Electronic Supplementary Information

Pillararene for fluorescence detection of *n*-alkane vapours

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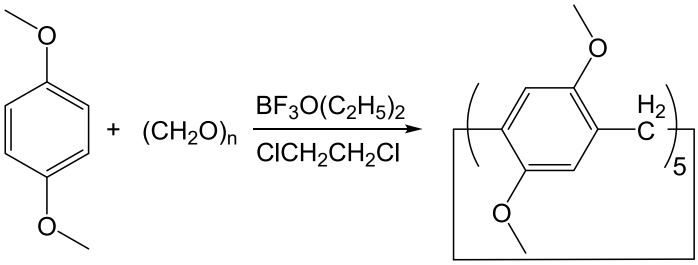
Experimental Section

Material and Methods

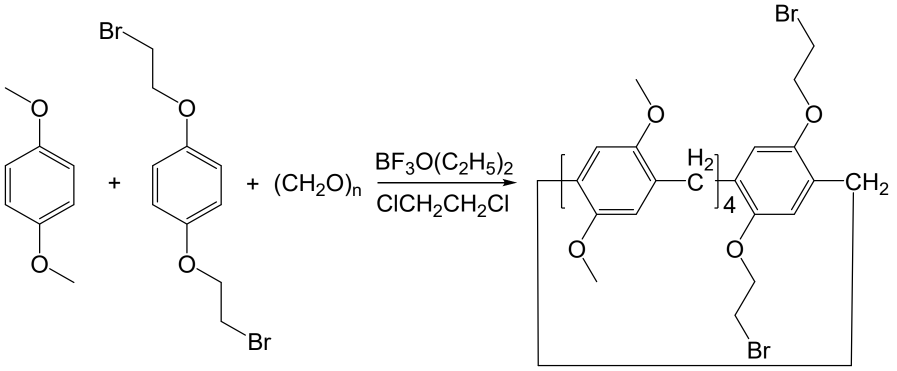
All starting materials and solvents were obtained from commercial sources and used without further purification unless otherwise indicated. All air-sensitive manipulations were performed under a N_2 atmosphere using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker BioSpin Avance III 400 MHz spectrometer. Mass spectrum was recorded on a Bruker ultrafleXtreme MALDI TOF/TOF mass spectrometer. Powder X-ray diffraction (PXRD) was measured on a Rigaku Smart Lab diffractometer at a rate of 2° min^{-1} (Bragg–Brentano geometry, Cu-Kα1 radiation, $\lambda = 1.54056$ Å, working voltage is 40 kV, working current is 15 mA). The transmittance of DBP[5] film and DBP[5]-hexane film were recorded on a Shimadzu 2600 UV-Vis spectrometer. The photoluminescence excitation and emission spectra were recorded using an Edinburgh FS-5 steady state fluorescence spectrometer. Thermogravimetric analysis (TGA) was performed on NETZSCH TG 209F1 Libra with a heating rate of 10 °C min^{-1} in N_2 atmosphere. Differential scanning calorimetry was recorded on NETZSCH DSC 214 with a heating rate of 10 °C min^{-1}.

Synthesis of DMP[5]



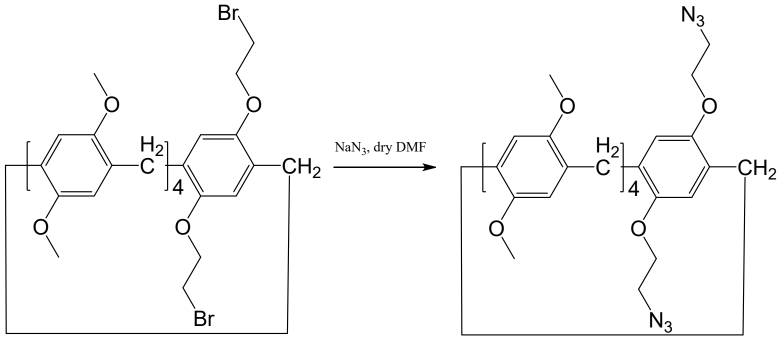
Synthesized according to the previously published method.[S1] Paraformaldehyde (0.93 g, 30 mmol) was added to a solution of 1,4-dimethoxybenzene (1.38 g, 10 mmol) in 1,2-dichloroethane (20 mL). The mixture was stirred at 30 °C for 30 min. Then, boron trifluoride diethyl etherate [$BF_3\cdot OEt_2$, 1.25 mL, 10 mmol] was added to the solution while the transparent solution turned into green. The resulting mixture was stirred at 30 °C for 3 h. The solution was poured into methanol, and the resulting precipitate was collected by filtration. The resulting solid was recrystallized from dichloromethane/methanol to yield a while solid (0.90 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (s, 10H), 3.77 (s, 10H), 3.65 (s, 30H).

Synthesis of DBP[5]



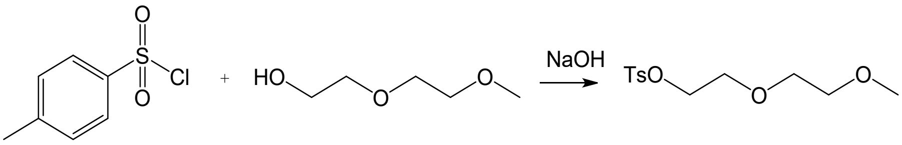
Synthesized according to the previously published method.[S2] Paraformaldehyde (1.50 g, 25 mmol) was added to a mixture of 1,4-bis(2-bromoethoxy)benzene (3.28 g, 5 mmol) and 1,4-dimethoxybenzene (2.76 g, 20 mmol) in 1,2-dichloroethane (100 mL) under the protection of nitrogen atmosphere. Boron trifluoride etherate (($BF_3{\cdot}OEt_2$), 3 mL, 25 mmol) was added to the mixture, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by MeOH (50 mL), and the solution was concentrated and dissolved in CH_2Cl_2 (100 mL). The raw product was purified by silica gel chromatography (2:1 petrol ether/CH_2Cl_2) to give a white solid (0.623 g, 13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (s, 8H), 6.77 (s, 2H), 4.10 (s, 4H), 3.81 (s, 10H), 3.70 (d, J = 17.2 Hz, 24H), 3.49 (s, 4H).

Synthesis of DAP[5]



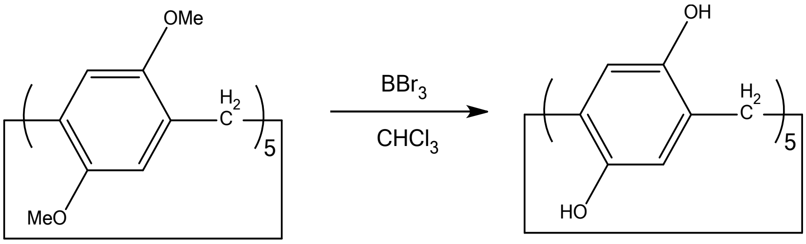
Synthesized according to the previously published method.[S3] Sodium azide (386 mg, 6.0 mol) was added to a solution of DBP[5] (560 mg, 0.6 mmol) in dry DMF (16 mL). The mixture was stirred at room temperature for 24 h under the protection of nitrogen. The mixture was poured into water (160 mL), and the precipitate was collected by filtration and washed with water to yield a white solid (0.422 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (m, 10H), 3.91 (t, 4H), 3.82 (m, 10H), 3.69 (m, 24H), 3.45 (t, 4H).

Synthesis of (2-methoxyethoxy)ethyltosylate



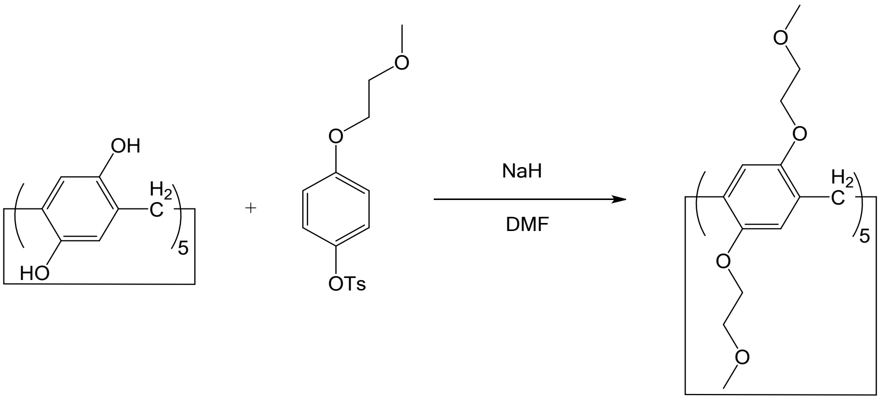
Synthesized according to the previously published method.[S4] Diethylene glycol monomethyl ether (6.0 g, 50 mmol, 1.0 eq) was dissolved in 35 mL of THF. Sodium hydroxide (7.0 g, 175 mmol, 3.5 eq.) was dissolved in 35 mL of H_2O, and then added slowly to the flask. After the reaction mixture was cooled down to 0 °C in an ice bath, *p*-toluenesulfonyl chloride (11.4 g, 60 mmol, 1.2 eq.) in 25 mL of THF was added dropwise to the mixture under vigorous stirring for 2 h, and then stirred at room temperature for 12 h. After completion of the reaction as indicated by TLC, the reaction mixture was poured to 5 wt% hydrochloric acid aqueous solution, and the product was extracted with dichloromethane (30 mL×3). The organic layer was then washed with saturated sodium hydrogen carbonate solution (50 mL × 3) and dried over anhydrous magnesium sulfate to obtain a yellow liquid (12.1 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 2H), 7.37 (s, 2H), 4.18 (s, 2H), 3.70 (s, 2H), 3.60 (s, 2H), 3.50 (s, 2H), 3.37 (s, 3H), 2.46 (s, 3H).

Synthesis of *per*-hydroxylated pillar[5]arene



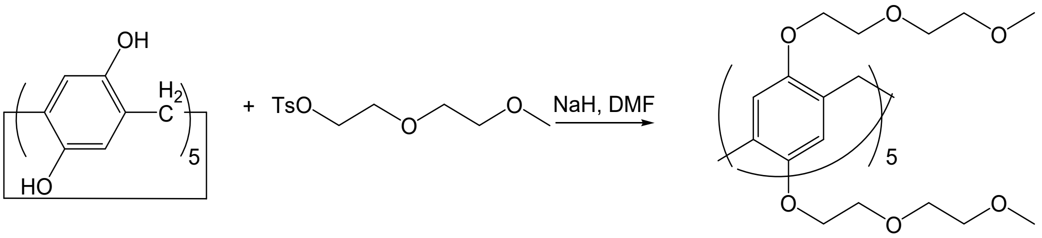
Synthesized according to the previously published method.[S1] To a solution of dimethoxypillar[5]arene (0.64 g, 0.75 mmol) in chloroform (37 mL), boron tribromide (4.52 g, 18.07 mmol) was added. The mixture was stirred at room temperature for 96 h while the transparent solution became turbid. Then the solid formed during the reaction was collected by filtration and washed with water. The raw product was purified by column chromatography (silica gel, dichloromethane-acetone, 50%:50%) to afford a white solid (0.21 g, 46%). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.98 (s, 1H), 6.67 (s, 5H), 3.58 (s, 5H).

Synthesis of EOP[5]



Synthesized according to the previously published method.^{S5} *per*-Hydroxylated pillar[5]arene (0.20 g, 0.328 mmol) was dissolved in DMF (7.5 mL) and THF (5 mL). Sodium hydride (0.25 g, 13.1 mmol) was added and the reaction mixture was stirred for 0.5 h. Then, 2-methoxyethyl *p*-toluenesulfonate (excess, 1.52 g, 6.58 mmol) was added and the reaction mixture was heated at 60 ^{o}C for 72 h under the protection of N_2. The solvent was evaporated to give a solid. The raw product was purified by column chromatography (silica gel; chloroform:methanol, 100:4) to afford a yellow solid (0.156 g, 40%). ^{1}HNMR (400 MHz, $CDCl_3$): δ 6.86 (s, 10H, phenyl), 4.03 (t, 20H, methylene), 3.78(s, 10H, methylene bridge), 3.66 (t, 20H, methylene), 3.34 (s, 30H, methoxy).

Synthesis of DEOP[5]



per-Hydroxylated pillar[5]arene (1.20 g, 1.47 mmol) was dissolved in a mixture of DMF (48 mL) and THF (30 mL). Sodium hydride (1.5 g, 78.6 mmol) was added and the reaction mixture was stirred. Then, excess of 2-methoxyethyl *p*-toluenesulfonate (11.00 g, 52.64 mmol) was added and the reaction mixture was heated at 60 ^{o}C for 72 h under the protection of N_2. After removal of the solvent, the resulting solid was dissolved in CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated to give a solid. The raw product was purified by column chromatography (silica gel; methanol:dichloromethane = 1:10) to afford a brown liquid (1.80 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (s, 10H), 4.05 (s, 20H), 3.86 (s, 20H), 3.78 (s, 10H), 3.72 (s, 20H), 3.52 (s, 20H), 3.28 (s, 30H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.80, 128.83, 115.34 (C of phenyl), 72.07, 70.64, 70.20, 68.12 (C of methylene), 58.93 (C of methyl), 29.37 (C of methylene bridge). MALDI-TOF-MS: *m/z* found (calcd.) for $C_{86}H_{130}O_{30}$ $[M]^+$: 1630.8675 (1630.8641).

Preparation of pillar[5]arene films

DBP[5] film. 12.5 mg of DBP[5] solid was dissolved in 1 mL of CH_2Cl_2, then the solution was drop-casted onto a 1 cm × 2.5 cm quartz slide and was dried in vacuum at 80 ^{o}C for 2 h.

DMP[5] film. 10.0 mg of DMP[5] solid was dissolved in 8 mL CH_2Cl_2, then the solution was drop-casted onto a 1 cm × 2.5 cm quartz slide and was dried in vacuum at 80 ^{o}C for 2 h.

DEOP[5] film. 20.0 mg of liquid DEOP[5] was dissolved in 8 mL CH_2Cl_2, then the solution was drop-casted onto a frosted groove in quartz slide and was dried in vacuum at 80 ^{o}C for 2 h.

Vapour-phase luminescence sensing measurements

1 mL of each analyte was placed in 20 mL glass vials for a few hours (the vial of undecane was heated with a heat gun for 30 s and then cooled down to room temperature) to reach the equilibrium vapour pressure of each analyte. The initial emission spectrum of each film was measured before it was exposed to vapour. Then, the sample slide was placed in the glass vial with the vapour of analyte. After specified exposure time, the quartz slide was taken out and mounted into the sample holder of the luminescence spectrophotometer to ensure the luminescence emission spectrum was recorded at the same area of the quartz slide.

Some analytes induced change in transparency of DBP[5] film to different degree, which corresponds to the crystallinity change of DBP[5]. The fine crystalline particles may cause the enhancement of stray light and lead to the shift of fluorescence baseline.

X-ray crystallography

5.0 mg of DBP[5] was added to *n*-hexane solution of iodine (6 mg mL^{-1}, 10 mL) and allowed to stand at room temperature for 48 h to obtain yellow crystals of DBP[5]$\supset$*n*-C_6H_{14}. 10 mg of DBP[5] was dissolved in acetonitrile (2 mL), the solvent was evaporated slowly, colourless prism crystals of DBP[5]$\supset$MeCN were successfully obtained after 2 d. A suitable crystal (0.40 × 0.25 × 0.15 mm^3 for DBP[5]$\supset$*n*-C_6H_{14}; 0.22 × 0.18 × 0.12 mm^3 for DBP[5]$\supset$MeCN) was selected and coated in paratone oil, and then attached to a glass silk with a stainless-steel stick inserted to the other end. After that it was quickly placed in the Agilent Technologies X-ray diffractometer with the enhance X-ray Source of Cu Kα radiation (λ = 1.54184 Å) using the ω–Φ scan technique. Data collection were collected at 149.98(10) and 150.00(10) K, respectively. Using Olex2,[S6] the structures were solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton minimisation.

Crystallographic data for DBP[5]$\supset$*n*-C_6H_{14}: $C_{56}H_{73}Br_2O_{10}$, FW = 1065.96, triclinic, space group *P*-1, a = 12.1481(3), b = 12.5650(2), c = 19.1794(5) Å, α = 91.434(2)°, β = 91.022(2)°, γ = 113.991(2)°, V = 2672.55(11) Å^3, Z = 2, T = 149.98(10) K, ρ_{calcd} = 1.325 g cm^{-3}, μ = 2.374 mm^{-1}, $F(000)$ = 1118.0, 19261 reflections were collected with 10363 unique for 7.706 < θ < 145.702, R_{int} = 0.0281, R_1 = 0.0526, wR_2 = 0.1440 ($I > 2\sigma(I)$), R_1 = 0.0560, wR_2 = 0.1477 (all data) for 624 parameters, GOF = 1.027. CCDC-2088012.

Crystallographic data for DBP[5]$\supset$MeCN: $C_{51}H_{58}Br_2N_2O_{10}$, FW = 1018.81, triclinic, space group *P*-1, a = 12.1504(2), b = 19.7551(4), c = 22.0947(4) Å, α = 102.955(2)°, β = 99.7860(10)°, γ = 102.0220(10)°, V = 4922.76(16) Å^3, Z = 4, T = 150.00(10) K, ρ_{calcd} = 1.375 g cm^{-3}, μ = 2.568 mm^{-1}, $F(000)$ = 2112, 40875 reflections were collected with 20085 unique for 3.575 < θ < 76.286, R_{int} = 0.0303, R_1 = 0.0374, wR_2 = 0.0963 ($I > 2\sigma(I)$), R_1 = 0.0431, wR_2 = 0.1013 (all data) for 1272 parameters, GOF = 1.025. CCDC-2088014.

References

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Table S1 Quenching efficiency $(I - I_0)/I_0$ of DMP[5] and DEOP[5] film at 450 nm upon exposure of various VOC vapours.

VOC vapour	DMP[5]	DEOP[5]
Nitrobenzene	>99%	>99%
Benzene	-43%	-17%
Toluene	-40%	+5%
Ethylbenzene	-38%	-27%
p-Xylene	-40%	-27%
m-Xylene	25%	0
o-Xylene	26%	0
Dichloromethane	-40%	-10%
Ethylene acetate	-31%	-11%
Hexane	-25%	-26%
Ethanol	0	-
Ethyl ether	-39%	0
Acetonitrile	-24%	-16%
Acetone	-51%	0
Diphenylmethane	-8%	0

Table S2 Time-resolved fluorescence of DMP[5] film, DBP[5]/acetone film, DBP[5]/toluene film, DBP[5]/nitrobenzene film (detected at 450 nm, $\lambda_{ex} = 345.1$ nm).

sample	τ_1/ns (%)	τ_2/ns (%)	τ/ns
DMP[5]	3.8980(19.16)	14.2373(80.84)	12.26
DMP[5] + acetone	3.7760(22.91)	13.5139(77.09)	11.36
DMP[5] + toluene	3.5766(20.66)	13.3810(79.34)	11.28
DMP[5] + nitrobenzene	2.8196(14.07)	12.7892(85.93)	11.39

Table S3 Emission properties of DMP[5] film, DMP[5]/acetone film, DBP[5]/toluene film, DBP[5]/nitrobenzene film.

Sample	Φ_F	τ/ns	$k_R{}^a/s^{-1}$	$k_{NR}{}^b/s^{-1}$
DMP[5]	22.49%	12.26	18.3×10^6	6.32×10^7
DMP[5]+acetone	7.78%	11.36	7.7×10^6	8.03×10^7
DMP[5]+toluene	8.75%	11.28	6.9×10^6	8.18×10^7
DMP[5]+nitrobenzene	0.42%	11.39	3.7×10^5	8.74×10^7

[a] $k_R = \Phi_F/\tau_F$; [b] $k_{NR} = (1 - \Phi_F)/\tau_F$.

Table S4 Bond angles and bond lengths of *n*-C_6H_{14} for DBP[5]⊃*n*-C_6H_{14}.

n-C_6H_{14} in the cavity

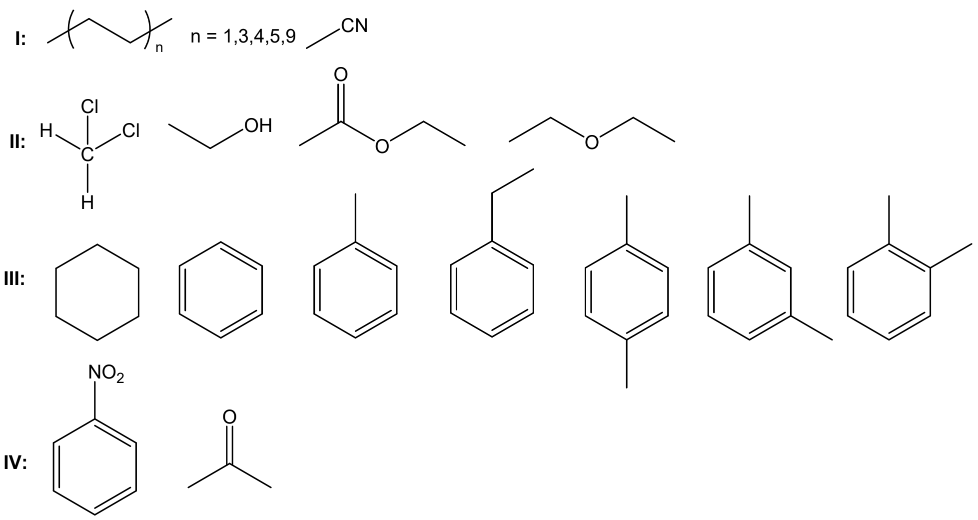
Atom	Atom	Atom	Angle/°	Atom	Atom	Length/Å
C53	C54	C55	129.0(8)	C54	C55	1.665(12)
C56	C55	C54	127.8(8)	C54	C53	1.519(14)
C54	C53	C52	121.5(8)	C55	C56	1.536(18)
C51	C52	C53	152.7(11)	C51	C52	1.556(13)
				C53	C52	1.640(15)

n-C_6H_{14} outside of the cavity

Atom	Atom	Atom	Angle/°	Atom	Atom	Length/Å
C49	C50	C50^1	116.1(4)	C50	C50^1	1.502(7)
C50	C49	C48	113.3(3)	C50	C49	1.499(5)
				C49	C48	1.518(5)

Table S5 Time-resolved fluorescence of DBP[5] film and DBP[5]/hexane film placed in the atmosphere of hexane for 20 min and 90 min.

	τ_1/ns (%)	τ_2/ns (%)	τ/ns (%)
DBP[5] film	15.02(100)	-	15.02
DBP[5]/hexane film-20min	16.39(84.69)	4.60(15.31)	14.58
DBP[5]/hexane film-90min	11.91(50.09)	0.40(49.91)	6.17



Scheme S1 Chemical structures of volatile organic compounds.

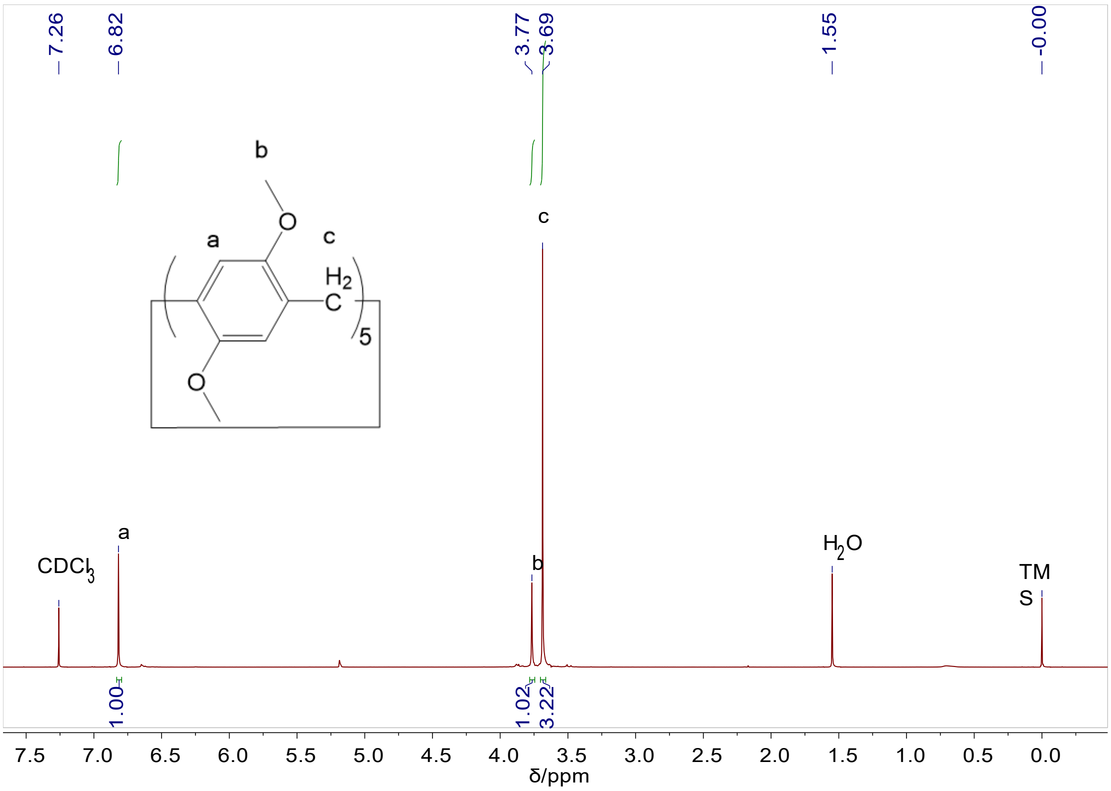


Fig. S1 ^{1}H NMR spectrum of dimethoxypillar[5]arene in $CDCl_3$ (400 MHz, 298 K).

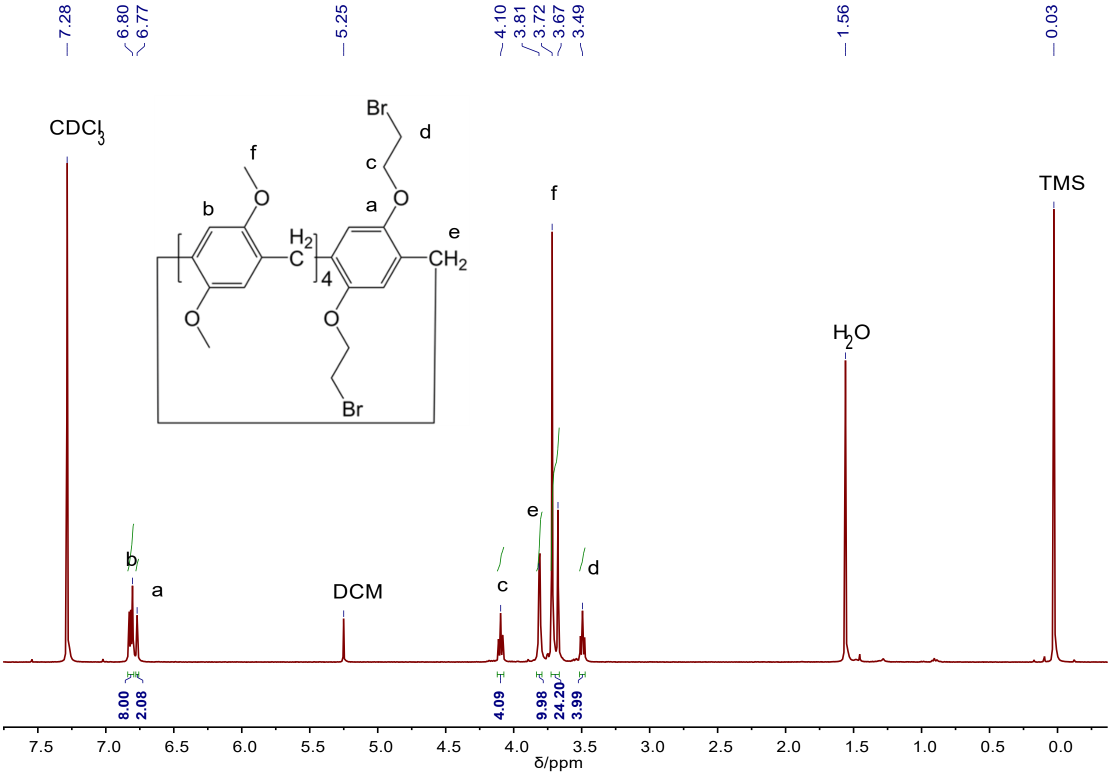


Fig. S2 ^{1}H NMR spectrum of DBP[5] in $CDCl_3$ (400 MHz, 298 K).

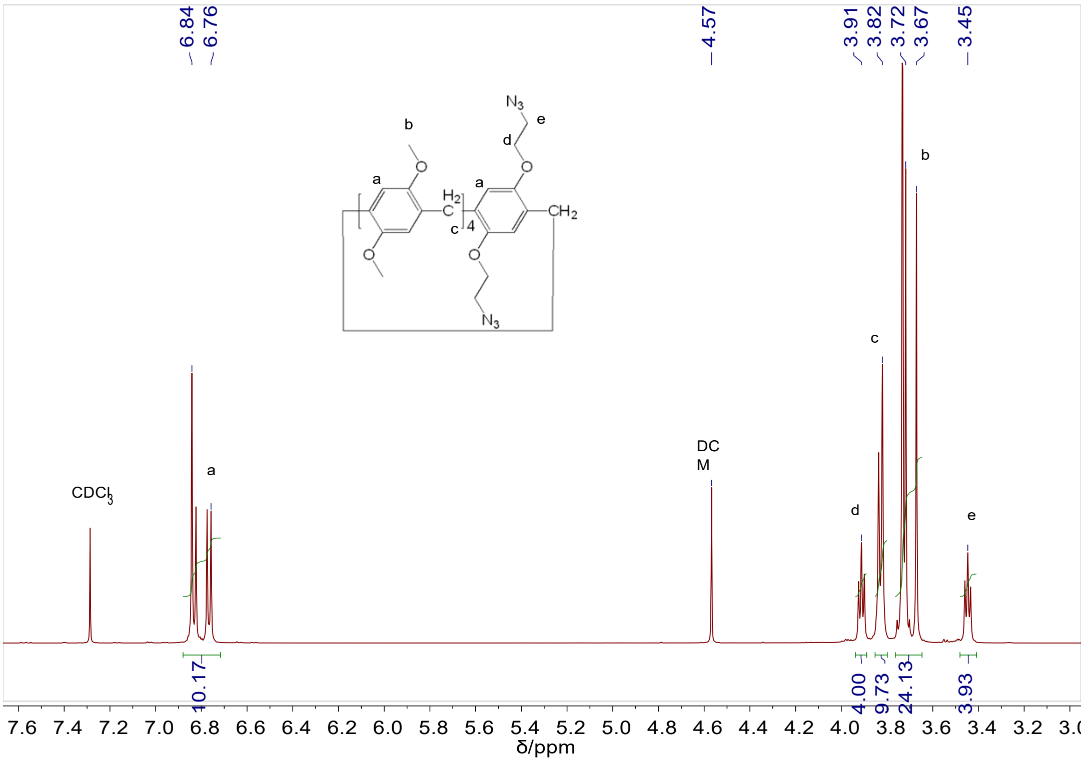


Fig. S3 ^{1}H NMR spectrum of DAP[5] in $CDCl_3$ (400 MHz, 298 K).

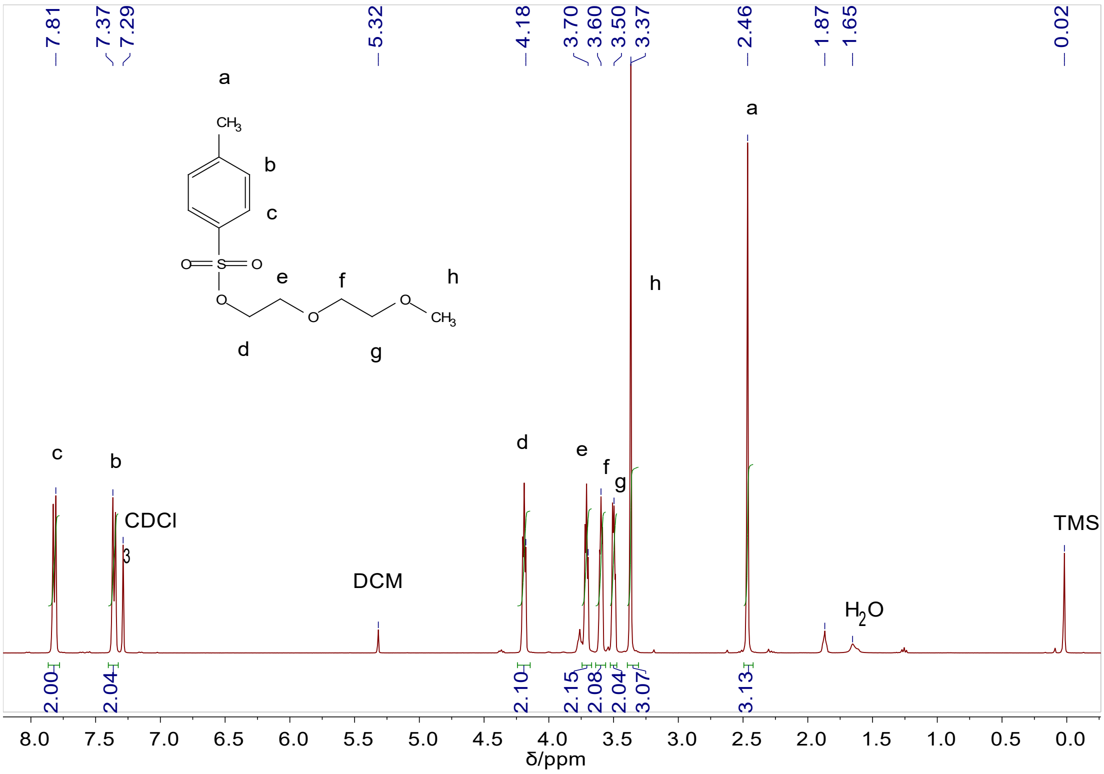


Fig. S4 ^1H NMR spectrum of (2-methoxyethoxy)ethyltosylate in $CDCl_3$ (400 MHz, 298 K).

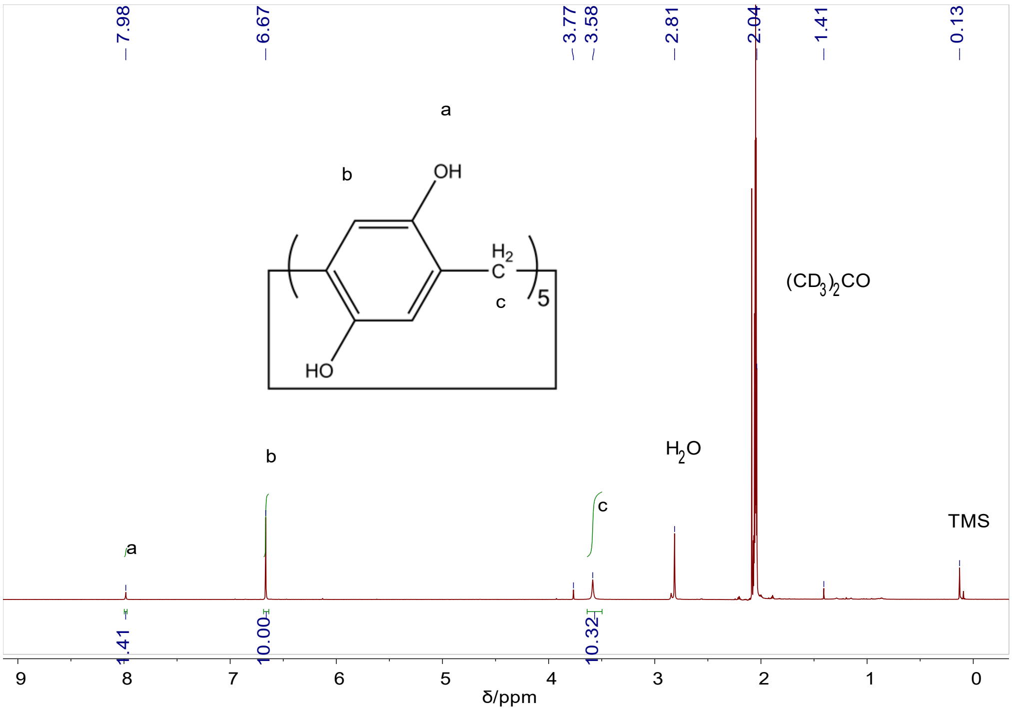


Fig. S5 ^1H NMR spectrum of *per*-hydroxylated pillar[5]arene in acetone-d_6 (400 MHz, 298 K).

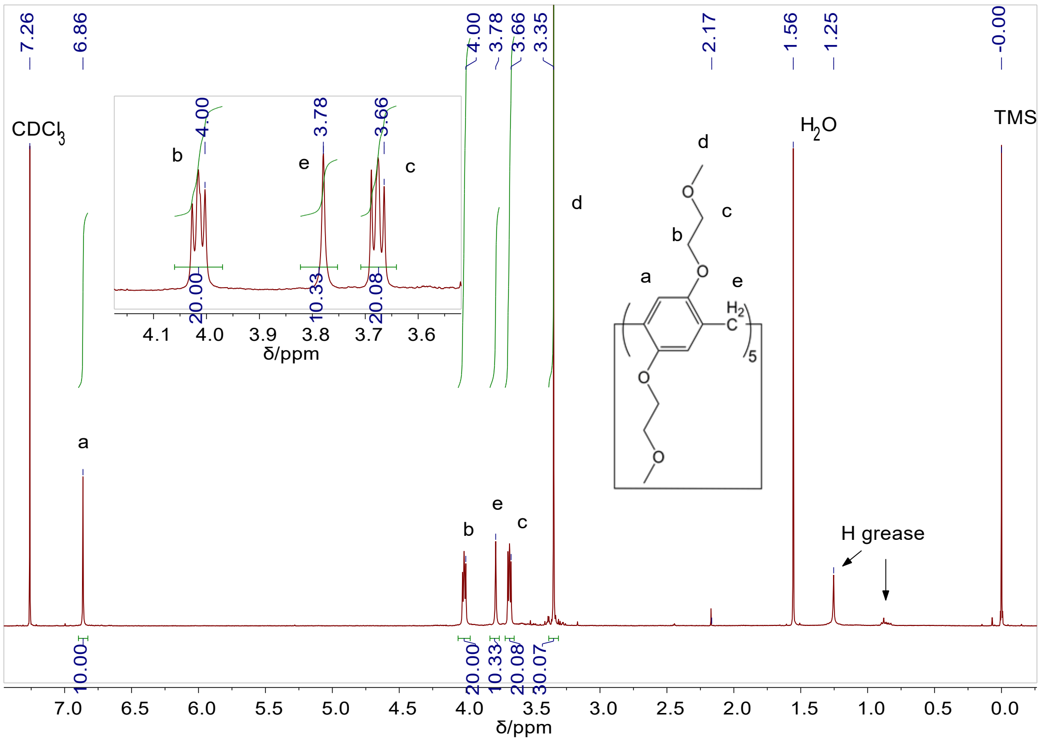


Fig. S6 ^{1}H NMR spectrum of EOP[5] in $CDCl_3$ (400 MHz, 298 K).

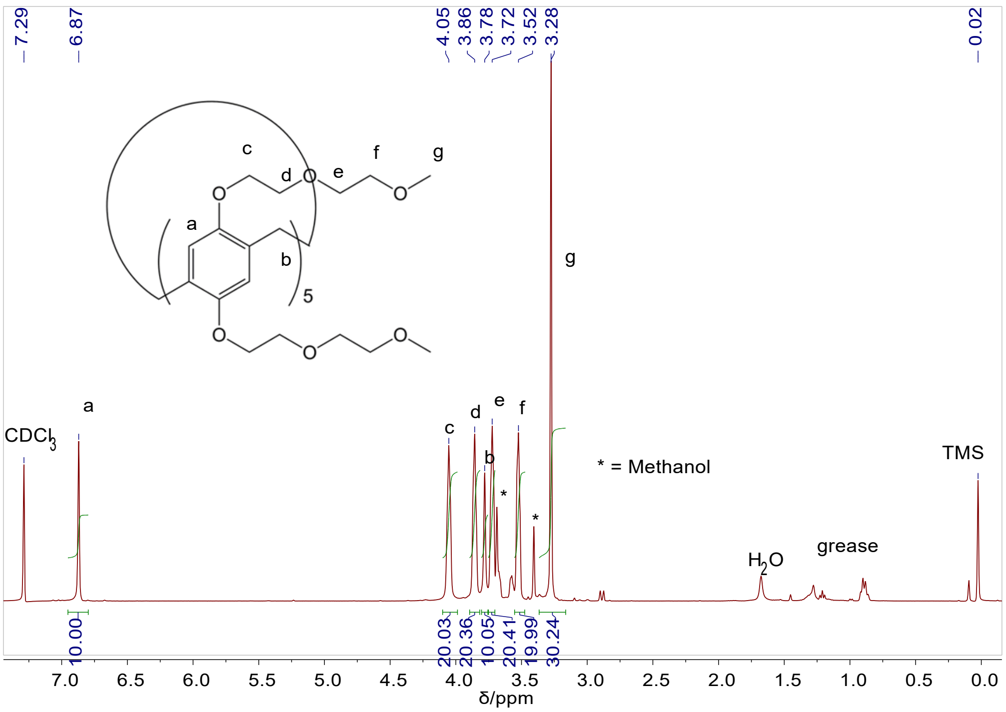


Fig. S7 ^{1}H NMR spectrum of DEOP[5] in $CDCl_3$ (400 MHz, 298 K).

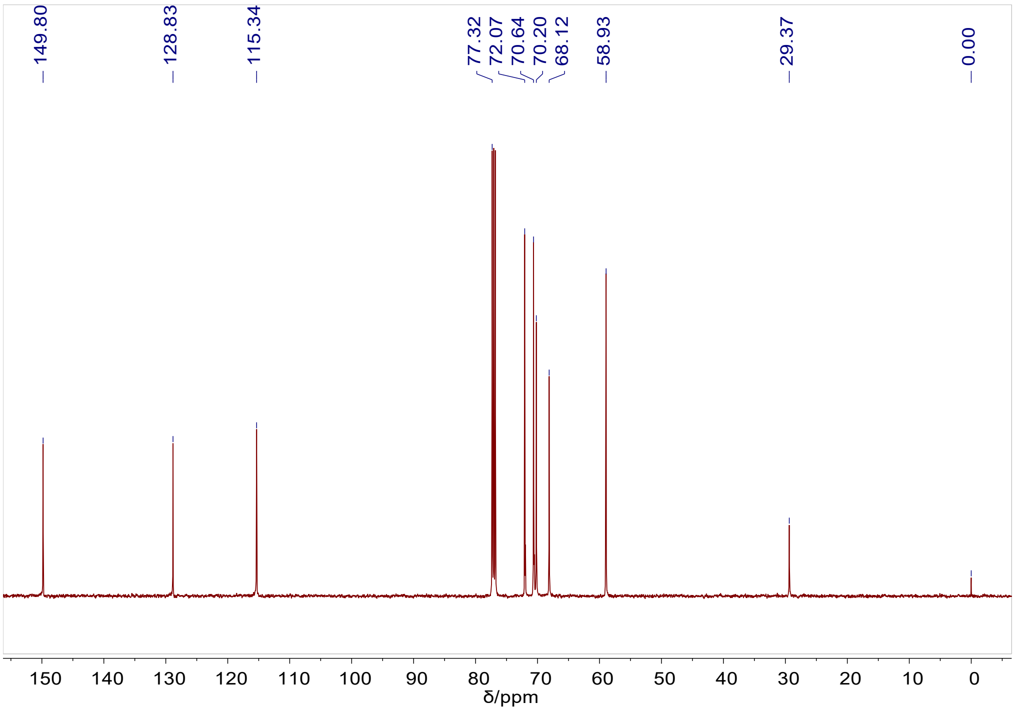


Fig. S8 ^{13}C NMR spectrum of DEOP[5] in $CDCl_3$ (100 MHz, 298 K).

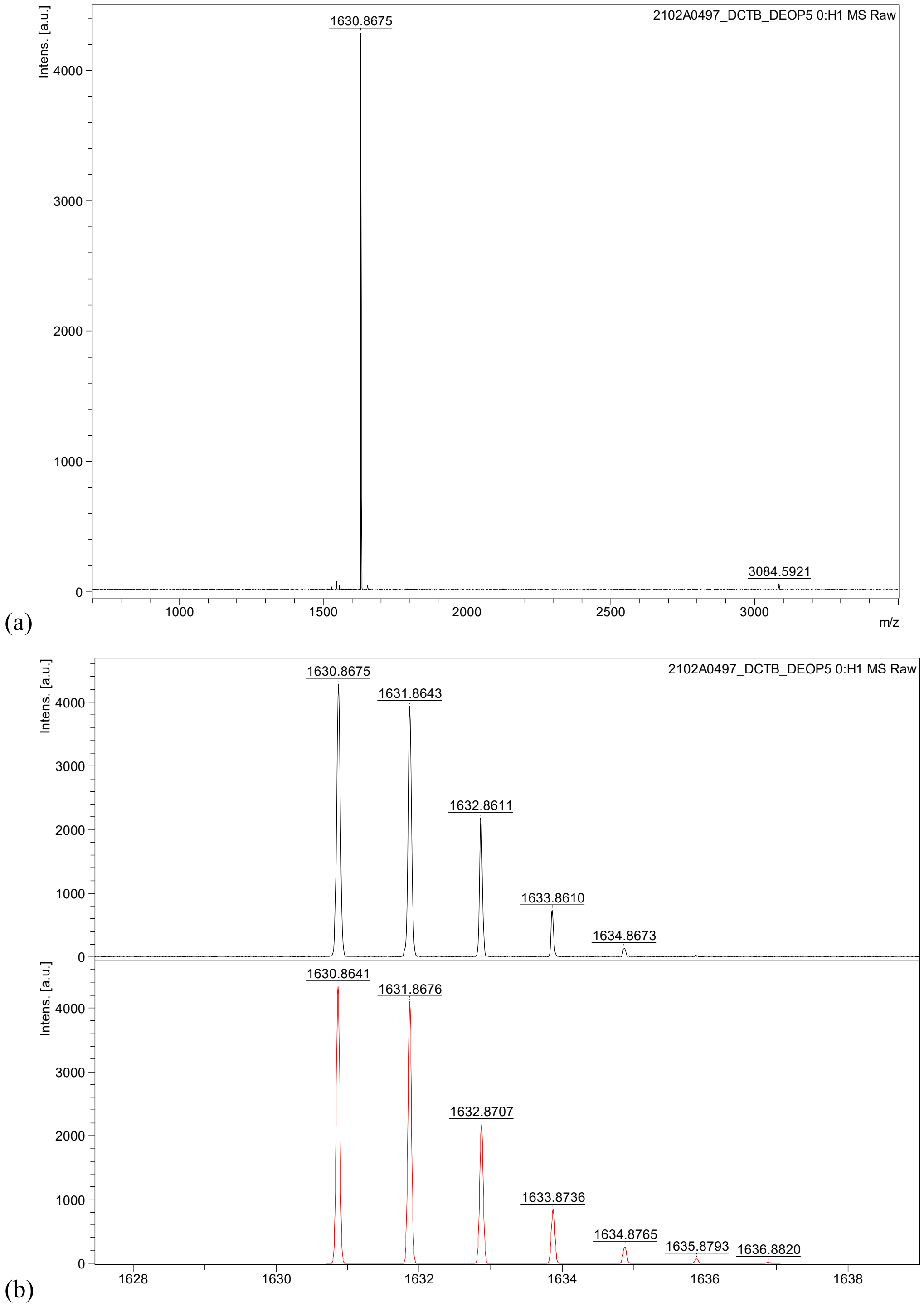


Fig. S9 (a) MALDI-TOF-MS full spectrum of DEOP[5], and (b) measured (top) and calculated (bottom) isotope patterns (*m*/*z* found (calcd.) for $[C_{86}H_{130}O_{30}]^+$, 1630.8675 (1630.8641)).

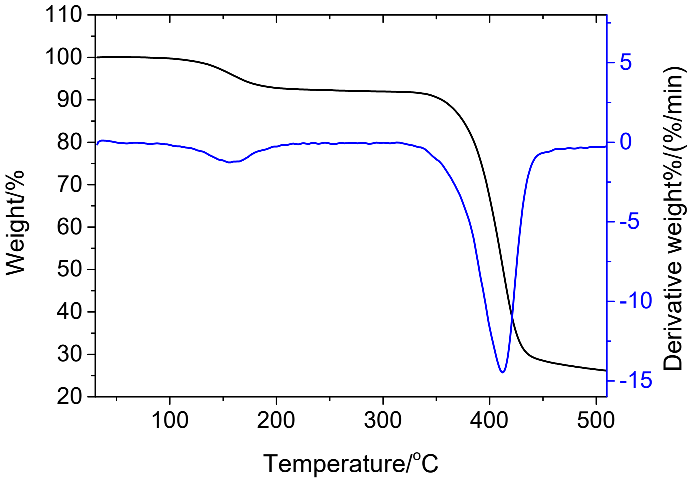


Fig. S10 TG and DTG curves of DEOP[5].

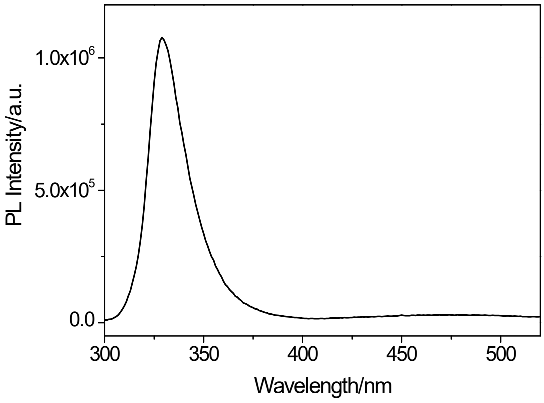


Fig. S11 Luminescence emission spectrum of 1,4-dimethoxybenzene in solid state at room temperature (λ_{ex} = 271 nm).

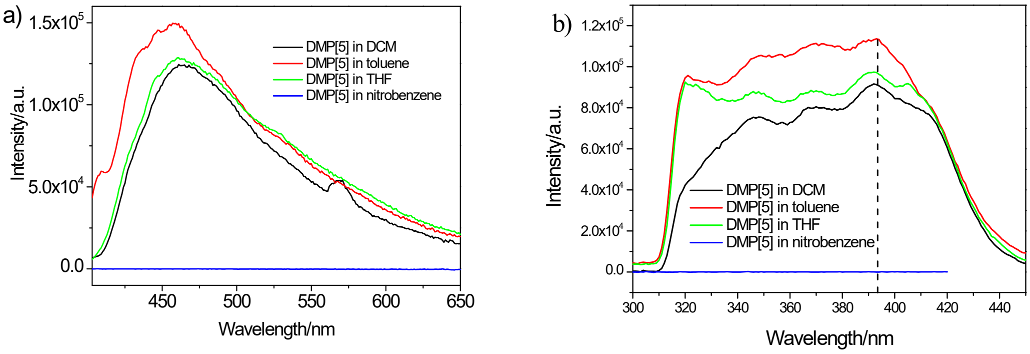


Fig. S12 (a) Emission and (b) excitation spectra of DMP[5] in dichloromethane (1.0 mmol L^{-1}), toluene, tetrahydrofuran and nitrobenzene (λ_{ex} = 393 nm, λ_{em} = 460 nm).

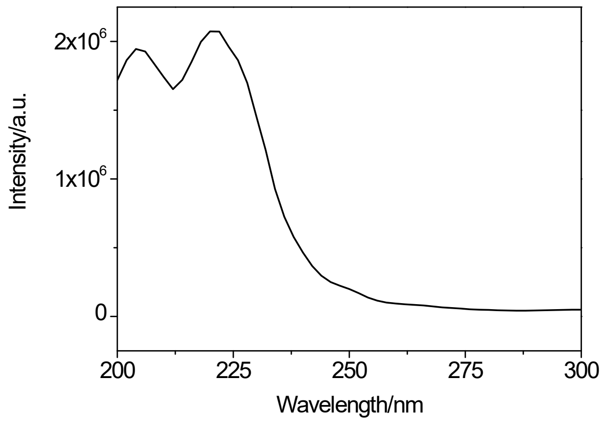


Fig. S13 Excitation spectrum of DMP[5] in solid state (λ_{em} = 450 nm).

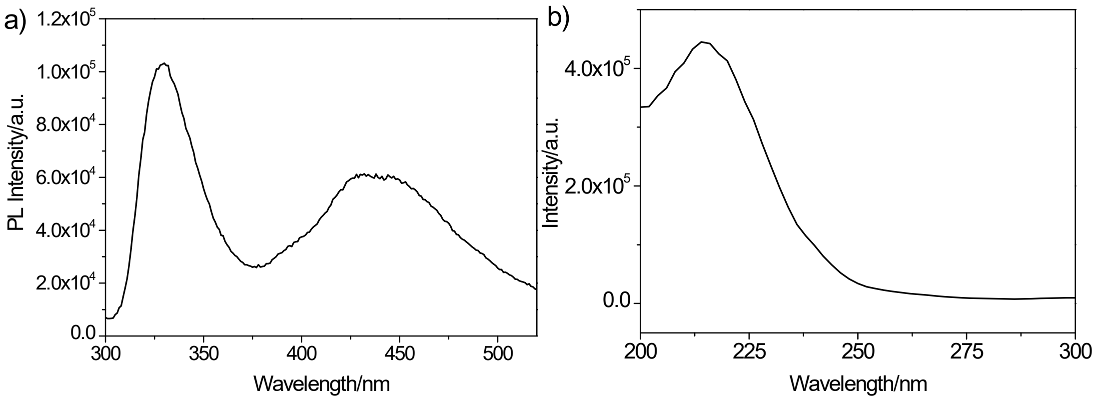


Fig. S14 (a) Emission and (b) excitation spectra of DBP[5] in solid state (λ_{ex} = 271 nm, λ_{em} = 450 nm).

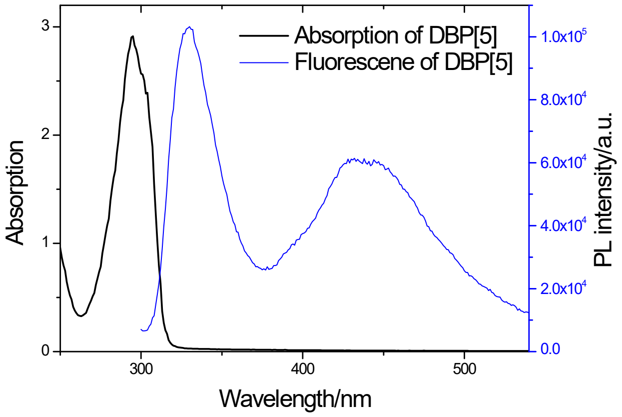


Fig. S15 Overlapping of the emission spectrum (λ_{ex} = 271 nm) of DBP[5] solid and UV-vis spectrum of DBP[5] in dichloromethane (0.04 mmol L^{-1}).

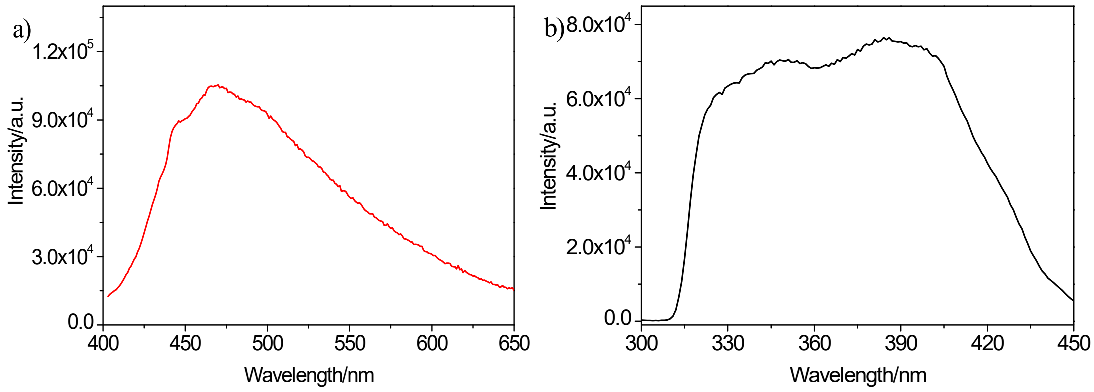


Fig. S16 (a) Emission and (b) excitation spectra of EOP[5] in dichloromethane (1.0 mmol L^{-1}, λ_{ex} = 393 nm, λ_{em} = 460 nm).

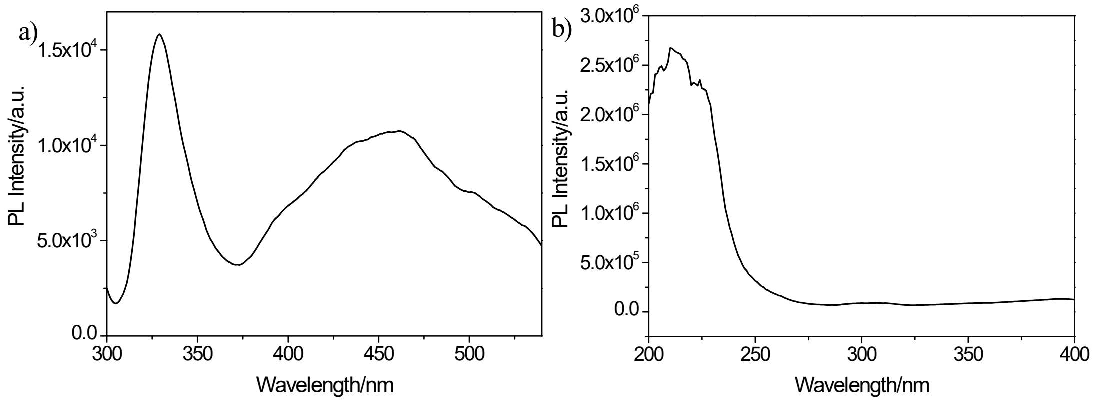


Fig. S17 (a) Emission and (b) excitation spectra of EOP[5] in solid state (λ_{ex} = 271 nm, λ_{em} = 450 nm).

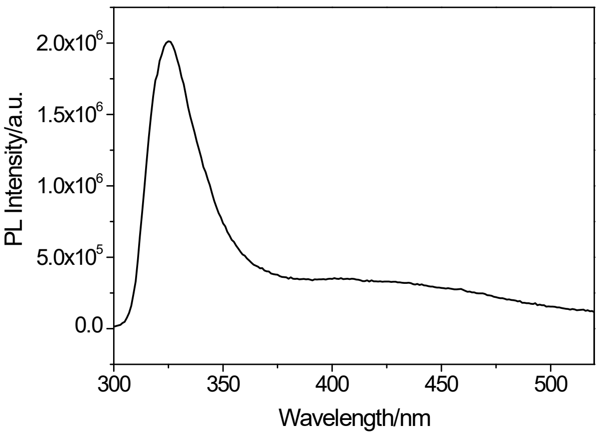


Fig. S18 Emission spectrum of DEOP[5] film (λ_{ex} = 271 nm).

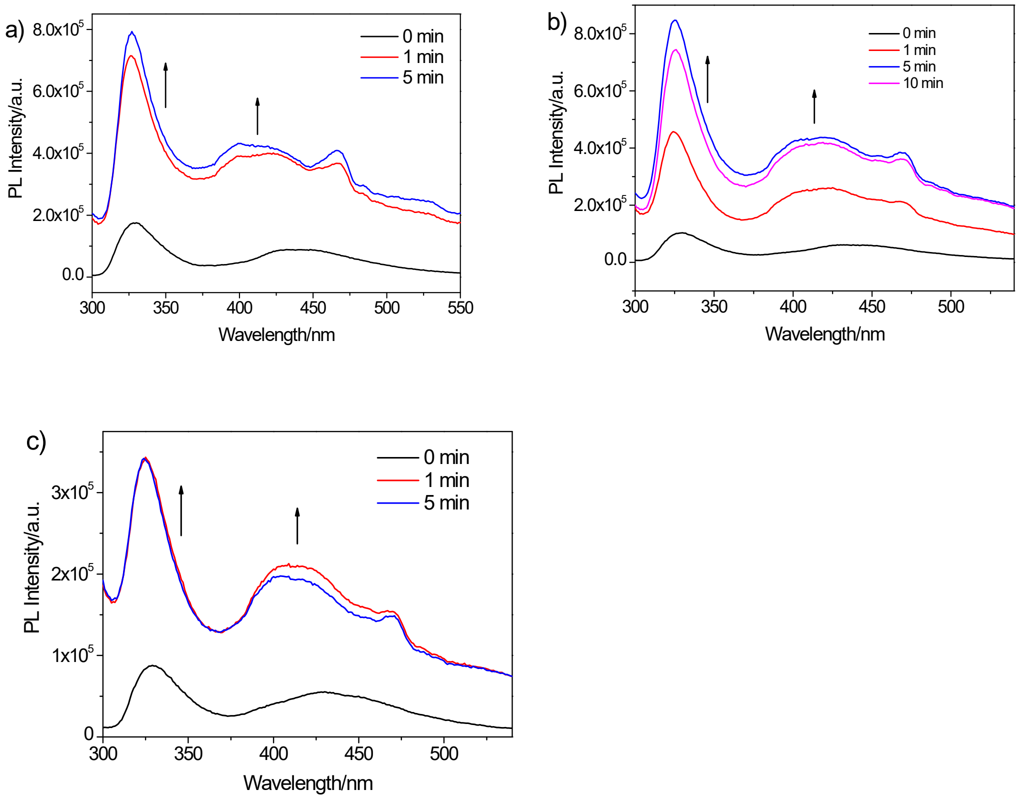


Fig. S19 Luminescence emission spectra of DBP[5] after exposure to (a) pentane, (b) heptane, and (c) undecane at room temperature (λ_{ex} = 271 nm).

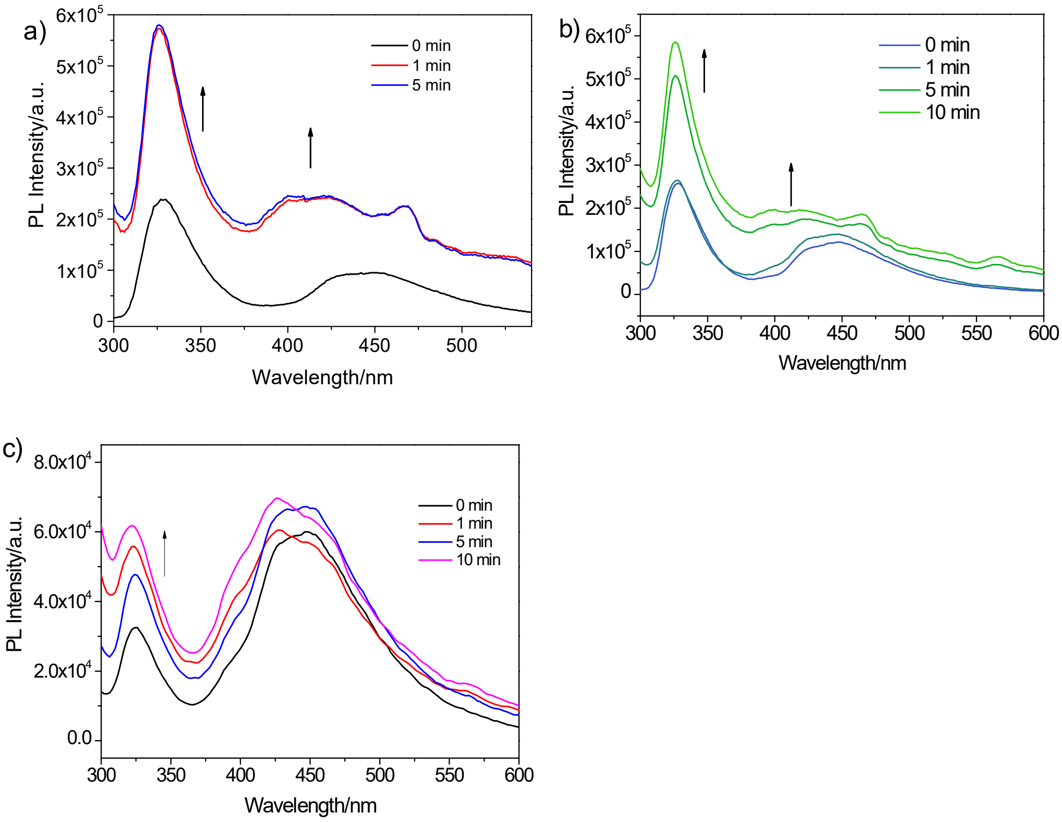


Fig. S20 Luminescence emission spectra of DBP[5] after exposure to (a) acetonitrile, (b) ethanol, and (c) diethyl ether at room temperature (λ_{ex} = 271 nm).

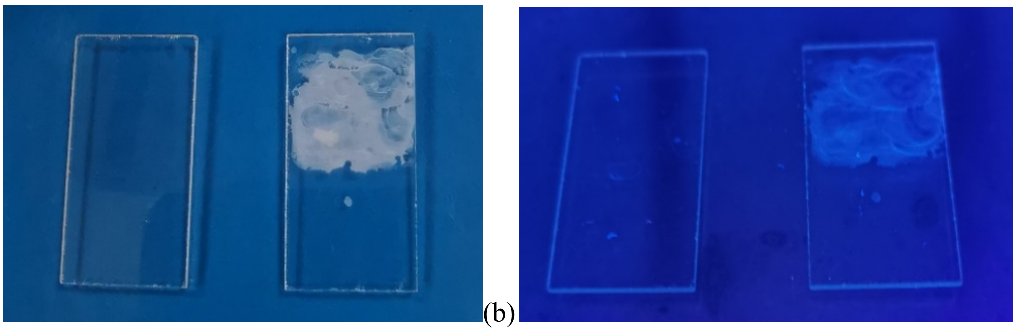

(a) (b)

Fig. S21 Photos of DBP5 film before (left) and after (right) exposure of hexane, (a) under daylight, and (b) under 365-nm UV light.

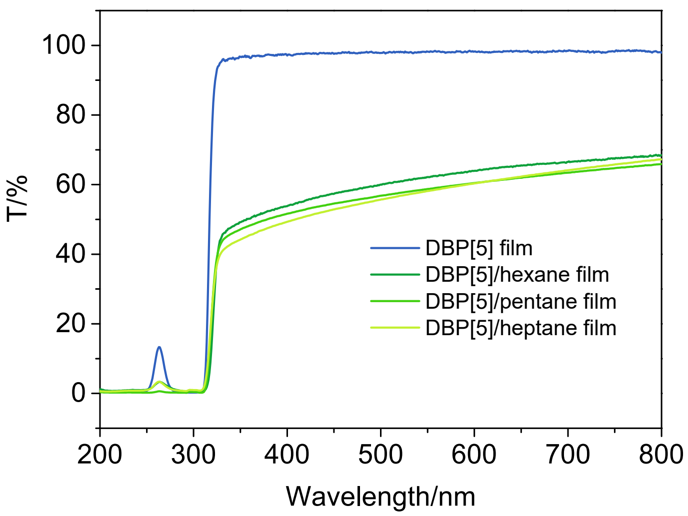


Fig. S22 Variation of the transmittance of DBP[5] film before and after exposed to hexane, pentane and heptane.

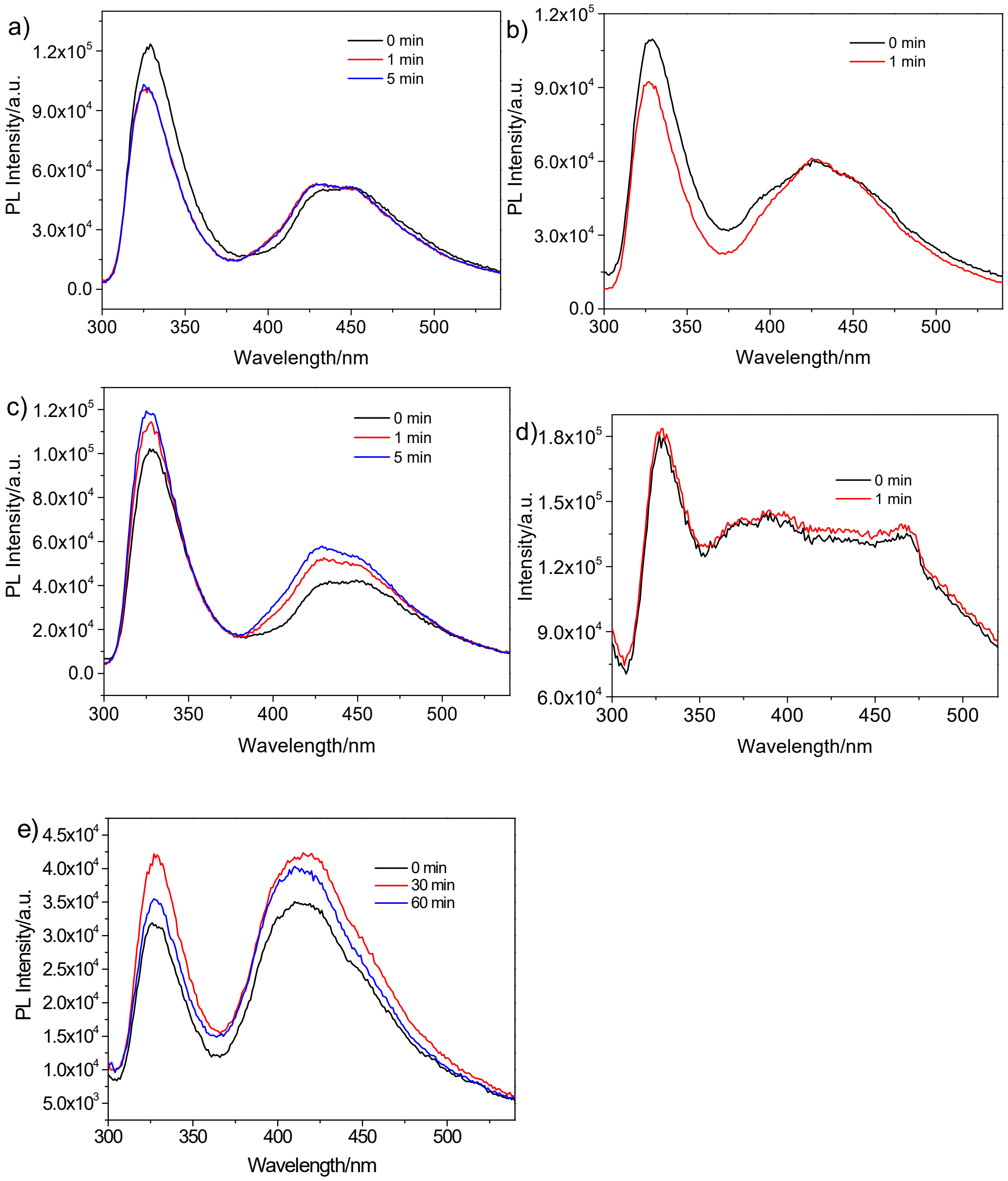


Fig. S23 Luminescence emission spectra of DBP[5] after exposure to (a) toluene, (b) *m*-xylene, (c) *o*-xylene, (d) dichloromethane, and e) propane at room temperature (λ_{ex} = 271 nm).

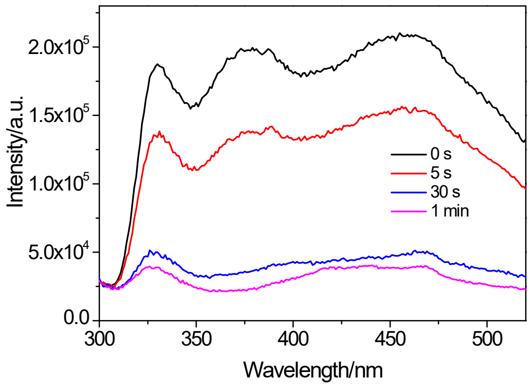


Fig. S24 Luminescence emission spectra of DBP[5] after exposure to nitrobenzene at room temperature (λ_{ex} = 271 nm).

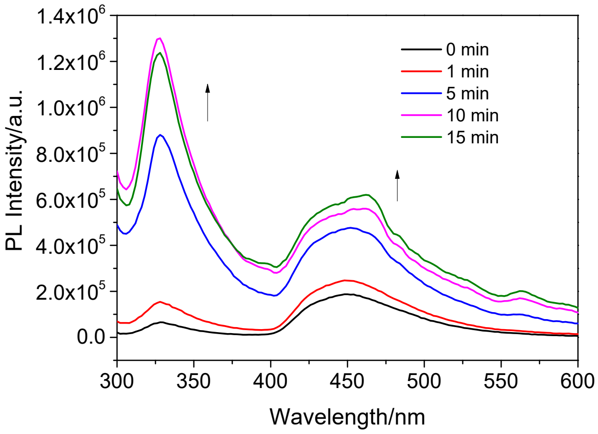


Fig. S25 Luminescence emission spectra of DAP[5] after exposure to hexane at room temperature (λ_{ex} = 271 nm).

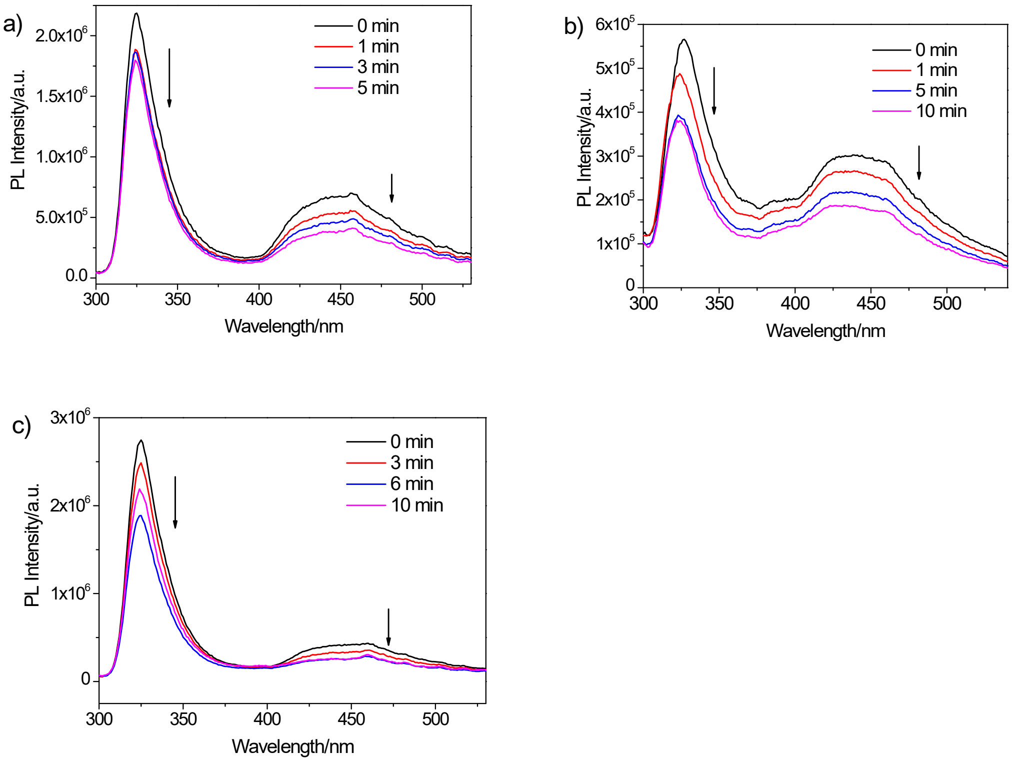


Fig. S26 Luminescence emission spectra of DMP[5] after exposure to (a) benzene, (b) toluene, and (c) ethylbenzene at room temperature (λ_{ex} = 271 nm).

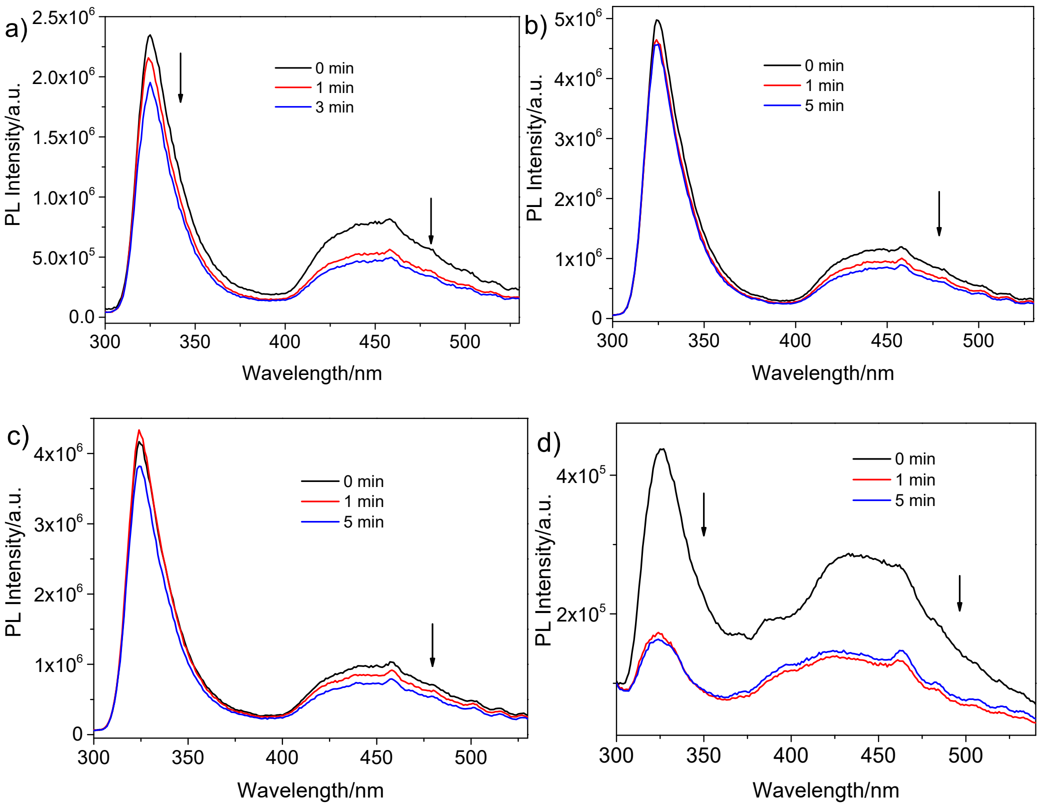


Fig. S27 Luminescence emission spectra of DMP[5] after exposure to (a) *p*-xylene, (b) *o*-xylene, (c) *m*-xylene, and (d) acetone at room temperature (λ_{ex} = 271 nm).

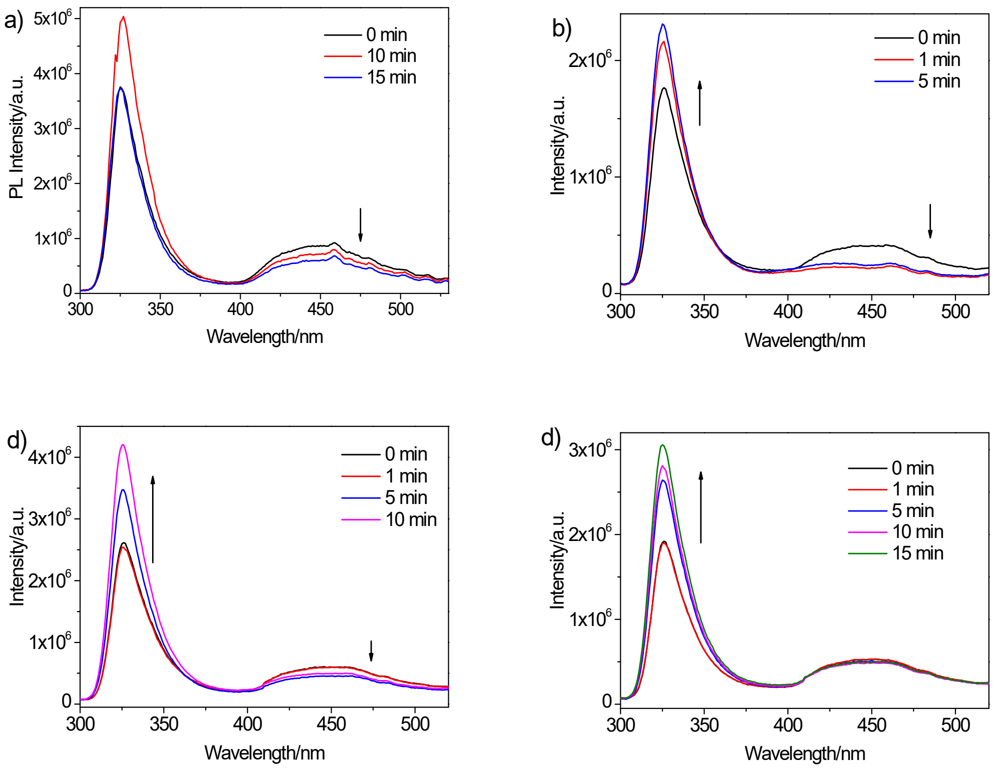


Fig. S28 Luminescence emission spectra of DMP[5] after exposure to (a) ethyl acetate, (b) dichloromethane, (c) acetonitrile, and (d) ethanol at room temperature (λ_{ex} = 271 nm).

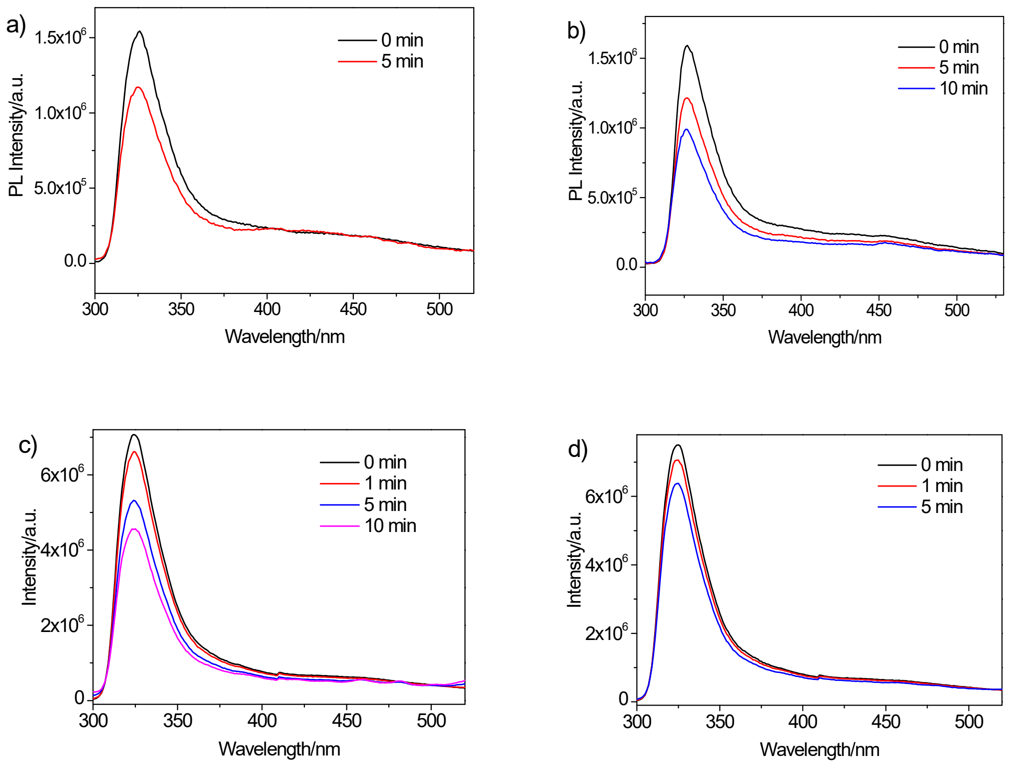


Fig. S29 Luminescence emission spectra of DEOP[5] after exposure to (a) toluene, (b) ethylbenzene, (c) acetonitrile, and (d) ethyl acetate at room temperature (λ_{ex} = 271 nm).

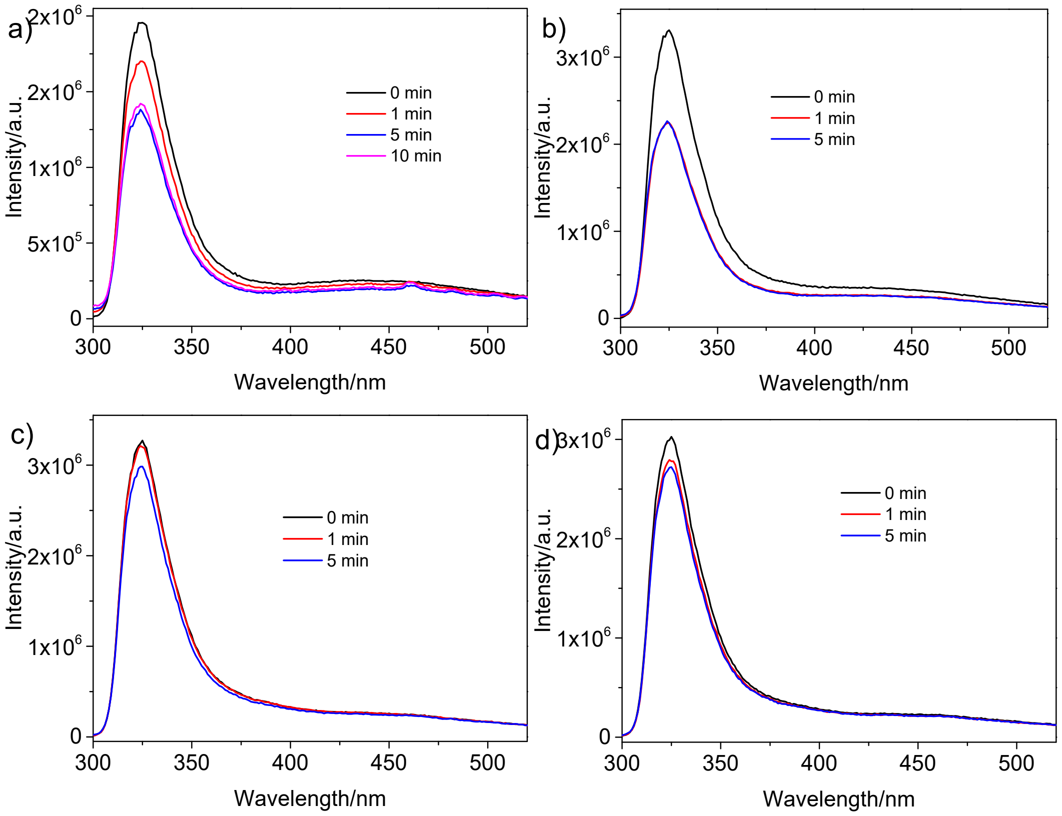


Fig. S30 Luminescence emission spectra of DEOP[5] after exposure to (a) benzene, (b) *p*-xylene, (c) *m*-xylene, and (d) *o*-xylene at room temperature ($\lambda_{ex} = 271$ nm).

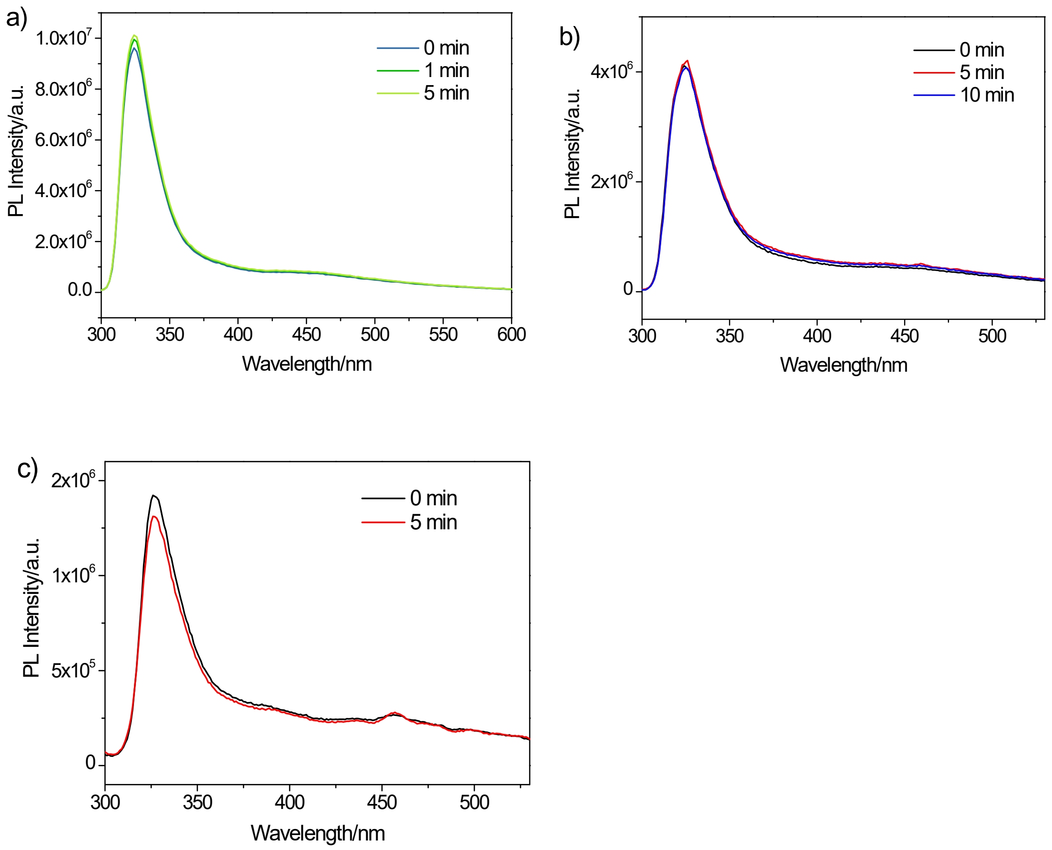


Fig. S31 Luminescence emission spectra of DEOP[5] after exposure to (a) hexane, (b) ethyl ether, and (c) acetone at room temperature (λ_{ex} = 271 nm).

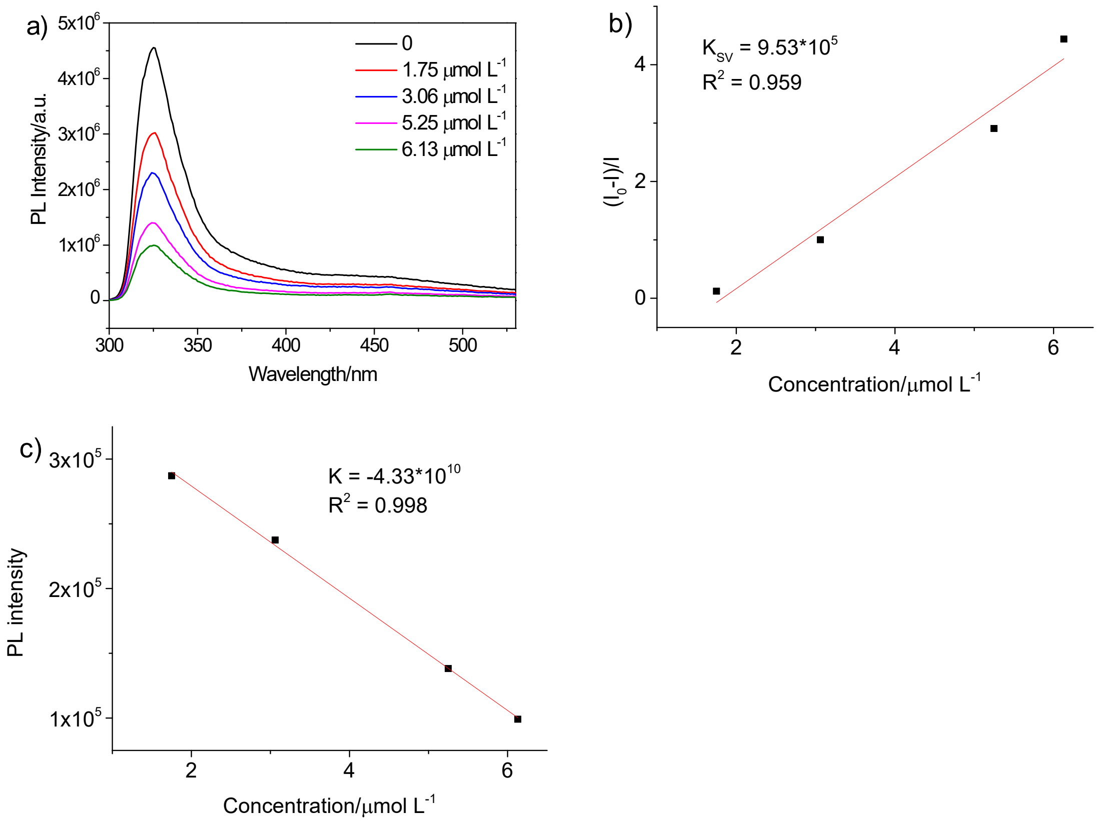


Fig. S32 (a) Concentration-dependent emission spectra at room temperature (λ_{ex} = 271 nm) after the DEOP[5] film device was exposed in nitrobenzene vapour for 5 s, (b) the plot of the fluorescence intensity $(I_0 - I)/I$ at 450 nm against c, and (c) the plot of the emission intensity at 450 nm against c ($K_{SV} = 9.06\times10^5$ L mol^{-1}).

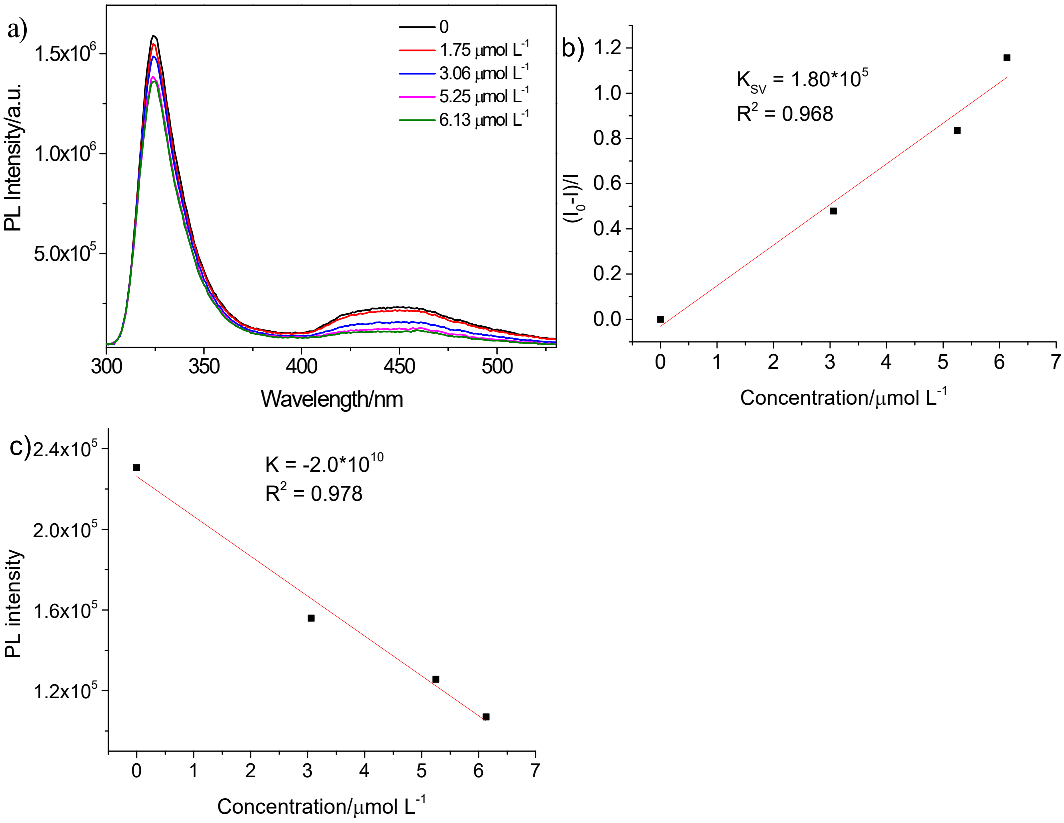


Fig. S33 (a) Concentration-dependent emission spectra at room temperature (λ_{ex} = 271 nm) after DMP[5] film device was exposed in nitrobenzene vapour for 5 s, (b) the plot of the fluorescence intensity $(I_0 - I)/I$ at 450 nm against *c*, and (c) the plot of the emission intensity at 450 nm against *c* ($K_{SV} = 1.5\times10^5$ L mol^{-1}).

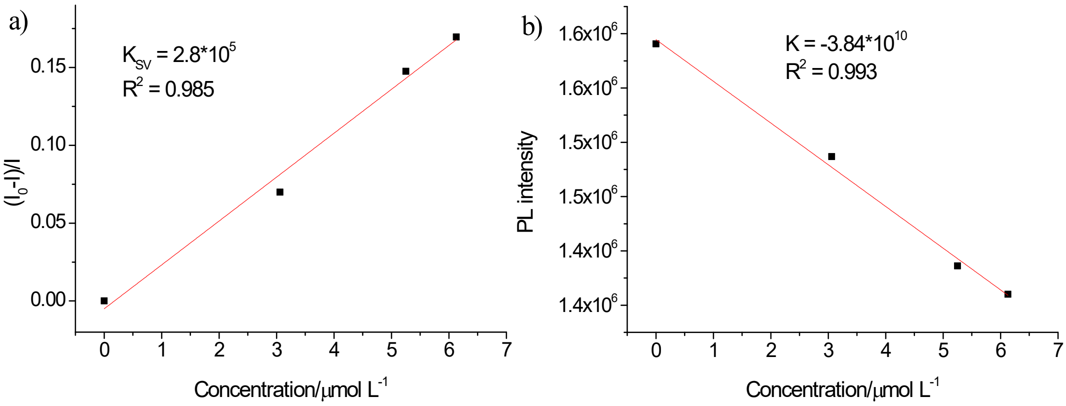


Fig. S34 (a) Plot of the fluorescence intensity $(I_0 - I)/I$ at 328 nm against *c*, and (b) plot of the emission intensity at 328 nm against *c* ($K_{SV} = 1.5\times10^5$ L mol^{-1}).

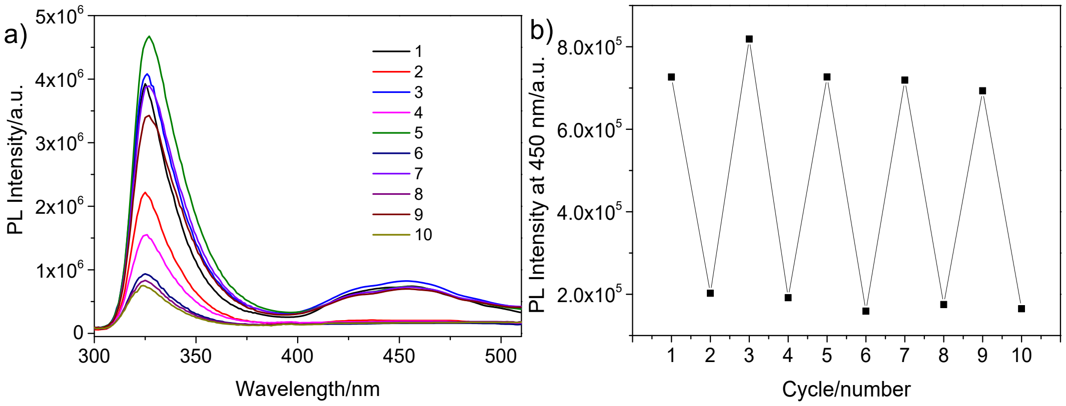


Fig. S35 Changes of (a) luminescence emission spectra and (b) fluorescence intensity at 450 nm of DMP[5] film after exposure to nitrobenzene at room temperature and then heated at 100 °C in vacuum for 5 times (λ_{ex} = 271 nm).

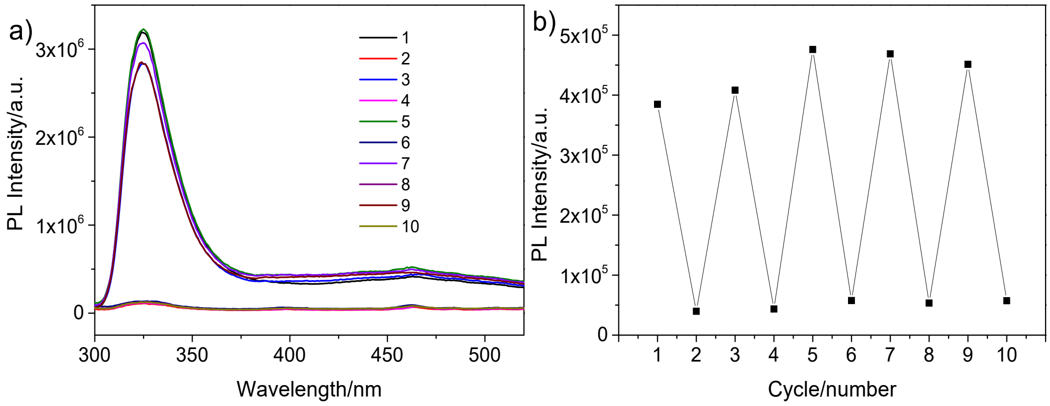


Fig. S36 Changes of (a) luminescence emission spectra and (b) fluorescence intensity at 450 nm of DEOP[5] film after exposure to nitrobenzene at room temperature and then heated at 100 °C in vacuum for 5 times (λ_{ex} = 271 nm).

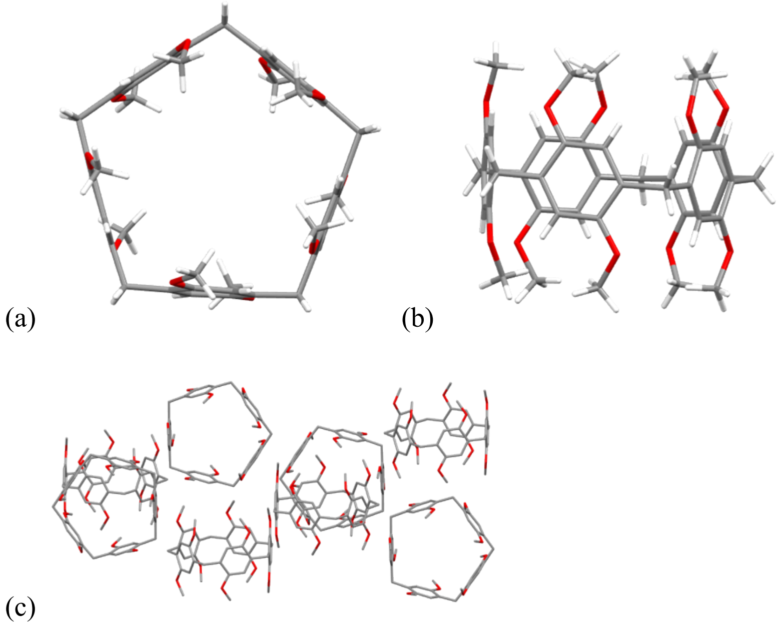


Fig. S37 X-ray crystal structure of DMP[5], (a) top view; (b) side view; (c) packing mode. Oxygen atoms are red, carbon atoms are medium grey, and hydrogen atoms are white.

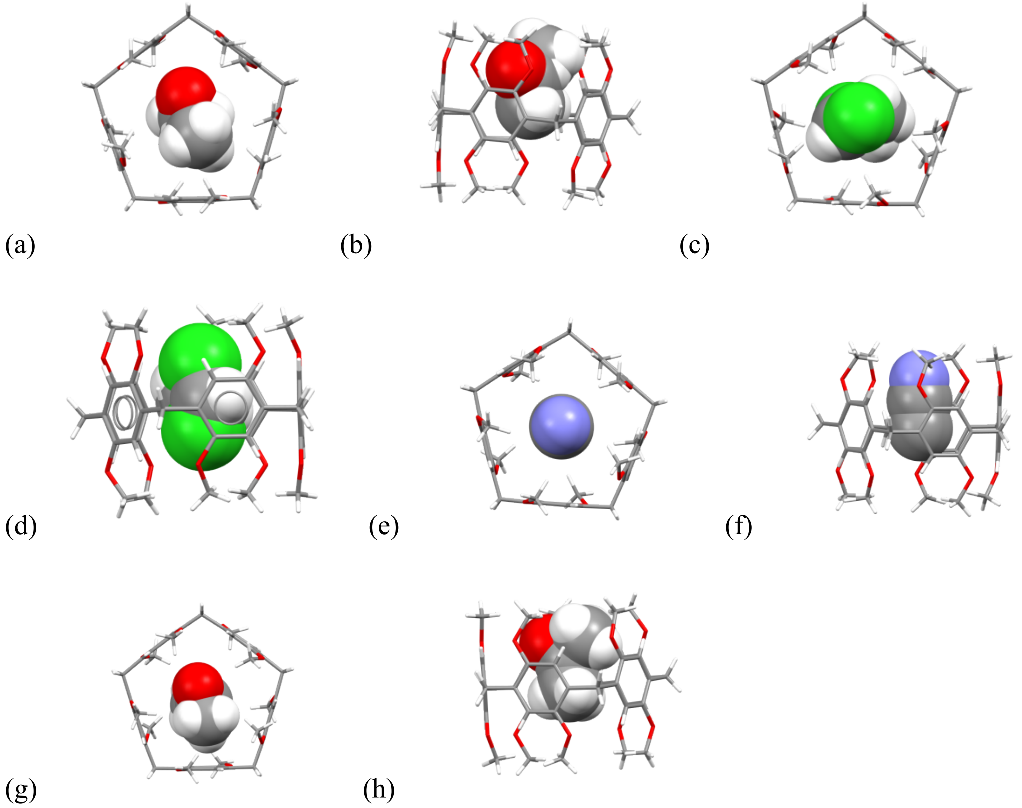


Fig. S38 X-ray crystal structures of ethyl acetate@DMP5, (a) top view, and (b) side view, dichloromethane@DMP5, (c) top view and (d) side view, acetonitrile@DMP5, (e) top view and (f) side view, and acetone@DMP5, (g) top view, and (h) side view.

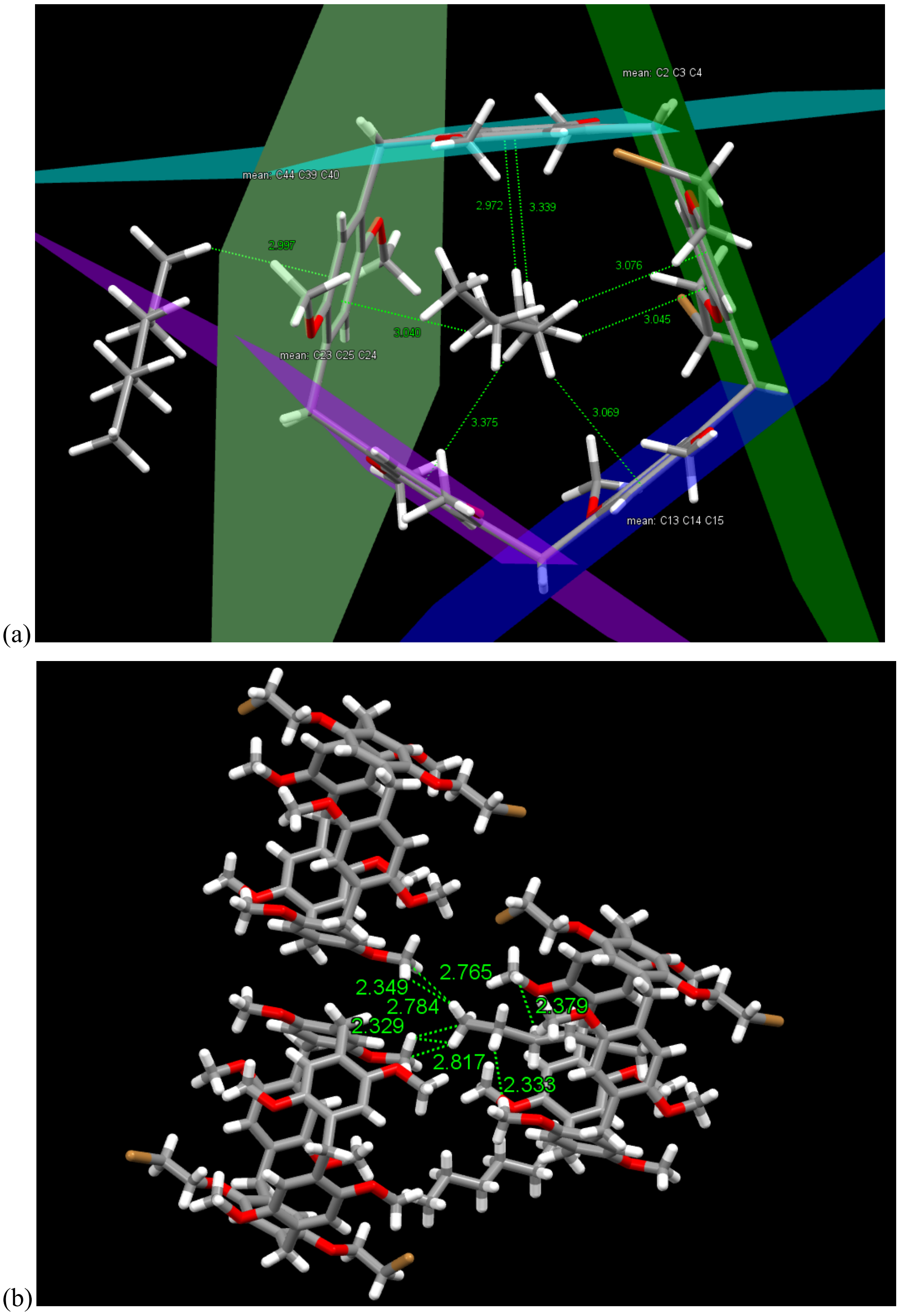


Fig. S39 (a) Distances between hydrogen atoms on the included *n*-hexane and phenyl planes of pillar[5]arene, and (b) distances between hydrogen atoms on the included *n*-hexane and the two adjacent pillar[5]arene molecules from X-ray crystal analysis of DBP[5]⊃*n*-C_6H_{14}. There are van der Waals interactions between *n*-hexane included the cavities and the methoxy groups of two adjacent DBP[5] molecules, of which the intermolecular distances are ranging from 2.33 Å to 2.82 Å.

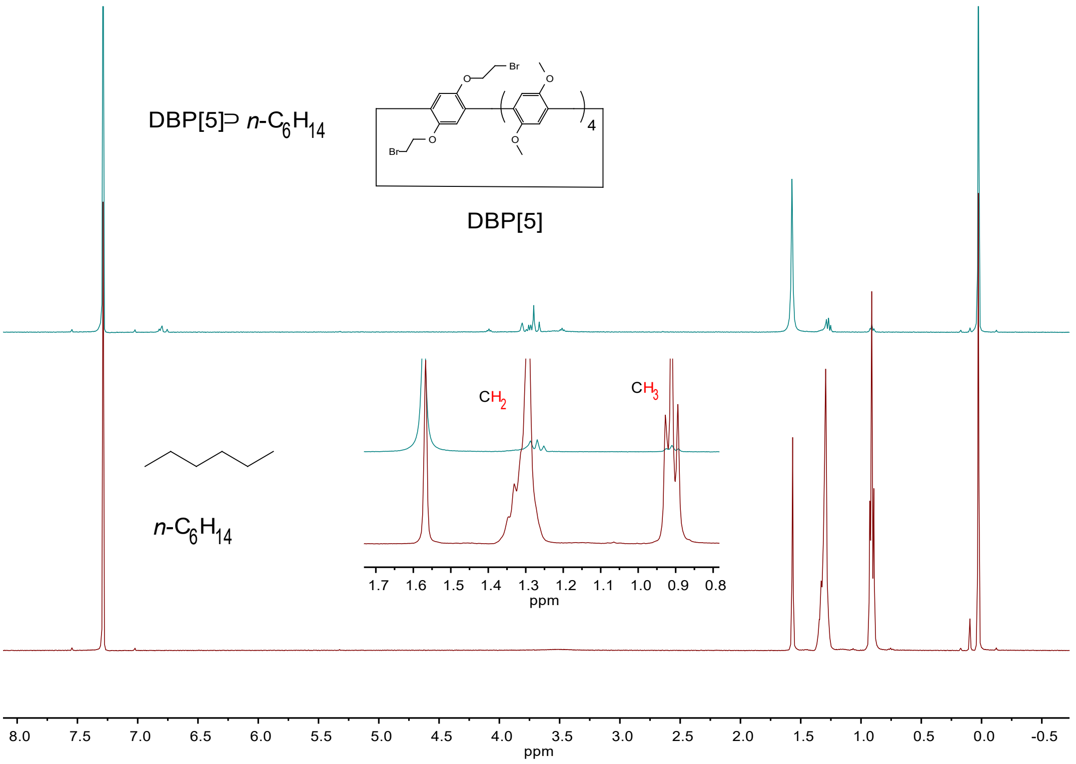


Fig. S40 ^{1}H NMR spectra of (a) DBP[5]⊃*n*-C_6H_{14} crystals, and (b) *n*-hexane in $CDCl_3$ (400 MHz, 298 K).

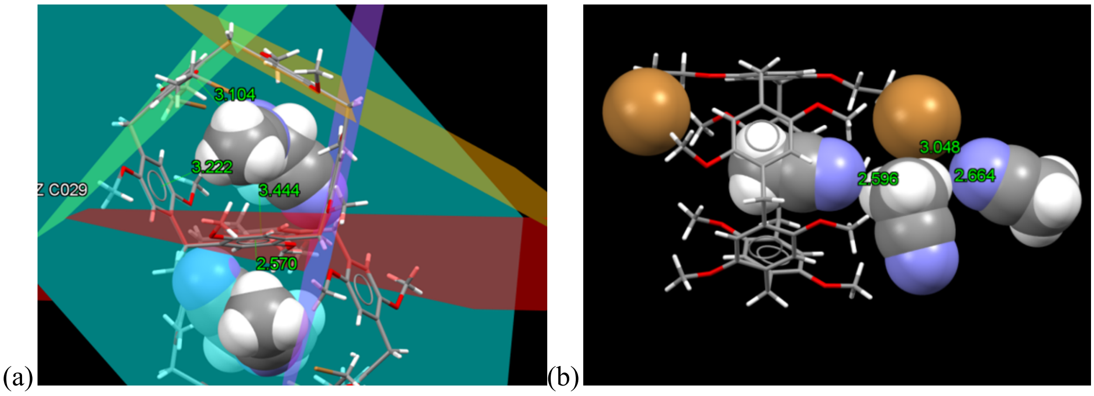


Fig. S41 (a) Distances between three hydrogen atoms on the included acetonitrile molecule and phenyl planes of pillar[5]arene, and (b) distances between the N atom of -CN group and H atoms of -CH_3 groups from the neighbouring acetonitrile molecule from the X-ray crystal analysis of DBP[5]⊃MeCN (C: gray, O: red, Br: yellow, N: blue). N···H distances, 2.60 and 2.66 Å. The distance between the H atom of the second acetonitrile molecule and Br atom is 3.05 Å.

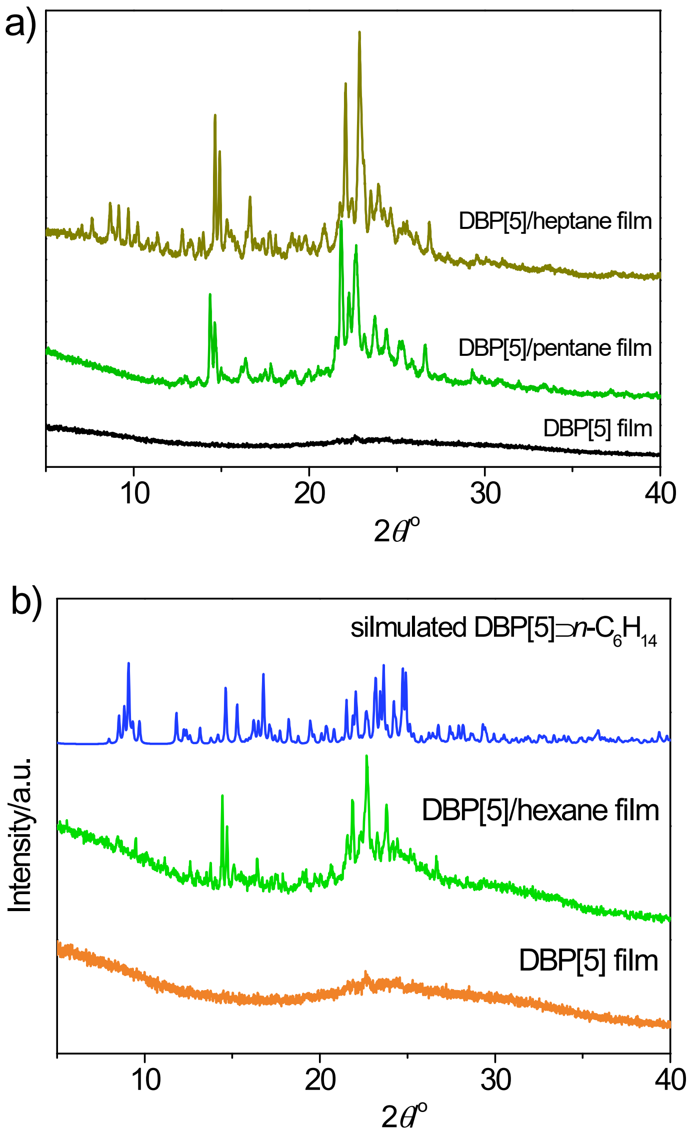


Fig. S42 Comparison of PXRD patterns of (a) DBP[5] film, DBP[5]/pentane film and DBP[5]/heptane film, and (b) DBP[5] film, DBP[5]/hexane film and simulated DBP[5]⊃*n*-C_6H_{14}. The PXRD pattern of DBP[5]/hexane film is consistent with that of simulated DBP[5]⊃*n*-hexane. There are some missing peaks in the experimental patterns of DBP[5]/hexane film compared to simulated DBP[5]⊃*n*-hexane, which may be owing to the poor crystallinity of DBP[5]/hexane film.

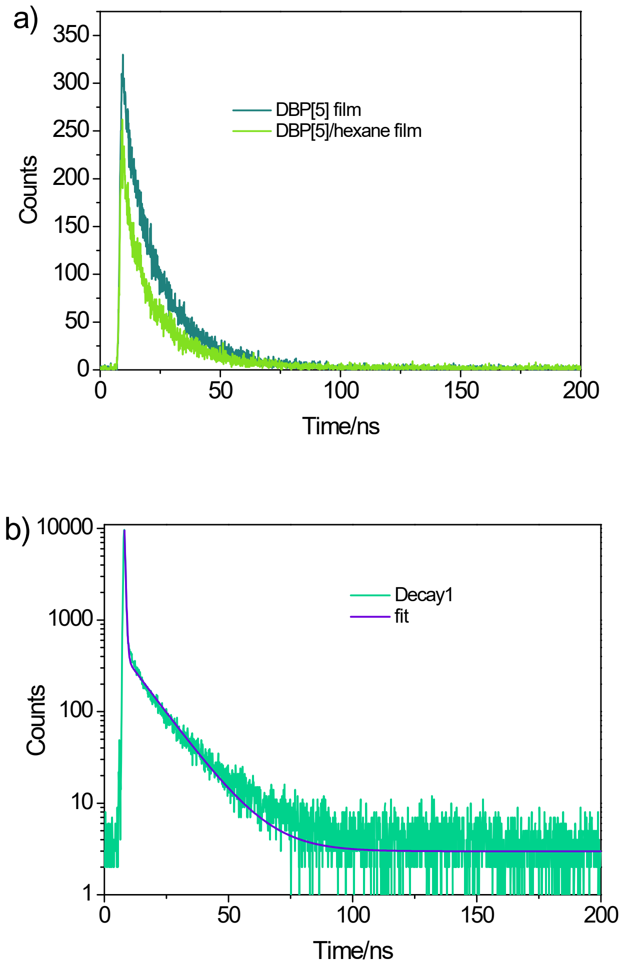


Fig. S43 Fluorescence lifetime spectra of a) DBP[5] film and DBP[5]/hexane film-20min (DBP[5] film was placed in the atmosphere of hexane for 20 min), and b) DBP[5]/hexane film-90min (DBP[5] film was placed in the atmosphere of hexane for 90 min) (detected at 450 nm, λ_{ex} = 406.2 nm).