Self-assembly of Positively Charged Discotic PAHs: From Nanofibers to Nanotubes

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Experimental Section

All starting materials were obtained from commercial suppliers and used as received unless otherwise specified. Irradiations with an external UV source were performed with a Rayonet reactor (RPR-200) with 3000 Å lamps in quartz flasks. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DPX 250 spectrometer with use of the solvent proton or carbon signal as an internal standard. MALDI-TOF mass spectra were measured using a Bruker Reflex II-TOF spectrometer using a 337 nm nitrogen laser and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix. A double graphite monochromator for the Cu-Kα radiation ($\lambda=0.154$ nm) was used for the WAXS experiments. SEM measurements were performed on a LEO 1530 field emission scanning electron microscope. TEM studies were conducted on a Philips Tecnai F20 electron microscope at an operating voltage of 200 kV. The sample was dissolved in methanol and the solution was dropped onto a copper grid covered with carbon film. Infrared (IR) spectra were recorded on Nicolet 730 FT-IR spectrophotometer using KBr pellet. DLS measurements were carried out on a laser light scattering...
spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 514 nm.

**Synthesis and characterization**

**PQPCl-n** and **PQPBF₄-n** was synthesized according to the literature method[1] with modification. Ethanol instead of methanol was used as the solvent for the dehydrogenation. The alkyl substituted PQP salts have poorer solubility in ethanol than in methanol and they could precipitate after the reaction. This modification could increase the yield and simplify the purification.

**1-(4-alklyphenyl)-2,4,6-triphenylpyridinium salts:**

2,4,6-triphenylpyrylium salt (2mmol) and 4-alkylaniline(2.2mmol) were added to 15ml absolute ethanol. The mixture was refluxed for 5 hours till the solution turned to transparent. After cooling the solution to room temperature, it was concentrated in vacuo to ca. 3ml. The concentrated solution was poured to 400ml hexane then. After filtration, the solid was recrystallized from 20ml hexane to give the target pyridinium salts.

**1-(4-hexylphenyl)-2,4,6-triphenylpyridinium chloride:** pale yellow solid (yield = 90%), \(^1\text{H} NMR\) (250MHz, CD\(_3\)OD, 25°C): \(\delta\) (ppm) = 8.43 (s, 2H, aromatic), 8.10-8.07 (m, 2H, aromatic), 7.60-7.58 (m, 3H, aromatic), 7.36-7.24 (m, 10H, aromatic), 7.10-7.07 (d, 2H, \(^3\text{J}(\text{H,H})=7.5\text{Hz},\) aromatic), 6.94-6.91 (d, 2H, \(^3\text{J}(\text{H,H})=7.5\text{Hz},\) aromatic), 2.43-2.37 (t, 2H, \(^3\text{J}(\text{H,H})=7.5\text{Hz},\) CH\(_2\)), 1.39-1.34 (t, 2H, \(^3\text{J}(\text{H,H})=7.5\text{Hz},\) CH\(_2\)), 1.22-1.00 (m, 6H, CH\(_2\)), 0.82-0.77 (t, 3H, CH\(_3\)); \(^13\text{C} NMR\) (250MHz, CD\(_3\)OD, 25°C): d (ppm): 14.45, 23.71, 29.31, 32.03, 32.74, 36.03, 126.87, 129.54, 129.69, 129.73, 130.00, 131.09, 131.40, 133.77, 134.65, 135.37, 138.22,
1-(4-hexylphenyl)-2,4,6-triphenylpyridinium tetrafluoroborate: white powder (yield = 98%), $^1$H NMR (250MHz, CD$_2$Cl$_2$, 25°C): $\delta$(ppm) = 8.20 (s, 2H, aromatic), 7.96-7.93 (m, 2H, aromatic), 7.67-7.64 (m, 3H, aromatic), 7.35 (s, 10H, aromatic), 7.07-7.03 (d, 2H, $^{3}J$(H,H)=10.0Hz, aromatic), 6.99-6.95 (d, 2H, $^{3}J$(H,H)=10.0Hz, aromatic), 2.50-2.44 (t, 2H, $^{3}J$(H,H)=7.5Hz, CH$_2$), 1.46-1.40 (t, 2H, $^{3}J$(H,H)=7.5Hz, CH$_2$), 1.29-1.07 (m, 6H, CH$_2$), 0.89-0.84 (t, 3H, CH$_3$); $^{13}$C NMR (250MHz, CD$_2$Cl$_2$, 25°C): d (ppm): 14.19, 22.94, 28.52, 31.08, 31.87, 35.44, 126.51, 128.42, 128.64, 128.89, 129.48, 129.97, 130.30, 130.73, 132.95, 133.13, 134.50, 136.62, 146.07, 157.32, 157.88.

1-(4-tetradecylphenyl)-2,4,6-triphenylpyridinium chloride: pale yellow solid (yield = 88%), $^1$H NMR (250MHz, CD$_3$OD, 25°C): $\delta$(ppm) = 8.45 (s, 2H, aromatic), 8.13-8.09 (m, 2H, aromatic), 7.63-7.60 (m, 3H, aromatic), 7.39-7.28 (m, 10H, aromatic), 7.13-7.09 (d, 2H, $^{3}J$(H,H)=7.5Hz, aromatic), 6.96-6.93 (d, 2H, $^{3}J$(H,H)=7.5Hz, aromatic), 2.45-2.39 (t, 2H, $^{3}J$(H,H)=7.5Hz, CH$_2$), 1.41-1.35 (t, 2H, $^{3}J$(H,H)=7.5Hz, CH$_2$), 1.01-1.23 (m, 22H, CH$_2$), 0.85-0.81 (t, 3H, CH$_3$); $^{13}$C NMR (250MHz, CD$_3$OD, 25°C): d (ppm): 14.49, 23.79, 29.66, 30.53, 30.83, 32.09, 33.13, 36.02, 121.36, 126.88, 129.53, 129.69, 129.74, 130.04, 131.02, 131.08, 131.38, 133.76, 134.66, 135.38, 138.23, 146.81, 158.52.

1-(4-tetradecylphenyl)-2,4,6-triphenylpyridinium tetrafluoroborate: white powder (yield = 95%), $^1$H NMR (250MHz, CD$_3$OD, 25°C): $\delta$(ppm) = 8.45 (s, 2H, aromatic), 8.12-8.09 (m, 2H, aromatic), 7.63-7.60 (m, 3H, aromatic), 7.39-7.26 (m,
10H, aromatic), 7.13-7.09(d, 2H, $^3$J(H,H)=7.5Hz, aromatic), 6.96-6.93 (d, 2H, $^3$J(H,H)=7.5Hz, aromatic), 2.45-2.39 (t, 2H, $^3$J(H,H)=7.5Hz, CH2), 1.42-1.36 (t, 2H, $^3$J(H,H)=7.5Hz, CH2), 1.23-1.02 (m, 22H, CH2), 0.84-0.82 (t, 3H, CH3); $^{13}$C NMR (250MHz, CD$_3$OD, 25°C): d (ppm): 14.48, 23.79, 29.66, 30.53, 30.83, 32.08, 33.13, 36.02, 126.89, 129.52, 129.68, 129.73, 130.03, 131.02, 131.06, 131.36, 133.73, 134.69, 135.42, 138.23, 146.80, 158.51, 158.56.

2-phenyl-9-alkylbenzoquinolizino[4,5,6,7-fed]phenanthridinylium salts (PQP salts)

2g 1-(4-alkylphenyl)-2,4,6-triphenylpyridinium salts was dissolved in 200ml absolute ethanol. The ethanolic solution was irradiated at 300nm wavelength. After 72 hours, the solid product was filtered off. The filtrate was concentrated in vacuo to give a 2nd corp. The combined solid was recrystallized in ethanol to give the PQP salts.

2-phenyl-9-hexylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium chloride PQPCl-6: yellow powder(yield = 47%), $^1$H NMR (250MHz, CD$_3$OD, 25°C): δ(ppm) = 9.35 (s, 2H, aromatic), 8.96-8.93 (d, 2H, $^3$J(H,H)=7.5Hz, aromatic), 8.69-8.65 (d, 4H, $^3$J(H,H)=10Hz, aromatic), 8.27-8.25 (m, 2H, aromatic), 7.98-7.92 (t, 2H, $^3$J(H,H)=7.5Hz, aromatic), 7.88-7.82 (d, 2H, $^3$J(H,H)=7.5Hz, aromatic), 7.70 (s, 3H, aromatic), 2.97-2.91 (t, 2H, $^3$J(H,H)=7.5Hz, CH2), 1.78-1.75 (m, 2H, CH2), 1.38-1.31 (m, 6H, CH2), 0.90-0.84 (t, 3H, CH3); $^{13}$C NMR (250MHz, CD$_3$OD, 25°C): d (ppm): 14.48, 23.79, 30.35, 32.75, 32.93, 37.14, 119.28, 124.73, 124.97, 125.27, 126.13, 127.40, 127.97, 129.70, 130.36, 131.10, 132.01, 133.11, 135.31, 136.00, 143.89, 147.14, 151.01.
MALDI-TOF-MS (MW=464.64 without anion): m/z: 464.04.

2-phenyl-9-hexylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium tetrafluoroborate PQPBF₄-6: yellow powder (yield = 66%), \(^1\)H NMR (250MHz, CD₂Cl₂, 25°C): \(\delta\) (ppm) = 9.31 (s, 2H, aromatic), 8.89-8.86 (d, 2H, \(^3\)J(H,H)=7.5Hz, aromatic), 8.69-8.67 (d, 4H, \(^3\)J(H,H)=7.5Hz, aromatic), 8.20-8.16 (m, 2H, aromatic), 8.10-8.04 (t, 2H, \(^3\)J(H,H)=7.5Hz, aromatic), 8.00-7.94 (t, 2H, \(^3\)J(H,H)=7.5Hz, aromatic), 7.76-7.73 (d, 3H, \(^3\)J(H,H)=7.5Hz, aromatic), 3.11-3.05 (t, 2H, \(^3\)J(H,H)=7.5Hz, CH₂), 1.90-1.84 (m, 2H, CH₂), 1.52-1.32 (m, 6H, CH₂), 0.95-0.89 (t, 3H, CH₃); \(^{13}\)C NMR (250MHz, CD₂Cl₂, 25°C): d (ppm): 14.21, 22.97, 29.42, 31.82, 32.04, 36.60, 118.61, 123.82, 123.97, 124.21, 125.17, 126.24, 126.89, 128.61, 129.40, 130.50, 131.58, 132.58, 134.71, 134.86, 142.69, 146.50, 150.37.

MALDI-TOF-MS (MW=464.64 without anion): m/z: 464.27.

2-phenyl-9-tetradecylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium chloride PQPCl-14: yellow powder (yield = 41%), \(^1\)H NMR (250MHz, CD₃OD, 25°C): \(\delta\) (ppm) = 9.53 (s, 2H, aromatic), 9.10-9.06 (d, 2H, \(^3\)J(H,H)=7.5Hz, aromatic), 8.85-8.82 (d, 4H, \(^3\)J(H,H)=7.5Hz, aromatic), 8.31-8.29 (m, 2H, aromatic), 8.06-8.00 (t, 2H, \(^3\)J(H,H)=7.5Hz, aromatic), 7.95-7.89 (d, 2H, \(^3\)J(H,H)=7.5Hz, aromatic), 7.72-7.69 (d, 3H, \(^3\)J(H,H)=7.5Hz, aromatic), 3.11-3.04 (t, 2H, \(^3\)J(H,H)=7.5Hz, CH₂), 1.89-1.84 (m, 2H, CH₂), 1.48-1.19 (m, 22H, CH₂), 0.84-0.79 (t, 3H, CH₃); \(^{13}\)C NMR (250MHz, CD₃OD, 25°C): d (ppm): 14.48, 23.78, 30.52, 30.61, 30.77, 30.81, 32.71, 33.12, 37.10, 119.34, 124.76, 125.02, 125.33, 126.19, 127.48, 128.00, 129.70, 130.43, 131.09, 132.00, 133.08, 135.31, 136.02, 143.96, 147.15, 151.07.
MALDI-TOF-MS (MW=576.85 without anion): m/z: 576.36.

2-phenyl-9-tetradecylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium tetrafluoroborate PQPBF$_4$-14: yellow powder (yield = 59%), $^1$H NMR (250MHz, CD$_3$OD, 25°C): $\delta$(ppm) = 9.56 (s, 2H, aromatic), 9.12-9.09 (d, 2H, $^3$J(H,H)=7.5Hz, aromatic), 8.88-8.85 (d, 4H, $^3$J(H,H)=7.5Hz, aromatic), 8.33-8.29 (m, 2H, aromatic), 8.06-8.02 (t, 2H, $^3$J(H,H)=7.5Hz, aromatic), 7.96-7.91 (d, 2H, $^3$J(H,H)=7.5Hz, aromatic), 7.72-7.69 (d, 3H, $^3$J(H,H)=7.5Hz, aromatic), 1.90-1.84 (m, 2H, CH$_2$), 1.47-1.19 (m, 22H, CH$_2$), 0.84-0.79 (t, 3H, CH$_3$); $^{13}$C NMR (250MHz, CD$_2$Cl$_2$, 25°C): d (ppm): 14.65, 23.46, 30.13, 30.18, 30.28, 30.43, 32.20, 32.69, 36.90, 118.83, 124.04, 124.17, 124.44, 125.35, 126.33, 127.40, 129.08, 129.49, 130.85, 132.01, 132.99, 134.79, 135.19, 142.81, 146.80, 150.55.

Figure S1. The intensity-weighted distribution of the aggregates formed by PQPCI-6 (a) and PQPCI-14 (b) obtained from the DLS measurements at 25 °C.

Figure S2. WAXS patterns of the dried powder of PQPCI-6 and PQPCI-14 obtained from methanolic solution.
Figure S3. Electron diffraction images of the PQP aggregates: (a) PQPCI-6; (b) PQPCI-14.

Figure S4. FTIR spectra of PQPCI-14 and PQPBF$_4$-14 in the 3000–3600 cm$^{-1}$ region.
Figure S5. WAXS patterns of a dried powder of PQPCI-6 and PQPBF₄-6 obtained from methanolic solution