

# Joint theoretical and experimental characterization of the structural and electronic properties of poly(dioctylfluorene-alt-N-butylphenyl diphenylamine)

J.C. Sancho-García<sup>1</sup>, C.L. Foden<sup>2</sup>, I. Grizzi<sup>2</sup>, G. Greczynski<sup>3</sup>,  
M.P. de Jong<sup>4</sup>, W.R. Salaneck<sup>4</sup>, J.L. Brédas<sup>5,1</sup>, and J. Cornil<sup>1,5</sup>

<sup>1</sup>Laboratory for Chemistry of Novel Materials  
Center for Research in Molecular Electronics and Photonics  
University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium

<sup>2</sup>Cambridge Display Technology  
Greenwich House, Madingley Rise  
Madingley Road, Cambridge CB3 0TX, UK

<sup>3</sup>Thin Films Electronics  
Westmansgatan 27  
S-582 16 Linköping, Sweden

<sup>4</sup>Department of Physics  
IFM, Linköping University  
S-581 83 Linköping, Sweden

<sup>5</sup>School of Chemistry and Biochemistry  
Georgia Institute of technology  
Atlanta, Georgia 30332-0400, USA

## Abstract

Fluorene-based copolymers are currently attracting considerable interest for use in a wide range of opto-electronic devices. Here, we present the results of a joint quantum-chemical and experimental characterization of the structural, electronic, and optical properties of an alternating fluorene-triphenylamine copolymer. We compare the results from this study with those from similar studies of polyfluorene. Although calculations are performed for the gas phase and experiments are performed on the solid state, the results from the two methodologies are in good agreement: the relevant electronic levels, HOMO and LUMO, of polyfluorene are found to be destabilized by incorporation of triphenylamine units in the conjugated backbone, whereas the optical properties of polyfluorene chains are largely unperturbed by the presence of triphenylamine.

## Introduction

The understanding and control of the organic electroluminescence phenomenon is undoubtedly one of the major achievements of recent years [1,2]. Current materials research in the field of organic light emitting diodes (LEDs) for displays is focused on the development of new high luminescence efficiency, and stable (long lifetime) materials. Poly(paraphenylenevinylene), PPV, and its derivatives are frequently the materials of choice for the active layer in organic LEDs [3,4]. More recently, polyfluorene (F) and fluorene-based copolymers have emerged as very promising systems. The growing number of experimental [5-12] and theoretical studies [13-16] dedicated to this new class of materials all indicate their suitability in LEDs for commercial applications: highly efficient emission in the whole UV-visible range, low-operating voltage, high stability, and long lifetime. Triarylamine-based derivatives have also reached a prominent position as

hole-transporting materials in OLEDs and incorporation of tertiary aromatic amines into a fluorene backbone has produced copolymers with hole mobilities reaching values as high as  $10^{-3} \text{ cm}^2/\text{Vs}$  [17], comparable with the mobility obtained for the widely used small-molecule hole-transporting material TPD. Therefore, fluorene-amine copolymers easily compete with small molecules in terms of mobility, but offer the additional advantage of solution processability; they can be deposited by spin coating or ink-jet printing. Finally, a recent study in which fluorene-amine hole-accepting copolymers were blended with electron-accepting polyfluorene derivatives showed that exciplex (*i.e.*, a stable excitonic charge-separated state that can emit light) formation in the blend plays a key role in determining the excellent device stability and lifetime [18], increasing interest in the properties of these materials.

Quantum-chemical calculations have proven useful in gaining insight into the optoelectronic properties of conjugated materials [19,20]. The results of quantum chemical calculations are used here in conjunction with experimental measurements to characterize the structural, electronic and optical properties of an alternating copolymer containing triphenylamine and fluorene moieties, TFB. The molecular structure of TFB is sketched in Fig. 1. The good agreement obtained in the results from the combined study clearly demonstrates how it is possible to design materials appropriate to the applications, by fine-tuning the key parameters prior to chemical synthesis. The paper is organized as follows: Sections 2 and 3 describe the experimental and theoretical methods, the main findings are reported in Section 4 and the summary and conclusions are in the last section.

## Experimental aspects

The cyclic voltammograms (CV) reported here were recorded with a computer-controlled EG&G potentiostat/galvanostat at a constant scan rate of 1000 mV/s. A three-electrode configuration undivided cell was used. The working electrode was glassy carbon (3 mm diameter), with a Pt wire auxiliary electrode and a non-aqueous reference electrode containing 0.01M  $\text{AgNO}_3$ , 0.1M tetrabutylammoniumperchlorate (TBAP) in acetonitrile, and silver wire. The electrolyte was 0.1M TBAP in acetonitrile. The oxidation voltage sweeping range was from -1.0V to 1.3V. The measurements are performed on a polymer film which is spin-coated directly on the working electrode from a toluene solution. A film of approximately 60 nm is typically obtained. HOMO and LUMO levels were measured at the onset of, respectively, the first oxidation and reduction events of the second cycle. The potentials were referenced to the ferrocene half-wave potential.

The absorption spectrum was measured on a Thermo Unicam UV2 UV/vis spectrometer. The spectra were recorded from 50-80 nm thick films spin coated from mixed xylene solutions on quartz substrates. The optical band gap was taken as the onset of the absorption spectrum.

The ultraviolet photoelectron spectroscopy (UPS) was carried out using a spectrometer of our own design and construction. The system employs monochromatized He-I (21.2 eV) and He-II (40.8 eV) radiation, and enjoys a based vacuum level below  $10^{-9}$  mBar. The energy resolution, as estimated from the Fermi edge of sputtered (*in-situ*) Au-substrate, is 0.1 eV. The polymer material was provided by Cambridge Display Technology. Ultra-thin films ( $<100\text{\AA}$ ) were spin-coated onto the native oxide Si substrates from a xylene 2mg/ml solution previously filtered with a 0.2  $\mu\text{m}$  PTFE syringe filter. Resulting film thickness was

determined by ellipsometry (HeNe laser), as well as from the attenuation of the substrate core-level XPS signal due to the presence of a thin organic over-layer.

### Theoretical methodology

Since the opto-electronic properties of conjugated oligomers converge rapidly with increasing chain size [21], we have considered oligomers of TFB and F containing from one to four and one to five repeat units, respectively (see Figure 1). In the calculations, the alkyl chains (attached to the conjugated backbone to improve solubility) are systematically replaced by hydrogen atoms since this does not affect the electronic and optical properties of the oligomers but significantly reduces calculation times. We have optimized the ground-state geometry of the chains using the semiempirical Hartree-Fock Austin Model 1 (AM1) method [22]; this choice is validated by the fact that the bond lengths and bond angles calculated with the AM1 method for the triphenylamine moiety compare remarkably well to those obtained at the correlated Hartree-Fock and Density Functional Theory (DFT) levels [23,24]. The experimental C–N bond lengths extracted from the crystal structure of triphenylamine [25] are in the range between 1.408–1.427 Å for the four independent molecules of the unit cell, in very good agreement with all the calculated values. Previous theoretical studies on phenylene-based [13,26] and alternating fluorene-based copolymers [16] also validate the choice of the AM1 method.

Using the AM1-optimized conformations, the electronic structure of the organic chains is generated with the spectroscopic version of the semiempirical Hartree-Fock Intermediate Neglect of Differential Overlap (INDO) [27] method, parameterized with the Mataga-Nishimoto potential for the electron-electron interaction terms. The INDO results are exploited to simulate the UPS spectra of the chains within Koopman's approximation [28,29]; the general procedure has been described in details in Ref. [28]. We have also coupled the INDO Hamiltonian to a Single Configuration Interaction (SCI) scheme to simulate the optical absorption spectra of the oligomers. All the singly excited configurations created by promoting a single electron from one of the  $\pi$ -occupied levels to one of the  $\pi$ -unoccupied levels are included in the CI expansion to ensure size-consistency. Note that we have used the Ohno-Klopman potential for the electron-electron interaction terms to calculate the energy of the lowest triplet excited state of the chains since this parameterization is known to give better agreement with experimental data [16].

## Results and discussion

### Structural characteristics

Knowledge of the structure adopted by TFB chains in thin films is a pre-requisite for understanding device optical and electrical performance. We have optimized the TFB geometry under three different conditions: (i) by imposing a fully planar conformation for the conjugated backbone; (ii) by optimizing all the degrees of freedom; and (iii) by considering an intermediate, partially relaxed, structure where two rings of the triphenylamine –the rings which form part of the polymer backbone– are fixed coplanar whilst the torsion angle associated with the third ring is optimized.

Figure 2 depicts the three AM1-optimized conformations and their relative energies. The fully relaxed conformation is the most stable and is lower in energy by 4 eV per repeat unit with respect to the planar conformation; note that the total energy of a fluorene

oligomer is stabilized by only 0.1 eV/unit when going from the planar structure to the most stable conformation in which the torsion angle between neighbouring fluorene moieties is 40°. The large energy difference in TFB arises from the strong steric repulsion between hydrogen atoms in the fully planarized geometry of the triphenylamine unit (the stabilization energy between structures evolving linearly with the number of units for both TFB and F chains). The lowest energy conformation of TFB is characterized by a torsion angle of 40° between a fluorene unit and adjacent benzene ring and by a torsion angle of 35° in triphenylamine between the plane defined by one of the benzene rings and the plane defined by the central nitrogen atom and the three connected carbon atoms (see zoom in Figure 2). The C–N–C bond angles in the triphenylamine units are close to 120° and have an almost pure sp<sup>2</sup> character, in agreement with recent DFT calculations [24,30] and AM1 results [31]. For the intermediate case, where two rings of the triphenylamine are fixed to be coplanar, the third ring of the triphenylamine unit rotates to be at 90° of the plane defined by the other two. This relaxed intermediate state is destabilized by 0.6 eV/unit with respect to the most stable structure. The large energy differences found for the structures that are not fully optimized lead us to conclude that the triphenylamine units of TFB chains adopt a propeller-like structure in the bulk, as also supported by X-ray data on triphenylamine [25] and closely related compounds [32].

The simulated UPS spectra of planar and fully optimized F oligomers show no significant difference in global line shape. In contrast, the calculated UPS spectra of the partially and fully optimized TFB oligomers show marked changes in their line shape in the low energy region, typically between 5 eV to 10 eV, where the highest occupied levels that govern both the electronic and optical properties of the polymer lie. The INDO-simulated UPS spectrum of TFB shows, for both partially and fully relaxed cases, an intense peak at ca. -8.0 eV arising from a broad set of occupied  $\pi$ -orbitals (Figure 3). The two resolved UPS features observed experimentally at lower energy ( $\sim -5.8$  and  $\sim -6.6$  eV) are only well reproduced by the fully optimized structure of TFB; the agreement is only partial for the intermediate structure. The simulation of the UPS spectra thus provides further evidence that the TFB chains adopt a twisted configuration in thin-film samples. We therefore focus on the fully relaxed conformation of F and TFB oligomers in deriving the electronic and optical properties.

## Electronic and optical properties

The energy of the frontier electronic levels of F and TFB chains is found to evolve linearly as a function of the inverse number of heavy atoms in the backbone (Figure 4). Whereas the HOMO orbital of both F and TFB oligomers is fully delocalized over the conjugated backbone, the delocalization of the LUMO orbital seen for F (and hence the width of the conduction band) is expected to be partly reduced on copolymerization with triphenylamine following the appearance of nodes in the wavefunction on the nitrogen atoms (Figure 5). The calculated energy of the LUMO of TFB is destabilized by 0.2 eV with respect to that of polyfluorene chains, in good quantitative agreement with the value of 0.2 eV found by CV. However, the destabilization of the HOMO level of TFB by some 0.15 eV with respect to that of F predicted by the calculations is not as large as the experimental value of 0.5 eV found by UPS and solid-state CV. This discrepancy can be attributed: (i) to problems inherent to the parameterization of the INDO method; and/or (ii) to the fact that the chains in the amorphous film do not adopt exactly the fully relaxed conformations found by the gas-phase calculations. It should be noted that small changes

in torsion angles between neighbouring moieties can result in rather large (tenths of eV) changes in frontier molecular orbital energies, which do not necessarily induce similar changes for the optical transition energies; moreover, any changes in torsion angles are unlikely to be the same for both F and TFB films. That some planarization of the molecules occurs on film formation is supported by the fact that the torsion angle between adjacent benzene rings in oligophenylenes is found to decrease from 40° to 20° on going from solution or gas phase to the crystalline state [33].

The chain-size evolution of the calculated energies of the lowest singlet ( $S_1$ ) and triplet ( $T_1$ ) excited states of F and TFB chains is reported in Figure 6. The linearity between the transition energies and the inverse number of heavy atoms in the backbone observed allows us to estimate, by extrapolation, the corresponding values for infinite chains. The lowest optical state for all the oligomers is principally constructed from a HOMO to LUMO transition ( $\pi$ - $\pi^*$  dipole-allowed transition).

Linear extrapolation of the  $S_1$  energy yields very similar transition energies for F and TFB at 3.35 and 3.37 eV, respectively. This result is fully consistent with the small red-shift (0.08 eV) in absorption onset found experimentally for the lowest absorption band peaking around 3.2 eV for both polymers (see Figure 7). The theoretical results are also supported by recent experimental studies indicating that the photoluminescence spectrum is largely unchanged on going from polyfluorene to alternating copolymers incorporating fluorene and tertiary aromatic amines [34-36]. Similar observations have also been made for PPV-triphenylamine copolymers [37,38]. This contrasts, however, with the observation of a significant red-shift in emission energy from the blue to the green when introducing benzothiadiazole units into a fluorene backbone [39]. The current results thus demonstrate how the choice of the co-monomer is critical in determining the electronic and/or optical properties of fluorene-based co-polymers.

The INDO/SCI calculations also reproduce the main differences between the optical absorption spectra of F and TFB, in the energy range between 2 and 6 eV, namely (see Figure 7): (i) the broadening of the lowest absorption band on incorporation of triphenylamine; from the theoretical spectra this can be seen to result from the appearance of a new band on the high energy side (around 3.8 eV) in TFB; (ii) the increase in the intensity of the absorption features located between 4.0 and 4.5 eV in TFB, that originates from a large number of highly correlated excited states (*i.e.*, described by a large mixing of one-electron excitations at the CI level); and (iii) a larger intensity for the peak around 6 eV observed when normalizing the intensity of the lowest absorption band. As expected, all the absorption features originate from electronic transitions between  $\pi$ -levels, as previously found for poly-paraphenylenevinylene (PPV) [40] and polyphenylene (PPP) chains [26].

The lowest triplet of both F and TFB also principally comprises a HOMO to LUMO transition. Extrapolation to the infinite chain limit yields energies of 2.58 and 2.60 eV for F and TFB respectively. This result is in good agreement with the experimental value of 2.2–2.3 eV reported for F chains in solution [41-43]. It is interesting to note that the calculated value of the exchange energy (defined as the difference between the energy of the lowest singlet and triplet excited states) has the same order of magnitude as the value around 0.7 eV obtained for a vast series of conjugated polymers [44]. The electron-hole probability distribution in the lowest singlet and triplet states is similar in F and TFB. For both materials, the singlet exciton extends over  $\sim 6$  phenylene rings with greatest amplitude/highest probability density on the central part of the chain segments [19]; the

lowest triplet excited state is much more confined, in agreement with previous theoretical studies [45].

## Conclusions

We have performed a theoretical characterization of the structural, electronic, and optical properties of an alternating copolymer containing triphenylamine and fluorene units in the gas phase, and compared the results with UPS, CV and UV absorption measurements in the amorphous solid state (thin films). Both the geometry optimization calculations and the agreement between the calculated electronic structure and the UPS data, indicate that the triphenylamine units adopt a propeller-like geometry. Our gas-phase calculations indicate that the HOMO and LUMO levels of TFB are both destabilized by 0.2 eV with respect polyfluorene; however, both the UPS and solid-state CV data point to a stronger destabilization of the HOMO level than that found theoretically, suggesting that the relaxation of the two materials is different in the solid state. This is to be expected as TFB is more highly twisted than F. The absence of any significant shift in the peaks of the absorption and emission bands suggested by the calculations is supported by the results from optical absorption measurements. The present study highlights the relevance of quantum-chemical approaches both for understanding the performance of materials in LEDs and also for design and selection of materials prior to synthesis.

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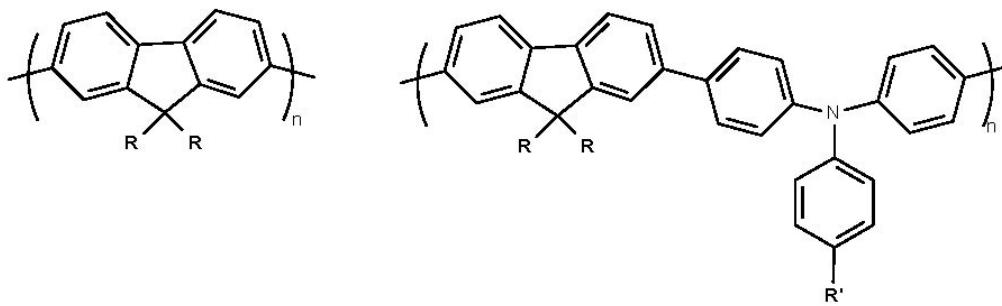


Figure 1: Chemical structure of polyfluorene (left) and poly(fluorene-co-N-(4-butylphenyl)diphenylamine) (right).

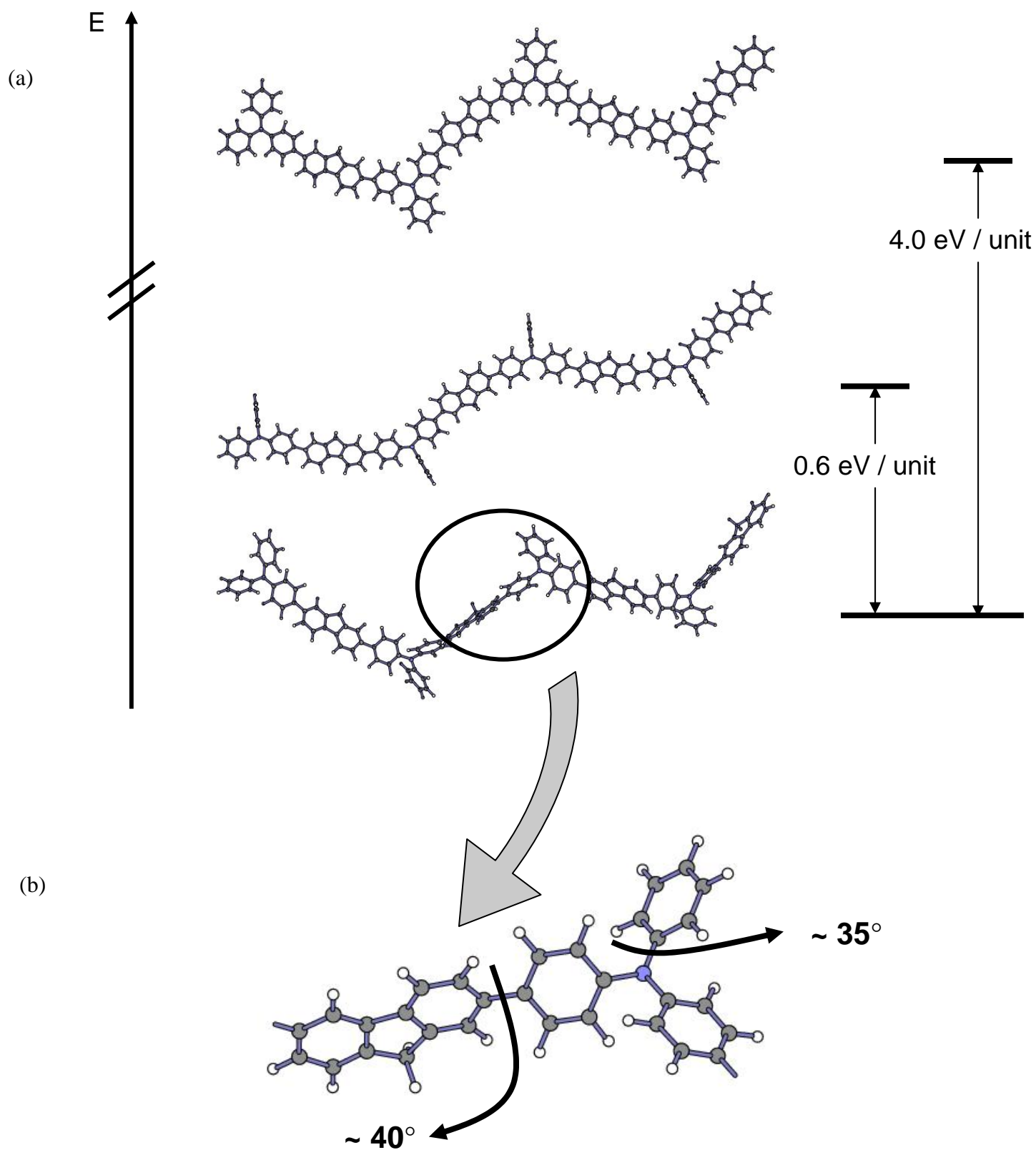


Figure 2: (a) AM1-optimized geometries of the three structures considered for a TFB tetramer: fully planar (top), partially relaxed (middle) and fully optimized (bottom); (b) AM1-calculated torsion angles in the fully optimized geometry of TFB.

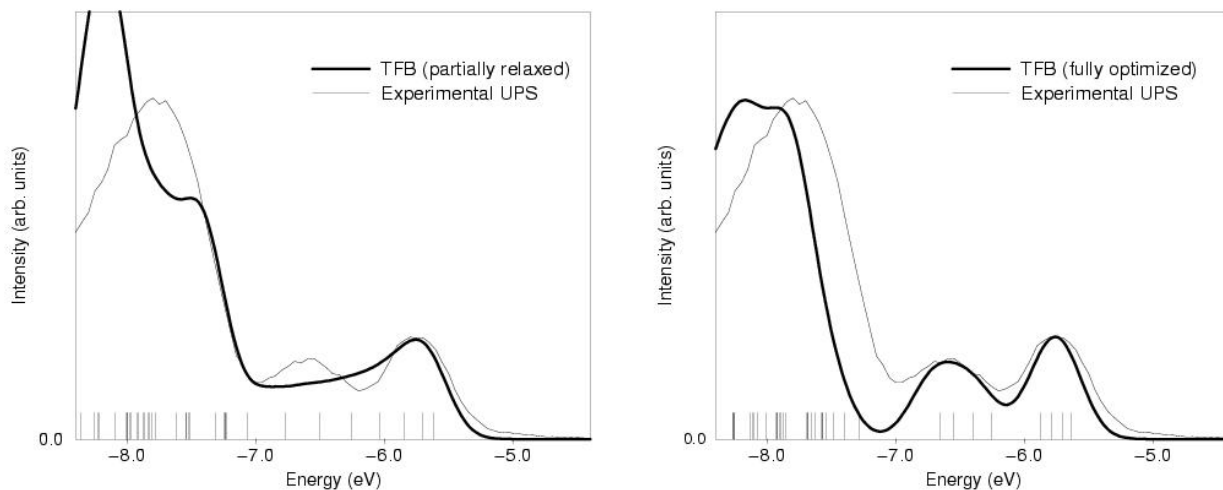


Figure 3: INDO-simulated UPS spectra of the partially relaxed (a) and fully optimized (b) tetramer of TFB compared to the experimental spectrum. In the simulations, we have scaled the energy axis by a factor of 0.9 and we have broadened the UPS features using Gaussian functions with a full-width at half-maximum (FWHM) of 0.4 eV chosen to match the experimental resolution; we also illustrate the distribution of the electronic levels before the broadening is applied.

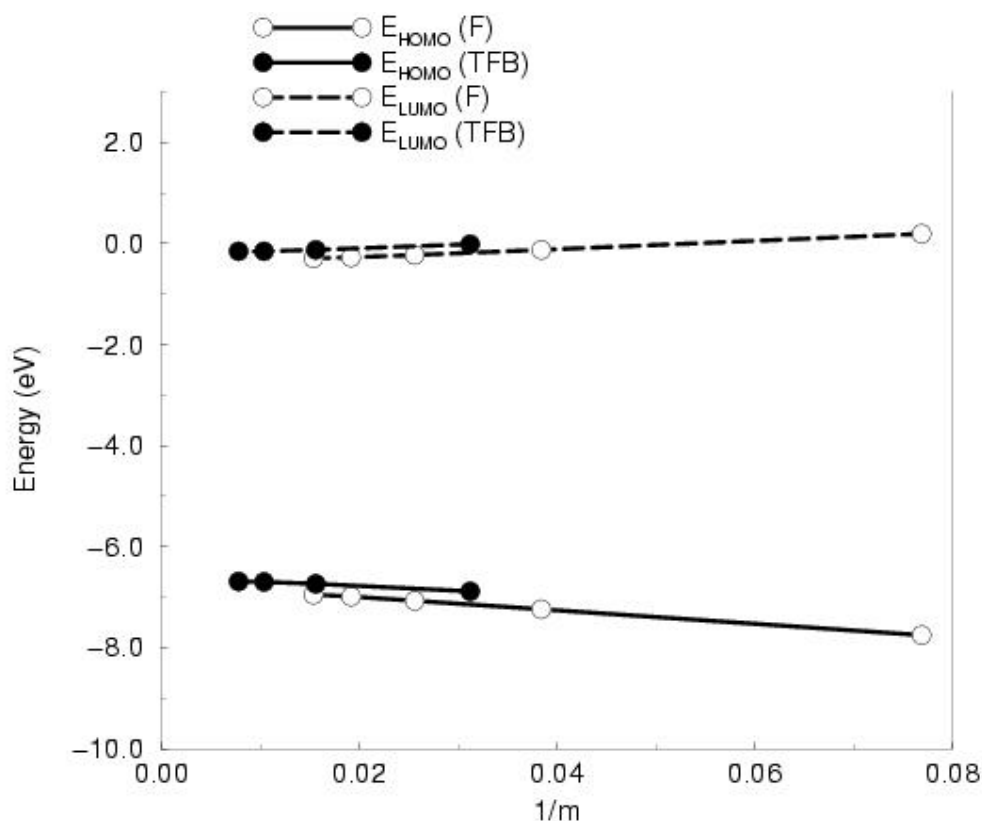


Figure 4: INDO-calculated evolution of the energy of the HOMO (solid lines) and LUMO (dashed lines) of the tetramer of TFB compared to the fully relaxed (F) and fully optimized (TFB) states.

(dashed lines) orbitals of F (open circles) and TFB (filled circles) oligomers as a function of the inverse number,  $m$ , of heavy atoms along the backbone.

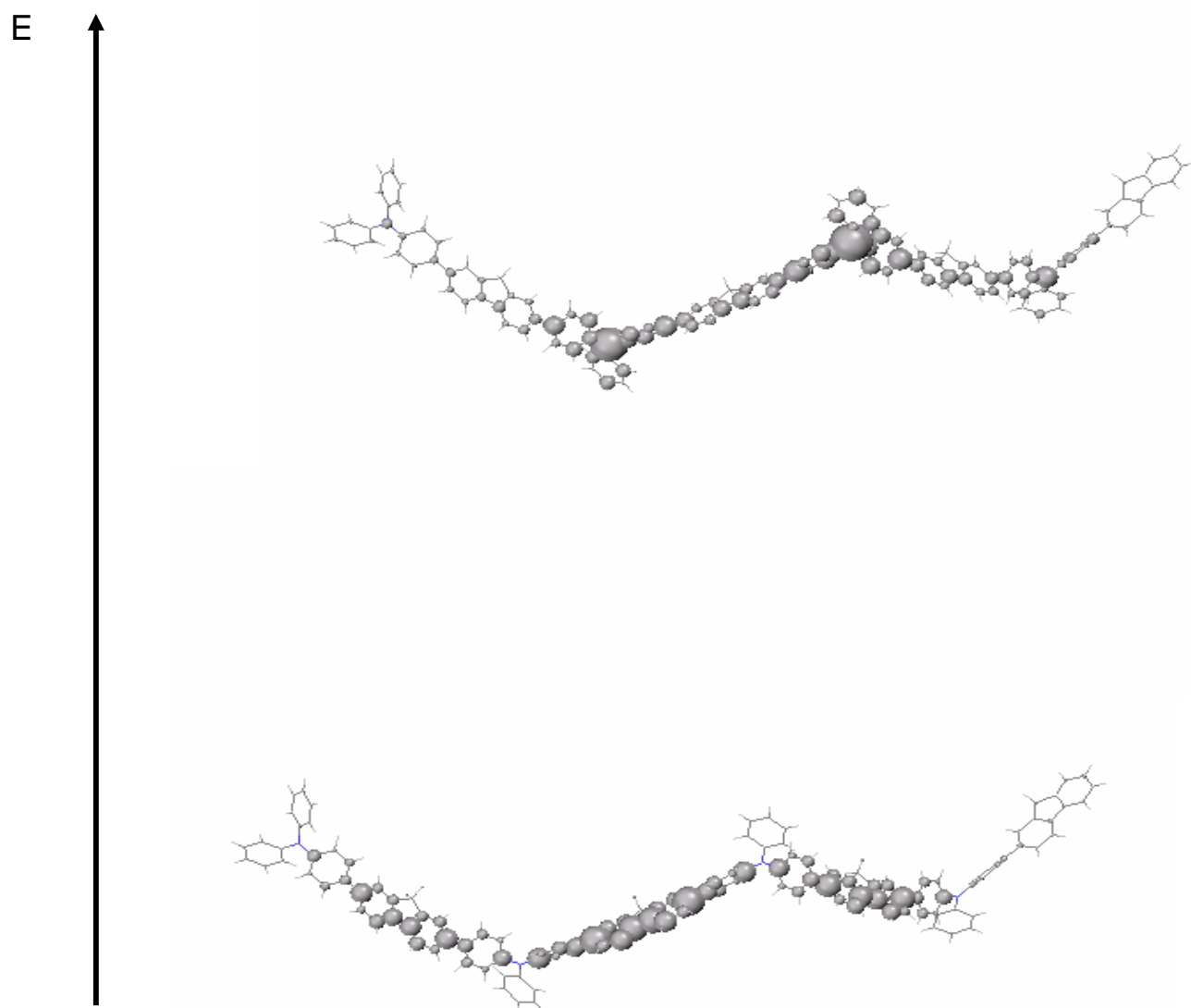


Figure 5: Representation of the distribution of the electronic density in the HOMO (bottom) and LUMO (top) orbitals of a TFB tetramer; the size of the spheres is proportional to the amplitude of the  $\pi$ -electron density.

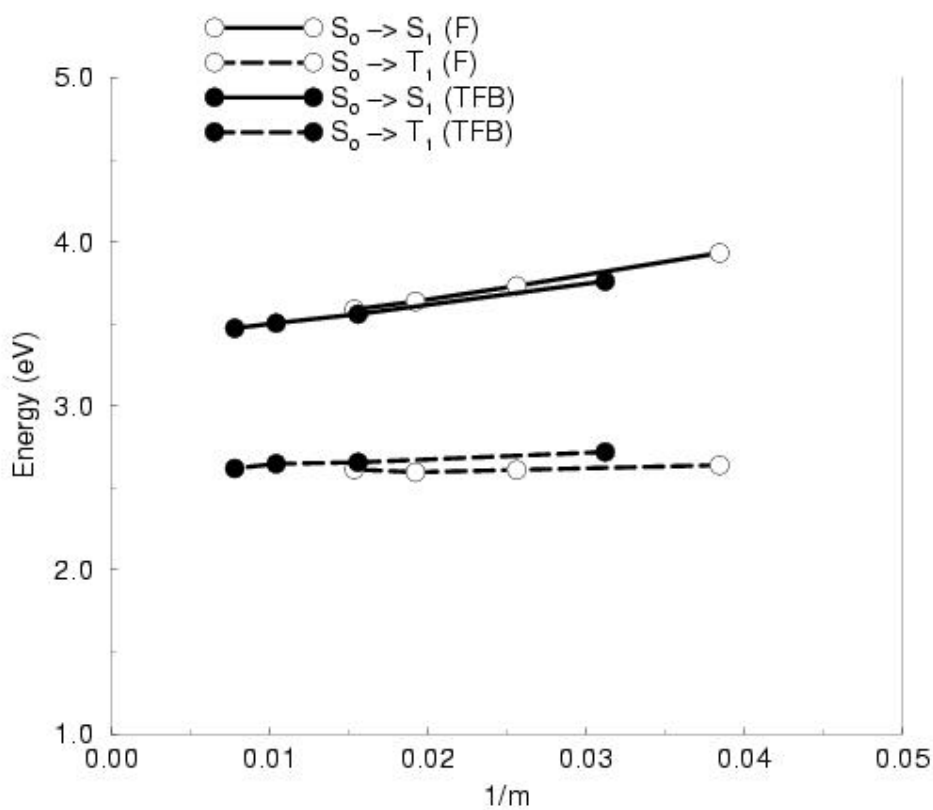


Figure 6: INDO/SCI-calculated evolution of the energy of the lowest singlet (solid lines) and triplet (dashed lines) excited states in F (open circles) and TFB (filled circles) oligomers as a function of the inverse number,  $m$ , of heavy atoms along the backbone.

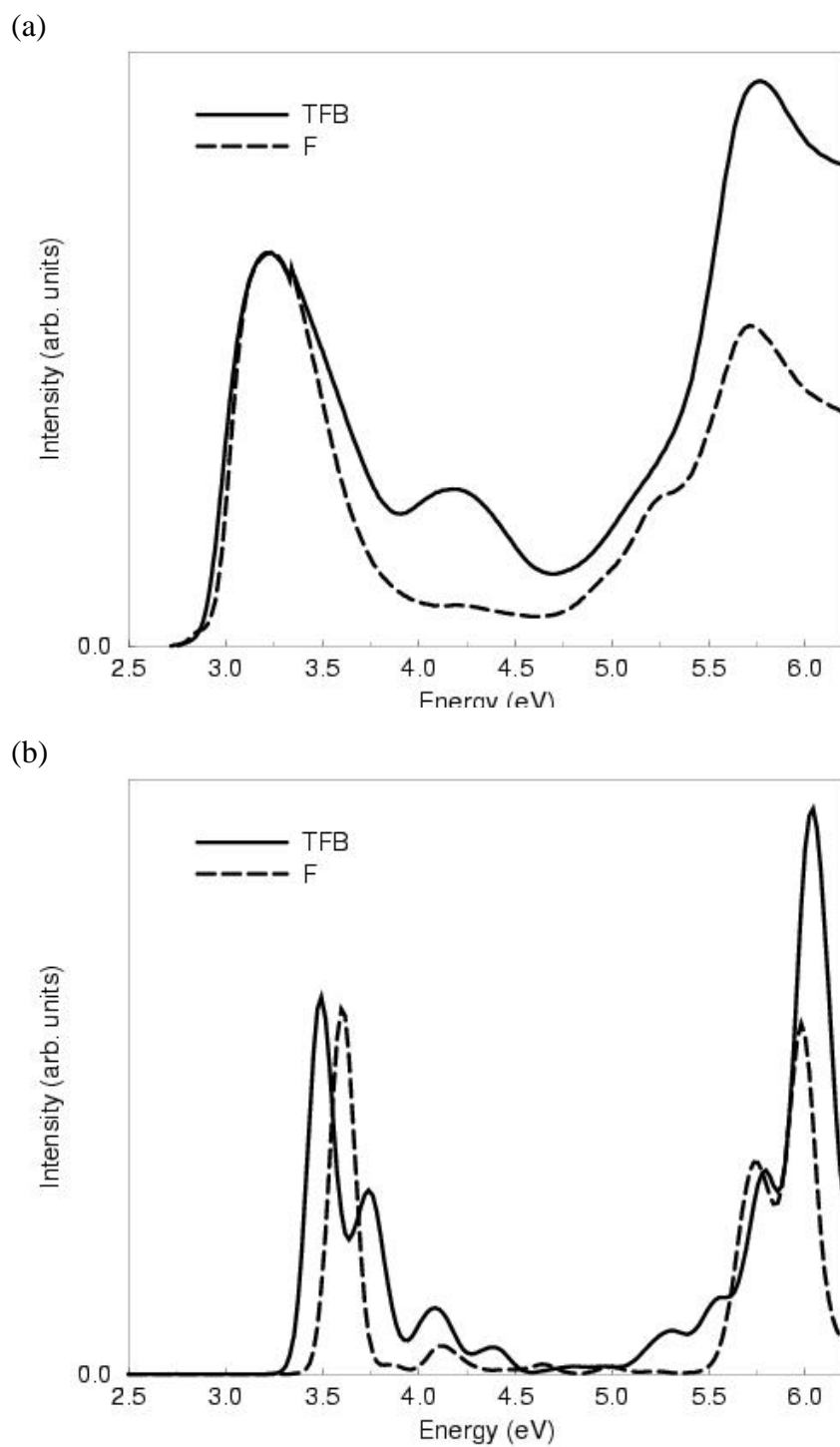


Figure 7: Experimental absorption spectra of TFB and F polymers (a) and corresponding INDO/SCI simulations performed on the longest oligomers (b). The absorption features are broadened by Gaussian functions with a FWHM set equal to 0.3 eV.