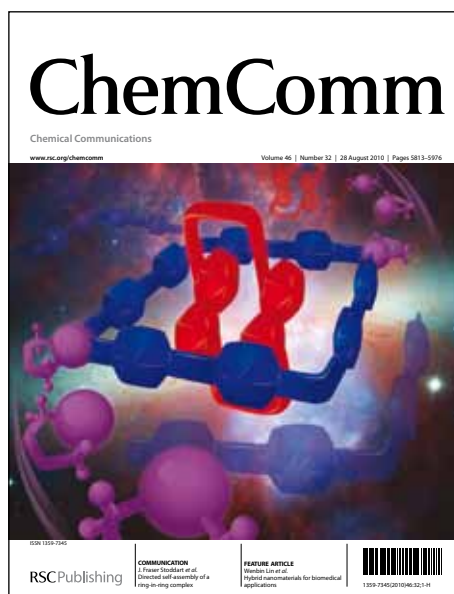


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COMMUNICATION**Vapochemically and Mechanochemically Reversible Polymerization/Depolymerization of S–Fe–Cu Carbonyl Clusters**

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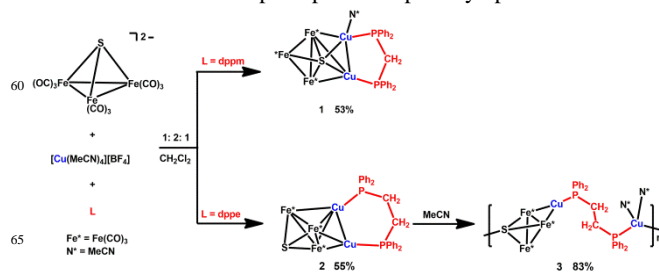
DOI: 10.1039/b000000x

A reversible vapochemical and mechanochemical solid-state transformation between a dppe-linked SFe_3Cu_2 -based cluster $[(\mu_3-S)Fe_3(CO)_9]Cu_2(dppe)$ (**2**) and its 1D polymer $[(\mu_4-S)Fe_3(CO)_9]Cu_2(dppe)(MeCN)_2$ (**3**), was demonstrated, in which polymer **3** exhibited semi-conducting properties with an energy gap of 1.69 eV.

Solid-state vapochemical and mechanochemical approaches provide efficient synthetic routes for many organic, inorganic, organometallic, and supramolecular materials.^{1–3} This type of solid-state reaction has gradually replaced traditional solution-based synthesis, mainly due to environmental concerns,² because it provides a green path to crystal engineering.^{2a,3a} Solid-state structural transformations of coordination polymers have now been extensively reviewed,^{2c,d,3} and to the best of our knowledge no reports concerning 0D to 1D transformation have addressed metal carbonyl complexes. However, the synthesis of 1D or pseudo-1D coordination polymers constructed from metal carbonyl ions connected with ligands or metal ions is attractive, because of the unique electrical and optical properties.⁴ A popular synthetic route employs solution-based self-assembly construction by using transition metal clusters as secondary building units (SBUs).^{4,5} Nevertheless, the direct solid-state transformation of metal carbonyl clusters in the formation of coordination polymers is yet to be explored. Herein, we present the first report of the solid-state reversible transformation between 0D and 1D carbonyl clusters via vapochemical and mechanochemical reactions.

When $[Et_4N]_2[SFe_3(CO)_9]$, $[Cu(MeCN)_4][BF_4]$, and bis(diphenylphosphino)methane (dppm) or bis(diphenylphosphino)ethane (dppe) were mixed in a 1: 2: 1 ratio in CH_2Cl_2 , the dicopper-bisphosphine-bridged clusters $[(\mu_5-S)Fe_3(CO)_9]Cu_2(dppm)(MeCN)$ (**1**) and $[(\mu_3-S)Fe_3(CO)_9]Cu_2(dppe)$ (**2**) were obtained in good yields (Scheme 1). Clusters **1** and **2** were fully characterized by spectroscopic methods and single-crystal X-ray diffraction analysis, and the ORTEP diagrams are shown in Fig. S1 and S2 (ESI†). Both **1** and **2** each consisted of a distorted $SFe_3(CO)_9Cu$ trigonal bipyramidal core with the SFe_2 or Fe_3 residing in the equatorial plane, whereas the $SFeCu$ or Fe_2Cu triangular plane was further capped by one copper atom and the $Cu-Cu$ bond was bridged by either dppm or dppe, respectively. In **1**, the five-membered $Cu-Cu-P-C-P$ ring assumed an envelope-like conformation, with the C(24) atom being above (or below) the

others, in which MeCN and C(24) sat in a *trans* orientation to reduce the steric hindrance. However, in **2**, the six-membered $Cu_2(dppe)$ ring had a nearly planar Cu_2P_2 arrangement with a mean deviation of 0.045 Å from the ideal plane, with the other two methylene groups located up and down across the ring. It is noteworthy that both Cu atoms in **1** were five-coordinated, while in **2**, the two Cu atoms were four- and five-coordinated, in which the four-coordinated Cu2 atom was in a nearly trigonal pyramidal environment with one apical position spatially open.

Scheme 1 Synthesis of complexes **1** and **2** and polymer **3**.

Based on the afore-mentioned geometric arrangement, when complex **2** was treated with MeCN, a polymeric complex $[(\mu_4-S)Fe_3(CO)_9]Cu_2(dppe)(MeCN)_2$ (**3**) was readily crystallized after the addition of hexanes/THF (Scheme 1). A similar treatment was carried out for **1**; however, no polymer was obtained. X-ray analysis showed that polymer **3** consisted of the repeating $SFe_3(CO)_9$ units that were connected by the $Cu(dppe)Cu$ moiety to give a 1D chain polymer, in which one Cu atom bridged one $Fe-Fe$ bond of the $SFe_3(CO)_9$ and the other Cu atom was S-bound with two coordinated MeCN molecules (Fig. S3, ESI†). According to a search of the Cambridge Crystallographic Data Centre, polymer **3** represented the first example of a $Cu(dppe)Cu$ -bridged metal carbonyl cluster-based polymer. As mentioned, the four-coordinated Cu2 atom was less hindered than the five-coordinated Cu1 atom in **2**. Hence, in the polymerization process, it was postulated that the σ -donor MeCN initially attacked the Cu2 atom of **2**, which induced $Fe-Cu$ and $Cu-Cu$ bond cleavages to form a reactive “ SFe_3Cu ” with the dangling $(dppe)Cu(MeCN)_2$ moiety that could then be further attacked by the sulfur atom of another “ SFe_3Cu ” unit, resulting in polymer **3**. This postulate was also supported by the more positive natural charge⁸ of the Cu2 atom (0.272) compared with Cu1 (0.092) and the relatively weaker Wiberg bond indices⁹ (0.200 and 0.143) of the $Fe-Cu$ and $Cu-Cu$ bonds in **2** (Table.

S1, ESI†). To understand the nature of polymer **3** in solutions, ESI-MS measurement was performed, which showed the major peaks corresponding to $[(\mu_3\text{-S})\text{Fe}_3(\text{CO})_9\text{Cu}]^-$ (514.9) and $[\{\text{SFe}_3(\text{CO})_9\}_2\text{Cu}_3]^-$ (1094.1), which indicated the degradation of polymer **3** in solutions.

Surprisingly, when the crystals of **2** were exposed to MeCN vapor, polymer **3** was formed (Fig. 1), and this formation was accompanied by a change in color from brownish-black to reddish-brown. This transformation was confirmed by powder X-ray diffraction, as shown in Fig. 2a. This is the first example of the vapor-driven 0D to 1D polymerization involving bond cleavages and formations in metal carbonyl complexes. However, this conversion was not a single-crystal to single-crystal transformation because the attempts to collect single crystal X-ray diffraction data on a fully converted sample failed. Meanwhile, the addition of a drop of MeCN into powder **2**, accompanied by a grinding of the mixture, resulted in its conversion to **3** (Fig. 2b). Furthermore, the depolymerization process from **3** to **2** was also achieved via mechanochemical grinding with the addition of drops of organic solvents, such as CH_2Cl_2 and THF (Fig. 2e and 2f), which could accelerate the conversion.^{2f,10}

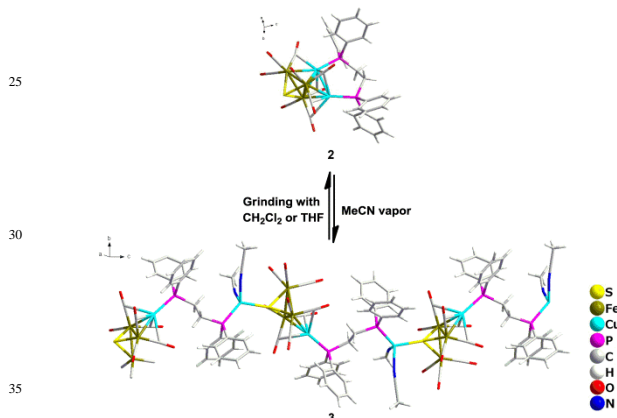


Fig. 1 The reversible transformation between cluster **2** and polymer **3**.

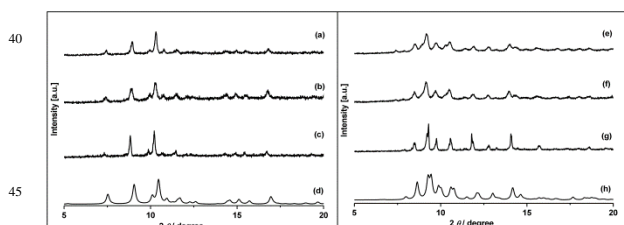


Fig. 2 Powder X-ray diffraction (PXRD) patterns for the following (a) As-synthesized **3** obtained from crystal **2** with MeCN vapor; (b) As-synthesized **3** after powder sample **2** was ground with one drop of MeCN; (c) As-synthesized **3**; (d) Calculated pattern for **3**; (e) As-synthesized **2** after powder sample **3** was ground in drops of CH_2Cl_2 ; (f) As-synthesized **2** after powder sample **3** was ground in drops of THF; (g) As-synthesized **2**; (h) Calculated pattern for **2**.

The thermal stability of **3** was also evaluated by thermogravimetric analysis (Fig. S4, ESI†). The TGA of polymer

3 showed a continuous weight loss of 32.03% at temperatures below 250 °C, corresponding to the loss of MeCN molecules and CO groups (theoretical 31.61%), and then a significant decrease in weight of approximately 31.14% at temperatures as high as 600 °C, which was consistent with the loss of phenyl and methylene groups (theoretical 31.78%), and left a residue with the composition $\text{SFe}_3\text{Cu}_2\text{P}_2$. It was noted that coordinated MeCN molecules were released at ~137 °C, which was lower than that for the MeCN-coordinated 1D Cu polymer $[(\text{Cu}_4\text{I}_4)\text{L}(\text{CH}_3\text{CN})_2]_n$ (L = calix[4]-bis-monothiacrown) (~150 °C),¹¹ which was indicative of the relative ease of the MeCN loss.

Moreover, the optical reflectance spectrum measurements showed that the band gaps of monomer **2** and polymer **3** were approximately 1.71 and 1.69 eV (Fig. S5, ESI†), respectively, indicating the energy gap was slightly decreased from **2** to **3**. The subtle difference was attributed to the bridging dppe, although this is traditionally not a good electron-transfer ligand. On the other hand, DFT calculations showed that the HOMO-10 of two units of **3** had a slight portion of the probability of electrons shifted to the adjacent cluster unit via the dppe ligand, implying that the bridging dppe could possibly enable the electron communication between adjacent $\text{SFe}_3(\text{CO})_9\text{Cu}_2$ -based units (Fig. S6, ESI†).

In summary, the syntheses and characterizations of bisphosphine-bridged $\text{SFe}_3(\text{CO})_9\text{Cu}_2$ -based clusters **1** and **2** were demonstrated. With the prolongation of the bridging C-chain from dpmp to dppe, the less-hindered **2** reacted readily with MeCN to give **3**. More importantly, the reversible solid-state polymerization/depolymerization between cluster **2** and polymer **3** was achieved via vapor-diffused-mediated and mechanochemical approaches. Furthermore, the dppe-bridged polymer **3** exhibited semi-conducting properties, with a band gap of 1.69 eV. These novel results may introduce new approaches to the construction of Fe—Cu chalcogenide cluster-based aggregates and extended frameworks with tunable optical properties. Further investigations into this issue are going.

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Notes and references

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† Electronic supplementary information (ESI) available: Experimental details, spectroscopic data, and calculated atomic coordinates. Crystallographic details of compound **1–3** can be found free of charge from the Cambridge Crystallographic Data Centre (CCDC 930774–930776). See DOI: 10.1039/b000000x/

- (a) T. Lasanta, M. E. Olmos, A. Laguna, J. M. López-de-Luzuriaga and P. Naumov, *J. Am. Chem. Soc.*, 2011, **133**, 16358; (b) I. O. Koshevoy, Y.-C. Chang, A. J. Karttunen, M. Haukka, T. Pakkanen and P.-T. Chou, *J. Am. Chem. Soc.*, 2012, **134**, 6564; (c) G. M. Espallargas, M. Hippler, A. J. Florence, P. Fernandes, J. van de Streek, M. Brunelli, W. I. F. David, K. Shankland and L. Brammer, *J. Am. Chem. Soc.*, 2007, **129**, 15606; (d) S. Libri, M. Mahler, G. M. Espallargas, D. C. N. G. Singh, J. Soleimannejad, H. Adams, M. D. Burgard, N. P. Rath, M. Brunelli and L. Brammer, *Angew. Chem. Int.*

- Ed., 2008, **47**, 1693; (e) L.-Q. Mo, J.-H. Jia, L.-J. Sun and Q.-M. Wang, *Chem. Commun.*, 2013, **48**, 8691; (f) Z. Huang, P. S. White and M. Brookhart, *Nature*, 2010, **465**, 598; (g) S. B. L. Vollrath, C. Hu, S. Bräse and K. Kirshenbaum, *Chem. Commun.*, 2013, **49**, 2317.
- 5 2 (a) D. Braga, S. L. Giaffreda, F. Grepioni, A. Pettersen, L. Maini, M. Curzi and M. Polito, *Dalton Trans.*, 2006, 1249; (b) T. Friščić and W. Jones, *Cryst. Growth Des.*, 2009, **9**, 1621; (c) T. Friščić, *Chem. Soc. Rev.*, 2012, **41**, 3493; (d) S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett,
- 10 W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell, *Chem. Soc. Rev.*, 2012, **41**, 413; (e) T. Friščić, *J. Mater. Chem.*, 2010, **20**, 7599; (f) G. A. Bowmaker, *Chem. Commun.*, 2013, **49**, 334. (g) E. Boldyreva, *Chem. Soc. Rev.*, 2013, **42**, 7719. (h) G.-W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 7668.
- 15 3 (a) G. K. Kole and J. J. Vittal, *Chem. Soc. Rev.*, 2013, **42**, 1755; (b) T. Friščić, I. Halasz, V. Štrukil, M. Eckert-Maksić and R. E. Dinnebier, *Croat. Chem. Acta*, 2012, **85**, 367; (c) J. J. Vittal, *Coord. Chem. Rev.*, 2007, **251**, 1781.
- 20 4 (a) M. Shieh, C.-Y. Miu, Y.-Y. Chu and C.-N. Lin, *Coord. Chem. Rev.*, 2012, **256**, 637; (b) S. Zacchini, *Eur. J. Inorg. Chem.*, 2011, 4125.
- 5 (a) T. Nakajima, A. Ishiguro and Y. Wakatsuki, *Angew. Chem. Int. Ed.*, 2001, **40**, 1066; (b) J. Bai, E. Leiner and M. Scheer, *Angew. Chem. Int. Ed.*, 2002, **41**, 783; (c) M. Scheer, L. Gregoriades, J. Bai,
- 25 M. Sierka, G. Brunklaus and H. Eckert, *Chem. Eur. J.*, 2005, **11**, 2163; (d) C. Femoni, F. Kaswalder, M. C. Iapalucci, G. Longoni and S. Zacchini, *Chem. Commun.*, 2006, 2135; (e) C. Femoni, R. D. Pergola, M. C. Iapalucci, F. Kaswalder, M. Riccò and S. Zacchini,
- 30 *Dalton Trans.*, 2009, 1509; (f) R. D. Pergola, A. Sironi, C. Manassero and M. Manassero, *Eur. J. Inorg. Chem.*, 2009, 4618; (g) P. Leoni, L. Marchetti, V. Bonuccelli, S. K. Mohapatra, A. Albinati, S. Rizzato, *Chem. Eur. J.*, 2010, **16**, 9468; (h) M. Shieh, M.-H. Hsu, W.-S. Sheu, L.-F. Jang, S.-F. Lin, Y.-Y. Chu, C.-Y. Miu, Y.-W. Lai,
- 35 H.-L. Liu and J. L. Her, *Chem. Eur. J.*, 2007, **13**, 6605; (i) M. Shieh, C.-H. Ho, W.-S. Sheu, B.-G. Chen, Y.-Y. Chu, C.-Y. Miu, H.-L. Liu and C.-C. Shen, *J. Am. Chem. Soc.*, 2008, **130**, 14114.
- 6 J.-J. Cherng, Y.-C. Tsai, C.-H. Ueng, G.-H. Lee, S.-M. Peng and M. Shieh, *Organometallics*, 1998, **17**, 255.
- 40 7 (a) G. J. Kubas, *Inorg. Synth.* 1979, **19**, 90; (b) M. G. Simmons, C. L. Merrill, L. J. Wilson, L. A. Bottomley and K. M. Kadish, *J. Chem. Soc., Dalton Trans.*, 1980, 1827.
- 8 (a) A. E. Reed and F. Weinhold, *J. Chem. Phys.*, 1983, **78**, 4066; (b) A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985,
- 45 **83**, 735.
- 9 K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083.
- 10 (a) N. Shan, F. Toda and W. Jones, *Chem. Commun.*, 2002, 2372; (b) G. A. Bowmaker, N. Chaichit, C. Pakawatchai, B. W. Skelton and A. H. White, *Dalton Trans.*, 2008, 2926; (c) A. V. Trask, W. D. S. Motherwell and W. Jones, *Chem. Commun.*, 2004, 890; (d) A. V. Trask, N. Shan, W. D. S. Motherwell, W. Jones, S. Feng, R. B. H. Tan and K. J. Carpenter, *Chem. Commun.*, 2005, 880; (e) T. Friščić,
- 50 A. V. Trask, W. Jones and W. D. S. Motherwell, *Angew. Chem. Int. Ed.*, 2006, **45**, 7546; (f) D. Braga, M. Curzi, A. Johansson, M. Polito, K. Rubini and F. Grepioni, *Angew. Chem. Int. Ed.*, 2006, **45**, 142; (g) D. Braga, S. L. Giaffreda and F. Grepioni, *Chem. Commun.*, 2006, 3877; (h) T. Friščić, L. Fábíán, J. C. Burley, W. Jones and W. D. S. Motherwell, *Chem. Commun.*, 2006, 5009.
- 55 11 J. Y. Lee, H. J. Kim, J. H. Jung, W. Sim and S. S. Lee, *J. Am. Chem. Soc.*, 2008, **130**, 13838.
- 60