Molecular Fullerenes Encapsulated in Metal-Organic Frameworks

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Fullerenes have many potential applications in various fields such as biomedicine, organic photovoltaics, molecular device, *et al.* However, it is still meaningful to explore more functional fullerene materials due to their special structures and attractive properties. In recent years, metal-organic frameworks (MOFs) have gained particular interest due to their potential applications in gas storage, catalysis, sensing, electronics, biomedicine, and so on. Considering the porous character of MOFs, it is fascinating to encapsulate molecular fullerenes into MOF pores and to construct new complex materials with unique properties and applications. In this minireview, we discuss the up-to-date study progress for the fullerene@MOF materials. We introduce firstly the preparation strategies, and then summarize the applications of these fullerene@MOF materials.

Keywords fullerenes, metal-organic frameworks, host-guest interaction, complex materials

Introduction

Fullerene, as the only one allotrope of elemental carbon with molecular form, has raised great attention since its discovery in 1985.^[1] One of the extraordinary characteristics of fullerenes is their aromatic structure, which endows them with unique photoelectrical properties and triggers many inspirations to investigate their applications.^[2-7] For example, fullerenes have been widely used as electron acceptors in polymeric solar cells (PSCs) due to their strong electron-accepting ability.^[7-9] Another unique structural character of fullerenes is their hollow interior, which can entrap atoms into the carbon cage to form endohedral fullerenes.^[10-12] The intramolecular charge transfer from entrapped species to the outer fullerene cage expands greatly the properties of fullerenes and their applications.^[13-16] In addition, fullerenes can be easily chemically functionalized,^[17-20] which could modulate their properties so as to promote their potential applications.^[2,16,21] Moreover, as spherical molecule, fullerenes have been studied as guest to construct supramolecular systems with many interesting electronic properties.^[22-25] In confined space, fullerenes exhibit different physical and chemical properties due to the host-guest interaction.^[26,27]

Recently, metal-organic frameworks (MOFs) attract great concern due to their porosity, high surface area, and so on.^[28-30] MOFs are crystalline materials consisting of periodically coordinated metal centers and organic ligands.^[30-33] MOFs have aromatic frameworks and hydrophobic pores, which enable them to accommodate many aromatic molecules through strong host-guest interactions.^[34-36] Moreover, the resulting assemblies could exhibit unique properties due to the confined effect on guest molecules.^[37] These studies inspire many interesting works with respect to the incorporation of fullerenes into MOFs.^[34,38-40] Considering the porous character of MOFs, it is fascinating to encapsulate molecular fullerenes into MOF pores and to construct new complex materials with unique properties and applications. Herein, we provide an overview of

preparation and applications for these fullerene@MOF materials.

The encapsulation of fullerenes into MOFs

Molecular fullerenes can be easily encapsulated into MOFs via the host-guest interaction originated from the aromatic and hydrophobic structures of them.^[22,31,39-49] In general, fullerenes can be encapsulated into MOFs through *in-situ* synthesis and post-synthesis method.

In 2004, Yaghi and co-workers^[31] designed and synthesized $\text{Zn}_4\text{O}(1,3,5\text{-benzenetribenzoate})_2$, a metal-organic framework with extremely high surface area estimated at $4500 \text{ m}^2 \cdot \text{g}^{-1}$. The MOF-177 with ordered structure has extra-large pores capable of binding polycyclic organic guest molecules. Especially, they reported the encapsulation of C_{60} into this MOF-177. The C_{60} @MOF-177 complex was synthesized by absorbing method, namely the post-synthesis method. After absorbing C_{60} , the crystals' shape and integrity of MOF-177 still remained intact, but the color became red. Moreover, Raman shifts of the complex compared with spectra of bulk C_{60} and with that of evacuated MOF-177 illustrated the presence of C_{60} in the pores of MOF-177 (Figure 1).

In 2010, Makoto Fujita *et al.*^[40] reported a crystalline coordination network generated from an infinite array of octahedral M_6L_4 cage subunits (M = metal, L = ligand). This coordination network is a crystalline molecular sponge engineered on the molecular level and retains similar guest recognition properties to those found in solution. The void spaces define alternating M_{12}L_8 and $\text{M}_{12}\text{L}_{24}$ cuboctahedral molecular cages and these large cages absorb up to 35 weight percent of C_{60} or C_{70} by simply soaking the crystals in a toluene solution of the fullerene (Figure 2). When the crystals are immersed in fullerene mixtures, C_{70} is preferentially absorbed.

In 2017, Wolfgang Brenner and co-workers^[44] reported the self-assembly of 4-fold-symmetric porphyrins with Fe^{II} or Zn^{II} , giving a cubic $\text{M}^{\text{II}}_8\text{L}_6$ cage framework with electron-deficient

Figure 1 (a) The structure of MOF-177 projected down [001]. ZnO₄ tetrahedra are shown in blue and O and C atoms are shown as red and black spheres, respectively. (b) A red crystal of C₆₀@MOF-177, and comparison of Raman spectra of a sliced crystal (D) and a whole crystal (C) with bulk C₆₀ (A) and an evacuated MOF (B).^[31]

Figure 2 Photographs of MOF generated from an infinite array of octahedral M₆L₄ cage subunits before (a) and after (b) inclusion of fullerene C₆₀. (c) An optimized model of C₆₀ in the cuboctahedral voids of network.^[40]

walls. This cage can encapsulate C₆₀-indene or C₆₀-anthracene bisadducts selectively other than un-functionalized fullerenes and monoadducts. In addition, The Fe^{II}₈L₆ cage can enable the reaction of C₆₀ and anthracene to yield the bisadducts selectively. These findings have relevance in the context of polymer solar cells.

In 2017, Escudero-Adán and co-workers^[46] reported two new supramolecular assemblies (**2** & **3**) using adequate Zn(II)-bisporphyrin cage, perylene bisimide and fullerene through *in-situ* synthesis method. According to single-crystal X-ray diffraction studies, the obtained MOF compounds consist of infinite 1D polymeric chain that aggregates to form 2D sheets in two directions, which in turn pack on top of another to generate the final 3D architecture. This investigation offered a new method of constructing fullerene@MOF complex, which may possess excellent photochemical and conducting properties in the solid state.

To realize the encapsulation of fullerenes within MOFs directly, other feasible ways have been developed.^[50,51] In 2013, Peng and co-workers^[52] designed and synthesized the first fullerene-linked 2D metal-organic framework based on a new hexakis-fullerene derivative possessing two pairs of phenyl pyridine groups. The framework contains two types of pores (I, II), non-coordinated hexakis-fullerene molecules serve as pillars between the 2D MOF layers, and they are located over the centers of two type I pores from adjacent layers (Figure 3). The results offered inspirations to build 3D MOF by connecting metal centers of the 2D fullerene layers.

Figure 3 2D layer of fullerene-linked 2D metal-organic framework viewed along the *b*-axis (H omitted for clarity). Cd gold, N blue, O red, C black.^[46]

In 2016, Williams and co-workers^[53] reported a crystalline metal-donor-fullerene framework, in which control of the donor-fullerene mutual orientation was achieved through metal coordination. The structure of fullerene-based acceptor, BPCF, was confirmed by the single-crystal X-ray Diffraction. The acquired PL data and theoretical calculations of this framework illustrated the specific photophysics of the prepared fullerene donor-acceptor scaffold.

In 2016, Andreas Kraft and co-workers^[54] designed and synthesized the first three-dimensional metal-fullerene frameworks MFF-1 and MFF-2 utilizing icosahedral hexakis adducts C₂ and C₃ as do-decatopic organic connectivity centers for MOF synthesis. The dodecatopic building blocks as a novel highly functionalized organic scaffold with a defined spatial arrangement of the peripheral reactive sites could be capable of forming densely cross-linked networks in the solid state.

Potential applications of the assemblies of fullerenes and MOFs

The encapsulation of molecular fullerenes into metal-organic frameworks *via* host-guest interaction could improve and expand the applications of fullerenes and MOFs greatly. In general, the encapsulation of molecular fullerenes can promote the applications of fullerenes or MOFs in magnetic, catalysis, gas storage, and so on.

Several works have focused on their applications in gas storage and separation.^[55] In 2009, Thornton and co-workers^[56] calculated the magnesium decorated fullerenes within metal-organic frameworks for storage hydrogen and methane using a new approach. Encapsulation of magnesium-decorated Mg₁₀C₆₀ fullerenes within MOF pores, denoted as Mg-C₆₀@MOF, endows exposed metal sites with high heats of gas adsorption into intimate contact with large surface area MOF structures. As a result, the capacity was found to increase despite an apparent loss of free volume derived from pore filling by fullerenes. In 2011, Rao and co-workers^[57] demonstrated theoretically that the hydrogen storage capacity is improved to be 6.3 wt% and 42 g·L⁻¹ at 100 bar and 243 K by the impregnation Li-coated C₆₀ in Li-decorated IRMOF-10. In addition, the gravimetric and volumetric hydrogen uptakes reach the 2015 DOE target at near ambient conditions. This strategy can be utilized with diverse buckyballs in other porous materials for enhancing hydrogen storage capacity.

In 2016, Yuan and co-workers^[38] prepared a series of fullerene-based porous aromatic frameworks (PAFs) and measured their adsorption capacity for H₂ and CO₂. The fullerene-based PAFs not only extend the surface area from C₆₀ molecules, but also keep their affinity to gases and they exhibit a good adsorption capacity for H₂ and CO₂, making them promising in gas separation and purification. These results

show that encapsulation of fullerenes into MOFs could improve the performance of MOFs in gas storage and separation.

The incorporation of fullerenes in MOFs has also potential applications in other fields. In 2011, Yang and co-workers^[42] reported the first example of the utilization of MOFs as the stationary phase for HPLC separation of fullerenes. MIL-101(Cr) has high surface area, large windows, mesoporous pores, and excellent chemical and solvents stability. As a result, MIL-101(Cr) showed very attractive for specific recognition and separation of fullerenes through adsorption-desorption method (Figure 4).

Figure 4 HPLC separation of C₆₀, C₇₀, C₇₆, and C₇₈ on a MIL-101(Cr) packed column (5 cm long × 4.6 mm i.d.) using CH₂Cl₂/CH₃CN (98 : 2) as the mobile phase at a flow rate of 1 mL·min⁻¹ with UV detection at 340 nm.^[42]

In 2017, Rizzuto and Nitschke^[58] reported a method for modulating the cooperativity of binding of a new Co^{II}₁₂L₆ cage assembly by the fullerene-mediated transformation of its stereochemistry. Upon binding C₆₀ or C₇₀, the stereochemistries of the capsule and cage morphologies have changed, resulting in the regulation of cooperative intermolecular interactions. The stereochemical transformations within this system can regulate long-range interactions between guests, modulating the specific modes and degrees of cooperativity (either positive or negative) expressed around the periphery of the cages.

In the following study in 2017, Nitschke and co-workers^[59] constructed a series of octanuclear supramolecular cages utilizing 5,10,15,20-tetrakis(4-aminophenyl)porphyrin or its zinc(II) complex, 1*H*-4-imidazolecarbaldehyde, and either zinc(II) or iron(II) salts. The coordination cages derived from iron(II) salts in the high-spin state at room temperature manifested spin- crossover in solution at low temperatures. After encapsulation of C₇₀, the spin-transition temperature *T*_{1/2} was lowered by 20 K and a remarkable high-spin-stabilizing effect was observed.

In 2016, Cao and co-workers^[60] studied the electron spin properties of a fulleropyrrolidine nitroxide radical incarcerated in the pores of MOF-177 and MIL-53. They found that the spatial confinement effect and intramolecular interactions induce distinctive spin dynamics in these two solid-state spin systems.

In 2017, Howarth and co-workers^[61] reported the incorporation of fullerene-based photosensitizer (PCBA) into a Zr₆-based MOF (NU-1000) *via* post-synthesis method. In this system, NU-1000 acts as an active platform for chromophore incorporation comparing with another Zr₆-based MOF, NU-1200. Both the organic linkers in the MOF and the incorporated fullerene-based photosensitizer contribute to the overall generation of singlet oxygen from the material upon UV irradiation, exhibiting selective oxidation for sulfur mustard (Figure 5).

Figure 5 Selective oxidation of sulfur mustard to bis(2-chloroethyl)sulfoxide using singlet oxygen produced by the photosensitizers NU-1000 and NU-1000-PCBA.^[61]

In 2017, Nitschke and co-workers^[62] reported the synthesis of metal-organic cage frameworks based on emissive BODIPY chromophores and the photophysical properties of these cages and their fullerene-encapsulated adducts (Figure 6). When cages were formed, the charge-transfer character exhibited by the bis(aminophenyl)-BODIPY subcomponents disappeared and strong excitonic interactions were observed, derived from the electronic delocalization through the metal centers. Upon the cages loaded with C₆₀ or C₇₀ fullerenes, the ultrafast host-to-guest electron transfer competed with the excitonic interactions, changing the photophysical behavior of the final complex.

Figure 6 Metal-organic cage frameworks based on emissive BODIPY chromophores and the photophysical properties of their fullerene-encapsulated complexes.^[62]

Recently, our group reported the magnetic properties of endohedral fullerenes within metal-organic frameworks. In 2015, Feng and co-workers^[63] reported a solid spin system composed of paramagnetic metallofullerene Y₂@C₇₉N and MOF-177. The incorporated Y₂@C₇₉N in MOF-177 show axisymmetric paramagnetic property, making it potential quantum bits for quantum information science and data storage. Later in 2018, Zhao and co-workers^[64] further reported the orientation-related paramagnetic properties of Y₂@C₇₉N in MOF-177 by the angular-dependent EPR spectroscopy. The results showed that the partially oriented molecules of Y₂@C₇₉N in MOF-177 caused the orientation-related EPR splitting. In addition, the N-effect of Y₂@C₇₉N can act as an anchor to build arrayed spin within the MOF matrix. In 2016, Li and co-workers^[65] found the controllable quantum tunneling of magnetism (QTM) for DySc₂N@C₈₀ by encapsulating it into MOF-177, which can expand its potential applications in high-density storage devices. In 2018, Meng and co-workers^[66] disclosed that the EPR

signals of $\text{Sc}_3\text{C}_2@\text{C}_{80}$ within MOF-177 can change under different temperatures and pressures and exhibit good reversibility under cycling temperature and pressure (Figure 7). These results revealed that the $\text{Sc}_3\text{C}_2@\text{C}_{80}$ can act as a paramagnetic molecular probe within MOF and other media.

Figure 7 Implanted paramagnetic $\text{Sc}_3\text{C}_2@\text{C}_{80}$ probe within MOF-177 under different temperatures and pressures.^[66]

Conclusions

The encapsulation of molecular fullerenes into MOFs and their applications up to date have been discussed. The inclusions of fullerenes were mainly realized through *in-situ* synthesis and post-synthesis methods. In addition, fullerenes can be chemically derived as ligands to form MOFs through metal coordination. All of the encapsulations of fullerenes into MOFs can improve the properties of fullerenes greatly as well as MOFs. On the one hand, the encapsulated fullerenes could improve the performance of MOFs in gas storage and separation. On the other hand, the inclusion of molecular fullerenes can promote the applications of fullerenes or MOFs in magnetic, catalysis, and so on. With the considerable advance in the field of fullerenes and MOFs, more solutions to encapsulate fullerenes into MOFs would be achieved, paving the way for the practical application of fullerenes and MOFs in more fields.

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