Confined Photoactive Substructures on a Chiral Scaffold: The design of an Electroluminescent Polyimide as Material for PLED**

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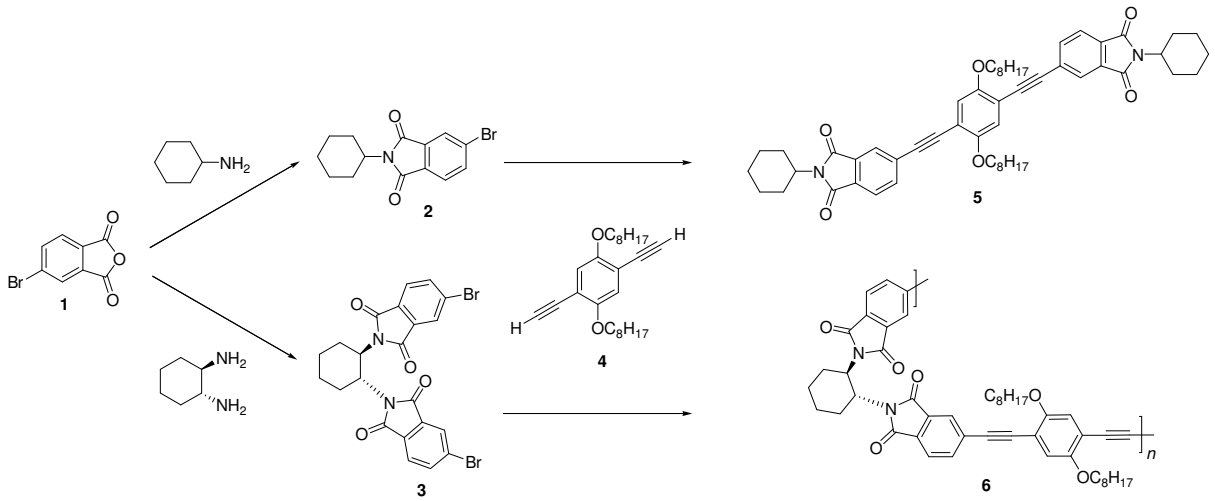
Supporting information

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 (NEt_3) and P_2O_5 (CH_2Cl_2) prior to use. Optically active *trans*-(1*R*,2*R*)-1,2-cyclohexyldiamine was obtained enantiomerically pure from the commercial racemic cis/trans mixture according to literature.[i] 4-Bromophthalic anhydride **(1)** was prepared according to Hollingsworth's procedure.[ii] 1,4-Bis(octyloxy)-2,5-di(ethynyl)benzene **(4)** was synthesized according to the reported procedure. [iii] Analytical data were in good agreement with the literature NMR (^1H and ^{13}C) spectra were recorded on a Bruker AC 200 spectrometer and $CDCl_3$ 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 at Perkin-Elmer 1000 FTIR spectrometer by preparing KBr pellets of the materials. 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 analysis 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 HR_2 and HR_3 styrragel columns using THF as eluent. Melting points were measured with an Electrothermal 9100 apparatus.

Organic 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 24h. The cold colorless solution was evaporated and the residue was recrystallized from MeOH. There was obtained 1 g (yield 74%) of **2** as a white crystalline solid, m.p. 140°C (MeOH); ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{14}H_{14}BrNO_2$: 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)-(1*R*,2*R*)-1,2-diaminocyclohexane (3).** To a solution of bromophthalic anhydride **1** (4.54 g, 20 mmol) in Toluene (150 mL) was added (1*R*,2*R*)-1,2-diaminocyclohexane (1.15 g, 10 mmol) followed by triethylamine (140 µL, 1 mmol). The mixture was refluxed under a Dean-Stark trap for 4h. 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 product of mono-addition. Concentration of the filtrate under reduce pressure gave a colorless oil which solidify on standing. The bisphthaloyl adduct was isolated by column chromatography on silicagel using methylene chloride as eluent. Yield 1.770 g (33%) of **3**, m.p. 245°C; Rf (silicagel, CH_2Cl_2) 0.4; ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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, $CHCl_3$ or THF); UV (MeCN) ε 21800 (278 nm), 32600 sh (250 nm), 42500 sh (240nm), 78000 (230 nm); Anal. Calcd for $C_{22}H_{16}Br_2N_2O_4$: 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);

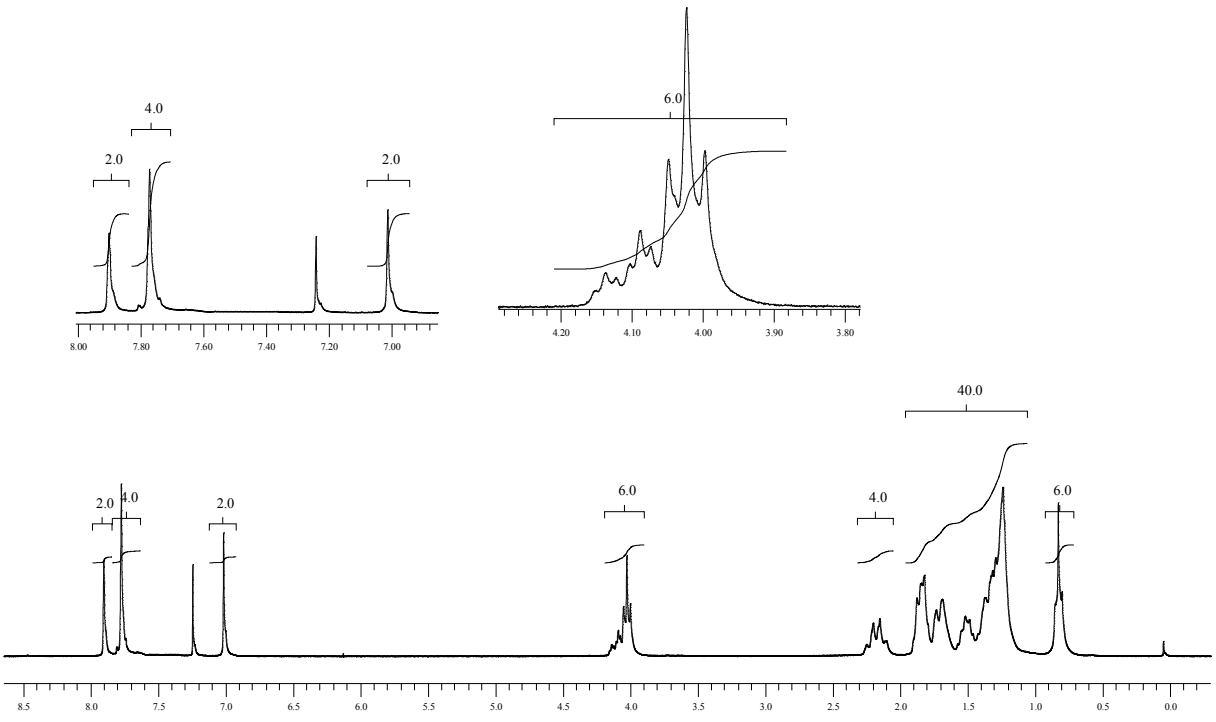
2-cyclohexyl-5-{[4-[(2-cyclohexyl-1,3-dioxo-2,3-dihydro-1*H*-isoindol-5-yl)ethynyl]-2,5-bis(octyloxy)phenyl]ethynyl}-1*H*-isoindole-1,3(2*H*)-dione (5): The organometallic coupling of the halo-phthalimide **2** (322.2 mg, 1.04 mmol) and the 1,4-

Diethynyl-2,5-bis(octyloxy)benzene **4** (200 mg, 0.523 mmol) was performed in the presence of $Pd_2dba_3(CHCl_3)$ (21.7 mg, 0.021 mmol), $P(C_6H_5)_3$ (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, the coupling occurred and the reaction is stirred for three days. The reaction mixture was filtered and concentrated under vaccum. 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. m.p. = 205-207°C; ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): 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 (CH_2Cl_2, nm): λ_{abs_max} = 403; UV-vis (film on quartz, nm): λ_{abs_max} = 448; Fluo (λ_{ex} = 400 nm): (CH_2Cl_2, nm): λ_{em_max} = 504; UV-vis (film on quartz, nm): λ_{em_max} = 508; Anal. Calcd for $C_{54}H_{64}N_2O_6$: 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): $M^{+\bullet}$ 837 (90), 507 (100);

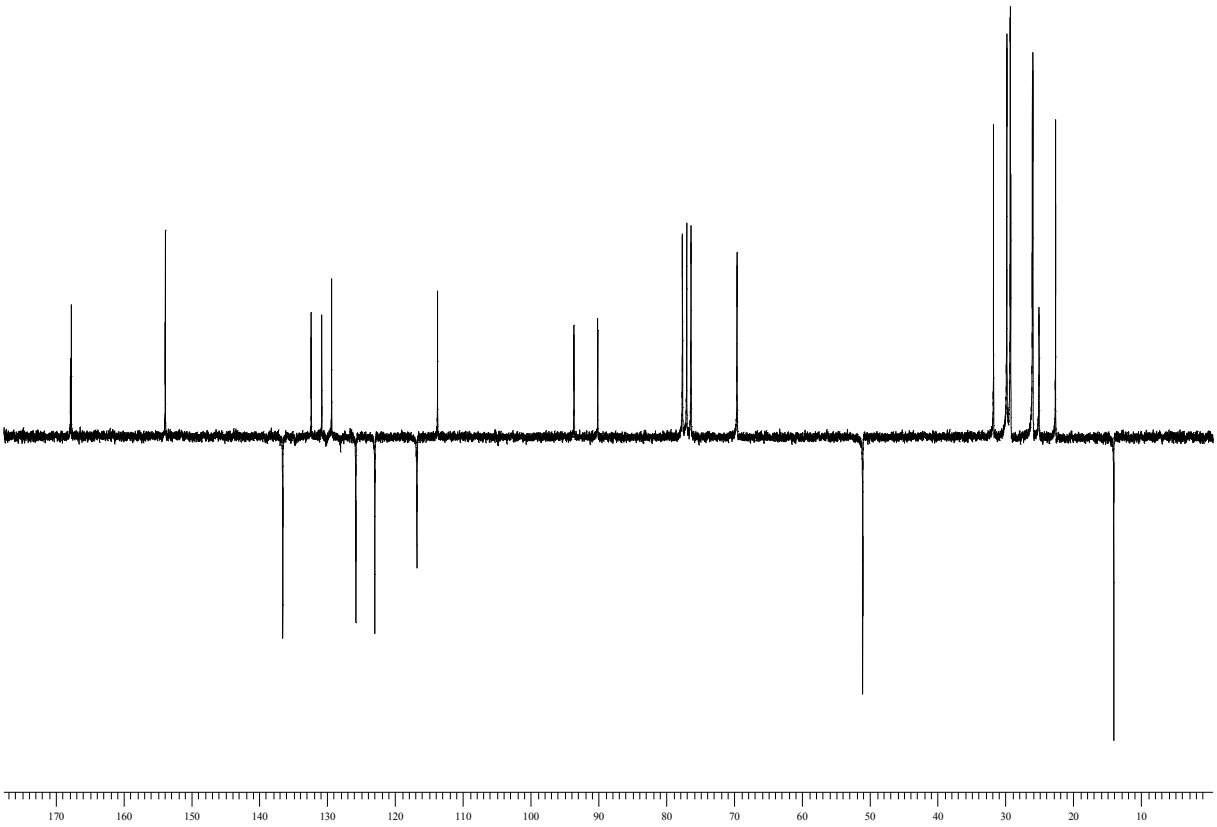
Polymer (6): The polymerization of the chiral halo-phthalimide **3** (278.3 mg, 0.523 mmol) and the 1,4-Diethynyl-2,5-bis(octyloxy)benzene **4** (200 mg, 0.523 mmol) was performed in the presence of $Pd_2dba_3(CHCl_3)$ (21.7 mg, 0.021 mmol), $P(C_6H_5)_3$ (22 mg, 0.084 mmol) and CuI (8 mg, 0.042 mmol) 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, CH_2Cl_2, CH_3CN, Xylene) and gel permeation chromatography (THF, polystyrene standard) analysis showed Mw = 15000 and Mn = 8500 (PDI = 1.76). These values correspond to an average of 11 repeating units per polymeric chain. $[\alpha]_D$ -452° (*c*=1, THF); GPC: Mw = 15000, Mn = 8500 (PDI= 1.76); ^{1}H NMR ($CDCl_3$): 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 (CH_2Cl_2, nm): λ_{abs_max} = 406 ; UV-vis (film on glass, nm): λ_{abs_max} = 406; Fluo (λ_{ex} = 400 nm):, (CH_2Cl_2, nm): λ_{em_max} = 508; UV-vis (film on glass, nm): λ_{em_max} = 524; Anal. Calcd for $C_{48}H_{52}N_2O_6$: 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.

NMR spectrum:

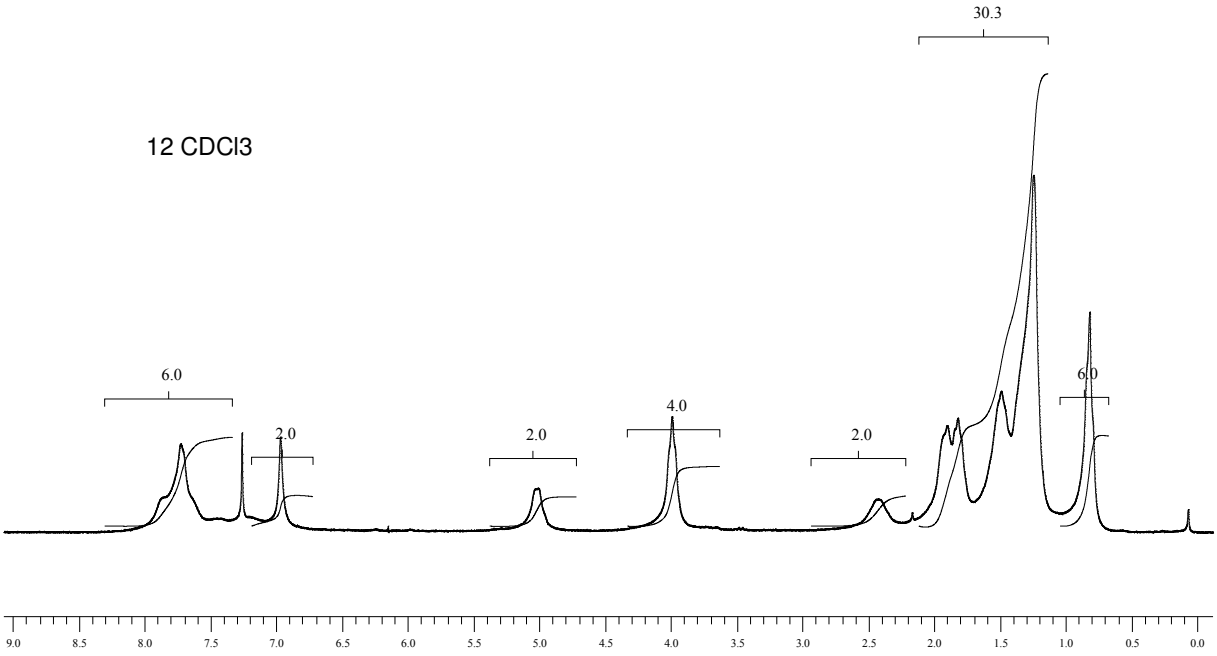
^{1}H spectrum of 5 in $CDCl_3$



^{13}C spectrum of 5 in $CDCl_3$



^{1}H spectrum of 6 in $CDCl_3$



GPC chromatograms: Gel permeation chromatography of **6** (THF (1 ml/min), polystyrene standard) analysis showed Mw = 15000 and Mn = 8500 (PDI = 1.76).

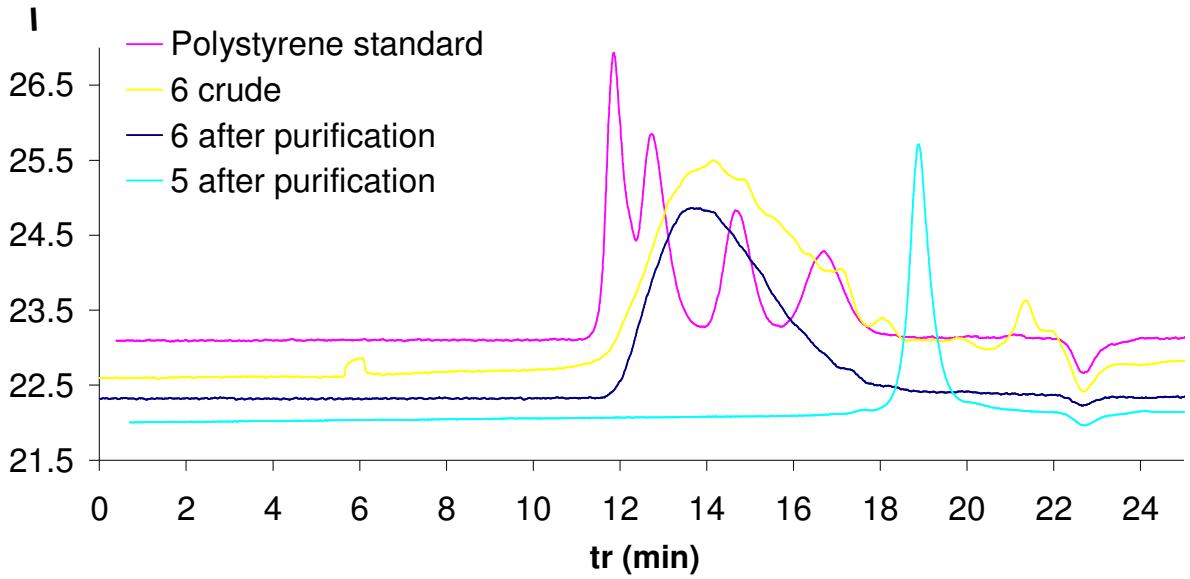


Figure 1. GPC chromatograms of **5** and **6**

Thermal stabilities: Thermal stabilities of the conjugated segment **5** and the polymer **6** were investigated by Thermogravimetry (TGA). This study was carried out under air with a heating rate of 10°C/min (cf. Figure 2a). The results are reported in table 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, is observed. After this stage, degradation continues but slower.

The isolated segment **5** and the polymer **6** were studied by Differential Scanning Calorimetry (DSC) in a range of temperature going from -120°C to 250 °C (cf. Figure 2b). Recordings were carried out under nitrogen with a heating rate of 20°C/min. DSC measurements on compound **5** showed endothermic transition at 211°C significant of its melt and an exothermic transition at 161°C indicative of its recrystallization. On the other hand, the thermogram dedicated to polymer **6** showed neither any crystalline transition nor T_g in the studied range of temperature.

Compound	Gas	Decomposition onset in °C Loss < 5%	Inflection point in °C	Weight loss in %
5	air	350	415 (1st step) 471 (2nd step)	31 (2 x OC_8H_{17}) 23 (2 x cyclohexylamine)
6	air	350	425 (1st step) 475 (2nd step)	35 (2 x OC_8H_{17}) 15 (cyclohexyldiamine)

Table 1

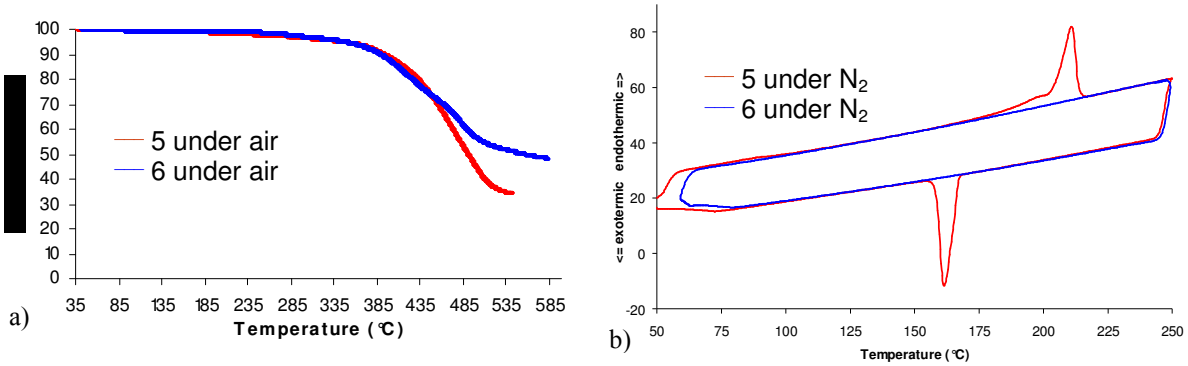
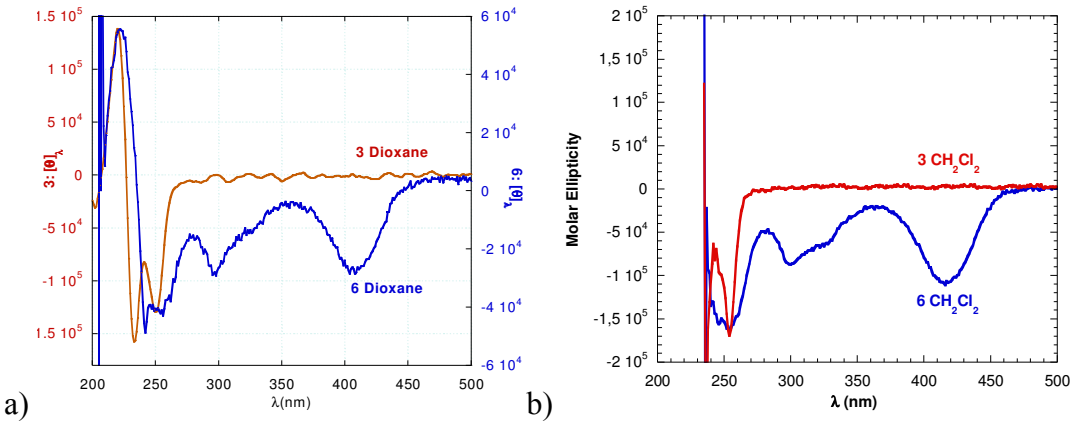


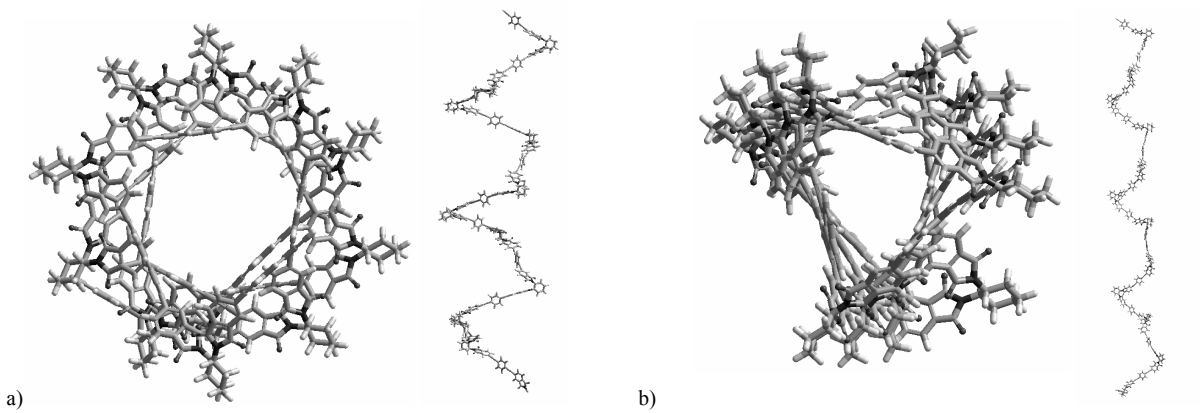
Figure 2. a) TGA Thermogram, b) Differential Scanning Calorimetry traces of **5** and **6**

CD measurements in a) Dioxane and b) CH_2Cl_2:



a) b)

MM2 calculated structures of the polyimide 6 constituted of 11 repeating units: a) C-Shape, b) S-Shape. The alkoxy-chains were omitted for clarity.



a) b)

Calculations were performed using Hyperchem™, Hypercube, Inc, 1115 NW 1114th Street, Gainesville, FL 32601, USA

X-ray Powder Diffraction properties. X-ray diffraction diagrams of **6** showed only 3 broad signals (2θ = 5.4, 12.2, 20.7°) characteristic of an amorphous material (Figure 3). Conversely, **5** revealed several diffraction peaks significant of a crystalline product.

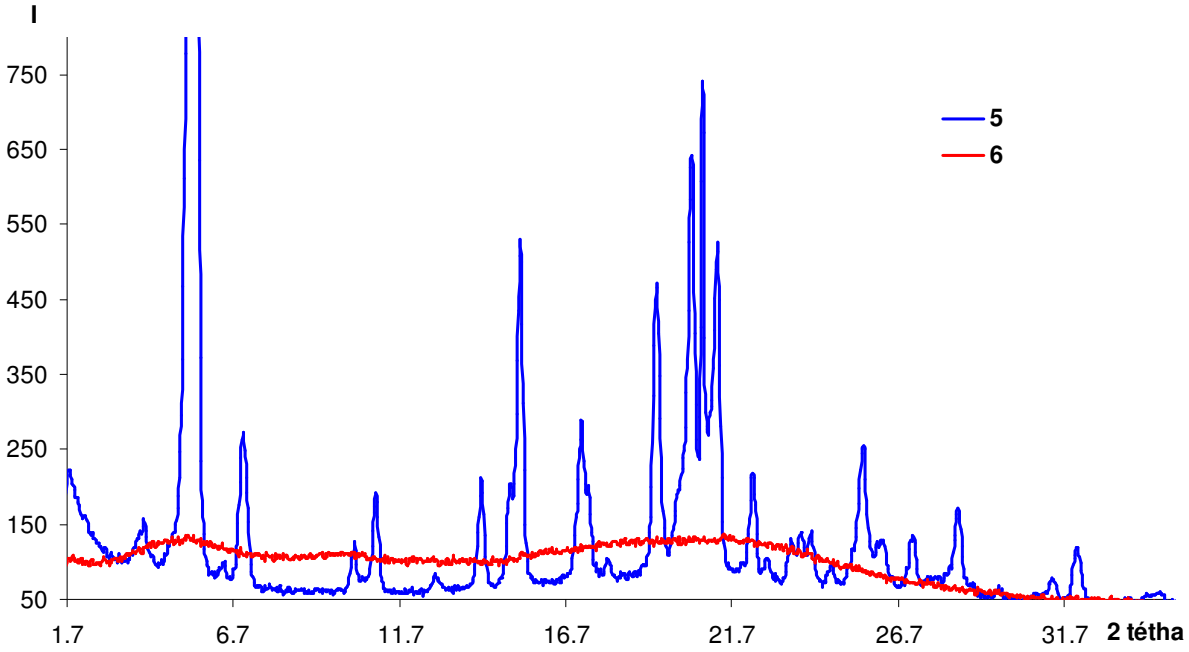
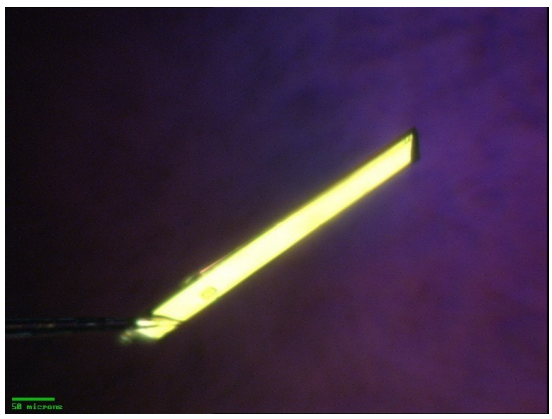


Figure 3. Normalized X-ray Powder Diffraction diagrams of **5** and **6**.

X-ray Diffraction on a monocristal of 5. Crystal structure of **5** was recorded on a microdiffractometer. The X-ray beam was 30 µm broad. The crystal sizes were about 450 x 30 x 30 μm^{-3}.

a) 

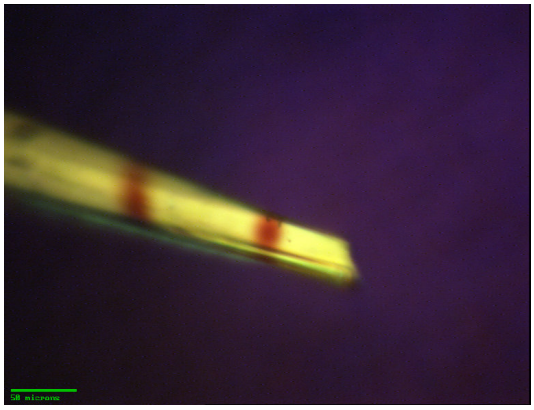
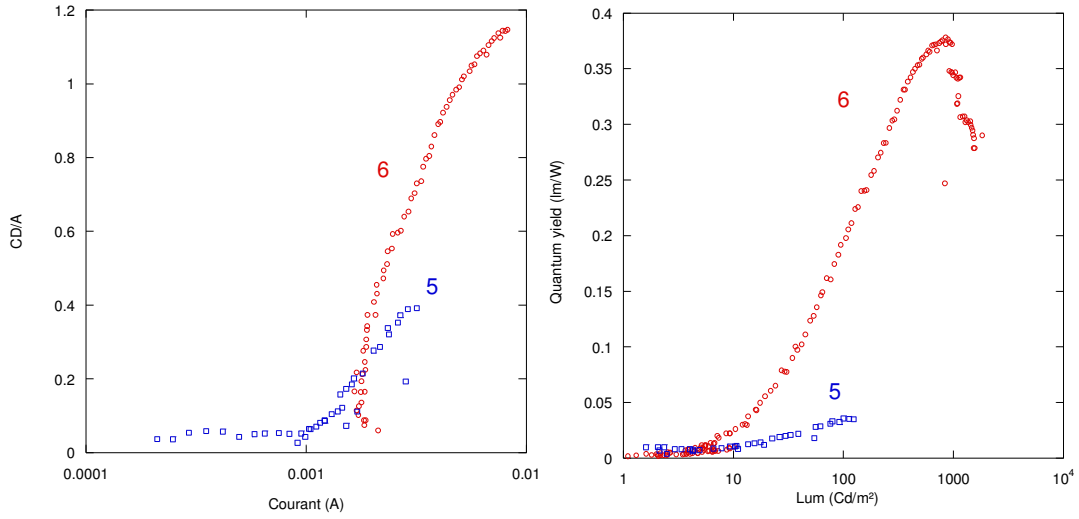
b) 

Figure 4. Single crystal of **5**: a) before X-ray irradiation; b) after X-ray irradiation.

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/▪. This substrate underwent a wet cleaning procedure of successive 30 minutes ultrasonic baths in trichloroethylene, ethanol and deionised water at room temperature. Then, a layer of poly(styrene sulfonate) doped poly(3,4-ethylene 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 performances of the device. Then, for PLEDs based on **6**, the layer of **6** was spin-coated from the 30 $mg.mL^{-1}$ from the xylene solution 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 aluminum layer (~ 150 nm thick) to minimize its oxidation. All devices investigated here had an active area of 10 mm^2. Samples were then stored and characterized under inert atmosphere (nitrogen glove box).



5 0.4 Cd/A and 0.036 Lum/W
6 1.15 Cd/A and 0.37 Lum/W

[i] E.N. Jacobsen, J.F. Larrow, *J. Org. Chem*. **1994**, *59*, 1939-1942.
[ii] M. H. Norman, J. L. Kelley, E. B. Hollingsworth, *J. Med. Chem*. **1993**, 36, 3417-3423.
[iii] Ruiz, J.P; Dharia, J.R.; Reynolds, J.R.; Buckley, L.J. *Macromolecules*, **1992**, *25*, 849.