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New optically active polyarylene vinylenes: control of chromophore separation by binaphthyl units

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New optically active copolymers containing binaphthyl units to control the conjugation length of the emitting chromophores show intense photoluminescence and high electron affinity.

The design of tailor-made π-conjugated polymers has been a subject of intensive research during the last decade due to their potential applications as novel materials for optoelectronics[1–5] given that they combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers.

The HOMO–LUMO gap in semiconducting polymers is roughly determined by the extent of π-delocalization along the backbone, the so-called effective conjugation length, which is responsible for the emitting properties of these materials. Introduction of non-conjugated segments into conjugated polymer backbones results in confinement of π-electrons in the conjugated fragment. Thus, the conjugation length of conjugated–non-conjugated multiblock copolymers can be effectively tailored by choice of the appropriate chromophores and spacers. Here we use functionalized chiral binaphthyl monomers as the non-conjugated spacer in conjugated–non-conjugated polymers **1**–**3** (Fig. 1).

Binaphthyl derivatives are optically active materials, their chirality being derived from the restricted rotation of the two naphthalene rings. The angle between the rings ranges from 60 and 120° and therefore, conjugation between the two naphthalene units is minimal.[6] Thus, the conjugated system in polymer containing binaphthyl units is confined to the region between two binaphthyl units [Fig. 1(*a*)].[7,8] The structure of these block-copolymers can be schematically represented as in Fig. 1(*b*) with consecutive conjugated systems linked to each other in a non-coplanar way.

In order to obtain processible polymeric materials, long alkoxy chains have been introduced as substituents on the monomeric units. Especially interesting is the presence of CN groups on the vinylene bridges of poly(arylenevinylenes), which is known to result in an increase in the electron affinity of polymeric materials for light emitting diodes (LEDs) with air stable electrodes.[9] The preparation of this prototype main chain chiral, cyano-containing binaphthyl-based copolymers was carried out using the Knoevenagel condensation[9] of appropriately functionalized binaphthyl (**4**, **5**) and naphthalene (**6**, **7**) monomers. Polymer **1** was obtained by reaction of the new bis(cyanomethyl)-substituted binaphthyl (**4**) with dialdehyde **5**. When **4** was reacted with 1,5-bis(hexyloxy)naphthalene-2,6-dicarbaldehyde (**7**)[10] under analogous conditions, polymer **2** was obtained. Reaction of binaphthyl dialdehyde (**5**) with 2,6-bis-(cyanomethyl)-1,5-bis(hexyloxy)naphthalene (**6**)[10] afforded polymer **3**.

Polymers **1**–**3** were obtained as orange solids in good yields (90, 80 and 75% respectively) with optical HOMO–LUMO onsets of 2.53 eV for **2**, 2.64 eV for **3** and 2.76 eV for **1**, measured *via* their UV-Vis absorption spectra (in CH_2Cl_2 solution). Gel permeation chromatography (GPC) against polystyrene revealed a weight average (M_w) of *ca.* 164 000 and a number average (M_n) of 22 000 (polydispersity (pd) = 7.62) for polymer **1**. Polymer **2** had the lowest mass (M_w = 15 300 and M_n = 9400, pd = 1.62). Polymer **3** presented M_w = 27 500 and M_n = 12 200 (pd = 2.27). Polymers were fully characterized using ^{1}H NMR, ^{13}C NMR, FTIR, and UV-Vis measurements. The infrared spectra displayed the characteristic CN stretching frequency at around 2212 cm^{-1} for the three polymers. ^{1}H NMR measurements exhibit the characteristic singlet of the vinylene proton at around δ 8.1 together with the expected signals of the naphthalene units and the alkoxy chains.†

Polymers were synthesized by using enantiomerically pure (*S*)-binaphthyl derivatives (**4**, **5**) and therefore main chain chiral polymers have been obtained. The observed optical rotations ($[\alpha]_D$) are 305 (*c* 0.2, $CHCl_3$) for (*S*)-**1**, 832 (*c* 1.3, $CHCl_3$) for (*S*)-**2** and 220 (*c* 0.7, $CHCl_3$) for (*S*)-**3**. Thus, these polymers rotate the plane of polarized light in the opposite direction to the binaphthyl dicyanomethyl-substituted species (*S*)-**4**, {$[\alpha]_D$ −34

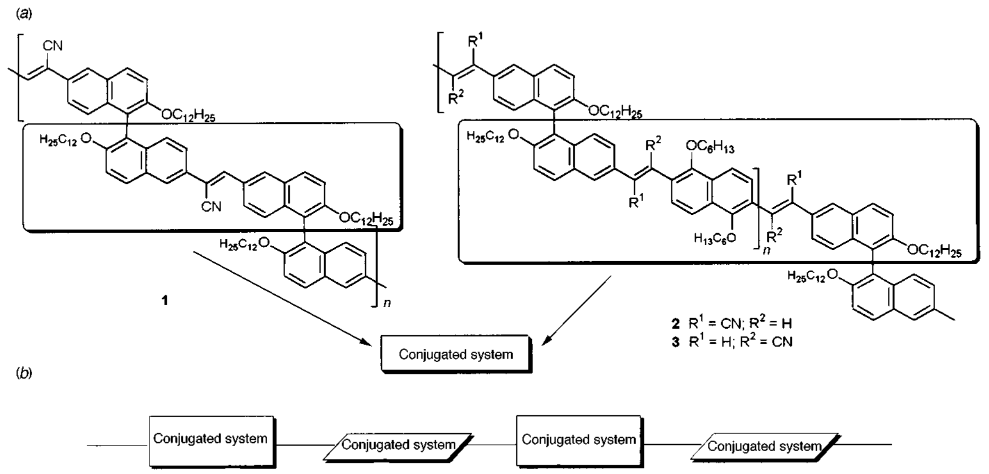
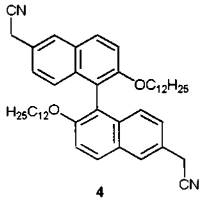


Fig. 1 (*a*) New block co-polymers showing the conjugated systems between binaphthyl units and (*b*) schematic representation of the polymers.



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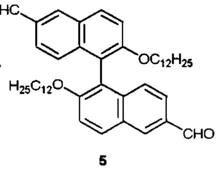

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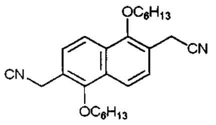

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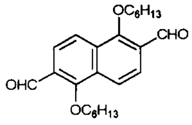

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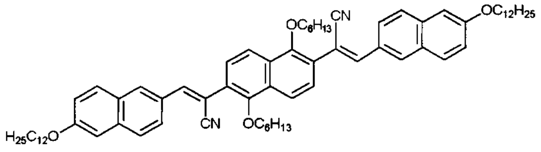

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(c 0.6, $CHCl_3$)} and in the same direction as the binaphthyldicarbaldehyde (S)-**5** {$[\alpha]_D$ 56 (c 0.7, $CHCl_3$)}.

Cyclic voltammetry studies of polymers **1–3** were carried out in CH_2Cl_2 at room temperature using Bu_4NClO_4 as supporting electrolyte (0.3 mg ml^{-1}, SCE reference electrode and glassy carbon as the working electrode). It was found that all the polymers are oxidized at potentials above 1.2 V (*vs.* SCE) which is high compared with other conjugated polymers (0.6–1.0 V).[11] On the other hand, all the polymers were found to be reducible at potentials around -1.5 V (*vs.* SCE). The relatively good acceptor ability of these polymers can be ascribed to the presence of the cyanovinylene moieties on the conjugated system. As it was previously stated, high electron affinity materials are of special interest for the manufacture of LEDs providing that they can be used in combination with air stable electrodes, thus increasing device life time.[9]

The absorption maximum of these polymers increases from **3** (λ_{max} 378 nm) to **1** (λ_{max} 382 nm) to **2** (λ_{max} 422 nm). These polymers emit strong blue–green light under an UV lamp. The fluorescence spectrum of **1** shows emission maxima at λ_{emi} 475 nm when excited at 382 nm. The fluorescence spectrum of **2** displays λ_{emi} 496 nm when excited at 422 nm and **3** exhibits an emission maxima of λ_{emi} 485 nm when excited at 378 nm. Two factors may be considered in order to rationalize the observed absorption and emission data. First, there is the extension of the conjugated system, which for polymer **1** comprises two naphthalene units linked by a cyanovinylene group and for polymers **2** and **3** includes three naphthalene units linked by two cyanovinylene moieties. Second, there is the steric hindrance of the hexyloxy substituents with respect to the cyano groups in polymer **3** which may cause torsion of the chain, reducing the planarity of the backbone and therefore decreasing the degree of conjugation.[12] Thus, the more red-shifted absorption and fluorescence values, which may be correlated to a longer effective conjugation length, are observed for polymer **2** which has three naphthalene units conjugated through two cyanovinylene bridges and does not have alkoxy substituents in positions adjacent to the cyano groups. In polymer **3** the absorption and emission values are blue shifted in comparison with polymer **2**, probably as a consequence of the already mentioned steric hindrance. The blue shift of the absorption and emission in polymer **1** with respect to polymer **2** may be rationalized in terms of a shorter conjugated system.

In order to ascertain that the conjugated system in the new polymers is really confined to the region between the two binaphthyl moieties (Fig. 1), we have determined by semiempirical calculations (PM3) the angle of rotation between the two naphthyl moieties of binaphthyl in a model compound constituted by the conjugated system of **3** end-capped by two naphthyl groups. The found values (85.7 and 92.1°) strongly suggest the lack of conjugation. Furthermore, we have synthesized compound **8**, which is the repetitive conjugated unit of polymer **3** (Fig. 1) in order to determine its UV-Vis spectrum. The data obtained (λ_{max} 380 nm) are in full agreement with that obtained for the related polymer **3** (λ_{max} 378 nm), showing the same onset value.

In summary, new optically active block copolymers containing binaphthyl units have been synthesized. They show an intense photoluminescence and a high electron affinity and therefore they are promising candidates for the fabrication of light emitting diodes. The main chain chiral character of these polymers may enable the observation of circularly polarized photo- and electroluminescence, which has not so far been reported.[13] Finally, a remarkable aspect of this contribution is that it might provide an effective approach to the synthesis of polymeric luminescent materials in which the emissive colors can be effectively tailored by reacting different appropriately functionalized fluorophores with binaphthyl monomers *via* Knoevenagel condensation polymerization.

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Notes and references

† Polymers **1**–**3** were characterized on the basis of the FTIR, ^1H and ^{13}C NMR analyses for which satisfactory results were obtained. *Selected data* for **2**: ν_{max}(KBr)/cm^{-1} 3060, 2855, 2214, 1682, 1621, 1593, 1038, 937, 762, 697, 603, 496; δ_H($CDCl_3$, 300 MHz) 8.44 (d, 2H, J 9), 8.30 (s, 2 H, =CH or Ar), 8.18 (s, 2H, Ar or =CH), 8.07 (d, 2H, J 9), 8.00 (d, 2H, J 8.8), 7.61 (d, 2H, J 9.2), 7.51 (d, 2H, J 9.2), 7.26 (d, 2H, J 8.8), 4.03 (m, 8H, OCH_2), 1.9 (m, 4H, CH_2), 1.5 (m, 4H, CH_2), 1.4–0.9 (m, 48H, CH_2), 0.8 (m, 12H, CH_2); δ_C($CDCl_3$, 75 MHz) 155.9, 155.6, 135.0, 134.2, 130.2, 129.3, 128.8, 126.7, 126.3, 125.0, 124.8, 122.4, 119.8, 119.1, 118.1, 117.5, 116.1, 112.6, 77.1, 69.4, 31.8, 31.6, 30.3, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 25.9, 25.6, 22.6, 22.5, 14.0, 13.9.

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