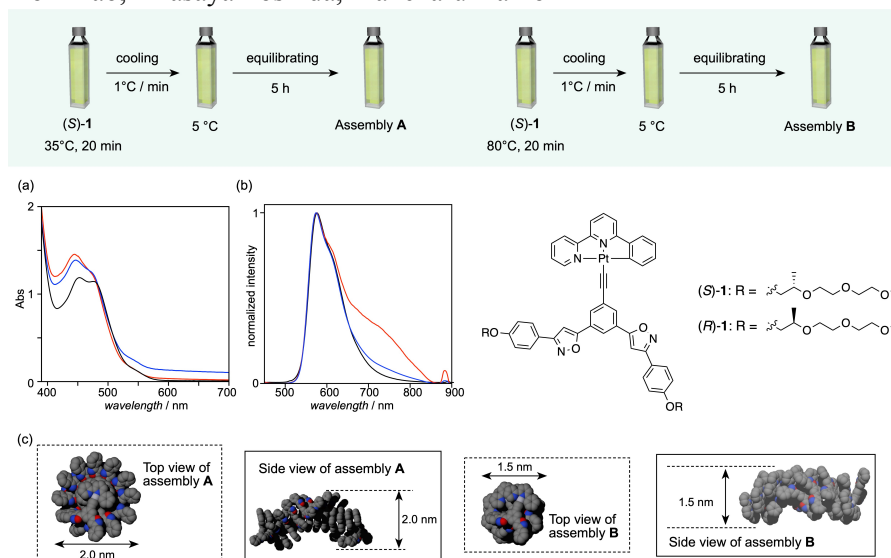


Pathway complexity in the self-assembly process of platinum complexes possessing TEG chains

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Aside from the most stable state, there are kinetically trapped metastable states in the supramolecular polymerization process, which is coined to be pathway complexity. Particular supramolecular polymers, which are commonly supramolecular polymers assembled in cooperative fashion, can be detected the metastable states as well as the most stable state. The pathway is determined by the preparation conditions, such as solvent, temperature, and concentration. Thus, two or more individually organized supramolecular assemblies can be prepared from one type of monomer molecules by varying the preparation conditions, which leads to information-rich functional materials. We have demonstrated that neutral platinum complexes with chiral TEG chains self-assembled to form helically stacked constructs in a cooperative fashion. We thus sought to gain the detailed insight into the self-assembly behavior of the platinum complexes (S)- and (R)-1.^[1]

Supramolecular assemblies of (S)-1 were prepared under two different conditions (Fig. 1 top). Both of the specimens exhibited blue-shifted peak in the absorption spectra, indicating assembled (S)-1 was formed in the solutions (Fig. 1a), where we defined the two assemblies as assembly **A** and assembly **B**, respectively. Clear MMLCT band was seen in the emission spectra of assembly **A** whereas relatively weak MMLCT band was observed in the solution of assembly **B** (Fig. 1b). The discernible difference between the emission spectra indicates that assembly **A** was formed primarily by Pt–Pt interactions, while assembly **B** was formed by π – π and dipole–dipole inter-actions (Fig. 1c).

[1] M. Yoshida, T. Hirao, T. Haino, *Chem. Commun.*, **2022**, 58, 8356-8359.