Supporting Information for

Radical Anionic versus Neutral 2,2’-Bipyridyl Coordination in Uranium Complexes Supported by Amide and Ketimide Ligands

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1. NMR spectra

Figure S1. $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 22 °C) of 1-(bipy)$_2$ and dmb immediately after mixing.

Figure S2. $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 22 °C) of 1-(bipy)$_2$ and dmb taken 3 h after mixing.
Figure S3. Selected regions of the $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 22 °C) of 1-(bipy)$_2$ and dmb taken 3 h after mixing.
Figure S4. $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 22 °C) of 1-(bipy)$_2$ and dmb taken 3 d after mixing.

Figure S5. A selected region of the $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 22 °C) of 1-(bipy)$_2$ and dmb taken 3 d after mixing.
**Figure S6.** $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 22 °C) of 3-(bipy)$_2$.

**Figure S7.** $^1$H NMR spectrum (300 MHz, C$_6$D$_6$, 22 °C) of 3-(bipy)$_2$ and dmb immediately after mixing.
2. X-ray crystallography

1-(bipy)$_2$

Figure S6. Thermal-ellipsoid (50% probability) representation of 1-(bipy)$_2$. Hydrogen and solvent atoms were omitted for clarity.

Crystals of 1-(bipy)$_2$ grown from a concentrated diethyl ether solution at -35 °C were coated with Paratone N oil (an Exxon product) on a microscope slide. A dark green plate of approximate dimensions 0.28 x 0.23 x 0.11 mm$^3$ was selected and mounted with wax on a glass fiber. A total of 16300 reflections (-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -21 ≤ l ≤ 12) were collected at 173(2) K in the θ range of 2.41 to 23.26°, of which 5904 were unique ($R_{int}$ = 0.0314). The structure was solved by Patterson methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated (d$_{CH}$ = 0.96 Å) positions except for the solvent atoms. The unit cell contains half of a molecule of diethyl ether as crystallization solvent. C1S of the solvent molecule was modeled as C1S and C1S', each with 50% occupancies. The residual peak and hole electron density were 1.04 and -1.49 e·Å$^{-3}$. The least squares refinement converged normally with residuals of (all data) $R_1 = 0.0310$, and GOF = 1.077. Crystal and refinement data: formula 2(C$_{44}$H$_{52}$N$_6$U)(C$_4$O), space group P-1, $a = 10.2945(7)$ Å, $b = 11.0569(7)$ Å, $c = 19.0658(12)$ Å, $α = 76.2790(10)^{°}$, $β = 85.6930(10)^{°}$, $γ = 86.8400(10)^{°}$, $V = 2100.7(2)$ Å$^3$, $Z = 1$, $D_{calc} = 1.478$ g·cm$^{-3}$, $F(000) = 932$, $R_1 = 0.0272$, $wR_2 = 0.0698$.  

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Inside the glove box, crystals of 2-bipy grown from a concentrated pentane solution at -35 °C were coated with Paratone N oil (an Exxon product) on a microscope slide. An orange brown plate of approximate dimensions 0.07 x 0.04 x 0.02 mm³ was selected and mounted with wax on a glass fiber. A total of 12729 reflections (-14 ≤ h ≤ 13, -14 ≤ k ≤ 14, -23 ≤ l ≤ 23) were collected at 173(2) K in the θ range of 2.07 to 23.30 °, of which 8818 were unique (Rint = 0.0703). All non-hydrogen atoms were refined anisotropically. The unit cell contains one and a half molecules of pentane as crystallization solvent. C3S lies on the inversion center. Hydrogen atoms were placed in calculated (dCH = 0.96 Å) positions, except for C3S, for which no hydrogen atoms were calculated. The residual peak and hole electron density were 2.58 and -2.62 e·Å⁻³, respectively. The least squares refinement converged normally with residuals of R1 = 0.0625, and GOF = 1.085. Crystal and refinement data: formula 2(C₆₄H₈₀N₅U)(C₅H₁₂)(C₅H₁₀), space group P-1, a = 12.7236(15) Å, b = 13.1198(16) Å, c = 21.535(3) Å, α = 96.427(2) °, β = 103.920(2) °, γ = 112.905(2) °, V = 3128.1(7) Å³, Z = 1, Dcalc = 1.343 g·cm⁻³, μ = 2.639 mm⁻¹, F(000) = 1306, Rf = 0.0681, and wR2 = 0.1569.
Inside the glove box, crystals of 3-(bipy)$_2$, obtained from a saturated pentane solution at –35 °C were coated with Paratone N oil (an Exxon product) on a microscope slide. A dark brown prism of approximate dimensions 0.55 x 0.10 x 0.06 mm$^3$ was selected and mounted with wax on a glass fiber. A total of 28057 reflections (-17 ≤ h ≤ 16, -13 ≤ k ≤ 19, -28 ≤ l ≤ 28) were collected at 183(2) K in the θ range of 2.50 to 23.32°, of which 10025 were unique ($R_{int} = 0.0499$). All non-hydrogen atoms were refined anisotropically. One of the t-butyl groups was disordered and the disorder was modeled over two sites. Hydrogen atoms were placed in calculated ($d_{C-H} = 0.96$ Å) positions. The unit cell contains large accessible voids; solvent molecules could not be modeled to fit this space (it is possible that some solvent was lost during crystal handling) and the program SQUEEZE was used. The residual peak and hole electron density were 0.72 and -0.65 e·Å$^{-3}$, respectively. The least squares refinement converged normally with residuals of $R_I = 0.0316$, and GOF = 1.056. Crystal and refinement data: formula C$_{62}$H$_{76}$N$_7$U, space group P2(1)/n, $a = 15.989(2)$ Å, $b = 17.137(2)$ Å, $c = 25.732(4)$ Å, $β = 98.460(2)^°$, $V = 6973.8(17)$ Å$^3$, $Z = 4$, $μ = 2.363$ mm$^{-1}$, $D_{calc} = 1.102$ g·cm$^{-3}$, $F(000) = 2356$, $R_I = 0.0417$, and $wR_2 = 0.0930$. 

Figure S8. Thermal-ellipsoid (50% probability) representation of 3-(bipy)$_2$. Hydrogen atoms were omitted for clarity.
Inside the glove box, crystals of 3-I-bipy, obtained from a saturated diethyl ether solution at –35 °C were coated with Paratone N oil (an Exxon product) on a microscope slide. A dark brown prism of approximate dimensions 0.37 x 0.35 x 0.28 mm³ was selected and mounted with wax on a glass fiber. A total of 21176 reflections (-13 ≤ h ≤ 14, -23 ≤ k ≤ 22, -21 ≤ l ≤ 21) were collected at 183(2) K in the θ range of 2.29 to 23.27°, of which 7764 were unique (R_{int} = 0.0318). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in calculated (d_{C-H} = 0.96 Å) positions. The unit cell contains large accessible voids; solvent molecules could not be modeled to fit this space (it is possible that some solvent was lost during crystal handling) and the program SQUEEZE was used. The residual peak and hole electron density were 0.57 and -0.57 e·Å⁻³, respectively. The least squares refinement converged normally with residuals of R_I = 0.0246, and GOF = 1.031. Crystal and refinement data: formula C₅₂H₆₈N₅UI, space group P2(1)/c, a = 12.987(3) Å, b = 21.245(4) Å, c = 25.732(4) Å, α = 90.0°, β = 97.038(3)°, γ = 90.0°, V = 5410.9(18) Å³, Z = 4, μ = 3.605 mm⁻¹, D_{calc} = 1.385 g·cm⁻³, F(000) = 2240, R_I = 0.0310, and wR₂ = 0.0625.

**Figure S9.** Thermal-ellipsoid (50% probability) representation of 3-I-bipy. Hydrogen atoms were omitted for clarity.
Figure S10. Space-filling model of 1-(bipy)$_2$ (top left), 2-bipy (top right), 3-(bipy)$_2$ (bottom left), 3-l-bipy (bottom right).
3. Electron absorption spectroscopy

Figure S11. UV-vis absorption spectrum of a 1-(bipy)$_2$ toluene solution at 25 ºC.

Figure S12. UV-vis absorption spectrum of a 2-bipy toluene solution at 25 ºC.
Figure S13. UV-vis absorption spectrum of a 3-(bipy)$_2$ toluene solution at 25 ºC.

Figure S14. UV-vis absorption spectrum of a 3-I-bipy toluene solution at 25 ºC.
4. Magnetic data

**Susceptibility measurements.** Reproducibility of the obtained data was ascertained using multiple samples from independent batches of a specific compound. Magnetic susceptibility measurements were recorded using a SQUID magnetometer at 5000 G. The samples were prepared in the glove box (50 – 100 mg) loaded in a gelatin capsule that was positioned inside a plastic straw and carried to the magnetometer in a tube sealed under N₂. The sample was quickly inserted into the instrument, centered and data obtained from 5 to 300 K. The contribution from the sample holders was not accounted for. The diamagnetic contributions were calculated using Pascal constants and subtracted from \( \chi_{\text{mol}} \). Effective magnetic moments were calculated either by linear regression from plots of \( 1/\chi_{\text{mol}} \) versus \( T \) (K) for Curie-Weiss behavior or by using the formula 2.828*\( \sqrt{T \chi_{\text{mol}}} \) for non-Curie-Weiss behavior.

**Figure S15.** Plots of \( \mu_{\text{eff}} \) versus \( T \) for 1-(bipy)₂ (top left), 3-(bipy)₂ (top right), 3-I-bipy (bottom left), 2-bipy (bottom right).
Figure S16. Plot of $\chi$ versus $T$ for 1-(bipy)$_2$.

Figure S17. Plot of $\chi$ versus $T$ for 3-(bipy)$_2$. 
Figure S18. Plot of $\chi$ versus T for 3-I-bipy.

Figure S19. Plots of $\chi$ (top) and $1/\chi$ (bottom) versus T for 2-bipy.