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Learning how planarization can affect dichroic patterns in polyfluorenes

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Abstract: The circular dichroism spectra of a single chain of polyfluorene was predicted for a *p*-twisted helix conformation and local planarized polymer sections in the presence and in the absence of thermal vibrations. Under thermal vibrations at 300 K, the planarized section of polyfluorene affords a red-shifted positive dichroic band between 446–456 nm, preserving a degree of chirality. The S1←S0 excitation energy decreases from 3.29 eV, for the *p*-twisted helix to 2.77 eV or 2.71 eV, for planarized sections with one or two coplanar twists, respectively. Thermal vibrations and intra-molecular rotations eventually affect the circular dichroism spectrum patterns, where planarized bent conformers induce a positive band towards 450 nm.

Keywords: chiral switch, chiral polymers, molecular dynamics, polymer simulations, circular dichroism spectra

Introduction

Conjugate polymers are continuously raising widespread attention owing to their versatile features spanning applications from organic electronics, photovoltaic devices towards nanomedicine.¹ Their flexible uses stem from the typical molecular organization, which confers them a specific chemical scaffold.^{2–11} For instance, amorphous arrangements have been so far related to spurious *cis*-defects arising during chemical synthesis¹² or owing to their backbone flexibility.¹³ The peculiar *cis* or *trans* orientation in the dihedrals of conjugated polymers have subtle effects on the observed properties including charge-transport mobility¹⁴ as well as absorbance or emission spectra.¹⁵ In these regards, absorbance and circular dichroism (CD) spectra of polyfluorenes are profoundly affected from the change in fluorene-fluorene dihedral orientations.⁸ For instance, the substituents at the C9 position¹⁶ together with the length of the alkyl side chains¹⁷ were shown to subtly influence the typical chiral assembly mechanism induced from a chiral solvent, resulting in effective chiral sensor frameworks.¹⁸ Amorphous silica support was also shown to be determinant to achieve a chiral arrangement of achiral chains of poly(9,9-dioctylfluorene) under circularly polarized light irradiation,¹⁹ owing to the specific interactions with the surface silanols.²⁰ In these regards, intramolecular rotations have been connected with blue shift in the UV or CD spectra, due to the excitation energy increase owing to the loss of conjugation.^{19,21}

Herein we focus our study on assessing how a local planarization of dihedral twist can affect the CD spectrum pattern. In order to predict this behavior, we considered a set of a 5-mer polyfluorene (PF) conformations sampled from enhanced sampling simulations in the framework of steered molecular dynamics (SMD)²² having all positive twist dihedrals, varying the intensity of the local dihedral twists, thereby rotating one or two coplanar angles.

The predicted ECD spectra show three specific patterns. The excitonic coupling is predicted only in the twisted conformation and it is related to the 5₁ helix conformation, as also previously shown by us¹⁹ and widely accepted as the most stable twisted conformation adopted in polyfluorenes.²³ Two positive red-shifted bands approaching 450 nm are detected only with coplanar dihedrals in the main chain subjected to thermal vibrations. A polymer chain with a flatter shape having a flexible, waved conformation leads to a smaller lowest-excitation energy, affording a red-shifted, monosignate, positive CD band.

Materials and Methods

Simulation details

An initial structure of the fluorene pentamer was obtained by ChemDraw software. The coordinates were optimized at the B3LYP/6-31G* level of theory,²⁴ with a relaxed scan for obtaining the planarization in a specific dihedral twist using Gaussian 16 package.²⁵ Furthermore, the coordinates were energy-minimized

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by using a steepest descent algorithm and then equilibrated by means of classical molecular dynamics (MD) simulation for 10 ns at 300 K, using a cell dimension of $48 \times 64 \times 16 \text{ nm}^3$. Steered molecular dynamics (SMD) were run following the simulation protocol that we validated in¹⁹ and successfully predicted polyfluorene chiral switching. In particular, the NVT ensemble was enforced at a temperature of 300 K by the velocity rescaling thermostat, as implemented in the GROMACS MD code - version 2016.3.²⁶ Electrostatic interactions were calculated using the Particle Mesh Ewald method.²⁷ The time-step was set to 2 fs. The LINCS algorithm²⁸ was applied to fix all bonds lengths. Periodic boundary conditions were applied. The torsional parameters and charges developed for oligofluorenes²⁹ reported by Raos and coworkers were used in combination with the CHARMM based General Force-Field³⁰ to treat the bond, angle and Lennard-Jones force field parameters. The four dihedral twists of the 5-mer polyfluorene were used as collective variables within PLUMED v.2.3.1,³¹ in order to sample twisted and coplanar conformations of the polymer. We obtained all twisted conformations having fluorene-fluorene dihedrals equal to 50 degrees and we thereby switched the value of fluorene-fluorene dihedrals to coplanar values (i.e. between 0 and 5 degrees).

Electronic CD spectra calculations

The intrinsic rotatory strengths were calculated for the sampled conformations of a 5-mer polyfluorene at the B3LYP/6-31G* level of theory. We chose the B3LYP functional owing to its good performance in predicting the electronic state energies of amorphous polyfluorenes.³² We also tested the Coulomb-attenuating correction of the B3LYP, the CAM-B3LYP³³ and the wB97XD³⁴ with dispersion corrections, in order to take into account possible charge transfer contributions that may arise in higher excited states. Those spectra are reported in the Supporting Information and do not significantly differ from the ones calculated at the B3LYP/6-31G* level of theory, apart from a blue shift of the spectra owing to an increase of the excitation energies. Furthermore, in order to assess the suitability of the force field parametrization in the ECD spectra predictions,³⁶ we calculated the UV and ECD spectra from the minimized MM coordinates through the steepest descent algorithm. The comparison with the ones calculated at the B3LYP/6-31G* level of theory does not show substantial differences, as highlighted from Figures S5 and S6 of the Supporting Information. ECD spectra calculations were run using Gaussian 16 package.²⁵ All the ECD spectra were calculated considering fifty singlet excited states. Rotatory strengths are reported in the usual c.g.s. units of $10^{-40} \text{ esu.cm.erg/Gauss}$ and calculated within the dipole-length formalism. The calculations of the ECD spectra at a given wavelength, λ , were done assuming Gaussian bands with 600 cm^{-1} full width at half-height (from 300 nm to 600 nm) for all transitions centered at a given excitation wavelength. A factor of 2.278 was applied during the conversion of rotatory strengths and $\Delta\epsilon$ values.³⁵

The calculated ECD spectra at CAM-B3LYP/6-31G* and wB97XD/6-31G* level of theory together with the related tables of rotational strengths are reported in the Supporting Information. The coordinates of the 5-mer polyfluorenes predicted at the B3LYP/6-31G* level of theory and sampled from SMD simulations are available at the following public repository:

https://github.com/adpietro/paolo/Chirality_Polyfluorenes/raw/master/PF_coordinates.zip

Results and Discussion

The effect of a local twist planarization in polyfluorenes was assessed through the calculation of ECD spectra at the B3LYP/6-31G* level of theory. Firstly, the ECD spectra were calculated from the optimized coordinates without any thermal effect. We started from the energy-minimized conformation with 37° , whose values are consistent with the one reported so far.^{29,32} From those coordinates a scan of the potential energy surface was carried out in a range of coplanar dihedrals (i.e. 0° - 5°), thereby rotating one, two or three consecutive dihedrals. From these planarized states we calculated the related ECD response.

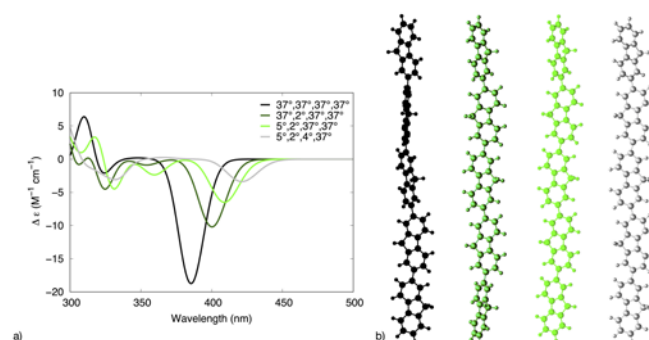


FIGURE 1. ECD spectra predicted at the B3LYP/6-31G* level of theory for a 5-mer polyfluorene with *p*-twisted or planarized conformations optimized at the same level of theory. The main chain dihedral twists identifying the optimized conformations are reported in the labels. The snapshots of the optimized coordinates for which ECD spectra were calculated are reported beside.

Figure 1 reports the ECD spectra predictions varying the number of the planarized dihedrals. The *p*-twisted polyfluorene helix conformation features a monosignate negative band approaching 380 nm. This band is red-shifted and accompanied by a decrease in intensity in the presence of coplanar dihedrals (Figure 1). It can be ascribed to an increase in polymer conjugation owing to the planarization.²¹

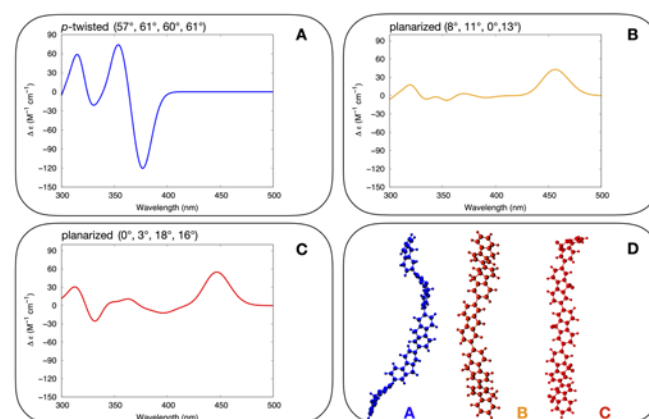


FIGURE 2. ECD spectra predicted at the B3LYP/6-31G* level for a 5-mer polyfluorene conformation sampled from SMD simulations at 300 K for *p*-twisted (A) and planarized conformations (B,C). The snapshots of the coordinates sampled from SMD at 300 K for which ECD spectra were calculated are reported beside in (D).

In the presence of thermal vibrations, the ECD spectrum related to the negative band centered at 380 nm of the *p*-twisted helix (Figure 2 A) does not significantly change with respect to the one calculated from the optimized coordinates within the DFT frameworks, however a positive band at 350 nm appears and it

features the excitonic coupling. Furthermore, the planarized coordinates obtained from SMD at 300 K afford an ECD spectrum with a red-shifted, positive band at 446 nm or 456 nm, with one (Figure 1B) or two coplanar twists (Figure 1C), respectively. Thermal vibrations counterbalance the strain of planarization allowing the polymer to bend towards the fluorene rings. Consequently, the polymer preserves a degree of chirality in the planarized polyfluorene conformations (Figure 2D).

In order to further analyze the Circular dichroism spectra predictions and because we detected a positive red-shifted band only in the presence of thermal vibrations, we clusterized the calculated rotational strengths for discriminating those of the planarized states with the one of the *p*-twisted conformation.

The clusterization of the related rotational strengths also shows specific dichroic spectral patterns for the *p*-twisted helix conformation, where a positive value is predicted at 350 nm and a negative value at 380 nm. At variance with the *p*-twisted helix conformation, the ECD spectra of the planarized polyfluorene scaffold feature positive rotational strengths predicted at 446 nm or 456 nm, with one or two coplanar twists, respectively (Figure 3).

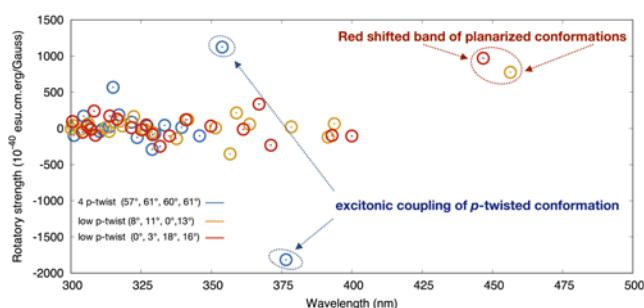


FIGURE 3. Rotational strengths calculated at the B3LYP/6-31G* level of theory for a 5-mer polyfluorene varying the dihedral twists. Positive rotational strengths are detected in the range 430–450 nm and are clusterized in red. The rotational strength values corresponding to the excitonic coupling predicted for the *p*-twisted conformation are clusterized in blue.

We analyzed the frontier orbitals (Figure 4) detecting a destabilization of the HOMO energy levels with respect to that one of the *p*-twisted conformation of 0.27 eV for the planarized conformation with one coplanar twist (conformation B in Figure 2) and 0.30 eV for the planarized conformation with two coplanar twists (conformation C in Figure 2).

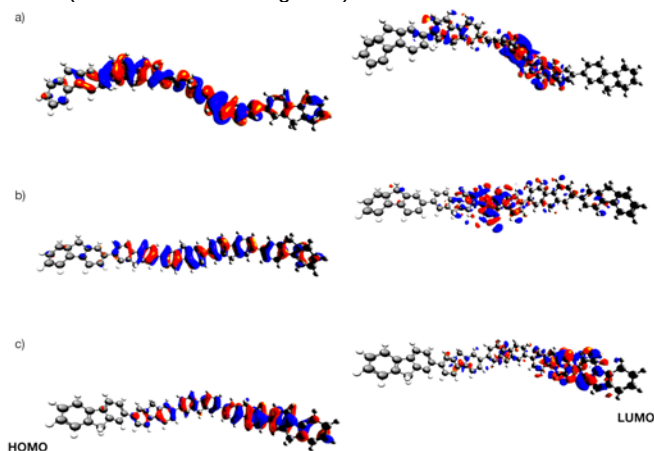


FIGURE 4. Frontier orbitals reconstructed at the B3LYP/6-31G* level of theory for the *p*-twisted polyfluorene a) and the planarized polyfluorene conformations with one b) or two coplanar twists c).

The LUMO energy levels turn out to be stabilized with respect to the one related to the *p*-twisted conformation of -0.30 eV in the presence of one coplanar twist (conformation B in Figure 2) and -0.35 eV in the presence of two coplanar twists (conformation C in Figure 2), with a total energy gap varying from 3.73 eV (*p*-twisted) to 3.16 eV or 3.08 eV, depending on the presence of one or two coplanar twists in the polymer main-chain. The former variation in the HOMO-LUMO energy gap is reflected in the S1←S0 excitation energy which respectively varies from 3.29 eV, corresponding to the Franck–Condon (FC) vertical transition from the ground state,³⁷ to 2.77 eV or 2.72 eV.

Conclusion

In summary we have disclosed how the planarization of polyfluorene conformations affect the ECD spectra patterns. Thermal vibrations introduce an extent of bending in the polymer main-chain, allowing a residual chirality. A red-shifted positive band at 446 nm is predicted for planarized polymer sections, which is subsequently red-shifted to 456 nm in the presence of two coplanar dihedrals in the polymer main-chain. The red-shift occurring in the planarized, dynamic conformations is due to the destabilization of the HOMO energy level of the coplanar conformations with respect to the *p*-twisted conformations (0.27 eV for the conformation with one coplanar twist and 0.30 eV for the conformation with two coplanar twists) accompanied by a concurrent stabilization of the LUMO energy level of the coplanar conformations with respect to the *p*-twisted conformations (-0.30 eV in the presence of one coplanar twist and -0.35 eV with two coplanar twists). Consequently, the total energy gap varies respectively from 3.73 eV (*p*-twisted) to 3.16 eV or 3.08 eV.

The variation in the energetics of the frontier orbitals causes the decreasing of the S1←S0 excitation energy from 3.29 eV for the *p*-twisted conformation to 2.77 eV or 2.72 eV, for the planarized conformations with one or two coplanar twists, respectively. Thermal vibrations coupled with intra-molecular rotations induce local changes that eventually impact the circular dichroism spectrum patterns.

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