Corannulene: A Curved Polyarene Building Block for the Construction of Functional Materials

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Conspectus

This Account describes a body of research in the design and synthesis of molecular materials prepared from corannulene. Corannulene ($C_{20}H_{10}$) is a molecular bowl of carbon that can be visualized as the hydrogen-terminated cap of buckminsterfullerene. Due to this structural resemblance, it is often referred to as a buckybowl. The bowl can invert, accept electrons, and form host-guest complexes. Due to these characteristics, corannulene presents a useful building block in materials chemistry.

In macromolecular science, for example, assembly of amphiphilic copolymers carrying a hydrophobic corannulene block enables micelle formation in water. Such micellar nanostructures can host large amounts of fullerenes (C_{60} and C_{70}) in their corannulene-rich core through complementarity of the curved π-surfaces. Covalent stabilization of the assembled structures then leads to the formation of robust water-soluble fullerene nanoparticles. Alternatively, use of corannulene in a polymer backbone allows for the preparation of electronic and redox-active materials. Finally, a corannulene-core enables polymer chains to respond to solution temperature changes and form macroscopic fibrillar structures. In this way, the corannulene motif brings a variety of properties to the polymeric materials.

In the design of non-fullerene electron acceptors, corannulene is emerging as a promising aromatic scaffold. In this regard, placement of sulfur atoms along the rim can cause an anodic shift in the molecular reduction potential. Oxidation of the sulfur atoms can further enhance this shift. Thus, a variation in the number, placement, and oxidation state of the sulfur atoms can create electron acceptors of tunable and high strengths. An advantage of this molecular design is that material solubility can also be tuned. For example, water-soluble electron acceptors can be created and is shown to improve the moisture-resistance of perovskite solar cells.

Host-guest complexation between corannulene and γ-cyclodextrin under flow-conditions of a microfluidic chamber allows for the preparation of water-soluble nanoparticles. Due to an oligosaccharide-based sugarcoat, the nanoparticles are biocompatible while the corannulene component renders them active towards non-linear absorption and emission properties. Together, these attributes allow the nanoparticles to be used as 2-photon imaging probes in cancer cells.

Finally, aromatic extension of the corannulene nucleus is seen as a potential route to non-planar nanographenes. Typically, such endeavors rely upon gas-phase synthesis or metal-catalyzed coupling protocols. Recently, two new approaches have been established in this regard. Photochemically-induced oxidative cyclization, the Mallory reaction, is shown to be a general method to access corannulenes with an extended π-framework. Alternatively, solid-state ball milling can achieve this goal in a highly efficient manner. These new protocols bring practicality and sustainability to the rapidly growing area of corannulene-based nanographenes.

In essence, corannulene presents a unique building block in the construction of functional materials. In this Account, we trace our own efforts in the field and point towards the challenges and future prospects of this area of research.

Key References

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- Barát, V.; Budanović, M.; Halilovic, D.; Huh, J.; Webster, R. D.; Mahadevegowda, S. H.; Stuparu, M. C. A General Approach to Non-Fullerene Electron Acceptors Based on the Corannulene Motif. *Chem. Commun.* **2019**, *55*, 3113–3116. This study describes oxidation of rim sulfur atoms as a practical strategy to access corannulene-based electron acceptors of tunable strengths.[3]
- Báti, G.; Csókás, D.; Yong, T.; Tam, S. M.; Shi, R. R. S.; Webster, R. D.; Pápai, I.; García, F.; Stuparu, M. C. Mechanochemical Synthesis of Corannulene-Based Curved Nanographenes. *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 21620–21626. This is the first study which explores the application of mechanochemistry in the synthesis of curved nanographenes.[4]

1. Introduction

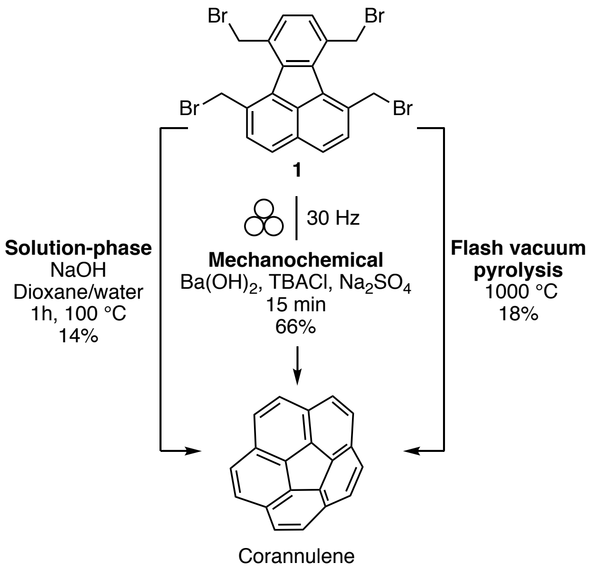
Corannulene[5-18] is often described as the smallest fragment of fullerene C_{60} which retains a curved molecular structure. However, it was envisaged and synthesized by Barth and Lawton nearly two decades before the discovery of fullerene C_{60}.[19] It is reasonable to assume that the synthetic difficulty in accessing corannulene deterred the scientific community from embracing this beautiful and unique molecular motif. Nonetheless, X-ray study was possible and confirmed that the molecule is shaped like a bowl with a depth of 0.87 Å.[20] Scott's pyrolytic synthesis was truly a turning point for corannulene chemistry.[21] It has allowed access to the molecule in an efficient manner[22] and thus numerous new studies could be carried out. These studies shed light on the dynamic nature of the bowl-inversion process and the capability to reduce the aromatic nucleus.[23-24] It is beyond a doubt that pyrolytic synthesis is the most successful method in accessing bowl-shaped polyarenes.[5-6] However, solution-phase synthesis offers milder conditions and higher selectivity. Therefore, solution-phase synthesis was developed by Siegel[25] and later improved by himself[26] and independently by Sygula and Rabideau.[27] In 2000, a major breakthrough in the solution-phase synthesis occurred when Sygula and Rabideau demonstrated that the crucial ring-closing step to corannulene required only reflux under a simple aqueous basic condition.[28] In 2012, Siegel presented a fully optimized solution-phase synthesis capable of producing corannulene at a kg-scale.[29] These synthetic developments empowered the scientific community with access to corannulene for new studies to come to the fore.

Table 1. Selected developments in the synthesis of corannulene.

	Research Group	Synthesis	Year	Reference
1	Barth and Lawton	First solution-phase synthesis	1966	19

2	Scott	First gas-phase synthesis	1991	21
3	Scott	Improved gas-phase synthesis	1997	22
4	Siegel	Second solution-phase synthesis	1996	25
5	Sygula and Rabideau	Improved solution-phase synthesis	2000	28
6	Siegel	Kg-scale solution-phase synthesis	2012	29
7	Stuparu	First solid-phase synthesis	2021	31

From the aforementioned discussion, it appears that the advancements of corannulene synthesis have concluded (Table 1). However, we believe that development of new synthetic routes is still required. While pyrolytic synthesis is great, the access to and the operation of a pyrolytic chamber may not be trivial. The solution-phase synthesis may produce kilograms of material but the use of toxic and expensive solvents and large amounts of a number of reagents is a concern. Therefore, new synthetic routes must continually be explored. For instance, mechanochemistry in which mechanical forces are applied to drive chemical reactions offers a third reaction space, the solid-phase, for synthetic purposes.[30] The advantage of mechanochemistry over the traditional gas-phase and solution-phase synthetic methods is that it is practically simple, mild, fast, high-yielding, and sustainable. Our results in this regard are very promising. For example, 15-minute ball milling of tetrabromomethylfluoranthene (**1**) with a solid base produces corannulene in 66% yield (Scheme 1).[31] In comparison, the pyrolytic synthesis gives 18% yield while the solution-phase chemistry provides a 14% yield.[32-33] This preliminary study confirms that mechanochemistry is capable of inducing molecular curvature and a worthy competitor of traditional syntheses. However, the tetrabromomethylfluoranthene precursor requires a multi-step synthesis. Therefore, the stage is now set to explore other precursors for mechanochemistry, preferably with a shorter and total solid-phase synthetic route to corannulene.



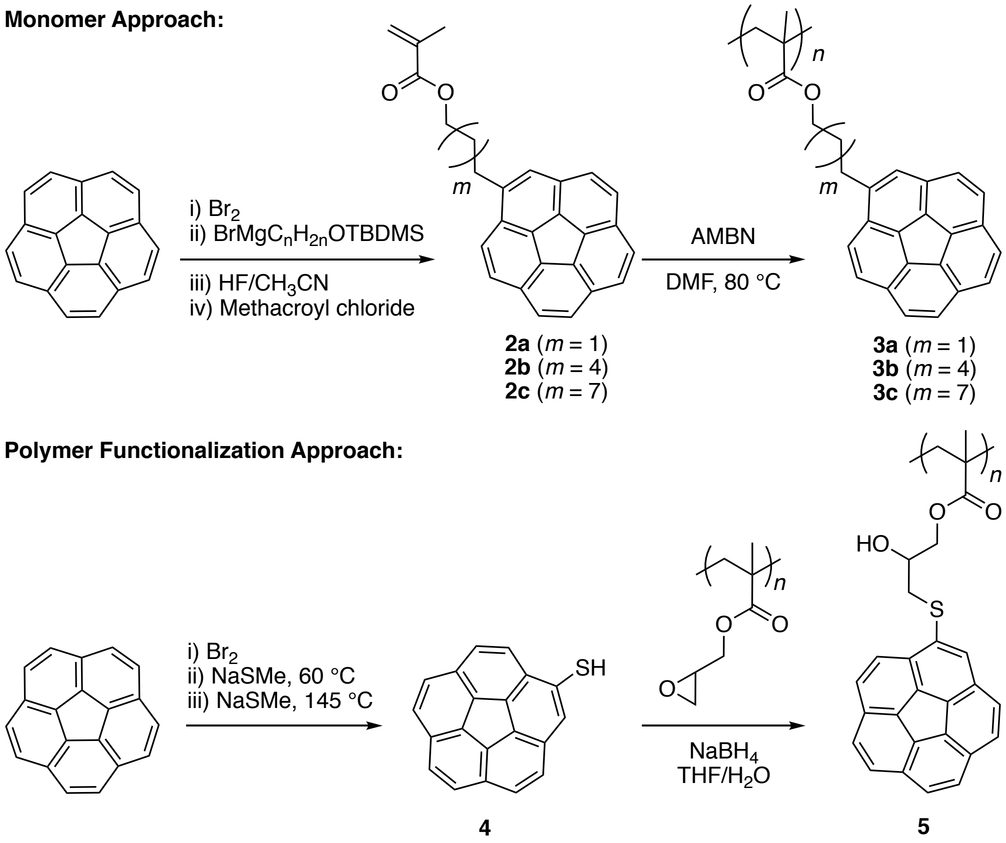
Scheme 1. Mechanochemical synthesis of corannulene and comparison with other synthetic strategies.

2. Discussion

2.1. Macromolecular Architectures

2.1.1. Side-Chain Polymers

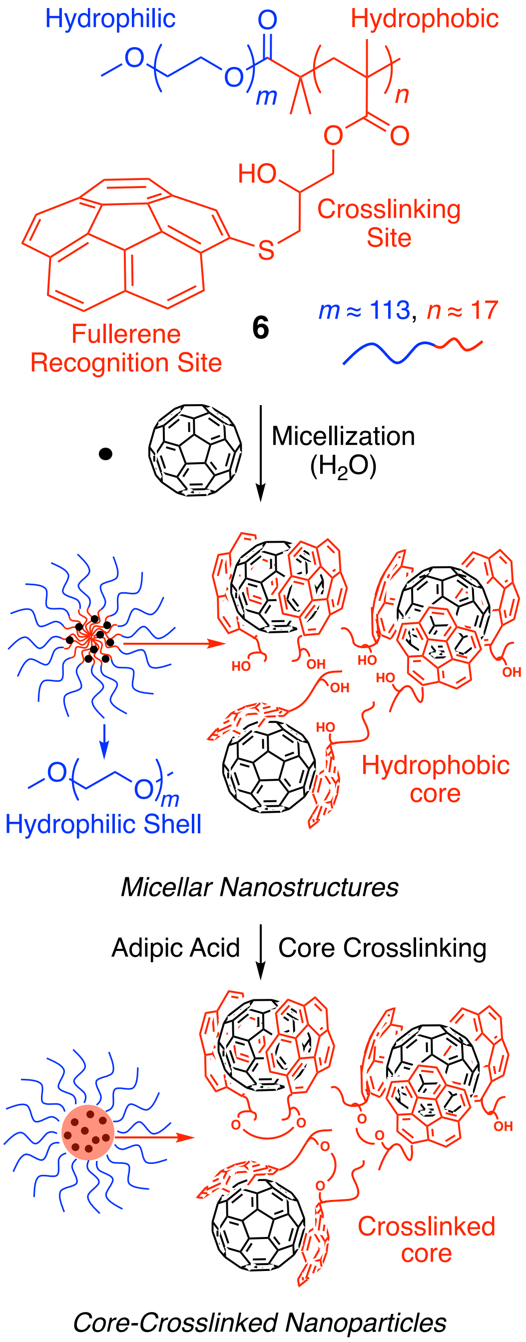
The properties of corannulene invoked a desire to incorporate this molecular motif into polymers.[34] Our first attempt in this direction was based on free radical polymerization due to its practicality.[1] For this, an acrylate group was installed onto corannulene through a multi-step organic synthesis to access monomers **2a-c** (Scheme 2).



Scheme 2. Different synthetic approaches to access corannulene polymers.

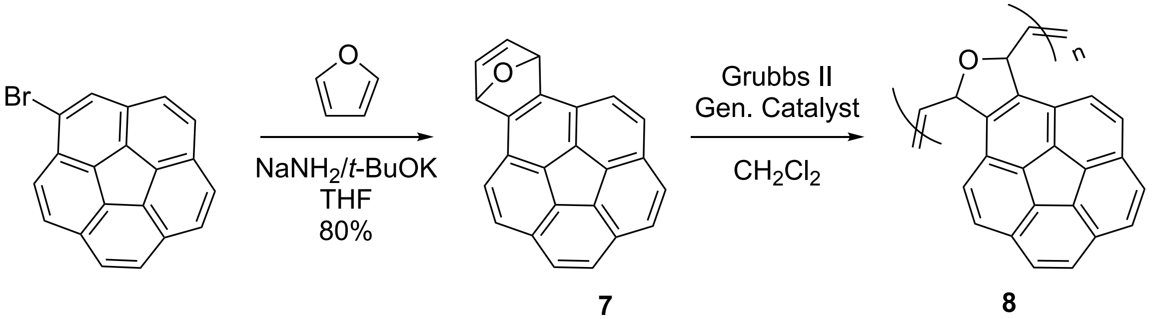
Figure 1. Encapsulation of fullerene C_{60} in corannulene-appended methacrylate polymers.

The polymerizations were successful and indicated that the corannulene nucleus did not interfere with the free radical chemistry. Therefore, homopolymers (**3a**-**c**) as well as block copolymers could be prepared with synthetic ease. A study on the properties indicated that these polymers are good hosts for fullerene C_{60} (Figure 1). While these advancements are significant, the synthesis of corannulene monomers is laborious. Furthermore, each monomer poses a different kinetic behavior during polymerization. A post-polymerization modification strategy solves this problem.[35] It involves the preparation of a reactive polymeric scaffold onto which corannulene is attached. In this synthetic scheme, the corannulene moiety is not involved in the polymerization reaction. However, to be able to achieve a full polymer functionalization, an efficient reaction is required to attach corannulene to the polymer chain. Therefore, thiol-epoxy reaction was chosen to achieve this goal.[36-37] Polymers with an epoxide group can be prepared from the commercially available glycidyl methacrylate monomer.[38] Mercaptocorannulene **4** can be accessed in three synthetic steps from corannulene. A base-catalyzed ring-opening reaction then provided the corannulene-functionalized polymer **5**. Once attached to a hydrophilic poly(ethylene glycol) segment, copolymer **6** could form a micellar structure in water due to amphiphilicity of the overall molecular structure (Scheme 3). The micellar core is enriched with corannulenes and can thus encapsulate fullerenes through complementarity of the curved π-surfaces. The micellar shell is formed by the poly(ethylene glycol) chains. This supramolecular structure can be stabilized by crosslinking of the core through esterification of the hydroxyl groups generated upon the ring-opening reaction. In this design, the specificity of the host-guest interactions between corannulene and fullerenes allows for a high fullerene loading capacity to be achieved (8%) while the flexibility and multivalency of the hosting block enables encapsulation of buckyballs with different molecular sizes (C_{60} and C_{70}). Covalent crosslinking of the core transforms the supramolecular micelles into robust nanoparticles.



Scheme 3. Preparation of water-soluble fullerene-containing core-shell polymer nanoparticles through assembly of corannulene-based amphiphilic copolymers.

The hemolysis and protein adsorption assay suggest compatibility of the core-crosslinked micellar nanoparticles with bio-relevant conditions and materials. Due to a molecularly defined non-crosslinked shell, the nanoparticles can be dried to a solid and re-dispersed in water without inducing inter-particle aggregation. The crosslinked nature of the core, on the other hand, endows thermal stability so that the nanoparticles can be heated at 100 °C for 72 hours without losing their structural integrity. In this way, corannulene polymers enable the construction of sophisticated fullerene-containing water-soluble nanoparticles. We anticipate that replacing conventional fullerenes in the present design with endohedral fullerenes containing for example Gd^{3+} could lead to new magnetic resonance imaging probes. Due to the nanometer size and a poly(ethylene glycol) shell, such probes are expected to circulate for long periods of time in the body. Furthermore, preparation of water-soluble nanoparticles with higher fullerenes (e.g., C_{84}) and studying their bio-relevant properties appears to be an appealing future research direction in this regard.



7 **8**

Scheme 4. Ring-opening metathesis polymerization of corannulene-based oxa-norbornadiene monomer.

In 2005, Sygula and coworkers presented the synthesis of corannulyne upon treatment of bromocorannulene with an excess of sodium amide and catalytic amount of potassium *tert*-butoxide.[39] This reactive species could be trapped with furan to give Diels-Alder adduct **7** in 80% yield (Scheme 4). **7** caught our attention as it represents a monomer for ring-opening polymerization process. The oxa-norbornadiene functionality can be subjected to a ring-opening metathesis polymerization with a ruthenium-based Grubbs' second-generation catalyst.[40] We observed, however, that polymerization of **7** resulted in the formation of spherical nanomaterials that were insoluble in organic solvents (Figure 2).

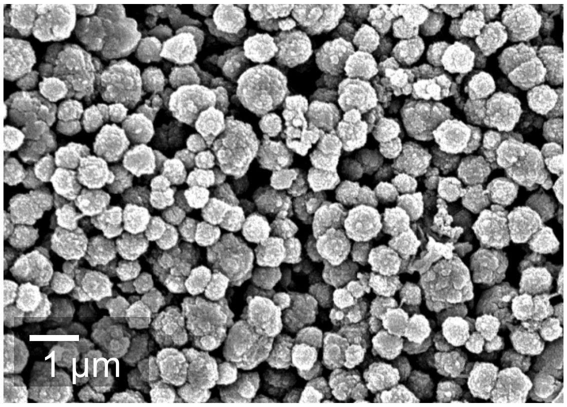
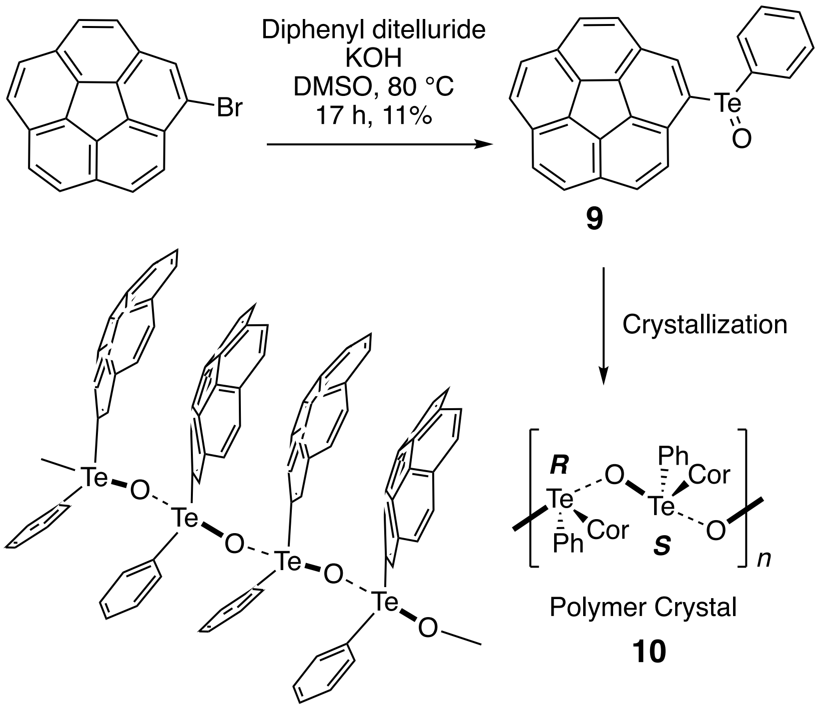


Figure 2. A scanning electron micrograph of polymer particles generated upon ROMP of monomer **7**.

Therefore, the structure of polymer **8** was confirmed in the solid-state with the help of ^{13}C cross-polarization magic angle-spinning (CP-MAS) NMR spectroscopy. The materials were nanoporous with an average pore size of approximately 1.4 nm and a surface area of 49.2 m^2/g. Their applications in the supercapacitor devices led to high retention of capacitance (90%) even after undergoing 10000 charging and discharging cycles. This work demonstrated that corannulene polymers are an attractive active component for the fabrication of electrochemical energy storage devices with long-term cyclability.



Scheme 5. Synthesis of corannulene-based tellurium oxide monomer **9**. The bottom shows the chemical structure of the syndiotactic polymer **10**.

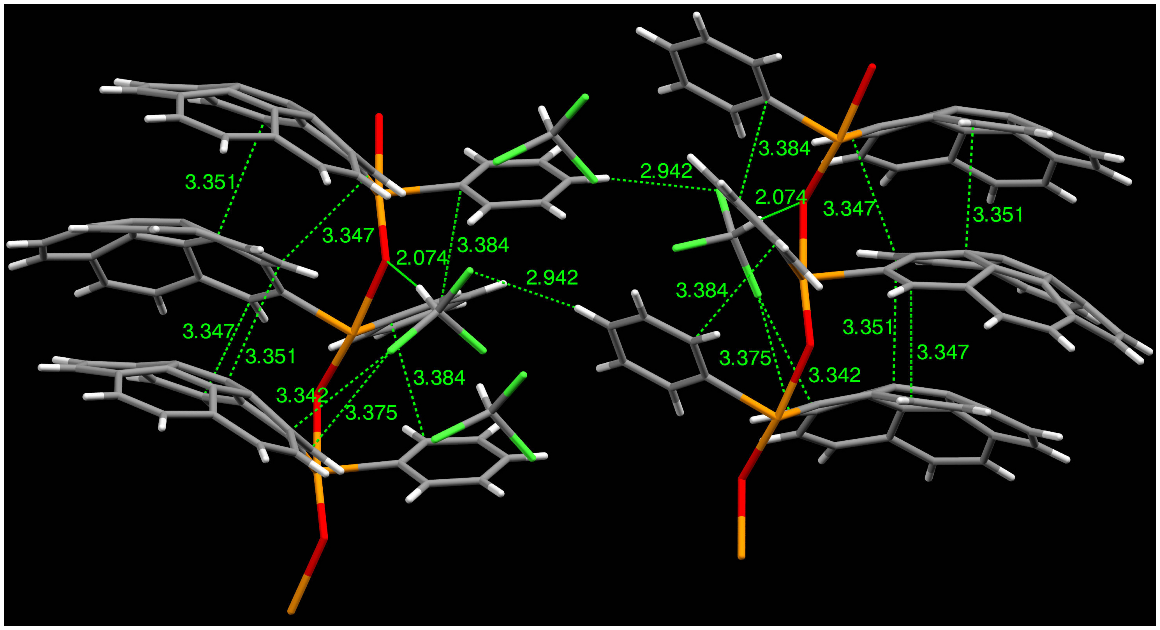


Figure 3. Single crystal structure of polymer **10**.

Our interest in corannulene chalcogenides (see section 2.2.) motivated us to synthesize a tellurium derivative[41] which was observed to oxidize to **9** either during the reaction or the purification process (Scheme 5). An examination with X-ray crystallography revealed that the oxide **9** gave rise to linear polymer chains (**10**) in the solid state. In these chains, Te-O constituted the polymer backbone around which the phenyl and corannulene groups were arranged as the polymer side-chains (Figure 3). The polymer crystal was stabilized by the intramolecular π-π stacking interactions of the side-chains and the intermolecular hydrogen and halogen bonding interactions with the chloroform (solvent) molecules. The polymer chains were found to be stereoregular with each pair of the repeating unit representing racemic diads. This work can be explored further for its potential generality towards the preparation of a new family of corannulene polymers based on chalcogen-bonding interactions.

2.1.2. Main-Chain Polymers

Traditionally, conjugated polymers are constructed by using planar aromatic building blocks. We started to explore utility of corannulene in this molecular design. Our initial efforts were directed at ladder polymers.[42] However, the complexity of synthesis motivated us to synthesize single-stranded structures (Figure 4). Furthermore, in order to establish a concrete structure-property relationship, we decided to build discrete oligomers **11**-**15**.[2] As for the molecular design, we opted for an acetylene bridge and a thiophene nucleus as linkers between the corannulene segments. The final structures comprised a combination of planar and non-planar structural motifs. The synthesis was carried out using palladium-catalyzed Sonogashira-Hagihara reaction.

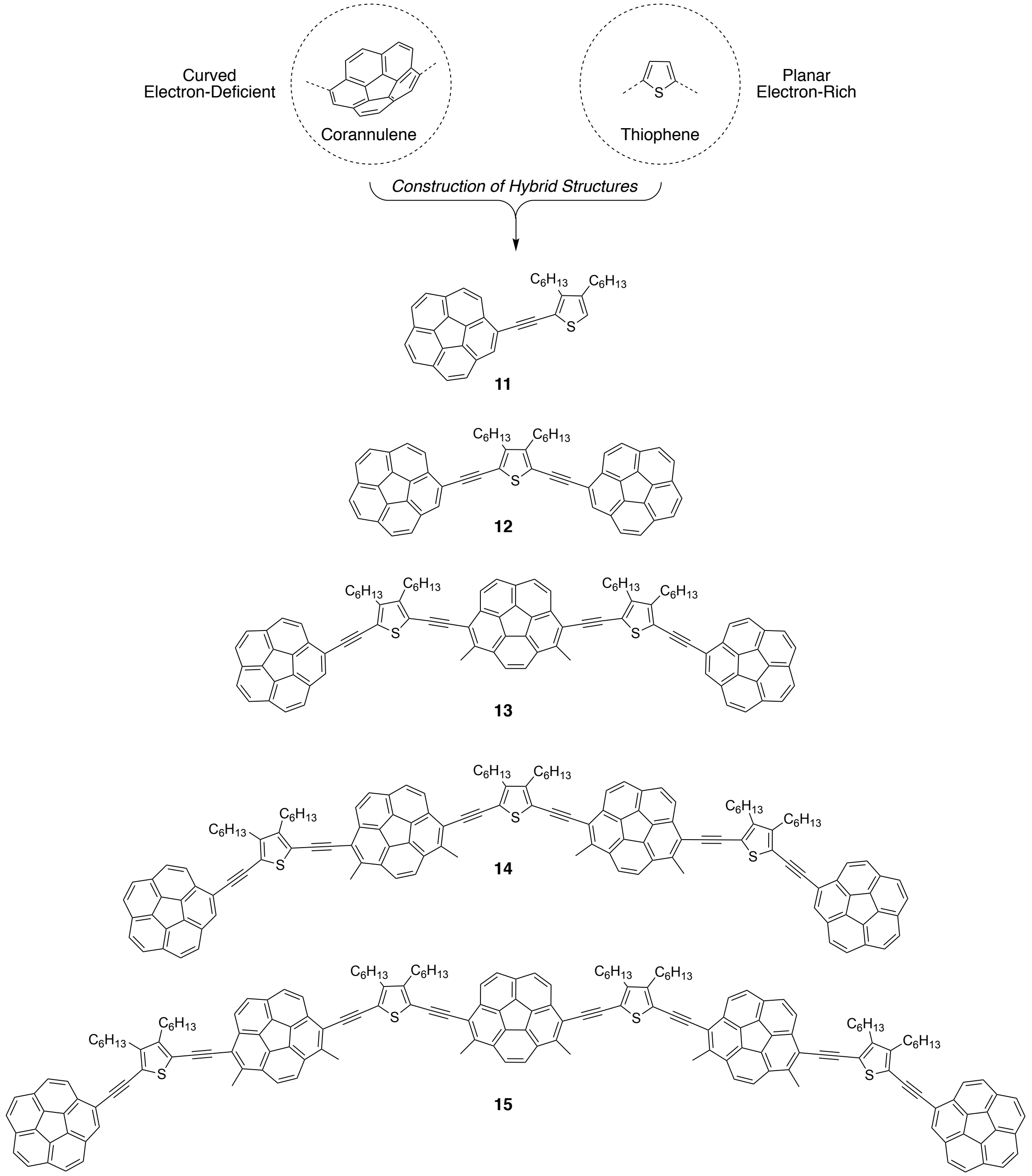


Figure 4. Combining planarity of thiophene and non-planarity of corannulene in discrete oligomers.

The oligomers were studied for their electronic properties. This examination revealed that the effective conjugation length had been reached at oligomer **13** which displayed the best optical properties. All the oligomers were found to exhibit non-linear absorption and emission properties (Figure 5). This study was the first demonstration of non-linear optical activity in corannulene chemistry. It also indicated that high molecular weight polymeric materials are not a necessity to observe optimum electronic properties in single-stranded corannulene structures.

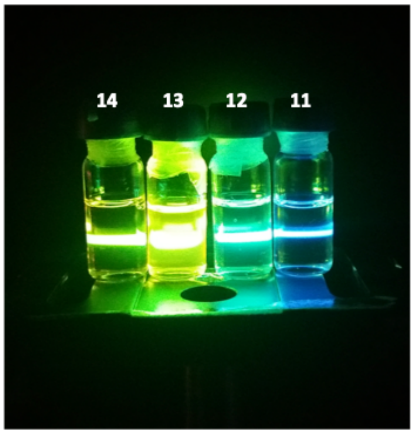
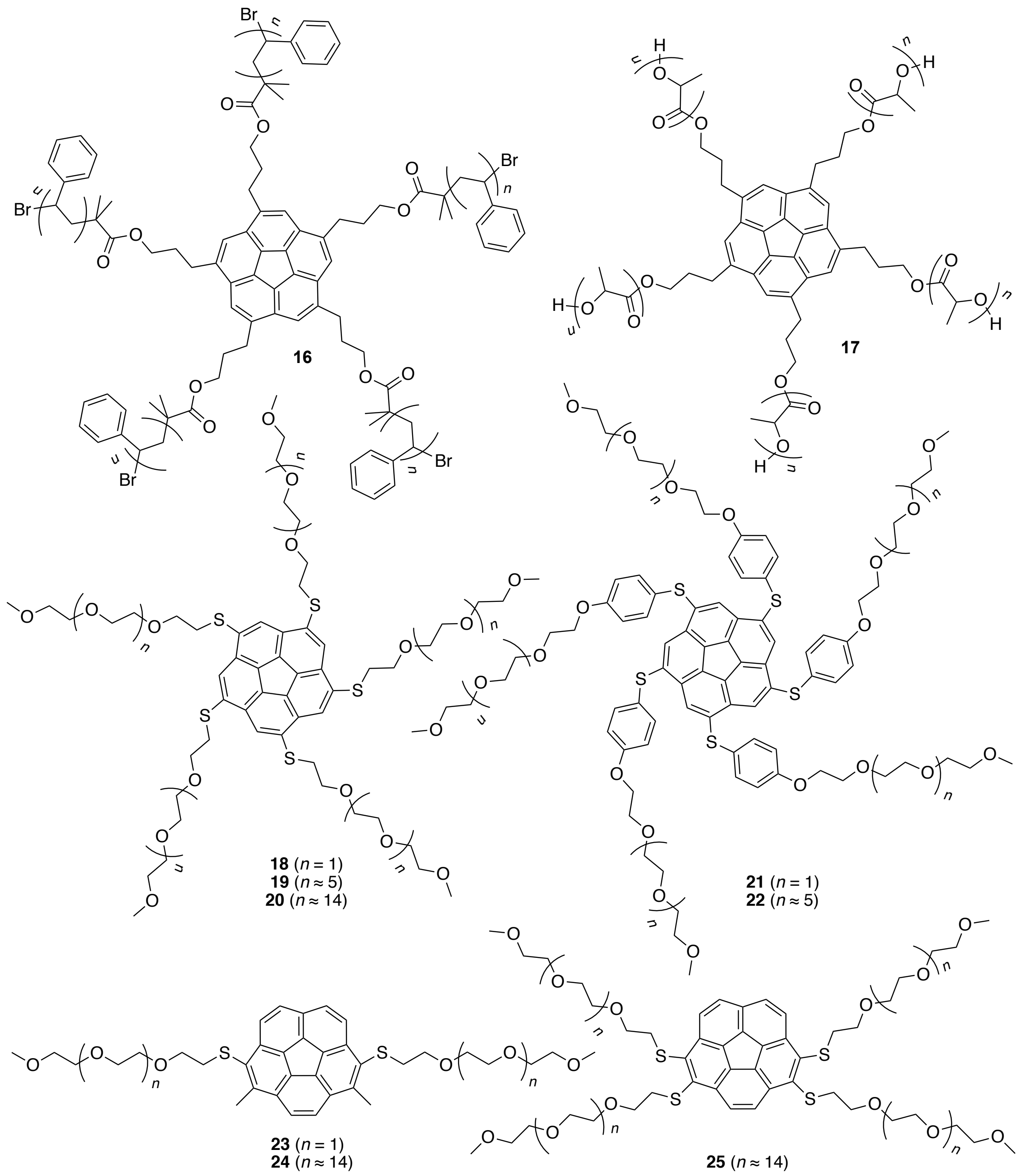


Figure 5. A digital picture showing 800 nm laser passing through solutions of corannulene-thiophene oligomers.

2.1.3. Star Polymers

The C_5-symmetric nature of corannulene lends itself as a perfect core around which polymer chains can be built to obtain star-shaped polymers. Our initial efforts in this direction were focused on using the core as a polymerization initiator.[43] This allowed for free radical and ring-opening polymerizations to be carried out and polystyrene (**16**) and polylactides (**17**) to be accessed with ease (Figure 6 top). Later work explored the attachment of ready-made polymer chains to the core via nucleophilic substitution reaction to give polymers **18-25** (Figure 6 bottom).[44-45] This synthetic route to star polymers is attractive since a variety of polymer chains can be obtained from commercial suppliers. We chose to use the thiol-terminated poly(ethylene glycol)s of varying lengths.



16

17

18 ($n = 1$)
19 ($n \approx 5$)
20 ($n \approx 14$)

21 ($n = 1$)
22 ($n \approx 5$)

23 ($n = 1$)
24 ($n \approx 14$)

25 ($n \approx 14$)

Figure 6. Chemical structures of corannulene-core star polymers.

Serendipitously, we discovered that warming aqueous solutions of polymer **18** turned it turbid (Figure 7). A scanning electron microscopy analysis revealed the formation of large fibres under these conditions (Figure 7). Upon cooling, the solutions returned to their normal (clear) appearance. The heating and cooling cycles could be repeated to obtain turbid and clear solutions.

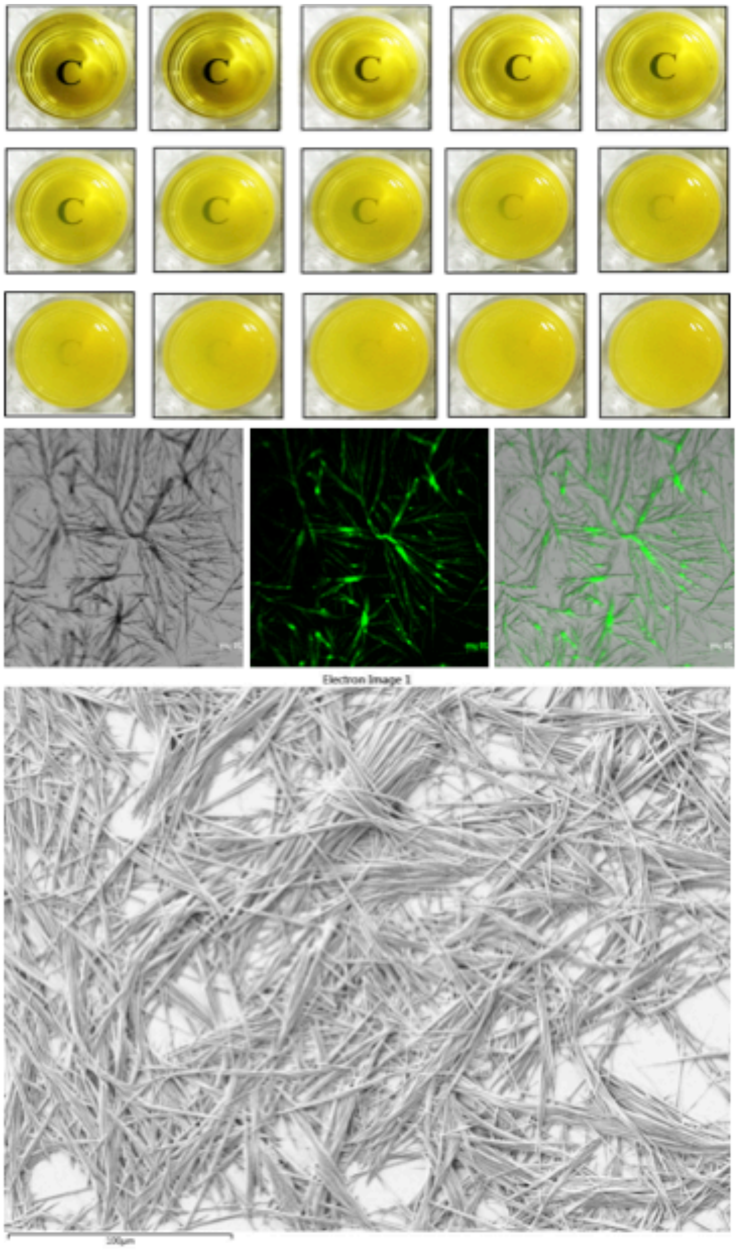


Figure 7. Digital picture showing turbidity in aqueous solution of **18** as temperature is raised (top). Optical micrographs showing green emission from the fibres (middle). Scanning electron micrograph of fibres formed upon heating of an aqueous solution of **18** (bottom).

The attachment of polar poly(ethylene glycol) chains to a non-polar corannulene core seems to invoke an amphiphilic character in polymer **18**. At room temperature, it is completely soluble in water through hydrogen bonding interactions with the oxygen atoms of the ethylene glycol chains. However, as the temperature of the solution is increased, water molecules withdraw from the structure thus making it insoluble and forcing it to precipitate out. Such a thermoresponsive character depends upon the hydrophilic/hydrophobic ratio in the molecule. Therefore, changing the length of the ethylene glycol chains and the chemical structure of the junction between the corannulene core and the polymer chain in **21**-**22**, the thermal transition temperature could be adjusted within the temperature range of 30 to 50 °C.

2.2. Non-Fullerene Electron Acceptors

Corannulene accepts four electrons while fullerene C_{60} accepts six.[24] Nonetheless, corannulene maintains some advantages over C_{60}. It can be synthesized at a large scale and in a cost-effective manner.[29] It has high solubility in a variety of common solvents used for device processing. It can be functionalized in a precise and controlled fashion without disrupting the electronic structure of the carbon scaffold. However, corannulene is not as strong an electron acceptor as fullerene C_{60}. To improve electron affinity, corannulene can be functionalized with electron withdrawing groups. In this regard, Boltalina's fluorinated corannulene[46] and Lentz's bis-imides/cyano derivatives[47] produces impressive anodic shifts of 1.23 and 1.42 V, respectively, in the first reversible reduction potential of corannulene. However, the synthesis and purification of some of these compounds may not be trivial. Furthermore, some compounds suffer from low solubility in common organic solvents. Therefore, a combination of good electron accepting capability with practical synthesis and high solubility continues to be an important research goal in corannulene chemistry.

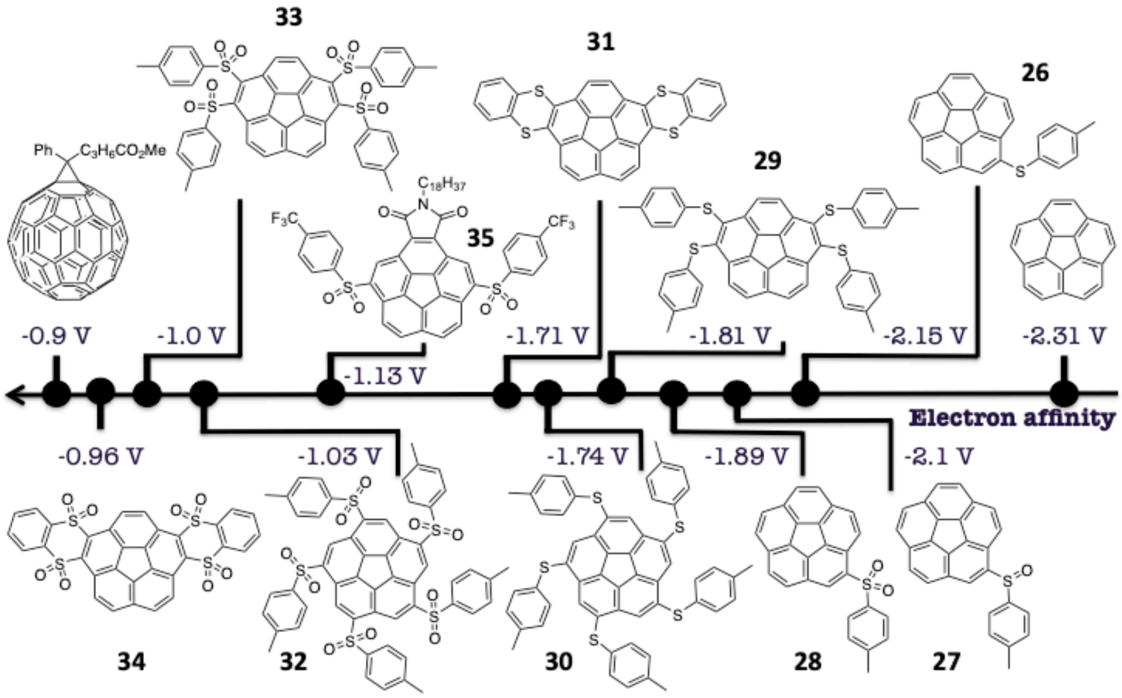
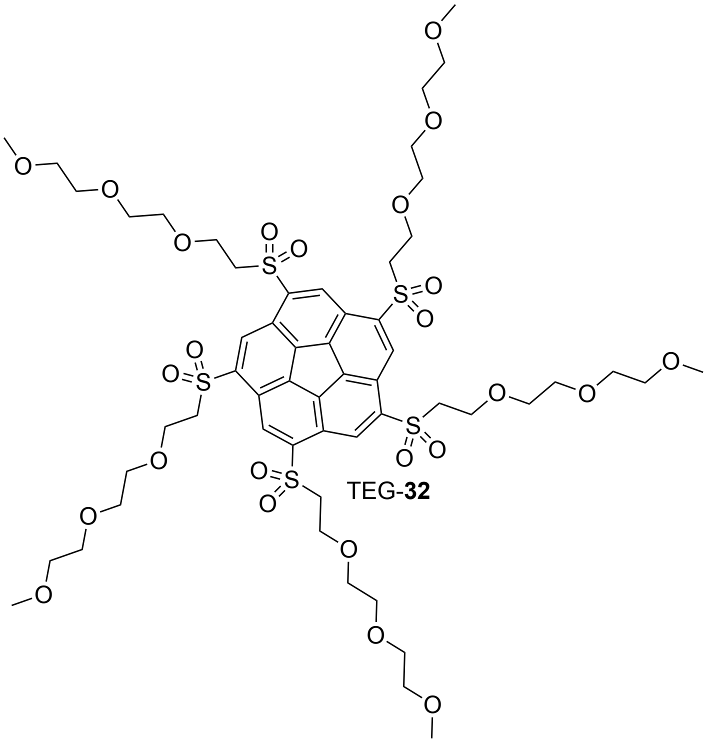


Figure 8. Systematic bridging of the electron affinity gap between corannulene and a fullerene derivative, $PC_{61}BM$, via oxidation of rim sulfur atoms.

Towards this end, we have been focusing on sulfide derivatives of corannulene.[3] They can be conveniently synthesized via nucleophilic aromatic substitution of halocorannulenes. For this purpose, a variety of aromatic thiols can be accessed from commercial sources. Furthermore, the complementary halogenated coupling partners are ubiquitous in corannulene chemistry. Once accessed, the sulfur atoms can be oxidized to electron withdrawing sulfoxide/sulfones to enhance the electron affinity of the central aromatic nucleus (Figure 8). Through a systematic variation of molecular structure (**26-35**), it could be established that the number, position, and oxidation state of sulfur atoms defines the strength of the electron acceptor. A higher number of sulfur atoms produce a greater anodic shift. Sulfones (**28**, **32**, **33**, **34**) are found to be better than sulfoxide (**27**) and sulfides (**26**, **29**, **30**, **31**). The cyclic tetrasulfone (**34**) is found to be better than non-cyclic-tetra and penta-sulfones (**32-33**). Overall, compounds **32**, **33**, and **34** could reach near the electron affinity of phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$). The best candidate in this series can be identified as **34** as it boasts the maximum anodic shift of 1.35 V in the first reduction potential as compared to bare corannulene. Furthermore, it can be easily accessed at a 0.5-gram scale from tetrabromocorannulene in two synthetic steps (overall yield = 46%), in which the second step does not require a chromatographic purification. These results are very encouraging as they point towards utility of sulfones in designing corannulene-based electron acceptors. However, the solubility of the best candidate (**34**) is less than optimal in common organic solvents. Therefore, a second molecular design is explored.[48] In this design, an imide group carrying a long solubilizing alkyl chain is introduced in the molecular structure. Furthermore, fluorinated thiols are used for the nucleophilic substitution reaction. Upon oxidation, **35** is obtained. Due to a combination of three electron-withdrawing groups, the molecule exhibits an anodic shift of 1.18 V as compared to pristine corannulene, which is comparatively less than in the case of **34**. However, compound **35** displays a much higher solubility in a range of organic solvents due to the long alkyl chain.



TEG-**32**

Figure 9. Water-soluble electron-acceptor for use in perovskite solar cells.

The future potential of the sulfone strategy lies in its modularity and possible avenue for further scaffold modification. This would allow for molecular level adaptations to be performed in order to meet the varied requirements of the organic electronics community. For instance, this concept can be readily adopted in the preparation of water-soluble electron acceptors.[49] This is achieved by replacing the phenyl groups from **32** with the triethylene glycol (TEG) chains (Figure 9). Remarkably, application of TEG-**32** as an additive in perovskite solar cells enhances the power conversion efficiency (PCE) from 15.4% to 16.8% and the devices retain 91% of their initial PCE over the course of 2 months. In comparison, the pristine device holds only 61% of its initial PCE. Remarkably, in a harsh humid environment, the devices containing TEG-**32** retains 87% of their initial efficiency while the pristine device suffers a significant deterioration in its performance.

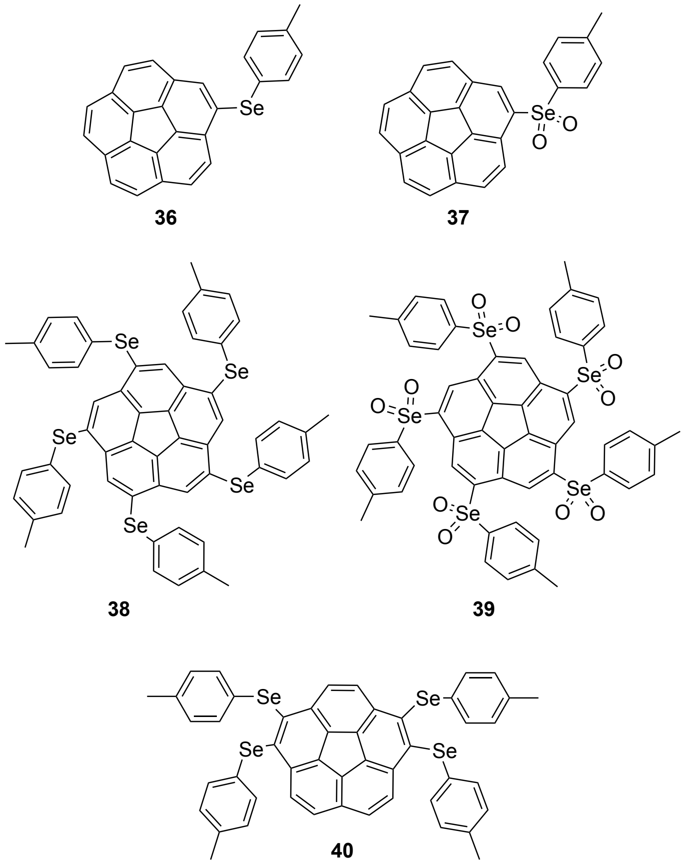


Figure 10. Selenoether derivatives of corannulene.

Encouraged by these studies, we planned the synthesis of selenoether analogues and their oxidation to selenones (**36-40**) in an effort to further enhance the electron affinity of the corannulene nucleus (Figure 10).[41] We observed that while the synthesis of some of the selenoethers are feasible, these compounds become unstable once they are oxidized. Therefore, they are of little value as electron acceptors. A potential strategy to improve their stability might lie in the preparation of heterocyclic structures with the selenium atoms being part of the aromatic structure.

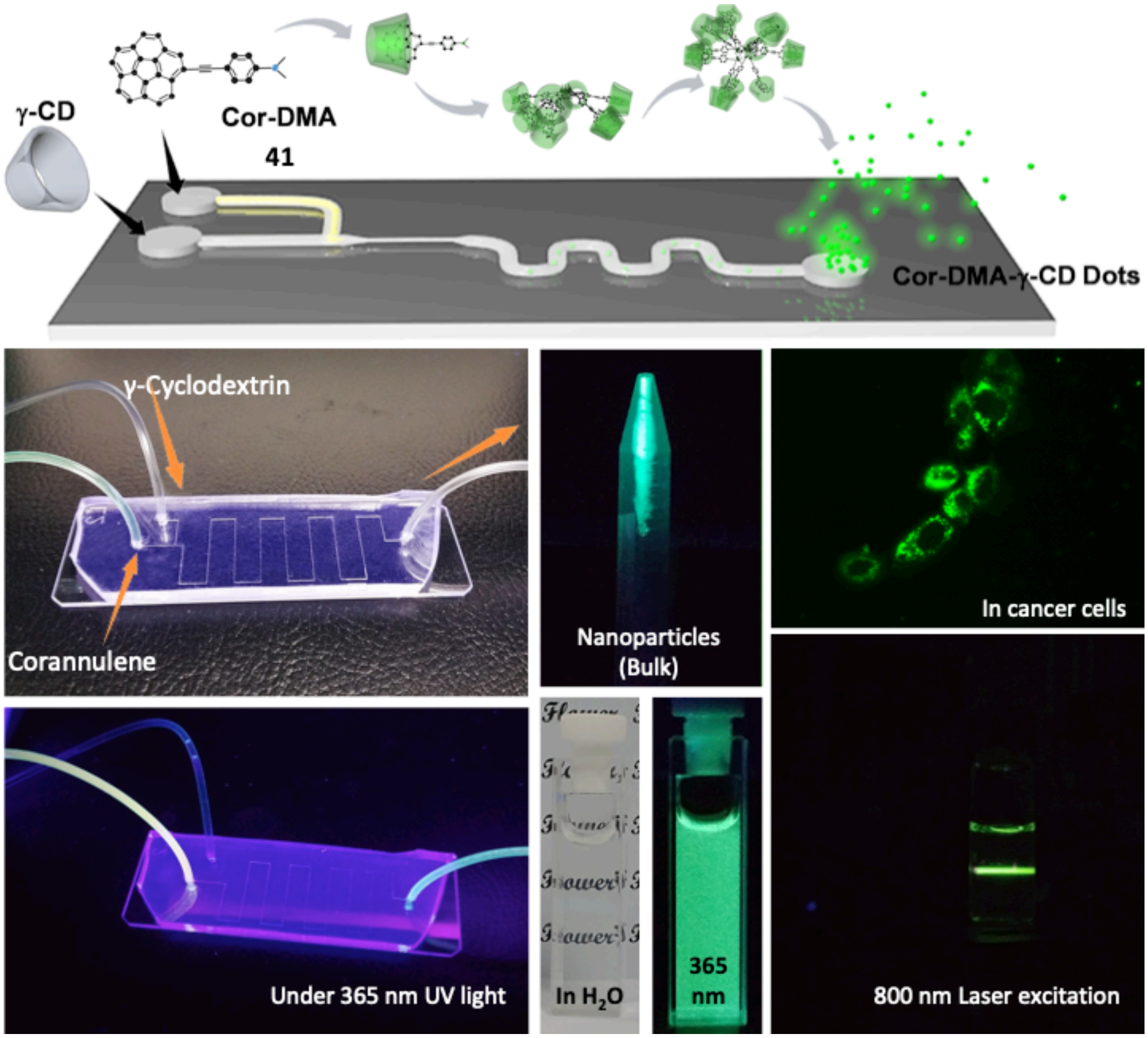


Figure 11. Schematic of a corannulene and cyclodextrin-based supramolecular nanoparticle synthesis under flow conditions (top). Digital pictures of the microfluidic device (bottom left), bulk nanoparticle (center) and nanoparticle solution in water (middle bottom), and upon excitation with an 800 nm laser (bottom right). Optical micrograph showing cancer cells upon uptake of the supramolecular nanoparticles (middle right).

2.3. Supramolecular Nanoparticles

The application of corannulene in biology is limited due to its restricted solubility in water. As seen in section 2.1.3., covalent functionalization with hydrophilic substituents such as poly(ethylene glycol) chains can alleviate this limitation. A more practical strategy is through supramolecular complexation with γ-cyclodextrin (γ-CD) (Figure 11).[50] This approach is general and functional corannulene derivatives can also be solubilized in water.[51] For instance, *N,N*-dimethylaminophenyl ethynylene derivative **41** shows excellent absorption and emission properties. Therefore, to harness its optical capabilities in biological applications such as imaging, it can be subjected to complexation with the cyclic oligosaccharide under flow conditions of a microfluidic chamber. Under such conditions, the hydrophobic **41** and hydrophilic γ-CD come in contact with each other and form an amphiphilic structure which assembles further into nano-sized particles. These particles exhibit water-solubility and non-toxicity due to the oligosaccharide shell. The corannulene component renders the particles active toward non-linear absorption and emission. Therefore, the nanoparticles can be applied for two-photon imaging purposes in cancer cells. Since the supramolecular functionalization strategy does not involve multistep organic synthesis and associated chromatographic purifications, it appears to be a promising route to corannulene-based water-soluble functional materials.

2.4. Curved Nanographenes

2.4.1. Photochemical Synthesis

The molecular curvature of corannulene makes it an ideal building block for the synthesis of non-planar nanographenes.[5-6] To achieve this goal, aromatic fragments are annulated to corannulene. Typically, flash vacuum pyrolysis and metal-catalyzed processes are employed to achieve this goal. These methods often suffer from harsh conditions, expensive and environmentally-unfriendly metal catalysts or low overall yields. As a practical alternative, we have recently established a simple synthetic strategy based on the Mallory reaction (Figure 12).[52]

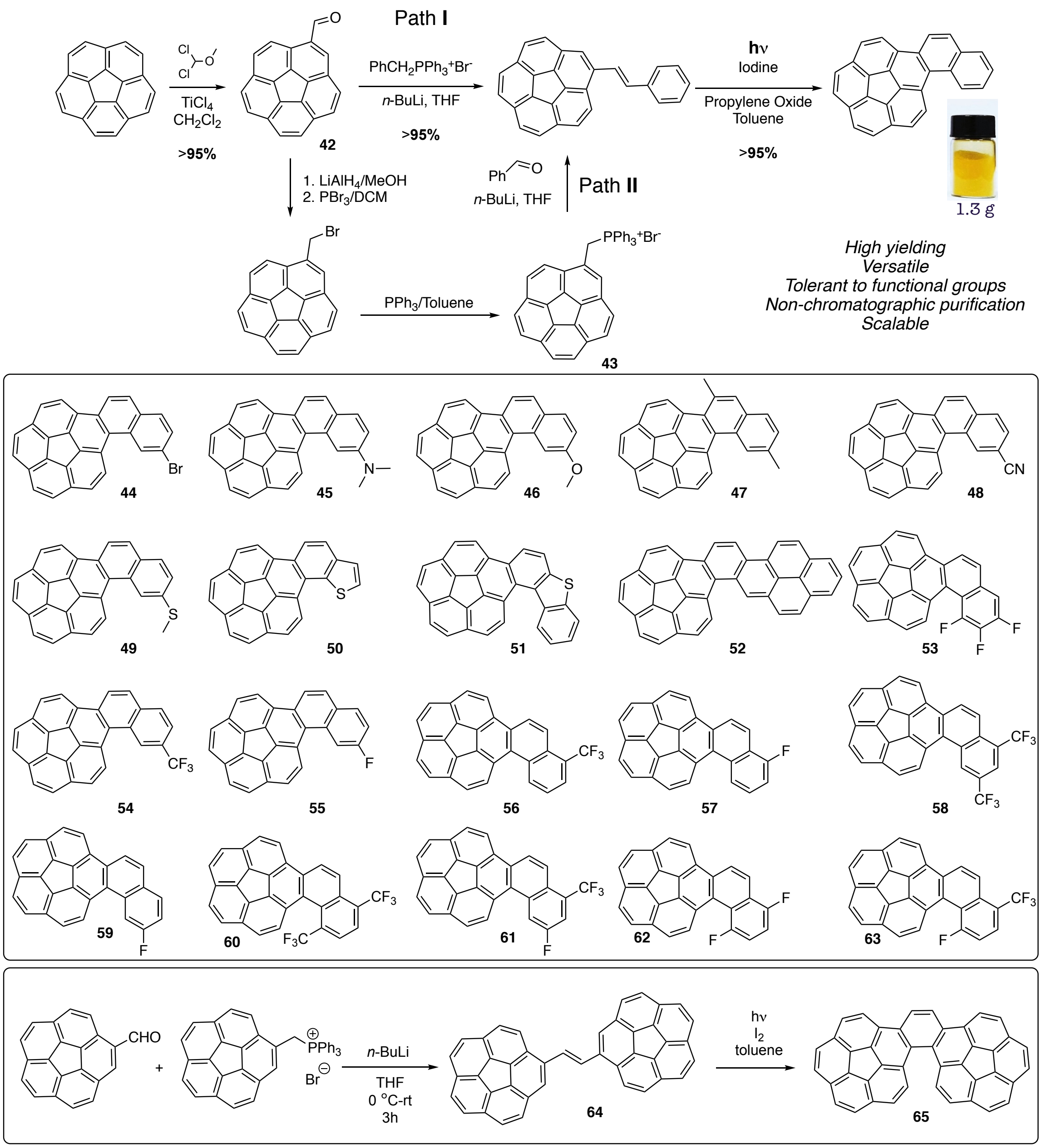


Figure 12. Photochemical synthesis of curved nanographenes.

In this approach, a corannulene-based aldehyde[53] (**42**) or ylide (**43**) is conjugated with an aromatic unit of choice through a Wittig reaction. The resulting stilbene-like precursor is subjected to the photochemically induced oxidative-cyclization process to extend π-framework.[54-55] The generality of this method allows for the preparation of a wide range of arenes and heteroarene structures (**44-63**). Meanwhile, the mild nature of the developed protocol permits for the incorporation of reactive (**44**, **48**, **49**) and functional (**53-63**)[54] substituents onto the extended aromatic scaffold. Furthermore, the high yielding synthesis ensures access to significant amounts of material in a facile manner. It is anticipated that increasing the number of annulations per corannulene unit can provide complex extended polycyclic aromatic structures that can potentially be used as precursors to the synthesis of higher buckybowl architectures.

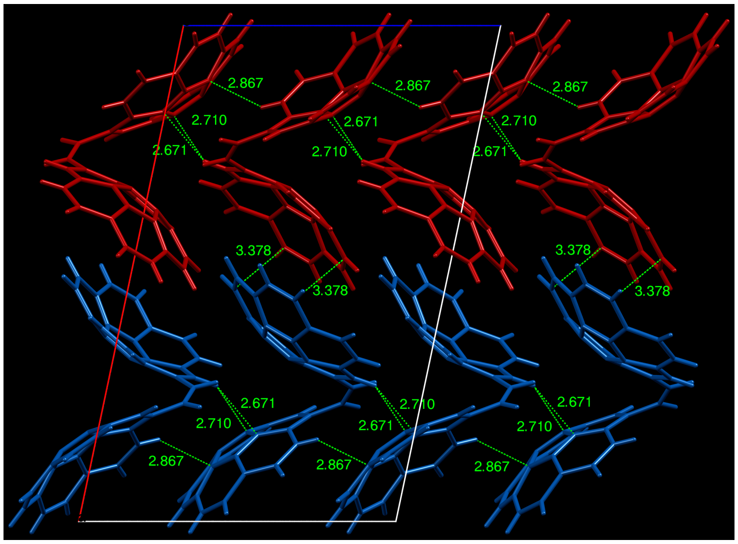


Figure 13. X-ray crystal structure of *cis* isomer of **64**.

An interesting possibility emerges when the Wittig precursors are both based on corannulene. This allows for the synthesis of dicorannulenylethene **64**[56] that produces *cis* and *trans* isomers. However, only the *cis* isomer crystallizes and displays a layered structure (Figure 13). The oxidative photocyclization of **64** leads to annulation of the corannulene nuclei to produce a $C_{42}H_{18}$ nanographene structure **65**. Interestingly, only the *trans* isomer of the dicorannulenylethene forms co-crystals with fullerene C_{60} through π-π stacking interactions (Figure 14). The crystalline arrangement is unique as a supramolecular box-like arrangement is formed with 4 molecules of the *trans* isomer enclosing 4 molecules of fullerene C_{60}.

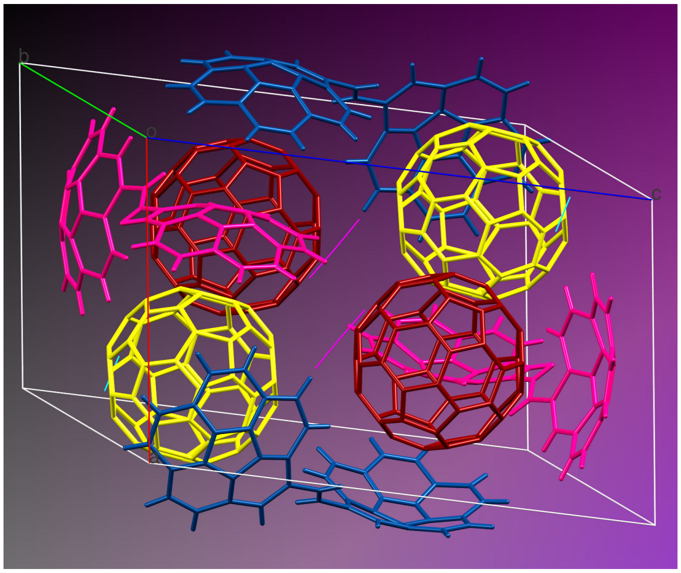
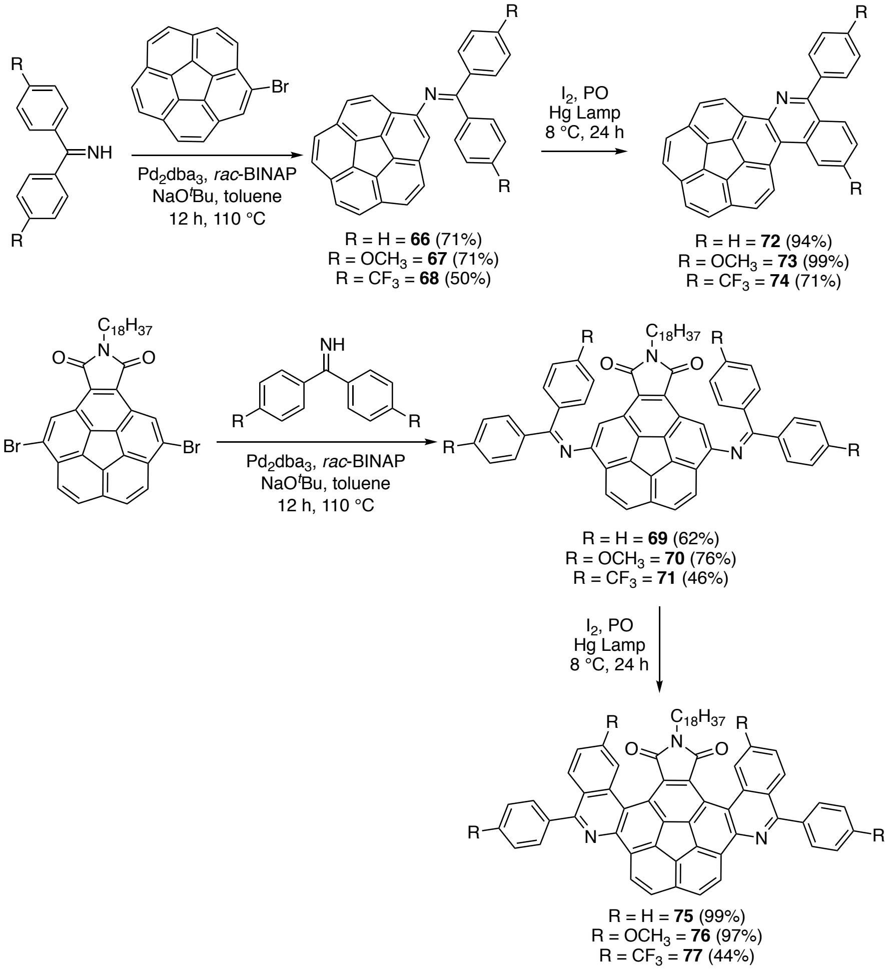


Figure 14. X-ray crystal structure of *trans*-isomer of **64** and fullerene C_{60}.

In **65**, the electrophilic halogenation of the bridge C=C bond is a potential route to introducing solubilizing groups and self-assembling synthons in the molecular structure. Such modifications will allow for further investigation into the covalent and non-covalent chemistries of the corannulene-based curved nanographenes.

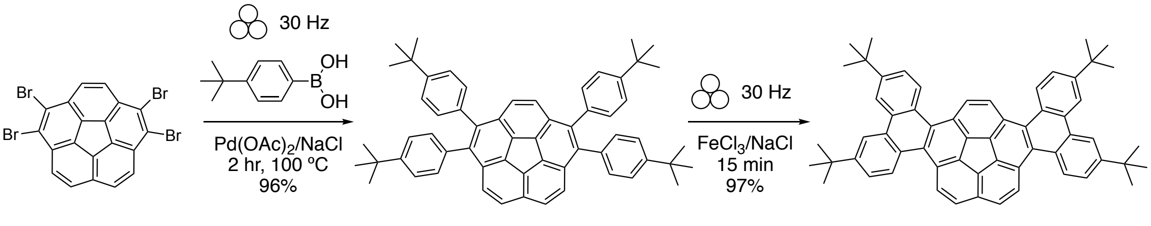
In Mallory reaction discussed thus far, stilbene-based precursors undergo an oxidative photocyclization reaction to join two adjacent aromatic nuclei into an extended aromatic structure. However, if a nitrogen atom replaces one of the carbon atoms in the central double bond, the Mallory reaction is known not to proceed under classic (chemically neutral) conditions.[57] It is likely that due to the involvement of the nitrogen lone pair, the photo-excitation energy decays rapidly through the internal conversion process. Surprisingly, however, corannulene-based imine precursors **66-71** successfully undergo oxidative photocyclization to produce single (**72-74**) and double (**75-77**) aza-helicenes in high yields (>90%) (Scheme 6).[58] It is reasonable to assume that corannulene helps in overriding the n-π* internal conversion process by lowering the product yielding π-π* excited state. Further work is required to support this notion and presents a good challenge for the future research in this area.



Scheme 6. Mallory reaction of corannulene-based imine precursors to access *N*-doped curved nanographenes.

2.4.2. Mechanochemical Synthesis

The photochemical approach represents a useful strategy in the aromatic extension of corannulene and the synthesis of non-planar nanographene structures. However, the use of organic solvents in such a synthesis poses sustainability issues. Mechanochemistry provides a potential alternative. In mechanochemical reactions, a solvent is not required. A simple ball milling of solids in a shaker mill is sufficient to perform the reaction and is known to be fast and high yielding. To examine this possibility, we chose to synthesize a corannulene-phenanthrene hybrid structure with positive and negative Gaussian curvatures (Scheme 7 and Figure 15).[4] The results show that solvent-less Suzuki and Scholl reactions were both successful in producing compounds **78** and **79** in isolated yields exceeding 95%. The former required 2 hours and the latter only 15 minutes for completion. Remarkably, sodium chloride can be used in both cases as the solid reaction medium which is a cheaper and greener alternative to organic solvents. These results demonstrate that mechanochemistry is an effective and sustainable synthetic tool in the preparation of curved corannulene-based nanographene structures.



78

79

Scheme 7. Mechanochemical synthesis of curved nanographenes.

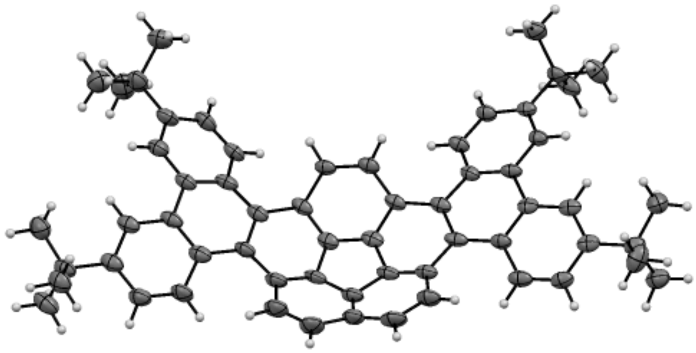


Figure 15. X-ray crystal structure of **79**.

3. Concluding Remarks

In this Account, we give a glimpse into our efforts of exploring the possibilities of materials chemistry with corannulene. It is clear that corannulene is a unique building block for functional material synthesis. Its uniqueness is rooted in its curved molecular structure and properties arising from this curvature. This distinction sets it apart from the plethora of other polycyclic aromatic building blocks in materials chemistry. We are confident that much is to be discovered in this regard and it is with this conviction that we look forward to the future with excitement and anticipation of new materials discovery based on this fascinating molecular motif.

Notes

The author declares no competing financial interest.

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Biography

A Romanian native, Mihaiela got her first taste of organic synthesis in the laboratories of Prof. Ion Grosu at the Babes-Bolyai University (Cluj-Napoca). Thereafter, she journeyed to Germany (Free University Berlin), Switzerland (ETH Zurich), and USA (University of Arizona at Tucson) for higher studies. It is upon her return to Zurich and the mentorship of Prof. Jay Siegel that she fell in love with corannulene. Since then her research has focused on introducing this beautiful molecule in the design of functional molecules and soft materials. In 2014, Mihaiela completed her habilitation thesis work at the University of Zurich and soon afterwards accepted the Nanyang Assistant Professorship from the Nanyang Technological University of Singapore.

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