Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Ultrafast charge separation and charge stabilization in vertically-linked 'tetrathiafulvalene - aluminum(III) porphyrin - gold(III) porphyrin' reaction center mimics

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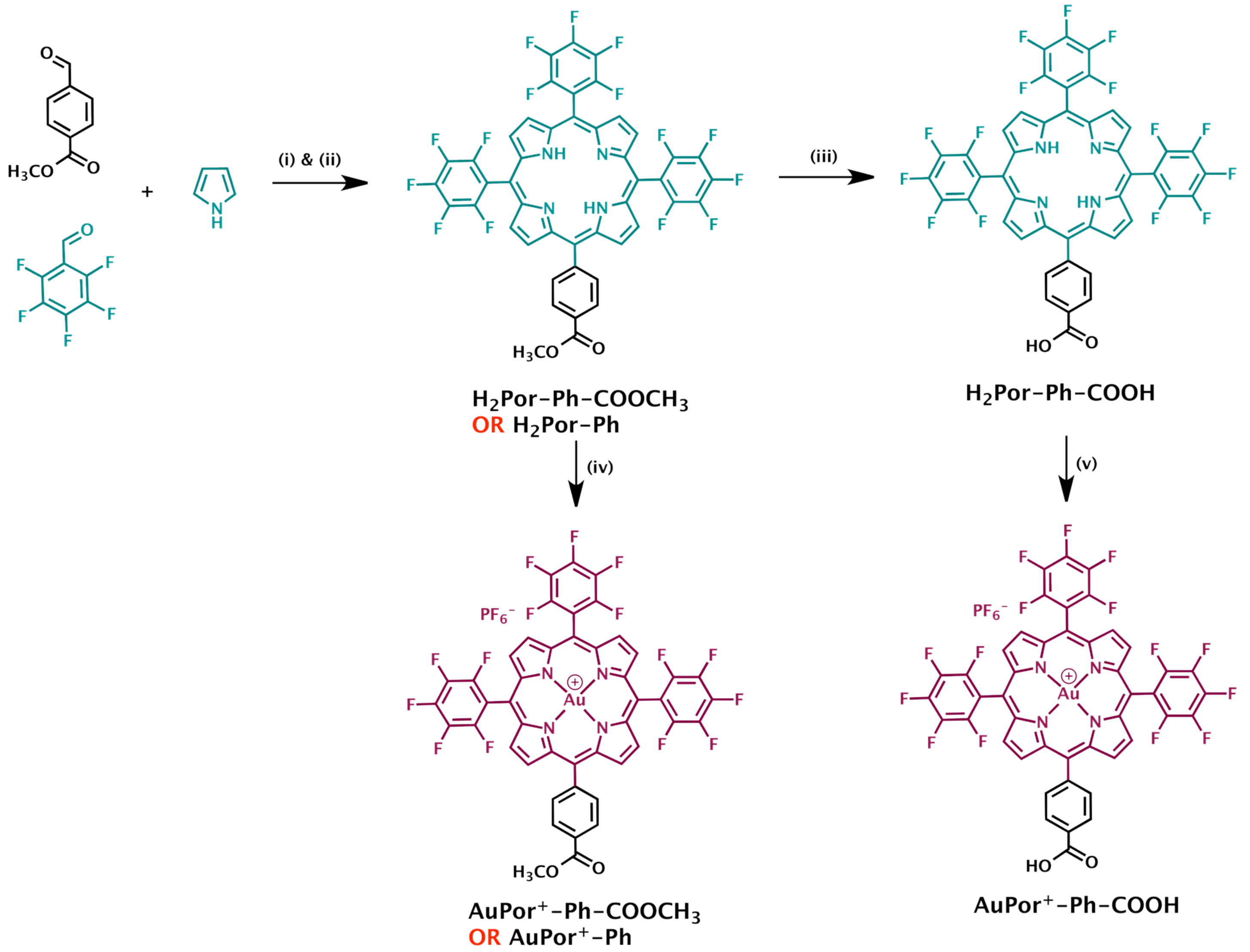
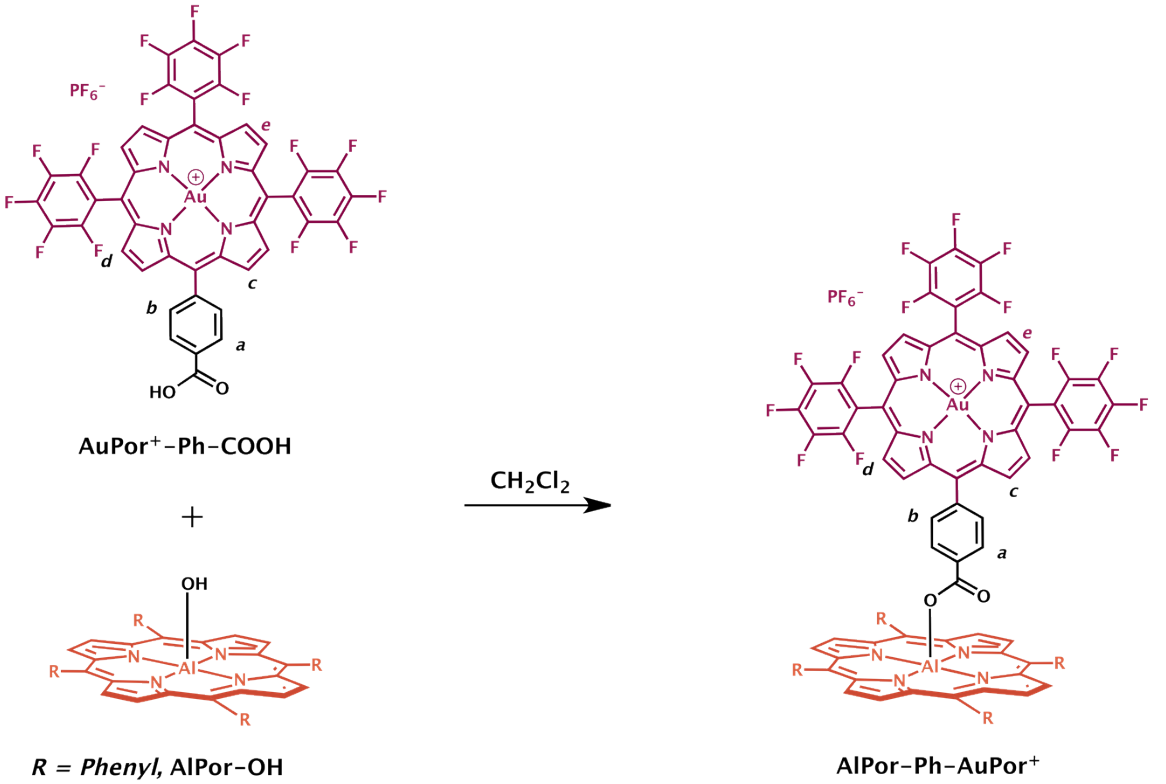


Scheme S1. Synthesis of gold(III) porphyrin derivatives. Reaction conditions: (i) $BF_3.OEt_2$, dichloromethane, 3 h, room temperature, N_2 (ii) p-chloranil, 12 h (iii) TFA, HCl, reflux, 48 h (iv) & (v) $AuCl_3$, AcOH, NaOAc, reflux, 16 h.



Scheme S2. Synthesis of the investigated dyad AlPor-Ph-AuPor$^+$. Reaction conditions: dichloromethane, 12 h, room temperature, N_2.

Preparation of AuPor-Ph-COOH.PF$_6$: **H_2Por-Ph-COOH (75 mg, 0.081 mmol), $AuCl_3$ (70 mg, 0.23 mmol) and NaOAc (260 mg, 3.23 mmol) were added to 10 mL of acetic acid. The resulting solution was refluxed for 16 h under nitrogen atmosphere. After reaction time, the reaction mixture was poured into water and extracted with dichloromethane. The collected organic layer was dried over Na_2SO_4 and then the solvent was removed under vacuum. The obtained solid was dissolved in methanol and precipated with aquous saturated NH_4PF_6. The obtained precipitate was collected by filtration and air-dried. The crude product was purified by silicagel column chromatography using dichloromethane:methanol (90:10) as an eluent. Yield: 20 mg (20%). ESI MS: *m/z* 1123.0444 for $[M-PF_6]^+$, calculated 1123.0459 for $C_{45}H_{13}AuF_{15}N_4O_2$.** ^1H NMR (300 MHz, CD_3CN): 9.69 (s, 4H), 9.62 (s, 4H), 8.61 (d, 2H, *J* = 7.8 Hz), 8.40 (d, 2H, *J* = 7.8 Hz). ^{31}P NMR (112 MHz, CD_3CN): −143.38 (sep). 1H NMR ($CDCl_3$, 300 MHz): 9.52 (d, 2H, *J* = 5.32 Hz), 9.47 (s, 4H), 9.39 (d, 2H, *J* = 5.32 Hz), 8.54 (d, 2H, *J* = 8.0 Hz), 8.25 (d, 2H, *J* = 8.0 Hz).

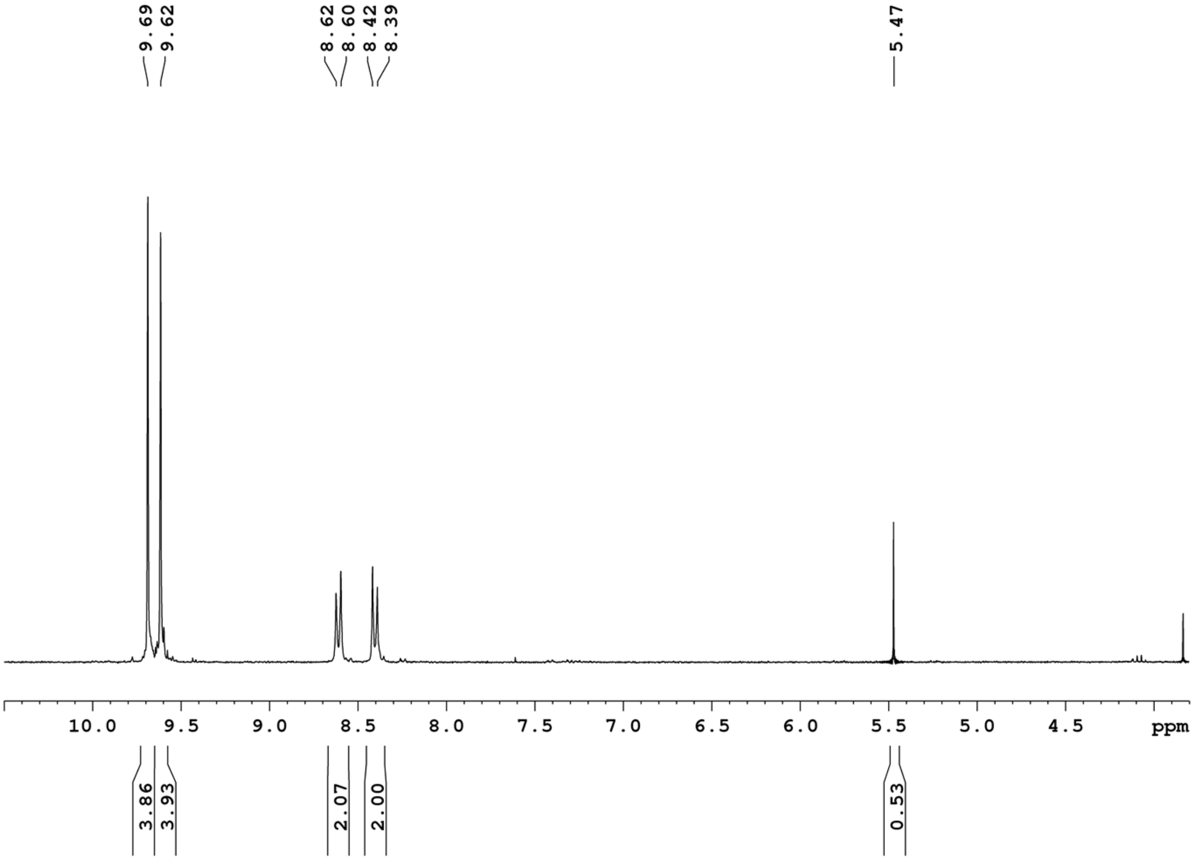


Fig. S1 ^{1}H NMR (300 MHz) spectrum of AuPor-Ph-COOH.PF_6 in CD_3CN. Note that the peaks at 5.45 and 3.81 ppm are due to solvent impurities.

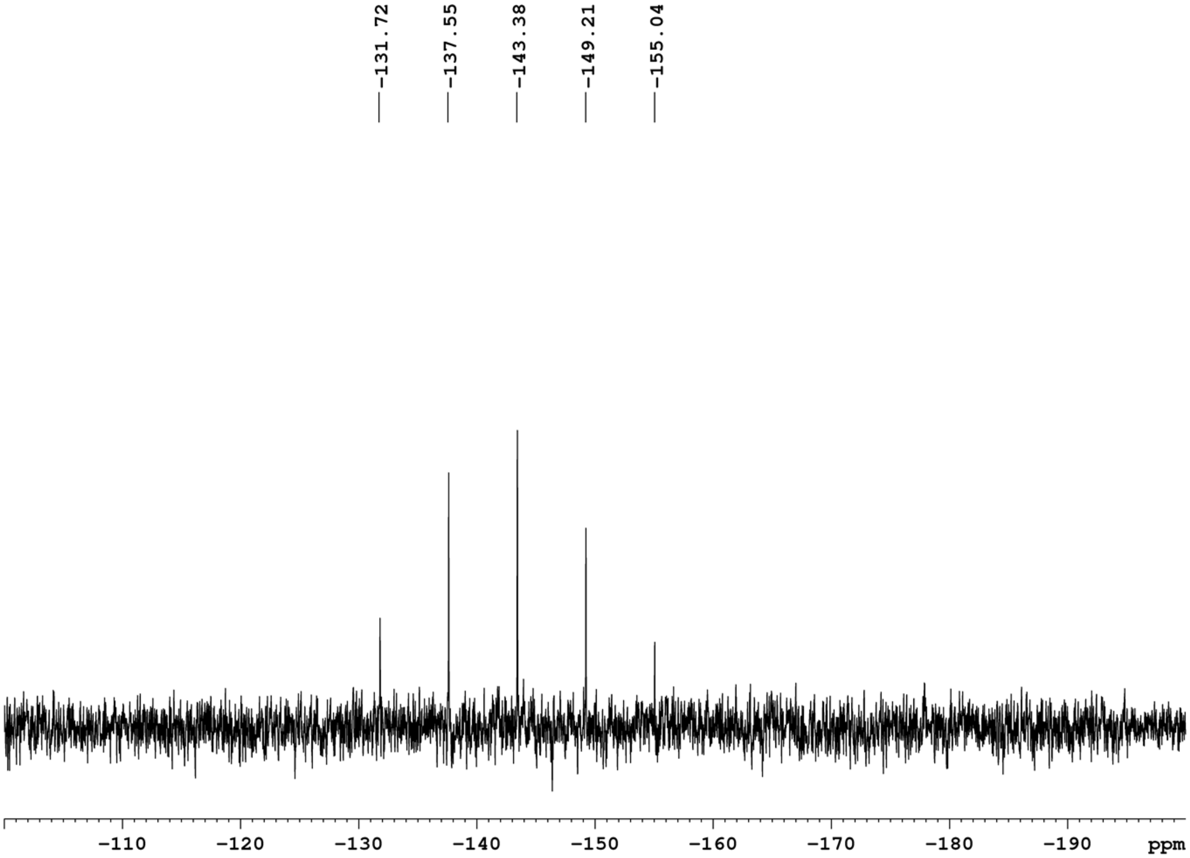


Fig. S2 ^{31}P NMR (121 MHz) spectrum of AuPor-Ph-COOH.PF$_6$ in CD$_3$CN

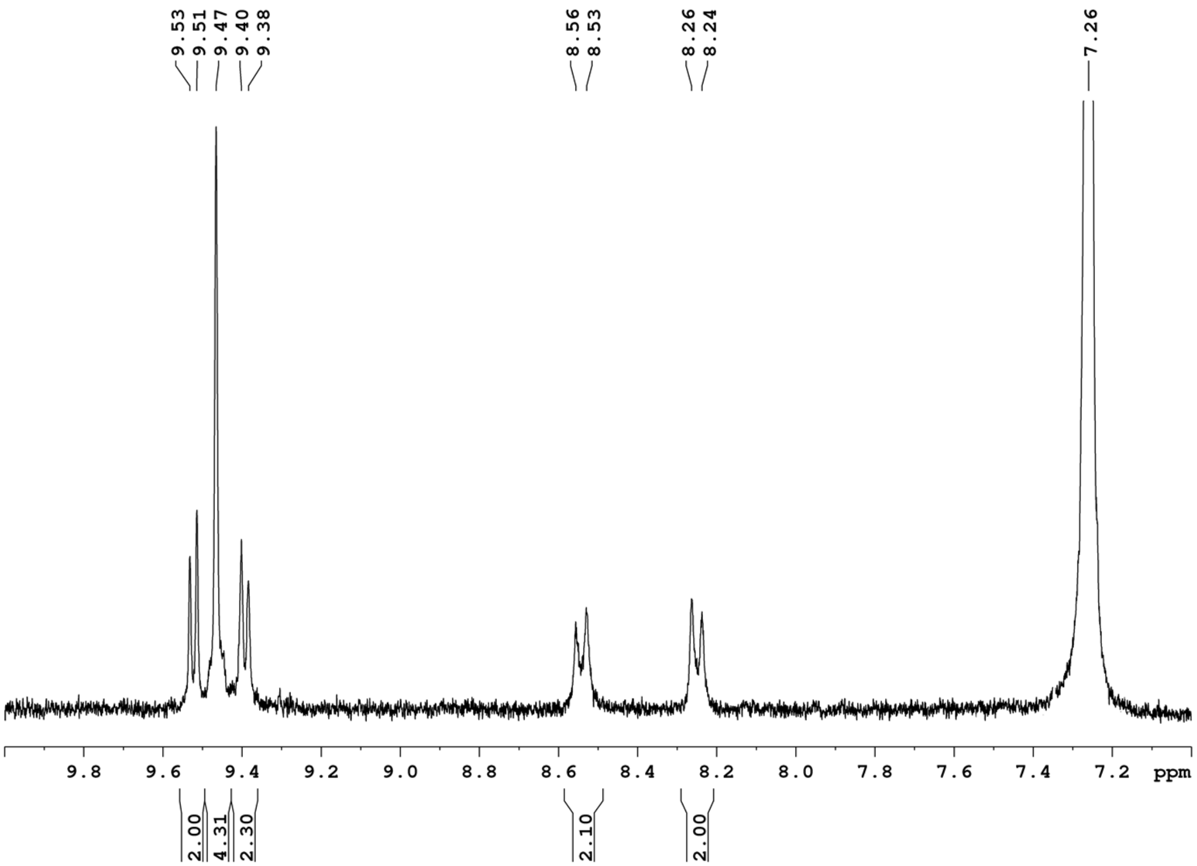


Fig. S3 ^{1}H NMR (300 MHz) spectrum of AuPor-Ph-COOH.PF$_6$ in CDCl$_3$.

Preparation of AuPor-Ph-COOCH$_3$.PF$_6$: **H$_2$Por-Ph-COOCH$_3$** (100 mg, 0.11 mmol), AuCl$_3$ (100 mg, 0.33 mmol) and NaOAc (300 mg, 3.65 mmol) were added to 10 mL of acetic acid. **The resulting solution was refluxed for 16 h under nitrogen atmosphere. After reaction time, the reaction mixture was poured into water and extracted with dichloromethane. The collected organic layer was dried over Na$_2$SO$_4$ and then the solvent was removed under vacuum. The obtained solid was dissolved in methanol and was precipated with aqueous saturated NH$_4$PF$_6$. The obtained precipitate was collected and air dried. The crude product was purified by silicagel column chromatography using dichloromethane:methanol (90:10) as an eluent. Yield: 34 mg (25%)**. FAB MS: m/z 1137.0607 for $[M-PF_6]^+$, calcualted 1137.0616 for $C_{46}H_{15}AuF_{15}N_4O_2$. ^{1}H NMR (300 MHz, CD$_3$CN): 9.68 (s, 4H), 9.61 (d, 2H, J = 6.0 Hz), 9.53 (d, 2H, J = 6.0 Hz), 8.56 (d, 2H, J = 6.0 Hz), 8.44 (d, 2H, J = 6.0 Hz), 4.12 (s, 3H).

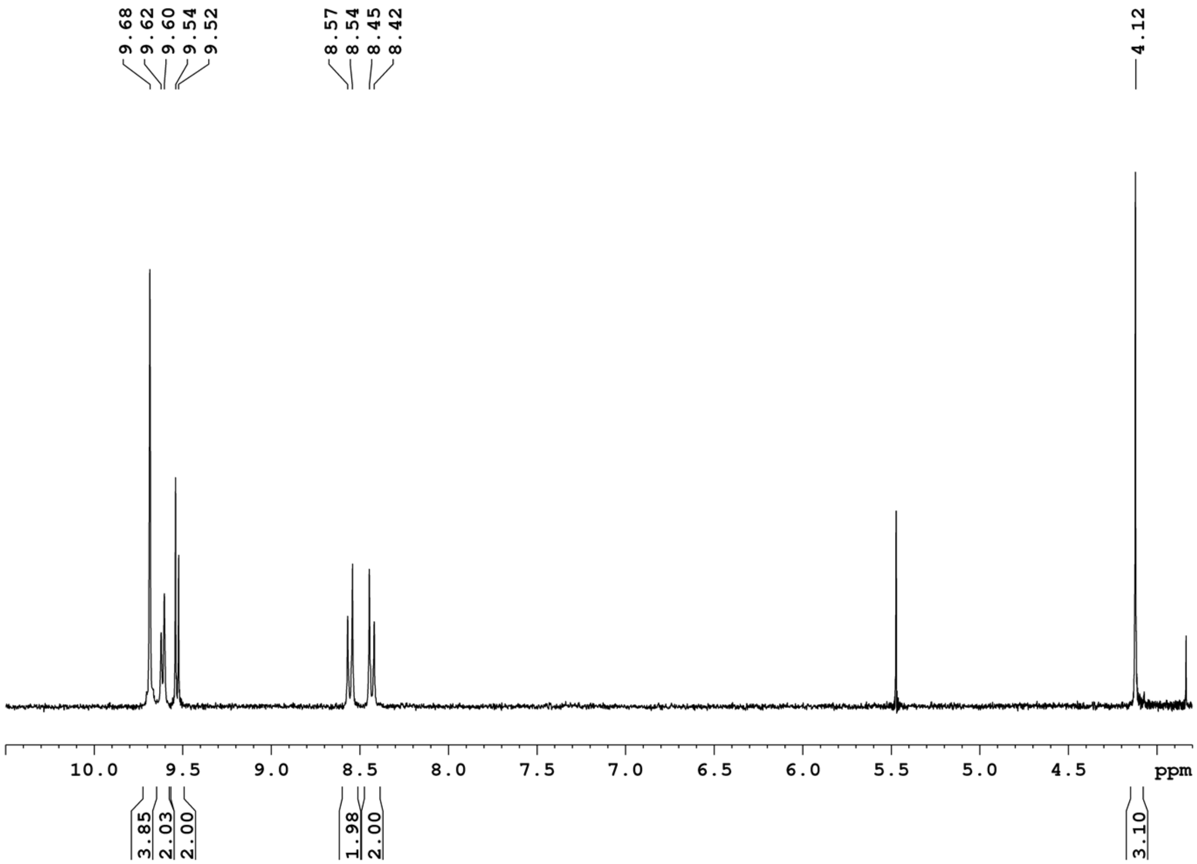


Fig. S4 ^{1}H NMR (300 MHz) spectrum of AuPor-Ph-COOCH$_3$.PF$_6$ in CD$_3$CN. Note that the peaks at 5.45 and 3.81 ppm are due to solvent impurities.

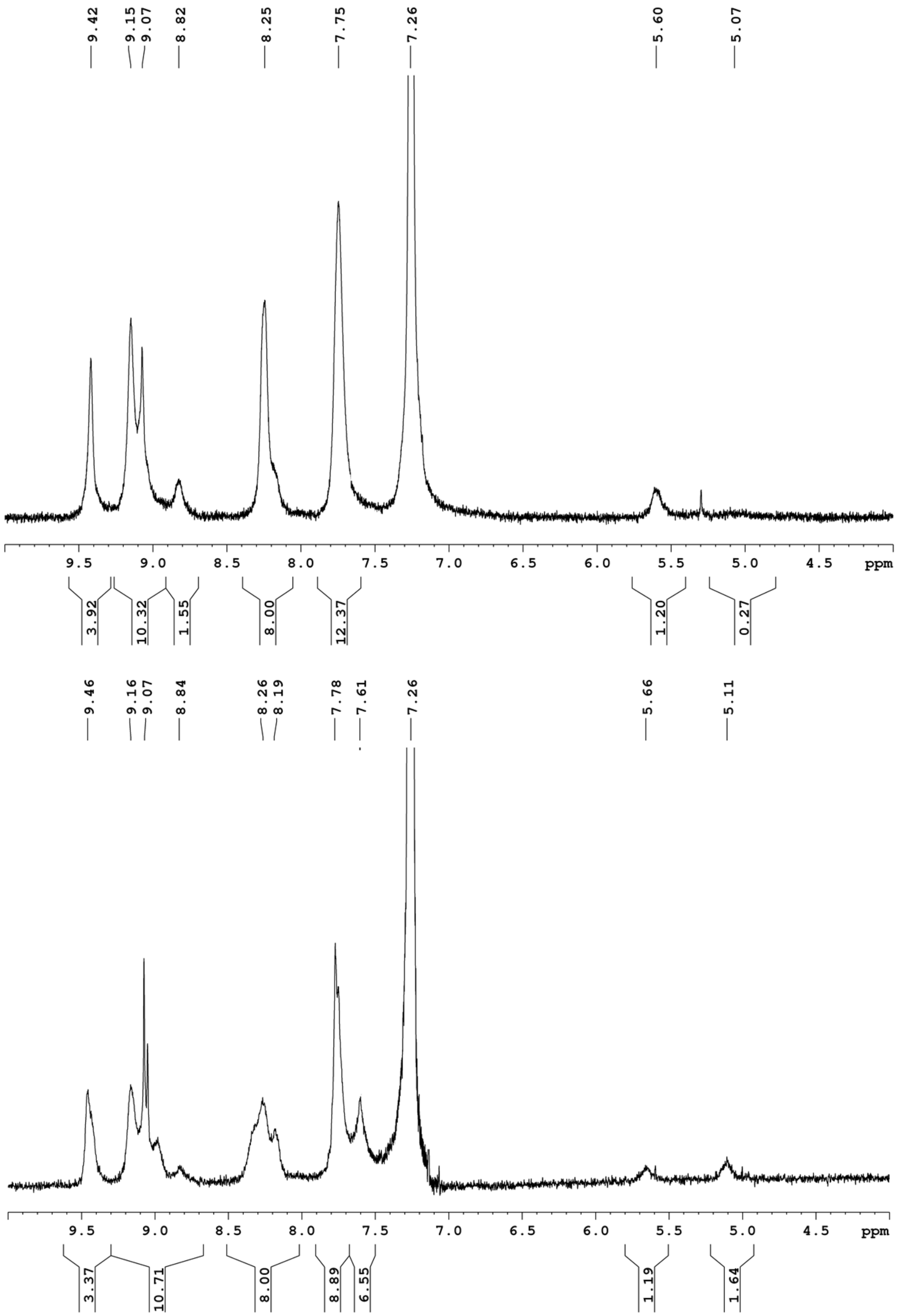


Fig. S5 ^{1}H NMR (300 MHz) spectra of AlPor-Ph-AuPor.PF$_6$ at ~1 mM (top) and ~2mM (bottom) concentrations in CDCl$_3$.

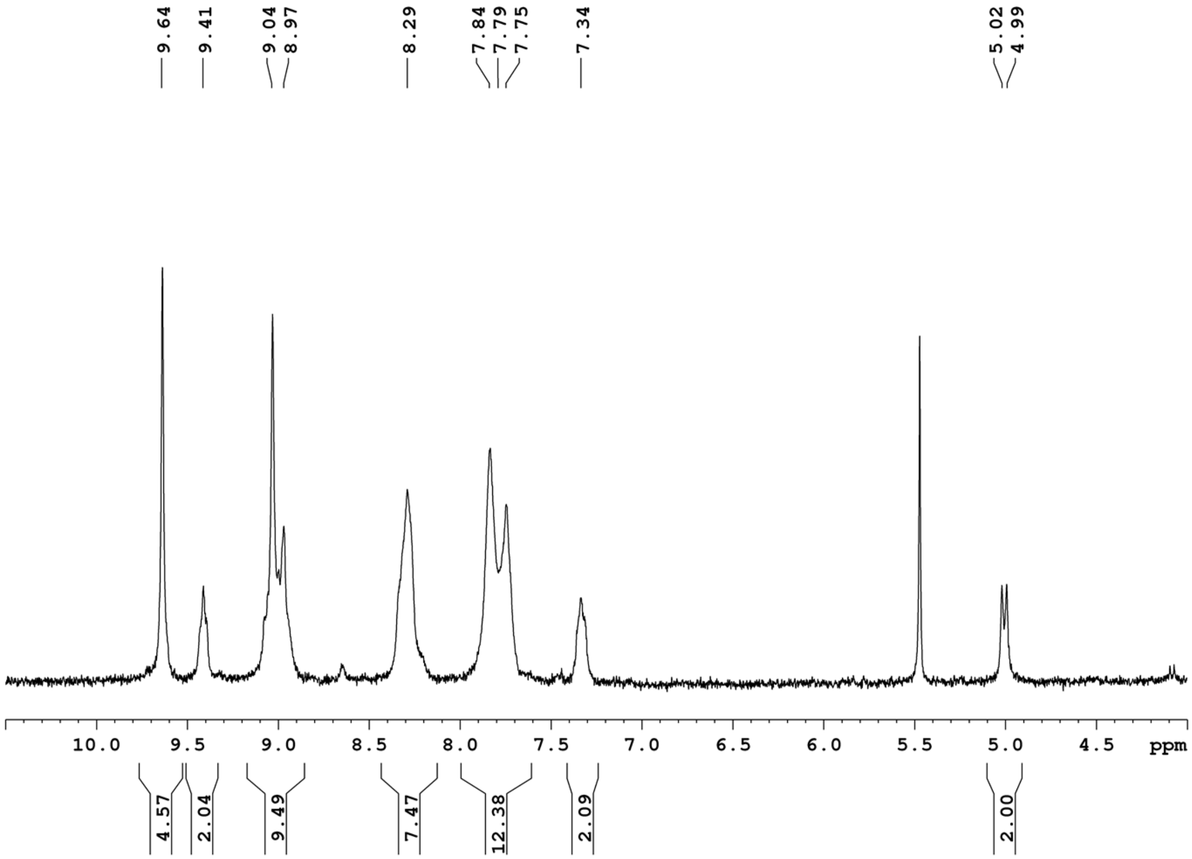


Fig. S6 ^{1}H NMR (300 MHz) spectrum of AlPor-Ph-AuPor.PF$_6$ (~2 mM) in CD$_3$CN.

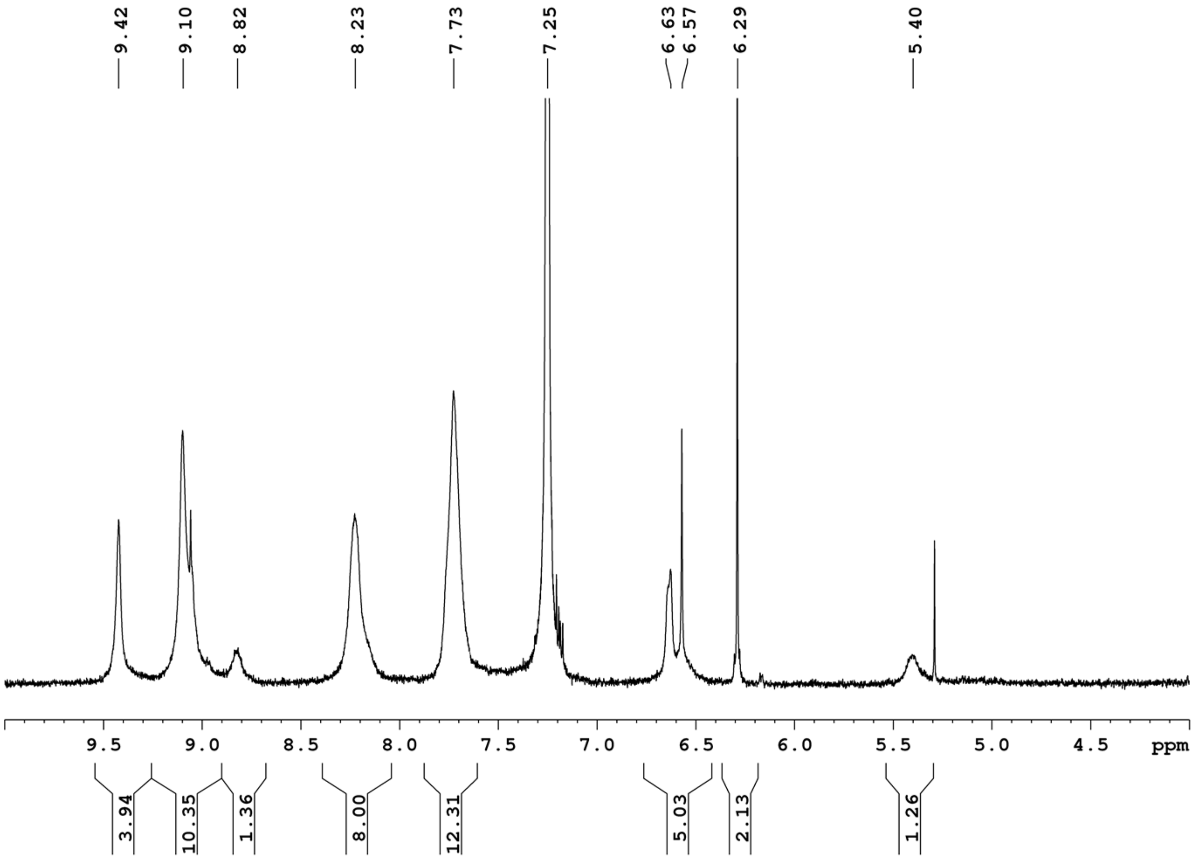


Fig. S7 ^{1}H NMR (300 MHz) spectrum of 1 mM TTF-py→AlPor-Ph-AuPor$^+$ in CDCl$_3$.

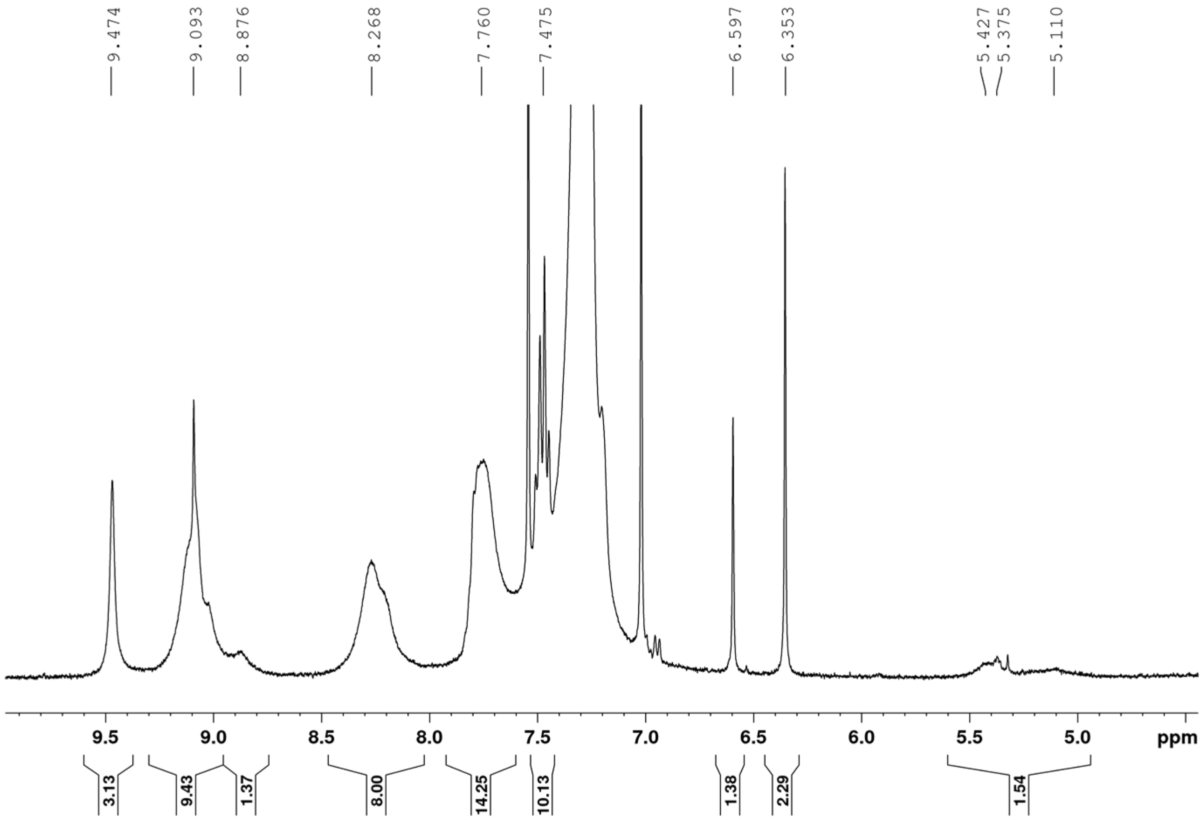


Fig. S8 ^{1}H NMR (400 MHz) spectrum of 0.6 mM TTF-Ph-py→AlPor-Ph-AuPor$^+$ in CDCl$_3$. Note that peaks at 7.55, 7.26 and 7.06 are due to the solvent.

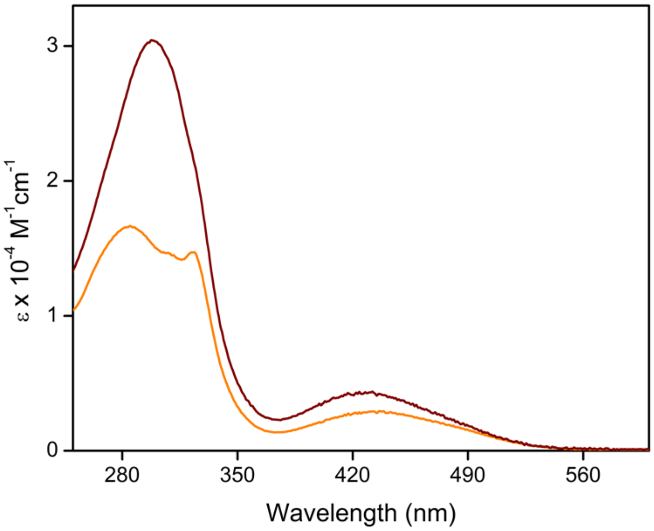


Fig. S9 UV-visible absorption spectra of TTF-py (orange) and TTF-Ph-py (maroon) in dichloromethane.

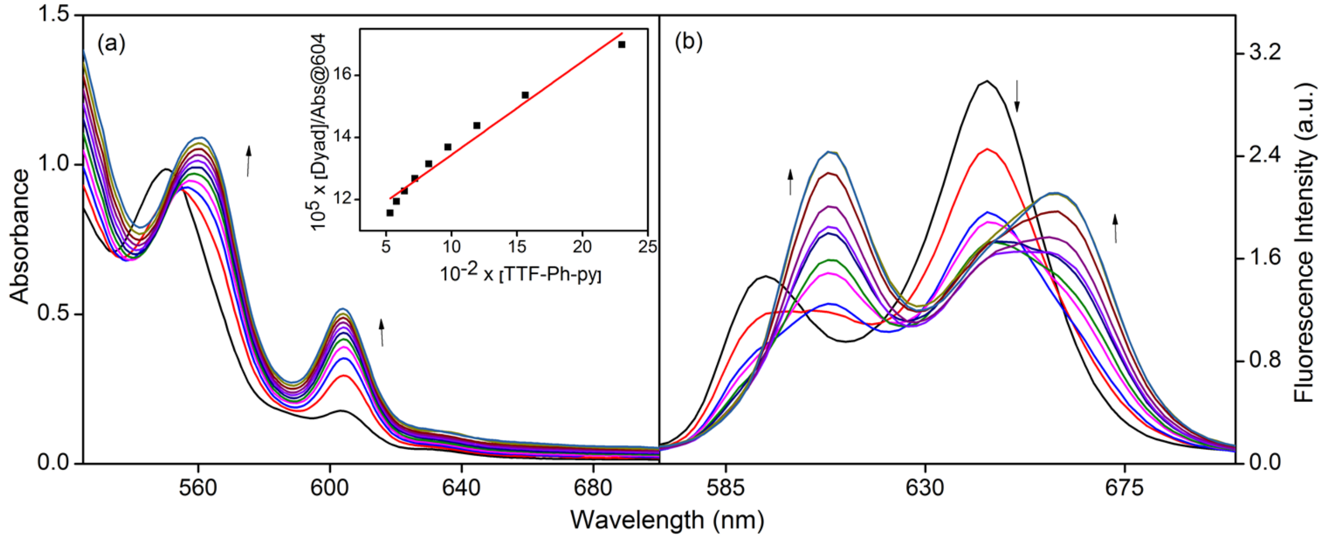


Fig. S10 (a) Absorption titrations and (b) fluorescence titration of AlPor-Ph-AuPor$^+$ with TTF-Ph-py in dichloromethane. The inset shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. TTF-Ph-py was added up to 1.88×10^{-3} M in 20 µL (2.22×10^{-4} M) increments to 1 mL (6×10^{-5} M) solution of dyad. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

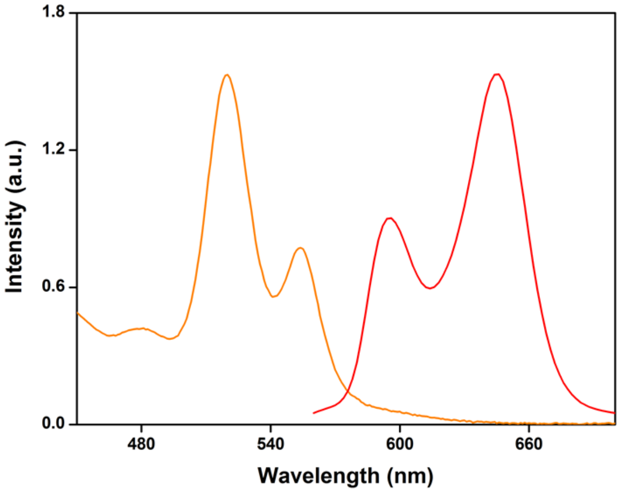


Fig. S11 Spectral overlap between the AlPor emission (red) and AuPor$^+$ absorption (orange) spectra in dichloromethane.

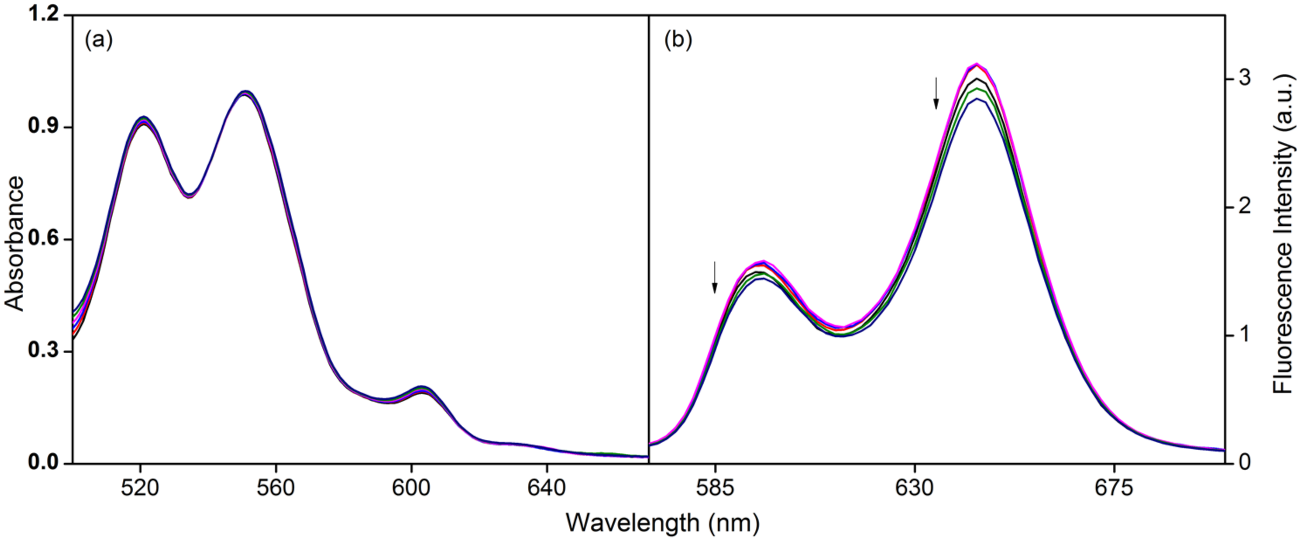


Fig. S12 (a) Absorption titrations and (b) fluorescence titration of AlPor-Ph-AuPor$^+$ with TTF in dichloromethane. TTF was added up to 1.88×10^{-3} M in 20 μL (2.22×10^{-4} M) increments to 1 mL (6×10^{-5} M) solution of dyad. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

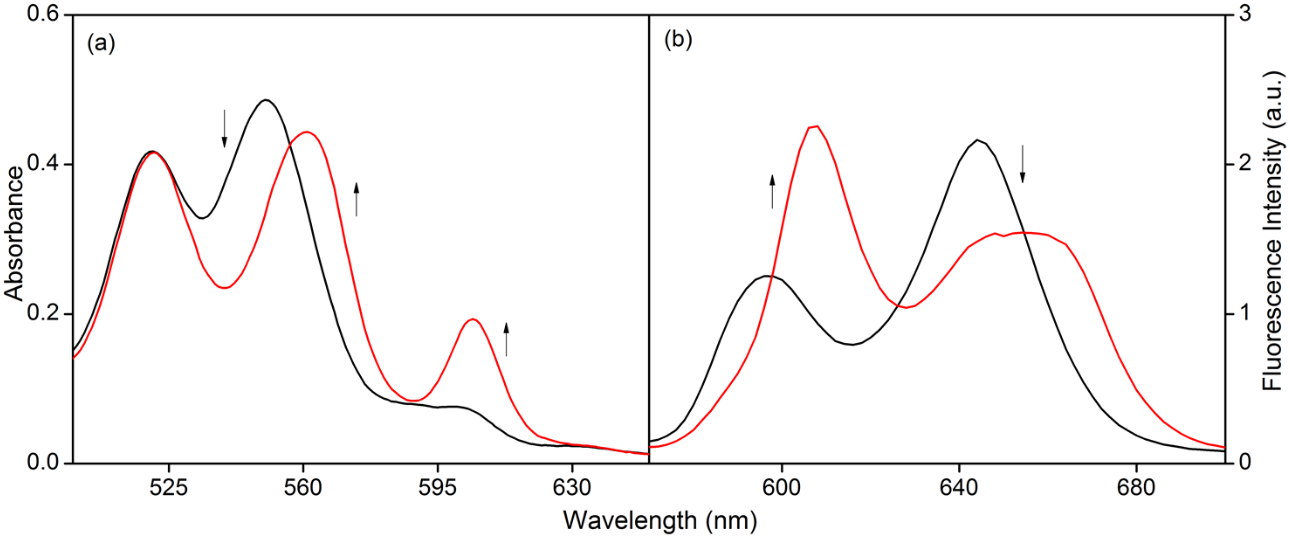


Fig. S13 (a) Absorption titrations and (b) fluorescence titration of AlPor-Ph-AuPor$^+$ with py in dichloromethane. Pyridine was added up to 3.80×10^{-3} M to 1 mL (2.4×10^{-5} M) solution of dyad. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

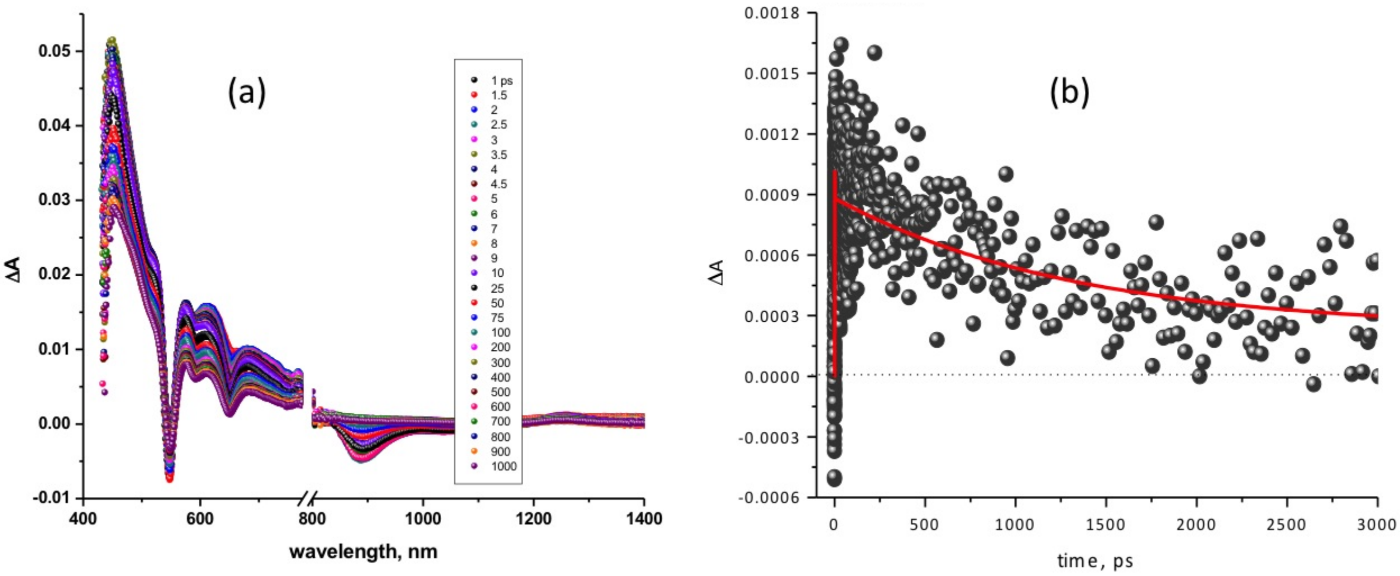


Fig. S14 (a) Femtosecond transient absorption spectra and (b) decay profile at 1247 nm of AlPor-Ph in *o*-DCB.