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Metallo-Network Polymers: Reversible CO Binding to an Immobilized Copper(I) Complex

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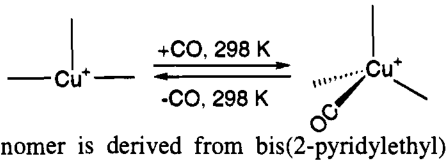
Copolymerization of molecular assemblies into organic hosts is an effective way of fabricating new materials having desirable chemical or physical properties. The assembly of the molecular species prior to polymerization is advantageous because of the greater control of the structure and amount of species incorporated into the polymer and the possibility of regulating their microenvironments. Recent examples of this method in the synthesis of new polymers include the monodispersal of metallic nanoclusters into organic polymer hosts[1] and molecular imprinting of selective binding sites into highly cross-linked network polymers.[2] We describe herein an application of this copolymerization approach for designing metal ion sites in network polymers.[3,4]

Our objective is to use the copolymerization process to synthesize sites in the polymer that can bind metal ions or stabilize metal−small molecule adducts. The macroporous character of these polymers should allow the incorporated metal ion to bind additional ligands not present during polymerization. In addition, the removal of the metal ion leaves the metal site with ligands arranged to rebind other metal ions not present during the polymerization process. Thus, the chemical and physical properties of the metal sites, and those of the polymer, can be changed through metal ion substitution. To test these proposals we have incorporated Cu(I) and Ag(I) complexes into network polymers and examined their ability to bind CO.

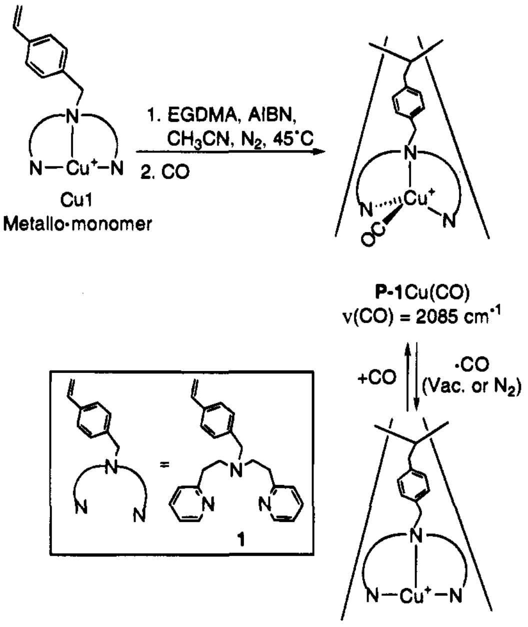
Since Cu(I) systems reversibly bind CO in solution[5] (eq 1), we reasoned that a similar reaction could occur within a network polymer, if the CO-free form has a coordinatively unsaturated three-coordinate Cu(I) center.[6] The ligand used in our metallo monomer is derived from bis(2-pyridylethyl)amine[7] through addition of a styrene group by treating the amine with 4-vinylbenzyl chloride to afford **1** (35%).[8] Allowing **1** to react with $[Cu(CH_3CN)_4]PF_6$ in acetonitrile and recrystallization from CH_3CN/ether produced Cu**1**PF_6 as a pale yellow microcrystalline solid in 85% yield.[9a,10]



(1)

The Cu**1** network polymer (**P**−**1**Cu) was synthesized using the protocol outlined in Scheme 1. Cu**1** (5 mol %) was copolymerized with ethylene glycol dimethacrylate (EGDMA) as the cross-linker (95 mol %) using CH_3CN as the porogenic agent and azobis(isobutyronitrile) (AIBN) as the radical initiator at 45 °C under a N_2 atmosphere. Continuous extraction of the crude solid with acetonitrile for 24 h afforded the insoluble macroporous polymer **P**−**1**Cu, which has an average surface area of 100 m²/g.

Scheme 1



The solid-state binding of CO to **P**−**1**Cu was monitored using diffuse reflectance infrared Fourier transformation (DRIFT) spectroscopy.[11] When **P-1**Cu (20 mass % in KBr) is exposed to CO, a new band at $\nu = 2085$ cm^{-1} appears in the DRIFT spectrum within 5 min (Figure 1b). This band is indicative of carbon monoxide coordination to a Cu(I) center.[5,9b,12] Reversion of **P-1**Cu(CO) to **P-1**Cu is accomplished by applying a vacuum or by flushing the polymer with a stream of N_2 for 15 min; this conversion is nearly quantitative with >85% of **P-1**Cu recovered (Figure 1c). Solid-state rebinding of CO to **P-1**Cu is also essentially quantitative, with >95% of the original signal for

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(6) Reversible CO binding to a Cu(I) complex bound to polystyrene has been reported: Balkins, K. J., Jr.; Kortz, A.; Drago, R. S. *Inorg. Chem.* **1988**, *27*, 2955.

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(8) Complete synthetic procedures are reported in the supporting information.

(9) (a) Cu**1**: ^1H NMR ($CO(CD_3)_3$) δ 8.70 (d, 2H, Py*H*), 7.99 (d, 2H, Py*H*), 7.56 (d, 2H, Py*H*), 7.46 (d, 2H, Py*H*), 7.39 (d, 2H, Ar*H*), 7.32 (d, 2H, Ar*H*), 6.68 (d, 2H, ArC*H*), 5.75 (d, 1H, *trans*-CH═C*H*H), 5.23 (d, 1H, *cis*-CH═C*H*H); 3.86 (s, 2H, NC*H*$_2$Ar), 3.32 (s, 4H, PyC*H*$_2$), 3.22 (s, 4H, C*H*$_2$). IR (Nujol): 1604 (s), 1568 (s), 1505 (s), 837 (s) cm^{-1}. Anal. Calcd for Cu**1**, $C_{23}H_{25}CuF_6N_3P$: C, 50.05; H, 4.57; N, 7.61. Found: C, 50.67; H, 4.13; N, 7.62. (b) Cu**1**(CO): ν(CO) = 2085 cm^{-1} (acetone); 2086 cm^{-1} (KBr). (c) Ag**1**: ^1H NMR ($CO(CD_3)_3$): δ 8.66 (m, 2 H, Py*H*) 7.95 (td, 2 H, Py*H*), 7.51 (m, 4 H, Py*H*), 7.23 (d, 2 H, Ar*H*), 7.16 (d, 2 H, Ar*H*), 6.67 (dd, 1 H, C*H*═CH$_2$), 5.73 (d, 1 H, *trans*-CH═C*H*H), 5.21 (t, 1 H, *cis*-CH═C*H*H), 3.60 (s, 2 H, NC*H*$_2$Ar), 3.25 (t, 4 H, PyC*H*$_2$), 3.08 (t, 4 H, C*H*$_2$). IR (Nujol): 1603 (s), 1569 (s), 1510 (s), 835 (s) cm^{-1}. Anal. Calcd for Ag**1**, $C_{23}H_{25}AgF_6N_3P$: C, 46.33; H, 4.23; N, 7.05. Found: C, 45.82; H, 3.97; N, 7.00. (d) **P-1**Cu: Anal. Found: C, 61.32; H, 6.65; N, 2.42; Cu, 0.34. (e) **P-1**Ag: Anal. Found: C, 61.69; H, 7.13; N, 1.66; Ag, 0.35.

(10) Benzyl form of Cu**1**: Blackburn, N. J.; Karlin, K. D.; Concannon, M.; Hayes, J. C.; Gultneh, Y.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1984**, 939. Sanyal, I.; Mahroof-Tahir; Nasir, M. S.; Ghosh, P.; Cohen, B. I.; Gultneh, Y.; Cruse, R. W.; Faroog, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 4322.

(11) Experimental details: Samples for all DRIFT experiments were prepared by crushing the polymer with KBr under an Ar atmosphere. DRIFT spectra were obtained using a Harrick Scientific diffuse reflectance accessory (DRA-PMI) with an environmental chamber (HVC-DRP) equipped with KBr windows. Infrared radiation was obtained from a resistively heated SiC source. The infrared radiation was collected using a Midac interferometer (M2401-C) with ZnSe optics and a 1 mm² wide-band MCT detector. The signals obtained were Fourier transformed and the Kubelka−Munk spectra generated using software provided by Midac (FT-IR Spectra Calc).

(12) (a) Villacorta, G. M.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 3672. (b) Blackburn, N. J.; Pettingill, T. M.; Seagraves, K. S.; Shigeta, R. T. *J. Biol. Chem.* **1990**, *31*, 4322.

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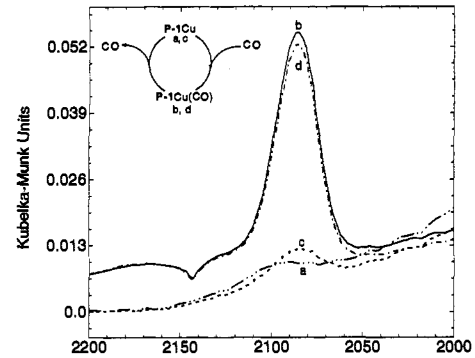


Figure 1. DRIFT spectra of (a) **P-1Cu**; (b) **P-1Cu(CO)**; (c) **P-1Cu-(CO)** under vacuum (10 min, 293K); (d) rebinding of CO to the polymer formed in spectrum c. The carbonyl polymers were formed by treating the **P-1Cu** with 5 mL of CO. Spectra of **P-1Cu(CO)** were recorded after a 15 s vacuum was applied to remove unbonded CO.

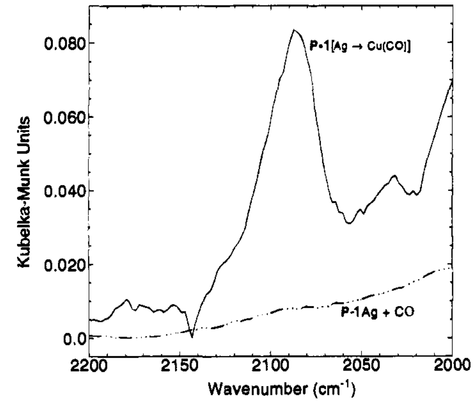


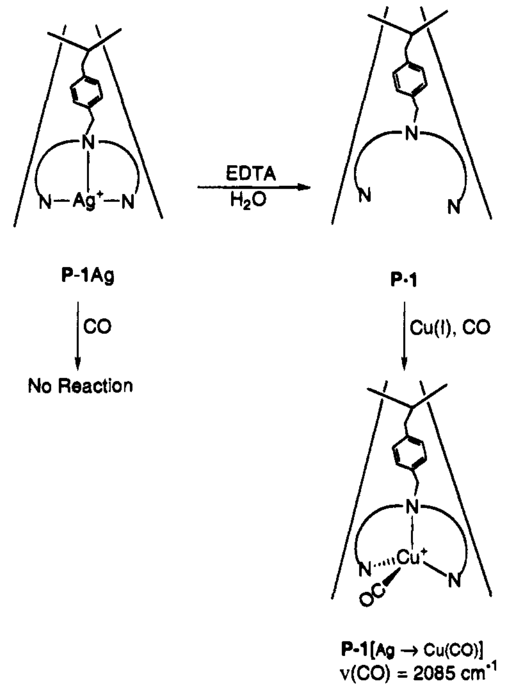
Figure 2. DRIFT spectra of **P-1Ag** under 1 atm of CO (—•••—) and **P-1**[Ag→Cu(CO)] (—).

P-1Cu(CO) obtained after re-exposure of the polymer to CO (Figure 1d). This process has been repeated for 10 cycles without any measurable loss in CO binding.

We have also synthesized Ag**1**[9c] and its corresponding network polymer **P-1Ag**. This silver(I) polymer serves as a structural *but not functional* mimic for the Cu(I) sites in **P-1Cu**. The polymeric metallo sites formed by Ag**1** and Cu**1** complexes should have analogous architecture since Ag(I) and Cu(I) complexes with nitrogenous ligands have similar structures.[13] However, CO binding to Ag(I) complexes is rare[14] and is unlikely to occur in the coordination environment provided by **1**. In fact, when **P-1Ag** is exposed to CO, there is no evidence in the DRIFT spectrum for CO binding to the Ag(I) immobilized sites, even when **P-1Ag** is exposed to 1 atm of CO for 30 min (Figure 2).

P-1Ag can be converted into a polymer which binds CO by replacing Ag(I) with Cu(I) ions in the metal binding sites. Silver ions were removed from the polymer by treating **P-1Ag** with an aqueous solution of EDTA, shaking for 6 days, washing with CH_3CN, and drying under vacuum (Scheme 2). This process removes ~66% of the Ag(I) from the polymer,[8,15] producing an apopolymer (**P-1**) that has binding sites (the immobilized tridentate ligand **1**) available to chelate metal ions. The reconstituted Cu(I) polymer **P-1**[Ag→Cu] is made by allowing **P-1** to react with an acetonitrile solution of $[Cu(CH_3CN)_4]^+$ under dinitrogen. Repeated washing of **P-1**[Ag→Cu] with acetonitrile (to remove unbound Cu(I) ions) yielded a polymer containing copper in 52% of the available sites (not optimized).

Scheme 2



When **P-1**[Ag→Cu] is exposed to CO (1 atm, 15 min), a peak at $\nu = 2085$ cm^{-1} is observed in the DRIFT spectrum (Figure 2), showing that this polymer is now competent to bind CO at its Cu(I) sites. Moreover, this CO-binding process is again reversible, making **P-1**[Ag→Cu] functionally similar to **P-1Cu**, the original network polymer containing Cu(I) immobilized sites.

In summary, our results demonstrate the reversible solid-state binding of CO to Cu(I) sites in a network polymer. The polymerization technique allows for the convenient incorporation of metal complexes, of known structure, into a polymeric matrix. Subsequent binding of exogenous ligands to the immobilized metal center can be used for initiating metal-based catalysis[3] and developing processes for the detection[16] or separation/storage of hazardous substances, such as CO.[17,18] Moreover, the chemical properties of the polymers can be modified by metal ion substitution within the immobilized sites.[19] Studies are in progress to extend this approach to other metal systems.

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Supporting Information Available: Synthetic procedures for the metal complexes and network polymers and the emission spectra of **P-1Cu** and **P-1Cu(CO)** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(15) **P-1Ag** is slightly light-sensitive, which causes oxidation of a small number of silver(I) imprinted sites.

(16) Preliminary room temperature experiments indicate that **P-1Cu** suspended in toluene or 2-MeTHF luminesces at 530 nm ($\lambda_{ex} = 345$ nm). This signal is quenched when CO is introduced into the system (Figure S1, supporting information).

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