

Directed assembly and reactivity of olefins within a one-dimensional ladder-like coordination polymer based on a dinuclear Zn(II) platform†

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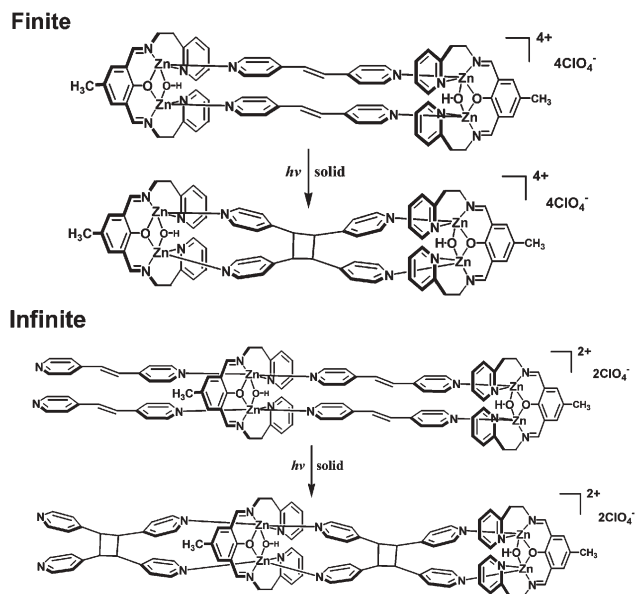
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A ladder-like coordination polymer involving a dinuclear Zn Schiff-base complex possesses organic linkers that undergo [2 + 2] photodimerisation in the solid state.

Methods that provide reliable control of chemical reactivity in the organic solid state can enable chemists to conduct stereoselective and solvent-free syntheses¹ by design² and construct functional solid-state materials (e.g. switches, nano-scale actuators).³ Unfortunately, reliable control of organic solid-state reactivity, particularly in the case of bimolecular reactions, has largely remained elusive owing to vexatious structure effects of molecular close packing.⁴

In this context, we have described a modular method to direct the [2 + 2] photodimerisation in the solid state.^{2,5} We have shown that rigid, bifunctional molecules (e.g. resorcinol) can be used as templates to juxtapose olefins (e.g. *trans*-1,2-bis(4-pyridyl)ethylene or 4,4'-bpe) *via* hydrogen bonds within finite molecular assemblies [e.g. 2(resorcinol)·2(4,4'-bpe)] for the photoreaction. That the olefins are assembled within finite assemblies means that the solid-state reactivity is largely 'insulated' from structural effects of close packing.⁴ To enable properties of transition-metal ions to be integrated within such reactive solids, we have recently extended the method to the dinuclear, cationic Zn complex [Zn₂L(OH)]²⁺ (**1**) (where LH = 2,6-bis[*N*-(2-pyridylethyl)formimidoyl]-4-methylphenol) which assembled 4,4'-bpe, *via* coordination bonds, within the finite tetranuclear complex [2(**1**)(4,4'-bpe)₂]⁴⁺ (Scheme 1).⁶ The positioning of the olefins was dictated by the separation distance of the Zn ions within **1**. The olefins of the tetranuclear assembly reacted *via* a single-crystal-to-single-crystal transformation to give *rac*-tetrakis(4-pyridyl)cyclobutane (4,4'-tpcb) stereospecifically in 100% yield.

During experiments to generalize **1** as a template to direct the [2 + 2] photodimerisation in the solid state,² we have discovered the ability of **1** to assemble with 4,4'-bpe to form an infinite, one-dimensional (1D) ladder-like coordination polymer in [(**1**)(4,4'-bpe)₂](ClO₄)₂·4H₂O (Scheme 1).⁷ A single-crystal X-ray structure analysis† of the solid reveals that the olefins are organized within the 1D polymer in a position suitable for a [2 + 2] photoreaction. Photoreactivity experiments demonstrate that the crystals are photoactive, reacting to give 4,4'-tpcb stereospecifically in near 100% yield. Whereas coordination polymers, or metal-organic frameworks (MOFs), have gained



Scheme 1

considerable attention owing to the ability of such extended structures to confer unique bulk physical properties (e.g. host-guest, magnetic) to solids,⁸ [(**1**)(4,4'-bpe)₂](ClO₄)₂·4H₂O represents a rare case of a MOF with organic units that undergo [2 + 2] photodimerisation in the solid state.^{9,10}

Pale yellow single crystals of [(**1**)(4,4'-bpe)₂](ClO₄)₂·4H₂O were obtained by slow evaporation of an ethanolic solution (25 mL) of [Zn₂L(OH)](ClO₄)₂ (0.32 g, 0.5 mmol) and 4,4'-bpe (0.91 g, 0.5 mmol) (molar ratio: 1:1) over a period of 2 days (yield: 72%). The composition of [(**1**)(4,4'-bpe)₂](ClO₄)₂·4H₂O was confirmed *via* single-crystal and powder X-ray diffraction data, as well as thermal gravimetric analysis.

A single-crystal X-ray structure analysis of [(**1**)(4,4'-bpe)₂](ClO₄)₂·4H₂O (Fig. 1) demonstrates that, similar to [2(**1**)(4,4'-bpe)₂](ClO₄)₄·4H₂O, the metal and organic components have assembled such that the bipyridines are organized, *via* Zn–N bonds, in a face-to-face stacked arrangement (Fig. 1). The two Zn atoms of **1** are separated by 3.19 Å (*cf.* [2(**1**)(4,4'-bpe)₂](ClO₄)₄·4H₂O: 3.14 Å) while the carbon–carbon double (C=C) bonds of the stacked olefins lie parallel and separated by 3.71 Å (*cf.* [2(**1**)(4,4'-bpe)₂](ClO₄)₄·4H₂O: parallel, 3.64 Å). The geometry of the stacked olefins conforms to criteria of Schmidt for [2 + 2] photoreaction in a solid.¹¹ In contrast to [2(**1**)(4,4'-bpe)₂](ClO₄)₄·4H₂O, however, each Zn ion of [(**1**)(4,4'-bpe)₂](ClO₄)₂·4H₂O lies in an octahedral, rather than a

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† Electronic supplementary information (ESI) available: Figs. S1–S5: TGA and XRD spectra. See <http://dx.doi.org/10.1039/b504477d>

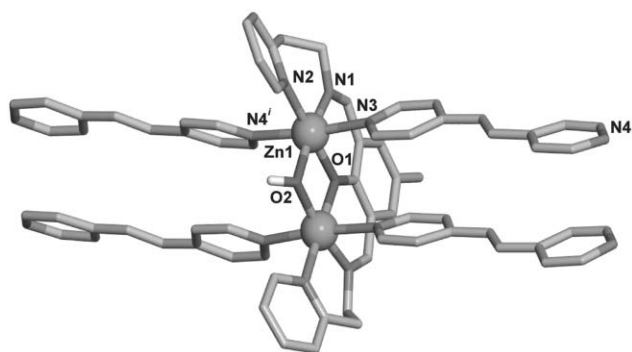


Fig. 1 X-Ray structure of $[(\mathbf{1})(4,4'\text{-bpe})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ displaying the coordination environment. Selected interatomic distances (Å): Zn(1)–N(1) 2.094(2), Zn(1)–N(2) 2.178(2), Zn(1)–N(3) 2.302(2), Zn(1)–N(4') 2.307(2), Zn(1)–O(1) 2.125(1), Zn(1)–O(2) 2.035(1). Symmetry operator $i: \frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$.

square-pyramidal, coordination environment such that two N-atoms of two 4-pyridyl groups adopt a *transoid* arrangement.⁶ The remaining coordination sites of each Zn ion are occupied by a single O- and two N-atoms of pentadentate L and a single O-atom of a $\mu\text{-OH}$ ion.

The *transoid* arrangement of the 4-pyridyl groups of $[(\mathbf{1})(4,4'\text{-bpe})_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ is propagated in space such that **1** and 4,4'-bpe assemble to form a 1D ladder-like coordination polymer along the crystallographic (101) direction (Fig. 2(a)). The pentadentate L units are oriented anti-parallel along the polymer backbone, with the Zn atoms being separated by 14.3 Å. The polymers are organized in a parallel and offset fashion such that nearest-neighbour C=C bonds of the olefins are separated by

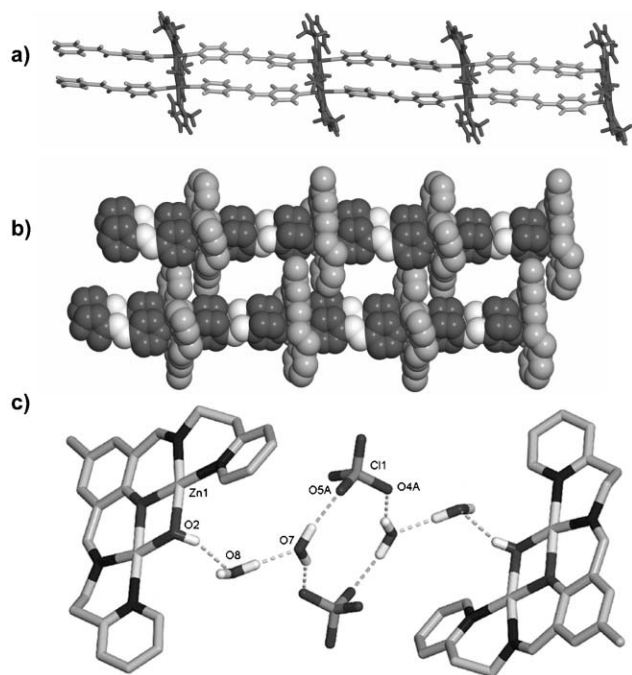


Fig. 2 X-Ray structure of $[(\mathbf{1})(4,4'\text{-bpe})_2] \cdot 4\text{H}_2\text{O}$: (a) 1D polymer, (b) neighbouring strands, and (c) intermolecular hydrogen bonds involving included water molecules. Selected interatomic distances (Å): O(7)···O(5A) 2.82(1), O(8)···O(7) 2.788(3), O(2)···O(8) 2.963(3).

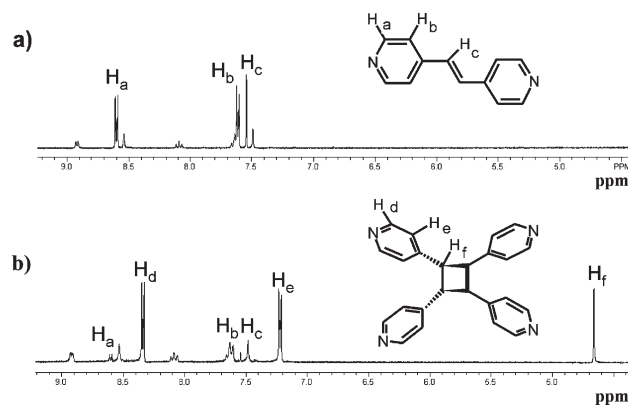


Fig. 3 ^1H NMR spectra of $[(\mathbf{1})(4,4'\text{-bpe})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$: (a) before and (b) after the photoreaction.

9.09 Å (Fig. 2(b)). The counter ClO_4^- ions and included water molecules are located between the polymer strands and assemble with the $\mu\text{-OH}$ ions to form a 1D network held together by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. Similar to $[2(\mathbf{1})(4,4'\text{-bpe})_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$, the network is composed of cyclic hydrogen-bonded arrays involving water molecules that bridge adjacent ClO_4^- ions (Fig. 2(c)).[§] This packing makes the C=C bonds of the 1D polymer the sole olefins of $[(\mathbf{1})(4,4'\text{-bpe})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ organized in the solid for [2 + 2] photoreaction.

UV-irradiation of a powdered crystalline sample of $[(\mathbf{1})(4,4'\text{-bpe})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (broadband medium pressure Hg-lamp) for a period of 32 h produced 4,4'-tpcb, as determined by ^1H NMR spectroscopy, in 95% yield (Fig. 3). The formation of 4,4'-tpcb was evidenced by a near complete disappearance of the olefinic singlet at 7.54 ppm and the appearance of a singlet at 4.66 ppm (solvent: $\text{DMSO}-d_6$). The latter peak is consistent with the *rect* stereochemistry of the cyclobutane ring of 4,4'-tpcb.¹² A thermogravimetric analysis revealed that the solid lost approximately half (*i.e.* two) of the included H_2O molecules during the photoreaction. The loss of the H_2O was accompanied by a loss of crystallinity, as demonstrated by powder X-ray diffraction data. Single crystals of $[(\mathbf{1})(4,4'\text{-bpe})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ also turned opaque during the photoreaction which, in contrast to $[2(\mathbf{1})(4,4'\text{-bpe})_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$,⁶ prohibited us from monitoring the reaction *via* single-crystal X-ray diffraction.¹³

In this report, a dimetal unit based on **1** has been shown to support a [2 + 2] photodimerization within a 1D ladder-like coordination polymer in the solid state. Given the variety of topologies available within the field of MOFs,⁸ we are now exploring the possibility of transferring the reactivity to other networks involving structurally diverse olefins and **1**. An ability to control reactivity using different solid-state architectures may open a door to yet unexplored crystal settings to develop functional MOFs and related materials.

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Notes and references

‡ Crystal data for $[(\mathbf{1})(4,4'\text{-bpe})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$: monoclinic, space group $C2/c$, $a = 11.909(2)$, $b = 17.257(3)$, $c = 23.920(4)$ Å, $\beta = 97.094(3)^\circ$, $Z = 8$, $U = 4878.6(1)$ Å³, $D_c = 1.57$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.079$ mm⁻¹. Least-square refinement based on 4325 reflections with $I_{\text{net}} > 2.0\sigma(I_{\text{net}})$ (out of

5522 unique reflections) led to a final value of $R = 0.034$. CCDC 267193. See <http://dx.doi.org/10.1039/b504477d> for crystallographic data in CIF or other electronic format.

§ Hydrogen bonding between O8 and the μ -OH can adopt two orientations.

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