

Guest-induced narcissistic self-sorting in water via imine formation

Supporting information

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1. Materials and General Methods

All reagents and solvents were purchased from commercial sources and used without further purification. Manipulations were performed under a normal laboratory atmosphere unless otherwise noted. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature using Bruker AVANCE NEO 600 spectrometers, with working frequencies of 600 and 150 MHz for ^1H and ^{13}C , respectively. Chemical shifts are reported in ppm relative to the residual internal non-deuterated solvent signals (CDCl_3 : $\delta=7.26$ ppm, D_2O : $\delta=4.80$ ppm). High-resolution mass spectra (HRMS) were measured on either a Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) or a Ultraflex extreme MALDI-TOF/TOF.

2. Synthetic Procedures

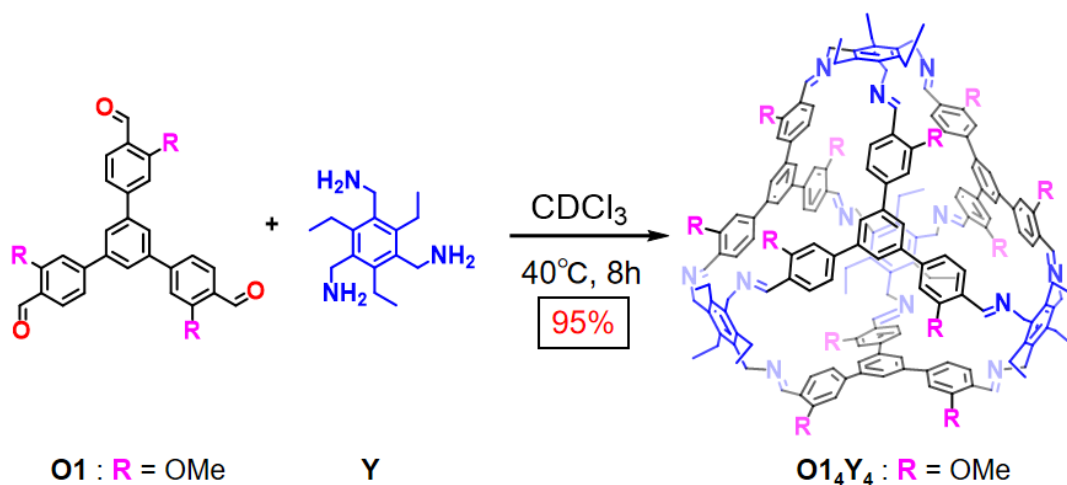


Figure S1. The synthesis of the tetrahedral cage **O1₄Y₄**.

O1₄Y₄: Trisbenzaldehyde **O1** (2.0 mg, 5.1 μmol , 1.0 equiv.), which was prepared according to the literature procedures^[1], and **Y** (1.4 mg, 5.6 μmol , 1.1 equiv.) were mixed in a CDCl_3 solution. After the mixture was heated at 40 °C for 8 h, the corresponding tetrahedral cage **O1₄Y₄** was formed as the only observable product without further purification. Removal of the solvent yielded the pure cage sample with a yield of 95%. ^1H NMR (600 MHz, CDCl_3) δ 8.68 (s, 12H), 7.98 (d, $J=8.0$ Hz, 12H), 7.54 (s, 12H), 7.07 (d, $J=8.0$ Hz, 12H), 6.97 (s, 12H), 4.93 (s, 24H), 3.90-3.86 (m, 24H), 3.72 (s, 36H), 2.89-2.77 (m, 36H). ^{13}C $\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 157.88, 154.75, 143.24, 142.28, 141.32, 131.57, 126.95, 124.53, 123.45, 118.95, 108.33, 54.56, 28.68, 14.85. MALDI-MS: m/z calcd for $[\text{M}+\text{H}]^+$ $[\text{C}_{180}\text{H}_{181}\text{N}_{12}\text{O}_{12}]^+$, 2704.399, found 2704.847.

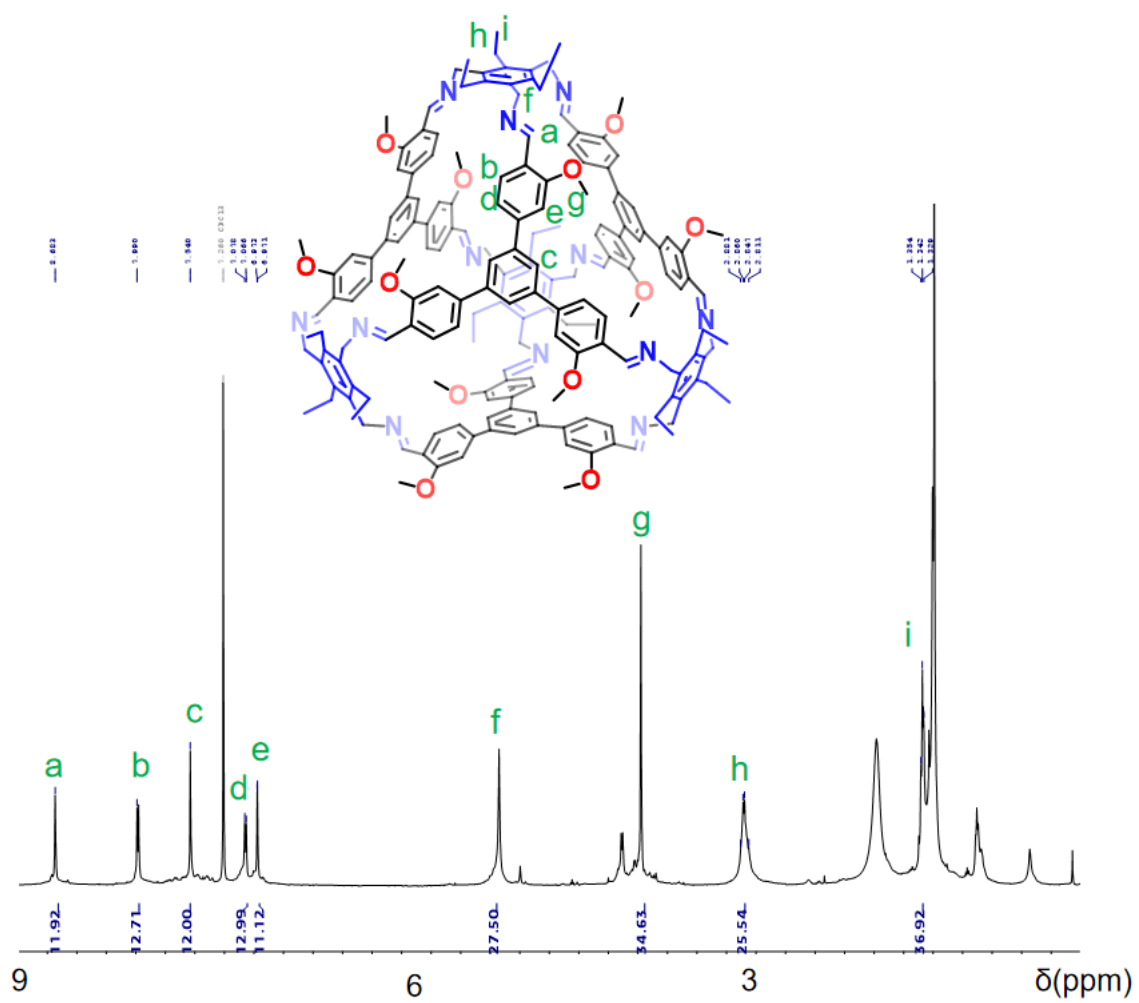


Figure S2. ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of **O14Y4**.

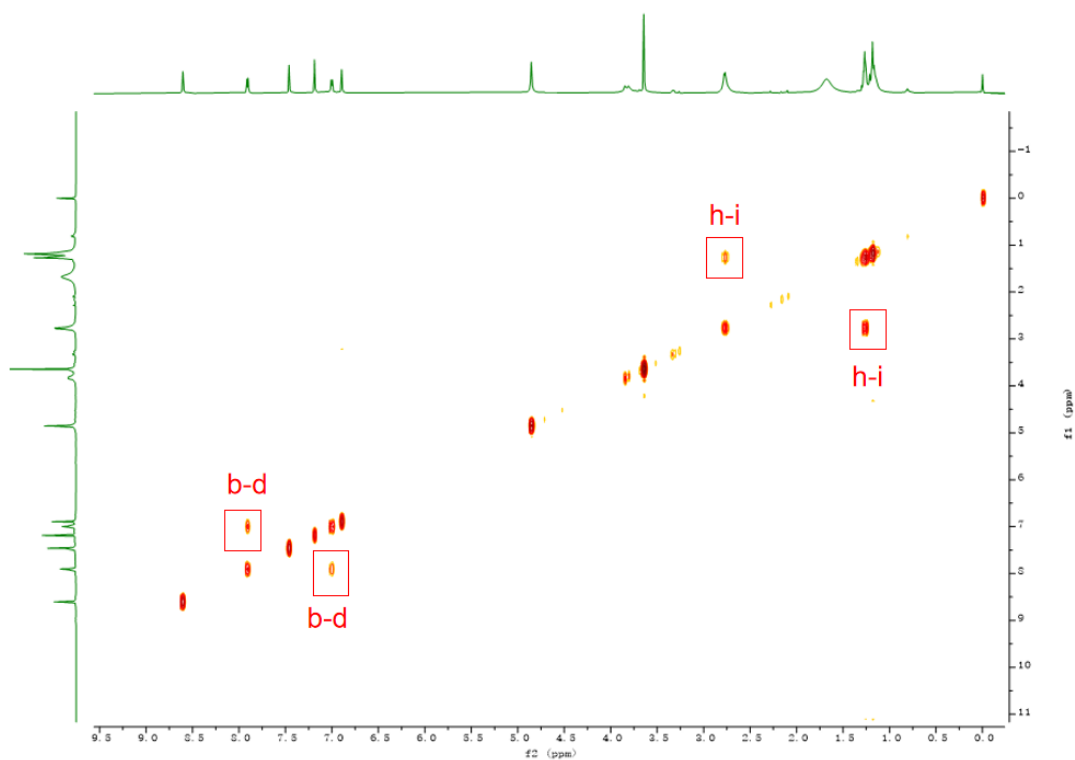


Figure S3. ^1H - ^1H COSY spectrum (600 MHz, CDCl_3 , 298 K) of **O14Y4**. The key correlation peaks are labelled in the spectrum.

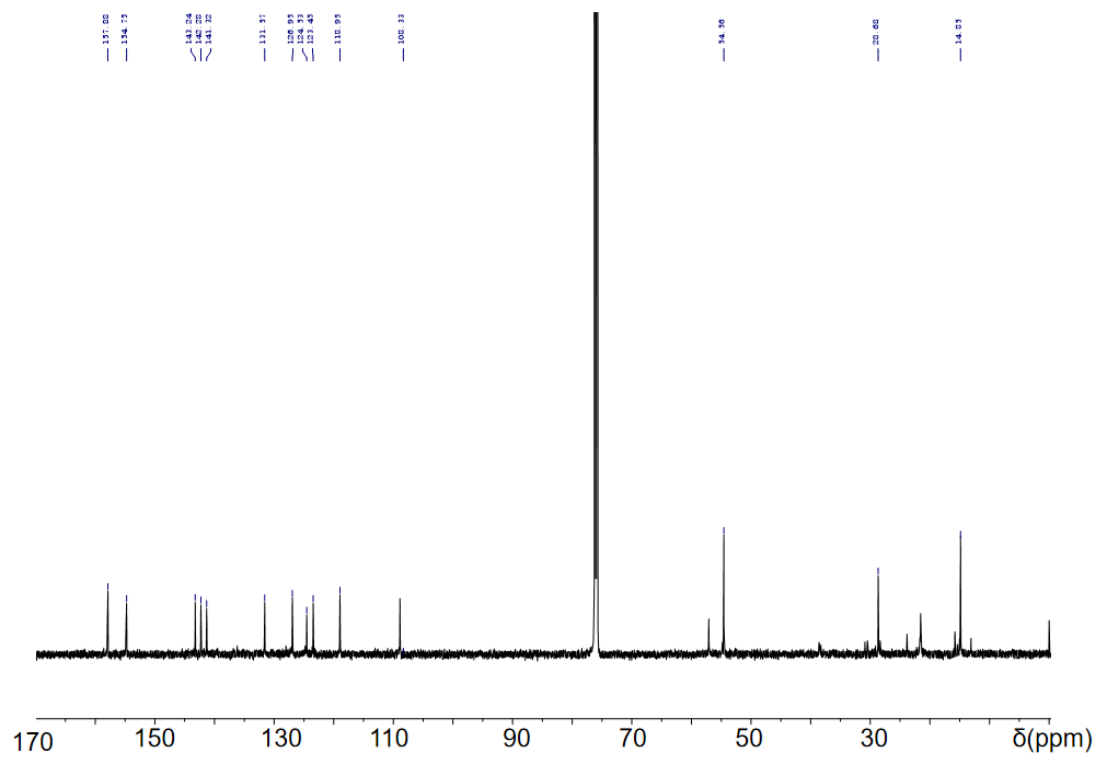


Figure S4. ^{13}C $\{^1\text{H}\}$ NMR spectrum (150 MHz, CDCl_3 , 298 K) of **O14Y4**.

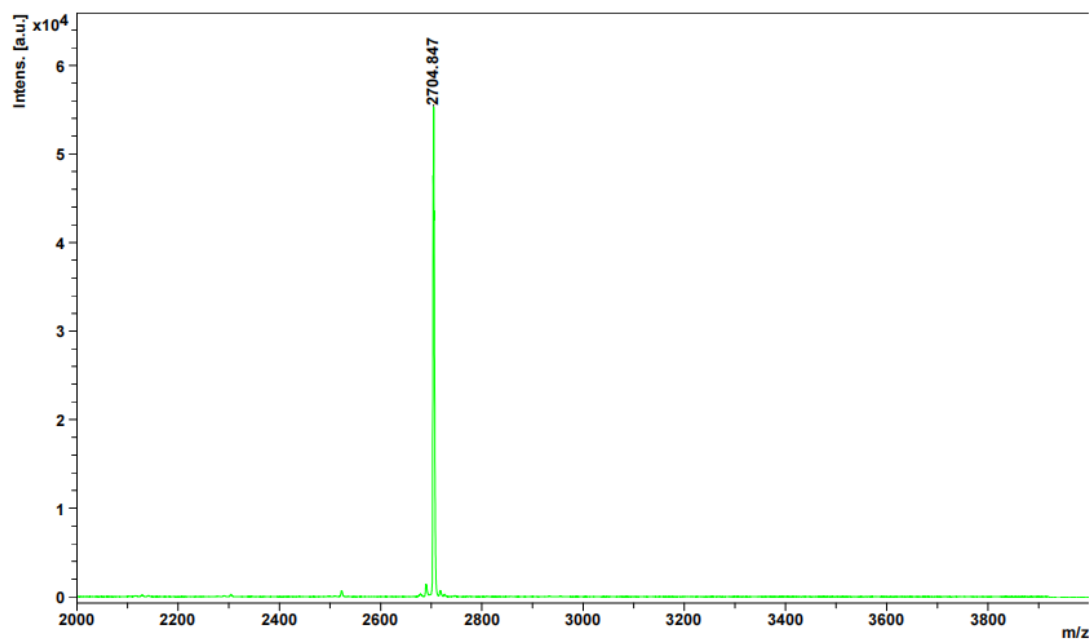


Figure S5. MALDI-MS of **O₁₄Y₄**: m/z calcd for [M+H]⁺ [C₁₈₀H₁₈₁N₁₂O₁₂]⁺, 2704.399; found 2704.847.

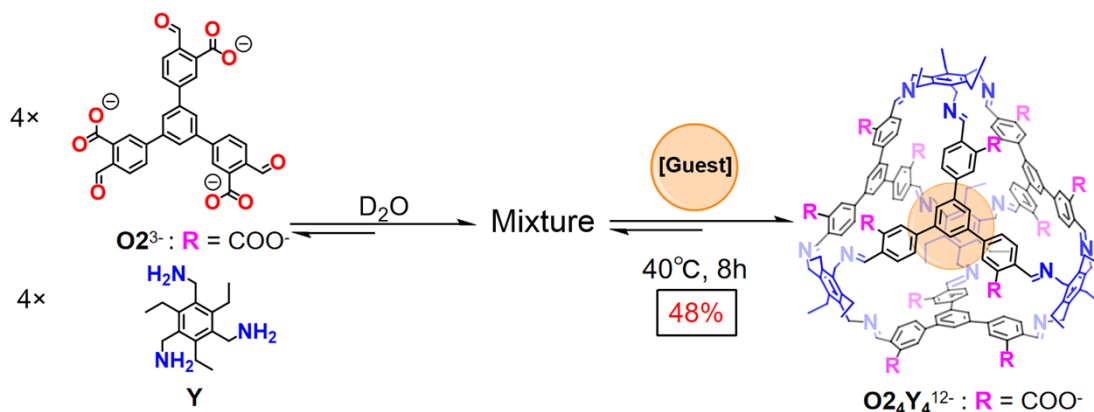


Figure S6. The synthesis of the tetrahedral cage $\text{O}_{24}\text{Y}_4^{12-}$.

$\text{O}_{24}\text{Y}_4^{12-}$: To a D_2O (0.5 mL) solution containing $\text{O}_2^{3-}\cdot 3\text{H}^+$ (2.0 mg, 3.8 μmol , 1.0 equiv.), which was the protonated form of O_2^{3-} prepared according to the literature procedures^[2], K_2CO_3 (2.0 mg, 0.014 mmol, 3.8 equiv), and $(n\text{-C}_4\text{H}_9)_4\text{N}^+\cdot\text{Cl}^-$ (2.0 mg, 7.2 μmol , 1.9 equiv.), **Y** (1.1 mg, 4.2 μmol , 1.1 equiv.) in D_2O was added. The mixture was heated at 40 °C for 8 h. ^1H NMR spectrum indicated that $\text{O}_{24}\text{Y}_4^{12-}$ was obtained as the only observable products containing $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ in its cavity. The yield of this cage was determined to be 48% by using DMF as the internal standard. ^1H NMR (600 MHz, D_2O) δ 9.01 (s, 12H), 8.02 (s, 12H), 7.96 (s, 12H), 7.90-7.88 (d, $J=7.8$ Hz, 12H), 7.68-7.66 (d, $J=7.8$ Hz, 12H), 5.00 (s, 24H), 4.00-3.97 (m, 24H), 1.23-1.17 (m, 36H). ESI-HRMS: m/z calcd for $[\text{M}+5\text{K}^+]^7-$ $[\text{K}_5\text{C}_{180}\text{H}_{144}\text{N}_{12}\text{O}_{24}]^7-$, 436.2672, found 436.2658.

Several trials to obtain the ^{13}C $\{^1\text{H}\}$ NMR spectrum of $\text{O}_{24}\text{Y}_4^{12-}$ were unsuccessful even though the sample was scanned for more than 10,000 times, probably because the solution of $\text{O}_{24}\text{Y}_4^{12-}$ was too dilute to record its ^{13}C NMR spectrum on account of its relatively low water-solubility.

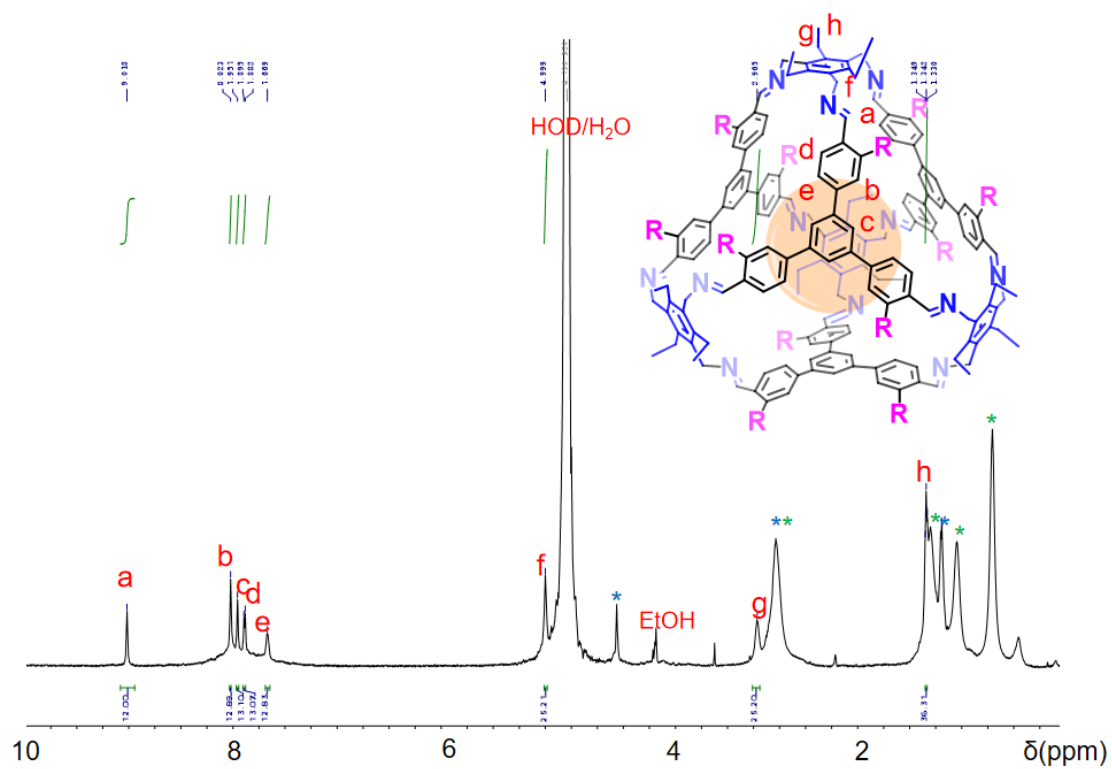


Figure S7. ^1H NMR spectrum (600 MHz, D_2O , 298 K) of $\text{O}_{24}\text{Y}_4^{12-}$. The resonances corresponding to unreacted Y and $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ are labelled with blue and green asterisks, respectively.

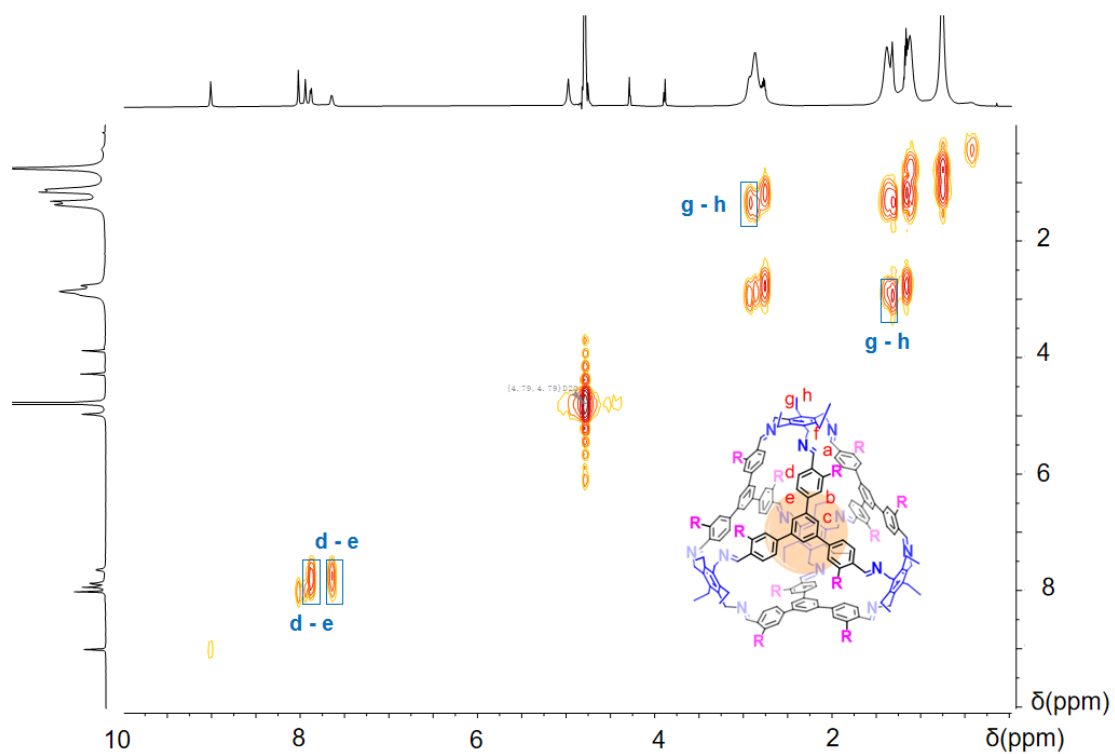
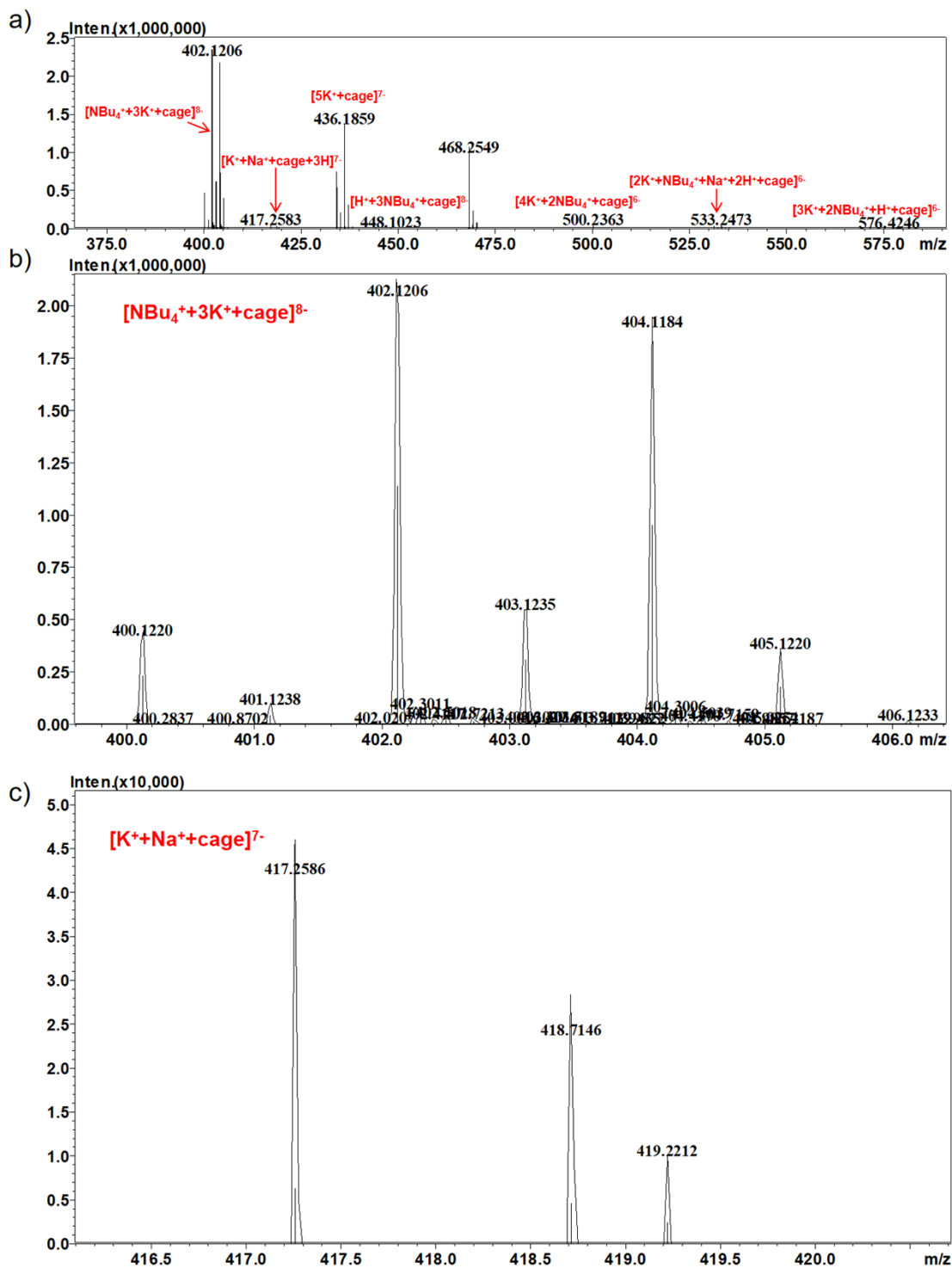


Figure S8. ¹H-¹H COSY spectrum (600 MHz, D₂O, 298 K) of **O₂₄Y₄¹²⁻**. The key correlation peaks are labelled in the spectrum.



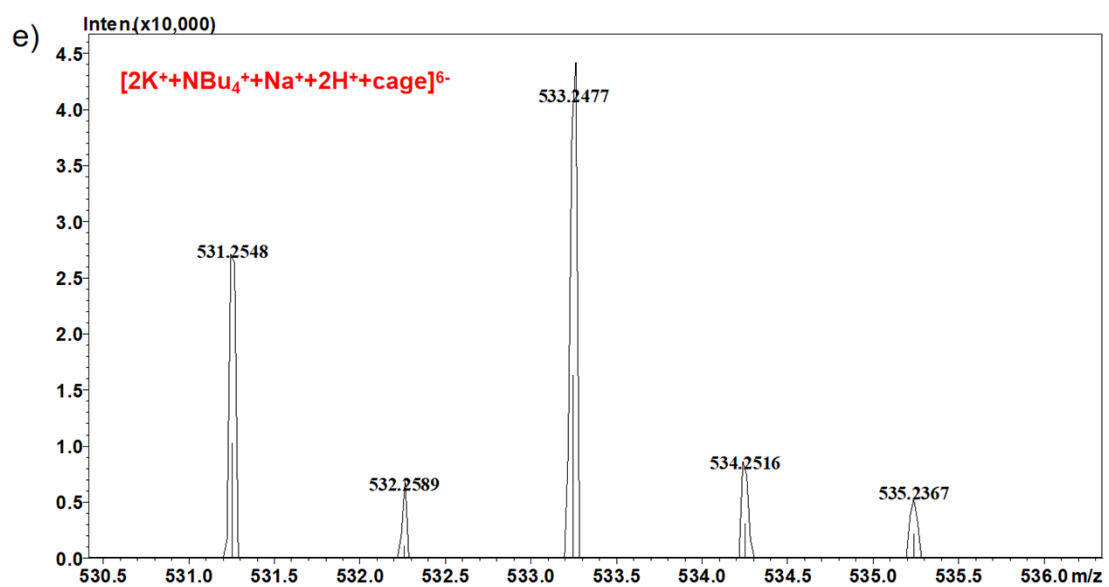
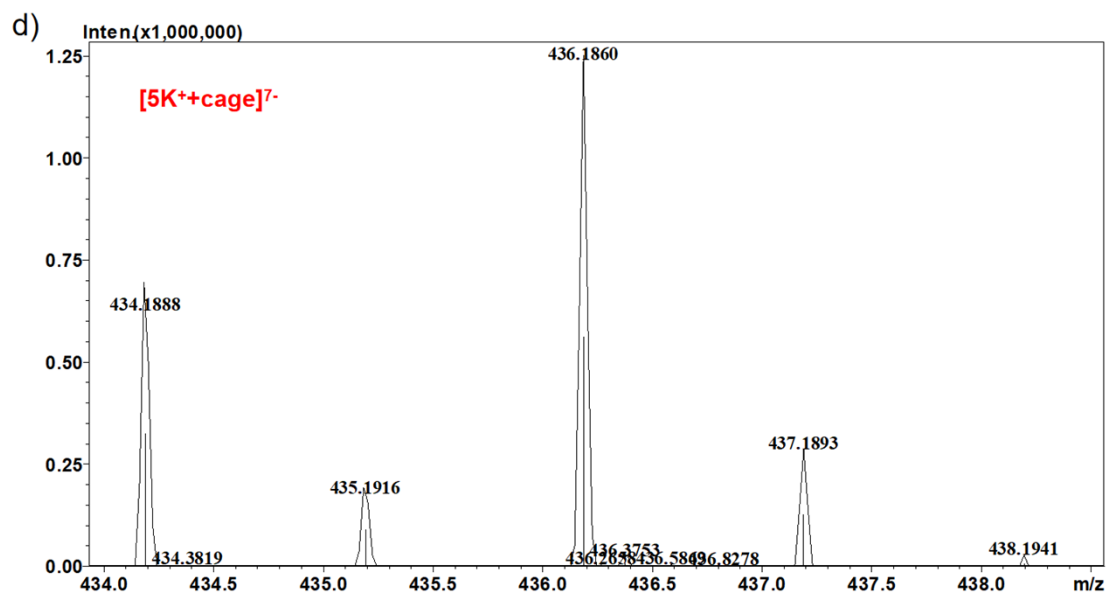


Figure S9. ESI-HRMS of $O_2Y_4^{12-}$.

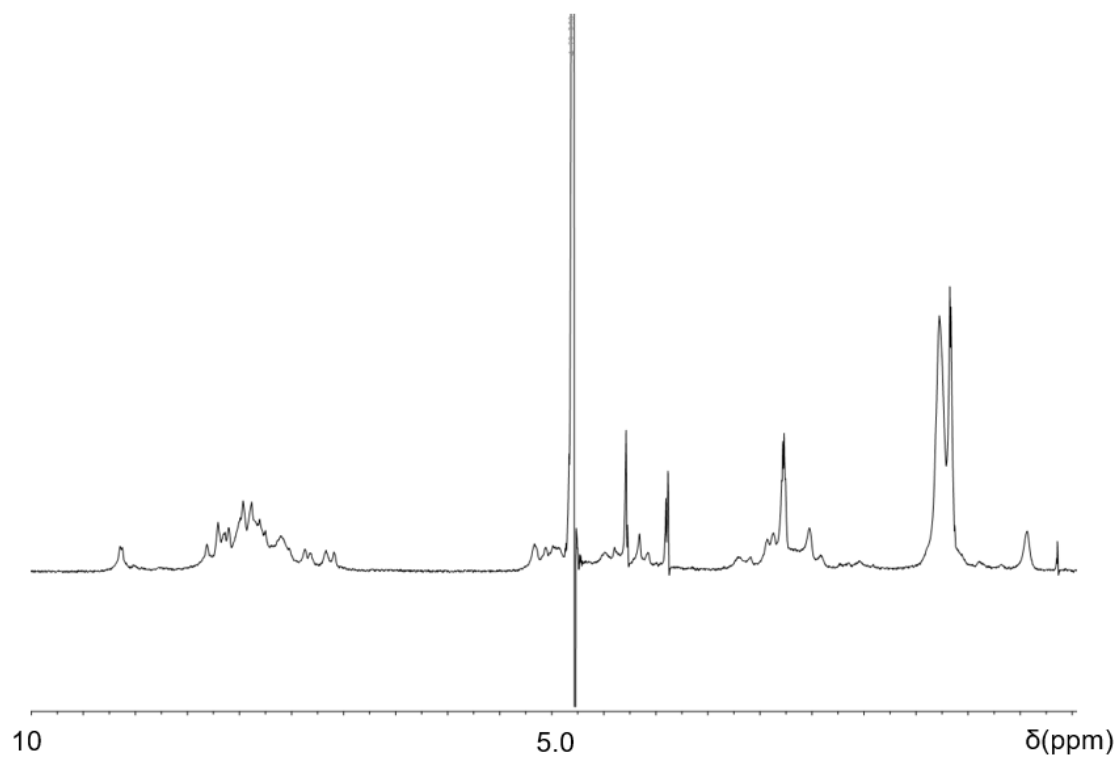


Figure S10. ¹H NMR spectrum (600 MHz, D₂O, 298 K) of a reaction mixture of **O2³⁻·3H⁺** (2.0 mg, 3.8 μmol, 1.0 equiv.), K₂CO₃ (2.0 mg, 0.014 mmol, 3.8 equiv.), and **Y** (1.1 mg, 4.2 μmol, 1.1 equiv.). The guest template (*n*-C₄H₉)₄N⁺·Cl⁻ was not added in this case, indicating that template is important in the cage formation.

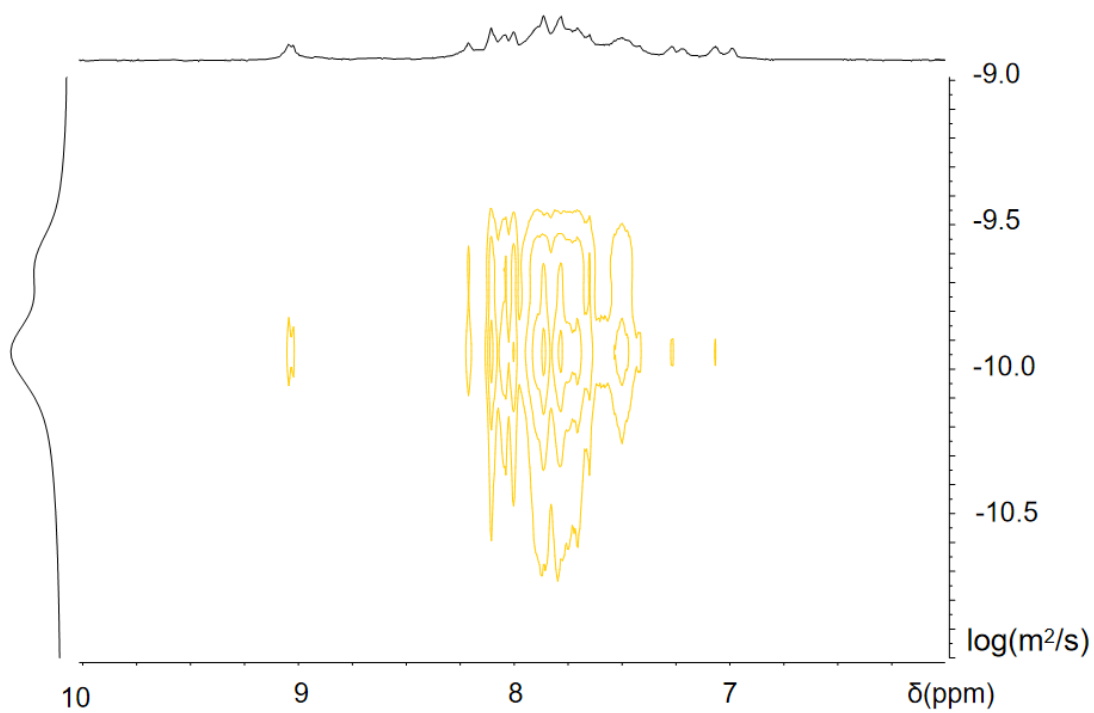


Figure S11. DOSY NMR spectrum (600 MHz, D_2O , 298 K) of a reaction mixture of $\text{O}_2^{3-}\cdot 3\text{H}^+$ (2.0 mg, 3.8 μmol , 1.0 equiv.), K_2CO_3 (2.0 mg, 0.014 mmol, 3.8 equiv.), and **Y** (1.1 mg, 4.2 μmol , 1.1 equiv.).

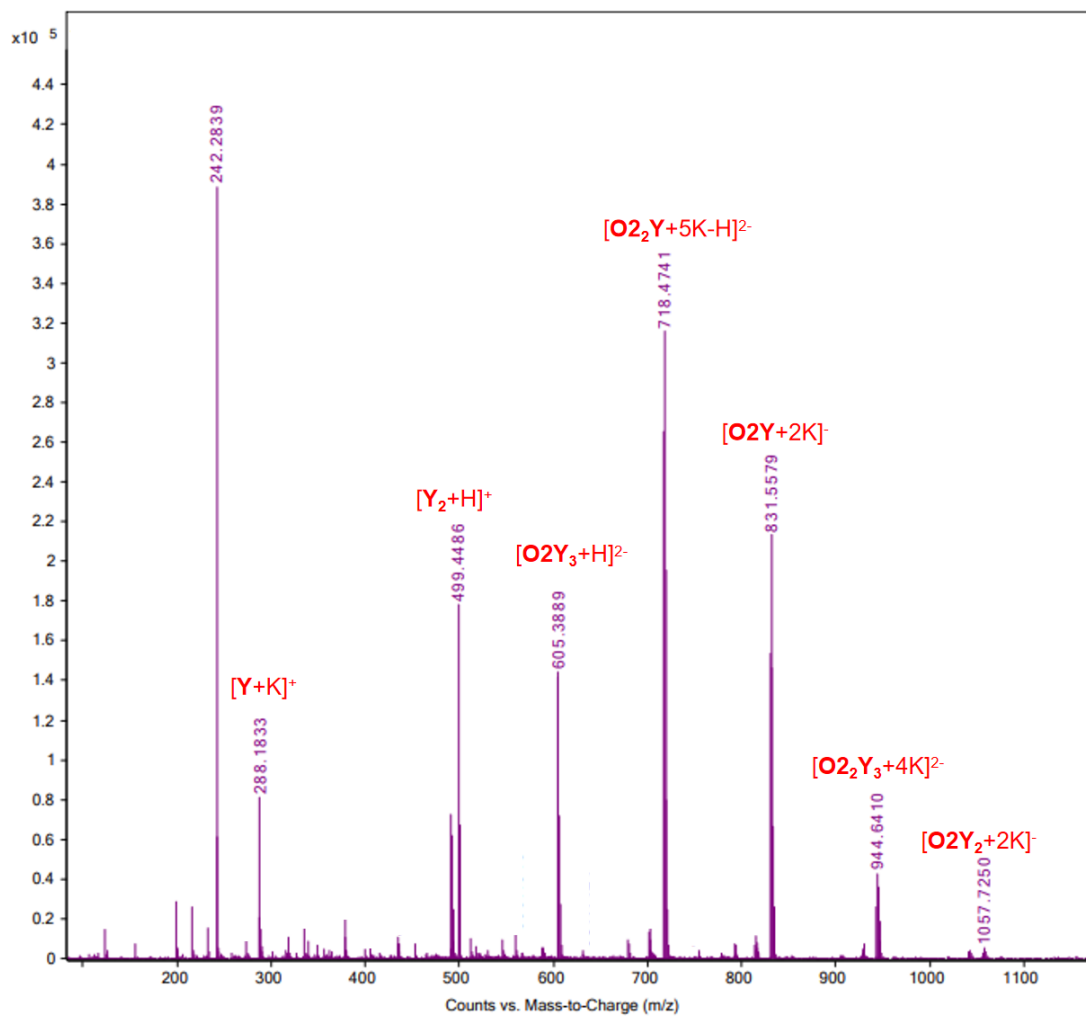


Figure S12. ESI-MS of the reaction mixture of $O_2^{3-}+3H^+$ (2.0 mg, 3.8 μmol , 1.0 equiv.), K_2CO_3 (2.0 mg, 0.014 mmol, 3.8 equiv.), and Y (1.1 mg, 4.2 μmol , 1.1 equiv.).

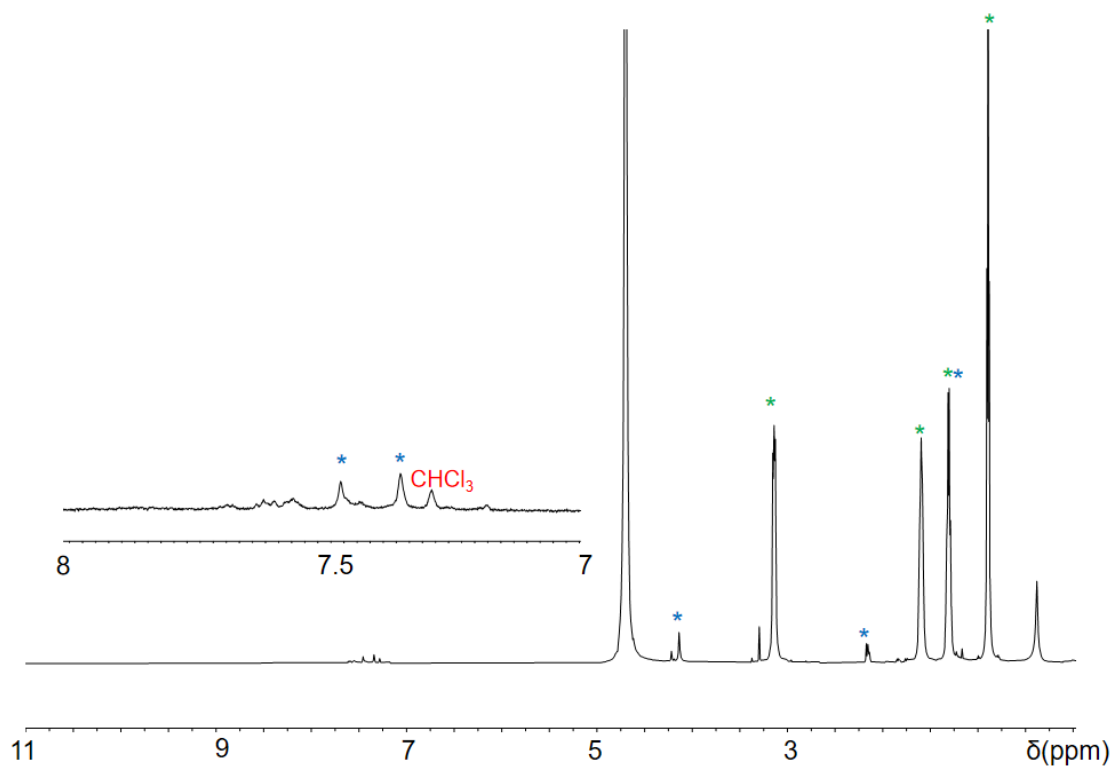


Figure S13. ¹H NMR spectrum (600 MHz, D₂O, 298 K) of the reaction mixture of **O2**³⁻•3H⁺ (2.0 mg, 3.8 μmol, 1.0 equiv.), K₂CO₃ (2.0 mg, 0.014 mmol, 3.8 equiv), benzene-1,3,5-triyltrimethanamine (1.1 mg, 4.2 μmol, 1.1 equiv.) and (*n*-C₄H₉)₄N⁺•Cl⁻ (2.0 mg, 7.2 μmol, 1.9 equiv.). The resonances corresponding to unreacted benzene-1,3,5-triyltrimethanamine and (*n*-C₄H₉)₄N⁺ are labelled with blue and green asterisks.

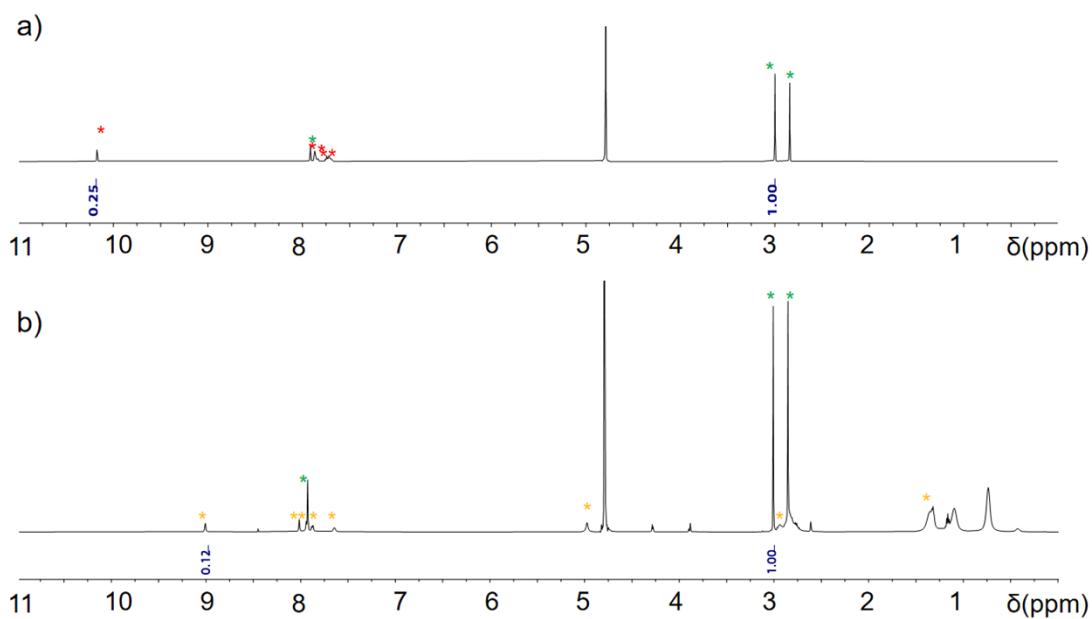


Figure S14. The ^1H NMR spectra (600 MHz, D_2O , 298 K) of a) a mixture of O_2^{3-} and DMF (as internal standard) a) before and b) after $(n\text{-C}_4\text{H}_9)_4\text{N}^+\cdot\text{Cl}^-$ and **Y** were added into the solution. The resonances corresponding to O_2^{3-} in a) and $\text{O}_2\text{Y}_4^{12-}$ in b) were integrated relative to one resonance corresponding to DMF, whose concentrations are identical in both spectra. The self-assembly yield of $\text{O}_2\text{Y}_4^{12-}$ was calculated to be $0.12/0.25$, which is 48%. The resonances corresponding to O_2^{3-} , $\text{O}_2\text{Y}_4^{12-}$ and DMF are labelled with red, yellow and green asterisks, respectively.

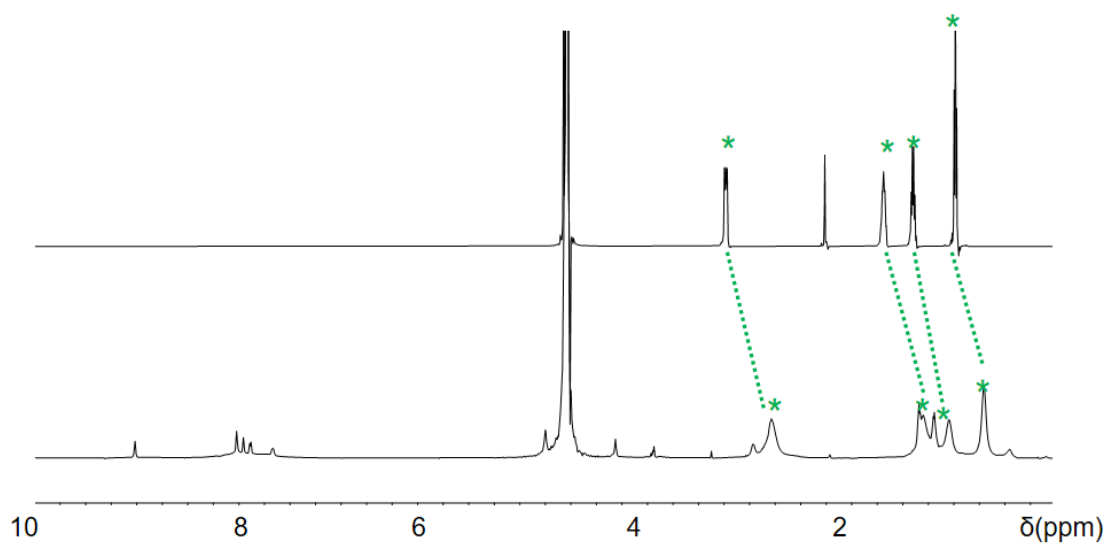


Figure S15. The ¹H NMR spectra (600 MHz, D₂O, 298 K) of (n-C₄H₉)₄N⁺ (top) and O₂₄Y₄¹²⁻ (bottom) whose formation was templated by using (n-C₄H₉)₄N⁺.

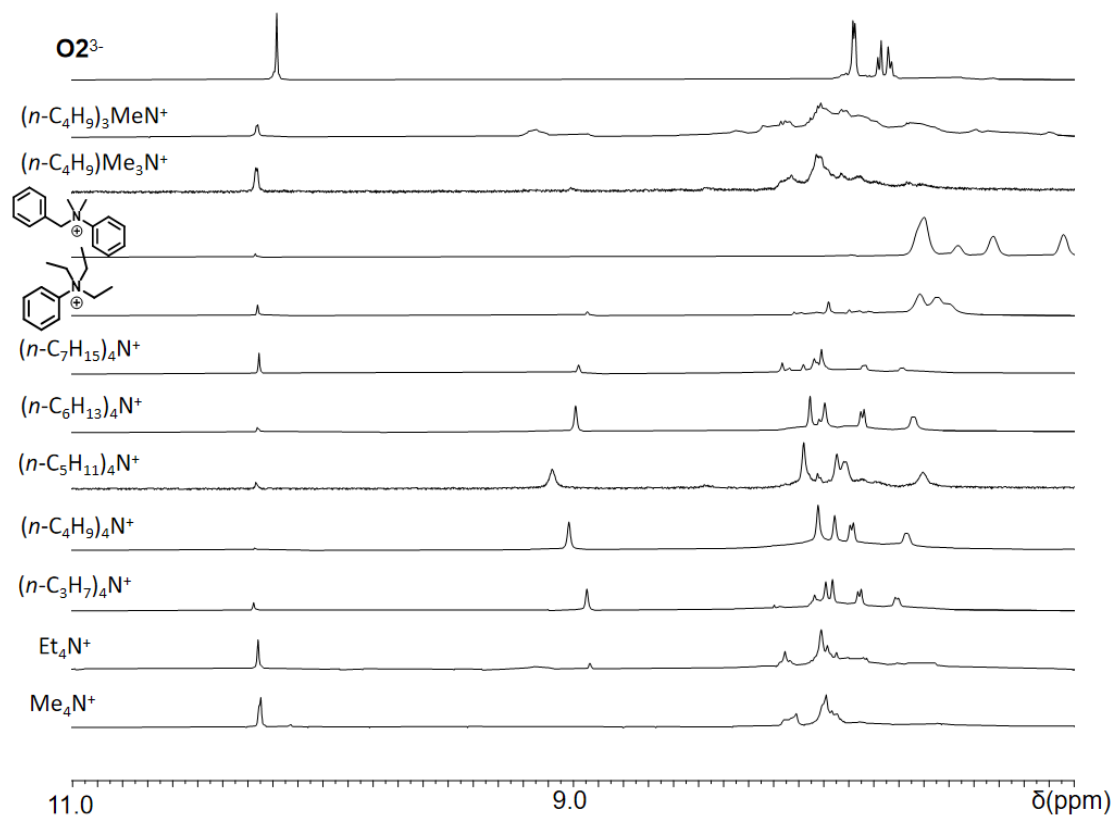


Figure S16. The ^1H NMR spectra (600 MHz, D_2O , 298K) of mixtures of O2^{3-} and Y , in the presence of different tetraalkylammonium cations, which was labelled in the corresponding spectra.

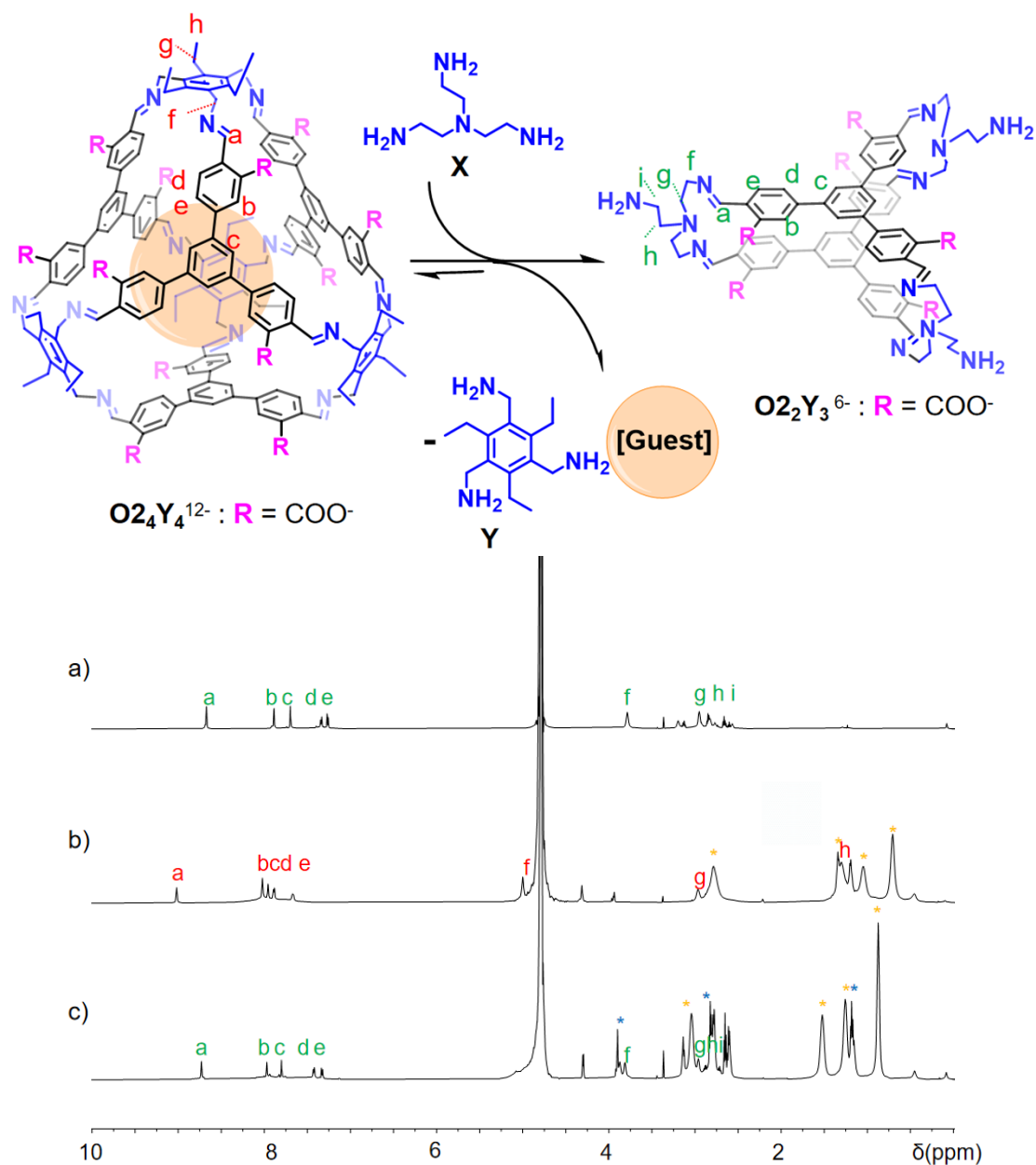


Figure S17. Partial ¹H NMR spectra (600 MHz, D₂O, 298 K) of a) **O₂X₃⁶⁻**, b) **O₂Y₄¹²⁻** containing (*n*-C₄H₉)₄N⁺ as the template, and c) the reaction mixture of the sample in b) and **X**. The spectrum in c) indicated that **O₂Y₄¹²⁻** was transformed into **O₂X₃⁶⁻**, after adding **X**, during which (*n*-C₄H₉)₄N⁺ and **Y** were released. The resonances corresponding to (*n*-C₄H₉)₄N⁺ and **Y** were labelled with yellow and blue asterisks, respectively. The resonances corresponding to **O₂X₃⁶⁻** and **O₂Y₄¹²⁻** were labelled with green and red letters, respectively.

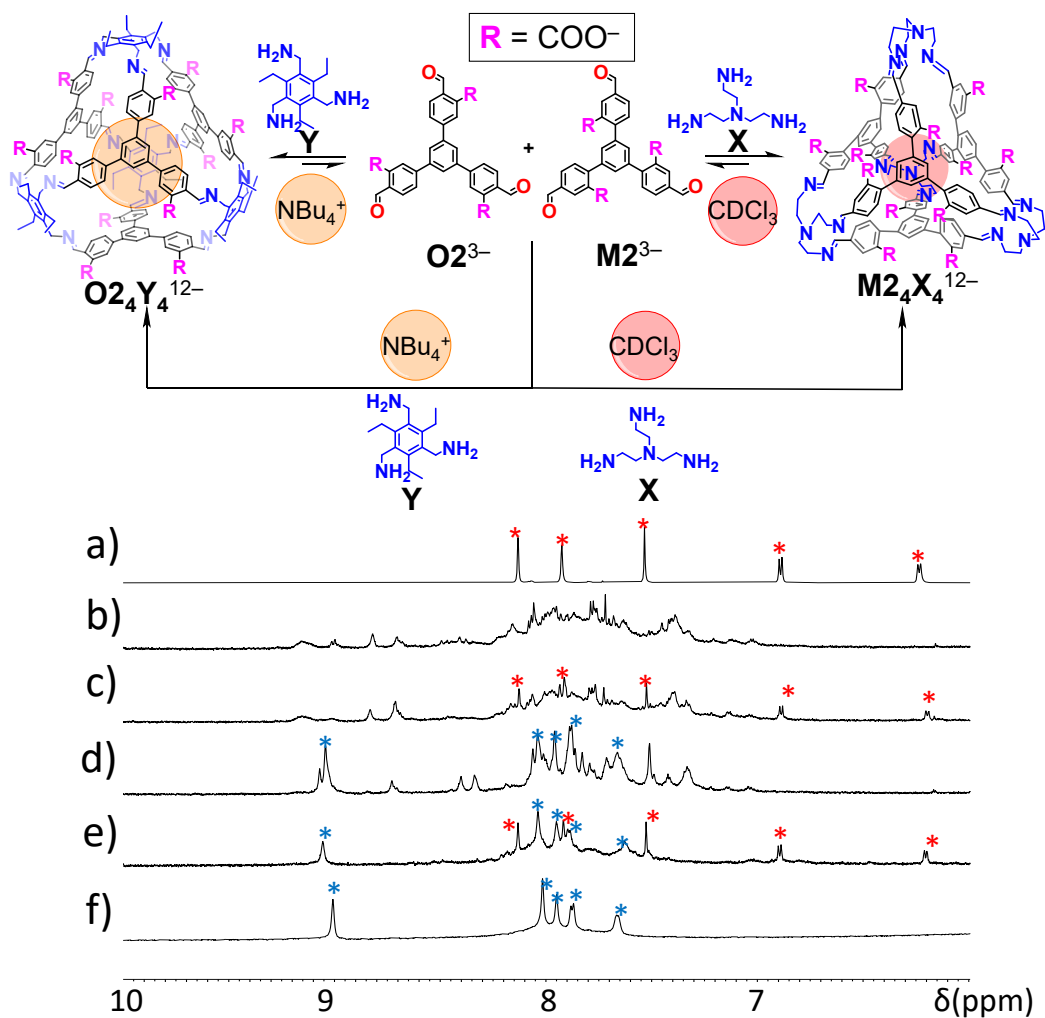


Figure S18. Partial ^1H NMR spectra (600 MHz, D_2O , 298 K) of a) $\text{M}2_4\text{X}_4^{12-}$ and f) $\text{O}2_4\text{Y}_4^{12-}$, b) a 2:1:2:1 mixture of **Y**, **X**, $\text{O}2_4\text{Y}_4^{12-}$ and $\text{M}2_4\text{X}_4^{12-}$, and the samples by adding c) CDCl_3 , d) $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Cl}^-$, as well as e) CDCl_3 and $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Cl}^-$ into the sample in b). The resonances corresponding to $\text{M}2_4\text{X}_4^{12-}$ and $\text{O}2_4\text{Y}_4^{12-}$ were labelled with red and blue asterisks, respectively.

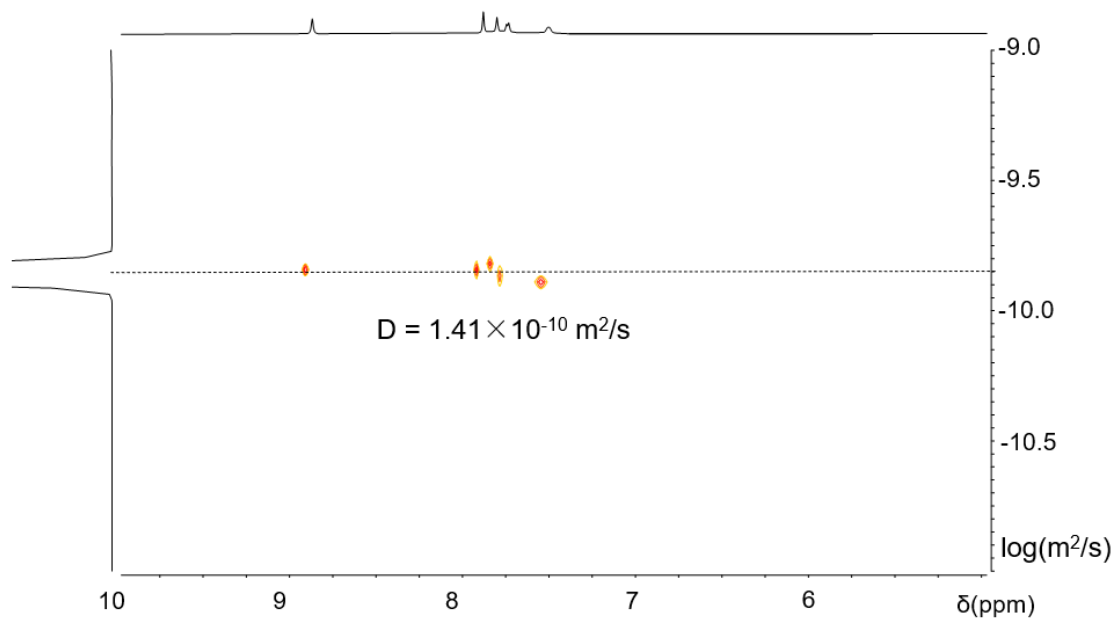


Figure S19. Partial ^1H DOSY spectrum (600 MHz, D_2O , 298 K) of $\text{M}_{24}\text{X}_4^{12-}$.

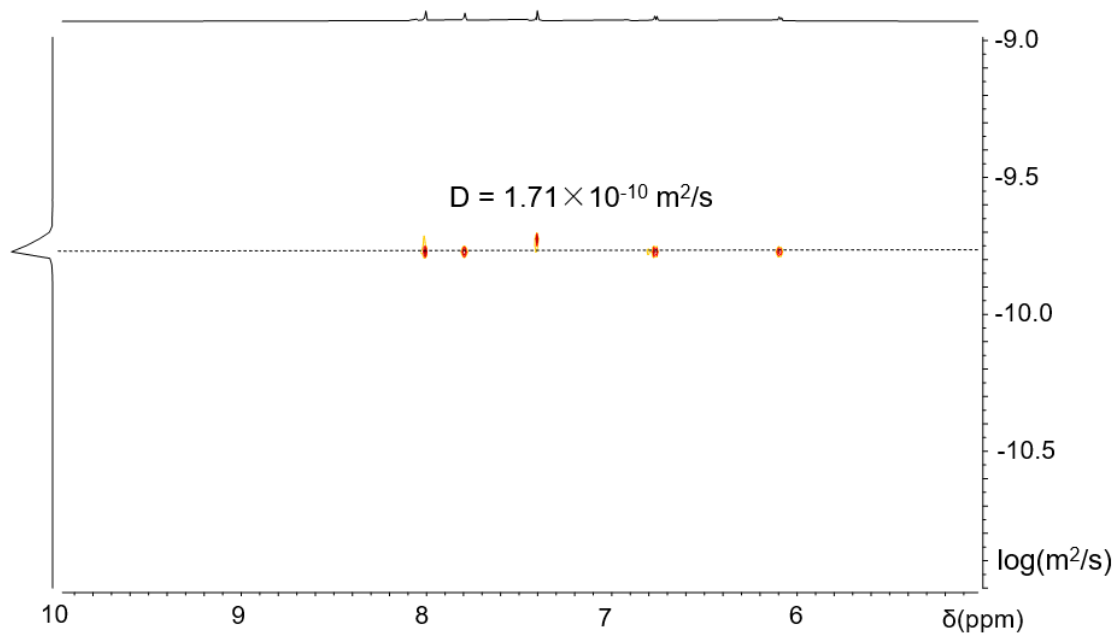


Figure S20. Partial ^1H DOSY spectrum (600 MHz, D_2O , 298 K) of $\text{O}_2\text{Y}_4^{12-}$.

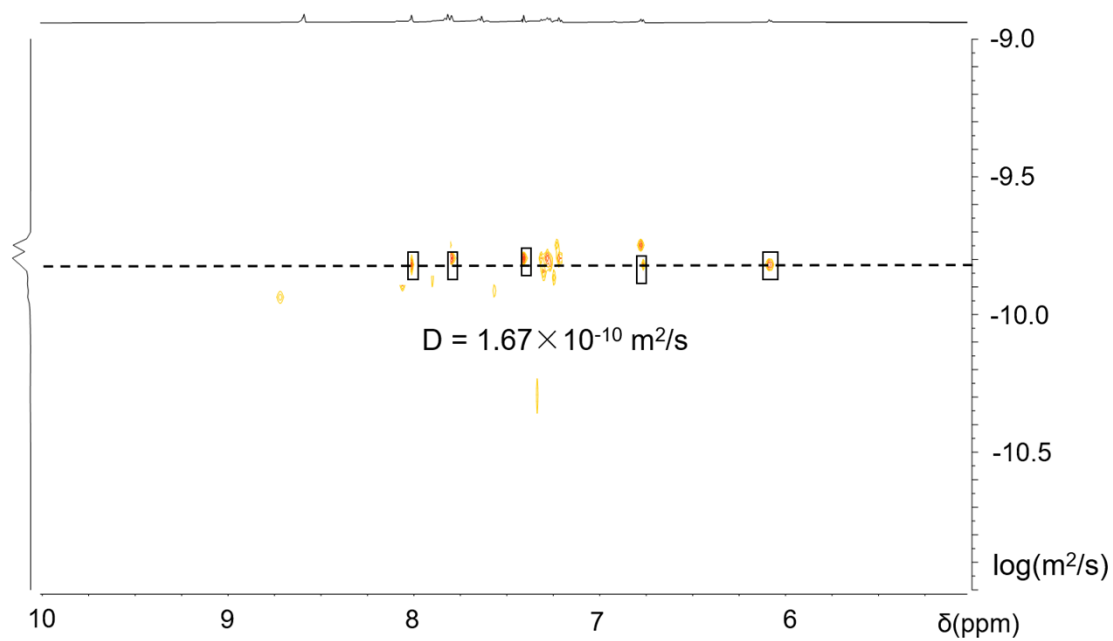


Figure S21. Partial ^1H DOSY spectrum (600 MHz, D_2O , 298 K) of a mixture of **M2**, **O2**, **X**, **Y** followed by adding CDCl_3 into the sample. The resonances corresponding to $\text{M}_2\text{X}_4^{12-}$ were marked.

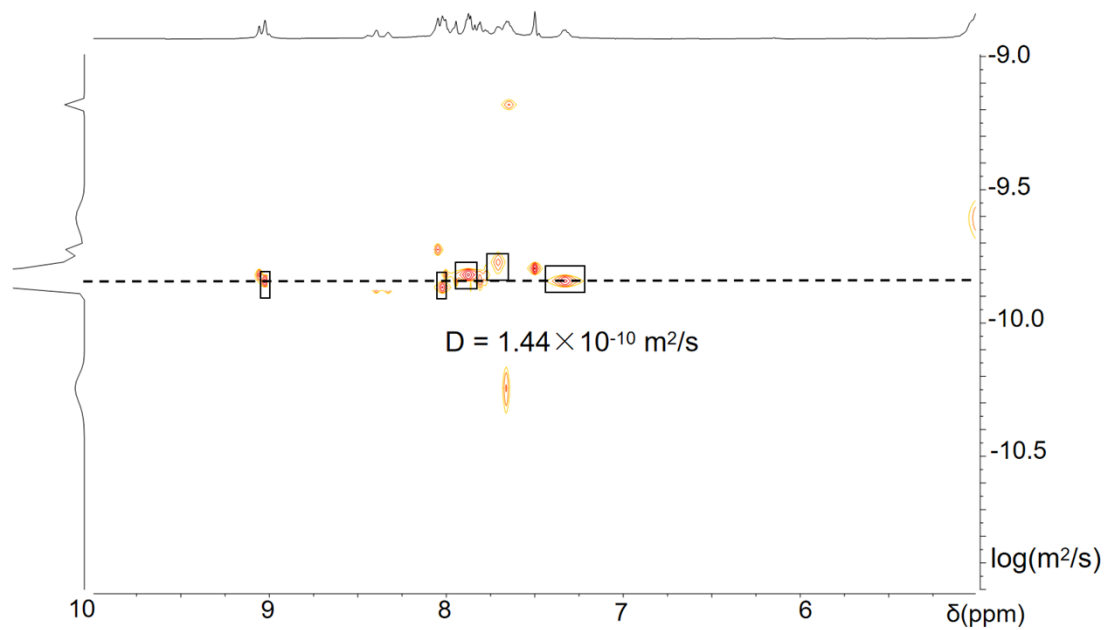


Figure S22. Partial ^1H DOSY spectrum (600 MHz, D_2O , 298 K) of a mixture of **M2**, **O2**, **X**, **Y** followed by adding $(n\text{-C}_4\text{H}_9)_4\text{N}^+\cdot\text{Cl}^-$ into the sample. The resonances corresponding to $\text{O2}_4\text{Y}_4^{12-}$ were marked.

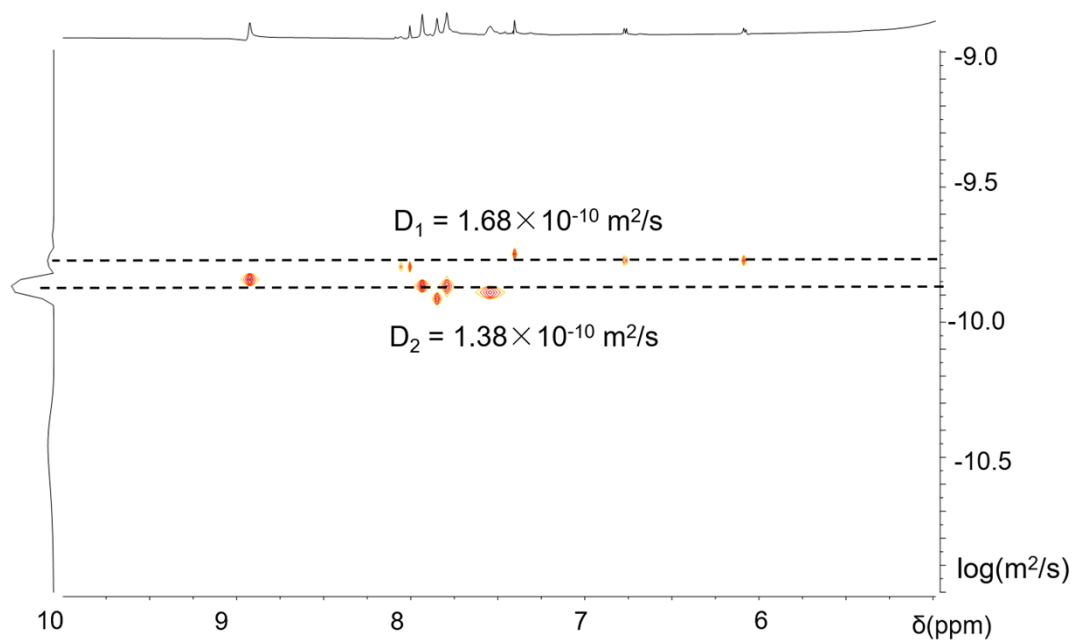


Figure S23. Partial ^1H DOSY spectrum (600 MHz, D_2O , 298 K) of a mixture of **M2**, **O2**, **X**, **Y** followed by adding $(n\text{-C}_4\text{H}_9)_4\text{N}^+\cdot\text{Cl}^-$ and CDCl_3 into the sample. The resonances corresponding to **M2₄X₄¹²⁻** and **O2₄Y₄¹²⁻** were marked.

Figure S24. Partial ^1H NMR spectra (600 MHz, CDCl_3 , 298 K) of a) **M1₄X₄** and c) **O1₄Y₄**, as well as b) a 1:2:1:2 mixture of **M1**, **O1**, **X** and **Y**. The spectrum in b) indicated that only **M1₄X₄** was self-assembled, while **O1₄Y₄** was not.

Figure S25. Partial ^1H NMR spectra (600 MHz, CDCl_3 , 298 K) of a) **O1₄Y₄**, c) $(n\text{-C}_4\text{H}_9)_4\text{N}^+$, and b) a mixture of **O1₄Y₄** and $(n\text{-C}_4\text{H}_9)_4\text{N}^+$. The spectrum in b) indicated that in organic solvent namely CDCl_3 , **O1₄Y₄** could not recognize $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ on account of the absence of hydrophobic effect.

References

- [1] Y. Zhang, Y. Zhao, C. Zhang, X. Luo, X. Liu, *CrystEngComm* **2022**, *24*, 4496-4499.
- [2] Y. Chen, G. Wu, B. Chen, H. Qu, T. Jiao, Y. Li, C. Ge, C. Zhang, L. Liang, X. Zeng, X. Cao, Q. Wang, H. Li, *Angew. Chem. Int. Ed.* **2021**, *60*, 18815-18820.