

## Electronic Supplementary Information

# Anthracene-Containing Crown Ether: Synthesis, Host–Guest Properties and Modulation of Solid-State Luminescence

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## Table of Contents

1. Materials and methods .....	S2
3. Synthesis of <b>An34C10</b> .....	S4
4. Fluorescence properties of <b>An34C10</b> in solution .....	S10
5. Characterization of <b>An34C10</b> under different stimuli .....	S11
6. Complexation of <b>An34C10</b> and <b>TCNB</b> in solution .....	S14
7. Characterization of <b>An34C10@TCNB</b> under different stimuli .....	S17
8. References .....	S25

## 1. *Materials and methods*

All chemicals were either employed as purchased or dried according to procedures described in the literature. Compounds **2** and **4** were prepared according to literature procedures.<sup>S1–S3</sup> A Bruker Avance DMX 400 spectrometer and a Bruker Avance DMX 600 spectrometer were used to record the <sup>1</sup>H and <sup>13</sup>C NMR spectra using the deuterated solvent as the lock. The internal reference was TMS or residual solvent. Quadrupole-time of flight (Q-TOF) mass spectrometry data were collected on an Agilent 6545 Q TOF mass spectrometer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultimate-IV X-ray diffractometer operating at 40 kV/30 Ma using the Cu K $\alpha$  line ( $\lambda = 1.5418 \text{ \AA}$ ). Data were measured over the range of 5–60° in 10 °/min steps over 5 min. Fourier transform infrared spectra (FT-IR) were recorded on KBr pellets containing ca. 1 mg of the compound in the range of 4000–400 cm<sup>-1</sup> on a Perkin–Elmer FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was carried out using a Q5000IR analyzer (TA instruments) with an automated vertical overhead thermobalance. The samples were heated at the rate of 10 °C/min using N<sub>2</sub> as the protective gas. Differential scanning calorimetry (DSC) was carried out using a DSC Q100 analyzer (TA Instruments). The samples were heated at 10 °C/min using N<sub>2</sub> as the protective gas. UV-vis spectra in solution were taken on a PerkinElmer Lambda 35 UV-vis spectrophotometer. Solid state UV-vis spectra were measured on a Shimadzu UV-VIS-NIR spectrometer (UV33600Plus). The fluorescence spectra in solution were recorded on a Shimadzu RF-5301PC fluorescence spectrophotometer. Solid state fluorescence spectra, fluorescence lifetime and quantum yield were measured on a spectrofluorimeter (Edinburgh FLS1000).

## 2. *Crystallographic data*

**Single Crystal Growth.** Single crystals of **An34C10** were grown by slow evaporation: 1.5 mg of dry **An34C10** powder were put in a small vial where 1.0 mL of ethyl acetate was added and the vial was heated until all the powder was dissolved. The resultant transparent solution was allowed to evaporate slowly to give crystals in

a few days. Single crystals of **An34C10@TCNB** were grown by slow evaporation: 1.5 mg of dry **An34C10** and 0.4 mg of **TCNB** were put in a small vial where 1.0 mL of acetone was added. The vial was heated until the two chemicals were dissolved. The resultant transparent solution was allowed to evaporate slowly to give dark purple crystals in a few days.

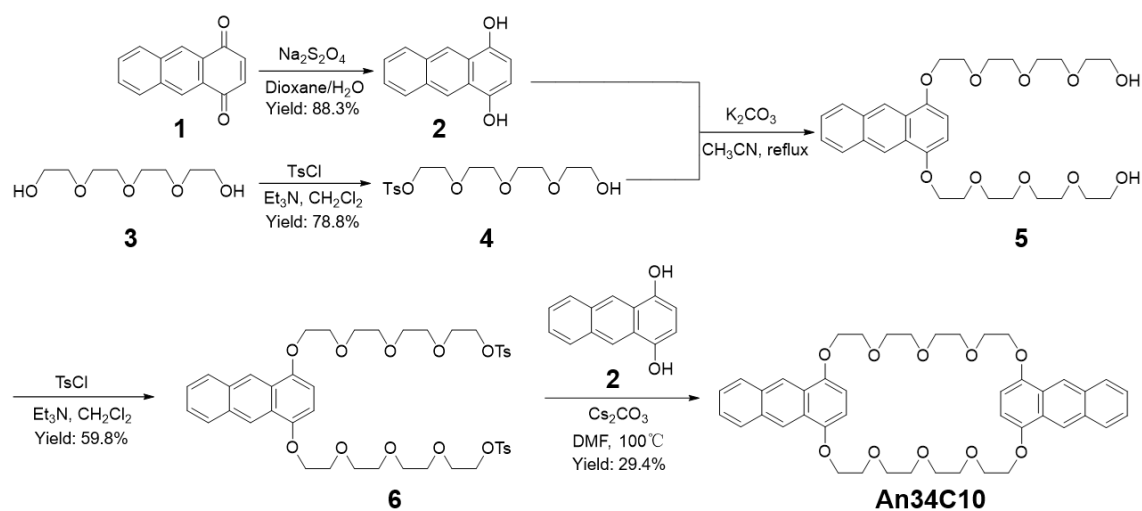
**Single Crystal X-Ray Diffraction.** Suitable crystals were selected and measured on a Bruker D8 Venture diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for cell determination. Supplementary CIFs, which include structure factors, are available free of charge from the Cambridge Crystallographic Data Centre (CCDC) via <https://www.ccdc.cam.ac.uk/structures/>.

**Table S1.** Experimental single crystal X-ray data for **An34C10** and **An34C10@TCNB** structures.

Formula	<b>An34C10</b>	<b>An34C10@TCNB</b>
Crystallization Solvent	Ethyl acetate	Acetone
Collection Temperature	170 K	277 K
Chemical Formula	C <sub>44</sub> H <sub>52</sub> O <sub>12</sub>	C <sub>54</sub> H <sub>48</sub> N <sub>4</sub> O <sub>10</sub>
Mr	772.85	912.96
Crystal Size [mm]	0.42 × 0.13 × 0.08	0.07 × 0.07 × 0.05
Crystal System	Monoclinic	Monoclinic
Space Group	<i>C2/c</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> [Å]	29.2025(13)	13.1957(8)
<i>b</i> [Å]	6.5188(2)	19.8927(13)
<i>c</i> [Å]	23.6035(11)	9.9873(6)
$\alpha$ [°]	90	90
$\beta$ [°]	116.6370(10)	112.009(4)
$\gamma$ [°]	90	90
<i>V</i> [Å <sup>3</sup> ]	4016.4(3)	2430.6(3)
<i>Z</i>	4	2
<i>D</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.278	1.247

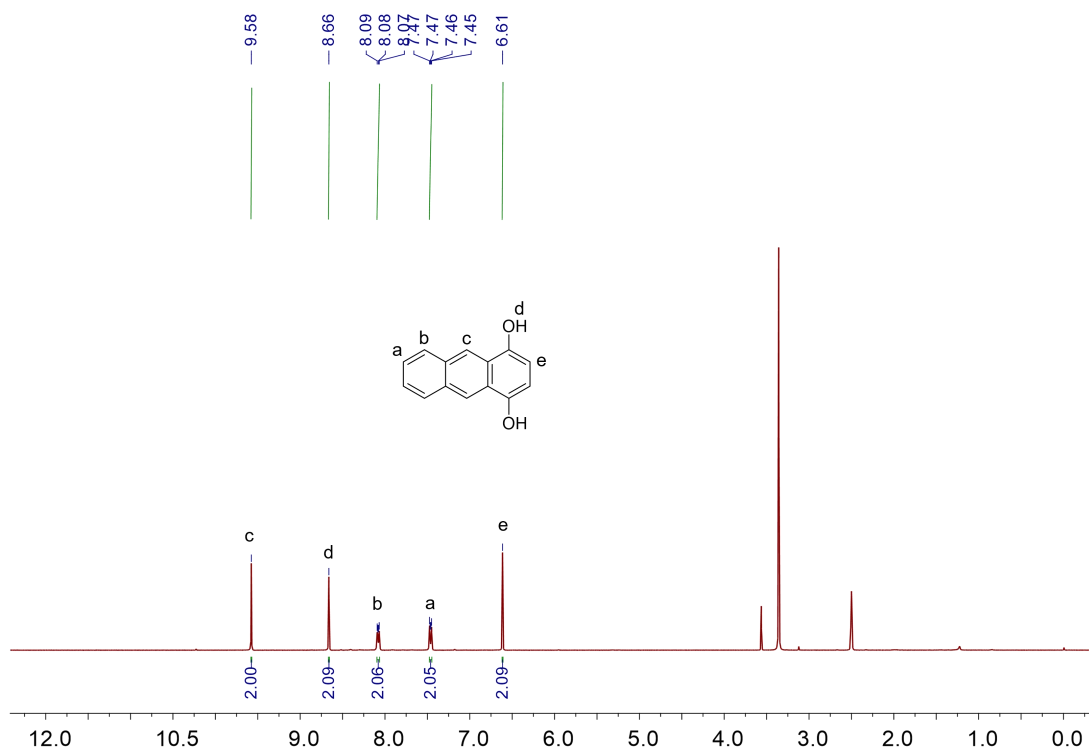
$\mu$ [mm <sup>-1</sup> ]	0.092	0.451
F(000)	1648	960
2 $\theta$ range [°]	5.680–54.348	7.732–110.128
Reflections collected	35919	20306
Independent reflections, $R_{int}$	4469, 0.0276	4506, 0.0803
Obs. Data [ $I > 2\sigma(I)$ ]	3540	2145
Data / restraints / parameters	4469 / 0 / 256	4506 / 84 / 358
Final $R_I$ values ( $I > 2\sigma(I)$ )	0.0422	0.1237
Final $R_I$ values (all data)	0.0569	0.1985
Final $wR(F_2)$ values (all data)	0.1178	0.3030
Goodness-of-fit on $F^2$	1.045	1.064
Largest difference peak and hole [e.A <sup>-3</sup> ]	0.189 / -0.415	1.241 / -0.282
CCDC	2226677	2226678

### 3. Synthesis of An34C10

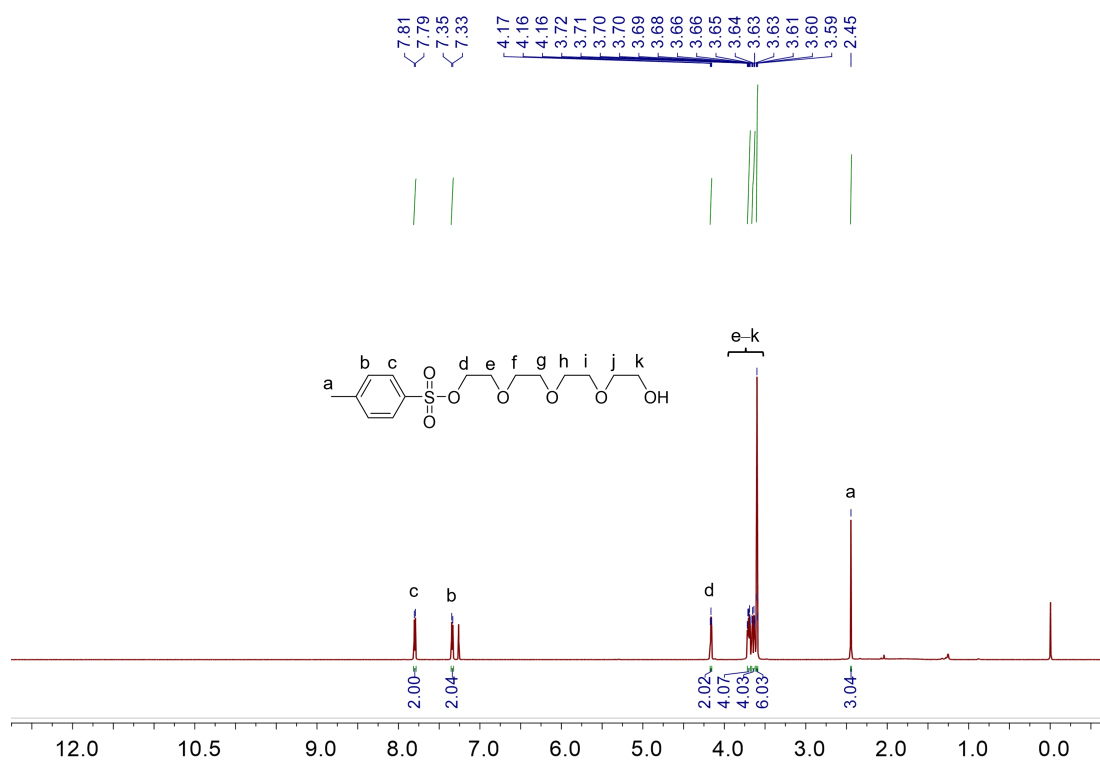


**Fig. S1.** Synthetic route to An34C10.

Compounds **2** and **4** were prepared according to a previous report.<sup>S1–S3</sup> They were all characterized by <sup>1</sup>H NMR.



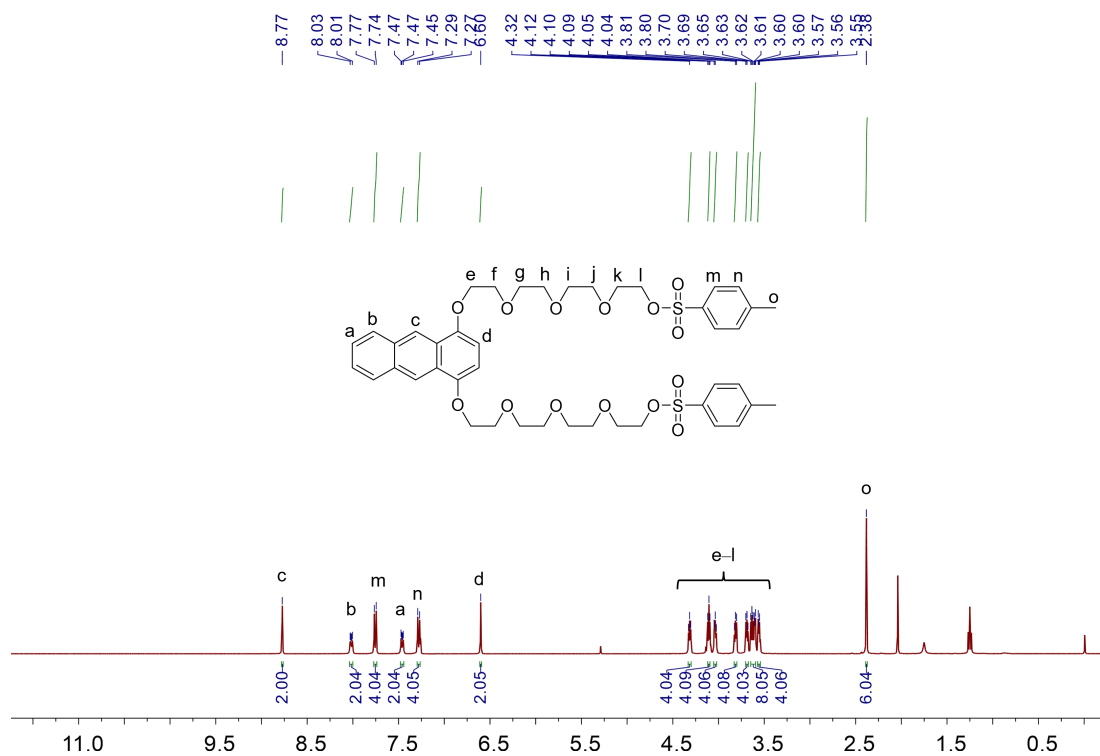
**Fig. S2.**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of compound 2.



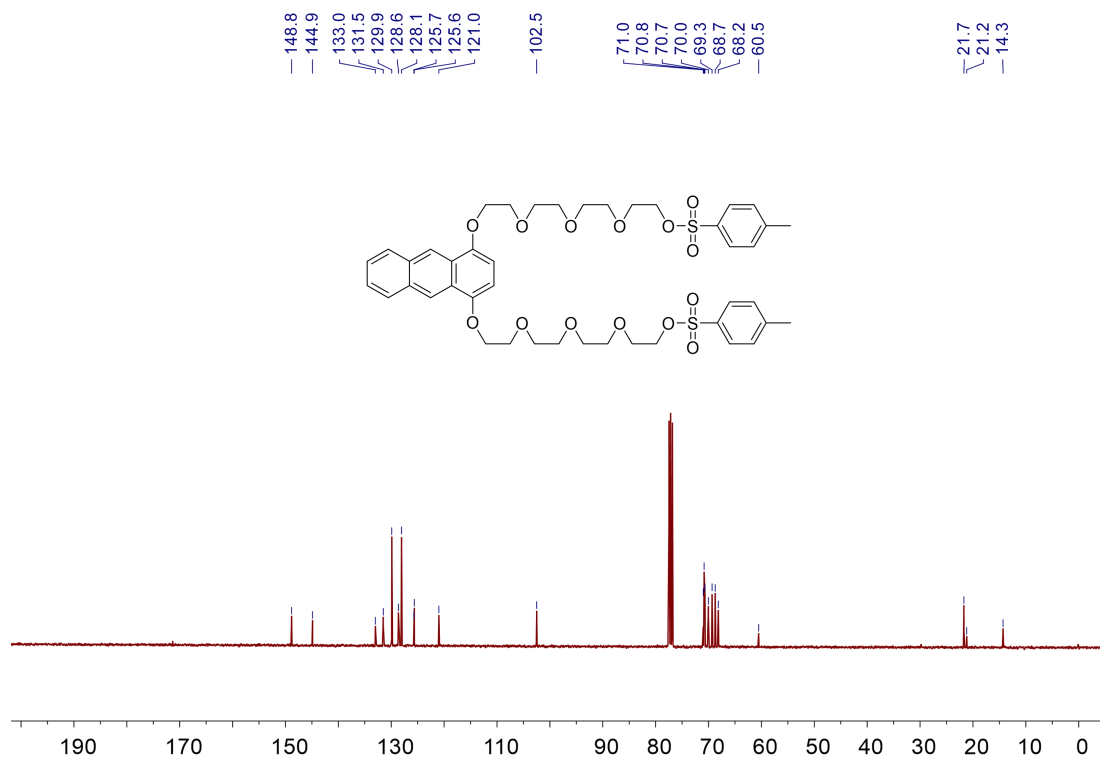
**Fig. S3.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{chloroform-}d$ , 298 K) of compound 4.

**Compounds 5 and 6:** A suspension of compound 2 (1.37 g, 6.50 mmol), compound 4 (4.98 g, 14.3 mmol), and  $\text{K}_2\text{CO}_3$  (3.61 g, 26.2 mmol) in  $\text{CH}_3\text{CN}$  (120 mL) was stirred

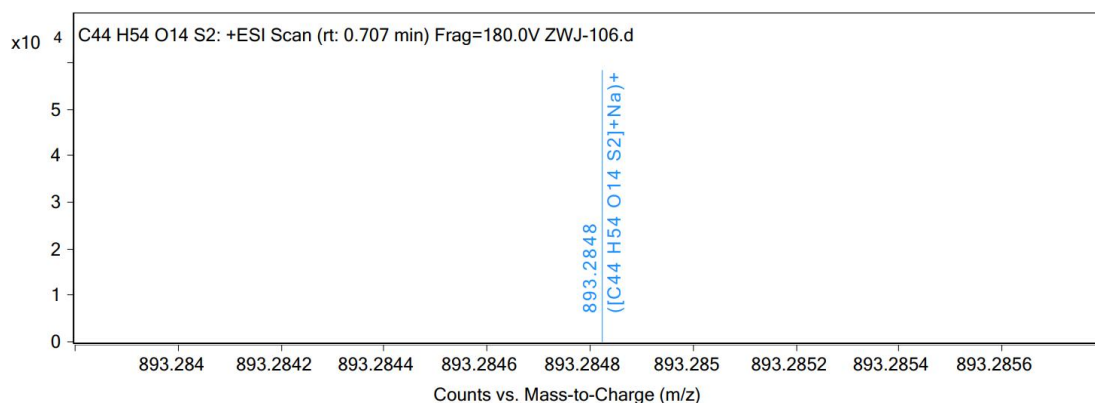
under reflux in an atmosphere of N<sub>2</sub> for 2 d. After cooling to room temperature, the insoluble materials were filtered off to give a light-yellow filtrate. It was dried under reduced pressure to give compound **5** as a yellow oil, which was treated directly with tosyl chloride (6.20 g, 32.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (75 mL) in the presence of Et<sub>3</sub>N (0.9 mL). The resulting mixture was stirred for another day. The organic phase was washed once with a saturated aqueous solution of NaCl (100 mL), twice with H<sub>2</sub>O (150 mL), and dried with MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the mixture was purified by silica gel column chromatography (petroleum ether/EtOAc = 1/2) to give the product **6** as a yellow oil (3.38 g, 60%). <sup>1</sup>H NMR (400 MHz, chloroform-*d*, 298 K)  $\delta$  (ppm): 8.77 (s, 2H), 8.02 (dd, *J* = 6, 3 Hz, 2H), 7.76 (d, *J* = 8 Hz, 4H), 7.46 (dd, *J* = 6, 3 Hz, 2H), 7.28 (d, *J* = 8 Hz, 4H), 6.60 (s, 2H), 4.33–4.30 (m, 4H), 4.10 (d, *J* = 4 Hz, 4H), 4.05–4.02 (m, 4H), 3.83–3.80 (m, 4H), 3.70–3.67 (m, 4H), 3.65–3.59 (m, 8H), 3.57–3.54 (m, 4H), 2.38 (s, 6H). <sup>13</sup>C NMR (100 MHz, chloroform-*d*, 298 K)  $\delta$  (ppm): 148.8, 144.9, 133.0, 131.5, 129.9, 128.6, 128.1, 125.7, 125.6, 121.0, 102.5, 71.0, 70.8, 70.7, 70.0, 69.3, 68.7, 68.2, 21.7, 21.2. Q-TOFMS: *m/z* calcd for [M + Na]<sup>+</sup> C<sub>44</sub>H<sub>54</sub>O<sub>14</sub>S<sub>2</sub>Na<sup>+</sup>, 893.2853, found 893.2848, error –1 ppm.



**Fig. S4.** <sup>1</sup>H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of compound **6**.



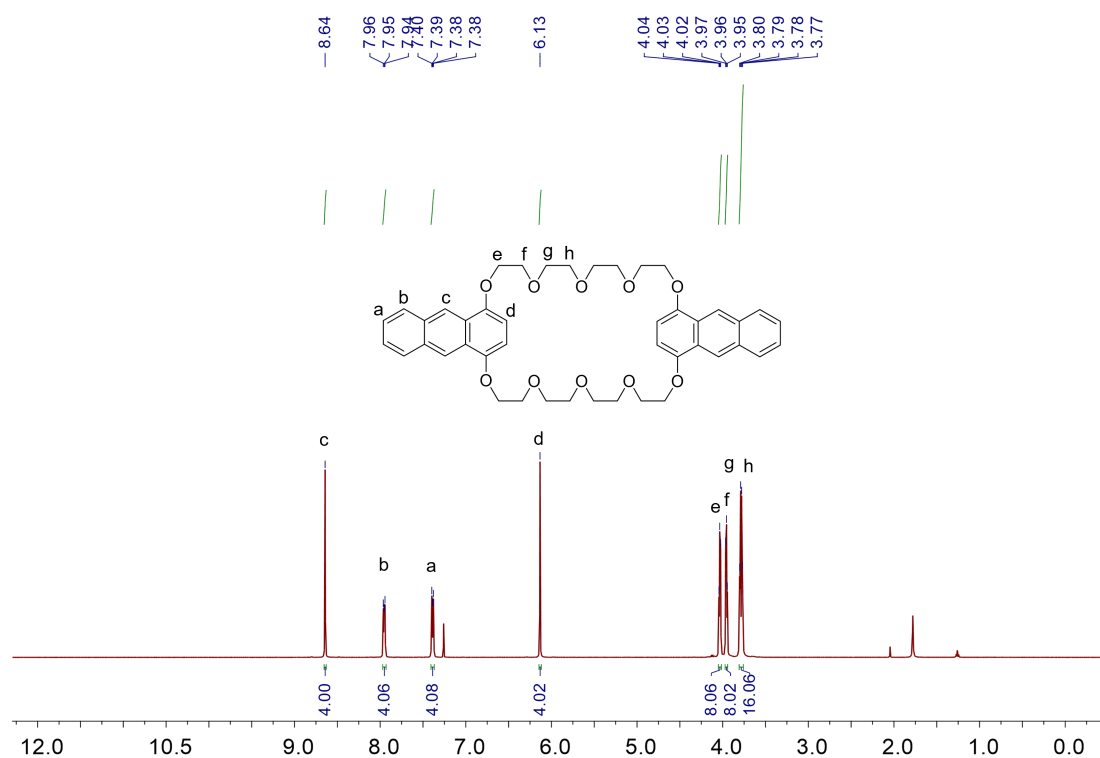
**Fig. S5.**  $^{13}\text{C}$  NMR spectrum (400 MHz, chloroform-*d*, 298 K) of compound **6**.



**Fig. S6.** Q-TOF mass spectrum of compound **6**.

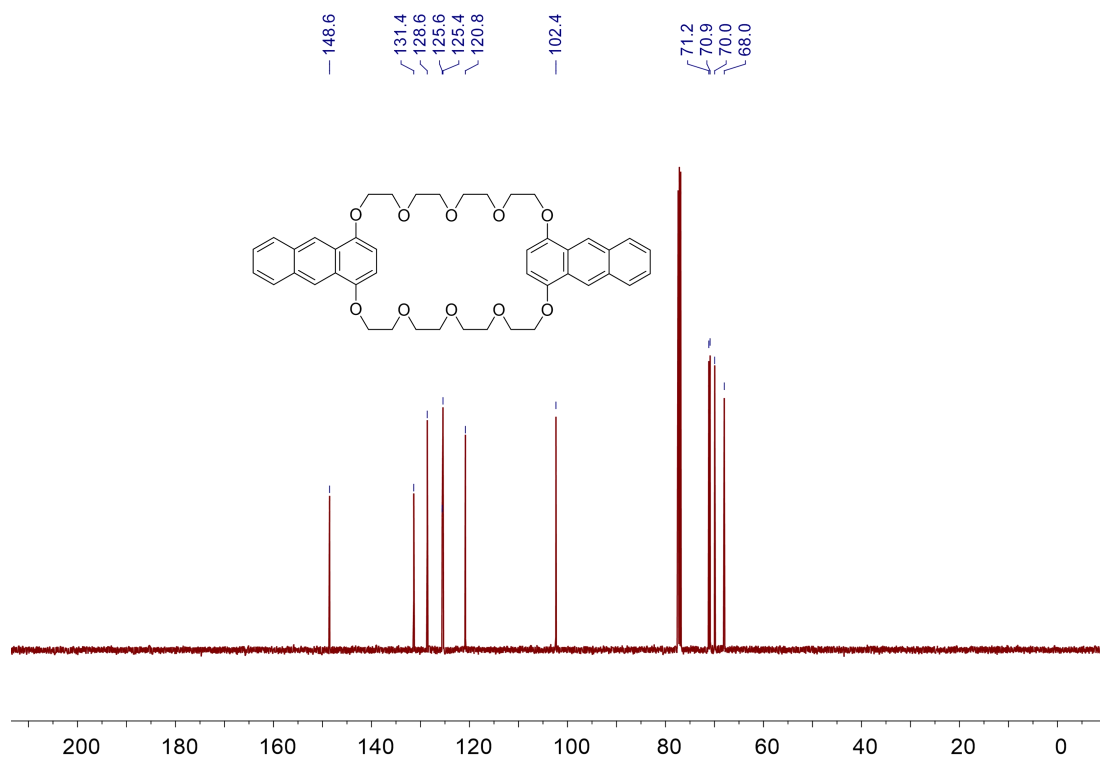
**An34C10:** A three-necked flask was equipped with a magnetic stirrer and a condenser under an inert atmosphere. The flask was charged with  $\text{Cs}_2\text{CO}_3$  (9.68 g, 29.7 mmol) and DMF (200 mL), and the reaction mixture was heated to  $100\text{ }^\circ\text{C}$ . A solution of compounds **2** (1.24 g, 5.90 mmol) and **6** (5.13 g, 5.90 mmol) in DMF (100 mL) was added slowly to the stirring  $\text{Cs}_2\text{CO}_3$  suspension within 12 h. After addition, the reaction mixture was stirred for 3 d at this temperature. After cooling to room temperature, the reaction mixture was filtered to remove the insoluble material, and

the solid was washed with DMF (50 mL). The filtrates were combined together and the solvent was removed under reduced pressure to obtain a dark residue. The mixture was purified by silica gel column chromatography (petroleum ether/EtOAc = 1/5) to give the product **An34C10** as a light yellow powder (1.28 g, 29%), mp 138 °C.  $^1\text{H}$  NMR (400 MHz, chloroform-*d*, 298 K)  $\delta$  (ppm): 8.64 (s, 4H), 7.95 (dd,  $J = 6, 3$  Hz, 4H), 7.39 (dd,  $J = 6, 3$  Hz, 4H), 6.13 (s, 4H), 4.05–4.02 (m, 8H), 3.96 (t,  $J = 5$  Hz, 8H), 3.78 (dd,  $J = 11, 6$  Hz, 16H).  $^{13}\text{C}$  NMR (100 MHz, chloroform-*d*, 298 K)  $\delta$  (ppm): 148.6, 131.4, 128.6, 125.6, 125.4, 120.8, 102.4, 71.2, 70.9, 70.0, 68.0. Q-TOFMS:  $m/z$  calcd for  $[\text{M}+\text{Na}]^+ \text{C}_{44}\text{H}_{48}\text{O}_{10}\text{Na}^+$ , 759.3145, found 759.3145, error 0 ppm.

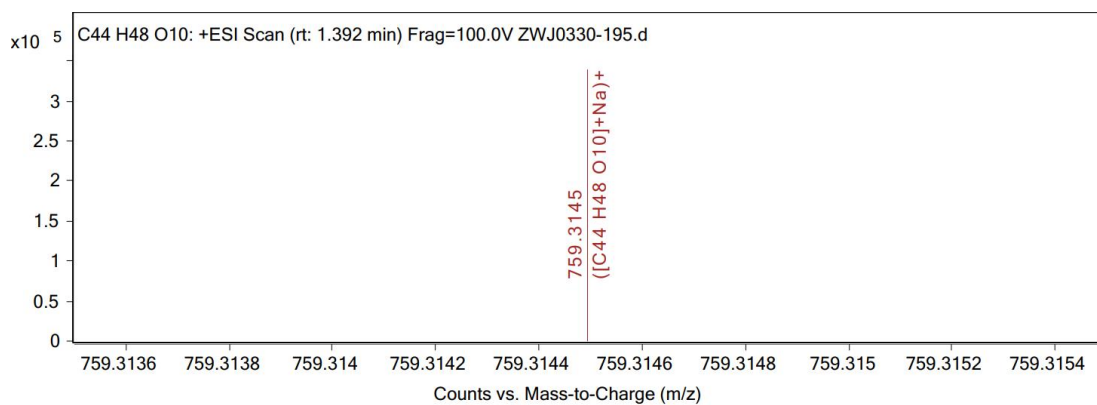


**Fig. S7.**  $^1\text{H}$  NMR spectrum (400 MHz, chloroform-*d*, 298 K) of **An34C10**.



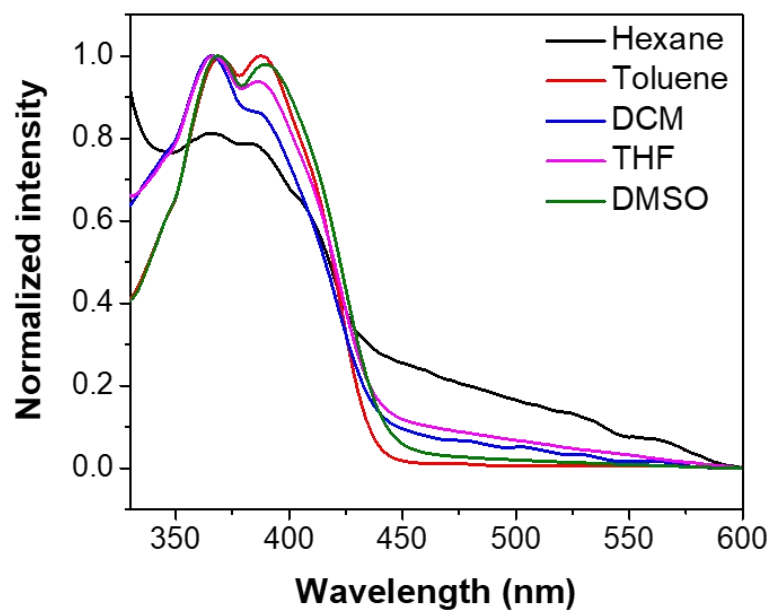


**Fig. S8.** <sup>13</sup>C NMR spectrum (400 MHz, chloroform-*d*, 298 K) of An34C10.

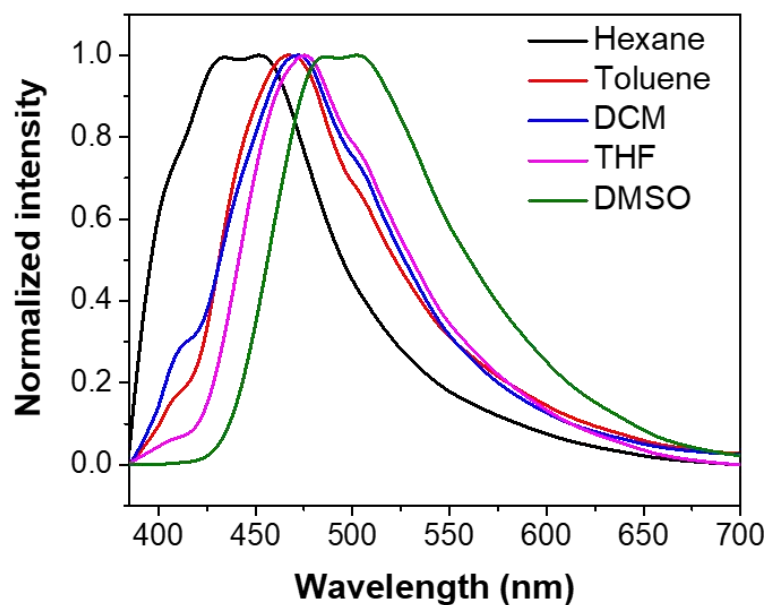


**Fig. S9.** Q-TOF mass spectrum of An34C10.

4. Fluorescence properties of **An34C10** in solution

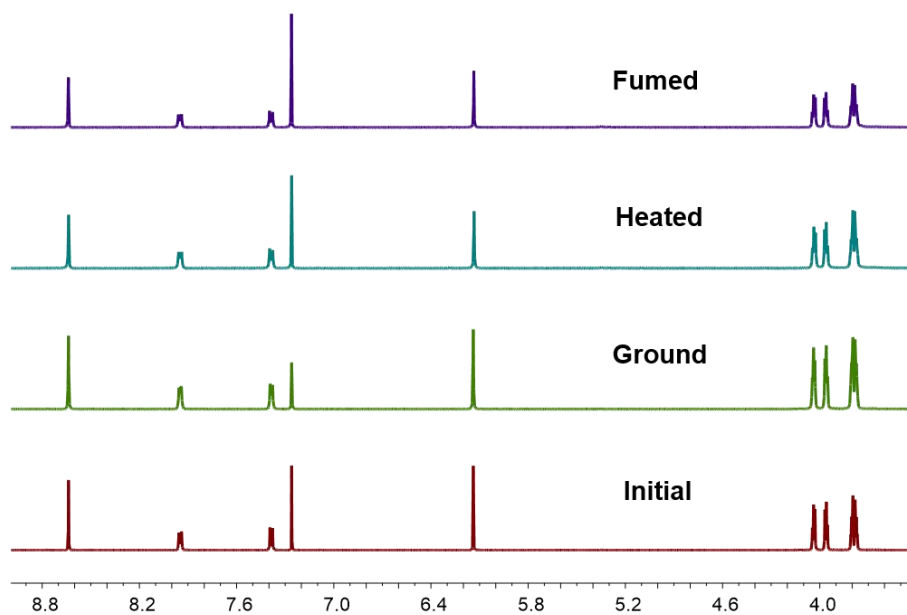


**Fig. S10.** Normalized UV-vis absorption spectra of **An34C10** in various solvents ( $c = 2 \times 10^{-5}$  M).

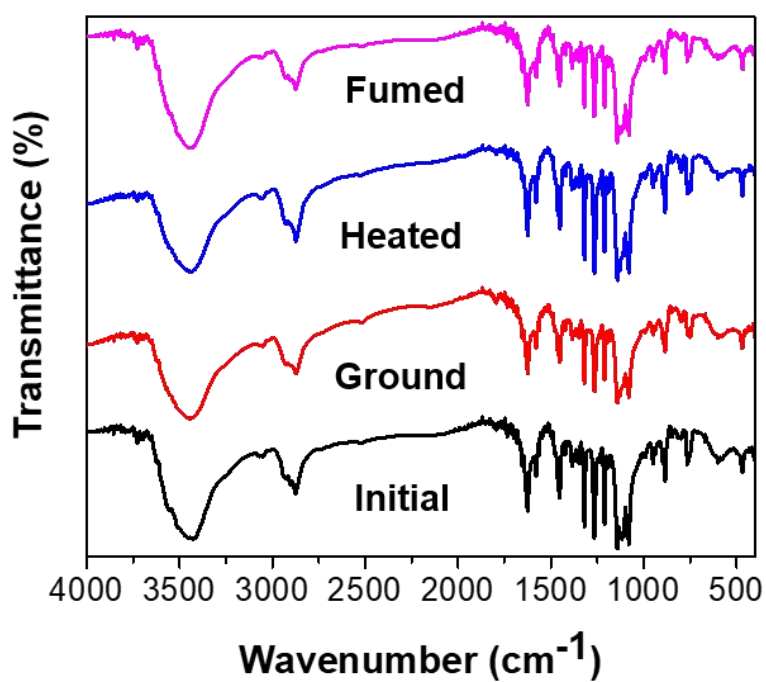


**Fig. S11.** Normalized fluorescence spectra of **An34C10** in various solvents ( $c = 2 \times 10^{-5}$  M).

5. Characterization of **An34C10** under different stimuli



**Fig. S12.** <sup>1</sup>H NMR (400 MHz, chloroform-*d*, 298 K) spectra of **An34C10** under different stimuli.



**Fig. S13.** FT-IR spectra of **An34C10** under different stimuli.

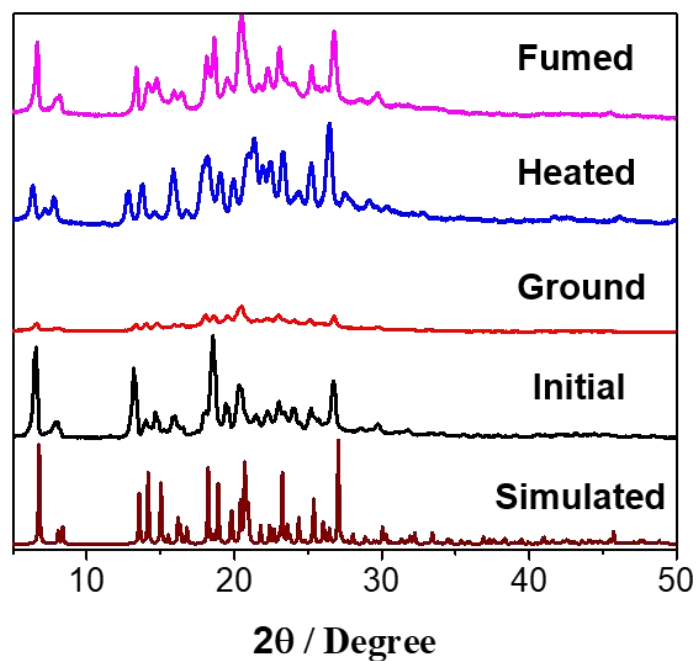


Fig. S14. PXRD patterns of An34C10 under different stimuli.

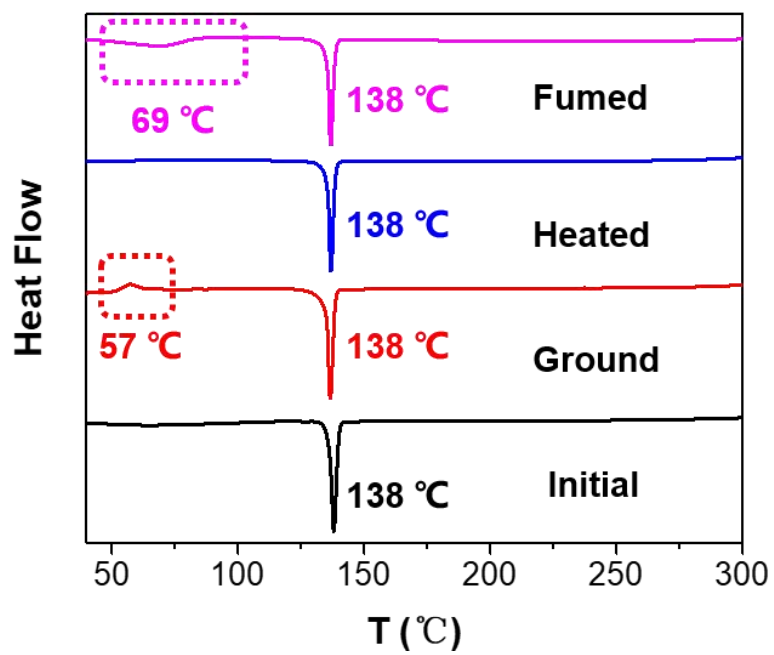
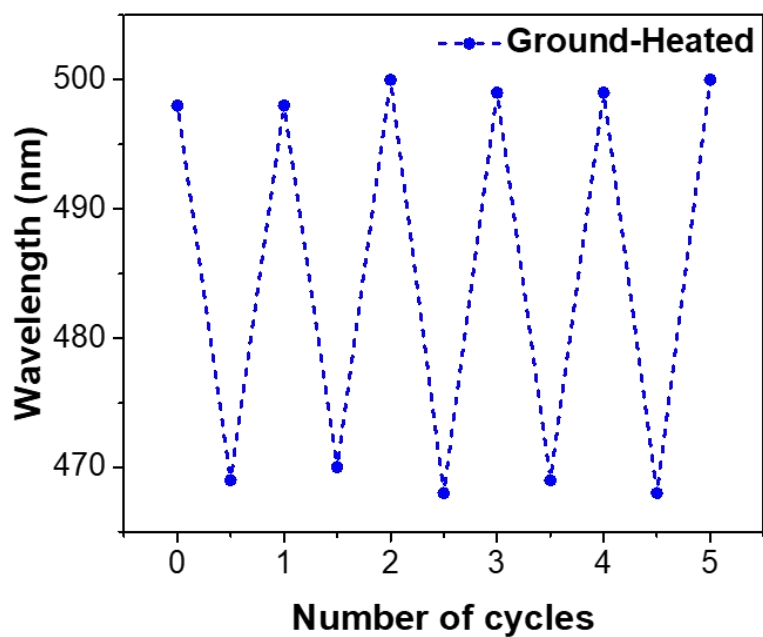
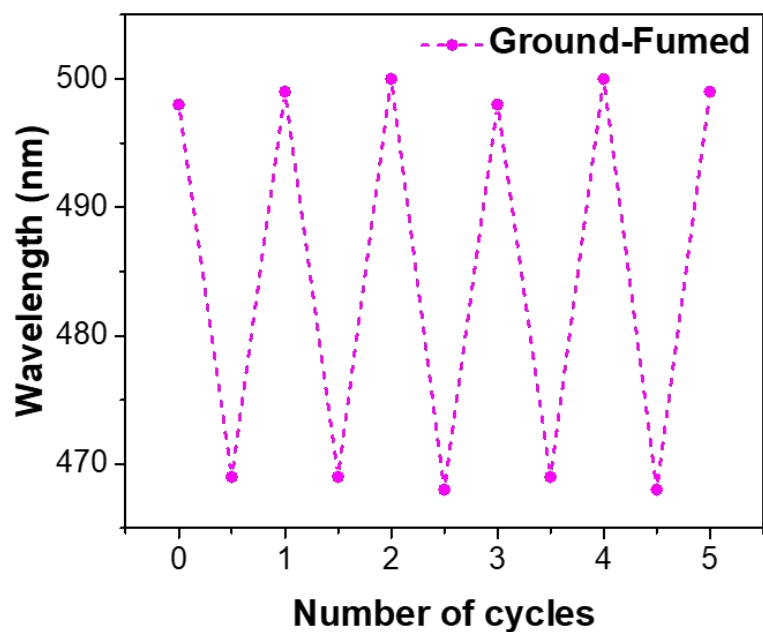


Fig. S15. DSC plots of An34C10 under different stimuli.

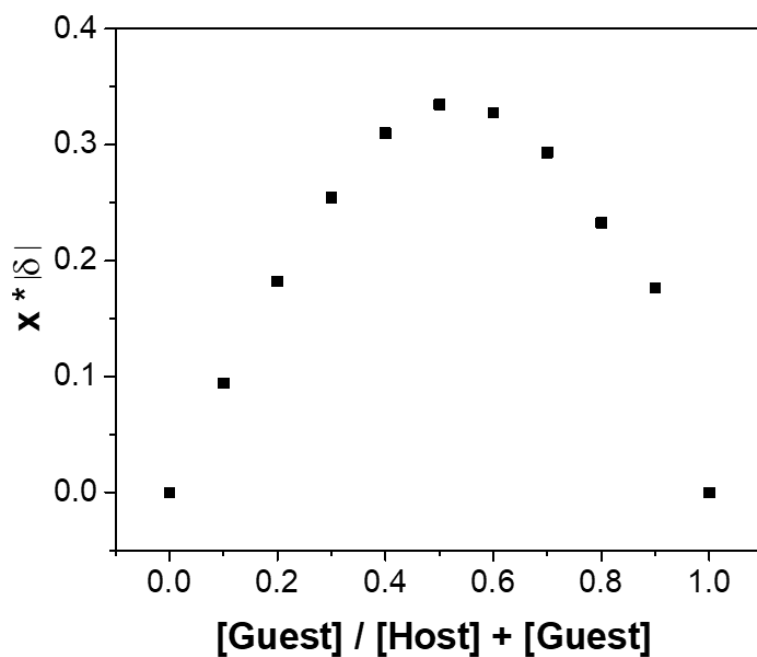


**Fig. S16.** Emission wavelength changes of An34C10 between ground and heated states in five cycles.

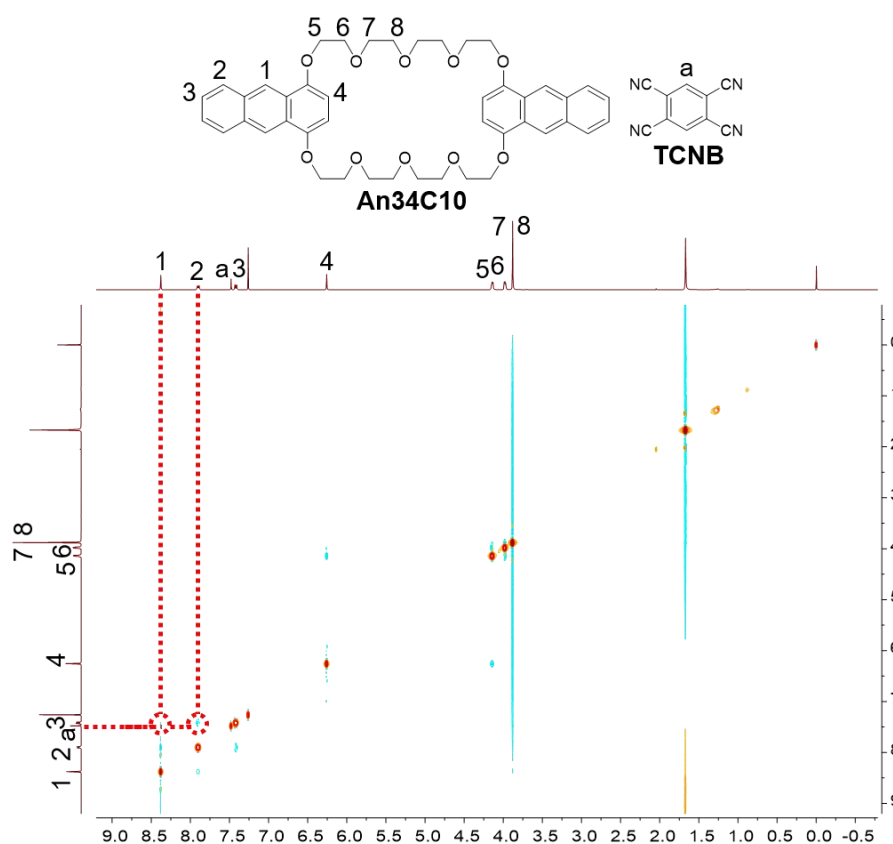


**Fig. S17.** Emission wavelength changes of An34C10 between ground and THF-fumed states in five cycles.

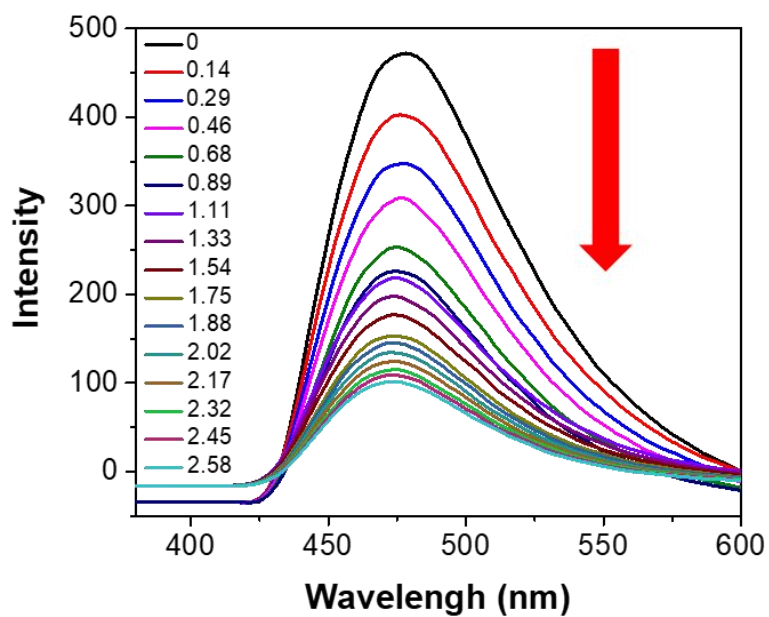
6. Complexation of **An34C10** and **TCNB** in solution



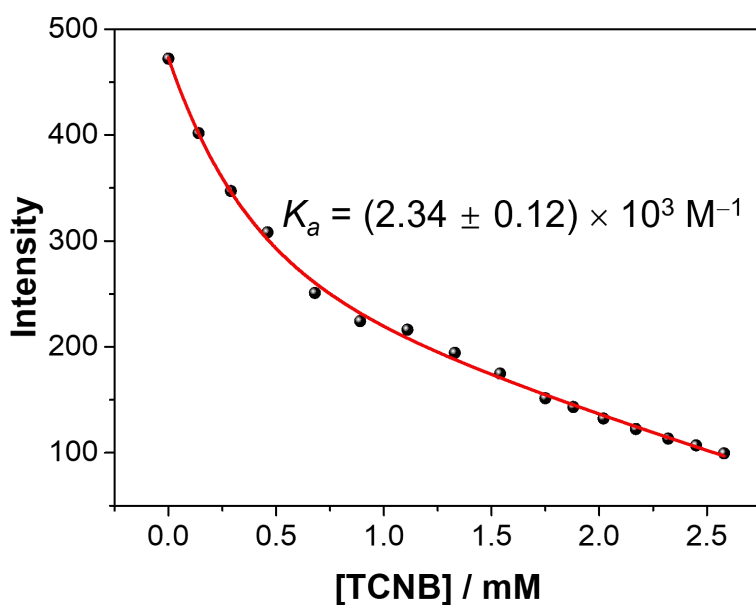
**Fig. S18.** Job plot showing that the complexation stoichiometry between **An34C10** and **TCNB** is 1:1. The total concentration of **An34C10** and **TCNB** was 5.00 mM.



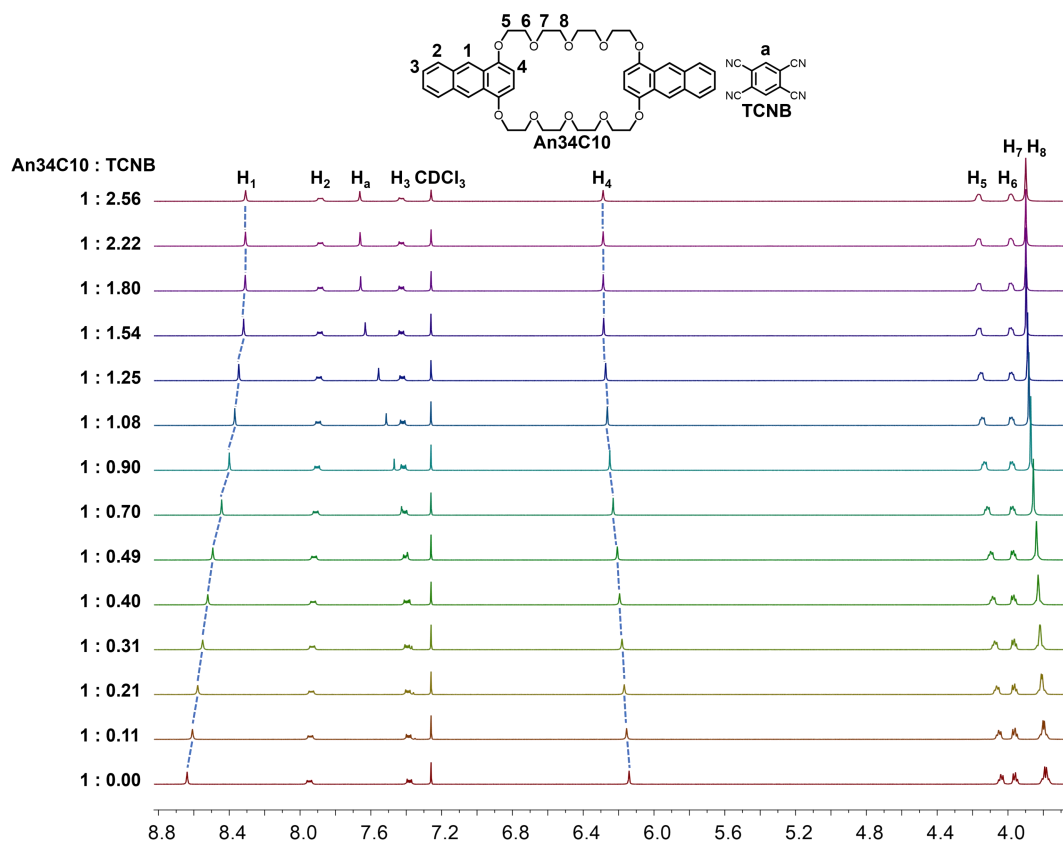
**Fig. S19.** 2D NOSEY spectrum (400 MHz, chloroform-*d*, 298 K) of **An34C10** (5.00 mM) and **TCNB** (5.00 mM).



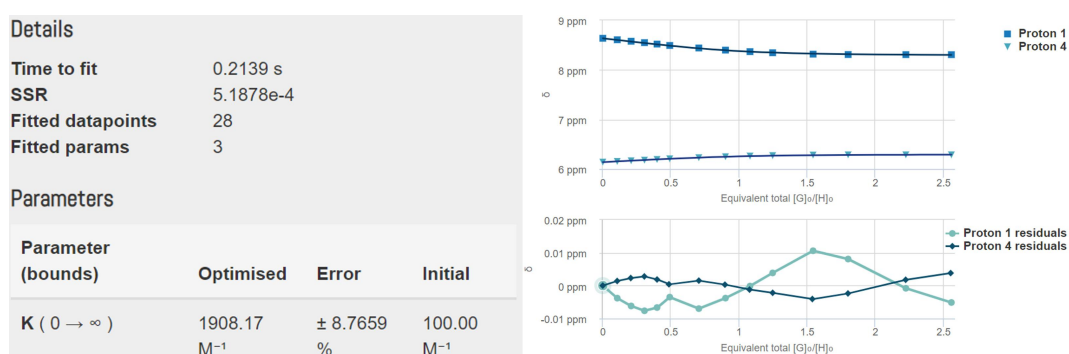
**Fig. S20.** Fluorescence of **An34C10** (0.50 mM) in chloroform at room temperature upon titration with **TCNB** (from 0 to 2.58 mM).



**Fig. S21.** Plot of **An34C10** fluorescence intensity vs. **TCNB** concentration. The binding constant was calculated by using a website, namely <http://supramolecular.org/>.



**Fig. S22.** Partial <sup>1</sup>H NMR (600 MHz) spectra of An34C10 (5.00 mM) in the presence of various molar equivalents of TCNB in chloroform-*d* at 298 K.



**Fig. S23.** Two plots of the resonance shifts corresponding to proton H<sub>1</sub> and H<sub>4</sub> in Fig. S22. These plots were then used to calculate the binding constant by using a website, namely <http://supramolecular.org/>. The binding constant was calculated to be  $(1.91 \pm 0.17) \times 10^3 \text{ M}^{-1}$ .



7. Characterization of *An34C10@TCNB* under different stimuli

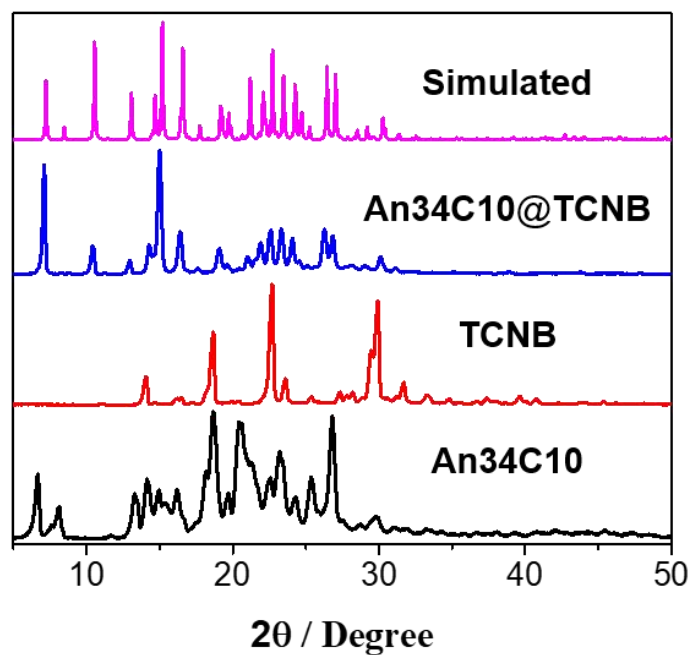


Fig. S24. PXRD patterns: *An34C10*; TCNB; *An34C10@TCNB*; simulated from the crystal structure of *An34C10@TCNB*.

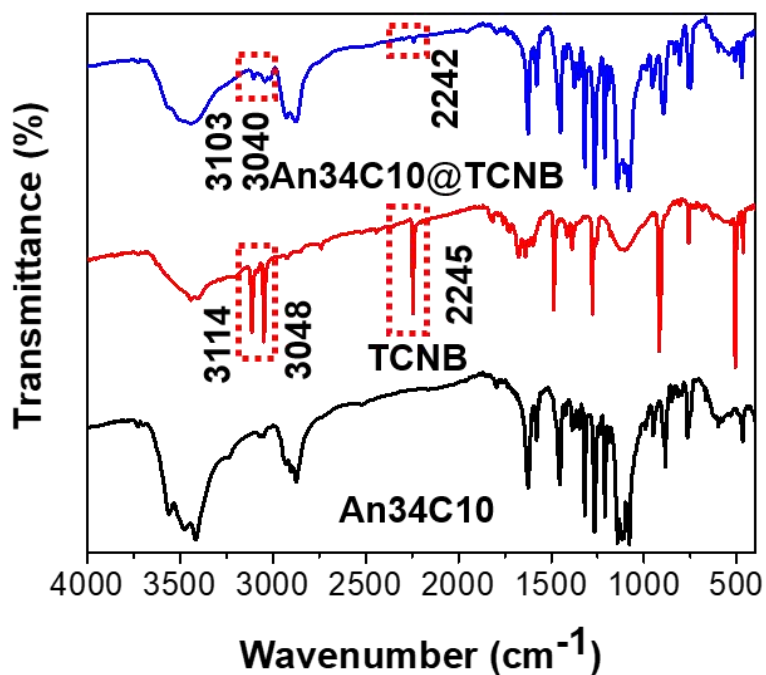


Fig. S25. FT-IR spectra of *An34C10*, TCNB and *An34C10@TCNB*.

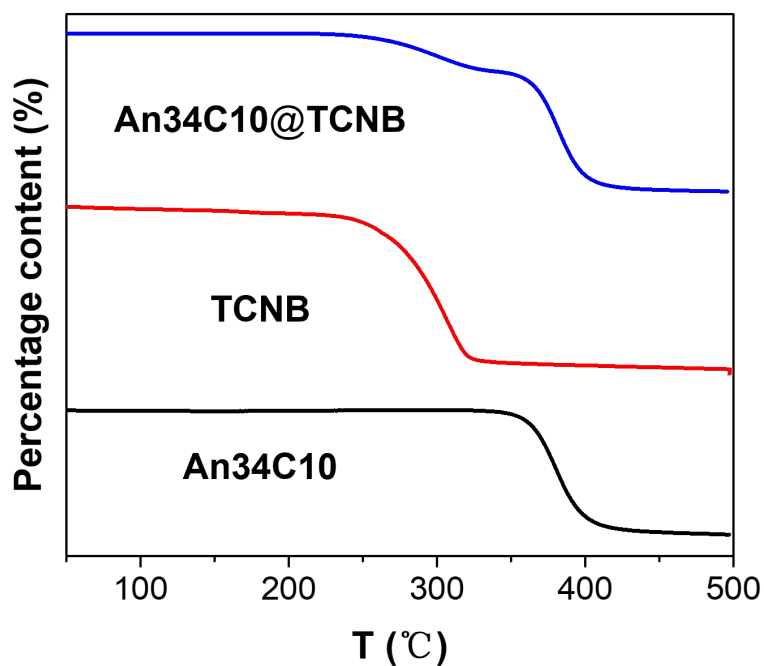


Fig. S26. Thermogravimetric analysis of An34C10, TCNB and An34C10@TCNB.

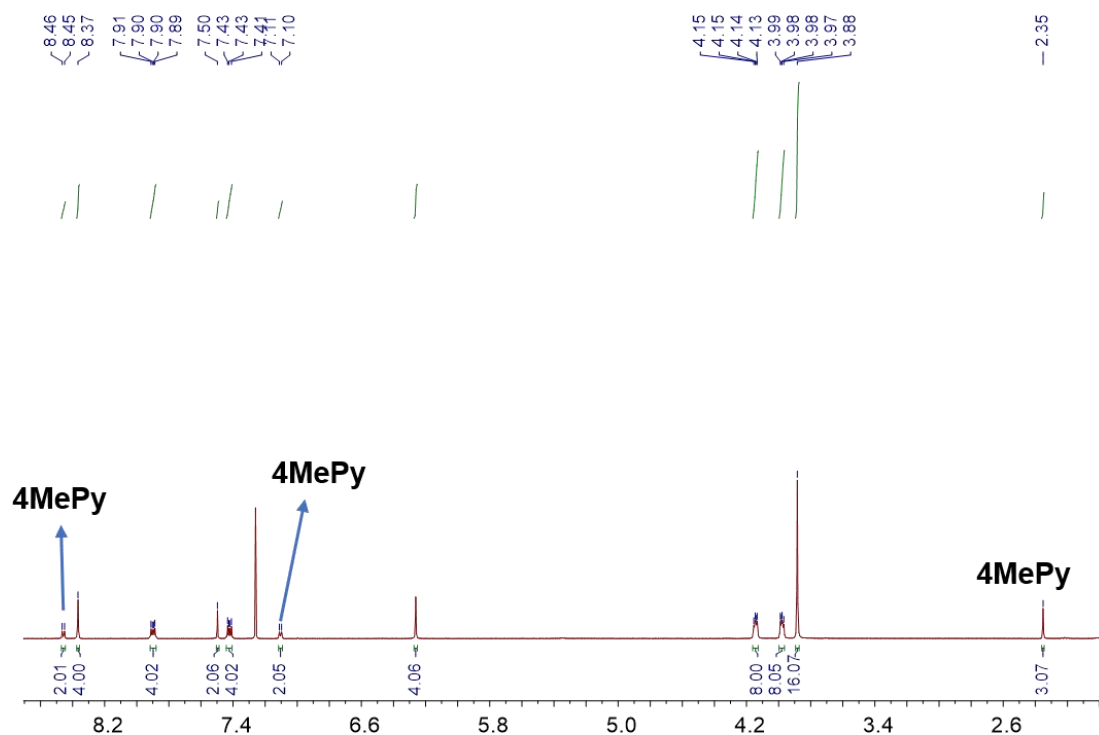
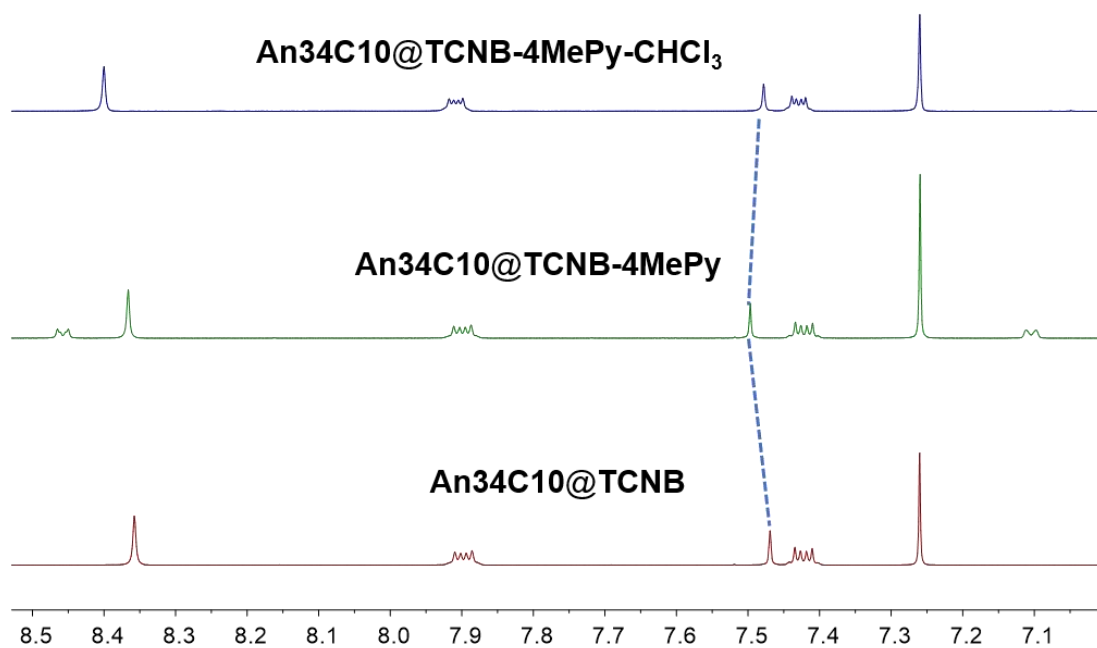
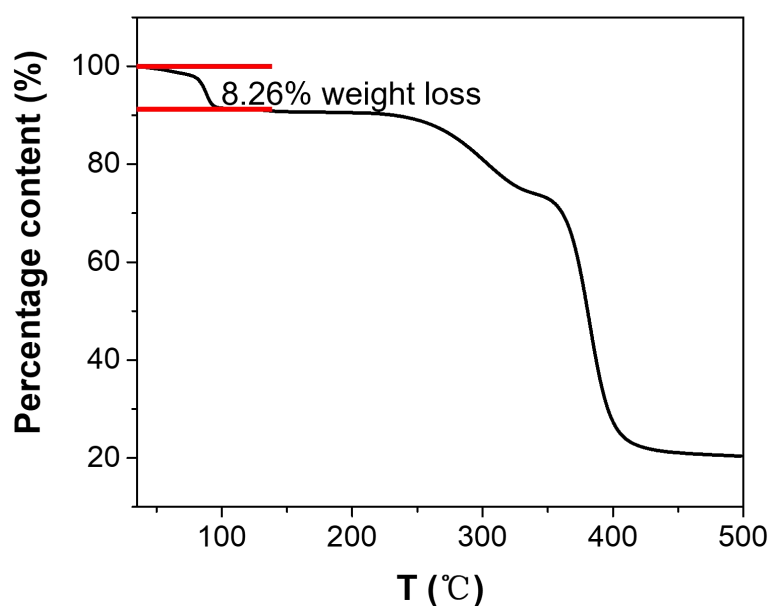


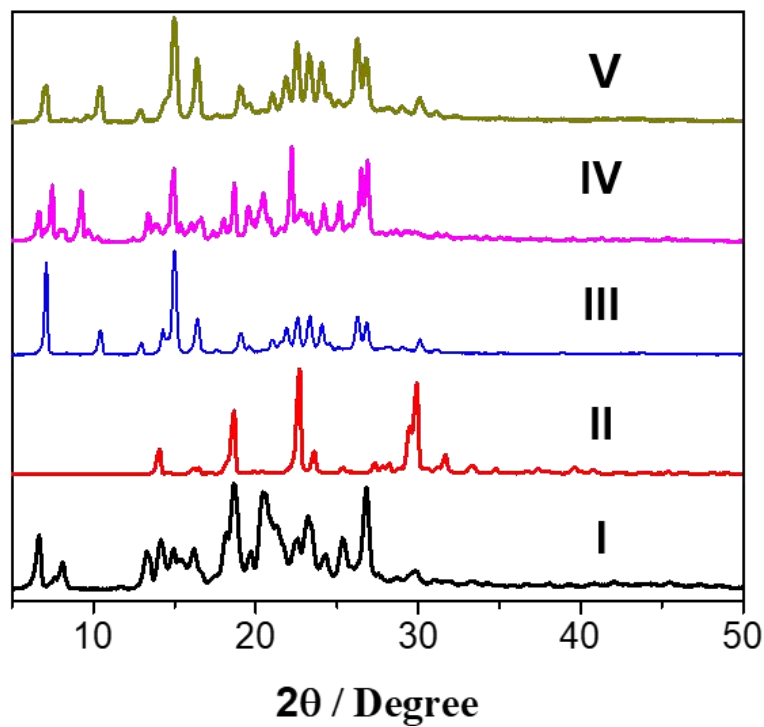
Fig. S27.  $^1\text{H}$  NMR spectra (400 MHz, chloroform-*d*, 298 K) of An34C10@TCNB-4MePy.



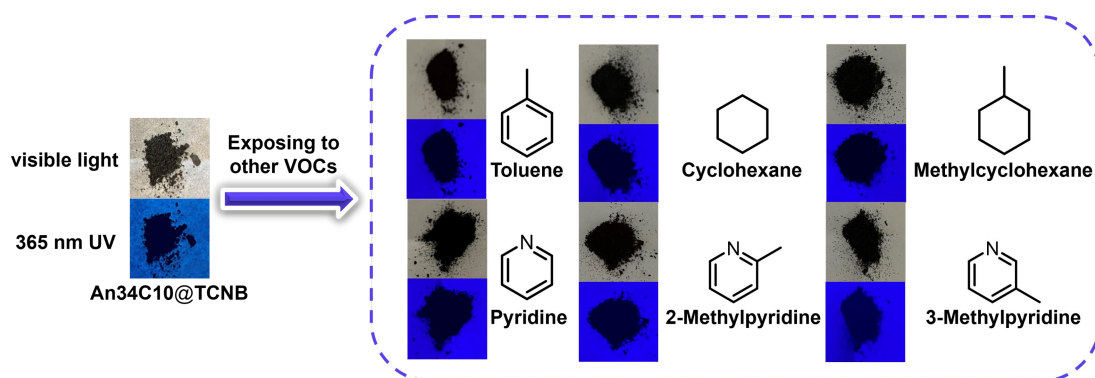
**Fig. S28.** Partial <sup>1</sup>H NMR spectra (400 MHz, chloroform-*d*, 298 K) of An34C10@TCNB, An34C10@TCNB-4MePy and An34C10@TCNB-4MePy-CHCl<sub>3</sub>.



**Fig. S29.** Thermogravimetric analysis of An34C10@TCNB-4MePy.



**Fig. S30.** PXRD patterns: (I) **An34C10**; (II) **TCNB**; (III) **An34C10@TCNB**; (IV) **An34C10@TCNB-4MePy**; (V) **An34C10@TCNB-4MePy-CHCl<sub>3</sub>**.



**Fig. S31.** The luminescence of **An34C10@TCNB** after exposure to other VOCs.

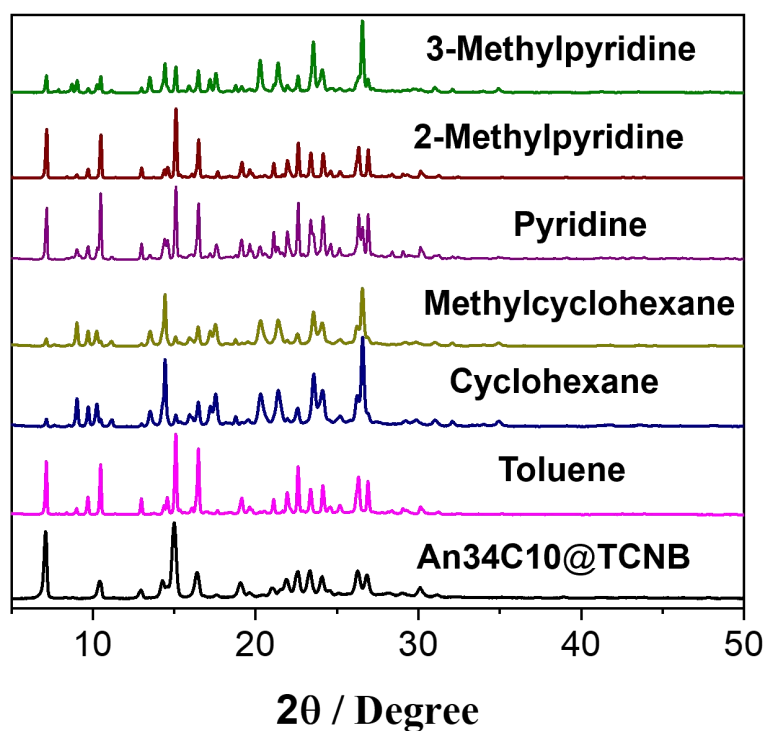


Fig. S32. PXRD patterns of An34C10@TCNB after exposure to other VOCs.

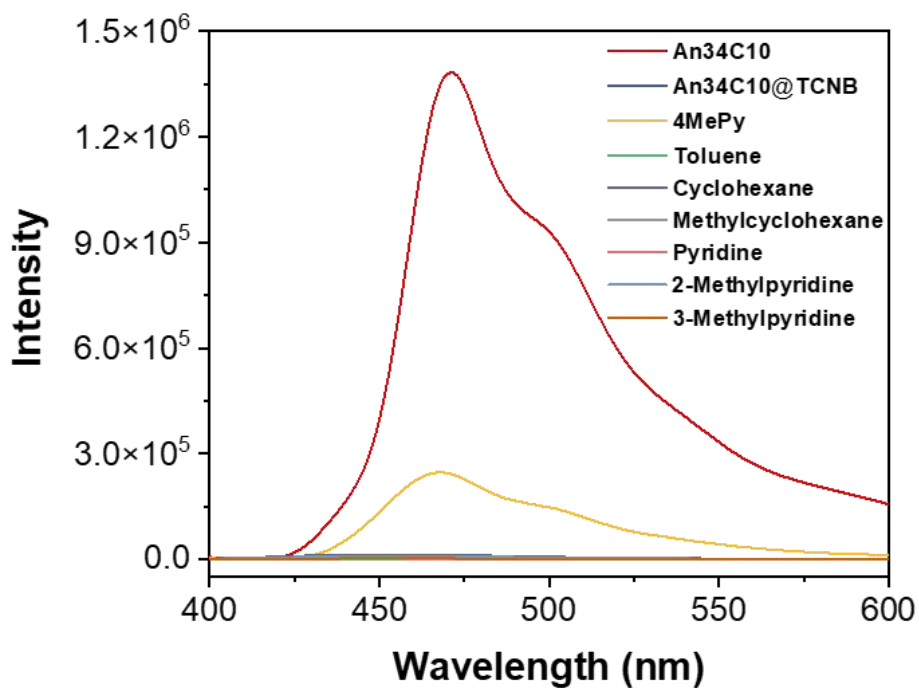
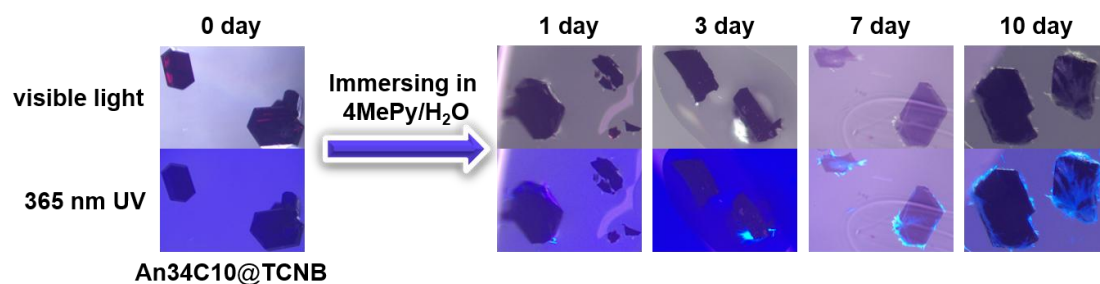
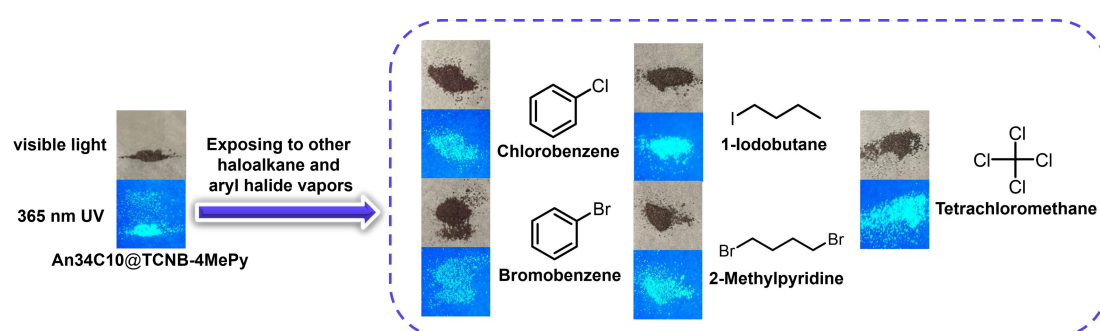


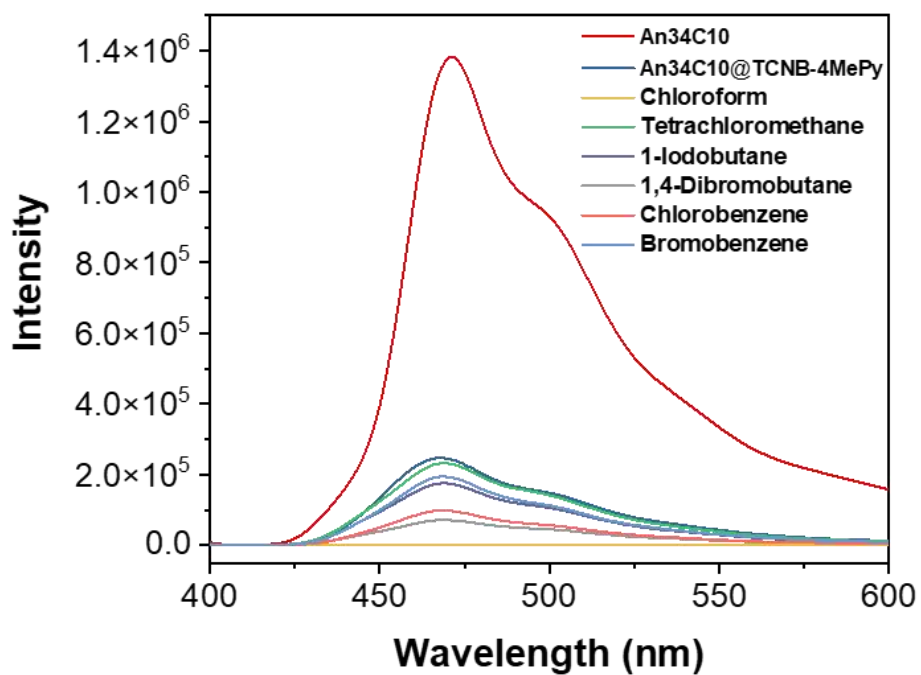
Fig. S33. Normalized solid state fluorescence spectra of An34C10@TCNB after exposure to other VOCs.



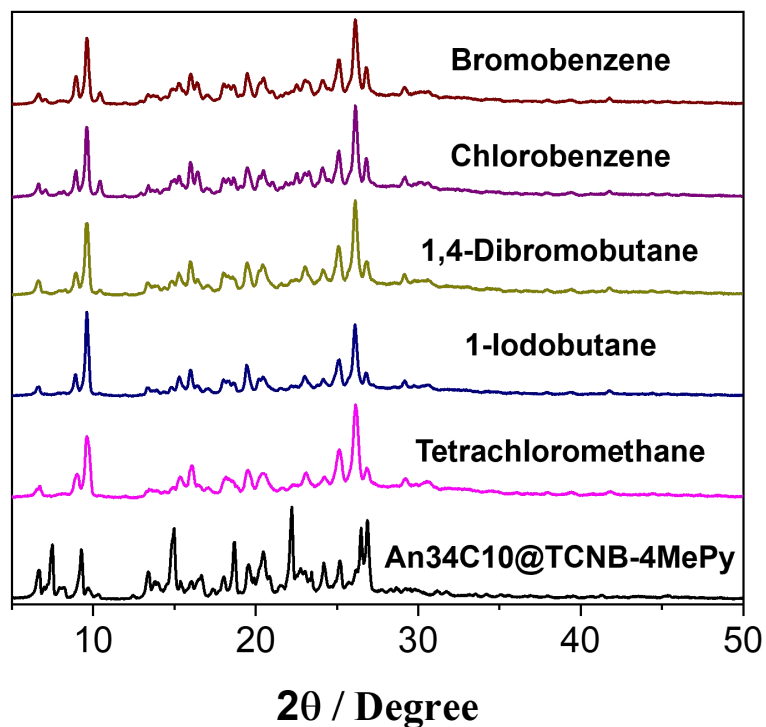
**Fig. S34.** Photographs showing single crystal changes when **An34C10@TCNB** co-crystals were immersed in a 4-methylpyridine aqueous solution (1.0 mol/L).



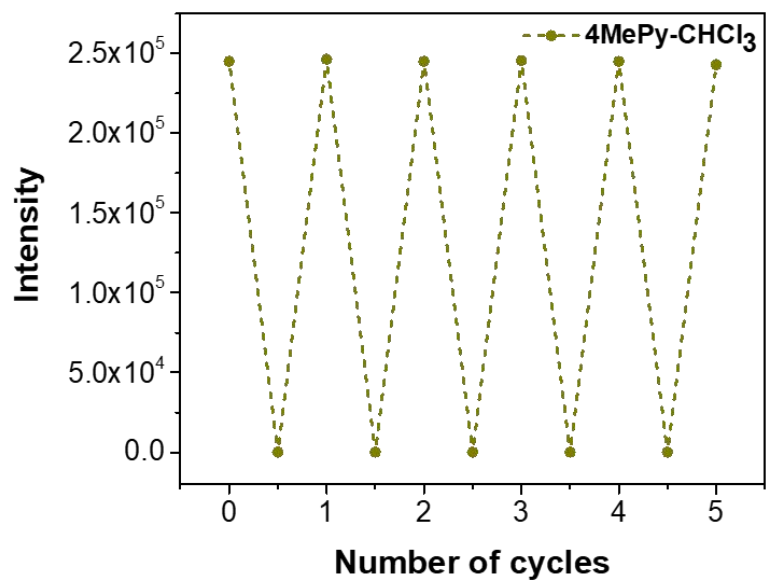
**Fig. S35.** The luminescence of **An34C10@TCNB-4MePy** after exposure to other haloalkane and aryl halide vapors.



**Fig. S36.** Normalized solid state fluorescence spectra of An34C10@TCNB-4MePy after exposure to other haloalkane and aryl halide vapors.



**Fig. S37.** PXRD patterns of An34C10@TCNB-4MePy after exposure to other haloalkane and aryl halide vapors.



**Fig. S38.** Fluorescence intensity changes between **An34C10@TCNB-4MePy** and **An34C10@TCNB-4MePy-CHCl<sub>3</sub>** over five cycles.



## 8. References

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