

Supporting information

for

**Controlled nitrite anion encapsulation and release in molecular cavity of
decamethylcucurbit[5]uril: Solution and solid state studies**

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Chemicals and materials

All chemicals and reagents were purchased from commercial suppliers and used without further purification except for decamethylcucurbit[5]uril ($\text{Me}_{10}\text{CB}[5]$) which was prepared and purified according to the procedure reported in the literature.^{S1}

Characterization methods

Elemental analyses of C, H, and N were carried out on an Elementar Vario EL III analyzer. Infrared (IR) spectra were recorded using KBr pellets on a PerkinElmer Spectrum One in the range 400–4000 cm^{-1} . Thermal gravimetric analyses (TGA) were performed under a flow of N_2 ($100 \text{ mL} \cdot \text{min}^{-1}$) with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ using a TA SDT–600 thermogravimetric analyzer. Aluminum oxide crucibles were used for all samples, and the instrument was calibrated using indium as standard. An empty crucible was used as reference. Miniflex600 powder X-ray diffractometer (PXRD) was employed for all measurements with experimental parameters as follows: room temperature, Cu–K α radiation ($\lambda = 1.54056 \text{ \AA}$), 2θ range $5\text{--}30^\circ$, Step size 0.02° (scanning rate with 2θ in $1^\circ \cdot \text{min}^{-1}$). Mass spectroscopy analysis was performed on a Bruker Impact II UHR–TOF mass spectroscopy. A water solution containing 1:10 equivalent of $\text{Me}_{10}\text{Q}[5]$ and sodium nitrite about 1 mM were electrosprayed and m/z of cationic species was recorded.

Synthesis of $[\text{Na}_2(\text{H}_2\text{O})_2(\text{NO}_2@\text{Me}_{10}\text{CB}[5])]^+ \cdot \text{NO}_2^- \cdot 14.75\text{H}_2\text{O}$ (Compound 1):

$\text{Me}_{10}\text{CB}[5]$ (198 mg, 0.2 mmol) was dissolved in 10 ml distilled water, and NaNO_2 (138 mg, 2.0 mmol) was then added. After sonication and magnetic stirring, the clear solution, with pH value of

7.0, was allowed to evaporate slowly at room temperature. Colorless crystals of compound **1** were obtained after three days. Anal. Calcd for $C_{40}H_{83.5}N_{22}Na_2O_{30.75}$ (%) (M = 1410.60): C, 34.14; H, 5.90; N, 21.90. Found (%): C, 34.67; H, 5.42; N, 22.26. IR (KBr, cm^{-1}): ν = 3450 (br, ν_{H_2O}), 2995 (w, ν_{CH_3}), 1741 [vs, $\nu(C=O)$], red shift compared to $\nu(C=O)$ on pure Me₁₀CB[5] at 1752], 1635 (w, δ_{H_2O}), 1477 (vs, δ_{CH_2}), 1406 (s), 1373 (m, δ_{CH_3}), 1309 (s), 1267 (m, NO_2^-), 1197 (m, asymmetric stretching of C-N), 1164 (w, symmetric stretching of C-N), 1072 (vs), 964 (w, stretching of C-C), 912 (m), 877 (s), 833 (s, NO_2^-), 759 (s, out-of-plane deformation of glycoluril ring), 721 (m), 699 (s, out-of-plane deformation of glycoluril ring). Crystallographic data of **1**: Monoclinic, space group P_2/n ; $a=10.9837(1)$ Å, $b=14.5848(1)$ Å, $c=19.3219(3)$ Å, $\beta=99.214(1)^\circ$; $V=3055.32(6)$ Å³, $Z=2$, GOOF=1.040. Total 29606 reflections measured ($7.64^\circ \leq 2\theta \leq 146.82^\circ$), 6097 unique ($R_{int} = 0.0231$, $R_{sigma} = 0.0155$) which were used in all calculations. The final R_1 was 0.0766 (all data)) and wR_2 was 0.2049 (all data).

Synthesis of $\{Na_2(H_2O)_{10}, CB[6]\}^{2+} \cdot 3(H_2O) \cdot 2(NO_2)^-$, (compound **2**)

CB[6] (200 mg, ~0.2 mmol) was dissolved in 10 ml distilled water, and NaNO₂ (138 mg, 2.0 mmol) was then added. After sonication and magnetic stirring, clear up-layer solution was moved to glass vial and was allowed to evaporate slowly at room temperature. Colorless crystals of compound **2** were obtained after two weeks. Crystallographic data of **2**: Orthorhombic, space group $Pna2_1$; $a=31.578(5)$ Å, $b=14.455(2)$ Å, $c=12.0570(17)$ Å, $V=5503.5(13)$ Å³, $Z=4$, GOOF=1.0458. Total 29673 reflections measured ($5.60^\circ \leq 2\theta \leq 136.74^\circ$), 9189 unique ($R_{int} = 0.0593$, $R_{sigma} = 0.0562$) which were used in all calculations. The final R_1 was 0.1169 (all data)) and wR_2 was 0.3177 (all data).

Crystallography

A crystal of compounds suitable for single crystal X-ray diffraction analysis was selected using a polarized light optical microscope. X-ray diffraction data was collected on an Agilent SuperNova diffractometer using Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$). Using Olex2,^{S2} the structure was solved with the olex2.solve structure solution program using Charge Flipping solution method and refined with the olex2.refine refinement package using Gauss-Newton minimisation method.^{S3} All non-hydrogen atoms except some disordered atoms were refined anisotropically. Hydrogen atoms on Me₁₀CB[5] or CB[6] were placed in geometrically calculated positions and included in the refinement process using a riding model. CIF files containing crystallographic data (CCDC 1554723 for compound 1, CCDC1845091 for compound 2) can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

PXRD characterization of compound 1

Phase purity of compound **1** was identified by powder X-ray diffraction (PXRD) study. The experimental PXRD pattern matches well with the one simulated from single crystal data of compound **1**, indicating the purity of bulk product.

Thermal stability of compound 1

Thermal stability of compound **1** was studied by thermal analysis in the temperature range of 30–600 °C. The TG curve showed that there are two major weight loss stages. The first weight loss occurred at 30-150 °C, which can be attributed to the release of H₂O molecules. The second weight loss around 430 °C can be assigned to the decomposition of the Me₁₀Q[5] host.

Table S1 Peaks found in mass spectra of Me₁₀CB[5]-NaNO₂, Me₁₀CB[5]-NaNO₂ after decomposition, CB[5]-NaNO₂ and CB[6]-NaNO₂ in water, and their proposed corresponding cationic species.

Sample	m/z	intensity	Proposed cationic species
Me ₁₀ CB[5]-NaNO ₂	1062.35	high	{2Na ⁺ +NO ₂ ⁻ +Me ₁₀ CB[5]} ⁺
	1034.40	low	{2Na ⁺ +OH ⁻ +Me ₁₀ CB[5]} ⁺
Me ₁₀ CB[5]-NaNO ₂ after decomposition	988.43	low	{H ₃ O ⁺ +Me ₁₀ CB[5]} ⁺
	993.38	low	{Na ⁺ +Me ₁₀ CB[5]} ⁺
	1034.41	low	{2Na ⁺ +OH ⁻ +Me ₁₀ CB[5]} ⁺
	503.23	high	{2H ₃ O ⁺ +Me ₁₀ CB[5]} ²⁺
	563.15	medium	{2Na ⁺ +K ⁺ +Cl ⁻ +2H ₂ O+Me ₁₀ CB[5]} ²⁺
	572.16	high	{2Na ⁺ +K ⁺ +Cl ⁻ +3H ₂ O+Me ₁₀ CB[5]} ²⁺
	577.15	medium	{2Na ⁺ +K ⁺ +NO ₃ ⁻ +2H ₂ O+Me ₁₀ CB[5]} ²⁺
CB[5]-NaNO ₂	911.19	high	{2Na ⁺ +Cl ⁻ +CB[5]} ⁺
	913.19	medium	{2H ₃ O ⁺ +NO ₂ ⁻ +CB[5]} ⁺
	438.11	medium	{2Na ⁺ +CB[5]} ²⁺
	922.21	low	{2Na ⁺ +NO ₂ ⁻ +CB[5]} ⁺
	927.16	low	{Na ⁺ +K ⁺ +Cl ⁻ +CB[5]} ⁺
CB[6]-NaNO ₂	539.14	high	{2Na ⁺ +2H ₂ O+CB[6]} ²⁺
	1013.31	low	{H ₃ O ⁺ +CB[6]} ⁺
	1037.29	low	{Na ⁺ +H ₂ O+CB[6]} ⁺
	1088.26	low	{2Na ⁺ +NO ₂ ⁻ +CB[6]} ⁺
	1106.27	low	{2Na ⁺ +NO ₂ ⁻ +H ₂ O+CB[6]} ⁺
	1156.25	low	{3Na ⁺ +2NO ₂ ⁻ +CB[6]} ⁺
	1174.25	low	{3Na ⁺ +2NO ₂ ⁻ +H ₂ O+CB[6]} ⁺

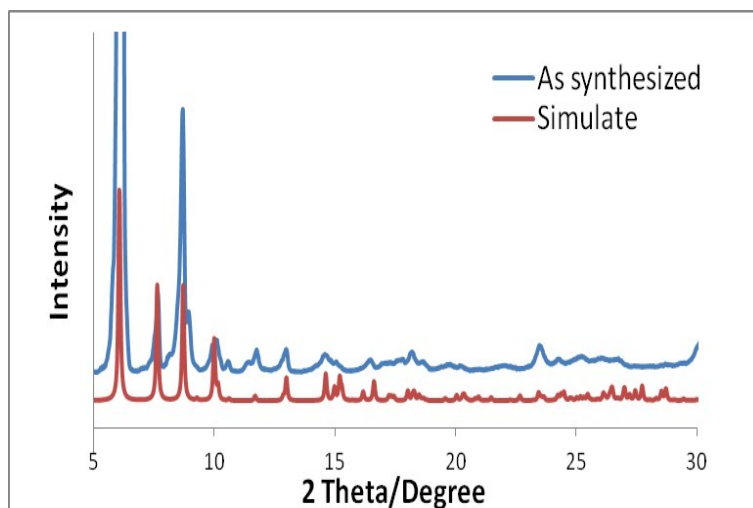


Fig. S1 Simulated and experimental PXRD of compound 1.

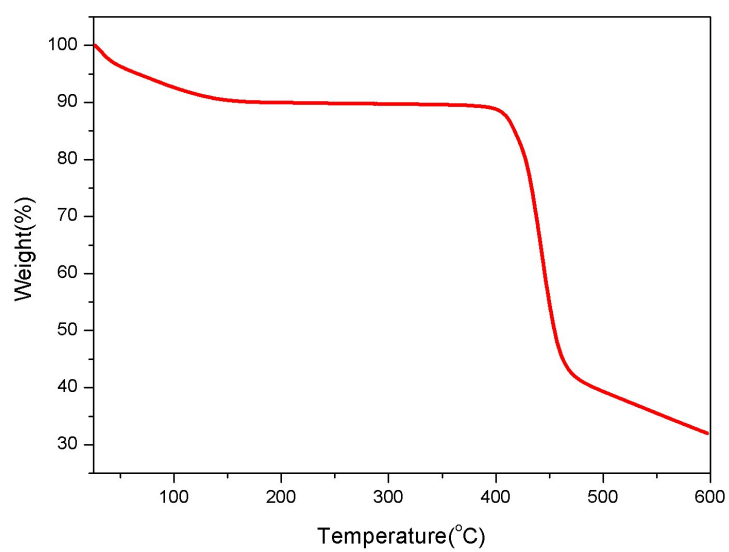


Fig. S2 TG curve of compound 1.

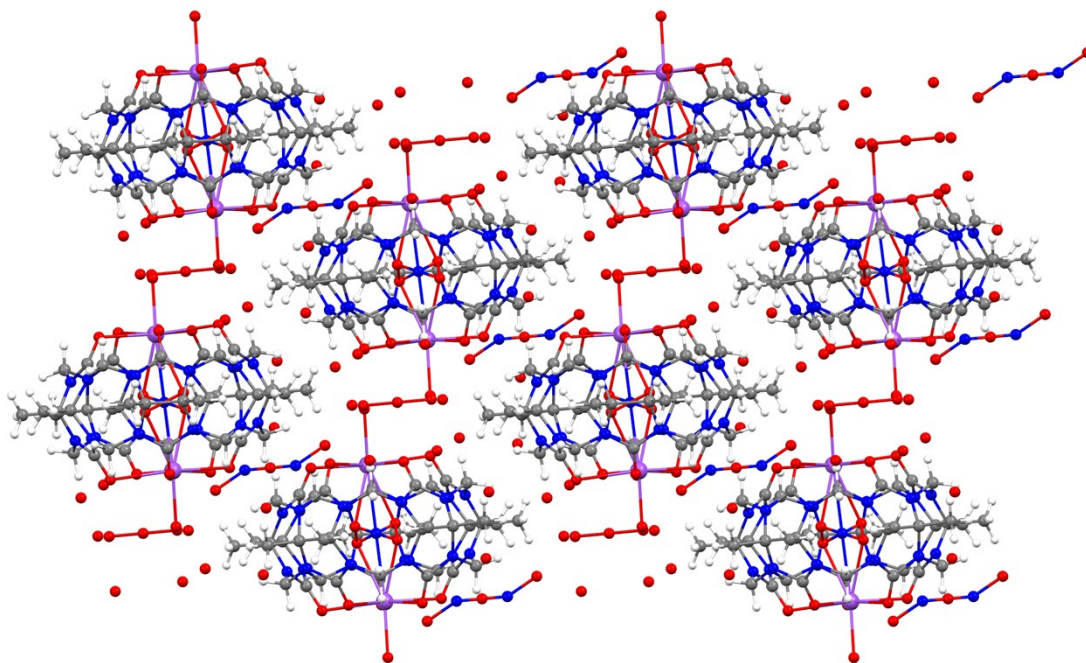


Fig. S3 A view of the 3 D packing diagram of compound **1** along the *b* axis.

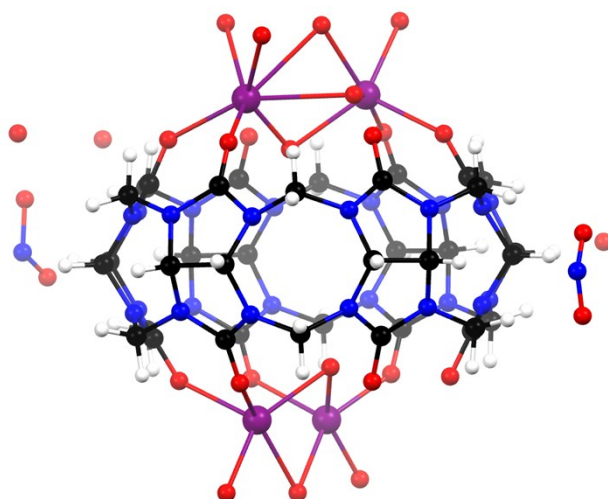


Fig. S4 The basic building unit in compound **2**

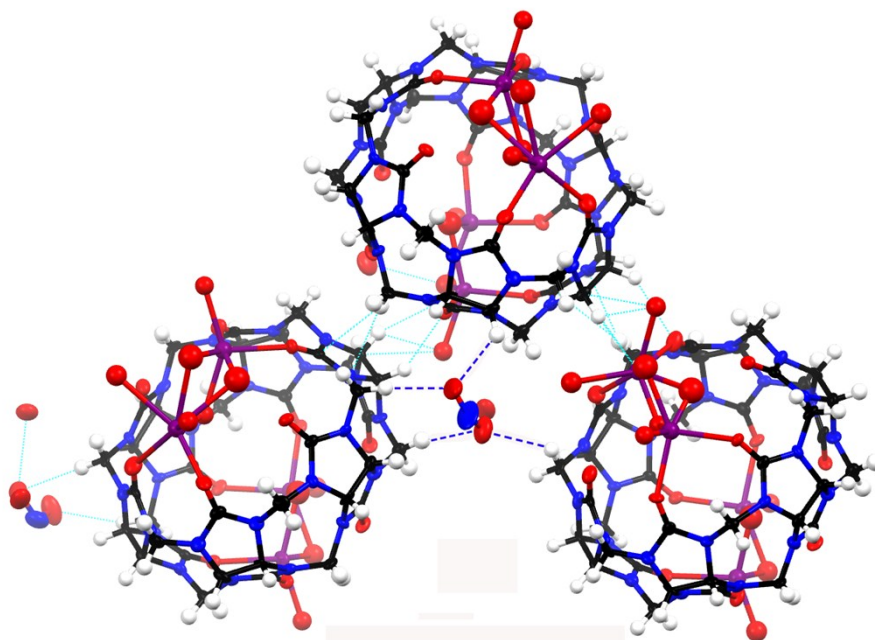


Fig. S5 Dashed blue lines show the noncovalent bonds formed between oxygen atoms of nitrite ion and hydrogen atoms of methylene and methine groups of CB[6] in compound **2**, with bond distances range from 2.461 Å to 2.532 Å.

References

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- (S2) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.
- (S3) L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst.*, 2015, **A71**, 59–75.