Electronic Supplementary Information

Macrocycle-based charge transfer co-crystals with specific selective vapochromism to benzene

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Contents

1. Materials and Methods.

All reactions were carried out with oven-dried glassware. Commercial reagents were used without further purification. ^{1}H NMR spectra were recorded on a Bruker DMX 400 NMR spectrometer. Single-crystal X-ray diffraction data were collected on a Bruker Smart APEXII CCD diffractometer using graphite monochromated Cu Kα (λ =1.54184 Å) radiation at 298 K.

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 Kα line (λ = 1.5418 Å). Data were measured over the range of 5-45° in 5°/min steps over 8 min.

Vapochromic experiments. An open 2 mL vial containing 25 mg of activated P2@TCNB was placed in a sealed 20 mL vial containing 1 mL of each vapor solution. Activated P2@TCNB powders were exposed under saturated vapor pressure in the closed vessel at room temperature. Obvious color changes were observed after 12 hours.

Sample preparation of P2@TCNB**.** P2 (10.4 mg) and TCNB (1.78 mg) were dissolved in 2 mL CH_2Cl_2, and then slowly evaporation of the solution at room temperature for 2 days, the red co-crystals P2@TCNB was obtained.

Large scale preparation of P2@TCNB**.** P2 (490 mg) and TCNB (84 mg) were dissolved in 50 mL CH_2Cl_2, and then slowly evaporation of the solution at room temperature for 3 days, the red co-crystals P2@TCNB was obtained.

Adsorption Experiments. In a typical solid-vapor adsorption experiment, an open vial (4 mL) containing 5 mg of activated P2@TCNB was placed into a sealed vial (20 mL) containing 1 mL of benzene or mixture vapor. The adsorption process was monitored over time by completely dissolving a portion of the crystals in $CDCl_3$ and measuring ^{1}H NMR spectra.

2. Characterization of Macrocycle-Based CT Cocrystals

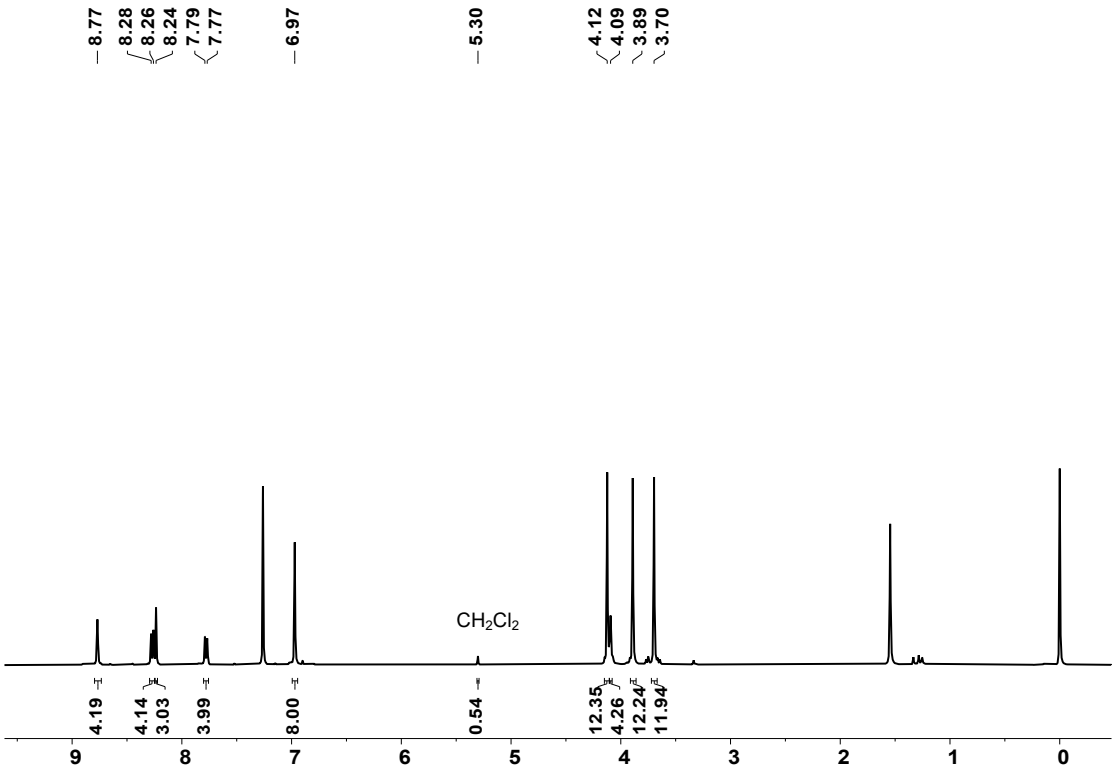

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB

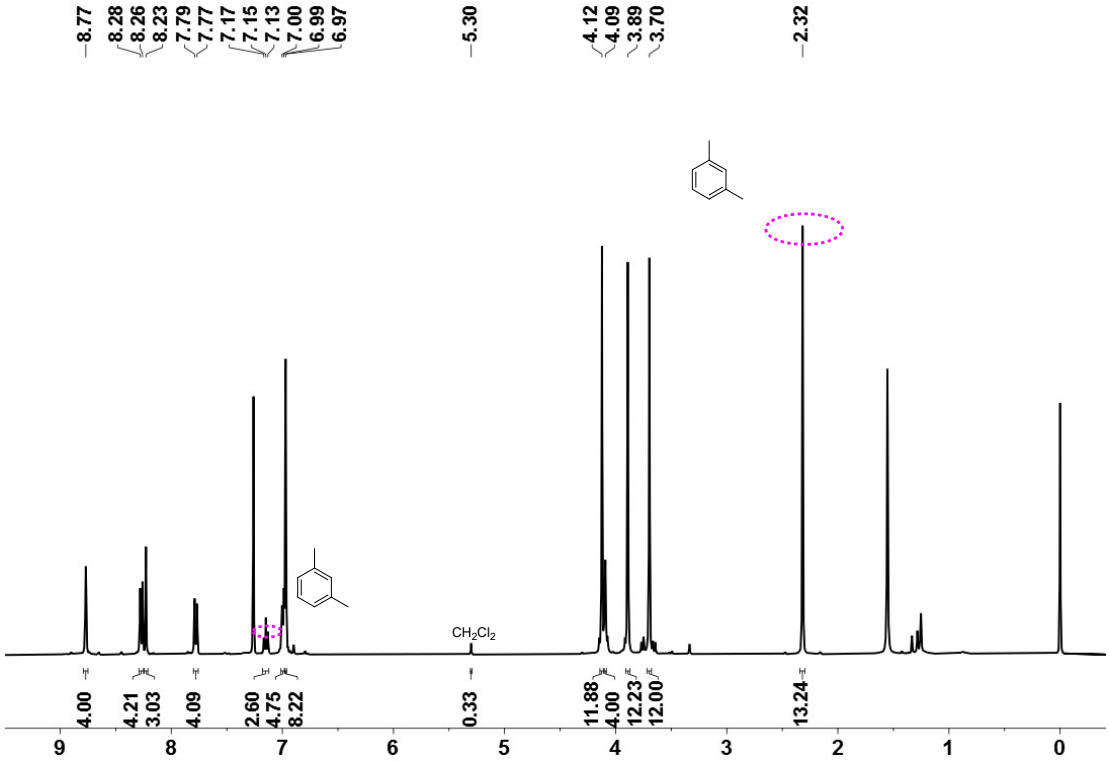

Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB after exposure to *m*-Xylene

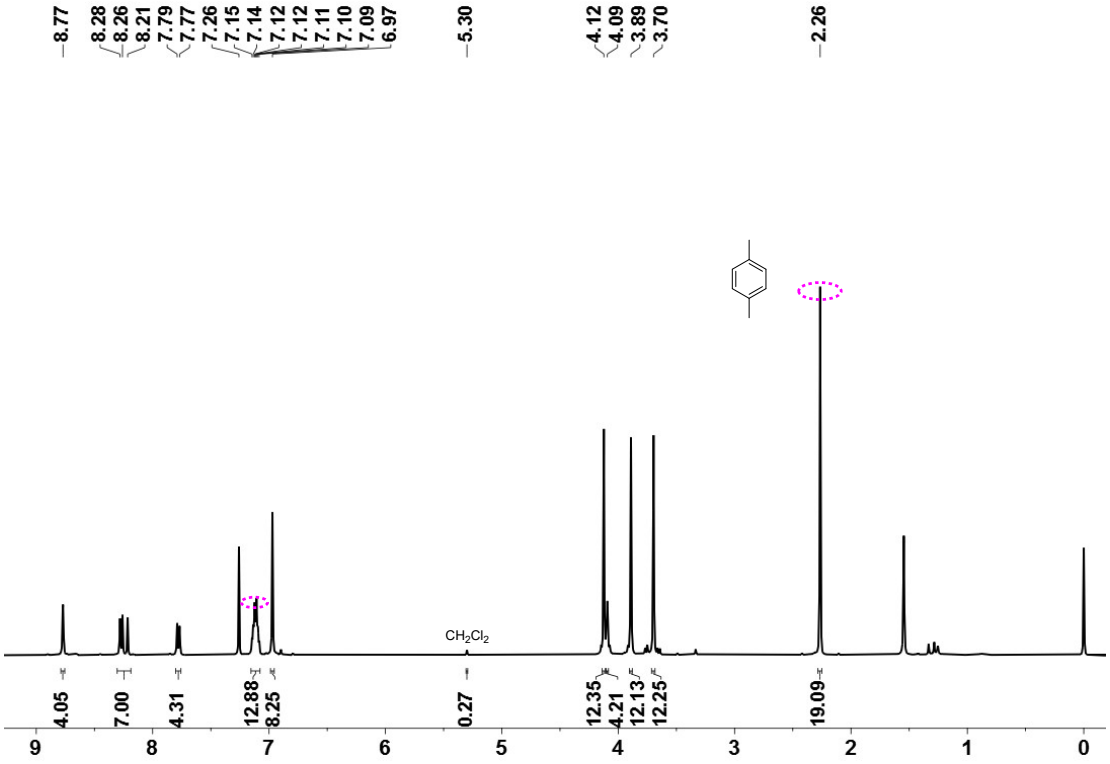

Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB after exposure to *p*-Xylene

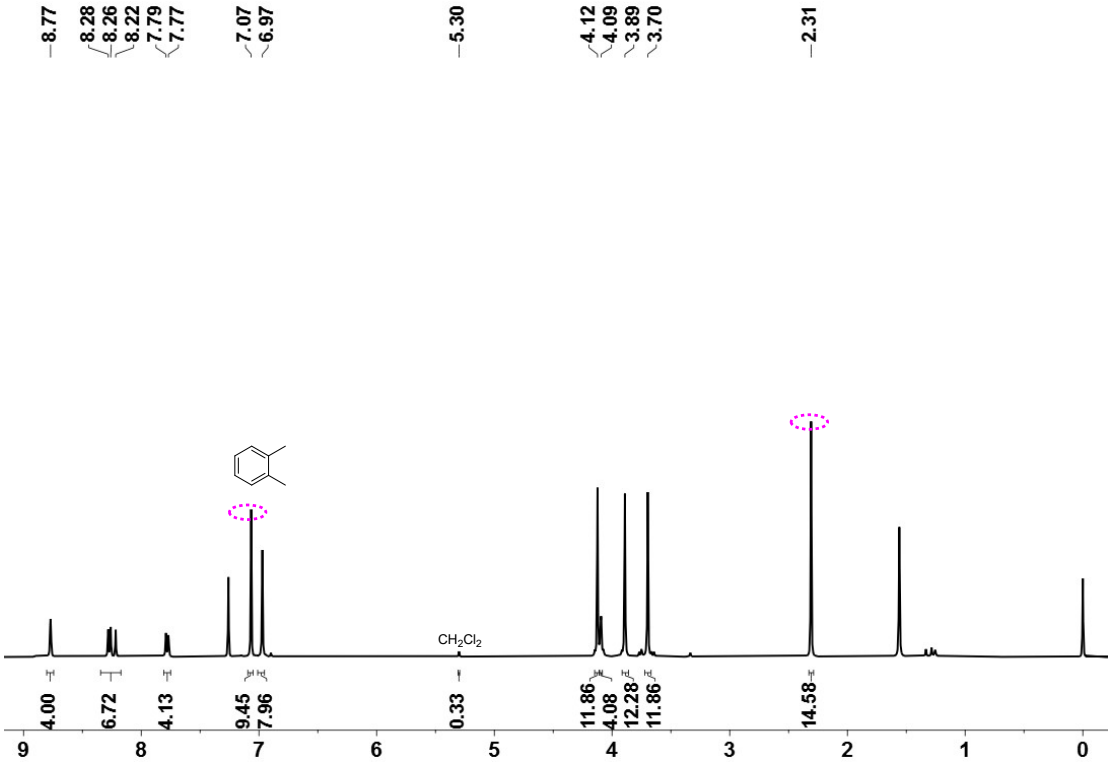

Figure S4.^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB after exposure to *o*-Xylene

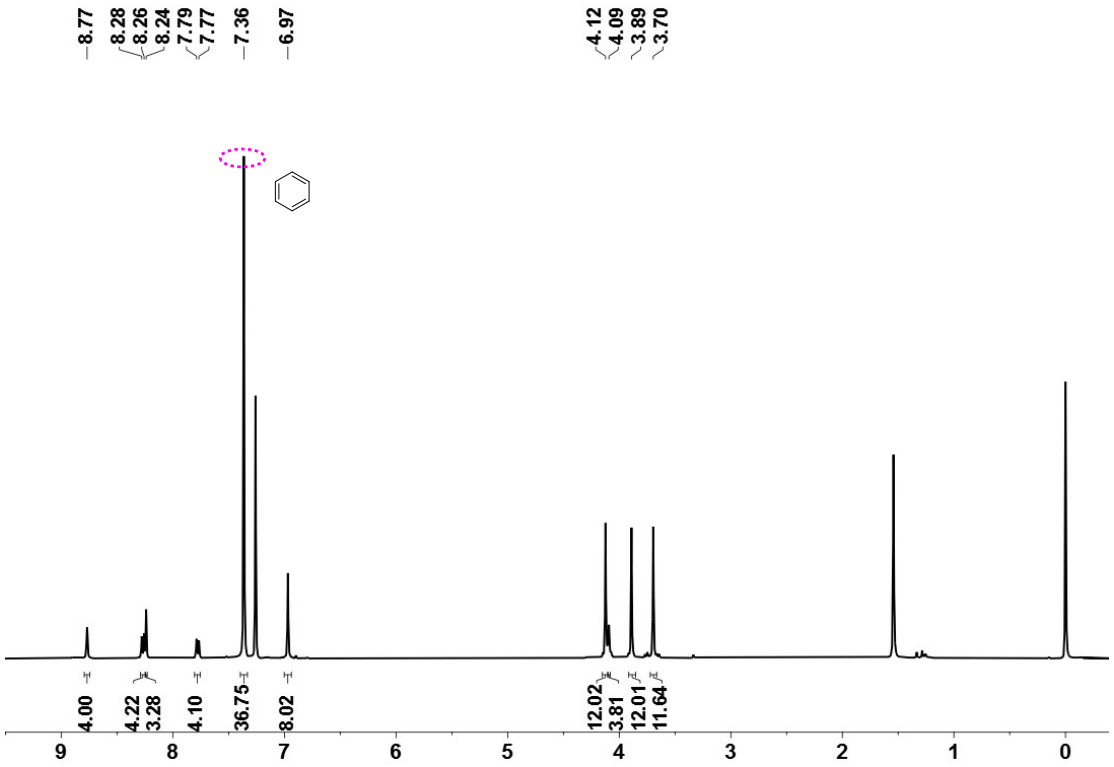

Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB after exposure to benzene

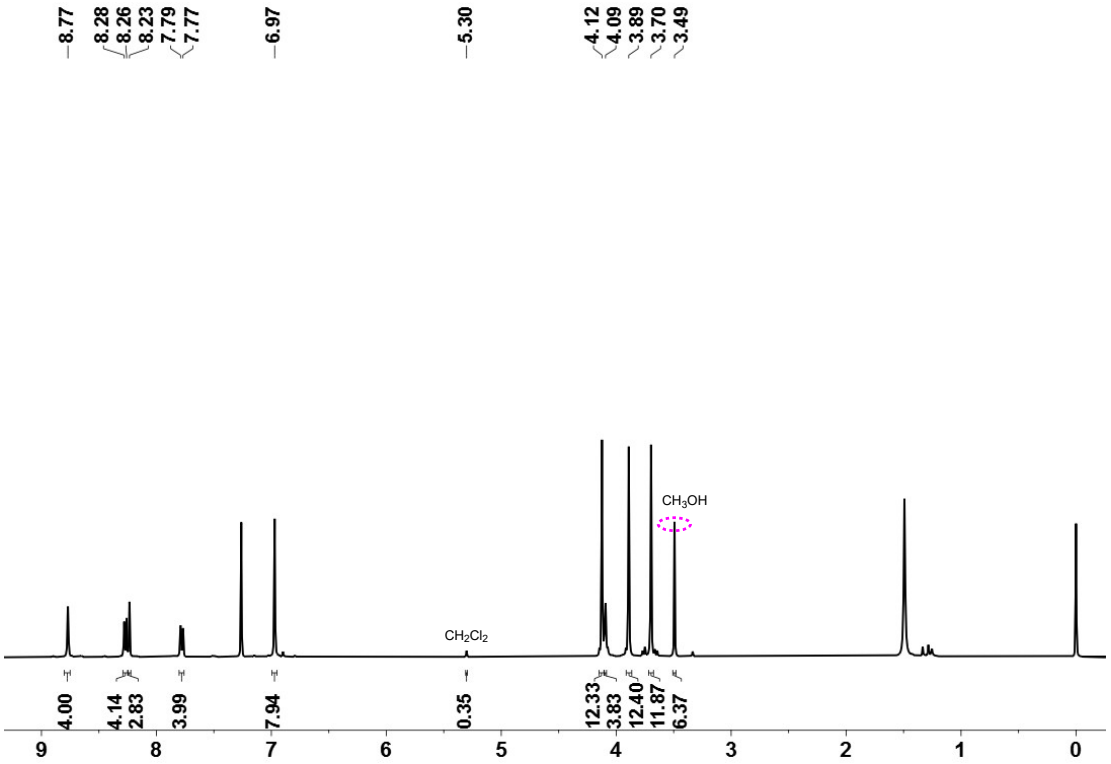

Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB after exposure to CH_3OH

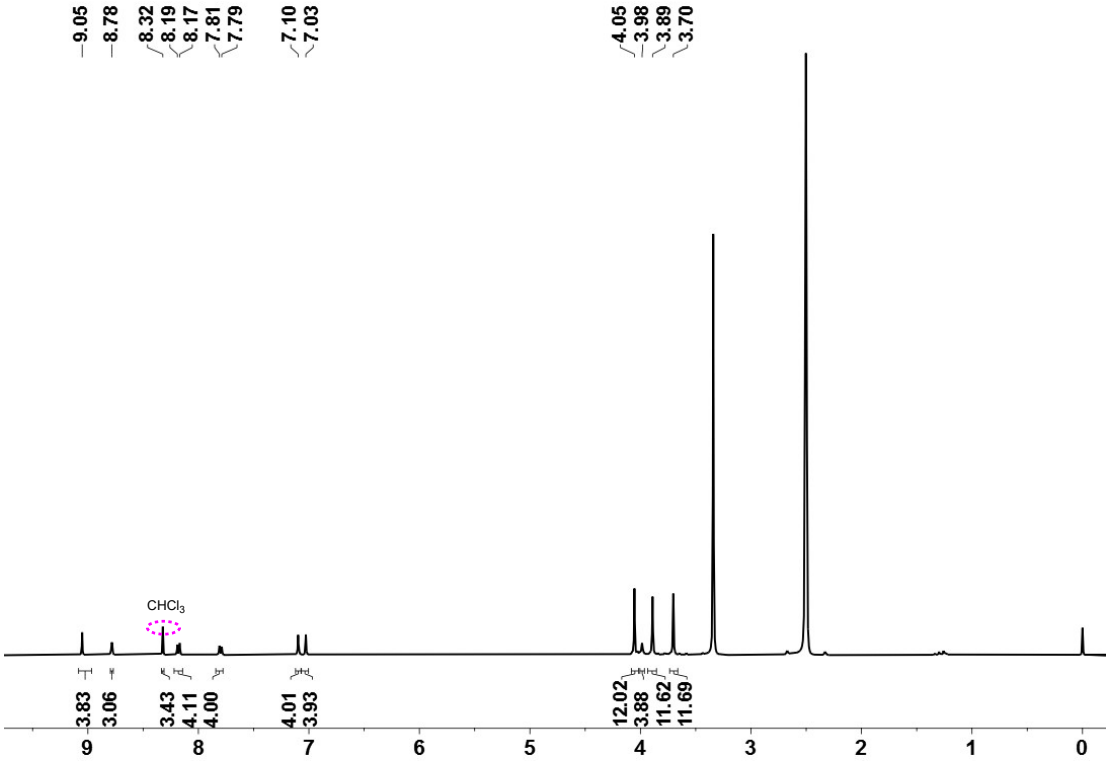

Figure S7.[1]H NMR spectrum (400 MHz, Dimethyl Sulfoxide-*d*6, 298K) of activated P2@TCNB after exposure to $CHCl_3$

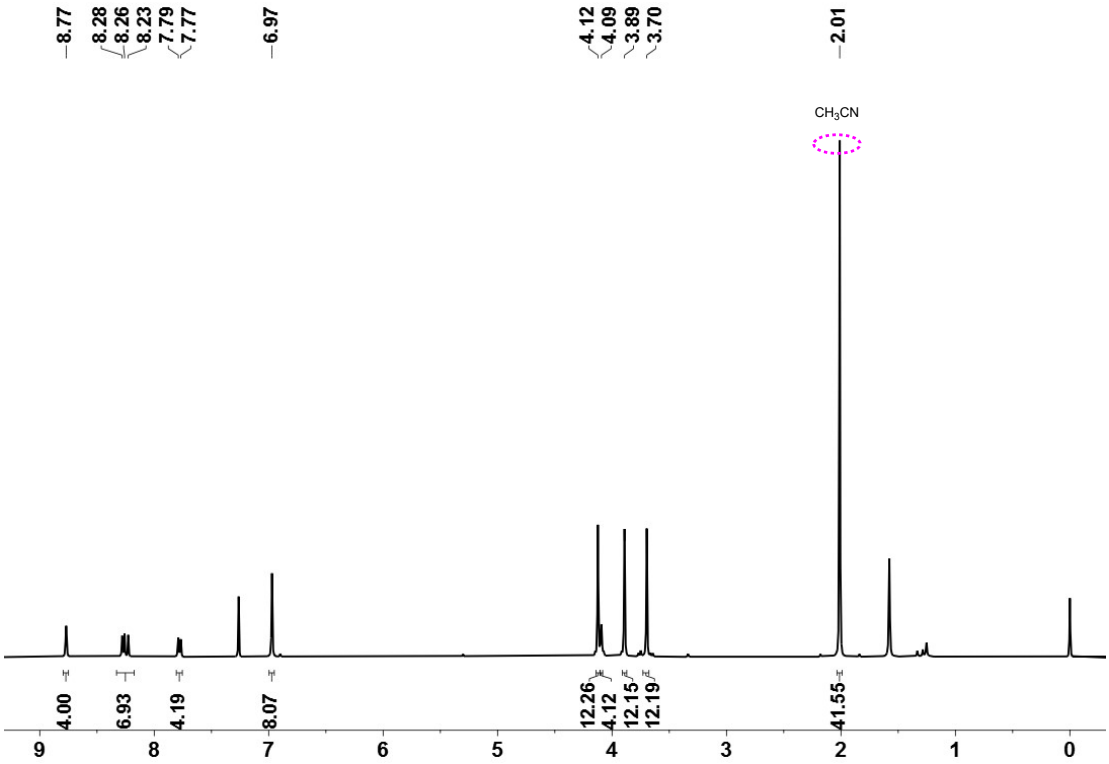

Figure S8.[1]H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB after exposure to CH_3CN

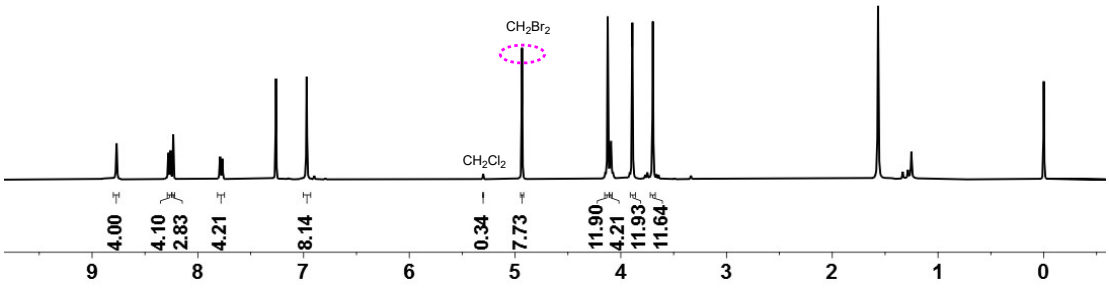

Figure S9.[1]H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB after exposure to CH_2Br_2

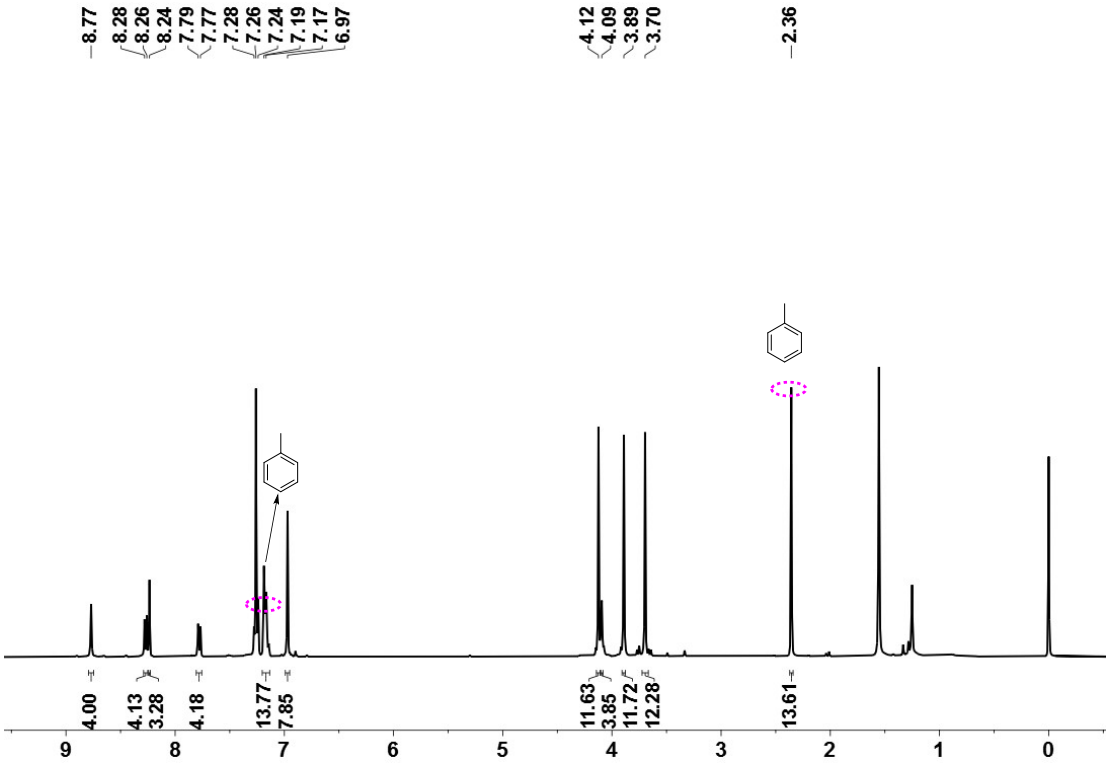

Figure S10.[1]H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB after exposure to toluene

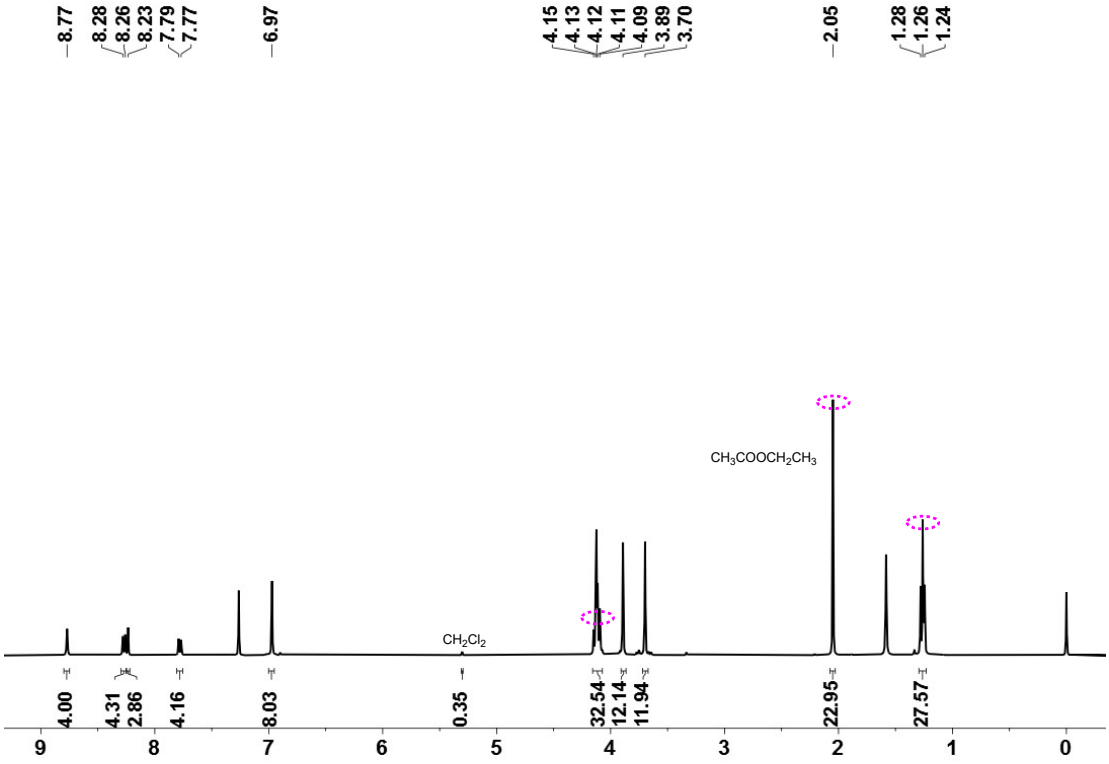

Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated P2@TCNB after exposure to ethyl acetate

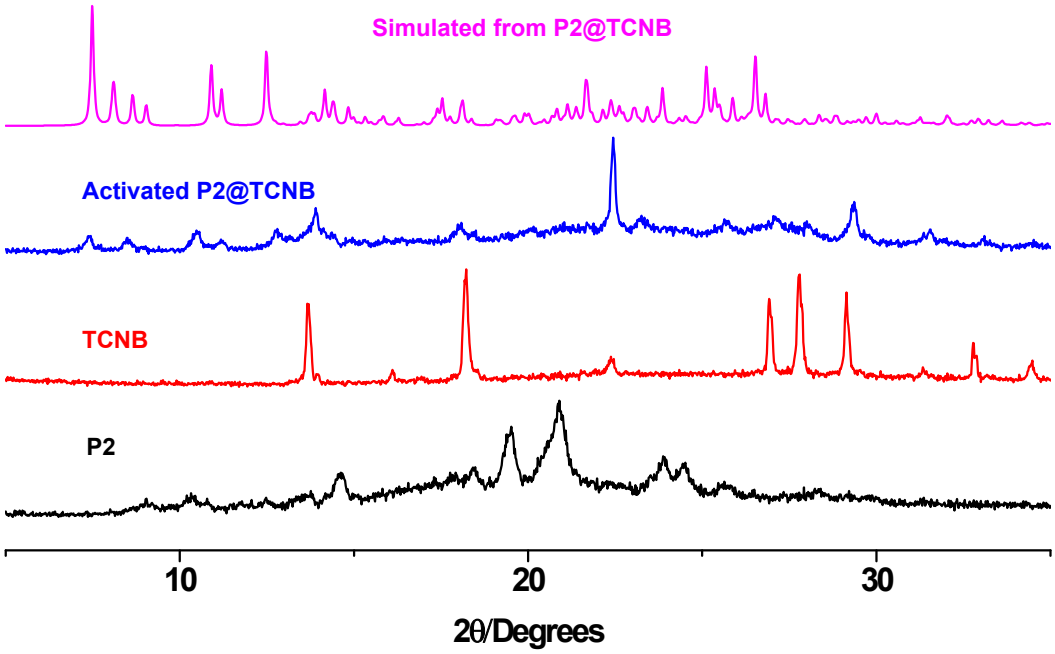

Figure S12. PXRD patterns of P2, activated P2@TCNB, TCNB and simulated from P2@TCNB

3. PXRD patterns and UV/Vis absorption spectra of activated P2@TCNB after exposure to VOCs

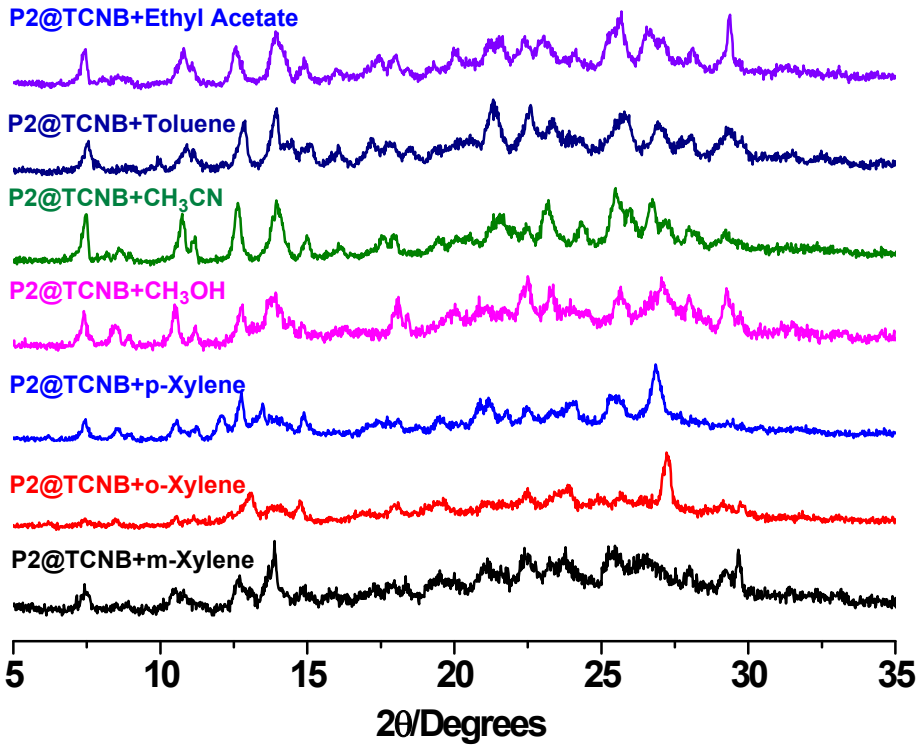

Figure S13. PXRD patterns of activated P2@TCNB after exposure to *o*-Xylene, *m*-Xylene, *p*-Xylene, toluene, CH_3OH and ethyl acetate

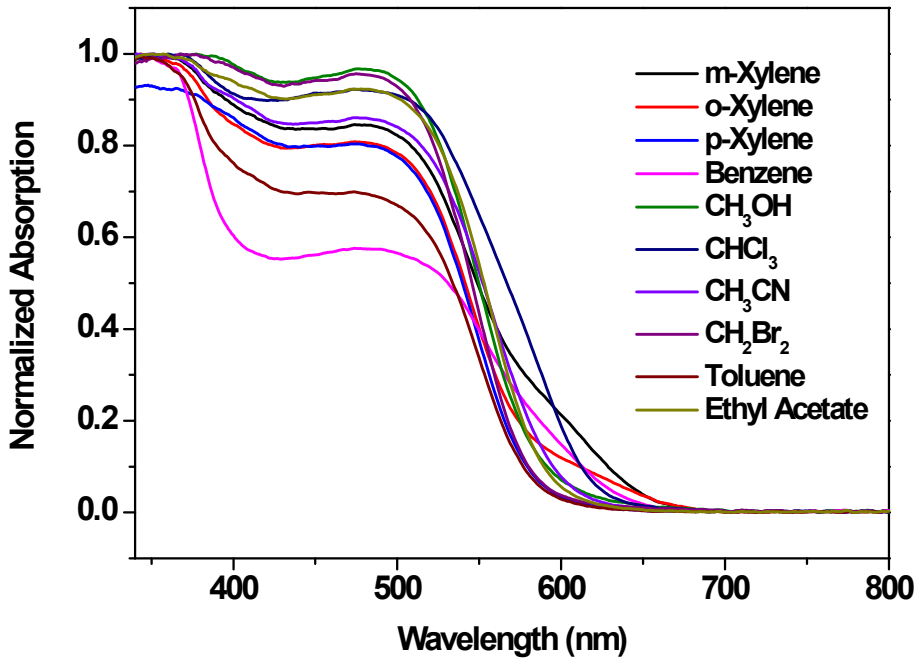

Figure S14. Solid-state UV/Vis absorption spectra of activated P2@TCNB after exposure to VOCs.

4. Crystal data and structures

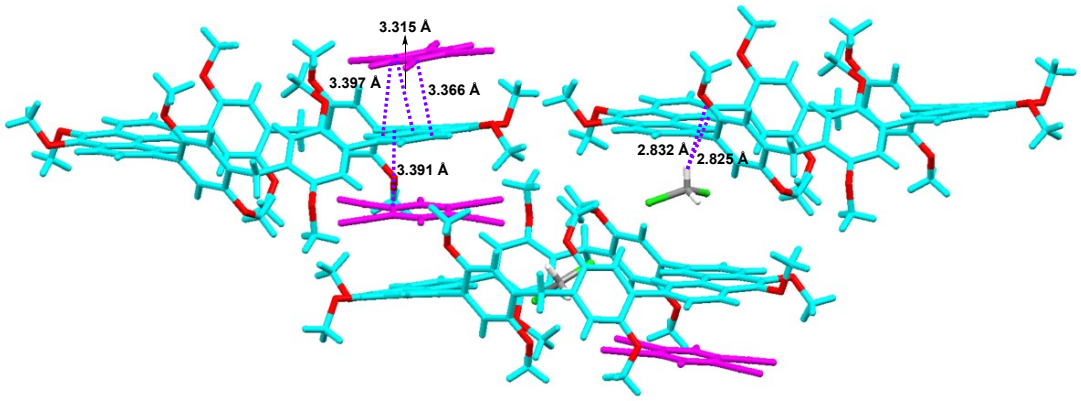

Figure S15. Crystal structure of P2@TCNB

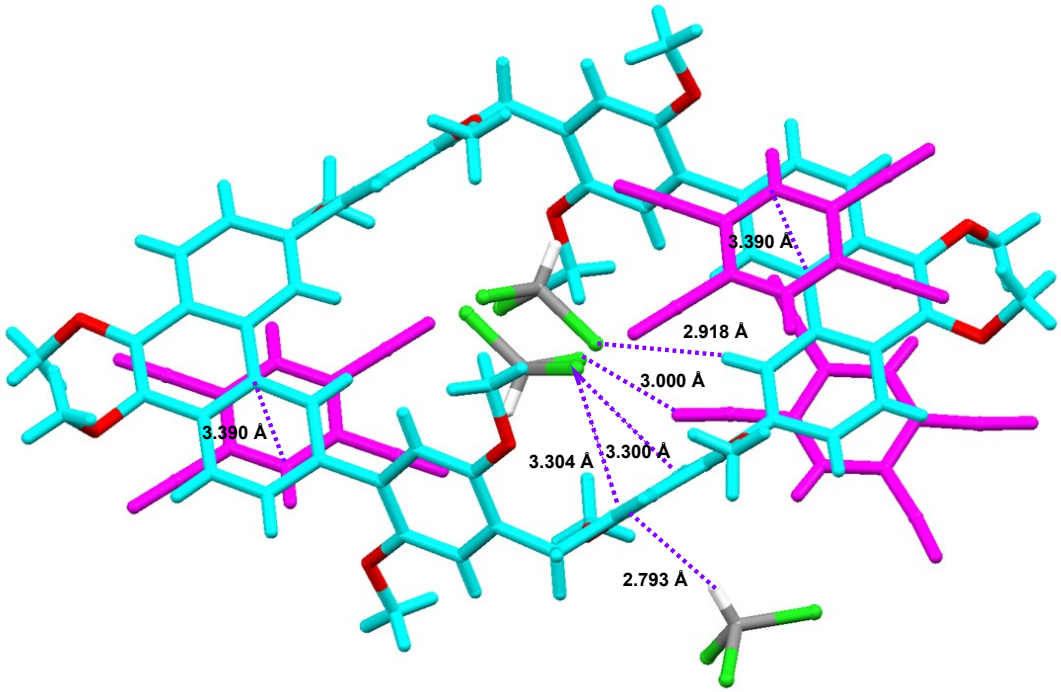

Figure S16. Crystal structure of P2@TCNB@$CHCl_3$

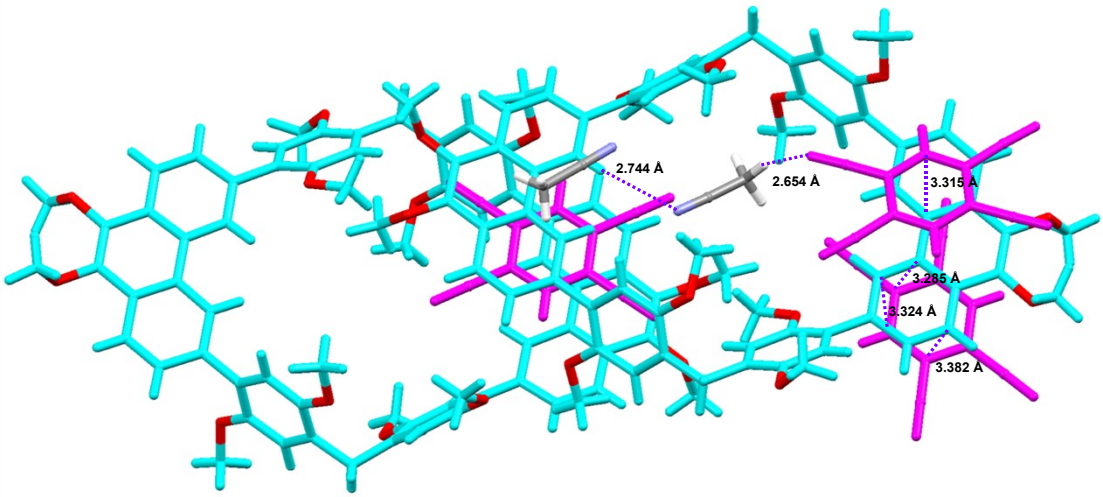

Figure S17. Crystal structure of P2@TCNB@CH_3CN

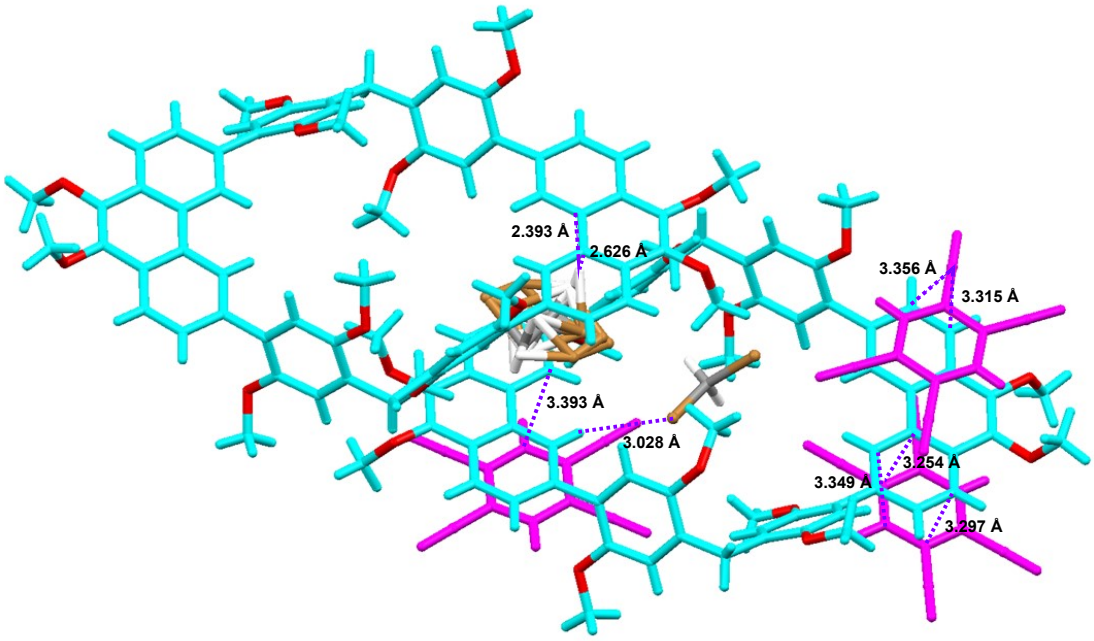

Figure S18. Crystal structure of P2@TCNB@CH_2Br_2

Figure S19. Picture of P2@TCNB single crystal

Table 1 Crystal data and structure refinement for P2@TCNB**.**

Identification code	P2@TCNB
Empirical formula	$C_{83}H_{67}Cl_4N_6O_{12}$
Formula weight	1482.22
Temperature/K	296.15(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.939(2)
b/Å	13.108(2)

c/Å	23.799(4)
α/°	95.070(2)
β/°	92.406(2)
γ/°	113.497(2)
Volume/Å^3	3673.8(11)
Z	2
ρ_{calc}g/cm^3	1.340
μ/mm^{-1}	0.230
F(000)	1542.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.41 to 50.054
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -28 ≤ l ≤ 28
Reflections collected	35507
Independent reflections	12938 [R_{int} = 0.0436, R_{sigma} = 0.0642]
Data/restraints/parameters	12938/302/1073
Goodness-of-fit on F^2	0.994
Final R indexes [I>=2σ (I)]	R_1 = 0.0657, wR_2 = 0.1759
Final R indexes [all data]	R_1 = 0.1455, wR_2 = 0.2247
Largest diff. peak/hole / e Å^{-3}	0.30/-0.38

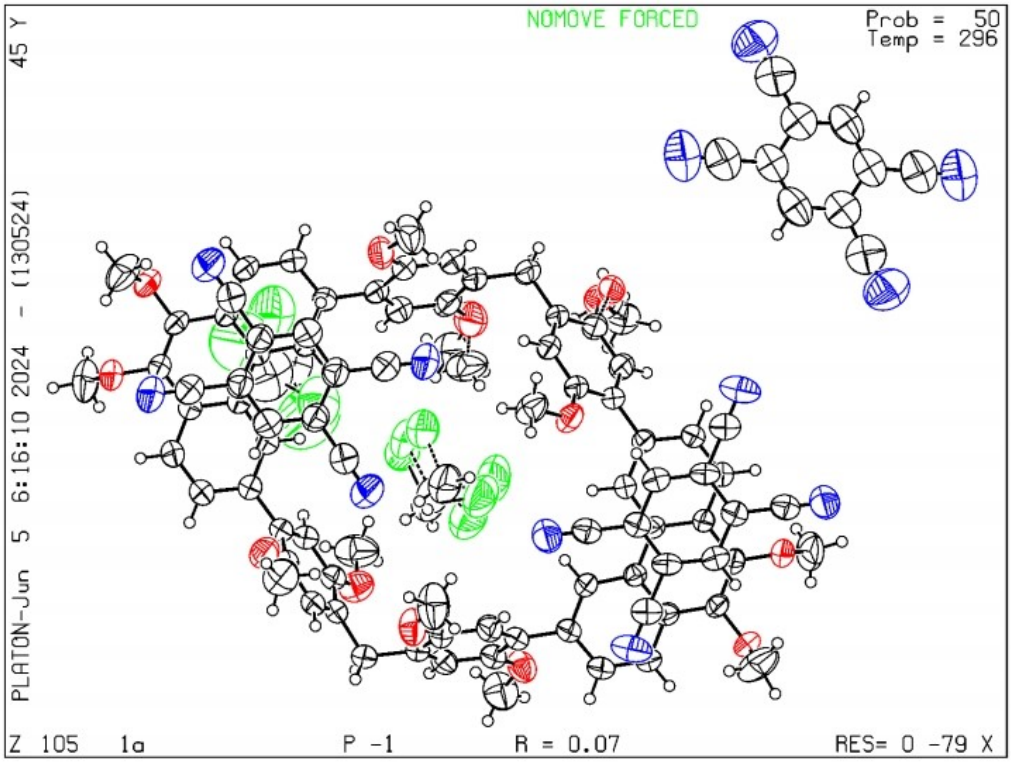

Table 2 Crystal data and structure refinement for P2@TCNB@$CHCl_3$**.**

Identification code	P2@TCNB@$CHCl_3$

Empirical formula	$C_{89}H_{67}Cl_9N_8O_{12}$
Formula weight	1759.55
Temperature/K	296.15(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.062(6)
b/Å	13.259(6)
c/Å	13.970(6)
α/°	70.993(6)
β/°	70.564(6)
γ/°	72.967(6)
Volume/Å^3	2110.4(16)
Z	1
ρ_{calc}g/cm^3	1.384
μ/mm^{-1}	0.366
F(000)	906.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.196 to 50.054
Index ranges	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
Reflections collected	20443
Independent reflections	7439 [R_{int} = 0.0703, R_{sigma} = 0.1264]
Data/restraints/parameters	7439/401/694
Goodness-of-fit on F^2	0.982
Final R indexes [I>=2σ (I)]	R_1 = 0.0820, wR_2 = 0.2156
Final R indexes [all data]	R_1 = 0.2047, wR_2 = 0.2927
Largest diff. peak/hole / e Å^{-3}	0.44/-0.31

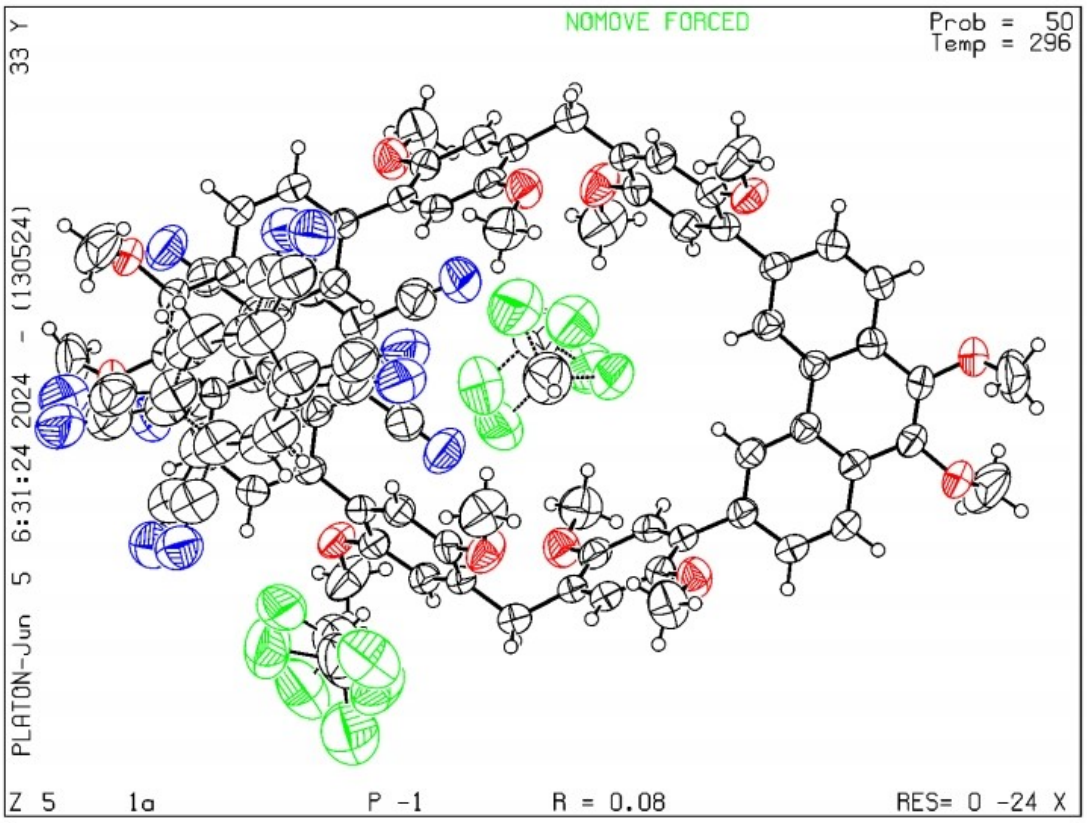

Table 3 Crystal data and structure refinement for P2@TCNB@CH_3CN**.**

Identification code	P2@TCNB@CH_3CN
Empirical formula	$C_{85}H_{69}N_8O_{12}$
Formula weight	1394.48
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	12.982(7)
b/Å	13.032(7)
c/Å	23.658(13)
α/°	91.171(8)
β/°	94.196(8)
γ/°	114.981(7)
Volume/Å^3	3612(4)
Z	2
ρ_{calc}g/cm^3	1.282
μ/mm^{-1}	0.087
F(000)	1462.0
Crystal size/mm^3	0.45 × 0.23 × 0.2
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	1.728 to 55.206
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-30 \leq l \leq 30$
Reflections collected	40489
Independent reflections	15989 [R_{int} = 0.0745, R_{sigma} = 0.1036]
Data/restraints/parameters	15989/48/960
Goodness-of-fit on F^2	0.944
Final R indexes [I>=2σ (I)]	R_1 = 0.0808, wR_2 = 0.2106
Final R indexes [all data]	R_1 = 0.1828, wR_2 = 0.2844
Largest diff. peak/hole / e $Å^{-3}$	0.37/-0.36

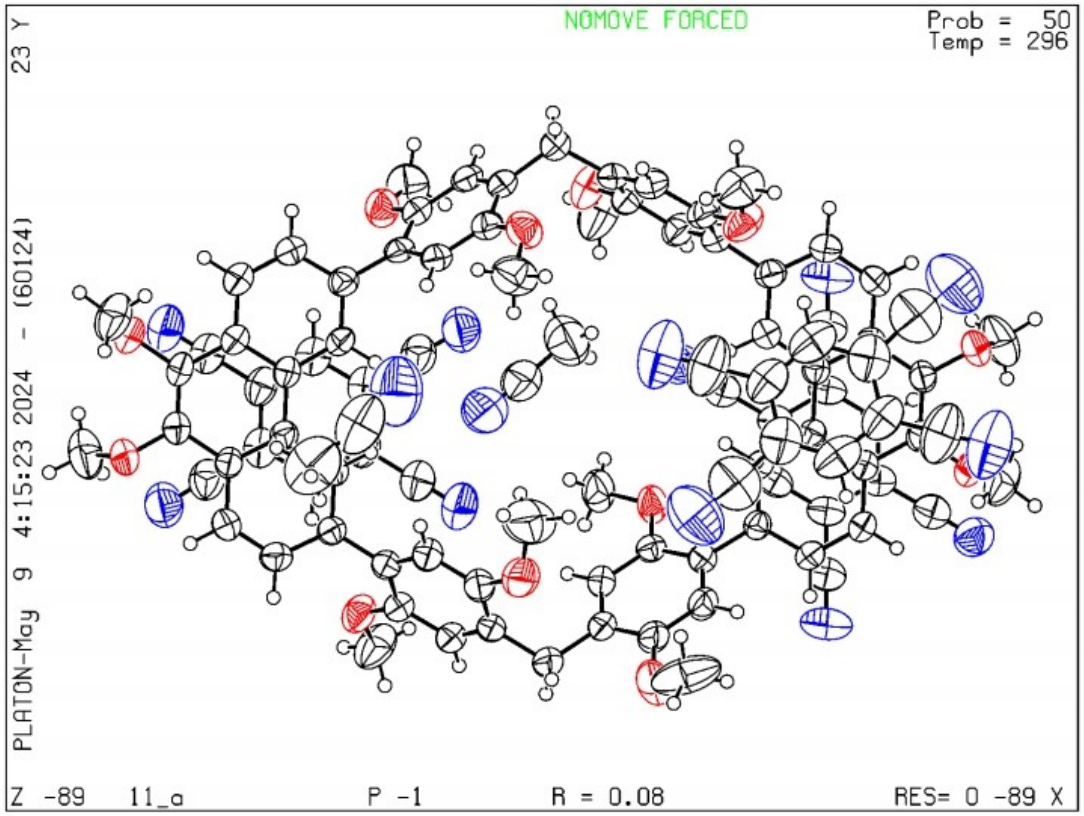

Table 4 Crystal data and structure refinement for P2@TCNB@CH_2Br_2**.**

Identification code	P2@TCNB@CH_2Br_2
Empirical formula	$C_{165}H_{132}Br_6N_{12}O_{24}$
Formula weight	3146.28
Temperature/K	296.15(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.903(3)
b/Å	13.152(3)
c/Å	23.932(6)
α/°	86.210(3)
β/°	88.225(3)

γ/°	64.678(3)
Volume/Å^3	3663.0(15)
Z	1
ρ_{calc}g/cm^3	1.426
μ/mm^{-1}	1.720
F(000)	1608.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.412 to 49.498
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -28 ≤ l ≤ 28
Reflections collected	34619
Independent reflections	12528 [R_{int} = 0.0737, R_{sigma} = 0.1096]
Data/restraints/parameters	12528/142/1025
Goodness-of-fit on F^2	1.002
Final R indexes [I>=2σ (I)]	R_1 = 0.0712, wR_2 = 0.1736
Final R indexes [all data]	R_1 = 0.1947, wR_2 = 0.2360
Largest diff. peak/hole / e Å^{-3}	0.69/-0.62

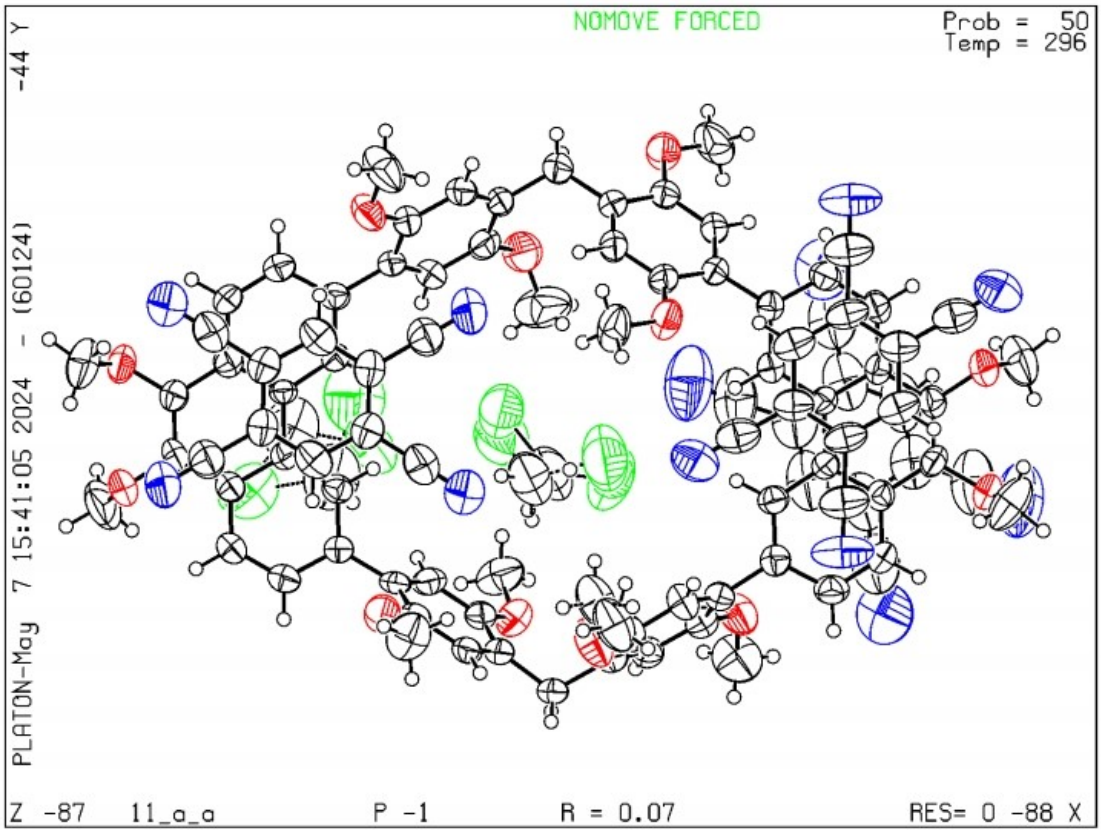

Table 1 Amount of VOCs absorption by activated P2@TCNB

VOCs	**Amount of VOCs over P2**
o-Xylene	2.43

m-Xylene	2.20
p-Xylene	3.18
benzene	6.13
toluene	4.54
CH_3OH	2.12
$CHCl_3$	3.43
CH_3CN	13.85
CH_2Br_2	3.87
ethyl acetate	7.65

5. Macrocycle-Based CT Cocrystals Adsorption Experiments

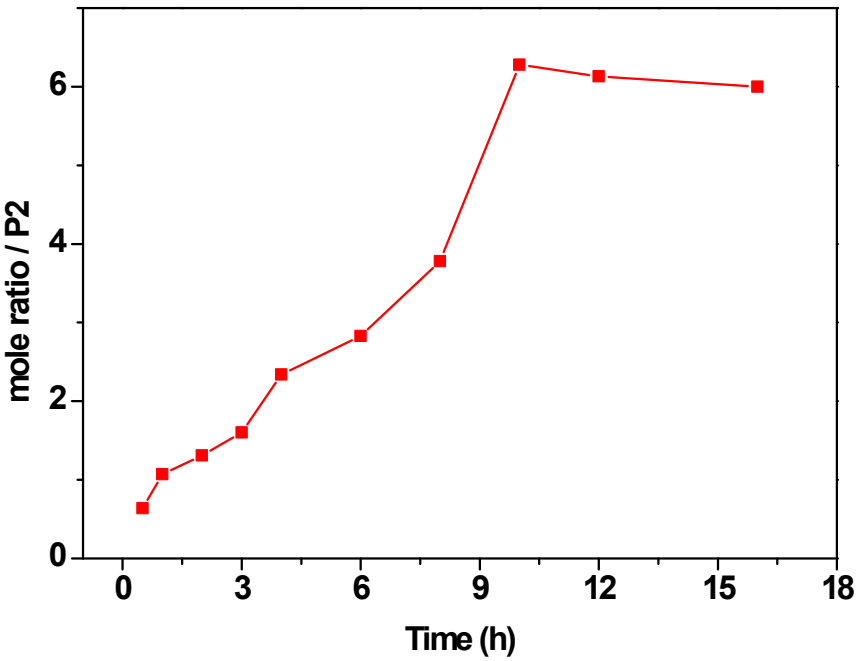

Figure S20. Time-dependent solid-vapor sorption plots of activated P2@TCNB for benzene vapor

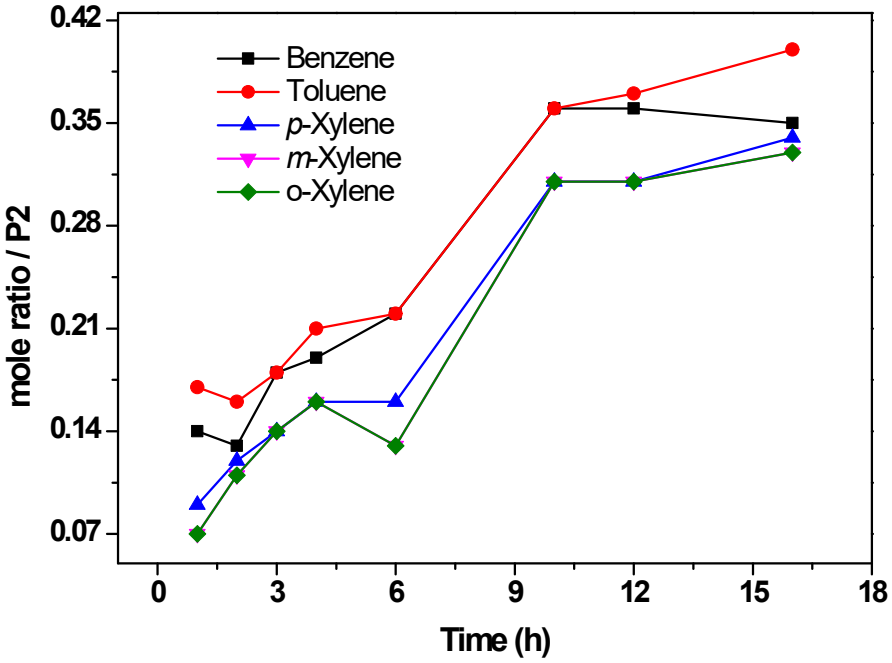

Figure S21. Time-dependent solid-vapor sorption plots of activated P2@TCNB for the mixture vapor (benzene : toluene : p-xylene : m-xylene : o-xylene = 1:1:1:1:1; v/v)