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Programming Rapid Functional Group Diversification into a Solid-State Reaction: Aryl Nitriles for Self-Assembly, Click Reactivity, and Discovery of Coexisting Supramolecular Synthons

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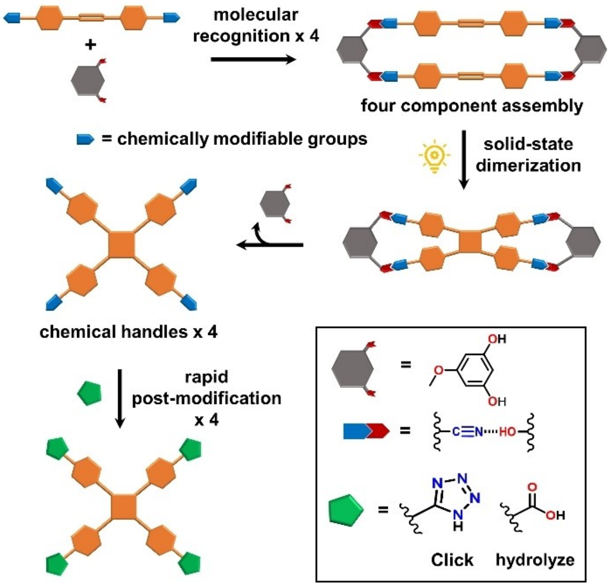
Abstract: A method to rapidly diversify the molecules formed in organic crystals is introduced, with aryl nitriles playing a novel dual role as both hydrogen-bond acceptors and modifiable organic groups. The discovery of coexisting supramolecular synthons in the same crystal is also described. The general concept is demonstrated by using a bis(aryl nitrile) alkene that undergoes a hydrogen-bond-directed intermolecular [2+2] photodimerization to form a tetra(aryl nitrile)cyclobutane. The product is readily converted by click reactivity to a tetra(aryl tetrazole) and by hydrolysis to a tetra(aryl carboxylic acid). The integration of aryl nitriles into solid-state reactions opens broad avenues to post-modify products formed in crystalline solids for rapid diversification.

Introduction

The organic solid state is a highly attractive medium (i.e., degree of organization, solvent-free) for directing the formation of covalent bonds to construct molecules.[1] While experiencing significant successes, the use of small-molecule templates to direct covalent bond formation in solids remains at a nascent stage of development.[2] In this context, we have shown how small-molecule templates based on 1,3-dihydroxybenzene, or resorcinol (**res**), can participate in hydrogen-bond-driven self-assembly to direct the formation of carbon–carbon single (C–C) bonds in solids through intermolecular [2+2] photodimerizations.[3] The templates assemble and preorganize alkenes within discrete four-component hydrogen-bonded assemblies for the photoreaction. The approach has been used to construct molecules in solids that are difficult to obtain from solution (e.g., ladderanes).[4]

While **res**-based templates have provided access to complex molecules in the solid state, a yet to be achieved goal is integration of an alkene with hydrogen-bond acceptor groups that can both: i) serve as "handles" for molecular recognition and self-assembly (Scheme 1, blue) and ii) be post-modified to a diverse range of functional groups (Scheme 1, green).[5] An organic functional group that meets these two conditions would satisfy structural and chemical requirements that sit at nexuses of molecular recognition, self-assembly, and organic synthesis, essentially programming the self-assembly process to support both reactivity and post-modification. To date, the majority of hydrogen-bond acceptors attached to reactive alkenes have been n-pyridyl groups (n = 2, 3 and 4), which are limited in terms of reactivity,[6] and corresponding capacity for post-modification.



Scheme 1. Integration of aryl nitriles for solid-state construction of covalent bonds and access to diverse chemical species by post-modification.

Herein, we report the first example of a templated reaction in the solid state that incorporates a functional group amenable to diverse post modifications. Specifically, we describe integration of the aryl nitrile group into a hydrogen-bond directed synthesis that can support rapid functional group diversification (Scheme 1). We show that cocrystallizations of 4,4′-dicyanostilbene (**DCSB**) with **res** templates afford binary cocrystals

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3(**res**)·5(**DCSB**) and (**MeO-res**)·(**DCSB**) (where: **MeO-res** = 5-methoxyresorcinol) wherein the C=C bonds of **DCSB** are preorganized by hydrogen bonds to the –C≡N group to undergo a [2+2] photodimerization. UV irradiation of each solid generates *rctt*-1,2,3,4-tetrakis-(4'-cyanophenyl)cyclobutane (**TCCB**) stereoselectively and in quantitative yield. Post-synthesis reactivity experiments demonstrate **TCCB** to be readily and fully converted to cyclobutanes decorated with tetrazole (**TZCB**) and carboxylic acid (**TACB**) groups. During our work, we have also discovered an unusual and novel case wherein two reported supramolecular synthons involving discrete assemblies and multiple components coexist in the *same binary cocrystal*. While the cocrystal is photoactive, the discovery illustrates inherent difficulties encountered to control crystal packing yet provides insight into new opportunities to construct and control properties of multi-component solids. Our introduction of aryl nitriles is expected to significantly advance the potential of reactions performed in solids as a means to generate diverse molecules and lead to innovations in organic synthesis, materials science, and medicinal chemistry.[7]

Results and Discussion

Aryl nitriles are one of the most versatile precursors in organic synthetic chemistry.[8] The –C≡N group can be readily elaborated to a variety of chemical functionalities (e.g., acid, aldehyde, amine, amidine, tetrazole),[9] with the click reaction to form a tetrazole being an important highlight.[10] The –C≡N group, however, is vastly underutilized as a participant in hydrogen bonds, particularly in the context of supramolecular synthesis and, more specifically, crystal engineering.[11] The latest Cambridge Structural Database (CSD) reveals limited examples of –C≡N groups acting as hydrogen-bond acceptors with mono- (8 hits) and di- (10 hits) hydroxybenzenes in the solid state,[12] yet the interaction is reasonably documented in solution.[13] The ability of aryl nitriles to participate in hydrogen bonds in the solid state to support the formation of covalent bonds has not been reported.

Photostability of native aryl nitrile

DCSB as a single component is photostable. The stilbene self-assembles in a herringbone motif to generate a layered structure with adjacent C=C double bonds parallel and separated by 4.75 Å (CSD refcode: WEFBIT;[14] Figure 1). When subjected to UV irradiation (40 h, Hg medium-pressure UV-lamp), crystalline **DCSB** was determined to be photostable (Figure S2 in the Supporting Information).

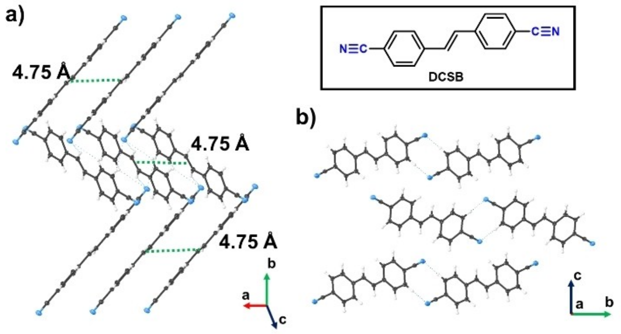


Figure 1. X-ray structure of **DCSB**: a) herringbone packing and b) view along the *a*-axis.

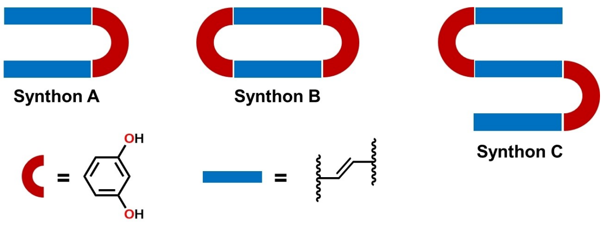
Photoactive hydrogen-bonded assemblies

Our approach to integrate the –C≡N group into a photoactive solid was carried out by cocrystallizing **DCSB** with a **res**-based template. Interactions of **res** molecules and aromatic hydrogen-bond acceptors can give rise to one of three supramolecular synthons in binary and higher-order cocrystals (Scheme 2). In all reported cases, the resulting cocrystals are composed exclusively of a single supramolecular synthon.[3,15] In this report, we describe a novel and unusual photoactive binary cocrystal composed of *both* three- (synthon **A**) and five-component (synthon **C**) discrete structures *in the same solid*. We also describe a binary cocrystal involving the predesigned four-component assembly (synthon **B**). Moreover, both solids were shown to be photoactive.

Unusual mixed three- and five-component assemblies

When **DCSB** (30 mg, 0.13 mmol) and parent **res** (14 mg, 0.13 mmol) (1:1 ratio) were subjected to liquid-assisted grinding (LAG; $CHCl_3$, 0.5 mL) using a mortar-and-pestle for a period of 10 min, powder X-ray diffraction (PXRD) revealed the formation of a new solid phase (Figure S7). Single crystals of 3(**res**)·5(**DCSB**) suitable for X-ray diffraction were obtained by slow evaporation (ca. 3 d) of a $CHCl_3$ solution (5 mL) of the ground powder (40 mg).

A single-crystal X-ray diffraction (SCXRD) analysis showed **res** and **DCSB** to crystallize in the triclinic non-centrosymmetric space group *P*1 (Figure 2). In contrast to our original design, **res** and **DCSB** form two distinct three- and five-component hydrogen-bonded assemblies (synthons **A** and **C**) in the solid 3(**res**)·5(**DCSB**). Each assembly is sustained by two and four O–H···N≡C hydrogen bonds, respectively (O···N distances:



Scheme 2. Supramolecular synthons involving **res** and **DCSB** for solid-state photodimerizations.

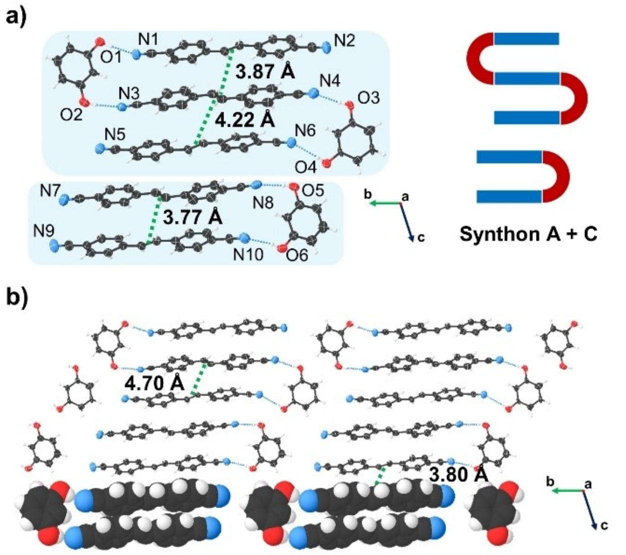


Figure 2. X-ray structure of 3(**res**)·5(**DCSB**): a) ORTEP of two distinct hydrogen-bonded assemblies in the solid at 50% probability and b) extended stacking.

O1···N1 2.814(8), O2···N3 2.839(8), O3···N4 2.831(9), O4···N6 3.001(9), O5···N8 2.851(8), O6···N10 2.877(9) Å; Figure 2a). In both assemblies, the C=C bonds lie anti-parallel, being separated by 3.87, 4.22, and 3.77 Å (centroid-to-centroid). The two different assemblies form infinite face-to-face stacks of **DCSB** molecules in a ladder-like pattern (Figure 2b). We are unaware of a case wherein two different supramolecular synthons based on hydrogen-bonded **res** molecule form in a solid.[3,16]

Designed four-component assembly

The success of using a **res** to direct reactivity in the solid state is predicated on the formation of four-component assemblies (i.e., synthon **B**). The synthon reliably localizes chemical reactivity and covalent bond formation within a discrete hydrogen-bonded structure. Whereas the case involving the parent **res** and **DCSB** afforded a combination of three- and five-component discrete assemblies in the same solid, the four-component assembly exclusively formed in the case of **MeO-res**.[17]

When **DCSB** (30 mg, 0.13 mmol) and **MeO-res** (18 mg, 0.14 mmol; 1:1 ratio) were subjected to LAG ($CHCl_3$, 0.5 mL) for a period of 10 min, a PXRD analysis revealed a formation of a new solid phase. Dissolution and slow evaporation of the ground powder (40 mg) from $CHCl_3$ (5 mL) afforded colorless plates over a period of 2 days. The composition of (**MeO-res**)·(**DCSB**) was confirmed by SCXRD and ^{1}H NMR spectroscopy (Figure S4).

The components of (**MeO-res**)·(**DCSB**) crystallize in triclinic space group $P\bar{1}$ (Figure 3). **DCSB** and **MeO-res** form a discrete four-component molecular assembly sustained by four O–H···N≡C hydrogen bonds (O···N distances: O1···N1 2.899(2), O2···N2 2.852(2) Å; Figure 3a). **DCSB** stacks approximately face-to-face with C=C bonds parallel and separated by 4.05 Å, which conforms to the geometry criteria for a [2+2] photodimerization.[18] The assemblies organize along the crystallographic *c*-axis to generate a ladder-like structure with **DCSB** and **MeO-res** as rungs and rails, respectively (Figure 3b). **DCSB** molecules assemble offset and participate in face-to-face π-π interactions (3.70 Å) between neighboring assemblies, with the C=C bonds separated by 7.29 Å.

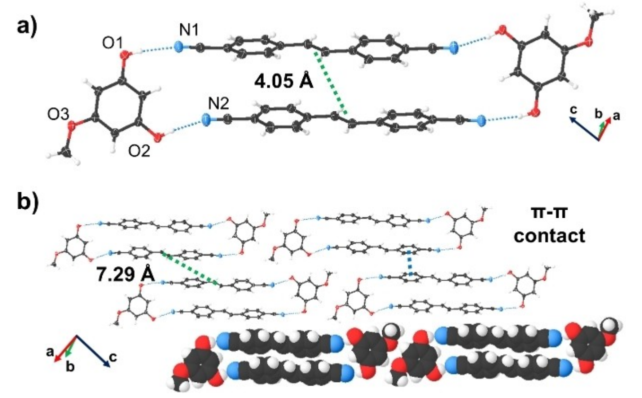


Figure 3. X-ray structure of (**MeO-res**)·(**DCSB**): a) view of the four-component assembly and b) extended stacking.

Photoreactivity and single-crystal-to-single-crystal reaction

When 3(**res**)·5(**DCSB**) and (**MeO-res**)·(**DCSB**) were each irradiated with UV radiation (30–40 h, 450 W medium-pressure Hg vapor lamp), **DCSB** reacted to form a cyclobutane in quantitative yield as evidenced by the complete disappearance of the alkene singlet at 7.56 ppm and appearance of a cyclobutane peak at 4.76 ppm on the ^{1}H NMR spectrum (Figures S3 and S4). We ascribe the formation of the cyclobutane photoproduct in 3(**res**)·5(**DCSB**) to the C=C bonds undergoing pedal-like rotation.[19] We note that the solid 3(**res**)·5(**DCSB**) exhibited a loss in crystallinity as evidenced by PXRD, with evidence of the solid becoming amorphous upon being exposed to the UV-light (Figure S6). In contrast to 3(**res**)·5(**DCSB**), a PXRD diffractogram showed (**MeO-res**)·(**DCSB**) to retain crystallinity (Figure S7). Moreover, when subjected to UV light using a Nail dryer lamp (20 h), optical microscopy was consistent with (**MeO-res**)·(**DCSB**) undergoing a single-crystal-to-single-crystal (SCSC) reaction.[20]

A SCXRD analysis of reacted (**MeO-res**)·(**DCSB**) revealed the stacked C=C bonds to undergo a partial SCSC reaction (overall yield: 30%, single-crystal conversion: 3%) to generate **TCCB** (Figure 4). In the solid, the structure of the hydrogen-bonded assembly remained intact, with the generation of **TCCB** being accompanied by weakening and strengthening of the hydrogen bonds (Figure 4a). The hydrogen-bonded assemblies extended along *c*-axis with neighboring **TCCB** molecules participating in displaced π-π interactions (3.80 Å; Figure 4b). We are unaware

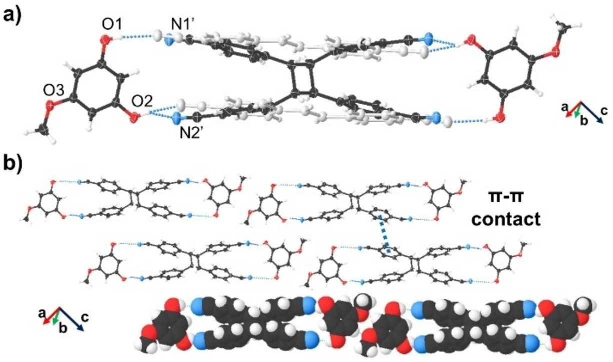


Figure 4. X-ray structure of photoreacted (**MeO-res**)·(**DCSB**): a) view of the formation of **TCCB** (dark gray) from **DCSB** (light gray) and b) extended stacking.

of an example wherein O–H···N≡C hydrogen bonds direct a photodimerization in the solid state.

Structure authentication, inclusion, and isolation

When photoreacted 3(**res**)·5(**DCSB**) was recrystallized in MeOH/DMF (2:1), single crystals as colorless lathes formed over a period of 4 days. SCXRD analysis revealed the composition of the single crystals as 2(**TCCB**)·(**res**)·(**DMF**).

The components of 2(**TCCB**)·(**res**)·(**DMF**) crystallize in the monoclinic space group $P2_1$ with two **TCCB** molecules, one **res** molecule, and one **DMF** molecule in the asymmetric unit (Figure 5). The cyclobutane **TCCB** exhibits a *rctt* stereochemistry consistent with two *trans* alkenes **DCSB** undergoing an intermolecular photodimerization. **Res** adopts an *anti–anti* conformation and interacts with **DMF** through O–H···O hydrogen bonds (O···O distance: O1···O3 2.728(9) Å; Figure 5a). As a consequence of the assembly process, the components of 2(**TCCB**)·(**res**)·(**DMF**) form an inclusion solid defined by 1D rhomboidal channels (dimensions: ~7.8×7.6 Å) along the crystallographic *b*-axis (Figure 5b). The channels are occupied by **res** and **DMF** molecules that sit at the center of the polygon and interact with **TCCB** backbone through weak O–H···N≡C hydrogen bonds (O···N distance: O1···N6 3.185(7) Å). The total solvent accessible volume (307.8 Å^3) with the exclusion of **res** and **DMF** was calculated to be 10.9% of the unit cell.[21] **TCCB** as a pure form was also isolated following treatment of irradiated (**MeO-res**)·(**DCSB**) with base (NaOH) and solvent extraction (CH_2Cl_2). The cyclobutane crystallizes to form close-packed tetrameric rectangular cages (Figure S1).

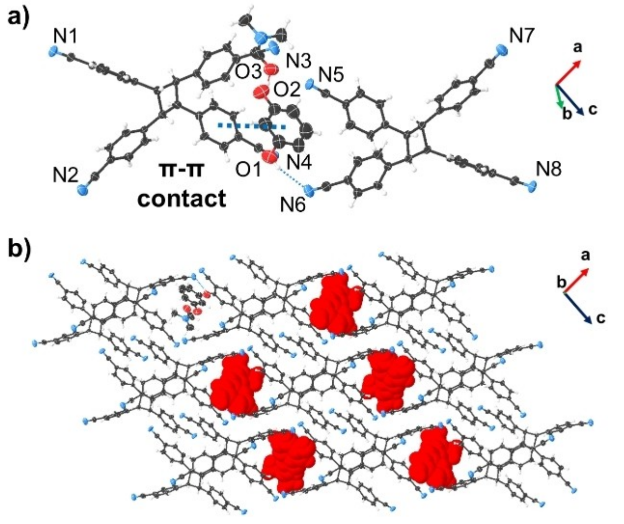


Figure 5. X-ray structure of 2(**TCCB**)·(**res**)·(**DMF**): a) ORTEP view of the asymmetric unit at 50% probability and b) space-filling of guests (red) along the *b*-axis.

Post-click modification

In line with our design, the hydrogen-bond-acceptor –C≡N groups employed for molecular recognition of **DCSB** to give **TCCB** are readily post-modifiable. Engineered into the solid-state reactivity is a capacity of the hydrogen-bond-acceptor –C≡N groups to undergo click reactivity. Tetrazoles, which form through 1,3-dipolar cycloadditions with azides, are important functional groups in organic synthesis,[22] the pharmaceutical industry,[23] and materials science (i.e., energetic materials).[24] While the click reaction has emerged ubiquitous as applied to organic chemistry performed in solution, we are unaware of a report that demonstrates the potential of molecules formed in crystals to be rapidly diversified using the transformation.

The cyclobutane **TCCB** readily undergoes a click reaction to give the tetratopic tetrazole-decorated cyclobutane **TZCB** (Figure 6). **TZCB** formed when **TCCB** (0.23 g, 0.5 mmol) was treated with NaN_3 (0.49 g, 7.5 mmol) in the presence of NEt_3·HCl (1.03 g, 7.5 mmol). Isolation of **TZCB** yielded a white powder (0.17 g, 0.34 mmol, 68% yield) (Figure 6a). When the solid was recrystallized in THF/EtOAc (3:1), single crystals formed as colorless blades upon slow evaporation over a period of 2 days. A SCXRD analysis demonstrated the solid as composition (**TZCB**)·2(**THF**)·2(**EtOAc**).

The components of (**TZCB**)·2(**THF**)·2(**EtOAc**) crystallize in the triclinic space group $P\bar{1}$ with a half **TZCB** molecule and full **THF** and **EtOAc** molecules in the asymmetric unit (Figure 6). The cyclobutane, which sits around a crystallographic center of inversion, is functionalized with four radially-oriented tetrazole groups with each being present in the 1H tautomeric form (Figure 6b).[25] The *rctt* configuration of the cyclobutane ring was retained following the post-click modification. **TZCB** self-assembles as zig-zag chains in the *ac*-plane through self-complementary N–H···N hydrogen bonds (N···N distance: N1···N8 2.845(4) Å) (Figure 6c). **TZCB** also participates in N–H···O hydrogen bonds with the included **EtOAc** molecules (N···O distance: N5···O2 2.737(5) Å) to give solvent-filled rhombic channels (Figure 6d). The solid (**TZCB**)·2(**THF**)·2(**EtOAc**) exhibits a solvent accessible volume (572.0 Å^3) that accounts for 48.2% of the unit cell volume, which is significantly larger than 2(**TCCB**)·(**res**)·(**DMF**) (10.9%). Reactivity experiments involving

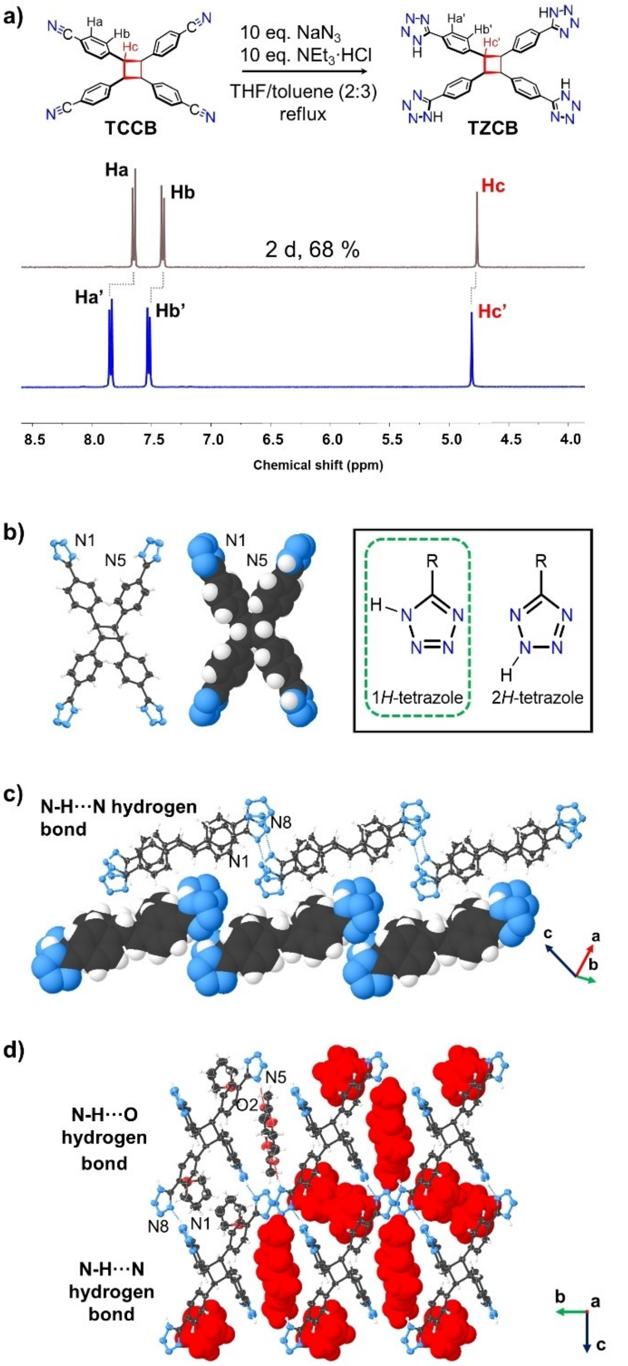


Figure 6. a) ^{1}H NMR spectroscopic comparison of **TCCB** and **TZCB** (400 MHz, [D$_6$]DMSO). X-ray structure of (**TZCB**)·2(**THF**)·2(**EtOAc**): b) ORTEP (50% probability) and space-filling models of **TZCB**, c) zig-zag chain sustained by N–H···N hydrogen bonds, and d) space filling of guests (red) along the *a*-axis.

TCCB with acid (e.g., HCl) also to generate the corresponding tetra(carboxylic acid) (Figure S5).[26]

Conclusion

In conclusion, aryl nitriles (–C≡N) have been used to support the formation of covalent bonds in the solid state. A tetracyano cyclobutane formed stereoselectively and in quantitative yield in a [2+2] photodimerization. The functionalized cyclobutane provides an attractive precursor for post-modification, as was demonstrated by the rapid generation of **TZCB**. We are now investigating the scope of products generated by using the –C≡N groups and the ability of these products to serve as multitopic linkers of porous frameworks (e.g., MOFs) and energetic materials. Efforts to elaborate the products with broad and diverse functionalities will be reported.[27]

Deposition Numbers 2152581 (for 3(**res**)·5(**DCSB**)), 2130586 (for (**TCCB**)·0.5(**res**)·0.5(**DMF**)), 2130583 (for (**MeO-res**)·(**DCSB**)), 2130584 (for 2(**MeO-res**)·(**TCCB**)), 2130585 (for **TCCB**), and 2130588 (for (**TZCB**)·2(**THF**)·2(**EtOAc**)) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: dimerization · molecular recognition · post-modification · self-assembly · solid-state reactions

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