

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/272111381>

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

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · FEBRUARY 2015

Impact Factor: 12.11 · DOI: 10.1021/ja512020w

CITATIONS

2

READS

129

4 AUTHORS:



Krishnendu Maity

Florida State University

2 PUBLICATIONS 2 CITATIONS

SEE PROFILE



Dillip Kumar Panda

University of Michigan

13 PUBLICATIONS 119 CITATIONS

SEE PROFILE



Eric Lochner

Florida State University

36 PUBLICATIONS 443 CITATIONS

SEE PROFILE



Sourav Saha

Florida State University

32 PUBLICATIONS 1,938 CITATIONS

SEE PROFILE

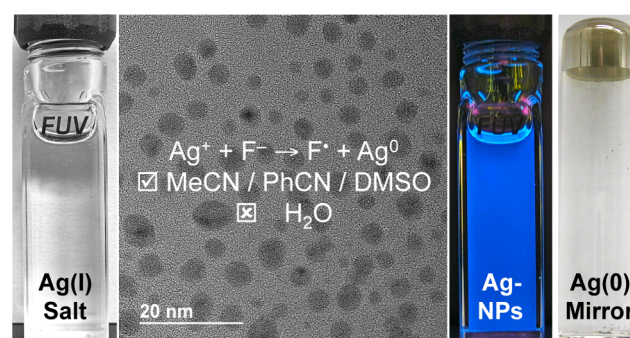
Fluoride-Induced Reduction of Ag(I) Cation Leading to Formation of Silver Mirrors and Luminescent Ag-Nanoparticles

Krishnendu Maity,[†] Dillip K. Panda,[†] Eric Lochner,[‡] and Sourav Saha^{*,†}[†]Department of Chemistry and Biochemistry, Florida State University, 95 Chieftan Way, Tallahassee, Florida 32306, United States[‡]Department of Physics, Florida State University, 77 Chieftan Way, Tallahassee, Florida 32306, United States**S** Supporting Information

ABSTRACT: In aprotic solvents, Lewis basic F[−] 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[−]-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[−] to \dot{F} radical, followed by its conversion to HF₂[−] via H-abstraction and H-bonding, was evident from ¹⁹F NMR spectroscopy. This redox reaction is deactivated in water, as the reducing power of hydrated F[−] diminishes drastically. Less Lewis basic Cl[−], Br[−], and I[−] 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 chemistry¹ entails the discovery of formal electron transfer (ET) from Lewis basic anions to π -acidic receptors,^{2,3} 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- π complexes⁴ emerged at the turn of this century and charge-transfer (CT) complexes of anions followed⁵ as soon as stronger π -acidic receptors were introduced, formal ET from strong Lewis basic anions, such as F[−] and OH[−] to strong π -acidic receptors was deemed ostensibly implausible until recently^{2,3} 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[−] > Cl[−] > Br[−] > I[−]), but because of a diminished reducing power of F[−] ions that become more extensively hydrated and stabilized in water than larger Cl[−], Br[−], and I[−] ions. This confusion impeded⁶ the understanding of

Scheme 1. Redox Reaction between Lewis Acidic Ag(I) and Lewis Basic F[−] in Aprotic Solvents Generates Luminescent AgNP Solutions and Ag(0) Mirrors



ET interactions between F[−] and π -acidic receptors and hindered the use of Lewis basic anions as reducing agents until recently.^{2,3}

Using UV/vis, NMR, EPR, and electrochemical experiments, we² and others³ have demonstrated that in aprotic solvents, strong Lewis basic anions (OH[−], F[−]) reduce π -acidic receptors to the corresponding paramagnetic radical anions via thermal ET, and less basic anions (AcO[−], Cl[−]) do so via photoinduced ET. In contrast, non-Lewis basic Br[−] and I[−] ions form CT complexes,^{2c,3c,5b} and TfO[−] and ClO₄[−] ions form anion- π complexes with π -acidic receptors.⁷ These studies not only revealed that in aprotic solvents, electron donating ability of anions closely follow their Lewis basicity trend,^{2,3c} but also presented us with a unique opportunity to discriminate them on the basis of their Lewis basicity through tunable electronic interactions with π -acidic receptors.

Despite strong similarities between organic π -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,⁸ the redox reactions between Lewis acidic metal ions and Lewis basic F[−] anion have remained largely unexplored⁹ (Scheme 1). Herein, we demonstrate that in aprotic solvents, F[−] 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[−] anion is oxidized to a highly reactive \dot{F} radical, which quickly transforms into HF₂[−] via H-abstraction, followed by H-bond formation between the HF intermediate and remaining F[−].

Received: November 25, 2014

Published: February 11, 2015

This redox reaction is deactivated in H₂O, as the hydrated F[−] anion ($\Delta H_{\text{hydration}} = -115 \text{ kcal/mol}$)¹⁰ 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).

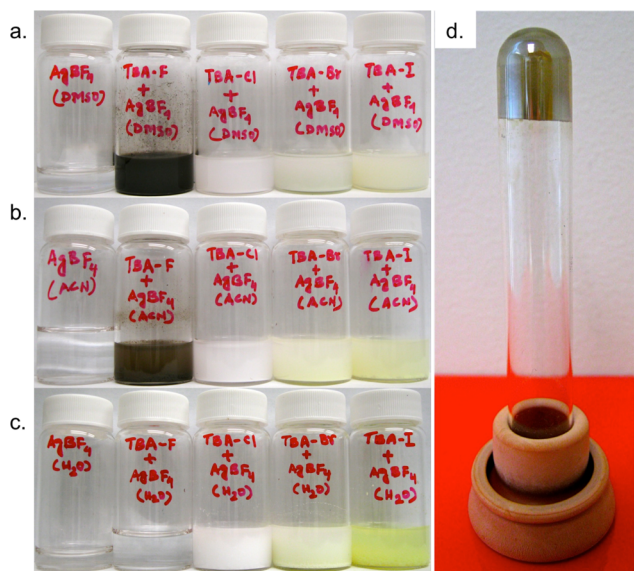


Figure 1. Photographs of 0.1 M AgBF₄ solutions in (a) DMSO, (b) MeCN, and (c) H₂O before and after the addition of Bu₄NF, Bu₄NCl, Bu₄NBr, and Bu₄NI salts (2 equiv). In aprotic solvents, F[−] reduces Ag(I) to metallic silver precipitates, while other anions produce corresponding Ag(I) halide precipitates. In H₂O, F[−] does not reduce Ag(I), as the solution remains clear. (d) Silver mirror formed by a redox reaction between AgBF₄ and Bu₄NF in DMSO.

To take advantage of the facile redox chemistry of Ag^{+/0} couple ($E_{\text{red}} = +215 \text{ mV}$ in DMSO and MeCN, Supporting Information, Figure S1),¹¹ AgBF₄, AgClO₄, and AgPF₆ salts were subjected to react with F[−] salts having different counterions. In aprotic solvents such as DMSO, MeCN, and PhCN and in H₂O, 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).¹² Upon addition of CsF, KF, Bu₄NF, or Et₄NF 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[−], 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 H₂O, however, neither the addition of F[−] salts into clear AgClO₄, AgBF₄, and AgPF₆ solutions, nor AgF itself, produced any metallic Ag(0) precipitation (Figure 1) due to a diminished reducing ability of hydrated F[−] 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[−] anion, whereas yellow AgBr and AgI precipitates remained intact due to much weaker electron

donating ability of Br[−] and I[−] than F[−] and Cl[−] ions.^{2,3c,13} Unlike AgCl, AgBr, and AgI that are insoluble in H₂O, AgF is soluble in H₂O, but it does not form any Ag(0) precipitate (Figure 1), indicating that the hydrated F[−] anions become so stabilized ($\Delta H_{\text{hydration}} = -115 \text{ kcal/mol}$ corresponds to -4.9 eV stabilization)¹⁰ that they are unable to reduce Ag(I) cations. These results are consistent with our previous studies that showed F[−]-induced reduction of π -acids in aprotic solvents, but the absence of such phenomenon in protic solvents² and when F[−] is H-bonded with a calix[4]pyrrole receptor.^{3c}

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

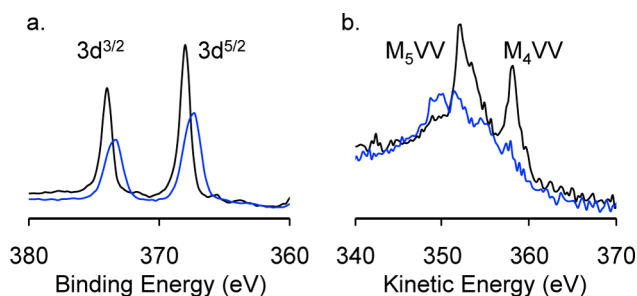


Figure 2. XPS shows (a) 3d binding energies (BE) and (b) M4VV kinetic energies (KE) of Ag(0) (black lines: 3d^{5/2} BE = 368.0 eV, $\Delta 3d = 6.00 \text{ eV}$; M₄VV KE = 358.1 eV) obtained from a redox reaction between AgBF₄ and CsF in DMSO, and Ag(I) cation (blue lines: 3d^{5/2} BE = 367.5 eV, $\Delta 3d = 6.02 \text{ eV}$; M₄VV KE = 355.2 eV).

and S3) characteristic Ag(0) signals (3d^{5/2} binding energy = 368.0 eV; M₄VV kinetic energy = 358.1 eV), which are distinct from characteristic Ag(I) signals (3d^{5/2} binding energy = 367.5 eV; M₄VV kinetic energy = 355.2 eV).¹⁴ The fact that in aprotic solvents Ag(I) salts do not form any Ag(0) unless F[−] is present in the medium and that F[−] reduces Ag(I) to Ag(0) irrespective of its counter cations (Cs⁺, K⁺, Bu₄N⁺, and Et₄N⁺) affirms that it is the Lewis basic F[−] anion, not solvent molecules nor counterions, which is responsible for the reduction of Ag(I). In H₂O, hydrated F[−] becomes stabilized^{3c} 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.¹⁵ For instance, the pale yellow AgNP solution (Figure S4: $\lambda_{\text{abs}} = \text{ca. } 350 \text{ nm}$) generated by a reaction between AgBF₄ and CsF in MeCN displays blue luminescence (Figure 3b: $\lambda_{\text{ex}} = 340 \text{ nm}$, $\lambda_{\text{em}} = 400 \text{ nm}$, quantum yield (Φ_{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*).¹⁵ None of the precursors, i.e., AgBF₄ and CsF solutions separately display any photoluminescence, leaving the AgNPs generated via F[−]-induced reduction of Ag(I) as the only viable source of the observed blue emission. While the reduction of Ag(I) salts by F[−] leading to the precipitation of larger Ag(0)

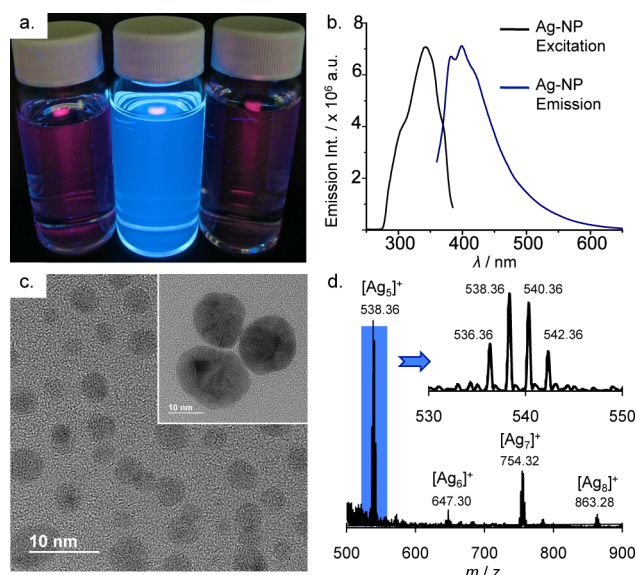


Figure 3. (a) Photographs of nonemissive MeCN solutions of AgBF₄ (left) and CsF (right) and luminescent MeCN solution of AgNPs (middle) obtained from a reaction between AgBF₄ and CsF. Samples are under UV irradiation (365 nm). (b) Excitation and emission spectra of AgNP solution in MeCN (from AgBF₄ + CsF reaction). (c) TEM of AgNPs produced by F[−]-induced reduction of Ag(I) in MeCN and PhCN (inset). (d) MALDI-TOF MS of AgNP solutions reveals [Ag_n]⁺ 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,¹⁶ our studies demonstrate for the first time that F[−] 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,^{16c} 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.¹⁵ 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[−] can reduce Ag(I) to Ag(0) in aprotic solvents, we turned our attention to determine the fate of the oxidized F[−] anion. The oxidation of F[−] anion (as Bu₄NF and CsF salts) by Ag(I) in DMSO-*d*₆ is evident from ¹⁹F NMR spectroscopy (Figure 4a), as the characteristic F[−] signal (δ = −106 ppm) disappears and a new signal corresponding to HF₂[−] anion appears at −154 ppm¹⁷ upon addition of a stoichiometric amount of AgClO₄. Interestingly, AgF does not display any characteristic F[−] peak in DMSO-*d*₆, instead it only shows the HF₂[−] signal (−154 ppm). The fact that in aprotic solvents the disappearance of F[−] signal and the emergence of HF₂[−] signal took place only in the presence of Ag(I) ruled out H⁺-

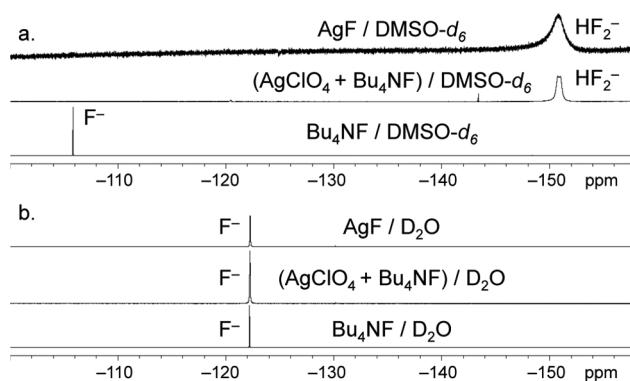


Figure 4. ¹⁹F NMR spectra (400 MHz, 298 K) of TBAF, a 1:1 mixture of TBAF and AgClO₄, and AgF in (a) DMSO-*d*₆ and (b) D₂O. In DMSO-*d*₆, the F[−] peak disappears in the presence of Ag(I), indicating oxidation of F[−] to \dot{F} , which ultimately forms HF₂[−] via H-abstraction and H-bond formation. In D₂O, the F[−] signal persists, ruling out any redox reaction between hydrated F[−] and Ag(I) ions.

abstraction by the F[−] anion as a means to HF₂[−] formation, as this process could have taken place even in the absence of Ag(I). Instead, this observation, coupled with F[−]-induced reduction of Ag(I) to Ag(0), suggests that Ag(I) first oxidizes F[−] anion to a highly reactive transitory \dot{F} radical that immediately abstracts a H atom from the medium forming a HF intermediate, which subsequently forms a H-bond with another F[−] ion to produce HF₂[−]. Bifluoride is a much less basic anion than F[−] in aprotic solvents^{3c,13} and may no longer be oxidized by Ag(I). In D₂O, the F[−] signal appears at ca. −122 ppm (Figure 4b) irrespective of its counterions (Bu₄N⁺, Cs⁺, and Ag⁺), and it remains unaffected even in the presence of Ag(I), demonstrating that hydrated F[−] ions are no longer oxidized by Ag(I), or in other words, hydrated F[−] ions cannot reduce Ag(I) anymore. It is worth noting that the fate of \dot{F} produced by ET from F[−] 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 \dot{F} radicals are consumed, a knowledge that would inspire new radical reactions.

The foregoing results demonstrate for the first time that, Lewis basic F[−] 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[−]-induced reduction of Ag(I) was determined by XPS, TEM, EDS, and MALDI-MS, whereas the Ag(I)-mediated oxidation of F[−] to \dot{F} radical, followed by its conversion to HF₂[−] via H-abstraction and H-bonding, was evident from ¹⁹F 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.¹⁸ Furthermore, the *in situ* generated \dot{F} radicals could trigger radical reactions,¹⁹ such as alkene polymerization that would afford new fluorine-capped polymers. Such diverse scopes of this novel redox reaction between Ag(I) and F[−] will open new frontiers of research in our laboratory and elsewhere.

■ ASSOCIATED CONTENT

⑤ 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>.

■ AUTHOR INFORMATION

Corresponding Author

*saha@chem.fsu.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Authors thank the donors of the American Chemical Society Petroleum Research Fund for funding this research through an ACS-PRF grant (S1734-DNI4). TEM analysis was conducted on an instrument funded and supported by FSU Research Foundation, NHMFL (NSF-DMR-0654118), and the State of Florida.

■ REFERENCES

- (1) (a) Sessler, J. L.; Gale, P.; Chow, W.-S. *Anion Receptor Chemistry*; RSC Publishing: Cambridge, UK, 2006. (b) Gale, P. A.; Busschaert, N.; Haynes, C. J. E.; Karagiannidis, L. E.; Kirby, I. L. *Chem. Soc. Rev.* **2014**, *43*, 205.
- (2) (a) Guha, S.; Saha, S. *J. Am. Chem. Soc.* **2010**, *132*, 17674. (b) Guha, S.; Goodson, F. S.; Roy, S.; Corson, L. J.; Gravenmier, C. A.; Saha, S. *J. Am. Chem. Soc.* **2011**, *133*, 15256. (c) Guha, S.; Goodson, F. S.; Corson, L. J.; Saha, S. *J. Am. Chem. Soc.* **2012**, *134*, 13679. (d) Goodson, F. S.; Panda, D. K.; Ray, S.; Mitra, A.; Guha, S.; Saha, S. *Org. Biomol. Chem.* **2013**, *11*, 4797.
- (3) (a) Alvey, P. M.; Iverson, B. L. *Org. Lett.* **2012**, *14*, 2706. (b) Ajayakumar, M. R.; Asthana, D.; Mukhopadhyay, P. *Org. Lett.* **2012**, *14*, 4822. (c) Aragay, G.; Frontera, A.; Lloveras, V.; Vidal-Gancedo, J.; Ballester, P. *J. Am. Chem. Soc.* **2013**, *135*, 2620. (d) Li, C.-Z.; Chueh, C.-C.; Ding, F.; Yip, H.-L.; Liang, P.-W.; Li, X.; Jen, A. K.-Y. *Adv. Mater.* **2013**, *25*, 4425. (e) Ley, D.; Guzman, C. X.; Adolfsen, K. H.; Scott, A. M.; Braunschweig, A. B. *J. Am. Chem. Soc.* **2014**, *136*, 7809.
- (4) (a) Frontera, A.; Gamez, P.; Mascal, M.; Mooibroek, T. J.; Reedijk, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 9564. (b) Ballester, P. *Acc. Chem. Res.* **2013**, *46*, 874. (c) Chifotides, H. T.; Dunbar, K. R. *Acc. Chem. Res.* **2013**, *46*, 894.
- (5) (a) Rosokha, Y. S.; Lindeman, S. V.; Rosokha, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 4650. (b) Chifotides, H. T.; Schottel, B.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 7202.
- (6) Dawson, R. E.; Hennig, A.; Weimann, D. P.; Emery, D.; Ravikumar, V.; Montenegro, J.; Takeuchi, T.; Gabutti, S.; Mayor, M.; Mareda, J.; Schalley, C. A.; Matile, S. *Nat. Chem.* **2010**, *7*, 533.
- (7) (a) Guha, S.; Goodson, F. S.; Corson, L. J.; Clark, R. J.; Saha, S. *CrystEngComm* **2012**, *14*, 1213. (b) Mitra, A.; Hubley, C. T.; Panda, D. K.; Clark, R. J.; Saha, S. *Chem. Commun.* **2013**, *49*, 6629. (c) Mitra, A.; Hubley, C. T.; Clark, R. J.; Saha, S. *Supramol. Chem.* **2014**, *26*, 296.
- (8) Saito, Y.; Wang, J. J.; Smith, D. A.; Batchelder, D. N. *Langmuir* **2002**, *18*, 2959.
- (9) Coetzee, J. F.; Campion, J. J.; Liberman, D. R. *Anal. Chem.* **1973**, *45*, 343.
- (10) Cametti, M.; Rissanen, K. *Chem. Commun.* **2009**, 2809.
- (11) Cyclic voltammetry (CV) shows that (Figure S1) the reduction of Ag(I) to Ag(0) is more difficult in DMSO and PhCN ($E^{1/2} = +215$ mV vs Ag/AgCl) than in H₂O ($E^{1/2} = +800$ mV); see Ahrlund, S.; Persson, I. *Acta. Chem. Scand. A* **1980**, *34*, 645.
- (12) While DMF can slowly reduce Ag(I) to Ag(0) (see: Pastoriza-Santos, I.; Liz-Marzán, L. M. *Langmuir* **1999**, *15*, 948), DMSO, MeCN, and PhCN are electron deficient solvents and do not reduce Ag(I) even after prolonged heating.
- (13) The calculated HOMO energies of anions in MeCN (ref 3c): F⁻ (-4.33 eV) > Cl⁻ (-5.25 eV) ≈ Br⁻ (-5.37 eV) ≈ I⁻ (-5.14 eV) > HF₂⁻ (-6.40 eV), which make F⁻ the strongest reducing agent among them.
- (14) (a) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Eden Prairie, MN, 1979. (b) Ferrara, A. M.; Carapeto, A. P.; do Rego, A. M. B. *Vacuum* **2012**, *86*, 1988.
- (15) (a) Hu, M. Z.; Easterly, C. E. *Mater. Sci. Eng. C* **2009**, *29*, 726. (b) Stamplecoskie, K. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **2010**, *136*, 1825. (c) Peng, S.; McMahon, J. M.; Schatz, G. C.; Gray, S. K.; Sun, Y. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 14530.
- (16) (a) Sun, Y.; Xia, Y. *Science* **2002**, *298*, 2176. (b) Yamamoto, M.; Kashiwagi, Y.; Nakamoto, M. *Langmuir* **2006**, *22*, 8581. (c) Muhammed, M. K. H.; Aldeek, F.; Palui, G.; Trapiella-Alfonso, L.; Mattoussi, H. *ACS Nano* **2012**, *10*, 8950. (d) Andrieux-Ledier, A.; Tremblay, B.; Courty, A. *J. Phys. Chem. C* **2013**, *117*, 14850. (e) Sun, Y. *Chem. Soc. Rev.* **2013**, *42*, 2497.
- (17) Sun, H.; DiMaggio, S. G. *J. Am. Chem. Soc.* **2005**, *127*, 2050.
- (18) (a) Eichelbaum, M.; Rademann, K. *Adv. Funct. Mater.* **2009**, *19*, 2045. (b) Chen, L. Q.; Xiao, S. J.; Peng, L.; Wu, T.; Ling, J.; Li, Y. F.; Huang, C. Z. *J. Phys. Chem. B* **2010**, *114*, 3655.
- (19) Deb, A.; Manna, S.; Modak, A.; Patra, T.; Maity, S.; Maiti, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 9747.