Highly selective colorimetric detection of cyanide anion in aqueous media by triphenylamine and phenanthro(9,10-d)imidazole based probes

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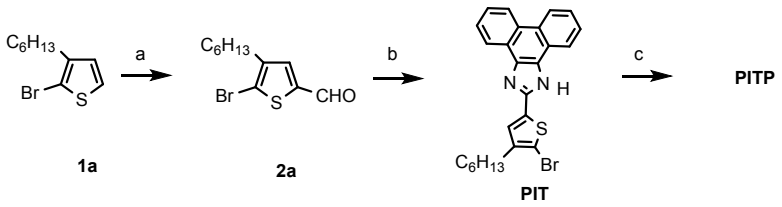
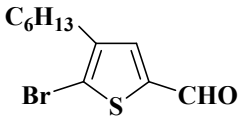
Experimental procedure:



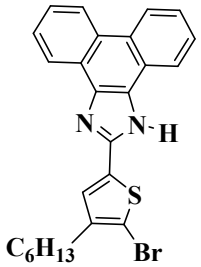
Scheme S1 (a) $POCl_3$, DMF, EDC, 80°C, (yield 95%) (b) 9,10-phenanthroquinone, NH_4OAc, AcOH, 120°C, (yield 90%) (C) 4-vinylpyridine, $Pd(OAc)_2$, DMF, 120°C, TBAB, K_2CO_3, (yield 45%).

Synthesis of 2-bromo-3-hexyl-5-carbaldehyde (2a)[1]



Mixture of phosphorous oxychloride 12.24 ml (48.6 mmol) and dimehtylformamide 5.84 ml (84.7 mmol) cooled to 0^0C and 2-bromo-3-hexyl-thiophene 0.8 ml (4.0 mmol) in 10 ml ethylene dichloride was added drop wise over 10 minutes into the reaction mixtures. Then heated to 80^0C for about 8 hrs. The reaction mass was quenched with ice cooled water and neutralized with sodium hydroxide and extracted with ethylacetate three times. Further, the organic layer was washed with brine and water dried over sodium sulfate and solvent was distilled over reduced pressure to give a dark brown solid, which was further purified by column chromatography using (9:1) pet ether and ethylacetate as an eluent. Yellow oily liquid was obtained; yield is 95%.^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.78 (s, 1H), 7.52 (s,1H), 2.60 (t, *J*= 9 Hz, 2H,), 1.63-1.58 (m, 2H), 1.2-1.5 (m, 6H), 0.89 (t, *J* = 6.6Hz, 3H).

Synthesis of 2-(5-bromo-4-hexylthiophen-2-yl)-1H-phenanthro(9,10-*d*)imidazole (PIT)[1]



2-bromo-3-hexyl-5-carbaldehyde 1.0 g (3.6 mmol) and 9,10-phenananthrodione 0.9 g (3.6 mmol) was dissolved in acetic acid 20 ml and added ammonium acetate 1.3 g (16.8 mmol) into the reaction flask and the reaction mass was reflux for about 12 hrs, the reaction mass was quenched with crushed ice to gave orange solid which was filtered and washed with hot dichloromethane to give a product as an off-white solid. Yield is 90% (m.p. 220 ^{0}C).^{1}H NMR (300 MHz, DMSO) δ 13.56 (s, 1H), 8.88 (t, *J* =

9 Hz, 2H), 8.48 (d, *J* = 6.0 Hz, 1H), 8.41(d, *J* = 9.0 Hz, 1H), 7.78 – 7.62 (m, 5H), 2.62 (t, *J*= 9.0 Hz, 2H), 1.67-1.62(t, 2H), 1.5-1.2 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H). ESI-MS m/z calcd for $C_{25}H_{23}BrN_2S$:$[M]^+$ 464.07, Found; LCMS-ESI $[M-H]^+$ = 463.19 m/z. Elemental Anal. Calcd for $C_{25}H_{23}BrN_2S$: C, 64.79; H, 5.00; N, 6.04, S, 6.92; Found: C, 64.75; H, 4.98; N, 6.07, S, 6.88%.

References

1. A. Jesin Beneto, V. Thiagarajan, and A. Siva, A Tunable Ratiometric pH Sensor Based on Phenanthro[9,10-d]imidazole covalently linked with vinylpyridine, *RSC Advances*, **2015**, 5, 67849–67852

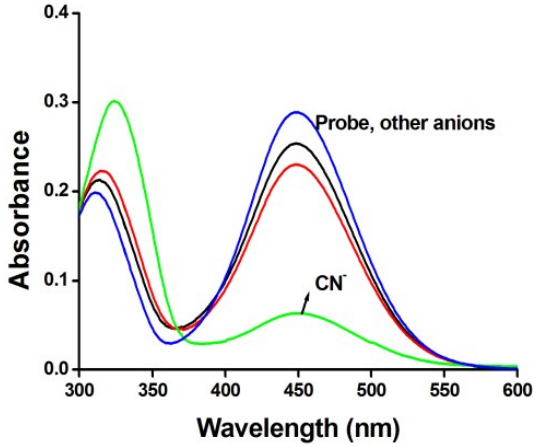


Figure S1. UV-visible spectra of TPC (10 μM) upon the addition of various anions.

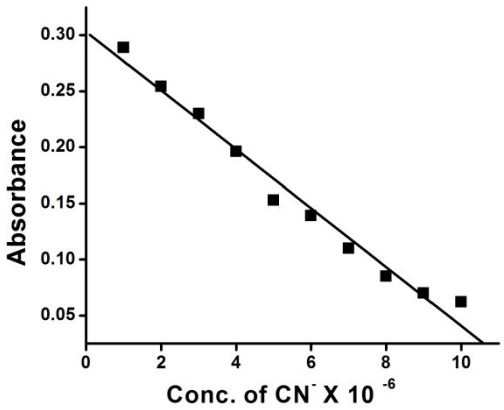


Figure S2. Linear plot of change in absorbance at 460 nm of TPC (10 μM) Vs. Various concentration of CN^- 1-10 μM.

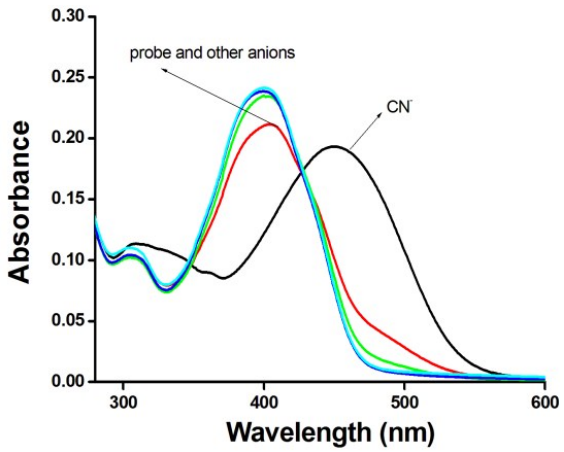


Figure S3. UV-visible spectra of PITP(10 μM) upon the addition of various anions.

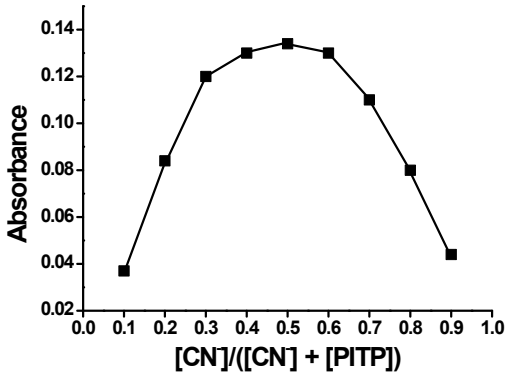


Figure S4. Jobs plot of PITP Vs. CN^-.

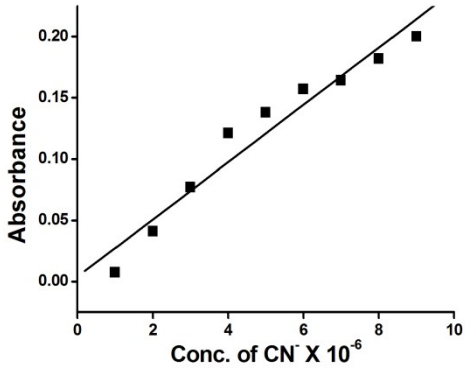


Figure S5. Linear plot of change in absorbance at 460 nm of PITP(10 μM) Vs. Various concentration of CN^- (1-10 μM).

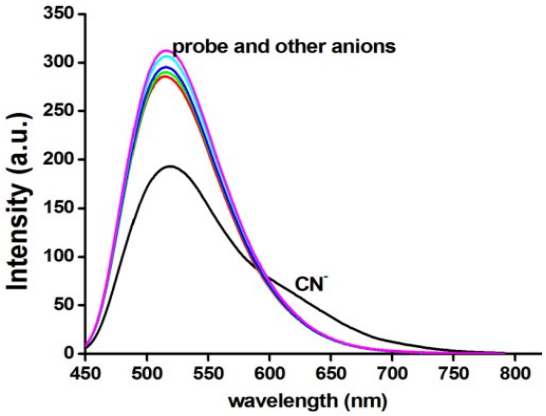
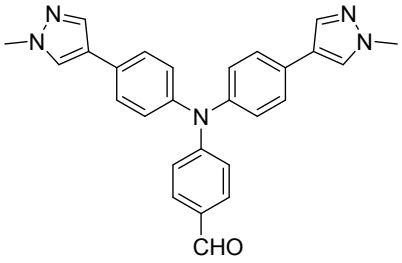


Figure S6. Fluorescence spectrum of PITP(10 μM) upon the addition of various anions, excited at 450 nm.



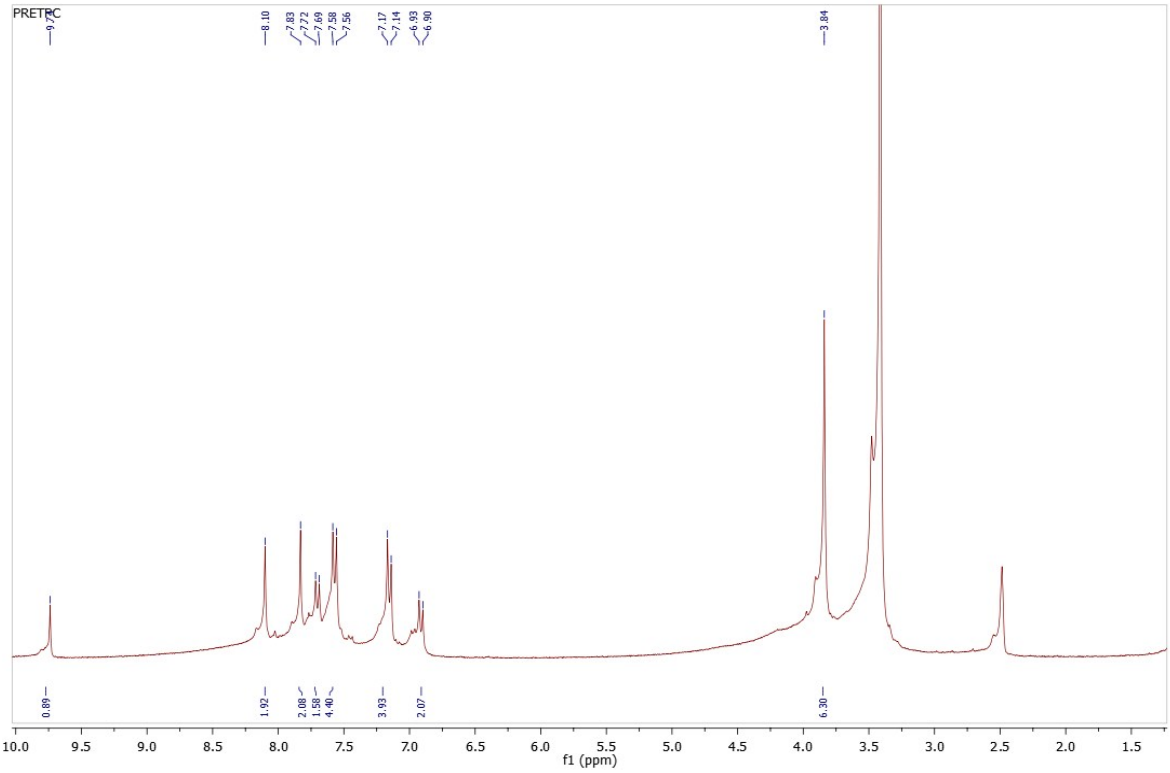
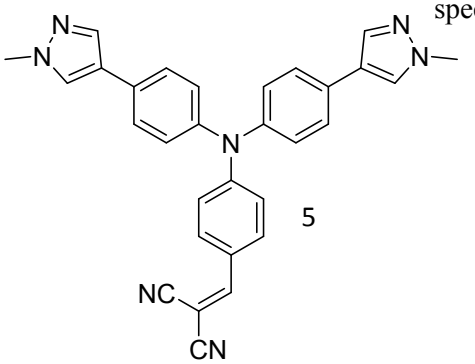


Figure S7. ^{1}H NMR spectrum of 4-(bis(4-1-methyl-1H-pyrazol-4-yl)phenylamino) benzaldehyde (2).



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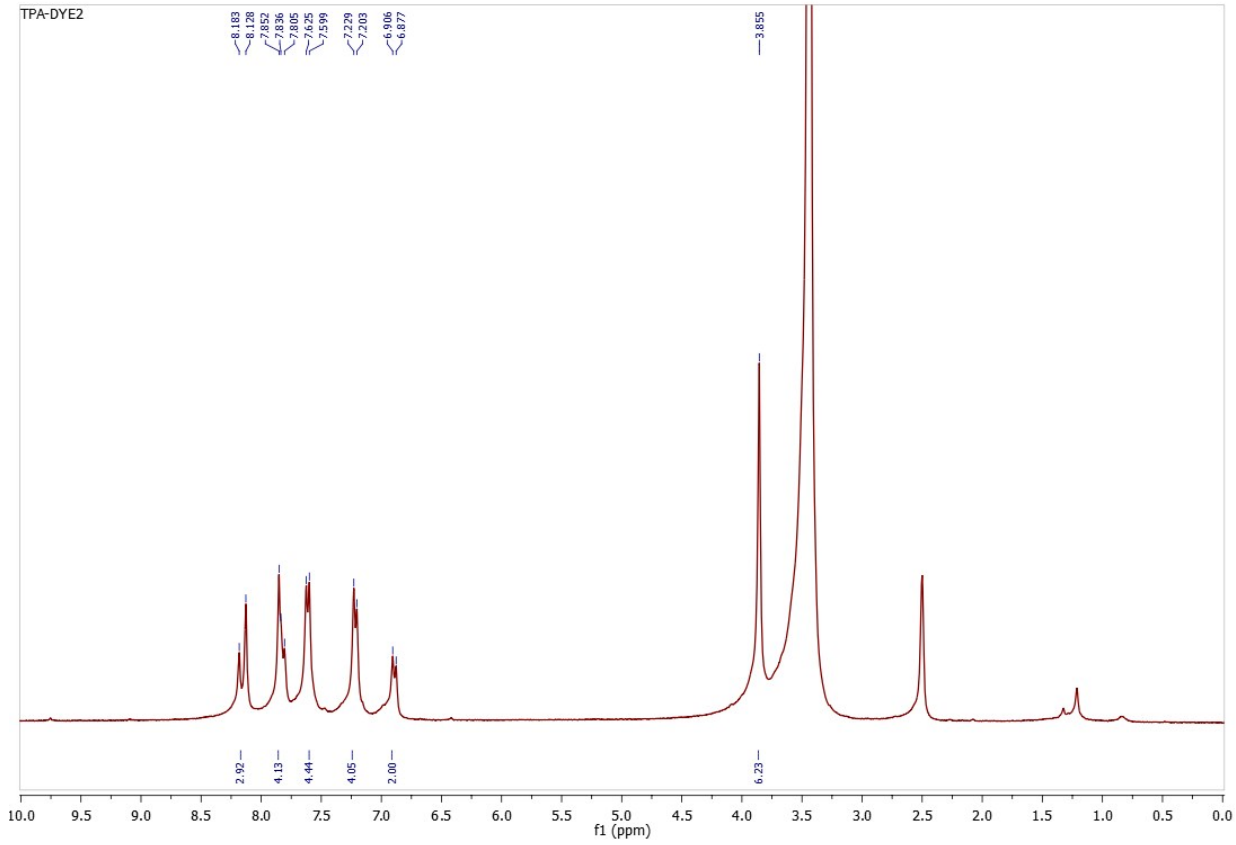
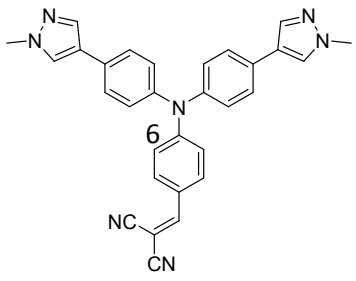


Figure S8. ^{1}H NMR spectrum of (2-(4-bis(4-(1-methyl-1H-pyrazol-4-yl)phenyl)amino)benzylidene)malononitrile) TPC.



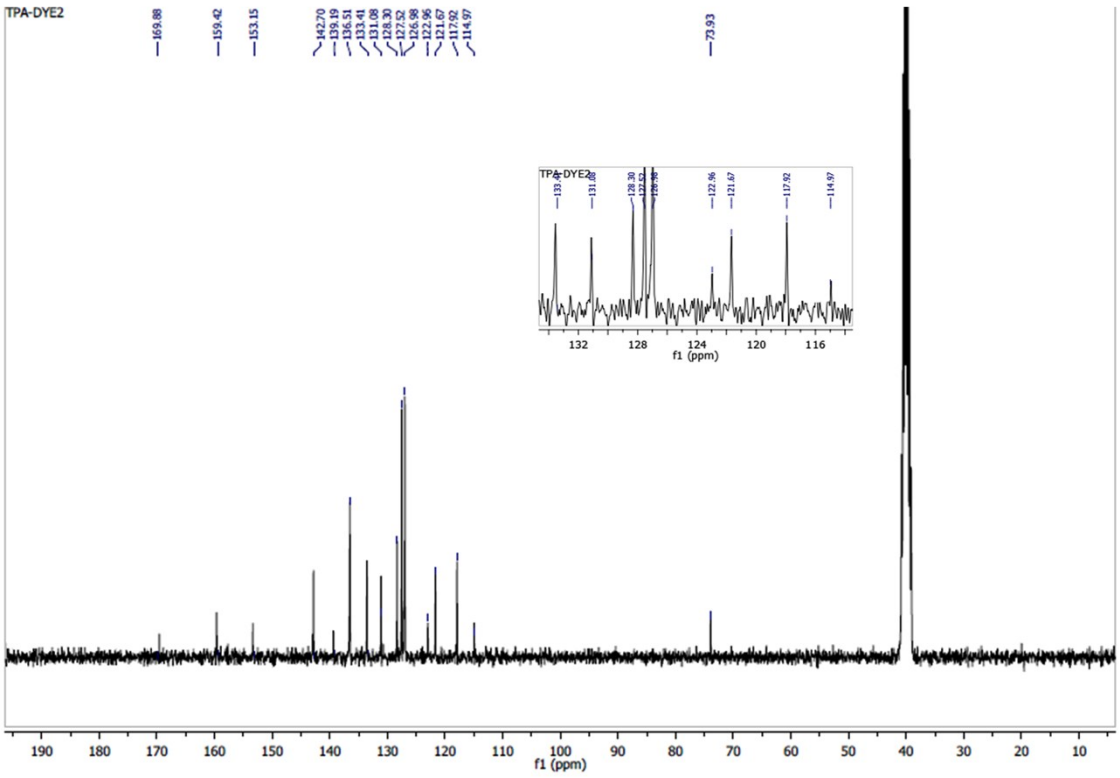


Figure S9. ^{13}C NMR spectrum of (2-(4-bis(4-(1-methyl-1H-pyrazol-4-yl)phenyl)amino)benzylidene)malononitrile) TPC.

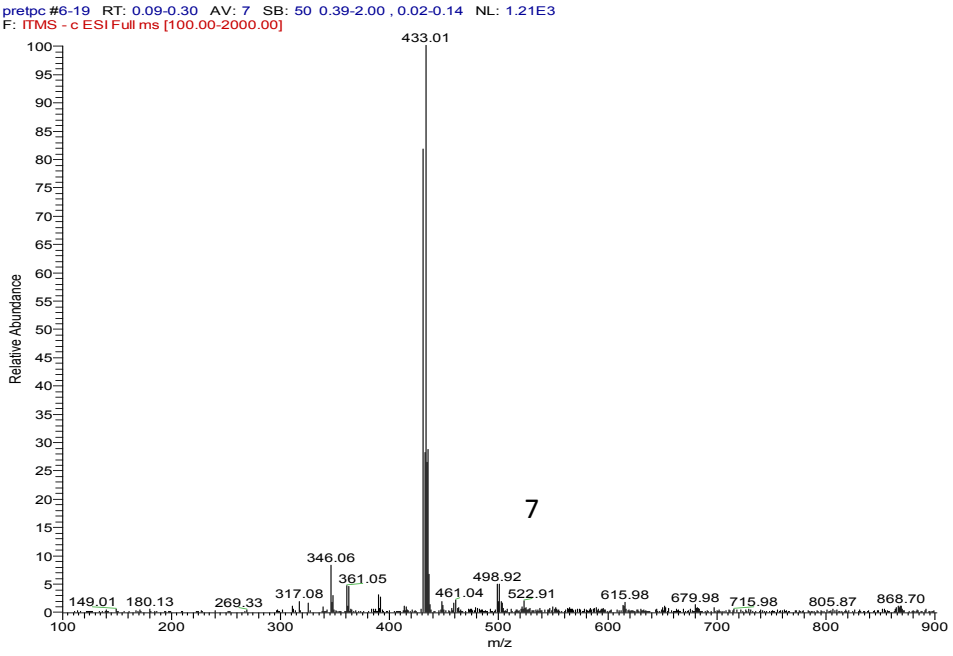


Figure S10. ESI-LCMS spectrum of 4-(bis(4-1-methyl-1H-pyrazol-4-yl)phenylamino) benzaldehyde (2).

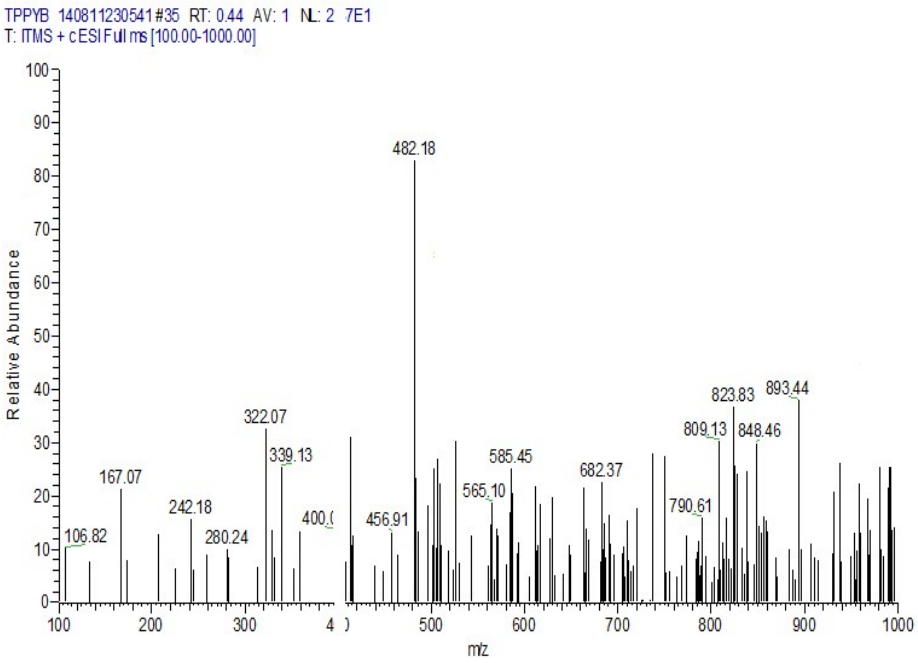
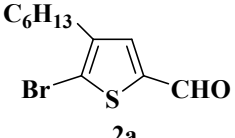


Figure S11. ESI-LCMS spectrum of (2-(4-bis(4-(1-methyl-1H-pyrazol-4-yl)phenyl)amino)benzylidene)malononitrile) (TPC).



2a

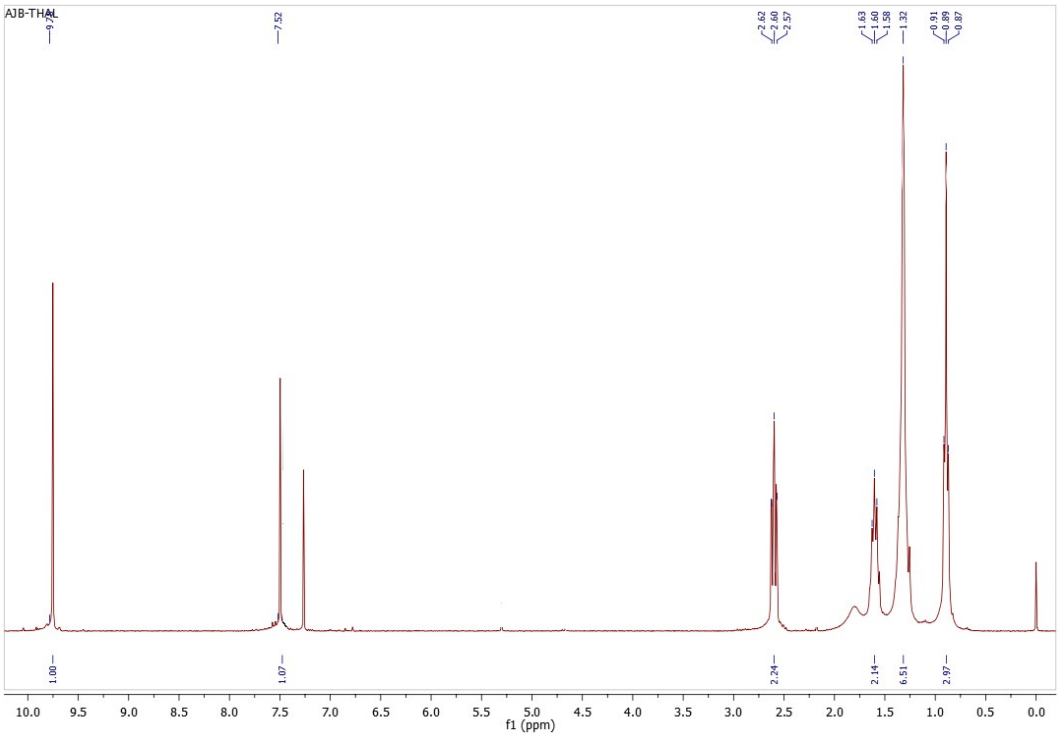
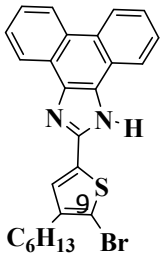


Figure S12. ^{1}H NMR spectrum of 2-bromo-3-hexyl-5-carbaldehyde (2a)



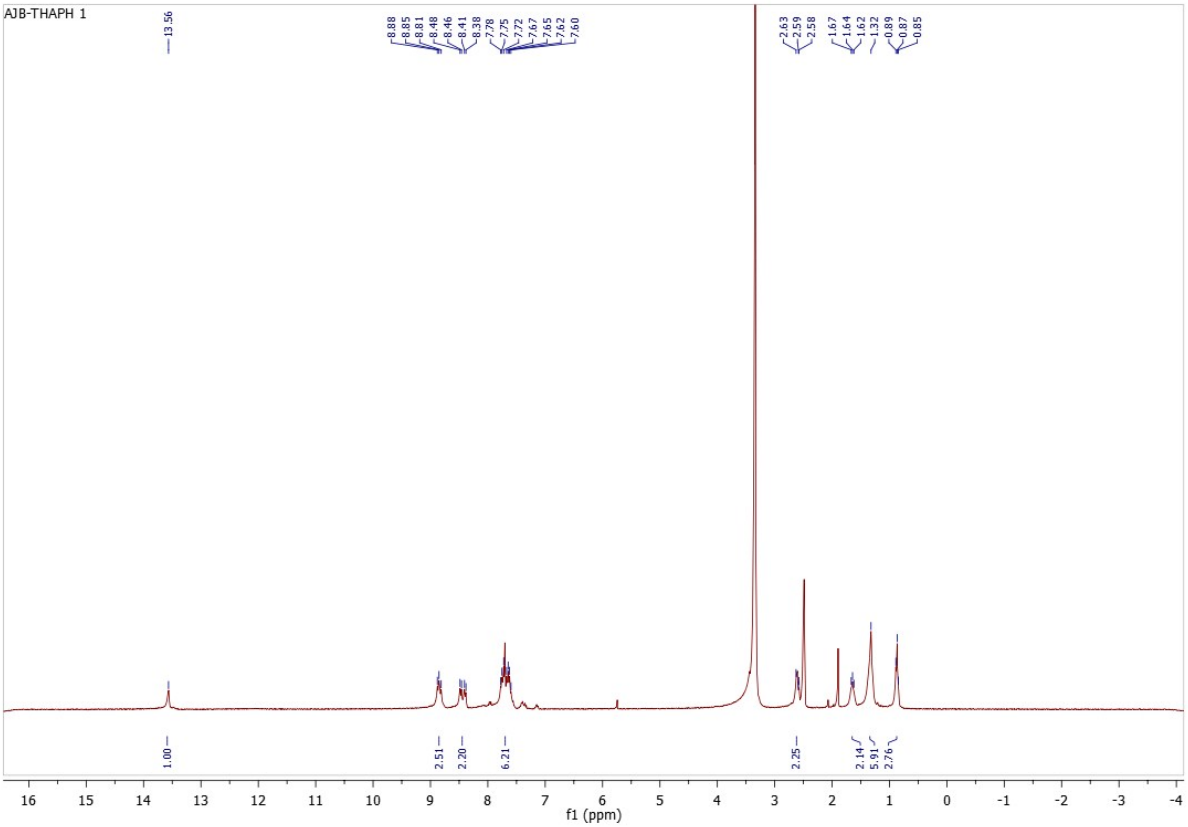
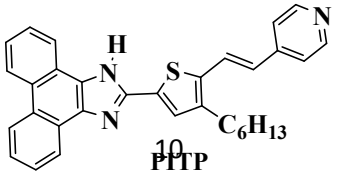


Figure S13. ^{1}H NMR spectrum of 2-(5-bromo-4-hexylthiophen-2-yl)-1H-phenanthro(9,10-d)imidazole (PIT).



PITP

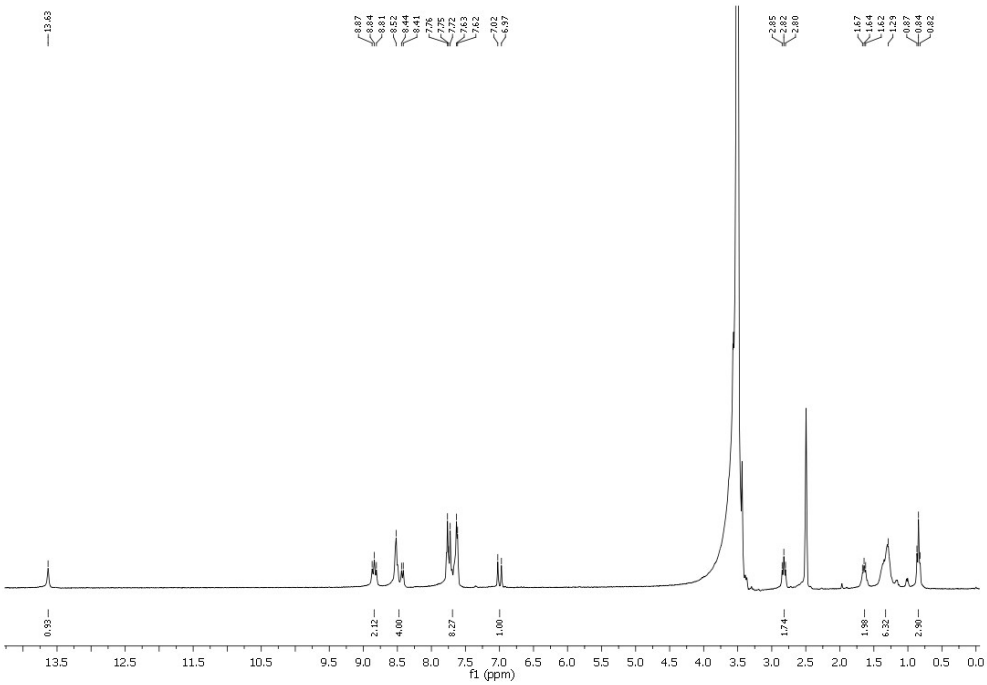
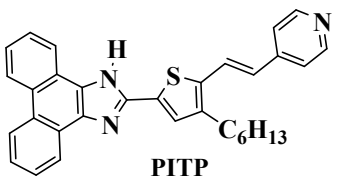


Figure S14. ^{1}H NMR spectrum of (E)-2-(4-hexyl-5-(2-(pyridin-4-yl)vinyl)thiphen-2-yl)-1H-phenanthro[9,10 d]imidazole (PITP)



PITP

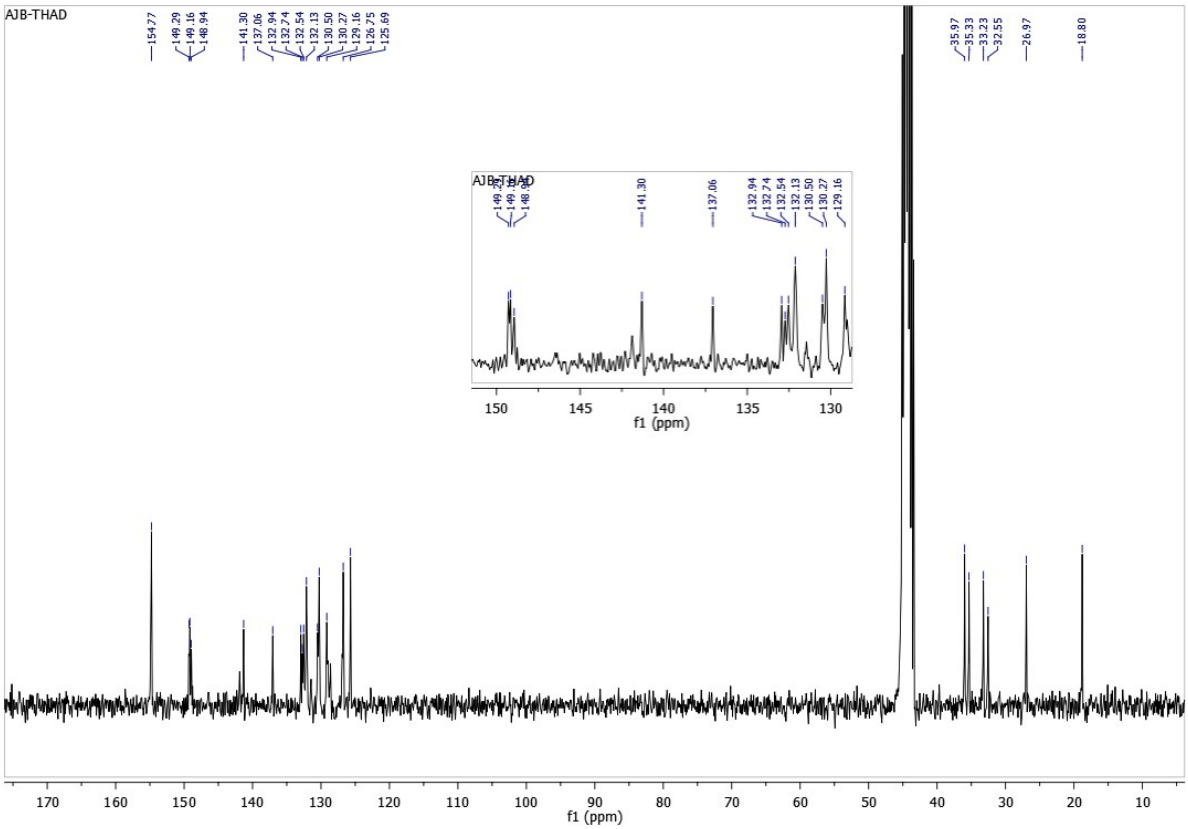


Figure S15. ^{13}C NMR spectrum of (E)-2-(4-hexyl-5-(2-(pyridin-4-yl)vinyl)thiphen-2-yl)-1H-phenanthro[9,10 d]imidazole (PITP).

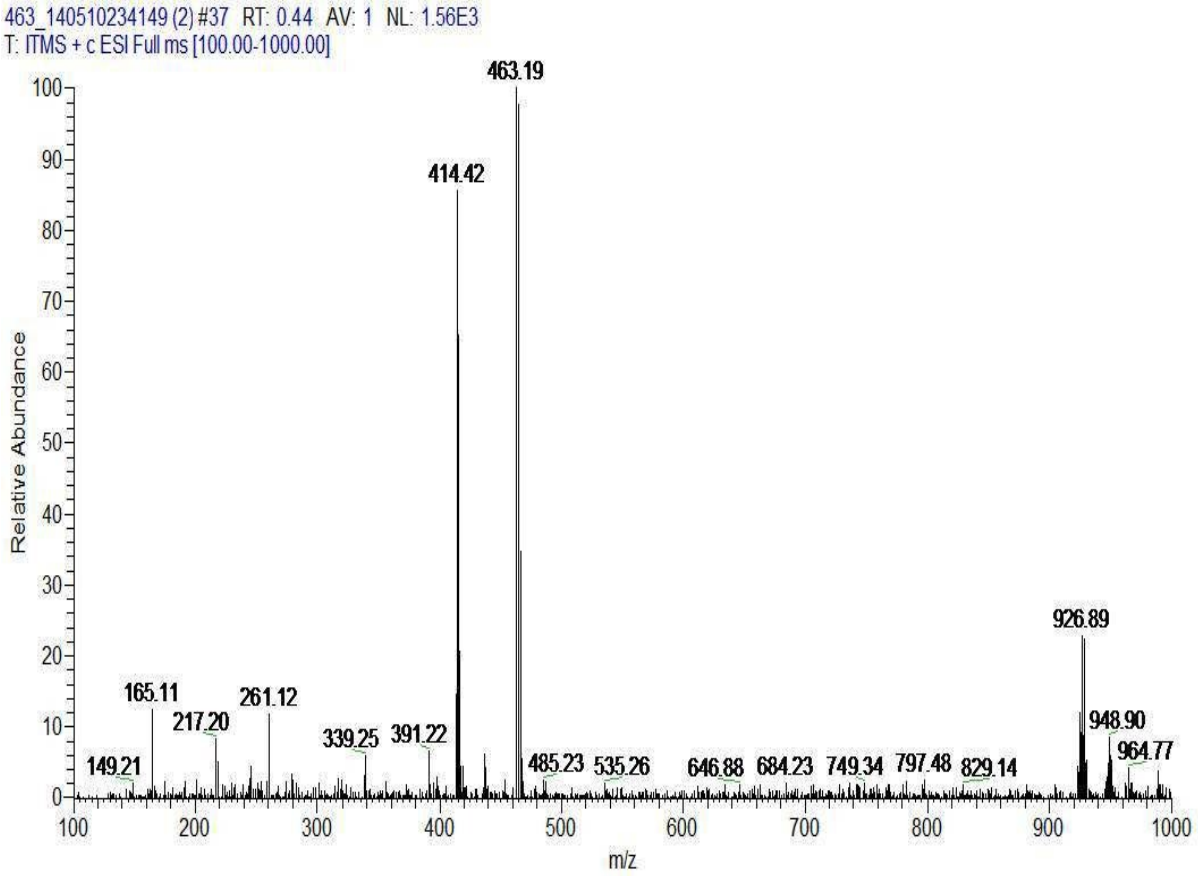


Figure S16. ESI-LCMS spectrum of 2 -(5-bromo-4-hexylthiophen-2-yl)-1H-phenanthro(9,10-d)imidazole (PIT)

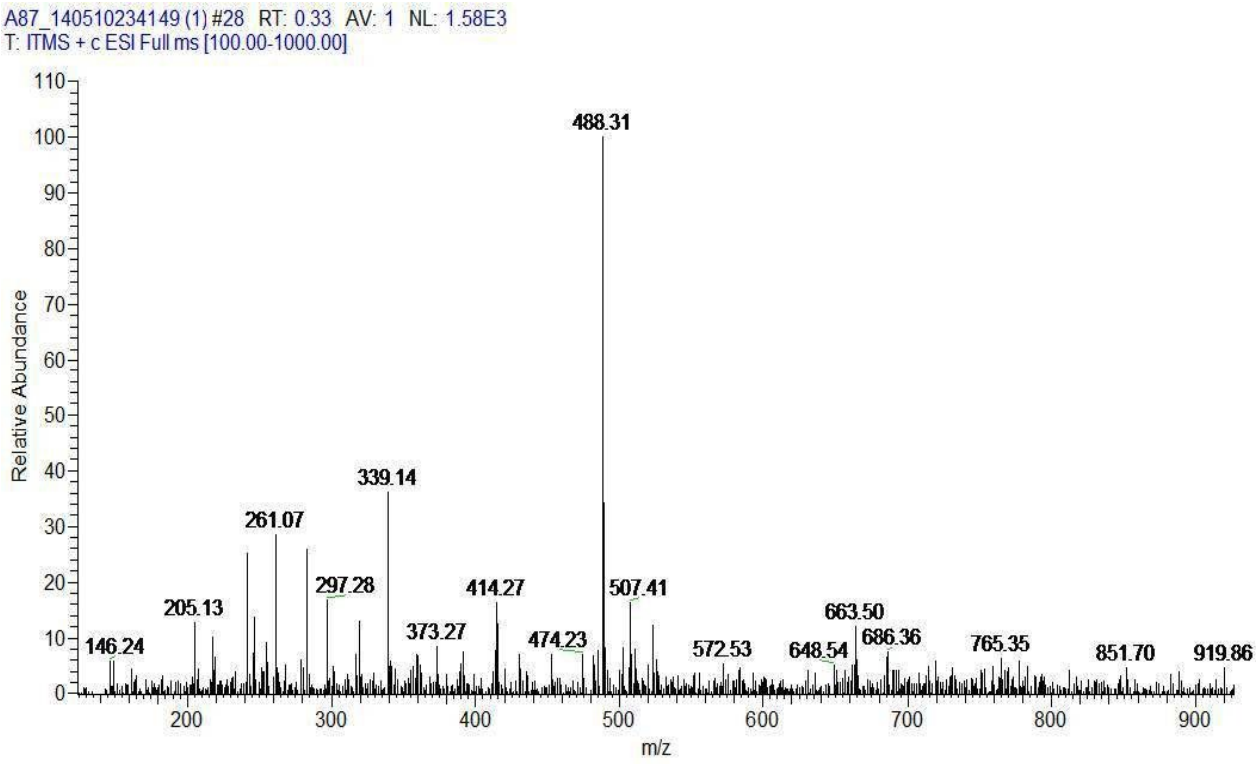


Figure S17. ESI-LCMS spectrum of (E)-2-(4-hexyl-5-(2-(pyridin-4-yl)vinyl)thiphen-2-yl)-1H-phenanthro[9,10 d]imidazole (PITP).