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One “Click” access to self-complementary molecular modules for halogen bonding†

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Novel D- π -A push-pull chromophores were synthesized in good yields by CuAAC coupling of 4-X-2,3,5,6-tetrafluorophenyl-1-azides (X = H, Br, I) with 4-ethynyl-dimethylaniline. Thanks to the self-complementary binding sites at the molecular ends, the iodo derivative self-organizes in the solid state forming head-to-tail halogen-bonded one-dimensional unlimited chains. The second-order NLO properties of the iodo compound have been investigated by the solution-phase electric field induced second-harmonic generation method (EFISH).

Over the past few years halogen bonding (XB) has quickly grown from a scientific curiosity to a key structural element in directing and controlling molecular self-assembly phenomena.^{1–3} First recognized as an effective tool in crystal engineering,^{4,5} the application of XB is nowadays moving towards a wide range of fields encompassing organocatalysis,⁶ biology and drug design,^{7–10} anion transport and recognition,^{11–15} and materials science.^{16–23} According to the IUPAC definition,²⁴ XB is an attractive non-covalent interaction occurring between an electrophilic halogen atom in a molecule and a nucleophile. The ability of halogen atoms to act as electrophiles relies on the anisotropic distribution of the electron density around halogen atoms involved in covalent bonds with one or more atoms:²⁵ a cap of positive electrostatic potential (the so-called σ -hole²⁶) is generated on the elongation of each covalent bond, and is responsible for the interaction with

nucleophiles. The strength and directionality of XB depend on both the magnitude and size of the σ -hole and can be easily tuned by modifying the electron-withdrawing ability of substituents in the vicinity of the halogen.²⁷

Haloperfluoroalkanes^{28,29} and haloperfluoroarenes^{30–32} have been largely applied as XB donors, since they form particularly short and directional interactions, thus allowing structural control over the final supramolecular aggregates. While the synthesis of haloperfluoroalkanes is not trivial, haloperfluoroarenes moieties have been easily appended to a wide diversity of organic compounds through nucleophilic aromatic substitution (S_NAr).^{33,34} In fact, the presence of strong electron-withdrawing substituents such as fluorine atoms, makes possible the nucleophilic substitution on aromatic rings, affording to new carbon-carbon or carbon-heteroatom bonds *via* the selective C-F bond cleavage.³⁵ The nucleophilic aromatic substitution (S_NAr) has been previously applied for the preparation of ditopic halogen-bonded donors,³³ and has proven to be an effective strategy to new tectons for XB-driven self-assembly.^{34,36}

In order to broaden the panel of accessible XB-donors, additional synthetic strategies are required for introducing halo-perfluorinated moieties on different molecular scaffolds, characterized by new electronic and structural properties. Hopefully these new synthetic methodologies should be chemoselective, utilize mild reaction conditions and result in high yields. According to Sharpless³⁷ the concept of click chemistry applies to reactions that are wide in scope, chemo- and stereoselective and highly efficient. Click reactions proceed smoothly under mild conditions, and the products are recovered in high yield with a minimum purification effort. Among the reactions fulfilling these criteria, the Cu-catalyzed azide-alkyne cycloaddition (CuAAC)^{38–40} has gained paramount importance. This reaction is in fact well suited to link together molecular building blocks and, accordingly, has found widespread application in the synthesis of dendrimeric structures.^{41–47} By contrast there are only few examples in which 1,2,3-triazoles prepared *via* CuAAC reaction have been used as π -conjugated linker in

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donor- π -acceptor (D- π -A) chromophores.⁴⁸⁻⁵³ These D- π -A push-pull molecules, in which D is an electron-donating group and A is an acceptor moiety, constitute an important class of compounds capable of second-order nonlinear optical (NLO) activities⁵⁴⁻⁵⁶ which are interesting for application in the electro-optical devices field.

The aim of the present study was to employ the CuAAC click chemistry in the synthesis of self-complementary molecular modules for halogen bonding. Specifically, we were intrigued to use the triazole-forming click reaction to link an aromatic XB-donor terminus, to a dimethylamine substituted aryl moiety acting as XB-acceptor (see Scheme 1). In the coupling product the triazole ring behaves as a π bridge linking a donor group to an acceptor one, resulting in novel D- π -A push-pull chromophores.

The presence of electron withdrawing substituents (EWS) on aryl moieties makes azides **1a-c**⁴⁵ particularly challenging substrates,⁴⁶⁻⁴⁸ however we found that they can be quite efficiently coupled with *N,N*-dimethylbenzenamine by employing the most usual CuSO₄·5H₂O/Na-ascorbate catalytic system. The sought 1,4-disubstituted 1,2,3-triazoles were obtained in moderately good yields (50-60%). Enhanced yields (up to 80%) in **2c** were obtained when the coupling was carried out by employing CuI as catalyst according to Recsei's methodology.⁵⁷ While the present work was in progress Zhang and co-workers reported⁵⁸ the synthesis of 1-polyfluoroaryl-1,2,3-triazoles *via* a copper-catalysed one-pot three-component reaction of polyfluoroarenes, sodium azide, and terminal alkynes. They found that the optimal conditions include the use of Cu(OAc)₂·H₂O as the catalyst and CH₃CN as solvent while other Cu sources used with the association of sodium ascorbate as the reducing agent were ineffective affording only to trace amounts of the desired products.

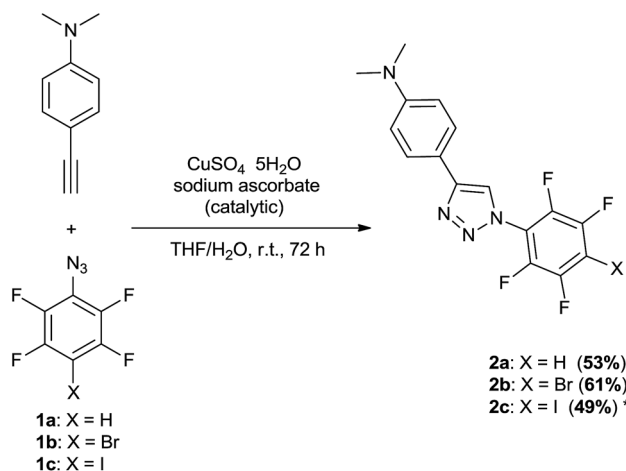
2a-c were characterized by ¹H, ¹³C and ¹⁹F NMR spectroscopy, UV-vis spectroscopy GC-MS and elemental analysis. Formation of the sought push-pull molecules is apparent from the presence in the ¹H NMR spectra of **2a-c** of a triplet (⁴J_{H-F} =

1.0 Hz) due to the proton of the triazole ring which couples with one of the F atoms of the fluorinated aryl moiety. Furthermore, upon formation of the triazole moiety, the aryl protons *o*- to the X group are displaced downfield of about 0.3 ppm, while the *m*-protons are shifted downfield of about 0.4 ppm. The ¹³C NMR spectra are in keeping with the proposed structures (ESI†).

The electronic absorption and emission spectra have been recorded at 298 K in CHCl₃ solution; as an example, the UV spectrum of **2c** is shown in Fig. 1. All the spectra show an absorption maximum at 290 nm indicating that the nature of the X atom does not affect significantly the optical activity. The corresponding emission spectra were obtained by excitation at the maximum absorbance frequency. All the excitation spectra display a maximum emission at 350 nm and result composed by a series of band and shoulders separated by about 1400 cm⁻¹, probably corresponding to the vibrational structure of the ground state.

Single crystals of the push-pull molecule **2c** have been obtained from chloroform solution, upon slow evaporation at room temperature. They were extremely thin plates, often curved and always twinned. One of the thickest crystal has been selected for single crystal X-ray analysis. Although it was twinned with large mosaicity, we were able to solve the structure with a good resolution, obtaining details about the supramolecular organization of the self-complementary molecules in the crystal lattices. CCDC no. 1453398, contains the supplementary crystallographic data for **2c**.

Compound **2c** crystallizes in the monoclinic space group *P2*₁/*n* with three independent molecules in the asymmetric unit. These three molecules, labelled as **A**, **B** and **C** in Fig. 2, differ essentially in the orientation of the two benzene rings with respect to the triazole ring. Looking at the N1-N2-C6-C5 and N3-C8-C9-C10 torsion angles in Fig. 2 (-32.4(9)° and 22.9(9)° for molecule **A**, 34.9(9)° and 18.9(9)° for **B** and 32.6(8)° and 18.7(9)° for **C**), it appears that the benzene rings are *anti*-rotated in molecule **A**, while they are *syn*-rotated in molecules **B** and **C**. The main interaction in the crystal packing is the I...N halogen bond between the iodine atom on the tetrafluoro-benzene ring and the nitrogen atom of the dimethylamino group, which produces a significant pyramidalization of the latter. In fact



Scheme 1 Synthesis of the novel D- π -A push-pull molecules *via* Cu-catalyzed azide-alkyne cycloaddition (CuAAC). *Yields up to 80% were obtained in the presence of CuI as catalyst.

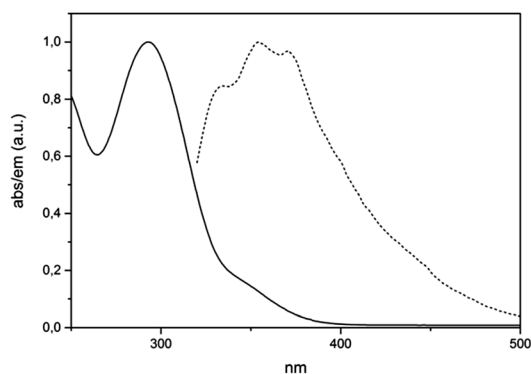


Fig. 1 Normalized UV-vis absorption (solid line) and fluorescence spectrum (dotted line) of **2c** in CHCl₃ (1×10^{-6} M).



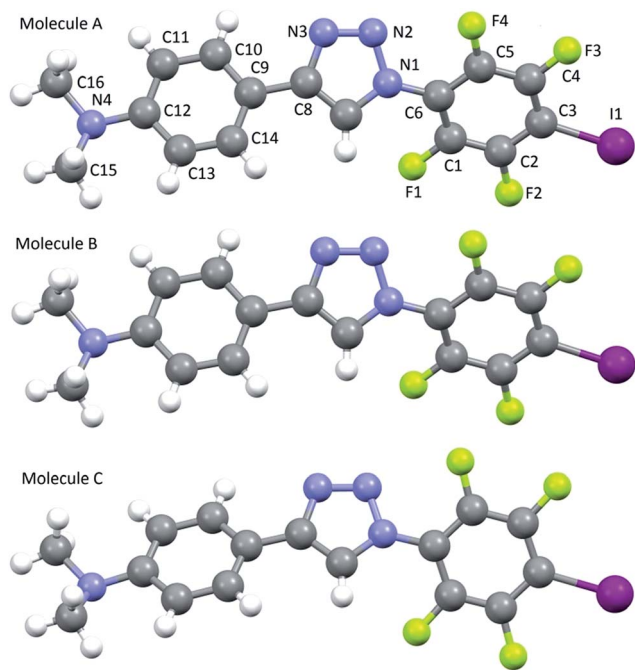


Fig. 2 The three independent molecules in the asymmetric unit of compound **2c**, showing the different conformation of **C** with respect to the similar **A** and **B**. The same labels have been assigned to chemically equivalent atoms. Colour code: C, dark grey; H, light grey; F, green; I, purple; N, blue.

a search for 4-dimethylaminophenyl groups in the CSD database (Version 5.36, November 2014 + 1 update, with $R < 0.005$, no disordered, no errors not polymeric, no ions, no powder structure, 572 hits, 836 data) revealed that the mean distance between N and the plane through its three bonded carbon atoms is 0.118(15) Å with the upper quartile of 0.154 Å, while in **2c** this distance is 0.298(7), 0.283(7) and 0.311(6) Å, for **A**, **B** and **C** molecules, respectively.

The occurrence of halogen bond between these self-complementary molecules produces two different unlimited zig-zag chains, the first made of alternating **A** and **B** molecules ($\cdots\mathbf{A}\cdots\mathbf{B}\cdots\mathbf{A}\cdots\mathbf{B}\cdots$), the second only of **C** molecules ($\cdots\mathbf{C}\cdots\mathbf{C}\cdots$) (see Fig. 3). The halogen bonds in these zig-zag chains are similar: the $\text{I}\cdots\text{N}$ distance is 2.940(5), 2.906(5) and 2.942(2) Å for the $\text{I1A}\cdots\text{N4B}$, $\text{I1B}\cdots\text{N4A}$ and $\text{I1C}\cdots\text{N4C}$ bonds, respectively. The corresponding $\text{C3-I1}\cdots\text{N4}$ angles are 170.0(2), 168.83(2) and 169.2(2)° while the $\text{I1}\cdots\text{N4-C12}$ are 96.9(4), 98.4(4) and 100.2(3)°. Parallel triplets of this chain, two of type $\cdots\mathbf{A}\cdots\mathbf{B}\cdots\mathbf{A}\cdots\mathbf{B}\cdots$ and the third of type $\cdots\mathbf{C}\cdots\mathbf{C}\cdots$ are linked together only by weak $\text{I}\cdots\text{H}$ and $\text{N}\cdots\text{H}$ contacts, producing a sort of waved tape, clearly shown in Fig. 3. No other significant contact is present in the structure. The head-to-tail assembly of these self-complementary XB modules ensures that each chain is polar, although the coupling of antiparallel dipoles generates a centrosymmetric structure, as clearly indicated by the centric space group ($P2_1/n$), where adjacent chains adopt an antiparallel arrangement.

It is well established, both experimentally and theoretically, that the environment strongly influences NLO responses of

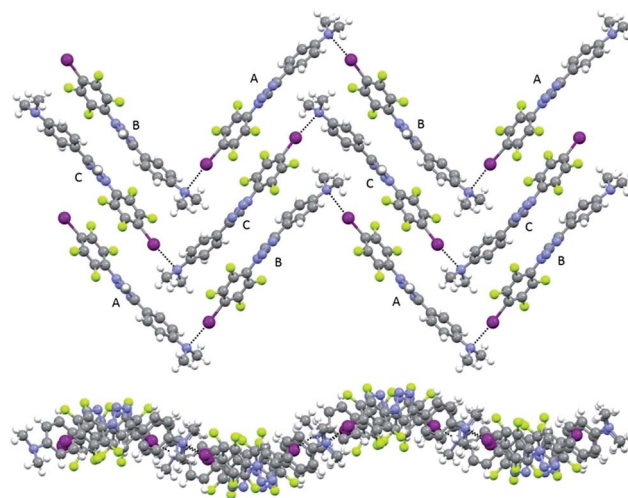


Fig. 3 Top: ball-and-stick view down the crystallographic *a* axis of three unlimited 1D halogen-bonded chains in **2c** structure; the labels point out the positions of the three independent molecules. Bottom: the same chains projected along the *c*-axis, showing their waving. Colours as follows: C, dark grey; H, light grey; F, green; I, purple; N, blue; XB, dotted black lines.

molecules.^{59,60} In fact, there are many examples of theoretical and experimental investigations describing that the formation of specific solute-solvent hydrogen bonding increases the value of β . Similarly, we have already demonstrated that the occurrence of XB influences the NLO properties of molecules in solution.^{61,62}

Here we have extended our analysis to compound **2c** whose second-order NLO properties were examined by the solution-phase electric field induced second-harmonic (EFISH) generation method.^{63,64} Measurements of $\mu\beta_\lambda$ (the product between the molecular dipole moment μ and the projection of the quadratic hyperpolarizability tensor β_{tot} along μ) were carried out in CHCl_3 and DMF solutions, at 1907 nm non-resonant wavelength. Interestingly, in agreement with previous studies,^{61,62} an inversion, from positive to negative, of the sign of the $\mu\beta_\lambda$ is observed on going from CHCl_3 ($+58 \times 10^{-48}$ esu) to DMF (-98×10^{-48} esu) due to the involvement of the I atom of **2c** in the formation of specific halogen-bonded adducts where the XB acceptor is DMF. Both the lower $\mu\beta_\lambda$ and absorption maximum of **2c** with respect to our previously investigated system bearing the same donor and acceptor moieties but a double bond conjugated bridge ($\mu\beta_\lambda$ equal to +124 and -380×10^{-48} esu in CHCl_3 and DMF respectively; λ_{max} equal to 382 nm) indicate the triazole ring as a less efficient π bridge.

Conclusions

In summary, we have described the synthesis of new heteroditopic self-complementary tectons designed in order to possess terminal halogen bond donor and acceptor groups connected by a 1,2,3-triazole ring as π -bridge. We found that 4-halo-tetrafluorobenzene-azides can be quite efficiently coupled with *N,N*-dimethylbenzamine, despite the presence of EWS



substituents on the aromatic ring, demonstrating the effectiveness of CuAAC “click chemistry” in the synthesis of a novel series of chromophores having A- π -D structure.

The crystal structure of the iodo-derivative **2c** show that the presence of self-complementary XB-donor and acceptor groups drives their self-assembly into head-to-tail halogen-bonded infinite polar chains. However, such polar chains aggregate according to a centrosymmetric crystal structure giving macroscopically a null second-order NLO response in the solid state. EFISH measurements in chloroform and DMF solutions confirm that the NLO responses in solution can be tuned thanks to solvent...chromophore XB interactions, since an inversion, from positive to negative, of the sign of the $\mu\beta_\lambda$ is observed on going from CHCl₃ to DMF.

Owing to the modular nature of the CuAAC reaction, it seems the new approach may be extended to the synthesis of other self-complementary molecular modules for halogen bonding driven self-assembly. Taking into account the effectiveness of XB in driving the formation of infinite polar chains, the synthetic approach described in this paper may be exploited for the synthesis of new organic chromophores showing high NLO activity in the solid state, provided a careful molecular design is applied in order to avoid the formation of centrosymmetric crystals.

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