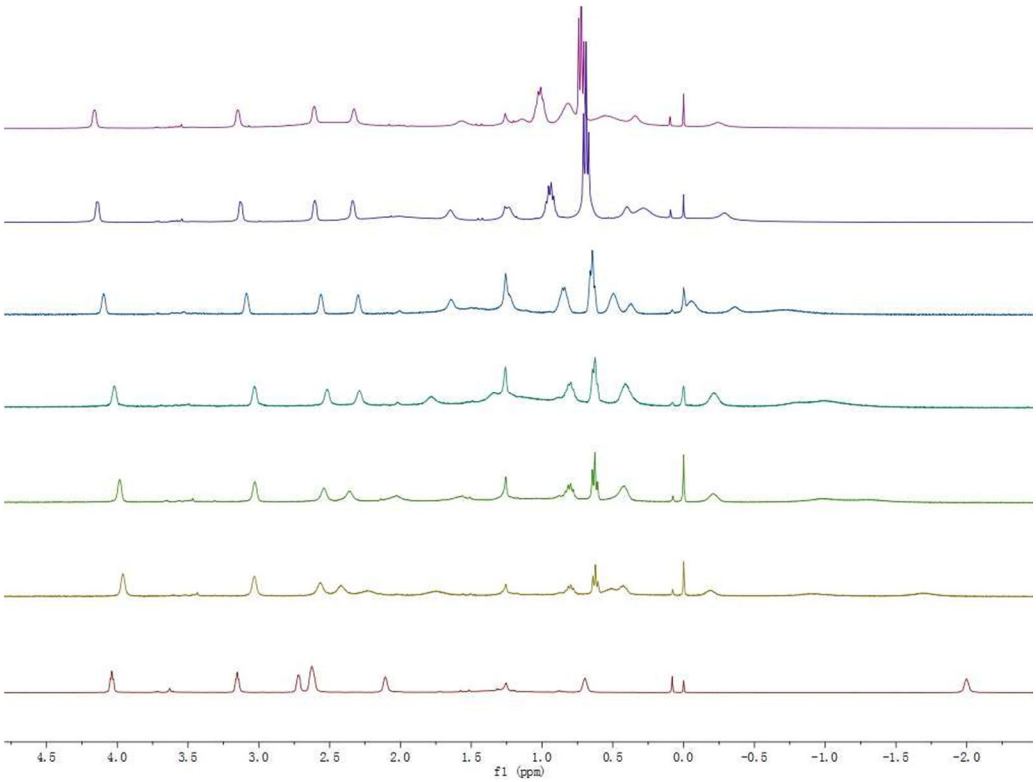


Figure S9. ^{1}H NMR titrations of host **OP3** (400 MHz, $CDCl_3$, 298 K) with the increment of **4c**: (a) 0.00 equiv., (b) 0.25 equiv., (c) 0.50 equiv., (d) 0.75 equiv., (e) 1.00 equiv., (f) 1.50 equiv., (g) 2.00 equiv., (h) 3.00 equiv.

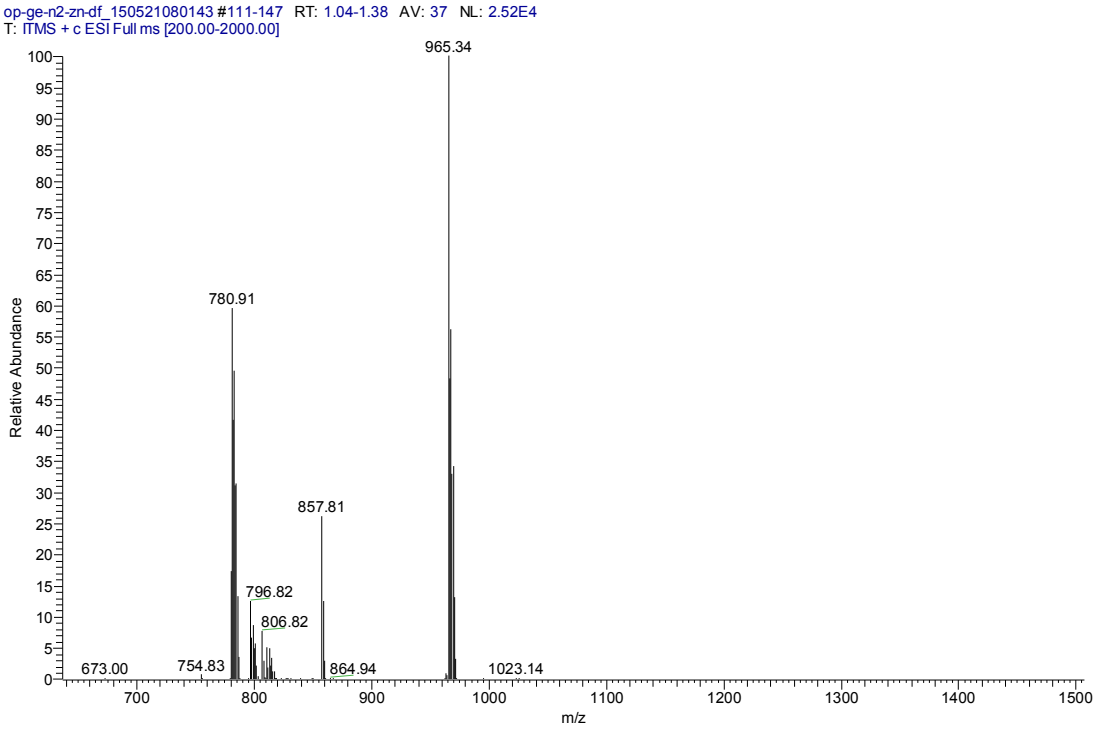


Figure S10. Mass spectrum of equimolar mixture of host **OP1** and **4c**.

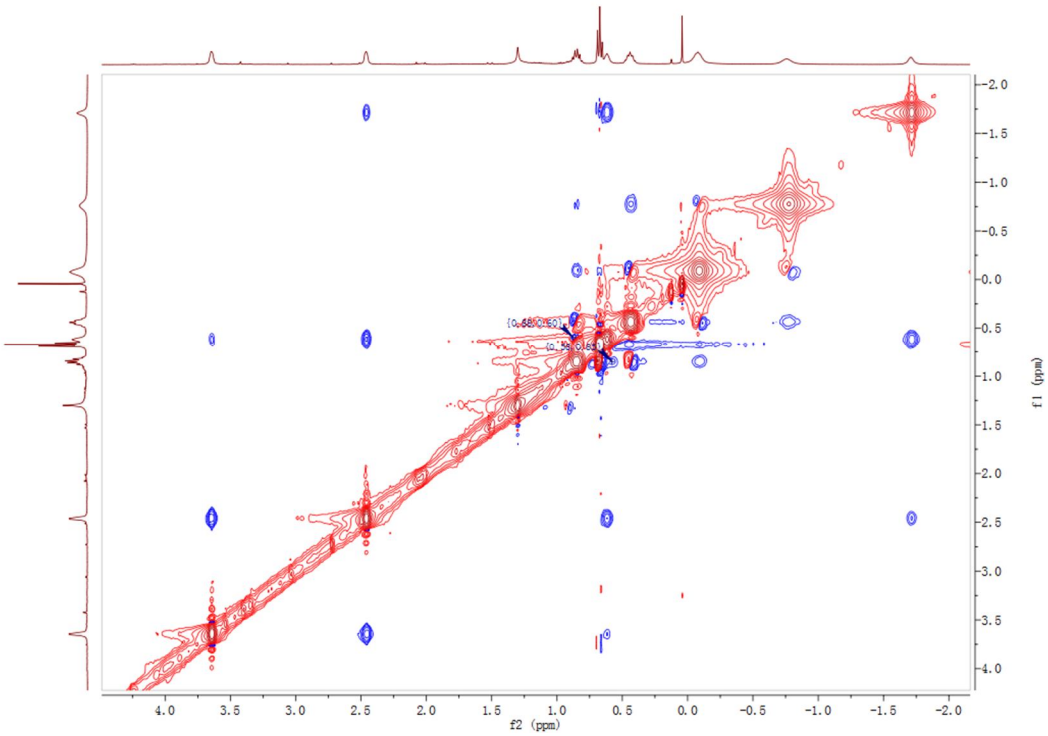


Figure S11. Partial 2D Noesy of equimolar mixture of host **OP1** and **4c** .

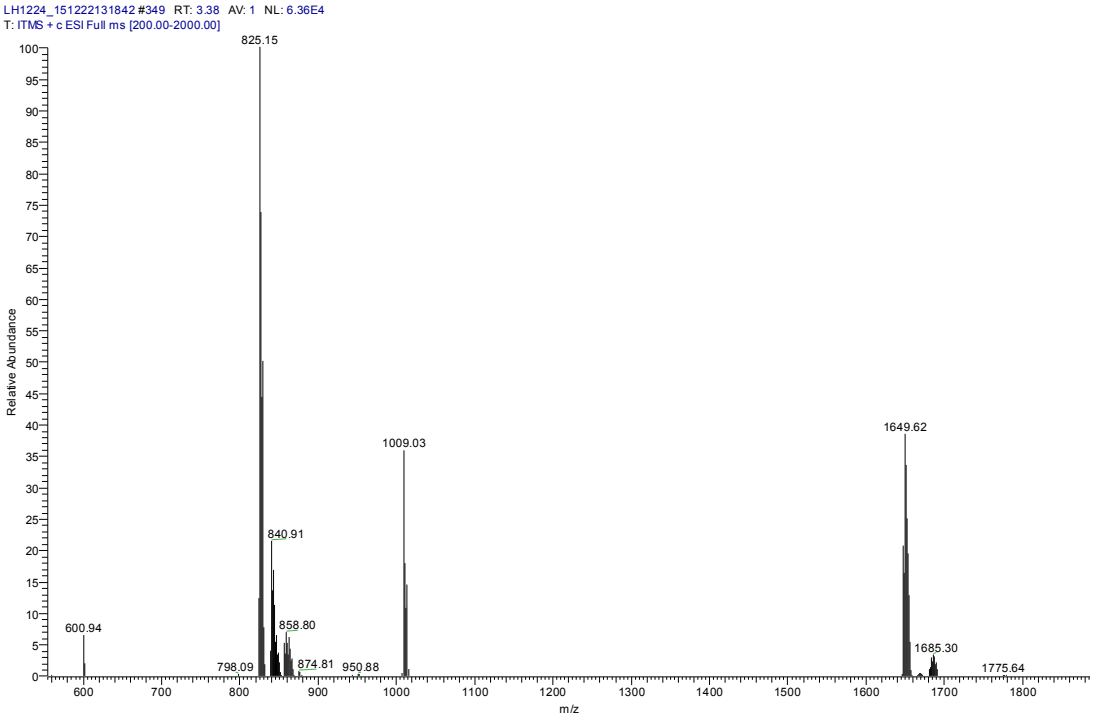


Figure S12. Mass spectrum of equimolar mixture of host **OP2** and **4c**.

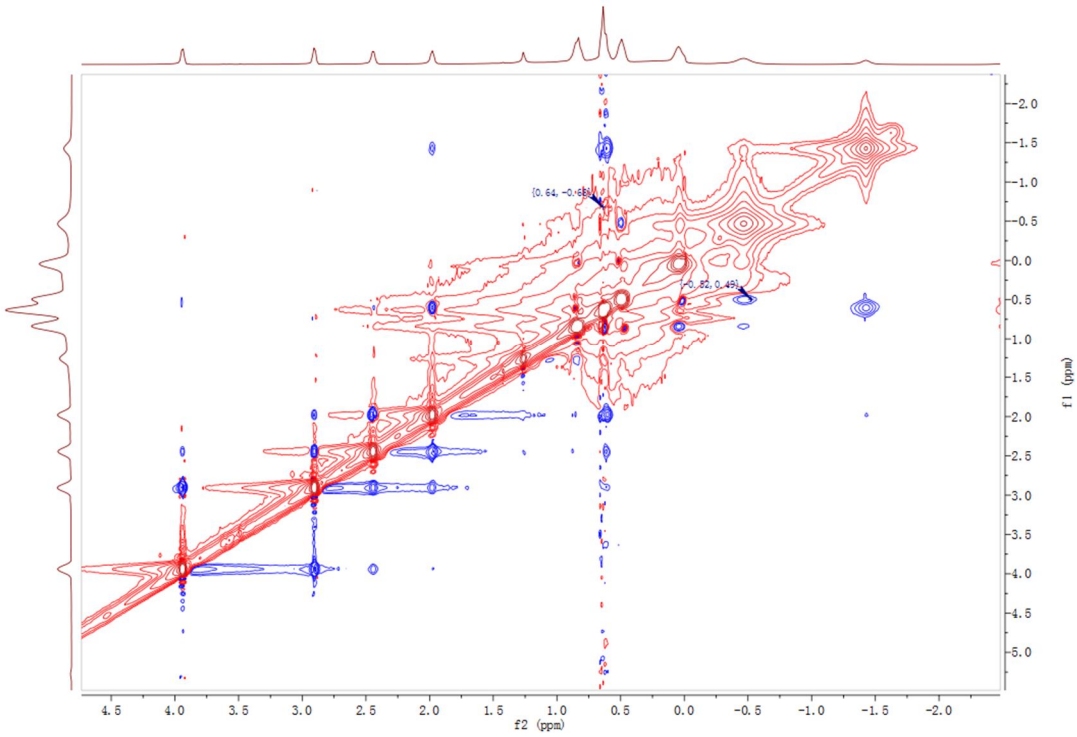


Figure S13. Partial 2D Noesy of equimolar mixture of host **OP2** and **4c**.

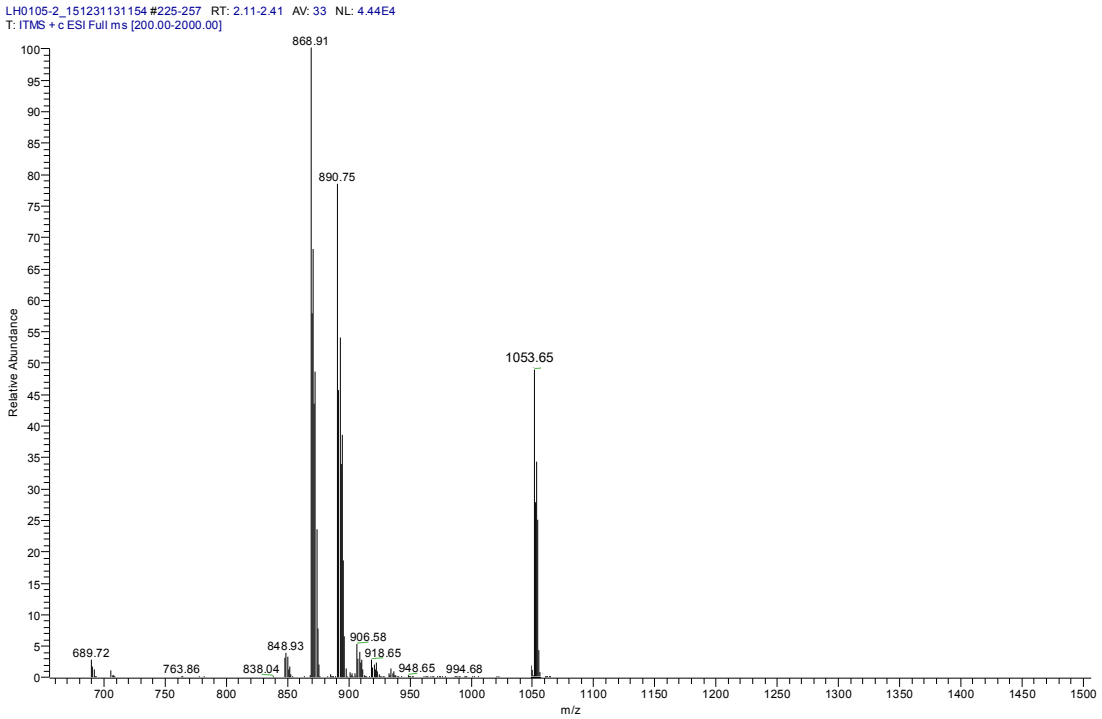


Figure S14. Mass spectrum of equimolar mixture of host **OP3** and **4c**.

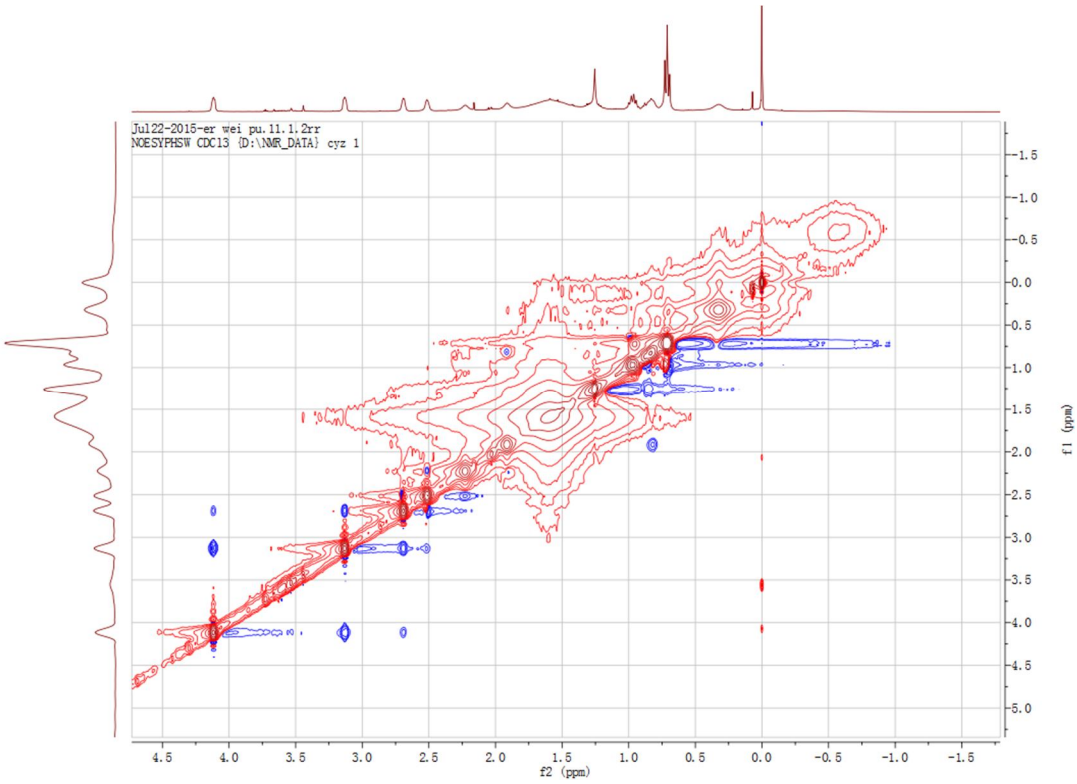


Figure S15. Partial 2D Noesy of equimolar mixture of host **OP3** and **4c**.

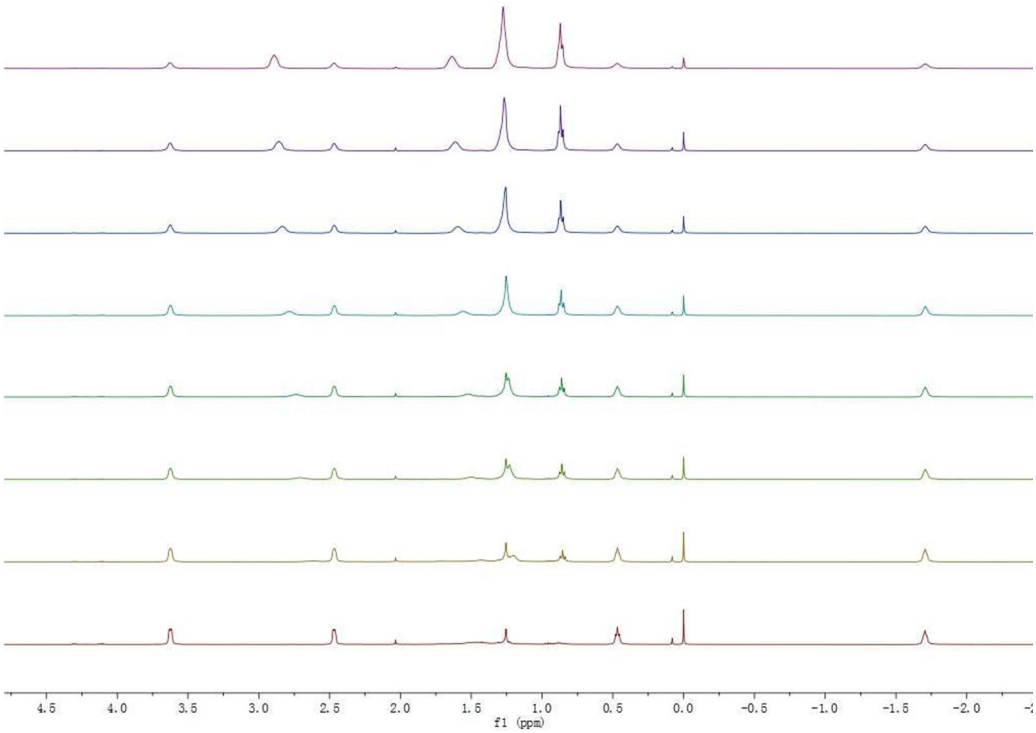


Figure S16. ^{1}H NMR titrations of host **OP1** (400 MHz, $CDCl_3$, 298 K) with the increment of **4b**: (a) 0.00 equiv., (b) 0.25 equiv., (c) 0.50 equiv., (d) 0.75 equiv., (e) 1.00 equiv., (f) 1.50 equiv., (g) 2.00 equiv., (h) 3.00 equiv.

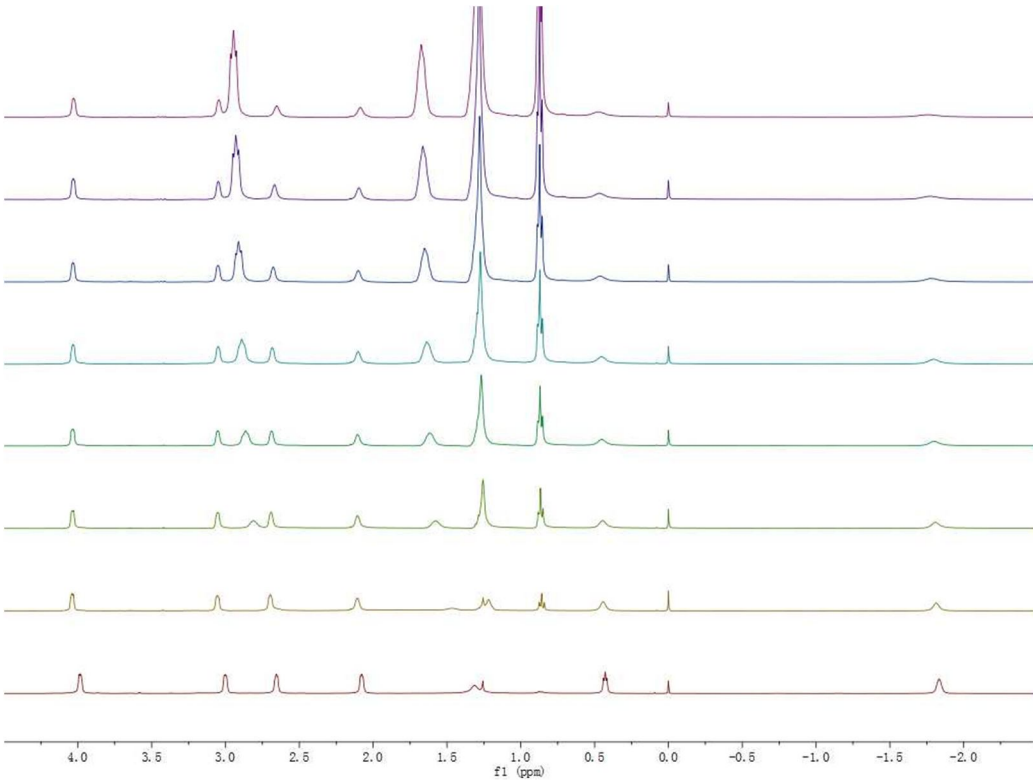


Figure S17. ^{1}H NMR titrations of host **OP2** (400 MHz, $CDCl_3$, 298 K) with the increment of **4b**: (a) 0.00 equiv., (b) 0.25 equiv., (c) 0.50 equiv., (d) 0.75 equiv., (e) 1.00 equiv., (f) 1.50 equiv., (g) 2.00 equiv., (h) 3.00 equiv.

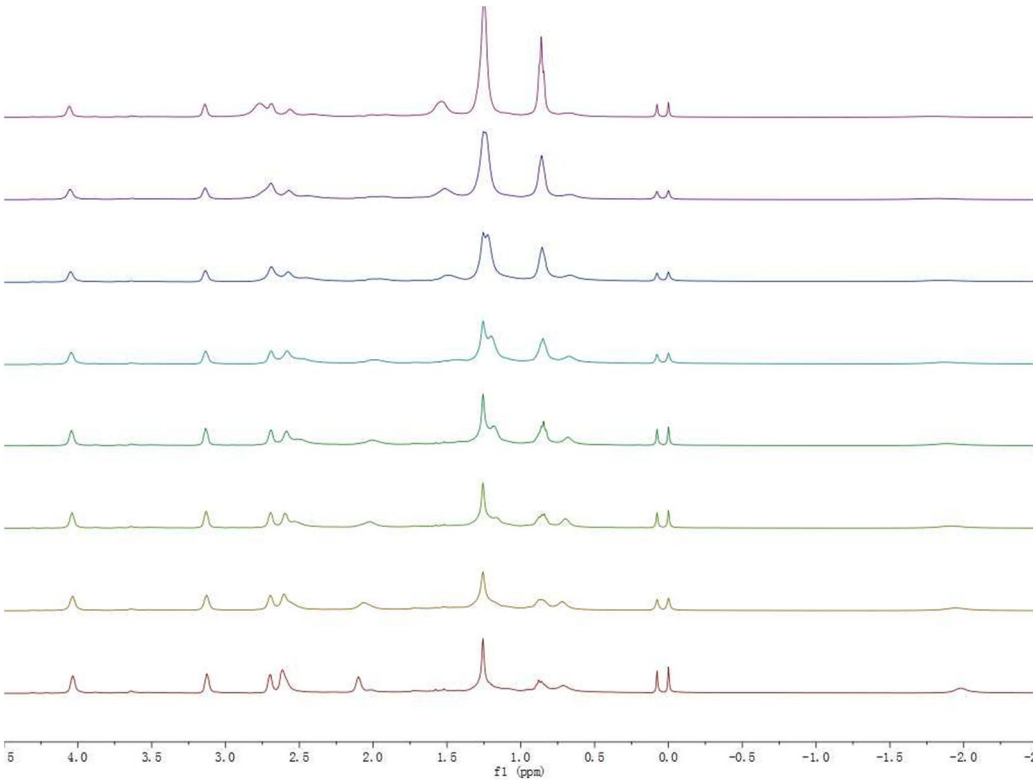
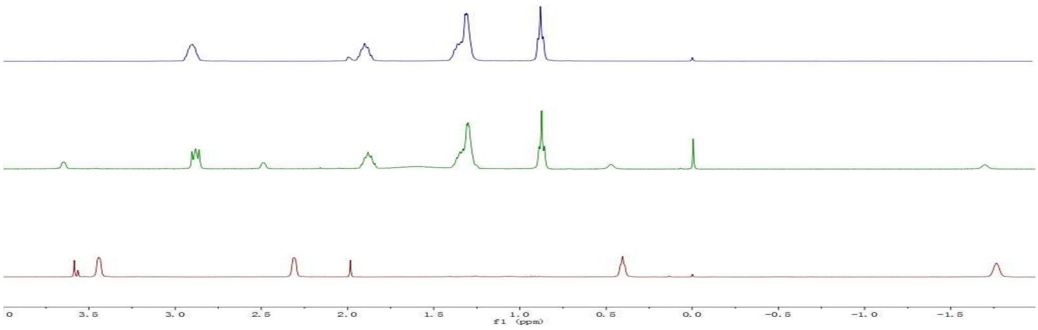
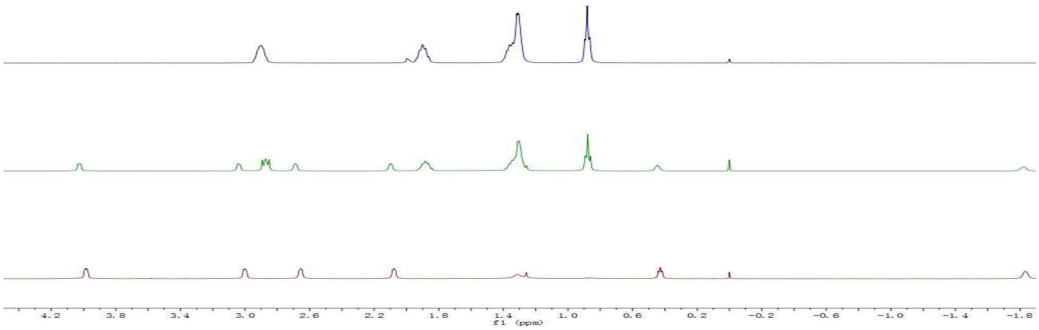


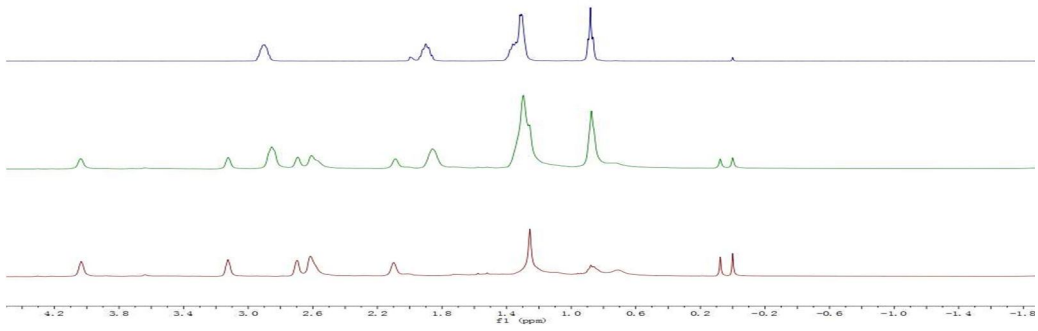
Figure S18. ^{1}H NMR titrations of host **OP3** (400 MHz, $CDCl_3$, 298 K) with the increment of **4b**: (a) 0.00 equiv., (b) 0.25 equiv., (c) 0.50 equiv., (d) 0.75 equiv., (e) 1.00 equiv., (f) 1.50 equiv., (g) 2.00 equiv., (h) 3.00 equiv.



OP1+4a

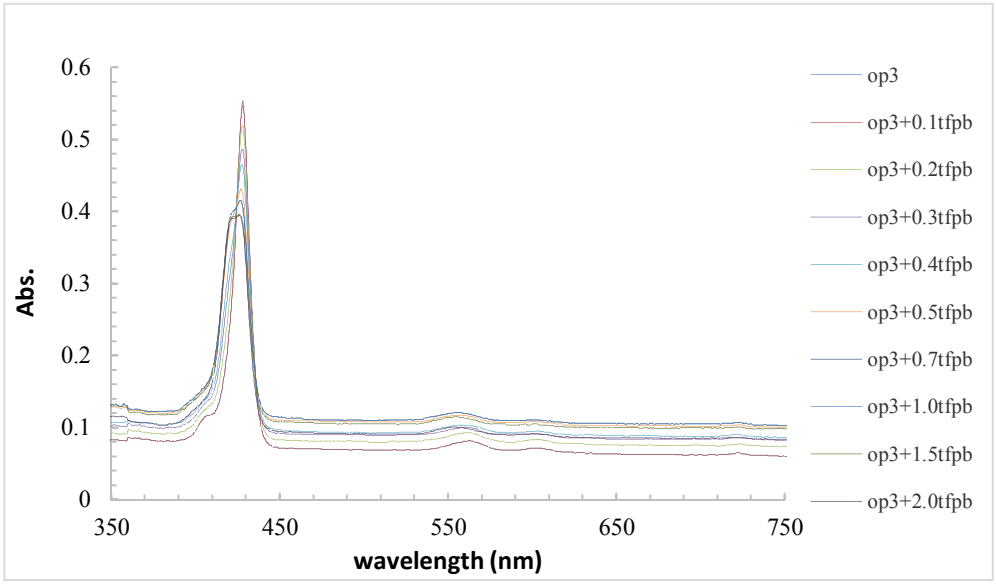


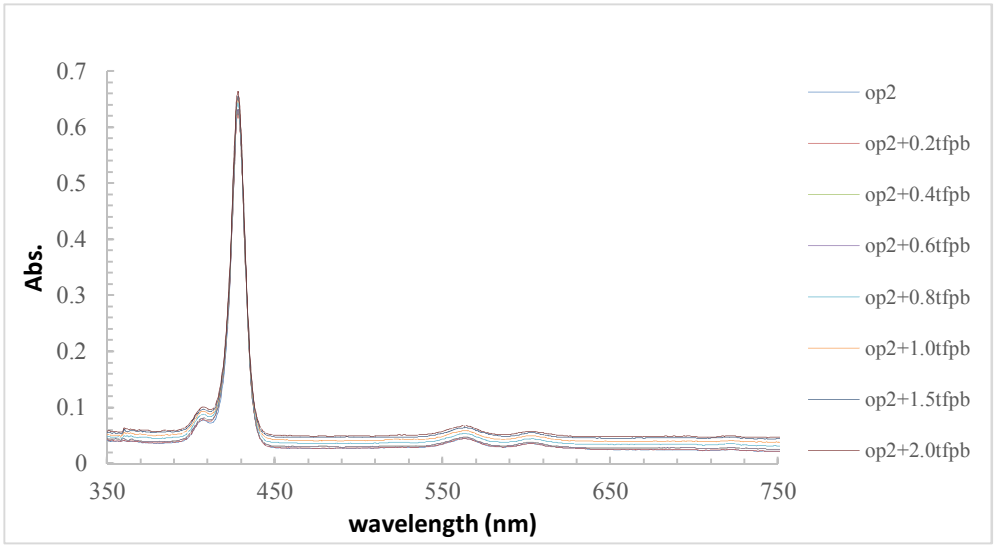
OP2+4a



OP3+4a

Figure S19. Partial ^{1}H NMR spectra of equimolar mixture of tailed porphyrin **OP** and **4a** (400 M Hz, $CDCl_3$, 298 K).





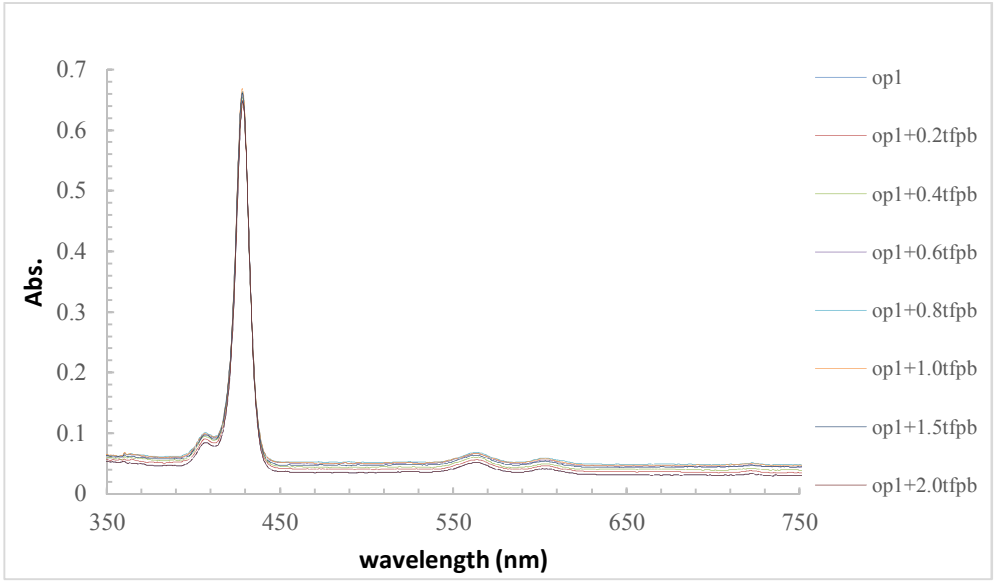


Figure S20. UV-Vis titration of host **OP** (1×10^{-6} mol/L in CH_2Cl_2 at 298 K) with the increment of **4c**.

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