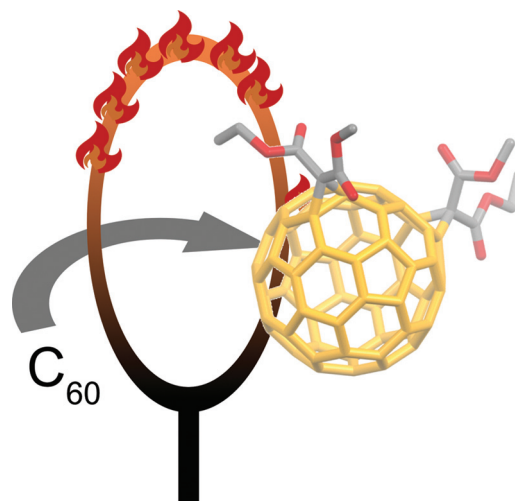


Supramolecular Approaches for Taming the Chemo- and Regiochemistry of C₆₀ Addition Reactions

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Dedicated to Prof. Peter Bäuerle on the occasion of his 65th birthday.

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Abstract The chemo- and regioselective functionalization of fullerenes is a long-standing problem of organic synthesis. Over the past five years, this fundamental challenge has gained technological relevance, because studies on single bis-adduct isomers in new-generation solar cells have demonstrated that the widespread use of isomer mixtures leads to suboptimal power conversion efficiencies. Herein, we review recent work on supramolecular approaches for achieving chemo- and regioselective syntheses of multiply functionalized derivatives of C₆₀.

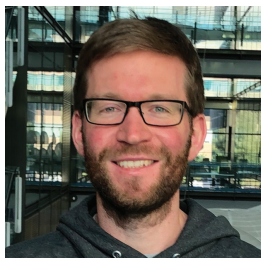
Key words fullerenes, template effect, supramolecular chemistry, regioselectivity, organic photovoltaics, host-guest chemistry

Introduction

Since the buckminsterfullerene C₆₀ became available in bulk,¹ a vast body of research has been dedicated to its chemical functionalization and modification.² Much of this research is motivated by the need to make fullerenes highly soluble and therefore enable the preparation of organic electronic devices by solution processing.³ Diels–Alder or Prato cycloadditions,⁴ the Bingel,⁵ Bingel–Hirsch⁶ as well as related cyclopropanation reactions⁷ represent the most

commonly used transformations, whose feasibility under mild conditions is mainly due to the unique reactivity of the fullerene double bonds.^{2a} In all these reactions, different numbers of addends can be installed at the fullerene core, such that the so-called mono, bis, tris, tetrakis, pentakis or hexakis products are obtained.⁸ In respect to this problem of chemoselectivity, herein we mainly focus on the formation of bis-adducts, since these derivatives represent a “sweet spot” regarding solubility and electron-acceptor capability.⁹ When forming bis-adducts with symmetrical reagents, up to eight different regioisomers are obtained, because the [6,6]-double bonds at the *cis*-1, *cis*-2, *cis*-3, *e*, and *trans*-1, *trans*-2, *trans*-3, *trans*-4 positions are in principle all accessible for addition reactions (Figure 1). When using unsymmetrical reagents, up to 37 different regioisomers can be obtained, which all possess (slightly) different optoelectronic properties. It is therefore important to ask the question whether the problem of regioselectivity is relevant to the performance of multiply functionalized fullerenes in bulk heterojunction or perovskite solar cells (PSCs). As we will outline in the following paragraph, this question has been addressed in the past decade by several research groups and the answer appears to be a clear “yes”. Against this background and while keeping the vastly decreased price of C₆₀ in mind, methods for the isomerically pure production of fullerene bis-adducts could lead to a revival of fullerene electron acceptors at a time when structurally complex, non-fullerene electron acceptors seem to be winning the race.¹⁰ The main focus of this short review is therefore a discussion of new approaches to tackle the chemo- and regioselectivity challenge associated with C₆₀ multiple additions.¹¹

Biosketches



Sebastian B. Beil studied chemistry in Kiel and Stockholm and finished his M.Sc. at the CAU Kiel in 2015 (Anne Staubitz) as a fellow of the Studienstiftung des Deutschen Volkes. Funded by a Kekulé fellowship and the Graduate School of Excellence Materials Science in Mainz, he joined

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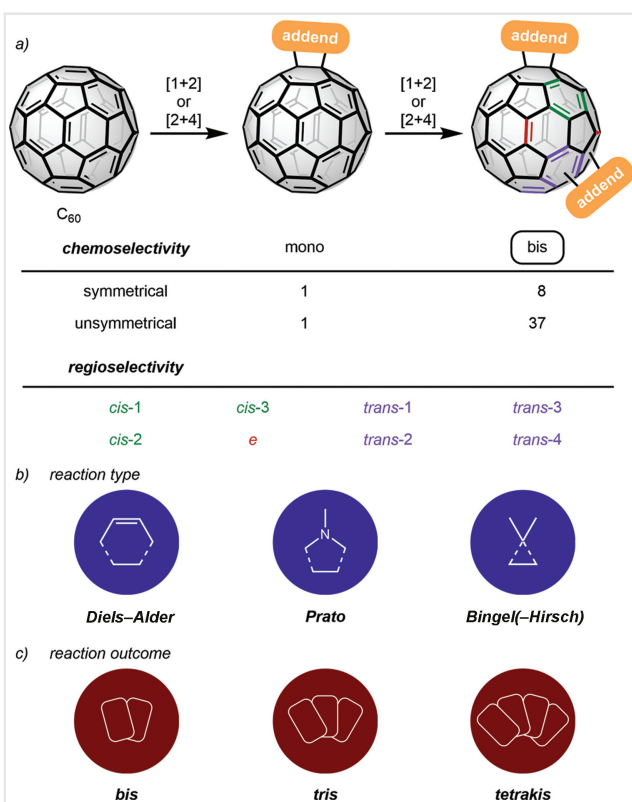


Figure 1 a) Chemoselective adduct formation (mono and bis) of C_{60} leads to distinct regioisomers (*cis*, *e* and *trans*) for bis-adducts. Icons used in this article to classify b) reactions types and c) reaction outcomes.

Effect of Fullerene Regioisomers on the Performance of Photovoltaic Devices

Mono-adducts generally have vastly increased solubilities when compared to unfunctionalized fullerenes, as exemplified by phenyl- C_{61} -butyric acid methyl ester (PCBM; Figure 2a),^{7b} which is commonly used as an electron acceptor in bulk heterojunction organic solar cells (BHJ-OSCs)¹² or as an n-type/ambipolar charge carrier in organic field-effect transistors.¹³ The widespread application of fullerenes and their derivatives in organic electronics is mainly due to their small reorganization energy upon electron transfer within the active layer of the device,¹⁴ which in turn is a result of their exceptionally rigid structure. Compared to silicon-based solar cells, power conversion efficiencies (PCEs, η) in solution-processed, fullerene-based solar cells are still somewhat lower, but single-layer devices now routinely exceed the 10% mark¹⁵ and in a tandem solar cell featuring PC[70]BM, a record PCE of 17.3% was reported (Figure 2b).¹⁶ As shown in Figure 2a, transforming C_{60} into a mono-adduct such as PCBM increases solubility in toluene by one order of magnitude. The addition of another phenyl-butyrate ester addend results in bis-PCBM, which exhibits even higher solubility and a higher LUMO energy as a result of the interrupted π -system.^{9,17} Due to their favorable properties, this class of fullerene bis-adducts found widespread application in BHJ-OSCs as well as PSC.¹⁸ Higher LUMO energies are beneficial in BHJ-OSC devices, since they are directly associated to improved open circuit voltages (V_{oc}),¹⁹ which

translate into higher PCE (Figure 2b).²⁰ The incorporation of substituents onto the methano-fullerene core not only leads to solution-processable devices,²¹ but also improves the chemical stability towards photo-dimerization.²² Aside from bis-PCBM, two widely used electron acceptors are indene- C_{60} -mono-adduct and the respective bis-adduct ICBA, which features an attractive LUMO energy level of -3.5 eV (Figure 2c).²³

Established syntheses of C_{60} bis-adducts (e.g. bis-PCBM, ICBA) unfortunately lack control of chemoselectivity and regioselectivity, which is exemplified by the HPLC trace depicted in Figure 2d, where each of the nine fractions (F1–F9) represents at least one isomer.²⁴ The conventional method to separate these isomers is HPLC purification with Buckyprep columns,²⁵ which is time-consuming and not particularly scalable. Nevertheless, a number of studies over the last few years have highlighted that isomer-pure C_{60} derivatives typically enhance device properties and that the widespread practice of using isomer mixtures leads to suboptimal device characteristics.²⁶ For instance, Dennis, Hummelen and coworkers have shown in a recent study on the HPLC separation of 18 bis-PCBM isomers that the optoelectronic properties of these regioisomers differ to a surprisingly large extent.²⁷ In 2017, two remarkable reports established the superiority of isomer-pure C_{60} bis-adducts in PSCs.^{18e} Huang and coworkers could show that an electron transport layer comprising isomer-pure *trans*-3-ICBA led to ideal charge extraction, enabling a stabilized PCE of 18.5%.²⁸ Grätzel, Bi and others

demonstrated that an isomer-pure bis-PCBM templating agent leads to better stability, efficiency, and reproducibility of a PSC and a PCE of 20.8%.²⁹

In arguably the most comprehensive case study to date on the use of fullerene bis-adducts in BHJ-OSCs, Li, Brabec and coworkers have isolated 12 individual ICBA regioisomers by three purification cycles of preparative HPLC (Figure 2d).^{24,30} Remarkably, the PCE in BHJ-OSCs was found to vary between 0.5% and 5.9%, even when only three different kinds of *trans*-3-ICBA isomers (a–c) were considered (Figure 2d–e).²⁴ This finding confirmed that slightly different fullerene regioisomers exhibit vast differences of performance in BHJ-OSCs, even though their LUMO levels are rather similar (Figure 2e). Most importantly, the *trans*-3(a)-ICBA isomer, which happens to be the most abundant in the original reaction mixture, did not only outcompete all other pure regioisomers, but also the mixture of isomers (as prepared). The authors tentatively explain these findings by the difference of solubility between the various ICBA regioisomers and by the importance of a match between acceptor and donor (here: P3HT) solubility.

Finally, it is worth noting that the issue of regioisomer mixtures is not limited to bis-adducts of the prototypical fullerene C_{60} . In fact, regioisomer mixtures are even more common in derivatives of higher fullerenes due to their intrinsically lower symmetry. For this reason, even the mono-adducts of C_{70} , as in the record-breaking electron acceptor PC[70]BM,¹⁶ exist as a mixture of regioisomers. Again, recent reports strongly suggest that these

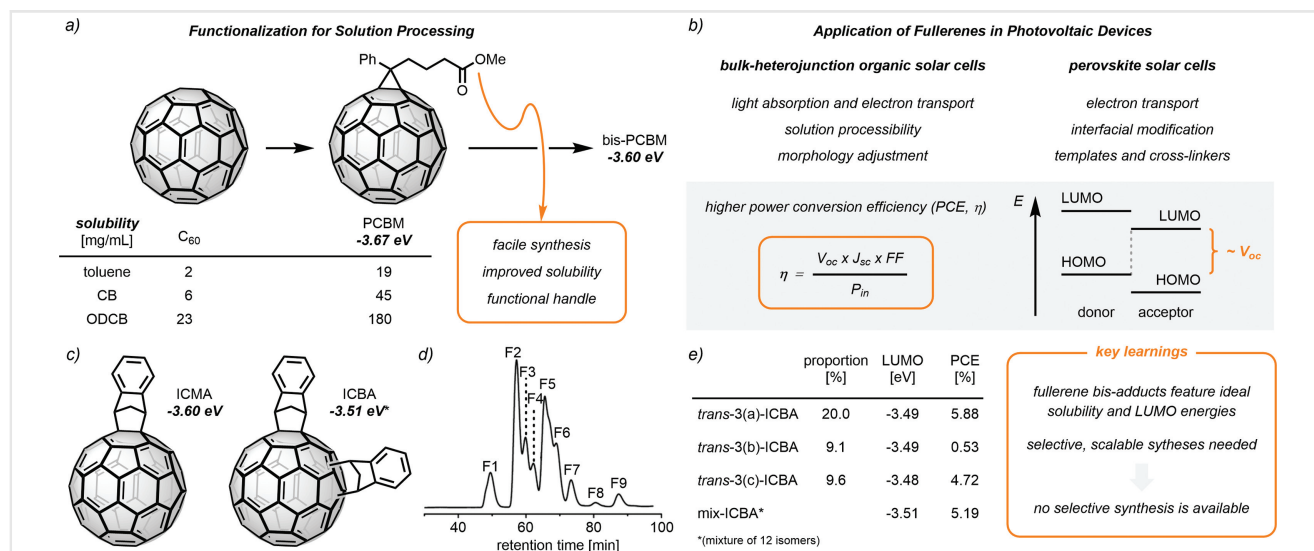


Figure 2 a) Structure of the most common fullerene mono-adduct used in organic photovoltaics (PCBM: phenyl- C_{61} -butyric acid methyl ester) and representative data on the effect of functionalization on the solubility in non-polar organic solvents.⁷ CB: chlorobenzene, ODCB: 1,2-dichlorobenzene. LUMO energy levels highlighted in bold. b) The use of fullerene adducts in bulk-heterojunction and perovskite solar cells is motivated by the opportunity to fine-tune solar cell characteristics, especially the power conversion efficiency (PCE).^{19d} Abbreviations: V_{oc} : open-circuit voltage, FF: fill factor, J_{sc} : short circuit current, P_{in} : incident solar power. c) Structures of common fullerene (bis-)adducts. ICMA: indene- C_{60} -mono-adduct, ICBA: indene- C_{60} -bis-adduct. d) HPLC chromatogram of ICBA, as synthesized, reproduced with permission from Ref. 24. Copyright The Royal Society of Chemistry. e) Comparison of PCEs obtained with different ICBA regioisomers in BHJ-OSCs.²⁴ Different *trans*-3 isomers (a–c) arise from the relative configuration of the unsymmetrical indene moieties, respectively.

regioisomers of C_{70} do not contribute equally to the performance of photovoltaic devices.^{26d,31}

From Conventional to Supramolecular and Photoresponsive Tethers

For the reasons outlined above, methods for the isomer-pure synthesis of C_{60} bis-adducts or C_{70} mono-adducts could have a large impact on the field of organic electronics. The first use of tethers to tackle this challenge was described by Diederich in 1994 (Figure 3a, left)³² and was followed by numerous studies since then.³³ Herein, we will focus on reports that deal with C_{60} as a substrate and are particularly noteworthy from a perspective of supramolecular chemistry. The first such study is Kräutler's ingenious solid-state synthesis of a Diels–Alder *trans*-1 C_{60} bis-adduct.^{33a} This remarkable reaction outcome is made possible by the linear stacking in the crystal structure of the mono-adduct of C_{60} with anthracene and the entropy-driven crystal-to-crystal transformation of the mono-adduct into a mixture of pristine C_{60} and the *trans*-1 bis-adduct.^{33a} Interestingly, Kräutler's approach was recently used to prepare an isomer-pure C_{60} bis-adduct that furnished a PCE of 8.1% in a polymer solar cell.³⁴

The use of a tether that harnessed a non-covalent interaction between a metallated porphyrin and C_{60} was described by Hirsch in 2006 (Figure 3a, right).³⁵ By using this Co^{II} porphyrin, a twofold Bingel³⁶ reaction towards the

respective bis-adduct was achieved with high *trans*-1 and *trans*-2 selectivity. The paramagnetic nature of the cobalt center was maintained and the solid-state structure revealed a C_{60} –Co distance of 2.7 Å, which is below the sum of the van der Waals radii and leads to a remarkable crystal packing featuring linear stacks of the molecules. Relying even more heavily on supramolecular chemistry, Torres and coworkers applied the strong π – π interactions between two porphyrins to enable a high regioselectivity for *cis*-substituted bis-adducts of C_{60} in a Prato cycloaddition reaction (Figure 3b, left).³⁷ This purely supramolecular tether approach resulted in the *cis*-1 regioisomer and an unidentified second isomer as sole reaction products in 38% and 62% relative yield, respectively. Notably, the formation of *trans*-isomers, which are usually the predominant reaction products in this reaction, was completely suppressed, highlighting the potential of strong supramolecular interactions to significantly affect the regiochemistry of this reaction.

Reporting an elegant example of a light-switchable tether, Đorđević et al. demonstrated that azobenzene-based tethers can deliver selectivity of C_{60} bis-addition depending on the configuration of the tether (Figure 3b).³⁸ The (*Z*)-tether was able to shift the typical distribution of the Bingel reaction (compare grey bars in the histograms of Figure 3b) towards the predominant formation of the *e* regioisomer (81% rel. yield), while the (*E*)-tether furnished the *trans*-4 regioisomer (91% rel. yield).

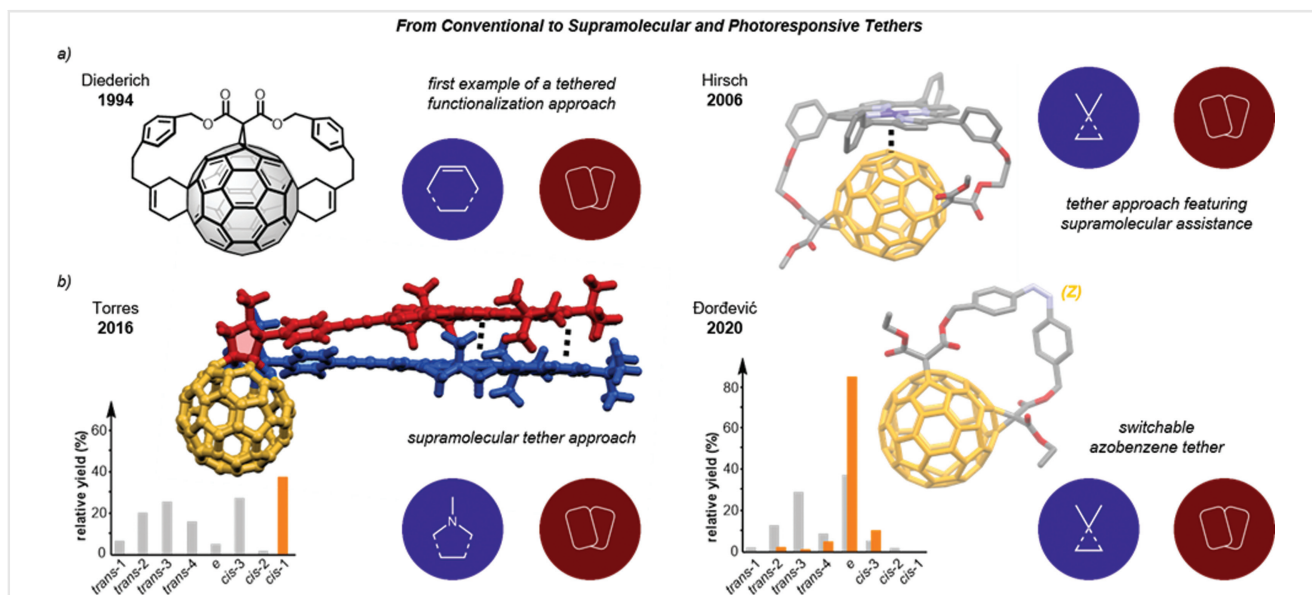
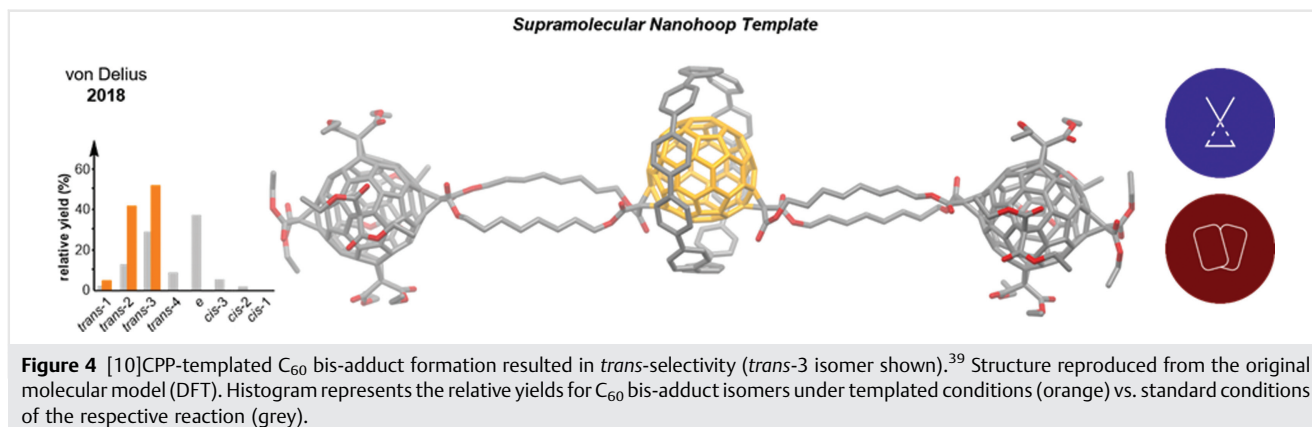


Figure 3 a) Conventional tether approaches for the formation of C_{60} bis-adducts. First example by Diederich using a prefucionalized C_{60} precursor.³² Templated twofold Bingel reaction of a Co^{II} porphyrin by Hirsch and coworkers.³⁵ π – π interaction indicated by the dashed line. Structure reproduced from CCDC 292094. b) Supramolecular tether approaches for the formation of C_{60} bis-adducts by porphyrin stacked *cis*-selective Prato reaction. Reproduced with permission from Ref. ³⁸. Azobenzene-templated twofold Bingel reaction to yield almost exclusively *e*-selective C_{60} bis-adduct.³⁷ Structure reproduced from CCDC 1911361. Histograms represent the relative yields for C_{60} bis-adduct isomers under templated conditions (orange) vs. standard conditions of the respective reaction (grey).



Nanohoop Template

A *trans*-selective approach for the synthesis of C₆₀ bis-adducts was reported in 2018 by von Delius and coworkers.³⁹ The method is based on the strong supramolecular interaction between commercially available nanohoop [10]CPP (cycloparaphenylene) and C₆₀,⁴⁰ which allowed for the preparation of two unprecedented [2]rotaxanes (Figure 4).³⁹ When carrying out a Bingel³⁶ reaction with the [10]CPP complex of a C₆₀ mono-adduct, the nanohoop acted as a template and directed the reaction to the *trans*-2 and *trans*-3 bis-adducts (43% and 52% rel. yield), accompanied by only a small amount of the *trans*-1 isomer (4% rel. yield). The presence of the nanohoop led to the complete suppression of the formation of the *e*-isomer, which typically represents the predominant product in Bingel reactions and importantly, the expensive nanohoop could be recycled after use. Transient absorption studies provided insights into the photo-induced electron transfer between the mechanically interlocked [10]CPP ring and the central C₆₀ bis-adduct. We expect that progress in the synthesis of novel CPPs^{40c,41} will lead to further examples of mechanically interlocked architectures featuring C₆₀ bis-adducts.

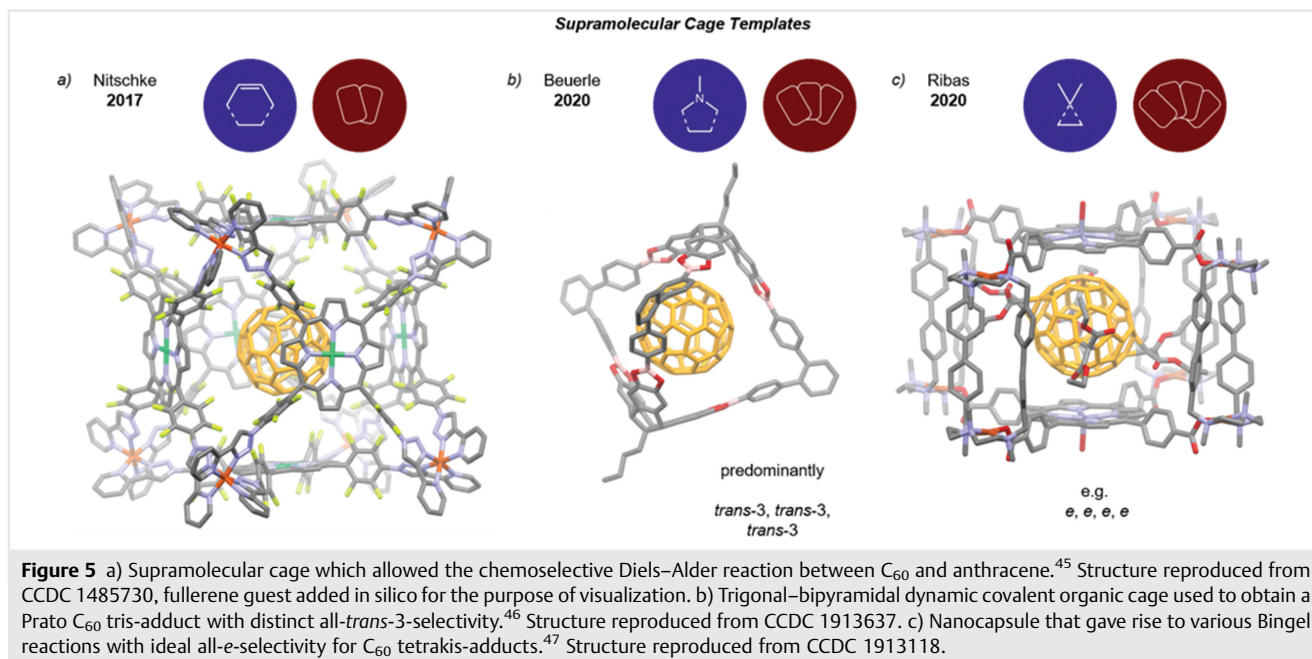
Self-Assembled Cages as Shadow Masks

Inspired by the strong π - π interaction between polyaromatic hydrocarbons or porphyrins and fullerenes (vide supra), a variety of capsules⁴² featuring these motives were designed to act as shadow masks for fullerene addition reactions. For instance, the confinement of C₆₀ in a metallo-supramolecular cage with a single orifice was used by Clever's group to halt the Diels-Alder reaction between C₆₀ and an excess of anthracene at the stage of mono-addition, representing an impressive case of chemoselectivity.⁴³ In an earlier study, Nitschke and coworkers used a self-assembled metallo-supramolecular cage to confine C₆₀⁴⁴ and thus changed the outcome of Diels-Alder reactions

(Figure 5a).⁴⁵ The authors were able to demonstrate the chemoselective formation of the bis-adduct between C₆₀ and indene or anthracene by Diels-Alder cycloaddition. Even though the regioselectivity of the addition reaction was not investigated, this study has inspired others in the field to utilize self-assembled cages for generating regioisomerically pure C₆₀ multiple adducts.

In 2020, Beuerle and coworkers described an organic, self-assembled cage that can act as a tripodal, dynamic covalent "shadow mask" and thus enables the remarkably selective all-*trans*-3 formation of a C₆₀ tris-adduct in 25% relative yield (Figure 5b).⁴⁶ The selectivity is a consequence of the threefold symmetry of the organic cage and is surprisingly high for this Prato reaction, which could theoretically furnish 46 distinct regioisomers. In a reaction featuring only 5 instead of 9 equivalents of the addition reagent, the authors were also able to obtain the *trans*-3 C₆₀ bis-adduct, albeit with somewhat lower chemo- and regioselectivity, indicating that the third addition reaction is the key for the selective formation of the all-*trans*-3 tris-adduct. The structure of the host-guest complex was elucidated by single-crystal X-ray diffraction (XRD; Figure 5b), and molecular modelling studies helped rationalize the formation of the three observed tris-adduct side products.

Also in 2020, Ribas and coworkers reported a sophisticated Pd-based nanocapsule,⁴⁷ which allowed the inclusion of C₆₀ and the stepwise performance of multiple Bingel reactions with exquisite equatorial (*e*) selectivity. It is remarkable that the self-assembled nanocapsule is stable under the reaction conditions that feature an excess of the strong base NaH, and it seems likely that the aforementioned molecular cages would not be compatible with this reaction mixture. Under optimized conditions, the shadow-mask approach led to the symmetry-matched *e,e,e,e*-C₆₀-tetrakis-adduct (Figure 5c), in astonishing 99% yield.⁴⁷ By varying the amount of malonate reagent the authors were able to obtain mono-, bis-(*e,e*) or tris (*e,e,e*)-adducts, and by carrying out the reaction in a two-step fashion a hexakis-adduct equipped with two different types of addends was accessible. Single-crystal XRD of the inclusion

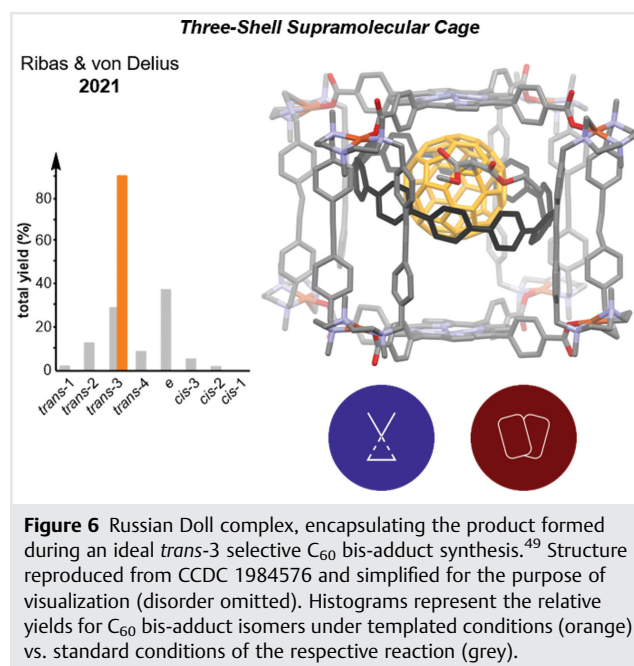


complex of the four-fold reaction product (Figure 5c) along with molecular dynamics simulations provided a deep understanding of the perfect regioselectivity based on strong inclusion and symmetry match. Finally, the authors demonstrated that a biphasic protocol based on anion metathesis enables the use of substoichiometric amounts of the Pd-based nanocapsule.⁴⁸

Russian Doll Shadow Mask

Building on their previously discussed nanohoop (Figure 4) and supramolecular mask approaches (Figure 5c), Ribas and von Delius have recently joined forces to investigate the tantalizing question whether a three-shell supramolecular complex can be used to generate isomerically pure C_{60} bis-adducts.⁴⁹ The authors therefore designed an extended Pd-based nanocapsule that was large enough to allow the inclusion of the $C_{60}C[10]CPP$ complex, as was clearly demonstrated by single-crystal XRD of the Russian Doll complex (Figure 6). The outcome of the corresponding Bingel³⁶ reaction was far from obvious, since the nanohoop by itself would favor the *trans*-2 and *trans*-3 bis-adducts, whereas the previously studied nanocapsule had exclusively produced *equatorial* multiple adducts. The observed perfect *trans*-3 selectivity in 90% yield is a promising finding in the context of organic photovoltaics (vide supra), where *trans*-3 isomers seem to be the most valuable fullerene bis-adducts.^{24,28} The result is also surprising, because the 120° angle between addends in a *trans*-3 C_{60} bis-adduct seemingly represents a symmetry mismatch with the nanocapsule that features four orthogonal openings. The solid-state structure of

the Russian Doll complex encapsulating the reaction product (Figure 6) shed light on this counter-intuitive result. Interestingly, the extended nanocapsule was large enough to allow the two substituents present in a fullerene *trans*-3 adduct to be accommodated in two contiguous windows, spanning an angle of 120° if one substituent is pointing to the top and the other to the bottom of the cage (Figure 6). The reaction result is therefore best understood such that the nanohoop completely shuts down any equatorial (e, 90°)



reactivity, while the symmetry of the nanocapsule is not reconcilable with the 144° angle between substituents in a *trans*-2 bis-adduct. The *trans*-3 bis-adduct (120°) is therefore the only possible reaction product, while the strong binding constants holding the three species together in acetonitrile are crucial for avoiding background reactivity (K_a ($C_{60}C[10]CPP$) = $5.7 (\pm 0.4) \times 10^6 \text{ M}^{-1}$ and K_a ($[10]CPP$ nanocapsule) = $1.1 (\pm 0.1) \times 10^5 \text{ M}^{-1}$, both determined in toluene:acetonitrile, 9:1). Isolation of the product was achieved by means of a workup protocol featuring washing with chloroform and displacement of the bis-adduct with pristine C_{60} , thus providing an opportunity for the recycling of $[10]CPP$ and nanocapsule, should a scale-up be desired. The scope of the reaction was demonstrated for substrates with low-to-moderate steric bulk, while the bulkiest substrate di-tert-butyl bromomalonate represents a limitation of the approach.

Conclusions and Outlook

In the past five years two developments have coincided that could potentially cross-fertilize during the 2020s: (i) researchers in the field of materials science have established that isomer-pure fullerene bis-adducts significantly outperform the previously used isomer mixtures in bulk heterojunction and PSCs. (ii) Supramolecular chemists have demonstrated that suitable host systems can be used to tame the chemo- and regioselectivity in C_{60} multiple addition reactions.

With the Bingel, Prato and Diels–Alder reactions, the described advances already cover some of the most important C_{60} addition reactions. While two supramolecular approaches have achieved partial regioisomeric control (von Delius: predominant *trans*-2 and *trans*-3 bis-adducts³⁹; Beuerle: predominant all-*trans*-3 tris-adduct⁴⁶), only two examples of exclusive selectivity have been reported to date (Ribas: *e* bis-adduct, *e,e,e* tris-adduct and *e,e,e,e*, tetrakis-adduct⁴⁷; Ribas & von Delius: *trans*-3 bis-adduct⁴⁹). This short summary shows that there are plenty of regioisomers still to be synthesized by supramolecular encapsulation (see Figure 1). Most notably, reports on fullerenes beyond C_{60} are still elusive. If the supramolecular toolbox can be further extended, we are optimistic that a dream of fullerene chemistry and organic materials science could become true, namely that virtually any fullerene multiple adduct can be obtained in high yield and as a single regioisomer, making chromatographic purification unnecessary.

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