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Solid-State Photochemical [2+2] Cycloaddition in a Hydrogen-Bonded Metal Complex Containing Several Parallel and Crisscross C═C bonds

Abdul Malik Puthan Peedikakkal and Jagadese J. Vittal*[a]

Abstract: One-dimensional hydrogen-bonded complex $[Zn(bpe)_2(H_2O)_4]$-$(NO_3)_2{\cdot}8/3\,H_2O{\cdot}2/3\,bpe$ (**1**, bpe = 4,4′-bipyridylethylene) containing coordination complex cations $[Zn(bpe)_2(H_2O)_4]^{2+}$ with parallel and crisscross double bonds undergoes photochemical [2+2] cycloaddition in the solid state and produces tetrakis(4-pyridyl)cyclobutane (tpcb) in up to 100 % yield with *rctt*-tpcb (**2a**) as major and *rtct*-tpcb (**2b**) as minor product. The bpe ligands with crisscross conformation of C═C bonds appear to undergo pedal-like motion prior to photodimerization. Grinding single crystals to powder accelerates the pedal motion of crisscrossed olefins in the bpe ligands to parallel alignment and provides the *rctt*-cyclobutane stereoisomer **2a** quantitatively. In addition, 100 % photodimerization of ground **1** indicates that the free bpe ligands, which are remote from each other in a pool of water, and NO_3^- ions moved toward each other to give a mixture of *rctt*- and *rtct*-tpcb isomers.

Keywords: cycloaddition · crystal engineering · solid-state reactions · stacking interactions · topochemistry

Introduction

Organic photochemistry has been evolving for the past fifty years, ever since Schmidt postulated conditions for the photochemical dimerization of C═C bonds in the solid state.[1,2] Although considerable progress has been made in this field, stacking of double bonds is still a challenge. Understanding of the principles of crystal engineering has had significant impact on solid-state photochemical [2+2] cycloaddition chemistry. Several weak but directional interactions have been successfully used to satisfy the Schmidt's geometric criteria for photoreactivity.[3] Recently, coordinative bonds have also been employed to align a pair of double bonds.[4,5] Although the use of directional hydrogen bonding to bring two C═C bonds closer for photochemical reactions is well documented, this strategy has rarely been used in inorganic complexes with ligands containing C═C bonds. Although most solid-state reactions follow the topochemical principle by maintaining the symmetry of monomers in the crystal lattice with small changes in dimension, some systems in which they satisfy the Schmidt criterion did not undergo photodimerization.[2a,b] Such reactions that require large molecular motion of atoms in the solid-state lattices are increasingly being discovered.[6–8] Kaupp highlighted the use of atomic force microscopy (AFM) and scanning near-field optical microscopy (SNOM) to detect such large molecular motions in crystal lattices.[6,7] This technique unraveled the concept of the phase-rebuilding mechanism in several nontopotactical photodimerization reactions or reactions that require large molecular motions such as the photodimerization of α-cinnamic acid[6a,b] anthracenes,[6a,c] and 2,5-dibenzylidenecyclopentanone.[6a,d] Intrinsic molecular movements include pedal motion,[8,9] bicycle pedal model,[10] hula twist[11] and crankshaft motion[12] in dimerization or isomerization reactions.

Molecular motion can be induced by external forces such as light irradiation or mechanical motion in the crystal lattice. For example, large pedal-like motion of double bonds in crystal lattice prior to dimerization[13a,b] and mechanically induced molecular migration have been detected in the crystal lattice by AFM techniques.[7] Anisotropic molecular migration has been observed within the crystal during reaction to remove the internal pressure caused by the change in molecular shape.[7] In *E*/*Z* isomerization of organic crystals large motion by internal rotation occurs on excitation by light irradiation.[10a,14,15] The presence of empty channels or

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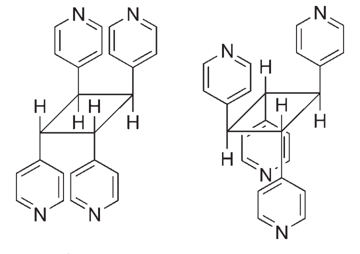
[a] A. M. P. Peedikakkal, Prof. J. J. Vittal
Department of Chemistry
National University of Singapore
3 Science Drive 3, 117543 (Singapore)
Fax: (+65) 6779-1691
E-mail: chmjjv@nus.edu.sg

Supporting information for this article (packing diagrams of **1**, tables of geometrical parameters, H-bond table, thermal analysis, XRPD, ^{1}H and ^{13}C NMR spectra, and product distribution table of tpcb isomers under various experimental conditions) is available on the WWW under http://www.chemeurj.org/ or from the author.

large void volume in loosely packed crystals with normally weak hydrogen bonds can promote molecular movement in the solid state.[14a,7a] The molecules can migrate easily among each other if they are not interlocked inside the crystal packing.

While exploring the coordination behavior of 4,4′-bipyridylethylene (bpe), we found that the double bonds in six bpe are aligned closely (ca. 4.0 Å) in crisscross and parallel orientations. Mechanically induced molecular alignment with pedal motion over the double bond and large molecular motion of bpe were observed in the crystal lattice, which on photoirradiation produced *rctt*- and *rtct*-tpcb isomers **2a** and **2b** (Scheme 1) in up to 100 % yield.



Scheme 1. Stereoisomers *rctt*-tpcb (**2a**) and *rtct*-tpcb (**2b**) observed in photoreactions of **1** in the solid state.

Results and Discussion

Single crystals of $[Zn(bpe)_2(H_2O)_4](NO_3)_2{\cdot}8/3\,H_2O{\cdot}2/3\,bpe$ (**1**) were grown by diffusing a methanolic solution of bpe into an aqueous solution of $Zn(NO_3)_2{\cdot}6\,H_2O$ in the ratio of 2:1. X-ray crystallography revealed that it contains 1D hydrogen-bonded chains of complex cations $[Zn(bpe)_2(H_2O)_4]^{2+}$. For $Z=3$ in the triclinic space group, the asymmetric unit of **1** contains one and a half formula units. A Co^{II} complex isotypical to **1** has been reported by Jung and co-workers.[16] The Zn^{II} ion in the half molecular unit is at the crystallographic inversion center. Each Zn^{II} ion in the $[Zn(bpe)_2(H_2O)_4]^{2+}$ ion has an N_2O_4 coordination environment with two bpe ligands in *trans* fashion which leaves two imine N atoms from each cation uncoordinated. These free N atoms form O−H···N hydrogen bonds with one of the hydrogen atoms of the neighboring water molecules to give a hydrogen-bonded 1D polymer (Figures 1–3). As a result the bpe pairs in the strands are aligned closely. For example, the distance between the centers of C=C bonds in the hydrogen-bonded strand containing Zn1 atoms is 3.796 Å (Figure 1) and the C=C bonds are aligned in parallel. On the other hand, adjacent C=C bond pairs are crisscrossed in the strand containing Zn2 atoms with a distance of 3.836 Å between the centers of the C=C bonds (Figure 2).

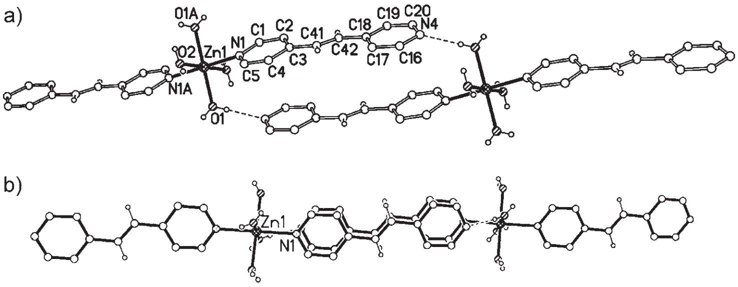


Figure 1. The hydrogen-bonded strands formed by Zn1 viewed approximately along the *a* axis (a) and the *c* axis (b) to show the parallel dispositions of C=C bonds. The aromatic CH hydrogen atoms have been omitted for clarity.

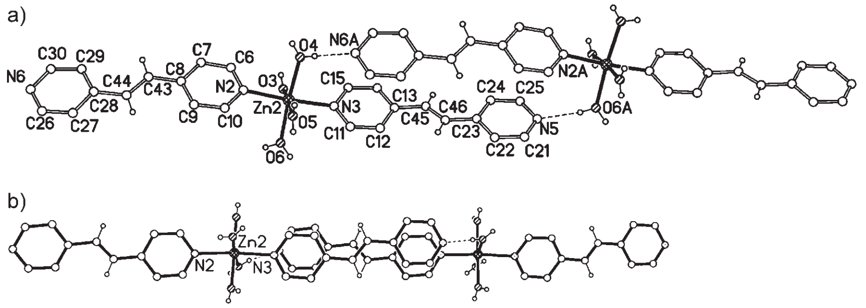


Figure 2. The hydrogen-bonded strands formed by Zn2 viewed approximately along the *a* axis (a) and the *c* axis (b) to show the crisscross alignment of C=C bonds. The aromatic CH hydrogen atoms have been omitted for clarity.

These hydrogen-bonded 1D polymers are propagated approximately along the *c* axis and stacked in the (101) plane. The olefin groups between Zn1 and Zn2 strands are lie antiparallel with distance of 3.595 Å between the centers of the olefinic bonds. Although the adjacent Zn2 strands are parallel, the strands are slip-stacked in such a manner that the carbon atom of the C=C bond is closer to the center of the adjacent pyridine ring (3.496 Å). Hence, overall, only three adjacent 1D hydrogen-bonded strands containing six bpe ligands are aligned roughly in a straight line approximately along the *c* axis (Figure 3).

The aqua ligands and lattice water molecules form two types of discrete water clusters stabilized by O−H···O bonds as a layer in the *ac* plane (Figure 4). The $(H_2O)_8$ cluster based on a cyclic hexamer with cyclohexane-like structure is propagated along the *a* axis by Zn1 atoms. Each $(H_2O)_8$ cluster is supported by four Zn^{II} ions. Another discrete $(H_2O)_5$ cluster with a “2-methylbutane-like” skeleton structure is sustained by three Zn^{II} ions between two rows of Zn2 atoms, of which three are coordinated water molecules. Water clusters and chains hosted by organic and inorganic lattices have attracted much attention.[17a] Although cyclic $(H_2O)_6$-based water clusters are very common, discrete acyclic water pentamers are little known.[17b,c] The crystal structure of **1** is a rare example containing two different discrete

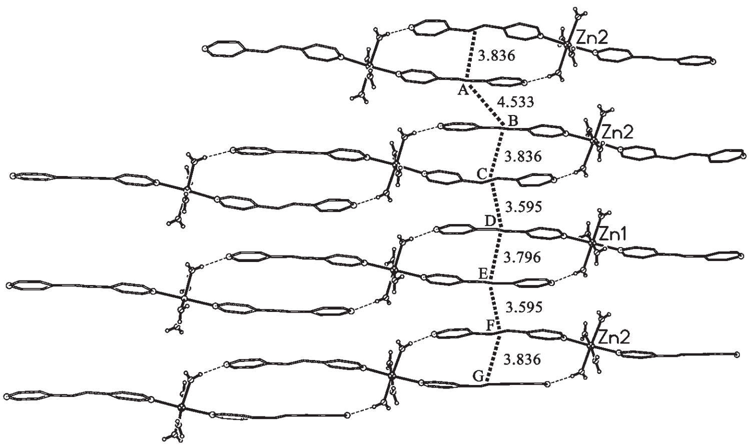


Figure 3. A view along the *a* axis showing the details of the alignments of double bonds in the hydrogen-bonded 1D polymeric structures present in **1**. The aromatic CH hydrogen atoms have been omitted for clarity.

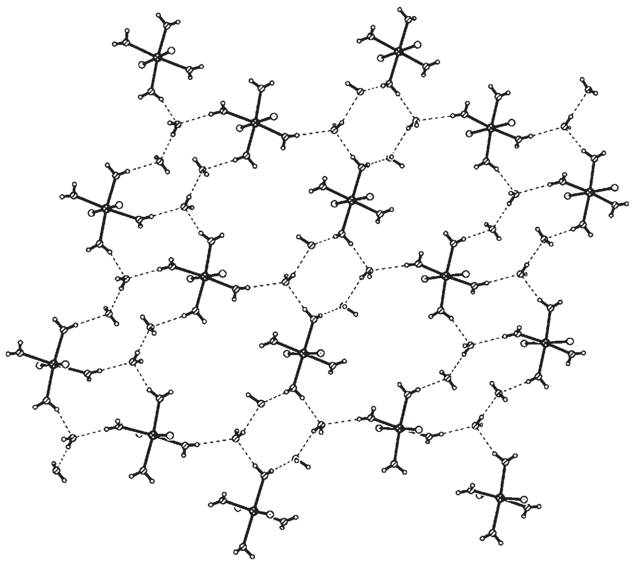


Figure 4. A perspective view showing the hydrogen-bonded connectivity in $(H_2O)_8$ and $(H_2O)_5$ clusters. Only relevant atoms are shown for clarity.

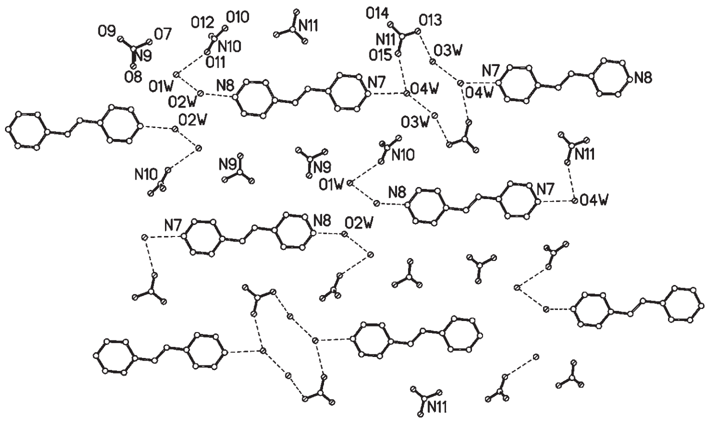


Figure 5. A view of the layer showing the interactions of NO_3^- anions, lattice water, and free bpe molecules that are sandwiched between the $[Zn(bpe)_2(H_2O)_4]^{2+}$ cationic layers in **1**.

water clusters, namely, cyclic and acyclic water clusters in the same lattice.[16]

The nitrate anions, lattice water, and free bpe molecules are sandwiched between the $[Zn(bpe)_2(H_2O)_4]^{2+}$ cationic layers in the (101) plane (Figure 5). The free bpe molecules are arranged roughly linearly, separated 7.14 and 9.49 Å from each other by one and two lattice water molecules, respectively. The closest C···C distance between adjacent bpe molecules separated by a row of NO_3^- ions is 6.09 Å.

The assembly of the olefin groups of six bpe ligands conforms to the distance criterion of Schmidt for [2+2] photoreactions, of which only one pair of olefins connected by Zn1 atoms lies parallel. When the single crystal of **1** was subjected to UV light for 25 h, 46% photochemical conversion was observed, of which 39% is due to *rctt*-tetrakis(4-pyridyl)-1,2,3,4-cyclobutane (*rctt*-tpcb, **2a**) and 7% due to *rtct*-tpcb isomer (**2b**, Scheme 1), as monitored by ^{1}H NMR spectroscopy. However, the percentage of isomer **2b** formed is much lower than expected based on the orientation of C=C bonds shown in Figure 3 and the C=C distances found in **1**. This can only be explained by assuming that C=C bonds of bpe ligands undergo pedal-like motion prior to photodimerization. Such dynamic behavior of C=C bonds in *trans*-stilbene was observed by Ogawa and co-workers.[8] Light-induced geometrical rearrangement by pedal motion has been observed in crystal lattices that exhibit photochromism.[18] Changes in conformation due to pedal motion prior to cyclobutane formation were also invoked to account for quantitative regiospecific formation of cyclobutane isomers.[14] Nevertheless, such motions are easier if the pair of molecules with C=C bonds are held on one side by weak interactions while the other side is left free. The sluggish reactivity of **1** may be attributed to difficulty of pedal motion in the single crystals due to the presence of coordinative bonds on one side and hydrogen bonds on the other. The incomplete pedal-like motion of bpe observed here is reflected in the residual formation of **2b** during photodimerization. However, when the single crystals were ground for 5 min to powder and subjected to UV irradiation for 4 h, 88% conversion of C=C bonds to cyclobutane rings was observed, and 100% conversion was achieved when UV irradiation was prolonged to 25 h.

The ^{1}H NMR spectrum of this product in [D$_6$]DMSO solution shows no signal at $\delta = 7.53$ ppm for olefinic protons but two singlets at $\delta = 4.65$ and 3.85 ppm due to two stereoisomers of cyclobutane rings, namely *rctt* (**2a**) and *rtct* (**2b**), respectively (Figure 6).[19,20] Hence, it is confirmed that all the bpe molecules including the six that are bonded to Zn^{II} ions and the two free ones present in the unit cell underwent photodimerization when **1** was ground into powder.

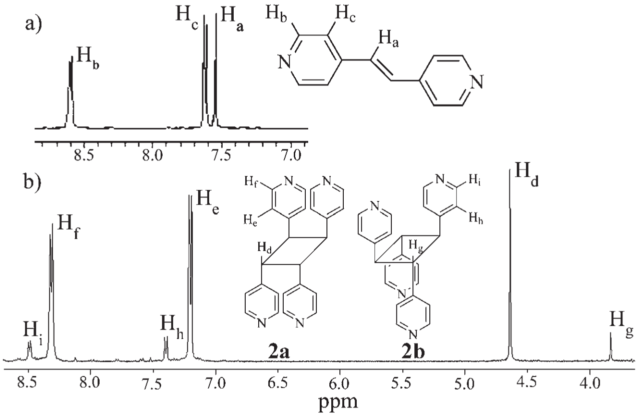


Figure 6. ^{1}H NMR spectra of **1** ground for 5 min (300 MHz, [D$_6$]DMSO, 25 °C, TMS) before UV irradiation (a) and after 25 h of UV irradiation (b).

Control experiments were carried out to separate the influence of grinding from the loss of the solvents. The results are compiled in Figure 7. The single crystals were dehydrated, and opaque single crystals obtained by heating **1** to 80 °C were subjected to UV radiation for 25 h, after which the ^{1}H NMR spectrum showed only 29 % photochemical conversion. This confirms that the increase in the reactivity and the formation of 100 % photodimerized product is due to grinding and not to water loss. Furthermore, thermogravimetric analysis of ground samples of **1** do not show significant loss of water (14.9 % for a sample ground for 5 min versus a theoretical weight loss of 15.1 % for 6.67 for all the water molecules), and the water loss was not significant even after these ground samples were subjected to UV irradiation.

Grinding increases the surface area, and greater reactivity is expected when a sample with a larger surface is exposed to UV irradiation. To test this hypothesis, bulk powder was synthesized by the same method, and its powder XRD pattern was successfully matched with the powder XRD pattern simulated from the single-crystal data. When this powder was subjected to UV light for 40 h, only 47 % conversion was observed (**2a**:**2b** 42:5). Hence, this result supports the notion that grinding accelerates the pedal-like motion of the C=C bonds of bpe molecules and thus accounts for the observed increase in reactivity by a factor of about ten (Figure 7). The powder XRD samples of ground powders have peaks with less intensity but maintain the same crystalline phase. The less crystalline nature of the powdered samples from single crystal may be due to movement of bpe ligands while maintaining the same crystal structure. The subject of solid-state reactions activated by grinding and milling has been extensively studied by Braga, Toda, Kaupp, and co-workers.[2c,21,22] Molecular migration in organic crystals is caused by mechanical pressure induced by nanoscratching.[6e,7b]

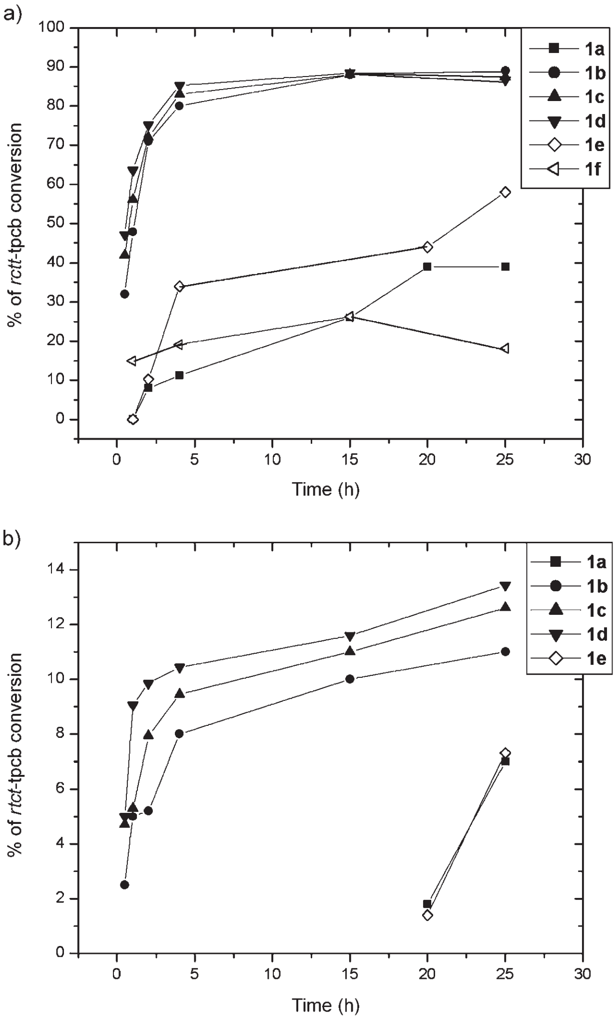


Figure 7. Plots showing the progress of photoconversion of **1** over various time intervals to a) *rctt*- and b) *rtct*-tpcb isomers, as monitored by ^{1}H NMR spectroscopy in [D$_6$]DMSO solution. **1a** = single crystal, **1b** = single crystal ground for 5 min, **1c** = single crystal ground for 10 min, **1d** = single crystal ground for 20 min, **1e** = crushed single crystals, **1f** = single crystal heated at 80 °C).

The photodimerized product still contains 11–13.4 % of isomer **2b** after 5–20 min of grinding and 25 h of UV exposure. This likely originated from the free bpe, since formation of **2b** requires movement of a bpe molecule along the C=C bond, which can easily occur for the free bpe molecule in the pool of water molecules and NO_3^- ions in the crystal lattice during grinding. The space between the stacked cationic layers provides enough room for translation of the bpe molecule along the C=C double bonds that exist in antiparallel fashion. This is in fair agreement with the 12.5 % expected for the random movement of free bpe molecules in the lattice and thus accounts for the observed photochemical behavior. Such molecular movements have been proposed in many cycloaddition reactions to rationalize the observed products.[6,7,13]

Conclusion

Hydrogen-bonded coordination complexes have been employed to align the C=C bonds in bpe for [2+2] cycloaddition reactions. To the best of our knowledge, photoreactivity has not been tested for solids containing more than one pair of well-aligned C=C bonds that satisfy the distance criterion. This is the first time that six olefins in a row satisfy the Schmidt distance criterion, of which four lie in crisscross conformation and two have parallel orientation. These bpe ligands with antiparallel C=C bonds undergo pedal-like motion prior to photodimerization. Grinding the single crystals into powder accelerates the pedal motion of crisscrossed olefins into parallel alignment as well as the motion of free bpe in the solid. Hence the olefin groups of bpe ligands undergo quantitative conversion to the cyclobutane derivative with exclusively *rctt* stereochemistry on UV irradiation of the ground sample. This is again an exceptional case in which the olefinic bonds need not be parallel under the Schmidt criterion to undergo photodimerization. Although the solid-state photoreaction stereospecifically produces cycobutane isomers, obtaining both *rctt*-tpcb and *rtct*-tpcb isomers from a single compound is not uncommon in the solid state.[2d,23,14c] Mechanical motion in the crystal may also facilitate movement of molecules to align in parallel, as required for photodimerization reaction such as light-induced electronic excitation. An internal pressure is exerted on the molecules by mechanical motion in the free volume between the cationic layers. Finally, two different types of water clusters, namely, $(H_2O)_8$ and $(H_2O)_5$, are trapped in the crystal structure of **1**.

Experimental Section

General: All chemicals were purchased from commercial sources and used as received for syntheses. All solvents used were of reagent grade. The yield of **1** is reported with respect to the metal salts. UV irradiation was conducted by using a Luzchem photoreactor. The ^{1}H NMR spectra were recorded with a Bruker ACF 300FT-NMR spectrometer with TMS as internal reference at 298 K. The yields observed on UV irradiation are reported in terms of the product distribution, obtained by integrating ^{1}H NMR spectra of the compounds. The IR spectra (KBr pellet) were recorded on a FTS 165 Bio-Rad FTIR spectrometer in the range 4000–400 cm^{-1}. ESI-MS spectra were recorded on a Finnigan MAT LCQ Mass Spectrometer by the syringe-pump method. Elemental analyses were performed in the Micro Analytical Laboratory, Department of Chemistry, and National University of Singapore.

Synthesis of $[Zn(bpe)_2(H_2O)_4](NO_3)_2\cdot 8/3H_2O\cdot 2/3bpe$ (1): $Zn(NO_3)_2\cdot 6H_2O$ (12 mg, 0.041 mmol) was dissolved in 0.6 mL of H_2O and carefully layered with 0.6 mL of an ethanolic solution of bpe (15 mg, 0.082 mmol). Colorless block crystals formed after three days and were decanted and dried in air. Yield: 27 mg (56 %); ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 8.60$ (d, 4H, Py-H), 7.61 (d, 4H, Py-H), 7.53 ppm (s, 2H, CH=CH); ^{13}C NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 150.52$ (C-Py), 143.82 (C-Py), 131.00 (C=C), 121.67 ppm (C-Py); IR (KBr): $\tilde{\nu} = 3433$(w), 1597(s), 1553(w), 1502(w), 1408(m), 1383(s), 1204(w), 1068(w), 1026(w), 992(m), 827(s), 552(s) cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{40}N_{7.33}O_{12.67}Zn$: C 48.32, H 5.07, N 12.91; found: C 48.58, H 4.95, N 12.69.

UV Irradiation of 1: In a typical experiment **1** (ca. 10 mg) was packed between two Pyrex glass slides and irradiated in a Luzchem photoreactor (8 W dark blue phosphor lamps, measured intensity ca. 1.75 mW cm^{-2}) at 350 nm. Single crystals, dehydrated crystals, crushed crystals, and samples manually powdered in a pestle and mortar for 5, 10, and 20 min were exposed to UV light for 0.5, 1, 2, 4, 15, and 25 h. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 8.50$ (d, 4H, Py-H for **2b**), 8.33 (d, 4H, Py-H for **2a**), 7.40 (d, 4H, Py-H for **2b**), 7.21 (d, 4H, Py-H for **2a**), 4.65 (s, 4H, CHCH for **2a**), 3.85 ppm (s, 4H, CHCH for **2b**); ^{13}C NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 149.57$ (C-Py for **2a**), 148.62 (C-Py for **2b**), 123.69 (C-Py for **2a**), 123.00 (C-Py for **2b**), 49.14 (CHCH for **2b**), 44.70 ppm (CHCH for **2a**); IR (KBr): $\tilde{\nu} = 1606$(m), 1556(w), 1503(w), 1383(s), 1224(w), 827(m) 551(m) cm^{-1}.

Crystal structure determination: Intensity data for **1** were collected on a Bruker APEX diffractometer equipped with a CCD detector and graphite-monochromated $Mo_{K\alpha}$ radiation by using a sealed tube (2.4 kW) at 223 K. Absorption corrections were made with the program SADABS[24] and the crystallographic package SHELXTL[25] was used for all calculations. Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 9.5695(5)$, $b = 14.5702(8)$, $c = 20.6012(11)$ Å, $\alpha = 87.089(1)$, $\beta = 82.869(1)$, $\gamma = 75.540(1)°$, $V = 2759.3(3)$ Å^3, $\rho_{calcd} = 1.434$ g cm^{-1}, and $Z = 3$. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1 = 0.0436$, $wR_2 = 0.1097$, GoF = 1.047 for 7784 ($I \geq 2\sigma(I)$) reflections. The two ethylenic carbon atoms were disordered in two sites with occupancies of 0.6 and 0.4. CCDC 631391 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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