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ARTICLE TYPE

Two act as one: unexpected dimers of catechol direct a solid-state [2+2] photodimerization in a six-component hydrogen-bonded assembly

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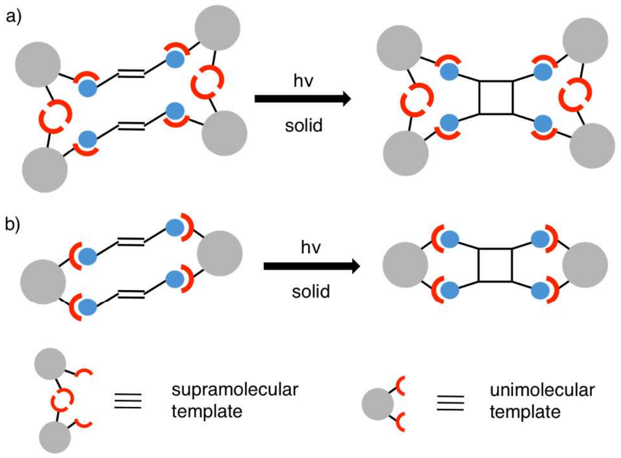
We describe hydrogen-bonded dimers of catechol that act collectively as a single template to direct an intermolecular [2+2] photocycloaddition in the solid state. The directed reactivity involves discrete, six-component hydrogen-bonded assemblies and a photoreaction that occurs stereoselectively and in quantitative yield.

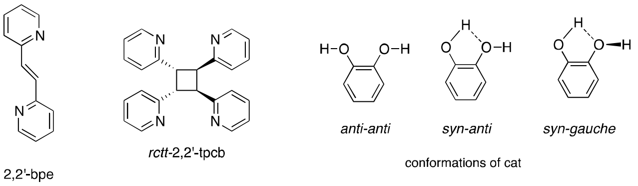
There is considerable interest in using small molecules to direct reactivity in the organic solid state.[1] The approach employs a ditopic molecule as a template - akin to an enzyme in Nature - to assemble olefins into the strict geometry of Schmidt[2] for an intermolecular photocycloaddition reaction. Principles of supramolecular chemistry are used to stack olefins into zero-dimensional (0D), or discrete, three- and four-component hydrogen-bonded assemblies that effectively decouple solid-state reactivity from unwanted effects of long-range packing.[3] In addition to synthesizing molecules difficult to achieve in solution, a major benefit of using the solid state as a medium to control reactivity – particularly, from a supramolecular perspective – is that one can effectively bypass structure effects of entropy and dissolution of the liquid phase[4] to investigate extents to which principles of supramolecular chemistry can direct reactivity in the solid state and beyond (*e.g.* solution).

In this context, a principle employed by Nature to control reactivity is the operation of multiple copies of macromolecules that collectively act as a single template for a chemical reaction.[5] In such a setting, two or more associated molecules utilize functional groups to both interact with each other and aid a substrate to assemble in an active site for reaction. With this in mind, we wish to report here an unexpected ability of multiple copies of the ditopic molecule catechol (**cat**) to act together as a template in the solid state (Scheme 1). The reactivity is achieved in a co-crystal of 4(**cat**)·2(**2,2'-bpe**) (where: **2,2-bpe** = *trans*-1,2-bis(2-pyridyl)ethylene) wherein hydrogen-bonded dimers of **cat** pre-organize **2,2'-bpe** into a novel, discrete, six-component assembly for an intermolecular [2+2] photodimerization (Scheme 1a). The olefin reacts to afford *rctt*-tetrakis(2-pyridyl)cyclobutane (**2,2'-tpcb**) stereoselectively and in quantitative yield. Whereas a single molecule is typically employed to stack olefins into the geometry for a [2+2] photodimerization in the solid state (Scheme 1b), we are unaware of a case wherein two or more copies of a single molecule unite to act as one to direct a cycloaddition reaction in a discrete assembly of molecules in a solid.



Scheme 1 Comparison: a) supramolecular (six components) and b) unimolecular (four components) templates for a [2+2] photocycloaddition.

The geometry requirements of Schmidt for a photodimerization provide foci for efforts to engineer covalent bonds in solids. Small ditopic hydrogen-bond-donor[6] and -acceptor[7] molecules with spatially-oriented functional groups have been useful in this regard to reliably stack olefins in solids for the photoreaction. Earlier work involving ditopic **cat**, however, suggested that the two hydroxyl groups were not suitably positioned to assemble and stack two olefins for the photoreaction.[8,9] Specifically, in (**cat**)·(**4,4'-bpe**), the diol adopts an *anti-anti* conformation in an unreactive 1D polymer. The idea that two copies of **cat** could stack two olefins to react also seemed unlikely given the disparity between the close proximity of the two hydroxyl groups of **cat** (~ 2.70 Å) and the larger separation distance that two carbon-carbon double (C=C) bonds generally must assume to react in a solid (i.e. 4.20 Å).



Scheme 2

Addition of **cat** (0.11 g) to MeCN (3 mL) in the presence of **2,2’-bpe** (0.10 g) yielded, upon standing for a period of *ca* 2 d, colorless crystals of 4(**cat**)·2(**2,2’-bpe**) **1** suitable for X-ray analysis. The formulation of **1** was confirmed by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction.[†]

A perspective of **1** is shown in Figure 1. The asymmetric unit consists of one **2,2’-bpe** and two **cat** molecules. The components assemble to form a discrete, six-component molecular assembly sustained by eight hydrogen bonds based on four O-H···N [O···N separations (Å): O(1)···N(1) 2.658(2), O(3)···N(2) 2.624(2)] and four O-H···O [O···O (Å): O(4)···O(1) 2.701(2), O(2)···O(3) 2.732(2)] forces (Fig. 1a). In the arrangement, the **cat** molecules self-assemble to effectively form hydrogen-bonded dimers that interact with face-to-face π-stacked bipyridines. Each **cat** molecule adopts a different conformation within a dimer. Specifically, one diol adopts a *syn-anti* conformation (Scheme 2)[10] wherein the *syn* and *anti* hydroxyl groups participate in intermolecular O-H···O and O-H···N hydrogen bonds, respectively. The second **cat** adopts a *syn-gauche* conformation[11] wherein the former and latter participate in intermolecular O-H···O and O-H···N hydrogen bonds, respectively, with the latter being twisted from the aromatic plane (105.5°). As a result of the assembly process, the C=C bonds of the two stacked olefins lie parallel and separated by 3.71 Å. The stacked geometry satisfies the requirements of Schmidt for a [2+2] photodimerisation in a solid.[2] The structure and composition of the six-component assembly contrasts those discrete four-component assemblies sustained by ditopic **res**.[1a] The assemblies pack as face-to-face π-stacked columns, with nearest-neighbor olefins being separated by 3.76 Å, which also satisfies the criteria of Schmidt for photoreaction.

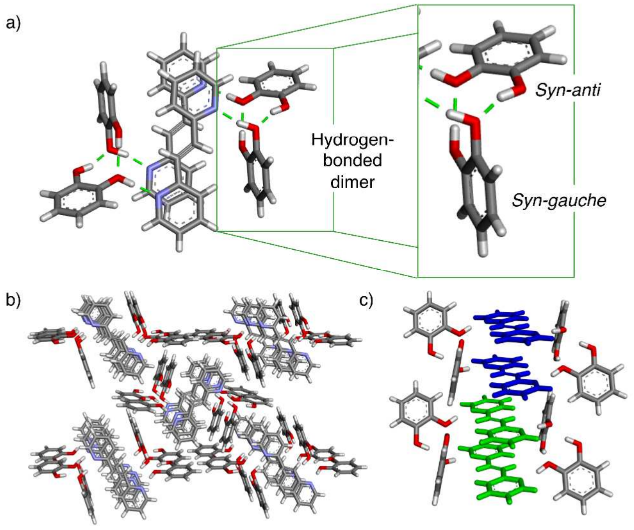


Fig. 1 Perspectives of **1**: a) six-component assembly, b) π-stacked columns, and c) nearest-neighbor assemblies.

The olefins of solid **1** are photoreactive. When a powdered crystalline sample of **1** was exposed to UV irradiation (broadband Hg lamp) for 50 h, **2,2’-bpe** reacted to form **2,2’-tpcb** quantitatively. The generation of the photoproduct was evidenced by the emergence of a cyclobutane peak at 4.93 ppm and complete disappearance of the olefin resonances.

The solid **1** also undergoes a single-crystal-to-single-crystal (SCSC) reaction,[1b,c] with the cyclobutane ring forming within the discrete hydrogen-bonded structures. In particular, X-ray diffraction data collected on a single crystal after being exposed to UV radiation using a curing lamp[12] after 35 h revealed electron density consistent with **2,2’-tpcb** having formed within the discrete hydrogen-bonded structures (cyclobutane occupancy: 10%).[8,13] The components of the reacted solid maintain the six-component assemblies compared to unreacted **1** [O···N (Å): O(1)···N(2B) 2.446(19), O(3)···N(1B) 2.437(18); O···O (Å): O(4)···O(1) 2.733(3), O(2)···O(3) 2.745(3)].

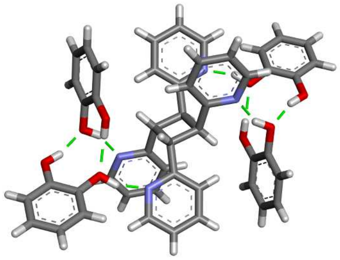


Fig. 2 SCSC transformation of **1** (unreacted olefins omitted for clarity).

Whereas **cat** interacts with **2,2’-bpe** and **2,2’-tpcb** in a six-component assembly, a structure determination of a recrystallized sample of reacted **1** (100% yield of **2,2’-tpcb**) reveals hydrogen-bonding different than the discrete structure. Specifically, recrystallisation of reacted **1** from MeNO$_2$ (4:1) afforded single crystals of 3(**cat**)·(**2,2’-tpcb**) **2** suitable for X-ray analysis.

The asymmetric unit of **2** contains two one-half **2,2’-tpcb** and three **cat** molecules. Similar to **1**, the components assemble *via* O-H···N and O-H···O hydrogen bonds. In contrast to **1**, the components form 1D chains [O···N (Å): O(5)···N(1) 2.682(2), O(1)···N(2) 2.753(2), O(4)···N(5) 2.761(3)] with **cat** molecules that self-assemble *via* O-H···O forces [O···O (Å): O(3)···O(1) 2.833(2), O(6)···O(3) 2.843(2), O(2)···O(5) 2.765(2)] to form trimers. Each trimer consists of one and two **cat** molecules in *syn-anti* and *syn-gauche* (-32.16°, 43.23°) conformations, respectively. Each trimer effectively donates two O-H···N hydrogen bonds to two 2-pyridyl groups in a *cisoid* conformation. A final hydroxyl group participates in an O-H···N force with a neighboring and crystallographically different **2,2’-tpcb** molecule, with the pyridines being in a *transoid* conformation. The cyclobutane rotamers alternate along the backbone of the 1D polymer.

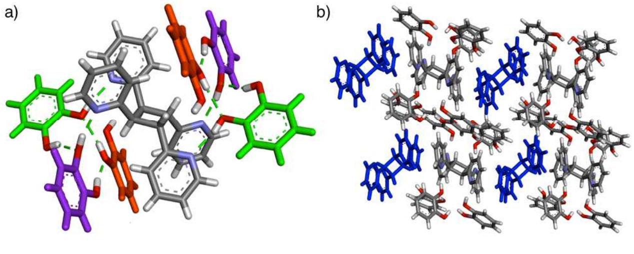


Fig. 3 Perspectives of **2**: a) **cat** trimers with conformation as *syn-anti* (green) and *syn-gauche* (purple and orange) and b) extended packing with alternating cyclobutane rotamers.

From the assembly **1**, as well as **2**, it is evident that the close proximity of the hydroxyl groups of a single **cat** molecules are not in a geometry favorable to preorganize two olefins for a [2+2] photodimerization as compared to **res**. The capacity of **cat** to self-assemble as a dimer and/or trimer, however, provides a structural flexibility that enables the geometry criteria of Schmidt to be achieved in a solid. Moreover, these observations are important since the assembly properties provide a further degree of structural freedom to utilize small-molecule templates to direct reactivity in the restricted environment of a crystalline solid.

In summary, we have demonstrated a [2+2] photodimerization in the solid state directed by assemblies of **cat** molecules that function as templates. The multi-component templates comprise **cat** dimers, with the reactivities occurring within discrete, six-component, hydrogen-bonded structures. We are now exploring the robustness of the self-assembly process involving dimers of **cat**, and related trimers, to afford reactive hydrogen-bonded structures. The ability of **cat** to afford such assemblies can provide an added and reliable means to achieve chemical reactivity in organic solid-state materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray structure data, ^{1}H NMR spectra, and X-ray powder patterns. See DOI: 10.1039/b000000x/

Crystal data for **1**: monoclinic, space group $P2_1/c$, a = 7.3687(7), b = 19.169(2), c = 14.7014(15) Å, β = 102.277(5) °, V = 2029.1(4) Å^3, D_c = 1.317 g/cm^3, Mo-Kα radiation (λ = 0.71070 Å) for Z = 4. Least-squares refinement based on 3329 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 4648 unique reflections) led to a final value of R = 0.043. CCDC reference number 1025307.

Crystal data for **1** SCSC (10% conversion): monoclinic, space group $P2_1/c$, a = 7.4665(8), b = 19.1328(19), c = 14.8336(15) Å, β = 102.249(5)°, V = 2070.81 Å^3, D_c = 1.291 g/cm^3, Mo-Kα radiation (λ = 0.71073 Å) for Z = 4. Least-squares refinement based on 2685 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 3631 unique reflections) led to a final value of R = 0.059 CCDC reference number 1025308.

Crystal data for **2**: triclinic, space group $P\bar{1}$, a = 11.9841(12) Å, b = 12.6106(13) Å, c = 13.7902(14) Å, α = 109.918(5) °, β = 103.137(5) °, γ = 102.958(5) °, V = 1801.6(3) Å^3, D_c = 1.281 g/cm^3, Mo-Kα radiation (λ = 0.71070 Å) for Z = 2. Least-squares refinement based on 4235 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 5711 unique reflections) led to a final value of R = 0.051. CCDC reference number 1025309.

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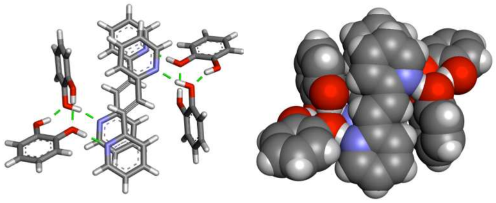
Graphical Abstract



Catechol self-assemblies as a dimer to function as template that directs a [2+2] photodimerization in the solid state.