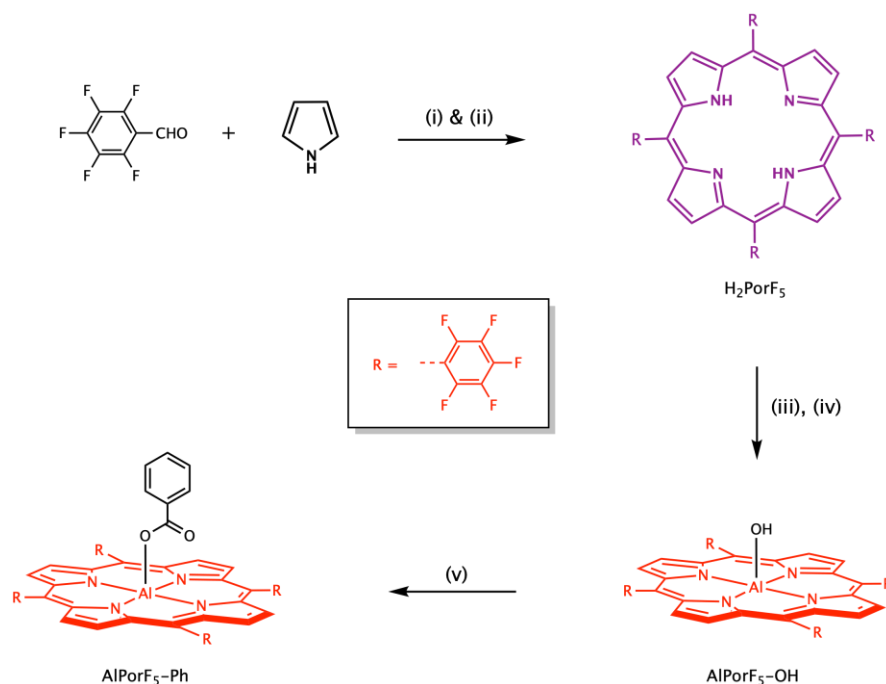


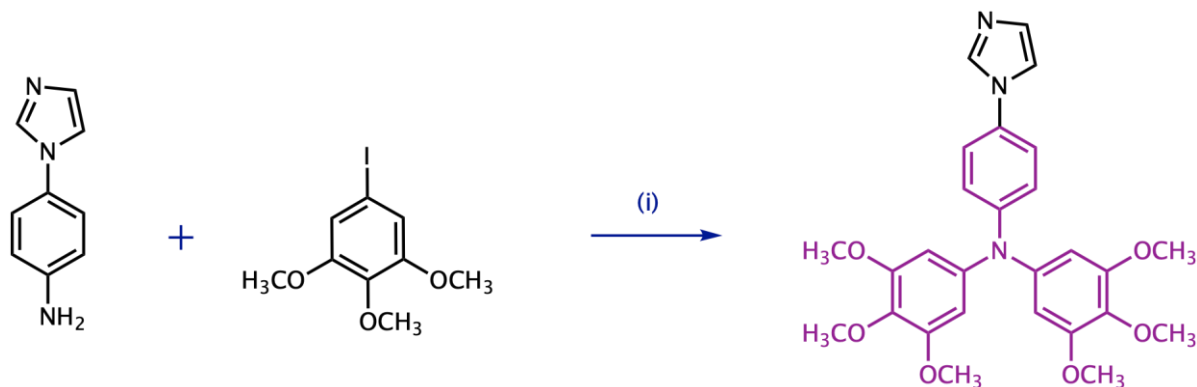
Decelerating Charge Recombination Using Fluorinated Porphyrins in *N,N*-bis(3,4,5-trimethoxyphenyl)aniline – Aluminum(III) Porphyrin – Fullerene Reaction Center Models

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Scheme S1. Synthesis of H_2PorF_5 , $\text{AlPorF}_5\text{-OH}$ and $\text{AlPorF}_5\text{-Ph}$. Reaction conditions: (i) $\text{BF}_3\cdot\text{Et}_2\text{O}$, dry dichloromethane, stirring at room temperature under nitrogen for 4-18 h, (ii) *p*-chloranil, stirring at room temperature under nitrogen for 12 h, (iii) AlMe_3 , dry toluene, stirring at room temperature under nitrogen for 1-5 days, (iv) H_2O , stirring at room temperature for 24 h, (v) Ph-COOH , dichloromethane and methanol, stirring at room temperature under nitrogen for 12h.



Scheme S2. Synthesis of BTMPA-Im. Reaction conditions: 1,10-phenanthroline, CuI , KOH , dry toluene, reflux under N_2 for 72 h.

Synthesis.

Preparation of BTMPA-Im. 1-(4-Aminophenyl)-1*H*-imidazole (199 mg, 1.25 mmol), 5-iodo-1,2,3-trimethoxybenzene (918 mg, 3.13 mmol), 1,10-phenanthroline (45 mg, 0.25 mmol), CuI (47 mg, 0.25 mmol) and KOH (561 mg, 10 mmol) were added to 10 mL of dry toluene. The resulting suspension was refluxed under nitrogen for 72 h. The reaction mixture was cooled to room temperature, filtered and washed with dichloromethane. The collected filtrate and solvent was removed under reduced pressure. The obtained crude

product was purified by Silica gel column chromatography. The column was eluted with CH₂Cl₂:EtOAc (50:50) and the desired compound was collected as the second band. Yield: 100 mg (16%). EI HRMS: m/z 491.27 for [M]⁺, calculated 491.2056 for C₂₇H₂₉N₃O₆. ¹H NMR (300 MHz, CD₂Cl₂): 7.98 (bs, 1H), 7.35 (bs, 1H), 7.30 (d, 2H, J = 8.92 Hz), 7.26 (bs, 1H), 7.14 (d, 2H, J = 8.92 Hz), 6.40 (s, 4H), 3.81 (s, 6H), 3.75 (s, 12H).

Preparation of H₂PorF₅. Pyrrole (1.35 g, 1.4 mL, 17.45 mmol) and pentafluorobenzaldehyde (3.42 g, 2.1 mL, 17.45 mmol) were dissolved in dry CH₂Cl₂ (1000 mL). The flask was flushed with N₂ for 30 min, followed by the addition of BF₃.Et₂O (0.1 mL) and the solution was stirred at room temperature under dark for 3h. *p*-Chloranil (1.50 g, 6.12 mmol) was added to the brown solution under N₂ stream then further stirred for 12h at room temperature. The dark solution was concentrated under reduced pressure and load on the Al₂O₃ column. Using CH₂Cl₂:hexane (50:50) as eluent, pure compound as purple solid was obtained. Yield: 1.30 g (31%). ESI HRMS: m/z 975.1144 for [M+1]⁺, calculated 975.0664 for C₄₄H₁₁F₂₀N₄. ¹H NMR (400 MHz, CDCl₃): δ , ppm 8.95 (s, 8H), -2.87 (s, 2H).

Preparation of AlPorF₅-OH. To a mixture of H₂PorF₅ (500 mg, 0.51 mmol) in 35 mL of dry toluene was added trimethylaluminum (1 mL, 2.0 M in hexane) under an atmosphere of N₂. The resulting solution was stirred at room temperature for 24 h, at which time 1 mL of water was added and stirring was continued overnight. The toluene was removed and the residue was purified by alumina column chromatography using CH₂Cl₂:CH₃OH (= 95:5) as eluent. Yield: 510 mg (98%). ESI MS: m/z 1017.0966 for [M+H]⁺, calculated 1017.0351 for C₄₄H₁₀F₂₀N₄OAl. ¹H NMR (400 MHz, CDCl₃+drops of CD₃OD): δ , ppm 9.03 (s, 8H).

Preparation of AlPorF₅-Ph. A mixture of AlPorF₅-OH (40 mg, 0.039 mmol) and benzoic acid (4.8 mg, 0.039 mmol) in dry CH₂Cl₂ (adequate methanol was added for solubility reasons) was stirred for 1 h under nitrogen atmosphere. After reaction time the solution was passed through anhydrous Na₂SO₄ and evaporated to dryness. Yield: 38 mg (86%). ESI HRMS: m/z 1040.0732 for [M-(PhCOO)+CH₃CN]⁺, calculated 1040.0510 for C₄₆H₁₁F₂₀N₅Al. ¹H NMR (400 MHz, CDCl₃): δ , ppm 9.17 (s, 8H), 6.65 (t, 1H), 6.33 (t, 2H), 5.09 (d, 2H, J = 7.77 Hz).

Preparation of AlPorF₃-Ph-C₆₀. A mixture of AlPorF₃-OH (9.7 mg, 0.011 mmol) and C₆₀-Ph-COOH (10 mg, 0.011 mmol) was dissolved in 5 mL of dry CH₂Cl₂ (adequate methanol was added for solubility reasons), the resulting solution was stirred at room temperature for 2 h. The solvent was subsequently removed and the residue was washed with hexane to yield the desired product in pure form. Yield: 18 mg (93%). ESI HRMS: m/z 896.1472 for [M-(C₆₀-PhCOO)+CH₃CN]⁺, calculated 896.6554 for C₄₆H₁₉F₁₂N₅Al. ¹H NMR (300 MHz, CDCl₃): δ , ppm

9.16 (s, 8H), 6.80 (bs, 2H), 5.13 (d, 2H, $J = 8.34$ Hz), 4.75 (d, 1H, $J = 9.26$ Hz), 4.42 (s, 1H), 3.99 (d, 1H, $J = 9.26$ Hz), 2.36 (s, 3H).

Preparation of AlPorF₅-Ph-C₆₀. A mixture of AlPorF₅-OH (30 mg, 0.029 mmol) and HOOC-Ph-C₆₀ (26.5 mg, 0.029 mmol) was dissolved in 9 mL of dry DCM (adequate methanol was added for solubility reasons, about 1 mL), the resulting solution was stirred at room temperature for 18 h. Solvent was evaporated and washed with hexane to yield the desired product in pure form. Yield: 45 mg (90%). ESI HRMS: m/z 1896.1031 for $[M+H]^+$, calculated 1896.1035 for C₁₁₄H₁₉F₂₀N₅O₂Al, 1040.0776 for $[M-(C_{60}-PhCOO)+CH_3CN]^+$. ¹H NMR (400 MHz, CDCl₃): δ , ppm 9.12 (s, 8H), 7.82 (t, 8H), 6.94 (bs, 2H), 5.23 (d, 2H, $J = 8.03$ Hz), 4.77 (d, 1H, $J = 9.26$ Hz), 4.49 (s, 1H), 4.02 (d, 1H, $J = 9.26$ Hz), 2.41 (s, 3H).

Methods.

NMR and mass spectroscopy. NMR spectra were recorded with Varian 500 MHz NMR spectrometer using CDCl₃ as the solvent. ESI mass spectra were recorded on a Bruker MicroTOF-III mass spectrometer.

Infrared studies. IR spectra were recorded with Perkin Elmer 100 FT IR Spectrometer. Samples were prepared as 1% dispersions in a KBr pellet.

Electrochemistry. Cyclic and differential pulse voltammetric experiments (CH₂Cl₂, 0.1 M tetrabutylammonium perchlorate, (TBA.ClO₄)) were performed on a BASi Epsilon electrochemical analyzer (working: glassy carbon, auxiliary electrodes: Pt wire, reference electrode: Ag wire). The Fc⁺/Fc (Fc = ferrocene) couple was used to calibrate the redox potential values. $E_{1/2}(Fc^+/Fc) = 0.84$ V vs Ag wire in *o*-DCB, 0.1M TBAP under our experimental conditions.

Steady-state spectroscopy. Steady-state UV-visible absorption spectra were recorded with a Cary 100 UV-VIS spectrometer. The concentration of the samples used for these measurements ranged from 10⁻⁶ M (porphyrin Soret band) to 10⁻⁵ M (Q-bands bands) solutions. Steady-state fluorescence spectra were recorded using a Photon Technologies International Quanta Master 8075-11 spectrofluorometer, equipped with a 75 W xenon lamp, running with FelixGX software. A wavelength of 550 nm, which exclusively excites the porphyrin, was used and the concentrations were held constant at 0.1 mM for all the compounds. The fluorescence lifetimes were evaluated using a Horiba Yvon Nanolog spectrofluorometer coupled with time-correlated single photon counting using nanoLED excitation sources. A right-angle detection method was used.

Absorption and fluorescence titrations. Absorption titrations were carried out in dichlorobenzene (*o*-DCB) at concentrations appropriate for measuring the porphyrin Soret band. A solution containing the acceptor (A = AlPorF_n-Ph-C₆₀ or AlPorF_n-Ph) derivative was placed in a cuvette and titrated by adding aliquots of a concentrated solution of the donor (D = BTMPA-Im or Me-Im). The donor solutions also contained the acceptor at its initial concentration so that the porphyrin concentration remained constant throughout the titration. The binding constants were calculated using the Benesi-Hildebrand equation, $[A]/\text{Abs} = (1/[D])(1/\varepsilon K) + (1/\varepsilon)$, where, [A] is the total concentration of bound and unbound acceptor and is kept fixed, Abs is the absorption of complex at the wavelength λ , [D] is the total concentration of the BTMPA-Im (or Me-Im) which is varied, K is binding constant and ε is the molar absorptivity of BTMPA \rightarrow AlPorF_n-Ph-C₆₀ or BTMPA \rightarrow AlPorF_n-Ph (where $n = 0, 3, 5$) complex. In an analogous manner, steady-state fluorescence titrations were carried out in *o*-DCB using solutions at constant concentration of AlPor derivative and varying concentration of BTMPA-Im (or Me-Im). The solutions were excited at the isosbestic point wavelength, which was obtained from the corresponding absorption titrations.

Femtosecond transient absorption spectroscopy. Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating a diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and a diode-pumped intracavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.5 W. For optical detection, a Helios transient absorption spectrometer provided by Ultrafast Systems LLC coupled with an optical parametric amplifier (OPA) provided by Light Conversion was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.5 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into the OPA, while the rest of the output was used for generation of the white light continuum. In the present study, the maximum absorption wavelength for each compound was used in all the experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

DFT calculations. All the dyads shown in Figs. S17 - S19 were optimized at the B3LYP/def2-SVP level of theory using an ultrafine grid in the Gaussian 16 software. The optimizations were performed in a CPCM dielectric continuum solvent model of dichlorobenzene as implemented in Gaussian 16. Dyads/ triads with AlPor, AlPorF₃, and AlPorF₅ are referred to as dyads/ triads 1, 2, and 3 respectively

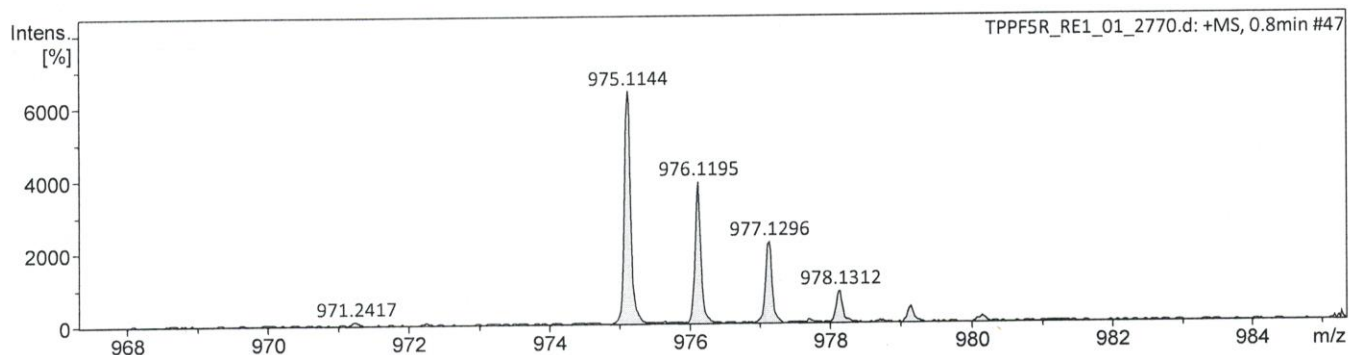


Figure S1. High resolution ESI mass spectrum of H_2PorF_5 .

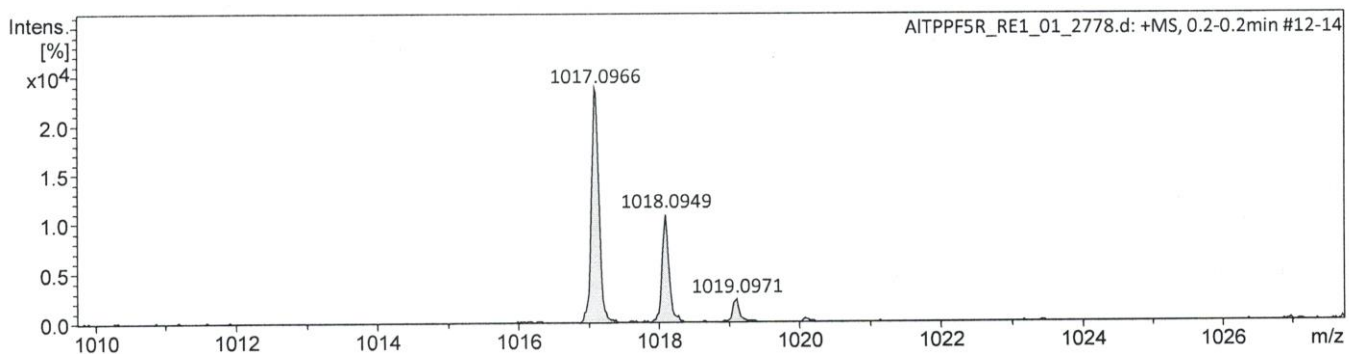


Figure S2. High resolution ESI mass spectrum of $\text{AlPorF}_5\text{-OH}$.

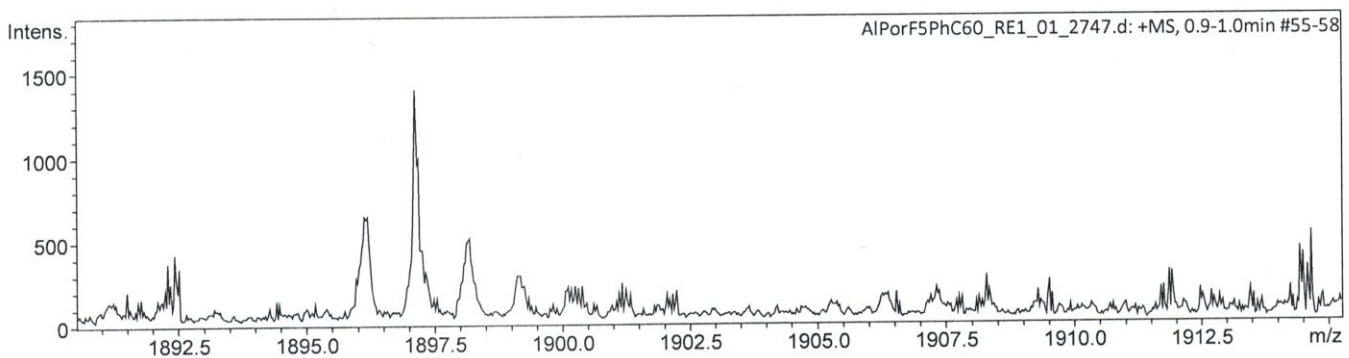


Figure S3. High resolution ESI mass spectrum of $\text{AlPorF}_5\text{-Ph-C}_{60}$.

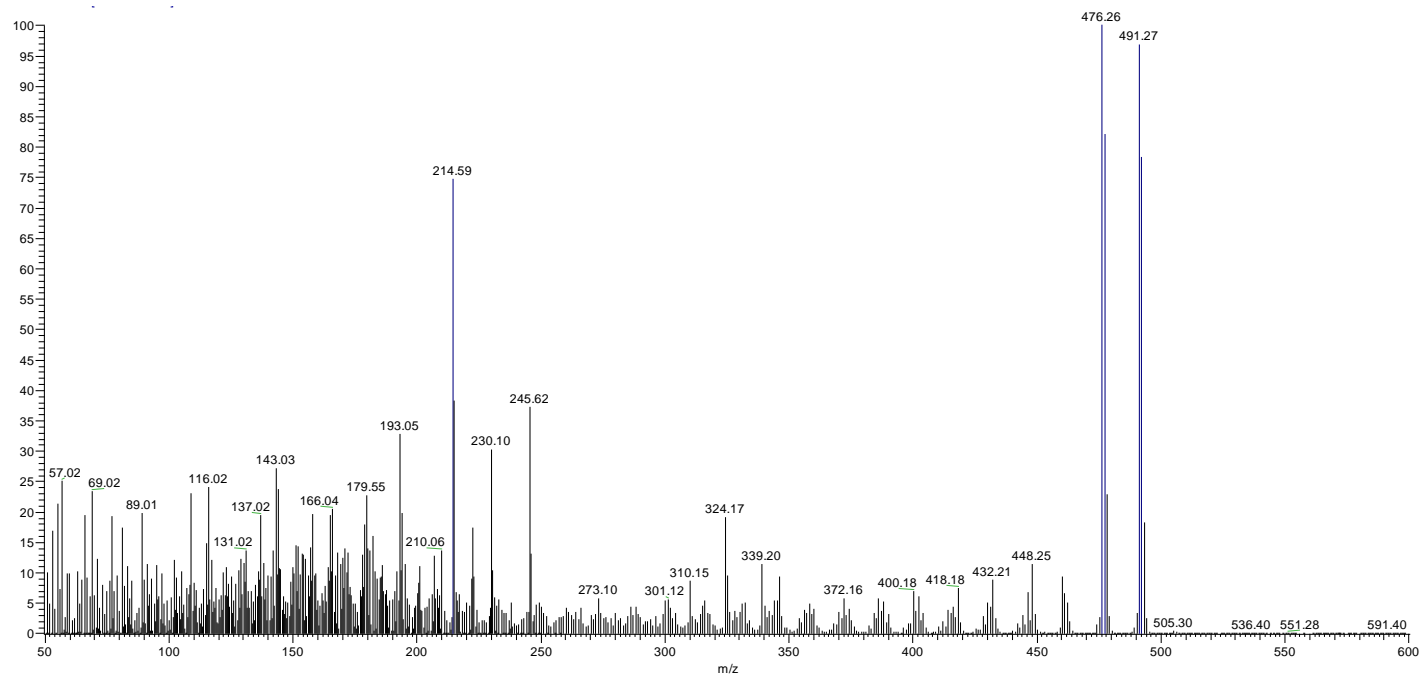


Figure S4. EI mass spectrum of BTMPA-Im.

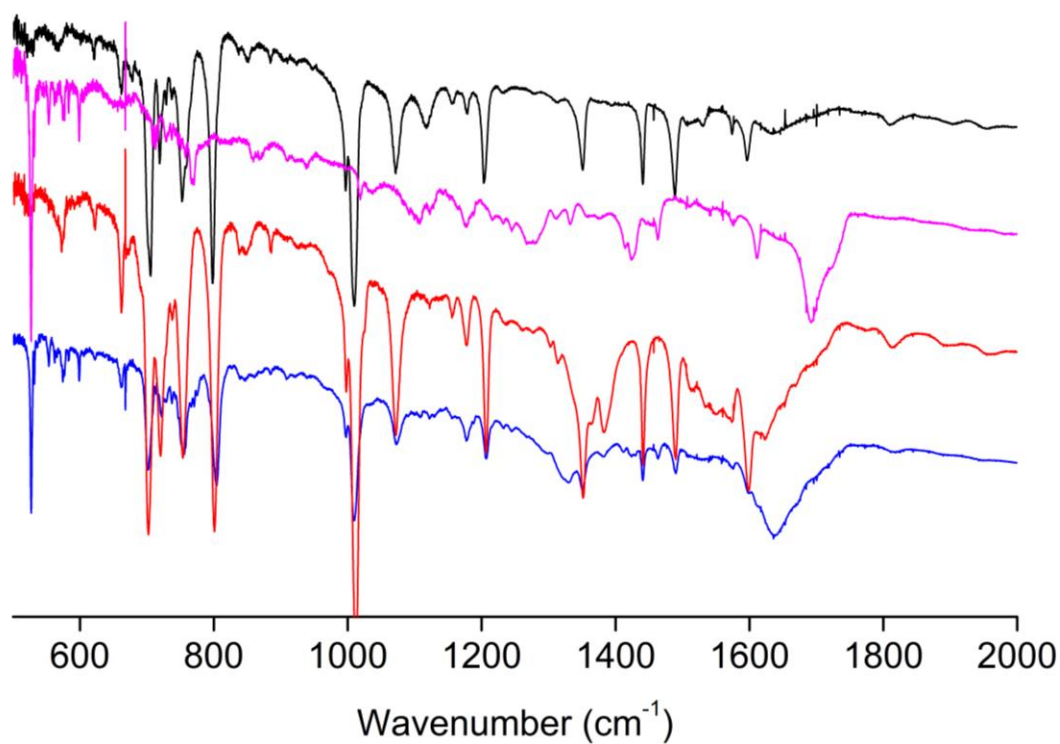


Figure S5. IR spectra (KBr pellets) of AlPor-OH (black), C₆₀-Ph-COOH (magenta), AlPor-Ph (red) and AlPor-Ph-C₆₀ (blue).

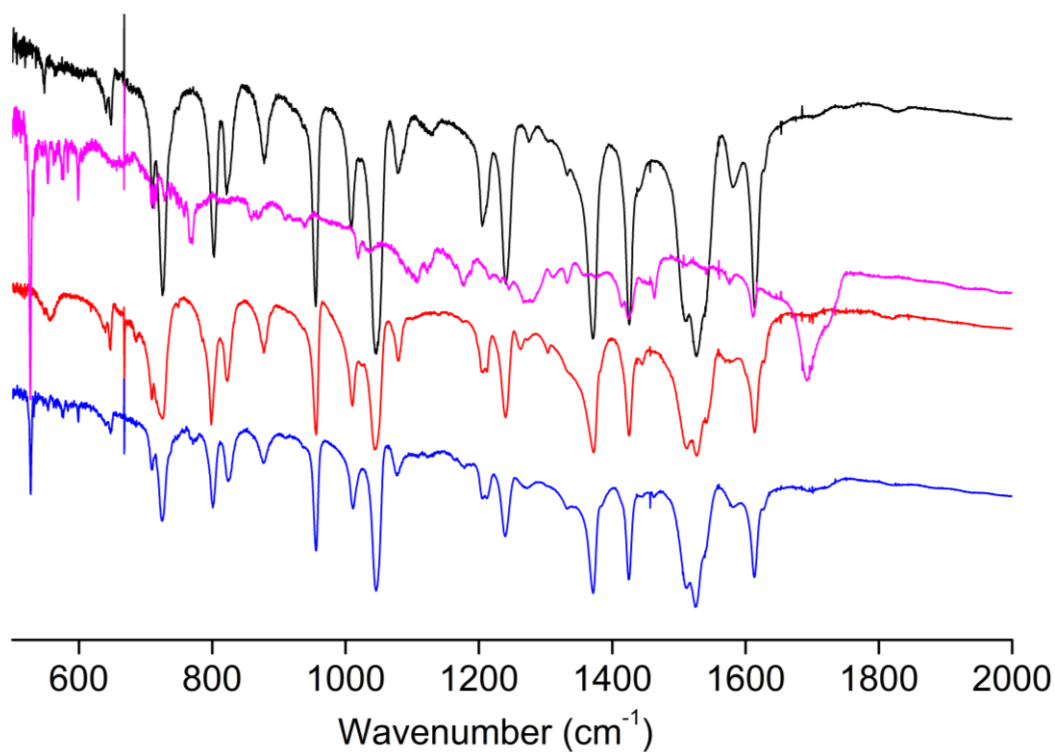


Figure S6. IR spectra (KBr pellets) of AlPorF₃-OH (black), C₆₀-Ph-COOH (magenta), AlPorF₃-Ph (red) and AlPorF₃-Ph-C₆₀ (blue).

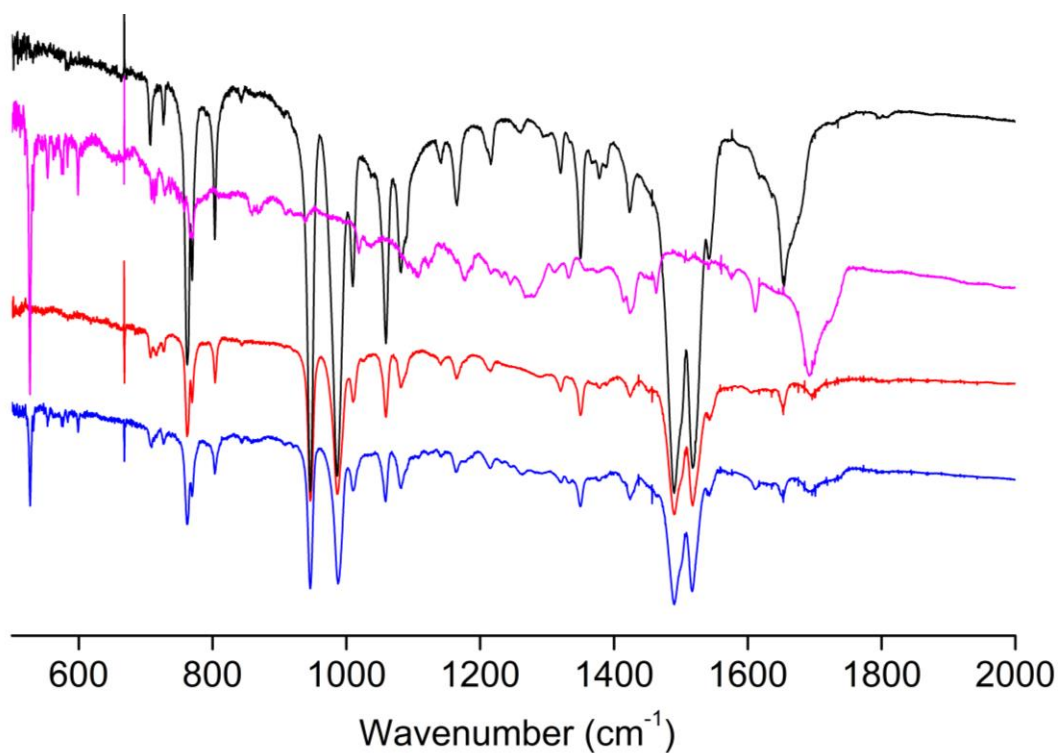


Figure S7. IR spectra (KBr pellets) of AlPorF₅-OH (black), C₆₀-Ph-COOH (magenta), AlPorF₅-Ph (red) and AlPorF₅-Ph-C₆₀ (blue).

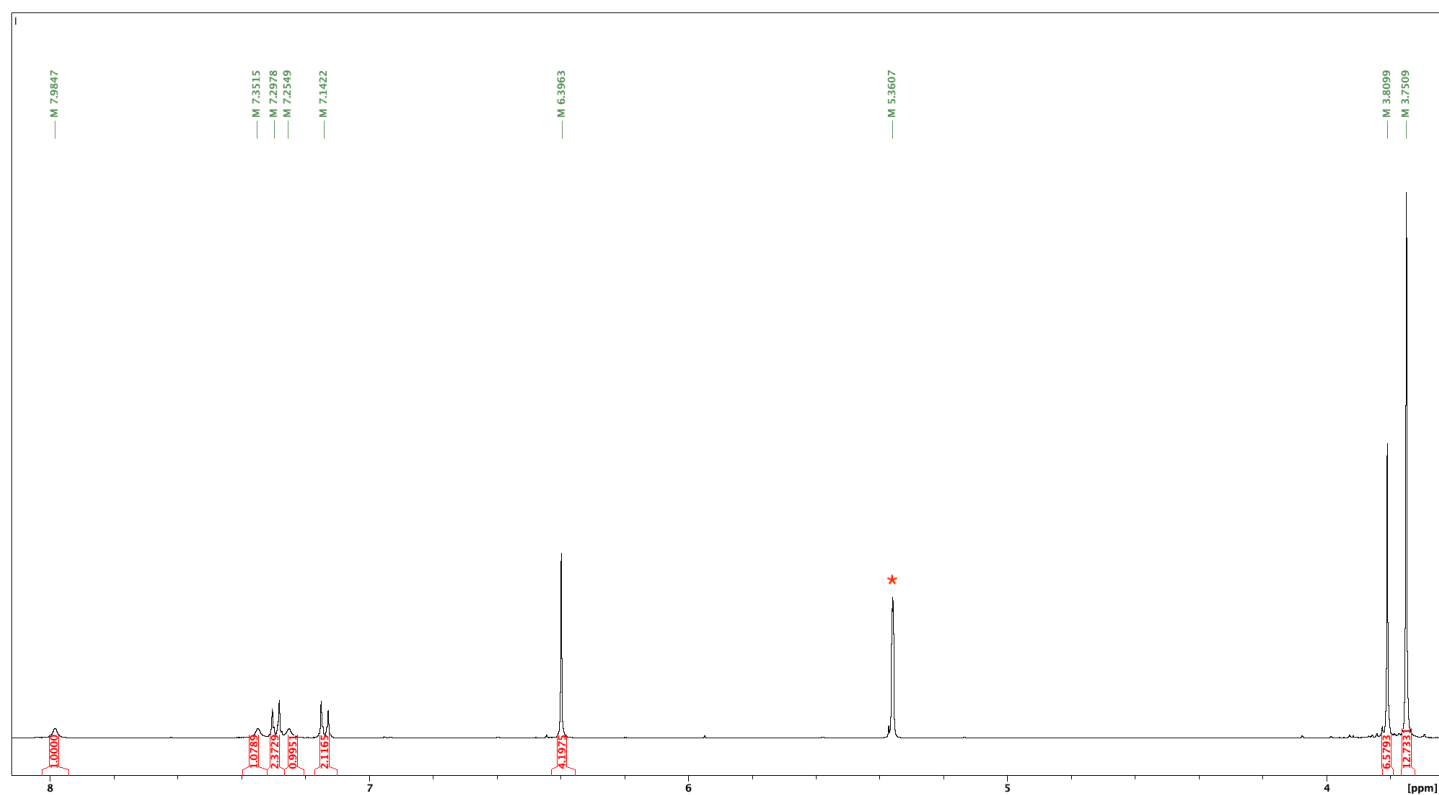


Figure S8. ^1H NMR spectrum of BTMPA-Im in CD_2Cl_2 . *Indicate solvent peaks.

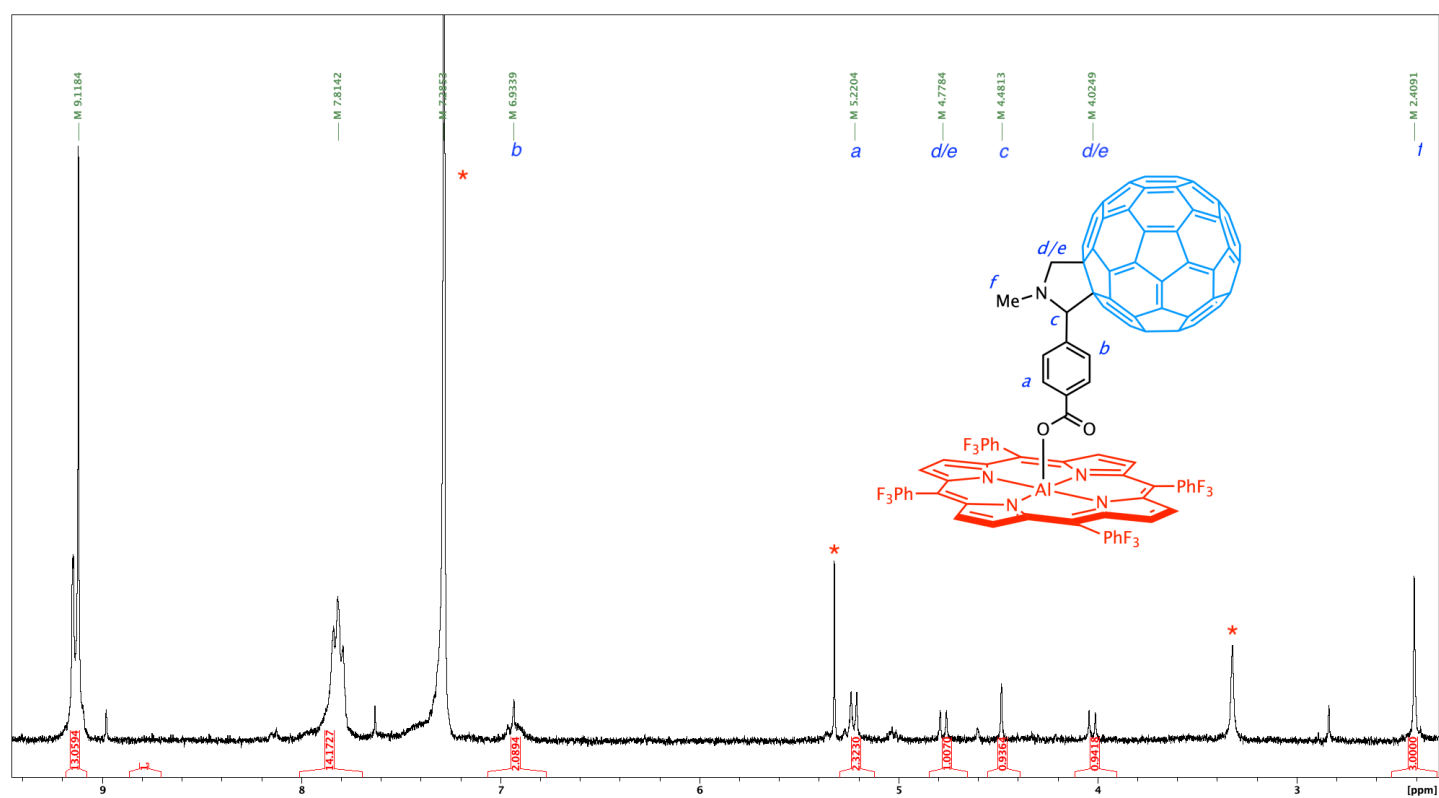


Figure S9. ^1H NMR spectrum of AlPorF₃-Ph-C₆₀ in CDCl_3 . *Indicate solvent peaks.

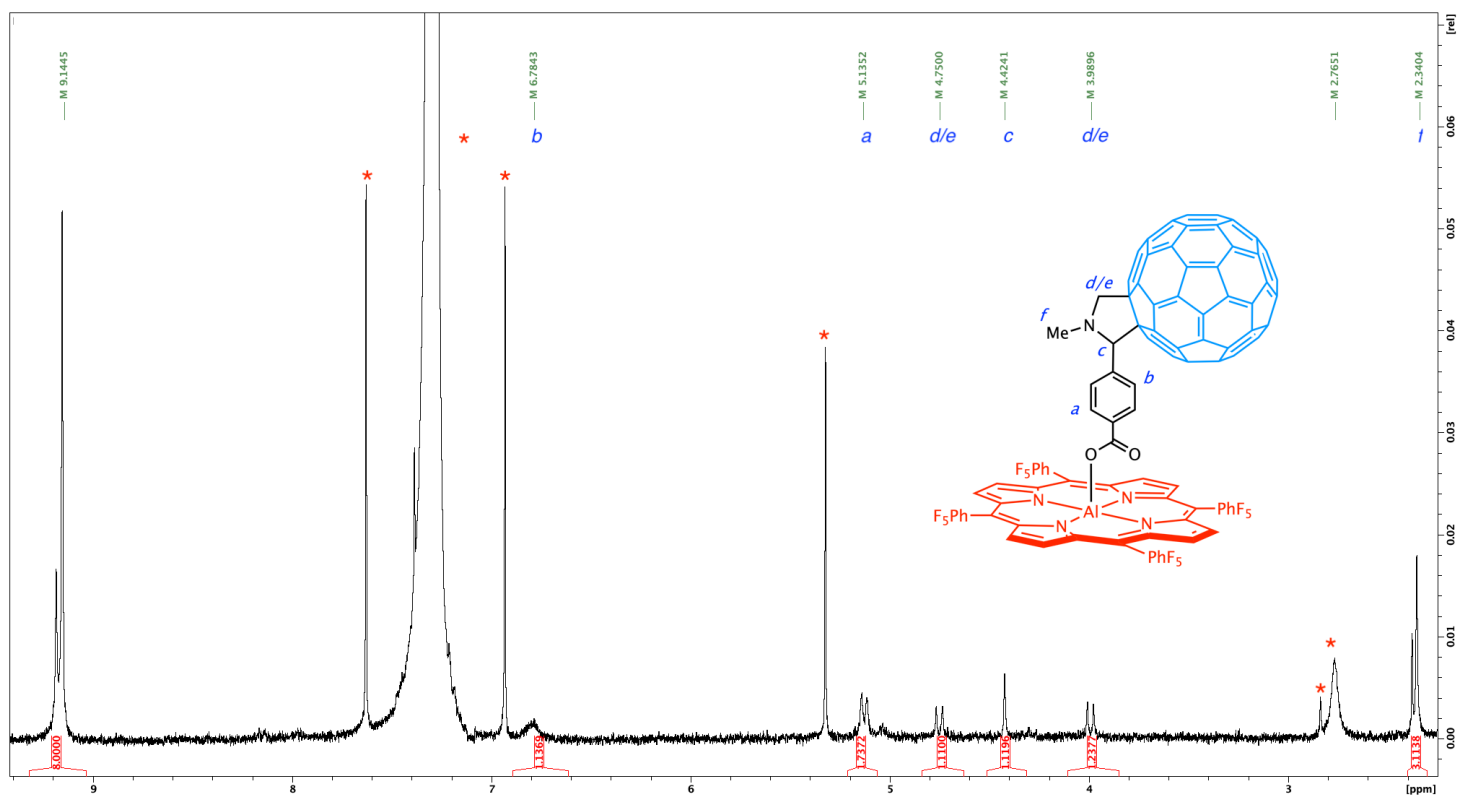


Figure S10. ^1H NMR spectrum of $\text{AlPorF}_5\text{-Ph-C}_{60}$ in CDCl_3 . *Indicate solvent peaks.

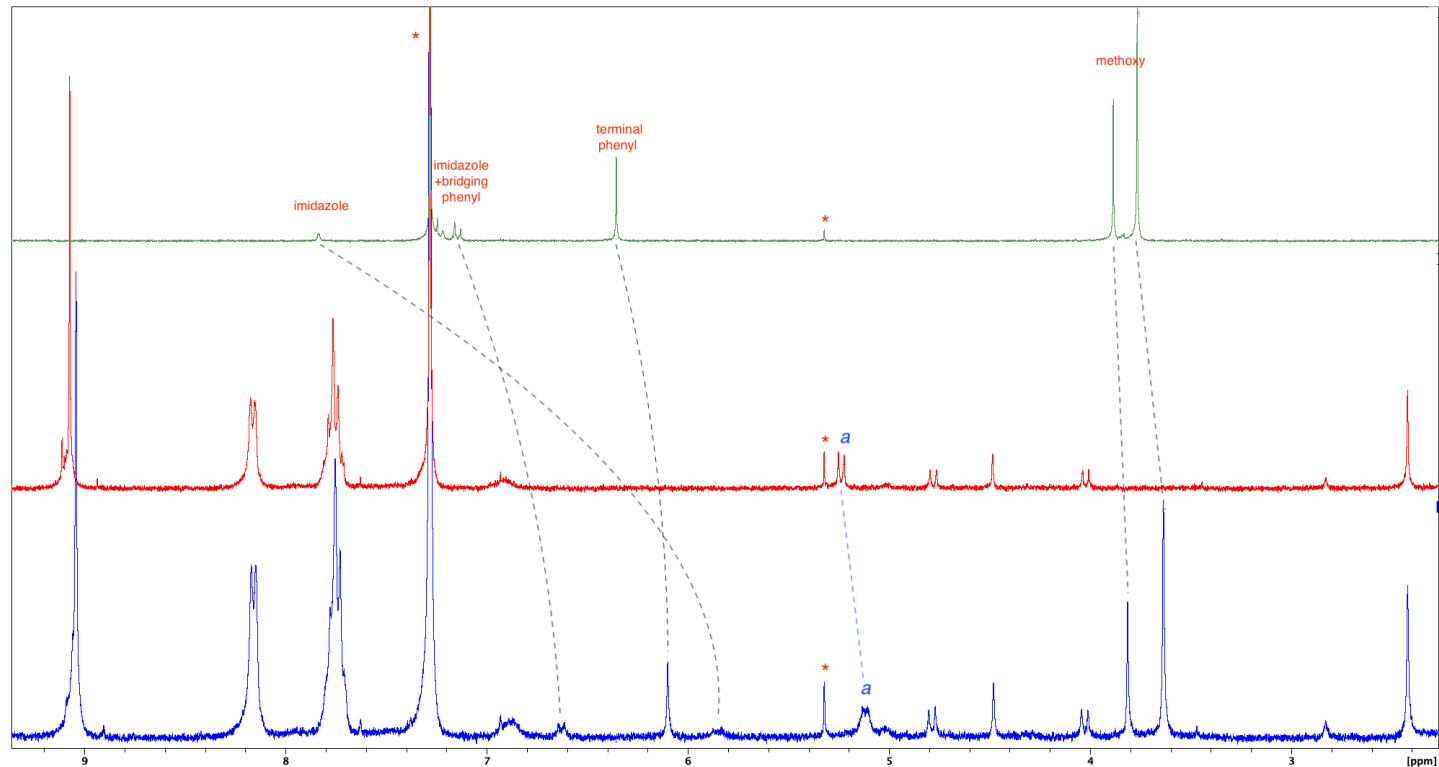


Figure S11. ^1H NMR spectra of BTMPA-Im (top), AlPor-Ph-C_{60} , and 1:1 mixture of AlPor-Ph-C_{60} and BTMPA-Im (bottom) in CDCl_3 .

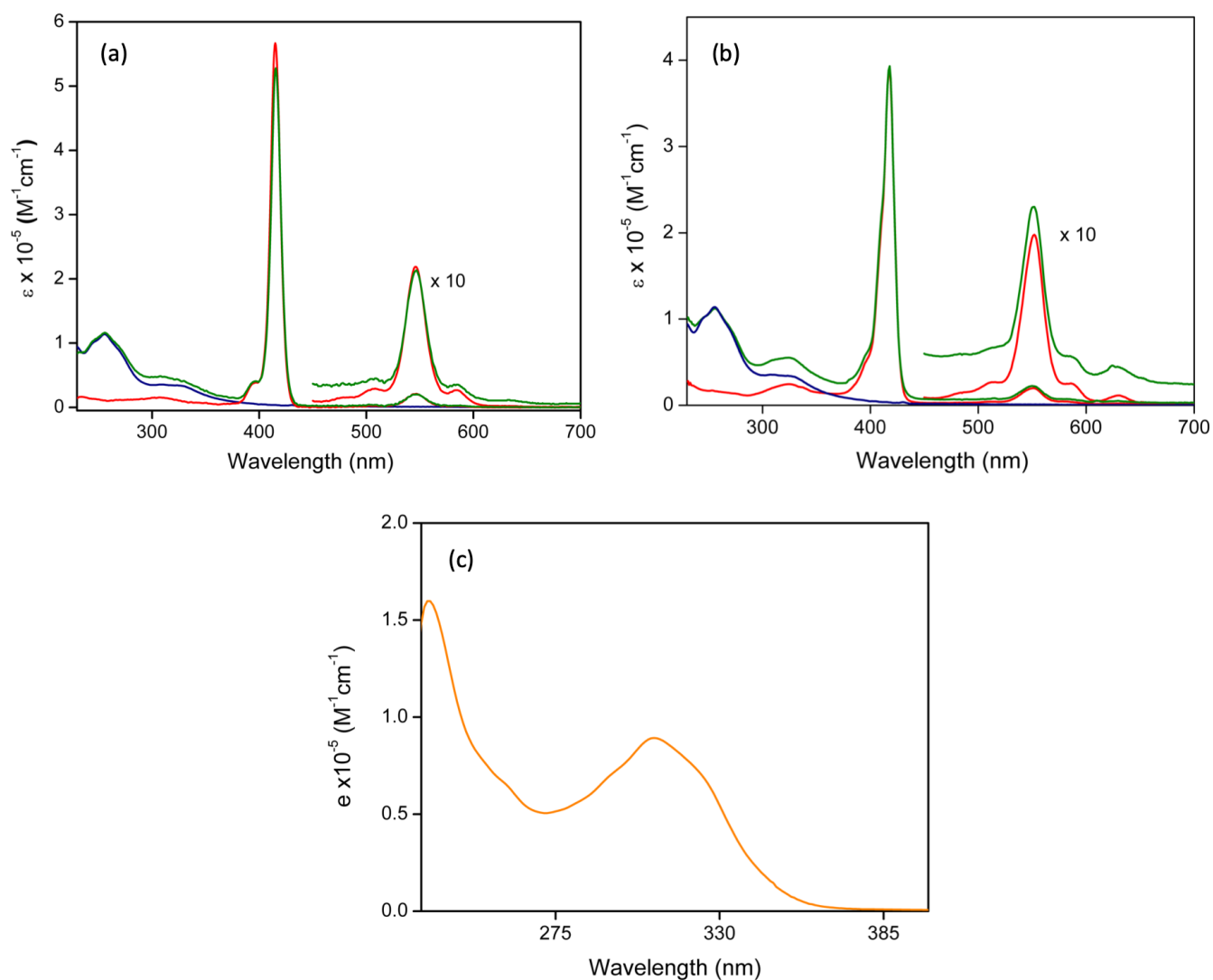


Figure S12. Absorption spectra of (a) AlPor-Ph-C₆₀ (green), AlPor-Ph (red) and C₆₀-Ph-COOMe (blue), (b) AlPorF₅-Ph-C₆₀ (green), AlPorF₅-Ph (red) and C₆₀-Ph-COOMe (blue), and (c) BTMPA-Im in dichloromethane. Note that for the dyad AlPorF₅-Ph-C₆₀ and its reference monomer AlPorF₅-Ph a sufficient amount methanol was added to the dichloromethane to allow to the compounds to dissolve.

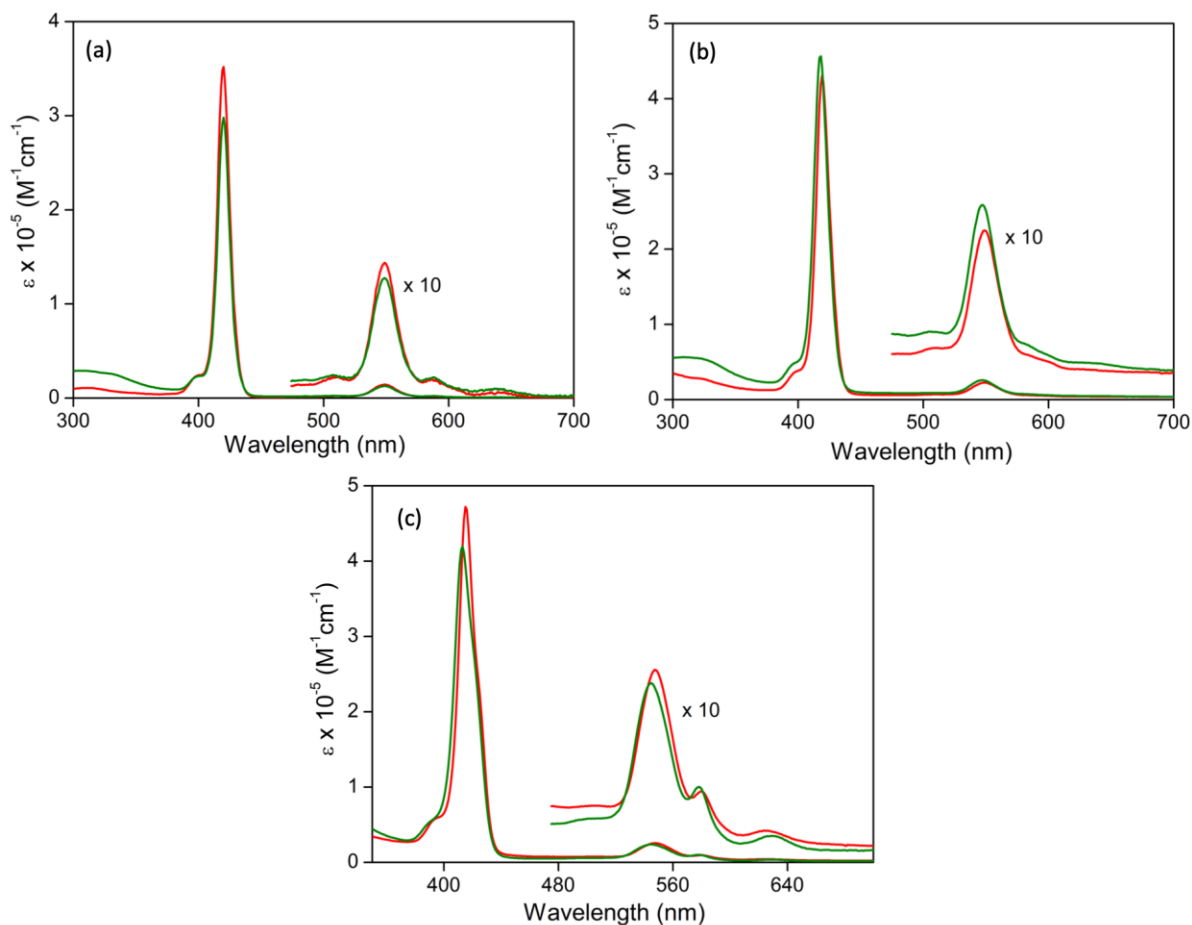


Figure S13. Absorption spectra of (a) AlPor-Ph-C₆₀ (green), AlPor-Ph (red) , (b) AlPorF₃-Ph-C₆₀ (green), AlPorF₃-Ph (red), and (c) AlPorF₅-Ph-C₆₀ (green), AlPorF₅-Ph (red) in *o*-DCB.

Table S1. Binding constant evaluated from the absorption titrations in *o*-DCB.

Titration	Binding constant (K , M^{-1})
BTMPA-Im \rightarrow AlPor-Ph- C_{60}	3.5×10^4
Me-Im \rightarrow AlPor-Ph- C_{60}	1.4×10^5
BTMPA-Im \rightarrow AlPor-Ph	3.1×10^4
Me-Im \rightarrow AlPor-Ph	6.4×10^4
BTMPA-Im \rightarrow AlPorF ₃ -Ph- C_{60}	1.7×10^5
Me-Im \rightarrow AlPorF ₃ -Ph- C_{60}	2.6×10^5
BTMPA-Im \rightarrow AlPorF ₃ -Ph	1.4×10^5
Me-Im \rightarrow AlPorF ₃ -Ph	8.9×10^4
BTMPA-Im \rightarrow AlPorF ₅ -Ph- C_{60}	4.3×10^5
Me-Im \rightarrow AlPorF ₅ -Ph- C_{60}	4.4×10^5
BTMPA-Im \rightarrow AlPorF ₅ -Ph	3.2×10^5
Me-Im \rightarrow AlPorF ₅ -Ph	2.6×10^5

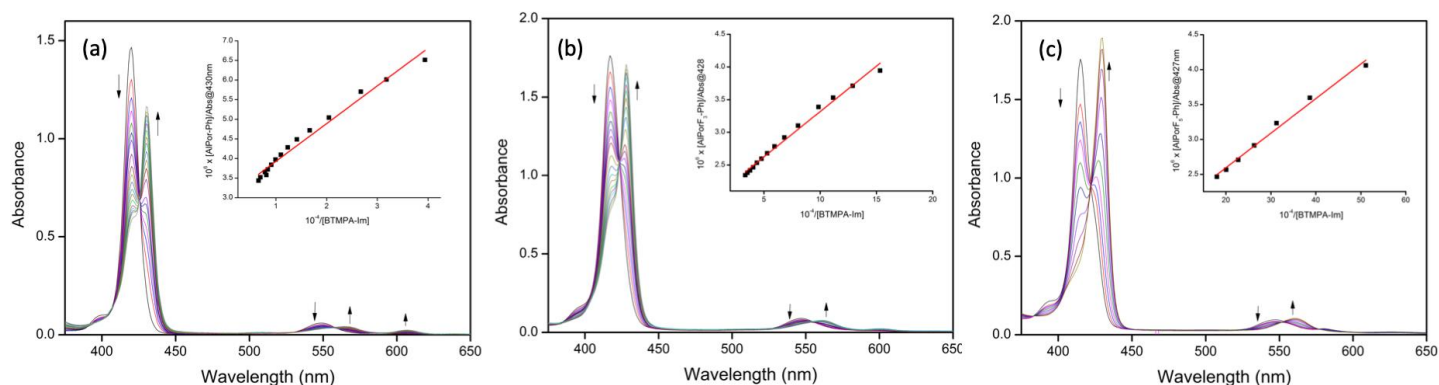


Figure S14. Absorption titrations of (a) AlPor-Ph vs BTMPA-Im: BTMPA-Im was added up to 1.52×10^{-4} M in 10 μ l (6.60×10^{-4} M) increments to a 1 ml (4×10^{-6} M) solution of AlPor-Ph, (b) AlPorF₃-Ph vs BTMPA-Im: BTMPA-Im was added up to 3.0×10^{-5} M in 10 μ l (1.37×10^{-4} M) increments to a 1 ml (4×10^{-6} M) solution of AlPorF₃-Ph, and (c) AlPorF₅-Ph vs BTMPA-Im: BTMPA-Im was added up to 5.54×10^{-6} M in 10 μ l (6.7×10^{-5} M) increments to a 1 ml (4×10^{-6} M) solution of AlPorF₅-Ph. All the titrations were performed in *o*-DCB. The inset shows the Benesi–Hildebrand plot.

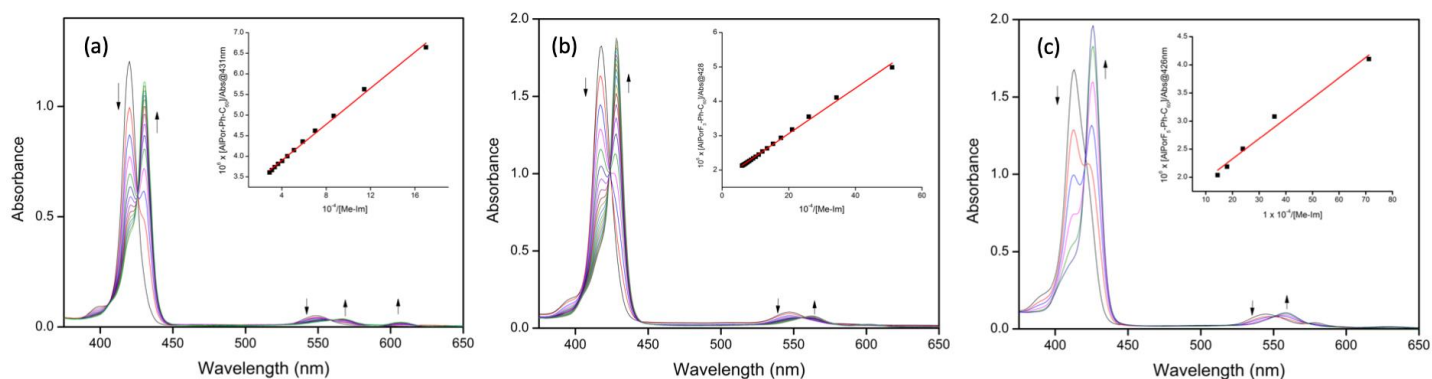


Figure S15. Absorption titrations of (a) AlPor-Ph-C₆₀ vs Me-Im: Me-Im was added up to 3.45×10^{-5} M in 10 μ l (3.0×10^{-3} M) increments to a 1 ml (4×10^{-6} M) solution of AlPor-Ph-C₆₀; (b) AlPorF₃-Ph-C₆₀ vs Me-Im: Me-Im was added up to 1.67×10^{-5} M in 10 μ l (1.0×10^{-4} M) increments to a 1 ml (4×10^{-6} M) solution of AlPorF₃-Ph-C₆₀; (c) AlPorF₅-Ph-C₆₀ vs Me-Im: Me-Im was added up to 6.92×10^{-6} M in 3.5 μ l (4.02×10^{-4} M) increments to a 1 ml (4×10^{-6} M) solution of AlPorF₅-Ph-C₆₀. All the titrations were performed in *o*-DCB. The inset shows the Benesi–Hildebrand plot.

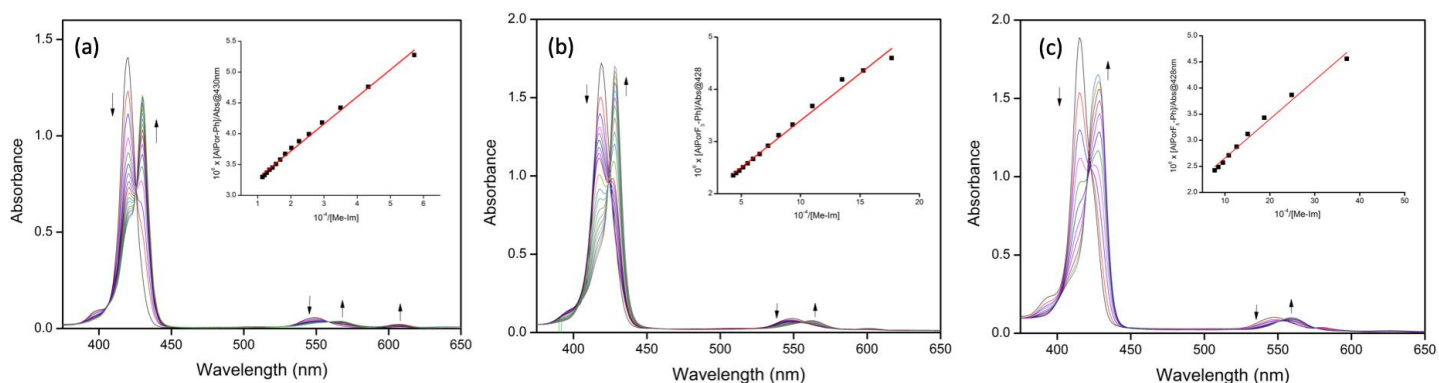


Figure S16. Absorption titrations of (a) AlPor-Ph vs Me-Im: Me-Im was added up to 8.7×10^{-5} M in 10 μ l (6.0×10^{-4} M) increments to a 1 ml (4×10^{-6} M) solution of AlPor-Ph; (b) AlPorF₃-Ph vs Me-Im: Me-Im was added up to 2.3×10^{-5} M in 10 μ l (1.0×10^{-4} M) increments to a 1 ml (4×10^{-6} M) solution of AlPorF₃-Ph; (c) AlPorF₅-Ph vs Me-Im: Me-Im was added up to 1.29×10^{-5} M in 5 μ l (2.72×10^{-4} M) increments to a 1 ml (4×10^{-6} M) solution of AlPorF₅-Ph. All the titrations were performed in *o*-DCB. The inset shows the Benesi–Hildebrand plot.

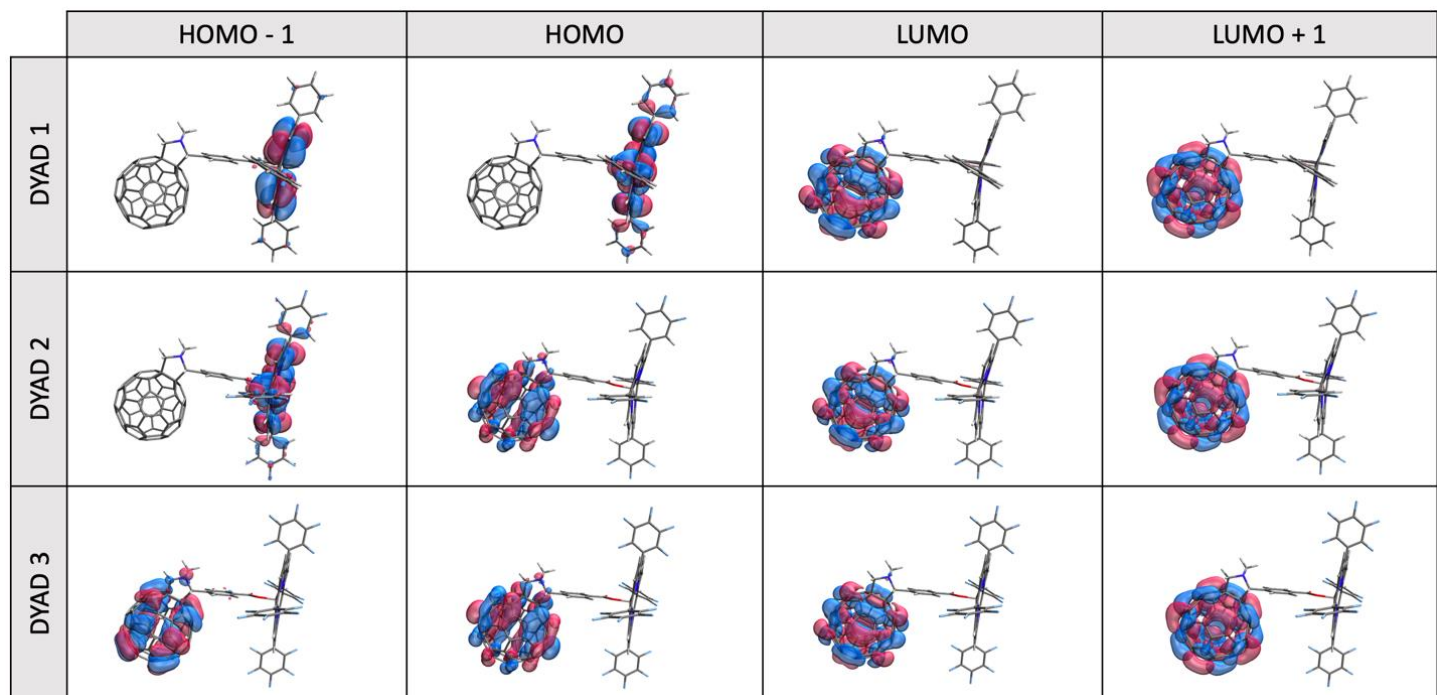


Figure S17. Frontier orbitals of AlPor-Ph-C₆₀ (Dyad 1), AlPorF₃-Ph-C₆₀ (Dyad 2) and AlPorF₅-Ph-C₆₀ (Dyad 3).

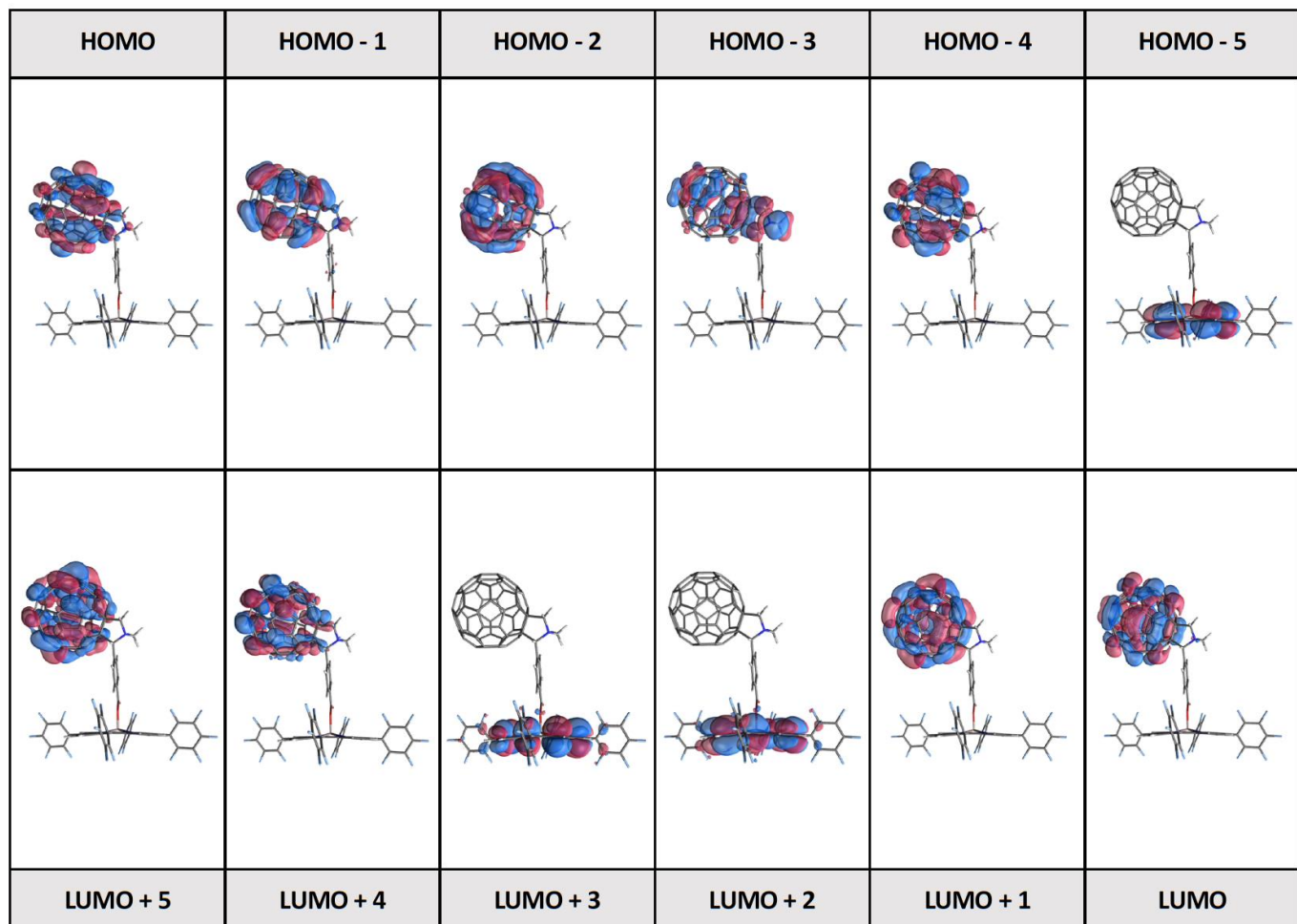


Figure S18. Frontier orbitals of the dyad AlPorF₅-Ph-C₆₀.

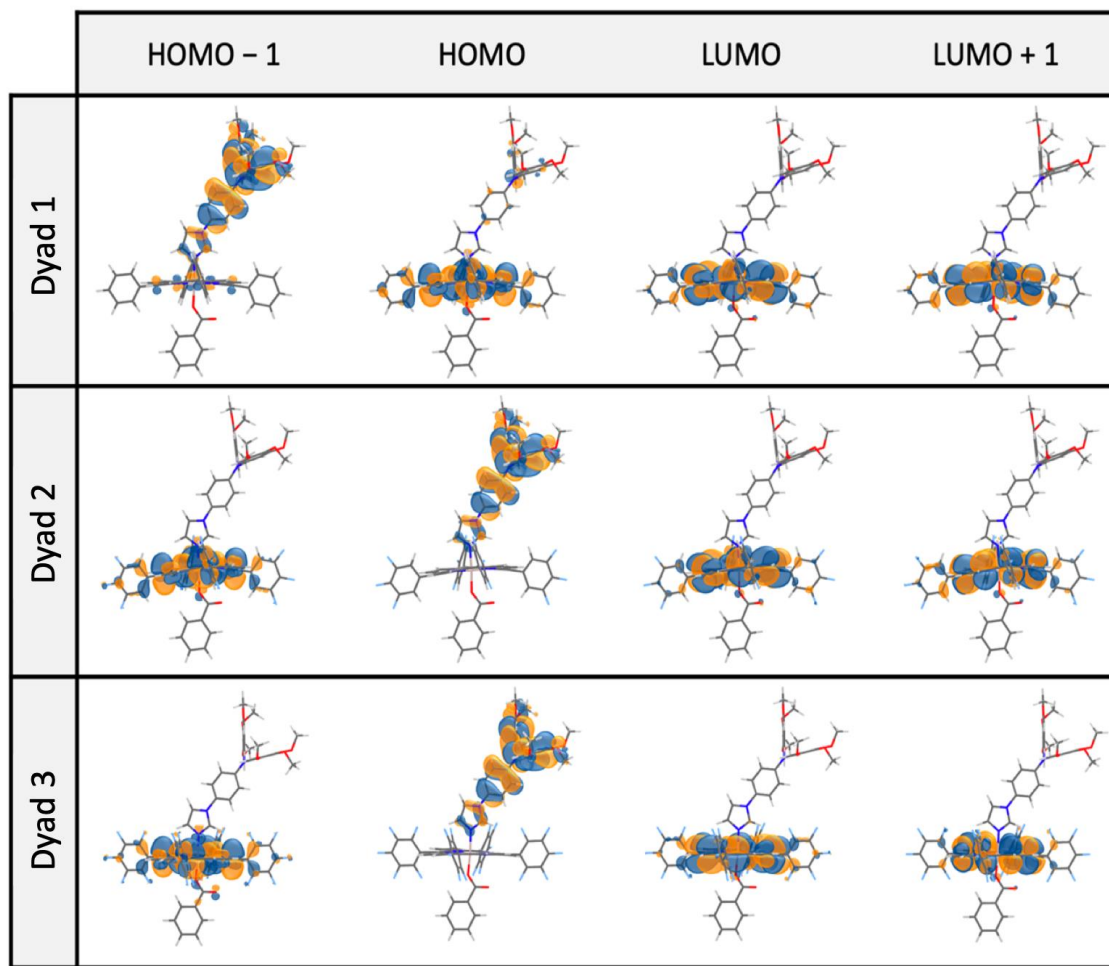


Figure S19. Frontier orbitals of the self-assembled dyads BTMPA-Im \rightarrow AlPor-Ph (Dyad 1), BTMPA-Im \rightarrow AlPorF₃-Ph (Dyad 2) and BTMPA-Im \rightarrow AlPorF₅-Ph (Dyad 3).

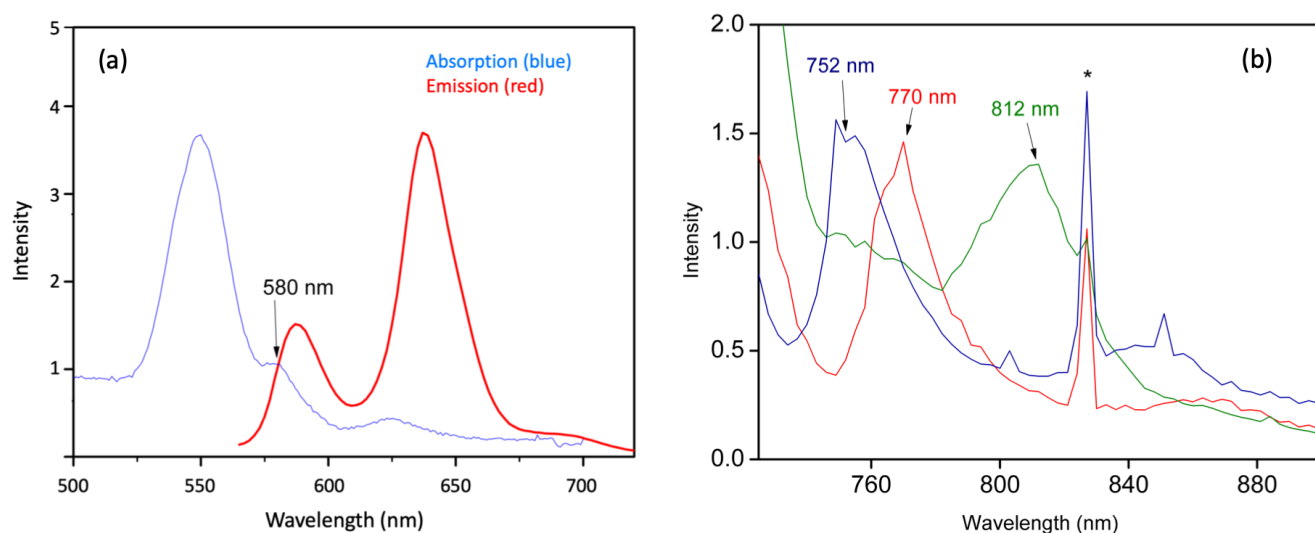


Figure S20. (a) Superposition of the absorption and fluorescence spectra of AlPorF₅-Ph in *o*-DCB. (b) Phosphorescence spectra of AlPor-Ph (red), AlPorF₃-Ph (blue) and AlPorF₅-Ph (green) in degassed CH₂Cl₂:C₂H₅OH (=1:1) mixture at 77K.

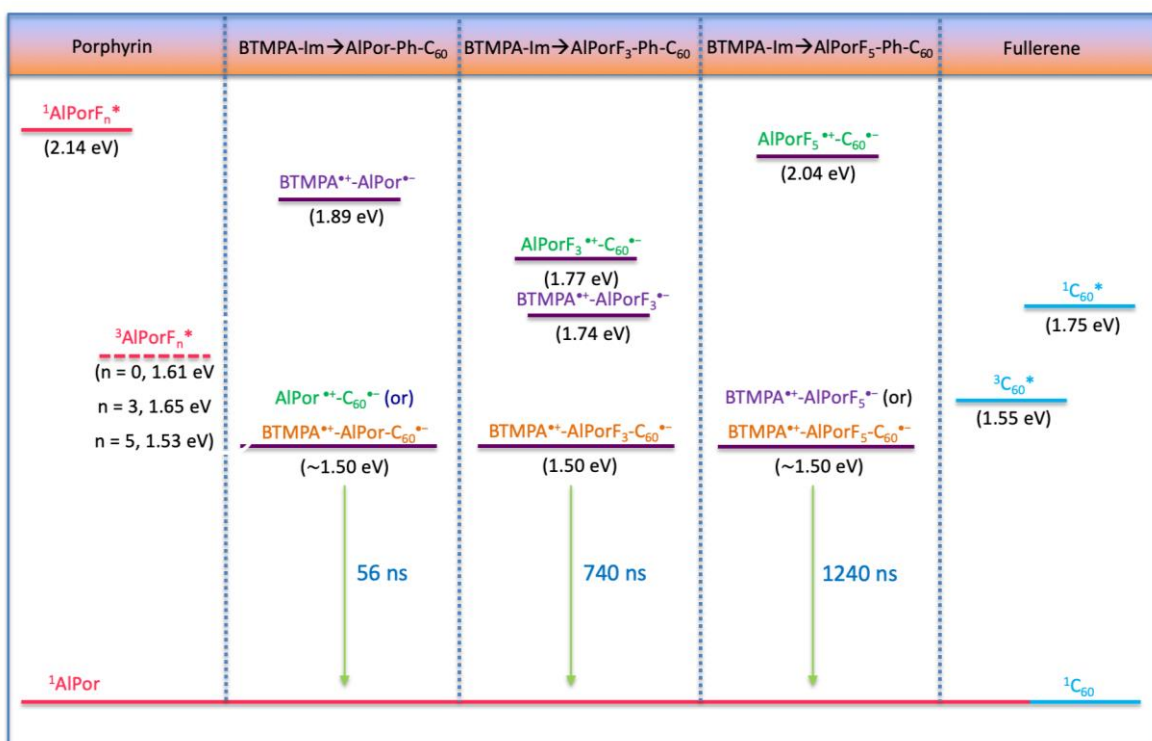


Figure S21. Energy level diagram of investigated triads in *o*-DCB.

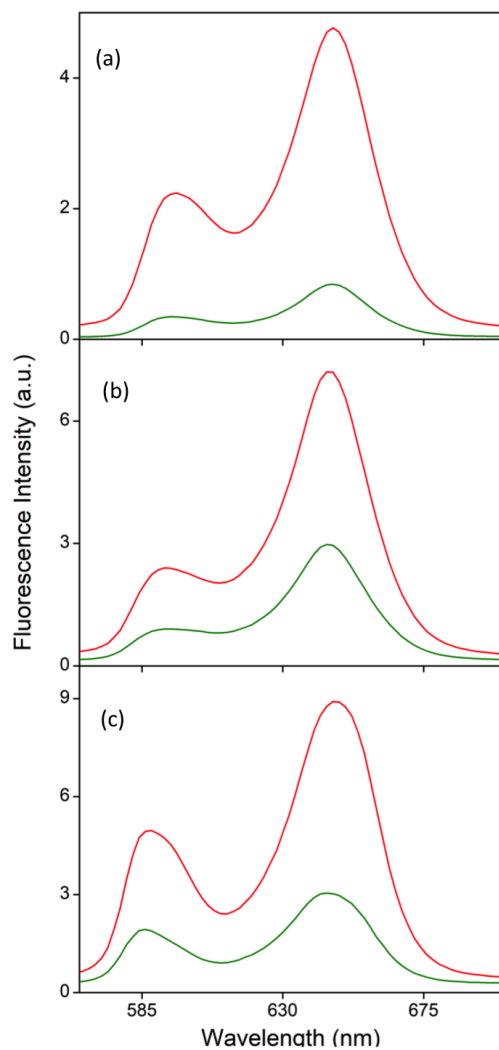


Figure S22. Fluorescence spectra of (a) AlPor-Ph (red) and AlPor-Ph-C₆₀ (green), (b) AlPorF₃-Ph (red) and AlPorF₃-Ph-C₆₀ (green), and (c) AlPorF₅-Ph (red) and AlPorF₅-Ph-C₆₀ (green) in toluene. Excitation wavelength = 550 nm.

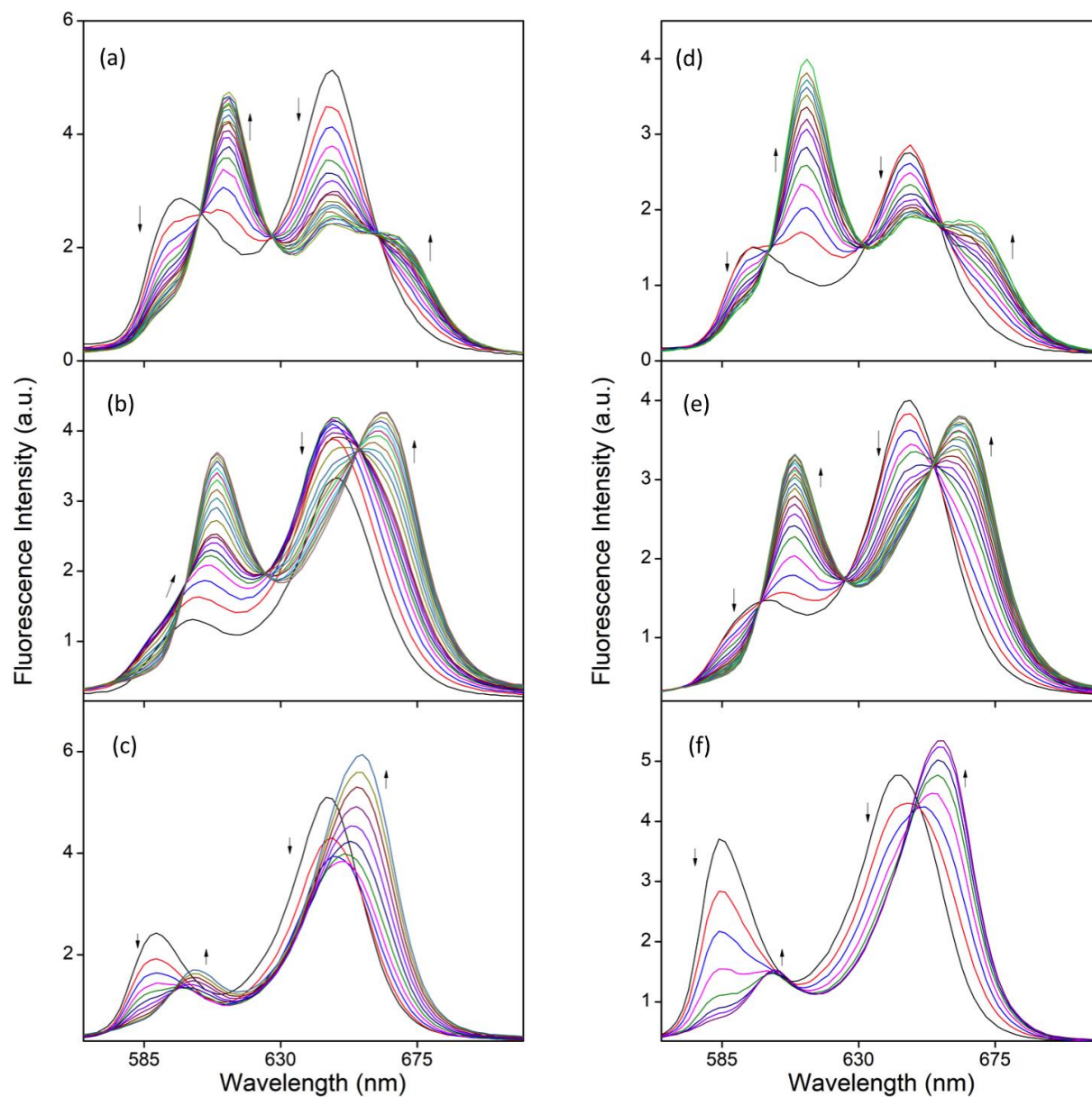


Figure S23. Fluorescence titration of Left: (a) AlPor-Ph vs Me-Im (b) AlPorF₃-Ph vs Me-Im, (c) AlPorF₅-Ph vs Me-Im. See Figure S16 for concentrations. Right: (d) AlPor-Ph-C₆₀ vs Me-Im (e) AlPorF₃-Ph-C₆₀ vs Me-Im, and (f) AlPorF₅-Ph-C₆₀ vs Me-Im. See Figure S15 for concentrations. All the titrations were performed in *o*-DCB.

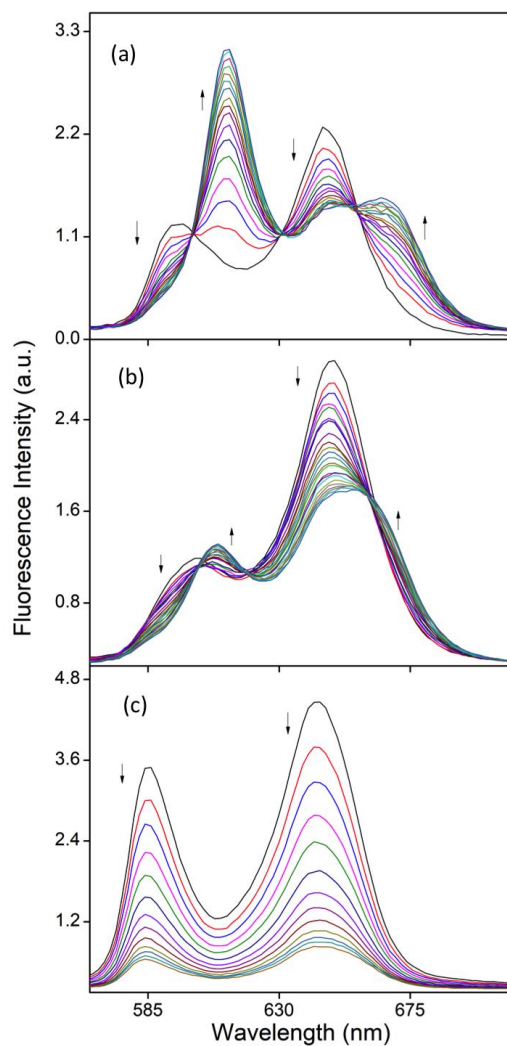


Figure S24. Fluorescence titration of (a) AlPor-Ph-C₆₀ vs BTMPA-Im, (b) AlPorF₃-Ph-C₆₀ vs BTMPA-Im, and (c) AlPorF₅-Ph-C₆₀ vs BTMPA-Im. See Figure 1 for concentrations. All the titrations were performed in *o*-DCB.

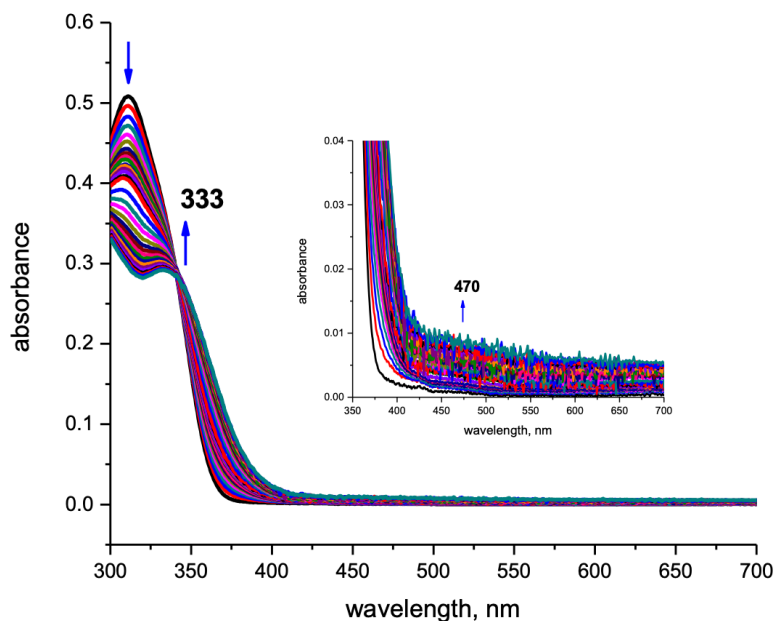


Figure S25. Spectral changes observed during the oxidation of BTMPA-Im in *o*-DCB with 0.2 M TBA.ClO₄.

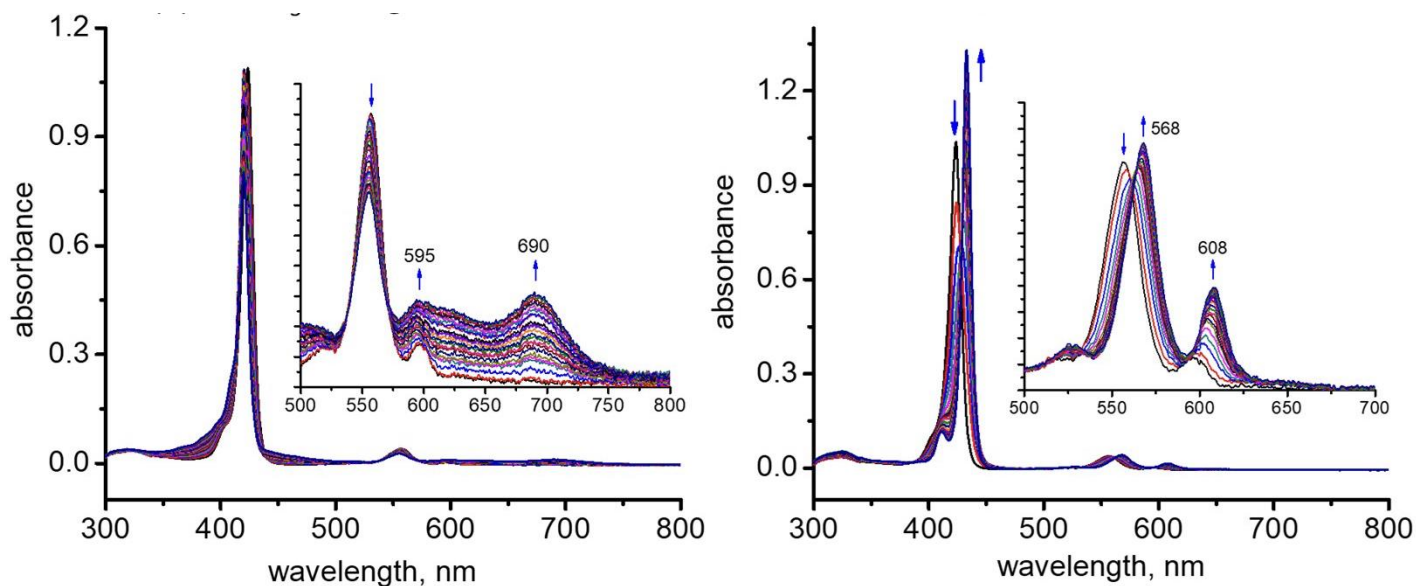


Figure S26. Spectral changes observed during first oxidation (right) and first reduction (left) of AlPorF₃-Ph in *o*-DCB containing 0.2 M TBA.ClO₄.

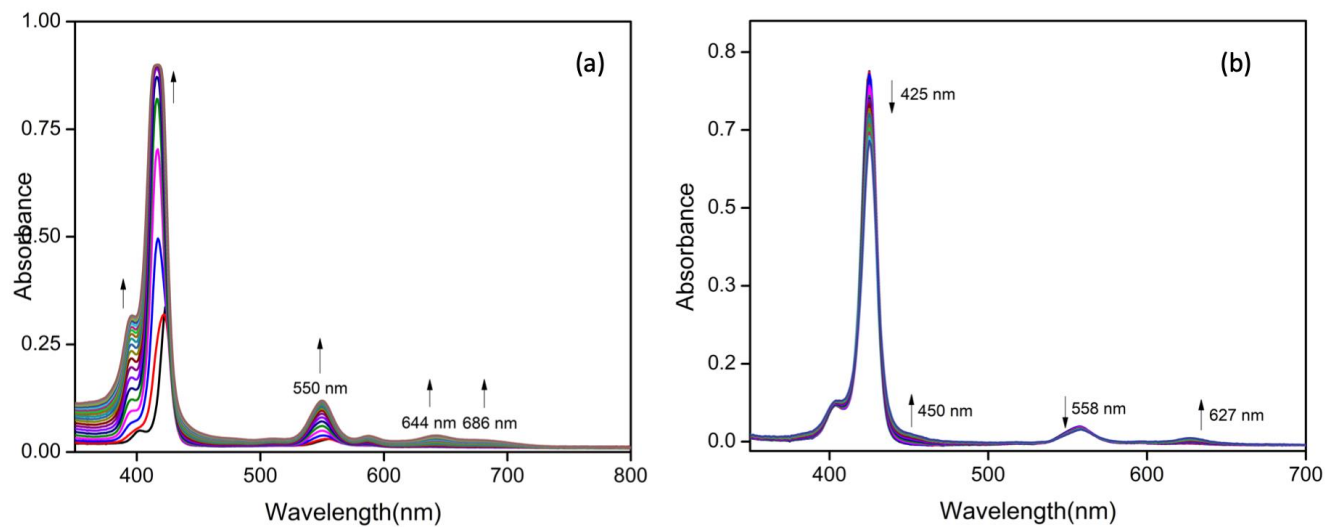


Figure S27. Spectral changes observed during first oxidation (right) and first reduction (left) of AlPorF₅-Ph in *o*-DCB containing 0.2 M TBA.ClO₄.