SUPPORTING INFORMATION

Chinese Journal of Structural Chemistry

Cyano and Isocyano-substituted Tetraphenylethylene with AIE Behavior and Mechanoresponsive Behavior

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Theoretical calculation method and results details. Density functional theory (DFT) calculations in this study were performed with the Gaussian 16 Rev. A03 package1. The geometrical structures of the ground states of two TPE derivatives were optimized by using PBE0 density functional methods. The def2-SVP basis set was used for all the atoms. The solvent effects, with tetrahydrofuran as solvent, were carried out by the self-consistent reaction field theory with solvent model based on density. Vibrational frequency analyses were performed on the optimized intermediates structures to ensure that they are local minima on the energy potential surface with no imaginary frequencies. Meanwhile, the electronic excitation properties of TPE-CN and TPE-NC compounds were investigated by using time-dependent DFT (TD-DFT) theory at PBE0/def2-SVP level. The calculated electronic absorption spectra of TPE-CN and TPE-NC compounds are shown in Figure S7. All the optimized structures were visualized by GaussianView 6.0 software 2.

High Performance Liquid Chromatography (HPLC) measurement. HPLC was performed on an Agilent Infinity II with a 90:10 elution system of acetonitrile and water, using a reversed column Poparis C18-Ether. The UV-visible detection wavelength is 340 nm. HPLC charts are in Figure S18-19.

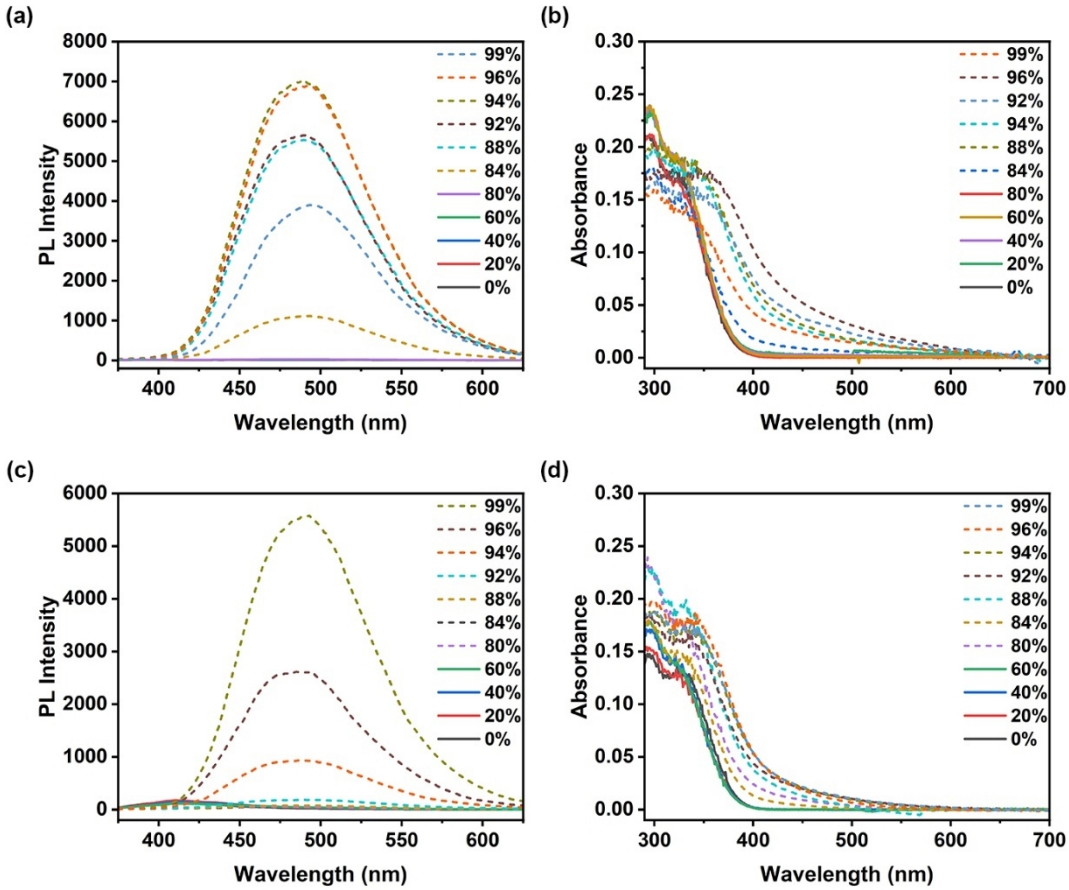

Figure S1. (a) The photoluminescence (PL) spectra of TPE-CN in acetonitrile/water mixture (1×10^{-5} M). (b) UV-visible spectra of TPE-CN in acetonitrile/water mixture (1×10^{-5} M). (c) PL spectra of TPE-CN in THF/water mixture (1×10^{-5} M). (b) UV-visible spectra of TPE-CN in THF/water mixture (1×10^{-5} M).

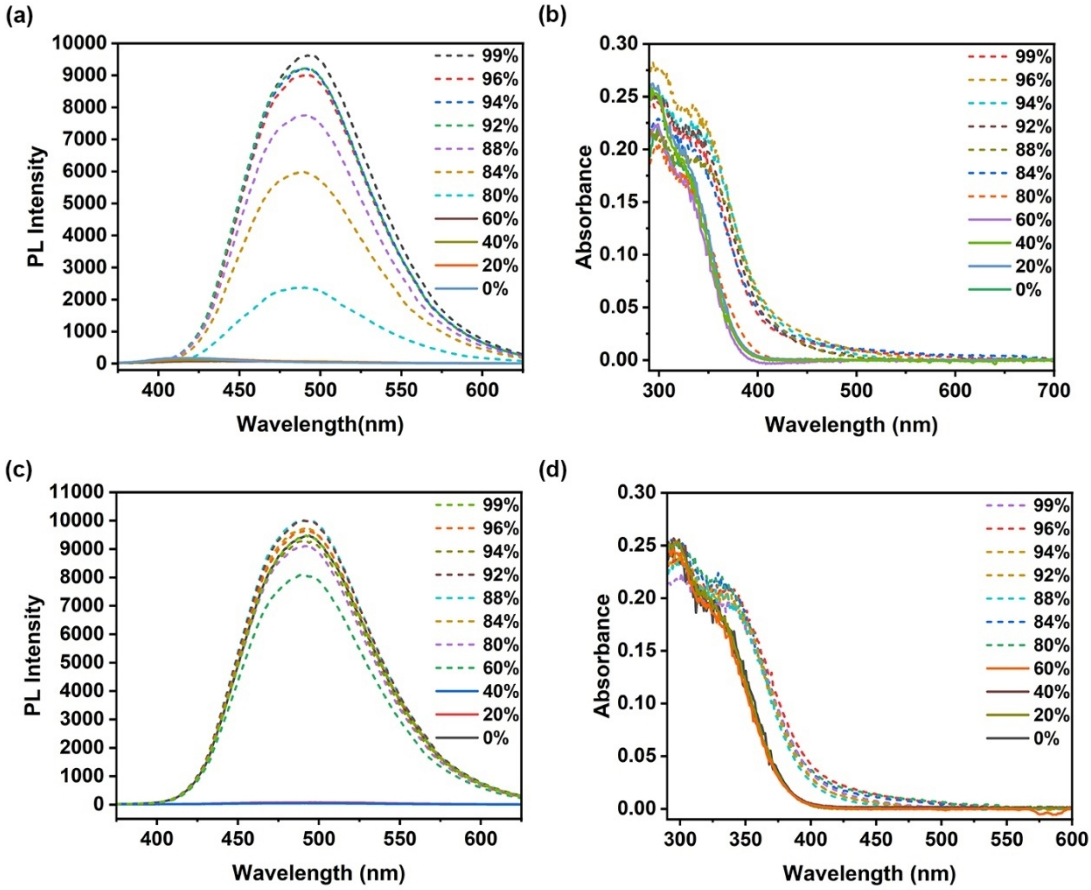

Figure S2. (a) The photoluminescence (PL) spectra of TPE-CN in DMF/water mixture (1×10^{-5} M). (b) UV-visible spectra of TPE-CN in DMF/water mixture (1×10^{-5} M). (c) PL spectra of TPE-CN in DMSO/water mixture (1×10^{-5} M). (b) UV-visible spectra of TPE-CN in DMSO/water mixture (1×10^{-5} M).

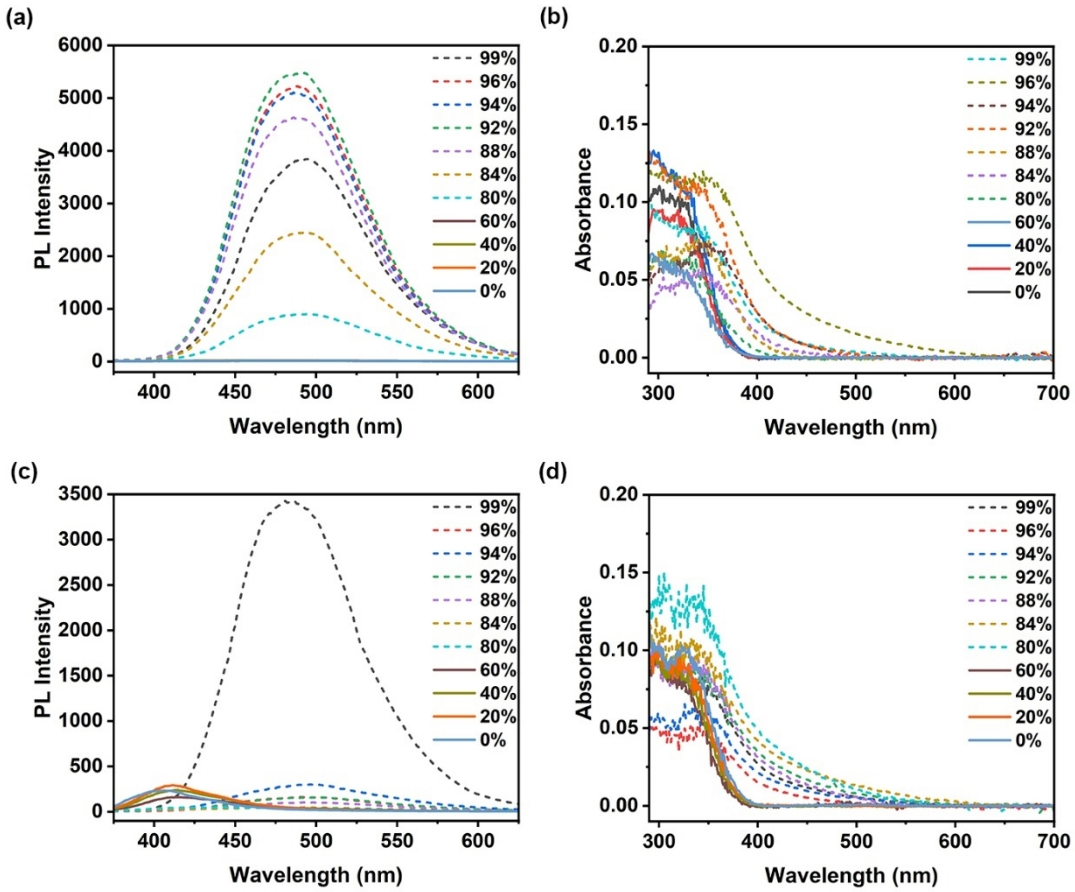

Figure S3. (a) The photoluminescence (PL) spectra of TPE-NC in acetonitrile/water mixture (5×10^{-6} M). (b) UV-visible spectra of TPE-NC in acetonitrile/water mixture (5×10^{-6} M). (c) PL spectra of TPE-NC in THF/water mixture (5×10^{-6} M). (b) UV-visible spectra of TPE-NC in THF/water mixture (5×10^{-6} M).

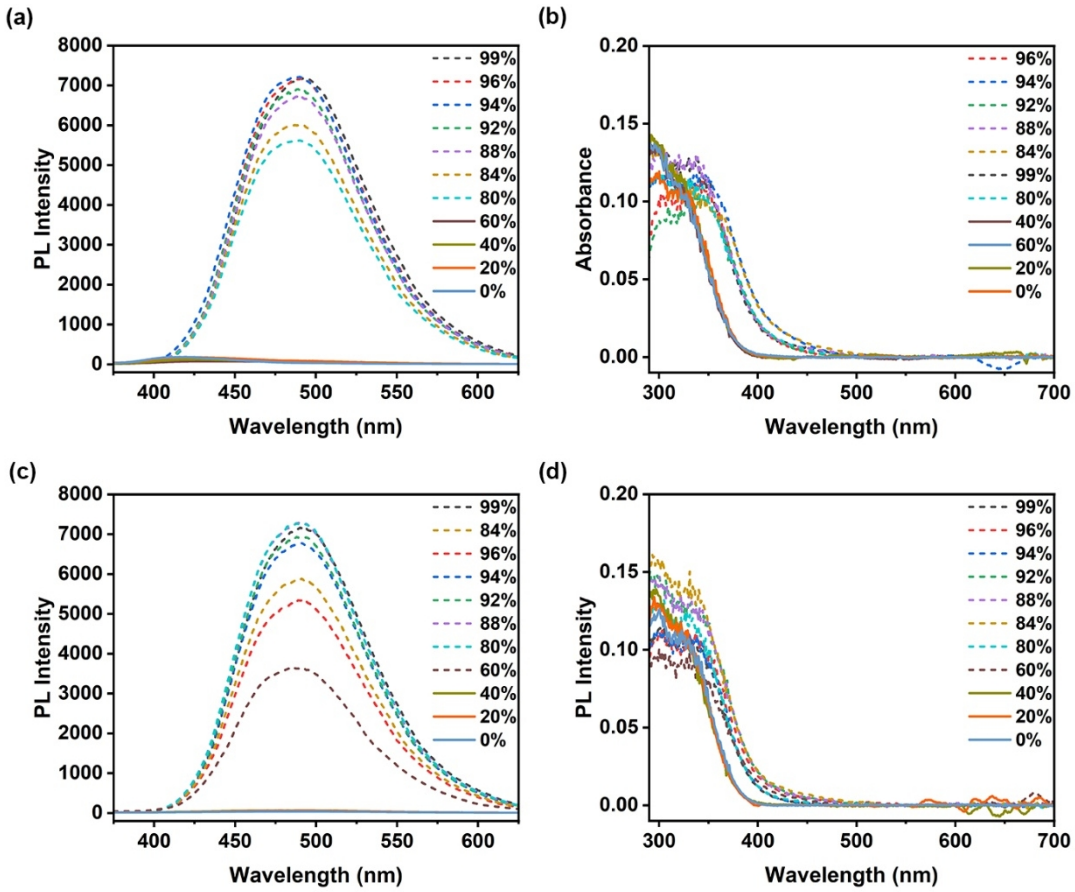

Figure S4. (a) The photoluminescence (PL) spectra of TPE-NC in DMF/water mixture (5×10^{-6} M). (b) UV-visible spectra of TPE-NC in DMF/water mixture (5×10^{-6} M). (c) PL spectra of TPE-NC in DMSO/water mixture (5×10^{-6} M). (b) UV-visible spectra of TPE-NC in DMSO/water mixture (5×10^{-6} M).

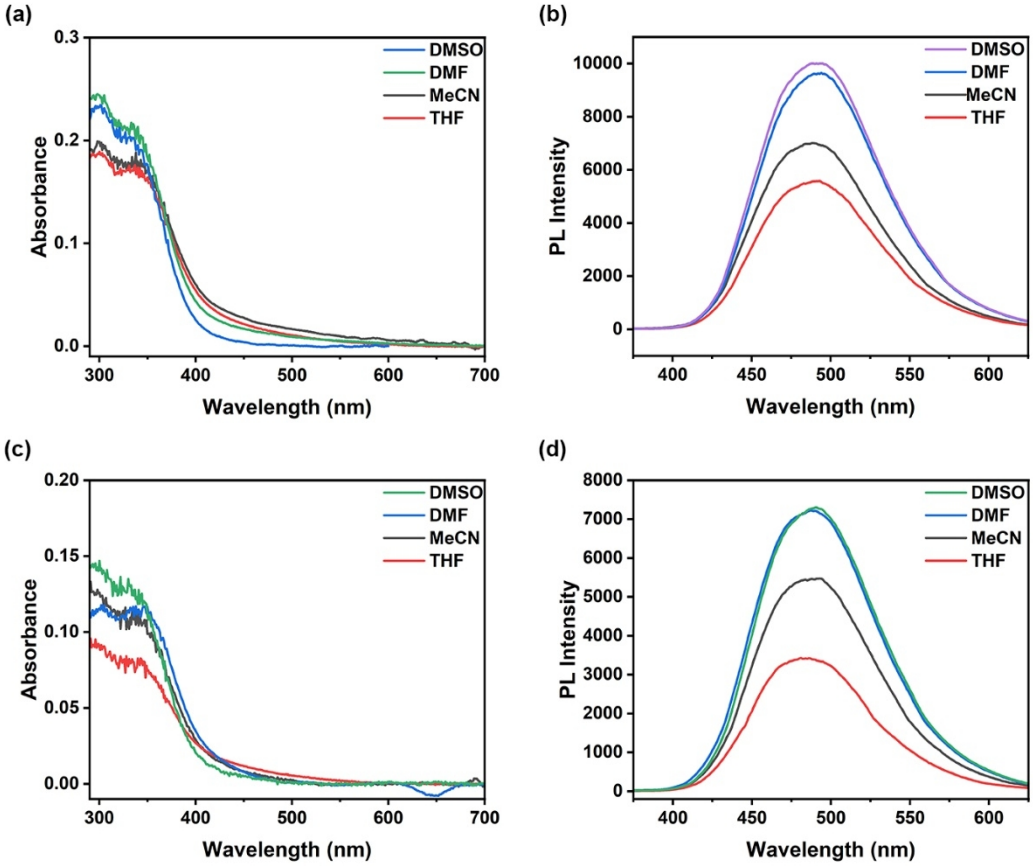

Figure S5. The photoluminescence (PL) spectra in different solvent and the corresponding UV-visible spectra. (a) the UV-visible spectra of TPE-CN (1×10^{-5} M) in acetonitrile (f_w = 94%), THF (f_w = 99%), DMF (f_w = 99%) and DMSO (f_w = 88%). (b) the PL spectra of TPE-CN (1×10^{-5} M) in acetonitrile (f_w = 94%), THF (f_w = 99%), DMF (f_w = 99%) and DMSO (f_w = 88%). (c) the UV-visible spectra of TPE-NC (5×10^{-6} M) in acetonitrile (f_w = 92%), THF (f_w = 99%), DMF (f_w = 94%) and DMSO (f_w = 88%). (d) the PL spectra of TPE-CN (5×10^{-6} M) in acetonitrile (f_w = 92%), THF (f_w = 99%), DMF (f_w = 94%) and DMSO (f_w = 88%). (Relative polarity for THF, MeCN, DMF, DMSO, and H_2O are 4.2, 6.2, 6.4, 7.2, and 10.2, respectively)

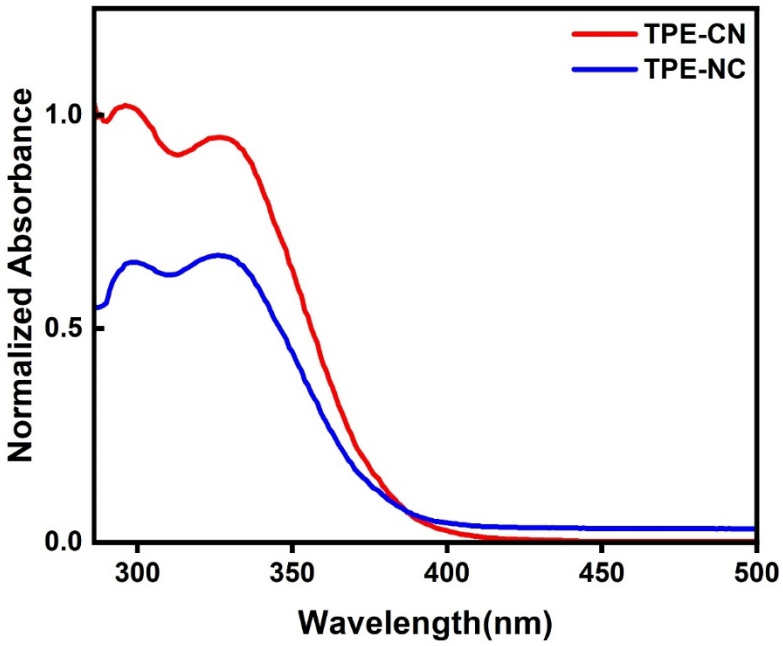

Figure S6. UV-visible absorption spectra of TPE-NC and TPE-NC in THF(1×10^{-5} M)

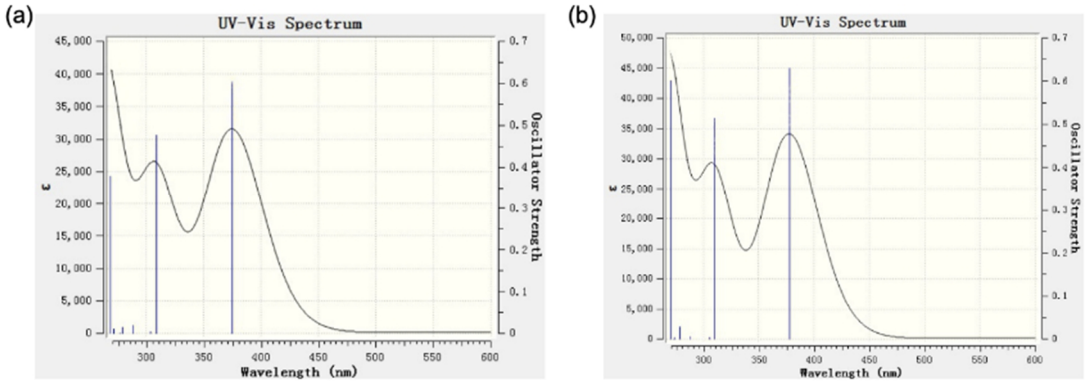

Figure S7. Calculated UV-visible spectrum of TPE-CN and TPE-NC (gray line) in THF accompanied with a simulated transitions (blue line) calculated by TD-DFT method at the PBE0/def2-SVP level.

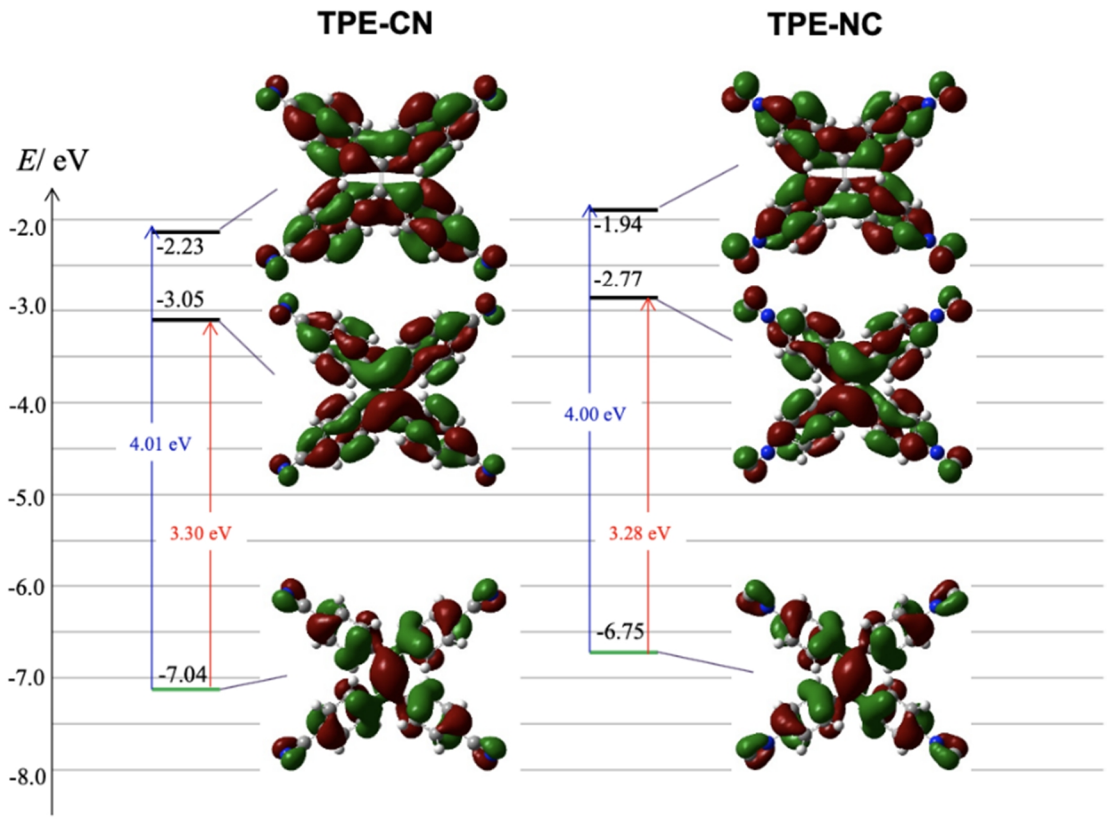

Figure S8. Energy diagram and distributions of frontier orbitals of TPE-CN and TPE-NC accompanied with the assignment of optical transitions.

Table S1. Absorption Wavelengths and Their Theoretical Assignments for TPE-CN and TPE-NC

	Observed absorption band (λ_{max})	Calculated by TD-DFT	Assigned transition[a]	Energy difference	Contri-bution	Oscillator strength (*f*)
TPE-CN	327 nm	376 nm	HOMO→LUMO	3.30 eV	0.71	0.60
	296 nm	309 nm	HOMO →LUMO + 1	4.01 eV	0.70	0.48
TPE-NC	327 nm	378 nm	HOMO→LUMO	3.28 eV	0.71	0.63
	298 nm	310 nm	HOMO→LUMO + 1	4.00 eV	0.70	0.51

[a] Assigned transitions and their corresponding energy difference were showed in Figure S8.

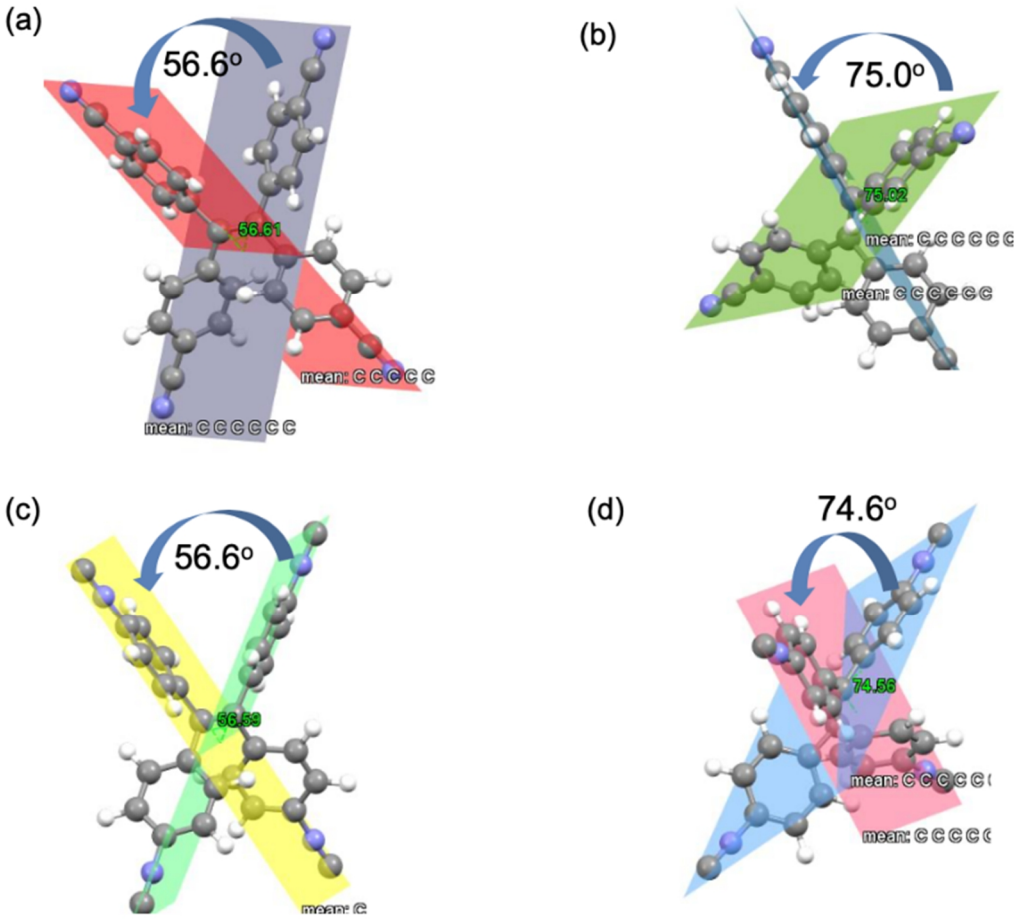

Figure S9. Dihedral angles of the neighbored phenyl rings of TPE-CN (a, b) and TPE-NC (c, d) in optimized molecular structures.

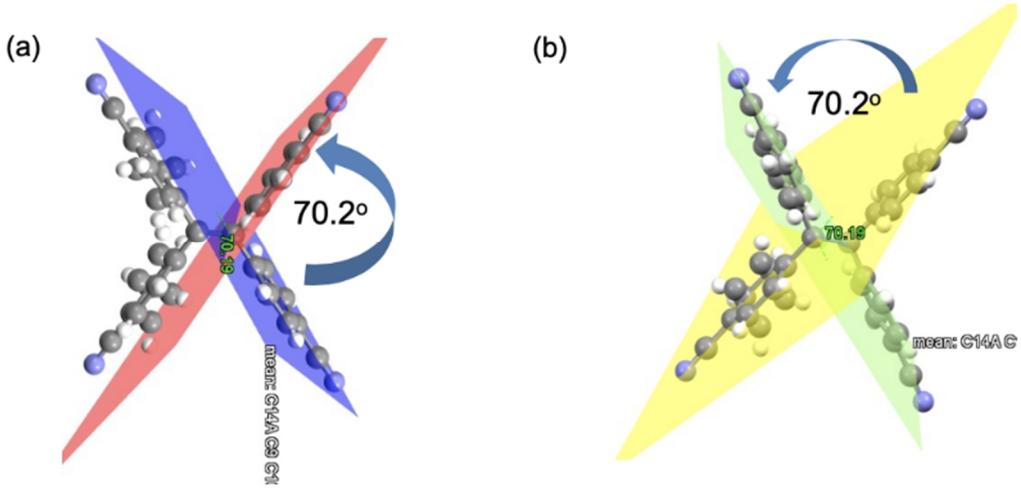

Figure S10. Dihedral angles of the neighbored phenyl rings of TPE-CN (a, b) in crystal molecular structures.

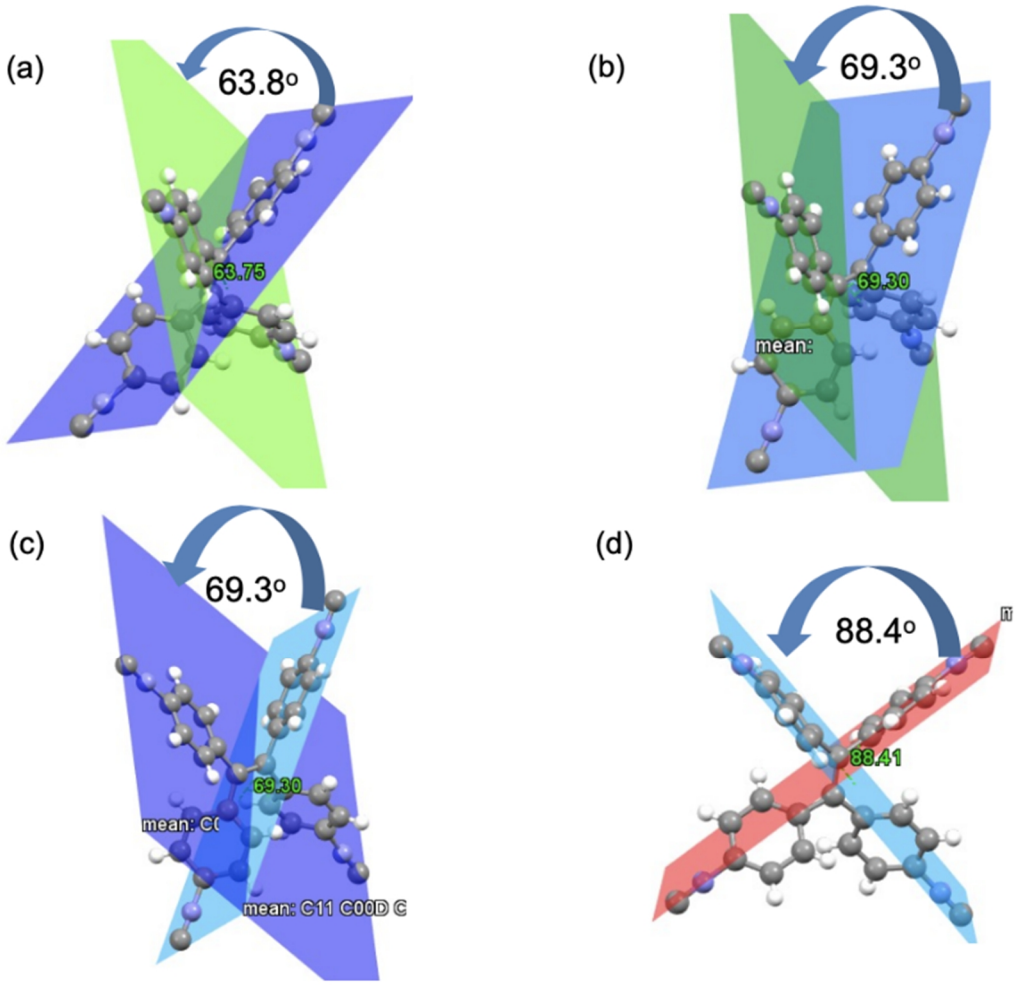

Figure S11. Dihedral angles of the neighbored phenyl rings of TPE-NC in crystal molecular structures of part I (with proportions of 75%).

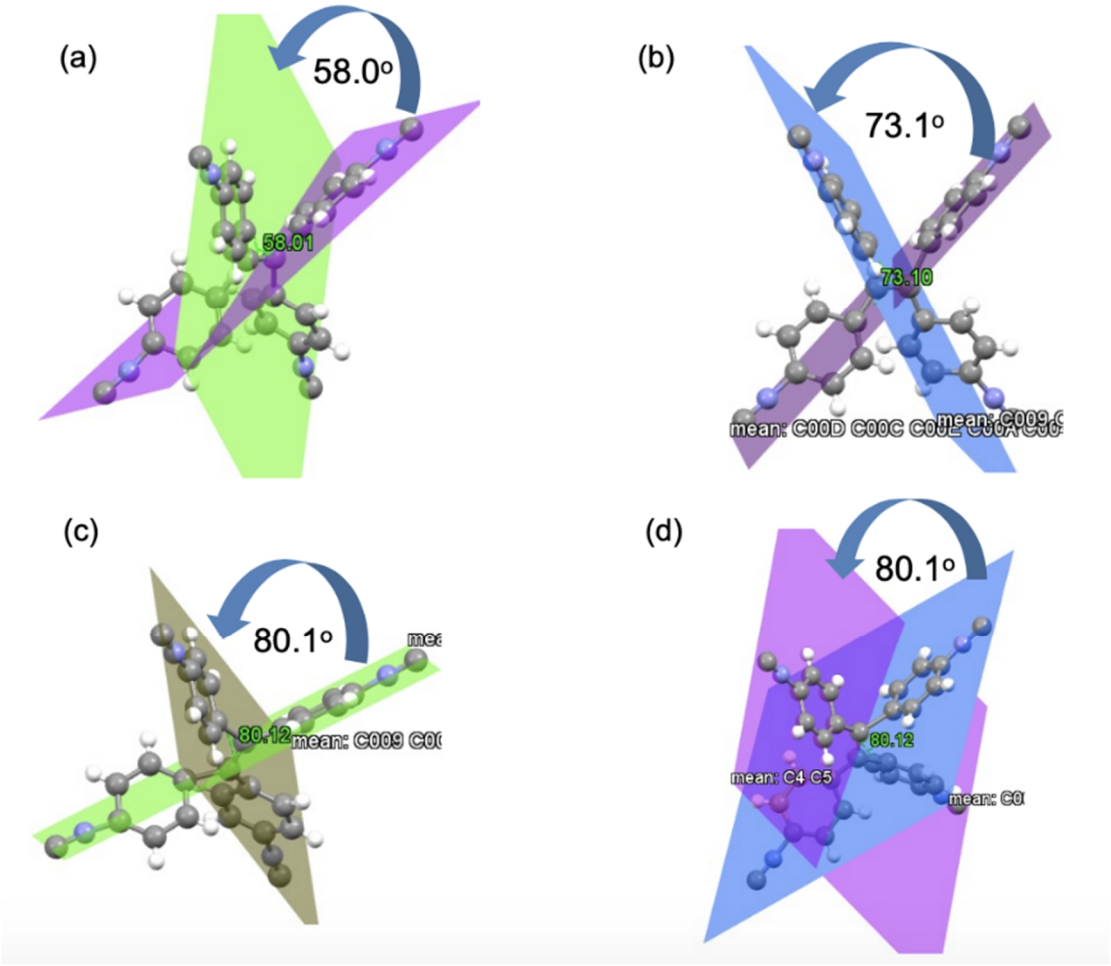

Figure S12. Dihedral angles of the neighbored phenyl rings of TPE-NC in crystal molecular structures of part I (with proportions of 25%).

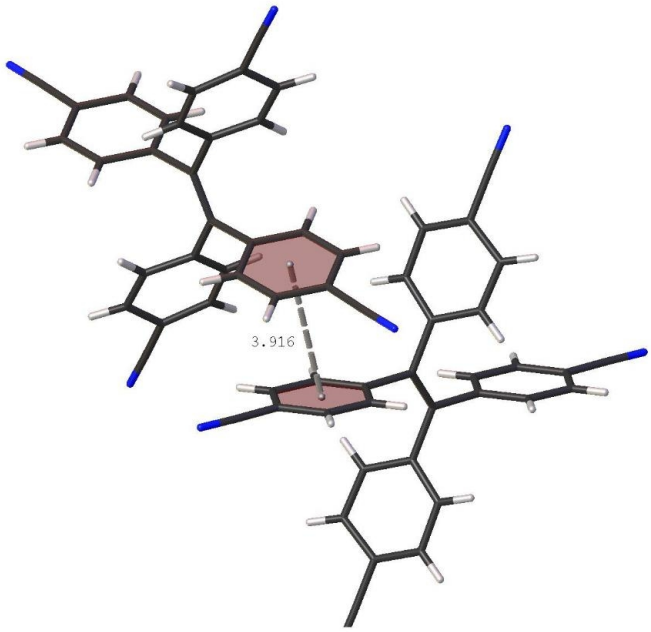

Figure S13. Intermolecular p-p stacking distance of TPE-CN (Å).

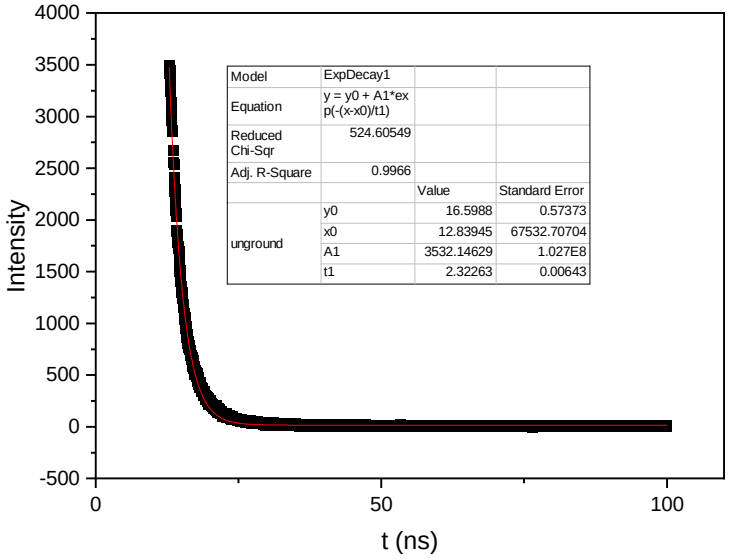

Figure S14. Lifetime of as-prepared sample of TPE-CN (2.32 ns)

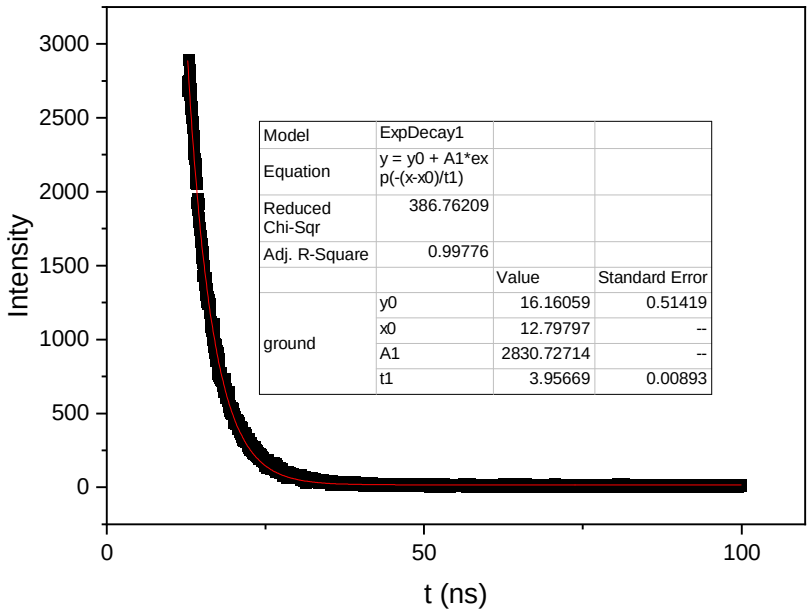

Figure S15. Lifetime of ground sample of TPE-CN (3.96 ns)

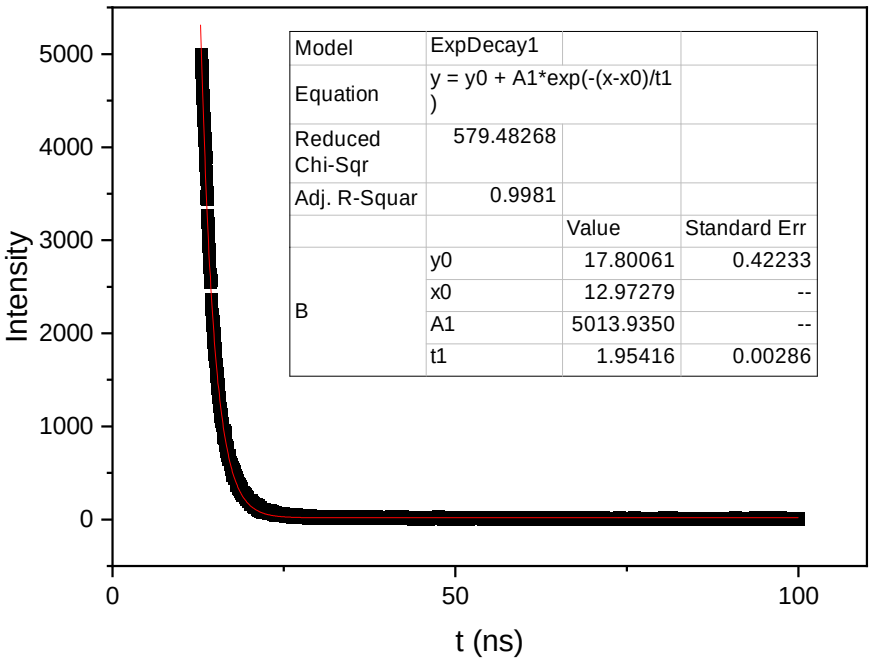

Figure S16. Lifetime of as-prepared sample of TPE-NC (1.95 ns)

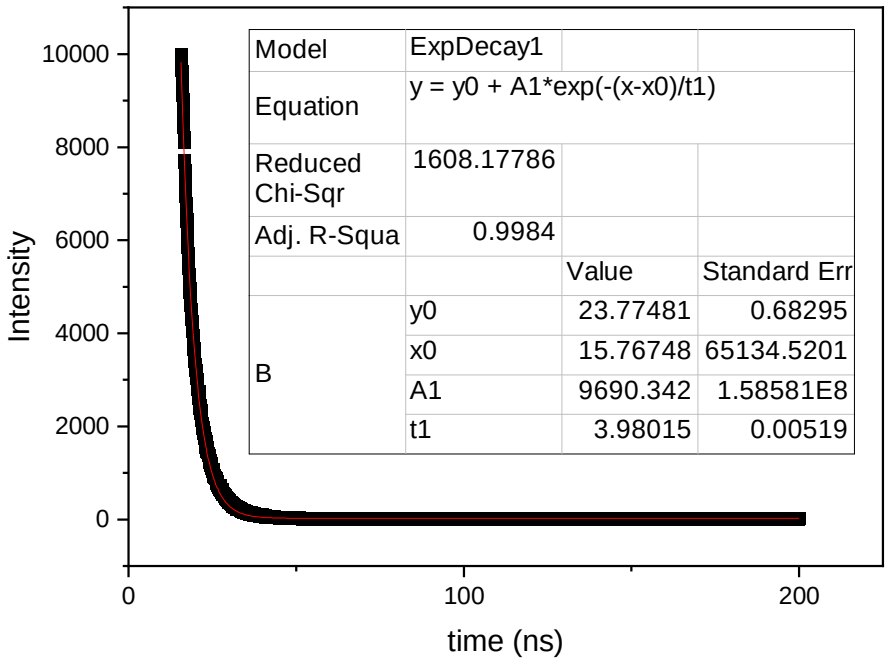

Figure S17. lifetime of ground sample of TPE-NC (3.98 ns)

Table S2. Cartesian Coordinates (in Angstrom) of DFT-Optimized Structures

TPE-CN, HF = -1369.177276 a.u.			
C	0.00007400	0.68341000	0.00003800
C	3.57804800	3.03801500	0.37888000
C	1.24758700	1.48225400	0.12571300
C	-1.24746200	1.48221200	-0.12561500
C	4.76559300	3.82864900	0.50603700
C	-2.19670500	1.19789700	-1.12029300
H	-2.02283500	0.36752300	-1.80736300
C	3.34752500	1.96326500	1.25111400
H	4.07463900	1.73661800	2.03300500
C	-2.63163100	3.34016500	0.61218800
H	-2.80669800	4.17896500	1.28838900
C	2.19674100	1.19810200	1.12052400
H	2.02283400	0.36781100	1.80768300
N	5.72695300	4.46885400	0.60801200
C	-1.47788300	2.57614200	0.72480600
H	-0.74209100	2.82514300	1.49307300
C	-3.57801700	3.03783600	-0.37872200
C	-4.76561100	3.82840100	-0.50585000
C	-3.34753600	1.96299500	-1.25085600
H	-4.07472100	1.73622400	-2.03264500
N	-5.72701200	4.46855000	-0.60780000
C	1.47803400	2.57611600	-0.72478900
H	0.74229900	2.82501000	-1.49314600
C	2.63173900	3.34019900	-0.61214800
H	2.80683100	4.17893800	-1.28841800
C	0.00006100	-0.68341100	0.00003000
C	-3.57808100	-3.03778300	0.37866200
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C	1.24755700	-1.48227600	-0.12565800
C	-4.76569100	-3.82833000	0.50574600
C	1.47797700	-2.57616800	0.72481200
H	0.74223100	-2.82507300	1.49315400
C	-2.63168700	-3.34009400	-0.61224600
H	-2.80676100	-4.17886700	-1.28847900
C	3.34750000	-1.96328500	-1.25105100
H	4.07462800	-1.73662500	-2.03292500
C	-1.47792500	-2.57608700	-0.72482300
H	-0.74212700	-2.82507500	-1.49308900
N	-5.72710000	-4.46847200	0.60766400
C	2.19672800	-1.19810800	-1.12044900

H	2.02284300	-0.36778900	-1.80758100
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H	2.80674100	-4.17903000	1.28840600
N	5.72688000	-4.46893500	-0.60800200
C	-2.19674600	-1.19789400	1.12031400
H	-2.02286800	-0.36755000	1.80741800
C	-3.34759100	-1.96297700	1.25083600
H	-4.07478200	-1.73622100	2.03262500

TPE-NC, HF = -1369.051299 a.u.

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H	-4.08106600	-1.73277500	-2.03760100
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C	-3.57488000	3.03252400	0.39270600
C	-3.34909700	1.95646900	1.25972900
H	-4.08102300	1.73278800	2.03757400
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H	4.08085500	-1.73336500	2.03802800
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C	2.19726500	1.19414300	-1.12361000
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C	3.34907100	1.95686000	-1.26006600
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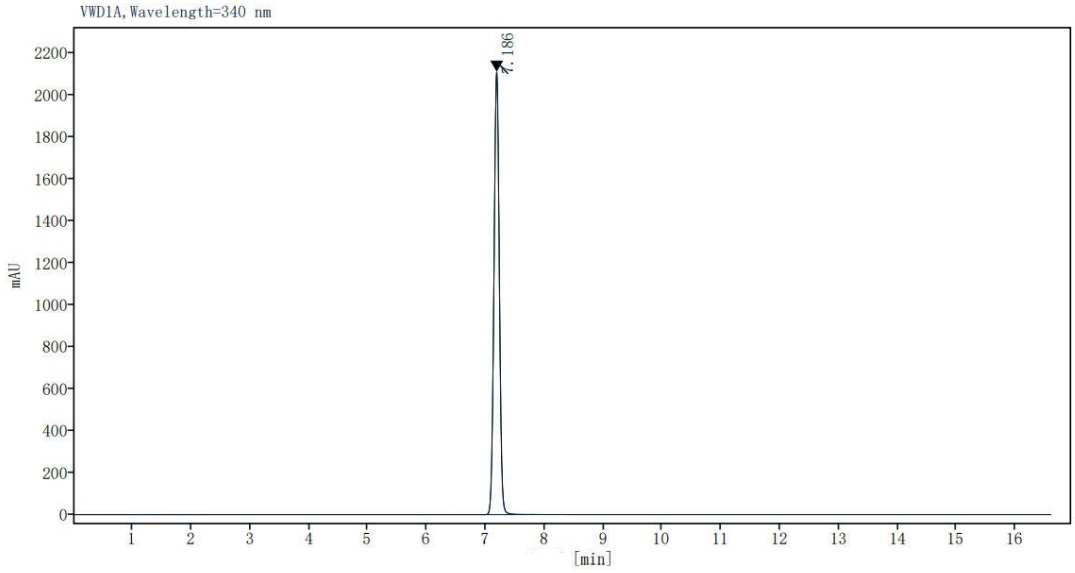
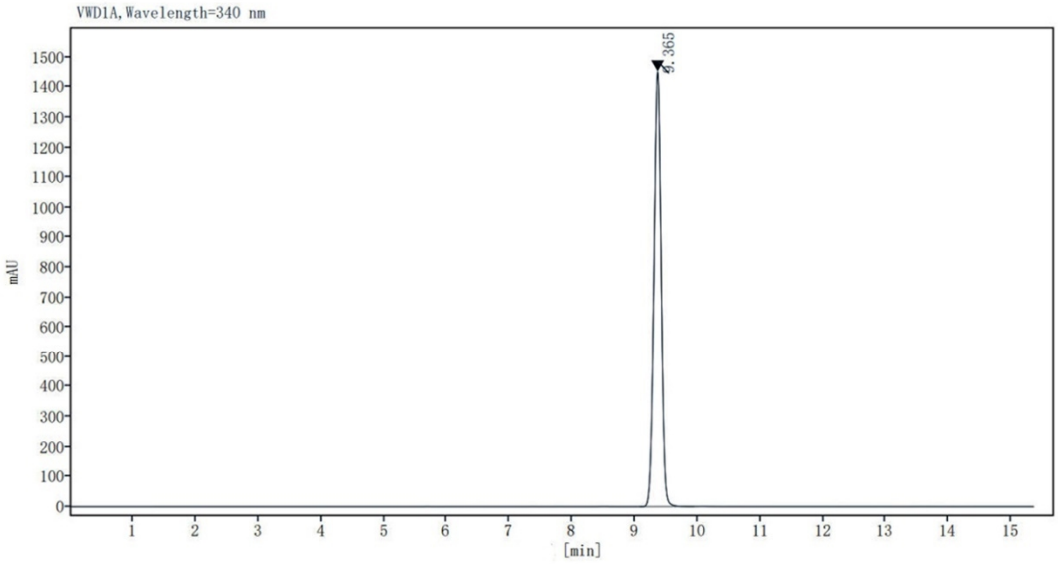


Name	Retention Time (min)	Type	Peak Width (min)	Area	Height	%Area	Resolution (R)	Noise Ratio (S/N)	Theoretical Plate Number (N)
	7.186	BV	0.76	13319.14	2111.78	100%			
	total			**13319.14**					

Fig S18. High performance liquid chromatography (HPLC) chart of TPE-CN



Name	Retention Time (min)	Type	Peak Width (min)	Area	Height	%Area	Resolution (R)	Noise Ratio (S/N)	Theoretical Plate Number (N)
	9.365	BB	0.87	11612.73	1452.28	100%			
	Total 11612.73								

Fig S19. High performance liquid chromatography (HPLC) chart t of TPE-NC

n REFERENCES

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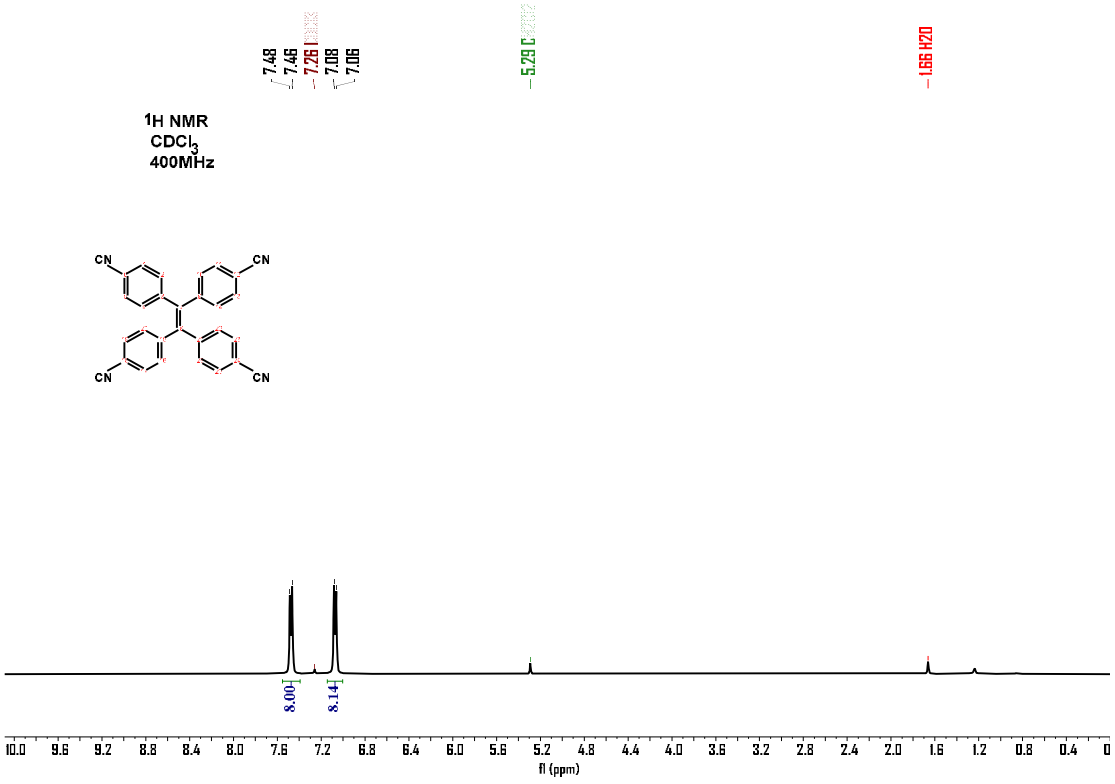
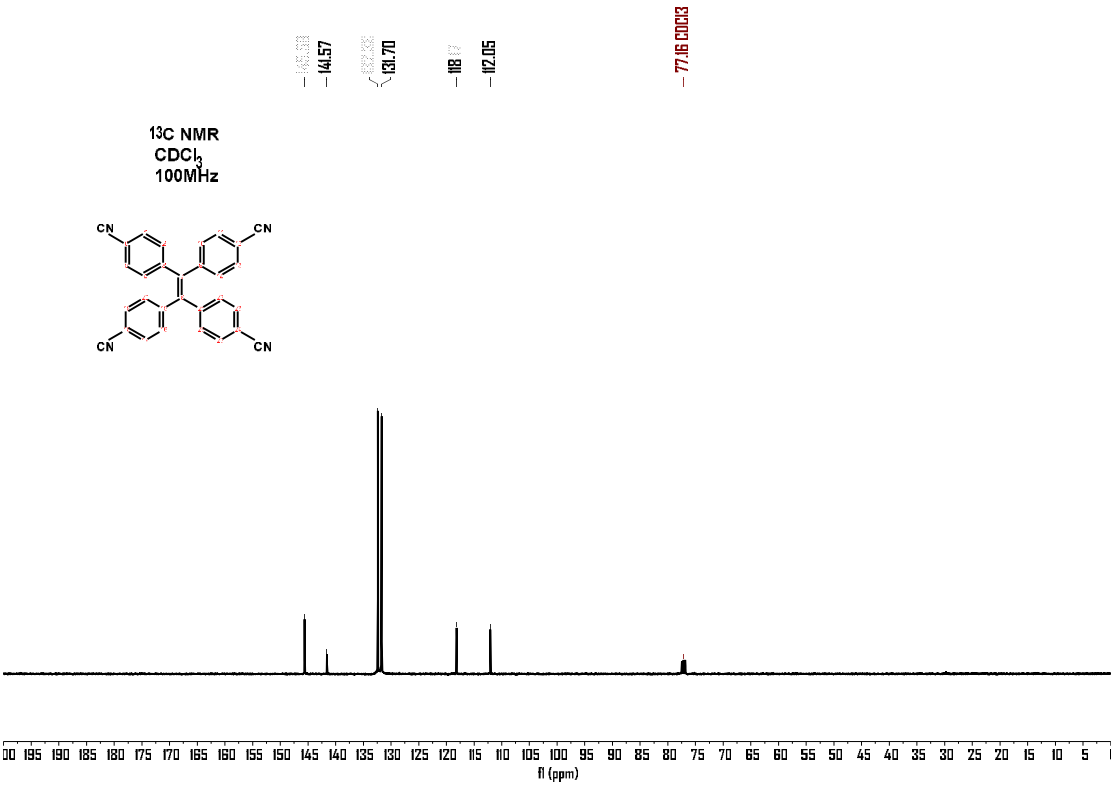
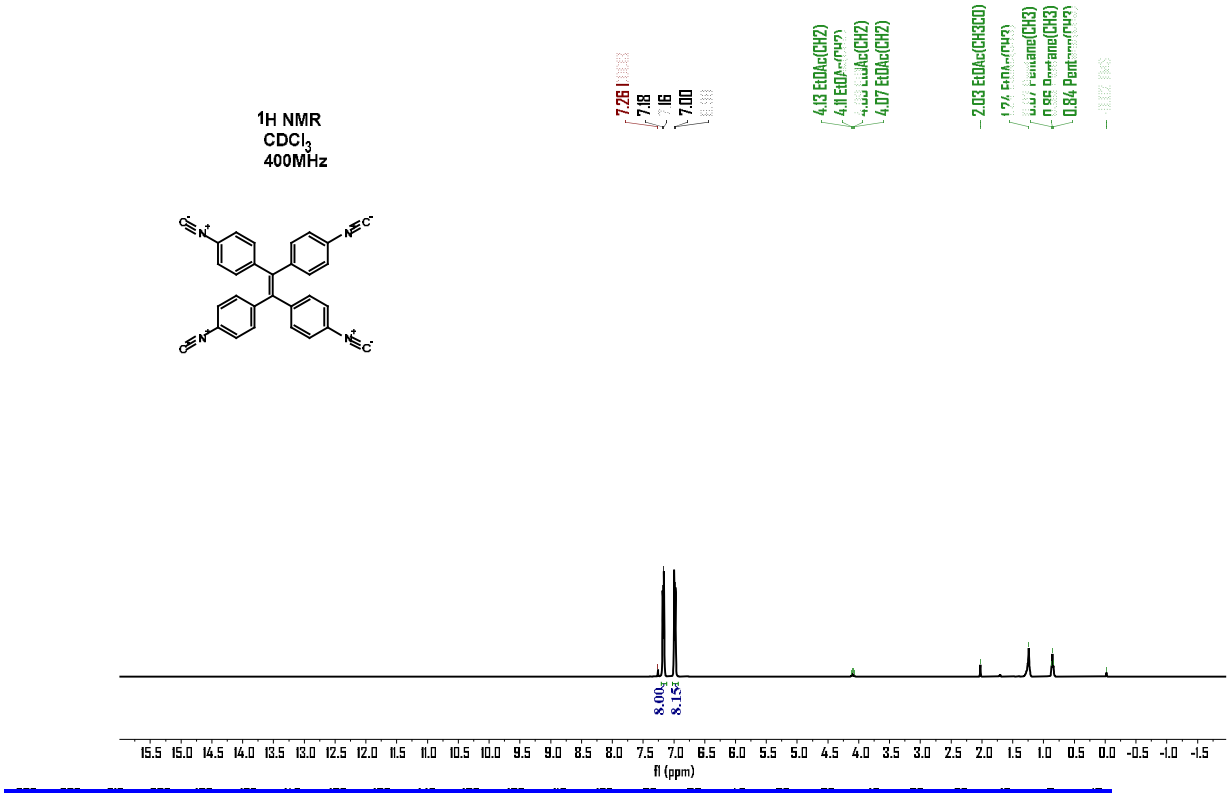
(2) Dennington, R.; Keith, T.; and Millam, J.; *Semichem Inc., Shawnee Mission, GaussView, Version 6.0,* **2016**

n NMR spectra



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7.18
7.16
7.00
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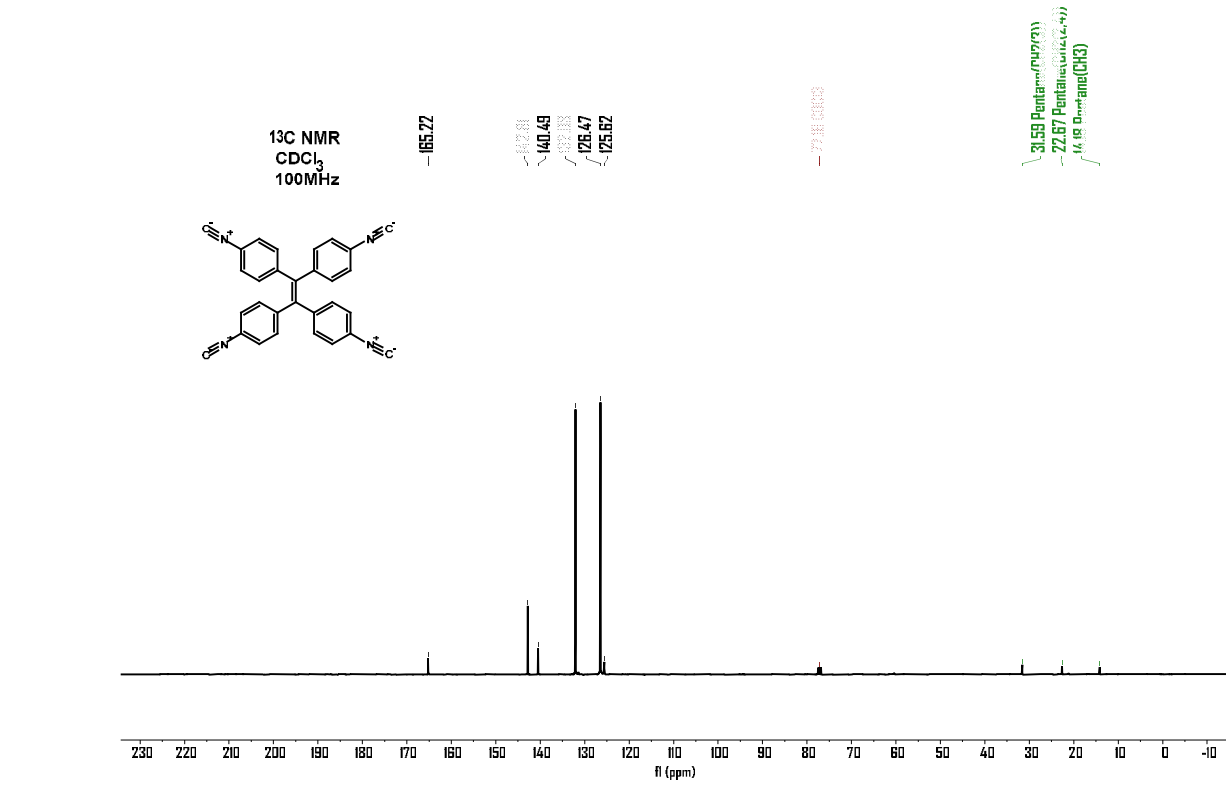
8.00
8.15
f1 (ppm)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CDCl3
100MHz
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140.49
126.47
125.62
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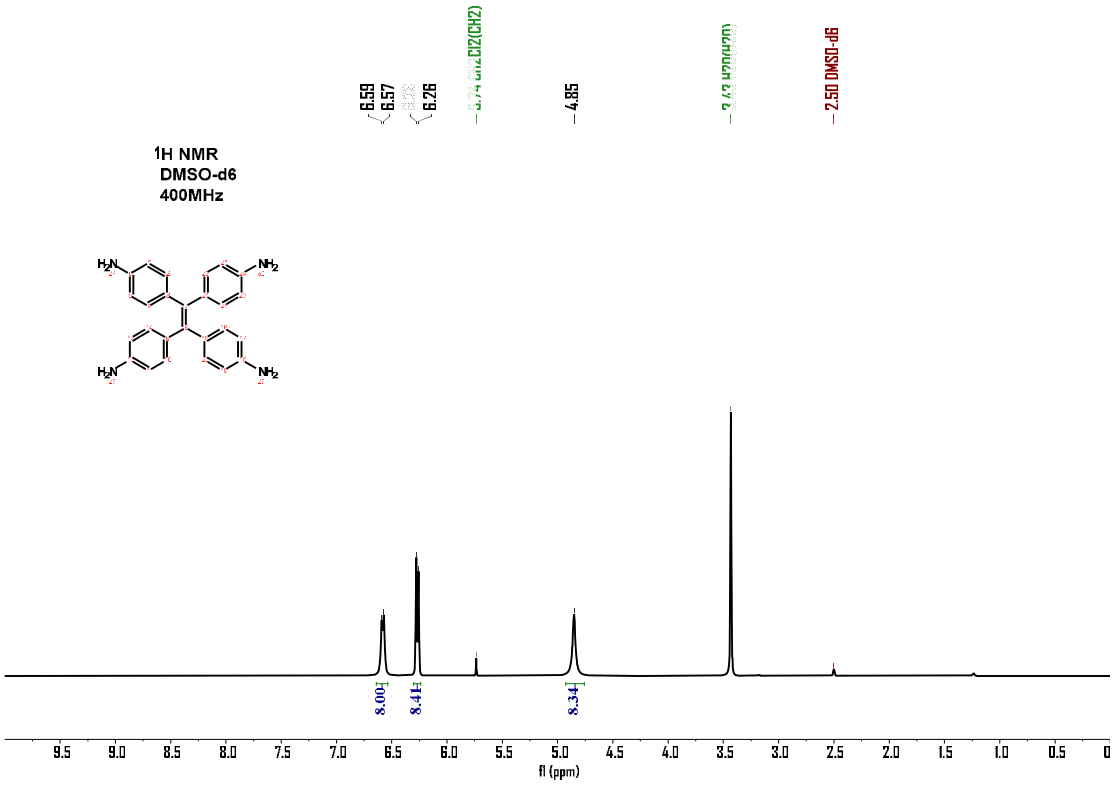
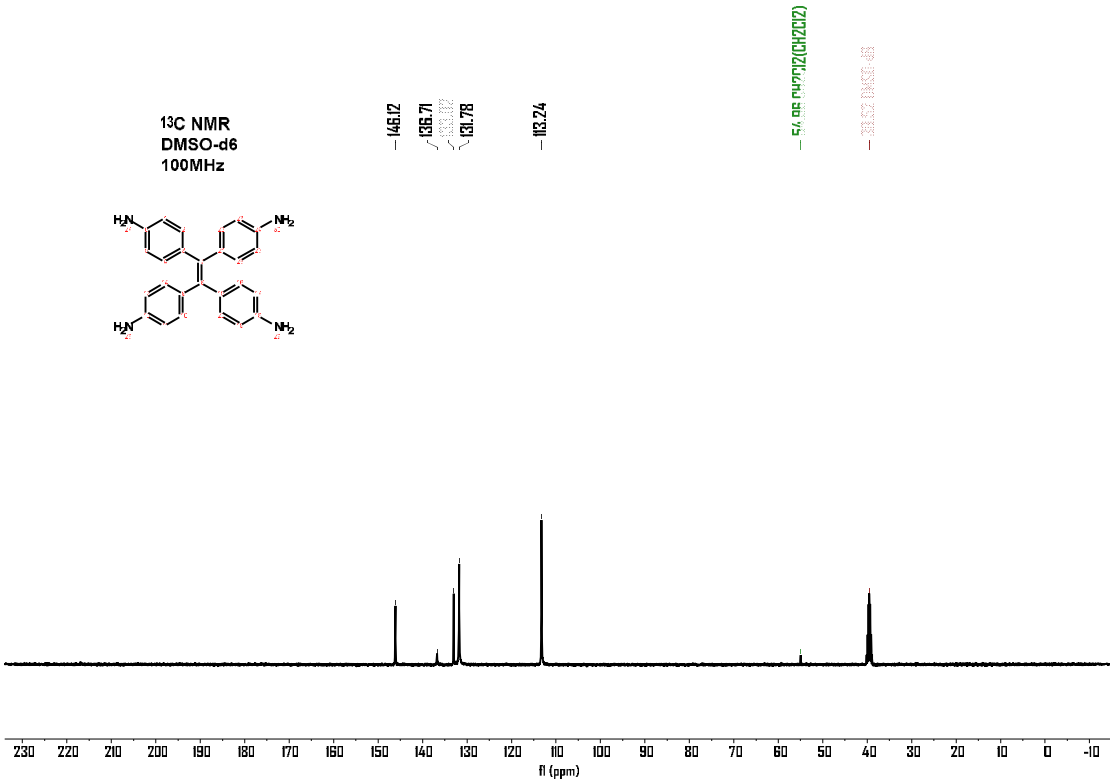
22.67 Pentane(CH2)
14.18 Pentane(CH3)
f1 (ppm)


1H NMR
DMSO-d6
400MHz
6.59
6.57
6.26
4.85
2.50 DMSO-d6
8.00
8.41
8.34
f1 (ppm)


13C NMR
DMSO-d6
100MHz
148.12
138.71
131.78
113.24
f1 (ppm)