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Solid-State Reversible Anion Exchange and Irreversible Anion Replacement in 1D Zinc(II) Coordination Polymers: Precursors for the Preparation of Zinc(II) Nanostructures

Mojtaba Khanpour[a] **and Ali Morsali***[a]

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Interesting solid-state reversible anion exchange and irreversible anion replacement in zinc coordination polymers from the ligand 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (bpdh) with different anions, $[Zn(\mu\text{-bpdh})(H_2O)_4](NO_3)_2\cdot 2bpdh$ (**1**), $[Zn(\mu\text{-bpdh})(H_2O)_4](ClO_4)_2\cdot 2bpdh$ (**2**), $[Zn(\mu\text{-bpdh})_2(NCS)_2]_n$ (**3**), $[Zn(\mu\text{-bpdh})_2(N_3)_2]_n$ (**4**), and $[Zn(\mu\text{-bpdh})(NO_2)_2]_n$ (**5**), were studied. Compounds **3**–**5** were prepared by irreversible solid-state anion replacement of either compound **1** or **2** with KSCN, NaN_3, or $NaNO_2$ under mixing or grinding. Compounds **1** and **2** undergo reversible solid-state anion exchange between ClO_4^- and NO_3^-. ZnO and ZnS nanoparticles were obtained by thermolyses of compounds **1**–**5** in oleic acid at 280 °C in air.

Introduction

The study of metal coordination polymers has gained great recognition as an important interface between synthetic chemistry and materials science, and it provides a solid foundation to help understand how molecules can be organized and how functions can be achieved.[1–14] To develop further our understanding of supramolecular architecture construction, it is interesting to investigate the effect that anions have on the fabrication of multidimensional polymers. During the course of the syntheses of the coordination polymers from ligand 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (bpdh) in our laboratory, we isolated two zinc(II) coordination polymers that undergo novel solid-state anion exchange and anion replacement: compounds $[Zn(\mu\text{-bpdh})(H_2O)_4](NO_3)_2\cdot 2bpdh$ (**1**) and $[Zn(\mu\text{-bpdh})(H_2O)_4](ClO_4)_2\cdot 2bpdh$ (**2**) can be converted into $[Zn(\mu\text{-bpdh})_2(NCS)_2]_n$ (**3**), $[Zn(\mu\text{-bpdh})_2(N_3)_2]_n$ (**4**), and $[Zn(\mu\text{-bpdh})(NO_2)_2]_n$ (**5**). It is well known that anions may have a major influence on constructing novel network geometries,[15] and anion exchange in the solid state has rarely been reported.[16,17] The solid-state reaction is a novel synthetic technique that has been developed in the last 10 years. It has received a considerable amount of attention because of its simplicity, low cost, high output, and low pollution.

Results and Discussion

The bpdh ligand was prepared by a reported method.[18] Single crystals of compounds **1** and **2** were isolated by slow evaporation of aqueous solutions obtained from the reaction of bpdh with a mixture of zinc(II) acetate and sodium nitrate or sodium perchlorate. Compounds **3**–**5** were prepared from the reaction of bpdh with a mixture of zinc(II) acetate and potassium thiocyanate, sodium azide, or sodium nitrite. Compounds **3**–**5** were also prepared by solid-state anion replacement from compounds **1** and **2** with KSCN, NaN_3, or $NaNO_2$ by grinding. The process of solid-state anion replacement is accompanied by a color change from yellow to white and orange for compounds **3** and **4** and without a color change for compound **5** (Figure 1; Supporting Information, Figure S1).

Single crystals of compounds **3** and **4** were isolated by the branched tube method, and single crystals of compound **5** were isolated by simple evaporation of a methanol solution. The structures of compounds **1**–**5** were determined by X-ray crystallography (Supporting Information, Table S1 and Figures S1–S3); substantial structural changes upon anion exchange between compounds **1** and **2** are not observed, but interesting substantial structural changes upon anion replacement between compounds **1** or **2** and KSCN, NaN_3, or $NaNO_2$ is observed. Compounds **1** and **2** are 1D coordination polymers, and the zinc atoms are linked by the oxygen atoms of four water molecules and the two nitrogen atoms of the bpdh ligands. There are two uncoordinated bpdh ligands that, along with the nitrate or perchlorate anions, form hydrogen bonds with the water molecules (Supporting Information, Figures S1 and S3). The X-ray struc-

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[a] Department of Chemistry, Faculty of Sciences, Tarbiat Modares University,
P. O. Box 14115-175, Tehran, Islamic Republic of Iran

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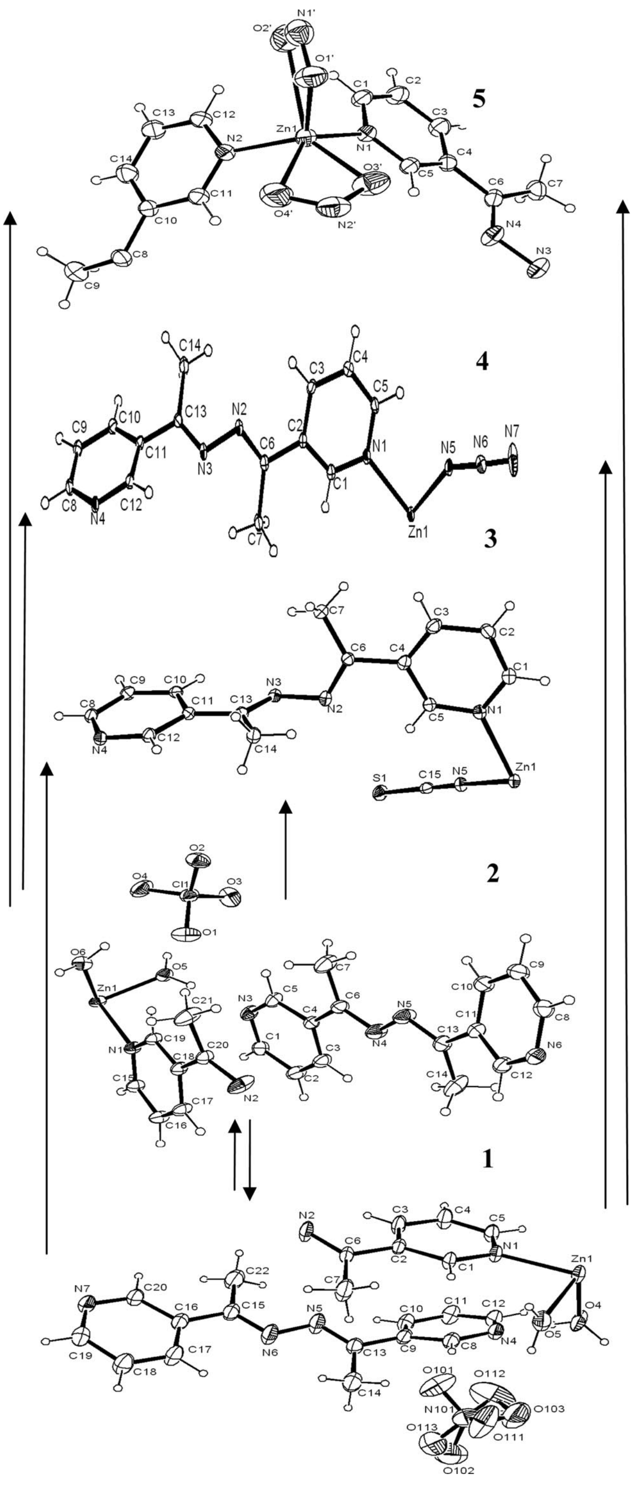

Figure 1. ORTEP diagram and a schematic diagram illustrating the structural conversions of 1D compounds {[Zn(μ-bpdh)$(H_2O)_4$]$(NO_3)_2$·2bpdh (**1**) and [Zn(μ-bpdh)$(H_2O)_4$]$(ClO_4)_2$·2bpdh (**2**)} into metallocycle 1D {[Zn(μ-bpdh)$_2$(NCS)$_2$]$_n$ (**3**) and [Zn(μ-bpdh)$_2$$(N_3)_2$]$_n$ (**4**)} and 1D zigzag {[Zn(μ-bpdh)$(NO_2)_2$]$_n$ (**5**)} coordination polymers by solid-state anion exchange. Ellipsoids are drawn at the 30% probability level.

tures of **3** and **4** reveal a number of unique features. Compounds **3** and **4** may be considered as coordination polymers of zinc(II) consisting of metallocyclic chains formed by bridging bpdh ligands, making a 1D array of Zn^{II} and bpdh in a 1:2 stoichiometry. The structures consists of a 1D polymer resulting from the connection of {Zn(NCS or N_3)$_2$} nodes with two bpdh spacers, and the Zn···Zn separations are 12.524 and 12.618 Å in **3** and **4**, respectively. The bpdh ligands in **3** and **4** act as bridging groups, yielding a 22-membered {Zn–N···N}$_2$ metallacycle (Supporting Information, Figures S1 and S3). These metallacycles are connected together, resulting in 1D chains. Each Zn^{II} atom has a distorted octahedral coordination sphere with an N_6 donor atom array; the apical positions are occupied by the nitrogen atoms of the thiocyanate or azide anions; the equatorial is occupied with four nitrogen atoms of the bpdh ligands. The structure of **5** may be considered as a polymer of zinc(II) atoms bridged by the bpdh ligand, and the Zn cations are also coordinated by two nitrite ions as bidentate ligands. All of this results in a structure consisting of 1D polymeric [Zn(μ-bpdh)$(NO_2)_2$] units. The coordination numbers of the zinc atoms is six with distorted octahedral ZnN_2O_4 coordination environments, and the two N-donor ligands and the nitrite ligands are in a *cis* position to each other, thus generating angular nodes of metal moieties. The structural supramolecular isomers are of the 1D zigzag chain type (Supporting Information, Figure S1).

Upon grinding with $NaClO_4$, compound **1** changes into compound **2**. The IR spectra and X-ray powder patterns show that anion exchange between compounds **1** and **2** is reversible. The IR spectra of **1** and those of the exchanged products are exhibited in Figure S4 (Supporting Information, traces 1 and 2). It can be seen clearly that an intense band around 1105 cm^{-1}, which originates from ClO_4^-, appears in the spectrum of **2**, whereas the intense band around 1381 cm^{-1} of the NO_3^- anion disappears. This indicates that the NO_3^- anions in compound **1** were completely exchanged by ClO_4^- anions. Solid **2** was grinded with $NaNO_3$ to allow reverse anion exchange, and product **1** was obtained. The band attributable to NO_3^- appeared in the IR spectrum, and the bands of ClO_4^- disappeared. Furthermore, the results of elemental analyses also confirmed complete anion exchanges.

Reversible anion exchange between compounds **1** and **2** was confirmed by X-ray powder patterns. Anion exchange by grinding results in a significant change in the powder pattern (Supporting Information, Figure S5), but acceptable matches were observed between the simulated pattern obtained from the single-crystal X-ray data and the experimental powder X-ray diffraction patterns obtained for the bulk crystalline samples prepared by anion exchange of compound **1** (Supporting Information, Figures S5d–S6f). These facts clearly indicate that compound **1** undergoes reversible anion exchange upon grinding to form **2**. The produced bpdh ligand and the $NaNO_3$ or $NaClO_4$ salts obtained after anion exchange and the transformation were removed by washing the products with an aqueous methanol solution.

Upon grinding of compound **1** or **2** with KSCN, NaN_3, or $NaNO_2$ for 1 h and with a reagent ratio of 1:4 [(compound **1** or **2**)/(KSCN, NaN_3, or $NaNO_2$)], compound **1** or

2 changes into compounds **3**–**5**. The IR spectra and X-ray powder patterns show that irreversible anion replacement takes place.

The nitrate or perchlorate bands in the IR spectra of the exchanged products were not observed, and the large broad band attributable to the O–H stretching vibrations is also significantly diminished (Supporting Information, Figure S4, traces 3–5).

For **3**, **4**, and **5**, the strong stretchings of the thiocyanate azide and the nitrite anions appear at ca. 2055, 2070, and 1262 cm^{-1} (Supporting Information, Figure S4, traces 3–5).

Irreversible anion replacement in compounds **1** and **2** was confirmed by X-ray powder patterns. Anion replacement by grinding results in a significant change in the powder pattern (Supporting Information, Figures S6–S11), but acceptable matches were observed between the simulated patterns obtained from the single-crystal X-ray data and the experimental powder X-ray diffraction patterns obtained for the bulk crystalline samples prepared by anion replacement in compounds **1** and **2**.

The X-ray structures of compounds **1**–**5** show that simple anion exchange without any major structural changes takes place between compounds **1** and **2**, whereas anion exchange in compounds **1** or **2** with thiocyanate azide and nitrite anions is accompanied by replacement of water molecules (Figure 1; Supporting Information, Figures S1–S3). The solid-state transformation starts from compound **1** or **2**. The uncoordinated bpdh ligands are oriented towards the neighboring units and form hydrogen bonds (Figure 1; Supporting Information, Figure S2). Dashed lines indicate the shortest nonbonding contacts between the OH groups of the coordinated water molecules and the N atoms of the unbridging bpdh ligands and the O atoms of the perchlorate anions of their neighbors. In compounds **1** and **2** there are two different types of hydrogen bonds: those formed between coordinated water molecules with the uncoordinated bpdh ligands, $N_{py}\cdots HO_{water}$ and nitrate or perchlorate anions $O_{anion}\cdots HO_{water}$, and those formed from neighboring complexes (Supporting Information, Figure S2). In compounds **3**–**5**, both types of hydrogen bonds are broken and two new types of coordination bonds between the bpdh ligand and thiocyanate, between the bpdh ligand and azide, or between the nitrite ligands and the zinc atoms, respectively, are formed.

However, removal of four water molecules from compound **1** or **2** and nitrate or perchlorate exchange with thiocyanate, azide, or nitrite in the solid state is accompanied by variation in the packing, metal-centered angles, and the original zinc-donor bonds. The rearrangement products $[Zn(\mu\text{-bpdh})_2(NCS)_2]_n$ (**3**), $[Zn(\mu\text{-bpdh})_2(N_3)_2]_n$ (**4**), and $[Zn(\mu\text{-bpdh})(NO_2)_2]_n$ (**5**) represent 1D coordination polymers in which there are no uncoordinated bpdh ligands. The formation of new $Zn\cdots N_{bpdh}$, $Zn\cdots N_{NCS/N_3}$, or $Zn\cdots O_{NO_2}$ bonds takes place along with the removal of $Zn–O_{water}$ bonds, which does not result in any change in the coordination number of the Zn atoms. This change in network topology starts when a mixture of solids **1** or **2** with potassium thiocyanate, sodium azide, or sodium nitrite is grinded. The reactions are not reversible and polymers **3**, **4**, or **5** are not converted back into **1** or **2** by rehydration and anion exchange.

The solid-state UV/Vis spectra of compounds **1**–**5**, as well as that of the pure bpdh ligand, were studied. The solid-state UV/Vis spectra of compounds **1**, **2**, **4**, and **5** display three absorption bands with a maximum intensity at ca. 220 to 420 nm (Supporting Information, Figure S12, traces a,b,d,e), whereas compound **3** displays two absorption bands with a maximum intensity at 220 and 320 nm (Supporting Information, Figure S12, trace c). The solid-state UV/Vis spectrum of the bpdh ligand is similar to that of compound **3** and also displays two absorption bands with maximum intensities at 210 and 310 nm, indicating that the two former electronic transitions in all five compounds are mostly of intraligand character and the last transition can be due to ligand-to-metal charge transfer (LMCT).

To examine the thermal stability of the five compounds, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700 °C (Supporting Information, Figures S13–S17). The TG curve of compound **1** indicates that release of H_2O molecules occurs in

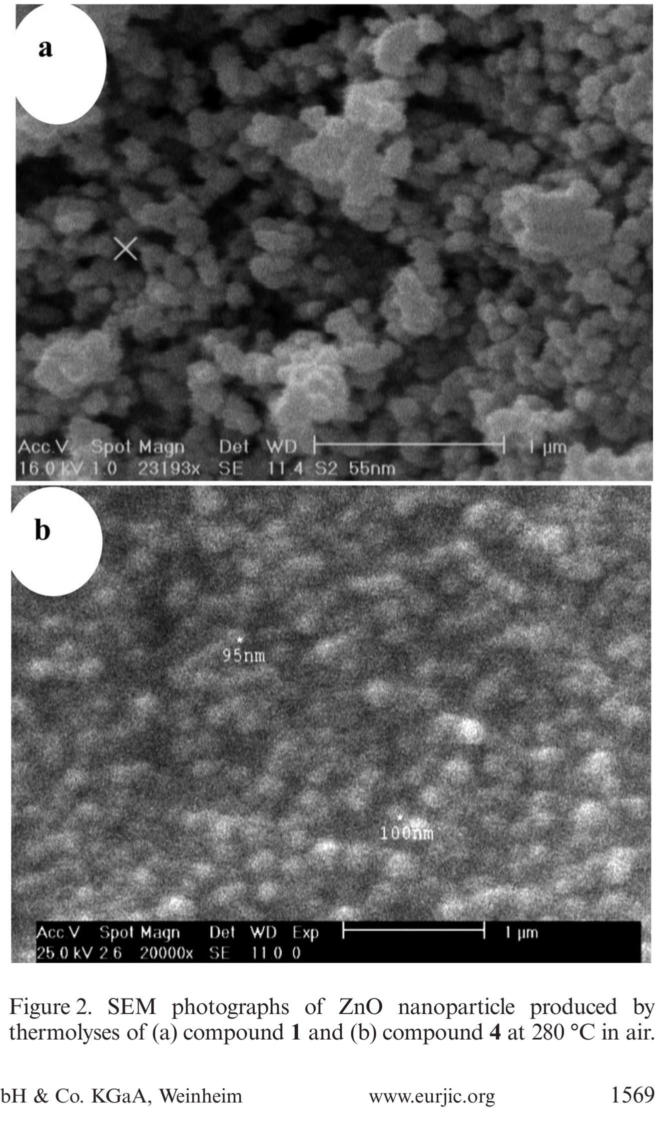

Figure 2. SEM photographs of ZnO nanoparticle produced by thermolyses of (a) compound **1** and (b) compound **4** at 280 °C in air.

one step at 120 °C (Supporting Information, Figure S13), whereas in compound **2** the H_2O and uncoordinated bpdh molecules release together at 200 °C. In contrast, thermogravimetric analysis shows that all five frameworks have remarkable thermal stability, as they do not melt and only decompose at temperatures above 170 °C, except for compound **1**, which releases water molecules at 120 °C.

ZnO and ZnS nanoparticles can be synthesized from the decomposition of precursors **1**–**5** in oleic acid. The morphologies and sizes of the as-prepared ZnO and ZnS samples were further investigated by using scanning electron microscopy (SEM). Figure 2 and Figures S18–S20 in the Supporting Information show the SEM images of the original morphology of the particles with diameters from 65 to 90 nm. The XRD pattern of ZnO (Supporting Information, Figure S21) produced by thermolyses of compounds **1**, **2**, **4**, and **5** is in agreement with the typical wurtzite structure ZnO diffraction (JCPDS No. 36-1451) and ZnS (Supporting Information, Figure S22) produced by thermolyses of compound **3** is in agreement with the hexagonal wurtzite structure ZnS diffraction (JCPDS No. 36-1450). This point demonstrates that coordination polymers may be suitable precursors for the preparation of nanoscale materials with interesting morphologies and sizes of particles, which may offer new insights into metal–organic supramolecular assemblies and nanochemistry.

Conclusions

In summary a reversible solid-state anion exchange between two isostructural 1D zinc(II) coordination polymers $[Zn(\mu\text{-bpdh})(H_2O)_4](NO_3)_2\cdot 2bpdh$ (**1**) and $[Zn(\mu\text{-bpdh})(H_2O)_4](ClO_4)_2\cdot 2bpdh$ (**2**) is reported. Also, a irreversible solid-state anion replacement of both compounds **1** and **2** with KSCN, NaN_3, or $NaNO_2$ for the preparation of $[Zn(\mu\text{-bpdh})_2(NCS)_2]_n$ (**3**), $[Zn(\mu\text{-bpdh})_2(N_3)_2]_n$ (**4**), and $[Zn(\mu\text{-bpdh})(NO_2)_2]_n$ (**5**), respectively, were studied. In the crystal lattice of compounds **1** and **2**, the coordination number of Zn^{II} does not change upon removal of four water molecules and new types of $Zn–N_{bpdh}$ and $Zn–N_{NCS/N_3}$ or $Zn\cdots O_{NO_2}$ bonds are formed. However, the following solid-state reactions are suggested for the anion exchange and replacement in this paper:
Compound **1** + $NaClO_4$ ⇄ Compound **2** + $NaNO_3$
Compound **1** or **2** + NaSCN or NaN_3 → Compound **3** or **4** + bpdh + $4H_2O$ + $NaNO_3$ or $NaClO_4$
Compound **1** or **2** + $NaNO_2$ → Compound **5** + 2bpdh + $4H_2O$ + $NaNO_3$ or $NaClO_4$
ZnO and ZnS nanoparticles were obtained by thermolyses of compounds **1**–**5** in oleic acid at 280 °C in air.

Experimental Section

Single crystals of compounds **1** and **2** were isolated by slow evaporation of an aqueous solution obtained from the reaction of bpdh with a mixture of zinc(II) acetate and sodium nitrate or sodium perchlorate.

Compound 1: Yield: 55% (m.p. >320 °C). $C_{42}H_{50}N_{14}O_{10}Zn$ (976.32): calcd. C 51.62, H 5.12, N 20.07; found C 51.50, H 4.90, N 20.10. IR: $\tilde{\nu}$ = 612 (m), 801 (m), 1381 (vs), 1415 (m), 1613 (s), 3410 (br.) cm^{-1}.

Compound 2: Yield: 65% (m.p. >320 °C). $C_{42}H_{50}ClN_{12}O_{12}Zn$ (1015.76): calcd. C 47.94, H 4.75, N 15.98; found C 47.30, H 4.73, N 15.60. IR: $\tilde{\nu}$ = 619 (m), 806 (m), 1105 (vs), 1411 (m), 1610 (s), 3400 (br.) cm^{-1}.

Compounds **3**–**5** were prepared from the reaction of bpdh with a mixture of zinc(II) acetate and potassium thiocyanate, sodium azide, or sodium nitrite. Compounds **3**–**5** were also prepared by solid-state anion replacement from compounds **1** and **2** with KSCN, NaN_3, or $NaNO_2$ by grinding for 1 h. Ground compounds **1** or **2** were mixed with KSCN, NaN_3, or $NaNO_2$ with a ratio of reagents of 1:4 (compounds **1** or **2**/KSCN, NaN_3, or $NaNO_2$) and ground by mortar for 1 h. The XRD and IR analyses before washing of the mixture showed that all of the peaks (compared to the simulated PXRD patterns of the products) due to products were created and the peaks of the reagents had disappeared. The powders obtained were washed repeatedly with an aqueous methanol solution.

Compound 3: Yield: 70% (m.p. >320 °C). $C_{30}H_{28}N_{10}S_2Zn$ (658.12): calcd. C 54.70, H 4.25, N 21.27; found C 54.60, H 4.45, N 21.30. IR: $\tilde{\nu}$ = 636 (m), 702 (m), 1041 (m), 1365 (m), 1609 (m), 2055 cm^{-1}.

Compound 4: Yield: 68% (m.p. >320 °C). $C_{28}H_{28}N_{14}Zn$ (626.00): calcd. C 53.67, H 4.47, N 31.30; found C 53.50, H 4.50, N 31.50. IR: $\tilde{\nu}$ = 635 (m), 706 (m), 1071 (m), 1385 (m), 1608 (m), 2070 cm^{-1}.

Compound 5: Yield: 60% (m.p. >320 °C). $C_{14}H_{14}N_6O_4Zn$ (395.68): calcd. C 42.45, H 3.53, N 21.23; found C 42.50, H 3.50, N 31.50. IR: $\tilde{\nu}$ = 630 (m), 721 (m), 1262 (s), 1382 (m), 1624 (m), 2040 cm^{-1}.

Precursors **1**–**5** (0.1 mmol) were dissolved immediately in oleic acid (1.35 mL) to form greenish black solutions. These solutions were degassed for 20 min and then heated to 280 °C for 2 h. At the end of the reaction, a white precipitate had formed. A small amount of toluene and a large excess of MeOH were added to the reaction solution and ZnO or ZnS nanostructures were separated by centrifugation. The solids were washed with EtOH and dried under an atmosphere of nitrogen.

CCDC-730692 (for **1**), -723322 (for **2**), -723325 (for **3**), -723324 (for **4**), and -730691 (for **5**) 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.

Supporting Information (see footnote on the first page of this article): Tables, packings, XRD patterns, and SEM photographs of compounds **1**–**5**.

Acknowledgments

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[1] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658.
[2] A. Morsali, M. Y. Masoumi, *Coord. Chem. Rev.* **2009**, *253*, 1882–1905.
[3] H. Ahmadzadi, F. Marandi, A. Morsali, *J. Organomet. Chem.* **2009**, *694*, 3565–3569.
[4] A. Aslani, A. Morsali, *Inorg. Chim. Acta* **2009**, *362*, 5012–5016.
[5] M. A. M. Abu-Youssef, A. Escuer, D. Gatteschi, M. A. S. Goher, F. A. Mautner, R. Vicente, *Inorg. Chem.* **1999**, *38*, 5716–5719.

[6] M. Fujita, Y. J. Kwon, S. Washizu, K. J. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152.

[7] Z. R. Ranjbar, A. Morsali, *J. Mol. Struct.* **2009**, *936*, 206–212.

[8] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, M. A. Novak, *Angew. Chem. Int. Ed.* **2001**, *40*, 1760–1763.

[9] N. Soltanzadeh, A. Morsali, *Ultrason. Sonochem.* **2010**, *17*, 139–144.

[10] K.-T. Wong, J.-M. Lehn, S.-M. Peng, G.-H. Lee, *Chem. Commun.* **2000**, 2259–2261.

[11] S. Khanjani, A. Morsali, *J. Mol. Struct.* **2009**, *935*, 27–31.

[12] N. Gimeno, R. Vilar, *Coord. Chem. Rev.* **2006**, *250*, 3161–3189.

[13] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375.

[14] D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. Rosseinsky, *J. Acc. Chem. Res.* **2005**, *38*, 273–282.

[15] S.-I. Noro, R. Kitaura, K. Mitsuru, S. Kitagawa, T. Ishii, H. Matsizaka, M. Yamashita, *J. Am. Chem. Soc.* **2002**, *124*, 2568–2583.

[16] J. J. Vittal, *Coord. Chem. Rev.* **2007**, *251*, 1781–1795.

[17] C. Hu, U. Englert, *Angew. Chem. Int. Ed.* **2006**, *45*, 3457–3459.

[18] D. M. Ciurtin, Y.-B. Dong, M. D. Smith, T. H.-C. Barclay, *Inorg. Chem.* **2001**, *40*, 2825–2834.

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