π-Electronic Ion Pairs：Ordered Arrangement Based on Noncovalent Interactions

(*College of Life Sciences, Ritsumeikan University*) ○Hiroki Tanaka, Yohei Haketa, Hiromitsu Maeda

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π-Electronic ion pairs are of interest for the fabrication of electronic materials with potential ferroelectric and electric conductive properties. Because of their appropriate sizes, geometries, and electronic states, π-electronic ions can achieve ordered ion-pair arrangements as dimension-controlled assemblies, including supramolecular gels and liquid crystals.[1] Despite numerous studies on assembling modes, the interactions between π-electronic ions are not well understood. This study focuses on the characteristic interactions operative in ion-pairing assemblies comprising porphyrin ions, which delocalize the charge in the core units. π-Electronic anions produced upon deprotonation of *meso*-hydroxy-substituted porphyrins (MHPs)[2] can form various π-electronic ion pairs in combination with π-electronic cations such as porphyrin–Au^{III} complexes[3] and triazatriangulenium cations ($TATA^+$). π-Electronic ion pairs were formed by mixing Na^+ salts of porphyrin anions, prepared from the CH_2Cl_2 solutions of MHPs with aqueous NaOH, and 1 equiv of chloride salts of desired countercations, followed by the removal of NaCl by washing with water (Fig. 1). The π-electronic ion pairs exhibited characteristic ^{1}H NMR signal shifts due to ion-pairing stacking in solution (Fig. 2). Furthermore, the energy decomposed analysis of single-crystal packing structures revealed that electrostatic and dispersion interactions were important for stabilizing the stacking π-electronic ions.

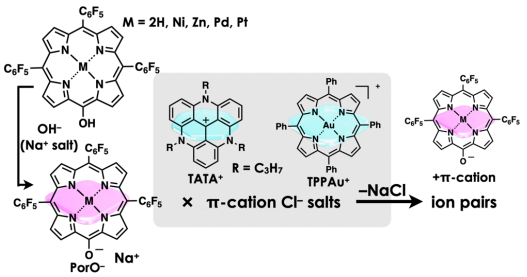

Fig. 1 Method for preparing π-electronic ion pairs.

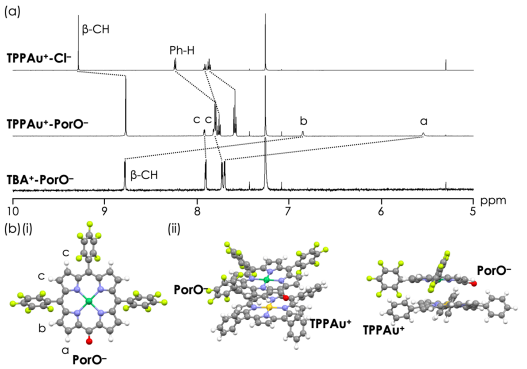

Fig. 2 (a) ^{1}H NMR spectra of $TPPAu^+$-Cl^-, $TPPAu^+$-$PorO^-$, and TBA^+-$PorO^-$ in $CDCl_3$ (1.0×10^{-3} M) and (b) optimized structures of (i) $PorO^-$ and (ii) $TPPAu^+$-$PorO^-$.

1) A recent review: Haketa, Y. et al., *Mol. Syst. Des. Eng.* **2020**, *5*, 757. 2) (a) Sasano, Y. et al., *Dalton Trans.* **2017**, *46*, 8924; (b) Sasano, Y. et al., *Chem. Eur. J.* **2019**, *25*, 6712. 3) (a) Haketa, Y. et al., *iScience* **2019**, *14*, 241; (b) Tanaka, H. et al., *Chem. Asian J.* **2019**, *14*, 2129.

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