

**Ethynyl Thiophene Appended Unsymmetrical Zinc Porphyrin Sensitizers for
Dye-Sensitized Solar Cells: Synthesis, Spectral, Electrochemical, and
Photovoltaic Properties**

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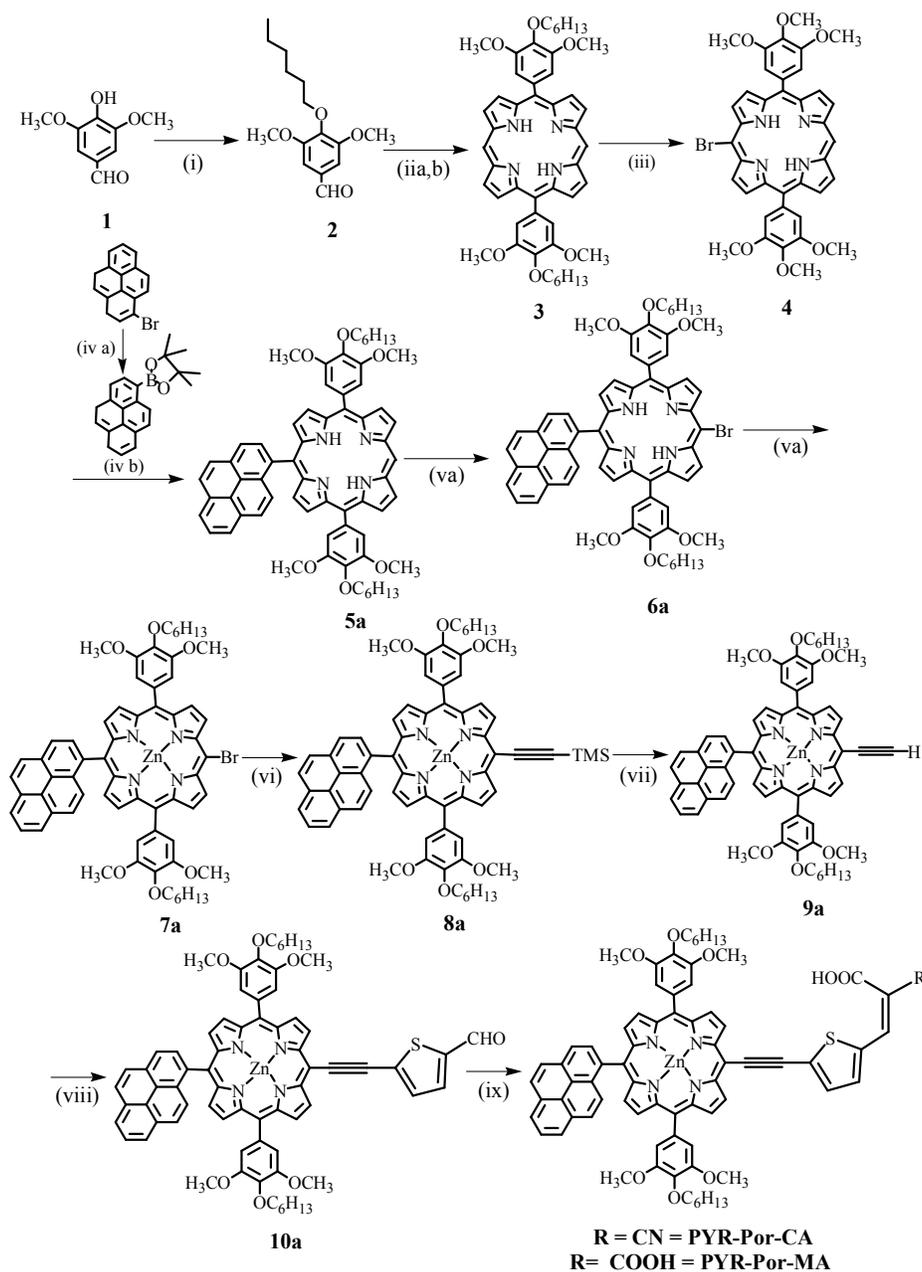
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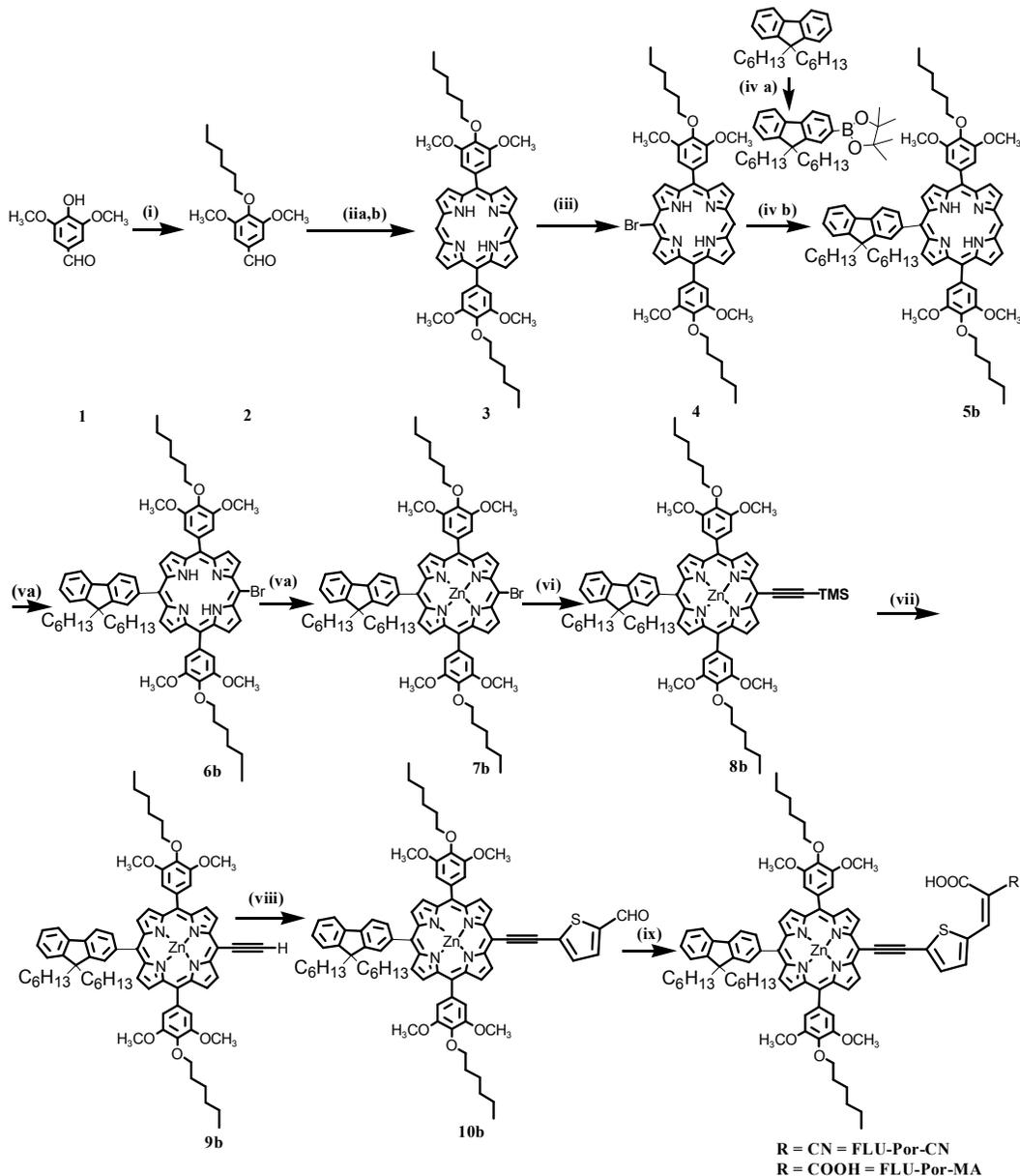
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Synthetic Scheme of PYR-Por-CA and PYR-Por-MA



(i) DMF, K_2CO_3 , reflux 4h (iia) Dipyrromethane, CH_2Cl_2 , TFA, RT (iib) DDQ, TEA, RT (iii) NBS, CH_2Cl_2 , RT (iva,b) $Pd(PPh_3)_4$, $Cs(CO)_3$, Toluene, reflux, 12h (va) NBS, CH_2Cl_2 , RT (vb) $Zn(OAc)_2$, $CHCl_3/CH_3OH$, reflux, 2h (vi) TMSA, TEA, $Pd(PPh_3)_2Cl_2$, CuI, 50 °C, 8h (vii) K_2CO_3 , CH_3OH/CH_2Cl_2 , RT, 3h (viii) 5-bromothiophene-2-carboxaldehyde, TEA, $Pd(PPh_3)_2Cl_2$, CuI, 50 °C, 8h (ix) Cyanoacetic acid (**PYR-Por-CA**) or malonic acid (**PYR-Por-MA**), $CHCl_3/CH_3CN$ (3:1), piperidine, reflux, 8h.

Synthetic Scheme of FLU-Por-CA and FLU-Por-MA



(i) DMF, K_2CO_3 , reflux 4h (iia) Dipyrromethane, CH_2Cl_2 , TFA, RT (iib) DDQ, TEA, RT (iii) NBS, CH_2Cl_2 , RT (iva,b) $Pd(PPh_3)_4$, $Cs(CO)_3$, Toluene, reflux, 12h (va) NBS, CH_2Cl_2 , RT (vb) $Zn(OAc)_2$, $CHCl_3/CH_3OH$, reflux, 2h (vi) TMSA, TEA, $Pd(PPh_3)_2Cl_2$, CuI , 50 °C, 8h (vii) K_2CO_3 , CH_3OH/CH_2Cl_2 , RT, 3h (viii) 5-bromothiophene-2-carboxaldehyde, TEA, $Pd(PPh_3)_2Cl_2$, CuI , 50 °C, 8h (ix) Cyanoacetic acid (**FLU-Por-CA**) or malonic acid (**FLU-Por-MA**), $CHCl_3/CH_3CN$ (3:1), piperidine, reflux, 8h.

Detailed Synthetic Procedure:

4-(hexyloxy)-3,5-dimethoxybenzaldehyde (2)

3,5-dimethoxy-4-hydroxy-benzaldehyde (5g, 0.0275 mole), 1-hexylbromide (7.7 ml, 0.055 mole) and K_2CO_3 were added to 10 ml of dried, dry DMF under nitrogen atmosphere. The reaction mixture was heated to reflux for 4h. After cooling to room temperature, the solution was extracted with ice cold water and ether. The organic phase was collected and evaporated to dryness. The brown liquid was purified by silica gel column using hexane/ $CHCl_3$ (2:1 v/v) mixture as eluent to yield pale yellow oil (92%). Elemental analysis of Anal. Calcd. For $C_{15}H_{22}O_4$ (266.33): C, 67.64; H, 8.33. Found: C, 67.60; H, 8.30. ESI-MS (m/z): $C_{15}H_{22}O_4$ [266.33]: M^+ 266 (100%). 1H NMR ($CDCl_3$, δ ppm): 9.87 (s, 1H), 7.05 (s, 2H), 3.94 (m, 2H), 3.73 (s, 6H), 1.75 (m, 2H), 1.29 (m, 6H), 0.96 (m, 3H).

5,15-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin (3)

Lindsey method was adopted for the synthesis of this porphyrin. This route involves the condensation of dipyrromethane and the substituted benzaldehyde in dry CH_2Cl_2 . The reaction mixture was degassed for 15min by purging with nitrogen, followed by drop wise addition of trifluoro acetic acid (TFA). The reaction mixture was protected from ambient light and allowed to stir at RT for 3h under nitrogen atmosphere. DDQ was added and the reaction mixture was allowed to stir for further 1h followed by quenching the acid catalyst using triethyl acetate (TEA). The product was purified by silica gel column chromatography using CH_2Cl_2 as the eluant to yield purple powder(15% yield). Elemental analysis of Anal. Calcd. For $C_{48}H_{54}N_4O_6$ (782.96): C, 73.63; H, 6.95; N, 7.16. Found: C, 73.60; H, 6.97; N, 7.20. ESI-MS (m/z): $C_{48}H_{54}N_4O_6$ [782.96]: M^+ 784 (100%). 1H NMR ($CDCl_3$, δ ppm): 10.35 (s, 2H), 9.05 (dd, 8H), 7.51 (s, 4H), 4.15 (m, 4H), 3.95 (s, 12H), 2.00 (m, 4H), 1.55 (m, 12H), 0.96 (m, 6H), -3.05 (b, 2H). UV-Vis (CH_2Cl_2) λ_{max} (nm) ($\log \epsilon$ $M^{-1} cm^{-1}$) : 410(5.81), 504(4.20), 539(3.8), 577(3.74), 632(3.21).

5-bromo-10,20- Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin (4)

Porphyrin (3) (100mg, 0.13mmol) was dissolved in 80ml of CH_2Cl_2 and the solution was cooled to 0° C. To this N-bromosuccinamide (28mg, 0.16mmol in 8 ml of CH_2Cl_2), was added drop

wise. The reaction was allowed to stir for 12 min, washed with water and purified by silica gel column chromatography using $\text{CHCl}_3/\text{Hexane}$ (3:1 v/v) as the eluent. The second band was the desired product (50% yield). Elemental analysis of Anal. Calcd. For $\text{C}_{48}\text{H}_{53}\text{BrN}_4\text{O}_6$ % (861.86): C, 66.89; H, 6.20; N, 6.50. Found: C, 66.90; H, 6.30; N, 7.50. ESI-MS (m/z): $\text{C}_{48}\text{H}_{53}\text{BrN}_4\text{O}_6$ [861.86]: M^+-Br 784 (100%). ^1H NMR (CDCl_3 , δ ppm): 10.35 (s, 1H), 9.82 (d, 2H), 9.15 (d, 2H), 9.00 (dd, 4H), 7.45 (s, 4H), 4.20 (m, 4H), 3.95 (s, 12H), 2.00 (m, 4H), 1.55 (m, 12H), 0.97 (m, 6H), -3.00 (b, 2H). UV-Vis (CH_2Cl_2) λ_{max} (nm) ($\log \epsilon \text{ M}^{-1} \text{ cm}^{-1}$) : 419(5.75), 514(3.30), 549(3.75), 589(3.71), 646(4.20).

5-pyrenyl-10,20- Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin (5a)

Monobromo porphyrin (**4**) (190 mg, 0.24 mmol) was dissolved in 40 ml of dry Toluene, to which CsCO_3 (393.6 mg, 1.2 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.25 equivalents) and 1-pyrenylborane (218 mg, 0.713 mmol) were added and the reaction mixture was refluxed under nitrogen atmosphere for 12 h. After cooling to RT, the crude mixture was purified using silica gel column with EtOAc/Hex (1:4 v/v) to afford the desired product (90% yield). Elemental analysis of Anal. Calcd. For $\text{C}_{64}\text{H}_{62}\text{N}_4\text{O}_6$ % (983.20): C, 78.18; H, 6.36; N, 5.70. Found: C, 78.20; H, 6.33; N, 5.68. ESI-MS (m/z): $\text{C}_{64}\text{H}_{62}\text{N}_4\text{O}_6$ [983.20]: M 984 (100%). ^1H NMR (CDCl_3 , δ ppm): 10.25 (s, 1H), 9.37 (d, 2H), 9.14 (d, 2H), 8.90 (dd, 2H), 8.70 (s, 1H), 8.46 (m, 6H), 8.05 (m, 2H), 7.45 (m, 6H), 4.28 (m, 4H), 3.95 (s, 12H), 1.99 (m, 4H), 1.55 (m, 12H), 0.97 (m, 6H), -2.78 (b, 2H). UV-Vis (CH_2Cl_2) λ_{max} (nm) ($\log \epsilon \text{ M}^{-1} \text{ cm}^{-1}$): 419 (5.81), 511 (4.44), 547(3.85), 584 (3.81), 640 (3.33).

5-fluorenyl-10,20- Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin (5b)

This compound was synthesized by adopting a similar procedure that was used to prepare **5a**. ^1H NMR(CDCl_3 , 300MHz): δ = 2.95 (s, 2H), 0.78 (m,12H), 0.98 (m, 8H), 1.25 (m, 8H), 1.45 (m, 10H), 1.60 (m, 4H), 2.1 (m, 8H), 3.95 (s, 12H), 4.31(t, 4H), 7.50 (m, 7H), 7.91-8.29 (m, 4H), 8.94(d, 4H), 9.13(d, 2H), 9.35 (s, 2H), 10.21 (s, 1H). ESI-MS: m/z $\text{C}_{73}\text{H}_{86}\text{N}_4\text{O}_6$: calculated : 1115.49, found : 1115 [M^+]. UV-Vis (CH_2Cl_2) λ_{max} (nm) ($\log \epsilon$): 272 (1.5), 306 (4.4), 418 (5.9), 512 (4.3), 547 (3.9), 587 (3.8), 641(3.5).

5-pyrenyl-15-bromo-10,20- Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin (6a)

Pyrenyl porphyrin (**5a**) (65mg, 0.065mmol) was dissolved in 30 ml of CH₂Cl₂ and the solution was cooled to 0° C. To this N-bromosuccinamide (14.3mg, 0.078 mmol dissolved in 3 ml of CH₂Cl₂), was added drop wise. The reaction was allowed to stir for 12 min, washed with water and purified by silica gel column chromatography using CHCl₃/Hexane (3:1 v/v) as the eluent to get the desired product in 80% yield. Elemental analysis of Anal. Calcd. For C₆₄H₆₁BrN₄O₆% (1060.37): C, 72.37; H, 5.79; N, 5.28. Found: C, 72.35; H, 5.80; N, 5.30. ESI-MS (m/z): C₆₄H₆₁BrN₄O₆ [1060.37]: M³⁺ 1057 (50%), [C₆₄H₆₁BrN₄O₆-Br] 984 (100%). ¹H NMR (CDCl₃, δppm): 9.71 (d, 2H), 9.14 (d, 2H), 8.90 (dd, 2H), 8.70 (s, 1H), 8.46 (m, 6H), 8.05 (m, 2H), 7.45 (m, 6H), 4.27 (m, 4H), 3.89 (s, 12H), 1.99 (m, 4H), 1.55 (m, 12H), 0.97 (m, 6H), -2.55 (b, 2H). UV-Vis (CH₂Cl₂) λ_{max} (nm) (log ε M⁻¹ cm⁻¹) : 427(5.90), 521(4.21), 557(3.80), 597(3.67), 654(3.50).

5-fluorenyl-15-bromo-10,20- Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin (6b)

This compound was synthesized by adopting a similar procedure that was used to prepare **6a** ¹H NMR(CDCl₃, 300MHz): δ = 0.81 (m, 12H), 0.99 (m, 8H), 1.22 (m, 8H), 1.42 (m, 10H), 1.62 (m, 4H), 2.04 (m, 8H), 3.99 (s, 12H), 4.29 (m, 4H), 7.24 (m, 7H), 7.98-8.27 (m, 4H), 8.99 (d, 4H), 9.05 (d, 2H), 9.29 (s, 2H). ESI-MS: m/z C₇₃H₈₅BrN₄O₆ : calculated : 1194.38, found : 1195[(M+H)⁺]. UV-Vis(CH₂Cl₂) λ_{max}(nm)(logε) : 268 (1.5), 307(4.4), 425(5.9), 521(4.3), 557(4.1), 599(3.7), 655(3.7).

5-pyrenyl-15-bromo-10,20- Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (7a)

Porphyrin (**6a**) (50mg, 0.051 mmol) and Zn(OAc)₂ (0.51 mmol) were dissolved in CHCl₃/MeOH (4:1 v/v) mixture and heated to reflux until Q-band absorption has changed. Then the reaction mixture cooled to RT, washed with water and recrystallised from CHCl₃/MeOH mixture to yield 95% of **7**. Elemental analysis of Anal. Calcd. For C₆₄H₅₉BrN₄O₆Zn% (1125.47): C, 68.30; H, 5.28; N, 4.98. Found: C, 68.32; H, 5.30; N, 5.00. ESI-MS (m/z): C₆₄H₅₉BrN₄O₆Zn [1125.47]: M 1126 (50%). ¹H NMR (CDCl₃, δppm): 9.77 (d, 2H), 9.10 (d, 2H), 8.81 (dd, 2H), 8.70 (s, 1H), 8.46 (m, 6H), 8.05 (m, 2H), 7.45 (m, 6H), 4.18 (m, 4H), 3.87 (s, 12H), 1.99 (m, 4H), 1.55 (m, 12H), 0.97 (m, 6H). UV-Vis (CH₂Cl₂) λ_{max} (nm) (log ε M⁻¹ cm⁻¹) 428(5.91), 554(4.22), 593(3.61).

*5-fluorenyl-15-bromo-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin
zinc(II) (7b)*

This compound was synthesized by adopting a similar procedure that was used to prepare **7a**. ¹H NMR(CDCl₃, 300MHz): δ = 0.88 (m,12H), 0.99(m, 8H), 1.30(m,8H), 1.45(m, 10H), 1.64 (m, 4H), 1.95 (m, 4H), 2.08 (m, 4H), 3.95(s, 12H), 4.26(t, 4H), 7.44(m, 7H), 7.92-8.20 (m, 4H), 8.97 (d, 4H), 9.10(d, 2H), 9.80 (s, 2H), 10.21(s, 1H) . ESI-MS: *m/z* C₇₃H₈₃BrN₄O₆ : calculated : 1257.789, found : 1258 [(M+H)⁺]. UV-Vis(CH₂Cl₂) λ_{max}(nm)(logε) : 263(4.4), 307(4.3), 426(5.9), 553(4.3), 594(4.4).

*5-pyrenyl-15-trimethylsilylethynyl-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin
zinc(II) (8a)*

Porphyrin (**7a**) (64 mg, 0.056 mmol) and Pd(PPh₃)₂Cl₂ (6.91mg, 0.006mmol) were dissolved in 10 ml of dry triethyl amine (TEA) to which trimethylsilylacetylene (0.036ml, 0.28mmol) and CuI (1.14 mg, 0.006 mmol) were added and the solution was heated to 50 °C for 8h. After cooling to RT, the crude mixture was washed with water and extracted with CHCl₃. The green product was subjected to silica gel column with CHCl₃/Hexane (3:1 v/v) as the eluent to afford the desired product (85% yield). Elemental analysis of Anal. Calcd. For C₆₉H₆₈N₄O₆SiZn% (1142.77): C, 72.52; H, 6.00; N, 4.90. Found: C, 72.55; H, 5.98; N, 4.91. ESI-MS (*m/z*): C₆₉H₆₈N₄O₆SiZn [1142.77]: M⁺ (35%). ¹H NMR (CDCl₃, δppm): 9.73 (d, 2H), 9.03 (d, 2H), 8.90 (dd, 2H), 8.70 (s, 1H), 8.46 (m, 6H), 8.05 (m, 2H), 7.45 (m, 6H), 4.18 (m, 4H), 3.96 (s, 12H), 1.93 (m, 4H), 1.44 (m, 12H), 0.97 (m, 6H), 0.63 (s, 9H). UV-Vis (CH₂Cl₂) λ_{max} (nm) (log ε M⁻¹ cm⁻¹) : 434(5.83), 561(4.22), 603(3.91).

*5-fluorenyl-15-trimethylsilylethynyl-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl] porphyrin
zinc(II) (8b)*

This compound was synthesized by adopting a similar procedure that was used to prepare **8a**. ¹H NMR(CDCl₃, 300MHz): δ = 0.64 (s, 9H), 0.87 (m,12H), 0.98(m, 8H), 1.16 (m,8H), 1.45(m, 10H), 1.46 (m, 4H), 1.99 (m, 4H), 2.11(m, 4H), 3.95(s, 12H), 4.26(t, 4H), 7.44(m, 7H), 7.92-8.20 (m, 4H), 8.97 (d, 4H), 9.10(d, 2H), 9.80 (s, 2H), 10.21(s, 1H) . ESI-MS: *m/z*

$C_{78}H_{92}N_4O_6SiZn$: calculated : 1275.08, found : 1275 $[M^+]$. UV-Vis(CH_2Cl_2) $\lambda_{max}(nm)$ (log ϵ) : 265(4.3), 307(4.3), 434(5.6), 563(4.2), 605(4.0).

5-pyrenyl-15-ethynyl-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (9a)

Porphyrin (**8a**) (65mg, 0.057mmol) and K_2CO_3 (0.5g) were dissolved in 30 ml of $CH_2Cl_2/MeOH$ mixture and allowed to stir at RT for 5h. The crude mixture was filtered to remove K_2CO_3 , washed with water and extracted with $CHCl_3$. Purification by silica gel column using $CHCl_3/Hexane$ (4:1 v/v) afforded a more polar green product (90% yield). Elemental analysis of Anal. Calcd. For $C_{66}H_{60}N_4O_6Zn$ (1070.59): C, 74.04; H, 5.65; N, 5.23. Found: C, 74.00; H, 5.68; N, 5.20. ESI-MS (m/z): $C_{66}H_{60}N_4O_6Zn$ [1070.59]: $M+Na$ (100). 1H NMR ($CDCl_3$, δ ppm): 9.82 (d, 2H), 9.12 (d, 2H), 8.80 (dd, 2H), 8.70 (s, 1H), 8.46 (m, 6H), 8.05 (m, 2H), 7.45 (m, 6H), 4.23 (m, 4H), 3.91 (s, 12H), 1.93 (m, 4H), 1.44 (m, 12H), 0.97 (m, 6H). UV-Vis (CH_2Cl_2) λ_{max} (nm) (log ϵ $M^{-1} cm^{-1}$) : 431(5.85), 557(4.54), 599(4.13).

5-fluorenyl-15-ethynyl-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (9b)

This compound was synthesized by adopting a similar procedure that was used to prepare **9a**. 1H NMR($CDCl_3$, 300MHz): δ = 0.86 (m,12H), 0.99(m, 8H), 1.44(m,8H), 1.55(m, 10H), 1.65 (m, 4H), 1.99 (m, 4H), 2.11 (m, 4H), 3.67 (s, 1H), 3.93(s, 12H), 4.33(t, 4H), 7.46(m, 7H), 7.90-8.25 (m, 4H), 8.98 (d, 4H), 9.12(d, 2H), 9.45 (s, 2H). ESI-MS: m/z $C_{75}H_{84}N_4O_6 Zn$: calculated : 1202.90 , found : 1204 $[(M+2H)^+]$. UV-Vis(CH_2Cl_2) $\lambda_{max}(nm)$ (log ϵ) : 267(4.5), 308(4.4), 430(5.7), 557(4.3), 600(5.0).

5-pyrenyl-15-(5-formylthiophene-2-yl)-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (10a)

Porphyrin **9a** (50 mg, 0.047 mmol) and $Pd(PPh_3)_2Cl_2$ (5.75 mg ,0.005 mmol) were dissolved in 10 ml of dry TEA to which 5-bromothiophene-2-carboxaldehyde (44.16 mg, 0.025 ml, 0.23 mmol) and CuI (0.95 mg, 0.005 mmol) were added and the solution was heated to 50 °C for 8h. After cooling to RT, the crude mixture was washed with water and extracted with $CHCl_3$. The green product was purified using silica gel column with $CHCl_3/Hexane$ (3:1 v/v) as the eluant to afford the desired product (85% yield). Elemental analysis of Anal. Calcd. For $C_{71}H_{62}N_4O_7SZn$ (1180.72): C, 72.22; H, 5.29; N, 4.75. Found: C, 72.20; H, 5.30; N, 4.70. ESI-MS (m/z):

$C_{71}H_{62}N_4O_7SZn$ [1180.59]: M (100%). 1H NMR ($CDCl_3$, δ ppm): 10.11 (s, 1H), 9.90 (d, 1H), 9.77 (s, 1H), 9.20 (d, 2H), 8.77 (m, 3H), 8.50 (m, 6H), 8.21 (m, 2H), 7.83 (m, 4H), 7.45 (m, 7H), 6.90 (s, 1H), 4.22 (m, 4H), 3.93 (s, 12H), 1.93 (m, 4H), 1.44 (m, 12H), 0.97 (m, 6H). UV-Vis (CH_2Cl_2) λ_{max} (nm) ($\log \epsilon M^{-1} cm^{-1}$): 426(5.83), 454(4.83), 566(3.82), 623(4.00).

5-fluorenyl-15-(5-formylthiophene-2-yl)-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (10b)

This compound was synthesized by adopting a similar procedure that was used to prepare **10a**. 1H NMR($CDCl_3$, 300MHz): δ = 0.87 (m,12H), 0.99(m, 8H), 1.43 (m,8H), 1.56(m, 10H), 1.63 (m, 4H), 2.00 (m, 4H), 2.12 (m, 4H), 3.92(s, 12H), 4.28 (t, 4H), 7.15 (d, 1H), 7.35 (d, 1H), 7.44(m, 7H), 7.92-8.23 (m, 4H), 9.03 (m, 4H), 9.48 (d, 2H), 9.54(s, 2H), 9.64 (s, 1H). ESI-MS: m/z $C_{80}H_{86}N_4O_7SZn$: calculated : 1313.04, found : 1315 [(M+H)⁺]. UV-Vis (CH_2Cl_2) λ_{max} (nm)($\log \epsilon$) : 267(4.5), 308(4.5), 423(5.6),453(sh, 5.1), 551(4.2), 621(4.0).

5-pyrenyl-15-[(5-formylthiophene-2-yl)-2-cyanoacrylicacid]-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) PYR-Por-CA: Porphyrin **10a** (50 mg, 0.042 mmol) was dissolved in 30 ml of $CH_3CN/ CHCl_3$ (3:1), to which piperidine and cyanoacetic acid (0.21 mmol) were added. The reaction mixture was refluxed for 8h. After cooling to RT, the reaction mixture was washed with water and 0.1M HCl and extracted with CH_2Cl_2 . The product was purified with silica gel column using $CH_2Cl_2/MeOH$ (3:1 v/v) as the eluant to afford the desired product (85% yield). Elemental analysis of Anal. Calcd. For $C_{74}H_{63}N_5O_8SZn\%$ (1247.77): C, 71.23; H, 5.09; N, 5.61 Found: C, 71.25; H, 5.10; N, 5.65. ESI-MS (m/z): $C_{74}H_{63}N_5O_8SZn$ [1246]: M⁺ (100%). 1H NMR ($CDCl_3$, δ ppm): 9.67 (s, 2H), 9.08 (s, 2H), 8.73 (m, 4H), 8.29 (m, 6H), 8.11 (m, 2H), 7.36 (m, 8H), 4.17 (m, 4H), 3.85 (s, 12H), 1.93 (m, 4H), 1.44 (m, 12H), 0.97 (m, 6H). UV-Vis (CH_2Cl_2) λ_{max} (nm) ($\log \epsilon M^{-1} cm^{-1}$) : 447(5.32), 575(4.04), 639(4.36).

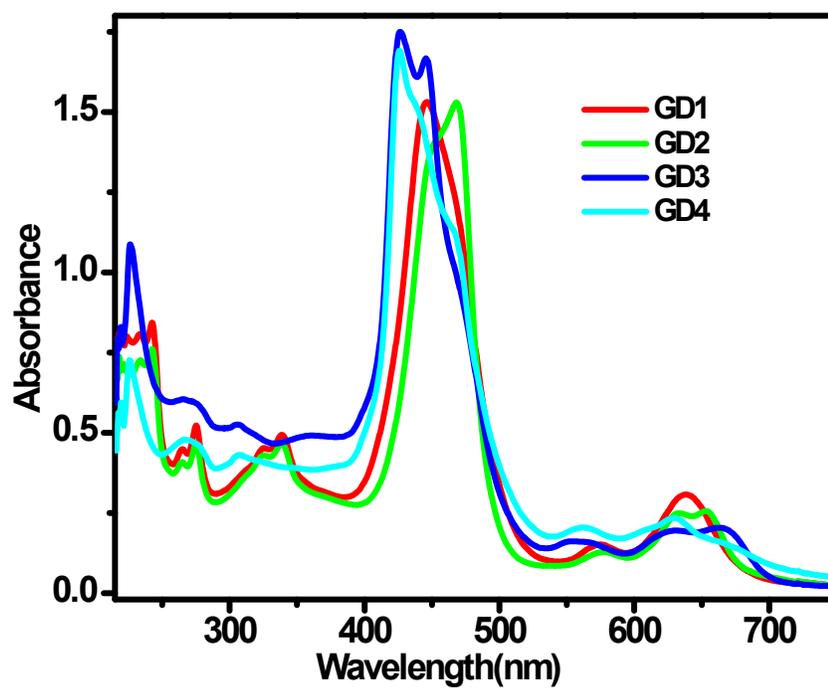
5-pyrenyl-15-[(5-formylthiophene-2-yl)methylene malonic acid]-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (PYR-Por-MA): This compound was synthesized by analogous procedure of the previous compound. The only difference is that here malonic acid was taken instead of cyanacrylic acid. Elemental analysis of Anal. Calcd. For $C_{74}H_{64}N_4O_{10}SZn\%$ (1266.77): C, 70.16; H, 4.49; N, 5.61 Found: C, 70.15; H, 5.10; N, 4.51. ESI-MS (m/z): $C_{74}H_{64}N_4O_{10}SZn\%$ (1266.77): [1264] M²⁺ (60%). 1H NMR ($CDCl_3$, δ ppm): 9.67 (s, 2H), 9.08 (s,

2H), 8.73 (m, 4H), 8.29 (m, 6H), 8.11 (m, 2H), 7.36 (m, 7H), 4.17 (m, 4H), 3.85 (s, 12H), 1.93 (m, 4H), 1.44 (m, 12H), 0.97 (m, 6H). UV-Vis(CH₂Cl₂) λ_{\max} (nm) (log ϵ M⁻¹ cm⁻¹) : 468 (5.12), 580 (4.01), 654 (4.46).

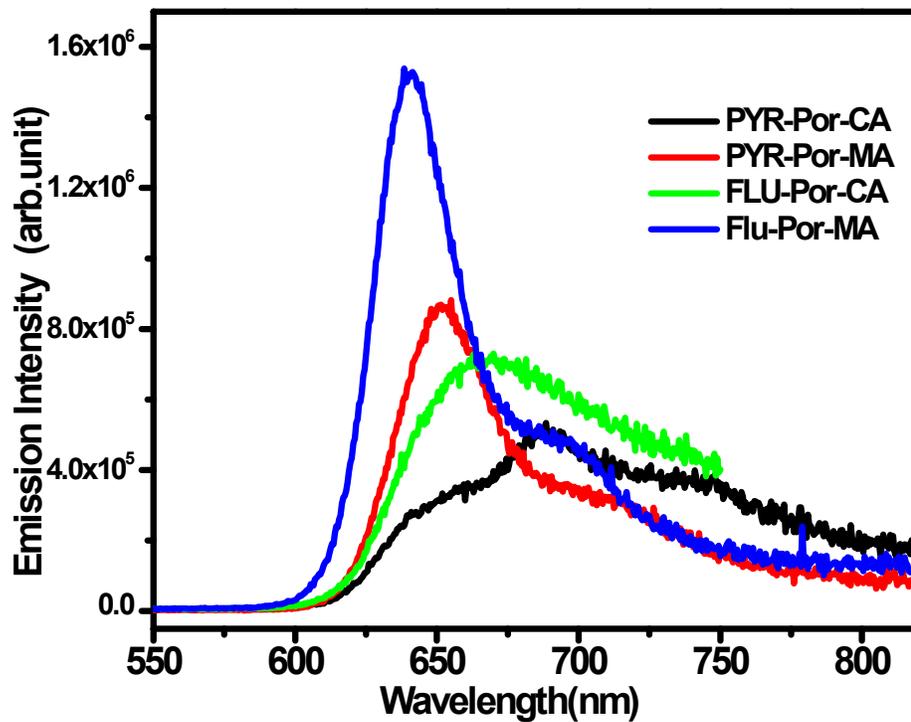
5-fluorenyl-15-[(5-formylthiophene-2-yl)-2-cyanoacrylicacid]-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (**FLU-Por-CA**): This compound was synthesized by adopting a similar procedure that was used to prepare **11a**. ¹H NMR(CDCl₃, 300MHz): δ = 0.65 (m,8H), 0.82(m, 12H), 1.23 (m,18H), 1.63 (m, 4H), 2.02 (m, 8H), 3.61(s, 12H), 4.23 (m, 4H), 6.85 (d, 2H), 7.42(m, 8H), 7.92-8.05 (m, 4H), 9.03 (m, 4H), 9.61 (m, 4H). MALDI-TOF MS: *m/z* C₈₃H₈₇N₅O₈SZn: calculated: 1380.08, found: 1381 [(M+H)⁺]. UV-Vis (CH₂Cl₂) λ_{\max} (nm)(log ϵ) : 267(4.6), 308(4.5), 444(5.2), 575(4.2), 638(4.5).

5-fluorenyl-15-[(5-formylthiophene-2-yl)methylene malonic acid]-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (**FLU-Por-MA**): This compound was synthesized by adopting a similar procedure that was used to prepare **12a**. ¹H NMR(CDCl₃, 300MHz): δ = 0.87 (m,12H), 0.99(m, 8H), 1.22 (m, 17H), 1.63 (m, 4H), 1.98 (m, 8H), 3.92(s, 12H), 4.23 (m, 4H), 7.03(d, 2H), 7.36 (m, 8H), 7.92-8.05 (m, 4H), 8.85 (m, 4H), 9.02 (d, 2H), 9.62(s, 2H). MALDI-TOF MS: *m/z* C₈₃H₈₈N₄O₁₀SZn: calculated: 1399.08, found: 1400 [(M+H)⁺]. UV-Vis (CH₂Cl₂) λ_{\max} (nm)(log ϵ) : 266 (4.6), 309(4.6), 448 (5.3), 572 (4.2), 632 (4.4).

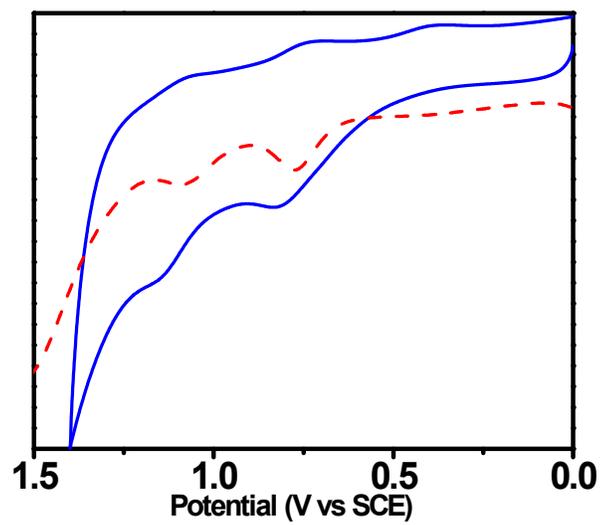
Absorption Spectra of Porphyrin Sensitizers in Dichloromethane



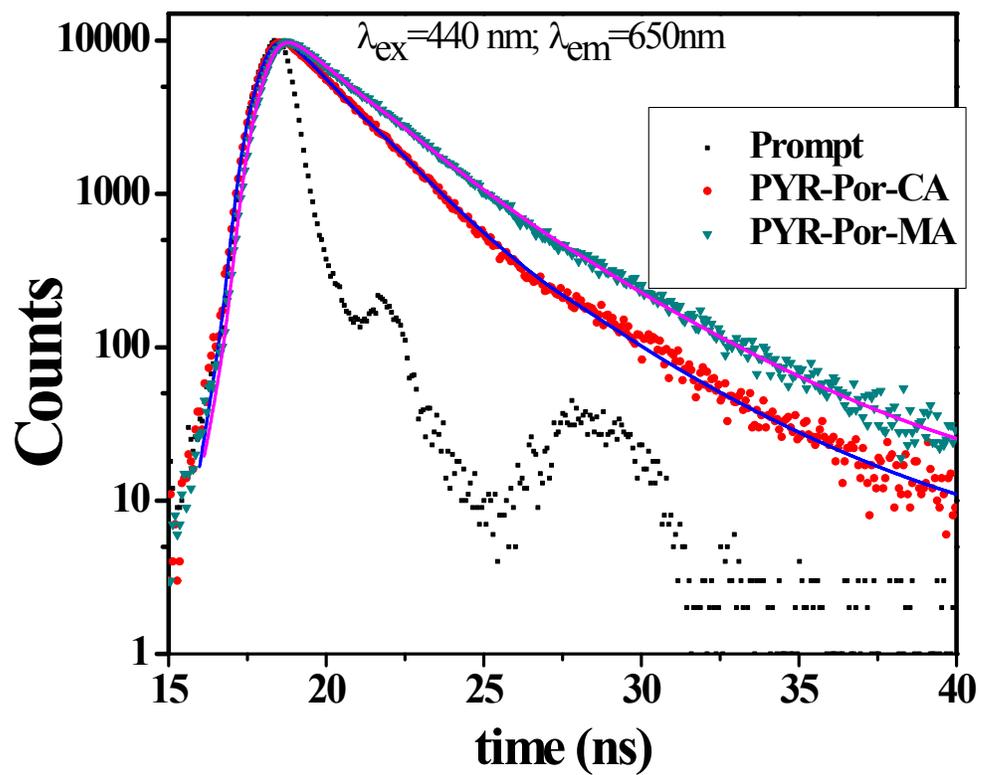
Emission Spectra of Sensitizers in Dichloromethane



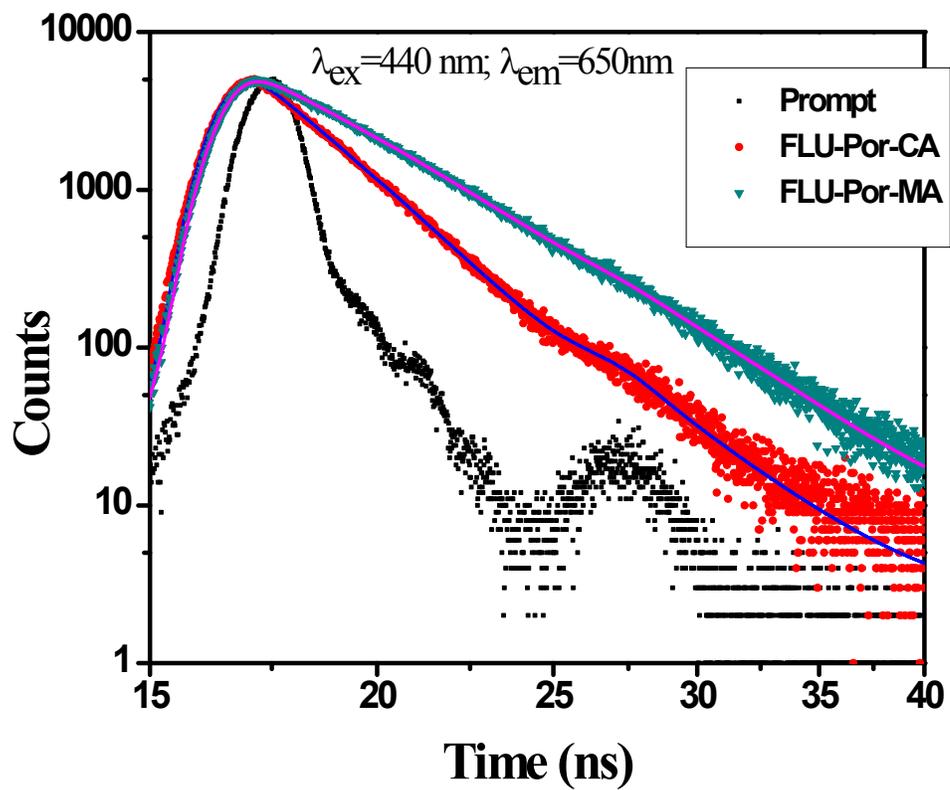
Cyclic voltammogram of PYR-Por-CA in CH₂Cl₂ solvent, scan rate 100 mV/s.



Fluorescence decay ($\lambda_{\text{ex}} = 440 \text{ nm}$, $\lambda_{\text{em}} = 650 \text{ nm}$) in Dichloromethane



Fluorescence decay ($\lambda_{\text{ex}} = 440 \text{ nm}$, $\lambda_{\text{em}} = 650 \text{ nm}$) in Dichloromethane



Electronic distribution computed in dichloromethane for the first occupied/unoccupied molecular orbitals of the PYR-Por-MA

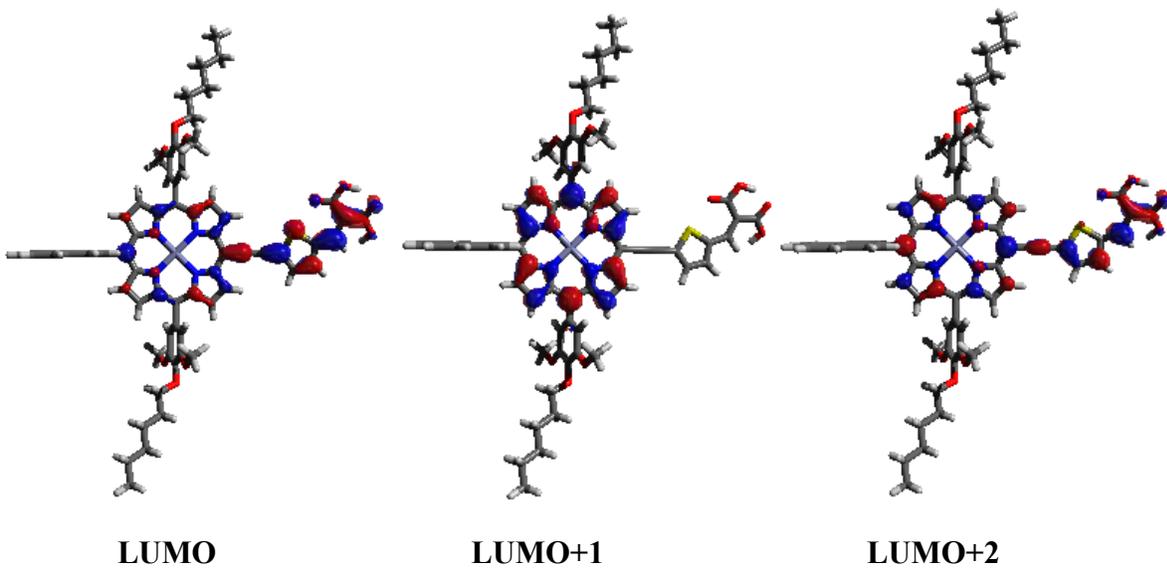
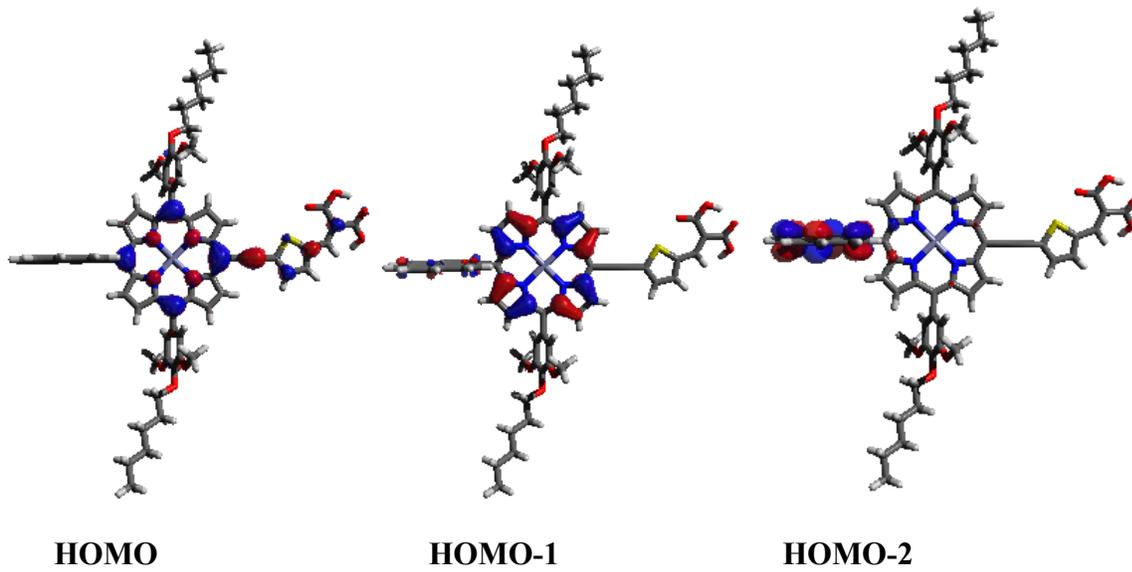


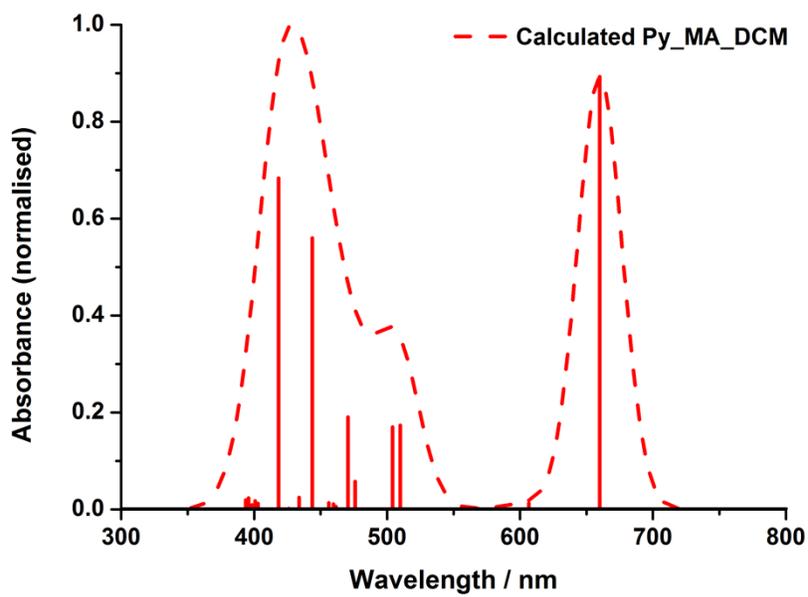
Table TD-DFT calculated visible absorption wavelengths for **PYR-Por-MA**, indicating the molecular orbitals involved and their relative contribution to the absorption.

Main Visible Absorbance / nm	Main Charge Transitions		Oscillator Strength	Relative Contribution
	MO from	MO to		
660	HOMO-1	LUMO+1	1.2618	17
	HOMO	LUMO		83
510	HOMO-1	LUMO+1	0.2452	36
	HOMO	LUMO		11
	HOMO	LUMO+2		53
504	HOMO-2	LUMO	0.2403	9
	HOMO-1	LUMO		23
	HOMO-1	LUMO+2		28
	HOMO	LUMO+1		40
444	HOMO-7	LUMO	0.7911	34
	HOMO-2	LUMO+1		16
	HOMO-1	LUMO+1		28
	HOMO	LUMO+2		22
419	HOMO-7	LUMO+1	0.9655	9
	HOMO-6	LUMO		7
	HOMO-4	LUMO+1		11
	HOMO-2	LUMO+2		17
	HOMO-1	LUMO		6
	HOMO-1	LUMO+2		30
	HOMO	LUMO+1		20

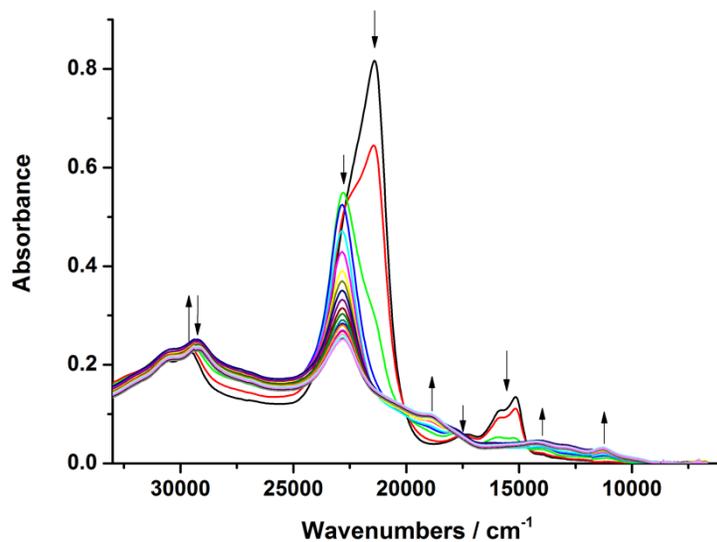
Table Percentage contributions from component parts of **PYR-Por-MA** to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals.(Ar-based = trimethoxyaryl unit; S-based = thiophene-bisacetic acid unit)

MO	MO energy / eV	% Contribution from				
		Zn-based	Porphyrin-based	Pyrene-based	S-based	Ar-based
HOMO-2	-5.51	0.01	13.18	85.61	0.12	1.08
HOMO-1	-5.45	0	82.37	10.40	0	7.23
HOMO	-5.19	0.85	61.82	3.06	23.88	10.39
LUMO	-3.04	0.15	33.89	1.95	62.28	1.73
LUMO+1	-2.42	0.23	88.47	1.46	0	9.84
LUMO+2	-2.33	0.14	51.78	3.11	42.71	2.26

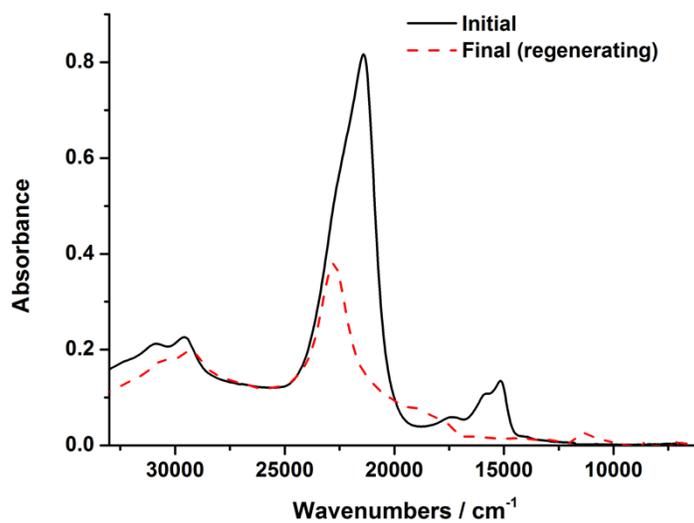
The red dash curve is the calculated spectrum of Py_MA in DCM and the solid columns are the calculated electronic transitions.



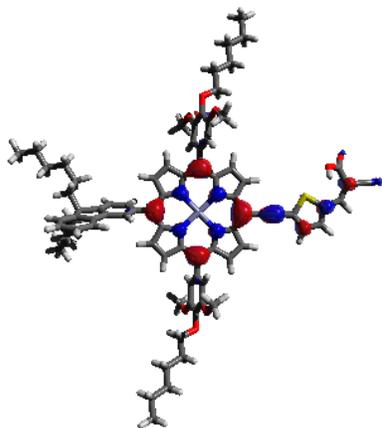
Oxidative OTTLE studies of **PYR-Por-MA** in 0.3 M TBABF₄/DCM with an applied potential of +1 V (vs. Ag/AgCl).



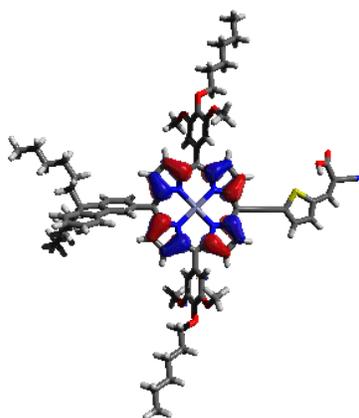
Overlay of initial and final spectra to show regeneration of **PYR-Por-MA** did not occur. The studies were carried out at -2 °C. The regeneration process was carried out at +0.2 V.



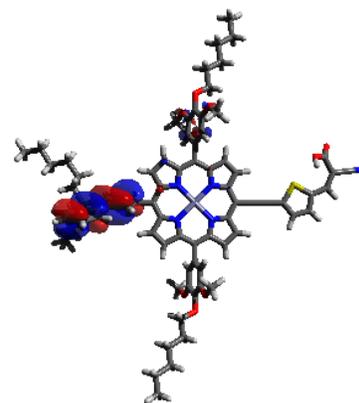
Electronic distribution computed in dichloromethane for the first occupied/unoccupied molecular orbitals of FLU-Por-CA



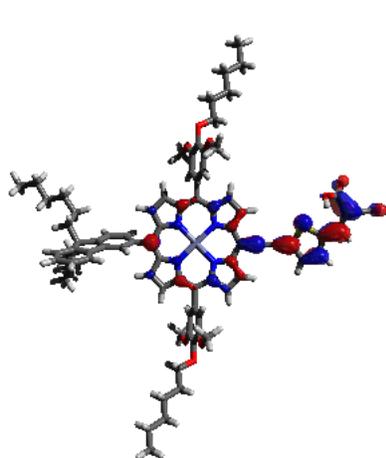
HOMO



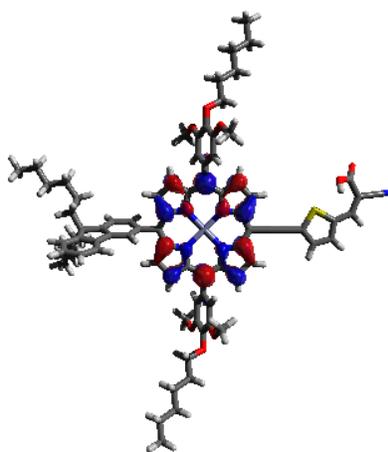
HOMO-1



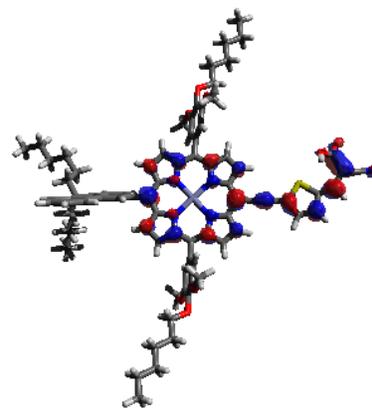
HOMO-2



LUMO



LUMO+1



LUMO+2

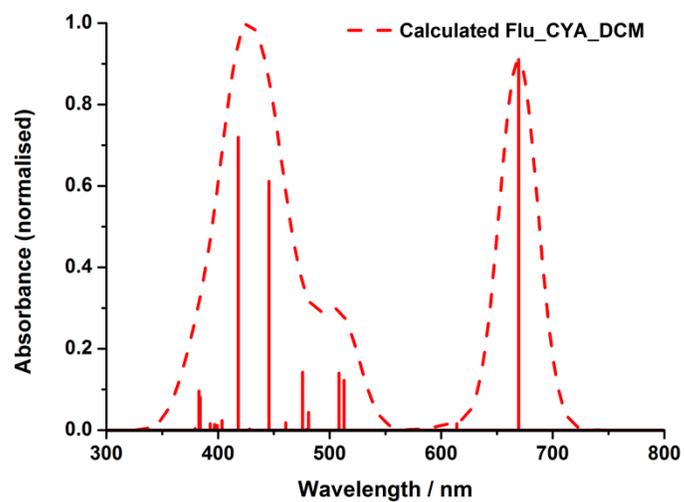
Table TD-DFT calculated visible absorption wavelengths for Flu-Por-CA indicating the molecular orbitals involved and their relative contribution to the absorption.

Main Visible Absorbance / nm	Main Charge Transitions		Oscillator Strength	Relative Contribution
	MO from	MO to		
669	HOMO-1	LUMO+1	1.3051	16
	HOMO	LUMO		84
513	HOMO-1	LUMO+1	0.1754	36
	HOMO	LUMO		10
	HOMO	LUMO+2		54
508	HOMO-1	LUMO	0.2007	25
	HOMO-1	LUMO+2		31
	HOMO	LUMO+1		44
446	HOMO-7	LUMO	0.8759	41
	HOMO-1	LUMO+1		35
	HOMO	LUMO+2		24
418	HOMO-7	LUMO+1	1.0313	9
	HOMO-6	LUMO		9
	HOMO-4	LUMO+1		14
	HOMO-1	LUMO		7
	HOMO-1	LUMO+2		38
	HOMO	LUMO+1		23

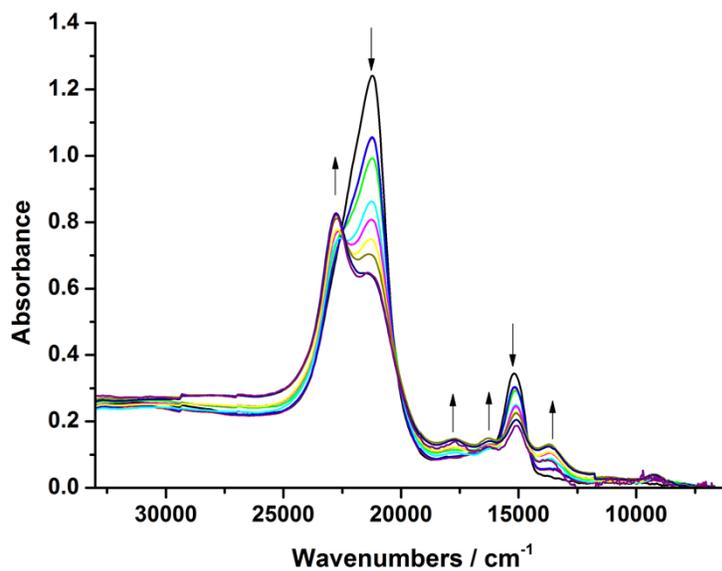
Table Percentage contributions from component parts of **Flu-Por-CA** to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals. (Ar-based = trimethoxyaryl unit; S-based = thiophene-cyanoacetic acid unit)

MO	MO energy / eV	% Contribution from				
		Zn-based	Porphyrin-based	Fluorene-based	S-based	Ar-based
HOMO-2	-5.95	0.01	5.66	88.26	1.29	4.78
HOMO-1	-5.47	0	89.12	3.00	0	7.88
HOMO	-5.20	0.87	62.41	3.92	23.31	9.49
LUMO	-3.08	0.16	31.66	1.77	64.90	1.51
LUMO+1	-2.43	0.23	88.11	2.08	0	9.58
LUMO+2	-2.36	0.14	54.15	3.14	40.49	2.08

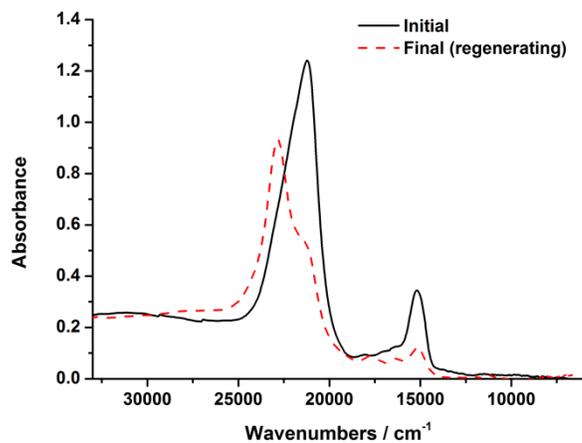
The red dash curve is the calculated spectrum of Flu-Por-CA in DCM and the solid columns are the calculated electronic transitions.



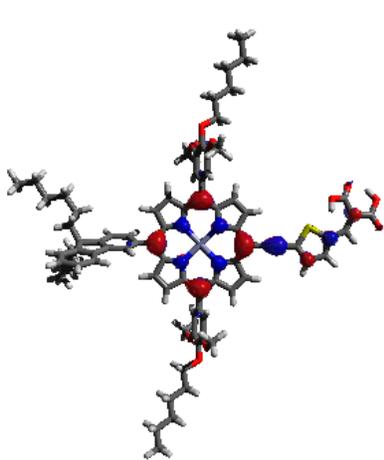
Oxidative OTTLE studies of **Flu-Por-CA** in 0.3 M TBABF₄/DCM with an applied potential of +1 V (vs. Ag/AgCl).



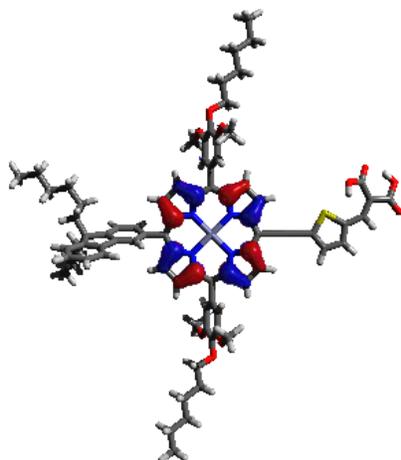
Overlay of initial and final spectra to show regeneration of **Flu-Por-CA** did not occur. The studies were carried out at -40 °C. The regeneration process was carried out at +0.15 V.



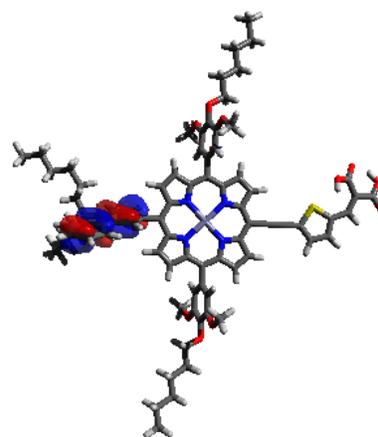
Electronic distribution computed in dichloromethane for the first occupied/unoccupied molecular orbitals of FLU-Por-MA



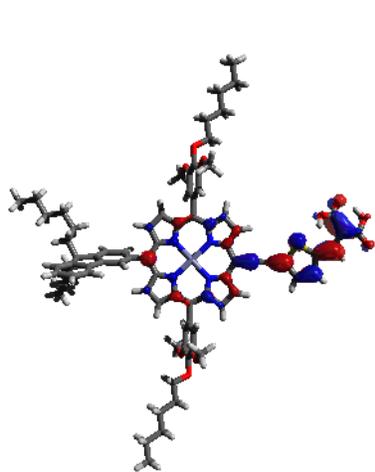
HOMO



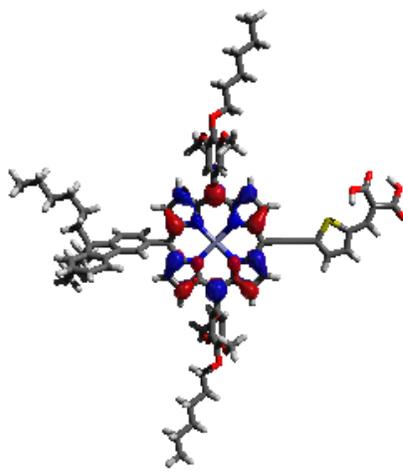
HOMO-1



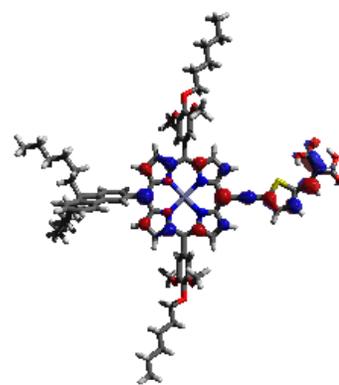
HOMO-2



LUMO



LUMO+1



LUMO+2

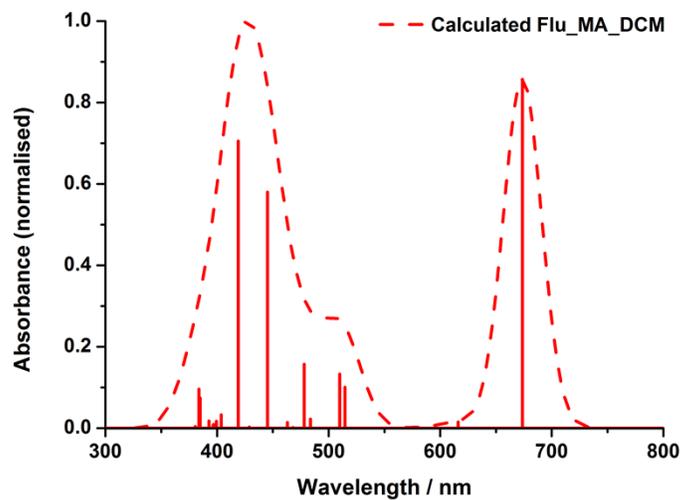
Table 1 TD-DFT calculated visible absorption wavelengths for **FLU-Por-MA**, indicating the molecular orbitals involved and their relative contribution to the absorption.

Main Visible Absorbance / nm	Main Charge Transitions		Oscillator Strength	Relative Contribution
	MO from	MO to		
674	HOMO-1	LUMO+1	1.2827	16
	HOMO	LUMO		84
515	HOMO-1	LUMO+1	0.1501	36
	HOMO	LUMO		10
	HOMO	LUMO+2		54
510	HOMO-1	LUMO	0.1990	24
	HOMO-1	LUMO+2		32
	HOMO	LUMO+1		44
445	HOMO-7	LUMO	0.8681	41
	HOMO-1	LUMO+1		36
	HOMO	LUMO+2		23
419	HOMO-7	LUMO+1	1.0557	9
	HOMO-6	LUMO		9
	HOMO-4	LUMO+1		16
	HOMO-1	LUMO+2		41
	HOMO	LUMO+1		25

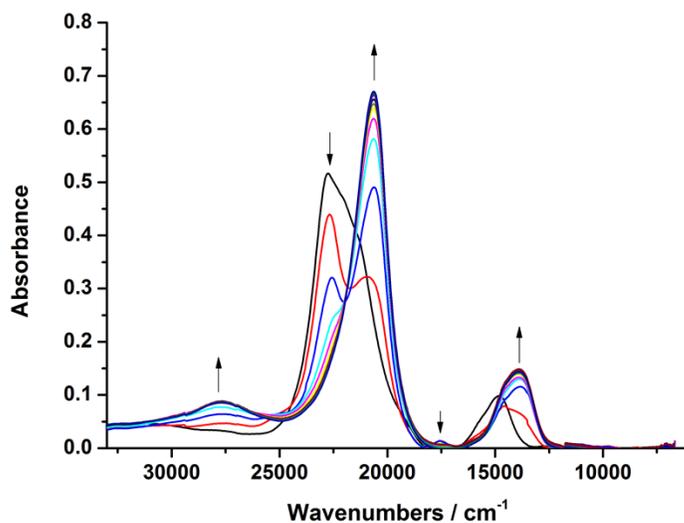
Table Percentage contributions from component parts of **FLU-Por-MA** to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals. (Ar-based = trimethoxyaryl unit; S-based = thiophene-bisacetic acid unit)

MO	MO energy / eV	% Contribution from				
		Zn-based	Porphyrin-based	Fluorene-based	S-based	Ar-based
HOMO-2	-5.95	0.01	5.71	88.55	0.89	4.84
HOMO-1	-5.47	0	89.19	2.81	0	8.00
HOMO	-5.20	0.86	62.25	3.99	22.69	10.21
LUMO	-3.09	0.16	30.97	1.76	65.54	1.57
LUMO+1	-2.43	0.23	87.90	2.19	0	9.68
LUMO+2	-2.37	0.14	54.70	3.23	39.66	2.27

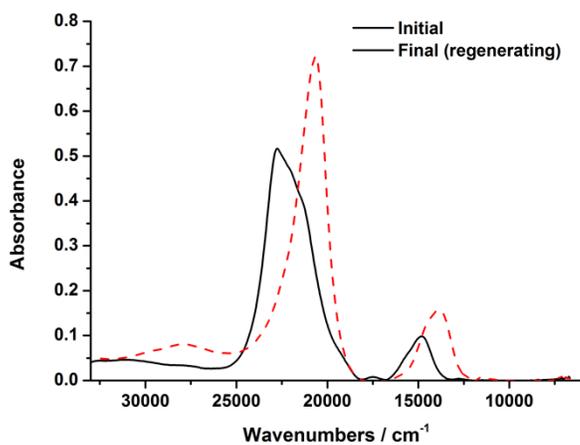
The red dash curve is the calculated spectrum of FLU-Por-MA in DCM and the solid columns are the calculated electronic transitions.



Oxidative OTTLE studies of **Flu_MA** in 0.3 M TBABF₄/DCM with an applied potential of +1 V (vs. Ag/AgCl).



Overlay of initial and final spectra to show regeneration of **Flu_MA** did not occur. The studies were carried out at -2 °C. The regeneration process was carried out at +0.2 V.



TG/DTG curves of **PYR-Por-MA** with heating rate of 10 °C min⁻¹ under Nitrogen atmosphere.

