

Supplementary Information

Synthesis of a luminescent macrocycle and its crystalline structure-adaptive transformation

Shuo Li,^a Zhi-Yuan Zhang,^b Haichang Zhang,^{*c} Yue-Ling Bai,^{*a} Lei Cui,^a and Chunju Li^{*a,b}

^aCollege of Science, Shanghai University, Shanghai 200444, P. R. China. E-mail: yuelingbai@shu.edu.cn

^bTianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China. E-mail: cjli@shu.edu.cn

^cScience and Technology on Power Sources Laboratory, Tianjin Institute of Power Sources, Tianjin, 300384, P. R. China. E-mail: hchzhang@tju.edu.cn

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1. Materials and methods

All reagents were purchased commercially and used without further purification unless otherwise noted. ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 500 MHz spectrometer. High-resolution mass spectra (HRMS) was determined on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Powder X-ray diffraction (PXRD) data were measured with a powder X-ray diffractometer (DX-2700).. PL spectra were obtained on RF-6000. Quantum efficiency and lifetime were measured on FLS1000. Melting points were obtained on an X-4 digital melting point apparatus without correction. ALL single crystal X-ray data were measured by direct methods using Bruker SMART APEX II). Thermogravimetric Analysis (TGA) was recorded using a Instrument NETZSCH STA 449F5 and the samples were heated under nitrogen gas at a rate of 10 °C/min. Diffuse reflectance spectra were recorded with a UV-3600iPlus spectrometer. Detailed experimental procedure: 1) about 20 mg of the sample was added to the integrating sphere to prepare a smooth film; 2) According to the instructions of UV-3600iPlus spectrometer, place Spectralon Reference Standard at the sampling port for reference scanning; 3) Remove Spectralon Reference Standard and place the sample at the sample port for diffuse reflectance spectrum scanning

2. Synthesis

Monomer. Under the protection of N₂ atmosphere, 2-(bis(4-bromophenyl)methylene)malononitrile (3.86 g, 10.0 mmol), 2,4-diethoxybenzeneboronic acid (5.25 g, 25.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.16 g, 1.00 mmol) were dissolved in tetrahydrofuran (200 mL). The sodium carbonate (4.24 g, 40.0 mmol) in water (20 mL) was added into the solution and stirred for 24 h at 82 °C. Upon cooling to room temperature, water (100 mL), dichloromethane (100 mL) was added and stirred. After filtration of the solution, the solution was partitioned between dichloromethane and water. The product was extracted from the organic layer. The aqueous layer was further extracted twice with dichloromethane (50 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The product was purified by column chromatography on silica gel (eluent: 2/1, v/v, dichloromethane:petroleum ether) to give yellow product monomer (4.91g, 87%). m.p. 123-124 °C; ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.69 (d, *J* = 5.0 Hz, 4H), 7.52 (d, *J* = 5.0 Hz, 4H), 7.31 (d, *J* = 10 Hz, 2H), 6.59 - 6.55 (m, 4H), 4.09 (q, *J* = 5.0 Hz, 4H), 4.06 (q, *J* = 5.0 Hz, 4H), 1.45 (t, *J* = 7.5 Hz, 6H), 1.38 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃, 298K) δ 175.0, 160.6, 157.2, 143.5, 133.9, 131.5, 130.7, 129.6, 121.7, 114.8, 105.8, 100.6, 79.4, 64.2, 63.8, 15.0, 14.8. HRMS (ESI) *m/z*: [M+Na]⁺ calculated for [C₃₆H₃₄N₂O₄Na]⁺, 581.2411; found, 581.2414.

MC. To the solution of monomer (2.28 g, 5.00 mmol) in chloroform (200 mL) was added paraformaldehyde (0.450 g, 30.0 mmol). Boron trifluoride diethyl etherate (0.650 ml, 10.0 mmol) was then added to the reaction mixture. The mixture was stirred at 25 °C for 25 minutes. Then the reaction was quenched by addition of 200 mL saturated aqueous NaHCO₃. The organic phase was separated and washed with saturated NaHCO₃ solution and brine. The organic layer was dried over anhydrous Na₂SO₄ and evaporated. The product was purified by column chromatography on silica gel (eluent: 100/1, v/v, dichloromethane: ethyl acetate) to obtain product MC (0.598g, 21%) as a yellow solid. m.p. > 320 °C; ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.57 (d, *J* = 10 Hz, 8H), 7.40 (d, *J* = 10 Hz, 8H), 6.94 (s, 4H), 6.55 (s, 4H), 4.09 (q, *J* = 5.0 Hz, 8H), 4.04 (q, *J* = 5.0 Hz, 8H), 1.41 (t, *J* = 7.5 Hz, 12H), 1.37 (t, *J* = 5.0 Hz, 12H). ¹³C NMR (125 MHz, CDCl₃, 298K) δ 175.2, 158.2, 155.5, 143.6, 133.8, 131.6, 130.6, 129.5, 122.6, 120.6, 114.8, 98.1, 79.1, 64.7, 64.2, 28.0, 15.0, 15.0. HRMS (ESI) *m/z*: [M+Na]⁺ calculated for [C₇₄H₆₈N₄O₈Na]⁺, 1129.4929; found, 1129.4923.

3. ^1H NMR, ^{13}C NMR, HMRS spectra

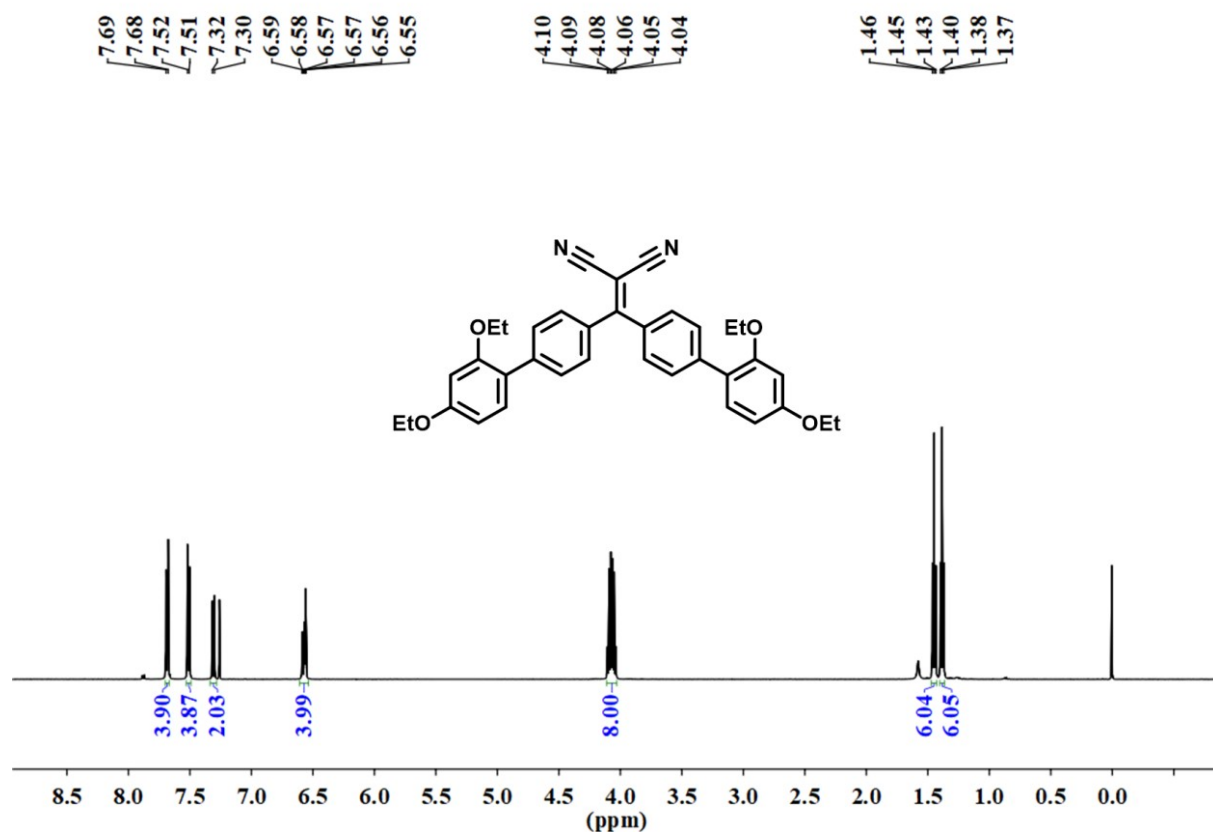


Fig. S1 ^1H NMR spectrum (500 MHz, CDCl_3 , 298K) of monomer.

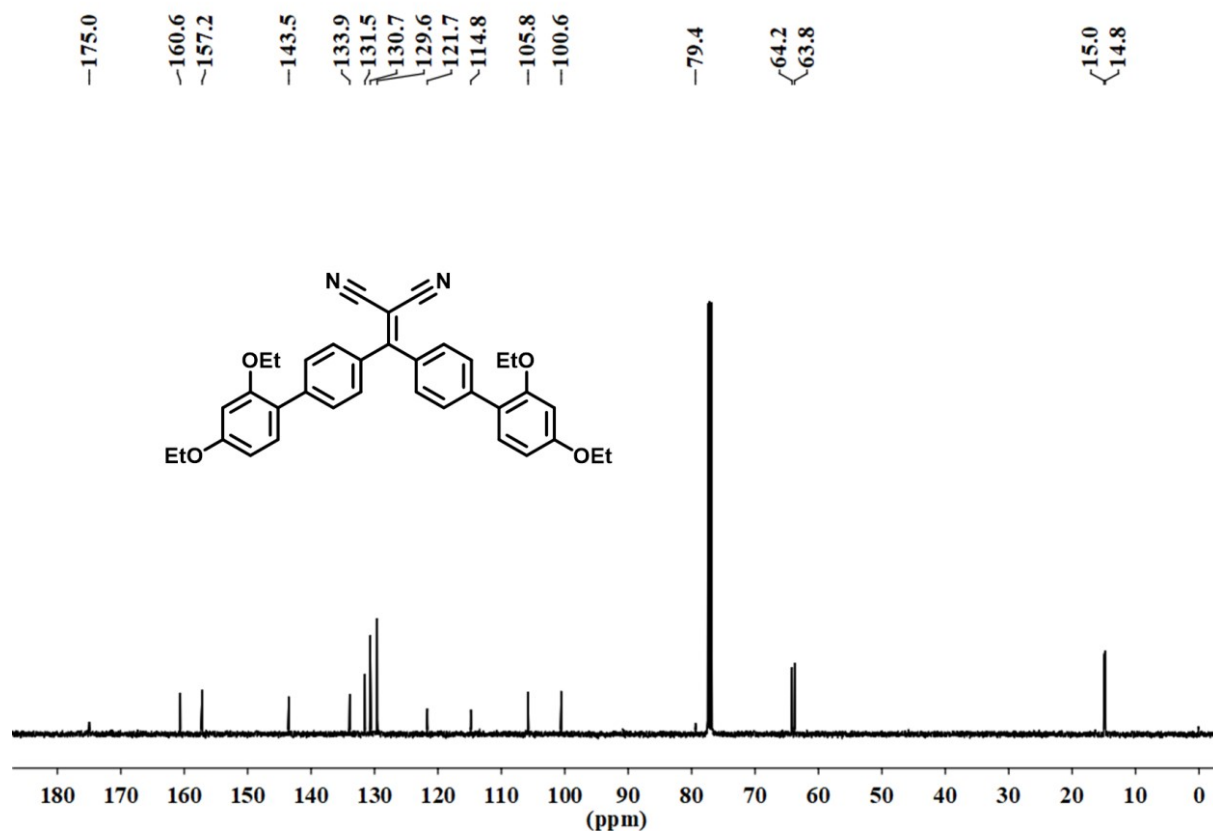


Fig. S2 ^{13}C NMR spectrum (125 MHz, CDCl_3 , 298K) of monomer.

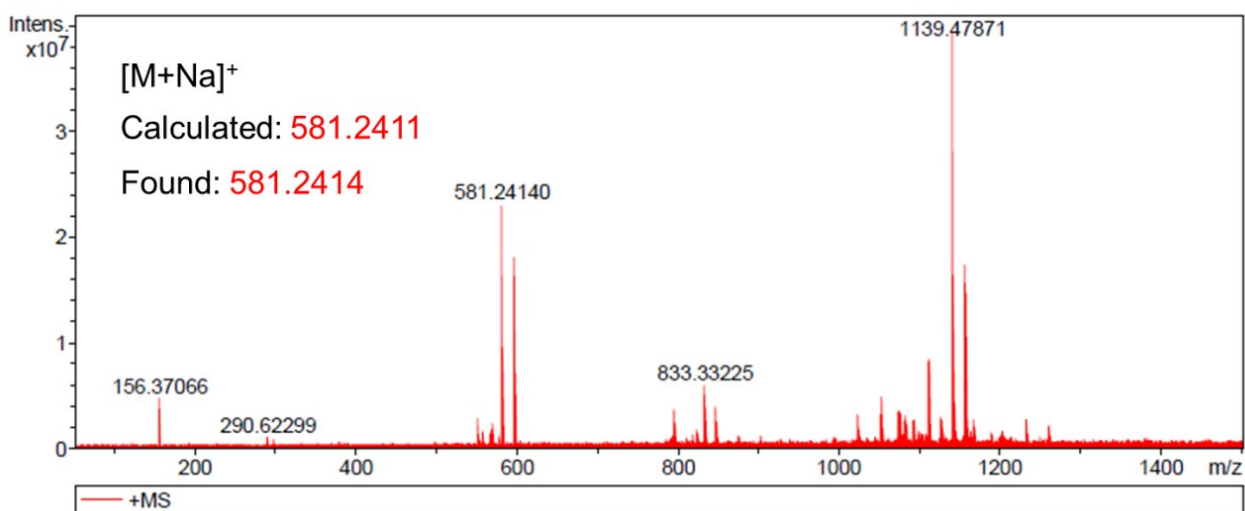


Fig. S3 HRMS spectrum of monomer.

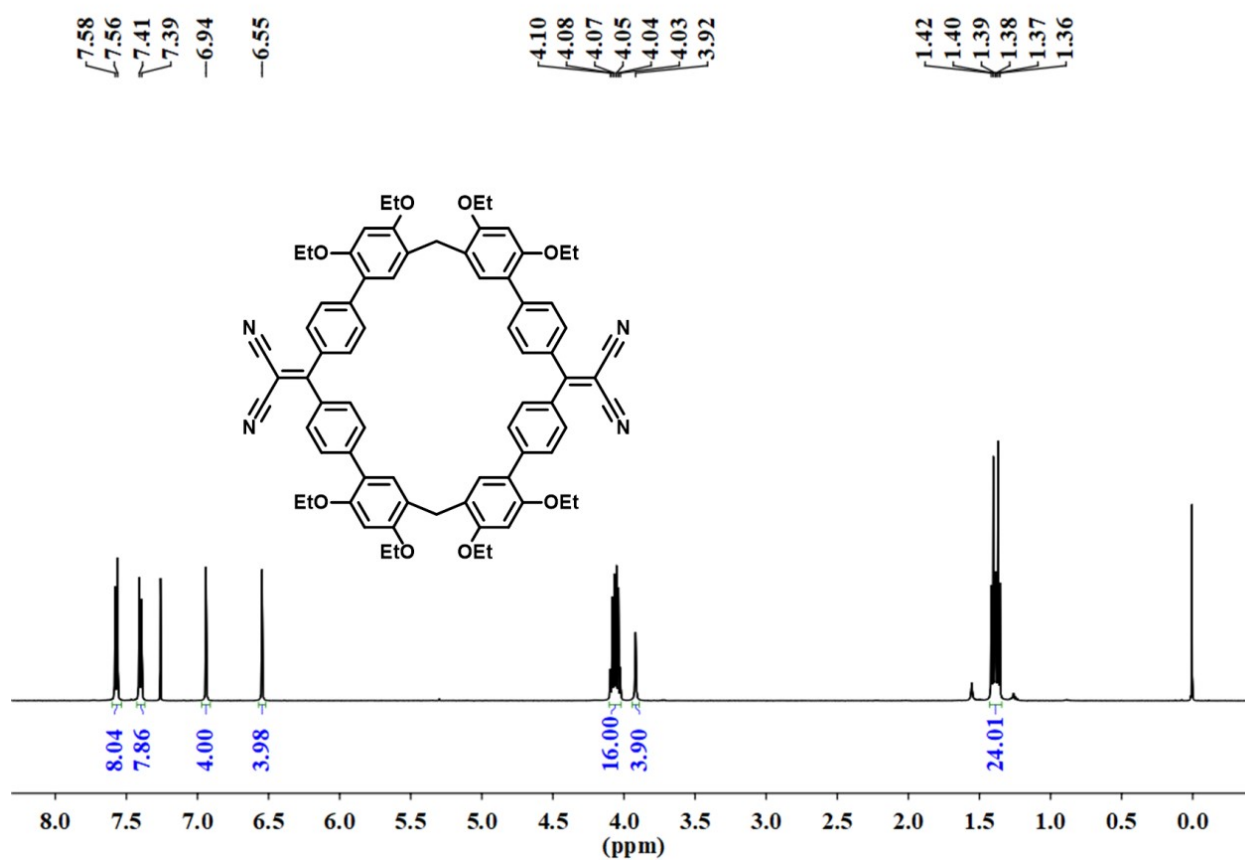


Fig. S4 1H NMR spectrum (500 MHz, $CDCl_3$, 298K) of MC.

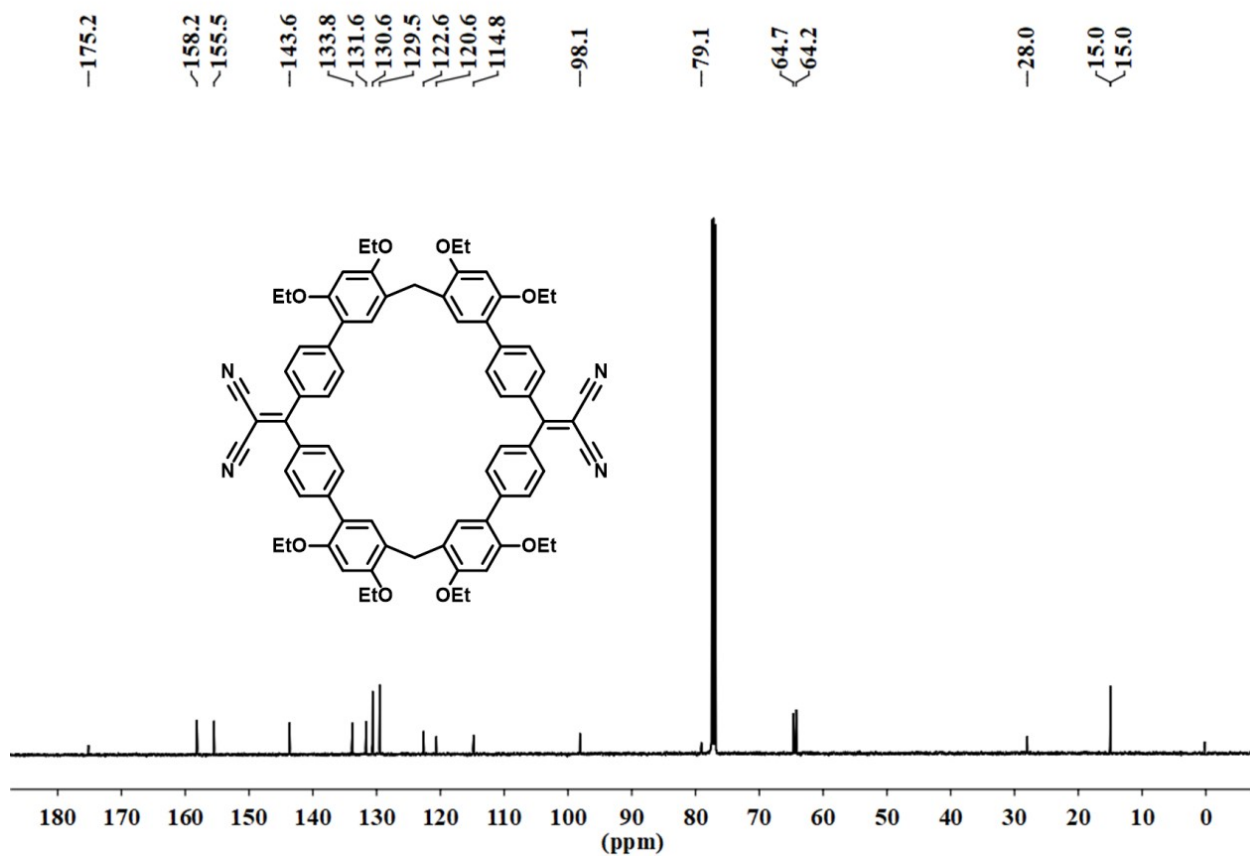


Fig. S5 ¹³C NMR spectrum (125 MHz, CDCl₃, 298K) of MC.

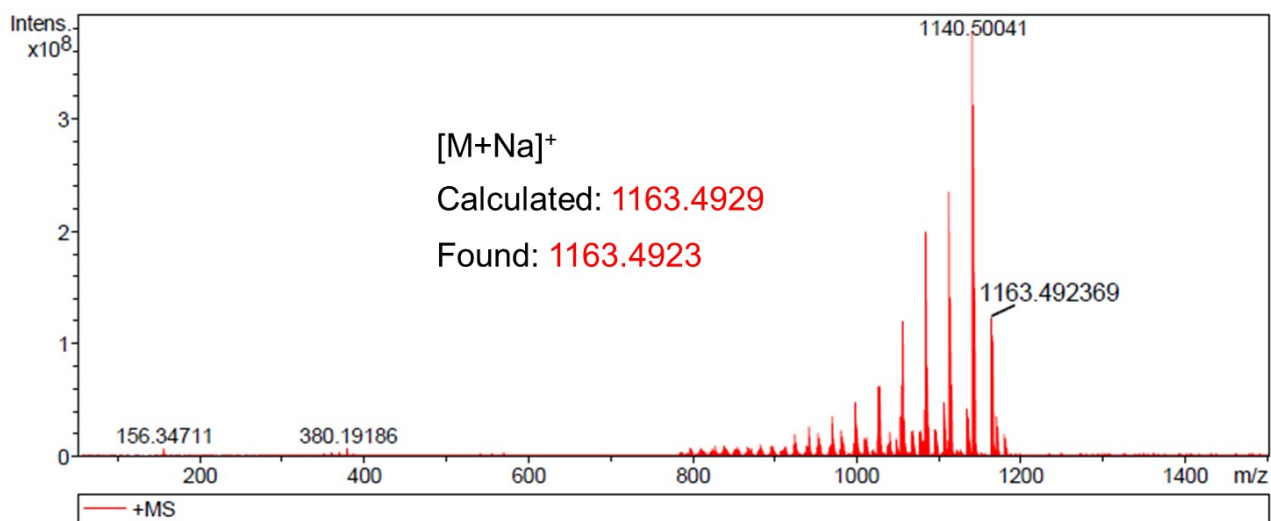


Fig. S6 HMRS spectrum of MC.

4. Photophysical Properties of macrocycle and monomer

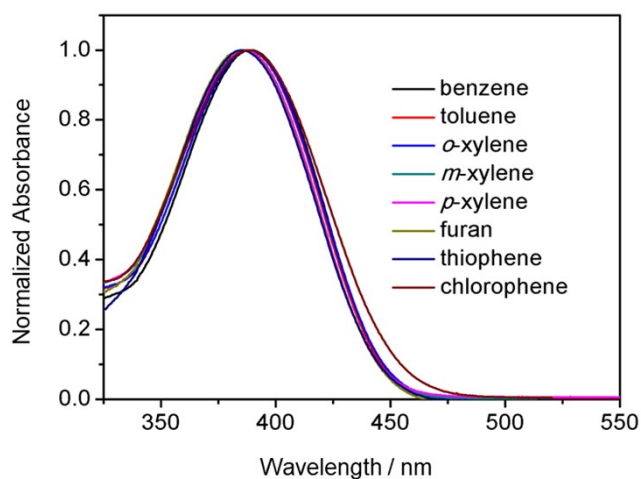


Fig. S7 The UV-vis spectra of the macrocycle MC in different solutions.

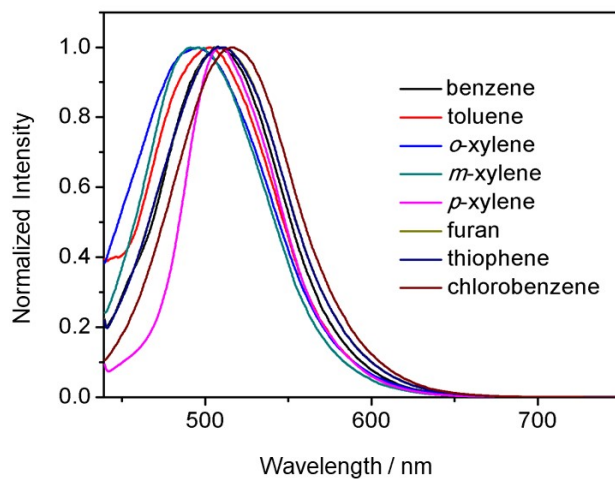


Fig. S8 Normalized photoluminescence spectrum of the macrocycle MC in different solutions.

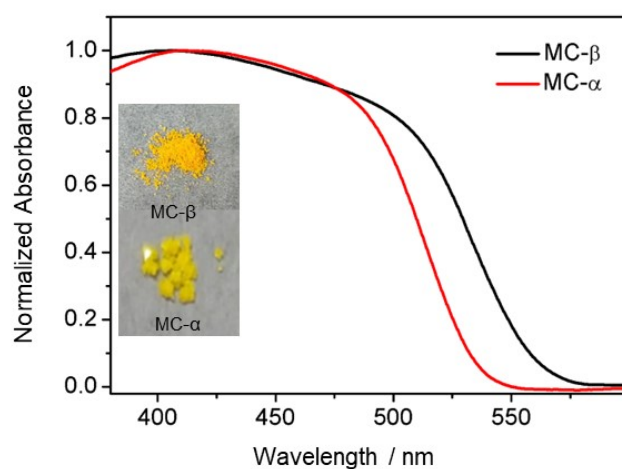


Fig. S9 Diffuse reflectance spectra of **MC-β** and **MC-α**. (Insets: photographs of **MC-β** and **MC-α** in the sunlight).

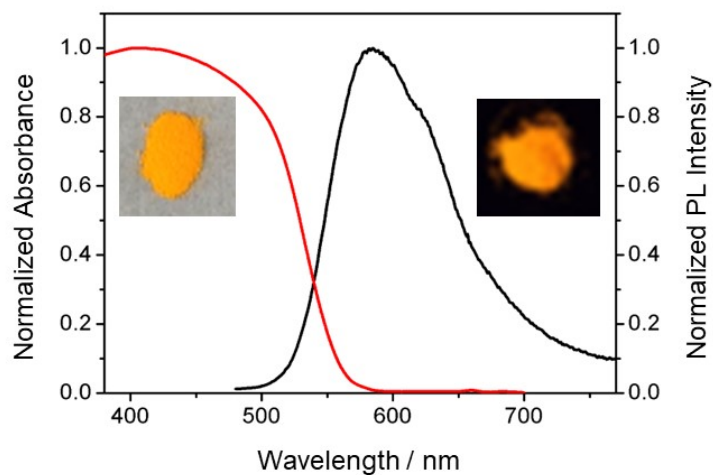


Fig. S10 Diffuse reflectance spectra and PL spectra of **MC-γ**. (Insets: photographs of **MC-γ** under 365 nm the sunlight and UV illuminations).

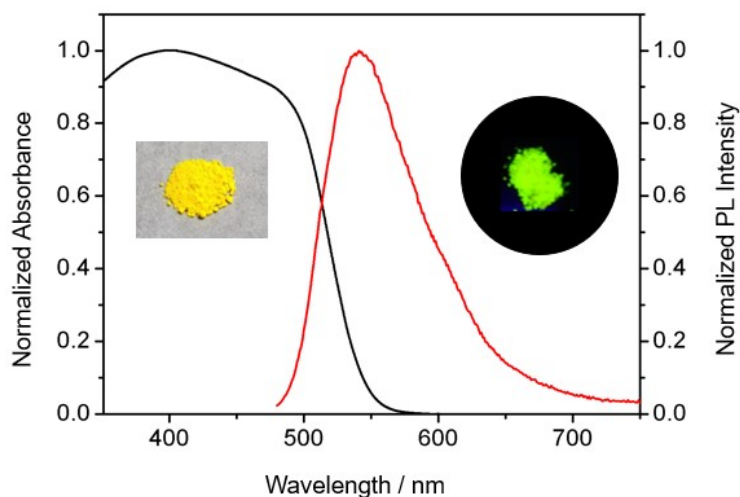


Fig. S11 Diffuse reflectance spectra and PL spectra of monomer crystals.

5. Powder XRD Patterns

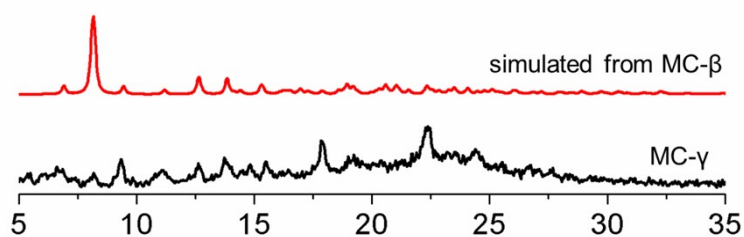


Fig. S12 PXRD patterns of **MC-γ** and simulated from **MC-β**.

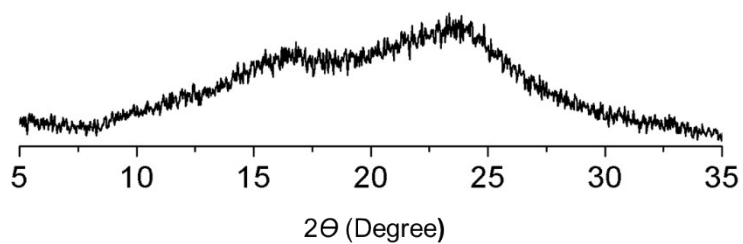


Fig. S13 PXR D patterns of MC- α in ground states.

6. Thermogravimetric Analysis

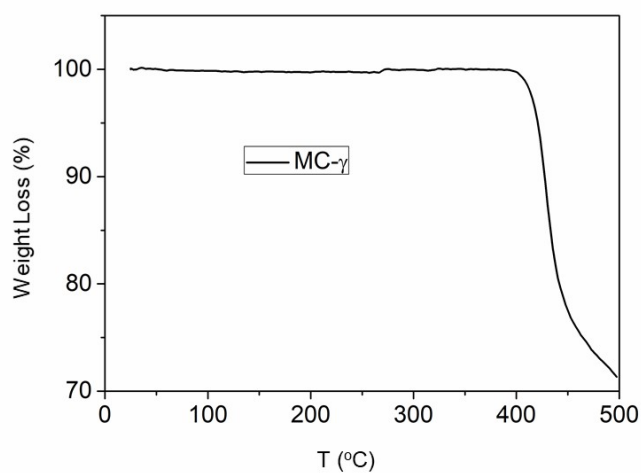


Fig. S14 TGA curve of MC- γ recorded under a nitrogen atmosphere.

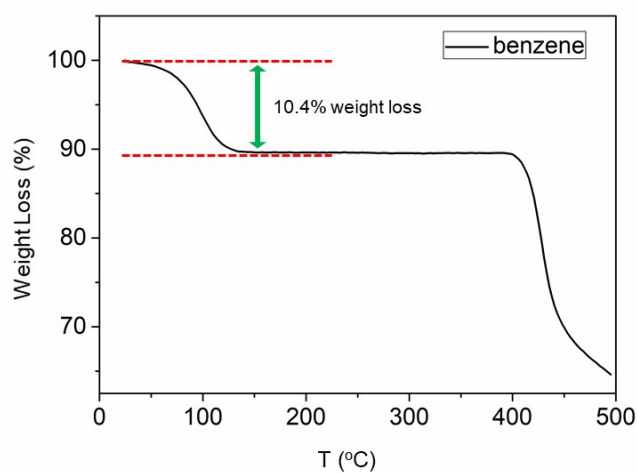


Fig. S15 TGA curve of MC- γ after uptake of benzene.

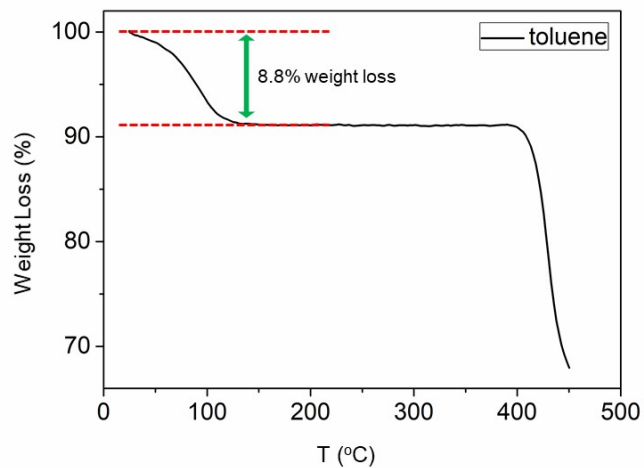


Fig. S16 TGA curve of MC- γ after uptake of toluene.

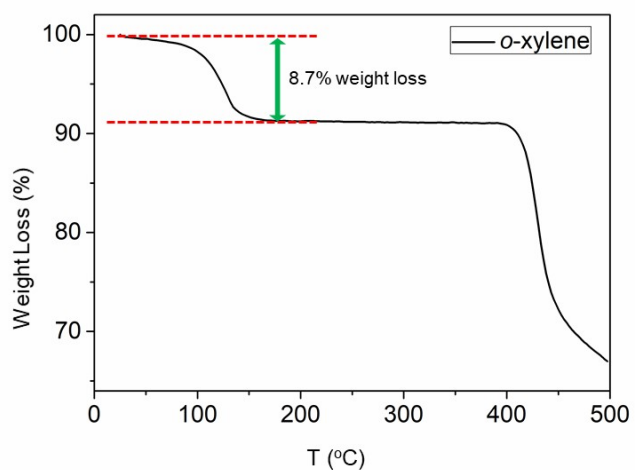


Fig. S17 TGA curve of MC- γ after uptake of *o*-xylene.

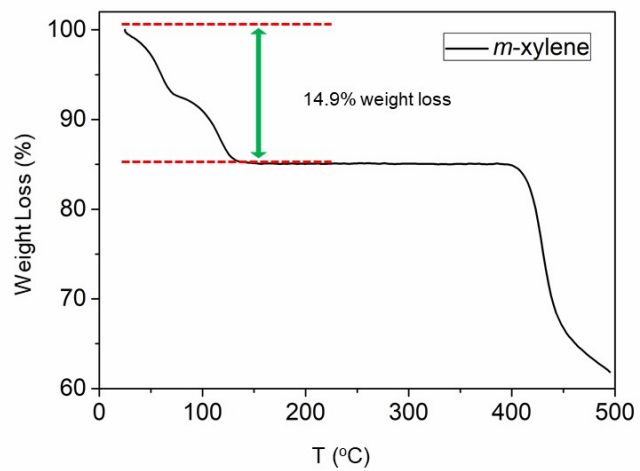


Fig. S18 TGA curve of MC- γ after uptake of *m*-xylene.

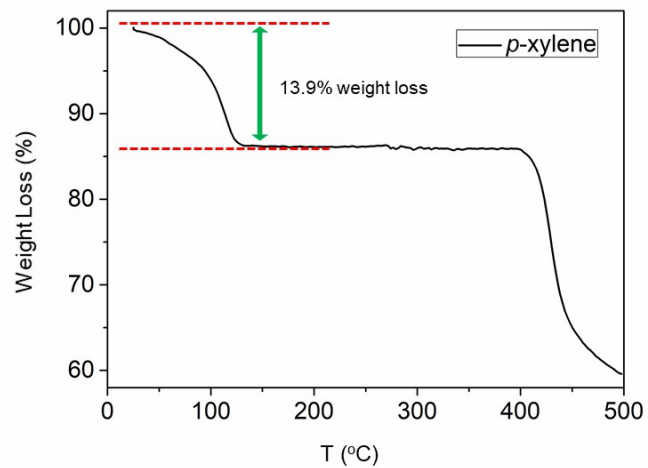


Fig. S19 TGA curve of MC- γ after uptake of *p*-xylene.

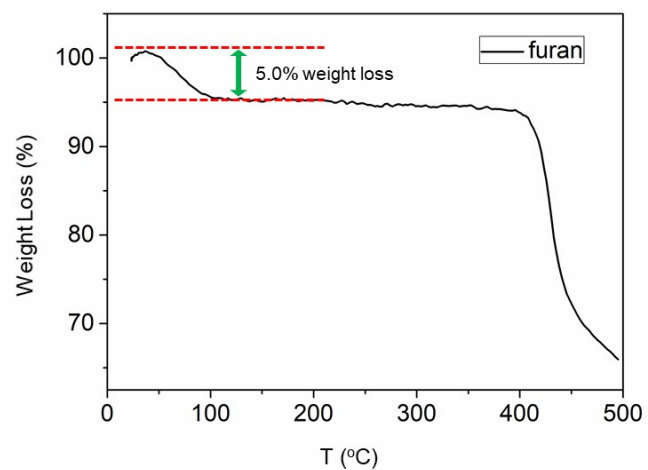


Fig. S20 TGA curve of MC- γ after uptake furan.

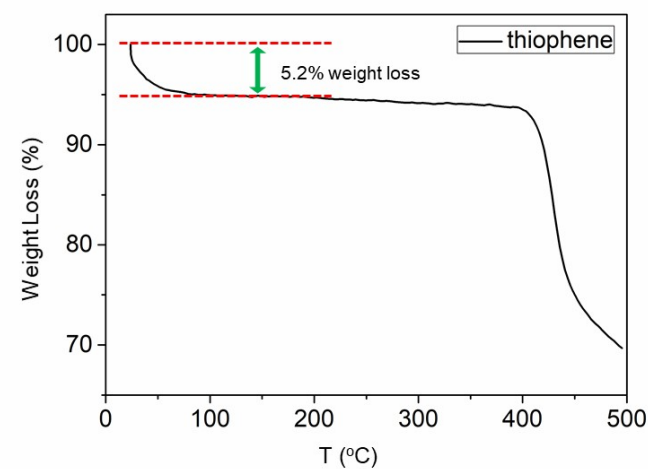


Fig. S21 TGA curve of MC- γ after uptake thiophene.

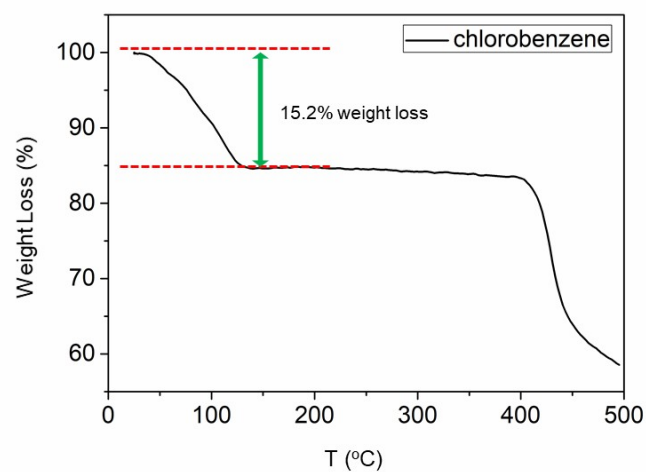


Fig. S22 TGA curve of MC- γ after uptake chlorobenzene.

7. Adsorption and desorption study of aromatic vapor

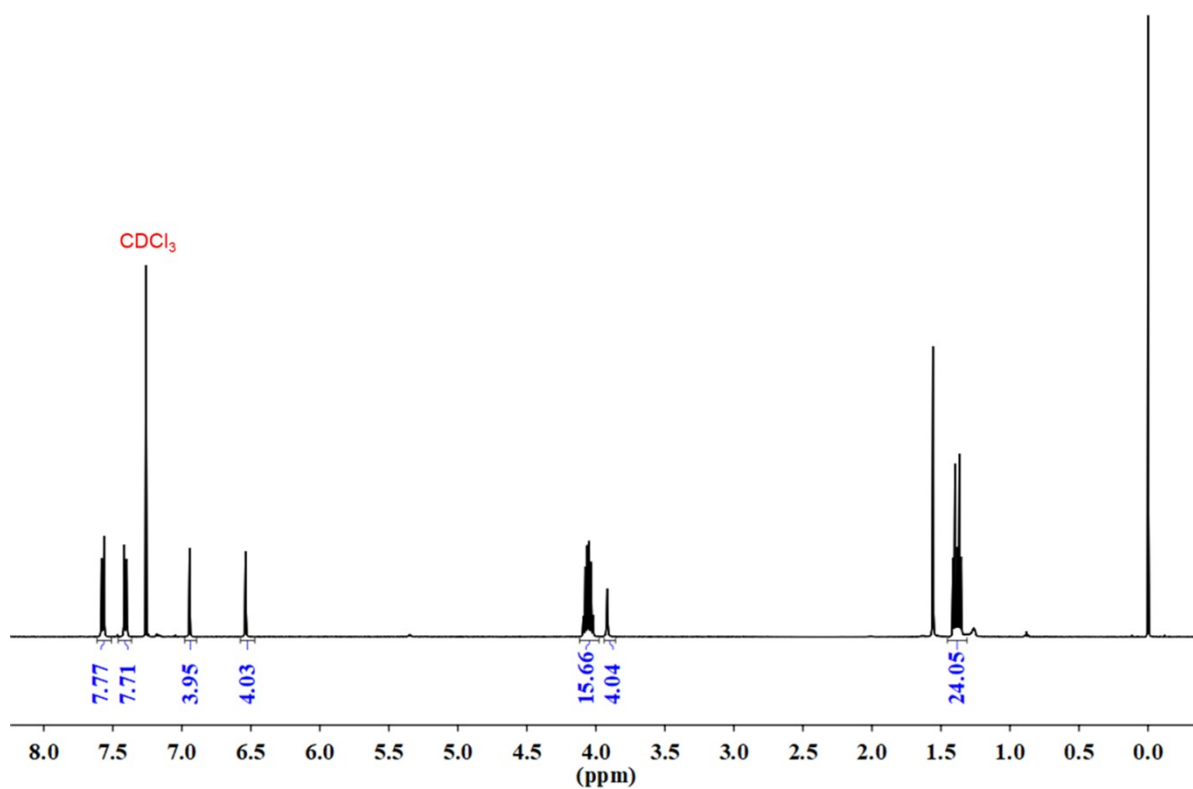


Fig. S23 ^1H NMR (500 MHz, CDCl_3) spectrum of MC- γ .

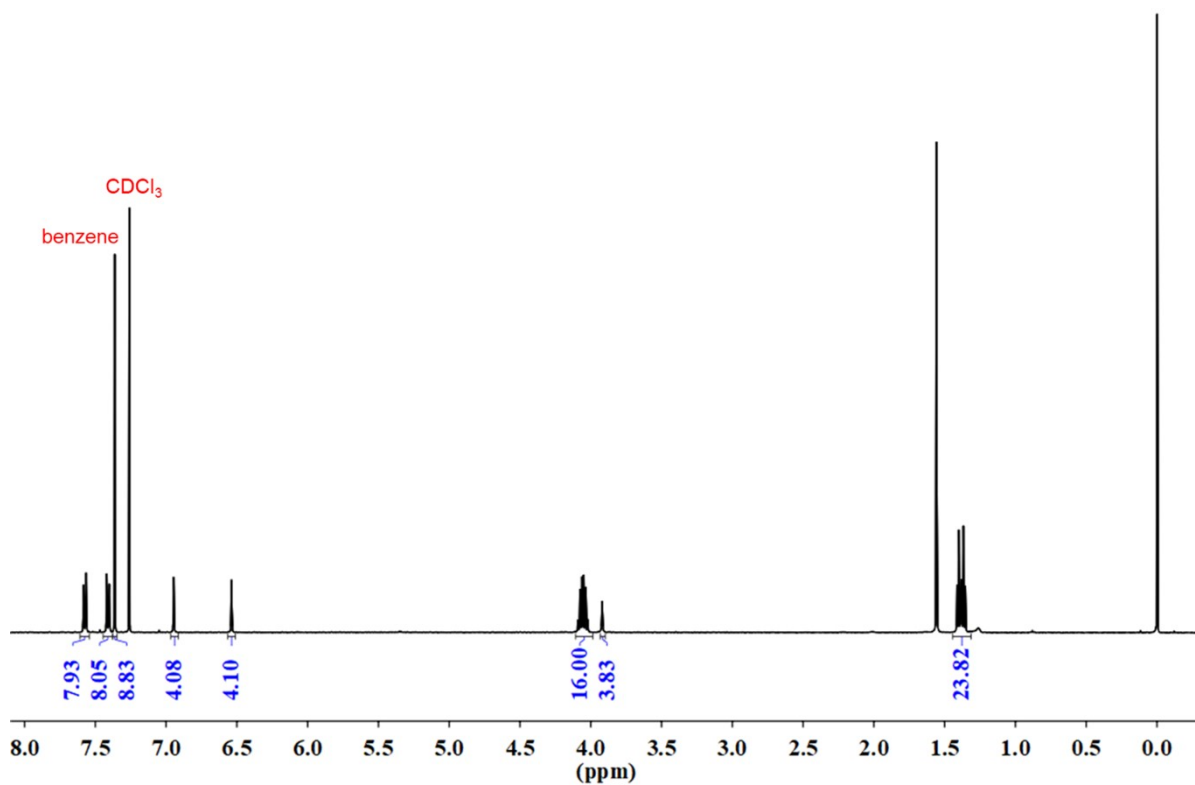


Fig. S24 ¹H NMR (500 MHz, CDCl₃) spectrum of MC- γ after uptake of benzene.

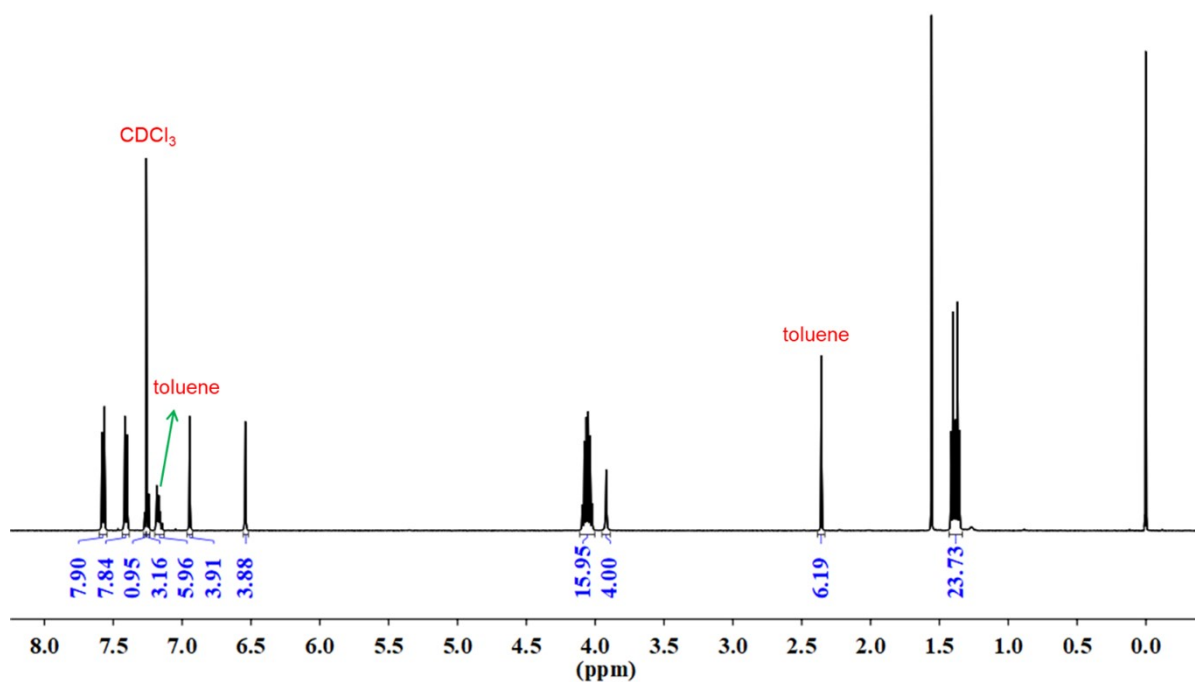


Fig. S25 ¹H NMR (500 MHz, CDCl₃) spectrum of MC- γ after uptake of toluene.

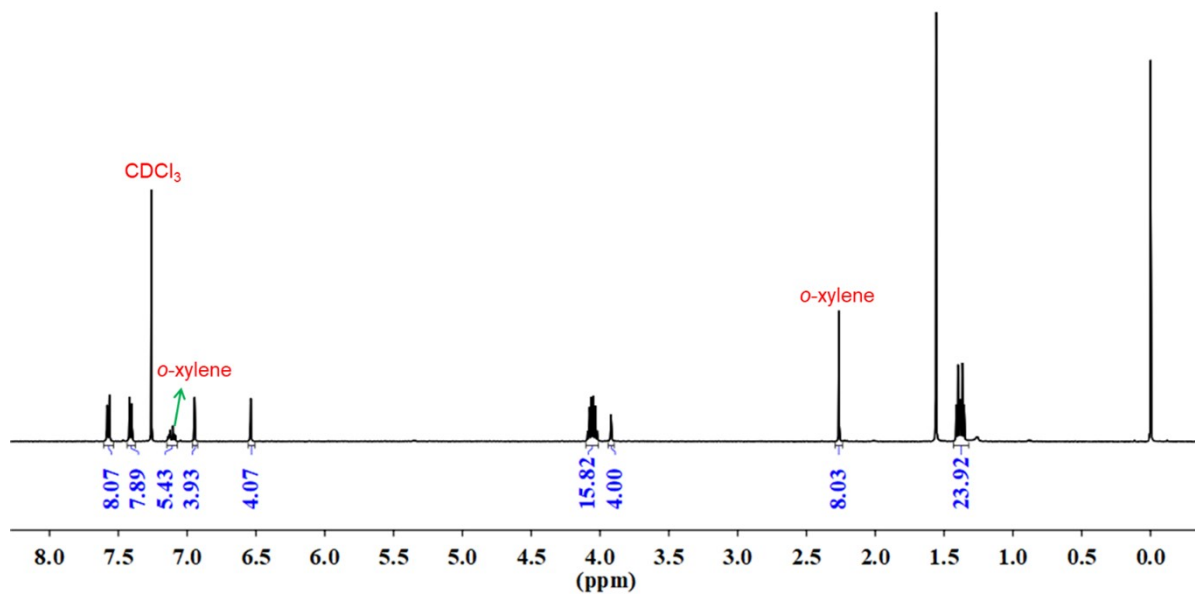


Fig. S26 ¹H NMR (500 MHz, CDCl₃) spectrum of MC- γ after uptake of *o*-xylene.

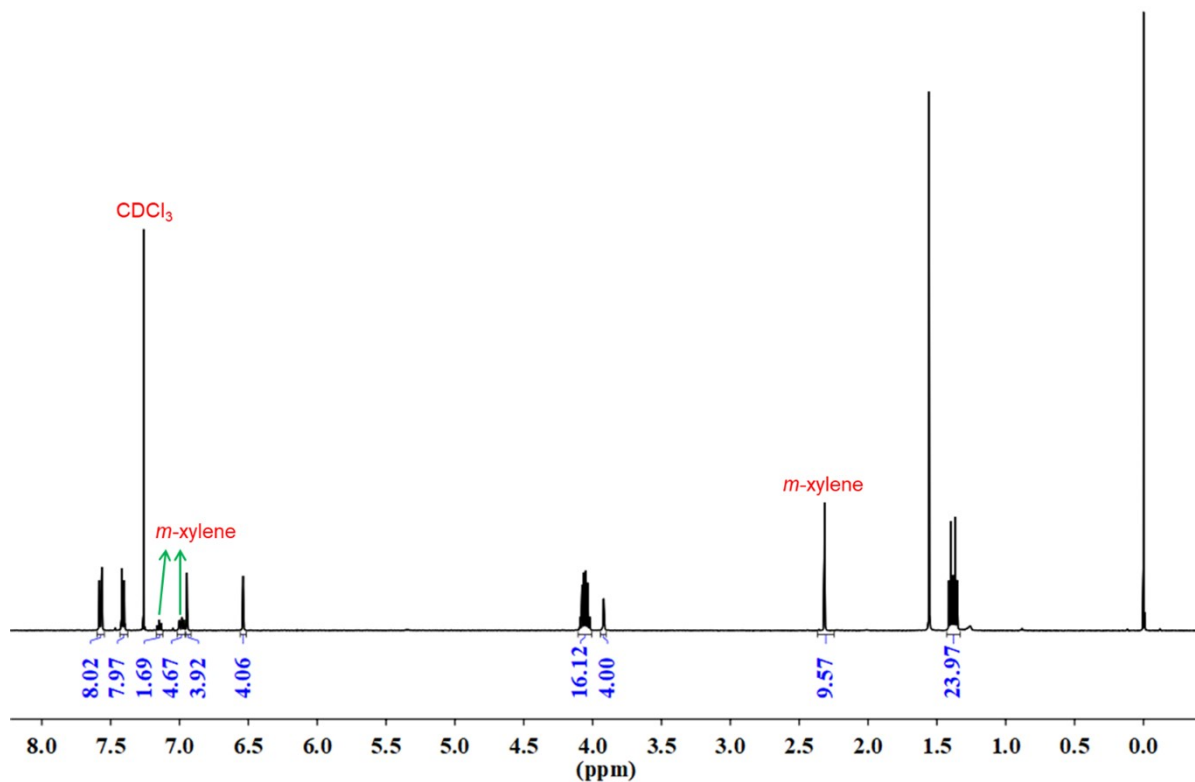


Fig. S27 ¹H NMR (500 MHz, CDCl₃) spectrum of MC- γ after uptake of *m*-xylene.

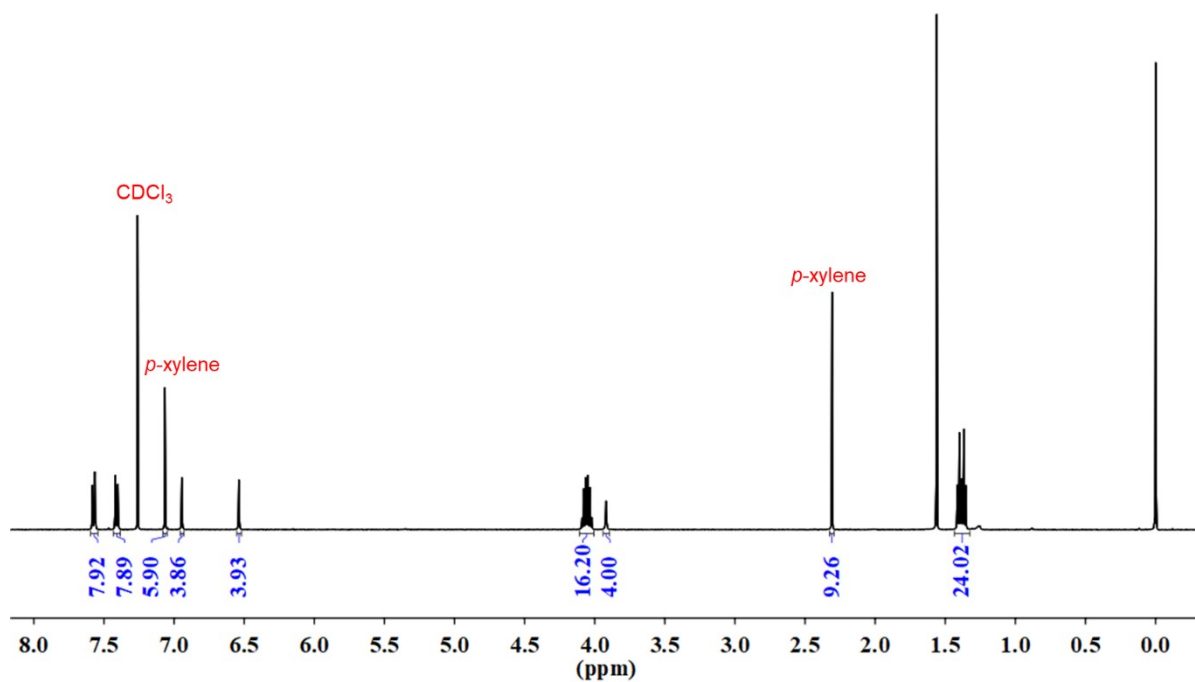


Fig. S28 ^1H NMR (500 MHz, CDCl_3) spectrum of MC- γ after uptake of *p*-xylene.

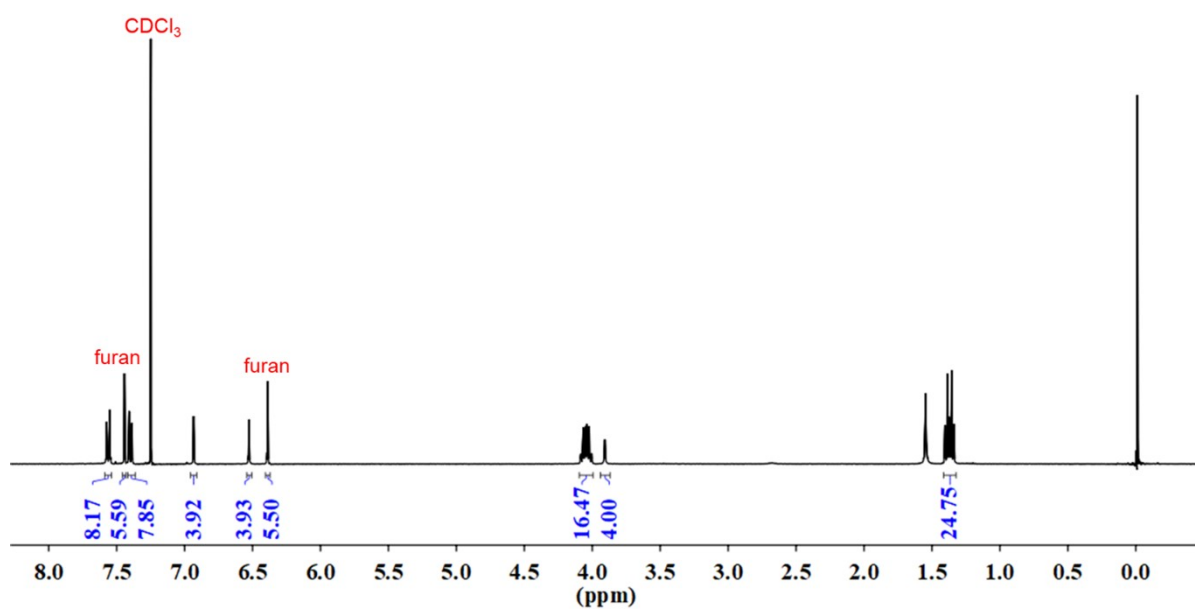


Fig. S29 ^1H NMR (500 MHz, CDCl_3) spectrum of MC- γ after uptake of furan.

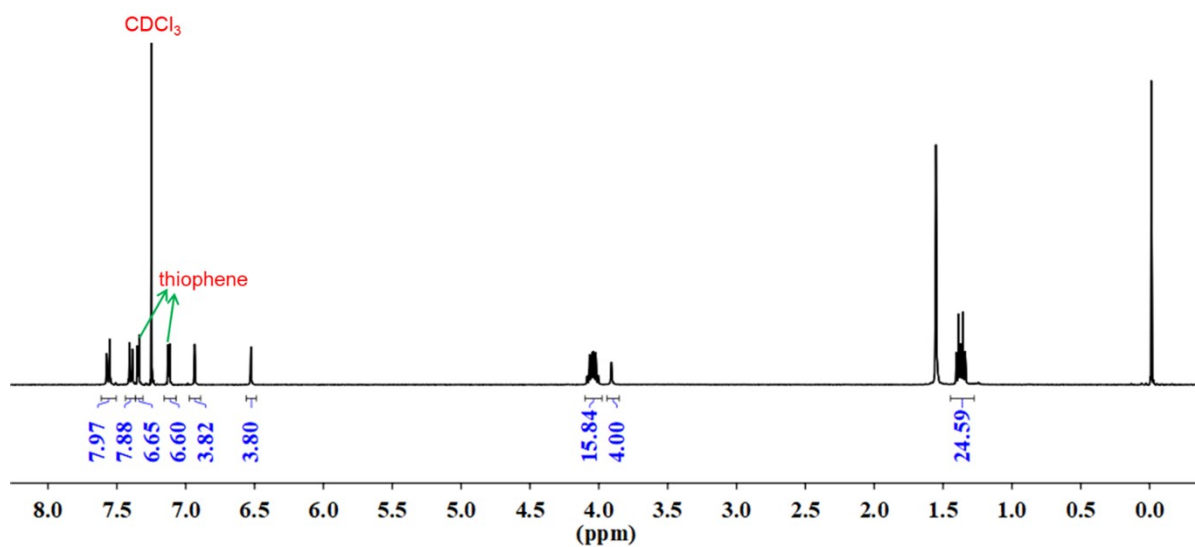


Fig. S30 ¹H NMR (500 MHz, CDCl₃) spectrum of MC-γ after uptake of thiophene.

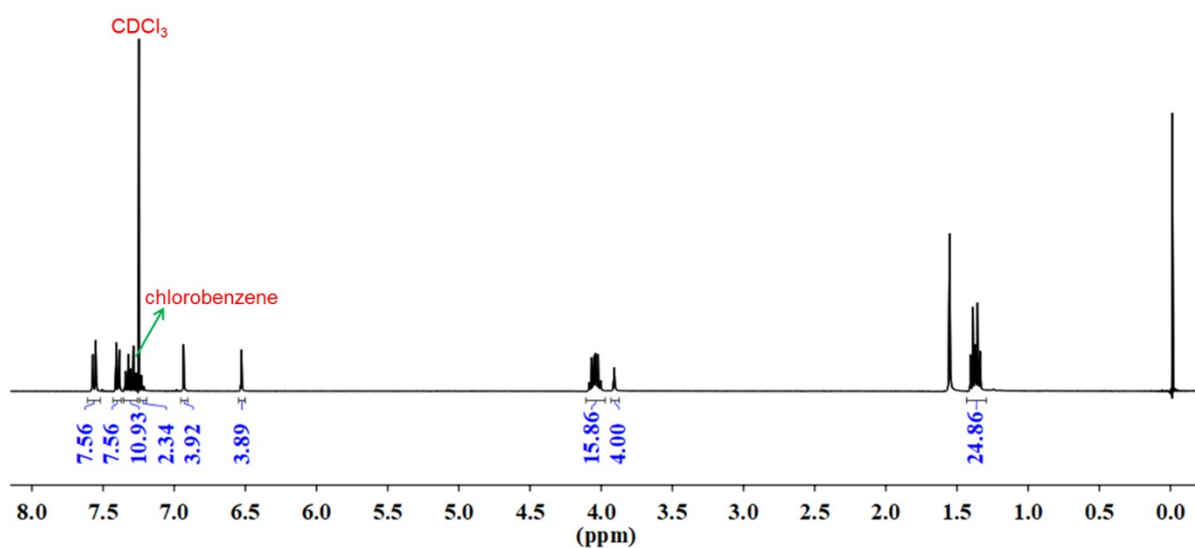


Fig. S31 ¹H NMR (500 MHz, CDCl₃) spectrum of MC-γ after uptake of chlorobenzene.

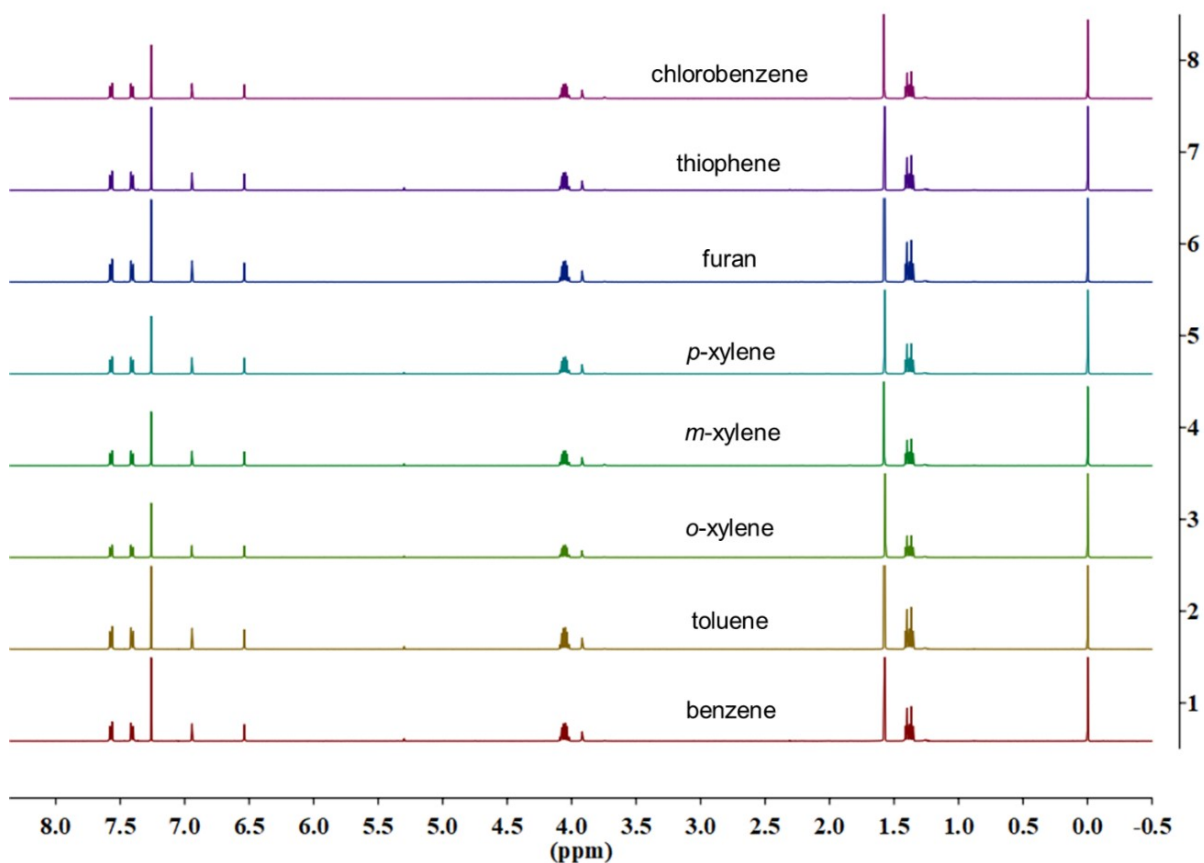


Fig. S32 ^1H NMR (500 MHz, CDCl_3) spectrum of aromatics-loaded $\text{MC-}\gamma$ after desorption of aromatics under vacuum at $65\text{ }^\circ\text{C}$ for 12 h.

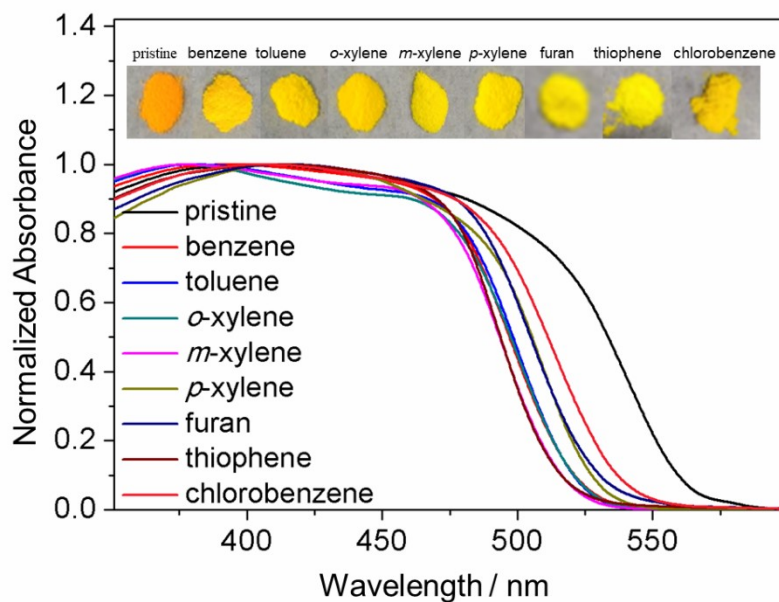


Figure S33 Normalized diffuse reflectance spectra of $\text{MC-}\gamma$ before and after uptake of aromatic vapors (insets: photographs of $\text{MC-}\gamma$ before and after exposure to various aromatic vapors in the sunlight).

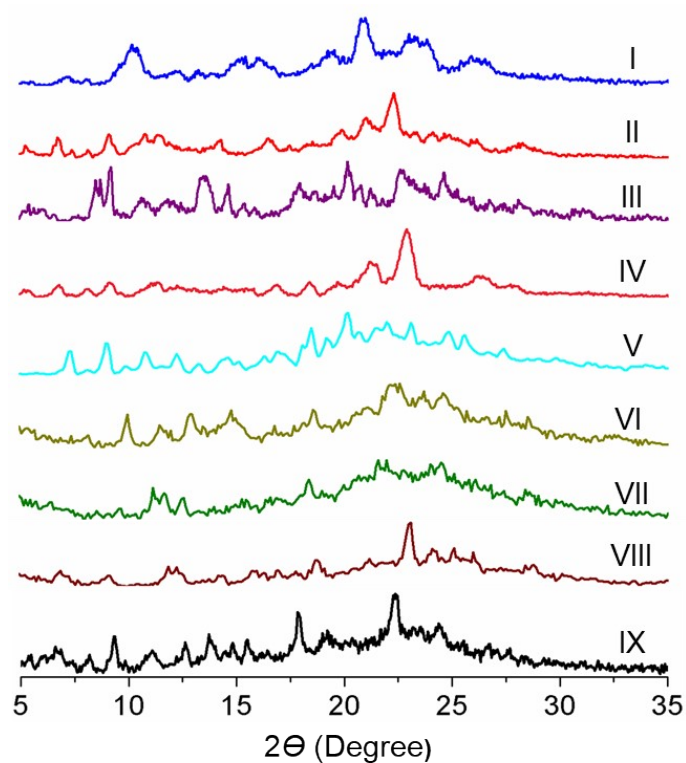


Fig. S34 PXR D patterns of MC- γ before (IX) and after capture of (I) benzene, (II) toluene, (III) o-xylene, (IV) m-xylene, (V) p-xylene, (VI) furan, (VII) thiophene, and (VIII) chlorobenzene.

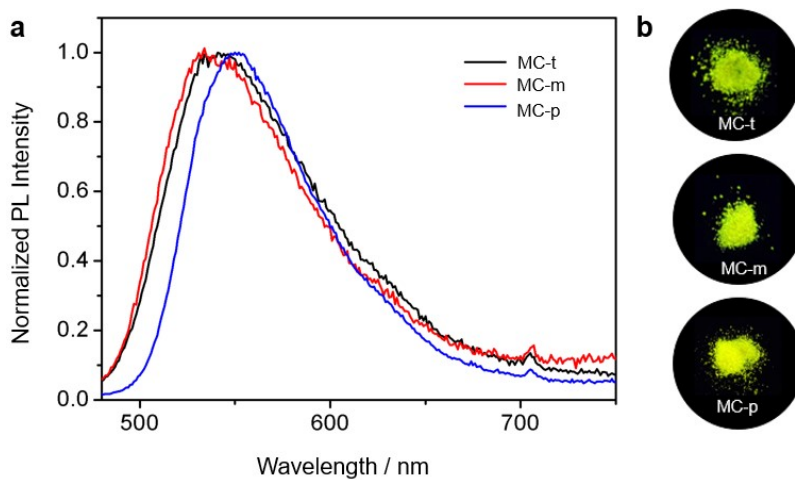


Fig. S35 (a) Normalized PL spectra of MC-t, MC-m and MC-p. (b) Photos of MC-t, MC-m and MC-p under 365 nm UV illuminations.

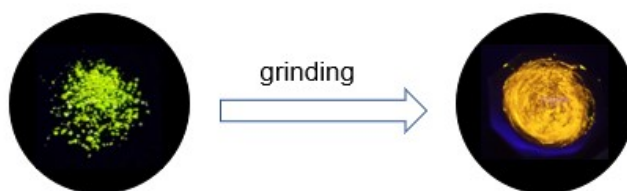


Fig. S36 Photographs of MC- α before and after grinding under 365 nm UV illuminations.

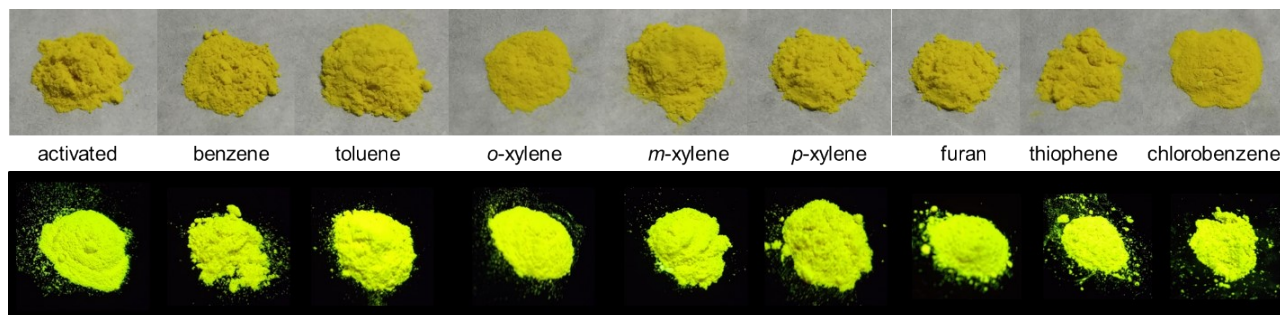


Fig. S37 Photographs of activated monomer crystals before and after exposing to various aromatic vapors. Top: sunlight; Bottom: 365 nm UV illuminations.

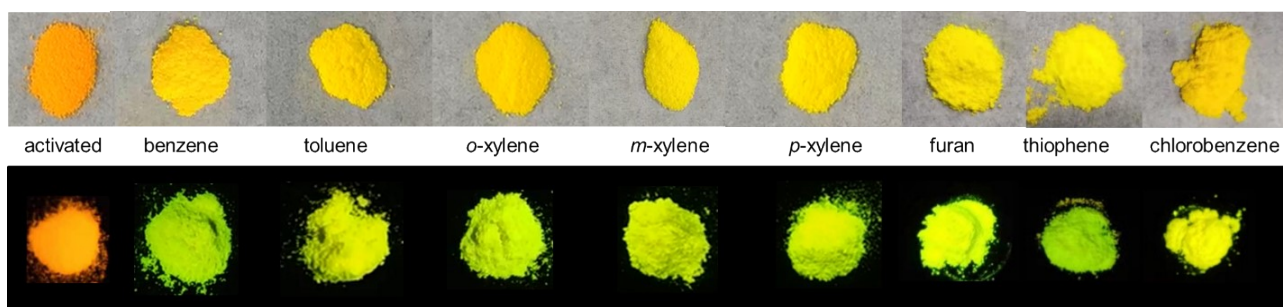


Fig. S38 Photographs of MC- γ before and after exposing to various aromatic vapors. Top: sunlight; Bottom: 365 nm UV illuminations.

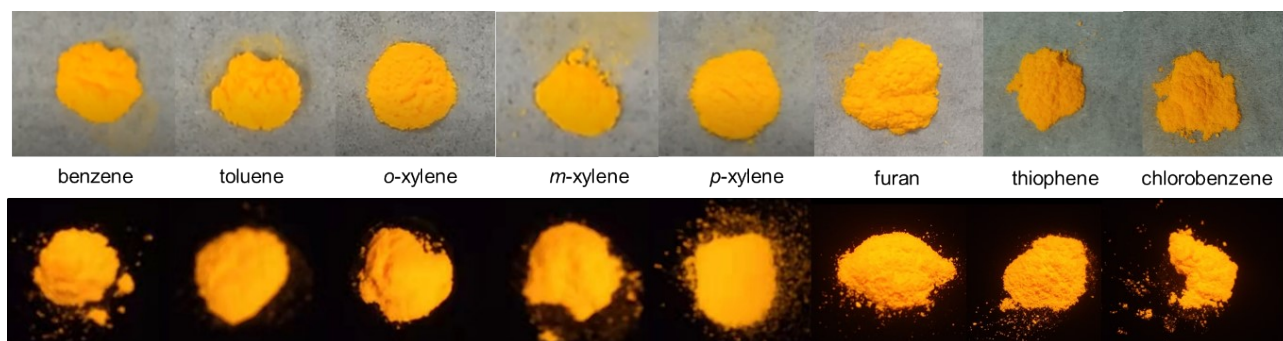


Fig. S39 Photographs of aromatics-loaded MC- γ after desorption of aromatics under vacuum at 65 °C for 12 h. Top: sunlight; Bottom: 365 nm UV illuminations.

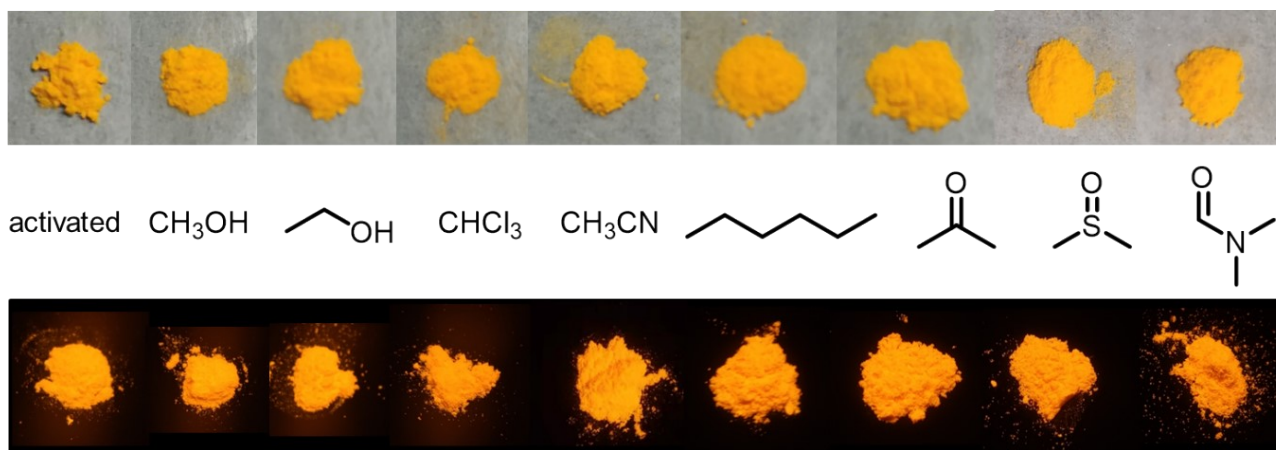


Fig. S40 Photographs of MC- γ after exposing to non-aromatic VOCs. Top: sunlight; Bottom: 365 nm UV illuminations.

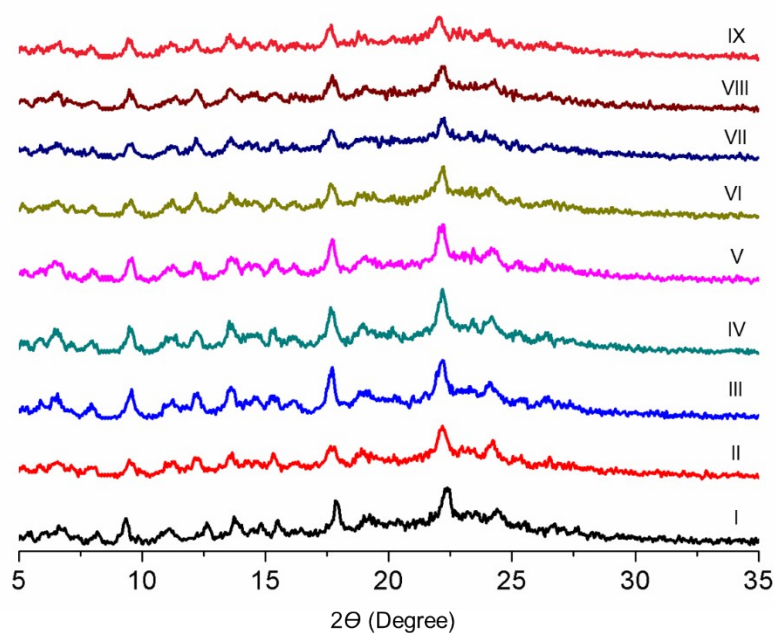


Fig. S41 PXRD patterns of aromatics-loaded MC- γ after desorption of aromatic vapors under vacuum at 65 °C for 12 h, (I) activated, (II) benzene, (III) toluene, (IV) *o*-xylene, (V) *m*-xylene, (VI) *p*-xylene, (VII) furan, (VIII) thiophene, and (IX) chlorobenzene.

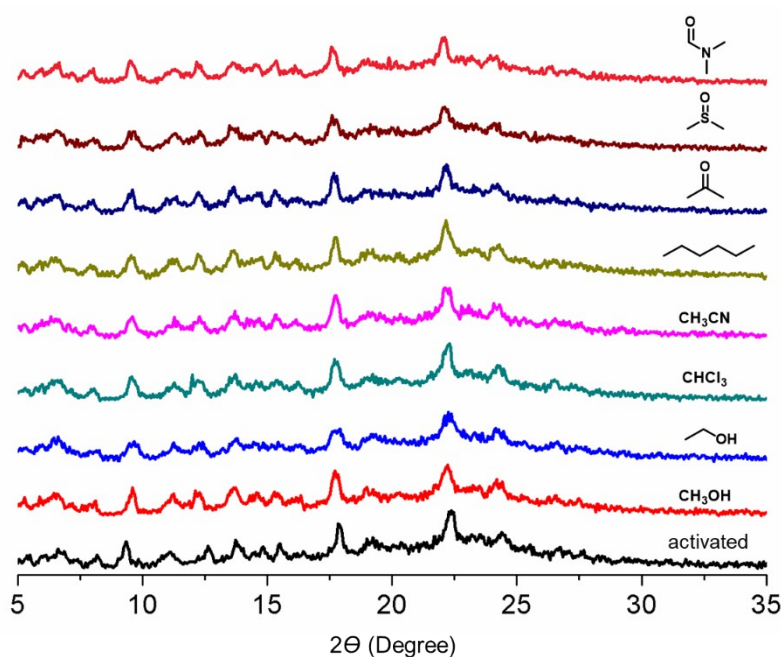


Fig. S42 PXRD patterns of MC- γ after exposing to other common VOCs.

8. Crystallography data

Monomer: Single crystals, suitable for X-ray crystallography, were obtained as yellow block by slow vapor diffusion of hexane (1 mL) into a dichloromethane (2 mL) solution of monomer (10 mg) at room temperature for 7 days. Crystal data of monomer was collected on Bruker smart Apex 2.

Table S1 Crystal data and structure refinement for monomer

CCDC	2106790	
Empirical formula	$C_{36}H_{34}N_2O_4$	
Formula weight	558.65	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 11.537(2)$ Å	$\alpha = 76.480(4)^\circ$.
	$b = 13.782(3)$ Å	$\beta = 80.728(3)^\circ$.
	$c = 22.883(4)$ Å	$\gamma = 69.280(3)^\circ$.
Volume	$3296.6(11)$ Å ³	
Z	4	
Density (calculated)	1.126 Mg/m ³	
Absorption coefficient	0.073 mm ⁻¹	
F(000)	1184	

Crystal size	0.120 x 0.110 x 0.090 mm ³
Theta range for data collection	0.919 to 25.010°.
Index ranges	-13<=h<=13, -16<=k<=15, -24<=l<=27
Reflections collected	24994
Independent reflections	11534 [R(int) = 0.0523]
Completeness to theta = 25.010°	99.1 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11534 / 662 / 872
Goodness-of-fit on F ²	1.136
Final R indices [I>2sigma(I)]	R ₁ = 0.0722, wR ₂ = 0.1460
R indices (all data)	R ₁ = 0.1253, wR ₂ = 0.1652
Extinction coefficient	n/a
Largest diff. peak and hole	0.299 and -0.466 e.Å ⁻³

MC- α : Single crystals, suitable for X-ray crystallography, were obtained as yellow block by slow vapor diffusion of diethyl ether (1 mL) into a 1,2-dichloroethane (2 mL) solution of **MC** (5 mg) at room temperature for 8 days. Crystal data was collected on Bruker smart Apex 2.

Table S2 Crystal data and structure refinement for **MC- α**

CCDC	2106793
Empirical formula	C ₇₄ H ₆₆ N ₄ O ₈
Formula weight	1139.30
Temperature/K	193.0
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 18.4433(14) Å α = 90°. b = 23.3947(17) Å β = 104.809(5)°. c = 19.9340(16) Å γ = 90°.
Volume/Å ³	8315.3(11)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	0.910
μ/mm^{-1}	0.301
F(000)	2408.0
Crystal size/mm ³	0.12 × 0.1 × 0.1

Radiation	GaK α ($\lambda = 1.34139$)
2 Θ range for data collection/ $^{\circ}$	4.312 to 104.194
Index ranges	$-21 \leq h \leq 20, -27 \leq k \leq 27, -23 \leq l \leq 23$
Reflections collected	62236
Independent reflections	14168 [$R_{\text{int}} = 0.1137, R_{\text{sigma}} = 0.0999$]
Data/restraints/parameters	14168/9/783
Goodness-of-fit on F^2	1.069
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1525, wR_2 = 0.3214$
Final R indexes [all data]	$R_1 = 0.2111, wR_2 = 0.3450$
Largest diff. peak and hole	0.77 and -0.38 e \AA^{-3}

MC- β : Single crystals, suitable for X-ray crystallography, were obtained as orange block by slow vapor diffusion of isopropyl ether (1 mL) into a chloroform (3 mL) solution of **MC** (5 mg) at room temperature for 10 days. Crystal data was collected on Bruker smart Apex 2.

Table S3 Crystal data and structure refinement for **MC- β**

CCDC	2106844
Empirical formula	$C_{75}H_{69}Cl_3N_4O_8$
Formula weight	1260.69
Temperature/K	193.0
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 43.827(7) \text{ \AA}$ $\alpha = 90^{\circ}$. $b = 6.3265(10) \text{ \AA}$ $\beta = 99.958(8)^{\circ}$. $c = 28.385(5) \text{ \AA}$ $\gamma = 90^{\circ}$.
Volume/ \AA^3	7752(2)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.080
μ/mm^{-1}	0.970
F(000)	2648.0
Crystal size/ mm^3	$0.12 \times 0.1 \times 0.1$
Radiation	GaK α ($\lambda = 1.34139$)
2 Θ range for data collection/ $^{\circ}$	3.562 to 107.814
Index ranges	$-52 \leq h \leq 52, -7 \leq k \leq 7, -32 \leq l \leq 34$

Reflections collected	31492
Independent reflections	7106 [$R_{\text{int}} = 0.0998$, $R_{\text{sigma}} = 0.0891$]
Data/restraints/parameters	7106/18/428
Goodness-of-fit on F^2	1.204
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1427$, $wR_2 = 0.4229$
Final R indexes [all data]	$R_1 = 0.1759$, $wR_2 = 0.4535$
Largest diff. peak and hole	1.46 and $-0.58 \text{ e } \text{\AA}^{-3}$

MC-t: Single crystals, suitable for X-ray crystallography, were obtained as yellow block by slow vapor diffusion of diethyl ether (1 mL) into a dichloromethane (3 mL) solution of **MC** (5 mg) at room temperature for 5 days. Crystal data was collected on Bruker smart Apex 2.

Table S4 Crystal data and structure refinement for **MC-t**

CCDC	2106866
Empirical formula	$\text{C}_{155}\text{H}_{142}\text{N}_8\text{O}_{16}$
Formula weight	2372.76
Temperature/K	141.0
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	$a = 14.645(5) \text{ \AA}$ $\alpha = 101.803(9)^\circ$. $b = 17.153(5) \text{ \AA}$ $\beta = 101.803(9)^\circ$. $c = 17.234(6) \text{ \AA}$ $\gamma = 111.239(7)^\circ$.
Volume/ \AA^3	3896(2)
Z	1
$\rho_{\text{calc}}/\text{cm}^3$	1.011
μ/mm^{-1}	0.331
F(000)	1256.0
Crystal size/ mm^3	$0.12 \times 0.1 \times 0.1$
Radiation	$\text{GaK}\alpha$ ($\lambda = 1.34139$)
2Θ range for data collection/ $^\circ$	4.62 to 107.798
Index ranges	$-17 \leq h \leq 17$, $-20 \leq k \leq 20$, $-20 \leq l \leq 17$
Reflections collected	36417
Independent reflections	14019 [$R_{\text{int}} = 0.1522$, $R_{\text{sigma}} = 0.1846$]
Data/restraints/parameters	14019/210/909

Goodness-of-fit on F ²	1.079
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.1449, wR ₂ = 0.3106
Final R indexes [all data]	R ₁ = 0.2512, wR ₂ = 0.3550
Largest diff. peak and hole	0.62/-0.37 e Å ⁻³

MC-m: Single crystals, suitable for X-ray crystallography, were obtained as yellow block by slow vapor diffusion of isopropyl ether (1 mL) into a chloroform (3 mL) solution of **MC** (5 mg) at room temperature for 6 days. Crystal data was collected on Bruker smart Apex 2.

Table S5 Crystal data and structure refinement for **MC-m**

CCDC	2106858
Empirical formula	C ₈₃ H ₇₉ Cl ₃ N ₄ O ₈
Formula weight	1366.85
Temperature/K	170.0
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 14.6237(13) Å α = 111.446(3)° b = 17.0225(18) Å β = 100.673(4)° c = 17.1904(15) Å γ = 100.673(4)°
Volume/Å ³	3863.6(6)
Z	2
ρ _{calc} /cm ³	1.175
μ/mm ⁻¹	0.175
F(000)	1440.0
Crystal size/mm ³	0.11 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.818 to 52.83
Index ranges	-18 ≤ h ≤ 17, -21 ≤ k ≤ 21, -21 ≤ l ≤ 21
Reflections collected	44193
Independent reflections	15674 [R _{int} = 0.0799, R _{sigma} = 0.1106]
Data/restraints/parameters	15674/0/902
Goodness-of-fit on F ²	1.025
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0761, wR ₂ = 0.1764
Final R indexes [all data]	R ₁ = 0.1605, wR ₂ = 0.2254

Largest diff. peak and hole

0.47/-0.75 e Å⁻³

MC-p: Single crystals, suitable for X-ray crystallography, were obtained as yellow block by slow vapor diffusion of diethyl ether (1 mL) into a dichloromethane (3 mL) solution of **MC** (5 mg) at room temperature for 6 days. Crystal data was collected on Bruker smart Apex 2.

Table S6 Crystal data and structure refinement for **MC-p**

CCDC	2106870	
Empirical formula	C ₉₈ H ₉₈ N ₄ O ₈	
Formula weight	1459.80	
Temperature/K	170.0	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.346(4) Å	α = 86.647(10)°.
	b = 16.214(5) Å	β = 74.030(10)°.
	c = 20.118(6) Å	γ = 78.328(9)°.
Volume/Å ³	4099(2)	
Z	2	
ρ _{calc} /cm ³	1.183	
μ/mm ⁻¹	0.074	
F(000)	1556.0	
Crystal size/mm ³	0.11 × 0.03 × 0.02	
Radiation	MoKα (λ = 0.71073)	
2θ range for data collection/°	4.212 to 50.054	
Index ranges	-14 ≤ h ≤ 15, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	
Reflections collected	40800	
Independent reflections	14384 [R _{int} = 0.1657, R _{sigma} = 0.2129]	
Data/restraints/parameters	14384/0/1005	
Goodness-of-fit on F ²	0.984	
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0980, wR ₂ = 0.2078	
Final R indexes [all data]	R ₁ = 0.2182, wR ₂ = 0.2678	
Largest diff. peak/hole	0.30/-0.37 e Å ⁻³	

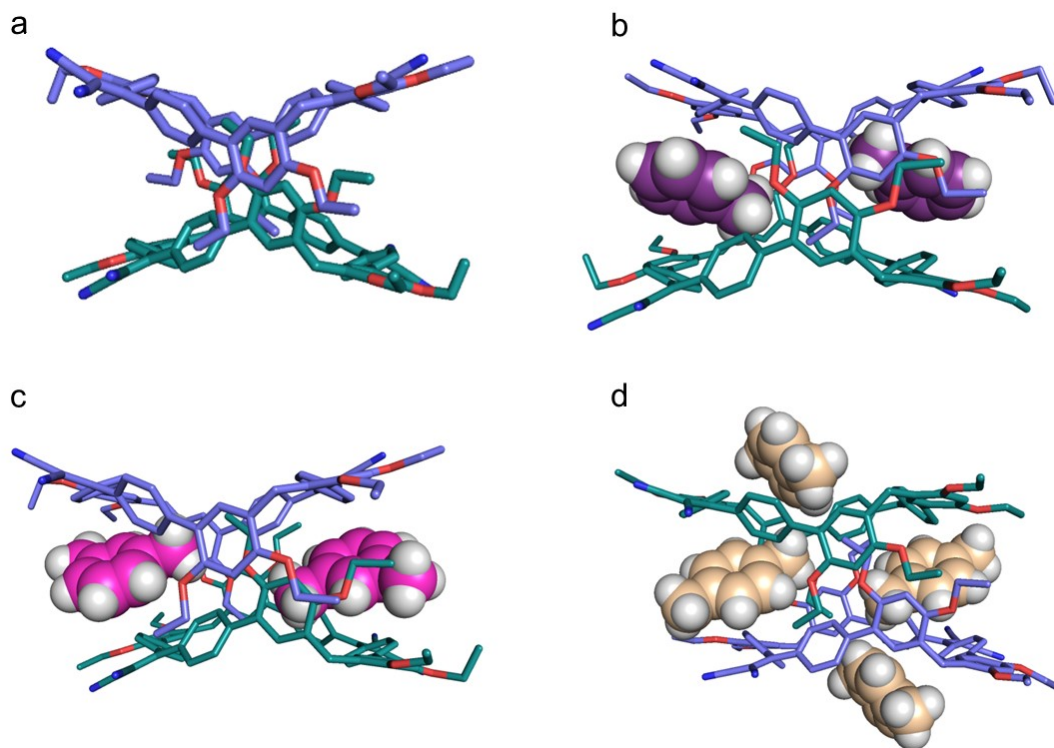


Fig. S43 Side view of the double-included geometry of (a) **MC- α** , (b) **MC-t**, (c) **MC-m** and (d) **MC-p**. Hydrogen atoms are omitted for clarity.

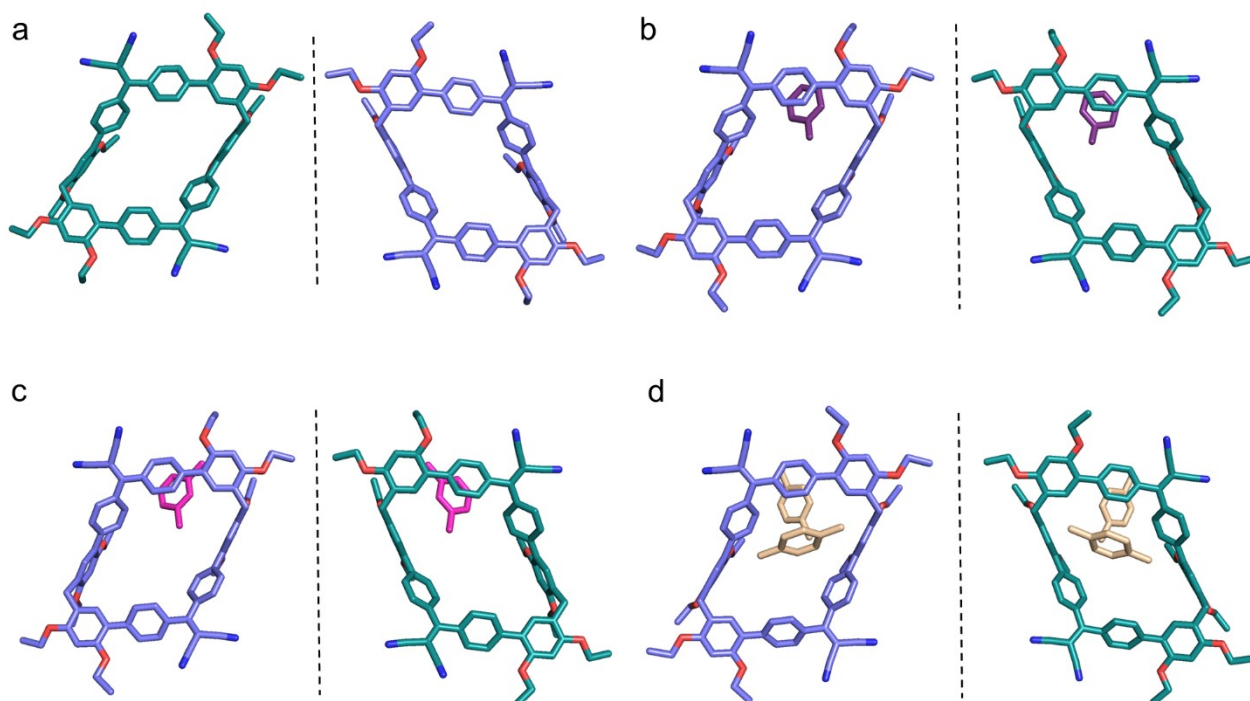


Fig. S44 A pair of enantiomers in (a) **MC- α** , (b) **MC-t**, (c) **MC-m** and (d) **MC-p**. The hydrogen atoms are omitted for clarity.

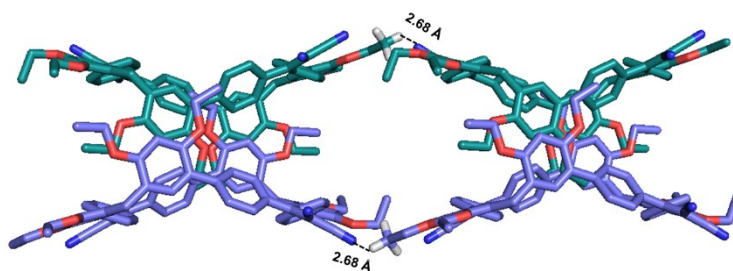


Fig. S45 Top view of the pseudo cavity of **MC- α** and the C-H \cdots N interactions (2.68 Å) between two double-included dimers. Part of the hydrogen atoms are omitted for clarity.

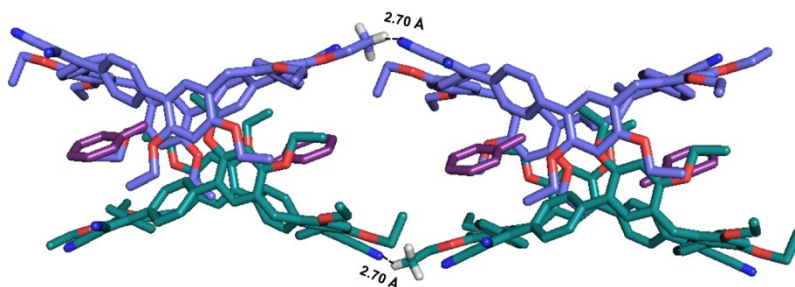


Fig. S46 Top view of the pseudo cavity of **MC-t** and the C-H \cdots N interactions (2.70 Å) between two double-included dimers. Part of the hydrogen atoms are omitted for clarity.

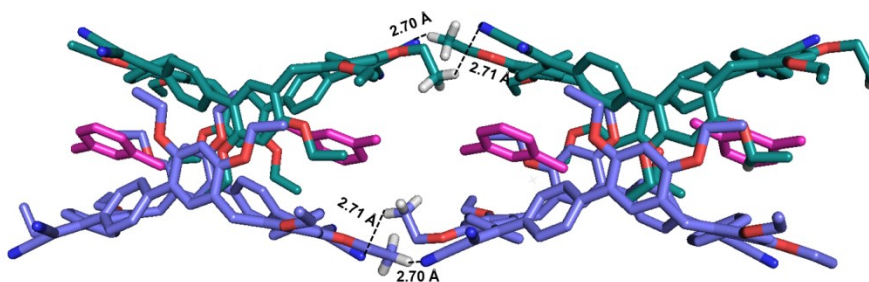


Fig. S47 Top view of the pseudo cavity of **MC-m** and the C-H \cdots N interactions (2.70 and 2.71 Å) between two double-included dimers. Part of the hydrogen atoms are omitted for clarity.

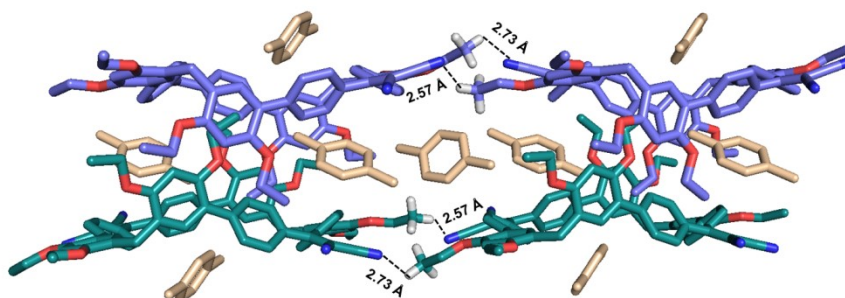


Fig. S48 Top view of the pseudo cavity of **MC-p** and the C-H \cdots N interactions (2.57 and 2.73 Å) between two double-included dimers. Part of the hydrogen atoms are omitted for clarity.

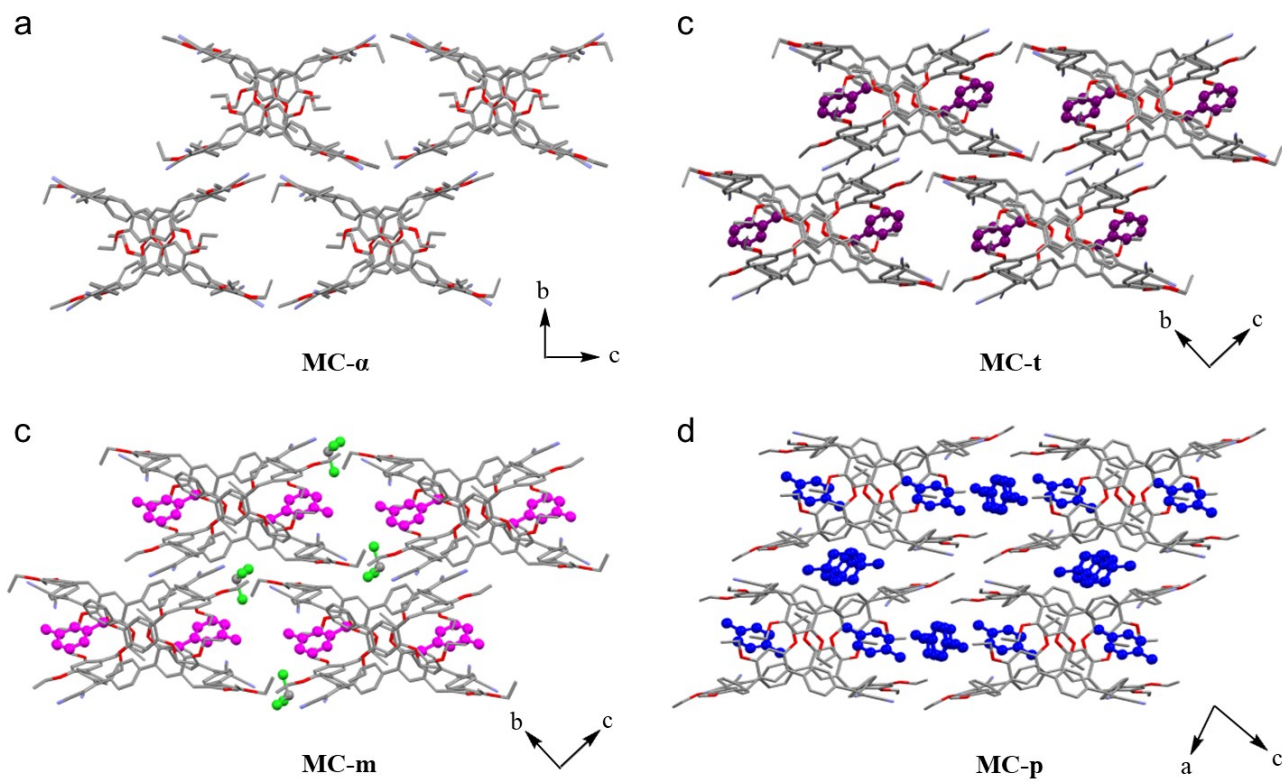


Fig. S49 The stacking mode of MC- α , MC-t, MC-m and MC-p. For clarity, some hydrogen atoms and solvents are omitted.