

Synthesis of Tetrazine-Tetracyanobutadienes and Their Transformation to Pyridazines *via* Inverse-electron Demand Diels-Alder Cycloaddition (IEDDA)

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Sr. no.	Content	Page no.
1	HR-MS spectra, ¹ H NMR, ¹³ C NMR, COSY NMR	2-11
2	DFT optimized TCNQ based molecules	12
3	DFT computed absorption spectra of 1 , 1T , 1DT , 1T-P & 1DT-P	12
4	Reduction and Oxidation potential of compound 1 , 1T , 1DT , 1T-P , 2T-P	13
5	Absorption spectra of 1DT with different anions.	14
6	UV-Vis spectra of 1T with CN ⁻	15

Sr. no.	Table	Page no.
1	Electrochemical data	14

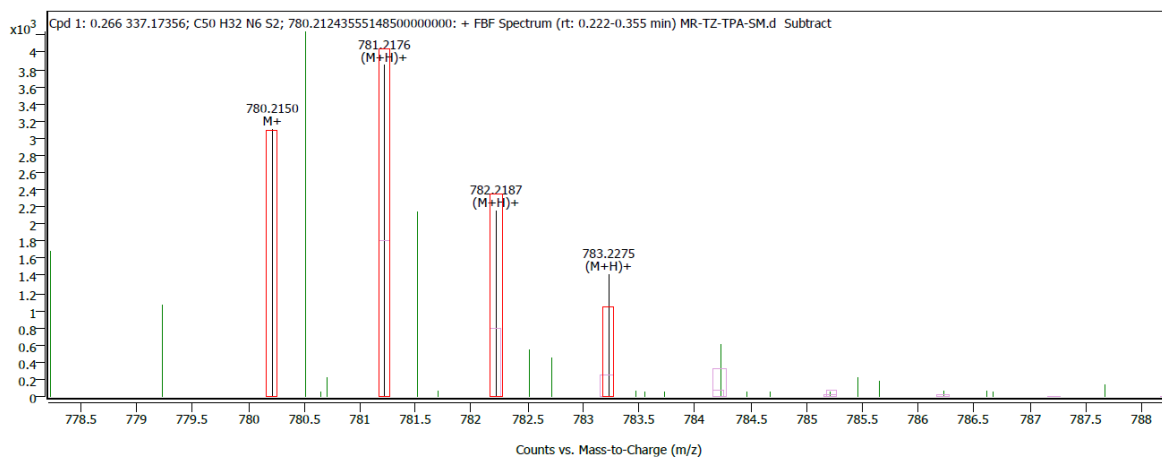


Figure S1. HR-MS spectra of compound **1**

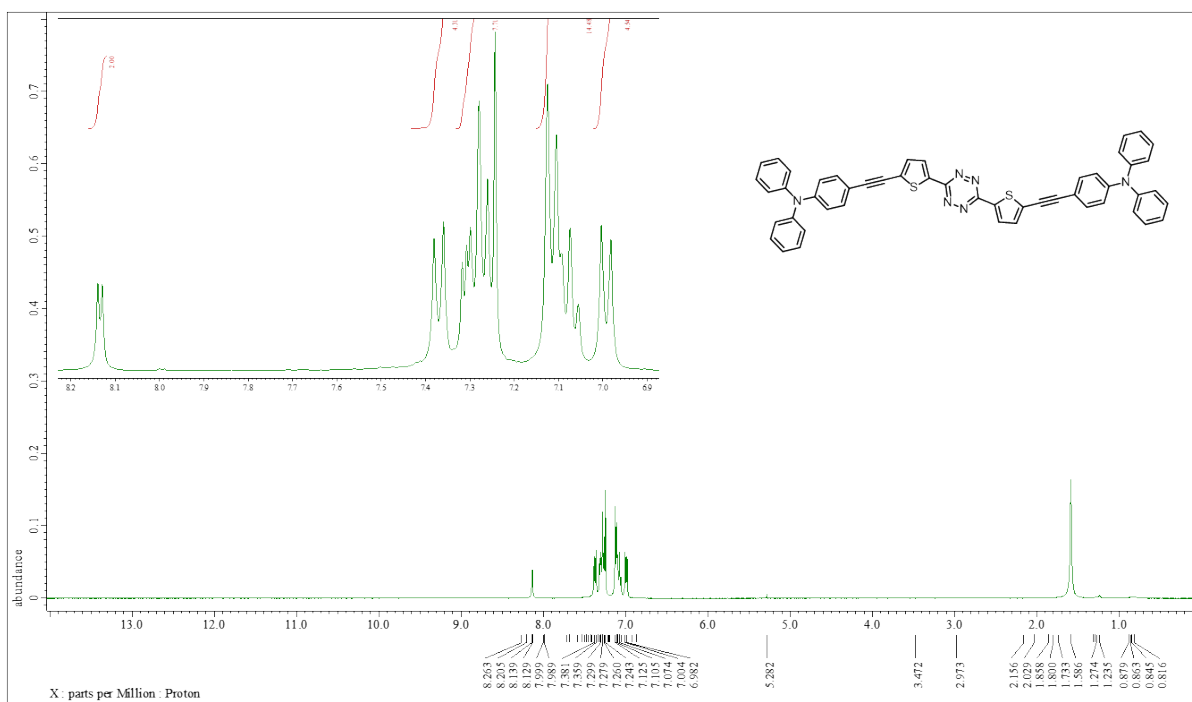


Figure S2. ^1H NMR spectra of compound **1**

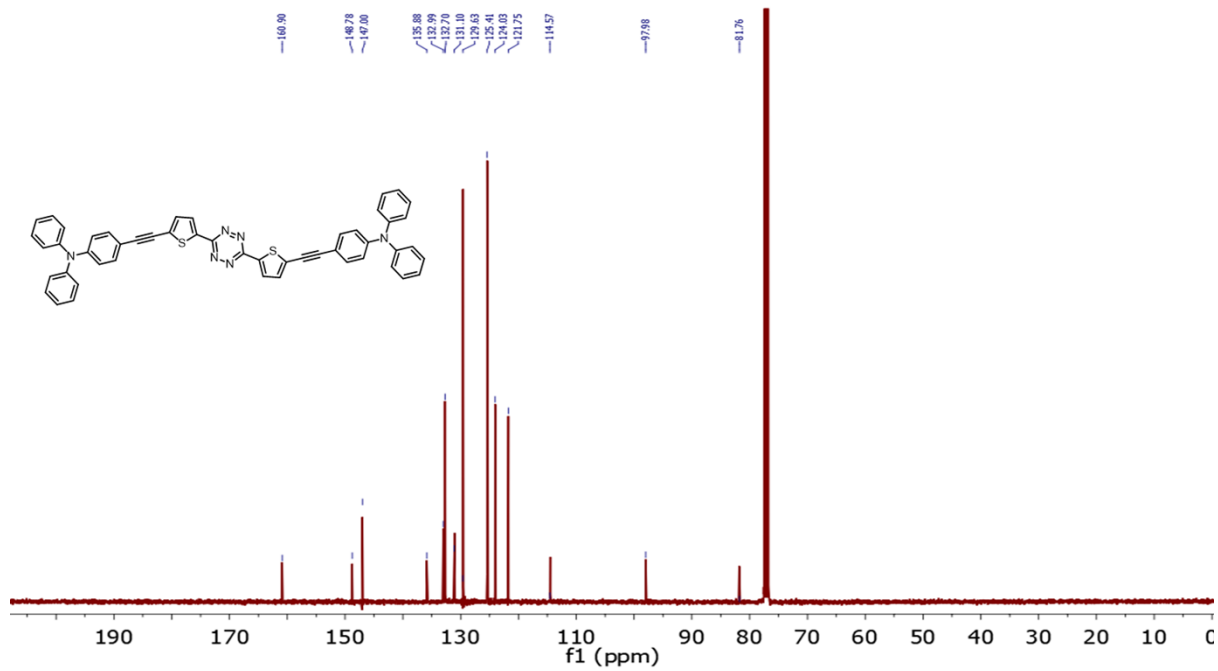


Figure S3. ^{13}C NMR spectra of compound 1

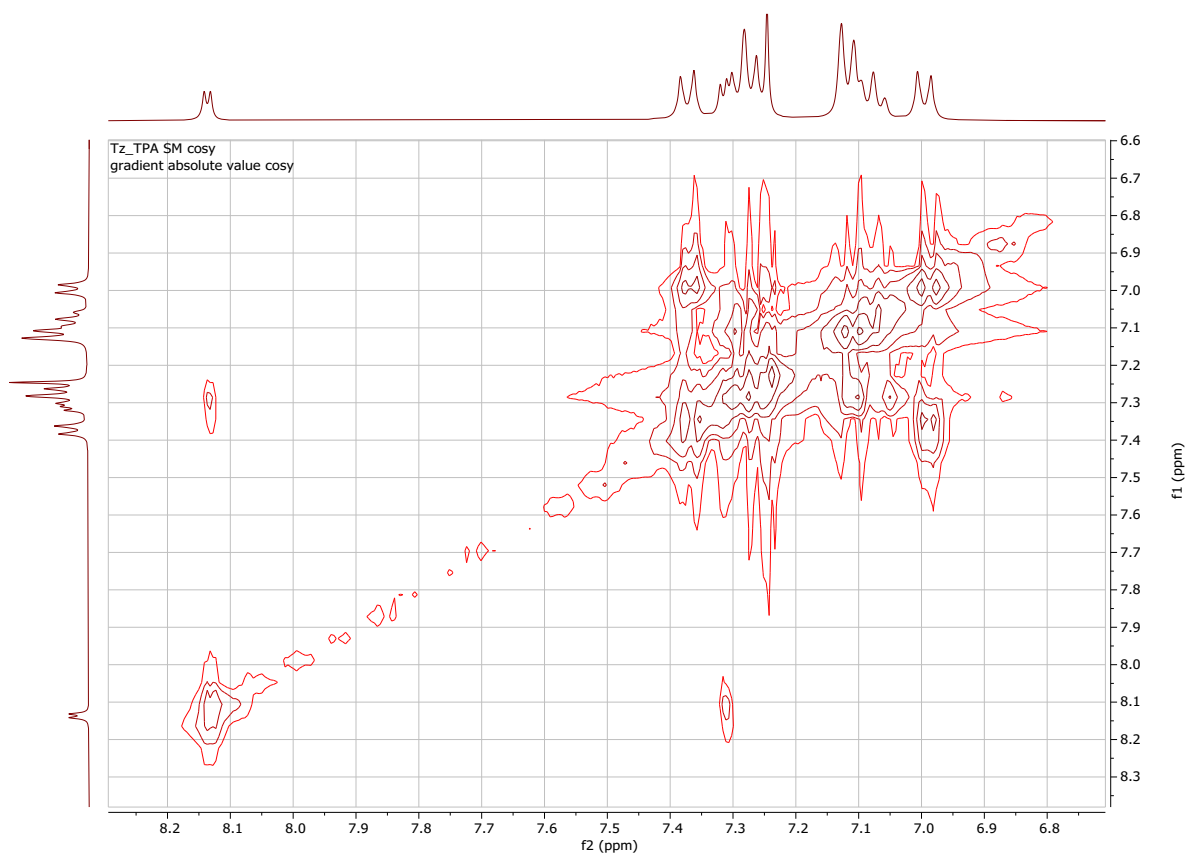


Figure S4. COSY NMR spectra of compound 1

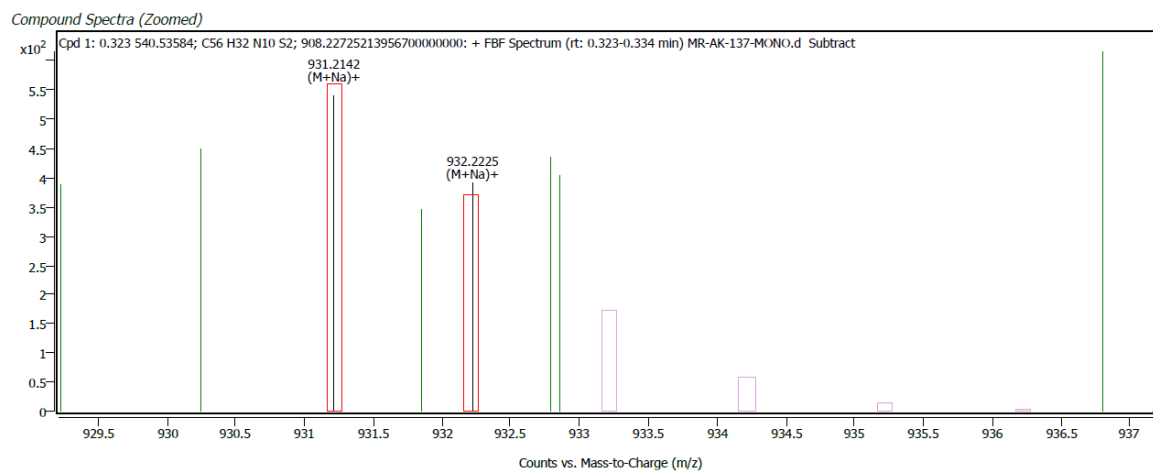


Figure S5. HR-MS spectra of compound 1T

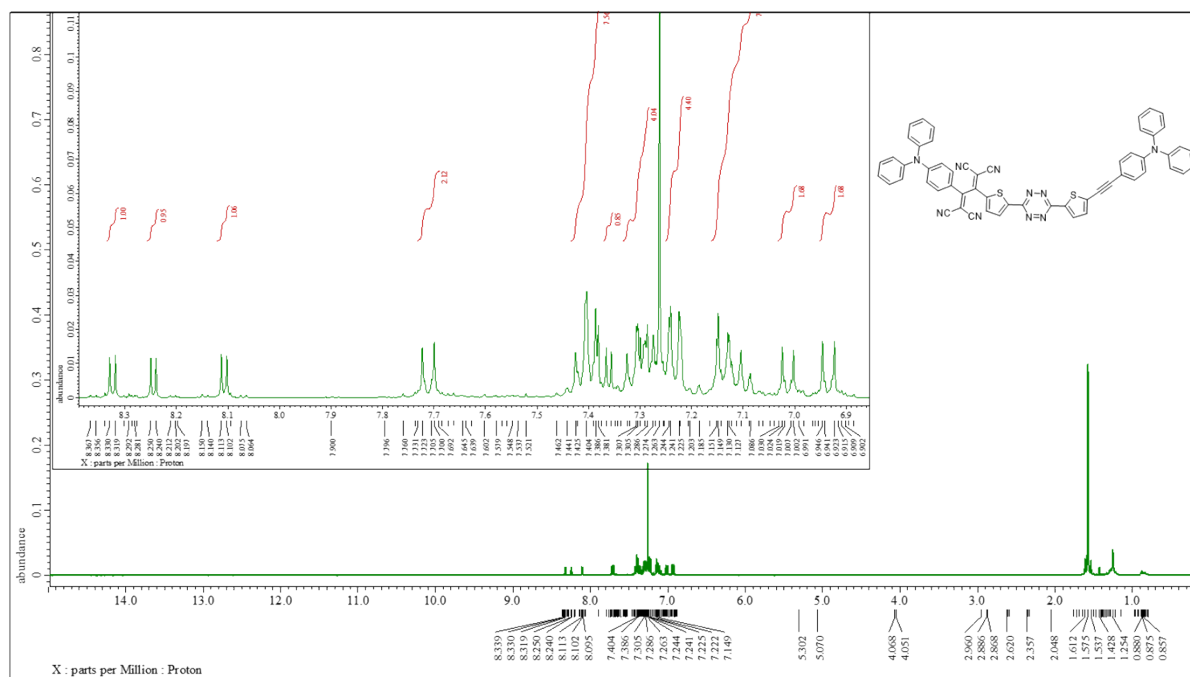


Figure S6. ^1H NMR spectra of compound 1T

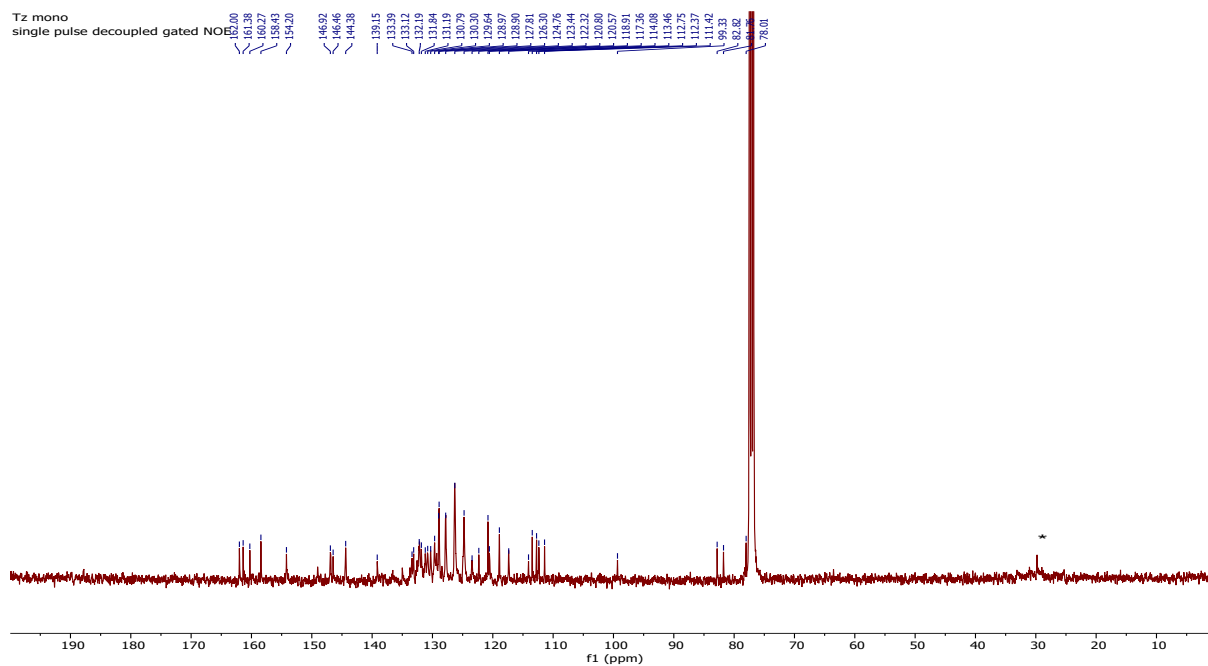


Figure S7. ^{13}C NMR spectra of compound **1T**

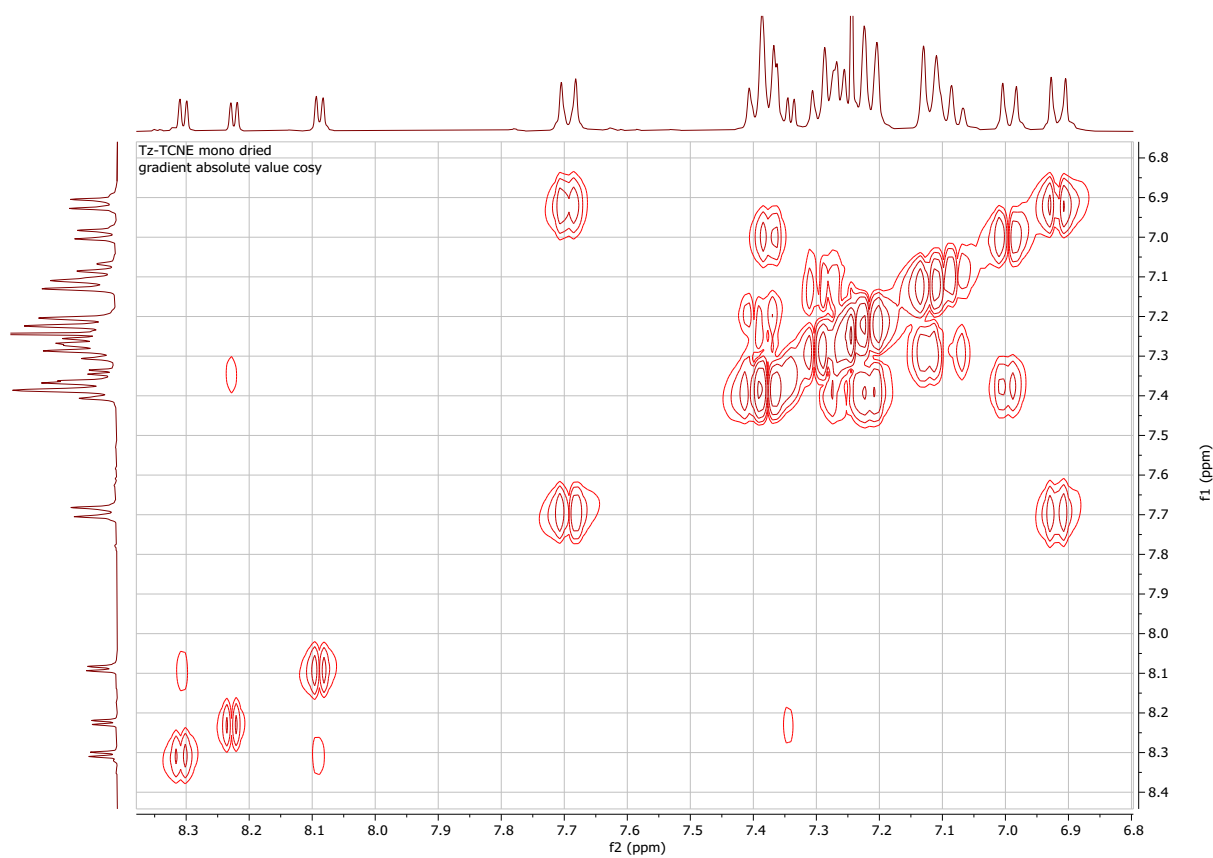


Figure S8. COSY NMR spectra of compound **1T**

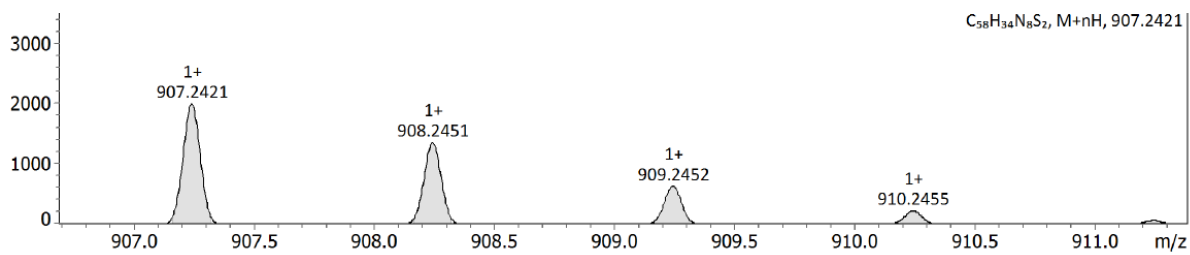


Figure S7. HR-MS spectra of compound 1T-P

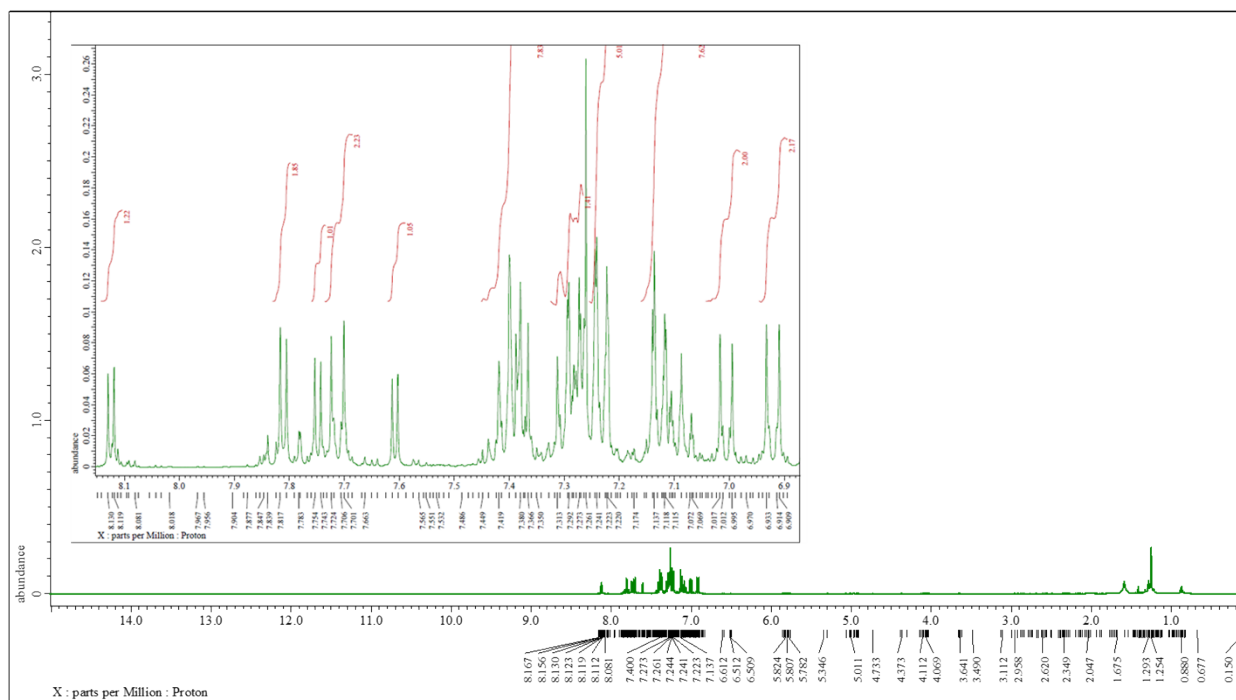


Figure S9. 1H NMR spectra of compound 1T-P

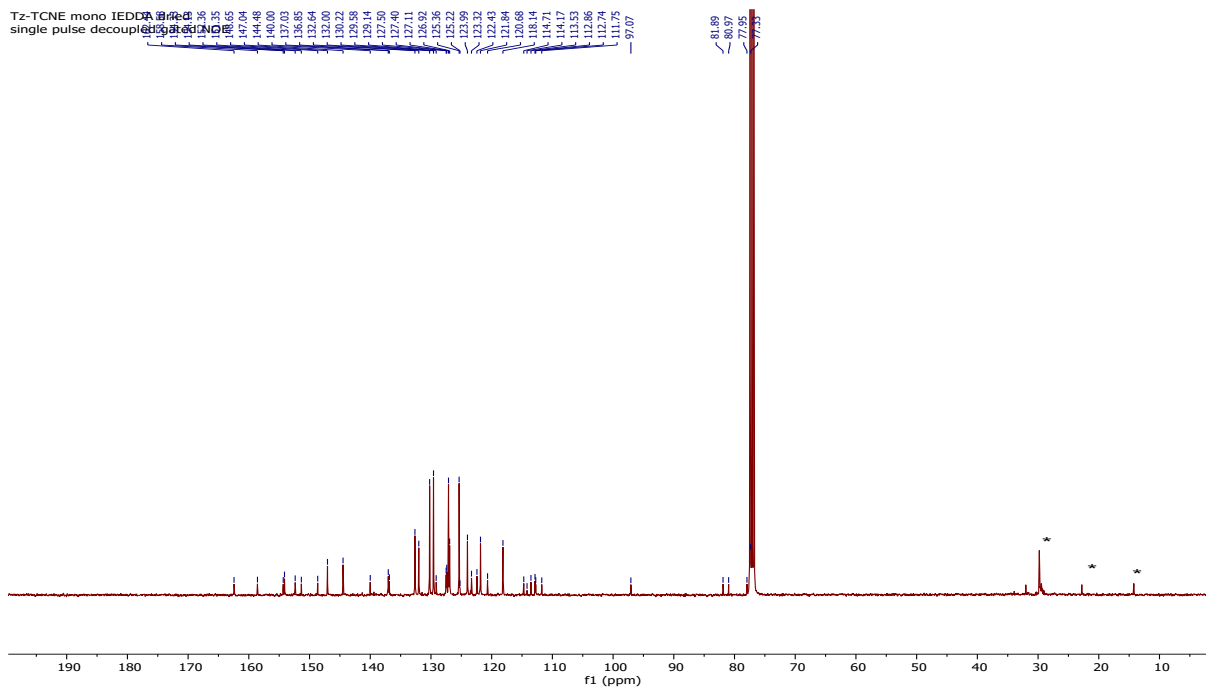


Figure S10. ^{13}C NMR spectra compound 1T-P

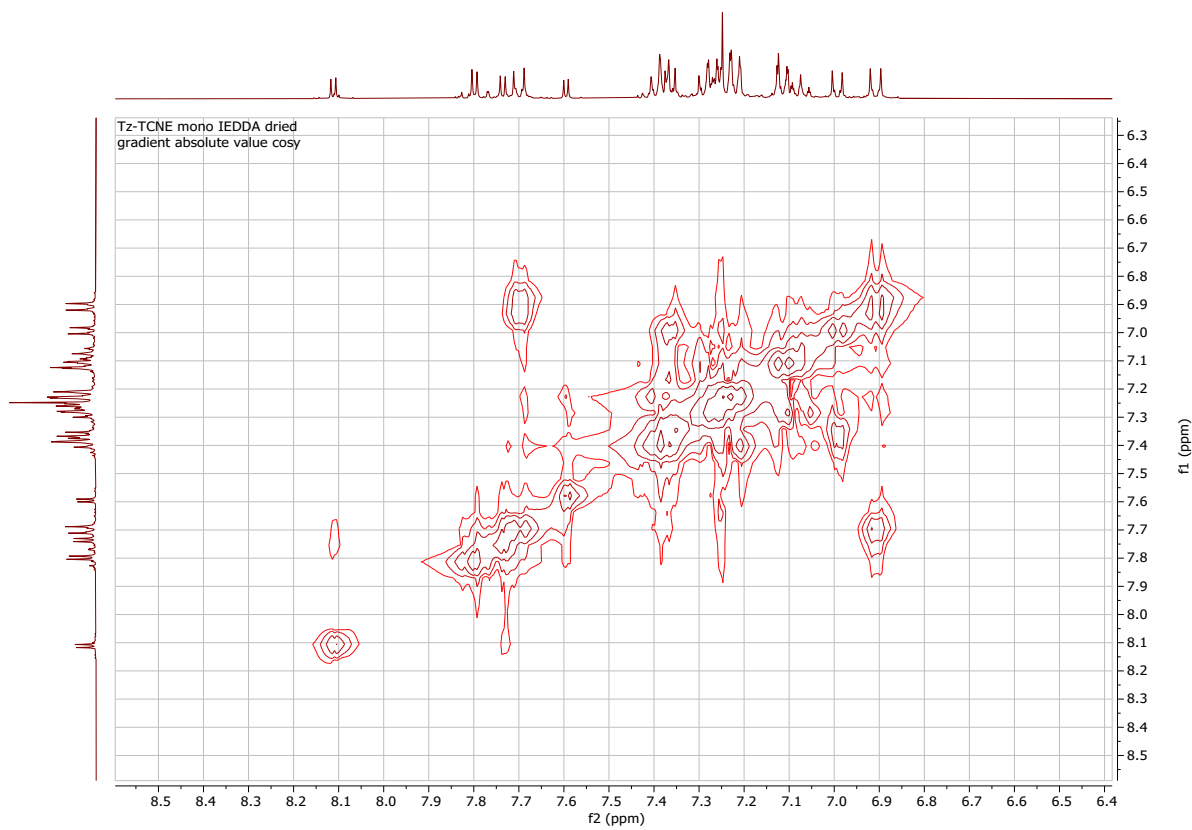


Figure S11. COSY NMR spectra of compound 1T-P

Compound Spectra (Zoomed)

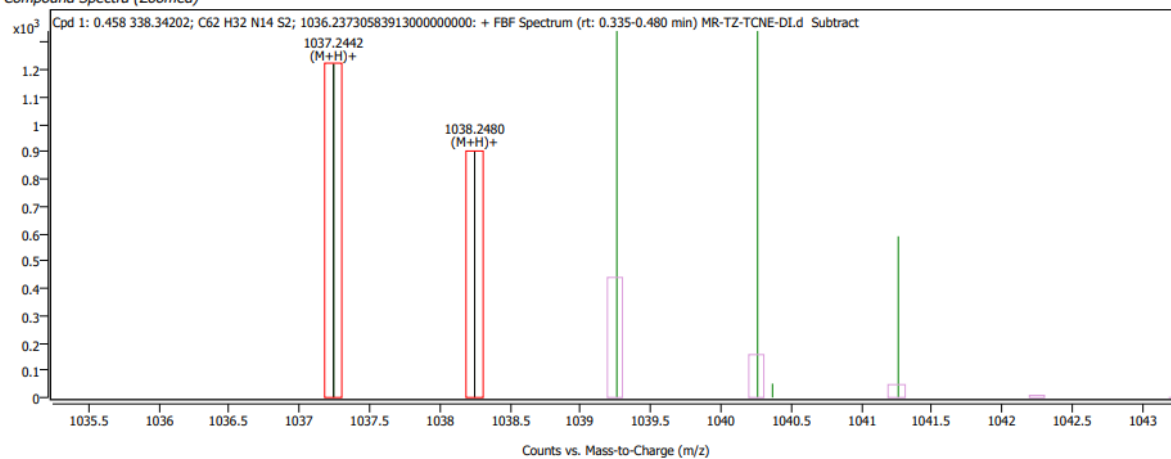


Figure S12. HR-MS spectra of compound 1DT

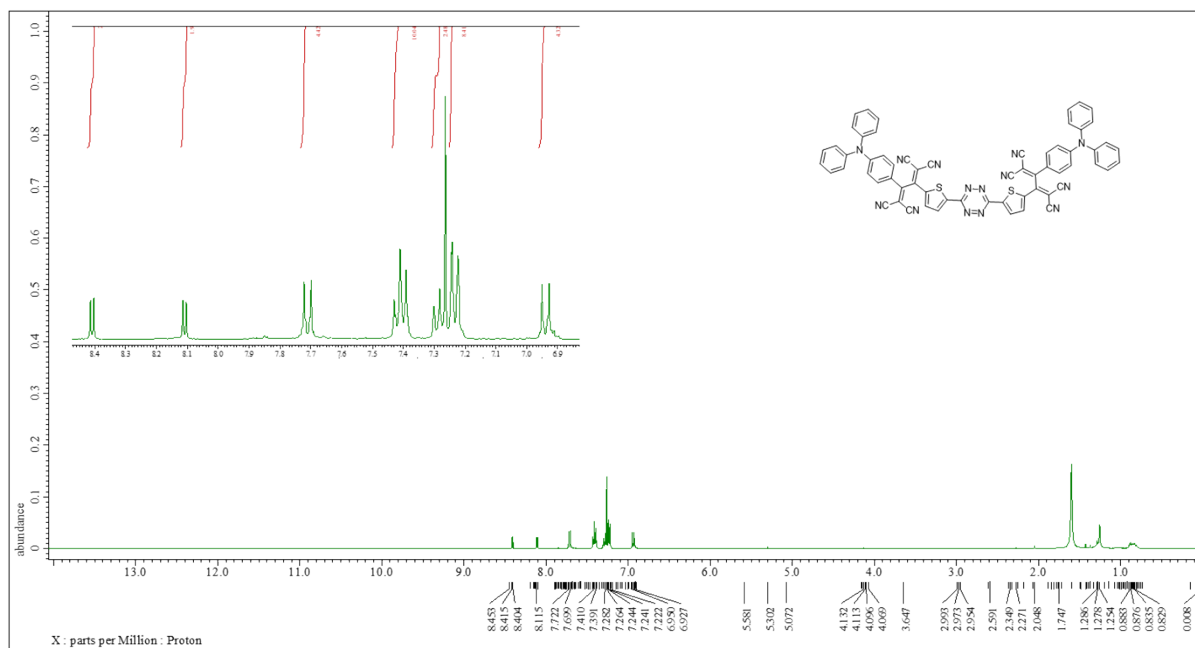


Figure S13. ¹H NMR spectra of compound 1DT

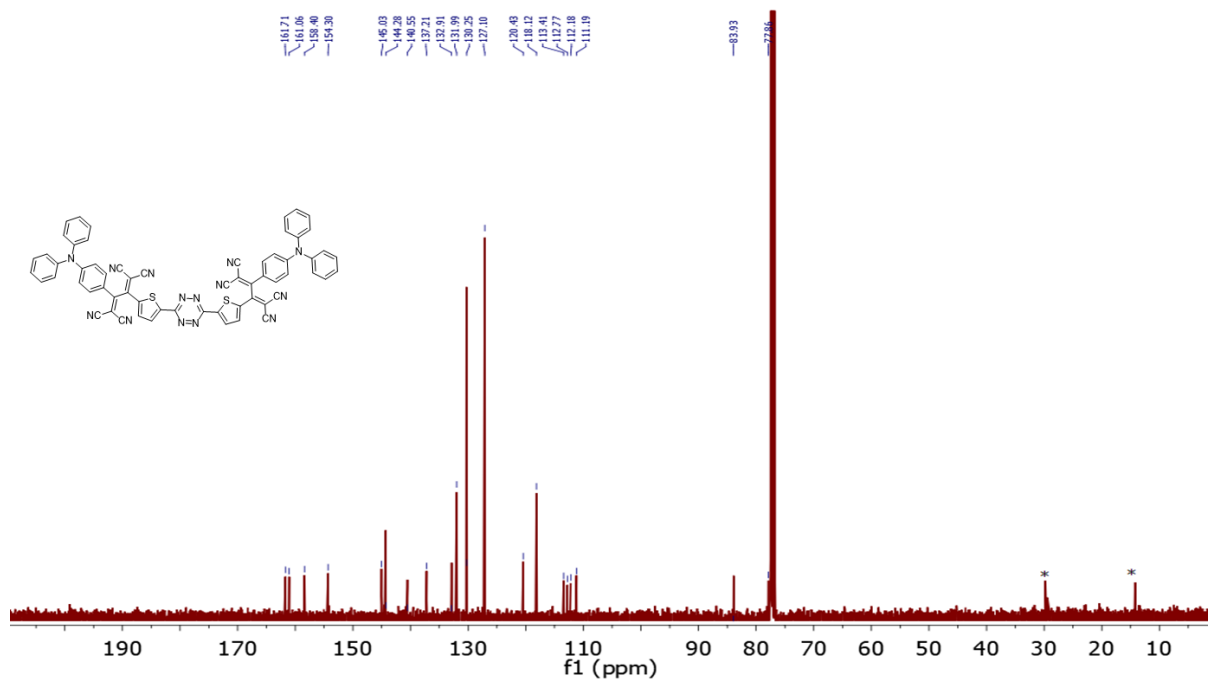


Figure S14. ^{13}C NMR spectra of compound **1DT**

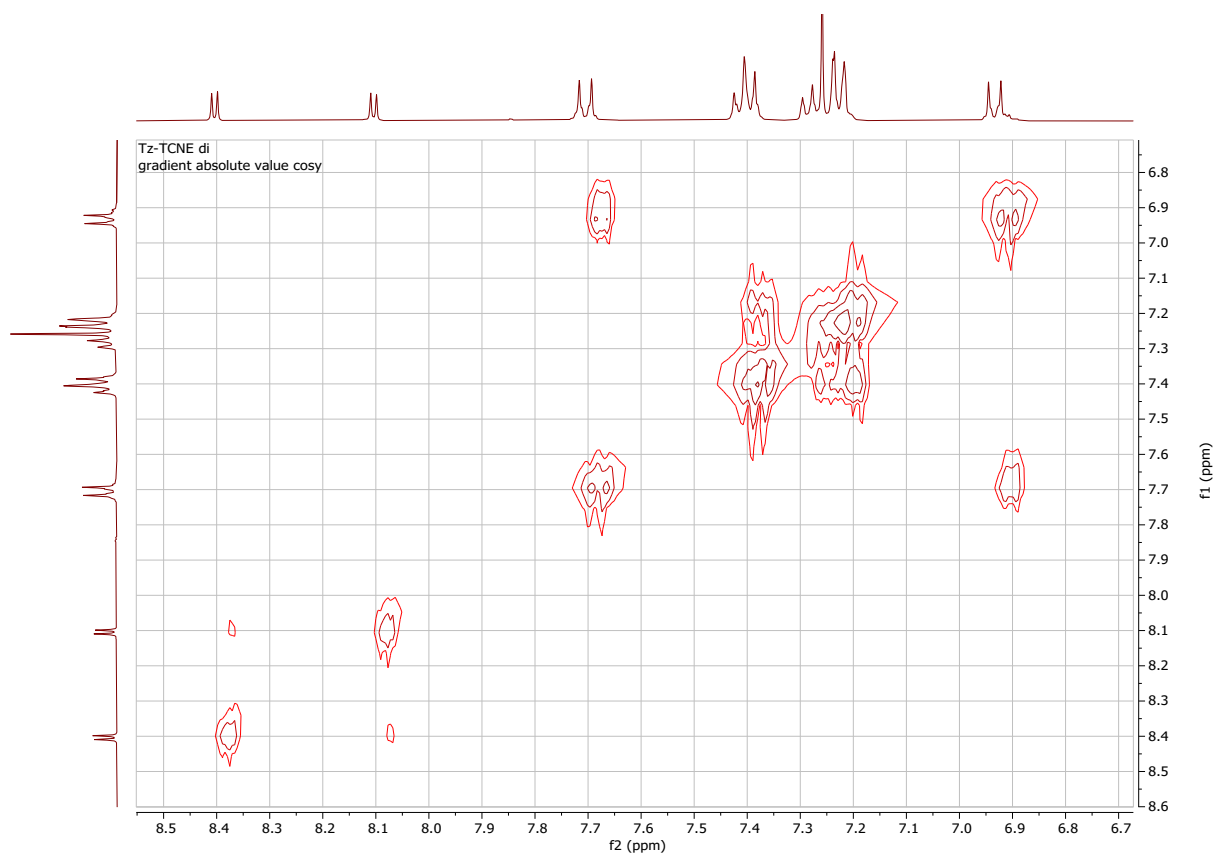


Fig. S15. COSY NMR spectra of compound **1DT**

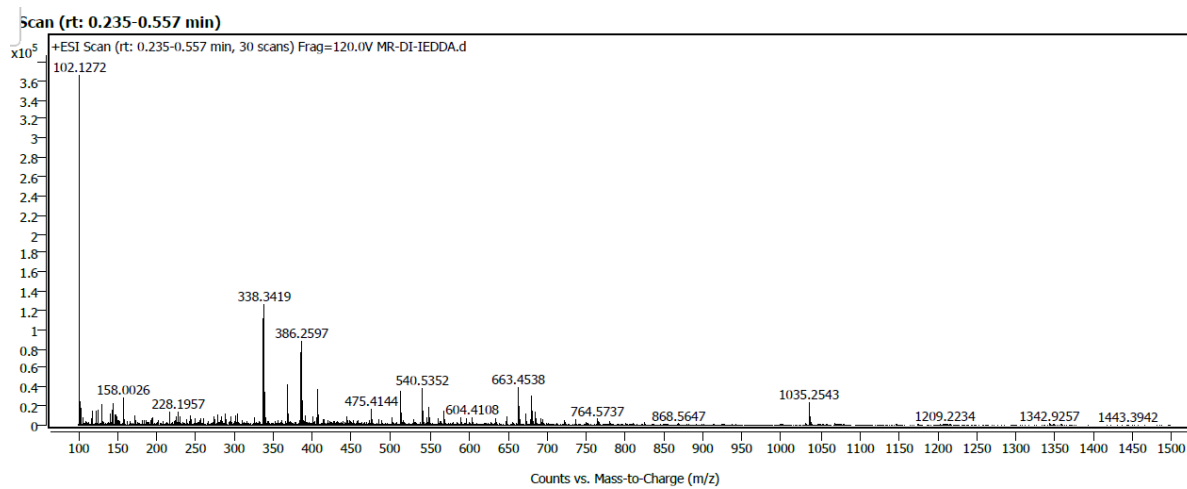


Fig. S16. HR-MS spectra of compound 1DT-P

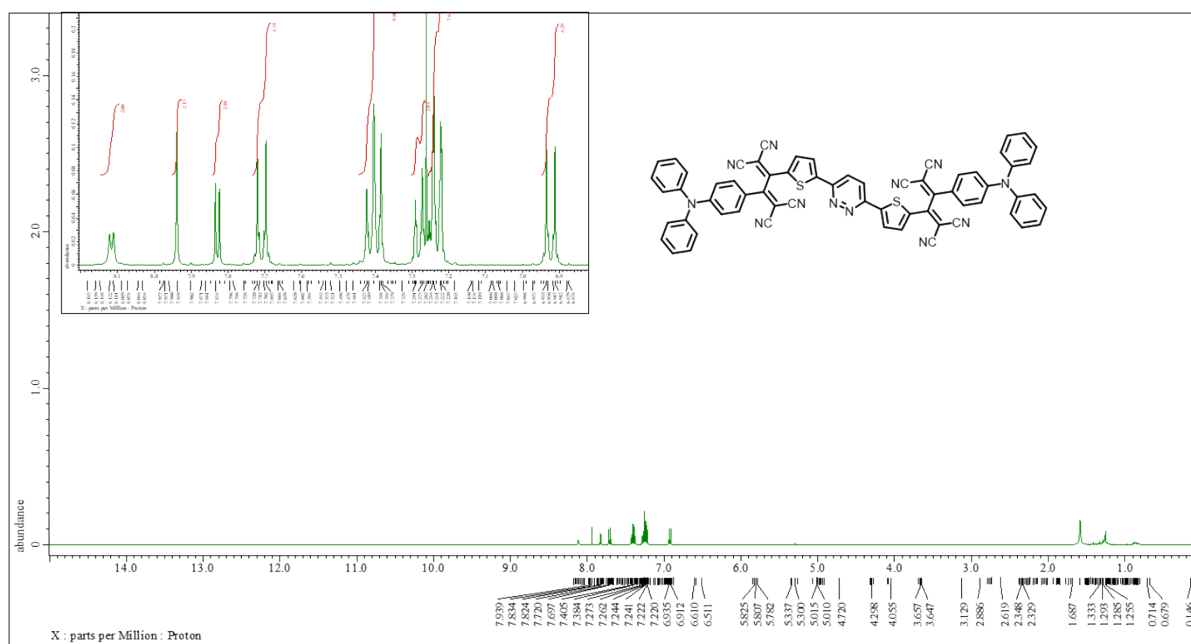


Fig. S17. ¹H NMR spectra of compound 1DT-P

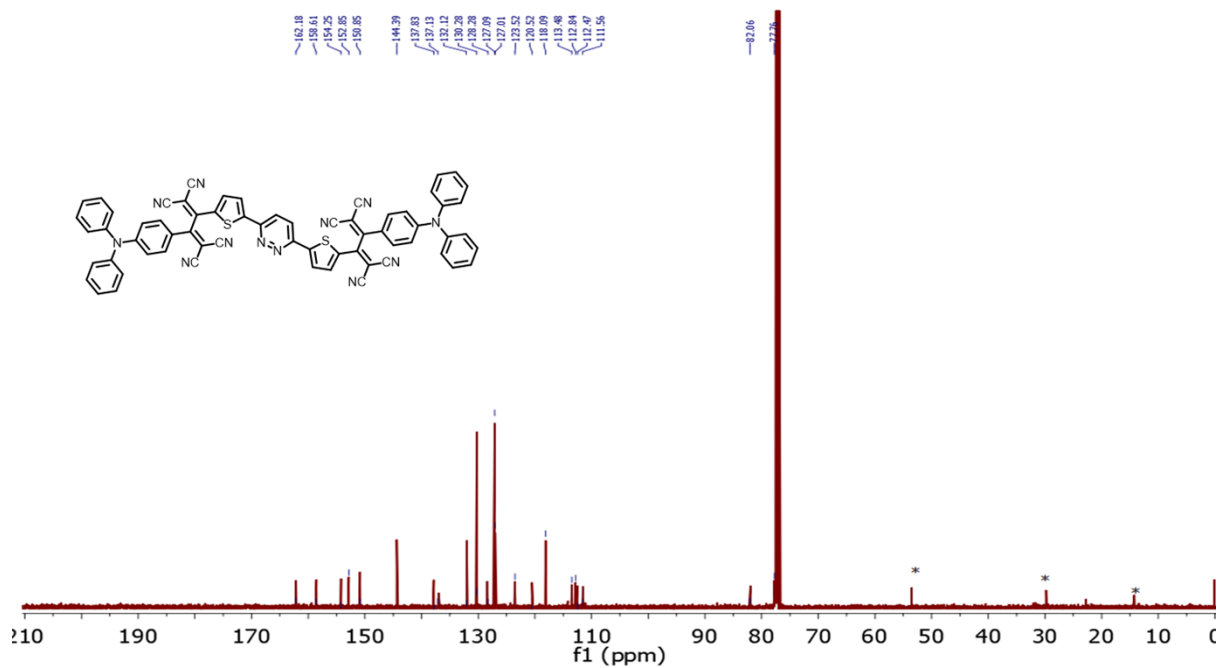


Fig. S18. ^{13}C NMR spectra of compound **1DT-P**

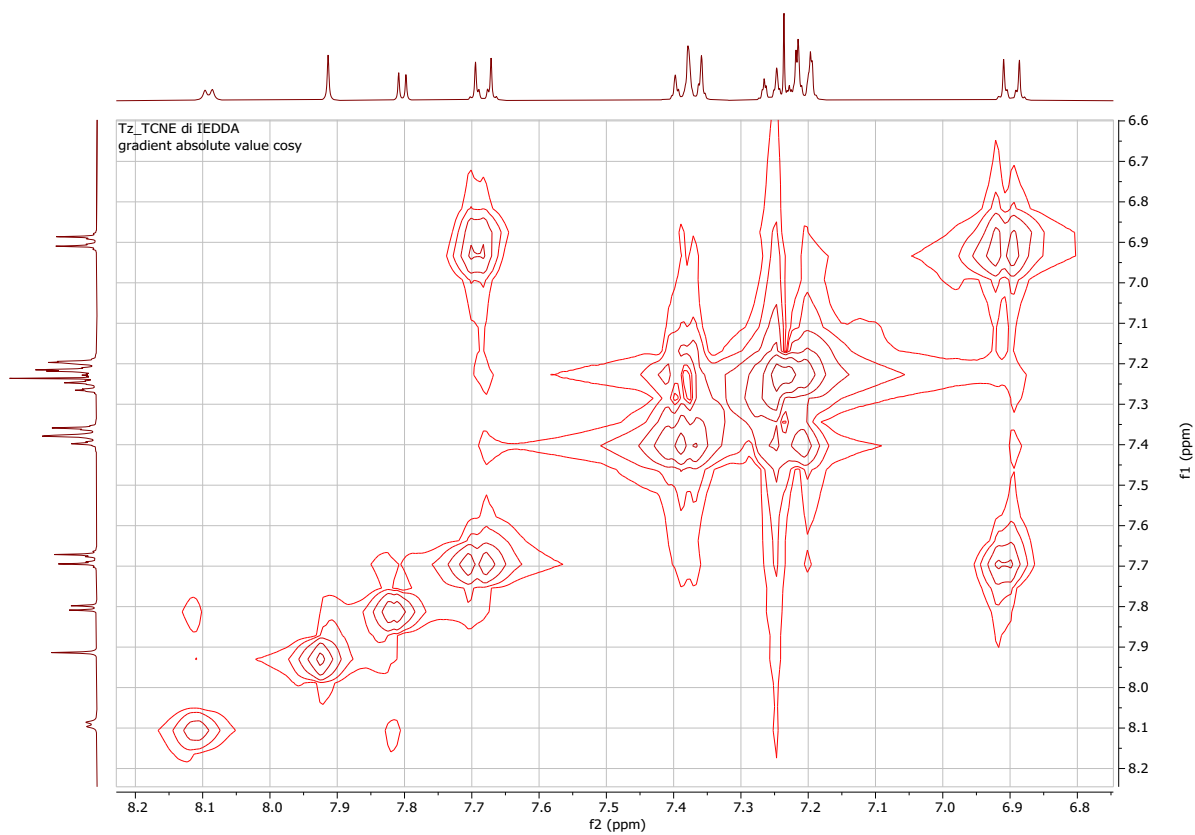


Fig. S19. COSY NMR spectra of compound **1DT-P**

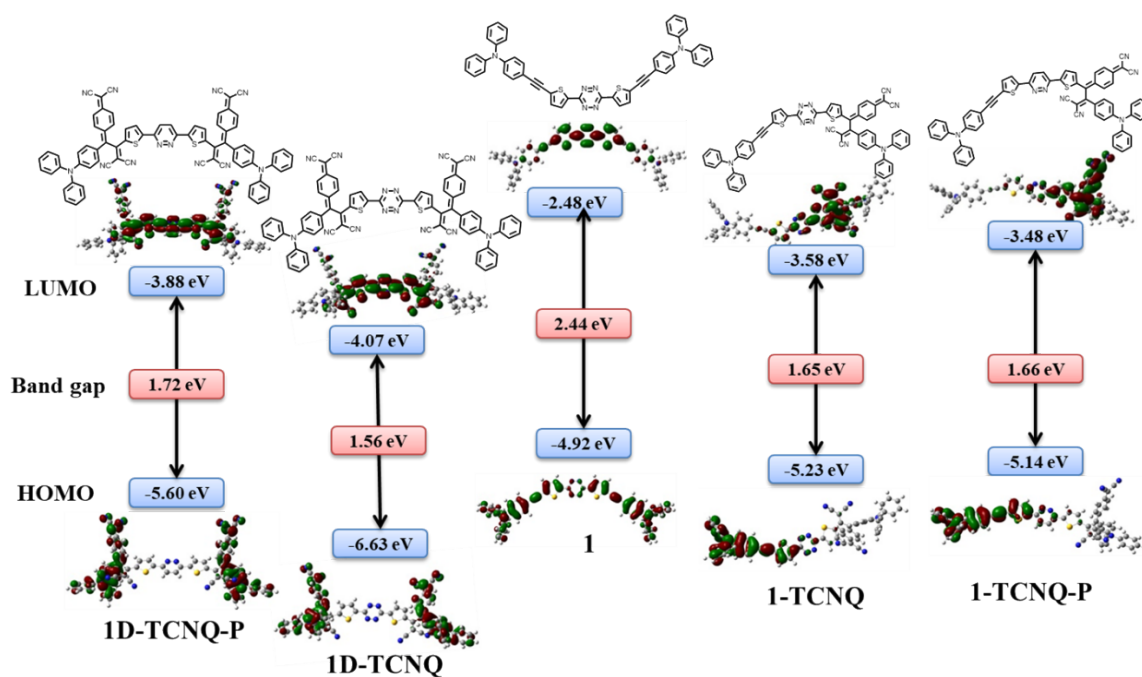


Fig. S20. DFT estimated HOMO-LUMO energies and the contours of **1**, cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD-based molecules (**1-TCNQ**, **1D-TCNQ**) and (**1-TCNQ-P**, **1D-TCNQ-P**).

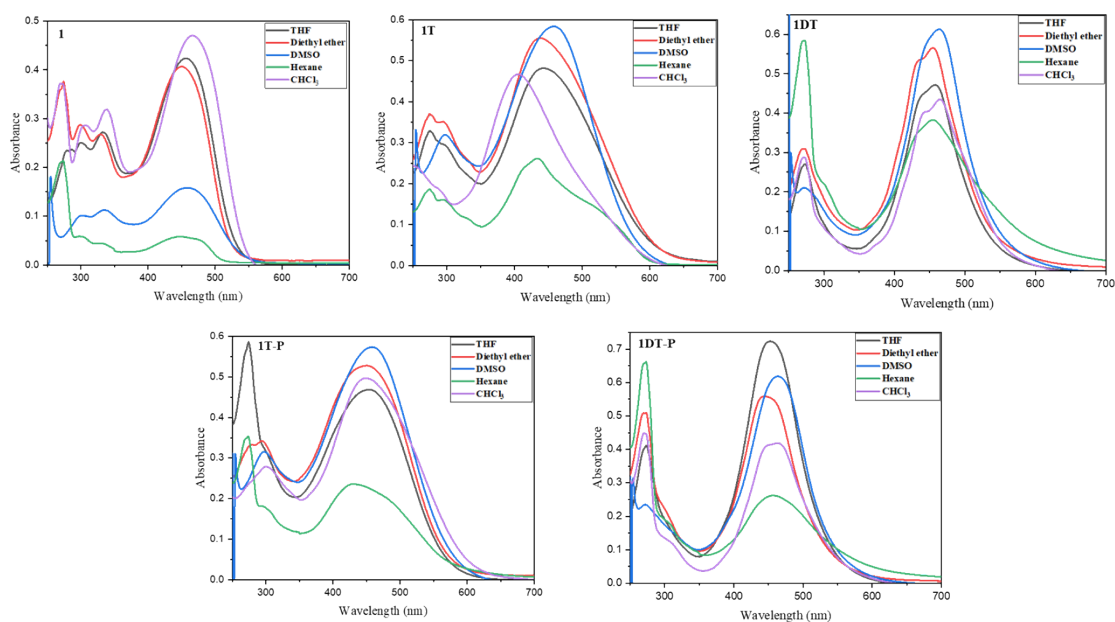


Fig. S21. Absorption spectra of **1**, **1T**, **1DT**, **1T-P** & **1DT-P** in different solvent

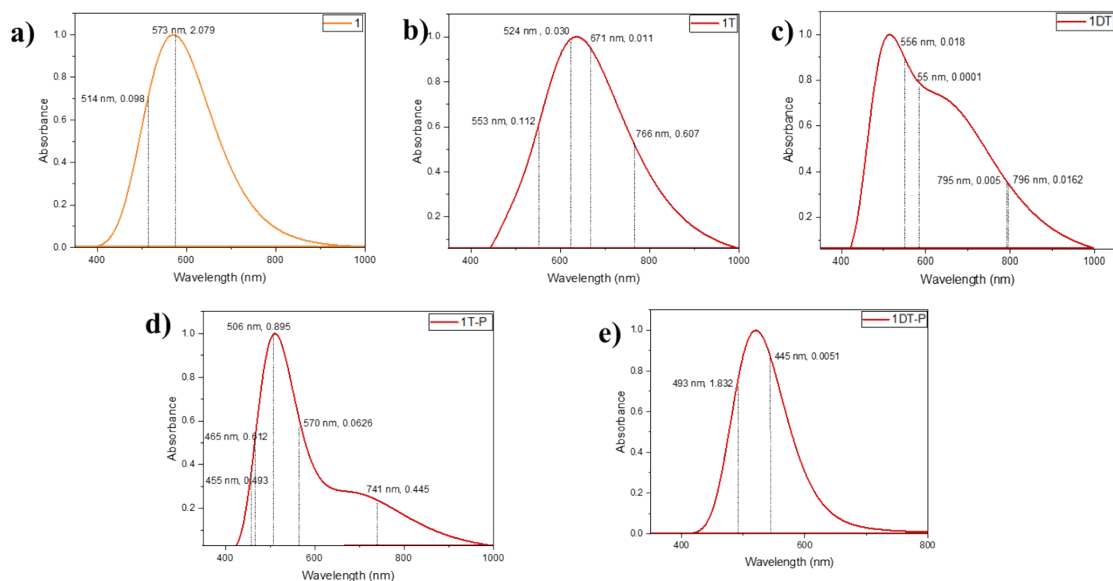


Fig. S22. Theoretically calculated UV-Vis absorption spectra obtained by time-dependent DFT at the B3LYP/6-31G level of theory

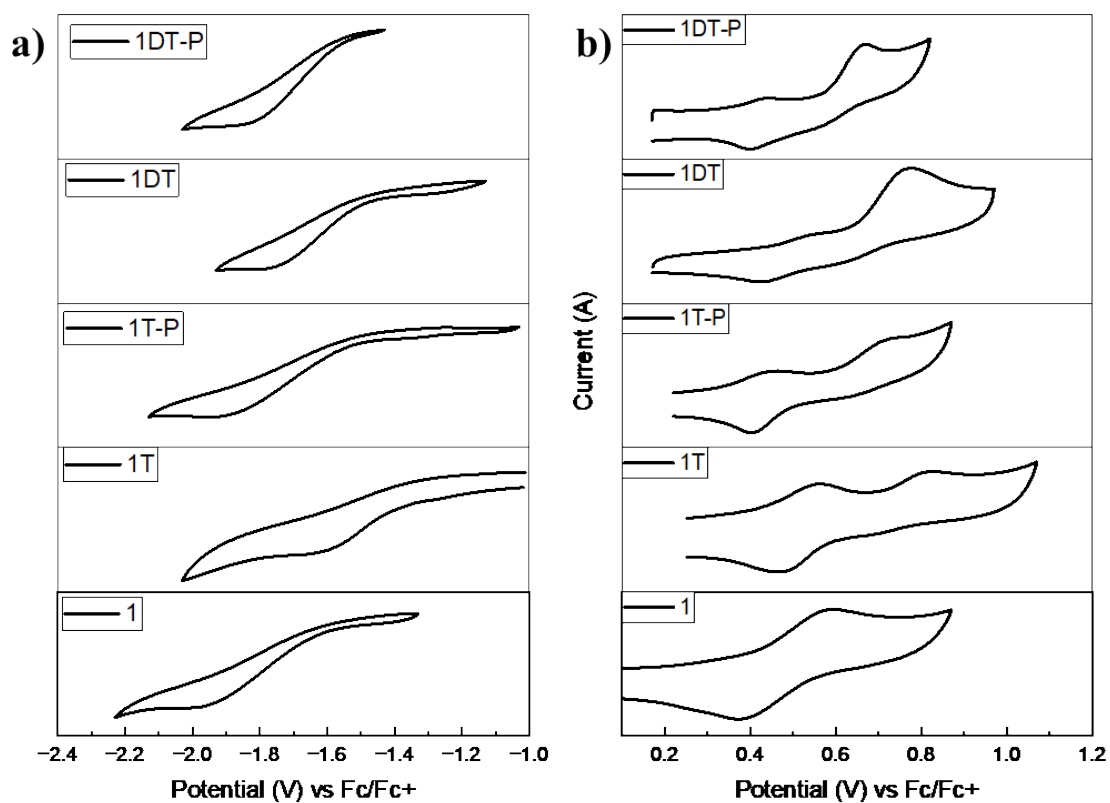
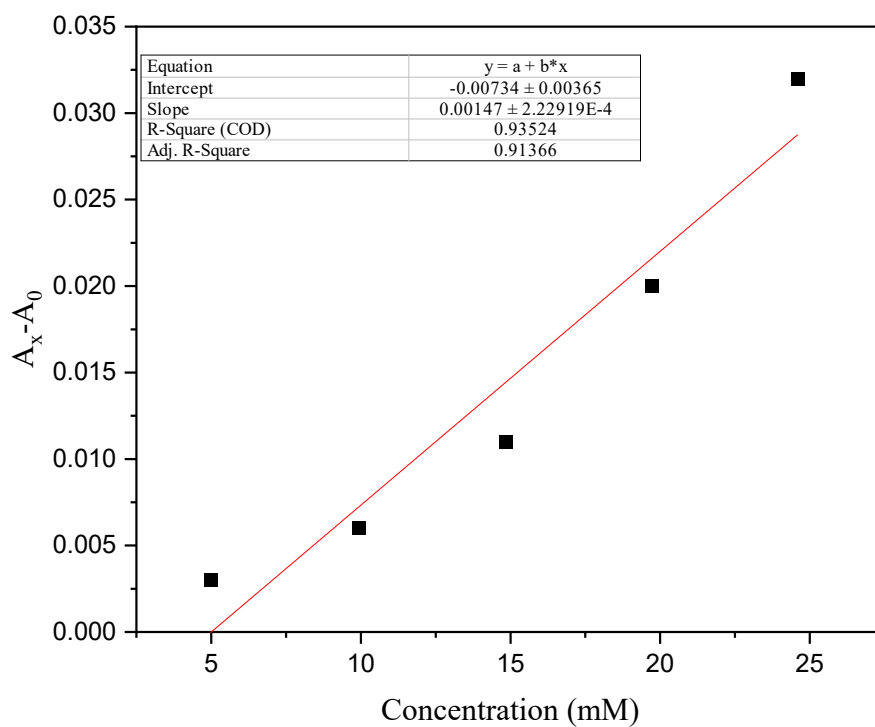


Fig. S23. a) Reduction potential of compound 1, 1T, 1DT, 1T-P, 1DT-P; b) Oxidation potential of compound 1, 1T, 1DT, 1T-P, 2T-P

Table S1. Electrochemical data of **1**, **1T**, **1DT**, **1T-P** & **1DT-P**

Compound	Oxidation		Reduction		HOMO	LUMO	Band gap (eV)
	Ag/AgCl	Ferrocene	Ag/AgCl	Ferrocene			
1	1.09	0.46	-1.15	-1.78	-5.26	-3.02	2.24
1T	1.12, 1.36	0.49, 0.73	-0.85	-1.48	-5.29, -5.53	-3.32	1.97
1T-P	1.05, 1.28	0.42, 0.65	-1.06	-1.69	-5.22, -5.45	-3.11	2.11
1DT	1.32	0.69	-0.98	-1.61	5.49	-3.19	2.30
1DT-P	1.24	0.61	-1.05	-1.68	-5.41	-3.12	2.29

**Fig. S24.** Limit of detection plot of 1DT with CN⁻

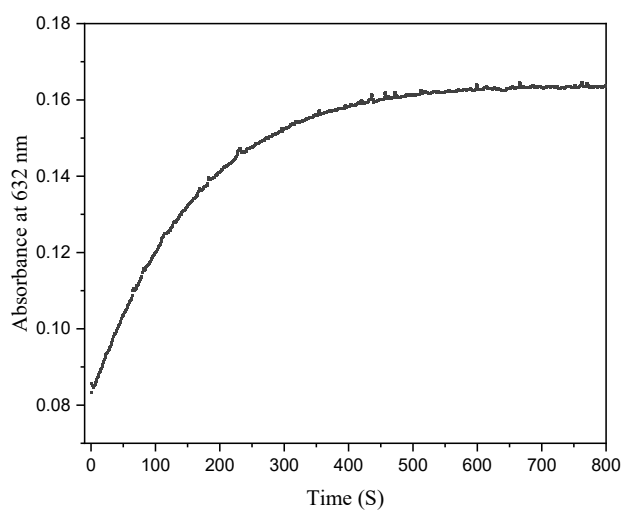


Fig. S25. Absorbance changes of 1DT at 632 nm as a function of time after CN⁻ addition.

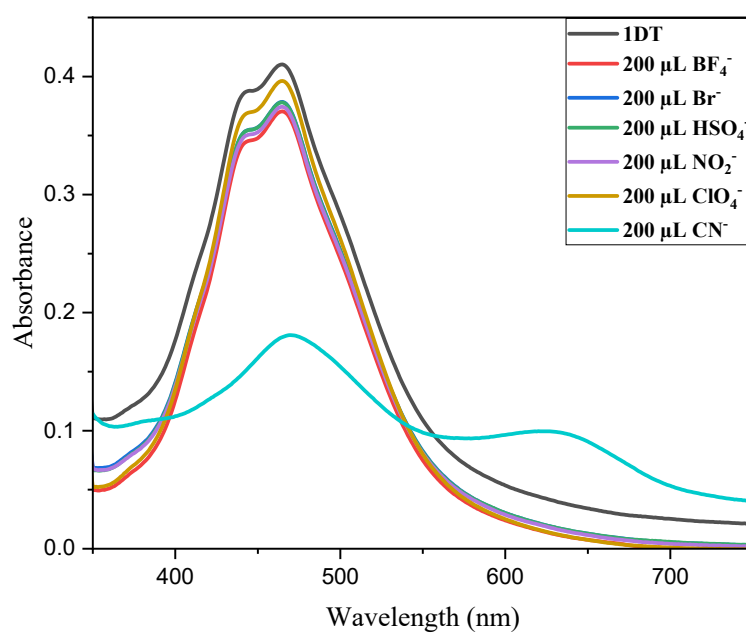


Fig. S26. Absorption spectra of 1DT (10⁻⁵ M in CHCl₃) with different anions.

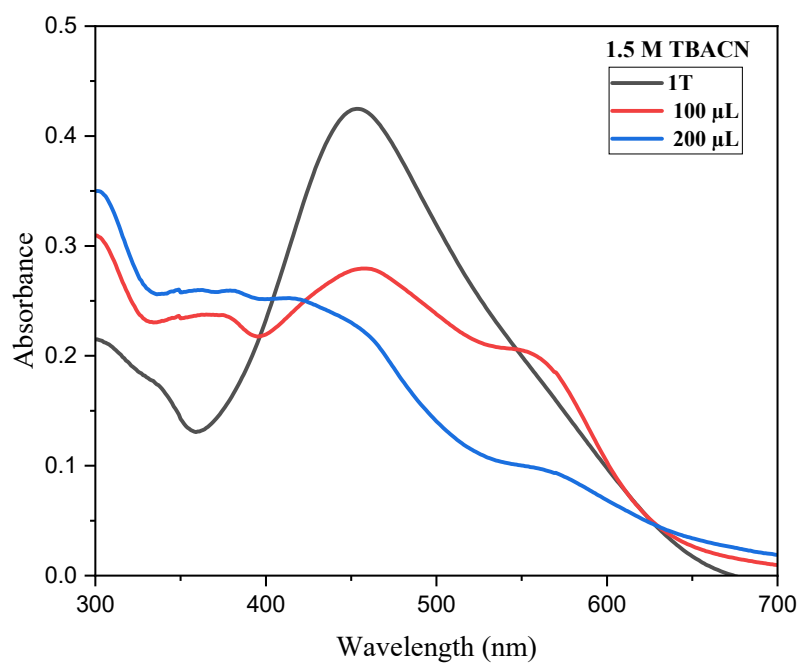


Fig. S27. UV-Vis spectra of **1T** (10^{-5} M) with CN^- (1.5 M)

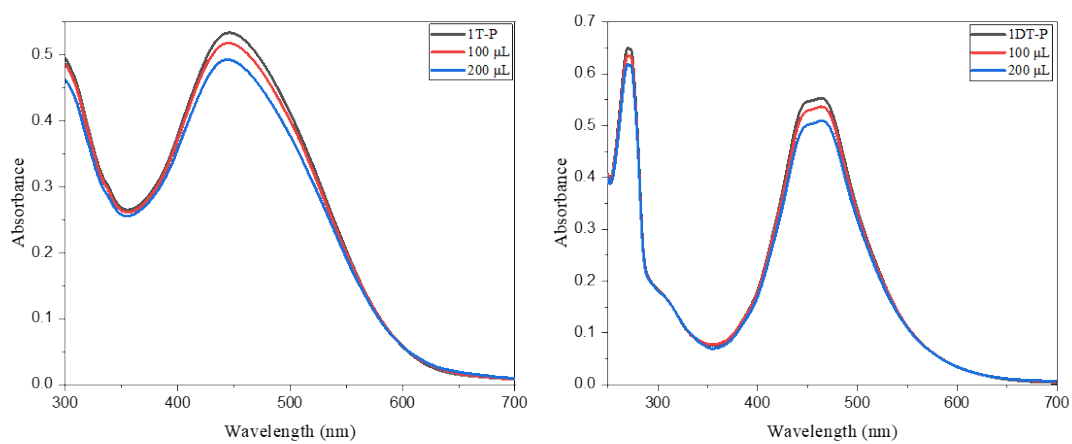


Fig. S28. UV-Vis spectra of **1T-P** & **1DT-P** (10^{-5} M) with CN^- (1.5 M)