Electronic supplementary information

Details of polymer synthesis and NMR analysis

Materials

Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. All reactions were carried out using standard and Schlenk techniques under an argon atmosphere. The solvents were used as commercial p.a. and HPLC quality.

3-(6-Bromohexyl)thiophene

3-Bromothiophene (10.0 g, 61.3 mmol) was dissolved in dry *n*-hexane (85 mL) and cooled to -50 °C. Then, 1.6 M *n*-butyl-lithium (38.3 ml, 61.3 mmol) was added drop-wise. After stirring for 10 min dry THF (8 mL) was introduced, yielding a white precipitate. The mixture was stirred for 1 h and allowed to warm up to room temperature. Additional THF (3 mL) was added along with an excess of 1,6-dibromohexane (38 mL, 81.7 mmol). The yellow mixture was stirred for 2 h followed by extraction with diethyl ether (three times). The organic phase was isolated, washed with water, and dried over magnesium sulfate. Following solvent removal, the excess alkylbromide was removed under reduced pressure. Further purification by vacuum distillation afforded 3-(6-bromohexyl)thiophene as a colourless oil (10.26 g, 68%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm): 7.17 (dd, J = 5.1 Hz and 3.0 Hz, 1H, Ar-H), 6.87 (dd, J = 5.1 Hz and 1.2 Hz, 1H, Ar-H), 6.86 (dd, J = 3.0 Hz and 1.2 Hz, 1H, Ar-H), 3.35 (t, J = 6.6 Hz, 2H, Br-CH_2), 2.56 (t, J = 7.6 Hz, 2H, Ar-CH_2), 1.78 (quint, J = 7.1 Hz, 2H, Br-CH_2-CH_2), 1.56 (quint, J = 7.6 and 7.1 Hz, 2H, Ar-CH_2-CH_2), 1.38 (quint, J = 8.1 Hz, J = 7.1 Hz, 2H, Ar-$(CH_2)_2$-CH_2), 1.28 (quint, J = 7.1 and 8.1 Hz, 2H, Br-$(CH_2)_2$-CH_2). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ (ppm): 143.3, 128.6, 125.5, 120.2, 34.7, 33.0, 30.6, 30.4, 28.7, 28.3.

2-Bromo-3-(6-bromohexyl)thiophene

3-(6-Bromohexyl)thiophene (4.95 g, 20.0 mmol) was dissolved in DMF (50 mL) in the dark at -20 °C. A solution of NBS (3.62 g, 20.5 mmol) in DMF (50 mL) was added drop-wise and the resulting mixture stirred for 30 min at -20 °C and overnight at room temperature. Then, the reaction mixture was quenched by pouring into ice (50 g). The resulting solution was extracted with dichloromethane three times. The combined organic layers were dried over magnesium sulfate, followed by the removal of volatile solvents at reduced pressure. The residue was purified by silica gel column chromatography (*n*-heptane) to afford 2-bromo-3-(6-bromohexyl)thiophene as a colourless oil (25.58 g, 73%). TLC: $R_f = 0.50$ (silica gel, *n*-heptane). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm): 7.13 (d, $J = 5.6$ Hz, 1H, Ar-H), 6.73 (d, $J = 5.6$ Hz, 1H, Ar-H), 3.34 (t, $J = 7.1$ Hz, 2H, Br-CH_2), 2.45 (t, $J = 7.6$ Hz, 2H, Ar-CH_2), 1.78 (quint, $J = 7.1$ Hz, 2H, Br-CH_2-CH_2), 1.56 (quint, $J = 7.6$ and 7.1 Hz, 2H, Ar-CH_2-CH_2), 1.38 (quint, $J = 7.6$ and 7.1 Hz, 2H, Ar-$(CH_2)_2$-CH_2), 1.27 (quint, $J = 7.1$ and 7.6 Hz, 2H, Br-$(CH_2)_2$-CH_2). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ (ppm): 142.0, 128.6, 125.7, 109.1, 34.7, 33.0, 29.7, 29.5, 28.6, 28.2. Elemental analysis: $C_{10}H_{14}Br_2S$, calculated (%): C 36.83, S 9.83, H 4.33, measured (%): C 36.95, S 9.72, H 4.59.

Poly[3-(6-bromohexyl)-2,5-thiophene] (P3BrHT)

Fresh lithium diisopropylamide (LDA) was prepared from freshly distilled diisopropylamine (1.6 mL) and 1.6 M *n*-butyllithium (6.25 mL in *n*-hexane). The product was added to dry THF (50 ml) under an Ar-atmosphere at -78 °C *via* syringe. The resulting solution was allowed to warm up to room temperature. The solution was stirred for 5 min at room temperature and again cooled down to -78 °C, followed by addition of 2-bromo-3-(6-bromohexyl)thiophene (3.26 g, 10.0 mmol). After stirring for 2 h the reaction mixture was added to a cooled solution (-78 °C) of dry tin(II) chloride (1.40 g, 10.3 mmol) in dry THF (3 mL) *via* a syringe, followed by additional stirring for 1 h at -78 °C. After warming up the mixture to room temperature the catalyst Ni(dppp)Cl_2 (43 mg, 0.0065 mmol) was added in the dark and the resulting reaction solution stirred for 30 min. The reaction product was poured into cold methanol (500 mL) and the precipitate isolated by filtration. The crude polymer was redissolved in $CHCl_3$ and washed with water, brine, and saturated $NaHCO_3$. Then, the solution was concentrated and the polymer reprecipitated by pouring the viscous solution into cold methanol (500 mL). The polymer was purified *via* Soxhlet extraction with methanol, acetone, and *n*-hexane. The residue was redissolved in chloroform and the polymer isolated by removing the chloroform under reduced pressure. The resulting polymer was dried under vacuum to yield P3BrHT as a dark red solid (1.82 g, 56%). ^{1}H-NMR (400 MHz, CD_2Cl_2). δ (ppm): 6.94 (s, 1H, Ar-H), 3.37 (t, 2H, J = 6.6 Hz, -CH_2), 2.87-2.74 (t, 2H, Ar-CH_2), 1.91-1.73 (m., 2H, Alkyl-H), 1.72-1.55 (m, 2H, Alkyl-H), 1.54-1.11 (m, 4H, Alkyl-H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ (ppm): 140.0, 133.9, 130.8, 128.9, 34.7, 33.0, 30.5, 29.6, 28.9, 28.3. Elemental analysis: $(C_{10}H_{13}BrS)_n$, calculated (%): C 48.92, S 13.08, H 5.34, measured (%):C 48.68, S 12.97, H 5.38. GPC Anal. (THF, 254 nm): M_n=5000 g/mol, M_w=7000 g/mol, PDI=1.4. UV-Vis ($CHCl_3$): $\lambda_{max, abs}$=435 nm. PL ($CHCl_3$, $\lambda_{ex.}$=380 nm): $\lambda_{max, em}$= 570 nm.

P3ImiHT

A large excess of *N*-methylimidazole (500 mg, 6.1 mmol) was added to a solution of P3BrHT (150 mg, 0.61 mmol, M_n=5000 g/mol) in dry THF (5 mL) at -78 °C. After stirring for 1 day at 80 °C the formation of a precipitate was observed, which was subsequently redissolved by addition of methanol (10 mL). After filtration to remove some insoluble material the solvents were removed under reduced pressure. The residue was purified by dialysis against water using a dialysis membrane with a cut-off of 3500 g/mol. The polymer was isolated by removing water under reduced pressure, reprecipitated into toluene and dried under vacuum to yield 134 mg (80 %) of P3ImiHT as a dark red solid. ^{1}H-NMR (400 MHz, D_2O). δ (ppm): 7.50-7.30 (m, 4H, Ar-H), 4.38-4.00 (m, 2H, N-CH_2), 3.96-3.87 (m, 3H, N-CH_3), 1.86-1.39 (m, 10 H, alkyl-H). Elemental analysis: $(C_{14}H_{19}BrN_2S)_n$, calculated (%): C 51.06, S 9.74, H 6.43, N 8.51, measured (%): C 50.40, S 9.42, H

6.35, N 8.54. DSC: T_g = 64.5 °C. UV-vis (H_2O): $\lambda_{max,\ abs}$=437 nm. PL (H_2O, $\lambda_{ex.}$=390 nm) $\lambda_{max,\ em}$=592 nm.

PL and photoexcitation spectra

Fig. s1 shows the PL spectra of P3ImiHT(SDS)$_x$-D_2O with an excitation wavelength of 500 nm. Fig. s2 shows the excitation spectra of P3ImiHT(SDS)$_x$-D_2O with an emission wavelength of 680 nm. The experiments correspond to those represented by Figs. 9b and 10.

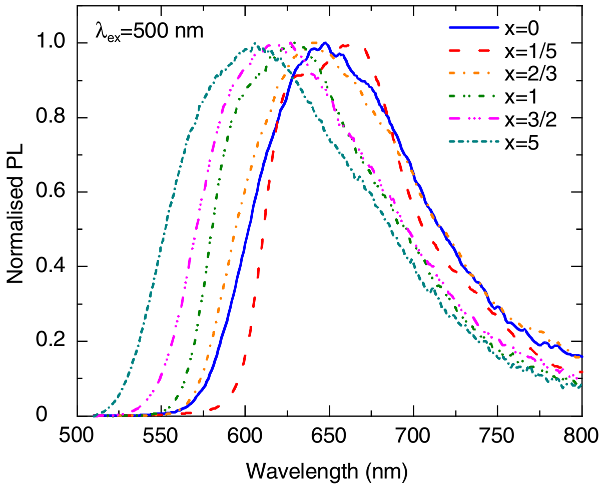

Fig. s1. PL spectra of P3ImiHT-D_2O (solid blue lines) and P3ImiHT(SDS)$_x$-D_2O x=1/5 (dashed red line), x=2/3 (dashed and dotted orange line), x=1 (dashed and double dotted green line), x=3/2 (dashed and triple dotted magenta line) for x=5 (double dashed and dotted cyan line). λ_{ex}=500 nm. The overall concentration of all samples was ~10 mg/mL.

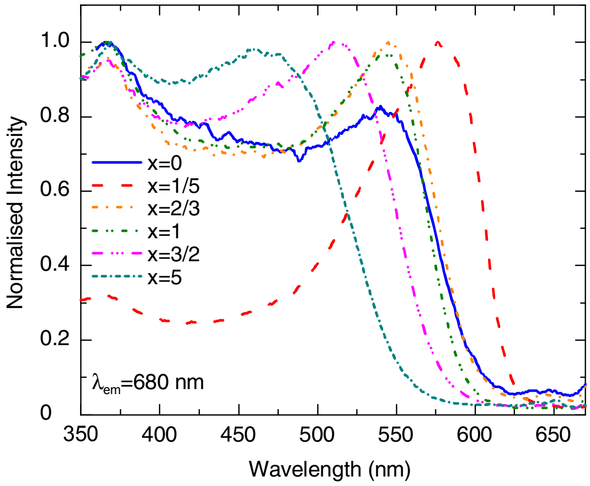

Fig. s2. Photoexcitation spectra of P3ImiHT-D_2O (solid blue line) and P3ImiHT$(SDS)_x$-D_2O x=1/5 (dashed red line), x=2/3 (dashed and dotted orange line), x=1 (dashed and double dotted green line), x=3/2 (dashed and triple dotted magenta line) for x=5 (double dashed and dotted cyan line). λ_{em}=680 nm. The overall concentration of all samples was ~10 mg/mL.

Photoabsorption, PL and excitation spectra upon 1000-fold dilution

Fig. s3 shows the UV/vis spectra of P3ImiHT(SDS)$_x$-D$_2$O. The experiments correspond to those represented by Fig. 9a but the samples were diluted by the factor of 1000 (from ~10 mg/mL to ~0.01 mg/mL).

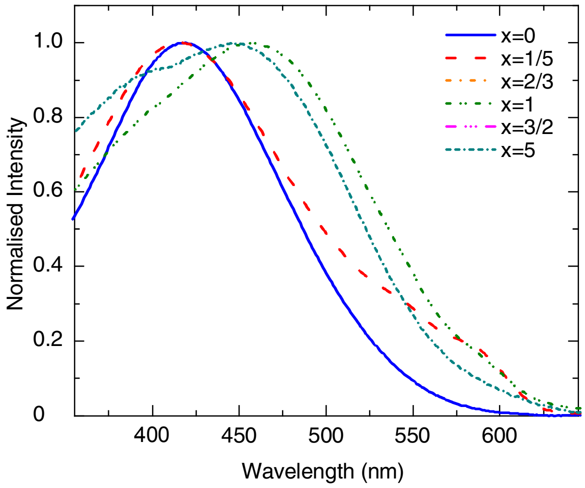

Fig. s3. UV/vis spectra of P3ImiHT-D$_2$O (solid blue line) and P3ImiHT(SDS)$_x$-D$_2$O x=1/5 (dashed red line), x=2/3 (dashed and dotted orange line), x=1 (dashed and double dotted green line), x=3/2 (dashed and triple dotted magenta line) for x=5 (double dashed and dotted cyan line). The overall concentration of all samples was ~0.01 mg/mL.

Fig. s4 shows the PL spectra of P3ImiHT(SDS)$_x$-D2O with the excitation wavelengths 450 nm (Fig. s4a) and 500 nm (Fig. s4b). The experiments correspond to those represented by Fig. 9b and Fig. s1 but the samples were diluted by the factor of 1000.

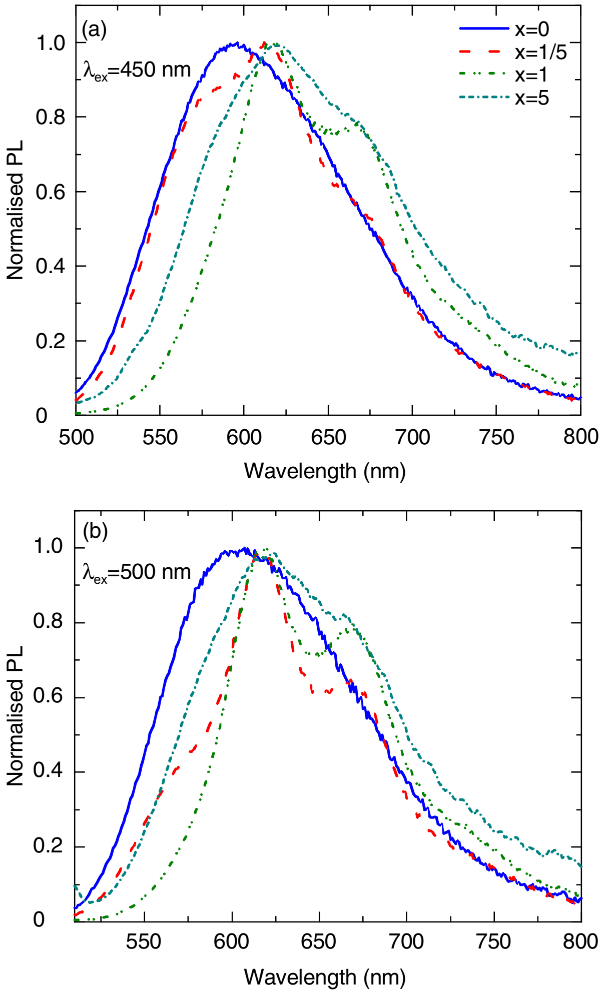

Fig. s4. PL spectra of P3ImiHT-D_2O (solid blue lines) and P3ImiHT(SDS)$_x$-D_2O x=1/5 (dashed red lines), x=2/3 (dashed and dotted orange lines), x=1 (dashed and double dotted green lines), x=3/2 (dashed and triple dotted magenta lines) for x=5 (double dashed and dotted cyan lines). The (a) λ_{ex} =450 nm. (b) λ_{ex} =500 nm. The overall concentration of all samples was ~0.01 mg/mL.

Fig. s5 shows the excitation spectra of P3ImiHT(SDS)$_x$-D2O with the emission wavelengths 620 nm (Fig. s5a) and 680 nm (Fig. s5b). The experiments correspond to those represented by Fig. 10 and Fig. s2 but the samples were diluted by the factor of 1000.

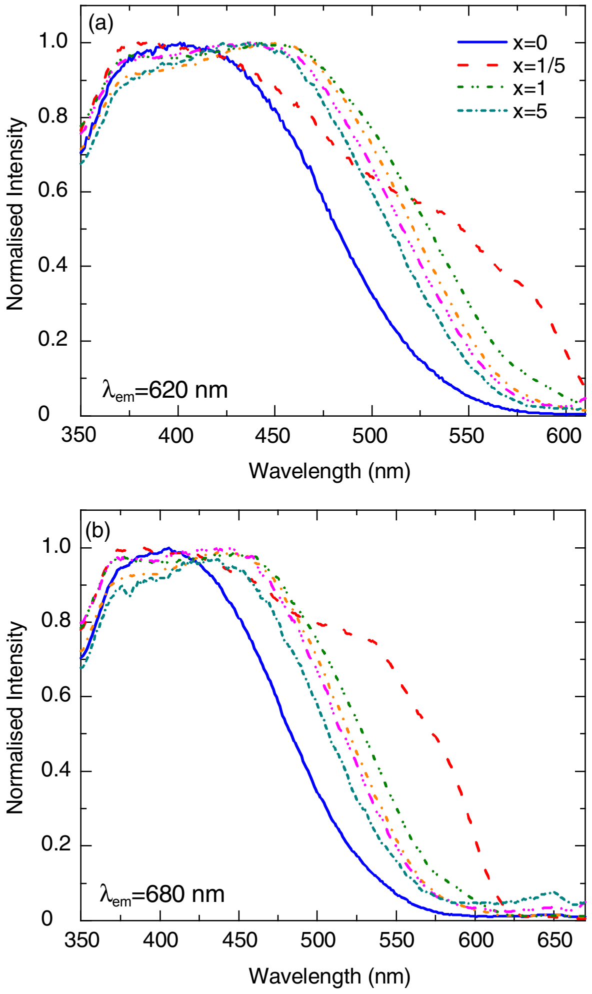

Fig. s5. Photoexcitation spectra of P3ImiHT-D$_2$O (solid blue lines) and P3ImiHT(SDS)$_x$-D$_2$O x=1/5 (dashed red lines), x=2/3 (dashed and dotted orange lines), x=1 (dashed and double dotted green lines), x=3/2 (dashed and triple dotted magenta lines) for x=5 (double dashed and dotted cyan lines). (a) λ_{em}=620 nm. (b) λ_{em}=680 nm. The overall concentration of all samples was ~0.01 mg/mL.