Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Charge-Separation in Panchromatic, Vertically Positioned Bis(donorstyryl)BODIPY – Aluminum(III) Porphyrin – Fullerene Supramolecular Triads

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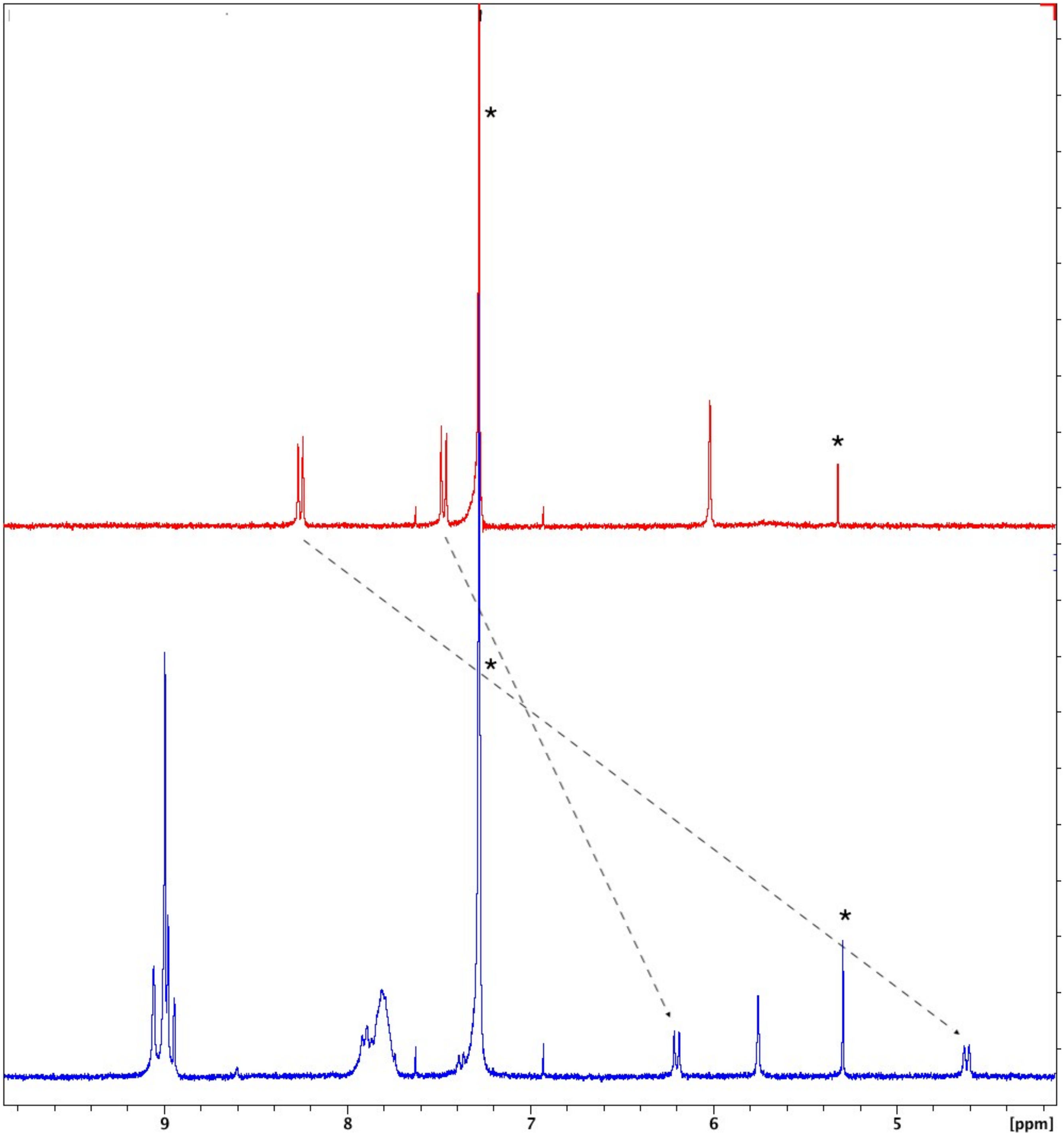

Figure S1. ^{1}H NMR spectra of (a) BDP-COOH and (b) BDP-AlPorF$_3$ in CDCl$_3$. Note: *Peaks represent solvent peaks or solvent impurities.

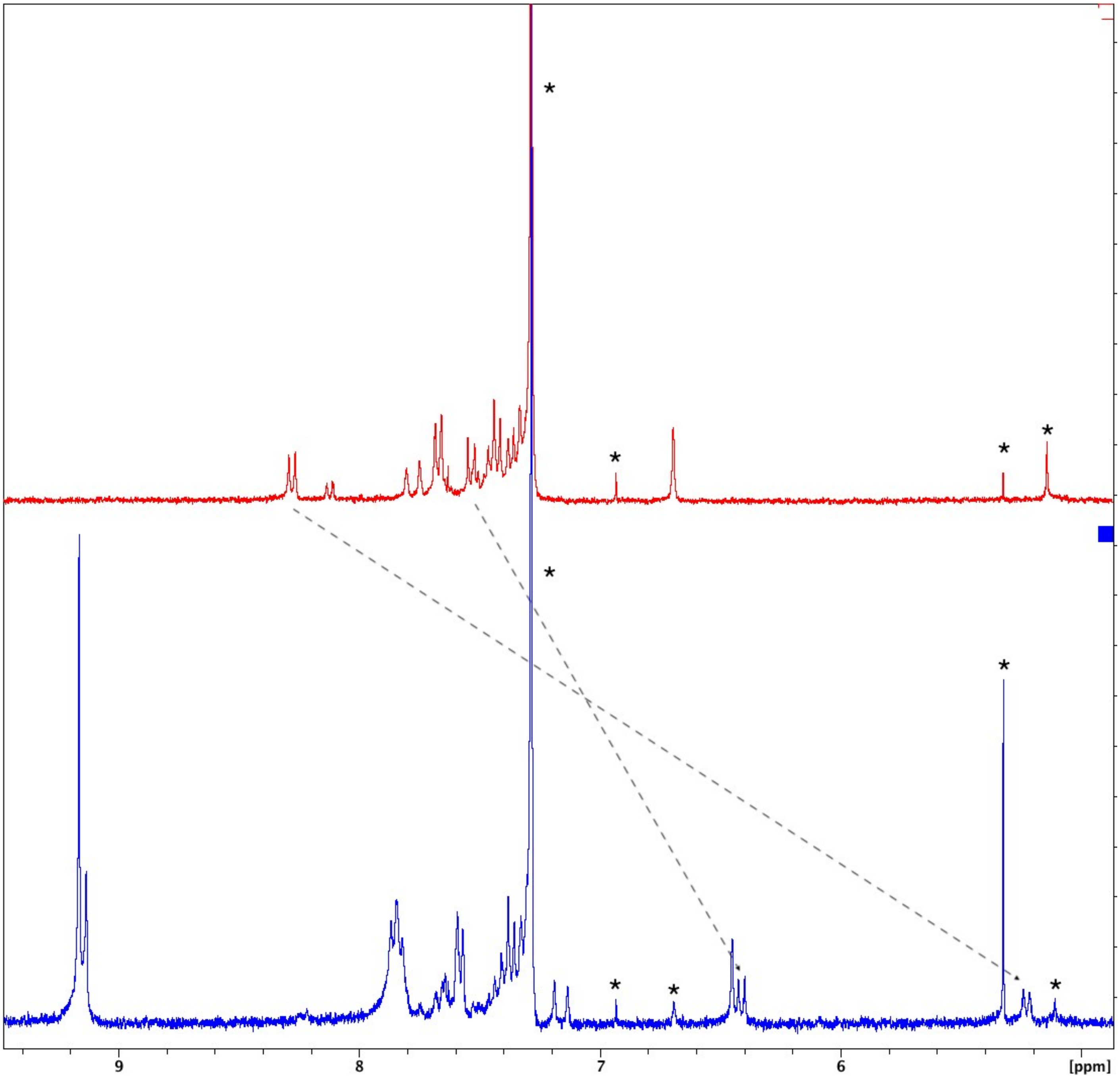

Figure S2. ^{1}H NMR spectra of (a) Ph$_2$-BDP-COOH and (b) Ph$_2$-BDP-AlPorF$_3$ in CDCl$_3$. Note: *Peaks represent solvent peaks or solvent impurities.

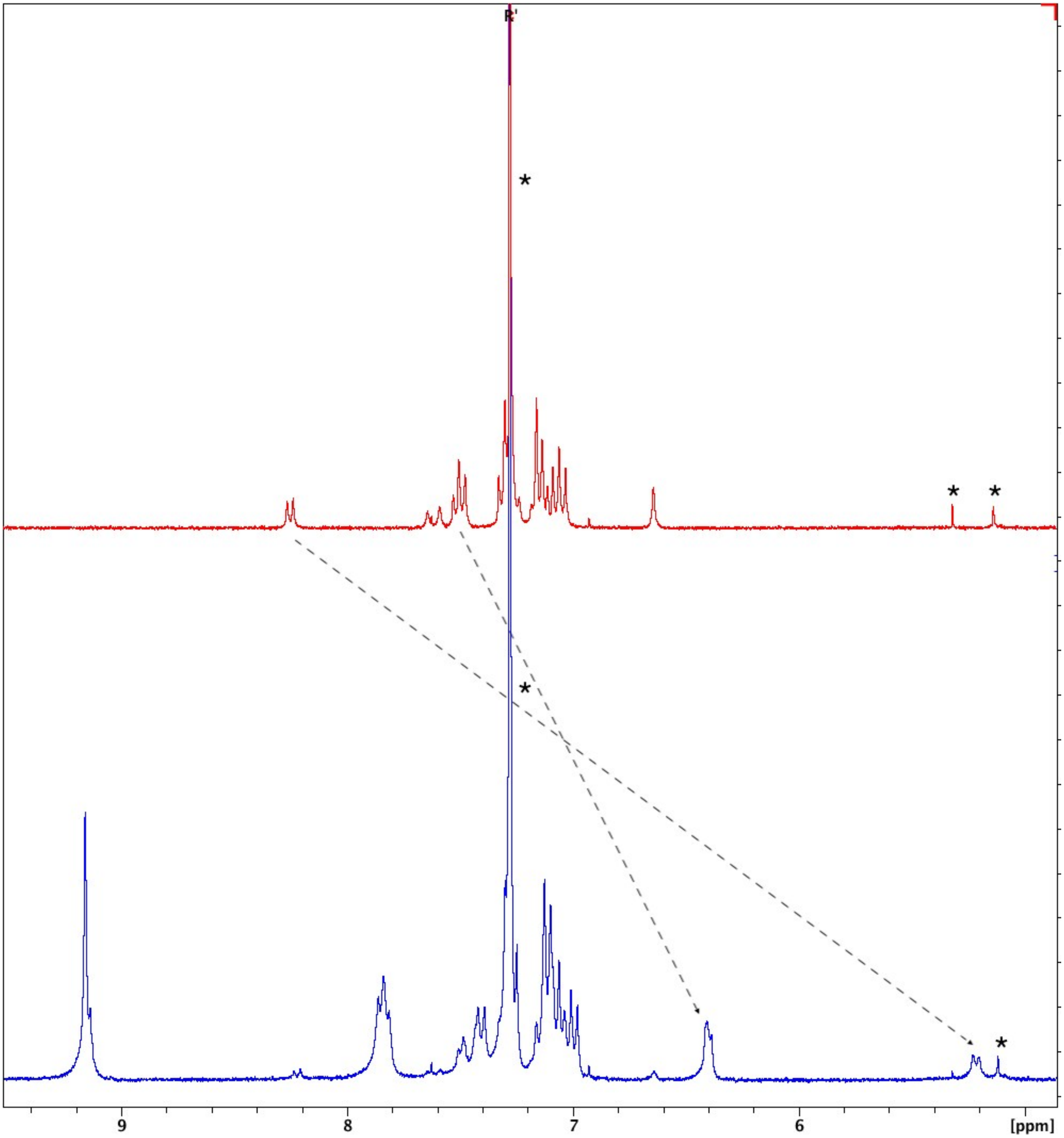

Figure S3. ^{1}H NMR spectra of (a) TPA$_2$-BDP-COOH and (b) TPA$_2$-BDP-AlPorF$_3$ in CDCl$_3$. Note: *Peaks represent solvent peaks or solvent impurities.

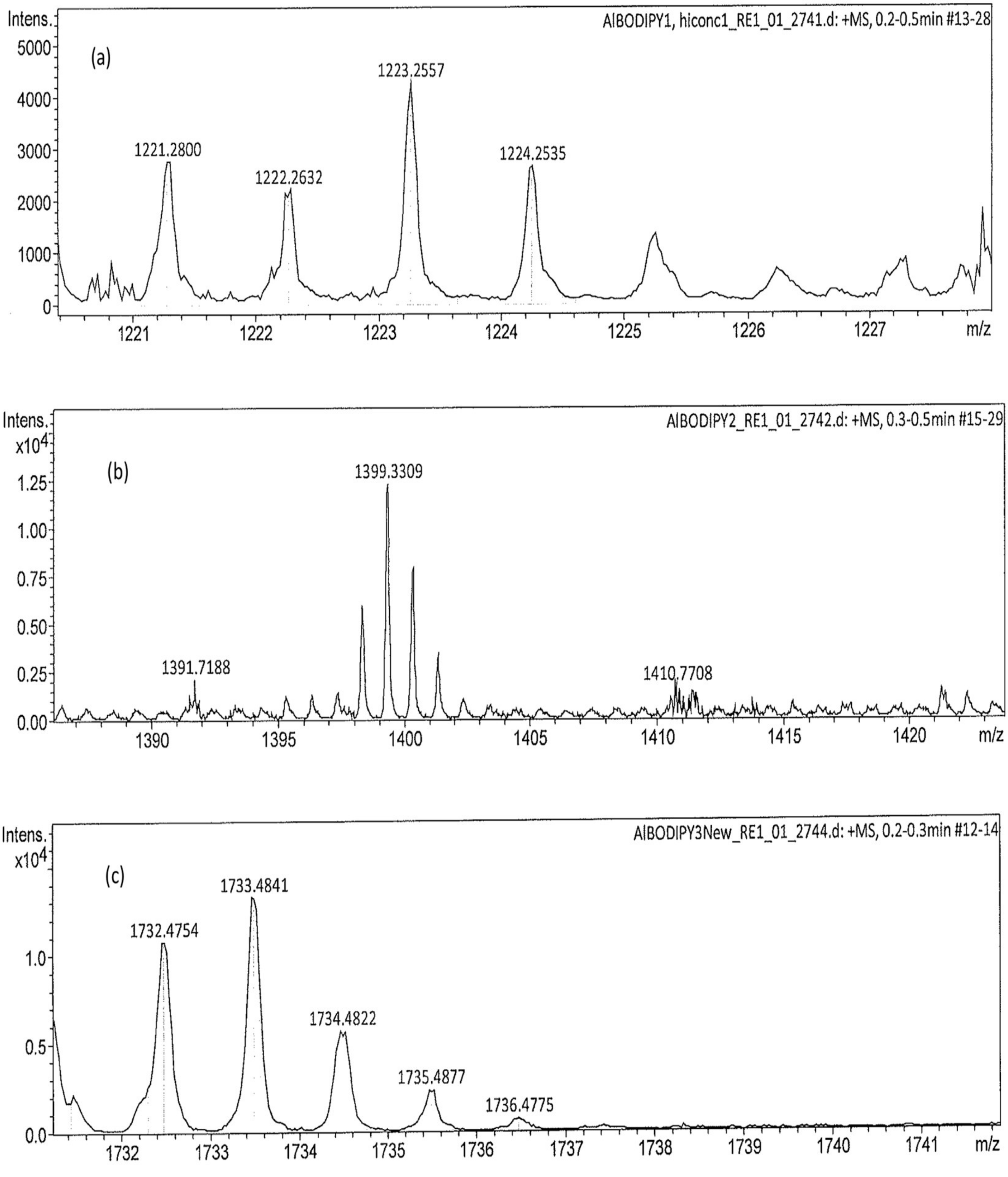

Figure S4. ESI high resolution mass spectra of (a) BDP-AlPorF$_3$ and (b) Ph$_2$-BDP-AlPorF$_3$ and (c) TPA$_2$-BDP-AlPorF$_3$.

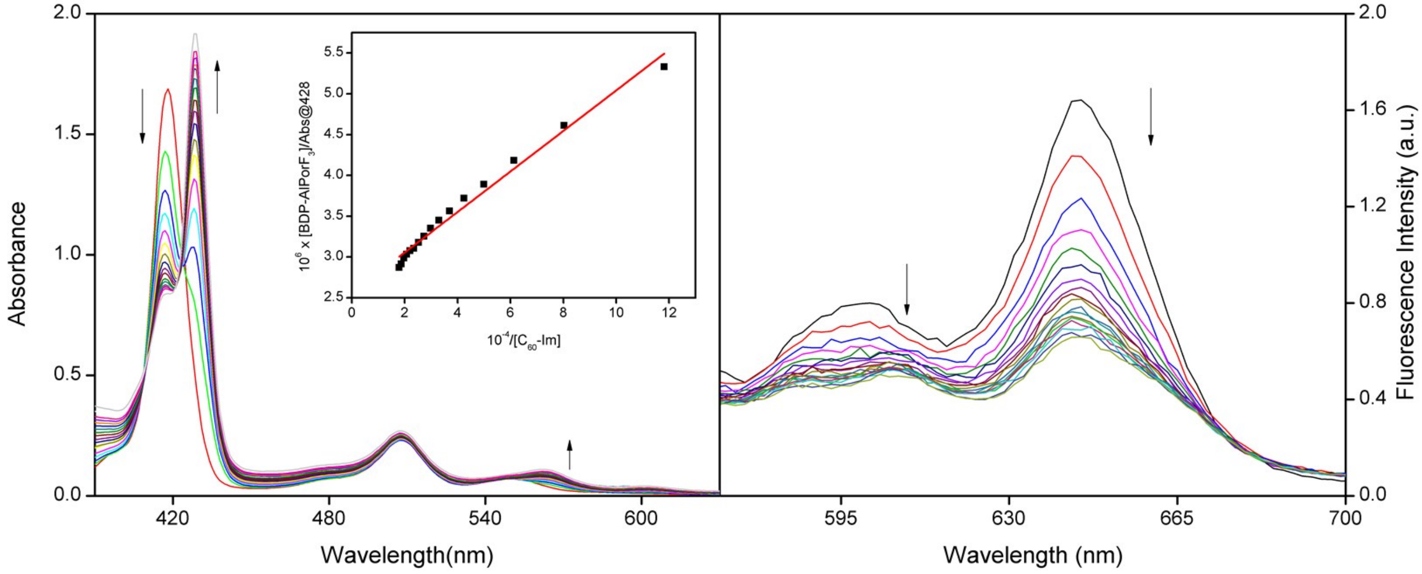

Figure S5. (a) Absorption and (b) fluorescence titrations of BDP-AlPorF$_3$ *vs* C$_{60}$-Im in *o*-DCB. The inset shows the Benesi–Hildebrand plot of the absorbance change at 429 nm. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. In titrations C$_{60}$-Im was added up to 4.31 × 10^{-6} M in 20 μl (2.20 × 10^{-4} M) increments to a 1 ml (5.5 × 10^{-6} M) solution of BDP-AlPorF$_3$.

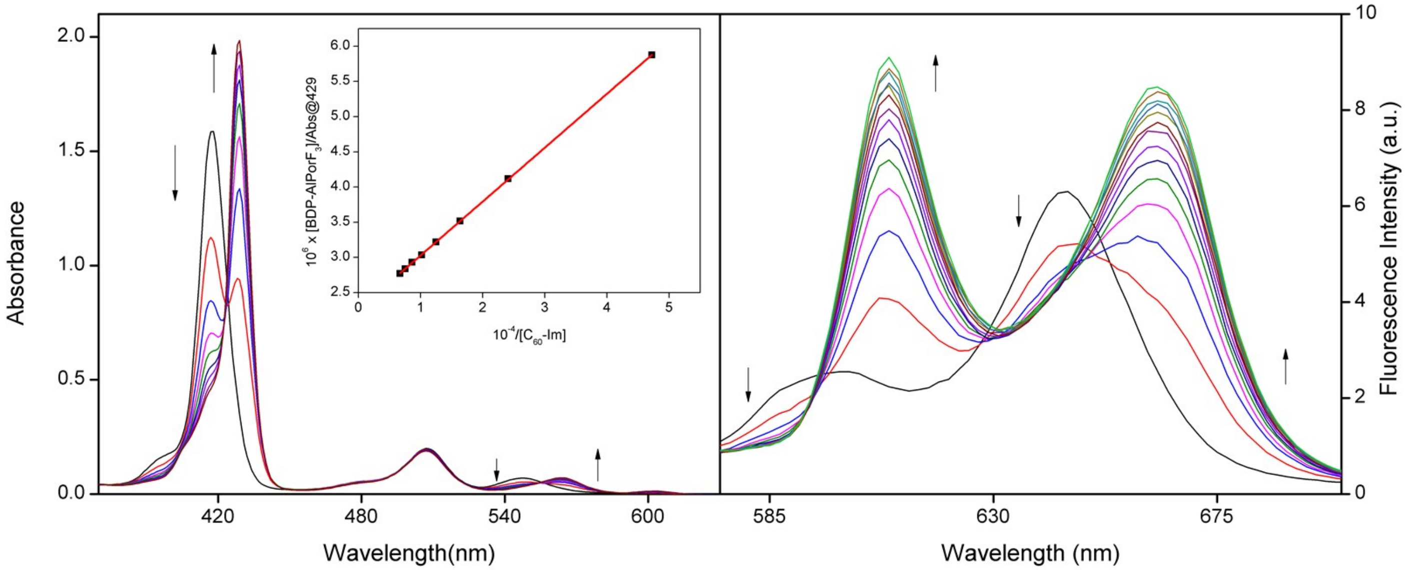

Figure S6. (a) Absorption and (b) fluorescence titrations of (BDP)-AlPorF$_3$ *vs* Me-Im in *o*-DCB. The inset shows the Benesi–Hildebrand plot of the absorbance change at 429 nm. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. In titrations Me-Im was added up to 2.12 × 10^{-6} M in 20 μl (1.08 × 10^{-4} M) increments to a 1 ml (5.5 × 10^{-6} M) solution of BDP-AlPorF$_3$.

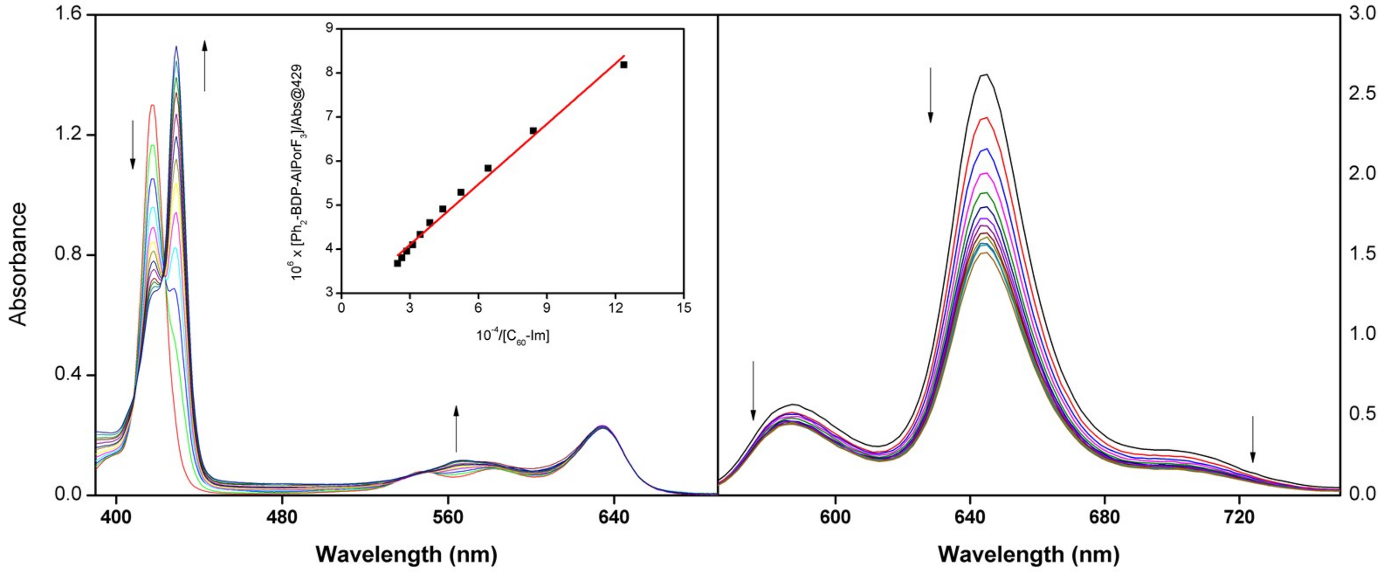

Figure S7. (a) Absorption and (b) fluorescence titrations of Ph_2-BDP-AlPorF$_3$ *vs* C_{60}-Im in *o*-DCB. The inset shows the Benesi–Hildebrand plot of the absorbance change at 429 nm. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. In titrations C_{60}-Im was added up to 4.12×10^{-6} M in 20 µl (2.1×10^{-4} M) increments to a 1 ml (5.5×10^{-6} M) solution of Ph_2-BDP-AlPorF$_3$.

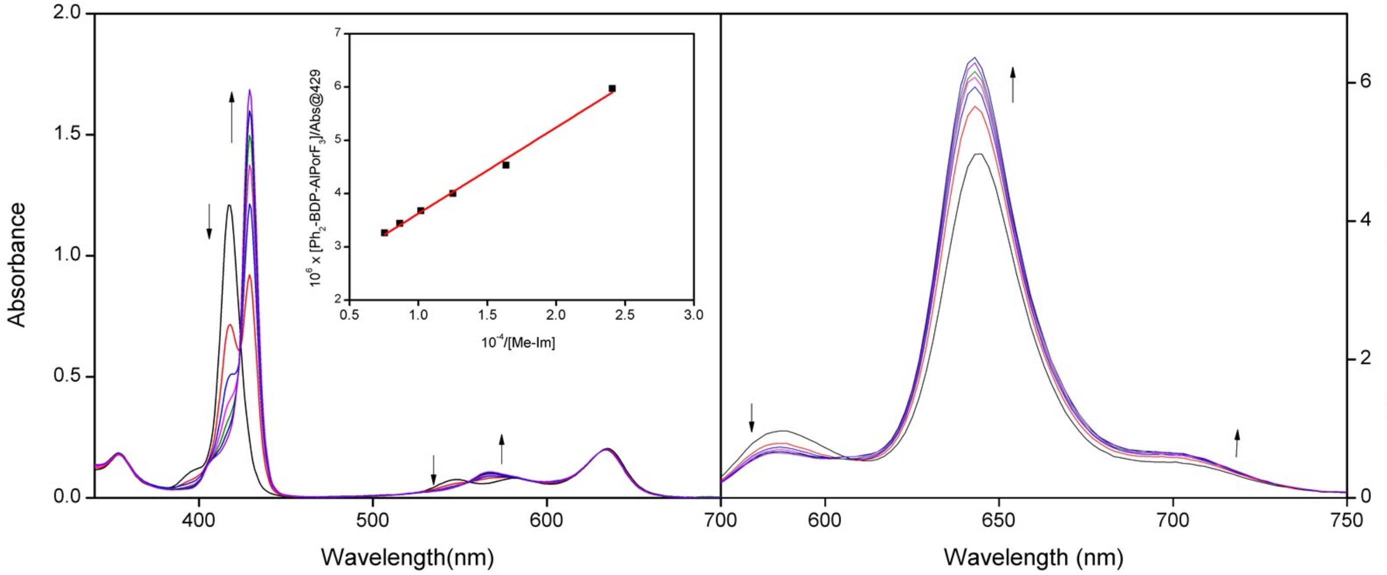

Figure S8. (a) Absorption and (b) fluorescence titrations of Ph_2-BDP-AlPorF$_3$ *vs* Me-Im in o-DCB. The inset shows the Benesi–Hildebrand plot of the absorbance change at 429 nm. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. In titrations Me-Im was added up to 2.12×10^{-6} M in 20 µl (1.08×10^{-4} M) increments to a 1 ml (5.5×10^{-6} M) solution of Ph_2-BDP-AlPorF$_3$.

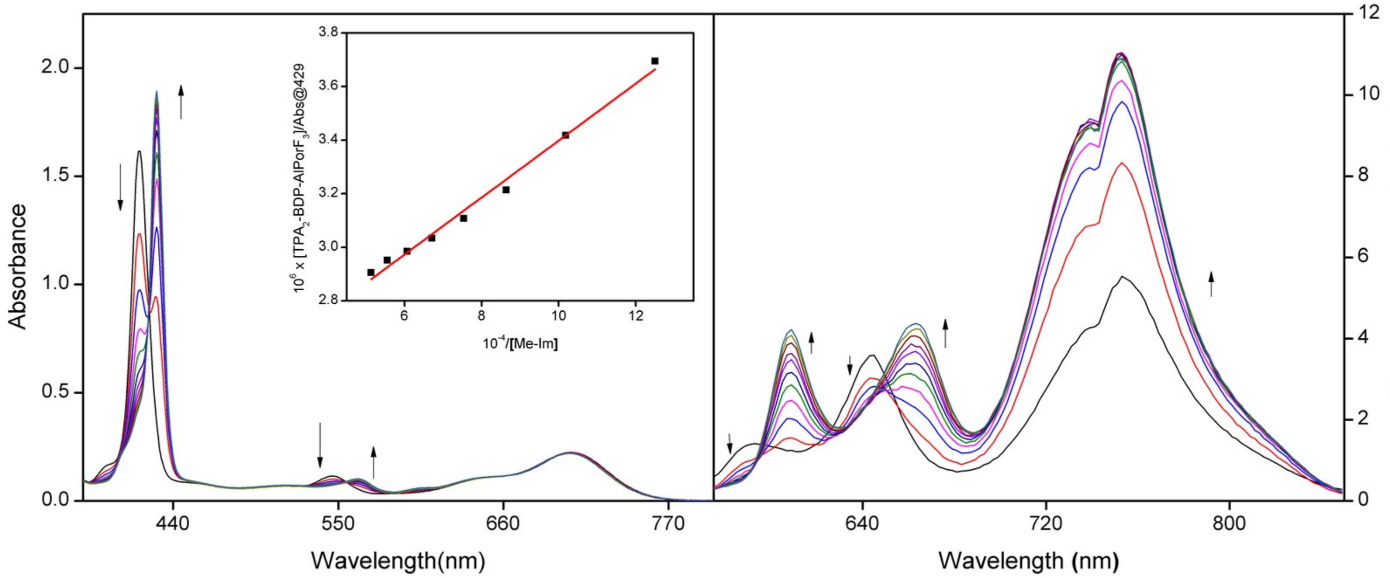

Figure S9. (a) Absorption and (b) fluorescence titrations of TPA$_2$-BDP-AlPorF$_3$ *vs* Me-Im in *o*-DCB. The inset shows the Benesi–Hildebrand plot of the absorbance change at 429 nm. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. In titrations Me-Im was added up to 5.5×10^{-6} M in 20 µl (1.08×10^{-4} M) increments to a 1 ml (5.5×10^{-6} M) solution of TPA$_2$-BDP-AlPorF$_3$.

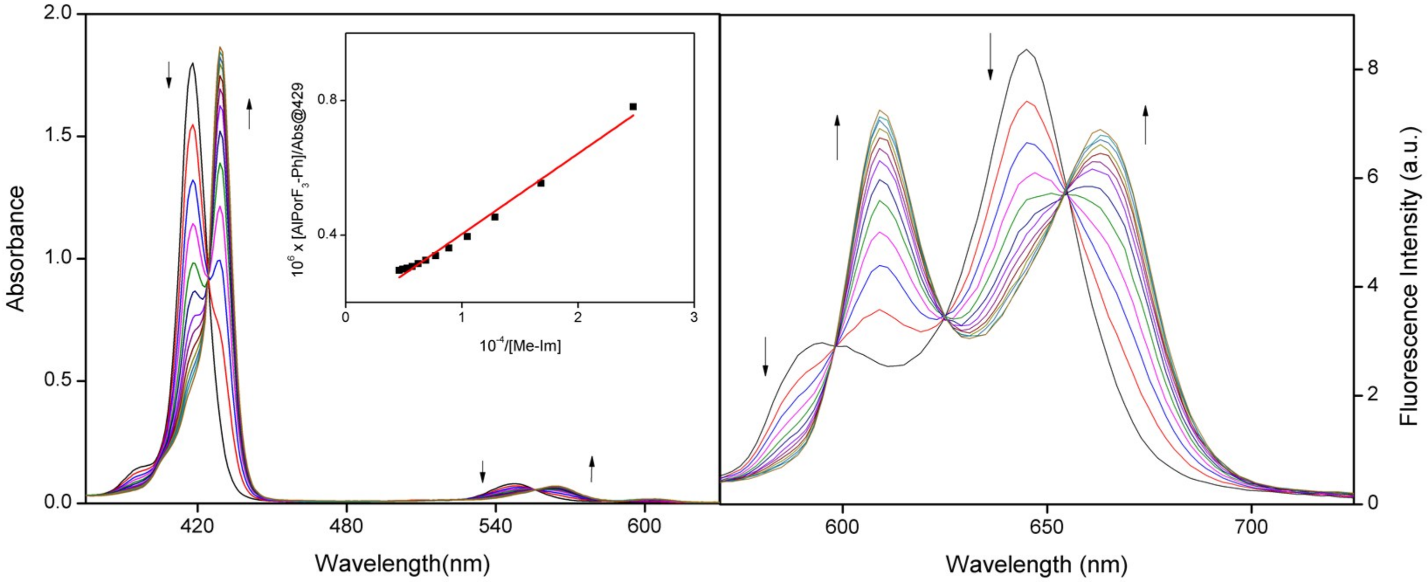

Figure S10. (a) Absorption and (b) fluorescence titrations of AlPorF$_3$-Ph *vs* Me-Im in *o*-DCB. The inset shows the Benesi–Hildebrand plot of the absorbance change at 429 nm. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. In titrations Me-Im was added up to 2.05×10^{-6} M in 20 µl (1.05×10^{-4} M) increments to a 1 ml (5.5×10^{-6} M) solution of AlPorF$_3$-Ph.

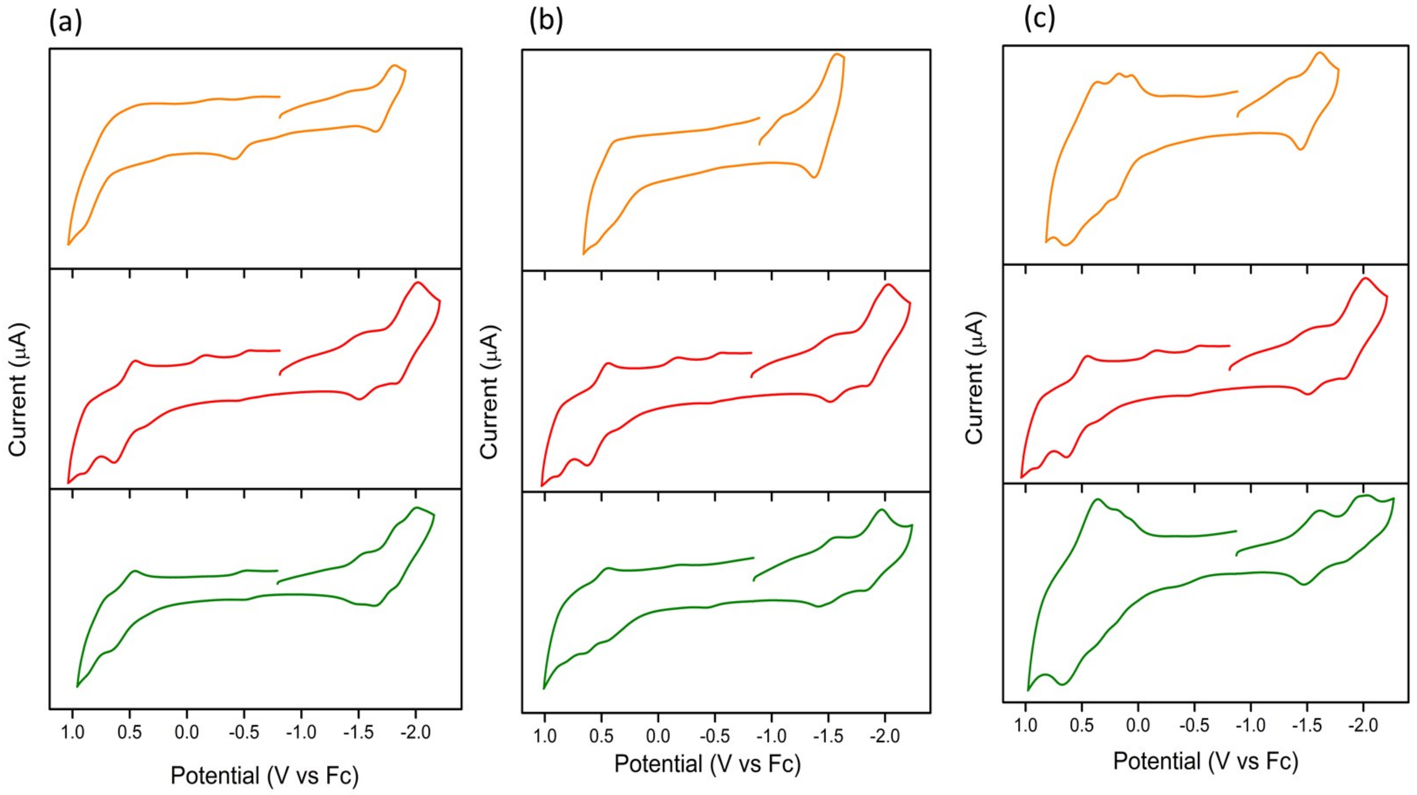

Figure S11. Cyclic voltammograms of (a) BDP-COOH (orange), AlPorF$_3$-Ph (red) and BDP-AlPorF$_3$ (green), (b) Ph$_2$-BDP-COOH (orange), AlPorF$_3$-Ph (red) and Ph$_2$-BDP-AlPorF$_3$ (green) and (c) TPA$_2$-BDP-COOH (orange), AlPorF$_3$-Ph (red) and TPA$_2$-BDP-AlPorF$_3$ (green) in *o*-DCB containing 0.1 M TBA.ClO$_4$. Scan rate = 100 mV/s.

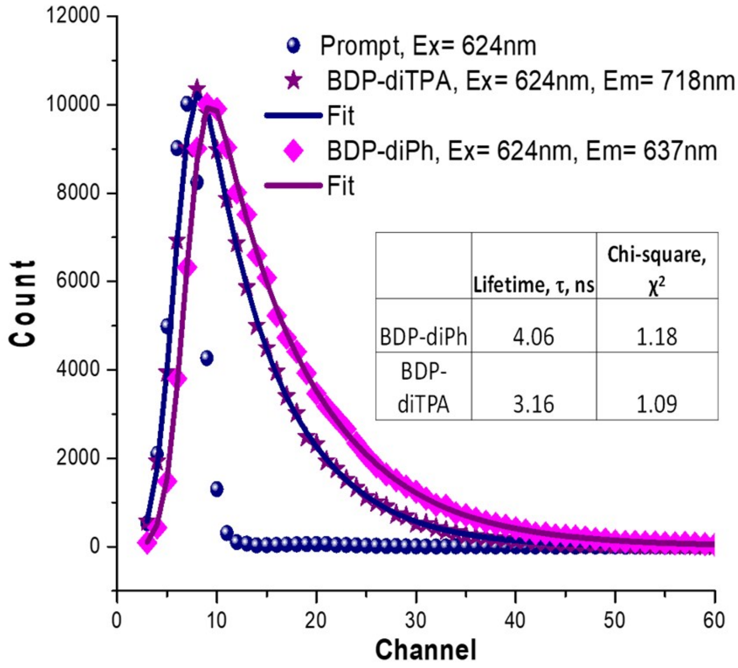

Figure S12. Fluorescence decay curves of representative BDP derivatives in toluene.

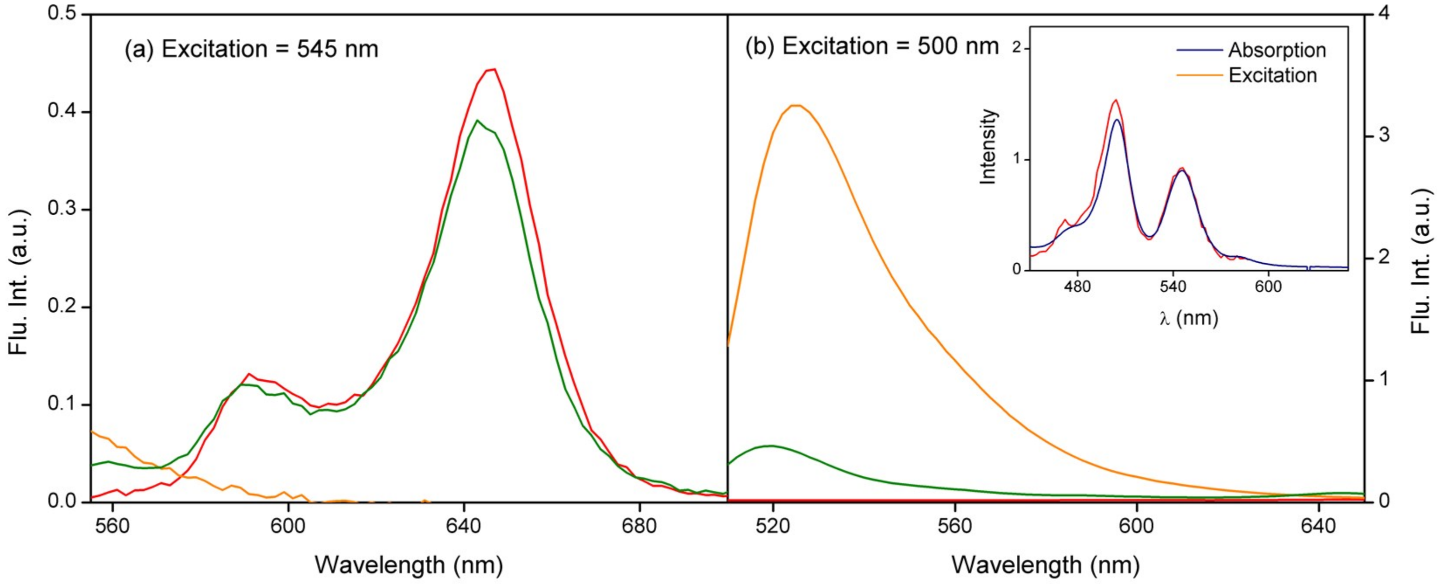

Figure S13. Steady-state fluorescence spectra of dyad BDP-AlPorF$_3$ in toluene: (a) & (b) BDP-AlPorF$_3$ (green), AlPorF$_3$-Ph (red) and BDP-COOH (orange). Inset: Absorption (blue) and corrected fluorescence excitation (red) spectra of dyad in toluene. The spectra were normalized between 525 and 575 nm. The excitation spectrum was collected at 660 nm corresponding to the emission of AlPorF$_3$.

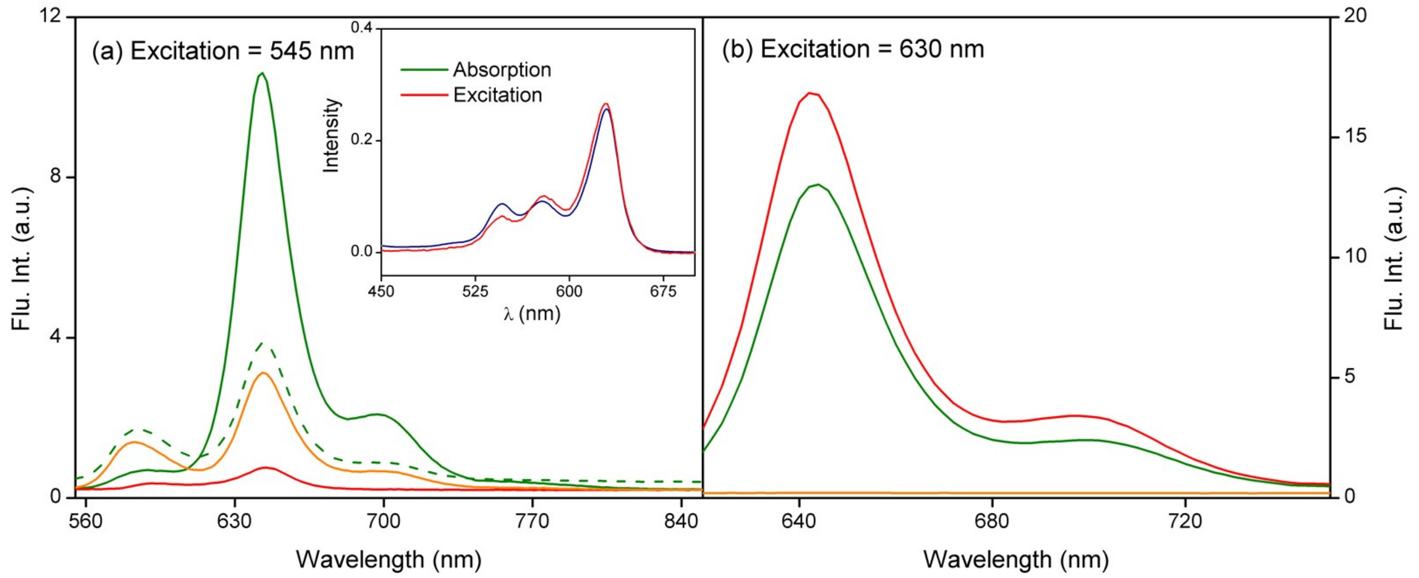

Figure S14. Steady-state fluorescence spectra of dyad Ph$_2$-BDP-AlPorF$_3$ in toluene: (a) & (b) Ph$_2$-BDP-AlPorF$_3$ (green), calculated mixture of AlPorF$_3$-Ph and Ph$_2$-BDP-COOH (dotted green), AlPorF$_3$-Ph (red) and Ph$_2$-BDP-COOH (orange). Absorption (blue) and corrected fluorescence excitation (red) spectra of (c) Ph$_2$-BDP-AlPorF$_3$ and (d) Ph$_2$-BDP-AlPorF$_3$✐Im-Me in toluene. The spectra were normalized between 600 and 675 nm. The excitation spectrum was collected at 710 nm corresponding to the emission of Ph$_2$-BDP.

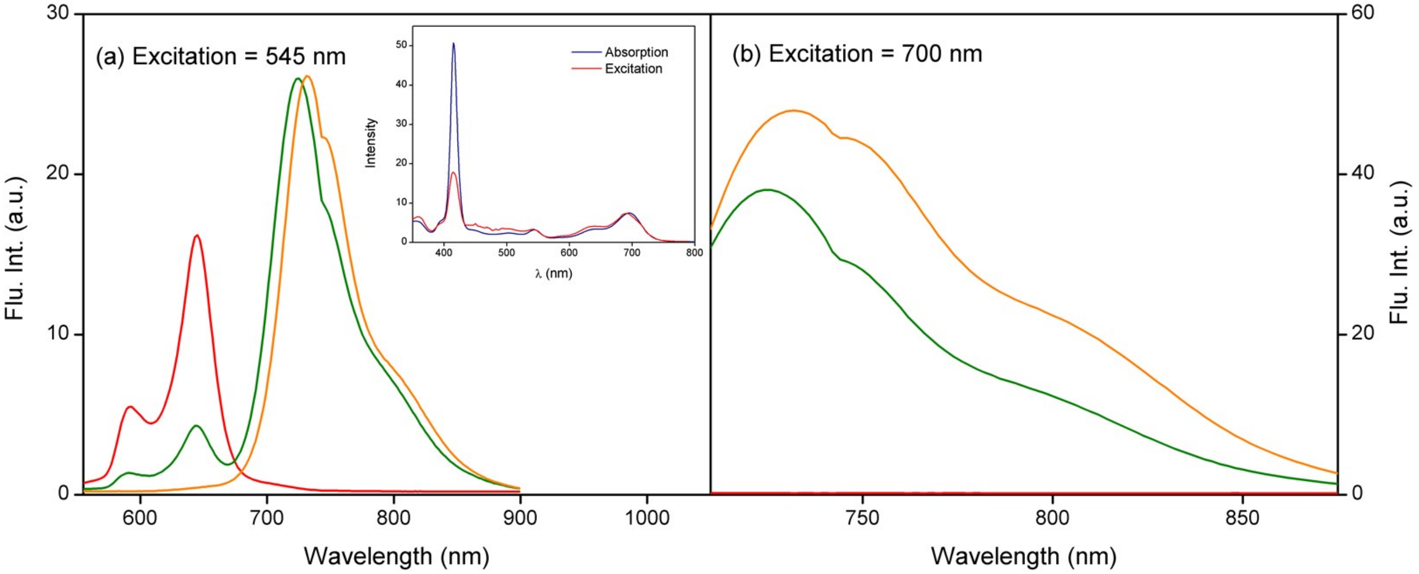

Figure S15. Steady-state fluorescence spectra of dyad TPA$_2$-BDP-AlPorF$_3$ in toluene: (a) & (b) TPA$_2$-BDP-AlPorF$_3$ (green), AlPorF$_3$-Ph (red) and TPA$_2$-BDP-COOH (orange). Inset: Absorption (blue) and corrected fluorescence excitation (red) spectra of (c) Ph$_2$-BDP-AlPorF$_3$ in toluene. The spectra were normalized between 650 and 800 nm.

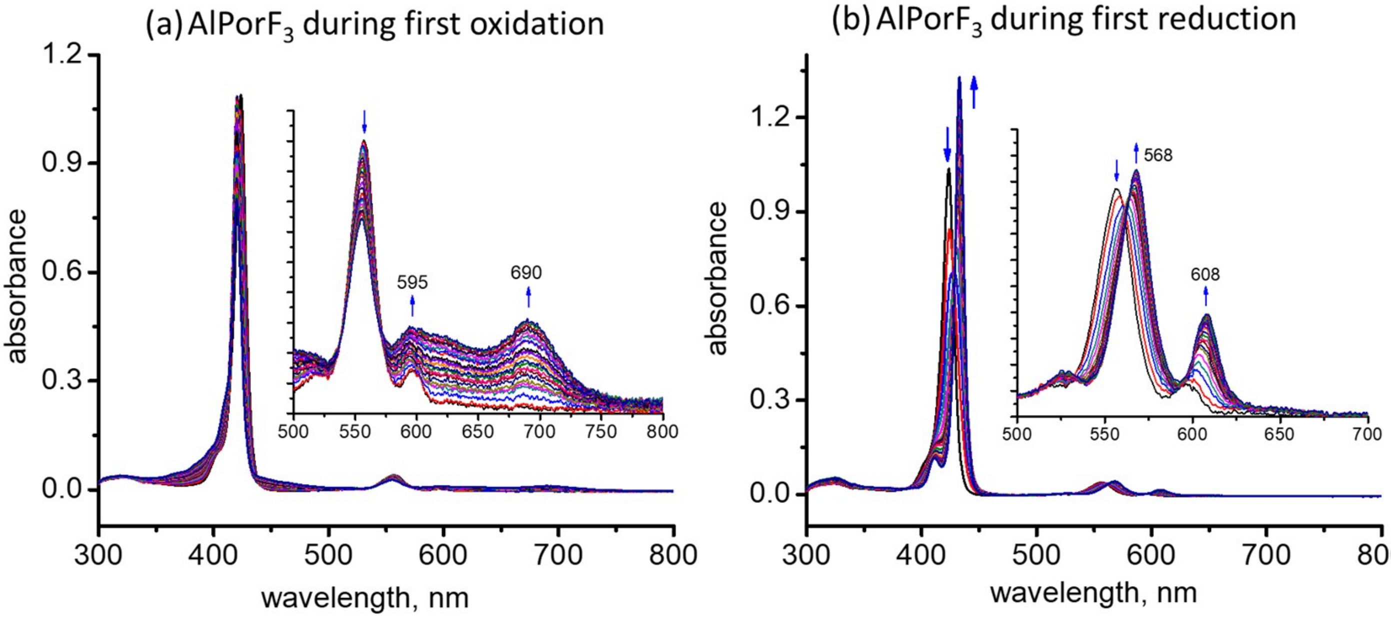

Figure 16. Spectral changes observed during (a) first oxidation and (b) first reduction of AlPorF$_3$ in *o*-DCB containing 0.2 M (TBA)ClO$_4$.

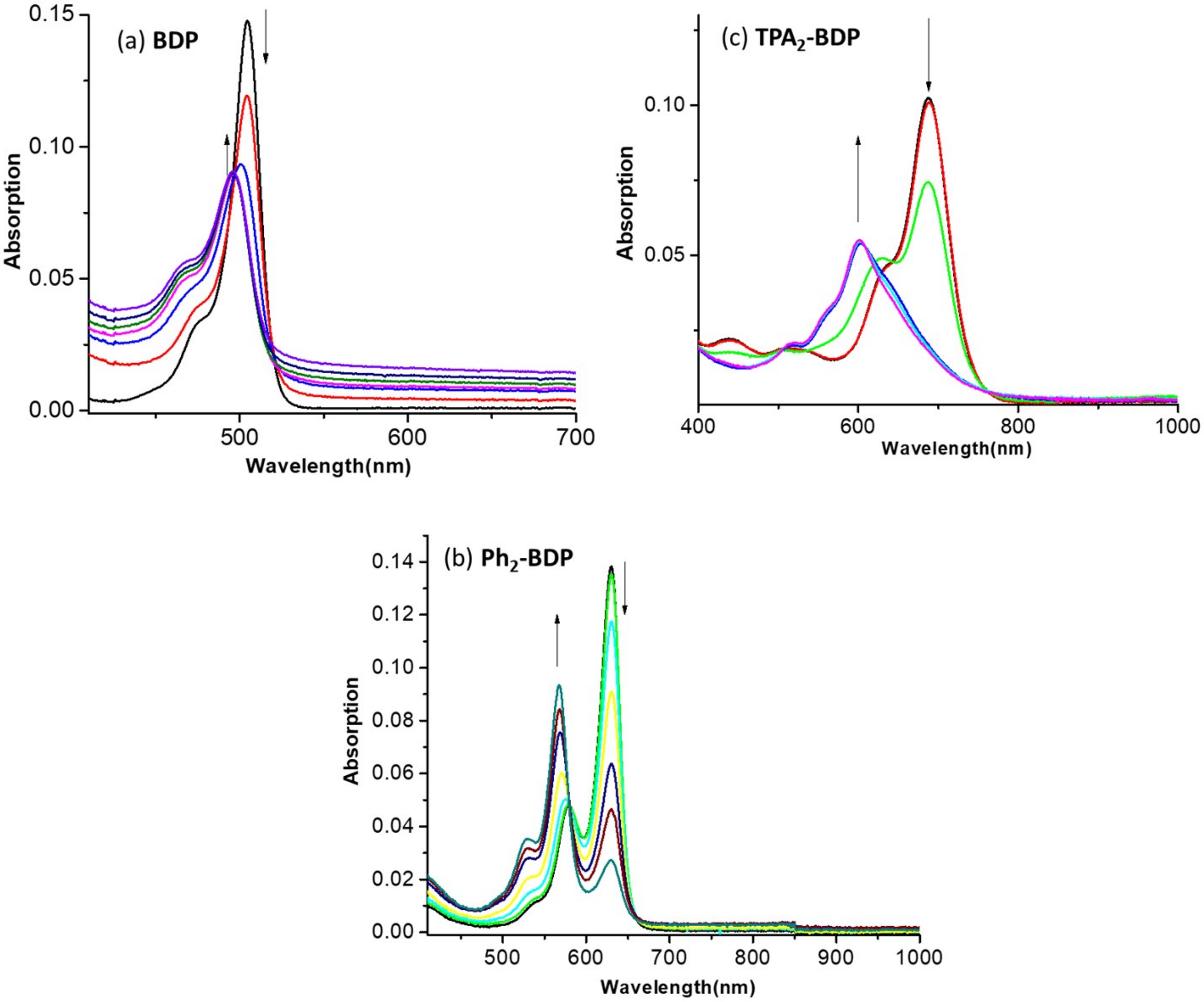

Figure S17. Spectral changes observed during chemical oxidation of (a) BDP, (b) Ph$_2$-BDP and (c) TPA$_2$-BDP in *o*-DCB. NOBF$_4$ was used as an oxidizing agent.

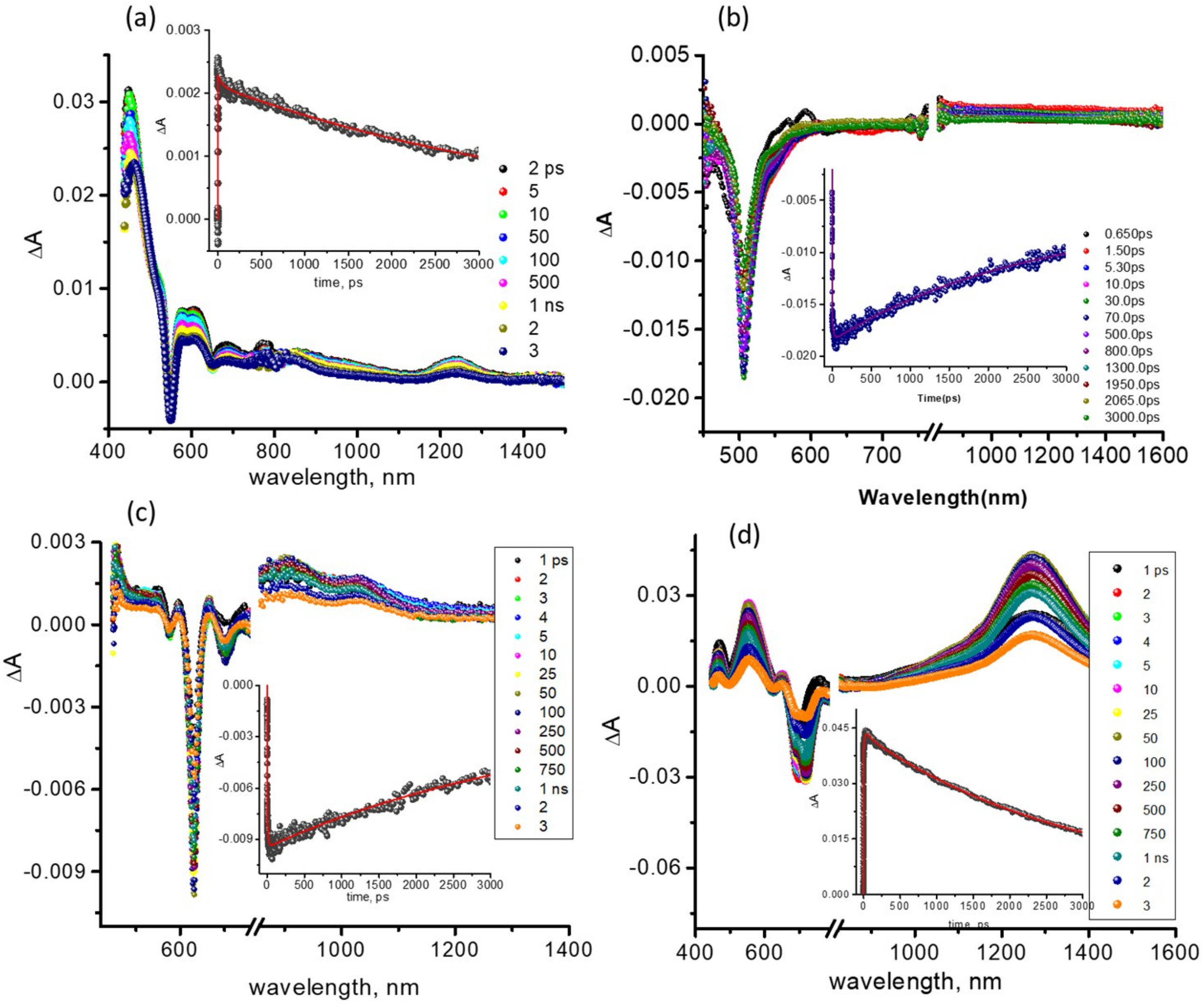

Figure S18. Femtosecond transient spectra of (a) AlPorF$_3$-Ph at the excitation wavelength of 550 nm (inset time profile of 1230 nm), (b) BDP at the excitation wavelength of 500 nm (inset: time profile of 505 nm), (c) (Ph)$_2$-BDP at the excitation wavelength of 555 nm (inset: time profile of the 630 peak), and (d) (TPA)$_2$-BDP at the excitation wavelength of 685 nm (inset: time profile of the 1280 nm). All spectra were recorded in toluene.

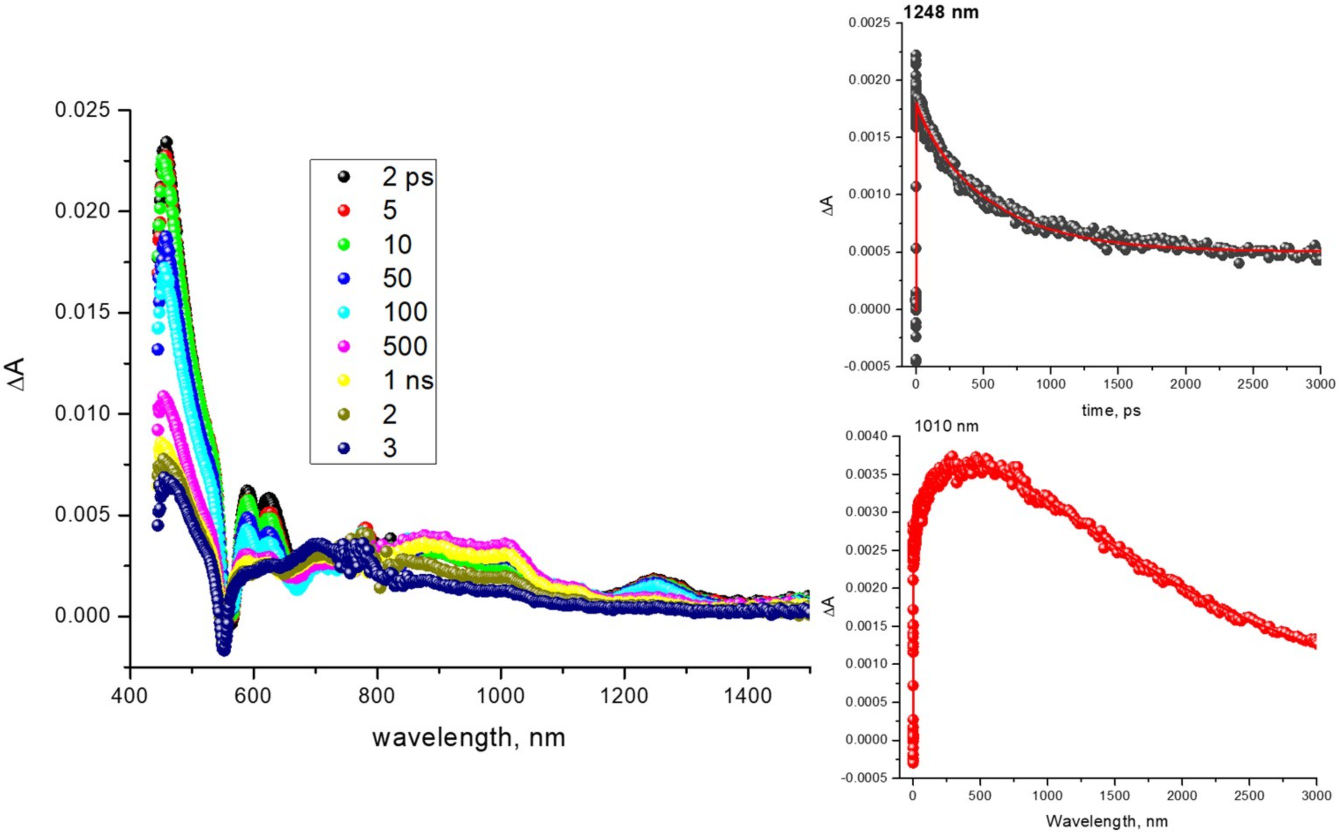

Figure S19. Femtosecond transient spectra at the indicated delay times of Ph-AlPorF$_3$←Im-C$_{60}$ dyad in toluene at the excitation wavelength of 550 nm. The time profile of 1250 and 1010 nm peaks are shown in the right-hand panel.