Role of Anion–π Interactions in the Supramolecular Assembly of Salts Containing Asymmetrical Bis(pyridyl) Cations

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Fig. S1 3-D supramolecular architectures of salts 1-8.

Fig. S2 Anion-π interactions in the 3-fold interpenetrated networks of 8.
**Powder X-ray diffraction (PXRD)**

Powder X-ray diffraction (PXRD) patterns for solid samples of salts 1-8 are measured at room temperature as illustrated in Fig. S4. The patterns are highly similar to their simulated ones (based on the single-crystal X-ray diffraction data), indicating that the single-crystal structures are really representative of the bulk of the corresponding samples.

**Thermogravimetric analysis (TGA)**

The thermal stability of the eight salts were analyzed on crystalline samples by thermogravimetric analyses (TGA) from room temperature to 600 °C at a rate of 10 °C min\(^{-1}\) under atmosphere. As shown in Fig. S5, the thermal stability of the hexafluorophosphates is lower than the thermal stability of the perchlorates but higher than the corresponding nitrates. The sharp weigh loss of the eight salts is falling in the range of 184-314 °C, 181-310 °C, 175-305 °C, 203-354 °C, 200-315 °C, 211-355 °C, 140-176 °C and 137-170 °C, respectively.

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**Fig. S3** Discrete motif in 2 formed by one PF\(_6^-\) and six HM2\(^+\) cations.
Fig. S4 PXRD patterns for salts 1-8.
Fig. S5 TG curves of salts 1-8 at atmosphere.