Supramolecular Construction of a Highly Elongated π-Conjugated Structure in the Solid State: Metal-Free Click Reaction Guided by C-H Hydrogen Bonding

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Abstract

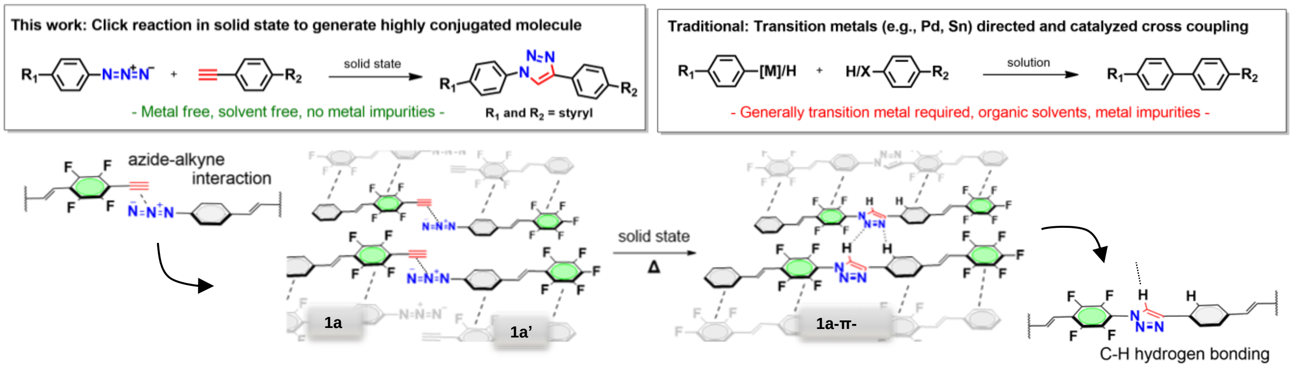
A planned topochemical azide-alkyne cycloaddition is developed in the organic solid state to generate a highly elongated π-conjugated 1,2,3-triazole by a metal-free click reaction. The triazole is generated using a binary cocrystal composed of stilbenes that are covalently adjoined in a single-crystal-to-single-crystal transformation. The click reaction is accompanied by a large-scale structural reorganization involving procession-like movements of 1D stacked columns into a 2D layered structure. The formation of the layered structure is guided by newly formed triazoles self-assembling via C-H···N hydrogen bonding.

Main

Extended π-conjugated structures (e.g., molecules, polymers) are of considerable interest academically and technologically, particularly in the field of electronics (e.g., electronic, mechanical, nonlinear optical, electrochemical properties).[1-3] Approaches to construct extended π-conjugated structures typically involve metal-mediated (e.g. Pd, Pt, Cu) coupling reactions performed in organic solvents (e.g. haloforms), which leave challenges related to sustainability.[4] Click approaches to form π-conjugated oligomers are also gaining increasing attention in solution albeit using metal catalysts (e.g. Cu).[5-7] In addition to the reactions being environmentally unfriendly owing to uses of organic solvents and precious metals, trace metals in the final products can be problematic[3,4] and reactions in solution are prone to afford mixtures (e.g., regioisomers, oligomers). Opportunities, therefore, exist to develop highly sustainable, reliable, regiospecific, and metal-free methods to generate these important extended π-conjugated structures.[8]

As we have been interested in expanding the boundaries of applying reactions that occur in organic crystals to form targeted products,[9] we attempted a planned synthesis of the highly elongated π-conjugated molecule **1a-π-1a'** in the solid state using the azide-alkyne click reaction (AAC) (**Scheme 1**).[10,11] To our knowledge, there have been no reports to use an AAC to form a highly elongated π-conjugated molecule such as **1a-π-1a'** in the solid state, although Ma has formed diaryl-1,2,3-triazoles with assistance of phenylperfluorophenyl (PFP) interactions.[12] The click-conjugated triazole (CCT) **1a-π-1a'** would consist of five aromatic rings in conjugation supported by the triazole ring and two flanking ethylene bridges.

Herein, we report on an AAC reaction of **1a** and **1a'** to proceed in the organic solid state to form **1a-π-1a'**. The reaction proceeds as a rare single-crystal-to-single-crystal (SCSC) transformation that involves a large-scale, precessional reorganization that is guided by newly generated of C-H hydrogen bonds to give one-dimensional (1D) polymer. In addition to confirming the formation of **1a-π-1a'**, the information from the SCSC reaction allows us to introduce an approach to develop crystalline solids based on supramolecular → molecular → supramolecular conversion of reactants to products. We expect the concept to be exploitable to generate novel π-rich hydrogen-bonded materials.[13]



Scheme 1. Solid-state here (upper left) and solution (upper right) approaches to form π-conjugated molecules and reported here (bottom) generation of a highly elongated π-conjugated structure using a binary cocrystal via metal-free click reaction.

In the solid state, an AAC reaction proceeds metal-free,[12,14] with the stereochemical outcome dictated by preorganization of the alkyne-azide groups.[15] From pioneering work of Ma [12,16-19] and Sureshan,[10,20] the proximity of the reacting groups and constrained environment of a crystal lattice obviate needs to use metals to control the regiochemical outcome. The electronic outcome contrasts a [2+2] photodimerization that also proceeds in the solid state yet affords saturated functionality (i.e., cyclobutane ring).[21]

Colorless laths of the binary cocrystal **1a·1a'** were generated by slow evaporation of a solution of THF/MeCN (4:1 *v*/*v*) during a period of two days. The composition of **1a·1a'** was confirmed by single-crystal and powder X-ray diffraction, as well as ^{1}H NMR spectroscopy.

A single-crystal X-ray analysis (SCXRD) revealed **1a·1a'** to cocrystallize in the triclinic space group *P*-1 (**Figure 1**). The stilbenes are nearly planar (twist angles: 4.17, 3.16°) and assemble by face-to-face PFP interactions (centroid-to-centroid: 3.72, 3.64 Å). The terminal -N=N=N (blue) and -C≡C-H (red) groups are antiparallel and in close proximity (closest C···N separations: 3.32 Å and 3.93 Å) (**Fig. 1a**). The aromatics form 1D stacked columns parallel to the crystallographic *b*-axis (**Fig. 1b**). The C=C bond of the alkyne **1a'** is disordered (relative occupancies: 0.92:0.08), with adjacent columns (**Fig. 1b**) interacting by C-H•••F contacts (C···F separations (Å): C···F 3.23(3), 3.34(2)).[22] The columns place the stilbenes in an offset, or 'out-of-plane', geometry, with the -N=N=N and -C≡C-H units preorganized for an intermolecular AAC reaction as outlined by Sureshan.[15] The cycloaddition would occur between columns involving the stilbenes in the out-of-plane geometry.

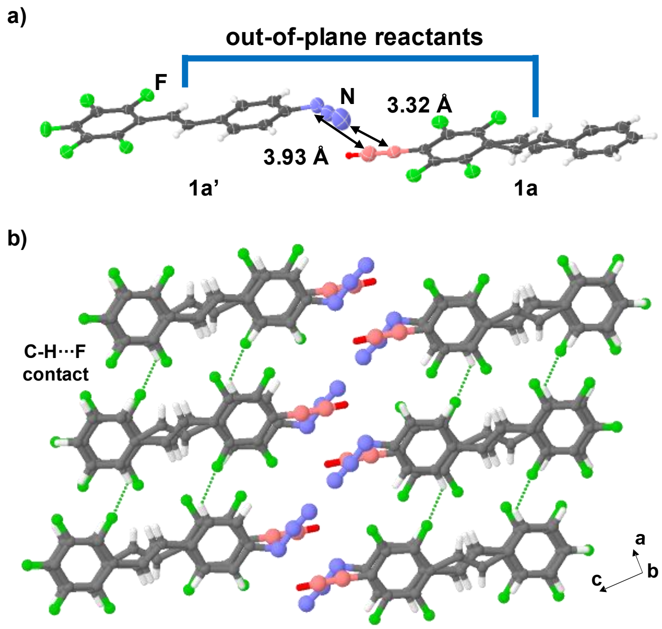


Figure 1. X-ray structure **1a·1a'**: (a) -N=N=N (blue) and -C≡C-H (red) groups and (b) overhead view of columns.

When **1a·1a'** was slowly heated, a DSC trace showed an exothermic peak at 105 ^{o}C consistent with triazole ring formation (see Supplementary Material). A shoulder peak at 110 ^{o}C was also present. An IR spectrum showed the azide (2126 cm^{-1}) and terminal alkyne (3310 cm^{-1}) to disappear. A Raman spectrum revealed the alkyne (2128 cm^{-1}) to also disappear, which was accompanied by the appearance of a triazole group (999 cm^{-1}). A ^{1}H NMR spectrum showed the alkyne (singlet, 5.16 ppm) to disappear with triazole ring formation (singlet at 9.20 ppm).

Optical inspection of **1a·1a'** revealed the single crystals to remain intact upon heating. A SCXRD analysis (**Fig. 2**) demonstrated the out-of-plane stilbenes to undergo an ACC reaction to generate the 1,2,3-triazole **1a-π-1a'** regiospecifically and in quantitative yield (**Fig. 2a**). The triazole consists of five aromatic rings in extended conjugation (total length: 26 Å or 2.6 nm),

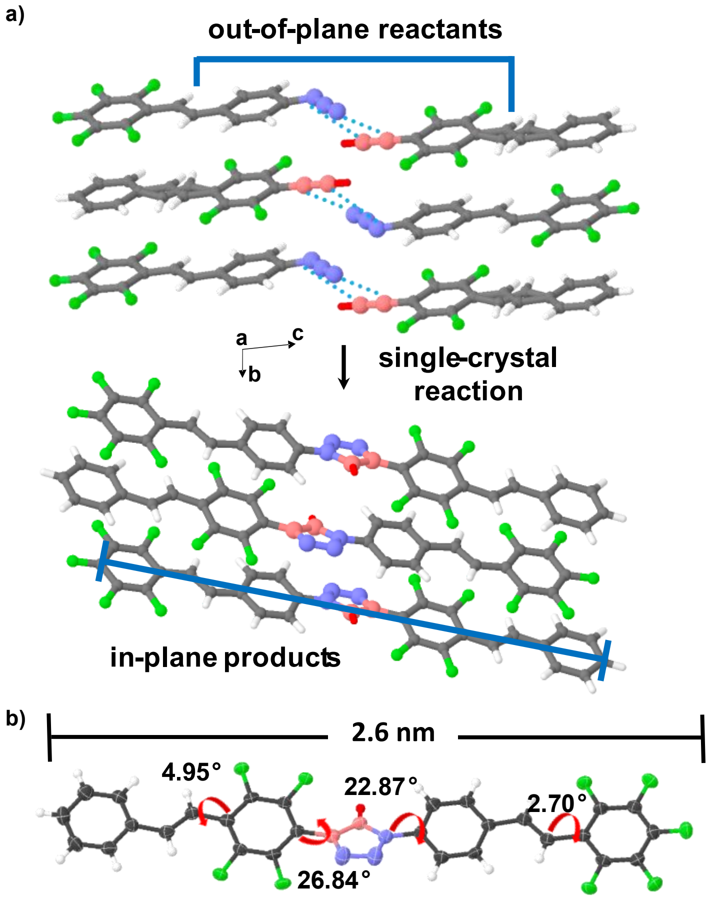


Figure 2. Single-crystal **1a·1a'** to **1a-π-1a'**: (a) triazole formation and (b) elongated π-structure.

being either slightly (stilbene) or appreciably (triazole) twisted from coplanarity (twists angles: 2.70° to 26.84°) (**Fig. 2b**). Thus, the out-of-plane stilbenes of **1a·1a'** moved 'in-plane' to form the triazole. Both -C=C- bonds of the ethylenes of the product, in contrast to the reactants, are ordered, which is consistent with the -C=C- linkages experiencing pedal-like motion.[23] We are unaware of an AAC reaction performed in the solid state that generates a highly elongated π-conjugated structure.[12] We note that DFT calculations (see Supplementary Material) reveal the extended π-conjugation of **1a-π-1a'** to exhibit a HOMO-LUMO gap (i.e., 3.8 eV) comparable to conventional oligomers (e.g. thiophenes, acenes). The transformation **1a·1a'** to **1a-π-1a'** represents the first example SCSC click reaction with reactants exclusively as aromatics.

The single-crystal nature of the AAC reaction provides details of structural changes of the aromatic components in the solid (**Figure 3**). Specifically, the conversion of **1a·1a'** to **1a-π-1a'** involved a remarkable large-scale solid-state reorganization wherein the formation of the triazole was accompanied by large rotations of the aromatic components about the crystallographic *a*- (36°) and *b*- (31°) axes (**Fig. 3a**). Overall, the rotations are akin to the stacked columns undergoing a gyroscopic precession[24,25] with a path (vertical displacement: 3.5 Å) that traces a partial turn of a helix. The triazole, however, shares the same space group (*P*-1) as the cocrystal and the PFP interactions remained intact (centroid-to-centroid: 3.75, 3.74 Å). The largest changes to the unit cell occurred along the *a*- and *c*-axes (ca. 3.2%), with the cell undergoing a modest reduction in volume (ca. 3%). The peak on the DSC at 110 °C can likely be ascribed to the large-scale movement to involve an accompanied phase transition.[26]

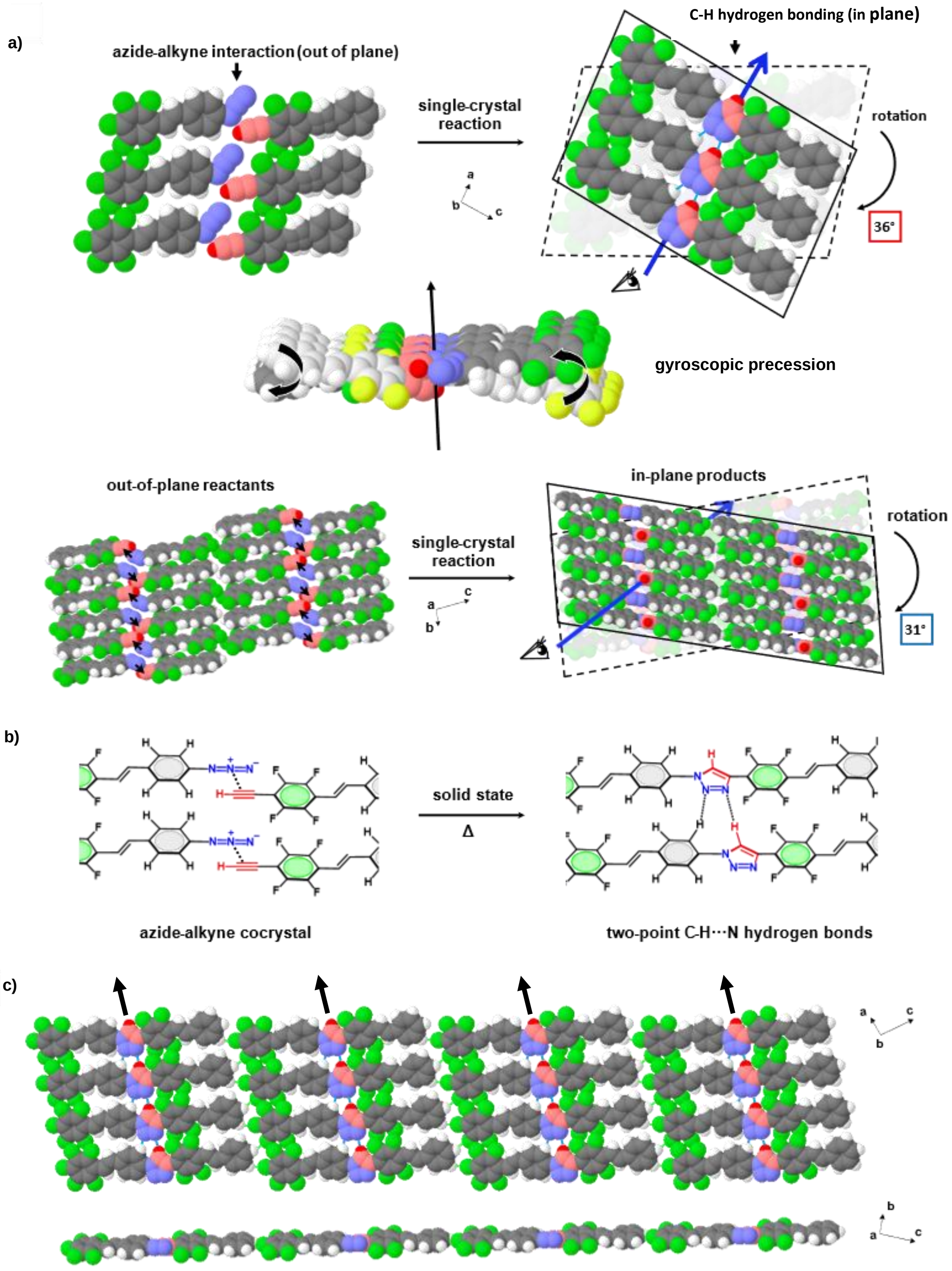
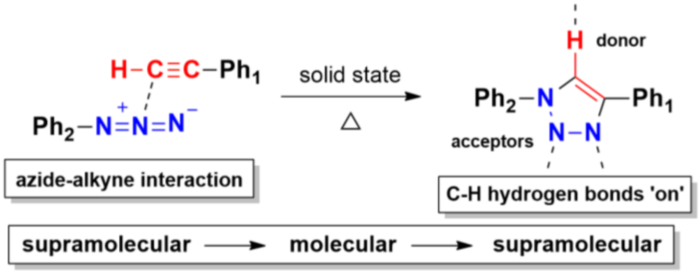


Figure 3. SCSC reaction of **1a·1a’** to **1a-π-1a'**: (a) gyroscopic precession (rotations *a*- and *b*-axes), (b) ‘conversion’ of azide-alkyne interaction to C-H hydrogen bonds, and (c) generated 2D structure above (top) and in plane (bottom) (arrow directions of C-H hydrogen bonding).

The large-scale reorganization can be attributed to the 'out-of-plane' to 'in-plane' transformation leading to the formation of C-H hydrogen bonding (**Fig. 3b**). The resulting triazole participates in a 1D network along the *a*-axis sustained by two-point C-H···N hydrogen bonds (C···N separations (Å): 3.32(3), 3.68(3) Å). The hydrogen bonds result in an 'induced fit' manifested as a planar 1D array. The C-H···N hydrogen bonds in combination with C-H···F interactions generate a 2D layered structure within the crystallographic *ac*-plane (**Fig. 3c**), with the C-H···N hydrogen bonds being parallel within a layer and antiparallel between layers. The 2D layers contrast the columnar structure prior to the AAC reaction.

In general, an AAC reaction of a terminal alkyne and azide as in **1a·1a'** will create one strong HB-donor (i.e., C-H ring group) and two strong HB-acceptors (i.e., N-ring atoms).[27] The hydrogen bonding capacity of a triazole allows for binding of anions as reported by Flood.[27,28] While the -C≡C-H group of the alkyne can act as a weak HB-donor,[29] the -N_3 group of an azide has only recently been described as a HB-acceptor in condensed phases and as related to click reactivity.[30] For **1a·1a'**, neither the -C≡C-H nor -N_3 group participate in hydrogen bonds; instead, the groups interact via the azide-alkyne interaction.[14] While the phenyl groups of **1a** and **1a'** can serve as weak HB-donors and HB-acceptors,[31] the groups participate in the PFP interactions.[12]



Scheme 2. C-H hydrogen bonds 'on' after ACC reaction with aromatic functionalization.

Thus, for **1a·1a'**, the AAC serves a dual role: (i) form the targeted extended π-conjugated triazole **1a-π-1a'** and (ii) populate the crystal with appreciably strong HB-donors and HB-acceptors (i.e., hydrogen bonds 'on') that 'trigger' the large-scale reorganization (**Scheme 2**). The reorganization presumably occurs to counterbalance energetic and structural costs of generating the HB-donors and HB-acceptors in a crystal lattice where originally there were none.[32]

In conclusion, we have demonstrated stilbenes to undergo a metal-free AAC reaction in the solid state to form a highly elongated π-conjugated structure. The click reaction resulted in a reorganization guided by C-H hydrogen bonding of the triazole product. We are now studying the reaction scope to afford novel aromatic-rich structures where the crystalline state allows for precise construction of large oligomers (e.g., controlled dispersity)[4] and novel solid-state architectures by triggered formation of hydrogen bonds. We also expect the interplay between supramolecular chemistry (i.e., alkyne-azide interaction), molecular (i.e., triazole formation), and supramolecular chemistry (i.e., hydrogen-bond formation) to be exploitable to generate novel hydrogen-bonded solids (e.g., higher dimensionality). The interplay could afford a supramolecular synthon[12] to generate aromatic-rich hydrogen-bonded polymers and materials.[32,33] Higher order cocrystals (e.g., ternary, quaternary) can also be developed to form aromatic covalent and noncovalent structures.[34] The observations can also be extended to covalent organic frameworks and related materials.[33]

Supporting Information

Full experimental details including materials, methods, synthesis, and analysis along with characterization data from ^{1}H NMR spectroscopy, thermogravimetric and infrared (TG-IR) Data, powder X-ray diffraction data, and single-crystal X-ray diffraction data have been provided in PDF format. Full crystallographic data have been provided in CIF format.

Author Contributions

SY performed and analyzed the original experiments and created drafts of the manuscript, CL conducted characterization experiments and created recent drafts of the manuscript, AC reviewed and edited the manuscript, and LRM directed the project and completed the manuscript. All authors have read and agreed to the published version of the manuscript.

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