

## Accessory Publication

### Physicochemical properties of new dicationic ether-functionalized low melting ammonium salts

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## 1. Capillary electrophoresis

### 1.1 Chemicals

Ultra pure water was obtained by passing distilled water through an ELGA Elgastat Maxima (Elga Ltd, UK) and it had a resistivity greater than 18.2 M $\Omega$ /cm. Benzylalcohol (>98%) was obtained from Fluka Chemika (Buchs, Switzerland), Ethyleneglycol (>98%) from Riedel-de Haën (Seelze, Germany), potassiumchloride (>99.5%) from Merck (Darmstadt, Germany) and methanol (HPLC Gradient Grade) from J.T. Baker (Deventer, Holland).

## **1.2 Measurements: UV-Vis spectrum, viscosity and conductivity**

Instrument control and data acquisition were performed with HP<sup>3D</sup> Chemstation software (Agilent, Rev 05.01.). Uncoated fused silica capillary (Composite Metal Services Ltd., The Chase, Worcester, UK) was 100  $\mu\text{m}$  i.d., 375  $\mu\text{m}$  o.d. and total length of 33 cm (8.5 cm to the detector). The capillary cassette temperature was adjusted to 25°C with air cooling. The instrument was placed in a temperature conditioned room (+20 °C). New capillaries were conditioned by successive flushes with 1 mol l<sup>-1</sup> and 0.1 mol l<sup>-1</sup> NaOH for 10 min each. Before each series of measurements, capillaries were cleaned with 0.1 mol l<sup>-1</sup> NaOH, ultra pure water and methanol for 3 minutes each. And after the daily measurements capillaries were cleaned with 0.1 mol l<sup>-1</sup> NaOH and ultra pure water and stored without vials for the next day. UV-Vis spectrum, viscosity and conductivity determinations were done by modifying the method of François *et al.* {{250 Francois,Y. 2006; }}. In viscosity and conductivity measurements the samples used were IL/methanol (v/v) mixtures of 5:95, 10:90, 25:75, 50:50, 75:25, 90:10, 95:5 and pure IL. For UV-Vis measurements, only pure ILs were used. Benzyl alcohol was used as flow marker for viscosity measurements and was detected at 254 nm.

In UV-Vis measurements, after capillary conditioning, capillary was first filled with ultra pure water and then hydrodynamic injection of the IL was performed under a pressure of 50 mbar for 5 seconds. Measurements were done by using the ultra pure water as a background electrolyte (BGE) and +20 kV voltage. After the sample zone of IL had passed the detector UV-Vis spectrum was recorded from 190 nm to 600 nm.

Before the conductivity measurements of the IL samples calibration of Capillary Electrophoresis (CE) power supply and microamperometer (I/V term in Equation 1.) was done with solutions of 0.1 mol L<sup>-1</sup> and 0.01 mol L<sup>-1</sup> KCl ( $\kappa=1.2931$  (1.288 [1]) and  $\kappa=0.1428$  (0.1413 [1]) S m<sup>-1</sup>). In IL conductivity determinations voltages successively applied were 0.2, 0.5, 1.0, 1.2 and 1.5 kV. All of the five voltages mentioned were used

for every sample (IL-methanol (v/v) mixtures of 5:95, 10:90, 25:75, 50:50, 75:25, 90:10, 95:5 and pure IL). All the measurements were repeated three times with same sample. Conductivity was obtained from the measured current intensity according to Ohm's law [1]:

$$\kappa = \frac{4LI}{\pi d_c^2 V} \quad (1)$$

Where L is the total capillary length, I is the measured intensity,  $d_c$  is the inner diameter of the capillary and V is the applied voltage.

The viscosity measurements began with calibration of both the pressure delivery system and inner diameter of the capillary ( $d_c^2 \Delta P$  term in Equation 2.) with solution of ethyleneglycol ( $\eta=16.04 \cdot 10^{-3}$  (16.1  $\cdot 10^{-3}$  [1]) Pa s at 25 °C). In the viscosity measurements the capillaries were first filled with IL and then a short plug of an IL sample including 0.05 % benzyl alcohol (flow marker) was injected under a pressure of 50 mbar for 3 seconds. The marker zone was displaced by IL sample without marker under 50 mbar. Viscosity measurements were repeated three times with same IL for precision evaluation. The detection time of the benzyl alcohol  $t_d$ , was used for calculation of viscosity according to Hagen-Poiseuille law [1]:

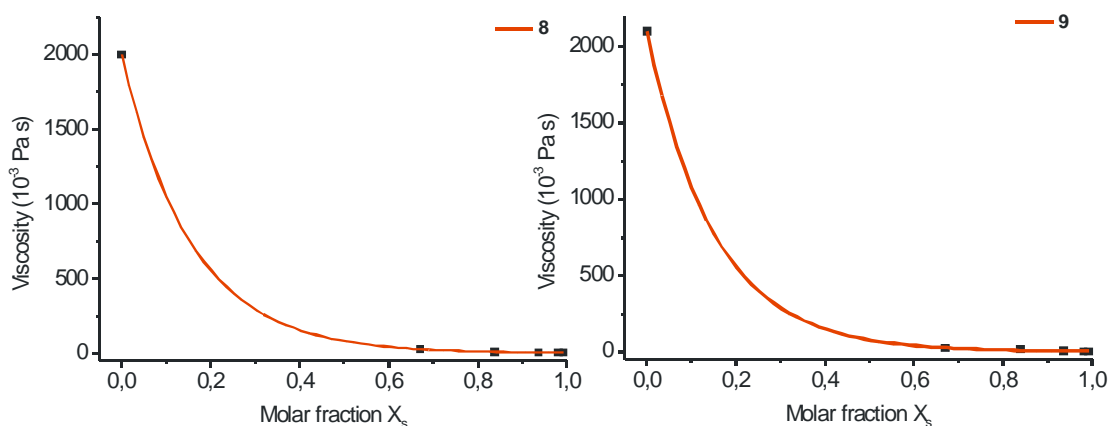
$$\eta = \frac{d_c^2 \Delta P t_d}{32lL} \quad (2)$$

Where  $\Delta P$  is the pressure applied and l capillary length to the detector.

### **1.3 Results and discussion**

The second approach to the viscosities of **8** and **9** was made by determining viscosities of IL/molecular solvent mixtures. In our case methanol was used, as both salts are fully miscible to it. Full series of IL/methanol mixtures (5:95, 10:90, 25:75, 50:50, 75:25, 90:10, 95:5 v/v) and pure IL was planned to be measured by capillary electrophoresis (CE). However, certain troubles appeared with pure IL, and with sample mixtures of 95:5 and 90:10 (v/v). The high viscosity of salts together with operational limitations of the CE apparatus, e.g. the inner diameter of capillary (100  $\mu\text{m}$ ) and the maximum injection pressure (50 mbar), caused blocks occasionally in the capillary. Therefore reliable

viscosities of pure ILs could not be acquired by CE, and the results of the rheometer measurements were used instead to visualize the change in viscosities of ILs as a function of the molar fraction of the methanol. The room temperature results of both CE and rheometer are presented in Fig. S1. In agreement with previously reported studies with monocationic ILs, {{250 Francois,Y. 2006; }} the viscosities of both dicationic salts decrease substantially by mixing with molecular solvent, in this case methanol, with a solvent molar fraction  $\geq 0.5$ , the viscosities are already below 100 mPa s (R.S.D in the range of 1 – 5%).

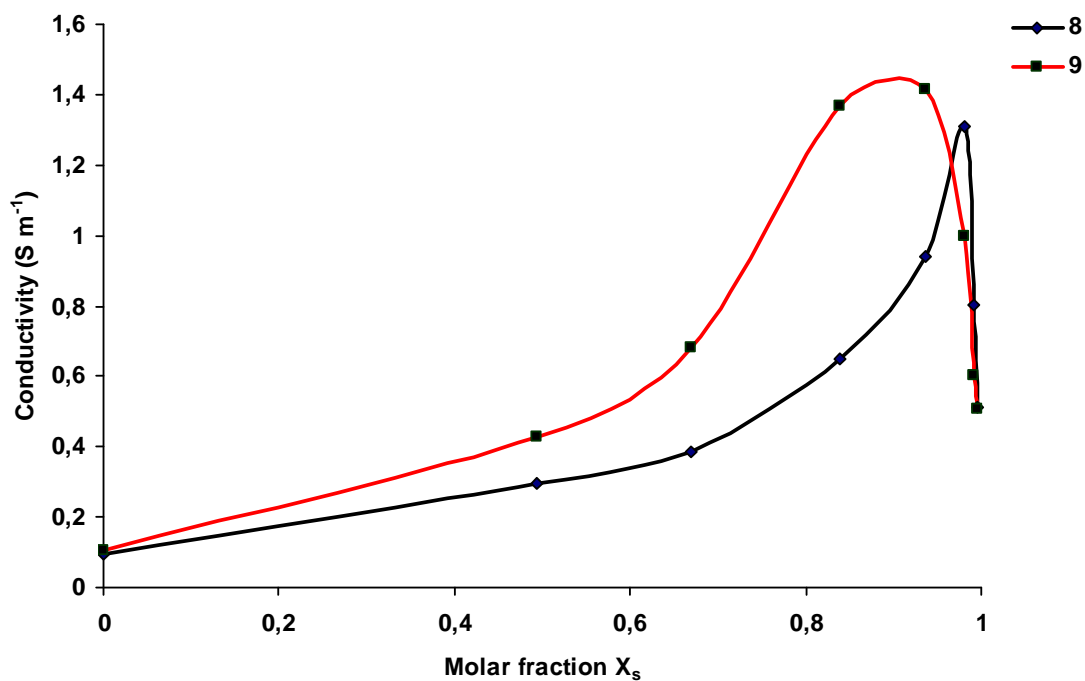


**Figure S1.** Variation of the viscosities for **8** and **9** in IL/methanol solvent mixtures as a function of the molar fraction of the methanol. Exponential function was fitted to the data.

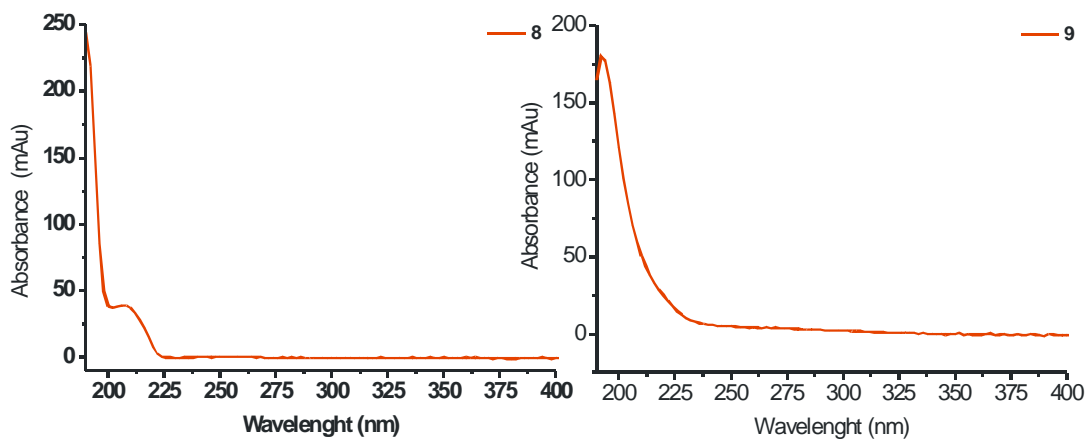
The high viscosity caused similar difficulties in the conductivity measurements with IL/methanol mixtures of 95:5 (v/v) and pure ILs. To diminish the effects of the capillary blocks, capillaries were changed frequently to improve accuracy and repeatability of the results. With successful measurements, conductivity values of  $\kappa = 0.094 \text{ S m}^{-1}$  and  $0.104 \text{ S m}^{-1}$  (R.S.D. in the range of 1-4%) were obtained for pure ILs **8** and **9**, respectively.

The variation of the conductivities of the ILs as a function of molar fraction of the methanol is presented in Fig. S2. For IL/methanol mixtures, behavior of conductivities have similar trend than on the imidazolium-based ILs reported by Francois *et al.* {{250 Francois,Y. 2006; }}. Conductivities of pure ILs are clearly lower than on IL/methanol mixtures with solvent molar fraction range of 0.80–0.98. Above that range, conductivities

decrease again substantially. It can be noted that particularly, salt **9** exhibit high conductivities (max  $\sim 1.4 \text{ S m}^{-1}$  at  $X_s = 0.8-0.9$ ) on a broad molar fraction range (0.6 – 0.95).



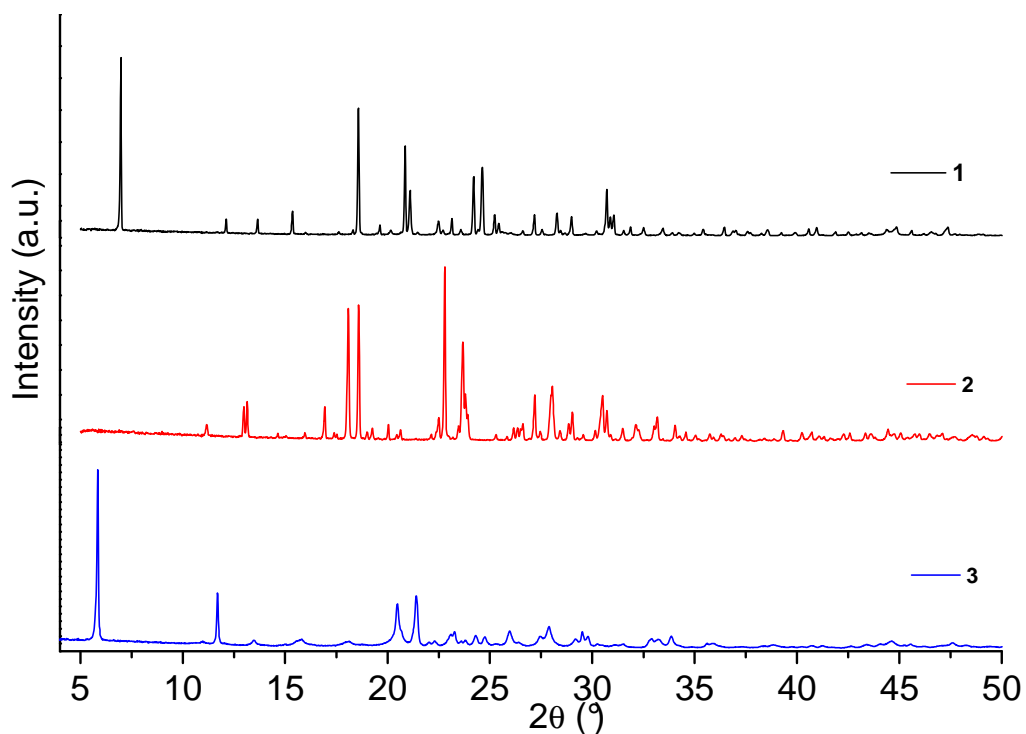
**Figure S2.** The conductivities of IL/methanol mixtures of salts **8** and **9** measured as a function of the methanol molar fraction.



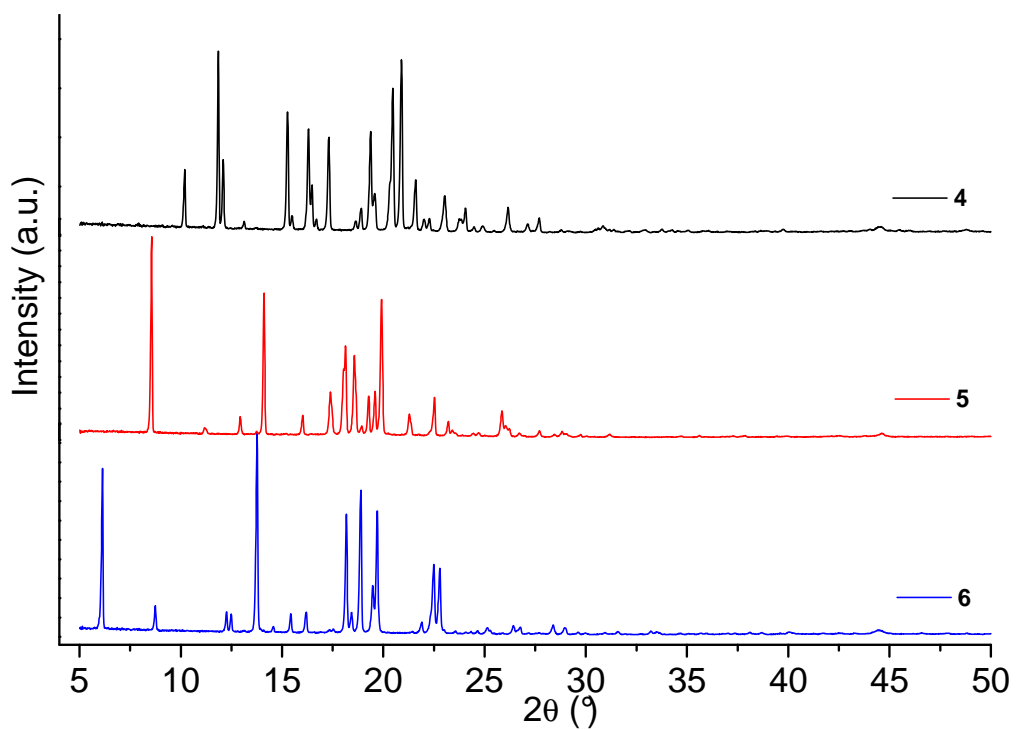
**Figure S3.** Uv-Vis spectra of compounds **8** and **9**.

The UV-Vis spectra of pure ILs **8** and **9** were acquired in the range 190–600 nm. However, only the range of 190–400 nm is presented in Fig. 2, because above 400 nm there was no change in absorption. The absorption maximum for **8** is below 190 nm. In addition a little shoulder appears between 200–225 nm. For **9** the absorption maximum is near 190 nm and no similar shoulder is noticed compared to the spectrum of **8**.

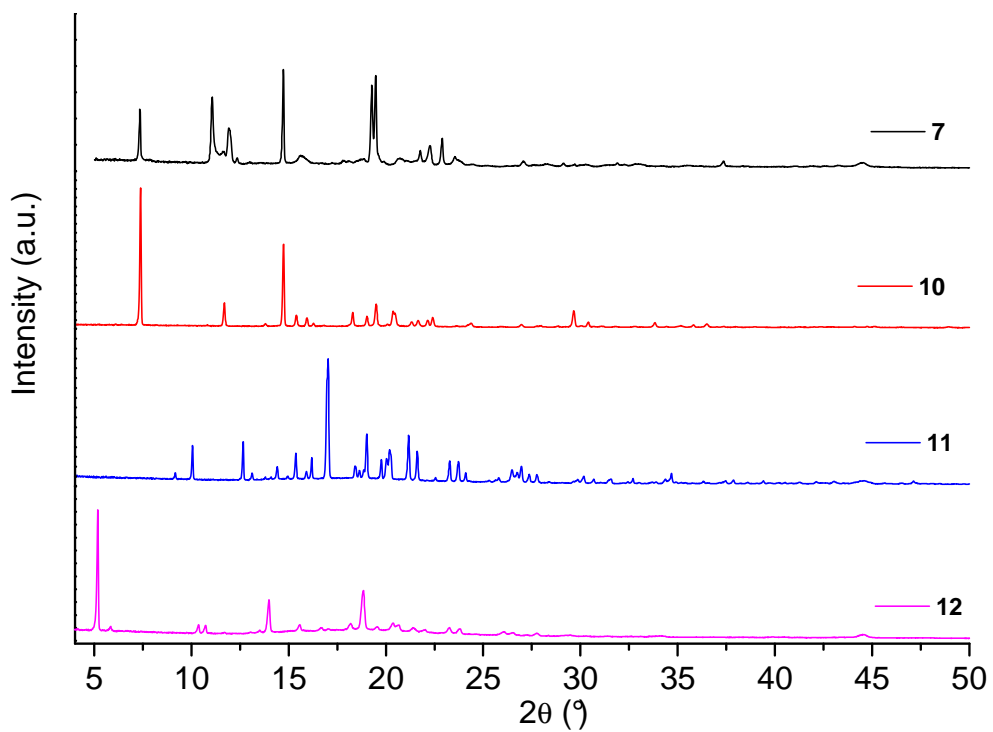
## 2. Powder X-ray diffraction



**Figure S4.** PXRD patterns of dicationic QA bromides **1** – **3**.

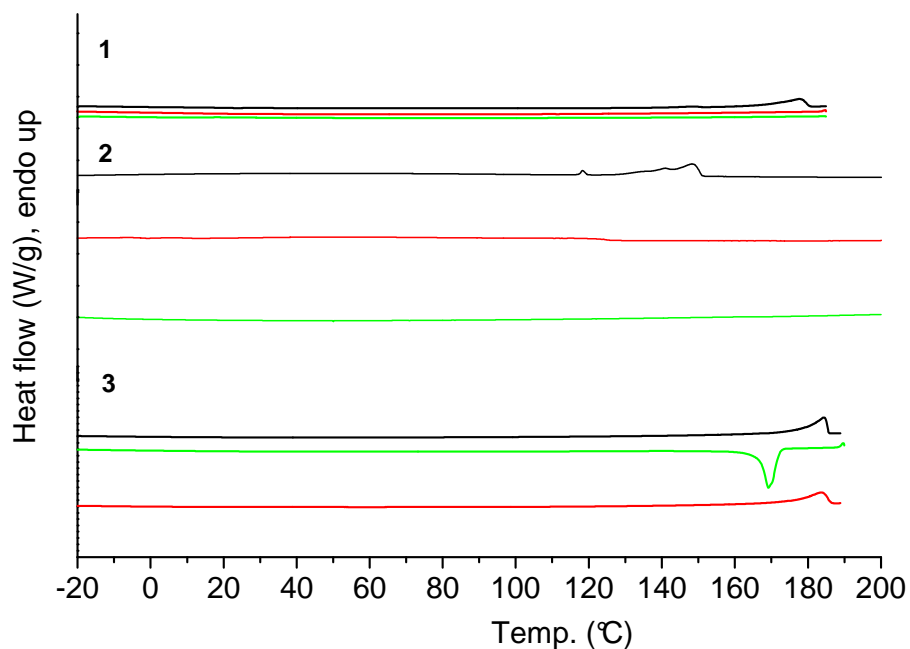


**Figure S5.** PXR D patterns of dicationic QA hexafluorophosphates **4 – 6**.

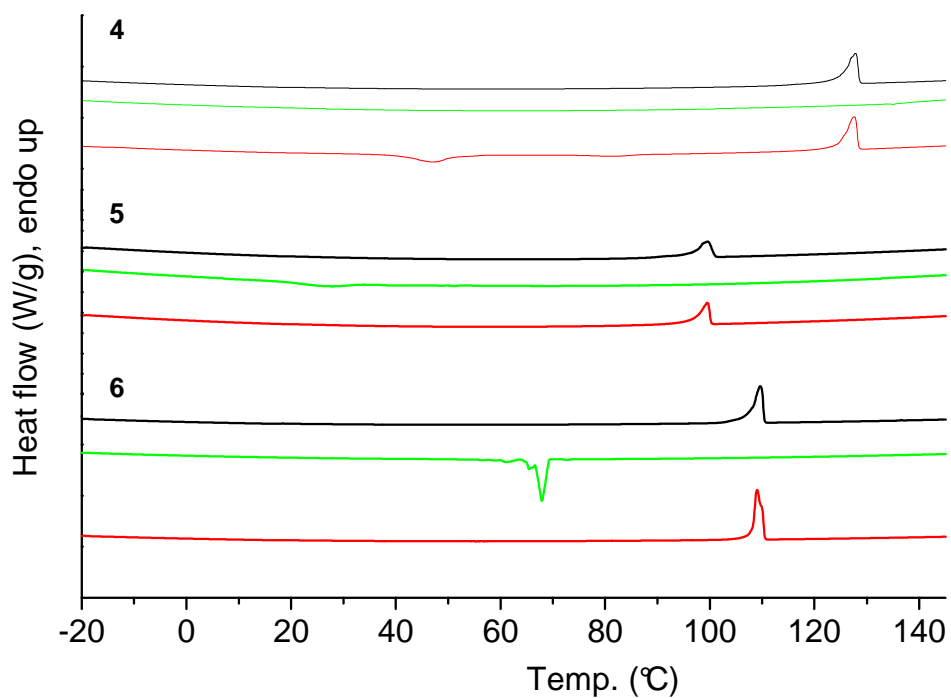


**Figure S6.** PXR D patterns of dicationic QA TFSI **7**, and TFMSs **10 – 12**.

### 3. Thermal analysis

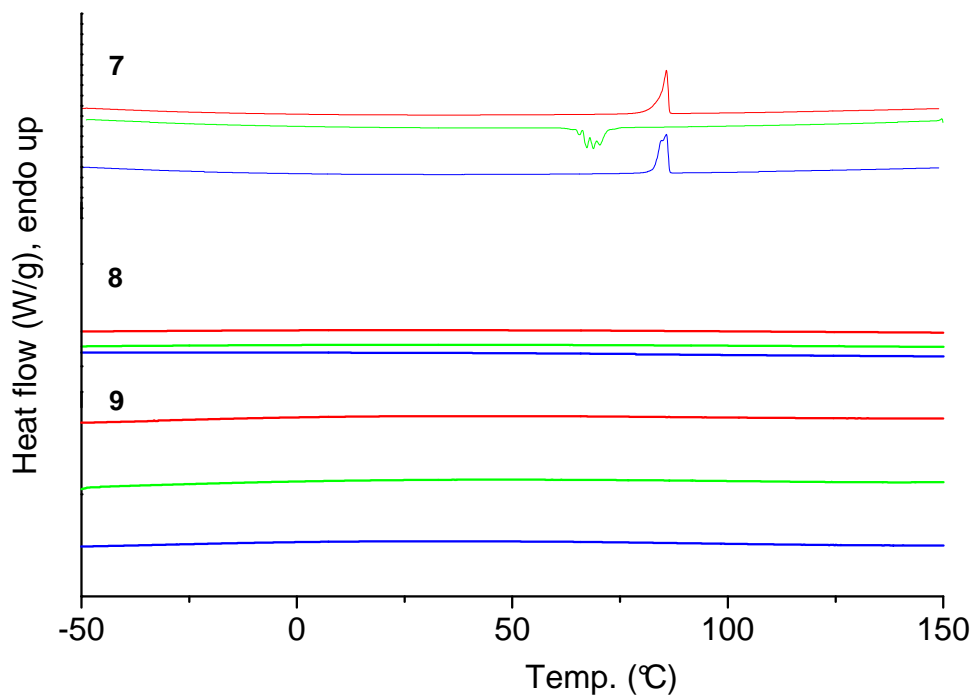


**Figure S7.** DSC scans of QA bromides **1** – **3** measured with a heating and cooling rate of 5 °C/min.

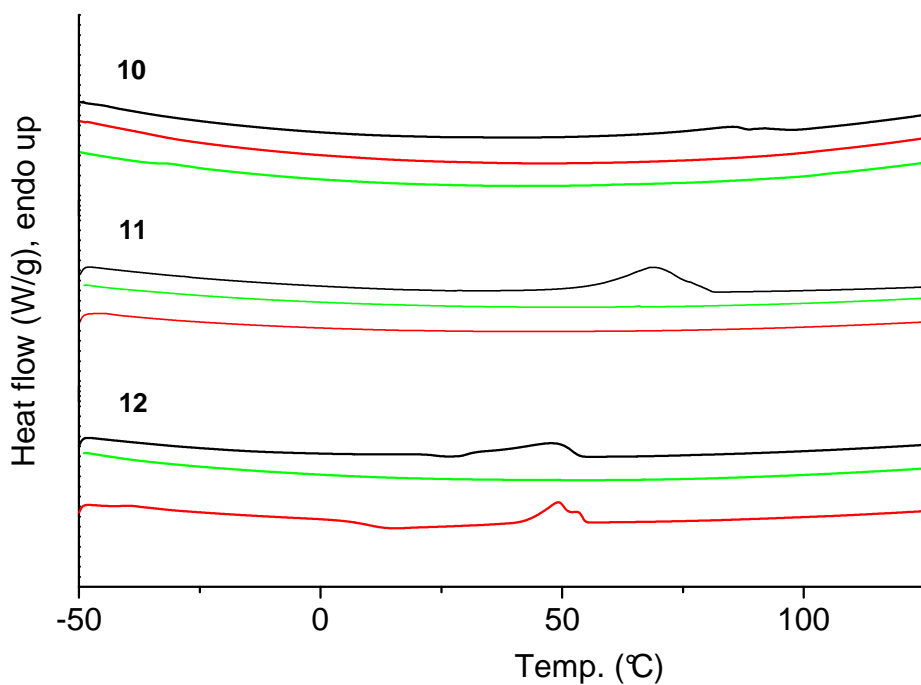


**Figure S8.** DSC scans of QA hexafluorophosphates **4** – **6** measured with a heating and cooling rate of 5 °C/min.

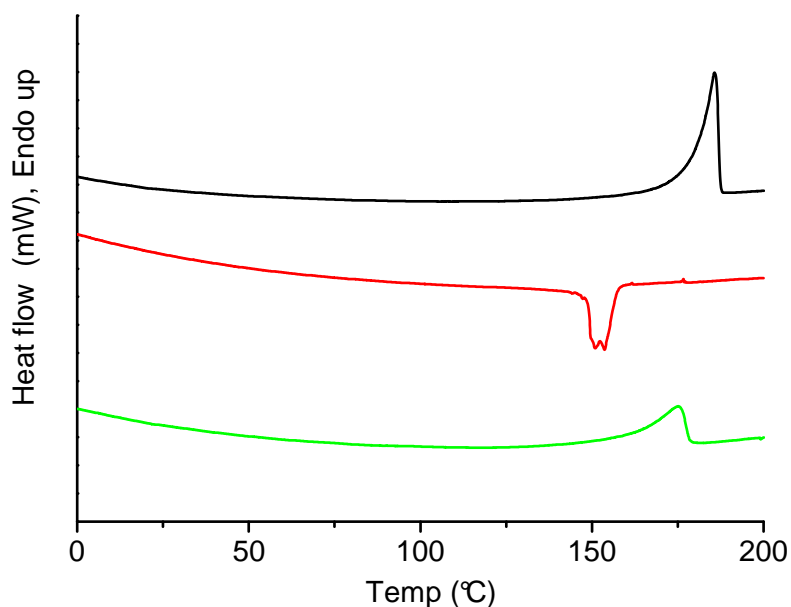




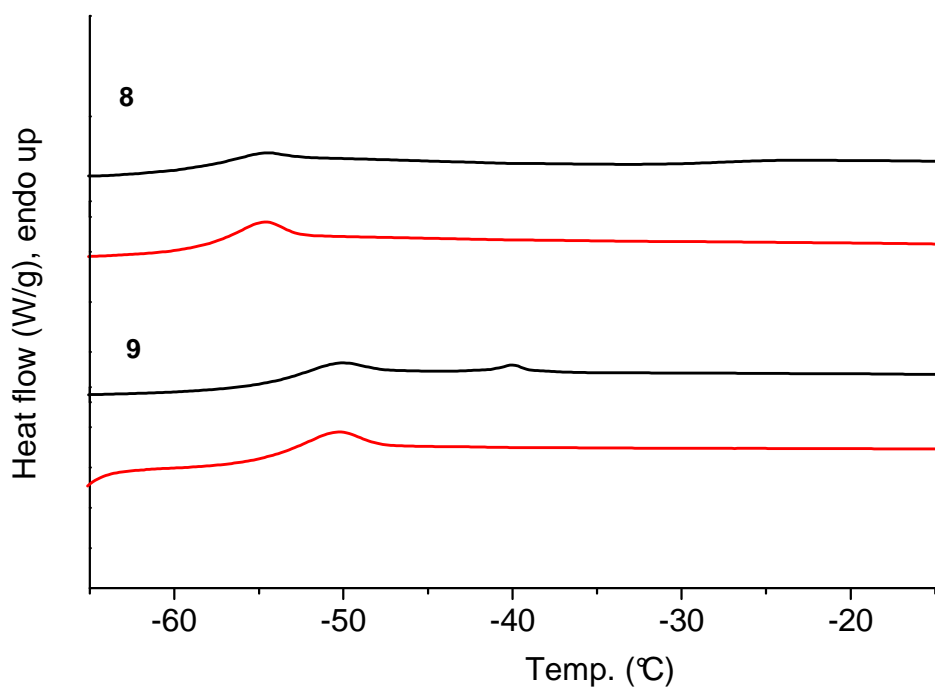
**Figure S9.** DSC scans of QA TFSIs 7 – 9 measured with a heating and cooling rate of 5 °C/min.



**Figure S10.** DSC scans of QA TFMSs 10 – 12 measured with a heating and cooling rate of 5 °C/min.



**Figure S11.** DSC scan of QA bromide **3** with heating rate of 5 °C/min and cooling rate of 10 °C/min. The melting enthalpies for the first and the second heating are 47.6 kJ/mol and 25.8 kJ/mol, respectively.



**Figure S12.** DSC scans of QA TFSIs **8** and **9** showing glass transitions with a heating rate of 10 °C/min.

## 4 .References

1. François, Y. , Zhang, K., Varenne, A., Gareil, P., *Anal. Chim. Acta* 562 (2006) 164-170.