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Controllable Columnar Organization of Positively Charged Polycyclic Aromatic Hydrocarbons by Choice of Counterions

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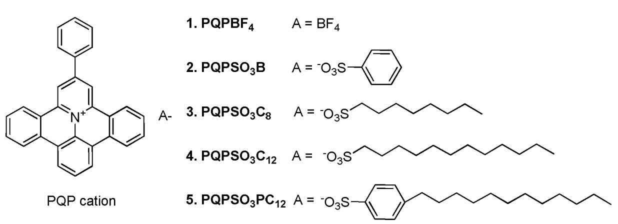
The organization of polycyclic aromatic hydrocarbons (PAHs) into columnar superstructures, which provides one-dimensional (1D) channels for energy/charge migration, has received great attention because of its potential applications in organic (opto)electronics and nanotechnology.[1] Besides $\pi-\pi$ interactions, various noncovalent intermolecular forces, such as hydrogen-bonding,[2] amphiphilic,[3] and charge-transfer interactions,[4] have been utilized as secondary forces to tailor the molecular arrangement of PAHs in columnar superstructures. Among them, ionic interactions are of paramount importance for creating new columnar systems and allowing one to tune liquid crystal (LC) properties.[5] Hierarchical columnar LCs have thus been constructed from PAHs consisting of charged substituents such as hexapyridinium (or hexaimidazolium)-substituted triphenylene[6] and *N*,*N′*-bis(ethylenetrimethylammonium)perylenediimide[7] with oppositely charged amphiphiles by a so-called ionic self-assembly (ISA) process.[5b] However, the charged substituents in these cases were located at the periphery of the aromatic cores. The design of novel columnar superstructures consisting of PAHs with charged aromatic cores is attractive and promising because such systems are expected to exhibit a unique self-organization into 1D ionic channels. This concept has rarely been addressed.

We recently described a class of positively charged 9-phenylbenzo[1,2]quinolizino[3,4,5,6-*fed*]phenanthridinylium (PQP) ions (Chart 1) for which the length of alkyl substituents as well as the size of inorganic anions critically influence the self-assembly behavior in solution, resulting in aggregates with different morphologies.[8] Here we report for the first time a controllable columnar organization of ionic PQP complexes containing a large charged aromatic core (Chart 1) in the crystalline and liquid-crystalline phases that is achieved simply by varying the organic counterions. A single crystal of the ionic complex **2** involving a benzenesulfonate anion exhibits a staggered dimer arrangement of PQP cations that further establishes columnar superstructures. Remarkably, the use of sulfonate anions with long alkyl tails leads to well-ordered discotic columnar mesophases with an identical staggered packing of the PQP complexes.

The new salts presented in Chart 1 were prepared from PQPBF$_4$ (**1**) and the sodium salts of various sulfonic acids by ion exchange. ^{1}H NMR spectroscopy and elemental analysis confirmed the chemical identities of the ionic complexes (see the Supporting Information). To investigate the stacking behavior of PQP derivates with different anions, single crystals of compounds **1** and **2** were first grown from their methanol solutions. Interestingly, the X-ray diffraction analysis indicated that **1** adopts a coplanar structure in which the phenyl ring and the large aromatic core remain in one plane, while they further organize into a condensed layered packing (Figure 1a and Figure S1a in the Supporting Information). Within each layer, two PQP cations stack into an interdigitated arrangement in which the phenyl ring is located at the bay position of its neighboring cation (as indicated by arrows in Figure 1a), whereas the BF$_4^-$ anions are distributed in the spaces between the dimers. On the other hand, every two PQP cations in neighboring layers adopt a staggered stacking, where the phenyl group is packed on the aromatic core of another cation. The intermolecular distance of ~0.35 nm is typical for a pronounced $\pi-\pi$ interaction (Figure S1b,c).

Chart 1. PQP Complexes Studied in This Work



In contrast to the layered packing of **1**, the benzenesulfonate salt **2** presents a highly ordered columnar stacking of PQP cations in the crystal. The asymmetric unit consists of two molecules (A and B) forming a dimer in which two PQP cations are packed in a cofacial, antiparallel arrangement. These are stacked along the *b* axis with centers of symmetry between the dimers. Thus, three different intermolecular contacts (A−B, B−B′, and A−A″; Figure 1b) with slightly different stacking distances of 3.40, 3.38, and 3.42 Å, respectively, are observed. In contrast to **1**, here the phenyl rings are not coplanar but arranged out-of-plane by an angle of 35° with respect to the aromatic core of the PQP cation. The projections along the columns are shown in Figure 1c and Figure S2. The anions

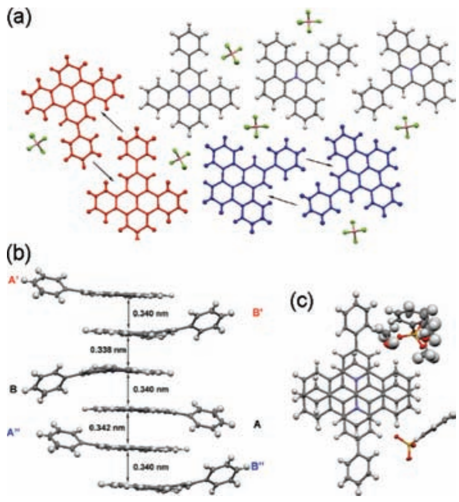


Figure 1. (a) Top view of the layered crystal structure of **1**; (b) side and (c) top views of the columnar structure of **2**.

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and methanol solvate molecules are located in the channels between the columns. Interestingly, three methanol molecules are bound by hydrogen bonds to only one of the two anions in the dimer (Figure S2b). We ascribe the dissimilar stacking behaviors of **1** and **2** to the different sizes of their anions. The small BF_4^- anions are located next to the cations, allowing the formation of a condensed layered structure. In contrast, the large benzenesulfonate anions require more space, leading to a better separation between the rigid aromatic cores. To the best of our knowledge, **2** is the first example of a single-crystal structure in which a columnar stacking of PAHs with charged aromatic cores has been observed.

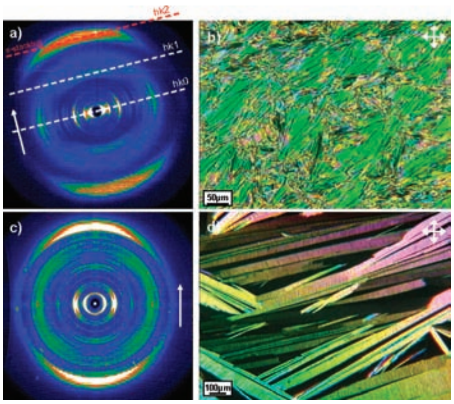

Figure 2. 2D WAXS patterns for (a) **5** and (c) **3** recorded at 30 °C [white arrows indicate the fiber orientation, and the dashed layer lines in (a) are assigned using Miller indices]. POM images with cross-polarizers recorded at 30 °C for (b) **5** and (d) **3** as each cooled from the isotropic phase at 1 °C/min.

Inspired by the single-crystal results, one may expect that the columnar superstructures of PQP complexes should be even established in the liquid-crystalline phase. Therefore, the behavior of LCs of PQP complexes **3**, **4**, and **5** containing sulfonate anions with long alkyl tails was subsequently investigated. Fiber wide-angle X-ray scattering (WAXS) experiments performed at 30 °C on both **5** (Figure 2a) and **4** (Figure S4) revealed 2D patterns typical of columnar discotics. The equatorial plane of the pattern, assigned as the *hk*0 layer line, indicates the intercolumnar arrangement whereby the columnar stacks are oriented along the fiber direction. In the case of both **4** and **5**, the X-ray scattering results did not allow one to distinguish clearly between a rectangular and a larger hexagonal unit cell (Figure S3). The broad, high-intensity wide-angle meridional reflection in the 2D pattern for each of three compounds **3**, **4**, and **5** is related to the π-stacking distance of 0.35 nm between individual molecules packed in the columns. Remarkably, the three compounds also showed additional reflections on the *hk*1 layer line corresponding to a spacing of 0.70 nm along the stacking axis, which is twice the π-stacking distance.[9] This intracolumnar correlation between every second molecule in the bulk confirms the above-described staggered arrangement of the PQP cations already observed in the single crystal. It should be noted that the intracolumnar staggered arrangement of the PQP cations is independent of the degree of steric demand of the substituents and remains unchanged in the mesophase and crystalline phase. Hence, the introduction of sulfonate anions with long alkyl tails through the ISA process allows one to control the thermal behavior in a relatively facile but efficient way while at the same time maintaining the columnar organization. This is a great advantage in comparison with systems in which substituents are covalently linked to the PAH core, where variation is often synthetically challenging and the molecular organization is less controlled.[1] In our present case, the intracolumnar staggered organization remains unchanged for **3**, **4**, and **5**, although the thermotropic properties of the compounds differ significantly. As expected, long chains result in the formation of discotic mesophases for **4** and **5** even at ambient temperatures. Each compound shows only one phase transition directly to the isotropic melt, at 180 °C for **4** and 210 °C for **5**. Images from polarized optical microscopy (POM) reveal that both compounds exhibit typical birefringent mesophase textures that are shearable as thin films (Figure 2b), confirming the soft mesophase character.[10] On the other hand, compound **3** shows only a crystalline state, as indicated by the highly optically anisotropic needles in the POM picture (Figure 2d) and the reflections in the 2D pattern with mixed indices in the first layer line (Figure 2c). A hexagonal unit cell with $a_{\text{hex}} = 2.78$ nm was determined for **3**.

In conclusion, an unprecedented columnar organization of ionic complexes based on PQP has been achieved via ionic self-assembly. These complexes represent the first family of PAHs containing a charged aromatic core with controllable columnar organization in the bulk state. Since the supramolecular organization of PAHs with charged aromatic cores can be easily tuned by their counterions, future work should include the use of more elaborate counterions that can incorporate hydrogen bonding, metal coordination, or chirality to further adjust their phase behavior. The influence of the charges of the aromatic cores could be investigated by the selection of charged PAHs with different core sizes, charges, or heteroatoms. The combination of their charged nature and well-organized columnar superstructure makes these materials promising for 1D anisotropic ion transport or construction of novel charge-transfer complexes.[11]

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Supporting Information Available: Preparation and characterization of ionic complexes, WAXS experiments, and single-crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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