Nanostructures

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# Self-Assembly of Positively Charged Discotic PAHs: From Nanofibers to Nanotubes**

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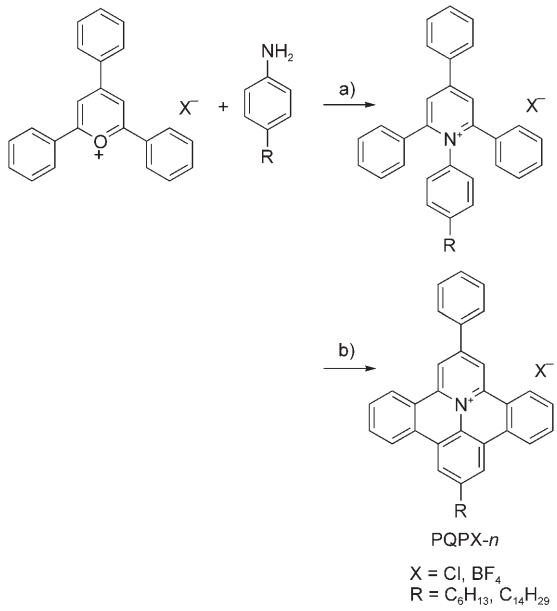
The self-assembly of polycyclic aromatic hydrocarbons (PAHs) to form nanostructures of different morphologies is attractive for supramolecular electronics.[1] The aggregates obtained from π–π interactions between PAHs can provide charge-transporting pathways and thus can be used as active materials in electronic and optoelectronic devices.[2] The appropriate functionalization of discotic PAHs such as triphenylene, dibenzonaphthacene, and hexa-*peri*-hexabenzocoronene improves both their ability to be processed and their aggregation behavior. The latter advantage comes from the presence of additional intermolecular forces, including van der Waals interactions, amphiphilic interactions, hydrogen bonding, or other noncovalent forces.[3] However, the introduction of substituents can only be done at the periphery of the discs. The incorporation of heteroatoms into the aromatic skeleton of such PAHs offers an opportunity to strongly influence their intermolecular carrier-transport properties when they are fabricated into nanoarchitectural devices.[3f,4] Although a few centrally charged discotic PAHs have been synthesized,[5] to the best of our knowledge, their aggregation behavior has not been reported.

Herein, we present a series of amphiphilic centrally charged discotic PAHs, 9-alkyl-2-phenylbenzo[8,9]quinolizino[4,5,6,7-*fed*]phenanthridinylium salts, abbreviated as PQPX-*n*, where X stands for the anion and *n* corresponds to the number of methylene units in the alkyl chain. The self-assembly behavior of these PQPs in solution as well as in the solid state has been investigated. One-dimensional (1D) nanoscaled fibers, ribbons, and tubular structures were formed simply and in a defined manner by varying the length of the alkyl chains and the counterions of the charged PAHs. Furthermore, the mechanism of PQP aggregation is proposed.

The synthesis of the 1-aryl-2,4,6-triphenylpyridinium salts and their subsequent dehydrogenations were carried out by a modified literature procedure[5] (see the Supporting Information). PQPX-6 and PQPX-14 with chloride and tetrafluoroborate as counterions were synthesized in this way (Scheme 1). The molecules were characterized by $^1$H NMR and $^{13}$C NMR spectroscopy as well as by MALDI-TOF mass spectrometry (see the Supporting Information).




***Scheme 1.*** Synthesis of PQPCl-*n* and PQPBF$_4$-*n*; a) ethanol, refluxing; b) ethanol, RT, *hν*.

Drop-casting methanolic solutions of PQPCl-6 and PQPCl-14 on a silicon wafer and removing the solvent quickly with a piece of filter paper resulted in 1D aggregates on the surface (Figure 1). Scanning electronic microscopy (SEM) and transmission electron microscopy (TEM) images indicated that PQPCl-6 aggregated to fibers with a uniform width of approximately 40 nm (Figure 1a). In contrast with the cylinderlike fibers formed from PQPCl-6, PQPCl-14 self-assembled into ribbonlike aggregates with a width of 80 nm and lengths ranging from 0.5 to 2 μm (Figure 1b). The different thickness of the ribbons (Figure 1c) suggested that the ribbons were composed of overlapping sheets to form a layer-by-layer structure (so-called lamellar packing). The occasionally twisted ribbons (Figure 1d) demonstrated the flexibility of these aggregates. Although environmental factors could influence the aggregation of the PQP molecules

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PAHs = polycyclic aromatic hydrocarbons.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

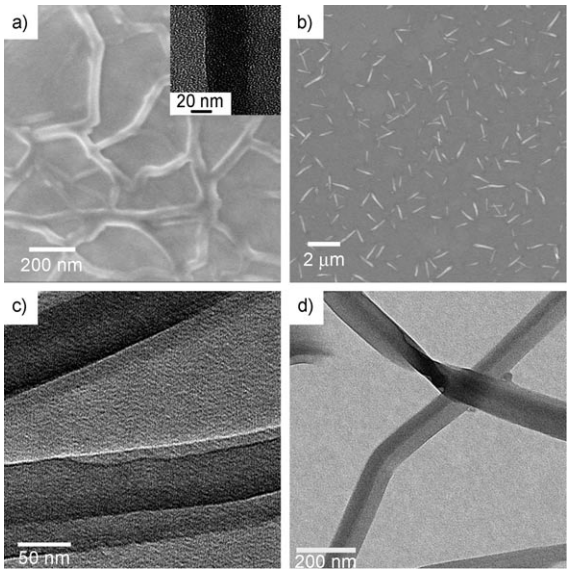


***Figure 1.*** a) SEM and TEM images (inset) of the solid fibers formed by PQPCl-6; b) SEM image of nanoribbons formed by PQPCl-14; c) and d) TEM images of nanoribbons formed by PQPCl-14 at different magnifications ($1\times10^{-3}$ mol $L^{-1}$ in methanol).

when they were transferred to the substrates,[6] aggregation already occurred in methanolic solution. This conclusion stems from dynamic light scattering (DLS) experiments performed on methanolic solutions of PQPCl-6 (0.4 g $L^{-1}$) and PQPCl-14 (0.24 g $L^{-1}$). According to their autocorrelation functions, both PQP salts indeed exhibited aggregation under these conditions. The hydrodynamic radii of the aggregates, $R_h$, were 28 nm and 77 nm, respectively (see Figure S1 in the Supporting Information). It should be noted that these nanostructures were reproducibly formed, even on different substrate surfaces such as silicon, glass, and highly ordered pyrolytic graphite (HOPG).

The morphological differences between PQPCl-6 and PQPCl-14 suggest a different packing mode for the two molecules, which is further supported by wide-angle X-ray scattering (WAXS) measurements of their dried powders obtained from methanolic solutions. The WAXS pattern of PQPCl-14 (see Figure 3 and Figure S2 in the Supporting Information) showed intense reflections with $d$ spacings of 40.1, 19.6, and 13.2 Å, which are characteristic of a lamellar structure.[7] Considering that the fully extended molecular length of PQPCl-14 is 28 Å,[8] each lamella may consist of two interdigitated PQPCl-14 molecular layers (Figure 4). In contrast, PQPCl-6 does not adopt such a lamellar structure according to WAXS analysis (see Figure S2 in the Supporting Information). Compared with PQPCl-14, PQPCl-6 exhibited a clear shift of its diffraction peaks to larger angles in the range of 10 to 30°, suggesting a more condensed packing of the discotic molecular units.[4b,e] According to Israelachivili's packing-parameter theory for amphiphiles, the ribbons from PQPCl-14 have a larger aggregation number $N$ than the fibers from PQPCl-6.[9a] This corresponds to a smaller optimal surface area per molecule $a_0$ and an increase in the aggregation parameter $P$.[9,10] Generally, for common surfactants, the tail length has no significant impact on the packing parameters, especially in the case of cylindrical and lamellar aggregates.[10] However, in this work, the transition from fibers to ribbons is observed upon changing the hexyl chains to tetradecyl chains. A possible reason could be the presence of the PAH part in the PQPs. Strong aromatic interactions between PQP molecules were detected by electron-diffraction analysis of the PQP aggregates (see Figure S3 in the Supporting Information). Compared with PQPCl-6, the less condensed but more ordered packing of PQPCl-14, which is obvious from WAXS, can be attributed to the increase in the length of the tails. The steric hindrance induced by the long alkyl chains probably prevents the aromatic part from getting closer.[3a,e] However, considering that the packing parameter $P$ of the ribbon increases, the head-group repulsion is presumably reduced, and other interactions such as solvophobic effects and attractive interactions between the chains[3a] become more important in achieving lower interaction free energies and a smaller optimal surface area per molecule $a_0$.[10b] It is known that differences in substituent groups can significantly influence the aggregation behavior of polypeptides and conjugated polymers,[11] and it is now evident that the same is true for the PQP salts described herein.

Besides changing the length of alkyl chain, changing the counterions also altered the morphology of the aggregates. Compared with the ribbons obtained from PQPCl-14, relatively long aggregates were formed from $PQPBF_4$-14 with a length of around 5 μm and a diameter ranging from 80 to 150 nm (Figure 2 a,b). Interestingly, some of these aggregates had helical structures with varying pitch (Figure 2 b). TEM characterization disclosed that many of the nonhelical aggregates were actually tubes with a wall thickness of 40–60 nm and an inner diameter of 20–50 nm (Figure 2 c,d). The different thickness of the tube walls (Figure 2 c) implied that the tubes were constructed by lamellar packing.

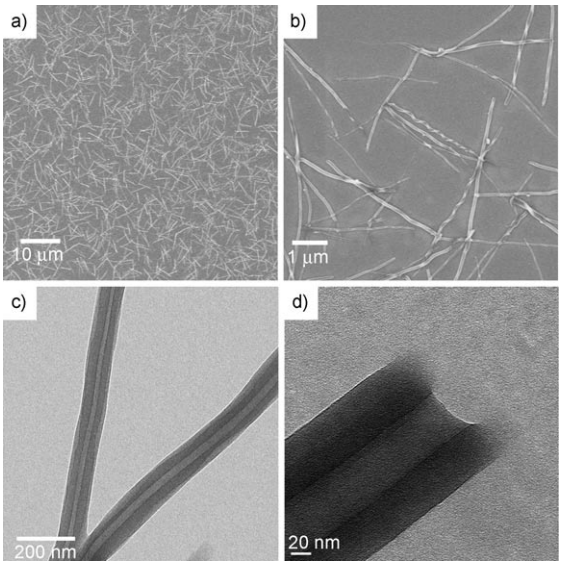


***Figure 2.*** SEM (a, b) and TEM (c, d) images of the aggregates formed by $PQPBF_4$-14 ($1\times10^{-3}$ mol $L^{-1}$ in methanol).

  

The aggregation behavior of PQPX-14 is affected by varying the inorganic counterion. Although organic counterions have previously been shown to influence the self-assembly of amphiphiles,[12] there is no previous example of purely inorganic counterions bringing about significant changes in morphology. The effect of the counterion-dependant change on the morphology was measured by the WAXS of PQPCl-14 and PQPBF$_4$-14 (Figure 3). Three sharp reflections, which are characteristic of lamellar stacking, appear at the same positions in their WAXS patterns. This provides evidence that both the ribbons from PQPCl-14 and the tubes from PQPBF$_4$-14 are formed from similar lamellar structures. However, their diffractions between 10 and 30° are different, suggesting different packing motifs within lamellae.

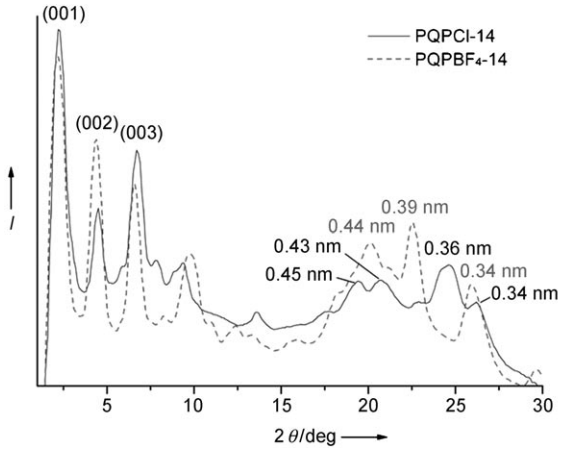


***Figure 3.*** WAXS pattern of the dried powder of PQPCl-14 and PQPBF$_4$-14 obtained from the methanolic solution.

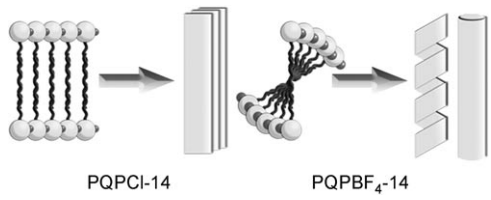


***Figure 4.*** Representation showing a change in the counterion from $Cl^-$ to $BF_4^-$ leading to a change from nanoribbons to helices and tubes.

The layered structure of the ribbon-shaped aggregates of PQPCl-14 is consistent with the stacking of the charged PAH head groups in a perfect face-to-face orientation with chloride ions (ionic radius = 1.21 Å in aqueous solution)[13] sandwiched between them (Figure 4). The helical and tubular aggregates of PQPBF$_4$-14 suggest that the replacement of the chloride ions with the larger tetrafluoroborate ions (ionic radius = 2.30 Å in aqueous solution)[14] disrupts the perfect face-to-face alignment of adjacent PQP cations and causes them to adopt a slipped face-to-face orientation (Figure 4). Consequently, neighboring pairs of PQP cations are rotated with respect to one another along the axis of the aggregate and a helical or tubular structure results. The different molecular alignment in the aggregates of PQPCl-14 and PQPBF$_4$-14 is further supported by WAXS and FTIR. The WAXS pattern of PQPCl-14 showed diffraction peaks at 0.45, 0.43, 0.36, and 0.34 nm, whereas the pattern of PQPBF$_4$-14 showed peaks at 0.44, 0.39, and 0.34 nm (Figure 3). The observation of weak bands at 3100 and 3350 $cm^{-1}$ in the FTIR spectrum of PQPCl-14 and the virtual absence of analogous bands in the spectrum of PQPBF$_4$-14 (see Figure S4 in the Supporting Information) suggest that hydrogen bonding may also play a role in the formation of ribbon or helical structures as it does in ammonium salts and ionic liquids.[15]

The WAXS patterns of PQPCl-6 and PQPBF$_4$-6 were consistent with an increase in distance between the PQP cations (see Figure S5 in the Supporting Information) upon going from $Cl^-$ to $BF_4^-$. However, aggregation of PQPBF$_4$-6 resulted in fibers (Figure 5), which were similar to those obtained from PQPCl-6, indicating that the change of the counterions has no significant effect on the self-assembly of PQP with short alkyl chains.

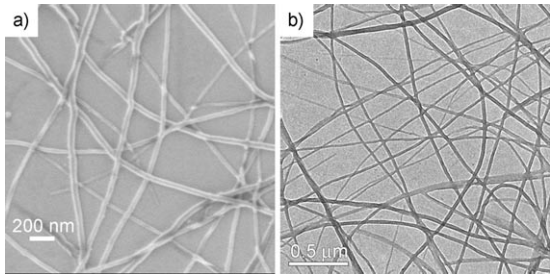


***Figure 5.*** SEM image (a) and TEM image (b) of the aggregates formed by PQPBF$_4$-6($1\times10^{-3}$ mol $L^{-1}$ in methanol).

In summary, the self-assembly behavior of positively charged PAHs (PQP salts) was investigated. One-dimensional nanofibers with a uniform size distribution were obtained from the aggregation of PQPCl-6 and PQPBF$_4$-6 in methanol. Increasing the alkyl chain length of the PQP salts reproducibly resulted in layered nanoscale structures, whereas changing the counterion of the PQP salts from $Cl^-$ to $BF_4^-$ led to a change in the morphology of the aggregate from nanoribbons to helices and tubes. This is interpreted as being due to the changes in intermolecular orientations within layers. Various ion-containing nano-objects can be controllably obtained by this method. The nano-objects reported herein are expected to be useful in the fabrication of miniaturized devices such as biosensors, electrochromic devices, or light-emitting diodes (LEDs).[16]

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[1] a) A. C. Grimsdale, K. Müllen, *Angew. Chem.* **2005**, *117*, 5732 – 5772; *Angew. Chem. Int. Ed.* **2005**, *44*, 5592 – 5629; b) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267 – 1300; c) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491 – 1546; d) J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718 – 747; e) X. Feng, J. Wu, M. Ai, W. Pisula, L. Zhi, K. Müllen, *Angew. Chem.* **2007**, *119*, 3093 – 3096; *Angew. Chem. Int. Ed.* **2007**, *46*, 3033 – 3036.

[2] E. W. Meijer, A. P. H. J. Schenning, *Nature* **2002**, *419*, 353 – 354.

[3] a) M. Kastler, W. Pisula, D. Wasserfallen, T. Pakula, K. Müllen, *J. Am. Chem. Soc.* **2005**, *127*, 4286 – 4296; b) W. Pisula, M. Kastler, D. Wasserfallen, J. W. F. Robertson, F. Nolde, C. Kohl, K. Müllen, *Angew. Chem.* **2006**, *118*, 834 – 838; *Angew. Chem. Int. Ed.* **2006**, *45*, 819 – 823; c) J. P. Hill, W. S. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii, T. Aida, *Science* **2004**, *304*, 1481 – 1483; d) F. Würthner, C. Thalacker, A. Sautter, W. Schärtl, W. Ibach, O. Hollricher, *Chem. Eur. J.* **2000**, *6*, 3871 – 3886; e) J. Wu, A. Fechtenkötter, J. Gauss, M. D. Watson, M. Kastler, C. Fechtenkötter, M. Wagner, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 11311 – 11321; f) X. H. Cheng, S. S. Jester, S. Höger, *Macromolecules* **2004**, *37*, 7065 – 7068; g) D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, D. Haarer, *Nature* **1994**, *371*, 141 – 143; h) H. Bengs, F. Closs, T. Frey, D. Funhoff, H. Ringsdorf, K. Siemensmeyer, *Liq. Cryst.* **1993**, *15*, 565 – 574.

[4] a) S. Kumar, E. J. Wachtel, E. Keinan, *J. Org. Chem.* **1993**, *58*, 3821 – 3827; b) S. Kumar, D. S. S. Rao, S. K. Prasad, *J. Mater. Chem.* **1999**, *9*, 2751 – 2754; c) D. J. Gregg, C. M. Fitchett, S. M. Draper, *Chem. Commun.* **2006**, 3090 – 3092; d) S. M. Draper, D. J. Gregg, R. Madathil, *J. Am. Chem. Soc.* **2002**, *124*, 3486 – 3487; e) R. I. Gearba, M. Lehmann, J. Levin, D. A. Ivanov, M. H. J. Koch, J. Barbera, M. G. Debije, J. Piris, Y. H. Geerts, *Adv. Mater.* **2003**, *15*, 1614 – 1618.

[5] A. R. Katritzky, Z. Zakaria, E. Lunt, *J. Chem. Soc. Perkin Trans. 1* **1980**, 1879 – 1887.

[6] a) M. Yang, W. Wang, F. Yuan, X. Zhang, J. Li, F. Liang, B. He, B. Minch, G. Wegner, *J. Am. Chem. Soc.* **2005**, *127*, 15107 – 15111; b) P. Jonkheijm, F. J. M. Hoeben, R. Kleppinger, J. van Herrikhuyzen, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2003**, *125*, 15941 – 15949.

[7] A. Ajayaghosh, R. Varghese, V. K. Praveen, S. Mahesh, *Angew. Chem.* **2006**, *118*, 3339 – 3342; *Angew. Chem. Int. Ed.* **2006**, *45*, 3261 – 3264.

[8] The MM2 force field was used to calculate the minimum-energy conformation during computer simulations.

[9] a) J. N. Israelachvili, D. J. Mitchell, B. W. Ninham, *Biochim. Biophys. Acta Biomembr.* **1977**, *470*, 185 – 201; b) J. N. Israelachvili, D. J. Mitchell, B. W. Ninham, *J. Chem. Soc. Faraday Trans. 2* **1976**, *72*, 1525 – 1568.

[10] a) C. Tanford, *The Hydrophobic Effect*, Wiley-Interscience, New York, **1973**; b) R. Nagarajan, *Langmuir* **2002**, *18*, 31 – 38.

[11] a) M. Reches, E. Gazit, *Phys. Biol.* **2006**, *3*, S10 – S19; b) H. Inouye, D. Sharma, W. J. Goux, D. A. Kirschner, *Biophys. J.* **2005**, *90*, 1774 – 1789; c) J. N. Wilson, W. Steffen, T. G. McKenzie, G. Lieser, M. Oda, D. Neher, U. H. F. Bunz, *J. Am. Chem. Soc.* **2002**, *124*, 6830 – 6831; d) D. Perahia, R. Traiphol, U. H. F. Bunz, *Macromolecules* **2001**, *34*, 151 – 155; e) R. Rulkens, G. Wegner, T. Thurn-Albrecht, *Langmuir* **1999**, *15*, 4022 – 4025.

[12] a) D. Franke, M. Vos, M. Antonietti, N. Sommerdijk, C. F. J. Faul, *Chem. Mater.* **2006**, *18*, 1839 – 1847; b) C. F. J. Faul, M. Antonietti, *Adv. Mater.* **2003**, *15*, 673 – 683; c) Y. Guan, M. Antonietti, C. F. J. Faul, *Langmuir* **2002**, *18*, 5939 – 5945; d) R. Oda, I. Huc, M. Schmutz, S. J. Candau, F. C. MacKintosh, *Nature* **1999**, *399*, 566 – 569; e) D. Berthier, T. Buffeteau, J. M. Leger, R. Oda, I. Huc, *J. Am. Chem. Soc.* **2002**, *124*, 13486 – 13494.

[13] M. Della Monica, L. Senatore, *J. Phys. Chem.* **1970**, *74*, 205 – 207.

[14] O. Hassel, H. Kringstad, *Z. Anorg. Allg. Chem.* **1932**, *209*, 281 – 288.

[15] a) V. P. Glazunov, A. A. Mashkovsky, S. E. Odinokov, *J. Chem. Soc. Faraday Trans. 2* **1979**, *75*, 629 – 635; b) K. Dong, S. Zhang, D. Wang, X. Yao, *J. Phys. Chem. A* **2006**, *110*, 9775 – 9782.

[16] a) T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem.* **2006**, *118*, 44 – 74; *Angew. Chem. Int. Ed.* **2006**, *45*, 38 – 68; b) K. Binnemans, *Chem. Rev.* **2005**, *105*, 4148 – 4204; c) C. A. Cutler, M. Bouguettaya, T. S. Kang, J. R. Reynolds, *Macromolecules* **2005**, *38*, 3068 – 3074; d) G. Sonmez, H. B. Sonmez, C. K. F. Shen, R. W. Jost, Y. Rubin, F. Wudl, *Macromolecules* **2005**, *38*, 669 – 675; e) X. Gong, S. Wang, D. Moses, G. C. Bazan, A. J. Heeger, *Adv. Mater.* **2005**, *17*, 2053 – 2058; f) S. Kim, J. Jackiw, E. Robinson, K. S. Schanze, J. R. Reynolds, J. Baur, M. F. Rubner, D. Boils, *Macromolecules* **1998**, *31*, 964 – 974; g) B. S. Gaylord, A. J. Heeger, G. C. Bazan, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 10954 – 10957.


  