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A Combined Experimental and Computational Investigation on Pyrene Based D-π-A Dyes

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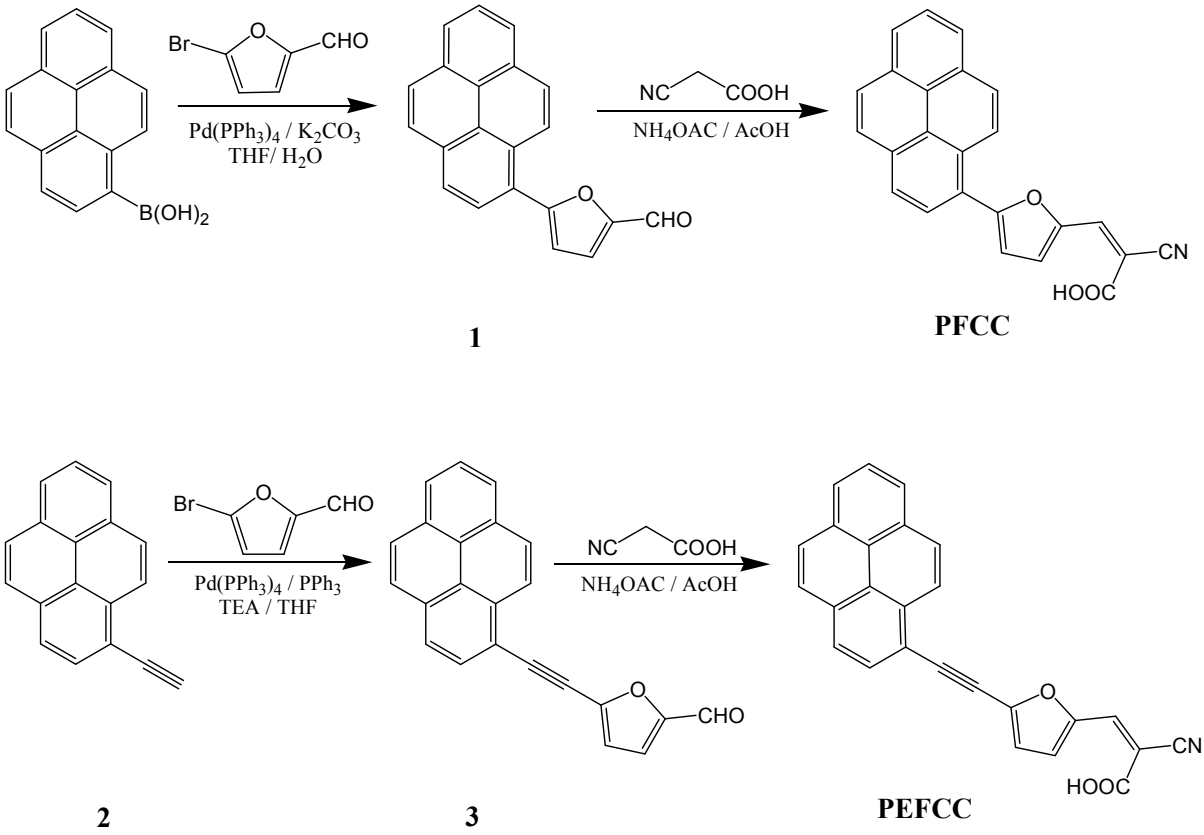

Scheme S1: Synthetic routes of pyrene derivatives.

Synthetic procedure:

5-pyren-1-yl-furan-2-carbaldehyde (1). Compound **1** was prepared according to our previous work[S1] starting from commercially available pyrene-1-boronic acid, 1-ethynylpyrene and 5-bromo-2-furaldehyde.

2-cyano-3-(5-pyren-1-yl-furan-2-yl)-acrylic acid (PFCC).A mixture of 5-pyren-1-yl-furan-2-carbaldehyde (0.296 g, 1.0 mmol), cyanoacetic acid (0.102g, 1.2mmol) and anhydrous ammonium acetate (0.038g, 0.5mmol) in 20 ml glacial acetic acid was heated under reflux for 8hours at argon atmosphere. After cooling, the reaction mixture was poured into the cold water; the precipitate formed was collected by filtration, washed with excess of water and dried. The crude product was purified in column chromatography ($CHCl_3$: MeOH) to give red solid product. (0.152 g, 51% yield);^{1}H NMR (DMSO-d_6, 500 MHz) δ ppm: 8.96-8.94 (d, 1H, *J* = 10 Hz), 8.53-8.52 (d, 1H, *J* = 5 Hz), 8.39-8.36 (t, 3H, *J* = 7.5 Hz), 8.31-8.26 (m, 2H), 8.23-8.21 (d, 1H, *J* = 10 Hz), 8.14-8.12 (t, 1H, *J* = 5 Hz), 7.99 (s, 1H), 7.51-7.49 (t, 2H, *J* = 5 Hz);^{13}C NMR (DMSO-d_6, 500 MHz) δ ppm: 157.2, 149.92, 131.81, 131.42, 129.36, 128.86,

127.77, 127.33, 127.17, 126.57, 126.52, 125.7, 125.06, 124.8, 124.25, 123.79, 114.13; EI-MS (*m/z*) 318 [M^+ - COOH]

5-pyren-1-ylethynyl-furan-2-carbaldehyde (3).A mixture of1-ethenylpyrene (0.50 g, 2.2 mmol), 5-bromo-2-furan carboxaldehyde (0.48 g, 3.3 mmol), $Pd(PPh_3)_4$ (25 mg, 0.02 mmol), CuI (42 mg, 0.22 mmol) and PPh_3 (50 mg, 0.22 mmol) were dissolved in 20 ml of freshly distilled THF and 10 ml of triethylamine and the resulting mixture was stirred at 100 °C overnight in an inert atmosphere. Finally the volatile solvent was evaporated in rotavapor and the residue was washed with brine and extracted from $CHCl_3$, dried in Na_2SO_4 and solvent was evaporated. The crude product was purified in column chromatography (Hexane: ethylacetate) to give yellow solid (0.422 g, 60% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm:9.7 (s, 1H), 8.6-8.58 (d, 1H, *J* = 10 Hz), 8.28-8.26 (d, 1H, *J* = 10 Hz), 8.25-8.20 (m, 3H), 8.16-8.14 (d, 2H, *J* = 10 Hz), 8.08-8.04 (t, 2H, *J* = 10 Hz), 7.34-7.33 (d, 1H, *J* = 5 Hz), 6.94-6.93 (d, 1H, *J* = 5 Hz); ^{13}C NMR ($CDCl_3$, 500 MHz) δ ppm: 177.21, 152.59, 142.35, 132.35, 132.29, 131.18, 130.97, 129.75, 129.08, 129.02, 127.18, 126.51, 126.18, 126.1, 125.09, 124.57, 124.39, 124.15, 117.16, 115.25, 96.14, 83.89.EI-MS (*m/z*)320 [M+].

2-cyano-3-(5-pyren-1-ylethynyl-furan-2-yl)-acrylic acid (PEFCC). The compound 5-pyren-1-ylethynyl-furan-2-carbaldehyde (0.20 g, 0.624 mmol), cyanoacetic acid (0.063g, 0.75mmol) and anhydrous ammonium acetate (0.02 g, 0.31mmol) in 20 ml glacial acetic acid was refluxed in oil bath at 120 °C overnight in an inert atmosphere. The mixture was cooled to room temperature, poured into ice cold water. The precipitate formed was filtered, washed with excess of water and dried. Finally red solid was obtained by purification through column chromatography ($CHCl_3$: MeOH, 95:5) to give red solid (0.31 g, 76 % yield).^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 8.36-8.32 (t, 1H, *J* = 8 Hz), 8.27-8.21 (m, 3H), 8.18-8.11 (m, 3H), 8.08-8.06 (d, 1H, *J* = 8 Hz), 8.02-7.98 (t, 1H, *J* = 8 Hz), 7.82 (s, 1H), 7.31-7.30 (d, 1H, *J* = 4 Hz), 7.22-7.21 (d, 1H, *J* = 4 Hz); ^{13}C NMR (DMSO-d_6, 400 MHz) δ ppm: 149.85, 131.50, 131.11,130.50, 130.18, 129.19, 126.96, 126.15, 124.76, 123.28, 123.02, 114.40, 95.43, 84.60, 72.21, 60.20; EI-MS (*m/z*) 343 [M^+ - COOH]

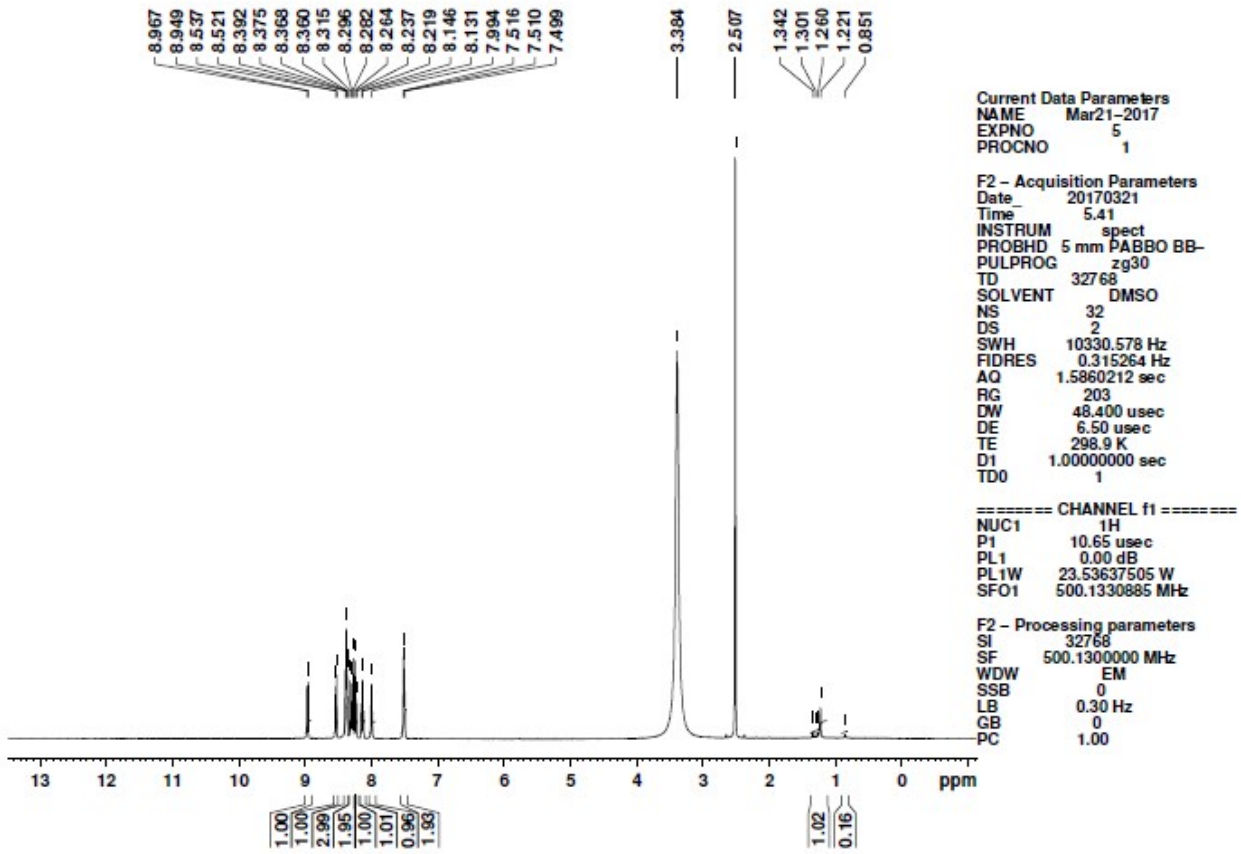

Fig.S1: ^{1}H NMR of 2-Cyano-3-(5-pyren-1-yl-furan-2-yl)-acrylic acid (PFCC) in DMSO-d_6

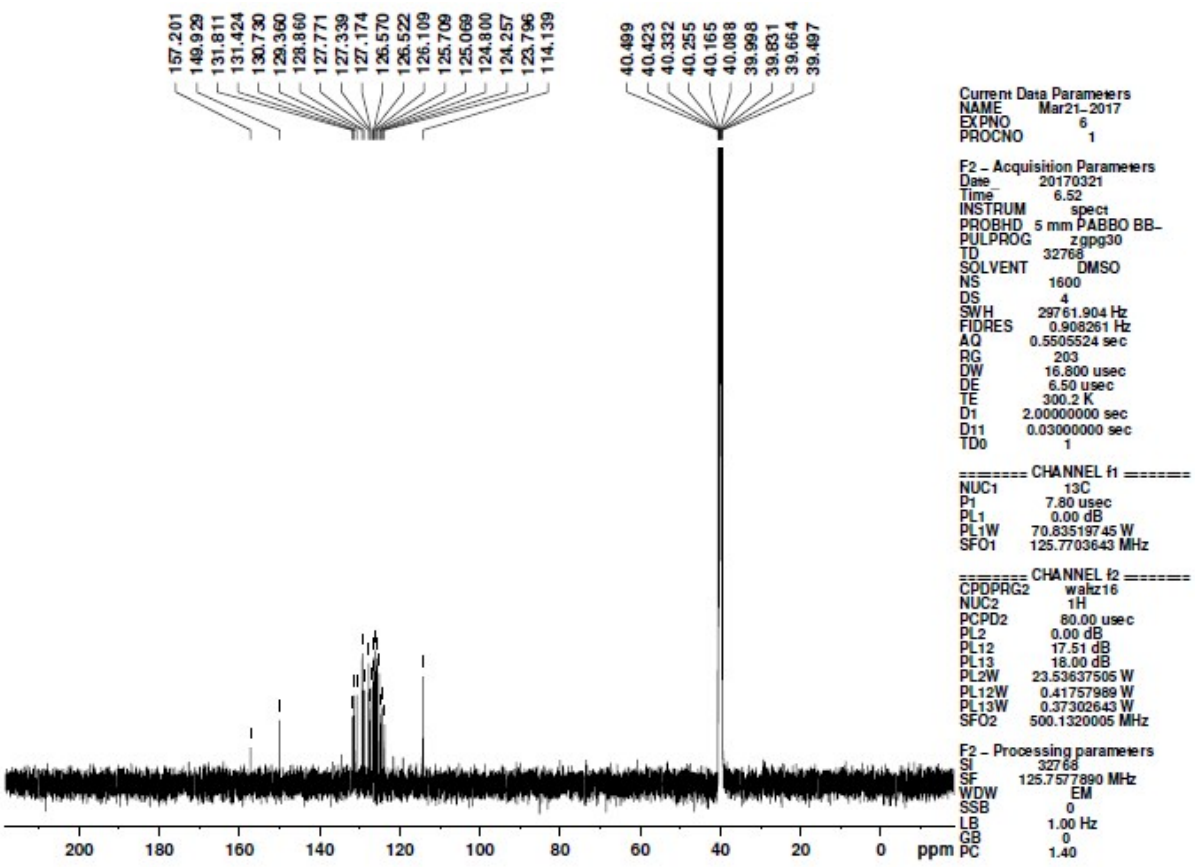

Fig. S2: ^{13}C NMR of 2-Cyano-3-(5-pyren-1-yl-furan-2-yl)-acrylic acid (PFCC) in DMSO-d_6

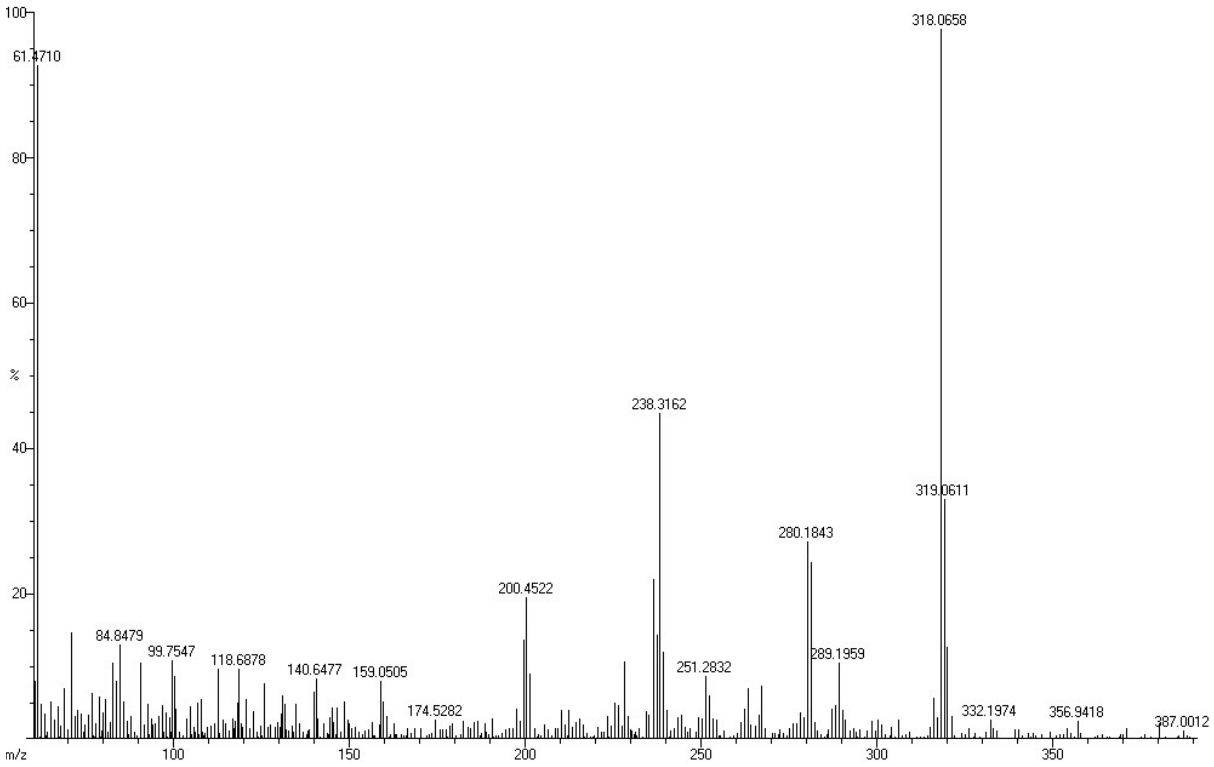

Fig. S3:EI-MASS Spectrum of 2-Cyano-3-(5-pyren-1-yl-furan-2-yl)-acrylic acid (PFCC).

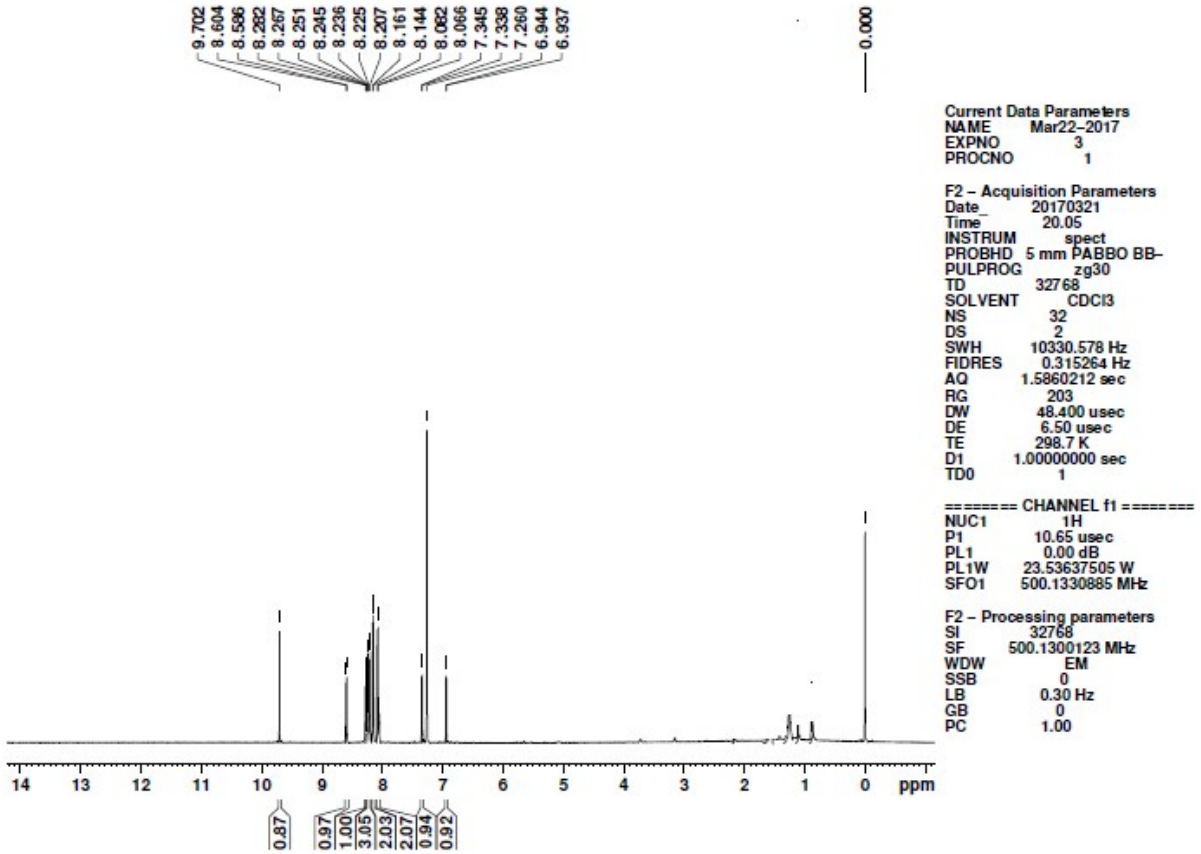

Fig.S4: ^{1}H NMR of 5-Pyren-1-ylethynyl-furan-2-carbaldehyde (**3**) in $CDCl_3$

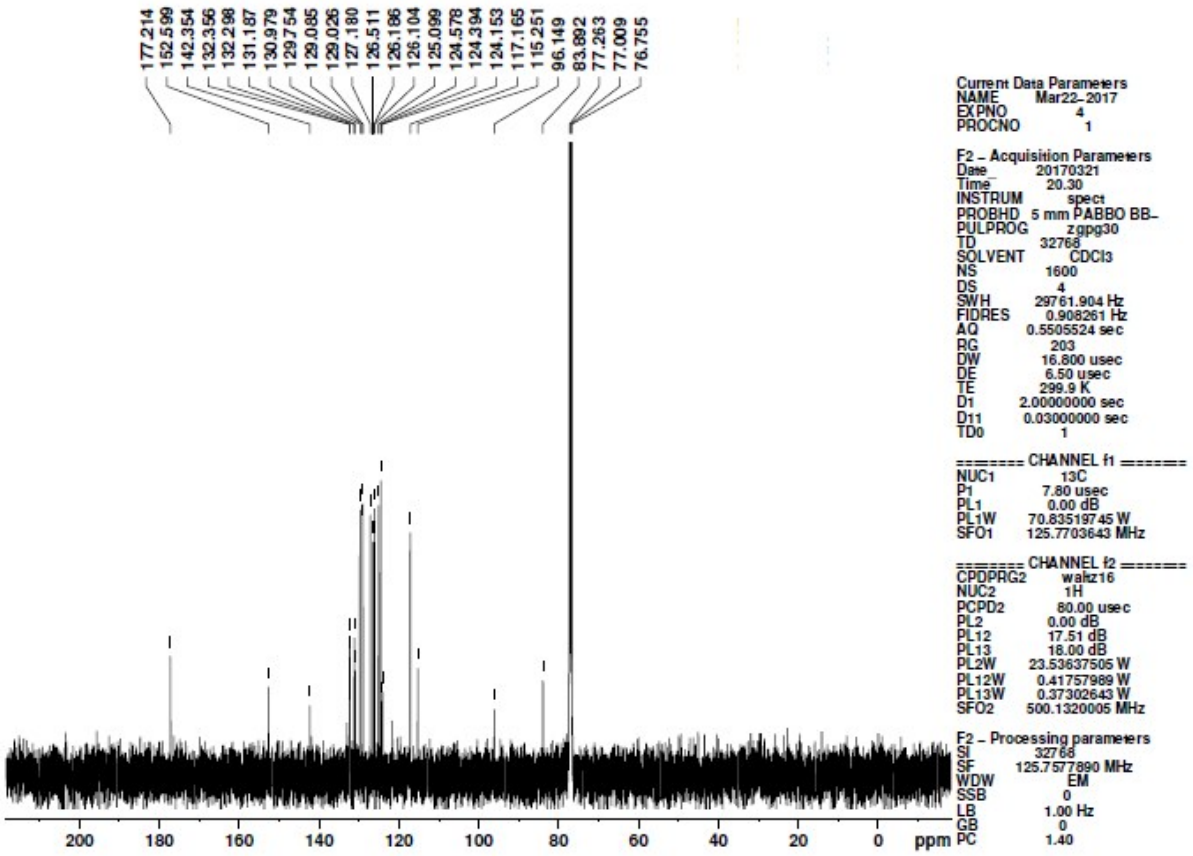

Fig.S5: ^{13}C NMR of 5-Pyren-1-ylethynyl-furan-2-carbaldehyde (**3**) in $CDCl_3$

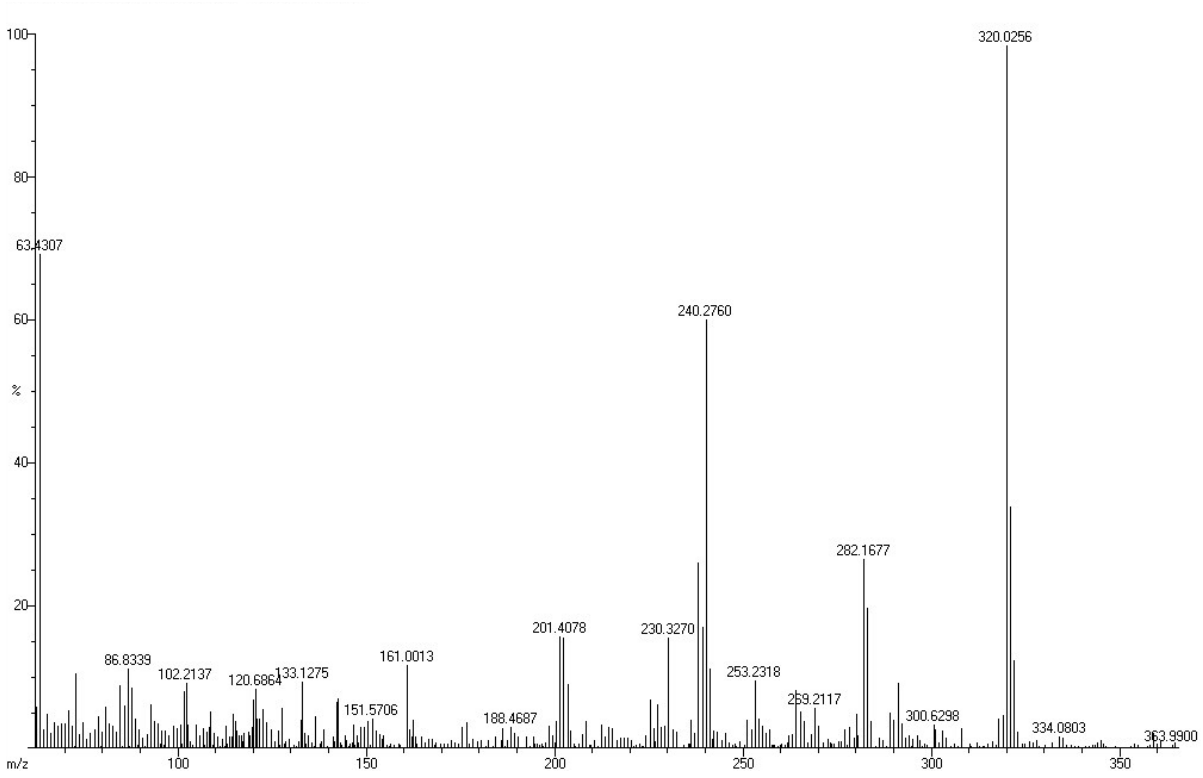

Fig. S6:EI-MASS Spectrum of 5-Pyren-1-ylethynyl-furan-2-carbaldehyde (**3**).

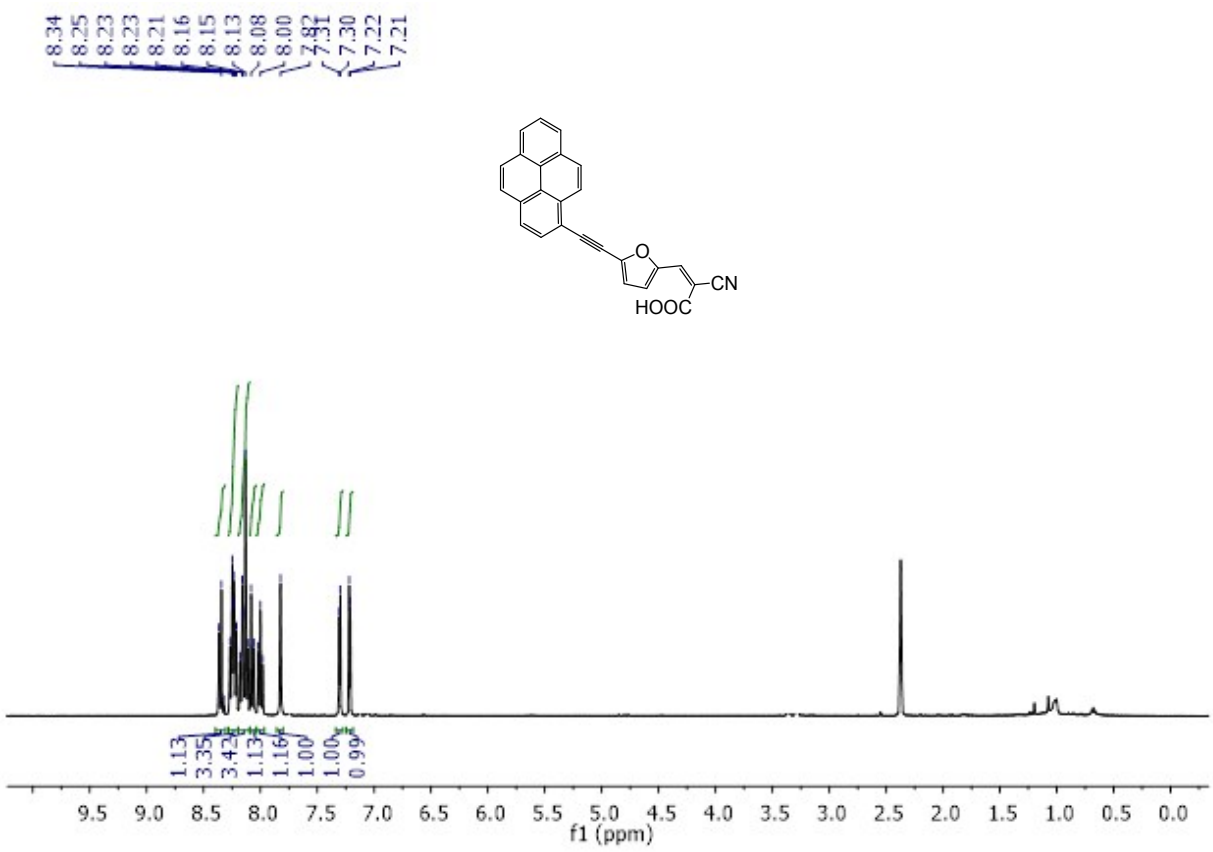

Fig.S7: ^{1}H NMR of 2-Cyano-3-(5-pyren-1-ylethynyl-furan-2-yl)-acrylic acid (PEFCC) in DMSO-d_6

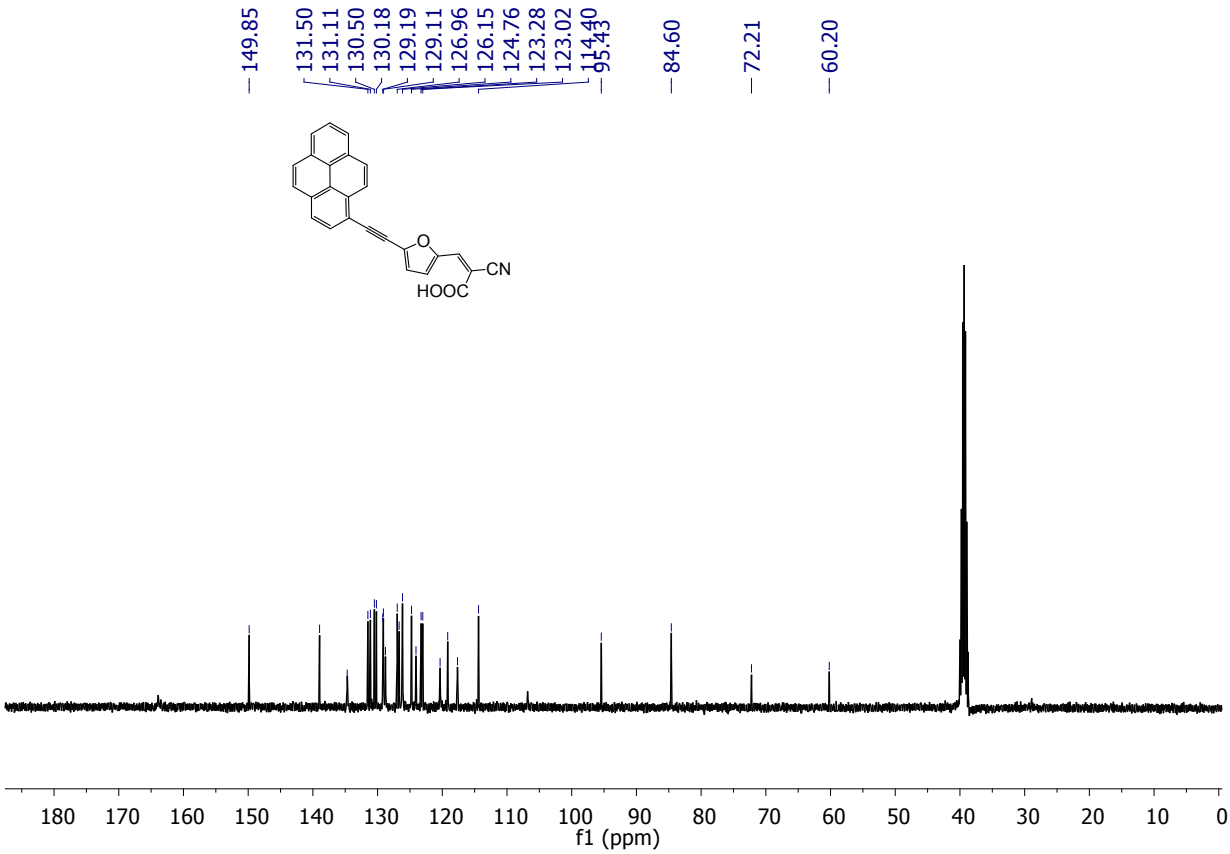

Fig.S8: ^{13}C NMR of 2-Cyano-3-(5-pyren-1-ylethynyl-furan-2-yl)-acrylic acid (PEFCC) in DMSO-d_6

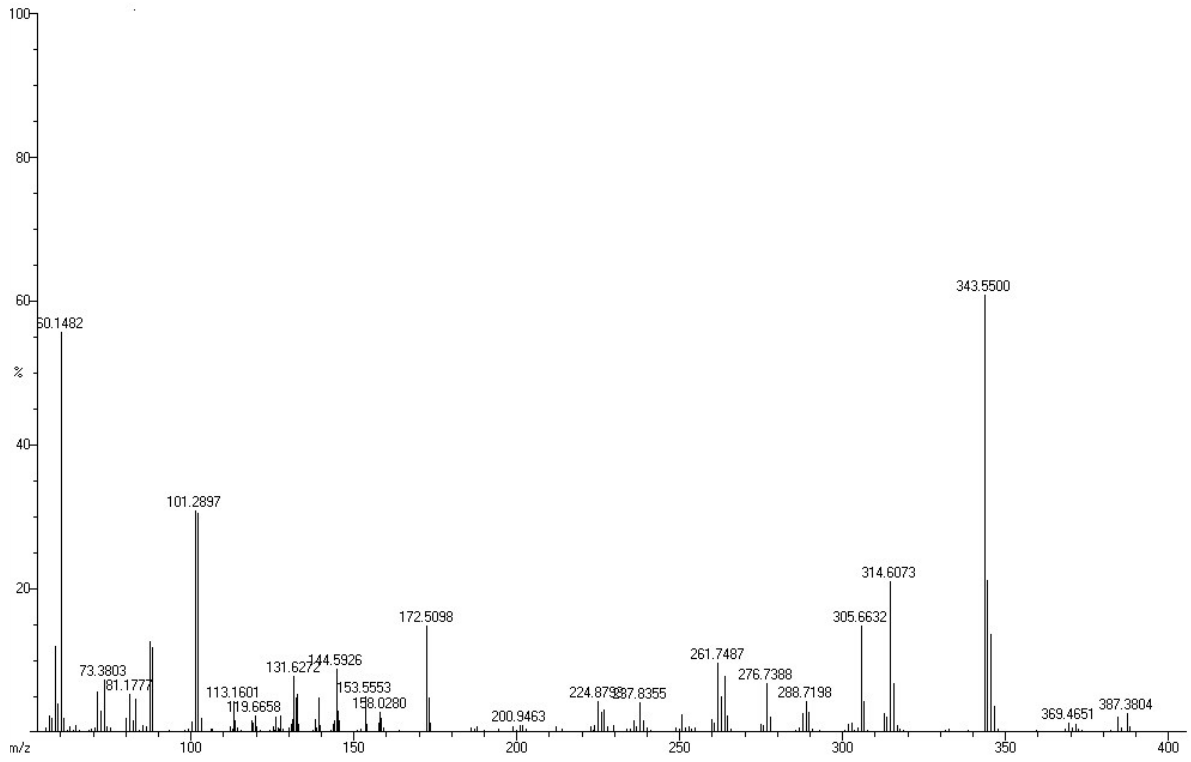

Fig. S9:EI-MASS Spectrum of 2-Cyano-3-(5-pyren-1-ylethynyl-furan-2-yl)-acrylic acid (PEFCC).

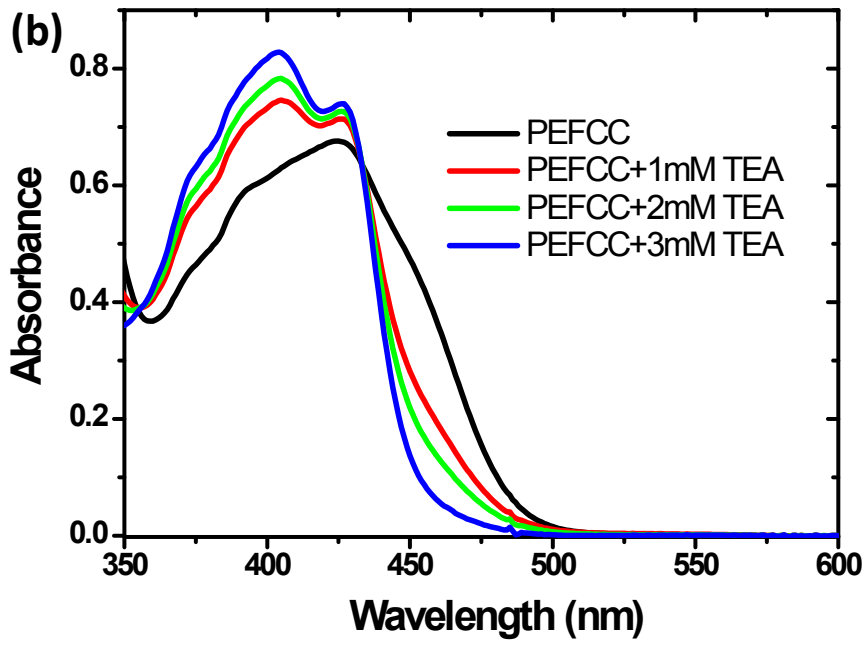

Figure S10: Absorption spectra of PEFCC with increasing concentrations of TEA.

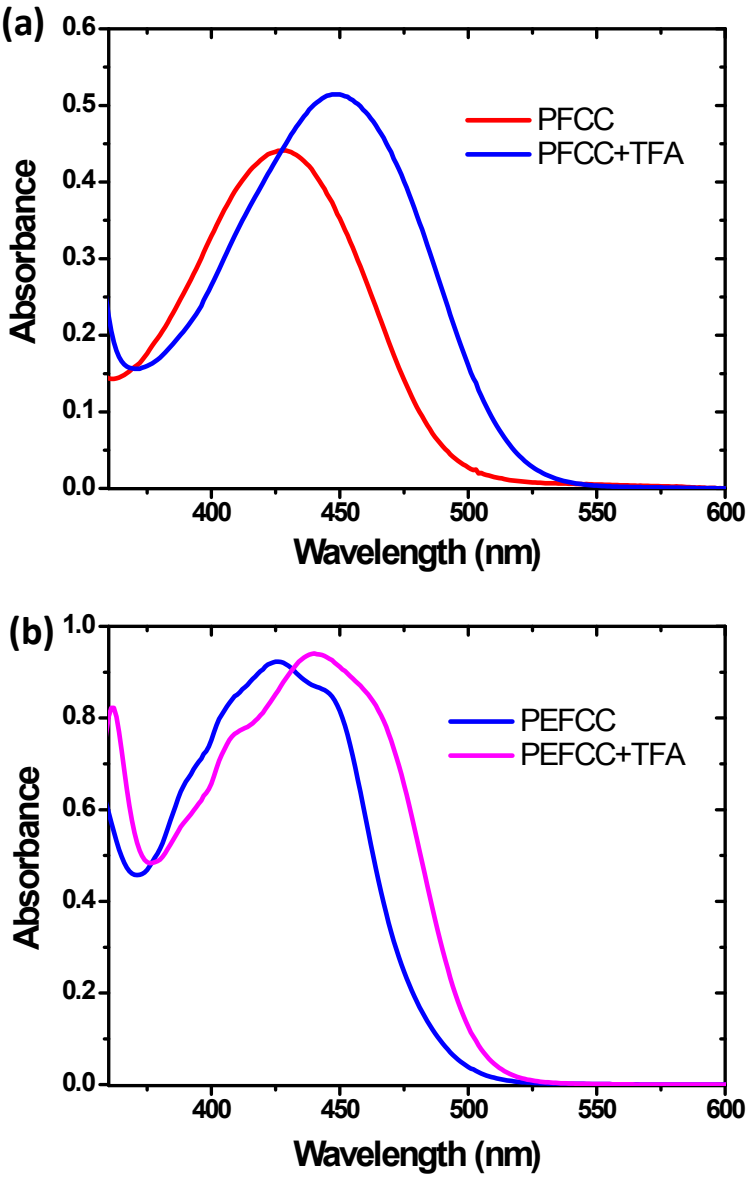

Figure S11: Absorption spectra of pyrene dyes recorded in THF before and after the addition of TFA.

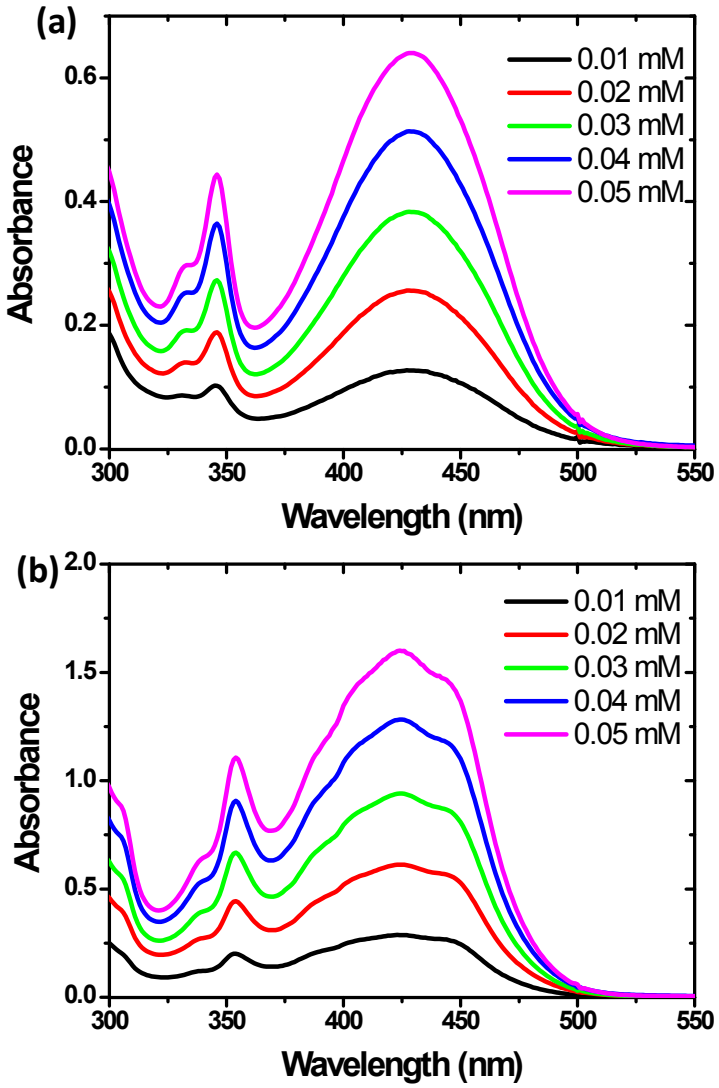

Fig. S12: Effect of dye concentration on the absorption spectra (a) PFCC (b) PEFCC

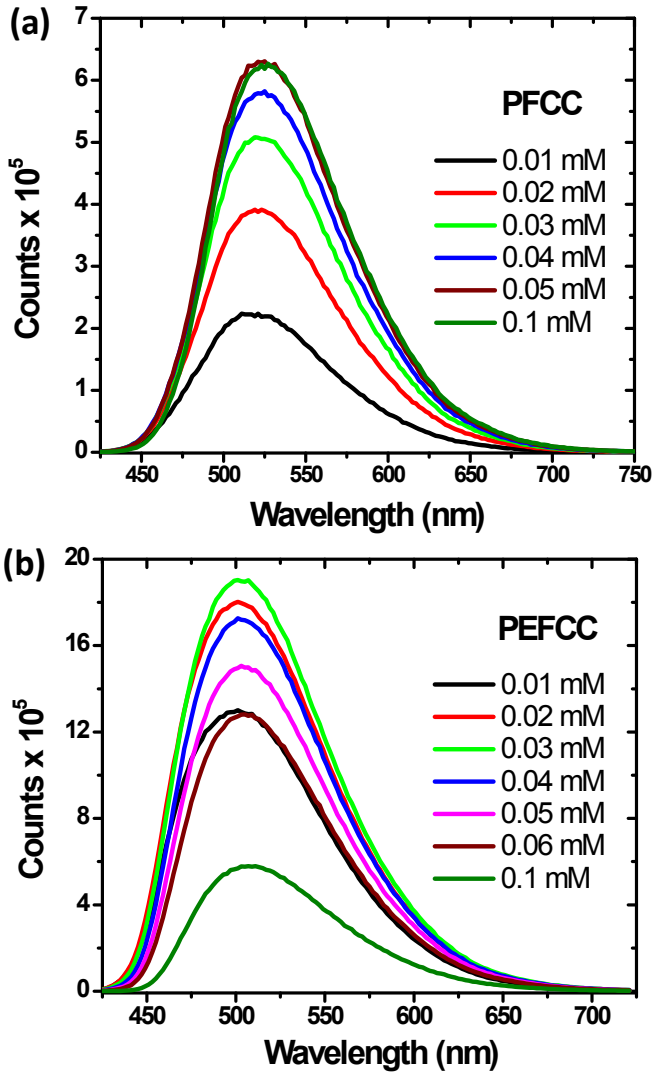

Figure S13: Effect of dye concentration on the emission spectra (a) PFCC (b) PEFCC

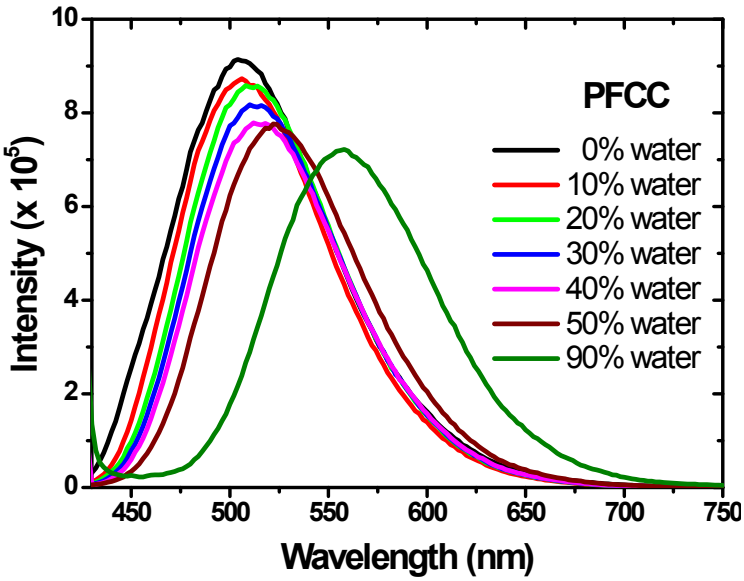

Figure S14: Aggregation induced emission changes of PEFCC dye with varying water fractions.

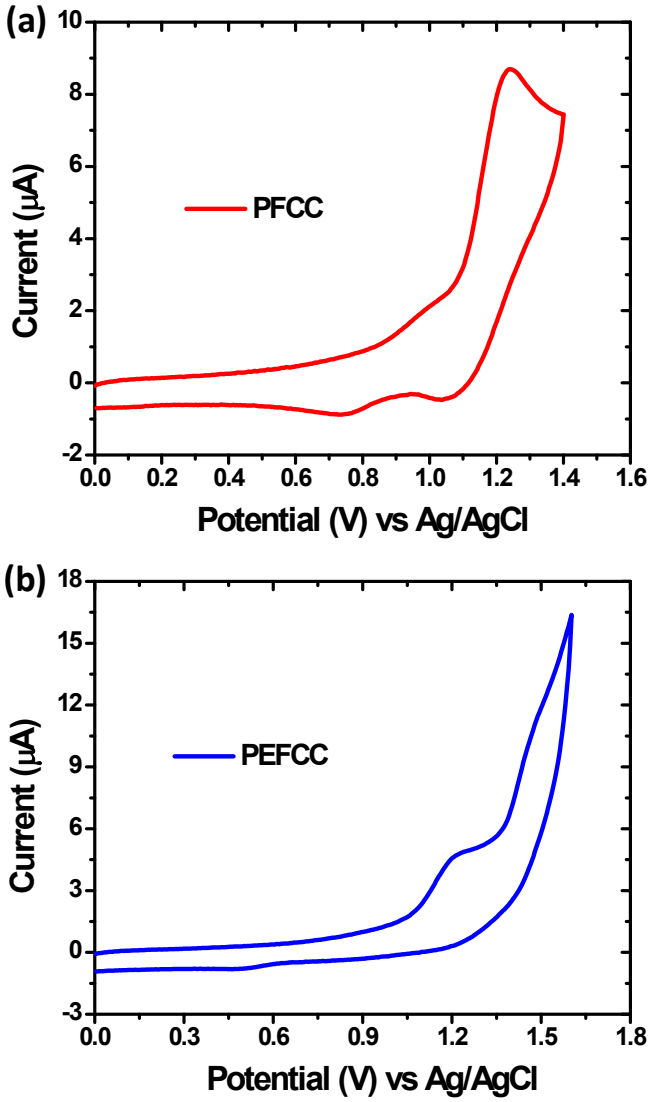

Figure S15: Cyclic voltammograms of pyrene derivatives(1 mM) in CH_3CN containing 0.1 M $TBAPF_6$ using Ag/AgCl as reference electrode with a scan rate of 0.10 V/s at 298 K. Potentials were measured vs Ag/AgCl and converted to a normal hydrogen electrode (NHE) by the addition of + 0.2 V.

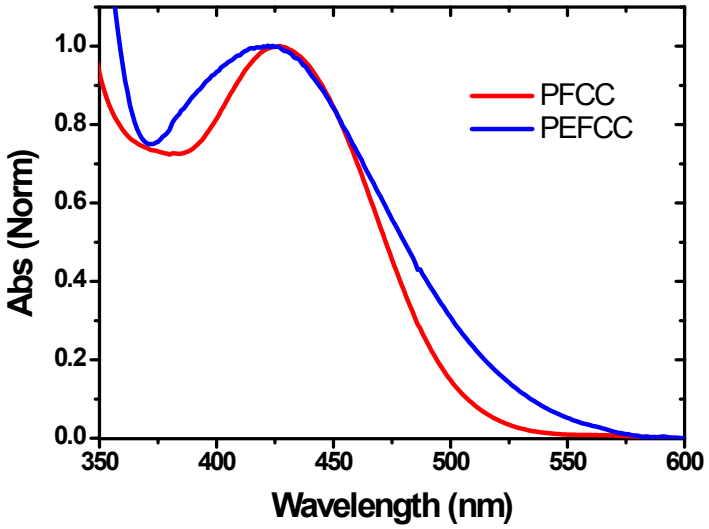

Figure S16: Normalized absorption spectra of pyrene derivatives on TiO_2 surface.

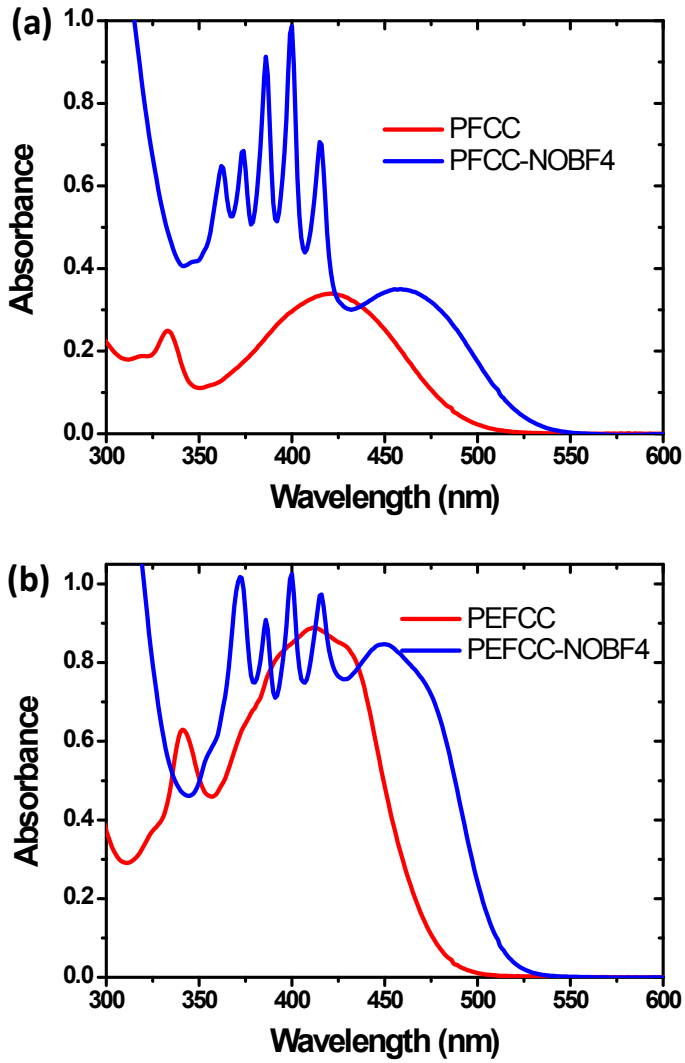

Fig. S17: Spectral changes of pyrene derivatives with nitrosonium tetrafluoroborate

Table S1: FMO molecular contributions

Molecule		Donor	Bridge-1	Bridge-2	Acceptor
PFCC	HOMO	83%	-	13%	4%
	LUMO	17%	-	28%	55%
PEFCC	HOMO	75%	9%	11%	5%
	LUMO	16%	9%	27%	48%

Reference:

S1. A. Kathiravan, V. Srinivasan, T. Khamrang, M. Velusamy, M. Jaccob, N. Pavithra, S. Anandan and K. Velappan, *Phys. Chem. Chem. Phys*., 2017, **19**, 3125-3135.