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Nanostructures

Two-Dimensional Nanostructures from Positively Charged Polycyclic Aromatic Hydrocarbons**

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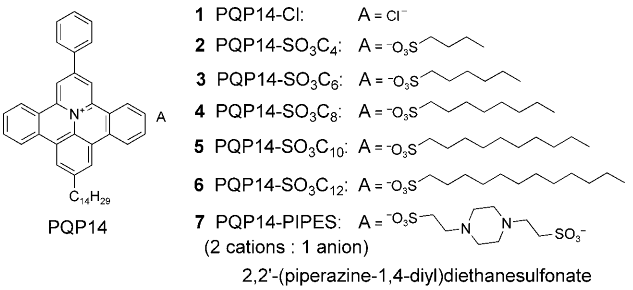
Over the last years, the rapid development of graphene, an ultrathin flat hexagonal lattice of carbon,[1] has led to increased interest in two-dimensional (2D) nanomaterials. These materials mainly refer to sheetlike structures that possess a high degree of anisotropy with a thickness that is a few orders of magnitude smaller than other dimensions.[2] The self-assembly of organic amphiphiles allows for the bottom-up fabrication of versatile nanostructures with controllable morphology by modification of the molecular structures or external conditions.[3] Thus this approach provides an appealing possibility for the template-free construction of novel 2D nanomaterials.[4] The organization of amphiphilic molecules with functional moieties, such as large aromatic cores or ionic species, into 2D nanostructures has been scarcely studied so far. Such 2D nanostructures can provide pathways for the transport of charges, ions, and energy.[5]

Positively charged polycyclic aromatic hydrocarbons (PAHs), like 9-phenyl-benzo[1,2]quinolizino[3,4,5,6-*fed*]phenanthridinylium (PQP, Scheme 1) salts, are particularly attractive building blocks for supramolecular chemistry because: 1) their extended aromatic frameworks offer aromatic interactions to enhance the stacking of molecules in the aggregated state;[6] 2) the introduction of hydrophobic alkyl chains to the hydrophilic aromatic cores of PQPs provides amphiphilic interactions, thus leading to molecules that form well-defined arrays in solution; 3) the arrangement of PQPs in superstructures can be controlled by choosing proper anions; and more importantly, 4) such self-organized superstructures of PQPs can serve as electrolytes to offer a channel for the transport of ionic species dissolved within.[7] Recently, we have made use of these advantages of PQPs to control their self-assembly behavior in solution as well as in the bulk. Nanostructures of alkylated PQPs with different morphologies such as fibers, ribbons, and tubes can be formed in methanol depending on the length of the alkyl substituents and the size of the inorganic anions.[8] On the other hand, well-ordered 1D columnar superstructures of PQPs are established in the bulk by the use of alkyl sulfonate anions through a so-called ionic self-assembly (ISA)[9] process.[10] Inspired by these results, we envision that the self-assembly of PQP salts into nanostructures with diversified morphologies would be experimentally feasible by the selection of different organic anions.



Scheme 1. PQP14 complexes studied herein.

Herein we demonstrate that the amphiphilic tetradecyl-substituted PQP (PQP14, Scheme 1) salts that contain alkyl sulfonate anions or disulfonate anions, can spontaneously organize into 2D nanostructures in solution. For PQP14 complexes with alkyl sulfonates, puckered 2D nanobelts with regular morphology are formed with the increase in the alkyl chain length of the anions, which can be ascribed to improved amphiphilic interactions during the coassembly of the cations and anions. By using a disulfonate anion, planar 2D aggregates are obtained, thus indicating that the "double anion" has a more profound impact on the 2D organization of PQP14 cations than the alkyl sulfonates. Notably, the different morphologies of these 2D nanostructures significantly affect the ionic conductivity of the mixture of PQP14 complexes and lithium salts, for which the planar aggregates exhibit a conductivity of two orders of magnitude higher than that of the puckered ones.

Ionic complexes **2**–**7** (Scheme 1) were prepared from PQP14-Cl **1** and the sodium salts of the corresponding sulfonate anions by an ion-exchange procedure described previously (see the Supporting Information).[10] To investigate their aggregation behavior, a phase transfer (PT) method with a methanol/water 1:1 binary solvent system was adopted to

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prepare nanostructures from the ionic complexes (see the Supporting Information).

The nanostructures of the ionic complexes **2**–**6**, which contain different alkyl sulfonate anions, were investigated by scanning electron microscopy (SEM). As shown in Figure 1 a and Figure S1 in the Supporting Information, 2D nanostructures can be found for all compounds. Among them, the aggregates formed by **2** show the most disordered shapes that consist of twisted 2D belts and 1D rods; compounds **3**, **4**, and **5** in contrast generate twisted beltlike nanostructures. The irregular morphologies of the nanostructures from **2**–**5** indicate that there is more than one type of supramolecular arrangement in their aggregates. It is worth noting that the puckered 2D aggregates formed by **6** are more uniform with a length of tens of micrometers and a width of 200 nm to 1 μm. Such a morphology is further confirmed by TEM (Figure 1 b)[11] and AFM (Figure 1 c). The thickness of these 2D nanobelts is around 80 nm (Figure 1 d and Figure S2a).

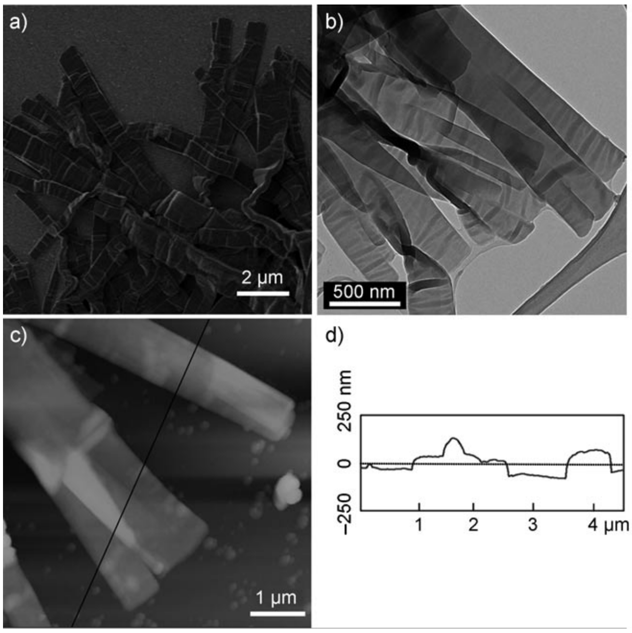

Figure 1. a) SEM, b) TEM, and c,d) AFM images of 2D aggregates formed by compound **6**.

Wide-angle X-ray diffraction (WAXD) measurements were employed to further analyze the aggregates from **2**–**6** and to elucidate the correlation between their supramolecular arrangements and macroscopic morphologies. Figure 2 a discloses that compounds **2**–**6** show two diffraction peaks at 2θ that range between 2 and 7°, which are indexed as (100) and (200) reflections associated with lamellar packing. As the longer alkyl chains of anions need more space in aggregates, it is reasonable that the *d* spacing of the (100) reflection increases from 2.61 (**2**–**5**) to 2.86 nm (**6**). For compounds **2**–**5**, the broad (100) reflections suggest that they may contain more than one peak, which is consistent with their irregular morphologies observed in SEM images. Moreover, with the increase in alkyl chain length, the intensity of the diffraction peak (200) becomes stronger and an additional weak diffraction peak attributed to the (300) reflection can be observed. This result suggests that **6** can establish a more ordered lamellar superstructure in comparison to **2**–**5**, which is in accordance with the observation of uniform nanostructures from **6**. This phenomenon is attributed to an improved amphiphilicity with an increased alkyl chain length of the anions, which subsequently enhances the coassembly of cations and anions.

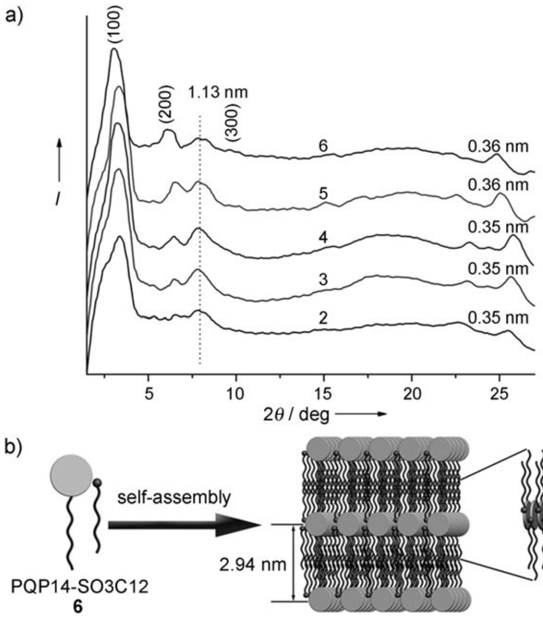

Figure 2. a) Wide-angle X-ray diffractograms of ionic complexes **2**–**6** (the peak related to the distance of 1.13 nm corresponds to the width of the PQP14 cation.[14]); b) Schematic illustration of the formation of 2D nanostructures from **6.**

It should be emphasized that compounds **2**–**6** belong to a class of ionic complexes called catanionic amphiphiles, which are traditionally referred to as mixtures of cationic and anionic surfactants.[12] It is well known that catanionic amphiphiles can easily form molecular bilayers (a membrane structure made of two layers of molecules) in solution caused by the compactness of the head groups.[12] However, exposition of the hydrocarbon tails to the aqueous phase at the edges of the bilayers requires more energy than bending them into closed vesicular structures. Thus, the 3D vesicle is normally a favorable morphology for self-assembly of catanionic amphiphiles,[13] while 2D nanostructures have been only observed under critical salt-free conditions.[4a] For compounds **2**–**6**, the diffraction peak of 2θ at approximately $25.4 \pm 0.5°$ corresponds to the typical π-stacking distance of about 0.35 nm (Figure 2 a), hence suggesting the existence of aromatic interactions. Therefore, we consider this additional noncovalent interaction to be the driving force for the prevention of the bending of the layered superstructures into vesicles, which is in stark contrast to the behavior of traditional catanionic amphiphiles.[6,13] Given the fully extended molecular length of 2.8 nm for a PQP14 cation,[14] each lamella of **6** (2.86 nm) should consist of two fully interdigitated layers of PQP14 cations.[15] Based on the above analysis, one possible packing model for **6** in the aggregates is proposed in Figure 2b. In this model, the coassembly of PQP14 and dodecane sulfonate (SO_3C_{12}) generates bilayer lamellae with the staggered cofacial stacking of the aromatic cores stabilizing the resulting superstructure. The alkyl chains of the cations and the anions arrange between the layers of aromatic cores and in this way reduce the rigidity of the lamellae,[16] thus leading to a wrinkled surface of the nanostructures.

When two conventional surfactants are linked by covalent bonds, the resulting amphiphiles usually show different supramolecular organization because the covalent bonds can direct the molecular orientation as well as increase the robustness of self-assembled superstructures.[17] With this in mind, we further investigated the effect of a “double anion” on the self-assembly behavior of PQP14 complexes. The short and rigid disulfonate anion of compound **7** can serve as a cross-linker to bind two neighboring PQP14 cations into a dimeric form,[18] which resembles the gemini amphiphiles obtained from two conventional surfactants chemically linked by a spacer.[17a] Such dimeric amphiphiles were reported to form anisotropic membranes in solution and on surfaces because of the orienting effect of the linker.[19] Indeed, almost perfect 2D nanostructures with sharp edges were derived from the self-assembly of **7**, as demonstrated by SEM and TEM (Figure 3a and b).[11] The width of these nanostructures is between 200 and 800 nm and the length is in the range of 800 nm to 8 μm. AFM characterization (Figure 3c and d) reveals that these planklike aggregates have smooth surfaces and their thickness is around 30 nm (Figure S2b), hence further confirming their flat 2D structure.

In comparison with the wrinkled nanobelts from **6**, the aggregates of **7** have a high-quality 2D anisotropic morphology with a planar surface. The difference can also be seen from their diffractograms (Figure 4a). The WAXD of the 2D planks from **7** contains three well-resolved diffraction peaks associated with the (100), (200), and (300) reflections, thereby suggesting a highly ordered lamellar superstructure. The *d* spacing is calculated to be 4.20 nm, hence indicating a much larger unit cell than that of **6** (2.86 nm). Based on the structural analysis and previous study on gemini amphiphiles,[19] a mechanism is proposed to explain the formation of 2D nanostructures from **7**. As shown in Figure 4b, the PQP14 dimers self-assemble into bilayer lamellae with interdigitated alkyl chains. The disulfonate anions prevent the overlap of aromatic cores in different layers, which thereby results in a repeat distance of 4.20 nm for each lamellar superstructure. In addition, a significant difference of the scattering intensities in the 2θ range of 18–22° between compounds **2**–**6** and **7** is obvious. In comparison to all other samples, **7** shows more crystalline reflections in this region, thus indicating ordered alkyl chains. This result confirms our proposed model for the organization of the anions. For **7**, the rigid disulfonate anions are located between the PQP14 cations (Figure 4b) and do not affect the side-chain crystallinity. In the case of **2**–**6**, the alkyl sulfonate anions arrange within the alkyl fraction of the PQP14 cation (Figure 2b) and in this way soften/disorder the alkyl substituents.

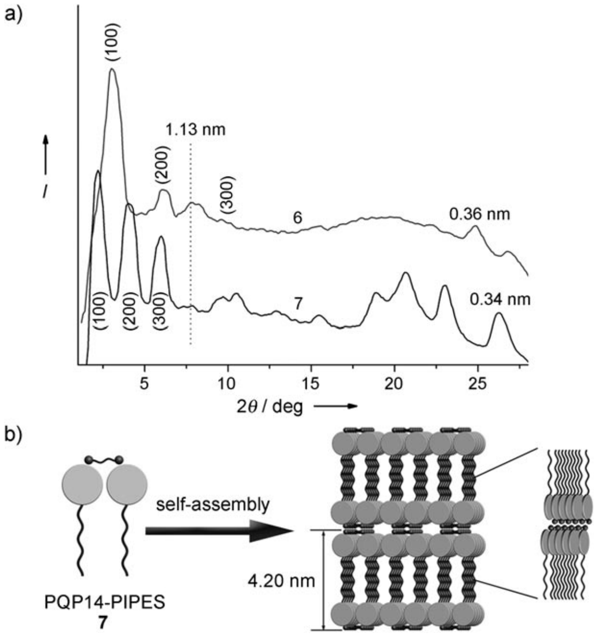

Figure 4. a) Wide-angle X-ray diffractograms of ionic complexes **6** and **7** (the peak related to the distance of 1.13 nm corresponds to the width of the PQP14 cation[14]); b) Schematic illustration of the formation of nanoplanks from the ionic complex **7**.

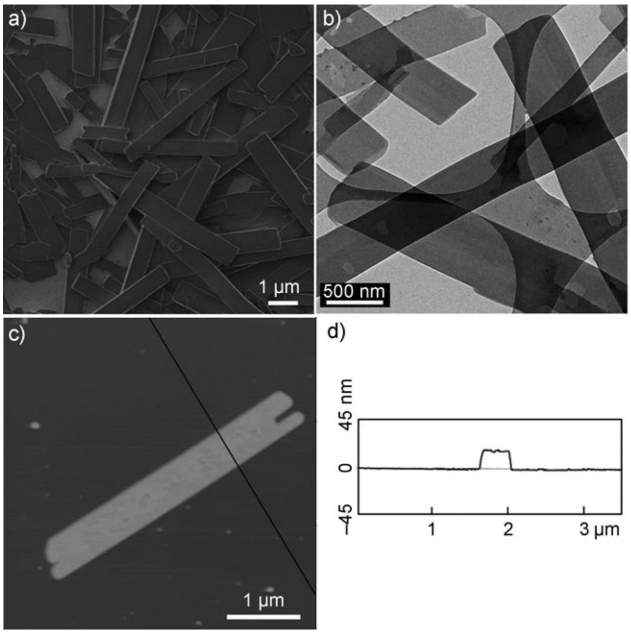

Figure 3. a) SEM, b) TEM and c,d) AFM images of nanoplanks obtained from the suspension of ionic complex **7**.

The nanostructures formed by PQP14 complexes have potential as ion conductors because of their phase-segregated structures.[5a] Therefore, the ionic conductivity of the PQP14 complexes (**6** and **7**) mixed with lithium salts were investigated (see the Supporting Information). A film of aggregates obtained from a mixture of **7** and $LiClO_4$ shows a conductivity of $\sigma = 7.3 \pm 0.5 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$ at ambient temperature, which is comparable to other supramolecular ion conductors.[7] This value is dramatically higher than that of the

2D nanobelts formed by **6** with $LiClO_4$ ($\sigma = 2.4 \pm 0.6 \times 10^{-7}$ $S\,cm^{-1}$). The obvious enhancement in the ionic conductivity has two reasons: Firstly, the highly ordered alignment of **7** in the aggregates offers a better channel for ion transport than **6**; secondly, compared to the puckered belts of **6** with $LiClO_4$, the planks from **7** with $LiClO_4$ have better contact with each other because of their flat surfaces, therefore effectively reducing the resistance of the film.

In summary, a controllable assembly of amphiphilic PQP14 complexes into 2D nanostructures has been achieved by choosing alkyl sulfonates or disulfonates as anions. For the first time, our results demonstrate that the 2D nanostructures with ordered morphology can lead to an improved ionic transport behavior. This work not only offers a new approach for the creation of 2D organic nanomaterials but also provides more insight into the self-assembly mechanism for the formation of stable planar aggregates with amphiphilic aromatic molecules.

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