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

Pyrene Based D-π-A Architectures: Synthesis, Density Functional Theory, Photophysics and Electron Transfer Dynamics

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Synthetic procedures

4-Pyren-1-yl-benzaldehyde (1). Pyrene-1-boronic acid (0.98 g, 4 mmol), 4-Bromobenzaldehyde (0.74 g, 4 mmol), $Pd(PPh_3)_4$ (0.46 g, 0.4 mmol), and K_2CO_3 (5.6 mL, 2M aqueous solution) in 20 mL dry THF was added and degassed with argon in 30 min and the mixture was refluxed at 80 ˚C for further 40 h. After cooling to room temperature, the mixture was extracted with DCM (3 × 20 mL). The organic phase was dried over anhydrous sodium sulfate. The solvent was removed with a rotary evaporator and the residue was purified on a silica gel column (hexane/ethylacetate = 9:1) to give greenish yellow solid (0.9 g, 73% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 10.05 (s, 1H), 8.08-8.14 (m, 3H), 7.92-8.04 (m, 7H), 7.85-7.87 (d, *J* = 8 Hz, 1H), 7.69-7.71 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 192.09, 147.73, 136.04, 135.22, 131.45, 131.30, 131.20, 130.87, 129.83, 128.34, 128.08, 127.96, 127.35, 127.28, 126.24, 125.54, 125.20, 124.96, 124.79, 124.73, 124.59. MS-EI m/z calcd for ($C_{23}H_{14}O$): 306.3567. Found: 306.3602.

5-Pyren-1-yl-thiophene-2-carbaldehyde (2). Yellow solid. Yield: 73 % (0.91 g). ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 9.99 (s, 1H), 8.39-8.41 (d, *J* = 8 Hz, 1H) 8.16-8.22 (m, 3H), 8.01-8.12 (m, 5H), 7.87-7.88 (d, *J* = 4 Hz, 1H), 7.45-7.46 (d, *J* = 4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 182.84, 153.07, 144.02, 136.63, 131.94, 131.38, 130.78, 129.09, 128.91, 128.68, 128.51, 128.11, 128.03, 127.24, 126.40, 125.88, 125.53, 124.97, 124.67, 124.58, 124.15. MS-EI m/z calcd for ($C_{21}H_{12}OS$): 312.3844. Found: 312.3800.

5-Pyren-1-yl-furan-2-carbaldehyde (3). Yellow solid. Yield: 76 % (0.9 g). ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 9.77 (s, 1H), 8.64-8.66 (d, *J* = 8 Hz, 1H), 8.28-8.30 (d, *J* = 8 Hz, 1H), 8.13-8.20 (m, 4H), 8.08-8.11 (d, *J* = 12 Hz, 1H), 7.99-8.03 (t, *J* = 8 Hz, 2H), 7.45-7.46 (d, *J* = 4 Hz, 1H), 7.03-7.04 (d, *J* = 4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm: 177.41, 159.90, 152.68, 132.30, 131.31, 130.66, 129.09, 128.72, 128.37, 127.24, 126.56, 126.37, 126.04, 125.70, 125.03, 124.82, 124.54, 124.09, 123.36, 123.03, 112.31. MS-EI m/z calcd for ($C_{21}H_{12}O_2$): 296.3188. Found: 296.3200.

A common procedure was adopted to obtained compounds **4 - 6** which involves the knoevenagel condensation of corresponding aldehydes **1 - 3** (0.4 g, 1.3 mmol) with rhodanine-3-acetic acid (0.37 g, 1.95 mmol) in the presence of acetic acid (5 mL) and ammonium acetate (0.004 g, 0.05 mmol) and the reaction mixture was heated to reflux at 120 ˚C for 15 h. The resulting solution was poured into ice-cold water, to produce precipitate.

This was filtered, washed thoroughly with ice-cold water and then dried. The crude product which was then purified by silica gel column chromatography using chloroform-methanol (v/v: 10:0.2) yielded the final product as solid.

[4-Oxo-5-(4-pyren-1-yl-benzylidene)-2-thioxo-thiazolidin-3-yl]-acetic acid (4). Orange solid. Yield: 68 % (0.42 g). ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 8.28-8.38 (m, 3H), 8.23-8.24 (d, J = 4 Hz, 2H), 8.17-8.20 (d, J = 12 Hz, 1H), 8.08-8.11 (m, 2H), 8.04-8.05 (d, J = 4 Hz, 1H), 7.9 (s, 1H), 7.81-7.87 (q, J = 8 Hz, 4H), 4.76 (s, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ ppm: 193.47, 167.78, 166.78, 143.49, 136.07, 133.86, 132.21, 131.80, 131.43, 131.39, 131.03, 130.79, 128.53, 128.25, 127.99, 127.77, 126.94, 126.06, 125.66, 125.45, 124.65, 124.59, 124.41, 122.25, 45.50. MS-EI m/z calcd for ($C_{28}H_{17}NO_3S_2$): 479.5695. Found: 479.5701. Elemental Anal. Calcd: C (70.13 %); H (3.57 %); N (2.92 %); S (13.37 %). Found: C (71.07 %); H (3.43 %); N (2.57 %); S (13.43 %).

[4-Oxo-5-(5-pyren-1-yl-thiophen-2-ylmethylene)-2-thioxo-thiazolidin-3-yl]-acetic acid (5). Red solid. Yield: 79 % (0.49 g). ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 8.47 (s, 1H), 8.35-8.39 (t, J = 8 Hz, 3H), 8.21-8.32 (m, 5H), 8.12-8.16 (t, J = 8 Hz, 1H), 7.97-7.98 (d, J = 4 Hz, 1H), 7.73-7.74 (d, J = 4 Hz, 1H), 4.75 (s, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ ppm: 192.40, 167.71, 166.49, 150.77, 138.46, 137.66, 131.82, 131.41, 131.05, 130.76, 129.40, 128.94, 128.64, 128.38, 128.02, 127.76, 127.26, 127.16, 126.57, 126.12, 125.58, 124.69, 124.27, 124.22, 119.65, 45.70. MS-EI m/z calcd for ($C_{26}H_{15}NO_3S_3$): 485.5972. Found: 485.6010. Elemental Anal. Calcd: C (64.31 %); H (3.11 %); N (2.88 %); S (19.81 %). Found: C (63.02 %); H (2.80 %); N (3.67 %); S (19.76 %).

[4-Oxo-5-(5-pyren-1-yl-furan-2-ylmethylene)-2-thioxo-thiazolidin-3-yl]-acetic acid (6). Brown solid. Yield: 65 % (0.41 g). ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 8.70-8.72 (d, J = 8 Hz, 1H), 8.35-8.46 (m, 5H), 8.24-8.29 (m, 2H), 8.13-8.17 (t, J = 8 Hz, 1H), 7.88 (s, 1H), 7.59-7.60 (d, J = 4 Hz, 1H), 7.54-7.55 (d, J = 4 Hz, 1H), 4.74 (s, 2H). MS-EI m/z calcd for ($C_{26}H_{15}NO_4S_2$): 469.5316. Found: 469.5300. Elemental Anal. Calcd: C (66.51 %); H (3.22 %); N (2.98 %); S (13.66 %). Found: C (66.84 %); H (3.00 %); N (2.77 %); S (13.77 %).

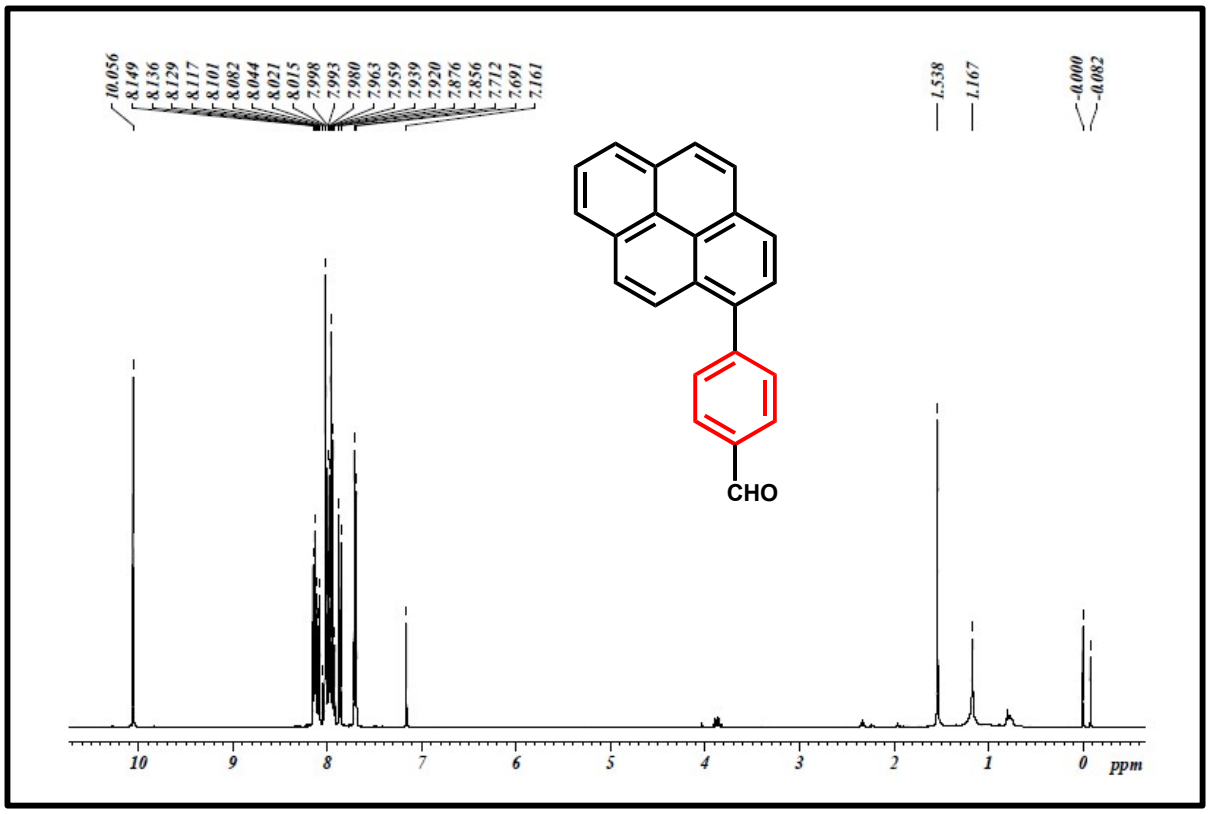


Figure S1: ^{1}H NMR spectrum of PBCA in $CDCl_3$

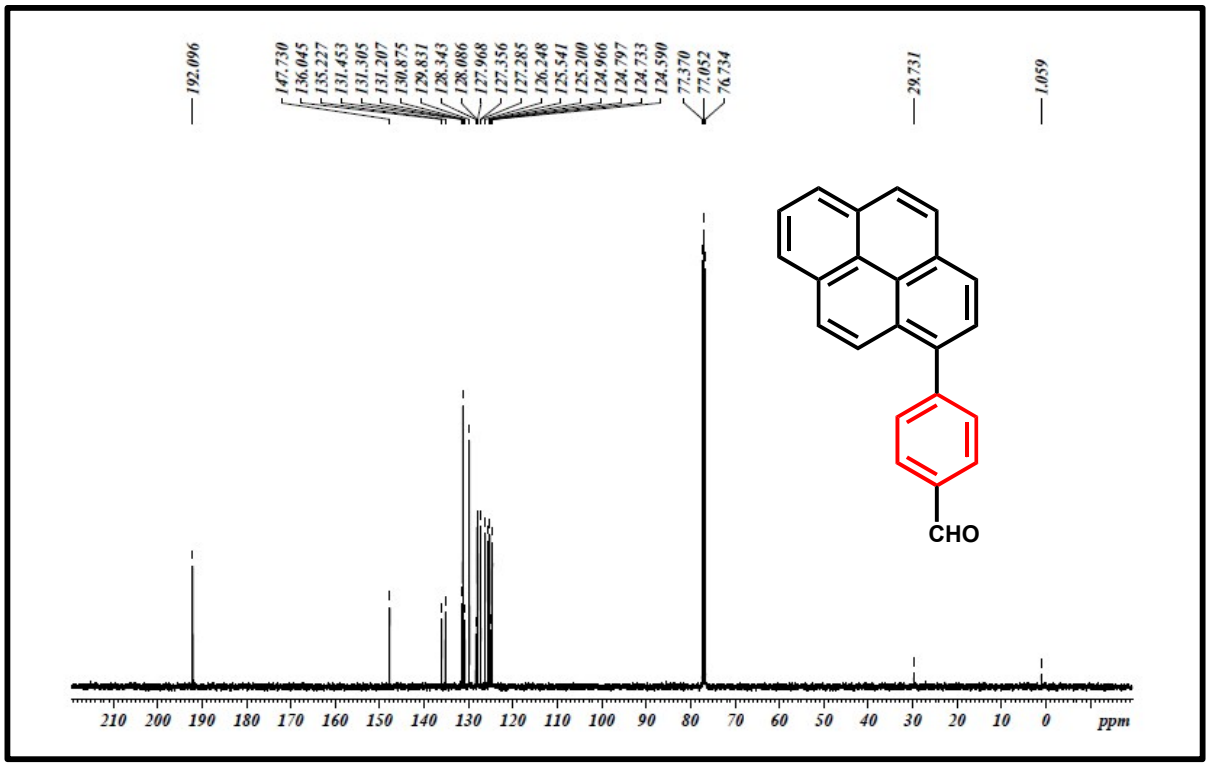


Figure S2: ^{13}C NMR spectrum of PBCA in $CDCl_3$

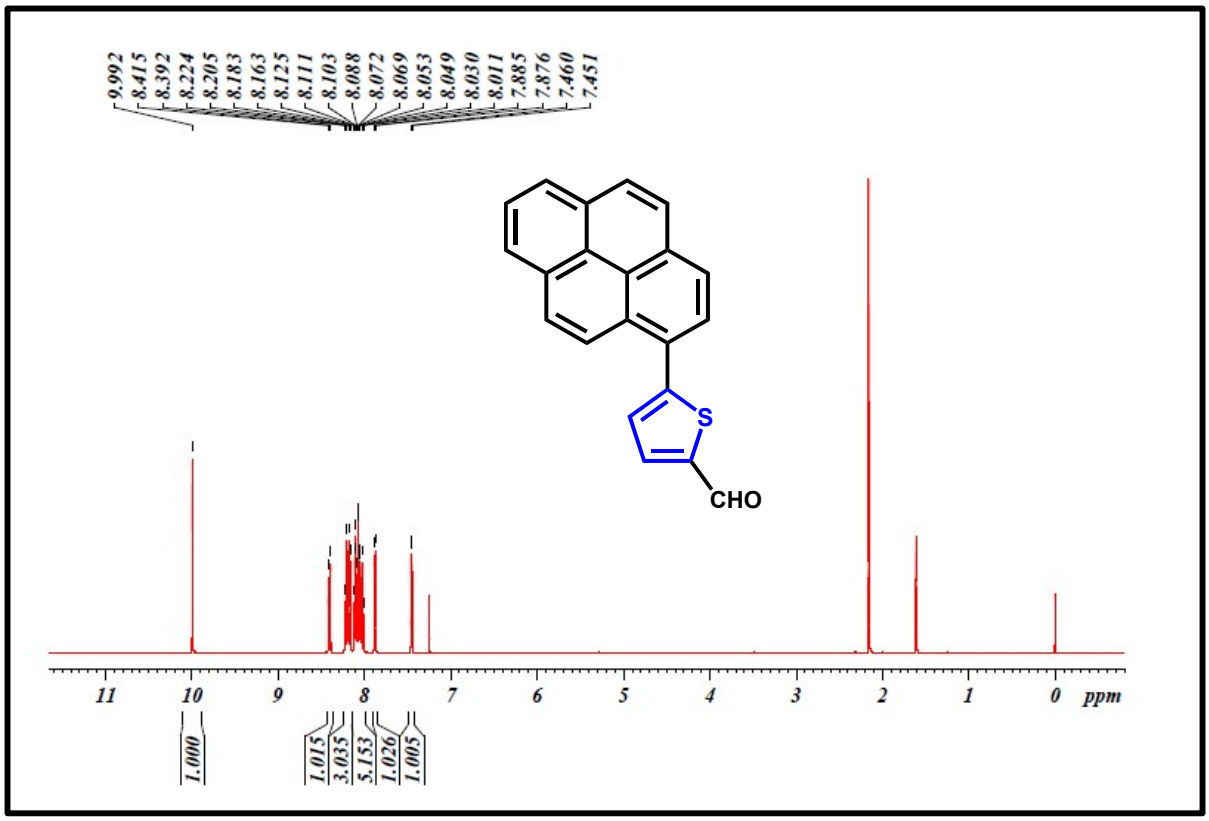


Figure S3: ^{1}H NMR spectrum of PTCA in $CDCl_3$

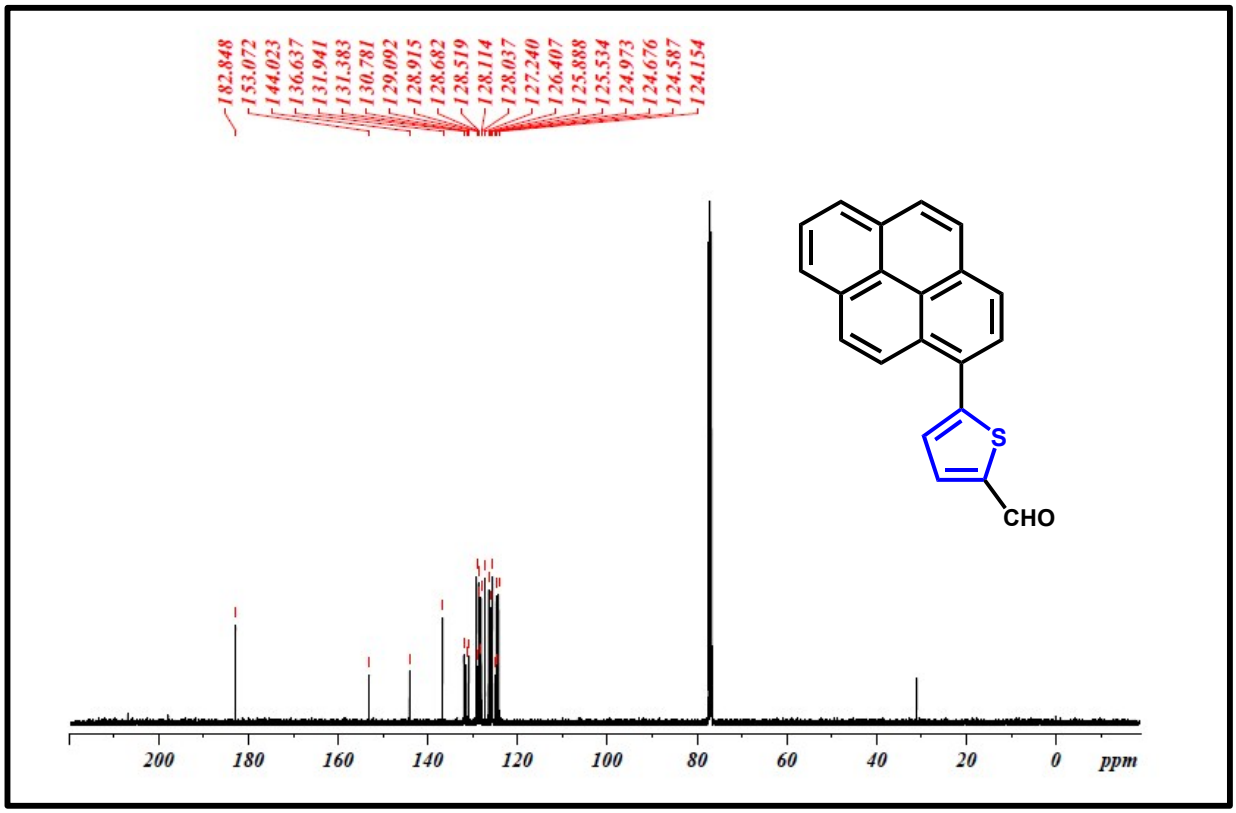


Figure S4: ^{13}C NMR spectrum of PTCA in $CDCl_3$

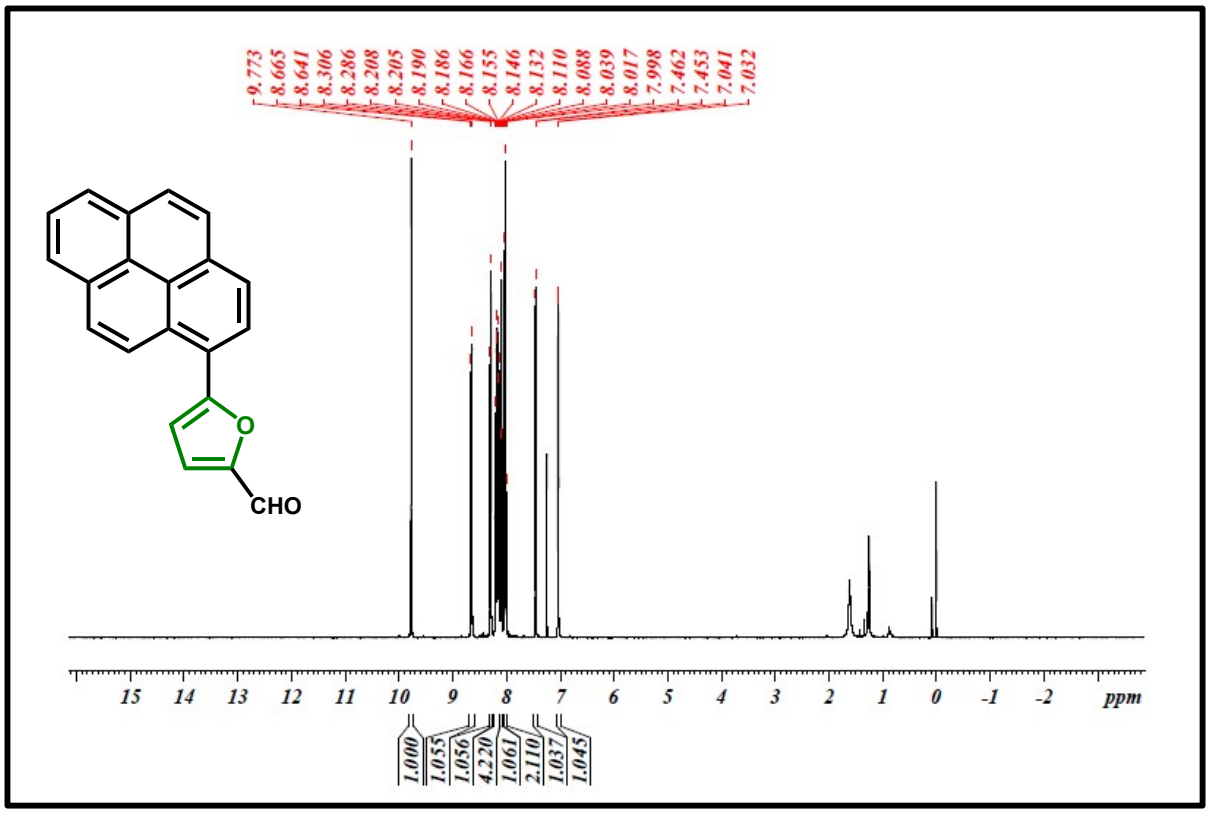


Figure S5: ^{1}H NMR spectrum of PFCA in $CDCl_3$

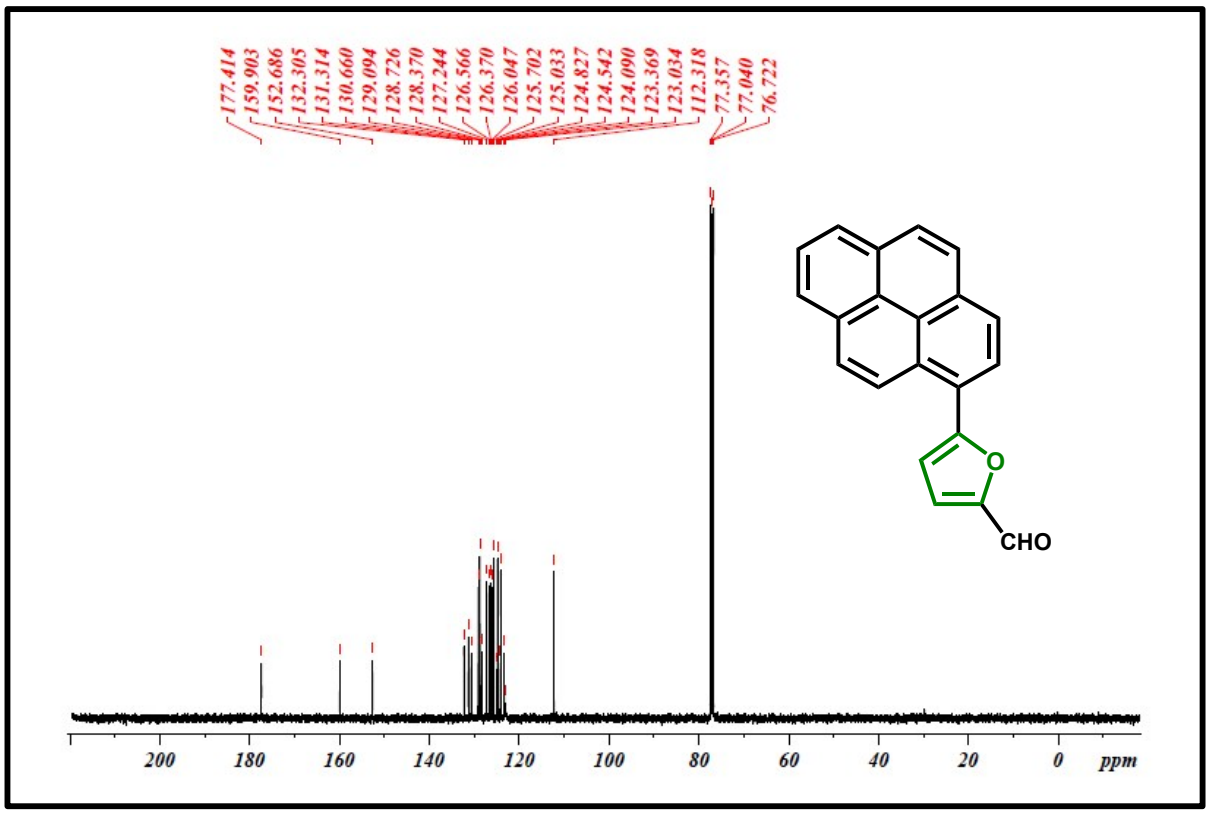


Figure S6: ^{13}C NMR spectrum of PFCA in $CDCl_3$

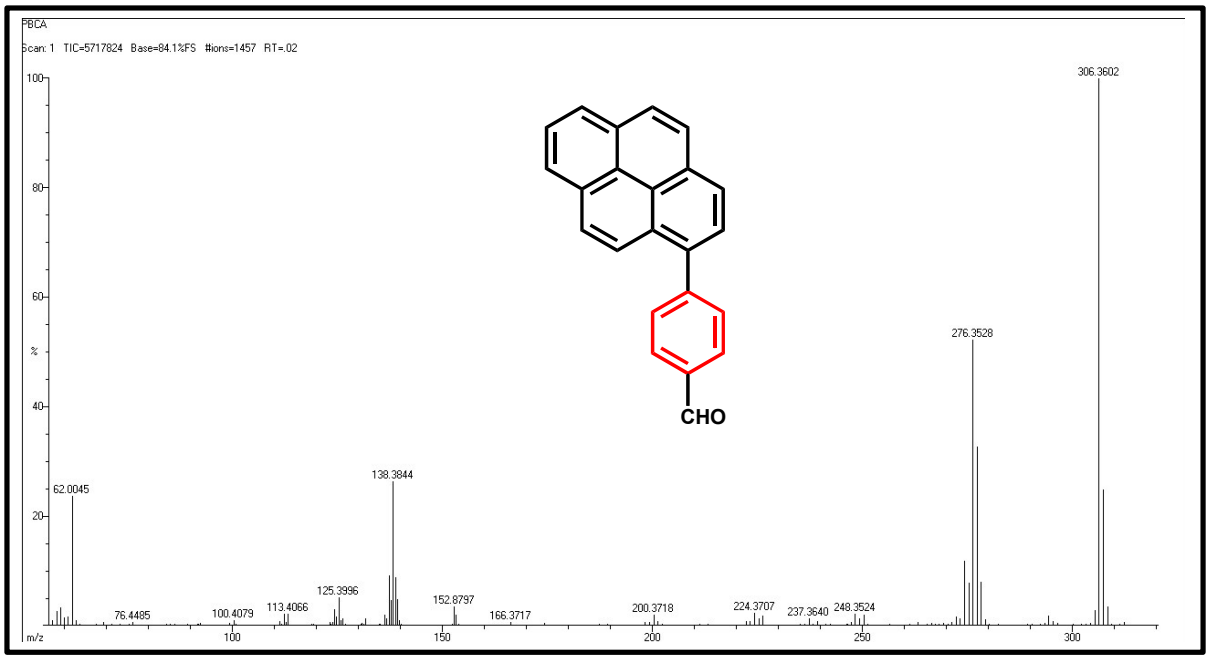


Figure S7: Mass spectrum of PBCA in DMSO – d_6

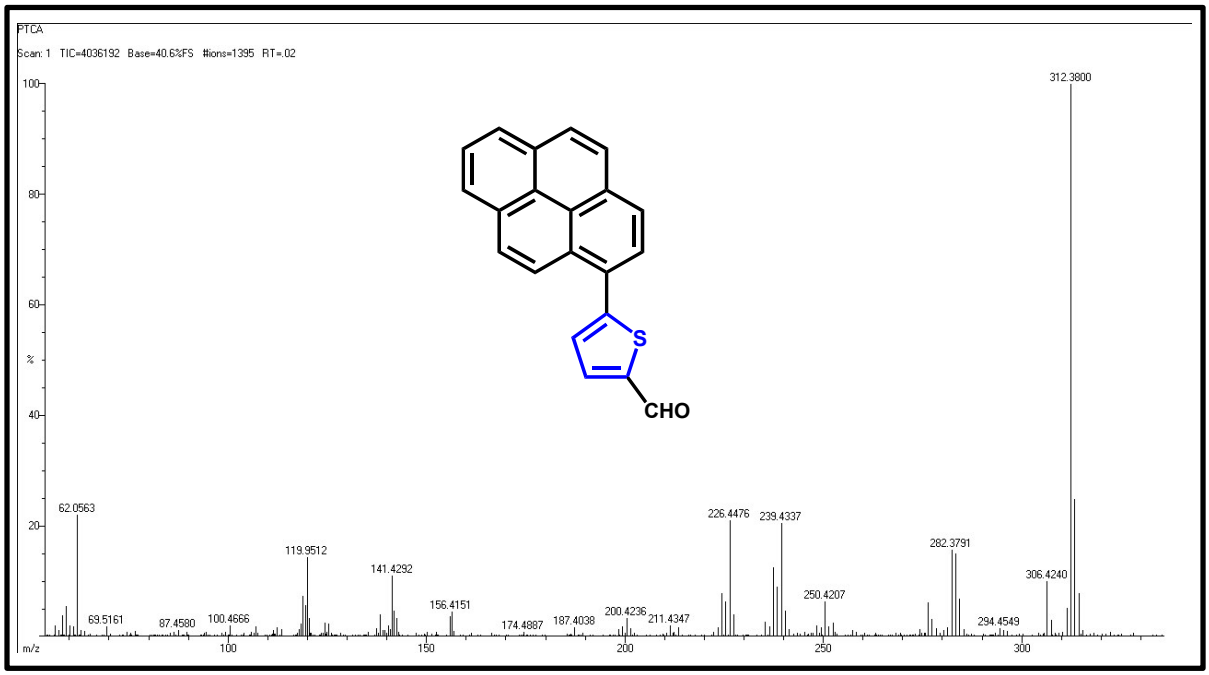


Figure S8: Mass spectrum of PTCA in DMSO – d_6

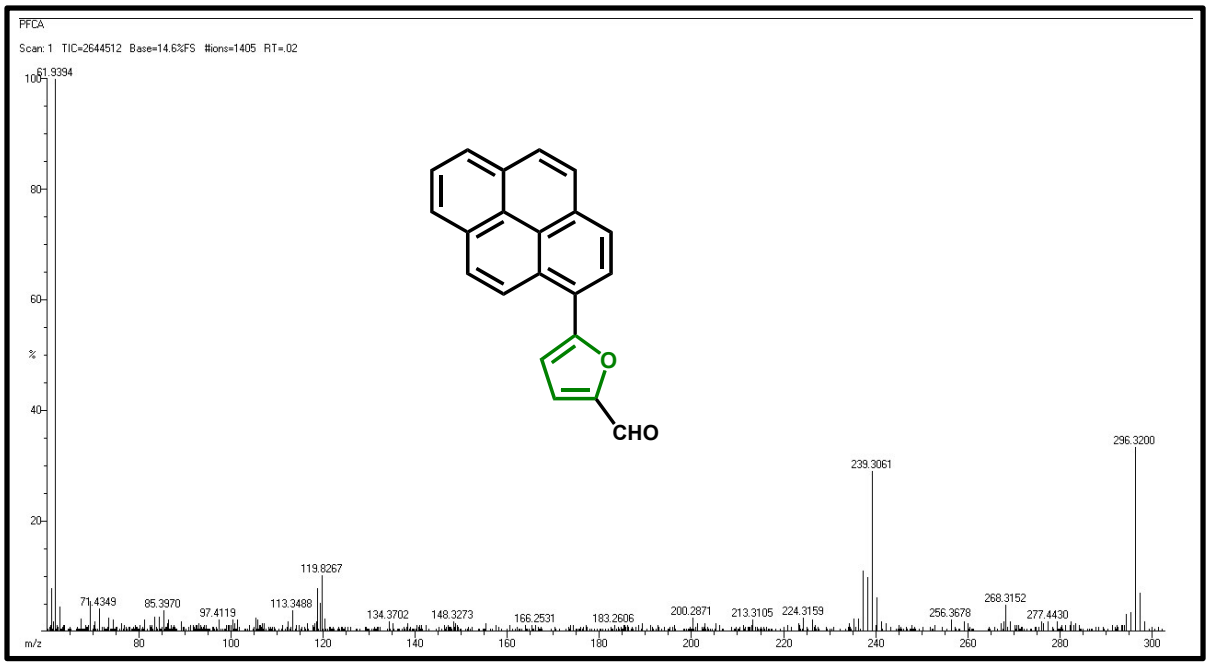


Figure S9: Mass spectrum of PFCA in DMSO – d_6

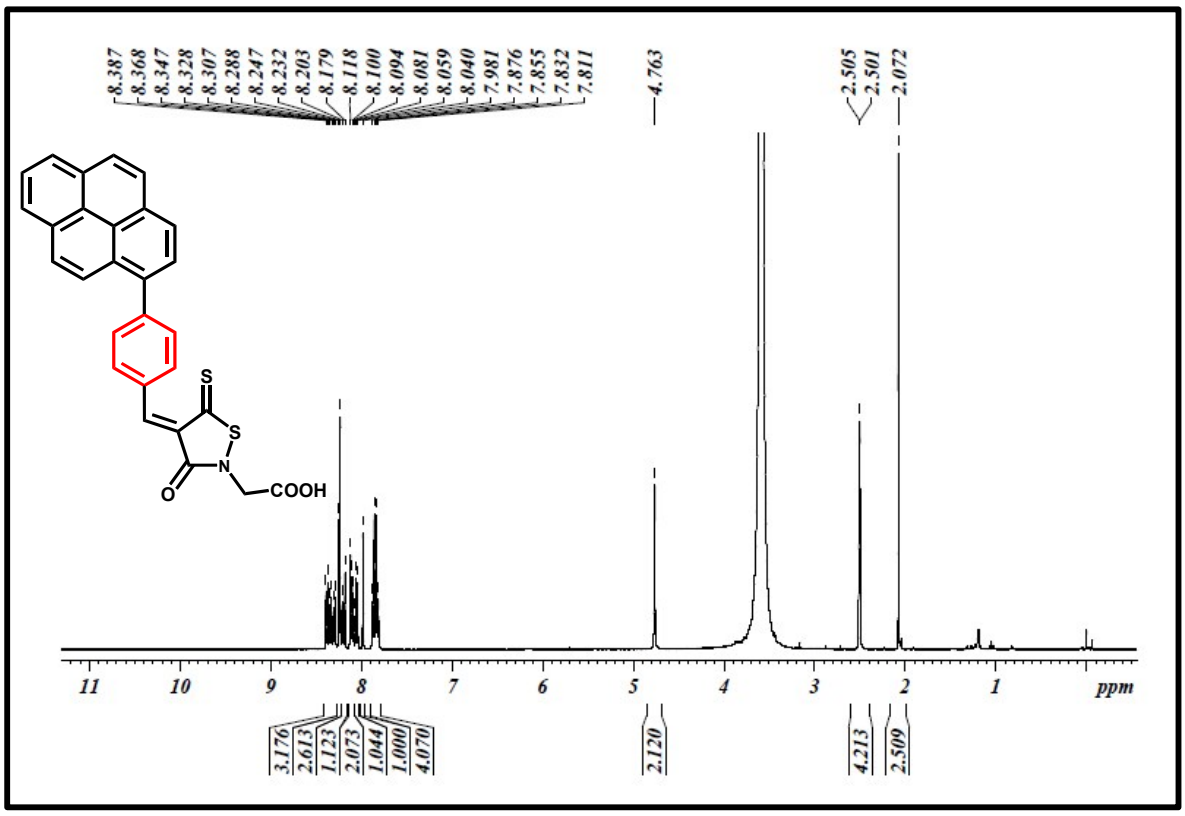


Figure S10: ^{1}H NMR spectrum of PBRA in DMSO – d_6

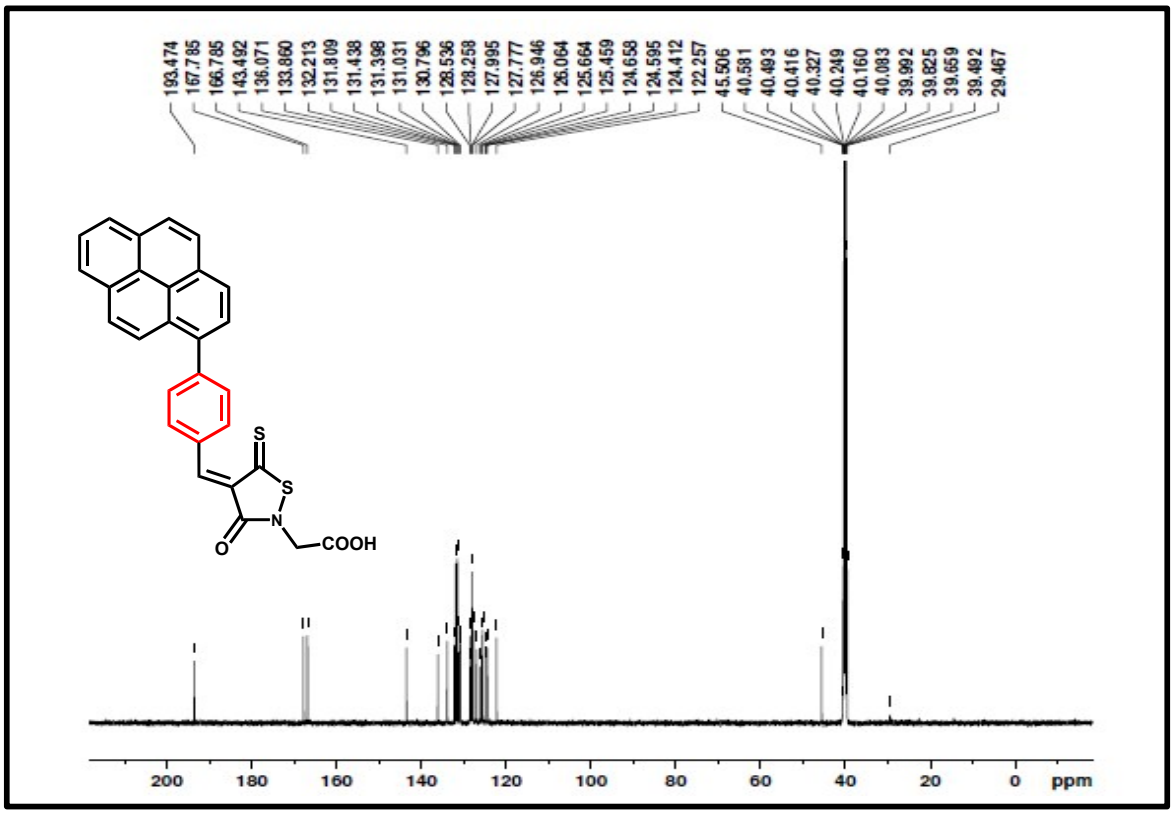


Figure S11: ^{13}C NMR spectrum of PBRA in DMSO – d_6

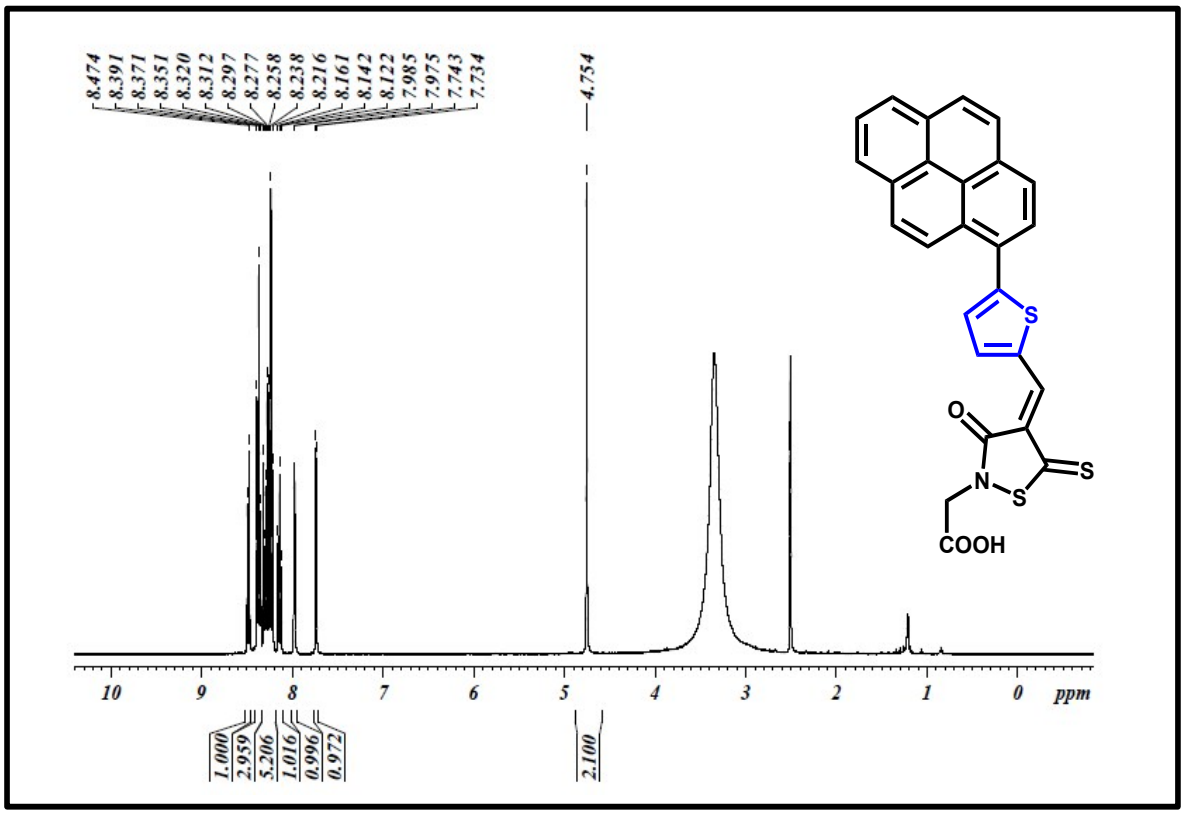


Figure S12: ^{1}H NMR spectrum of PTRA in DMSO – d_6

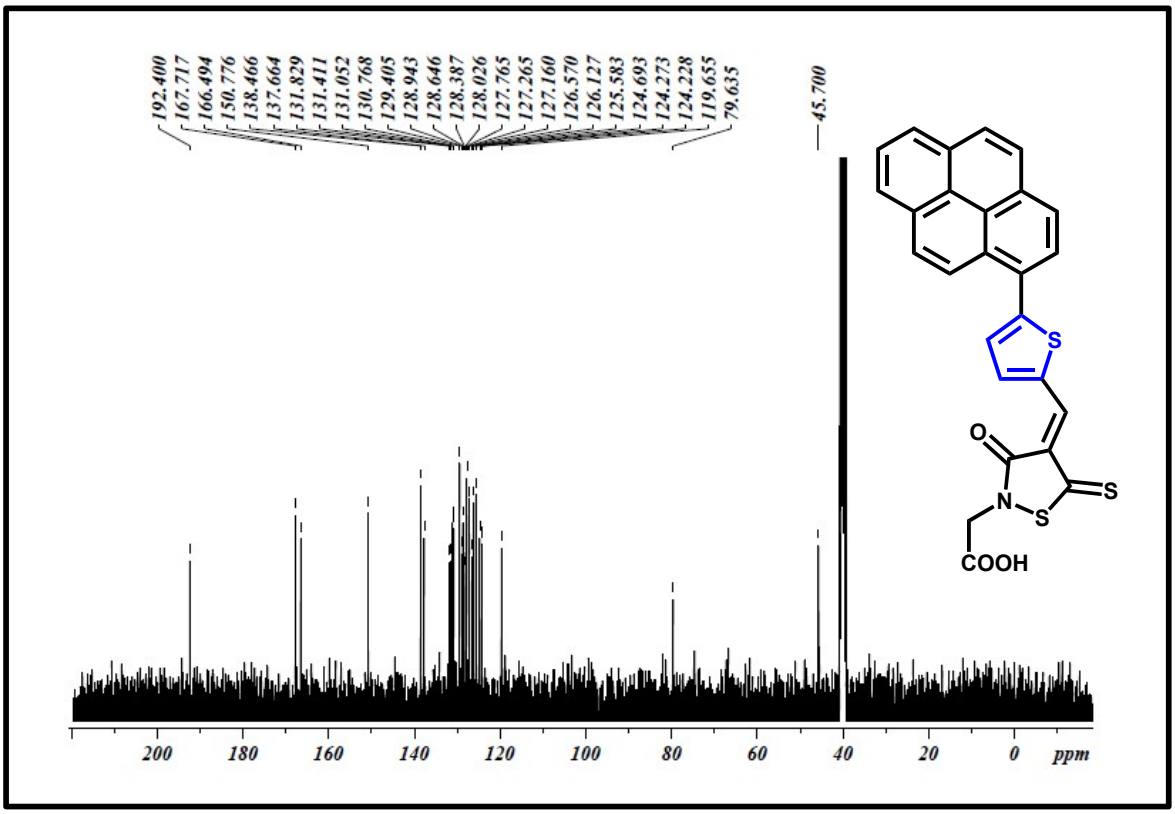


Figure S13: ^{13}C NMR spectrum of PTRA in DMSO – d_6

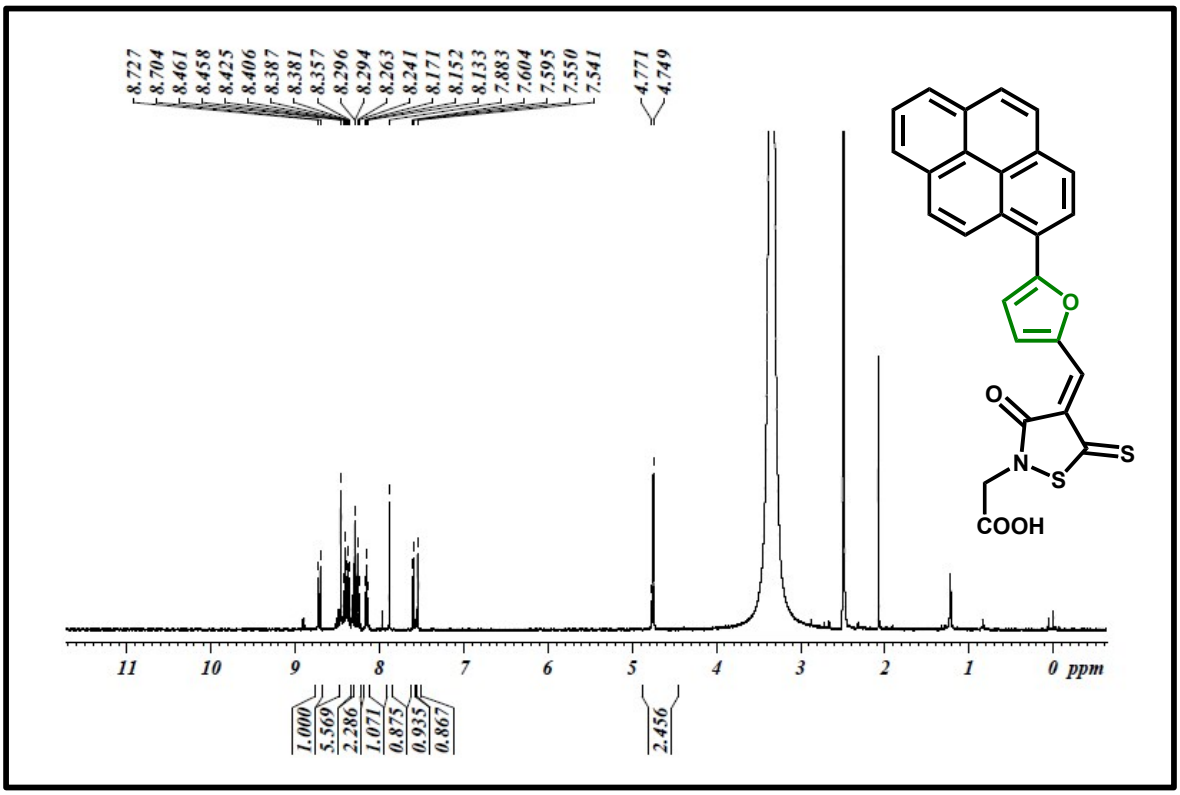


Figure S14: ^{1}H NMR spectrum of PFRA in DMSO – d_6

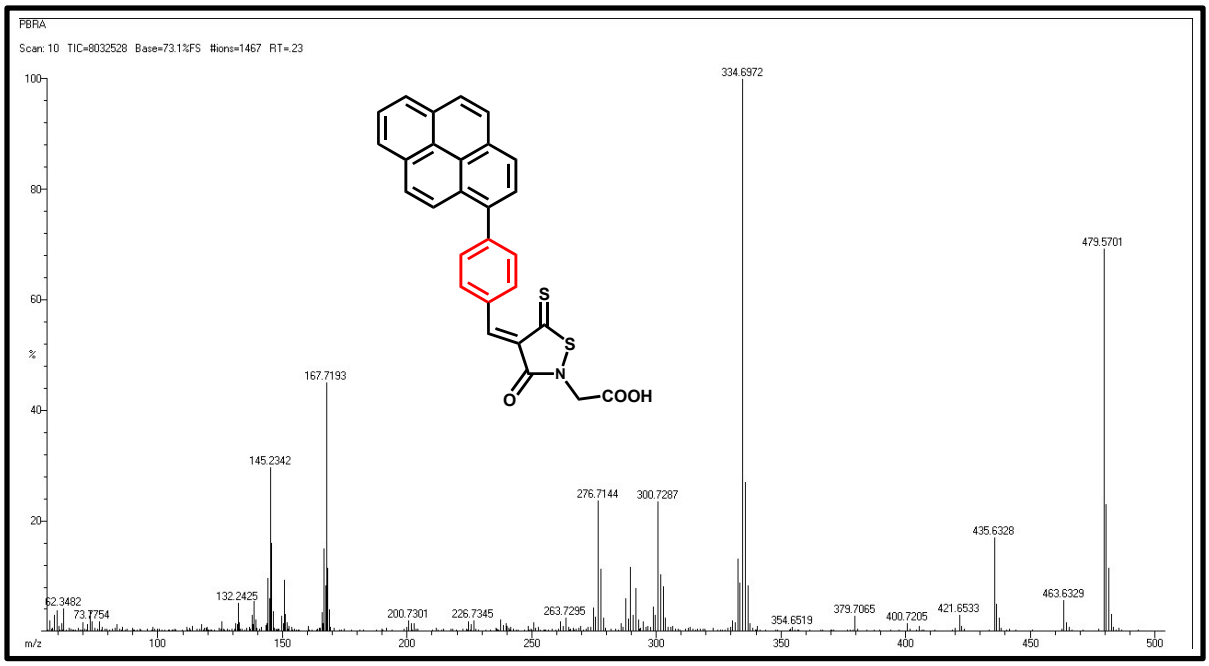


Figure S15: Mass spectrum of PBRA in DMSO – d_6

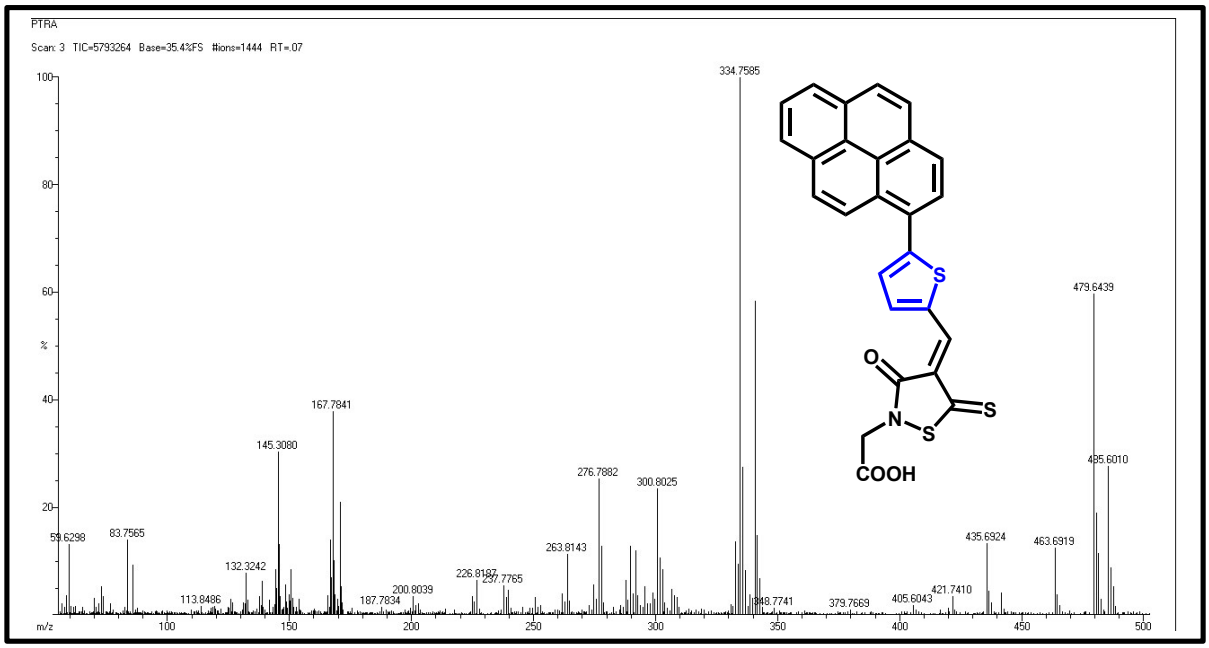


Figure S16: Mass spectrum of PTRA in DMSO – d_6

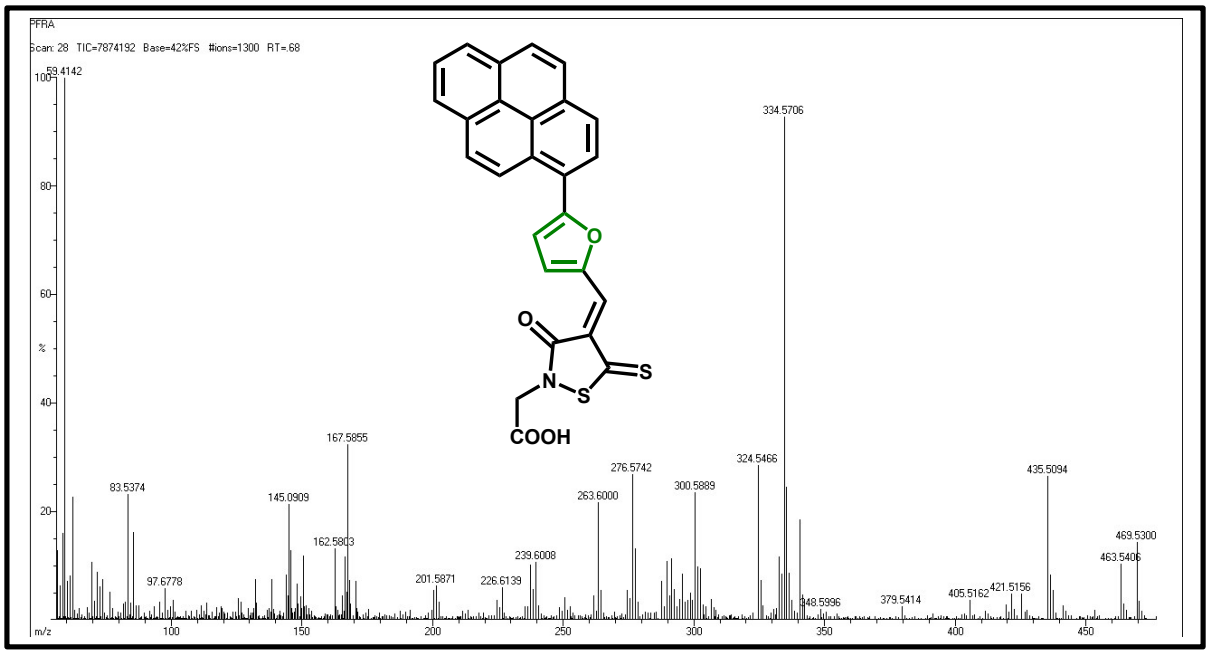


Figure S17: Mass spectrum of PFRA in DMSO – d_6

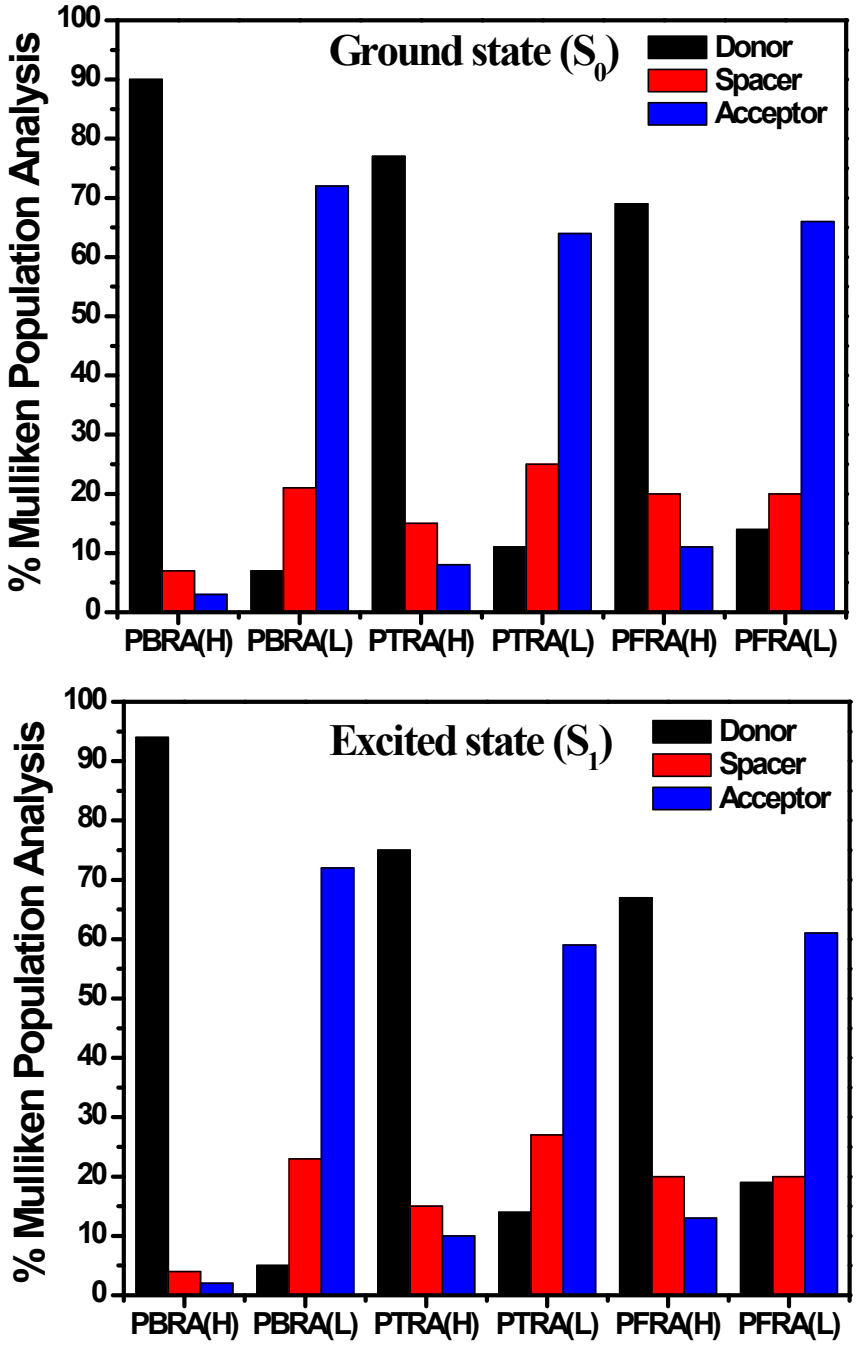


Figure S18: Mulliken population analysis of pyrene derivatives.

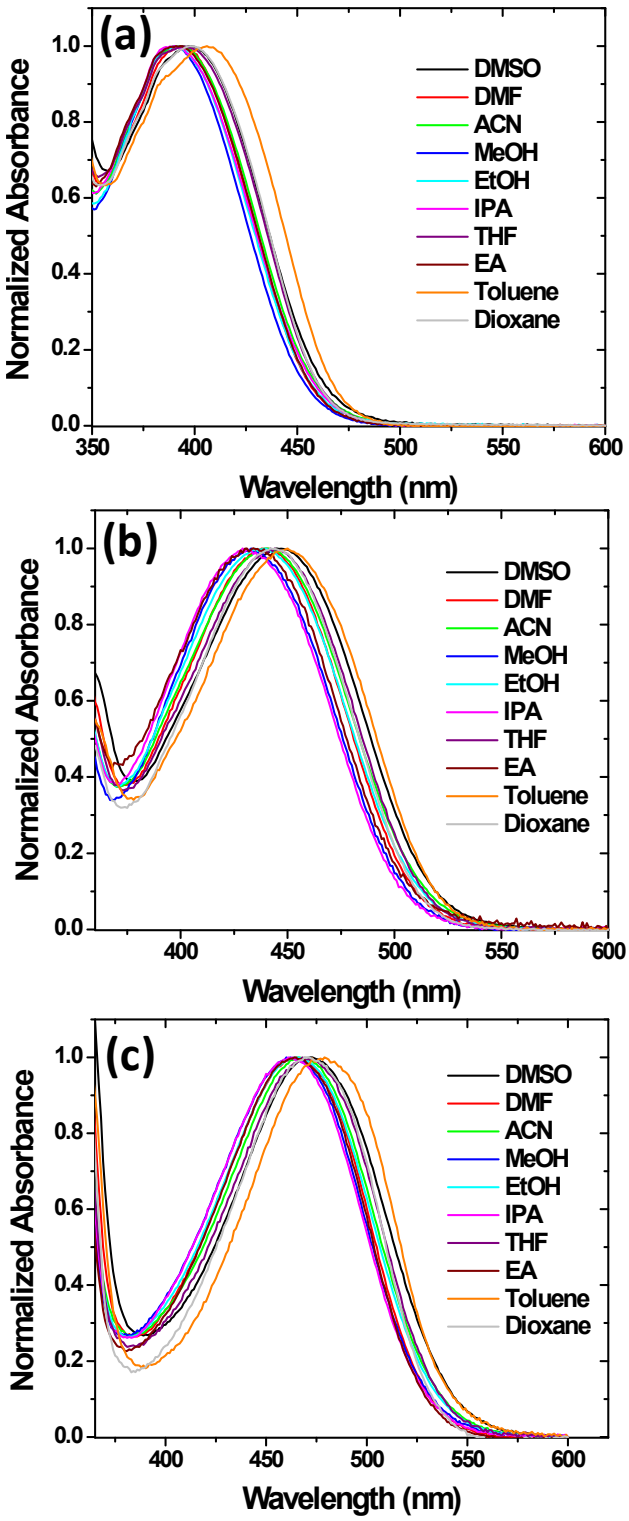


Figure S19: The absorption spectra of pyrene derivatives in various solvents. (a) PBRA (b) PTRA and (c) PFRA

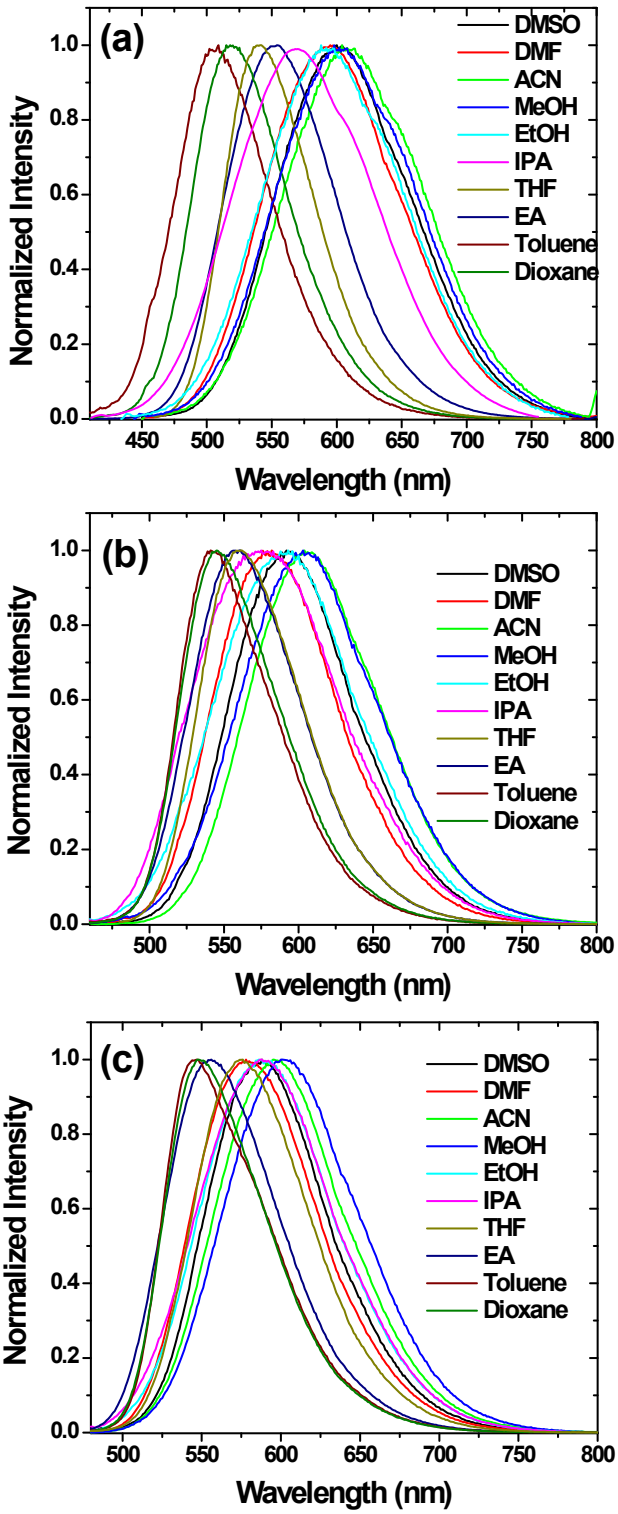


Figure S20: The emission spectra of pyrene derivatives in various solvents. (a) PBRA (b) PTRA and (c) PFRA

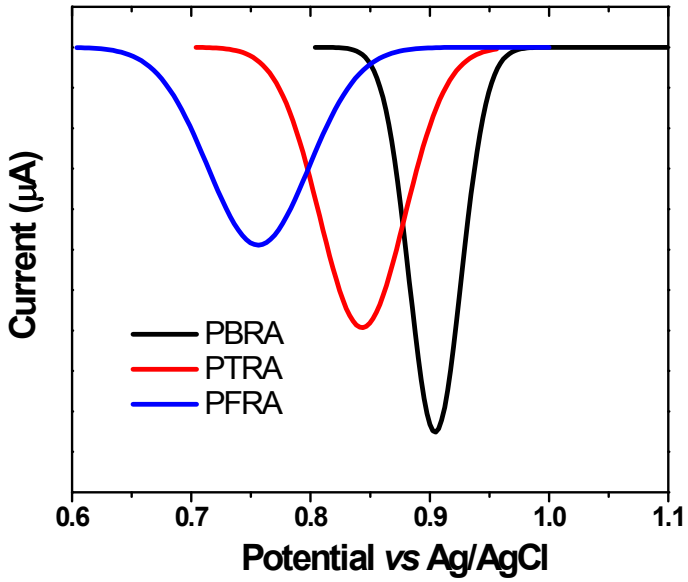


Figure S21: Differential pulse voltammogram of pyrene derivatives in THF solution at 25 °C. Supporting electrolyte: 0.1 M *tetra*-butylammonium hexafluorophosphate. Scan rate: 5 mV s^{-1}

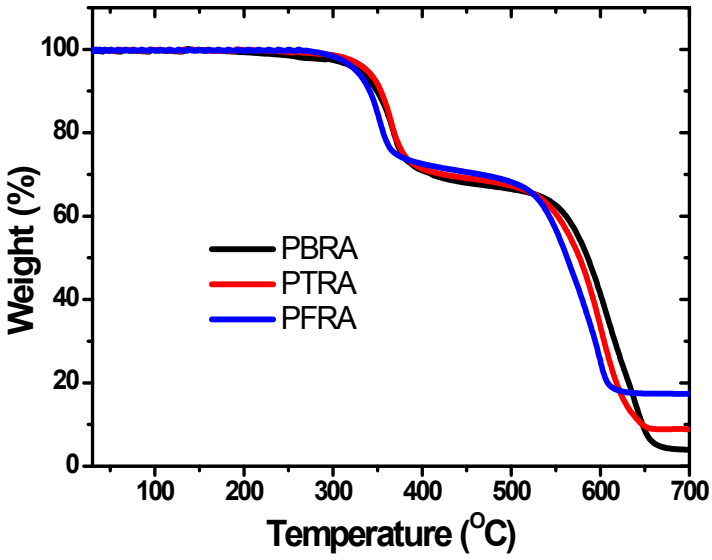


Figure S22: TGA spectrum of pyrene derivatives at a heating rate of 10 °C/min under N_2 atmosphere.

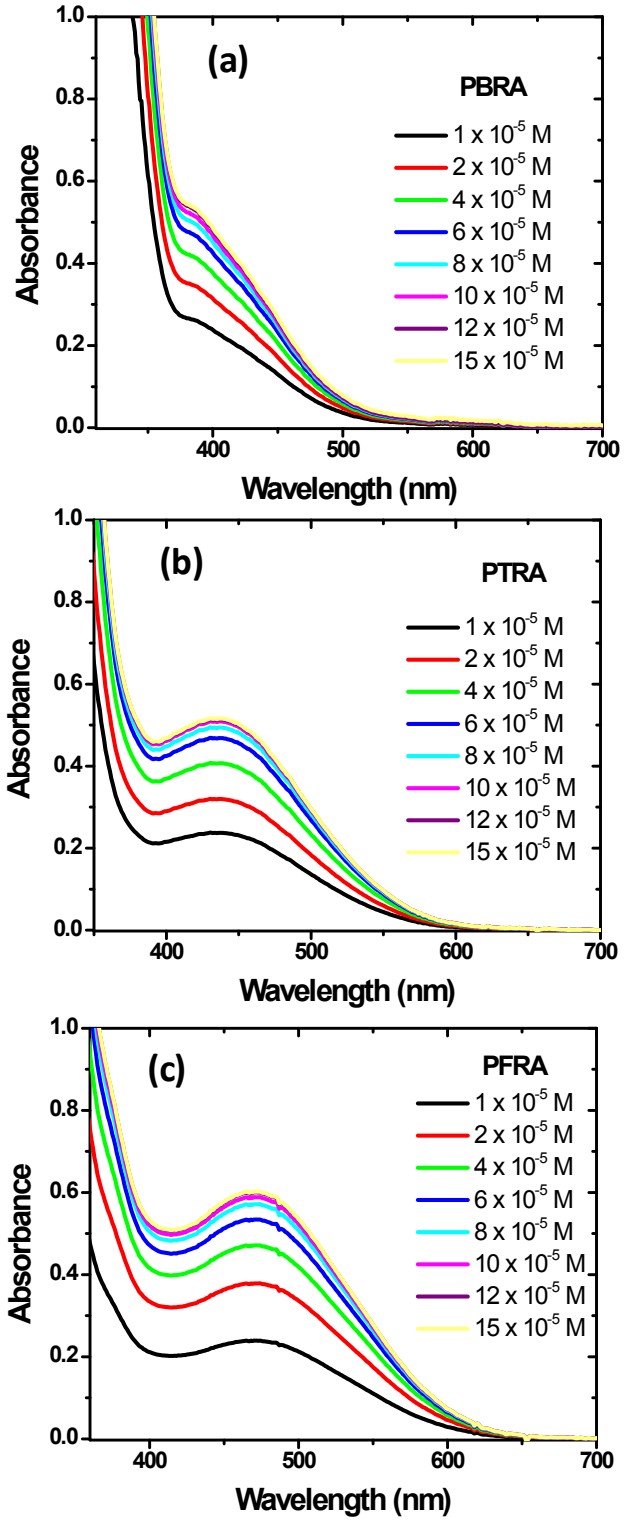
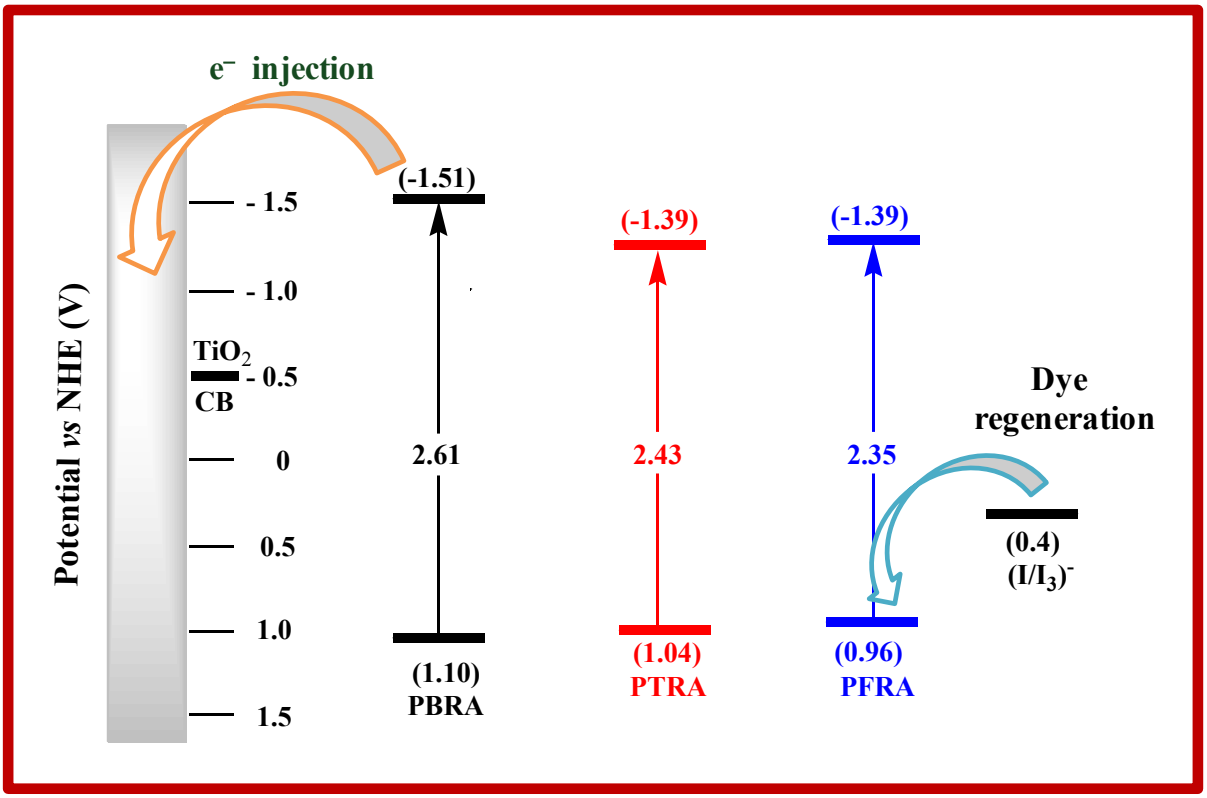


Figure S23: Absorption spectra of pyrene derivatives anchored on TiO_2 films. (a) PBRA, (b) PTRA and (c) PFRA

Table S1: Computed absorption maxima (in nm), energy (E in *eV*) and oscillator strength (*f*) at Cam-B3LYP/6-311+G(d,p) level of theory in THF continuum.

Parameters	PBRA	PTRA	PFRA
λ_{max} (nm)	392	433	445
E in eV	3.16	2.86	2.79
Oscillator strength	1.407	1.611	1.765
Electronic Transition	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_1$
Nature of Transition	ICT	ICT	ICT



Scheme S1: Schematic energy levels for the electron transfer between pyrene derivatives and the conduction band of TiO_2