Noncentrosymmetric Packings Influenced by Electronic Properties of Products of Click Reactions

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**S** Supporting Information

ABSTRACT: Though 1,4-disubstituted 1,2,3-triazole rings have been utilized as electronic bridges in the solution phase, the use of a triazole ring to serve as an electronic bridge of small molecules in the crystalline state has been underdeveloped. Here two compounds with a central 1,4-disubstituted 1,2,3-triazole ring are synthesized to investigate the electronic bridging between terminal stilbazole and pyridine groups in the crystalline phase. The electronic properties of the molecules are characterized through solution phase UV−vis spectroscopy, single crystal X-ray diffractions, and density-of-state and gas-phase DFT calculations. We show that the electronic bridging behavior of a 1,4-disubstituted 1,2,3-triazole ring derived from a click reaction is maintained in the solid state by rare head-to-head (hh) packing in noncentrosymmetric crystal environments.
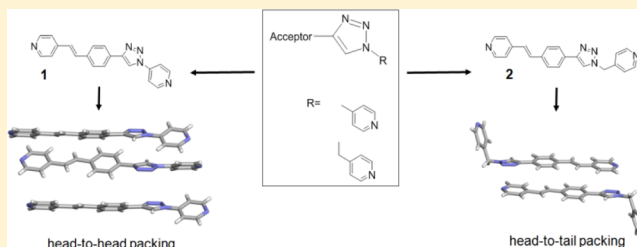
Whereas the copper-catalyzed azide−alkyne cycloaddition (CuAAC) click reaction[1,2] has experienced great promise with widespread applications in organic synthesis and materials chemistry (e.g., fluorescence),[3] less is known with regard to how electronic information is propagated by the triazole ring itself. In this context, recent studies have reported the triazole ring to bridge electron-donor and -acceptor groups as part of charge-transfer conduits in solution.[4] Triazole rings have, thus, been incorporated into branched dendrimers to bridge donors and acceptors and enhance tunable photoluminescence. Moreover, substitution patterns of donor and acceptor groups of triazoles are now being studied to discern modes of electronic bridging. For example, triazole rings have been utilized to bridge an electron donor in the form of a fullerene to an acceptor in the form of a Zn(II) porphyrin.[4c] Very recently, the triazole moiety has been revealed to support enhanced optical properties involving pyrimidine as an electron acceptor.[4d] There has been only one report, however, that suggests that a triazole serve as an electronic bridge of small molecules in the crystalline state. In the report, the triazole acted as a bridge in starburst triphenylamines.[5] Without crystal packing information, however, correlations to electronic spectra can be difficult.

Our interests in triazoles lie in an ability of 1-[2-(4-pyridyl)ethenyl]-4-[3-(4-pyridyl)-1H-1,2,3-triazol-4-yl] benzene (**1**) and 1-[2-(4-pyridyl)ethenyl]-4-[3-(pyridin-2-yl-methyl)-1H-1,2,3-triazol-4-yl] benzene (**2**) (Scheme 1) to function as building blocks for applications in self-assembly and supramolecular syntheses.[6] During studies to understand the solid-state structures of the bipyridines, we discovered that,

Scheme 1. 1,4-Triazole Rings As Bridges Involving Stilbazole and Pyridine
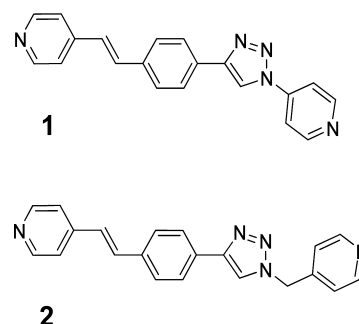
while both compounds assemble in noncentrosymmetric space groups, **1** exhibits rare head-to-head (hh) stacking in the crystalline state manifested as edge-to-face π-stacking. The hh stacking contrasts a more typical form of head-to-tail (ht) stacking encountered in **2**. Using electronic crystalline calculations, we show the packings to be consistent with electronic communication to take place across the central triazole rings of **1** and **2**, which support the hh geometry of **1** in the solid. The solution and solid-state properties make **1** and **2** attractive for developments in optoelectronics applications (e.g nonlinear optics).

Bipyridines **1** and **2** were synthesized through the CuAAC click reaction in either one-pot (**2**) or two-step reactions (**1**).[7] The terminal stilbazole and pyridine groups were integrated to provide opportunities for hydrogen bonding and/or metal coordination in more downstream supramolecular applications.[7a] Thus, both **1** and **2** possess end groups that can be easily tailored, with the two molecules differing by either the presence or absence of a saturated CH_2 linkage between the triazole and pyridine rings. The incorporation of the sp³-hybridized C atom between the triazole and pyridine rings in **2** would, moreover, disrupt possible electron communication and bridging.

To begin our investigation, UV−vis spectra were determined in both dimethylformamide (DMF) (40 μM) and dichloromethane (DCM) (40 μM) (Figure 1).[8] For **1**, significant
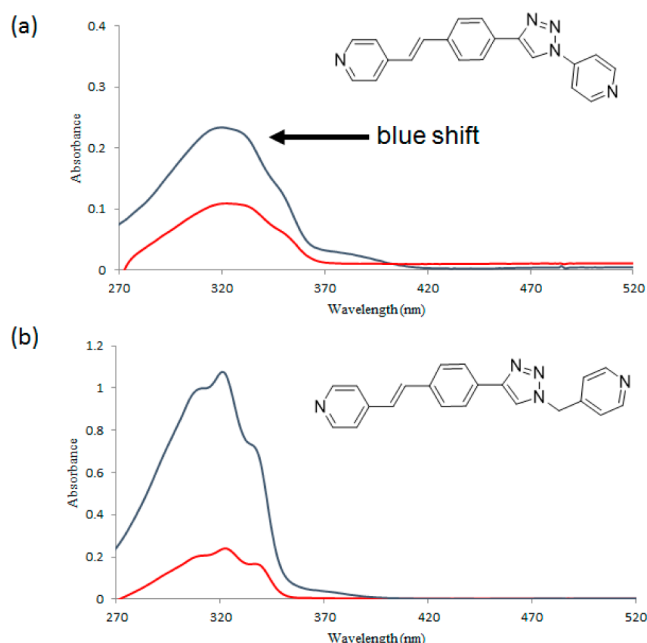

Figure 1. UV−vis spectra: (a) **1** in 40 μM DMF (red) and 40 μM DCM (blue) and (b) **2** in 40 μM DMF (red) and 40 μM DCM (blue).

changes in wavelength and intensity were observed for the peak at 323 nm (DMF) that underwent an increase in intensity and blue shift to 317 nm (DCM). In the case of **2**, no significant change in the λ_{max} was observed. An increase in intensity of the peak at 323 nm for **2**, however, was observed in less polar DCM. Additional UV−vis spectra were collected in DMF and DCM at dilutions of 20 μM (see the Supporting Information).

The spectra exhibit similar trends as those seen at 40 μM concentrations. The differences in the UV−vis spectra of **1** are consistent with solvochromatic behavior, which is typical for a molecule that is easily polarizable.[9]

Whereas evidence for the 1,4-disubstituted 1,2,3-triazole ring of **1** to act as an electronic bridge was realized in the solution phase, that the electronic behavior is maintained in the solid state originates from crystal structures of both **1** and **2**.

Single crystals of **1** (8.5 mg) were grown from slow solvent evaporation in ethanol (9 mL). Thin colorless plates formed over a period of approximately 3 h.[10]

The asymmetric unit of **1** consists of a full molecule that crystallizes in the noncentrosymmetric space group *Cc* (Figure 2). The stilbazole moiety is planar with a 24.4° rotation from the triazole ring, while the pyridyl "R" group exhibits a 23.6° rotation from the triazole. The overall twist of **1** is 47.6°, as measured with respect to the central benzene ring. Importantly, **1** exhibits atypical hh stacking in the solid, which is sustained by edge-to-face π forces, with neighboring molecules canted at 48.2°, as measured from the plane of the central benzene ring (Figure 2a). In the arrangement, the triazole rings of neighboring molecules are separated by 3.8 Å, with the molecular dipoles being effectively aligned in the same direction. The hh alignment is further manifested through C−H···N forces (3.6 Å) between triazole rings of neighboring molecules (Figure 2b). Similar C−H···X⁻ forces involving triazole rings to support anion binding have been reported.[11] Collectively, the hh packing of **1** is propagated throughout the entire crystal, which accounts for the noncentrosymmetric packing.

In contrast to **1**, ht packing was realized for **2**. Single crystals of **2** (8.0 mg) were grown from slow solvent evaporation of toluene (5 mL). Colorless plates formed after approximately 5 days.[12]

Similar to **1**, triazole **2** also crystallizes in the noncentrosymmetric space group *Cc* (Figure 3). The asymmetric unit of **2**, however, consists of two full molecules. Each molecule exhibits rotation from planarity between the central benzene ring and the triazole ring (molecule A: 9.6° and molecule B: 10.2°). The presence of the saturated linkage results in a dihedral twist between the triazole ring and the pyridyl "R" group (molecule A: 112.5° and molecule B: 110.4°). In contrast to **1**, the two molecules are present as dimers that display an ht arrangement sustained by face-to-face π forces (ca. 3.7 Å). Adjacent triazole rings within the dimer are separated by 12.0 Å. C−H···N interactions are not present between neighboring triazole rings, as with **1**. The dimers pack ht, with adjacent dimers being canted at approximately 37.6°
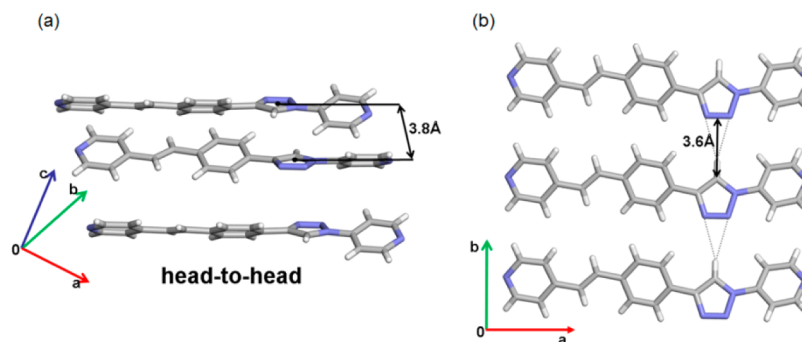

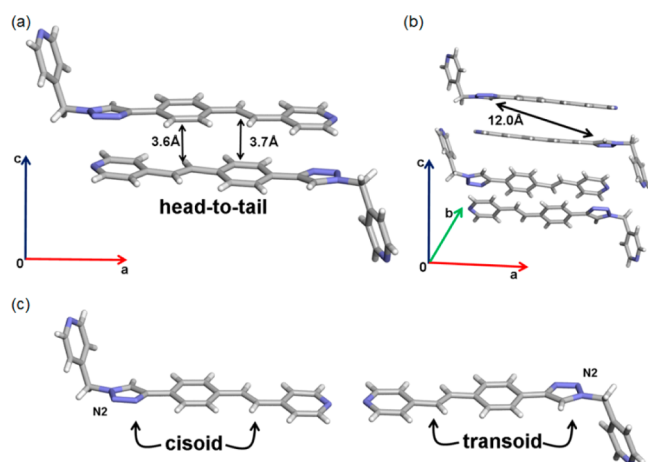**Figure 2.** Packing of **1**: (a) hh stacking via edge-to-face forces and (b) CH···N interactions.

Figure 3. Packing of **2**: (a) ht packing via face-to-face π forces, (b) extended packing, and (c) conformations of molecules of the dimer.

Figure 4. Density of states plots in crystalline environment: (a) **1** and (b) **2**. Highest crystalline-filled band (orbital) is aligned with 0 eV. Gas-phase DFT calculations: (c) HOMO and LUMO of **1** and **2**. Note the presence and absence of delocalized electron density in the LUMO of **1** and **2**, respectively. Isosurface density parameter was 0.03.

with respect to the plane of the central benzene ring. The ht packing of nonconjugated **2** is consistent with typical behavior of molecules to pack to cancel dipole moments. An origin of the noncentrosymmetric packing of **2**, however, lies in the conformations of the alkene units. In particular, whereas the C═C bonds of stacked molecules of **1** adopt cisoid conformations with respect to the N2/N3 N atoms of each triazole ring, the two molecules present in the asymmetric unit of **2** adopt either a cisoid or transoid conformation (Figure 3c).

Molecules in organic solids typically assemble ht or antiparallel, so as to promote cancellation of molecular dipole moments.[13] For **1**, we attribute the hh packing to the ability of the 1,4-disubstituted 1,2,3-triazole to serve as an electronic bridge between the two pendant stilbazole and pyridine groups. In effect, the bridge enables charge distribution to be spread throughout the molecule and, thus, support a hh π-stacked structure. The crystal packing is consistent with a bipyridine that is "electronically soft", with the electron density being easily polarized by bridging behavior of the triazole.[14] Notably, in a survey of the Cambridge Structural Database (CSD) (version 5.34, update 3, November 2012) of structurally analogous triazoles, we determined 6 of 32 molecules to exhibit noncentrosymmetric packing based on hh stacking geometries.[15]

Insight into the nature of the hh packing in **1** was gained by periodic density-of-state (DOS) calculations derived directly from optimized crystal structures of **1** and **2** (Figure 4, panels a and b). Specifically, for the LUCO of **1**, contributions from the stilbazole, pyridine, and triazole involve crystalline band overlap in the 3.5 to 4.5 eV region, which supports the triazole ring to act as an electronic bridge. For **2**, there are negligible contributions from triazole and pyridyl moieties to the LUCO. Gas-phase DFT calculations for single molecules of **1** and **2** are consistent with the triazole ring, acting as a bridge between the stilbazole and the pyridine (Figure 4c). Electron density of the HOMO of **1** is localized on the stilbazole and triazole, while electron density of the LUMO is delocalized throughout the entire molecule. Similar to **1**, the electron density for the HOMO of **2** is localized on both the stilbazole and triazole. Unlike **1**, however, electron density is not present on the pendant pyridyl "R" group in the LUMO of **2**. Gas-phase DFT calculations also demonstrate the hh face-to-face dimer of **1** to exhibit a binding energy that is relatively stable and comparable to alternative ht geometries. The binding
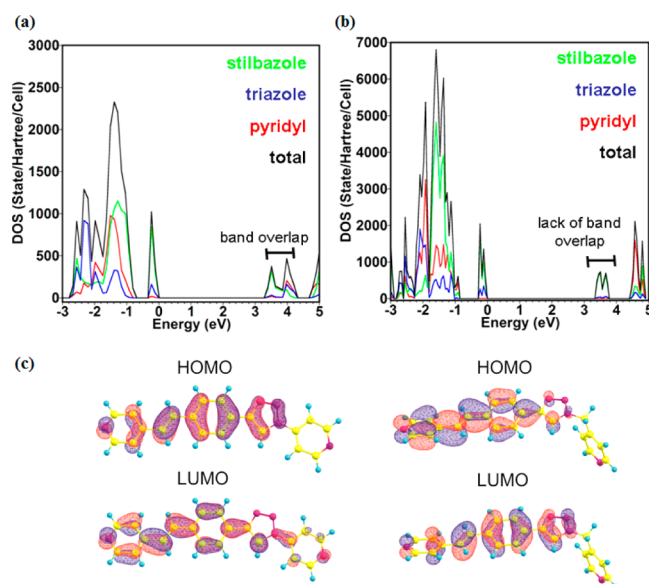
energy for the ht dimer of **2** reflects a relatively stable geometry with hh orientations being consistently less stable in energy (see Table S1 of the Supporting Information). The calculations are also consistent with the relative planarities exhibited by the stilbazole and triazole moieties of **1** and **2** in the solids.

In this report, we have shown that the electronic bridging behavior of a 1,4-disubstituted 1,2,3-triazole ring derived from a click reaction is maintained in the solid state. Both molecules crystallize in the same noncentrosymmetric space group that involve different stacking geometries. For **1**, unusual hh packing is supportive of electronic charge being distributed throughout the molecule via bridging, while **2** exhibits a more typical ht geometry. We are now studying more complex triazole donor-to multiple-acceptor click-based products with a goal to develop electronically functional complex solids.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, spectroscopic data, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(10) Crystal data for **1**: monoclinic; *Cc*; chemical formula: $C_{20}H_{15}N_5$; formula weight: 325.37; unit-cell dimensions: $a = 37.700(4)$ Å, $b = 5.7148(6)$ Å, $c = 7.2827$ (8) Å, $\alpha = 90.00°$, $\beta = 96.164°$, $\gamma = 90.00°$ $V = 1560.0(3)$ Å^3; temperature = 293(2) K; $Z = 4$; $\mu = 0.086$ mm^{-1}; $\rho_{calcd} = 1.39$ g/cm^3; $R = 0.0454$ for 1375 reflections with $I > 2\sigma(I)$.

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(12) Crystal data for **2**: monoclinic; *Cc*; chemical formula: $C_{21}H_{17}N_5$; formula weight: 339.40; unit-cell dimensions: $a = 42.009(5)$ Å, $b = 5.9508(6)$ Å, $c = 13.5541(14)$ Å, $\alpha = 90.00°$, $\beta = 92.817(5)°$, $\gamma = 90.00°$, $V = 3384.3(6)$ Å^3; temperature = 293(3) K; $Z= 8$; $\mu = 0.083$ mm^{-1}; $\rho_{calcd} = 1.33$ g/cm^3; $R = 0.0377$ for 2967 reflections with $I > 2\sigma(I)$.

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