Electronic supplementary information

Supramolecular assembly of H-bonded copolymers/complexes/nanocomposites and fluorescence quenching effects of surface-modified gold nanoparticles on fluorescent copolymers containing pyridyl H-acceptors and acid H-donors

Tzung-Chi Liang and Hong-Cheu Lin*

Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan (ROC)

Synthesis of H-acceptor monomer PBT

The synthetic route for monomer **PBT** is shown in Scheme S1, and its synthetic procedure is described as follows:

4-Bromo-2,5-dimethylbenzaldehyde (2). 2,5-Dibromo-*p*-xylene **1** (Lancaster) (6.9 g, 26.3 mmol) was dissolved in 60 mL of dry THF (TEDIA) purged with nitrogen. A solution of n-BuLi (ACROS) (13.7 mL, 34.2 mmol, 2.5 M in hexane) was added dropwise to a rapidly stirred THF at -78°C. The rate of addition was adjusted to keep the temperature below -78°C. After the solution was stirred to react at -78°C for 2 h, a solution of DMF (ACROS) (4.1 mL, 52.6 mmol) was added dropwise, following the same temperature control. After 2 h, the reaction was quenched with water and extracted with ethyl acetate (TEDIA). The organic extracts were dried over Na_2SO_4 (SHOWA) and then evaporated. The crude product was purified and recrystallized

from n-hexane to give a white crystal. Yield: 5.0 g (90 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 10.19 (s, 1H), 7.63 (s, 1H), 7.47 (s, 1H), 2.60 (s, 3H), 2.43 (s, 3H).

4-Bromo-2,5-dimethylbenyl alcohol (3). To a stirred solution of compound **2** (5.0 g, 23.7 mmol) in 100 mL of THF/MeOH (TEDIA) (1:1), $NaBH_4$ (Lancaster) (0.9 g, 23.7 mmol) was added very slowly and reacted at room temperature. After 1 h, the solution was cooled to 0°C by a ice bath, acidified with a dilute HCl solution, and extracted with ethyl acetate. The resulting extracts in organic phase were combined and washed with water. The organic extracts were dried over Na_2SO_4 and evaporated. The crude product was purified and recrystallized from dichloromethane/2-propanol to give a colorless crystal. Yield: 4.1 g (80 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 7.33 (s, 1H), 7.21 (s, 1H), 4.61 (s, 2H), 2.35 (s, 3H), 2.27 (s, 3H).

1-Bromo-4-chloromethyl-2,5-dimethoxybenzene (4). A stirred solution of compound **3** (4.1 g, 19 mmol) in 1,4-dioxane (150 mL) was added with concentrated HCl (20 mL, 3N), and then the mixture was refluxed for 10 h. After the reaction was completed, the crude mixture was added with water. The organic layer was extracted with ethyl acetate, dried over Na_2SO_4 and evaporated. The crude product was purified by flash column chromatography (silica gel, n-hexane/ethyl acetate 40:1) to give a white solid. Yield: 4.0 g (89 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 7.36 (s, 1H), 7.15 (s, 1H), 4.51 (s, 2H), 2.36 (s, 6H).

4-Bromo-2,5-dimethylbenzyldiethylphosphonate (5). To a stirred solution of compound **4** (4.0 g, 17.1 mmol), and an excess of triethylphosphite (Lancaster) (20 mL) were mixed and heated to reflux for 12 h. The excess of triethylphosphite was removed under reduce pressure and the crude product was purified and washed with hot hexane to give a white solid. Yield: 5.1 g (90 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 7.28 (s, 1H), 7.07 (s, 1H), 4.08-3.95 (m, 10H), 3.06 (s, 1H), 2.99 (s, 1H), 2.28 (s, 3H), 2.26 (s, 3H).

1-Bromo-2,5-dimethyl-4-[2-(4-pyridyl)ethenyl]benzene (6). Compound **5** (5.1 g, 15.1 mmol) was dissolved in 60 mL of dry THF purged with nitrogen. A solution of lithium diisopropylamide (Lancaster) (22.7 mL, 45.3 mmol, 2.5 M in hexane) was added dropwise to a rapidly stirred solution at -78°C. The rate of addition was adjusted to keep the temperature below -78°C. After the solution was stirred to react at -78°C for 30 min, a solution of pyridine-4-carboxaldehyde (Aldrich) (2 mL, 21.1 mmol) was added dropwise and stirred for 30 min to come back to room temperature. Then, the mixture was stirred to react for 18 h at room temperature. The reaction was quenched with water and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (silica gel, dichloromethane/acetone 20:1) to give a yellow solid. Yield: 3.7 g (85 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 8.56 (d, J = 4.8 Hz, 2H), 7.42 (s, 1H),

7.40 (d, *J* = 16.2 Hz, 1H), 7.36 (s, 1H), 7.35 (d, *J* = 4.8 Hz, 2H), 6.88 (d, *J* = 16.2 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H).

10-(4-Bromophenoxy)-decan-1-ol (8). A mixture of compound **7** 4-bromophenol (Lancaster) (4.9 g, 28.5 mmol), potassium carbonate (8.7 g, 62.7 mmol), 10-bromodecanol (7.4 g, 31.4 mmol), and a few amounts of potassium iodide (SHOWA) in acetone (200 mL) was heated to reflux and stirred under nitrogen for 48 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was taken up in water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (silica gel, n-hexane/ethyl acetate 3:1) to give a white solid. Yield: 8.3 g (88 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 7.33 (d, *J* = 9.0 Hz, 2H), 6.75 (d, *J* = 9.0 Hz, 2H), 3.89 (t, *J* = 6.3 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 1.78-1.69 (m, 2H), 1.59-1.50 (m, 2H), 1.41-1.29 (m, 12H).

4-[4-(10-Hydroxy-decyloxy)-phenyl]-2-methyl-3-butyn-2-ol (9). A solution of compound **8** (8.3 g, 25.3 mmol), PPh_3 (Lancaster) (13.1 mg, 0.51 mmol), and CuI (ACORS) (73 mg, 0.38 mmol) in dry triethylamine (TEDIA) (80 mL) was degassed with nitrogen for 5 min. 2-Methyl-3-butyn-2-ol (ACORS) (3.7 mL, 38 mmol) and $Pd(PPh_3)_2Cl_2$ (Lancaster) (180 mg, 0.25 mmol) were added to the solution at room temperature and the mixture was stirred to react at 70 ^{o}C for 12 h. The mixture was

filtered and the solvent was removed in vacuum. The crude mixture was extracted by dichloromethane. The organic solution was washed with water, dried over Na_2SO_4, and then evaporated. The crude product was purified by column chromatography (silica gel, n-hexane/ethyl acetate 2:1) to give a light yellow solid. Yield: 4.7 g (56 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 7.31 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 1.77-1.70 (m, 2H), 1.60 (s, 6H), 1.58-1.50 (m, 2H), 1.42-1.29 (m, 12H).

4-Ethynyl-1-(10-hydroxydecan-1-yloxy)benzene (10). A solution of compound **9** (4.7 g, 14.2 mmol) and finely powdered KOH (SHOWA) (2.39 g, 42.6 mmol) in 1,4-dioxane (80 mL) was refluxed under nitrogen for 3 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was taken up in water and extracted with ethyl acetate, and then acidified with 150 mL of HCl (3 N). The organic solution was washed with water, dried over Na_2SO_4, andevaporated. The crude product was purified by column chromatography (silica gel, n-hexane/ethyl acetate 4:1) to give a light yellow solid. Yield: 3.6 g (92 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 7.39 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.97 (s, 1H), 1.80-1.70 (m, 2H), 1.57-1.50 (m, 2H), 1.42-1.29 (m, 12H).

10-{4-[2,5-Dimethyl-4-(2-pyridin-4-yl-vinyl)-phenylethynyl]-phenoxy}-decan-1-ol (11). A mixture of compound **6** (3.7 g, 12.7 mmol)**,** PPh_3 (170 mg, 0.64 mmol), and CuI (120 mg, 0.64 mmol) in dry triethylamine (80 mL) was degassed with nitrogen for 5 min. After addition of compound **10** (3.6 mL, 13.3 mmol) and $Pd(PPh_3)_2Cl_2$ (90 mg, 0.13 mmol) to the solution at room temperature, the reaction mixture was stirred to react at 70 ^oC for 12 h. The mixture was filtered and the solvent removed in vacuum. The crude mixture was extracted by dichloromethane. The organic solution was washed with water, dried over Na_2SO_4, and then evaporated. The crude product was purified by column chromatography (silica gel, dichloromethane) to give a light yellow solid. Yield: 4.4 g (72 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 8.61 (d, *J* = 6.0 Hz, 2H), 7.56 (d, *J* = 15.9 Hz, 1H), 7.51 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 6.0 Hz, 2H), 7.36 (s, 1H), 6.98 (d, *J* = 15.9 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.68 (t, *J* = 6.6 Hz, 2H), 2.53 (s, 3H), 2.44 (s, 3H), 1.82 (m, 2H), 1.60 (m, 2H), 1.49-1.16 (m, 12H).

2-Methyl-acrylic acid 10-{4-[2,5-dimethyl-4-(2-pyridin-4-yl-vinyl)-phenylethynyl]-phenoxy}-decyl ester PBT. Compound **11** (1.0 g, 2.1 mmol), vinyl methacrylate (TCI) (1.24 ml, 0.01 mmol), 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane (92 mg, 0.83 mmmol), 2,6-di-tert-butyl-4-methyl phenol (Lancaster) (27 mg, 1.3 mmmol), and 2 ml of THF

were added to a round-bottom flask. The solution was stirred to react at 50 ^{o}C for 48 h. The crude product was purified by column chromatography (aluminium oxide, n-hexane/dichloromethane 4:1) to give a light yellow solid. Yield: 0.54 g (47 %). ^{1}H-NMR (ppm, $CDCl_3$): δ 8.57 (d, *J* = 5.4 Hz, 2H), 7.51 (d, *J* = 16.2 Hz, 1H), 7.46 (s, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 5.4 Hz, 2H), 7.31 (s, 1H), 6.93 (d, *J* = 16.2 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.08 (s, 1H), 5.53 (s, 1H), 4.12 (t, *J* = 6.9 Hz, 2H), 3.96 (t, *J* = 6.9 Hz, 2H), 2.49 (s, 3H), 2.39 (s, 3H), 1.93 (s, 3H), 1.77 (m, 2H), 1.65 (m, 2H), 1.49-1.20 (m, 12H). ^{13}C NMR (ppm, $CDCl_3$): δ 167.34, 159.30, 149.92 (2C), 145.09, 137.62, 136.58, 134.60, 133.63, 133.60, 132.96 (2C), 130.52, 127.20, 126.47, 125.20, 123.72, 121.00 (2C), 115.30, 114.59 (2C), 94.65, 87.04, 68.09, 64.84, 29.49, 29.46, 29.37, 29.25, 29.21, 28.62, 26.03, 25.99, 20.39, 19.20, 18.37. MS (EI): *m*/*z* [M^+] 549.3, calcd *m*/*z* [M^+] 549.32. Anal. Calcd. for $C_{37}H_{43}NO_3$: C 80.84, H 7.88, N 2.55. Found: C 80.56, H 7.95, N 2.77.

Chemical characteristics of monomers M1-M6

4-(10-Acryloyloxy-decyloxy)-benzoic acid (M1). Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.32-1.46 (m, 12H), 1.65-1.69 (m, 2H), 1.76-1.83 (m, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 4.15 (t, *J* = 6.6 Hz, 2H), 5.83 (d, *J* = 9.0 Hz, 1H), 6.14 (m, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H). Anal. Calcd for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 68.80; H, 7.96.

3-(10-Acryloyloxy-decyloxy)-benzoic acid (M2). Yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.25-1.99 (m, 16H), 4.01 (t, *J* = 6.6 Hz, 2H), 4.15 (t, *J* = 6.9 Hz, 2H), 5.80 (d, *J* = 9.0 Hz, 1H), 6.07-6.16 (m, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 8.1 Hz, 1H), 7.59 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 1H). Anal. Calcd for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 68.88; H, 8.18.

2-(10-Acryloyloxy-decyloxy)-benzoic acid (M3). Yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.20-1.47 (m, 12H), 1.58-1.64 (m, 2H), 1.83-2.00 (m, 2H), 4.08 (t, *J* = 6.5 Hz, 2H), 4.21 (t, *J* = 6.8 Hz, 2H), 5.79 (d, *J* = 9.0 Hz, 1H), 6.03-6.13 (m, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H). Anal. Calcd for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 68.44; H, 7.85.

4-(10-Acryloyloxy-decyloxy)-benzoic acid methyl ester (M4). Yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.21-1.53 (m, 12H), 1.57-1.71 (m, 2H), 1.72-1.83 (m, 2H), 3.86 (s, 3H), 3.98 (t, *J* = 6.6 Hz, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 5.78 (d, *J* = 10.2 Hz, 1H), 6.05-6.14 (m, 1H), 6.37 (d, *J* = 17.4 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 7.95 (d, *J* = 9.0 Hz, 2H). Anal. Calcd for $C_{21}H_{30}O_5$: C, 69.59; H, 8.34. Found: C, 69.68; H, 8.26.

3-(10-Acryloyloxy-decyloxy)-benzoic acid methyl ester (M5). Yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.19-1.59 (m, 12H), 1.59-1.71 (m, 2H), 1.71-1.84 (m,

2H), 3.88 (s, 3H), 3.97 (t, *J* = 6.6 Hz, 2H), 4.12 (t, *J* = 6.6 Hz, 2H), 5.77 (d, *J* = 10.5 Hz, 1H), 6.04-6.16 (m, 1H), 6.36 (d, *J* = 17.1 Hz, 1H), 7.04-7.08 (m, 1H), 7.23-7.33 (m, 1H), 7.52-7.60 (m, 2H). Anal. Calcd for $C_{21}H_{30}O_5$: C, 69.59; H, 8.34. Found: C, 69.83; H, 8.38.

2-(10-Acryloyloxy-decyloxy)-benzoic acid methyl ester (M6). Yield: 71%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.19-1.46 (m, 12H), 1.57-1.63 (m, 2H), 1.73-1.88 (m, 2H), 3.83 (s, 3H), 3.98 (t, *J* = 6.6 Hz, 2H), 4.11 (t, *J* = 6.8 Hz, 2H), 5.80 (d, *J* = 9.1 Hz, 1H), 6.04-6.15 (m, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 6.83-6.94 (m, 2H), 7.35-7.44 (m, 1H), 7.75 (d, *J* = 8.4 Hz, 1H). Anal. Calcd for $C_{21}H_{30}O_5$: C, 69.59; H, 8.34. Found: C, 69.77; H, 8.20.

Chemical characteristics of copolymers P1-P6

P1. Yield: 67%. ^{1}H NMR (300 MHz, *d*-THF, δ): 0.92-1.86 (m, 35H), 2.33-3.57 (m, 6H), 3.84-4.03 (b, 8H), 6.81-7.62 (m, 12H), 7.92 (d, 2H), 8.49 (d, 2H). The copolymer composition of x / y = 1 / y = 1 / [(16.78 - 12) / 4] = 1 / 1.2, where 16.78 was obtained from the total integration areas of aromatic protons in copolymer **P1** from Fig. S1(a).

P2. Yield: 65%. ^{1}H NMR (300 MHz, *d*-THF, δ): 0.90-1.91 (m, 35H), 2.31-3.61 (m, 6H), 3.86-4.00 (b, 8H), 6.80-7.63 (m, 14H), 8.49 (s, 2H). The copolymer composition of x / y = 1 / y = 1 / [(17.40 - 12) / 4] = 1 / 1.35, where 17.40 was obtained from the

total integration areas of aromatic protons in copolymer **P2** from Fig. S1(b).

P3. Yield: 63%. ^{1}H NMR (300 MHz, *d*-THF, δ): 0.95-1.95 (m, 35H), 2.39-3.58 (m, 6H), 3.86-4.15 (b, 8H), 6.80-7.88 (m, 14H), 8.49 (s, 2H). The copolymer composition of x / y = 1 / y = 1 / [(16.46 - 12) / 4] = 1 / 1.12, where 16.46 was obtained from the total integration areas of aromatic protons in copolymer **P3** from Fig. S1(c).

P4. Yield: 53%. ^{1}H NMR (300 MHz, *d*-dioxane, δ): 0.90-1.84 (m, 35H), 2.30-3.49 (m, 6H), 3.81-4.07 (m, 11H), 6.79-7.83 (m, 14H), 8.52 (s, 2H). The copolymer composition of x / y = 1 / y = 1 / [(17.94 - 12) / 4] = 1 / 1.49, where 17.94 was obtained from the total integration areas of aromatic protons in copolymer **P4** from Fig. S1(d).

P5. Yield: 50%. ^{1}H NMR (300 MHz, *d*-dioxane, δ): 0.86-1.81 (m, 35H), 2.29-3.45 (m, 6H), 3.75-4.05 (m, 11H), 6.77-7.60 (m, 14H), 8.50 (s, 2H). The copolymer composition of x / y = 1 / y = 1 / [(18.34 - 12) / 4] = 1 / 1.59, where 18.34 was obtained from the total integration areas of aromatic protons in copolymer **P5** from Fig. S1(e).

P6. Yield: 45%. ^{1}H NMR (300 MHz, *d*-dioxane, δ): 0.85-1.81 (m, 35H), 2.30-3.49 (m, 6H), 3.75 (s, 3H), 3.81-4.05 (b, 8H), 6.79-7.68 (m, 14H), 8.50 (s, 2H). The copolymer composition of x / y = 1 / y = 1 / [(17.69 - 12) / 4] = 1 / 1.42, where 17.69 was obtained from the total integration areas of aromatic protons in copolymer **P6**

from Fig. S1(f).

Chemical characteristics of homopolymers PBT1 and P7-P9

PBT1. Yield: 49%. ^{1}H NMR (300 MHz, *d*-dioxane, δ): δ 0.89-1.75 (b, 18H), 1.93 (s, 3H), 2.33 (s, 3H), 2.46 (s, 3H), 3.84-4.03 (b, 4H), 6.78-7.61 (m, 10H), 8.51 (s, 2H).

P7 (PBAp). Yield: 85%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 1.12-1.75 (m, 16H), 3.84-4.04 (b, 4H), 6.93 (s, 2H), 7.83 (s, 2H).

P8 (PBAm). Yield: 80%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 1.17-1.75 (m, 16H), 3.80-4.01 (b, 4H), 6.95-7.18 (b, 1H), 7.21-7.42 (m, 2H), 7.47 (s, 1H).

P9 (PBAo). Yield: 53%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.27-2.25 (m, 16H), 3.85-4.05 (b, 4H), 6.85-7.08 (b, 2H), 7.32-7.45 (b, 1H), 7.58 (d, 1H).

Synthesis of surface-functionalized gold nanoparticles AuSC10 and AuSCOOH

The surface-functionalized gold nanoparticles (**AuSC10** bearing acid-free surfactants) used in this study were prepared through standard Brust-Schiffrin methodology.[1] Hydrogen tetrachloroaurate aqueous solution (30 mL, 30 mmol) was mixed with tetraoctylammonium bromide (TOAB) in toluene solution (80 mL, 50 mmol). The two-phase mixture was vigorously stirred until all tetrachloroaurate was transferred into the organic layer, and then dodecanethiol (20 μL) was added to the organic phase. A freshly prepared aqueous solution of sodium borohydride (25 ml, 0.4 mol) was

slowly added with vigorous stirring. After further stirring for 3 h, the organic phase was separated, and the standard Brust reaction mixture was evaporated without removing TOAB and dried completely under reduced pressure. The black solid obtained was heat-treated at 165°C at a heating rate of 2°C/min and held at this temperature for 30 min.[2] The thermally 'ripened' product was dissolved in toluene and washed with methanol to remove excess thiol ligands and TOAB, then **AuSC10** nanoparticles with alkyl surfactants were obtained. In the subsequent Murray place exchange reaction,[3] **AuSC10** nanoparticles (60 mg) were combined with the proper amount of 11-mercaptoundecanoic acid in dichloromethane (3 mg of **AuSC10**/mL) and reacted for 48 h. After the exchange reaction was completed, the reaction mixture was concentrated using a rotary evaporator. After washing these products with a large amount of ethanol and acetone, no further purifications were conducted on these samples. Then, the acid-functionalized gold nanoparticles (**AuSCOOH**) with a diameter ca. 5 ~ 6 nm were obtained, and the monolayer compositions of **AuSCOOH** nanoparticles with both acid and alkyl surfactants were characterized by ^{1}H NMR featured 79% decanethiol and 21% carboxylic acid thiol functionalities.[4] In our studies of nanocomposites, both THF-soluble gold nanoparticles, i.e., alkyl-functionalized gold nanoparticles (**AuSC10** bearing acid-free surfactants) and acid-functionalized gold nanoparticles (**AuSCOOH** bearing acid surfactants), were

used.

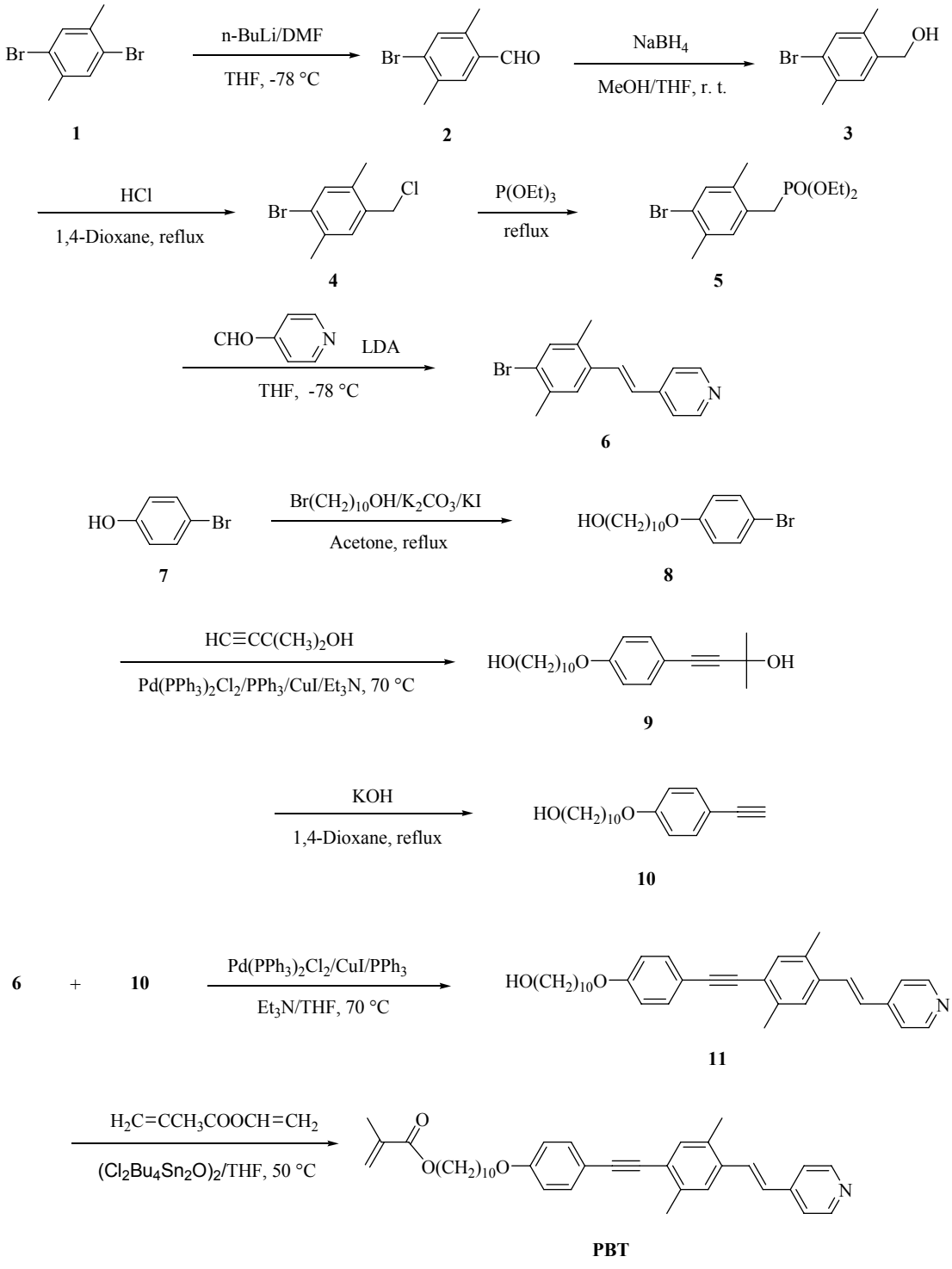
References

1. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.

2. T. Teranishi, S. Hasegawa, T. Shimizu and M. Miyake, *Adv. Mater.*, 2001, **13**, 1699.

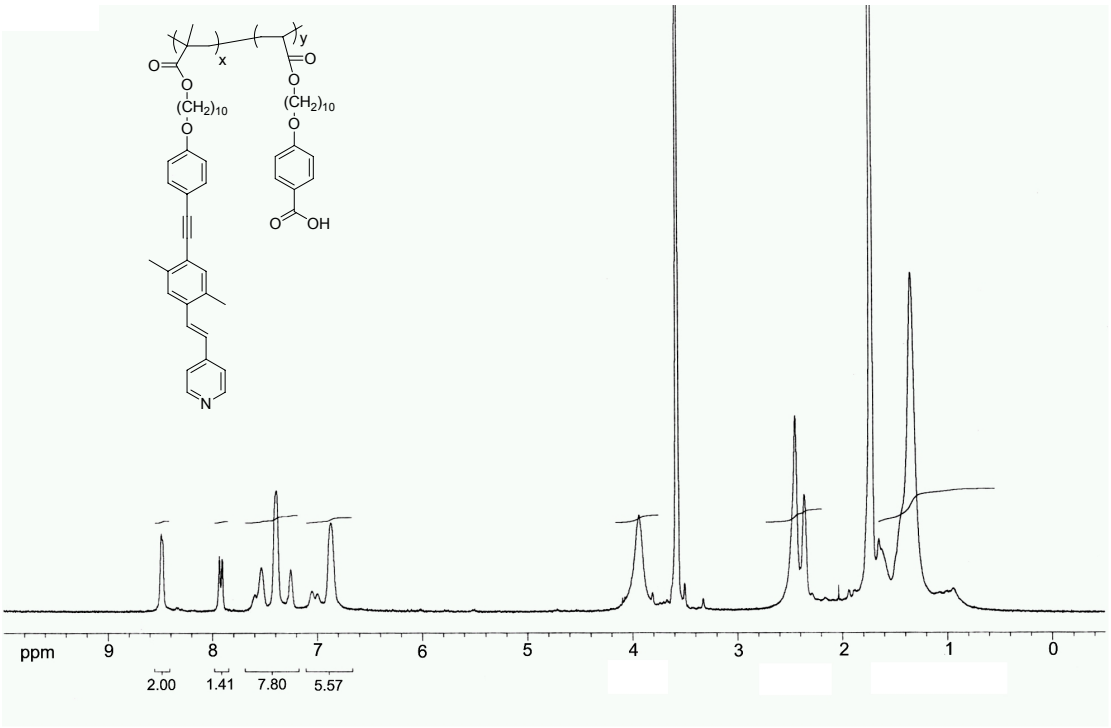
3. R. S. Ingram, M. J. Hostetler and R. W. Murray, *J. Am. Chem. Soc.*, 1997, **119**, 9175.

4. A. W. Shaffer, J. G. Worden and Q. Huo, *Langmuir*, 2004, **20**, 8343.

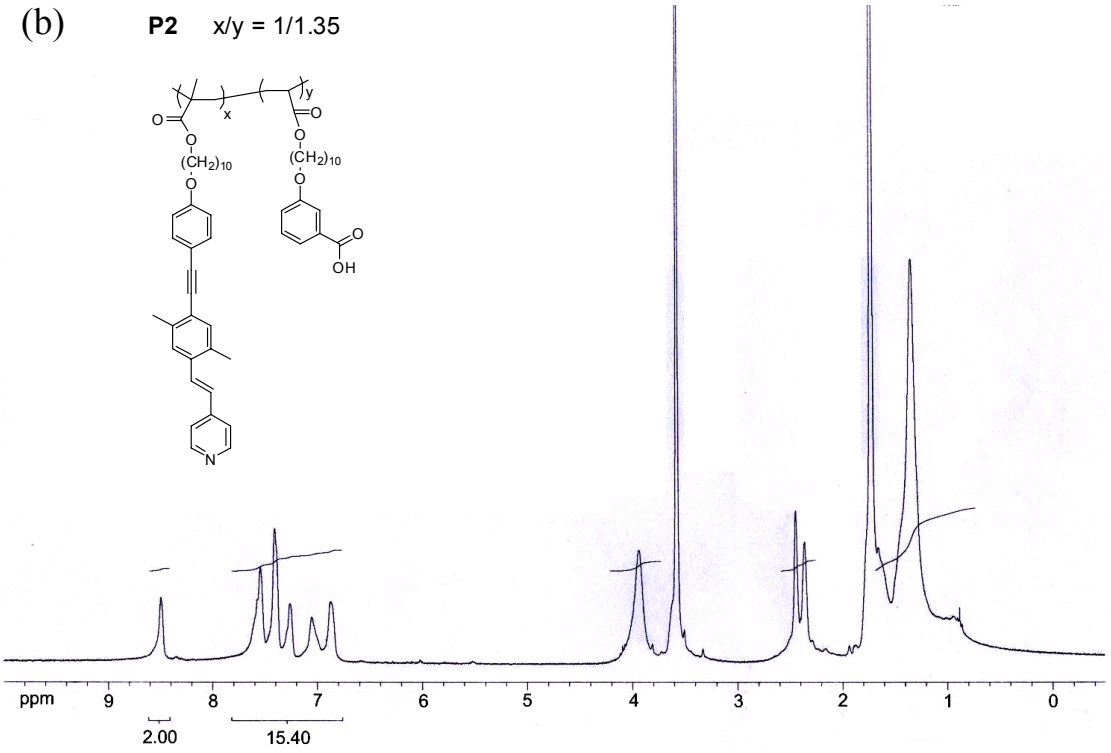


Scheme S1 Synthetic routes for monomer **PBT**

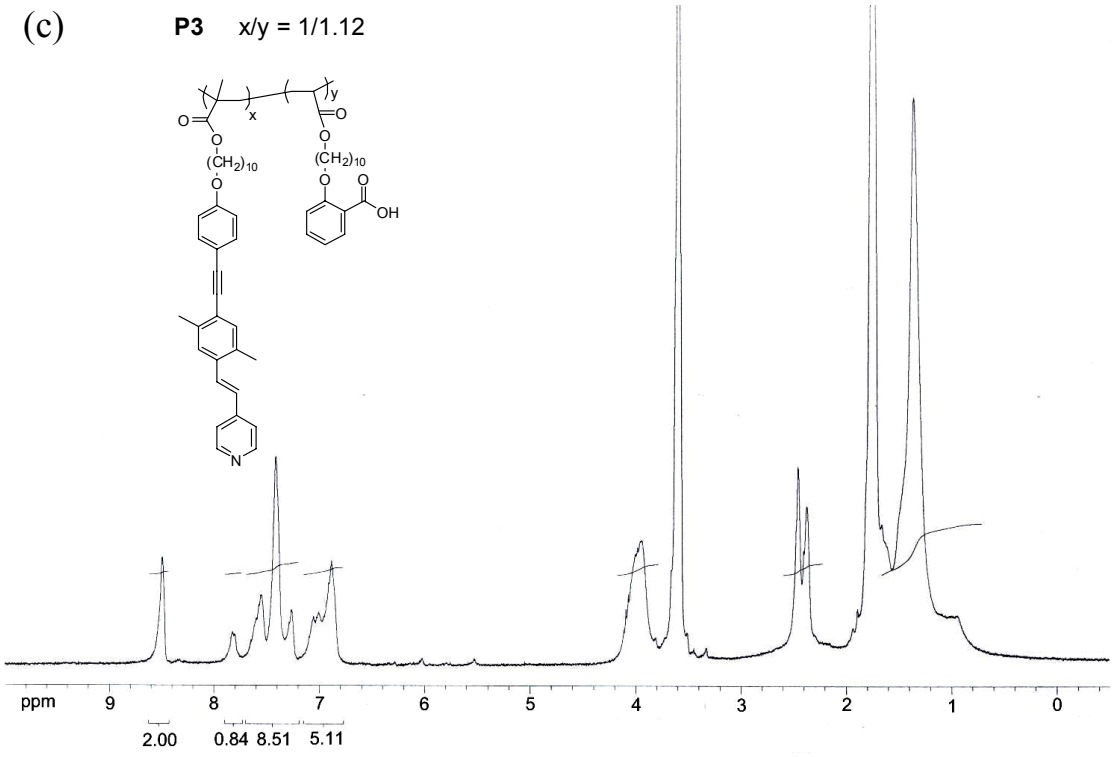
(a) **P1** x/y = 1/1.20



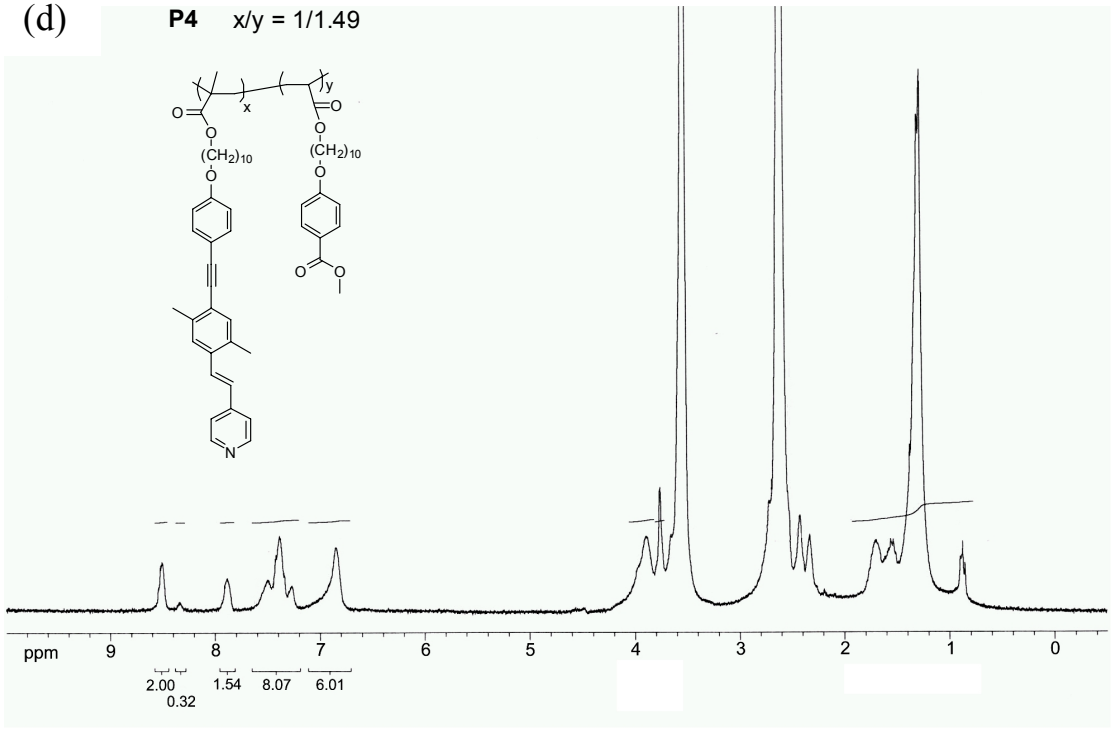
(b) **P2** x/y = 1/1.35

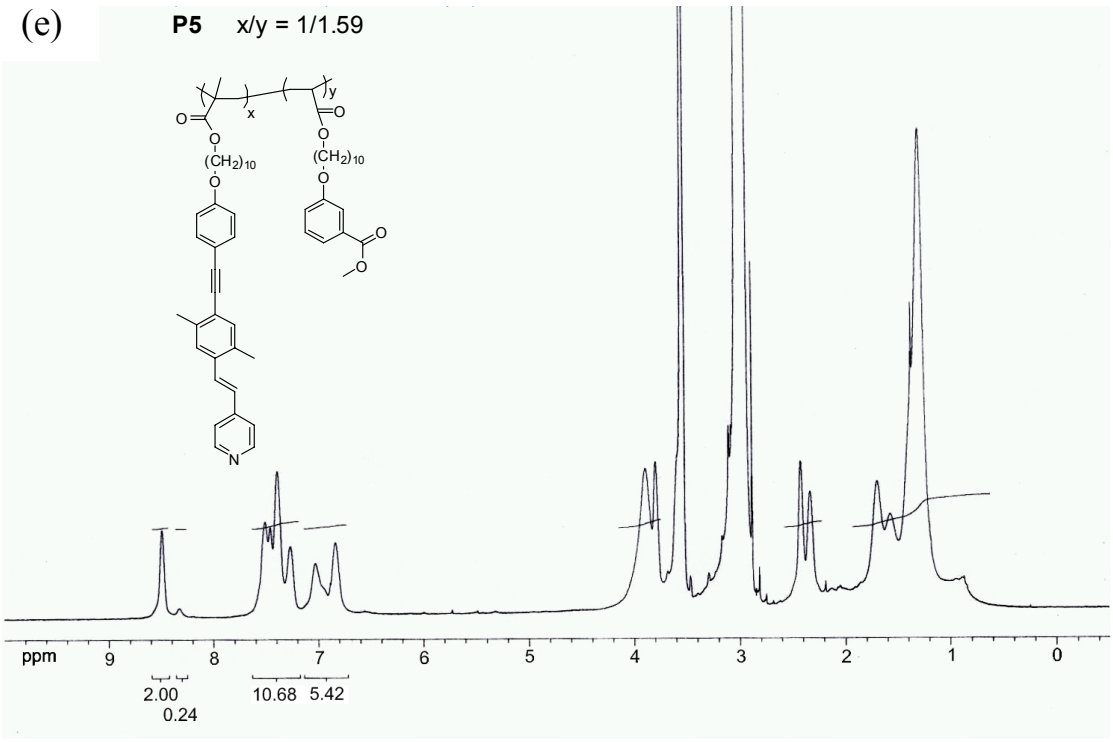


(c) **P3** x/y = 1/1.12



(d) **P4** x/y = 1/1.49





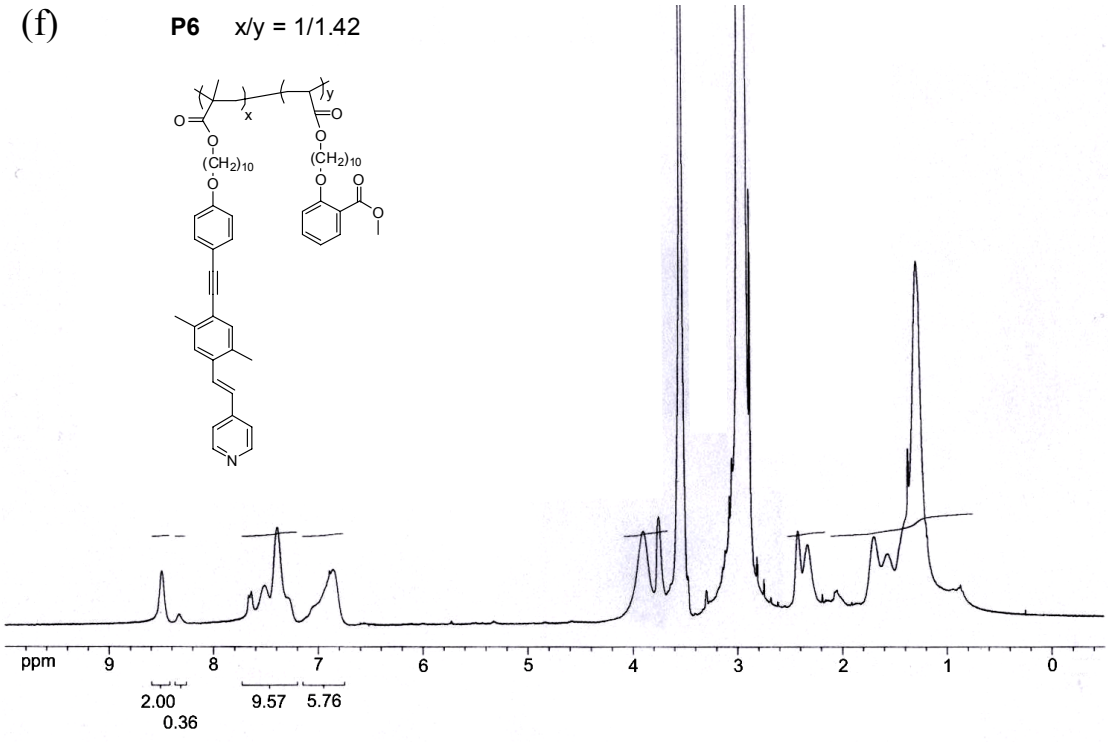


Fig. S1 ^{1}H-NMR spectra of copolymers (a) **P1** (b) **P2** (c) **P3** in *d*-THF and (d) **P4** (e) **P5** (f) **P6** in *d*-dioxane.

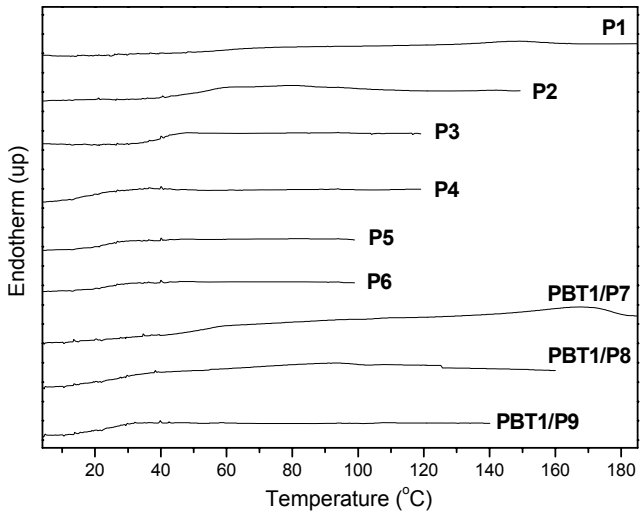
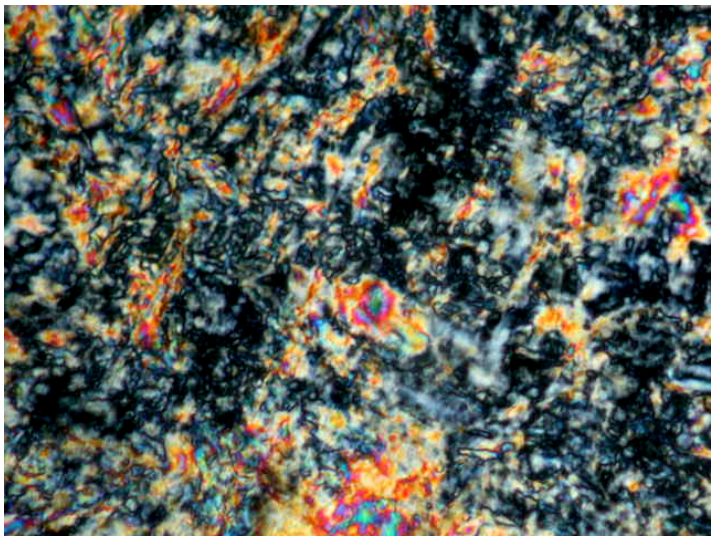
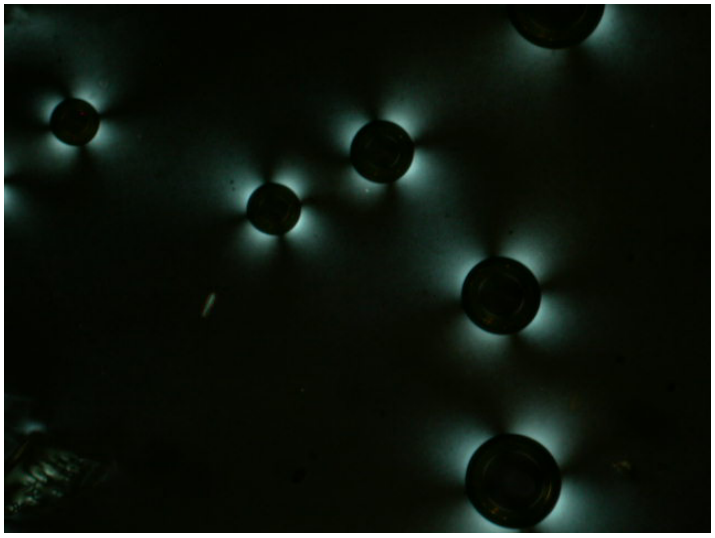


Fig. S2 DSC heating curves (the second heating) of copolymers **P1-P6** and H-bonded homopolymer complexes **PBT1/P7-P9**.

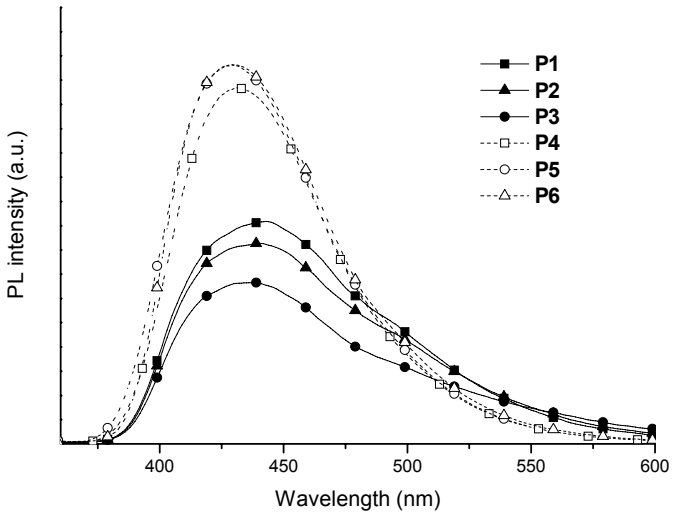


(a)

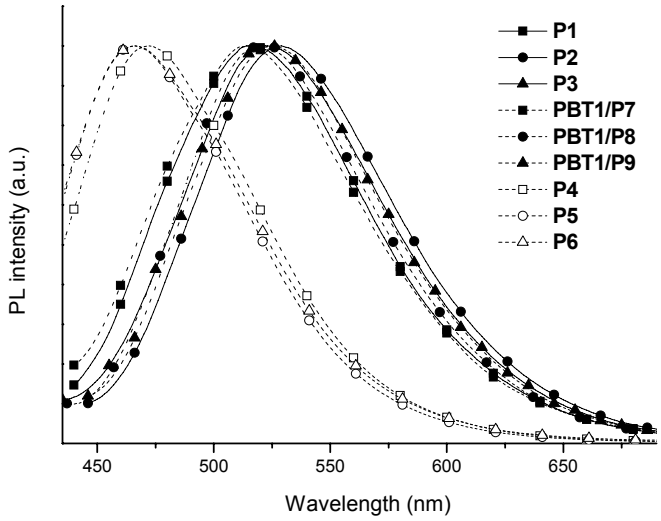


(b)

Fig. S3 Optical texture of (a) the Sc phase of copolymer **P1** observed by POM at 130°C (cooling) and (b) the nematic phase of copolymer **P2** observed by POM at 70°C (cooling).

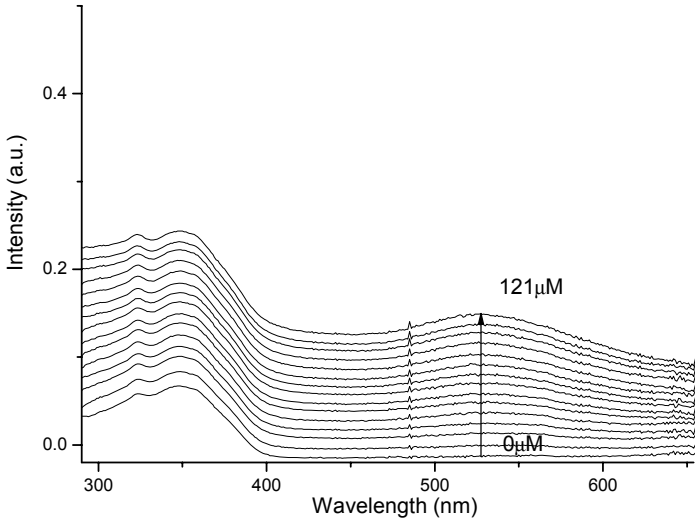


(a)

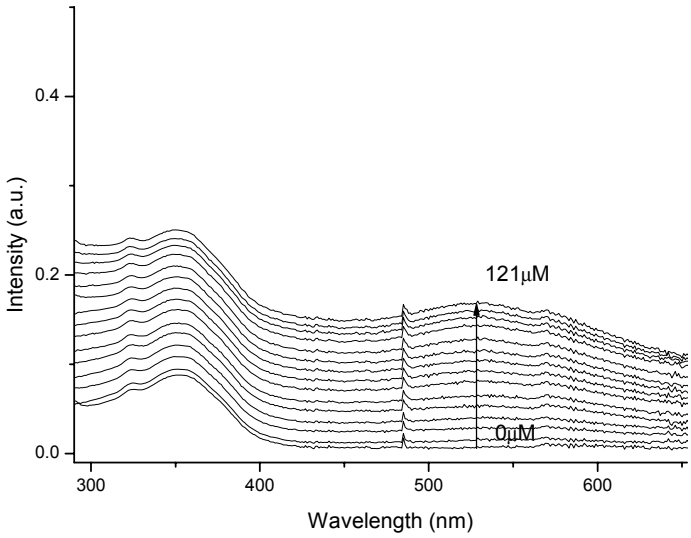


(b)

Fig. S4 (a) PL spectra of copolymers **P1**-**P6** in THF solutions (b) normalized PL spectra of copolymers **P1**-**P6** and H-bonded homopolymer complexes **PBT1/P7**, **PBT1/P8**, and **PBT1/P9** in solid films.



(a)



(b)

Fig. S5 UV-visible spectra of copolymers **P1** and **P4** titrated by surface-functionalized nanoparticles (**AuSCOOH**) in THF solutions: (a) **P1** and (b) **P4** by varying the concentration of acid-donor-modified gold nanoparticles (**AuSCOOH**).

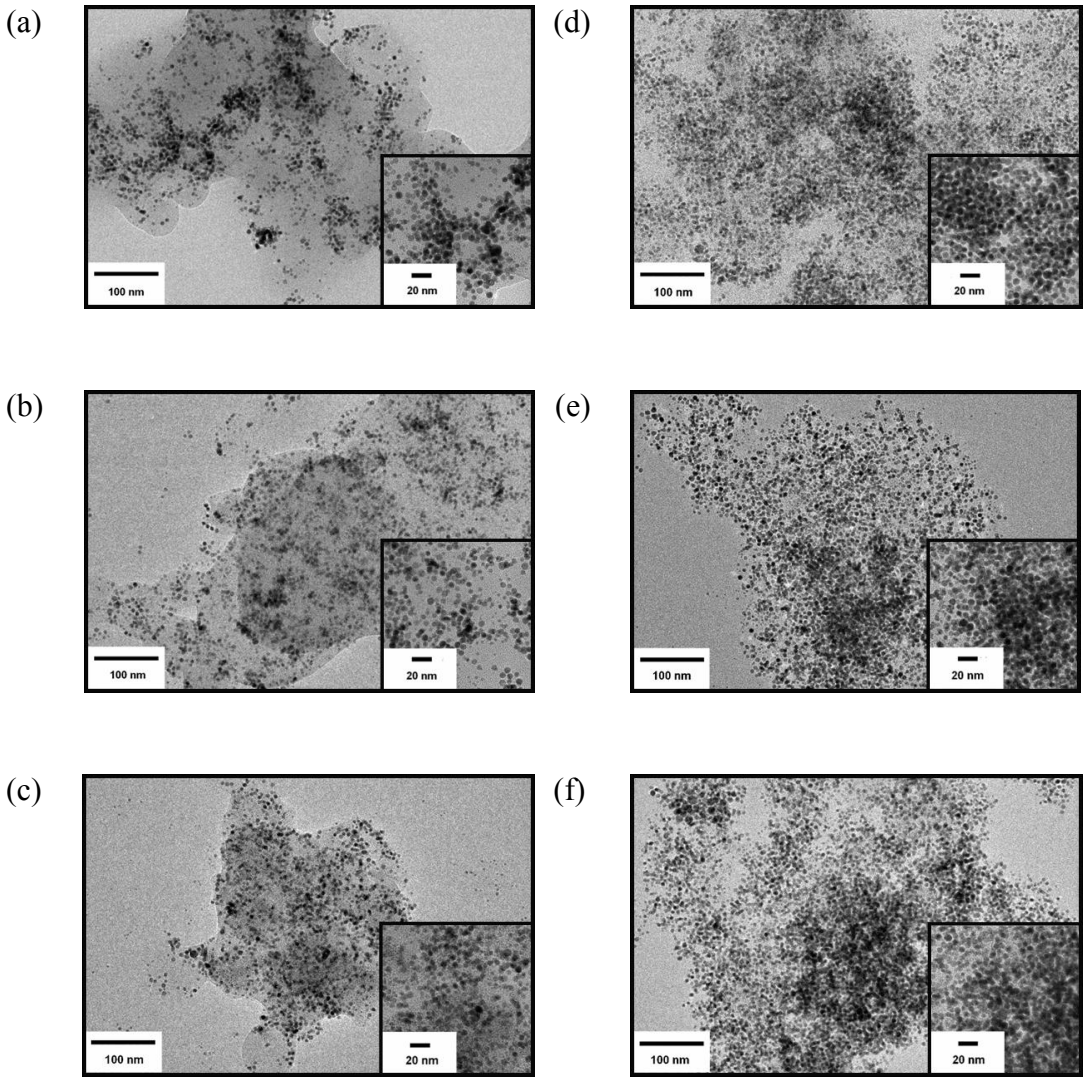


Fig. S6 TEM images of nanocomposites containing various copolymers (self-H-bonded copolymers **P1-P3** and non-self-H-bonded copolymers **P4-P6**) and acid-modified **AuSCOOH** nanoparticles: (a) **P1-AuSCOOH**, (b) **P2-AuSCOOH**, (c) **P3-AuSCOOH**, (d) **P4-AuSCOOH**, (e) **P5-AuSCOOH**, and (f) **P6-AuSCOOH**.

Table S1 Characterization of copolymers P1-P6 and H-donor homopolymers P7-P9

polymer	molar ratio of **PBT** in feed[a]	molar ratio of **PBT** in output copolymer[b]	M_n[c]	M_w[c]	PDI[c]	T_d[d](°C)
PBT1	1	1	8800	20300	2.3	389
P1	0.5	0.45 (1/1.20)	5300	8100	1.5	389
P2	0.5	0.43 (1/1.35)	6200	10800	1.7	374
P3	0.5	0.47 (1/1.12)	6800	9600	1.4	284
P4	0.5	0.40 (1/1.49)	7100	13000	1.8	344
P5	0.5	0.39 (1/1.59)	5600	14900	2.6	345
P6	0.5	0.41 (1/1.42)	5800	12600	2.1	315
P7	-	-	6000	11700	1.9	357
P8	-	-	7100	12200	1.7	346
P9	-	-	6300	10300	1.6	294

[a] Molar ratio of monomer **PBT** in the feed before copolymerization.

[b] Molar ratio of monomer **PBT** in the output copolymers determined by NMR.

[c] Molecular weights were determined by GPC in DMF, based on polystyrene standards.

[d] Decomposition temperatures (°C) at 5% weight loss were measured by TGA at a heating rate of 20°C/min under nitrogen.