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Chiral bifacial indacenodithiophene-based π -conjugated polymers with chirality-induced spin selectivity

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Novel optically active π -conjugated polymers having a chiral bifacial indacenodithiophene backbone were synthesized by Suzuki-Miyaura cross coupling polymerization with benzothiadiazole comonomer. The obtained C₂-chiral polymers form amorphous thin films on HOPG and exhibit good chirality-induced spin selectivity with spin polarization of nearly 70%.

Chiral π -conjugated molecules and polymers are attractive owing to the added values derived from their chirality, including chiral recognition ability and circularly polarized luminescence properties^{1–6}. Of growing interest among chirality-related properties is chirality-induced spin selectivity (CISS)^{7–9}, where up or down spin-polarized current preferentially passes through an optically active chiral substance to generate spin-polarized current useful for various fields including spintronics applications, asymmetric reactions, and oxygen reduction. In general, chiral π -conjugated polymers are synthesized by attaching chiral side chains or introducing axially chiral moieties in the main chain^{1–4}. Recently, our group reported new chiral skeletons namely “bifacial” chiral π -conjugated molecules such as C₂-chiral bifacial indenofluorenes¹⁰ and C₃-chiral bifacial truxenes¹¹ having two different substituent groups on their bridging sp³-carbon atoms, and investigated their function as surface passivation reagents for perovskite solar cells and circularly polarized luminescence emitters. To develop a new class of chiral “bifacial” π -conjugated polymers, we focus on C₂-chiral bifacial indacenodithiophene (IDT) (*e.g.*, **1**, Fig. 1), having the same structural symmetry as indenofluorene¹⁰, due to its high potential as a constituent for high performance organic electronic materials, such as semiconducting donor-acceptor

copolymers^{12,13}, hole transporting molecules^{12,14}, and non-fullerene acceptors¹⁵. There are several reports^{16,17} on the IDT derivatives having different substituent groups on their bridging sp³-carbon atoms, but the enantiomer resolution is unprecedented. To our best knowledge, chiral IDT-containing conjugated copolymers have not been reported, except for helicene-containing IDT copolymer in the main chain¹⁸. Here we report the first isolation of enantiomers of a chiral bifacial IDT derivative and application to the Suzuki-Miyaura cross coupling polymerization with a benzothiadiazole comonomer. The resultant optically active bifacial IDT-based π -conjugated copolymers formed amorphous thin films and showed clear CISS property with spin polarization of 30~60% as well as bisignate Cotton effect on the main chain charge-transfer (CT) absorption band.

A C₂-chiral bifacial IDT derivative was synthesized according to the scheme in Fig. 1. Widely-used indacenodithiophene dione **3**¹² was reacted with phenyl lithium to give diol **4** in 77% yield as a mixture of *syn* (chiral but racemic) and *anti* (*meso*) isomers in ca. 1:3 ratio. Since the diol **4** was poorly soluble in organic solvents, after washing with hexane, the crude diol **4** was used in the next reaction without further purification or separation of isomers. The Williamson-ether synthesis reaction between diol **4** and methoxy-

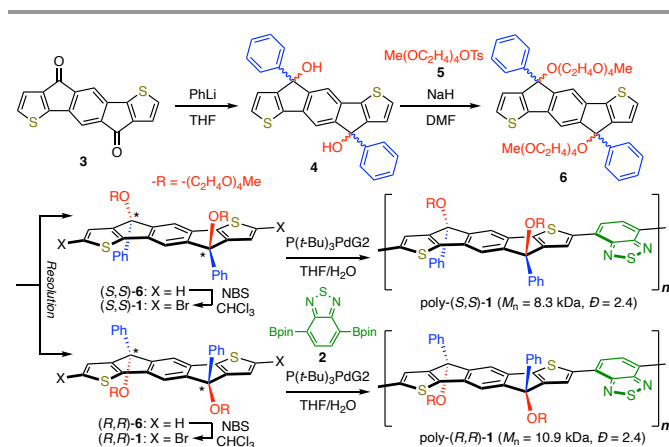


Fig 1. Synthesis of chiral bifacial IDT monomers and polymers.

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terminated tetraethylene glycol mono tosylate **5** using NaH as a base gave IDT derivative **6** having phenyl and tetraethylene glycol groups on the bridging sp^3 -carbon atoms as a mixture of *syn* and *anti* isomers in 69% yield. Silica gel column chromatography allowed isolation of *syn* isomer of **6**. Chiral resolution of *syn*-**6** was successfully conducted by preparative chiral HPLC separation using chiral stationary phase to provide enantiomerically pure (*S,S*)-**6** and (*R,R*)-**6** (Fig. 2a). We estimated their chirality by calculating their circular dichroism (CD) spectra by TD-DFT with B3LYP/6-311G(d,p) level of theory. Fig. 2b shows the observed (solid lines) and calculated (dotted lines) CD spectra of **6s**. The enantiomers showed mirror-imaged CD spectra of each other, and the theoretically calculated CD spectra of **6s** agree with the observed CD spectra to estimate the first and second fractions as (*S,S*)-**6** and (*R,R*)-**6**, respectively (Fig. 2). The **6s** were brominated with *N*-bromo succinimide (NBS) in $CHCl_3$ to afford enantiomerically pure (*S,S*)-**1** and (*R,R*)-**1** in 90% yield (Figs. 1 and S1). The chemical structures of newly synthesized compounds were unambiguously characterized by NMR and FT-IR spectroscopy, as well as high-resolution MALDI-TOF mass spectrometry (ESI⁺). Thus, we successfully obtained the enantiomer pair of the dibrominated optically active bifacial C_2 -chiral IDT monomers (*S,S*)-**1** and (*R,R*)-**1** that can be used for transitional metal catalysed coupling polymerization.

As a coupling partner, we decided to use a benzothiadiazole(BT)-based comonomer because copolymers of electron donating IDT and electron accepting BT units are popular as high performance semiconducting polymers.^{12,13} The obtained optically active (*S,S*)-**1** and (*R,R*)-**1** were polymerized with dibrominated benzothiadiazole **2** comonomer by Pd-catalysed Suzuki-Miyaura cross coupling polymerization using $P(t-Bu)_3$ Pd G2 catalyst in aqueous tetrahydrofuran (THF) to give corresponding π -conjugated copolymers, poly-(*S,S*)-**1** and poly-(*R,R*)-**1** in 30% and 33% yield, respectively (Fig. 1). The chemical structures of the polymers were confirmed by NMR and FT-IR spectroscopy (ESI⁺). For their number-average molecular weight (M_n) and dispersity (\mathcal{D}), analytical size exclusion chromatography (SEC) indicated that poly-(*S,S*)-**1** has $M_n = 8.2$ kg/mol and $\mathcal{D} = 2.4$, while poly-(*R,R*)-**1** has $M_n = 10.9$ kg/mol and $\mathcal{D} = 2.4$, respectively. In THF, these polymers exhibited clear bisignate Cotton effect on the main chain charge-transfer (CT) absorption band in the long wavelength region around

600 nm (Fig. 3a). The physical and structural properties of the polymers in solid and thin film state were investigated. From the differential scanning calorimetry (DSC) measurement, these polymers do not show any clear sign of phase transition in the temperature range of $-50 \sim 200$ °C (Figs. S2 and S3), indicating their amorphous nature. We fabricated thin films of the polymers on quartz by spin coating their chlorobenzene solutions (10 mg/mL) at 3000 rpm. Smooth, blue-coloured thin films were obtained and displayed slightly red-shifted UV-vis absorption and CD spectra (Figs. 3b and S4) compared to the spectra in solution state. The spectral shapes of CD spectra in the film state are similar to those obtained in the solution state, suggesting that the polymers did not form higher-ordered structure in thin-film state. The absence of clear diffraction in grazing-incident X-ray diffraction (GI-XRD) measurements (Fig. S5) of the thin films also support their amorphous nature.

To investigate CISS properties of the polymers, we fabricated thin films of the polymers on HOPG by spin coating their chlorobenzene solutions (3 mg/mL) at 1500 rpm. By atomic force microscopy (AFM), we confirmed that relatively smooth thin films with root mean square roughness of 0.60 nm for poly-(*S,S*)-**1** and 0.54 nm for poly-(*R,R*)-**1** were obtained (Fig. 4a,b). We estimated the thickness of the thin films to be 23.2 ± 3.2 nm for poly-(*S,S*)-**1** and 23.4 ± 4.4 nm for poly-(*R,R*)-**1** (Fig. 4f) by AFM measurement of several height gaps that were made by partial scratching (Fig. S6). The CISS properties of the thin films of the polymers were investigated by spin-polarized magnetic conductive (mc)-AFM technique with an experimental setup shown in Fig. 4f. We used a CoCr cantilever (Bruker, MESP-V2) as a ferromagnetic electrode and put a Nd magnet on the top of the cantilever during the measurement with "up" or "down" directions to maintain the magnetization of the cantilever (Fig. S7). Current-voltage (*I*-*V*) curves were measured with either up and down polarized conditions more than 50 sweeps in different places to obtain two averaged *I*-*V* curves for up and down (I_{up} and I_{down}) spin-polarized currents. As a result, the thin film of poly-(*S,S*)-**1** exhibited

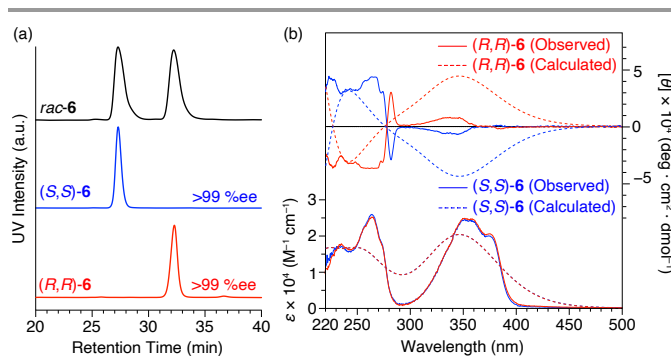


Fig. 2. (a) Chiral HPLC profiles (DAICEL Co., Ltd., CHIRALPAK IG-3[®], EtOAc:*n*-hexane = 1:2, flow rate = 0.5 mL/min) of *rac*-**6**, (*S,S*)-**6** and (*R,R*)-**6**. (b) Experimentally observed (solid lines) and theoretically calculated (dotted lines) CD and UV-vis absorption spectra of (*S,S*)-**6** (blue) and (*R,R*)-**6** (red) (15 μ M, THF, 25 °C).

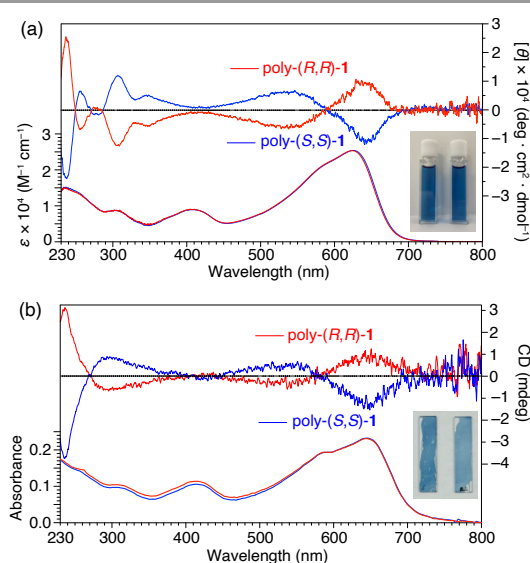


Fig. 3. CD and UV-vis absorption spectra and photographs of poly-(*S,S*)-**1** (spectra; blue, photograph; left) and poly-(*R,R*)-**1** (spectra; red, photograph; right) (a) in THF (15 μ M for monomer unit, 25 °C) and (b) on quartz.

higher current for I_{down} than I_{up} (Figs. 4c and S8a), while the thin film of poly-(*R,R*)-1 exhibited higher current for I_{up} than I_{down} (Fig. 4d and S8b), indicating the successful observation of CISS behavior of the chiral polymers.¹⁹ The spin polarization (SP), defined as $SP = [(I_{\text{up}} - I_{\text{down}})/(I_{\text{up}} + I_{\text{down}})]$, is shown in Fig. 4e as an indicator of degree of spin-filtering function. The average SP values of the thin films of poly-(*S,S*)-1 and poly-(*R,R*)-1 were $-62 \pm 7\%$ and $+69 \pm 4\%$, respectively²⁰; these are the highest class of SP values among chiral π -conjugated polymers.^{21–23} Fontanesi, Naaman and coworkers reported that the spin-coat film of chiral polythiophene with L-cysteine-derived side chains could not act as a spin filter, whereas the carefully prepared monolayer of the same polymer exhibited SP of ca. 34%.²¹ Similarly, Naaman reported that the monolayer film of poly(fluorene-co-thiophene) with chiral sulfide side groups exhibited SP of ca. 30%, but its spin-coat film displayed no spin-selective transporting property.²² Naaman, Maeda, Nishimura and coworkers reported that the vertically aligned helical polyacetylenes whose one terminal was covalently immobilized onto the substrate exhibited CISS with SP of ca. 50%.²³ It is noteworthy that the amorphous thin films of poly-(*S,S*)-1 and poly-(*R,R*)-1, where the alignment of the polymer chains are random, simply prepared by spin coating show the highest class of SP value without special synthetic or fabrication protocols.

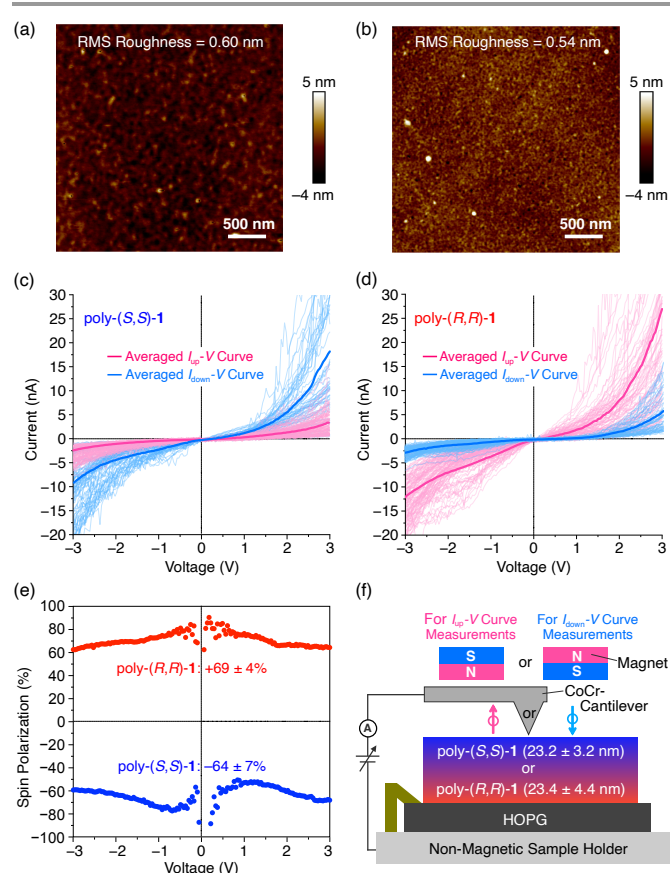


Fig. 4. AFM height images of spin-coat thin films of (a) poly-(*S,S*)-1 and (b) poly-(*R,R*)-1 on HOPG. Up (pink) or down (sky blue) spin-polarized current-voltage curves of the thin film of (c) poly-(*S,S*)-1 and (d) poly-(*R,R*)-1 on HOPG. Unaveraged curves are shown as thin red and blue lines. (e) Spin polarization as a function of the applied voltage for poly-(*S,S*)-1 (blue) and poly-(*R,R*)-1 (red). (f) Schematic illustration of spin-polarized mc-AFM measurement. The directions of the arrows in panel f represent the directions of spins.

Recently, spin-coat thin films of chiral organic small molecules such as chiral subphthalocyanines²⁴ and topologically chiral molecular knots²⁵ with high SP values of 50–88% have been reported, while spin-coat films of chiral polymer systems may have their advantages because thin films of polymers generally have higher mechanical, thermal and chemical toughness than the spin-coat films of small molecules.

We also tried to evaluate the CISS properties of the corresponding monomers [(*S,S*)-1 and (*R,R*)-1] in the same way on HOPG (Fig. S10). However, it was difficult to fabricate smooth thin films on HOPG (Fig. S10a–d), we found the formation of amorphous aggregate on HOPG probably due to poor matching of interfacial property between the monomers and HOPG, and higher mobility of monomers than polymers on HOPG. We tried spin-polarized mc-AFM measurements of the monomer thin films, but the observed currents were very low, and almost no spin selectivity was obtained (Fig. S10e,f). Thus, chiral polymers with good film-forming property have advantage as spin filtering materials over small molecular system, because we can fabricate amorphous polymer films on various substrates by simple spin coating or related methods to endow substrates with spin filtering function.

In conclusion, we developed chiral bifacial π -conjugated polymers based on newly synthesized bifacial IDT units, and found a good CISS effect of their thin films. We also demonstrated the usefulness of chiral π -conjugated polymers as spin filtering materials owing to their good film-forming property. In this year, an interesting phenomena of inverse chirality-induced spin selectivity effect in chiral assemblies of π -conjugated polymers was reported,²⁶ thus spintronic research using chiral organic semiconducting materials is a growing field. Since IDT unit is a popular building block for high-performance organic electronic materials, chiral bifacial IDT unit would be promising for next generation chiral spintronic materials.

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Data availability

The data supporting this article have been included as part of

the ESI.†

Conflicts of interest

There are no conflicts to declare.

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The data supporting this article have been included as part of the Electronic Supplementary Information.