

Supporting Information

**Stable and soluble oligomers of porous organic cage
through post-synthesized modification**

Chenjuan Yu,^{a,b} Yanpin Yang^{*a} and Youfu Wang^{*b}

^a. School of Materials Engineering, Shanghai University of Engineering Science, 333

Longteng Road, Shanghai 201620, PR China. E-mail: yangc0709@126.com

^b. School of Chemistry and Chemical Engineering, Frontiers Science Center for

Transformative Molecules, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai

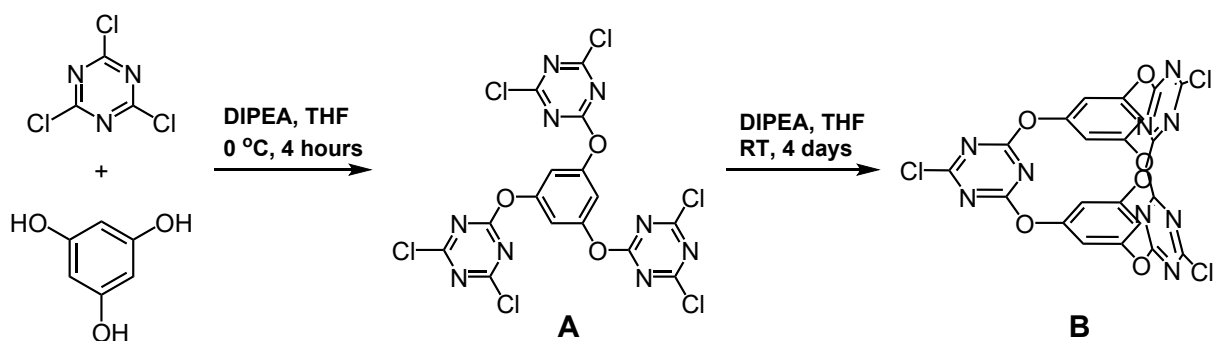
200240, PR China. E-mail: wyfown@sjtu.edu.cn

1. Materials and general procedures

All chemical reagents were commercially available and used as received. The nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 400 (400 MHz for ^1H -NMR and 100 MHz for ^{13}C -NMR) in CDCl_3 at ambient probe temperature. Matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectra were performed on a Bruker Speed MALDI-TOF 7090 (Bruker, Germany). The Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 FT-IR using ATR measurements for solids as neat samples. The dynamic light scattering (DLS) was performed with a Size and Zeta Potential Analyzer (Malvern, UK).

2. Synthesis Procedure

2.1 Synthesis of the Triazine molecular cage

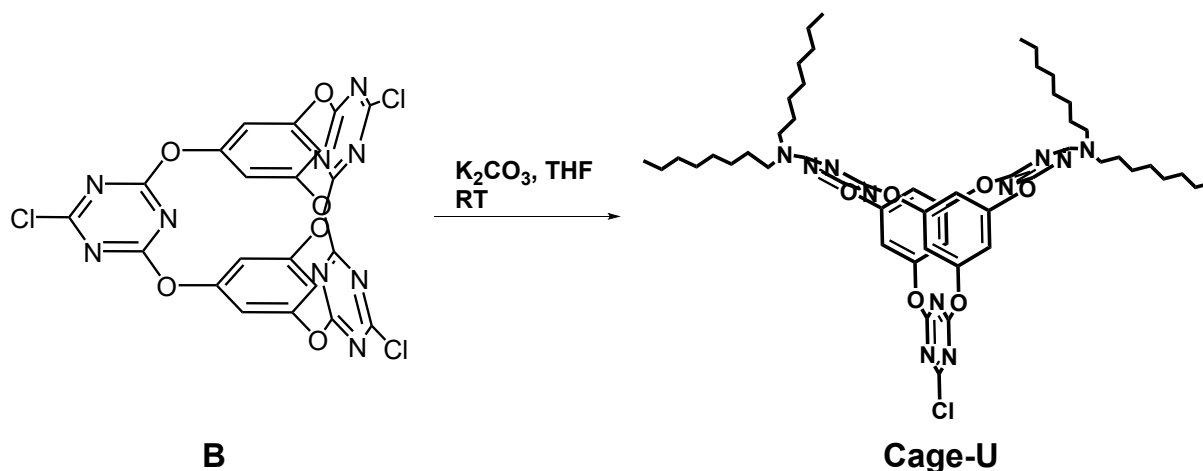


A: A solution of 1,3,5-benzenetriol (1.26 g, 10 mmol, 1.0 eq.) and N,N-diisopropylethylamine (DIPEA, 4.86 g, 37.6 mmol, 3.76 eq.) were dissolved in THF (60 mL). The THF (100 mL) solution containing cyanuric chloride (8.30 g, 45 mmol, 4.5 eq.) was added dropwise at 0 °C for 20 minutes. The resulting mixture was further stirred at 0 °C for 4 hours. The suspensions were filtered to remove insoluble precipitates. After removal of the solvent, the crude product was purified by column chromatography on silica gel (petroleum ether: acetone = 18: 1) to afford **A** as a white solid (4.45 g, yield 78.1%).

B: 1,3,5-benzenetriol (0.50 g, 4 mmol, 1.0 eq.) and **A** (2.28 g, 4 mmol, 1.0 eq.) were dissolved in THF (200 mL), respectively. The above two solutions were added dropwise to THF (400 mL) containing DIPEA (1.86 g, 14.4 mmol, 3.6 eq.) at the same rate for 4 h at room temperature. After the two solutions were added, the mixture was stirred at room temperature for another 4 days. The organic layer was collected through filtration and solvent was removed under reduced pressure. The crude product was subjected to silica gel chromatography with PE: EtOAc (3: 1,

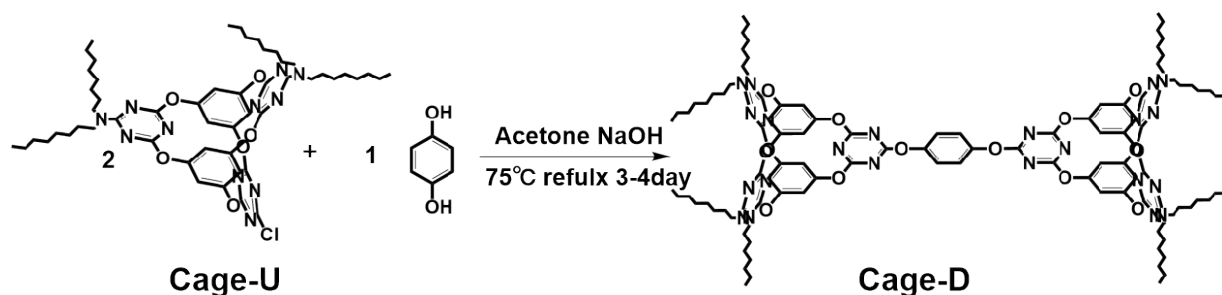
v/v) as eluent to afford the final product **B** as white solid (0.90 g, yield 38.4%).

2.2 Synthesis of the Cage-Unimer (Cage-U)



Cage-U: **B** (0.50 g, 0.85 mmol, 1.0 eq.) and K_2CO_3 (0.42 g, 3.06 mmol, 3.6 eq.) were added to THF (40 mL) and the mixture was cooled to 0 °C. Dioctylamine (0.45 g, 1.88 mmol, 2.2 eq.) was dissolved in THF (60 mL) and added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. After that, the reaction mixture was filtered to remove the precipitate. Then solvent was removed under reduced pressure. The residue was subjected to column chromatography with PE: EtOAc (40: 1, v/v) as eluent to afford **Cage-U** (0.38 g, yield 44.8%). 1H NMR (400 MHz, $CDCl_3$) δ 6.63 (t, $J = 2.0$ Hz, 2H), 6.56 (d, $J = 2.0$ Hz, 4H), 3.57 (t, $J = 8.0$ Hz, 8H), 1.63 (br, 8H), 1.33-1.25 (m, 40H), 0.88 (t, $J = 6.8$ Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.48, 172.93, 172.07, 167.45, 153.67, 152.16, 116.43, 114.44, 47.70, 31.85, 29.45, 29.31, 27.62, 26.91, 22.70, 14.15. MS (Maldi TOF): Calculated for $C_{53}H_{74}N_{11}O_6Cl$ $[M+H]^+$ 996.5590, found 996.5564. The 1H - and ^{13}C -NMR spectra and Maldi-TOF mass spectrum of **Cage-U** are exhibited in **Figure S1**, **S5** and **S9**, respectively.

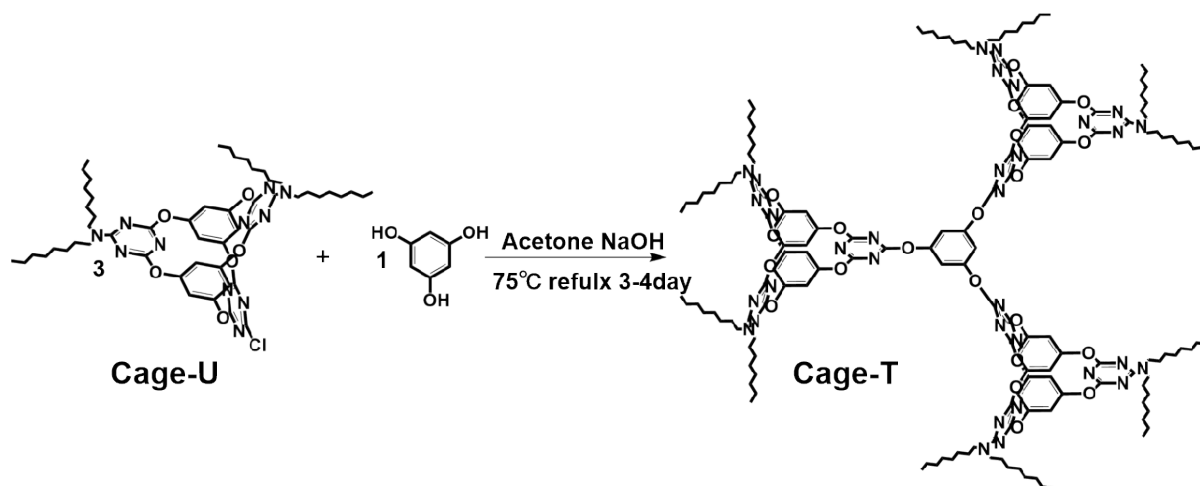
2.3 Synthesis of the Cage-Dimer (Cage-D)



Cage-D: **Cage-U** (0.20 g, 0.20 mmol, 2.1 eq.) was dissolved in anhydrous acetone (10 mL).

Under reflux condition, 10 mL solution (acetone: H₂O= 1:1) containing hydroquinone (0.01 g, 96 μ mol, 1.0 eq.) and NaOH (8 mg, 0.21 mmol, 2.2 eq.) was added within 10 minutes. The resulting solution was heated to reflux for 3 days. The organic layer was separated, and the aqueous layer was extracted with DCM (3 \times 30 mL). The combined organic extracts were washed with water (3 \times 30 mL). After removal of the solvent, the crude product was purified by column chromatography on silica gel (PE:EtOAc = 15:1, v/v) to afford **Cage-D** as a white solid (0.16 g, yield 82.0%). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (s, 4H), 6.60 (t, *J* = 2.0 Hz, 4H), 6.55 (d, *J* = 2.0 Hz, 8H), 3.57 (t, *J* = 8.0 Hz, 16H), 1.63 (br, 16H), 1.35-1.24 (m, 80H), 0.87 (t, *J* = 6.8 Hz, 24H). ¹³C NMR (100 MHz, CDCl₃) δ 174.26, 174.06, 172.12, 167.48, 153.49, 152.50, 149.27, 122.88, 116.04, 114.67, 47.66, 31.85, 29.45, 29.31, 27.62, 26.91, 22.69, 14.14. MS (Maldi TOF): Calculated for C₁₁₂H₁₅₂N₂₂O₁₄ [M+H]⁺ 2031.1970, found 2031.1925. The ¹H- and ¹³C-NMR spectra and Maldi-TOF mass spectrum of **Cage-D** are exhibited in **Figure S2, S6 and S10**.

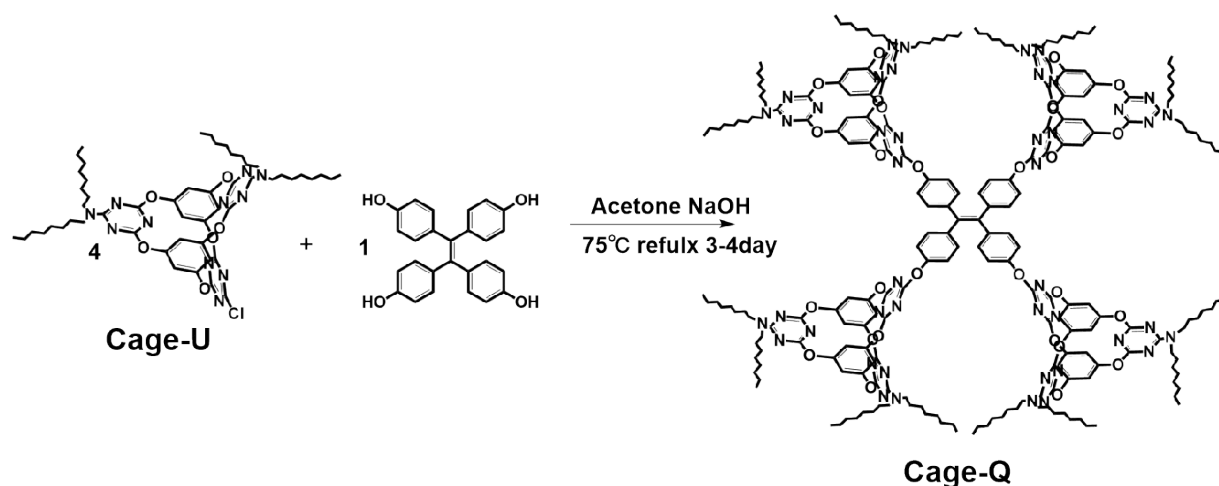
2.4 Synthesis of the Cage-Trimer (Cage-T)



Cage-T: **Cage-U** (0.30 g, 0.30 mmol, 3.2 eq.) was dissolved in anhydrous acetone (10 mL). Under reflux condition, 10 mL solution (acetone: H₂O= 1:1) containing 1,3,5- benzenetriol (12 mg, 94 μ mol, 1.0 eq.) and NaOH (13 mg, 0.32 mmol, 3.4 eq.) was added within 10 minutes. The resulting solutions were heated to reflux for 3 days. The organic layer was separated, and the aqueous layer was extracted with DCM (3 \times 30 mL). The combined organic extracts were washed with water (3 \times 30 mL). After removal of the solvent, the crude product was purified by column chromatography on silica gel (PE: EtOAc = 10: 1, v/v) to afford **Cage-T** as a white

solid (99 mg, yield 35.0%). ^1H NMR (400 MHz, CDCl_3) δ 7.25 (s, 3H), 6.60 (t, $J = 2.0$ Hz, 6H), 6.55 (d, $J = 2.0$ Hz, 12H), 3.57 (t, $J = 8.0$ Hz, 24H), 1.63 (m, 24H), 1.35-1.25 (m, 120H), 0.87 (t, $J = 6.8$ Hz, 36H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.07, 173.67, 172.11, 167.47, 153.52, 152.47, 152.02, 116.08, 114.62, 113.85, 47.66, 31.83, 29.43, 29.30, 27.61, 26.90, 22.68, 14.13. MS (Maldi TOF): Calculated for $\text{C}_{165}\text{H}_{225}\text{N}_{33}\text{O}_{21}$ $[\text{M}+\text{H}]^+$ 3006.7665, found 3006.7680. The ^1H - and ^{13}C -NMR spectra and Maldi-TOF mass spectrum of **Cage-T** are exhibited in **Figure S3, S7 and S11**.

2.5 Synthesis of the Cage-Quadruplex (Cage-Q)



Cage-Q: **Cage-U** (0.30 g, 0.30 mmol, 4.2 eq.) was dissolved in anhydrous THF (20 mL). Under reflux condition, 20 mL solution ($\text{THF}:\text{H}_2\text{O} = 1:1$) containing tetrakis(4-hydroxyphenyl)ethylene (28 mg, 71.4 μmol , 1.0 eq.) and NaOH (13 mg, 0.32 mmol, 4.4 eq.) was added within 10 minutes. The resulting solution was heated to reflux for 3 days. After removal of the solvent, the crude product was purified by column chromatography on silica gel (PE: EtOAc = 13: 1, v/v) to afford **Cage-Q** as a white solid (68 mg, yield 22.3%). ^1H NMR (400 MHz, CDCl_3) δ 7.17 (d, $J = 8.6$ Hz, 8H), 7.03 (d, $J = 8.6$ Hz, 8H), 6.58 (d, $J = 1.9$ Hz, 8H), 6.56 (d, $J = 1.9$ Hz, 16H), 3.56 (t, $J = 8.0$ Hz, 32H), 1.62 (br, 32H), 1.33-1.25 (m, 160H), 0.87 (t, $J = 6.6$ Hz, 48H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.19, 174.01, 172.12, 167.47, 153.46, 152.57, 150.35, 140.89, 140.13, 132.80, 121.01, 115.94, 114.73, 47.62, 31.83, 29.43, 29.29, 27.60, 26.89, 22.68, 14.13. MS (Maldi TOF): Calculated for $\text{C}_{238}\text{H}_{312}\text{N}_{44}\text{O}_{28}$ $[\text{M}+\text{H}]^+$ 4237.4488, found 4237.061. The ^1H - and ^{13}C -NMR spectra and Maldi-TOF mass spectrum of **Cage-Q** are exhibited in **Figure S4, S8 and S12**, respectively.

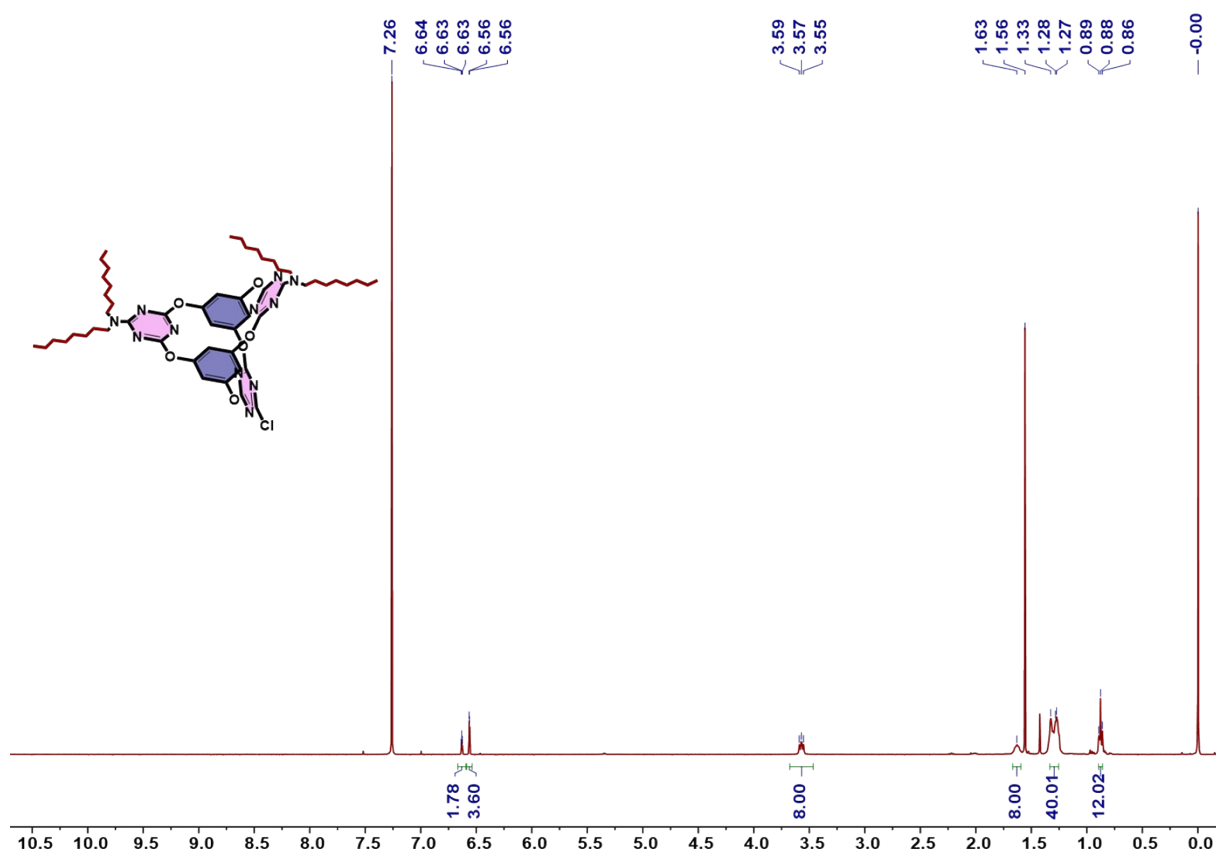


Fig. S1 The ^1H -NMR spectrum of the **Cage-U** in CDCl_3 .

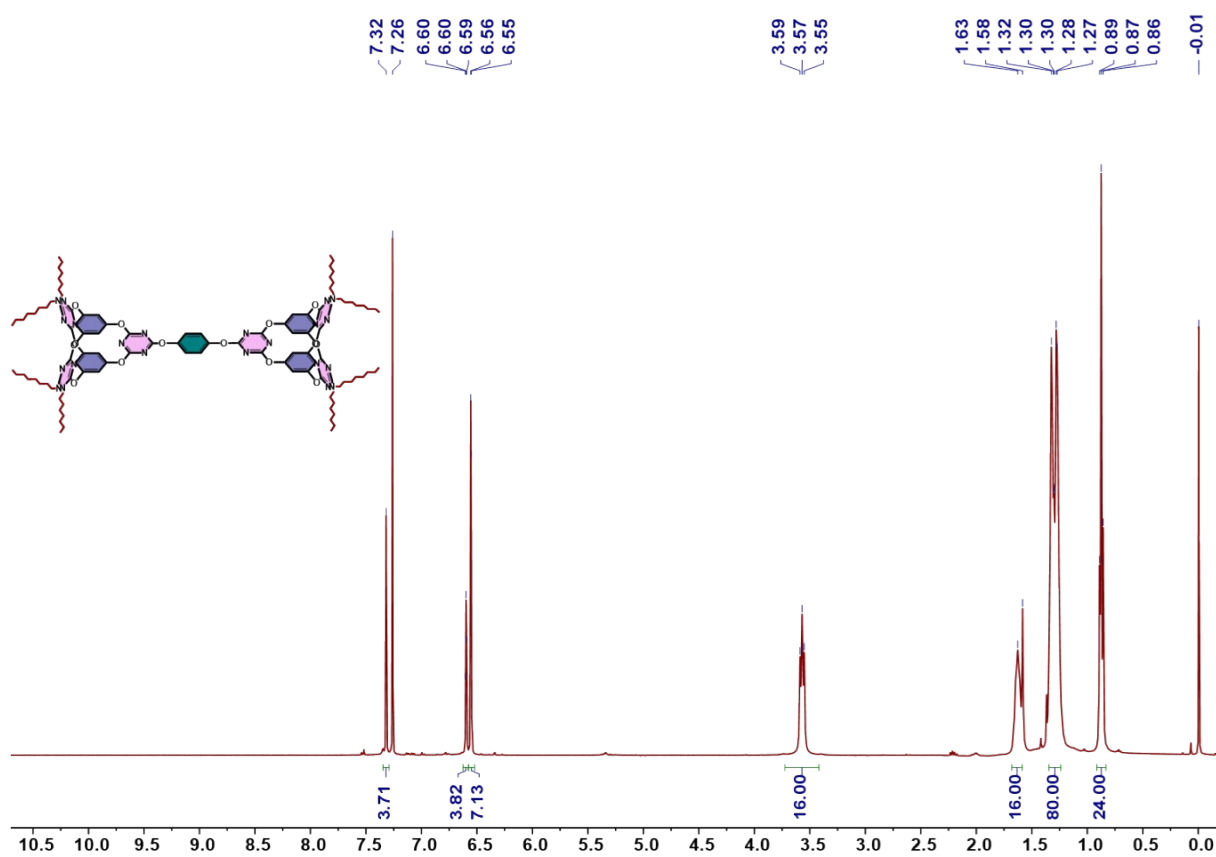


Fig. S2 The ^1H -NMR spectrum of the **Cage-D** in CDCl_3 .

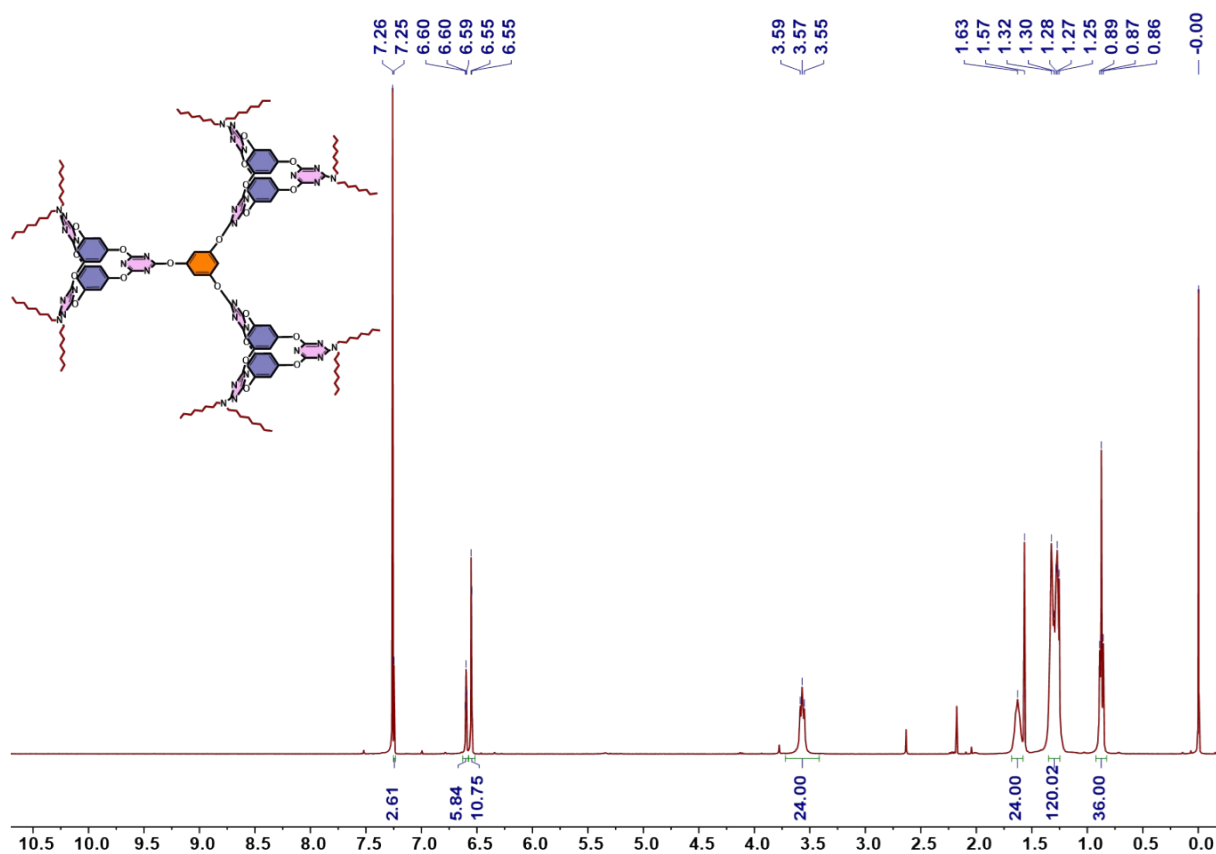


Fig. S3 The ¹H-NMR spectrum of the **Cage-T** in CDCl₃.

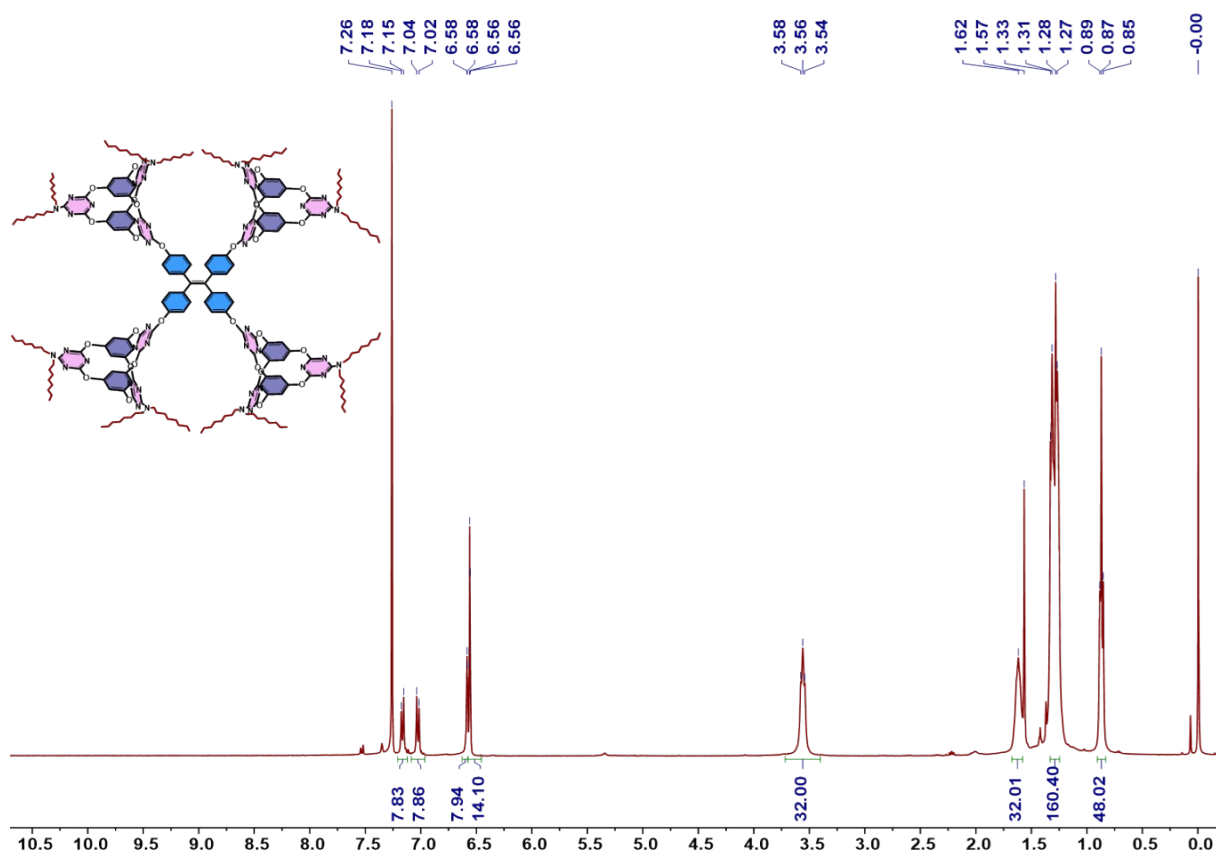


Fig. S4 The ¹H-NMR spectrum of the **Cage-Q** in CDCl₃.

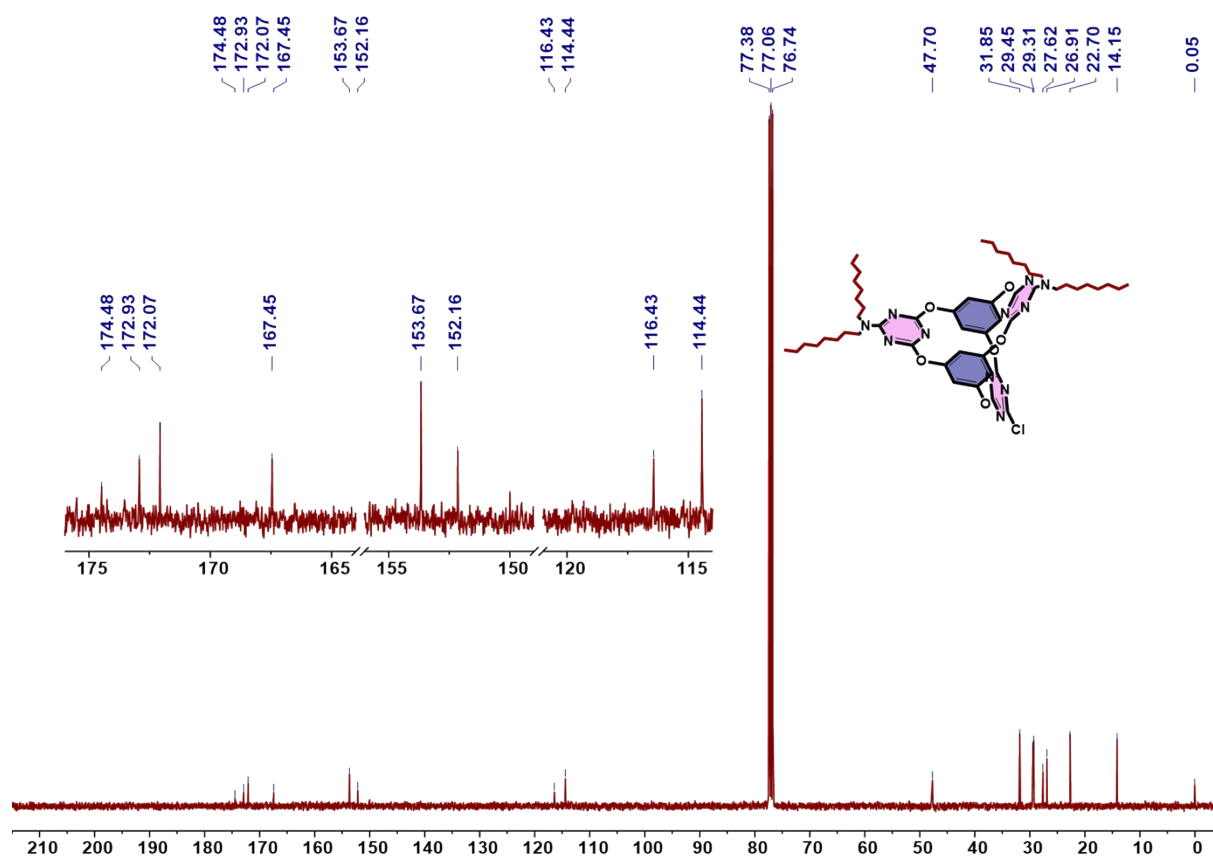


Fig. S5 The ¹³C-NMR spectrum of the **Cage-U** in CDCl₃.

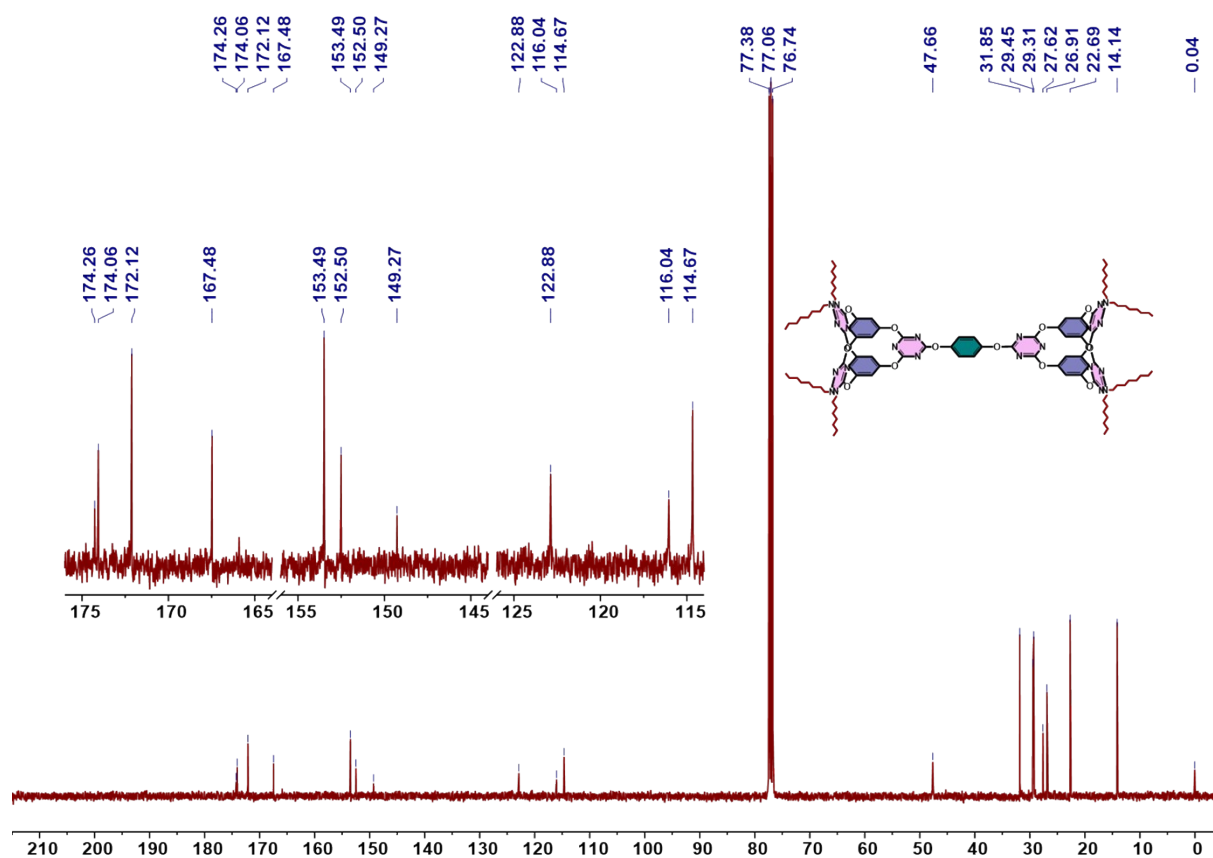


Fig. S6 The ¹³C-NMR spectrum of the **Cage-D** in CDCl₃.

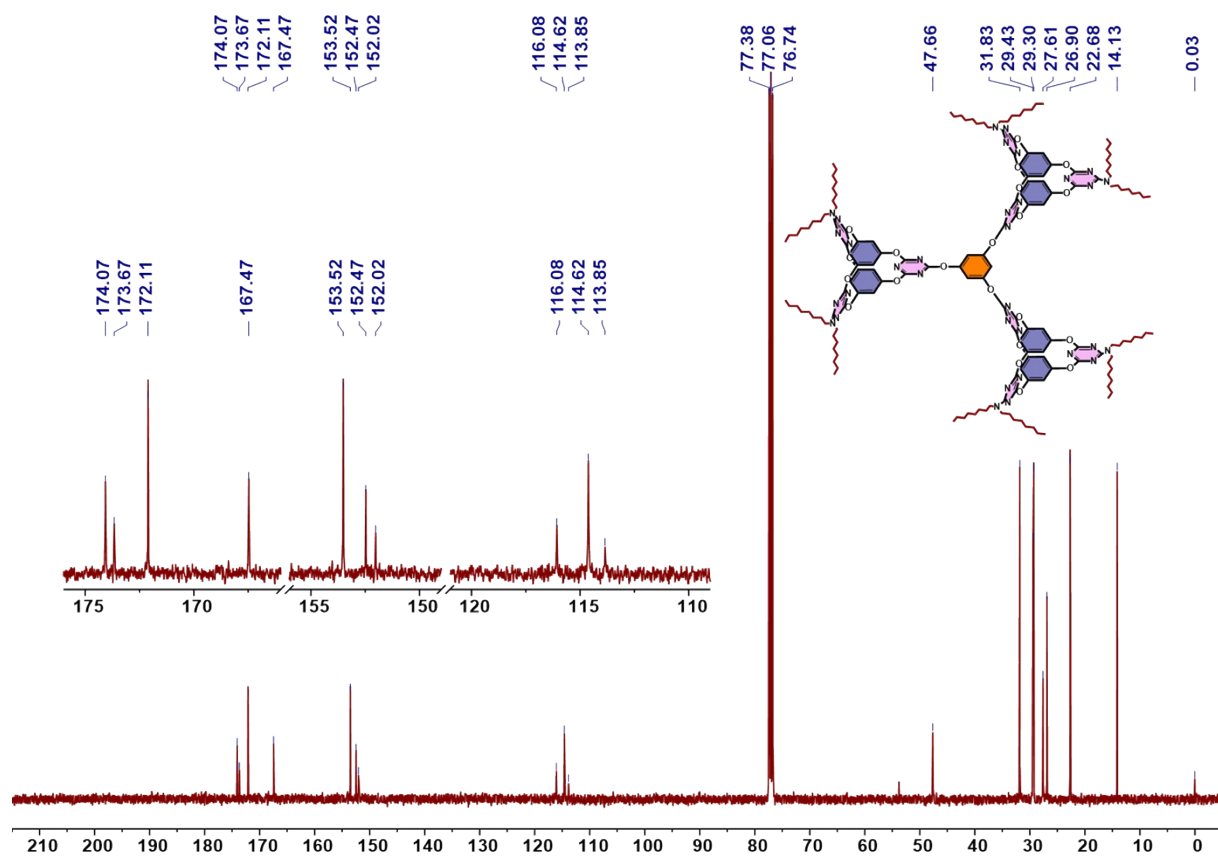


Fig. S7 The ^{13}C -NMR spectrum of the **Cage-T** in CDCl_3 .

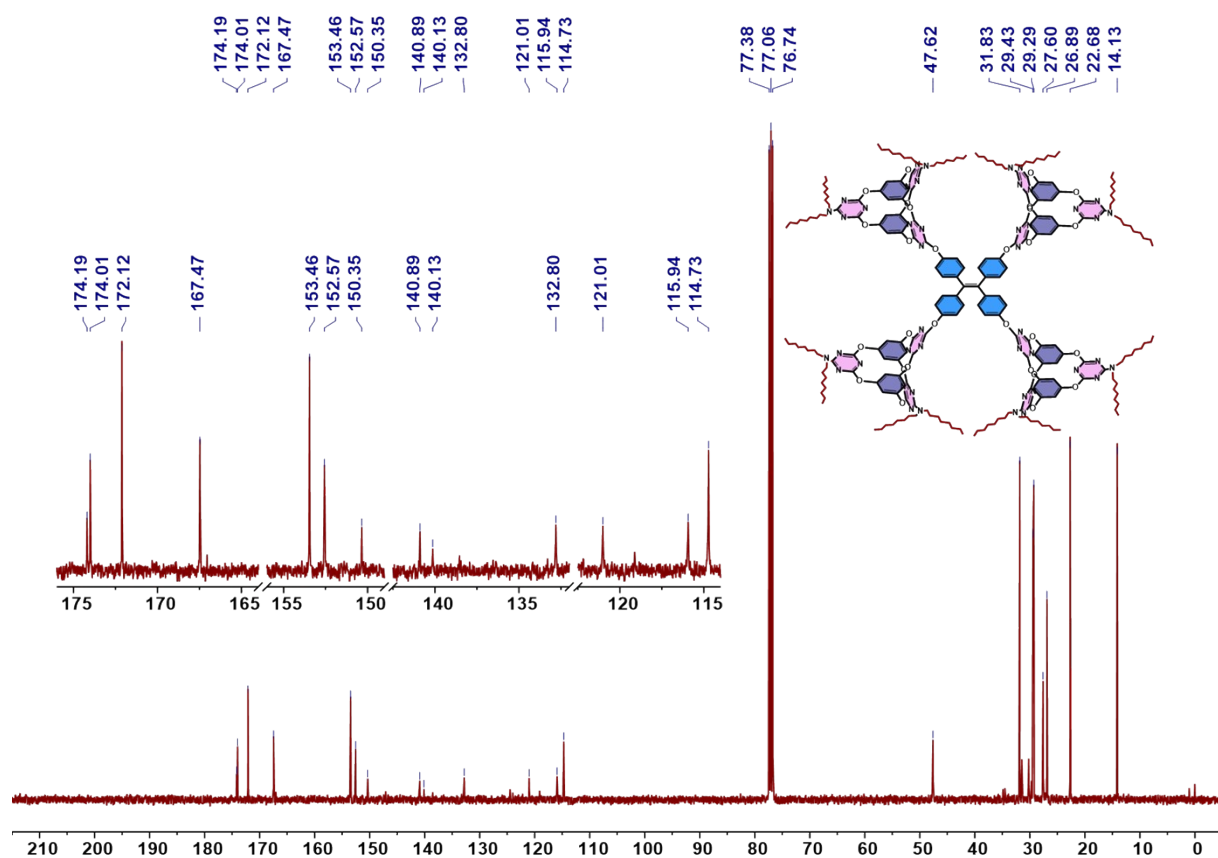


Fig. S8 The ^{13}C -NMR spectrum of the **Cage-Q** in CDCl_3 .

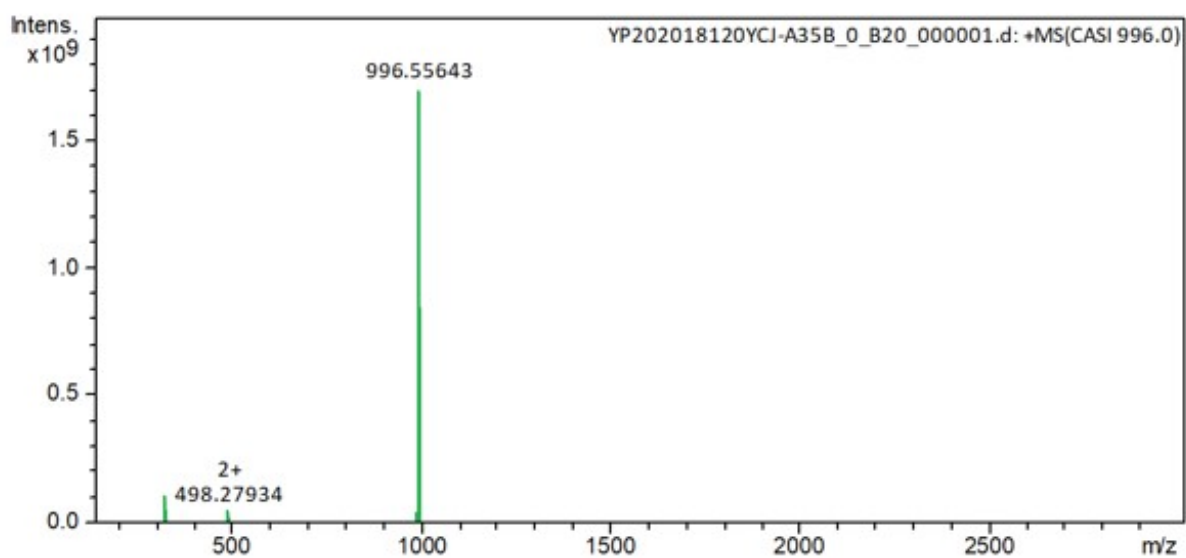


Fig. S9 The MALDI-TOF mass spectrum of the **Cage-U**.

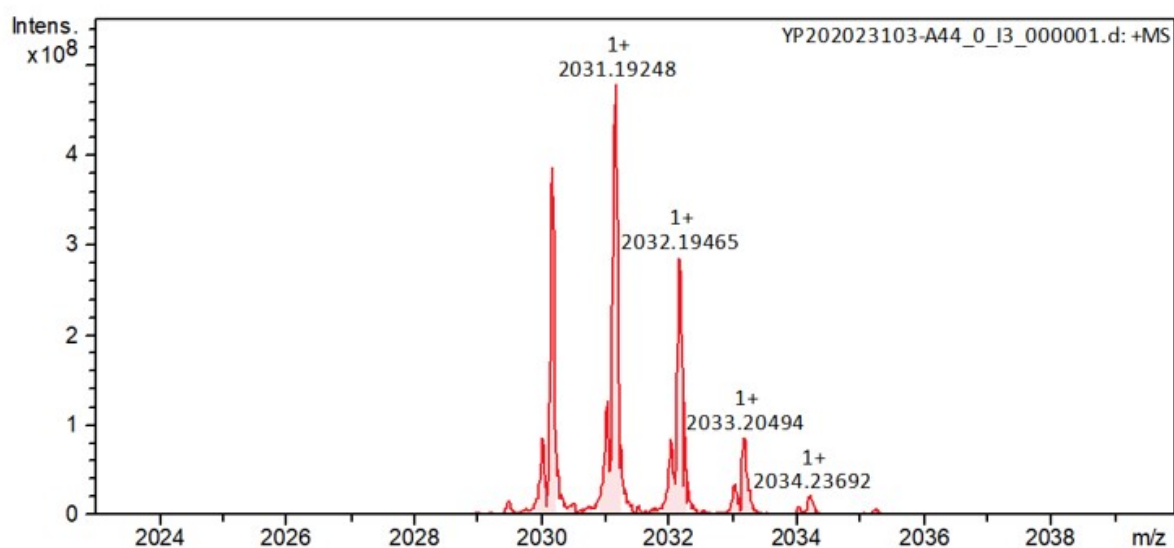


Fig. S10 The MALDI-TOF mass spectrum of the **Cage-D**.

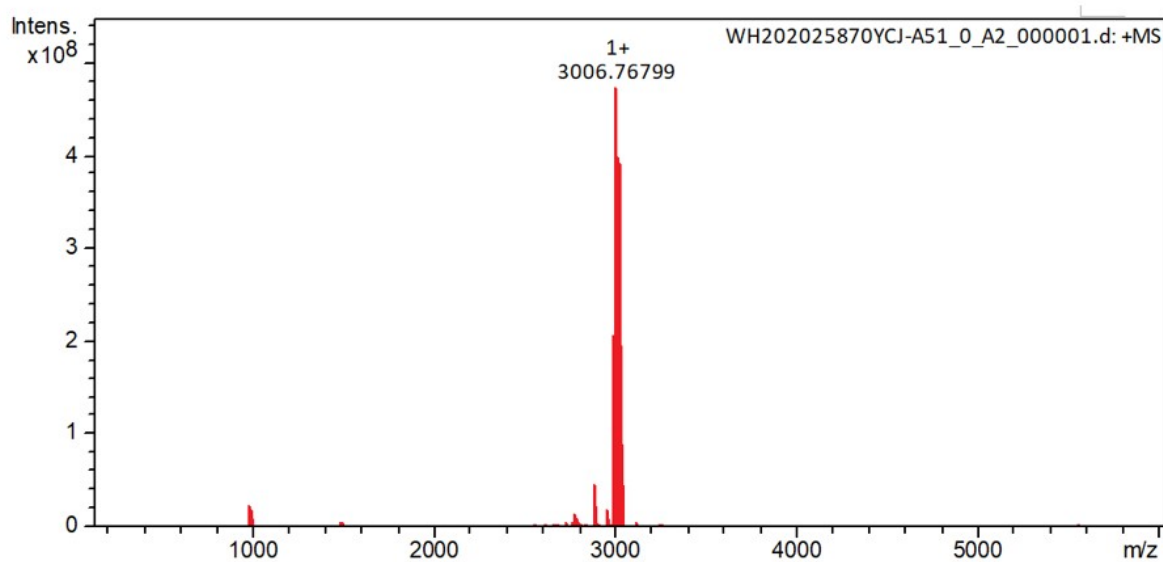


Fig. S11 The MALDI-TOF mass spectrum of the **Cage-T**.

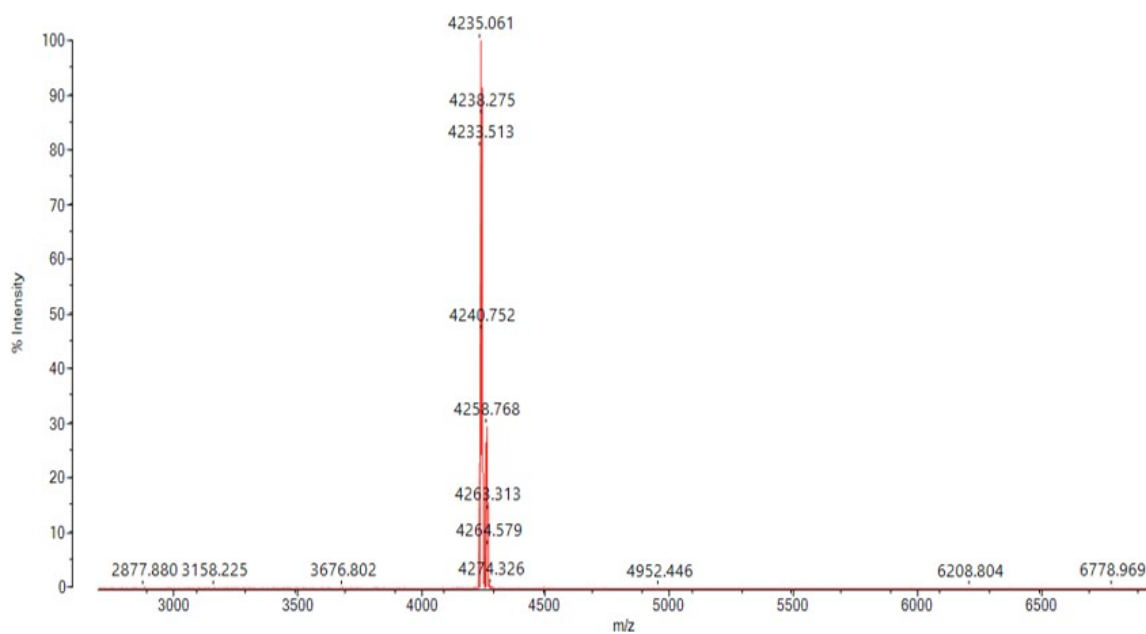


Fig. S12 The MALDI-TOF mass spectrum of the **Cage-Q**.

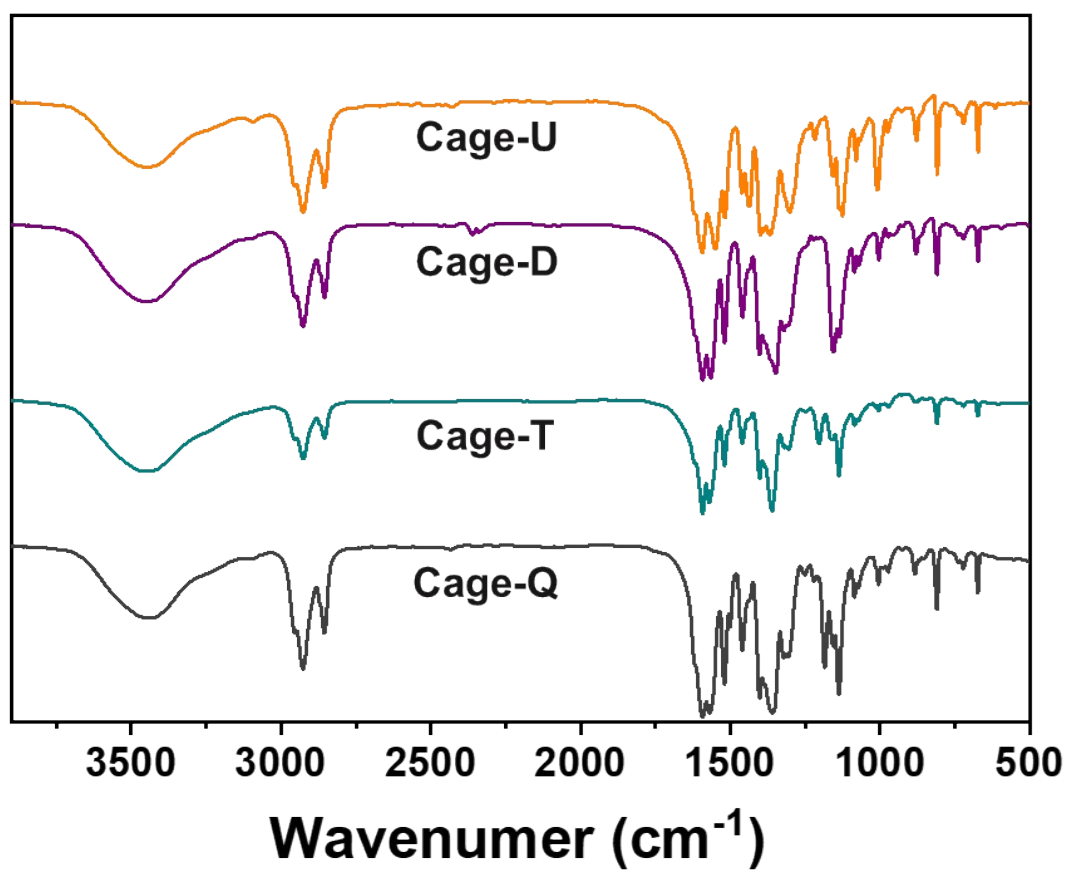


Fig. S13 The FT-IR spectra of cage oligomers.

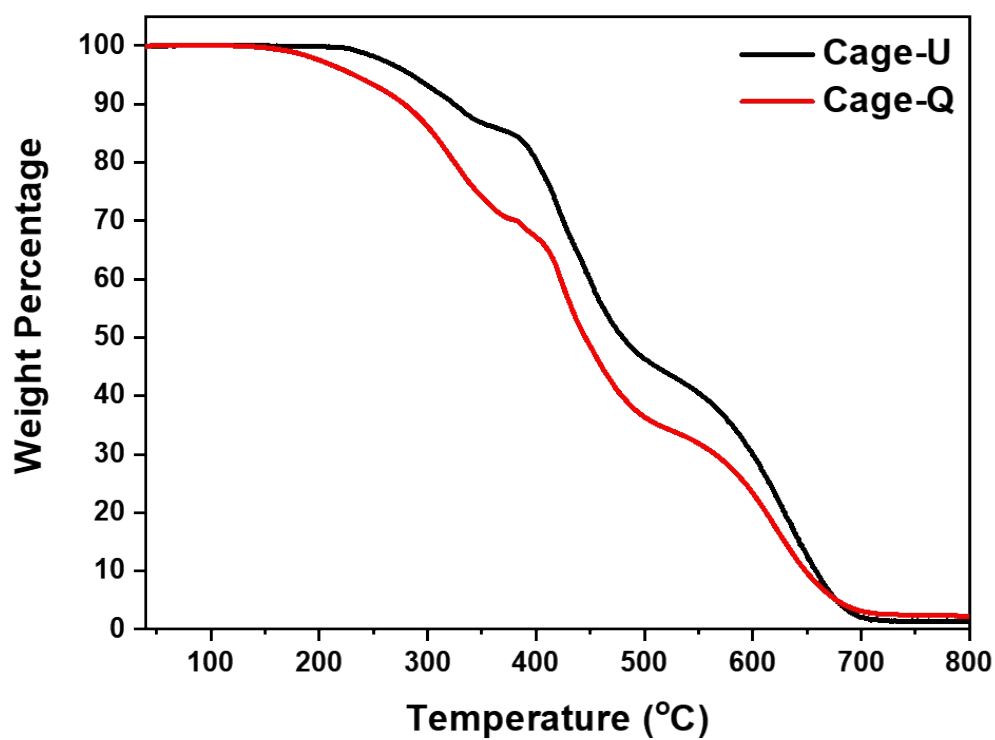


Fig. S14 TGA profiles of **Cage-U** and **Cage-Q** (Air, Heating rate: 10 °C/min).

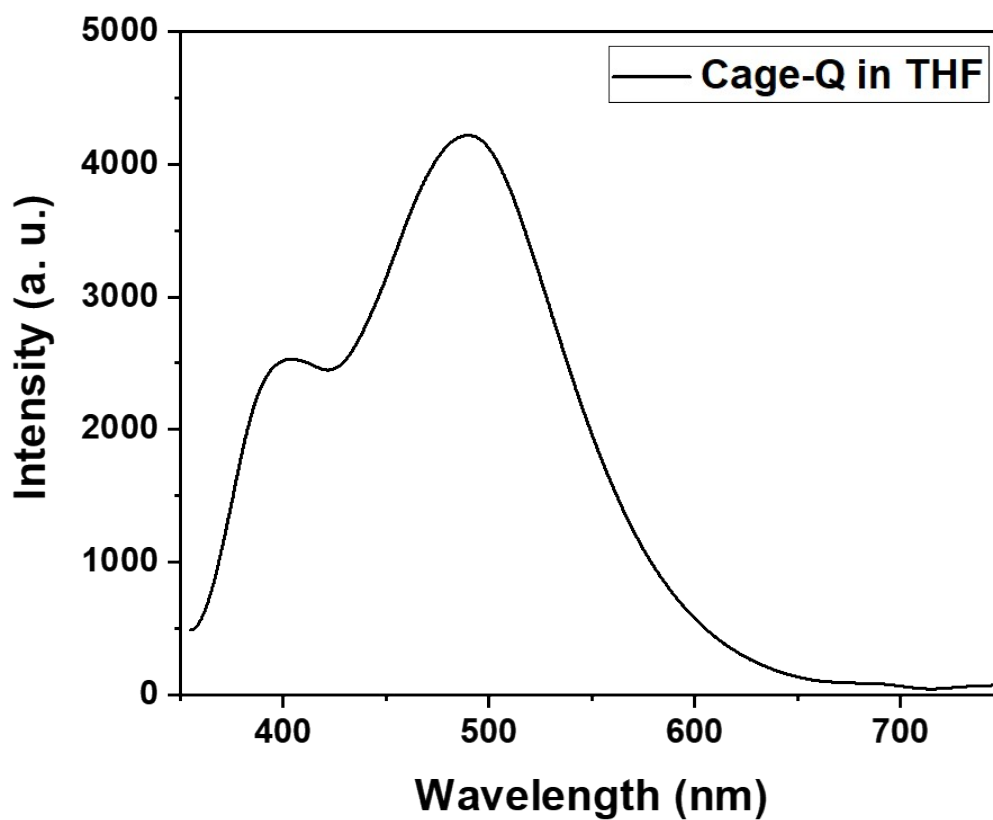


Fig. S15 The photoluminescent plot of **Cage-Q** in THF solution. ($\lambda_{\text{ex}} = 340$ nm)

Table S1. The sizes and distributions of cage oligomers from DLS.

	Cage-U	Cage-D	Cage-T	Cage-Q
D (nm)	5.576	5.981	7.001	7.695
PDI	0.430	0.345	0.063	0.425