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Light-induced dipole moment modulation in diarylethenes: a fundamental study

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The dipole moment of photochromic diarylethenes is determined in solution for both the coloured and uncoloured form by measuring the capacitance of a capacitor filled with a photochromic solution as the dielectric material. Diarylethenes with different electroactive substituents are investigated and the modulation of dipole moment is related to the different chemical structure. We determine a modulation of the dipole moment up to 4 Debye. We discuss the model used to obtain the dipole moment from the capacitance measurements and we compare the experimental results with the outcomes from DFT calculations. The results highlight the importance of conformational effects in the description of the dipole moment of diarylethenes.

Introduction

Interesting works have recently shown how the modulation of dipole moment in photochromic materials can be effectively used to tune the electric behaviour of organic thin film transistors¹, the mobility in organic semiconductors², the doping of graphene³, the wettability of surfaces^{4,5} or to generate electrical current in a light-triggered electret⁶. In spite of this large interest, only a few experimental values of dipole moments of photochromic materials can be found in the literature⁷. Generally, papers report the calculated values of dipole moment for diarylethenes^{8,9}, spiropyrans^{10,11}, fulgides^{12,13}.

The experimental evaluation of the dipole moment gives a tool for the validation of the theoretical calculations. Even more important, it provides the actual characterization of the photochromic system in a specific environment and allows discussing the modulation of the dipole moment upon photoconversion in real conditions.

In this paper, symmetrical and asymmetrical substituted diarylethenes are considered, to highlight the effect of a push-pull structure in actually enhancing the dipole moment of the coloured form. We compare the results with the analogous symmetrically substituted molecules with donor groups. The diarylethene bearing acceptors at both sides are ruled out as the dipole moment is expected to be very low in both forms, as demonstrated in ref 8. We found that modulation of dipole moment up to 4 D can be obtained with push-pull diarylethenes. Worth noting we demonstrate that the analysis of the dipole moment by DFT calculation fails for the push-pull derivatives if the contribution of all the conformers of the open form to the total dipole moment is not considered.

Experimental

Theory of molecular dipole moment measurement

There are different methods to measure the dipole moment for molecules in liquid phase and some of them are well-established. Probably, the most important one consists in the exploitation of the Debye equation (written adopting SI units)¹⁴:

$$\frac{\epsilon-1}{\epsilon+2} \frac{M}{d} = P_m = \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu^2}{3kT} \right) \quad (1)$$

Where P_m is the molar polarization¹⁵. The dipole moment μ can be calculated by measuring the quasi-static relative permittivity ϵ , knowing the molecular polarizability α and the density d (M is the molar mass, N_A the Avogadro's number, ϵ_0 is the vacuum permittivity, k the Boltzmann constant and T the temperature). This approach is definitely valid only for samples in the gas phase, but it has been successfully applied to solutions of polar molecules in apolar solvents. In this peculiar case, the molar polarization of the solution (P_{12}) can be written as (supposing no solute-solvent interactions and additivity of the molar polarization):

$$P_{12} = X_1 P_1 + X_2 P_2 = \frac{\epsilon_{12}-1}{\epsilon_{12}+2} \frac{X_1 M_1 + X_2 M_2}{d_{12}} \quad (2)$$

Where X_i and M_i are the molar fraction and molar mass of the solvent (1) and solute (2), ϵ_{12} is the relative permittivity of the solution, d_{12} its density.

Since P_{12} can be measured and P_1 is determined by the solvent properties, we can in principle determine P_2 and hence the dipole moment.

Actually, equation 1 deserves important considerations regarding the molar polarization P_m . Indeed, P_m results from different contributions, namely the orientation contribution (P_O) related to the permanent dipole moment, the electronic contribution (P_E) related to the electronic polarizability (α_e) and the vibrational contribution (P_V) related to the vibrational polarizability (α_v). Therefore, eq. 1 can be written as follow:

$$\frac{\epsilon-1}{\epsilon+2} \frac{M}{d} = P_E + P_V + P_O = \frac{N_A}{3\epsilon_0} \left(\alpha_e + \alpha_v + \frac{\mu^2}{3kT} \right) \quad (3)$$

Usually, P_V is much smaller than P_E and can be neglected. This approximation cannot be applied in the case of highly polar molecules¹⁶, especially for conjugated polar molecules with a very strong IR spectrum, for which α_v can be computed from the absorption intensities of the vibrational transitions¹⁷.

The electronic contribution to the molar polarization, P_E , is usually determined by the refractive index measurements. Actually, refractive index is measured at optical frequencies, whereas dipole moment measurements are carried out at almost static electric field.

Here, we investigate molecules with intense IR spectrum which remarkably changes upon photo irradiation¹⁸; we calculate both P_E and P_V contributions by using density-functional theory (DFT). Data on the selected solvent (n-hexane) are taken from the literature¹⁶.

Capacitance measurement

The dipole moment is calculated using equations 1 and 2 starting from the measurement of the relative permittivity of the solvent ϵ_1 and of the liquid solution ϵ_{12} . Relative permittivity is determined by measuring three times the capacitance of the same capacitor filled with air (C_{air}), pure solvent (C_1) and solution (C_{12}), respectively. The solvent and solution permittivity as a function of the relative permittivity of air (ϵ_{air}), are given by:

$$\epsilon_1 = \epsilon_{air} \frac{C_1}{C_{air}}, \quad \epsilon_{12} = \epsilon_{air} \frac{C_{12}}{C_{air}} \quad (4)$$

The determination of the relative permittivity with respect to a reference (ϵ_{air}) allows to achieve a high accuracy without requiring a detailed knowledge of the capacitor geometry.

The experimental set-up has been specifically designed to perform measurements with a small volume samples (less than 2 ml) and a low concentration of photochromic molecules (0.1 – 5 mM).

This is a fundamental feature since it makes possible to overcome the risk of possible aggregation of polar molecules that could occur upon increasing the concentration.

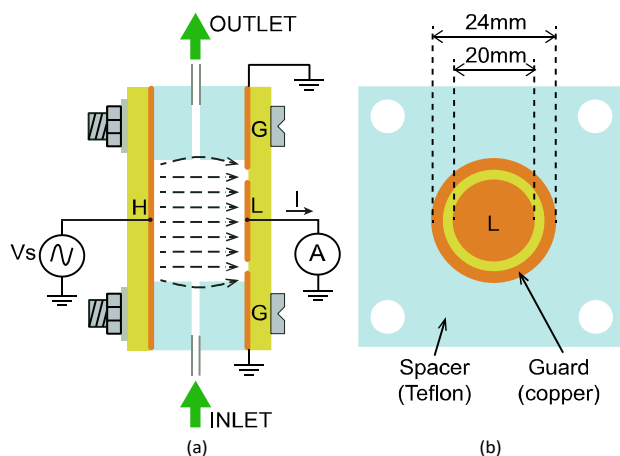


Figure 1. (a) Three-terminal cell for the dipole moment determination. The dashed lines show the electric field lines. (b) Top view of the printed circuit board with the Teflon spacer and the electrodes L and G (Guard).

The small values of capacitance of the photochromic solutions (1-2 pF) are measured using a custom three-terminal cell connected to a precision LCR meter (E4980A by Agilent) as shown in Fig. 1. A sinusoidal voltage V_s is forced to the electrode H and the current I flowing through the electrode L is acquired. The capacitance is extracted by the analysis of the amplitude and phase of I with respect to V_s . The voltage V_s is independent of the stray capacitance of the cable connecting the terminal H to the instrument. Similarly, the sensed current is not affected by the cables because the potential of terminal L is kept fixed to 0 V. Thus, this technique allows for measurements with high accuracy of small capacitances. The third electrode G is kept to the same potential of L (0 V) to obtain a uniform electric field in the volume of the cell between the H and L electrodes. Consequently, the measured capacitance is insensitive to the effect of fringing fields which are the main source of inaccuracy using a simpler two-terminal cell¹⁹. Copper electrodes, fabricated using a standard printed circuit board technology, are used. The internal diameter of the cell is 24 mm and the gap between the electrodes H and L-G is 3 mm, defined by a Teflon spacer. The total volume of the cell is only 1.4 ml and the capacitance in air is of $C_{air} \approx 0.9$ pF. A thinner cell would be beneficial in terms of both volume (lower) and capacitance (higher). However, by using thinner cell we have experienced a lower reproducibility of the measurements maybe due to a higher

sensitivity to mechanical arrangement of the components. The liquid is injected in the cell through two metallic tubes inserted in the Teflon spacer.

An example of capacitance recording during an experiment for the measurement of the dipole moment is reported in figure 2. The solvent is slowly injected in the void cell using a syringe pump. A low flow rate (100 – 300 $\mu\text{l}/\text{min}$) is used to prevent the formation of air bubbles and to avoid the mechanical stress given by the pressure. The capacitance reaches a plateau when the solvent has totally filled the cell. The cell is emptied after a few minutes and then the procedure is repeated using the solution with photochromic molecules. The analysis of the recorded data allows for the extraction of C_{air} , C_1 and C_{12} and the dipole moment is computed according to the previous equations (eqs. 2-4). The error in the measurement of the capacitance (δC) propagates to the evaluation of the dipole moment as follows:

$$\delta\mu \approx \frac{1}{2\mu} \cdot \frac{27kT}{cN} \cdot \frac{\epsilon_0\epsilon}{(\epsilon+2)^2} \cdot \frac{\delta C}{C} \quad (5)$$

where c is the concentration. The main source of error in the measurement of the capacitance is the change of the capacitor geometry whenever the cell is opened and closed. This error is of the order of few fF and it is comparable to the contribution given by the photochromic molecules. We obtained a reduction of the capacitance error down to $\delta C \approx 0.1$ fF by maintaining the cell closed during the whole experiment and properly filling/emptying it as required. Consequently, by making use of equation (5) the error on the evaluation of the dipole moment is $\delta\mu \approx 0.5/\mu c$, where μ and $\delta\mu$ are expressed in Debye and c is the concentration (mM).

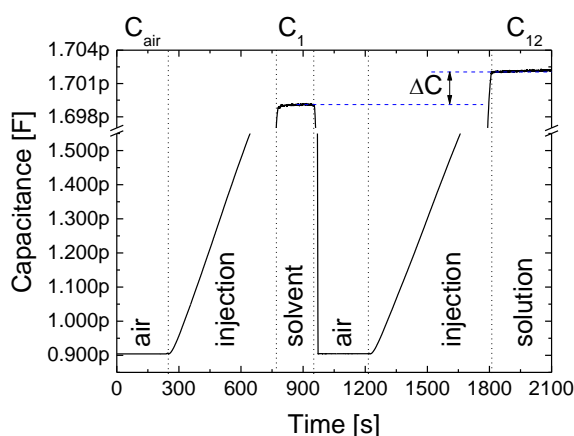


Figure 2. Example of capacitance measurement during an experiment for retrieving the relative permittivity of air, solvent (n-hexane) and the photochromic solution. The upper part of the graph has a different scale in order to magnify the difference between C_1 and C_{12} .

Photochromic molecules

We considered diarylethenes differing in the lateral substitution to highlight the effect of the push- π -pull structure in enhancing the dipole moment of the closed form. Their chemical structure is reported in figure 3.

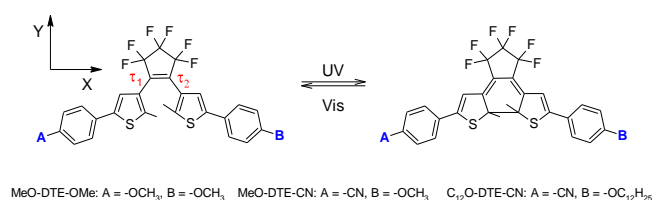


Figure 3. Chemical structure of the photochromic diarylethenes studied with the reference coordinates and the two torsional angles τ_1 and τ_2 .

The MeO-DTE-OMe is characterized by the presence of two donor groups. MeO-DTE-CN and $C_{12}O$ -DTE-CN show a donor-acceptor structure and they differ only in the length of the alkyl chain.

Synthesis

The photochromic diarylethenes derivatives have been synthesized as previously reported²⁰.

DFT calculations

The calculation of the Potential Energy Surfaces (PES), equilibrium geometry and vibrational spectra and of the molecular models considered in this work were carried out using Gaussian09 code²¹, adopting the B3LYP density functional and the 6-31G(d,p) basis set. The electronic contribution to the polarizability (α_e) at static electric field is readily available from the calculations and it has

been shown that this approach provides reliable results^{22–24}. The vibrational contribution to the polarizability (α_v) was computed starting from the frequencies and intensities of the calculated IR spectrum¹⁷.

In the case of MeO-DTE-CN, to find the average dipole moment of the open form we have considered the dynamical interconversion between the two conformers C_2 (antiparallel) and C_s (parallel). The rigid PES calculations on MeO-DTE-CN were carried out by varying the two torsional angles (τ_1 , τ_2) between the perfluorinated unit and the two lateral rings (see figure 3) while keeping the other internal degrees of freedom at the optimized values found for the C_2 reference conformation. The direct inspection of the PES allowed the identification of the minima, which were subsequently fully optimized starting from the corresponding values of the torsional angles (τ_1 , τ_2). Hence, the dipole moments of the conformers have been weighted according to the Boltzmann distribution (based on relative energies) to obtain the average dipole moment. From the point of view of the dipole moments, we did not find significant differences between the complete alkylated model ($C_{12}O$ -DTE-CN) and its simplified version, MeO-DTE-CN. This is expected since the two models possess essentially the same electroactive substituents.

Results and discussion

The dipole moment of all the considered diarylethenes (figure 3) was calculated as described in the experimental section. Calculation for the closed form is straightforward, since only one conformation is possible. For the open form we initially considered the C_2 (antiparallel) conformer, which is the only one undergoing the photoisomerisation²⁵. Table 1 reports the calculated values of the dipole moment, including the components along the Cartesian axes defined in figure 3.

Molecule	Isomer	μ_x (D)	μ_y (D)	μ_z (D)	μ (D)
MeO-DTE-MeO	C	0.02	-3.05	-0.24	3.06
	O – C_2	0.01	-2.05	-0.20	2.06
MeO-DTE-CN	C	8.66	-1.59	0.07	8.80
	O – C_2	7.06	-1.49	-1.47	7.36
$C_{12}O$ -DTE-CN	C	9.67	-0.49	-0.27	9.69
	O – C_2	7.95	-1.13	-0.51	8.05

Table 1. Calculated dipole moments for the diarylethenes in the closed form and in the C_2 (antiparallel) open form. The definition of the axes is reported in figure 3.

In order to discuss the values of the dipole, we split the molecules in three fragments, as depicted in figure 4.

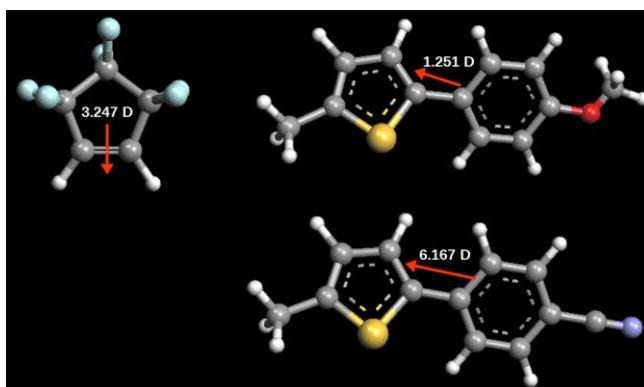


Figure 4. Chemical structure of the fragments with the corresponding dipole moment.

By adopting the reference system of figure 3, we notice that the two lateral fragments show a dipole moment that lies almost along the X-axis. However, the cyano group shows a much larger value (6.17 D) than in the case of methoxy group (1.25 D). The perfluorinated fragment gives a remarkable contribution with a dipole moment of 3.25 D that is directed along the Y-axis.

In the closed form, the symmetrical MeO-DTE-MeO has a dipole moment directed along the Y-axis. Indeed, there is compensation between the dipole moment of the two methoxy fragments along the X-axis, whereas the dipole moment of the perfluorocyclopentene is slightly compensated by the MeO dipole along the Y-axis.

A different behaviour occurs for the asymmetric diarylethenes, with a dipole moment value of about 9 D for the closed form, which is much larger than for the symmetric molecule; in addition, the dipole moment points almost along the X-axis. This is due to the direction of the dipole moment of the two fragments with a predominance of the cyanobenzene over the alkoxybenzenes. An effect that further increases the dipole moment is the possible internal charge transfer between the acceptor cyano group and the donor methoxy group.

Considering the open form in the C_2 conformation (antiparallel), smaller values of the dipole moment characterise all the molecules, with the same direction of the dipole moment in the closed form. Since the decrease of the dipole moment in the open

form, we expect a modulation of this properties upon photoisomerization. Moreover, such modulation should be larger for the asymmetric molecules as predicted by the calculations (see table 1).

To retrieve the dipole moment from the experimental capacitance measurements, according to the Debye equation (3), it is necessary to know the polarizabilities (electronic and vibrational). The calculated data are reported in table 2.

Molecule	Isomer	$\alpha_e(\text{\AA}^3)$	$\alpha_v(\text{\AA}^3)$
MeO-DTE-MeO	C	71.28	19.86
	O – C ₂	58.10	12.85
MeO-DTE-CN	C	73.35	12.24
	O – C ₂	58.93	11.47
C ₁₂ O-DTE-CN	C	94.16	15.94
	O – C ₂	78.69	16.33

Table 2. Calculated values of the electronic and vibrational contributions to the polarizability for the three photochromic diarylethenes. The values are given in \AA^3 . Conversion to SI units (Cm^2/V) requires the factor 1.11×10^{-40} .

For all the molecules, α_e is larger for coloured isomers than the open form, due to the increase of the π -conjugation. As expected, the molecule with the C₁₂ chain (C₁₂O-DTE-CN) shows a higher value, since the electronic polarizability is proportional to the number of electrons. As for the vibrational contribution, α_v , the values are of the order of 20-25% of the electronic term, hence it cannot be neglected in the Debye equation.

In the experimental measurements, the capacitance of the cell filled with the photochromic derivative dissolved in hexane was measured according to the procedure described in the experimental section, both for the uncoloured and coloured forms. The change in capacitance ΔC of the photochromic solution and the pure solvent is reported in table 3.

Molecule	ST	c [mM]	ΔC [fF]	ϵ_{sol}
MeO-DTE-MeO	C	1.1	3	1.8837
	O	1	1.9	1.8820
MeO-DTE-CN	C	0.25	2.5	1.8806
	O	0.25	0.9	1.8781
C ₁₂ O-DTE-CN	C	0.14	1.4	1.8820
	O	0.13	0.7	1.8830

Table 3. Experimental values for the photochromic molecules under test: the concentration c of the photochromic solutions, the change in capacitance (ΔC) between the pure solvent and the photochromic solution; the relative permittivity is calculated according to eq. 3 for the solution under measurement (ϵ_{sol}).

The change of capacitance (ΔC) between solvent and solution, of the order of fF, is consistent with the low concentration of the photochromic molecules and the tiny geometry of the capacitor. Moreover, the modulation ΔC is larger for the coloured (closed) form than the open one, meaning that also the relative permittivity is larger. According to the theoretical method above described, this increase in permittivity can result both from an increase of the dipole moment and of the polarizability. In addition, the modulation of the relative permittivity (see table 3) is proportional to the concentration of the photochromic molecule in solution. From the data reported in table 3, the experimental values of the dipole moment of the dithienyethenes were calculated and reported in table 4 both considering and neglecting the polarizability terms α_e and α_v .

Molecule	State	μ [D]	μ [D]	μ [D]	$\Delta\mu$ [D]
		Neglecting α_e and α_v	Neglecting α_v		
MeO-DTE-MeO	C	5.4	4.5	4.2±0.2	0.9
	O	4.4	3.5	3.3±0.15	
MeO-DTE-CN	C	10.3	9.9	9.8±0.75	4.6
	O	6.0	5.4	5.2±0.65	
C ₁₂ O-DTE-CN	C	10.5	10	9.9±0.2	3.5
	O	7.3	6.6	6.4±0.4	

Table 4. Experimental values of the dipole moment for the three photochromic derivatives in the open and closed forms. The reported uncertainty of μ refers to the variation in repeated measurements.

We notice that neglecting polarizability turns into a higher value of the dipole moment both for the open and closed forms. Nevertheless, as the polarizability contribution is similar for both the photochromic forms, the $\Delta\mu$ is weakly affected. Moreover, the effect of the electronic polarizability is larger than the effect of the vibrational polarizability and this is consistent with the values reported in table 2.

Values of dipole moment larger for the closed form than for the open form were obtained for all the diarylethenes, as expected. Moreover, smaller values resulted for the symmetric species (MeO-DTE-MeO) than for the asymmetric molecules. Both these

findings are in good agreement with the calculations. However, only MeO-DTE-MeO is correctly modelled in both the isomeric states, with a modulation of about 1 D between the coloured and the uncoloured form.

On the other hand, there is a remarkable discrepancy between the experimental and theoretical values of dipole moments for the two asymmetrical species. Indeed, the modulation of dipole moment ($\Delta\mu$) resulted between 3.5 and 4.6 D from the capacitance measurements and only of about 1.5 from the DFT calculation. By comparing the absolute values of dipole moment, the discrepancy mainly springs from the open form.

Therefore, we considered the dynamical interconversion that occurs when diarylethenes in the open form are dissolved in a solvent. We chose to perform the analysis of one asymmetrical diarylethene since the electronic influence of the side groups on the dipole is the same in MeO-DTE-CN and C₁₂O-DTE-CN, the only difference being the length of the alkoxy chain. As the intrinsic disorder of long chains makes heavy calculation we selected MeO-DTE-CN for the conformational analysis. By DFT calculation we computed the PES of MeO-DTE-CN starting from the C₂ conformation and varying the two torsional angles τ_1 and τ_2 between the perfluorocyclopentene and the thienyls units (see figure 3). The result is reported in figure 5.

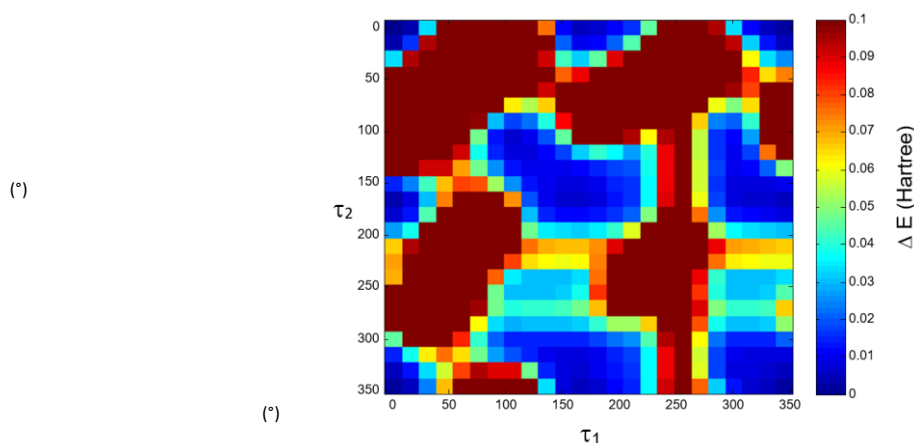


Figure 5. Potential energy map for the MeO-DTE-CN as function of the two torsional angles τ_1 and τ_2 . The 0 value of the two torsional angles corresponds to the values at the equilibrium geometry in the C₂ form.

Four regions can be identified in fig. 5 where the energy is locally minimum, hence where the most stable conformers are located. Starting from the optimized geometry corresponding to the values of these relative minima, the dipole moment, polarizabilities (both vibrational and electronic) were calculated and then weighted according to a Boltzmann distribution of the conformers. Table 5 reports the values for the four conformers.

Conformer	Energy (Hartree)	ΔE (Hartree)*	μ (D)	α_e (Å ³)	α_v (Å ³)
1	-2641.9139	1.0E-04	7.36	58.93	11.47
2	-2641.9121	1.90E-3	5.21	57.13	14.45
3	-2641.9140	0	2.70	57.25	15.57
4	-2641.9123	1.70E-3	3.78	56.20	16.40
Average value			4.85	57.85	13.89

* It is the difference in energy in respect to the absolute minimum.

Table 5. values of energy, dipole moment and polarizabilities calculated for the different minima of the molecule MeO-DTE-CN in the open form.

Such values of polarizability are very similar among the different conformers and this is due to the fact that the polarizability is mainly driven by the extent of π -conjugation, which is limited to the phenyl-thienyl dimer in all conformers. In this way, by applying the Debye equation for the open form of MeO-DTE-CN, we determine a dipole moment of 4.85 D, which is much smaller than the value calculated for just the C₂ isomer. Hence, by adopting this comprehensive approach, one can reconcile the theoretical and experimental values of the dipole.

Conclusions

The dipole moment of different photochromic diarylethenes was evaluated in solution by measuring the relative permittivity according to the Debye theory. A tailored set-up, characterized by a low electric noise, was designed and built to carry out such measurements in dilute solutions.

For all the diarylethenes under investigation, the dipole moment of the closed form was higher than that of the open form, as expected. Moreover, the push- π -pull structure of the asymmetrically-substituted derivatives led to very large modulation of the

dipole moment (*ca.* 4 Debye), which is desired for applications in electronic devices and surfaces with light-switching wettability. The experimental results also showed a change in the dielectric constant of the photochromic solution.

Dipole moment values were also determined by DFT calculations and showed that the electronic polarizability is larger for the coloured form and this is ascribed to the increase of π -conjugation. Moreover, both the vibrational and electronic contributions to the polarizability have to be taken into account when the dipole moment is calculated using the Debye equation.

The experimental and theoretical values of the dipole moment were in agreement, except for the asymmetric molecule in the uncoloured open form. Such discrepancy was rationalized by taking into account the dynamical interconversion that occurs in solution among the conformers. By considering the contributions to the dipole arising from the different conformers, a good agreement was then found.

In conclusion, this combined experimental and theoretical study allowed both to measure the dipole moment of diarylethenes and to highlight the failing of the theoretical predictions if the dynamical interconversion between the different conformers in the open state is not accounted.

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