Reactivity of NO2 with Porous and Conductive Copper Azobispyridine Metallopolymers

Naomi E. Clayman,†⊥ Mary Anne Manumpil,†⊥ Benjamin D. Matson,†§ Shengkai Wang,‡ Adam H. Slavney,† Ritimuka Sarangi,*,§ Hemamala I. Karunadasa,*,† and Robert M. Waymouth*†

†Department of Chemistry, Stanford University, Stanford, California 94305, United States
‡Department of Mechanical Engineering, Stanford University, Stanford, California 94305, United States
§Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

Supporting Information

ABSTRACT: We report the reactivity of copper azobispyridine (abpy) metallopolymers with nitrogen dioxide (NO2). The porous and conductive [Cu(abpy)]n mixed-valence metallopolymers undergo a redox reaction with NO2, resulting in the disproportionation of NO2 gas. Solid- and gas-phase vibrational spectroscopy and X-ray analysis of the reaction products of the NO2-dosed metallopolymer show evidence of nitrate ions and nitric oxide gas. Exposure to NO2 results in complete loss of porosity and a decrease in the room-temperature conductivity of the metallopolymer by four orders of magnitude with the loss of mixed-valence character. Notably, the porous and conductive [Cu(abpy)]n metallopolymers can be reformed by reducing the Cu-nitrate species.

INTRODUCTION

Combustion of fossil fuels that powers much of the transportation and industry in today’s society results in the release of toxic gases into the atmosphere. Among these gases is NO2, a dangerous brown gas found in smog. Continued exposure to low concentrations (∼1 ppm) of NO2 can result in chronic respiratory problems; short-term exposure to 10 ppm induces acute respiratory difficulties, and concentrations nearing 100 ppm can result in death.1 These biological and environmental concerns have motivated studies to identify materials that can sense or react with and capture NO2.1−5 Sensor technologies have been developed to detect small amounts of NO2 gas.1−5 Materials that react with NO2 without interfering reactions with more abundant gaseous species (N2, O2, CO2) also have potential environmental applications for the capture and sequestration of these toxic gases.

We previously described6 the electrically conductive and porous copper azobispyridine (abpy) metallopolymers [Cu(abpy)]n. These metallopolymers exhibit an unusual combination of substantial conductivity (0.18 S·cm−1 at room temperature) and porosity (90 m2·g−1). The conductivity of the neutral polymer, with oxidation states formally assigned as [Cu+(abpy•−)]n, was attributed to its mixed-valence character.6 The [Cu(abpy)]n metallopolymers can be reversibly oxidized at −0.8 V vs Ag/AgNO3 to the insulating (<10−10 S·cm−1) and nonporous cationic metallopolymer, formally assigned as [Cu(abpy)X+]n (X = monanion). As a reducing, porous material, we anticipated that the neutral metallopolymer might react with oxidizing gases such as NO2.

Herein, we report the reaction of the porous and conductive [Cu(abpy)]n with NO2 gas (Scheme 1). This gas/solid redox reaction results in oxidation of the metallopolymer and the reductive disproportionation of NO2 gas into nitric oxide (NO) gas and nitrate anions (NO3−). Notably, after exposure to NO2 gas, the resulting oxidized material can be reduced to regenerate [Cu(abpy)]n with approximately 75% recovery of the porosity and conductivity of the original metallopolymer.

Received: April 23, 2019

Scheme 1. Proposed Reaction of [Cu(abpy)]n with NO2 Gas
RESULTS AND DISCUSSION

Metallopolymer [Cu(abpy)]n, generated from the chemical reduction of [Cu(abpy)PF6]n with Cp2Co, was used for all NO2 reactivity studies. Black powders of [Cu(abpy)]n were dosed with either a mixture of NO2 (1%) in dry air (99%) or a mixture of NO2 (2%) in dry N2 (98%) at room temperature for variable amounts of time. Solid [Cu(abpy)]n is insoluble in water and organic solvents. After exposure to NO2, the resulting green powders become soluble in most polar organic solvents such as acetonitrile (CH3CN) to afford a dark purple/black solution. Analysis of the headspace of a sample of [Cu(abpy)]n after exposure to an atmosphere of 2% NO2 in N2 reveals the presence of NO gas (approximately 0.6 mol %; Figure 1), as determined by mid-IR tunable diode laser absorption near 1920 cm\(^{-1}\). The evolution of NO gas is very fast, occurring within the first 0.2 s of NO2 exposure. Under the conditions used for monitoring, the NO concentration in the reactor headspace reaches about 0.2 mol % in the first 0.2 s (Figure S1).

Several experiments were carried out to identify the other nitrogen oxides generated from the reaction of the metallopolymer [Cu(abpy)]n with NO2. The reaction products were dissolved in CH3CN and analyzed by electrospray-ionization mass spectrometry (ESI-MS, see Supporting Information). The most intense peak in the spectrum in negative mode is an absorption near 1920 cm\(^{-1}\). Of the ions observed for samples with and without oxygen exposure, and no isotopic shifts were observed in any peaks when \(^{18}\)O2 was dosed with either a mixture of NO2 (1%) in dry air (99%) or a mixture of NO2 (2%) in dry N2 (98%), corresponding to the formation of \([Cu(azpy)NO_3]^+\) (Figure S6). Fragmentative collision-induced dissociation (CID) performed on the ion at 491 m/z resulted in the loss of one of the azpy ligands, and the complex fragmented into \([Cu^{159+}(azpy^{16}NO_3)^+]\). This observation implies that the nitrate anion is coordinated to the CuII center and is more strongly bound to the metal center than one of the azpy ligands. This strong coordination of nitrate could facilitate the fragmentation of the polymer chain upon NO2 exposure.

Reduction of the powder obtained through exposure of [Cu(abpy)]n to NO2 gas with cobaltocene (Cp2Co) results in the precipitation of a black solid and yellow supernatant. Slow vapor diffusion of pentane into the dichloromethane/CH3CN supernatant held at \(-20\) °C afforded yellow needles of cobaltocenium nitrate (CoIII(Cp2NO3); Cp = C6H5C") as confirmed by single-crystal X-ray diffraction (Figure S8). The isolation of a nitrate salt further verifies the oxidation of NO2 to NO3\(^-\) by the metallopolymer. We obtained crystals of CoIII(Cp2NO3) regardless of whether the reaction with NO2 was performed in dry air or dry N2. The crystallization of Cp2CoNO3 under O2-free conditions indicates that all three oxygen atoms in NO3\(^-\) originate from the NO2 and not from O2. Confirmation of the origin of the oxygen atoms in NO3\(^-\), was obtained by IR spectroscopy analysis of three samples of [Cu(abpy)]n, dosed with different gas mixtures: one was dosed with only 2% NO2 in N2, one with 2% NO2 in N2 and codosed with \(^{18}\)O2, and one codosed with \(^{16}\)O2. The IR spectra of all three samples (Figure S9) are identical: no differences could be observed for samples with and without oxygen exposure, and no isotopic shifts were observed in any peaks when \(^{18}\)O2 was introduced into the system, confirming that the oxygens in NO3\(^-\) are derived from NO2.

We probed the solid-phase–gas-phase reaction between [Cu(abpy)]n and NO2 by a variety of spectroscopic techniques. Powders of [Cu(abpy)]n display a broad absorbance around \(\approx 2500\) cm\(^{-1}\) in the mid-infrared region (Figure S10). This absorbance is the low-energy tail of the band we assign as a predominantly ligand-based intervalence charge transfer (IVCT) band. This IVCT band is absent in the IR spectrum of [Cu(azpy)NO3]+ (Figure S6), suggesting that the product no longer possesses radical abpy ligands. Upon NO2 dosing, we also observe the emergence of a new peak at 1273 cm\(^{-1}\) (Figure S10), which has been previously attributed to coordinated nitrate (NO3\(^-\)) in anhydrous cupric nitrate.

Changes in electronic structure after NO2 exposure were observed by electron paramagnetic resonance (EPR) spectroscopy. The EPR spectrum of [Cu(abpy)]n features a broad peak with a g value of 2.08, corresponding to radical abpy ligands with possible contribution from the copper centers due to electronic delocalization. The solid-state EPR spectrum of major ion observed in positive mode exhibited an m/z value of 429, corresponding to Cu(azpy)\(^{159+}\) (Figure S4). After exposure of powders of Cu(azpy)\(_2\) to NO2 gas, the ESI-MS spectrum of Cu(azpy)\(_2\) changes. A new ion with a m/z of 491, corresponding to [Cu(azpy)NO3]++, emerges (Figure S5), in addition to an ion at 308 m/z, corresponding to the formation of [Cu(azpy)NO3]+ (Figure S6). Fragmentative collision-induced dissociation (CID) performed on the ion at 491 m/z resulted in the loss of one of the azpy ligands, and the complex fragmented into [Cu\(^{159+}\)(azpy^{16}NO3)]. This observation implies that the nitrate anion is coordinated to the CuII center and is more strongly bound to the metal center than one of the azpy ligands. This strong coordination of nitrate could facilitate the fragmentation of the polymer chain upon NO2 exposure.

Figure 1. Mid-IR laser absorption analysis of the gas product of [Cu(abpy)]n, dosed with NO2 (red). The strong characteristic absorption of NO appears near 1920.71 cm\(^{-1}\). In this example, the final NO mole fraction in the reactor headspace was determined to be 6150 ppm. As a control, the 2% NO2/N2 mixture was also introduced to the reactor without [Cu(abpy)]n (purple). The background NO mole fraction, determined from this control test, was less than 100 ppm.

absorption of NO near 1920 cm\(^{-1}\). The evolution of NO gas is very fast, occurring within the first 0.2 s of NO2 exposure. Under the conditions used for monitoring, the NO concentration in the reaction headspace reaches about 0.2 mol % in the first 0.2 s (Figure S1).
[Cu(abpy)]ₙ after 16 h of NO₂ (2%) exposure reveals that this broad, symmetrical signal in [Cu(abpy)]ₙ diminishes upon exposure to NO₂. We also observe the emergence of a new signal with characteristic rhombic Cu⁰⁰ spectral shape (Figure S12A). There is literature precedent for disproportionation of NO₂ on electron-rich surfaces, and in fact, Addison et al. report the isolation of Cu⁰⁰(NO₃)₂ and NO gas when copper metal is treated with NO₂ in the form of liquid N₂O₄.

Cu K-edge X-ray absorption spectroscopy (XAS) was used to further evaluate the oxidation state of Cu in samples of [Cu(abpy)]ₙ before and after NO₂ dosing, as well as in [Cu(abpy)PF₆]ₙ. The Cu K rising edge region is dominated by Cu 1s → 4p⁺ continuum transitions (~8979 eV) and is therefore strongly modulated by the effective nuclear charge \( Z_{\text{eff}} \) on Cu. The rising edge of [Cu(abpy)PF₆]ₙ measured as the maximum of the first derivative, occurs at an energy of 8982.6 eV and is very similar in energy and shape measured as the maximum of the derivative of Cu(abpy)PF₆ signal with characteristic rhombic CuII spectral shape (Figure 2.).

The rising edge of both [Cu(abpy)PF₆]ₙ and [Cu(abpy)PF₆] (bpy = 2,2'-bipyridine), indicating an increase in \( Z_{\text{eff}} \) on Cu as the bipyridine ligand is replaced with more redox-active azpy or abpy ligands, indicating that [Cu(abpy)PF₆]ₙ is better represented as [Cu₁⁺(abpy)²⁻PF₆]ₙ. The rising edge of the reduced species [Cu(abpy)]ₙ shows a distinct change in shape with a slight increase in rising edge energy (8982.9 eV, Figure 2A). Remarkably, this shift in rising edge energy is indicative of an increase in the \( Z_{\text{eff}} \) on Cu upon reduction of [Cu(abpy)].

\[
\text{Cu}^{(\text{abpy}^-)} + 4\text{NO}_2 \rightarrow \text{Cu}^{II}(\text{abpy})^2(\text{NO}_3^-)_2 + 2\text{NO}
\]

Solid [Cu(abpy)]ₙ has a room-temperature conductivity of 0.18 S·cm⁻¹, which increases up to 0.46 S·cm⁻¹ upon heating to 125 °C, and an activation energy for conduction of 98 meV. Upon exposing powders of [Cu(abpy)]ₙ to NO₂ for 1 h, the room-temperature conductivity of the material drops to 8.5 × 10⁻² S·cm⁻¹. After 16 h of exposure, the room-temperature conductivity value decreases to 6.4 × 10⁻⁴ S·cm⁻¹. Likewise, the activation energy increases up to 290 meV upon NO₂ dosing. Electrical conductivity in [Cu(abpy)]ₙ is thought to arise from electron hopping between radical mixed-valence abpy ligands. From the EPR and IR spectra, we infer that the redox reaction between NO₂ and [Cu(abpy)]ₙ results in a loss of mixed valency. A decrease in conductivity upon NO₂ exposure is consistent with this interpretation and confirms the loss of electronic communication across the material.

We also observe changes in the surface area of [Cu(abpy)]ₙ upon NO₂ exposure. Fine powders of [Cu(abpy)]ₙ have a Brunauer–Emmett–Teller (BET) surface area of 90 m²·g⁻¹. Concomitant with loss of conductivity, we also observe a complete loss of porosity after NO₂ dosing for 16 h (Figure 3).

The observed lack of porosity in NO₂-dosed [Cu(abpy)]ₙ is
consistent with the oxidation of the material to a cationic species associated with NO$_3^-$ anions and likely also to the fragmentation of the polymer chains upon gas exposure.

As the reaction between [Cu(abpy)]$_n$ and NO$_2$ is a redox reaction, we sought to regenerate [Cu(abpy)]$_n$ from the oxidized product using a chemical reductant. The addition of a solution of Cp$_2$Co to a solution of the polymer after exposure to NO$_2$ results in the isolation of black powders with properties reminiscent of [Cu(abpy)]$_n$. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and combustion analysis reveal that the approximate formula of the black powders is [Cu(abpy)]$_n$ (see Supporting Information). The solid-state EPR spectrum of the reformed polymer shows a broad peak with a $g$ value of 2.08, similar to that of [Cu(abpy)]$_n$ (Figure S13).

To confirm that we successfully regenerated the [Cu(abpy)]$_n$ polymer’s properties upon chemical reduction after exposure to NO$_2$, we measured the optical, electronic, and gas sorption properties of the reformed material. The fingerprint region of the IR spectrum of the reformed material matches that of the original polymer (Figure S14). Significantly, we observe the return of the low-energy tail of the IVCT band in the IR spectrum that disappeared upon NO$_2$ exposure. The re-emergence of the IVCT indicates the reformation of radical abpy ligands upon reduction.

The regenerated material has a room-temperature conductivity ($7.8 \times 10^{-2}$ S·cm$^{-1}$) and an activation energy for conductivity (160 meV) similar to that of [Cu(abpy)]$_n$ generated from [Cu(abpy)PF$_6$]$_n$ (0.18 S·cm$^{-1}$ and 98 meV, respectively). Furthermore, we find that the regenerated material retains a significant fraction of the porosity with a BET surface area of 70 m$^2$·g$^{-1}$ (vs 90 m$^2$·g$^{-1}$ for [Cu(abpy)]$_n$). We have shown that the porosity of [Cu(abpy)]$_n$ arises from expulsion of charge-balancing anions upon reduction of the [Cu(abpy)X]$_n$ ($X = \text{Br}^-$, PF$_6^-$, BArF$_6^-$) from which it is generated. The slightly lower conductivities and surface areas of the regenerated materials may be due to the templating effect mediated by the extrusion of different anions (NO$_3^-$ vs PF$_6^-$) upon reduction. To test this hypothesis, we prepared a sample of [Cu(abpy)]$_n$ from [Cu(abpy)NO$_3$]$_n$ to see if the porosity of the reformed material can be attributed to the anion templating effect. Reduction of [Cu(abpy)NO$_3$]$_n$ yields [Cu(abpy)]$_n$ with a BET surface area of 60 m$^2$·g$^{-1}$ (Figure S15).

The lower porosity of the [Cu(abpy)]$_n$ generated from [Cu(abpy)NO$_3$]$_n$ compared to that generated from [Cu(abpy)PF$_6$]$_n$ is consistent with the previously observed templating effect because PF$_6^-$ is larger than NO$_3^-$.$^6$ Because we expect the polymer to fragment upon NO$_3^-$ coordination to the Cu centers, this templating effect may not be as strong when reforming [Cu(abpy)]$_n$ from the NO$_2$ reaction product mixture. The 10 m$^2$·g$^{-1}$ difference in surface area between the [Cu(abpy)]$_n$ polymer generated from [Cu(abpy)NO$_3$]$_n$ and the [Cu(abpy)]$_n$ polymer reformer from the NO$_2$ reaction may also be within experimental error as the surface area of these soft materials is very sensitive to handling conditions.$^6$

**CONCLUSIONS**

In conclusion, we report the reactivity of the porous and electrically conductive copper azobispyridine metallopolymer, [Cu(abpy)]$_n$, with NO$_2$. Intriguingly, XAS analysis indicates that the oxidation state of the copper ions increases upon reduction of [Cu(abpy)PF$_6$]$_n$ to generate [Cu(abpy)]$_n$, indicating that the abpy ligands are actively engaged in the redox reactions of these materials. The redox reaction between NO$_2$ and [Cu(abpy)]$_n$ results in the disproportionation of NO$_2$ into nitrate and NO gas, as evidenced by vibrational spectroscopy and single-crystal X-ray diffraction. EPR and XAS provide evidence for the oxidation of both the ligand and the copper center upon reaction of [Cu(abpy)]$_n$ with NO$_2$. Upon exposure to NO$_2$, the metallopolymer’s room-temperature conductivity value drops by four orders of magnitude as it loses its mixed-valence character. Additionally, NO$_2$ dosing causes the metallopolymer to completely lose porosity. Lastly, [Cu(abpy)]$_n$ metallopolymer may be regenerated after oxidation by NO$_2$ by chemical reduction, recovering much of the electrical conductivity, porosity, and optical properties of the parent polymer. These promising findings make [Cu(abpy)]$_n$ a good platform for developing materials for NO$_2$ sensing and sequestration.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01190.

Experimental descriptions, synthetic procedures, and material characterization (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: waymouth@stanford.edu.
*E-mail: hemamala@stanford.edu.
*E-mail: ritits@slac.stanford.edu.

**ORCID**
Naomi E. Clayman: 0000-0002-4894-2174
Benjamin D. Matson: 0000-0001-5733-0893
Shengkai Wang: 0000-0003-0947-4643
Ritumika Sarangi: 0000-0002-2764-2279
Hemamala I. Karunadasa: 0000-0003-4949-8068
Robert M. Waymouth: 0000-0001-9862-9509

**Author Contributions**
*N.E.C and M.A.M. contributed equally.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

N.E.C. and R.M.W. thank the Office of Naval Research (ONR N000141410551) and the Center for Molecular Analysis and Design (CMD) for a graduate fellowship. Work by M.A.M., A.H.S., and H.I.K. was funded by an NSF CAREER award (DMR-1351538). M.A.M. thanks CMD, the National Science Foundation (NSF; award DGE-114747), and Stanford’s Diversifying Academia, Recruiting Excellence Program for fellowships. B.D.M. was supported by the Precourt Institute for Energy (2017-4-Waymouth). Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract DE-AC02-76SF00515. Single crystal X-ray diffraction was performed on Beamline 11.3.1 at the Advanced Light Source, which is a DOE Office of Science User Facility under Contract DE-AC02-05CH11231. We thank Prof. Matteo Cargnello and Dr. Michael Aubrey for...
helpful discussions. We thank Dr. Abraham Saldivar Valdes, Dr. Michael Aubrey, Dr. Matthew D. Smith, Kurt Lindquist, and Katherine Walker for experimental assistance. We thank Prof. Edward I. Solomon and Prof. Ronald K. Hanson for access to equipment. XAS measurements were performed at beamline 7-3 at the Stanford Synchrotron Radiation Light-source (SSRL).

References


