Electronic Supplementary Information for:

Factors Controlling the Spectroscopic Properties and Supramolecular Chemistry of an Electron Deficient 5,5-Dimethylphlorin Architecture

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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] Column chromatography was preformed with 40-63 μm silica gel with the eluent reported in parentheses. Analytical thin-layer chromatography (TLC) was performed on precoated glass plates and visualized by UV or by staining with $KMnO_4$. 5,5-Dimethyl-1,9-bis(pentafluorobenzoyly)dipyrromethane **(1)** was prepared using previously published method.[2]

Compound Characterization. ^1H 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 77.16). 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. Low resolution MS data was obtained using either a LCQ Advantage from Thermofinnigan or a Shimadzu LC/MS-2020 single quadrupole MS coupled with an HPLC system, with dual ESI/APCI source. High-resolution mass spectrometry analyses were either performed by the Mass Spectrometry Laboratory in the Department of Chemistry and Biochemistry at the University of Delaware.

UV-vis Absorption Experiments. UV/visible absorbance spectra were acquired on a StellarNet CCD array UV-vis spectrometer using screw cap quartz cuvettes (7q) of 1 cm pathlength from Starna. All absorbance spectra were recorded at room temperature. All samples for spectroscopic analysis were prepared in dry solvent within a N_2 filled glovebox. TBAF titrations were conducted by placing 2.0 mL of a 10 μM solutions of **3H(PhI^{CF_3})** into a screw cap quartz cuvette. Following the recording of an initial UV-vis absorbance spectrum, 10 μL aliquots of a 0.25 mM solution of TBAF and phlorin (10 μM) were added to the cuvette and changes in the UV-vis profile were monitored. Since the aliquots were all 10 μM in **3H(PhI^{CF_3})**, the concentration of phlorin did not change over the course of the experiment, which significantly simplifies analysis of the titration data. Job analysis for fluoride binding to **3H(PhI^{CF_3})** was carried out using solutions containing 10 μM of total analyte (TBAF + **3H(PhI^{CF_3})**). The ratio of **3H(PhI^{CF_3})** to fluoride was systematically varied by combining the appropriately sized aliquots of 10 μM stock solutions of TBAF and phlorin. Titrations and Job analyses conducted for binding of **3H(PhI^{CF_3})** to carboxylate salts were carried out using analogous methods.

Electrochemical Measurements. All electrochemistry was performed using either a CHI-620D potentiostat/galvanostat or a CHI-760D bipotentiostat. Differential pulse voltammetry (DPV) was performed for a N_2 sparged solution using a standard three-electrode configuration for quiescent solutions using a glassy carbon working disk electrode (3.0 mm diameter), a platinum wire auxiliary electrode and a Ag/AgCl reference electrode. DPV experiments were performed in

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1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
2. Pistner, A. J.; Lutterman, D. A.; Ghidiu, M. J.; Ma, Y.-Z.; Rosenthal, J. *J. Am. Chem. Soc.* **2013**, *135*, 6601–6607.

acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. Concentrations of the phlorin analyte was 1 mM and a scan rate of 50 mV/s and sensitivity of 10 mA/V were maintained during data acquisition.

Steady-State Fluorescence Measurements. Spectra were recorded on an automated Photon Technology International (PTI) QuantaMaster 40 fluorometer equipped with a 75-W Xenon arc lamp, a LPS-220B lamp power supply and a Hamamatsu R2658 photomultiplier tube. Samples for fluorescence analysis were prepared in an analogous method to that described above for the preparation of samples for UV-vis spectroscopy. Samples of **3H(PhI^{CF3})** were excited at λ = 650 nm and emission was monitored from 680–850 nm with a step size of 0.5 nm and integration time of 0.25 seconds. Reported spectra are the average of at least three individual acquisitions.

Emission quantum yields were calculated using Nile Blue in ethanol (Φ_{ref} = 0.27)[3] as the reference actinometer using the expression below,[4]

$$\Phi_{em} = \Phi_{ref}\left(\frac{A_{ref}}{A_{em}}\right)\left(\frac{I_{em}}{I_{ref}}\right)\left(\frac{\eta_{em}}{\eta_{ref}}\right)^2$$

where Φ_{em} and Φ_{ref} are the emission quantum yield of the sample and the reference, respectively, A_{ref} and A_{em} are the measured absorbance of the reference and sample at the excitation wavelength, respectively, I_{ref} and I_{em} are the integrated emission intensities of the reference and sample, respectively, and η_{ref} and η_{em} are the refractive indices of the solvents of the reference and sample, respectively.

Time-Resolved Fluorescence Measurements. The experimental setup for picosecond time-correlated single-photon-counting (TCSPC) measurements has been described in detail previously[5] and only a brief account will be given here. The detection system includes an actively quenched single photon avalanche photodiode (PDM 50CT module, Micro Photon Devices) and a TCSPC module (PicoHarp 300, PicoQuant). The light source was an optical parametric amplifier pumped by a 250 kHz Ti:Sapphire regenerative amplifier. Excitation was at 650 nm with typically 50 fs (full width at half maximum, fwhm) pulse duration and < 10 nJ pulse energy. Fluorescence emission was selected by using a 10 nm (fwhm) bandpass filter centered at 750 nm (CVI, F10-750.0-4-1.00), which were chosen according to the peak wavelength of the fluorescence emission spectra. The instrument response function (IRF) showed a fwhm of ~ 40 ps as recorded at the excitation wavelength using a dilute water suspension of coffee creamer. A 4.0-ps channel time was chosen and typically more than 10,000 counts were collected in the peak channel in order to obtain an acceptable signal-to-noise ratio. The polarization of the excitation beam was set to the magic angle (54.7°) with respect to an emission linear polarizer, which enables us to eliminate any depolarization contribution. Quantitative analysis of the time-resolved fluorescence data were performed by employing a least squares deconvolution fitting algorithm with explicit consideration of the finite IRF (FluoFit, PicoQuant) and a reduced chi-squares (χ^2) value is used to judge the quality of each fit.

X-Ray Crystallography. Crystals of **3H(PhI^{CF3})** were mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). Unit

3. Brouwer, A. M. *Pure Appl. Chem.* **2011**, *83*, 2213.
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5. Ma, Y.; Shaw, R.; Yu, X.; O'Neil, H. M.; Hong, K. *J. Phys. Chem. B* **2012**, *116*, 14451.

cell parameters were obtained from 36 data frames, 0.3° ω, from three different sections of the Ewald sphere. The systematic absences in the diffraction data are uniquely consistent with the reported space group. The data sets were treated with absorption corrections based on redundant multiscan data. The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL 6.12 program library The CIF has been deposited under CCDC 960702.

Computations. All density functional calculations were performed using the Gaussian 09 (G09) program package,[6] with the Becke three-parameter hybrid exchange and Lee-Yang-Parr correlation functional (B3LYP).[7–9] A 6-31G* basis set was used for all atoms. All geometry optimizations were performed in C_1 symmetry with subsequent vibrational frequency analysis to confirm that each stationary point was a minimum on the potential energy surface. A polarizable continuum model was utilized in the geometry optimization to model the solvent effects of the system.[10–14] The vertical singlet transition energies of the complexes were computed at the time-dependent density functional theory (TDDFT) level in methanol within G09 by using the optimized ground state structure. Molecular orbital were visualized using Visual Molecular Dynamics (VMD) software.[15]

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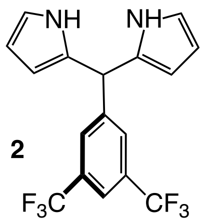
15. www.ks.uiuc.edu

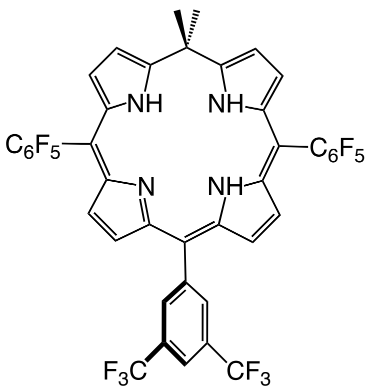
Synthetic Protocols

5-(3,5-bis(trifluoromethyl)phenyl)dipyrromethane (2). This compound was prepared by adapting a literature method.[16] Pyrrole (25 mL, 360 mmol) and 3,5-bis(trifluoromethyl)benzaldehyde (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 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 $C_{17}H_{12}F_6N_2$, 358.09; found, 358. HR-EI-MS: m/z: calcd for $C_{17}H_{12}F_6N_2$, 358.0905; found, 358.0895

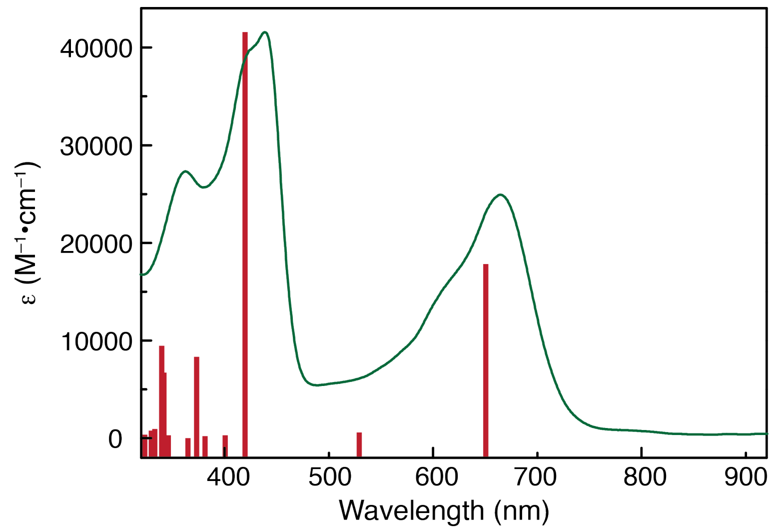


2

5,5-Dimethyl-10,20-bis(pentafluorophenyl)-15-(bis-3,5-trifluoromethylphenyl)phlorin (3H(Phl^{CF_3})). This compound was prepared by amending a previously described method.[Error! Bookmark not defined.] 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 time, the reaction was quenched with H_2O and extracted with dichloromethane. The organic layer was washed sequentially with H_2O and brin e 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 173 mg (0.50 mmol) of compound **2** and 1.54 mL (20.0 mmol) of trifluoroacetic acid. 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 (100 mmol) of triethylamine 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 (2:1) as the eluent to deliver 183 mg of the title compound as an deep green powder (41%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm: 8.17 (s, 2H), 8.05 (s, 1H), 7.38 (d, J = 5.0 Hz, 2H), 7.18 (d, J = 5.0 Hz, 2H), 6.99 (d, J = 3.8 Hz, 2H), 6.84 (d, J = 3.9 Hz, 2H), 4.98 (s, 3H), 1.44 (s, 6H) ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ/ppm: –63.49 (s), –139.09 to –139.60 (m), –153.73 (t, *J* = 21.0 Hz), –162.35 (td, *J* = 23.3, 8.0 Hz). HR-ESI-MS: $[M + H]^+$ m/z: calcd for $C_{42}H_{21}F_{16}N_4$, 885.1511; found, 885.1496.



16. 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.



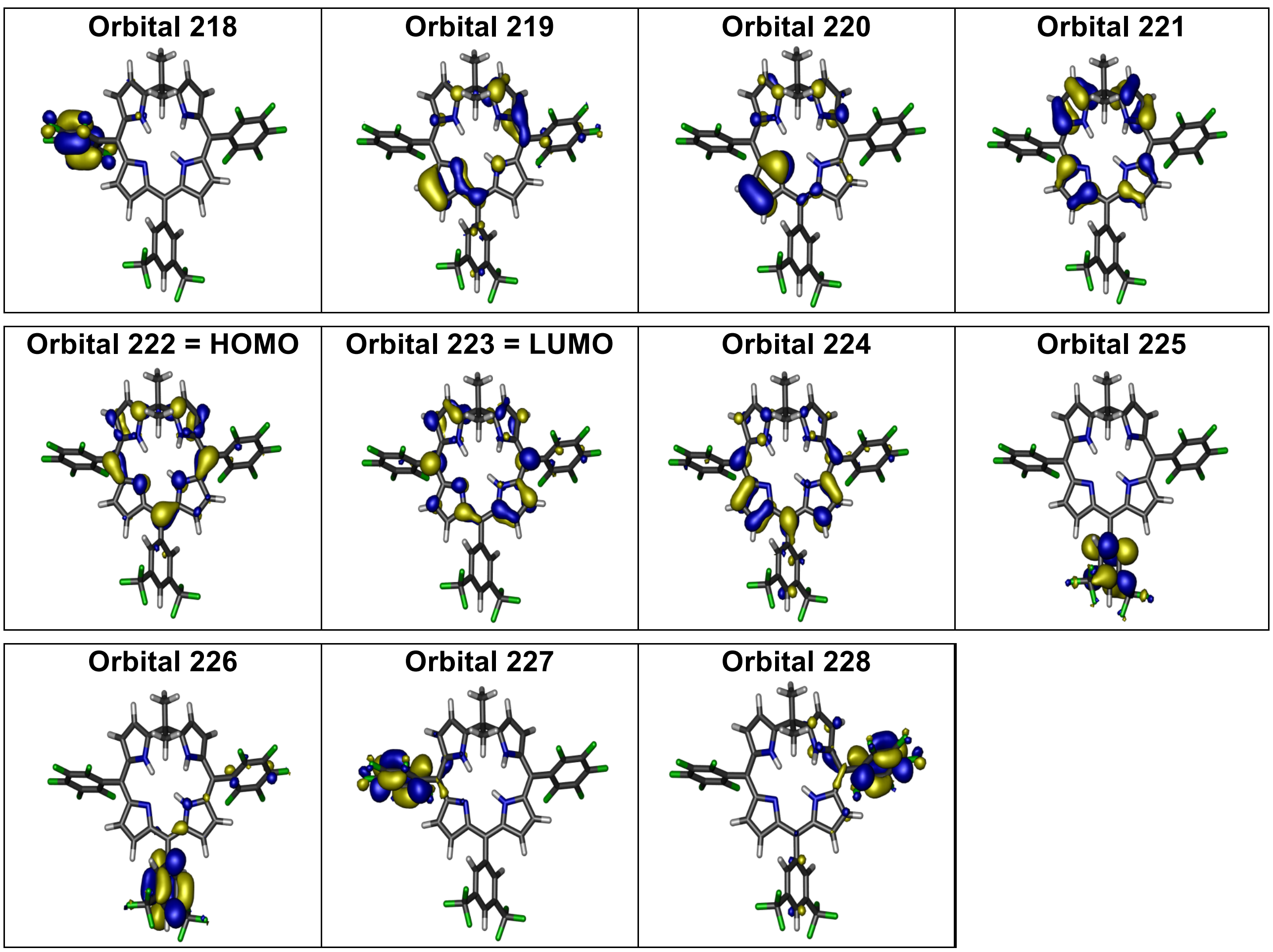


Figure S1. UV-vis absorbance spectrum of **3H(PhI^{CF_3})** in CH_2Cl_2 (green). The red lines indicate the 30 most intense electronic transitions in that solvent as calculated by TD-DFT. The orbitals involved in these 30 transitions are illustrated above and listed in Table S5.

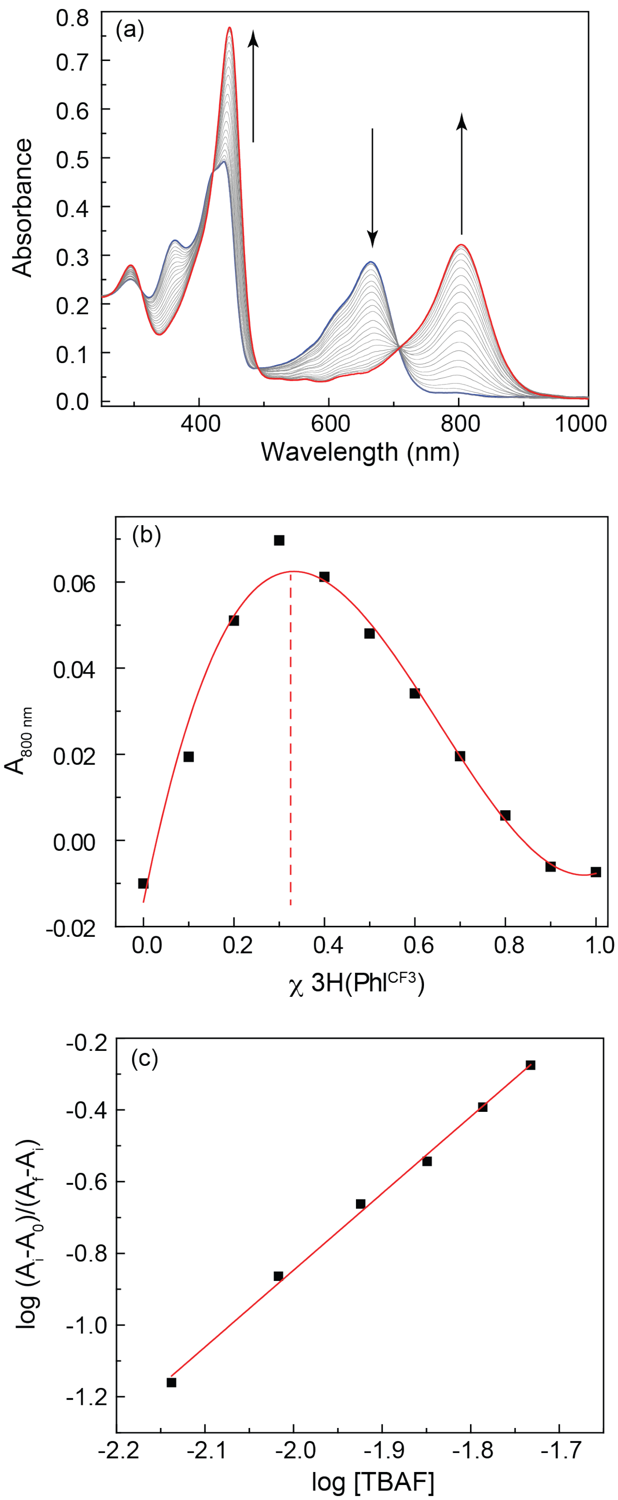


Figure S2. Changes in the UV-vis absorption profile of **3H(PhI^{CF3})** upon titration with TBAF in CH_2Cl_2. (b) Job plot for fluoride binding to **3H(PhI^{CF3})**. (c) Hill plot confirming the allosteric formation of **3H(PhI^{CF3})•2F$^-$**.

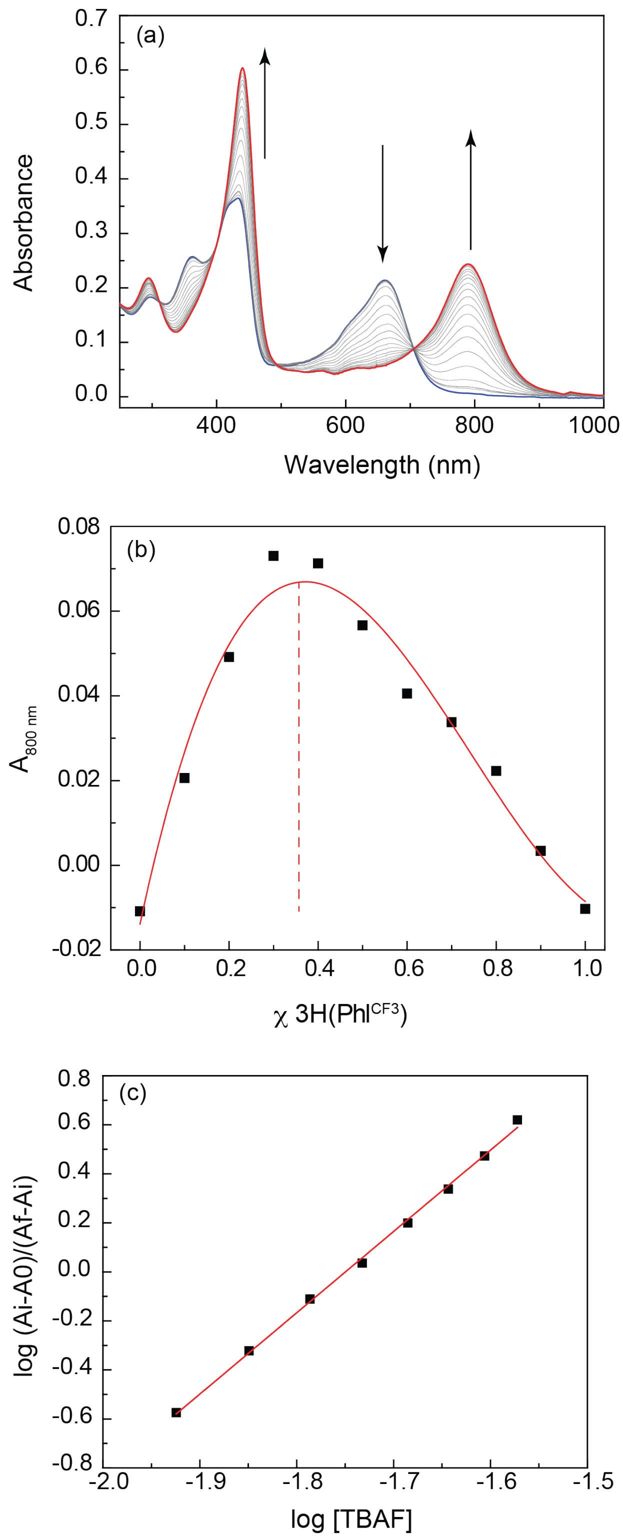


Figure S3. Changes in the UV-vis absorption profile of **3H(PhI^{CF3})** upon titration with TBAF in CH_3CN. (b) Job plot for fluoride binding to **3H(PhI^{CF3})**. (c) Hill plot confirming the allosteric formation of **3H(PhI^{CF3})•2F^{-}**.

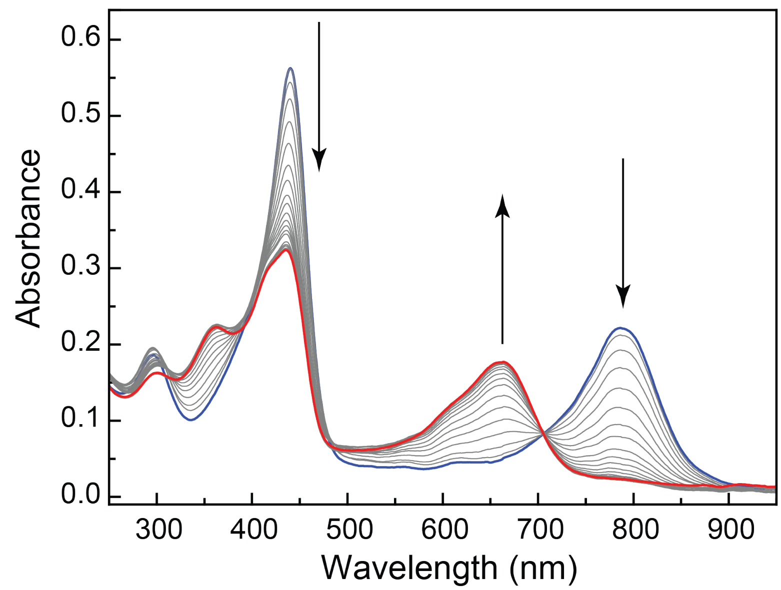


Figure S4. Changes in the UV-vis absorbance spectrum of **3H(PhI^{CF3})•OAc^{-}** in MeCN upon addition of aliquots of MeOH.

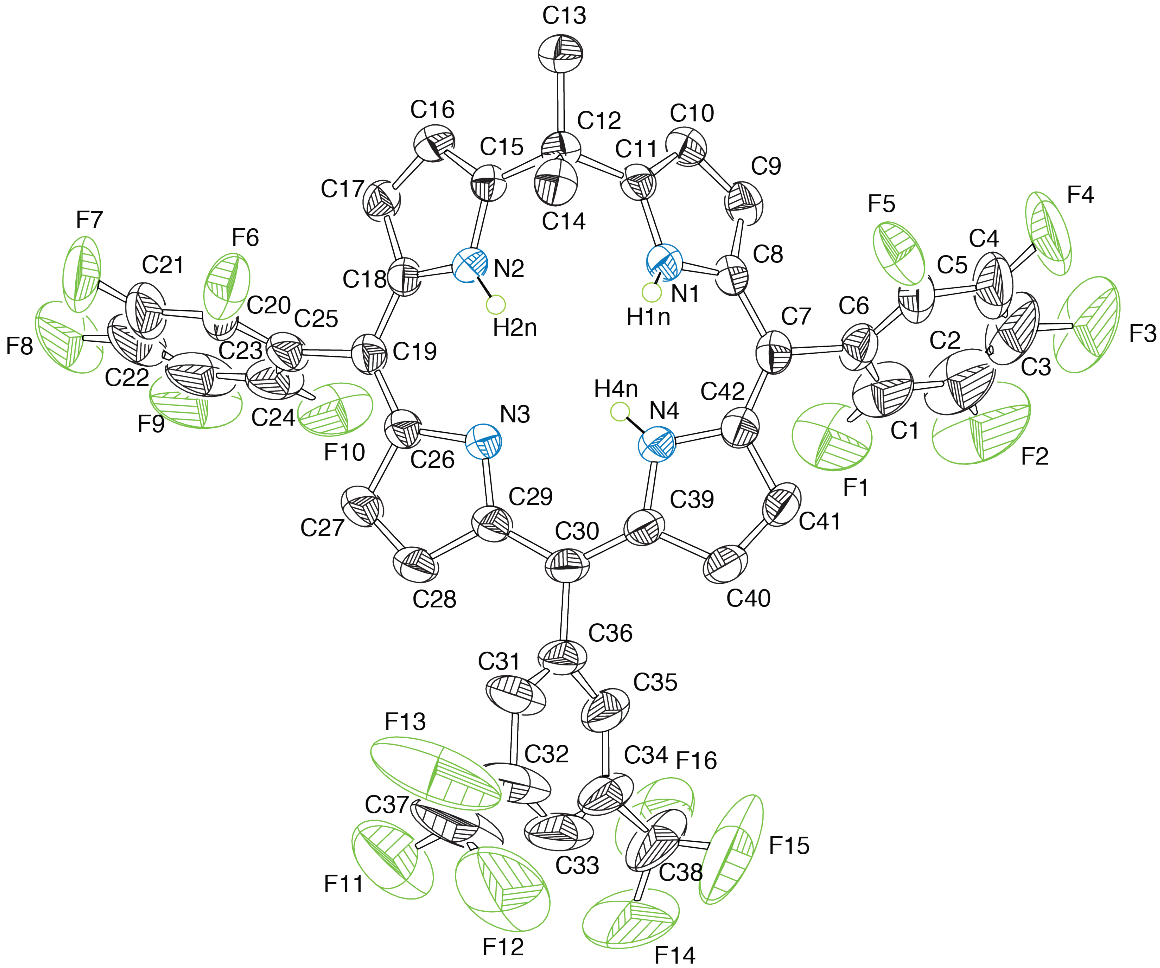


Figure S5. Fully labeled solid-state structure of **3H(PhI^{CF_3})**. Ellipsoids are shown at the 50% probability level and all non-nitrogen hydrogen atoms are omitted for clarity.

Table S1 Crystallographic Data for **3H(PhI^{CF_3})**.

Formula	$C_{42}H_{24}F_{16}N_4$
F_w	884.62
Crystal System	Monoclinic
Space Group	$P2_1/n$
a	15.454(8) Å
b	9.361(5) Å
c	27.907(14) Å
α	90°
β	96.211(8)°
γ	90°
V	4014(3) Å^3
Z	4
Temp	200(2) K
D_{calcd}	1.464 mg/m^3
2θ range	3.16 – 50.00°
μ (Mo Kα)	0.139 mm^{-1}
Relections	41796
Unique	7066
R(int)	0.0527
R_1	0.0826
wR_2	0.2360

Table S2 Bond Lengths (Å) Determined for **3H(PhI^{CF_3})**.

Bond	Length	Bond	Length
C(1)-F(1)	1.340(10)	C(22)-C(23)	1.397(16)
C(1)-C(6)	1.371(9)	C(23)-F(9)	1.344(11)
C(1)-C(2)	1.387(12)	C(23)-C(24)	1.408(10)
C(2)-F(2)	1.326(12)	C(24)-F(10)	1.356(9)
C(2)-C(3)	1.357(17)	C(24)-C(25)	1.356(9)
C(3)-C(4)	1.347(17)	C(26)-N(3)	1.391(6)
C(3)-F(3)	1.355(9)	C(26)-C(27)	1.443(7)
C(4)-F(4)	1.343(11)	C(27)-C(28)	1.343(7)
C(4)-C(5)	1.362(9)	C(28)-C(29)	1.447(7)
C(5)-F(5)	1.333(8)	C(29)-N(3)	1.350(6)
C(5)-C(6)	1.377(8)	C(29)-C(30)	1.421(7)
C(6)-C(7)	1.479(6)	C(30)-C(39)	1.394(7)
C(7)-C(42)	1.373(7)	C(30)-C(36)	1.493(6)
C(7)-C(8)	1.442(6)	C(31)-C(36)	1.349(9)
C(8)-C(9)	1.375(6)	C(31)-C(32)	1.391(8)
C(8)-N(1)	1.379(6)	C(32)-C(33)	1.377(16)
C(9)-C(10)	1.397(7)	C(32)-C(37)	1.501(17)
C(10)-C(11)	1.368(6)	C(33)-C(34)	1.353(16)
C(11)-N(1)	1.367(5)	C(34)-C(35)	1.362(9)
C(11)-C(12)	1.513(6)	C(34)-C(38)	1.503(17)
C(12)-C(15)	1.511(6)	C(35)-C(36)	1.381(9)
C(12)-C(13)	1.529(6)	C(37)-F(11')	0.99(3)
C(12)-C(14)	1.538(7)	C(37)-F(11)	1.249(13)
C(15)-N(2)	1.362(5)	C(37)-F(13)	1.271(18)
C(15)-C(16)	1.380(6)	C(37)-F(12)	1.341(14)
C(16)-C(17)	1.393(7)	C(37)-F(13')	1.37(4)
C(17)-C(18)	1.387(6)	C(37)-F(12')	1.39(3)
C(18)-N(2)	1.363(6)	C(38)-F(16)	1.266(19)
C(18)-C(19)	1.419(6)	C(38)-F(15)	1.291(10)
C(19)-C(26)	1.382(6)	C(38)-F(14)	1.349(14)
C(19)-C(25)	1.499(6)	C(39)-N(4)	1.375(6)
C(20)-F(6)	1.318(8)	C(39)-C(40)	1.441(7)
C(20)-C(21)	1.375(9)	C(40)-C(41)	1.356(7)
C(20)-C(25)	1.409(9)	C(41)-C(42)	1.429(7)
C(21)-F(7)	1.346(11)	C(42)-N(4)	1.388(6)
C(21)-C(22)	1.346(15)	C(1)-F(1)	1.340(10)
C(22)-F(8)	1.325(8)	C(1)-C(6)	1.371(9)
C(1)-C(6)	1.371(9)	C(26)-N(3)	1.391(6)
C(1)-C(2)	1.387(12)	C(26)-C(27)	1.443(7)
C(2)-F(2)	1.326(12)	C(27)-C(28)	1.343(7)
C(2)-C(3)	1.357(17)	C(28)-C(29)	1.447(7)

Bond	Length	Bond	Length
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C(9)-C(10)	1.397(7)	C(32)-C(33)	1.377(16)
C(10)-C(11)	1.368(6)	C(32)-C(37)	1.501(17)
C(11)-N(1)	1.367(5)	C(33)-C(34)	1.353(16)
C(11)-C(12)	1.513(6)	C(34)-C(35)	1.362(9)
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C(12)-C(13)	1.529(6)	C(35)-C(36)	1.381(9)
C(12)-C(14)	1.538(7)	C(37)-F(11')	0.99(3)
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C(19)-C(26)	1.382(6)	C(38)-F(15)	1.291(10)
C(19)-C(25)	1.499(6)	C(38)-F(14)	1.349(14)
C(20)-F(6)	1.318(8)	C(39)-N(4)	1.375(6)
C(20)-C(21)	1.375(9)	C(39)-C(40)	1.441(7)
C(20)-C(25)	1.409(9)	C(40)-C(41)	1.356(7)
C(21)-F(7)	1.346(11)	C(41)-C(42)	1.429(7)
C(21)-C(22)	1.346(15)	C(42)-N(4)	1.388(6)
C(22)-F(8)	1.325(8)		

Table S3 Bond Angles (°) Determined for **3H(PhI^{CF_3})**.

Atoms	Angle	Atoms	Angle
F(1)-C(1)-C(6)	120.3(6)	F(6)-C(20)-C(21)	118.1(7)
F(1)-C(1)-C(2)	118.4(8)	F(6)-C(20)-C(25)	120.6(5)
C(6)-C(1)-C(2)	121.3(9)	C(21)-C(20)-C(25)	121.2(8)
F(2)-C(2)-C(3)	119.5(10)	F(7)-C(21)-C(22)	119.2(8)
F(2)-C(2)-C(1)	120.7(13)	F(7)-C(21)-C(20)	120.0(10)
C(3)-C(2)-C(1)	119.7(9)	C(22)-C(21)-C(20)	120.8(9)
C(4)-C(3)-F(3)	121.5(14)	F(8)-C(22)-C(21)	122.9(12)
C(4)-C(3)-C(2)	120.5(7)	F(8)-C(22)-C(23)	116.8(11)
F(3)-C(3)-C(2)	117.7(13)	C(21)-C(22)-C(23)	120.3(7)
F(4)-C(4)-C(3)	120.3(8)	F(9)-C(23)-C(22)	123.2(8)
F(4)-C(4)-C(5)	120.8(10)	F(9)-C(23)-C(24)	118.7(10)
C(3)-C(4)-C(5)	118.9(10)	C(22)-C(23)-C(24)	118.0(8)
F(5)-C(5)-C(4)	117.0(7)	F(10)-C(24)-C(25)	119.5(6)
F(5)-C(5)-C(6)	119.4(5)	F(10)-C(24)-C(23)	117.9(7)
C(4)-C(5)-C(6)	123.6(8)	C(25)-C(24)-C(23)	122.6(8)
C(1)-C(6)-C(5)	115.9(6)	C(24)-C(25)-C(20)	117.1(6)
C(1)-C(6)-C(7)	122.3(6)	C(24)-C(25)-C(19)	122.8(6)
C(5)-C(6)-C(7)	121.8(5)	C(20)-C(25)-C(19)	120.1(5)
C(42)-C(7)-C(8)	124.6(4)	C(19)-C(26)-N(3)	125.3(4)
C(42)-C(7)-C(6)	120.0(4)	C(19)-C(26)-C(27)	125.3(4)
C(8)-C(7)-C(6)	115.3(4)	N(3)-C(26)-C(27)	109.4(4)
C(9)-C(8)-N(1)	106.7(4)	C(28)-C(27)-C(26)	107.1(4)
C(9)-C(8)-C(7)	130.7(4)	C(27)-C(28)-C(29)	107.0(4)
N(1)-C(8)-C(7)	122.6(4)	N(3)-C(29)-C(30)	125.3(4)
C(8)-C(9)-C(10)	107.8(4)	N(3)-C(29)-C(28)	110.5(4)
C(11)-C(10)-C(9)	108.3(4)	C(30)-C(29)-C(28)	124.0(4)
N(1)-C(11)-C(10)	107.1(4)	C(39)-C(30)-C(29)	124.0(4)
N(1)-C(11)-C(12)	121.3(4)	C(39)-C(30)-C(36)	119.0(4)
C(10)-C(11)-C(12)	131.3(4)	C(29)-C(30)-C(36)	117.0(4)
C(15)-C(12)-C(11)	105.6(3)	C(36)-C(31)-C(32)	122.4(8)
C(15)-C(12)-C(13)	110.0(4)	C(33)-C(32)-C(31)	119.8(10)
C(11)-C(12)-C(13)	109.9(4)	C(33)-C(32)-C(37)	120.6(8)
C(15)-C(12)-C(14)	110.4(4)	C(31)-C(32)-C(37)	119.6(10)
C(11)-C(12)-C(14)	111.6(4)	C(34)-C(33)-C(32)	119.5(7)
C(13)-C(12)-C(14)	109.1(4)	C(33)-C(34)-C(35)	118.2(9)
N(2)-C(15)-C(16)	106.5(4)	C(33)-C(34)-C(38)	123.3(10)
N(2)-C(15)-C(12)	122.2(4)	C(35)-C(34)-C(38)	118.5(12)
C(16)-C(15)-C(12)	131.2(4)	C(34)-C(35)-C(36)	125.2(8)
C(15)-C(16)-C(17)	108.4(4)	C(31)-C(36)-C(35)	114.9(5)
C(18)-C(17)-C(16)	107.4(4)	C(31)-C(36)-C(30)	123.5(5)
N(2)-C(18)-C(17)	106.8(4)	C(35)-C(36)-C(30)	121.6(6)

Atoms	Angle	Atoms	Angle
N(2)-C(18)-C(19)	122.6(4)	F(11')-C(37)-F(11)	137(2)
C(17)-C(18)-C(19)	130.4(4)	F(11')-C(37)-F(13)	46(3)
C(26)-C(19)-C(18)	126.0(4)	F(11)-C(37)-F(13)	111.5(16)
C(26)-C(19)-C(25)	119.0(4)	F(11')-C(37)-F(12)	62(4)
C(18)-C(19)-C(25)	114.9(4)	F(11)-C(37)-F(12)	106.0(8)
F(13)-C(37)-F(12)	105.4(12)	F(16)-C(38)-F(14)	102.2(9)
F(11')-C(37)-F(13')	121(2)	F(15)-C(38)-F(14)	102.2(9)
F(11)-C(37)-F(13')	46(3)	F(16)-C(38)-C(34)	119.5(10)
F(13)-C(37)-F(13')	139(3)	F(15)-C(38)-C(34)	112.6(9)
F(12)-C(37)-F(13')	64(3)	F(14)-C(38)-C(34)	109.6(14)
F(11')-C(37)-F(12')	118(3)	N(4)-C(39)-C(30)	125.0(4)
F(11)-C(37)-F(12')	51(3)	N(4)-C(39)-C(40)	105.9(4)
F(13)-C(37)-F(12')	73(3)	C(30)-C(39)-C(40)	129.0(4)
F(12)-C(37)-F(12')	149.5(16)	C(41)-C(40)-C(39)	108.3(4)
F(13')-C(37)-F(12')	97(2)	C(40)-C(41)-C(42)	109.0(4)
F(11')-C(37)-C(32)	111.0(17)	C(7)-C(42)-N(4)	126.3(4)
F(11)-C(37)-C(32)	112.1(11)	C(7)-C(42)-C(41)	127.9(4)
F(13)-C(37)-C(32)	113.6(8)	N(4)-C(42)-C(41)	105.8(4)
F(12)-C(37)-C(32)	107.7(13)	C(11)-N(1)-C(8)	109.9(4)
F(13')-C(37)-C(32)	107(2)	C(18)-N(2)-C(15)	110.8(3)
F(12')-C(37)-C(32)	100.5(11)	C(29)-N(3)-C(26)	106.0(3)
F(16)-C(38)-F(15)	108.8(16)	C(39)-N(4)-C(42)	110.8(4)

Table S4 Cartesian coordinates for DFT optimized structure of **3H(PhI^{CF_3})**.

Atom	x-coordinate	y-coordinate	z-coordinate
C	5.316298	-0.89153	1.564584
C	6.639974	-0.9655	1.987412
C	7.577042	-1.63523	1.207088
C	7.181295	-2.22081	0.007552
C	5.855101	-2.12958	-0.39994
C	4.879532	-1.46621	0.361121
C	3.462565	-1.4046	-0.0693
C	2.801457	-2.64307	-0.36661
C	3.048611	-3.9501	0.063831
H	3.796975	-4.23657	0.790118
C	2.132932	-4.80186	-0.58428
H	2.044617	-5.86985	-0.44444
C	1.344437	-4.02484	-1.43141
C	0.161935	-4.38969	-2.31074
C	0.235111	-5.8799	-2.69082
H	0.247833	-6.5265	-1.80895
H	1.143291	-6.07218	-3.26956
H	-0.62985	-6.1551	-3.30206
C	0.141025	-3.55288	-3.6132
H	0.038071	-2.47745	-3.43188
H	-0.70984	-3.85524	-4.2317
H	1.061635	-3.71586	-4.18329
C	-1.08143	-4.12254	-1.48213
C	-2.03343	-5.00861	-0.95678
H	-2.03387	-6.08072	-1.09039
C	-2.98228	-4.25665	-0.25413
H	-3.85239	-4.63413	0.264516
C	-2.60128	-2.90308	-0.33292
C	-3.2303	-1.73051	0.169049
C	-5.67719	-2.33109	-0.02043
C	-6.94702	-2.51081	0.519255
C	-7.16059	-2.26516	1.872586
C	-6.10318	-1.84279	2.672339
C	-4.84095	-1.672	2.111117
C	-4.59053	-1.90756	0.754116
C	-2.68093	-0.44747	0.129576
C	-3.41044	0.770348	0.431161
H	-4.44548	0.830574	0.739582
C	-2.55268	1.801148	0.213065
H	-2.74805	2.856145	0.344977
C	-1.28119	1.20785	-0.18524

C	-0.07799	1.969939	-0.35349
C	-0.94038	4.068578	-1.4295
H	-1.41668	3.451862	-2.18459
C	-1.06667	5.457752	-1.48944
C	-0.44556	6.270156	-0.54167
H	-0.54258	7.347818	-0.5916
C	0.299628	5.670254	0.473818
C	0.418257	4.281305	0.545397
H	0.976061	3.832098	1.359693
C	-0.19451	3.45642	-0.41077
C	-1.92276	6.068625	-2.56638
C	1.024376	6.528933	1.475525
C	1.199871	1.409095	-0.37948
C	2.482637	2.072128	-0.41481
H	2.624347	3.135176	-0.54316
C	3.460304	1.132598	-0.25796
H	4.528127	1.301606	-0.25295
C	2.843948	-0.16602	-0.17809
F	4.447553	-0.25831	2.367097
F	7.01205	-0.40968	3.147837
F	8.850448	-1.71351	1.604242
F	8.083358	-2.85139	-0.75603
F	5.530987	-2.68239	-1.57792
F	-5.51966	-2.5616	-1.33241
F	-7.9646	-2.90723	-0.25642
F	-8.37655	-2.43238	2.401199
F	-6.30321	-1.61188	3.976366
F	-3.84782	-1.2778	2.921548
F	-3.24061	5.981851	-2.26417
F	-1.64802	7.376805	-2.7581
F	-1.75694	5.441445	-3.7532
F	0.410335	7.717573	1.664176
F	2.289893	6.801848	1.073967
F	1.12068	5.926036	2.681103
N	1.739989	-2.72109	-1.26096
H	1.50223	-1.96388	-1.88699
N	-1.44198	-2.86659	-1.08586
H	-0.96312	-1.98298	-1.23636
N	-1.37774	-0.14275	-0.24667
N	1.472914	0.057512	-0.29805
H	0.725177	-0.59908	-0.08814

Table S5 MOs Involved in the 30 Most Intense Electronic Transitions for **3H(PhI^{CF_3})** in CH_2Cl_2.

Excited State	Molecular Orbitals	Energy	f value
Excited State 1	222 → 223	1.9058 eV 650.56 nm	f = 0.4962
Excited State 2	221 → 223 222 → 224	2.9548 eV 419.60 nm	f = 0.0166
Excited State 3	221 → 223 222 → 224 222 → 226 222 → 228	2.9548 eV 419.60 nm	f = 1.1573
Excited State 4	222 → 225	3.0961 eV 400.45 nm	f = 0.0088
Excited State 5	220 → 223 221 → 224	3.2528 eV 381.16 nm	f = 0.0057
Excited State 6	219 → 223 220 → 223 221 → 224 222 → 228	3.3236 eV 373.04 nm	f = 0.2324
Excited State 7	222 → 226	3.3991 eV 364.76 nm	f = 0.0005
Excited State 8	222 → 227 222 → 228	3.5837 eV 345.96 nm	f = 0.0083
Excited State 9	219 → 223 221 → 223 222 → 227 222 → 228	3.6266 eV 341.88 nm	f = 0.1875
Excited State 10	216 → 223 219 → 223 221 → 224	3.6500 eV 339.68 nm	f = 0.2639
Excited State 11	216 → 223 218 → 223 219 → 223	3.7232 eV 333.00 nm	f = 0.0270
Excited State 12	216 → 223 218 → 223 222 → 229	3.7580 eV 329.92 nm	f = 0.0177
Excited State 13	217 → 223 218 → 223 222 → 229	3.7620 eV 329.57 nm	f = 0.0217

Excited State	Molecular Orbitals	Energy	f value
Excited State 14	214 → 223 215 → 223 217 → 223 222 → 229 222 → 230	3.8552 eV 321.61 nm	f = 0.0031
Excited State 15	214 → 223 215 → 223 217 → 223 222 → 229	3.8676 eV 320.57 nm	f = 0.0102
Excited State 16	214 → 223 215 → 223 222 → 229 222 → 230	3.8955 eV 318.28 nm	f = 0.0007
Excited State 17	214 → 223 215 → 223 221 → 225 222 → 230	3.9147 eV 316.72 nm	f = 0.0574
Excited State 18	214 → 223 215 → 223 221 → 225 222 → 230	3.9328 eV 315.25 nm	f = 0.0031
Excited State 19	210 → 223 211 → 223 212 → 223 213 → 223 214 → 223	4.0019 eV 309.82 nm	f = 0.0277
Excited State 20	219 → 224 220 → 224	4.0323 eV 307.47 nm	f = 0.0380
Excited State 21	221 → 223 213 → 223	4.0942 eV 302.83 nm	f = 0.0335
Excited State 22	211 → 223 212 → 223 221 → 226	4.1689 eV 297.40 nm	f = 0.0177
Excited State 23	212 → 223 221 → 226	4.1905 eV 295.87 nm	f = 0.0480
Excited State 24	221 → 227	4.3321 eV 286.20 nm	f = 0.0440
Excited State 25	210 → 223 221 → 228 222 → 233	4.3794 eV 283.11 nm	f=0.0612

Excited State	Molecular Orbitals	Energy	f value
Excited State 26	210 → 223 219 → 224 220 → 224 222 → 231 222 → 233	4.4532 eV 278.42 nm	f = 0.0274
Excited State 27	209 → 223 210 → 223 219 → 224 222 → 231	4.4860 eV 276.38 nm	f = 0.0376
Excited State 28	209 → 223 210 → 223 211 → 223 222 → 231	4.5081 eV 275.03 nm	f = 0.0197
Excited State 29	209 → 223 219 → 224 211 → 228 222 → 231	4.5449 eV 272.80 nm	f = 0.0430
Excited State 30	216 → 224 218 → 224 221 → 230	4.6380 eV 267.32 nm	f = 0.0062