

# Fluoride-Induced Reduction of Ag(I) Cation Leading to Formation of Silver Mirrors and Luminescent Ag-Nanoparticles

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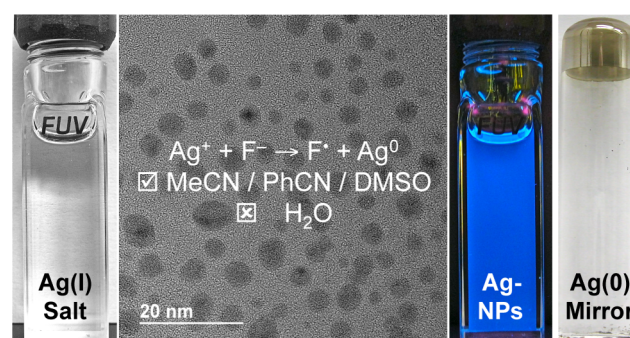
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**S** Supporting Information

**ABSTRACT:** In aprotic solvents, Lewis basic F<sup>-</sup> anion reduces Lewis acidic Ag(I) cation to Ag(0), forming metallic silver mirrors on the inner surfaces of reaction vessels and luminescent Ag-nanoparticles (AgNPs) in supernatant solutions, which emit blue light upon UV irradiation. The F<sup>-</sup>-induced formation of silver mirrors and AgNPs was confirmed through X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), fluorescence spectroscopy, and mass spectrometry, whereas the Ag(I)-induced oxidation of F<sup>-</sup> to  $\dot{F}$  radical, followed by its conversion to HF<sub>2</sub><sup>-</sup> via H-abstraction and H-bonding, was evident from <sup>19</sup>F NMR spectroscopy. This redox reaction is deactivated in water, as the reducing power of hydrated F<sup>-</sup> diminishes drastically. Less Lewis basic Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> ions do not reduce Ag(I) to Ag(0), instead they can only form Ag(I) halide precipitates irrespective of protic or aprotic solvents. The Ag-coated surfaces, luminescent AgNPs, and  $\dot{F}$  radicals produced by this unprecedented redox reaction could be exploited as electrodes, light-emitting materials, and radical initiators, respectively.

One of the latest and perhaps the most intriguing revelations of anion recognition chemistry<sup>1</sup> entails the discovery of formal electron transfer (ET) from Lewis basic anions to  $\pi$ -acidic receptors,<sup>2,3</sup> which takes place in aprotic solvents where anions are less solvated but gets deactivated in protic solvents where they become stabilized upon solvation. Although anion- $\pi$  complexes<sup>4</sup> emerged at the turn of this century and charge-transfer (CT) complexes of anions followed<sup>5</sup> as soon as stronger  $\pi$ -acidic receptors were introduced, formal ET from strong Lewis basic anions, such as F<sup>-</sup> and OH<sup>-</sup> to strong  $\pi$ -acidic receptors was deemed ostensibly implausible until recently<sup>2,3</sup> on the basis of a presumption that anions derived from strong electronegative elements could not act as electron donors. Coincidentally, while this assumption appears true in water and protic solvents, it is not for the reason it was surmised, as in a given group electronegativity of elements (F > Cl > Br > I) has little to do with the Lewis basicity, i.e., electron donating ability of the corresponding anions (F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>), but because of a diminished reducing power of F<sup>-</sup> ions that become more extensively hydrated and stabilized in water than larger Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> ions. This confusion impeded<sup>6</sup> the understanding of

## Scheme 1. Redox Reaction between Lewis Acidic Ag(I) and Lewis Basic F<sup>-</sup> in Aprotic Solvents Generates Luminescent AgNP Solutions and Ag(0) Mirrors



ET interactions between F<sup>-</sup> and  $\pi$ -acidic receptors and hindered the use of Lewis basic anions as reducing agents until recently.<sup>2,3</sup>

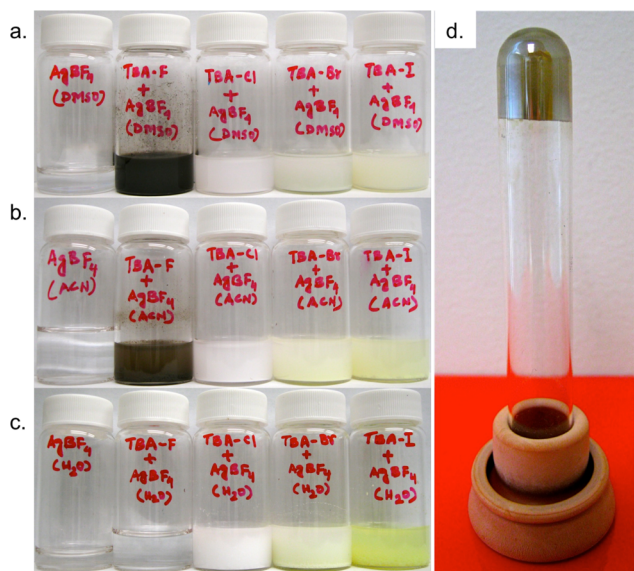
Using UV/vis, NMR, EPR, and electrochemical experiments, we<sup>2</sup> and others<sup>3</sup> have demonstrated that in aprotic solvents, strong Lewis basic anions (OH<sup>-</sup>, F<sup>-</sup>) reduce  $\pi$ -acidic receptors to the corresponding paramagnetic radical anions via thermal ET, and less basic anions (AcO<sup>-</sup>, Cl<sup>-</sup>) do so via photoinduced ET. In contrast, non-Lewis basic Br<sup>-</sup> and I<sup>-</sup> ions form CT complexes,<sup>2c,3c,5b</sup> and TfO<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> ions form anion- $\pi$  complexes with  $\pi$ -acidic receptors.<sup>7</sup> These studies not only revealed that in aprotic solvents, electron donating ability of anions closely follow their Lewis basicity trend,<sup>2,3c</sup> but also presented us with a unique opportunity to discriminate them on the basis of their Lewis basicity through tunable electronic interactions with  $\pi$ -acidic receptors.

Despite strong similarities between organic  $\pi$ -acids and Lewis acidic transition metal ions in terms of their electron accepting abilities and the fact that the latter is known to serve as oxidizing agents,<sup>8</sup> the redox reactions between Lewis acidic metal ions and Lewis basic F<sup>-</sup> anion have remained largely unexplored<sup>9</sup> (Scheme 1). Herein, we demonstrate that in aprotic solvents, F<sup>-</sup> reduces Ag(I) salts to Ag(0), forming silver mirrors on the inner surfaces of reaction vessels and luminescent AgNPs in supernatant solutions. Conversely, the F<sup>-</sup> anion is oxidized to a highly reactive  $\dot{F}$  radical, which quickly transforms into HF<sub>2</sub><sup>-</sup> via H-abstraction, followed by H-bond formation between the HF intermediate and remaining F<sup>-</sup>.

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This redox reaction is deactivated in H<sub>2</sub>O, as the hydrated F<sup>-</sup> anion ( $\Delta H_{\text{hydration}} = -115 \text{ kcal/mol}$ )<sup>10</sup> becomes stabilized and loses its reducing power. Weaker Lewis basic halide ions are unable to reduce Ag(I) to Ag(0), but they form precipitates of corresponding Ag(I) halides irrespective of solvents (Figure 1).



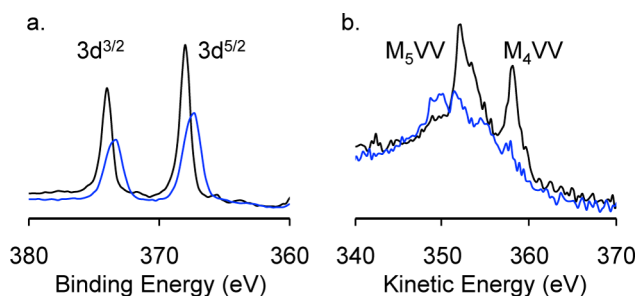
**Figure 1.** Photographs of 0.1 M AgBF<sub>4</sub> solutions in (a) DMSO, (b) MeCN, and (c) H<sub>2</sub>O before and after the addition of Bu<sub>4</sub>NF, Bu<sub>4</sub>NCl, Bu<sub>4</sub>NBr, and Bu<sub>4</sub>NI salts (2 equiv). In aprotic solvents, F<sup>-</sup> reduces Ag(I) to metallic silver precipitates, while other anions produce corresponding Ag(I) halide precipitates. In H<sub>2</sub>O, F<sup>-</sup> does not reduce Ag(I), as the solution remains clear. (d) Silver mirror formed by a redox reaction between AgBF<sub>4</sub> and Bu<sub>4</sub>NF in DMSO.

To take advantage of the facile redox chemistry of Ag<sup>+0</sup> couple ( $E_{\text{Red}} = +215 \text{ mV}$  in DMSO and MeCN, Supporting Information, Figure S1),<sup>11</sup> AgBF<sub>4</sub>, AgClO<sub>4</sub>, and AgPF<sub>6</sub> salts were subjected to react with F<sup>-</sup> salts having different counterions. In aprotic solvents such as DMSO, MeCN, and PhCN and in H<sub>2</sub>O, these Ag(I) salts form colorless solutions and do not form any Ag(0) precipitation, demonstrating that these solvents and counterions do not reduce Ag(I) to Ag(0).<sup>12</sup> Upon addition of CsF, KF, Bu<sub>4</sub>NF, or Et<sub>4</sub>NF salts into clear solutions of Ag(I) salts in DMSO, MeCN, and PhCN, metallic silver particles began to precipitate immediately, and characteristic silver mirrors formed gradually on the inner surfaces of reaction vessels (Figure 1). Unlike the aforesaid Ag(I) salts of charge diffuse anions that do not produce any Ag(0) in the absence of F<sup>-</sup>, yellow AgF immediately turned metallic gray in polar aprotic solvents, and metallic silver mirror appeared on the surface of reaction vessels as the resulting Ag(0) particles slowly deposited on the surface (Figure S2). In H<sub>2</sub>O, however, neither the addition of F<sup>-</sup> salts into clear AgClO<sub>4</sub>, AgBF<sub>4</sub>, and AgPF<sub>6</sub> solutions, nor AgF itself, produced any metallic Ag(0) precipitation (Figure 1) due to a diminished reducing ability of hydrated F<sup>-</sup> anions.

In contrast, addition of other halide ions into clear Ag(I) salt solutions led to precipitation of AgCl, AgBr, and AgI salts instead of metallic Ag(0) (Figures 1 and S2). In aprotic solvents, the white AgCl suspension turned gray over time, possibly because of a slow reduction of Ag(I) to Ag(0) by a weak Lewis basic Cl<sup>-</sup> anion, whereas yellow AgBr and AgI precipitates remained intact due to much weaker electron

donating ability of Br<sup>-</sup> and I<sup>-</sup> than F<sup>-</sup> and Cl<sup>-</sup> ions.<sup>2,3c,13</sup> Unlike AgCl, AgBr, and AgI that are insoluble in H<sub>2</sub>O, AgF is soluble in H<sub>2</sub>O, but it does not form any Ag(0) precipitate (Figure 1), indicating that the hydrated F<sup>-</sup> anions become so stabilized ( $\Delta H_{\text{hydration}} = -115 \text{ kcal/mol}$  corresponds to  $-4.9 \text{ eV}$  stabilization)<sup>10</sup> that they are unable to reduce Ag(I) cations. These results are consistent with our previous studies that showed F<sup>-</sup>-induced reduction of  $\pi$ -acids in aprotic solvents, but the absence of such phenomenon in protic solvents<sup>2</sup> and when F<sup>-</sup> is H-bonded with a calix[4]pyrrole receptor.<sup>3c</sup>

The metallic silver particles and mirrors produced by the reactions between Ag(I) and F<sup>-</sup> in aprotic solvents were analyzed by XPS to confirm their chemical composition and oxidation state through a Wagner plot.<sup>14</sup> The XPS data of silver mirrors and metallic precipitates generated by F<sup>-</sup>-induced reduction of Ag(I) salts in aprotic solvents display (Figures 2

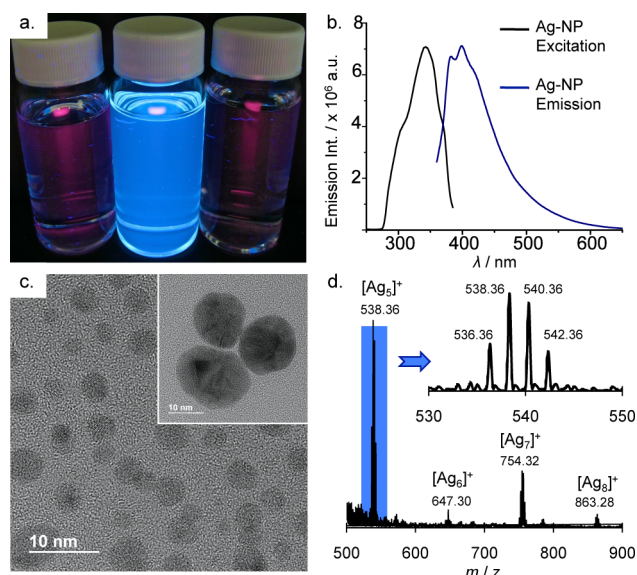


**Figure 2.** XPS shows (a) 3d binding energies (BE) and (b) M4VV kinetic energies (KE) of Ag(0) (black lines: 3d<sup>5/2</sup> BE = 368.0 eV,  $\Delta 3d = 6.00 \text{ eV}$ ; M<sub>4</sub>VV KE = 358.1 eV) obtained from a redox reaction between AgBF<sub>4</sub> and CsF in DMSO, and Ag(I) cation (blue lines: 3d<sup>5/2</sup> BE = 367.5 eV,  $\Delta 3d = 6.02 \text{ eV}$ ; M<sub>4</sub>VV KE = 355.2 eV).

and S3) characteristic Ag(0) signals (3d<sup>5/2</sup> binding energy = 368.0 eV; M<sub>4</sub>VV kinetic energy = 358.1 eV), which are distinct from characteristic Ag(I) signals (3d<sup>5/2</sup> binding energy = 367.5 eV; M<sub>4</sub>VV kinetic energy = 355.2 eV).<sup>14</sup> The fact that in aprotic solvents Ag(I) salts do not form any Ag(0) unless F<sup>-</sup> is present in the medium and that F<sup>-</sup> reduces Ag(I) to Ag(0) irrespective of its counter cations (Cs<sup>+</sup>, K<sup>+</sup>, Bu<sub>4</sub>N<sup>+</sup>, and Et<sub>4</sub>N<sup>+</sup>) affirms that it is the Lewis basic F<sup>-</sup> anion, not solvent molecules nor counterions, which is responsible for the reduction of Ag(I). In H<sub>2</sub>O, hydrated F<sup>-</sup> becomes stabilized<sup>3c</sup> and cannot reduce Ag(I) to Ag(0) anymore.

In addition to forming silver mirrors on surfaces, the redox reactions between Ag(I) salts and CsF in MeCN, PhCN, and DMSO also generate luminescent AgNP solutions (Figures 3a and S4) that display size-dependent excitation and emission spectra.<sup>15</sup> For instance, the pale yellow AgNP solution (Figure S4:  $\lambda_{\text{Abs}} = \text{ca. } 350 \text{ nm}$ ) generated by a reaction between AgBF<sub>4</sub> and CsF in MeCN displays blue luminescence (Figure 3b:  $\lambda_{\text{ex}} = 340 \text{ nm}$ ,  $\lambda_{\text{em}} = 400 \text{ nm}$ , quantum yield ( $\Phi_{\text{em}}$ ) = 3.5% using coumarin-440 as a standard), whereas the AgNPs produced by the same reaction in PhCN display excitation and emission at slightly longer wavelengths (Figure S4:  $\lambda_{\text{ex}} = 350 \text{ nm}$ ,  $\lambda_{\text{em}} = 410 \text{ nm}$ ). The slight red-shift ( $\Delta\lambda = \text{ca. } 10 \text{ nm}$ ) displayed by the AgNPs formed in PhCN compared to that in MeCN can be attributed to a larger particle size in the former (*vide infra*).<sup>15</sup> None of the precursors, i.e., AgBF<sub>4</sub> and CsF solutions separately display any photoluminescence, leaving the AgNPs generated via F<sup>-</sup>-induced reduction of Ag(I) as the only viable source of the observed blue emission. While the reduction of Ag(I) salts by F<sup>-</sup> leading to the precipitation of larger Ag(0)



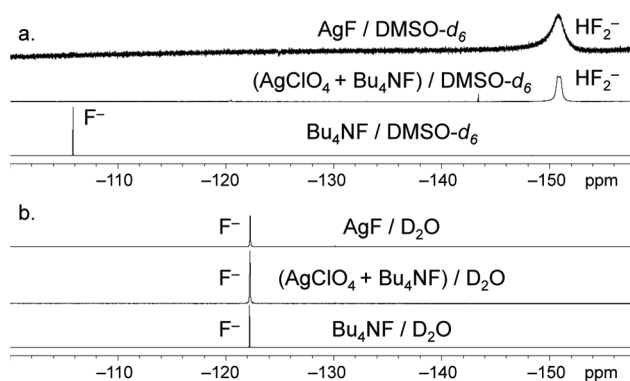


**Figure 3.** (a) Photographs of nonemissive MeCN solutions of AgBF<sub>4</sub> (left) and CsF (right) and luminescent MeCN solution of AgNPs (middle) obtained from a reaction between AgBF<sub>4</sub> and CsF. Samples are under UV irradiation (365 nm). (b) Excitation and emission spectra of AgNP solution in MeCN (from AgBF<sub>4</sub> + CsF reaction). (c) TEM of AgNPs produced by F<sup>-</sup>-induced reduction of Ag(I) in MeCN and PhCN (inset). (d) MALDI-TOF MS of AgNP solutions reveals [Ag<sub>n</sub>]<sup>+</sup> clusters.

particles and formation of Ag-mirror takes place at room temperature, the formation of luminescent AgNP solutions is facilitated upon heating the reaction mixtures at ca. 100 °C (Figure S5). Under this condition, the nascent Ag(0) clusters disperse uniformly forming AgNPs that absorb and emit at particular wavelengths. Although luminescent AgNPs are known to form via reduction of Ag(I) salts in the presence of additional capping agents that control their size and optical properties,<sup>16</sup> our studies demonstrate for the first time that F<sup>-</sup> can reduce Ag(I) salts in aprotic solvents to generate emissive AgNPs even in the absence of such capping agents. These ligand-free luminescent AgNPs are stable under ambient conditions, and like other AgNPs,<sup>16c</sup> their emission intensity is diminished upon continuous UV irradiation (Figure S5).

TEM images show (Figure 3c) that the AgNPs formed in MeCN (~5 nm) are smaller than those in PhCN (~15 nm). These observations are consistent with slightly red-shifted excitation and emission spectra displayed by the latter.<sup>15</sup> Furthermore, EDS analysis confirmed that the luminescent NPs are indeed composed of Ag (Figure S6), and MALDI-MS revealed the presence of Ag-clusters in the luminescent supernatant solutions (Figure 3d).

Having demonstrated that F<sup>-</sup> can reduce Ag(I) to Ag(0) in aprotic solvents, we turned our attention to determine the fate of the oxidized F<sup>-</sup> anion. The oxidation of F<sup>-</sup> anion (as Bu<sub>4</sub>NF and CsF salts) by Ag(I) in DMSO-*d*<sub>6</sub> is evident from <sup>19</sup>F NMR spectroscopy (Figure 4a), as the characteristic F<sup>-</sup> signal (δ = -106 ppm) disappears and a new signal corresponding to HF<sub>2</sub><sup>-</sup> anion appears at -154 ppm<sup>17</sup> upon addition of a stoichiometric amount of AgClO<sub>4</sub>. Interestingly, AgF does not display any characteristic F<sup>-</sup> peak in DMSO-*d*<sub>6</sub>, instead it only shows the HF<sub>2</sub><sup>-</sup> signal (-154 ppm). The fact that in aprotic solvents the disappearance of F<sup>-</sup> signal and the emergence of HF<sub>2</sub><sup>-</sup> signal took place only in the presence of Ag(I) ruled out H<sup>+</sup>-



**Figure 4.** <sup>19</sup>F NMR spectra (400 MHz, 298 K) of TBAF, a 1:1 mixture of TBAF and AgClO<sub>4</sub>, and AgF in (a) DMSO-*d*<sub>6</sub> and (b) D<sub>2</sub>O. In DMSO-*d*<sub>6</sub>, the F<sup>-</sup> peak disappears in the presence of Ag(I), indicating oxidation of F<sup>-</sup> to Ḟ, which ultimately forms HF<sub>2</sub><sup>-</sup> via H-abstraction and H-bond formation. In D<sub>2</sub>O, the F<sup>-</sup> signal persists, ruling out any redox reaction between hydrated F<sup>-</sup> and Ag(I) ions.

abstraction by the F<sup>-</sup> anion as a means to HF<sub>2</sub><sup>-</sup> formation, as this process could have taken place even in the absence of Ag(I). Instead, this observation, coupled with F<sup>-</sup>-induced reduction of Ag(I) to Ag(0), suggests that Ag(I) first oxidizes F<sup>-</sup> anion to a highly reactive transitory Ḟ radical that immediately abstracts a H atom from the medium forming a HF intermediate, which subsequently forms a H-bond with another F<sup>-</sup> ion to produce HF<sub>2</sub><sup>-</sup>. Bifluoride is a much less basic anion than F<sup>-</sup> in aprotic solvents<sup>3c,13</sup> and may no longer be oxidized by Ag(I). In D<sub>2</sub>O, the F<sup>-</sup> signal appears at ca. -122 ppm (Figure 4b) irrespective of its counterions (Bu<sub>4</sub>N<sup>+</sup>, Cs<sup>+</sup>, and Ag<sup>+</sup>), and it remains unaffected even in the presence of Ag(I), demonstrating that hydrated F<sup>-</sup> ions are no longer oxidized by Ag(I), or in other words, hydrated F<sup>-</sup> ions cannot reduce Ag(I) anymore. It is worth noting that the fate of Ḟ produced by ET from F<sup>-</sup> to π-acids has been unknown and that its final product has been elusive so far. The current studies depicted a clear picture as to how the resulting Ḟ radicals are consumed, a knowledge that would inspire new radical reactions.

The foregoing results demonstrate for the first time that, Lewis basic F<sup>-</sup> anion can reduce Lewis acidic Ag(I) cation to Ag(0) in aprotic solvents, while the hydrated ions no longer engage in such redox chemistry. The formation of Ag(0) mirrors and AgNPs via F<sup>-</sup>-induced reduction of Ag(I) was determined by XPS, TEM, EDS, and MALDI-MS, whereas the Ag(I)-mediated oxidation of F<sup>-</sup> to Ḟ radical, followed by its conversion to HF<sub>2</sub><sup>-</sup> via H-abstraction and H-bonding, was evident from <sup>19</sup>F NMR spectroscopy. The metallic silver-coated surfaces can be used as electrodes, while the blue-emitting AgNP solutions could be useful for a number of imaging and nanotechnology applications.<sup>18</sup> Furthermore, the *in situ* generated Ḟ radicals could trigger radical reactions,<sup>19</sup> such as alkene polymerization that would afford new fluorine-capped polymers. Such diverse scopes of this novel redox reaction between Ag(I) and F<sup>-</sup> will open new frontiers of research in our laboratory and elsewhere.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental conditions, electrochemical, XPS, TEM, EDS, UV/vis absorption, and luminescence data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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