Poster Presentation

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Binder-modulated Morphology and Photo-responsive White-light-emission in MOC-derived Hydrogel

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Charge-assisted hydrogen bonds (CAHBs) is a type of non-covalent interaction(X-H(+)•••Y(-)) that play important role in the structure-property correlation of bio-macromolecules and in various biological molecular recognition processes.1 CAHB is also widely employed in the construction of discrete organic cages, extended crystalline metal-organic architectures and soft supramolecular gels. The reason behind such versatility of CAHB is essentially the intrinsic strength (stronger than neutral X-H•••Y bond) and directionality that results in wide range of materials with array of exciting and complementary properties. In this regard, CAHB driven self-assembly of predesigned metal-organic cage, into soft supramolecular hydrogel is unprecedented. Recently, a new class of metallogels (PolyMOC gels), consists of metal-organic cages as junction between the polymeric ligands, have been developed which exhibit higher branch functionality (f) and enhanced mechanical property compared to other conventional metallogels.2,3 Although this approach is inspiring, attempts to derive hydrogels based on supramolecular self-assembly of metal-organic cages in presence of different molecular binder have not been documented before. Herein, we report synthesis of a new supramolecular porous framework, {(Me2NH2)12[Ga8(ImDC)12].24H2O} (1), consists of anionic metal-organic cubes [Ga8(ImDC)12]12- (Ga-MOC) that are connected to each other through CAHB interaction with Me2NH2+ (DMA) cations. Though 1 is highly soluble in water, the discrete Ga-MOC cubes having 24 peripheral carboxylate oxygens, remain unbroken in solution. This particular phenomenon provides us an opportunity to crosslink the Ga-MOCs with a wide range of molecular binders that could lead to the formation of ion-pair-assisted hydrogels. Moreover, the nano or mesoscale morphologies and properties of the resulting hydrogels could be tuned by deliberately choosing different kinds of molecular binders. When ammonium cation (NH4+) is used as binder, self-assembly of Ga-MOC results in hydrogel with tubular nanostructures which has been exploited for column chromatographic separation of oppositely charged species. Furthermore, self-assembly of Ga-MOC is also achieved with other molecular binders including N-(2-aminoethyl)-1,3-propanediamine, guanidine hydrochloride, and β-alanine that generates different nanostructures (bouquet, sheet, cube). We also extend the concept to form stimuli responsive luminescent hydrogel by rationally designing an AIE-active chromophoric molecular binder containing tetraphenylethene (TPE) core. The characteristic photocyclization behaviour of TPE renders the hydrogel highly photoresponsive. Such photoresponsive behaviour of the hydrogel is explored for tuning the excitation energy transfer from TPE segment to encapsulated acceptor dye and finally a pure white-light-emitting hydrogel with Commission Internationale de L'Eclairage (CIE) coordinates of (0.33, 0.32) is achieved.

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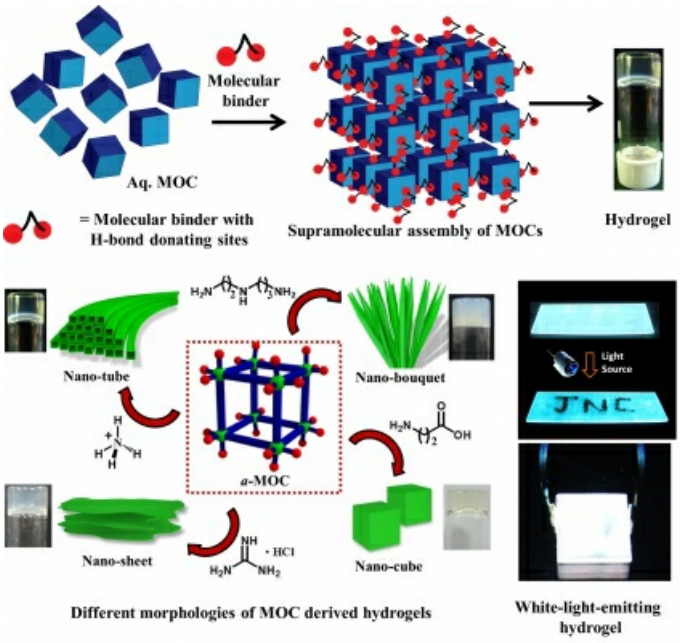

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