

# Spectroscopic signatures for planar equilibrium geometries in methyl-substituted oligothiophenes

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In recent studies it was demonstrated that temperature-dependent optical spectroscopy is a valuable tool for revealing the differences in the geometries of flexible molecules like oligothiophenes (OTs) in the ground ( $S_0$ ) and first excited ( $S_1$ ) electronic states, by examining the symmetry relations between the absorption and emission spectra: while at low temperature the spectra show mirror symmetry, pointing to planar geometries in  $S_0$  and  $S_1$ , the symmetry relation breaks down at ambient temperature due to thermal population of torsional modes. In the present joint spectroscopic and theoretical study, we demonstrate that this behavior is also observed for di- and tetramethyl-substituted OTs, suggesting an essentially planar equilibrium geometry not only in  $S_1$  but also in  $S_0$ , despite the increasing sterical hindrance which is imposed by the substituents. This rather surprising result is rationalized by the softness of the carbon–sulfur bond, which is able to adapt to the geometrical constraints.

## Introduction

Conjugated oligomers have received much attention due to their use in (opto)electronic devices.<sup>1–5</sup> Among others, oligothiophenes (OTs) are widely studied since it is possible to tune their functional properties by minor structural modifications or conformational changes.<sup>6–10</sup> There are two classes of (opto)electronic devices in which OTs have found applications as active materials, namely organic light-emitting devices (OLEDs) and field-effect transistors (OFETs). The conformation of the molecules controls their properties and hence the performance of these devices; in OFETs, the conformation affects the crystal packing and therefore the carrier mobility and in OLEDs, the intersystem crossing rate and therefore the fluorescence quantum yield, as well as the electronic transition energies by modifying the effective conjugation length. Especially intriguing is the role of small substituents in oligomers with torsional degrees of freedom that are often used, for instance, to prevent aggregation. It is commonly assumed that large differences in the geometric structure occur between substituted and unsubstituted OTs and that, depending on the length and substitution pattern, quite different results are obtained concerning the planarity of the alkyl-substituted

molecules and the conformation of the thiophene rings.<sup>11–13</sup> In the case of alkyl-substituted quaterthiophenes (4T) in the solid state, depending on the number and position of the alkyl-side-chain substituents, coplanar molecules, molecules with non-coplanar inner rings, with coplanar inner rings but with non-coplanar outer rings, with *syn* and *anti* configurations as well as distortion from planarity in inner rings by a displacement of the sulfur atom out of the molecule plane, could be observed.<sup>14</sup> Regarding isolated molecules in solution, Lanzani *et al.*, Durocher *et al.*, Di Paolo *et al.* as well as Egelhaaf *et al.*<sup>12,15–18</sup> explored the optical properties of 4T and related compounds in order to elucidate the role of substituents in determining the position of both optical absorption and emission maxima. In this paper, we focus our interest on the torsional potential energy of 4T and its methyl derivatives in (frozen) solution and its impact on their optical properties. Our spectroscopic studies demonstrate that in  $S_0$  all these molecules, despite the sterical hindrance induced by the methyl substituents, have a very flat torsional potential corresponding to a quasi-planar conformation, as in  $S_1$ . As will be shown, this phenomenon is not predicted by standard gas-phase quantum-chemical calculations; however, the theoretical models account well for the observed spectral changes (mirror symmetry breakdown) induced by the temperature in the optical absorption and emission spectra. Our approach could be of significant interest for the interpretation of experimental results in related conjugated oligomers.<sup>17,18</sup>

## Experimental and computational details

Three unsubstituted and alkyl-substituted OTs (see Scheme 1), namely 4Ts, 3,3'''-dimethylquaterthiophene (DMe4T) and

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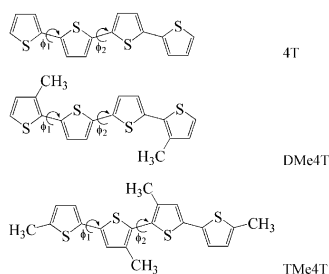
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**Scheme 1** Molecular structure of 4Ts under investigation, along with dihedral angles  $\phi_1$  and  $\phi_2$  involved in quantum-chemical calculations.

3'',4',5,5'''-tetramethylquaterthiophene (TMe4T), have been synthesized in accordance with literature.<sup>19</sup> Samples were studied in solution using *n*-tetradecane as a solvent, at a concentration of about  $10^{-6}$  mol l<sup>-1</sup> or lower to avoid self-absorption and aggregation phenomena in the PL measurements at low temperature (LT).

Absorption and PL spectra at RT were collected with a Varian Cary 50 Scan spectrophotometer (bandwidth 1 nm) and a Varian Cary Eclipse spectrofluorimeter (bandwidth 1 nm), respectively. LT PL and excitation (PLE) measurements were performed on frozen solutions in a bath cryostat using a monochromated Xe lamp as excitation source (bandwidth 1 nm), and a N<sub>2</sub>-cooled CCD camera coupled with a 190 mm polychromator (bandwidth 0.5 nm) for the signal detection. All optical measurements have been corrected for the instrumental spectral responses.

Quantum-chemical calculations using (time-dependent) density functional theory, (TD-)DFT, were performed in the gas-phase in order to obtain the equilibrium geometries and vibrational normal modes of both S<sub>0</sub> and S<sub>1</sub> as well as the adiabatic and vertical transition energies. All calculations have been performed with the TURBOMOLE V5.7.1 program package.<sup>20,21</sup> The geometries were converged with the BHHLYP (50% of Hartree–Fock exchange)<sup>22</sup> exchange–correlation kernel since hybrid functionals are expected to provide much more reliable performance for the optical and photophysical properties of this kind of systems.<sup>23–26</sup> In order to study the effect of the conformational disorder, two different symmetries were imposed at both the DFT and TD-DFT levels: C<sub>2h</sub> (planar conformation) and C<sub>2</sub> (non-planar conformation). The cost-effective 6-31G\* basis set was consistently employed in the calculations<sup>27,28</sup>, and the *m4* numerical quadrature grid was used. The SCF convergence criterion was set to 10<sup>-7</sup>. The typical difficulties encountered<sup>29,30</sup> when applying TD-DFT methods for the description of transition energies are not expected to largely affect the results presented here since long-range charge-transfer excitations are not involved.

The simulation of LT absorption spectra for the planar molecules was done within the harmonic approximation with displaced undistorted oscillators (linear coupling), following the procedure described in literature.<sup>31</sup> The Huang-Rhys factors were calculated using a modified version of the Dushin program.<sup>32</sup>

For RT spectra, thermal excitation of out-of-plane modes have to be included in order to correctly describe the band shapes.<sup>31</sup> For undisplaced distorted oscillators, when both the S<sub>0</sub> and S<sub>1</sub> torsional potentials are harmonic (quadratic coupling), this can be done by numerical convolution of the

low temperature spectra with a spectral distribution function<sup>31</sup>,

$$G'(E) = \exp[-E/(D - 1)kT] \quad (1)$$

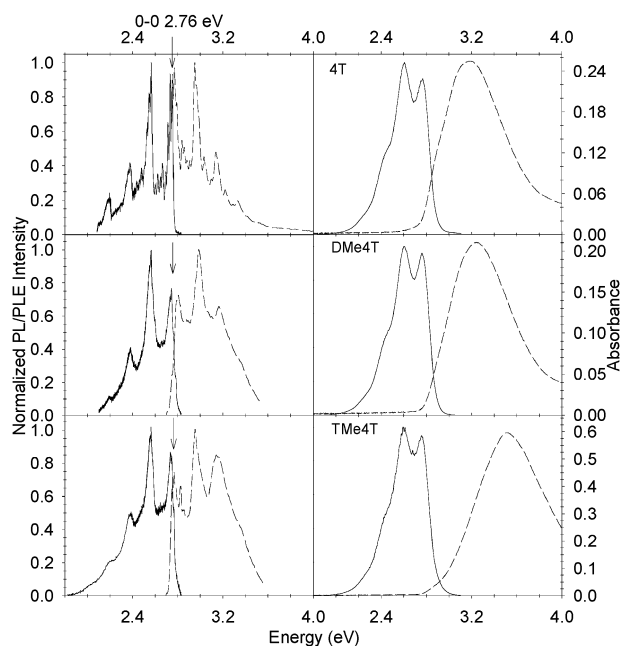
where  $G'(E)$  is an exponential distribution which takes into account the thermal population of low-frequency (torsional) modes.  $D$  accounts for the difference in the potential energy surfaces in S<sub>0</sub> and S<sub>1</sub> and is defined as the ratio of the force constants of the modes involved; it is set here to obtain the best agreement with experiment. The spectra were additionally convoluted by a Gaussian function of bandwidth  $\gamma$  to account for the (dynamic) inhomogeneities of the environment.

In order to get a deeper insight into the differences in the potential energy surfaces of the molecules under study, bithiophene (2T), 3-methylbithiophene (Me2T), and 3,3''-dimethylbithiophene (DMe2T) have been taken as model compounds. The torsional potential energy surfaces in S<sub>0</sub> have been calculated by obtaining the equilibrium geometries at different torsional angles ( $\phi = 0-180^\circ$ ). In S<sub>1</sub>, the energy surface has been calculated from the vertical transition energies from the ground state at the different torsional angles. All these calculations have been made at the DFT level with the BHHLYP functional using the triple-zeta quality basis set with polarization functions added on all atoms (cc-pVTZ), which appears to be the best compromise between accuracy and computational cost in the determination of potential surfaces for this kind of compounds.<sup>33–35</sup>

## Optical spectra

### Room temperature spectra

In Fig. 1 the PL and PLE/absorption spectra of 4T, DMe4T and TMe4T at RT and at 4 K are reported. At RT, the optical



**Fig. 1** Normalized PL (solid line) and PLE/absorption spectra (dashed line) collected at 4 K (left) and 300 K (right) for 4T, DMe4T and TMe4T (from top to bottom).

spectra show a typical behavior<sup>11,18,36</sup> characterized by broad and unstructured  $S_0 \rightarrow S_1$  absorption bands, with a significant Stokes-shift with respect to the corresponding PL spectra. There is a complete breakdown of the mirror symmetry rule since the PL spectra of all three molecules, contrary to the absorption spectra, exhibit a well-defined vibronic progression with a separation of about 0.18–0.19 eV essentially built from two vibrational modes.<sup>37</sup> The purely electronic PL transition from  $S_1$  to  $S_0$  ( $E_{00}$ ) is at 2.76 eV for all the molecules under the same experimental conditions (*i.e.* the same solvent) and is thus unaffected by the presence of the substituents. This finding suggests a similar conformational geometry for  $S_1$  for the three oligomers. For unsubstituted OTs,  $S_1$  has always been assumed to possess a planar geometry<sup>18,36</sup> due to the significant shortening of the interring bond. Our results therefore suggest that, also for methyl substituted OTs, planarity in  $S_1$  is attained upon photoexcitation, thus implying that the conjugation is strong enough to overcome steric hindrance effects.

The effect of substituents is more evident in the absorption spectra. Indeed, the absorption maximum energy shifts towards higher values as the number of methyl groups increases; they are located at 3.19, 3.24 and 3.51 eV for 4T, DMe4T and TMe4T, respectively (Table 1). The absorption bandwidth shows a similar trend and is the largest for the tetra-methylated oligomer. Since the position of the 0–0 transition in the PL spectra is the same for all the 4Ts, the amplitude of the Stokes-shift (measured from the 0–0 energy to the absorption maximum) increases with the number of methyl groups from 0.43 eV for 4T to 0.46 eV for DMe4T to 0.75 eV for TMe4T.

The breakdown of the mirror symmetry rule between optical absorption and emission spectra as well as a large Stokes-shift are usually explained in the case of non-rigid conjugated moieties (such as OTs, oligophenylenes, *etc.*) by taking into account the torsional degrees of freedom which lead to a non-planar structure in  $S_0$ .<sup>18,38,39</sup> In the case of substituted chromophores, a more pronounced  $S_0$  distortion is expected due to steric hindrance effects.<sup>40</sup> Previous geometry optimization data of similar isolated molecules give inter-ring dihedral angles larger than  $40^\circ$ , which—in a simple picture—leads to shifts in the excitation energy as large as several hundred meV.<sup>11</sup> For sterically non-hindered systems, it was shown at a later stage

that the room temperature features have to be correctly described by thermal population of planar equilibrium structures, leading to an *on average* distorted structure.<sup>31,41</sup>

### Low temperature spectra

While our measurements suggest that the presence of methyl groups and their number can affect the  $S_0$  geometry of the oligomer at RT, this situation is drastically changed at low temperature where the substitution seems to play a minor role. The most striking difference between room and low-temperature measurements is that the mirror symmetry rule is recovered at LT (Fig. 1 left) for all molecules under study. Moreover, both the PL and PLE spectra of all molecules show the same vibronic progressions with negligible Stokes-shift. In the PL spectra, the main peak positions and relative intensities are the same as those observed at RT without any energy shift related to solvent freezing. The spectral features are more resolved at LT, thus allowing, at least in the case of 4T, to recognize the vibronic replica due to all vibrational modes efficiently coupled with the purely electronic transition.<sup>42</sup> The only difference between the PL spectra of the investigated OTs is the increased broadening and the lack of details in DMe4T and TMe4T PL traces which are probably due to a larger disorder in the co-crystallization of OTs/*n*-tetradecane mixture induced by the methyl groups, which do not allow for a uniform environment. For this reason, only small changes are observed in the PL of methyl-substituted OTs in the temperature range between 4 and 100 K (not reported here). We can therefore conclude that the  $S_1$  states of the investigated systems are influenced by temperature only in terms of an increased inhomogeneous broadening, without any effect on their average geometry.

As outlined before, the PLE spectra at LT are the mirror images of the PL spectra. They show the same reduced fine structure in the presence of the substituents, with the half-width of each vibronic peak slightly increasing with the number of methyl groups. From the overall comparison between the PLE and PL spectra of the frozen solutions at 4 K, the following observations can be drawn: (i) in both absorption and emission spectra, the intensities and positions of the vibronic progressions do not change with methyl substitution, thus suggesting that both the vibrational frequencies and the coupling to the  $\pi$ - $\pi^*$  electronic transition are very similar in  $S_0$  and  $S_1$ ; (ii) in the

**Table 1** Experimental electronic origin ( $E_{00}$ ) of PL and PLE and absorption maxima ( $A_{\max}$ ) at RT and LT; TD-DFT-calculated (BHHLYP/6-31G\*) adiabatic, and vertical transition energies for absorption ( $S_0 \rightarrow S_1$ ) and emission ( $S_1 \rightarrow S_0$ ) spectra of two conformers ( $C_2$  and  $C_{2v}$ ) of 4T, DMe4T and TMe4T ( $\phi_1$  and  $\phi_2$  dihedral angles, see Scheme 1). The oscillator strengths are given in parentheses.<sup>a</sup> All the energies are in eV

|       | Experimental |      |                |      | Calculated      |                |                |                  |                |                |                |          |     |
|-------|--------------|------|----------------|------|-----------------|----------------|----------------|------------------|----------------|----------------|----------------|----------|-----|
|       | PL           |      | $A_{\max}/PLE$ |      | PLANAR $C_{2v}$ |                |                | NON-PLANAR $C_2$ |                |                |                |          |     |
|       | RT           | LT   | RT             | LT   | $E_{00}$        | $E_{Em}$       | $E_{Abs}$      | $E_{00}$         | $E_{Em}$       | $E_{Abs}$      | $\phi_1$       | $\phi_2$ |     |
| 4T    | 2.76         | 2.76 | 3.19           | 2.76 | 2.99            | 2.70<br>(1.29) | 3.31<br>(1.24) | 3.00             | 2.70<br>(1.29) | 3.43<br>(1.23) | 19             | 17       |     |
| DMe4T | 2.76         | 2.78 | 3.24           | 2.81 | 2.98            | 2.69<br>(1.31) | 3.30<br>(1.25) | 3.02             | 2.69<br>(1.31) | 3.63<br>(1.17) | 39             | 21       |     |
| TMe4T | 2.76         | 2.77 | 3.51           | 2.77 | 2.95            | 2.67<br>(1.43) | 3.26<br>(1.36) | <i>anti</i>      | 3.05           | 2.67<br>(1.43) | 3.99<br>(1.18) | 20       | 71  |
|       |              |      |                |      |                 |                |                | <i>syn</i>       | 3.20           | 2.73<br>(1.21) | 3.73<br>(1.18) | 10       | 127 |

<sup>a</sup> Geometry optimization with the 6-311G\* basis set yields in general somewhat larger torsional angles, but a qualitative similar picture.

three cases, a reasonable mirror symmetry with almost zero Stokes-shift (when considered as the energy spacing between the 0–0 electronic transitions) is observed. These observations suggest similar conformational geometries in  $S_0$  and  $S_1$  for the three oligomers.

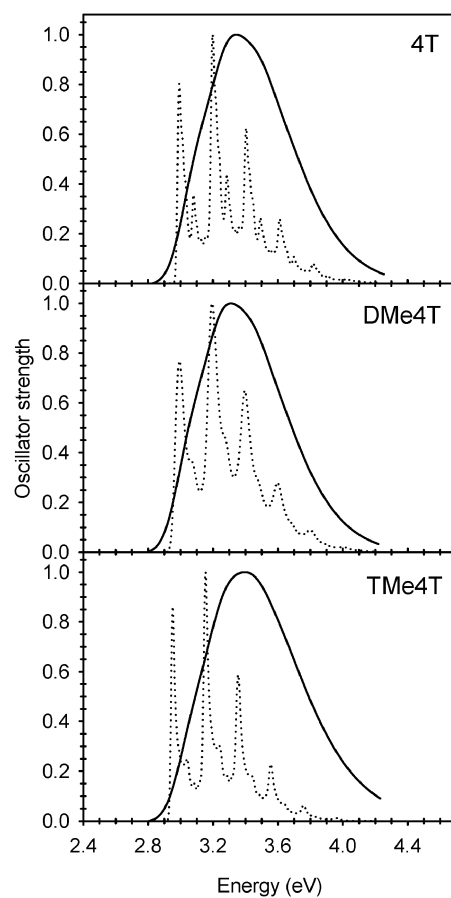
## Quantum-chemical approach

### Low temperature limit

The calculated vertical emission (absorption) energies  $E_{Em}$  ( $E_{Abs}$ ) as well as the adiabatic transition energies ( $E_{00}$ ) are given in Table 1 for the set of molecules considered here. Vertical emission energies were obtained as excitation energies from the first singly-excited state of the molecules at  $T \rightarrow 0$  K. All the reported ( $\pi$ – $\pi^*$ ) transitions are strongly dipole-allowed and characterized by a dominant HOMO to LUMO excitation, in general agreement with previous calculations reported for 4T at different levels of theory.<sup>43,44</sup>

Comparison between the results obtained for planar and non-planar *anti*-conformations (see Table 1) indicate that the adiabatic transition energy  $E_{00}$  and the vertical emission  $E_{Em}$  show practically no differences among the systems, and do practically not change independently of the conformation. This can be explained by the fact that the emission starts from a planar  $S_1$  state in both symmetries, and the energy difference between the  $S_0$  equilibrium geometries of the planar and non-planar conformations is very small (0.014, 0.034 and 0.104 eV for 4T, DMe4T and TMe4T, respectively). On the contrary, striking differences are found for  $E_{Abs}$ : whereas the differences among the systems are negligible for planar conformations, they become as large as  $\sim 0.6$  eV for the non-planar conformers. Since all quantum-chemical calculations are done at 0 K, these results must be compared to the experimental recordings at low temperature, but not at ambient temperature. In the low temperature limit, no major differences between the compounds regarding the position and structure of both the experimental emission and absorption bands are found. Thus, the first conclusion that can be extracted from the calculations is that the equilibrium structures of all systems in this study are rather planar in both  $S_0$  and  $S_1$ . The calculated LT absorption spectra of the compounds, based on strictly planar  $S_0$  and  $S_1$  states, confirm these results by showing a very similar intensity distribution compared to the experimental spectra (Fig. 2); this also points to small distortions in the normal modes upon substitution.

Conclusive evidence of a (nearly) planar  $S_0$  state of DMe4T and TMe4T—at least in frozen solution—arises from the mirror symmetry between absorption and emission at LT: this is only possible if not only  $S_1$  but also  $S_0$  is planar, or the energy difference between the equilibrium and the planar geometry in  $S_0$  is vanishingly small. Mirror symmetry was indeed demonstrated for longer unsubstituted oligothiophenes such as 5T,<sup>36</sup> and oligophenylenevinylenes in solid matrices.<sup>31</sup> On the other hand, no mirror symmetry in the LT limit was observed for systems where geometric repulsion does not permit planarization, such as oligophenylenes.<sup>40</sup> The direct proof for a planar ground state of DMe4T and TMe4T in frozen solution is difficult. Arguments might arise from crystal

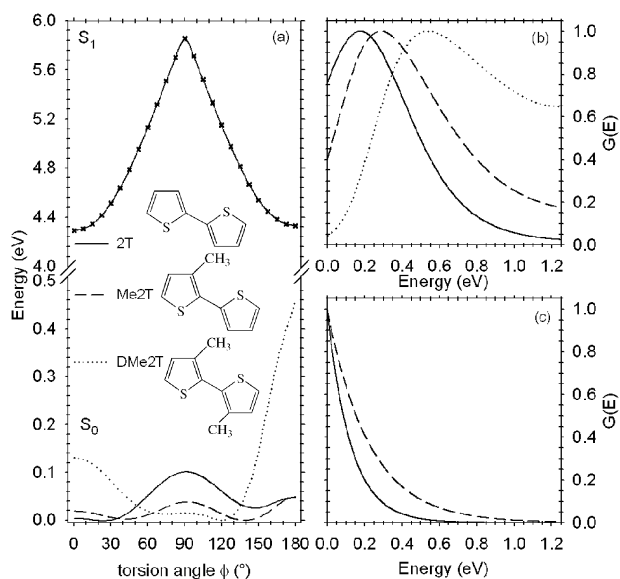


**Fig. 2** Simulated low (dotted line) and room (solid line) temperature absorption spectra of 4T, DMe4T and TMe4T (from the top to the bottom). Inserted Gaussian half-widths (LT) 4T: 150  $\text{cm}^{-1}$ , DMe4T: 300  $\text{cm}^{-1}$ , TMe4T: 300  $\text{cm}^{-1}$ . The RT spectra were convoluted with a Gaussian distribution (half-widths: 1500  $\text{cm}^{-1}$ ), and with an exponential distribution ( $D[4T, DMe4T] = 6.0$ ,  $D[TMe4T] = 10.0$ ,  $T = 293$  K).

structure analysis, although dense packing can lead to a substantial reduction of the torsional angles, *e.g.* for 2T which is co-planar in the crystal,<sup>45–46</sup> but shows a dihedral angle of  $\phi = 21^\circ$  (*anti*-conformation) in the gas phase (from jet experiments),<sup>47</sup> reproduced by gas-phase quantum-chemical calculations.<sup>48–51</sup> Interestingly, dihedral angles in the crystal structure of differently methylated 4T molecules—all with the same substitution pattern for the central thiophene units as in TMe4T—can vary from  $\phi_2 = 0^\circ$ ,<sup>56</sup> to  $\phi_2 = 30^\circ$  or  $\phi_2 = 46^\circ$ ,<sup>57</sup> all showing *anti* conformation. This variability apparently originates from the easily polarizable unshared electrons of the sulfur atoms that allow for the deformation of the thiophene rings to give significantly longer C–S bond lengths in the presence of strong steric interactions induced by substitutions next to the  $\alpha$ ,  $\alpha'$  junctions.<sup>56,57</sup>

This effect is not fully recognized by our gas-phase calculations on methylated bithiophene (2T): for a comparison, we

† Previous experimental gas-phase electron diffraction results showed a dihedral angle of  $\phi = 32^\circ$  (*anti*-conformation) in the gas phase at 370 K, to which several gas-phase quantum-chemical calculations refer.<sup>33–35,48–55</sup>



**Fig. 3** (a) Potential energy surfaces for inter-ring torsion of 2T, Me2T and DMe2T as a function of the torsional angle, calculated at the BHHLYP/cc-pVTZ level; first excited ( $S_1$ ) (top) and electronic ground ( $S_0$ ) state (bottom). (b) Convolution function calculated from the potential energy surfaces for 2T (solid line), Me2T (dashed line) and DMe2T (dotted line). (c) Exponential distribution function according to eqn (1), for  $D = 6.0$  (solid line) and  $D = 10.0$  (dashed line), at  $T = 293$  K.

have calculated the potential curves of 2T as well as the mono- and bi-methylated compounds (Me2T, DMe2T), see Fig. 3. Me2T can partly compensate the constraints imposed by mono-substitution, thus leading to a minimum at  $\phi = 42^\circ$  (*anti*) and just a slight increase of the barrier at  $\phi = 0^\circ$  compared to 2T, which would still allow planarization under external constraints like in solid solution or in the crystal. This is not possible for bi-substitution: in DMe2T the barrier at  $\phi = 0^\circ$  is very high, and the minimum is now found at  $120^\circ$  (*syn*), however with a rather low potential barrier (0.015 eV at  $90^\circ$ ) for the flip to the *anti*-conformation (local minimum at  $74^\circ$ ), in essential agreement with a former study by Raos *et al.*<sup>58</sup>

Geometry optimization of TMe4T gives a similar picture,  $\phi_2 = 127^\circ$  (*syn*), being here however only slightly more stable (0.012 eV) than the *anti*-conformation at  $71^\circ$ . The large barrier height at  $0^\circ$  of 0.13 eV makes efficient planarization under external constraints (like in solid solution or, even more, in the crystal) rather unlikely, inconsistent with the X-ray structure in ref. 56 and 57, and thus likely due to an underestimation of the softness of the C–S bond by the calculations. A closer inspection of the calculated C–S bond lengths shows that the inner C–S bond slightly increases when going from an *anti*- to an *anti*-coplanar conformation in both, DMe2T and TMe4T. Such a small deformation appears to be insufficient to compensate the stress imposed by the sterical hindrance in the planar conformer.

### Thermal population of torsional modes

When the temperature increases, minimization of the free energy  $G$  should be considered, with  $G = H - TS$ , where

$H$  and  $S$  are the enthalpy and the entropy of the system, respectively. At RT, the contribution of the entropic factor becomes dominant: the  $S$  term, which is directly related to the availability of different conformational states, should affect the energy of the optical transitions by lowering the energy ( $G$ ) of distorted conformers. Upon substitution, a larger number of non-planar states can be populated at high temperature due to the reduction of the torsional barriers (*vide supra*), thus shifting the position of the main absorption band to higher energy. As an example, we deduced the convolution functions for the methylated 2Ts of the absorption process by taking into account the shape of the torsional potentials in  $S_0$  and  $S_1$ , see Fig. 3. These functions were found by representing the population in  $S_0$  at different torsional angles according to a Boltzmann population, against the vertical energy difference  $S_1 - S_0$  at every torsional angle considered.<sup>31</sup> The results displayed in Fig. 3(b) show a clear trend towards a strongly broadened distribution upon substitution, which implies increasingly broadened and blue-shifted spectra in the series 2T  $\rightarrow$  Me2T  $\rightarrow$  DMe2T. With the potentials derived for 2T and substituted derivatives, it can already be seen that OTs containing DMe2T units will have the most broadened and blue-shifted absorption spectra, in agreement with previous experimental results for substituted 2T where a progressive blue-shift of the absorption maxima is observed when going from 2T to 4,4'- to 3,4'- and to 3,3'-dimethyl-2,2'-bithiophene (DMe2T);<sup>59,60</sup> this explains qualitatively the evolution of the RT spectrum going from 4T to TMe4T.

In order to simulate the absorption spectra of the three 4T oligomers at room temperature, we use the idea described above taking into account that a more planar equilibrium structure of  $S_0$  is expected for methyl-substituted 4T in solution compared with the substituted 2T models. A simple convolution function based on planar, harmonic torsional potential (eqn (1))<sup>31</sup> is expected to suitably describe the thermal effects: the resulting spectra are shown in Fig. 2 (solid lines), where the parameter  $D$  has been chosen to best match the experimental spectrum in each case. An increase in  $D$  is observed when going from 4T *via* DMe4T to TMe4T; this reflects the decrease in the slope of the potential hypersurface (*i.e.*, in the energy barrier between the local minima) in  $S_0$  torsional potential, in agreement with the trends provided by the quantum-chemical calculations. The convolution functions for the different  $D$  are displayed in Fig. 3c and show the same trend as the convolution functions obtained from the potential hypersurfaces with our model (Fig. 3a).

## Conclusion

We have demonstrated in a combined spectroscopic and quantum-chemical approach that the presence of methyl substituents in OTs does not appreciably distort the  $S_0$  conformation from planarity for molecules in solution at LT. This is supported by the observation of a clear mirror symmetry between absorption and emission spectra at LT.

This somewhat unexpected result is rationalized by the ability of the thiophene ring to adapt to the constraints induced by methylation thanks to the easy polarizability of

the sulfur atom and long C–S bonds. At RT, mirror symmetry is lost and a significant Stokes shift is obtained, which is ascribed to thermal population of distorted conformations, *i.e.* in an average non-planar ground state geometry, due to the shallow torsional barrier in  $S_0$ . Although the herein presented gas-phase quantum-chemical calculations cannot provide a detailed quantitative description of the experimental results in solid solution, they provide a reasonable qualitative insight into the mechanisms of thermally induced mirror-symmetry breakdown in these systems. An extension of the theoretical approach to more space-filling substituents and their role in excited state torsional relaxation as observed experimentally,<sup>17,18,61,62</sup> might be of interest for future studies. This should possibly also include a better quantitative description by using more sophisticated methods such as (doubly-) hybrid density functionals, DFT augmented with empirical dispersion terms, approximated coupled-cluster CC2/CC3, or multi-reference Møller–Plesset calculations based on CASSCF.

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