Systematic Rim Cyano Functionalization of Pillar[5]arene and Corresponding Host-Guest Property Varieties

Guo Wang, Hui Qiang, Yun-Zhe Guo, Jie Yang, Ke Wen, and Wei-Bo Hu

Shanghai Advanced Research Institute, Chinese Academy of Science, Shanghai 201210, China
School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
Department of Chemistry, Shanghai University, Shanghai 200444, China

Correspondence Address
Dr. Wei-Bo Hu and Prof. Dr. Ke Wen
Shanghai Advanced Research Institute, Chinese Academy of Science, Shanghai 201210, China
Tel: +86-21-20608039; Fax: +86-21-20325173
Email address: huwb@sari.ac.cn, wenk@sari.ac.cn

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Materials and Methods:

Unless otherwise noted, all commercial reagents and solvents were used without purification. Separation by flash column chromatography was performed on silica gel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were recorded at a 500 MHz spectrometer with TMS as the reference. Mass spectra (ESI analysis) were recorded on an Esquire 6000 spectrometer (LC/MS). Single crystal X-ray diffraction data were collected on a SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube (λ = 0.71073 Å) and data reduction included absorption corrections by the multi-scan method. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added at their geometrically ideal positions and refined isotropically. Microwave synthesis was conducted in a MCR-3 microwave reactor (Supporting Information, Fig. S32). The reaction vessel was an open one, and the temperature was monitored by an internal probe.

Synthesis of **P5**[1]

Hydroquinone dimethyl (0.2 mol) and polyoxymethylene (0.6 mol) were added into CH_2ClCH_2Cl (750 mL) in turn. The mixture was stirred at 30 °C for 10min, and followed, $BF_3.Et_2O$ (0.21 mol) was added into the mixture for once. The reaction was further stirred at 30 °C for another 30 min, and then quenched by adding MeOH (200 mL). The resulting reaction solution was concentrated and purified by column chromatography to afford **P5** as write solid (22.5 g, 75%).

Synthesis of **nQ-P5**[2] **(n=1, 2, 3, 4)**

To a CH_2Cl_2 (300 mL) solution of **P5** (15.0 g，20 mmol), a solution of $(NH_4)_2[Ce(NO_3)_6]$ (2n mmol) in water (50 mL) was added dropwise. The mixture was stirred at r.t. for 30 min, washed with water (100 mL x 3), removed solvent under vacuum and purified by column chromatography to nQ-P5 as red solid. The reaction yields of **1Q-P5**, **2Q-P5**, **3Q-P5** and **4Q-P5** were 65%, 40%, 39% and 28% respectively.

Synthesis of **10H-P5**[3]

To a CH_2Cl_2 (300 mL) solution of **P5** (7.5 g，10 mmol), BBr_3 (27.5 g, 110 mmol) was

added dropwise at 0 °C. The resulting mixture was stirred at rt for 3d. Water was added into the reaction mixture dropwise, giving a suspension, which was filtered. The filtration was washed with HCl (1 M, 3*20 mL) and water (3*20 mL) in turn to give the crude product as pink solid quantitively, which could be used for next reaction after dried without purification.

Synthesis of 2nOH-P5 (n=1, 2, 3, 4):

$NaHB_4$ (4n mmol) was added into a solution of **nQ-P5** (1.0 mmol) in CH_2Cl_2/MeOH (20 mL/ 10 mL). The mixture tuned to be a colorless one in minutes. HCl (1 M) was added into the mixture (adjusting the PH to 7), followed by water (20 mL). The organic solvents of mixture were removed, and the obtained suspension was filtered to give the crude product as pink solid quantitively, which could be used for next reaction after dried without purification.

Synthesis of 2nOTf-P5 (n=1, 2, 3, 4, 5):

To a solution of **2nOH-P5** (1 mmol) in CH_2Cl_2 (100 mL) pyridine (3n mmol) was added, resulting in a mixture which was stirred at 0 °C for 10 min. After triflic anhydride (2.4 n mmol) was added at 0 °C, and the mixture was stirred at room temperature for 4 h and washed with aqueous HCl solution (1.0 M, 3×50 mL). The solvent was removed under reduced pressure resulting in a residue which was purified by column chromatography to afford the desired product **2nOTf-P5** as white solid.

4OTf-P5:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.81 (s, 1H), 6.96 (s, 1H), 6.85 (s, 1H), 6.82 (s, 1H), 4.28 (s, 1H), 4.03 (s, 2H), 3.81 (s, 5H), 3.75 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.65, 150.59, 150.55, 146.30, 146.25, 134.05, 133.63, 129.51, 125.69, 124.66, 124.60, 124.35, 122.42, 122.40, 119.87, 119.85, 117.33, 117.31, 114.76, 114.01, 113.55, 113.25, 55.73, 55.17, 55.05, 30.72, 30.40, 29.41; HRMS (ESI) calcd for $C_{45}H_{36}F_{12}NO_{18}S_4[M+NH_4^+]$ = 1240.1088, found 1240.1084.

6OTf-P5:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.29 (s, 1H), 7.22 (s, 1H), 6.75 (s, 1H), 6.74 (s, 1H), 4.00 (s, 1H), 3.95 (s, 2H), 3.92 (s, 2H), 3.72 (s, 3H), 3.70 (s, 3H); ^{13}C

NMR (126 MHz, $CDCl_3$) δ 150.72, 150.46, 146.16, 146.12, 146.09, 135.91, 133.89, 130.49, 126.09, 125.65, 125.06, 124.56, 124.49, 113.80, 113.20, 55.34, 55.29, 30.49, 30.38; HRMS (ESI) calcd for $C_{45}H_{36}F_{18}NO_{22}S_6$ [M+NH_4^+] = 1475.9760, found 1475.9825.

8OTf-P5:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 2H), 7.26 (d, *J* = 1.1 Hz, 1H), 7.23 (s, 1H), 7.19 (s, 1H), 6.77 (s, 1H), 4.07 (s, 1H), 4.04 (s, 2H), 3.97 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.67, 146.15, 146.07, 145.94, 136.30, 132.87, 132.21, 130.21, 126.12, 125.10, 124.92, 124.46, 113.48, 55.50, 30.72, 30.16; HRMS(ESI) calcd for $C_{45}H_{30}F_{24}NO_{26}S_8$ [M+NH_4^+] = 1711.8433, found 1711.8264; calcd for $C_{45}H_{26}F_{24}O_{26}S_8Na$ [M+Na^+] = 1716.7987, found 1716.7891.

Cyanation reactions

Oil bath method:

A mixture of **2nOTf-P5** (1.0 mmol)、$Zn(CN)_2$ (2.2n mmol) and $Pd[P(C_6H_5)_3]_4$ (0.1n mmol) in DMF (20 mL) was heated at 170 °C under nitrogen for 24 h, and then cooled to room temperature. The mixture was poured into water (200 mL), filtered and the filtration was collected and purified by chromatography to give the target molecules. (n= 1, 2, or 3)

Microwave method:

A mixture of **2nOTf-P5** (1.0 mmol)、$Zn(CN)_2$ (2.2n mmol) and $Pd[P(C_6H_5)_3]_4$ (0.1n mmol) in DMF (20mL) was heated at 153 °C using microwave-heating method under nitrogen for 5 h, and then cooled to room temperature. The mixture was poured into water (200mL), filtered and the filtration was collected and purified by chromatography to give the target molecules. (n= 1, 2, 3, 4 or 5)

2CN-P5：68.1 % (oil bath method) and 90.8 % (microwave method).

^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ:7.71 (s, 2H), 6.93(s, 2H), 6.81(s, 4H), 6.80 (s, 2H), 4.01 (s, 4H), 3.80 (s, 6H), 3.79 (s, 6H), 3.71 (s, 6H), 3.70 (s, 6H), 3.68 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ: 150.8, 150.5, 150.4, 150.1, 143.4, 134.7, 129.9, 128.4, 127.9, 124.6, 118.1, 115.7, 113.6, 113.5, 113.4, 113.0, 77.3, 77.1, 76.8, 55.7, 55.6, 55.5, 55.4, 39.7, 34.0, 29.2, 29.1; HRMS (ESI): calcd for $C_{45}H_{45}N_2O_8$ [M + H^+]

= 741.3170, found 741.3167.

Crystallographic Data of 2CN-P5: [C95H95.50N6.50O16]; *Mr* = 1584.270; T = 149.99 K; Monoclinic; space group P 1 21 1; *a* = 12.2850(4); *b* = 28.8977(11); *c* = 25.3483(9) Å; α =90.000; β = 103.049(1); γ =90.000; *V* = 8766.5(5) Å^3; Z = 4; ρcalcd = 1.200 g/cm^3;μ = 0.082 mm^{-1}; reflections collected 114039; unique reflections 31014; data/restraints/parameters 31014 / 3 / 2163; *GOF* on *F2* 0.991; *Rint* for independent data 0.0627; final *R1 = 0.0453, wR2 = 0.1030*; R indices (all data) *R1 = 0.0787, wR2 = 0.1195*; largest diff. peak and hole: 0.391 and -0.265 e.Å^{-3}.

4CN-P5： 50.4 % (oil bath method) and 68 % (microwave method)

^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ:7.73 (s, 2H), 7.71 (s, 2H), 7.00 (s, 2H), 6.95 (s, 2H), 6.83 (s, 2H), 4.03 (s, 4H), 4.02 (s, 4H), 3.84 (s, 6H), 3.83 (s, 8H), 3.73 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ: 150.7, 150.5, 150.4, 143.5, 143.0, 134.9, 134.7, 129.7, 125.1, 118.0, 118.0, 116.0, 115.9, 113.7, 113.6, 113.5, 77.4, 77.1, 76.8; HRMS: calcd for $C_{45}H_{42}N_5O_6$ [M + NH_4^+] = 748.3130, found 748.3129.

6CN-P5: 39.4 % (oil bath method) and 67.5 % (microwave method)
^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ: 7,73 (s, 2H), 7.71 (s, 2H), 7.00 (s, 2H), 6.95 (s, 2H), 6.83 (s, 2H), 4.03 (s, 4H), 4.02 (s, 4H), 3.84 (s, 6H), 3.83 (m, 8H), 3.73 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ: 150.7, 150.5, 150.4, 143.5, 143.0, 134.9, 134.7, 129.7, 126.3, 125.1, 118.1, 118.0, 118.0, 116.0, 115.9, 113.7, 113.6, 113.6, 77.3, 77.1, 76.8, 56.2, 55.9, 55.6, 34.0, 34.0, 29.1; HRMS (ESI): calcd for $C_{45}H_{33}N_6O_4$ [M + H^+] = 721.2558, found 721.2555.

Crystallographic Data of 6CN-P5: [C47 H35 Cl5 N6 O4]; *Mr* = 925.06; T = 150.0 K; triclinic; space group P $\bar{1}$; *a* = 11.8381(5); *b* = 12.1136(5); *c* = 16.2757(8) Å; α =91.438(3); β = 99.204(2); γ =99.741(2); *V* = 2267.44(18) Å^3; Z = 2; ρcalcd = 1.355 g/cm^3; μ = 0.370 mm^{-1}; reflections collected 52356; unique reflections 9894; data/restraints/parameters 9894/0/564; *GOF* on *F2* 1.191; *Rint* for independent data 0.1333; final *R1* = 0.1147, *wR2* = 0.3011; R indices (all data) *R1* =0.1953, *wR2* = 0.3600; largest diff. peak and hole: 1.301 and -1.432 eÅ^{-3}.

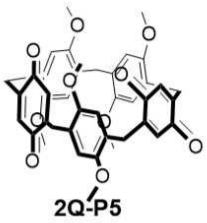
8CN-P5: 58.2 % (microwave method)

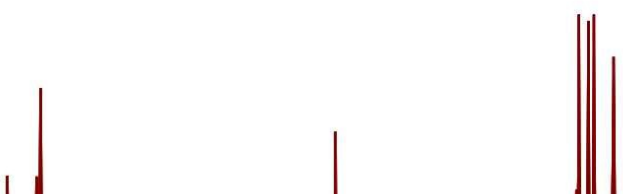
^{1}H NMR (500 MHz, CDCl3, 298K) δ: 8.07 (s, 2H), 7.99 (s, 2H), 7.91 (s, 2H), 7.87 (s, 2H), 7.07 (s, 2H), 4.37 (s, 2H), 4.35 (s, 4H), 4.10 (s, 4H), 3.89 (s, 6H); ^{13}C NMR (101 MHz, DMF) δ 151.2, 144.7, 142.0, 141.8, 140.5, 136.1, 135.8, 135.7, 135.6, 127.1, 117.2, 116.7, 116.5, 114.4, 79.4, 55.8, 36.8, 33.8; HRMS (ESI): calcd for $C_{45}H_{26}N_8O_2Na$ [M + Na^+] = 733.2071, found 733.2207.

Synthesis of 10CN-P5: 47.4 % (microwave method)

^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ: 7.77 (s, 10H), 4.38 (s, 10H); ^{13}C NMR (126 MHz, CD_3CN, 298K) δ: 146.6, 140.9, 140.7, 121.5, 121.2, 41.4. HRMS (ESI): calcd for $C_{45}H_{30}N_{11}$ [M+NH_4^+] = 718.2211, found 718.2195.

Crystallographic Data of 10CN-P5: [C51 H29 N13]; *Mr* = 823.87; T = 149.99 K; triclinic; space group P $\bar{1}$; *a* = 13.9003(17); *b* = 13.9234(16); *c* = 13.9234(16) Å; *α* = 78.58; *β* = 63.598(2); *γ* = 63.598(2); *V* = 2161.9(4) Å^3; Z = 2; *ρ*calcd = 1.266 g/cm^3; *μ*= 0.080 mm^{-1}; reflections collected 40087; unique reflections 7607; data/restraints/parameters 7607/23/581; *GOF* on *F2* 0.901; *Rint* for independent data 0.1300; final *R1* = 0.0655, *wR2* = 0.1480; R indices (all data) *R1* = 0.1494, *wR2* = 0.1715; largest diff. peak and hole: 0.467 and -0.283 eÅ^{-3}.





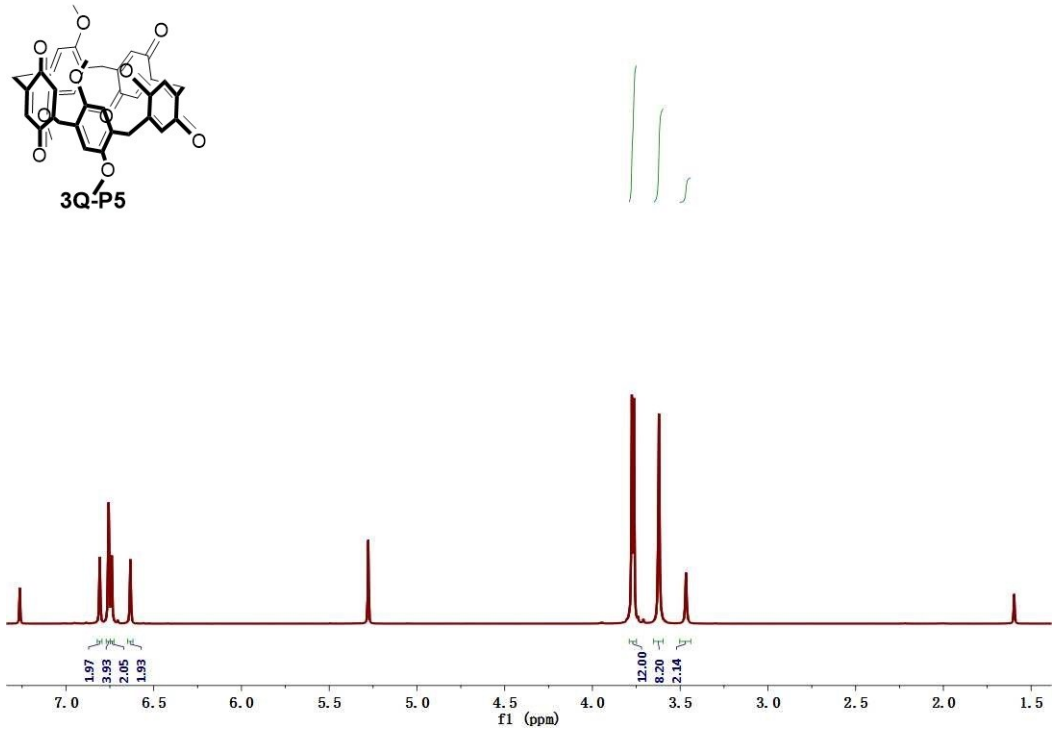


Fig. S2 ^{1}H NMR spectrum of 3Q-P5 in $CDCl_3$

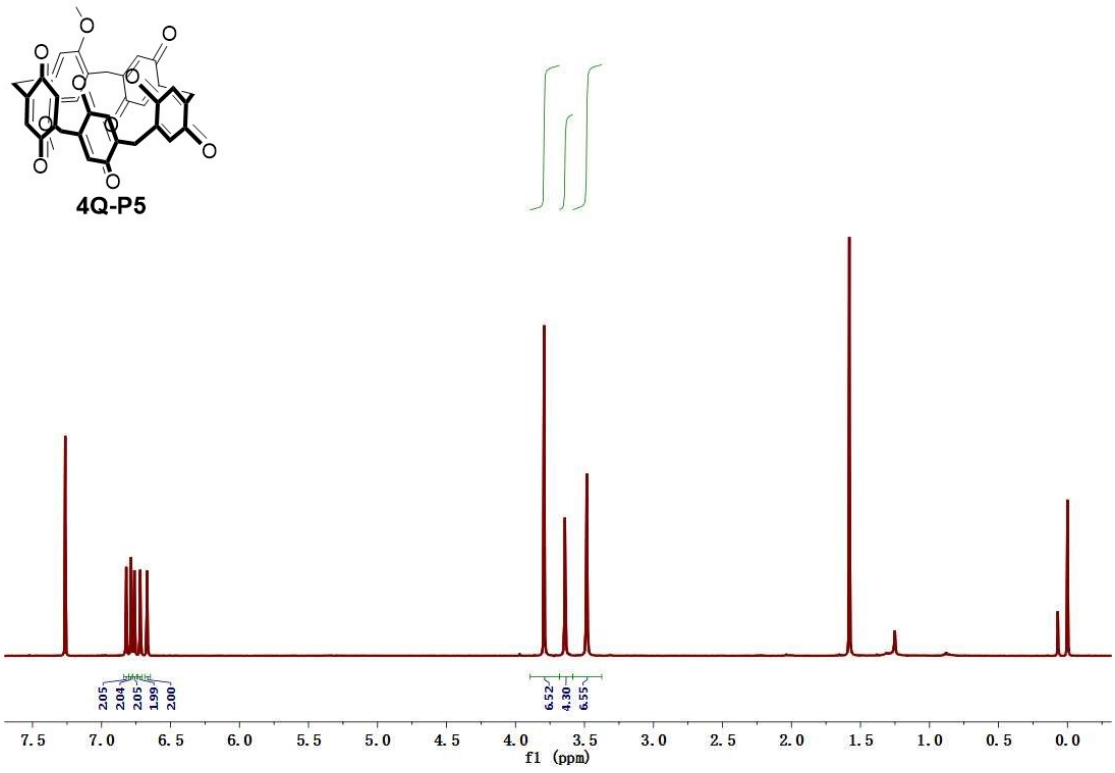


Fig. S3 ^{1}H NMR spectrum of 4Q-P5 in $CDCl_3$

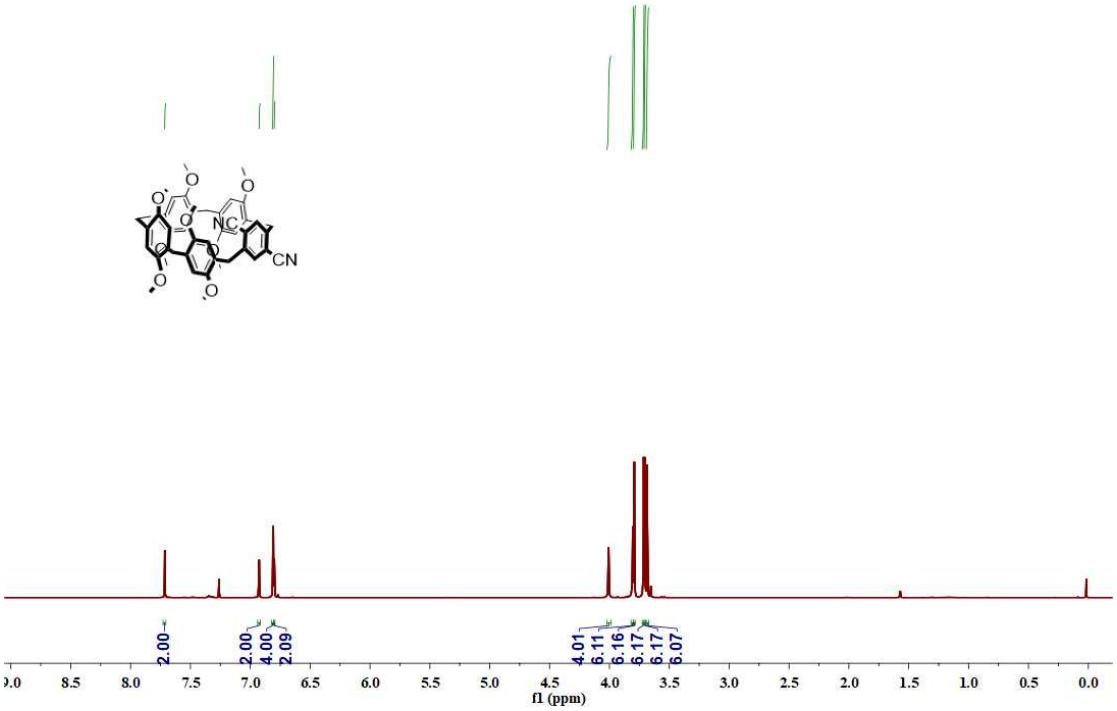


Fig. S4 ^{1}H NMR spectrum of 2CN-P5 in $CDCl_3$

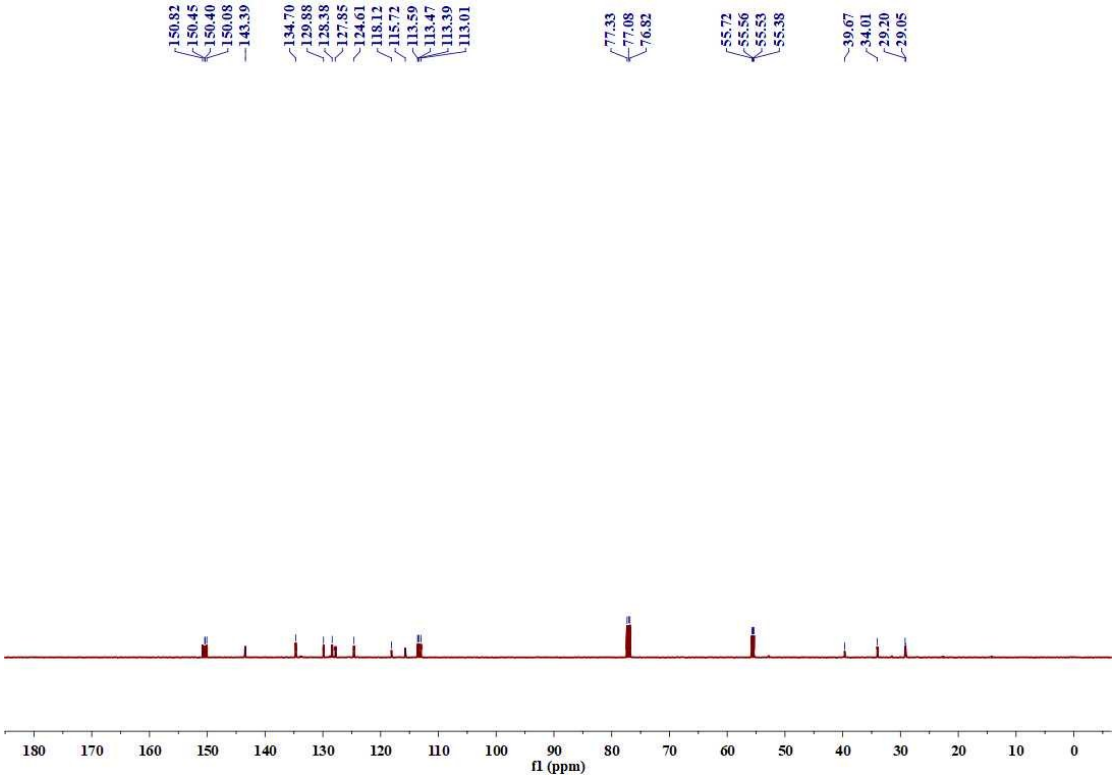


Fig. S5 ^{13}C NMR spectrum of 2CN-P5 in $CDCl_3$.

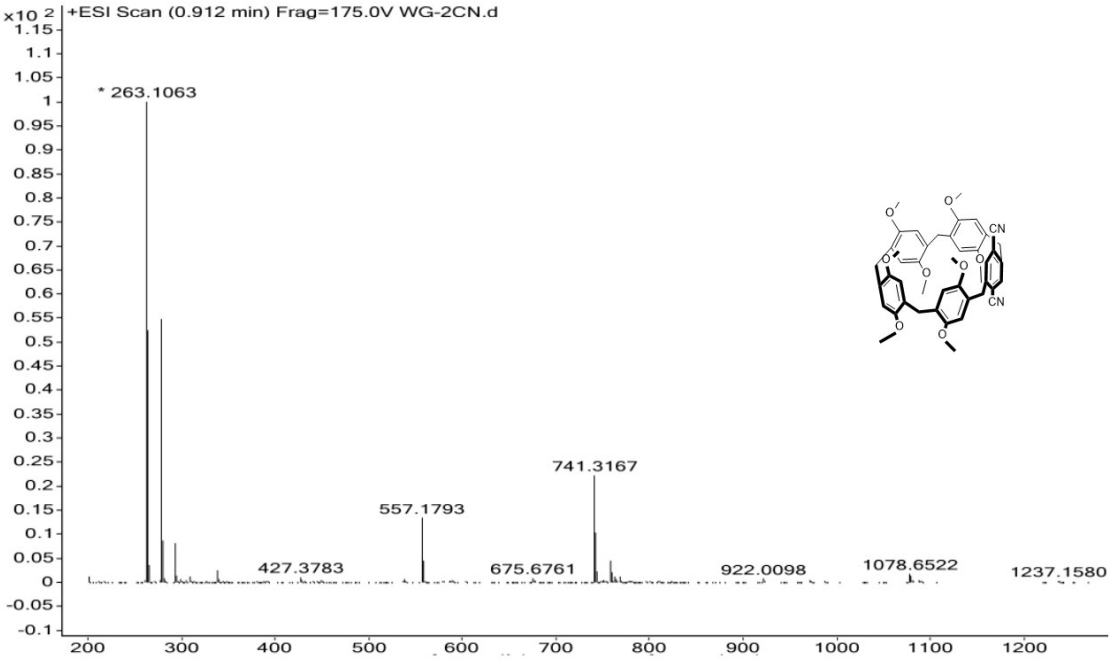


Fig. S6 HRMS (ESI) of 2CN-P5：calcd for $C_{46}H_{44}N_2O_8$[M+H$^+$] m/z 741.3177, found 741.3167.

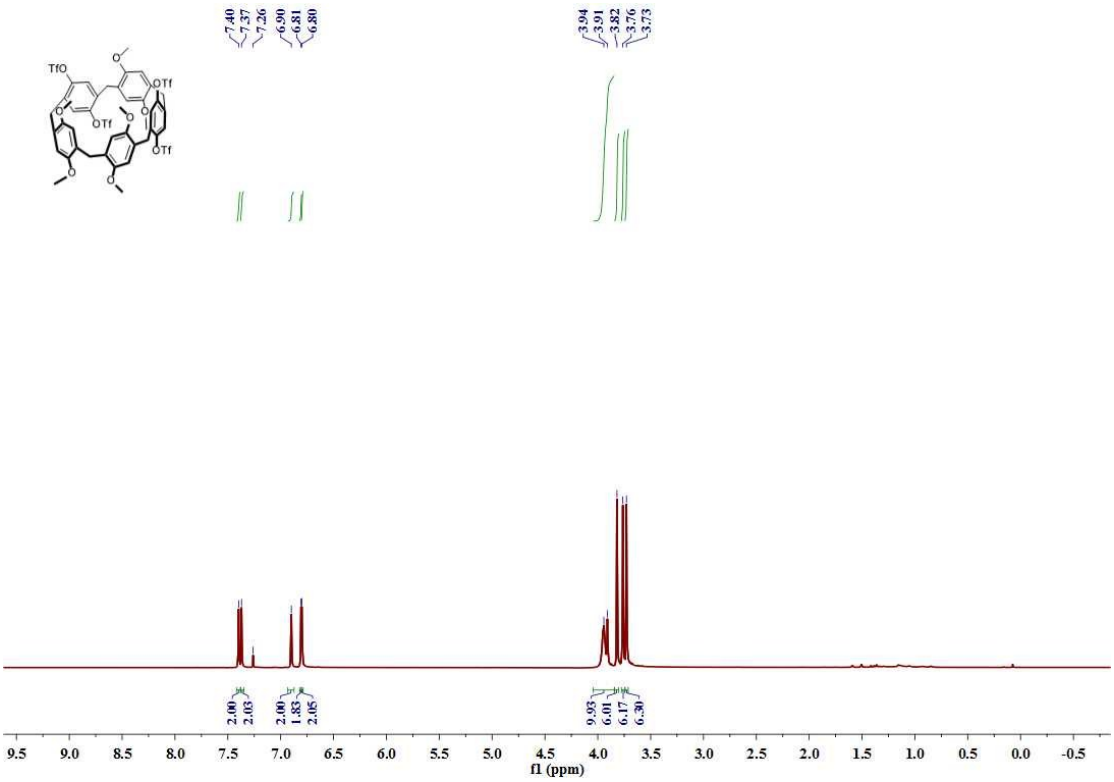


Fig. S7 ^{1}H NMR spectrum of 4OTf-P5 in $CDCl_3$.

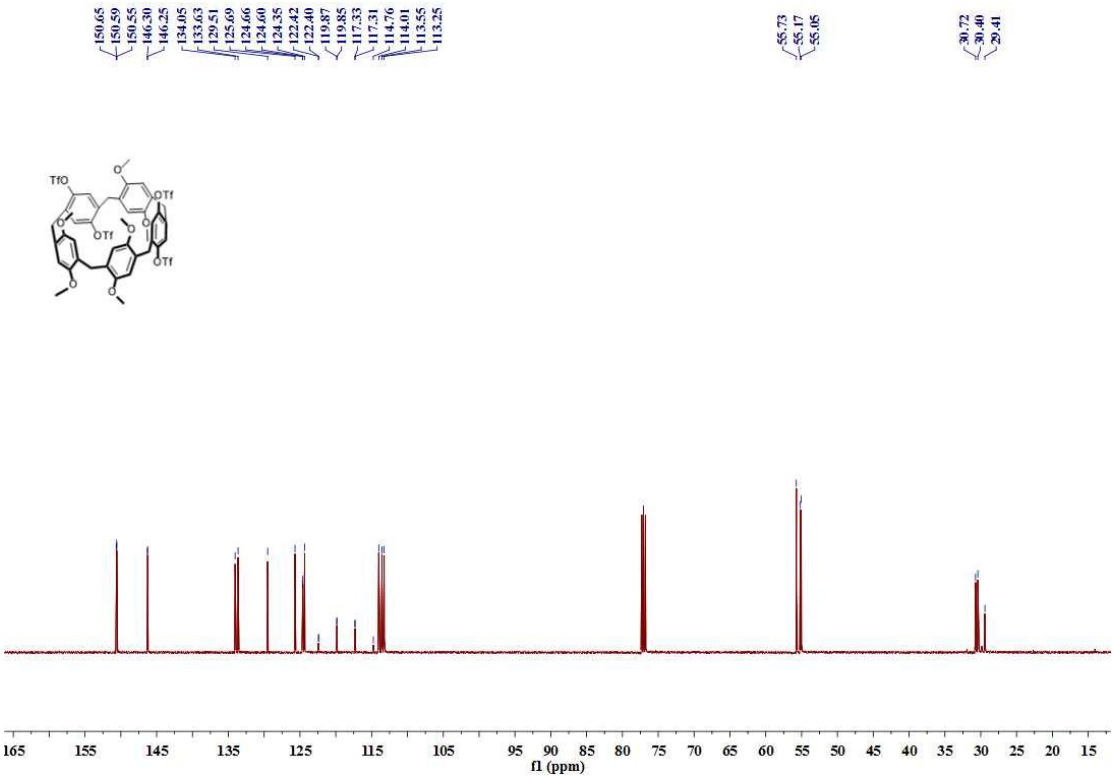


Fig. S8 ^{13}C NMR spectrum of 4OTf-P5 in $CDCl_3$.

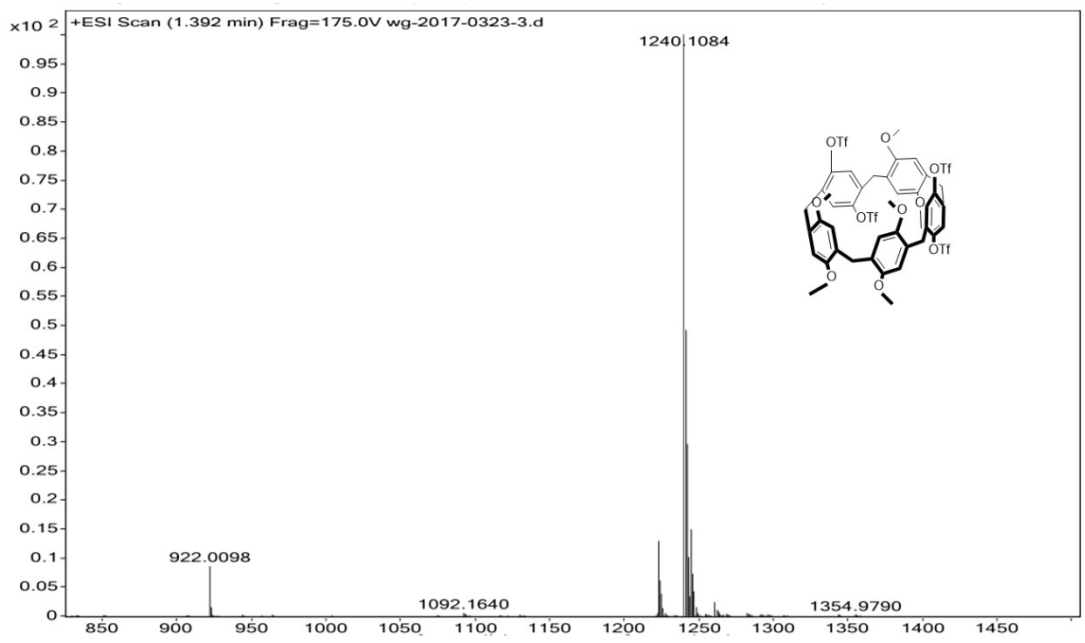


Fig. S9 HRMS(ESI) of 4OTf-P5: calcd for $C_{45}H_{36}F_{12}NO_{18}S_4[M+NH_4^+]$ m/z 1240.1088, found 1240.1084.

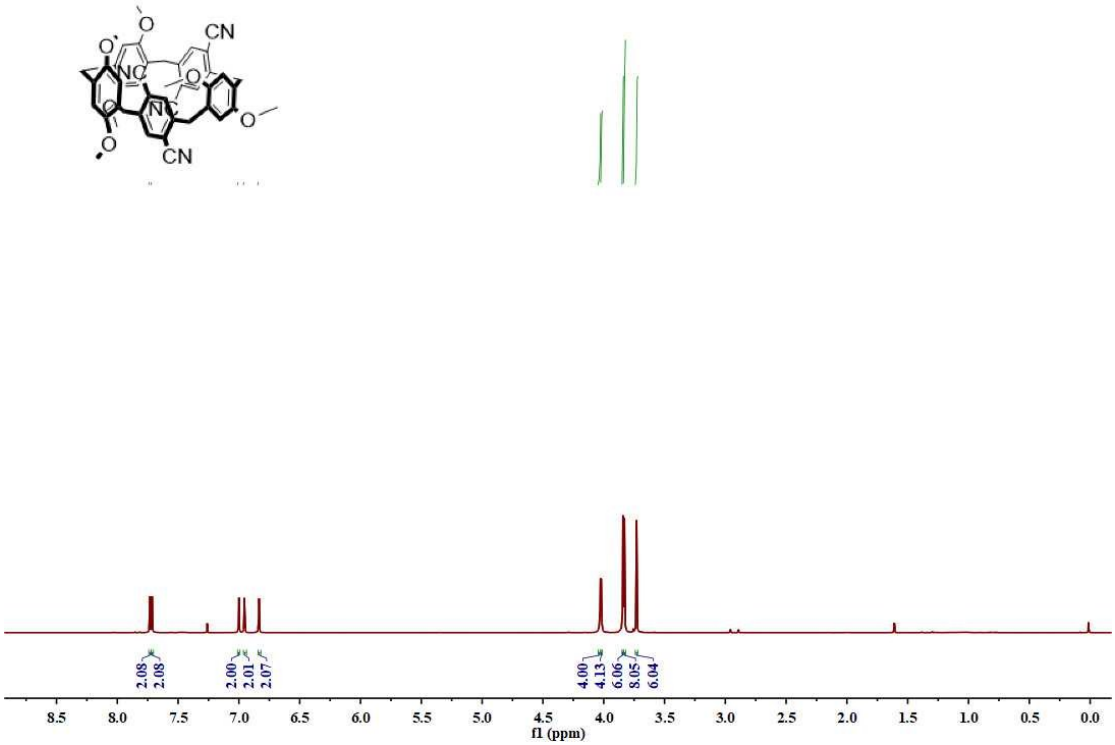


Fig. S10 ^{1}H NMR spectrum of 4CN-P5 in $CDCl_3$.

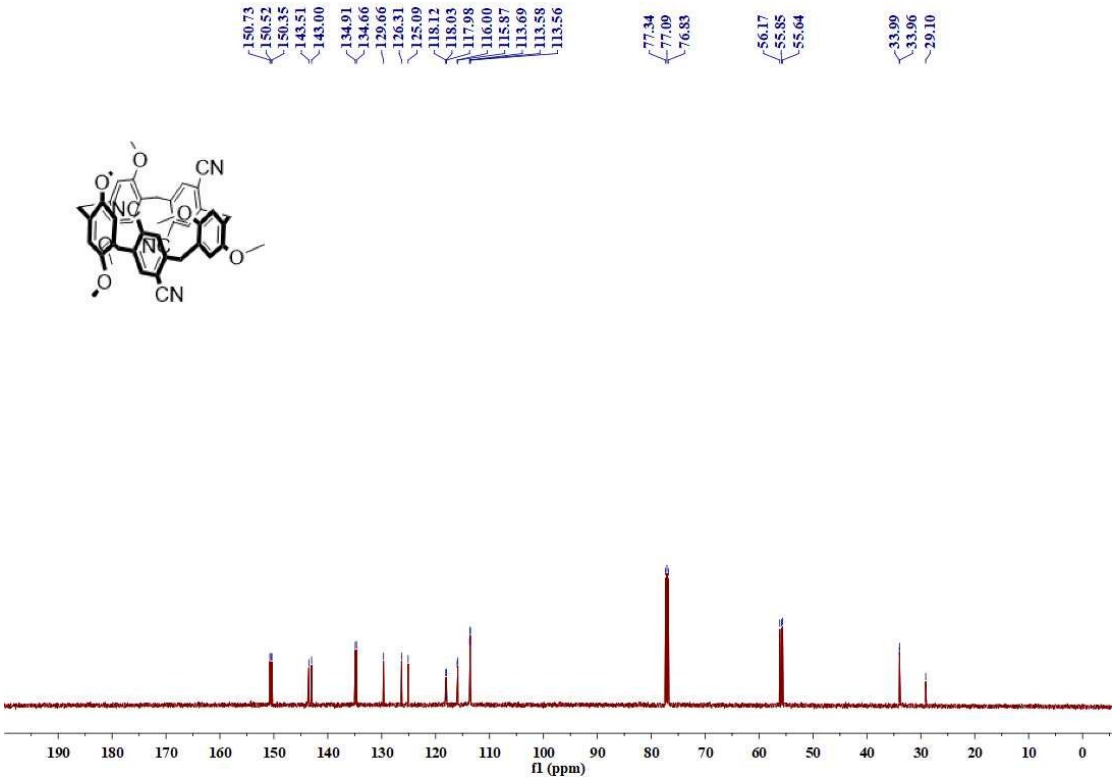


Fig. S11 ^{13}C NMR spectrum of 4CN-P5 in $CDCl_3$.

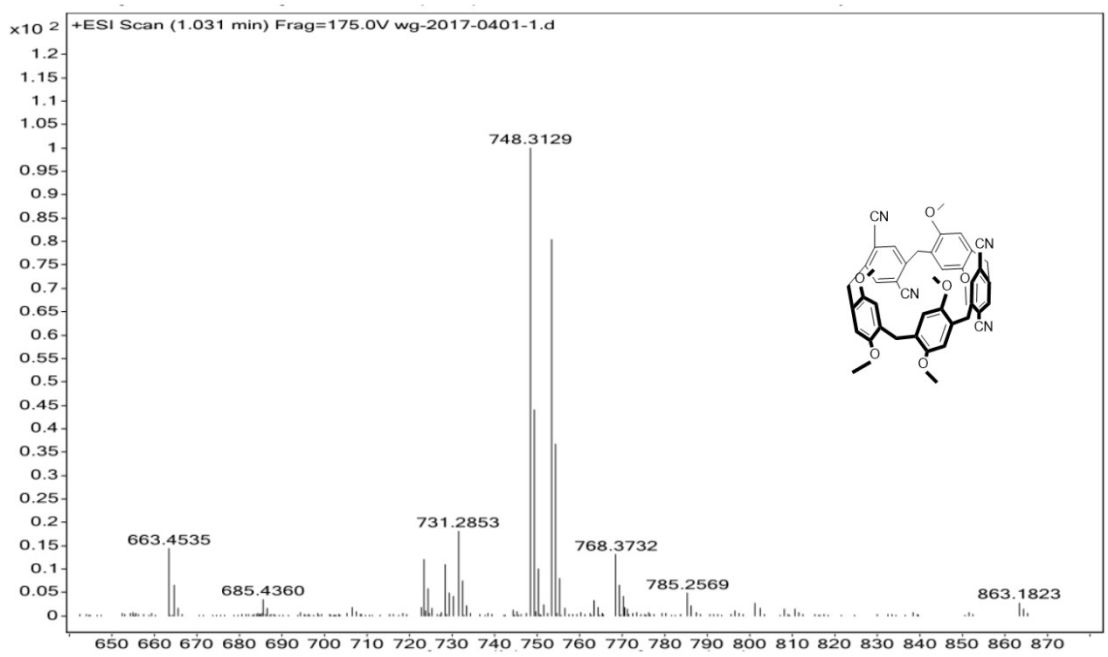


Fig. S12 HRMS(ESI) of 4CN-P5: calcd for $C_{45}H_{42}N_5O_6[M+NH_4^+]$ m/z 748.3130, found 748.3129.

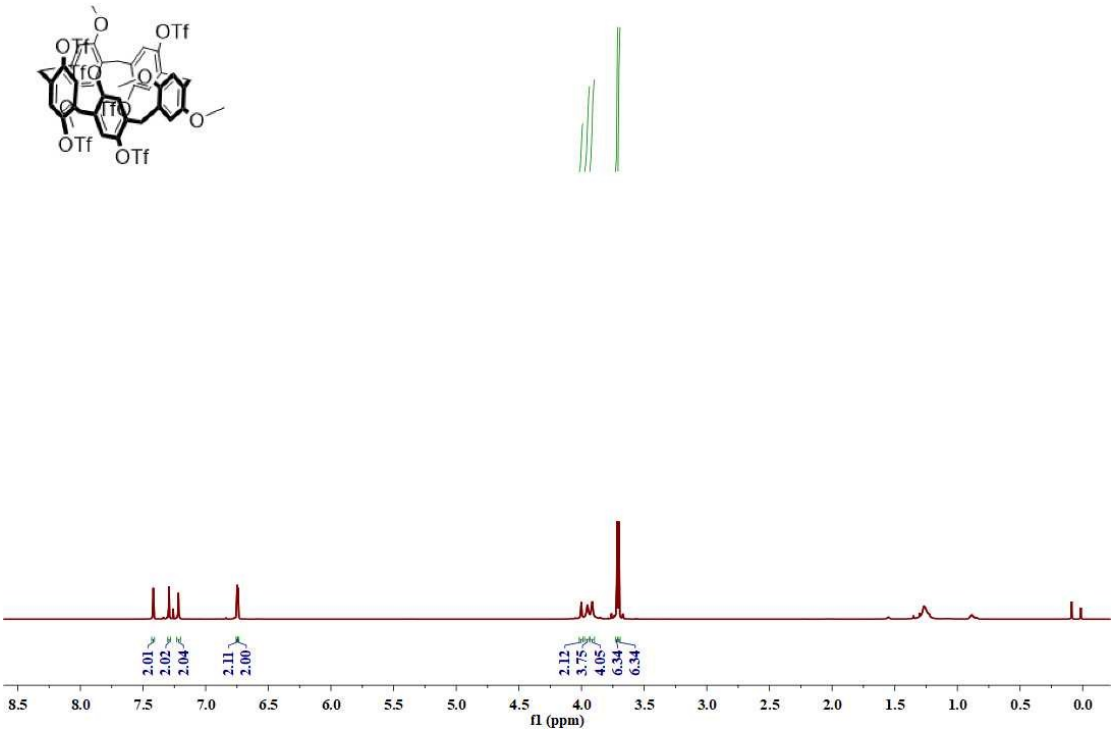


Fig. S13 ^{1}H NMR spectrum of 6OTf-P5 in $CDCl_3$.

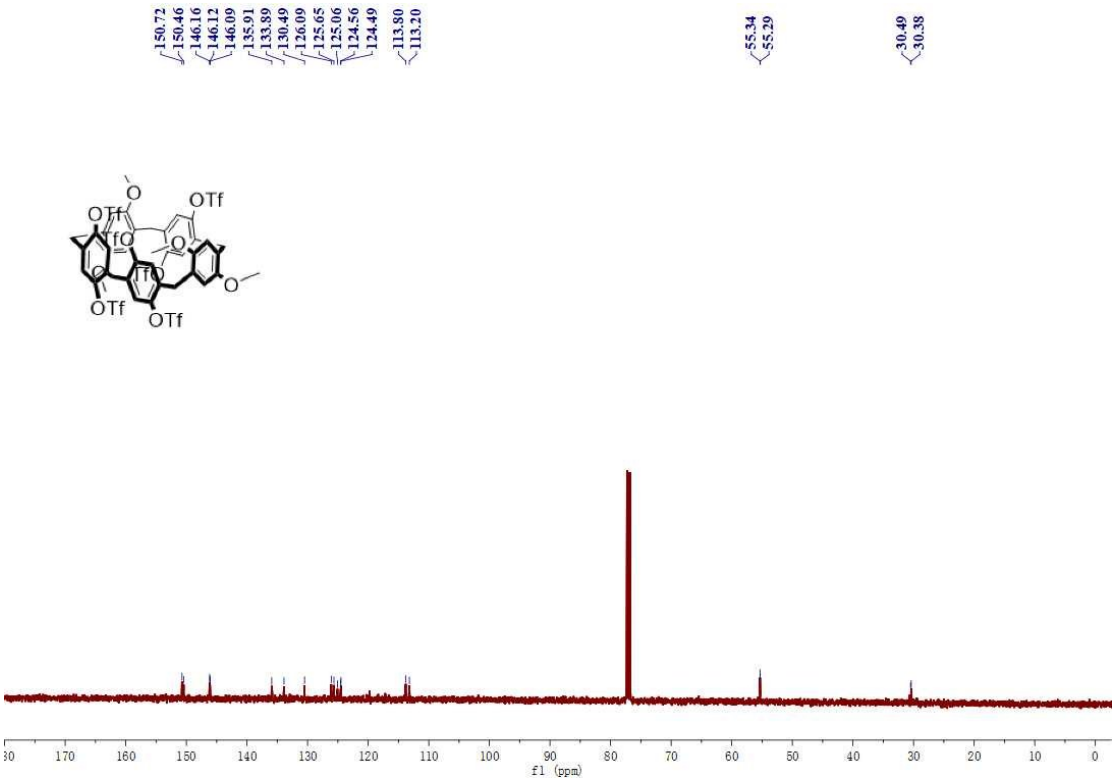


Fig. S14 ^{13}C NMR spectrum of 6OTf-P5 in $CDCl_3$.

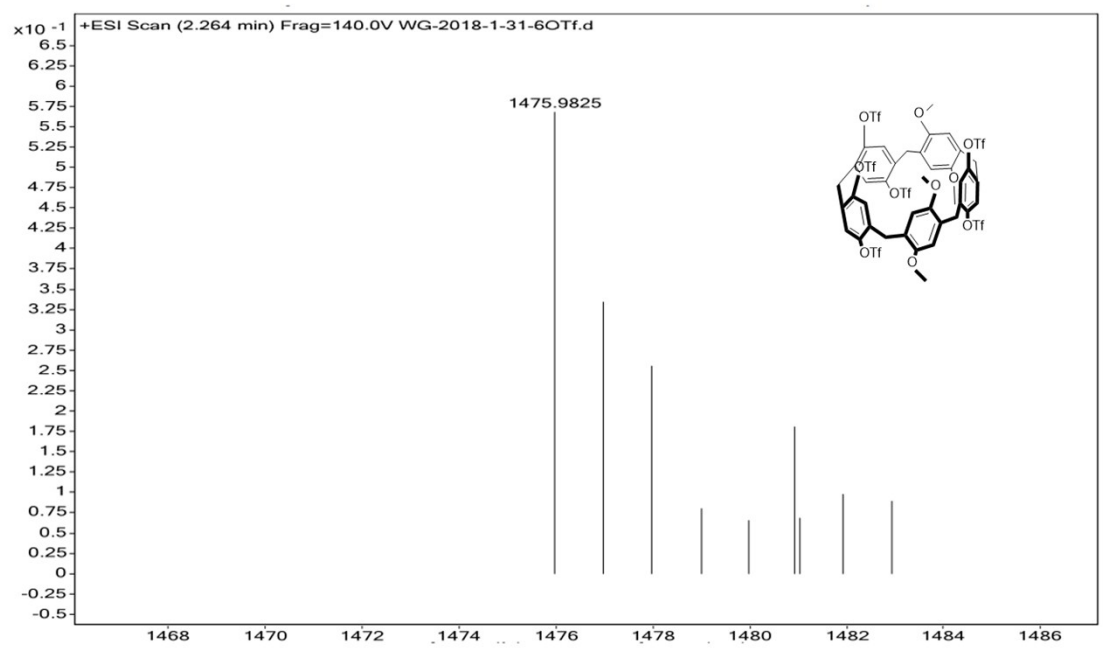


Fig. S15 HRMS (ESI) of 6OTf-P5: calcd for $C_{45}H_{36}F_{18}NO_{22}S_6[M+NH_4^+]$ m/z 1475.9760, found 1475.9825.

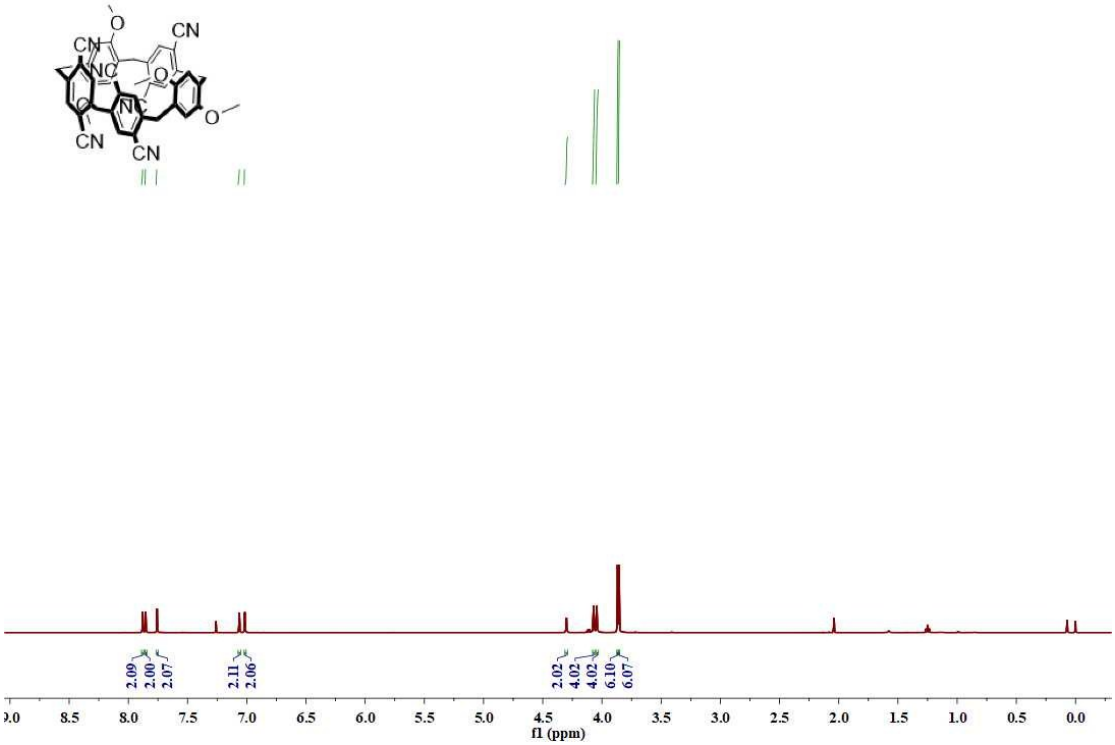


Fig. S16 ^{1}H NMR spectrum of 6CN-P5 in $CDCl_3$.

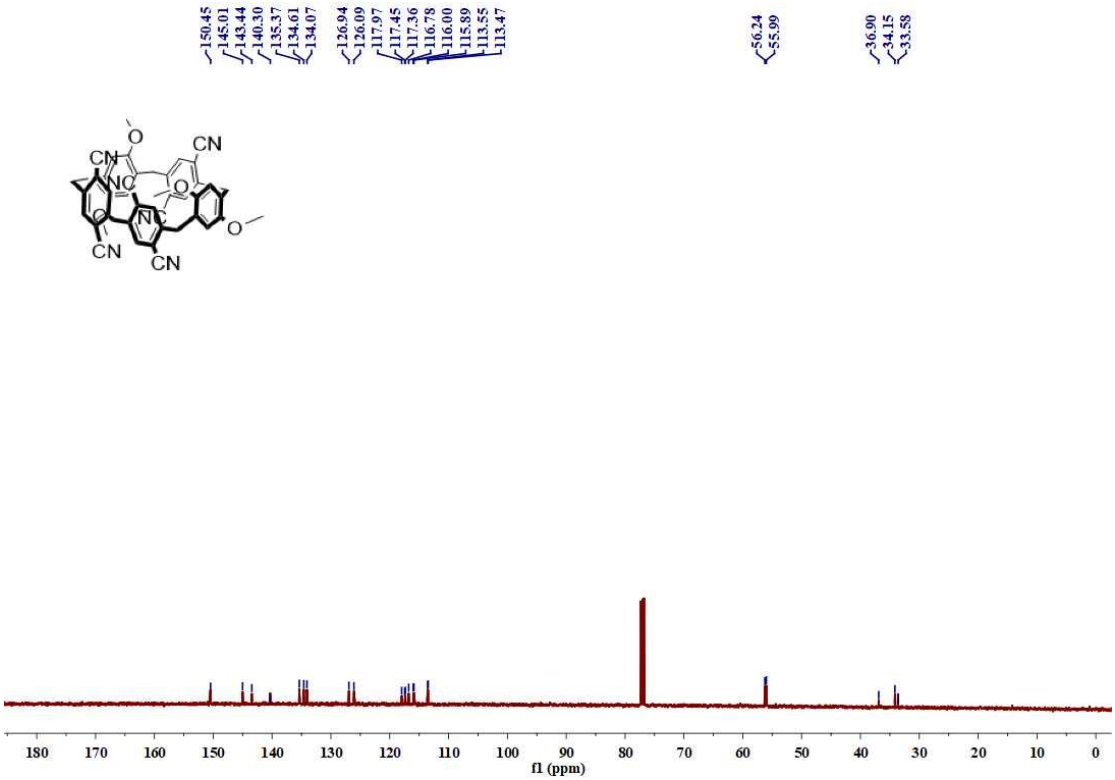


Fig. S17 ^{13}C NMR spectrum of 6CN-P5 in $CDCl_3$.

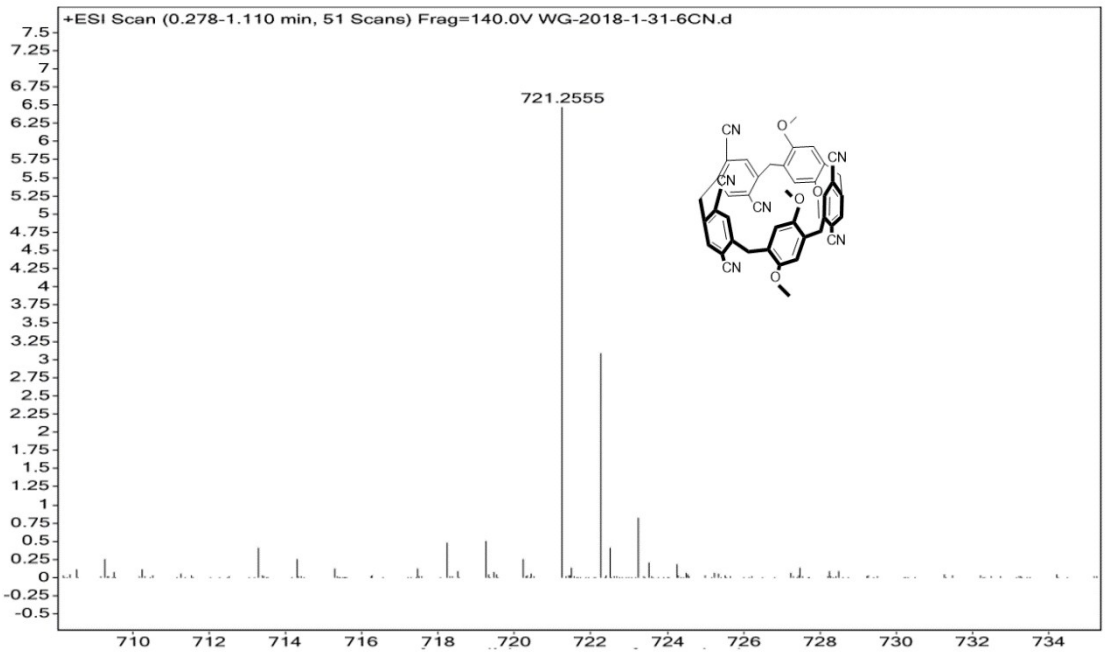


Fig. S18 HRMS(ESI) of 6CN-P5: calcd for $C_{45}H_{33}N_6O_4[M+H^+]$ m/z 721.2558, found 721.2555.

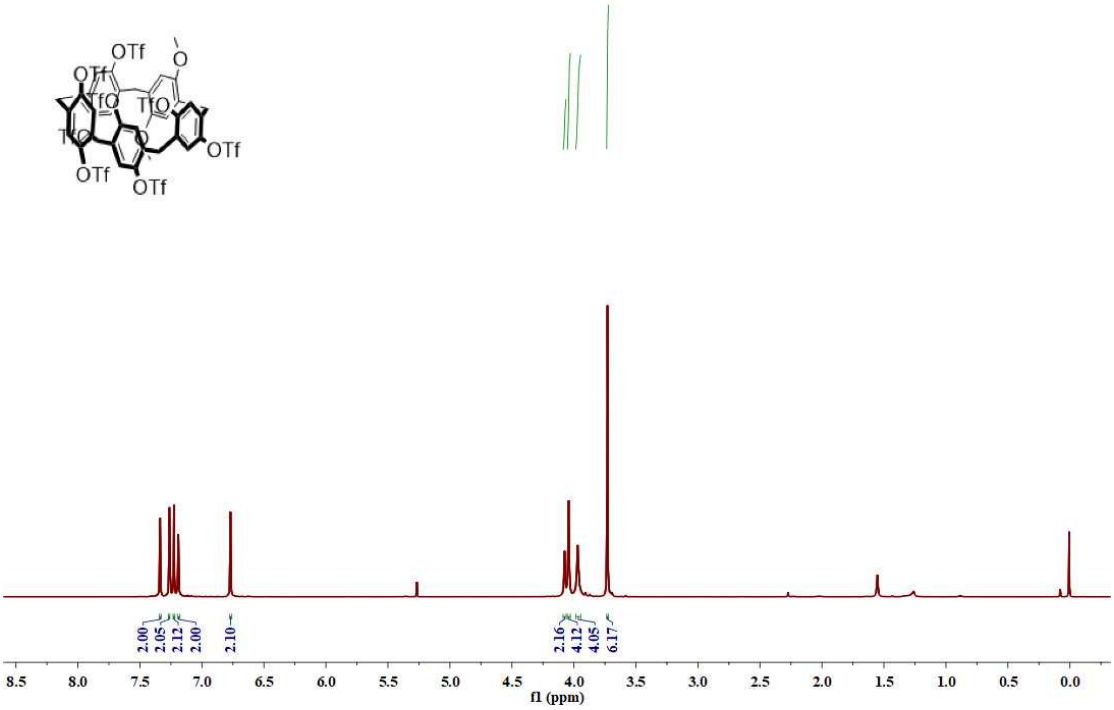


Fig. S19 ^{1}H NMR spectrum of 8OTf-P5 in $CDCl_3$.

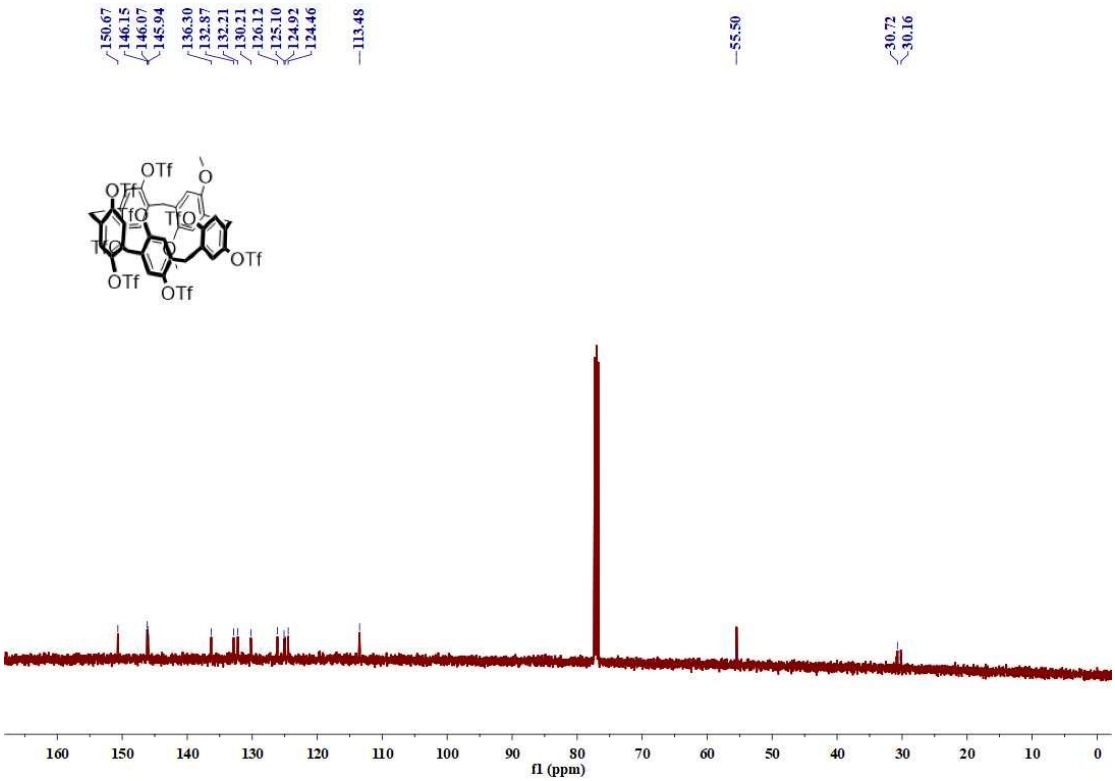


Fig. S20 ^{13}C NMR spectrum of 8OTf-P5 in $CDCl_3$.

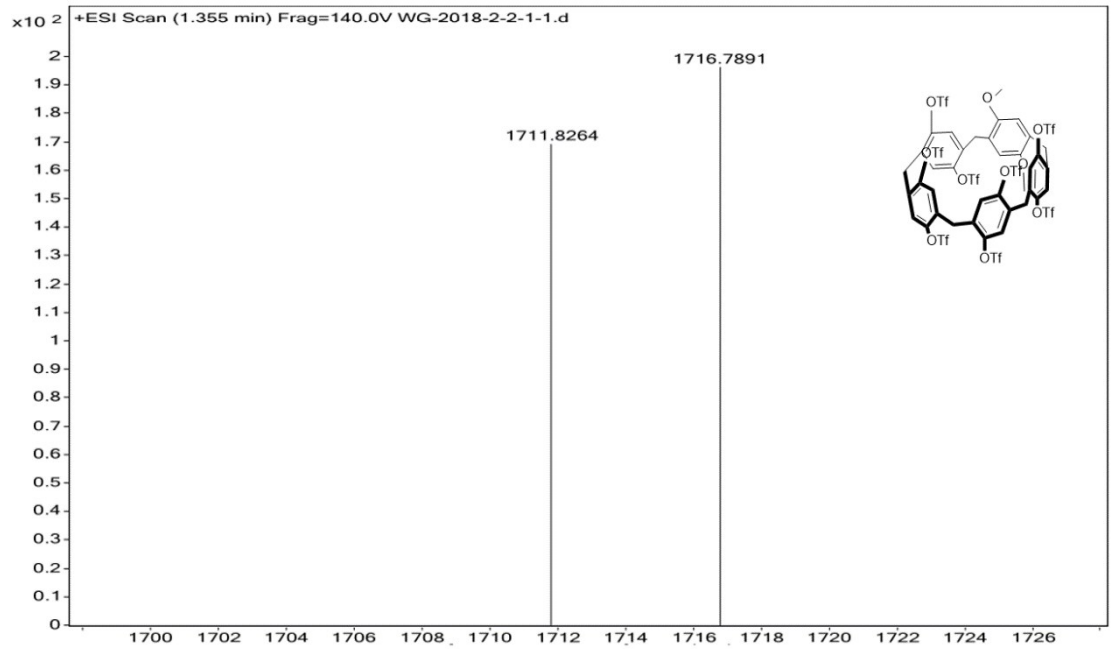


Fig. S21 HRMS(ESI) of 8OTf-P5: calcd for $C_{45}H_{30}F_{24}NO_{26}S_8[M+NH_4^+]$ m/z 1711.8433, found 1711.8264, calcd for $C_{45}H_{26}F_{24}O_{26}S_8Na[M+Na^+]$ m/z 1716.7987, found m/z1716.7891.

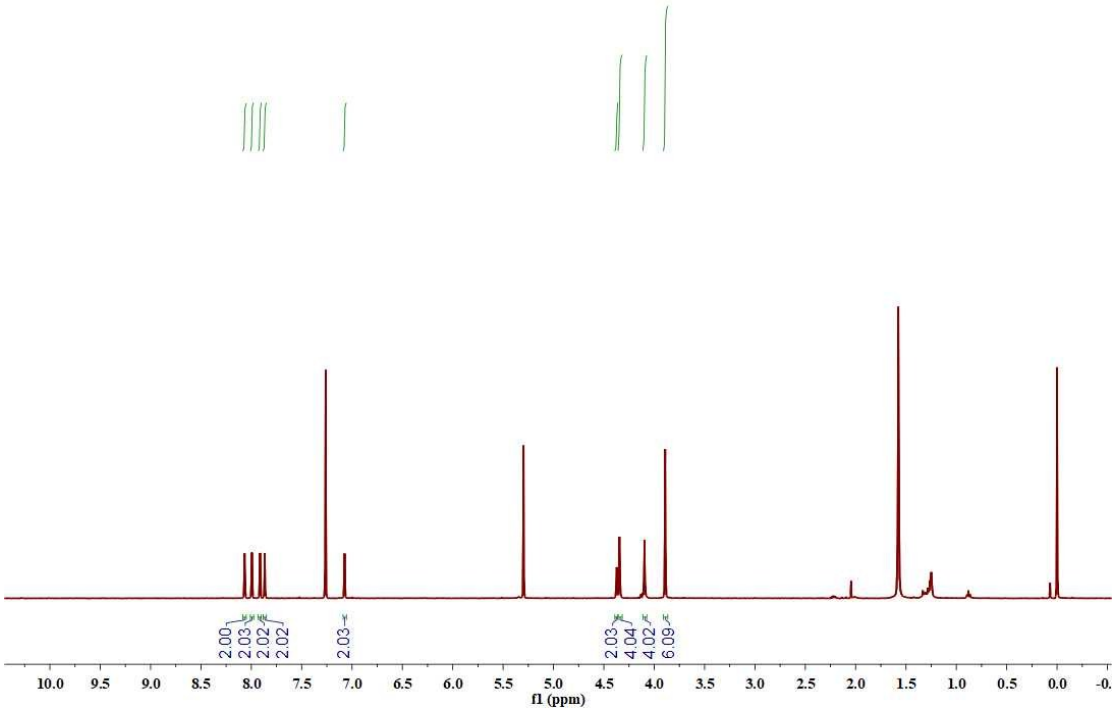


Fig. S22 ^{1}H NMR spectrum of 8CN-P5 in $CDCl_3$

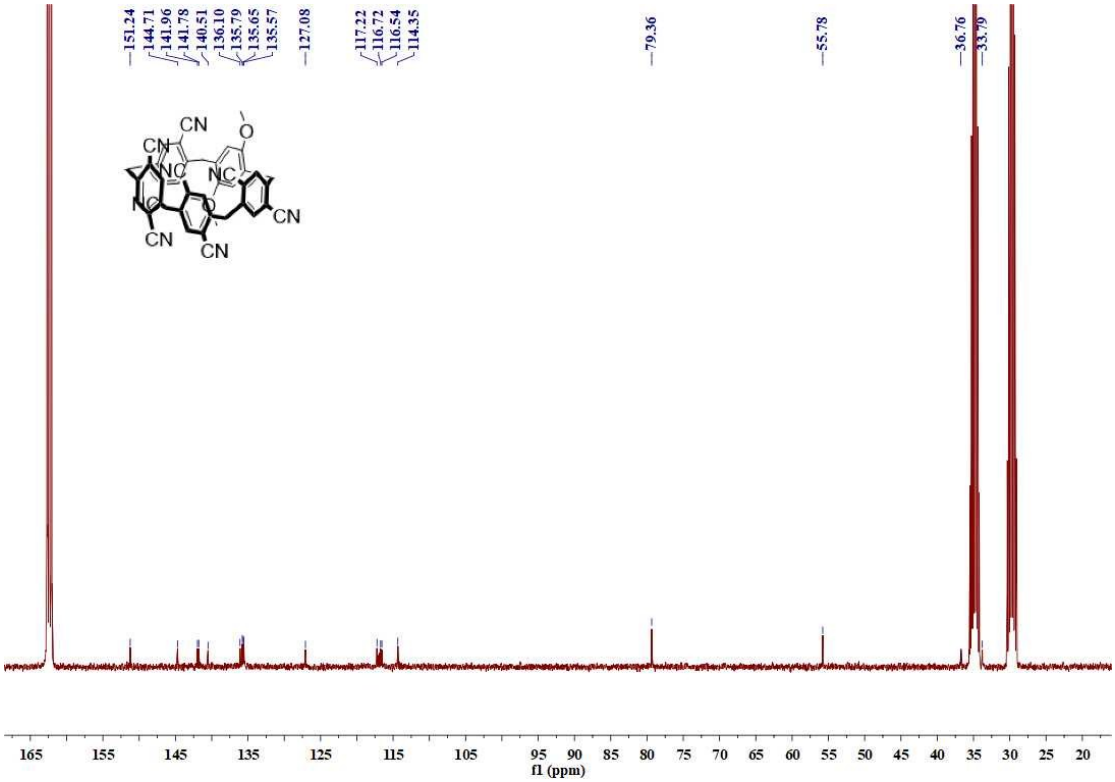


Fig. S23 ^{1}H NMR spectrum of 8CN-P5 in DMF

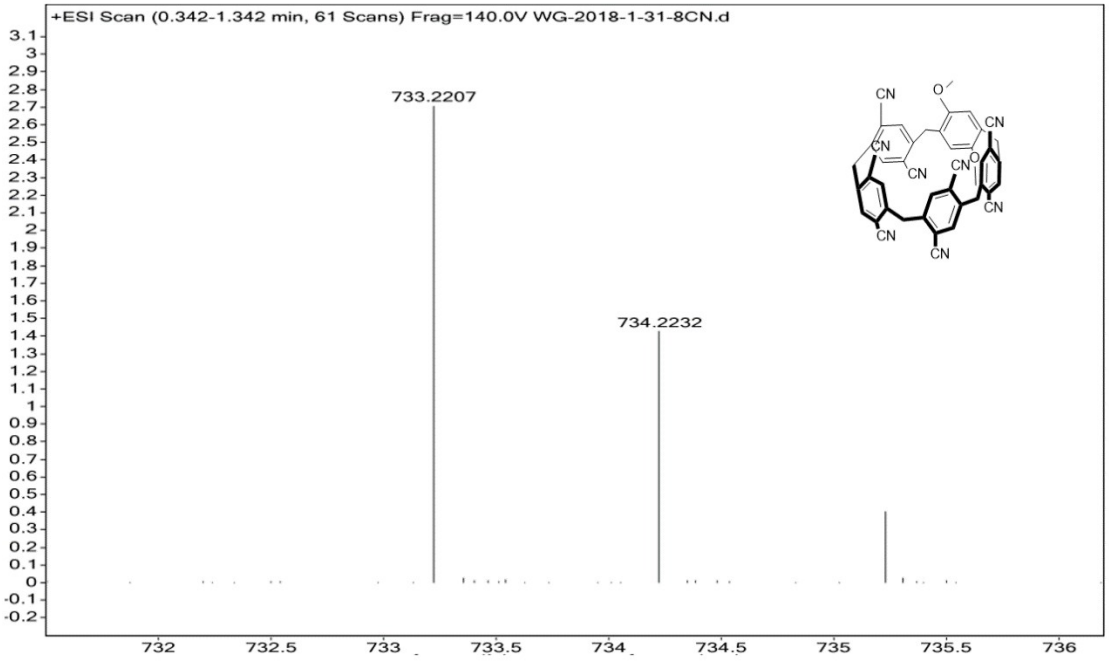


Fig. S24 HRMS(ESI) of 8CN-P5: calcd for $C_{45}H_{26}N_8O_2Na[M+Na^+]m/z$ 733.2071, found 733.2207.

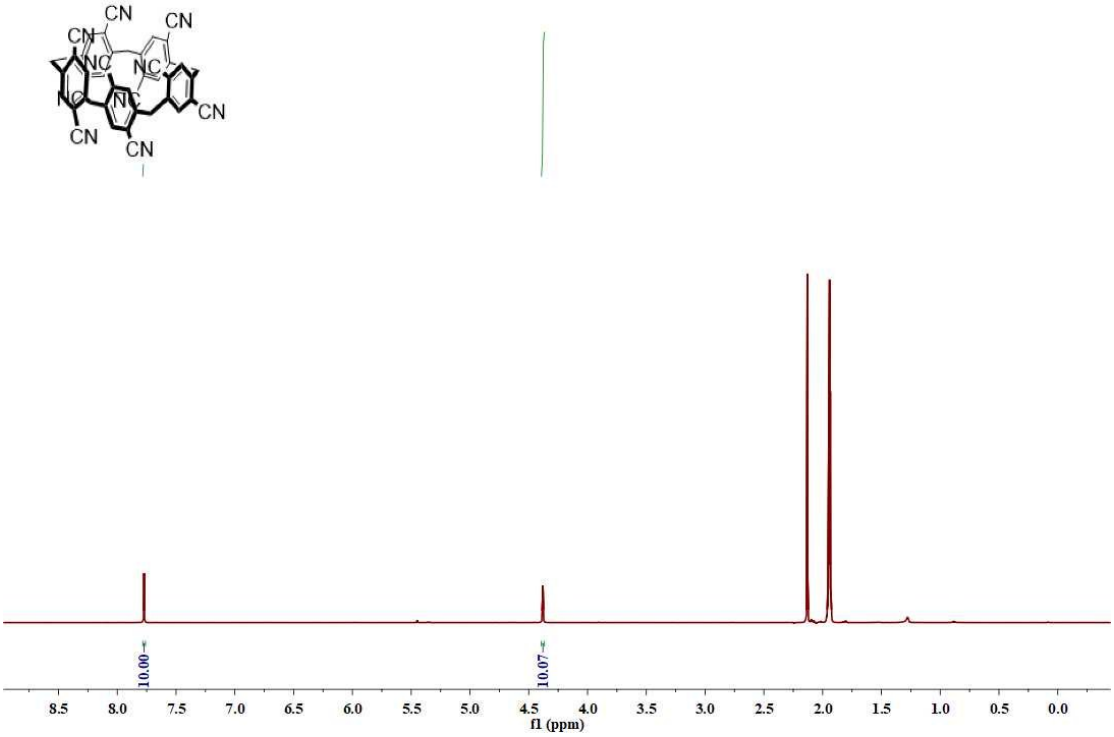


Fig. S25 ^1H NMR spectrum of 10CN-P5 in CD_3CN.

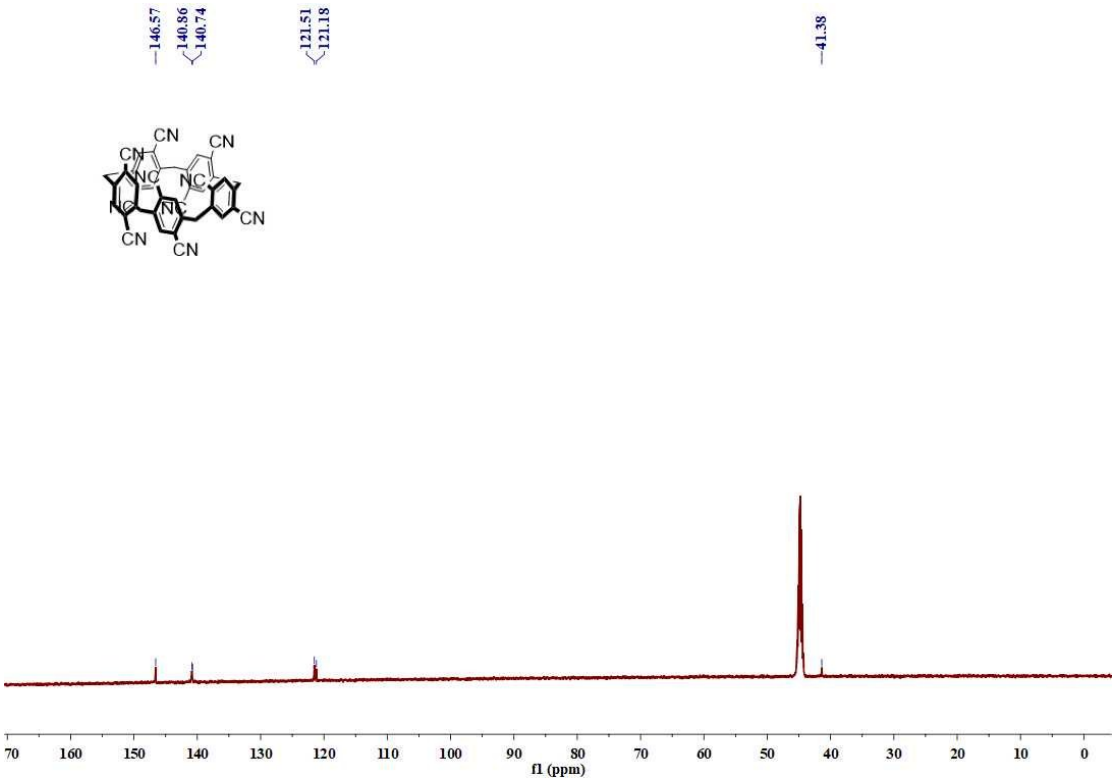


Fig. S26 ^{13}C NMR spectrum of 10CN-P5 in CDCN.

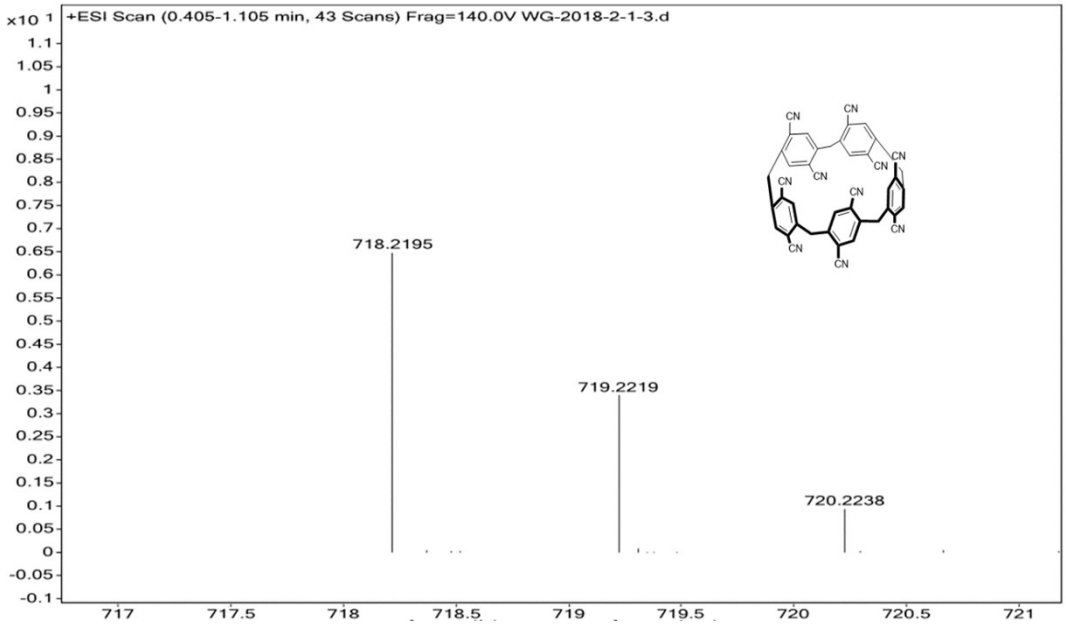


Fig. S27 HRMS(ESI) of 10CN-P5: calcd for $C_{45}H_{30}N_{11}[M+NH_4^+]$ m/z 718.2211, found 718.2195.

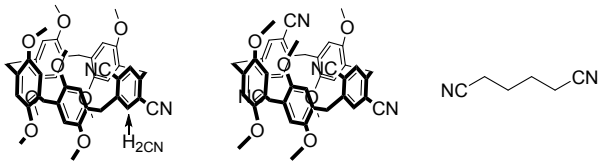
Host-guest complexation of 2nCN-P5 (n=1 or 2) and DB in $CDCl_3$

Stoichiometry and association constant determination for the complexation between 2nCN-P5 (n=1 or 2) and G

To determine the stoichiometry and association constant between 2**nCN-P5** and **DB**, ^{1}H NMR titration was carried out with solutions which had a constant concentration of 2**nCN-P5** (5.0 mM) and varying concentrations of **DB**. By a non-linear curve-fitting method, the association constant between the guest **DB** and host 2**nCN-P5** was calculated. The non-linear curve-fitting was based on the equation:[4]

$$\Delta\delta = (\Delta\delta_\infty/[\mathbf{2nCN\text{-}P5}]_0)\ (0.5[\mathbf{DB}]_0 + 0.5([\mathbf{2nCN\text{-}P5}]_0+1/Ka)-(0.5([\mathbf{DB}]_0^2+(2[\mathbf{DB}]_0(1/Ka-[\mathbf{2nCN\text{-}P5}]_0)) + (1/Ka + [\mathbf{2nCN\text{-}P5}]_0)^2)^{0.5}))$$

Where $\Delta\delta$ is the chemical shift change of H_{2nCN} on 2**nCN-P5** at $[\mathbf{DB}]_0$, $\Delta\delta_\infty$ is the chemical shift change of H_{2nCN} when **2nCN-P5** is completely complexed, $[2\mathbf{nCN\text{-}P5}]_0$ is the fixed initial concentration of 2**nCN-P5**, and $[\mathbf{DB}]_0$ is the varying concentrations of guest (Fig. S29, Fig. S32).



2CN-P5 **4CN-P5** **DB**

Fig. S28 Chemical structures of **2CN-P5**, **4CN-P5** and **DB**

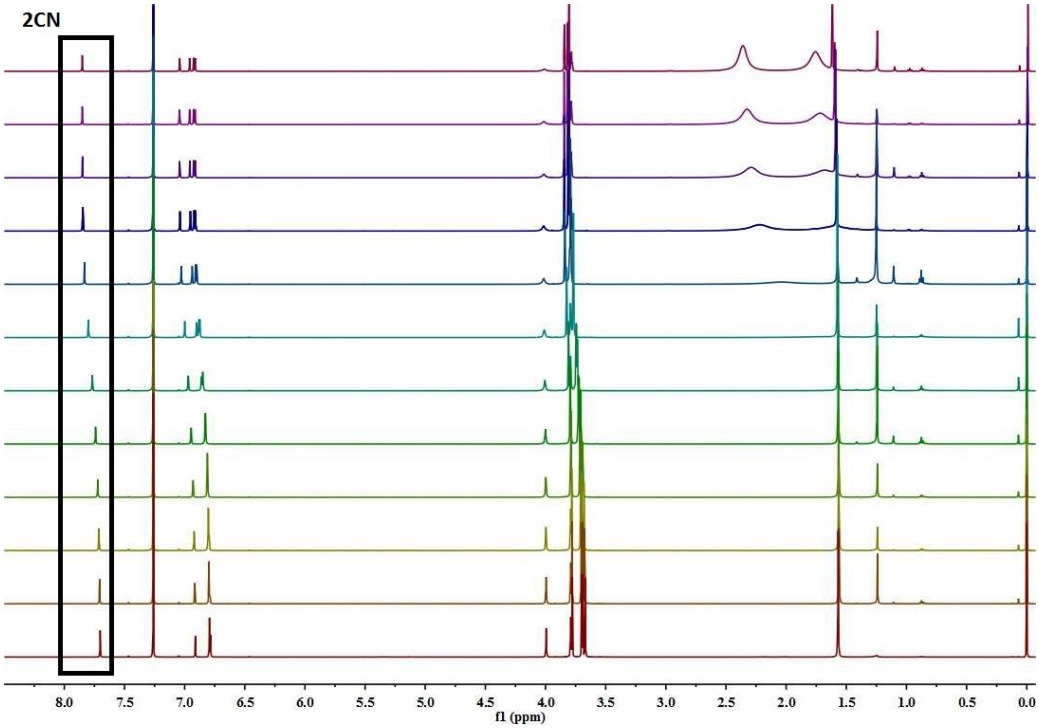


Fig. S29 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of **2CN-P5** at a concentration of 5.0 mM upon addition of **DB**. From bottom to top, the concentrations of **DB** were 0, 0.2, 0.6, 1.0, 2.0, 4.0, 8.0, 22.1, 44.1, 66.2, 88.2, 132.3 mM, respectively

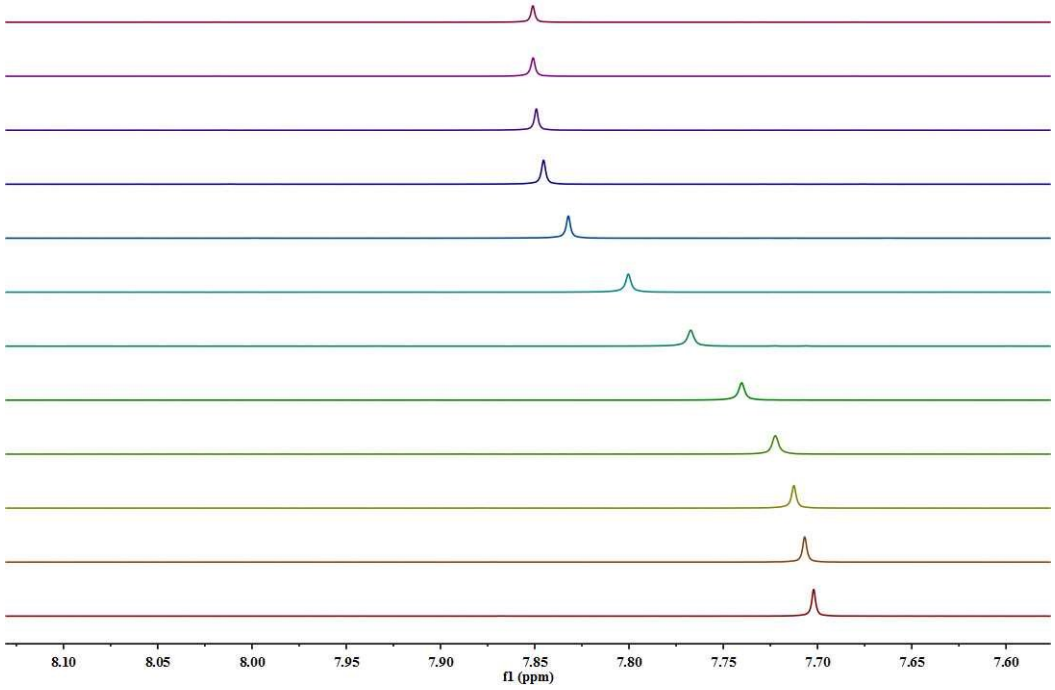


Fig. S30 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of H_{2CN} peak shift of **2CN-P5** at a concentration of 5.0 mM upon addition of **DB**. From bottom to top, the concentrations of **DB** were 0, 0.2, 0.6, 1.0, 2.0, 4.0, 8.0, 22.1, 44.1, 66.2, 88.2, 132.3 mM, respectively.

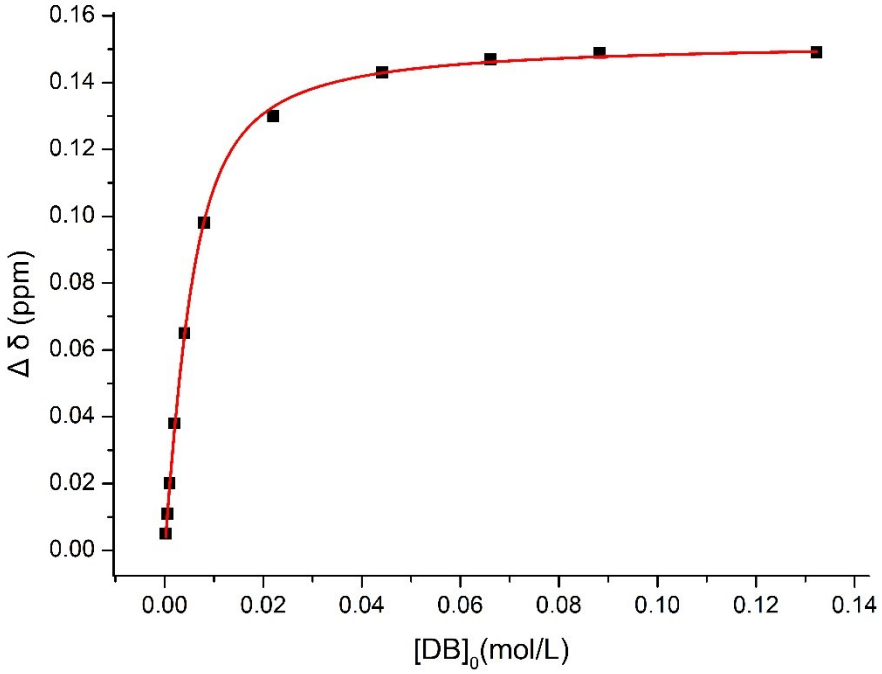


Fig. S21 The non-linear curve-fitting (NMR titrations, $\Delta\delta$ of H_{2CN}) for the complexation of **2CN-P5** (5.0 mM) with **DB** in $CDCl_3$ at 298 K. The concentrations of **DB** were 0, 0.2, 0.6, 1.0, 2.0, 4.0, 8.0, 22.1, 44.1, 66.2, 88.2, 132.3 mM, respectively. The *K*a value for **DB⊂2CN-P5** complex in $CDCl_3$ at 298 K is determined to be 383.5 ± 16.0 M^{-1} (Adj. R-Square: 0.99949).

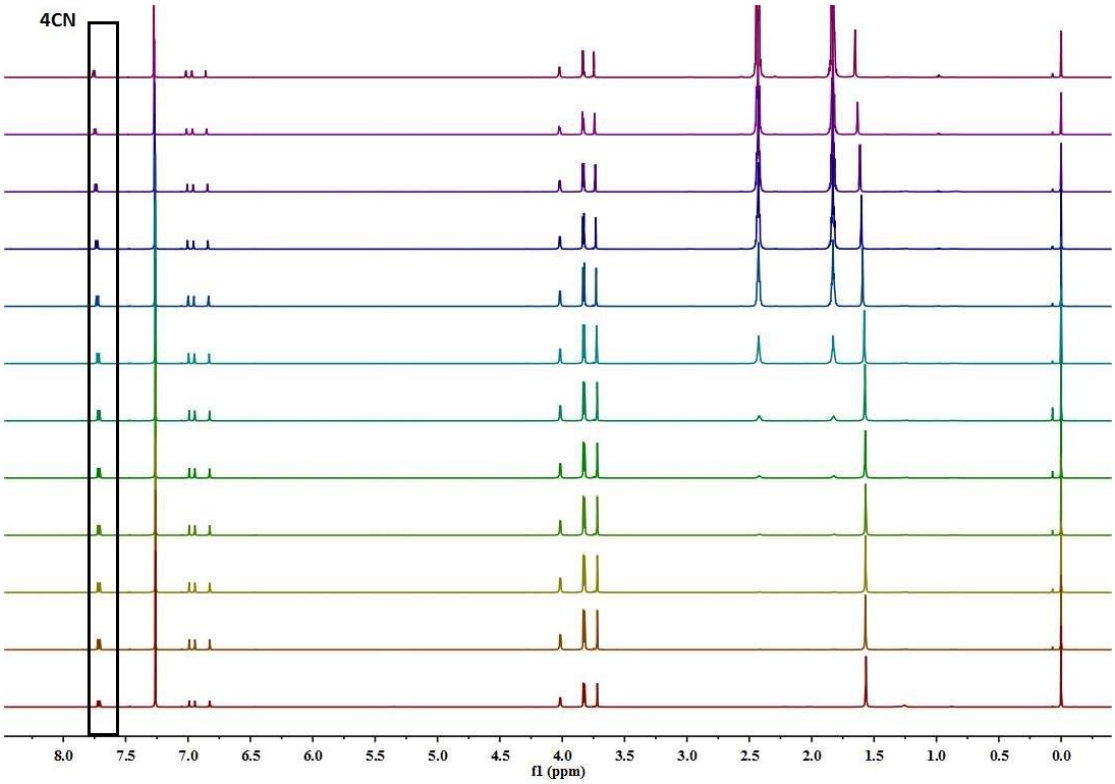


Fig. S32 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of **4CN-P5** at a concentration of 5.0 mM upon addition of **DB**. From bottom to top, the concentrations of **DB** were 0, 0.6, 1.0, 2.0, 4.0, 8.0, 22.1, 44.1, 66.2, 88.2, 132.3, 176.43 mM, respectively

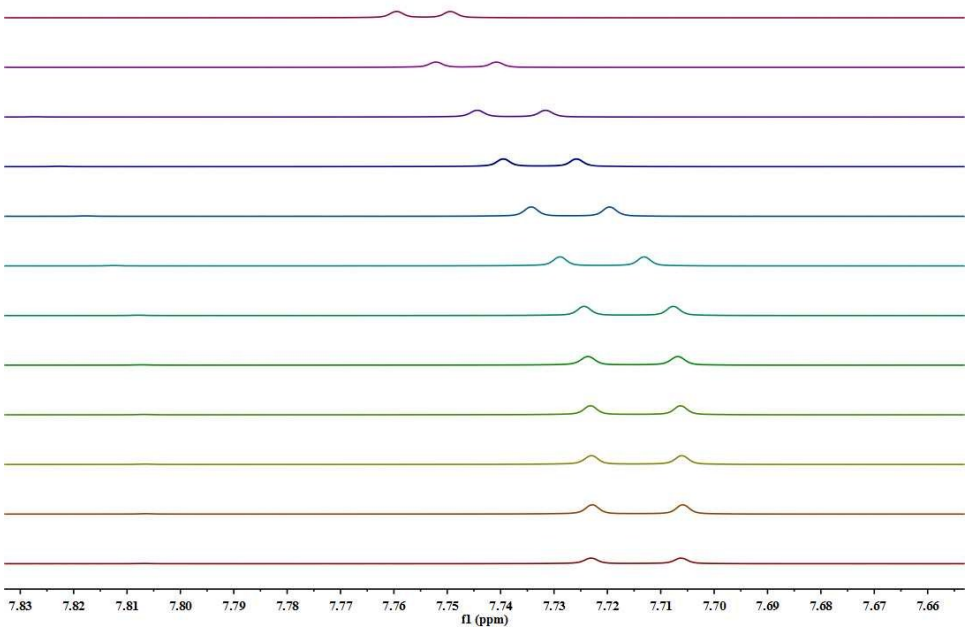


Fig. S33 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of H_{4CN} peak shift of **4CN-P5** at a concentration of 5.0 mM upon addition of **DB**. From bottom to top, the concentrations of **DB** were 0, 0.6, 1.0, 2.0, 4.0, 8.0, 22.1, 44.1, 66.2, 88.2, 132.3, 176.43 mM, respectively

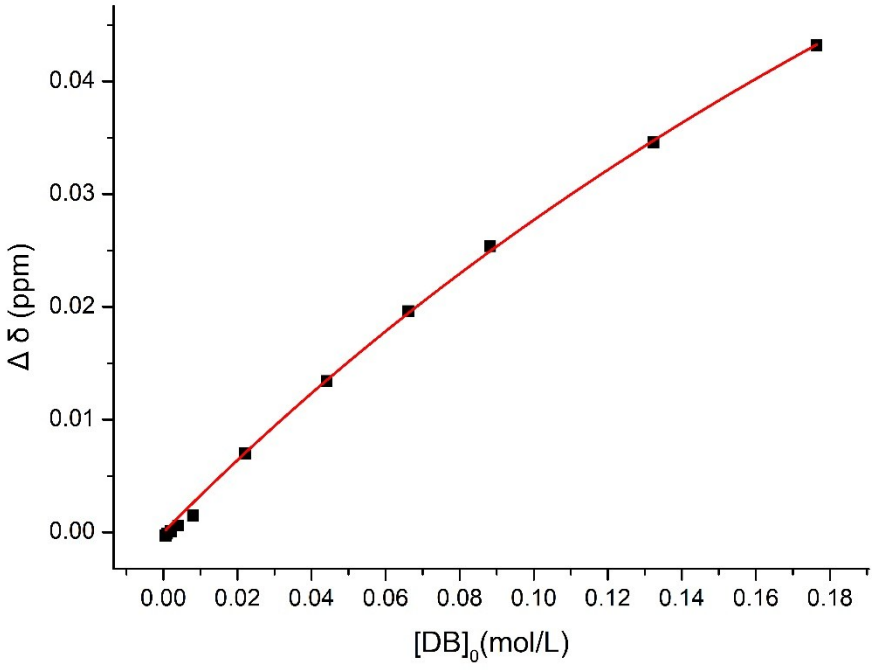


Fig. S34 The non-linear curve-fitting (NMR titrations, $\Delta\delta$ of H_{4CN}) for the complexation of **4CN-P5** (5.0 mM) with **DB** in $CDCl_3$ at 298 K. The concentrations of **DB** were 0, 0.6, 1.0, 2.0, 4.0, 8.0, 22.1, 44.1, 66.2, 88.2, 132.3, 176.43 mM, respectively. The *K*a value for **DB⊂ 2CN-P5** complex in $CDCl_3$ at 298 K is determined to be 2.1 ± 0.3 M^{-1} (Adj. R-Square: 0.9987).

Fig. S35 The MCR-3 microwave reactor.

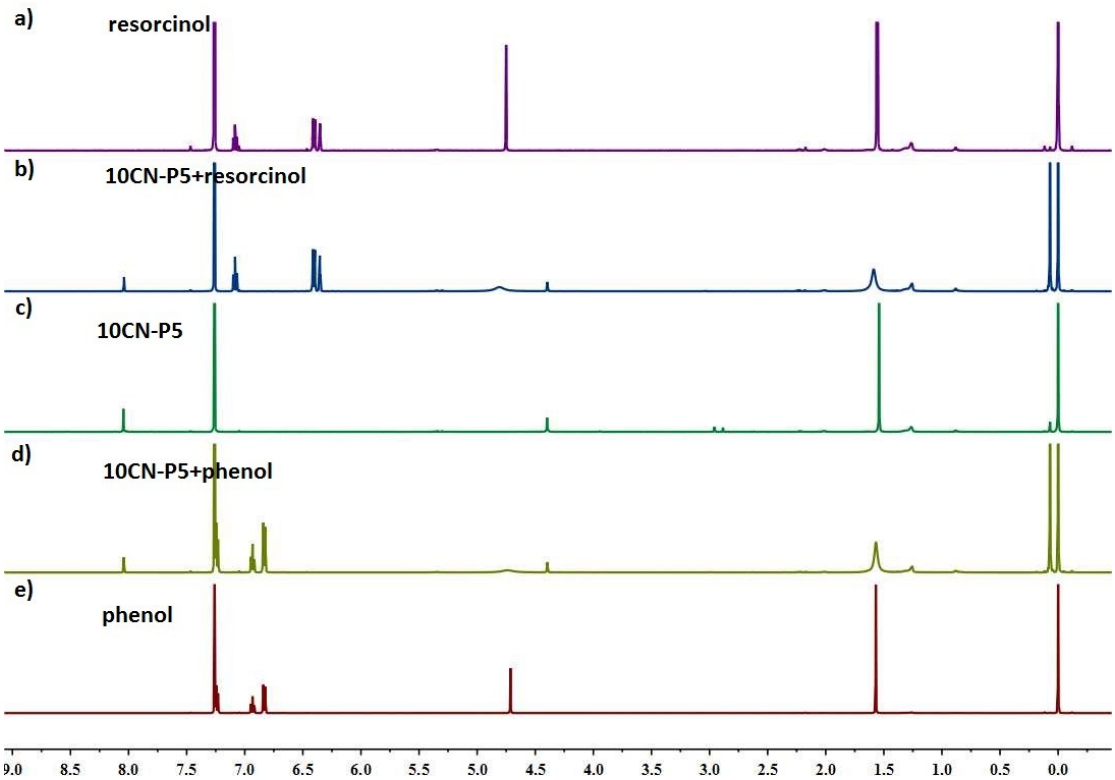


Fig. S36 ^{1}H NMR spectra (500 MHz, $CDCl_3$) of a) resorcinol, b) **10CN-P5** + resorcinol, c) **10CN-P5**, d) **10CN-P5** + phenol and d) phenol

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2 C. Xie, W. Hu, W. Hu, Y. A. Liu, J. Huo, J. Li, B. Jiang and K. Wen, *Chin. J. Chem.*, 2015, **33**, 379-383.

3 T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022-5023.

4 (a) K. A. Connors, *Binding Constants*, Wiley, New York, 1987; (b) R. P. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.,* 1996, **118**, 4931–4951; (c) Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang and H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1807−1816.