Supplementary Material (ESI) for Chemical Communications

Supplementary Inforrmation

Color and fluorescence expression at the interface of two different dynamic polymers

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1. General aspects

All reagents and solvents were purchased at the highest commercial quality and were used without further purification unless otherwise noted. ^{1}H NMR spectra were recorded on Bruker Avance 400 spectrometers. Coupling constants are given in Hz. The spectra were internally referenced to the residual proton solvent signal. Microanalyses were performed by the Service de Microanalyse, Institut de Chimie, Université Louis Pasteur. FAB mass spectrometric measurements were performed by the Service de Spectrométrie de Masse, Institut de Chimie, Université Louis Pasteur. Absorption spectra were recorded on a Varian Cary-3 UV-visible spectrometer. Fluorescence measurements were performed on a HORIBA JOBIN YVON Fluorolog-3 Spectrofluorometer equipped with a sample holder for solid state.

2. Synthesis of monomers

Compound A

N,N-dibenzylhydrazine was purchased from Tokyo Chemicals Industry. The compound (1.5 g) was recrystallized from hot n-heptane (20 mL) to give compound **A** as a colorless crystal (0.31 g).

Compound B

2,5-thiophenedicarboxyaldehyde was purchased from Aldrich. The compound (2.0 g) was recrystallized from hot water (20 mL), followed by active carbon treatment to give compound **B** as a white powder (1.55 g).

Compound 1

The purified compound **A** (N,N-dibenzylhydrazine; 129 mg, 0.61 mmol) and the purified compound **B** (2,5-thiophenedicarboxyaldehyde; 42 mg, 0.3 mmol) was dissolved in $CHCl_3$ (0.6 mL) and the stirred mixture was kept at room temperature for 3 h under argon atmosphere, followed by evaporation of $CHCl_3$ at room temperature with slight argon stream. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3$/n-heptane, 2:1) affording desired compound **1** (103 mg) in 64% yield as a pale yellow powder. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.37-7.25 (m, 22H), 6.71 (s, 2H), 4.50 (s, 8H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 529.2420; found 529.2374; elemental analysis calcd (%) for $C_{34}H_{32}N_4S$: C 77.24, H 6.10, N 10.60; found: C 77.02, H 6.11, N 10.42.

Compound C

An aqueous solution of N-benzyl-N-phenylhydrazine hydrochloride (2.35 g), purchased from Alfa Aezar, was neutralized with 1N-NaOH aqueous solution, followed by extraction with $CHCl_3$. The solution was dried over Na_2SO_4 and the solvent were evaporated to dryness to give a crude compound **C** (1.75 g). The crude was purified by column chromatography on silica gel (eluent: $CHCl_3/CH_3CN$, 50:1) affording purified compound **C** (0.22 g) as a white powder.

Compound 2

The purified compound **C** (N-benzyl-N-phenylhydrazine; 202 mg, 1.02 mmol) and the purified compound **B** (2,5-thiophenedicarboxyaldehyde; 70 mg, 0.50 mmol) was dissolved in $CHCl_3$ (10 mL) and the stirred mixture was kept at room temperature for 3 h under argon atmosphere, followed by evaporation of $CHCl_3$ at room temperature with slight argon stream. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3/CH_3CN$, 50:1) affording desired compound **2** (282 mg) in 56% yield as dark tango oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.78 (s, 2H), 7.42-7.32 (m, 12H), 7.27 (t, J = 7.33 Hz, 2H), 7.19 (d, J = 7.28 Hz, 4H), 7.00 (s, 2H), 6.97-6.90 (m, 2H), 5.31 (s, 4H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 501.2107; found 501.2070; elemental analysis calcd (%) for $C_{32}H_{28}N_4S$: C 76.77, H 5.64, N 11.19; found: C 76.70, H 5.41, N 11.00.

Compound D

Phenylacetic acid hydrazide (2.32 g, 0.015 mol) and propionaldehyde (1.56 mg, 0.027 mol) was dissolved in the mixture of CH_2Cl_2 (20 mL) and $CHCl_3$ (10 mL) with Na_2SO_4, and the stirred mixture was kept at room temperature for 1 day under argon atmosphere, followed by filtration and evaporation of $CHCl_3$ at room temperature with slight argon stream, affording crude compound **D** (2.93 g) as white solid. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 11.14, 10.92 (s, 1H), 7.52-7.15 (m, 6H), 3.83 (s, 1H), 3.44 (s, 1H), 2.27-2.19 (m, 2H), 1.32-0.67 (m, 3H). Something aggregate of the compound B was observed in NMR spectrum.

Compound E

The crude compound **B** (1.90 g) and benzyl bromide (0.86 g, 0.005 mol) were added to a suspension of K_2CO_3 (3.20 g, 0.023 mol) in DMF (6 mL) and the stirred mixture was heated to 60 °C for 4 h under argon atmosphere, followed by filtration and evaporation of DMF. The crude product was roughly purified by column chromatography on silica gel (eluent: $CH_2Cl_2/C_2H_5OCOCH_3$, 30:1) affording crude compound **E** (0.91 g). ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.40-7.19 (m, 8H), 7.16 (t, J = 4.54 Hz, 1H), 7.10 (d, J = 8.22 Hz, 2H), 5.09 (s, 1H), 4.13 (s, 1H), 2.22 (dq, J = 7.40, 4.51 Hz, 2H), 0.98 (t, J = 7.42 Hz, 2H).

Compound F

Crude compound **E** (0.42 g) and O-methylhydroxylamine hydrochloride (0.50g, 6 mmol) were dissolved in DMF (8 mL), then 1N-HCl aqueous solution (2.3 g) was added. The stirred mixture was kept at room temperature for 2 h under argon atmosphere. The mixture was taken up in 0.5N-NaOH aqueous solution (25 mL) / $CHCl_3$ (80 mL). The organic layer was washed with H_2O (500 mL) 2 times, dried over Na_2SO_4 and the solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: $CHCl_3/CH_3CN$, 10:1) affording purified compound **F** (0.24 g) as colorless crystal. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.40-7.14 (m, 10H), 4.70 (s, 2H), 4.49 (br, 2H), 3.93 (s, 2H).

Compound 3

The purified compound **F** (147 mg, 0.61 mmol) and the purified compound **B** (2,5-thiophenedicarboxyaldehyde; 42 mg, 0.30 mmol) was dissolved in the mixture of $CHCl_3$ (0.4 mL) and MeOH (0.2 mL) with acid type ion-exchange resin (Amberlyst^{TM} 15, 1.5 mg), then the stirred mixture was kept at 60 °C for 5 h under argon atmosphere, followed by evaporation of the solvents. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3$/CH_3CN, 25:1) affording almost purified compound **3** (160 mg). Furthermore, the compound (160 mg) was recrystallized from the mixture of $CHCl_3$ (1.6 g) and MeOH (1.9 g) to give yellow crystal (90 mg) in 51 % yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 8.02 (s, 2H), 7.39 (d, *J* = 7.07 Hz, 4H), 7.33- 7.20 (m, 14H), 7.15 (d, *J* = 7.07 Hz, 4H), 5.23 (s, 4H), 4.22 (s, 4H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 585.2319; found 585.2300; elemental analysis calcd (%) for $C_{36}H_{28}N_4O_2S$: C 73.95, H 5.52, N 9.58; found: C 74.11, H 5.51, N 9.65.

Compound 4

The purified compound **C** (N-benzyl-N-phenylhydrazine; 198 mg, 1.0 mmol) and 2-thiophenecarboxyaldehyde (144 mg, 1.28 mmol) was dissolved in $CHCl_3$ (1 mL) and the stirred mixture was kept at room temperature for 3 h under argon atmosphere, followed by evaporation of $CHCl_3$ at room temperature with slight argon stream. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3$) affording desired compound **4** (250 mg) in 85% yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.84 (s, 1H), 7.44 (d, *J* = 5.07 Hz, 1H), 7.41-7.10 (m, 10H), 7.02 (dd, *J* = 5.05, *J'* = 3.56 Hz, 1H), 6.95-6.87 (m, 1H), 5.29 (m, 2H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 293.1107; found 293.1003; elemental analysis calcd (%) for $C_{18}H_{16}N_2S$: C 73.94, H 5.52, N 9.58; found: C 73.94, H 5.50, N 9.63.

Compound 5

The purified compound **C** (N-benzyl-N-phenylhydrazine; 119 mg, 0.6 mmol) and butyraldehyde (64 mg, 0.89 mmol) was dissolved in $CHCl_3$ (0.6 mL) and the stirred mixture was kept at room temperature for 3 h under argon atmosphere, followed by evaporation of $CHCl_3$ at room temperature with slight argon stream. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3$) affording desired compound **5** (129 mg) in 51% yield as colorless oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.33 (t, *J* = 7.46 Hz, 2H), 7.26-7.23 (m, 5H), 7.13 (d, *J* = 7.31 Hz, 2H), 6.97-6.61 (m, 2H), 5.10 (s, 2H), 2.22 (dt, *J* = 7.22, *J'* = 5.29 Hz, 2H), 1.45 (sext., *J* = 7.34 Hz, 2H), 0.84 (t, *J* = 7.37 Hz, 3H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 253.1699; found 253.1706; elemental analysis calcd (%) for $C_{17}H_{20}N_2$: C 80.91, H 7.99, N 11.10; found: C 80.96, H 7.99, N 11.14.

Compound G

3–Hydroxybenzaldehyde (12.23 g, 0.10 mol) and bis[2–(2–chloroethoxy)ethyl]ether (9.37 g, 0.040 mol) were added to a suspension of K_2CO_3 (17.45 g, 0.126 mol) and NaI (1.20 g, 0.008 mol) in DMF (60 mL) and the stirred mixture was heated to 90 °C for 21 h under argon atmosphere. The mixture was taken up in H_2O (200 mL) / $CHCl_3$ (300 mL). The organic layer was washed with H_2O (200 mL) 4 times, dried over Na_2SO_4 and the solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/$C_2H_5OCOCH_3$, 3:1) affording purified compound **G** (8.43 g, 0.021 mol) in 49% yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 9.98 (s, 2H), 7.55-7.50 (m, 4H), 7.42 (d, *J* = 2.94 Hz, 2H), 7.33-7.26 (m, 4H), 4.18 (t, *J* = 4.67 Hz, 4H), 3.77 (t, *J* = 4.51 Hz, 4H), 3.63-3.53 (m, 8H); elemental analysis calcd (%) for $C_{22}H_{26}O_7$: C 65.66, H 6.51; found: C 65.14, H 6.50.

Compound H

Powder of $NaBH_4$ (3.78g, 0.10 mol) was added gradually into a stirred mixture of compound **G** (8.00 g, 0.020 mol) in MeOH (300 mL) at 0 °C. The mixture was kept stirred for 20 min at 0 °C after the addition, followed by for 1 h at 25 °C. HCl aqueous solution (1N, 170 mL) was added carefully into the stirred mixture at 0 °C, then MeOH was removed from the mixture solution in vacuo. The residue was taken up in H_2O (300 mL) and extracted with $CHCl_3$ (200 mL) 3 times. The $CHCl_3$ solution combined was dried over Na_2SO_4 and the solvents were evaporated to afford crude compound **H** (7.05 g, 0.017 mol) in 87% yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.22 (t, *J* = 7.92 Hz, 2H), 6.91-6.86 (m, 4H), 6.80 (d, *J* = 6.95 Hz, 2H), 5.16 (t, *J* = 5.79 Hz, 2H), 4.47 (d, *J* = 5.80 Hz, 4H), 4.06 (t, *J* = 4.78 Hz, 4H), 3.74 (t, *J* = 4.51 Hz, 4H), 3.63-3.52 (m, 8H).

Compound I

PBr_3 (5.42g, 0.020 mol) in CH_2Cl_2 (35 mL) was added dropwise into a stirred mixture of compound **H** (7.05 g, 0.017 mol) in CH_2Cl_2 (250 mL) at 0 °C. The mixture was kept stirred for 1 h at 0 °C after the addition, followed by for 18 h at 25 °C. H_2O (100 mL) was added to the mixture at 0 °C, then NaOH aqueous solution (1N, 320 mL) was added carefully until pH of the mixture reached to around 10. The organic layer was separated after adding NaCl aqueous solution (saturated, 175 mL) and dried over Na_2SO_4. Solvents were evaporated to afford crude compound **I** (8.77 g, 0.016 mol) in 95% yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.27 (t, *J* = 8.00 Hz, 2H), 7.04-7.00 (m, 4H), 6.92-6.87 (m, 2H), 4.66 (s, 4H), 4.08 (t, *J* = 4.75 Hz, 4H), 3.74 (t, *J* = 4.53 Hz, 4H), 3.61-3.55 (m, 8H).

Compound J

Propionaldehyde (7.0 g, 0.121 mol) was added dropwise into a stirred mixture of phenylhydrazine (10.8 g, 0.10 mol) in CH_2Cl_2 (50 mL) at 25 °C, followed by adding Na_2SO_4 (20 g). After stirred for 1 h at 25 °C, Na_2SO_4 was isolated by filtration. The filtrate mixture was evaporated to afford crude compound **J** (14.2 g, 0.096 mol) in 96% yield as mixture of the *E* and *Z* isomers. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 9.59 and 9.02 (s, 1H), 7.18-6.32 (m, 6H), 2.26-2.18 (m, 2H), 1.08-1.02 ppm (m, 3H).

Compound K

The crude compound **I** (2.08 g, 0.004 mol) and the crude compound **J** (2.37 g, 0.016 mol) were added to a suspension of K_2CO_3 (1.26 g, 0.009 mol) in DMF (12 mL) and the stirred mixture was heated to 60 °C for 3 h under argon atmosphere. The mixture was taken up in H_2O (400 mL), then extracted with $CHCl_3$ (100 mL) twice. The combined $CHCl_3$ solution was dried over Na_2SO_4 and the solvent was evaporated to dryness. The residue (4.12g, a hard red oil) was roughly purified by column chromatography on silica gel (eluent: $CHCl_3$/AcOEt, 20:1) affording crude compound **K** (1.10 g, 1.7 mmol) in 42 % yield as a hard orange oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.22-7.18 (m, 10H), 6.86 (t, *J* = 4.76 Hz, 2H), 6.79-6.75 (m, 4H), 6.67–6.64 (m, 4H), 5.01 (s, 4H), 4.00-3.98 (m, 4H), 3.68–3.66 (m, 4H), 3.54–3.45 (m, 8H), 2.25 (dq, *J* = 7.44, *J'* = 4.76 Hz, 4H), 0.98–1.02 (t, *J* = 7.45 Hz, 6H).

Compound L

The crude compound **K** (750 mg, 1.13 mmol) and *O*-Methoxylamine hydrochloride (0.97 g, 11.6 mmol) were dissolved in the mixture of DMF (7 mL) and HCl aqueous solution (1N, 3.5 mL). The solution was stirred for 2 h at 25 °C, then taken up in $CHCl_3$ (400 mL). After adding NaOH aqueous solution (0.5N, 40 mL) to the bilayer solution, the organic layer was washed with H_2O (400 mL) 3 times followed by dryness with Na_2SO_4. Crude

product (590 mg) was obtained after evaporation. Column chromatographies were performed 3 times on silica gel (eluent: CH_2Cl_2/CH_3CN, 3:1) to afford pure compound **L** (260 mg, 0.44 mmol) in 39 % yield as a faintly yellow oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.22 (t, *J* = 7.95 Hz, 2H), 7.13 (dd, *J* = 8.70, 7.23 Hz, 4H), 6.96 (d, *J* = 7.94 Hz, 4H), 6.86-6.84 (m, 4H), 6.80 (d, *J* = 7.12 Hz, 2H), 6.62 (t, *J* = 7.20 Hz, 2H), 4.58 (s, 4H), 4.36 (br, 4H), 4.01 (dd, *J* = 4.4 Hz, *J'* = 4.9 Hz, 4H), 3.68 (dd, *J* = 4.4 Hz, *J'* = 4.9 Hz, 4H), 3.58-3.52 (m, 8H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 587.3228; found 587.3224; elemental analysis calcd (%) for $C_{34}H_{42}N_4O_5$: C 68.54, H 7.10, N 9.40; found: C 68.97, H 7.23, N 9.27.

Compound M

Methyl *p-tert*-butylphenylacetate (12.38 g, 0.06 mol) in MeOH (15 mL) was added dropwise into a stirred mixture of hydrazine monohydrate (15 g, 0.3 mol) in MeOH (40 mL) at room temperature. The mixture was stirred at 50 °C for 2 h followed by cooled to 0 °C to give precipitate. After adding H_2O (200 mL), the precipitate was isolated by filtration to give crude compound **M** (8.67 g). ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 9.19 (s, 1H), 7.31 (d, *J* = 8.25 Hz, 2H), 7.18 (d, *J* = 8.22 Hz, 2H), 4.20 (s, 2H), 3.30 (br, 2H), 1.27 (s, 9H).

Compound N

Propionaldehyde (3.48 g, 0.06 mol) was added dropwise into a stirred mixture of the crude compound **M** (8.24 g, 0.04 mol) in CH_2Cl_2 (50 mL) at 25 °C, followed by adding Na_2SO_4 (10 g). After stirred for 1 h at 25 °C, Na_2SO_4 was isolated by filtration. The filtrate mixture was evaporated to afford crude compound **N** (9.85 g). ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 11.14, 10.93 (s, 1H), 7.54-7.17 (m, 6H), 3.78 (s, 1H), 3.39 (s, 1H), 2.28-2.18 (m, 2H), 1.07-1.00 (m, 3H).

Compound O

The crude compound **I** (2.34 g, 0.0044 mol) and the crude compound **N** (4.95 g, 0.02 mol) were added to a suspension of K_2CO_3 (9.03 g, 0.065 mol) in DMF (12 mL) and the stirred mixture was heated to 60 °C for 4 h under argon atmosphere. The solid portion of the mixture was isolated by filtration and the solution was evaporated. The residue (8.34 g) was roughly purified twice by column chromatography on silica gel (eluent: CH_2Cl_2/CH_3CN, 5:1) affording compound **O** (1.10 g, 1.28 mmol) in 29 % yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.33 (d, *J* = 8.26 Hz, 4H), 7.24 (d, *J* = 8.25 Hz, 4H), 7.20-7.13 (m, 4H), 6.78 (d, *J* = 8.08 Hz, 2H), 6.67-6.65 (m, 4H), 5.03 (s, 4H), 4.09 (s, 4H), 3.98 (dd, *J* = 5.43, *J'* = 3.74 Hz, 4H), 3.71 (dd, *J* = 5.29, *J'* = 3.73 Hz, 4H), 3.59-3.53 (m, 8H) 2.21 (dq, *J* = 7.40, *J'* = 4.46 Hz, 4H), 1.26 (s, 18H), 0.99 (t, *J* = 7.40 Hz, 6H).

Compound P

Compound **O** (0.43 g, 0.5 mmol) and *O*-Methoxylamine hydrochloride (0.84 g, 10 mmol) were dissolved in DMF (4 mL). The solution was stirred for 4 h at 25 °C, then taken up in $CHCl_3$ (30 mL). After adding NaOH aqueous solution (0.5N, 30 mL) to the solution, the organic layer was evaporated. The residue (0.36 g) was purified three times by column chromatography on silica gel (eluent: CH_2Cl_2/CH_3CN/MeOH, 100:50:1) affording purified compound **P** (105 mg, 0.13 mmol) in 29 % yield as a colorless oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.31 (d, *J* = 8.21 Hz, 4H), 7.24-7.19 (m, 6H), 6.84 (d, *J* = 8.36 Hz, 2H), 6.81-6.79 (m, 4H), 4.65 (s, 4H), 4.50 (br, 4H), 4.08 (dd, *J* = 5.32, *J'* = 4.06 Hz, 4H), 3.88 (s, 4H), 3.76 (dd, *J* = 5.39, *J'* = 4.19 Hz, 4H), 3.64-3.56(m, 8H), 1.30 (s, 18H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 783.4691; found 783.4645; elemental analysis calcd (%) for $C_{46}H_{62}N_4O_7$: C 70.56, H 7.98, N 7.16; found: C 70.43, H 8.11, N 6.73.

3. General method for the synthesis of polymers

Equimolar amounts of the bis-hydrazine and the dialdehyde at concentrations around 0.04 M each were dissolved in the mixture of $CHCl_3$ and THF(8 : 2 in volume ratio; for the polymer **P1**) or $CHCl_3$ (for the polymer **P2**, **P3**), followed by addition of pentadecafluorooctanoic acid in 0.1 molar ratio with respect to the resulting total hydrazone bonds. The solution was heated to 60 °C for 12 h, then poured into a petri dish of 50 mm diameter made of fluoroplastic, followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared and then kept at 60 °C in vacuo for 12 h. About 200 mg of the total amounts of monomers were used to obtain the polymer film of around 0.04–0.06 mm thickness.

Polymer P1

^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.22-7.00 (br, 10H), 6.73 (br, 5H), 6.63 (br, 5H), 4.96 (br, 4H), 3.92 (br, 4H), 3.61 (br, 4H), 3.45 (br, 8H), 2.15 (br, 4H), 1.56(br, 2H)

Polymer P2

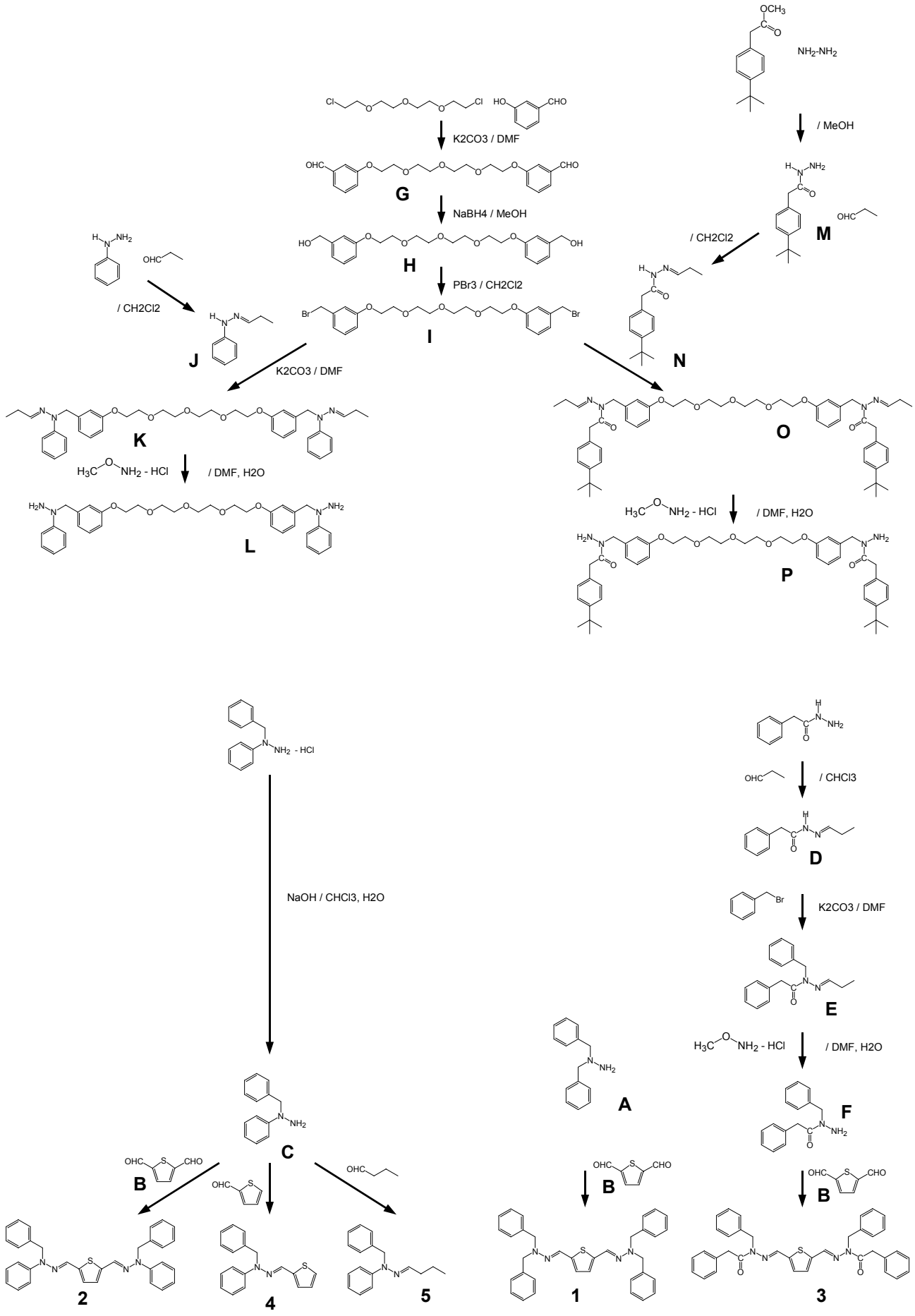
^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.96 (br, 2H), 7.33-7.12 (m, 12H), 6.75-6.64 (m, 6H), 5.12 (br, 4H), 4.14 (br, 4H), 3.92 (br, 4H), 3.63 (br, 4H), 3.48 (br, 8H), 1.14(br, 18H)

Polymer P3

^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.78-7.71 (br, 2H), 7.36-7.18 (m, 10H), 6.92-6.69 (m, 10H), 5.18 (br, 4H), 3.94 (br, 8H), 3.61 (br, 4H), 3.43(br, 8H)

4. Preparation of polymer thin layers

Polymer thin layers were prepared using a 2 wt% THF solution of the polymer by spin-coating onto 5 cm square quartz plates, which was rinsed with acetone prior to use. The spin-speed and the period were 500 rpm and 60 sec, respectively. These layers were subsequently dried *in vacuo* at 60 °C for 12 hr.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G
NaBH4 / MeOH
H
PBr3 / CH2Cl2
I
/ MeOH
M
/ CH2Cl2
N
/ CH2Cl2
J
K2CO3 / DMF
K
O
H3C-O-NH2 - HCl
/ DMF, H2O
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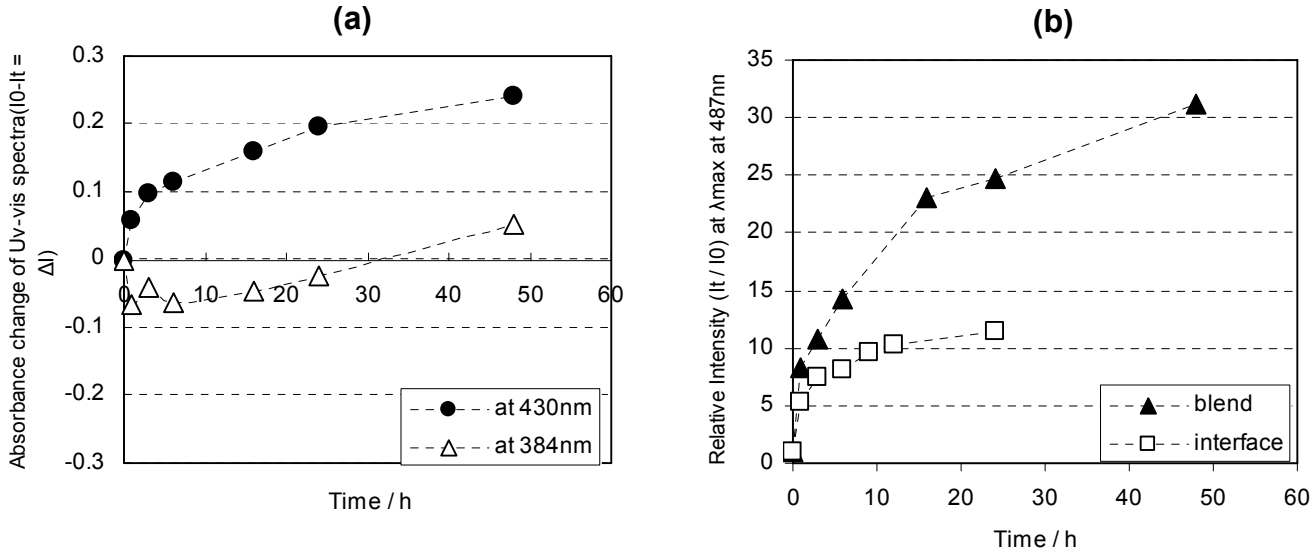

Figure S1. Exchange reaction as a function of heating time between **P1** and **P2** plotted for (a)the absorbance change($\Delta I = I_0 - I_t$) at the indicated wavelengths of UV-vis spectra in Fig.4, (b)the relative intensity at λ max 487 nm(I_t / I_t) of the fluorescence spectra in Fig.4 and Fig.7. Absorbance at 384 nm of the starting polymer **P2** does not decrease significantly during exchange due to overlap with the new absorption of the exchanged polymer **P3**. (molar extinction coefficient ε of **P2** = 31,000 at λ max 368 nm and **P** = 34,000 at λ max 420 nm)

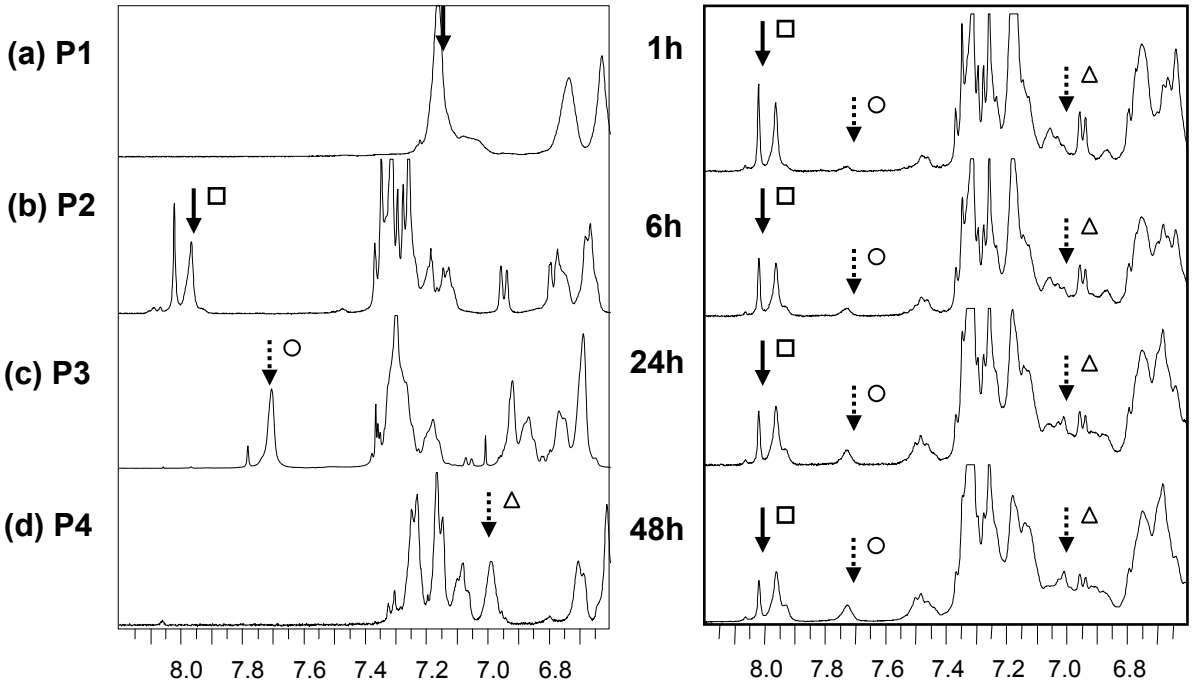

Figure S2. Left: ^{1}H NMR spectra of the dynamic polymers (a) **P1**, (b) **P2**, (c) **P3** and (d) **P4**. Right:^{1}H NMR spectra of the polymer blend between **P1** and **P2** as a function of heating time in a DMSO-d_6(ca. 10mM) showing the CH=N proton signals. The proton NMR spectra showed that the proportions of **P2** : **P3** was about 3 : 1 after 48 h heat treatment.