Electronic Supplementary Information for

Redox-induced fluoride ligand dissociation stabilized by intramolecular hydrogen bonding

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Synthetic Preparations

General Considerations

All commercially-available reagents were used as received without further purification. H_3 thpa and $CuCl(H_3$ thpa),¹ tpa² and K[Fe(CO)₂Cp]³ were synthesized as previously described. All manipulations were carried out under a purified atmosphere of nitrogen using standard Schlenk techniques or in an MBraun Lab Master 130 or Innovative Technologies Pure LabHE GP-1 glovebox, unless otherwise stated. NMR spectra were recorded on either a Varian MR400 or a Varian vnmrs 500 spectrometer and are referenced to residual solvent peaks. IR spectra were collected using a Nicolet iS10 spectrometer using a diamond attenuated total reflectance (ATR) accessory or as KBr pellets. EPR spectra were collected on a Varian Cary-50 spectrophotometer. Elemental analyses were performed by Midwest Microlabs, LLC, Indianapolis, IN. Voltammetry experiments were conducted under N₂ in a cell consisting of a glassy carbon working electrode, platinum counter electrode and a silver wire reference and introduced at the end of the experiment, then voltammograms were referenced to SCE (ferrocene/ferrocenium = 0.46 V / SCE in CH₂Cl₂).

CuF(H₃thpa)BF₄ (1)

In the open air, methanol (30 mL) was added to H₃thpa (0.400 g; 1.18 mmol) and NaBF₄ (0.285 g; 0.259 mmol) and stirred. Cu(SO₄)·5H₂O (0.295 g; 1.18 mmol) was added to the mixture and stirred for *ca*. 5 min, producing a cloudy green mixture, at which time CsF (0.198 g; 1.30 mmol) was added and stirring was continued for 2 h. The turquoise mixture was then filtered and the filtrate was concentrated to dryness. The residue was extracted with dichloromethane (*ca*. 30 mL) and filtered. The filtrate was concentrated to yield the title compound as a microcrystalline turquoise solid (0.462 g; 77%). Crystals of **1** suitable for X-ray diffraction were grown from vapor diffusion of diethyl ether into a dichloromethane solution of **1**. IR (ATR, cm⁻¹): 3159 (OH), 3125 (OH), 1629, 1578, 1459, 1312, 1046 (BF₄), 717. EPR (1:1 CH₂Cl₂:toluene, 77 K): $g_x = 2.210$, $g_y = 2.182$, $g_z = 1.945$, $A_x = 100$ G, $A_y = 103$ G, $A_z = 67$ G. UV-vis (CH₂Cl₂): 889 nm (240 cm⁻¹M⁻¹), 683 (53). Anal. cald (C₁₈H₁₈BCuF₅N₄O₃): 42.58 C, 3.57 H, 11.04 N%. Found: 43.05 C, 3.67 H, 11.13 N%.

CuF(H₃thpa) (2)

Complex 1 (199.5 mg; 0.393 mmol) was suspended in dimethoxyethane (*ca.* 25 mL) and K[Fe(CO)₂Cp] (81.0 mg dissolved in *ca.* 2 mL dimethoxyethane; 0.375 mmol) was added dropwise to the mixture and stirred for *ca.* 15 min. The dark orange mixture was then filtered and the filtrate was concentrated to dryness. The residue was washed with 1:1 dimethoxyethane:diethyl ether (*ca.* 10 mL) and filtered, then the filter cake was washed with diethyl ether until the eluent became colorless. The collected solids were then extracted with tetrahydrofuran and filtered until the eluent became colorless. The tetrahydrofuran filtrate was then concentrated to give a yellow solid, which after trituration with pentane and drying under vacuum yielded the title compound as a yellow powder (94.4 mg; 60%). Analytical samples and crystals of **2** suitable for X-ray diffraction were grown from vapor diffusion of diethyl ether into a dichloromethane solution of **2**. ¹H NMR, 400 MHz (CD₂Cl₂): 12.90 (br s, 3 H), 7.51 (t, *J*

= 7.6, 3 H), 6.67 (d, J = 8, 6 H), 3.90 (s, 9 H). ¹³C NMR, 100 MHz (CD₂Cl₂):164.5, 154.0, 139.7, 114.4, 111.3, 58.5. ¹⁹F NMR, 377 MHz (CD₂Cl₂): -109.0 (br s). IR (ATR, cm⁻¹): 2909, 2848, 2644, 2609, 2570, 2536, 2501, 2473, 1614, 1570, 1440, 1154, 789. Anal. cald (C₁₈H₁₈CuFN₄O₃): 51.36 C, 4.31 H, 13.31 N%. Found: 51.05 C, 4.29 H, 13.23 N%.

CuF(tpa)PF₆ (3)⁴

This compound was previously prepared by reaction of Cu(tpa)⁺ with O₂ in the presence of PF₆^{-,4} This procedure provided low and variable yields and we therefore sought an alternative, more reliable preparation. Acetonitrile (*ca*. 5 mL) was added to a mixture of tpa (48.9 mg; 0.168 mmol), CuF₂ (17.5 mg; 0.172 mmol) and NaPF₆ (30.4 mg; 0.181 mmol) and stirred for 2 h. Over this time, the mixture gradually became blue and nearly homogeneous. The mixture was filtered and the filtrate was concentrated to a blue oil under vacuum. The oil was extracted with dichloromethane (*ca*. 5 mL), filtered and concentrated to again give a blue oil. The oil was triturated with copious amounts of diethyl ether and dried under high vacuum, giving a blue foam. Prolonged drying of the foam under high vacuum and crushing provided the title compound as a sky blue powder (50.2 mg; 58%). IR (KBr, cm⁻¹): 1614, 1446, 838 (PF₆), 767, 558, 498 (Cu-F). EPR (1:1 CH₂Cl₂:toluene, 77 K): g₁ = 2.210, g_{||} = 1.940, A₁ = 92 G, A_{||} = 67 G. UV-vis (CH₂Cl₂): 894 nm (170 cm⁻¹M⁻¹), 700 (84). The characterization data are consistent with those previously reported by Karlin and co-workers.⁴



Figure S1. X-band EPR spectra of **1** (left) and **3** (right). Spectra collected in 1:1 dichloromethane:toluene at 77 K. The * notes an impurity present in the spectrometer cavity and the background spectra are presented for reference.



Figure S2. UV-vis spectra of 1 (left) and 3 (right) collected in dichloromethane.



Figure S3. Cyclic voltammograms of **1** collected at varying scan rates (left) and dependence of peak current on scan rate (right). Voltammograms collected in 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane.



Figure S4. Cyclic voltammogram of **1** in the presence of ferrocene highlighting similar peak separations (ΔE) under identical conditions (left) and overlay of cyclic voltammograms of **2** and CuCl(H₃thpa) (right). Voltammograms collected in 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane at 100 mV/s scan rate.



Figure S5. Cyclic voltammograms of **3** at varying scan rates (left) and cyclic voltammogram of **3** at 100 mV/s with inset highlighting the return wave at *ca.* -0.20 V is not reversible (right). Voltammograms collected in 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane.



Figure S6. ATR-IR spectrum of crystalline 1.



Figure S7. ATR-IR spectrum of crystalline 2.



Figure S8. 400 MHz ¹H NMR spectrum of **2** collected at 25 °C in CD_2Cl_2 . The * notes residual tetrahydrofuran in the spectrum.



Figure S9. 377 MHz ¹⁹F NMR spectrum of 2 collected at 25 °C in CD₂Cl₂.



Figure S10. OH region of the 500 MHz ¹H NMR spectrum of **2** collected at -25 °C in CD_2Cl_2 (*J* = 49.5 Hz). Note a methanol temperature calibration was performed to accurately determine the sample temperature.

Proton Spectrum											
Sample Name:											
Data Collected on: te.chem.lsa.umich.edu-vnmrs500 Archive directory:											
Sample directory:											
FidFile: CM-V-167-1H-19Fdec-neg25C											
Pulse Sequence: FHdec Solvent: cd2cl2 Data collected on: Mar 19 2014					-12.850						
Temp15.0 C / 258.1 K Operator: morecam											
Relax, delay 2.000 sec					- C						
Acq. time 1.300 sec					1						
Width 7485.0 Hz					A						
16 repetitions OBSERVE H1 500 0004572 MHz					A						
DECOUPLE F19, 470,4958757 MHz					- 11						
Power 44 dB					11						
on during acquisition					11						
off during delay E19dar: WUBST40 & kHz durbe: 0.40 modulated					11						
DATA PROCESSING					П						
Line broadening 0.3 Hz					11						
FT size 65536											
Total time 0 min 59 sec					11						
						-					
արարարություն	undun	1000 lun	do reference	mulun	1000 luna	muhun	mulun	սուրու	donalian.	1000 from	huun
14.4 14.2 14.0 13.8	13.6	13.4	13.2	13.0	12.8	12.6	12.4	12.2	12.0	11.8	ppm

Figure S11. OH region of the 500 MHz ${}^{1}H{}^{19}F{}$ NMR spectrum of **2** collected at -25 °C in CD₂Cl₂. Note a methanol temperature calibration was performed to accurately determine the sample temperature.



Figure S12. Top: OH region of the 400 MHz ¹H NMR spectrum of **2** in CD_2Cl_2 before and immediately after addition of 100 eq. of deoxygenated D₂O. Bottom: 377 MHz ¹⁹F NMR spectrum of **2** in CD_2Cl_2 before and immediately after addition of 100 eq. of deoxygenated D₂O. Note that decomposition of **2** slowly occurs upon addition of deoxygenated D₂O to an as yet unidentified copper species.

Computational details

All calculations were performed using Gaussian 09⁵ and visualized using ChemCraft.⁶ Becke's threeparameter hybrid function⁷ using Lee, Yang and Parr's correlation function⁸ (B3LYP) was used for all calculations using the triple-zeta basis set TZVP.⁹ Structures were freely optimized in C_1 symmetry and were confirmed to be minima based on the absence of imaginary frequencies in the calculated vibrational spectra. Computed vibrational frequencies have been scaled according to the appropriate factors reported by Merrick and co-workers.¹⁰ Compositions of molecular orbitals were calculated using AOMix (Rev. 6.51).¹¹ NBO analysis was performed using NBO Version 3.1 as implemented in Gaussian 09.¹² For the NBO analysis of the Cu-F interaction, weak F(2p) \rightarrow Cu(4p) and F(2p) \rightarrow Cu(4s) donoracceptor interactions were found. The second order stabilization energy of these interactions are 18.8 kcal/mol and 7.8 kcal/mol, respectively. We assign these interactions as electrostatic in nature as the NBO analysis did not find bonding orbitals between Cu and F. These interactions likely contribute to the observed Wiberg bond index of 0.12.



Figure S13. DFT-optimized geometries of 1 (left) and 2 (right).

Table S1. Summary of DFT-optimized structures and comparison to solid state structures.

		1	2		
	TZVP	Experiment	TZVP	Experiment	
Cu-F	1.964	1.925(2)	2.347	2.469(2)	
Cu-N _{ax}	2.036	1.995(3)	2.289	2.218(3)	
Cu-N _{eq} avg.	2.083	2.049	2.051	2.006	
N-Cu-Cl	179.83	178.71	179.82	178.02	

Table S2. Experimental and calculated OH stretching frequencies for 1 (cm⁻¹).

		1	H ₃ thpa ¹	
	TZVP	Experiment	TZVP	
v _{он} (asym)	3233	3125	3620	
v _{он} (sym)	3314	3159	-	

Crystallographic Details

Crystals were mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187$ A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 240(1) K (for 1) and 85(1) K (for 2) with the detector placed at a distance 42.00 mm from the crystal. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0¹³ and corrected for absorption. The structures were solved and refined with the Bruker SHELXTL (version 2008/4) software package.¹⁴ All nonhydrogen atoms were refined anisotropically with the hydrogen atoms placed in a mix of idealized and refined positions. For the data collection on crystals of 1, it was found the crystals underwent a destructive phase change upon cooling below 240 K and therefore data collection was performed at 240 K.



Figure S14. Solid state structure of 1 showing disordered BF₄ anions (50% probability ellipsoids).

Compound	1	2
Empirical Formula	C ₁₈ H ₁₈ CuFN ₄ O ₃ BF ₄	C ₁₈ H ₁₈ CuFN ₄ O ₃
Formula Weight	507.71	420.91
Temperature	240(2) K	85(2) K
Wavelength	1.54178 Å	1.54178 Å
Crystal system	Monoclinic	Monoclinic
Space group	I2/a	P21/n
Unit cell dimensions	a = 15.4006(3) Å	a = 8.7930(2) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	b = 9.5362(2) Å	b = 14.8014(3) Å
	$\beta = 90.988(6)^{\circ}$	$\beta = 93.525(7)^{\circ}$
	c = 20.090(2) Å	c = 13.3814(9) Å
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume	4124.8(3)Å ³	1738.28(13) Å ³
Ζ	8	4
Density (calc.)	1.635 g/cm ³	1.608 g/cm ³
Absorption coefficient	2.179 mm ⁻¹	2.117 mm ⁻¹
F(000)	2056	864
Crystal size	0.18 x 0.14 x 0.02 mm ³	0.16 x 0.14 x 0.08 mm ³
Theta range for data	3.15 to 68.24°	4.46 to 68.23°
Index ranges	-17<=h<=18	-10<=h<=9
	-11<=k<=11	-17<=k<=17
	-33<=]<=33	-16<=1<=16
Reflections collected	56602	44126
Independent reflections	3776	3182
Completeness	100.0 %	100.0 %
Absorption correction	Semi-empirical from	Semi-empirical from
	equivalents	equivalents
Max. and min. transmission	0.958 and 0.695	0.844 and 0.748
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints /parameters	3776 / 0 /339	3169 / 0 /257
Goodness-of-fit on F ²	1.152	1.276
Final R indices	R1 = 0.0559	R1 = 0.0533
[I>2sigma(I)]	wR2 = 0.1636	wR2 = 0.1413
R indices (all data)	R1 = 0.0631	R1 = 0.0539
	wR2 = 0.1712	wR2 = 0.1415
Largest diff neak and hole	$0.355 \text{ and } -0.616 \text{ p} ^{3-3}$	0.995 and -0.553 e.Å ⁻³
Largest and peak and note	0.555 and -0.010 C.A	0.775 unu -0.555 C.M
	1	1

Table S3. Atomic coordinates for optimized structures calculated using the TZVP basis set.

	CuF(H₃	thpa)+ - 1			CuF(H₃	thpa) - 2	
atom	х	v	z	atom	х	v	Z
Cu	10.16477	1.305169	2.720842	Cu	7.538313	4.618811	9.971113
F	9.684599	2.503607	1.240593	F	7.387888	2.280629	9.834226
N	10.66457	0.058973	4.251306	N	7.692328	6.899186	10.10433
N	8.514473	1.719334	3.920909	N	9.566708	4.771477	10.24212
N	11.99155	2.199328	3.173914	N	6.330943	4.905558	11.60207
0	12.14782	3.55013	1.312888	N	6.788661	5.080091	8.118854
N	10.16845	-0.45706	1.60885	0	9.975012	2.539457	9.839069
С	7.547489	1.103991	6.013782	0	6.140321	2.66139	12.08899
н	7.523237	0.445734	6.870679	0	6.133435	2.922665	7.642152
0	7.736423	3.545092	2.749238	с	8.980933	7.096522	10.76748
С	8.454697	0.901467	4.996963	н	8.804618	7.048575	11.84552
С	12.5364	1.683012	4.29941	н	9.406907	8.087659	10.56617
С	7.668493	2.748784	3.815551	с	10.01826	6.030049	10.43195
0	9.184494	0.379008	-0.29998	C	11.36872	6.327401	10.40095
С	9.396087	-0.27885	4.956453	н	11.70789	7.344699	10.54257
н	9.605524	-0.65616	5.959432	c	12.27835	5.287361	10.18501
н	8.917713	-1.08543	4.396594	н	13.34142	5.491717	10.15856
С	11.60953	0.817549	5.118583	C	11.81947	3,999068	10.00227
н	12.1681	0.136156	5.763444	н	12,48852	3.167742	9.829989
н	11.01141	1.464272	5.763854	C	10,43465	3.777672	10.02965
С	6.709026	3.010157	4.803177	C C	6.515819	7.249164	10.8997
н	6.041658	3.851306	4.682946	н	5.672341	7.338692	10,20972
С	12.69678	3.046045	2.417633	н	6.619137	8.223187	11,3944
С	10.63753	-1.50355	2.327026	C	6.136389	6.199125	11.93831
С	14.00411	3.417032	2.7609	C C	5.545702	6.554658	13,13736
н	14.54271	4.104837	2.12517	н	5.410929	7.597097	13.39279
С	6.661224	2.182621	5.903882	C	5.128167	5.539802	14.00435
н	5.936059	2.367314	6.68578	н	4.660601	5.789961	14,94848
С	10.57049	-2.79641	1.856031	C	5.315241	4.217642	13.65702
н	10.9409	-3.61947	2.450541	н	5 009079	3 404003	14 29944
C	9.63788	-0.6607	0.399187	C	5,937895	3,934997	12,43235
C	13.8206	1.989481	4.692216	C C	7.642295	7.307052	8,700523
н	14.24029	1.555587	5.588748	н	8.663897	7.267531	8.312659
С	9.54827	-1.9461	-0.15252	н	7,303458	8.343648	8.577954
н	9.114117	-2.07132	-1.13398		6 791126	6 397344	7 82087
C	14.56021	2.876189	3.899742	C C	6 116264	6 892078	6 719576
н	15.5718	3.13778	4.181902	н	6 120654	7 9527	6 507165
C	10.0131	-3.01029	0.589189		5 434692	5 99334	5 892908
Н	9.947776	-4.01436	0.190506	н	4.900254	6.353306	5.022638
C	11.30225	-1.13704	3.632818	C C	5 440976	4 645708	6 189076
н	11.29841	-1.97725	4.330607	н	4 925127	3 918559	5 577935
H	12.3453	-0.88261	3.432274	,	6,1323229	4,221072	7,333143
Н	11.21961	3.234078	1.20015	н	8 972724	2 485472	9 85952
H	8.426835	3.234474	2.115766	н	6 608523	2.403472	11 20677
H	9.336948	1.226291	0.183407	н	6 639526	2 721235	8 484686

Cu(H₃thpa)⁺							
atom	х	у	Z				
Cu	2.776	1.9868	2.0576				
Ν	1.388	3.536	1.8922				
Ν	4.4086	2.2517	3.3344				
0	-0.0479	2.8873	3.5774				
0	3.9205	0.5963	4.8677				
0	1.4314	-0.9039	1.1023				
N	2.9886	0.668	0.4517				
N	3.9499	3.2892	0.761				
С	5.2689	3.1899	2.8629				
С	2.428	-1.1489	-1.0138				
н	1.8419	-2.0427	-1.1714				
С	2.2975	-0.4394	0.1824				
С	5.9747	1.7192	5.0745				
н	6.2025	1.1114	5.9382				
С	-0.4413	4.9546	2.5292				
н	-1.2987	5.1002	3.1702				
С	3.8508	1.1422	-0.4829				
С	2.9426	4.1069	0.0768				
н	2.5591	3.5226	-0.7637				
н	3.3682	5.0243	-0.3451				
С	0.321	3.7902	2.6496				
С	4.7629	1.5382	4.4033				
С	1.7671	4.4571	0.9703				
С	-0.0483	5.888	1.5932				
н	-0.6067	6.8077	1.4766				
С	4.0237	0.5076	-1.6981				
н	4.7086	0.9146	-2.429				
С	4.6743	2.3622	-0.1148				
н	5.5557	2.0156	0.4306				
н	5.0374	2.8498	-1.0264				
С	1.0767	5.6422	0.8031				
Н	1.4088	6.363	0.0689				
С	6.8464	2.6696	4.5865				
Н	7.7999	2.8319	5.0721				
С	4.8044	4.0348	1.6914				
Н	4.2121	4.8618	2.0915				
Н	5.6721	4.4803	1.1924				
С	6.4945	3.4158	3.4597				
Н	7.1653	4.1605	3.0543				
С	3.3024	-0.659	-1.961				
H	3.4243	-1.1746	-2.9048				
Н	0.5726	2.1424	3.564				
Н	1.4352	-0.3127	1.8708				
Н	3.1298	0.5647	4.3077				

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