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# Reactivity of NO<sub>2</sub> with Porous and Conductive Copper **Azobispyridine Metallopolymers**

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**S** Supporting Information

ABSTRACT: We report the reactivity of copper azobispyridine (abpy) metallopolymers with nitrogen dioxide  $(NO_2)$ . The porous and conductive  $[Cu(abpy)]_n$  mixed-valence metallopolymers undergo a redox reaction with NO<sub>2</sub>, 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 NO<sub>2</sub> results in complete loss of porosity and a decrease in the roomtemperature 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 NO<sub>2</sub> 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.<sup>1</sup> These biological and environmental concerns have motivated studies to identify materials that can sense or react with and capture  $NO_2$ .<sup>1-5</sup> Sensor technologies have been developed to detect small amounts of NO<sub>2</sub> gas.<sup>1-5</sup> Materials that react with NO<sub>2</sub> without interfering reactions with more abundant gaseous species  $(N_2,$  $O_{2}$ ,  $CO_{2}$ ) also have potential environmental applications for the capture and sequestration of these toxic gases.

We previously described<sup>6</sup> the electrically conductive and porous copper azobispyridine (abpy) metallopolymers [Cu- $(abpy)]_n$ . These metallopolymers exhibit an unusual combination of substantial conductivity (0.18  $\,S{\cdot}cm^{-1}$  at room temperature) and porosity (90  $m^2 \cdot g^{-1}$ ). The conductivity of the neutral polymer, with oxidation states formally assigned as  $[Cu^+(abpy^{-\bullet})]_n$ , was attributed to its mixed-valence character.<sup>6</sup> The  $[Cu(abpy)]_n$  metallopolymer can be reversibly oxidized at –0.8 V vs Ag/AgNO\_3 to the insulating (<10  $^{-10}~{\rm S}{\cdot}{\rm cm}^{-1})$  and nonporous cationic metallopolymer, formally assigned as  $[Cu^{+}(abpy^{0})X]_{n}$  (X = monoanion). As a reducing, porous



material, we anticipated that the neutral metallopolymer might react with oxidizing gases such as NO<sub>2</sub>.

Herein, we report the reaction of the porous and conductive  $[Cu(abpy)]_n$  with NO<sub>2</sub> 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 (NO<sub>3</sub><sup>-</sup>). Notably, after exposure to NO<sub>2</sub> gas, the resulting oxidized material can be reduced to regenerate [Cu(abpy)]<sub>n</sub> with approximately 75% recovery of the porosity and conductivity of the original metallopolymer.

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# RESULTS AND DISCUSSION

Metallopolymer  $[Cu(abpy)]_n$ , generated from the chemical reduction of  $[Cu(abpy)PF_6]_n$  with  $Cp_2Co,^6$  was used for all  $NO_2$  reactivity studies. Black powders of  $[Cu(abpy)]_n$  were dosed with either a mixture of  $NO_2$  (1%) in dry air (99%) or a mixture of  $NO_2$  (2%) in dry  $N_2$  (98%) at room temperature for variable amounts of time. Solid  $[Cu(abpy)]_n$  is insoluble in water and organic solvents. After exposure to  $NO_2$ , the resulting green powders become soluble in most polar organic solvents such as acetonitrile ( $CH_3CN$ ) 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%  $NO_2$  in  $N_2$  reveals the presence of NO gas (approximately 0.6 mol %; Figure 1), as determined by mid-IR tunable diode laser



**Figure 1.** Mid-IR laser absorption analysis of the gas product of  $[Cu(abpy)]_n$  dosed with NO<sub>2</sub> (red). The strong characteristic absorption of NO appears near 1920.71 cm<sup>-1</sup>. In this example, the final NO mole fraction in the reactor headspace was determined to be 6150 ppm. As a control, the 2% NO<sub>2</sub>/N<sub>2</sub> 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 near 1920 cm<sup>-1</sup>. The evolution of NO gas is very fast, occurring within the first 0.2 s of NO<sub>2</sub> 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).

Several experiments were carried out to identify the other nitrogen oxides generated from the reaction of the metal-lopolymer  $[Cu(abpy)]_n$  with NO<sub>2</sub>. The reaction products were dissolved in CH<sub>3</sub>CN and analyzed by electrospray-ionization mass spectrometry (ESI-MS, see Supporting Information). The most intense peak in the spectrum in negative mode is an ion at 61 m/z, corresponding to NO<sub>3</sub><sup>-</sup> (Figure S2). Of the ions observed in positive mode, one corresponds to Cu(abpy)<sub>2</sub><sup>+</sup> (431 m/z, Figure S3), indicating fragmentation of the polymer chain upon exposure to NO<sub>2</sub>. We also observe adducts of copper, azobispyridine ligand, and NO<sub>3</sub><sup>-</sup>. The ESI-MS indicates that [Cu(abpy)]<sub>n</sub> is oxidized by NO<sub>2</sub>, and the copper speciates as a NO<sub>3</sub><sup>-</sup> adduct. No nitrate is observed in the ESI-MS of acetonitrile saturated with 2% NO<sub>2</sub> in N<sub>2</sub>.

To better understand the metallopolymer's reactivity with NO<sub>2</sub>, we carried out similar studies with  $(Cu(azpy)_2)^6$  (1) (azpy = phenylazo-2-pyridine), a molecular analogue of  $[Cu(abpy)]_n$  where one pyridyl ring per Cu center is replaced by a phenyl ring to prevent bridging to another Cu center. Here, the ligand-based mixed valence is formally designated as  $Cu^+(azpy^{0.5-})_2$ .<sup>6</sup> Before exposure of  $Cu(azpy)_2$  to NO<sub>2</sub>, the



major ion observed in positive mode exhibited an m/z value of 429, corresponding to  $Cu(azpy)_2^+$  (Figure S4). After exposure of powders of  $Cu(azpy)_2$  to NO<sub>2</sub> gas, the ESI-MS spectrum of  $Cu(azpy)_2$  changes. A new ion with a m/z of 491, corresponding to  $[Cu(azpy)_2NO_3]^+$ , emerges (Figure S5), in addition to an ion at 308 m/z, 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  $[Cu^{2+}(azpy^0)NO_3]^+$ . This observation implies that the nitrate anion is coordinated to the Cu<sup>II</sup> 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 NO<sub>2</sub> exposure.

Reduction of the powder obtained through exposure of  $[Cu(abpy)]_n$  to NO<sub>2</sub> gas with cobaltocene (Cp<sub>2</sub>Co) results in the precipitation of a black solid and yellow supernatant. Slow vapor diffusion of pentane into the dichloromethane/CH<sub>3</sub>CN supernatant held at -20 °C afforded yellow needles of cobaltocenium nitrate ( $Co^{III}Cp_2NO_3$ ;  $Cp = C_5H_5^-$ ) as confirmed by single-crystal X-ray diffraction (Figure S8). The isolation of a nitrate salt further verifies the oxidation of NO2 to NO<sub>3</sub><sup>-</sup> by the metallopolymer. We obtained crystals of  $Co^{III}Cp_2NO_3$  regardless of whether the reaction with NO<sub>2</sub> was performed in dry air or dry N2. The crystallization of Cp<sub>2</sub>CoNO<sub>3</sub> under O<sub>2</sub>-free conditions indicates that all three oxygen atoms in NO<sub>3</sub><sup>-</sup> originate from the NO<sub>2</sub> and not from  $O_2$ . Confirmation of the origin of the oxygen atoms in  $NO_3^$ 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  ${}^{16}O_2$ , and one codosed with  ${}^{18}O_2$ . 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 <sup>18</sup>O<sub>2</sub> was introduced into the system, confirming that the oxygens in  $NO_3^-$  are derived from  $NO_2$ .

We probed the solid-phase–gas-phase reaction between  $[Cu(abpy)]_n$  and  $NO_2$  by a variety of spectroscopic techniques. Powders of  $[Cu(abpy)]_n$  display a broad absorbance around ~2500 cm<sup>-1</sup> in the mid-infrared region (Figure S10).<sup>6</sup> This absorbance is the low-energy tail of the band we assign as a predominantly ligand-based intervalence charge transfer  $(IVCT)^7$  band. This IVCT band is absent in the IR spectrum of  $[Cu(abpy)]_n$  after  $NO_2$  dosing (Figure S10), suggesting that the product no longer possesses radical abpy ligands. Upon  $NO_2$  dosing, we also observe the emergence of a new peak at 1273 cm<sup>-1</sup> (Figure S10), which has been previously attributed to coordinated nitrate  $(NO_3^-)$  in anhydrous cupric nitrate.<sup>8</sup>

Changes in electronic structure after NO<sub>2</sub> 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.<sup>6</sup> The solid-state EPR spectrum of  $[Cu(abpy)]_n$  after 16 h of NO<sub>2</sub> (2%) exposure reveals that this broad, symmetrical signal in  $[Cu(abpy)]_n$  diminishes upon exposure to NO<sub>2</sub>. We also observe the emergence of a new signal with characteristic rhombic Cu<sup>II</sup> spectral shape (Figure S12A).<sup>9</sup> There is literature precedent for disproportionation of NO<sub>2</sub> on electron-rich surfaces, and in fact, Addison et al.<sup>10</sup> report the isolation of Cu<sup>II</sup>(NO<sub>3</sub>)<sub>2</sub> and NO gas when copper metal is treated with NO<sub>2</sub> in the form of liquid N<sub>2</sub>O<sub>4</sub>.

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 NO<sub>2</sub> dosing, as well as in  $[Cu(abpy)PF_6]_n$ . The Cu K rising edge region is dominated by Cu 1s  $\rightarrow$  4p+ continuum transitions (~8979 eV) and is therefore strongly modulated by the effective nuclear charge  $(Z_{eff})$  on Cu.<sup>11-14</sup> The rising edge of  $[Cu(abpy)PF_6]_n$ , measured as the maximum of the first derivative, occurs at an energy of 8982.6 eV and is very similar in energy and shape to that of the molecular model compound  $[Cu(azpy)_2][PF_6]_{n}^{15}$ which has a slightly higher rising edge energy of 8983.4 eV.

The rising edge of both  $[Cu(abpy)PF_6]_n$  and  $[Cu(azpy)_2]$ - $[PF_6]^{15}$  occur at an energy higher than that of  $[Cu(bpy)_2]$ - $[PF_6]$  (bpy = 2,2'-bipyridine), indicating an increase in  $Z_{eff}$  on Cu as the bipyridine ligand is replaced with more redox-active azpy or abpy ligands, indicating that  $[Cu(abpy)PF_6]_n$  is better represented as  $[Cu^{1+\delta}(abpy^{-\delta})PF_6]_n$ . 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  $Z_{eff}$  on Cu upon reduction of [Cu(abpy)-



**Figure 2.** Normalized Cu–K edge XAS spectra of (A)  $[Cu^{I}(abpy)-PF_{6}]_{n}$  (teal),  $[Cu(abpy)]_{n}$  (blue), and  $Cu^{I}(bpy)_{2}PF_{6}$  (bpy = 2,2'-bipyridine; orange), a Cu<sup>I</sup> standard, and (B)  $Cu^{II}(bpy)_{2}(BF_{4})_{2}$  (purple), a Cu<sup>II</sup> standard, and  $[Cu(abpy)]_{n}$  after exposure to NO<sub>2</sub> gas for 24 h (red).

PF<sub>6</sub>]<sub>n</sub>: the Cu metal centers appear to be more oxidized after a bulk reduction of the material, resulting in  $[Cu^{1+\Delta}(abpy^{-(1+\Delta)})]_n$ , where  $\Delta > \delta$ . Although rare, a similar phenomenon has been observed in molybdenum and tungsten compounds with sulfur-based redox noninnocent ligands, wherein a net oxidation of the compound resulted in a reduction of the metal center.<sup>16–19</sup> Dosing  $[Cu(abpy)]_n$  with NO<sub>2</sub> results in a dramatic blue-shifting of the rising edge energy to 8986.2 eV. Thus, the reaction of  $[Cu(abpy)]_n$  with NO<sub>2</sub> yields copper species with rising edge energies similar to that of the Cu<sup>II</sup>(bpy)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> (8986.3 eV, Figure 2B), indicating that the oxidation states of the products of NO<sub>2</sub> exposure are most reasonably formulated as Cu<sup>II</sup> species.

Combining evidence from IR spectroscopy, EPR, and XAS, we propose that  $[Cu(abpy)]_n$  reacts with four equivalents of NO<sub>2</sub> gas per copper center, where NO<sub>2</sub> oxidizes both the Cu and the abpy ligand and disproportionates to form NO<sub>3</sub><sup>-</sup> and NO. Although approximate oxidation state assignments are given below, we note that there is considerable electronic delocalization between Cu and the abpy ligand, as discussed above:

$$Cu^{I}(abpy^{-}) + 4NO_{2} \rightarrow Cu^{II}(abpy^{0})(NO_{3}^{-})_{2} + 2NC_{2}$$

Solid  $[Cu(abpy)]_n$  has a room-temperature conductivity of 0.18 S·cm<sup>-1</sup>, which increases up to 0.46 S·cm<sup>-1</sup> upon heating to 125 °C, and an activation energy for conduction of 98 meV.<sup>6,20</sup> Upon exposing powders of  $[Cu(abpy)]_n$  to NO<sub>2</sub> (2%) for 1 h, the room-temperature conductivity of the material drops to  $8.5 \times 10^{-2}$  S·cm<sup>-1</sup>. After 16 h of exposure, the room-temperature conductivity value decreases to  $6.4 \times 10^{-5}$  S·cm<sup>-1</sup>. Likewise, the activation energy increases up to 290 meV upon NO<sub>2</sub> dosing. Electrical conductivity in  $[Cu(abpy)]_n$  is thought to arise from electron hopping between radical mixed-valence abpy ligands.<sup>6</sup> From the EPR and IR spectra, we infer that the redox reaction between NO<sub>2</sub> and  $[Cu(abpy)]_n$  results in a loss of mixed valency. A decrease in conductivity upon NO<sub>2</sub> 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 NO<sub>2</sub> exposure. Fine powders of  $[Cu(abpy)]_n$  have a Brunauer–Emmett–Teller (BET) surface area of 90 m<sup>2</sup>·g<sup>-1.6</sup> Concomitant with loss of conductivity, we also observe a complete loss of porosity after NO<sub>2</sub> dosing for 16 h (Figure 3). The observed lack of porosity in NO<sub>2</sub>-dosed  $[Cu(abpy)]_n$  is



**Figure 3.** Nitrogen isotherms measured at 77 K of  $[Cu(abpy)]_n$  before exposure to NO<sub>2</sub> gas (blue), after NO<sub>2</sub> exposure (red), and after regeneration of the material by Cp<sub>2</sub>Co reduction (green). Surface areas are 90 m<sup>2</sup>/g, ~0 m<sup>2</sup>/g, and 70 m<sup>2</sup>/g, respectively.

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  $Cp_2Co$  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<sub>2</sub>, 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<sub>2</sub> exposure. The reemergence of the IVCT indicates the reformation of radical abpy ligands upon reduction.

The regenerated material has a room-temperature conductivity  $(7.8 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1})$  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<sup>-1</sup> and 98 meV, respectively). Furthermore, we find that the regenerated material regains a significant fraction of the porosity with a BET surface area of 70 m<sup>2</sup>·g<sup>-1</sup> (vs 90 m<sup>2</sup>·g<sup>-1</sup> 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 = Br<sup>-</sup>,  $PF_6^-$ ,  $BAr_4^{F_4^-}$ ) from which it is generated.<sup>6</sup> 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<sup>2</sup> g<sup>-1</sup> (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  $NO_3^-$ .<sup>6</sup> 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<sup>2</sup>·g<sup>-1</sup> difference in surface area between the  $[Cu(abpy)]_n$  polymer generated from  $[Cu(abpy)NO_3]_n$  and the  $[Cu(abpy)]_n$  polymer reformed 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.<sup>6</sup>

# CONCLUSIONS

In conclusion, we report the reactivity of the porous and electrically conductive copper azobispyridine metallopolymer,  $[Cu(abpy)]_n$ , with NO<sub>2</sub>. 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 NO2 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<sub>2</sub>. Upon exposure to NO<sub>2</sub>, the metallopolymer's room-temperature conductivity value drops by four orders of magnitude as it loses its mixed-valence character. Additionally, NO<sub>2</sub> dosing causes the metallopolymers to completely lose porosity. Lastly,  $[Cu(abpy)]_n$  metallopolymers can be regenerated after oxidation by NO<sub>2</sub> 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<sub>2</sub> sensing and sequestration.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

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

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

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#### Notes

The authors declare no competing financial interest.

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