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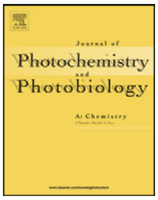

Enhancing the light driven modulation of the refractive index in organic photochromic materials: A quantum chemical strategy

Niccolò Adami[a], Daniele Fazzi[b,*], Andrea Bianco[a,c], Chiara Bertarelli[a,b], Chiara Castiglioni[a,b]

[a] Dipartimento di Chimica, Materiali e Ing. Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy, and INSTM, Milano, Italy
[b] Center for Nano Science and Technology (CNST) of IIT@PoliMi, Via Pascoli 70/3, 20133 Milano, Italy
[c] INAF, Istituto di Astrofisica Spaziale e Fisica Cosmica, via Bassini 15, 20133 Milano, Italy

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ABSTRACT

A theoretical investigation based on DFT predictions on 1,2-dithienylperfluorocyclopentene derivatives is presented. Molecules of this class have been demonstrated to show efficient thermally irreversible photochromism for developing optical switches. In particular, by doping a glassy polymer matrix with 1,2-dithienylperfluorocyclopentene derivatives, an optical element with a light induced modulation of the refractive index can be obtained.

Here, a simple model is proposed allowing the correlation between the change of the molecular polarizability, upon photoisomerization, to the modulation of the refractive index of the bulk material.

Based on this model and on DFT simulations, we suggest criteria for the optimization and design of the *bulk material property* (i.e. *refractive index modulation*) by modifying, with suitable chemical substitutions, the molecular and electronic structure of the photochromic species (that is by changing the *molecular property*, i.e. the *molecular polarizability*).

A systematic analysis of the polarizability changes upon photoisomerization (from the uncolored to the colored form) is carried out for 24 different molecules and correlations with the changes of the electronic and molecular structure are proposed and discussed.

1. Introduction

Photochromic molecules switch between two different stable molecular structures (usually named *colored* and *uncolored* form) under a suitable light stimulus: this property can be exploited for the design of new functional materials whose optical features can be tuned by photon irradiation [1].

Among the families of organic photochromic compounds [1,2] diarylethenes, as the 1,2-dithienylperfluorocyclopentene derivatives, have been widely investigated in the past two decades [3].

Thanks to their good stability, high quantum yield and high fatigue resistance, molecules belonging to the diarylethene family are very attractive for the development of electro-optical devices, such as optical switches [4–7], optical memories [8–12], active waveguides [13–15] and rewritable optical elements for astronomical instrumentation [16,17].

1,2-Dithienylethenes exist in an open (usually uncolored) form which shows the thiophene rings linked to the perofluorocyclopentene bridge twisted out of the molecular plane: in spite of the fact that a *cis*-hexatriene conjugation path exists across the bridge, an effective π electrons conjugation is prevented by the lack of planarity; therefore, the molecule consists of two independent π electron systems localized on the two molecular arms borne by the cyclopentene unit. Upon UV light irradiation, the closed form is obtained where a CC single bond is formed between the two thiophene units with a subsequent rearrangement of the π-electron system, giving rise to a sequence of alternated single and double CC bonds connecting the two heterocycles. Moreover, as a consequence of the photoinduced closing reaction, a more flat and planar structure is obtained, with an enhancement in the electron delocalization. This remarkable increment in the degree of π-electron conjugation determines the peculiar electro-optical properties of the photochromic materials; in particular the transition from a transparent material (in the visible range) to a colored one [18,19].

The strong changes in the molecular and electronic structure of the two photochromic isomers turn into different photo-physical and chemical properties [7], such as the optical absorption and fluorescence emission [20], the ionization potential/electron affinity and, of primary importance for the present study, the refractive index [14,20–22].

The refractive index modulation (Δn) in the near infrared and/or visible range is at the basis of several technological applications

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* Corresponding author. Tel.: +39 02 2399 3383; fax: +39 02 2399 3231.
E-mail address: daniele.fazzi@iit.it (D. Fazzi).

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proposed for these materials, such as linear and non-linear optical devices (i.e. waveguides, holographic gratings, wavelength tunable filters, holographic memories).

It has been already shown [21,22] that by doping a transparent polymer matrix (e.g. poly-methylmethacrylate glass) with 1,2-diarylethenes it is possible to obtain a material showing light driven modulation of the refractive index in the near infrared, whose value depends on the chemical structure of the photochromic molecules (it has been demonstrated that side groups play a relevant role in enhancing Δn) [21,22]. Δn values suitable for technological applications have been already reached thanks to the synthesis of photochromic polymers with a backbone constituted by 1,2-dithienylperfluorocyclopentenes units.[16,23], or with amorphous materials made of low molecular weight diarylethenes with bulky groups [20].

The key *technological parameter*, for the above reported optical applications, is the difference in the refractive index between the *open* and the *closed* form ($\Delta n = n^{\text{open}} - n^{\text{closed}}$) of the photochromic molecule. In order to enhance Δn, according to the technological requirements, two strategies can be followed:

(i) increase the *concentration* of the active photochromic molecules embedded in the polymer matrix;
(ii) optimize the *intrinsic molecular properties*, by adding some specific chemical group (electron withdrawing/donor groups) to the photochromic molecular unit.

The former is severely limited by the solubility of the photochromic species in the host polymer [24]; for the latter instead the chemical design offers several opportunities of changing the intrinsic molecular properties by suitable functionalization; it has been preliminarily shown that the molecular polarizability change ($\Delta\alpha$), from the *open* to the *closed* form, is correlated to the light induced modulation of the refractive index Δn [25].

Since the polarizability is mainly determined by the π-electron conjugation of the molecule, substituents bound to the photochromic unit can remarkably modify its value and hence the refractive index; in particular, electron acceptor/donor groups able to withdraw/donate the electronic charge, as well as chemical groups containing sequences of polarizable CC double/triple bonds or aryls, have been shown to enhance the molecular polarizability in the colored *closed* form [25].

In order to optimize this *molecular property* (α), for achieving a large modulation of the refractive index n, several aspects have to be considered:

(a) the overall photochromic properties must be preserved;
(b) the molecule has to be *stable* in a wide range of temperatures and concentrations (compatible with the host polymer matrix);
(c) the molecule has to be *functionalized* with proper chemical groups able to control and tune the π-electron conjugation.

The last point (c) will be investigated in detail in this paper using quantum chemical simulations.

These methods have been applied only recently to the case of diarylethene to predict different molecular properties (i.e. absorption spectrum and kinetic of isomerization [8,26,27]).

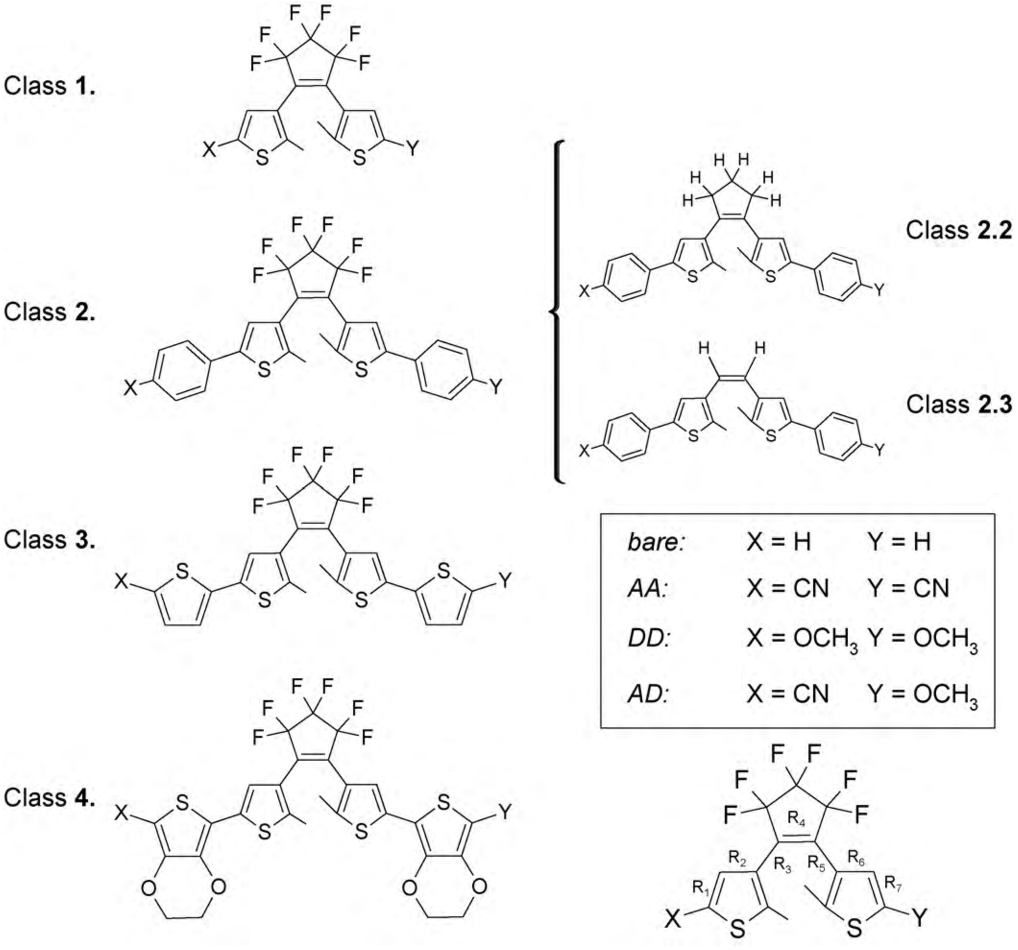

Fig. 1. Sketches of the diarylethene molecular structures studied in this work and (bottom right) numbering of CC bonds considered for the definition of the Bond Length Alternation (BLA) parameter (see text).

In this work we firstly introduce a relationship which has been developed to link together the technological parameter Δn and the molecular property $\Delta\alpha$ (Section 2); this relationship allows to clarify the role of the material parameters which are relevant to achieve enhanced device performances.

On this basis, we will conclude that the molecular polarizability of photochromic molecules, and in particular the figure of merit $\Delta\alpha/\alpha_{\text{open}}$, predicted using DFT simulations, is a key parameter for designing the optimal chemical structure to achieve large modulation of the refractive index (Δn).

In Section 3 we will analyze a wide series of functionalized 1,2-dithienylethene derivatives (see Fig. 1), which have been chosen in a systematic way in order to identify the best photochromic structures with improved opto-electronic properties. This method provides useful criteria and general guidelines for the design of optimized photochromic materials.

It has to be mentioned that once the optimal molecular structures to enhance the modulation of the refractive index are identified, other relevant properties dependent on the chemical structure have also to be taken into account. In particular, it should be verified that the photochromic features which are sensitive to π-electrons conjugation, such as cyclization/cycloreversion quantum yields, are preserved.

2. Methods

2.1. Theoretical methodology

Molecular structures, molecular polarizabilities and electronic structures of the diarylethene derivatives (both the *open* and the *closed* form) have been calculated using density functional theory (DFT) simulations with a hybrid exchange-correlation potential including both Becke and Hartree-Fock exchange and Lee, Yang and Parr correlation (B3LYP) [28], and the split-valence 6-31G(p,d) Pople basis set [29]. The theoretical framework is the same used in a recent paper we published on the same subject [25]. All the optimized molecular structures are validated by vibrational frequencies calculations; no imaginary frequencies are found for each optimized geometry. All simulations were carried out with the Gaussian03 program [30].

For conjugated diarylethenes, it has recently been shown that the range-separated hybrid functional CAM-B3LYP [31] provides results in very good agreement with experimental data yielding also accurate polarizabilities and bond length alternations values [32–34]. Further works are still in progress, which take into account a detailed comparison with this new DFT functional regarding the evaluation of the molecular properties herein considered.

2.2. Relationship between the variation of the molecular polarizability $\Delta\alpha$ and the modulation of the refractive index Δn

In a previous work [25] we adopt the classical Lorentz–Lorentz model [35], to describe in a simple way the relationship between the molecular polarizability α and the refractive index n of a molecular material. For the case of a blend, on the hypothesis that the contribution of the different chemical species is *additive*, the Lorentz–Lorentz model can be generalized as:

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}N_\nu^{\text{ph}}\alpha^{\text{ph}} + \frac{4\pi}{3}N_\nu^{\text{matr}}\alpha^{\text{matr}} \tag{1}$$

where N_ν^{ph} and N_ν^{matr} are the molar concentrations and $\alpha^{\text{ph/matr}}$ the molecular polarizabilities of the two species, namely the photochromic molecule and the matrix.

Eq. (1) has been used [25] for predicting the refractive index of several functionalized diarylethene-based photochromic compounds embedded in a PMMA matrix. The trend found by the experimental Δn values [22] showed a clear dependence on the chemical nature of the functional groups. However, the values of n (in particular those obtained for the *closed* forms) have been always overestimated by the theory. Discrepancies between the predicted values of the refractive index (Eq. (1)) and those experimentally obtained, can be also ascribed to phenomena which can be hardly quantified, such as the actual fraction of photochromic molecules in the *closed* (or *open*) form after light irradiation [36]. In spite of these difficulties, a simple look to the *molecular parameters*, namely the molecular polarizability (α), allowed an improved rationalization of the observed trends. In the present work we consider only the molecular polarizability of the two forms, without an explicit prediction of the refractive index of the material.

In order to give a sound justification of our choice, we have shown (see Appendix A) that, starting from Eq. (1) (or Eq. (A1), see Appendix A), it is possible to obtain simple expressions which establish a *linear* correlation between Δn and $\Delta\alpha^{\text{ph}}$ value.

These expressions (see Eqs. (2) and (3)) are derived under the hypothesis that: $\Delta n/n_{\text{open}} \ll 1$, where n_{open} is the refractive index of the material before photoisomerization, namely with photochromic molecules in their *open* form. This hypothesis is reasonable as explained in Appendix A.

After some manipulation of Eq. (1) (see Appendix A) we obtain the following results for the two cases considered:

1. pure photochromic material

$$\Delta n = \frac{(n_{\text{open}}^2+2)(n_{\text{open}}^2-1)}{6n_{\text{open}}}\left(\frac{\Delta\alpha^{\text{ph}}}{\alpha_{\text{open}}^{\text{ph}}}\right) \tag{2}$$

2. photochromic molecules embedded in a polymer matrix

$$\Delta n = \frac{(n_{\text{open}}^2+2)(n_{\text{open}}^2-n_{\text{matr}}^2)}{2n_{\text{open}}(n_{\text{matr}}^2+2)}\left(\frac{\Delta\alpha^{\text{ph}}}{\alpha_{\text{open}}^{\text{ph}}}\right) \tag{3}$$

Eqs. (2) and (3) clarify the relationship between the technological parameter (Δn) and the molecular property ($\Delta\alpha^{\text{ph}}/\alpha_{\text{open}}^{\text{ph}}$).

The term $\Delta\alpha^{\text{ph}}/\alpha_{\text{open}}^{\text{ph}}$ is an adimensional quantity which describes the effectiveness of the photoinduced isomerization in changing the molecular polarizability. The refractive index of a material is indeed independent of the volume occupied by the molecule, being related to the polarization *density* of the material. Moreover, the $\Delta\alpha^{\text{ph}}/\alpha_{\text{open}}^{\text{ph}}$ parameter fully describes the effect of the photochromic reaction on the change of the refractive index of the material, since the other factors of Eqs. (2) and (3) contain only information about the optical properties of the material *before* the closure reaction. Interestingly, in the case of a blend (Eq. (3)) the difference ($n_{\text{open}}^2 - n_{\text{matr}}^2$) clearly depends on the relative concentration of the photochromic species in the material and can be, in principle, increased as far as the percentage of the dopant photochromic molecules increases [37].

Accordingly, we can state that Eqs. (2) and (3) express, in an analytical form, the two different strategies mentioned in Section 1 (i and ii) for optimizing the performances of a photochromic material.

3. Results and discussion

In order to derive general information on the molecular polarizability of diarylethene derivatives, both in the *open* and in the *closed* form and on the effects of chemical functionalization, a systematic study of the diarylethene derivatives reported in Fig. 1 has been carried out. The dithienylethenes are classified according to four different classes, namely: **1.** *Base*, **2.** *Phenyl* (Ph), **3.** *Thienyl* (Th), **4.** *3,4-Ethylenedioxy thienyl* (EDOT).

Starting from the simplest molecular structures belonging to class **1.**, the other classes are derived from it by attaching various chemical groups (namely phenyl, class **2.**; thienyl, class **3.**; EDOT, class **4**) to the 5,5′ positions of the two thienyl rings. In this way the molecules belonging to classes **2.**–**4.** can be regarded as derived from class **1.**, in which an increase of the π-electron conjugation along the two molecular arms is obtained adding further aromatic rings. These chemical units will be referred in the following as *conjugation enhancing* (CE) end groups.

Within each class (**1.**–**4.**) we have analyzed four different cases:

(a) without any acceptor/donor end-group, named *bare*;
(b) symmetric end-substituted with two cyano groups (CN, acceptor), named *AA*;
(c) symmetric end-substituted with two methoxy groups (OCH_3, donor), named *DD*;
(d) asymmetric end-substituted with a methoxy and a cyano group (push–pull), named *DA*;

Another molecular site which can be chemically modified in order to induce a change of the molecular polarizability is the bridge between the two thienyls; we have explored, only for the class **2.**, the following three cases:

2.1 octafluorocyclopentene (this class coincides with the *bare* class **2.**);
2.2 cyclopentene;
2.3 ethene.

Also for series **2.1**, **2.2**, **2.3** we have studied the four cases described above (points a–d), namely *bare*, *AA*, *DD* and *DA*.

*3.1. Tuning the polarizability by functionalizing the diarylethene backbone: from class **1.** to class **4.***

In Table 1 we report the predicted DFT molecular polarizability values for diarylethene derivatives belonging to the classes **1.**, **2.**, **3.** and **4.** for both the *open* and the *closed* form, considering each of the four cases mentioned before: *bare*, *AA*, *DD* and *DA* (see Fig. 1).

Comparing the polarizability values for the classes **1.** and **2.** it is well evident that the addition of the phenyl rings increases of about three times the value of $\Delta\alpha$, then raising the relative parameter $\Delta\alpha/\alpha^{\text{open}}$. If we compare the *bare* molecules belonging to class **1.** and to class **2.** respectively, we find an increase of the polarizability of 130 bohr^3 in the *open* form and of 177 bohr^3 in the *closed* form. This effect is due to the phenyl rings which act as *conjugation enhancing* groups increasing the π electrons conjugation path both in the *open* and in the *closed* form. While in the *open* form the phenyl rings belong to two non-interacting π systems, in the *closed* form they are strongly coupled through the conjugated bridge, thus allowing a more effective enhancement of the polarizability value.

This last effect parallels the structural relaxation occurring upon the closure reaction. Structural changes have been investigated by calculating the Bond Length Alternation parameters, which are defined as $\text{BLA}_{\text{open}} = (R_2+R_3+R_5+R_6)/4-(R_1+R_4+R_7)/3$ and $\text{BLA}_{\text{closed}} = (R_2+R_4+R_6)/3-(R_1+R_3+R_5+R_7)/4$ (see Fig. 1, bottom right panel, for the CC bonds numbering). Notice that the above BLA definitions are the same for all the different classes considered (**1.**–**4.**), since they involve only the central dithienylethene moiety, thus allowing a direct structural comparison. Nevertheless, the so defined BLA parameters are also sensitive to the changes of π-electron conjugation due to the added CE groups; indeed, the presence of a longer CC bonds sequence indirectly affects the BLA of the central dithienylethene unit.

In fact BLA values reported in Table 2 indicate that for molecules of class **2.**, *closed* form, there is a more pronounced bond length equalization along the conjugated CC bond sequence (smaller BLA value in the closed form and higher ΔBLA) with respect to class **1.**, as a consequence of a higher delocalization of π electrons along the molecular backbone (see also Fig. 2). Another relevant structural parameter related to the enhancement of conjugation is the dihedral angle (θ) between the thienyl units and the perfluorocyclopendadiene ring, which passes from approximately 50° to about 8° upon photoisomerization.

By adding the chemical groups, electron acceptor (A = CN) or donor (D = OCH_3), in a symmetric way (*AA* or *DD*), both the polarizability value and the parameter $\Delta\alpha/\alpha_{\text{open}}$ increase for class **2.**

Table 1
Computed (DFT B3LYP/6-31G**) molecular polarizabilities of diarylethene molecules belonging to the class: **1.**, **2.**, **3.** and **4.** (see Fig. 1), in their *open* and *closed* structure.

Molecule	α (bohr^3)		$\Delta\alpha$ (bohr^3)	$\Delta\alpha/\alpha_{\text{open}}$
	Open	*Closed*		
1.				
bare	214	230	16	0.075
AA	226	258	32	0.142
DD	225	241	16	0.071
DA	226	255	29	0.128
2.				
bare	343	407	64	0.187
AA	402	489	87	0.216
DD	392	481	89	0.227
DA	398	494	96	0.241
FF	344	412	68	0.198
3.				
bare	337	419	82	0.243
AA	397	512	115	0.290
DD	389	496	107	0.275
DA	394	515	121	0.307
4.				
bare	404	507	103	0.255
AA	468	604	136	0.291
DD	452	584	132	0.292
DA	462	602	140	0.303

Table 2
Computed (DFT B3LYP/6-31G**) Bond Length Alternation (BLA) for diarylethene molecules belonging to the class: **1.**, **2.**, **3.** and **4.** (see Fig. 1), in their *open* and *closed* structure. For the definition of BLA see text.

Molecule	BLA (Å)		ΔBLA (Å)
	Open	*Closed*	
1.			
bare	0.093	0.081	0.012
AA	0.083	0.069	0.014
DD	0.093	0.073	0.020
DA	0.088	0.062	0.026
2.			
bare	0.086	0.067	0.019
AA	0.084	0.065	0.019
DD	0.086	0.065	0.021
DA	0.085	0.063	0.022
FF	0.086	0.067	0.019
3.			
bare	0.085	0.060	0.025
AA	0.084	0.059	0.025
DD	0.084	0.058	0.026
DA	0.083	0.055	0.028
4.			
bare	0.082	0.057	0.025
AA	0.081	0.055	0.026
DD	0.082	0.054	0.028
DA	0.081	0.052	0.029

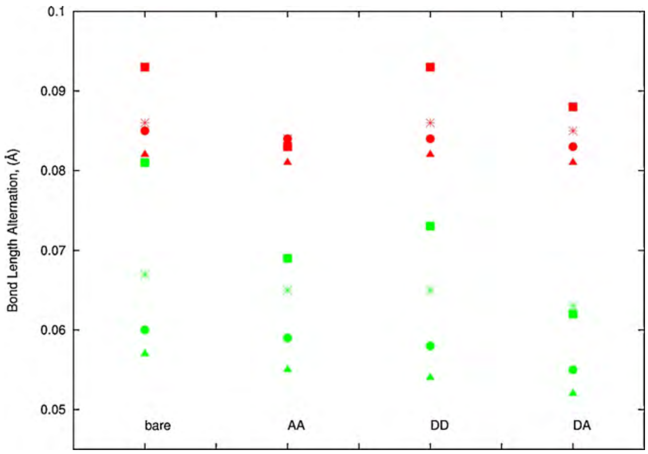

Fig. 2. Bond Length Alternation trends of the whole set of photochromic molecules studied in this works: squares, class **1.**; asterisks, class **2.**; circles, class **3.**; triangles, class **4.** Red symbols, *open* form; green symbols, *closed* form.

In the case of donor substituents (OCH_3) the increase in the polarizability value α can be rationalized as due to the injection of additional electron charge in the π system. For the same reason, the polarizability variation $\Delta\alpha$ increases of 25 bohr^3 with a subsequent enhancing of the $\Delta\alpha/\alpha_{\mathrm{open}}$ parameter.

If we consider the withdrawing feature of the perfluorinated ring, it is not immediately clear why the presence of an electron acceptor such as the CN group, able to attract the electronic charge too, determines again an increase in the polarizability change.

To better clarify this point we replace both CN groups with another acceptor group, namely with fluorine atom (case **2.** *FF* in Table 1).

In this case the polarizability change $\Delta\alpha$ is much closer to the value obtained for the parent *bare* molecule, thus suggesting that the marked increase in $\Delta\alpha$ obtained by the introduction of the CN group is mainly ascribed to the presence of π electrons of the triple bond, which contribute to further extend the conjugation path, independently by the acceptor character of the cyano group. This is also the reason why, the trend in $\Delta\alpha/\alpha_{\mathrm{open}}$, showing the hierarchy *DD* > *AA* > *bare* for the class **2.** is not reproduced for the class **1**. (for the class **1.** the trend is *AA* > *DD* > *bare*). Indeed, $\Delta\alpha$ is poorly enhanced in case of **1.** *DD* because of the narrow π-electron conjugation of the molecule, also in the *closed* form; on the other hand, in the **1.** *AA* case the polarizability results to be more effectively enhanced thanks to the increased π-electron conjugation due to the CN triple bond, which overwhelms the effect related to its electron withdrawing ability. This same effect also explains why within class **1**. the best performance is reached by **1.***AA*, while for molecules belonging to class **2**. the largest $\Delta\alpha$ and $\Delta\alpha/\alpha_{\mathrm{open}}$ values are obtained by non-symmetric functionalization, i.e. in the case of the donor–acceptor molecule (*DA*). The π electrons bridge indeed allows the end groups to communicate via a through-bond interaction: it is well known [38] that the introduction of a suitable pair of electron donor (*push*) and electron acceptor (*pull*) end substituents can remarkably enhance the degree of π electrons delocalization along a conjugated carbon atoms chain.

From the above considerations we can conclude that the strategy to increase the refractive index variation (Δn) by controlling the modulation of the molecular polarizability during the photochromic reaction, can be pursued in a first two steps route:

(1) introducing *conjugation enhancing* (*CE*) systems (as the case of phenyl rings, from *class* **1.** to *class* **2.**)
(2) performing a push–pull substitutions (as the case **2.** *DA*).

Following these guidelines we decided to deeply investigate the effect of different *CE groups* by replacing phenyl rings (class **2.**) with thienyl rings (class **3.**) (see Table 1).

Comparing the *bare* **2.** and *bare* **3.** molecules we notice that both $\Delta\alpha$ and $\Delta\alpha/\alpha_{\mathrm{open}}$ parameters increases by virtue of the thienyl rings which are more effective than phenyl in providing mobile electrons to the conjugation path (see Table 2).

Moreover, when the two thienyl units are in *trans* configuration (as illustrated in the sketch of Fig. 1) the repulsion between non-bonded H atoms (which is always present for the phenyl-substituted molecules belonging to class **2.**) is reduced and the two rings are almost coplanar in the *closed* form. For instance, the value of the torsional angle between thienyl and phenyl unit of **2.***bare closed* molecule is $\theta = 158^\circ$, while the torsional angle between the two thienyl units of **3.***bare closed* molecule is $\theta = 178^\circ$. This fact also contributes to an enhanced electron delocalization over the whole molecule in the *closed* form. As expected, the changes of the BLA parameters, taken as a measure of the π electron delocalization confirm the above conclusions.

The effect of adding electron donor and acceptor groups to the thiophene rings has been investigated and it is illustrated by the data reported in Table 1. The trend found for $\Delta\alpha/\alpha_{\mathrm{open}}$ is parallel to that already described for the class **2.** (i.e. *DA* > *DD* ≈ *AA* > *bare*).

It is worthwhile noting that for class **3.**, the formation of an acceptor-π bridge-donor (A-π-D) system in the *closed* form, obtained by a non-symmetric substitution, provides the best result, showing $\Delta\alpha$ and $\Delta\alpha/\alpha_{\mathrm{open}}$ values exceeding of about 30% those of **2.***DA*. According to Eqs. (2) and (3), molecule **3.***DA* will have the best refractive index modulation, either as pure photochromic material or embedded in polymer matrix system.

Inspired by the encouraging results found by the introduction of thiophene *CE groups* we have also considered the possibility to add mobile electronic charge to the system by replacing the end thienyls with 3,4-ethylenedioxidethienyls (EDOT). It is indeed known that the presence of the ethylenedioxide provides excess of electronic charge to the aromatic system, which can be beneficial in increasing molecular polarizability.

The increased *total* number of electrons present in the molecules of class **4.** determines a remarkable enhancement of the molecular polarizability in both *closed* and *open* forms (compared with the corresponding molecules of class **3.**).

This behavior is also reflected by the parameter $\Delta\alpha$ which suggests that EDOT is a more efficient *CE* substituent than only thienyl rings. However, if we look to the values of the adimensional parameter $\Delta\alpha/\alpha_{\mathrm{open}}$ we conclude that thiophene and EDOT are almost indistinguishable. However, a closer look to the $\Delta\alpha/\alpha_{\mathrm{open}}$ values indicates that the presence of the donor ehylenedioxide group determines an improvement in the presence of donor end groups (see **4.***DD* with **3.***DD* case), while it is not beneficial when acceptor groups are added in 5-position (see **4.***AA*). We can ascribe this behavior to the electron withdrawing effect of CN groups, which attract out of the aromatic system the excess of negative charge injected by ethylenedioxide.

As already mentioned the molecular polarizability α is, in a first approximation, roughly proportional to the total number of electrons in the molecule [For this same reason in our previous paper [25] we introduced another kind of parameter, namely ΔPPE (it is obtained from $\Delta\alpha$ by normalization over the total number of electrons in the given molecule); ΔPPE values behave in a very similar way as the figure of merit $\Delta\alpha/\alpha^{\mathrm{open}}$ proposed in this work for the first time], as shown in the past on the basis of a large amount of experimental data [39]. As a consequence, the introduction of bulky substituents carrying many electrons is obviously reflected by higher values of $\Delta\alpha$ and the increase in the Δn simply depends on the increase of the weight concentration of active molecules

Table 3
Computed (DFT B3LYP/6-31G**) molecular polarizabilities of diarylethene molecules belonging to the class: **2.1**, **2.2** and **2.3** (see Fig. 1), in their *open* and *closed* structure.

Molecule	α (bohr^3)		$\Delta\alpha$ (bohr^3)	$\Delta\alpha/\alpha_{open}$
	Open	*Closed*		
2.1				
bare	343	407	64	0.187
AA	402	489	87	0.216
DD	392	481	89	0.227
DA	398	494	96	0.241
2.2				
bare	341	405	64	0.188
AA	403	495	92	0.228
DD	389	465	76	0.195
DA	397	491	94	0.237
2.3				
bare	312	365	53	0.170
AA	373	452	79	0.212
DD	360	427	67	0.186
DA	367	449	82	0.223

in the polymer matrix. This cannot be definitively considered an "efficient" way.

Interestingly, the fact that the conjugated path is scarcely sensitive to the substitution of a thiophene moiety with an EDOT group can be inferred looking at the structural data in Table 3, which show very similar ΔBLA values for classes **3** and **4**.

3.2. *Effects of the cyclopentene bridge on the polarizability values*

While it is well know that the photochromic molecules under investigation benefit from the presence of a fluorinated cyclopentenyl group in terms of fatigue resistance and photochromism at the solid state, we considered of relevant importance also to study if the fluorine atoms have some active role in determining changes in the molecular polarizability after the photoisomerization.

In Table 3 we report the computed DFT polarizability for the three classes **2.1**, **2.2**, **2.3** described at the beginning of Section 3. We can notice that the removal of a cyclic bridge (class **2.3**) turns into a general decrease of the molecular polarizability in the *open* form as well as in the *closed* form; also in this case this behavior can be simply ascribed to the lower number of electrons available in the molecules.

Molecules of class **2.2**, with an unsubstituted cyclopentene, show polarizability values close to those of class **2.1**. This result leads to the hypothesis that electronegative atoms (like fluorine) tend to withdraw electrons and, as a consequence, the $C{=}C$ bond belonging to the cyclopentene, which is involved in the π-conjugation path, may result partially depleted of electronic charge.

Considering the fact that the contribution of conjugated electrons to the molecular polarizability is usually larger with respect to that of localized electrons [39,40] the negligible effect on the polarizability values while passing from class **2.1** to class **2.2** can be justified with a sort of balance between two effects. Indeed, in the case of the unsubstituted cyclopentene the decrease of the total number of electrons tends to lower the α value, but the availability of a larger amount of mobile electronic charge in the π system tends to increase its value.

In spite of the differences discussed above, the values of $\Delta\alpha$ as well as those of the adimensional parameters $\Delta\alpha/\alpha_{open}$ can be suitably considered similar for the *bare* molecules of the three classes **2.1**, **2.2** and **2.3**.

Interestingly we found an inversion of the trend while passing from donor end groups (*DD*) to acceptor end groups (*AA*). In the case of perfluocyclopentene, one of the highest $\Delta\alpha$ is found in the presence of donor groups (*DD*), while for classes **2.2** and **2.3** the *AA* case is more effective. This behavior suggests that the presence of fluorine atoms on the bridge is not negligible with respect to the choice of the most effective end groups; this can be explained considering that in the case of donor end groups (*DD*), the whole molecules can be thought as made by two moieties (the two symmetric arms) characterized by a *push-π-pull* structure, where the pull unit is the perfluorinated cyclopentene.

On the other hand, since the presence of the perfluorinated ring is motivated by the already mentioned advantages in the overall photochromism, we can conclude that chemical modifications of this group can be discarded in our screening of molecular structures for the optimization of Δn.

In summary, inspired by the model described by Eqs. (2) and (3), we can conclude that, in order to enhance the relative polarizability modulation $\Delta\alpha/\alpha_{open}$ of 1,2-dithienylethenes and hence the refractive index change Δn, some specific chemical and structural variations are suggested, as:

- addition of conjugation enhancing groups as phenyl and, overall, thienyl rings (classes **2.** and **3.**);
- addition of donor (OCH_3) and acceptor (CN) groups, yielding a push–pull bridge after photoisomerization to the closed form (*DA* class **3.**);

Moreover, modification of the "ethene bridge" turned out to be weakly effective.

4. Conclusions

A deep theoretical analysis of 1,2-dithienylperfluorocyclopentene derivatives has been carried out with the aim of establishing relationships between the chemical structure and the enhancement of the modulation of the refractive index of the material through the calculation of the molecular polarizability.

A simple model based on Lorentz–Lorentz equation has been developed (see Appendix A); the model explicitly links the molecular polarizability α to the macroscopic refractive index n in the case of both pure photochromic materials and doped polymer matrix. An adimensional quantity $\Delta\alpha/\alpha_{open}$ has been proposed as a figure of merit of the photochromic systems in order to enhance the refractive index change (Δn) by passing from the *open* to the *closed* form.

It has been shown that the extension of the conjugation path plays an important role: the increase of the number of π electrons available for conjugation and the choice of aromatic rings with a greater propensity to establish inter-rings conjugation (thienyl rings are better than phenyl ones) have been demonstrated to enhance the $\Delta\alpha/\alpha_{open}$ parameter (hence Δn). Also the end groups are of great relevance in affecting $\Delta\alpha/\alpha_{open}$; in this sense it is worth to combine the asymmetric substitutions, made by a donor (OCH_3) and a withdrawing (CN) group, with a dithienylethene moiety which is characterized by a well-extended conjugation.

We are hopeful that the guidelines drawn in this work could suggest useful criteria and general guidelines, rationalized on the base of DFT simulations, for the design of optimized photochromic materials

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Appendix A.

The classical Lorentz–Lorentz model used to describe in a simple way the relationship between the molecular polarizability α and the refractive index n of a molecular material, is reported in Eq. (A1):

$$\frac{n^2-1}{n^2+2}=\frac{4\pi}{3}N_\nu\alpha \tag{A1}$$

where $N_\nu = N_A/V$, is the molar concentration, N_A is the Avogadro number and V is the molar volume. The α term appearing in Eq. (A1) is the average molecular polarizability, obtained from the polarizability tensor α as: $\alpha = 1/3$ Trace (α); the scalar equation (Eq. (A1)) holds for a random orientation of molecules, as the case of amorphous materials and blends whit glassy polymers.

For the case of a blend, Eq. (A1) turns out as:

$$\frac{n^2-1}{n^2+2}=\frac{4\pi}{3}N_\nu^{\mathrm{ph}}\alpha^{\mathrm{ph}}+\frac{4\pi}{3}N_\nu^{\mathrm{matr}}\alpha^{\mathrm{matr}} \tag{A2}$$

where N_ν^{ph} and N_ν^{matr} are the molar concentration of the two species, namely the photochromic species and the matrix.

Eq. (A2) can be written for the material in the two limiting cases, namely before photoisomerization with all the photochromic molecules in their *open*, uncolored form and after photoisomerization, with all the photochromic molecules in their *closed* form.

The refractive index in the two cases will be n_{open} and n_{closed} respectively and can be expressed using Eq. (A2), provided that the values $\alpha_{\mathrm{open}}^{\mathrm{ph}}$ and $\alpha_{\mathrm{closed}}^{\mathrm{ph}}$ are explicitly introduced.

In the hypothesis that N_ν^{ph} and N_ν^{matr} do not change appreciably by virtue of the photochromic reaction, we can now evaluate the quantity:

$$\frac{n_{\mathrm{closed}}^2-1}{n_{\mathrm{closed}}^2+2}-\frac{n_{\mathrm{open}}^2-1}{n_{\mathrm{open}}^2+2}=\frac{4\pi}{3}N_\nu^{\mathrm{ph}}(\alpha_{\mathrm{closed}}^{\mathrm{ph}}-\alpha_{\mathrm{open}}^{\mathrm{ph}})=\frac{4\pi}{3}N_\nu^{\mathrm{ph}}\Delta\alpha^{\mathrm{ph}} \tag{A3}$$

The left hand term of Eq. (A3) can be worked out introducing the relationship: $n_{\mathrm{open}} = n_{\mathrm{closed}} + \Delta n$. After linearization of the expression obtained (hypothesis of small Δn) we can write:

$$\frac{6n_{\mathrm{open}}\Delta n}{(n_{\mathrm{open}}^2+2)^2}=\frac{4\pi}{3}N_\nu^{\mathrm{ph}}\Delta\alpha^{\mathrm{ph}} \tag{A4}$$

Eq. (A4) describes a relatively simple linear relationship between Δn and $\Delta\alpha^{\mathrm{ph}}$.

Moreover, notice that this expression is correct also for a material consisting of the only photochromic species, as far as Δn is small. It can be indeed obtained starting from Eq. (A1), instead of Eq. (A2), where now n and Δn refer to a material made by the only photochromic molecules.

We can further worked out Eq. (A4) in order to remove the parameter N_ν^{ph}. This can be easily done by writing Eq. (A2) explicitly for the case of the *open* material (i.e. $\alpha^{\mathrm{ph}} = \alpha_{\mathrm{open}}^{\mathrm{ph}}$) and in the case of the pure matrix. In this last case we have:

$$\frac{n_{\mathrm{matr}}^2-1}{n_{\mathrm{matr}}^2+2}=\frac{4\pi}{3}N_\nu^{\mathrm{matr}}\alpha^{\mathrm{matr}} \tag{A5}$$

Eq. (A5) can be exploited in order to describe the contribution of the matrix (which appears in Eq. (A2)) simply by means of its characteristic refractive index, n_{matr}. This can be safely done, provided that the molar concentration of the pure matrix is very close to that of the matrix in the blend, as expected for blends at low concentration of photochromic molecules (usually the concentration is kept lower than 10% to avoid segregation phenomena).

We obtain:

$$\frac{n_{\mathrm{open}}^2-1}{n_{\mathrm{open}}^2+2}-\frac{n_{\mathrm{matr}}^2-1}{n_{\mathrm{matr}}^2+2}=\frac{4\pi}{3}N_\nu^{\mathrm{ph}}\alpha_{\mathrm{open}}^{\mathrm{ph}} \tag{A6}$$

We can now divide the two members of Eq. (A4) by the corresponding members of Eq. (A6), thus yielding the final expression:

$$\Delta n=\frac{(n_{\mathrm{open}}^2+2)-(n_{\mathrm{open}}^2-n_{\mathrm{matr}}^2)}{2n_{\mathrm{open}}(n_{\mathrm{matr}}^2+2)}\left(\frac{\Delta\alpha^{\mathrm{ph}}}{\alpha_{\mathrm{open}}^{\mathrm{ph}}}\right) \tag{A7}$$

A similar expression can be obtained in the case of a pure photochromic materials by simply dividing the two members of Eq. (A4) by the two corresponding members of Eq. (A1), written for the case of a fully photochromic material in its *open* form.

In this case:

$$\Delta n=\frac{(n_{\mathrm{open}}^2+2)-(n_{\mathrm{open}}^2-1)}{6n_{\mathrm{open}}}\left(\frac{\Delta\alpha^{\mathrm{ph}}}{\alpha_{\mathrm{open}}^{\mathrm{ph}}}\right) \tag{A8}$$

As already stated, this equation holds only for pure photochromic material where we have a relatively small change in the value of the refractive index upon photoisomerization, namely $\Delta n/n_{\mathrm{open}} \ll 1$ This is undoubtedly a good approximation, since the modulations of the refractive index measured for backbone photochromic polymers are smaller than 0.1 and for doped polymer matrix are one order of magnitude smaller. If we consider the refractive index of the material in between 1.5 and 1.6, the ratio in the worst case is approximately 0.06.

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