Tuning second-order NLO responses through halogen bonding†

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In the field of electrooptic materials, a strategy based on hydrogen bonding (HB)-driven self-assembly, among others, has already demonstrated its great potential for the design of transparent organic thin films with very high electrooptical responses.[1] Halogen bonding (XB),[2] any noncovalent interaction involving halogens as electrophilic sites, is a rather new item in the supramolecular toolbox and shares numerous properties with the better known HB. The great potential of XB in the design of new and high-value functional materials is now emerging clearly.[3]

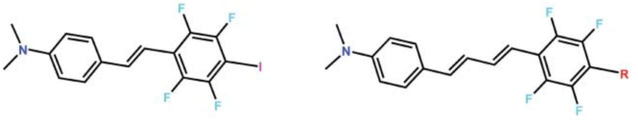
Keen to extend the use of XB to the self-assembly of organic thin films for nonlinear optical (NLO) and optoelectronic applications,[4] we have synthesized the XB-based self-complementary tectons *N*,*N*-dimethyl-4-[(*E*)-2-(2,3,5,6-tetrafluoro-4-iodophenyl)vinyl]aniline (**1a**) and *N*,*N*-dimethyl-4-[(1*E*,3*E*)-4-(2,3,5,6-tetrafluoro-4-iodophenyl)buta-1,3-dien-1-yl]aniline (**1b**) (Scheme 1). These tectons self-organize in the crystal giving rise to head-to-tail halogen-bonded polymers thanks to the self-complementary binding sites at the molecular ends.[5] Before studying the electrooptical activities of the halogen-bonded 2D films that these modules form, we decided to evaluate their NLO properties at the molecular level.

Here we report on the measurement, by the solution-phase electric field induced second-harmonic (EFISH) generation method,[6] of the second-order NLO properties of the two members **1a,b** of this new class of XB-based NLO-phores. From the EFISH data on the two chromophores **1a,b** in different solvents, and in comparison with the NLO data for *N*,*N*-dimethyl-4-[(1*E*,3*E*)-4-(2,3,5,6-tetrafluorophenyl)buta-1,3-dien-1-yl]aniline **2** (chosen as a control compound, which lacks the I atom on the tetrafluorophenyl fragment and is not capable of XB) it has been possible to show for the first time that both the value and the sign of second-order NLO responses in solution can be tuned thanks to solvent··· chromophore XB. As a function of the ability of the solvent to behave as XB-acceptor, the NLO-phores under study give rise to $\mu\beta_\lambda$ values ranging from +192 × 10^{-48} esu to −465 × 10^{-48} esu. Rationalization of these results at the molecular level is fully supported by density functional theory (DFT) and time dependent DFT (TDDFT) calculations.

The two chromophores **1a,b** possess terminal XB-donor and -acceptor groups and incorporate a conjugated π-electron spacer between electron-rich and electron-poor aromatics (push–pull effect), in analogy with most of the molecular materials for NLO applications.[7] Iodotetrafluorophenyl residue was chosen as it is a strong XB-donor group; moreover, it can easily be appended to a wide variety of C frameworks with high yield and regioselectivity.[5] Furthermore, it could be expected that the electron withdrawing ability of F contributes to enhance second-order NLO response.[8]

The measurements of $\mu\beta_\lambda$, the product of the molecular dipole moment and the projection of $\boldsymbol{\beta}_{\mathrm{tot}}$, the 'vectorial part' of the quadratic hyperpolarizability tensor, along $\boldsymbol{\mu}$, for the chromophores **1a,b** and **2** were firstly carried out in $CHCl_3$ solutions at 1907 nm non-resonant wavelength. The obtained $\mu\beta_\lambda$ values were similar and positive (see Table 1), and very close to those measured for the pentafluoro analogues of **1a** and **1b** (**3a** and **3b**, which showed $\mu\beta_\lambda$ values of +100 and +200 × 10^{-48} esu, for **3a** and **3b**, respectively; see ESI,† Scheme 2).[8a] The good agreement among the $\mu\beta_\lambda$ values of **1a,b**, **2** and **3a,b** allows to exclude any specific role of the I atom substitution on the molecular NLO properties of chromophores **1a,b** in $CHCl_3$.

The UV-vis absorption spectra of **1a,b** and **2** in $CHCl_3$ show one major band at 382, 406, and 392 nm, respectively (see Fig. 1) with a small solvatochromic behavior. This band can be attributed to the intramolecular charge-transfer (CT) transition to the lowest-energy excited state emanating from the NMe_2 donor-end of the molecule. The attribution of the UV major band has been confirmed by TDDFT calculations performed with ADF[9] on **1a**, whose geometry was previously optimized at the B3LYP/3-21G** level with Gaussian 98.[10] We relied here on the observation that, an increase in the π-spacer length improves the NLO response of



1a

1b 2
R = I, H

Scheme 1 The NLO-phores under study in this work.

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Table 1 Computed μ(D) and experimental $\mu\beta_\lambda$ values ($\times 10^{-48}$ esu) and CT bands (nm) of NLO-phores **1a,b** and **2** in $CHCl_3$ and DMF

		$CHCl_3$		DMF	
Compound	μ	$\mu\beta_\lambda$	λ_{max}	$\mu\beta_\lambda$	λ_{max}
1a	6.31	+124	382	−380	387
1b	7.25 (6.8)[a]	+192	406	−465	410
2	6.10	+173	392	+70	396

[a] Experimental value in $CHCl_3$.

chromophores without modifying, however, their electronic peculiarities.[8] Calculations predicted one major band (see ESI,† Table 5), corresponding to the HOMO → LUMO transition. The HOMO and LUMO were both π orbitals, the former localized on the electron-rich NMe_2-substituted aromatic ring, the N atom, and the ethylenic bond, and the latter on the electron-poor perfluorinated ring and the ethylenic bond (see ESI,† Table 6). This transition is therefore associated with an increase of the ground state dipole moment or, in other words, to a positive $\Delta\mu_{eg}$, the difference between the dipole moment moduli of the excited and ground states. According to the phenomenological Oudar two-level model,[11] giving the CT contribution to the quadratic hyperpolarizability, $\beta_{CT} \propto (\mu^2_{eg}\Delta\mu_{eg}/\Delta E^2_{eg})$, wherein μ_{eg} is the transition dipole moment and ΔE_{eg} the excitation energy, a positive projection β_λ is then to be expected, explaining the positive $\mu\beta_\lambda$ experimental values. The sign of β_λ was reproduced by TDDFT calculations on **1a** at the same frequency as used in the experimental set-up ($\mu\beta_\lambda = +613 \times 10^{-48}$ esu, where $\mu = 6.31$ D is the B3LYP/3-21G** ground state dipole, see Table 1).

It is well established, both experimentally and theoretically, that the environment strongly influences NLO responses of molecules.[12] In fact, there are many examples of theoretical and experimental investigations of the HB-effects on the NLO response of molecular systems. In particular, Huyskens *et al.*[12a,b] have shown that the formation of specific HB solute–solvent interactions always increases the value of β. We then decided to investigate the effect of XB on the NLO properties of chromophores **1a,b** and **2** by performing the EFISH measurements in solutions of the strong XB acceptor solvent DMF. A slightly lower $\mu\beta_\lambda$ value, compared to the one in $CHCl_3$, was measured for **2** ($\mu\beta_\lambda = +70 \times 10^{-48}$ esu). On the other hand, a much higher and unexpected negative $\mu\beta_\lambda$ value was measured for **1a,b** ($\mu\beta_\lambda = -380$ and -465×10^{-48} esu, respectively, Table 1). In our hypothesis, this intriguing finding can be somehow related to the involvement of the I atom of NLO-phores **1a,b** in the formation of O···I XB with DMF. The involvement of **1b** in XB with the solvent has been clearly demonstrated by ^{19}F NMR studies in $CDCl_3$, DMF, as well as in stronger XB-acceptor solvents like piperidine (PIP) and quinuclidine (QUI).[13] These measurements predicted the formation of halogen-bonded adducts of increasing stability in the order $CDCl_3 \ll DMF \ll PIP < QUI$ (see ESI,† Table 3). We have reproduced the same order of stability by B3LYP/3-21G** geometry optimizations on the complexes of **1a** with the above-mentioned bases, giving interaction energies, corrected for basis set superposition error,[14] equal to 4.26, 7.28 and 7.40 kcal mol^{-1} for DMF, PIP and QUI.

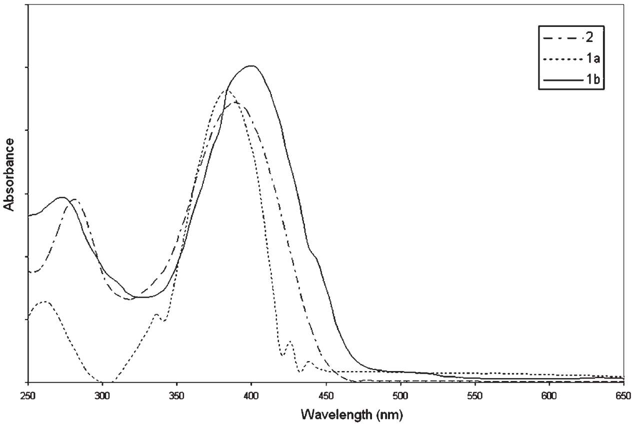

Fig. 1 UV-vis spectra of **2**, **1a** and **1b** in $CHCl_3$.

In order to substantiate the effect of XB-acceptor solvents on the NLO responses of chromophores **1a,b**, we performed the EFISH measurements in $CHCl_3$ solutions of **1b** in the presence of the three Lewis bases. Using a molar ratio base/**1b** equal to 200, a negative $\mu\beta_\lambda$ value was obtained for the strongest base QUI ($\mu\beta_\lambda = -149 \times 10^{-48}$ esu), while a molar ratio equal to 250 was necessary to observe such sign inversion with PIP and DMF ($\mu\beta_\lambda = -118$ and -103×10^{-48} esu, respectively, see Table 2). Consistent with the role of XB in the change of $\mu\beta_\lambda$ sign, this value remained positive in the case of **2** also when the PIP/**2** ratio was 300.

Aimed at giving a phenomenological interpretation to these results, we measured the UV spectra of **1b** and **2** in $CHCl_3$ added with PIP (1 : 150 and 1 : 300 molar ratios, respectively) and in DMF (see Tables 1 and 2). For both solvents, the CT band did not show either significant shift or intensity variation with respect to the corresponding spectra registered in pure $CHCl_3$. Therefore, the XB occurrence does not modify the nature of the HOMO → LUMO transition in the NLO-phore **1b**, as also evidenced by the computed TDDFT properties of this transition for dimers of **1a** with DMF, PIP and QUI (see ESI,† Tables 5 and 7–9). This suggests that β_{CT} of chromophores **1a,b** does not undergo significant changes in the presence of XB-acceptors. The sign inversion in $\mu\beta_\lambda$ is then imputable to a change in the direction of $\boldsymbol{\mu}$, as a consequence of the simultaneous presence, in the halogen-bonded complexes, of two competitive electron-donor sites, the intramolecular (–NMe_2) and the intermolecular ones (solvent), placed on either sides of the electron-acceptor iodoperfluorinated ring.

This hypothesis was confirmed by DFT calculations on the three complexes of **1a** with DMF, PIP and QUI. In all of the three cases, the dipole moments point approximately towards opposite directions with respect to that determined for isolated **1a**, while maintaining unvaried the direction of $\boldsymbol{\beta}_{tot}$. The sign inversion was in fact well reproduced in the case of the dimer of **1a** with DMF

Table 2 $\mu\beta_\lambda$ values ($\times 10^{-48}$ esu) of $CHCl_3$ solutions of **1b** and **2** added with excess XB-acceptor solvent

	Ratio	$\mu\beta_\lambda$
QUI/**1b**	200	−149
	250	−487
PIP/**1b**	200	+49
	250	−118
	300	−298
DMF/**1b**	250	−103
PIP/**2**	300	+220

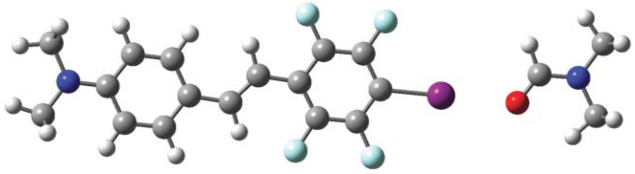

Fig. 2 Optimized geometry of the halogen-bonded complex **1a**·DMF.

(Fig. 2) ($\mu\beta_\lambda = -120 \times 10^{-48}$ esu, where $\mu = 2.90$ D). On the other hand, in the cases of the complex of **1a** with PIP and QUI, the calculated $\mu\beta_\lambda$ values, while negative, were very low ($\mu\beta_\lambda = -38$ and -39×10^{-48} esu, respectively) owing to their small computed dipoles ($\mu = 0.66$ and 0.78 D, respectively). In our opinion, this disagreement with experiment can be ascribed to (i) the neglecting of bulk solvent effects,[12d] and/or (ii) the occurrence of multiple XB, which is expected to increase the dipole moment of the real system and then the $\mu\beta_\lambda$ magnitude.[15]

In conclusion, in this work, for the first time, a theoretical and experimental approach to describing the influence of XB on the NLO properties of molecules in solution is given. Reasonable agreement between theory and experiment substantiates the role XB plays in tuning[16] both the value and the sign of $\mu\beta_\lambda$. This observation may be used for the rational design of new electrooptic materials. At a more fundamental level, it has been illustrated how the neglecting of the XB occurrence may lead to serious misinterpretations of results in NLO studies.

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Notes and references

1 B. Kippelen, *Nat. Mater.*, 2004, **3**, 841; A. Facchetti, E. Annoni, L. Beverina, M. Morone, P. Zhu, T. Marks and G. Pagani, *Nat. Mater.*, 2004, **3**, 910; R. U. A. Khan, O.-P. Kwon, A. Tapponnier, A. N. Rashid and P. Gunter, *Adv. Funct. Mater.*, 2006, **16**, 180.

2 P. Metrangolo, H. Neukirch, T. Pilati and G. Resnati, *Acc. Chem. Res.*, 2005, **38**, 386.

3 R. Liantonio, P. Metrangolo, F. Meyer, T. Pilati and G. Resnati, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 1.

4 P. K. Thallapally, G. R. Desiraju, M. Bagieu-Beucher, R. Masse, C. Bourgogne and J. F. Nicoud, *Chem. Commun.*, 2002, 1052; A. D. Bond, J. Griffiths, J. M. Rawson and J. Hulliger, *Chem. Commun.*, 2001, 2488; A. R. P. S. Jagarlapudi, F. H. Allen, V. J. Hoy, J. A. K. Howard, R. Thaimattam, K. Biradha and G. R. Desiraju, *Chem. Commun.*, 1997, 101.

5 G. Marras, P. Metrangolo, F. Meyer, T. Pilati, G. Resnati and A. Vij, *New J. Chem.*, 2006, **30**, 1397.

6 (*a*) B. F. Levine and C. G. Bethea, *Appl. Phys. Lett.*, 1974, **24**, 445; (*b*) K. D. Singer and A. F. Garito, *J. Chem. Phys.*, 1981, **75**, 3572; (*c*) I. Ledoux and J. Zyss, *Chem. Phys.*, 1982, **73**, 203.

7 T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays and A. Persoons, *J. Mater. Chem.*, 1997, **7**, 2175.

8 (*a*) A. Papagni, S. Maiorana, P. Del Buttero, D. Perdicchia, F. Cariati, E. Cariati and W. Marcolli, *Eur. J. Org. Chem.*, 2002, 1380; (*b*) P. Romaniello and F. Lelj, *J. Fluorine Chem.*, 2004, **125**, 145.

9 G. Te Velde, F. M. Bickelhaupt, S. J. A. Van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931.

10 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *GAUSSIAN 98 (Revision A.11.3)*, Gaussian, Inc., Pittsburgh, PA, 2002.

11 J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664.

12 (*a*) F. L. Huyskens, P. L. Huyskens and A. P. Persoons, *J. Chem. Phys.*, 1998, **108**, 8161; (*b*) F. L. Huyskens, P. L. Huyskens and A. Persoons, *J. Mol. Struct.*, 1998, **448**, 161; (*c*) A. Abbotto, L. Beverina, S. Bradamante, A. Facchetti, C. Klein, G. A. Pagani, M. Redi-Abshiro and R. Wortmann, *Chem. Eur. J.*, 2003, **9**, 1991, and references therein; (*d*) W. Bartkowiak and P. Lipkowski, *J. Mol. Model.*, 2005, **11**, 317, and references therein; (*e*) K. E. Riley and K. M. Merz, Jr., *J. Phys. Chem. A*, 2007, **111**, 1688.

13 M. T. Messina, P. Metrangolo, W. Panzer, G. Resnati and E. Ragg, *Tetrahedron Lett.*, 1998, **39**, 9069.

14 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.

15 S. J. Grabowski and E. Bilewicz, *Chem. Phys. Lett.*, 2006, **427**, 51.

16 R. Andreu, M. J. Blesa, L. Carrasquer, J. Garín, J. Orduna, B. Villacampa, R. Alcalá, J. Casado, M. C. Ruiz Delgado, J. T. López Navarrete and M. Allain, *J. Am. Chem. Soc.*, 2005, **127**, 8835.