Supramolecular Chemistry

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Coordination-Driven Self-Assembly of PEO-Functionalized Perylene Bisimides: Supramolecular Diversity from a Limited Set of Molecular Building Blocks**

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dyes/pigments · nanowires · molecular electronics ·
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Advances in the field of functional organic materials will rely on a combination of synthetic chemistry and materials science. Supramolecular chemistry may serve as the bridge between these different fields, as noncovalent interactions dominate the intermolecular packing of the constituent molecules in the final material and, hence, control its physical properties. Taking the formation of hierarchical structures in biology as a model,[1] organic materials with complex functions might be obtained from a small number of simple molecular building blocks through a limited set of highly efficient reactions, as long as the information necessary for the system to adopt a higher ordered structure is encoded at the molecular level. Sophisticated processing procedures may, finally, guide the system to find the desired hierarchical structure among the manifold of energetically similar alternatives. However, such an approach only seems feasible if intermolecular interactions can be used deliberately to induce structure formation in a predictable fashion. For this purpose, different types of supramolecular synthons need to be systematically investigated to develop a comprehensive set of supramolecular methods comparable to the large toolbox of reliable organic synthetic methods used in the synthesis of complex covalent structures. In particular, directed interactions such as aromatic interactions[2] or hydrogen bonding[3] have recently been investigated for the rational or even predictable formation of supramolecular assemblies. A particularly instructive example was recently reported by Rybtchinski and co-workers, who investigated the self-assembly of poly(ethylene oxide)-substituted perylene bisimide derivatives, some of which were equipped with terpyridine ligands for the coordination of transition metals.[4] In their investigations, the authors combined amphiphilicity, polymer attachment, π–π stacking, and metallo-supramolecular interactions to prepare optoelectronically active organic materials with different supramolecular morphologies from essentially the same simple set of molecular building blocks.

Organized assemblies of organic dyes play a major role in electron-transfer processes in biological systems, and they are essential in photovoltaic and other organic electronic applications. For this reason, the solution-phase self-assembly of functionalized perylene bisimide dyes has been a popular subject of investigation in recent years, because their promising n-type semiconducting properties render them interesting substrates for the preparation of organic semiconducting nanowires or nanostructured bulk materials.[5] In one of the most elaborate examples, Würthner, Meijer, and co-workers reported perylene bisimides to which two oligo(phenylene vinylene) segments with chiral substituents were attached through complementary multiple hydrogen-bonding interactions.[6] The resulting donor–acceptor–donor dye triads were found to form well-defined, helical nanoscopic fibrils that showed photoinduced electron transfer and may be regarded as "double-cable" nanowires. Further examples include liquid-crystalline phases from perylene bisimides with bulky terminal tris(dodecyloxy)phenyl substituents,[7] organogels from related hydrogen-bonded derivatives,[8] and helical fibrils from perylene bisimides with tris(dodecyloxy)phenyl residues attached as side groups at the "bay area" (1,6,7,12-positions), which gave rise to strongly fluorescent J-aggregates.[9] Li and co-workers reported the controlled folding of macromolecules obtained by linking perylene bisimides to oligonucleotides,[10] while Finlayson et al. covalently attached perylene bisimides to poly(isocyanopeptide)s as rigid 4_1-helical scaffolds.[11]

Metal-coordination-directed self-assembly has been thoroughly investigated as a means to obtain multicomponent

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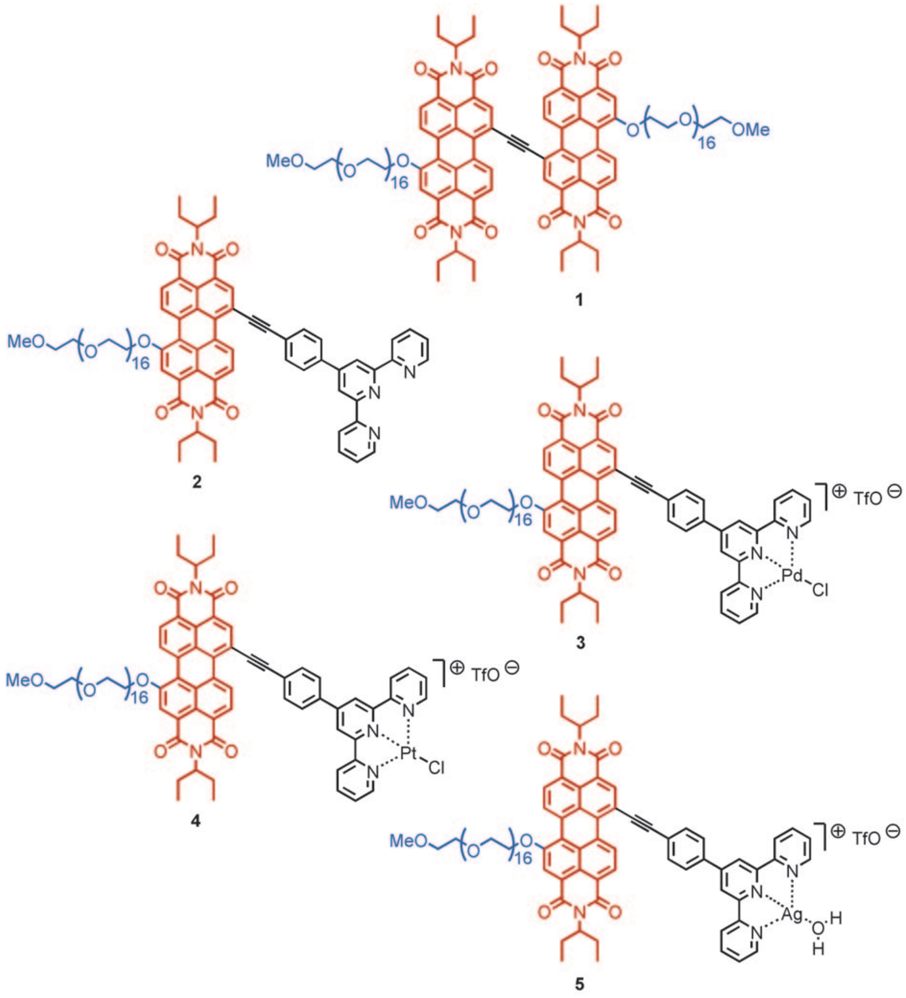
macrocycles,[12] metallo-supramolecular polymers,[13] including hierarchically structured materials from folded polymers[14] or polyrotaxanes,[15] and two-dimensional lattices.[16] Metal coordination to pyridine- or terpyridine-substituted perylene bisimide derivatives has been used to prepare defined multichromophoric nano-objects and supramolecular polymers.[17]

The attachment of amorphous polymer segments to monodisperse self-assembling segments is a versatile tool to create well-defined nanostructures, for example from otherwise insoluble hydrogen-bonded oligopeptides and oligo(aramide)s.[3] The polymer segments serve to 1) provide solubility in an increased variety of chemical environments, 2) prevent the premature precipitation of ill-defined, insoluble aggregates, and 3) guide the molecules toward the formation of well-defined nanoscopic structures by "frustration" of the self-assembling segments' crystallization. Thus, the enthalpy of crystallization is counterbalanced by the entropy penalty associated with the required chain extension of the attached, noncrystalline polymer segments, thus resulting in a thermodynamic equilibrium structure with lateral dimensions on the molecular length scale.



Scheme 1. Perylene bisimide derivatives **1**–**5** containing hydrophilic poly(ethylene oxide) (PEO) segments. Some of them also contain terpyridine ligands and transition-metal fragments to tune their self-assembly behavior. OTf = CF_3SO_3.

Rybtchinski and co-workers combined the different supramolecular elements outlined above in their target molecules **1**–**5** (Scheme 1) and were, thus, able to create a versatile and adaptive set of optoelectronically active supramolecular materials. The covalently linked symmetric derivative **1**, for example, was observed to self-assemble into nanoscopic fibrils that were several micrometers long. Their "necklace" morphology is a rarely observed feature (Figure 1 a), suggesting stacking of the chromophores perpendicular to the fibril axis. While the width of these "necklace" fibrils was defined by the length of the chromophore, their uniform height was, supposedly, controlled by "frustration" of the crystallization by the attached polymer segments. The well-known formation of stable perylene bisimide anions upon reduction was then exploited to induce controlled and reversible deaggregation. Reduction led to the formation of micelles (Figure 1 b), which was accompanied by a color change from green to blue and a significant decrease in viscosity. Apparently, the originally hydrophobic dye became hydrophilic, and the charges introduced repulsive electrostatic interactions. The reductive deaggregation was found to be reversible upon exposure to air, yielding the same nanoscopic fibrils as before and allowing the self-assembly of **1** to be easily switched on and off. The authors have created a stimuli-responsive supramolecular polymer which forms or depolymerizes under oxidative or reductive conditions, respectively, and changes its optoelectronic properties accordingly.

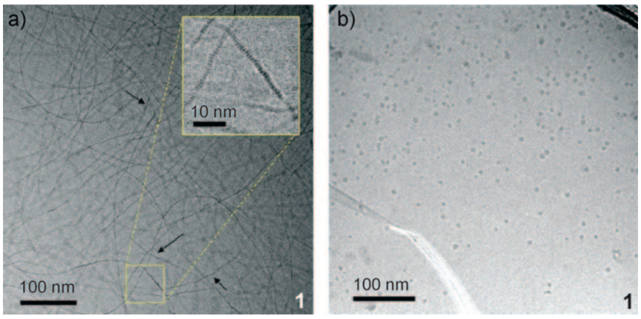


Figure 1. a) Cryo-transmission electron microscopy (TEM) images of "necklace" fibrils formed from **1** (after exposure to air). b) Micelles after reduction of **1** to the anion.

Extending the scope of supramolecular structures afforded by a single covalent building block, Rybtchinski and co-workers proceeded to combine the PEO-substituted perylene bisimides as a "permanent" supramolecular motif with a "tunable" one, that is, a terpyridine ligand which forms planar complexes with Pd, Pt, and Ag ions. Interestingly, the uncomplexed derivative **2** formed "necklace" fibrils (Figure 2a) closely related to those obtained from **1**, indicating the formation of loosely bonded dimers (owing to the hydrophobic effect) which then stacked perpendicularly to the fibril's axis.

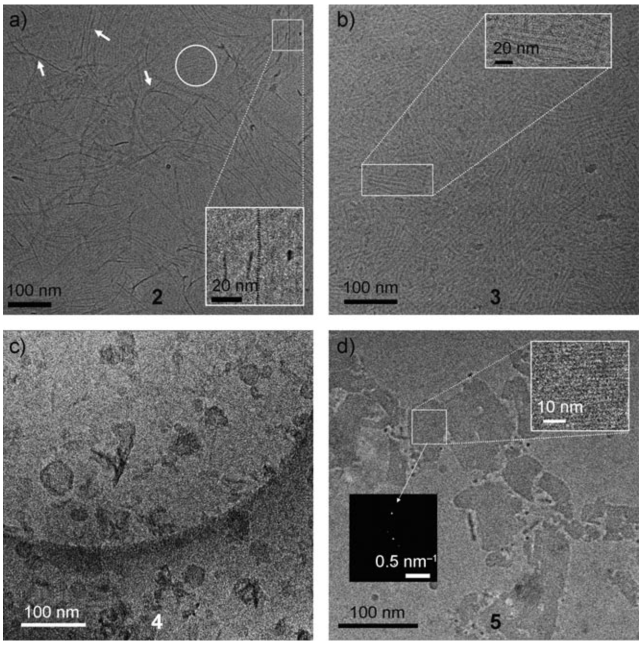


Figure 2. Cryo-TEM images of **2**–**5** revealing a) "necklace" fibrils, b) hollow tubules, c) vesicular aggregates, and d) lamellar platelets.

This self-assembly behavior changed upon the addition of transition-metal salts, and nanoscopic tubules, vesicles, or platelets were obtained from the complexes **3**–**5**. The Pd complex **3**, for example, formed nanoscopic tubules (Figure 2b). Apparently, the perylene bisimides stacked to form hollow cylinders such that the inner surface was covered with the Pd complexes and the hydrophilic PEO segments were placed on the outside to shield the self-assembled structures from the hydrophilic solvent (water/THF). Interestingly, the isovalent Pt complex **4** gave rise to bilayer vesicles about 30 nm in diameter (Figure 2c). The authors proposed that the formation mechanism was similar to that observed for **1** and **2**, with the difference that the stacking of the perylene bisimides perpendicular to the fibril axis appeared to be infinitely extended, yielding two-dimensional bilayers (closing to form vesicles) instead of one-dimensional fibrils. UV/Vis spectra indicated the presence of Pt–Pt interactions, which seem to provide a sufficient additional enthalpy contribution to overcome the entropy-driven "frustration" of crystallization. Finally, the Ag derivative **5** formed bilayer platelets several dozens of nanometers in diameter (Figure 2d). On the basis of the fine structure of these bilayers, the authors proposed a structure model related to the previous case, assuming additional hydrogen bonding of complexed water molecules to be responsible for the extension from one- to two-dimensional aggregates. The directional nature of these hydrogen-bonding interactions as opposed to the Pt–Pt interactions in **4** was proposed to induce an increased rigidity of the resulting bilayer, decreasing the curvature and precluding the formation of closed vesicles.

The aggregates of **2**–**4** exhibited energy-transfer properties similar to those observed in natural photosynthetic complexes, suggesting that they might be good candidates for artificial light-harvesting systems. In particular, the Pt complex **4** exhibited an excellent coverage of the solar spectrum, and the photofunctional properties of derivative **1** could be switched off by reduction of the perylene groups and restored under oxidation by air.

In conclusion, Rybtchinski and co-workers prepared a variety of nanostructured materials derived from a limited set of closely related, optoelectronically active, supramolecular building blocks. Furthermore, they were able to provide a reasonable explanation for the different observed superstructures. While this, of course, does not imply predictability of nanostructure formation, it may still serve as a valuable guideline for how to utilize the employed supramolecular motifs in a rational way for the preparation of highly ordered materials. The interesting optoelectronic properties of the obtained materials and their dependence on the type of superstructure, combined with the elegant and simple processing into the desired morphology, could make these materials interesting candidates for future applications in photovoltaics.

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