Hexabenzocoronene-Based Coordination Polymers

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Polycyclic aromatic hydrocarbons (PAHs), large π-conjugated systems, have been recognized as one of the key materials in the field of structural organic chemistry due to their high thermal and chemical stability, unique electronic and optical properties, *etc*. Previously, our group reported a nanographene MOF that exhibits unique crystal-to-crystal structural transitions by cooperatively rotating its large planer π-system upon guest uptake and release.[1] Among nanosized graphite segments, coronene is known as an attractive long-lived phosphorescent emitter.[2,3] Herein, we report crystalline frameworks composed of hexabenzocoronenes and characterize their photophysical behaviors.

While substitution of coronene usually affords a complicated mixture, for its extended hexa-*peri*-hexabenzocoronene, direct functionalization protocols have been recently emerged.[4] First, we synthesized hexabenzocoronene-based dicarboxylic acid ligand ($^{HBC}LH_2$).[1] The phosphorescence lifetime of $^{HBC}LH_2$ in DMF at 100 K was found to be comparable to that reported for unmodified coronene (τ_{phos} ~ 6 s), and long-lasting afterglow was observed. Besides, while bulk solid $^{HBC}LH_2$ doesn't show visible emission after stopping the photoexcitation, the MOF powder comprising $^{HBC}LH_2$ maintains the afterglow behavior, suggesting the HBC units are well-dispersed and their molecular motion is suppressed in the crystalline framework. We also report an HBC-based tricarboxylic acid ligand ($^{HBC}LH_3$) and discuss the photophysical properties in detail.

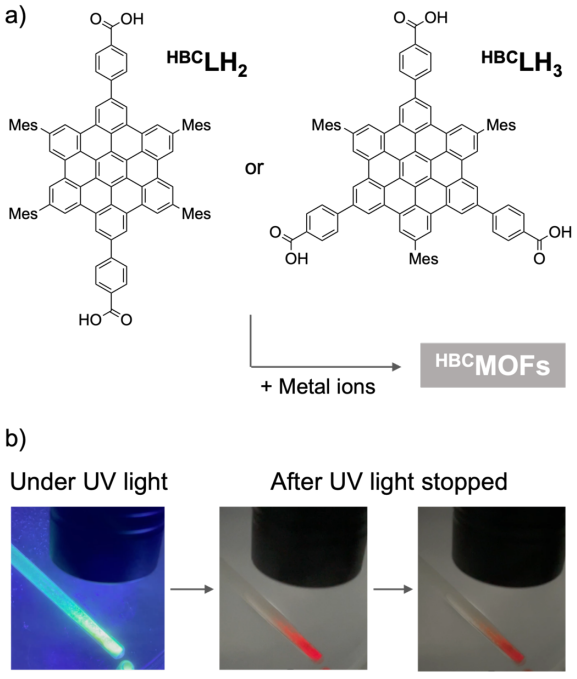

Fig. (a) Chemical structure of HBC ligands for coordination polymers. (b) Afterglow from MOF crystals composed of $^{HBC}LH_2$ at 77 K.

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