

Conjugated aromatic systems

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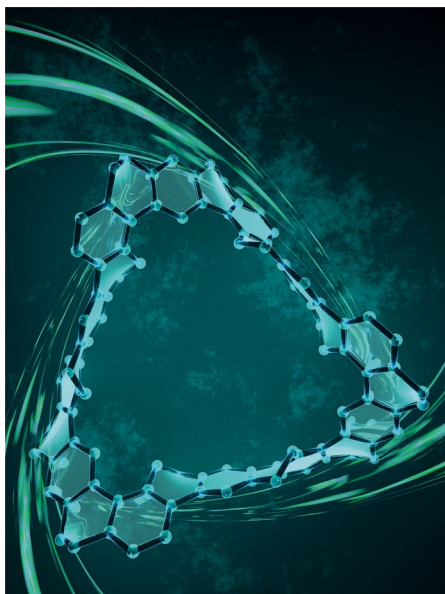
The synthesis of conjugated aromatic molecules and polymers with tailored properties provides a useful range of materials for electronic devices.

Conjugated molecules and polymers with their extended, delocalized π systems are well known for their optoelectronic properties. They are often strong absorbers of visible light and can show semiconductor behaviour, making them sought-after synthetic targets. In this issue, we explore the design and synthesis of conjugated structures with aromatic rings.

Conceptually, if these polycyclic aromatic systems (PAS) are composed of hydrogen and carbon only, they can be considered as fragments of graphene. It is therefore unsurprising that the electronic properties of these molecules and polymers are intriguing. These properties, together with typically high stability, have led to their application as active layers in devices including organic light-emitting diodes (OLEDs), organic thin film transistors (OTFTs) and photovoltaic cells.

Most conjugated small aromatic molecules with no pendant substituents are planar and, as their size increases, their solubility in common organic solvents decreases. Also, as molecular size or complexity increases, the structures can experience steric congestion, and the conjugated aromatic molecules become contorted, with curved π surfaces (M. Ball et al., *Acc. Chem. Res.* **48**, 267–276; 2015). Compared with planar aromatic molecules, these contorted structures have more diverse intermolecular interactions in the solid state, leading to enhanced charge transport properties. Moreover, if PAS are modified with hydrocarbon side chains, they can self-assemble into superstructures, some examples forming liquid-crystalline films which can be used as conductive materials in OTFTs (M. Ball et al., *Acc. Chem. Res.* **48**, 267–276; 2015). These distortions and modifications make it possible to tune and improve the electronic properties and solution processability of conjugated aromatic systems for a particular target application.

Acenes – comprising benzene rings fused together – are a simple form of conjugated



aromatic system. The member of the family with five fused benzenes, pentacene, is a semiconductor and commonly used in OTFTs. Following its discovery in the early 1900s, pentacene and its derivatives were well explored for use in organic electronics and since, attention has drifted to longer acenes. However, it is challenging to prepare acenes longer than hexacene because of their low solubility and poor stability, and only after several decades was it possible to extend the length to 12 fused benzenes (F. Eisenhut, *ACS Nano* **14**, 1011–1017; 2020).

In an Article in this issue, Uemura and co-workers report the synthesis of a polyacene (with around 18 fused benzenes) within the spatial constraints of a metal–organic framework (MOF). Inside the nanoscale channels of the MOF, sequential coupling reactions form a precursor polymer and then, dehydro-aromatization gives the polyacene. There will undoubtedly be wide interest in this polyacene owing to the known evolution of electronic properties as the length of the acene increases. Uemura and co-workers observe that the polyacene absorbs light ranging from the visible to the near infrared, as the polymer is a mixture of chains of different lengths. A News & Views by Schmidt discusses these MOF-made polyacenes further.

Also in this issue, from computational studies of fused benzenes, Renana Gershoni-Poranne discusses in a Q&A how the longest

linear length of fused benzenes closely influences the electronic properties, including the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), ionization potential and electron affinity. The longer the longest linear stretch, the smaller the HOMO–LUMO gap, and this is not affected by the total number of rings in the molecule. The Q&A outlines how useful computational studies are in the elucidation of structure–property relationships of PAS. Alongside the properties investigated for electronic applications, the development of PAS as ligands in catalysts is probed.

The synthesis of graphene-like molecules by stacking naphthalene blocks is reported in an Article by Yu Lan, Jingsong You and co-workers. Using rhodium-catalysed C–H activation–annulation, naphthalene ketones sequentially extend to form zigzag π -extended nanographenes. The nanographenes are then incorporated into n-type organic semiconductors for either OTFT or OLED applications.

Two Articles in this issue report the synthesis of twisted Möbius carbon nanobelts using different synthetic strategies. The strategies and structures in these approaches are compared in a News & Views by Miao and Casado. In the Article by Hiroyuki Isobe, Jishan Wu and co-workers, triply twisted nanobelts are formed by Suzuki coupling-mediated macrocyclization, followed by Bi(OTf)₃-catalysed cyclization of vinyl ethers and oxidative dehydrogenation. In the second Article, Daisuke Hashizume, Ken Tanaka and co-workers make twisted nanobelts that can have up to four twists by first forming cyclic polyynes consisting of linear paraphenylene and curved metaphenylene units. Then, these polyynes undergo rhodium(I)-catalysed [2 + 2 + 2] cycloaddition reactions to form the nanobelts. Also on the theme of cyclic aromatic molecules, a Q&A by Birgit Esser discusses the synthetic hurdles to make nanohoops and nanobelts, and highlights their use as charge storage components in organic batteries.

We hope you enjoy our Focus issue on conjugated aromatic systems and following the journey from computational prediction to synthesis, and through to the investigation and tuning of properties and applications.

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