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Through space charge transfer and quadratic nonlinear optical (NLO) properties in alternated stacks of 2-amino-1,3-benzothiazole–ethylcoumarin-3-carboxylate charge transfer complexes: from the molecular to the bulk NLO response

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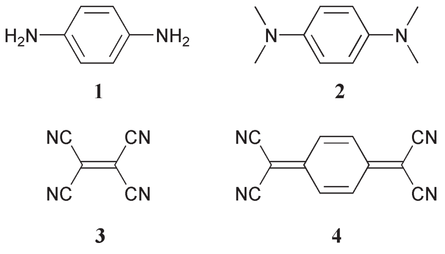
Received (in Montpellier, France) 21th October 2003, Accepted 10th December 2003
First published as an Advance Article on the web 15th March 2004

The title compound is a charge transfer complex with an experimental low lying excitation located around 420 nm. It is used as a model compound for the investigation of a possible strategy towards NLO materials obtained by "through space" charge transfer. Its solid state structure (*Pc* space group) reveals non-centrosymmetric alternating chains of donor-acceptor entities, built from the two independent 2-amino-1,3-benzothiazole entities hydrogen-bonded in the crystal unit cell. Each independent chain gives rise to a one-dimensional charge transfer, and therefore a non-vanishing NLO response along the chain. The angle between the glide mirror and the charge transfer direction is close to the optimized value (61°) and leads to two extended lattices of high NLO capability over the whole extent of the crystal. Unfortunately, an angle of 175° is observed between the two lattices, because of the unexpected effect of the hydrogen bonding, thus cancelling most of the NLO response. The efficiency of the material is therefore limited to 0.15 times that of urea in second harmonic generation (SHG). Nevertheless, this investigation indicates that charge transfer complexes could be envisioned for an alternative approach to molecular materials with SHG capabilities.

Introduction

The last three decades have witnessed a growing interest in molecules having quadratic nonlinear optical (NLO) properties,[1] which possess the potential to supplant the inorganic ferroelectric materials currently available (*e.g.*, KH_2PO_4 and $LiNbO_3$)[2] by virtue of their large molecular hyperpolarizabilities (β). Beside the famous stilbene and stilbazolium skeletons, which have been the benchmark NLO candidates during the 1980's,[3] more elaborated molecules have recently been proposed, such as octupolar structures,[4,5] while alternative approaches to chromophore optimization have also been envisioned based on the concept of bond length alternation (BLA).[6] Nevertheless, these attempts towards NLO materials with enhanced capabilities all lead to molecules having the same basic electronic features: an extended π electron cloud highly delocalized between donor and acceptor substituents on an organic skeleton. This ensures the indispensable prerequisite for a large NLO response: the existence of a strong charge transfer excitation.[7]

Beside this broad class of NLO materials exhibiting intramolecular charge transfer, alternative approaches are based on intermolecular interactions between chromophores. For instance, Nicoud *et al.* have reported on co-crystals obtained from phenol and pyridine-based molecules in which a proton transfer was evidenced, giving rise to an enhanced hyperpolarizability and an efficiency higher than that of urea in second harmonic generation.[8] Another strategy could be envisioned on the basis of intermolecular (or "through space") charge transfer, a concept that has lead to important classes of molecular materials (*e.g.*, molecular metals and superconductors).[9] Di Bella *et al.* have reported on a computational investigation that explored this strategy in detail.[10] Among a variety of donor-acceptor pairs, they have found a sizeable NLO response in charge transfer complexes based on *p*-phenylenediamine (**1**), *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (**2**), tetracyanoethylene (TCNE) (**3**) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) (**4**) all shown in Scheme 1. On the other hand, the search for an actual NLO charge transfer complex



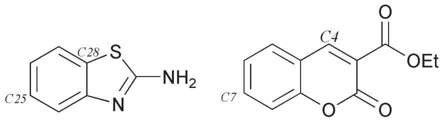
Scheme 1

DOI: 10.1039/b313294c

has received very limited attention, from a synthetic point of view. Sironi *et al.* have investigated the structure of stilbazole crystals in which NLO properties and intermolecular charge transfer are present.[11] Nevertheless, the NLO response was not attributed to interchromophore delocalization in this material. Zyss *et al.* have reported on an organic chromophore in which a paracyclophane has been shown to provide a significant ''through space'' charge transfer pathway between a donor and an acceptor unit.[12a] The authors also reported on through space octupolar contributions to the hyperpolarizability of such chromophores.[12b] However, this result was obtained within a single molecular unit, and measured in solution. Recently, the polymerization of thiophene-substituted paracyclophane has been reported for designing polymeric chains with π-π through space interactions and potential NLO applications,[13] but to the best of our knowledge, the issue related to the bulk NLO response has not been addressed yet for these alternative materials.

In the present contribution, we wish to focus on charge transfer complexes built up from stacks of donor and acceptor entities engineered in the solid state in a non-centrosymmetric environment. Two kinds of materials can be found in the literature, depending on the nature of the stacks. (*i*) Segregated donor (–D–D–D–) and acceptor (–A–A–A–) stacks are usually obtained by using planar precursors with strong donor-acceptor capabilities, such as TCNQ (**4**). They usually lead to semiconducting or conducting materials with long range charge delocalization.[14] They are highly absorbent and therefore may be of limited value for optical applications. In addition, they possess high molecular and crystal symmetries, with almost all of them crystallizing in centrosymmetric space groups, and therefore are NLO inactive. (*ii*) Alternated (–D–A–D–) or highly distorted donor-acceptor stacks are obtained when the precursors exhibit reduced symmetry and planarity, or modest donor-acceptor capabilities.[15] Their range of transparency is large and their organization into infinite chains could result in a macroscopic one-dimensional NLO response, once this has been achieved on the scale of the asymmetric unit cell.

As an illustration for this latest and more promising family, the charge transfer complex selected for the present investigation is the 1:1 complex 2-amino-1,3-benzothiazole–ethylcoumarin-3-carboxylate (ABT–CC, whose components are shown in Scheme 2).[16] The reasons for choosing this material were first motivated by the yellow color of the crystals, which strongly contrasts with the perfectly white color of its individual 2-amino-1,3-benzothiazole (ABT) and ethylcoumarin-3-carboxylate (CC) starting components, providing initial evidence for a charge transfer behavior. Furthermore, the structure reveals regular, but non-centrosymmetric alternated stacks in the solid state, which is an important structural prerequisite in quadratic nonlinear optics, while the compound crystallizes in the non-centrosymmetric *Pc* monoclinic space group. The experimental optical properties will be analyzed within the semi-empirical INDO formalism and the possibilities for a bulk NLO response will be discussed in relation to the intermolecular charge transfer behavior. Finally, a critical evaluation of the strategy based on using the ''through space'' approach in alternated donor-acceptor stacks for the design of NLO materials will be proposed.



ABT **CC**

Scheme 2

Experimental

Materials and equipment

A microcrystalline powder of 2-amino-1,3-benzothiazole–ethylcoumarin-3-carboxylate (1:1) was obtained by simple co-crystallization of ethycoumarin-3-carboxylate (CC)[17] and 2-aminobenzothiazole (ABT), as previously described.[16]

The UV-vis diffuse reflectance spectra were recorded on a CARY SE UV-VIS-NIR spectrophotometer with 10^{-1} mol (3.8, 5.5 and 9.3 mg) of ABT, CC and the complex, respectively) in KBr discs (250.0 mg IR spectroscopic grade in every case).

Second harmonic generation (SHG) measurements were carried out by the Kurtz–Perry powder test,[18] using a nanosecond pulsed Nd-YAG (10 Hz) laser. The fundamental radiation was used as the incident laser beam for SHG. The second harmonic signal was detected by a photomultiplier and read on an ultrafast Tektronic TDS 620B oscilloscope. The samples were uncalibrated microcrystalline powders obtained by grinding and put between two glass plates.

Computational details

The all-valence INDO (intermediate neglect of differential overlap) method[19] was employed for the calculation of the electronic spectra for the interacting pair of 2-amino-1,3-benzothiazole and ethylcoumarin-3-carboxylate. The mono-excited configuration interaction (MECI) approximation was employed to describe the excited states. The 100 lowest energy one-electron transitions between the 10 highest occupied molecular orbitals and the 10 lowest unoccupied ones were chosen to undergo CI mixing. Calculations were performed using the INDO/1 Hamiltonian incorporated in the commercially available MSI software package INSIGHT II (4.0.0).[20] Metric parameters used for the calculation were taken from the crystal structure data. Two independent adducts are found in the asymmetric unit of 2-amino-1,3-benzothiazole–ethylcoumarin-3-carboxylate. In the present paper, the reported calculations were made by using the interacting pair built up from the 3-carboxycoumarin labelled A in the crystal structure. However, we carefully checked that the second pair leads to a similar spectrum. The calculation of the molecular hyperpolarizability was performed within the sum-over-state (SOS) formalism.[21] Details of the computationally efficient INDO-SOS-based method for describing second-order molecular optical nonlinearities have been reported elsewhere.[22]

Results and discussion

Optical spectra

While ABT and CC are colorless compounds, the 2-amino-1,3-benzothiazole–ethylcoumarin-3-carboxylate molecular complex forms yellow crystals. The diffuse reflectance electronic spectra for the three compounds are shown in Fig. 1. The individual ABT donor and CC acceptor components exhibit absorption maxima located at 361 and 370 nm, respectively. The spectrum of the molecular complex reveals a broad band overlapping the individual components, a significant shoulder being observed at higher wavelength, in agreement with the yellow color of the powder. A change in color observed in molecular crystals is frequently associated with donor-acceptor associations.[23]

At this point, the details of the packing observed in the crystal structure of ABT–CC have to be emphasized. ABT and CC components can be described as regularly packed along their six-membered carbon rings [Fig. 2(a)], parallel to the *b* crystallographic axis. However, there is no π-overlap between these rings and, therefore, no pathway for a possible intermolecular electronic interaction. By contrast, the packing reveals

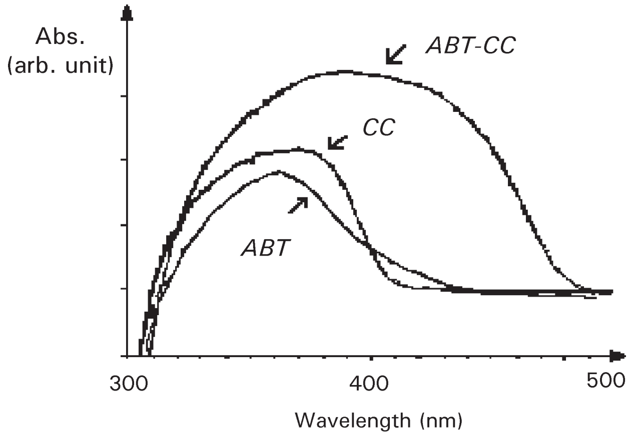


Fig. 1 Diffuse reflectance electronic spectra of the supramolecular ABT–CC complex, in KBr discs, *versus* those of the pristine ABT and CC starting components.

Table 1 Low-lying intense transitions observed in the INDO calculated electronic spectra of 2-amino-1,3-benzothiazole–ethyl-coumarin-3-carboxylate (ABT–CC)

Transition	Wavelength/nm	Composition of the CI mixing[a]
$1 \rightarrow 3$	328	0.869 $\chi_{66\rightarrow67}$
$1 \rightarrow 5$	307	0.836 $\chi_{65\rightarrow67}$
$1 \rightarrow 8$	270	0.884 $\chi_{66\rightarrow68}$

[a] Orbital 66 is the HOMO and orbital 67 the LUMO.

important π-contacts between the lactone ring of CC and the six-membered ring of one of its ABT neighbors [Fig. 2(b)]. In order to correlate this structural feature and the experimental spectrum, the INDO calculation is presented in Table 1. While the calculation performed on the individual ABT and CC components indicates single absorption maxima located at 275 and 306 nm, respectively, the calculated spectrum of the π-overlapping ABT–CC adduct is composed of three major transitions, at 270, 307, and 328 nm. For each of these, a single excitation is dominant in the configuration interaction (CI) mixing, as indicated in Table 1. The nature of these transitions is analyzed in Fig. 3. The $1 \rightarrow 8$ transition mainly involves the ABT fragment, without any "through space" charge transfer character. The CC counterpart is dominant in the $1 \rightarrow 5$ transition, but ABT clearly provides an additional donor component (43.8% of the electron density in orbital 65), giving the transition partial charge transfer behavior. Furthermore, the description of the new, low-lying $1 \rightarrow 3$ transition at 328 nm reveals that 97% of the electron density is localized on the ABT fragment (HOMO-based ground state) and 99% on the CC counterpart (LUMO-based excited state). This leaves no doubt that ABT–CC strongly behaves as a charge transfer complex, as anticipated from the experimental reflectance spectrum.

NLO response in the ABT–CC charge transfer complex

In their analysis of the origin of the NLO response in charge transfer complexes, Di Bella *et al.* have shown that β is largely determined by the lowest energy "through space" charge transfer excitation. It is worth remembering that, in terms of perturbation theory, a two-level model for β is a widely used guideline for rationalizing the NLO response, according to the following equation[24]

$$\beta_{zzz} = \frac{3e^2\hbar^2 f(\Delta\mu)_z}{2mE^3} \times \frac{E^4}{\left(E^2 - (2\hbar\omega)^2\right)\left(E^2 - (\hbar\omega)^2\right)} \qquad (1)$$

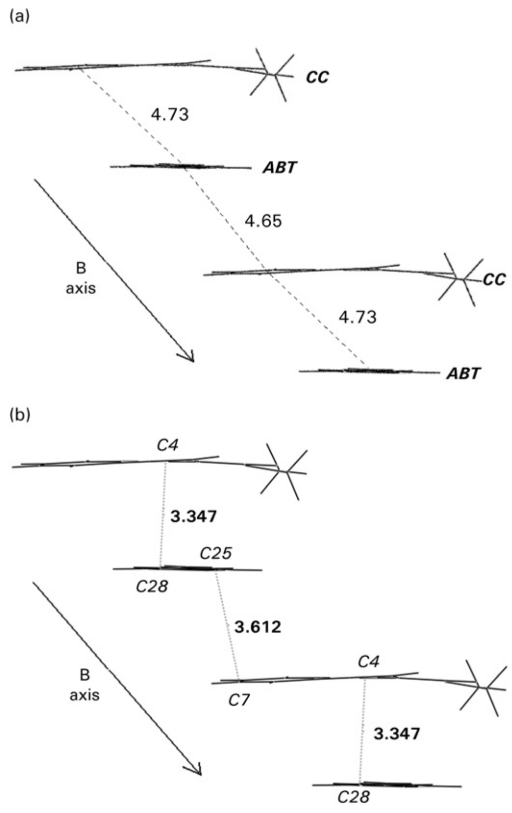


Fig. 2 Packing along the *b* crystallographic axis for ABT–CC. The intermolecular distances (in Angström) are measured (a) between the centroids of the six-membered carbon rings and (b) between the carbon atoms with the shortest intermolecular contacts.

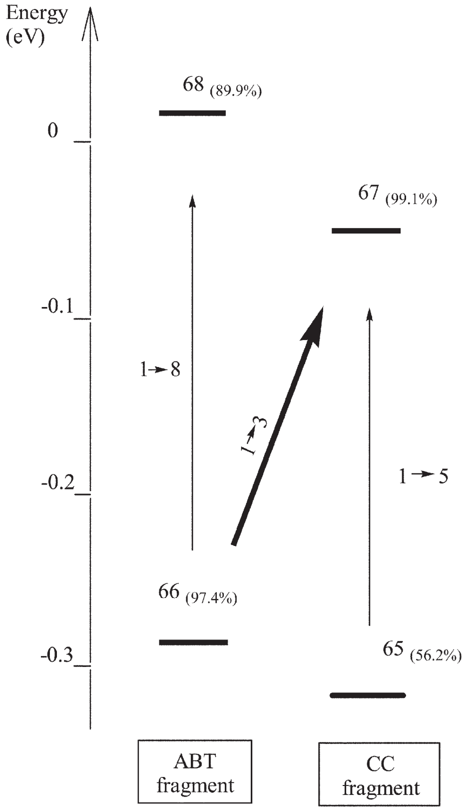


Fig. 3 Energies of the molecular orbitals involved in the optical spectrum of ABT–CC. Orbitals 65 and 67 are mainly localized on CC, while orbitals 66 and 68 are on ABT (the electron density % on the dominant fragment is given in parentheses).

which relates the β value to the energy ($\hbar\omega$) of the incident laser beam. In eqn. (1), E is the energy of the charge transfer transition occurring along the z charge transfer axis, f is the oscillator strength and $\Delta\mu$ is the change in dipole moment between the excited and the ground state. As previously pointed out,[10] the main electronic feature making intermolecular charge transfers relevant in terms of potential NLO response is provided by an unusually large $\Delta\mu$ parameter. In the present case, the intensity of the transition is modest ($f = 0.05$), but the $\Delta\mu$ parameter is extremely large (11.9 D), despite a very short distance (3.57 Å) between the donor and acceptor molecular units. However, due to the modest oscillator strength and pale yellow color (high E value), the calculated hyperpolarizability remains modest and equal to 4.5×10^{-30} cm^5 esu^{-1} at 1.064 μm for the ABT–CC charge transfer unit.

Towards bulk NLO response in donor-acceptor stacks?

To the best of our knowledge, the issue of crystal state NLO response has never been addressed in the case of "through space charge transfer". The previously investigated **1**–**4** donor and acceptor entities have been the basis of numerous crystal structures, which will briefly be reviewed in the following section. The Cambridge Crystallographic Data Base (CDB) reveals a number of entries equal to 23, 30, 180 and 593, for structures based on compounds **1** to **4**, respectively. In the case of **1**, all of them belong to centrosymmetric space groups. Compound **2** leads to two non-centrosymmetric crystals, in which it does not behave as an electron donor.[25,26] Among the 180 reported structures containing TCNE (**3**) units, 8 actually belong to non-centrosymmetric space groups, while only 1 reveals alternated stacks, but with no charge transfer transitions.[27] Finally, TCNQ (**4**) is by far the molecule that has provided the largest number of crystal structures in the series, with 593 entries. Most non-centrosymmetric entries are observed in the triclinic $P1$ space group (20 entries), with pseudo-centrosymmetric segregated stacks. Indeed, we have found only 4 structures in which TCNQ is embodied in alternated stacks in non-centrosymmetric space groups.[28–31]

It appears clear from this literature survey that these highly symmetric entities possess a strong tendency for centrosymmetric charge transfer behavior and therefore vanishing bulk NLO response. In the case of molecules with lower symmetry (*e.g.*, C_{2v}), it is interesting to note that an alternated stack would necessarily result in a non-centrosymmetric chain. This difference is illustrated in Fig. 4. In the situation depicted on the top of the picture, the high molecular symmetry and regular packing lead to identical $D_i \rightarrow A_{i+1}$ and $D_i \rightarrow A_{i-1}$ donor-acceptor charge transfers. Therefore, vanishing NLO properties are expected over the whole extent of the chain. By contrast, the stack presented at the bottom with molecules of reduced symmetry corresponds to the situation encountered in ABT–CC. Each donor is surrounded by two acceptors, but for symmetry reasons, $D_i \rightarrow A_{i+1}$ and $D_i \rightarrow A_{i-1}$ are likely different. Furthermore, the repeating units along the entire extent of the chain ensure a non-zero SHG efficiency.

After the observation of non-centrosymmetric stacks in the solid state, the relationships between this charge transfer direction and the crystal symmetries have to be analyzed in order to clarify if the donor-acceptor axis can give rise to a macroscopic NLO effect. In particular, modest NLO chromophores such as urea ($\beta = 0.3$ to 0.5×10^{-30} cm^5 esu^{-1})[32] can lead to potential candidates for NLO devices, for reasons related to their optimized solid state structure or phase matchable characteristics.[33] The present ABT–CC charge transfer complex exhibits a rather modest β value equal to 4.5×10^{-30} cm^5 esu^{-1}, but it crystallizes in the Pc monoclinic space group (point group 2, which is the one providing the best optimization for the angular orientation of chromophores in the solid state).[34] In the case of efficient NLO materials with birefringence phase matching properties found in this point group [*e.g.*, *N*-(4-nitrophenyl)-L-prolinol, NPP][35] and with the assumption of a one-dimensional molecular NLO response along the charge transfer axis z of the complex ($\beta = \beta_{zzz}$), the model leads to:

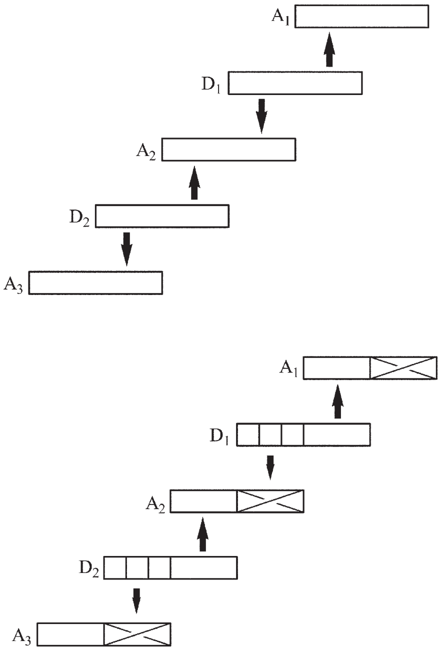


Fig. 4 Charge transfer along regular stacks of donor-acceptor molecular entities with (top) D_{2h} or (bottom) C_{2v} symmetry.

$$d_{31} = N\beta_{zzz} \times \cos\theta \sin^2\theta \qquad (2)$$

All other d components of the crystalline NLO tensor are negligible or of no use for birefringence phase matching.[35] (θ is defined as the angle between the charge transfer axis and the *ac* glide mirror of the crystal). The optimization of d_{31} can be achieved for $\theta = 55°$, which gives an angular factor equal to 0.38. In ABT–CC, we observed a θ value of 61°, which correspond to an angular factor equal to 0.37. For symmetry reasons, each donor-acceptor stack present in the crystal is therefore perfectly oriented to give rise to a bulk NLO effect. Surprisingly, the SHG measurement indicates a very modest efficiency for ABT–CC, being equal to 0.15 times that of urea (a chromophore with a molecular NLO response ten times lower than that of the present charge transfer complex). The explanation can be found from the overall description of the crystal unit cell, in which two ABT donors units are hydrogen-bonded by their amino groups, which results in two independent donor-acceptor stacks. Each of them certainly gives rise to an optimized macroscopic sub-lattice, by virtue of repeated chains and *ac* glide mirrors. However, both sub-lattices are oriented with an angle equal to 175°, with the result that most of the SHG signal is cancelled out.

Possible strategies for the design of efficient materials based on the "through space" approach

A critical evaluation of the present ABT–CC material reveals two severe weakness, which have to be addressed: the modest β value of the donor-acceptor unit and the deleterious effect of the presence of two independent ABT–CC pairs in the unit cell.

In order to investigate a possible modulation of the β value, the donor-acceptor interactions have been modified by changing the interplanar ABT–CC distances. Owing to the observation of a pseudo-regular stack of the six-membered carbon rings along the *b* crystallographic axis [Fig. 2(a)], the translation is assumed to occur along the *b* direction for the calculation. The results are gathered in Fig. 5. Within the framework of the two-level model, it is interesting to observe the effect of a translation on the E, $\Delta\mu$ and f parameters. The energy of the transition, E_{LUMO} (CC-based) – E_{HOMO} (ABT-based), is not affected by the translation, while the change in dipole moment increases with the donor-acceptor distance. In any case, the oscillator strength remains roughly constant. This latter effect, which prohibits a large charge transfer intensity and hence a large β value, is probably due to the very low symmetry (C_s) of the individual fragments. In order to ensure both non-centrosymmetry of the fragments (to favor non-centrosymmetric stacks) and large overlaps (to favor large f), C_{2v} molecular structures should be preferred as the most promising targets for the design of donor and acceptor starting components.

As is well-known, crystal structures cannot be predicted from molecular structures.[36] One may tentatively suggest that, in order to avoid the pseudo-centrosymmetric solid state organization arising from hydrogen bonding, the possibility for interactions between donors (*e.g.*, ABT in the present case) or acceptors should be avoided. This could be achieved by simply using dimethylamino donor groups instead of $-NH_2$. In addition to the intermolecular interaction, this would increase the donor power and hopefully enhance the charge transfer behavior.

Conclusion

ABT–CC is a charge transfer complex with two hydrogen-bonded ABT donor units in the crystal asymmetric unit cell. From each of them a non-centrosymmetric stack is generated, which results in a non-vanishing charge transfer behavior over the entire chain. Furthermore, the symmetries of the crystal (glide mirror) give rise to two macroscopic sub-networks with angle values between the charge transfer axis and the mirrors around 60°, close to the optimized angular value for large NLO efficiencies. Nevertheless, the pseudo-centrosymmetric organization of the two independent ABT entities in the asymmetric unit cell is such that most of the properties of each sub-network cancel those of the other one, the resulting SHG signal being non-zero, but finally very weak, in the present material.

Crystal engineering is highly laborious, with the outcome of many tedious syntheses frequently being uncertain. Nevertheless, the present investigation indicates that charge transfer complexes could be envisioned as an alternative family of molecular materials with solid state SHG properties.

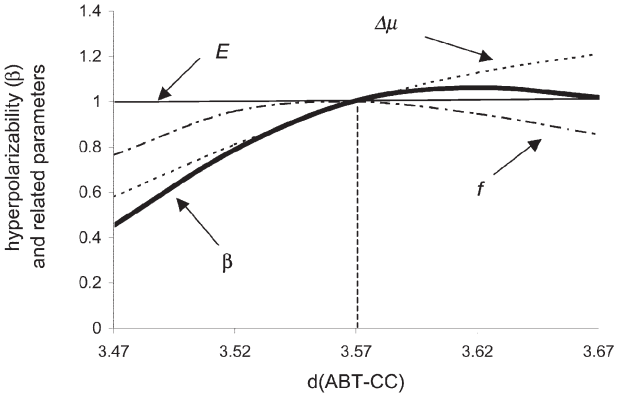


Fig. 5 Modulation of the charge transfer parameters (energy E, oscillator strength f, and dipole moment change $\Delta\mu$) and the related 2-level based hyperpolarizability (β) as a function of the intermolecular ABT–CC distance, assuming a translation along the *b* crystallographic axis. The intermolecular distances are measured between the centroids of the lactone ring of CC and the phenyl ring of ABT. The values for β, E, f and $\Delta\mu$ are normalized to 1, which corresponds to the actual crystal structure in which the intermolecular distance is equal to 3.57 Å.

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