Supplementary Information for:

Triarylboron-Functionalized 8-Hydroxyquinolines and their Aluminum(III) Complexes

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General Information and Materials:

Dry solvents were obtained from a solvent purification system (Innovative Technologies, Inc.). Reactions that required oxygen-free environments were conducted under an inert nitrogen atmosphere in oven-dried glassware using standard Schlenk techniques unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded using Bruker Avance 300, 400 or 500 MHz spectrometers. UV-Vis measurements were acquired using a Varian Cary 50 Bio Spectrometer. Excitation and emission spectra were recorded using a Photon Technologies International Quanta Master model C-60 spectrometer. High-resolution mass spectra were obtained using a Water/Micromass GC-TOF EI-MS spectrometer. Elemental analyses were conducted by Canadian Microanalytical Service Ltd. Cyclic voltammetry measurements were acquired using a BAS CV-50W analyzer with a typical sample concentration of 4 mg of sample and 50mg of NBu_4PF_6 (TBAP) as supporting electrolyte in 3 mL of DMF using a standard Ag/AgCl reference electrode, Pt working electrode, and Pt auxiliary. The ferrocenium/ferrocene couple was used as an internal standard (E_o=0.55V). Aside from 8-hydroxyquinoline, ordered from TCI, all reagents were obtained from the Sigma-Aldrich chemical company. 8-tert-butoxycarbonyloxy-5-ethynylquinoline[S2], 5,5'-dibromo-3,3'-dihexyl-2,2'-bithiophene[S3] and 5-bromo-8-(methoxymethoxy)quinoline[S4] were synthesized as outlined in literature.

Synthesis:

Synthesis of 1:

(p-iodophenyl)dimesitylborane: Diiodobenzene (3g, 9.09 mmol) was dissolved into 60 mL of dry THF at room temperature. The temperature of the reaction flask was reduced to -78°C to which a hexane solution of nBuLi (1.6 M, 5.2 mL, 8.18 mmol) was added and the contents of the flask reacted for 2hrs. A solution of dimesitylboron fluoride (2.20g, 8.18mmol) in 20mL of THF was added to the reaction flask and allowed to react for 2 hours at -78°C and then at room temperature overnight. The solvent was removed under vacuum and the product purified using column chromatography on silica gel (hexane) and then recrystallized in hexane to give white crystalline product in 50% yield. ^{1}H NMR ($CDCl_3$, 25°C): δ (ppm) = 7.70 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 4H), 2.30 (s, 6H), 1.98 (s, 12H). This data matches literature spectral data.[S1]

1: A mixture of (p-iodophenyl)dimesitylborane (604 mg, 1.34 mmol), 8-tert-butoxycarbonyloxy-5-ethynylquinoline (300 mg, 1.11 mmol), $Pd(PPh_3)_4$ (64 mg, 0.056 mmol), CuI (21 mg, 0.11 mmol) and DIPEA (5 mL) was stirred in THF (40 mL) overnight at room temperature. The THF was removed *in vacuo*. Water was added to the mixture and the product was extracted with $CHCl_3$. **1-Boc** was purified by column chromatography on silica gel (hexane/acetone = 9:1) and then recrystallized using hexane in 67% yield. Then to a stirred solution of **1-Boc** (100 mg, 0.17 mmol) in 1 mL of dry $CHCl_3$, piperidine (49.9 μL, 0.50 mmol) was added and allowed to stir for approximately 10 minutes at room temperature. The $CHCl_3$ was removed *in vacuo* and the product was recrystallized in acetone resulting in quantitative yield of **1**. ^{1}H NMR (CD_2Cl_2, 25°C): 8.89 (d, *J* = 3.0 Hz, 1H), 8.75 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.64 (m, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.89 (s, 4H), 2.35 (s, 6H), 2.05 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 25°C): δ (ppm) = 153.7, 149.0, 141.2, 139.3, 138.4, 136.6, 135.3, 133.0, 131.2, 129.3, 128.6, 127.0, 123.1, 111.5, 110.2, 93.5, 88.9, 23.5, 21.3. HRMS of $C_{35}H_{32}BNO$: calcd [$M+H^+$] *m/z* = 494.2655, found [$M+H^+$] *m/z* = 494.2661.

Synthesis of 2:

5-bromo-5'-dimesitylboryl-3,3'-dihexyl-2,2'-bithiophene: 5,5'-dibromo-3,3'-dihexyl-2,2'-bithiophene (1.92 g, 3.89 mmol) was dissolved into 20 mL of dry THF at room temperature. The temperature of the reaction flask was reduced to -78°C to which a hexane solution of nBuLi (1.6 M, 2.55 mL, 4.08 mmol) was added and the contents of the flask reacted for ~2 hrs. A solution of dimesitylboron fluoride (1.28 g, 4.28 mmol) in 15 mL of THF was added to the reaction flask and allowed to react for 2 hours at -78 °C and then at room temperature overnight. The solvent was removed *in vacuo* and the product purified using column chromatography on silica gel using hexanes as eluent (80% yield). ^{1}H NMR ($CDCl_3$, 25°C): δ (ppm) = 7.30 (s, 1H), 6.91 (s, 1H), 6.84 (s, 4H), 2.49 (m, 4H), 1.48 (m, 4H), 1.22 (m, 12H), 0.86 (m, 6H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 25 °C): δ (ppm) 145.3, 143.2, 142.7, 142.0, 141.2, 139.6, 138.8, 131.9, 128.4, 31.9, 31.8, 31.1, 30.8, 29.3, 29.0, 23.8, 22.8, 21.5, 14.3. HRMS of $C_{38}H_{50}BBrS_2$: calcd *m/z* = 660.2630, found *m/z* = 660.2645.

2: To a solution of 5-bromo-5'-dimesitylboryl-3,3'-dihexyl-2,2'-bithiophene (1.10g, 1.66mmol) in THF (15mL) at -78 °C, was added nBuLi (1.6M, 1.14mL, 1.82mmol). The mixture was allowed to react for 2 hrs. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.42 mL, 2.08 mmol) was added slowly at -78 °C. The reaction mixture was allowed to react for 2 hours at -78°C before it was warmed to room temperature and allowed to react overnight. The product was purified using column chromatography on silica gel using hexane and ethyl acetate sequentially, resulting in a yield of 69% of **5-pinacolboryl-5'-dimesitylboryl-3,3'-dihexyl-2,2'-bithiophene**. Into a 20 mL schlenk flask was added the above boronic ester (750 mg, 1.06 mmol), 5-bromo-8-(methoxymethoxy)quinoline (190 mg, 0.71 mmol), K_3PO_4 (567 mg, 2.13 mmol), $Pd(CH_3COO)_2$ (8.00 mg, 0.035 mmol), and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (29 mg, 0.07 mmol) in toluene (3 mL). The reaction proceeded overnight under reflux. The product was purified using column chromatography on silica gel (ethyl acetate/hexane = 1:2) to give **2-MOM** in 95% yield, which was then deprotected according to literature methods.[S4] ^{1}H NMR ($CDCl_3$, 25°C): δ (ppm) = 8.83 (d, *J* = 4.0 Hz, 1H), 8.66 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 8.5 Hz, 4.0 Hz, 1H), 7.467,374 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.03 (s, 1H), 6.86 (s, 4H), 2.63 (m, 4H), 2.33 (s, 6H), 2.20 (s, 12H), 1.58 (m, 4H), 1.27 (m, 12H), 0.90 (m, 6H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 25°C): δ (ppm) = 152.4, 149.6, 147.9, 144.6, 142.8, 142.7, 142.1, 141.0, 140.6, 138.6, 138.4, 134.7, 129.4, 129.3, 129.0, 128.3, 127.0, 123.0, 122.2, 109.7, 31.7, 31.7, 31.0, 30.9, 29.4, 29.2, 29.1, 28.9, 23.6, 22.7, 21.3, 14.2. HRMS of $C_{47}H_{56}BNOS_2$: calcd *m/z* = 725.3896, found *m/z* = 725.3905.

Aluminum Complexes

Al(1)$_3$: To a solution of 1 (100 mg, 0.203 mmol) in toluene (30 mL) at 25°C, $Al(Me)_3$ (33.8 μL, 0.068 mmol) was added. The reaction was allowed to proceed for 15 minutes at which point the toluene was removed *in vacuo* and the product was recrystallized using hexanes in 80% yield. ^{1}H NMR ($CDCl_3$, 25°C): δ (ppm) 8.82 (m, 5H), 7.82 (d, J= 8.14 Hz, 3H), 7.63 (m, 1H), 7.56 (m, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.40 (m, 1H), 7.33 (d, J = 5.1 Hz, 1H), 7.05 (d, J = 8.15 Hz, 1H), 7.02 (d, J = 8.15 Hz, 1H), 6.93 (d, J = 8.15 Hz, 1H), 6.83 (s, 4H), 2.30 (s, 18H), 2.00 (s, 36H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 25°C): δ (ppm) = 160.8, 160.5, 160.1, 146.2, 145.5, 143.7, 141.9, 141.2, 140.0, 139.6, 139.5, 139.3, 139.3, 139.1, 139.0, 136.6, 136.4, 136.2, 131.1, 130.4, 130.3, 129.4, 128.6, 127.6, 127.4, 127.3, 125.6, 123.2, 123.1, 122.6, 113.4, 113.2, 113.0, 105.7, 105.6, 105.2, 93.2, 93.1, 93.0, 89.7, 89.4, 89.1, 66.1, 23.6, 21.3, 15.5, 1.2. HRMS of $C_{105}H_{93}B_3N_3O_3Al$: calcd [M+Na$^+$] *m/z* = 1526.7209, found [M+Na$^+$] *m/z* = 1526.9110.

Al(2)$_3$: To a solution of 2 (100 mg, 0.138 mmol) in toluene (30 mL) at 25^{o}C, Al(Me)$_3$ (23.0 μL, 0.0460 mmol) was added. The reaction was allowed to proceed for 15 minutes at which point the toluene was removed *in vacuo* and the product purified by centrifugation in hexanes in quantitative yield. ^{1}H NMR ($CDCl_3$, 25^{o}C): δ (ppm) = 8.80 (m, 5H), 7.65 (m, 3H), 7.51 (m, 1H), 7.42 (m, 1H), 7.34 (s, 3H), 7.22 (m, 1H), 7.16 (m, 4H), 6.93 (m, 3H), 6.83 (s, 12H), 2.59 (m, 12H), 2.30 (s, 18H), 2.17 (s, 38H), 1.56 (m, 12H), 1.24 (m, 36H), 0.84 (m, 18H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 25^{o}C): δ (ppm) = 159.7, 159.5, 159.1, 149.9, 149.8, 145.7, 145.2, 144.9, 144.8, 144.8, 143.5, 143.3, 143.1, 143.1, 143.0, 142.5, 141.7, 141.3, 141.2, 140.5, 139.9, 139.8, 138.9, 138.9, 138.8, 138.7, 138.3, 133.3, 133.1, 132.8, 129.5, 129.2, 129.1, 129.0, 128.7, 128.6, 128.4, 128.1, 125.8, 122.5, 121.9, 118.0, 117.8, 117.6, 113.9, 113.4, 112.9, 32.1, 32.0, 31.4, 31.3, 31.3, 31.2, 29.7, 29.6, 29.5, 29.3, 24.0, 23.1, 23.1, 21.9, 21.7, 21.2, 14.6, 14.5. HRMS of $C_{141}H_{165}B_3N_3O_3S_6Al$: calcd [M+H$^+$] *m/z* = 2021.1343, found [M+H$^+$] *m/z* = 2201.1396.

^{1}H NMR and COSY Spectra of Ligands and Complexes

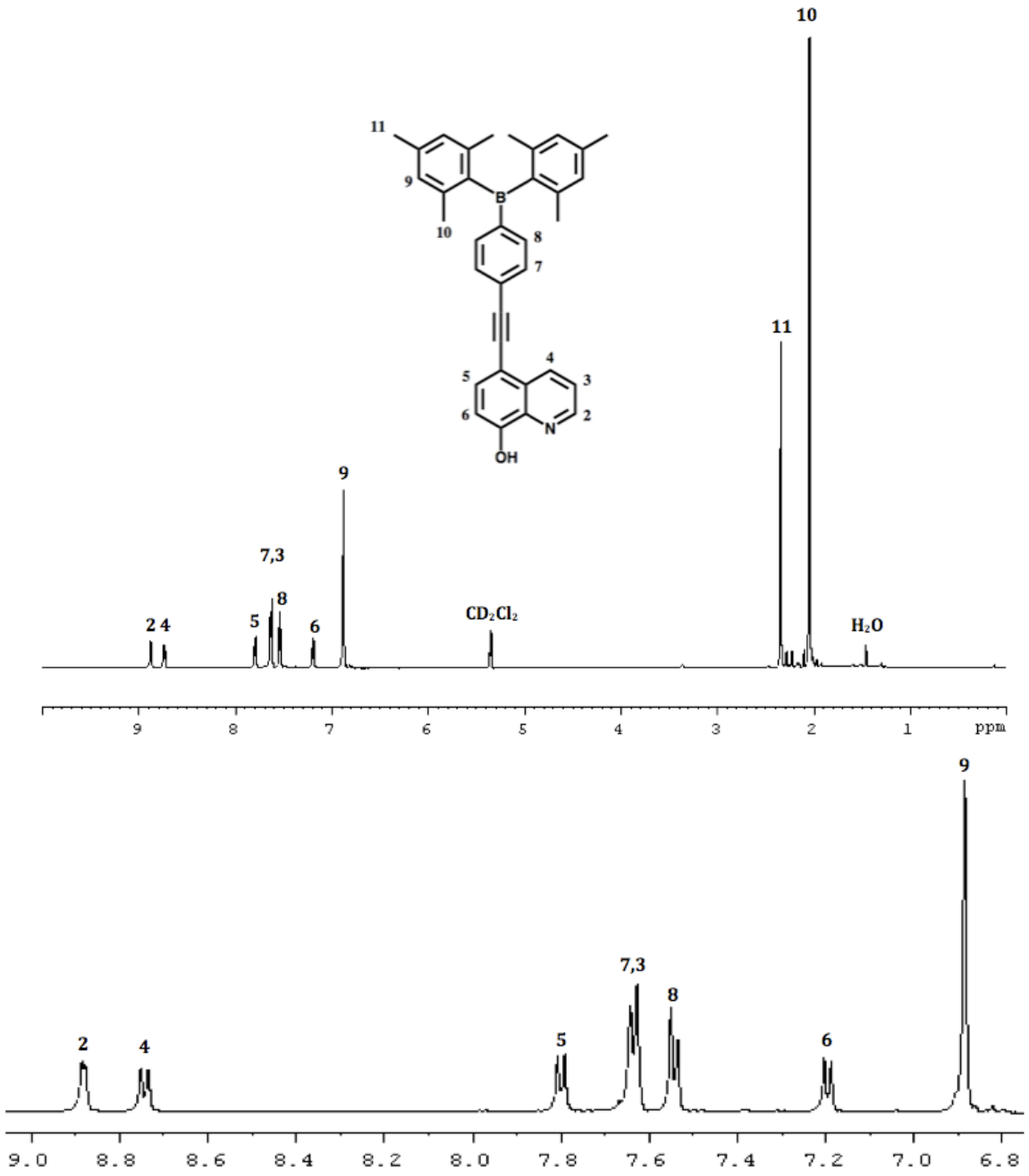

Figure S1. (Top) ^{1}H NMR spectrum of **1** and (bottom) the aromatic region of the spectrum, enlarged for clarity (CD_2Cl_2, 25^{o}C).

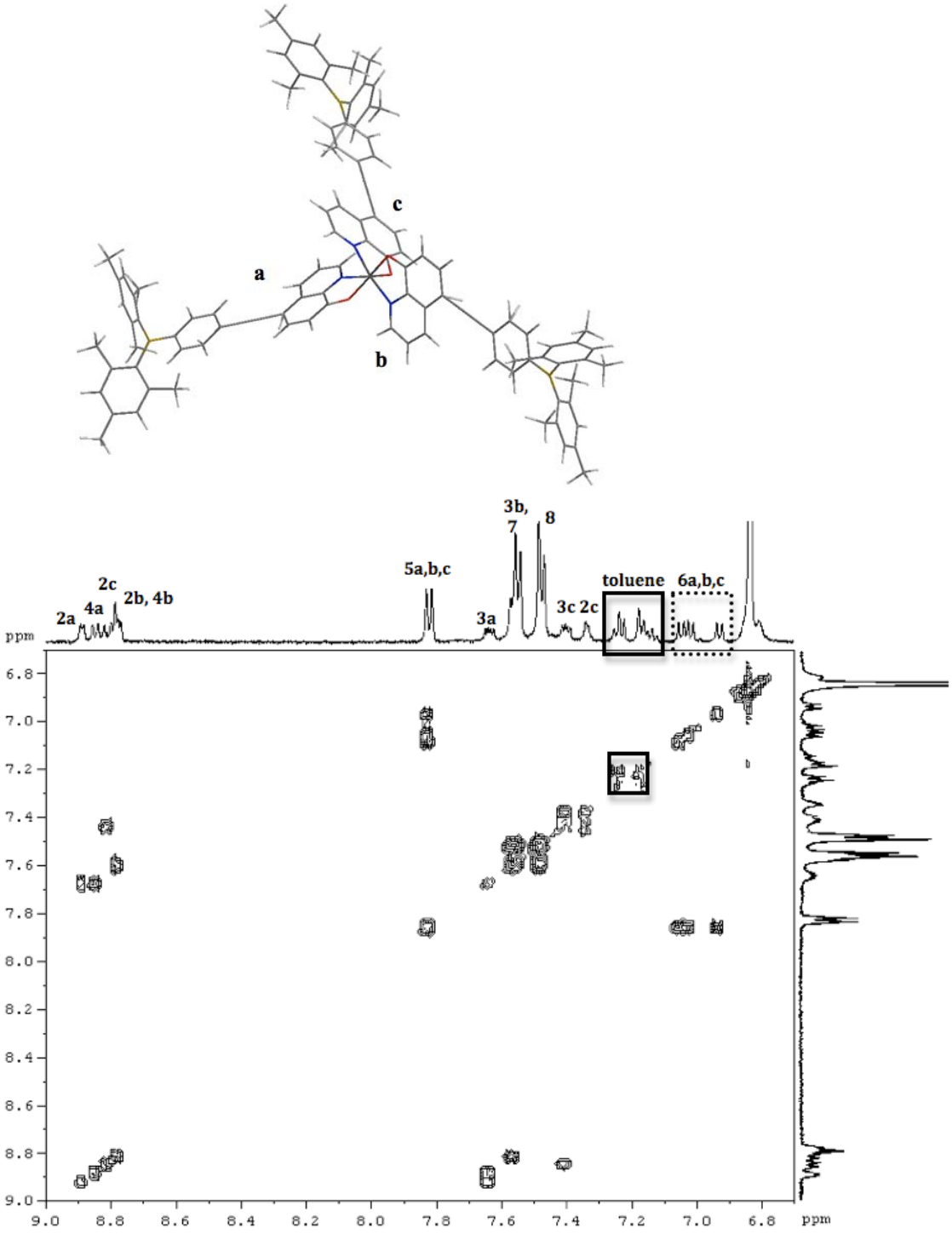

Figure S2. (Top) The isomeric form of **Al(1)$_3$** was found to be meridional, possessing C_1 symmetry. Due to the C_1 symmetry of this structure, the three ligands are chemically inequivalent (a to c). (Bottom) COSY spectrum of the aromatic region of Al(**1**)$_3$.

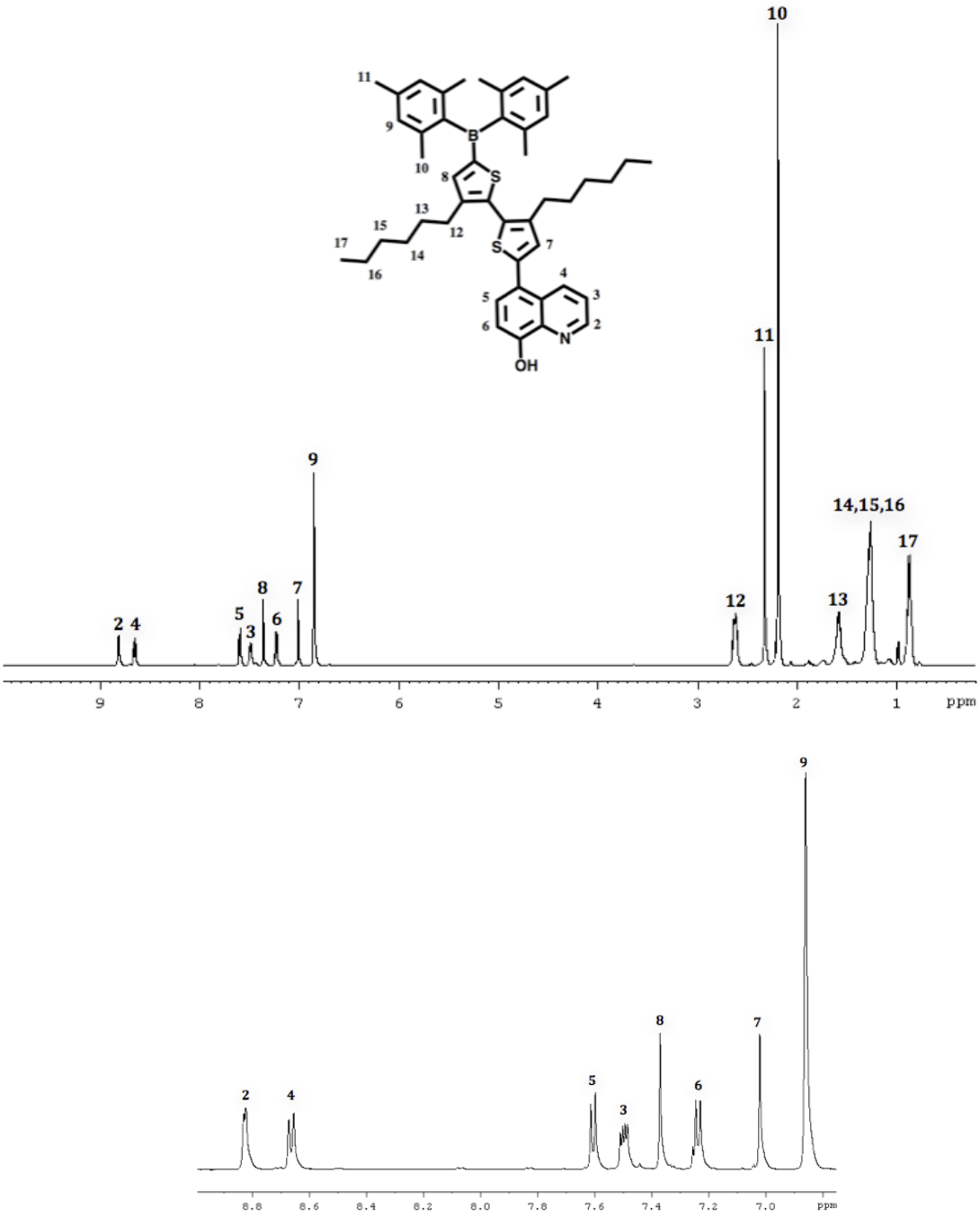

Figure S3. (Top) ^{1}H NMR spectrum of **2** and (bottom) the aromatic region of the spectrum, enlarged for clarity ($CDCl_3$, 25°C).

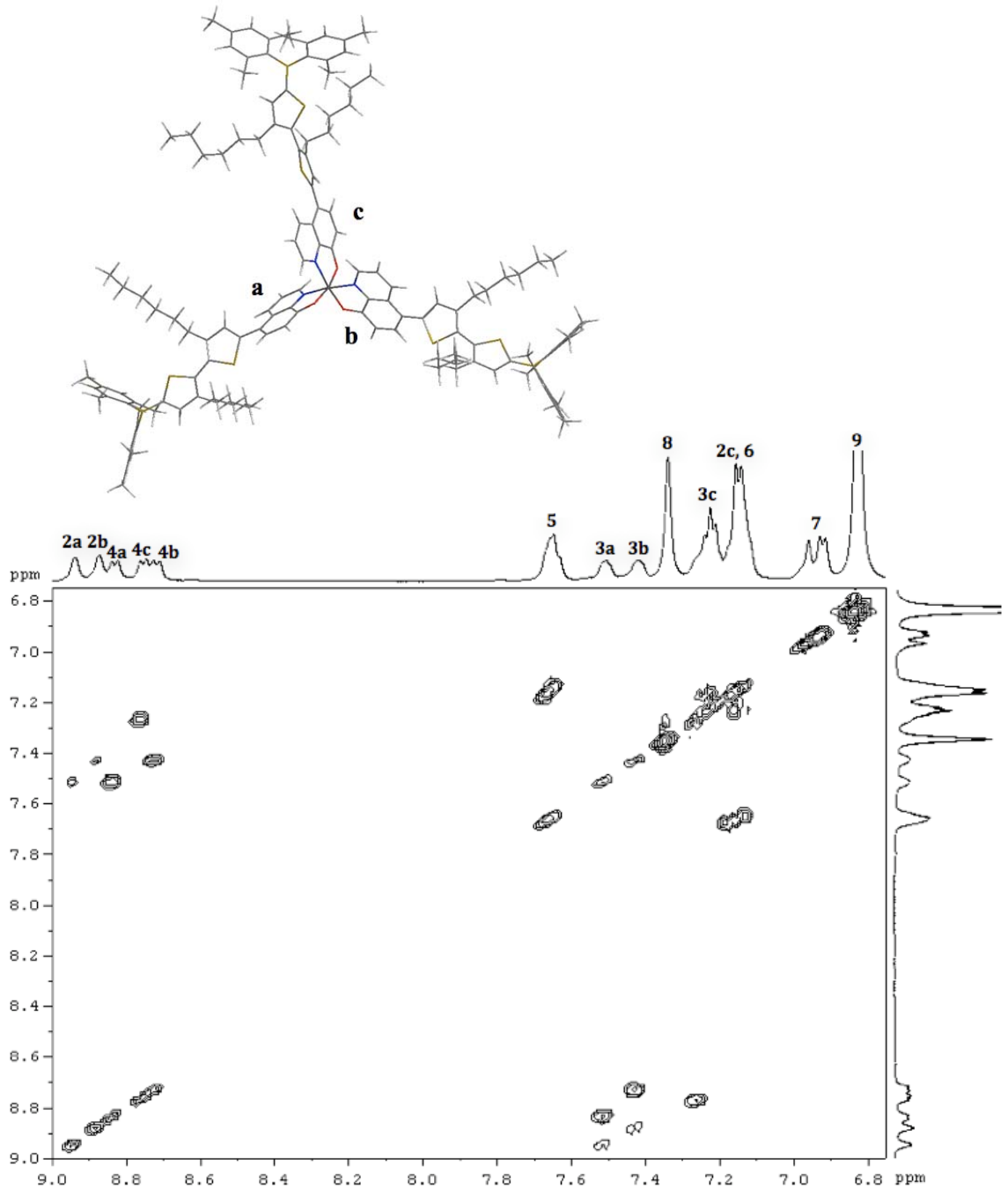

Figure S4. (Top) The isomeric form of **Al(2)$_3$** was found to be meridional, possessing C_1 symmetry. Due to the C_1 symmetry of this structure, the three ligands are chemically inequivalent (a to c). (Bottom) COSY spectrum of the aromatic region of Al(**2**)$_3$.

Photophysical Properties

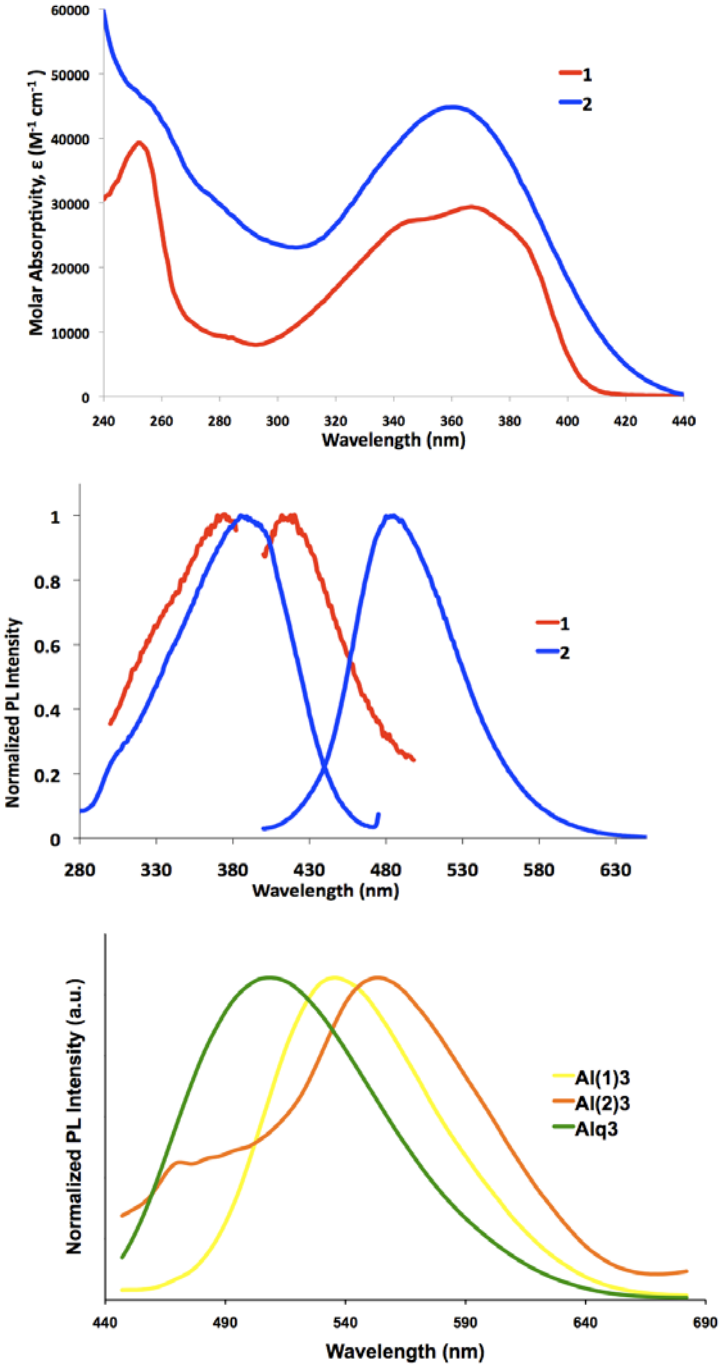

Figure S5. UV-Vis absorption spectra (top), normalized excitation and emission spectra (middle) of **1** and **2** (1.0 x 10^{-5}M) in CH_2Cl_2 at room temperature and (bottom) solid state emission spectra with λ_{ex} = 365 nm.

Table S1. The Spectroscopic Properties of free ligands **1** and **2**.

a

Compound	**A, nm (ε, M^{-1} cm^{-1})**	**λ_{ex}, nm CH_2Cl_2, rt**	**λ_{em}, nm CH_2Cl_2, rt**	**Φ Solution[a]/solid**
1	254 (38600), 368 (29300)	373	413	<0.1%/0.3%
2	363 (44800)	385	480	0.56%/<0.01%

Quantum efficiency measurements in CH_2Cl_2 used 9,10-diphenylanthracene as standard.

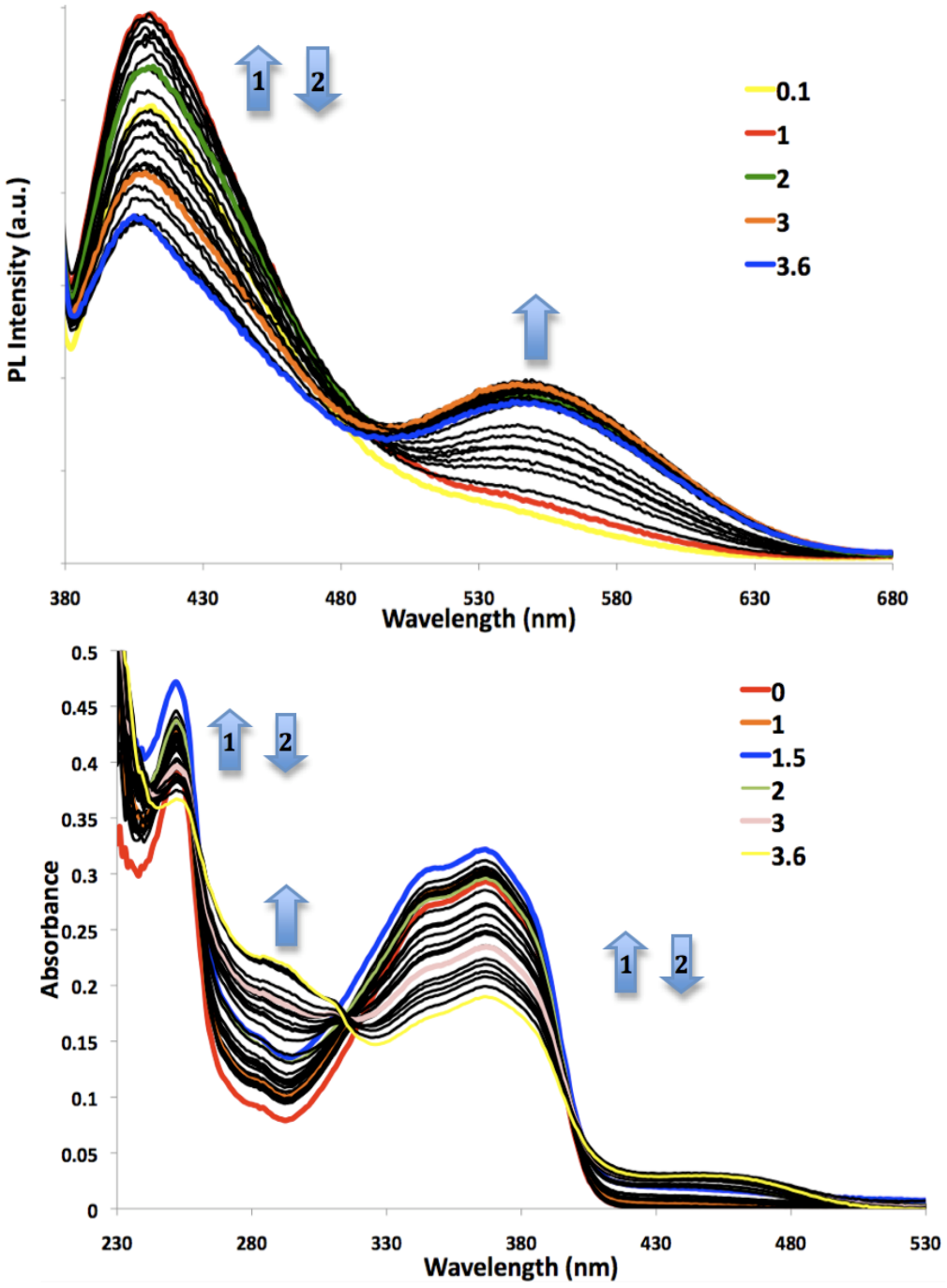

Figure S6. The UV absorption (bottom) and fluorescent titration (top) spectra of free ligand **1** (1 x 10^{-5} M) by TBAF (0-3.6 eq), in CH_2Cl_2 at 298 K (λ_{ex} = 373 nm). Wherever two arrows are present is an indication that there were two distinct phases in the spectral changes during the course of the titration.

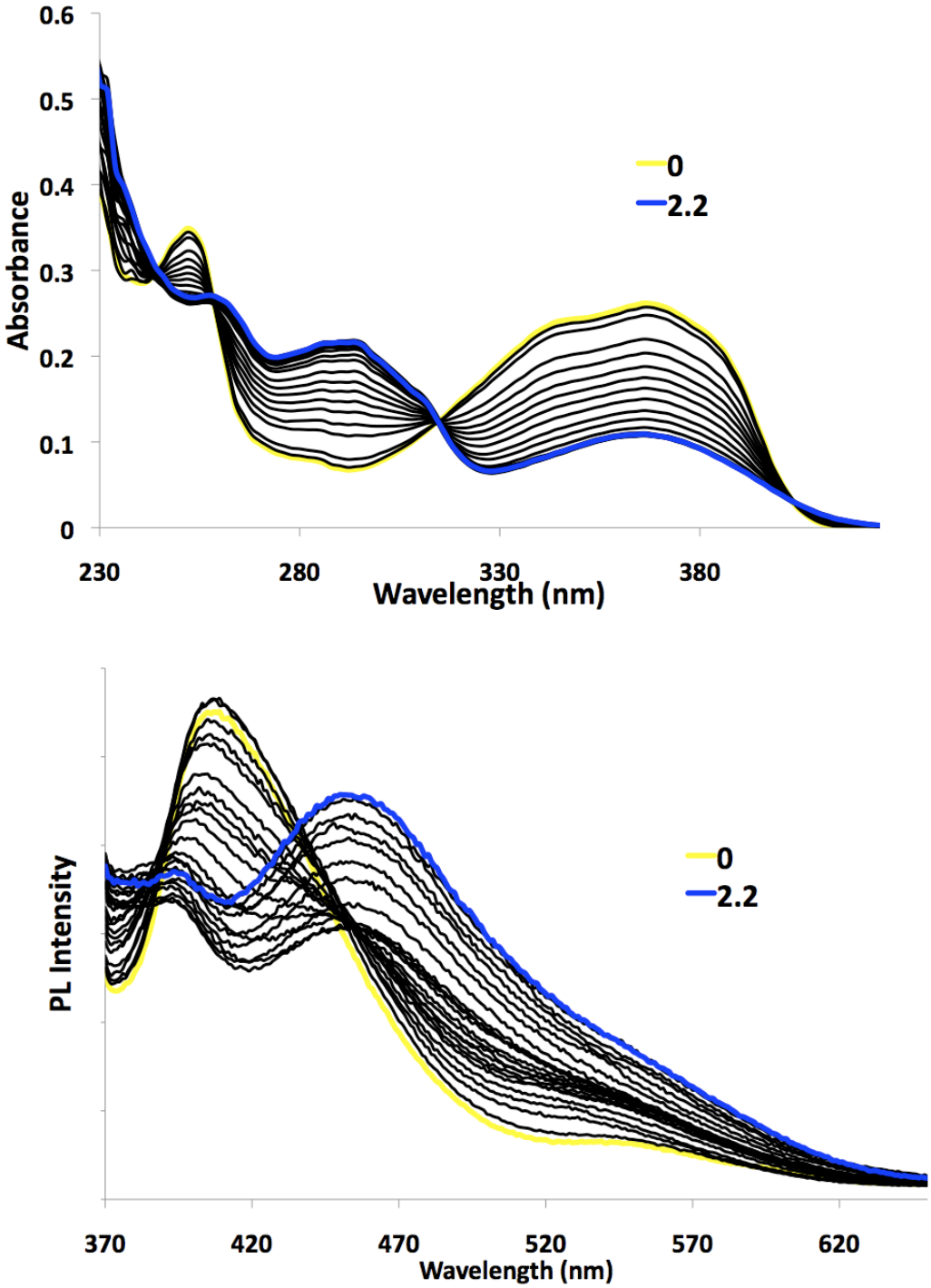

Figure S7. The UV-vis (top) and fluorescent titration (bottom) spectra of free ligand **1** (1 x 10^{-5} M) by tetraethylammonium cyanide, in CH_2Cl_2 at 298 K (λ_{ex} = 373 nm).

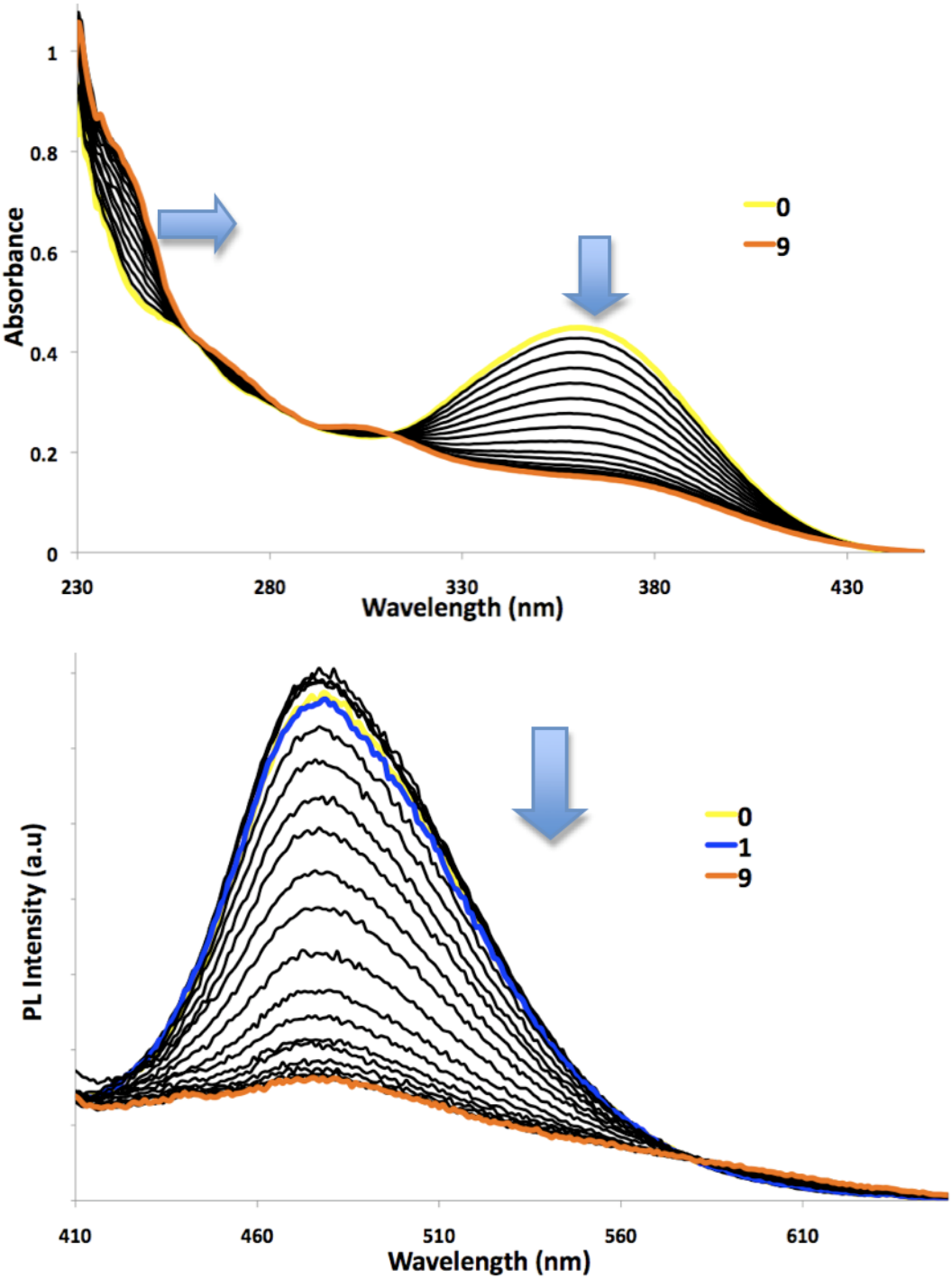

Figure S8. The UV-vis (top) and fluorescent titration (bottom) (λ_{ex} = 385 nm) spectra of free ligand **2** (1 x 10^{-5} M) by TBAF in CH_2Cl_2 at 298 K.

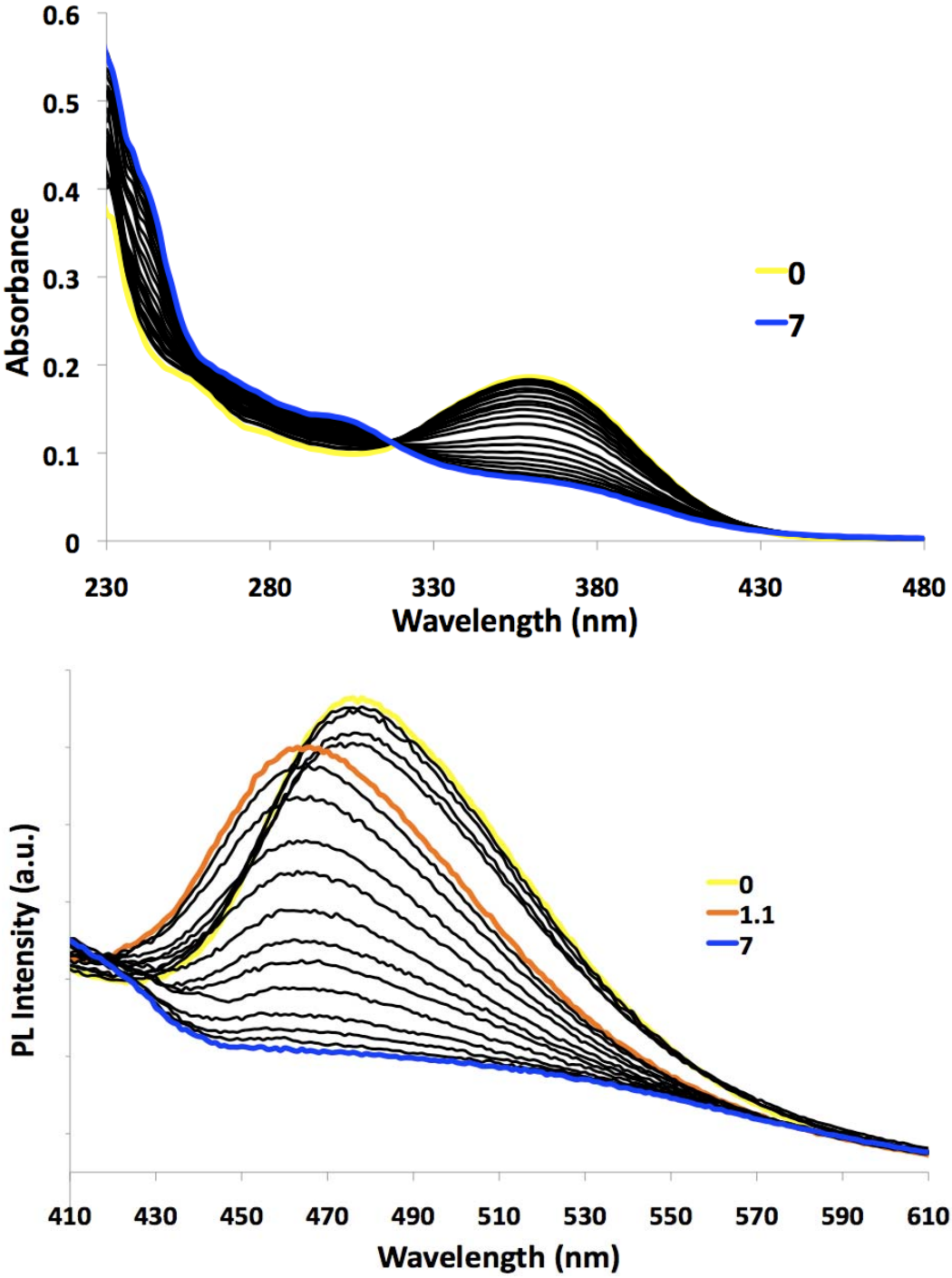

Figure S9. The UV-vis absorption (top) and fluorescence (bottom) titration (λ_{ex} = 385 nm) spectra of free ligand **2** (1 x 10^{-5} M) by tetraethylammonium cyanide in CH_2Cl_2 at 298K.

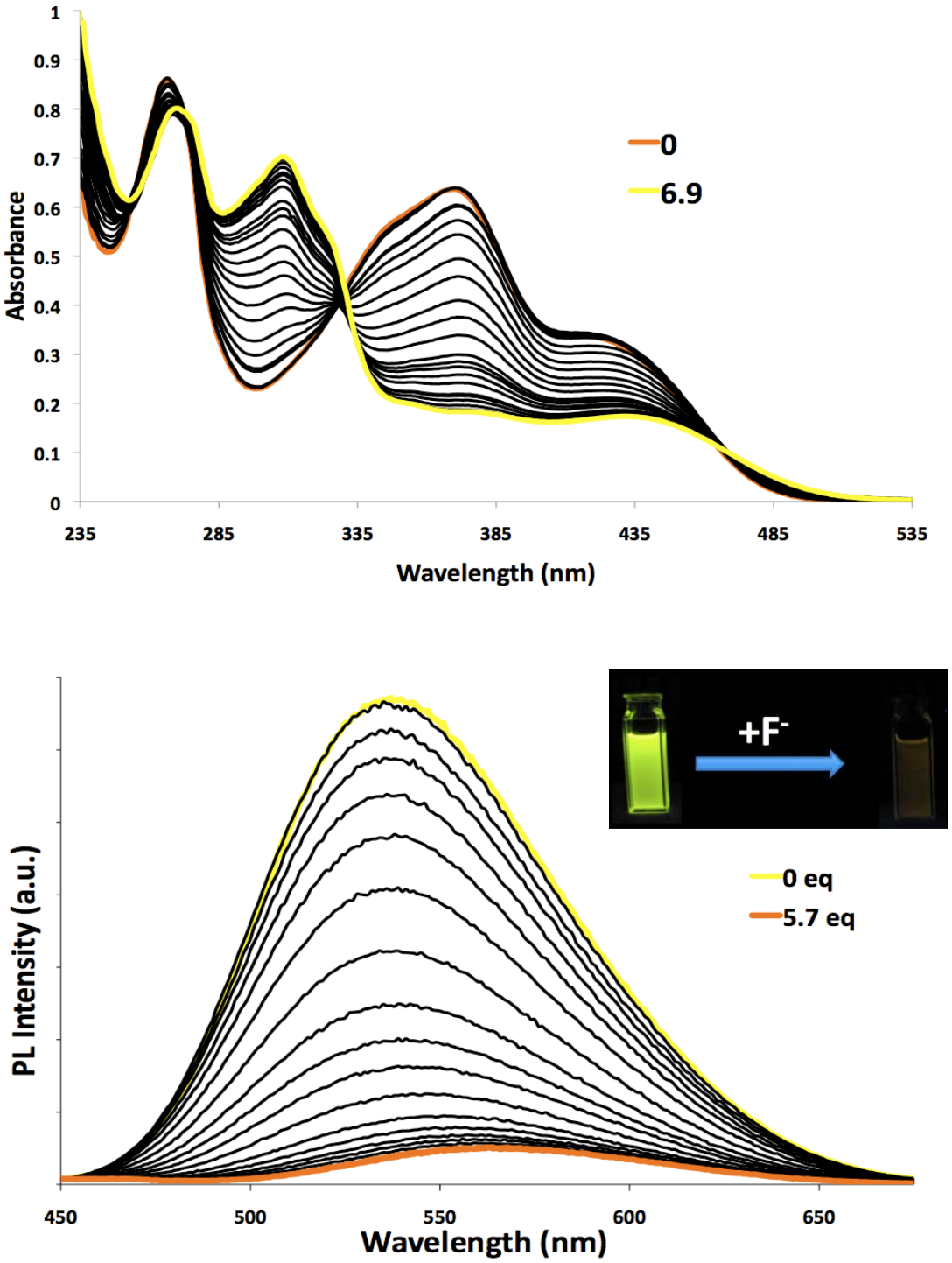

Figure S10. The UV-vis absorption (top) and fluorescence (bottom) titration (λ_{ex} = 420 nm) spectra of **Al(1)$_3$** (1 x 10^{-5} M) by TBAF in CH_2Cl_2 at 298 K.

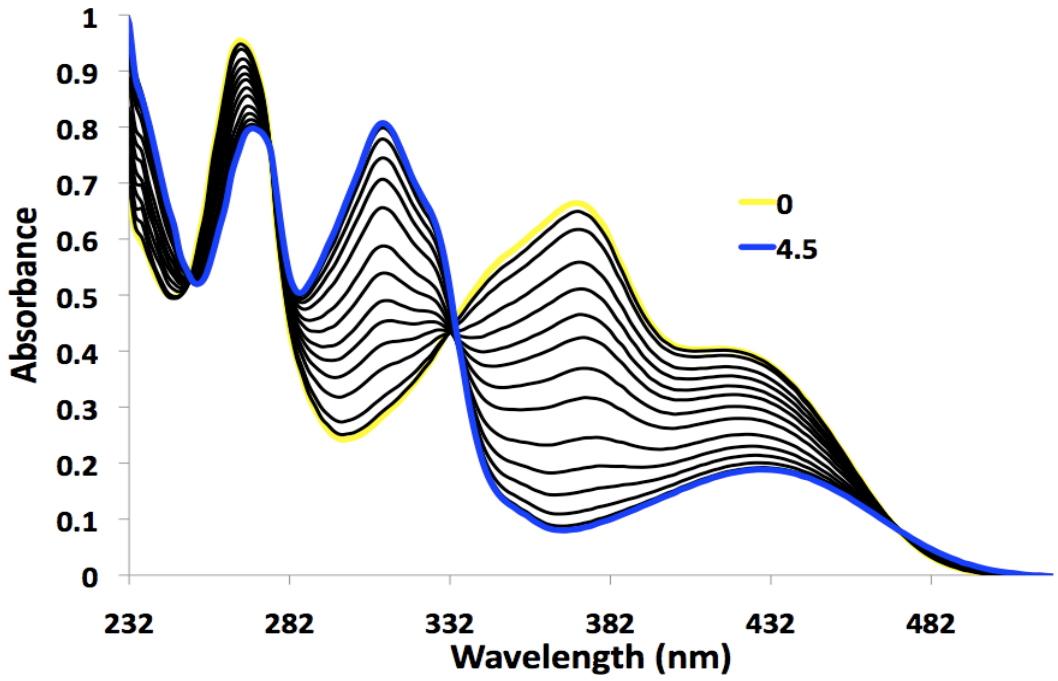

Figure S11. The UV-vis titration spectra of **Al(1)$_3$** (1 x 10^{-5} M) by tetraethylammonium cyanide (TEACN) in CH_2Cl_2 at 298 K.

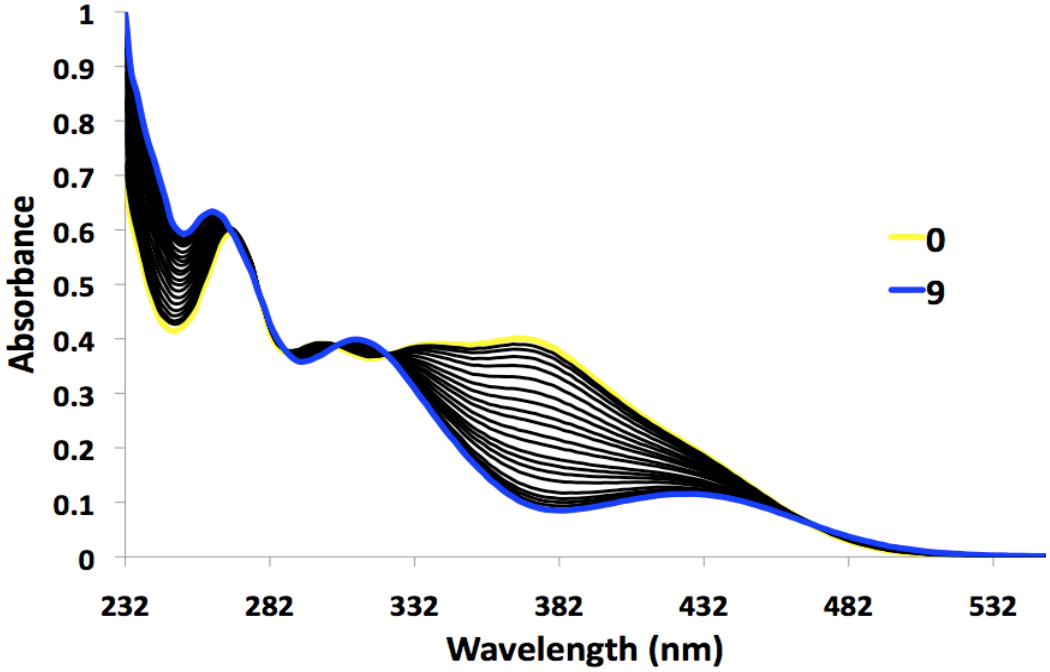

Figure S12. The UV-vis absorption spectra of **Al(2)$_3$** (1 x 10^{-5} M) titrated by tetraethylammonium cyanide in CH_2Cl_2 at 298 K.

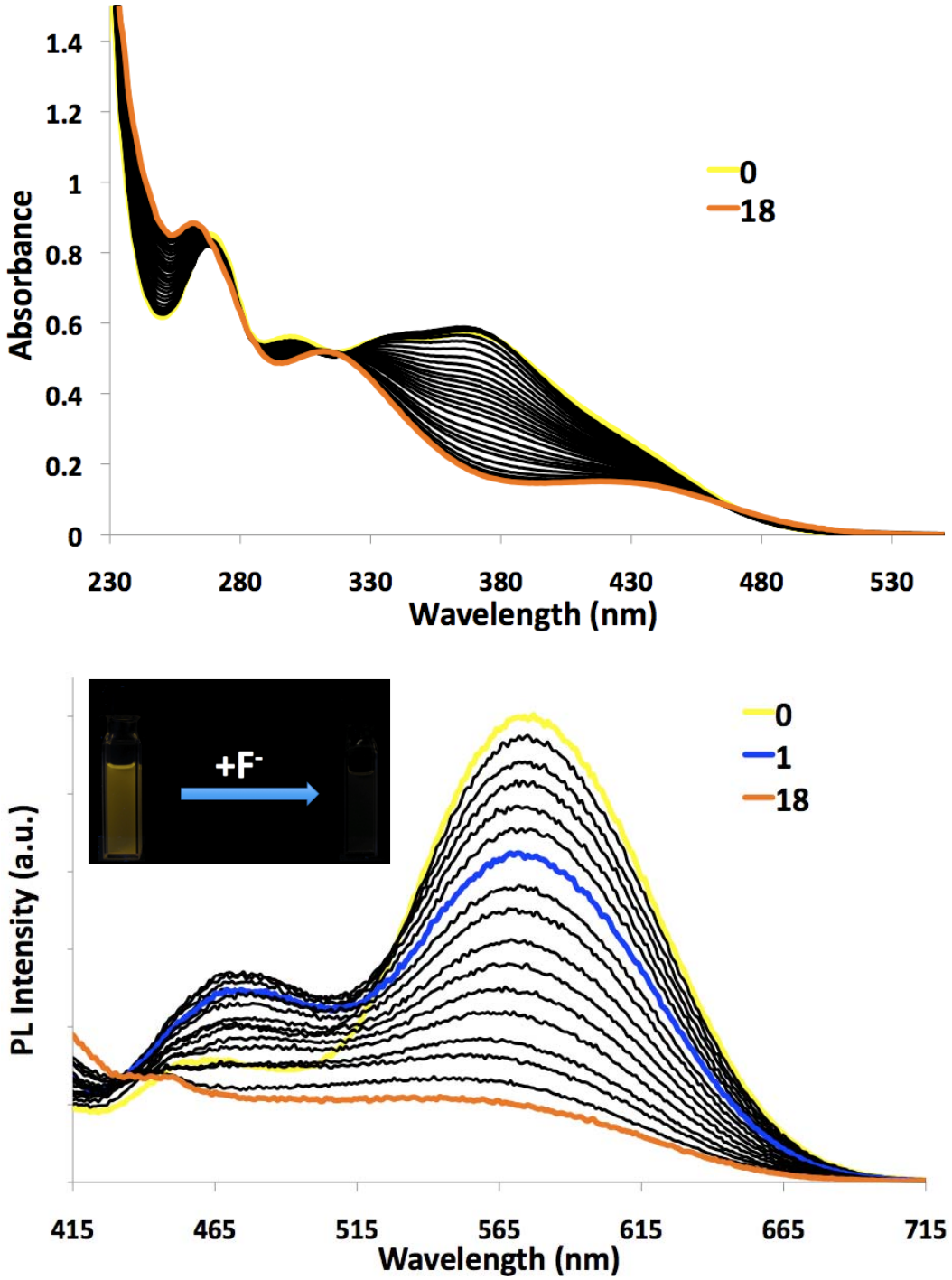

Figure S13. The UV-vis (top) and fluorescence (bottom) titration (λ_{ex} = 395 nm) spectra of **Al(2)$_3$** (1 x 10^{-5} M) by TBAF in CH_2Cl_2 at 298 K.

Electrochemical Properties

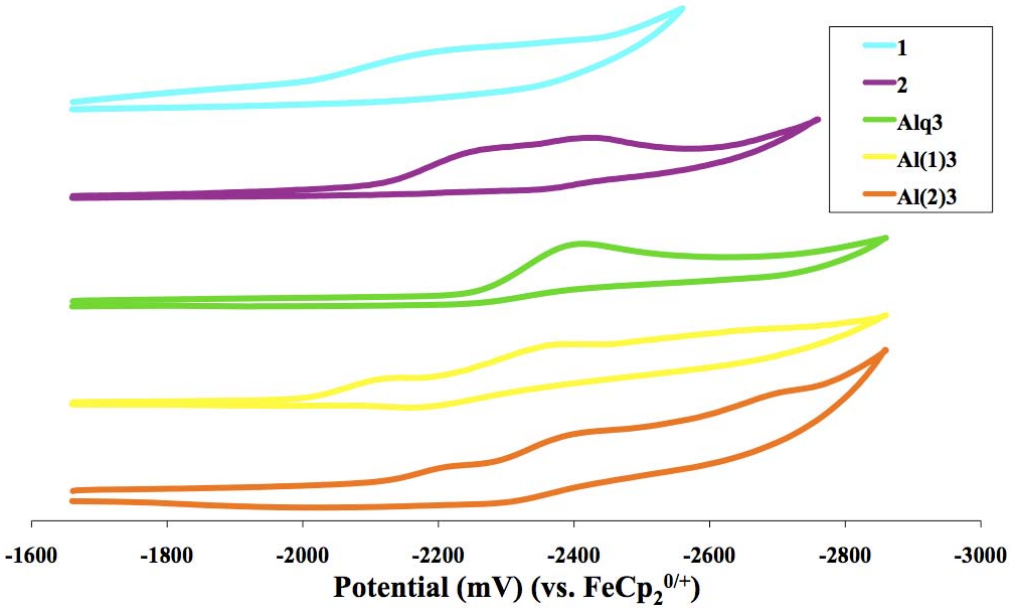

Figure S14. CV diagrams of Alq_3, **1** and **2** and their aluminum complexes in DMF with NBu_4PF_6 as the electrolyte and scanning rates 200-500 mV/s.

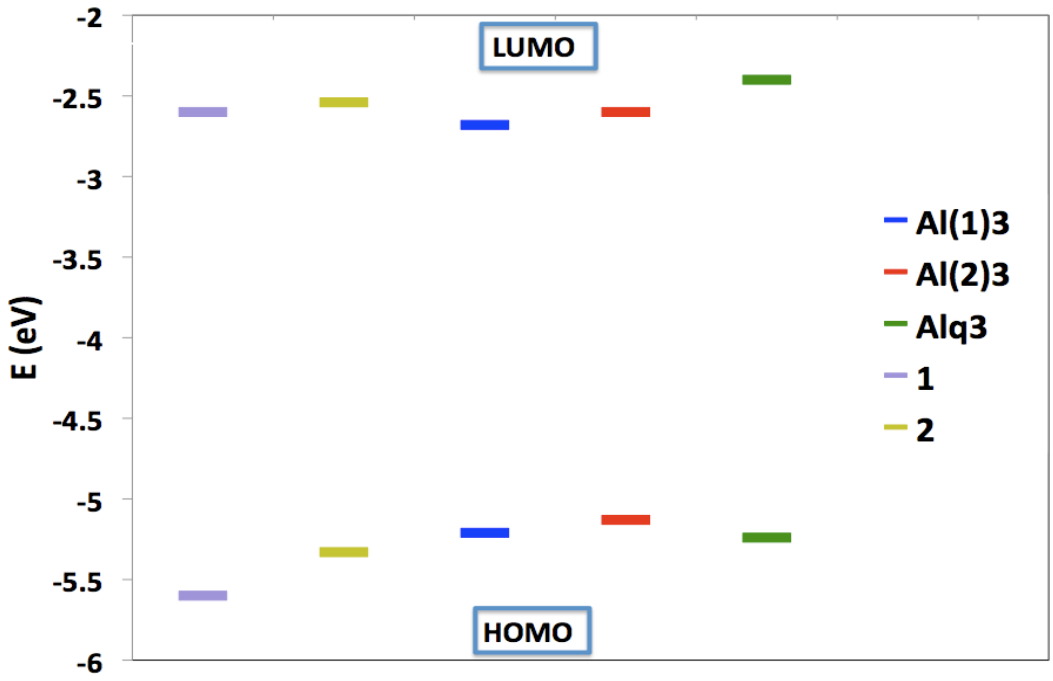

Figure S15. The HOMO-LUMO levels obtained from the CV data and UV-Vis measurements of the free ligands and their Al(III) complexes.

Table S3. HOMO and LUMO Energies of the Free Ligands.

Experimental Energy (eV)			
Compound	**Homo[a]**	**Lumo[b]**	**Band Gap[c]**
1	-5.60	-2.60	3.00
2	-5.33	-2.54	2.79

[a] Obtained from the calculated LUMO level and the HOMO-LUMO band gap. [b] From reduction values in DMF.
[c] Using the band edge of the UV-Vis spectra.

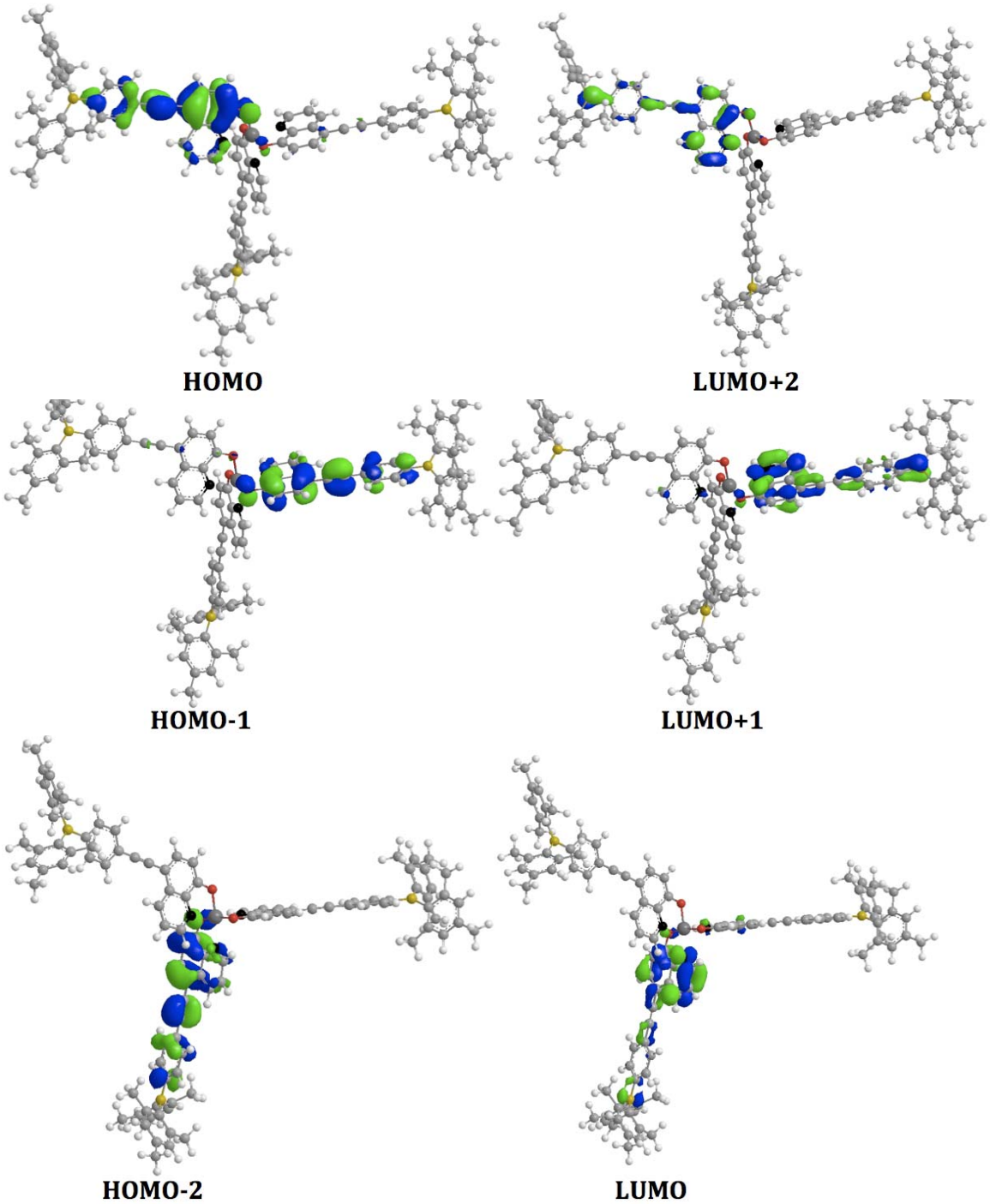

Figure S16. HOMO and LUMO frontier molecular orbitals of **Al(1)$_3$**.

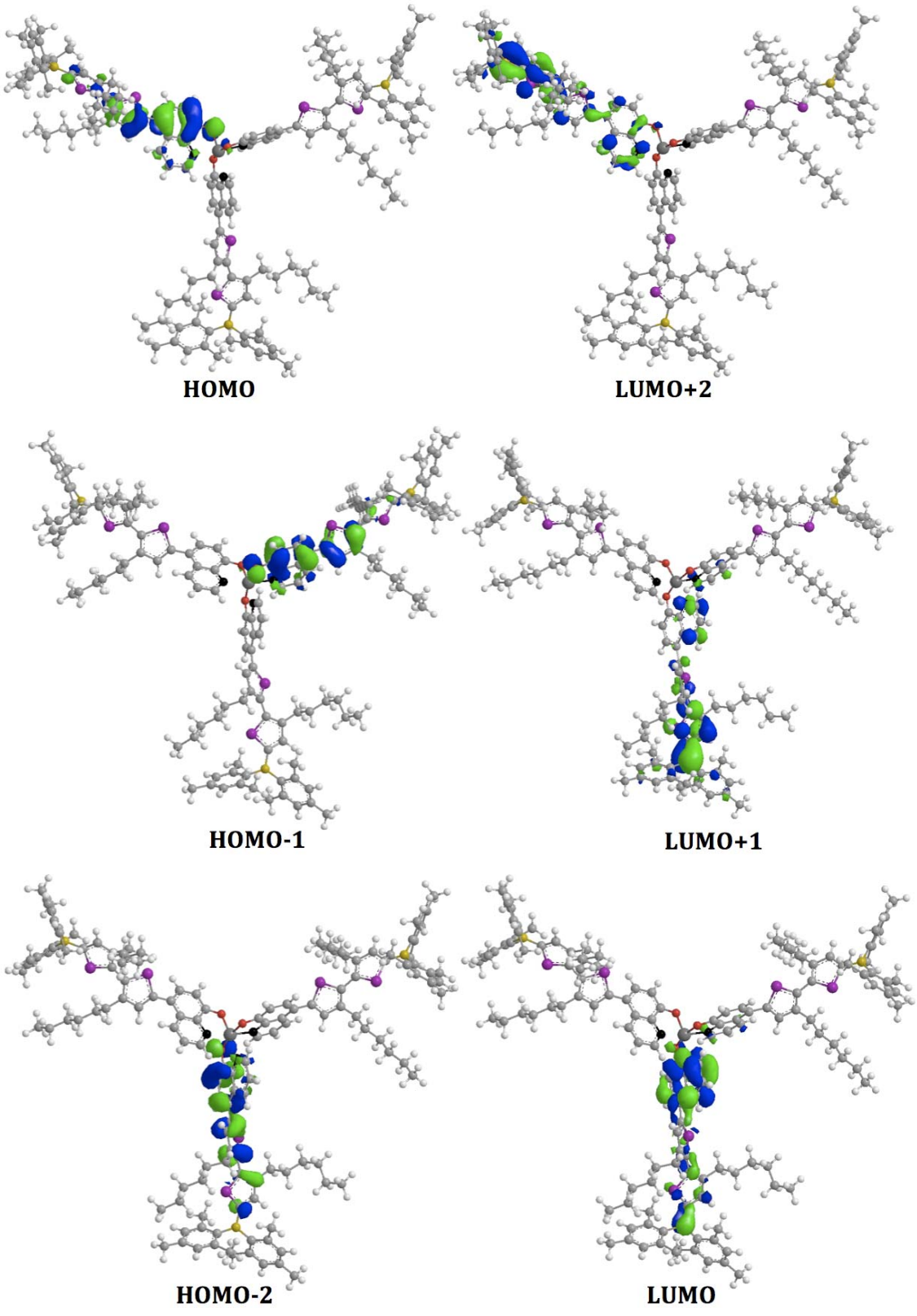

Figure S17. HOMO and LUMO frontier molecular orbitals of **Al(2)$_3$**.

Table S4. HOMO and LUMO Frontier Molecular Orbitals for $Al(1)_3$ and $Al(2)_3$.

Calculated Energy (eV)						
Compound	**HOMO-2**	**HOMO-1**	**HOMO**	**LUMO**	**LUMO+1**	**LUMO+2**
$Al(1)_3$	-5.31	-5.21	-5.06	-2.24	-2.09	-2.00
$Al(2)_3$	-5.37	-5.26	-5.05	-2.18	-2.04	-1.97

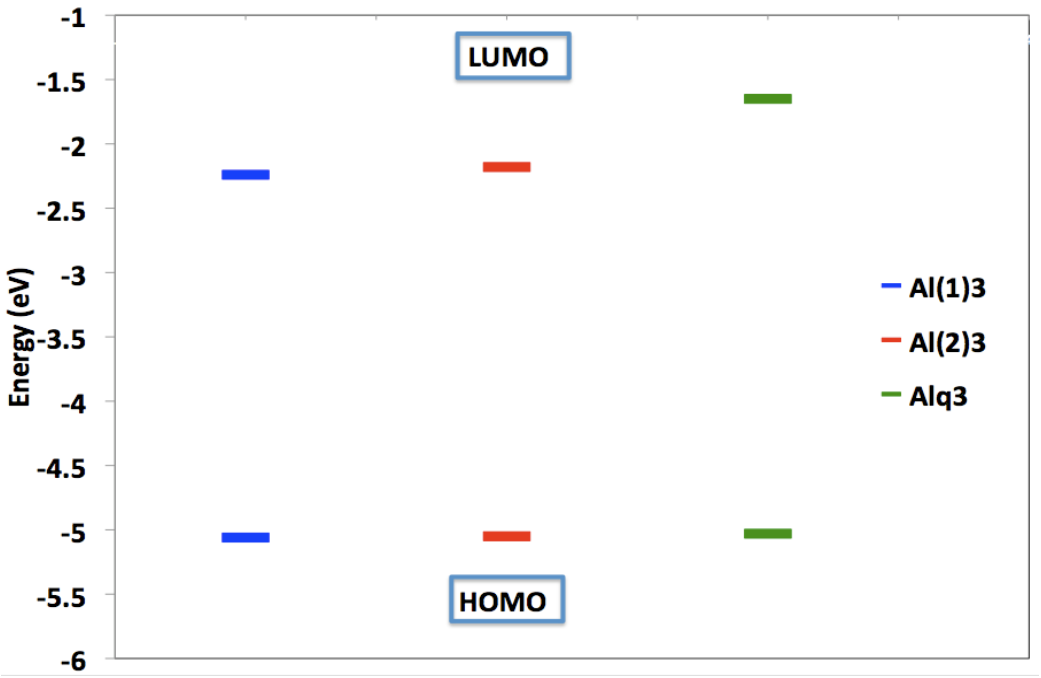

Figure S18. The HOMO-LUMO levels obtained from DFT calculations (B3LYP 6-31G*) for the Al(III) complexes—the calculated energy levels for Alq_3 were obtained from literature.[S6]

Titration of Alq_3 with TBAF and TEACN

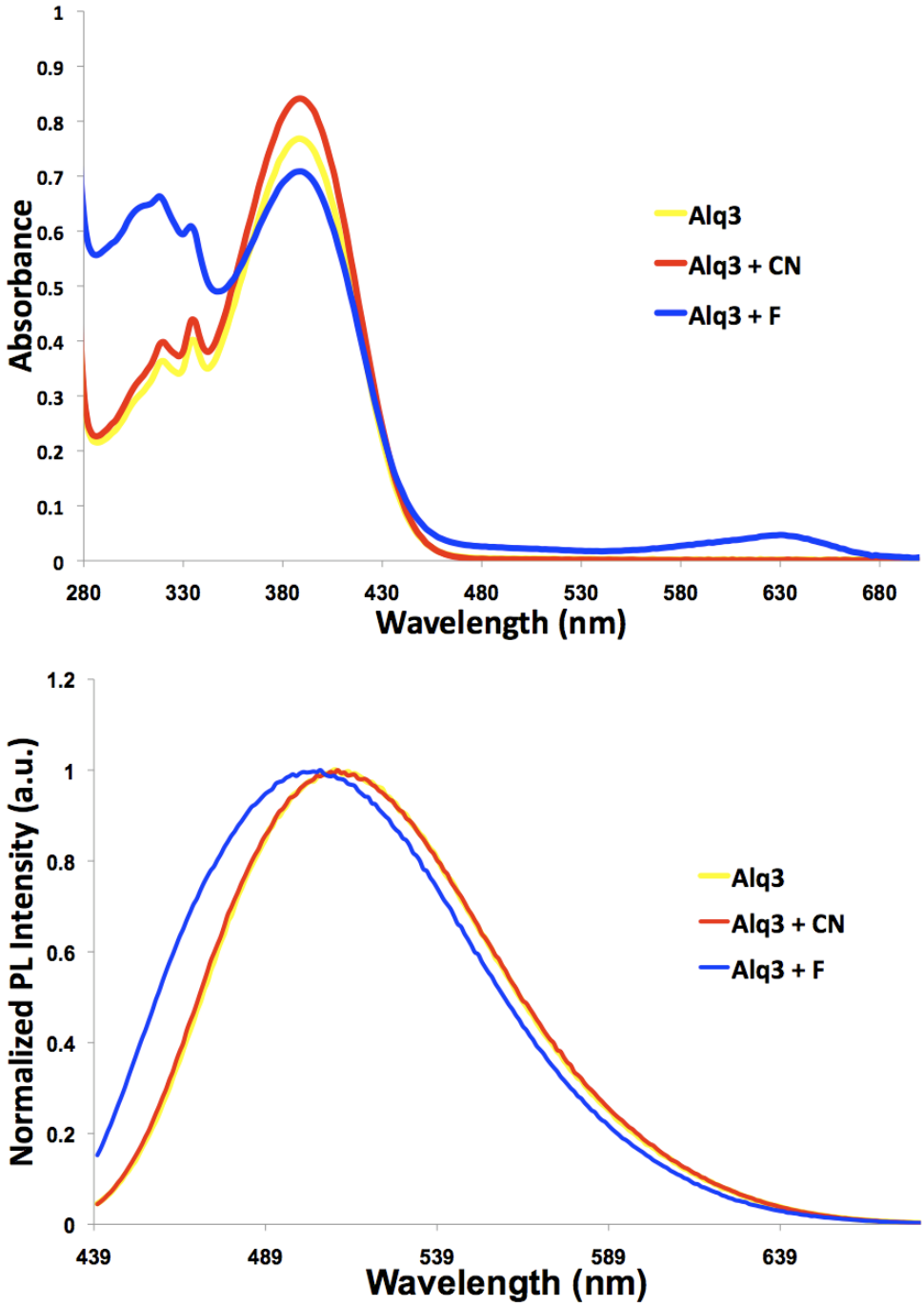

Figure S19. The UV (top) and fluorescent (bottom, λ_{ex} = 420nm) spectra of Alq_3 after the addition of either tetraethylammonium cyanide or tetrabutylammonium fluoride in CH_2Cl_2 at 298K.

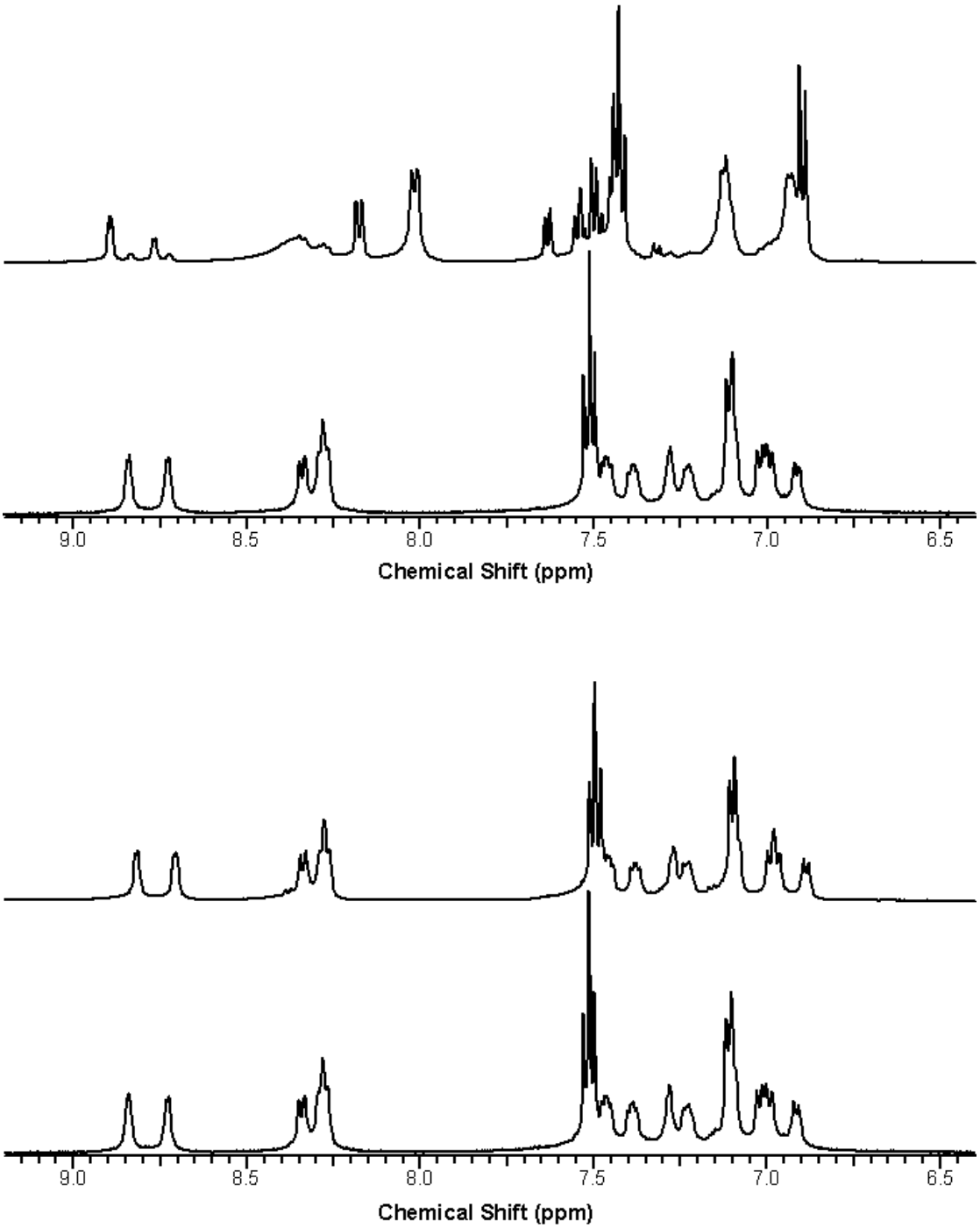

Figure S20. ^{1}H NMR spectral change of Alq_3 titrated with excess tetrabutylammonium fluoride (top) and tetraethylammonium cyanide (bottom) in CD_2Cl_2.

References

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