Electronic Supplementary Information

A pentipycene-based bis(crown ether) host: synthesis and its complexation with cyclobis(paraquat-*p*-phenylene)

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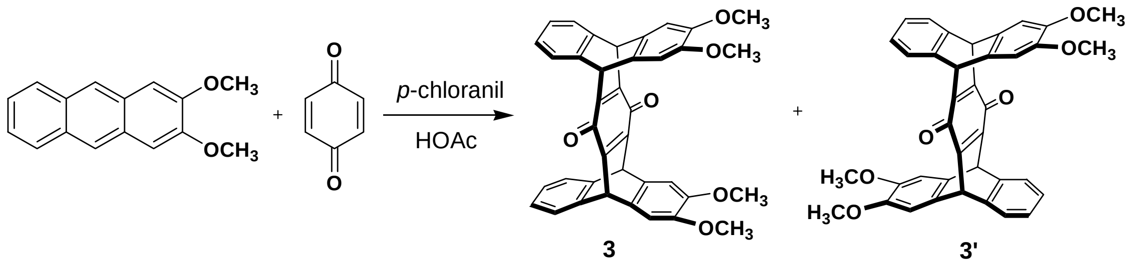
Contents

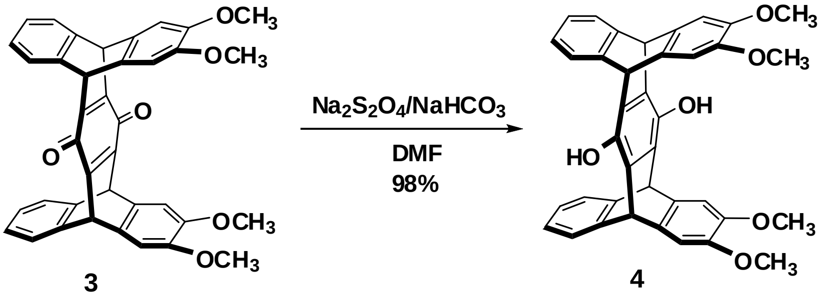
1. Synthetic procedure for host 1

General methods. Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^1H NMR, ^{13}C NMR and ^1H-^1H COSY spectra were recorded on a DMX300 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. UV spectrum was recorded on a UV-2041PC Shimadzu photometer. Materials obtained commercially were used without further purification. Cyclobis(paraquat-*p*-phenylene) tetra(hexafluorophosphate) **2** was prepared according to literature procedure.[S1] The association constant for the complex **1·2** was determined according to the literature method.[S2]

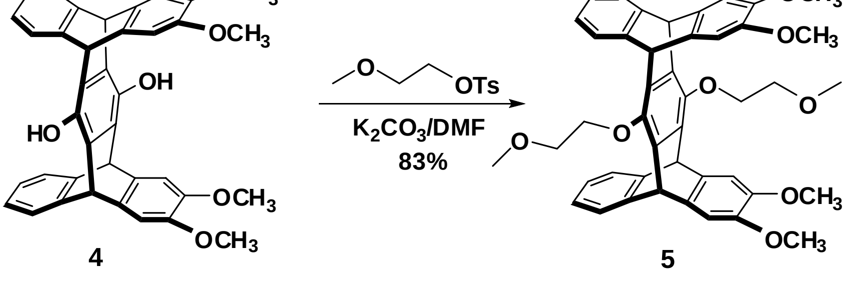


Compound **3**. A mixture of 2,3-dimethoxyanthracene (1.213 g, 5.1 mmol), benzoquinone (0.27 g, 2.5 mmol) and *p*-chloranil (1.24 g, 5.0 mmol) in HOAc (120 mL) was refluxed for 48 hr. The reaction mixture was concentrated under reduced pressure, and then resolved by CH_2Cl_2, washed by water for several times, after which the organic layer was dried over anhydrous sodium sulfate. The solvent was concentrated under reduced pressure, and the crude product was purified by column chromatography over silica gel (eluent: CH_2Cl_2 and then 50:1 CH_2Cl_2/ethyl acetate) to give **3** (0.62 g) in 41% yield and **3**′ (0.64 g) in 43% yield, respectively. Mp: >300 °C. IR: ν 1643 cm^{-1}. ^1H

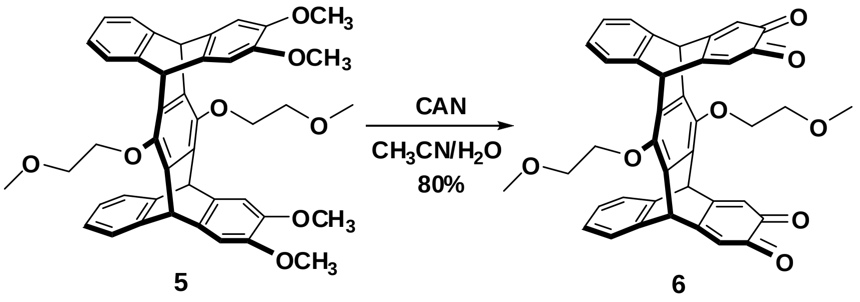
NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 12H), 5.67 (s, 4H), 6.91-6.98 (m, 8H), 7.31-7.36 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.2, 56.3, 109.4, 123.9, 125.3, 136.5, 144.2, 146.5, 151.6, 180.1. MALDI-TOF MS: *m/z* 580.3 $[M]^+$, 603.2 $[M+Na]^+$. Anal. Calcd for $C_{38}H_{28}O_6 \cdot 3/4CH_2Cl_2$: C, 72.23; H, 4.61. Found: C, 72.26; H, 4.76.



Compound **4**. $NaHCO_3$ (0.59 g, 7 mmol) and $Na_2S_2O_4$ (5.7 g, 33 mmol) were added to a solution of **3** (0.58 g, 1 mmol) in DMF (20 mL). The mixture was heated under Ar at 100 °C overnight. The cooled solution was poured into 300 mL of water, and the white precipitate was collected and dried under vacuum to afford **4** in 98% yield as white solid. ^1H NMR (300 MHz, $CDCl_3$): δ 3.67 (s, 12H), 5.58 (s, 4H), 6.86-6.89 (m, 8H), 7.24-7.26 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.3, 56.3, 109.1, 123.2, 124.9, 131.6, 138.4, 139.7, 145.9, 146.0. MALDI-TOF MS: *m/z* 582.2 $[M]^+$, 605.2 $[M+Na]^+$, 621.1 $[M+K]^+$.

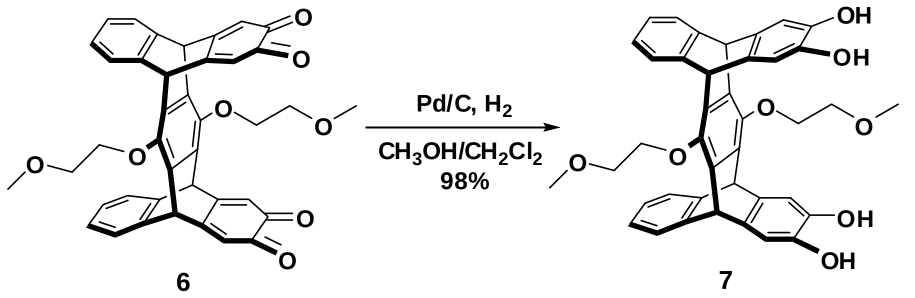


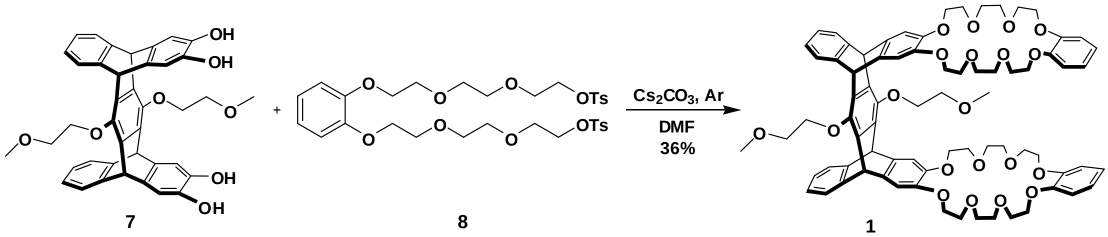
Compound **5**. A mixture of pentiptycene hydroquinone **4** (509 mg, 0.87 mmol), 2-methoxyethyl 4-methylbenzenesulfonate (431 mg, 1.87 mmol), and K_2CO_3 (972 mg, 7.04 mmol) in 50 mL of dry DMF was refluxed under Ar for 2 days. The mixture was filtered and the filtration was concentrated under reduced pressure, then 50mL CH_2Cl_2 was added and the solution was washed by diluted HCl, dried over anhydrous sodium sulfate, after which the solvent was concentrated under reduced pressure. Column chromatography using 20:1 CH_2Cl_2/ethyl acetate as eluent afforded **5** (580 mg, 83%) as a white solid. Mp: 138-139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.67 (s, 6H), 3.77 (s, 12H), 3.88-3.90 (t, 4H), 4.00-4.28 (t, 4H), 5.67 (s, 4H), 6.89-6.96 (m, 8H), 7.28-7.33 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.9, 56.4, 59.3, 71.9, 74.8, 109.1, 123.2, 125.0, 136.9, 138.2, 145.7, 146.0, 146.2. MALDI-TOF MS: *m/z* 698.2 $[M]^+$, 721.3 $[M+Na]^+$, 737.2 $[M+K]^+$. Anal. Calcd for $C_{44}H_{42}O_8 \cdot 0.5H_2O$: C, 74.66, H, 6.12. Found: C, 74.84; H, 6.36.



Compound **6**. A mixture of **5** (300 mg, 0.43 mmol) and CAN (1.43 g, 2.61 mmol) in acetonitrile (30 mL) and water (6 mL) was stirred at room temperature for 30 min. The reaction mixture was extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate and then concentrated under reduced pressure, the crude product was further purified by column chromatography over silica gel (eluent: 10:1 CH_2Cl_2/ethyl acetate) to give **6** (220 mg) in 80% yield as an orange solid. Mp: >300 °C. IR: ν 1644 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63 (s, 6H), 3.86-3.87 (t, 4H), 4.07

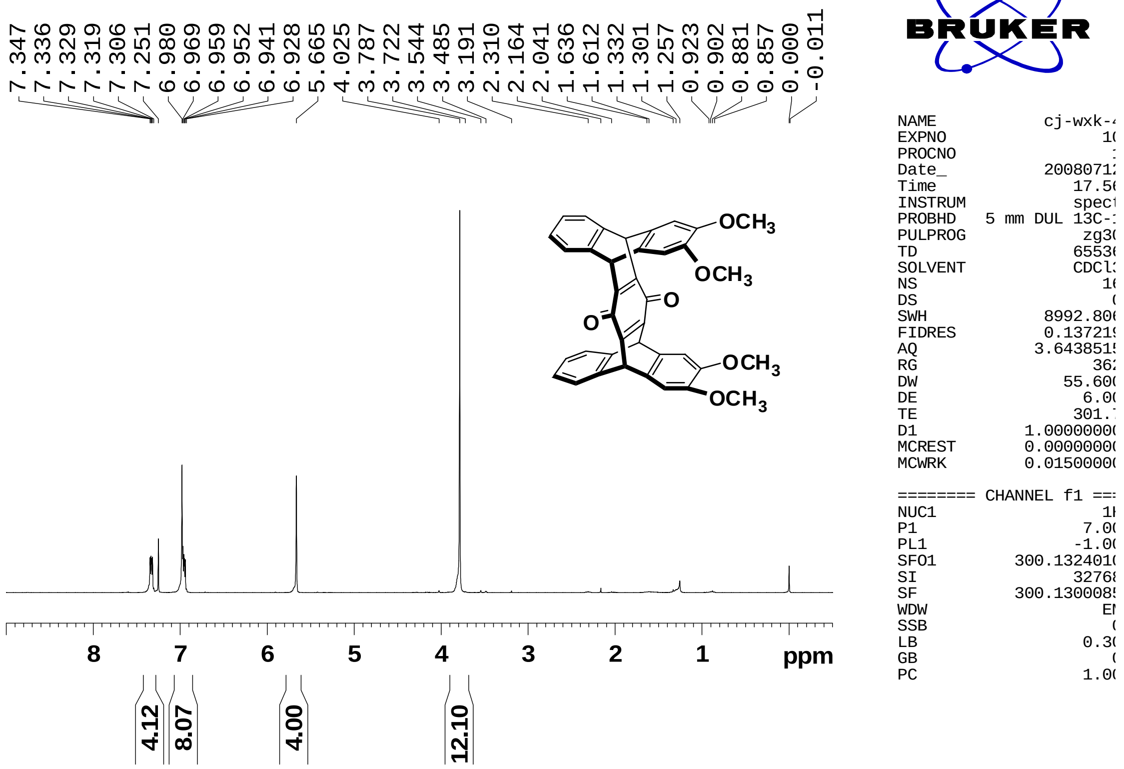
(brs, 4H), 5.63 (s, 4H), 6.38 (s, 4H), 7.20-7.23 (m, 4H), 7.37-7.40 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.2, 59.3, 71.6, 75.9, 122.0, 124.7, 128.2, 132.9, 138.6, 146.4, 152.4, 179.8. MALDI-TOF MS: *m/z* 642.3 $[M+4H]^+$. Anal. Calcd for $C_{40}H_{30}O_8 \cdot 1.2H_2O$: C, 72.76; H, 4.95. Found: C, 72.50; H, 4.81.





Compound **1**. Reduction of the *o*-quinone **6** (0.40 g, 0.61 mmol) with catalytic hydrogenation gave **7** (0.397 g, 0.62 mmol) as a white solid in 98% yield, which was used in the next reaction without further purification. A suspension of cesium carbonate (1.66 g, 5.1 mmol) in anhydrous DMF (70 mL) under argon atmosphere was stirred vigorously for 10 min and then heated to 100 °C. To the mixture was added dropwise a solution of **7** (0.397 g, 0.62 mmol) and bistosylate **8**[S2a] (0.847 g, 1.24 mmol) in anhydrous DMF (70 mL) over 12h. The reaction mixture was stirred at 100 °C for another 3d. After cooling down to ambient temperature, the mixture was filtered and washed with CH_2Cl_2 (60 mL). The filtrate was concentrated under reduced pressure to give a gray solid, which was dissolved in CH_2Cl_2 (250 mL) and washed with diluted HCl. The organic layer was dried over anhydrous sodium sulfate. Removal of the solvent, the resulting oil was subjected to successive column chromatography over silica gel (eluent: 100:1 CH_2Cl_2/CH_3OH and then 60:1 CH_2Cl_2/CH_3OH) 0.295 g (36 %) of **1** as an off-white solid was obtained. Mp: 78-79 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 3.55-3.57 (m, 22H), 3.64-3.69 (m, 16H), 3.82-3.83 (m, 4H), 3.96-4.01 (m, 20H), 5.70 (s, 4H), 6.84 (s, 8H), 6.91-6.93 (m, 4H), 7.00 (s, 4H), 7.28-7.32 (m, 4H). ^{13}C NMR (75 MHz, CD_3CN): δ 47.0, 58.2, 68.4, 69.0, 69.2, 69.3, 70.2, 70.3, 71.2, 74.8, 111.4, 113.7, 120.9, 123.0, 124.7, 137.0, 138.2, 145.3, 145.6, 145.7, 148.5. MALDI-TOF MS: *m/z* 1341.6 $[M+Na]^+$. Anal. Calcd for $C_{76}H_{86}O_{20}$: C, 69.18; H, 6.57. Found: C, 69.13; H, 6.72.

2. ^{1}H NMR and ^{13}C NMR spectra of compounds 1, 3-6



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FIDRES         0.13721
AQ            3.643851
RG                   36
DW                55.60
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TE                 301.
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MCREST       0.00000000
MCWRK        0.01500000

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PL1                -1.0
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SI                 3276
SF           300.130008
WDW                   E
SSB
LB                  0.3
GB
PC                  1.0
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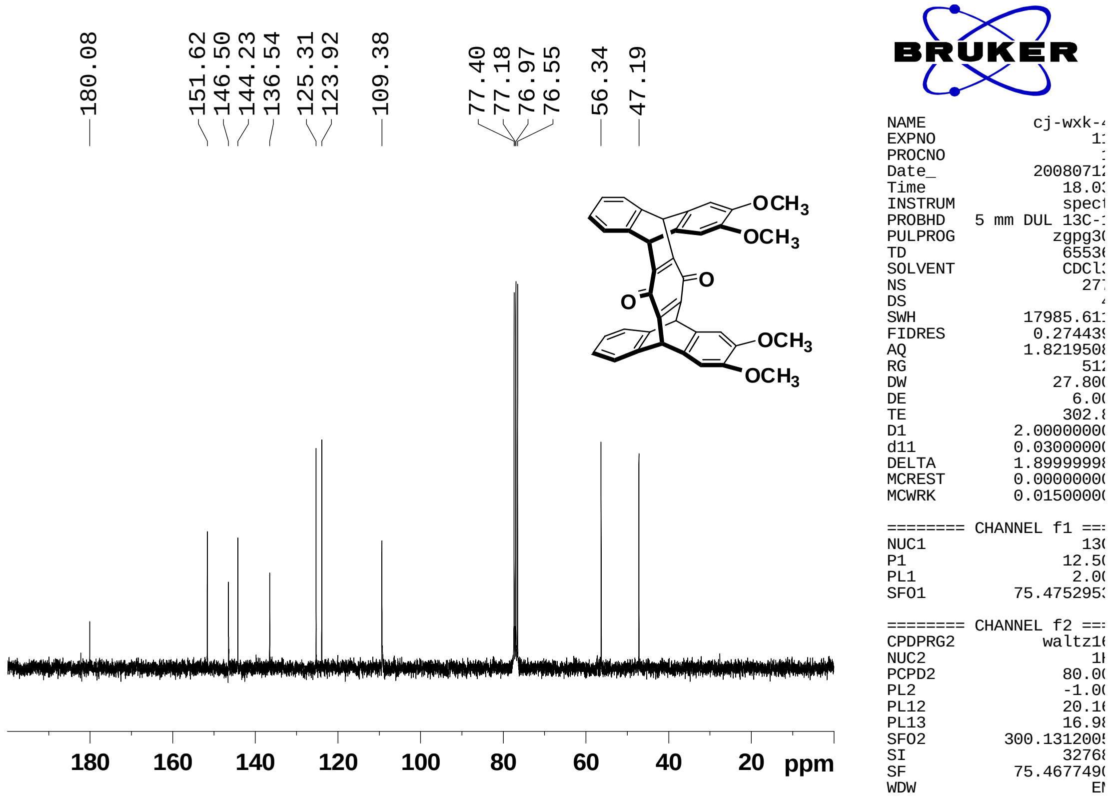
Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3**.



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TD                 6553
SOLVENT            CDCl
NS                   27
DS
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FIDRES         0.274443
AQ            1.8219508
RG                   51
DW                27.80
DE                 6.0
TE                 302.
D1           2.00000000
d11          0.03000000
DELTA        1.89999999
MCREST       0.00000000
MCWRK        0.01500000

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P1                 12.5
PL1                 2.0
SFO1         75.4752950

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PL12               20.1
PL13               16.9
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SI                 3276
SF           75.4677490
WDW                   E
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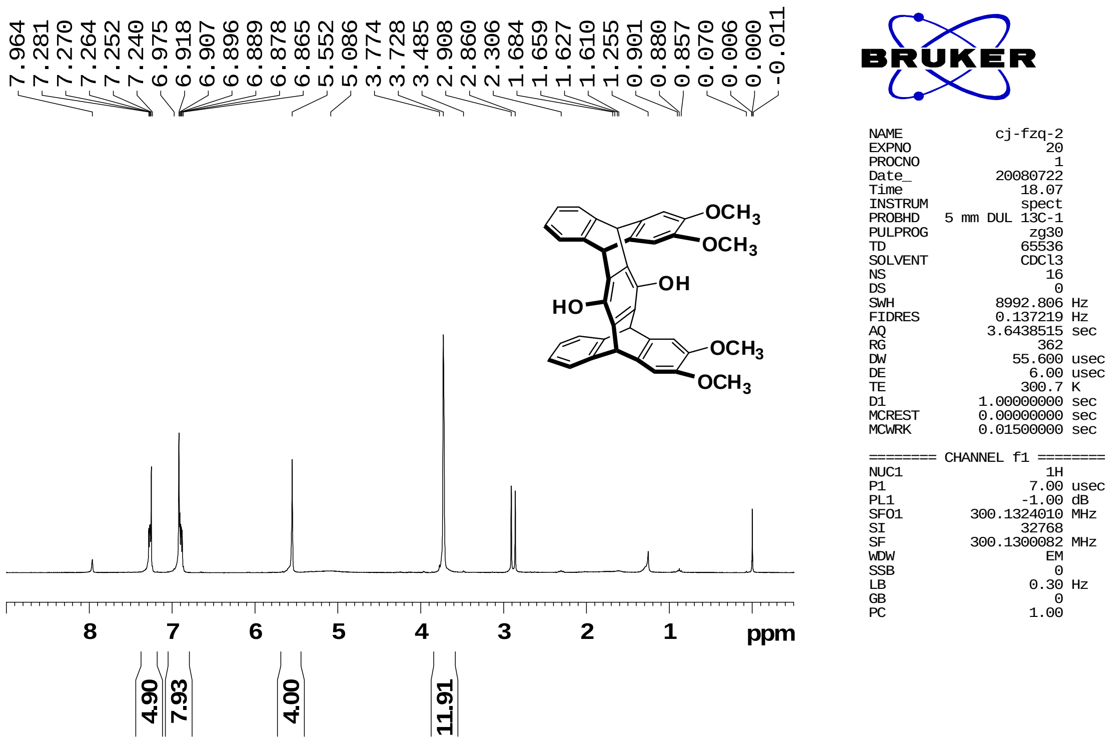
Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **3**.



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TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ            3.6438515 sec
RG                  362
DW               55.600 usec
DE                 6.00 usec
TE                300.7 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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PL1               -1.00 dB
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SI                32768
SF          300.1300082 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
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PC                 1.00
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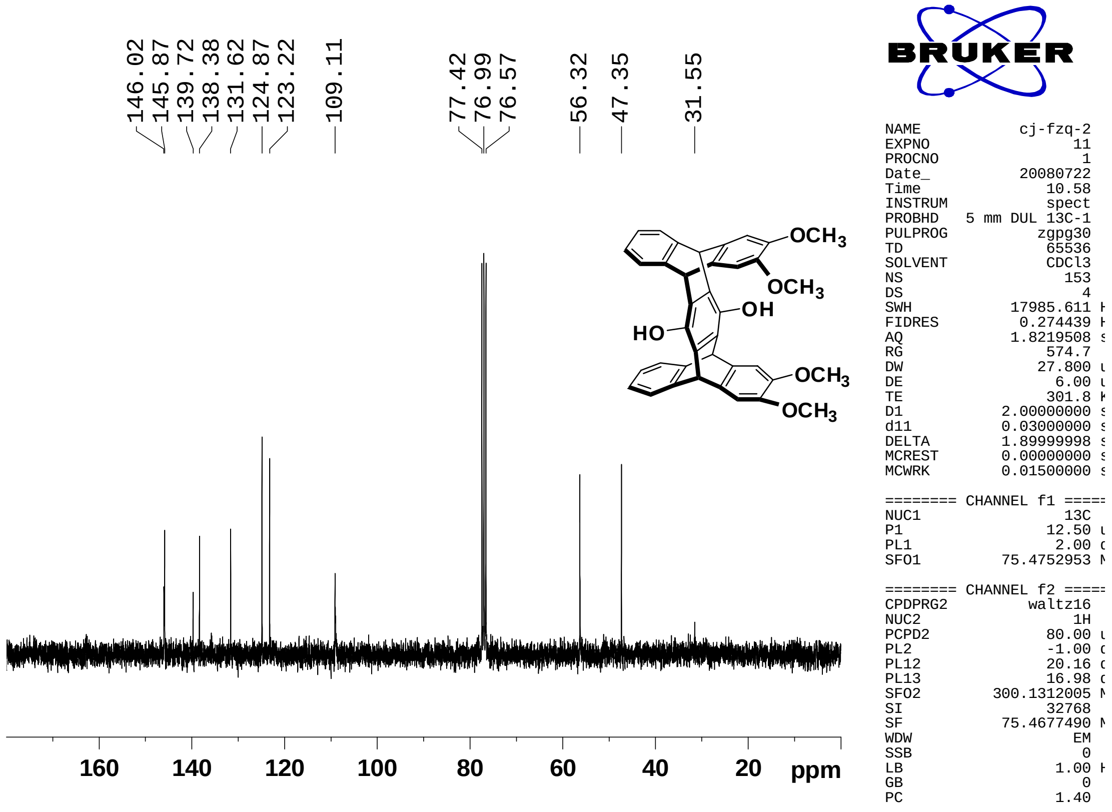
Figure S3. ^{1}H NMR spectrum (300 MHz, CDCl$_3$) of **4**.



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PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   153
DS                     4
SWH            17985.611 H
FIDRES          0.274439 H
AQ             1.8219508 s
RG                 574.7
DW                27.800 u
DE                  6.00 u
TE                 301.8 K
D1            2.00000000 s
d11           0.03000000 s
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MCREST        0.00000000 s
MCWRK         0.01500000 s

======== CHANNEL f1 =====
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P1                 12.50 u
PL1                 2.00 d
SFO1          75.4752953 M

======== CHANNEL f2 =====
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PCPD2              80.00 u
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PL12               20.16 d
PL13               16.98 d
SFO2         300.1312005 M
SI                 32768
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WDW                   EM
SSB                    0
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GB                     0
PC                  1.40
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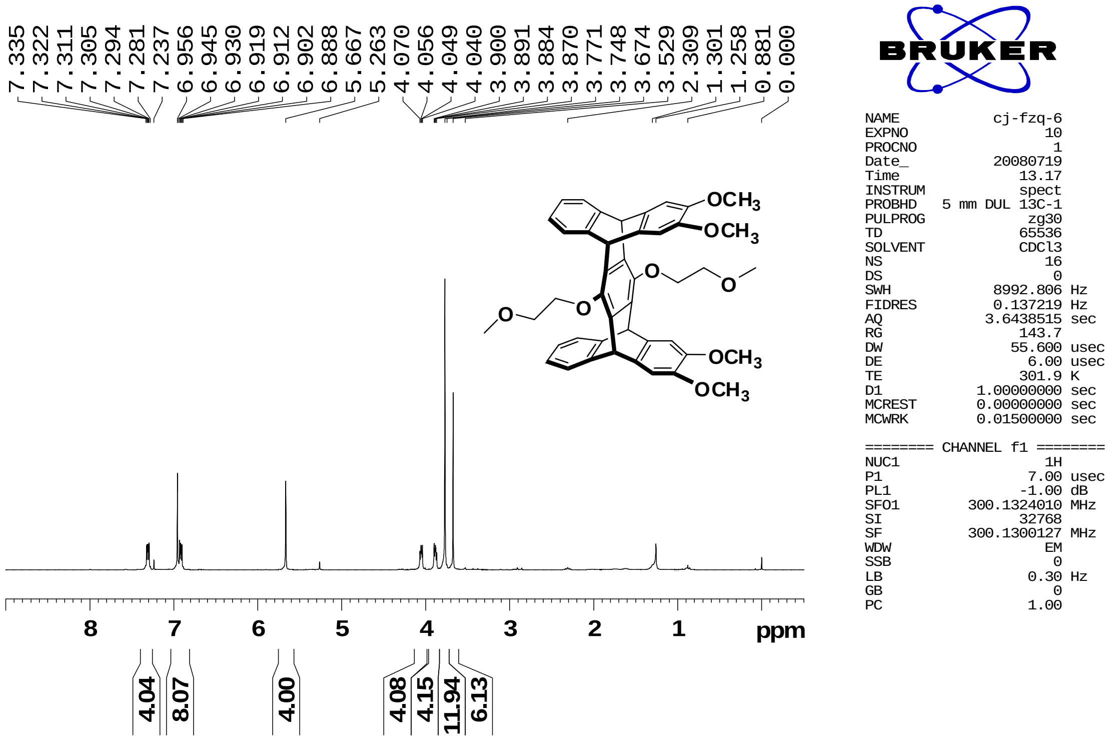
Figure S4. ^{13}C NMR spectrum (75 MHz, CDCl$_3$) of **4**.



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SOLVENT          CDCl3
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DS                   0
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FIDRES        0.137219 Hz
AQ           3.6438515 sec
RG               143.7
DW              55.600 usec
DE                6.00 usec
TE               301.9 K
D1          1.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

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PL1              -1.00 dB
SFO1       300.1324010 MHz
SI               32768
SF         300.1300127 MHz
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LB                0.30 Hz
GB                   0
PC                1.00
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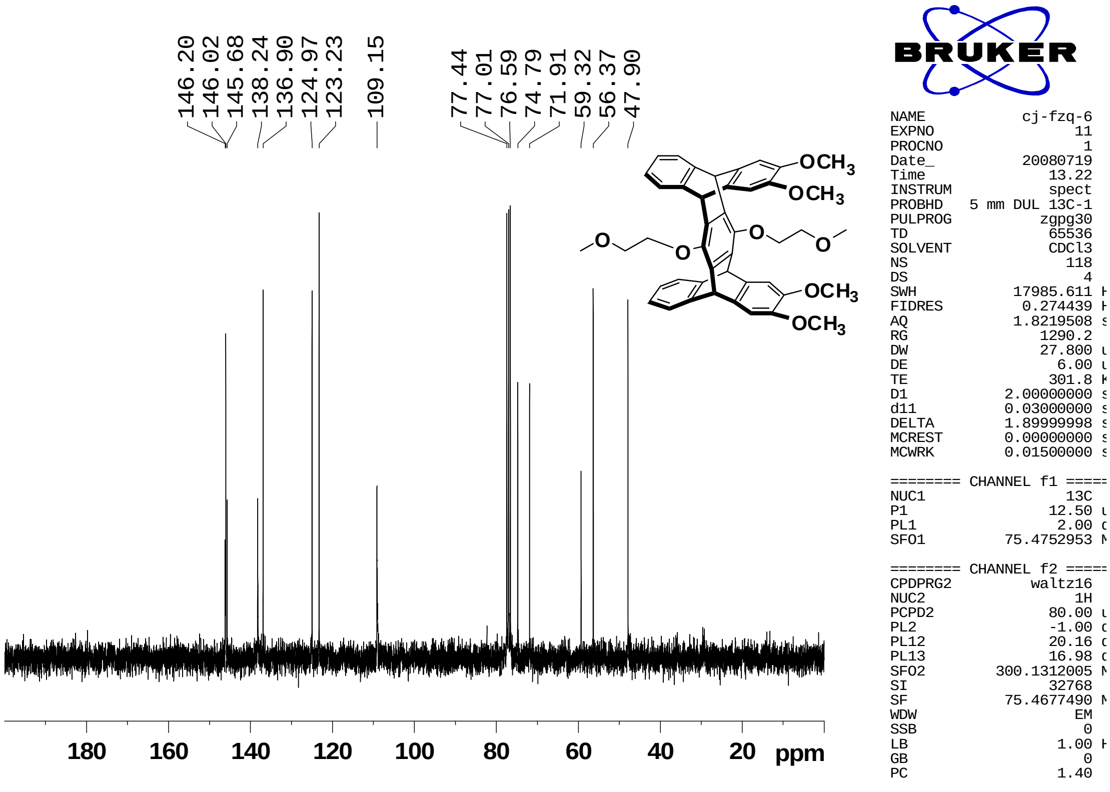
Figure S5. ^{1}H NMR spectrum (300 MHz, CDCl$_3$) of **5**.



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TD               65536
SOLVENT          CDCl3
NS                 118
DS                   4
SWH          17985.611
FIDRES        0.274439
AQ           1.8219508
RG              1290.2
DW              27.800
DE                6.00
TE               301.8
D1          2.00000000
d11         0.03000000
DELTA       1.89999998
MCREST      0.00000000
MCWRK       0.01500000

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P1               12.50
PL1               2.00
SFO1        75.4752953

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NUC2                1H
PCPD2            80.00
PL2              -1.00
PL12             20.16
PL13             16.98
SFO2       300.1312005
SI               32768
SF          75.4677490
WDW                 EM
SSB                  0
LB                1.00
GB                   0
PC                1.40
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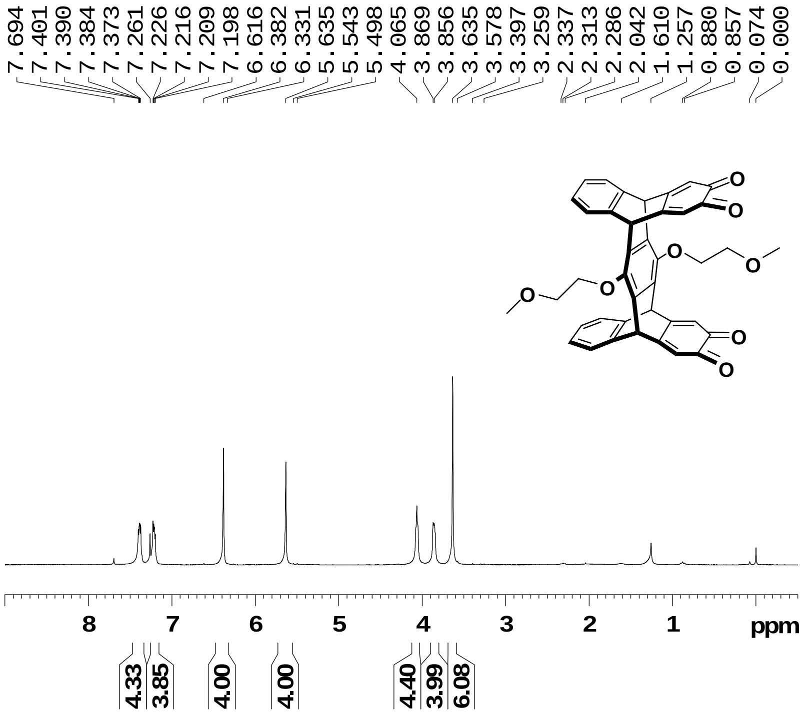
Figure S6. ^{13}C NMR spectrum (75 MHz, CDCl$_3$) of **5**.



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TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
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FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                   181
DW                55.600 usec
DE                  6.00 usec
TE                 300.6 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.00 usec
PL1                -1.00 dB
SFO1         300.1324010 MHz
SI                 32768
SF           300.1300053 MHz
WDW                   EM
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LB                  0.30 Hz
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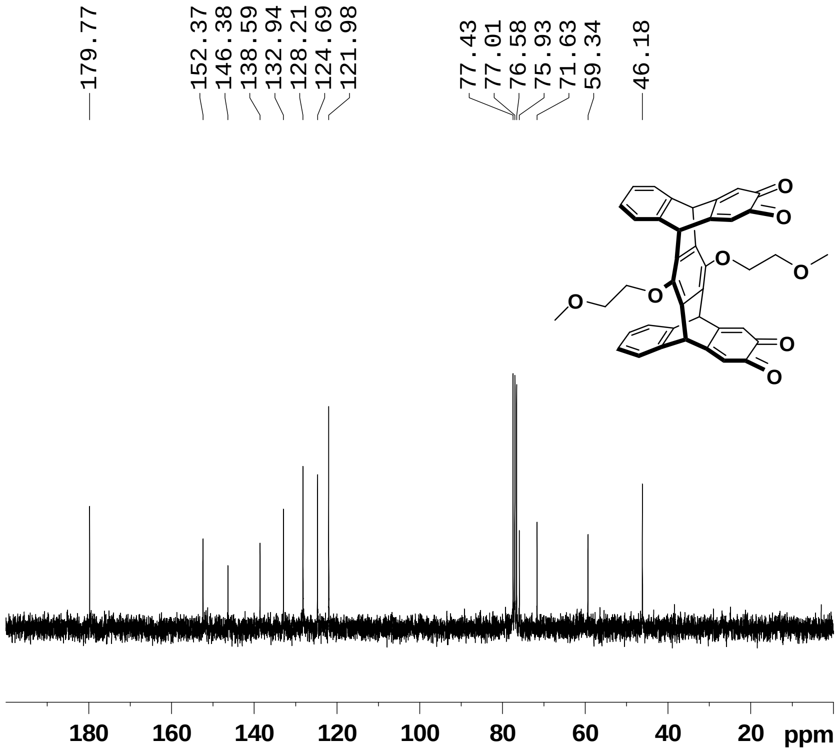
Figure S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6**.



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TD                 65536
SOLVENT            CDCl3
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FIDRES          0.274439
AQ             1.8219508
RG                1824.6
DW                27.800
DE                  6.00
TE                 302.1
D1            2.00000000
d11           0.03000000
DELTA         1.89999998
MCREST        0.00000000
MCWRK         0.01500000

======== CHANNEL f1 ====
NUC1                 13C
P1                 12.50
PL1                 2.00
SFO1          75.4752953

======== CHANNEL f2 ====
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NUC2                  1H
PCPD2              80.00
PL2                -1.00
PL12               20.16
PL13               16.98
SFO2         300.1312005
SI                 32768
SF            75.4677490
WDW                   EM
SSB                    0
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GB                     0
PC                  1.40
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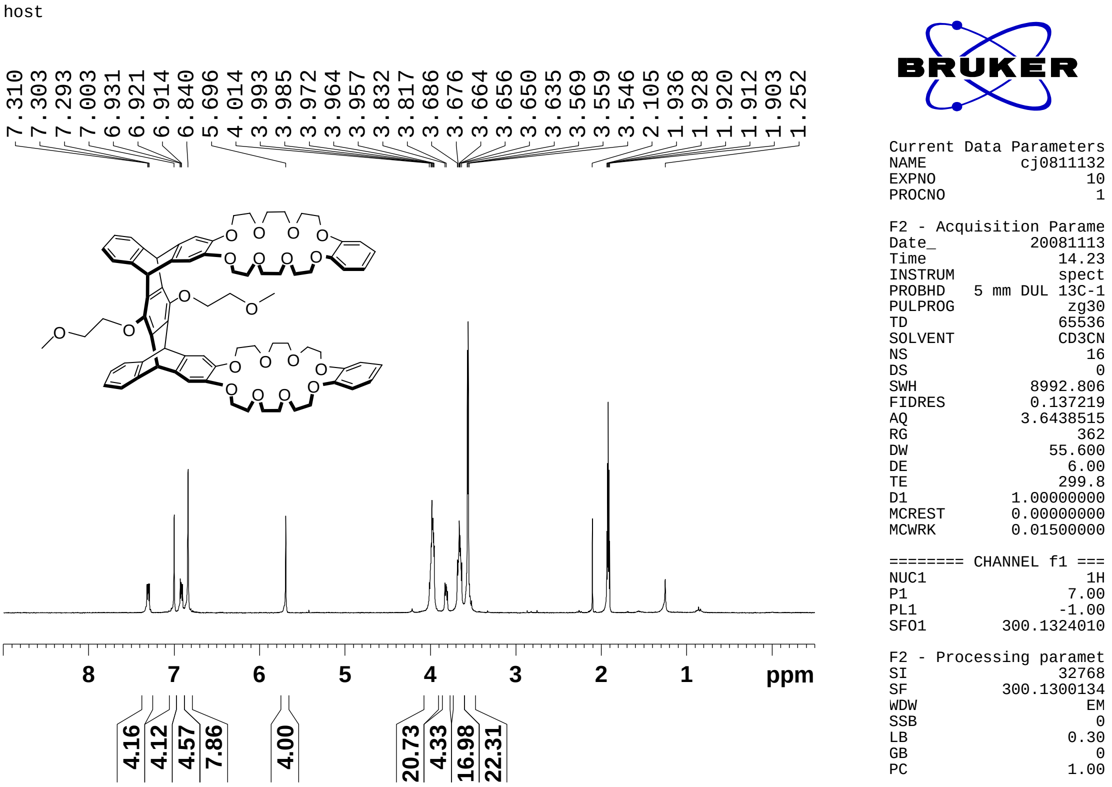
Figure S8. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6**.



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SFO1          300.1324010

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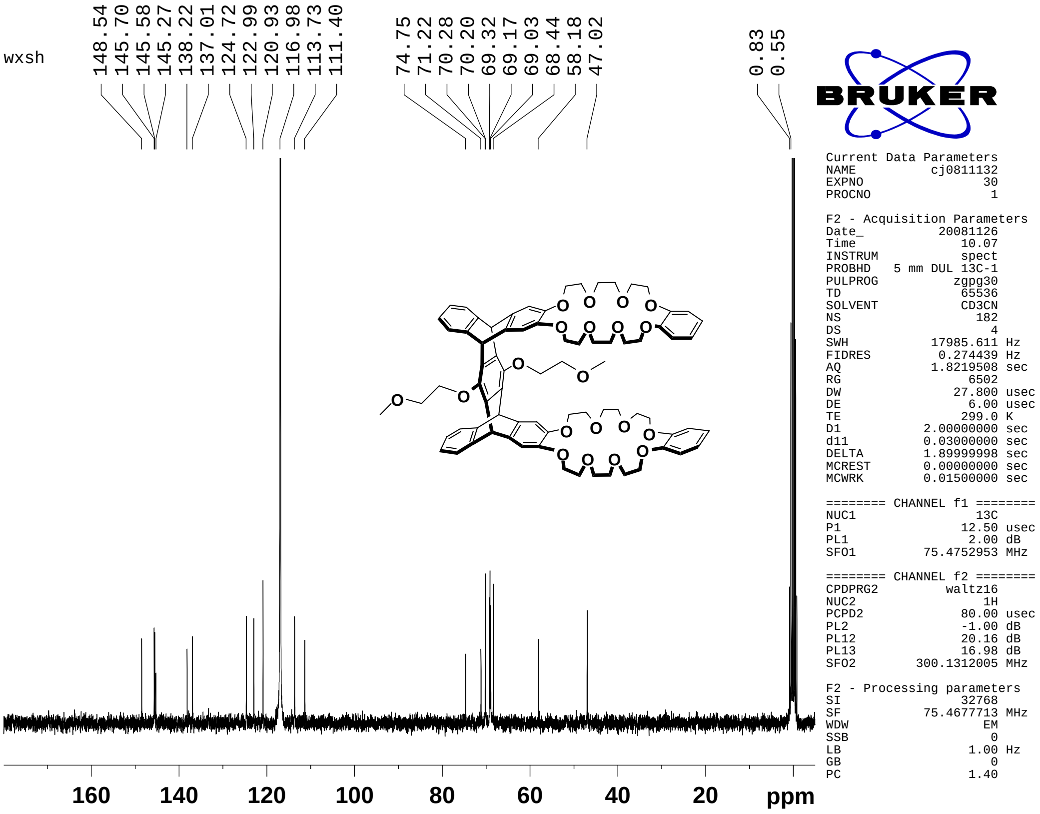
Figure S9. ^{1}H NMR spectrum (300 MHz, CD_3CN) of **1**.



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NS                    182
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FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                   6502
DW                 27.800 usec
DE                   6.00 usec
TE                  299.0 K
D1             2.00000000 sec
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DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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P1                  12.50 usec
PL1                  2.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                 -1.00 dB
PL12                20.16 dB
PL13                16.98 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677713 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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Figure S10. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **1**.

3. ^{1}H-^{1}H COSY spectrum of complex 1·2

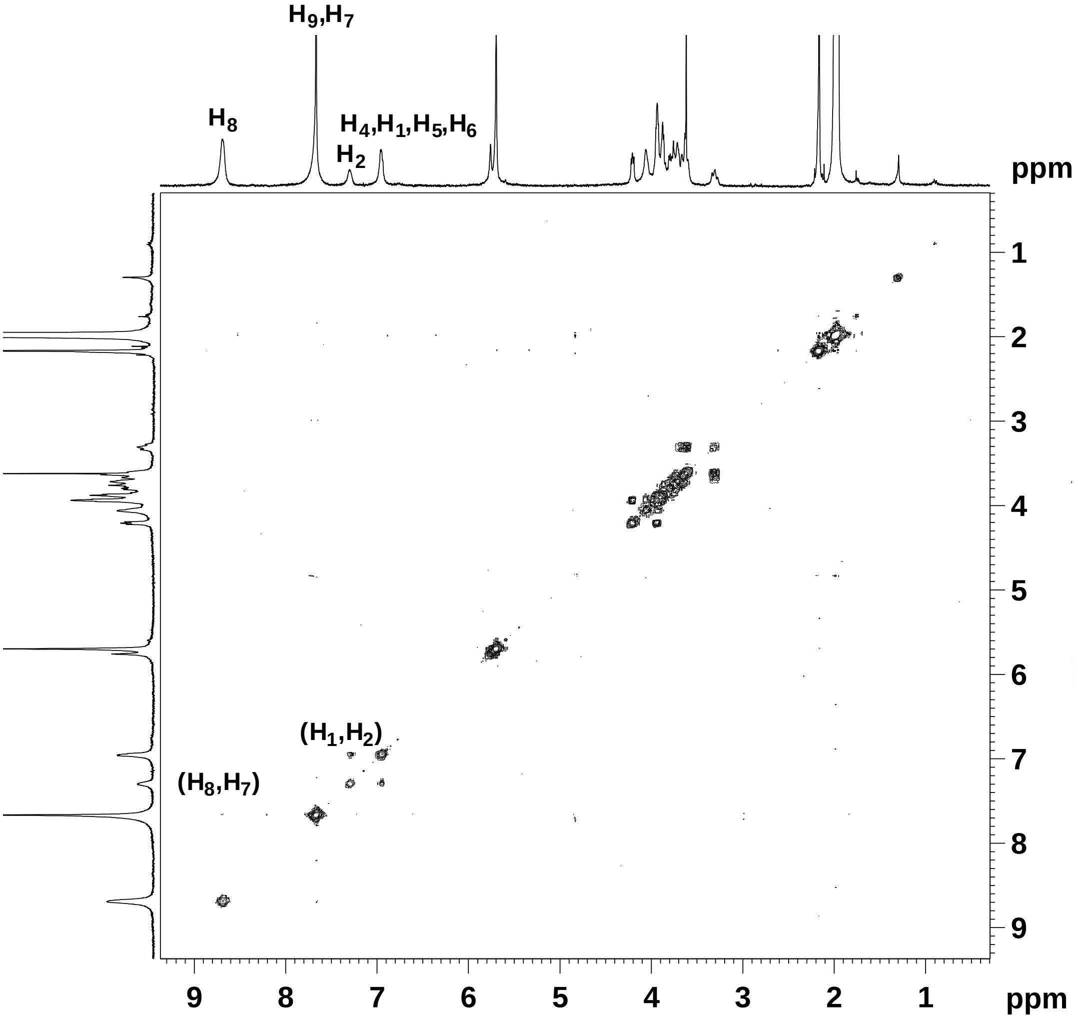

Figure S11. ^{1}H-^{1}H COSY spectrum (300 MHz, CD_3CN) of a solution of **1** and 1 equiv of **2**. $[\mathbf{1}]_0$ = 1 mM.

4. ^{1}H NMR spectra of complex 1·2 at low temperatures

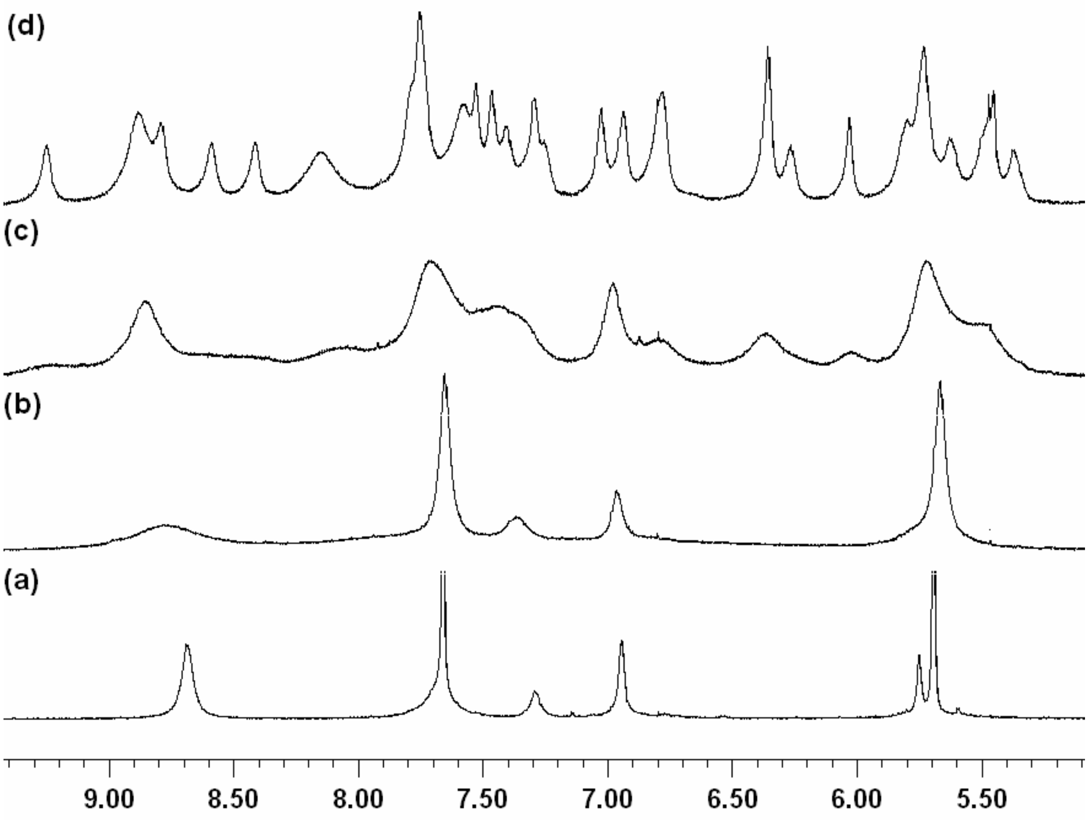

Figure S12. Partial ^{1}H NMR spectra (600 MHz, CD_3CN) of a solution of **1** and 1 equiv of **2** at (a) 293 K, (b) 273 K, (c) 253 K, and (d) 233 K. $[\mathbf{1}]_0 = 1$ mM.

5. CV curves for a solution of the host in the absence and presence of the guest

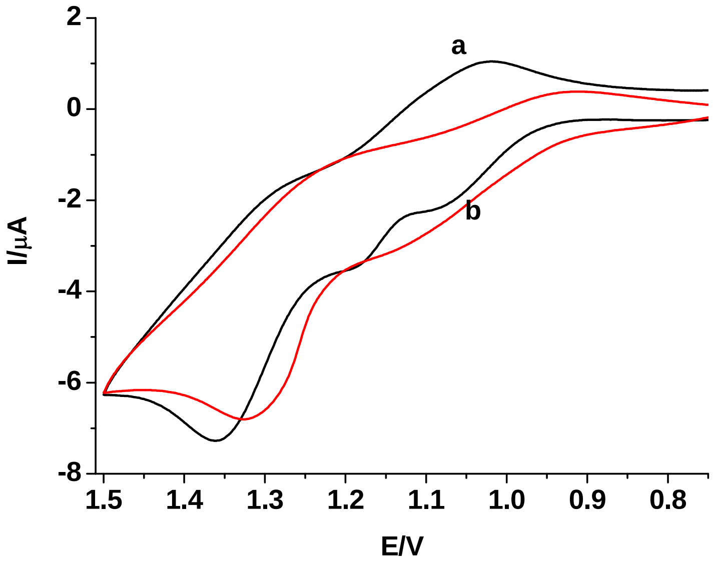

Figure S13. CV curves for a solution of **1** (2.5×10^{-4} M) in CH_3CN-$(NBu_4)PF_6$ (0.1 M) in the absence (black line) and the presence (red line) of guest $\mathbf{2}^{4+}$ (1.0×10^{-3} M). Working electrode: Pt. Reference electrode: $Ag/AgNO_3$. Scan rate: $0.2 Vs^{-1}$.

6. Determination of the association constant

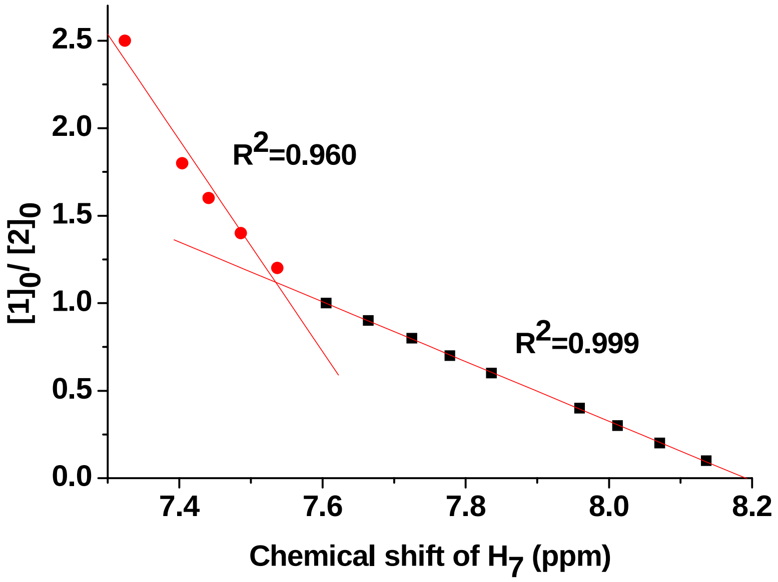

Figure S14. Mole ratio plot for the complexation of **1** and **2** in CD_3CN at 298 K.

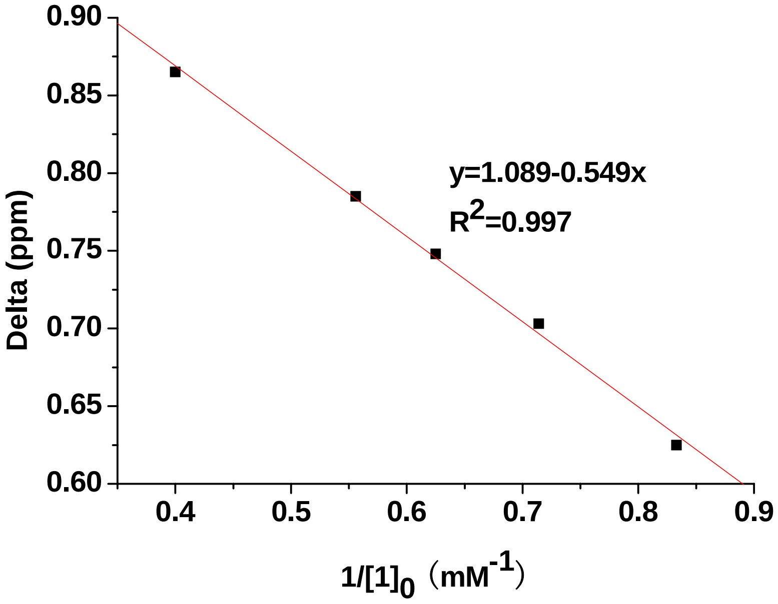

Figure S15. Determination of Δ_0 of H_7 for the complexation of **1** and **2** in CD_3CN at 298 K.

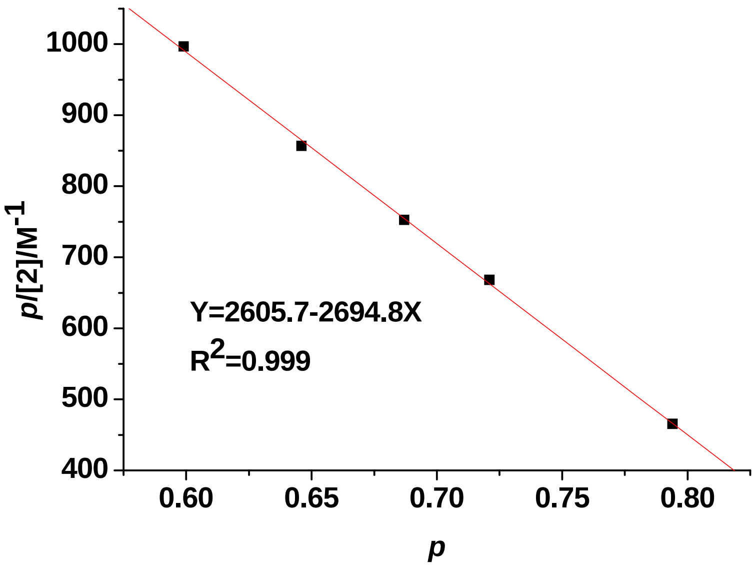

Figure S16. Scatchard plot for the complexation of **1** and **2** in CD_3CN at 298K.

7. ESI-MS spectrum of complex 1·2

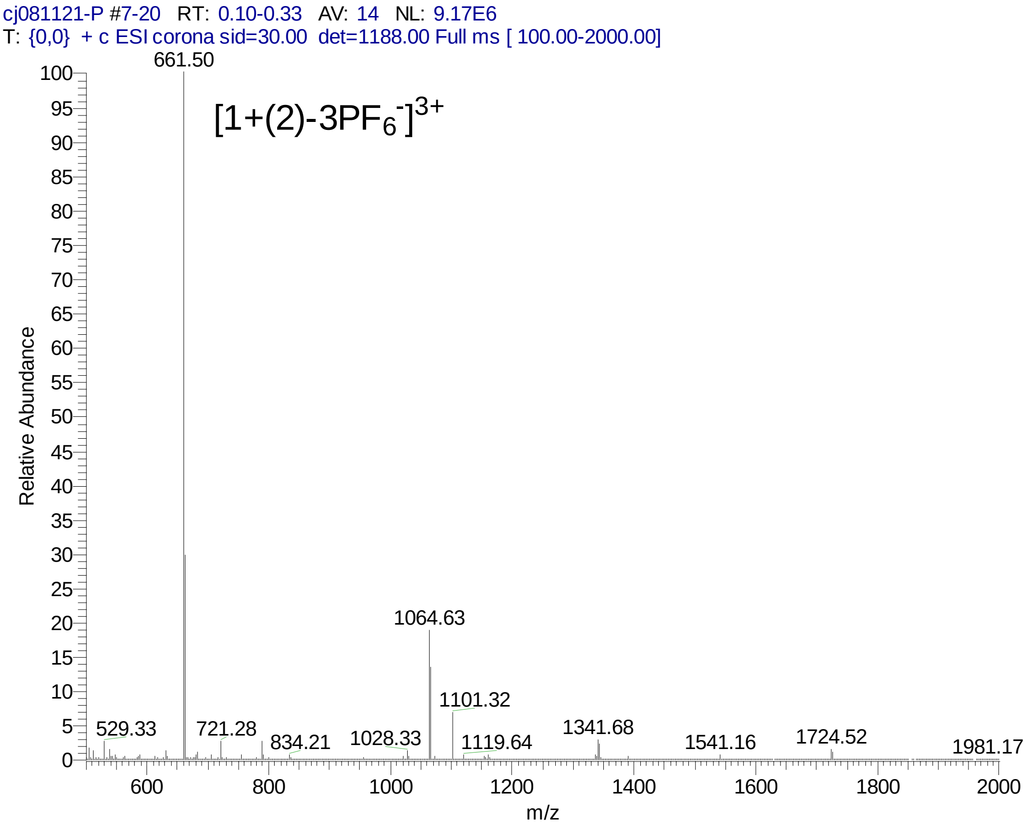

Figure S17. ESI-MS spectrum of the complex **1·2**.

8. Color change and UV spectra of 1, 2 and complex 1·2

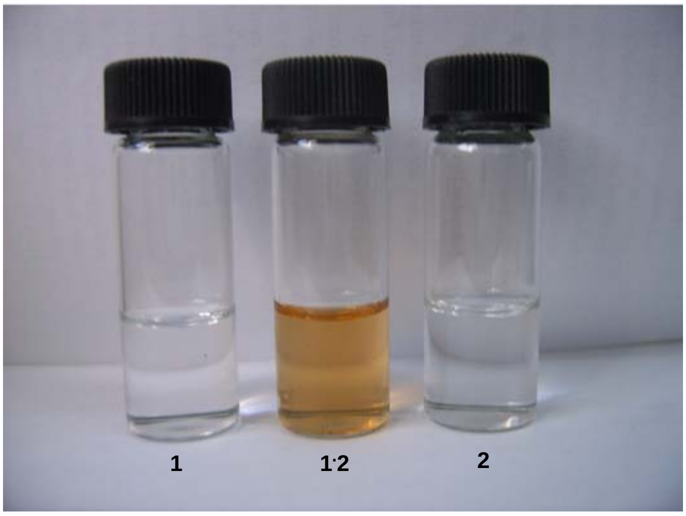

Figure S18. Color change from colorless of **1** (1×10^{-3} moldm^{-3}) to orange on complexation with **2** (colorless, 1×10^{-3} moldm^{-3}).

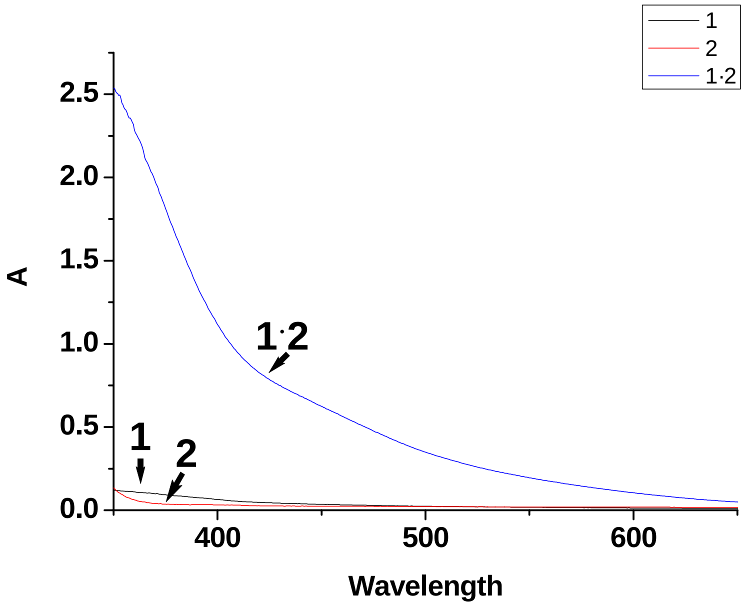

Figure S19. Absorption spectra of **2** (1×10^{-3} moldm^{-3}) in the absence and presence of **1** (1×10^{-3} moldm^{-3}) in CH_3CN at 298K.

9. Single crystal analysis of complex 1·2

Application of 108 least-squares restraints is for confining the thermal vibration parameters of fluoride atom of the disorder PF_6 ion, which can make them be isotropic.

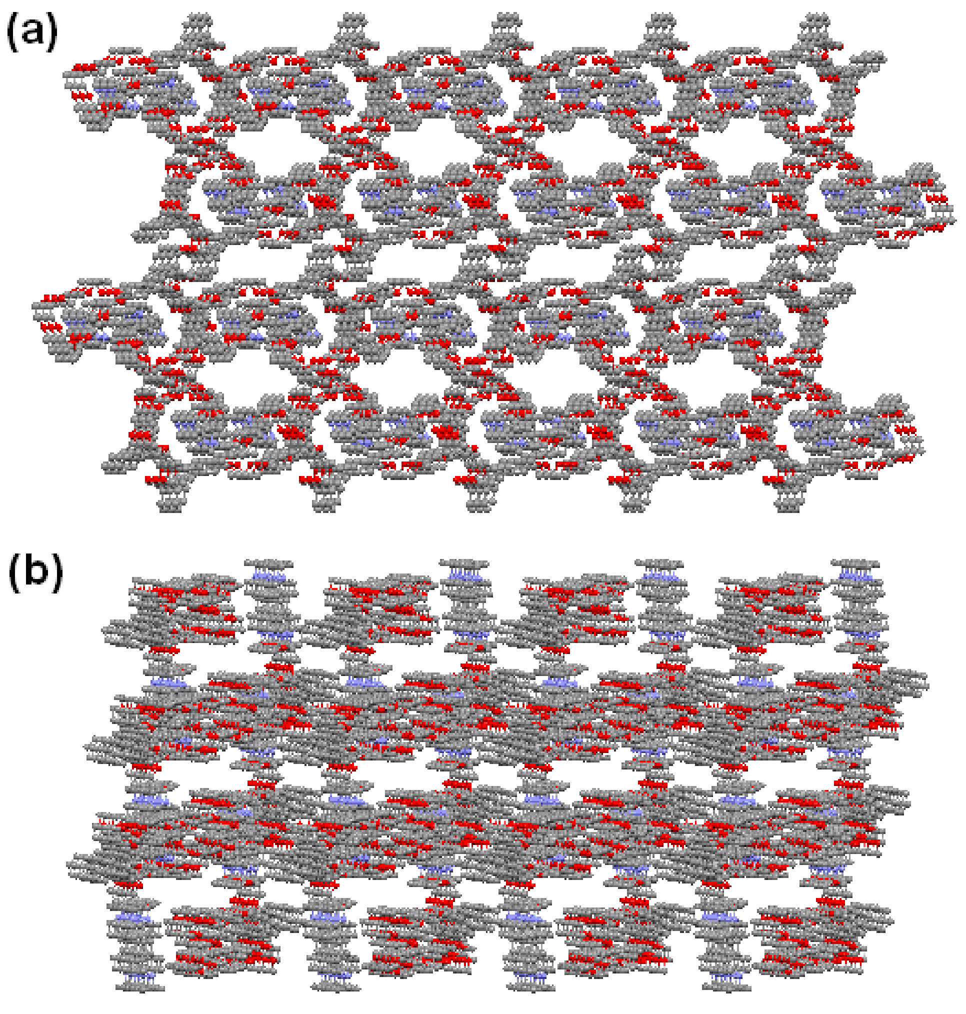

Figure S20. Crystal packing of the complex viewed along the *a*-axis (a), and *b*-axis (b). Solvent molecules, PF_6^- counterions and hydrogen atoms were omitted for clarity.

9. References

S1. B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1547.

S2. (*a*) T. Han and C.-F. Chen, *Org. Lett.*, 2006, **8**, 1069; (*b*) Connors, K. A. *Binding Constants*; J. Wiley and Sons: New York, 1987.