

Electronic Supplementary Information for

A donor-acceptor cage for circularly polarized TADF emission

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1. Materials and Instruments

Reagents and solvents were purchased from commercial suppliers and used without further purification, unless otherwise indicated. The catalyst Pd(PPh₃)₄ and 2-(hydroxymethyl)phenylboronic acid were purchased from Bide Pharma Ltd., China. Potassium carbonate, cesium carbonate and phosphorus tribromide were purchased from General-Reagent®, China. Flash column chromatography was performed on silica gel (200-300 mesh) and the compounds were visualized under 254 nm on thin-layer chromatography (TLC) plates. Compounds 2,7,12-tribromo-5,10,15-triethyltriindole (**1**) and 4,4',4''-(1,3,5-triazine-2,4,6-triyl)triphenol (**P1**) were synthesized according to the literature procedure.^[S1-S2]

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance III HD 400, Bruker Avance III HD 500 and Quantum-I Plus 400 spectrometer. Chemical shift values (δ) are reported in ppm relative to the internal reference tetramethylsilane (TMS), and coupling constants (J) are reported in Hertz (Hz). The multiplicity in the ¹H NMR spectra are described as s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). MALDI-TOF mass spectrometry was performed on a Bruker Autoflex speed TOF/TOF mass spectrometer and operated in reflective mode with (trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propene]-malononitrile (DCTB) as the matrix. The single crystal data of cage **DA-2** was collected on Bruker D8 VENTURE at 173 K. The structures were solved by direct methods using the OLEX-2 software. All nonhydrogen atoms were refined using anisotropic thermal parameters.

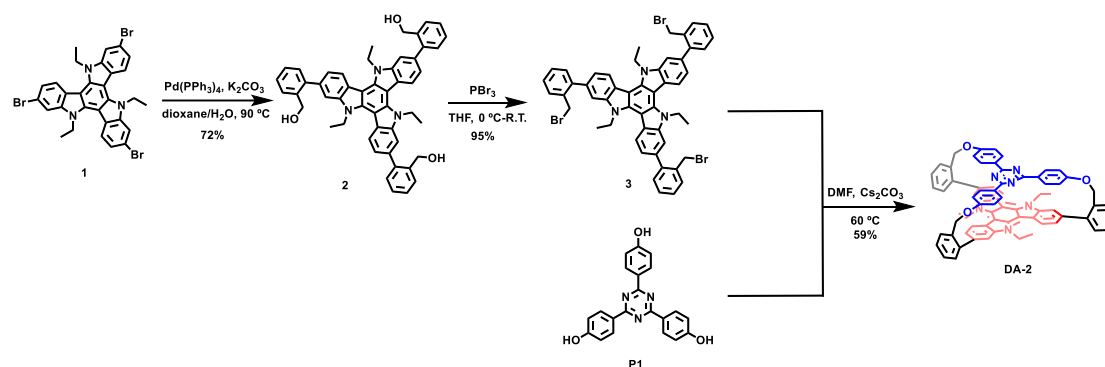
UV-vis absorption spectra were recorded on a Shimadzu UV 3600 and Perkin-Elmer Lambda 950-PKA spectrometers. The steady state photoluminescence (PL) spectra, and fluorescence lifetimes were measured on a JASCO FP-8600 and an Edinburgh FLS1000 PL spectrometer, as well as on a Hamamatsu Photonics Quantaaurus-Tau C11367-03. The absolute PL quantum efficiencies (Φ) of the samples were measured with a Hamamatsu Photonics Quantaaurus-QY C11347-01. The solutions for the UV-vis and PL measurements were charged in transparent quartz cuvettes with a width of 10 mm and they were degased with O₂ or N₂ during 15 min. The neat film, PMMA film (2 wt%) and host-guest doped films (6 wt%) of **DA-2** were prepared by spin coating from chloroform solutions on quartz substrates with a spin rate of 1000 rpm.

Chiral HPLC was conducted on a Shimadzu LC-20AD device with a CHIRALPAK IG (IG00CE-UC011) column and hexane/DCM/DEA = 30/70/0.1 (V/V/V) as the

mobile phase with a flow rate of 1 mL/min. The column temperature was set at 35 °C. Circular dichroism (CD) was performed with a JASCO J-1500 spectrometer. CD spectra of the solution of **DA-2** were recorded in 10 mm quartz cuvettes at 25 °C using toluene and DCM as the solvent. A scan rate of 200 nm min⁻¹ with a response time of 1 s and a bandwidth of 5 nm were adopted. CPL spectra were measured on a JASCO CPL-200 spectrophotometer.

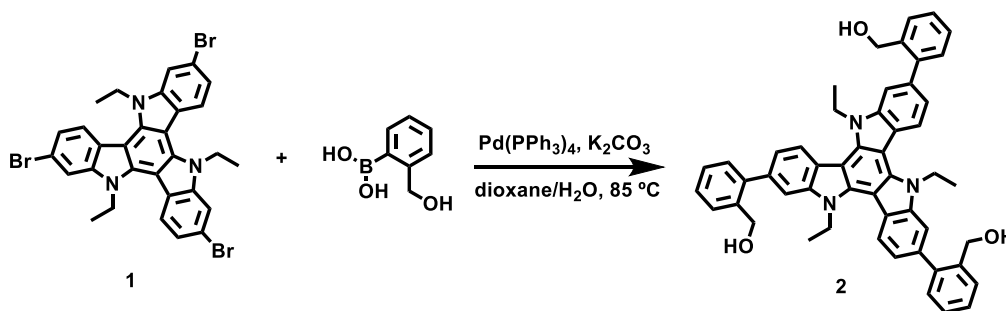
2. Synthetic Procedures

The syntheses of all chemical compounds are described as follows. ¹H and ¹³C NMR resonances of all compounds are listed after their synthetic procedures and their assignments are given in their NMR spectra.



Scheme S1. Synthetic routes for cage **DA-2**.

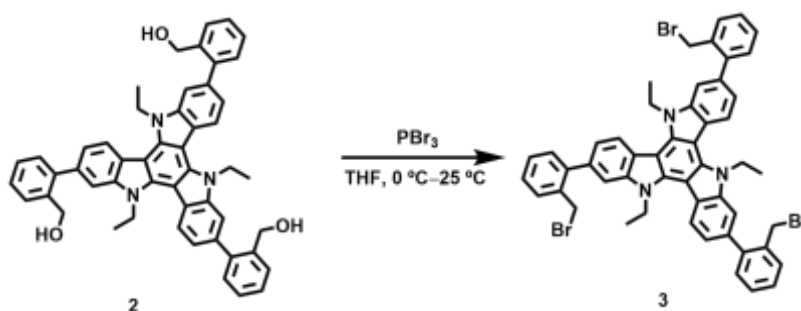
Synthesis of compound 2



Compound **1** (2664 mg, 4 mmol), 2-(Hydroxymethyl)phenylboronic acid (2432 mg, 16 mmol), Pd(PPh₃)₄ (462 mg, 0.4 mmol) and K₂CO₃ (3312 mg, 24 mmol) were added into a schrenk flask which was evacuated and backfilled with N₂ for three times. Dioxane (96 mL) and H₂O (24 mL) were bubbled with N₂ for 15 minutes and then added into the flask under N₂. The reaction was kept at 85 °C with stirring for 24 hours. After the reaction, the solvents were removed by rotary evaporation and the residue was extracted with DCM and brine. The organic phase was collected and dried over

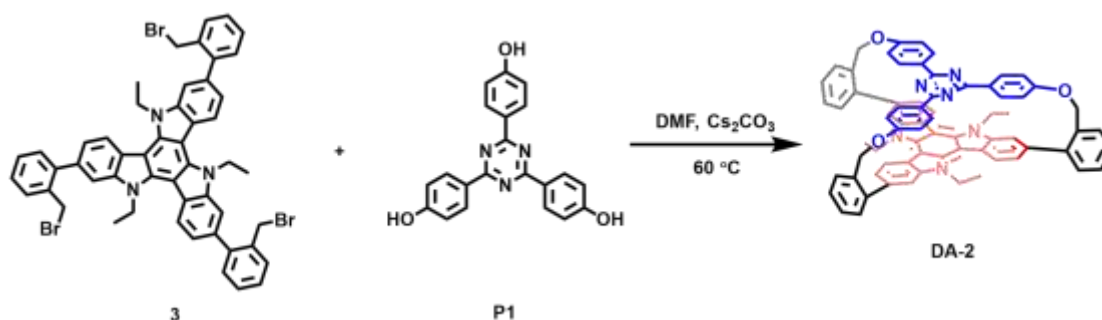
anhydrous MgSO_4 to get the crude product which was purified by column chromatography with EA/PE (1/2) as the eluents to yield the compound **2** (2141 mg, 72%) as yellow powder. ^1H NMR (400 MHz, CDCl_3): δ 8.41 (d, $J = 8.0$ Hz, 3H), 7.69–7.65 (m, 3H), 7.56–7.52 (m, 3H), 7.51–7.46 (m, 6H), 5.11 (q, $J = 8.0$ Hz, 6H), 4.83 (s, 6H), 1.72 (t, $J = 8.0$ Hz, 9H). ^{13}C NMR (125 MHz, CDCl_3): δ 142.22, 140.83, 139.16, 138.47, 135.58, 130.71, 128.84, 127.90, 127.70, 122.64, 121.35, 121.30, 111.16, 103.23, 63.71, 41.89, 15.82.

Synthesis of compound **3**



Compound **2** (2141 mg, 2.86 mmol) was charged into a 200 mL Schrenk flask which was evacuated and backfilled with N_2 for 3 times. Then THF (80 mL) was added by syringe to form a yellow solution. Phosphorus tribromide (PBr_3 , 1.1 mL, 11.5 mmol) was diluted in THF (5 mL) and added drop by drop into the THF solution of compound **2** under ice bath. Then the reaction was slowly warmed to 25 °C and further reacted for 8 hours with stirring. After the reaction, 2 mL deionized water was added to quench the residual PBr_3 . THF was removed by rotary evaporation and the residue was dissolved in DCM to get a concentrated solution. Then the solution was added into MeOH drop by drop. The precipitation in MeOH was collected by centrifugation to get the pure product as light-green powder (2341 mg, 87%). ^1H NMR (400 MHz, CDCl_3): δ 8.42 (d, $J = 8.0$ Hz, 3H), 7.90 (d, $J = 4.0$ Hz, 3H), 7.64–7.61 (m, 3H), 7.52–7.49 (m, 3 H), 7.46–7.41 (m, 9 H), 5.13 (q, $J = 8.0$ Hz, 6H), 4.65 (s, 6 H), 1.73 (t, $J = 8$ Hz, 9H). ^{13}C NMR (125 MHz, CDCl_3): δ 142.91, 140.72, 139.28, 135.57, 135.07, 131.34, 131.08, 128.77, 127.98, 122.80, 121.48, 121.33, 110.91, 103.26, 42.01, 33.28, 15.96.

Synthesis of cage DA-2



Compound **P1** (229 mg, 0.64 mmol) and cesium carbonate (1252 mg, 3.84 mmol) were dissolved in DMF (256 mL) in a round flask. The reaction mixture was stirred at 60 °C for 0.5 hour. Then the powder of compound **3** (600 mg, 0.64 mmol) was added into the solution and the mixture was reacted for further 24 hours. After the reaction, the mixture was extracted with DCM and brine. The organic phase was washed with brine for 3 times and then dried over anhydrous Na₂SO₄. The concentrated DCM solution was added into MeOH and the precipitate was collected by centrifugation to get the crude product. Pure product **DA-2** (400 mg, 59%) was obtained by column chromatography with DCM/PE 2/1 as the eluents. ¹H NMR (400 MHz, CDCl₃): δ 8.25–8.01 (m, 9H), 7.58–7.42 (m, 12H), 7.14–7.00 (m, 6H), 6.75 (d, *J* = 4.0 Hz, 4 H), 6.43–6.13 (m, 4 H), 5.22–5.00 (m, 6H), 4.65 (s, 3 H), 1.99 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 168.95, 163.48, 144.41, 139.75, 138.46, 136.40, 135.51, 131.42, 130.80, 130.25, 128.97, 128.60, 127.97, 127.67, 121.84, 121.09, 120.63, 119.24, 118.20, 112.75, 111.80, 101.48, 71.34, 41.00, 17.41. MALDI-TOF: Calcd. for C₇₂H₅₄N₆O₃ [M]⁺ 1050.425; Found, 1050.289.

3. Quantum Chemical Calculations

All calculations have been performed with the Gaussian09 A.02 program^[S3] using default procedures, algorithms and integration grids. The initial structure obtained from single crystal analysis was optimized with the range-separated dispersion-corrected hybrid functional ωB97X-D^[S4] in conjunction with the 6-31G(d,p) basis level since it includes a dispersion correction for efficient description of weak interactions.^[S5] In order to maintain consistency with UV-Vis absorption and CD experiments, ground state and excited state optimizations were carried out using dichloromethane ($\epsilon = 8.93$) as the solvent within the framework of the Conductor-like Polarizable Continuum Model (CPCM). Concurrently, time-dependent DFT (TD-DFT) calculations of the

excited state properties were conducted utilizing toluene ($\epsilon = 2.37$, CPCM) as the solvent, in accordance with time-resolved and temperature-dependent photophysical studies.^[S6] Calculated frontier orbitals (two HOMO and two LUMO because the molecule was found of C_3 symmetry) of **DA-2** are displayed in Fig. S1 (Please note that the ethyl groups have been replaced with methyl groups in order to alleviate the computational workload). Frequency calculation was performed with no imaginary frequency found for the optimized molecular geometry.

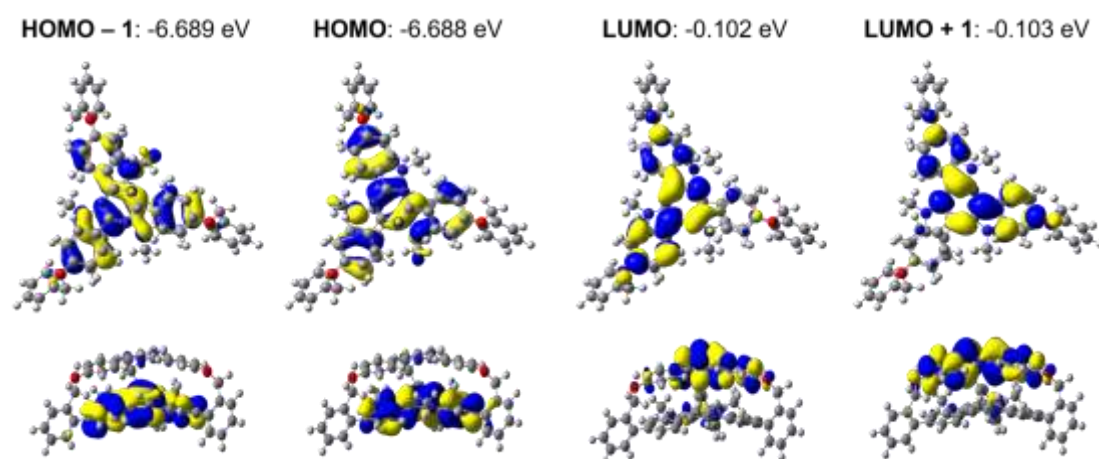


Fig. S1 Calculated frontier orbitals of **DA-2**.

TD-DFT calculations were performed using optimized molecular geometry for the first 20 (singlet:triplet = 50:50) transitions considering toluene as solvent (CPCM). Specifically, TD-DFT calculations were performed under B3LYP/6-311G(d,p) level^[S7] in combination with the Becke-Jonson (BJ) damping (-D3(BJ)) which includes an intramolecular non-covalent interactions correction^[S8] with an additional keyword of IOP(9/40=4).

Table S1. Calculated energy level for **DA-2** model compound.

HOMO -1 (eV)	HOMO (eV)	LUMO (eV)	LUMO +1 (eV)	S ₁ (eV)	T ₁ (eV)	ΔE_{ST} (eV)	OS S ₁ (f)
-6.689	-6.688	-0.102	-0.103	2.757	2.624	0.133	0.0018

Table S2. The contribution of the molecular orbitals (MOs) of the transition from ground (S_0) to excited singlet (S_1 and T_1) for **DA-2** model compound.

Transition	OS (f)	Major contributions				λ (nm)
S_1	0.0018	H-1->LUMO	H-1->L+1	HOMO->LUMO	HOMO->L+1	449.74
		(20%)	(23%)	(34%)	(22%)	
T_1	0.0000	H-1->LUMO	H-1->L+1	HOMO->LUMO	HOMO->L+1	472.52
		(22%)	(14%)	(16%)	(22%)	

Excited state geometry optimization were performed under CAM-B3LYP^[S9]/6-311G(d,p) level in combination with the Becke-Jonson (BJ) damping (-D3(BJ)) which includes an intramolecular non-covalent interactions correction with an additional keyword of IOP(9/40 = 4) considering DCM as solvent (CPCM). Hole/electron analysis, transition dipole moment analysis and magnetic transition dipole moment analysis were done by Multiwfn Ver 3.8. ^[S10]

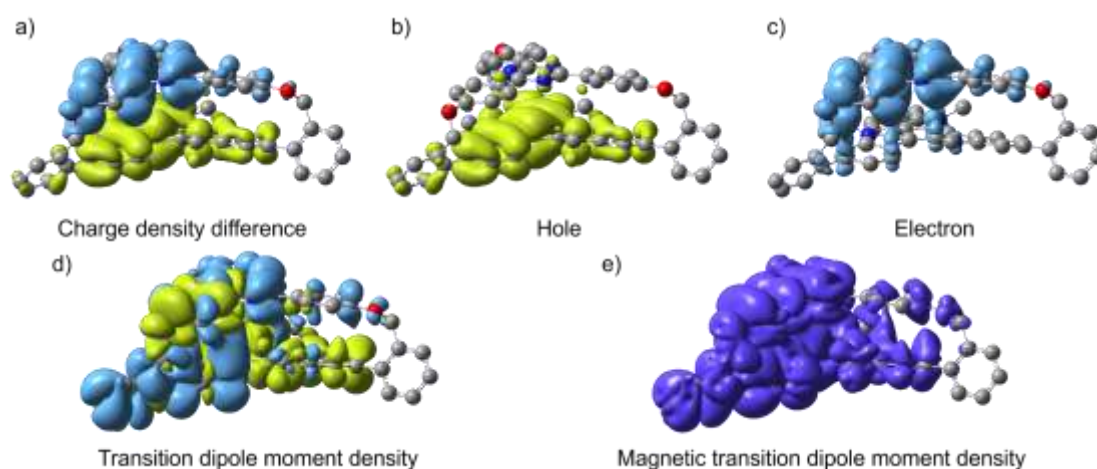


Fig. S2 Excited state analysis of optimized S_1 geometry for **DA-2** with isovalue = 0.0004, (a) charge density difference analysis and S_1 transition; (b) and (c) hole/electron analysis of S_1 state; (d) and (e) electronic and magnetic transition dipole moment analysis of S_1 state.

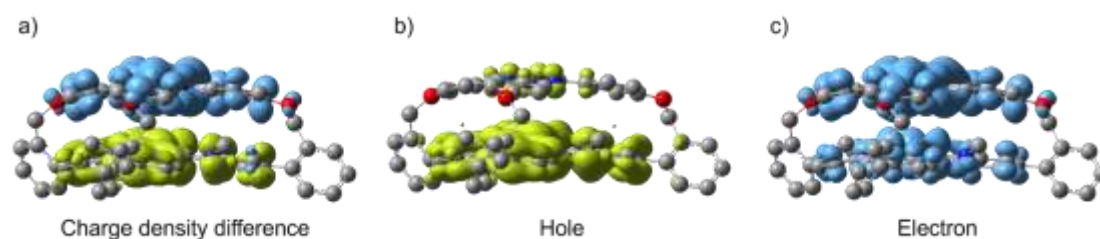


Fig. S3 (a) Charge density difference analysis and T_1 transition; (b) and (c) hole/electron analysis of T_1 state

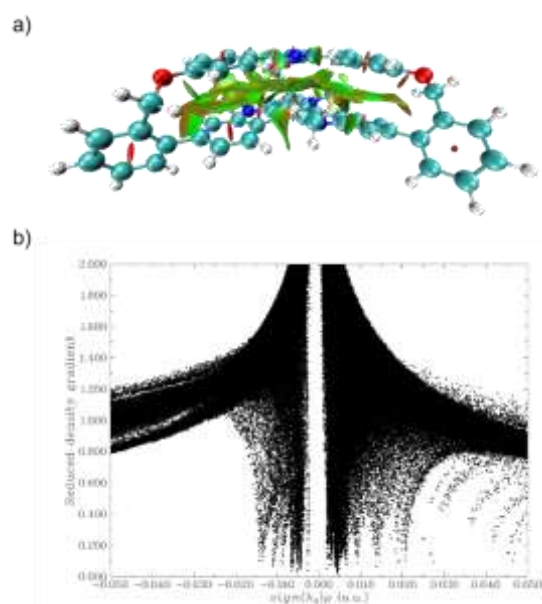


Fig. S4 (a) Reduced density gradient (RDG) isosurface map (isovalue = 0.50) and (b) corresponding scatter diagram (plots of RDG to $\text{sign}(\lambda_2)\rho$) for **DA-2**.

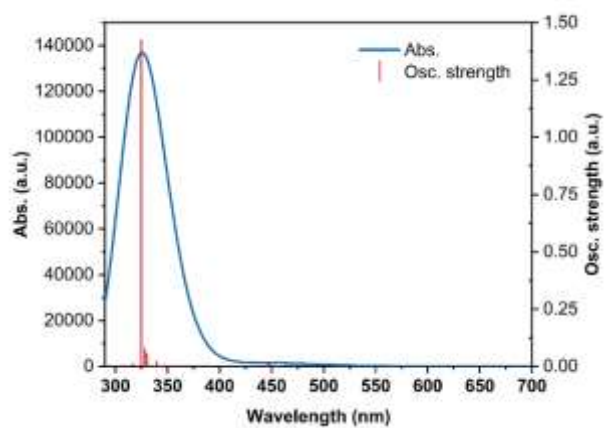


Fig. S5 Predicted UV-Vis absorption spectrum and oscillator strength of major transitions.

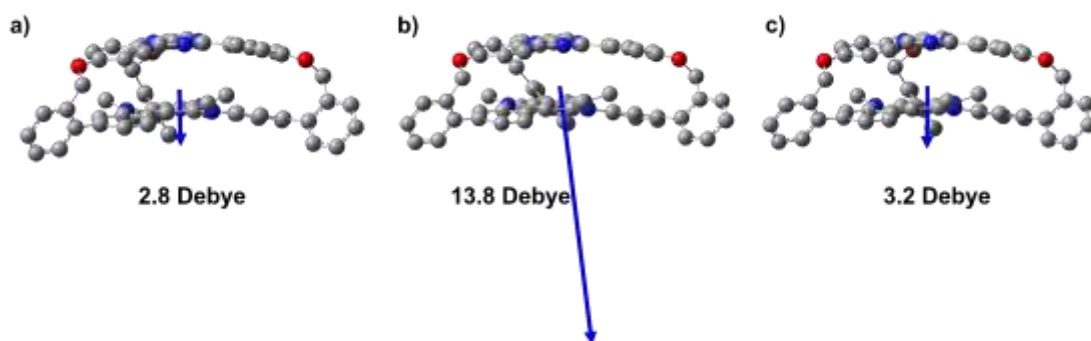


Fig. S6 Dipole moments of (a) ground state, (b) S_1 excited state and (c) T_1 excited state.

4. Photophysical Experiments

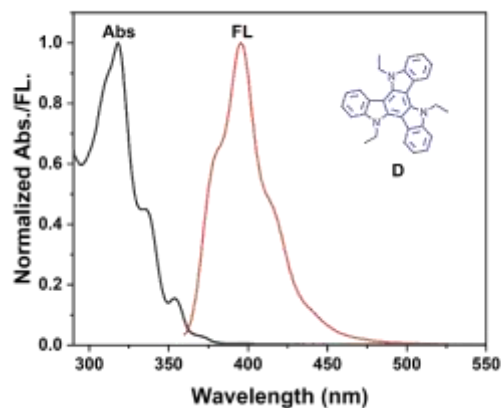


Fig. S7 Absorption and fluorescence spectra of reference electron donor **D** in toluene solution.

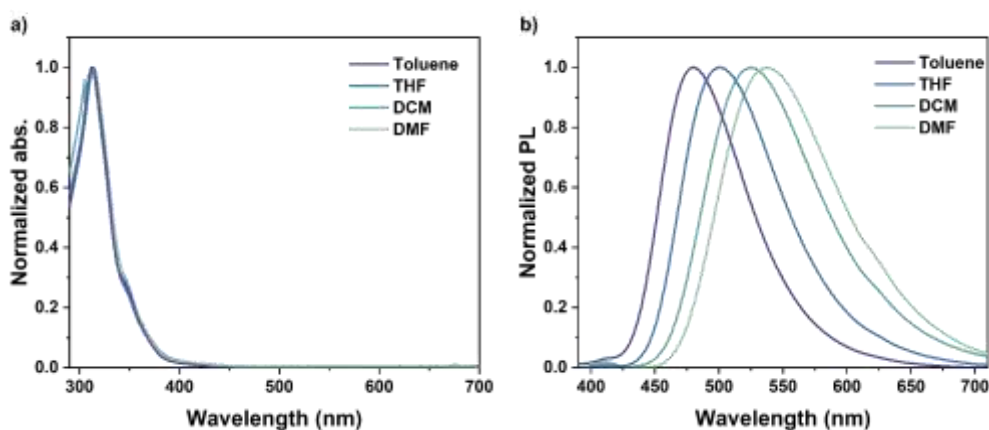


Fig. S8 Absorption (a) and photoluminescence (Excitation wavelength: 310 nm) (b) spectra of DA-2 in different solvents.

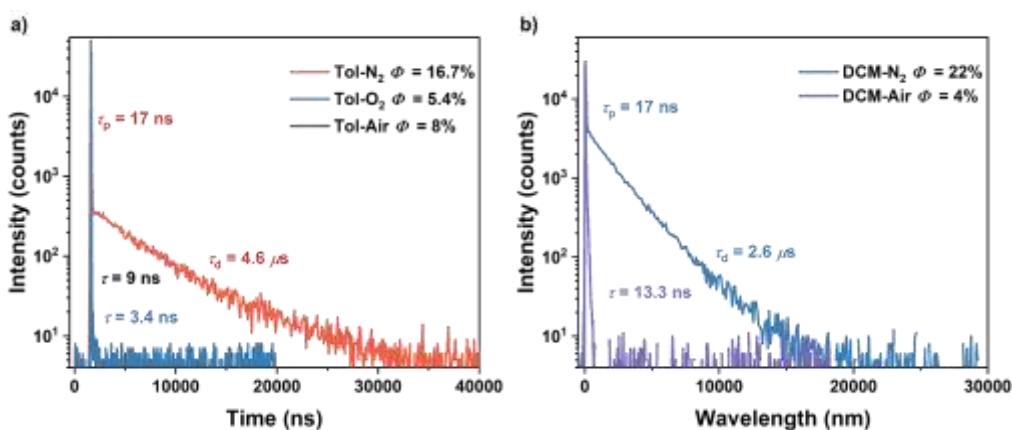


Fig. S9 Time resolved PL of DA-2 in toluene (a) and DCM (b) solution at 298 K. (Excitation wavelength: 340 nm)

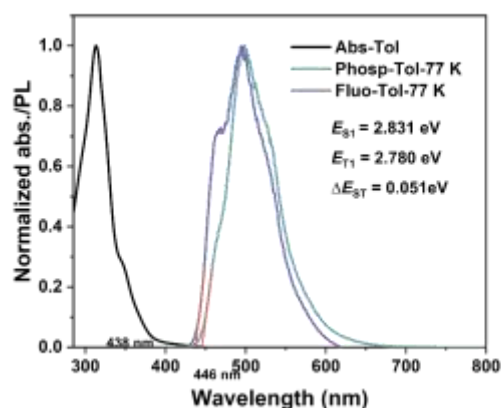


Fig. S10 Absorption, fluorescence and phosphorescence spectra of **DA-2** in toluene solution. The energy levels of S_1 and T_1 excited states were calculated from the onset of fluorescence and phosphorescence spectra.

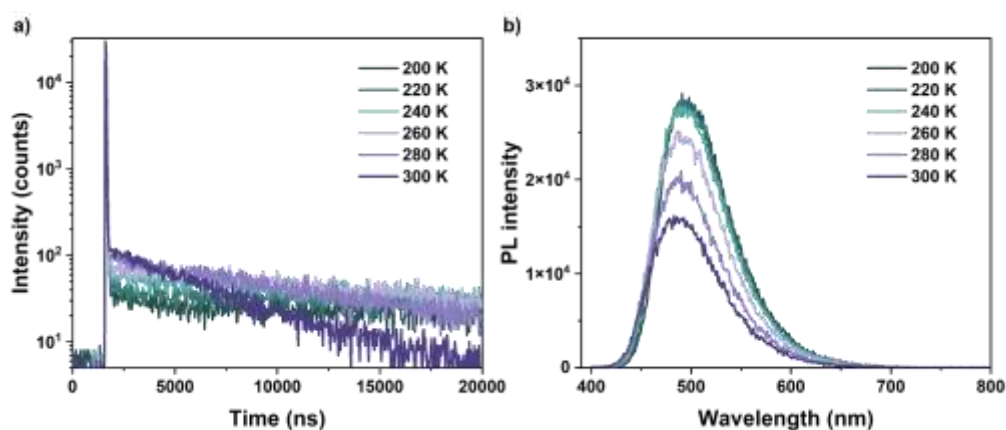


Fig. S11 mperature dependence of time resolved PL in toluene (a) and the corresponding PL spectra at each temperature (b).

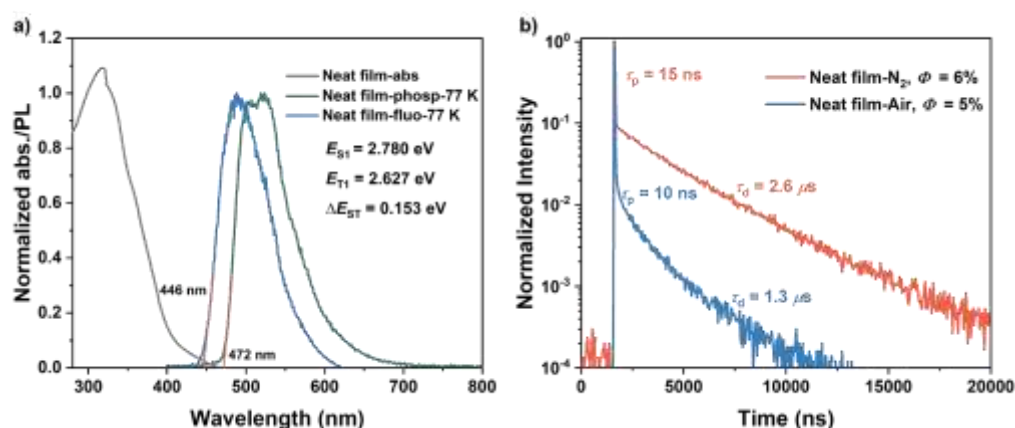


Fig. S12 (a) Solid-state absorption (298 K), fluorescence and phosphorescence (77 K) spectra of **DA-2** in neat film. The energy difference of S_1 and T_1 excited states were calculated as 0.015 eV from the onset of fluorescence and phosphorescence spectra. (b) The time resolved PL spectra at 298 K in N_2 and air condition.

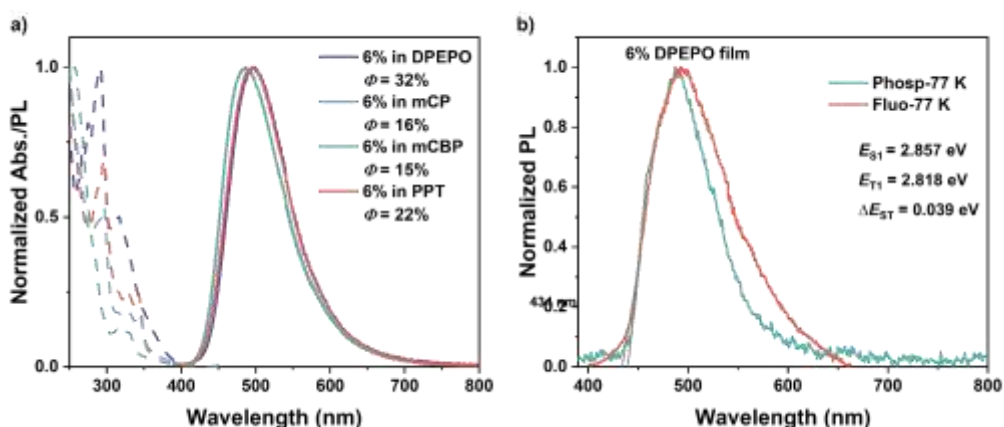


Fig. S13 Solid-state absorption and photoluminescence of **DA-2** doped in different host materials (a) and the fluorescence and phosphorescence spectra of **DA-2** in neat film at 77 K (b). The energy levels of S_1 and T_1 excited states were calculated from the onset of fluorescence and phosphorescence spectra.

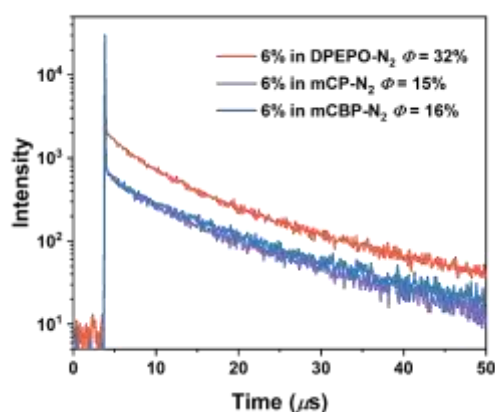


Fig. S14 Time resolved PL of **DA-2** in different host materials (6 wt%). In DPEPO host matrix, the proportion of delayed component was obviously increased which is consistent with the increase of PLQY.

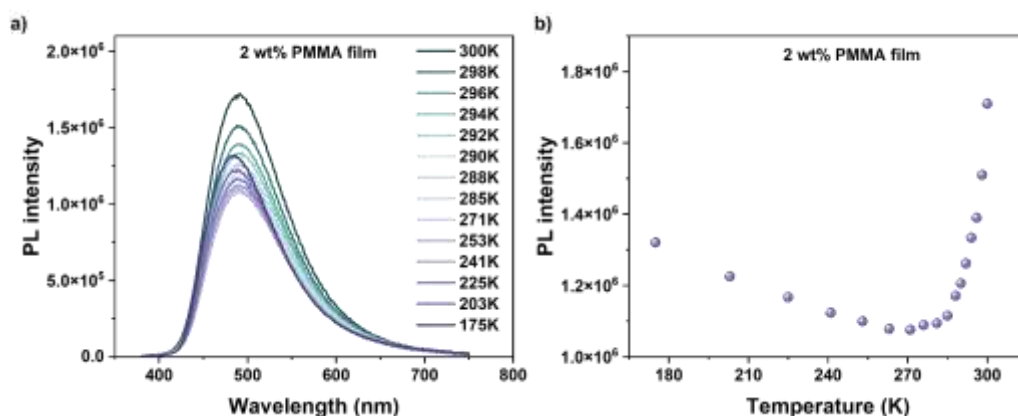


Fig. S15 Temperature-dependence of PL spectra of **DA-2** in 2 wt% doped PMMA film.

Table S3. Summary of photophysical properties of **DA-2** in different conditions.

	Tol			DCM		Neat	PMMA	DPEPO	PPT	mCP	mCBP
						film	film	film	film	film	film
λ_{\max} (nm)	485			520		490	480	495	495	485	485
Φ_{PLQY} (%)	N ₂	Air	O ₂	N ₂	Air	6	20	32	22	15	16

5. Chiroptical Properties

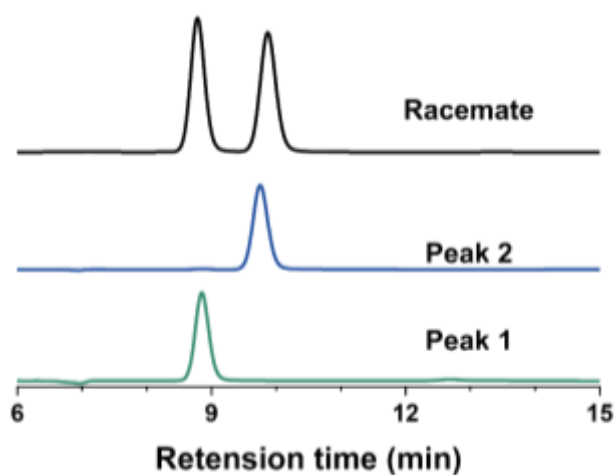


Fig. S16 Chiral HPLC results of compound **DA-2**.

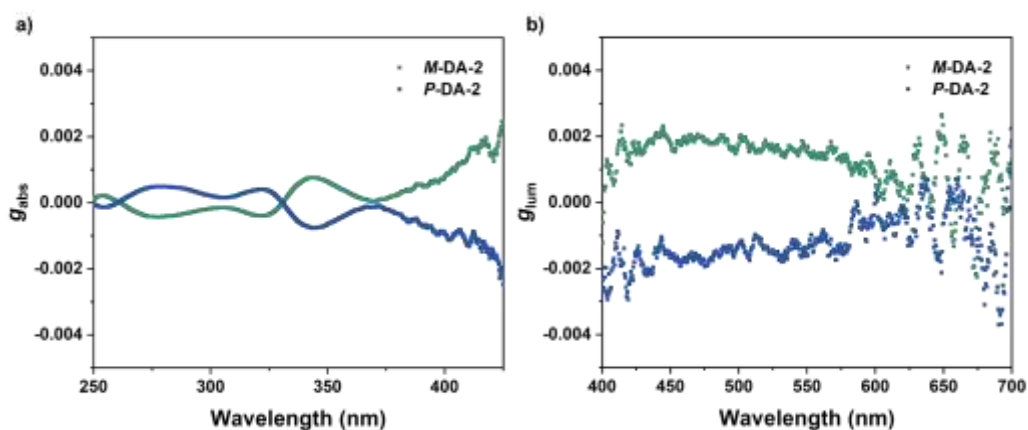


Fig. S17 Experimental g factors of absorption in DCM solution (a) and luminescence in PMMA film (b) of **DA-2** enantiomers.

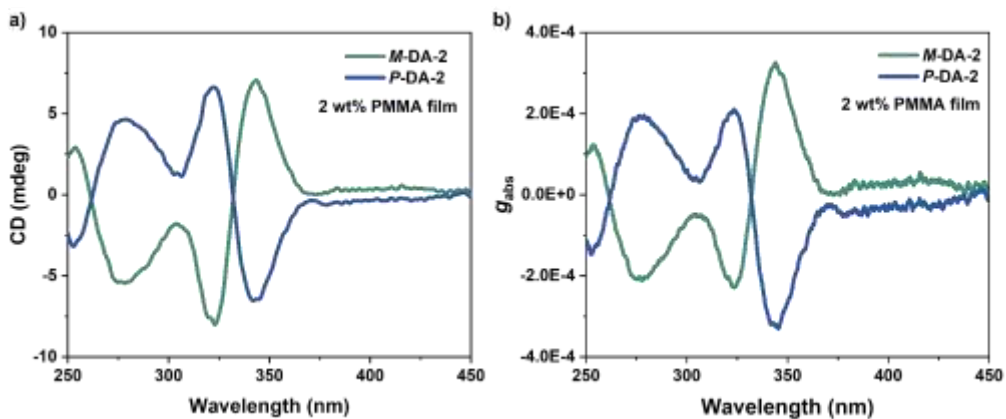


Fig. S18 CD spectrum (a) and the corresponding g factor (b) of DA-2 enantiomers in 2 wt% doped PMMA film.

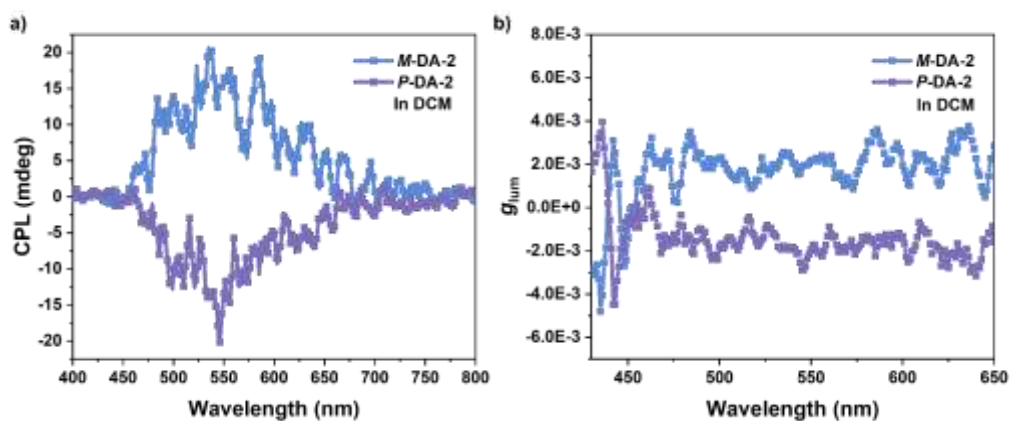
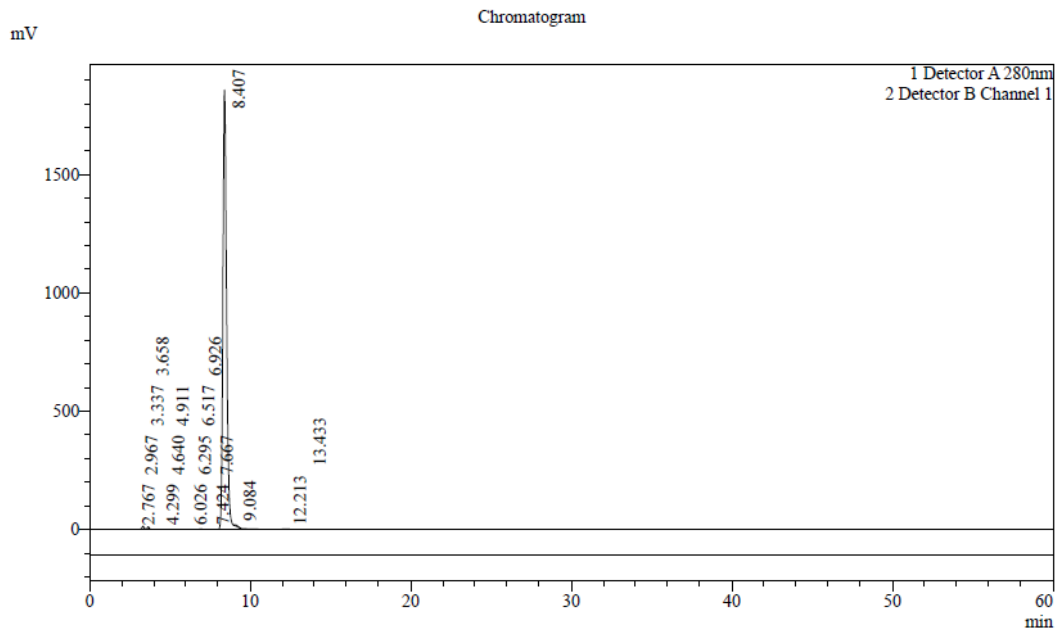


Fig. S19 CPL spectrum (a) and the corresponding g factor (b) of DA-2 enantiomers in DCM solution.

Sample Information

Acquired by : System Administrator
 Sample Name : DA-2-PK1--DCM-Hex-60-40
 Sample ID :
 Tray# : 1
 Vial# : 77
 Injection Volume : 20
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 Method File : Method-20211124.lcm
 Batch File :
 Report Format File : DEFAULT.lsr
 Date Acquired : 12/12/2023 6:35:48 PM
 Date Processed : 12/12/2023 7:35:51 PM



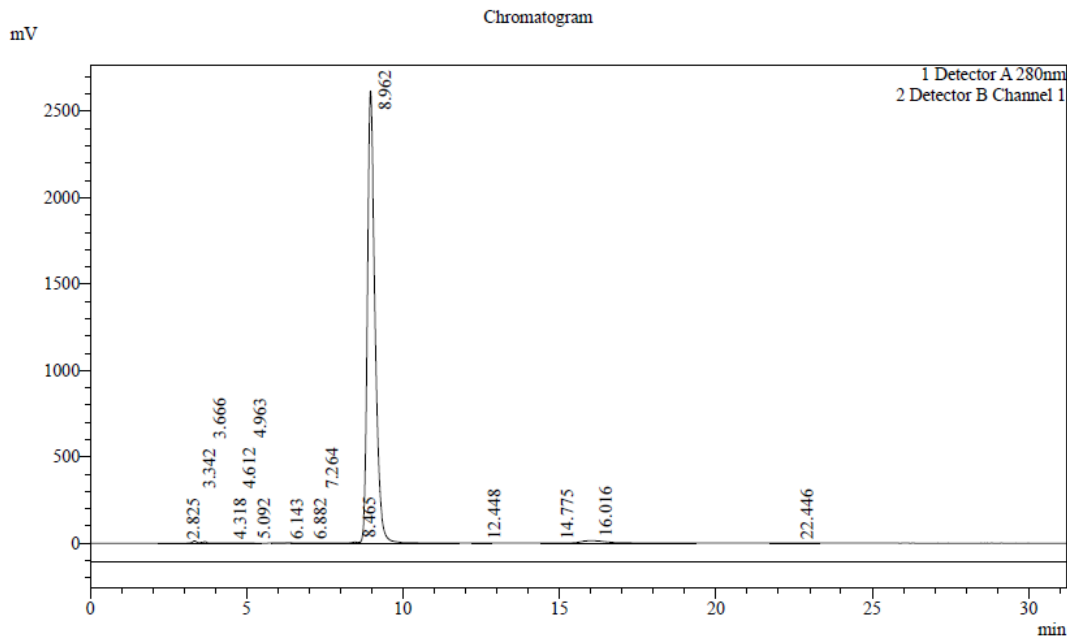
Peak Table

Detector A 280nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	2.767	1768	78	0.006	0.004
2	2.967	1115	99	0.004	0.005
3	3.337	127297	13631	0.423	0.720
4	3.658	95426	11493	0.317	0.607
5	4.299	10526	677	0.035	0.036
6	4.640	4068	283	0.014	0.015
7	4.911	1363	137	0.005	0.007
8	6.026	3107	285	0.010	0.015
9	6.295	2641	196	0.009	0.010
10	6.517	1104	145	0.004	0.008
11	6.926	21635	1330	0.072	0.070
12	7.424	6980	427	0.023	0.023
13	7.667	5329	332	0.018	0.018
14	8.407	29692116	1858709	98.746	98.208
15	9.084	52690	3835	0.175	0.203
16	12.213	31559	587	0.105	0.031
17	13.433	10546	383	0.035	0.020
Total		30069270	1892628	100.000	100.000

Fig. S20 HPLC diagram of the one enantiomer of DA-2.

Acquired by : System Administrator
 Sample Name : DA-2-PK2--DCM-Hex-60-40
 Sample ID :
 Tray# : 1
 Vial# : 76
 Injection Volume : 20
 Data File : DA-2-PK2--DCM-Hex-60-41.lcd
 Method File : Method-20211124.lcm
 Batch File :
 Report Format File : DEFAULT.lsr
 Date Acquired : 12/12/2023 4:26:25 PM
 Date Processed : 12/12/2023 4:57:37 PM

Sample Information



Peak Table

Peak#	Ret. Time	Area	Height	Area%	Height%
1	2.825	3701	110	0.008	0.004
2	3.342	134958	13664	0.296	0.513
3	3.666	82686	9531	0.181	0.358
4	4.318	11498	859	0.025	0.032
5	4.612	5903	349	0.013	0.013
6	4.963	1623	167	0.004	0.006
7	5.092	1665	145	0.004	0.005
8	6.143	3321	210	0.007	0.008
9	6.882	7409	445	0.016	0.017
10	7.264	15638	957	0.034	0.036
11	8.465	88363	6355	0.194	0.238
12	8.962	44360945	2616392	97.224	98.186
13	12.448	2142	121	0.005	0.005
14	14.775	1775	72	0.004	0.003
15	16.016	889486	14985	1.949	0.562
16	22.446	16340	382	0.036	0.014
Total		45627452	2664744	100.000	100.000

Fig. S21 HPLC diagram of the other enantiomer of DA-2.

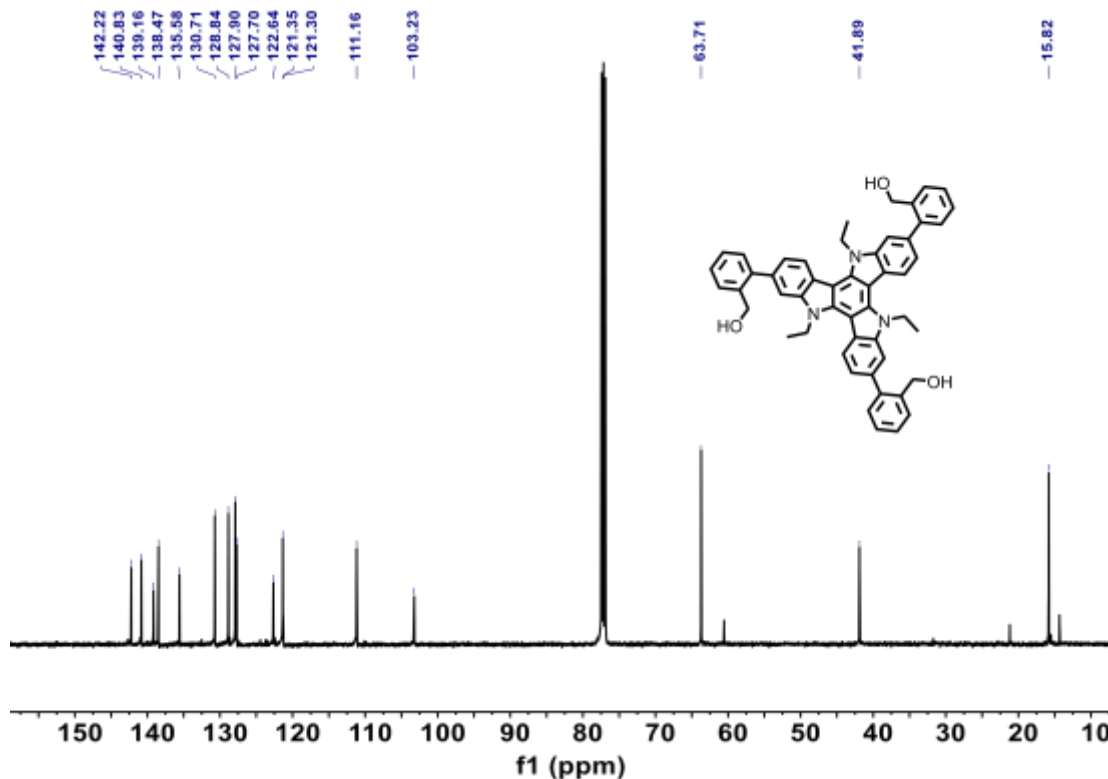
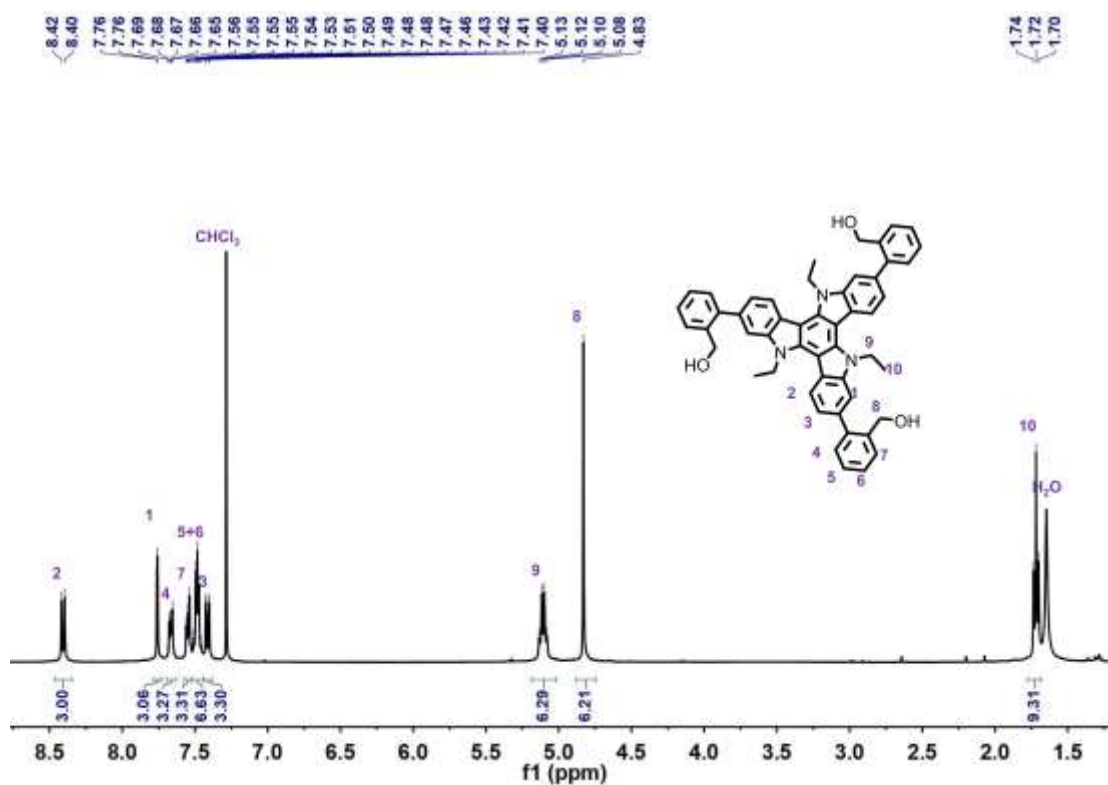
6. X-Ray Crystallography

CCDC deposition number 2308211.

Table S4. Crystal data and structure refinement for **DA-2 • CHCl₃**.

Identification code	DA-2 • CHCl₃
Empirical formula	C ₇₃ H ₅₅ Cl ₃ N ₆ O ₃
Formula weight	1170.58
Temperature	173 K
Wavelength	1.54178 Å
Crystal system, space group	Orthorhombic, <i>Pca</i> 2 ₁
Unit cell dimensions	$a = 24.6915 (5) \text{ \AA}, \alpha = 90^\circ$ $b = 14.7339 (3) \text{ \AA}, \beta = 90^\circ$ $c = 15.6091 (3) \text{ \AA}, \gamma = 90^\circ$
Volume	5678.6 (2)
Z, Calculated density	4, 1.369 g/cm ³
Absorption coefficient	1.921 mm ⁻¹
F (000)	2440.0
Crystal size	0.18×0.16×0.14 mm ³
Theta range for data collection	2.999 to 68.217 deg
Limiting indices	-29≤h≤28, -17≤k≤17, -18≤l≤18
Reflections collected / unique	58493/10368 [R(int) = 0.0670]
Completeness to theta = 67.679	100.0%
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	0.7631 and 0.6359
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10368/2/769
Goodness-of-fit on F ²	1.038
Final R indices [I > 2 sigma (I)]	R1 = 0.0519, wR2 = 0.1404
R indices (all data)	R1 = 0.0605, wR2 = 0.1490
Extinction coefficient	n/a
Largest diff. peak and hole	1.067 and -0.665 e.Å ⁻³

7. NMR and MALDI-TOF MS Spectra of Precursors and Cage DA-2



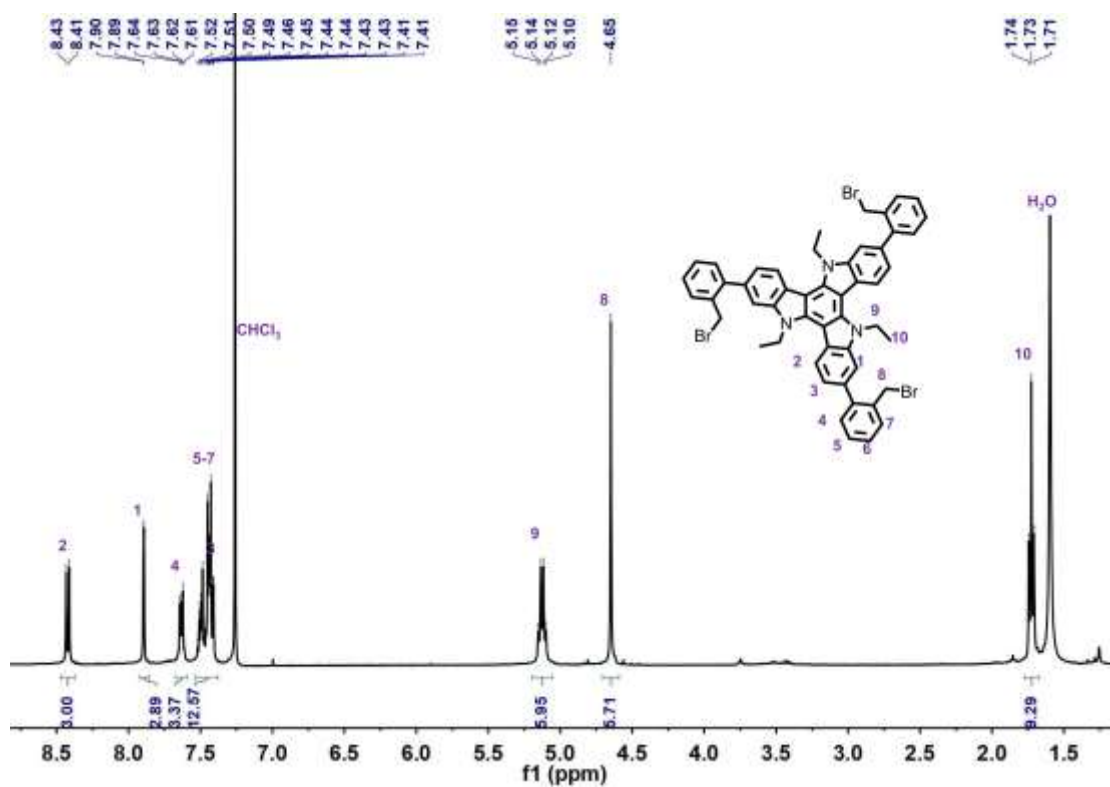


Fig. S24 ^1H NMR spectrum of compound 3 in CDCl_3 (400 MHz, 298 K).

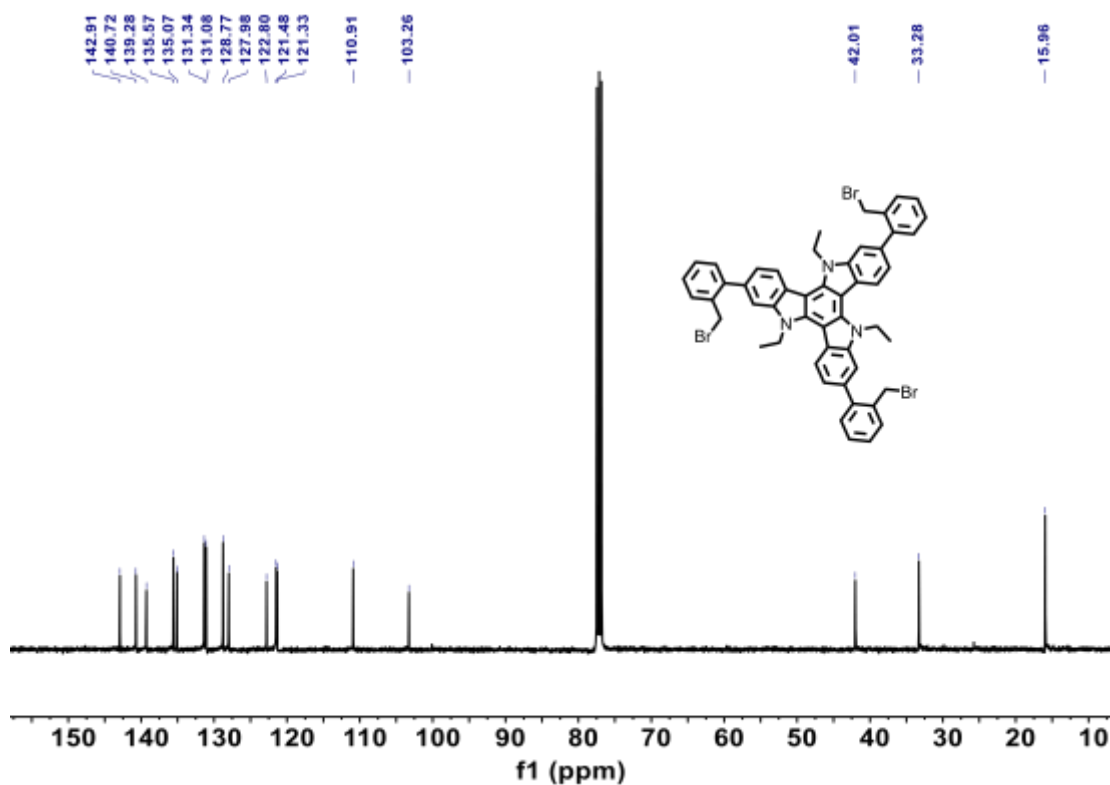


Fig. S25 ^{13}C NMR spectrum of compound 3 in CDCl_3 (125 MHz, 298 K).

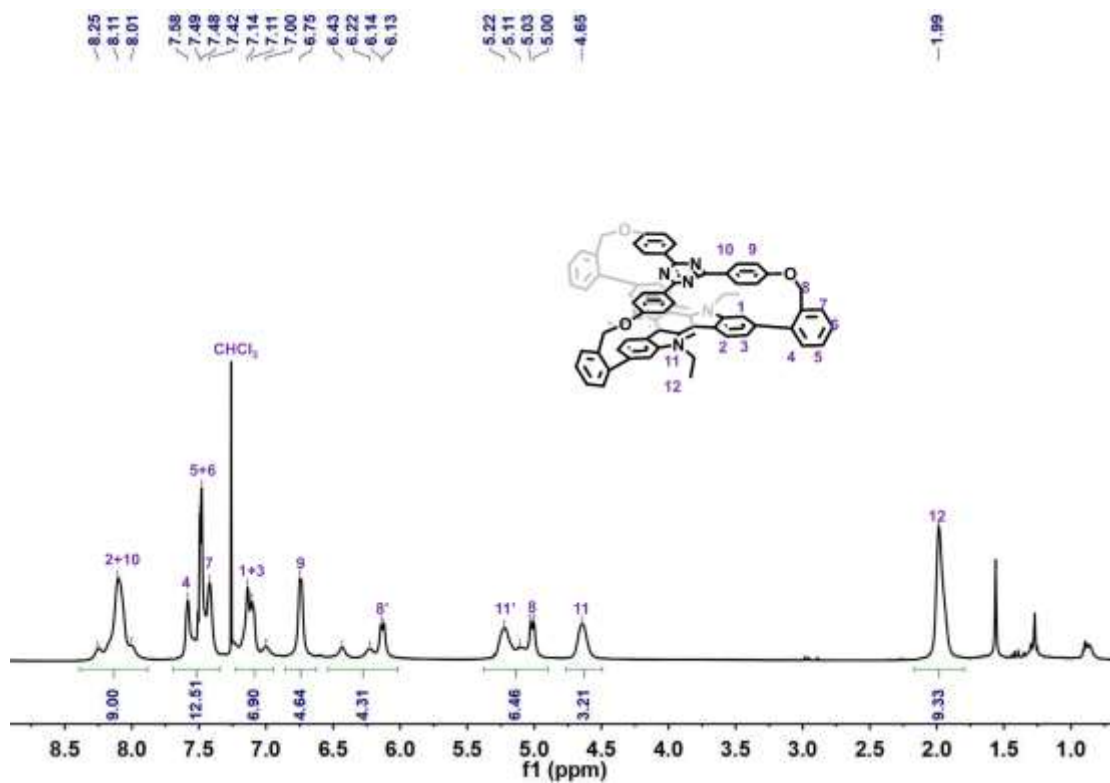


Fig. S26 ¹H NMR spectrum of compound DA-2 in CDCl₃ (400 MHz, 298 K).

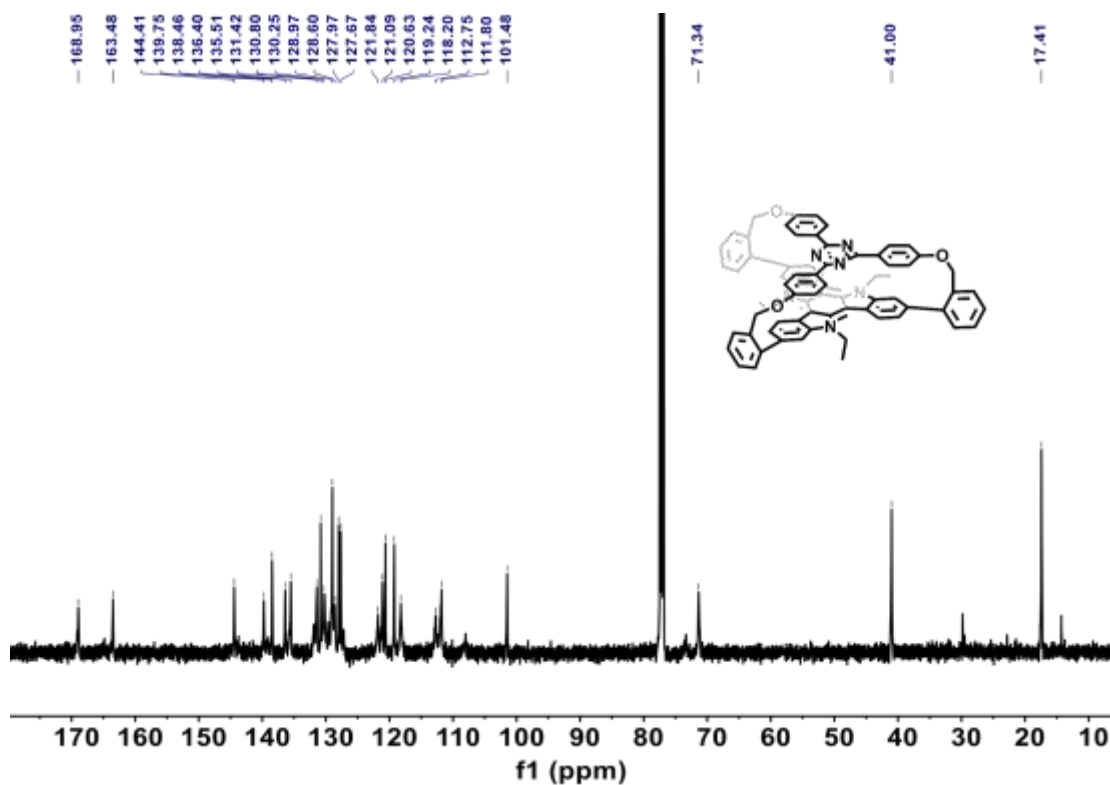


Fig. S27 ¹³C NMR spectrum of compound DA-2 in CDCl₃ (125 MHz, 298 K).

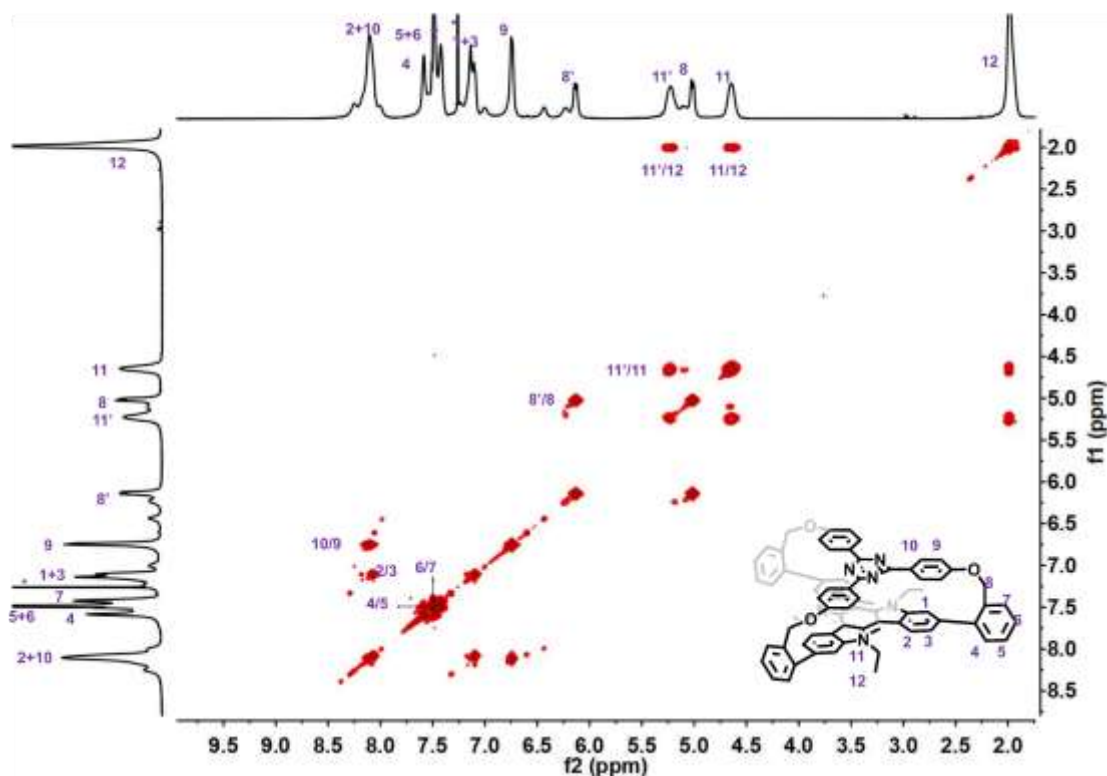


Fig. S28 ^1H - ^1H COSY spectrum of compound **DA-2** in CDCl_3 (400 MHz, 298 K).

The racemic compound and two enantiomers have the same ^1H NMR spectrum, and we think the small peaks in Figure S17 were signals from different rotational conformers with unequal populations of the sample instead of from impurities. The rotational conformers can originate from the rotation of phenyl linker and ethyl group which influences the chemical shift. To prove this, we changed the deuterated solvent from CDCl_3 to $\text{C}_2\text{D}_2\text{Cl}_4$ and conducted following additional NMR experiments which have been added as Fig S29–S35. NOESY spectrum of the sample in Fig S30 indicates the distances between protons on the acceptor, donor and benzyl group are close enough to influence the chemical shift of each other. In variable temperature ^1H NMR from 228 K to 338 K in $\text{C}_2\text{D}_2\text{Cl}_4$ (Fig. S29), at lower temperature, both the main peak and side peaks assigned to proton 2 and 10 shows more splitting which can be attributed to the lower exchange rate between different conformers at lower temperature. With temperature increases, the exchange rate increases which leads to the broadening and merging of peaks from different conformers. At a higher temperature of 373 K (Fig S33), the peaks split clearer which can be well assigned together with the COSY spectra at 373 K. Additionally, DOSY NMR of the sample in ESI Fig S33 also displays that only one dominant species of **DA-2** with the residue of solvents.

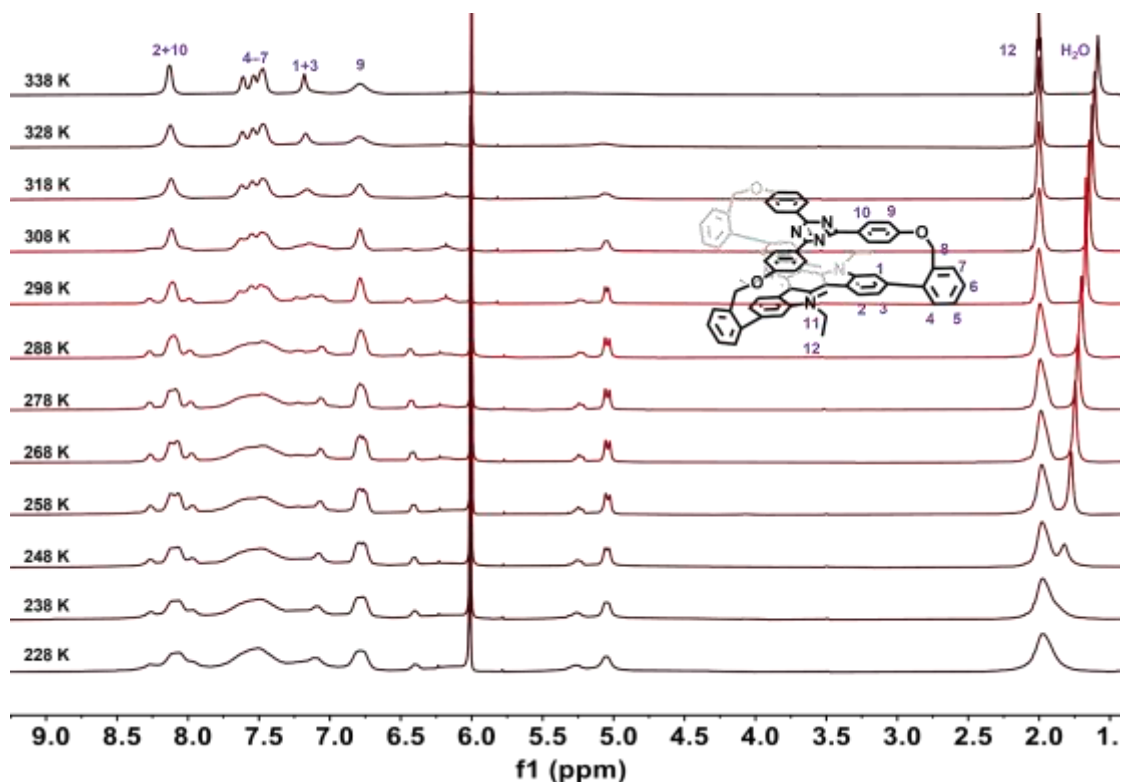


Fig. S29 Variable temperature ^1H NMR spectra of compound DA-2 in $\text{C}_2\text{D}_2\text{Cl}_4$ (500 MHz). At higher temperature, signals are broadened and merged. This can be attributed to the chemical exchange between different conformers resulted from the rotation of ethyl and benzyl groups. The exchange rate is increased at higher temperature which leads to the averaging of signals from different conformers and thus the broadening and merging of peaks.^{S11,S12}

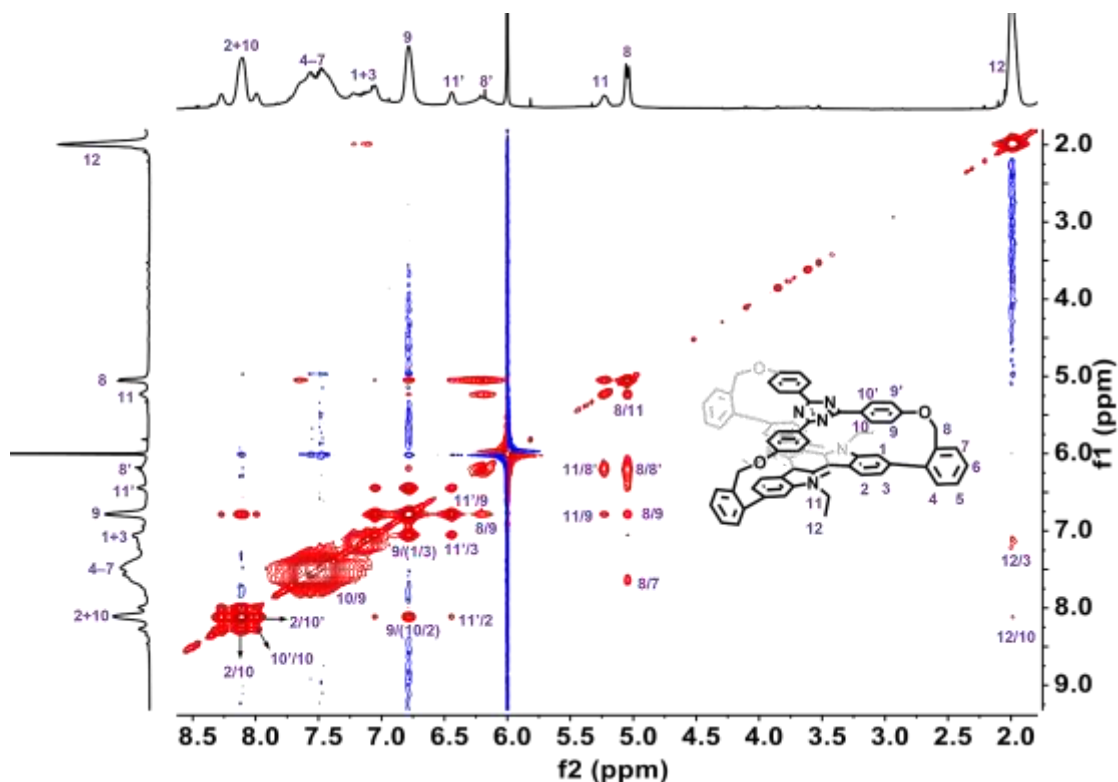


Fig. S30 ^1H - ^1H NOESY NMR spectrum of compound DA-2 in $\text{C}_2\text{D}_2\text{Cl}_4$ (500 MHz, 298 K).

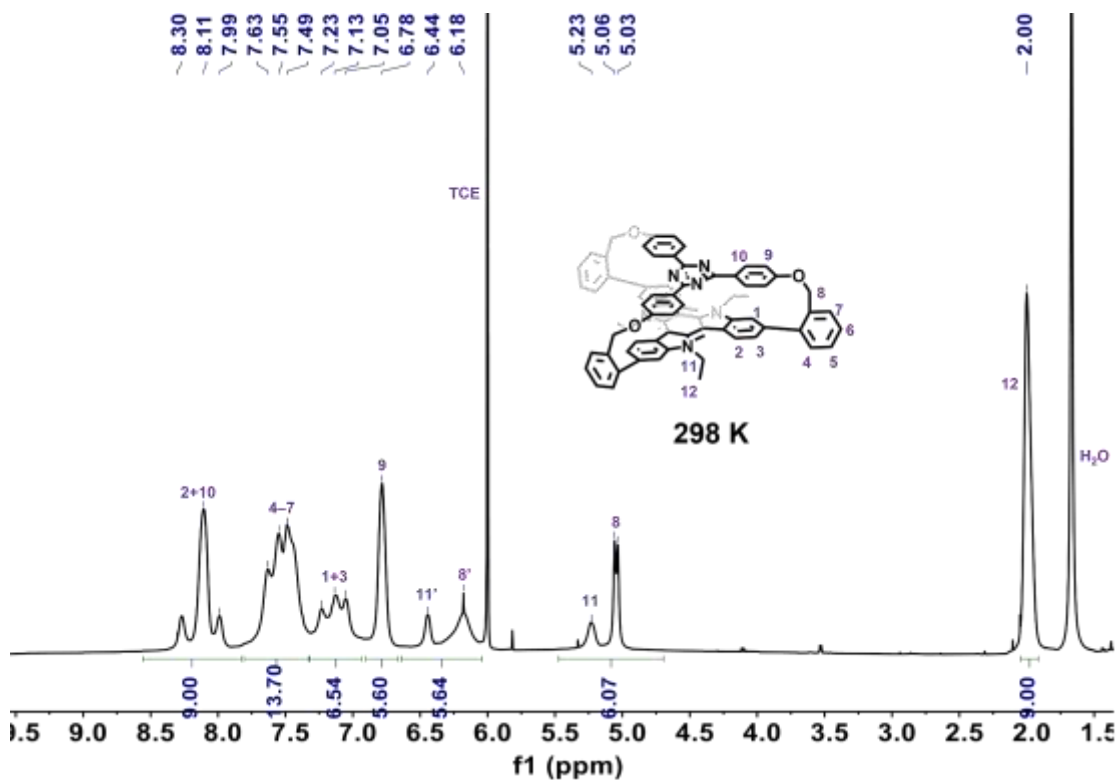


Fig. S31 ¹H NMR spectrum of compound DA-2 in C₂D₂Cl₄ (500 MHz, 298 K).

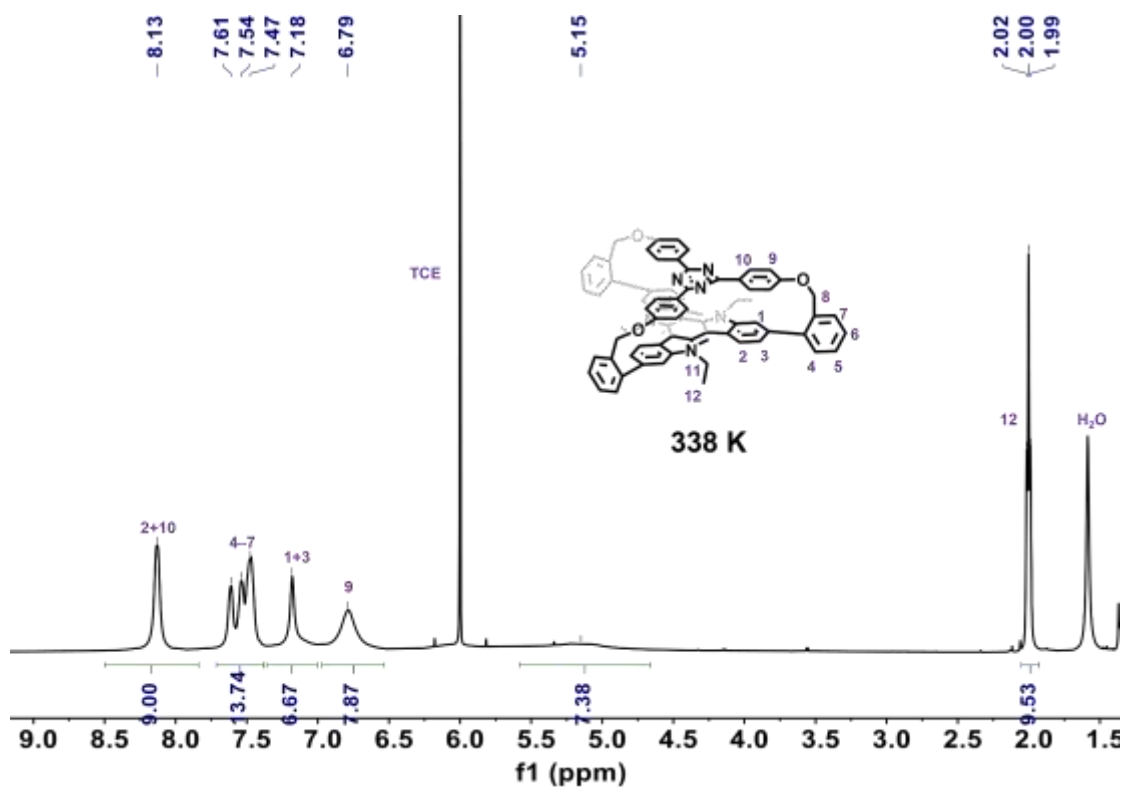


Fig. S32 ¹H NMR spectrum of compound DA-2 in C₂D₂Cl₄ (500 MHz, 338 K). The broad flat peak at 5.15 ppm is assigned to proton 8 and 11 and the integrate is smaller because of the peak broadening and overlapping with solvent peaks.

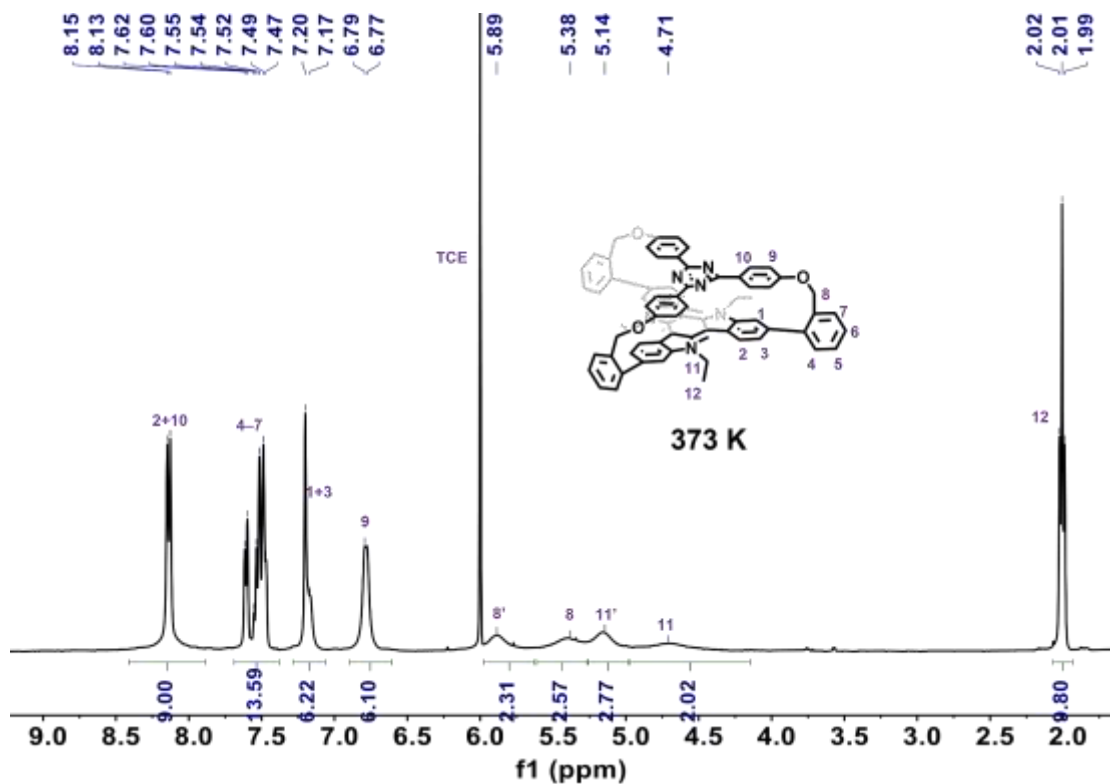


Fig. S33 ^1H NMR spectrum of compound DA-2 in $\text{C}_2\text{D}_2\text{Cl}_4$ (400 MHz, 373 K).

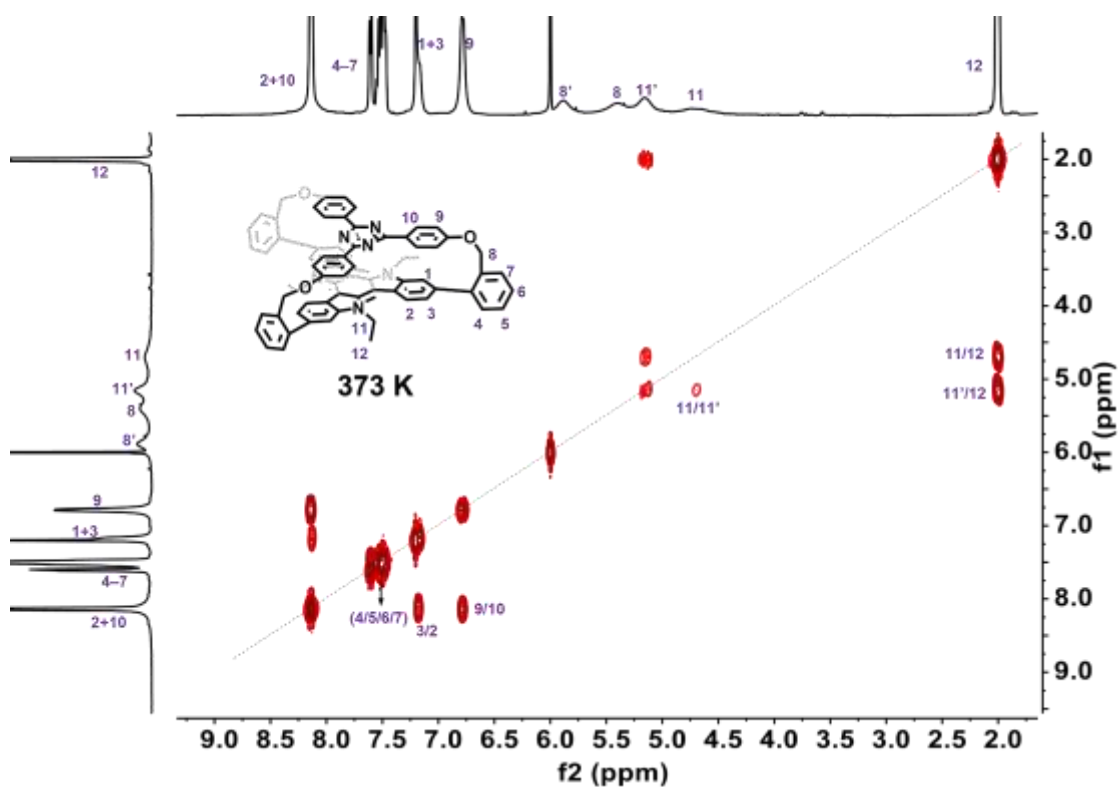


Fig. S34 ^1H - ^1H COSY NMR spectrum of compound DA-2 in $\text{C}_2\text{D}_2\text{Cl}_4$ (400 MHz, 373 K).

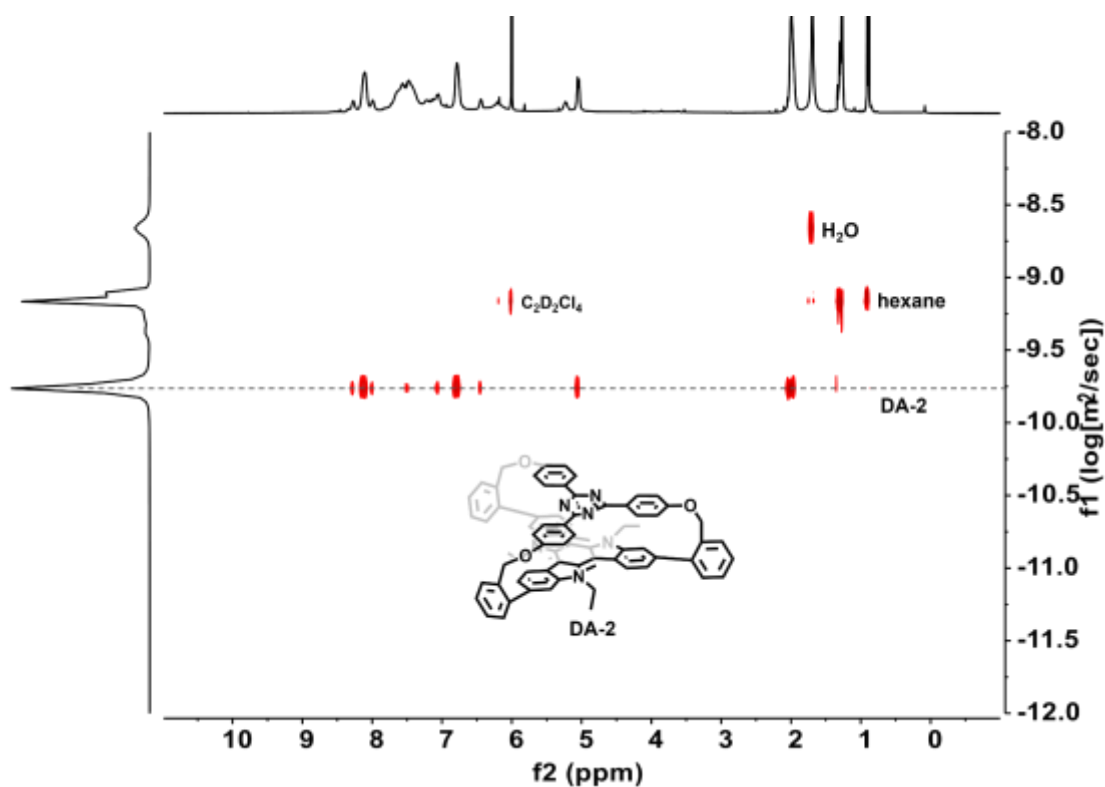


Fig. S35 DOSY NMR spectrum of compound **DA-2** in $C_2D_2Cl_4$ (500 MHz, 298 K).

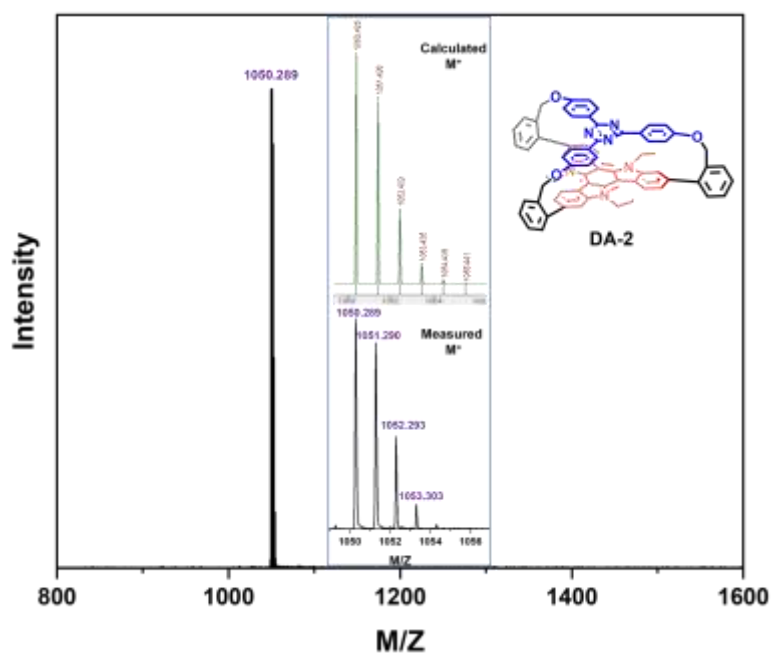


Fig. S36 MALDI-TOF MS spectrum of cage **DA-2**, and the inset are the calculated and experimental isotopic distributions of the cage.

8. References

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9. Optimized Geometry of DA-2

O	-4.49096105	-5.17944382	1.63754720
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