Engineering the Assembly and Elasticity of Isoreticular Disulfide-Based Metal–Organic Nanotubes

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Metal–organic nanotubes (MONTs), a fascinating subclass of metal–organic frameworks (MOFs), have garnered significant attention due to their unique tubular 1D architectures and tunable physicochemical properties.[1] Compared with the well-developed 2D[2] and 3D[3] MOFs, MONTs are still in their infancy due to the synthetic difficulties. A limited number of MONTs have been synthesized, and while a majority of reports have focused solely on structural details. Regulating the elasticity of MONTs through precise modulation of their inter-tube interactions remains a significant challenge, as it requires a deep understanding of their assembly mechanisms.

In this study, we reported the rational design and synthesis of isoreticular MONTs through the self-assembly of cadmium ions (Cd^{2+}), 4,4'-Dipyridyl Disulfide(^{py}DS), and isophthalate derivatives (Hip^{2-} or $OHip^{2-}$). The crystal structures revealed that two Cd^{2+} were connected by two ^{py}DS to form a coordination square $[Cd^{2+}(^{py}DS)_2]^{4+}$, which one-dimensionally connected with the assistant of isophthalate to form a metal−organic nanotube. Moreover, the substituents at 5 positions of isophthalate pointed out to the adjacent nanotube, offering a powerful strategy for tuning the inter-tube interactions. In MONT-DS-OHip, robust hydrogen bonding between neighboring nanotubes, with hydroxyl groups as donors, enhanced mechanical properties and minimized solvent effects on elasticity (Fig. 1a). In contrast, MONT-DS-Hip, lacking this network, displayed solvent-dependent stacking and significant variability in elasticity (Fig. 1b). This approach provides a versatile strategy for designing responsive MONT systems.

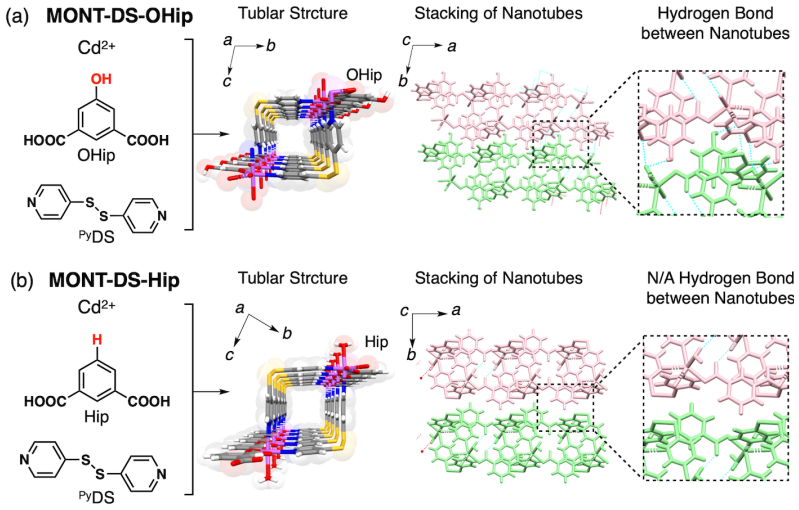

Fig. 1 The constituent components and crystal structures of (a) MOF-DS-OHip and (b) MOF-DS-Hip.

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