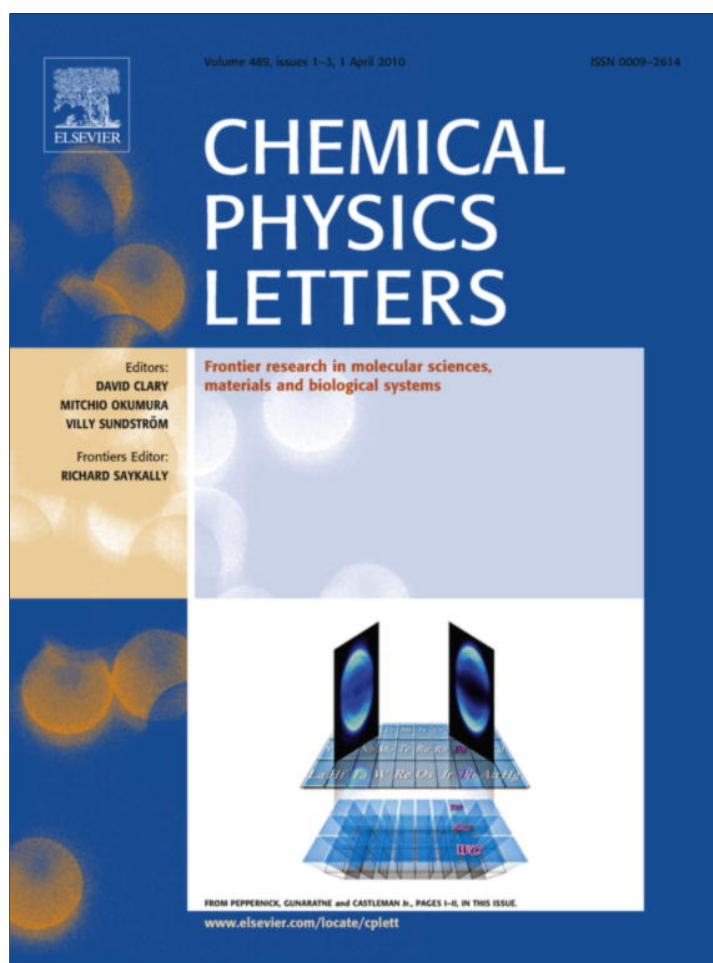


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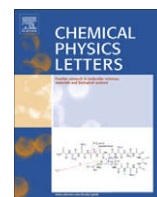
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## Fluorescence light emission at 1 eV from a conjugated polymer

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## ABSTRACT

While polymer light-emitting diodes are currently finding commercial applications in displays and lighting, the development of low bandgap polymers emitting in the infrared has received much less attention in spite of potential applications for instance in the field of communication technologies. We report here a light emission at 1 eV from a low bandgap polymer made of an alternation of dialkoxy-phenylene units and a low bandgap monomer composed of an electron accepting 2-thia-1,3,5,8-tetraaza-cyclopenta[b]naphthalene group fenced with electron donating thiophene units. The electronic structure of the polymer chains has been characterized at a quantum-chemical level to shed light into the experimental results.

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## 1. Introduction

Conjugated polymers are optically active materials whose photoluminescence (PL) and electroluminescence (EL) properties have received a great deal of interest over the last fifteen years. Applications have already entered the manufacturing process with the first polymer light-emitting diodes (PLEDs) becoming part of colour displays. One of the main advantages of using polymers as active materials is the ability to control important features such as the desired colour emission and their intensity via bandgap engineering through chemical synthesis. Infrared absorption from discrete molecules with an extended  $\pi$ -system [1] and organic NIR absorbing dyes has been reported in the past [2]. In contrast, little attention has been paid on the synthesis of low bandgap polymers, i.e., with a gap lower than 1.8 eV [3], that can emit light in the near infrared (NIR) for applications in telecommunication. Conjugated polymers are attractive for their processibility from solution leading to homogeneous thin films without cracks or pin-holes. A promising strategy to engineer at the molecular level low bandgap polymers is to introduce along a backbone an alternation of donor and acceptor units [4,5]. In such alternating copolymers, a low energy gap is created between the highest occupied molecular orbital (HOMO) of the donor unit and lowest unoccupied molecular orbital (LUMO) level of the acceptor moiety. Note, however, that a full localization of the HOMO/LUMO levels over their respective units would lead to a vanishingly small transition dipole moment for this transition, thus precluding efficient absorption and emission pro-

cesses. The width of the energy gap depends on factors such as the conjugation length, the solid-state ordering, and the intra-chain charge transfer character.

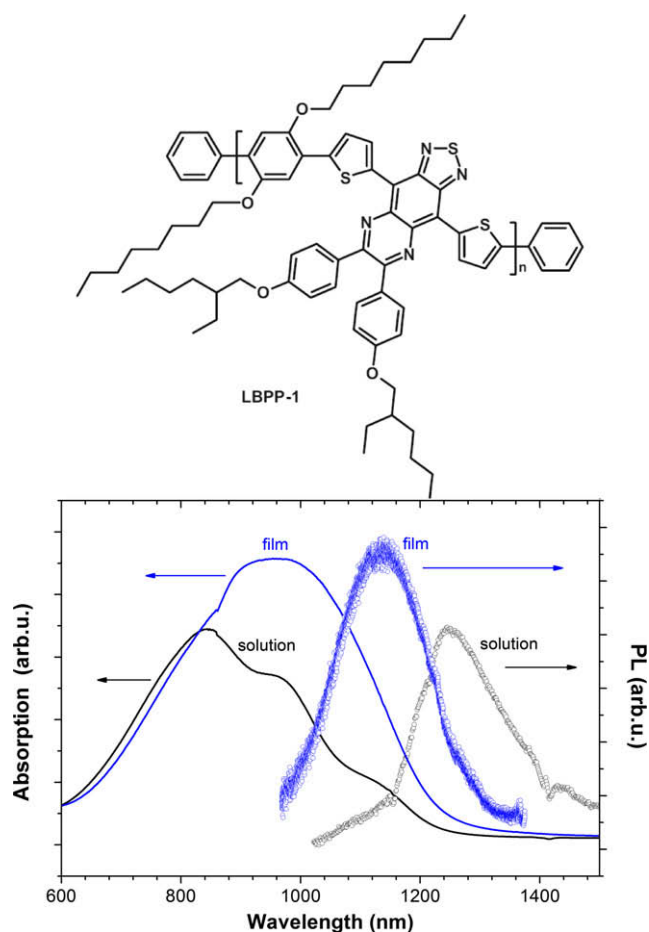
Reports on polymers with low bandgap demonstrated from absorption spectroscopy abound and are motivated by their use in solar cells [5–7]; however, to the best of our knowledge, light emission in the NIR down to 1 eV from a conjugated polymer has not been reported yet, probably as a result of the strongly competing internal conversion processes. In this Letter, we report the photoluminescence properties of the low bandgap polymer LBPP-1 in thin film and solution (see chemical structure in Fig. 1a). This polymer is photostable, solution processible, and emits in the NIR region.

## 2. Experimental

The synthetic route towards this low bandgap polymer has been described in details elsewhere [8]. LBPP-1 films were drop casted on glass substrates from a solution of LBPP-1 in chloroform (5 mg/ml). The films were a couple of micrometers thick. The temperature-dependent photoluminescence (PL) measurements of LBPP-1 films were performed inside a cryostat under vacuum ( $\sim 10^{-5}$  mbar). In this way, photo-oxidative damage was not an issue and temperatures as low as 3.6 K were attained. The beam spot size on the sample was  $5 \mu\text{m}^2$  and the intensity of the beam before entering the cryostat approximately 28 mW. The excitation wavelength was 750 nm. The infrared detector was a Horiba Linear InGaAs array detector (IGA-1024). PL measurements of the LBPP-1 solution in chloroform were taken under atmospheric pressure using the same setup. The absorption spectra of LBPP-1 in film

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**Fig. 1.** (a) Chemical structure of LBPP-1. (b) Room-temperature absorption and PL spectra of LBPP-1 film and solution. The absorption and PL spectra of both the film and solution have been normalized to the respective maxima.

and in solution were taken using a Perkin Elmer Lambda 900 UV-VIS-NIR spectrometer.

### 3. Results and discussion

LBPP-1 is built from two different types of monomer units: a low bandgap unit and a dialkoxy-phenylene unit. The low band gap monomer is composed of an electron accepting group, 2-thia-1,3,5,8-tetraaza-cyclopenta[*b*]naphthalene, fenced with electron donating thiophene units. For sake of simplicity, LBPP-1 can be seen as being made of an alternation of donor–acceptor (D–A) segments, with D the thiophene-dialkoxyphenylene-thiophene segment, and A the 2-thia-1,3,5,8-tetraaza-cyclopenta[*b*]naphthalene group.

#### 3.1. Optical properties

Fig. 1b shows the absorption and PL spectra of a drop-casted LBPP-1 film on glass (black lines). There is an absorption maximum at 954 nm, similar to the values reported previously [8], while the emission maximum is lying at 1140 nm. Both spectra are featureless, with the emission spectrum red shifted by 186 nm. The Stokes shift reflects a significant structural relaxation in the excited state while the lack of vibronic structures in the spectra is attributed to torsional motions that dynamically regulate the conjugation length [9]. The narrowing of the emission band further suggests the occurrence of intra- and inter-chain energy transfer processes to-

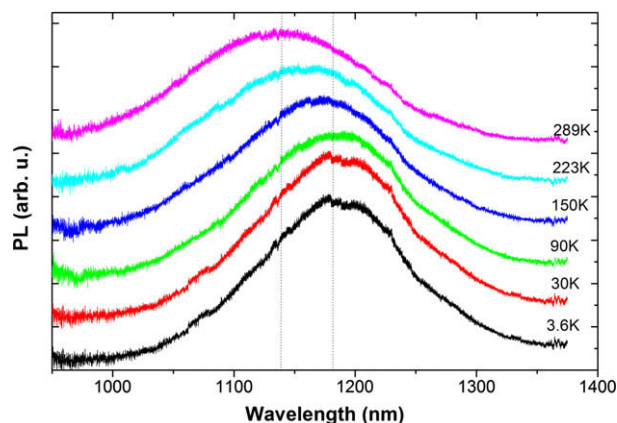
wards chromophores with the largest effective conjugation length and hence lowest HOMO–LUMO energy gaps [10]. The fluorescence quantum efficiency is estimated to be about  $4 \times 10^{-8}\%$  for the thin film.

Fig. 2 displays the PL spectra of a LBPP-1 film at different temperatures. The overall spectrum blue shifts by  $\sim 45$  nm and becomes broader with increasing temperature from 289 K to 4 K. The blue shift is explained by the decrease in the effective conjugation length upon amplification of torsional motions between the polymer segments [10]. Similar spectral shifts with temperature have been observed with other conjugated polymers [11], albeit with emission peaks at almost half the wavelength compared to LBPP-1.

A deeper insight into the nature of the emitting species can be inferred by comparing the room-temperature PL spectrum of the LBPP-1 film with that of a solution in chloroform, see Fig. 1b. In the absorption spectrum of the solution, the two peaks that can be resolved at 955 nm and at 846 nm, do not necessarily correspond to different excited vibrational levels since they tend to merge in one main peak when the same absorption spectrum is taken using a less polar solvent (e.g. hexane) than chloroform. A rather atypical feature of these spectra is the fact that the emission of the solution (peak at 1247 nm) is red shifted compared to the emission of the film (peak at 1140 nm) by approximately 107 nm. Typically, chains in the solid state possess a lower bandgap than in solution due to an increase in planarity, as supported by the red shift observed for the absorption spectrum. Moreover, the impact of intermolecular interactions is also expected to induce a red shift of the emission [12].

#### 3.2. Theoretical modeling

Quantum-chemical calculations have been performed on model oligomers of LBPP-1 versus oligothiophenes to characterize their electronic properties and rationalize the experimental measurements. The ground-state geometry of the oligomers has been optimized at the Hartree–Fock semi-empirical Austin Model 1 (AM1) level by imposing the planarity of the backbone and by replacing the long alkyl chains of LBPP-1 by hydrogen atoms. Fig. 3 shows the shape of the frontier orbitals of the donor and acceptor building blocks of LBPP-1 and their relative energies. Owing to the large energy difference between the LUMO levels of the two units (1.20 eV), the LUMO of the repeat unit of LBPP-1 is predominantly localized over the acceptor part (14% on D and 86% on A) and is slightly stabilized with respect to the LUMO level of the accepting unit. In contrast, the smaller energy separation between the HOMO levels ( $\sim 0.7$  eV) of the D and A segments and the large electronic



**Fig. 2.** Temperature-dependent PL spectra of LBPP-1.

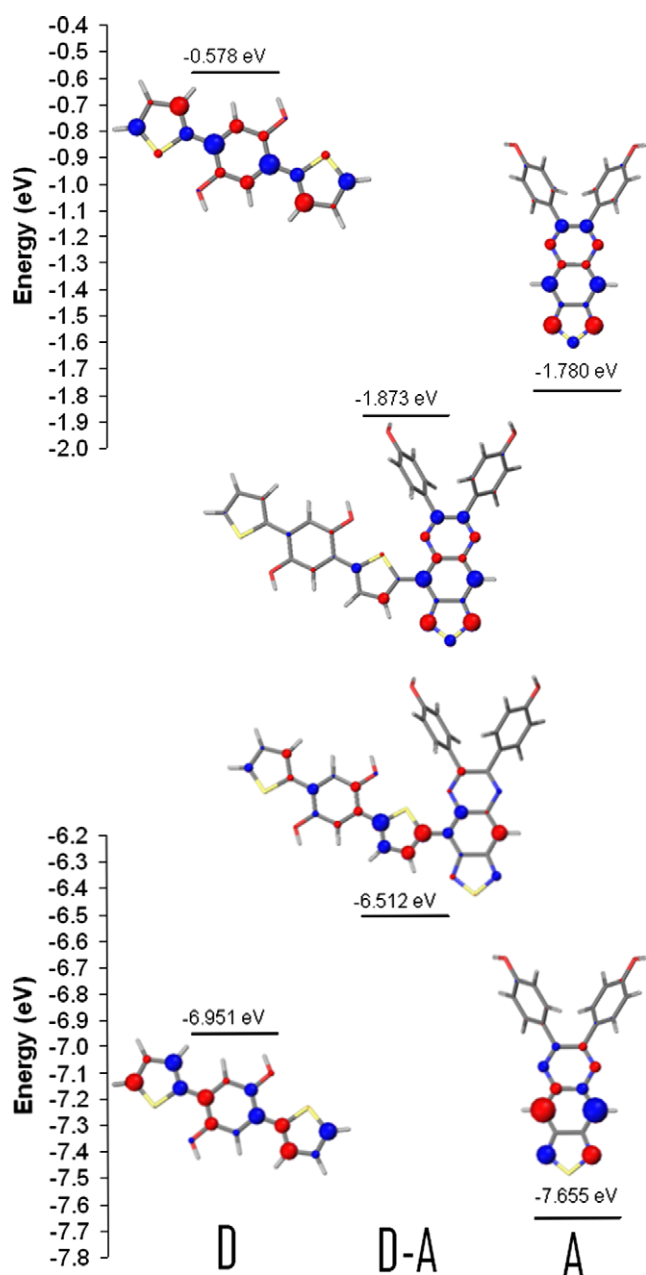


Fig. 3. Schematic representation of the energy and shape of the HOMO (bottom) and LUMO (top) levels of the donor and acceptor segments and of the corresponding repeat unit of LBPP-1.

density on the connected atoms of the acceptor unit promotes a strong interaction between the two moieties; this translates into a more delocalized character for the HOMO level in the repeat unit (66% on D and 34% on A) and to a strong energy destabilization compared to the HOMO level of the building blocks. The same picture is obtained for other donor/acceptor copolymers [13,14]. Note that the delocalized character of the HOMO level ensures a significant transition dipole moment (and hence oscillator strength) for the lowest optical transition. In a second stage, we have computed the energy of the lowest optical transition on the basis of the optimized geometries by using the semi-empirical Hartree–Fock INDO (Intermediate Neglect of Differential Overlap) method coupled to a Single Configuration Interaction (SCI) scheme [15]; the active space includes  $M \times M$  orbitals for the oligothiophenes, with  $M$  corresponding to half the number of  $\pi$  electrons, and  $10n \times 10n$  orbitals

for the LBPP-1 series, with  $n$  the number of oligomers. Fig. 4 displays the evolution of the lowest optical transition energy as a function of  $1/n_d$  (with  $n_d$  the minimal number of bonds connecting the two extremities of the molecules) for the LBPP-1 oligomers and oligothiophenes. The extrapolation of the results based on a Kuhn fit [16,17] provides an optical gap of about 2 eV for polythiophene, in full consistency with corresponding experimental measurements [18]. The extrapolated value obtained for LBPP-1 is significantly lower than that for polythiophene (1.51 eV versus 1.94 eV, respectively) but does not match the experimental value around 1 eV. This is attributed to the fact that the lowest optical transition creates an intra-chain charge transfer in the LBPP-1 backbone, owing to the strong localization of the LUMO level over the accepting unit. The INDO/SCI calculations give a total amount of about 0.35 |e| transferred from the donating to the accepting units upon photoexcitation. In turn, this charge transfer induces an extra stabilization of the excited state by polarizing electronically the neighbouring chains, an effect neglected in our gas-phase calculations. Interestingly, oligothiophenes and LBPP-1 oligomers with a similar  $n_d$  value exhibit a similar oscillator strength for the lowest optical transition as a result of the participation of delocalized levels in the description of the state.

The charge transfer promoted in the lowest excited state might also rationalize the blue shift of the emission band when going from solution to the solid state. As a matter of fact, a recent study on polymer blends has shown that the Coulomb interactions between the charge distribution of an excited chain and that of an adjacent neutral chain can lead to a blue shift of the emission in the repulsive regime [19]. The localization of the excitation upon geometry relaxation is a prerequisite for the manifestation of such environmental effects since a cancellation of attractive and repulsive forces is expected to prevail for the delocalized excitations initially generated upon photoexcitation [19]. However, Coulomb interactions in the attractive regime should also give rise to chains

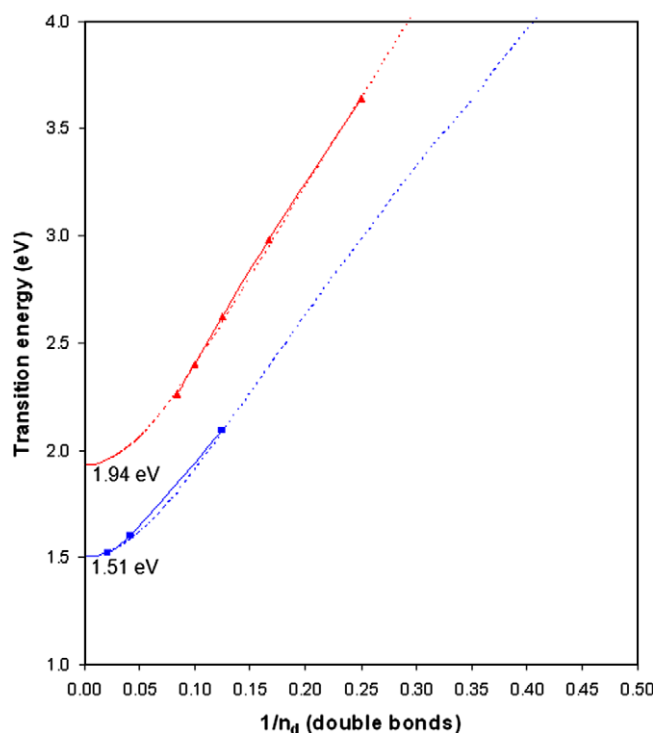


Fig. 4. Evolution of the energy of the first optical transition of LBPP oligomers (blue) and oligothiophenes (red) as a function of  $1/n_d$  (with  $n_d$  the smallest number of double bonds going from one side of the molecule to the other). The dashed lines show the Kuhn's fits of the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

emitting at lower energy compared to solution; this discrepancy can be reconciled with the experimental measurements by conjecturing at this stage that such excitations are actually converted into inter-chain exciplexes that are known to be generally weakly emissive [20] in agreement with the low quantum efficiency recorded. More experiments are in progress to verify such hypotheses.

#### 4. Conclusion

Low bandgap conjugated polymers are potentially interesting to fabricate NIR diodes sending optical signal in telecommunication networks. Here, we have reported the extraordinary emission properties of the low bandgap polymer LBPP-1, which emits NIR radiation between 1000 nm and 1400 nm ( $\sim 1$  eV). This low bandgap is obtained by using monomer with donor–acceptor segments. The delocalized character of the HOMO on the donor and acceptor segments, together with the localized character of the LUMO on the acceptor, promotes a significant transition dipole moment (and hence oscillator strength) for the lowest optical transition of LBPP-1 chains. The significant charge transfer occurring in the lowest excited state and the resulting intra-chain and inter-chain Coulombic interactions are likely to be at the origin of the unexpected blue shift of the emission band when going from solution to the solid state, as well as the low fluorescence efficiency.

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