Halogen Bonding Enhances Nonlinear Optical Response in Poled Supramolecular Polymers†

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We demonstrate that halogen bonding strongly enhances the nonlinear optical response of poled supramolecular polymer systems. We compare three nonlinear optical chromophores with similar electronic structures but different bond-donating units, and show that both the type and the strength of the noncovalent interaction between the chromophores and the polymer matrix play their own distinctive roles in the optical nonlinearity of the systems.

The halogen bond can be defined as an attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity[1]. Most properties of halogen bonds, such as directionality, strength, and tunability, can be rationalized by considering the anisotropic molecular electrostatic potential (MEP) distribution around halogen atoms. In fact, this is characterized by a region of positive MEP, denoted as the σ-hole[2], which develops along the extension of the covalent bond involving the halogen atom, and a belt of negative MEP orthogonal to it. Consequently, an electron donor (*e.g.*, a Lewis base) will be attracted by the σ-hole and repelled by the rest of the atom surface. This explains the high directionality and linearity of halogen-bonded structures, both in the gas phase[3] and in the solid state[4]. The strength of the halogen bonding depends on the polarizability of the halogen atom – the higher the polarizability, the greater the interaction strength – and on the moiety attached to the halogen atom.

The benefits of halogen bonding have been recognized in crystal engineering[5], medicinal chemistry[6], and more recently in the design of functional materials[7,8]. In particular, halogen-bonded supramolecular complexes provide an excellent platform for inducing macroscopic mechanical movements in azobenzene-containing material systems[9,10], in particular light-induced surface topography patterns in azopolymer films[11,12]. Such patterns are generated through photoinitiated mass transport triggered by *cis-trans* isomerization of the embedded photoactive azobenzene molecules. Halogen-bonded low-molecular-weight complexes were found to allow for an exceptionally efficient mass transport[9], and halogen-bonded supramolecular polymers were found to surpass similar hydrogen-bonded polymers in surface-patterning efficiency[12].

Azopolymers are an exceptional platform for organic nonlinear optical materials, due to the high nonlinear optical (NLO) response of push-pull-type azobenzenes that can be tuned through photoisomerization[13]. A purely optical method for controlling the NLO response in azopolymers is all-optical poling[14], in which a dual-frequency optical field is used to selectively excite azobenzene molecules in a polar fashion (*i.e.*, there is a unique direction in which the molecules need to be oriented for high probability of excitation). After repeated *cis-trans* isomerization cycles, the originally isotropic and thus centrosymmetric structure of an azopolymer is turned into a noncentrosymmetric one. The main motivation for breaking the symmetry are second-order NLO effects, such as second-harmonic generation and the electro-optic effect, that occur only in noncentrosymmetric media[15]. These NLO effects are of high interest in the field of photonics, where they allow several essential functionalities. Cost-effective polymeric materials with high and tunable second-order response would therefore open new possibilities for photonic technology.

Studies on poled polymer systems have largely focused on materials with the light-responsive molecules covalently attached to the polymer backbone[14,16]. However, the tedious

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synthesis required to prepare such polymers has triggered the search for supramolecular materials with high optical nonlinearities [17,18]. We have earlier shown using hydrogen-bonded supramolecular azopolymers that the chromophore content and thereby the photoactive properties can be greatly enhanced through noncovalent interactions [19]. Herein, we show that the benefits of supramolecular interactions in poled polymers can be further boosted by making use of halogen bonds, and that the NLO response inscribed by all-optical poling is superior in halogen-bonded polymer-azobenzene complexes compared to their hydrogen-bonded counterparts. We also demonstrate that the response scales with the strength of halogen bonding, and depends delicately on the ability of the support polymer matrix to act as a noncovalent-bond acceptor. The study is complemented by theoretical calculations that further elucidate the different performance of halogen- and hydrogen-bonded complexes.

The compounds used in this work are shown in Fig. 1. What is unique about the azobenzene molecules employed is that by changing the bond-donor atom X, we profoundly alter the type and strength of noncovalent interaction with the polymer matrix while maintaining the electronic and photochemical properties of the molecules practically unchanged [11,12]. For the

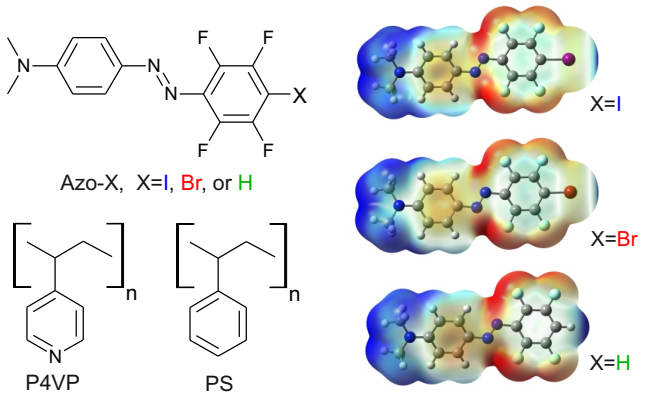

Fig. 1 Chemical structures of the components used in the studied material systems (left) and M062X/6-311++G(d,p) MEP maps (right). Potentials are mapped on the respective isosurfaces (0.001 a.u.) of electron density. Values of electrostatic potential range from -0.03 (red) to 0.03 (blue) a.u., with most positive local values on X equal to 0.037, 0.033 and 0.041 a.u. for X=I, Br and H, respectively. Atom color scheme: C, gray; H, light gray; N, dark blue; Br, red; F, sky blue, I, magenta.

support matrix, poly(4-vinylpyridine) (P4VP) was chosen as each of the chromophores is able to interact with the free electron pair of the nitrogen atom in the pyridine ring, giving rise to a R–X$\cdots$N noncovalent bond. The molecules Azo-I and Azo-Br form halogen bonds of different interaction strength with P4VP (I > Br) whereas the acidic hydrogen atom of Azo-H forms a weak hydrogen bond with P4VP. As a reference polymer, we chose polystyrene (PS), which lacks the electron-donating nitrogen atom and is therefore expected to give rise to weaker and less specific interactions with the chromophores, involving the halogen/hydrogen species and the aromatic ring π electrons arranged in a T-shaped configuration [20,21]. In principle, such R–X$\cdots\pi$ interaction could take place also in the P4VP matrix but in that case, the stronger R–X$\cdots$N interaction is expected to prevail.

To verify the formation and characteristics of the involved noncovalent bonds, we modelled the material systems using density functional theory (DFT) at the M062X/6-311++G(d,p) level. We calculated the interaction energies between the Azo-X molecules and either 4-methylpyridine or methylbenzene, used as model compounds for P4VP and PS, respectively. In the case of 4-methylpyridine, both collinear and T-shaped arrangements of the interacting molecules were considered. Interaction energies, corrected for Basis Set Superpositions Error (BSSE), were found to be -5.689, -4.248, and -4.128 kcal mol^{-1} for Azo-I$\cdots$N, Azo-Br$\cdots$N, and Azo-H$\cdots$N, respectively. The MEP maps of the Azo-X molecules (see Fig. 1) elucidate the different bonding characteristics of Azo-I and Azo-Br compared to Azo-H. The positive electrostatic potential on the halogen species is localized in a small area along the extension of the C–X bond. In contrast, for the Azo-H, the area of positive potential is rather hemispherically distributed around the hydrogen atom. This difference accounts for greater directionality of halogen bonding compared to hydrogen bonding.

When considering the Azo-X$\cdots\pi$ interaction, a local energy minimum with T-shaped configuration was obtained only for the halogenated Azo-I and Azo-Br molecules, with interaction energies amounting respectively to -3.298 and -2.997 kcal mol^{-1} in the case of 4-methylpyridine and to -4.064 and -3.464 kcal mol^{-1} in the case of methylbenzene. These energies are lower than those obtained for the Azo-X$\cdots$N interaction, indicating that the T-shaped configuration is unlikely in P4VP matrix in favour of the collinear one. On the other hand, the Azo-X$\cdots\pi$ interaction, while weaker, is expected to take place in PS matrix, though presumably the optimal T-shaped arrangement is sterically hindered in the real system owing to the presence of the polymeric backbone, making the contribution of such interaction even less significant. Finally, unlike Azo-I and Azo-Br, Azo-H was unable to give rise to a stable T-shaped configuration with either 4-methylpyridine or methylbenzene, indicating that the Azo-H molecule interacts with P4VP exclusively through Azo-H$\cdots$N interaction while no directional interaction with PS is to be expected.

The NLO response was studied in spin-coated azopolymer thin films denoted as P4VP(Azo-X)$_y$ where y stands for the number of azobenzenes per each polymer repeat unit. Prior to the experiments, the samples were verified to be homoge-

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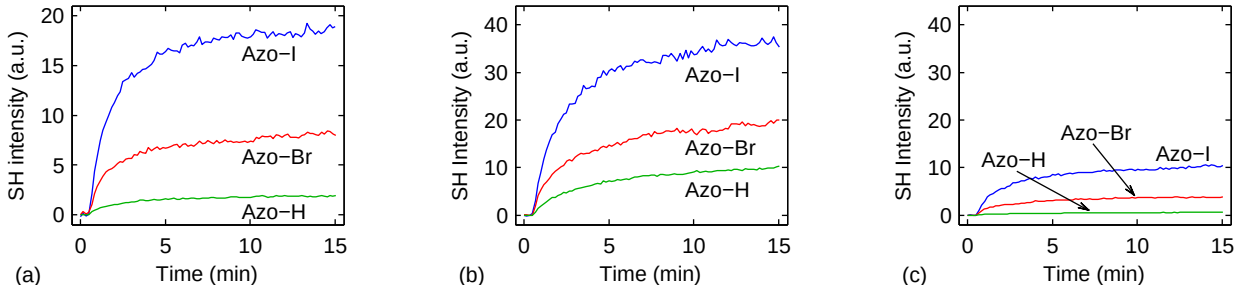

Fig. 2 Evolution of second-order nonlinearity during all-optical poling for P4VP(Azo-X)$_{0.1}$ (a), P4VP(Azo-X)$_{0.05}$ (b), and PS(Azo-X)$_{0.05}$ (c). The poling process is started at 30 s and continued up until 15 min where near-saturation is reached. Generally lower values of NLO response in P4VP(Azo-X)$_{0.1}$ compared to P4VP(Azo-X)$_{0.05}$ are due to much lower thickness and slight deterioration in the 10 mol-% samples due to dozens of poling cycles needed for all-optical poling optimization (see ESI for optimization details).

neous and amorphous using optical microscopy. Figure 2(a) presents the evolution of the second-order nonlinearity during all-optical poling for P4VP(Azo-X)$_{0.1}$ samples with thicknesses of 280 nm $\pm$10 %. The poling is performed with 1064 nm fundamental and 532 nm seeding beam wavelengths and the NLO response is measured with 1064 nm fundamental (See ESI for details). The nonlinearity is seen to depend drastically on the substituent X, developing in the order I $>$ Br $>$ H. In other words, in samples of equal thickness and containing the same amount of azobenzene chromophores, (i) stronger halogen bonding between the active molecules and the support matrix yields higher optical nonlinearity (Azo-I vs. Azo-Br), and (ii) the halogen-bonded systems surpass the hydrogen-bonded system P4VP(Azo-H)$_{0.1}$ in terms of the optical nonlinearity. To the best of our knowledge, this is the first indication of the significance of halogen bonding in developing solid-state organic NLO materials.

To verify the generality of this observation, we prepared another set of samples with lower, 5 mol-%, azobenzene content. Reducing the azobenzene concentration allowed us to compare the NLO response obtained in P4VP to that in a weakly interacting PS matrix: if strong halogen bonds boost the optical nonlinearity, a strong matrix dependence is expected. The poling results for P4VP(Azo-X)$_{0.05}$ and PS(Azo-X)$_{0.05}$ are presented in Figs. 2(b) and 2(c), respectively. Two important observations can be made. Firstly, the NLO response still develops in the order I $>$ Br $>$ H. Secondly, the second-order NLO response is greatly diminished when replacing P4VP with PS, becoming negligible with Azo-H. Note, however, that the same hierarchy (I $>$ Br $>$ H) still remains following the order of Azo-X$\cdots\pi$ interaction energies given by DFT calculations. Overall, this gives us two independent verifications on the significance of halogen bonding on the NLO response: (i) Azo-I vs. Azo-Br in P4VP and (ii) Azo-I in P4VP vs. PS.

When considering the significance of halogen bonding in all-optical poling, several things have to be accounted for. Firstly, the process is based on photoinduced polar reorientation of the azobenzene molecules and therefore closely related to photoinduction of anisotropic (yet centrosymmetric) chromophore alignment[22,23]. The photoinduced anisotropy can be monitored by measuring the birefringence of the films upon irradiation with linearly polarized light, which we did using 532 nm excitation to match the seeding beam in the poling process. The measurement details and results are presented in the ESI. The main conclusion from these measurements is that photoinduced birefringence also greatly benefits from stronger chromophore-polymer bonding and halogen bonding yields higher anisotropy compared to hydrogen bonding. The qualitative differences are therefore same as they are for photoinduced NLO effects but the differences between the material systems are smaller.

Secondly, as the optical poling process is driven by repeated cycling between the *trans* and *cis* isomers of the azobenzene units, an accurate comparison between different material systems requires that their spectroscopic/photochemical properties are approximately equal. We verified this for the 5 mol-% sample series by pumping the thin films with a 532 nm laser (5 s, 20 mW/cm^2), matching the seeding beam wavelength of the poling process. The absorption spectra are given in the ESI (Fig. S2 and Table S1). For each chromophore, a 14–18 nm blue shift in the peak near 450 nm is seen when moving from P4VP to PS. This shift can be attributed to solvatochromic effects due to change in polarity of the molecular environment[24,25]. After excitation, a 14–23 % drop in absorbance at peak and a smaller increase at 350–400 nm are seen. These changes are characteristic for azobenzenes as they isomerize from *trans* to *cis* form[26] and prove that effective photoinduced isomerization takes place during 532 nm excitation. Most of the photoinduced changes were seen to vanish in a few hours. This, together with clearly evident isosbestic points in the spectra reveal that no photodegradation occurs during irradiation. The effective photoisomerization at 532

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nm together with lack of permanent changes in the absorption spectra suggest that the results obtained from all-optical poling at 1064/532 nm and photoinduced birefringence at 532 nm truly provide information on the influence of intermolecular interactions and their effects on the efficiency of photoinduced molecular realignment.

Based on the results, we can conclude that stronger halogen bonding leads to enhanced NLO response as well as to higher photoinduced birefringence. In each case, similar-strength hydrogen-bonding is not as beneficial. In each of the chromophores, the bond-donating atom is attached to the highly electronegative tetrafluorinated aromatic ring, due to which the single-atom mutation or a noncovalent bond formation have only minor effects on the molecular properties. Therefore, no significant changes in the photochemical or electronic properties are to be expected within the Azo-X series, which is verified by the absorption spectra (Fig. S2), computed dipole moments and molecular hyperpolarizabilities (Table S2). This leads us to the conclusion that the noncovalent interaction must be the defining factor. Bonding strength has earlier been found to enhance both linear and nonlinear optical properties in supramolecular systems [19] and the comparison of Azo-I and Azo-Br in this study strongly supports this. Nevertheless, the superior performance of Azo-Br compared to Azo-H in P4VP is not explained by bonding strength as DFT calculations reveal that the interaction energy is essentially the same. We suggest that the directional nature of the halogen bond leads to a more rigid supramolecular structure that allows the formation of higher molecular order. We note that theoretical calculations have been made that suggest notably modified dipole moments of stilbene-based halogenated NLO molecules in the presence of halogen-bond acceptors. [27] Yet the conclusion of these calculations was that halogen bonding does not significantly change the molecular-level NLO response. In our future studies, we plan to study the molecular hyperpolarizability through hyper-Rayleigh scattering experiments [28] to (i) gain further understanding on the results presented herein, and (ii) find the limits of halogen bonding in enhancing the NLO response of poled polymer systems.

To summarize, we have studied the second-order NLO response in halogen-bonded supramolecular polymers using all-optical poling. Our results demonstrate that stronger chromophore-polymer halogen bonding results in increased NLO response when the bond strength is the only variable. Furthermore, we have shown that a halogen-bonded supramolecular system is superior to a hydrogen-bonded one even when the bonding strengths are essentially equal. Together, these findings yield the conclusion that both the interaction strength and type have their own distinct effects for NLO response in supramolecular polymer systems and provide new implications for the design of second-order NLO materials.

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References

1 G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati and K. Rissanen, *Pure Appl. Chem.*, 2013, **85**, 1711–1713.
2 T. Clark, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2013, **3**, 13–20.
3 A. C. Legon, *Angew. Chem. Int. Ed.*, 1999, **38**, 2686–2714.
4 M. Saccone, G. Cavallo, P. Metrangolo, A. Pace, I. Pibiri, T. Pilati, G. Resnati and G. Terraneo, *CrystEngComm*, 2013, **15**, 3102–3105.
5 R. W. Troff, T. Mkel, F. Topić, A. Valkonen, K. Raatikainen and K. Rissanen, *Eur. J. Org. Chem.*, 2013, **2013**, 1617–1637.
6 R. Wilcken, M. O. Zimmermann, A. Lange, A. C. Joerger and F. M. Boeckler, *J. Med. Chem.*, 2013, **56**, 1363–1388.
7 A. Priimagi, G. Cavallo, P. Metrangolo and G. Resnati, *Acc. Chem. Res.*, 2013, **46**, 2686–2695.
8 F. Meyer and P. Dubois, *CrystEngComm*, 2013, **15**, 3058–3071.
9 A. Priimagi, M. Saccone, G. Cavallo, A. Shishido, T. Pilati, P. Metrangolo and G. Resnati, *Adv. Mater.*, 2012, **24**, OP345–OP352.
10 O. S. Bushuyev, T. C. Corkery, C. J. Barrett and T. Friscic, *Chem. Sci.*, 2014, **5**, 3158–3164.
11 A. Priimagi, G. Cavallo, A. Forni, M. Gorynsztejn-Leben, M. Kaivola, P. Metrangolo, R. Milani, A. Shishido, T. Pilati, G. Resnati and G. Terraneo, *Adv. Funct. Mater.*, 2012, **22**, 2572–2579.
12 M. Saccone, V. Dichiarante, A. Forni, A. Goulet-Hanssens, G. Cavallo, J. Vapaavuori, G. Terraneo, C. J. Barrett, G. Resnati, P. Metrangolo and A. Priimagi, *J. Mater. Chem. C*, 2015, **3**, 759–768.
13 S. K. Yesodha, C. K. S. Pillai and N. Tsutsumi, *Prog. Polym. Sci.*, 2004, **29**, 45–74.
14 C. Fiorini, F. Charra, J. M. Nunzi and P. Raimond, *J. Opt. Soc. Am. B*, 1997, **14**, 1984–2003.
15 R. W. Boyd, *Nonlinear Optics*, Academic Press, San Diego, 2008.
16 G. Xu, J. Si, X. Liu, Q. Yang, P. Ye, Z. Li and Y. Shen, *Opt. Commun.*, 1998, **153**, 95–98.
17 M. J. Banach, M. D. Alexander, S. Caracci and R. A. Vaia, *Chem. Mater.*, 1999, **11**, 2554–2561.
18 A. Facchetti, E. Annoni, L. Beverina, M. Morone, P. Zhu, T. J. Marks and G. A. Pagani, *Nat. Mater.*, 2004, **3**, 910–917.
19 A. Priimagi, M. Kaivola, M. Virkki, F. J. Rodríguez and M. Kauranen, *J. Nonlinear Opt. Phys. Mater.*, 2010, **19**, 57–73.
20 D. Hauchecorne, N. Nagels, B. J. van der Veken and W. A. Herrebout, *Phys. Chem. Chem. Phys.*, 2012, **14**, 681–690.
21 N. Nagels, D. Hauchecorne and W. A. Herrebout, *Molecules*, 2013, **18**, 6829–6851.
22 A. Natansohn, S. Xie and P. Rochon, *Macromolecules*, 1992, **25**, 5531–5532.
23 J. A. Delaire and K. Nakatani, *Chem. Rev.*, 2000, **100**, 1817–1846.
24 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319–2358.
25 E. Rusu, D.-O. Dorohoi and A. Airinei, *J. Mol. Struct.*, 2008, **887**, 216–219.
26 Z. Sekkat and W. Knoll, *Photoreactive organic thin films*, Academic Press, San Diego, 2002.

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27 E. Cariati, A. Forni, S. Biella, P. Metrangolo, F. Meyer, G. Resnati, S. Righetto, E. Tordin and R. Ugo, *Chem. Commun.*, 2007, 2590–2592.
28 K. Clays and A. Persoons, *Phys. Rev. Lett.*, 1991, **66**, 2980–2983.

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