

## Supporting Information S1

### Preparation of Q[5]KI

Q[5]2KCl<sup>1</sup> (1.45g) was dissolved in hot water (10mL) filtered while still hot. KI (780mg) dissolved in hot water (2mL) was added. Crystals began to form within 5min but the sample was set aside to cool overnight and the crystals were collected by filtration, washed with a little water and air-dried to yield pale yellow crystals 1.29g. Found: C, 28.7; H, 3.9; N, 21.8; I, 20.3. C<sub>30</sub>H<sub>30</sub>N<sub>20</sub>O<sub>10</sub> K<sub>2</sub>I<sub>2</sub>.6H<sub>2</sub>O requires C, 28.4; H, 3.3; N, 22.0; I, 20.0

### Optimal method for the preparation of Q[5]KI templated crystals

Template molecule (200mg) was dissolved in hot water (50mL). The temperature of the solution was maintained between 60-70°C and KI (950mg) was added, followed by Q[5].2KI (1.7g). The hot solution was then filtered and set aside to cool overnight. The pale amber crystals were collected by filtration and air dry for 24hr.

### **Q[5] KI HObzCOOH**

Yield 1.63g. Found: C, 29.7; H, 3.7; N, 19.7; I, 18.6. C<sub>104</sub>H<sub>102</sub>N<sub>60</sub>O<sub>36</sub> K<sub>6</sub>I<sub>6</sub>.24H<sub>2</sub>O requires C, 29.8; H, 3.6; N, 20.0; I, 18.1. <sup>1</sup>H NMR (D<sub>2</sub>O) δ 4.37(Q methylene protons), 5.57 (Q methine protons), 5.69 (Q methylene protons), 6.96 (Ar H<sub>3,5</sub>) 7.95 (Ar H<sub>2,6</sub>), mole ratio of Q[5]:HObenzCOOH, 3:2.

### **Q[5] KI HObzCN**

Yield 1.6g. Found: C, 29.7; H, 3.6; N, 20.9; I, 18.7. C<sub>104</sub>H<sub>100</sub>N<sub>62</sub>O<sub>32</sub> K<sub>6</sub>I<sub>6</sub>.24H<sub>2</sub>O requires C, 30.0; H, 3.6; N, 20.9; I, 18.3. <sup>1</sup>H NMR (D<sub>2</sub>O) δ 4.37 (Q methylene protons), 5.57 (Q methine protons), 5.69 (Q methylene protons), 6.96 (Ar H<sub>3,5</sub>) 7.65 (Ar H<sub>2,6</sub>), mole ratio of Q[5]:HObenzCN, 3:2.

### Alternative experimental procedure for Q[5]KI templated crystals

Q[5] 4.87g KI 8.69g, hydroxybenzoic acid 4.3g, 500mL water to dissolve Q[5] heat 60°C and KI 100mL water same temp. the acid is dissolved in water 400mL heated 100°C. Q solution poured into KI solution with stirring at 60°C then 400mL acid solution is added with stirring. Allow to cool slowly to rt and stand several days. Crystals are light yellow become darker with time. Yield 70-80%

### Template removal

The crystals are powdered placed in a soxhlet extraction apparatus and the template removed using either ethanol or 1,4-dioxane as the solvent. The completion of the extraction was determined by <sup>1</sup>H NMR, where the sample was completely dissolved in D<sub>2</sub>O. The general time period is 12-18hr. Dioxane is slightly more efficient than ethanol.

### **Q[5] KI HObenzCOOH removed.**

Found: C, 28.7; H, 3.4; N, 22.1; I, 20.0. C<sub>30</sub>H<sub>30</sub>N<sub>20</sub>O<sub>10</sub> K<sub>2</sub>I<sub>2</sub>.5H<sub>2</sub>O requires C, 28.8; H, 3.2; N, 22.4; I, 20.3.

Table S1. Miscellaneous absorption profiles of the porous Q[5]. KI materials prepared with the template 4-hydroxybenzonitrile (HObzCN) or the template 4-hydroxybenzoic acid (HObzCOOH).

Volatile <sup>b</sup>	Q[5].KI.HObzCN	Q[5].KI.HObzCOOH
THF	0.21 (3.75hr)	0.96 (24hr) <sup>c</sup>
		0.21 (14hr)
THF	3.97 (72hr)	1.59 (72h)
Dioxane	0.35 (22hr)	0.29 (22hr)
Dioxane	0.41 (22hr) <sup>c</sup>	0.31 (3hr) <sup>c</sup>
		0.33 (22hr) <sup>c</sup>

a) A solid sample and a volatile in separate vials was placed in a seal vessel at room temperature at the pressure of the vapour for the time as specified. b) The proportion of the volatile absorbed is expressed as a mole ratio relative to Q[5]. c) The solid absorption material was air dried only. All other samples were pre-dried at 90°C *in vacuo*.

Table S2. Comparative absorption of Q[5].KI.HObzCOOH as a powder and as crystals (~0.2-0.5mm) of air-dried samples.

Volatile <sup>b</sup>	Q[5].KI.HObzCOOH
MeOH	0.74 (16hr)
MeOH	0.69 (16hr) <sup>a</sup>

a) Powdered samples. b) The proportion of the volatile absorbed is expressed as a mole ratio relative to Q[5]. c) The solid absorption material was air dried only.

Table S3. MeOH displacement by dioxane – a comparative absorption of Q[5].KI.HObzCOOH as a powder and as crystals (~0.2-0.5mm) of air-dried samples which had pre-absorbed MeOH (above table S2).

Samples	Q[5].KI.HObzCOOH per-absorbed MeOH		Q[5].KI.HObzCOOH control <sup>a</sup>
	Dioxane <sup>b</sup> absorbed	MeOH <sup>b</sup> remaining	
Crystals			Dioxane absorbed <sup>b</sup>
	1 hr	0.08	0.006 <sup>e</sup>
	2.2 hr	0.11	0.09
	3.45 hr	0.14	0.12 <sup>f</sup>
	5.45 hr	0.18	0.16
Powder	24.6 hr	0.22 <sup>d</sup>	0.23
		< 0.001	
	1 hr	0.12	
	2.2 hr	0.18	
	3.45 hr	0.18	

a) The control was crystals that were air-dried and had not pre-absorbed MeOH. b) The proportion of the volatile absorbed is expressed as a mole ratio relative to Q[5]. c) These results were collected concurrently for all three samples, with all samples placed in the same vapour chamber. d) Crystals appear stable. e) Displaced MeOH

from other samples absorbed by this sample 0.05 moles. f) No MeOH; vapour chamber flushed with N<sub>2</sub> and fresh dioxane used as source.

Table S4. Vapor pressures of the volatile organic molecules studied for absorption.<sup>2</sup>

Volatile	mmHg @20°C
MeOH	126.7
EtOH	59.0
THF	162.0
Acetone	231.0
1,4-dioxane	37.1
Benzene	95.3

### X-ray powder diffraction patterns

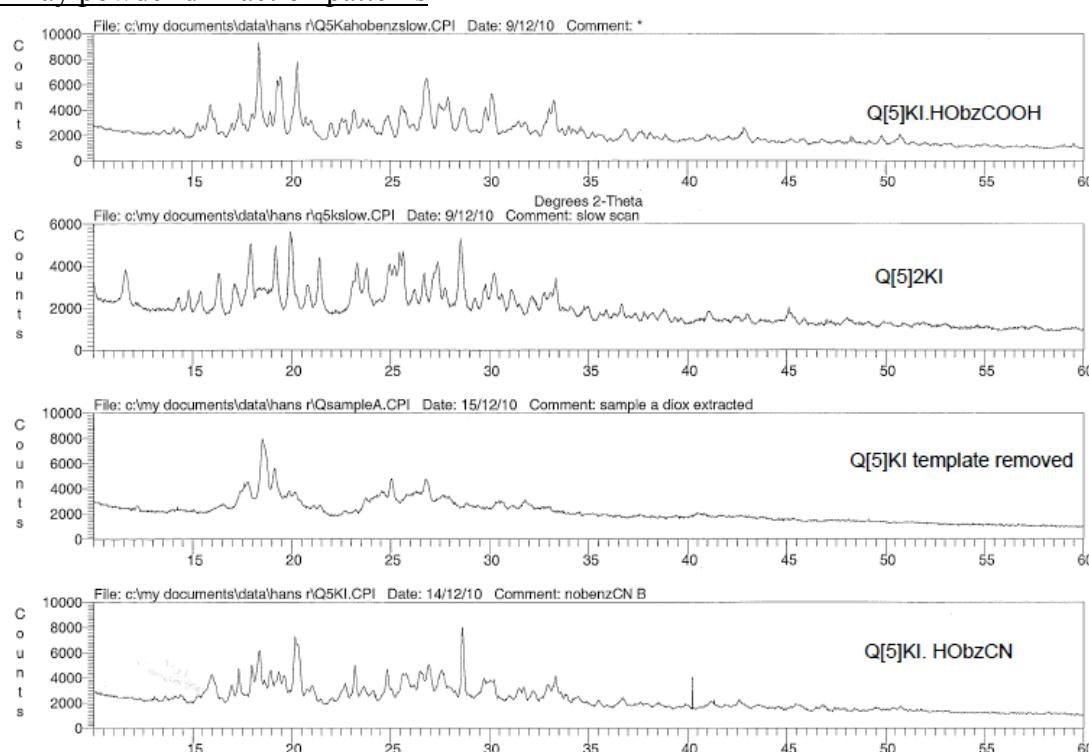


Figure S1. X-ray powder diffraction patterns of the solid materials Q[5].KI. HObzCOOH; Q[5].2KI; Q[5]KI template removed; and Q[5].KI. HObzCN (in order top to bottom).

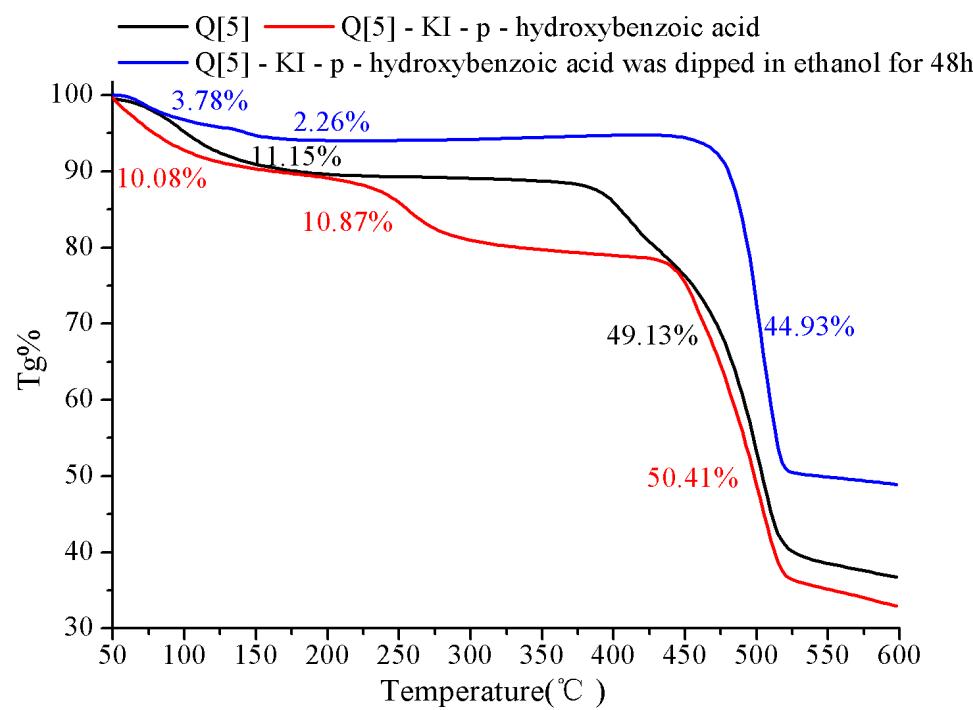


Figure S2. Thermal gravimetric analysis of Q[5]; Q[5].KI. HObzCOOH; and Q[5].KI. HObzCOOH dipped in ethanol.

Crystallographic Information

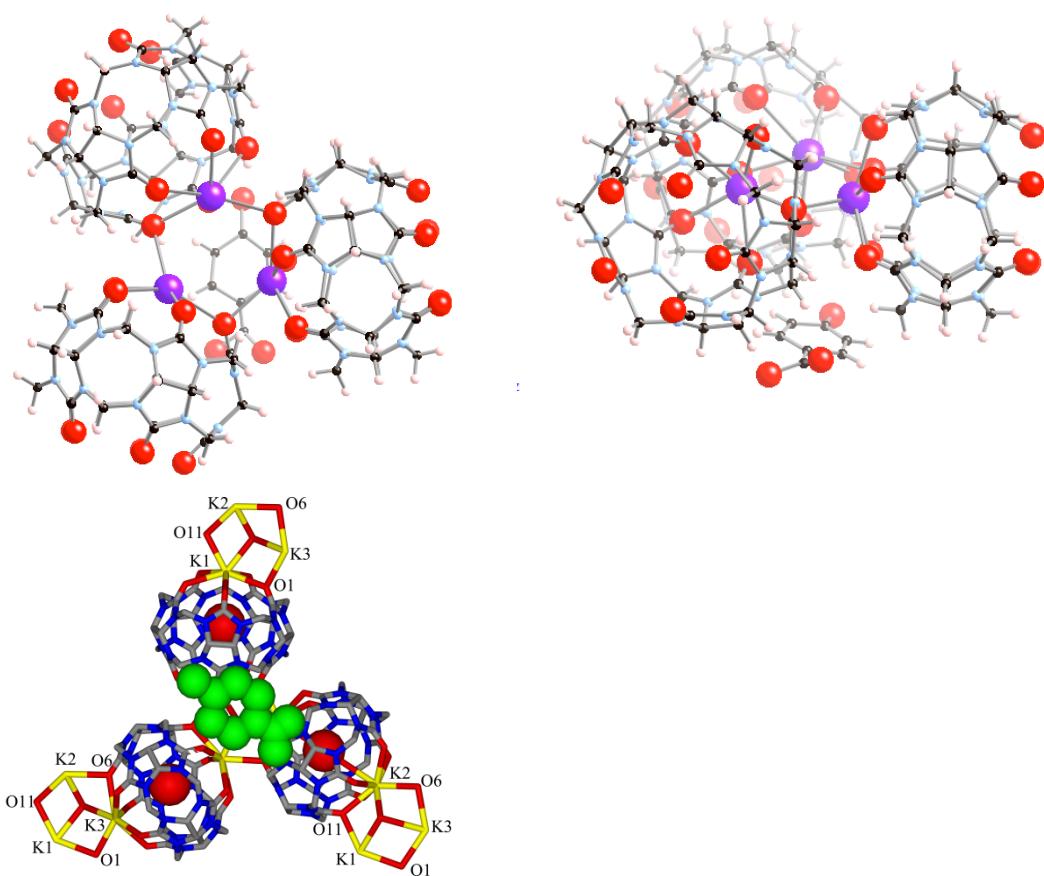


Figure S3. Trigonal node showing 3 Q[5] bonded by 3 K with the junction situated over the template molecule 4-hydroxybenzoic acid. On the Left, plan views; On the right, a side view. H<sub>2</sub>O have been omitted for clarity except for the cavity encapsulated H<sub>2</sub>O shown at the left-hand bottom.

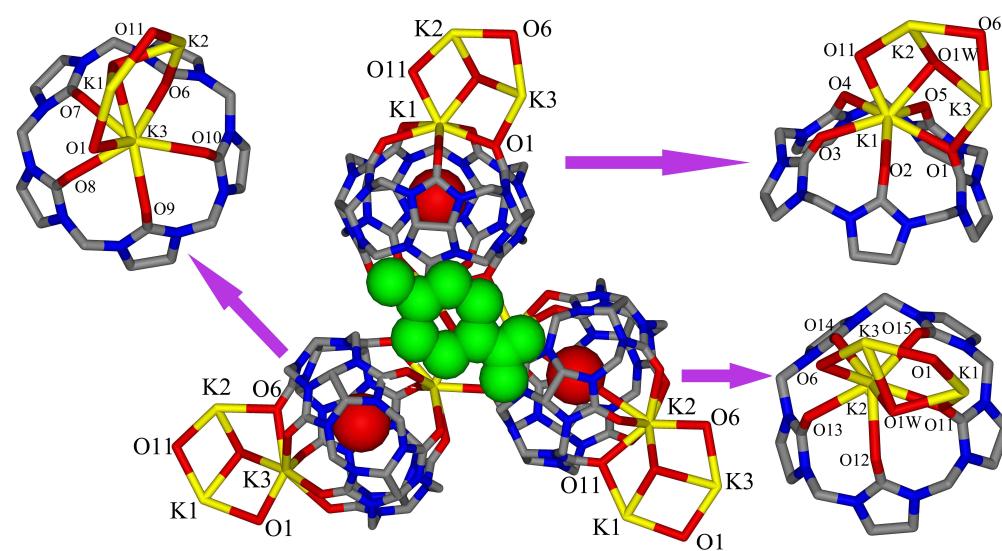


Figure S4. Trigonal node with the oxygen and potassium atoms identified.

### Symmetry and Constraints

The unit cell contains a symmetric mirror about the equatorial plane of Q[5] along the *a* axis (ie the ten methine carbons in the equatorial plane of Q[5]). The symmetric operation code is *a*: *x*,  $1/2-y$ , *z*, such as K2 and K2<sup>a</sup>, O8 and O8<sup>a</sup> and so on.

Six DFIX commands were used to fix the phenyl ring of the template HObzCO<sub>2</sub>H molecule.

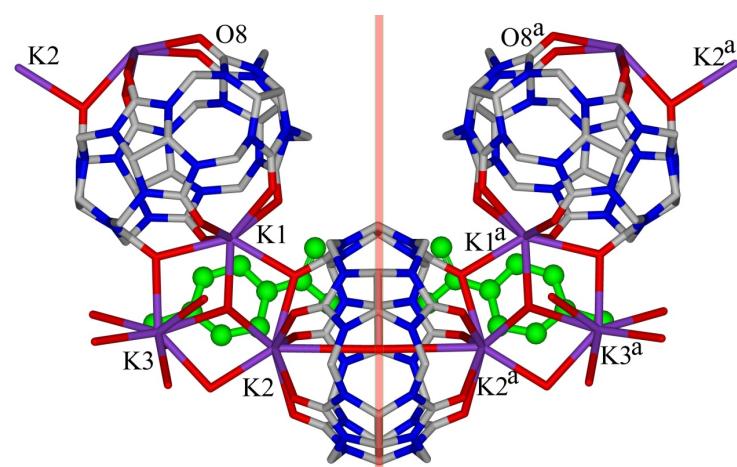


Figure S5 Shows the symmetric orientation of Q[5] as they form the ring.

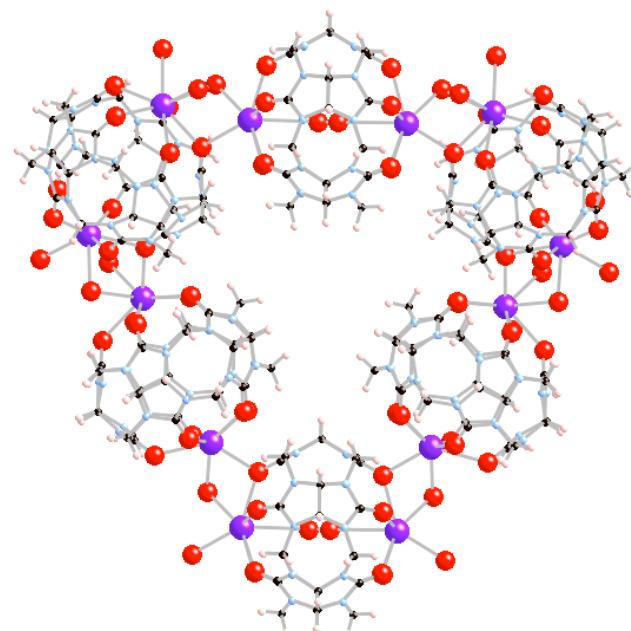


Figure S6. A perspective of the Q[5] 'beaded' structure forming a 6-membered ring.

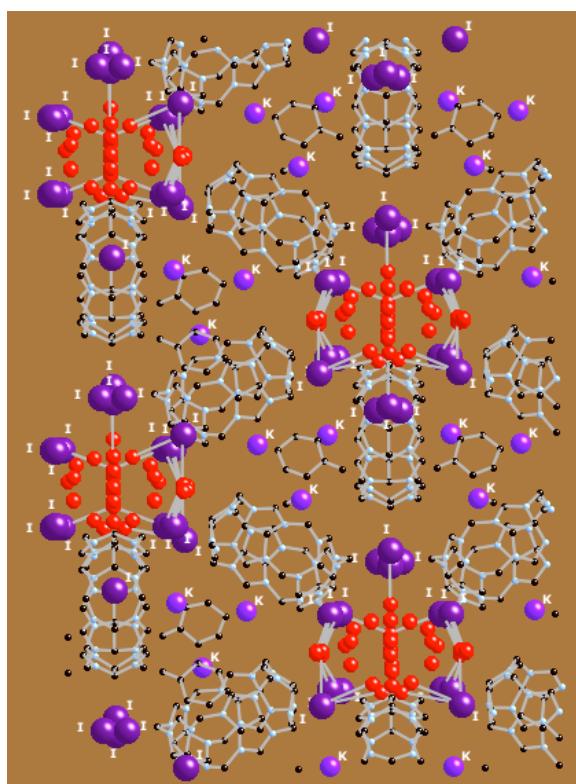


Figure S7. Plan view of the water channels. The location of potassium ions (K) and iodide ions are shown all other water, hydrogen atoms and Q[5] oxygen atoms are omitted for clarity. The carbon-nitrogen structural frames of Q[5] are shown and the carbon frames of the template p-hydroxybenzoic acid. This image shows that the water channels are free of ions.

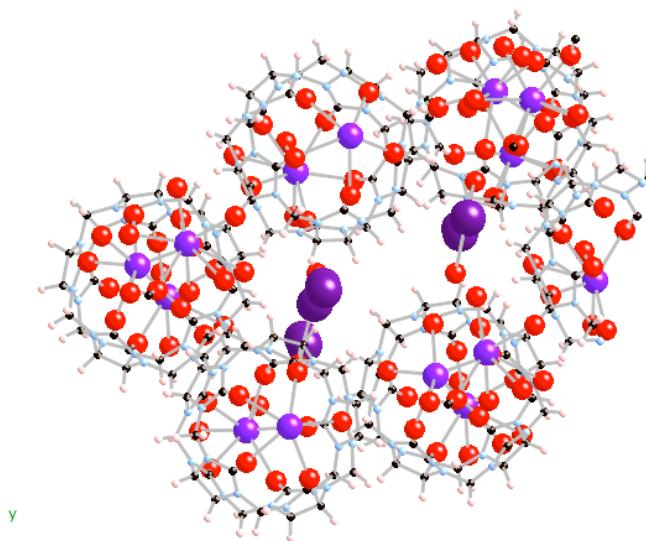


Figure S8. A segment of the structure of Q[5]2KI crystals prepared in the absence of a template molecule.<sup>3</sup>

## References

1. A. I. Day, A. P. Arnold, R. J. Blanch and A. Coe, "Alkali Metals and the Ratio of Cucurbit[n]urils in Synthesis", *J Incl. Phenom. Macrocyclic Chem.* **2002**, 43, 247-250.
2. CRC Handbook of Chemistry and Physics 91<sup>st</sup> Ed. 2010-2011  
<http://www.hbcpnetbase.com/>
3. Feng, X.; Du, H.; Xiao, X.; Luo, S.-X.; Xue, S.-X.; Zhang, Y.-Q.; Zhu, Q.-J.; Tao, Z.; Zhang, X.-Y.; Gang, W. *Cryst. Growth Des.* **2010**, 10 (7), 2901-7.