



A chiral polymer with alternating conjugated segments and (1*R*,2*R*)-1,2-diaminocyclohexane as a unit with C_2 symmetry

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Abstract—A chiral conjugated polymer was prepared via the palladium catalysed coupling reaction between 1,4-di-ynyl-2,5-dialkoxybenzene and a bis-5-bromothieryl derivative of (1*R*,2*R*)-1,2-diaminocyclohexane as a chiral unit with C_2 symmetry and a unit with complexing properties. The resulting chiral polymer of which its backbone consists of alternating conjugated segments and chiral complexing units, showed intense luminescence properties and was used as a ligand in the rhodium-catalysed hydride transfer reduction. © 2001 Elsevier Science Ltd. All rights reserved.

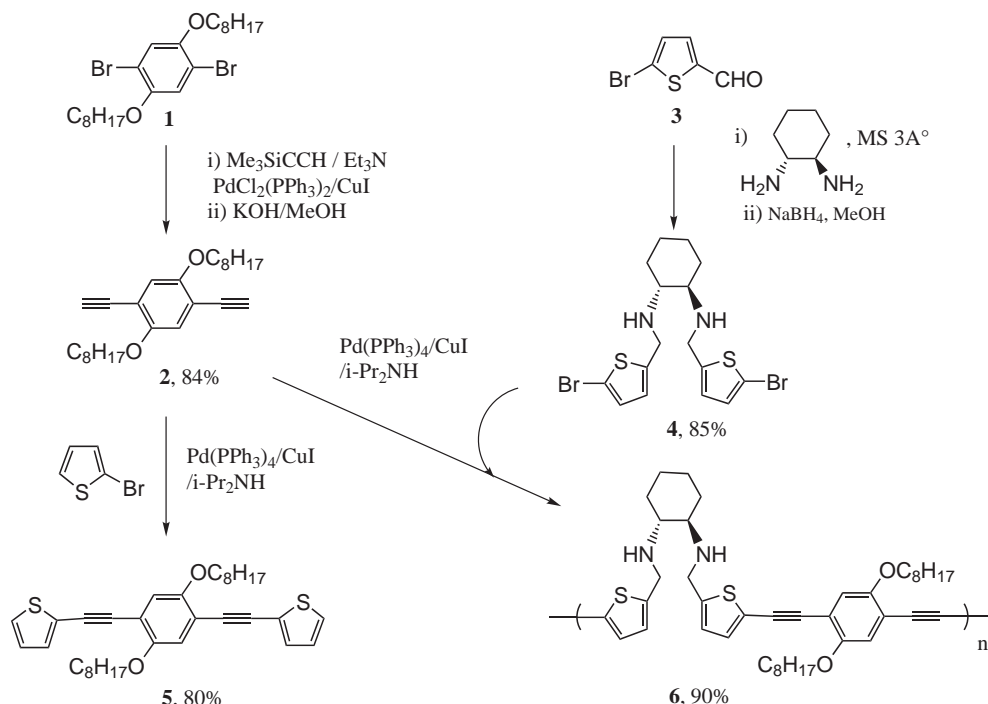
Owing to their remarkable electronic and photonic properties, which result from the existence of an extended conjugated π -system, conjugated organic polymers are receiving much attention and very diverse applications of these materials have emerged.^{1–4} Many efforts are being made to control the bulk properties of these materials by a design strategy based on molecular engineering.^{5–9} The tuning of the optical properties of conjugated polymers results from the control and variation of the structure of the chain unit. For example, the use of organometallic coupling reactions allowed a controlled synthesis of various polymers and nano-architectures.^{6,7,10} Additionally, the arrangement of the polymeric chain in the solid is also of great importance since interchain interactions and dimensionality also play a determining role in the physical properties of the material^{11,12} which are critically dependent on supramolecular features such as molecular packing. High-charge mobility arose from well-defined arrangement of the conjugated segments in supramolecular assemblies.¹³ Conversely, solid-state quantum efficiency is related to the degree of long-range order, decreasing with increasing order.¹⁴ The coplanar orientation of conjugated polymer backbones is assumed to lead to the formation of excimer complex which provides a non emissive decay channel for the excited state. A helical polymer, which conformation arises from the main chain chirality¹⁵ may exhibit lower interactions which may help to prevent the polymer chain from packing.¹⁶ Also, chiral conjugated polymers¹⁷ are potentially useful in areas such as photo- or electroluminescence, non-linear optics, enantioselective sensing, molecular recognition or asymmetric catalysis. Our current interest in the optical and

electro-optical properties of thienylene–phenylene copolymers,^{12,18} for which emission with high quantum yields was observed in solution,¹⁹ has led us to study the synthesis of chiral structures as a means to decrease interchain interaction in the solid state. We have been interested in developing a quite general route from a readily available chiral di-amine, having C_2 symmetry which could lead to helical conformation and which would be capable of metal complexation for catalysis.

We prepared a chiral conjugated polymer using the easily accessible (1*R*,2*R*)-1,2-diaminocyclohexane²⁰ as described in Scheme 1. The preparation of the conjugated segment was achieved from 2,5-dibromo-1,4-dioctoxybenzene **1**. It was first reacted with trimethylsilylacetylene (3 mol equiv.) in triethylamine in the presence of (PPh₃)₂PdCl₂/CuI which led to 1,4-bis[(trimethylsilyl)ethynyl]-2,5-bis-(octoxy)benzene in 90% yield. Subsequent treatment with MeOH/THF in the presence of KOH as base gave the desilylated di-yne **2** in 84% isolated yield. The palladium catalysed coupling of **2** in the presence of Pd(PPh₃)₄, with 2-bromothiophene gave **5** which was isolated in 80% yield.[†]

[†] Selected characterisation data of **5**: mp: 66.5°C; ¹H NMR (δ , ppm, CDCl₃): 7.27–7.32 (m, 4H, -H_{th}), 7.02 (dd J =4.9, 3.8 Hz 2H, H_{th}), 6.99 (s, 2H, H_{ph}), 4.01 (t, J =6.3, 4H, O-CH₂), 1.85 (m, 4H, CH₂), 1.28–1.54 (m, 20H, CH₂), 0.88 (t, J =6.1 Hz 6H, CH₃); ¹³C NMR (δ , ppm, CDCl₃): 14.1, 22.7, 25.9, 26.1, 29.3, 29.4, 31.8, 69.7, 88.1, 89.8, 113.8, 116.6, 123.5, 127.1, 127.4, 131.8, 153.5; MS (FAB⁺): 546 (M); absorption (CHCl₃) λ_{\max} nm (ϵ_{\max} /l mol⁻¹ cm⁻¹) 325 (21300); 377 (26800); emission (CHCl₃) λ_{\max} (nm) 430 (excitation λ_{\max} =385 nm). Anal. calcd for C₃₄H₄₂O₂S₂: C, 74.68; H, 7.74%. Found: C, 74.69; H, 8.04%.

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Scheme 1. Synthesis of monomeric units of **4** and **5** and of polymer **6**.

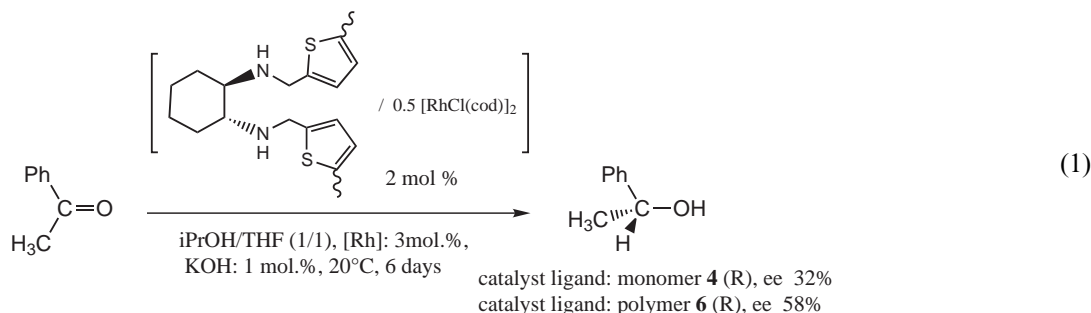
The chiral unit **4** was then prepared from (1*R*,2*R*)-1,2-diaminocyclohexane which upon reaction with 5-bromo-2-thiophenecarboxaldehyde **3** in CH_2Cl_2 using 3 Å molecular sieves gave 84% yield of an intermediate (1*R*,2*R*)-*N,N'*-bis(5-bromothiophen-2-ylmethyl)-1,2-diiminocyclohexane. The latter was reduced by sodium borohydride in dry methanol at room temperature to give (1*R*,2*R*)-*N,N'*-bis(5-bromothiophen-2-ylmethyl)-1,2-diaminocyclohexane **4** in 85% yield.[‡] The polycondensation reaction was then achieved using equimolar quantities of **4** (1.02 mmol, 474 mg) and **2** (390 mg) in the presence of palladium tetrakis(triphenylphosphine) (4 mol %) and cuprous iodide (4 mol %) in a toluene/di-isopropyl amine mixture (25 mL/10 mL).²¹ The resulting polymer **6** was soluble in THF, CHCl_3 and CH_2Cl_2 . THF solutions of **6** were purified by preparative gel permeation chromatography (GPC), over polystyrene bio-beads S-X1 (200–400 mesh) with THF as the eluent. The ^1H NMR spectrum recorded at 400 MHz and infrared spectroscopy data of **6** are consistent with the polymer structure shown in Scheme 1.[§] The molecular weights of

the collected fractions of **6** were evaluated by analytical GPC column calibrated with polystyrene standards: $M_w = 11900$, $M_w/M_n = 1.7$, corresponding to an average degree of polymerisation of ten. Solutions of **6** in THF showed specific optical rotation $[\alpha]_D^{25} = -65^\circ$ ($c = 0.9$, THF), higher than that of the monomeric chiral unit **4** $[\alpha]_D^{25} = -38.6^\circ$ ($c = 1.33$, CHCl_3).

The absorption–emission properties of the conjugated structure were studied. We compared the properties of the rigid conjugated molecule **5** with those of the polymeric material **6**. The latter contains the same unsaturated unit as an alternating conjugated substructure separated by the chiral unit which limits conjugation length by isolating the unsaturated segments. The UV–vis spectrum of CHCl_3 solutions of **5** showed absorption for values of $\lambda_{\text{max}} = 325$ nm ($\epsilon = 21300$), 377 nm ($\epsilon = 26800$). The emission spectrum (CHCl_3 solutions) revealed $\lambda_{\text{max}} = 438$ nm ($\lambda_{\text{excitation}} = 385$ nm). The absorption spectrum of polymer **6** in dilute CHCl_3 solutions showed π – π^* transition maxima at $\lambda_{\text{max}} = 329$ nm ($\epsilon = 18700$), 385 nm ($\epsilon = 25000$). It is quite similar to that of the isolated structure **5**, indicating similar conjugation properties in the two cases in agreement with a confinement of the conjugated length within the region between the chiral units. The polymer emitted strong fluorescence in the green region under UV irradiation ($\lambda_{\text{excitation}} = 385$ nm) in dilute CHCl_3 solutions and showed two photoluminescent bands at $\lambda_{\text{max}} = 497$ and 519 (shoulder) nm. A very large Stokes shift (112 nm) is observed for the polymer **6**. The photoluminescence emission of **6** also remains very strong in the solid state ($\lambda_{\text{max}} = 556$ and 580 nm), consistent with the absence of π -stacking interactions in the solid material. The observed intense photoluminescence is probably related to the non-planar structure of the polymeric material resulting from the

[‡] Selected characterisation data of **4**: $[\alpha]_D^{25} = -38.6^\circ$ ($c = 1.33$, CHCl_3); ^1H NMR (δ , ppm, CDCl_3): 6.86 (d, $J = 3.67$, 2H, H_{th}), 6.65 (d, $J = 3.7$ Hz, 2H, H_{th}), 4.02 (d, $J = 15.3$ Hz, 2H, $-\text{NH}-\text{CH}_2$), 3.80 (d, $J = 15.28$ Hz, 2H, $-\text{NH}-\text{CH}_2$), 2.06–2.26 (m, 4H, cyclohexyl), 1.95 (s, 2H, $-\text{NH}-$), 1.68–1.74 (m, 2H, cyclohexyl), 0.97–1.25 (m, 4H cyclohexyl); ^{13}C NMR (δ , ppm, CDCl_3): 24.8, 31.4, 45.8 (CH_2-NH), 60.3 ($\text{CH}-\text{NH}$), 110.6, 124.5, 129.3, 141.1; ν_{max} (KBr)/ cm^{-1} : 3299 (N–H); MS (FAB⁺): 465 (M+1). Anal. calcd for $\text{C}_{16}\text{H}_{20}\text{Br}_2\text{N}_2\text{S}_2$: C, 41.39; H, 4.34; N, 6.03%. Found: C, 41.57; H, 4.39; N, 6.16%.

[§] Selected characterisation data of **6**: ^1H NMR (δ , ppm, CDCl_3): 7.12 (s, 2H, H_{th}), 6.94 (s, 2H, H_{ph}), 6.83 (s, 2H, H_{th}), 4.12–3.75 (broad singlet, 8H, CH_2), 2.31–2.08 (broad singlet, 4H, cyclohexyl), 1.84–1.78 (broad singlet, 8H, NH and CH_2), 1.49–1.25 (broad singlets, 28 H, CH_2), 0.85 (broad singlet, 6H, CH_3); ν_{max} (KBr)/ cm^{-1} : 3298 (N–H), 2199 ($\text{C}\equiv\text{C}$). Raman shift (solid state) cm^{-1} : 2201 ($\text{C}\equiv\text{C}$). Anal. calcd for $\text{C}_{42}\text{H}_{56}\text{N}_2\text{O}_2\text{S}_2$: C, 73.64; H, 8.24; N, 4.09 %. Found: C, 73.0; H, 8.15; N, 3.61 %.



presence of alternating chiral units in the main chain. It leads to lower interchain interactions and limits the π -stacking¹⁴ of the photo-luminescent centre.

Also, *trans*-1,2-diamino-cyclohexane derivatives are of great interest as ligands for catalysis.²² Rhodium complexes of (1*R*,2*R*)-1,2-diaminocyclohexane ligands have been used in asymmetric hydrogen-transfer reduction of prochiral ketones.^{23,24} Rhodium complexes of **4** and **6** were formed upon reaction with 0.5 mol of [Rh(cod)Cl]₂ in THF,[†] and these were used as catalysts in the asymmetric reduction of acetophenone[‡] (Eq. (1)). Under identical conditions, the use of monomer **4** as a ligand gave (*R*)-1-phenylethanol (93% yield; ee=33%) and the use of polymer **6** as a ligand led to lower conversion but higher enantioselectivity (46% yield; ee=58%). The enhanced selectivity may arise from a helical conformation of the polymeric structure arising from the presence of alternating chiral C₂ units and a rigid conjugated segment in the main chain. It provides an additional contribution to the chirality of the catalytic species and results in higher ee compared to the value obtained using the isolated monomeric chiral unit.

In conclusion, compared to the monomeric units, chiral conjugated polymers containing a chiral diamine unit and a conjugated unit exhibit upgraded properties. The chiral unit can serve as a catalyst ligand, leading to enhanced selectivity, also strong photoluminescence was observed. We are currently studying the physical properties of polymer **6** and its use to prepare electroluminescent diodes, owing to the observed large Stokes shift and intense solid state photoluminescence.²⁵ Also, the reported synthetic route can be extended to a variety of diamines as chiral units and to a variety of conjugated segments using palladium catalysed coupling reactions.

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[†] Evidence for the complexation of the ligand **4** was obtained by UV–vis spectroscopy. THF solutions of [Rh(cod)Cl]₂ exhibited an absorption at 350 nm which was red-shifted to 375 nm in the presence of **4**. The high absorption of **6** in this range, prevents measurements for the polymer.

[‡] The experiments were performed at room temperature using a 1/1 THF/*i*-PrOH solvent mixture, molar ratios Rh/substrate: 0.03; Rh/KOH: 0.1. The reaction was followed by capillary GC and the enantioselectivity was determined by HPLC using a Chiracel-OD column.

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