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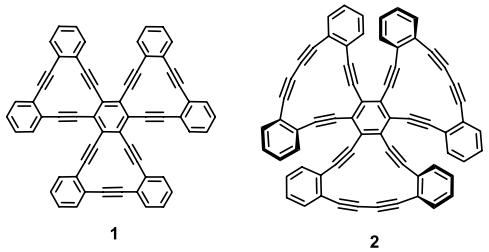
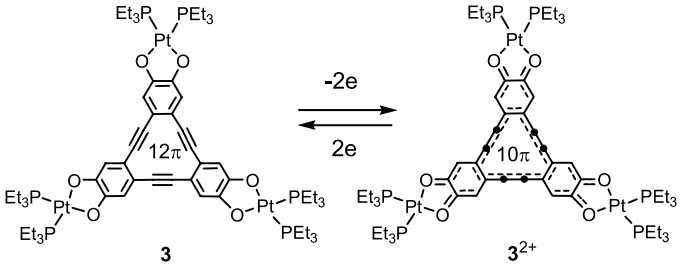
Synthesis of Structurally Novel Conjugated π-Systems

We have been studying the synthesis and properties of structurally novel, conjugated π-electronic systems of the nanometer regime, aiming at the creation of new materials with optoelectronic functions for use in nanotechnological applications. In particular, we have been focusing our attention on two- and three-dimensionally extended π-systems consisting of sp- and sp^2-hybridized carbon atoms.

For example, the trefoil-shaped molecule **1**, consisting of three dehydrobenzo[12]annulene ([12]DBA) units and possessing a partial structure of hitherto unknown two-dimensional carbon network *graphyne*, was synthesized utilizing a new synthetic method developed by us. Compound **1** was shown to exhibit a large two-photon absorption cross-section that facilitates π-electron delocalization due to its planar structure. The larger homolog **2** consisting of three dehydrobenzo[14]annulene ([14]DBA) units adopts a propeller-like nonplanar structure of C_{3v} symmetry. Because of its propeller shape and the readily polarizable [14]DBA units, compound **2** could serve as a component of a molecular motor when immobilized on a solid surface. Moreover, in order to develop a new redox-active ligand for transition metal complexes, we synthesized the platinum(II) complex **3** of catechol type [12]DBA and investigated its redox properties by means of both electrochemical and chemical oxidation.



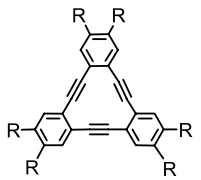
1 **2**



3 **3^{2+}**

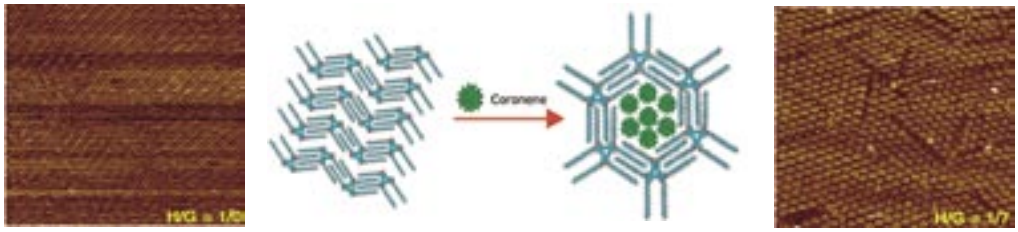
Self-Assembly of Shape-Persistent Macrocycles

Self-assembly of molecular building blocks on surfaces is a technique that has been widely employed to produce well-defined, two-dimensional (2D) molecular networks. In particular, molecular networks with void spaces (so-called *2D porous networks* with an intrinsic cavity within the molecules and/or void spaces formed between molecules) are of great interest because such networks would serve as templates for the controlled self-assembly of single-molecule-based devices, which will be of use in future nanotechnological applications. To build molecular networks with large intermolecular voids at the interface between highly oriented pyrolytic graphite (HOPG) and 1,2,4-trichlorobenzene (TCB), we employed [12]DBA derivatives **4a-f** with different alkoxy chains located on the periphery of triangle-shaped DBA cores and used a scanning tunnelling microscope (STM) as a tool to examine the molecular networks. DBAs **4a-b** with shorter alkyl chains formed porous honeycomb-type networks, whereas compounds **4c-f** with C_{14}-C_{20} chains exhibited nonporous linear

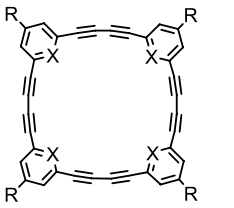


4a R=$OC_{10}H_{21}$
4b R=$OC_{12}H_{25}$
4c R=$OC_{14}H_{29}$
4d R=$OC_{16}H_{33}$
4e R=$OC_{18}H_{37}$
4f R=$OC_{20}H_{41}$

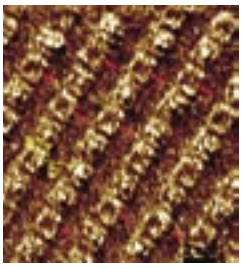
type structures. Surprisingly, however, upon adding an excess amount of guest coronene molecules to the already formed linear type pattern of **4c**, a nearly complete transformation into the honeycomb structure was observed. Whereas the linear structure of **4d** did not completely transform into the honeycomb structure with coronene, complete transformation was accomplished when a larger triangle-shaped molecule was employed as a guest.



Square-shaped macrocycles **5a-b,** having an intrinsic cavity, served as templates for controlled nanopatterning. The 2D molecular network of pyridine macrocycle **5a,** formed at the HOPG-TCB interface, binds tropylium ions, forming a two-dimensional array of the organic cation on the surface. More interestingly, **5a** formed a mixed 2D network with square macrocycle **5b** in which **5a** and **5c** were aligned alternately. Selective binding of tropylium ions by **5a** led to the formation of the alternating alignment of open and filled voids of the macrocycles.



5a X=N, R=$CO_2C_8H_{17}$
5b X=CH, R=$CH_2OC_8H_{17}$



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