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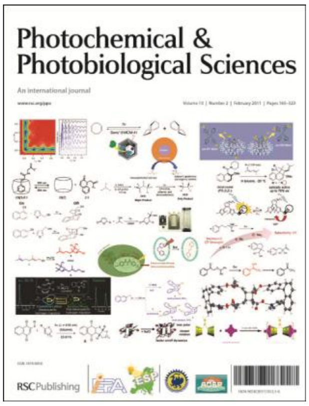

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Applications of hydrogen-bond-acceptor templates to direct 'in-phase' reactivity of a diene diacid in the solid state†‡

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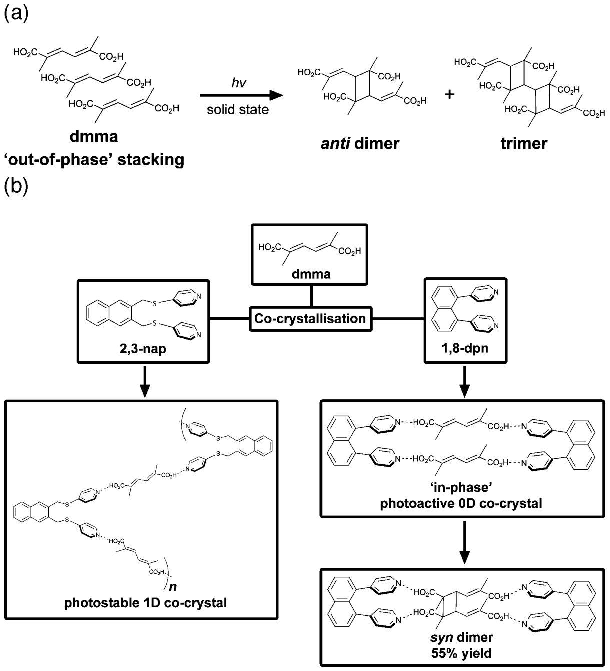
The hydrogen-bond-acceptor (HBA) templates 2,3-bis(4-methylenethiopyridyl)naphthalene (2,3-nap) and 1,8-bis(4-pyridyl)naphthalene (1,8-dpn) are used to assemble (*E*,*E*)-2,5-dimethylmuconic acid (dmma) in the solid state for an intermolecular [2 + 2] photocycloaddition. Co-crystallisation of 2,3-nap with dmma affords an 1D hydrogen-bonded polymer that is photostable while 1,8-nap affords a 0D hydrogen-bonded assembly that is photoactive. The diene stacks in-phase and reacts to give a *syn* monocyclobutane in up to 55% yield.

Small ditopic molecules that act as hydrogen-bond templates have emerged as tools to control intermolecular [2 + 2] photodimerisations of olefins in solids.[1] The templates can serve as molecular equivalents of two hands to assemble and stack alkenes within discrete, or 0D, co-crystalline supramolecular assemblies into the appropriate geometry[2] for photoreaction. To date, hydrogen-bond-donor (HBD) templates (*e.g.* resorcinol) have gained the most attention, providing efficient access to molecules difficult to achieve in solution (*e.g.* [2.2]paracyclophane, ladderanes).[3,4]

In this manuscript, we describe our initial work to employ hydrogen-bond-acceptor (HBA) templates, in the form of 2,3-bis(4-methylenethiopyridyl)naphthalene (2,3-nap)[5] and 1,8-bis(4-pyridyl)naphthalene (1,8-dpn),[6] to direct the reactivity of a 1,3-diene, in the form of (*E*,*E*)-2,5-dimethylmuconic acid (dmma), in the solid state. We have reported that pure dmma undergoes both a dimerisation and trimerisation in the solid state to afford a mixture of products; namely, a monocyclobutane dimer and an unusual bicyclobutyl trimer.[7] The products arise from 'out-of-phase' stacking of the diene in the solid (Scheme 1a).[8] 1,3-Dienes such as dmma are familiar reactants in organic solid-state photochemistry,[9] known to undergo cycloadditions, polymerizations,[10] and isomerizations.[11] The acid groups also make the resulting cyclobutanes attractive as ligands in coordination-driven self-assembly[12] and, in principle, amenable to a variety of post-synthetic transformations.[13] Both 2,3-nap and 1,8-dpn have been demonstrated by us, and others, to assemble the monoolefin fumaric acid (fum) within 0D co-crystalline hydrogen-bonded assemblies that undergo [2 + 2] photodimerisation to give *rctt*-1,2,3,4-tetracarboxylic acid (cbta) in up to quantitative yield. Here, co-crystallisations of dmma with 2,3-nap and 1,8-dpn afford 1D and 0D hydrogen-bonded assemblies (2,3-nap)·(dmma)¶ and (1,8-nap)·(dmma)‖ that are photostable and photoactive, respectively (Scheme 1b). In contrast to the pure solid, 1,8-dpn enforces the diene into a stacked in-phase geometry that reacts to give the *syn* monocycobutane *rctt*-3,4-bis((*E*)-2-carboxyprop-1-enyl)-1,2-dimethylcyclo-butane-1,2-dicarboxylic acid (cbda) stereospecifically in up to 55% yield. The formation of the photostable 1D polymer is attributed to the conformational flexibility of 2,3-nap, which adopts an *anti* conformation in the solid. Our results, thus,



Scheme 1 Reactivity of dmma and involving 2,3-nap and 1,8-dpn.

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‡ Electronic supplementary information (ESI) available: Details of ^{1}H NMR studies and structure solutions by single-crystal X-ray diffraction. CCDC reference numbers 802315 (2,3-nap)·(dmma), 802316 (1,8-dpn)·(dmma), and 802317 2(1,8-dpn)·(cbda). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1pp05077j

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also emphasize a critical role of template conformation to direct the reactivity of alkenes in solids.[14,15]

We have recently shown that dmma self-assembles in the solid state to form 1D hydrogen-bonded polymers sustained by carboxylic acid dimers.[7] Neighbouring 1D strands packed such that the nearest-neighbour carbon-carbon double (C=C) bonds assembled parallel and in close proximity. The stacking of the olefins placed the dienes in an out-of-phase geometry that, upon UV-irradiation, afforded both an *anti* monocyclobutane dimer and a bicyclobutyl trimer as products. A total of two HBA templates have been reported to date. More specifically, 2,3-nap and 1,8-dpn have been used to assemble fum face-to-face in 0D assemblies that react to generate cbta. The ability of the bipyridines to enforce face-to-face stacking of fum for a photodimerisation prompted us to determine whether each HBA template could be used to achieve in-phase reactivity of dmma.

When 2,3-nap was co-crystallised with dmma (ratio: 1 : 1) from acetonitrile, light-brown needles of (2,3-nap)·(dmma) formed during a period of 24 h. The composition of (2,3-nap)·(dmma) was confirmed by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction.

As shown in Fig. 1, the components of (2,3-nap)·(dmma) self-assemble to form a 1D polymer held together by O–H···N hydrogen bonds (O(1)···N(1) 2.584(2) Å) (Fig. 1a). In this arrangement, 2,3-nap adopts, in contrast to (2,3-nap)·(fum) yet similar to the pure bipyridine,[5] an *anti* conformation (dihedral angle: 42.1°) with the S-atoms pointing in opposite directions. Neighbouring 1D polymers lie parallel and offset, with the naphthalene units participating in edge-to-face π–π forces with 4-pyridyl groups. As a consequence of the assembly process, the C=C bonds of the dienes are separated by approximately 9.6 Å within and 9.7 Å between adjacent 1D polymers, respectively (Fig. 1b). The geometries lie well outside the criteria of Schmidt for a photodimerisation in a solid. In line with the structure of (2,3-nap)·(dmma), exposure of a powdered crystalline sample of the co-crystal to UV-irradiation (450 W broad-band UV lamp) revealed the solid to be photostable.

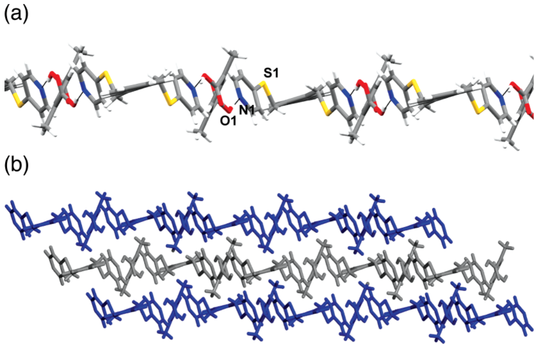

Fig. 1 Perspective of (2,3-nap)·(dmma): (a) 1D polymer and (b) offset stacking along crystallographic *ac*-plane.

Whereas (2,3-nap)·(dmma) is photostable, the co-crystal (1,8-dpn)·(dmma) is photoactive. When 1,8-dpn was co-crystallised with dmma (ratio: 1 : 1) from 1 : 10 (v/v) methanol–ethyl acetate, light-yellow cubes of (1,8-dpn)·2(dmma) formed after a period of 24 h. The composition of 2(1,8-dpn)·2(DMMA) was confirmed by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction.

As shown in Fig. 2, the components of (1,8-dpn)·(dmma) form, in contrast to (2,3-nap)·(dmma), a discrete hydrogen-bonded assembly, which sits around a crystallographic centre of inversion, sustained by four O–H···N hydrogen bonds (O(1)···N(1) 2.676(2) Å) (Fig. 2a). In this arrangement, 1,8-dpn, being more rigid than 2,3-nap, enforces the diene into an in-phase stacked geometry wherein the C=C bonds lie parallel and separated by 3.69 Å. The geometry places each C=C bond in a position suitable for [2 + 2] photodimerisation. Nearest-neighbour assemblies lie orthogonal and separated at a distance >10 Å (Fig. 2b), which means the olefins within the 0D hydrogen-bonded structures possess the C=C bonds able to undergo photoreaction.

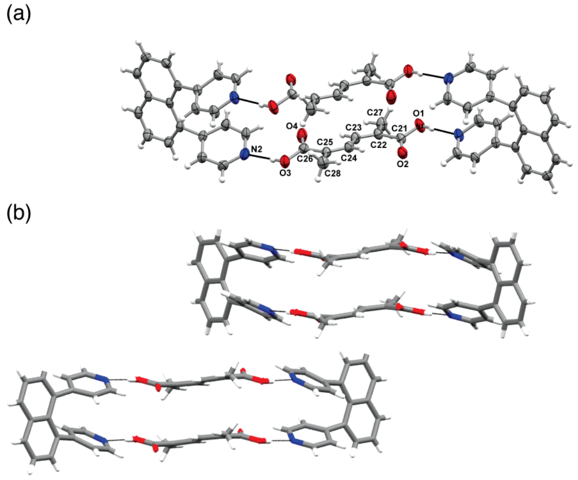

Fig. 2 Perspective of (1,8-dpn)·(dmma): (a) four-component assembly and (b) nearest-neighbour assemblies along crystallographic *b*-axis.

To determine the reactivity of the solid, a powdered crystalline sample of 2(1,8-dpn)·2(dmma) was subjected to UV-irradiation (450 W broad-band UV lamp) for a period of approximately 70 h. As determined by ^{1}H NMR spectroscopy (solvent: DMSO-d_6), a monocyclobutane formed stereospecifically in 55% yield. The generation of a monocyclised product was evidenced by the emergence of both alkene and cyclobutane protons at 6.36 ppm and 3.70 ppm, respectively (ratios: 1 : 1). The chemical shifts of the peaks were different than the recently reported *anti* photodimer.[7] Moreover, given that dmma was assembled in-phase in 2(1,8-dpn)·2(dmma) for reaction, the cyclobutane product was assigned as the *syn* photodimer.

The structure of the cyclobutane photoproduct was confirmed *via* single-crystal X-ray diffraction. When the reacted solid was dissolved in 4 : 1 hexanes:ethyl acetate (v/v), a white precipitate involving 1,8-dpn and the cyclobutane (ratio: 2 : 1) immediately formed. Recrystallisation from methanol afforded light-yellow needles after a period of 24 h. As shown in Fig. 3, cbda and 1,8-dpn assemble to form a three-component complex** sustained by four O–H···N hydrogen bonds (O(1)···N(1) 2.717(3) Å, O(3)···N(2) 2.661(3) Å) (Fig. 3a). The pairs of acid groups attached to the unsymmetrical cyclobutane ring lie splayed, with each type of acid group interacting with an identical template molecule. The complexes pack in the crystallographic *ab*-plane to form 2D layers sustained by edge-to-face π–π interactions involving pyridyl and naphthalene units of the templates (Fig. 3b).

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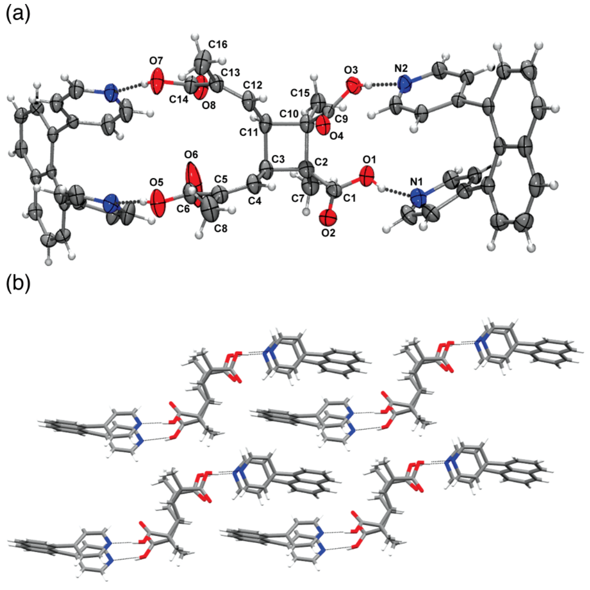

Fig. 3 Perspective of 2(1,8-dpn)·(cbda): (a) discrete three-component assembly and (b) packing of assemblies in *ab*-plane.

In summary, we have demonstrated that 1,8-dpn assembles dmma for an in-phase intermolecular [2 + 2] photodimerisation that generates cbda. The conformationally more flexible 2,3-nap results in a 1D hydrogen-bonded polymer that is photostable. With the reactivity of a diene diacid achieved, we are currently developing derivatives of both families of HBA templates so that libraries of bipyridines are available and can be applied in template switching[16] for the construction of more complex product molecules.

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Notes and references

¶ Crystal data for (2,3-nap)·(dmma): $C_{22}H_{18}N_2S_2 \cdot C_8H_{10}O_4$, $M_r = 544.66$ g mol^{-1}, monoclinic, $a = 12.8295(14)$ Å, $b = 14.5618(16)$ Å, $c = 14.3340(15)$ Å, $\alpha = 90°$, $\beta = 95.724(5)°$, $\gamma = 90°$, $V = 2664.5(5)$ Å^3, $T = 150(2)$ K, space group $C2/c$, $Z = 4$, 8919 reflections measured, 2351 independent reflections ($R_{int} = 0.0324$). The final R_1 values were 0.0361 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.0946 ($I > 2\sigma(I)$). The final R_1 values were 0.047 (all data). The final w$R(F^2)$ values were 0.099 (all data) (CCDC 802315).

‖ Crystal data for (1,8-dpn)·(dmma): $C_{20}H_{14}N_2 \cdot C_8H_{10}O_4$, $M_r = 452.49$ g mol^{-1}, monoclinic, $a = 14.5252(16)$ Å, $b = 6.9630(8)$ Å, $c = 23.665(3)$ Å, $\alpha = 90°$, $\beta = 102.029(5)°$, $\gamma = 90°$, $V = 2340.9(5)$ Å^3, $T = 190(2)$ K, space group $P2_1/n$, $Z = 4$, 15098 reflections measured, 4117 independent reflections ($R_{int} = 0.0388$). The final R_1 values were 0.0394 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.0994 ($I > 2\sigma(I)$). The final R_1 values were 0.0597 (all data). The final w$R(F^2)$ values were 0.1078 (all data) (CCDC 802316).

** Crystal data for (1,8-dpn)·(cbda): $C_{16}H_{20}O_8 \cdot 2(C_{20}H_{14}N_2)$, $M_r = 904.98$ g mol^{-1}, monoclinic, $a = 31.686(4)$ Å, $b = 9.6115(11)$ Å, $c = 29.601(3)$ Å, $\alpha = 90°$, $\beta = 93.685(5)°$, $\gamma = 90°$, $V = 8996.3(18)$ Å^3, $T = 150(2)$ K, space group $C2/c$, $Z = 8$, 27238 reflections measured, 7918 independent reflections ($R_{int} = 0.0601$). The final R_1 values were 0.0579 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1483 ($I > 2\sigma(I)$). The final R_1 values were 0.0963 (all data). The final w$R(F^2)$ values were 0.1634 (all data) (CCDC 802317).

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