Anion-induced self-assembly of positively charged polycyclic aromatic hydrocarbons towards nanostructures with controllable two-dimensional morphologies†

Chongqing Yang,a Dongqing Wu,*a Wuxue Zhao,a Weizhen Ye,b Zhixiao Xu,a Fan Zhanga and Xinliang Fengac

A controllable self-assembly strategy of positively charged polycyclic aromatic hydrocarbons (PCPAH) towards the formation of rectangle sheets and ribbon-like nanostructures has been achieved by choosing divalent anions with different sizes. In contrast, only rod-like nanostructures are obtained from PCPAH with univalent anions. It is revealed that the divalent anions play a key role in guiding the packing of PCPAH, which provides an unprecedented route to fabricate two-dimensional nanostructures.

Over the last decade, the enthusiasm of scientific researchers towards two-dimensional (2D) nanomaterials has been boosted by graphene and its analogues due to their unique flat morphology and anisotropic chemical/physical behavior.1 However, the delicate fabrication of 2D materials with desired compositions and properties is still challenging.2 In this respect, the self-assembly of organic molecules provides a mild and solution processable strategy for the bottom-up fabrication of freestanding 2D soft nanomaterials.3 More importantly, the chemical and physical properties of these organic nanosheets,4 including electronic/photonic properties,5 porosity6 and metal or protein recognition activities7 can be precisely defined by the rational design of molecular building blocks.

Combining the extended aromatic frameworks with the incorporation of a charged heteroatom, PCPAH offer both strong π–π interactions to enhance the molecular stacking and good affinity with polar solvents, making them attractive building blocks in supramolecular chemistry.8 Thus, one can tune the self-assembly behavior and optoelectronic properties of PCPAH via the modification of their aromatic core, substituents and associated anions, which render them highly desirable candidates for the bottom-up synthesis of 2D soft nanomaterials. In our previous work, it was found that a typical PCPAH molecule, the 2-phenyl-9-benzo[8,9]quinoxalino-[4,5,6,7-fed]phenanthridinylium salt (PQP) containing a tetradecyl chain (shortened as PQPC14), can spontaneously self-organize into 2D ribbon-like nanostructures in solution with the short and rigid disulfonate anion serving as the cross-linker to direct the orientation of the neighbouring PQPC14 cations. More importantly, the ribbon morphologies of the PQPs exhibited strong dependence on the rigidity and valences of the organic anions.9 Inspired by these results, we envision that the proper selection of inorganic divalent counteranions may also guide the packing behavior of PQPs with short alkyl chains and facilitate the formation of nanostructures with controlled 2D sheet-like morphologies.

Herein, the self-assembly behavior of hexyl-substituted PQPs (PQPC6, Scheme 1) with divalent anions including tetrachloroplatinate (PtCl42−) and hexachloropalladate (PdCl62−) as well as univalent tetrachloroaurate (AuCl4−) in a binary solvent system (DMF/MeOH 1 : 7) was investigated. Interestingly, rectangle nanosheets were formed from PQPC6 salts employing PtCl42− as the counteranion. Moreover, the

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Scheme 1 The ion-exchange route for preparing PQPC6-based ionic complexes with different counter ions.
control over the packing of PQPC$_6$ cations could be further achieved by tuning the steric hindrance and valence of the counteranions with PdCl$_6^{2-}$ and AuCl$_4^-$, resulting in morphology variation from 2D ribbons to one-dimensional (1D) rods. Based on these results, it is revealed that the divalent anions (PtCl$_4^{2-}$ and PdCl$_6^{2-}$) played a key role in adjusting the non-covalent interactions between the adjacent PQPC$_6$ cations, thus giving rise to the unequal growth rates of the aggregates along different dimensions.

The ionic complexes of PQPC$_6$–M (PQPC$_6$–PtCl$_4$, PQPC$_6$–PdCl$_6$ and PQPC$_6$–AuCl$_4$; Scheme 1) were prepared from PQPC$_6$–BF$_4$ with potassium tetrachloroplatinate (K$_2$PtCl$_4$), potassium hexachloropalladate (K$_2$PdCl$_6$) and potassium tetrachloroaurat (K[AuCl$_4$]) in a one-to-one charge ratio via a facile ion-exchange procedure. Typically, PQPC$_6$–BF$_4$ was first dissolved in a binary solvent system (DMF/MeOH 1 : 7) and the aqueous solution containing the potassium salts of the corresponding anions was then added drop-wise (see the ESI†). Due to the amphiphilic nature of the ionic complex, aggregates with an ordered packing in such a mixed solvent were obtained as direct precipitate from the solution. The compositions of the obtained three ionic complex aggregates were confirmed by the elemental analysis results (Table S1†).

Fig. 1a and b, rectangle-shaped 2D nanosheets with sharp edges were obtained. The width of the nanosheets is between 200 and 400 nm, while the length is in the range of 200 nm–1 μm. The atomic force microscopy (AFM) image (Fig. 1c) reveals that the nanosheets of PQPC$_6$–PtCl$_4$ have a smooth surface with a height of ~23 nm, further confirming their 2D morphology. It should be noted that the mixed solvent in this work is essential for the formation of the above mentioned 2D aggregates and that the aggregates do not form when either DMF or MeOH alone was used as the solvent (Fig. S2†).

The wide-angle X-ray diffraction (WAXD) patterns of PQPC$_6$–PtCl$_4$ show intense peaks at 4.2, 7.6, 8.5 and 9.7° (Fig. 2a), corresponding to the (100), (101), (200) and (010) facets of a monoclinic packing, respectively. The diffraction peak at approximately 25.2° is attributed to the π–π stacking of the aromatic frameworks of PQPC$_6$ cations. Based on these results, Pawley refinement on the Reflux Plus module of the Materials Studio program version 6.1 was subsequently executed to calculate the unit cell parameters of PQPC$_6$–PtCl$_4$ in the rectangular nanosheets. With the profile-fitting factors $R_p$ and $R_p$ being 6.35 and 4.58 % respectively, the unit cell parameters of PQPC$_6$–PtCl$_4$ are calculated to be $a = 23.10$ Å, $b = 9.08$ Å, and $c = 11.70$ Å (Table S2†).

Accordingly, the packing behavior of PQPC$_6$–PtCl$_4$ in the rectangular nanosheets could be proposed by considering the previously reported packing mode of PQPs with different counteranions. As illustrated in Fig. 2b, two neighbouring PQPC$_6$ cations can form a dimer structure in the aggregates with their aromatic core arranged in a slipped head-to-head manner and the PtCl$_4^{2-}$ anion shared by two cations located at their bay position. Driven by the local micro-phase separation between their soft and rigid parts, these dimers can further stack together via non-covalent forces including π–π interactions, ionic interactions, etc.

The simulated packing model from a quantum chemical calculation on CASTEP (Cambridge Sequential Total Energy Package) suggests that the stacking of the molecules along the three dimensions is mainly dominated by three kinds of non-covalent forces: solvophobic interactions along the X-axis, electrostatic effects between the PQPC$_6^{+}$–PtCl$_4^{2-}$ ion pairs along the Y-axis, and the π–π interactions along the Z-axis (Fig. 2c). Under polar experimental conditions, the solvophobic interactions between the alkylic moieties will be enhanced along the X-axis, and the strong electrostatic interactions between the cation–anion pairs greatly inhibit the repulsion between the adjacent dimers along the Y-axis. However, the centrally charged aromatic core would prefer to expose themselves to the solvent, thus causing a slipped face-to-face structure between the adjacent cations and greatly reducing π–π interactions along the Z-axis. Driven by these interactions, the packing of the PCPAH in the direction parallel to the X–Y interfaces should be much faster than that in

Fig. 1. (a) SEM and (b) TEM images; (c) AFM image and height profile of rectangular nanosheets formed by ionic complex PQPC$_6$–PtCl$_4$.
the direction along the Z-axes, hence leading to the formation of 2D nanostructures.

The formation of 2D nanostructures from PQPC$_{6}^-$-PtCl$_{4}^{-}$ inspired us to further study the self-assembly behavior of PQPC$_{6}^-$-PdCl$_{6}^{2-}$, which also contains a divalent complex anion with a larger volume (ionic radius PtCl$_{4}^{2-}$ = 3.07 Å, PdCl$_{6}^{2-}$ = 3.33 Å). As demonstrated in the SEM and TEM images, the aggregates of PQPC$_{6}^-$-PdCl$_{6}^{2-}$ are uniform nanoribbons with a length of 600 nm to several micrometres and a width of 100 to 300 nm (Fig. 3a and b). AFM characterization shows that the thickness of the nanoribbons is around 47 nm (Fig. 3c).

Different from PQPC$_{6}^-$-PtCl$_{4}^{-}$, the WAXD patterns of PQPC$_{6}^-$-PdCl$_{6}^{2-}$ exhibit obvious diffractions at 6.06, 9.00, 10.80 and 12.12°, which are typical for the (001), (010), (101) and (002) facets of a triclinic packing. Additionally, the diffraction at 25.4° is attributed to the π-π interactions among the aromatic frameworks of PQPC$_{6}^-$ cations. The lattice parameters of the triclinic space group formed by PQPC$_{6}^-$-PdCl$_{6}^{2-}$ are calculated as $a = 8.40$ Å, $b = 14.93$ Å and $c = 21.39$ Å with the wR$_{p}$ and R$_{p}$ converged to 12.80 and 9.26 %, separately (Fig. 4a).

According to the XRD patterns, the structural simulation suggests that the aggregates of PQPC$_{6}^-$-PdCl$_{6}^{2-}$ have a similar packing model to that of PQPC$_{6}^-$-PtCl$_{4}^{-}$ with their anions embedded between the solvophilic interfaces (Fig. 4b). However, since the ionic radius of PdCl$_{6}^{2-}$ is larger than that of PtCl$_{4}^{2-}$, the steric hindrance caused by the anions will push them away from the PQPC$_{6}^-$ cations. As a result, the packing of PQPC$_{6}^-$-PdCl$_{6}^{2-}$ along the Y-axis is restricted since there is not enough space for the accommodation of PdCl$_{6}^{2-}$ to balance the increased positive charge density along the Y-axis. Thus, the width of the aggregates is shorter than that of the nanosheets from PQPC$_{6}^-$-PtCl$_{4}^{-}$, resulting in the ribbon-like morphology. Although different anions can cause varied morphologies, our experimental results indicate that the combination of PtCl$_{4}^{2-}$ and PdCl$_{6}^{2-}$ won’t lead to the formation of aggregates with a new morphology and only the mixture of nanosheets and nanoribbons can be obtained (Fig. S3†).

We further explored the impact of the counteranions with different charges on the PQP-based ionic complexes; the self-assembly behavior of PQPC$_{6}^-$-AuCl$_{4}^{-}$ was thus investigated in this work. Interestingly, only rod-like aggregates with a length in the range from 600 nm to 1 μm and a diameter ranging from 60 to 100 nm were obtained (Fig. 5a and b). AFM characterization (Fig. 5c) reveals a thickness of ~67 nm. Different from PQPC$_{6}^-$-PtCl$_{4}^{-}$ and PQPC$_{6}^-$-PdCl$_{6}^{2-}$, the WAXD patterns of PQPC$_{6}^-$-AuCl$_{4}^{-}$ contain four sharp diffraction peaks at 6.32, 8.36, 9.60, and 12.74°, corresponding to the (001), (010), (100), (002) facets of the triclinic structure. The simulation profile of PQPC$_{6}^-$-AuCl$_{4}^{-}$ (Fig. 5d) also fits well with the experimental data with wR$_{p}$ and R$_{p}$ converged to 11.74 and 8.63 % and the parameters of the unit cell for PQPC$_{6}^-$-AuCl$_{4}^{-}$ are determined to be $a = 10.63$ Å, $b = 10.67$ Å, and $c = 16.00$ Å.

According to the above calculation, the simulated packing model of PQPC$_{6}^-$-AuCl$_{4}^{-}$ is shown in Fig. 5e. Compared with PQPC$_{6}^-$-PtCl$_{4}^{-}$, the electrostatic repulsion between the adjacent dimers of PQPC$_{6}^-$-AuCl$_{4}^{-}$ along the Y-axis would increase significantly since AuCl$_{4}^{-}$ is a monovalent anion, which would remarkably restrict the growth rate along the Y-axis. Thus, the 1D rod-like aggregates are derived from PQPC$_{6}^-$-AuCl$_{4}^{-}$.

In conclusion, we have demonstrated the synthesis and self-assembly of three hexyl-substituted PQP salts with different inorganic anions. By using counter-anions with different...
sizes and valances, the packing of PQPC₆ cations along different dimensions could be easily tuneable, giving rise to different morphologies from 2D nanosheets to 1D nanorods. In line with these arguments, it could be concluded that the divalent inorganic anions (PtCl₄²⁻ and PdCl₆²⁻) in the PQPC₆-based ionic complexes can effectively adjust the non-covalent interactions between the adjacent PQPC₆ cations and direct the packing of the PQPC₆ salts into 2D aggregates. Thus, it is anticipated that this approach can be applied to restructure the order and arrangement of the functional organic molecules in their aggregates, which will provide new opportunities for the fabrication of miniaturized optoelectronic devices.

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Notes and references

1 (a) X. Huang, C. Tan, Z. Yin and H. Zhang, Adv. Mater., 2014, 26, 2185; (b) R. Mas-Balleste, C. Gomez-Navarro, J. Gomez-Herrero and F. Zamora, Nanoscale, 2011, 3, 20; (c) C. N. R. Rao, H. S. S. Ramakrishna Matte and U. Maitra, Angew. Chem., Int. Ed., 2013, 52, 13162; (d) J. Sakamoto, J. van Heijst, O. Lukin and A. D. Schluter, Angew. Chem., Int. Ed., 2009, 48, 1030.
2 (a) M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh and H. Zhang, Nat. Chem., 2013, 5, 263; (b) T. Govindaraju and M. B. Avinash, Nanoscale, 2012, 4, 6102.
3 X. Zhuang, Y. Mai, D. Wu, F. Zhang and X. Feng, Adv. Mater., 2015, 27, 403.
4 (a) T. Bauer, Z. Zheng, A. Renn, R. Enning, A. Stemmer, J. Sakamoto and A. D. Schlüter, Angew. Chem., 2011, 123, 8025; (b) Y. Zheng, H. Zhou, D. Liu, G. Floudas, M. Wagner, K. Koynov, M. Mezger, H.-J. Butt and T. Ikeda, Angew. Chem., 2013, 125, 4945.
5 W. Yao, Y. Yan, L. Xue, C. Zhang, G. Li, Q. Zheng, Y. S. Zhao, H. Jiang and J. Yao, Angew. Chem., 2013, 125, 8875.
6 G. Das, B. P. Biswal, S. Kandambeth, V. Venkatesh, G. Kaur, M. Addicoat, T. Heine, S. Verma and R. Banerjee, Chem. Sci., 2015, 6, 3931.
7 E. J. Robertson, G. K. Olivier, M. Qian, C. Proulx, R. N. Zuckermann and G. L. Richmond, Proc. Natl. Acad. Sci. U. S. A., 2015, 112, 338.
8 (a) D. Wu, X. Feng, M. Takase, M. C. Haberecht and K. Mullen, Tetrahedron, 2008, 64, 11379; (b) D. Wu, W. Pisula, V. Enkelmann, X. Feng and K. Mullen, J. Am. Chem. Soc., 2009, 131, 9620; (c) D. Wu, W. Pisula, M. C. Haberecht, X. Feng and K. Mullen, Org. Lett., 2009, 11, 5686; (d) D. Wu, L. Zhi, G. J. Bodwell, G. Cui, N. Tsao and K. Mullen, Angew. Chem., Int. Ed., 2007, 46, 5417.
9 D. Wu, R. Liu, W. Pisula, X. Feng and K. Mullen, Angew. Chem., Int. Ed., 2011, 50, 2791.
10 J. Zhang, Y. Yan, M. W. Chance, J. Chen, J. Hayat, S. Ma and C. Tang, Angew. Chem., 2013, 125, 13629.
11 E. L. Spitler and W. R. Dichtel, Nat. Chem., 2010, 2, 672.
12 S. Ghosh, A. Roy, D. Banik, N. Kundu, J. Kuchlyan, A. Dhir and N. Sarkar, Langmuir, 2015, 31, 2.
13 W. M. Haynes, T. J. Bruno and D. R. Lide, CRC Handbook of Chemistry and Physics, Internet Version, 85th edn, 2004.