

## Fluorinated leaning pillar[6]arene: synthesis, structure and selective iodide anion binding by anion- $\pi$ interactions

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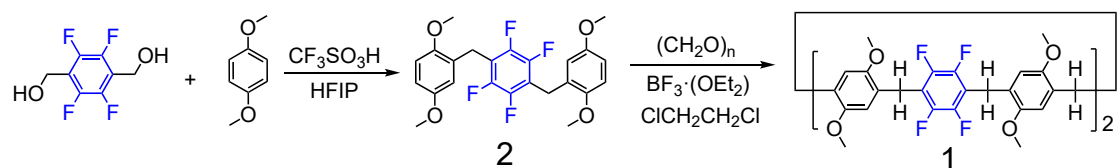
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## 1. Materials and instrumentations

All reagents were commercially available and used as supplied without further purification.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR were recorded with Agilent 600 MHz and 400 MHz Direct Drive instrument with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. High-resolution mass spectrometric (HRMS) experiments were performed with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Single crystal X-ray data were obtained on an Oxford Diffraction Xcalibur Atlas Gemini captra instrument. The electrostatic potential surfaces (ESP) of computed species were generated with Gaussview 6.0. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer.

## 2. Synthesis and characterizations of compounds



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

### Synthesis of compound 2.

1,4-Dimethoxybenzene (8.29 g, 60 mmol), 2,3,5,6-tetrafluoro-1,4-benzenedimethanol (2.10 g, 10.0 mmol), 0.500 mL of trifluoromethanesulfonic acid and 40 mL of hexafluoroisopropanol (HFIP) were added in a 100 mL pressure flask and the reaction mixture was stirred at 100 °C for 24 h. Then, the solvent was concentrated by rotary evaporation and the resulting residue was purified by column chromatography on silica gel using a mixture of petroleum ether and dichloromethane ( $v : v = 2 : 1$ ) as the eluent to give 3.42 g (76 % yield) of **2** as a white solid. Mp: 135.8–136.6 °C. The  $^1\text{H}$  NMR spectrum of compound **2** is shown in Fig. S1.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 6.77–6.79 (d,  $J = 12$  Hz, 2 H), 6.71–6.73 (m, 2 H), 6.60–6.61 (d,  $J = 6$  Hz, 2 H), 4.01 (s, 4 H), 3.80 (s, 6 H), 3.72 (s, 6 H). The  $^{13}\text{C}$  NMR spectrum of **2** is shown in Fig. S2.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 156.1, 154.2, 130.0, 118.8, 114.2, 113.9, 56.6, 25.7. The  $^{19}\text{F}$  NMR spectrum of **2** is shown in Fig. S3.  $^{19}\text{F}$  NMR spectrum

of **2** (565 MHz, 298 K) in  $\text{CDCl}_3$   $\delta$  (ppm):  $-144.13$ . The HR ESI-MS of **2** is shown in Fig. S4. HR ESI-MS of **2** calcd for  $[\text{M} + \text{H}^+]$   $\text{C}_{24}\text{H}_{23}\text{F}_4\text{O}_4^+$ , 451.1532, found 451.1580.

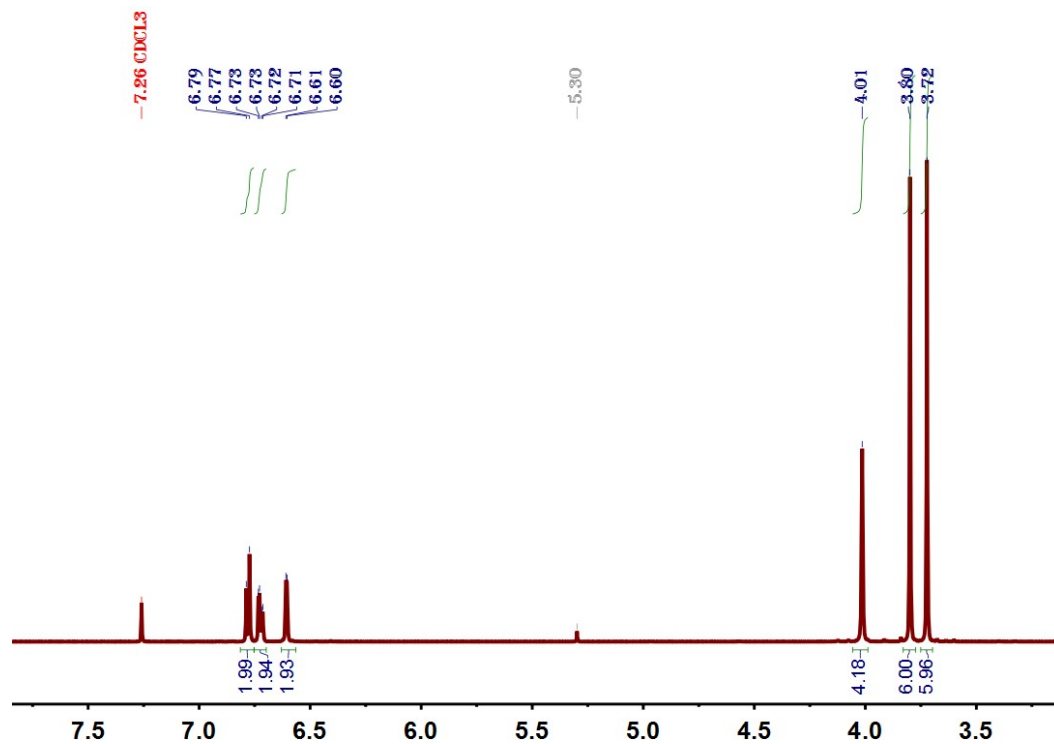


Fig. S1  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ , 298 K) of **2**.

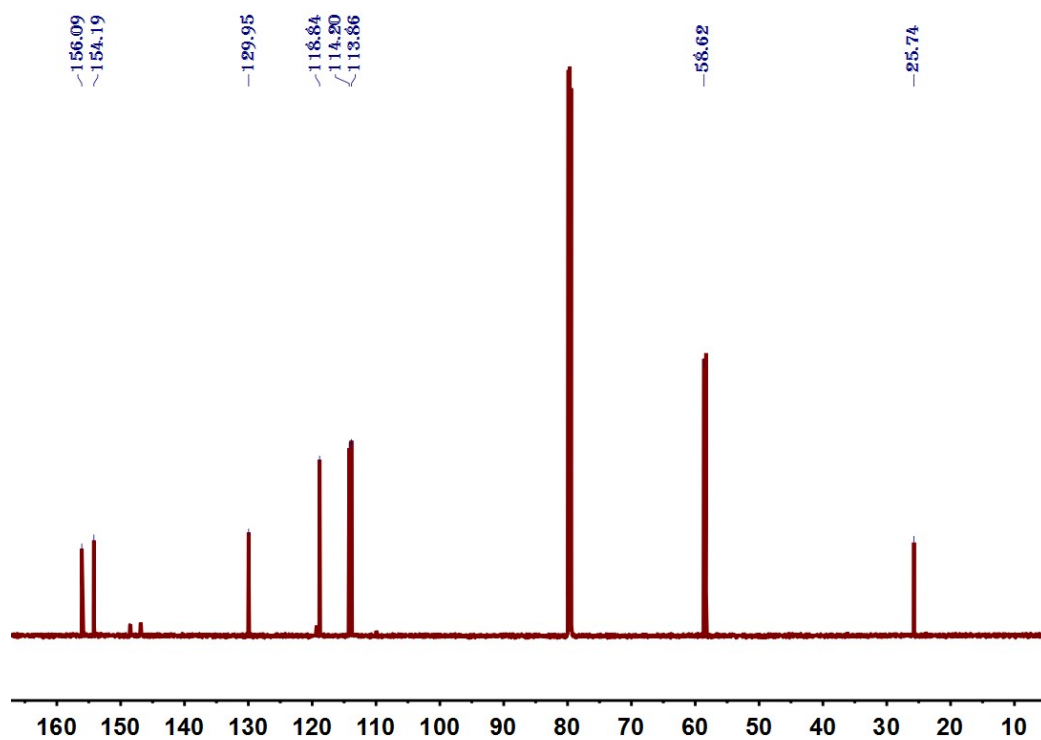
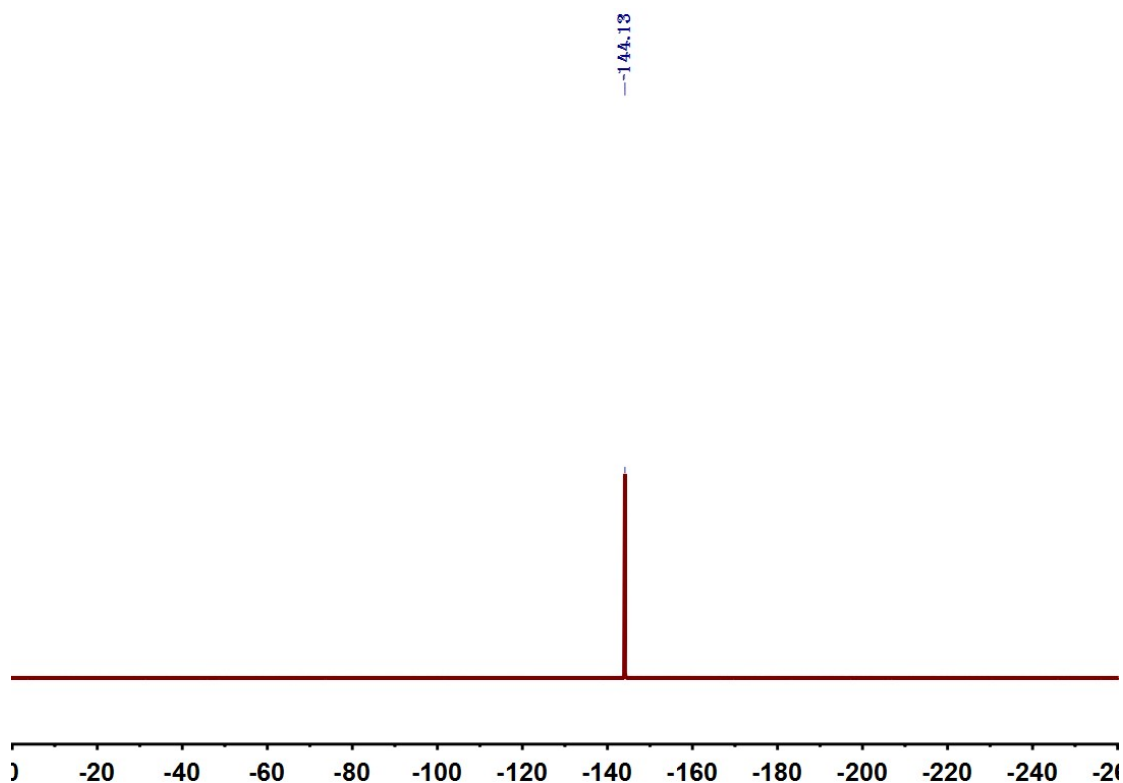
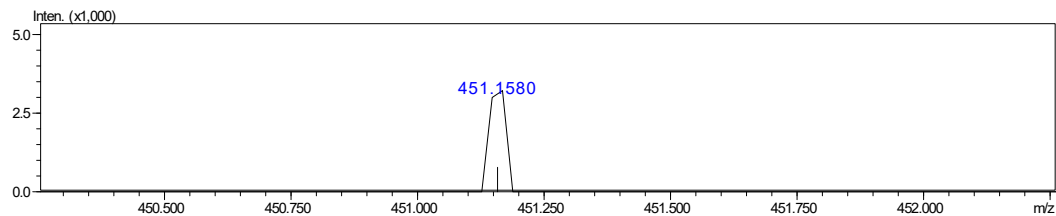


Fig. S2  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ , 298 K) of **2**.



**Fig. S3**  $^{19}\text{F}$  NMR spectrum (565 MHz,  $\text{CDCl}_3$ , 298 K) of **2**.



**Fig. S4** HR ESI-MS spectrum of **2**.

### Synthesis of **1**.

To a 100 mL round bottom flask, compound **2** (540 mg, 1.20 mmol), paraformaldehyde (108 mg, 3.60 mmol) and 60 mL of 1,2-dichloroethane were added. Then,  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  (1.00 mL, 7.80 mmol) was added to the solution and the mixture was stirred at room temperature for 1.5 h. Then, the reaction was quenched with  $\text{Na}_2\text{CO}_3$  solution. The organic layer was washed with water and saturated  $\text{NaCl}$  solution, and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After concentrating the dried organic layer to a minimum volume by rotary evaporation, the resulting residue was purified by column chromatography on silica gel using a mixture of petroleum ether and dichloromethane

( $v : v = 3 : 2$ ) as the eluent to give 293 mg (53 % yield) of **1** as a white solid. Mp: 276.4–277.9 °C. The  $^1\text{H}$  NMR spectrum of compound **1** is shown in Fig. S5.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 6.72 (s, 4 H), 6.58 (s, 4 H), 3.91 (s, 8 H), 3.83 (s, 4 H), 3.73 (s, 12 H), 3.60 (s, 12 H). The  $^{13}\text{C}$  NMR spectrum of **2** is shown in Fig. S2.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 153.8, 131.0, 126.7, 116.4, 58.7, 32.9, 26.4. The  $^{19}\text{F}$  NMR spectrum of **1** is shown in Fig. S7.  $^{19}\text{F}$  NMR spectrum of **1** (565 MHz, 298 K) in  $\text{CDCl}_3$   $\delta$  (ppm):  $-144.81$ . The HR ESI-MS of **1** is shown in Fig. S8. HR ESI-MS of **1** calcd for  $[\text{M} + \text{Na}^+]$   $\text{C}_{50}\text{H}_{44}\text{F}_8\text{O}_8\text{Na}^+$ , 947.2801, found 947.2782, error  $-2$  ppm.

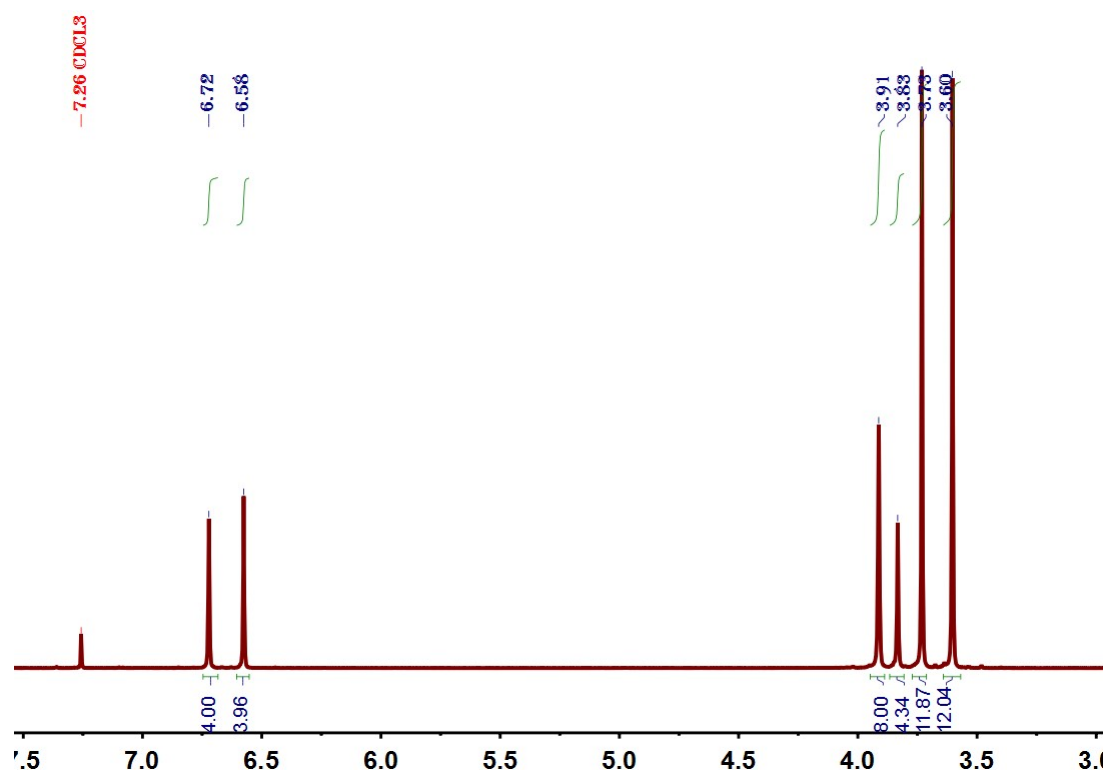


Fig. S5  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ , 298 K) of **1**.

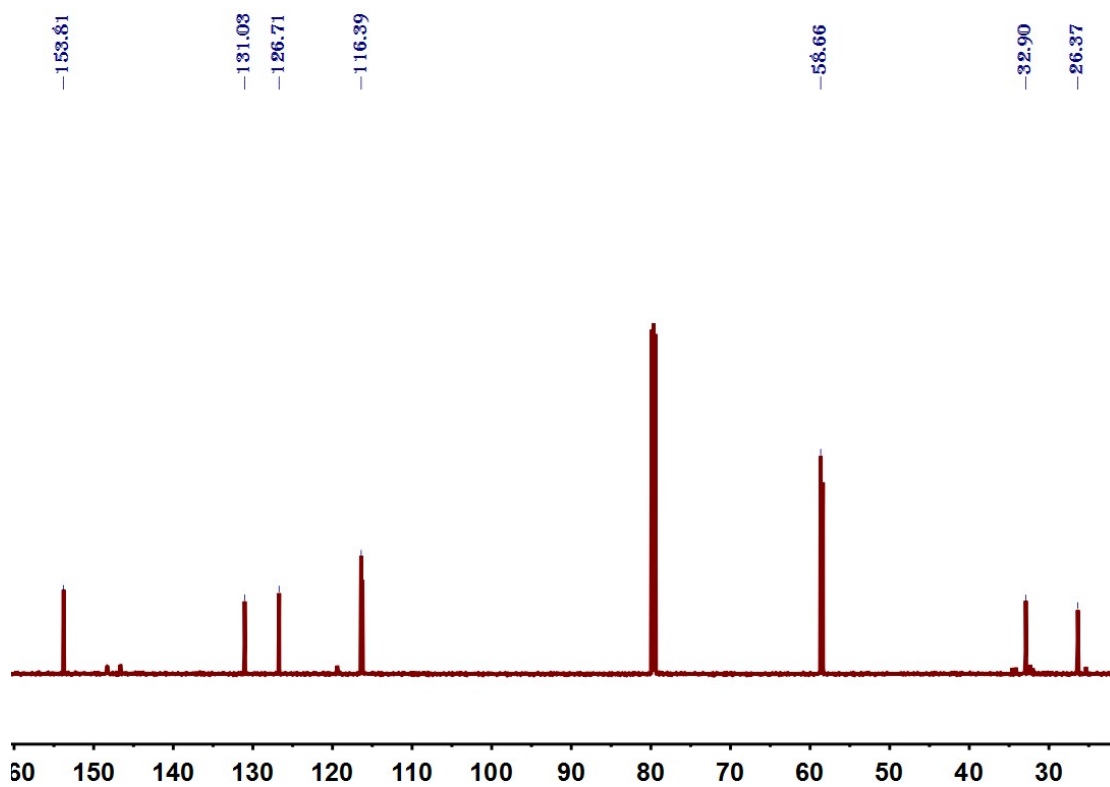


Fig. S6  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ , 298 K) of **1**.

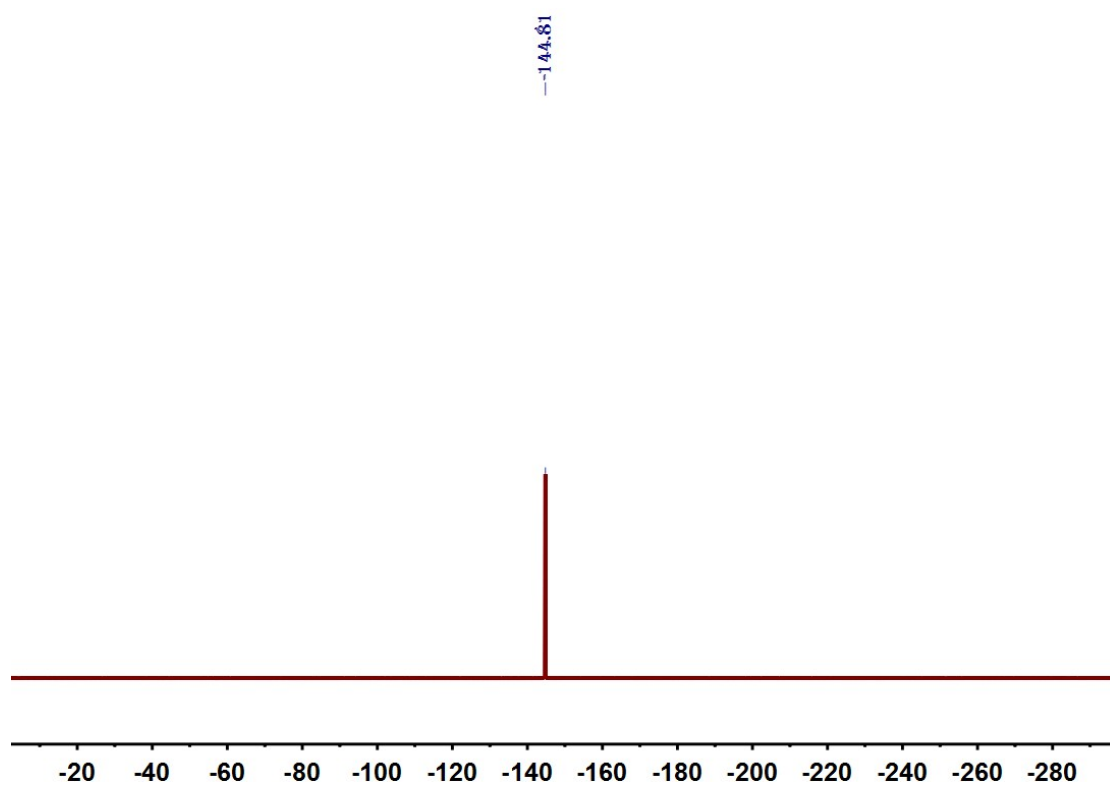
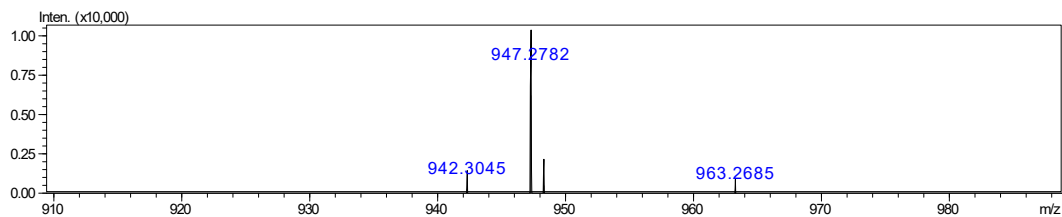


Fig. S7  $^{19}\text{F}$  NMR spectrum (565 MHz,  $\text{CDCl}_3$ , 298 K) of **1**.



**Fig. S8** HR ESI-MS spectrum of **1**.

### 3. Crystallographic data for **1**

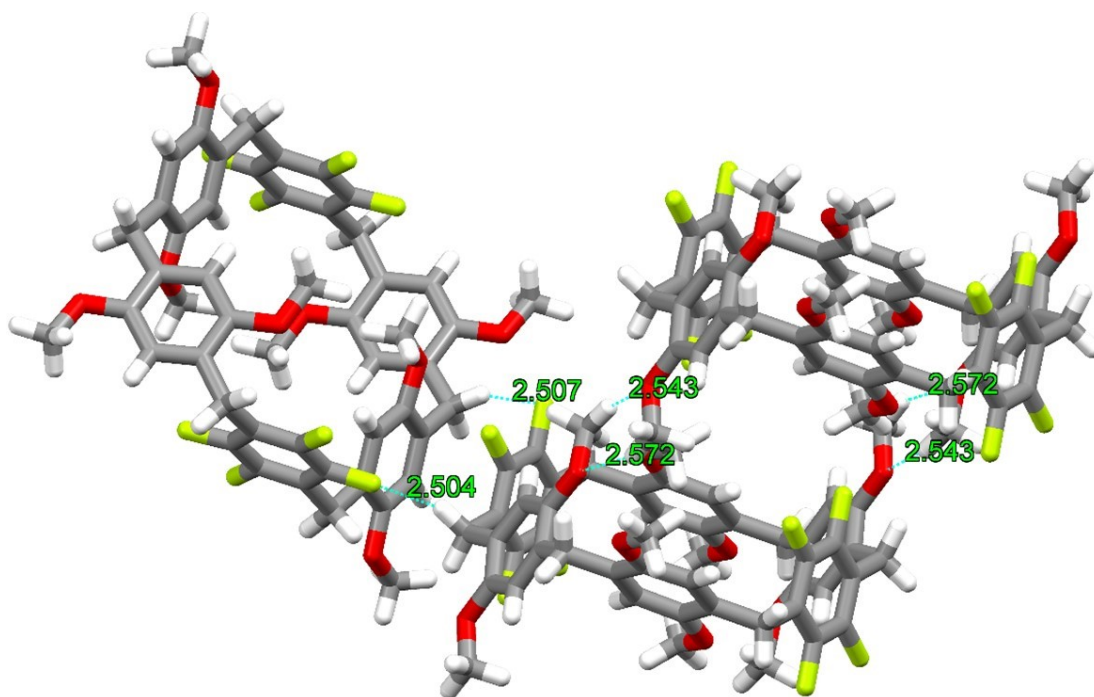
The method to get single crystals of **1** suitable for X-ray single crystal diffraction analysis: Compound **1** (10 mg) was dissolved in acetonitrile to make a hot saturated acetonitrile solution. The resultant solution was allowed to evaporate slowly to give crystals within 2 days.

**Table S1.** Experimental single crystal X-ray data for **1**.

Formula	<b>1</b>
Crystallization Solvent	acetonitrile
Collection Temperature	169.98 K
Formula	$C_{50}H_{44}F_8O_8$
<i>Mr</i>	924.85
Crystal Size [mm <sup>3</sup> ]	0.15 × 0.1 × 0.05
Crystal System	triclinic
Space Group	P-1
<i>a</i> [Å]	9.1525(2)
<i>b</i> [Å]	13.3382(3)
<i>c</i> [Å]	20.1751(4)
$\alpha$ [°]	86.3770(10)
$\beta$ [°]	88.4620(10)
$\gamma$ [°]	73.9160(10)
<i>V</i> [Å <sup>3</sup> ]	2361.68(9)
<i>Z</i>	2

Dcalcd [g cm <sup>-3</sup> ]	1.301
$\mu$ [mm <sup>-1</sup> ]	0.594
F(000)	960.0
2 $\theta$ range [°]	6.01 – 109.784
Reflections collected	30529
Independent reflections, <i>Rint</i>	8894, 0.0476
Data / restraints / parameters	8894/0/603
Final <i>R</i> 1 values ( $I > 2\sigma(I)$ )	0.0443
Final <i>R</i> 1 values (all data)	0.0443
Goodness-of-fit on $F^2$	1.026
Largest difference peak and hole [e.Å <sup>-3</sup> ]	0.26/–0.28
CCDC	2024931

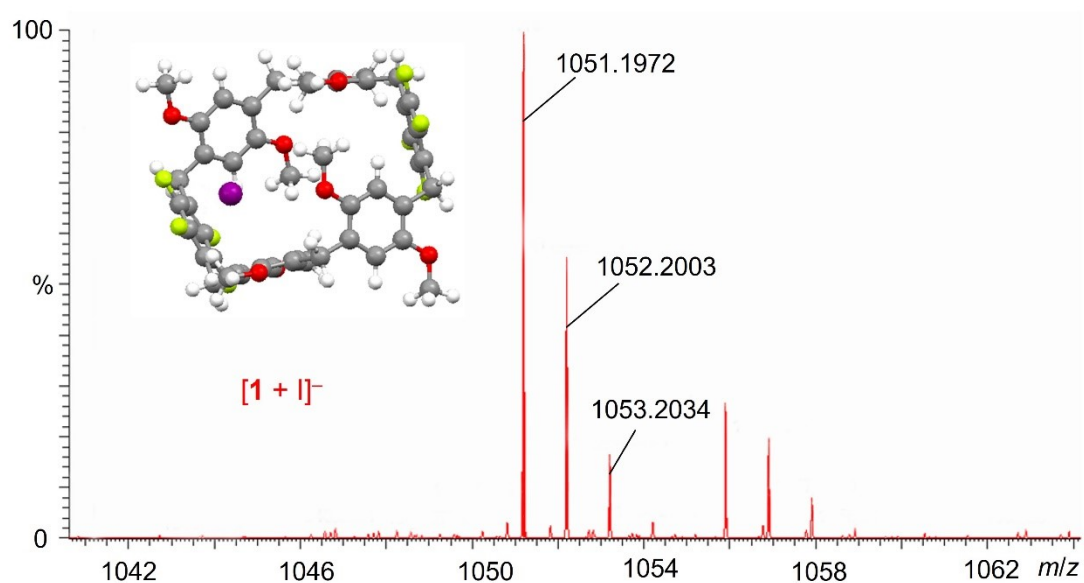
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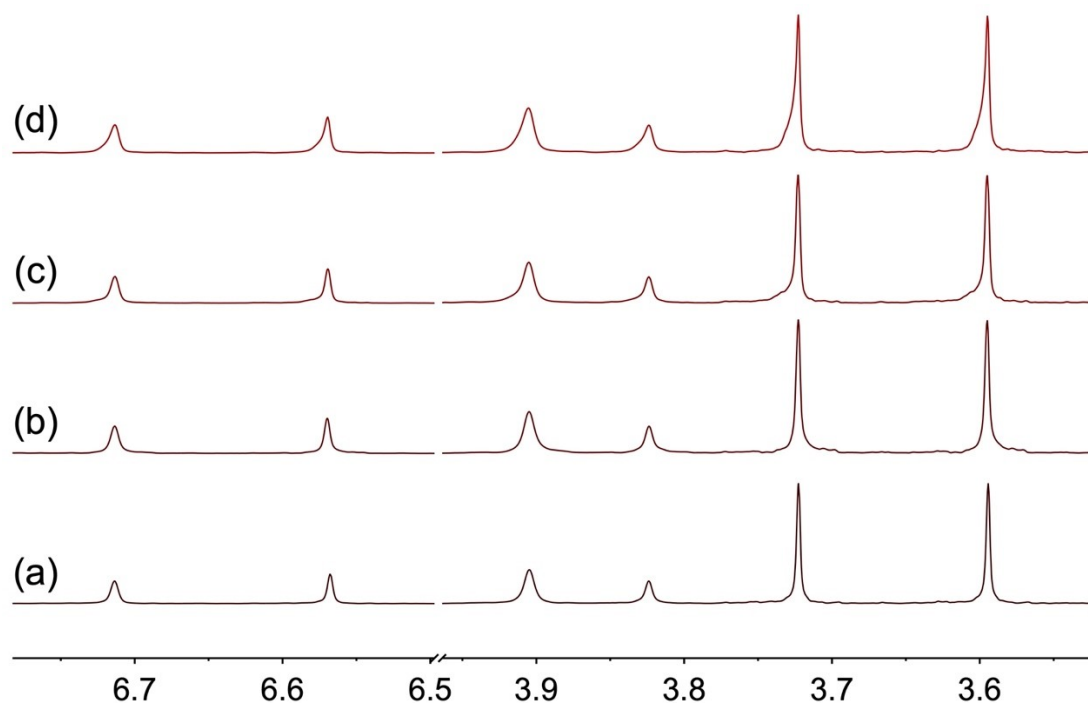
**Fig. S9** Single crystal structure of **1**. C gray, O red, H white, F yellow. C–H···F interactions with H···F distances of 2.507, 2.504 Å; C–H···O interactions with H···O distances of 2.543, 2.572 Å.



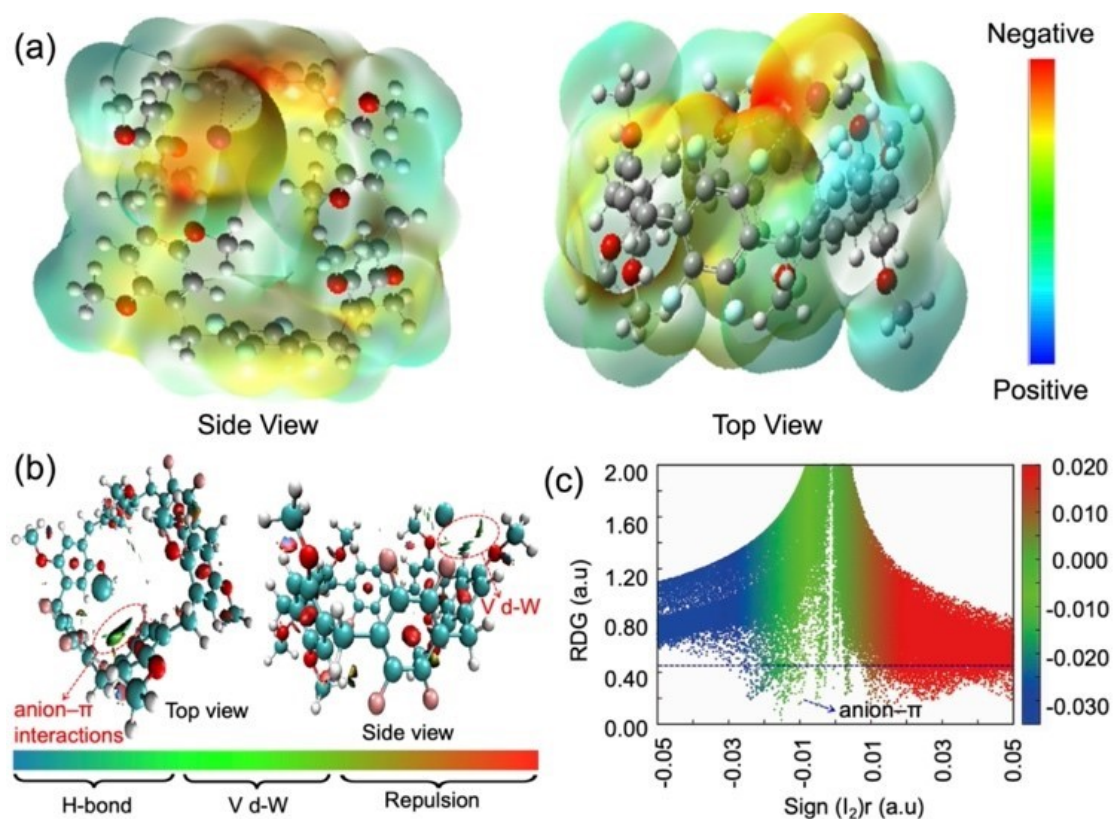
4. Host-guest complexation study between **1** and halide anions



**Fig. S10** The high-resolution ESI-MS spectrum of the host-guest complex  $[1 + I]^-$  in  $\text{CHCl}_3$ .



**Fig. S11** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ , 298 K) of **1** (0.0130 M) upon the addition of 5.00 equivalents of halide anions (0.0650 M): (a) **1**; (b) **1** + TBAF; (c) **1** + TBAC; (d) **1** + TBAB.



**Fig. S12** (a) Molecular electrostatic potential surfaces maps of the host-guest complex; (b) plots of the IGM of the host-guest complex; (c) plots of RDG of the host-guest complex.

### 5. Association constant determination

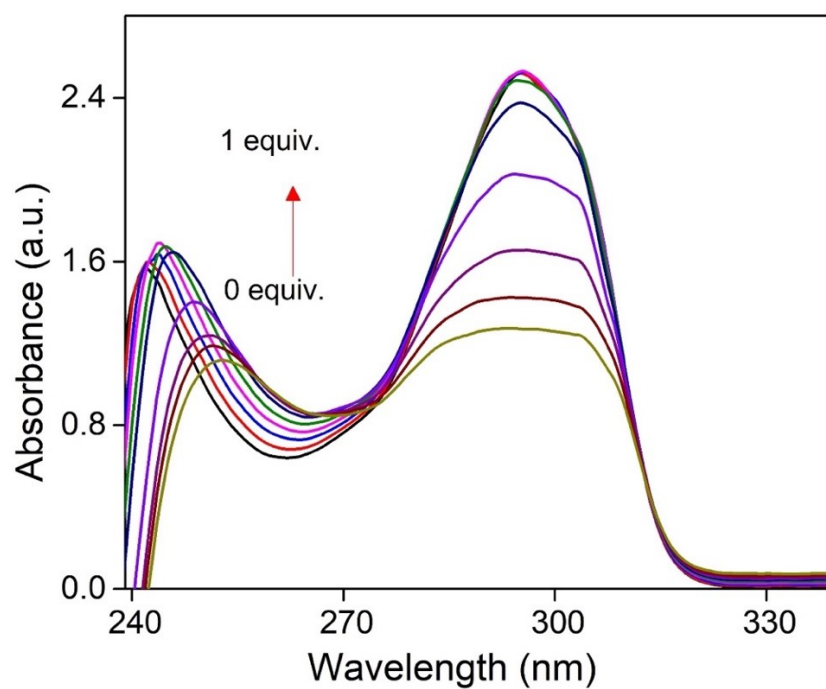
To determine the association constant between **1** and TBAI, UV-vis absorption titration was done with solutions which had a constant concentration of the **1** ( $1.00 \times 10^{-4}$  mol/L) and varying concentrations of the guest molecules. By a non-linear curve-fitting method, the association constant ( $K_a$ ) was determined.

The non-linear curve-fitting was based on a previous report.<sup>S1</sup>

$$\Delta A = (\Delta A_\infty / [H]_0) (0.5[G] + 0.5([H]_0 + 1/K_a) - (0.5([G]^2 + (2[G](1/K_a - [H]_0) + (1/K_a + [H]_0)^2)^{0.5}))$$

Where  $\Delta A$  is the absorbance change of **1** at different concentrations of the guest TBAI,  $\Delta A_\infty$  is the absorbance change when **1** is completely complexed,  $[H]_0$  is the fixed initial

concentration of **1**, and [G] is the concentration of the guest.



**Fig. S13** UV-vis absorption titration spectra ( $\lambda_{em} = 261.5$  nm) of **1** ( $1.00 \times 10^{-4}$  mol/L) in the presence of different concentration of TBAI (0–1.00 equiv.) in  $\text{CHCl}_3$  solution.

#### 6. Calculated potential profile

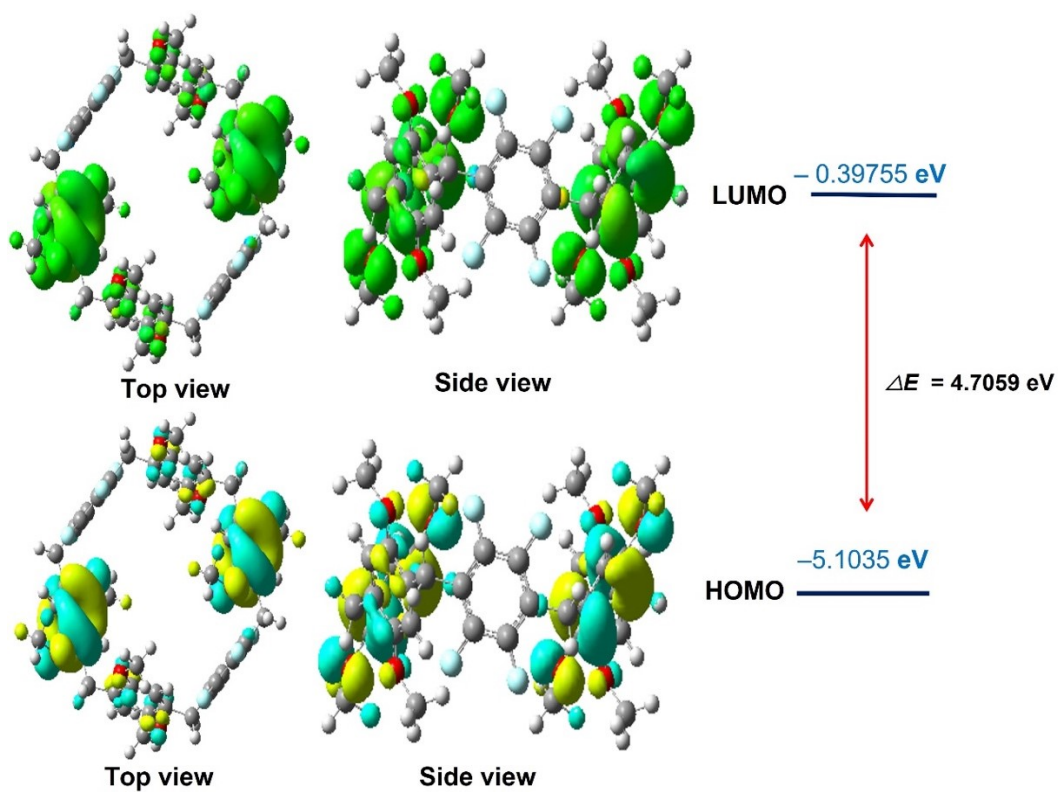


Fig. S14 Frontier molecular orbital energy gap of **1**.

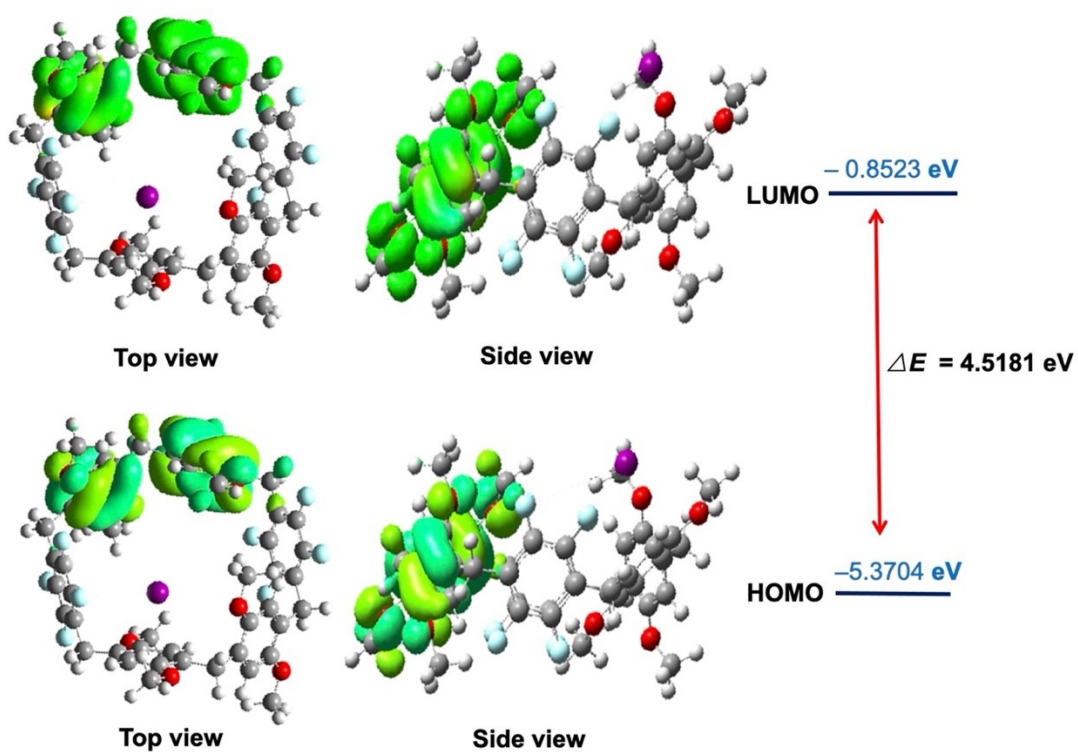


Fig. S15 Frontier molecular orbital energy gap of the host-guest complex.

## 7. References

S1. (a) P. R. Ashton, R. Ballardini, V. Balzani, M. Bělohradský, 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. (b) Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Org. Lett.*, 2014, **16**, 2066–2069.