

Supplementary Information

Anion-induced Self-Assembly of Positively Charged Polycyclic Aromatic Hydrocarbons towards Nanostructures with Controllable Two-dimensional Morphologies

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Experimental Section

Materials:

All chemicals were obtained from commercial suppliers such as Aldrich, Aladdin, and Adamas and used without purification. Irradiations with an external UV source were performed with a 254 nm lamp (38 W).

Characterizations:

¹H Nuclear Magnetic Resonance (NMR) spectra was recorded on the Mercury Plus 400 (400 MHz) spectrometer with tetramethylsilane as the internal reference and DMSO-d₆ as the solvent. The elemental analysis was measured on Vario EL Cube for N element and on the inductively coupled plasma optical emission spectrometer (iCAP6300, Thermo) for the noble metals. Fourier transform infrared spectroscopy (FTIR) was performed on a Spectrum 100 (Perkin Elmer, Inc., USA) spectrometer with a scan range of 4000 - 400 cm⁻¹. The sample powders were pulverized with KBr, and pressed into disks. The morphology analysis of the samples was acquired by field-emission scanning electron microscope (FESEM, FEI, Sirion 200, 25 KV) and transmission electron microscope (TEM, JEOL, JEM-2010, 200 KV). The WAXD experiments were performed on a Rigaku D/Max 2500 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$) with a scanning speed of 0.5°/min from 3 to 30 °. The molecular modeling and Pawley Refinement were performed by Reflux, implemented in the Material Studio program package version 6.1.

Synthesis of PQPC₆-BF₄:

The synthesis of 2-phenyl-9-alkylbenzoquinolizino[4,5,6,7-*fed*] phenanthridinium tetrafluoroborate salts (PQPC₆-BF₄, Scheme 1) was carried out according to the previously reported method¹.

PQPC₆-BF₄: Yellow powder. ¹H NMR (400MHz, DMSO-*d*₆, 25°C): δ(ppm) = 9.55 (s, 2H, aromatic), 9.27-9.24 (d, 2H, *J*=8.4Hz, aromatic), 8.86-8.84 (d, 4H, *J*=8.4Hz, aromatic), 8.51-8.49 (dd, 2H, *J*=6.4, 2.8Hz aromatic), 8.02-7.98 (t, 2H, *J*=7.6 Hz, aromatic), 7.91-7.87 (t, 2H, *J*=7.7 Hz, aromatic), 7.75-7.73 (m, 3H, aromatic), 2.96-2.92 (t, 2H, *J*=8.0 Hz, CH₂), 1.80-1.75 (m, 2H, CH₂), 1.37-1.30 (m, 6H, CH₂), 0.89-0.86 (t, 3H, *J*=7.0 Hz, CH₃).

Preparation of PQPC₆-M ionic complexes:

Preparation of PQPC₆-PtCl₄: To the DMF/MeOH (V/V=5 ml/35 ml) solution of PQPC₆-BF₄ (55 mg), the aqueous solution of K₂PtCl₄ (0.5eq, 20 mL) was added drop by drop in 15min. Then, the mixture was gently stirred for 4h at 298 K before certification. At last, the collected precipitates were washed by water and methanol subsequently. After drying in vacuum, the yellowish powders were grinded and collected (yield = 87.2%).

Preparation of PQPC₆-PdCl₆: To the DMF/MeOH (V/V=5ml/35ml) solution of PQPC₆-BF₄ (55mg), the aqueous solution of K₂PdCl₆ (0.5eq, 20 mL) was added drop by drop in 15min. Then, the mixture was gently stirred for 4h at 298K before certification. At last, the collected precipitates were washed by water and methanol subsequently. After vacuum drying, the yellowish powders were grinded and collected (yield = 88.6%).

Preparation of PQPC₆-AuCl₄: To the DMF/MeOH (V/V=5ml/35ml) solution of PQPC₆-BF₄ (55mg), the aqueous solution of K₂AuCl₄ (0.5eq, 20 mL) was added drop by drop in 15min. Then, the mixture was gently stirred for 4h at 298K before certification. At last, the collected precipitates were washed by water and methanol subsequently. After vacuum drying, the yellowish powders were grinded and collected (yield = 82.8%).

Table S1. The calculated and found elemental analysis of the ionic complexes

PQPC₆-M.

Ionic Complexes	Calculated (%)			Found (%)		
	C	H	N	C	H	N
PQPC ₆ -PtCl ₄	66.40	4.78	2.21	64.45	4.61	2.39
PQPC ₆ -PdCl ₆	67.35	4.84	2.24	65.21	4.61	2.27
PQPC ₆ -AuCl ₄	52.32	3.76	1.74	52.79	3.87	1.81

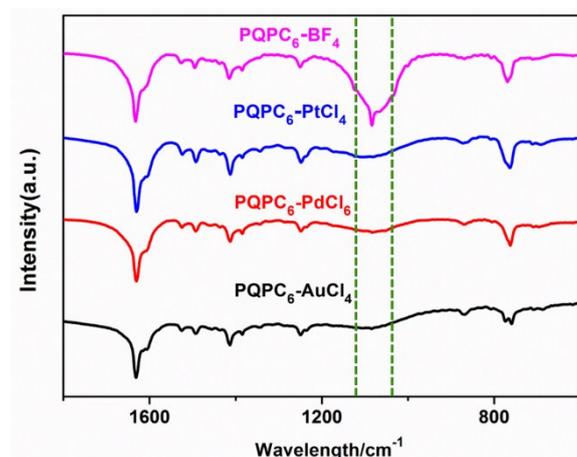


Fig. S1. The FTIR analysis of PQPC₆-BF₄ and PQPC₆-M. All the F-B-F vibrational frequencies at about 1085 cm⁻¹ were totally absent in Fourier transform infrared spectroscopy (FTIR) spectra of PQPC₆-PtCl₄.

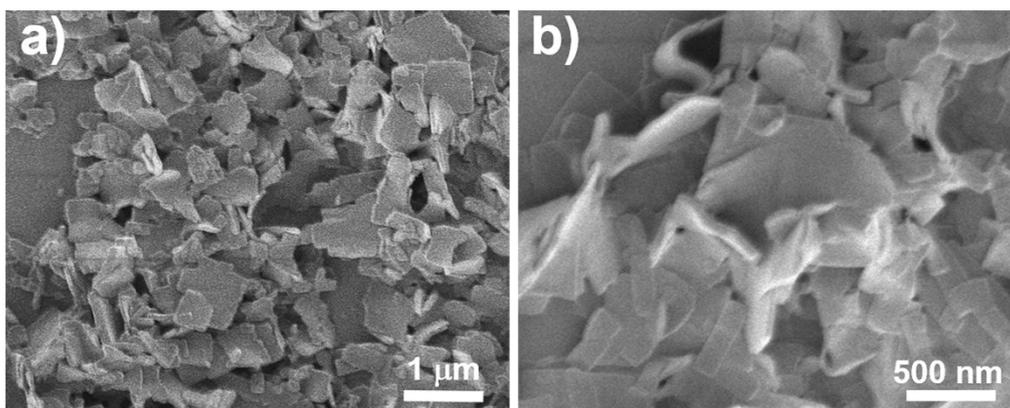


Fig. S2 a) SEM images of ionic complex PQPC₆-PtCl₄ formed in DMF; b) SEM images of ionic complex PQPC₆-PtCl₄ formed in MeOH.

Table S2. The simulated crystal parameters of PQPC₆-Pt, PQPC₆-PdCl₆, PQPC₆-AuCl₄ and PQPC₆-BF₄ extracted from the WAXS.

Name	Crystal System	a/Å	b/Å	c/Å	α	β	γ	Volume
PQPC ₆ -PtCl ₄	Monoclinic	23.32	9.11	11.71	90.00	114.66	90.00	2258.71
PQPC ₆ -PdCl ₆	Triclinic	8.40	14.93	21.39	47.89	78.65	102.11	1722.34
PQPC ₆ -AuCl ₄	Triclinic	10.63	10.67	16.00	85.13	119.66	97.27	1565.09

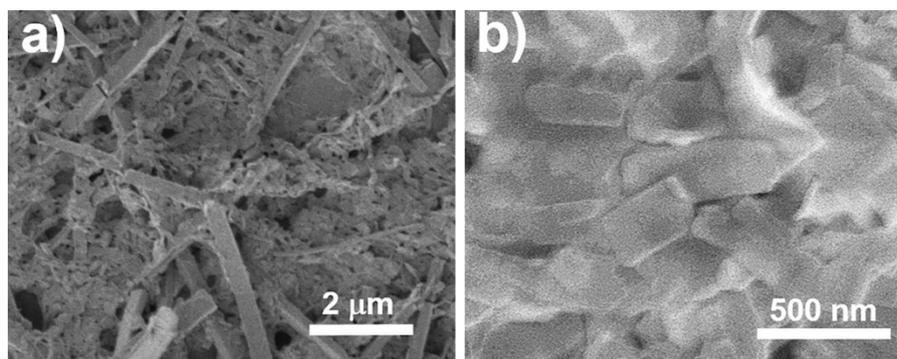


Fig. S3 a) and b) SEM images of the aggregates from PQPC₆ with both PtCl₄²⁻ and PdCl₆²⁻ as anions (molar ratio of anion = 1:1).

Reference

- 1 D. Wu, L. Zhi, G. J. Bodwell, G. Cui, N. Tsao and K. Müllen, *Angew. Chem. Int. Ed.*, 2007, 46, 5417.