Pergamon

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Tetrahedron Letters 44 (2003) 3687–3689

TETRAHEDRON LETTERS

Identification of supramolecular templates: design of solid-state photoreactivity using structural similarity

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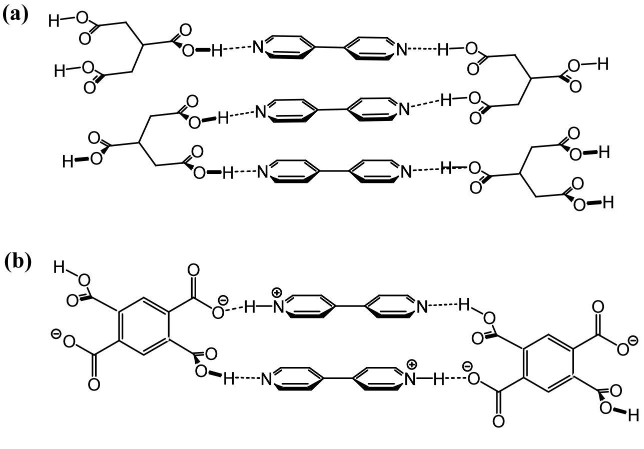
Received 24 January 2003; revised 25 February 2003; accepted 7 March 2003

Abstract—Structural similarity has been used to identify multifunctional templates for topochemically controlled solid-state photodimerisation. By examination of co-crystal structures of 4,4′-bipyridine with various acids, tricarballylic acid and 1,2,4,5-benzenetetracarboxylic acid have been identified as supramolecular templates for the alignment in the solid-state of 1,2-bis(4-pyridyl)ethylene. As a result, photodimerisation in the solid-state proceeds smoothly and with high yield. © 2003 Elsevier Science Ltd. All rights reserved.

Supramolecular control of solid-state photodimerisation involves the combined use of molecular recognition, self-assembly and topochemistry.[1] Bi-functional supramolecular templates, that hydrogen bond to monomer molecules to establish appropriate monomer alignments,[2,3] enable stereo- and regio-control[4] during photoreaction. Various olefins, using diols and dicarboxylic acids as pre-organisation agents, thereby undergo topochemical photodimerisation with extremely high selectivity. For example, 100% conversion to the *syn*-dimer of 1,2-bis(4-pyridyl)ethylene (**bpe**) readily results from irradiation in the solid-state of co-crystals of **bpe** with resorcinol or 1,8-naphthalenedicarboxylic acid.[2] To date, the strategy has been limited to bifunctional templates. We wondered from earlier work performed in our group whether trifunctional or multifunctional templates would also be successful. Clearly from the synthetic viewpoint, increasing functionality will lead to less template being required. There was also the question as to whether the increase in the number of functional groups on the templates might lead to the formation of other competitive synthons (e.g. acid–acid interactions in the case of carboxylic acids) and the breakdown of supramolecularly controlled photodimerisation.

In this paper, we outline an approach to identify suitable multi-functional templates for [2+2] photodimerisation of **bpe**. We have used the concept of structural similarity,[4] i.e. the design of comparable three-dimensional crystal packing arrangements from building blocks that have very similar molecular structures. 4,4′-Bipyridine (**bipy**), with a comparable molecular shape and functionality to **bpe**, was selected as an ideal candidate for the identification of potential multifunctional template molecules. A search of the Cambridge Structural Database (CSD)[5] showed that co-crystal structures of **bipy** with two multi-functional molecules, tricarballylic acid (**tca**)[6] and 1,2,4,5-benzenetetracarboxylic acid (**bta**),[7] possessed **bipy** molecules with appropriate alignment and separation distances of reactive centres of ca. 3.7 Å (Scheme 1). We therefore conjectured that co-crystals of **bpe** with **tca** and **bta**, would have similar supramolecular arrangements to the corresponding **bipy** co-crystals, and furthermore, such co-crystals would be photoactive. Co-crystals of **bpe**



Scheme 1.

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doi:10.1016/S0040-4039(03)00685-3

with **tca** and **bta** were obtained, therefore, from 1:1 (acid:base) molar ratio mixtures in dimethylsulfoxide (DMSO) solution at room temperature. Single crystal diffraction and ^{1}H NMR analyses were carried out in order to determine the crystal structures of the resulting **tca**·1.5**bpe** and **bta**·2**bpe** complexes and their reaction products.[8]

In agreement with our expectations the structures of the acid/**bipy** and acid/**bpe** crystals are very similar. In the structure of **tca**·1.5**bpe** (Fig. 1), each **tca** is hydrogen-bonded to three **bpe** molecules such that supramolecular tapes are formed [O1···N3, H101···N3, O1-H101···N3 ($-x+1$, $-y$, $-z+1$): 2.600(2), 1.59 Å, 169°; O3···N1, H103···N1, O3–H103···N1: 2.575(2), 1.57 Å, 171°; O5···N2, H105···N2, O5–H105···N2 (x, $y-2$, $z+1$): 2.604(2), 1.60 Å, 169°].[9,10] Within one tape, three **bpe** molecules adopt a 'sandwich' formation between two adjacent acids, with separation distances of ca. 3.82 and 3.80 Å, respectively. In addition, adjacent tapes pack upon one another with an inter-tape distance of ca. 3.59 Å. These intra- and inter-tape distances of **bpe** are within the criteria proposed by Schmidt for successful [2+2] photodimerisation to occur.[11] UV irradiation (TM G8T5 UV lamp, 366 nm) of powdered crystalline samples[12] of **tca**·1.5**bpe** stereospecifically produced the *syn*-dimer, *rctt*-tetrakis(4-pyridyl)cyclobutane (**tpcb**). In the case of the three-layer arrangement of **bpe**, 100% **bpe** photodimerisation is unlikely to be achieved, and a kinetic analysis of photodimerisation is presented in Figure 2 with the final conversion being ca. 90%. It is noted that, in contrast to the solid-state synthesis of **tpcb** reported previously, fine needle-like crystals of *pure* **tpcb** (i.e. not a co-crystal of **tpcb** and acid) without further purification, were obtained by recrystallisation of the irradiated sample of **tca**·1.5**bpe** from DMSO, as evidenced by single-crystal X-ray diffraction analysis.[13] The **tca** component remains in the solution and can therefore be readily separated from the dimer.

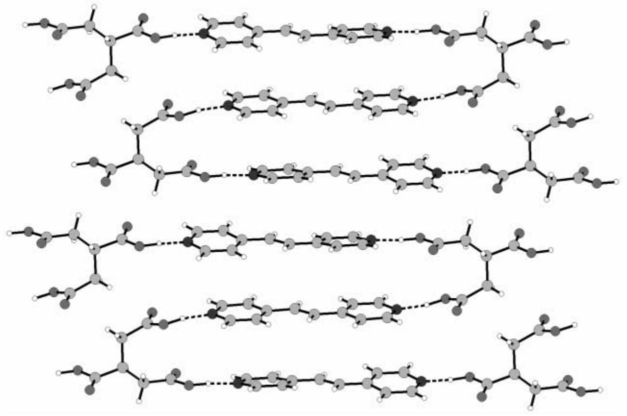

Figure 1. Co-crystal structure of **tca**·1.5**bpe**.

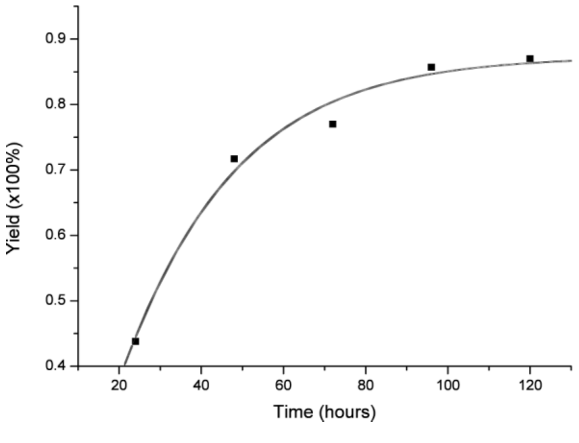

Figure 2. The kinetic analysis of solid-state photodimerisation of **bpe** in **tca**·1.5**bpe**.

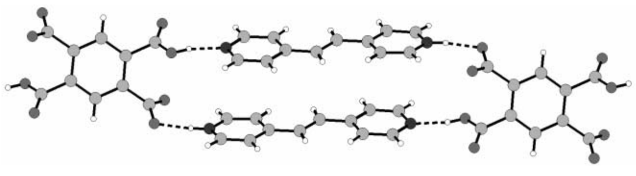

Figure 3. Co-crystal structure of **bta**·2**bpe**.

Figure 3 illustrates **bta**·2**bpe**, which forms one-dimensional supramolecular tapes, with the linkage of O–H···N hydrogen bonds [O1···N2, H101···N2, O1–H101···N2 ($x-1$, $y-2$, z): 2.537(2), 1.54 Å, 164°; N1···O3, H1···O3, N1–H1···O3 ($x-1$, y, $z-1$): 2.570(2), 1.57 Å, 168°]. The **bpe** molecules stack in pairs, similar to that of **bta**·2**bipy**, within these tapes and the separation distances of **bpe** molecules also satisfy the criteria for [2+2] photodimerization. A conversion of 100% was achieved after 48 h UV irradiation of **bta**·2**bpe**. For this system, yellow needle-like co-crystals of **bta** and **tpcb** (**bta**·**tpcb**) were obtained by recrystallisation of the irradiated sample from DMSO, with disordered DMSO and water molecules within the supramolecular channels (Fig. 4).

In conclusion, we have demonstrated a potential route using known structures of **bipy** co-crystals to identify multi-functional molecular templates for efficient solid-state photodimerisation to occur. Using this approach

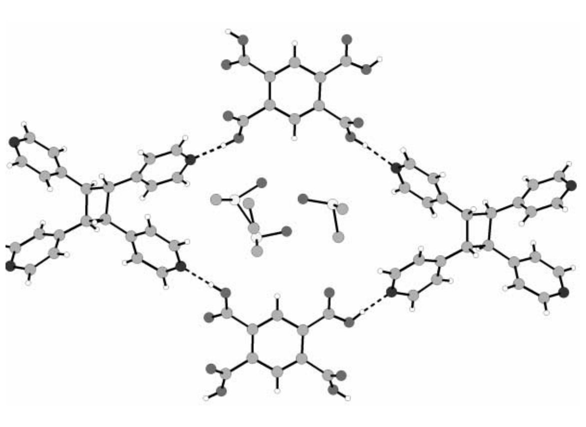

Figure 4. Two-dimensional supramolecular network of **bta**·**tpcb** with disordered DMSO molecules occupying the cavities. The water molecule and methyl H atoms on DMSO have been omitted for clarity.

of structural similarity, **bpe** photodimerised within an extended one-dimensional tape in the solid-state as opposed to the previous reports of dimerisation of discrete molecular assemblies. Finally, the use of **tca** provided a facile procedure for the synthesis of **tpcb** and one that does not require complicated separation and purification procedures.

Acknowledgements

We are grateful for a DWEF Cambridge Scholarship and ORS Award (N.S.) as well as financial assistance from EPSRC towards the purchase of the CCD diffractometers. We also thank Dr. J. E. Davies for data collection and assistance.

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   Crystal data for **tca**·1.5**bpe**: $C_{24}H_{23}N_3O_6$, $M = 449.45$, colourless block, triclinic, space group P-1, $a = 10.6604(6)$ Å, $b = 10.8439(8)$ Å, $c = 11.1166(9)$ Å, $\alpha = 66.145(3)°$, $\beta = 65.463(3)°$, $\gamma = 80.744(3)°$, $V = 1069.12(13)$ Å^3, $Z = 2$, $D_{calcd} = 1.396$ Mg/m^3, $\mu = 0.102$ mm^{-1}, $F(000) = 472$, crystal size 0.23×0.18×0.07 mm^3, 10338 reflections collected, 3739 independent reflections ($R_{int} = 0.0443$), $R_1 = 0.0516$, $wR_2 = 0.1213$ for $I > 2\sigma(I)$, $R_1 = 0.0765$, $wR_2 = 0.1335$ for all data.
   Crystal data for **bta**·2**bpe**: $C_{17}H_{13}N_2O_4$, $M = 309.29$, colourless block, triclinic, space group P-1, $a = 7.2831(3)$ Å, $b = 8.9753(4)$ Å, $c = 11.3939(6)$ Å, $\alpha = 101.1990(14)°$, $\beta = 90.2830(14)°$, $\gamma = 107.869(3)°$, $V = 693.71(6)$ Å^3, $Z = 2$, $D_{calcd} = 1.481$ Mg/m^3, $\mu = 0.107$ mm^{-1}, $F(000) = 322$, crystal size 0.25×0.12×0.07 mm^3, 6505 reflections collected, 2460 independent reflections ($R_{int} = 0.0336$), $R_1 = 0.0507$, $wR_2 = 0.1279$ for $I > 2\sigma(I)$, $R_1 = 0.0731$, $wR_2 = 0.1423$ for all data.
   Crystal data for **bta**·**tpcb**·3DMSO·H$_2$O: $C_{40}H_{46}N_4O_{12}S_3$, $M = 870.99$, yellow block, orthorhombic, space group $Pna2_1$, $a = 37.1339(7)$ Å, $b = 9.1474(1)$ Å, $c = 12.3413(2)$ Å, $V = 4192.08(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.380$ Mg/m^3, $\mu = 0.244$ mm^{-1}, $F(000) = 1832$, crystal size 0.12×0.10×0.07 mm^3, 23321 reflections collected, 6103 independent reflections ($R_{int} = 0.0879$), $R_1 = 0.1291$, $wR_2 = 0.3496$ for $I > 2\sigma(I)$, $R_1 = 0.1806$, $wR_2 = 0.3813$ for all data.
   Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 194975–194977. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
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