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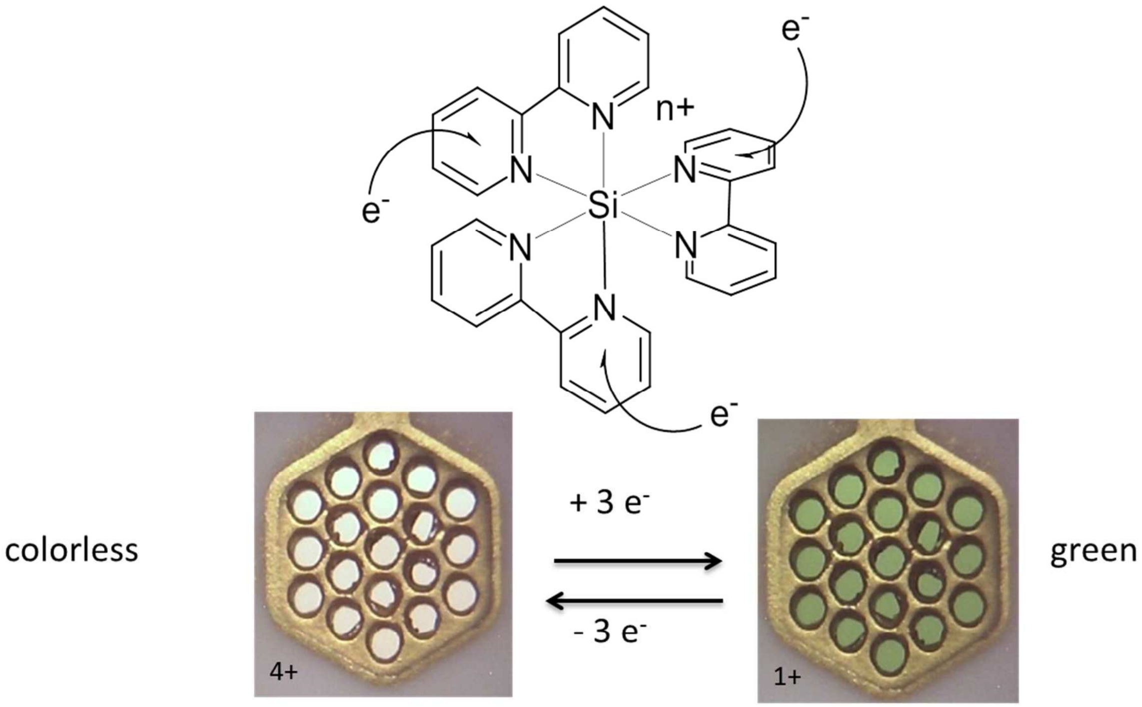
Graphical Abstract:

Tris(bipyridyl)silicon(IV) was electrochemically reduced in acetonitrile to obtain the UV-vis spectra of its reduced species. Three stable, reversible reduced states (3+, 2+, and 1+) were observed with distinct isosbestic points for each of the redox reactions. The fully oxidized state (4+) is colorless, while the reduced states were green. The absorbance spectra for the three reduced states are consistent with ligand localized reductions. Potential advantages of using these complexes in electrochromic applications are discussed.



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Tris(bipyridyl)silicon(IV) was electrochemically reduced in acetonitrile to obtain the UV-vis spectra of its reduced species. Three stable, reversible reduced states (3+, 2+, and 1+) were observed with distinct isosbestic points for each of the redox reactions. The fully oxidized state (4+) is colorless, while the reduced states were green. The absorbance spectra for the three reduced states are consistent with ligand localized reductions. Potential advantages of using these complexes in electrochromic applications are discussed.

The non-innocence of the 2,2'-bipyridine ligand has led to extensive experimental and theoretical research in recent years to assign oxidation states to reduced species of coordination complexes containing this ubiquitous ligand.[1-10] UV-vis/NIR spectroscopy has often been used to distinguish neutral bipyridine ligands from singly or doubly reduced ligands.[11-13] In the case of bipyridine complexes of silicon, DFT calculations by Wieghardt and co-workers indicate a strong preference for the central atom to remain tetravalent with ligand localized reductions.[1] Their calculations predict that $Si(bpy)_3^{1+}$, for example, should contain three ligand-localized SOMOs (≤3% Si character), and Mulliken spin density population analysis places one unpaired spin on each ligand and <0.01 on the silicon atom. It therefore has the predicted electronic structure $[Si(bpy^{\bullet})_3]^+$.

In a previous study,[14] we explored the electrochemistry of $[Si(bpy)_3]^{4+}$ using cyclic voltammetry (Figure 1) and found that it exhibits three chemically reversible, one-electron reductions ($E^o_{(4+/3+)}$ = -0.530 V, $E^o_{(3+/2+)}$ = -0.758 V, and $E^o_{(2+/1+)}$ = -1.001 V vs. Fc/Fc^+ at a platinum disk working electrode in acetonitrile/N(n-Bu)$_4$PF$_6$ solution). These reduction potentials are much less negative than those of other bipyridine coordination complexes due to the tetravalent silicon center. Three additional reductions were observed, but they were only partially chemically reversible on the timescale of the CV. The difference between the reduction potentials is large enough to allow for the electrochemical preparation of nearly pure samples of each state, as seen in the mole fraction distribution (Figure 2). The 3+ and 2+ species reach 98% mole fraction and the 4+ and 1+ can each exceed 99.9% at 25 °C. Consequently, an *in situ* spectroelectrochemical analysis of the first three reduced states $Si(bpy)_3^{n+}$ (n = 3, 2, 1) is possible.

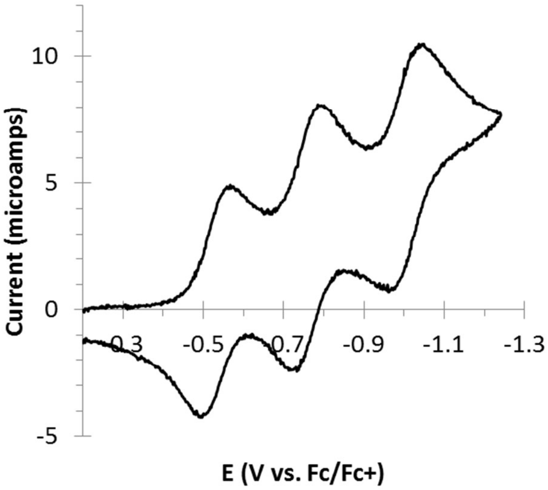

Figure 1. CV scan of $[Si(bipy)_3](PF_6)_4$in acetonitrile/0.10 M N(n-Bu)$_4$PF$_6$ vs. Fc/Fc$^+$. Scan rate = 200 mV/s with iR compensation.

The UV-vis spectrum of each state was obtained using an argon flushed spectroelectrochemical cell with a 1.0 mm pathlength that consisted of a printed gold honeycomb working electrode, a gold counter electrode, and a Ag/AgCl reference electrode standardized to the ferrocene/ferrocenium couple. Samples of $[Si(bpy)_3](PF_6)_4$ were dissolved in an anhydrous acetonitrile solution that was 0.10 M in $[(n\text{-}Bu)_4N][PF_6]$. The mole fraction distribution predicts that from -300 mV to -640 mV only the 4+ and 3+ species should be present in solution, which is consistent with a smooth transition in the UV-vis spectra with clear isosbestic points

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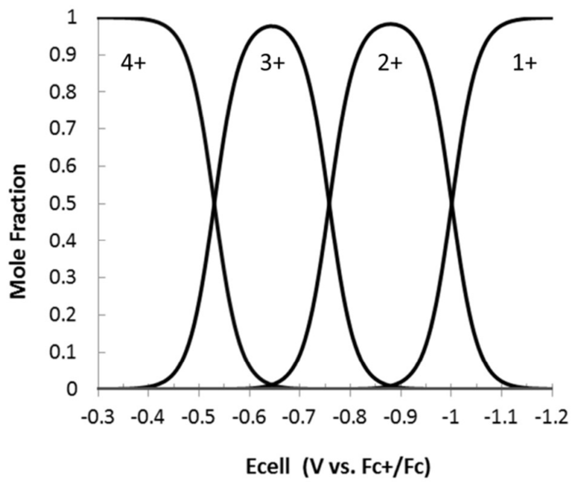

Figure 2. Mole fraction of Si(bpy)$_3$$^{4+}$ calculated from observed reduction potentials at 25 °C.

at 216, 237, 314, and 352 nm (Figure 3). Likewise, clean transitions appear for the other two redox processes as well, which allows for the confident assignment of the UV-vis spectra for each of the reduced species (Figure 4). The fully oxidized 4+ species can be recovered completely after each reduction.

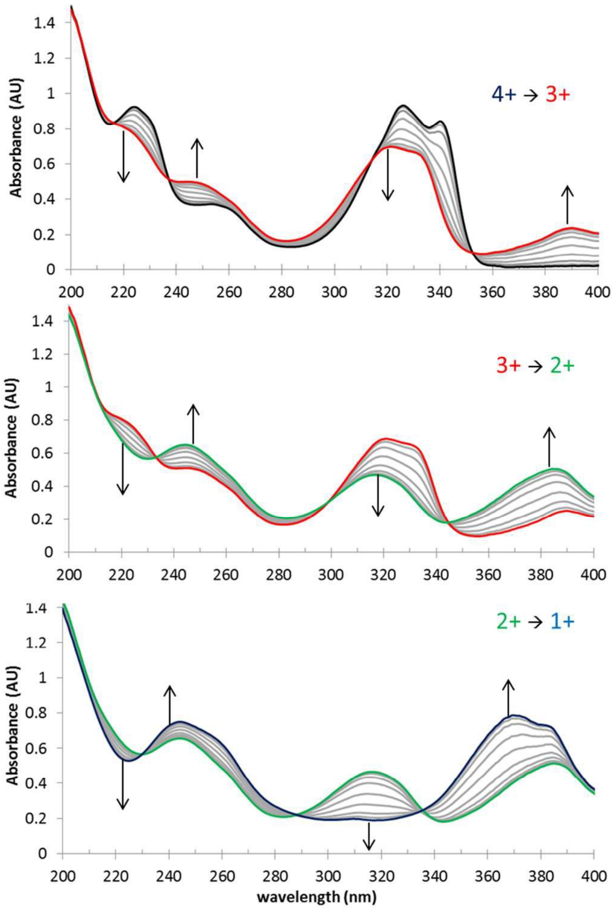

Figure 3. UV-vis spectra recorded at 25 mV intervals from -445 to -645 mV (top), -670 to -870 (middle), and -895 to -1120 mV (bottom).

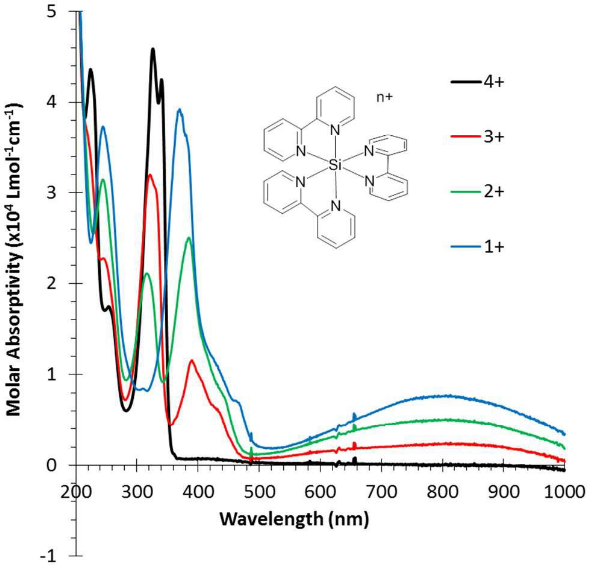

Figure 4. UV-vis spectra of Si(bpy)$_3$$^{n+}$ states generated electrochemically at -445 mV (black line, n=4), -645 mV (red line, n=3), -895 mV (green line, n=2), and -1095 mV vs. Fc/Fc$^+$ (blue line, n=1).

The 4+ state (black line) possesses two unresolved peaks at 327 nm and 341 nm, which are consistent with pi → pi* transitions of bipyridine ligands in other coordination complexes. Upon reduction the intensity of this peak decreases (and slightly blue shifts) as each of the bipyridine ligands becomes reduced. At the same time a peak around 390 nm and a broad absorbance from 600-1000 nm consistent with pi → pi* transitions for a bipyridine radical anion emerge. Attempts to reduce [Si(bpy)$_3$](PF$_6$)$_4$ further to the neutral species, resulted in an irreversible, overall decrease in absorbance without isosbestic points, consistent with a plating out of [Si(bpy)$_3$]^0 on the electrode. This may not be a problem in an electrochemical device with the Si(bpy)$_3$$^{n+}$ dye already attached to the electrode, but it prevents accurate spectroscopic characterization with our current set-up. Note that in the presence of oxygen, one electron reduction led to an irreversible chemical reaction and the appearance of an unidentified species that absorbs at 400 nm and does not absorb in the region 500 – 1000 nm (see ESI). This species is avoided with degassed samples.

The results suggest that polypyridylsilicon(IV) complexes may be excellent candidates for cathodic coloring materials. Cathodic coloring materials are an important component of dual-active electrochromic windows, in which an electrochromic dye attached to an anode is reinforced by a complimentary electrochromic dye at the cathode[15-17]. The cathodic coloring material should be colorless (or nearly colorless) in its oxidized or bleached state and intensely colored upon reduction. The N,N'-dialkyl and N,N'-diaryl-4,4'-bipyridinium salts, also known as viologens, are excellent examples, with robust and reliable spectroelectrochemistry.[18-19] However, the color range of the single reduced viologens tends to be limited to shades of blue and violet.

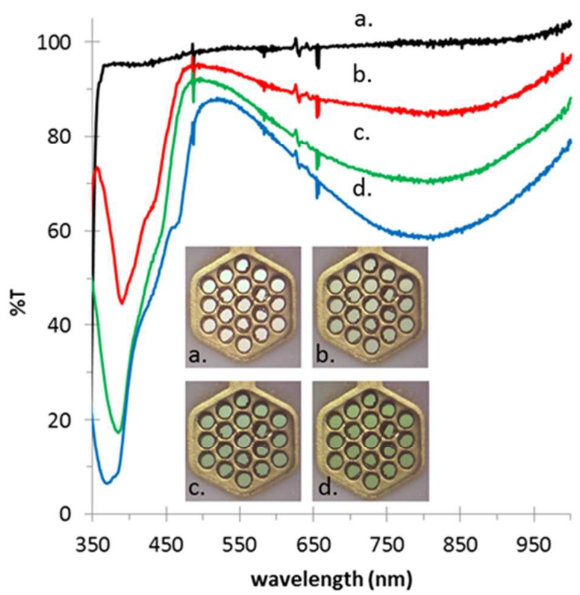

Figure 5. Transmittance and photos (inset) of (a) $Si(bpy)_3^{4+}$, (b) $Si(bpy)_3^{3+}$, (c) $Si(bpy)_3^{2+}$, and (d) $Si(bpy)_3^{1+}$.

The reduced $Si(bpy)_3^{4+}$ species appear green (Figure 5), which has traditionally been a more challenging color to obtain in electrochromic materials since it requires the presence of both red and blue absorption bands.[21] It is possible to obtain very large Δ%Ts for both bands: > 85% (362-387 nm) and > 40% (751-857).

Polypyridyl transition metal complexes have been extensively explored for potential electrochromic applications and reviewed by Mortimer.[22] In the most studied complex, $Ru(bpy)_3^{2+}$, the first three one-electron reductions lead to a stepwise decrease in the pi → pi* transition of the neutral ligand and the appearance of new bands associated with the reduced bipyridine ligand[23] similar to those seen here with $Si(bpy)_3^{4+}$. The MLCT transition also exhibits a bathochromic shift through the visible portion of the spectrum upon reduction. Subsequent studies demonstrated that the synthetic versatility of bipyridine ligands affords a broad spectrum of colors and electrochromic switching opportunities.[24,25] Also, polymerization schemes have been developed to deposit films of polypyridyl transition metals for electrochromic devices.[22] However, the presence of MLCT transitions is generally undesirable for electrochromic applications requiring a colorless oxidized state. In this communication, we demonstrate that polypyridylsilicon(IV) complexes present an excellent alternative, by providing several advantages: (1) they exhibit multiple stable oxidation states with well-behaved chemically reversible electrochemistry, (2) they are often colorless in the fully oxidized (+4) state, (3) they have very low reduction potentials attributed to the tetravalent silicon center, which could enable low-voltage devices and applications, (4) their reduced ligand based transitions appear in the visible portion of the spectrum, and (5) they can be synthesized easily from earth-abundant elements.

Acknowledgements

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References

1 J. England and K. Wieghardt, *Inorganic Chemistry*, 2013, **52**, 10067-10079.
2 A. C. Bowman, J. England, S. Sproules, T. Weyhermueller and K. Wieghardt, *Inorganic Chemistry*, 2013, **52**, 2242-2256.
3 J. England, C. C. Scarborough, T. Weyhermueller, S. Sproules and K. Wieghardt, *European Journal of Inorganic Chemistry*, 2012, 4605-4621.
4 P. Milko and M. A. Iron, *Journal of Chemical Theory and Computation*, 2014, **10**, 220-235.
5 C. C. Scarborough and K. Wieghardt, *Inorganic Chemistry*, 2011, **50**, 9773-9793.
6 M. Wang, J. England, T. Weyhermueller and K. Wieghardt, *Inorganic Chemistry*, 2014, **53**, 2276-2287.
7 M. Wang, T. Weyhermueller and K. Wieghardt, *Chemistry-a European Journal*, 2014, **20**, 9037-9044.
8 M. Wang, J. England, T. Weyhermueller and K. Wieghardt, *European Journal of Inorganic Chemistry*, 2015, 1511-1523.
9 C. Wolff, A. Gottschlich, J. England, K. Wieghardt, W. Saak, D. Haase and R. Beckhaus, *Inorganic Chemistry*, 2015, **54**, 4811-4820.
10 M. Irwin, L. R. Doyle, T. Kraemer, R. Herchel, J. E. McGrady and J. M. Goicoechea, *Inorganic Chemistry*, 2012, **51**, 12301-12312.
11 P. S. Braterman and J. I. Song, *Journal of Organic Chemistry*, 1991, **56**, 4678-4682.
12 E. Koenig and S. Kremer, *Chemical Physics Letters*, 1970, **5**, 87-90.
13 Y. Torii, T. Yazaki, Y. Kaizu, S. Murasato and Kobayash.H, *Bulletin of the Chemical Society of Japan*, 1969, **42**, 2264-2267.
14 B. Suthar, A. Aldongarov, I. S. Irgibaeva, M. Moazzen, B. T. Donovan-Merkert, J. W. Merkert and T. A. Schmedake, *Polyhedron*, 2012, **31**, 754-758.
15 V. K. Thakur, G. Ding, J. Ma, P. S. Lee and X. Lu, *Advanced Materials*, 2012, **24**, 4071-4096.
16 J. Jensen, M. Hosel, A. L. Dyer and F. C. Krebs, *Advanced Functional Materials*, 2015, **25**, 2073-2090.
17 R. H. Bulloch, J. A. Kerszulis, A. L. Dyer and J. R. Reynolds, *Acs Applied Materials & Interfaces*, 2014, **6**, 6623-6630.
18 P. M. Beaujuge, C. M. Amb and J. R. Reynolds, *Accounts of Chemical Research*, 2010, **43**, 1396-1407.
19 R. J. Mortimer and T. S. Varley, *Chemistry of Materials*, 2011, **23**, 4077-4082.
20 R. J. Mortimer and T. S. Varley, *Solar Energy Materials and Solar Cells*, 2012, **99**, 213-220.
21 G. Sonmez, C. K. F. Shen, Y. Rubin and F. Wudl, *Angewandte Chemie-International Edition*, 2004, **43**, 1498-1502.
22 R. J. Mortimer, in *Annual Review of Materials Research, Vol 41*, eds. D. R. Clarke and P. Fratzl, Annual Reviews, Palo Alto, 2011, vol. 41, pp. 241-268.

23 G. A. Heath, L. J. Yellowlees and P. S. Braterman, *Journal of the Chemical Society-Chemical Communications*, 1981, 287-289.
24 C. M. Elliott and E. J. Hershenhart, *Journal of the American Chemical Society*, 1982, **104**, 7519-7526.
25 F. Pichot, J. H. Beck and C. M. Elliott, *Journal of Physical Chemistry A*, 1999, **103**, 6263-6267.