Anion Exchange Dynamics in the Capture of Perchlorate by a Cationic Ag-Based MOF

Ian R. Colinas, Kenneth K. Inglis, Frédéric Blanc and Scott R.J. Oliver

We report a detailed study of the host-guest interaction for a cationic metal-organic framework that can reversibly capture perchlorate. The structural transformation and flexibility of silver 4,4′-bipyridine nitrate (SBN) upon formation of silver 4,4′-bipyridine perchlorate (SBP) was evaluated by monitoring the anion exchange dynamics using a combination of powder X-ray diffraction (PXRD) with multinuclear 13C, 15N and 109Ag solid-state NMR spectra at different time intervals of the anion exchange. The structural transformation from SBN to SBP is complete within 70 minutes and was determined to take place by a solvent-mediated process. This pathway is confirmed by the morphological changes of the two crystalline materials observed by SEM. This key understanding may lead to application of this material towards perchlorate capture.

Recently, MOFs have been under intense investigation due to their ability to exchange their intrapore or interlayer ions with other ionic species in solution. Their structural integrity is not compromised, which make these materials excellent candidates for the separation of pollutants. The adsorptive separation of pollutant species in the gas phase, such as carbon dioxide or methane, is driven by the reversible dynamic behavior of the network, often referred to as "breathing". This action results in a change of interaction strength between the guest molecules and host framework due to framework displacement accompanied by a change in the unit cell volume. There has been much less effort into understanding the structural flexibility and dynamic transformations that solid MOFs exhibit during adsorption and/or ion exchange. The mechanism by which such ion exchange processes take place has been proposed to be either by a solid state or a solvent-mediated transformation. In the case of a solid state transition, the ion exchange proceeds through the diffusion of free ions within the channels of the coordination polymer crystals. In contrast, the solvent-mediated process involves the dissolution of the initial coordination polymer followed by the formation and crystallization of a new coordination polymer from the solution phase.

The structural transformations that coordination polymers undergo during ion exchange processes can be monitored by single crystal or powder X-ray diffraction (PXRD) of the MOF in combination with analytical measurements of the solution towards incoming and outgoing guests. If possible, single crystal X-ray crystallographic methods are preferred for the exact structural determination of the new MOF phase upon adsorption. This methodology, however, provides limited structural information regarding the dynamic behavior of the framework during exchange due to the absence or sufficient size/quality of crystals. In contrast, magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy
provides structural information about the local environment. Organic linkers of the MOFs. Hence, NMR spectroscopy could be used in conjunction with XRD methods as a complement. This technique for analyzing the exchange dynamics of M@N materials. NMR is well suited to probe the structural flexibility and reversible dynamic behavior of a framework undergoing ion exchange. Jiang et al. reported the structural flexibility of a Cu(bipy)$_2$(H$_2$O)$_2$(BF$_4$) (bipy = 4,4'-bipyridine) framework by chemisorption of probe molecules that could induce reversible structural changes. The transitions could be monitored by $^{13}$B MAS NMR as a result of the change in polarization of the probe molecule and its interaction with Cu(I) sites. In our previous work, we reported the successful capture of aqueous perchlorate by Silver 4,4'-Bipyridine Nitrate (SBN) to yield a Silver 4,4'-Bipyridine Perchlorate (SBP) MOF. We showed that SBM effectively exchanged guest NO$_3^-$ ions to ClO$_4^-$ ions at a record capacity of 354 mg/g within 90 minutes. The solubilities of the complex pairs as well as the relative stabilities of the complex pairs were determined by 31P NMR spectroscopy. All other experimental details are given in Table S1. The structural transformation is followed by analysis of the [Ag(bipy)]$^+$ material at different time intervals using PXRD, Ion Chromatography (IC) analysis was performed at a Wide Bore 400 MHz 9.4 T Bruker Avance III HD NMR spectrometer equipped with a 4 mm HXY triple-resonance MAS probe (in double resonance mode) for $^{13}$C and $^{15}$N and with a 4 mm HX MAS probe for $^{109}$Ag or on a Wide Bore 850 MHz 20 T Bruker AVANCE 600 MHz NMR spectrometer equipped with a 3.2 mm HXY triple-resonance MAS probe (in double resonance mode) for $^{13}$C. Data acquisition was performed with cross polarization (CP) and SPINAL-64 heteronuclear decoupling. Recycle delays ranging from 30 to 180 s were used and correspond to 1.3 $\times$ $^{1}$H $T_1$ (measured by $^{1}$H saturation recovery experiments). All other experimental details are given in Table S1. The 13C, 15N and 109Ag chemical shifts were referenced to the CH carbon of adamantane at 29.45 ppm, glycine at 33.44 ppm (corresponding to liquid NH$_4$ at 0 ppm) and a saturated solution of AgNO$_3$ in D$_2$O [with 0.24 M of Fe(NO$_3$)$_3$] at 0 ppm, respectively. All samples were packed in air. Using the Haeberlen convention, the principal components $\delta_{11}$, $\delta_{22}$, $\delta_{13}$ of the chemical shift tensors were defined such that $|\delta_{11} - \delta_{22}|$ $>$ $\delta_{13}$ $>$ $|\delta_{12} - \delta_{13}|$. $\delta_{13}$ is the isotropic chemical shift and related to the principal components of the shielding tensor by $\delta_{13} = (\delta_{11} + \delta_{22} + \delta_{12})/3$. The chemical shift anisotropy $\delta_{ani}$ is defined as $\delta_{ani} = \delta_{13} - \delta_{iso}$ and the deviation from axial symmetry given by the asymmetry parameter $\eta = (\delta_{22} - \delta_{11})/\delta_{ani}$.

2. Experimental

2.1 Synthesis. In short, a mixture of AgNO$_3$ (AgNO$_3$, Fisher, 99%, 0.1 g, 0.59 mmol), 4,4'-bipyridine (Acros Organics, 98%, 0.1 g, 0.64 mmol) and deionized water (10 ml) was stirred at room temperature for 3 days in a sealed beaker. Pale gray crystals were isolated after filtration and rinsed with water (10 ml) and acetone (5 ml) to yield SBM (0.187 g, 97.6 % based on silver nitrate). Batch anion exchange experiments were carried out under ambient conditions by mildly stirring the ground SBM (80 mg, 0.25 mmol) with 50 ml deionized water and NaClO$_4$ (Fluka Analytical, 98 %, 35 mg, 0.25 mmol). The post-exchange crystalline SBP product was recovered at the different time intervals by vacuum filtration and rinsed with water (10 ml) and acetone (5 ml).

2.2 Regeneration. The regeneration of SBM from SBP was carried out by stirring the ground SBM (80 mg, 0.22 mmol) in a 0.1 M NaNO$_3$ solution (NaNO$_3$, Fisher, 99 %) at 70 °C for 24 h. The regeneration of the SBM was studied by recording the PXRD, $^{13}$C, $^{15}$N, $^{109}$Ag CP MAS NMR data and SEM images after treatment of the SBM material with excess nitrate at 70 °C under stirring...

2.3 Characterization. PXRD data were measured on a Rigaku Americas Miniflex Plus diffractometer, scanning from 2 to 40 ° (2θ) at a rate of 2 °/min with a 0.04 ° step size under Cu Ka radiation ($\lambda = 1.5418$ Å). Ion Chromatography (IC) analysis was performed to assess the perchlorate concentration using a Dionex ICS-3000 with an IonPac AS20 column and a detection limit of 3 μg/L (ppb). SEM data were collected with a FEI Quanta 3D Dualbeam microscope. Solid-state NMR: experiments were performed at room temperature on a Wide Bore 400 MHz 9.4 T Bruker Avance III HD NMR spectrometer equipped with a 4 mm HXY triple-resonance MAS probe (in double resonance mode) for $^{13}$C and $^{15}$N and with a 4 mm HX MAS probe for $^{109}$Ag or on a Wide Bore 850 MHz 20 T Bruker AVANCE spectrometer equipped with a 3.2 mm HXY triple-resonance MAS probe (in double resonance mode) for $^{13}$C. Data acquisition was performed with cross polarization (CP) and SPINAL-64 heteronuclear decoupling. Recycle delays ranging from 30 to 180 s were used and correspond to 1.3 $\times$ $^{1}$H $T_1$ (measured by $^{1}$H saturation recovery experiments). All other experimental details are given in Table S1. The 13C, 15N and 109Ag chemical shifts were referenced to the CH carbon of adamantane at 29.45 ppm, glycine at 33.44 ppm (corresponding to liquid NH$_4$ at 0 ppm) and a saturated solution of AgNO$_3$ in D$_2$O [with 0.24 M of Fe(NO$_3$)$_3$] at 0 ppm, respectively. All samples were packed in air. Using the Haeberlen convention, the principal components $\delta_{11}$, $\delta_{22}$, $\delta_{13}$ of the chemical shift tensors were defined such that $|\delta_{11} - \delta_{22}|$ $>$ $\delta_{13}$ $>$ $|\delta_{12} - \delta_{13}|$. $\delta_{13}$ is the isotropic chemical shift and related to the principal components of the shielding tensor by $\delta_{13} = (\delta_{11} + \delta_{22} + \delta_{12})/3$. The chemical shift anisotropy $\delta_{ani}$ is defined as $\delta_{ani} = \delta_{13} - \delta_{iso}$ and the deviation from axial symmetry given by the asymmetry parameter $\eta = (\delta_{22} - \delta_{11})/\delta_{ani}$.
initial dissociation of silver nitrate followed by the self-assembly of the cationic polymer chains, charge balanced by nitrate ions. This can undergo quantitative anion exchange upon exposure to ClO₄⁻ solution to yield SBP with a 99% conversion as determined by monitoring the concentration of ClO₄⁻ in solution from chromatography (IC). The PXRD data confirms the identity of two crystalline phases as they match the theoretical patterns based on the single crystal solution (Figure S1). After 10 minutes of exposure to ClO₄⁻, the intensity of the low angle (002) peak decreases and a new set of peaks [e.g. 22°, 28°], corresponding to the (211) plane of the SBP crystalline phase begin to appear, indicating initiation of the process.

Based on the above structural considerations, it is clear that the two coordination polymers are structurally different in the arrangement of the cationic layers as well as the location of the anions. Such structural differences suggest that the anion exchange may proceed by a solvent-mediated process involving the initial dissolution of the SBN T-shaped polymers followed by the crystallization of eclipsed SBP polymers from the perchlorate solution (Figure S2). In order to support this hypothesis, the anion exchange was monitored versus time by both PXRD (Figure 2) and multinuclear MAS NMR (Figure 3).

After 25 minutes, the PXRD pattern is an approximately equal mixture of both the SBN and SBP crystal phases, indicating that the anions have been partially exchanged. The relative amounts of both phases were verified by measuring the residual concentration of perchlorate in the anion exchange solution at different time intervals with ion chromatography (Figure S3). The predominance of the SBP phase is observed after 40 minutes, where the low angle peaks corresponding to (001) and (100) of SBP are now higher intensity relative to the peaks of SBN. After 70 minutes, the anion exchange is complete and the PXRD pattern is pure phase SBP (see below for recovery to SBN). In addition, a shift in the (001) and (100) phases to a higher 2-theta indicates that the d-spacing decreased, likely due to a contraction of the structure upon completion of the anion exchange.

The ¹³C CP MAS NMR spectra of SBN and SBP (black and purple spectra, Figure 3a) obtained at 20 T show three different isotropic resonances δiso at 153.3-152.7, 144.1-143.8 and 123.3-121.7 ppm for the individual carbons in the asymmetric unit and correspond to the

### Table 1. Structural properties of SBN and SBP

<table>
<thead>
<tr>
<th>Property</th>
<th>SBN</th>
<th>SBP</th>
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<tr>
<td>Ag(I)/Ag(II)/Å</td>
<td>2.97(1)</td>
<td>3.60(1)</td>
</tr>
<tr>
<td>Anion O/Ag(II)/Å</td>
<td>2.826(17), 2.782(10)</td>
<td>2.945(15), 2.863(10)</td>
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<tr>
<td>Anion O-Ch(V)/Å</td>
<td>3.374(10)</td>
<td>3.352(10)</td>
</tr>
<tr>
<td>n-stacking / Å</td>
<td>3.55</td>
<td>3.47</td>
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Figure 1. (a) Crystallographic view of SBN in the "a" plane and (b) "b" plane. (b) Crystallographic view of SBP in the "a" plane, and (d) "c" plane. The nitrate oxygens are disordered between two sites (Ag, magenta; N, blue; O, red; C, black; Cl, green).

Figure 2. PXRD patterns of the SBN/SBP anion exchange of SBN pre-exchange (black), after 10 min (red), 25 min (blue), 40 min (green), complete exchange to SBP after 70 min (purple), and regeneration to SBN (grey).

Both SBN and SBP structures consist of Ag(I) chelated by the nitrogens of two different (µ-2)-4,4'-bipyridine units that result in extended polymeric chains. The chains align parallel into a non n-stacked layer where the rings are coplanar with the plane of the page. The two structures differ in the arrangement of their subsequent layers. For SBN, the cationic layers are rotated by 90°, forming a crisscross or T-shaped pattern in which half the pyridine rings n-stack in a staggered manner with a distance of 3.55 Å from the next layer (Figure 1). In addition, half of the Ag(I) centers are dimerized and cross linked to the next layer by the formation of Ag-Ag bonds with a distance of 2.97(1) Å. In contrast, the cationic layers in SBP are eclipsed, resulting in n-stacking of all the pyridine rings and a shorter interlayer distance of 3.47 Å (Figure 1). The Ag(I) centers have a long contact distance of 3.60(1) Å, which is well above the covalent range. These longer Ag-Ag distances allow for the spherical ClO₄⁻ anions to be more spread out between the polymeric interlayers. The ClO₄⁻ to Ag(I) distance is therefore greater for SBP than for SBN but closer contact of the anions to the bipyridine CHC⁺ in SBP (Table 1).
Figure 3. (a) $^{13}$C, (b) $^{15}$N and (c) $^{109}$Ag CP MAS NMR of the SBN/SBP anion exchange of SBN pre-exchange (black), after 10 min (red), 25 min (blue), complete exchange to SBP (purple) and regeneration back to SBN (grey). Spectral assignments are given in the figure. The $^{13}$C spectra were obtained at 20 T while the $^{15}$N and $^{109}$Ag were obtained at 9.4 T. In (b), the insets show magnified views of the 280–250 ppm isotropic region of the AgN resonances. In (c), the insets show magnified views of the first left spinning sidebands in the 650–450 ppm region. Spinning sidebands are marked with asterisks (*).

$^{13}$C, $^{15}$N and $^{109}$Ag ions in the 4,4'-bipyridine ligand respectively. As the NO$_3^-$ – ClO$_4^-$ anion exchange progresses by dissolution of SBN and subsequent capture of the ClO$_4^-$ by the crystallization of SBP, a downfield shift of around 1.6 ppm is clearly observed in the signal of the CHCIV carbon (Figure 3a) at 121.7 ppm. The spinning sideband manifold yields an axially symmetric chemical shift tensor ($\delta_\text{iso}$) = 438.5 ppm and is consistent with a single silver atom environment in SBP. This resonance is a quintet with a spacing of 61 Hz, corresponding to the indirect scalar coupling between $^{109}$Ag and $^{14}$N (99.63 % nat. ab., I = 1). The approximate 1:2:3:2:1 relative intensity of the quintet is expected for coupling to two equivalent I = 1 nuclei and the crystal structure of SBP presenting a silver atom nitrogen-bonded by two bipy ligands. Note that the $^J_{15N-109Ag}$: $^J_{109Ag-14N}$ ratio is 1.38, close to the expected $^{15}$N : $^{14}$N magnetic moment ratio of 1.40. Additionally, the spinning sideband manifold yields an axially symmetric chemical shift tensor (i.e. $\eta = 0$). This observation agrees well with the almost linear environment of the N–Ag(1)–N moiety in the bipy–Ag–bipy polymers (173.73°, Table 1).

As SBN is converted into SBP by addition of ClO$_4^-$, the relative ratio of the NO$_3^-$ anions and the bipy ligand signals at 379.3 and 263.9 ppm in the $^{15}$N CP MAS NMR spectra decreases, until a single nitrogen environment is detected. The $^{109}$Ag CP MAS NMR spectrum (purple, Figure 3c) shows a doublet with $^J_{15N-109Ag}$ = 81 Hz for the former resonances and results from the indirect scalar coupling arising from coordination of the nitrogen atoms of bipy to the silver atoms, as expected from the crystal structure (Figure 1)

The $^{109}$Ag CP MAS NMR spectra of SBN (purple, Figure 3c) shows a series of intense spinning sidebands spanning over approximately 1000 ppm, in agreement with the large chemical shift anisotropy of $^{109}$Ag of $\delta_\text{iso} = -774$ ppm. Note that the relative low signal to noise ratio of this $^{109}$Ag spectrum arises from the very low magnetic moments of this nucleus. A single isotropic resonance appears at $\delta_\text{iso} = 438.5$ ppm and is consistent with a single silver atom environment in SBP. This resonance is a quintet with a spacing of 61 Hz, corresponding to the indirect scalar coupling between $^{109}$Ag and $^{14}$N (99.63 % nat. ab., I = 1). The approximate 1:2:3:2:1 relative intensity of the quintet is expected for coupling to two equivalent I = 1 nuclei and the crystal structure of SBP presenting a silver atom nitrogen-bonded by two bipy ligands. Note that the $^J_{15N-109Ag}$: $^J_{109Ag-14N}$ ratio is 1.38, close to the expected $^{15}$N : $^{14}$N magnetic moment ratio of 1.40. Additionally, the spinning sideband manifold yields an axially symmetric chemical shift tensor (i.e. $\eta = 0$). This observation agrees well with the almost linear environment of the N–Ag(1)–N moiety in the bipy–Ag–bipy polymers (173.73°, Table 1).
Hz centred at $\delta_{iso} = 261.4$ ppm. This signal is due to the nitrogen atoms of bipy that are bonded to Ag. No resonance could be detected at 379.3 ppm in SBP, consistent with the complete NO$_3^-$ - ClO$_4^-$ anion exchange as seen by PXRD. The very small difference in chemical shift between the nitrogen atoms of bipy in SBN and SBP likely arises from the greater deshielding of the bipy nitrogen in SBN by the NO$_3^-$ that is in closer proximity to the silver atom. The $^{15}$N CP MAS NMR spectra for SBN and SBP are therefore consistent with the $^{13}$C CP MAS NMR spectra in the arrangement of the Ag-bipy cationic layers upon exchange of NO$_3^-$ for ClO$_4^-$ perchlorate anions.

Upon SBN/SBP anion exchange, the $^{109}$Ag CP MAS NMR spectra (Figure 3c) reveal the appearance of an additional isotropic resonance at approximately $\delta_{iso} = 341$ ppm. Its intensity increases with ClO$_4^-$ content and is attributed to the [Ag-bipy]$^+$ moiety in SBP. Upon total exchange, the $^{109}$Ag signal of SBN completely disappears, in agreement with the PXRD $^{13}$C and $^{15}$N data discussed above. Note that no $^{1}J$(H$_{Ag}$, $^{14}$N) scalar coupling could be clearly detected in the $^{109}$Ag CP MAS NMR spectrum of SBP, probably resulting from slightly broader NMR lines and disorder. An axially symmetric $^{109}$Ag chemical shift tensor with $\delta_{iso}$ = -776 ppm and $\eta$ = 0 is also obtained, with the later value in agreement with the linear N - Ag(I) - N angle in SBP (Table 1).

The change in morphology of the SBN crystals during anion exchange with ClO$_4^-$ was investigated by performing batch tests experiments, stopping the reaction at various time intervals to analyze the resulting crystals by SEM (Figure 4). Initially, the synthesis of SBN yields smooth block-shaped crystals with an average width of 4 to 10 µm (black, top left, Figure 4). Upon 10 min of exposure of the SBN crystals to the ClO$_4^-$ aqueous solution, the smooth block shaped crystals began to display indentations at the surface (red, Figure 4). These indentations show that the new SBP phase is beginning to form on the SBN crystals, similar to that reported by Schröder and coworkers for [Ag(4,4-bipy)$^+$][BF$_4^-$] to [Ag(4,4-bipy)$^+$][NO$_3^-$]. After 25 min, small needles corresponding to the SBP crystal phase are observed in addition to SBP blocks with indentations (blue, Figure 4). After 40 min, the crystals have lost their block-shaped morphology and consist primarily of bundles of needles that appear to be nucleated from the SBN block crystals (green, Figure 4). The anion exchange is complete after 70 minutes and only long SBP needles could be identified (purple, Figure 4), with average length 12 to 15 µm and width 2 to 4 µm.

The gradual change in morphology of the SBN block crystals to SBP needles upon exposure to ClO$_4^-$ solution confirms that the structural transformation between the two coordination polymers occurs by a solvent-mediated process consistent with the PXRD and MAS NMR spectra described above. The self-propagating growth of a new crystal phase from a parent phase has been proposed to facilitate exchange of anions in the inside core of [Ag(4,4-bipy)$^+$][BF$_4^-$] crystals undergoing the structural transformation to [Ag(4-bipy)$^+$][NO$_3^-$].

Figure 4. SEM images of SBN pre-exchange (black, top left) and the solid after 10 min (red), 25 min (blue), 40 min (green), complete exchange to SBP (purple), and the first regeneration to SBN (grey).

The reversibility of the anion exchange was demonstrated in our previous work and seven cycles of perchlorate uptake were monitored by PXRD. The metastability of the [Ag-bipy]$^+$ solids allows for the reversible solvent mediated transformation that can be controlled by the concentration of the incoming anions and temperature. The lower solubility of SBP as well as its higher stability due to the greater degree of π-stacking account for the rapid SBN to SBP transition. In contrast, the re-intercalation of nitrate is a less favoured process due to the larger hydration energy of nitrate. Additionally, SBN has a lower stability due to the partial π-stacking.

The regeneration of the SBN was further studied by recording the PXRD, $^{13}$C, $^{15}$N, $^{109}$Ag CP MAS NMR data and SEM images after treatment of the SBP material with excess nitrate at 70 °C under stirring (grey spectra, Figures 3-4). The heat promotes the dissolution of the SBP polymers, while the excess nitrate shifts the dynamic equilibrium of the exchange to return to block shaped crystals with morphology identical to the as-synthesized SBN material (cf. black and grey SEMs, Figure 4). The corresponding PXRD, $^{13}$C and $^{109}$Ag NMR data showed that although SBN has been mostly regenerated, approximately 10 % of SBP is still present (as evidenced by integration of the NMR spectra and PXRD peaks).

4. Conclusion

This work shows by multiple complementary solid state methods that ClO$_4^-$ uptake by Silver 4,4’-Bipyridine Nitrate (SBN) [Ag-bipy]$^+$][NO$_3^-$] occurs via a solvent-mediated process to yield Silver 4,4’-Bipyridine Perchlorate (SBP). The structural features of the silver coordination polymers in terms of π-stacking and electrostatics concur with the dynamics of the anion exchange process. All three characterization methods show that the two crystalline phases are present throughout the anion exchange process. This study provides evidence of the structural flexibility displayed by the interaction of cationic [Ag-bipy]$^+$ MOFs with different adsorbates upon anion exchange. Such understanding of
structural dynamics is crucial for the rational design of these materials. The use of reagents such as perchlorate, chromate and arsenate is important in the formation of new crystals through the exchange of ions. Each exchange cycle circumvents the degradation issues of current ion exchange solids such as resins and LDHs that force them to single-use.

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References

TOC Synopsis:

The perchlorate capture process by a cationic Ag-based MOF was carefully studied using a combination of powder X-ray diffraction (PXRD), multinuclear $^{13}$C, $^{15}$N and $^{109}$Ag solid state NMR and SEM.