

## Supporting Information

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### 1. List of Compounds:

#### Compounds of class a

- 1a:** “[K<sub>4</sub>(DB18C6)<sub>8</sub>(H<sub>2</sub>O)<sub>8</sub>(I<sub>3</sub>)<sub>4</sub>]<sub>n</sub>”  
**1’:** [{"KI(DB18C6)}<sub>2</sub>(DB18C6)]  
**2a:** [Na<sub>2</sub>(DB18C6)<sub>2</sub>(H<sub>2</sub>O)(OH)I<sub>3</sub>]  
**3a:** [Na(DB18C6)(H<sub>2</sub>O)<sub>2</sub>(DB18C6)I<sub>3</sub>]

#### Compound of class b

- 1b:** “[K<sub>4</sub>(DB18C6)<sub>8</sub>(H<sub>2</sub>O)<sub>8</sub>(IBr<sub>2</sub>)<sub>4</sub>]<sub>n</sub>”  
**2b:** [Na<sub>2</sub>(DB18C6)<sub>2</sub>(H<sub>2</sub>O)(OH)IBr<sub>2</sub>]  
**3b:** [Na(DB18C6)(H<sub>2</sub>O)<sub>2</sub>(DB18C6)IBr<sub>2</sub>]

#### Compound of class c

- 1c:** “[K<sub>4</sub>(DB18C6)<sub>8</sub>(H<sub>2</sub>O)<sub>8</sub>(BrI<sub>2</sub>)<sub>4</sub>]<sub>n</sub>”  
**2c:** [Na<sub>2</sub>(DB18C6)<sub>2</sub>(H<sub>2</sub>O)(OH) BrI<sub>2</sub>]  
**3c:** [Na(DB18C6)(H<sub>2</sub>O)<sub>2</sub>(DB18C6)BrI<sub>2</sub>]

### 2. Syntheses

#### Compounds of class a

**1a:** In a Schlenk tube, 0.133 g (0.37mmol) of dibenzo-18-crown-6 were dissolved in 20 ml THF and 20 ml 0.05 M aqueous (KI + I<sub>2</sub>)-solution was added. The obtained solution was transferred into a beaker which was closed with parafilm and the solution was allowed to stand at room temperature for several weeks. After evaporation of solvent, crystals **1a** in form of dark red-brown needles were isolated, and used for single crystal diffraction and conductivity measurements. Yield: ca, 86% referring to halides.

**<sup>1</sup>H-NMR:** (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 6.95 (ArH), 4.15 (m, CH<sub>2</sub>), 3.93 (m, CH<sub>2</sub>), 2.13 (H<sub>2</sub>O). **<sup>1</sup>H-NMR:** (THF-d<sub>8</sub>, 360MHz): δ [ppm] 7.13 (ArH), 7.04 (ArH), 4.19 (m, CH<sub>2</sub>), 4.34 (m, CH<sub>2</sub>), 2.64 (H<sub>2</sub>O). **<sup>13</sup>C-NMR** (THF-d<sub>8</sub>, 360 MHz): δ [ppm] 69.076 (CH<sub>2</sub>), 70.702(CH<sub>2</sub>), 113.1413(C-Ar), 122.285(C-Ar), 148.902(C-Ar).

**IR** ν [cm<sup>-1</sup>] 3611(w), 3545(w), 2927(w), 1594(m), 1504(s), 1449(m), 1327(m), 1250(s), 1124(s), 941(s), 846(w), 780(m), 740(s), 633(w).

**Thermal decomposition product of 1a: [KI(DB18C6)]<sub>2</sub>(DB18C6), 1'**

Compound **1a** was slowly heated from 20° to 180°C. The temperature was stabilized at 180°C for two hours. Single crystals of **1'** in form of dark needles were obtained with 80 % yield and used for single diffraction. <sup>1</sup>H-NMR: (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 6.950(ArH), 6.891(ArH), 4.207(CH<sub>2</sub>), 4.134(CH<sub>2</sub>), 4.134(CH<sub>2</sub>), 4.125(CH<sub>2</sub>), <sup>13</sup>C-NMR (CD<sub>3</sub>CN, 300 MHz): δ [ppm] 67.988(CH<sub>2</sub>), 69.974(CH<sub>2</sub>), 112.242(C-Ar), 118.25(C-Ar), 122.281(C-Ar).

**IR** ν [cm<sup>-1</sup>] 2926.26(w), 1594 (s), 1506.47(s), 1452.47(s), 132964 (m), 1289.60(m), 1217.13(m), 1122.44(s), 1062.46(m), 994.37 (s), 957.38(m), 932.52(s), 820.81(m), 778.26(m), 738.03(s), 595.65(s), 557.56(w).

**2a:** A single crystal of **1a** was immersed into a 0.1 M aqueous NaOH-solution. After one day, it is extracted from solution, washed and re-measured by X-ray diffraction. **2a** is obtained with ca. 100% yield.

<sup>1</sup>H-NMR (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 7.3(ArH), 4.4 (m CH<sub>2</sub>), 2.7(OH), 1.5 (H<sub>2</sub>O). <sup>13</sup>C-NMR (THF-d<sub>8</sub>, 360 MHz): δ [ppm] 68.74(CH<sub>2</sub>), 70.21 (CH<sub>2</sub>), 121.62 (C-Ar).

**IR** ν [cm<sup>-1</sup>] 3611(w), 3546(w), 3060(w), 2925(m), 1595(s), 1504(s), 1451(s), 1356(m), 1328(m), 1288(m), 1252(s), 1124(s), 1062(S), 995(s), 941(s), 854(m), 821(m), 738(s).

**3a:** The synthesis of compound **3a** is identical to that of compound **1a**, except that potassium iodide (KI) is replaced by sodium iodide (NaI) and sodium hydroxide (NaOH) in equal proportions or with KI only. Compound **3a** crystallises in form of dark red-brown needles with a yield of 83%.

<sup>1</sup>H-NMR (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 6.42(ArH), 2.92(CH<sub>2</sub>), 2.00(H<sub>2</sub>O).

**IR** ν [cm<sup>-1</sup>] 3627(w), 3560(w), 3064(w), 2905(w), 2835(w), 1594(m), 1504(s), 1451(S), 1430(m), 1382(w), 1330(m), 1254(s), 1219(s), 1125(s), 1065(m), 949(s), 911(m), 850(w).

**1b:** **1b** was synthesized in the same style and under the same conditions as that of **1a**. 0.133 g (0.37mmol) of dibenzo-18-crown-6 were dissolved in 20 ml THF and 20 ml 0.05 M aqueous (KI + Br<sub>2</sub>)-solution. The beaker was closed with parafilm and the solution was allowed to stand at room temperature for several weeks. After evaporation of solvent, crystals of compound **1b** in form of red-brown needles were isolated and used for single crystal diffraction. Yield: ca, 86% referring to halides.

<sup>1</sup>H-NMR: (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 6.95 (ArH), 4.15 (m, CH<sub>2</sub>), 3.93 (m, CH<sub>2</sub>), 2.13 (H<sub>2</sub>O) ; <sup>1</sup>H-NMR: (THF-d<sub>8</sub>, 360MHz): δ [ppm] 7.13 (ArH), 7.04 (ArH), 4.19 (m, CH<sub>2</sub>), 4.34 (m, CH<sub>2</sub>), 2.64 (H<sub>2</sub>O) ; <sup>13</sup>C-NMR (THF-d<sub>8</sub>, 360 MHz): δ [ppm] 69.076 (CH<sub>2</sub>), 70.702(CH<sub>2</sub>), 113.1413(C-Ar), 122.285(C-Ar), 148.902(C-Ar).

**IR** ν [cm<sup>-1</sup>] 3611.81 (w), 2927.44 (w), 1620.96 (w), 1595.48 (m), 1504.19 (s), 1450.59 (s), 1381.55 (w), 1327.11(w), 1280 (s), 1215.51 (s), 1162.80(s), 1059.54 (s), 851.54 (w), 738.82 (s).

**2b:** Like compound **2a**, a single crystal of **1b** was immersed into a 0.1 M aqueous NaOH-solution. After one day, it is extracted from solution, washed and re-measured by X-ray diffraction. **2b** was obtained with 100% yield.

<sup>1</sup>H-NMR: (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 6.940(ArH), 6.934(ArH), 4.13 (m, CH<sub>2</sub>), 3.903(m, CH<sub>2</sub>), 2.14 (H<sub>2</sub>O). <sup>13</sup>C-NMR (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 68.194(CH<sub>2</sub>), 70.052(CH<sub>2</sub>), 112.496(C-Ar), 121.99(C-Ar).

**IR** ν [cm<sup>-1</sup>] 3610.14(w), 3544.83(w), 3065.07(w), 2926.15(w), 1621.04(w), 1597.38(m), 1504.08(s), 1449.59(s), 1397.13(w), 1328.24(m), 1251.94(s), 1218.41(s), 1100.29(s), 1060.01(s), 942.22(s), 910.53(m), 846.56(w).

**3b:** Compound **3b** is synthesized as compound **1b**, replacing potassium iodide (KI) by sodium iodide (NaI). Compound **3b** with yield around 85 %, crystallises in form of red-brown needles.

<sup>1</sup>H-NMR (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 7.3(ArH), 4.4 (m CH<sub>2</sub>), 2.7(OH), 1.5 (H<sub>2</sub>O), <sup>13</sup>C-NMR (THF-d<sub>8</sub>, 360 MHz): δ [ppm] 68.74(CH<sub>2</sub>), 70.21 (CH<sub>2</sub>), 121.62 (C-Ar).

**IR** ν [cm<sup>-1</sup>] 3611(w), 3546(w), 3060(w), 2925(m), 1595(s), 1504(s), 1451(s), 1356(m), 1328(m), 1288(m), 1252(s), 1124(s), 1062(S), 995(s), 941(s), 854(m), 821(m), 738(s).

**1c:** Compound **1c** was synthesized in the same manner and under the same conditions as that of **1a** or **1b**. 0.133 g (0.37mmol) of dibenzo-18-crown-6 were dissolved in 20 ml THF and 20 ml 0.05 M aqueous (KBr + I<sub>2</sub>)-solution. The beaker was closed with parafilm and the solution was allowed to stand at room temperature for several weeks. After evaporation of solvent, crystals of compound **1c** in form of dark red-brown needles were isolated and used for single crystal diffraction. Yield: ca, 83 % referring to halides.

<sup>1</sup>H-NMR: (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 6.949(ArH), 4.147(m, CH<sub>2</sub>), 3.923(m, CH<sub>2</sub>), 2.14(H<sub>2</sub>O). <sup>13</sup>C-NMR (CD<sub>3</sub>CN, 300 MHz): δ [ppm] 68.129(CH<sub>2</sub>), 70.053(CH<sub>2</sub>), 112.418(C-Ar), 122.128(C-Ar).

**IR** ν [cm<sup>-1</sup>] 3609.50 (w), 3547.11(w), 3064.48 (w), 2931.41 (w), 2876.38 (w), 1619.89(w), 1595.97 (m), 1504.30 (s), 1451.09(s), 1357.51 (m), 1251.29 (m), 1126.38 (s), 1050.91(m), 943.62 (s), 853.91 (w), 782.45 (m), 734.83 (s).

**2c:** A single crystal of **1c** was immersed into a 0.1 M aqueous NaOH-solution. After one day, it is extracted from solution, washed and re-measured by X-ray diffraction. **2c** was obtained with 100% yield.

<sup>1</sup>H-NMR: (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 6.936(ArH), 6.930(ArH), 4.130 (m, CH<sub>2</sub>), 3.896(m, CH<sub>2</sub>), 2.14 (H<sub>2</sub>O), 1.58 (OH). <sup>13</sup>C-NMR (CD<sub>3</sub>CN, 300 MHz): δ [ppm] 70.046 (CH<sub>2</sub>), 68.202 (CH<sub>2</sub>), 112.506(C-Ar), 121.968(C-Ar).

**IR** ν [cm<sup>-1</sup>] 3621.12 (w), 3547.11(w), 3064.48 (w), 2931.41 (w), 2876.38 (w), 1619.89(w), 1595.97 (m), 1504.30 (s), 1451.09(s), 1357.51 (m), 1251.29 (m), 1126.38 (s), 1050.91(m), 943.62 (s), 853.91 (w), 782.45 (m), 734.83 (s).

**3c:** In a Schlenk, 0.133 g (0.37mmol) of dibenzo-18-crown-6 were dissolved in 20 ml THF and 20 ml 0.05 M aqueous (NaBr + I<sub>2</sub>)-solution. The obtained solution was transferred into a beaker which was closed with parafilm and the solution was allowed to stand at room temperature for several weeks. After evaporation of solvent, crystals **3c** in form of red-brown needles were isolated, and used for single crystal diffraction. Yield: ca, 86% referring to halides.

<sup>1</sup>H-NMR: (CD<sub>3</sub>CN, 360 MHz): δ [ppm] 6.936(ArH), 6.930(ArH), 4.130 (m, CH<sub>2</sub>), 3.896(m, CH<sub>2</sub>), 2.14 (H<sub>2</sub>O), 1.58 (OH); <sup>13</sup>C-NMR (CD<sub>3</sub>CN, 300 MHz): δ [ppm] 70.046 (CH<sub>2</sub>), 68.202 (CH<sub>2</sub>), 112.506(C-Ar), 121.968(C-Ar).

**IR** ν [cm<sup>-1</sup>] 3621.12(w), 3547.11(w), 2931.41(w), 1619.89(m), 1504.30(s), 1451.09(s), 1382.50(m), 1357.51(m), 1251.29(m), 1219.24(m), 1126.38(s), 1065.50(m), 943.62(s), 910.20(w), 853.91 (w), 782.45(m), 734.83(s), 637.44(w).

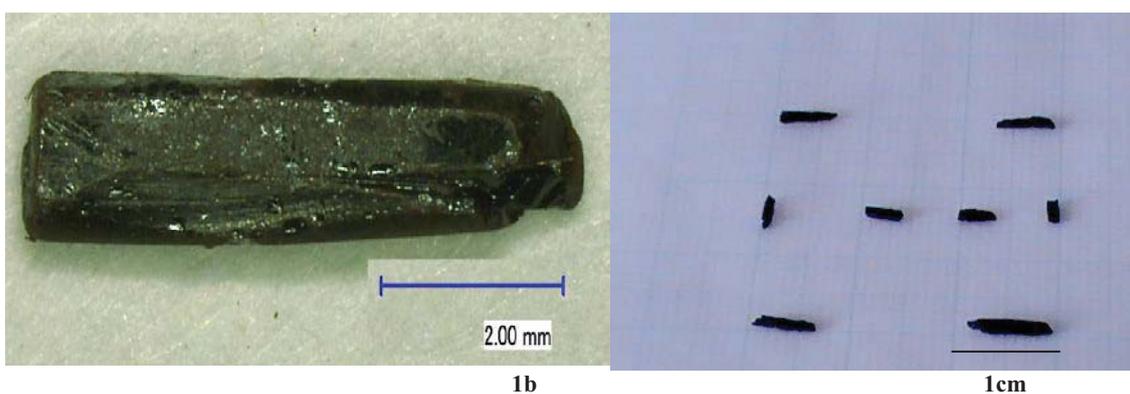
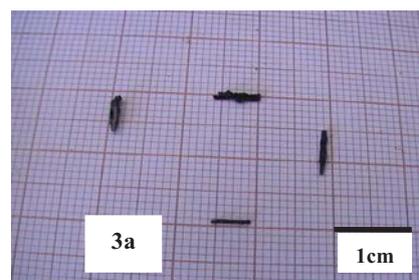
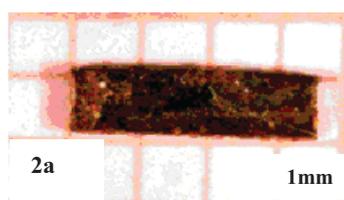
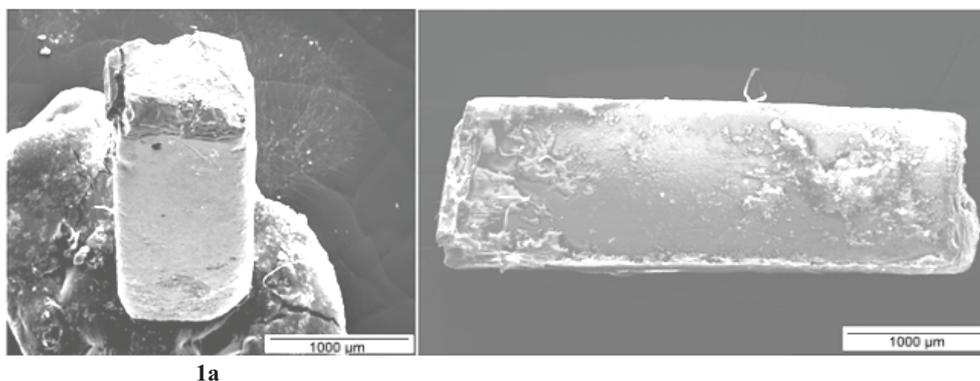
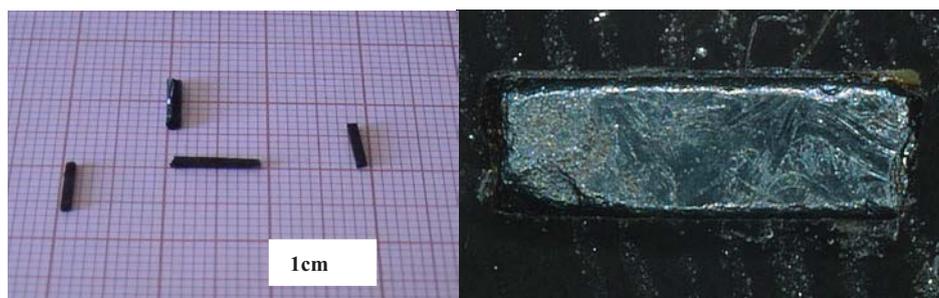
### 3. ICP-OES measurements.

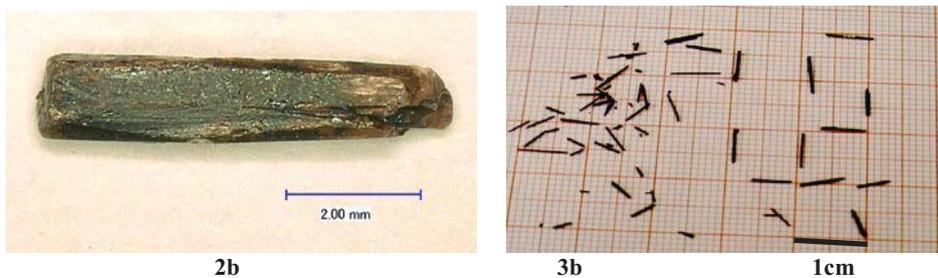
**Table 1.** Sodium and potassium concentration inside the compounds of class **b**. for a concentration of 150mg/L

Class <b>b</b>	<b>1b</b>	<b>2b</b>	<b>3b</b>
Na- Concentration (mg/L)	0.019	1.146	1.465
K- Concentration (mg/L)	3.632	1.061	0.225

A single crystal of each compound, **1b**, **2b** and **3b** was weighed and dissolved such as to obtain a concentration of 150 mg of compound per litre. The concentration of Na<sup>+</sup> and K<sup>+</sup> was determined with an ICP-OES instrument. Similar effects were obtained for the other series as well. For the **2b** crystals obtained after immersion, these values are obtained after 24h. It can be seen that conversion is apparently not 100%, however, we could not confirm this in the single crystal structure data.

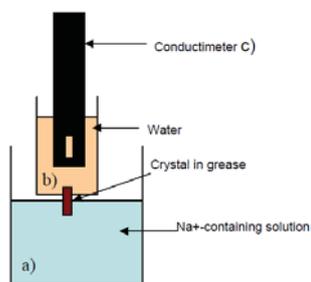
### 4. Photos of crystals



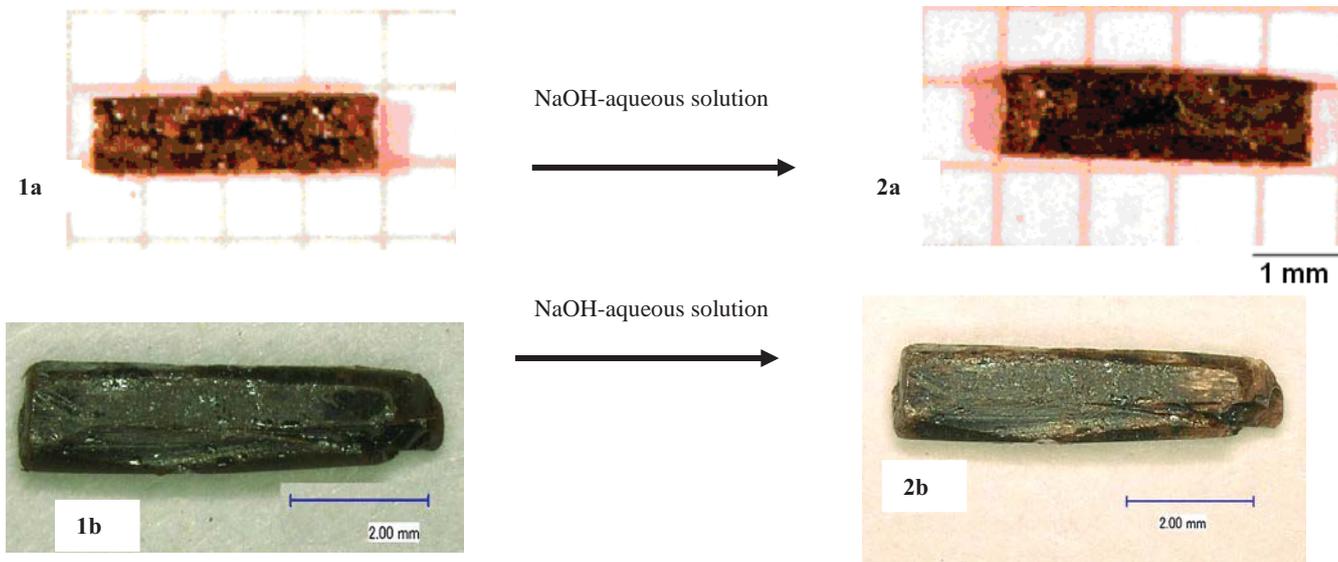


### 5. Conductivity measurement of crystals

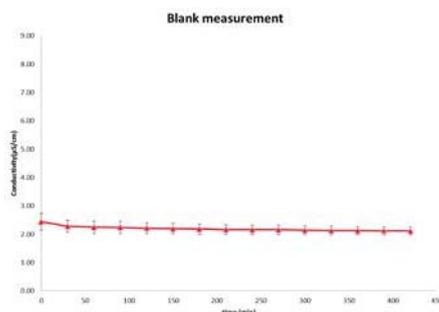
Conductivity analysis of ion exchange in our single crystalline material was determined using device A (Scheme 1). It is composed of three parts: one reservoir (a) containing a 1 M in  $\text{Na}^+$  solution (NaOH), one compartment (b) filled with deionised water on which crystal **1** is fixed, and one conductimeter (c) in this latter. A single crystal of compound **1** bridges the two compartments. In the upper one, the deionised water will be enriched with  $\text{Na}^+$  due to osmotic pressure. The measurement of the conductivity was recorded by MeterLab CDM 210 conductivity meter. Upon NaOH transport of crystal **1**, transformation into compound **2** occurs (Figure 1). In order to make sure the grease is not conducting and nothing can pass via interface grease-single crystal, a long crystal of **1** (size: 0.7cm x 0.1cmx0.1cm) was used to the experiment. Furthermore, we also measured blanks by using deionized water in both compartments, (a) and (b) and found the ionic conductivity to be constant, hence the crystal does not dissolve itself over time in water.



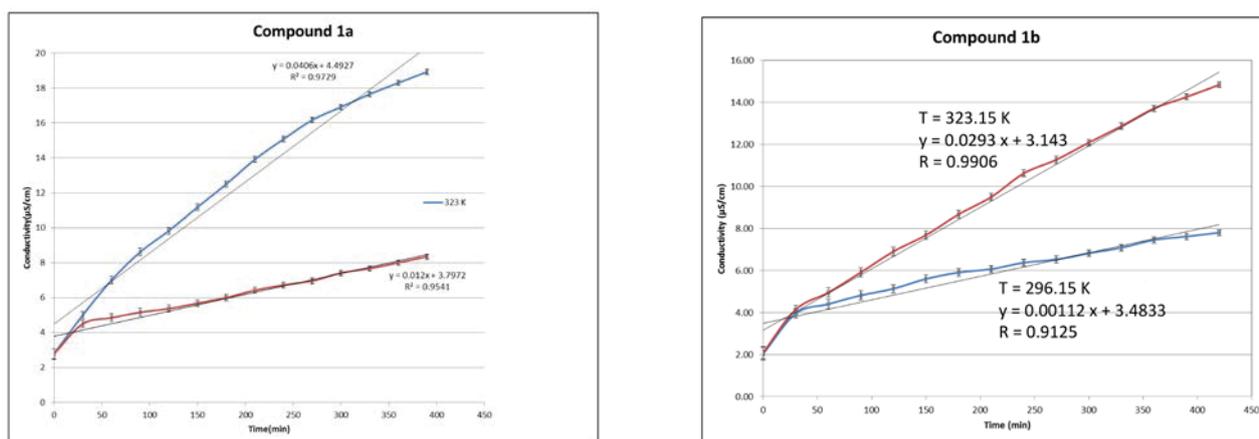
**Scheme 1.** Device A for sodium cation conductivity measurement



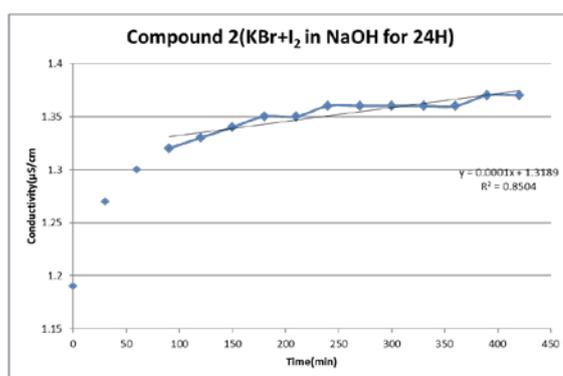
**Figure 1.** Transformation of single crystal **1** to single crystal **2** after sodium hydroxide transport



**Figure 2:** Blank measurement with a crystal of **1b** with deionized water in both compartments (a) and (b) of device A.



**Figure 3a.** Conductivity measurements through single crystals of **1a** (left) and **1b** (right), showing the kinetic law of sodium conductivity at 296 and 323K. The ratio of the slopes gives directly the ratio of kinetic constants.



**Figure 3b.** Conductivity measurements through single crystals of **2c**, showing the kinetic law of potassium conductivity at 296K. The ratio of the slopes gives directly the ratio of kinetic constants.

The crystal size of all the compounds for conductivity measurement and the kinetic and thermodynamic studies are: Length = 7 mm, width = 1mm and thickness = 1mm. So the area of crystals is  $1\text{mm}^2$  and the volume is  $7\text{mm}^3$ .

All values of conductivity ( $\sigma$ ) are experimental, they are given by the conductimeter (c) immersed in the deionised water of compartment (b) see device A (scheme 1). The values of sodium conductivity ( $\sigma$ ) in compartment b) after 420 min of compound **1a** at 296 and 323 K are respectively 10.4 and 20.97  $\mu\text{S}/\text{cm}$  while those of compound **1b** are 9.84 and 16.88  $\mu\text{S}/\text{cm}$ .

After conductivity measurement, the  $\text{Na}^+$  concentration of 4 mL of water of compartment (b) (scheme 1) was determined using a Perkin Elmer, Optical Emission Spectrometer Optima 7000 DV. The result is contained in the following table 2.

**Table 2.** Concentration of the sodium ions after 7 hours of measurement

Compound/T(K)	296	323
<b>1a</b>	0.307±0.04 (mg/L)	0.488 ± 0.049 (mg/L)
	13.347x10 <sup>-6</sup> (mol/L)	21.217x10 <sup>-6</sup> (mol/L)
<b>1b</b>	0.227±004 (mg/L)	0.581± 0.008 (mg/L)
	9.869x10 <sup>-6</sup> (mol/L)	25.260 x10 <sup>-6</sup> (mol/L)

The number of sodium ions transported after 7 hours through the compound can be determined, and the results are listed in the table 3 below:

**Table 3.** Number of sodium ions transported through the crystal after 7 hours.

Compound / T(K)	296	323
<b>1a</b>	$5.338 \times 10^{-8}$ mol	$8.486 \times 10^{-8}$ mol
<b>1b</b>	$3.947 \times 10^{-8}$ mol	$10.104 \times 10^{-8}$ (mol/L)

This number of mole of sodium ions can be reported to the surface of single crystals. This allows to determine the flow of sodium ions per hour (Table 4).

**Table 4.** Flow of sodium ions in one hour.

Compounds / T(K)	296	323
<b>1a</b> (KI <sub>3</sub> )	$7.625 \times 10^{-9}$ mol/mm <sup>2</sup> /h	$12.122 \times 10^{-9}$ mol/mm <sup>2</sup> /h
<b>1b</b> (KBr <sub>2</sub> I)	$5.638 \times 10^{-9}$ mol/mm <sup>2</sup> /h	$14.434 \times 10^{-9}$ mol/mm <sup>2</sup> /h

Total number of the channels and also the number of different channels in the compound **1a** and **1b** can be estimated from the single crystal size (table 5).

**Table 5.** Determination of the number of channels in the crystals **1a** and **1b**

	Volume of the crystal	Volume of unit cell	Total number of channels	Number of C1-channels	Number of C2-channels	Number of C3-channels
Compound <b>1a</b>	7mm <sup>3</sup> or $7 \times 10^{21}$ Å <sup>3</sup>	4488.6 Å <sup>3</sup>	$1.56 \times 10^{18}$	$3.9 \times 10^{17}$	$7.8 \times 10^{17}$	$3.9 \times 10^{17}$
Compound <b>1b</b>	7mm <sup>3</sup> or $7 \times 10^{21}$ Å <sup>3</sup>	4534.3 Å <sup>3</sup>	$1.54 \times 10^{18}$	$3.85 \times 10^{17}$	$7.7 \times 10^{17}$	$3.85 \times 10^{17}$

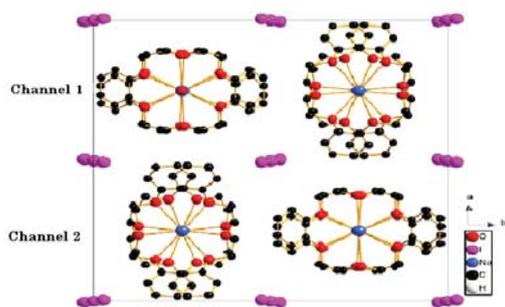
The three sorts of channels in **1a** transport sodium ions, thus, the number of sodium cations going through a single channel can be determined. And those values are in the following table 6.

**Table 6.** Number of sodium ions transported per single channel

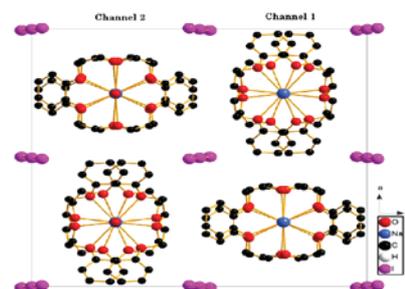
Compounds / T(K)	296	323
<b>1a</b>	$4.88 \times 10^{-27}$ mol/h	$7.77 \times 10^{-27}$ mol/h
<b>1b</b>	$3.66 \times 10^{-27}$ mol/h	$9.37 \times 10^{-27}$ mol/h

The measurement of sodium ions conductivity at 7 hours of crystals of compound **1a** and **1b** has been realized. Sodium ions in the crystals can be determined. The same crystals **1a** and **1b** using for the experiment were utilized. The weight of each of the two compounds is 1.2 mg. Each crystal of both compounds was dissolved in a mixture of 9 mL of deionised water and 1 mL of 65% HNO<sub>3</sub>. These solutions obtained were used to determine the sodium concentration by ICP-OES measurement with a Perkin Elmer, Optical Emission Spectrometer Optima 7000 DV. The amount of sodium ions in the crystals **1a** and **1b** is respectively  $0.413 \pm 0.001$  mg/L and  $0.453$  mg/L.

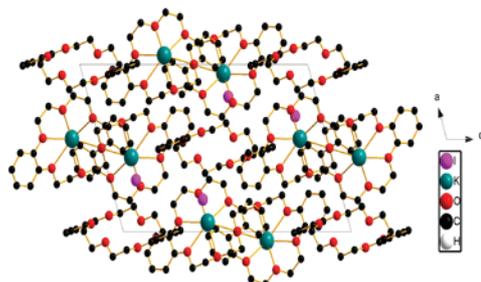
## 6. Unit cells of the compounds.



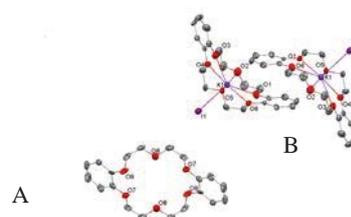
**Figure 4.** Unit cell of **2a**, view down the *c*-axis of the channels



**Figure 5.** Unit cell of **3a**, view down the *c*-axis of the channels



**Figure 6.** Unit cell of **1'**, view down the (o,a,c)-plane



**Figure 7.** Crystal structure of **1'**

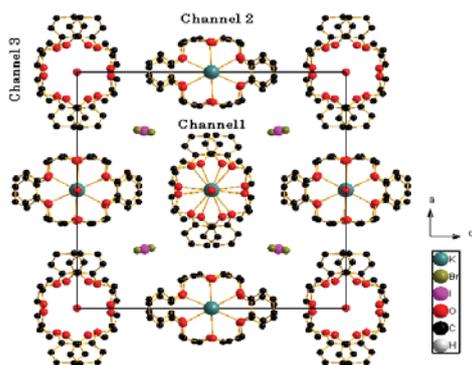


Figure 8. Unit cell of 1b, view down the *b*-axis of the channels

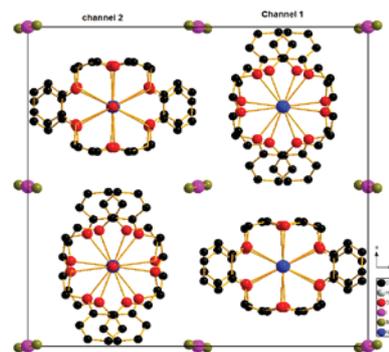


Figure 9. Unit cell of 2b, view down the *c*-axis of the channels

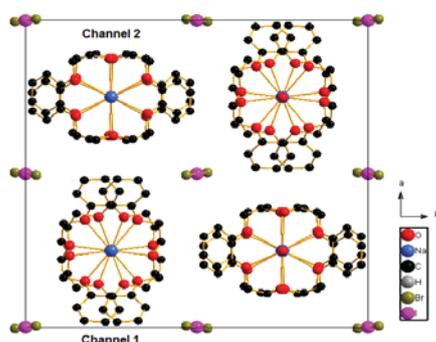


Figure 10. Unit cell of 3b, view down the *c*-axis of the channels

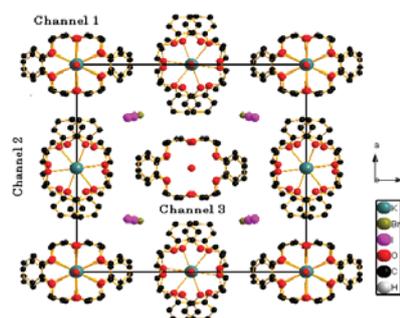


Figure 11. Unit cell of 1c, view down the *b*-axis of the channels

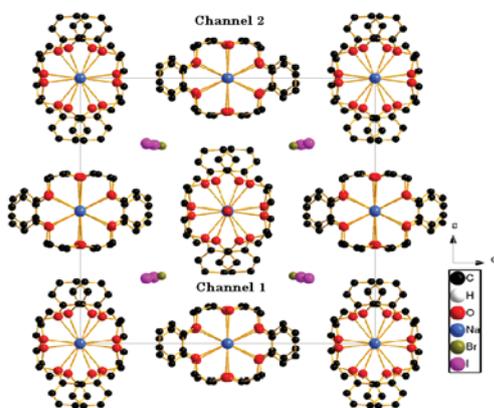


Figure 12. Unit cell of 2c, view down the *b*-axis of the channels

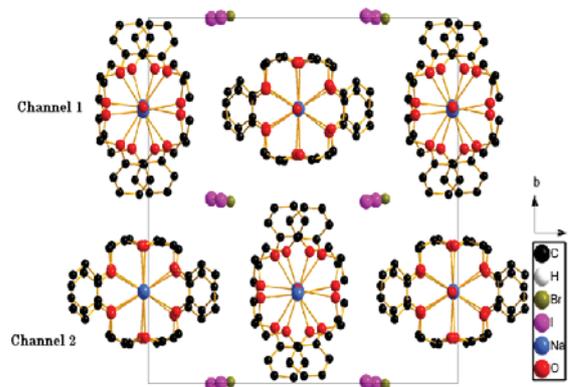


Figure 13. Unit cell of 3c, view down the *a*-axis of the channels

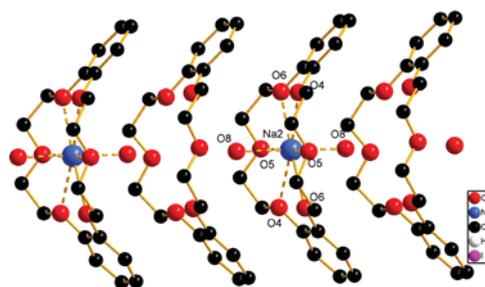


Figure 14. Side view of the two different channels of 3a along *a*-axis



**7. Crystallographic data of Compounds:** Details in common: Mo-K $\alpha$  radiation ( $\lambda=0.71073\text{\AA}$ ), T= 200(2)K, CAD4 diffractometer,  $\omega-2\theta$  scans. Refinement method: Full-matrix least-squares on F<sup>2</sup>, M=K for **1** and Na for **2**, **3**. C1, C2 and C3 denote Channels one, two and C3 in the compound.

**Table 7.** Crystallographic and characteristic data of single crystals class **a**

Crystal class (a)	<b>1a</b>		<b>2a</b>		<b>3a</b>	
Empirical Formula	C <sub>120</sub> H <sub>156</sub> I <sub>9</sub> K <sub>3</sub> O <sub>42</sub>		C <sub>40</sub> H <sub>51</sub> I <sub>3</sub> Na <sub>2</sub> O <sub>14</sub>		C <sub>80</sub> H <sub>104</sub> I <sub>6</sub> Na <sub>2</sub> O <sub>28</sub>	
Formula weight (g/mol)	3529.998		1182.56		2321.136	
Crystal system	Monoclinic		Orthorhombic		Orthorhombic	
Space Group	P2		Pccn		Pccn	
a(Å)	21.9132(9)		21.9810(3)		a = 22.0440(3)	
b(Å)	9.3473(3)		22.0058(3)		b = 22.0952(9)	
c(Å)	21.9139(9)		9.37090(10)		c = 9.2199(6)	
$\beta$ (°)	90.067(3)		90		90	
V(Å <sup>3</sup> )	4488.6(3)		4532.79(10)		4490.7(4)	
Z	2		4		4	
Density (calculated)(Mg/m <sup>3</sup> )	1.741		1.733		1.711	
Absorption coefficient(mm <sup>-1</sup> )	2.245		2.150		2.160	
F(000)	2328		2336		2280	
Theta range for data collection(°)	2.08 to 27.50°.		1.31 to 24.66		1.30 to 25.00°	
Reflections collected	39441		14096		3893	
Independent reflections	20555 [R(int) = 0.1119]		3764 [R(int) = 0.1030]		3893 [R(int) = 0.0000]	
Completeness to theta = 25.00°	99.9 %		98.2%		98.5 %	
Data / restraints / parameters	20555/1/438		3764/0/271		3893 / 0 / 270	
Goodness-of-fit on F <sup>2</sup>	0.761		1.194		0.555	
Final R indices [I>2sigma(I)]	R1 = 0.0637, wR2 = 0.0617		R1 = 0.0569, wR2 = 0.1258		R1 = 0.0578, wR2 = 0.1230	
R indices (all data)	R1 = 0.1836, wR2 = 0.0842		R1 = 0.0679, wR2 = 0.1321		R1 = 0.0786, wR2 = 0.0678	
Largest diff. peak and hole(Å <sup>-3</sup> )	1.315 and -1.446 e		1.026 and -0.960 e		0.472 and -0.538 e	
Index ranges	-28<=h<=28, -12<=k<=12, -28<=l<=28		-25<=h<=25, 0<=k<=25, -10<=l<=10		0<=h<=26,0<=k<=26, 0<=l<=10	
M-O <sub>(DB18C6)</sub> (Å) (M = K <sup>+</sup> or Na <sup>+</sup> )	2.613(10)-2.779(10) C1 2.699(10)-2.814(10) C2		2.641(3)-2.791(5) C1 2.690(6)-2.802(5) C2		2.556(3)-2.794(3) C1 2.633(3)-2.794(3) C2	
M-Plan (O <sub>x</sub> O <sub>y</sub> O <sub>z</sub> O <sub>x'</sub> O <sub>y'</sub> O <sub>z'</sub> ) (Å)	0.0009(1)- 0.059(1) C1 0.025(1)-0.089(1) C2		0.018(5) C1 0.038(6) C2		0.07(4) C1 0.103(4) C2	
Angle (I-I-I) (°)	179.13(3)-179.10(3)		180		180	
M-O <sub>axial</sub> (OH)(Å)	1.668(15)-2.873(13) C1		2.178(17)-2.507(17) C1		Na-H <sub>2</sub> O: 2.299(7)-2.311(7) C1	
M-O <sub>axial</sub> (H <sub>2</sub> O)(Å)	2.694(17)-2.877(17) C2		2.313(16)-2.372(16) C2		Na-H <sub>2</sub> O :293(7)-2.317(7) C2	
O <sub>axial</sub> -plan(O <sub>x</sub> O <sub>y</sub> O <sub>z</sub> O <sub>x'</sub> O <sub>y'</sub> O <sub>z'</sub> ) (Å)	1.883(1)-2.757(1) C1 2.642(1)-2.857(1) C2 1.979(1)-2.095(2) C3		2.121(16)-2.564(16) C1 2.282(15)-2.403(15) C2		2.224(4)-2.385(4) C1 2.214(4)-2.395(4) C2	
Distances(Å) I-I	2.941(3)-2.898(3)		2.922(5) (symmetry)		2.9124(10) (Symmetry)	
Angle between the planes of two phenyl groups	85.2(3)-85.55(4) C1 81.65(4)-88.83(4) C2 82.73(4)-85.06(4) C3		85.05(1) C1 85.35(1) C2		82.98(10) C1 80.96(10) C2	
Distance between two terminals I <sub>3</sub> (Å)	3.791(2)		3.826(7)		3.803(6)	
Angle of Two adjacent I-I-I(°)	150.19(7)		150.69(1)		145.63(14)	

**Table 10.** Crystallographic and characteristic data of single crystals class **b**

Crystal class (b)	1b		2b		3b	
Empirical Formula	C <sub>120</sub> H <sub>156</sub> Br <sub>6</sub> I <sub>3</sub> K <sub>3</sub> O <sub>42</sub>		C <sub>40</sub> H <sub>51</sub> Br <sub>2</sub> INa <sub>2</sub> O <sub>14</sub>		C <sub>80</sub> H <sub>104</sub> I <sub>2</sub> Br <sub>4</sub> Na <sub>2</sub> O <sub>28</sub>	
Formula weight (g/mol)	3248.76		1088.56		2087.136	
Crystal system	Monoclinic		Orthorhombic		Orthorhombic	
Space Group	P2		Pccn		Pccn	
a(Å)	21.9848(7)		21.9740(5)		22.0982(6)	
b(Å)	9.3733(2)		22.0037(16)		22.1153(17)	
c(Å)	22.0038(7)		9.3786(11)		9.211(2)	
β(°)	89.995(2)°		90		90	
V(Å <sup>3</sup> )	4534.3(2)		4534.6		4501.3(10)	
Z	2		4		4	
Density (calculated)(Mg/m <sup>3</sup> )	1.580		1.594		1.568	
Absorption coefficient(mm <sup>-1</sup> )	2.622		2.550		2.558	
F(000)	2168		2192		2136	
Theta range for data collection(°)	1.85 to 25.00°		2.93 to 25.00		1.30 to 25.00	
Reflections collected	88711		3854		3858	
Independent reflections	15898 [R(int) = 0.1119]		3854 [R(int) = 0.0000]		3858 [R(int) = 0.0000]	
Completeness to theta = 25.00°	100 %		96.2 %		97.5	
Data / restraints / parameters	15898/0/4044		3854 / 0 / 270		3858 / 0 / 270	
Goodness-of-fit on F <sup>2</sup>	1.252		0.669		0.683	
Final R indices [I>2sigma(I)]	R1=0.1125,wR2 =0.3044		R1 = 0.0567, wR2 = 0.1297		R1 = 0.0567, wR2 = 0.1297	
R indices (all data)	R1=0.1493,wR2 =0.3481		R1 = 0.1259, wR2 = 0.1488		R1 = 0.1435, wR2 = 0.1395	
Largest diff. peak and hole(Å <sup>-3</sup> )	7.678 and -2.528 e.		1.171 and -0.878 e.		1.045 and -0.494 e.	
Index ranges	26<=h<=26,11<=k<=10, -26<=l<=26		0<=h<=26,0<=k<=26,0<=l<=11		0<=h<=26,0<=k<=26,0<=l<=10	
M-O <sub>(DB18C6)</sub> (Å)	2.613(10)-2.779(10) C1 2.699(10)-2.814(10) C2	C1 C2	2.641(3)-2.791(5) C1 2.690(6)-2.802(5) C2	C1 C2	2.572(6)-2.789(6) C1 2.628(6)-2.793(6) C2	C1 C2
M-Plan (O <sub>x</sub> O <sub>y</sub> O <sub>z</sub> O <sub>x'</sub> O <sub>y'</sub> O <sub>z'</sub> ) (Å)	0.0009(1)-0.059(1) C1 0.025(1)-0.089(1) C2	C1 C2	0.018(5) C1 0.038(6) C2	C1 C2	0.075(9) C1 0.117(9) C2	C1 C2
Angle (Br-I-Br) (°)	179.13(3)		180		180	
M-O <sub>axial</sub> (OH)(Å)	1.668(15)-2.873(13) C1	C1	2.16(3)-2.53(3) C1	C1	Na-H <sub>2</sub> O:2.284(14)-2.321(14)C1	C1
M-O <sub>axial</sub> (H <sub>2</sub> O)(Å)	2.694(17)-2.877(17) C2	C2	2.29(3)-2.40(3) C2	C2	Na-H <sub>2</sub> O:2.299(15)-2.307(15) C2	C2
O <sub>axial</sub> -plan(O <sub>x</sub> O <sub>y</sub> O <sub>z</sub> O <sub>x'</sub> O <sub>y'</sub> O <sub>z'</sub> ) (Å)	1.669(0)-3.035(0) C1 2.712(2)-2.902(1) C2 1.451(1)-3.012(1) C3	C1 C2 C3	2.143(2)-2.545(2) C1 2.253(2)-2.453(2) C2	C1 C2	2.209(1)-2.396(1) C1 2.18(1)-2.424(1) C2	C1 C2
Distances I-Br(Å)	2.897(3)-2.941(3)		2.9278(9) (symmetry)		2.9124(10)(Symmetry)	
Angle between the planes of two phenyl groups	85.2(3)-85.55(4) C1 81.65(4)-88.83(4) C2 82.73(4)-85.06(4) C3	C1 C2 C3	84.62(2) C1 84.39(2) C2	C1 C2	81.59(2) C1 81.20(2) C2	C1 C2
Distance between two terminals IBr <sub>2</sub> (Å)	3.82(1)		3.82(1)		3.80(1)	
Angle of two adjacent Br-I-Br(°)	150.58(3)		150.65(3)		145.32(3)	

**Table 11.** Crystallographic and characteristic data of single crystals class **c**

Crystal class (c)	1c	2c	3c
Empirical Formula	C <sub>120</sub> H <sub>156</sub> I <sub>6</sub> Br <sub>3</sub> K <sub>3</sub> O <sub>42</sub>	C <sub>80</sub> H <sub>102</sub> I <sub>4</sub> Br <sub>2</sub> Na <sub>4</sub> O <sub>28</sub>	C <sub>80</sub> H <sub>104</sub> I <sub>4</sub> Br <sub>2</sub> Na <sub>2</sub> O <sub>28</sub>
Formula weight (g/mol)	3388.998	2271.12	2181.136
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space Group	<i>P2</i>	<i>P2</i>	<i>Pna2<sub>1</sub></i>
<i>a</i> (Å)	21.9780(6)	21.96 98(5)	9.2082(3)
<i>b</i> (Å)	9.3770(2)	9.3665(3)	22.0527 (8)
<i>c</i> (Å)	22.0090(6)	21.9960(8)	22.0889(8)(8)
$\beta$ (°)	4535.8(2)	4526.3(3)	4485.42(3)
<i>V</i> (Å <sup>3</sup> )	89.943(2)	89.974(3)	90
<i>Z</i>	2	2	4
Density (calculated)(Mg/m <sup>3</sup> )	1.654	1.662	1.643
Absorption coefficient(mm <sup>-1</sup> )	2.421	2.354	2.365
F(000)	2256	2252	2208
Theta range for data collection(°)	1.85 to 25.00°.	1.85 to 25.00	1.84 to 29.26°
Reflections collected	118046	42783	83178
Independent reflections	15752 [R(int) = 0.0973]	15884 [R(int) = 0.0477]	11880 [R(int) = 0.1019]
Completeness to theta = 25.00°	99.6 %	99.4	98.9
Absolute structure parameter	0.510(19)	0.490(15)	0.523(17)
Data / restraints / parameters	15752 / 1 / 438	15884 / 1 / 748	11880 / 1 / 527
Goodness-of-fit on F <sup>2</sup>	1.055	1.054	1.002
Final R indices [I>2sigma(I)]	R1=0.0737, wR2= 0.2004	R1 = 0.0730, wR2 = 0.2084	R1 = 0.0650, wR2 = 0.1710
R indices (all data)	R1=0.1125, wR2= 0.2392	R1 = 0.0897, wR2 = 0.2265	R1= 0.1023, wR2 = 0.1908
Largest diff. peak and hole(Å <sup>-3</sup> )	3.910 and -1.714 e.	2.864 and -2.304 e.	1.910 and -1.447 e
Index ranges	26<=h<=26, -10<=k<=11, -26<=l<=26	-26<=h<=24, -11<=k<=11, -26<=l<=26	-12<=h<=12, -30<=k<=30, -29<=l<=30
M–O <sub>(DB18C6)</sub> (Å)	2.678(8)-2.810(8) C1 2.594(8)-2.826(8) C2	2.620(7)-2.793(7) C1 2.668(7)-2.797(6) C2	2.431(9)-2.846(8) C1 2.603(12)-2.807(11) C2
M–Plan (O <sub>x</sub> O <sub>y</sub> O <sub>z</sub> O <sub>x'</sub> O <sub>y'</sub> O <sub>z'</sub> )( Å)	0.069(3)-0.095(4) C1 0.043(4)-0.052(4) C2	0.028(6)-0.043(6) C1 0.101(6)-0.108(6) C2	0.07(3) C1 0.12(3) C2
Angle (I–I–Br) (°)	179.72(7)	179.85(5)	
M–O <sub>axial</sub> (OH)(Å)	1.805(13)-2.863(14) C1	1.78(2)-3.00(2) C1	Na–H <sub>2</sub> O:2.251(6)-2.365(8) C1
M–O <sub>axial</sub> (H <sub>2</sub> O)(Å)	2.604(13)-2.966(14) C2	1.56(2)-2.95(2) C2	Na–H <sub>2</sub> O:2.295(7)-2.314(7) C2
O <sub>axial</sub> -Plan(O <sub>x</sub> O <sub>y</sub> O <sub>z</sub> O <sub>x'</sub> O <sub>y'</sub> O <sub>z'</sub> )(Å)	1.736(13)-2.958(13) C1 2.553(12)-3.008(1) C2 1.787(12)-2.674(13) C3	1.752(1)-2.953(1) C1 1.670(1)-3.050(1) C2	2.164(4)-2.433(4) C1 2.174(6)-2.429(6) C2
Distances I–Br(Å)	2.913(2)	2.909(1)	2.9007(15)
Distances I–I(Å)	2.929(2)	2.930(1)	2.9084(4)
Angle between the planes of two phenyl groups	82.43(3)-85.04(3) C1 80.11(3)-89.63(9) C2 85.67(3)-86.92(3) C3	85.07(2)-86.92(2) C1 86.08(2)-86.65(2) C2	83.21(2) C1 80.86(1) C2
Distance between two terminals BrI <sub>2</sub> (Å)	3.83(1)	3.82(1)	3.81(1)
Angle of two adjacent I–I–Br(°)	150.93(5)	150.85(4)	145.47(3)

**Table 12.** Crystallographic and characteristic data of single crystals **1'**

Crystal	<b>1'</b>
Empirical Formula	C <sub>60</sub> H <sub>72</sub> I <sub>2</sub> K <sub>2</sub> O <sub>18</sub>
Formula weight (g/mol)	1413.18
Crystal system	Monoclinic
Space Group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	<i>a</i> = 12.6488(9) Å
<i>b</i> (Å)	<i>b</i> = 12.5348(5)
<i>c</i> (Å)	<i>c</i> = 20.4930(14)
$\beta$ (°)	108.019(5)°.
<i>V</i> (Å <sup>3</sup> )	3089.8(3)
<i>Z</i>	2
Density (calculated)(Mg/m <sup>3</sup> )	1.519
Absorption coefficient(mm <sup>-1</sup> )	1.222
F(000)	1440
Theta range for data collection(°)	1.69 to 25.00°.
Reflections collected	5380
Independent reflections	5380[R(int)=0.0000]
Completeness to theta = 25.00°	98.9 %
Max. and min. transmission	0.9086 and 0.7921
Data / restraints / parameters	5380 / 0 / 370
Goodness-of-fit on F <sup>2</sup>	0.725
Final R indices [I>2sigma(I)]	R1 = 0.0545, wR2 = 0.0631
R indices (all data)	R1 = 0.1331, wR2 = 0.0745
Largest diff. peak and hole(Å <sup>-3</sup> )	0.384 and -0.543 e
Index ranges	-15<= <i>h</i> <=14, 0<= <i>k</i> <=14, 0<= <i>l</i> <=24
K–O(DB18C6) (Å)	2.740(4)-2.801(4)
K-Plane (O <sub>1</sub> O <sub>2</sub> O <sub>3</sub> O <sub>4</sub> O <sub>5</sub> O <sub>6</sub> )( Å)	0.5611(17)
K–I(Å)	3.4639(18)
I-plane (O <sub>1</sub> O <sub>2</sub> O <sub>3</sub> O <sub>4</sub> O <sub>5</sub> O <sub>6</sub> )(Å)	4.0166(5)
Angle between the planes of two phenyl groups	00 for A 66.58(20) for B

## 8 Description of the structures of single crystals

### Compounds of class a

**Developed formula:** [ $\{K_C(DB18C6)(\mu-H_2O)\}_{2n}-\{K(H_2O)_2C(DB18C6)(DB18C6)\}_n\{(DB18C6)(H_2O)\}_{2n}\}(I_3)_{3n}$ , **1a**

This compound **1a** was obtained by reacting crown ether dibenzo-18-crown-6 with potassium tri-iodide using water-tetrahydrofuran as solvent. After evaporation of solvent at room temperature, single crystals of **1a** were formed and were used for X-ray diffraction. [ $\{K_C(DB18C6)(\mu-H_2O)\}_{2n}-\{K(H_2O)_2C(DB18C6)(DB18C6)\}_n\{(DB18C6)(H_2O)\}_{2n}\}(I_3)_{3n}$ , **1a** crystallises as dark red-brown needles in the monoclinic space group *P*2 (*n*° 3) with four independent molecules per asymmetric unit (Figure 1 of the article).

The structure of **1a** is formed of three parallel, differently filled 1D-channels of DB18C6. The triiodide anions act as scaffolds in between the channels (Figure 1 of the article). These anions are asymmetric with I–I distances between 2.925(3) and 2.972(3) Å contrary to those of other compounds which are symmetric [2, 3]. However, the distance of 3.791(2) Å between two anions is long but testifies to weak interactions between polyiodide anions. The angle defined between terminal iodide I<sub>3</sub> and the atoms I<sub>1</sub> and I<sub>2</sub> of the next I<sub>3</sub><sup>-</sup> is around 150°, similar to what has been reported previously [2, 3, 4]. The counter ions I<sub>3</sub><sup>-</sup> is almost linear with angle 179.4 (1) °. One of the channels, C1, is filled with a linear chain of alternating water molecules and potassium ions bridged by hydrogen bonds. All potassium ions are placed in the cavity defined by the six oxygen atoms of the crown ether ligand and are almost included in it (only a difference of between 0.013 (3) and 0.064 (3) Å). Every potassium ion is thus linked with the next one via a water molecule and the angle K<sup>+</sup>–H<sub>2</sub>O–K<sup>+</sup> is 180°.

In the second channel type, C2, alternately one crown ether molecule remains empty, while a second is filled with a potassium ion, to which two water molecules are coordinated in axial positions with distances of 2.707(12) and 2.828 (16) Å relative to the central atom of potassium. Here again, the later is included in the cavity of the ligand with a deviation between 0.013(3) Å and 0.029(3) Å as shown by table 9.

The third channel, C3, contains alternating DB18C6 and water molecules (Figure 2 of the article). The distances, between water molecules and the plan formed with six oxygen atoms of crown ether, are around 2 Å. This shows that all molecules of water are outside the

cavity of the ligand. In this case, all water molecules are not coordinated. They are simply aligned with an average distance of 4.075(3) Å between two consecutive molecules.

All three channels run parallel to the *b*-axis, with one C1, two C2 and one C3-type channels per unit cell. The orientation of the DB18C6 ligands is opposite in channels C1 and C3, while the two C2 run antiparallel to each other. The channels C2 are almost perfectly stacked with respect to the phenyl groups of the DB18C6 ligands, while in C1 and C3, the aromatic rings are offset by 10° ca.

With our synthetic approach, large quantities of air-stable single crystals of cm-dimensions in length were obtained (Photo of crystals, **1a**). The red-brown colour is typical for the triiodide absorption (molar absorptivities of I<sub>3</sub><sup>-</sup> at 288 and 350 nm were determined to be 3.52 × 10<sup>-4</sup> and 2.32 × 10<sup>-4</sup> L.mol<sup>-1</sup>.cm<sup>-1</sup>, respectively.) [4 b]. To our knowledge, compound **1a** is the first example of dibenzocrown ether in which the ligands are so well stacked by such a triple unidirectional π-stacking. Single and double uni-dimensional π-stacking is usually observed [5]. Most of the time, monomeric complexes have been described [6, 7]. In these compounds, the potassium cation is situated at around 0.3(1) Å out of the plane of the oxygen atoms of the crown ether. In **1a**, it is well coordinated by the crown ether.

**1'**: Developed formula [ {K<sub>c</sub>(DB18C6)I }<sub>2n</sub>(DB18C6) ]

When **1a** was heated from 20° to 180°C, single crystals of **1'** in form of dark needles was obtained with chemical formula [ {K<sub>c</sub>(DB18C6)I }<sub>2n</sub>(DB18C6) ] **1'**. It crystallises in monoclinic space group *P*2<sub>1</sub>/*n* with two independent molecules A and B per unit cell. The volume of unit cell of **1'** is 3089.8(3)Å<sup>3</sup>. This volume is 1.44 times lower than the volume of **1a**. This seems normal. In fact, if **1a** is heated until 145°C (See thermogravimetric analysis below), it loses some of its components, in particular water molecules and its volume decreases. As shown in Figure 7, the molecule A is empty crown ether in form of chair configuration. The torsion angle is 7.75(3)°. The planes formed with two aromatic groups in A are parallel and are situated to 3 Å to each other. The molecule B is formed of one potassium ion coordinated by crown ether but shifted by 0.561(1) Å of plane formed by six oxygen atoms of this later. The assembly forms a hexagonal pyramid with the potassium cation on the summit linked by an iodide anion. This later assures the neutrality of the edifice. The potassium ion is then heptacoordinated. Molecule B is presented in form of a sail boat with the bond K–I of distance 3.4639(3)Å as main pillar. The six bonds K–O(DB18C6) of distances between 2.740(4) Å and 2.801(4) Å, the same with Na–O(DB18C6) distances[8], serve as the basic pillars. There is an interaction π-π between two successive molecules of A with a length of 3.81Å. One molecule of A is surrounded by several (four) pairs of molecules B (Figure 6). In molecule B, the angle between the planes formed of two phenyl group is 66.6(2)°. This angle is lower than that of **1a**. This means that the heat progressively deforms the molecules of the ligand while the water molecules are removed from the crystals.

**Developed formula:** [ {Na<sub>c</sub>(DB18C6)(μ-H<sub>2</sub>O) }<sub>n</sub>{Na<sub>c</sub>(DB18C6)(μ-HO)<sub>2/2</sub> }<sub>n</sub> ] (I<sub>3</sub>)<sub>n</sub>, **2a**

When single crystals of **1a** are exposed to an aqueous solution of NaOH, they are not dissolved. Ions exchange was occurred, and compound [ {Na<sub>c</sub>(DB18C6)(μ-H<sub>2</sub>O) }<sub>n</sub>{Na<sub>c</sub>(DB18C6)(μ-HO)<sub>2/2</sub> }<sub>n</sub> ] (I<sub>3</sub>)<sub>n</sub>, **2a** was found. This compound **2a** was previously described by Fromm et al [2, 3]. It was obtained by immersing compound ∞[(H<sub>2</sub>O)(DB18C6)(μ<sub>2</sub>-H<sub>2</sub>O)<sub>2/2</sub>]<sub>∞</sub>[(H<sub>3</sub>O)(DB18C6)(μ<sub>2</sub>-H<sub>2</sub>O)<sub>2/2</sub>] (I<sub>3</sub>) in aqueous sodium hydroxide solution. Ion exchange and of H<sub>2</sub>O or H<sub>3</sub>O<sup>+</sup> by NaOH is observed without dissolution of the single crystals. This compound **2a** is not isostructural to **1a**. Since it is the basis of the results described further on, its structure is briefly discussed again here and will be also compared by **1a**. Compound **2a** crystallizes as dark red-brown needles in the orthorhombic space group *P*ccn (n° 56) with two independent half-molecules in the asymmetric unit (Figure 4). Instead of three channels like **1a**, it filled of two different channels in a crystallographic point of view. Its unit cell parameters are slightly higher than **1a**, which reflects a volume a little larger of 44 Å<sup>3</sup>. The two channels are anti-parallel to each other and arranged in alternating manner along *c*-axis, surrounded by parallel triiodide anions which anions are symmetric with a bond length of 2.922(5) (Table 9). There is the same angle between two adjacent triiodides. The angle is still 150° in **2a**.

Channel C1 of compound **2a** is filled of a linear and alternating chain of hydroxide and sodium ions in which the cations are all strongly coordinated by ligand crown ether DB18C6 (only a deviation of 0.056 Å out of the plane formed by the six oxygen atoms of the crown ether). It formed of neutral complexes [ {Na<sub>c</sub>(DB18C6)(μ-OH) } ] linked one to the next via hydroxide ion (OH<sup>-</sup>) with distances Na–OH between 2.17(1) Å and 2.50(1) Å. These values are more or less shorter than of those of K–H<sub>2</sub>O in **1a**. This effect results probably from the attractive dipole-dipole interactions between sodium cation and hydroxide anions. In **2a**, the Na–O(DB18C6) distances, between 2.687(4) Å and 2.779(3) Å correspond well to average values in the literature [3]. These values are close to those of K–O(DB18C6) in **1a**. This means that both of alkali metals are well coordinated by the ligand crown ether in the two compounds. Those distances are given in table 9.

Channel C2 for its, is filled of an alternating chain of water molecules and sodium ions. The cations are always coordinated by ligand crown ether DB18C6. Therefore, this channel is filled with cationic complexes [ {Na<sub>c</sub>(DB18C6)(μ-H<sub>2</sub>O) } ]<sup>+</sup> linked one to the next via a water molecule with distances Na–H<sub>2</sub>O between 2.31(2) Å and 2.37(2) Å. It is formed of linear chain of cationic complexes which charge is neutralized by the charge of I<sub>3</sub><sup>-</sup>. The Na–O(water) distances fit also with literature[3], They are shorter than those of K–O(water) in **1a** with 2.71(1)Å and K–O<sub>(water, bridging)</sub> with a distance of 2.828(16). The angle between the planes formed by two phenyl groups in channel C2 is around 85(1)° going well with that of literature [3]. This confirms the coordination of sodium ions by crown ether [2, 3, 7]. The differences between **1a** and **2a** are summed up in Table 9.

**Developed formula:** [ {Na<sub>c</sub>(DB18C6)(μ-H<sub>2</sub>O) (DB18C6)(H<sub>2</sub>O) }<sub>2n</sub> ] (I<sub>3</sub>)<sub>2n</sub>, **3a**

Direct attempts of synthesis of the sodium analogue of compound **1a** lead to [ {Na<sub>c</sub>(DB18C6)(μ-H<sub>2</sub>O) (DB18C6)(μ-H<sub>2</sub>O) }<sub>2n</sub> ] (I<sub>3</sub>)<sub>2n</sub>, **3a**. It was obtained by reacting crown ether dibenzo-18-crown-6 with sodium tri-iodide using water-tetrahydrofuran as solvent. After evaporation of solvent at room temperature, single crystals of **3a** were formed and were used for X-ray diffraction. It is isostructural to **2a** and it “crystallizes” as dark red-brown needles in the orthorhombic space group *P*ccn (n° 56) with two independent half-molecules in the asymmetric unit. As shown in Figure 5, compound **3a** has almost identical unit cell as **2a**. However, there are significant differences in the Na–O(axial) distances for **3a** as these distances are more symmetric than in **2a**. Thus, in **2a**, Na1–O7 and Na1–O7' are 2.17(2) and 2.51(2) Å, and Na2–O8 and Na2–O8' are 2.37(2) and 2.31(2) Å long, respectively, while the same values in **3a** vary between 2.293(7) and 2.317(7) Å. This is indicative of the absence of NaOH in **3a**. Also, in **3a**, only every second crown ether ligand of a channel is filled with sodium in average, the sodium ions being split over two crown ether ligands (Figure 14). The two channels of **3a** are almost identical. The difference between both of them is situated in the packing of the ligand and also in the localization of the cations in the cavity of this later. In channel

C1 of **3a**, all sodium ions are situated at 0.07(3) Å out of the cavity of DB18C6, more the angle between the planes of two phenyl groups is 83.0(1)° while in channel C2, this angle is 2° lower. Crystallographic data and the distances of the different bonds in crystal **3a** are summarized in table 9. On the other side, sodium cations are offset by 0.03 Å more of the cavity of the ligand. All this confers to channel C2, a well interaction  $\pi$ -stacking of phenyl groups of the polymer while they are offset in Channel C1. As in compound **2a**, the two channels of **3a** are aligned antiparallel and surrounded by linear triiodide anions to ensure the neutrality of the compound. These anions with a I-I distance of 2.913(4) Å, also in accord with that of the literature [3] are still symmetric. Nevertheless, the angle 145.6(1)°, between two adjacent triiodides is 5° less than of compound **2a**. In this compound **3a**, the distance between two anions is 3.803(6) Å. It indicates the weak interactions between polyiodide anions.

**Developed formula**  $[\{K\subset(DB18C6)(\mu-H_2O)\}_{2n}-\{K(H_2O)_2\subset(DB18C6)(DB18C6)\}_n\{(DB18C6)(H_2O)\}_{2n}](IBr_2)_{3n}$ , **1b**.

When dibenzo-18-crown-6 reacts with potassium iodine dibromide (made with mixture of potassium iodide and dibromine) in aqueous-tetrahydrofuran solvent, single crystal of  $[\{K\subset(DB18C6)(\mu-H_2O)\}_{2n}-\{K(H_2O)_2\subset(DB18C6)(DB18C6)\}_n\{(DB18C6)(H_2O)\}_{2n}](IBr_2)_{3n}$ , **1b** in form of needles were formed. **1b**, like **1a**, crystallises as dark red-brown in monoclinic space group  $P2$  ( $n^\circ 3$ ) with four independent molecules per unit cell (Figure 8). The two compounds, **1a** and **1b** are isostructural. They have the same number of channels arranged in the same manner in their structure. The only difference in view of eye in the two structures is in the formation of contour halide ions. While the three channels of **1a** are surrounded by asymmetric tri-iodide ions ( $I_3^-$  or I-I-I), these of **1b** are encapsulated by non symmetric Br-I-Br ions with an angle of 179.13(7)° which are also almost linear. The angle between two adjacent Br-I-Br is still 150°. The distance Br-I, 2.941(3) Å is shorter than the distance I-I of **1a**. However, distance Br-I<sub>(bridging)</sub> 2.897(3) Å is longer than I-I<sub>(bridging)</sub>. When the structure of **1b** is closely viewed in terms of crystallographic, it seems slightly different to **1a**. For example, the volume of its unit cell is larger than that of **1a** of 55 Å<sup>3</sup> even if the distances of K-O<sub>(CE)</sub> which are between 2.61(1) Å and 2.814(4) Å remain identical. The K-O<sub>(H<sub>2</sub>O)</sub> distances, 2.69(1)-2.81(4) in channel C2 are identical in both of the structures whereas, the same K-O<sub>(H<sub>2</sub>O)</sub> distances in channel C1 are different. They are 0.07 Å more or less longer from each other. Crystallographic and characteristic data of single crystal **1b** are contained in table 10.

**Developed formula**  $[\{Na\subset(DB18C6)(\mu-H_2O)\}_n\{Na\subset(DB18C6)(\mu-HO)_{2/2}\}_n](IBr_2)_n$ , **2b**

When single crystals of **1b** are immersed into an aqueous solution of NaOH, they are transformed into compound **2b** of chemical formula  $[\{Na\subset(DB18C6)(\mu-H_2O)\}_n\{Na\subset(DB18C6)(\mu-HO)_{2/2}\}_n](IBr_2)_n$ , without being dissolved. All potassium cations in **1b** are exchanged by sodium ions. Even though the volume remains unchanged, compound **2b** is very different of compound **1b** of that it is derived, with different structural parameters and composition. **2b** is not also isostructural to **1b**. However, not only compound **2b** is isostructural to **2a**, it has almost the same crystallographic parameters and the same volume of the unit cell which is 4534.6(6) Å<sup>3</sup> (table 9 and 10). These values are very in agreement with those of the literature [2, 3]. Therefore, besides the tri-halide anions, the two compounds, **2a** and **2b** are the same composition and constitution. Thus, like **2a**, compound **2b** contains two different channels. One channel, C1, is filled of linear and alternative Na<sup>+</sup> and OH. Na<sup>+</sup> is in the cavity of the ligand (only a deviation of 0.018(5)° of this cavity). Each sodium ion coordinated is linked to its neighbor by hydroxide ion. Thus the assembly forms a linear chain of neutral edifice of  $[Na\subset(DB18C6)(\mu-HO)_{2/2}]_n$ . Na-OH distances of **2b** which are 2.29(3)-2.40(3) Å, the same of those of **2a** are more or less longer than these of K-H<sub>2</sub>O of **1b**.

Channel C2 is linear arrangement of the cationic complexes  $[\{Na\subset(DB18C6)(\mu-H_2O)\}]^+$  in the same geometry as Channel C1 linked by water molecules. In channel C1 of **2b**, Na-O(water) distances 2.690(6) Å- 2.802(5) Å are larger than those of C1 of compound **2a**. This is due to the fact that in **2b**, both channels are surrounded by symmetric anions Br-I-Br with distance of 2.927(9) Å and linearly distributed throughout the crystal. Those anions also ensure the neutrality of the crystal. The distance I-Br is the same of that of I-I in compound **2a**.

Compound **2b** crystallizes as dark red-brown needles in the orthorhombic space group  $Pccn$  ( $n^\circ 56$ ) with two independent half-molecules in the asymmetric unit (Figure 9). The angle between two adjacent Br-I-Br is around 150° (150.65(3)). The distance between two external ions is 3.82(1) Å. The angle between the planes of two phenyl groups is 84°. And then the distances Na-O(DB18C6) are between 2.641(3) Å and 2.802(5) Å. These values of the angles and the distances of the lengths are in accordance with those the literature [2, 3, 7].

**Developed formula**  $[\{Na\subset(DB18C6)(\mu-H_2O)(DB18C6)(H_2O)\}_{2n}](IBr_2)_{2n}$ , **3b**.

The reaction of with dibenzo-18-crown-6 with (KI+Br<sub>2</sub>)-aqueous-tetrahydrofuran leads to the formation of compound **3b** with chemical formula  $[\{Na\subset(DB18C6)(\mu-H_2O)(DB18C6)(H_2O)\}_{2n}](IBr_2)_{2n}$  after the evaporation of solvent at room temperature. Compound **3b** is isostructural to **2b** and **3a**. It also crystallizes as red brown-needles in orthorhombic space group  $Pccn$  ( $n^\circ 56$ ) with two molecules per unit cell. It is formed of two different channels from the stacking of crowns ether (Figure 10). The two channels are aligned surrounded by linear and symmetric anions Br-I-Br like in compound **2b**. The distance Br-I, 2.9124(10) Å, in **3b** is the same of that of **2b**. In compound **3b**, the distances Na-O(axial), 2.22(4) Å-2.39(4) are identical. This suggests that both channels of **3b** are filled of the same elements. Na-O(axial) distances in **3a** and **3b** are equal (Table 9 and 10). Both of **3a** and **3b** are filled of the same channels. Each channel is filled with linear infinite chain which the unit is composed of one sodium ion coordinated by crown ether  $[Na\subset DB18C6]$  followed by empty crown ether non-coordinated  $[(DB18C6)]$ , both elements are linked each other by one water molecule forming a stable edifice (Figure 14). In channel C2, there is a well interaction  $\pi$ -stacking of phenyl groups of the polymer while in Channel C1; the aromatic rings are offset by ca. 10°. The distances Na-O(DB18C6) between 2.628(6) Å and 2.793(6) Å of **3b** are the same as **3a**. This corresponds to average values in the literature [9]. Na-O(axial) distances are also the same in the both compounds. Even though **3b** contains the same channels filled with the chemical elements in the same manner and with the same bond lengths that compound **3a**, it differs from this later by the polyanions. While **3b** is filled by linear anions Br-I-Br ensuring the neutrality of this compound, **3a** is filled of linear tri-iodide anions I-I-I. The channels of compounds **3b** and **2b** are surrounded by the same linear anions Br-I-Br but they have different bond lengths of the constituent elements. The later show the difference between these two compounds **3b** and **2b**. In **3b** the angle 81.59(2)° between the planes of two aromatic groups, similar in **3a** is shorter than that of **2b**. In **3b** and **3a**, the angle 145° between two adjacent tri-anions and the distance 3.80 Å between two tri-anions are lower than those of **2b** by ca. 5° and 0.02 Å respectively. In channel C1 of **3b**, the sodium Na1 is 0.075(9) Å out of the mean plane formed by the six surrounding oxygen atoms of the crown ether, slightly exo of the folding of the later oxygen atoms. In channel

C2 the deviation out of the plane is 0.117(9) Å. This shows that Na<sup>+</sup> ions are more coordinated by the ligand in Channel C1 than in channel C2.

**Developed formula**  $[\{K\subset(DB18C6)(\mu-H_2O)\}_{2n}-\{K(H_2O)_2\subset(DB18C6)(DB18C6)\}_n\{(DB18C6)(H_2O)\}_{2n}](I_2Br)_{3n}, 1c$

Polymer dibenzo-18-crown-6 reacts with (KBr+I<sub>2</sub>) in aqueous-tetrahydrofuran solution to give after slow evaporation of solvent at room temperature, a red-brown single crystal in form of needles of compound **1c** with chemical formula  $[\{K\subset(DB18C6)(\mu-H_2O)\}_{2n}\{K(H_2O)_2\subset(DB18C6)(DB18C6)\}_n\{(DB18C6)(H_2O)\}_{2n}](I_2Br)_{3n}$ . Compound **1c** is isostructural to compounds **1a** and **1b**. All are crystallized in monoclinic *P2* (*N*<sup>o</sup> 3) with four molecules per unit cell. The volume of unit cell of **1c** which is 4535 Å<sup>3</sup> is the same of that of **1b** but slightly different of **1a** of 47 Å<sup>3</sup>. The organization of the texture and the structure of **1c** are identical to **1a** and **1b**. The three compounds have the same three channels composed of same elements and arranged in the same manner. Channel C1 is still filled with a linear chain of water molecule and coordinated potassium ions by the ligand DB18C6. Regarding channel C2, it filled of linear chain of alternating coordinated crown ether and non-coordinated crown ether linked each other by water molecule. This channel looks like the channel of compounds **3a** and **3b**. The difference is situated on the metal ion. While channels C2 of compounds **1** are filled of potassium cations those of compounds **3** contained sodium ions. Channel C3 are unique. They are filled with linear empty crown ether linked by water molecule. The three channels disposed in the same manner antiparallel thereby showing the similarity in the three structures. The very main difference in these structures is situated on the polyhalide anions. The stability and the neutrality of channels of compound **1c** are realized by the anions I–I–Br<sup>-</sup> (Figure 11) while those of **1a** and **1b** are respectively insured by I–I–I<sup>-</sup> and Br–I–Br<sup>-</sup> anions. In **1c**, the I–I distance 2.93 Å is constant and it is the same value found in the literature [4a]. This I–I distance is between that of compound **1a**, 2.888(3) Å and 2.972(3) Å. Those values are closed to that of Chekhov [7]. In this same compound **1c**, I–Br distance also constant is 2.913(2) Å is between 2.898 Å and 2.941 Å of that of compound **1b**. In compound **1c**, like **1a** and **1b**, the angle between the planes of two aromatic groups and also the distance between two tri-anions which are respectively 150° and 3.82 are not change and still identical.

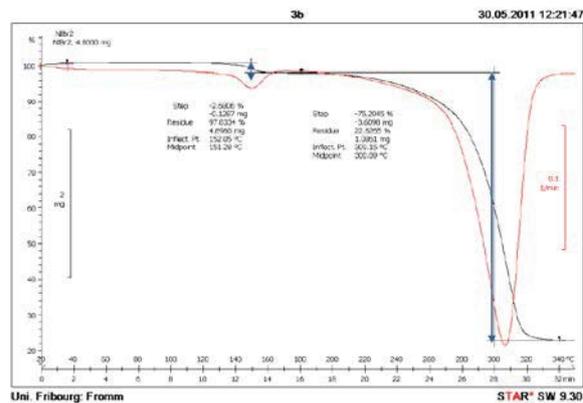
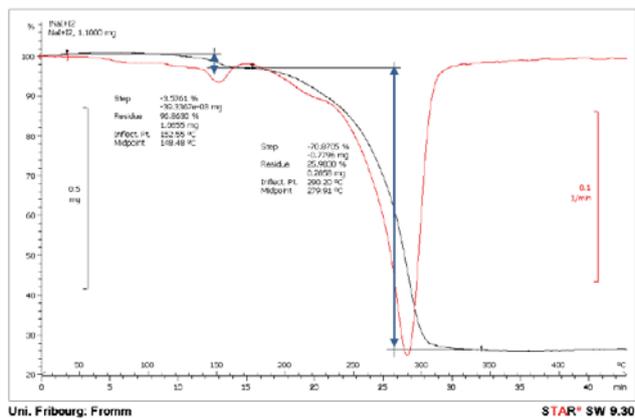
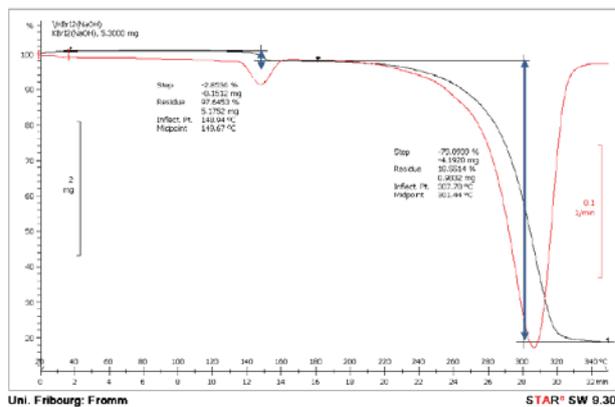
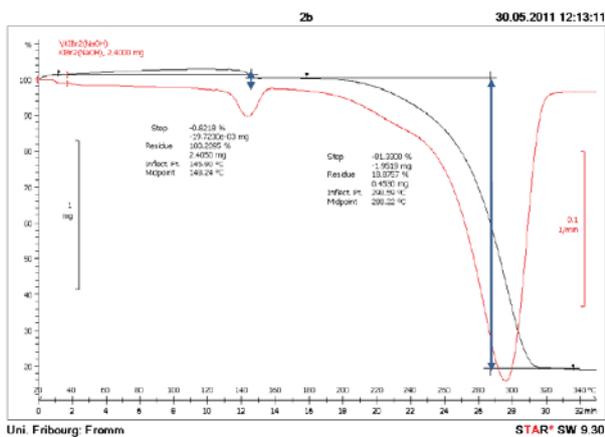
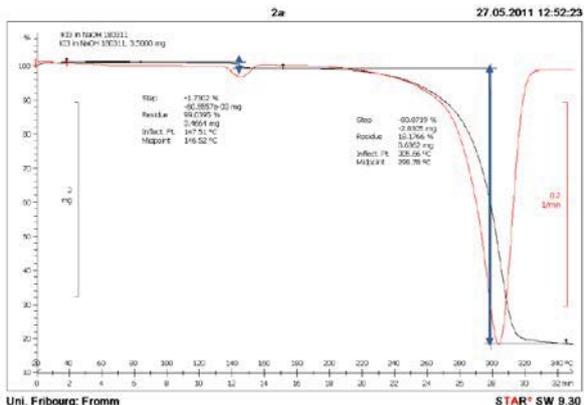
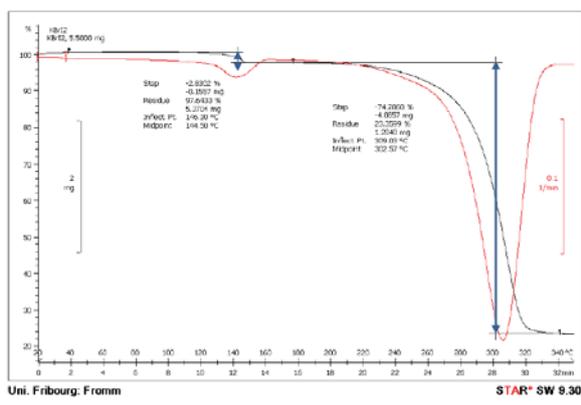
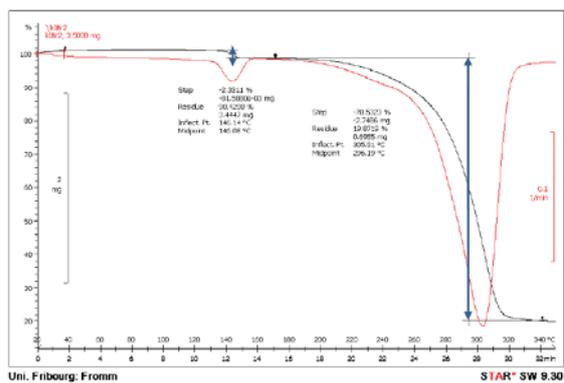
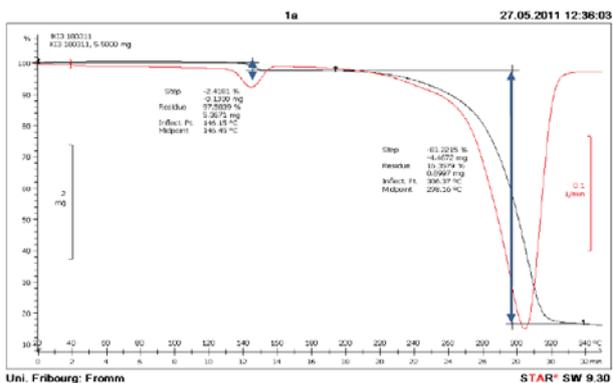
**Developed formula**  $[\{Na\subset(DB18C6)(\mu-H_2O)\}_n\{Na\subset(DB18C6)(\mu-HO)_{2/2}\}_n](I_2Br)_n 2c$

Single crystals of compound **1c** are immersed into an aqueous solution of NaOH, ion ex-change and substitution of H<sub>2</sub>O by NaOH is observed without dissolution of those single crystals and compound **2c** isostructural to **1c** is obtained as red-brown needles in monoclinic space group *P2* with two molecules per unit cell (Figure 12). Chemical formula of **2c** is  $[\{Na\subset(DB18C6)(\mu-H_2O)\}_n\{Na\subset(DB18C6)(\mu-HO)_{2/2}\}_n](I_2Br)_n$ . There are two different channels in **2c**, Channel C1 and channel C2. Both of channels C1 and C2 are antiparallel and are stabilized by parallel antisymmetric I–I–Br<sup>-</sup> anions. The distances between metal ions and the axial oxygen atoms (M<sup>+</sup>–O<sub>(axial)</sub>) in channel C1 and C2 are respectively 1.78(2) Å–3.00(2) Å and 1.56(2) Å–2.95 Å. Those distances are different that of these K–H<sub>2</sub>O of compound **1c** which are 1.805(13) Å –2.863(14) Å and 2.604(14) Å–2.966(14) Å. Moreover the volume of unit cell of **2c**, 4526 Å<sup>3</sup> is different to that of **1c** which is 4536 Å<sup>3</sup>. It is the same as for the distances I–I and I–Br. This information proves that even though **1c** and **2c** are isostructural; compound **2c** does not contain potassium ions. The metal ions contained in **2c** are sodium ions. The Na–O(axial) distances are different from Na–O distances of **2a** and **2b** because **2c** is not only isostructural to the two compounds (**2a** and **2c**) but also its counter ions (I–I–Br asymmetric) are different to the counter ions of **2a** (I–I–I, symmetric) and **2b** (Br–I–Br, also symmetric). Like **2a** and **2b**, channel C1 of **2c** is still filled of linear coordinated sodium ions by DB18C6 linked to each other by OH<sup>-</sup> ions. And channel C2 contains sodium ions coordinated linked by water molecules. The distance between two anions (I–I–Br) is 3.82(1) Å rest the same those of polyanions of other compounds. The angle between the planes of two aromatic groups around 86° is also close of that literature [3]. The angle defined between terminal bromide Br<sub>2</sub> and the atoms I3 and I1 of the next anions is 150.85°. This value is the same as that we find in the other compounds in literature [4].

**Developed formula**  $[\{Na\subset(DB18C6)(\mu-H_2O)(DB18C6)(H_2O)\}_{2n}](I_2Br)_{2n}, 3c$

Dibenzo-18-crown-6 is reacted with (KBr+I<sub>2</sub>) in aqueous-tetrahydrofuran solvent. After evaporation of solvent, single crystals of compound **3c** in form of needles are grown. Its colour is red-brown and its chemical formula which is  $[\{Na\subset(DB18C6)(\mu-H_2O)(DB18C6)(H_2O)\}_{2n}](I_2Br)_{2n}$ , **3c** is not isostructural to any structures already described. It crystallizes in orthorhombic space group *Pna2*<sub>1</sub> with two molecules per unit cell (Figure 13). Its volume which is 4485(3) Å<sup>3</sup> is the lowest volume of the compounds directly synthesized. Like to compounds **3a** and **3b**, **3c** is formed of two channels C1 and C2 anti parallel distributed throughout the structure and stabilized by linear parallel polyanions I–I–Br<sup>-</sup>. The polyanions also allow the neutrality of the crystalline complex. The distance I–Br in **3c** of 2.90(1) Å is equal to that of **2c** but differs from that of **1c**. I–I distance measuring also 2.90(1) Å is lower to I–I distance of **3a** and **3c**. In **3c**, Na–O(axial) distances is comprised between 2.29 Å and 2.31 Å. These Na–O(axial) distances are equal to the Na–O(H<sub>2</sub>O) distances in Channels C2 of compounds **3a** and **3b**. Or channel C2 of **3a** and **3b** are filled of sodium cations and water molecules. So, both of channels (C1 and C2) of **3c** contained also sodium ions and water molecules. The channel are filled in the same manner with linear and alternative elements  $[\{Na\subset(DB18C6)\}$  and  $[DB18C6]$ . The two elements are linked by a water bridge forming cationic complex  $[\{Na\subset(DB18C6)(\mu-H_2O)(DB18C6)(H_2O)\}_{2n}]^+$ . This complex consists of a sodium cation coordinated to which a DB18C6-ligand in equatorial, and two water molecules in axial position of a hexagonal bipyramidal coordination sphere followed by another empty DB18C6-ligand always in equatorial position. As in **3a** and **3b**, the main difference between channels C1 and C2 in **3c** is situated stacking of aromatic groups of the ligands. Channels C2 are almost perfectly stacked with the phenyl groups of the ligand. In channel C2 the sodium ions are slightly deviated of 0.12(3) Å from the cavity formed by the six oxygen atoms of DB18C6. Also, the angle between the planes of two phenyl groups which is 80.86(1)° is the same that of channel C2 in **3a**. In channels C1 of **3c**, the aromatic group are offset. In **3c**, Na–O(DB18C6) distances are situated between 2.431(9) Å–2.846(10) Å are in accord with the average value in the other compounds in literature[8]. The distances between O(H<sub>2</sub>O) and the plane formed by the six oxygen atoms of the ligand are between 2.164(14) Å and 2.433(4) Å. These values are identical to those of **3a** and **3b** which are filled with the same sodium cations as **3c**. Compounds **3a**, **3b**, **3c** have the same cations, the same channel, crystallized in orthorhombic but differ by the space group and the polyanions. Channels of **3a** are stabilized by tri-iodide ions. Those of **3b** by Br–I–Br<sup>-</sup> and finally those of **3c** by I–I–Br<sup>-</sup>.

## 9. Thermogravimetric analysis of the compounds



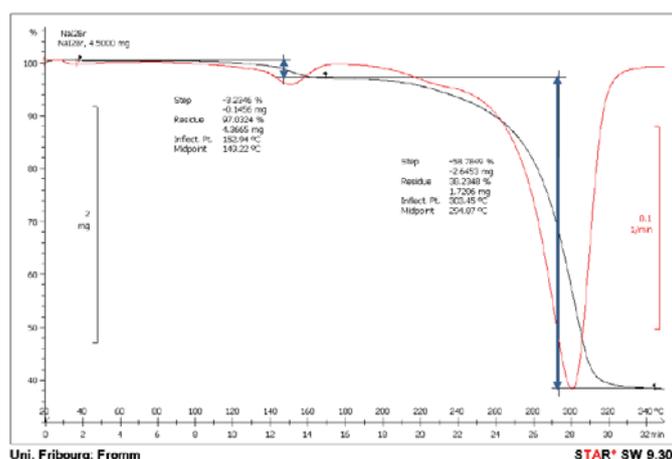


Figure 23. Curve of Loss water molecules and thermal decomposition of compound 3b

Compounds **1a**, **1b**, **1c** have the same framework. These metal-organic frameworks contain three channels filled with a total of six water molecules, three potassium ion, three polyanions ( $\text{I}_3^-$  for **1a**,  $\text{IBr}_2^-$  for **1b** and  $\text{I}_2\text{Br}^-$  for **1c**) and six molecules of ligand dibenzo-18-crown-6. These three compounds have been submitted to heat treatment ( $10^\circ\text{C}/\text{min}$ . until  $340^\circ\text{C}$ , under  $\text{N}_2$ ) to perform thermogravimetric analyses. This gives an indication on the behaviour of these compounds to the heat and allows to determine the temperatures of vaporization and decomposition of molecules in the crystals. The decreasing curves obtained (Figures 15, 16, 17) all show a first level at  $146^\circ\text{C}$  where the weight loss corresponds to the loss of six water molecules that bind potassium ions coordinated by crown ethers and also empty crown ethers by a thermal process. The elimination of the water molecules is therefore done at a fairly high temperature ( $146^\circ\text{C}$ ), which implies that the compounds **1a**, **1b** and **1c** are stable at room temperature. In fact, for the molecules strongly linked as the water in these crystals **1**, we often observed temperatures significantly higher than the boiling point of water [8]. The removal water in these crystal **1** leads to the formation of new compound **1'** previously described. Around  $306^\circ\text{C}$ , we observe a second level which can correspond to the loss of the six molecules of crown ether causing a degradation of these crystals.

Compounds **2** (**2a**, **2b**, **2c**) are the same building blocks. They contained two sodium ions, one water molecule, one hydroxide ion two DB18C6 and one polyanion. Thermogravimetric analysis of these compounds **2** shows a loss of water molecule and hydroxide ion around  $146^\circ\text{C}$  and a degradation of molecules of crown ether around  $305^\circ\text{C}$  (Figures 18, 19, 20).

Compounds **3** (**3a**, **3b**, **3c**) are composed of two sodium cations, four water molecules and four molecules of DB18C6 ligands. The curve of thermograms of these crystals show a loss of water in the crystals at  $152^\circ\text{C}$  and degradation of the molecules of crown ether around  $303^\circ\text{C}$  (Figures 21, 22, 23). Water loss at  $152^\circ\text{C}$  in compounds **3** is higher than that of in compounds **1** and **2**. This means that water molecules are strongly and regularly distributed in crystals **3** than in crystals **1** and **2**.

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