Supporting Information

Highly selective recognition of the $Al(ClO_4)_3$ molecule by a mono-pyrene substituted thiacalix[4]arene chemosensor

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S01. Materials and methods

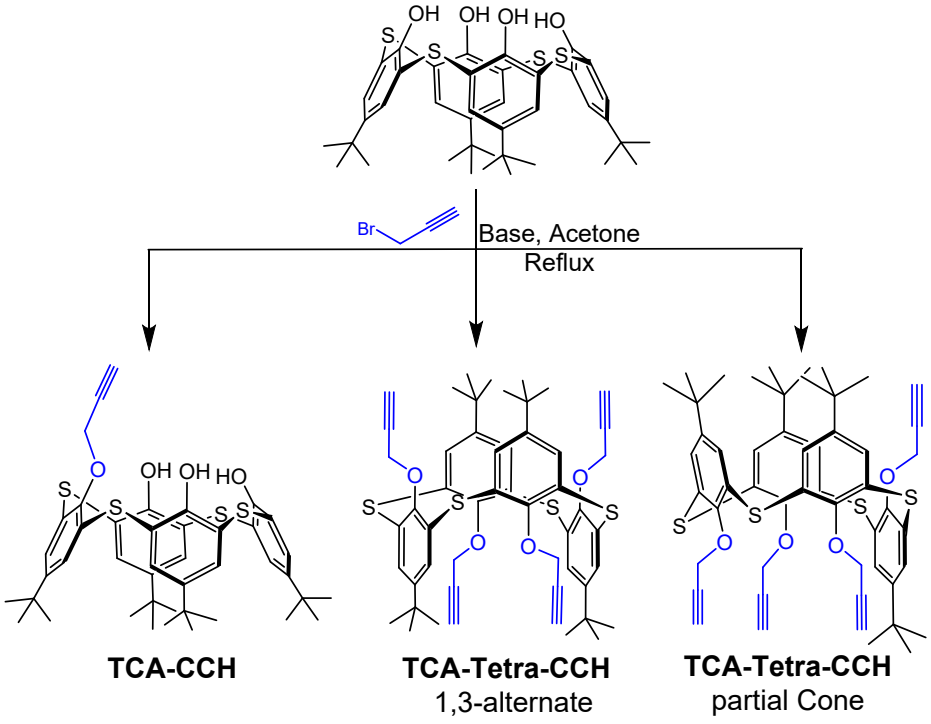
Unless otherwise stated, all reagents used were purchased from commercial sources and were used without further purification. Double distilled water was used throughout. UV-Vis absorption spectra were conducted on a UV-2700 spectrophotometer (Shimadzu) in a 1 cm quartz cell. Fluorescence spectral measurements were performed on fluorescence spectrophotometer (Edinburgh Instruments FS920 or FS5) using a 1 cm quartz cell. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 400 NMR spectrometer at room temperature using TMS as an internal standard. MALDI-TOF mass spectra were measured on a Bruker autoflex 3 system.

S02. Spectral measurement

To a 10 mL volumetric flask containing different ions, the appropriate amounts of the CH_2Cl_2 solution of sensor **TCA-Py** were added using a micropipette. The mixture was diluted with EtOH to 10 mL, and then the fluorescence sensing of the ions was conducted. The fluorescence spectra were measured after addition of the ions at room temperature and when equilibrium was reached. Fluorescence measurements were carried out with an excitation and emission at 344 nm and 396 nm.

S03. Synthesis of compounds

S03.1 Synthesis of the propargyl substituted compounds based on thiacalix[4]arene



Scheme S1. The products for the condensation of thiacalix[4]arene with 3-bromoprop-1-yne.

Table S1. Screening Conditions.

entry	Starting compounds		Base			Reaction time	Yield[b]		
	TCA (eq.)[a]	$BrCH_2CCH$ (eq.)[a]	Na_2CO_3 (eq.)[a]	K_2CO_3 (eq.)[a]	Cs_2CO_3 (eq.)[a]		mono-[d] TCA	Tetra-[e] TCA	Recover TCA
1	1.0	1.1	2.1	□-	□-	48 h	0	0	100%
2	1.0	3.2	□-	2.1	□-	17 h	29%	34%	8%
3	1.0	2.0	□-	1.1	□-	17 h	33%	7%	20%
4	1.0	1.0+1.0[c]	□-	1.1	□-	24h	38%	2%	10%
5	1.0	5.0	-	□-	10	24h	0	85%	0
6	1.0	1.1	□-	□-	2.1	6h	20%	0	50%
7	1.0	0.6+0.5[c]	□-	□-	0.6+0.5[c]	20 h	70%	0	0

[a] The mol ratio for the reagents; [b] Isolated yield from column chromatography; [c] The reagents were added portion wise while stirring; [d] Mono-propargyl substituted thiacalix[4]arene; [e] Tetra-propargyl substituted thiacalix[4]arene.

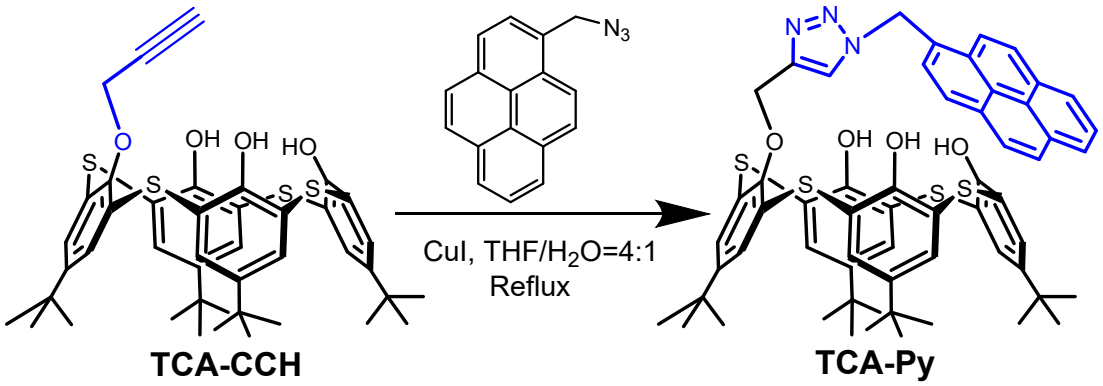
The synthesis of the propargyl substituted compounds based on thiacalix[4]arene were prepared following the general procedure: A mixture of p-*tert*-butylthiacalix[4]arene (**TCA**) and base (as shown in table S1) in dry acetone was heated under reflux for 1 h under an N_2 atmosphere. On cooling to room temperature, 3-bromoprop-1-yne (**$BrCH_2CCH$**) was added while stirring. The mixture heated at reflux for an additional reaction time as shown in table S1. After the prescribed reaction time, the mixture was cooled to room temperature, and the acetone removed under reduced pressure. The system was then diluted with 2 M HCl and extracted with CH_2Cl_2. The organic layer was washed with water and dried over anhydrous $MgSO_4$. The mixture was filtered and the filtrate evaporated to leave a residue, which was purified by column chromatography with Hexane–CH_2Cl_2 (3:1, 2:1, 1:1) as the eluent to afford the products.

Mono-propargyl substituted thiacalix[4]arene (**TCA-CCH**): M.p. 235 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ = δ 9.22 (s, 1H, OH), 8.80 (s, 2H, OH), 7.63 (d, J = 2.5 Hz, 2H, Ar-H), 7.59 (d, J = 2.4 Hz, 2H, Ar-H),7.58 (s, 2H, Ar-H), 7.54 (s, 2H, Ar-H), 5.27 (d, J = 3.1 Hz, 2H), 2.69 (t, J = 2.4 Hz, 1H), 1.23 (s, 18H), 1.20 (s, 9H) and 1.13 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ =156.40, 156.32, 156.01, 149.25, 143.95, 143.66, 136.02, 135.86, 135.83, 135.80, 128.88, 120.95, 120.65, 120.47, 78.02, 63.73, 34.41, 34.14, 34.12, 31.31, 31.26 and 30.99 ppm. HRMS: *m/z* calcd for $C_{43}H_{50}O_4S_4$ $[M]^+$: 758.2592; found:758.2599. (Fig. S1~S3)

Tetra-propargyl substituted thiacalix[4]arene (**TCA-Tetra-CCH**): ^{1}H NMR study revealed that the tetra-propargyl substituted thiacalix[4]arene was comprised of both the partial cone and the 1,3-alternate conformations in $CDCl_3$ solution at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) partial cone: δ = 7.90 (s, 2H), 7.57 (s, 2H), 7.53 (s, 2H), 7.05 (s, 2H), 4.80 (s, 6H), 4.49

(s, 2H), 2.53 (t, J = 2.1 Hz, 2H), 2.46 (d, J = 1.8 Hz, 1H), 2.19 (t, J = 2.1 Hz, 1H), 1.43 (s, 9H), 1.31 (s, 9H) and 1.08 (s, 18H) ppm; 1,3-alternate: δ 7.58 (s, 8H), 4.69 (s, 8H), 2.43 (s, 4H) and 1.27 (s, 36H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ =135.37, 134.30, 133.53, 133.08, 132.16, 131.57, 128.96, 128.68, 128.63, 127.89, 80.57, 80.47, 79.92, 75.23, 74.45, 74.43, 74.40, 61.54, 59.53, 58.38, 57.84, 34.48, 34.37, 34.25, 34.13, 313.36, 31.32, 31.24 and 31.19 ppm. (Fig. S4~S6, The ^{1}H NMR data is the same as the previous report.[1])

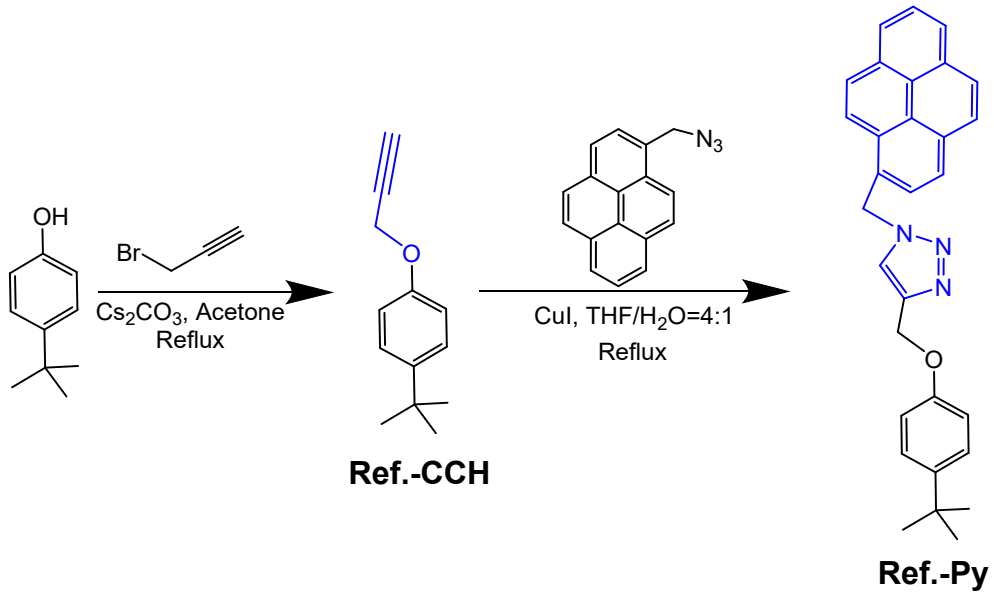
S03.2 Synthesis of Mono-pyrene substituted thiacalix[4]arene (TCA-Py)



Copper iodide (20 mg) and DIPEA (46μL) were added to a mixture of **TCA-CCH** (200 mg, 0.263 mmol) and 1-(azidomethyl)pyrene (135 mg, 0.527 mmol) in 35 ml THF/H_2O (4:1) solution and heated at reflux for 24 h. The resulting solution was cooled and diluted with water and extracted with CH_2Cl_2. The organic layer was separated and dried (Mg_2SO_4) and evaporated to give the solid crude product. The residue was eluted from a column chromatography of silica gel with (CH_2Cl_2/Hexane 1:1 to 1:0) to afford the desired product, **TCA-Py** (123 mg, 46%). Recrystallization from CH_2Cl_2–Methanol afforded X-ray quality colourless crystals. M.p. 186-187°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49 (s, 2H), 8.38 (d, J = 9.2 Hz, 1H), 8.33 – 8.14 (m, 5H), 8.07 (d, J = 7.5 Hz, 1H), 7.97 (dd, J = 12.4, 8.2 Hz, 2H), 7.90 (d, J = 8.9 Hz, 1H), 7.82 (t, J = 7.6 Hz, 1H), 7.55 (s, 2H), 7.48 (d, J = 2.5 Hz, 2H), 7.34 (d, J = 2.5 Hz, 2H), 7.29 (s, 2H), 6.41 (s, 2H), 5.49 (s, 2H), 1.21 (s, 9H), 1.13 (s, 18H) and 1.12 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.97, 156.26, 155.35, 149.50, 143.84, 143.39, 143.16, 136.70, 136.00, 135.93, 135.31, 132.46, 130.92, 130.71, 129.67, 129.57, 128.89, 128.12, 127.86, 127.40, 126.45, 125.84, 125.75, 125.38, 125.34, 124.63, 124.58, 121.82, 120.65, 120.02, 119.83, 70.68, 52.87, 34.40, 34.01, 33.99, 31.33, 31.19 and 30.99 ppm. HRMS: *m/z* calcd for $C_{60}H_{62}N_3O_4S_4$ $[M+H]^+$: 1016.3623; found:1016.4345. (Figs. S7~S9)

S03. 3 Synthesis of reference compound (Ref.-Py)

Compounds **Ref.-CCH**[2] and **Ref.-Py**[3] were prepared by following our previously reported procedures, and their structural identification was verified by ^{1}H NMR spectroscopy (Figs S10-S11).



Scheme S2. Synthetic route to **Ref.-Py**.

S04. Characterization of compounds

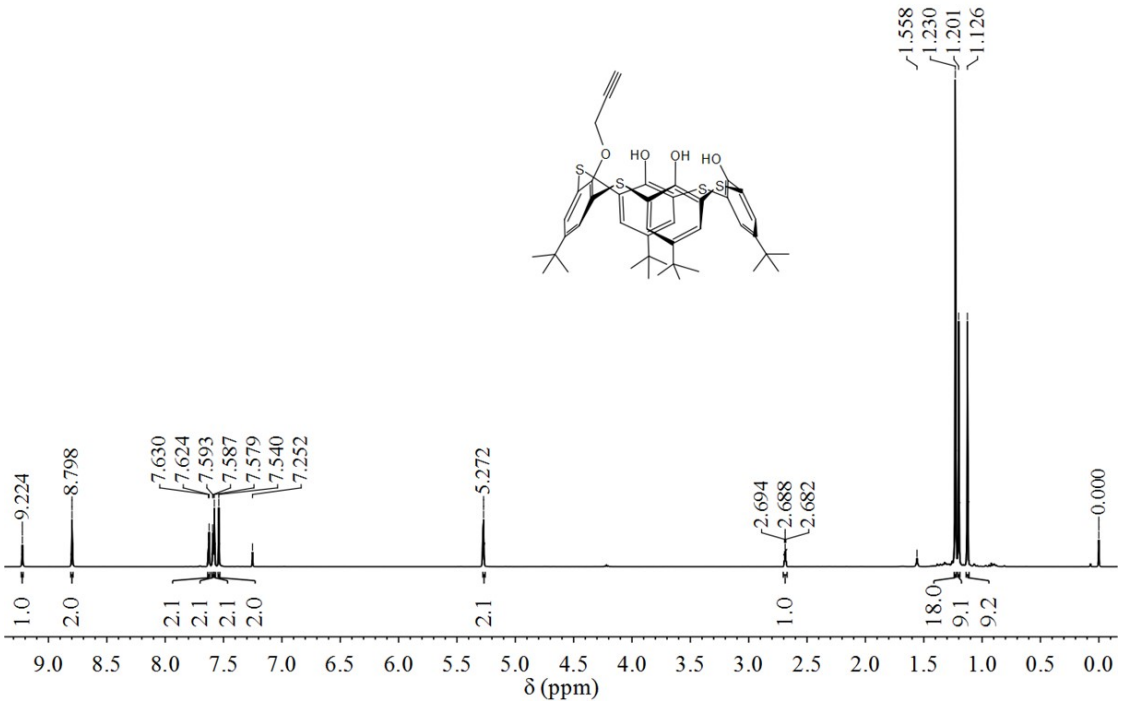


Figure S1. ^{1}H NMR spectrum of **TCA-CCH** (400 MHz, $CDCl_3$, 293 K).

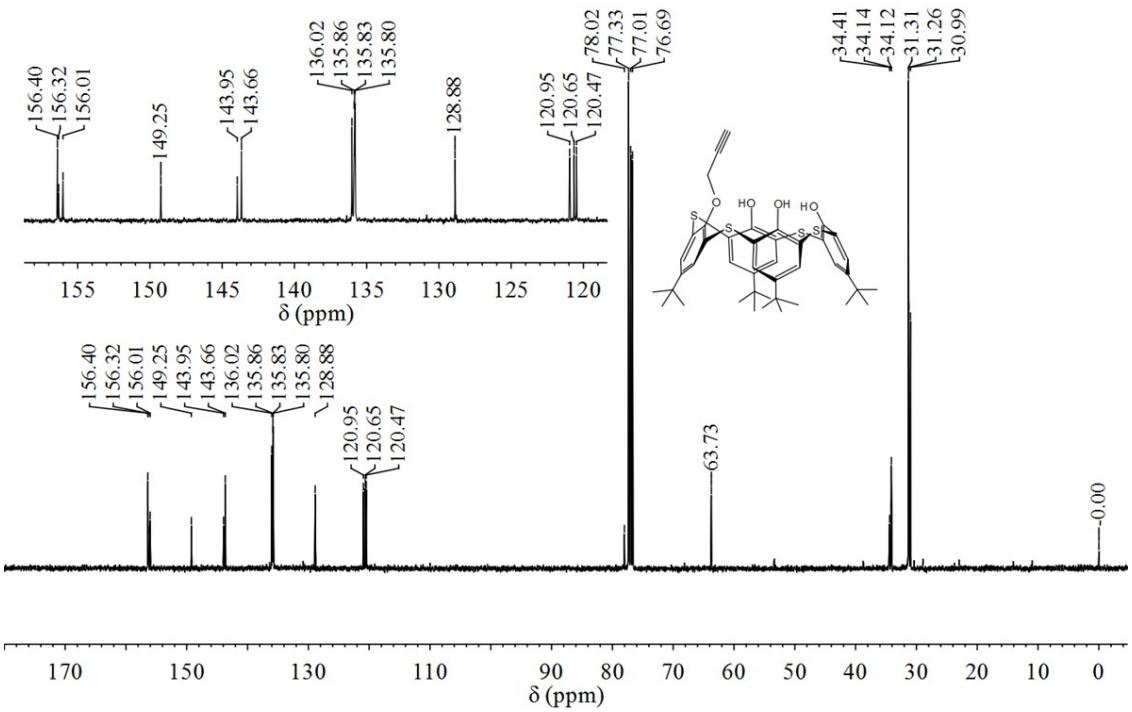


Figure S2. ^{13}C NMR spectrum of **TCA-CCH** (100 MHz, $CDCl_3$, 293 K).

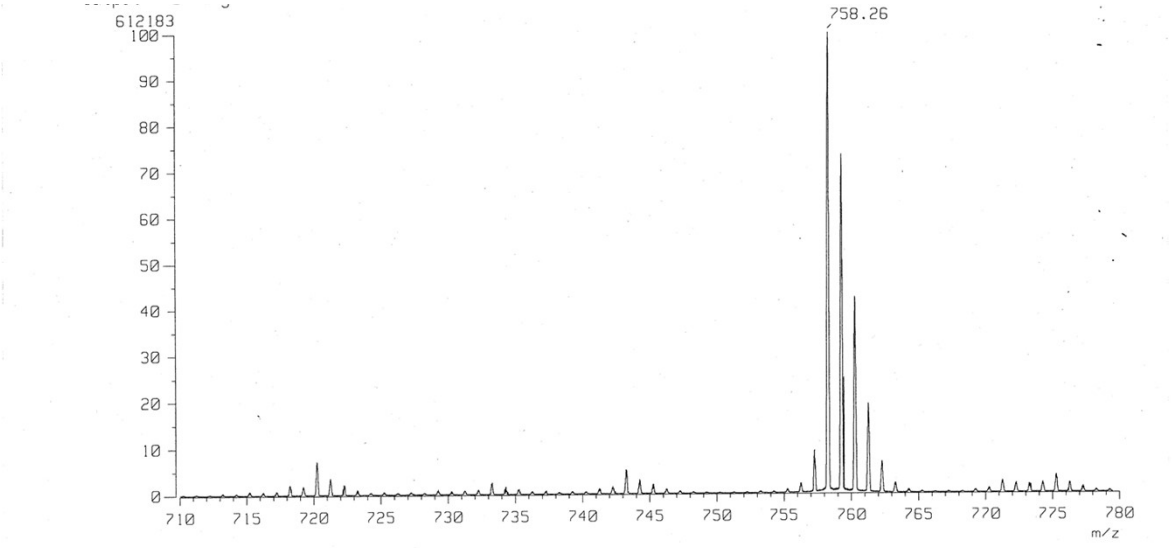


Figure S3. ESI-HRMS spectrum of **TCA-CCH**.

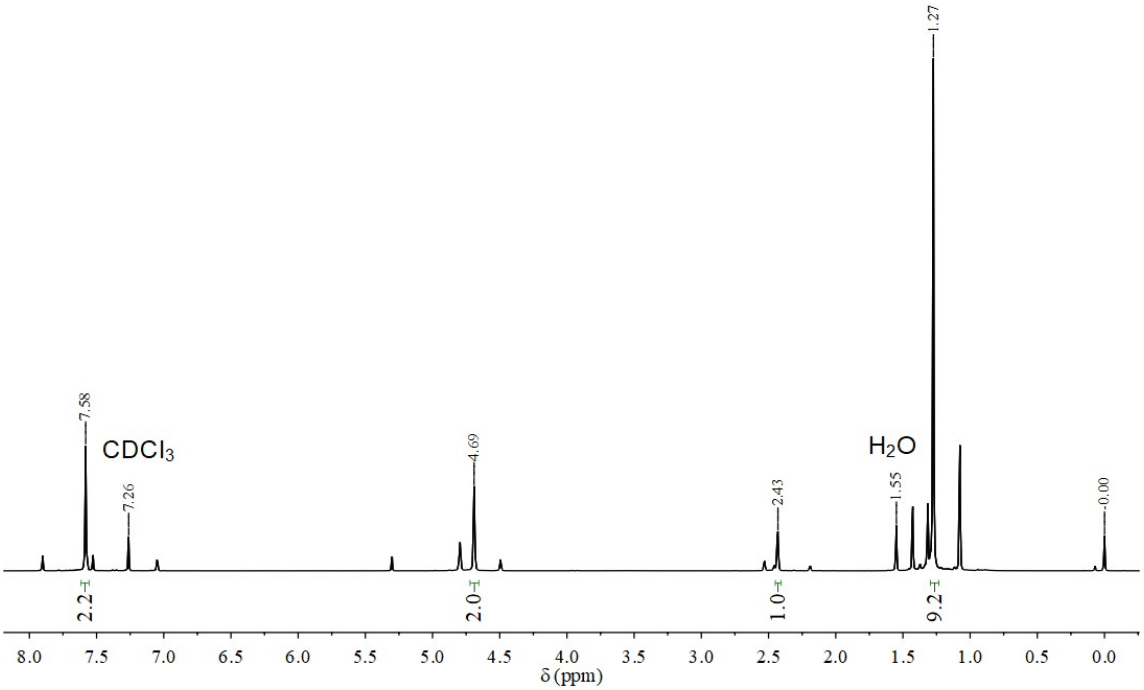


Figure S4. ^{1}H NMR spectrum of 1,3-alternate **TCA-Tetra-CCH** (400 MHz, $CDCl_3$, 293 K). Note: The ^{1}H NMR study revealed that the tetra-propargyl substituted thiacalix[4]arene was comprised of both the partial cone and the 1,3-alternate conformations in $CDCl_3$ at room temperature. Although it is difficult to isolate these two isomers, they can readily be identified. Here, the only labeled peaks correspond to the 1,3-alternate **TCA-Tetra-CCH.**

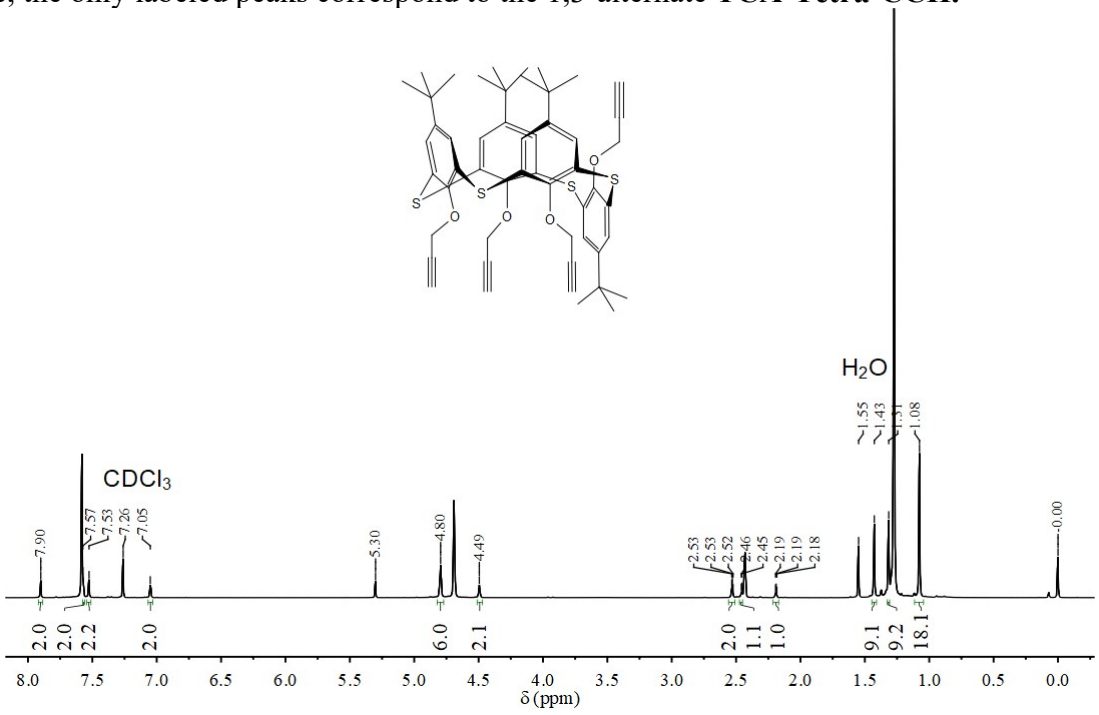


Figure S5. ^{1}H NMR spectrum of partial cone **TCA-Tetra-CCH** (400 MHz, $CDCl_3$, 293 K). Note: The ^{1}H NMR study revealed that the tetra-propargyl substituted thiacalix[4]arene was comprised of both the partial cone and the 1,3-alternate conformations in $CDCl_3$ at room temperature. Although it is difficult to isolate these two isomers, we can easily identify these two isomers. Here, the only labeled peaks correspond to the partial cone **TCA-Tetra-CCH.**

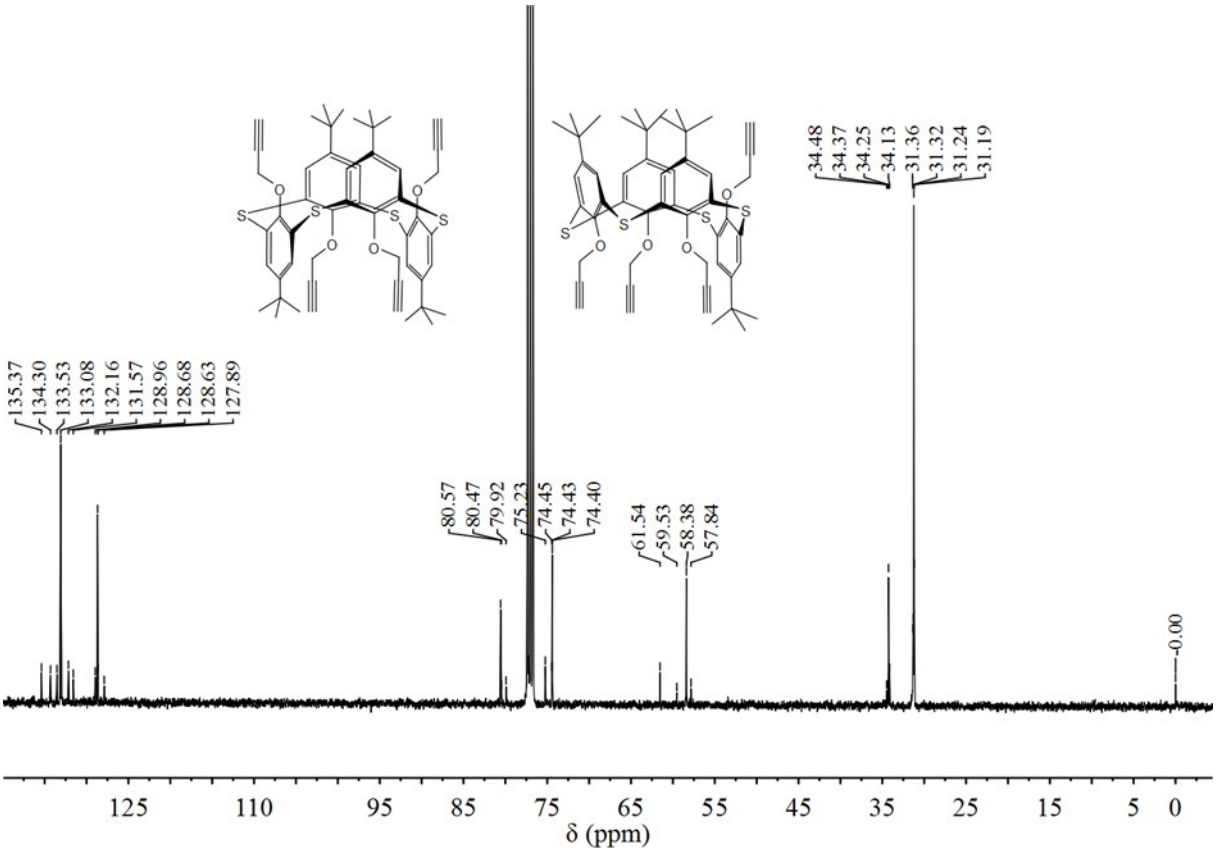


Figure S6. ^{13}C NMR spectrum of **TCA-Tetra-CCH** (100 MHz, $CDCl_3$, 293 K).

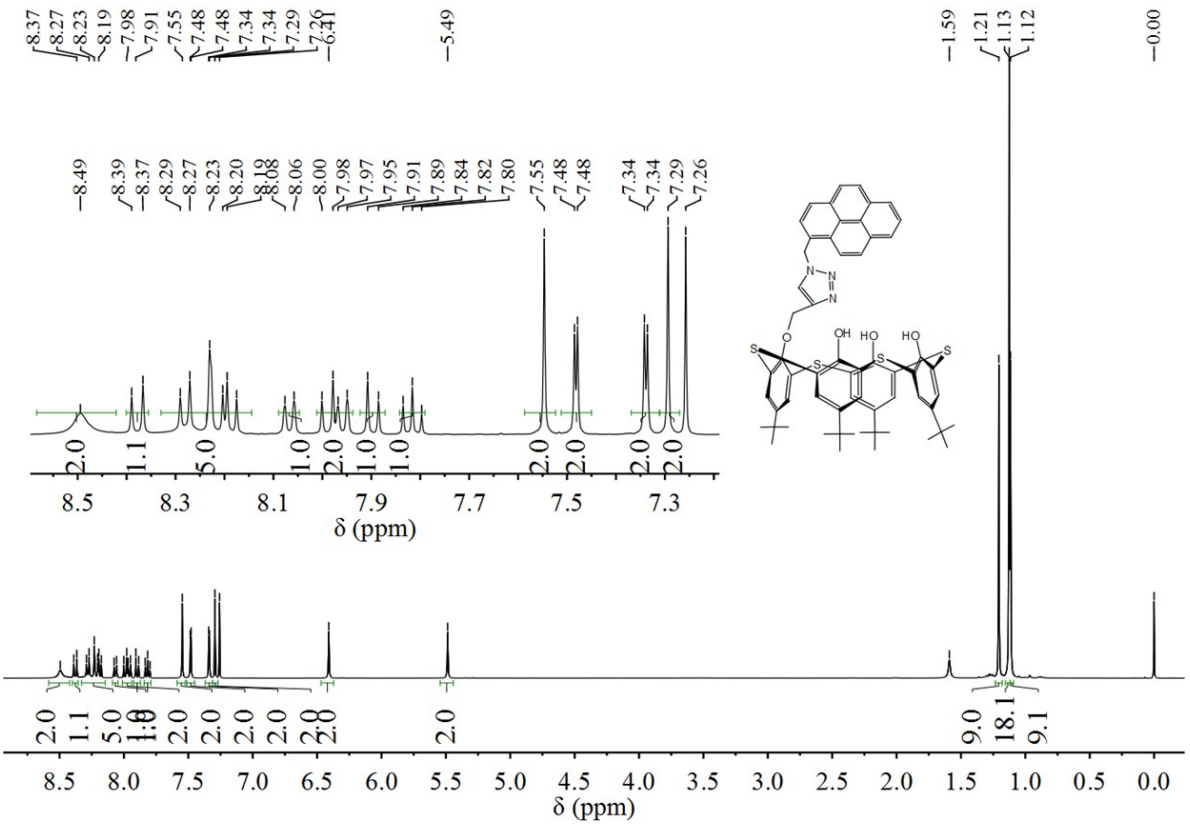


Figure S7. ^{1}H NMR spectrum of **TCA-Py** (400 MHz, $CDCl_3$, 293 K).

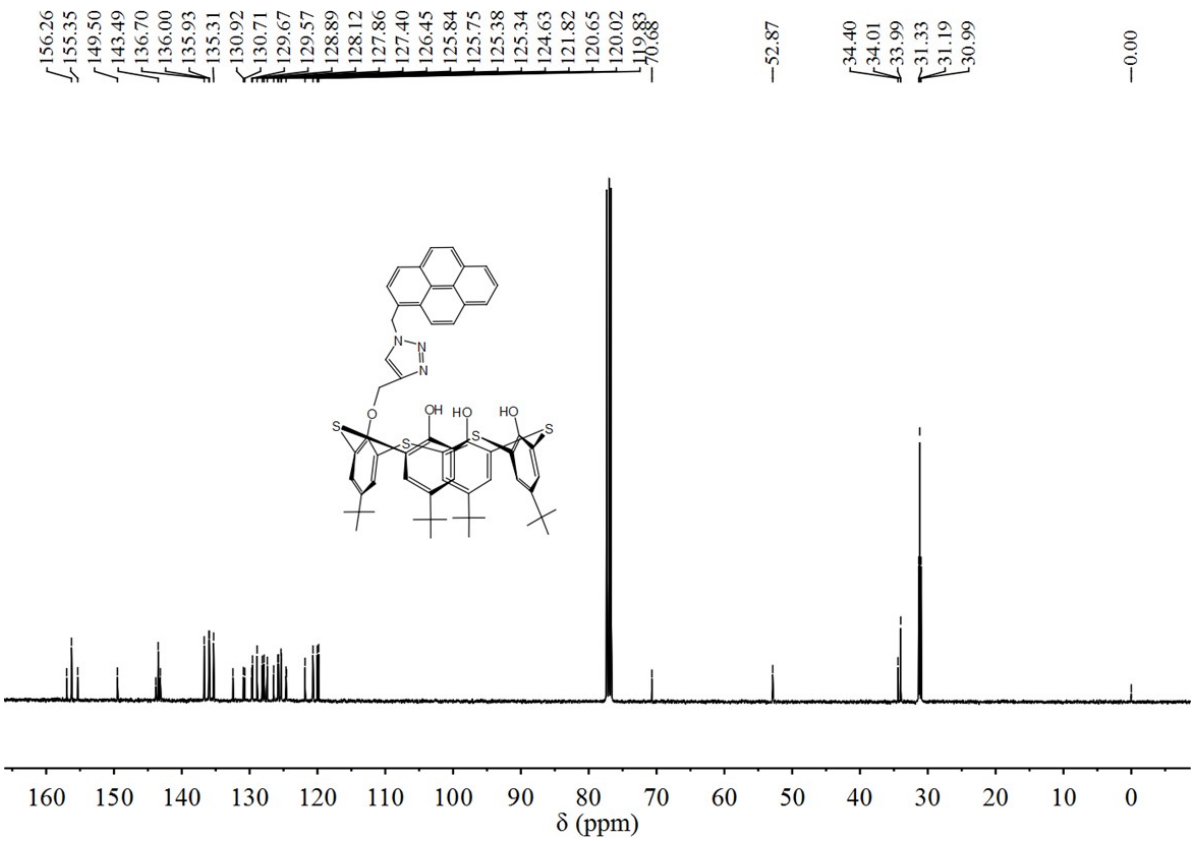


Figure S8. ^{13}C NMR spectrum of **TCA-Py** (100 MHz, $CDCl_3$, 293 K).

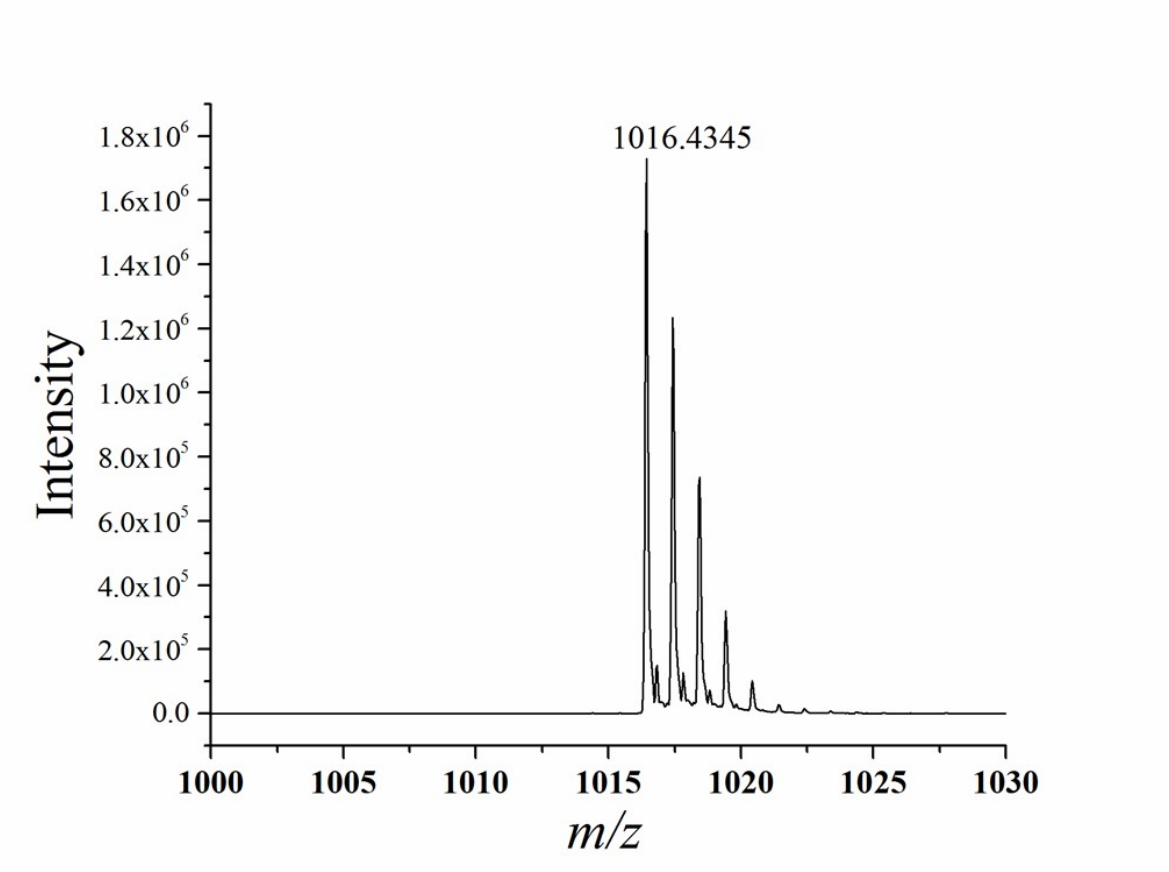


Figure S9. ESI-HRMS spectrum of **TCA-Py**.

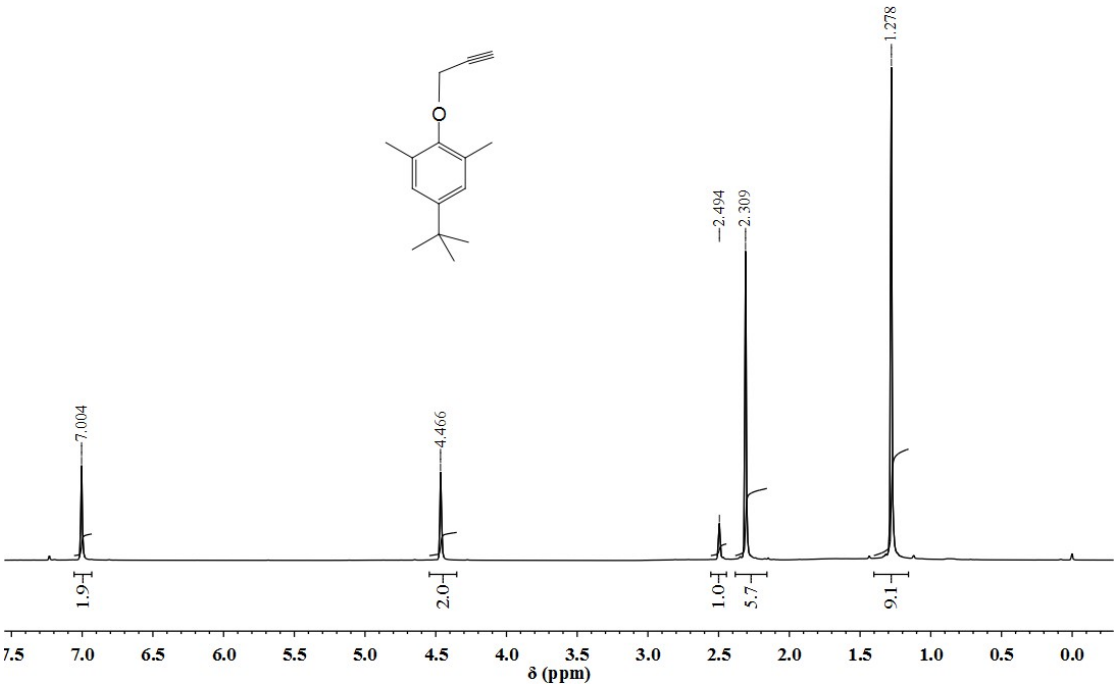


Figure S10. ^{1}H NMR spectrum of compound **Ref.-CCH** (400 MHz, $CDCl_3$, 293 K).

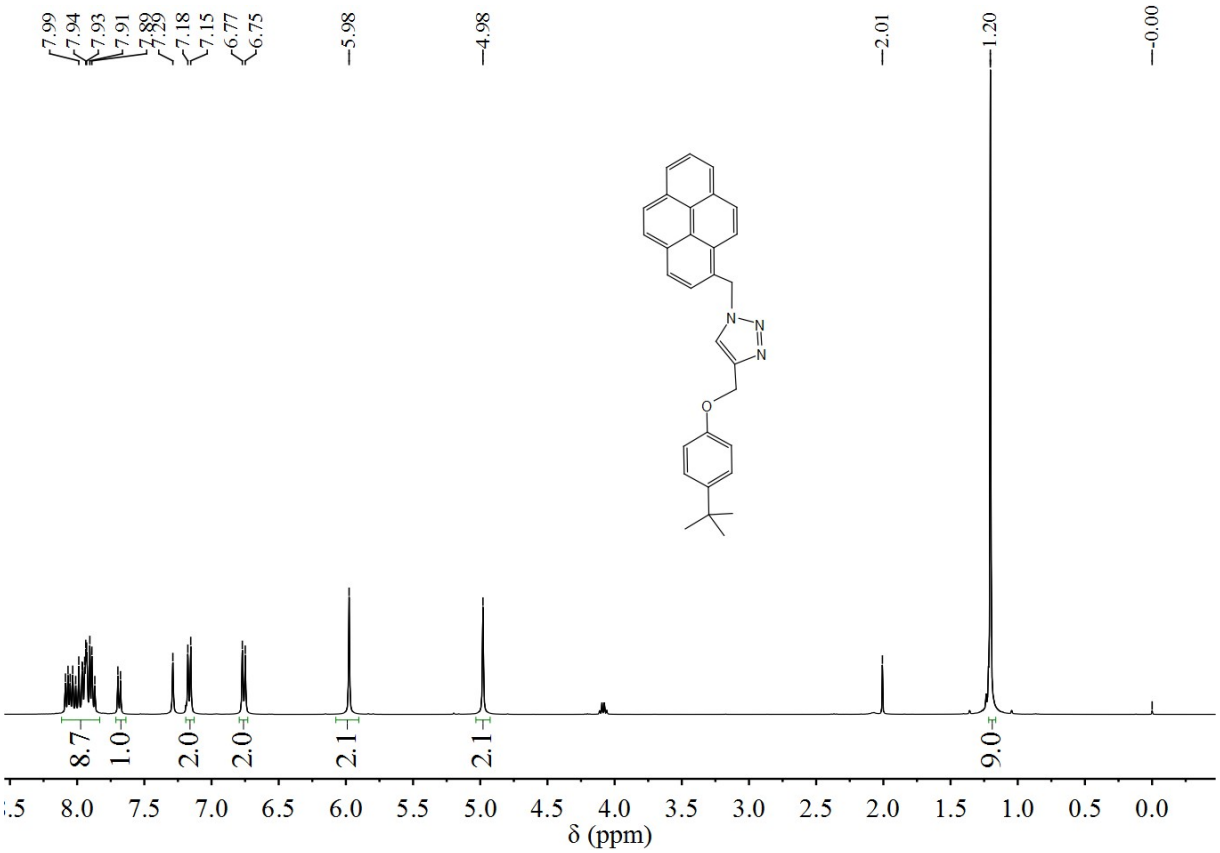


Figure S11. ^{1}H NMR spectrum of compound **Ref.-Py** (400 MHz, $CDCl_3$, 293 K).

S05. X-ray characterization of TCA-Py

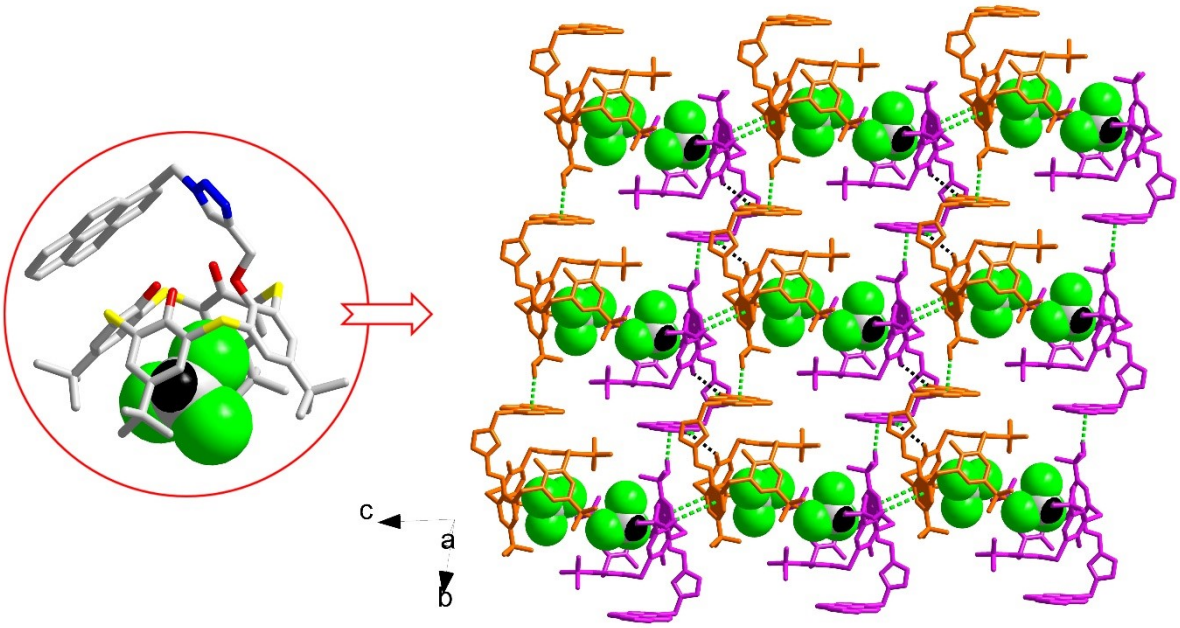


Figure S12. 2D layer of **TCA-Py** with $CHCl_3$ molecules constructed from 1D chains via non-covalent interactions.

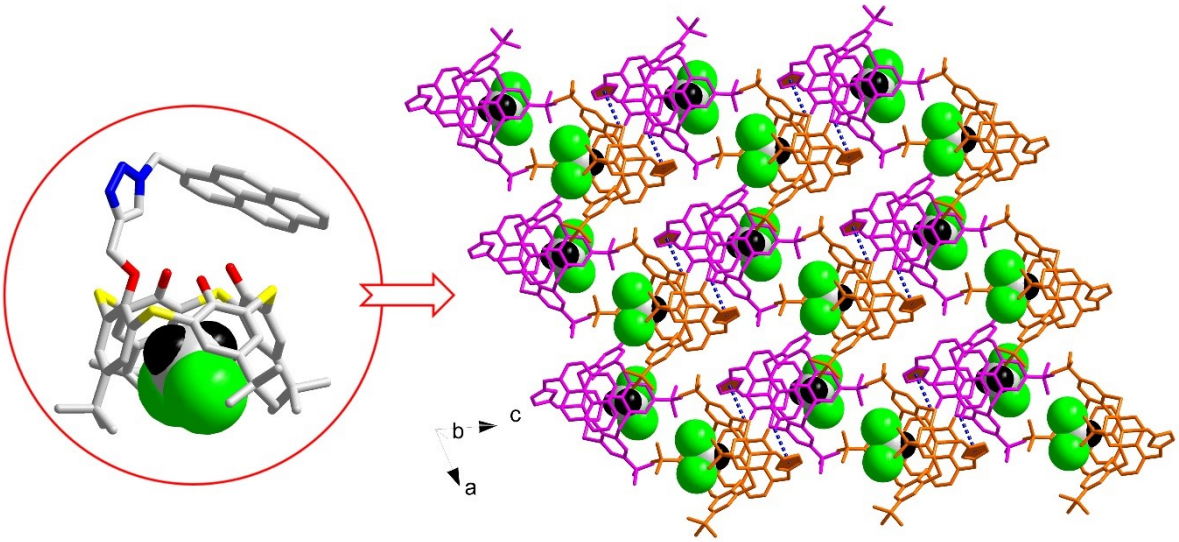


Figure S13. 2D layer of **TCA-Py** with CH_2Cl_2 molecules constructed from 1D chains via non-covalent interactions.

Table S2. Crystal Data and Structure Refinements for sensor **TCA-Py** obtained from $CHCl_3$ (**TCA-Py·CH_2Cl_2**) and CH_2Cl_2 (**TCA-Py·CH_2Cl_2**).

Compound	**TCA-Py·$CHCl_3$**	**TCA-Py·CH_2Cl_2**
chemical formula	$C_{61}H_{62}N_3O_4S_4Cl_3$	$C_{60}H_{63}N_3O_4S_4Cl_2$
formula weight	1135.72	1103.28
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a /Å	13.168(3)	13.6599(17)
b /Å	15.978(4)	15.397(2)
c /Å	17.170(4)	15.955(2)
α /°	78.706(7)	73.023(6)
β /°	82.726(7)	69.682(5)
γ /°	74.748(7)	71.576(5)
temperature /K	293	193
volume /Å^3	3407.0(14)	2922.3(7)
Z	2	2
D_c /g cm^{-3}	1.107	1.254
μ /mm^{-1}	0.299	1.792
F(000)	1192	1162
reflections collected/unique	11906/ 8025	10238/ 8395
data / restraints / parameters	11906/ 20/ 688	10238/ 682 /12
GOF	1.029	1.093
R_1, wR_2 [$I > 2\sigma(I)$][a,b]	0.0796/ 0.1659	0.0741/ 0.2176
R_1, wR_2 (all data)	0.1086/ 0.1755	0.0890 /0.2336

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$

S06. Fluorescence spectra of Ref.-py and TCA-Py

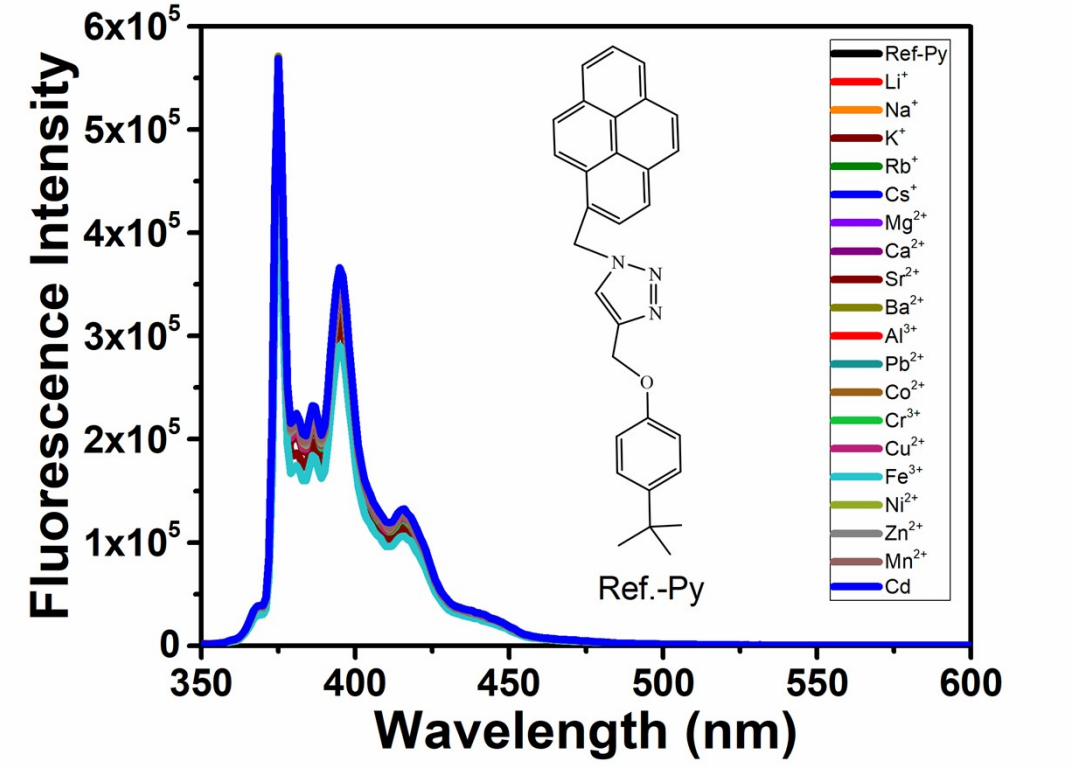


Figure S14. Fluorescence spectra (λ_{ex} = 344 nm) of sensor **Ref.-Py** (10 μM, EtOH/CH_2Cl_2/H_2O = 94/1/5) with or without 10 equiv. of the various guest ((the perchlorate of Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Fe^{3+}, Al^{3+} and $Cr(NO_3)_3$).

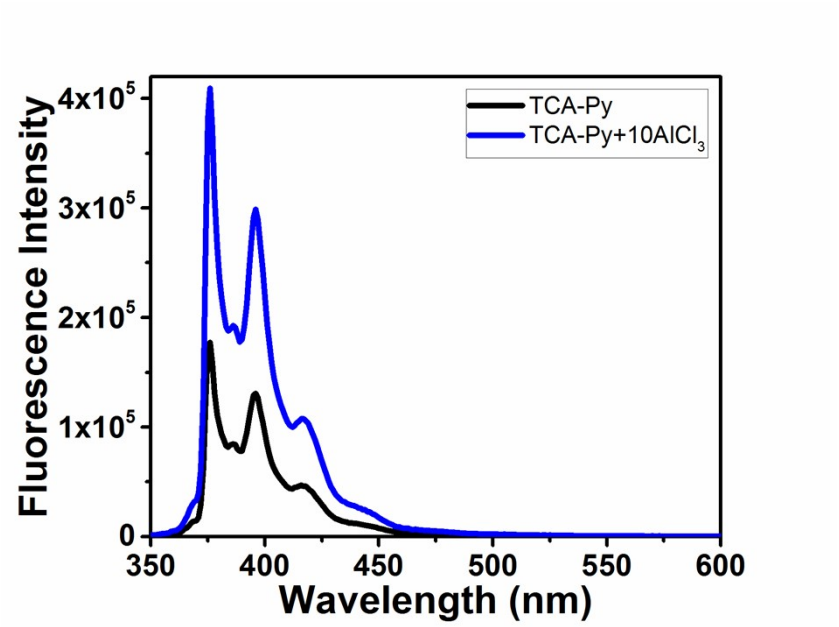


Figure S15. Fluorescence spectra (λ_{ex} = 344 nm) of sensor **TCA-Py** (10 μM, EtOH/CH_2Cl_2/H_2O = 94/1/5) with or without 10 equiv. of $AlCl_3$ solution.

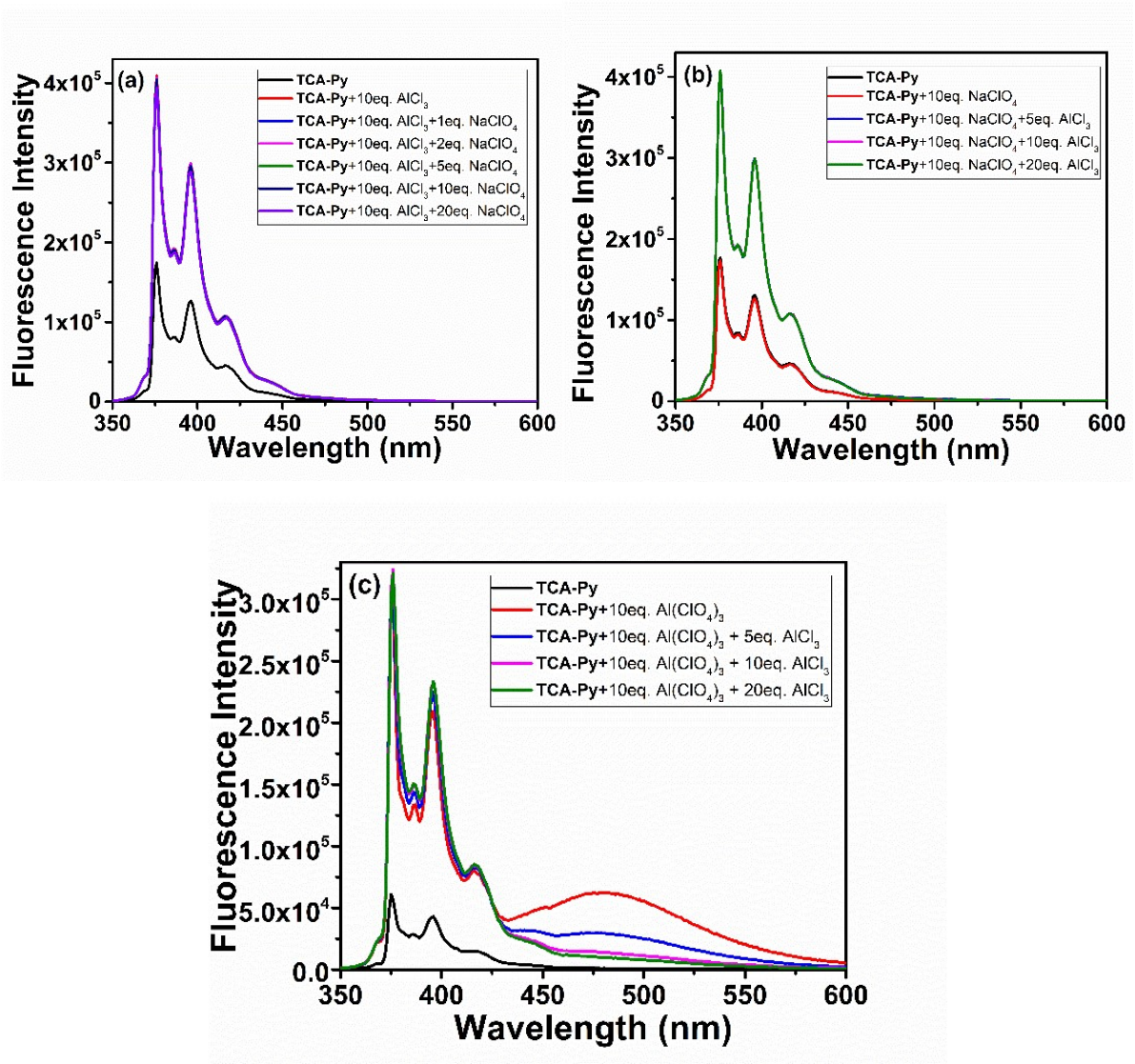


Figure S16. a) Fluorescence spectra of sensor **TCA-Py** (10 μM, EtOH/CH_2Cl_2/H_2O = 94/1/5) with 10 equiv. of $AlCl_3$ solution, and then gradually increasing the concentration of $NaClO_4$ solution; b) Fluorescence spectra of sensor **TCA-Py** (10 μM, EtOH/CH_2Cl_2/H_2O = 94/1/5) with 10 equiv. of $NaClO_4$ solution, and then gradually increasing the concentration of $AlCl_3$ solution; c) Fluorescence spectra of sensor **TCA-Py** (10 μM, EtOH/CH_2Cl_2/H_2O = 94/1/5) with 10 equiv. of $Al(ClO_4)_3$ solution, and then gradually increasing the concentration of $AlCl_3$ solution.

S07. Binding constant

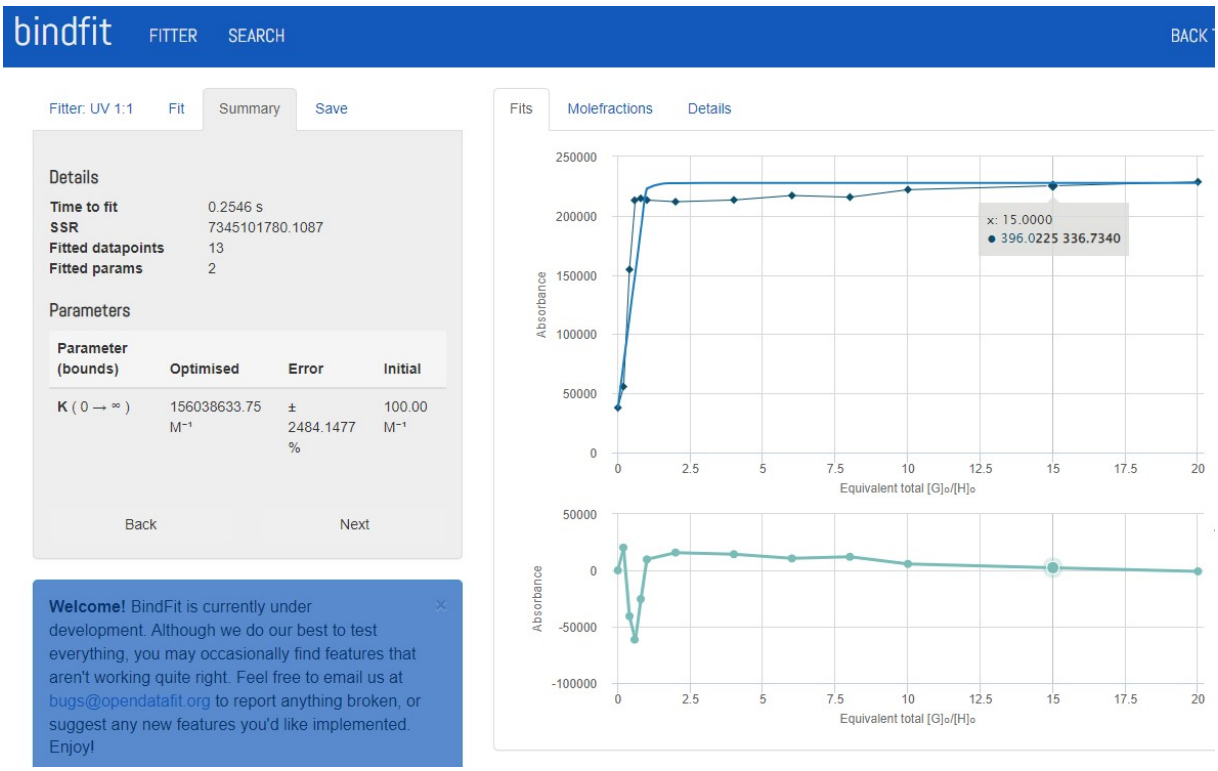


Figure S17. The binding constant of **TCA-Py**-$AlCl_3$ complex was calculated using the online supramolecular chemistry research and analysis tools[4] reported in 2015 by Prof. Pall Thordarson[5] at UNSW to extract the binding constant. The binding constant was calculated to be $1.56\times10^8 \pm 243$ M^{-1}.

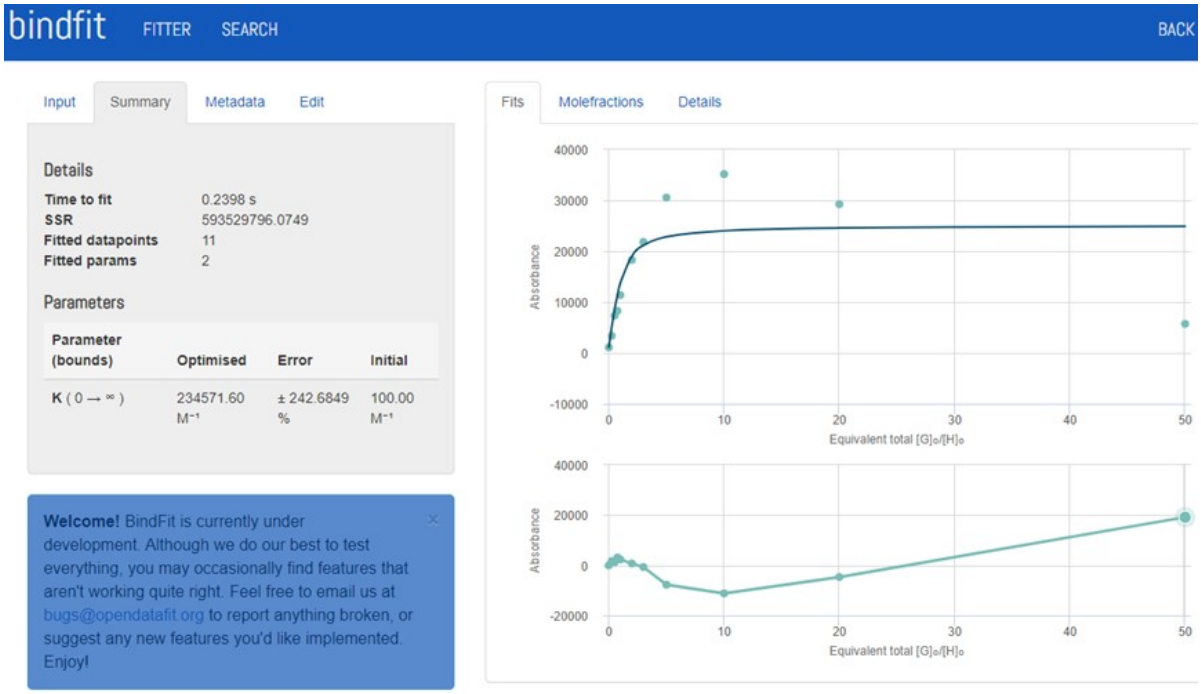


Figure S18. The binding constant of **TCA-Py**-$Al(ClO_4)_3$ complex was calculated using the online supramolecular chemistry research and analysis tools[4] which was reported in 2015 by Prof. Pall Thordarson[5] at UNSW to extract the binding constant. The binding constant was

calculated to be $2.35\times10^5 \pm 243$ M^{-1}.

S08. References

1. X. Li, H. W. Han and X. G. Meng, *Acta Crystallogr Sect E Struct Rep Online*, 2009, **65**, o3007.
2. J. L. Zhao, C. Wu, H. Tomiyasu, X. Zeng, M. R. J. Elsegood, C. Redshaw and T. Yamato, *Chem Asian J*, 2016, **11**, 1606-1612.
3. X.-L. Ni, X. Zeng, C. Redshaw and T. Yamato, *Tetrahedron*, 2011, **67**, 3248-3253.
4. http://supramolecular.org/.
5. a) P. Thordarson, *Chem. Soc. Rev*., 2011, 40, 1305-1323; b) D. B. Hibbert and P. Thordarson, *Chem. Commun*., 2016, 52, 12792-12805