Confined photoactive substructures on a chiral scaffold: the design of an electroluminescent polyimide as material for PLED**†

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The optical and electroluminescent properties of a new chiral electroluminescent polyimide consisting of alternating conjugated segments and chiral units is described. The synthesized polymer exhibited high thermal stability (Td = 350 °C), high electron affinity, and good thin-film forming ability. The C2 symmetry of the chiral unit induces a secondary structure which reduces all types of intra and interchain interactions. The incorporation of a well-defined phenyleneethynylene substructure within the chiral backbone allowed the fabrication of a monolayer electroluminescent polymeric diode with high performance which compares most favorably to related poly-phenyleneethynylene.

Introduction

During the past decade, several polymeric materials suitable for light-emitting devices have been developed.¹ Such devices require highly efficient luminescent materials with good thermal and photochemical stability.

Although aromatic polyimides (APIs) have been extensively studied as high-performance polymers for their unique mechanical, dielectric and optical properties as well as thermal and chemical stability,² few attempts have been made to use them for the purpose of light-emitting diodes. Uses are limited to the transporting layer or dye doped matrix in electroluminescent devices.³

On the other hand, chiral polymers today are of great interest owing to their structure and supramolecular arrangement controlling their optoelectronic properties.⁴ Recently, conjugated polymers incorporating a C_2 symmetry binaphtyl unit were reported for diverse applications such as electroluminescence, non-linear optics, chiral sensors and asymmetric catalysis.⁵ In a previous paper, we reported the synthesis of a soluble chiral conjugated polyimine based on *trans*-(1*R*,2*R*)-1,2-cyclohexyldiamine with good luminescence properties.⁶ The incorporation of a well-defined conjugated segment in the chiral backbone prevents stacking of the conjugated units minimizing the self-quenching processes of excitons. Unfortunately, their low glass transition and HOMO–LUMO levels precluded the fabrication of a polymeric light emitting diode (PLED).

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We describe here the first synthesis and electroluminescent characterization of a novel phenyleneethynylene-based polyimide which combines thermal stability and a C_2 chiral structure with a confined chromophore. We focus on conjugated oligophenyleneethynylenes which are chemically and thermally more stable than polyphenylenevinylenes but usually afford low efficiency devices. Its incorporation in a chiral backbone should allow control of the undesired inter- and intrachain interactions.

Results and discussion

Synthesis and characterisation

In order to avoid the high temperature treatment usually required in the classical synthesis and casting of polyimides, we designed a different strategy involving low temperature organometallic coupling of aromatic and conjugated units (cf. Scheme 1). Thus, the imide function was first introduced on the chiral unit by condensation of the bromophthalic anhydride 1^7 and the *trans*-(1*R*,2*R*)-1,2-cyclohexyldiamine⁸ to give the chiral halo-imide 3.[†] Finally, 3 readily underwent coupling with the conjugated 1,4-diethynyl-2,5-bis(octyloxy)benzene 4⁹ in the presence of palladium catalyst and provided high molecular weight conjugated polymer 6. The polymer was separated from the low weight oligomers by a precipitation with methanol from a THF solution and gel permeation chromatography (THF, polystyrene standard) analysis showed $M_{\rm w} = 15000$ and $M_{\rm n} = 8500$ (PDI = 1.76). These values correspond to an average of 11 repeating units per polymeric chain. Unlike conventional fully aromatic polyimides, this new material with a confined chromophore alternating with chiral units is highly soluble in common organic solvents, highly fluorescent and emits greenish blue light when irradiated. The related low molecular weight model compound 5 was synthesized for comparison in a similar manner using the haloimide 2 instead of 3.†

Thermal stability is one of the most important requirements in PLEDs, because the joule-heat generated by the device

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Scheme 1 Synthetic route of 5 and 6.

severely relaxes and damages organic materials. Thermogravimetry (TGA) of the conjugated segment **5** and the polymer **6** were studied in air with a heating rate of 10 °C min⁻¹.† Both products show a decomposition onset above 350 °C; the losses of mass below this temperature are lower than 5%. Beyond 350 °C, a first weight loss, corresponding to the fragmentation of the side chains (C₈H₁₇), was observed. After this stage, degradation occurred at a slower rate. Thus, the polymer shows a very good thermal stability bearing in mind that this property could be optimized quite simply by modifying the nature of side chains since the C–O bond constitutes a breaking point.

Moreover, to use polyimide 6 as an electroluminescent layer, it is necessary to detect the existence of a crystalline or glass (T_g) transition. Indeed, this type of transition in the range of operating temperatures of diodes affects their lifetime. We studied the isolated segment 5 and the polymer 6 by Differential Scanning Calorimetry (DSC) in a range of temperatures from -120 °C to 250 °C.† Recordings were carried out in nitrogen with a heating rate of 20 $^{\circ}$ C min⁻¹. DSC measurements on polymer 6 showed neither any crystalline transition nor T_{g} in the studied range of temperature. On the other hand, the thermogram dedicated to compound 5 showed an endothermic transition at 211 °C signifying its melt and an exothermic transition at 161 °C indicative of its recrystallization. The stabilization of the polymer 6, in the solid state, can be explained by the rigidity introduced by imide functions but also by the cooperative effect of Van der Waals interactions existing between side chains. These latter interactions reduce polymeric inter-chain slips. In any case, considering its thermal, chemical and morphological stability, the polymer is an excellent candidate for future applications.

Structural properties

X-Ray diffraction diagrams of **6** only showed 3 broad signals ($2\theta = 5.4, 12.2, 20.7^{\circ}$) characteristic of an amorphous material.† Conversely, **5** revealed several diffraction peaks indicative of a crystalline product. This behavior is consistent

with lower order and stacking of the conjugated segment in the polymer compared to the isolated segment in the monomer. Small needles of **5** were grown from the evaporation of a chloroform solution and microdiffraction patterns were recorded at the Microfocus Beamline ID13 (European Synchrotron Radiation Facility – ESRF, Grenoble). **5** crystallizes in a triclinic system with a $P\bar{1}$ space group. One independent half molecule is located on an inversion centre (Fig. 1).

The three benzene rings (**A**, **B** and **B**') linked by triple bonds are mostly coplanar with a dihedral angle C(15)–C(14)–C(10)– C(9) 14.06(18)°. On the other hand, the plane defined by the cyclohexane ring is orthogonal to this aromatic system (**B**–**A**–**B**') with a rotation angle C(23)–C(27)–C(14)–C(16) 90.47(12)°. Substitution in position 4 of phthalimides **B** and **B**' can be at the origin of two conformations, both groups **B** and **B**' can be in *trans* position relative to the **B**–**A**–**B**' axis or in *cis* position. The *trans* conformation appears to be the most stable geometry in the solid state. In the crystal, molecules form layers separated by side chains and the cyclohexyl fragments along the *c* axis (Fig. 2). Each molecule belongs to a



Fig. 1 Molecular structure of compound 5: anisotropic displacement parameters are drawn at the 50% probability level. Distances [Å] and angles [°] (with standard deviations in parentheses): C(12)-C(13) 1.216(2) Å, C(13)-C(14) 1.433(2) Å, C(18)-C(21) 1.504(2) Å, C(19)-C(20) 1.503(2) Å, C(15)-C(14)-C(10)-C(9) 14.06(18)°, C(23)-C(22)-N(1)-C(21) 62.63(23)°, C(23)-C(27)-C(14)-C(16) 90.47(12)°.



Fig. 2 Packing arrangement of 5: layers separated by the side chains and the cyclohexyl fragments developing along the c axis.

chain of interactions (dotted lines) which develops along the *b* axis through phthalimide groups. The layers are stabilized by π -stacking interactions in the *ab* plane between phthalimide residues **B** and **B'** (dotted lines) and between aryl rings **A** and the triple bonds (broken lines) (Fig. 2).

The perpendicular distance (3.25 Å) between two molecules and the shortest intermolecular contact distances C(17)– C(15)_(1+x, y, z) 3.275 Å and C(16)–C(21)_(1-x, 2-y, 1-z) 3.378 Å indicate very strong intermolecular interactions and large orbital overlap between neighbouring parallel molecules although the overlap between aromatic rings is small. This behaviour should result in an enhanced conjugation length due to these intermolecular π -stacking interactions.

An indication of the structure of the polymeric material 6 can be deduced from the specific optical rotation and circular dichroism measurements.

The specific optical rotation of **6**, $[\alpha]_D^{20} = -452^\circ$ (c = 1, dioxane), was found to be higher in comparison with the chiral bis-phthalimide **3** ($[\alpha]_D^{20} = -186.5^\circ$ (c = 0.97, CHCl₃ or dioxane). This value, three times higher, could be the result of a secondary structure of helix type.

In addition, unambiguous determination of the stereostructure of the bichromophoric system and, hence, consistency of the (1R, 2R) absolute configuration and conformation of the cyclohexyldiamine was given by circular dichroism spectroscopy carried out on polymer 6. Indeed, the absolute configuration of chiral β -bis-phthalimides is readily correlated with the degenerate exciton Cotton effects resulting from the intramolecular interaction of the electric-dipole-allowed transition moments of two vicinal phthalimide chromophores linked by a cyclohexyldiamine (below 260 nm, π – π * band).¹⁰ The CD spectrum of a 10 μ M solution of 6 in dioxane (Fig. 3) displays four sets of Cotton effects around 232 (exciton-type), 254, 298 and 404 nm which correspond to the position of the absorption maxima in the UV spectrum (see below). Its molecular ellipiticities were: $[\theta]_{\lambda} = 5.55 \times 10^4$ (222 nm) and $-4.90 \times$ 10^4 (242 nm), -4.22×10^4 (254 nm), -2.93×10^4 (298 nm), -2.85×10^4 (404 nm). Based on correlations established by Gawroński,¹¹ the negative sign of the exciton Cotton effect corresponding to the π - π * charge-transfer transition located at 232 nm ($\varepsilon = 77300 \text{ M}^{-1} \text{ cm}^{-1}$), is in agreement with the (1*R*, 2R) absolute configuration and reveals that transition dipole



Fig. 3 CD spectra of 3 and 6 in dioxane at 20 °C ($c \approx 10 \ \mu\text{M}$) and relation between the sign of the exciton Cotton effects and the absolute configuration.

moments of two vicinal phthalimide chromophores linked by a cyclohexyldiamine are coupled. This implies that imides are in close proximity allowing charge mobility (Fig. 3).

For polymer **6**, the characteristic features of the di-imide linkage are observed. The negative Cotton effect observed at lowest wavelength is in full agreement with the exciton theory of chiral bichromophoric systems as described by Harada and Nakanishi.¹² However, a bisignate CD effect is not observed in the region of absorption of the π conjugated chromophore (404 nm). For a helical polymer one would expect a so-called bisignate Cotton effect at the π - π * transition.¹³

Molecular modeling using the MM2 force field of polyimide 6 consisting of 11 repeating units (value deduced from the GPC analysis) yielded two low-energy structures of C₂ symmetry which could be described by two types of helical shapes: C-shape and S-shape.[†] In both cases, the phthalimide groups connected by the 1,4-diethynyl-2,5-bis(octyloxy)benzene segment are in a trans geometry and the C or S conformations are the result of a rotation of these phthalimides around the C-N bond. The aromatic segments are fully isolated from each other. Owing to the CD measurements, 6 certainly adopts less ordered secondary structures. Indeed, due to the substitution of the phthalimide group in position 4, other polymeric arrangements could be considered, but in this case, their low degree of symmetry results in an increase of their total energy. This is supported by the crystal structure of 5 which reveals a trans configuration of the phthalimide functions along the long axis of the conjugated segment (cf. Fig. 1).

Optical and photoluminescence properties

The UV-vis spectra of **5** and **6** in solution (CH₂Cl₂) and as thin films (obtained by spin coating from a 20 mg mL⁻¹ chloroform solution) are shown in Fig. 4. The confinement of the conjugated chromophore between two chiral units resulted in very similar optical absorption and emission properties for the monomer **5** (CH₂Cl₂, $\lambda_{abs_max} = 403$ nm; $\lambda_{em_max} = 504$ nm ($\lambda_{ex} = 400$ nm)) and the polymer **6** [CH₂Cl₂, $\lambda_{abs_max} = 406$ nm; $\lambda_{em_max} = 508$ nm ($\lambda_{ex} = 400$ nm)] in solution. By comparing the ratio of the fluorescence emission intensity maximum to UV absorbance at the excitation wavelength used for the sample with that of a standard,¹⁴ the relative fluorescence

Fig. 4 UV-vis absorption and emission spectra of 5 and 6: solution in on 5.

CH₂Cl₂ and thin films.

quantum yields of **5** and **6** were measured in chloroform solutions. Very similar values were obtained ($\Phi_{\rm f5} = 0.28$ and $\Phi_{\rm f6} = 0.31$).¹⁵

In the solid state, thin films of 5 and 6, realized by spincoating from 20 mg mL⁻¹ solutions in CHCl₃ on a quartz substrate, exhibited different behaviors. Compared to the solution, the absorption of the isolated conjugated unit 5 showed a red-shift of the maximum wavelength ($\Delta \lambda = 45$ nm). This behavior can be attributed to an enhanced conjugation due to intermolecular π -stacking interactions in the solid state as already deduced from the X-ray diffraction study. It is worth noticing that the polymer showed identical absorption bands in CH₂Cl₂ solution and in the solid state, signifying the absence of interchain π -stacking interactions within the polymeric solid. This is consistent with the presumed helical structure deduced from the molecular modeling. The C_2 symmetry, introduced by the chiral unit, results in the transposition of the optical properties from the solution to the solid. This behavior indicates that the conjugated segments are fully isolated in the solid state. However CD measurements showed that charge transport should be effective through the overlap of the two vicinal phthalimide moieties. The use of such a chiral polymer is a very convenient and interesting way to circumvent problems arising from the recrystallization of small molecules or aggregation of polymeric chains during LED processing. Although phenyleneethynylenes are chemically and thermally more stable than phenylenevinylenes (PPVs), they offer devices with poor performances (300 Cd m⁻² for the best one compared to 2000 Cd m⁻² for most PPVs).¹⁶ This is the result of their rod like structure which favors fully aggregated and well packed chains giving very low luminescence quantum yield efficiency. The coplanar orientation of the conjugated polymer backbones is assumed to lead to the formation of excimer complexes which provide nonemissive decay channels for excited states. Nonemissive orientations are more significant in materials with a higher degree of long range order.¹⁷

Electroluminescence properties

Light emitting diodes have been made using polymer **6** and using monomer **5**. **6** was dissolved in xylene which is a commonly used solvent. The solution (30 mg mL⁻¹) is homogeneous and transparent. **6** was highly soluble compared to related PPVs. Conversely, **5** was not soluble in xylene. Therefore, to enable the comparison of the LEDs, thin films of **5** were prepared by vacuum evaporation, whereas thin films of **6** were obtained by spin-coating. Both films were controlled to be 100 nm thick. The structures of the LEDs, described in Scheme 2, are as follows: ITO/PEDOT-PSS/**6**/Ca/A1 and ITO/PEDOT-PSS/**5**/Ca/A1.

LUMO and HOMO levels have been measured by cyclic voltammetry at -3.64 eV and -5.76 eV, respectively, for **6** and at -3.04 eV and -5.46 eV, respectively, for **5** (Scheme 2). From such electronic structures, it is believed that charge carrier injection may differ. The energetic barrier at the anodic interface is higher in a PLED based on **6** than in a device based on **5**. Hole injection is then easier in **5**. At the cathodic interface, electron injection from calcium is not limited by any





Scheme 2 PLED and OLED structures of (a) 5 and (b) 6.

energetic barrier in both cases. As a consequence, charge balance is better in **5** than in **6**. On only this basis, higher performances were expected with **5**.

Fig. 5 shows the measured current-voltage-luminance characteristics (I-V-L) of devices based on 5 and on 6. With 6, good luminance levels are obtained for voltages lower than 20 V (1500 Cd m⁻² @ 10.5 V) and the onset voltage is observed at 5.5 V. With 5, a 27 V onset voltage is revealed. Much smaller luminances are observed due to smaller current densities. Values of 125 Cd m⁻² are only observed at 35 V. Such very high applied voltages are consistent with poor performances of 5-based devices. As a consequence, the injection related data reported above are not sufficient to predict the performance of PLEDs. We believe that 5 present a poor ability to emit light due to π -stacking which induces quenching of luminescence. The use of 6 is therefore an interesting alternative to avoid such π -stacking and to significantly increase LEDs performances. Another parameter controlled by the use of 6 lies in the quality of the electroluminescent layer deposited. Indeed, the small molecule 5 tends to crystallise during the vacuum evaporation process and generates some grain boundaries known to be drastic for the OLEDs performances.

Electroluminescence (EL) spectra have been measured with both materials **5** and **6**. They are centred at 510 nm and 564 nm respectively. These EL spectra are in agreement with HOMO and LUMO level positions deduced by cyclic voltammetry since they provide a bandgap width of 2.45 eV for **5** and



Fig. 5 I-V-L Curves of ITO/PEDOT/5 or 6/Ca/Al diodes. Inset: electroluminescence and photoluminescence spectra of 6.

2.20 eV for 6. The observed light is blue and pale green for 5 and 6 respectively. The chromatic coordinates calculated from the EL spectra are reported at x = 0.27/y = 0.55 for 5 and at x = 0.46/y = 0.51 for 6 following the CIE-1964 chromaticity diagram. The red shift observed only in the emission spectra (photoluminescence and electroluminescence) of 6 could find its origin in the fact that two imide functions grafted on the same cyclohexyl fragment are in interaction. Indeed the C2 symmetry of the chiral unit bring them in close contact and CD measurements showed that they are coupled in the excited state. The red shift observed in the photoluminescence spectrum of 6 from the solution to the solid state (Fig. 4, $\Delta \lambda = 10$ nm) is even bigger in the electroluminescence spectrum (Inset Fig. 5, $\Delta \lambda = 40$ nm) suggesting that the electric field induced by the electroluminescence process activates this exciton coupling. This effect related to built-in electric fields has already been observed.¹⁸

Conclusion

In summary, the synthesis and characterization of a new chiral conjugated polyimide 6 was carried out. This new polymer is soluble in common organic solvents and emits green light upon irradiation. Its optical behaviour was also evaluated by comparison with its respective repeat unit. The C_2 symmetry of the chiral unit induces secondary structures which reduce all types of intra and interchain interactions. The high thermal stability, the ability to cast thin polymer layers directly from solution with excellent film-forming properties and efficient EL make the chiral polyimide of potential interest for technological applications. The incorporation of a well-defined oligo-phenyleneethynylene structure within the chiral backbone allowed fabrication of monolayer electroluminescent polymeric diodes with high performance, whereas the corresponding poly-phenyleneethynylene is not efficient when used as an emissive layer in electroluminescent devices.

Experimental

Materials and methods

All the reactions were performed under nitrogen atmosphere using Schlenk tube techniques. The solvents were distilled under nitrogen over Na-benzophenone (THF), KOH (NEt₃) and P₂O₅ (CH₂Cl₂) prior to use. Optically active trans-(1R,2R)-1,2-cyclohexyldiamine was obtained enantiomerically pure from the commercial racemic cis/trans mixture according to literature procedure.¹⁹ 4-Bromophthalic anhydride (1) was prepared according to Hollingsworth's procedure.²⁰ 1,4-Bis(octyloxy)-2,5-di(ethynyl)benzene (4) was synthesized according to the reported procedure.²¹ Analytical data were in good agreement with the literature. NMR (¹H and ¹³C) spectra were recorded on a Bruker AC 200 spectrometer and CDCl₃ was used as solvent. Chemical shifts (δ), reported in parts per million, are relative to tetramethylsilane. Signal multiplicities: s(singlet), bs(broad singlet), d(doublet), dd(doublet of doublet), t(triplet), tt(triplet of triplet), m(multiplet). IR spectra were recorded on a Perkin-Elmer 1000 FTIR spectrometer using KBr pellets. UV-vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F2500. Optical rotation were measured on a Perkin-Elmer Polarimeter 241. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS in Vernaison (France). Mass spectra were measured on a JOEL MS-DX 300 mass spectrometer utilising *m*-nitrobenzyl alcohol (3-NOBA) as the matrix. GPC measurements were made on a Waters device equipped with HR₂ and HR₃ styrragel columns using THF as eluent. Melting points were measured with an Electrothermal 9100 apparatus.

Synthesis

N-(4-Bromophthaloyl)-cyclohexylamine (2). To a solution of bromophthalic anhydride 1 (1 g, 4.4 mmol) in toluene (150 mL) was added cyclohexylamine (0.5 mL, 4.4 mmol) followed by triethylamine (0.5 mL, 3.6 mmol). The mixture was refluxed under a Dean-Stark trap for 24 h. The cold colorless solution was evaporated and the residue was recrystallized from MeOH. 1 g (yield 74%) of 2 was obtained as a white crystalline solid, mp 140 °C (MeOH); ¹H NMR (CDCl₃) δ 1.29 (m, 2H), 1.80 (m, 4H), 2.18 (m, 2H), 4.05 (tt, J = 3.6, 12 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.78 (dd, J = 1.8, 8.0 Hz, 1H), 7.89 (d,J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 24.97, 25.87, 29.69, 51.07, 124.30, 126.27, 128.48, 130.48, 133.61, 136.62, 166.89, 167.45; IR (KBr) 3084, 2932, 2856, 1768, 1708, 1369, 1351, 1092, 739 cm⁻¹; UV (MeCN) ε 12 (301 nm), 16400 sh (251 nm), 22000 sh (242 nm) 48300 (230 nm); Anal. Calcd for C₁₄H₁₄BrNO₂: C, 54.56; H, 4.58; N, 4.55; O, 10,38. Found C, 54.63; H, 4.25; N, 4.42; O, 10.66%; m/z (FAB+) (%): 308 (M + H, 100), 309 (15), 310 (94).

N,N'-Bis(4-bromophthaloyl)-(1R,2R)-1,2-diaminocyclohexane (3). To a solution of bromophthalic anhydride 1 (4.54 g, 20 mmol) in toluene (150 mL) was added (1R,2R)-1,2diaminocyclohexane (1.15 g, 10 mmol) followed by triethylamine (140 µL, 1 mmol). The mixture was refluxed under a Dean-Stark trap for 4 h. A white precipitate of the monophthalyol adduct formed. The reaction mixture was cooled to room temperature and the white solid was filtered off to give 700 mg (yield 22%) of the mono-addition product. Concentration of the filtrate under reduced pressure gave a colorless oil which solidified on standing. The bisphthaloyl adduct was isolated by column chromatography on silicagel using methylene chloride as eluent. Yield 1.770 g (33%) of 3, mp 245 °C; $R_{\rm f}$ (silicagel, CH₂Cl₂) 0.4; ¹H NMR (CDCl₃) δ 1.53 (m, 2H), 1.92 (m, 4H), 2.40 (m, 2H), 4.96 (m, 2H), 7.59 (m, 2H), 7.77 (m, 2H), 7.89 (m, 2H); ¹³C NMR (CDCl₃) δ 24.85, 29.12, 51.02, 124.64, 126.60, 128.84, 130.00, 132.50, 136.86, 166.50, 167.05; IR (KBr) 3081, 2933, 2861, 1769, 1719, 1374, 1355, 1098, 739 cm⁻¹; $[\alpha]_D^{20}$ -186.5° (c = 0.97, CHCl₃ or THF); UV (MeCN) & 21800 (278 nm), 32600 sh (250 nm), 42500 sh (240 nm), 78000 (230 nm); Anal. Calcd for C₂₂H₁₆Br₂N₂O₄: C, 49.65; H, 3.03; N, 5.26; O, 12,03. Found C, 50.89; H, 2.83; N, 5.32; O, 12.27%; m/z (FAB+) (%): 531 (M + H, 49), 533 (100), 535 (51).

2-Cyclohexyl-5-{[4-[(2-cyclohexyl-1,3-dioxo-2,3-dihydro-1*H*-isoindol-5-yl)ethynyl]-2,5-bis(octyloxy)phenyl]ethynyl}-1*H*-isoindole-1,3(2*H*)-dione (5). The organometallic coupling of

the halo-phthalimide 2 (322.2 mg, 1.04 mmol) and the 1,4diethynyl-2,5-bis(octyloxy)benzene 4 (200 mg, 0.523 mmol) was performed in the presence of Pd₂dba₃(CHCl₃) (21.7 mg, 0.021 mmol), P(C₆H₅)₃ (22 mg, 0.0837 mmol) and CuI (8 mg, 0.0418 mmol) in a mixture of THF (10 mL) and triethylamine (5 mL). At 70 °C, coupling occurred and the reaction was stirred for three days. The reaction mixture was filtered and concentrated under vacuum. Further purification of the residue by column chromatography on silicagel using a 1 : 1 mixture of cyclohexane and methylene chloride as eluent provided 5 (420 mg, 96%) as a yellow solid. mp = $205-207 \degree C$; ¹H NMR (CDCl₃): δ 7.90 (s, 2H), 7.77 (s, 4H), 7.02 (s, 2H), 4.09 (tt, J = 2.8, 6.8 Hz, 2H), 4.02 (t, J = 5 Hz, 4H), 2.15 (m, 4H), 1.24–1.90 (m, 40H), 0.83 (m, 6H); ¹³C NMR (CDCl₃): δ 167.82, 167.72, 153.86, 136.55, 132.35, 130.80, 129.35, 125.77, 122.98, 116.77, 113.74, 93.62, 90.13, 69.59, 51.07, 31.78, 29.83, 29.33, 29.31, 29.25, 26.06, 25.98, 25.08, 22.64, 14.07; UV-vis (CH₂Cl₂, nm): $\lambda_{abs_max} = 403$; UV-vis (film on quartz, nm): $\lambda_{abs max} = 448$; Fluo ($\lambda_{ex} = 400 \text{ nm}$) (CH₂Cl₂, nm): $\lambda_{em max} =$ 504; UV-vis (film on quartz, nm): $\lambda_{em_max} = 508$; Anal. Calcd for C₅₄H₆₄N₂O₆: C, 77.48; H, 7.71; N, 3.35; O, 11,47. Found C, 77.43; H, 7.83; N, 3.48; O, 11.10%; FAB (*m/z*): M^{+•} 837 (90), 507 (100).

Polymer (6). The polymerization of the chiral halophthalimide 3 (278.3 mg, 0.523 mmol) and the 1,4-diethynyl-2,5-bis(octyloxy)benzene 4 (200 mg, 0.523 mmol) was performed in the presence of Pd₂dba₃(CHCl₃) (21.7 mg, 0.021 mmol), P(C₆H₅)₃ (22 mg, 0.084 mmol) and CuI (8 mg, 0.042 mmol) in a mixture of THF (15 mL) and triethylamine (5 mL). At 70 °C the coupling occurred and provided 6 as an orange solid after five days of heating. The polymer was separated from the low weight oligomers by a precipitation with methanol from a THF solution. This new material 6 was soluble in common organic solvents (THF, CH₂Cl₂, CH₃CN, xylene) and gel permeation chromatography (THF, polystyrene standard) analysis showed $M_{\rm w} = 15000$ and $M_{\rm n} = 8500$ (PDI = 1.76). These values correspond to an average of 11 repeating units per polymeric chain. $[\alpha]_D - 452^\circ$ (c = 1, THF); GPC: $M_{\rm w} = 15000$, $M_{\rm n} = 8500$ (PDI = 1.76); ¹H NMR (CDCl₃): δ 7.72 (m, 6H), 6.97 (s, 2H), 5.00 (m, 2H), 3.99 (m, 4H), 2.41 (m, 2H), 1.23-1.89 (m, 30H), 0.81 (m, 6H); UV-vis (CH₂Cl₂, nm): $\lambda_{abs max} = 406$; UV-vis (film on glass, nm): $\lambda_{abs_max} = 406$; Fluo ($\lambda_{ex} = 400 \text{ nm}$) (CH₂Cl₂, nm): $\lambda_{em_max} =$ 508; UV-vis (film on glass, nm): $\lambda_{em max} = 524$; Anal. Calcd for C₄₈H₅₂N₂O₆: C, 76.57; H, 6.96; N, 3.72; O, 12,75. Found C, 74.04; H, 6.69; N, 3.81; O, 11.87%.

Crystal data for 5

C₅₄H₆₄O₆N₂, triclinic, $P\bar{1}$ (no. 2), a = 5.254(3) Å, b = 14.407(4) Å, c = 16.820(3) Å, $\alpha = 112.813(4)^{\circ}$, $\beta = 90.918(43)^{\circ}$, $\gamma = 99.076(72)^{\circ}$, V = 1154.72 Å³, T = 100(2) K, $R_1 = 0.0658$ for 4426 independent observed reflections [$F > 4\sigma(F_0)$], S = 0.982. Data collection for 11: φ scans, 2° oscillation range, 5 passes of 1.5 s exposure time per image, 90 images, $\lambda = 0.7305$ Å. CCDC reference number 256242. See http://dx.doi.org/10.1039/b503284a for crystallographic data in CIF or other electronic format.

Devices fabrication methods

The structure of the device includes a layer of Indium Tin Oxide (ITO) which is the commonly used transparent electrode for such applications with a sheet resistance of approximately 17 Ω/\blacksquare . This substrate underwent a wet cleaning procedure of successive 30 minute ultrasonic bath treatments in trichloroethylene, ethanol and deionised water at room temperature. Then, a layer of poly(styrene sulfonate) doped poly(3,4ethylene dioxythiophene) (PEDOT-PSS) was spun, from a 3 wt% water dispersion at 5000 rpm to form a 50 nm layer. This conducting polymer layer was cured at 80 °C under rotary pump vacuum for 1 hour. This layer improves hole injection from the ITO to the HOMO level of the organic material and increases the performance of the device. Then, for PLEDs based on 6, the layer of 6 was spin-coated from the 30 mg mL^{-1} solution in xylene at 1000 rpm to form a 100 nm-thick layer. For PLEDs based on 5, the organic layer (100 nm) was thermally evaporated at 10^{-6} mbar at a rate of 1 nm s⁻¹. Finally, a calcium cathode was thermally evaporated under vacuum (10^{-6} mbar) through a shadow mask. This calcium layer (~ 40 nm thick) was capped with an aluminium layer $(\sim 150 \text{ nm thick})$ to minimize its oxidation. All devices investigated here had an active area of 10 mm². Samples were then stored and characterized under inert atmosphere (nitrogen glove box).

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