Supramolecular Chemistry

Topochemical Photodimerization in the Coordination Polymer $[\{(CF_3CO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-bpe})_2]_n$ through Single-Crystal to Single-Crystal Transformation**

*Ni Lian Toh, Mangayarkarasi Nagarathinam, and Jagadese J. Vittal**

Solid-state photochemical [2+2] cycloadditions of organic molecules have been very well studied in the past.[1] Although the geometric criteria for such topochemical dimerizations are well established, it has been a challenge to organize the two double bonds in the solid state.[2] MacGillivray and coworkers had considerable success in aligning the double bonds in small organic molecules by using the strength and directionality of the hydrogen bonds.[3] Serendipitous single-

---

[*] N. L. Toh, Dr. M. Nagarathinam, Prof. J. J. Vittal
Department of Chemistry
National University of Singapore
Science Drive 3
Singapore 117543 (Singapore)
Fax: (+65) 6779-1691
E-mail: chmjjv@nus.edu.sg

[**] We thank the National University of Singapore for financial support (Grant No. R143-000-153-112) and Professor Wai Yip Fan for the Xe lamp and his interest in this project. bpe = 4,4′-bipyridylethylene.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

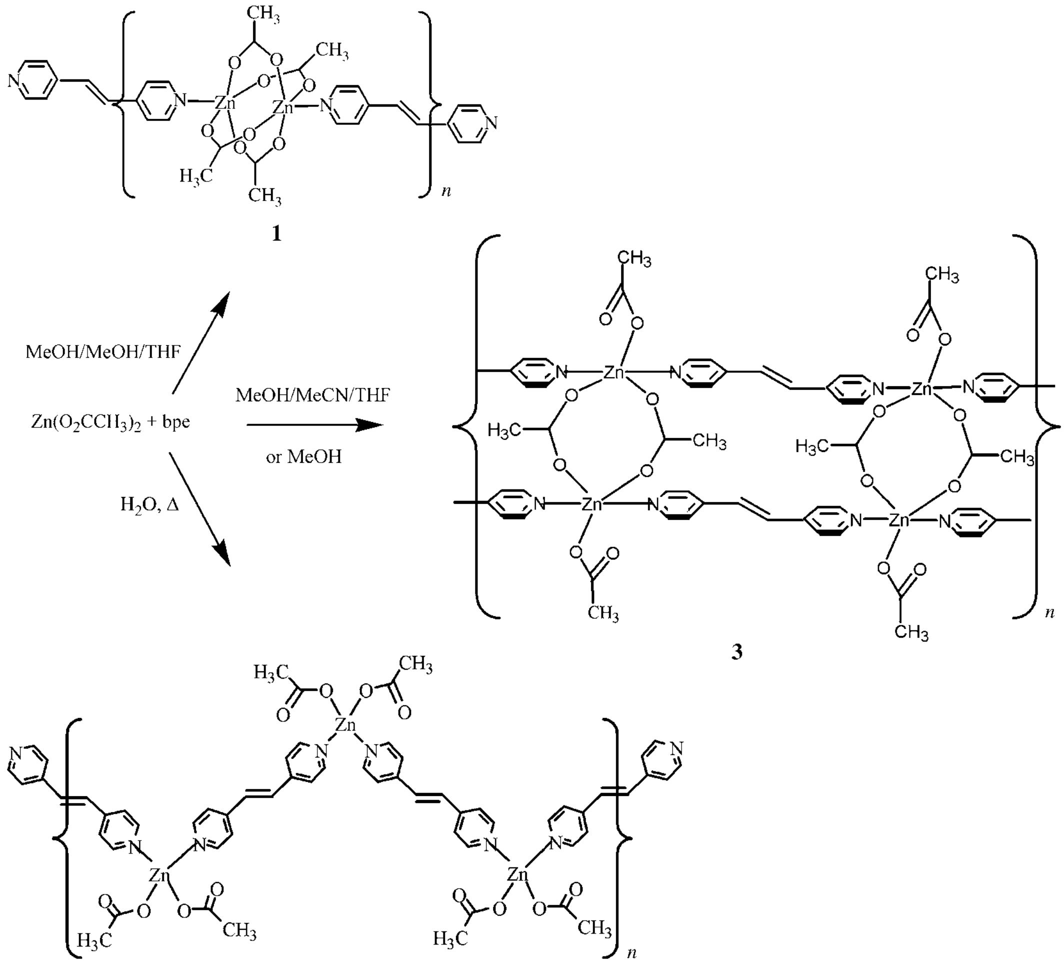
DOI: 10.1002/ange.200462673

crystal to single-crystal (SCSC) polymerization of 1,6-triacetylene has been reported to occur, assisted by π–π stacking.[4] Metal complexes have also been successfully used for dimerization, oligomerization, and polymerization of olefins and acetylenes.[5,6] This includes solid-state polymerization of the monomeric metal complex, aquabis(3-butenoato)calcium by ^{60}Co γ irradiation.[5a]

Compared to the solid-state photochemical reactions involving mostly two molecules, the transformations of one coordination polymeric structure to another are very rare in solid-state supramolecular reactions as the breaking and forming of bonds should occur in more than one direction simultaneously. Most of the reversible topotactic solid-state reactions involve the removal of guest solvent molecules from cavities.[7] Iordanidis and Kanatzidis reported SCSC structural transformations based on the redox-induced zipper action of selenium atoms by iodine.[8] A few more interesting solid-state supramolecular transformations including SCSC have been reported recently.[9]

One dimensional metal coordination polymers with molecular ladder structures can easily be prepared by self-assembly.[10] Hence these structures provide another interesting possibility to align photoreactive double bonds in the solid state as the distance between the vertical strands can be manipulated by a judicious choice of the bridging ligands or metallophilic interactions. Such metal coordination polymeric structures have not been exploited for this purpose before. Here, we report the topochemical transformation of a 1D metal coordination polymer, $[\{(F_3CCO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-bpe})_2]_n$ (bpe = 4,4′-bipyridylethylene), which has a molecular ladder structure, through [2+2] photochemical cycloaddition across the vertical strands into $[\{(F_3CCO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-tpcb})_2]_n$ (tpcb = tetrakis(4-pyridyl)-cyclobutane) in up to 100% yield. This cycloaddition is accompanied by SCSC transformation.

When $Zn(O_2CCH_3)_2{\cdot}2\,H_2O$ was treated with an equimolar amount of bpe, compounds $[\{(\mu\text{-}O_2CCH_3)_4Zn_2\}(\mu\text{-bpe})]_n$ (**1**), $[\{Zn(O_2CCH_3)_2\}(\mu\text{-bpe})]_n{\cdot}n\,H_2O$ (**2**), and $[\{(H_3CCO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-bpe})_2]_n$ (**3**) were isolated. Their composition and solid-state structures depend on the way in which the crystals were grown as illustrated in Scheme 1. Compound **1** forms a linear 1D coordination polymer and has a zinc/bpe-ligand stoichiometry of 2:1, whereas **2** and **3** are supramolecular isomers that have a 1:1 ratio of metal to linear spacer ligand.[11] Light-yellow hexagonal crystals of **1** were obtained by diffusion of a solution of bpe in THF into Zn-



Scheme 1. The formation of different products upon reaction of $Zn(O_2CCH_3)_2$ with bpe in various solvents and under various conditions.

$(O_2CCH_3)_2{\cdot}2H_2O$ in solution in MeOH at room temperature. A buffer layer of MeOH was added between these two solutions to avoid instant precipitation. When a layer of MeCN was used as the buffer, colorless rodlike crystals of **3** were isolated from the solvent junction in a day. A mixture of **1** and **3** were furnished in a ratio of approximately 60:40 if the crystals were allowed to grow for 4 days. The colorless long, thin, platelet crystals of **3** were separated by hand-picking from the clusters of **1** under a microscope. Compound **2** was formed as colorless distorted cubic crystals by cooling a clear filtered solution of boiled aqueous solution containing an equimolar ratio of $Zn(O_2CCH_3)_2{\cdot}2H_2O$ and bpe.

Compound **2** forms a zigzag polymer in which Zn^{II} has tetrahedral geometry. On the other hand, the Zn^{II} ions present in the two linear infinite polymers $[\{(O_2CCH_3)Zn\}(bpe)]_n$ in **3** are bridged by two acetate ligands to provide a molecular ladder polymeric structure. The Zn^{II} ion has, therefore, distorted trigonal bipyramidal geometry with the two pyridyl nitrogen atoms occupying the axial positions. The Zn···Zn distance in **3** (3.82 Å) is longer than that found in **1** (2.900(1) Å). This may be caused by the fact that four acetate ligands bridging the two Zn^{II} ions provide a paddle-wheel structure in **1** with *trans* O-Zn-O angles of 158.4(3) and 162.0(3)°. A crystallographic center of inversion is present in all of the structures. The two bpe ligands in the adjacent chains in **3** are aligned parallel, but are slightly slip-stacked. The nonbonding distances between the double bonds of the two bpe ligands in the parallel chains (C···C distance 3.63 Å, and C-C···C angles 74.0 and 106.0°) are congenial for the [2+2] cycloaddition to take place in the solid state.[2,3]

The powdered crystalline compound **3** was subjected to UV irradiation using a xenon lamp for a period of 14 hours. The cycloaddition was accompanied by a color change from colorless to pale yellow. The quantitative photoreactivity of the molecular ladder polymer **3** is evident from the ^1H and ^{13}C NMR spectra of the irradiated product in [D$_6$]DMSO. The ^1H NMR spectrum shows complete disappearance of the signals for the olefinic protons at $\delta = 7.56$ ppm, the appearance of signals for cyclobutane protons at $\delta = 4.68$ ppm, and a shift in the resonances of the bipyridyl protons from $\delta = 8.61$ and 7.63 ppm to $\delta = 8.35$ and 7.26 ppm. However, single crystals of **3** after irradiation were found to split into two, and the much anticipated SCSC structural transition was not successful.

Long rodlike colorless crystals of $[\{(F_3CCO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-bpe})_2]_n$, **4** were obtained exclusively from a solution containing an equimolar ratio of $Zn(O_2CCH_3)_2{\cdot}2H_2O$, bpe, and CF_3CO_2H in DMF (*N,N*-dimethylformamide). A perspective view of a portion of the molecular ladder polymer as determined by X-ray crystallography is shown in Figure 1. Two acetato ligands bridge a pair of Zn^{II} ions in $[Zn_2(\mu\text{-bpe})_2]_n$ with a Zn···Zn distance of 3.848(1) Å to form a molecular ladder polymer. A trifluoroacetate anion chelates each Zn^{II} center to complete the distorted octahedral geometry at the metal center. A crystallographic inversion center is present in the middle of the $[Zn_2(\mu\text{-}O_2CCH_3)_2]$ ring, and the polymer propagates in the [011] direction. As in **3**, the linear spacer ligands are disposed facing each other, but are slightly slip-stacked. This is evident from the deviation from 90° of Zn-Zn-N angles (i.e. 78.8 and 100.0°). The C···C nonbonding distance between the two ethylene carbon atoms of the bpe ligands in the parallel chains is 3.747 Å and the C-C···C angles are 78.9 and 101.1°. In the crystal structure of **4**, the bpe ligands are free from disorder, unlike **3**, and are employed for SCSC transformation studies. The adjacent ladders are also slip-stacked such that the pyridyl rings are close to the ethylene carbon atoms while the closest C···C distance between ethylenic carbon atoms is 7.10 Å.

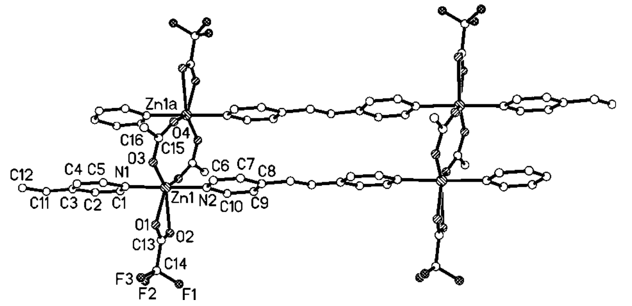


Figure 1. A perspective view of a portion of the 1D molecular ladder polymeric structure of **4**. The hydrogen atoms and disordered; fluorine atoms have been omitted for clarity. Selected bond parameters [Å, °]: Zn(1)–N(1) 2.143(3), Zn(1)–N(2) 2.146(3), Zn(1)–O(1) 2.234(4), Zn(1)–O(2) 2.431(5), Zn(1)–O(3) 2.013(3), Zn(1)–O(4a) 2.019(3), C(3)–C(11) 1.458(5), C(8)–C(12b) 1.463(5), C(11)–C(12) 1.321(6), Zn(1)···Zn(1a) 3.848(1), N(1)-Zn(1)-N(2) 178.6(1), O(3)-Zn(1)-O(4a) 129.5(1), O(1)-Zn(1)-O(2) 53.9(1), O(1)-Zn-O(4a) 138.0(1), O(3)-Zn(1)-O(2) 146.2(1). The symmetry operators are: $a = 1-x, 1-y, 1-z$; $b = x, y-1, z-1$; $c = x, y+1, z+1$.

UV irradiation of single crystals of **4** for about 3 hours did not change its single-crystal nature, morphology, transparency, or its diffracting power of X-rays. Hence, an irradiated single crystal of **4** ($[\{(F_3CCO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-tpcb})_2]_n$ (**5**) was selected for structure determination by single-crystal X-ray diffraction experiments. The X-ray crystallographic analysis confirmed the formation of new bonds across the vertical strands shown in Figure 2. The two pyridyl rings are bent towards each other with an interplanar angle of 27.4°. As a result, the Zn···Zn distance increased from 3.747 Å in **4** to 4.162 Å in **5**, and other bond parameters in **5** have also changed to accommodate the formation of new single bonds across the ethylene bonds. The formation of tpcb from two bpe ligands in the bulk of **5** was also confirmed by ^1H NMR spectroscopy.

Recently bpe ligands have been successfully oriented in parallel to form an infinite 1D ribbonlike polymer by utilizing the N···I interactions with an iodo derivative of pentaerythritol ether, and photochemical dimerization has also been accomplished through SCSC transformation.[12] While this work was in progress, a [2+2] cycloaddition reaction in cadmium fumarate dehydrate, which has a square-grid 2D structure, was reported;[13] however, it appears that neither complete photoconversion nor SCSC were observed. A discrete metal complex has been employed previously to orient the molecules for cycloaddition to take place in the solid state.[5b] In this present work, $Zn(O_2CCH_3)_2$ has been used to align the bpe ligands in a parallel fashion in a metal

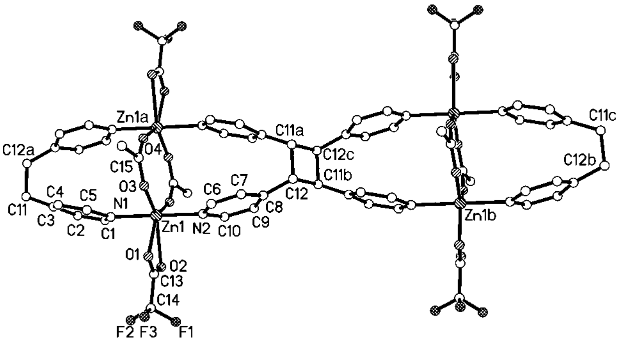


Figure 2. A view showing a part of the 1D polymeric structure of **5**. The hydrogen atoms have been omitted for clarity. Selected bond parameters [Å, °]: Zn(1)–N(1) 2.138(4), Zn(1)–N(2) 2.127(4), Zn(1)–O(1) 2.157(4), Zn(1)–O(2) 2.500(4), Zn(1)–O(3) 2.018(5), Zn(1)–O-(4a) 2.030(5), C(3)–C(11) 1.497(7), C(8)–C(12) 1.505(7), C(11)–C(12b) 1.536(7), Zn(1)···Zn(1a) 4.162(1), N(1)-Zn(1)-N(2) 178.3(2), O(3)-Zn-(1)-O(4a) 122.8(2), O(1)-Zn(1)-O(2) 55.2(2), O(1)-Zn-O(4a) 141.7(2), C(3)-C(11)-C(12b) 119.4(4), C(3)-C(11)-C(12a) 114.3(4), C(8)-C(12)-(C11c) 120.1(4), C(8)-C(12)-C(11a) 114.3(4), C(11c)-C(12)-C(11a) 89.6(4). The symmetry operators are: $a=1-x$, $1-y$, $1-z$; $b=x$, $1+y$, $1+z$; $c=x$, $y-1$, $z-1$.

coordination polymer, and expectedly, the coordination polymer has been found to exhibit photochemical reactivity. Furthermore, solid-state supramolecular transformation of one type of coordination polymer into another has been accompanied by photodimerization across the strands. The SCSC transformation has been successfully accomplished by partially replacing the acetate anion with trifluoroacetate ions to eliminate the problem of disorder in bpe.

In summary, the use of coordination polymers in topochemical photodimerization reactions has been illustrated. A number of other metal coordination network structures may also be used to preorganize the double bonds in the spacer ligands. Further new interesting network structures can be synthesized from a number of metal coordination polymeric structures in the SCSC structural transformation. Such new exciting coordination polymers are waiting to be explored.

Experimental Section

1: A solution of $Zn(O_2CCH_3)_2{\cdot}2H_2O$ (0.110 g, 0.5 mmol) in methanol (2 mL) was layered over a solution of bpe (0.090 g, 0.5 mmol) in THF (2 mL), with methanol (8 mL) as a middle buffer layer. Hexagonal crystals were obtained after 2 days (0.07 g, 26%). IR (KBr): $\tilde{\nu}=$ 1611(s), 1506(m), 1400(s), 1226(w), 1071(w), 1026(s), 830(s), 675(m), 621(m) cm^{-1}; ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 298 K): $\delta=$ 8.61 (d, 4H, Py-H), 7.63 (d, 4H, Py-H), 7.56 (s, 4H, CH=CH), 1.81 ppm (s, 6H, CH_3COO); Elemental analysis (%) calcd. for $C_{20}H_{22}N_2O_8Zn_2$: C, 43.74; H, 4.03; N, 5.10; found: C, 44.07; H, 4.34; N, 5.06.

2: Bpe (0.182 g, 1 mmol) in DMF (2 mL) was added to $Zn(O_2CCH_3)_2{\cdot}2H_2O$ (0.220 g, 1 mmol) in DMF (4 mL), and the white precipitate which immediately separated out was filtered and redissolved in hot water. The clear solution was filtered and allowed to slowly evaporate; yellow cubic crystals separated out after a week and were collected, washed with ether, and dried under vacuum (0.140 g, 36%). IR (KBr): $\tilde{\nu}=1637$(s), 1504(m), 1420(s), 1064(m), 1031(w), 830(m), 719(s) cm^{-1}; Elemental analysis (%) calcd. for $C_{16}H_{18}N_2O_5Zn$: C, 50.08; H, 4.73; N, 7.30; found: C, 50.38; H, 4.65; N, 7.23. A NMR spectrum was not recorded owing to the insolubility of the complex in common deuterated solvents.

3: A solution of $Zn(O_2CCH_3)_2{\cdot}2H_2O$ (0.11 g, 0.5 mmol) in methanol (2 mL) was layered over a solution of bpe (0.09 g, 0.5 mmol) in THF (2 mL), with CH_3CN (4 mL) as a middle buffer layer. Colorless rodlike crystals that formed in the junction were separated out the next day (0.12 g, 38%). In another method, equimolar amounts of $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.22 g) and bpe (0.18 g) in CH_3OH (4 mL and 2 mL, respectively) were mixed, and after stirring for a minute at room temperature, the clear solution was filtered and allowed to evaporate slowly. Colorless rodlike crystals separated out after two days; these were collected, washed with ether, and dried under vacuum (75%). IR (KBr): $\tilde{\nu}=1610.6$(vs), 1429.3(vs), 1251.8 (vw), 1209.0(vw), 1070.5(w), 1026.1(m), 929.7(vw), 839.0(s, bpeth), 686.7(w), 553.7(m) cm^{-1}; ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 298 K): $\delta=8.61$ (d, 4H, Py-H), 7.64 (d, 4H, Py-H), 7.56 (s, 4H, CH=CH), 1.83 ppm (s, 6H, CH_3COO); ^{13}C NMR: ([D$_6$]DMSO, 300 MHz, 298 K): $\delta=176$ (O=CO), 150.05 (C-Py), 143.55 (C-Py), 130.63 (C=C), 121.30 (C-Py), 22.30 ppm (CH_3); Elemental analysis (%) calcd. for $C_{32}H_{32}N_4O_8Zn_2$: C, 52.55; H, 4.41; N, 7.66; found: C, 51.45; H, 4.35; N, 7.23%.

UV Irradiation of **3:** A powdered sample of **3** (30 mg) was placed between two glass slides and was irradiated using a Xe lamp (60 W) for approximately 18 h. IR (KBr): $\tilde{\nu}=1622$(s), 1590(s), 1508(m), 1410(m), 1381(m), 1232(w), 1060(m), 1026(m), 825(m), 675(m) cm^{-1}; ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 298 K): $\delta=8.35$ (d, 4H, Py-H), 7.24 (d, 4H, Py-H), 4.68 (s, 4H, CH-CH), 1.81 ppm (s, 6H, CH_3COO); ^{13}C NMR: ([D$_6$]DMSO, 300 MHz, 298 K): $\delta=176.48$ (O=CO), 149.14 (C-Py), 148.24 (C-Py), 123.26 (C-Py), 44.31 (CH-CH), 22.31 ppm (CH_3).

4: Trifluoroacetic acid (0.1 mL, 1.2 mmol) and bpe (0.186 g, 1 mmol) in DMF (2 mL) were added consecutively to a solution of $Zn(O_2CCH_3)_2{\cdot}2H_2O$ (0.220 g, 1 mmol) in DMF (4 mL). After stirring for 1 min at RT, the clear solution was filtered and allowed to evaporate slowly. Colorless rodlike crystals separated out after two days; these were collected, washed with ether, and dried under vacuum (0.21 g, 53%). IR (KBr): $\tilde{\nu}=1690.3$(m), 1610.6(vs,), 1430.9(m), 1205.5(m), 1126.4(m), 1070.1(vw), 1018.3(w), 979.8(vw), 832.8(s), 726.0(w), 617.6(vw), 552.9(m) cm^{-1}; ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 298 K): $\delta=8.60$ (d, 4H, Py-H), 7.63 (d, 4H, Py-H), 7.56 (s, 4H, CH=CH), 1.85 ppm (s, 3H, CH_3COO); Elemental analysis (%) calcd. for $C_{32}H_{26}N_4O_8F_6Zn_2$: C, 45.79; H, 3.12; N, 6.07; found: C, 45.63; H, 3.32; N, 6.07.

5: A powdered sample of **4** (10 mg) placed between two glass slides was irradiated using a Xe lamp for approximately 12 h. IR (KBr): $\tilde{\nu}=1686$(s), 1613(s), 1502(m), 1430(m), 1205(m), 1129(m), 1068(m), 1018(m), 832(m), 725(m) cm^{-1}; ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 298 K): $\delta=8.35$ (d, 4H, Py-H), 7.26 (d, 4H, Py-H), 4.69 (s, 4H, CH–CH), 1.85 ppm (s, 3H, CH_3COO).

Crystal data for **1**: Monoclinic space group $C2/c$, $a=10.530(3)$ Å, $b=16.345(3)$ Å, $c=12.901(2)$ Å, $\beta=101.140(5)°$, $V=2178.5(7)$ Å^3, $Z=4$, $\rho_{\text{calcd}}=1.674$ g cm^{-3}. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1=0.0678$, $wR2=0.1650$, and GOF $=1.168$ for 1451 reflections with $F_o>4\sigma(F_o)$ and 151 parameters. Crystal data for **2**: Monoclinic space group $P2/n$, $a=9.5526(6)$ Å, $b=5.6572(3)$ Å, $c=16.034(1)$ Å, $\beta=98.492(1)$, $V=857.00(9)$ Å^3, $Z=2$, $\rho_{\text{calcd}}=1.487$ g cm^{-3}. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1=0.0293$, $wR2=0.0802$, and GOF $=1.086$ for 1463 reflections with $F_o>4\sigma(F_o)$ and 120 parameters. Crystal data for **3**: Triclinic space group $P\bar{1}$, $a=7.9853(7)$ Å, $b=9.3552(9)$ Å, $c=11.099(1)$ Å, $\alpha=95.792(2)$, $\beta=99.325(2)$, $\gamma=105.797(2)°$, $V=778.0(1)$ Å^3, $Z=1$, $\rho_{\text{calcd}}=1.561$ g cm^{-3}. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1=0.0404$, $wR2=0.1042$, and GOF $=1.039$ for 2459 reflections with $F_o>4\sigma(F_o)$ and 233 parameters. Crystal data for **4**: Triclinic space group $P\bar{1}$, $a=8.179(1)$ Å, $b=9.528(1)$ Å, $c=11.373(1)$ Å, $\alpha=98.922(3)$, $\beta=97.602(3)$, $\gamma=103.846(3)°$, $V=836.8(2)$ Å^3, $Z=2$, $\rho_{\text{calcd}}=$

1.665 g cm^{-3}. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1 = 0.0526$, $wR2 = 0.1382$, and GOF = 1.058 for 2508 reflections with $F_o > 4\sigma(F_o)$ and 263 parameters. Crystal data for **5**: Triclinic space group $P\bar{1}$, $a = 8.4414(9)$ Å, $b = 9.806(1)$ Å, $c = 10.799(1)$ Å, $\alpha = 99.066(2)$, $\beta = 99.101(2)$, $\gamma = 105.796(2)°$, $V = 830.1(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.679$ g cm^{-3}. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1 = 0.0534$, $wR2 = 0.1415$, and GOF = 1.037 for 2456 reflections with $F_o > 4\sigma(F_o)$ and 236 parameters.

Crystal data for **1**–**5** were collected on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated Mo$_{K\alpha}$ radiation (2.4 kW) using a sealed tube at 223(2) K. Absorption corrections were made with the program SADABS,[14] and the crystallographic package SHELXTL[15] was used for all calculations. CCDC-255233–255237 contain 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.

Received: November 19, 2004

Keywords: cycloaddition · photochemistry · self-assembly · topochemistry · zinc

---

[1] a) G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647 – 678; b) C. R. Theocharis, W. Jones in *Organic Solid State Chemistry* (Ed.: G. R. Desiraju), Elsevier, **1987**, chap. 2, pp. 47 – 68; c) D. Braga, F. Grepioni, *Angew. Chem.* **2004**, *116*, 4092 – 4102; *Angew. Chem. Int. Ed.* **2004**, *43*, 4002 – 4011.

[2] a) V. Ramamurthy, K. Venkatesan, *Chem. Rev.* **1987**, *87*, 433 – 481; b) P. Wagner, B.-S. Park in *Organic Photochemistry, Vol. 11* (Ed.: A. Padwa), Marcel Dekker, New York, **1991**, chap. 4; c) W. Jones, *Organic Molecular Solids: Properties and Applications*, CRC, Boca Raton, FL, **1997**; d) B. S. Green, R. M. Lahav, D. Rabinovich, *Acc. Chem. Res.* **1979**, *12*, 191 – 197; e) F. Toda, *Acc. Chem. Res.* **1995**, *28*, 480 – 486; f) A. E. Keating, M. A. Garcia-Garibay in *Organic and Inorganic Photochemistry* (Eds.: V. Ramamurthy, K. S. Schanze), Marcel Dekker, New York, **1998**, pp. 195 – 248; g) K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100*, 1025 – 1074.

[3] a) X. Gao, T. Friščič, L. R. MacGillivray, *Angew. Chem.* **2004**, *116*, 234 – 238; *Angew. Chem. Int. Ed.* **2004**, *43*, 232; b) T. Friščič, L. R. MacGillivray, *Chem. Commun.* **2003**, 306 – 307; c) B. Dushyant, G. Papaefstathiou, L. R. MacGillivray, *Chem. Commun.* **2002**, 1964 – 1965; d) L. R. MacGillivray, J. L. Reid, J. A. Ripmeester, *J. Am. Chem. Soc.* **2000**, *122*, 7817 – 7818; e) L. R. MacGillivray, *CrystEngComm* **2002**, *4*, 37 – 47.

[4] T. Hoang, J. W. Lauher, F. W. Fowler, *J. Am. Chem. Soc.* **2002**, *124*, 10656 – 10657.

[5] a) M. J. Vela, B. B. Snider, B. M. Foxman, *Chem. Mater.* **1998**, *10*, 3167 – 3171; b) G. S. Papaefsthathiou, Z. Zhong, L. Geng, L. R. MacGillivray, *J. Am. Chem. Soc.* **2004**, *126*, 9158 – 9159; c) F. D. Lewis, S. L. Quillen, P. D. Hale, J. D. Oxman, *J. Am. Chem. Soc.* **1988**, *110*, 1261 – 1267; d) M. J. Vela, V. Buchholz, V. Enkelmann, B. B. Snider, B. M. Foxman, *Chem. Commun.* **2000**, 2225 – 2226; e) N. W. Alcock, P. de Meester, T. J. Kemp, *J. Chem. Soc. Perkin Trans. 2* **1979**, 921 – 926; f) G. Cao, T. E. Mallouk, *J. Solid State Chem.* **1991**, *94*, 59 – 71; g) C. R. Theocharis, A. M. Clark, S. E. Hopkin, P. Jones, *Mol. Cryst. Liq. Cryst.* **1988**, *156 (Pt.A)*, 85 – 91.

[6] For polymerization without metals, see: a) V. Enkelmann, *Adv. Polym. Sci.* **1984**, *63*, 92 – 136; b) G. W. Coats, A. R. Dunn, L. M. Henling, J. W. Ziller, E. B. Lobkovsky, R. H. Grubbs, *J. Am. Chem. Soc.* **1998**, *120*, 3641 – 3649; c) W. L. Dilling, *Chem. Rev.* **1983**, *83*, 3 – 47; d) M. Hasegawa, *Chem. Rev.* **1983**, *83*, 507 – 518.

[7] For example, see: a) S. Rabe, U. Müller, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1367 – 1370; b) U. Englert, B. Ganter, B, T. Wagner, W. Kläui, *Z. Anorg. Allg. Chem.* **1998**, *624*, 970 – 974; c) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1999**, 375 – 376; d) H. Li, M. Eddaoudi, M. O'Keefe, O. M. Yaghi, *Nature* **1999**, *402*, 276 – 279; e) D. V. Soldatov, E. V. Grachev, J. A. Ripmeester, *Cryst. Growth Des.* **2002**, *2*, 401 – 408; f) C. J. Kepert, T. J. Prior, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2000**, *122*, 5158 – 5168; g) E. Y. Lee, M. P. Suh, *Angew. Chem.* **2004**, *116*, 2858 – 2861; *Angew. Chem. Int. Ed.* **2004**, *43*, 2798 – 2801.

[8] a) L. Iordanidis, M. G. Kanatzidis, *Angew. Chem.* **2000**, *112*, 2004 – 2006; *Angew. Chem. Int. Ed.* **2000**, *39*, 1928 – 1930; b) L. Iordanidis, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2000**, *122*, 8319 – 8320.

[9] a) D. M. Shin, I. S. Lee, D. Cho, Y. K. Chung, *Inorg. Chem.* **2003**, *42*, 7722 – 7724; b) O. S. Jung, S. H. Park, K. M. Kim, H. G. Jang, *Inorg. Chem.* **1998**, *37*, 5781 – 5785; c) X. Xue, X.-S. Wang, R.-G. Xiong, X.-Z. You, B. F. Abrahams, C.-M. Che, H.-X. Ju, *Angew. Chem.* **2002**, *114*, 3068 – 3070; *Angew. Chem. Int. Ed.* **2002**, *41*, 2944 – 2946; d) B. Rather, B. Moulton, R. D. B. Walsh, M. J. Zaworotko, *Chem. Commun.* **2002**, 694 – 695; e) B. Rather, M. J. Zaworotko, *Chem. Commun.* **2003**, 830 – 831; f) M.-H. Zeng, X.-L. Feng, X.-M. Chen, *Dalton Trans.* **2004**, 2217 – 2223; g) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem.* **2002**, *114*, 3545 – 3548; *Angew. Chem. Int. Ed.* **2002**, *41*, 3395 – 3398; h) K. Biradha, M. Fujita, *Angew. Chem.* **2002**, *114*, 3542 – 3545; *Angew. Chem. Int. Ed.* **2002**, *41*, 3392 – 3395; i) J. D. Ranford, J. J. Vittal, D. Wu, *Angew. Chem.* **1998**, *110*, 1159 – 1162; *Angew. Chem. Int. Ed.* **1998**, *37*, 1114 – 1116; j) J. D. Ranford, J. J. Vittal, D. Wu, X. Yang, *Angew. Chem.* **1999**, *111*, 3707 – 3710; *Angew. Chem. Int. Ed.* **1999**, *38*, 3498 – 3501.

[10] a) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629 – 1658; b) M. J. Zaworotko, *Chem. Commun.* **2001**, 1 – 10; c) M. J. Zaworotko in *Crystal Engineering: The Design and Application of Functional Solids, NATO ASI Ser. C-539* (Eds.: M. J. Zaworotko, K. R. Seddon), Kluwer, Dordrecht, **1999**, pp. 383 – 408; d) A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk, M. Schröder, *Coord. Chem. Rev.* **2001**, *222*, 155 – 192; e) N. R. Champness, M. Schröder, *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 419 – 424.

[11] Compound **3** is strictly a pseudosupramolecular isomer of **2** as it has one lattice water molecule in the asymmetric unit. For the definition of supramolecular isomer, see Ref. [10a].

[12] T. Caronna, R. Liantonio, T. A. Logothetis, P. Metrangolo, T. Pilati, G. Resnati, *J. Am. Chem. Soc.* **2004**, *126*, 4500 – 4501.

[13] A. Michaelides, S. Skoulika, M. G. Siskos, *Chem. Commun.* **2004**, 2418 – 2419.

[14] G. M. Sheldrick, SADABS, Software for Empirical Absorption Corrections, University of Göttingen (Germany), **2000**.

[15] SHELXTL Reference Manual, version 5.1, Bruker AXS, Analytical X-Ray Systems, Madison, WI, USA, **1997**.