Electronic Supplementary Information for:

A Tetrapyrrole Macrocycle Displaying a Multielectron Redox Chemistry and Tunable Absorbance Profile

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General Experimental Methods

General Materials and Methods. Reactions were performed in oven-dried round-bottomed flasks unless otherwise noted. Reactions that required an inert atmosphere were conducted under a positive pressure of N_2 using flasks fitted with Suba-Seal rubber septa or in a nitrogen filled glove box. Air and moisture sensitive reagents were transferred using standard syringe or cannula techniques. Reagents and solvents were purchased from Sigma Aldrich, Acros, Fisher, Strem, or Cambridge Isotopes Laboratories. Solvents for synthesis were of reagent grade or better and were dried by passage through activated alumina and then stored over 4 Å molecular sieves prior to use.[1] Control compounds 5,10,15,20-tetra-pentafluorophenylporphyrin (2H(TpFPP)[2] and 5,10,15-tris-pentafluorophenylcorrole (3H(TpFPC)[3] were prepared using published methods. All other reagents were used as received.

Compound Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Proton spectra are referenced to the residual proton resonance of the deuterated solvent ($CDCl_3$ = δ 7.26) and carbon spectra are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.23). All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. LR-GCMS data were obtained using an Agilent gas chromatograph consisting of a 6850 Series GC System equipped with a 5973 Network Mass Selective Detector. LR-ESI MS data was obtained using either a LCQ Advantage from Thermofinnigan or a Shimadzu LCMS-2020. HR-ESI mass spectrometric analyses were performed by the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign.

Synthetic Protocols

5,5-Dimethyldipyrromethane. This compound was prepared using a literature method.[4] Pyrrole (87.0 mL, 1.25 mol) and acetone (3.7 mL, 50.0 mmol) were combined in a round bottom flask and the resulting mixture was sparged with N_2 for 10 minutes. To the degassed solution was added trifluoroacetic acid (380 µL, 5 mmol) and the mixture was stirred for 5 min, following which time, the reaction was quenched with 100 mL of 0.1 M NaOH. The product was then extracted into ethyl acetate and this organic layer was washed with water and dried over sodium sulfate. Following removal of the solvent by rotary evaporation, the desired product was purified via vacuum distillation to give 4.15 g of the title compound as a white solid (47% based on acetone starting material). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm: 7.71 (br s, 2H), 6.61 (m, 2H), 6.14 (m, 2H), 6.10 (m, 2H), 1.64 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) δ/ppm: 139.22, 117.21, 107.82, 103.83, 77.16, 35.46, 29.43. GCMS: $[M]^+$ m/z: calcd for $C_{11}H_{14}N_2$, 174.12; found, 174.

5-(Pentafluorophenyl)dipyrromethane. This compound was prepared using a literature method.[4] Pyrrole (25 mL, 360 mmol) and pentafluorobenzaldehyde (1.76 mL, 14.4 mmol) were combined in a round bottom flask and the resulting mixture was sparged with N_2 for 10 minutes. To the degassed solution was added trifluoroacetic acid (110 µL, 1.4 mmol) and the mixture was stirred for 5 min, following which time, the reaction was quenched with 100 mL of 0.1 M NaOH. The product was then extracted into ethyl acetate and this organic layer was washed with water

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[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1996**, *15*, 1518–1520.

[2] Lindsey, J. S.; Wagner, R. W. J. Org. *Chem.* **1989**, *54*, 828–836.

[3] Reith, L. M.; Stiftinger, M.; Monkowius, U.; Knör, G.; Schoefberger, W. *Inorg. Chem.* **2012**, *50*, 6788–6797.

[4] Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391–1396.

and dried over sodium sulfate. Following removal of the solvent by rotary evaporation, the desired product was purified via vacuum distillation to give 3.1 g of the title compound as a white solid (69%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm: 8.14 (br s, 2H), 6.73 (m, J = 2.7, 1.6 Hz, 2H), 6.17 (q, J = 6.1, 2.7 Hz, 2H), 6.03 (m, 2H), 5.90 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) δ/ppm: 128.23, 118.26, 108.81, 107.77, 77.16, 33.18. GCMS: $[M]^+$ m/z: calcd for $C_{15}H_9F_5N_2$, 312.17; found, 312.

5,5-Dimethyl-1,9-bis(pentafluorobenzoyly)dipyrromethane. This compound was prepared by amending a previously described method.[5] To 5,5-dipyrromethane (0.871 g, 5.00 mmol) was added 100 mL of dry toluene under an atmosphere of N_2. To the resulting solution was added ethyl magnesium bromide (25 mL, 25.0 mmol, 1 M in THF) in dropwise fashion and the resulting mixture was stirred for 30 min at room temperature. A solution of 1.80 mL of pentafluorobenzoyl chloride (12.5 mmol) in 12.5 mL of dry toluene was then added to the stirred reaction in dropwise fashion and the resulting solution was stirred for an additional 30 min. The reaction was quenched with 75 mL of saturated NH_4Cl and the organic layer was then separated, washed sequentially with water and brine, and then dried over Na_2SO_4. Following solvent removal under reduced pressure, the crude product was purified by flash chromatography on silica using hexanes and ethyl acetate (2:1) as the eluent. Recrystallization of the product at –35 °C from CH_2Cl_2/hexanes delivered 843 mg of the title compound as a white solid (30%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm: 9.77 (br s, 2H), 6.66 (d, 2H), 6.24 (d, J = 4.0 Hz, 2H), 1.81 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) δ/ppm: 172.4, 148.3, 144.1, 142.5, 137.7, 131.6, 122.6, 113.9, 109.8, 36.5, 28.4. ESI-MS: $[M + H]^+$ m/z: calcd for $C_{25}H_{13}F_{10}N_2O_2$, 563.08; found, 563.

5,5-Dimethyl-10,15,20-tris(pentafluorophenyl)phlorin (3H(Phl^F)). This compound was prepared by amending a previously described method.[5] To a solution of 5,5-Dimethyl-1,9-bis(pentafluorobenzoyly)dipyrromethane (281 mg, 0.50 mmol) dissolved in 40 mL of THF and MeOH (3:1) was added 946 mg of $NaBH_4$ (25.0 mmol). The resulting mixture was stirred at room temperature for 2 hrs, following which, the reaction was quenched with H_2O and extracted with dichloromethane. The organic layer was washed sequentially with H_2O and brine and then dried over Na_2SO_4. The solvent was then removed via rotary evaporation and the resulting residue was dissolved in 200 mL of dichloromethane and combined with 156 mg of 5-(pentafluorophenyl)dipyrromethane (0.50 mmol) and 1.54 mL of trifluoroacetic acid (20.0 mmol). The resulting solution was stirred at room temperature for 15 min, after which time 167 mg of DDQ (0.730 mmol) was added to the reaction. After stirring the reaction for an additional 5 min, 14 mL triethylamine (100 mmol) was added. After stirring the solution for an additional 30 min, the reaction was filtered through a pad of silica and eluted with CH_2Cl_2 until the mobile phase was no longer green. Following removal of the solvent under reduced pressure, the crude green colored material was purified by flash chromatography on silica using hexanes and CH_2Cl_2 (3:1) as the eluent to deliver 200 mg of the title compound as an deep green powder (48%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm: 7.37 (d, J = 5.0 Hz, 2H), 7.14 (d, J = 5.0 Hz, 2H), 6.94 (d, J = 3.9 Hz, 2H), 6.78 (d, J = 3.9 Hz, 2H), 5.16 (br s, 3H), 1.42 (s, 6H). HR-ESI-MS: $[M+ H]^+$ m/z: calcd for $C_{40}H_{18}F_{15}N_4$, 839.1292; found, 839.1286.

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[5] O'Brien, A. Y.; McGann, J. P.; Geier III, G. R. *J. Org. Chem.* **2007**, *72*, 4084–4092.

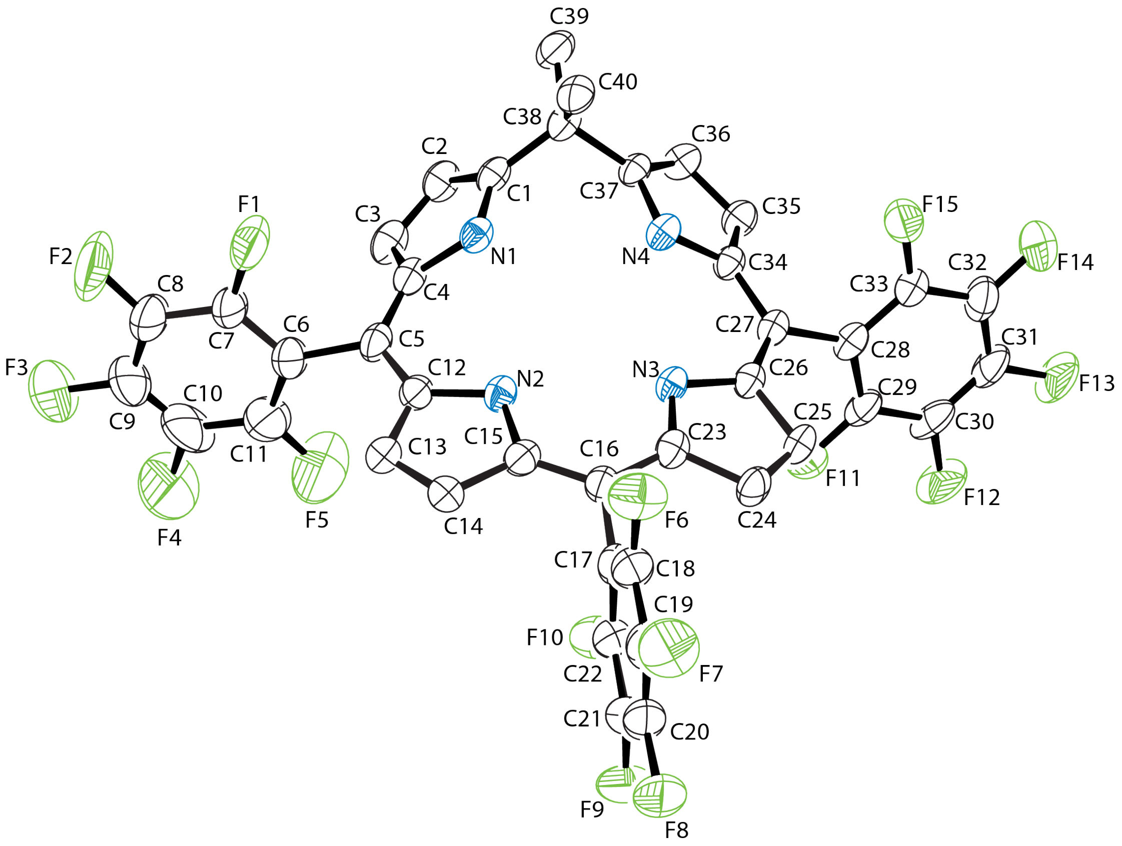

Figure S1. Fully labeled thermal ellipsoid plot of the solid-state structure of 3H(PhI^{F}). Ellipsoids are shown at the 50% probability level. Cocrystallized solvent and hydrogen atoms are omitted for clarity.

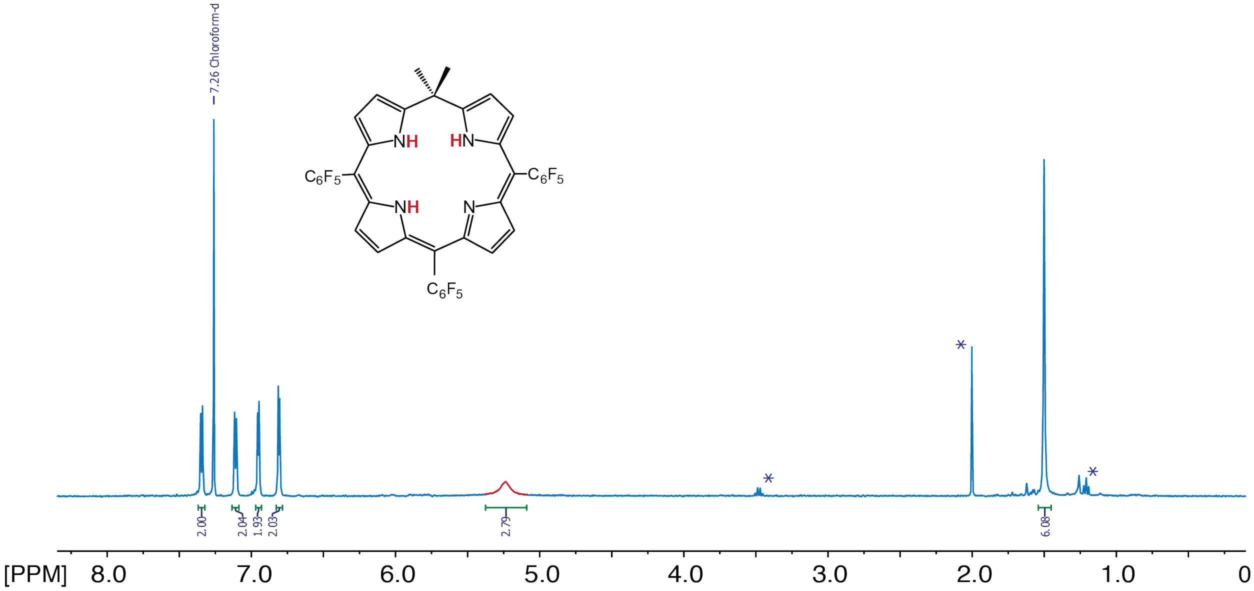

Figure S2. ^{1}H NMR spectrum for 3H(Phl^F) in CDCl$_3$. Note resonances for N–H protons at ~5.15 ppm. Asterisks denote peaks attributed to adventitious solvent.

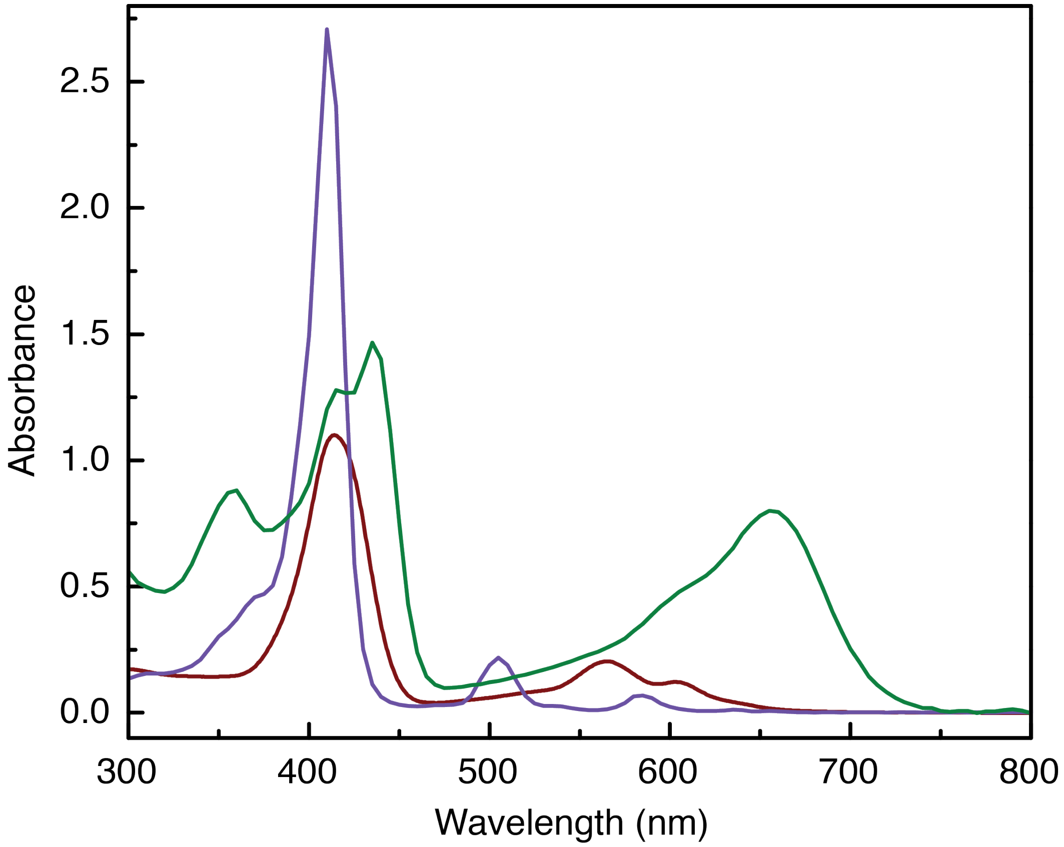

Figure S3. Comparison of UV-vis absorption profiles for a 50 μM solution of 3H(PhI^F) in THF (green) and the homologous porphyrin (2H(TpFPP), purple) and corrole (3H(TpFPC), maroon) in THF (10 μM).

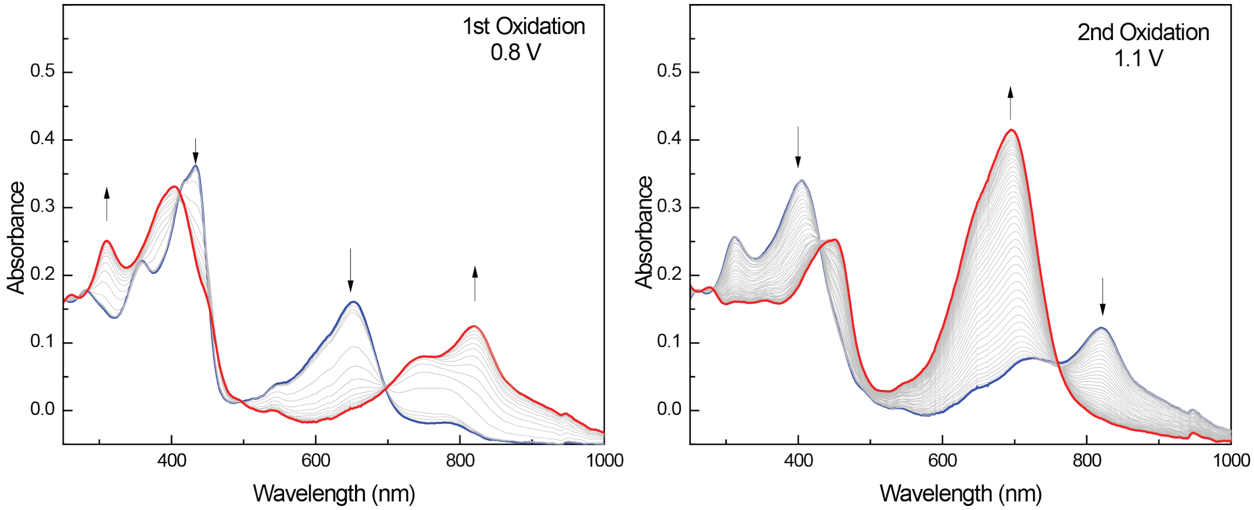

Figure S4. UV-vis spectroelectrochemistry recorded for a 100 μM solution of $3H(PhI^F)$ in THF containing 0.1 M $TBAPF_6$. (left) Spectral changes associated with oxidation of $3H(PhI^F)$ by a single electron at 0.8 V versus Ag/AgCl. (right) Spectral changes associated with oxidation of $3H(PhI^F)^{\bullet +}$ by a second electron at 1.1 V versus Ag/AgCl.

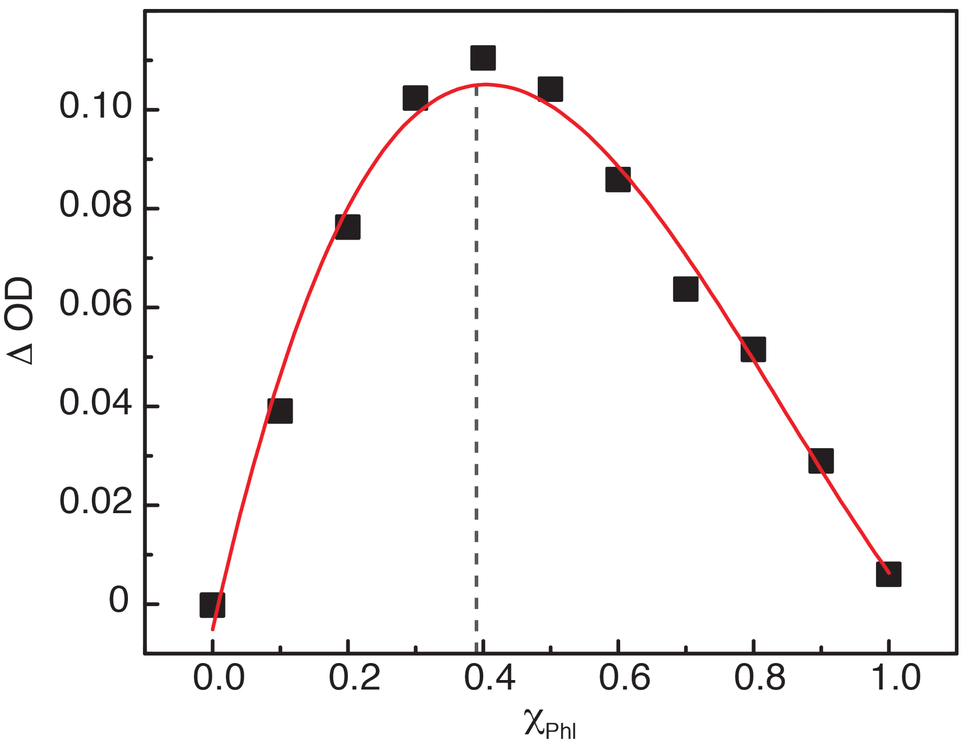

Figure S5. Job plot constructed for titration of 3H(PhI^F) with TBAF in THF. Total concentration of analyte in solution was maintained at 10 μM for the entire titration.

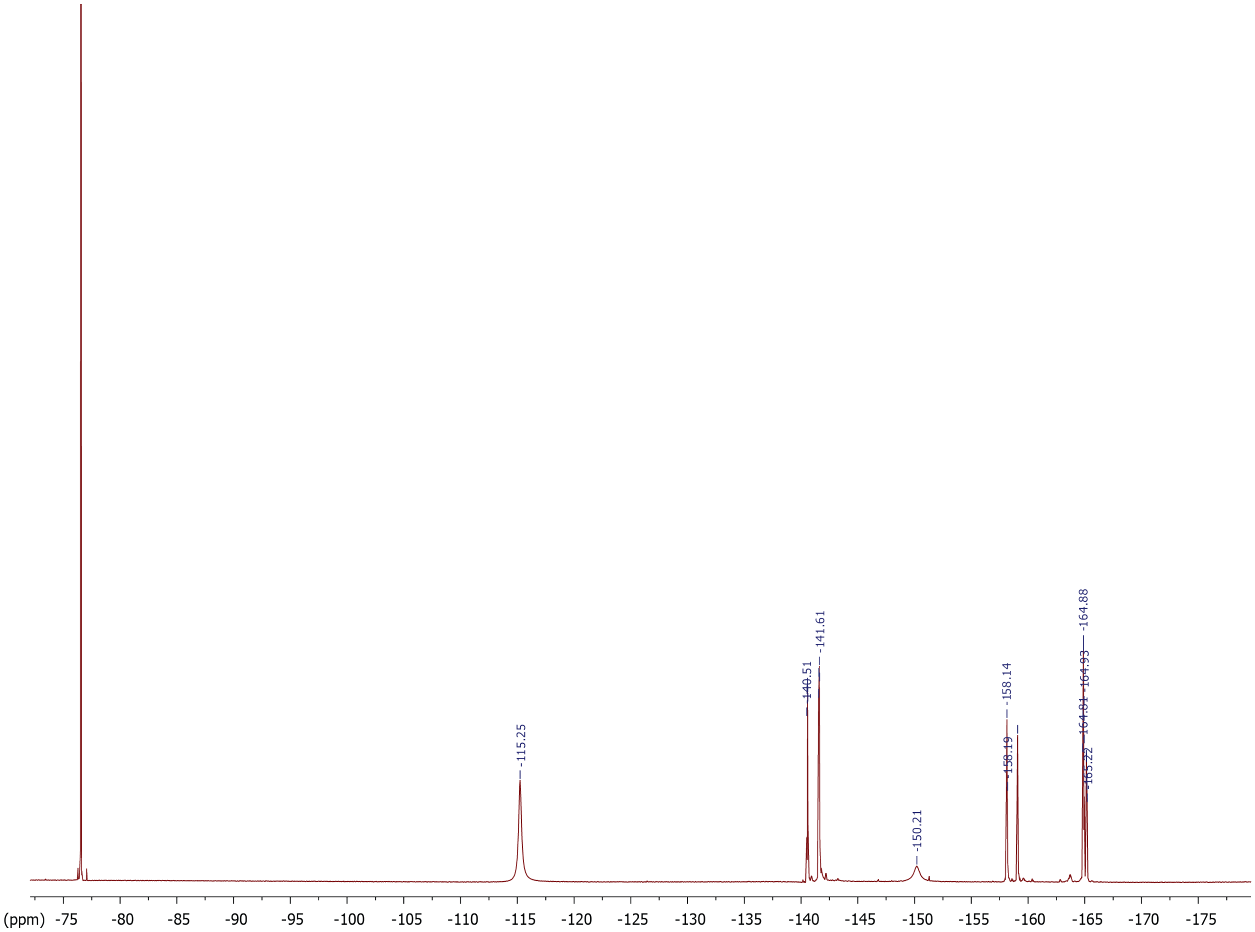

Figure S6. ^{19}F NMR spectrum for 3H(PhI^{F}) and 10 equivalents of TBAF in CD_3CN. Note resonance corresponding to bound and unbound F^{-} at –150.21 and –115.25 ppm, respectively. The large peak at –76.55 ppm is due to an internal TFA standard.

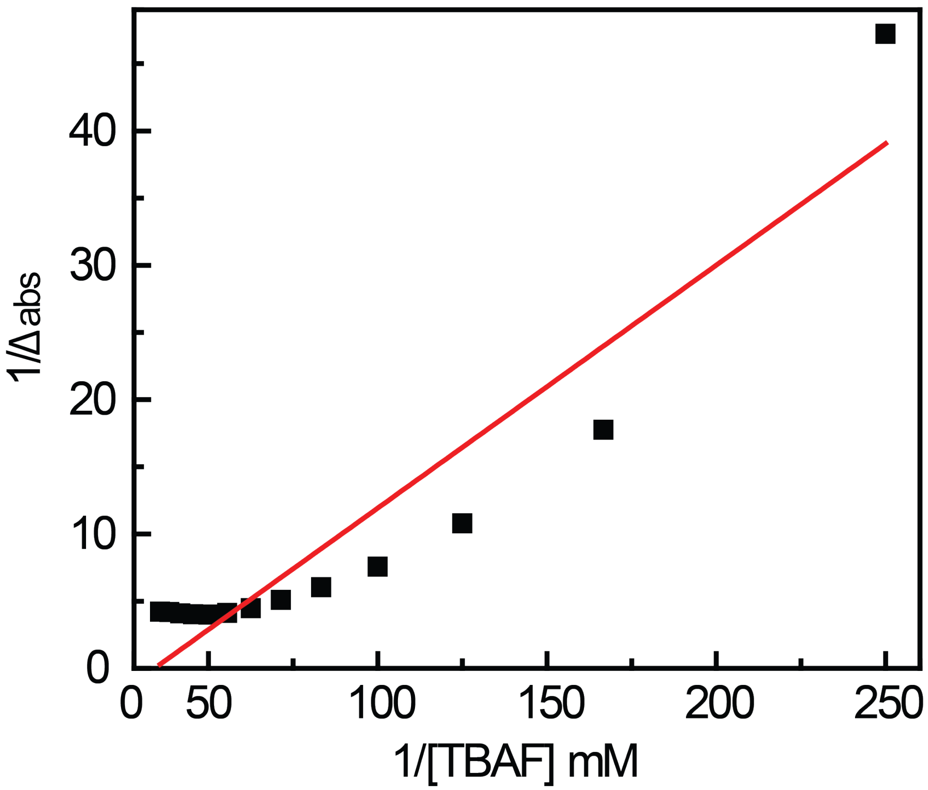

Figure S7. Benesi-Hildebrand plot constructed from the titration data shown in Figure 5 of the main text. Fluoride binding is not accurately modeled by this plot indicating that binding to the 3H(PhI^{F}) cannot be of 1:1 stoichiometry.

Table S1. Bond Lengths (Å) for 3H(PhI^{F}).

N(1)-C(1)	1.373(5)
N(1)-C(4)	1.390(5)
N(1)-H(1N)	0.9943
C(1)-C(2)	1.384(5)
C(1)-C(38)	1.502(5)
C(2)-C(3)	1.399(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.391(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.423(6)
C(5)-C(12)	1.374(6)
C(5)-C(6)	1.496(5)
C(6)-C(7)	1.371(6)
C(6)-C(11)	1.395(7)
C(7)-F(1)	1.312(6)
C(7)-C(8)	1.374(6)
C(8)-F(2)	1.303(7)
C(8)-C(9)	1.404(9)
C(9)-F(3)	1.328(6)
C(9)-C(10)	1.344(11)
C(10)-F(4)	1.350(8)
C(10)-C(11)	1.390(8)
C(11)-F(5)	1.322(8)
C(12)-N(2)	1.397(4)
C(12)-C(13)	1.421(6)
N(2)-C(15)	1.380(5)
N(2)-H(2N)	0.9890
C(13)-C(14)	1.352(6)
C(13)-H(13)	0.9500
C(14)-C(15)	1.430(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.382(5)
C(16)-C(23)	1.429(5)
C(16)-C(17)	1.493(5)

C(17)-C(18)	1.373(7)
C(17)-C(22)	1.393(6)
C(18)-F(6)	1.327(6)
C(18)-C(19)	1.397(6)
C(19)-F(7)	1.338(7)
C(19)-C(20)	1.369(8)
C(20)-F(8)	1.337(5)
C(20)-C(21)	1.353(9)
C(21)-F(9)	1.339(7)
C(21)-C(22)	1.398(7)
C(22)-F(10)	1.334(6)
C(23)-N(3)	1.335(5)
C(23)-C(24)	1.461(5)
N(3)-C(26)	1.393(4)
C(24)-C(25)	1.336(6)
C(24)-H(24)	0.9500
C(25)-C(26)	1.453(5)
C(25)-H(25)	0.9500
C(26)-C(27)	1.381(5)
C(27)-C(34)	1.423(5)
C(27)-C(28)	1.496(5)
C(28)-C(33)	1.375(6)
C(28)-C(29)	1.389(6)
C(29)-F(11)	1.332(5)
C(29)-C(30)	1.382(6)
C(30)-F(12)	1.337(5)
C(30)-C(31)	1.364(8)
C(31)-F(13)	1.345(5)
C(31)-C(32)	1.380(7)
C(32)-F(14)	1.317(6)
C(32)-C(33)	1.382(6)
C(33)-F(15)	1.341(5)
C(34)-N(4)	1.377(5)
C(34)-C(35)	1.391(5)
N(4)-C(37)	1.355(5)
N(4)-H(4N)	0.8634

C(35)-C(36)	1.400(5)
C(35)-H(35)	0.9500
C(36)-C(37)	1.378(5)
C(36)-H(36)	0.9500
C(37)-C(38)	1.518(5)
C(38)-C(40)	1.521(6)
C(38)-C(39)	1.527(5)
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-Cl(2)	1.716(10)
C(41)-Cl(1)	1.739(10)
C(41)-Cl(3)	1.743(10)
C(41)-H(41)	1.0000
C(42)-Cl(5)	1.719(12)
C(42)-Cl(4)	1.736(13)
C(42)-Cl(6)	1.764(12)
C(42)-H(42)	1.0000

Table S2. Bond angles (°) of 3H(PhI^F).

C(1)-N(1)-C(4)	109.6(3)
C(1)-N(1)-H(1N)	123.7
C(4)-N(1)-H(1N)	123.9
N(1)-C(1)-C(2)	107.9(3)
N(1)-C(1)-C(38)	121.3(3)
C(2)-C(1)-C(38)	130.5(3)
C(1)-C(2)-C(3)	107.5(3)
C(1)-C(2)-H(2)	126.3
C(3)-C(2)-H(2)	126.3
C(4)-C(3)-C(2)	108.6(4)
C(4)-C(3)-H(3)	125.7
C(2)-C(3)-H(3)	125.7
N(1)-C(4)-C(3)	106.3(4)
N(1)-C(4)-C(5)	122.3(3)
C(3)-C(4)-C(5)	131.3(4)
C(12)-C(5)-C(4)	125.7(3)
C(12)-C(5)-C(6)	119.1(4)
C(4)-C(5)-C(6)	115.1(3)
C(7)-C(6)-C(11)	116.8(4)
C(7)-C(6)-C(5)	120.8(4)
C(11)-C(6)-C(5)	122.1(4)
F(1)-C(7)-C(6)	118.5(4)
F(1)-C(7)-C(8)	117.0(4)
C(6)-C(7)-C(8)	124.4(5)
F(2)-C(8)-C(7)	122.3(5)
F(2)-C(8)-C(9)	120.1(5)
C(7)-C(8)-C(9)	117.2(5)
F(3)-C(9)-C(10)	122.8(6)
F(3)-C(9)-C(8)	117.7(6)
C(10)-C(9)-C(8)	119.5(5)
C(9)-C(10)-F(4)	119.3(6)
C(9)-C(10)-C(11)	122.5(6)
F(4)-C(10)-C(11)	118.3(7)
F(5)-C(11)-C(10)	120.1(6)

F(5)-C(11)-C(6)	120.5(5)
C(10)-C(11)-C(6)	119.3(6)
C(5)-C(12)-N(2)	126.2(4)
C(5)-C(12)-C(13)	128.3(4)
N(2)-C(12)-C(13)	105.5(3)
C(15)-N(2)-C(12)	110.3(3)
C(15)-N(2)-H(2N)	121.9
C(12)-N(2)-H(2N)	122.6
C(14)-C(13)-C(12)	109.4(4)
C(14)-C(13)-H(13)	125.3
C(12)-C(13)-H(13)	125.3
C(13)-C(14)-C(15)	108.6(4)
C(13)-C(14)-H(14)	125.7
C(15)-C(14)-H(14)	125.7
N(2)-C(15)-C(16)	125.0(3)
N(2)-C(15)-C(14)	105.9(3)
C(16)-C(15)-C(14)	128.9(3)
C(15)-C(16)-C(23)	124.7(3)
C(15)-C(16)-C(17)	117.4(3)
C(23)-C(16)-C(17)	117.3(3)
C(18)-C(17)-C(22)	117.0(4)
C(18)-C(17)-C(16)	123.0(4)
C(22)-C(17)-C(16)	119.9(4)
F(6)-C(18)-C(17)	120.5(4)
F(6)-C(18)-C(19)	117.6(5)
C(17)-C(18)-C(19)	121.8(5)
F(7)-C(19)-C(20)	121.1(4)
F(7)-C(19)-C(18)	119.5(5)
C(20)-C(19)-C(18)	119.3(5)
F(8)-C(20)-C(21)	119.9(5)
F(8)-C(20)-C(19)	119.3(5)
C(21)-C(20)-C(19)	120.8(4)
F(9)-C(21)-C(20)	121.5(5)
F(9)-C(21)-C(22)	119.0(6)
C(20)-C(21)-C(22)	119.5(5)
F(10)-C(22)-C(17)	119.7(4)

F(10)-C(22)-C(21)	118.8(5)
C(17)-C(22)-C(21)	121.5(5)
N(3)-C(23)-C(16)	125.9(3)
N(3)-C(23)-C(24)	111.6(3)
C(16)-C(23)-C(24)	122.3(3)
C(23)-N(3)-C(26)	105.5(3)
C(25)-C(24)-C(23)	106.2(3)
C(25)-C(24)-H(24)	126.9
C(23)-C(24)-H(24)	126.9
C(24)-C(25)-C(26)	107.2(3)
C(24)-C(25)-H(25)	126.4
C(26)-C(25)-H(25)	126.4
C(27)-C(26)-N(3)	125.5(3)
C(27)-C(26)-C(25)	124.9(3)
N(3)-C(26)-C(25)	109.5(3)
C(26)-C(27)-C(34)	125.9(3)
C(26)-C(27)-C(28)	118.6(3)
C(34)-C(27)-C(28)	115.4(3)
C(33)-C(28)-C(29)	117.4(3)
C(33)-C(28)-C(27)	122.0(4)
C(29)-C(28)-C(27)	120.6(4)
F(11)-C(29)-C(30)	117.9(4)
F(11)-C(29)-C(28)	120.7(3)
C(30)-C(29)-C(28)	121.3(4)
F(12)-C(30)-C(31)	119.9(4)
F(12)-C(30)-C(29)	120.4(5)
C(31)-C(30)-C(29)	119.6(4)
F(13)-C(31)-C(30)	120.1(5)
F(13)-C(31)-C(32)	119.2(5)
C(30)-C(31)-C(32)	120.7(4)
F(14)-C(32)-C(31)	120.5(4)
F(14)-C(32)-C(33)	120.9(5)
C(31)-C(32)-C(33)	118.6(4)
F(15)-C(33)-C(28)	119.8(3)
F(15)-C(33)-C(32)	117.9(4)
C(28)-C(33)-C(32)	122.3(4)

N(4)-C(34)-C(35)	106.5(3)
N(4)-C(34)-C(27)	122.9(3)
C(35)-C(34)-C(27)	130.6(3)
C(37)-N(4)-C(34)	110.6(3)
C(37)-N(4)-H(4N)	127.3
C(34)-N(4)-H(4N)	121.8
C(34)-C(35)-C(36)	107.4(3)
C(34)-C(35)-H(35)	126.3
C(36)-C(35)-H(35)	126.3
C(37)-C(36)-C(35)	108.2(3)
C(37)-C(36)-H(36)	125.9
C(35)-C(36)-H(36)	125.9
N(4)-C(37)-C(36)	107.3(3)
N(4)-C(37)-C(38)	121.4(3)
C(36)-C(37)-C(38)	131.2(3)
C(1)-C(38)-C(37)	106.3(3)
C(1)-C(38)-C(40)	111.8(3)
C(37)-C(38)-C(40)	110.0(3)
C(1)-C(38)-C(39)	110.2(3)
C(37)-C(38)-C(39)	109.7(3)
C(40)-C(38)-C(39)	108.8(3)
C(38)-C(39)-H(39A)	109.5
C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(38)-C(40)-H(40A)	109.5
C(38)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(38)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
Cl(2)-C(41)-Cl(1)	111.8(7)
Cl(2)-C(41)-Cl(3)	111.4(6)
Cl(1)-C(41)-Cl(3)	111.0(7)

Cl(2)-C(41)-H(41)	107.5
Cl(1)-C(41)-H(41)	107.5
Cl(3)-C(41)-H(41)	107.5
Cl(5)-C(42)-Cl(4)	110.0(10)
Cl(5)-C(42)-Cl(6)	109.7(9)
Cl(4)-C(42)-Cl(6)	109.9(9)
Cl(5)-C(42)-H(42)	109.1
Cl(4)-C(42)-H(42)	109.1
Cl(6)-C(42)-H(42)	109.1