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## A water-soluble naphthalenediimide-containing hexacationic cage

Shuai Fang, Errui Li, Dingsheng Zhu, Guangcheng Wu, Qinhao Zhang, Chuhao Lin, Feihe Huang, Hao Li\*

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#### **S1. General Methods**

All reagents and solvents were purchased from commercial sources and used without further purification. KI<sub>3</sub> was prepared by sonicating a 1:1 mixture of I<sub>2</sub> and KI in water. Manipulations were performed under a normal laboratory atmosphere unless otherwise noted. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature using Bruker AVANCE III 400/500 and Agilent DD2 600 spectrometers, with working frequencies of 400/500/600 and 100/125/150 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. Chemical shifts are reported in ppm relative to the residual internal non-deuterated solvent signals (D<sub>2</sub>O:  $\delta = 4.70$  ppm, DMSO-*d*<sub>6</sub>:  $\delta = 2.50$  ppm, one methyl of DMF-*d*<sub>7</sub>:  $\delta = 2.08$  ppm). High-resolution mass spectra (HRMS) were recorded on a Fourier transform ion cyclotron resonance mass spectrometery (FT-ICR MS). X-ray crystallographic data were collected on a Bruker D8 Venture diffractometer.

### S2. Synthesis and Characterization of Compounds



Scheme S1. Synthesis of 1.

**Compound 1**: It was synthesized based on previous literature<sup>[1]</sup>.

1,2,4,5-Benzenetetracarboxylic dianhydride (2.68 g, 10.0 mmol) and

3-aminopyridine (2.35 g, 25.0 mmol) were added to a reaction flask containing

anhydrous DMF (30ml). The solution was refluxed overnight under the protection

N<sub>2</sub>. The reaction mixture was then cooled to 0 °C by using an ice bath, leading to a yellow precipitate which was collected via filtration. The solid was washed with CH<sub>2</sub>Cl<sub>2</sub> and acetone, followed by drying under vacuum, yielding a light brown powder (3.80 g, 90%). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  8.77 (s, 4H), 8.69 (m, 4H), 7.96 (m, 2H), 7.65 (m, 2H). The <sup>1</sup>H NMR spectrum of **1** is fully consistent with that reported in the literature<sup>[1]</sup>.



Scheme S2. Synthesis of M1<sup>2+.</sup> 2Br<sup>-</sup>

M1<sup>2+.</sup> 2Br<sup>-</sup>: 1 (420 mg, 1.0 mmol) and (bromomethyl)benzene (427.5 mg, 2.5 mmol) were combined in a reaction flask. Anhydrous DMF (15 mL) was added, and the solution was refluxed overnight under protection of N<sub>2</sub>. After the reaction mixture was cooled to 0 °C, the yellow slurry was collected via filtration, and washed with CH<sub>2</sub>Cl<sub>2</sub> and acetone. The product was then dried under vacuum to yield a light-yellow powder (724 mg, 90%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ9.49 (d, J=6.1, 2H), 9.50 (s, 2H), 8.88 (d, J=8.5, 2H), 8.82(s, 4H), 8.51(m, 2H), 7.60(d, J=6.6, 2H), 7.48(m, 3H), 6.06(s, 4H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 162.4, 147.0, 145.5, 145.0, 135.5, 133.8, 131.0, 129.6, 129.3, 129.0, 128.9, 126.8, 126.6, 63.9. HRMS (ESI) (m/z): calculated for C<sub>90</sub>H<sub>54</sub>Br<sub>6</sub>N<sub>12</sub>O<sub>12</sub>: 301.0972; found: 301.0981.



Scheme S3. Synthesis of 2<sup>6+</sup>·6Br<sup>-</sup>

2<sup>6+</sup>•6Br<sup>-</sup>: 1 (630 mg, 1.5 mmol) and 1,3,5-tris(bromomethyl)benzene (357 mg, 1.0 mmol) were combined a reaction flask. Anhydrous DMF (150 mL) was added \, and the solution was refluxed for 2 days under protection of N<sub>2</sub>, during which light was avoided. After the reaction mixture was cooled to 0 °C, the yellow slurry was collected via filtration and washed with CH<sub>2</sub>Cl<sub>2</sub> and acetone. The product was then dried under vacuum to yield a little dark yellow powder (390 mg, 40%). <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O): δ 9.26 (d, J=6, 6H), 8.92(s, 6H), 8.66 (d, J=8.15, 6H), 8.37 (t, J=6.35, 6H), 8.24(s, 12H), 7.18(s, 6H), 6.06(s, 6H). (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.90 (s, 6H), 9.49 (d, J=5.85, 6H), 8.86 (d, J=8.15, 6H), 8.54(t, J=6.35, 6H), 8.34(s, 6H), 7.88(s, 6H), 6.95(s, 6H), 6.29(s, 6H), 5.97(s, 6H). (500 MHz, DMF- $d_7$ ):  $\delta$  10.07 (s, 6H), 9.76 (d, J=6.12, 6H), 9.00 (d, J=8.34, 6H), 8.66(m, 6H), 8.39(s, 6H), 7.11(s, 6H), 6.53(s, 6H), 6.16(s, 6H), 5.97(s, 6H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 162.5, 147.7, 147.2, 145.5, 136.1, 135.9, 130.4, 129.4, 128.1, 128.0, 126.4, 124.8, 63.4. HRMS (ESI) (m/z): calculated for C<sub>90</sub>H<sub>54</sub>N<sub>12</sub>O<sub>12</sub><sup>6+</sup> [M]<sup>6+</sup>: 249.2331, found: 249.2301.  $C_{90}H_{52}N_{12}O_{12}^{4+}$  [M-2H]<sup>4+</sup> 373.0951, found: 373.0964.  $C_{90}H_{53}BrN_{12}O_{12}^{4+}$  $[M+Br-H]^{4+}$  393.5762, found: 393.5747.  $C_{90}H_{53}BrN_{12}O_{12}^{4+}[M+2Br]^{4+}$  413.5577, found: 413.5578.

# S3. <sup>1</sup>H NMR, <sup>13</sup>C NMR and 2D NMR Spectra of Compounds



Figure S1. Partial <sup>1</sup>H NMR spectrum (500 M Hz, 298 K,  $D_2O$ ) of  $2^{6+} \cdot 6Br^{-}$ .



Figure S2. Partial <sup>1</sup>H NMR spectrum (500 M Hz, 298 K, DMSO- $d_6$ ) of  $2^{6+} \cdot 6Br^-$ .



Figure S3. Partial <sup>1</sup>H NMR spectrum (500 M Hz, 298 K, DMF- $d_7$ ) of  $2^{6+} \cdot 6Br^-$ .



Figure S4. Partial <sup>13</sup>C NMR spectrum (125 M Hz, 298 K, DMSO- $d_6$ ) of  $2^{6+} \cdot 6Br^-$ .





Key coupling peaks were labelled in the spectrum.



Figure S6. Partial <sup>1</sup>H NMR spectrum (500 M Hz, 298 K,  $D_2O$ ) of  $M1^{2+.}2Br^{-}$ .



Figure S7. Partial <sup>1</sup>H NMR spectrum (500 M Hz, 298 K, DMSO- $d_6$ ) of M1<sup>2+.</sup> 2Br<sup>-</sup>.



Figure S8. Partial <sup>13</sup>C NMR spectrum (500 M Hz, 298 K, DMSO-*d*<sub>6</sub>) of M1<sup>2+.</sup> 2Br<sup>-</sup>.

## S4. Variable Temperature <sup>1</sup>H NMR Spectroscopic Analysis



**Figure S9.** Partial <sup>1</sup>H NMR spectra (500 M Hz, 298K, DMF-*d*<sub>7</sub>) of **2<sup>6+</sup>**⋅6Br<sup>-</sup> based on Variable Temperature <sup>1</sup>H NMR experiment.

**S5. Mass Spectra** 



Figure S10. Mass spectrum of  $2^{6+} \cdot 6Br^{-}$ .



Figure S11. Mass spectrum of M1<sup>2+.</sup> 2Br<sup>-</sup>.

# S6. <sup>1</sup>H NMR Titrations, Job-Plot, and Binding Constant calculation





pyridinium units barely shifted.





Figure S13. Partial <sup>1</sup>H NMR spectra (600 M Hz, 298 K, D<sub>2</sub>O) of

2,6-dihydroxynaphthalene  $\subset 2^{6+} \cdot 6Br^{-}$  recorded in the presence of different amount

of 2,6-dihydroxynaphthalene. The spectrum in the top is corresponding to 2,6-dihydroxynaphthalene.



Figure S14. The Job-Plot corresponding to the binding between 2,6-dihydroxynaphthalene and  $2^{6+} \cdot 6Br^-$ , which was made based on <sup>1</sup>H NMR spectroscopic results. [Host]+ [Guest]= 0.50 mM. The maximum value of the Y axis is obtained at 0.66, indicating a 2:1 (host: guest) binding stoichiometry.



Figure S15. A plot of the upfield shifts of the resonance corresponding to proton f in the cage versus the guest/host ratio, namely [2,6-dihydroxynaphthalene]/[ $2^{6+}$ ], in which [ $2^{6+}$ ] was kept constant, namely 1 mM. This plot was then used to calculate the binding constants of 2,6-dihydroxynaphthalene $\subseteq 2^{6+} \cdot 6Br^-$  in D<sub>2</sub>O, by using a

website namely http://supramolecular.org/. The binding constants of 2,6-dihydroxynaphthalene  $\subseteq 2^{6+} \cdot 6Br^{-}$  are calculated to be  $K_{11} = 3.4 \pm 0.3 \times 10^{4}$  and

$$K_{21} = 1.4 \pm 0.2 \times 10^4 \,\text{M}^{-1}$$
 in water.





**Figure S16.** Partial <sup>1</sup>H NMR spectra (600 M Hz, 298 K,  $D_2O$ ) of

2-hydroxynaphthalene  $\subset 2^{6+} \cdot 6Br^{-}$  recorded in the presence of different amount of

2-hydroxynaphthalene. The spectrum in the top is corresponding to

2-hydroxynaphthalene.



Figure S17. The Job-Plot corresponding to the binding between 2-hydroxynaphthalene and 2<sup>6+</sup>•6Br<sup>−</sup>, which was made based on <sup>1</sup>H NMR spectroscopic results. [Host]+ [Guest]= 0.50 mM. The maximum value of the Y axis is obtained at 0.50, indicating a 1:1 (host: guest) binding stoichiometry.



**Figure S18.** A plot of the upfield shifts of the resonance corresponding to proton f in the cage versus the guest/host ratio, namely [2-hydroxynaphthalene]/[ $2^{6+}$ ], in which [ $2^{6+}$ ] was kept constant, namely 1 mM. This plot was then used to calculate the binding constants of 2-hydroxynaphthalene  $\subseteq 2^{6+} \cdot 6Br^-$  in D<sub>2</sub>O, by using a

website namely http://supramolecular.org/. The binding constants of 2-hydroxynaphthalene  $\subseteq 2^{6+} \cdot 6Br^{-}$  are calculated to be  $K = 5.0 \pm 0.2 \times 10^4 M^{-1}$  in



Figure S19. Partial <sup>1</sup>H NMR spectra (600 M Hz, 298 K, D<sub>2</sub>O) of 4,7–dihydroxy–

coumarin  $\subset 2^{6+} \cdot 6Br^{-}$  recorded in the presence of different amount of







**Figure S21.** A plot of the upfield shifts of the resonance corresponding to proton f in the cage versus the guest/host ratio, namely  $[4,7-dihydroxy-coumarin]/[2^{6+}]$ , in which  $[2^{6+}]$  was kept constant, namely 1 mM. This plot was then used to calculate the binding constants of 4,7-dihydroxy-coumarin  $\subseteq 2^{6+} \cdot 6Br^-$  in D<sub>2</sub>O, by using a

website namely http://supramolecular.org/. The binding constants of 4,7–dihydroxy–coumarin  $\subseteq 2^{6+} \cdot 6Br^{-}$  are calculated to be  $K_{11}=2.4 \pm 0.2 \times 10^{4}$ , and  $K_{21}=7.5 \pm 0.9 \times 10^{3} M^{-1}$  in water.



**Figure S22.** Partial <sup>1</sup>H NMR spectra (600 M Hz, 298 K, D<sub>2</sub>O) of 5,7–dihydroxy– coumarin  $\subset 2^{6+} \cdot 6Br^{-}$  recorded in the presence of different amount of



**Figure S23.** The Job-Plot corresponding to the binding between 5,7–dihydroxy–coumarin and **2<sup>6+•</sup>6Br<sup>-</sup>**, which was made based on <sup>1</sup>H NMR spectroscopic results. [Host]+ [Guest]= 0.50 mM. The maximum value of the Y axis is obtained at 0.50, indicating a 1:1 (host: guest) binding stoichiometry.



Figure S24. A plot of the upfield shifts of the resonance corresponding to proton f in the cage versus the guest/host ratio, namely  $[5,7-dihydroxy-coumarin]/[2^{6+}]$ , in which  $[2^{6+}]$  was kept constant, namely 1 mM. This plot was then used to calculate the binding constants of 5,7-dihydroxy-coumarin  $\subseteq 2^{6+} \cdot 6Br^-$  in D<sub>2</sub>O, by using a

website namely http://supramolecular.org/. The binding constants of 5,7-dihydroxy-coumarin  $\subseteq 2^{6+} \cdot 6Br^{-}$  are calculated to be K=  $9.9 \pm 1.5 \times 10^{3} \text{ M}^{-1}$  in





coumarin  $\subset 2^{6+} \cdot 6Br^-$  recorded in the presence of different amount of

7-hydroxy- coumarin.



Figure S26. The Job-Plot corresponding to the binding between 7–hydroxy– coumarin and  $2^{6+}\cdot 6Br^{-}$ , which was made based on <sup>1</sup>H NMR spectroscopic results. [Host]+ [Guest]= 0.50 mM. The maximum value of the Y axis is obtained at 0.50,

indicating a 1:1 (host: guest) binding stoichiometry.



Figure S27. A plot of the upfield shifts of the resonance corresponding to proton f in the cage versus the guest/host ratio, namely [7–hydroxy–coumarin]/[2<sup>6+</sup>], in which [2<sup>6+</sup>] was kept constant, namely 1 mM. This plot was then used to calculate the binding constants of 7–hydroxy–coumarin $\subseteq 2^{6+} \cdot 6Br^-$  in D<sub>2</sub>O, by using a website namely http://supramolecular.org/. The binding constants of 7–hydroxy–coumarin $\subseteq 2^{6+} \cdot 6Br^-$  are calculated to be K= 4.6 ± 0.6 × 10<sup>3</sup> M<sup>-1</sup> in



Figure S28. Partial <sup>1</sup>H NMR spectra (600 M Hz, 298 K,  $D_2O$ ) of  $2^{6+}\cdot 6Br^-$  (0.5 mM)

in the presence of different amount of KI<sub>3</sub>.

The binding constant of  $2^{6+} \cdot 6Br^-$  to recognize a  $I_3^-$  anion was also determined by <sup>1</sup>H NMR titration experiments. Because the host-guest exchange occurs slow on the <sup>1</sup>H NMR timescale, we measured the integration of resonances corresponding to both the free  $2^{6+} \cdot 6Br^-$ , and  $I_3^- \subset 2^{6+} \cdot 6Br^-$ , which provided the resonance ratio, namely  $[I_3^- \subset 2^{6+} \cdot 6Br^-]/[2^{6+} \cdot 6Br^-]$ . KI<sub>3</sub> was prepared by sonicating a 1:1 mixture of I<sub>2</sub> and KI in water. As a consequence,  $[KI_3]_0$  is thus equal to [KI]. The "free"  $[KI_3]$  in titration experiments was calculated to be  $[KI_3]_0 - [I_3^- \subset 2^{6+} \cdot 6Br^-]$ .  $K_a = 1.5 \pm 0.4 \times 10^4 \,\mathrm{M}^{-1}$  was obtained by using the following equation.

 $K_a = [I_3 \subset 2^{6+} \cdot 6Br^-]/([2^{6+} \cdot 6Br^-][KI_3])$ 

# **S7.** Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) experiment



**Figure S29.** Photographs showing color change before (left) and after (right) 5 mg of cage was exposed to iodine vapor for 8 h.



Figure S30. Thermogravimetric analysis of desolvated  $2^{6+} \cdot 6Br^{-}$ .



Figure S31. Thermogravimetric analysis of  $2^{6+} \cdot 6Br^{-}$  after adsorption of iodine



Figure S32. Differential scanning calorimetry (DSC) experiment of desolvated

**2**<sup>6+</sup>•6Br<sup>−</sup>.

## **S8.** X-ray crystallography

#### Methods

Single crystals, suitable for X-ray crystallography, were grown by slow vapor diffusion of cage's solution in water over the course of days. Data were collected at 173 K on a Bruker D8 Venture Diffractometer equipped with a GaK $\alpha$  I $\mu$ S source and MX optic.

## 1) 2<sup>6+</sup>·6Br<sup>-</sup>

a) Crystal parameters

 $C_{90}H_{60}Br_6N_{12}O_{15}$ , Yellow block, monoclinic, space group P 21, a = 14.159(7) Å, b = 23.995(13) Å, c = 14.229(7) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 104.068(14)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 4689(4) Å3, Z = 2, T = 173 K, pcalc = 1.437 g/cm<sup>3</sup>,  $\mu$ (GaK $\alpha$ ) = 2.500 mm<sup>-1</sup>. Final R1(I > 2 $\sigma$ (I)) = 0.0870 and wR2 = 0.2689 (all data). The structure was solved by direct method and different Fourier syntheses. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. CCDC number: 2076466.

b) Solid-state structure



**Figure S33.** Different views of the solid-state structure of  $2^{6+} \cdot 6Br^-$ . Color code: C gray, N green, O red, I purple, H white. Counterions, not necessary hydrogen atoms, disordered and partial guest molecules have been omitted for clarity.

# (2) 2,6-dihydroxynaphthalene $\subset 2^{6+} \cdot 6Br^{-}$

#### a) Crystal parameters

 $C_{150}H_{108}Br_6N_{12}O_{27}$ , Yellow block, monoclinic, space group P -1, a = 14.4602(5) Å, b = 14.4602(5) Å, c = 14.4602(5) Å,  $\alpha$  = =106.980(1)°,  $\beta$  = 100.140(1)°,  $\gamma$  = 109.181(1)°, V = 7049.7(5) Å3, Z = 2, T = 173 K, pcalc = 1.409 g/cm<sup>3</sup>,  $\mu$ (GaK $\alpha$ ) = 1.785 mm<sup>-1</sup>. Final R1(I > 2 $\sigma$ (I)) = 0.1393 and wR2 = 0.3485 (all data). The structure was solved by direct method and different Fourier syntheses. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. CCDC number: 2076470.

b) Solid-state structure



**Figure S34.** Different views of the solid-state structure of naphthalene–2,6–diol  $\subset$  2<sup>6+</sup>·6Br<sup>-</sup>. Color code: C gray, N green, O red, I purple, H white. Counterions, hydrogen atoms that are not involved in hydrogen bonding, disordered counterions, guests and solvent molecules have been omitted for clarity.

# (3) 2-hydroxynaphthalene $\subset 2^{6+} \cdot 6Br^{-}$

#### a) Crystal parameters

 $C_{100}H_{65}Br_6N_{12}O_{15}$ , Yellow block, monoclinic, space group C 2, a = 18.8016(17) Å, b = 21.9859(17) Å, c = 28.453(2) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 108.666(6)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 11143.0(16) Å3, Z = 2, T = 170 K, pcalc = 1.284 g/cm<sup>3</sup>,  $\mu$ (GaK $\alpha$ ) = 2.046 mm<sup>-1</sup>. Final R1(I > 2 $\sigma$ (I)) = 0.1777 and wR2 = 0.4512 (all data). The structure was solved by direct method and different Fourier syntheses. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. CCDC number: 2076467.

b) Solid-state structure



**Figure S35.** Different views of the solid-state structure of naphthalene $-2-ol \subset 2^{6+} \cdot 6Br^{-}$ . Color code: C gray, N green, O red, I purple, H white. Counterions, hydrogen atoms that are not involved in hydrogen bonding, disordered counterions, guests and solvent molecules have been omitted for clarity.

## (4) 5,7-dihydroxy coumarin $\subset 2^{6+} \cdot 6Br^{-}$

a) Crystal parameters

 $C_{233}H_{147}Br_{12}N_{24}O_{49}$ , Yellow block, space group P -1, a = 21.620(3) Å, b = 25.189(3) Å, c = 26.682(3) Å,  $\alpha = 99.495(9)^{\circ}$ ,  $\beta = 108.239(7)^{\circ}$ ,  $\gamma = 105.860(7)^{\circ}$ , V = 12767(3) Å3, Z = 2, T = 173 K, pcalc = 1.307 g/cm<sup>3</sup>,  $\mu$ (GaK $\alpha$ ) = 1.873 mm<sup>-1</sup>. Final R1(I > 2 $\sigma$ (I)) = 0.1431 and wR2 = 0.3198 (all data). The structure was solved by direct method and different Fourier syntheses. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and

refined with the ShelXL refinement package using Least Squares minimization. CCDC number: 2076468.

b) Solid-state structure



**Figure S36.** Different views of the solid-state structure of 5,7–hydroxy coumarin  $\subset$  2<sup>6+</sup>·6Br<sup>-</sup>. Color code: C gray, N green, O red, I purple, H white. Counterions, hydrogen atoms that are not involved in hydrogen bonding, disordered counterions, guests and solvent molecules have been omitted for clarity.

## (5) $I_3^- \subset 2^{6+} \cdot 6Br^-$

#### a) Crystal parameters

 $C_{90}H_{54}Br_{2}I_{6}N_{12}O_{12}$ , Yellow block, monoclinic, space group P 21/n, a = 12.1313(8) Å, b = 23.4871(17) Å, c = 31.769(2) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 99.440(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 8929.3(10) Å3, Z = 4, T = 173 K, pcalc = 1.798 g/cm<sup>3</sup>,  $\mu$ (GaK $\alpha$ ) = 12.320 mm<sup>-1</sup>. Final R1(I > 2 $\sigma$ (I)) = 0.1652 and wR2 = 0.3825 (all data). The structure was solved by direct method and different Fourier syntheses. Using Olex2, the structure

was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. CCDC number: 2076469.

b) Solid-state structure



**Figure S37.** Different views of the solid-state structure of  $I_3^- \subset 2^{6+} \cdot 6Br^-$ . Color code: C gray, N green, O red, I purple, H white. Counterions, hydrogen atoms that are not involved in hydrogen bonding, disordered counterions, guests and solvent molecules have been omitted for clarity.

## (6) $I_2 \subset 2^{6+} \cdot 6Br^-$

## a) Crystal parameters

 $C_{90}H_{54}Br_6I_2N_{12}O_{12}$ , Yellow block, monoclinic, space group P 21/n, a = 12.102(2) (8) Å, b = 23.347(6) Å, c = 31.702(9) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 99.798(16)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 8827(4) Å3, Z = 4, T = 173 K, pcalc = 1.677 g/cm<sup>3</sup>,  $\mu$ (GaK $\alpha$ ) = 6.315 mm<sup>-1</sup>. Final R1(I > 2 $\sigma$ (I)) = 0.1368 and wR2 = 0.3416 (all data). The structure was solved by direct method and different Fourier syntheses. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. CCDC number: 2076465.

b) Solid-state structure



**Figure S38.** Different views of the solid-state structure of  $I_2 \subset 2^{6+} \cdot 6Br^-$ . Color code:

C gray, N green, O red, I purple, H gray. Counterions, hydrogen atoms that are not involved in hydrogen bonding, disordered counterions, guests and solvent molecules have been omitted for clarity.



**Figure S39.** Packing mode of 5,7–dihydroxy coumarin  $\subset 2^{6+} \cdot 6Br^{-}$  single crystal structure along an axis in different direactions. Color code:  $2^{6+} \cdot 6Br^{-}$  blue, guest red.

Counterions, and hydrogen atoms have been omitted for clarity.

# **S9. Reference**

[1] Guha, S. and Saha, S., J. Am. Chem. Soc. 2010, 132, 17674-17677.