Ionic-Guests-Assisted Charge–Transfer Assemblies Based on the Electron-Donor Pillar[5]arene and the Electron-Acceptor Cyanostar

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Macrocycle-based charge–transfer assemblies (MCTAs) have gained increasing interest due to their potentials for guest recognition and the structural aesthetics. In most cases, MCTAs have been created by co-crystallization, using the rigid steric structures of macrocyclic molecules as the main backbone. However, when the sizes or shapes of the electron-donor and acceptor molecules are quite different, achieving close assembly of the molecules to effectively form MCTAs becomes significantly challenging.

Herein, we report the creation of MCTAs based on two macrocycles with different sizes and shapes; pillar[5]arene (**PA**) and cyanostar (**CS**). **PA**, composed of five alkoxy benzene units, provides an electron-rich cavity, thus exhibiting electron donor property (Fig. 1a). In contrast, **CS**, containing electron-withdrawing cyanostilbene units, displays electron acceptor properties (Fig. 1b). Therefore, by mixing **PA** and **CS**, charge–transfer assemblies can be formed. However, MCTAs obtained by mixing only **PA** and **CS** could not achieve effective CT emission. This would be because the structures of **PA** and **CS** differ significantly– **PA** has a 3D pillar-like shape and **CS** has a 2D planar shape (Fig. 1c). To address these issues, we focused on the fact that **PA** and **CS** are excellent receptors for cation and anion guest molecules, respectively, due to their electron-rich or electron-deficient cavities. By introducing ionic guest molecules into the **PA**–**CS** system, the cationic guests can be encapsulated by **PA**, while the anionic guests can be sandwiched by two **CS** (Fig. 1d). The electrostatic interaction between ionic guests allowed the **PA** and **CS** to assemble closely, resulting in an improvement of the quantum yield and enabling the observation of CT emission even in the solution state, which cannot be accessed without ionic guests.

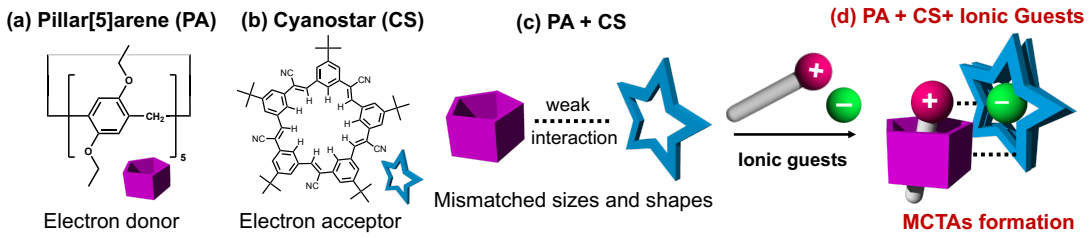

Fig.1 Chemical structures of (a) pillar[5]arene (**PA**) and (b) cyanostar (**CS**). CT assembly formation of (c) **PA**+**CS** and (d) **PA**+**CS**+ionic guests.

Reference: 1) J.-R. Wu, G. Wu, D. Li, Y.-W. Yang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202218142.