Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Spectroelectrochemistry of tris(bipyridyl)silicon(IV): ligand localized reductions with potential electrochromic applications

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Synthesis of tris(2,2'-bipyridyl)silicon(IV) hexafluorophosphate.

$[Si(bpy)_3](PF_6)_4$ was synthesized according to the procedure published by Suthar, et al.,[1] by combining 1.00 g of SiI_4 (1.87 mmol) with 1.16 g of 2,2'-bipyridine (7.47 mol, 4 eq.) in 5.00 g of 2-picoline in a heavy-wall glass pressure tube under inert atmosphere. The tube was then sealed and placed in a silicone oil bath at 125 ˚C for 3 hours, producing a dark brown solid. At the end of the heating period, the tube was opened, and a small addition of methanol was added to quench incomplete reaction byproducts. Centrifugation and subsequent multiple rinses of the solid with methanol, chloroform, and ether yielded $[Si(bpy)_3]I_4$ as a brown solid that was dried under vacuum. Conversion to the hexafluorophosphate salt was done by dissolving $[Si(bpy)_3]I_4$ in water followed by precipitation of $[Si(bpy)_3](PF_6)_4$ after addition of saturated NH_4PF_6 in water. The solid was rinsed with methanol and ether before drying under vacuum. ^{1}H NMR(CD_3CN): δ 7.43 (d, 6H, *J* = 5.6 Hz), 8.11 (m, 6H), 8.91 (m, 6H), 9.07 (d, 6H, *J* = 8.1Hz). ^{13}C NMR (CD_3CN): δ 129.0 ppm, 134.5 ppm, 144.3 ppm, 147.5 ppm, and 152.3 ppm. ^{29}Si NMR (CD_3CN): δ -155 ppm. ESI-MS: $[Si(bipy)_3]^{4+}(PF_6^-)_3$: $C_{30}H_{24}N_6SiP_3F_{18}^+$ 931.55 m/z; $[Si(bipy)_3]^{4+}\bullet(PF_6^-)_2$: $C_{30}H_{24}N_6SiP_2F_{12}^{2+}$ 393.29 m/z; $[Si(bipy)_3]^{4+}$: $C_{30}H_{24}N_6Si^{4+}$ 124.16 m/z.

Spectroelectrochemical Experiments

The spectroelectrochemical cell was purchased from Pine Instruments and consisted of a covered quartz cuvet with a 1.0 mm pathlength with a printed gold honeycomb working electrode (Pine Instruments), a gold counter electrode, and a Ag/AgCl reference electrode standardized to the ferrocene/ferrocenium couple. Samples of $[Si(bpy)_3](PF_6)_4$ (2.8×10^{-4} M) were prepared in anhydrous acetonitrile with tetra-n-butylammonium hexafluorophosphate (0.1 M). Solutions were potentiostated with a Princeton Applied Research model 173 potentiostat/galvanostat and analyzed with an Agilent 8453 Diode Array Spectrometer.

Note that in our previous manuscript[1], reduction potentials for $Si(bpy)_3^{4+}$ were measured vs. Fc/Fc^+ and then converted to V vs. SCE using the conversion $E^o_{1/2}$ (Fc/Fc^+) = +0.400 V vs. SCE. In the current manuscript all reported values are vs. the internal Fc/Fc^+ standard.

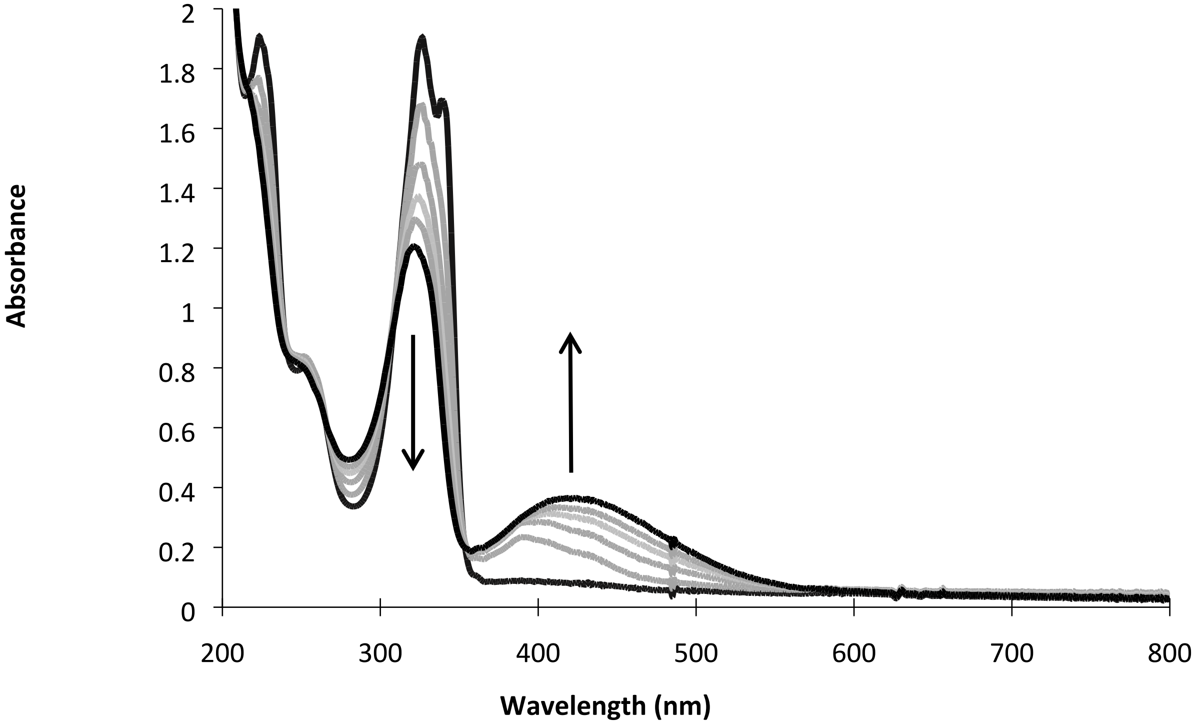

Figure S1. UV-vis spectra of $[Si(bpy)_3](PF_6)_4$ in acetonitrile/0.10 M tetra-n-butylammonium hexafluorophosphate **without** thorough degassing taken at 15 second intervals between -445 mV and -645 mV vs. Fc/Fc^+.

References:

1 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.