

New chiral π -conjugated polymers based on a (*1R,2R*)-diiminocyclohexane chiral unit with weak interchain π stacking[†]

Jean-Pierre Lère-Porte,* Joël J. E. Moreau, Françoise Serein-Spirau and Salem Wakim

UMR CNRS 5076 Hétérochimie moléculaire et macromoléculaire, E.N.S.C.M., 8 rue de l'École Normale, 34096 Montpellier Cedex 05, France. E-mail: lere@cit.enscm.fr; Fax: +33(0)467144353; Tel: +33(0)467147213

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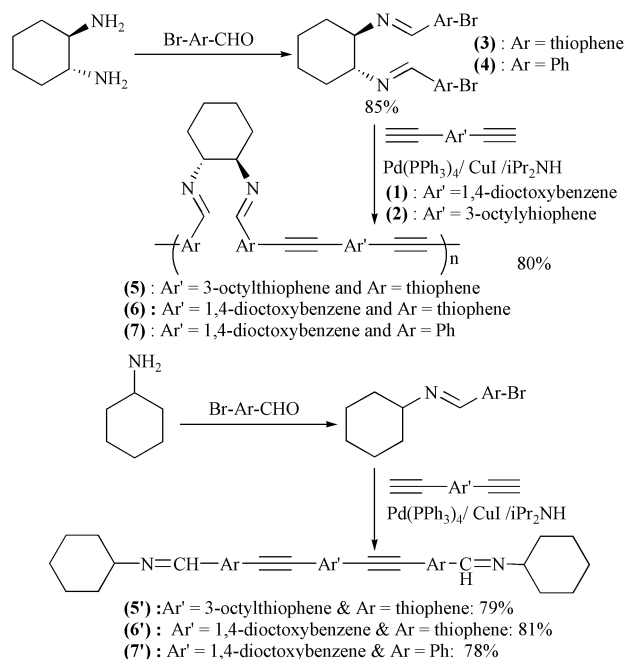
New chiral π -conjugated polymers consisting of alternating conjugated segments and (*1R,2R*)-diiminocyclohexane units with C_2 symmetry were prepared by a palladium-catalyzed coupling reaction, they exhibited very high specific optical rotations ($[\alpha]$ up to -3000°) and strong Cotton effects ($[\theta]$ 10^6 deg $\text{cm}^2 \text{mol}^{-1}$).

π -Conjugated organic polymers have attracted considerable attention owing to their interesting properties as materials for charge transport,^{1–4} for non linear optics,⁵ for electronics and optoelectronics.^{1–3,6} Particularly, they are attractive emissive materials for light emitting diodes (LEDs) because they are easily processed and their optical properties can be easily tuned by chemical engineering.⁷ The stacking of the π -conjugated polymer chains plays a determining role in the physical properties of these materials.^{8,9} The introduction of a chiral unit into a π -conjugated polymer can lead to a backbone with a helical secondary structure and has been explored as a route to enantioselective sensors and catalysts.^{10,11} In addition, the secondary structure of the chain prevents π -stacking of the conjugated segments leading to enhanced electroluminescence efficiency.^{7,12} Circularly polarized electroluminescence was also reported for these materials.¹³ π -Conjugated polymers bearing optically active side groups have been extensively studied, but few examples of π -conjugated polymers possessing chiral units in the main chain have been reported. The latter polymers were shown to have a more stable helical secondary structure with less dependence on temperature and solvent.^{14,15} In this paper we report a versatile synthesis of a new class of chiral polymers which have a backbone consisting of alternating conjugated segments and (*1R,2R*)-1,2-diiminocyclohexane. We explored the use of the more rigid diiminocyclohexane compared to diaminocyclohexane as a means to induce stable helical secondary structure in the chain. The optical and electro-optical properties associated with a tunable π -conjugated segment located between the chiral units are reported.

Chiral conjugated polymers containing (*1R,2R*)-diiminocyclohexane were obtained as shown in Scheme 1. 1,4-Diethynyl-(2,5-dioctoxy)benzene (**1**) and 2,5-diethynyl (3-octyl)thiophene (**2**) were prepared by palladium-catalyzed coupling of trimethylsilylacetylene with the appropriate aromatic derivative followed by a KOH-promoted deprotection. The reaction of (*1R,2R*)-diaminocyclohexane and 5-bromo-2-thiophene carboxaldehyde or 4-bromobenzaldehyde in CH_2Cl_2 using 3 Å molecular sieves¹⁶ afforded (*1R,2R*)-*N,N'*-bis(5-bromothiophene-2-ylmethyl)diiminocyclohexane (**3**) and (*1R,2R*)-*N,N'*-bis(bromobenzylidene)diiminocyclohexane (**4**). The polycondensation reaction was achieved using equimolar quantities (1 mmol) of chiral units (**3**) or (**4**) and diethynyl conjugated moieties (**1**) or (**2**) in the presence of palladium tetrakis(triphenylphosphine) (4 mol%) and cuprous iodide (4 mol%) in a toluene-diisopropylamine mixture (25 mL/10 mL)¹⁷ (Scheme 1). The resulting polymers[‡] (**5–7**) were soluble in toluene, DMF, THF, CHCl_3 and CH_2Cl_2 and insoluble in

alcohols and CH_3CN . THF solutions of polymers were purified by preparative gel permeation chromatography (GPC), over polystyrene bio-beads S-X1 (200–400 mesh) with THF as the eluent. The average molecular weights of the collected fractions of (**5–7**) were evaluated by analytical GPC column calibrated with polystyrene standards; they varied from 12000 to 23000 suggesting an average degree of polymerization (DP_n) from 13 to 19. Solutions of polymers in THF showed specific optical rotations up to 3200° , four to five times higher than those of the isolated chiral unit.

The absorption and emission properties of the polymers **5–7** are indicated[‡]. For comparison, those of the isolated conjugated segments **5'**, **6'**, **7'** (Scheme 1) have been evaluated. The absorption and emission properties of **5'–7'** (cf. ESI[†]) are identical to those of **5–7**[‡] in agreement with a confinement of the conjugation length between two chiral units.¹⁸ Under visible irradiation in dilute THF solutions the polymers emitted strong fluorescence in the blue region and showed two bands around 425–470 nm for $\lambda_{\text{excitation}} \cong 400$ nm. Thin films of polymers **5–7** and of repeating units **5'–7'** on a glass substrate were realized by spin-coating from saturated solutions in CHCl_3 and the optical properties were studied and compared to the solution. The absorption of the isolated conjugated units shows a red-shift of the wavelength maximum in the solid state **5'–7'**. This behaviour can be attributed to an enhanced conjugation in the solid state, due to favoured π -stacking interchain interactions. Interestingly the polymers **5–7** showed absorption bands exactly identical in CHCl_3 solutions and in the solid state (Fig. 1a,b). This result is consistent with the absence of π -stacking interactions of the conjugated units in the polymeric solid material. Moreover X-ray diffraction diagrams of **7** showed



Scheme 1

[†] Electronic supplementary information (ESI) available: selected characterization data for **2–4**, and **5'–7'**. See <http://www.rsc.org/suppdata/cc/b2/b208869j/>

only one diffraction signal at small angles ($2\theta = 3.4^\circ$) and a broad signal ($2\theta = 21^\circ$) characteristic of semi-crystalline material. Conversely $7'$ revealed several diffraction peaks significant of a crystalline product. This behaviour is consistent with lower order and stacking of the conjugated segment in the polymer compared to the isolated segment in the monomer.

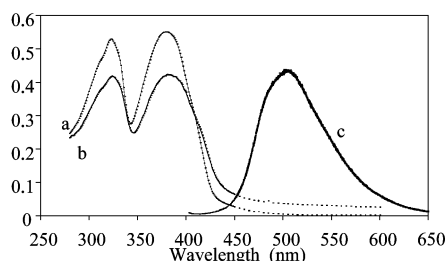


Fig. 1 Absorption spectrum of **7** in CHCl_3 (a) and in solid state (b). Fluorescence spectrum of **7** in the solid state (c).

The circular dichroism spectra have been recorded. Chiral conjugated copolymers (**5**–**7**) display strong Cotton effects and the molar ellipticity values $[\theta]$, calculated using the molecular weight of the polymer repeating unit, are very high from 1.2 to $3.4 \times 10^6 \text{ deg cm}^2 \text{ mol}^{-1}$, an example is given in Fig. 2. The CD spectrum of the polymer chain may arise from a contribution of the helical secondary structure which could be responsible for the observed low degree of interchain interactions in the material.

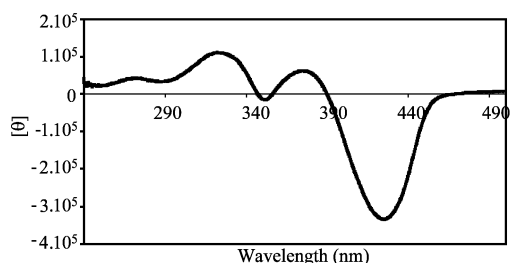


Fig. 2 CD spectrum of (**6**).

In the solid state, the polymers emitted strong photoluminescence in the green region ($\lambda_{\text{max}} = 505 \text{ nm}$) under visible irradiation ($\lambda_{\text{excitation}} = 381 \text{ nm}$) (Fig. 1c). Photoluminescence quantum yields were measured for the three copolymers. Moderate or low values were observed for **5** (2%) and **6** (3%), it can be explained by the heavy-atom effect of sulfur atoms contained in the polymeric chain.¹⁹ Interestingly, a quite high value (32%) was obtained for **7** and it is as high as those reported for phenylene–vinylene based copolymers currently used to develop electroluminescent diodes.⁹ Very large Stokes shifts from 100 to 180 nm are observed for all polymers. The intense photoluminescence can be related to the non-planar structure of the polymeric chain leading to lower chain interactions and preventing photoluminescent centres from packing.¹²

In summary, chiral conjugated polymers containing the rigid (*1R,2R*)-diiminocyclohexane showed physical characteristics and properties consistent with a low degree of interaction between the conjugated segments. They are highly soluble and show very high specific optical rotation, strong Cotton effect, low crystallinity and similar absorption spectra in solution and in the solid state. These results support low π -stacking interactions which can be derived from the existence of a helical conformation of the polymer chain. The high photoluminescence quantum yield (30%) observed for **7**, associated with its good ability to form homogeneous films on glass, opens interesting possibilities to fabricate green light emitting diodes.

Notes and references

† Selected characterization data for **5**: Yield: 79%; GPC: $M_w = 22830$ and $M_n = 10870$ (PDI = 2.1), $DP_n = 19$; $[\alpha]_D = -3194^\circ$ ($c = 0.72$, THF); $^1\text{H NMR}$ (δ , ppm, CDCl_3): 0.86 (3H, t, $J = 5 \text{ Hz}$, CH_3), 1.28 (12 H, broad singlet, H_{octyl} and $\text{H}_{\text{cyclohexyl}}$), 1.6 (2H, m, H_{octyl}), 1.84 (6H, broad singlet, $\text{H}_{\text{cyclohexyl}}$), 2.65 (2H, t, $J = 6.6 \text{ Hz}$, th- CH_2), 3.28 (2H, broad singlet, $-\text{CH}-\text{N}$), 7.02 (1H, s, H_{th}), 7.05 (2H, broad singlet, H_{th}), 7.10 (2H, broad singlet, H_{th}), 8.17 (2H, s, $-\text{CH}=\text{N}-$). ν_{max} ($\text{KBr}/\text{cm}^{-1}$): 1627 (C=N); absorption (CHCl_3) λ_{max} (nm) ($\epsilon_{\text{max}}/\text{l mol}^{-1} \text{ cm}^{-1}$) 403 (39075), 280 (14890), 242 (14681); absorption (film on glass) λ_{max} (nm) 403; emission (THF) λ_{max} (nm) 447, 474 (excitation $\lambda_{\text{max}} = 400 \text{ nm}$); solid state emission λ_{max} (nm) 584 (excitation $\lambda_{\text{max}} = 405 \text{ nm}$); CD(CHCl_3) λ_{max} (nm) ($\theta/10 \text{ deg cm}^2 \text{ mol}^{-1}$) 415.8 (-2.87×10^5), 363.2 (6.82×10^4), 305.9 (1.58×10^4), 280.9 (5.58×10^4).

Selected characterization data of **6**: Yield: 79%; GPC: $M_w = 25800$ and $M_n = 12500$ (PDI = 2.06), $DP_n = 18$; $[\alpha]_D = -2200^\circ$ ($c = 0.95$, THF); $^1\text{H NMR}$ (δ , ppm, CDCl_3): 0.85 (6H, broad singlet, CH_3), 1.20–1.5 (22 H, multiplet, H_{octyl} and $\text{H}_{\text{cyclohexyl}}$), 1.78–1.85 (10H, broad singlet, H_{octoxy} and $\text{H}_{\text{cyclohexyl}}$), 3.31 (2H, broad singlet, $-\text{CH}-\text{N}$), 3.98 (4H, t, $J = 6 \text{ Hz}$, O- CH_2), 6.93 (2H, s, H_{phenyl}), 7.05 (2H, s, H_{th}), 7.11 (2H, s, H_{th}), 8.17 (2H, s, $-\text{CH}=\text{N}-$); ν_{max} ($\text{KBr}/\text{cm}^{-1}$): 2196 (C=C), 1627 (C=N); absorption (CHCl_3) λ_{max} (nm) ($\epsilon_{\text{max}}/\text{l mol}^{-1} \text{ cm}^{-1}$) 403 (41270), 342 (24300), 261 (15333), 241 (16700); absorption (film on glass) λ_{max} (nm) 404; emission (THF) λ_{max} (nm) 449, 473 (excitation $\lambda_{\text{max}} = 402 \text{ nm}$); solid state emission λ_{max} (nm) 505 (excitation $\lambda_{\text{max}} = 400 \text{ nm}$); CD(CHCl_3) λ_{max} (nm) ($\theta/10 \text{ deg cm}^2 \text{ mol}^{-1}$) 425.4 (-3.36×10^5), 374.4 (6.23×10^4), 351.7 (-1.69×10^4), 322.5 (1.11×10^5), 271.5 (4.30×10^4).

Selected characterization data of **7**: Yield: 79%; GPC: $M_w = 13600$ and $M_n = 8500$ (PDI = 1.45), $DP_n = 13$; $[\alpha]_D = -825^\circ$ ($c = 0.78$, THF); $^1\text{H NMR}$ (δ , ppm, CDCl_3): 0.83 (6H, broad singlet, CH_3), 1.20–1.5 (22 H, multiplet, H_{octyl} and $\text{H}_{\text{cyclohexyl}}$), 1.78–1.85 (10H, broad singlet, H_{octoxy} and $\text{H}_{\text{cyclohexyl}}$), 3.41 (2H, broad singlet, $-\text{CH}-\text{N}$), 3.98 (4H, t, $J = 6 \text{ Hz}$, O- CH_2), 6.97 (2H, s, H_{phenyl}), 7.46 (4H, d, $J = 8.6 \text{ Hz}$, H_{ph}), 7.57 (4H, d, $J = 8.3 \text{ Hz}$, H_{ph}), 8.18 (2H, s, $-\text{CH}=\text{N}-$); ν_{max} ($\text{KBr}/\text{cm}^{-1}$): 2198 (C=C), 1641 (C=N); absorption (CHCl_3) λ_{max} (nm) ($\epsilon_{\text{max}}/\text{l mol}^{-1} \text{ cm}^{-1}$) 379 (39154), 323 (37667), 243 (24534); absorption (film on glass) λ_{max} (nm) 323, 382; emission (THF) λ_{max} (nm) 428, 446 (excitation $\lambda_{\text{max}} = 380 \text{ nm}$); solid state emission λ_{max} (nm) 505 (excitation $\lambda_{\text{max}} = 381 \text{ nm}$); $\gamma = 1.04^\circ$; CD(CHCl_3) λ_{max} (nm) ($\theta/10 \text{ deg cm}^2 \text{ mol}^{-1}$) 394.5 (-1.21×10^5), 333 (-7.97×10^4), 304 (4.09×10^4), 247.5 (6.16×10^4).

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