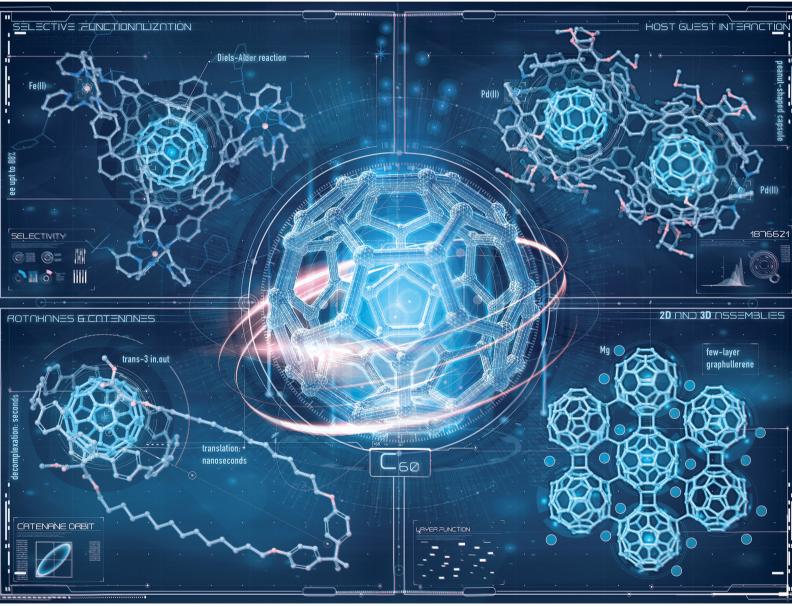
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Recent advances in supramolecular fullerene chemistry†

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Fullerene chemistry has come a long way since 1990, when the first bulk production of C_{60} was reported. In the past decade, progress in supramolecular chemistry has opened some remarkable and previously unexpected opportunities regarding the selective (multiple) functionalization of fullerenes and their (self)assembly into larger structures and frameworks. The purpose of this review article is to provide a comprehensive overview of these recent developments. We describe how macrocycles and cages that bind strongly to C_{60} can be used to block undesired addition patterns and thus allow the selective preparation of single-isomer addition products. We also discuss how the emergence of highly shapepersistent macrocycles has opened opportunities for the study of photoactive fullerene dyads and triads as well as the preparation of mechanically interlocked compounds. The preparation of two- or threedimensional fullerene materials is another research area that has seen remarkable progress over the past few years. Due to the rapidly decreasing price of C_{60} and C_{70} , we believe that these achievements will translate into all fields where fullerenes have traditionally (third-generation solar cells) and more recently been applied (catalysis, spintronics).

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1. Introduction

Carbon allotropes come in many different forms and flavours (Fig. 1), all of which have distinct properties that are exploited in diverse functional organic materials. Diamond and graphite occur naturally and are both polymeric, but exhibit very different mechanical and electronic properties mainly as a



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Diamond Graphite y-Graphyne Carbon nanotube Cyclocarbon

C_n fullerenes

Endohedral metallofullerene Heterofullerene

Fig. 1 Selected examples for carbon allotropes (top row): diamond, graphite, γ -graphyne, 4 carbon nanotube and cyclo[18]carbon. 6 Selected examples for fullerenes C_n . $^{12.13}$ Grey box: the most abundant endohedral metallofullerene $Sc_3N \subset I_h - C_{80}$ and heterofullerene $(C_{59}N)_2$ as examples for relevant compounds beyond carbon allotropes. $^{10.14}$

result of $\operatorname{sp}^3 vs. \operatorname{sp}^2$ hybridization of carbon. One of the unique aspects of graphene is that it can be made by exfoliation from natural graphite² and by chemical bottom-up synthesis (*e.g.* by chemical vapour deposition).³ Synthetic carbon allotropes have seen important new arrivals such as γ -graphyne, which was prepared in bulk thanks to dynamic covalent synthesis,⁴ and a discrete, sp-hybridized member of the cyclocarbon family (cyclo[18]carbon, C18),⁵ which so far is only accessible *via* on-surface synthesis.⁶ Fullerenes⁷ and carbon nanotubes⁸ can be prepared in bulk and comprise sp^2 -hybridized carbon frameworks as well as a significant degree of curvature that influences reactivity, optoelectronic properties and non-covalent interactions. While C_{60} is the most abundant member of the fullerene family, higher fullerenes,⁹ endohedral metallofullerenes (EMFs)¹⁰

D_{5h}-C₇₀

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Grant ("SUPRANET") and has received the Cram-Lehn-Pedersen Prize (2022) and the Prix Forcheurs Jean-Marie Lehn (2023).

and heterofullerenes¹¹ have unique properties due to their lower symmetry, anisotropic curvature and the incorporation of elements other than carbon (Fig. 1, grey box).

 $(C_{59}N)_2$

Sc3NCIn-Can

Fullerenes are engaged in a long-standing relationship with supramolecular chemistry. Concerning higher fullerenes and EMFs, this relationship is built on necessity, because their isolation from complex soot mixtures is far from trivial and requires specialized HPLC columns or innovative uses of hostguest chemistry. What makes C60 special as a supramolecular guest is its high symmetry (I_h) , relatively large size, complete rigidity, well-defined curvature and lack of heteroatoms. While its high symmetry and large size implies that sometimes C₆₀ is used as a "guest of last resort" (e.g. in a relatively large selfassembled cage), we found that the majority of recent studies goes beyond proof-of-principle science. In this article, we therefore aim to put emphasis on advances showing exceptional originality either from the perspective of fullerene or supramolecular chemistry (or ideally: both). Because we focus mainly on advances from the past decade and we do not discuss all aspects of the field in equal detail, we wish to direct the reader to relevant work here. A book entitled "Supramolecular Chemistry of Fullerenes and Carbon Nanotubes" (edited by Martin and Nierengarten) comprises the state-of-the-art until 2012. 15 Older review articles include overviews on metalloporphyrin hosts (2007),16 curved fullerene receptors (2008),17 open-cage fullerenes (2010),18 fullerene assemblies (2010)19 and endohedral fullerenes (2013). 10 Among the more recent review articles, several rather narrow articles focus on methods for fullerene binding/release (2016), ²⁰ fullerene purification (2017, 2020)^{21,22} and selective functionalization (2020, 2021).22,23

It is our hope that this review article will lend further momentum to the promising research directions described herein. For the first time since 1990, two dreams of fullerene

chemists have come within reach: (i) the purification of fullerene mixtures (incl. EMFs) without use of chromatography and (ii) the selective synthesis of single-isomer addition products thanks to the use of supramolecular templates. Due to the rapidly decreasing price of C₆₀ (currently as low as 20 USD per gram) and C70, further progress towards these aims could make a real difference in key 21st century technologies, including photovoltaics, photocatalysis and quantum information processing.24,25

2. Selective fullerene functionalization

Exploiting the properties of the most abundant fullerenes C₆₀ and C₇₀ in solution-processed devices typically requires their covalent functionalization. Attaching one or two substituents to the fullerene core increases solubility, lowers the LUMO level, which is important for any application relying on electron transport, and modulates the morphology of solid-state materials. In this section, we will provide a brief introduction into unique challenges associated with the selective (multiple) functionalization of fullerenes and discuss supramolecular approaches towards meeting these challenges.

Phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) are typical examples of fullerene mono-adducts acting as electron acceptors or electron transport materials in bulk heterojunction or perovskite solar cells, respectively.26,27 Fig. 2 gives an overview on the most common methods used for the functionalization of C₆₀, such as the Bingel(-Hirsch) reaction, the Prato reaction, the Diels-Alder reaction and trifluoromethylation.²⁸ C₇₀ has a lower symmetry

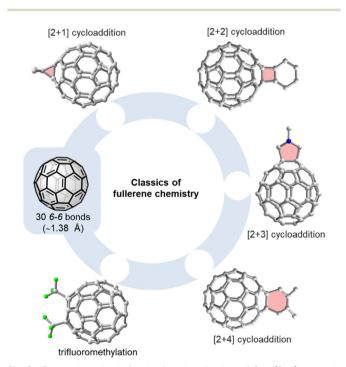


Fig. 2 Selected methods for the functionalization of C_{60} : [2+1] cycloaddition (e.g. Bingel–Hirsch reaction^{29,30}), [2+2] cycloaddition,^{31,32} [2+3] cycoaddition (e.g. Prato reaction³³), or trifluoromethylation.³⁴

than C₆₀ and therefore has four different types of reactive sites $(\alpha$ -, β -, γ -, and δ -site, see Fig. 4). This implies that even monoadducts of C70 (such as the above mentioned PC71BM) are obtained as mixture of (regio)isomers that are hard to separate. With spherical C₆₀, complex isomer mixtures are obtained whenever 2-5 groups are added to the fullerene core.

Recent work by diverse groups in materials science established that significantly higher device efficiencies can be obtained when using isomerically pure fullerenes rather than mixtures of regioisomers, diastereomers or racemates. 23,35-37 The classic approach to address the regioisomer problem in C₆₀ bis-addition is the use of a tether. Pioneered by Diederich, this method has the disadvantage that the tether remains attached to the fullerene, thus restricting the scope of products, unless degradable linkers are used, such as the dialkoxysilanes recently employed by Nierengarten. 38-40 Tethers can also be stimuli-responsive, 41 and their regioisomer-directing effect can be enhanced by a non-covalent interaction, as in the example by Hirsch shown in Fig. 3a.42

While Kräutler's highly selective synthesis of a trans-1 bisadduct (96%) in the solid-state can be regarded as a supramolecular strategy, 43 it took until 2016 for researchers to strategically employ non-covalent interactions for addressing the regioisomer problem. Torres and coworkers relied on strong intermolecular π - π interactions between two porphyrins to achieve a high regioselectivity for cis-substituted C₆₀ bisadducts in a Prato reaction.44 In 2018, our group utilized [10]CPP as a supramolecular template to synthesize [2]rotaxanes comprising a central fullerene bis-adduct as binding site for the CPP ring. The regioselectivity was not perfect, with the trans-1, trans-2 and trans-3 bis-adducts formed in 4%, 43% and 52% relative yield, respectively (Fig. 3b). 45 Beuerle and Ribas independently developed the "supramolecular shadow mask" strategy that is particularly powerful, wherever a multi-addition product is desired that matches the symmetry and number of "windows" in the cage (e.g. tris-addition and trans-3 relationship between substituents in the case of the Beuerle cage shown in Fig. 3c). However, when a bis-adduct is desired, supramolecular shadow masks either give a suboptimal reaction outcome (Fig. 3c) or the reaction progress has to be stopped at precisely the right time.22 By combining our [10]CPP strategy and Ribas' nanocapsule approach, we were able to achieve exclusive trans-3 regioselectivity for the Bingel bis-addition reaction to C₆₀. 46 This three-shell supramolecular mask strategy (Fig. 3d) required the design of an extended Pdbased cage to allow the encapsulation of the [10]CPP⊃C₆₀ complex. Interestingly, the trans-3 C₆₀ bis-adduct is symmetrymismatched with the outer shell (three-fold vs. four-fold symmetry), and scope studies revealed that Rebek's 55% rule⁴⁷ can be used to rationalize and predict the limitations of the approach.

Because C₇₀ has the shape of an American football, multiadducts to this second most abundant fullerene present a particular challenge. 48-50 Due to the decreased symmetry of the molecule eight distinct types of C-C double bonds (6,6 and 5,6), such that even mono-addition reactions give rise to isomer

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a) m-m interaction assistance

Continuous Cls-1

Cis-2

Cis-3

Cis-3

Frans-2

Irans-2

Irans-2

Irans-1

Three-shell supramolecular cage template

Fig. 3 Selected methods for regioselective twofold addition reactions to C_{60} . (a) $\pi-\pi$ interaction assistance. (b) Supramolecular nanohoop template. (c) Supramolecular cage template, 3 equiv. *N*-methylglycine was used. (d) Three-shell supramolecular mask strategy.

mixtures. While supramolecular approaches for the selective mono-functionalization of C_{70} are still elusive, Echegoyen and coworkers achieved an impressive yield of 68% for the C_{70} bisaddition 1 and obtained only one regioisomer using Kräutler's solvent-free Diels–Alder reaction process (Fig. 4). The researchers found that the C_{70} bis-adducts can be converted into the " α "-mono-adduct 2 at a temperature of 190 °C, which represents an indirect solution to the mono-addition challenge. Moreover, both mono- and bis-adducts can be reverted to pristine C_{70} at 250 °C. This anthracene addition strategy may prove beneficial as a way of protecting groups to guide multiple fullerene additions.⁵¹

In fullerene tris- or higher addition reactions it is notoriously difficult to achieve itero- and regioselectivity. So far, only a few successful strategies have been developed based on

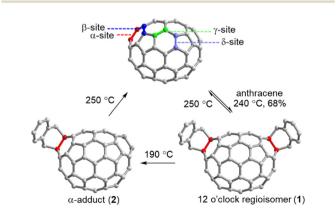


Fig. 4 Four distinct types of double bonds in C_{70} and dynamic multi-additions of C_{70} resulting from Diels-Alder reactions in molten anthracene.

privileged addition patterns of C60 encapsulated inside supramolecular masks. For instance, Beuerle and coworkers synthesized a trigonal bipyramidal covalent organic cage and observed strong affinity for $C_{60/70}$ ($K_a > 10^5 \text{ M}^{-1}$) in CHCl₃. Thanks to the threefold symmetry of the cage (Fig. 3c), to the authors were able to obtain the trans-3-trans-3-trans-3 C₆₀ Prato tris-adduct in an impressive relative yield of 25%.52 In a Pd-based nanocapsule shadow mask, Ribas and coworkers reported the first synthesis of an e,e,e,e-tetrakis-C₆₀ Bingel adduct in quantitative yield (Fig. 5).53 The nanocapsule's four perpendicular "windows" led to the observed regioselectivity, and the authors were also able to achieve the selective and quantitative formation of exclusively tetrakis-adducts using a biphasic protocol and catalytic amounts of the nanocapsule. More recently, Torres, Torre and coworkers realized the efficient Diels-Alder reaction between C60 and anthracene in water by using a metallo-organic Pd(II)-subphthalocyanine (SubPc) capsule as the catalytic host.54 In summary, supramolecular masks represent a promising new approach to achieve selective fullerene addition reactions, but atom economy is an obvious problem of this approach, because the masks typically have a higher molecular weight than the encapsulated fullerene and/ or contain precious metals. It is therefore noteworthy that the masks can be recovered, and an important next goal is to develop methods that only require catalytic quantities in homogeneous solution.

Because most fullerene multi-adducts are chiral, achieving enantioselectivity is a formidable challenge whose importance has been underscored by recent work by Fuchter demonstrating that homochiral fullerenes outperform the corresponding racemates as electron transport layers in perovskite solar cells.³⁷

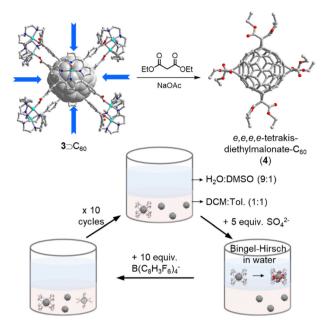


Fig. 5 Biphasic catalytic protocol for the synthesis of e,e,e,e-tetrakisdiethylmalonate-C₆₀ adduct **4** by using a sophisticated Pd-based nanocapsule 3 as the mask.

While this challenge has been approached previously using chiral reagents/catalysts,55 one recent report by Nitschke and coworkers demonstrated the first supramolecular approach enabling the enantioselective functionalization of fullerenes (Fig. 6).⁵⁶ The authors utilized an enantiopure metal-organic cage (5) that was self-assembled from Fe(NTf₂)₂, chiral 2-formylpyridine, and 1,5-anthracene-based dianiline. The cage was shown to react with encapsulated C60 to produce a highly diastereoselective e,e,e-tris adduct (6) via a chemo-, regio-,

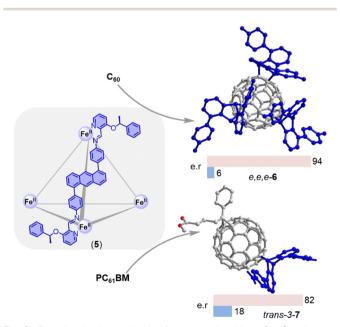


Fig. 6 Enantioselective synthesis of an e,e,e-tris adduct-C₆₀ 6 and trans-3-bisadduct-PC₆₁BM 7 through stereochemical information transfer from a chiral self-assembled cage 5

and enantio-selective Diels-Alder cycloaddition with the anthracene component of the cage. Encouraged by the successful diastereoselective reaction observed with C₆₀, the researchers investigated the reaction with PC61BM. They found that PC61BM reacted with only one of the six anthracene components on the opposite hemisphere to the original substituent, resulting in an adduct (7) that exhibited excellent diastereoselectivity for trans-3 addition. The chiral adducts produced by this method were released from the cage by adding excess tris(2-aminoethyl)amine, which led to disintegration of the cage. The chiroptical properties of these adducts were also investigated, which make them promising materials for chiral organic electronics.⁵⁷ While these findings represent a significant advance in the field of enantioselective fullerene functionalization, a method that facilitates enantioselective addition reactions with external reagents (rather than with components of the cage) would be the next logical step.

3. Supramolecular fullerene dyads and triads

Electrochemical experiments show that C₆₀ exhibits six equidistant reduction waves, with the lowest reduction potential at ca. -0.44 V (vs. SCE). The unique spherical and rigid framework of sp² carbon atoms in C₆₀ offers exceptional properties as an electron acceptor. 58,59 It has been established that C₆₀ derivatives possess relatively small reorganization energies during an electron transfer process, which makes them ideal electron acceptors for energy conversion and storage applications.⁶⁰ In this section, we will review recent work on the electronaccepting properties of fullerenes in supramolecular dyads and triads with electron donors.

To mimic the multicomponent photosynthesis process, various covalently/non-covalently bridged C60-based donoracceptor (D-A) dyads have been developed since the first pioneering work revealed that charge-recombination is considerably slower than charge-separation in porphyrin-fullerene dyads. 32,61 The design of efficient photoinduced electron transfer systems depends on several factors, including aromaticity, planarity, and energetics of the electron donor, the distance and orientation between the donor and acceptor, and the nature of the bridging unit. Numerous C₆₀-based D-A systems, containing donors such as porphyrin, ferrocene, platinum complex, tetrathiafulvalene (TTF), boron dipyrromethene (BODIPY), oligothiophene, phenothiazine or phthalocyanine have been studied to investigate the photoinduced charge separation and solar cell characteristics of these dyads. 62-65

Although covalently bridged D-A systems based on fullerenes have shown promising results, non-covalently bridged D-A systems resemble more closely natural photosynthetic systems, particularly in respect to the bridge between donor and acceptor. A wide range of non-covalent interactions (e.g. π - π , electrostatic, metal-ligand, H bonds) have been employed for the construction of D-A assemblies.⁶⁶ [10]Cycloparaphenylene ([10]CPP) exhibits a strong supramolecular association **Review Article**

electron π interactions 8⊃fullerene electron

Fig. 7 (a) Efficient electron transfer in modular $\mathbf{8} \supset$ fullerene complexes. (b) Selected examples of hydrogen bond bridged C_{60} -based D-A dyads ($\mathbf{9}$ and 10) and corresponding charge transfer process. (c) Supramolecular complexation between ditopic porphyrin receptor 11 and fullerene derivative 12.

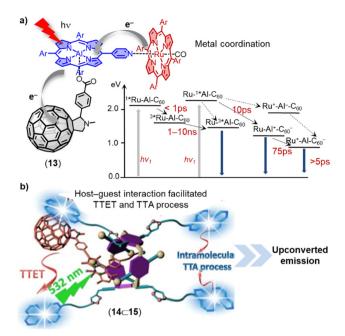
transfer

with fullerenes due to concave–convex π – π interactions.⁶⁷ Our group has used [10]CPP as a supramolecular junction to create modular dyads between zinc porphyrin and five representative fullerenes (Fig. 7a).⁶⁸ Fluorescence titrations revealed that all fullerene derivatives have a remarkably high association constant with 8 ($K_a > 10^5 \,\mathrm{M}^{-1}$). Time-resolved transient absorption studies showed efficient charge separation and recombination across the non-covalent [10]CPP junction. This efficient supramolecular connection allowed studying the electron-accepting properties of the rather unstable dimer $(C_{60})_2$, and interesting stoichiometry and concentration dependent effects on charge recombination were observed. For example, desymmetrization of the C₆₀ moieties resulted in two distinct charge recombination processes in the 1:1 complex. While only one electronrecombination process was observed in the more symmetric 2:1 complex, a lifetime of up to 542 ns was observed, which is among the longest-lived charge-separated states in porphyrinfullerene containing D-A systems found to date.

Hydrogen bonding-based noncovalent interactions have been widely employed to control the electronic coupling between D-A dyads. For instance, Hirsch and coworkers have reported the assembly of a C60-based Hamilton receptor and metalloporphyrin-based cyanuric acid motifs.⁶⁹ Sessler and coworkers have reported zinc porphyrin-appended cytidine and fullerene-appended guanosine (9).⁷⁰ In these supramolecular wires, the photoinduced charge transfer processes have occurred exclusively through the hydrogen bonding bridges. The attenuation factor (β) is a key parameter of a molecular bridge that determines the magnitude of the electronic coupling between the redox sites and the energy of the charge transfer states localized at the two ends. Martín and colleagues have reported a series of noncovalent C60-based hybrids (10), which combine a zinc porphyrin with p-(2fulleropyrrolidinyl)benzoates of different lengths (Fig. 7b).⁷¹ The authors achieved an exceptionally small β value of ca. 0.07 Å^{-1} , benefitting from the strong supramolecular interactions in the carboxylate/amidinium salt bridge. Nierengarten and coworkers have investigated the supramolecular complexation of a C₆₀ derivative 12 (Fig. 7c) with a porphyrin dimer and a porphyrin tape (11) endowed with two crown ether rings. 72,73 Both ditopic porphyrin systems formed complexes with 1:1 and 1:2 stoichiometry and exhibit negative cooperativity, indicating a reduced binding constant for the complex of the second fullerene unit. The formation of these complexes is driven by the complementary π - π interactions and ammonium-crown ether hydrogen bonding interactions between the porphyrin tape and the C₆₀ moieties.

Hydrogen bonding & π - π interactions

The use of fullerenes and carbon nanotubes to mimic natural photosynthesis in supramolecular multicomponent D-A assemblies via metal-ligand coordination is another promising field of research.^{74,75} Porphyrins and phthalocyanines have been extensively employed as electron donors in the construction of fullerene-based dyads/triads due to their exceptional photophysical and photochemical properties, as well as their capacity to form metal-ligand coordination bonds. 76-79 For instance, Lengo and coworkers effectively fabricated a threecomponent multichromophoric assembly 13, which consists of a fullerene monoadduct, an aluminium(III)-monopyridylporphyrin, and a ruthenium(II)-tetraphenylporphyrin (Fig. 8a).80 The photophysical properties of this triad have been examined on the femtosecond-nanosecond timescale using pump-probe spectroscopy. Upon excitation of the aluminium(III)-monopyridylporphyrin, the strong emission characteristic of this moiety was guenched. The transient absorption experiments provided evidence for the occurrence of stepwise photoinduced electron and hole transfer processes, resulting in the formation of a charge-separated state between the fullerene acceptor and the ruthenium-porphyrin donor (see Fig. 8a for the Jablonski diagram). Architectures of higher complexity such as tetrads, pentads, and hexads have also shown promise for photoinduced electron-transfer processes.81-84 The non-covalent assembly between multiple



Self-assembled ruthenium(||)porphyrin-aluminium(|||)porphyrin-fullerene triad 13. Insert: Photophysical processes occurring in the triad (in CH₂Cl₂). (b) Schematic illustration of host-guest complexation facilitated triplet-triplet annihilation upconversion (TTA-UC) of 15 ⊃ 14. Adapted from ref. 88 with permission from American Chemical Society. copyright 2016.

fullerenes or chromophores is another promising approach for preparing organic photosensitizers.85-87

The process of triplet-triplet annihilation upconversion (TTA-UC) is of interest for efficiently harvesting diffuse visible/ near-IR light and achieving high upconversion quantum yields.⁸⁹ To improve TTA-UC efficiency, Yang and coworkers developed a new strategy using host-guest complexation between an alkyl nitrile chain functionalized C_{60} -BODIPY sensitizer (14) and a tetraperylene-based pillar[5]arene emitter (15) (Fig. 8b).88 This supramolecular complexation facilitated triplet-triplet energy transfer (TTET) and TTA processes between the sensitizer and emitter, resulting in a significant increase in TTA-UC intensity and a high upconversion quantum yield ($\Phi_{\rm UC}$) of up to 3.2% even at a very low emitter concentration of 6×10^{-5} M. This innovative supramolecular approach for bringing several components into spatial proximity improves TTA-UC efficiency without altering the intrinsic photophysical properties of the sensitizers and emitters.

Fullerene-based materials are being increasingly recognized for their electrophilic nature and their ability to stabilize radicals, which makes suitable C₆₀ derivatives promising in the field of (photo)catalysis. 66,90 For instance, Heredia and coworkers have synthesized a novel boron pyrrol hydrazine-C₆₀ (BOPHY-C₆₀) dyad that not only produces singlet oxygen (1O2) and superoxide radical anion (O2 • under irradiation with visible light (470 nm), but also demonstrates the ability to photoinactivate microorganisms. 91 Similarly, Martín and coworkers have employed metallo-fulleropyrrolidines as homogeneous/heterogeneous catalysts for hydrogen transfer reactions (Fig. 9a), which resulted in a quantitative yield of ketone reduction and alcohol

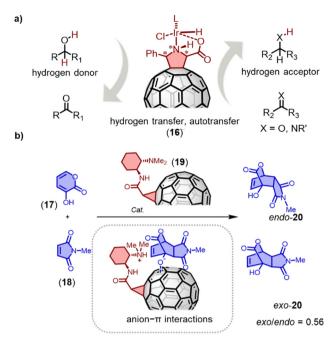


Fig. 9 (a) Transfer hydrogenation by metallo-fulleropyrrolidine 16. (b) Anionic Diels-Alder reaction of 17 and 18; insert: proposed anionic transition state for exo products on C₆₀ surfaces.

N-alkylation with only 0.5 mol% and 0.125 mol% iridiumfulleropyrrolidine catalyst 16 loading, respectively. 92 The catalyst is easily separable from the reaction mixture and has also been successfully utilized for the alkylation of aniline with aliphatic alcohols in the presence of MgSO₄. For example, benzylamine underwent quantitative alkylation with cyclohexanol using a 1.25% iridiumfulleropyrrolidine catalyst.

Anion- π catalysis involves stabilizing anionic transition states and intermediates through anion- π interactions on aromatic surfaces. 93,94 Fullerenes, which offer a highly symmetric π system devoid of heteroatoms, provide an excellent platform to investigate the importance of polarizability in anion- π catalysis, without the complications of substituents, positive quadrupole moments or inplane dipoles. 95 Matile and coworkers discovered that a fullerene mono-adduct catalyst 19 exhibited good selectivity for enolate addition and improved the exo/endo diastereoselectivity of the Diels-Alder reaction. 96 Using the anionic [4+2] cycloaddition of dienophile 18 and 3-hydroxy-2-pyrones 17 as an example, strong endo selectivity was observed. Fullerenes with flexible tethers failed to alter this intrinsic selectivity. The best exo-20/endo-20 ratio of 0.56 with 55% ee was achieved using fullerene 19 with conformationally constrained tethers as catalysts. The experimental data suggests that anion- π stabilization persists during the subsequent charge delocalization in the intrinsically disfavored exo transition state of the [4+2] cycloaddition.

4. Fullerene host-guest chemistry

4.1. Fullerenes as hosts

Open-cage fullerenes with their extremely rigid, all-carbon backbones exhibit unique cavities for the binding of neutral

or charged guests. ^{10,97–100} Although endohedral metallofullerenes (EMFs) do not meet the definition of a supramolecular complex but rather of a carceplex, ¹⁰¹ we will also discuss this compound class, because non-covalent interactions in opencage intermediates are relevant during statistical or rational EMF syntheses.

Since the first report of a metal-encapsulating fullerene in 1985, 102 endohedral fullerenes have been studied extensively. 97-99,103 Endohedral fullerenes can be classified according to their "imprisoned" guests as (i) endohedral metallofullerenes (EMFs) and (ii) nonmetal endohedral fullerenes. 10 The first category includes mono-, di-, and trimetallofullerenes, 104-109 as well as cluster metallofullerenes¹¹⁰ (e.g. oxide clusters, ¹⁰³ nitride clusters, 111-113 cyano clusters, 114 sulfide clusters, and carbide clusters), 10,97-99,115-120 while the second category includes H₂, noble gases, 121 water and other non-metal guests. 10,100 (Fig. 10) The synthesis of endohedral fullerenes is a challenging task, for which several strategies have been developed, including the vaporization of graphite in the presence of additives, the implantation of atoms through the walls of the pre-existing carbon framework, as well as multi-step chemical synthesis involving the opening of orifices in the fullerene scaffold.

The first open-cage fullerene was synthesized by using singlet oxygen to oxidize an azafullerene. The Pioneering work by a number of research groups 18,127,128 led to a wide scope of open-cage fullerenes, which offer the possibility to encapsulation and entrap guests within their cavity. The encapsulation of H_2 , O_2 , CO_2 , NH_3 , CH_4 , HF, HCN, HCCH, CH_3OH , and H_2O was achieved in this way and progress in this field has been reviewed recently by $Gan.^{127,129}$ In addition to the neutral molecules listed above, halide anions, LiF ([$LiF \subset 20$]₂, Fig. 10), and cationic [BeF]⁺ have also been encapsulated in the fullerene cage by Gan and coworkers. The authors demonstrated that a 19-membered open-cage fullerene with four carbonyl groups, an ether oxygen and a quinoxaline moiety on the rim of the orifice could act as the container for F^- , Cl^- , Br^- ([$Br \subset 21$]₂, Fig. 10) and I^- . Fullerenes containing halide anions exhibit higher polarity

compared to the respective empty fullerenes. The functional groups attached to open-cage fullerenes, such as amines, alcohols, and aromatic moieties, not only enable the selective recognition of guests, but also provide possibilities for further assembling higher-order structures or enabling the study of fundamental guest properties. For example, hydrogen-bonded fullerene dimers were obtained utilizing amide- 125 ([H₂O=22]₂, Fig. 10) and bis(hemiketal)- 130 containing open-cage[60]fullerenes. Dimers were also found in other work due to coordination between metal ions (such as Na, Ag, and Pt) and donor atoms as well as intermolecular π – π interactions. $^{123,124,131-133}$ Murata and coworkers constructed a supramolecular complex by encapsulating a 3 O₂ molecule into an open-cage C₆₀ derivative, of which the EPR spectra exhibited triplet state character as well as the anisotropy of the 3 O₂. 134

Endohedral fullerenes, while technically not host-guest complexes, nevertheless offer a unique opportunity to study metal-fullerene interactions, 135,136 unusual metal-metal interactions, 107,109,116,137 and other special bonds within fullerenes. These effects can give rise to single-molecule magnetism. 138-141 For example, lanthanide dimetallofullerenes featuring a single-electron Ln-Ln bond behave like singlemolecule magnets and are therefore potential qubits for molecule-based quantum computing.99 Recently, Popov and coworkers discovered that anionic metallofullerenes can react with the Umemoto reagent II, resulting in the addition of CF₃ groups to fullerenes, indicating electrophilic trifluoromethylation might be a useful method to derivate fullerenes. 142 By employing this approach, $M_2 \subset C_{80}(CF_3)$ (M = Tb, Y) monoadducts were synthesized, of which $Tb_2 \subset C_{80}(CF_3)$ exhibits robust and remarkable magnetic properties with magnetic hysteresis up to 27 K. Apart from encapsulation of metals by larger fullerenes, Shinohara successfully obtained crystalline C_{60} -based metallofullerenes $Gd \subset C_{60}(CF_3)_5$ and $La \subset C_{60}(CF_3)_5$ from their CS₂ solution by vapor diffusion, in which CF₃ groups highly improved the stability of these metallofullerenes. 143 The electronic properties of endohedral fullerenes are tunable by

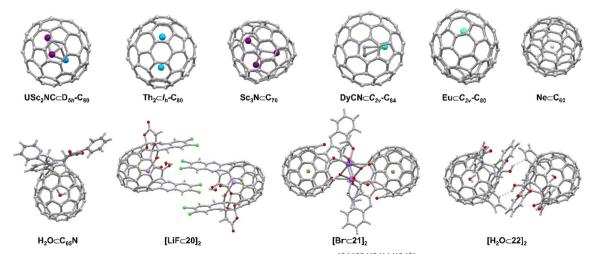


Fig. 10 Selected endohedral fullerenes and open-cage fullerenes acting as hosts 104,109,112,114,119,121 and supramolecular open cage fullerene-based dimers. 122-125

the insertion of different metals or metal clusters. 144,145 For instance, Lu₃N⊂C₈₀, a typical structure within the trimetallic nitride template (TNT) family, has a lower oxidation potential than C₆₀ and exhibits high stability compared to other EMFs. This property makes it an ideal electron donor, and in 2019, Martin and coworkers used $Lu_3N \subset C_{80}$ in combination with C_{60} as an acceptor to construct an "all-fullerene" donor-acceptor system. 146

4.2. Molecular tweezers as fullerene hosts

Molecular tweezers are molecular hosts with an open cavity and two identical binding sites for capturing guests (Fig. 11). By controlling the balance between rigidity and flexibility in the tweezers, distinct advantages can be provided for molecular recognition. 147 Generally, the two binding sites can be bridged by a pH-responsive (e.g. pyridyl), ion-responsive (e.g. dipyridyl and crown ether), or photo-responsive (e.g. dithienylethene and azobenzene) linker, allowing the molecular tweezers to capture and release guests. 148-150 This controllable recognition property has made molecular tweezers attractive tools in sensing, drug delivery and mixture separation. In the field of fullerene chemistry, tweezers have been studied for selectively extracting C_{60}/C_{70} or other higher fullerenes from carbon soot. ^{151–164}

Porphyrins have a strong affinity for fullerenes, thanks to their large π surface and the capability to undergo charge transfer interactions. For instance, Boyd and colleagues devised molecular tweezers for binding C₆₀ and C₇₀, using porphyrin units connected via a metal coordination bond. Alvarez and colleagues synthesized double-tweezers with a single porphyrin core containing eight pyrene units, capable of binding with C₆₀ (and C₇₀) and forming a 1:2 complex. Interestingly, the double-tweezers can transform into single-tweezers by coordinating the porphyrin core with Zn²⁺. ¹⁶⁷ Meanwhile, π-extended tetrathiafulvalene (exTTF), with its concave geometry and high electron-donating capacity, has been extensively utilized for binding fullerenes and carbon nanotubes. 168,169 Notably, Martín and colleagues have shown that exTTF-based molecular tweezers can be covalently linked to carbon

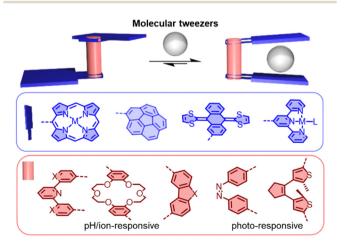


Fig. 11 Schematic representation of switchable molecular tweezers (based on various linkers and binding motifs)

nanotubes. By binding C_{60} relatively strongly ($\log K_a \approx$ 3.0-3.1), interesting non-covalent C₆₀/CNT hybrid materials can be obtained.170

Corannulene is a bowl-shaped polycyclic aromatic hydrocarbon (PAH), which is predisposed for the binding fullerenes, because it represents a fragment of C_{60} . In recent years, several π-extended and N-embedded "buckybowls" have been synthesized. 151 These buckybowls exhibit high affinity towards fullerenes through concave-convex π - π interactions when incorporated in tweezers architectures. 171,172 Sygula and coworkers provided the first strong evidence of supramolecular binding between a corannulene-based molecular tweezers and C_{60} in solution and in the solid state. The authors found that this double concave host strongly binds to C₆₀ to form a stable complex $(K_a = 8600 \text{ M}^{-1} \text{ in tolulene-} d_8).^{173} \text{ Stuparu}$ and coworkers designed a family of corannulene-based amphiphilic polymers that can yield fullerene-rich water-soluble materials. 174,175 Shinokubo and coworkers reported two types of azabuckybowl-based molecular tweezers that exhibited different affinities towards C_{60} and C_{70} . The carbazole-linked tweezers preferentially binds to C₇₀ over C₆₀, while the phenanthrene-linked tweezers associated with C60 more strongly than with C₇₀. Most host-guest systems can recognize guests, but releasing the guest without destroying the host structure is often a significant challenge. Alvarez and coworkers designed 2,2'-bipyridine-bridged molecular tweezers 23 that can capture and release fullerenes through in situ Cu(1) complexation and decomplexation. In the presence of Cu(1), the tweezers exhibited good binding affinities with C_{60} and C_{70} (K_a (C_{60}) = 2 \times $10^3 \,\mathrm{M}^{-1}$, $K_{\rm a} \,(\mathrm{C}_{70}) = 5 \times 10^3 \,\mathrm{M}^{-1}$ (Fig. 12a), and the reversibility of the fullerene capture and release was demonstrated. 176

In addition to PAH motifs, macrocycles can also act as binding sites in molecular tweezers. Haino and coworkers showed that biscalix[5] arenes covalently tethered together possess an ideal cavity for accommodating fullerenes. The K_a between the biscalix[5]arenes tweezers and C60 was found to be approximately 10⁴ M⁻¹ in toluene, significantly higher than the K_a between a single calix[5] arene and C_{60} . The When a molecule is equipped with two or more biscalix[5] arene tweezers, as demonstrated by molecule 24, supramolecular polymers and networks can be formed simply by addition of the dumbbell fullerene 25 (Fig. 12b). These hierarchically assembled supramolecular architectures are expected to pave the way for the development of stimuli-responsive fullerene-containing polymeric materials. 177,179

4.3. Macrocycles as fullerene hosts

Pedersen, Lehn, and Cram's pioneering work on macrocyclic compounds, such as crown ethers and cryptands, established the foundations of supramolecular chemistry. Since then, there have been significant advances in the design and synthesis of new macrocyclic molecules, which have in many cases led to applications in drug delivery, sensing, and chemical separation technologies. Examples include cyclodextrins, 180 calixarenes, cucurbiturils, pillar[n]arenes, pagoda[n]arene and cyclobis-(paraquat-p-phenylene). 181-190 Additionally, fully conjugated

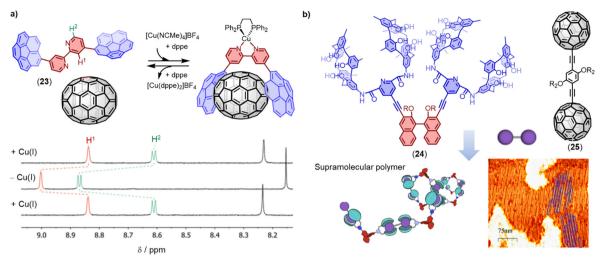


Fig. 12 (a) Chemical structure of 2,2'-bipyridine-bridged molecular tweezers 23 and its in situ coordination/decoordination of C_{70} as monitored using ¹H-NMR in CD₂Cl₂ at 298 K. Adapted from ref. 176 with permission from Royal Society of Chemistry, Copyright 2021. (b) Schematic representation of the formation of supramolecular polymers based on biscalix[5]arenes tweezers 24 and dumbbell fullerenes 25. Adapted from ref. 177 with permission from American Chemical Society, copyright 2021.

macrocycles like [n]CPPs, cyclo-porphyrins, and [n]cyclo-2,8chrysenylenes with well-defined diameters and unique radial conjugation exhibit fascinating electronic and optical properties. 191-204 These shape-persistent macrocycles offer significant advantages in constructing 1D nanotubes, 2D networks, and 3D complexes via self-assembly.205

This review article primarily focusses on covalent macrocycles and metallomacrocycles, which have demonstrated their effectiveness as hosts for fullerene recognition (Fig. 13). 162,206-243 These include highly strained and π-conjugated compounds such as [10]CPP and its derivatives, 244-251 [4]cyclo-2,8-chrysenylene (26), $^{252-254}_{252-254}$ porphyrinylene nanohoop (31), $^{255}_{255}$ and [n] cyclodibenzopentalenes (33), 256,257 which all exhibit exceptionally high affinity towards fullerenes ($K_a > 10^5 \text{ M}^{-1}$). Among these macrocycles, [4]cyclo-2,8-chrysenylene (26) and porphyrinylene nanohoop (31) exhibit outstanding fullerene affinity ($K_a > 10^8 \text{ M}^{-1}$) due to an extended π surface that maximizes concave-convex π - π interactions and further decreases the degrees of freedom in the host. One powerful strategy for constructing macrocyclic structures is coordination-driven self-assembly. 258,259 For instance, Peris and coworkers synthesized a palladium-cornered metallomacrocycle 42 with four pyrene-bis(imidazolylidene) bridging ligands, which can encapsulate both C_{60} and C_{70} to form $42 \supset C_{60}$ ($K_a = 5.4 \times$ $10^3 \text{ M}^{-1} \text{ in CD}_3\text{CN}$) and $42 \supset \text{C}_{70} (K_a = 7.1 \times 10^4 \text{ M}^{-1} \text{ in CD}_3\text{CN})$ complexes.²⁶⁰ By introducing additional homo-/hetero-macrocyclic structures to the backbone of macrocycles, e.g. in bismacrocycles, compounds with the capability to bind to multiple, distinct guests can be obtained.261-266 For example, Cong and coworkers reported a conjugated figure-of-eight oligoparaphenylene nanohoop (40) with adaptive cavities that can form 1:2 host-guest complexes with C_{60} and $C_{70}.^{267}$ More recently, Xu, Yam and von Delius reported the synthesis of two [n]cycloparaphenylenepillar[5]arene ([n]CPP-P[5]A, n = 8 and 10) bismacrocycles by integrating P[5]A into the [n]CPP backbone. [n]CPP-P[5]A exhibits multiple guest recognition and promising properties of circularly

polarized luminescence ($g_{lum} \approx 0.02$), with [10]CPP-P[5]A showing potential for use in supramolecular polymer preparation.²⁶⁸

Nano-Saturn complexes consist of a fullerene molecule as a planetary body surrounded by a macrocycle featruing a perpendicular π -system. Achieving such complexes is not trivial, because the perpendicular arrangement of π -system limits the strength of the van der Waals (vdW) dispersion interaction. Toyota and coworkers have nevertheless demonstrated that a cyclo-2,7-anthrylene hexamer can form a disktype nano-Saturn complex with C_{60} through multiple CH- π interactions $(K_a = 2.3 \times 10^3 \text{ M}^{-1} \text{ in toluene}).^{269}$ Another promising candidate for preparing nano-Saturn complexes with fullerene is metal coordination macrocycles. However, constructing a stable and size-compatible disk-type metallomacrocycle is challenging because of the inherent lability of coordination interactions and the effects of steric crowding in the planar metallomacrocycle. Zhan and coworkers have recently reported the selective synthesis of [Cu₁₀(2-methylimidazolate)₁₀] 46 using C₆₀ as a template.²⁷⁰ Remarkably, the ten methyl groups of the metallomacrocycle provide almost thirty CH- π interactions with the C₆₀ or C₇₀ molecule, stabilizing the disk-type metallomacrocycle (Fig. 14a). The interaction energy of their nano-Saturn complex is calculated to be much larger than that of most reported disk-type nano-Saturn complexes.

In addition to their direct use as fullerene hosts, macrocyclic molecules can also serve as backbones to prepare molecular cavitands, cages and nanotubes that enable fullerene encapsulation in the third dimension. For example, Tiefenbacher and coworkers have recently reported a megalo-cavitand 47 with volumes of up to 814 Å³ by using an acridane[4]arene and four triptycenes as building blocks (Fig. 14b).²⁷¹ They found that 47 exhibits a higher affinity for C_{70} ($K_a = 1.2 \times 10^6 \text{ M}^{-1}$ in toluene) than C_{60} ($K_a = 6.5 \times 10^4 \,\mathrm{M}^{-1}$ in toluene). Moreover, the authors discovered that cavitand 47 can selectively bind to C70 in the

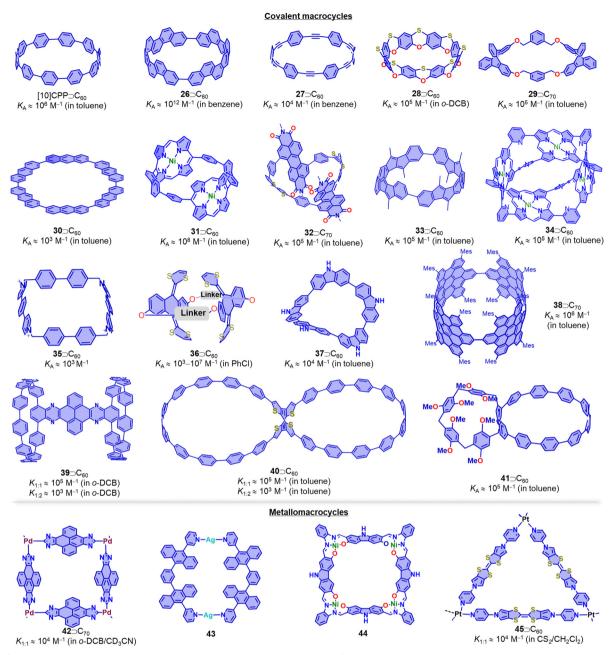


Fig. 13 Selected fullerene hosts: covalent macrocycles and metallomacrocycles. Side-chains are omitted for clarity

presence of C₆₀, which may be useful for fullerene purification. Tanaka and coworkers have described the synthesis of a supramolecular double-decker cage 48 composed of two shape-persistent imine-bridged tetranuclear ZnII-macrocycles and four 1,4-diazabicyclo-[2.2.2] octane molecules for the specific recognition of ellipsoidal fullerenes (Fig. 14c).²⁷³ Additionally, Tani and coworkers have designed a family of phenothiazine/ alkynyl-bridged cyclic porphyrin dimers bearing self-assembling 4-pyridyl groups (Fig. 14d). The phenothiazine-bridged dimers exhibit a higher affinity with both C_{60} ($K_a \approx 10^6 \text{ M}^{-1}$ in toluene) and C_{70} ($K_a \approx 10^7 \text{ M}^{-1}$ in toluene), and these dimers can selfassemble into a nanotube through π - π interactions of the pyridyl groups and C-H···N hydrogen bonds between porphyrin β-CH groups and pyridyl nitrogen donors. 272,274 Thus, macrocycle-based cavitands, macrocyclic double-deckers and self-assembled nanotubes offer opportunities for the specific recognition of fullerene derivatives.275

The importance of fullerene radicals in energy conversion and storage applications has been highlighted in photoinduced charge transfer processes in fullerene-based D-A systems. However, these radicals are typically short-lived and labile under air. To address this challenge, Tagmatarchis and coworkers developed a supramolecular approach to stabilize fullerene radicals.²⁷⁶ By continuously illuminating a mixture of $[10]\text{CPP} \supset (C_{59}\text{N})_2 \subset [10]\text{CPP}$ in 1-chloronaphthalene, the highly reactive azafullerene radical (C59N°) was generated and

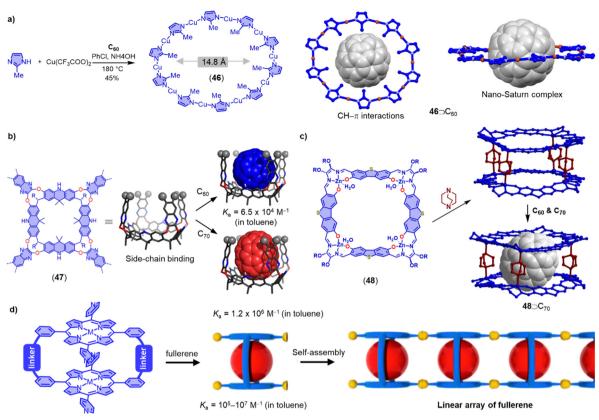


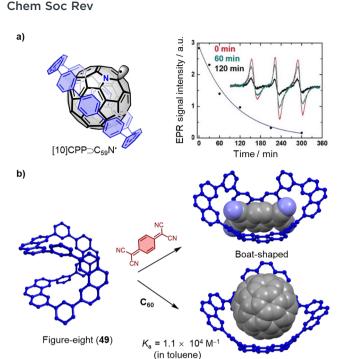
Fig. 14 (a) Selective synthesis of [Cu₁₀(2-methylimidazolate)₁₀] 46 utilizing C₆₀ as the template, and the solid-state structure of nano-Saturn complex $\mathbf{46} \supset C_{60}$. (b) Molecular models of megalo-cavitands $\mathbf{47}$ and corresponding C_{60} and C_{70} complexes. Adapted from ref. 271 with permission from Wiley-VCH, copyright 2022. (c) Synthesis of a supramolecular double-decker cage 48 and its selectively recognition with C_{70} . (d) Formation of linear array of fullerenes in self-assembled porphyrin nanotube. Adapted from ref. 272 with permission from American Chemical Society, copyright 2014.

immediately shielded by formation of the stable [10]CPP⊃C₅₉N[•] complex. This shielding effect leads to exceptionally long-lived C₅₉N[•] radicals, which are of interest for quantum information processing technologies, 277 because dimerization is prevented (Fig. 15a). Additionally, Tao, Du and coworkers introduced [9]CPP to the active layer of fullerene organic solar cells (OSCs). This not only promotes charge transfer between poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene-co-3-fluorothieno[3,4-b]-thiophene-2-carboxylate] (PTB7-Th) and PC₇₁BM, but also enhances charge transport between the $PC_{71}BM$ molecules by adjusting intermolecular π - π stacking. As a result, the ternary OSCs made from PTB7-Th, [9]CPP, and PC₇₁BM achieved a high power conversion efficiency (PCE) of around 11%, almost one fifth higher than the PTB7-Th and PC₇₁BM binary OSC devices.²⁷⁸

Conjugated macrocycles typically have rigid, inflexible cavities that restrict their ability to recognize a wide range of guest molecules and sometimes limit them to bind only a single type of guest. However, in 2021, Liu and coworkers reported a remarkable "Figure-eight" macrocycle 49, that possesses the ability to flexibly adjust its conformation in response to changes in the external environment, allowing it to accommodate a variety of guest molecules (Fig. 15b).²⁷⁹ This unique property of macrocycle 49 was demonstrated through its ability to assemble with planar, electron-deficient guest molecules,

such as 7,7,8,8-tetracyanoquinodimethane, by adopting a boat-shaped conformation. The K_a of this complex was determined to be $1.0 \times 10^3 \,\mathrm{M}^{-1}$ in toluene at 323 K. Furthermore, the macrocycle demonstrated an even higher affinity towards C_{60} , with a K_a of 1.1 \times 10⁴ M⁻¹ in toluene at 323 K, and single crystal X-ray diffraction (SCXRD) confirmed that the macrocycle changed into a belt-shaped conformation in the presence of C₆₀. These results suggest that macrocycle 49 is a promising candidate for the development of versatile host molecules capable of accommodating a diverse range of guest molecules.

Compared to covalent macrocycles, metallomacrocycles have demonstrated greater synthetic efficiency and diversity due error correction during their formation from small subcomponents. Metal coordination-driven self-assembly is a highly efficient strategy for constructing supramolecular architectures. 280,281 Thanks to their kinetic reversibility, metallomacrocycles have wide applications in host-guest chemistry, particularly in the encapsulation and release of fullerenes. 282-285 In 2020, Oppel reported a new torus-shaped metallomacrocycle **50** with an outer diameter of 31.7 Å. Zn(II) ions are octahedrally coordinated between two ligands of alternating orientation which in solution, bind fullerenes C₆₀ and C₇₀ in their spherical cavities (Fig. 16a).²⁰⁸ The fullerene encapsulations were characterized by SCXRD and NMR spectroscopy, and theoretical



chloronaphthalene after the illumination at 532 nm has been switched off of [10]CPP ⊃ C₅₉N[•]. Adapted from ref. 276 with permission from Wiley-VCH, copyright 2019. (b) Conformation transformation of "Figure-eight" macrocycle 49 by adding guest 7,7,8,8-tetracyanoguinodimethane and C₆₀, the side-chains are omitting for clarity.

Fig. 15 (a) Structure and time dependence of the X-band EPR signal in 1-

Belt-shaped

calculations were conducted to gain a deep understanding of host-guest interactions in these metallomacrocycles.

For certain applications of fullerene hosts, the release of encapsulated guest molecules from the host molecule is necessary. Although many macrocycles exhibit excellent fullerene recognition ability, the subsequent release of fullerenes remains challenging, especially in cases where the binding constant is very high. Typically, guest release from host-guest complexes can be triggered by chemical, electrochemical, heat stimuli, or the addition of secondary guests in a guestexchange process. Yoshizawa and coworkers developed a method for releasing captured C_{60} upon UV-vis irradiation (Fig. 16b).²¹⁴ Metallomacrocycle 51 was formed only in the presence of guest C₆₀. A pale-yellow solution with a powdery suspension of solids was observed after exposing 51⊃C₆₀ in CH₃CN to UV-vis irradiation produced by a 36 W incandescent light bulb at room temperature for 1.5 h. The broad UV-vis absorption band of $52 \supset C_{60}$ (400-700 nm) disappeared, indicating the release of C₆₀ from the metallomacrocycle. A recovery yield of 68% was determined for C₆₀, and the complex can be regenerated in ca. 60% yield from the UV-vis irradiated sample by adding AgNO₃ at room temperature.

4.4. Cages as fullerene hosts

Cages are a unique class of supramolecular hosts due to their three-dimensional and rigid molecular structure, typically exhibiting a well-defined cavity. In contrast to covalent or

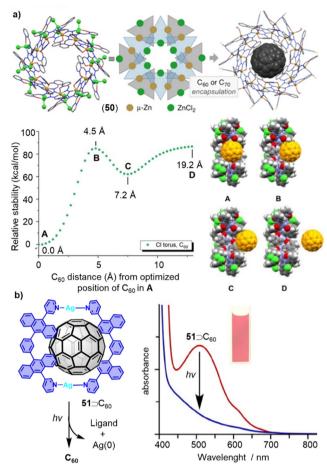


Fig. 16 (a) Supramolecular metallocycle 50, schematic drawing and inclusion complex $51 \supset C_{60}$ as well as energy diagram showing the relative stability as a function of the C₆₀ distance from its position at the BP86/ 6-31G level of theory (A). Adapted from ref. 208 with permission from Wiley-VCH, copyright 2020. (b) Fullerene release from 51⊃C₆₀ complex by photoirradiation. Adapted from ref. 214 with permission from American Chemical Society, copyright 2013.

metal-organic frameworks, cages are discrete and can be characterized with solution-based techniques. Syntheses are typically achieved by self-assembly, which is why cages often feature dynamic covalent bonds, 286 labile metal-ligand bonds 280,287 or weak non-covalent interactions. 288 In recent years, the encapsulation of fullerenes in cages has been pursued by a large number of groups. 16,20,289-292 This research is typically motivated by the desire to explore new host-guest chemistry and to endow the encapsulated fullerene with unusual properties. For instance, encapsulated fullerenes can exhibit improved solubility, (radical) stability, catalytic activity or modulated redox potentials.²⁹³⁻²⁹⁵ As discussed in section 2, encapsulated fullerenes can also undergo itero-, regioand stereoselective addition reactions. 52,296,297 The selective encapsulation of fullerenes is of interest for obtaining pure fullerenes from complex mixtures (e.g. soot). 298-300

PAH moieties are often employed as the core building blocks incorporated into cages due to their strong π - π or charge transfer interactions with fullerenes. Examples of such moieties include porphyrin, 16,301,302 pyrene, 303 anthracene, 304 tetrathiafulvalene, 305

carbon bowls, as well as some electron-deficient groups like naphthalene diimide (NDI), and perylene bisimide (PBI), etc. 306 Coordination-driven self-assembled cages, with diverse shapes and sizes, also known as metallocages or metal-organic cages, have been constructed and widely used for the encapsulation of fullerenes. 20,22,307,308 The dynamic nature of metallocages, owing to labile coordination bonds (e.g. Pd-N) allows large fullerene guests to enter cages with small windows and transformations between different complexes, 207,302,309-312 Some exceptionally large metallocages were shown to bind multiple fullerenes,313 offering an opportunity to study cluster of fullerenes. 302,314-316 For example, a large tetrahedron metallocage 52 containing nickel(II) porphyrins and Zn metals assembled by Nitschke and coworkers was used to encapsulate 1-4 equiv. of C₆₀. 316 Interestingly, coencapsulation within the metallocage made it easier to reduce C₆₀ to the $C_{60}^{\bullet -}$ radical anion, in which according to theory is due to vdW interactions between multiple fullerenes (Fig. 17a). In related work, Yoshizawa and coworkers used a peanut-shaped polyaromatic metallocage 53,282,317 assembled from "W" ligands and Pd(II) metals, which allowed the encapsulation of two fullerenes separated by a distance of 6.4 Å (Fig. 17b). This discrete, noncontacted fullerene dimer undergoes sequential reduction in the cavity of the metallocage to generate $(C_{60}^{\bullet-})_2$, $C_{60}^{\bullet-}$ $\cdot C_{60}^{2\bullet-}$, and $(C_{60}^{2\bullet-})_2$. Furthermore, the stepwise encapsulation of two C_{60} molecules was achieved in a temperature-controlled fashion.

Purely organic cages have been synthesized using the wellestablished toolbox of dynamic covalent chemistry (DCvC). 286,318,319 DCvC cages are typically more robust than metallocages and the products of self-assembly can be kinetically inert. The encapsulation of fullerenes into organic cages can therefore depend on the size of the cage windows, unless the cage is still dynamic, as in Beuerle's boronic ester cage.⁵² As an example for an organic cage with large windows, Zhang and coworkers synthesized a porphyrin and carbazole moieties-contained rectangular prismatic organic cage by utilizing alkyne metathesis. 320 This cage exhibits highly selective encapsulation of C₇₀ over C₆₀ $(K_{\rm C70}/K_{\rm C60} > 1000)$, which was successfully used to isolate C₇₀ from a mixture with C_{60} . Of note, the encapsulated C_{70} was released by addition of excess trifluoroacetic acid and encapsulation of the fullerene was possible upon addition of triethylamine, highlighting the robustness of organic cages, which in this case enables the controlled a repeated guest encapsulation and release.

Trigonal prism-shaped cages also offer the opportunity to encapsulate fullerenes, as long as their size is in a suitable range. Recently, a trigonal prismatic nanobarrel constituted by three pyrene panels and two triangular windows with a diameter of 12.7 Å was synthesized by employing dynamic imine bond.³²¹ This pyrene cage allows the encapsulation of C₆₀ in poor solvents for the fullerene, which is a useful method for dissolving C₆₀ in non-aromatic solvents (such as dichloromethane, chloroform, and 1,1,2,2-tetrachloroethane). In order to provide a better prediction for rational design of DCvC cages for C₆₀, Jelfs and coworkers used an evolutionary algorithm to identify potential hosts for C₆₀. The study showed that promising imine-based cages for encapsulation of C60 need to have suitable size, planar tri-topic aldehyde units with a low number of rotating single bonds, di-topic amine building blocks with functionality on adjacent carbon atoms and overall a highly symmetrical structure. 322 Besides self-assembly based on reversible interactions, organic cages can also be synthesized by high-yielding irreversible reactions.323 Wu and coworkers reported a three-dimensional π -conjugated polyradicaloid prism-like cage consisting two benzene-1,3,5-triyl and three Chichibabin's hydrocarbon motifs as linker, which was prepared by Ni(COD)₂-mediated Yamamoto homocoupling. ³²⁴ The large cavity in the conjugated cage allowed selective encapsulation C_{70} over C_{60} .

A new class of organic cationic viologen/porphyrin cages was developed by Stoddart and coworkers in recent years.325 A tetragonal organic porphyrin cage 54 with 8 positive charges was utilized to encapsulate C₆₀ or C₇₀ due to the suitable cavity within cage and the favorable D-A interaction between the porphyrins and fullerene guests (Fig. 18a).326 More recently, Lipke and coworkers reported the gram-scale synthesis of a

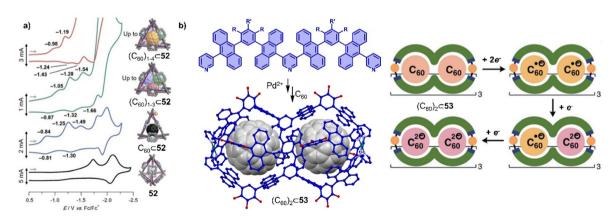


Fig. 17 Selected redox properties of fullerenes encapsulated within the cages. (a) Cyclic voltammograms porphyrin cage 52 encapsulating 0-4 equiv. C₆₀. Adapted from ref. 316 with permission from American Chemical Society, copyright 2017. (b) Assembly of peanut-shaped polyaromatic metallocage- C_{60} complex [crystal structure of $(C_{60})_2 = 53$] and schematic representation of the sequential reduction processes of $(C_{60})_2 = 53$. Adapted from ref. 282 with permission from Wiley-VCH, copyright 2020.

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a) 55 b) 0.1 mM Gram-scale synthesis 0 -**4**0 55 ⊃C₆₀ 0.1 mM -120 -2.415 2 V/s 55 -1.6 -1.1 -0.6

Fig. 18 Organic cationic cages encapsulating fullerenes. (a) Selective extraction of C70 by a tetragonal prismatic porphyrin cage 54 (crystal structures). (b) Tetracationic cage 55 and cyclic voltammograms of 55 in comparison with $C_{60} \subset 55$. Adapted from ref. 327 with permission from Royal Society of Chemistry, copyright 2020.

different cationic porphyrin cage by the formation of pyridinium linkages between two complementary porphyrin "bowls" in the last step. This new cage 55 was found to bind fullerenes very strongly ($K_a > 10^8 \text{ M}^{-1}$ in MeCN) (Fig. 18b).³²⁷ Interestingly, although the cage binds C₆₀ or C₇₀ with strong affinities, the redox properties of fullerenes are not affected due to encapsulation, which is in contrast to other porphyrin metallocages. As both cages 54 and 55 exhibit stronger binding ability towards C₇₀ over C₆₀, the selective extraction of C₇₀ from C₆₀/C₇₀ mixtures has also been achieved.

Encapsulation of fullerenes within cages has not only improved the solubility in common solvents, 321 but also may tune the electronic properties of fullerenes due to strong π - π interactions with cage, which provide a reaction platform to modify fullerenes. Kim and coworkers constructed a series of well-defined 3D porphyrin boxes by employing dynamic covalent chemistry approach, 328 of which the large cavity and suitable windows allow to encapsulate fullerenes and even occur those harsh condition reactions (Fig. 19a). Recently, they successfully conducted the inverse-electron-demand Diels-Alder reaction between fullerenes and 1,2,4,5-tetrazine within a Zn-porphyrin box 56, a reaction that normally requires very harsh reaction condition and longer reaction time with low yield. Interestingly, C60-tetrazine adduct is transferred to a bent-shaped C₆₀-pyrazoline adduct through a hydration reaction and then released from the box with the addition of excess axle. The confined microenvironment within a cage also allows for photoredox chemical transformations of encapsulated fullerenes. Recently, a self-assembled subphthalocyanine capsule 57 was used as a reactor to accelerate the additions of (diaryl) methylamine and trifuoroethyl radicals to C60 under green light

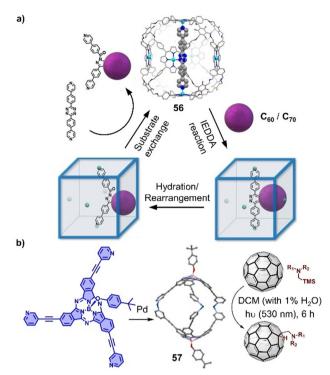


Fig. 19 Tuning the reactivity of fullerenes within cages. (a) Representation of insertion of tetrazine-based linear axle inside a porphyrin box 56 and functionalization of C_{60}/C_{70} inside box. Adapted from ref. 328 with permission from Wiley-VCH, copyright 2022. (b) Assembly of a subphthalocyanine capsule-based molecular reactor (57) and the photoredox transformations of fullerenes.

irradiation, which are typically photoredox transformations that occur within a cage (Fig. 19b). 329,330

Traditionally, electron-rich moieties are adopted as the main components to build hosts for electron-deficient fullerenes, which enhances host-guest interactions through charge transfer. However, electron-deficient moieties like PBI, 309,314 NDI, 331 and triptycene carboxylic dianhydride^{294,332} can also be employed to construct cages, resulting in different host-guest interactions with fullerenes. For example, Würthner and coworkers found that a Fe₄(PBI)₆ tetrahedron cage assembled from octahedral Fe(II) ions and linear 2,2'-bipyridine modified PBI at the imide positions was capable of encapsulating two equivalents of C₆₀.³¹⁴ Encapsulation of C₆₀ exhibits almost no effect on the absorption of cage, indicating weak interaction between PBI and C₆₀ at the ground state, possibly because bulky groups at bay positions prevent the contact. Stang, Fang and coworkers also observed encapsulation of fullerenes in a PBI-based trigonal prism, 309 assembled from Pt(II) and tetrapyridyl connected PBI at ortho positions. Similar as in Würthner's study, C₆₀ or C₇₀ encapsulation had a negligible effect on the both absorption and fluorescence spectra of the trigonal prism, indicating that the interaction is mainly based on dispersion. The encapsulation of fullerenes in cages comprising electron deficient subcomponents offers the opportunity to stabilize fullerene or cage once either of the two is reduced to the radical anion due to the favourable interaction between acceptor and the newly

formed donor (radical anion). For example, Nitschke and colleagues constructed an NDI-based ZnII4L6 cage 58,331 where the NDIs could be reduced to the radical anion and used as the catalyst for the oxidative coupling of different tetraaryl borates to give biaryls (Fig. 20a). Furthermore, the catalytic reactivity of the radical cage was further enhanced by the presence of the C₆₀ guest that plays an important role in stabilizing the NDI radical. $C_{60}^{\bullet -}$ could act as a carrier for efficient charge harvesting and can be generated by obtaining single electrons from suitable electron donors. Generally, the lifetime of $C_{60}^{\bullet-}$ is rather short (<1 s) in solution. Recently, Clever and coworkers found that a self-assembled electron-deficient cage 59 consisting of four triptycene carboxylic dianhydride ligands and two Pd(II) cations²⁹⁴ stabilized the $C_{60}^{\bullet-}$ radical anion, which was attributed to the strong interaction between C₆₀ • and electrondeficient cage 59 (Fig. 20b). The chemical reduction of encapsulated C₆₀ was achieved by adding 1-benzyl-1,4-dihydronicotinamide as a reducing regent with the 2 min irradiation of a white LED, and encapsulation which extended the half-life of C₆₀•- to 14 min in air and 893 min under inert conditions.

The interaction between cages and fullerenes not only affects their electronic properties, but also their spin state properties. For example, Lützen and coworkers reported a metallocage with spin crossover behavior, assembled by using 5,10,15,20-tetrakis(4-aminophenyl)porphyrin or its zinc(II) complex, 333 1H-4-imidazolecarbaldehyde, and iron(II) salts. The iron(II) centers in this metallocage 60 exhibit the highspin state at room temperature and low-spin state in solution at low temperature. More interestingly, a "high-spin-stabilizing effect" through encapsulation of C₇₀ was observed (Fig. 21).

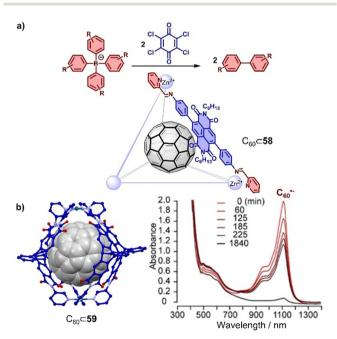


Fig. 20 (a) C-C bond formation catalyzed by $C_{60} \subset 58$. (b) Solid state structure of $C_{60} \subset$ 59 and the UV-Vis-NIR spectra of $C_{60}^{\bullet-} \subset$ 59 measured under N₂ atmosphere over time. Adapted from ref. 294 with permission from American Chemical Society, copyright 2021

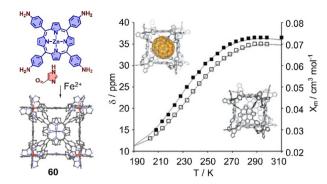


Fig. 21 Self-assembly of an octanuclear metallocage 60 and chemical shift of selected protons in temperature-dependent ¹H NMR experiments in CD₃OD. Black lines represent the calculated molar susceptibility γ_m based on the ideal solution model. Adapted from ref. 333 with permission from Wiley-VCH, copyright 2017.

4.5. Other fullerene hosts

Hosts for fullerene binding are not just limited to tweezers, macrocycles and cages. The recent use of other types of hosts will be summarized in this section, including curved or bowlshaped molecules, 17 proteins, 334-336 polymers 337,338 and carbon nanotubes.339,340

Curved or bowl-shaped π-conjugated molecules are inherently more shape-complementary to fullerenes than planar compounds and possess other unique properties. 17,341-354 For instance, many curved molecules are chiral and are more soluble than comparable planar analogues. Corannulene, which has already been discussed in the section on tweezers, is a prototypical curved π -conjugated molecule. As a fragment of C₆₀, it has been a building block of choice for the binding of fullerenes. 355,356 Dibenzo-[a,g]corannulene, 357 a simple corannulene derivative, formed a co-crystal with C₆₀ and C₇₀ in 1:1 and 2:1 stoichiometry, respectively. The solid state structures indicated a strong interaction between corannulene and the fullerenes, with the shortest distance being only 3.14 Å. Shinokubo and coworkers used a nitrogen-embedded buckybowl as host for C₆₀, and the 1:1 association of was supported by X-ray diffraction and UV-vis absorption and fluorescence titration experiments in 1,2-dichlorobenzene. 348 A flexible decapyrrylcorannulene (DPC) host, 358 developed by Zhang, Yang, Xie and coworkers, possesses ten pyrrole groups which resemble flexible 'fingers' on the periphery of the corannulene core. This host could bind 15 different fullerenes, including almost all commonly known types of fullerenes, such as pristine (C_{60} , C_{70} , C90), exohedral (six methanofullerene derivatives, three fullerene hydride derivatives, and one fulleroid derivative), endohedral (Sc₃N@C₈₀), dimeric and heteroderivatized [(C₅₉N)₂] structures, fulleroid and pentagon-fused fullerenes. Crystal structures of fullerenes with DPC reveal the high adaptivity that results from the presence of ten electron-rich 'fingers' at the outer rim of corannulene. Corannulene was also incorporated into organometallic complexes with the purpose of binding fullerenes. Peris and coworkers used a corannulene-functionalized di-N-heterocyclic carbene-Au^I complex as

receptor for C_{60} . The binding was found to be on the order of 103 M⁻¹ (toluene) and a host-guest ratio of up to 3:1 was confirmed by NMR spectroscopy and ITC titrations. Apart from corannulene derivatives, 359-361 Nabeshima and colleagues developed a series of chiral concave π -systems comprising phosphorus atoms, 343,347 which bind C₆₀ due to the concaveconvex interactions. In addition to buckybowls, 362-365 a bowlshaped nanobelt reported by Wu and coworkers, which could selectively capture C_{70} with a large binding constant ($log(K_a) \approx$ 5; in toluene) from a mixture of C₆₀/C₇₀ due to size and shape complementarity.366 Isobe and coworkers synthesized a nanometer-sized geodesic phenylene bowl comprising 20 phenylene units, which forms a 1:1 ball-in-bowl complex with C₆₀. The association constant in chloroform was found on the order of 10⁴ M⁻¹ by ¹H NMR spectroscopy and the complex structure was confirmed by SCXRD. Osuka, Kim and coworkers reported a series of porphyrin trimers, bearing additional carbonyl groups or methylene groups inserted between one of the β - β linkages of the porphyrin tapes. Among these hosts for C₆₀, the methylene-linked syn-Ni(II) porphyrin trimer exhibited the strongest association constant of ca. 107 M-1 in toluene at 25 °C. 368,369

 π -Extended nanographenes with suitably sized cavities have also been utilized as hosts for fullerenes. 370-372 For example, Wang and coworkers reported a Janusarene 61,342 possessing nineteen phenyl rings (seven constituting the hexaphenylbenzene core and the other twelve forming a "fence" around the two faces of the core), which was synthesized via an efficient cobalt-catalyzed cyclotrimerization of alkyne precursors. Hostguest complexation of 61 and C60 was supported by SCXRD, which revealed a ratio of 1:1 in the solid state. The crystal packing showed a 1D alternating supramolecular polymer (Fig. 22a), ³⁷³ in which fullerene nestles inside the cavity formed by two janusarene molecules, indicating concave-convex interactions between $\mathbf{61}$ and C_{60} . Wei and coworkers also reported a 'Janus' hexabenzocoronene derivative consisting of three triptycene units fused onto the periphery of coronene. 350 The synthesis featured the condensation of syn-triveratrylbenzene and 2-formyltriptycene in one pot with high yield, and the product was found to host C_{60} ($K_a = 4.9 \times 10^3 \text{ M}^{-1}$) and C_{70} ($K_a = 6.9 \times 10^3 \text{ M}^{-1}$) in toluene. Wust and coworkers designed a series of D_4 -symmetric tetraoxa[8]circulenes, 374 which possess an extended planar π -conjugation due to the introduction of oxygen atoms. One [8]circulene 62 was fused with four triptyceno subunits and could therefore serve as host for C₆₀, which was demonstrated by SCXRD (Fig. 22b). Recently, Würthner and coworkers observed the co-assembly of C₆₀ and a negatively curved polycyclic aromatic hydrocarbon 63, forming a supramolecular complex with an unusual 1:4 stoichiometry, which was characterized and analyzed by SCXRD and theoretical calculations.³⁷⁵ Interestingly, the complex topologically resembles of the fascinating carbon allotrope Schwarzite (Fig. 22c).376

In addition to using large π -conjugated molecules, some small molecules also form host-guest complexes with fullerenes due to hydrogen bonding. 377-383 For instance, Stefankiewicz and coworkers reported a hydrogen-bonded capsule, selfassembled by eight amino acid functionalized molecules 64 through 48 hydrogen bonds between the carboxyl and amine moieties of adjacent monomers (Fig. 23a), which was confirmed by SCXRD and multiple NMR methods in chlorinated solvents.384 The crystallographic analysis revealed that the monomer 64 formed an octameric supramolecular nanocapsule with the cavity volume up to 1719 Å³. The large inner cavity of capsule has been used to selectively encapsulate C₇₀ from a mixture of C_{60}/C_{70} in tetrachloroethane. Orentas, Wärnmark and coworkers developed a series of ureidopyrmidinone (UPy)based hydrogen bonding tubes that exhibit intriguing dynamic behavior, such as self-sorting and solvent/guest-induced rearrangement. 380,381,385,386 By adding C₆₀, an octameric tube

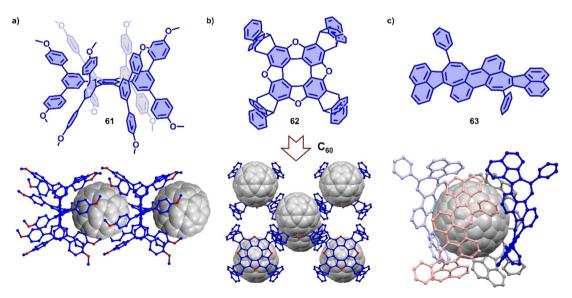


Fig. 22 Co-crystals of Janusarene 61 (a), tetraoxa[8]circulene 62 (b) and negatively curved polycyclic aromatic hydrocarbon 63 (c) with C₆₀.

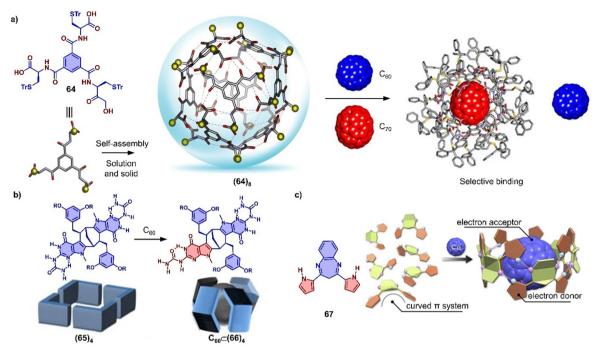


Fig. 23 Hydrogen bond associated, adaptive systems. (a) Self-assembly of supramolecular nanocapsule (64)₈ from compound 64 and selective encapsulation of C_{70} from a mixture of C_{60}/C_{70} . Adapted from ref. 384 with permission from Springer Nature, copyright 2017. (b) The symmetry breaking of monomer by rearrangement and schematic representation of starting tetramer (65)₄ and capsular complex $C_{60} = (66)_4$ Adapted from ref. 386 with permission from Springer Nature, copyright 2017. (c) Structure of DPB 67 and schematic representation of supramolecular polymer to macrocycle transformation with addition of C₆₀. Adapted from ref. 387 with permission from American Chemical Society, copyright 2020.

(65)4 comprising multiple hydrogen bonds was rearranged to capsular complex $C_{60} \subset (66)_4$ due to encapsulation of C_{60} (Fig. 23b), which was investigated by multiple NMR measurements.386 Recently, Maeda and coworkers reported a selfassociating curved π -system, ³⁸⁷ dipyrrolylbenzodiazepines (67), which forms a 1D supramolecular polymer in the solid state driven by the hydrogen bonds between a pyrrole NH as H bond donor and the diazepine nitrogen atom as H bond acceptor (Fig. 23c). The crystal structures revealed that this supramolecular polymer was successfully transformed into a large supramolecular macrocycle by the addition of C₆₀, forming a supramolecular complex assembled by six compound 67 and one C₆₀. The arrangement of monomer units and the strong concave-convex D-A interactions between 67 and C60 result in ultrafast electron transfer from 67 to C₆₀.

Fullerenes are typically hosted by molecules with a rigid backbone, large π system and a suitably sized cavity. However, encapsulation of fullerenes by proteins, driven by multiple weak interactions, was also reported. 388,389 The interactions between proteins with fullerenes and their derivatives include a very broad range, such as π - π , dispersion, hydrophobic, surfactant-like, cation- π , anion- π , hydrogen bonding, as well as electrostatic interactions, and are presumably acting synergistically, 334 involving multiple functional groups. For instance, aliphatic moieties from amino acids like methionine, proline, alanine, leucine, valine, and isoleucine interact with the surface of C_{60} , ^{390,391} while amino acids with aromatic rings (e.g. phenylalanine) establish strong π - π stacking interactions with the fullerene.³⁹² In addition, functional groups possessing positive and/or negative charges (e.g. lysine, aspartate and others) undergo surfactant-like interactions. 391,393 Understanding the interaction between fullerene and protein by multiple methods (such as SCXRD, NMR, UV-vis, and fluorescence) is a complex challenge that promises insights into protein structure and dynamics.334

Utilizing multiple weak interactions to host fullerenes also represents a new method to construct capsules. 394,395 Remarkably, Yoshizawa and coworkers achieved the encapsulation of fullerene in water by using a water-soluble adamantane capsule,³⁹⁴ where the driving force was the hydrophobic effect, dispersion and CH- π interactions. This approach demonstrates the potential of using weak interactions to create highly selective and efficient encapsulation systems.

5. Mechanically interlocked molecules

The mechanical bond³⁹⁶ is of interest for 21st century material science because it offers access to unique structural and dynamic properties as well as the ability to respond to external stimuli. Among the various types of mechanically interlocked molecules (MIMs), fullerenes are evidently good candidates as stoppers in rotaxanes, because the large and rigid carbon scaffold can prevent the dissociation of a macrocycle from a thread. 397-399 Furthermore, fullerene-based D-A systems have been found to exhibit rapid charge separation and low

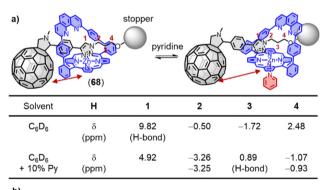
reorganization energy values during photoinduced processes (see above). 400 This unique property allows for the investigation of molecular motion and control of intramolecular photoinduced charge separation processes, which are essential steps in natural photosynthesis. As a result, the development of molecular fullerene-based MIM photosynthetic systems has gained considerable attention in recent years. 398,400 The first fullerene-based mechanically interlocked molecule was reported in 1995 by Sauvage and colleagues, 401 and since then, several methodologies have been developed to effectively incorporate fullerenes into pseudorotaxanes, rotaxanes, and catenanes. Metal-ligand exchange, hydrogen bonding and π - π

interactionshave been instrumental for achieving these MIM

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syntheses.402-404

Porphyrin-fullerene MIMs are the most frequently employed in photosynthetic model systems because they reliably provide photoinduced charge separation. On many occasions, both fullerenes and porphyrins have been utilized as stoppers in rotaxanes. In 2019, Weiss and coworkers reported a novel rotaxane 68 containing a strapped porphyrin as the shuttle and a fullerene stopper at the end of a mobile dumbbell (Fig. 24a). 405 The position of the porphyrin-based shuttle was fixed via metal-ligand coordination and could be switched by the addition of coordinating ligands such as 10% pyridine- d_5 in benzene- d_6 . Pyridine binds to the Zn-center opposite to the triazole, relocating the triazole outside of the phenanthroline pocket. The motion of the shuttle was clearly supported by comparing the chemical shifts of the alkyl protons. Moreover, transient absorption measurements revealed that solvent polarity influenced molecular motion of the rotaxanes upon charge separation.



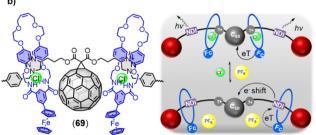
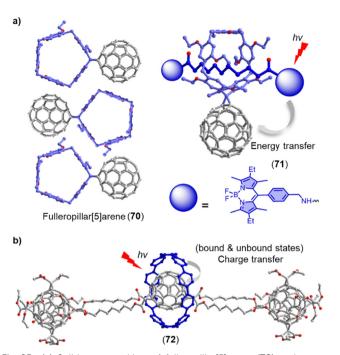


Fig. 24 (a) Comparison of the chemical shifts and position of the dumbbell of **68** in benzene- d_6 upon addition of 10% pyridine- d_5 . (b) Schematic depiction of a switchable D-A four-station C₆₀-based [3]rotaxane 69 via anion-induced molecular motion

Beer and coworkers have developed a multicomponent [3]rotaxane 69 as part of their efforts to create photoactive devices with multiple switching capabilities. The rotaxane includes a four-station bis-NDI axle, a centrally positioned C₆₀ bis-triazolium component, and two macrocycles containing ferrocenyl-isophthalamide. The rotaxane was prepared using a chloride anion template methodology (Fig. 24b). 406 In the chloride form, two ferrocenyl-functionalized macrocycles reside at the center of the axle, which triggers the activation of the NDI fluorophore and formation of a C₆₀ fullerene-based chargeseparated state. Conversely, when the chloride anions were replaced with hexafluorophosphate anions, the ferrocenylfunctionalized macrocycles shuttle to the peripheral NDI axle stations, leading to the formation of an NDI-containing chargeseparated state and quenching of the NDI emission.

Macrocyclic arenes have garnered significant attention in supramolecular chemistry due to their easy synthesis and ability to selectively recognize guests. 407 The small, electronrich cavity of macrocyclic arenes allows them to capture electron-deficient molecules such as alkyl nitriles, pyridinium salts, and urea derivatives, making them ideal for developing stimuli-responsive materials and constructing MIMs. 408,409 Nierengarten and coworkers functionalized C₆₀ with pillar[5]arene (P[5]A) to create a fulleropillar[5]arene derivative 70, where each fullerene moiety interacts with three P[5]A subunits through intermolecular π - π and electrostatic interactions in the solid state. 410,411 By encapsulating a diacyl chloride in P[5]A and carrying out a stoppering reaction, the authors were able to synthesize a photoactive [2]rotaxane 71 that comprises a central fullerene moiety and two terminal BODIPY stoppers (Fig. 25a). Even though the C_{60} moiety and the BODIPY stoppers are not covalently connected, efficient through-space excited state interactions have been observed in this architecture. In 2020, Wu and coworkers reported a "fulleropillar[4]arene": a pillararene in which one arene moiety has been replaced by a trans-4 fullerene bisadduct. Interestingly, this unusual macrocycle exhibits significantly higher association ($K_a \approx 6600 \text{ M}^{-1}$ in DMSO) with viologen derivatives than P[5]A,412 which allowed the authors to prepare a new type of pseudorotaxane.

Constructing MIMs with large size and shape-persistent cavities, such as those found in prototypical carbon nanohoops or nanobelts, presents significant challenges, not least because these componds typically lack heteroatoms. In 2018, the von Delius group overcame this difficulty by reporting the successful synthesis of two discrete [2]rotaxanes (72) that feature a strained carbon nanoring [10]CPP, which exhibited intriguing photoinduced charge transfer properties (Fig. 25b).45 The strong concave-convex π - π interactions between [10]CPP and C_{60} monoadduct ($K_a = 1.8 \times 10^6 \text{ M}^{-1}$ in toluene) enabled the highly efficient and regioselective synthesis of these two rotaxanes (trans-2: 10% and trans-3: 26%). Transient absorption studies revealed snapshots of the macrocycle's "bound" and "unbound" states along the trajectory of the thread. The exceptionally slow dissociation of the CPP ring from the fullerene binding site, along with very fast translation along the thread was later confirmed in high-level meta dynamics



(a) Solid state packing of fulleropillar[5]arene (70) and corresponding photoactive [2]rotaxane 71. (b) Optimized structure of [10]cycloparaphenylene-fullerene [2]rotaxane 72

simulations⁴¹³ and could pave the way towards MIMs in which the ring is transporting charge, which would have relevance for photovoltaics and photocatalysis.

Recently, the Ribas and von Delius groups used their Matryoshka approach (see Fig. 3) for the trans-3 selective bisfunctionalization of C₆₀ to achieve the synthesis of a new type of [2]catenane 74.414 These catenanes comprise a [10]CPP ring that is mechanically interlocked with a larger macrocycle that is formed in the final step of the synthetic route by Bingel bisaddition to C_{60} . Because the malonate esters (73) are unsymmetric, this reaction could lead to an astonishingly complex reaction mixture with up to 22 spectroscopically distinguishable isomeric products. The combination of nanocapusle shadownask (degraded in a controlled fashion after the reaction), [10]CPP template (ring incorporated into the product) and tether effect (use of bismalonates connected through a long spacer) was thus necessary to obtain > 97% selectivity for trans-3 isomers along with ca. 30% yield (Fig. 26a). The authors demonstrate that for the optimal tether length (C14) an isomer fraction of up to 87% was obtained for one out of the three distinct trans-3 diastereomers (in,out-trans-3). The dynamic properties of this type of catenane were explored in silico by the Pavan group, who reported extremely fast translation of the [10]CPP along the non-fullerene parts of the larger macrocycle as well as a very long average residence time of 30 s on the fullerene binding site (Fig. 26b and C).

2D and 3D assemblies

Fullerenes and their derivatives have emerged as valuable building blocks to construct functional carbon materials, which are widely used in different fields, such as sensors, liquid crystals, optoelectronics, catalysts, and energy conversion. 19,171,415,416 To obtain highly ordered fullerene 2D or 3D fullerene materials, numerous approaches have been developed. 417,418 While covalent cross-linking establishes robust 2D frameworks, the principles of supramolecular chemistry are vital for establishing order during synthesis and can be harnessed to generate 3D vdW (hetero)structures.

6.1. Assembly of ordered fullerene materials

2D carbon materials have attracted increasing attention due to their unique fundamental properties that promise applications in electronic and optical devices, as well as in charge storage, heterojunctions, hydrogenation and photovoltaic applications. 417,418 Within the fullerene family, C₆₀ has been widely used as a building block to construct 2D structures owing to its

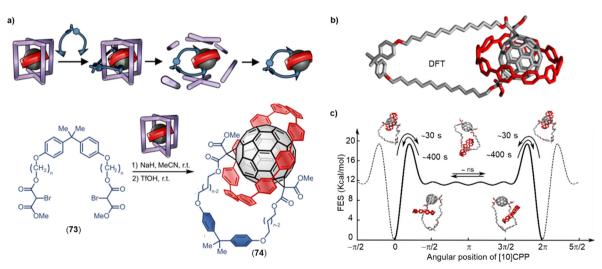


Fig. 26 (a) The synthetic strategy of C₆₀/[10]CPP-catenanes (74). (b) Atomistic molecular model of the C14-C₆₀/[10]CPP-catenane. (c) Free-energy diagram as a function of the angular position of [10]CPP along the larger ring of the catenane.

spherical shape and commercial availability. While the band gap of crystalline C_{60} is around 2.3 eV, 419 theoretical studies predict that the band gap of both polymeric and vdW-based C₆₀ monolayers ranges from 0.6 to 1.0 eV, 420 which is significantly lower than that of any experimentally isolated monolayer of an organic semiconductor. Furthermore, the band gap of C₆₀-based 2D materials highly depends on the symmetry of the structure and the distance between individual C_{60} moieties. 420,421 Recently, some important advances have been made in preparations of highly ordered 2D fullerene-based materials, representing a new approach to synthesize 2D materials with novel (optoelectronic) properties. 422-424 For example, Zheng and coworkers successfully synthesized covalently bonded C₆₀ networks by using an organic cation slicing strategy.422 C60 molecules formed radical anions upon heating with Mg, and new C-C bonds formed between adjacent C₆₀ moieties through [2+2] cycloaddition reactions. X-ray diffraction studies revealed that the bulk crystals exhibit a layered structure of alternative polymeric C₆₀ layers and Mg atomic layers. The Mg layers act as linkers between the adjacent C₆₀ layers by Mg-C bonds with the length of 2.22-2.37 Å, which made the C_{60} layers cannot be exfoliated by simple mechanical exfoliation.

Thus, the authors used an organic cation slicing strategy treating the bulk crystals with tetrabutylammonium salicylate (TBAS). This led to cleavage of the Mg-C bonds and the

formation of magnesium salicylate and tetrabutylammonium cations (NBu₄⁺) that replaced the Mg cations. (Fig. 27a) The NBu₄⁺-intercalated C₆₀ crystals were subsequently exfoliated by gentle manual shaking furnishing a few-layer quasi-tetragonal phase (qTP) and a monolayer quasi-hexagonal phase (qHP). Both two 2D materials exhibit great crystallinity and unique topological structures. Compared with graphene and individual fullerene molecules, the monolayer polymeric C₆₀ possesses a moderate band gap of 1.6 eV and good thermodynamic stability. The asymmetric lattice structure of the monolayer induces significant in-plane anisotropic properties, such as anisotropic phonon modes and conductivity, which can be attributed to the unique structure of the monolayer. Later in the same year, Peng rationalized the experimental band gap of these polymeric C_{60} materials in silico. The calculations also suggested that these monolayer C₆₀ materials have suitable band gaps, charge carrier mobilities and band edges for photocatalytic water splitting.425

Recently, Roy, Nuckolls and coworkers reported on "graphullerene",423 a graphene-like hexagonal layer of polymeric C_{60} linked by covalent bonds (Fig. 27b), synthesized using the chemical vapour transport (CVT) method to grow single crystals of a $(Mg_4C_{60})_n$ network, followed by removal of magnesium by dilute acid. This material exhibits a much higher thermal

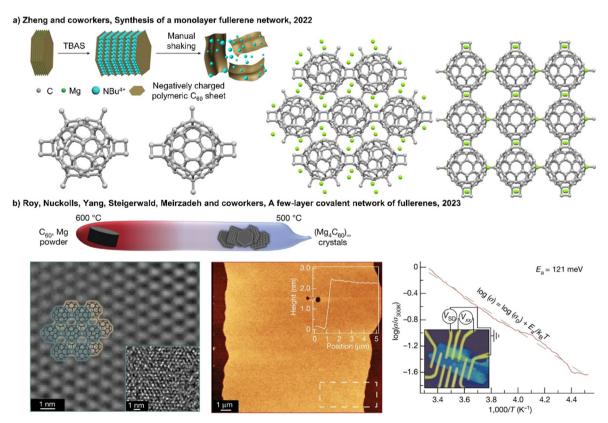


Fig. 27 (a) Schematic of organic cation slicing exfoliation and crystal structures of the bulk single crystal of qHP-C₆₀ and qTP-C₆₀ as well as their monomer C₆₀. Adapted from ref. 422 with permission from Springer Nature, copyright 2022. (b) Schematic of the CVT technique used for the growth of $(Mg_4C_{60})_{\infty}$ single crystals, iFFT and AFM image of a few-layer "graphullerene" flake, the log of the conductance (σ) versus temperature (T) for a 70 nm-thick $(Mg_4C_{60})_{\infty}$ -based device (a fit to a thermally activated (Arrhenius) model (dashed green line), inset is a typical device and corresponding four-terminal measurement scheme). Adapted from ref. 423 with permission from Springer Nature, copyright 2023.

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conductivity compared to molecular C₆₀, likely due to the inplane covalent bonding of layered polymeric C₆₀. In addition, Moiré-type superlattices were found by high-resolution transmission electron microscopy (HR-TEM) and near-field nanophotoluminescence spectroscopy. However, the methods used for small-scale preparation of carbon structures with covalently cross-linked C60 limit detailed characterization and represent a hurdle for applications. In this respect, an important advance was made in 2023 by Zhu, Ruoff and coworkers who reported the gram-scale synthesis of long-range ordered porous carbon (LOPC), 424 a new type of carbon. The synthesis started from C_{60} and was catalyzed by α -Li₃N at 550 $^{\circ}$ C and ambient pressure (Fig. 28). LOPC consists of broken C₆₀ cages mostly bonded via sp² carbon atoms, as evidenced by X-ray diffraction, Raman spectroscopy, magic-angle spinning solid-state NMR spectroscopy, aberration-corrected transmission electron microscopy and neutron scattering. LOPC possesses remarkable conductivity, with a value of $1.17 \times 10^{-2} \,\mathrm{S \, cm^{-1}}$ at room temperature and the conduction is close to the result from a combination of metalliclike transport over short distances punctuated by carrier hopping at a temperature lower than 30 K. Simulations of LOPC reveal that graphullerene is a metastable structure that exists as intermediate during the transformation from a fullerene-type to a graphene-type carbon allotrope and represents a transition from semiconducting

to metallic property with increasing temperature. Recently, Du and

coworkers explored the photocatalytic water splitting properties of a

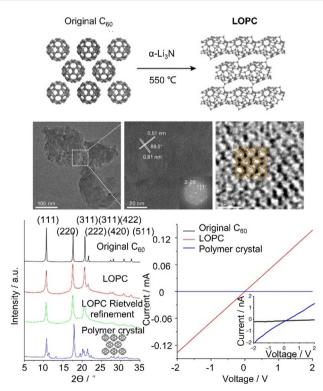


Fig. 28 Atomic structure of LOPC, TEM images of LOPC particles, Cu Ka (λ = 0.15418 nm) X-ray diffraction patterns with simulation for LOPC, and direct current voltage-current curves of three membranes made by mixing each carbon material with 5 wt%; polytetrafluoroethylene. Adapted from ref. 424 with permission from Springer Nature, copyright 2023.

few-layer C₆₀ network, which furnished production rates of H₂ and H₂O₂ of 91 and 116 μmol g⁻¹ h⁻¹, respectively. 426 Collectively, these recent breakthroughs offer new opportunities for exploring the fundamental properties, supramolecular properties and potential applications of covalently bonded 2D carbon materials.

2D or 3D fullerene crystals are different from these covalently cross-linked 2D materials, because they rely only on non-covalent forces such as π - and vdW interactions. 19,417,418,427,428 A large amount of 2D fullerene crystals with great diversity of shapes, such as 2D hexagons, 2D nanorhombus or hexagonal 2D nanosheets have been obtained by using the liquid-liquid interfacial participation (LLIP) method. 429-431 For example, Ariga and coworkers obtained a new class of C₆₀ crystals with bimodal pore architectures by employing LLIP with the use of solvents isopropyl alcohol (IPA), benzene and carbon tetrachloride (CCl₄). By changing the ratio of benzene and CCl₄, the shapes of 2D crystals were tuned. Interestingly, the bimodal pore crystals exhibited 2D hexagonal plate-like morphology and offered enhanced electrochemically active surface areas compared to pristine C₆₀. 432 Sathish and coworkers reported 2D hexagonal C₆₀ nanosheets using the LLIP method at the CCl₄/alcohol interface. The size of 2D C₆₀ crystals could be tuned by changing the alcohol (anti)solvent and the diameters of hexagonal nanosheets varied from \sim 7.5 µm, \sim 2.5 µm, and \sim 500 nm (IPA, ethanol, and methanol, respectively).433

The synthesis of 3D fullerene crystals, which are mostly based on C₆₀ or C₇₀ and their derivatives, is highly dependent on the shapes of fullerenes.434 C70 3D crystals were first prepared by Choi and coworkers in 2010 by using the precipitation approach. 435 Since then, several other methods have been developed to obtain fullerene 3D crystals, including static liquid-liquid precipitation, re-precipitation, solvent vapor annealing, and drop-drying.417 When using different methods, polymorphic structures of 3D fullerene crystals can be obtained that exhibit distinct properties such as enhanced fluorescence emission, hydrophobicity and photocurrent response, high surface-to-volume ratio beneficial for electrocatalytic hydrogen evolution reaction and sensing.417,418 Recently, Yang and coworkers developed a universal approach based on the LLIP method associated with ultrasonication to prepare the endohedral fullerene-based 3D crystals with tunable crystal shape. 434 Three metal nitrile "clusterfullerene" ($M_3N \subset I_h$ - C_{80} , M = Tb, Er, and Sc) 3D crystals were successfully obtained, and the shape of crystals could be easily switched by changing the solvent ratio of solvent to antisolvent. The crystal shape-dependent emission of the three clusterfullerenes was studied, revealing that crystals with dice shape emit stronger light than the cube-shaped crystals (Fig. 29a). Such an enhancement of photoluminescence in highly crystalline C₇₀ and higher fullerene C₇₈ relative to their powder states was also found by others, and was attributed to the increased crystallinity of fullerenes together with the decreased intermolecular interactions. 435-437 The formation of fullerene-based 3D materials not only provides an ordered arrangement of carbon cages, but also produces a regular network of pores that are typically larger in the case of less symmetric C_{70} . By changing the crystal preparation method, the

porous structure can also be tuned. Shrestha, Ariga and coworkers prepared highly crystalline C₇₀ cubes with the average edge lengths of *ca.* \sim 3.4 \pm 0.4 μm that possess holes extending 1-1.5 μm deep from the surfaces via dynamic LLIP. 438 Interestingly, the holes on the surfaces of the C₇₀ cube could be closed by regrowing a thin layer of fullerene, and subsequently be reopened by local irradiation via electron beam.

In addition to the formation of 3D crystalline materials by using pristine fullerenes, fullerene derivatives have also been utilized as building blocks to construct 3D frameworks or porous materials. 440-445 These frameworks are assembled by non-covalent interactions, and their structures can be tuned by manipulating the dynamic interactions within frameworks. Beuerle and coworkers reported a series of hexakis-substituted C₆₀ adducts bearing twelve carboxylic acid groups, and their incorporation as the polytopic organic linker into the hydrogen-bonding frameworks in solid state 446,447 and MOFs interlinked by metal ions (such as Zn2+, Ca2+, Cu2+, and Cd²⁺). 448,449 The interfullerene distances within the frameworks could be controlled by either alkyl space length between C₆₀ and carboxylic acid group or the type of cross-linking. 446-449 Recently, Martin, Costa and coworkers created dynamic molecular crystalline frameworks by using weak "sticky fingers" vdW interactions 439,450 based on a hexakis-substituted C60 adduct 75 synthesized using the Bingel-Hirsch reaction (Fig. 29b). The hexakis-substituted C₆₀ adduct 75 forms two different crystals from ethanol with and without Fe(BF₄)₂. Transformation between two polymorphs could be achieved by heating with and without ethanol. These materials are highly

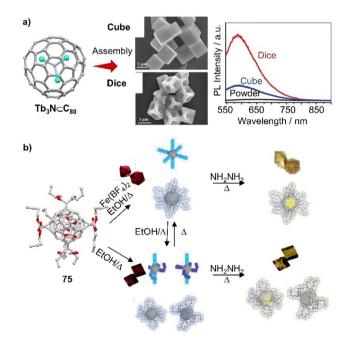


Fig. 29 (a) SEM images of cube- and dice-shaped $Tb_3N \subset C_{80}$ microcrystals and fluorescence spectra of $Tb_3N \subset C_{80}$ dice, cube, and powder. Adapted from ref. 434 with permission from Wiley-VCH, copyright 2019. (b) Dynamic behavior of a hexakis[60] fullerene 75. Adapted from ref. 439 with permission from Royal Society of Chemistry, copyright 2021.

dynamic, such that exposure to hydrazine vapor induced the selective hydrogenation of crystalline materials and a structural change. The molecular movements in the lattice and the selective reaction can be observed directly by single-crystal to single-crystal diffraction (Fig. 29b).

Self-assembled monolayers (SAMs) have been widely used for surface modification and act as the crucial interlayers and electronically active layers in organic electronic devices (such as organic light emitting diodes, organic photovoltaics, and organic thin film transistors). Not surprisingly, C60-functionalized SAMs exhibit interesting properties. 451-456 For example, Peukert and coworkers tuned the molecular order of C₆₀ functionalized phosphonic acid monolayers by changing the ratio of alkyl phosphonic acids (PA) and C60-functionalized octadecyl phosphonic acids (C₆₀-PA) on alumina substrates. 455 A pronounced maximum in sum-frequency intensity of the C₆₀ band is observed for SAMs with \sim 75% C₆₀-PA and \sim 25% PA. By using the same method, Clark, Halik and coworkers further confirmed that a mixture of C60-functionalized and nonfunctionalized spacer molecules can lead to a morphology with improved charge transport in self-assembled monolayer fieldeffect transistors. 453 By changing the ratio of C60-PA and PA from 100:0, 70:30, 50:50, and 30:70, the maximum drain currents of these monolayers were successfully tuned and quantum mechanical calculations revealed conduction pathways within the fullerene monolayers.

A series of fullerene amphiphiles have been synthesized, 457-459 different from neutral derivatives, whose relevant interfacial chemistry has been summarized in 2019.460 Recently, Nakamura and coworkers described a pseudo-C₅ symmetric fullerene amphiphile 76 attached with five 4-benzoic acid groups. The toluene/1-butanol/water solution of this compound spontaneously forms a 3 nm thick, free-standing 2D film as 1-butanol and toluene are evaporating gradually during a few hours at the water/air interface. (Fig. 30) The film was stabilized by hydrogen bonding between two fullerene layers. The size of this large-area film was up to several tens of cm2 and the photoconductivity of this film (transferred to a gold comb electrode) was determined as 1.4×10^{-4} S cm⁻¹. Furthermore, the film was laminated into a multilayer film either by using large amount of 76 solution or repeating the preparation procedure several times. 461

Fullerene liquid crystals (LCs) have attracted considerable attention, because they offer a combination of the excellent optoelectronic properties of fullerenes and the unique properties of liquid crystals. There are two approaches to construct fullerene LCs: the "molecular LC approach" is based on the covalent linking of fullerenes with large liquid crystal mesogens. The "supramolecular LC" method is based on supramolecular self-assembly.462 Using the molecular LC approach, nematic, cholesteric, smectic, and columnar phases could be achieved by introducing cholesterol and other functional groups to C₆₀ via flexible spacers or via a rigid "shuttlecock" geometry.463 However, the molecular LC approach is limited by the low content of fullerenes, which "dilutes" the optical and photophysical properties of fullerenes. The supramolecular LC approach was first developed by Nakamura and coworkers in

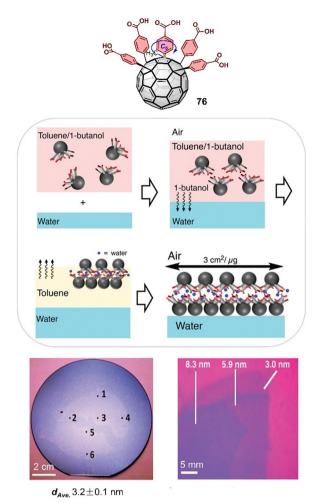


Fig. 30 Structure of pseudo- C_5 symmetric fullerene amphiphile 76, assembly of 2D film, the 2D film on 160.6 \pm 0.1 nm thick SiO₂/Si wafer (φ = 10.2 cm) (the thickness of six points were calculated by interference fringe shifts from visible-light reflection spectra), and sequential lamination of film on 288.8 nm thick SiO_2/Si wafer to form single, double, and triple films. Adapted from ref. 461 with permission from Wiley-VCH, copyright 2022.

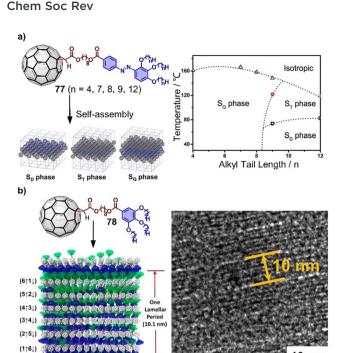
2002464 and further refined by other groups.465 This method relies on fullerene derivatives consisting of two parts: fullerenes and/or other PAHs provide π - π interactions between aromatic moieties, whereas and soft parts such as long alkyl chains provide vdW interactions. Both parts facilitate the assembly of highly ordered supramolecular structures with high aspect ratios, which exhibit liquid crystalline behaviour. The high fullerene content endows the fullerene-based LC with optoelectronic properties that are difficult to achieve with conventional molecular LCs. 466 Combining fullerene LCs with 2D crystals or superlattices takes these materials properties even further. 467 Recently, Tu, Li and coworkers employed a series of tetrablockmimic azobenzene-containing C_{60} dyads 77 (n = 4, 7, 8, 9, 12) to construct supramolecular LCs.468 This approach allows the manipulation of smectic supramolecular LC phases by changing the alkyl tail length of dyads (Fig. 31a). These materials exhibit excellent electron mobility of ca. 1.5×10^{-3} cm² V⁻¹ s⁻¹

due to the favourable combination of LC properties and 2D crystals. In a more recent study, well-defined superlattices were observed in supramolecular fullerene LCs by utilizing hierarchical self-assembly with a sphere-cone molecule as the building block 78. The formation of the superlattice was shown to improve the transient electron conductivity of the material (Fig. 31b).463

Self-assembled fullerene materials can act as sensors, catalysts, photoconductors or semiconductors in field-effect transistors.417,418 For instance, Li and coworkers prepared long-range $M_3N \subset C_{80}$ (M = Sc, Lu) single-crystal microwires by utilizing a pillar-structured template, which exhibited highly sensitive photoconductivity with a response time as low as 0.1 s, and also were employed in field-effect transistors. 469 Molecular gels have been used as spatially confined templates for the growth of C₆₀ crystals to obtain super-long crystalline C₆₀ fibers and large-area 2D crystals, which were utilized as photodetectors with high performance by Liu, Fang, and coworkers. 470,471 The dice-shaped Sc₃N ⊂ C₈₀ 3D crystals have been utilized as a support for the Pt-catalyzed methanol oxidation by Yang and coworkers. Catalyst performance was shown to be improved due to the larger surface area when compared with the cube shape crystals. 472 Shrestha, Ariga and coworkers prepared hierarchically structured C70 cubes and corn-husk-shaped fullerene C₆₀ crystals, which have been successfully applied as sensors for volatile aromatic solvents and acid vapors, respectively.473,474

6.2. Co-assembly of fullerenes and organic molecules

Fullerenes and their derivatives have been studied as building blocks to construct supramolecular (co)polymers in solution. Beside the work by Haino on helically organized fullerene arrays (see Section 4.2 or Fig. 12b), 177 many other groups have made efforts to construct fullerene-based supramolecular polymers. For example, Langa and coworkers synthesized a fullerene-bis-Zn-porphyrin e-bisadduct as the monomer, 475 which assembled into large donut structures driven by charge transfer interactions between porphyrin-bearing arms and fullerenes. This self-assembled D-A polymer possesses long-lived charge separated states upon light irradiation, specially, the lifetime of final charge-separated state is upon to 40 µs, which is relevant for single-component light harvesting devices. Sessler and coworkers employed a thiopropyl-functionalized tetrathiafulvalene-annulated calix[4]pyrrole (TTP-C[4]P) and phenyl C₆₁ butyric acid (PCBA) as monomers to assemble an alternating supramolecular polymer in a 7:3 mixture of CHCl₃ and CS2. The self-assembly is driven by the charge transfer interaction between electron rich pocket of TTF-C[4]P and fullerene and the hydrogen bonding between TTF-C[4]P and carbolic acid moiety.476 The supramolecular polymer could be disaggregated by addition of organic acid or electrolysis. Later, Sessler and coworkers reported an extended tetrathiafuvaleneporphyrin macrocycle, which acts as a ball-and-socket receptor for C₆₀ and C₇₀. This macrocycle and fullerenes assemble into 3D supramolecular organic frameworks (SOFs) in the solid state. The C70-based SOF exhibits remarkable electrical



Molecular structure of tetrablock-mimicazobenzenecontaining C_{60} dyads 77 (n = 4, 7, 8, 9, 12), molecular packing model for dyads in the S_{T} phase and S_{Q} phase, with face-centered tetragonal fullerene packing in the 2D crystals viewed along the [001] zone and the [110] zone (blue dots indicate voids between the packed molecules and orange rectangles alkyl-tail-substituted azobenzene moieties). Adapted from ref. 468 with permission from Wiley-VCH, copyright 2018. (b) The sphere-cone molecule 78, representation of molecular packing, and TEM image of layered superlattice structure. Adapted from ref. 463 with permission from American Chemical Society, copyright 2020.

conductivity ($\sigma = 1.3 \times 10^{-8} \text{ S cm}^{-1} \text{ at } 298 \text{ K}$). These supramolecular polymers offer unique advantages over traditional covalent polymers due to the reversible nature of noncovalent interactions, such as response to the redox, pH, heating, light, or small molecules.

Pristine fullerenes have been successfully co-assembled with molecules to fabricate novel functional materials. For example, Jeong, Jang, and coworkers prepared well-defined hierarchical nanostructures, consisting of a host-guest complex between pyrene-based tweezers 79 and C₆₀. Due to its layered structure that comprises a 2D array of C₆₀ moieties, the material exhibited high electron mobility of 1.7 \times 10⁻² cm² V⁻¹ s⁻¹ (Fig. 32a).477 Although several porphyrin/fullerene supramolecular co-assemblies/crystals have been reported, 478-481 photoinduced charge transfer between these two organic semiconductors was rarely studied, and these co-assemblies/crystals exhibited short lifetimes of charger transfer states and low charge mobility. In a co-crystal of a zinc-metalated porphyrin box 80 with C_{60}/C_{70} , 482 Kim and coworkers observed a tightly packed square-planar core of four C₆₀ or C₇₀ surrounded by six porphyrin boxes. This tight packing pattern provides high charge mobility and allows for forming long-lived chargeseparated states. Relative to crystalline box 80, a significant

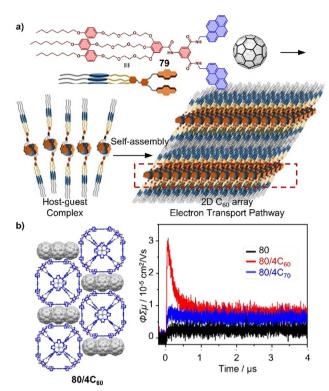


Fig. 32 (a) Hierarchical assembly of bispyrene tweezers 79 and fullerene. Adapted from ref. 477 with permission from American Chemical Society, copyright 2019. (b) Co-assembly of porphyrin box 80 with four equivalents C₆₀ and flash-photolysis time-resolved microwave conductivity of 80, 80/4C₆₀, and 80/4C₇₀. Adapted from ref. 482 with permission from American Chemical Society, copyright 2020.

enhancement of photoconductivity was observed in architectures, 10-fold and 3-fold enhancement in $\varphi \Sigma \mu$ for 80/4C₆₀ and 80/4C₇₀, respectively. The photoconductivity of C₇₀-based material is lower than C₆₀-based material, which was ascribed to different electronic couplings between porphyrins and C_{60}/C_{70} . (Fig. 32b).

Metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) have emerged as promising materials with potential applications in a wide range of research fields. 483 Because most MOFs or COFs have relatively large pores, the encapsulation of guests has been widely explored and fullerenes are an evident choice due to their relatively large size and optoelectronic properties. 484-494 Berna and coworkers employed a flexible benzylic amide macrocycle attached with two carboxylic acid groups as the ligand to prepare copper(II)and zinc(II)-based MOFs, which could selectively encapsulate C_{60} from a mixture of C_{60} and C_{70} . The encapsulation of fullerenes was used to modulate the optoelectronic properties of MOFs due to the electronic interaction with hosts, leading to the unique properties and applications. For instance, Zhu and colleagues employed a zirconium-based MOF 81 as a host, 489 composed of 1,3,6,8-tetrakis(4-benzoate) pyrene (TBAPy) linkers and Zr-oxo nodes, to encapsulate C₆₀ (Fig. 33a). The uneven charge distribution in C₆₀⊃81 provides a robust built-in electric field, which is 10.7 times higher than that in 81. Using this

material, photocatalytic hydrogen evolution was found to be significantly enhanced thanks to the encapsulation of C₆₀. The interplay between MOF hosts and fullerenes was also demonstrated to boost photoelectric conductivity. 486,488 Heinke and coworkers constructed a crystalline porphyrin-based MOF (82) incorporating C₆₀, 487 providing rapid charge separation. Thanks to the efficient formation of holes and electrons, good photoconductivity was observed with an on-off photocurrent ratio of two orders of magnitude (Fig. 33b). The chirality of complex fullerene derivatives (e.g. certain fullerene bis-adducts) is a fascinating topic. However, imparting chirality to pristine C₆₀ without installation of substituents is far from trivial. To this end, Uemura and coworkers employed a chiral MOF (83) hosting the highly symmetric C₆₀ using a self-assembly strategy (Fig. 33c), of which C₆₀ could be incorporated into the chiral channels of MOF. 485 This approach can therefore endow highly symmetric, achiral compounds with chirality.

Surface co-assembly is a powerful method for creating wellorganized 2D arrays that exhibit excellent performance in photovoltaic devices, sensors, and catalysts. 427 For example, the Rabe group used hydrogen bonding to self-assemble a trimesic acid monolayer as the template for mono- or bilayers of complexes of fullerenes and oligothiophene macrocycles. 206 Recently, Tanaka and coworkers reported the formation of a periodic monolayer of spatially separated C₆₀ moieties on an Au(111) surface using carbazole-salphens or Ni-salphens containing macrocycles as fullerenes hosts. The pattern of discrete C₆₀ units on the surface was thermally stable up to 200 °C under ambient pressure.212 In related work, Zeng and coworkers created ordered 2D C₆₀

patterns on a highly oriented pyrolytic graphite (HOPG) surface using host-guest complexes of aggregation-induced emissive macrocycles and fullerenes. 495 Rosei and coworkers employed a 2D covalent organic framework as surface-confined template to host the C₇₀ moieties, imposing anchoring effects on the LC growth of C70 molecules, forming several fullerene-based LC mesophases, which cannot be observed under other conditions. 496 These findings highlight the potential of fullerene-based surface co-assemblies for developing advanced materials and functional devices.

Summary and outlook

Thanks to the rapidly decreasing price of C₆₀ (as low as 20 USD per gram) and the relevance of fullerenes as organic electronic materials, fullerene-based supramolecular chemistry has witnessed remarkable advances in the past decade. For instance, selective fullerene functionalization methods were developed by encapsulating fullerenes in supramolecular hosts and thus shutting down undesired reaction pathways or enhancing reactivity. With the help of such selectively modified fullerenes, supramolecular dyads and mechanically interlocked architectures have been prepared that exhibit unique optoelectronic systems. Endohedral fullerenes and open-cage fullerenes offer not only an opportunity to tune fundamental properties of fullerenes, but also a unique "playground" for the creation of functional supramolecular architectures.

Over the past decade, a large number of effective hosts for fullerenes have been synthesized, and the relevant host-guest

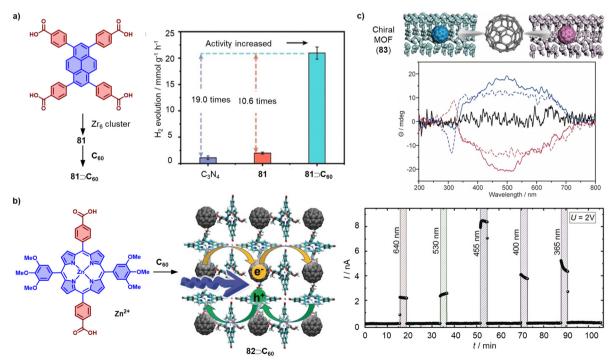


Fig. 33 Selected encapsulations of fullerenes into MOFs to achieve: (a) improved photocatalytic hydrogen evolution, (b) improved photoconduction, (c) chirality transfer from MOF to C₆₀. Adapted from ref. 489, 487 and 485 with permission from Wiley-VCH, copyright 2023, 2019, 2021 for (a), (b) and (c), respectively.

complexes have shown significant potential in selective functionalization reactions, catalysis, the stabilization of short -lived compounds and the tuning of spin properties. Fullerenes have also been utilized as building blocks to construct covalent or non-covalent 2D/3D carbon materials, which show great potential for electron transport, conductivity, liquid crystallinity and catalysis. We expect that the recent trend towards the preparation of ordered, high-performance fullerene materials will continue and that increasing effort will be devoted towards harnessing the unique spin properties of nonconventional fullerenes, which will require further advances in both synthesis and supramolecular chemistry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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