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Selective anion-induced helical aggregation of chiral amphiphilic polythiophenes with isothiuronium-appended pendants

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An optically active isothiuronium-attached polythiophene **1_{poly}** has been prepared for the first time by oxidative polymerisation of (*S*)-3-(3-(*N*-(2-(2-methoxyethoxy)ethyl)-*N*-(1-phenylethyl)-*S*-isothiuronio)propoxy)-4-methylthiophene **1** with FeCl₃. The analysis carried out using gel-permeation chromatography allows us to estimate the number average molecular weight (M_n) and the polydispersity index as 5.53×10^5 and 1.4, respectively. Although the polymer showed an absorption band at 420 nm with circular dichroism (CD) silence in H₂O–MeOH (1:1, v/v) at 25°C, the addition of anions as a chemical stimulus was found to cause not only a bathochromic shift but also a split-type-induced CD (ICD) in the π – π^* transition region. This phenomenon is anion selective; the most enhanced ICD spectra were obtained when hydrophobic anions such as PF₆[–] were added to the solution. As inferred from field emission-scanning electron microscopy observation, the anion-ICD spectra arose from chiral aggregation of the polymer, which was effected by solvophobic effect via the exchange with hydrophobic anions at isothiuronium pendants. Solvent polarity and temperature dependencies on the chirality induction were investigated, the obtained results suggested that the dynamic helical aggregation of the polythiophene backbone is based on planar interchain interactions.

Keywords: polythiophene; isothiuronium unit; chirality; anion

Introduction

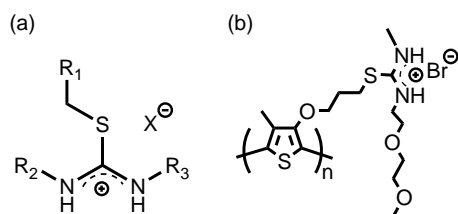
It is one of the fascinating research areas in material science to study how to arrange highly ordered structures of π -conjugated polymers because the conformation and organisation would affect their electrical and optical properties (1). This subject is a significant issue in their applications such as field effect transistors (2), electroluminescence devices (3), solar cells (4), chemosensors (5). Of particular interest in this field is the supramolecular chirality control of optically active conjugated polymers from the stand point of not only the more understanding of stereochemical aspects in biological systems but also potential applications to chiroptical materials (6). The use of amphiphilic π -conjugated polymers has a merit towards this end; the interplay of hydrophilic and hydrophobic interactions could lead to supramolecular organisation in aqueous solution. Nilsson et al. (7) reported chiral amino acid-appended polythiophenes wherein the zwitterionic side chain which acts as a hydrophilic site regulates the conformation of the polymer backbone in water, resulting in a helical *syn* conformation. In addition, amphiphilic polythiophenes bearing enantiometrically pure oligo(ethylene oxide) side chains have been prepared and characterised (8). Although achiral amphiphilic polythiophenes

capable of interacting chiral guest species could induce helical conformer through such an interaction (9), Shinkai et al. (10) have proposed a new way that a certain water-soluble polythiophene is insulated by a natural helix-forming polysaccharide, schizophyllan, to induce a predominantly one-handed helical structure. Despite such intriguing approaches, the investigation of chirality manipulation on amphiphilic conjugated polymers still remains of worth because obtained knowledge would contribute to the methodology for structure control of chiroptical polymers.

Currently, we have focused on synthesis and characteristics of polythiophenes with isothiuronium groups as a pendant unit. The high synthetic susceptibility of the cationic isothiuronium unit could allow us to introduce functional groups at *R*₁, *R*₂ and *R*₃ sites (Scheme 1(a)). With this in mind, we previously reported the related polythiophene (Scheme 1(b)) which exhibited a phytate sensing in water (11). Its highly sensitive aggregation property triggered by anion as a chemical stimulus motivated us to prepare the next target.

Herein, we report a new type of optically active polythiophene **1_{poly}** which has been readily prepared by introducing (*S*)-phenylethylamino unit into the

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Scheme 1. Structures of isothiuronium derivatives.

isothiuronium pendant. The amphiphilic properties led to a selective anion-induced helical aggregation in aqueous solution.

Results and discussion

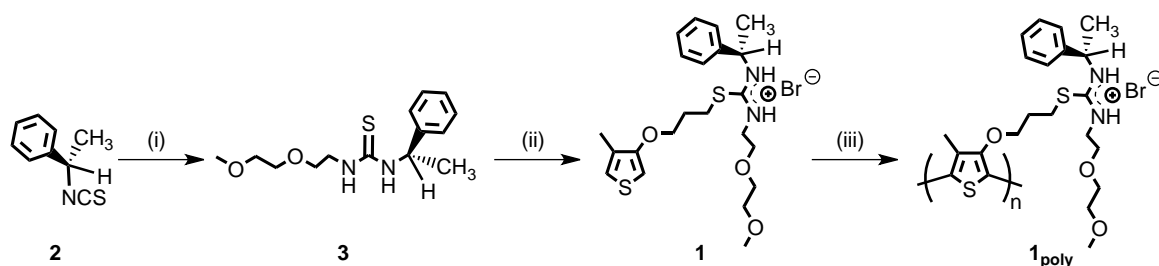
Synthesis

The synthetic path towards **1_{poly}** is shown in Scheme 2. Because a variety of isothiocyanate derivatives are commercially available, chiral functional group can be appended into the pendant segment. We thus decided to employ (*S*)-(1-isothiocyanatoethyl)benzene **2** as starting material (*12*). It was allowed to react with 2-(2-methoxyethoxy)ethylamine (*13*) to afford the corresponding thiourea **3** in 54% yield, being followed by the reaction with 3-(3-bromopropoxy)-4-methylthiophene (*10*) to afford the desired monomer **1** in 46% yield. The structure assignment of monomer **1** was carried out using several spectroscopic data (see Experimental section); the insertion of an isothiuronium unit was identified by means of the ¹H NMR measurement (δ = 8.74–8.76, 10.37 ppm). The polymerisation of **1** using FeCl₃ as an oxidising agent was carried out in dry CHCl₃. The ¹H NMR measurement allowed us to observe the disappearance of signals arising from the terminal thiophene ring, which implied that the polymerisation of **1** proceeded. We reasoned that under the reaction conditions using dry CHCl₃ as a solvent no anion exchange reaction occurred on the cationic side chain (*14*). The obtained polymer **1_{poly}** was then analysed by using gel-permeation chromatography (GPC) with a polystyrene standard, where the number average molecular weight (M_n) and

the polydispersity index were estimated to be 5.53×10^5 and 1.4, respectively. The obtained **1_{poly}** is soluble not only in water and MeOH but also aprotic solvents such as acetone and acetonitrile. The optical properties were estimated by means of UV–vis and fluorescence spectroscopy. After several examinations, a stable aqueous dispersion was obtained when H₂O–MeOH (1:1, v/v) was employed; the absorption and fluorescence maxima were observed at 420 and 535 nm (λ_{ex} = 420 nm), respectively (Figure 1). In the latter case, the fluorescence quantum yield was estimated to be 2.4% using fluorescein as the reference (*15*).

Anion-induced helical chirality

The introduction of chirality into the pendants allowed us to use circular dichroism (CD) spectroscopy to estimate the conformational process occurring in the formation of supramolecular structures. In H₂O–MeOH (1:1, v/v) at 25°C, the polythiophene **1_{poly}** (1.0×10^{-4} M/unit) exhibits no CD pattern in the π – π^* transition region, which indicates that **1_{poly}** adopts a random-coil conformation under these conditions. Taking the cationic character of isothiuronium unit into account, we investigated how the addition of an anion into the solution would affect the conformation of **1_{poly}**. Figure 2 shows the change in CD and UV–vis spectra of **1_{poly}** upon addition of incremental amounts of PF₆[–] as a putative chemical stimulus in H₂O–MeOH (1:1, v/v) at 25°C where 10 mM of NaCl was added into the solution to maintain the ionic strength of the reaction solution. The PF₆[–] addition caused a significant red shift in the absorption spectra with an apparently isosbestic point at 460 nm, appearing as a new absorption band with well-resolved vibronic transitions at λ = 510, 540 and 590 nm. The spectral change brought about a colour change from yellow to purple. In addition, an intense split-type-induced CD (ICD) was observed upon the addition of PF₆[–] (Figure 2(a)), where the zero-crossing point close to the absorption maximum at 543 nm indicates the presence of strong exciton coupling between polythiophene backbones. Taken together, the distinct red shift in the absorption band and the appearance of



Scheme 2. Reagents and conditions: (i) 2-(2-methoxyethoxy)ethylamine, MeOH, room temperature, 21 h, 54%; (ii) 3-(3-bromopropoxy)-4-methylthiophene, dry EtOH, 70°C, 93 h, 46% and (iii) FeCl₃, dry CHCl₃, room temperature, 12 h.

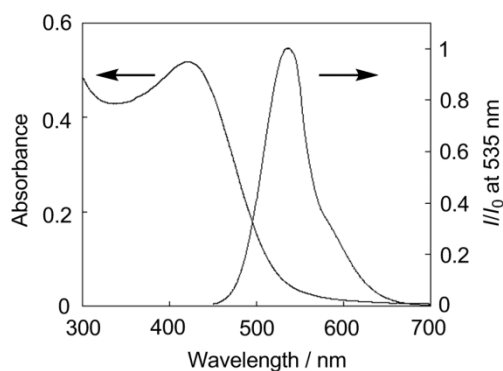


Figure 1. UV-vis and fluorescence spectra of $\mathbf{1}_{\text{poly}}$ (1.0×10^{-4} M/unit) in H_2O -MeOH (1:1, v/v) at 25°C . $\lambda_{\text{ex}} = 420$ nm.

bisignate CD spectra (Davydov splitting) are characteristic of the π -stacked chiral aggregation of the polythiophene (16), the ICD pattern being assigned as a *p*-helix.

The evidence of PF_6^- -induced aggregation came from a field emission-scanning electron microscopy (FE-SEM). The images were taken from the samples obtained by drying the H_2O -MeOH (1:1, v/v) solution on an aluminium foil. Whereas $\mathbf{1}_{\text{poly}}$ indicates a well-isolated state without any aggregation (Figure 3(a)), the image of the solution after PF_6^- addition clearly indicates a networked structure consisting of fibril-like aggregates (Figure 3(b)).

Anion selectivity for the chirality induction

Our interest is to see whether such a dynamic aggregation would be anion selective. We carried out CD titration

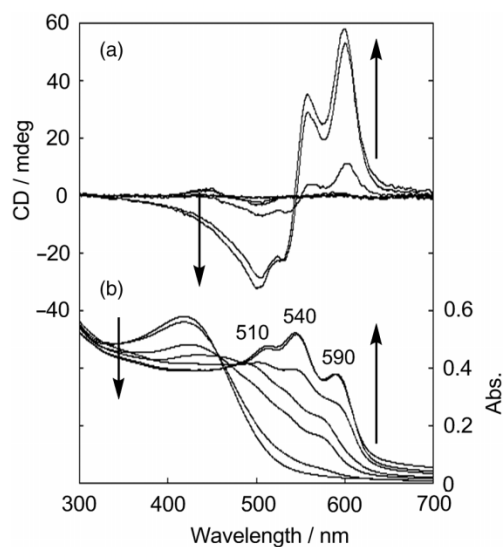


Figure 2. CD (a) and UV-vis (b) spectra of $\mathbf{1}_{\text{poly}}$ (1.0×10^{-4} M/unit) in the addition of an incremental amount of KPF_6 in H_2O -MeOH (1:1, v/v) with NaCl (10 mM) at 25°C . $[\text{KPF}_6] = 0, 0.3, 0.6, 1, 2, 3$ and 5 mM. The data was collected within 10 min after mixing $\mathbf{1}_{\text{poly}}$ with KPF_6 .

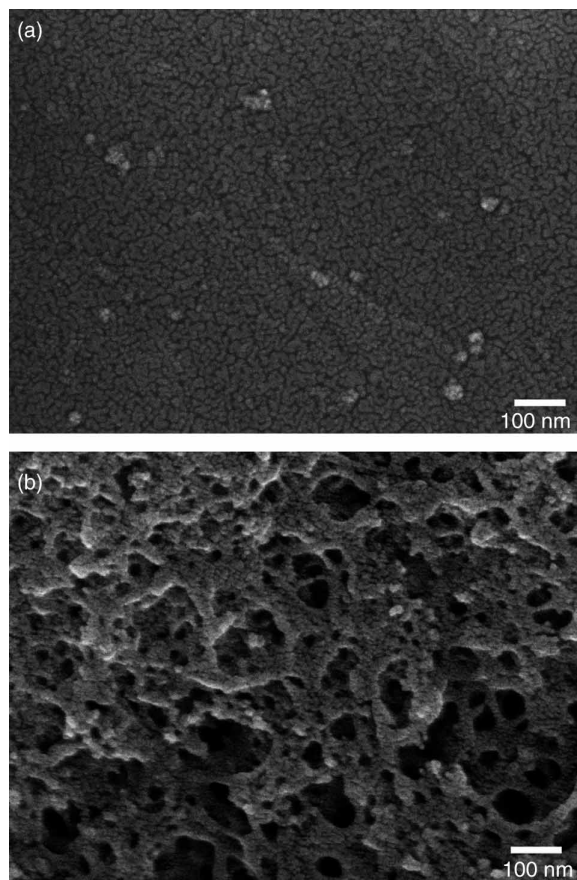


Figure 3. FE-SEM images of (a) $\mathbf{1}_{\text{poly}}$ (1.0×10^{-4} M/unit) and (b) $\mathbf{1}_{\text{poly}}$ (1.0×10^{-4} M/unit) aggregated by adding KPF_6 (5 mM). The scale bar corresponds to 100 nm.

experiments in H_2O -MeOH (1:1, v/v) at 25°C ; change in the intensity at 600 nm in the CD spectra was plotted as a function of the concentration of added anion where F^- , Cl^- , Br^- , I^- , AcO^- , HPO_4^{2-} (equilibrating with H_2PO_4^- under neutral conditions), adenosine 5-triphosphate (ATP), BF_4^- , ClO_4^- and PF_6^- were employed as guest anions. As shown in Figure 4, a steep increase in CD intensity was observed upon addition of $> 1 \times 10^{-3}$ M of PF_6^- into the solution, meaning that chiral aggregation switched on at the anion concentration. We thus defined the concentration as aggregation point which, consequently, was dependent on anions used in the following order: PF_6^- (1×10^{-3} M) $>$ ClO_4^- (5×10^{-3} M) $>$ BF_4^- (3×10^{-2} M), I^- (4×10^{-2} M). Indeed, the addition of I^- did not induce such aggregation so efficiently; the CD intensity in the presence of 1.0×10^{-1} M of I^- was 5.6 times lower than that when 5×10^{-3} M of PF_6^- was added into the solution. On the other hand, there was no change in the CD spectra upon addition of F^- , Cl^- , Br^- , AcO^- , HPO_4^{2-} and ATP. From these results, the addition of hydrophobic anions was effective for the chiral aggregation behaviour, suggesting that anion exchange with hydrophobic anions at isothioronium units should diminish the hydrophilicity of the side

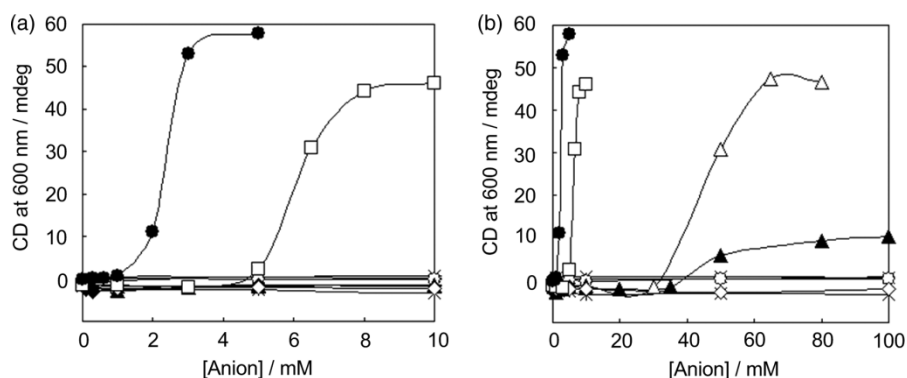


Figure 4. ICD of $\mathbf{1}_{\text{poly}}$ (1.0×10^{-4} M/unit) by anions at various concentrations in H_2O -MeOH (1:1, v/v) with NaCl (10 mM) at 25°C . The CD intensities were monitored at 600 nm. The data was collected within 10 min after mixing $\mathbf{1}_{\text{poly}}$ with anions. The guest concentration ranges from (a) 0 to 10 mM and (b) to 100 mM. KPF_6 (●), NaClO_4 (□), KF (*), KCl (×), KBr (+), KI (▲), ATP with sodium counterion (◆), K_2HPO_4 (◇), AcOK (○) and NaBF_4 (△).

chains to induce chiral aggregation. This behaviour, in turn, might be utilised as an anion-detectable method by means of CD spectroscopy (17).

Solvent-dependencies and temperature-dependencies on the chirality induction

The effect of polar solvents on the chiral aggregates of $\mathbf{1}_{\text{poly}}$ induced by PF_6^- was investigated by CD and UV-vis spectroscopic methods. Figure 5 shows the obtained spectra of $\mathbf{1}_{\text{poly}}$ in the presence of PF_6^- in a mixture of H_2O and MeOH with various ratios of H_2O . Although the CD spectrum was almost silent when 5 or 10% (v/v) H_2O -MeOH solution $\mathbf{1}_{\text{poly}}$ with PF_6^- was employed, the intensity of the ICD signal dramatically increased as the ratio of H_2O in the solution was increased. Also, the increase in

the ratio of H_2O led the absorption maximum to be red shifted from 380 to 540 nm with showing an isosbestic point. Taken together, the observed CD is attributable to a biased helical aggregation of the polythiophene, the aggregation being prompted not only by the exchange of the isothiuronium counterion (Br^-) with the hydrophobic anion (PF_6^-) but also by an increase in hydrophilicity of the bulk environment. In addition, temperature-dependent CD and UV-vis spectra were measured in the presence of PF_6^- in H_2O -MeOH (1:1, v/v). As temperature was increased, the CD intensities decreased significantly which became optically silent at 70°C (Figure 6(a)), being accompanied with the thermochromic behaviour as shown in Figure 6(b). These results strongly indicate the dynamic helical aggregation, where planarisation of the polymer occurred with interchain interactions.

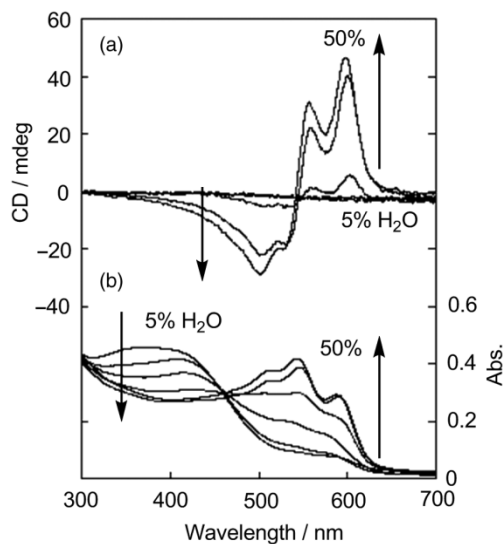


Figure 5. CD (a) and UV-vis (b) spectra of $\mathbf{1}_{\text{poly}}$ (1.0×10^{-4} M/unit) in the presence of KPF_6 (5 mM) in H_2O -MeOH of various ratios at 25°C .

Conclusions

Taking advantage of the synthetic susceptibility of the isothiuronium unit, we have succeeded in synthesising optically active polythiophenes with (*S*)-phenylethylisothiuronium pendants. Although H_2O -MeOH solution of $\mathbf{1}_{\text{poly}}$ is CD silent, selective anion-ICD spectra were detected where the addition of hydrophobic anions such as PF_6^- was most effective. To the best of our knowledge, $\mathbf{1}_{\text{poly}}$ is a new type of chiral amphiphilic polythiophene in which helical aggregation is promoted by hydrophobic anions in aqueous solution. The findings would provide a new approach to obtain polythiophene-based chiroptical materials.

Experimental section

General

NMR spectra were recorded on JEOL JNM-EX 270 (270 MHz) and JEOL Lambda 500 (500 MHz) spectrometers. Chemical shifts (δ) are reported downfield from the internal standard Me_4Si . Fast atom bombardment

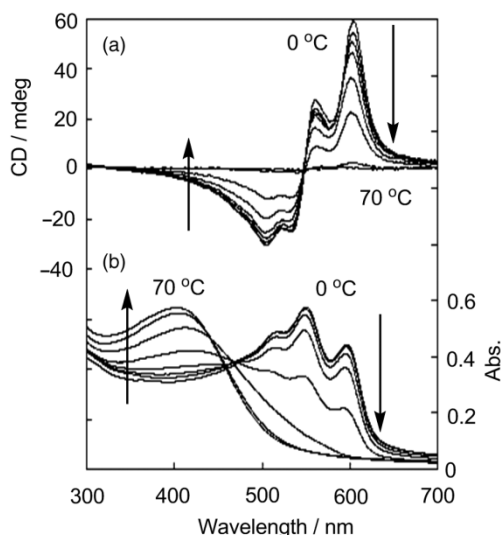


Figure 6. Temperature-dependent CD (a) and UV-vis (b) spectra of I_{poly} (1.0×10^{-4} M/unit) in the presence of KPF_6 (5 mM) in H_2O -MeOH (1/1, v/v) with NaCl (10 mM).

(FAB) mass spectra were obtained on a JEOL JMS-700 spectrometer where 3-nitrobenzyl alcohol was used as a matrix. Infrared spectra were recorded on JASCO FT/IR-5300. Elemental analyses were obtained on a Yanaco CHNcoder MT-5. GPC was performed using a JAI recycling preparative HPLC equipped with RI-5 RI detector. JAIGEL-5H-A column was used for the system where *N,N*-dimethylformamide (DMF) was employed as an eluent containing lithium bromide (100 mM) and phosphoric acid (60 mM). The number average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of polystyrene calibration. CD spectra were recorded on JASCO J-820 spectropolarimeter. Fluorescence and absorption spectra were measured using a JASCO FP-6300 and Shimadzu UV-3100PC spectrophotometers, respectively.

Materials

Unless otherwise indicated, reagents and solvents used for this study were commercially available and used as supplied (Tokyo Kasei [Chuo-ku, Tokyo, Japan], Kanto Kagaku [Chuo-ku, Tokyo, Japan], Wako [Osaka, Osaka, Japan], Aldrich [St Louis, MO, USA]). The water and methanol for spectroscopic as for well as SEM measurements were purchased in analytical grade and used as received.

(*S*)-1-(2-(2-Methoxyethoxy)ethyl)-3-(1-phenylethyl)thiourea **3**

(*S*)-1-(Isothiocyanatoethyl)benzene (1.92 g, 11.8 mmol) **2** was dissolved in MeOH (14 ml). After 2-(2-methoxyethoxy)ethylamine (1.39 g, 11.6 mmol) was added to the

solution, the mixture was stirred at room temperature for 21 h. The resulting solution was evaporated and chromatographed on silica gel (Wakogel C-300, 5% (v/v) MeOH in $CHCl_3$). In this way, 1.78 g of **3** was obtained (54% yield).

1H NMR (270 MHz, $CDCl_3$) δ (ppm): 1.53 (d, $J = 6.91$ Hz, 3H), 3.33 (s, 3H), 3.36–3.39 (m, 2H), 3.43–3.63 (m, 6H), 4.98 (br, 1H), 6.04 (br, 1H), 6.26 (br, 1H), 7.27–7.38 (m, 5H); MS (FAB) m/z 283 $[M + H]^+$.

(*S*)-3-(3-(*N*-(2-(2-Methoxyethoxy)ethyl)-*N*-(1-phenylethyl)-*S*-isothiuronio)propoxy)-4-methylthiophene **1**

Under N_2 atmosphere, 3-(3-bromopropoxy)-4-methylthiophene (424 mg, 6.79 mmol) was dissolved in dry EtOH (16 ml). (*S*)-1-(2-(2-Methoxyethoxy)ethyl)-3-(1-phenylethyl)thiourea **3** (560 mg, 1.98 mmol), dissolved in dry EtOH (10 ml), was added to the solution. The resulting mixture was stirred at 70 °C for 93 h. After the removal of solvent *in vacuo*, the residue was chromatographed on silica gel (Wakogel C-300) using a gradient of MeOH (0–5% (v/v)) in $CHCl_3$ as an eluent, and further purified by GPC using $CHCl_3$ as an eluent. In this way, 426 mg of **1** was obtained (46% yield).

1H NMR (270 MHz, $CDCl_3$) δ (ppm): 1.62 (d, $J = 8.07$ Hz, 3H), 2.03 (d, $J = 0.84$ Hz, 3H), 2.18 (quint, $J = 6.21$ Hz, 2H), 3.25 (s, 3H), 3.47–3.50 (m, 2H), 3.69 (t, $J = 4.21$ Hz, 2H), 3.75 (t, $J = 6.18$ Hz, 2H), 3.86 (br, 4H), 4.00 (t, $J = 4.77$ Hz, 2H), 4.87 (quint, $J = 6.60$ Hz, 1H), 6.12 (d, $J = 3.29$ Hz, 1H), 6.79–6.81 (m, 1H), 7.23–7.41 (m, 5H), 8.74–8.76 (br, 1H), 10.37 (br, 1H); MS (FAB) m/z 437 $[M - Br]^+$; Anal. calcd for $C_{22}H_{33}BrN_2O_3S_2 \cdot 0.5CHCl_3$: C, 45.78; H, 5.85; N, 4.85. Found: C, 45.61; H, 5.93; N, 4.95.

Polymer preparation (I_{poly})

$FeCl_3$ (316 mg, 1.95 mmol) was dissolved in dry $CHCl_3$ (12 ml) under N_2 atmosphere. Monomer **1** (336 mg, 0.649 mmol), dissolved in dry $CHCl_3$ (10 ml), was added to the solution. The mixture was then stirred for 12 h at room temperature. The resulting precipitate was washed with Et_2O (20 ml \times 3). The product was purified by extraction through a soxhlet extractor with Et_2O (150 ml) for 47 h and then with acetone (150 ml) for 5 h. After evaporation, the residue was further washed with $CHCl_3$ (30 ml) and dried *in vacuo*. In this way, 113 mg of I_{poly} was obtained.

1H NMR (500 MHz, $DMSO-d_6$) δ (ppm): 1.24–1.44 (br, 3H), 1.97 (s, 3H), 2.23 (br, 2H), 3.13 (s, 3H), 3.37 (br, 10H), 3.83 (br, 2H), 4.87 (br, 1H), 7.17–7.25 (br, 5H), 9.61 (br, 2H); IR (KBr): $\nu = 3364, 2922, 1179$ cm^{-1} ; GPC: M_n 5.53×10^5 $gmol^{-1}$, polydispersity: 1.4; UV-vis:

$\lambda_{\text{max}} = 420 \text{ nm}$ in H_2O – MeOH (1:1, v/v); fluorescence:
 $\lambda_{\text{em}} = 535 \text{ nm}$ ($\lambda_{\text{ex}} = 420 \text{ nm}$) in H_2O – MeOH (1:1, v/v).

FE-SEM measurements

The samples were dissolved in H_2O – MeOH (1:1, v/v) and dried under reduced pressure on an aluminium foil. They were shielded by Au and examined with a JEOL JSM-7500F scanning electron microscope.

Acknowledgements

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