

Electronic Supplementary Information (ESI):

**High-performance dielectric ionic ladderphane-derived triblock
copolymer with self-assembled unique nanostructure**

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Experimental Procedures

Synthesis of *endo*-N-(4-hydroxy phenyl)-norbornene-pyrrolidine (*endo*-HPNP)

To a slurry of LiAlH_4 (2.43 g, 64 mmol) in THF (50 mL), *endo*-NDI (4.08 g, 16 mmol) in THF (40 mL) was added slowly under nitrogen atmosphere at 0 °C, and the mixture was stirred at room temperature for 24 h. EtOAc (5 mL) was added, and then water (5 mL) was carefully introduced. The resulting suspension was filtered, washed with CH_2Cl_2 (100 mL \times 3). The organic phase was dried with MgSO_4 and the solvent was removed in decompression to give the crude product as a solid. After drying, the yellow powder was obtained (2.98 g, 81.1% yield). M.p.: 184-186 °C. ^1H NMR (500 MHz, CDCl_3 , ppm): δ 7.21-7.20 (d, 2H, $J = 9.00$ Hz, NCCH), 6.89-6.87 (d, 2H, $J = 9.00$ Hz, CHCOCO), 6.39 (s, 2H, CH=CH), 3.95 (s, 1H, ArOH), 3.43 (s, 4H, CH_2NAr), 3.04 (s, 2H, =CHCHCH), 2.65 (s, 2H, =CHCHCH), 1.90-1.73 (dd, 2H, $J = 8.50$ Hz, =CHCHCH $_2$). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 137.79, 129.83, 122.03, 117.12, 59.40, 54.34, 45.26, 44.81.

Synthesis of *endo*-N-(4-hydroxy phenyl)-norbornene pyrrolidinium (*endo*-HPNP- PF_6)

To a solution of *endo*-HPNP (0.456 g, 2 mmol) in THF (20 mL), CH_3I (0.852 g, 6 mmol) was added under nitrogen atmosphere, and the mixture was stirred at room temperature for 18 h. The resulting suspension was filtered and the solid was washed with THF (10 mL \times 3). The solid was dissolved in 60 mL MeOH, KPF_6 solution (10 mL, 0.12 wt%) was added, and the mixture was stirred at room temperature for 24 h. The mixture was evaporated to remove solvent and the solid was washed with water (100 mL \times 3). The colourless powder was obtained (0.575 g, 73% yield). ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, ppm): δ 7.60-7.45 (d, 2H, $J = 10.00$ Hz, NCCH), 6.98-6.83 (d, 2H, $J = 9.50$ Hz, CHCOCO), 6.27 (s, 2H, CH=CH), 4.38 (s, 1H, ArOH), 3.32-3.25 (br,

7H, $\text{CH}_2\text{NAr} + \text{NCH}_3$), 3.04 (s, 2H, =CHCHCH), 2.86-2.77 (t, 2H, =CHCHCH), 1.76-1.67 (dd, 2H, $J = 10.00$ Hz, =CHCHCH₂). ¹³C NMR (125 MHz, (CD₃)₂SO, ppm): δ 139.39, 137.39, 122.54, 116.09, 68.09, 56.42, 53.43, 43.89.

As shown in Scheme 1, *endo*-NDI was easily transformed into *endo*-N-4-phenol-norbornene-pyrrolidine (*endo*-HPNP) by reduction reaction with LiAlH₄. Ionic compound *endo*-N-4-phenol-norbornene-pyrrolidine (*endo*-HPNP-PF₆) was obtained firstly by the reaction of *endo*-HPNP with CH₃I, and then the anion exchange of I⁻ by hexafluorophosphate. The crude product was purified by crystallization from ethanol to give a colourless crystal, and characterized by ¹H and ¹³C NMR spectroscopy. The ¹H NMR spectra of *endo*-HPNP and *endo*-HPNP-PF₆ (Fig. S1 and S2, ESI[†]) indicated the presence of characteristic two groups of methylene (proton e) adjacent to the norbornene ring at 3.47-3.41 and 3.32-3.25 ppm, respectively, meant carbonyl group was completely reduced to methylene. Moreover, ¹H NMR spectrum of *endo*-HPNP-PF₆ (Fig. S2, ESI[†]) showed new resonance signals appeared at 3.34 ppm from methyl carbon (proton i) in contrast to the ¹H NMR spectrum of *endo*-HPNP, and the integration ratio for methylene (proton e) and methyl (proton i) was 4:3.2, which was agreed well with the theoretical value of 4:3.

Synthesis of bisnorbornene-based monomer 2

To a solution of PBI-COOH (1.85 g, 2 mmol) in 50 mL of anhydrous CH₂Cl₂, *endo*-HPNP (1.12 g, 4.8 mmol) and DMAP (0.15 g, 1.2 mmol) were added under stirring at ice-water bath for 5 min, then EDCI•HCl (1.15 g, 6 mmol) was added to the mixture, stirred at room temperature for 3 days. The solvent was removed under reduced pressure. The solid was purified by column chromatography on silica gel using CH₂Cl₂/CH₃OH (200:1) as eluent. The red powder (1.93 g, 72%) was obtained. ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.68 (s, 4H, pery), 6.89-6.85 (d, 4H, $J = 6.82$ Hz,

NCCH), 6.40-6.35 (d, 4H, $J = 6.82$ Hz, CHCOCO), 6.31 (s, 4H, CH=CH), 4.22-4.19 (t, 4H, $J = 8.70$ Hz, CH_2NCO), 3.21-3.05 (m, 8H, CH_2NAr), 2.95 (s, 4H, =CHCHCH), 2.88-2.83 (d, $J = 9.50$ Hz, 4H, =CHCHCH), 2.50-2.47 (t, 4H, $J = 9.02$ Hz, $OCOCH_2$), 1.77-1.26 (m, 40H, =CHCHCH₂ + $OCOCH_2(CH_2)_9CH_2N$). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 173.16, 162.26, 145.73, 140.69, 135.85, 135.36, 132.94, 131.44, 128.59, 127.27, 121.79, 52.21, 50.85, 46.52, 45.63, 40.98, 34.31, 29.49, 29.46, 29.41, 29.31, 29.23, 29.13, 28.10, 27.06, 25.07; elemental analysis calcd (%) for C₇₈H₈₂Cl₄N₄O₈: C 69.64, H 6.14, N 4.16; found: C 69.95, H 6.03, N 3.95. IR (KBr): 2928 (CH₂), 2850 (C=C), 1756 (C=O), 1702, 1665, 1585, 1510, 1367, 1283, 1234, 1195, 905, 795 cm⁻¹.

Synthesis of bisnorbornene-based ionic monomer 3

To a solution of **PBI-COOH** (0.5 g, 0.5 mmol) in 60 mL of anhydrous CH₂Cl₂, *endo*-**HPNP-PF₆** (0.5 g, 1.27 mmol) and DMAP (0.036 g, 0.3 mmol) were added under stirring at ice-water bath for 5 min, then EDCI•HCl (0.286 g, 1.5 mmol) was added to the mixture, stirred at room temperature for 3 days. The solvent was removed under reduced pressure. The solid was washed with toluene (3×30 mL). The red powder (0.586 g, 65%) was obtained. ¹H NMR (500 MHz, (CD₃)₂SO, ppm): δ 8.75-8.45 (br, 4H, pery), 7.87-7.69 (d, 4H, $J = 6.82$ Hz, NCCH), 7.46-7.26 (d, 4H, $J = 6.82$ Hz, CHCOCO), 6.25 (s, 4H, CH=CH), 4.51-4.41 (m, 4H, CH_2NCO), 4.17-3.81 (br, 8H, CH_2NAr), 3.43 (s, 6H, NCH₃), 3.00 (s, 4H, =CHCHCH), 2.95-2.87 (t, $J = 8.5$ Hz, 4H, =CHCHCH), 2.66-2.55 (t, 4H, $J = 7.05$ Hz, $OCOCH_2$), 1.77-1.16 (m, 40H, =CHCHCH₂ + $OCOCH_2(CH_2)_9CH_2N$). ¹³C NMR (125 MHz, (CD₃)₂SO, ppm): δ 171.79, 144.95, 137.59, 140.69, 129.36, 128.66, 125.59, 125.08, 123.87, 123.07, 113.80, 68.23, 56.01, 53.51, 44.37, 44.23, 29.45, 29.16, 26.92, 28.78, 26.89, 24.65, 21.46, 21.18, 17.89; elemental analysis calcd (%) for C₈₀H₈₈Cl₄F₁₂N₄O₈P₂: C 57.70, H

5.33, N 3.36; found: C 57.99, H 5.13, N 3.24. IR (KBr): 2928 (CH₂), 2850 (C=C), 1756 (C=O), 1702, 1662, 1584, 1500, 1396, 1293, 1234, 1175, 914, 840, 600 cm⁻¹.

Polymerization of 1. A 250 mL of Schlenk tube was charged with monomer **1** (143 mg, 0.1 mmol) dissolved in CHCl₃ (17 mL). In another 25 mL of Schlenk tube, **Ru-III** (3.6 mg, 4 μmol) was dissolved in CHCl₃ (1 mL). After degassed in three freeze-vacuum-thaw cycles, the catalyst solution of **Ru-III** was then injected into the monomer solution via a syringe under vigorous stirring at 30 °C for 3 h. The corresponding PBI-bridged homopolymer ladderphane **P1**₂₅. The number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) of **P1**₂₅ were 48,300 and 1.6, respectively. ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.72-8.55 (br, pery), 7.29-6.87 (br, CH=CH on phenyl), 5.92-5.64 (br, *trans*-CH on backbone), 5.63-5.42 (br, *cis*-CH on backbone), 4.43-4.03 (br, CH₂NCO), 3.33-3.00 (br, =CHCHCH), 2.98-2.71 (br, =CHCHCH), 2.68-2.17 (br, OCOCH₂), 1.97-1.20 (br, =CHCHCH₂ + CH₂OCO(CH₂)₉CH₂N). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 176.72, 171.62, 162.18, 150.14, 135.28, 132.90, 131.45, 129.21, 128.49, 127.55, 127.26, 123.21, 122.05, 51.11, 46.01, 40.91, 30.94, 29.09, 27.95, 26.82, 24.72.

Polymerization of 2. Monomer **2** (134 mg, 0.1 mmol) and **Ru-III** (3.6 mg, 4 μmol) were stirred in 17 mL of CHCl₃ at 30 °C for 3 h. The corresponding PBI-bridged homopolymer ladderphane **P2**₂₅. The M_n and PDI of **P2**₂₅ were 45,800 and 1.5, respectively. ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.72-8.51 (br, pery), 6.95-6.38 (br, CH=CH on phenyl), 5.55-5.30 (br, *trans*-CH on backbone), 4.31-4.02 (br, CH₂NCO), 3.31-2.94 (br, CH₂NAr), 2.95-2.77 (br, =CHCHCH), 2.76-2.61 (br, =CHCHCH), 2.60-2.40 (br, OCOCH₂), 1.97-0.96 (br, =CHCHCH₂ + OCOCH₂(CH₂)₉CH₂N). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 187.50, 169.20, 146.24, 139.80, 134.83, 133.93, 132.67, 132.05, 131.43, 127.46, 123.14, 53.26, 59.69, 54.76, 50.78, 43.41, 38.75,

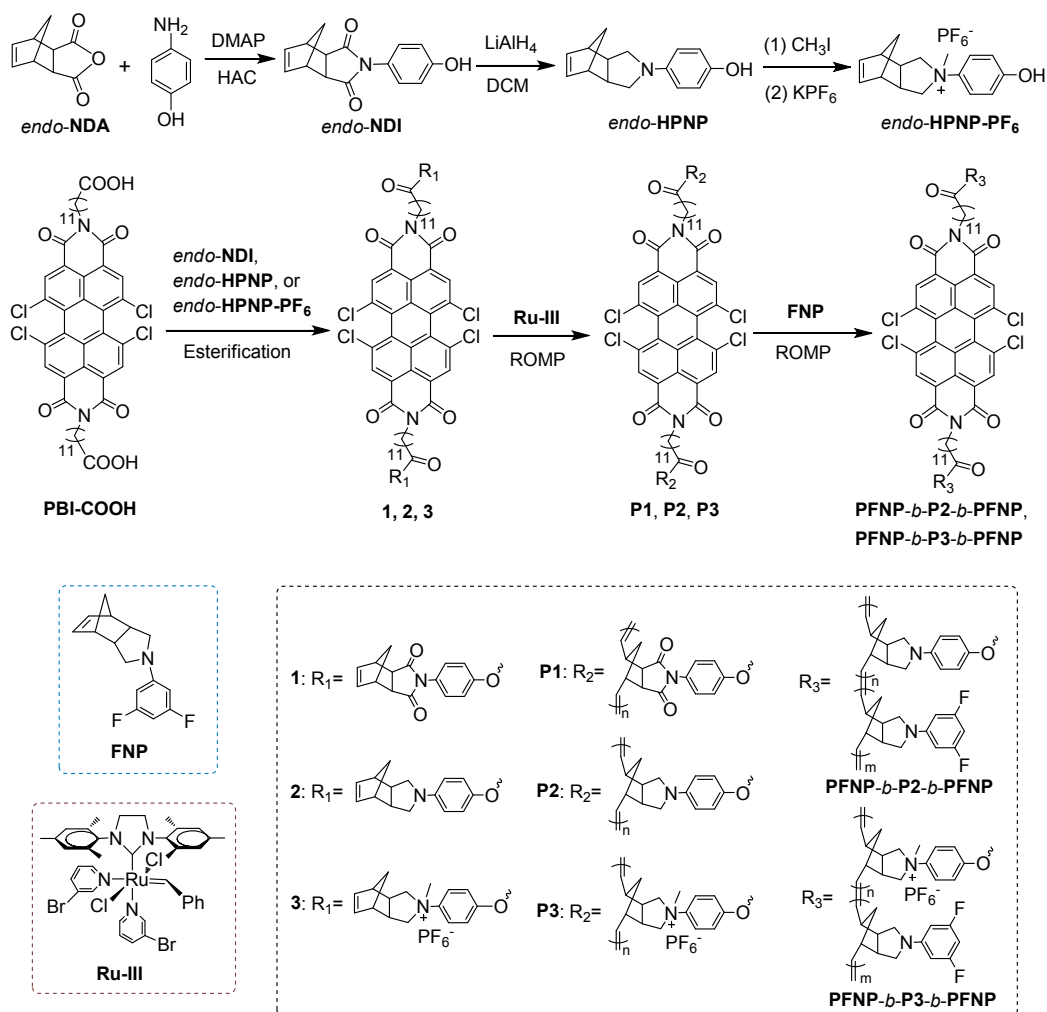
30.47, 25.51, 24.27, 21.94, 20.93, 19.40. IR (KBr): 2933 (CH₂), 2850 (C=C), 1756 (C=O), 1707, 1589, 1515, 1392, 1362, 1288, 1238, 1204, 1170, 1101, 970, and 810 cm⁻¹.

Synthesis of triblock copolymer ladderphane PFNP₅₀-*b*-P2₂₅-*b*-PFNP₅₀. A 50 mL of Schlenk tube was charged with monomer **2** (134 mg, 0.1 mmol) dissolved in CHCl₃ (16 mL), **Ru-III** (3.6 mg, 4 μmol) was dissolved in CHCl₃ (1 mL) in a 25 mL of Schlenk tube, and **FNP** (49.4 mg, 0.2 mmol) was dissolved in CHCl₃ (1 mL) in a 25 mL of Schlenk tube. After degassed in three freeze-vacuum-thaw cycles, the catalyst solution of **Ru-III** was then injected into the solution of monomer **2** via a syringe under vigorous stirring at 30 °C for 0.5 h. After that, the solution of **FNP** was injected into the reaction solution via a syringe under vigorous stirring at 30 °C for 2.5 h. The corresponding triblock copolymer ladderphane, referred to as **PFNP₅₀-*b*-P2₂₅-*b*-PFNP₅₀**, was obtained by precipitating the reaction mixture from excess petroleum ether. The *M_n* and PDI of **PFNP₅₀-*b*-P2₂₅-*b*-PFNP₅₀** were 81500 and 1.4, respectively. ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.75-8.55 (br, pery), 6.92-6.35 (br, CH=CH on phenyl), 6.21-5.95 (br, CH on *m*-difluorophenyl), 5.54-5.20 (br, *trans*-CH on backbone), 4.30-4.01 (br, CH₂NCO), 3.35-2.99 (br, CH₂NAr), 2.98-2.58 (br, =CHCHCH + =CHCHCH), 2.57-2.35 (br, OCOCH₂), 1.99-0.70 (br, =CHCHCH₂ + OCOCH₂(CH₂)₉CH₂N). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 171.75, 165.20, 162.64, 161.55, 149.93, 135.35, 132.84, 131.50, 131.34, 129.17, 128.46, 127.37, 122.98, 121.89, 95.36, 51.35, 46.50, 40.78, 34.37, 30.58, 29.02, 28.08, 27.71, 26.63, 24.78. IR (KBr): 2928 (CH₂), 2850 (C=C), 1756 (C=O), 1707, 1667, 1633, 1584, 1510, 1475, 1392, 1362, 1288, 1234, 1209, 1165, 1106, 972, and 815 cm⁻¹.

Syntheses of bisnorbornene-type monomers

Bisnorbornene-type monomers **1**, **2**, and **3** were synthesized via the esterification of

dicarboxy-contained PBI (**PBI-COOH**) with *endo*-N-(4-hydroxyphenyl)-norbornene dicarboximide (*endo*-**NDI**), *endo*-N-(4-hydroxyphenyl)-norbornene pyrrolidine (*endo*-**HPNP**), and ionic *endo*-N-(4-hydroxyphenyl)-norbornene pyrrolidinium hexafluorophosphate (*endo*-**HPNP-PF₆**), respectively (Scheme S1, ESI†).



Scheme S1 Syntheses of functional monomers and polymers.

These PBI-functionalized bisnorbornene monomers were characterized by ¹H NMR, ¹³C NMR, and elemental analysis (ESI†). The ¹H NMR spectra of monomers **2** and **3** (Fig. S3 and S4, ESI†) showed the resonance signals of methylene protons (h) adjacent to the ester group at 2.50-2.47 and 2.66-2.55 ppm, respectively, and the integration ratio for methylene protons (e) and methylene protons (h) was nearly 2:1, meant *endo*-**HPNP** and *endo*-**HPNP-PF₆** were connected to **PBI-COOH** completely.

Similarly, in ^{13}C NMR spectra of monomers **2** and **3** (Fig. S3 and S4, ESI †), the resonance of ester carbons appeared at 173.16 and 171.19 ppm, respectively, which also proved *endo*-HPNP and *endo*-HPNP- PF_6 were connected to PBI-COOH. Elemental analysis suggested that **2** and **3** have the right element content. Apparently, all these points confirmed the successful preparation of **2** and **3** with the expected structure.

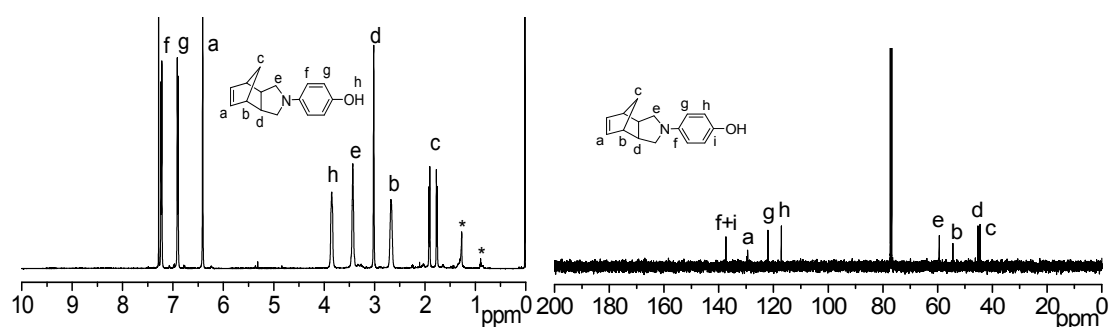


Fig. S1 ^1H and ^{13}C NMR spectra of *endo*-HPNP.

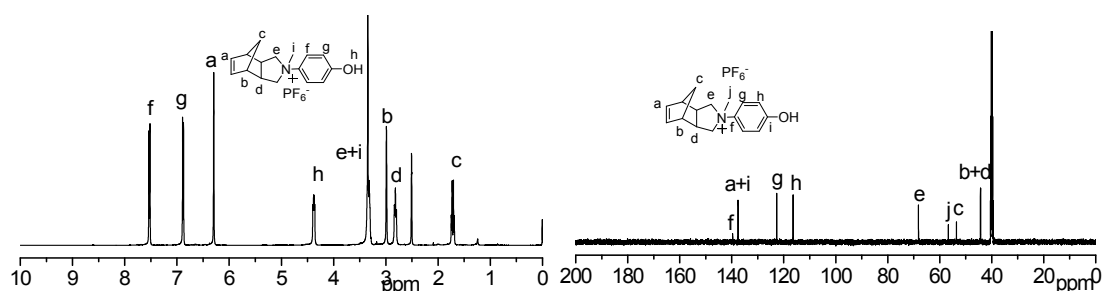


Fig. S2 ^1H and ^{13}C NMR spectra of *endo*-HPNP- PF_6 in $\text{DMSO-}d_6$.

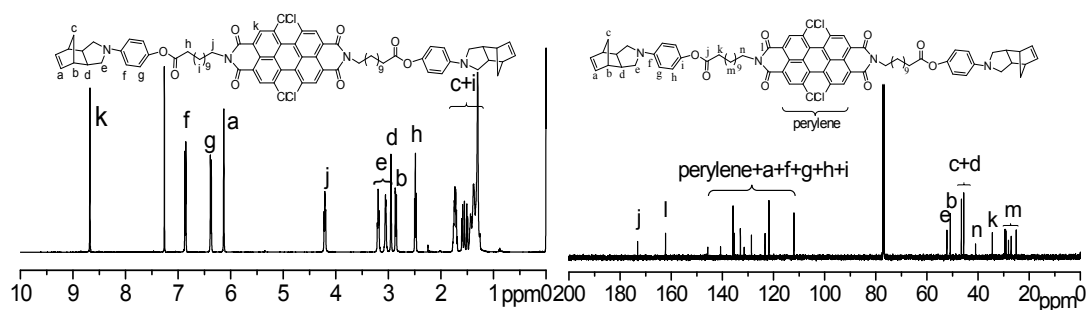


Fig. S3 ^1H and ^{13}C NMR spectra of monomer **2**.

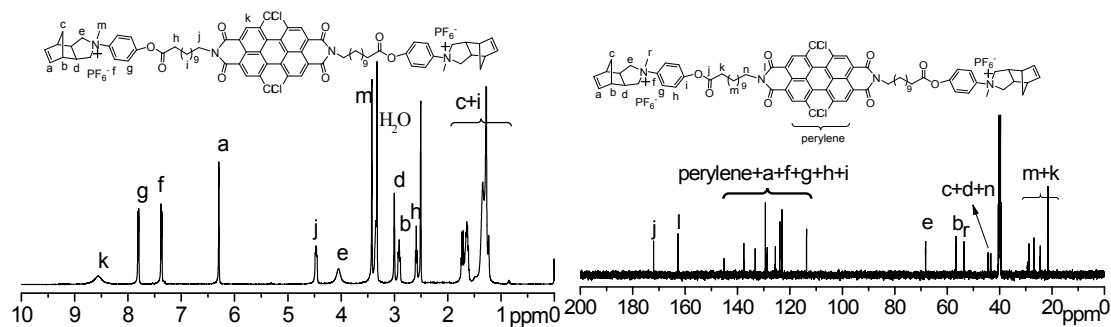


Fig. S4 ^1H and ^{13}C NMR spectra of monomer **3** in $\text{DMSO-}d_6$.

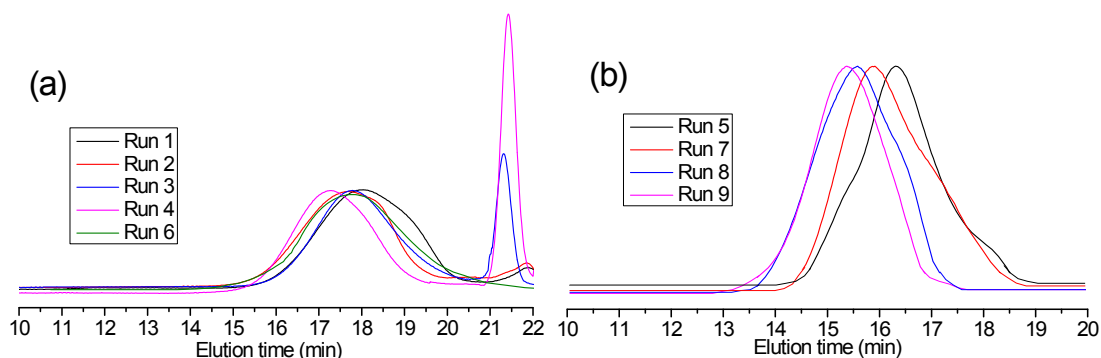


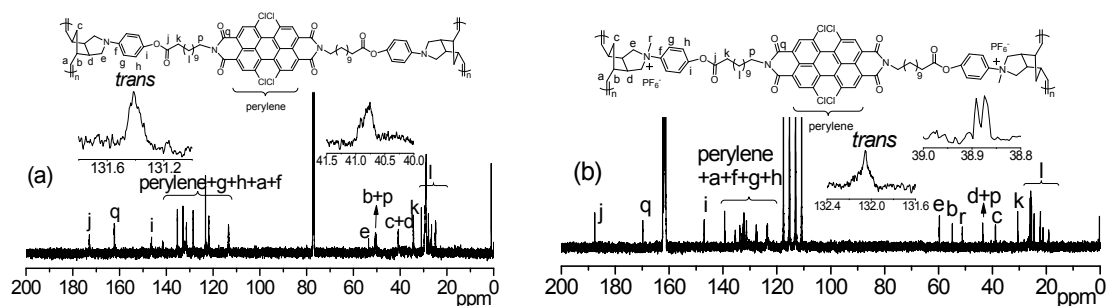
Fig. S5 GPC traces of (a) homopolymers and (b) copolymers.

Table S1 Solubility of monomers and polymers in various solvents at room temperature*

Samples	CH_2Cl_2	CHCl_3	THF	Toluen e	CH_3OH	Acetone
1	++	++	++	+	–	+–
2	++	++	++	+	–	+–
3	++	+–	+–	–	+–	+–
P1 ₂₅	++	++	++	+	+–	–
P2 ₂₅	++	++	++	+	+–	–
PFNP ₅₀ - <i>b</i> - P2 ₂₅ - <i>b</i> - PFNP ₅₀	++	++	+	+–	+–	+–
P3 ₂₅	+	+–	+–	–	+–	+–
PFNP ₅₀ - <i>b</i> - P3 ₂₅ - <i>b</i> - PFNP ₅₀	+	+	+	+–	+–	+–
PFNP ₁₀₀ - <i>b</i> - P3 ₂₅ - <i>b</i> - PFNP ₁₀₀	++	++	+	+–	–	–
PFNP ₂₀₀ - <i>b</i> - P3 ₂₅ - <i>b</i> - PFNP ₂₀₀	++	++	++	+	–	–

*1 mg of polymer or monomer in 1 mL of solvent.

–: insoluble; +–: partially soluble; +: soluble; ++ easily soluble.



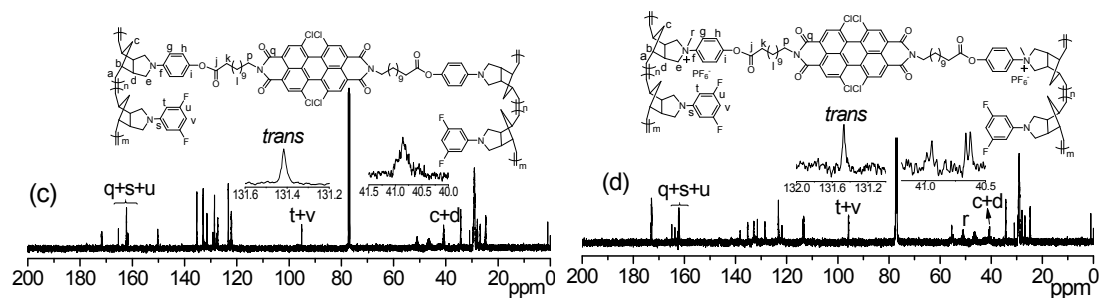


Fig. S6 ^{13}C NMR spectra of **P2₂₅** (a), **P3₂₅** (b, in CF_3COOD), **PFNP₅₀-b-P2₂₅-b-PFNP₅₀** (c), and **PFNP₅₀-b-P3₂₅-b-PFNP₅₀** (d).

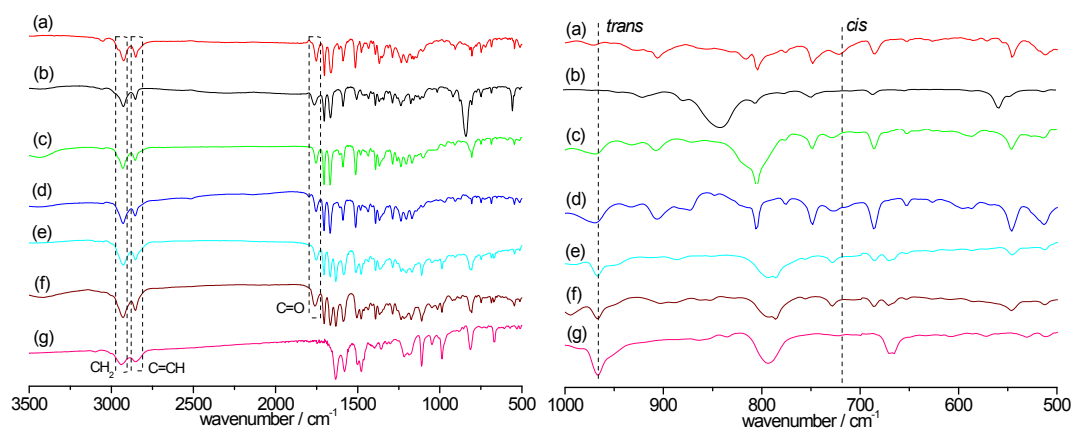
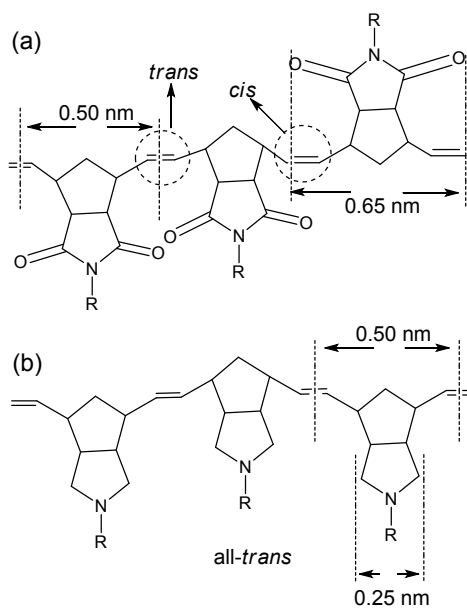


Fig. S7 IR spectra of **2** (a), **3** (b), **P2₂₅** (c), **P3₂₅** (d), **PFNP₅₀-b-P2₂₅-b-PFNP₅₀** (e), and **PFNP₅₀-b-P3₂₅-b-PFNP₅₀** (f), and **PFNP₇₅** (g).



Scheme S2 Schematic illustrations of the backbone of (a) **P1₂₅** and (b) **P2₂₅**.

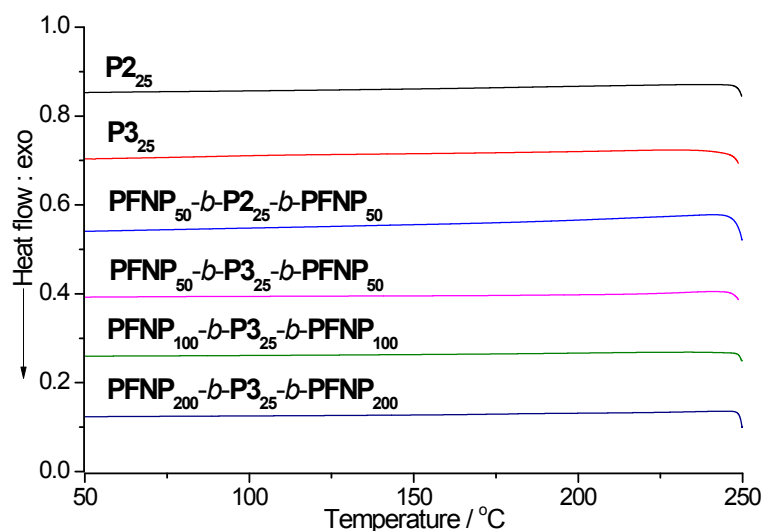


Fig. S8 DSC curves of polymers in the cooling process.

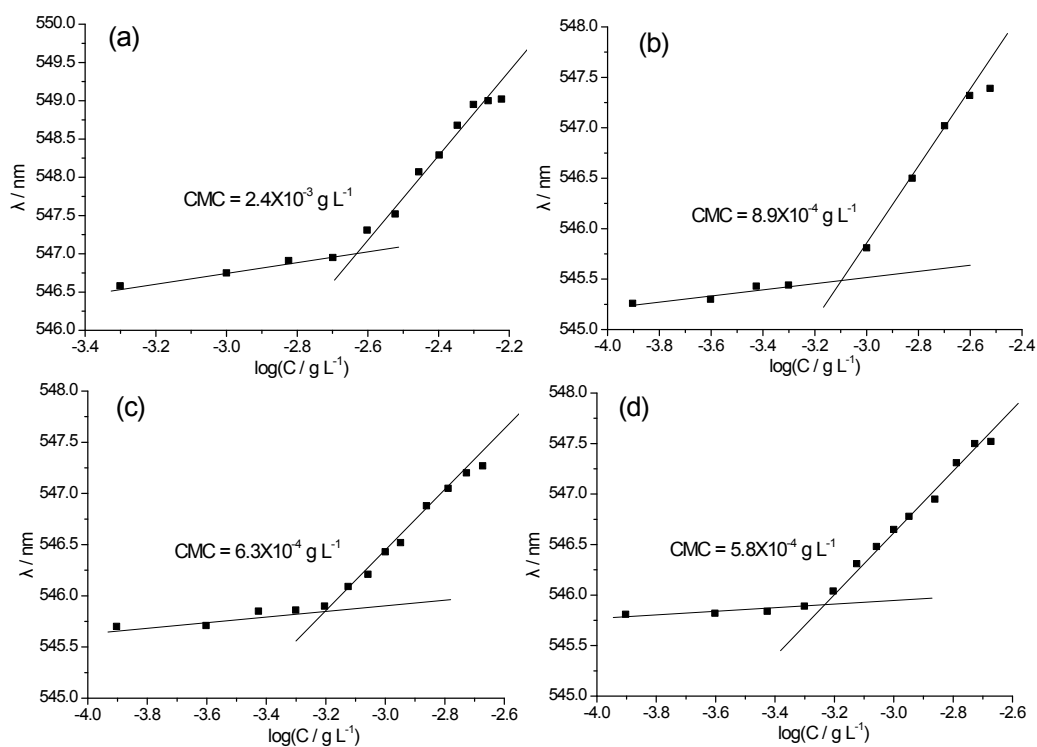


Fig. S9 Determination of the CMC by fluorimetry measurement for (a) $\text{PFNP}_{50}\text{-}b\text{-P}_{25}\text{-}b\text{-PFNP}_{50}$, (b) $\text{PFNP}_{50}\text{-}b\text{-P}_{325}\text{-}b\text{-PFNP}_{50}$, (c) $\text{PFNP}_{100}\text{-}b\text{-P}_{325}\text{-}b\text{-PFNP}_{100}$, and (d) $\text{PFNP}_{200}\text{-}b\text{-P}_{325}\text{-}b\text{-PFNP}_{200}$.

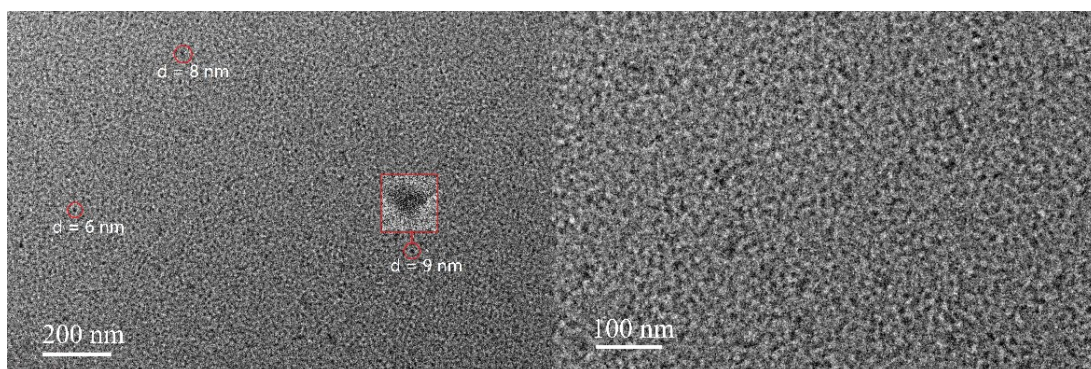


Fig. S10 TEM images of **P2₂₅** at 0.005 mg mL⁻¹ in THF.

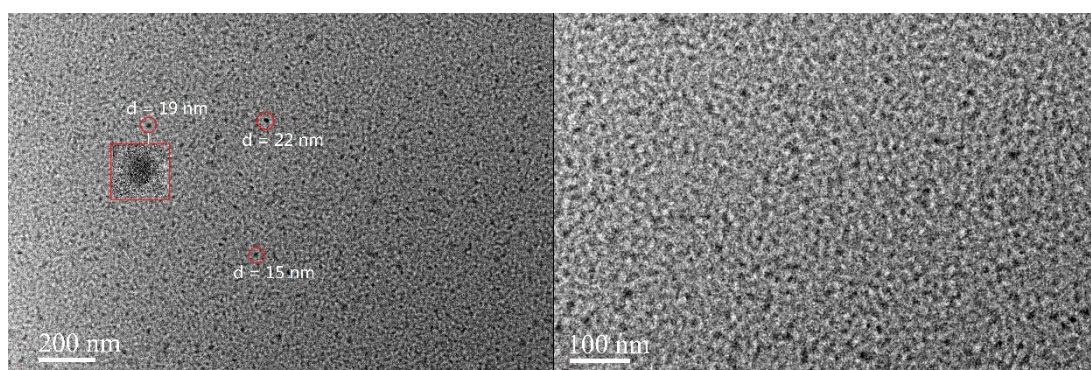


Fig. S11 TEM images of **P3₂₅** at 0.005 mg mL⁻¹ in THF.

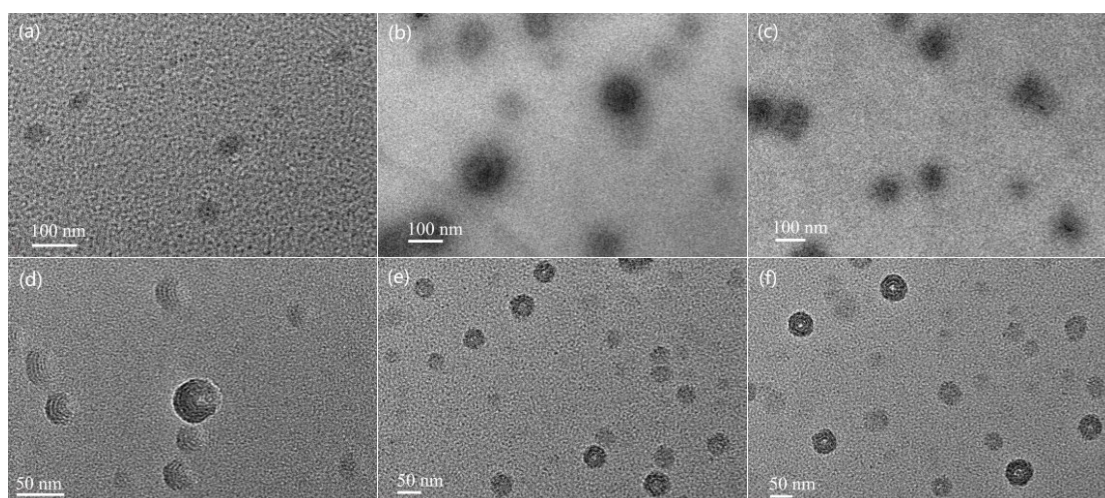


Fig. S12 TEM images of **PFNP₅₀-*b*-P2₂₅-*b*-PFNP₅₀** (a-c) and **PFNP₅₀-*b*-P3₂₅-*b*-PFNP₅₀** (d-f) at 0.005 (a,d), 0.01 (b,e), and 0.02 (c,f) mg mL⁻¹ in THF.

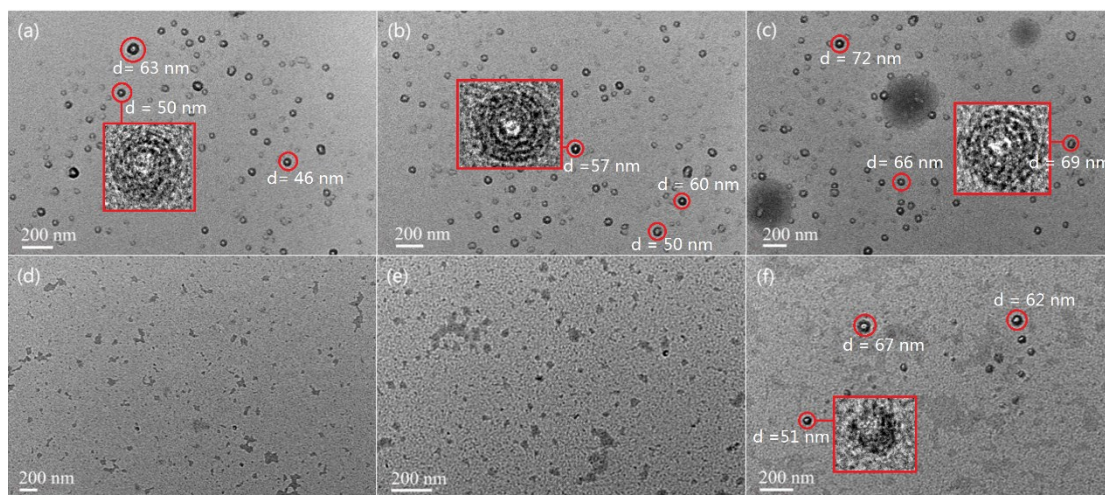


Fig. S13 TEM images of $\text{PFNP}_{100}\text{-}b\text{-P3}_{25}\text{-}b\text{-PFNP}_{100}$ (a-c) and $\text{PFNP}_{200}\text{-}b\text{-P3}_{25}\text{-}b\text{-PFNP}_{200}$ (d-f) at 0.005 (a,d), 0.01 (b,e), and 0.02 (c,f) mg mL^{-1} in THF.

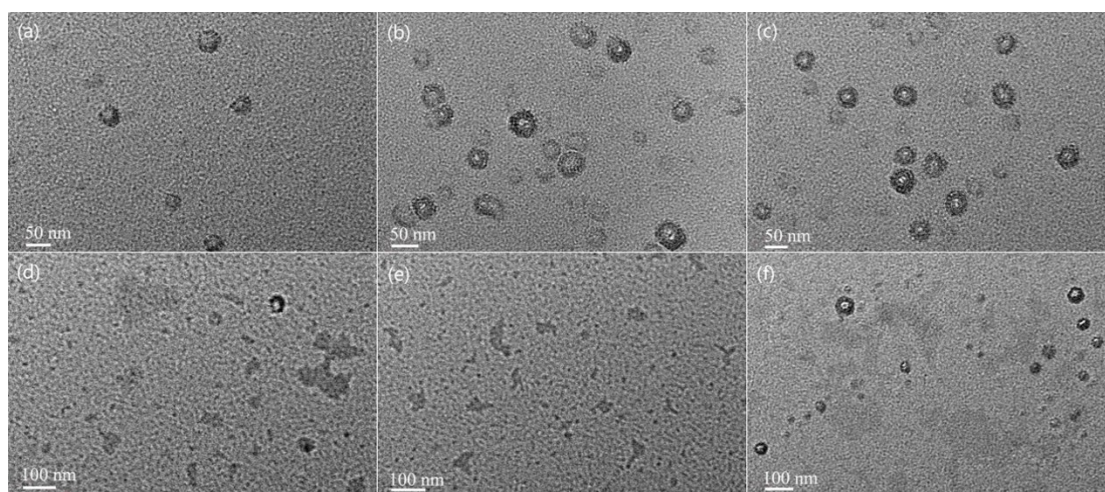


Fig. S14 TEM images of $\text{PFNP}_{100}\text{-}b\text{-P3}_{25}\text{-}b\text{-PFNP}_{100}$ (a-c) and $\text{PFNP}_{200}\text{-}b\text{-P3}_{25}\text{-}b\text{-PFNP}_{200}$ (d-f) at 0.005 (a,d), 0.01 (b,e), and 0.02 (c,f) mg mL^{-1} in THF.

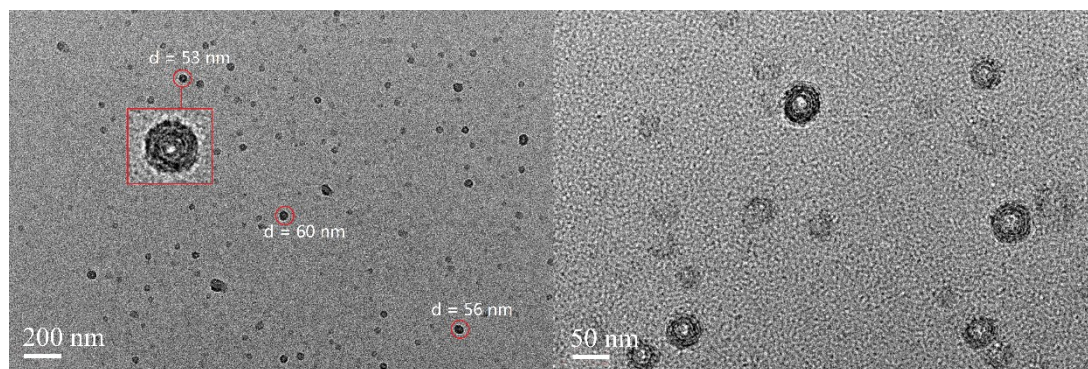
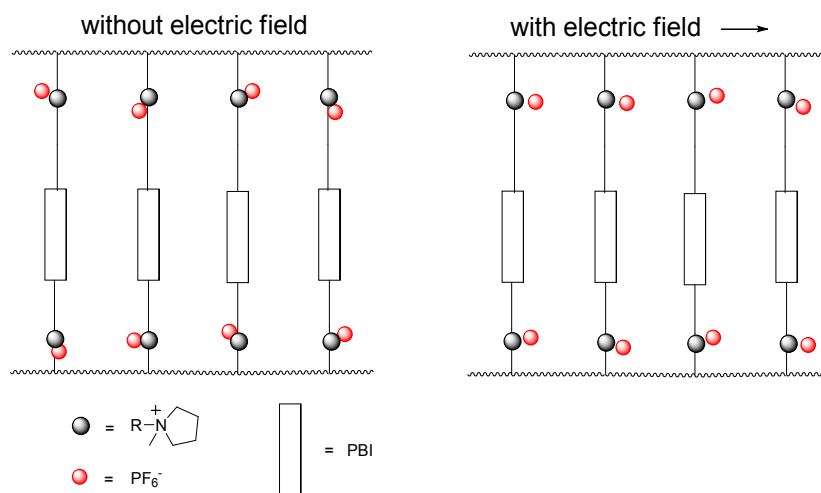


Fig. S15 TEM images of $\text{PFNP}_{50}\text{-}b\text{-P3}_{25}\text{-}b\text{-PFNP}_{50}$ at 0.005 mg mL^{-1} in THF by frozen-dried process.



Scheme S3 Schematic illustrations of small relative displacements of the ions under the applied electric field.

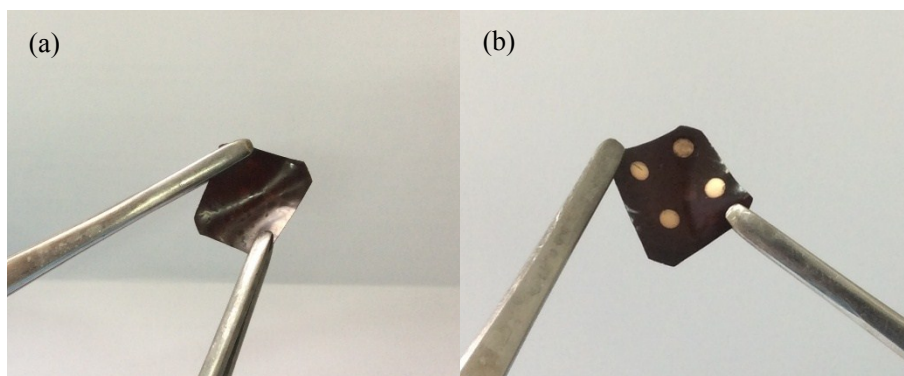


Fig. S16 Photographs for free-standing film of **PFNP₂₀₀-*b*-P3₂₅-*b*-PFNP₂₀₀** before (a) and after (b) plating.