

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

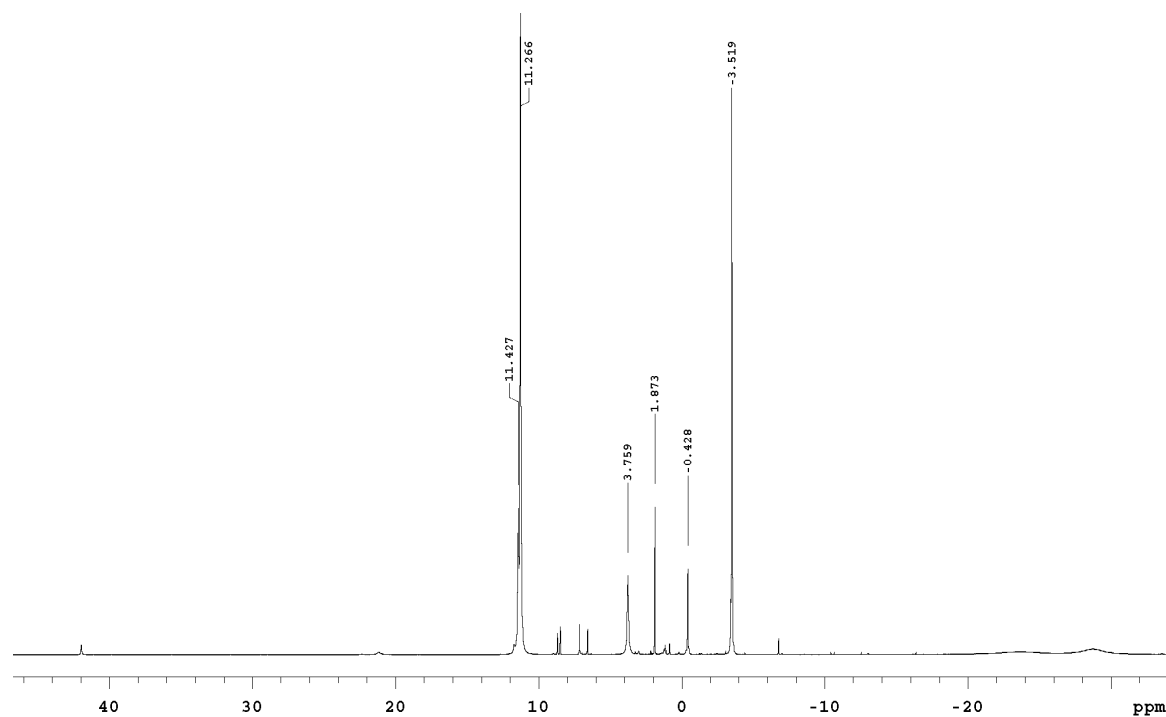


Figure S1. ^1H NMR spectrum (300 MHz, C_6D_6 , 22 $^\circ\text{C}$) of **1**-(bipy) $_2$ and dmb immediately after mixing.

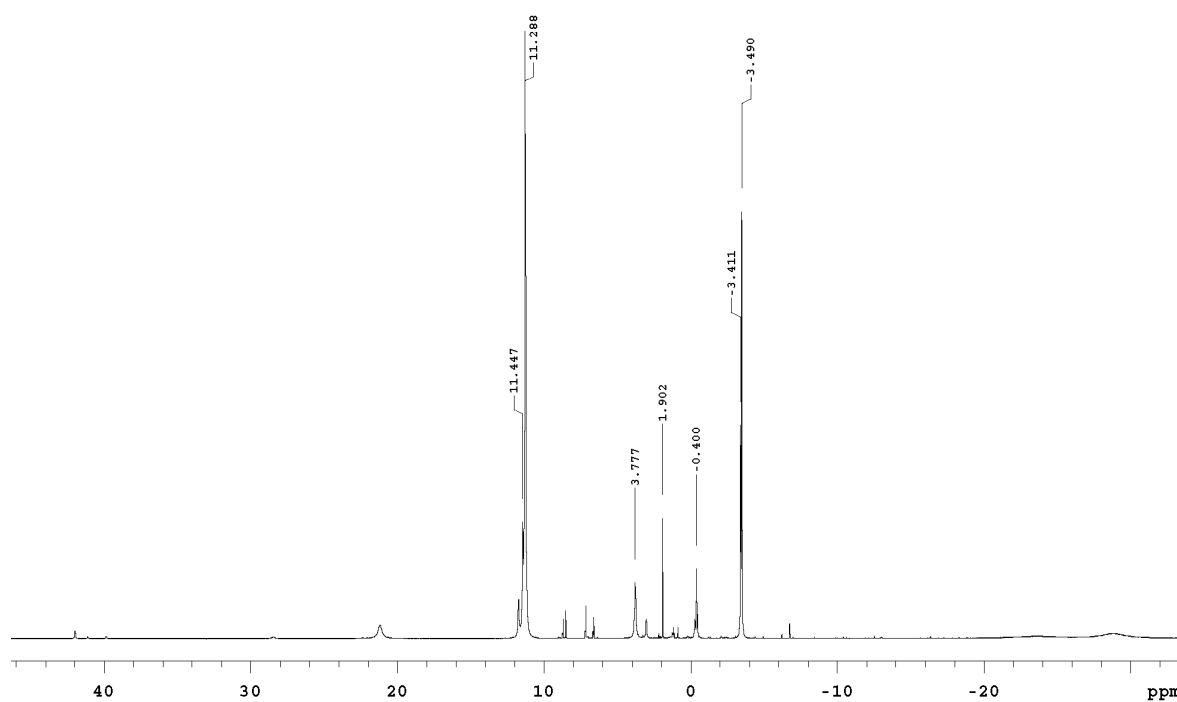


Figure S2. ^1H NMR spectrum (300 MHz, C_6D_6 , 22 $^\circ\text{C}$) of **1**-(bipy) $_2$ and dmb taken 3 h after mixing.

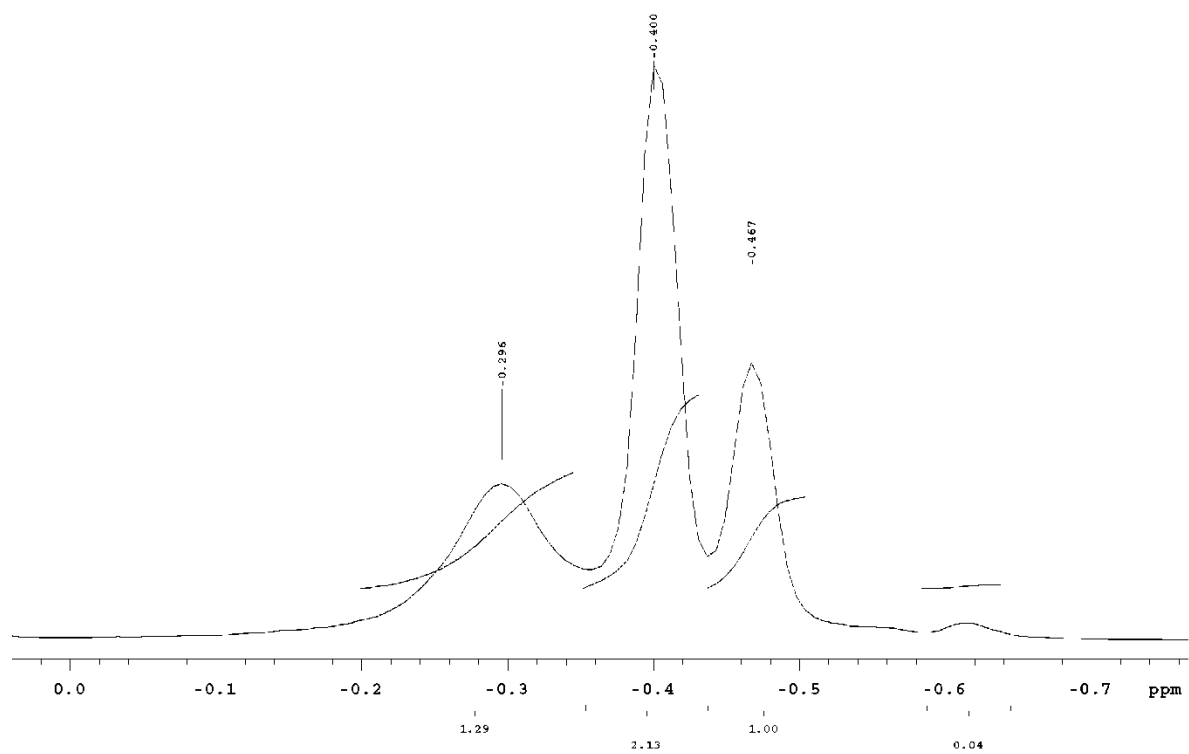
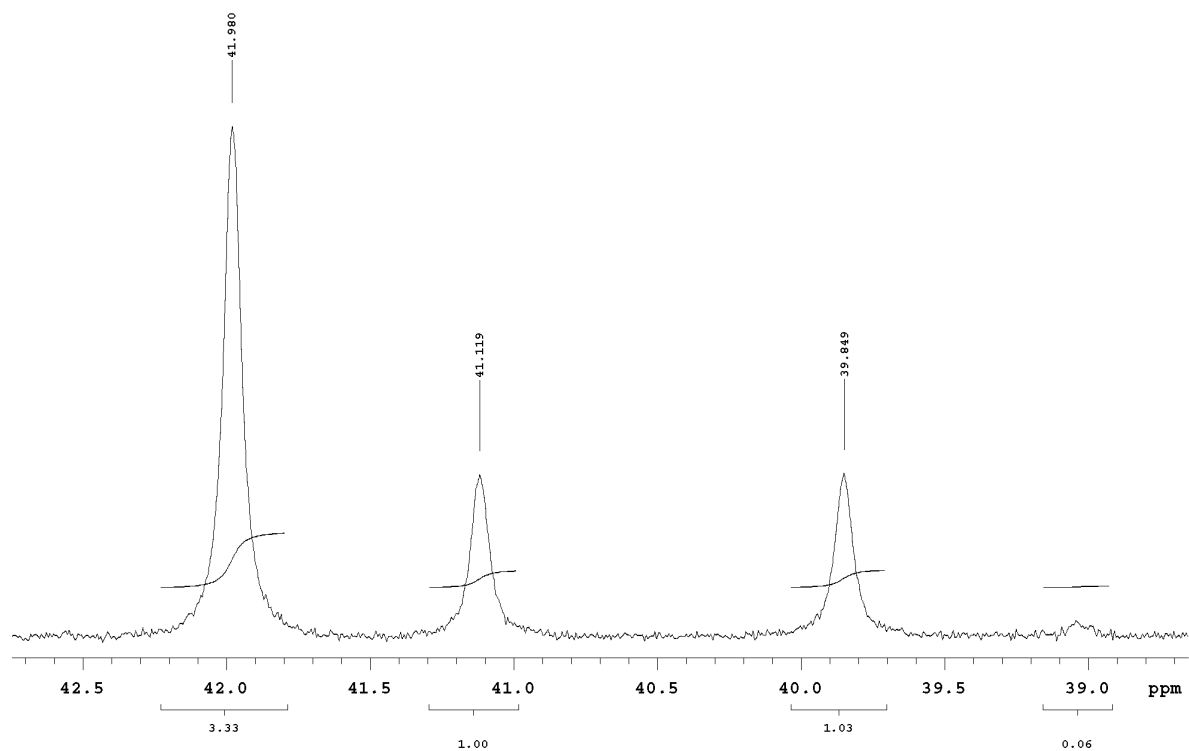


Figure S3. Selected regions of the ¹H NMR spectrum (300 MHz, C₆D₆, 22 °C) of 1-(bipy)₂ and dmb taken 3 h after mixing.

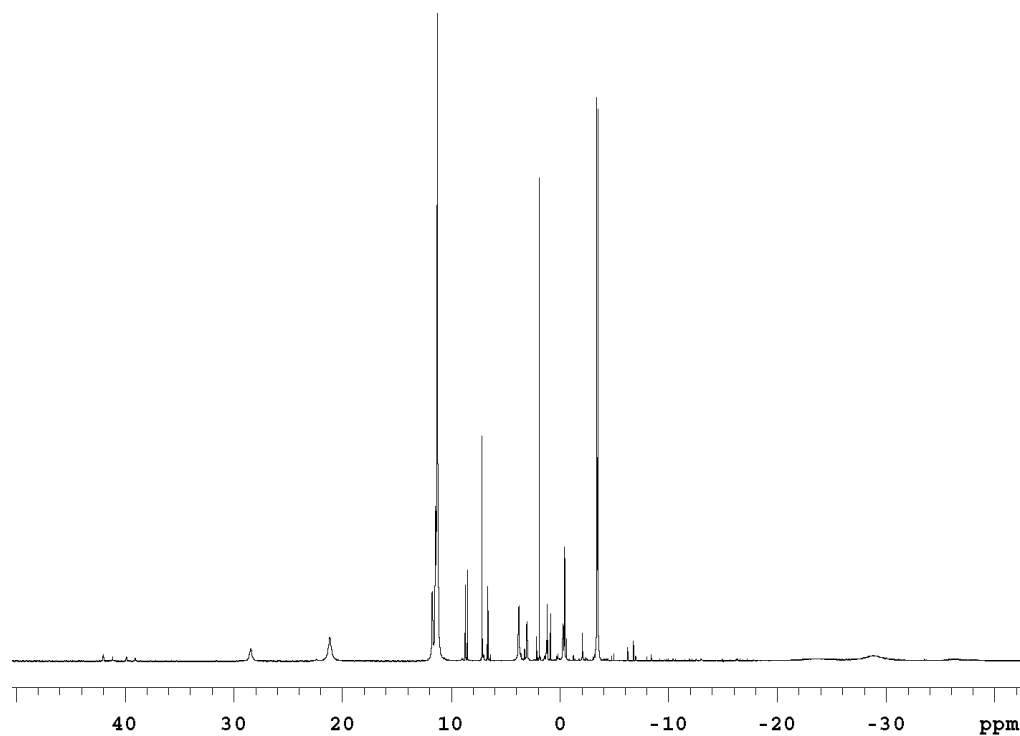


Figure S4. ^1H NMR spectrum (300 MHz, C_6D_6 , 22 $^\circ\text{C}$) of **1**-(bipy) $_2$ and dmb taken 3 d after mixing.

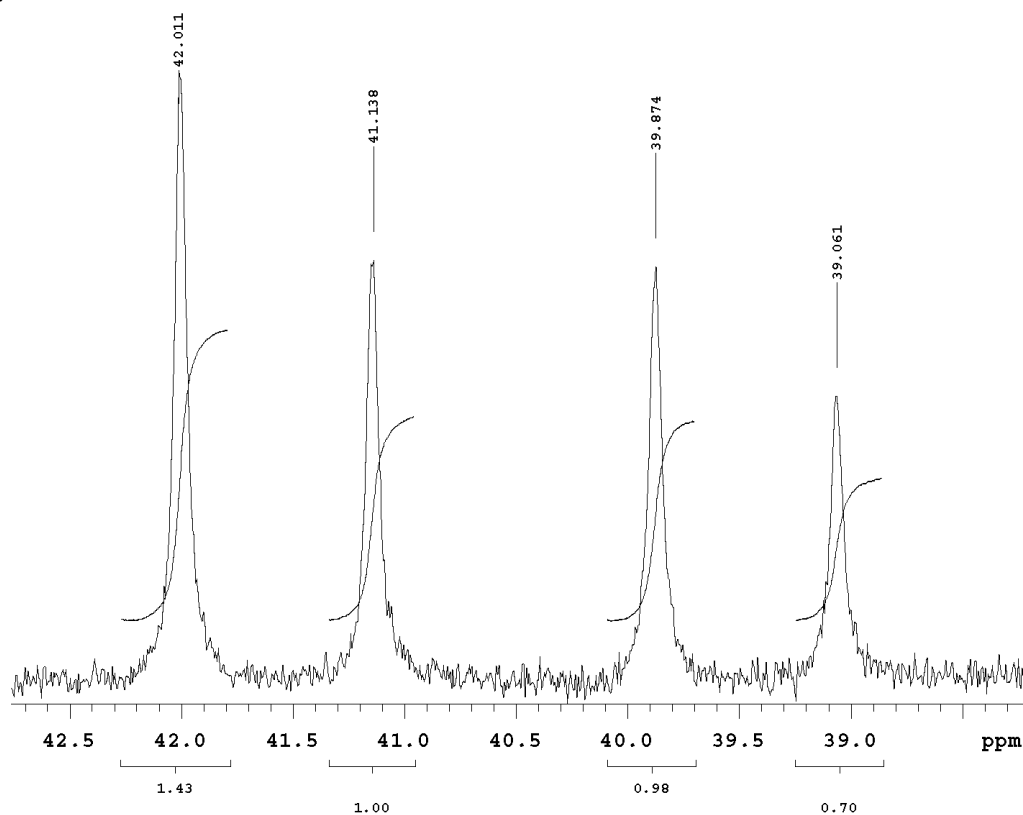


Figure S5. A selected region of the ^1H NMR spectrum (300 MHz, C_6D_6 , 22 $^\circ\text{C}$) of **1**-(bipy) $_2$ and dmb taken 3 d after mixing.

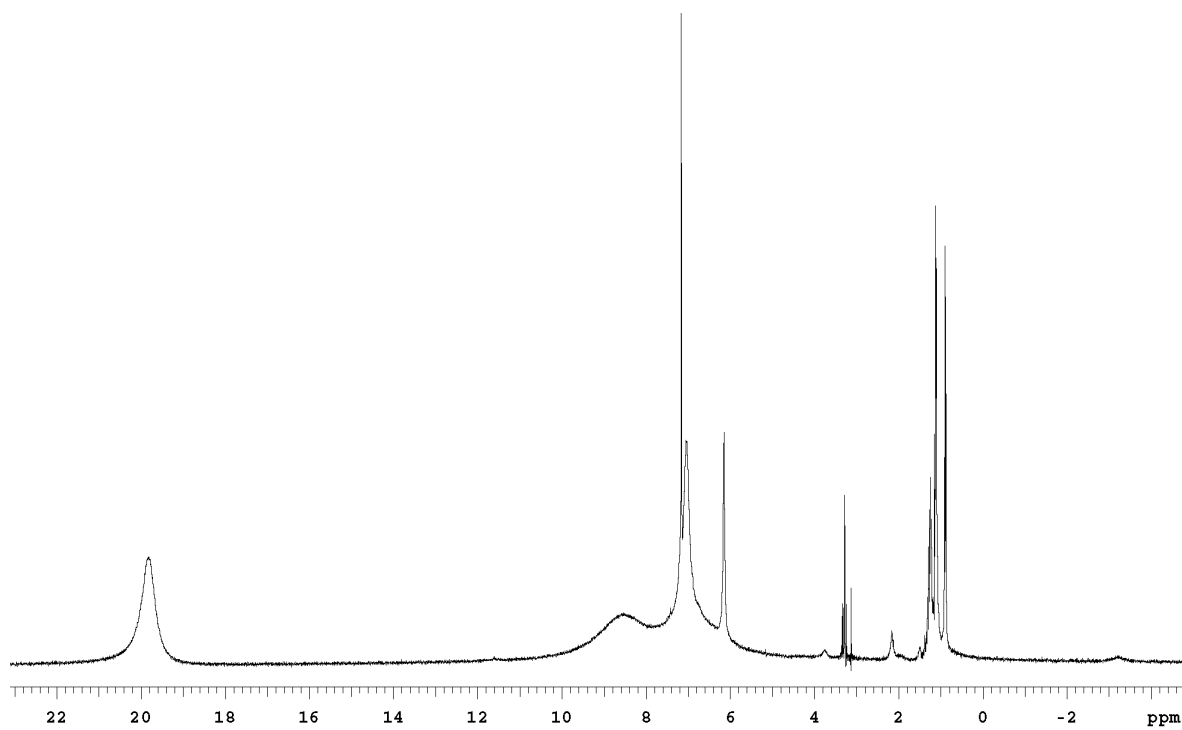


Figure S6. ^1H NMR spectrum (300 MHz, C_6D_6 , 22 $^\circ\text{C}$) of 3-(bipy) $_2$.

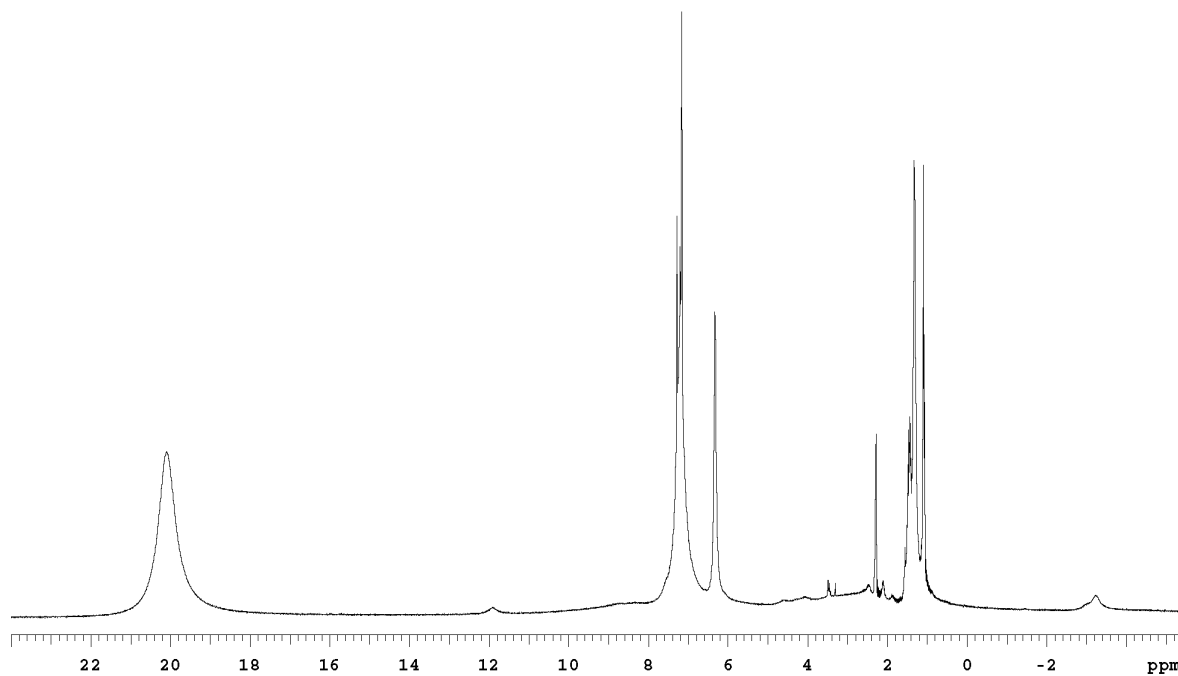


Figure S7. ^1H NMR spectrum (300 MHz, C_6D_6 , 22 $^\circ\text{C}$) of 3-(bipy) $_2$ and dmb immediately after mixing.

2. X-ray crystallography

1-(bipy)₂

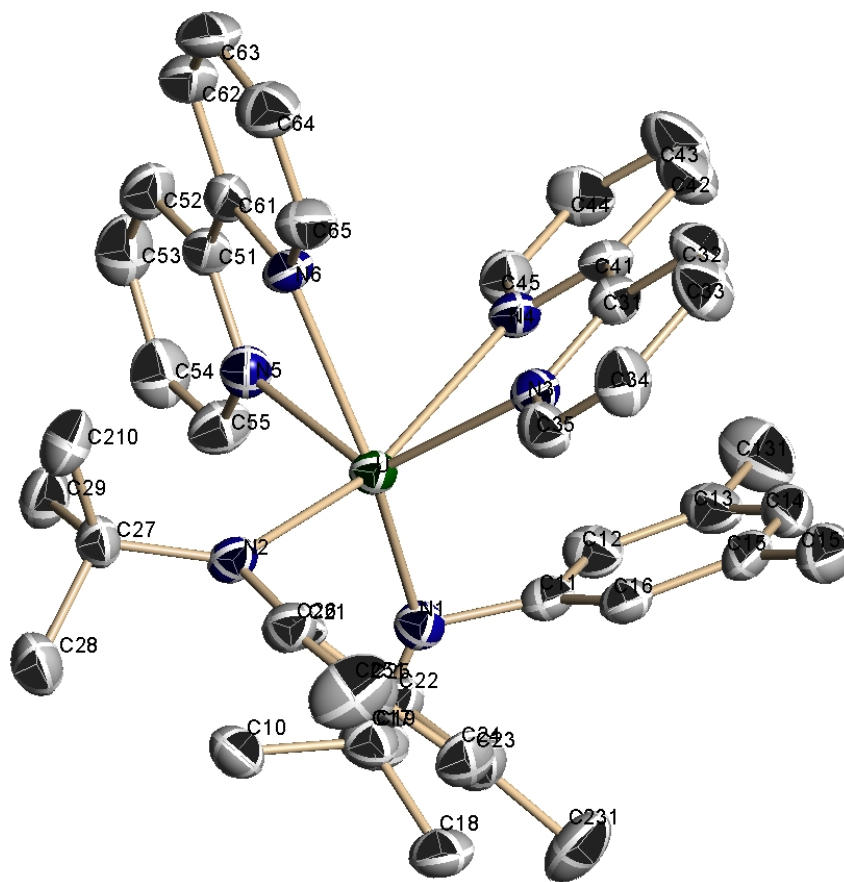


Figure S6. Thermal-ellipsoid (50% probability) representation of 1-(bipy)₂. Hydrogen and solvent atoms were omitted for clarity.

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 mm³ was selected and mounted with wax on a glass fiber. A total of 16300 reflections ($-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-21 \leq l \leq 12$) 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(C₄₄H₅₂N₆U)(C₄O), space group P-1, $a = 10.2945(7)$ Å, $b = 11.0569(7)$ Å, $c = 19.0658(12)$ Å, $\alpha = 76.2790(10)^\circ$, $\beta = 85.6930(10)^\circ$, $\gamma = 86.8400(10)^\circ$, $V = 2100.7(2)$ Å³, $Z = 1$, $D_{calc} = 1.478$ g·cm⁻³, $F(000) = 932$, $R_1 = 0.0272$, $wR_2 = 0.0698$.

2-bipy

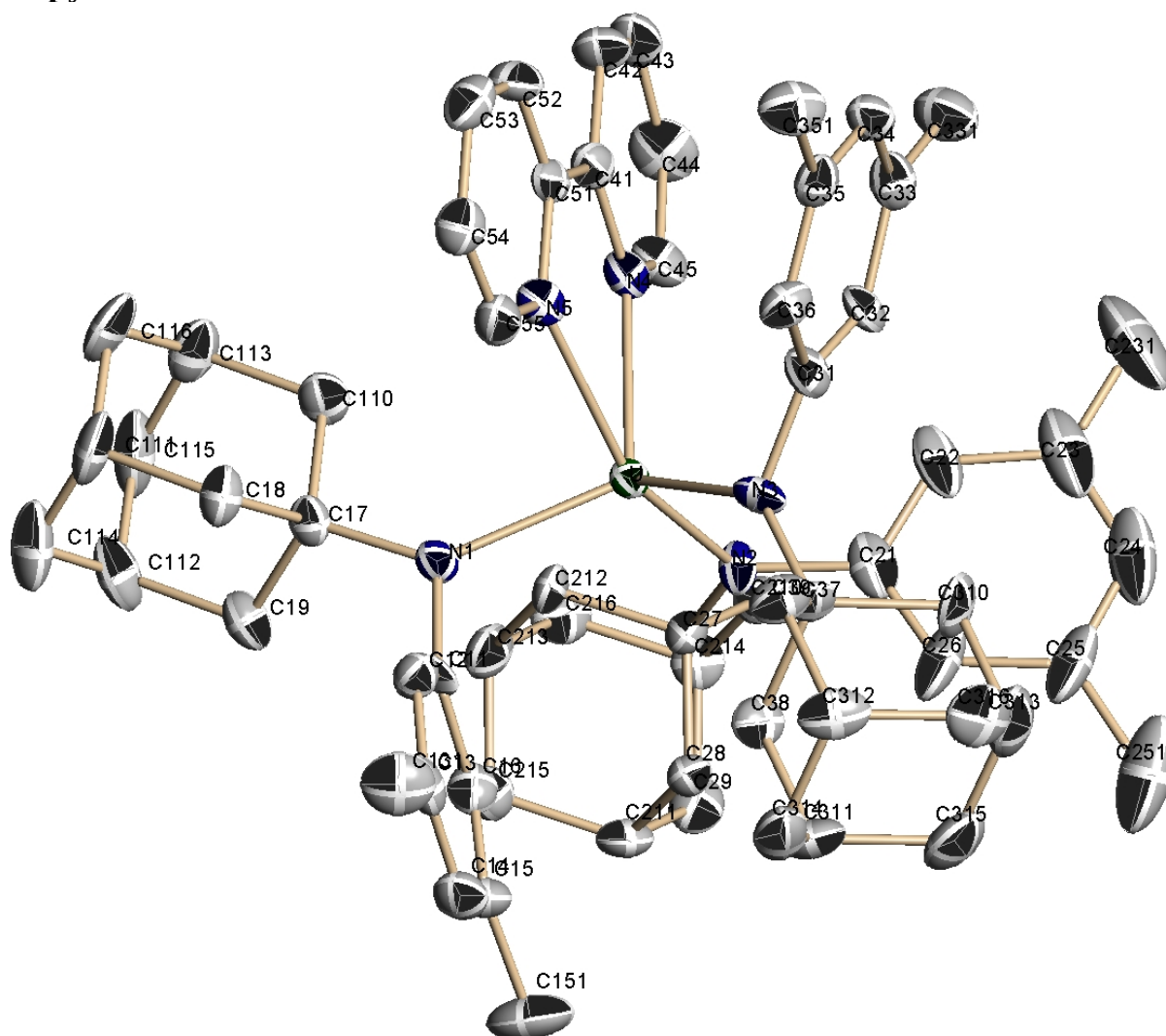


Figure S7. Thermal-ellipsoid (50% probability) representation of **2-bipy**. Hydrogen and solvent atoms were omitted for clarity.

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 ($-14 \leq h \leq 13$, $-14 \leq k \leq 14$, $-23 \leq l \leq 23$) were collected at 173(2) K in the θ range of 2.07 to 23.30 °, of which 8818 were unique ($R_{\text{int}} = 0.0703$). 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 ($d_{\text{CH}} = 0.96$ 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 $\cdot$ Å⁻³, respectively. The least squares refinement converged normally with residuals of $R_1 = 0.0625$, and GOF = 1.085. Crystal and refinement data: formula 2(C₆₄H₈₀N₅U)2(C₅H₁₂)(C₅H₁₀), space group P-1, $a = 12.7236(15)$ Å, $b = 13.1198(16)$ Å, $c = 21.535(3)$ Å, $\alpha = 96.427(2)^\circ$, $\beta = 103.920(2)^\circ$, $\gamma = 112.905(2)^\circ$, $V = 3128.1(7)$ Å³, $Z = 1$, $D_{\text{calc}} = 1.343$ g $\cdot$ cm⁻³, $\mu = 2.639$ mm⁻¹, $F(000) = 1306$, $R_I = 0.0681$, and $wR_2 = 0.1569$.

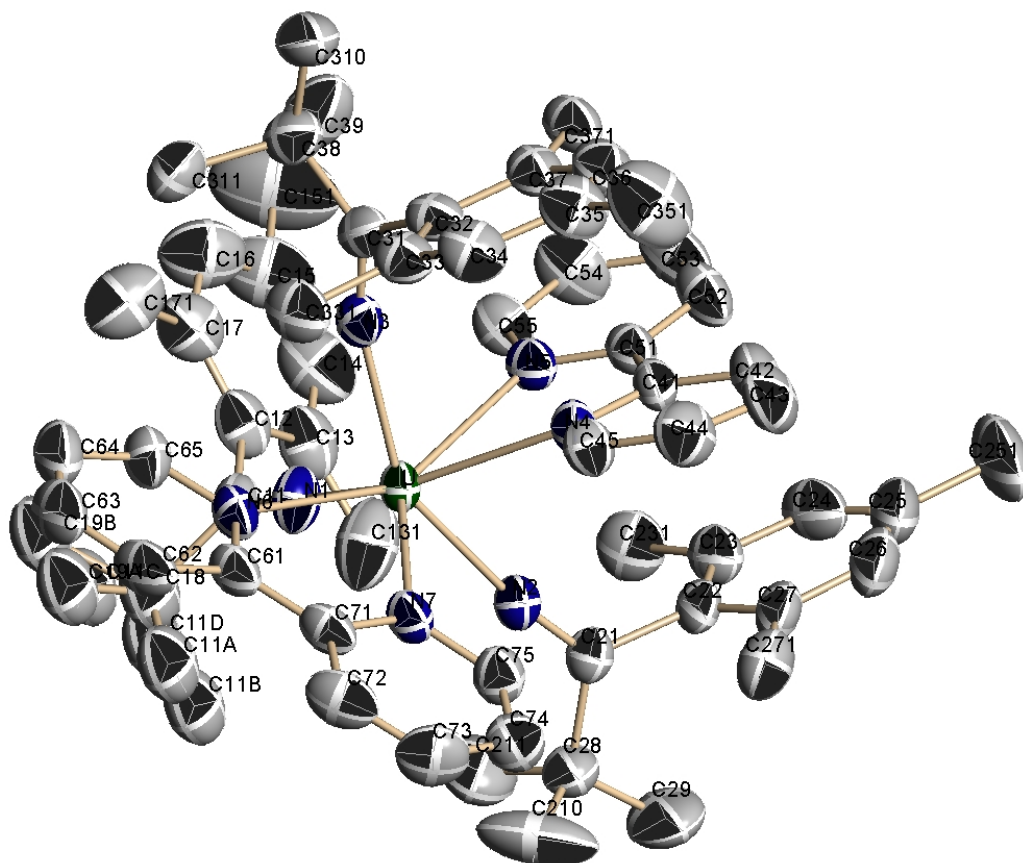
3-(bipy)₂

Figure S8. Thermal-ellipsoid (50% probability) representation of 3-(bipy)₂. Hydrogen atoms were omitted for clarity.

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 mm³ was selected and mounted with wax on a glass fiber. A total of 28057 reflections ($-17 \leq h \leq 16$, $-13 \leq k \leq 19$, $-28 \leq l \leq 28$) were collected at 183(2) K in the θ range of 2.50 to 23.32°, of which 10025 were unique ($R_{\text{int}} = 0.0499$). 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 ($d_{\text{C-H}} = 0.96$ 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 $\text{GOF} = 1.056$. Crystal and refinement data: formula C₆₂H₇₆N₇U, space group P2(1)/n, $a = 15.989(2)$ Å, $b = 17.137(2)$ Å, $c = 25.732(4)$ Å, $\beta = 98.460(2)^\circ$, $V = 6973.8(17)$ Å³, $Z = 4$, $\mu = 2.363$ mm⁻¹, $D_{\text{calc}} = 1.102$ g·cm⁻³, $F(000) = 2356$, $R_I = 0.0417$, and $wR_2 = 0.0930$.

3-I-bipy

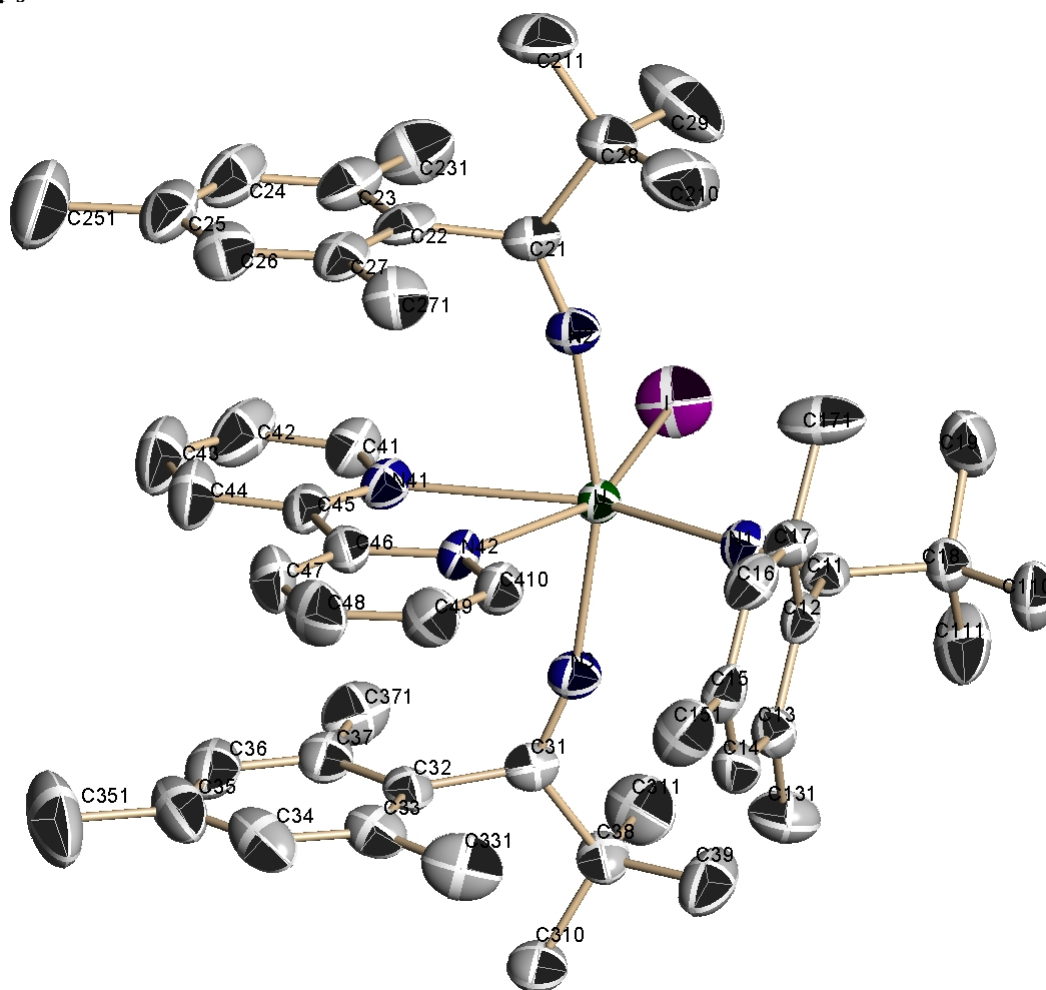


Figure S9. Thermal-ellipsoid (50% probability) representation of 3-I-bipy. Hydrogen atoms were omitted for clarity.

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 $0.37 \times 0.35 \times 0.28 \text{ mm}^3$ was selected and mounted with wax on a glass fiber. A total of 21176 reflections ($-13 \leq h \leq 14$, $-23 \leq k \leq 22$, $-21 \leq l \leq 21$) were collected at 183(2) K in the θ range of 2.29 to 23.27° , of which 7764 were unique ($R_{\text{int}} = 0.0318$). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in calculated ($d_{\text{C-H}} = 0.96 \text{ \AA}$) 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 $-0.57 \text{ e}^{-}\cdot\text{\AA}^{-3}$, respectively. The least squares refinement converged normally with residuals of $R_1 = 0.0246$, and $\text{GOF} = 1.031$. Crystal and refinement data: formula $\text{C}_{52}\text{H}_{68}\text{N}_5\text{UI}$, space group P2(1)/c , $a = 12.987(3) \text{ \AA}$, $b = 21.245(4) \text{ \AA}$, $c = 25.732(4) \text{ \AA}$, $\alpha = 90.0^{\circ}$, $\beta = 97.038(3)^{\circ}$, $\gamma = 90.0^{\circ}$, $V = 5410.9(18) \text{ \AA}^3$, $Z = 4$, $\mu = 3.605 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.385 \text{ g}\cdot\text{cm}^{-3}$, $F(000) = 2240$, $R_1 = 0.0310$, and $wR_2 = 0.0625$.

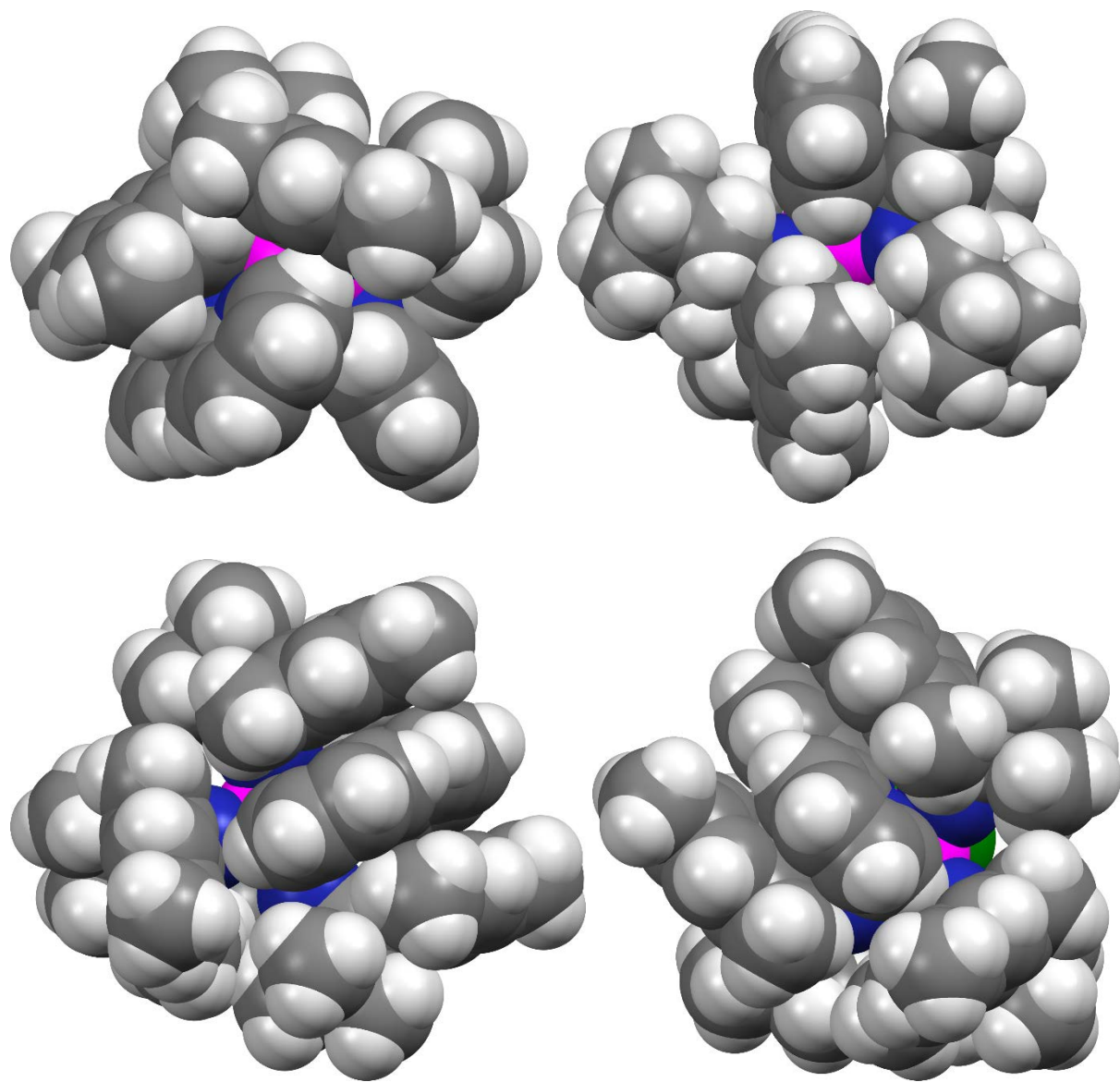


Figure S10. Space-filling model of **1**-(bipy)₂ (top left), **2**-bipy (top right), **3**-(bipy)₂ (bottom left), **3-I**-bipy (bottom right).

3. Electron absorption spectroscopy

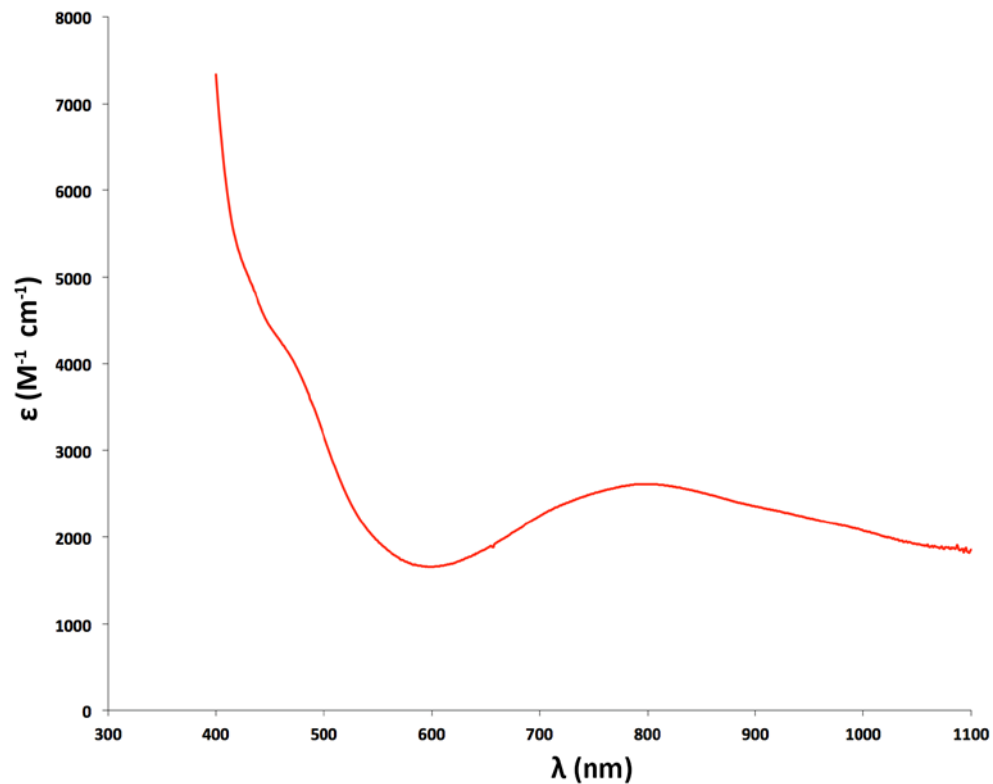


Figure S11. UV-vis absorption spectrum of a 1-(bipy)₂ toluene solution at 25 °C.

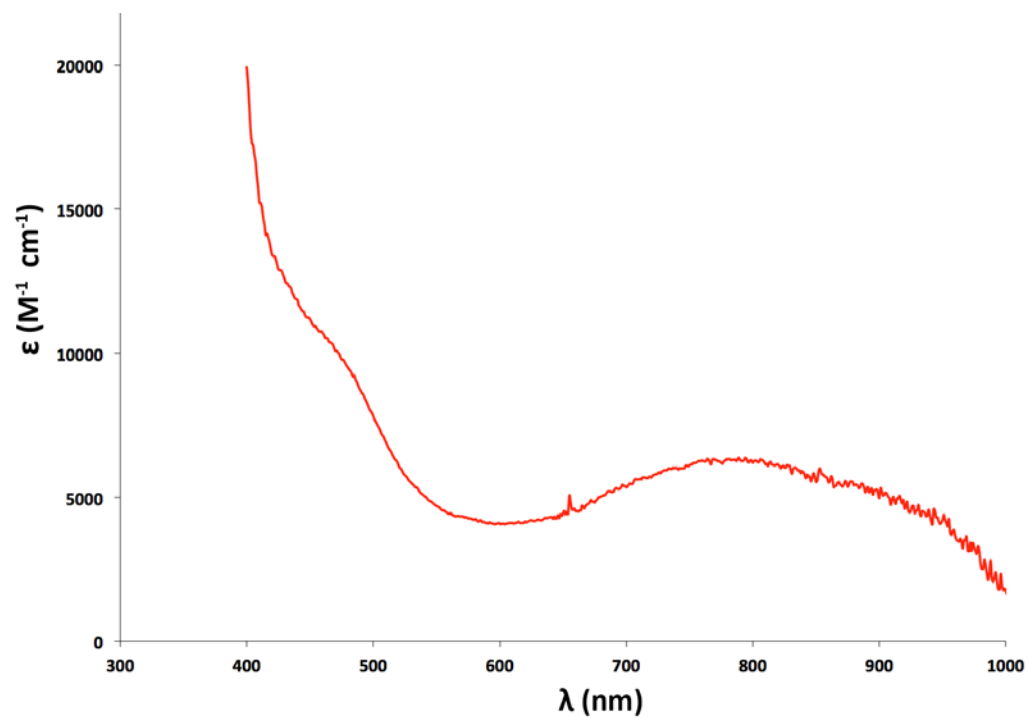


Figure S12. UV-vis absorption spectrum of a 2-bipy toluene solution at 25 °C.

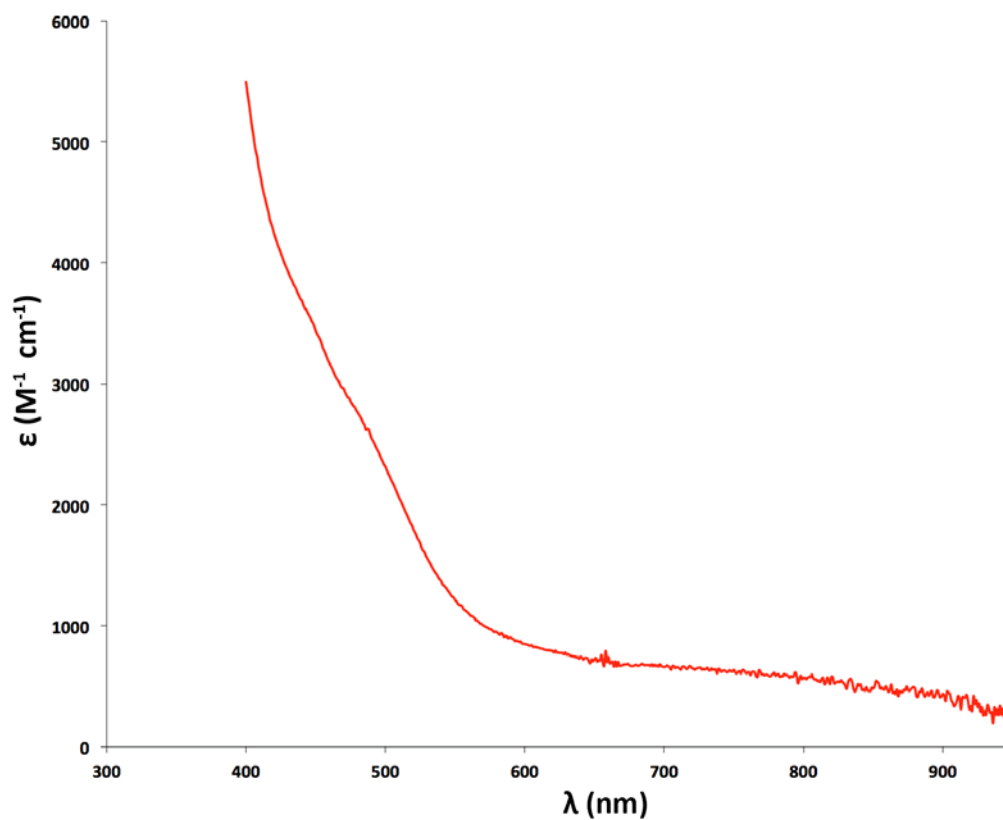


Figure S13. UV-vis absorption spectrum of a 3-(bipy)₂ toluene solution at 25 °C.

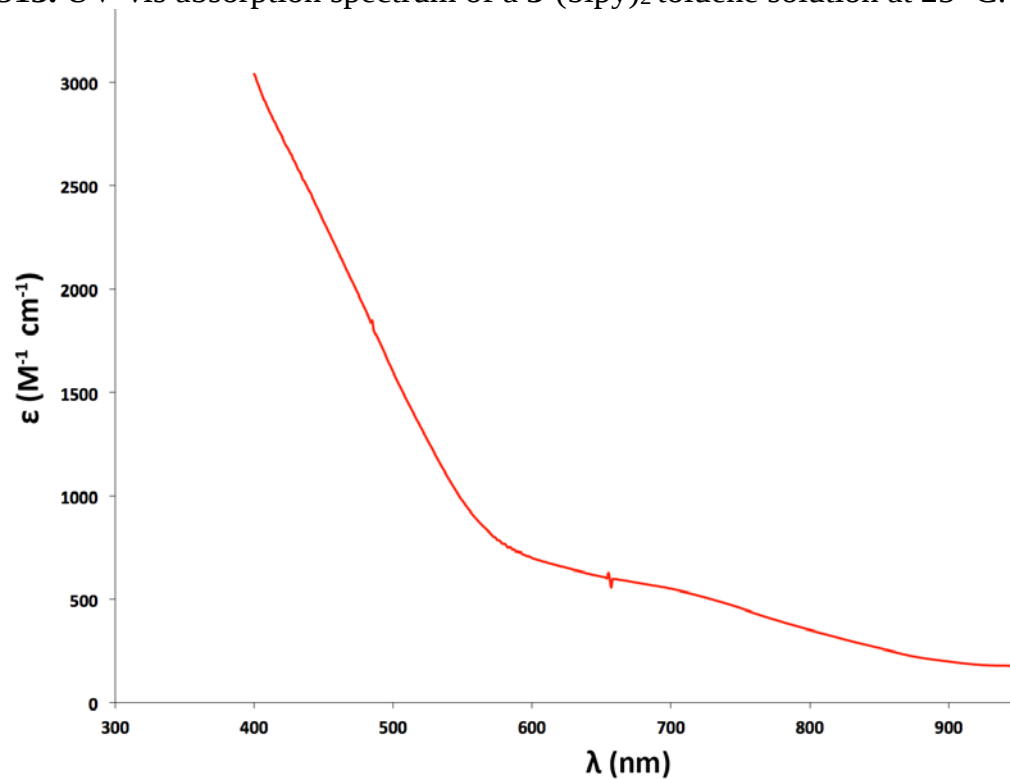


Figure S14. UV-vis absorption spectrum of a 3-I-bipy toluene solution at 25 °C.

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 N_2 . 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 χ_{mol} . Effective magnetic moments were calculated either by linear regression from plots of $1/\chi_{mol}$ versus T (K) for Curie-Weiss behavior or by using the formula $2.828 \cdot \sqrt{(T \cdot \chi_{mol})}$ for non-Curie-Weiss behavior.

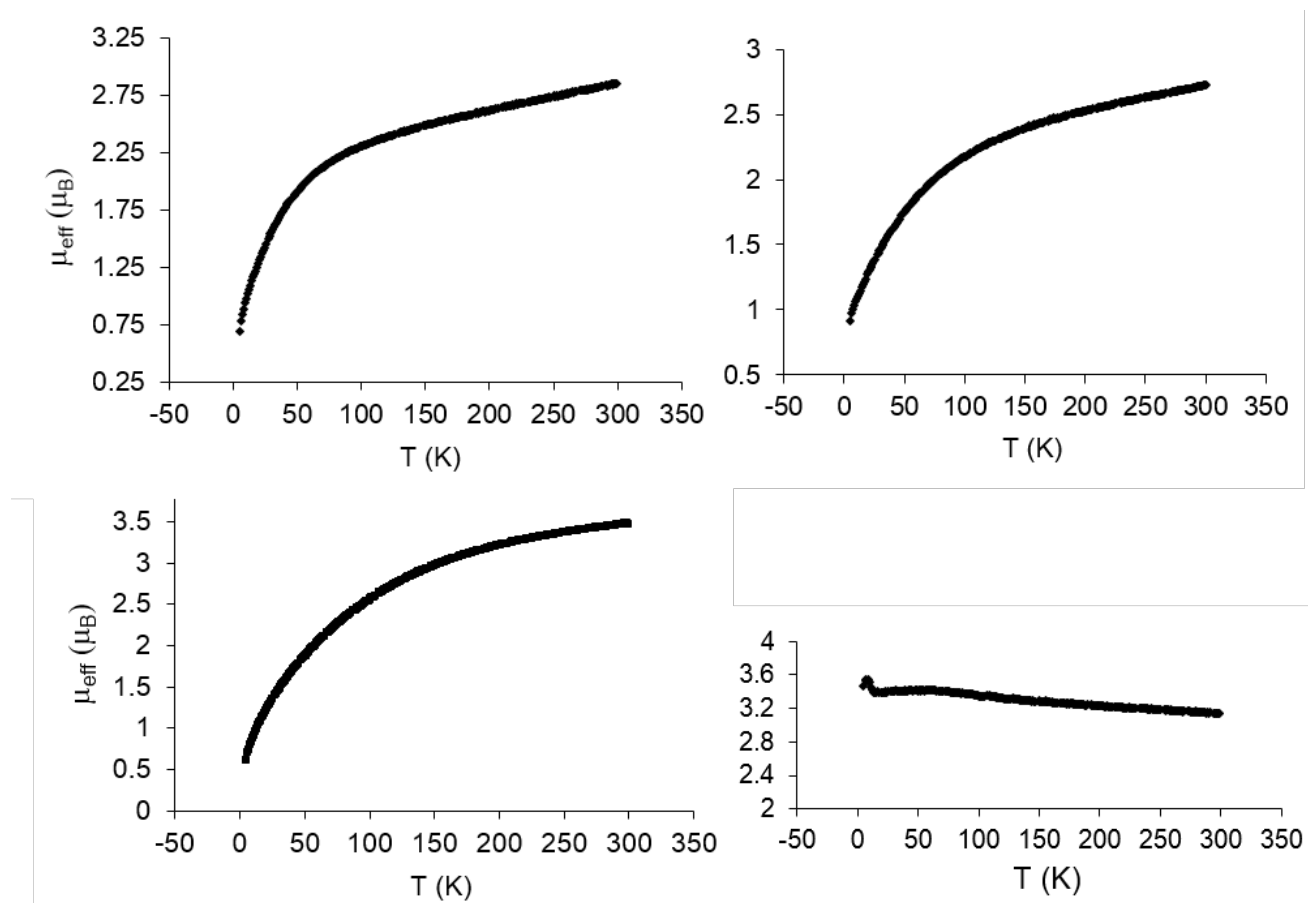


Figure S15. Plots of μ_{eff} versus T for $1-(bipy)_2$ (top left), $3-(bipy)_2$ (top right), $3-I-bipy$ (bottom left), $2-bipy$ (bottom right).

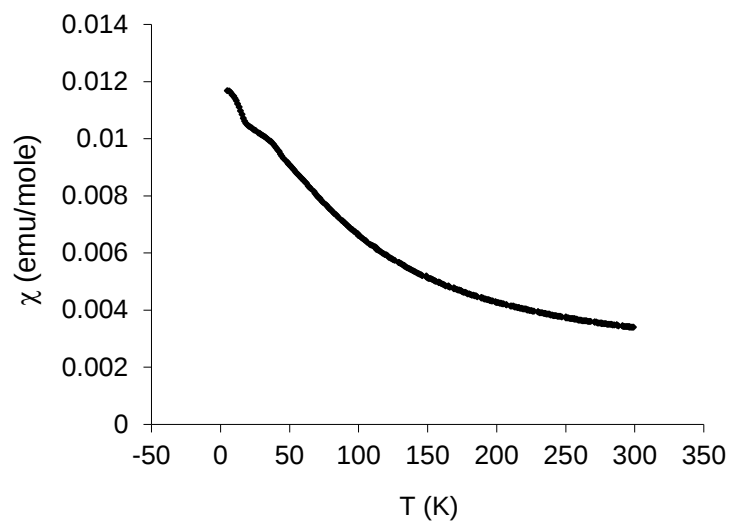


Figure S16. Plot of χ versus T for 1-(bipy)₂.

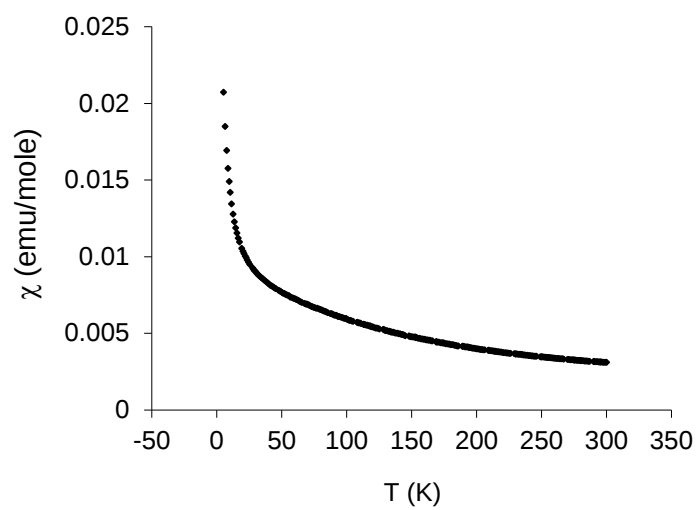


Figure S17. Plot of χ versus T for 3-(bipy)₂.

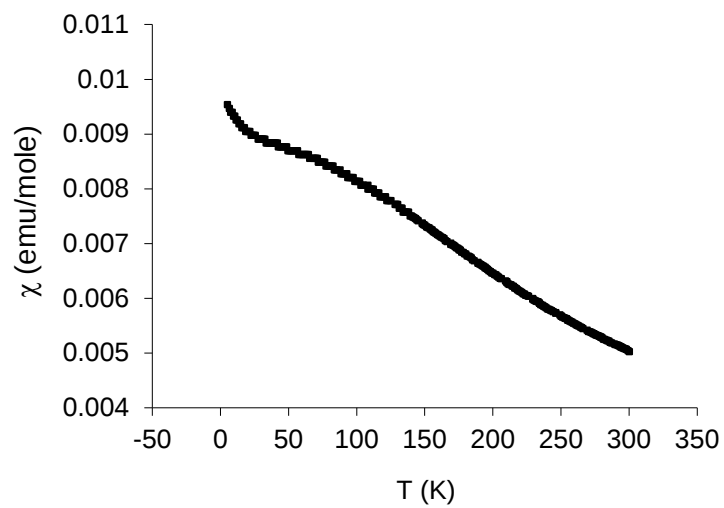


Figure S18. Plot of χ versus T for 3-I-bipy.

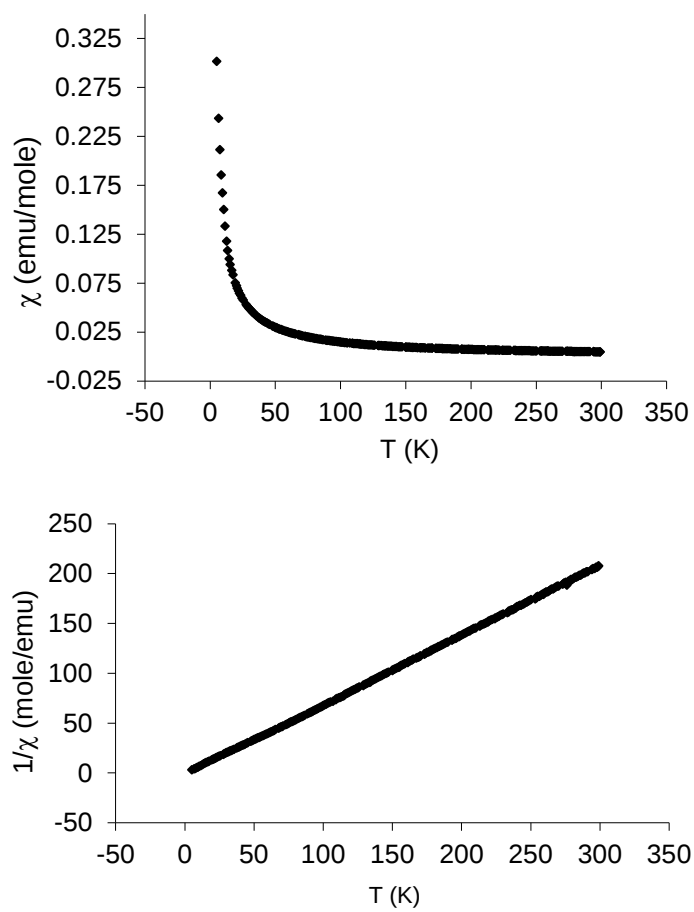


Figure S19. Plots of χ (top) and $1/\chi$ (bottom) versus T for 2-bipy.