

Supporting Information for

**Triphenylethylenyl–Based Donor–Acceptor–Donor Molecules:
Structural and Optical Properties Studies, and AIE Properties for
Cyanide Detection**

Ming Hui Chua,^{a,b} Hui Zhou,^a Ting Ting Lin,^a Jishan Wu,^{*a,b} and Jianwei Xu^{*a}

^a *Institute of Materials Research and Engineering, A*STAR, 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634*

^b *Department of Chemistry, National University of Singapore, Block S8 Level 3, 3 Science Drive 3, Singapore 117543*

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S1. Photo-physical and Aggregation Induced Emission Properties

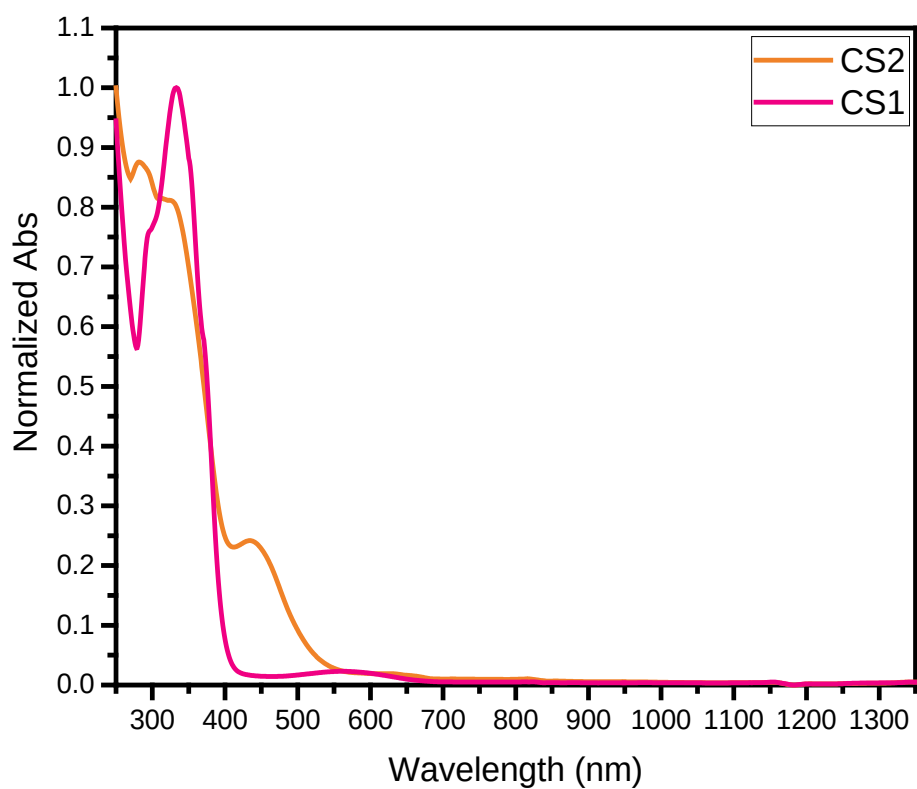


Figure S1. Normalized absorption spectra of CS1 and CS2 measured to long wavelengths. No absorption peaks were observed/measured beyond 700nm unlike calculated by TD-DFT.⁴

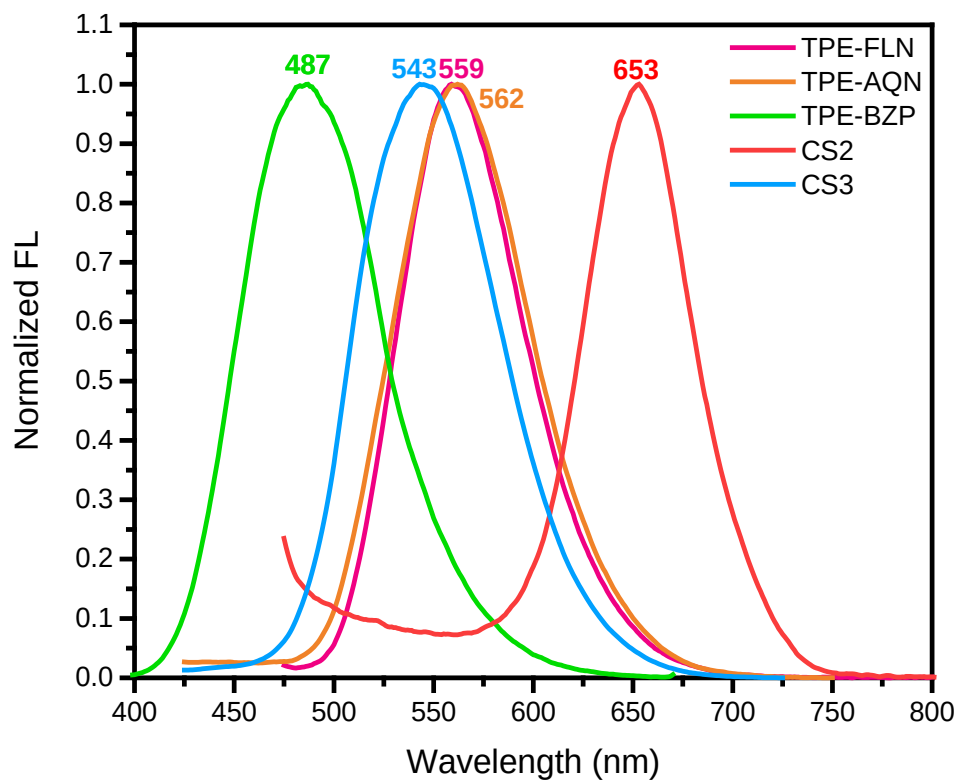


Figure S2. Normalized thin film fluorescence spectra of TPE-FLN, TPE-AQN, TPE-BZP, CS2 and CS3 samples prepared by drop-casting on quartz, measured in N₂ atmosphere.

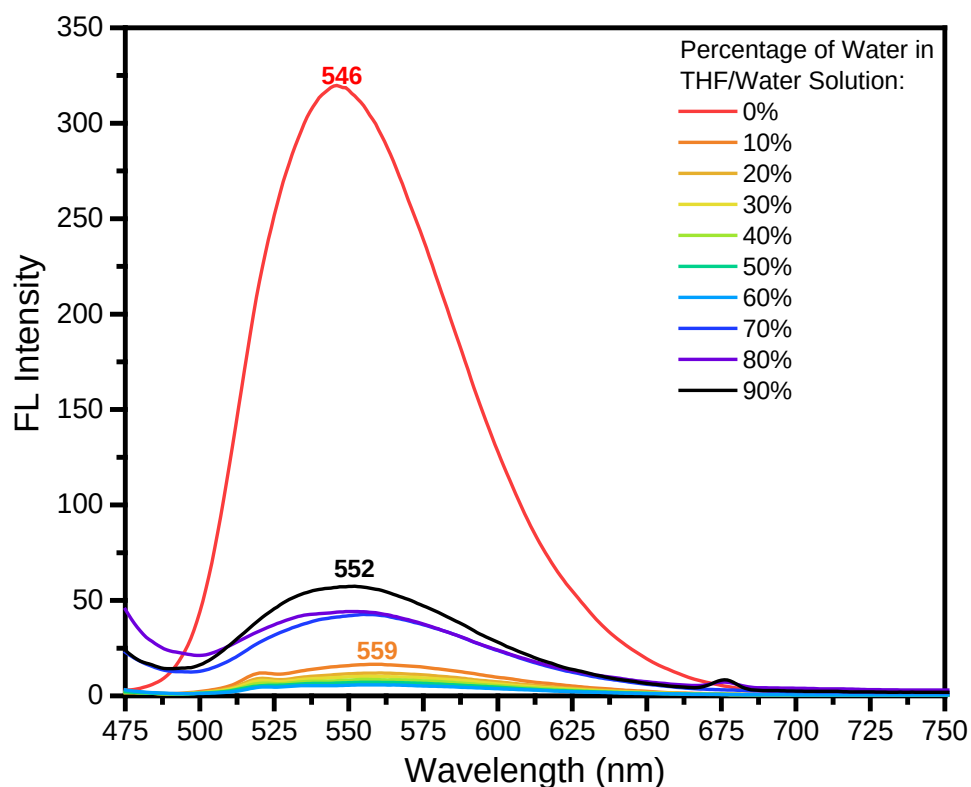


Figure S3. Fluorescence spectra of TPE-FLN solution (10 μ M) in THF/Water solutions of different proportions. Excitation wavelength 450nm.

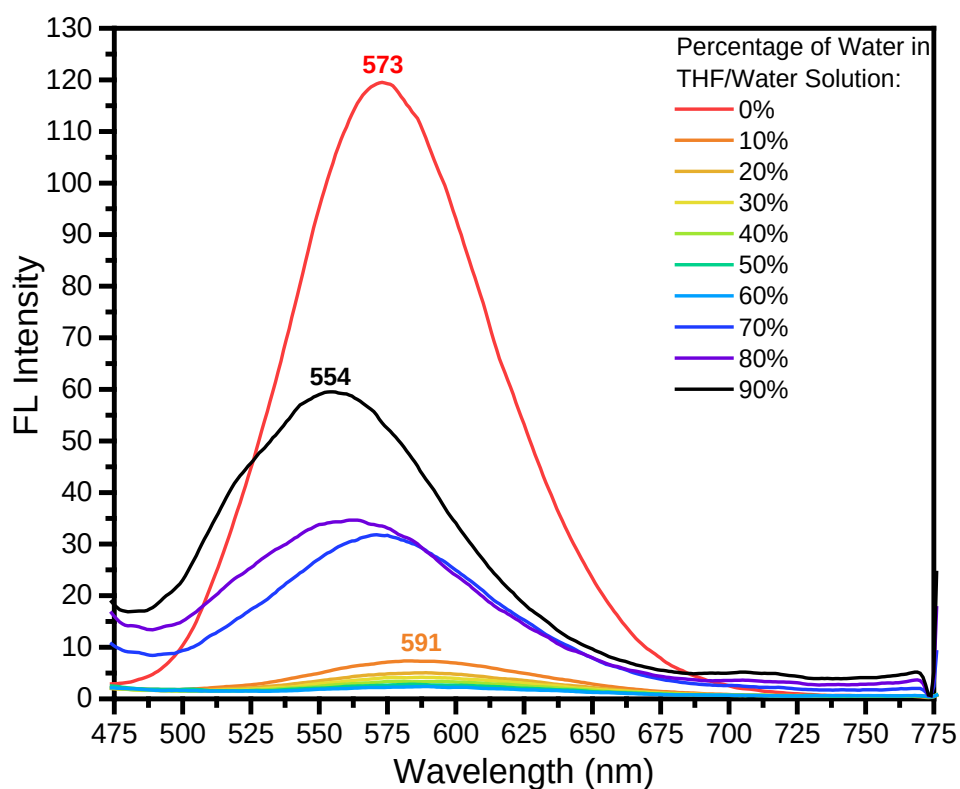


Figure S4. Fluorescence spectra of **TPE-AQN** solution (10 μ M) in THF/Water solutions of different proportions. Excitation wavelength 440nm.

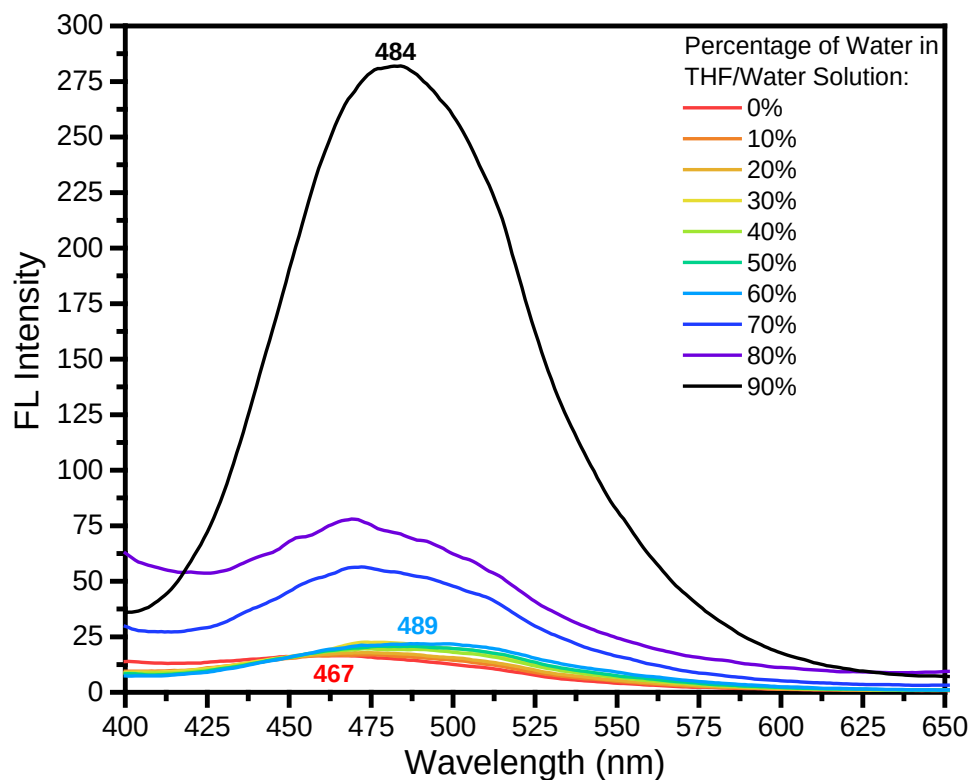


Figure S5. Fluorescence spectra of **TPE-BZP** solution (10 μ M) in THF/Water solutions of different proportions. Excitation wavelength 350nm.

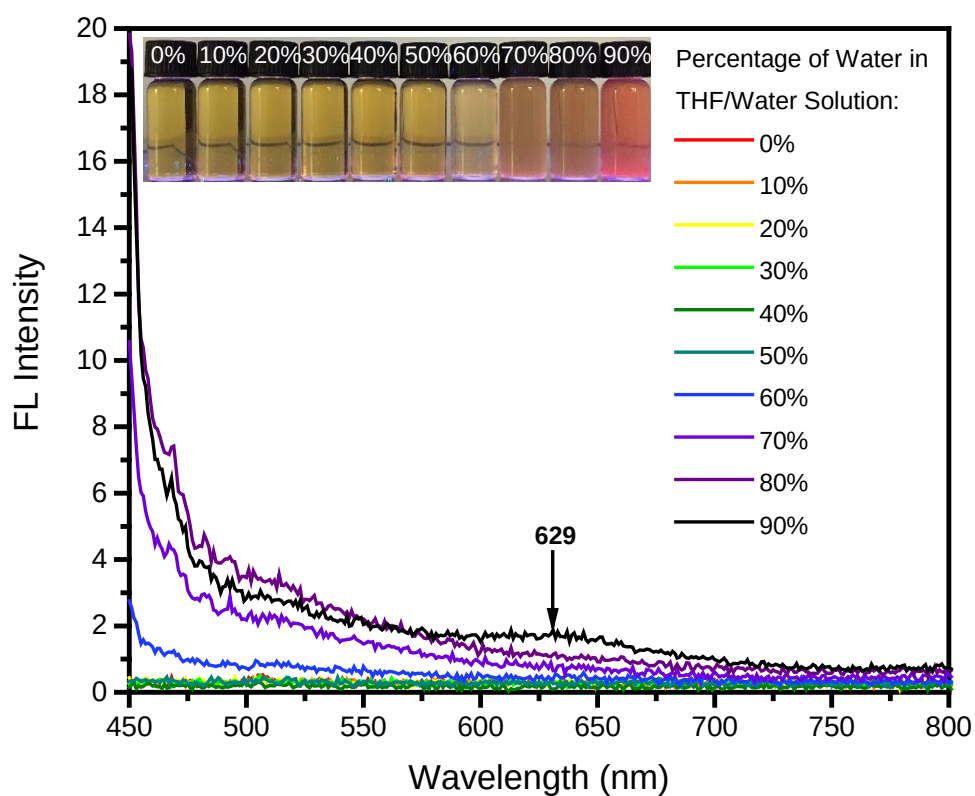


Figure S6. Fluorescence spectra of **CS2** solution (100 μ M) in THF/Water solutions of different proportions. Excitation wavelength 440nm. Insert is photo of the solutions taken under UV irradiation (365nm)

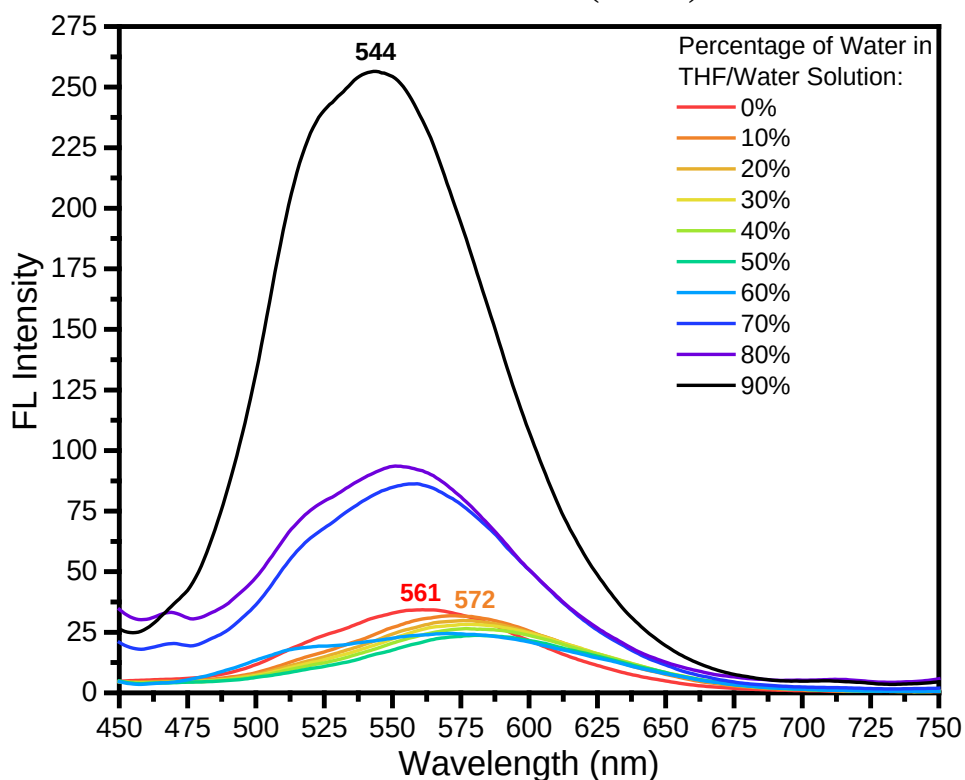


Figure S7. Fluorescence spectra of **CS3** solution (10 μ M) in THF/Water solutions of different proportions. Excitation wavelength 390nm.

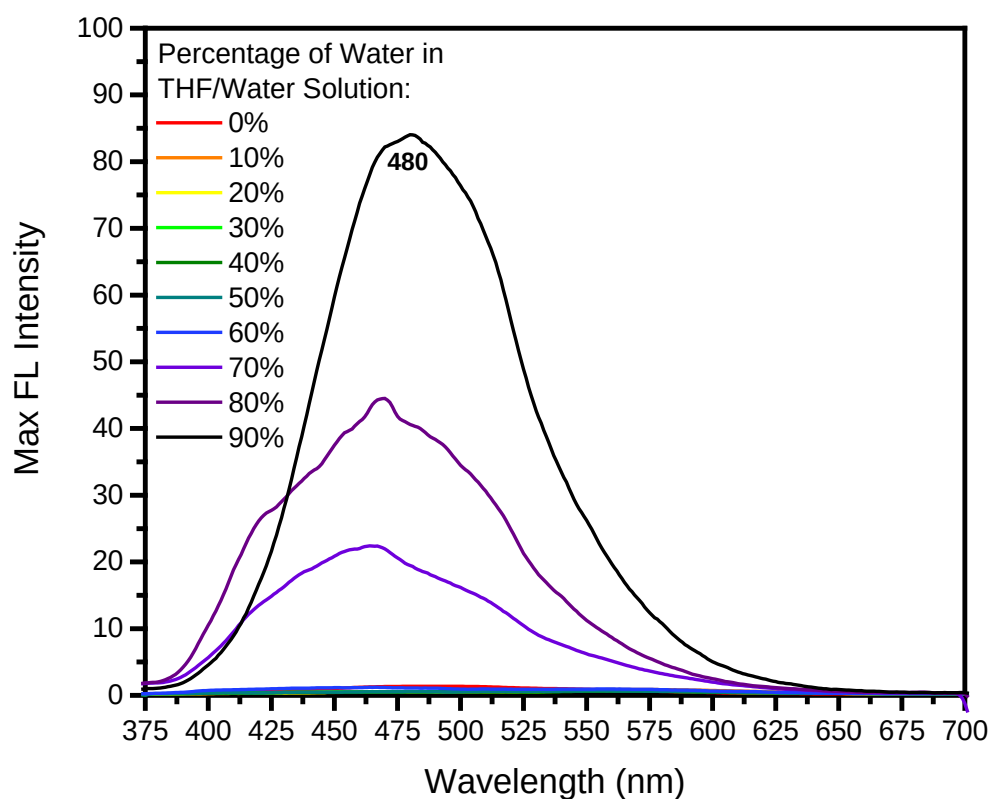


Figure S8. Fluorescence spectra of **CS1-CN** solution (10 μ M) in THF/Water solutions of different proportions. Excitation wavelength 350nm.

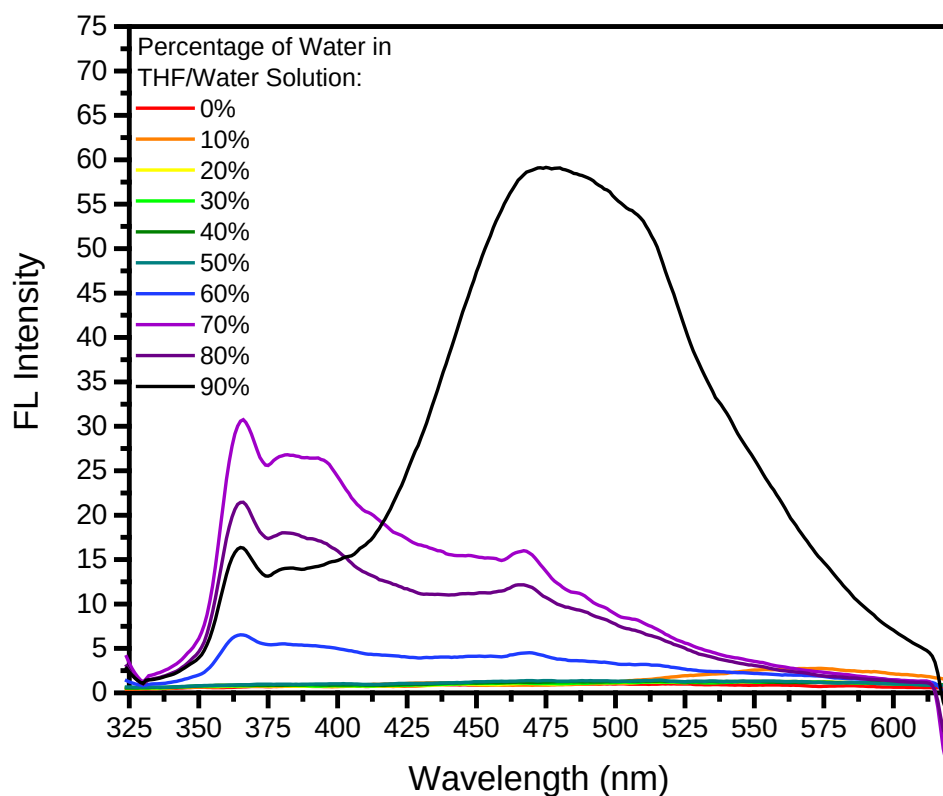


Figure S9. Fluorescence spectra of **CS3-CN** solution (10 μ M) in THF/Water solutions of different proportions. Excitation wavelength 320nm.

Table S1. Relative quantum yields of compounds **TPE-FLN**, **TPE-AQN**, **TPE-BZP**, **CS3**, **CS1-CN** and **CS3-CN** in aggregate states, in comparison to quantum yields in pure THF.

THF/water Composition	Relative Quantum Yield, Φ					
	TPE-FLN	TPE-AQN	TPE-BZP	CS3	CS1-CN	CS3-CN
0% Water	0.120	0.020	0.004	0.004	0.003	0.003
70% Water	0.017	0.006	0.035	0.011	0.060	0.110
80% Water	0.018	0.007	0.048	0.012	0.110	0.080
90% Water	0.024	0.011	0.110	0.030	0.220	0.210

Measurements are obtained in reference to quinine sulphate in 0.5M H₂SO₄ ($\Phi = 0.54$), subjected to $\pm 10\%$ error.

S2. Crystallographic Analysis

Table S2. Crystal data and structure refinement for **TPE-FLN**, **TPE-AQN** and **TPE-BZP**

	TPE – FLN	TPE - AQN	TPE - BZP
Empirical formula	C ₅₆ H ₄₅ O _{2.75}	C ₅₈ H ₄₄ O ₃	C ₅₃ H ₃₈ O
Formula weight	761.92	788.93	690.83
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	1.54178 Å	1.54178 Å	1.54178 Å
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P21/n	C2/c	P-1
Unit cell dimensions	a = 12.1439(5) Å, α = 90°. b = 9.0734(3) Å, β = 90.014(2)°. c = 37.6521(14) Å, γ = 90°.	a = 22.5855(14) Å, α = 90°. b = 15.8549(10) Å, β = 92.183(2)°. c = 11.8676(7) Å, γ = 90°.	a = 10.7918(4) Å, α = 76.3590(10)°. b = 10.8195(4) Å, β = 81.0290(10)°. c = 17.2771(6) Å, γ = 74.8090(10)°.
Volume	4148.8(3) Å ³	4246.6(5) Å ³	1882.35(12) Å ³
Z	4	4	2
Density (calculated)	1.220 Mg/m ³	1.234 Mg/m ³	1.219 Mg/m ³
Absorption coefficient	0.569 mm ⁻¹	0.580 mm ⁻¹	0.541 mm ⁻¹
F(000)	1612	1664	728
Crystal size	0.351 x 0.255 x 0.108 mm ³	0.441 x 0.333 x 0.174 mm ³	0.437 x 0.352 x 0.123 mm ³
Theta range for data collection	2.347 to 66.585°.	3.407 to 66.430°.	2.645 to 74.887°.
Index ranges	-14 ≤ h ≤ 14, - 10 ≤ k ≤ 10, - 44 ≤ l ≤ 44	-26 ≤ h ≤ 26, - 18 ≤ k ≤ 18, - 14 ≤ l ≤ 13	-13 ≤ h ≤ 13, - 13 ≤ k ≤ 13, - 21 ≤ l ≤ 21
Reflections collected	48891	15627	32282
Independent reflections	7311 [R(int) = 0.0287]	3723 [R(int) = 0.0359]	7646 [R(int) = 0.0516]
Completeness to theta = 66.585°	99.90%	99.50%	99.10%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6994	n.d.	0.7538 and 0.5944
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7311 / 64 / 588	3723 / 230 / 298	7646 / 0 / 488
Goodness-of-fit on F ²	1.027	1.049	1.055
Final R indices [I > 2σ(I)]	R1 = 0.0448, wR2 = 0.1165	R1 = 0.0466, wR2 = 0.1281	R1 = 0.0500, wR2 = 0.1270
R indices (all data)	R1 = 0.0500, wR2 =	R1 = 0.0507, wR2 = 0.1314	R1 = 0.0541, wR2 = 0.1304

	0.1208		
Extinction coefficient	n/a	n/a	0.0053(5)
Largest diff. peak and hole	0.392 and -0.540 e.Å ⁻³	0.326 and -0.287 e.Å ⁻³	0.377 and -0.287 e.Å ⁻³
CCDC Number	1573521	1573522	1573523

Table S3. Crystal data and structure refinement for **CS1**, **CS2** and **CS3**

	CS1	CS2	CS3
Empirical formula	C ₅₆ H ₃₆ N ₂	C ₆₀ H ₃₆ N ₄	C ₅₆ H ₃₈ N ₂
Formula weight	736.87	812.93	738.88
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	1.54178 Å	0.71073 Å	1.54178 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P21/c	P-1	C2/c
Unit cell dimensions	a = 18.8041(6) Å, α = 90°. b = 12.7049(4) Å, β = 112.4250(10)°. c = 19.0559(7) Å, γ = 90°.	a = 7.9503(4) Å, α = 80.314(2)°. b = 16.0571(6) Å, β = 88.214(2)°. c = 17.4515(7) Å, γ = 84.116(2)°.	a = 14.0044(3) Å, α = 90°. b = 12.8632(3) Å, β = 92.2880(10)°. c = 22.7228(5) Å, γ = 90°
Volume	4208.3(2) Å ³	2184.29(16) Å ³	4090.05(16) Å ³
Z	4	2	4
Density (calculated)	1.163 Mg/m ³	1.236 Mg/m ³	1.200 Mg/m ³
Absorption coefficient	0.514 mm ⁻¹	0.072 mm ⁻¹	0.529 mm ⁻¹
F(000)	1544	848	1552
Crystal size	0.450 x 0.275 x 0.096 mm ³	0.340 x 0.260 x 0.042 mm ³	0.211 x 0.166 x 0.078 mm ³
Theta range for data collection	2.542 to 66.592°.	2.368 to 28.281°.	3.894 to 66.581°.
Index ranges	-22 ≤ h ≤ 21, - 13 ≤ k ≤ 15, - 18 ≤ l ≤ 22	-10 ≤ h ≤ 10, - 21 ≤ k ≤ 17, - 23 ≤ l ≤ 23	-16 ≤ h ≤ 16, - 15 ≤ k ≤ 15, - 27 ≤ l ≤ 27
Reflections collected	33370	49778	20720
Independent reflections	7390 [R(int) = 0.0660]	10843 [R(int) = 0.0541]	3616 [R(int) = 0.0220]
Completeness to theta = 66.585°	99.40%	99.90%	99.80%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.4821	0.7459 and 0.7014	0.7538 and 0.7004
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7390 / 131 / 582	10843 / 0 / 577	3616 / 0 / 263
Goodness-of-fit on F ²	1.056	1.019	1.069
Final R indices [I > 2σ(I)]	R1 = 0.0869, wR2 = 0.2301	R1 = 0.0528, wR2 = 0.1270	R1 = 0.0359, wR2 = 0.0913
R indices (all data)	R1 = 0.0972, wR2 = 0.2408	R1 = 0.0836, wR2 = 0.1424	R1 = 0.0388, wR2 = 0.0935
Extinction coefficient	0.0020(3)	n/a	n/a

Largest diff. peak and hole	0.607 and -0.406 e.Å ⁻³	0.521 and -0.312 e.Å ⁻³	0.222 and -0.174 e.Å ⁻³
CCDC Number	1573518	1573519	1573520

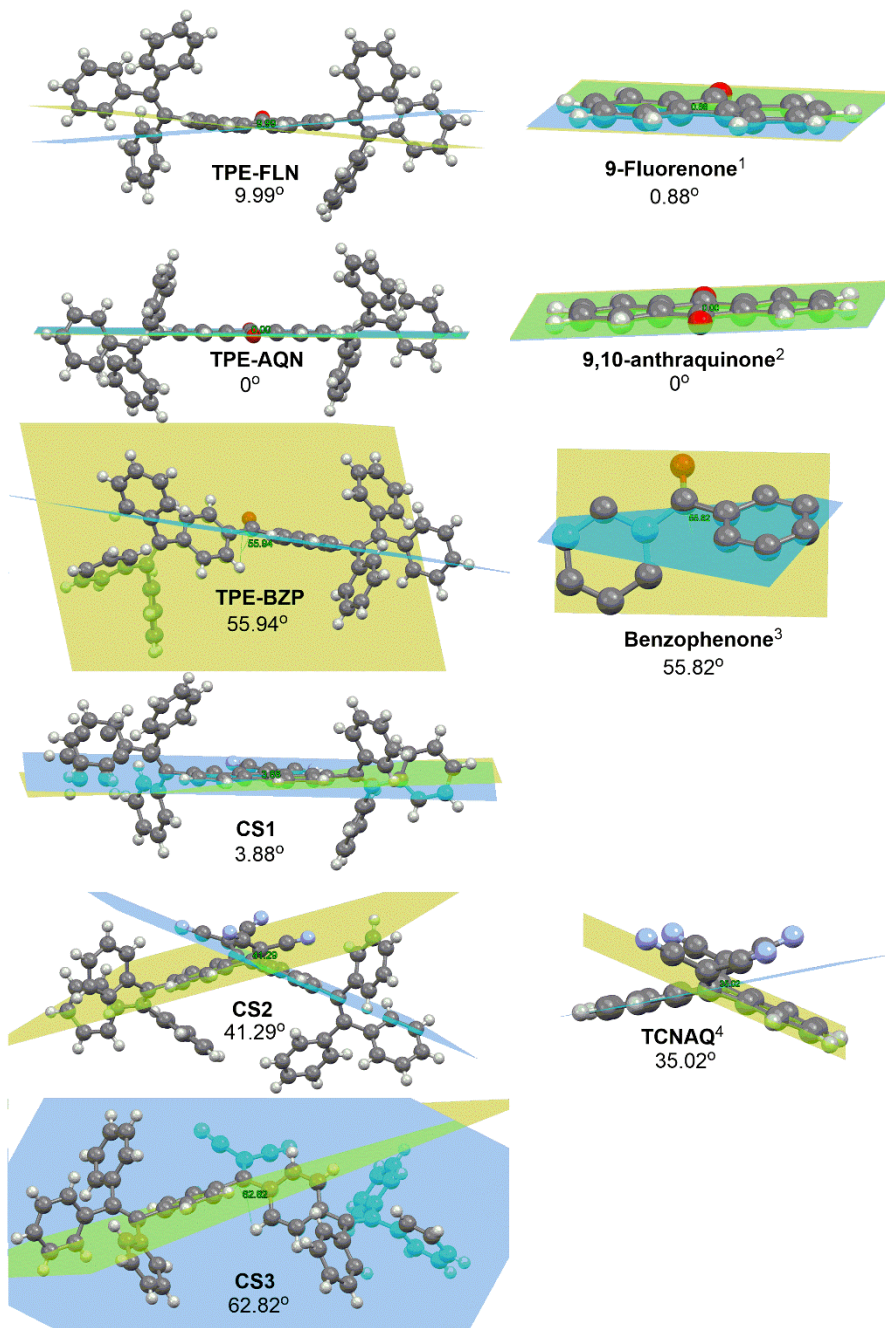
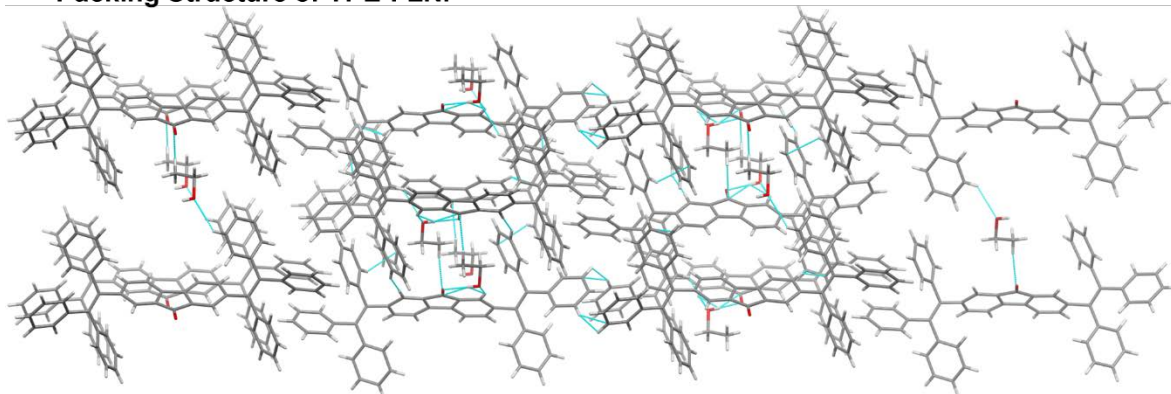


Figure S10. Structural distortion and deviation from planarity of triphenylethylenyl-functionalized molecules, **TPE-FLN**, **TPE-AQN**, **TPE-BZP**, **CS1**, **CS2** and **CS3**, in comparison with reported structures of unsubstituted analogues.

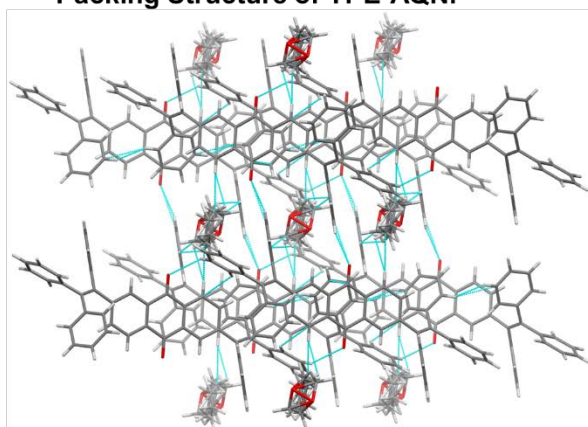
The structural distortion and deviation from planarity of the molecules are quantified by the angle between the planes of two adjacent phenyl rings constituting part of the centre acceptor moiety. The angle, θ , is as shown in Figure 8. Comparisons were made with available reported crystal structures, which θ was also determined using the same method, of unsubstituted analogues, i.e. 9-fluorenone, 9,10-anthraquinone, benzophenone and TCNAQ.

References: ^[1] Luss, H. R. and Smith, D. L, Acta Crystallographica Section B, 1972, 28, 884–889. DOI: 10.1107/S056774087200336X. (CCDC No. 1157855) ^[2] K.Lonsdale, H.J.Milledge, K.E.Sayed, Acta Crystallographica, 1966, 20, 1. DOI: 10.1107/S0365110X6600001X. (CCDC No. 1103145) ^[3] E. B. Fleischer, N. Sung, and S. Hawkinson, J. Phys. Chem., 1968, 72, 4311–4312. DOI: 10.1021/j100858a065. (CCDC No. 1114984) ^[4] N. E. Heimer and D. L. Mattern, J. Am. Chem. Soc., 1993, 115, 2217–2220. DOI: 10.1021/ja00059a016. (CCDC No. 1136376)

Packing Structure of TPE-FLN:



Packing Structure of TPE-AQN:



Packing Structure of TPE-BZP:

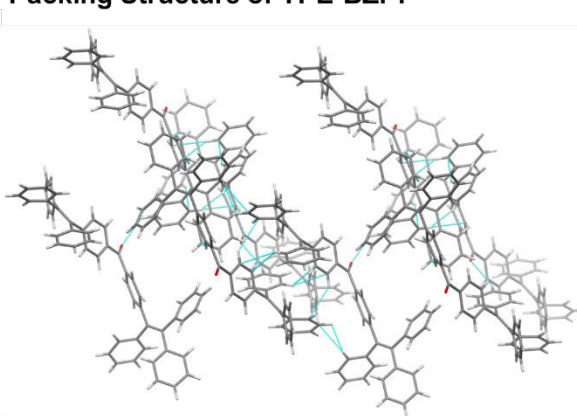


Figure S11. Packing structure of **TPE – FLN**, **TPE-AQN** and **TPE-BZP** obtained from single crystal XRD analysis.

All three carbonyl-containing compounds, **TPE-FLN**, **TPE-AQN** and **TPE-BZP**, involved their carbonyl groups in intermolecular hydrogen bonding in crystal packing as shown in **Figure 11**. **TPE-FLN** packs in an anti-parallel fashion. Ethanol solvent molecules serve as bridges between adjacent molecules of **TPE-FLN**. Each ethanol molecular participated in hydrogen bonding between its a terminal methyl proton and the carbonyl group of one **TPE-FLN** molecule. Also, ethanol’s hydroxyl group participated in hydrogen bonding with a terminal phenyl ring proton of one **TPE-FLN** molecule, and the fluorenone proton of another **TPE-FLN** molecule. Likewise, solvent molecules also participated in the crystal packing of **TPE-AQN**. Each THF solvent molecule interacts with an anthraquinone proton of four adjacent **TPE-AQN** molecules *via* short interactions. In addition, adjacent molecules of **TPE-AQN** also interact *via* hydrogen bonding between the carbonyl groups and terminal phenyl protons. No solvent molecules were involved in the crystal packing of **TPE-BZP**. The

carbonyl group of each **TPE-BZP** molecule interacts with the terminal phenyl protons of two adjacent molecules.

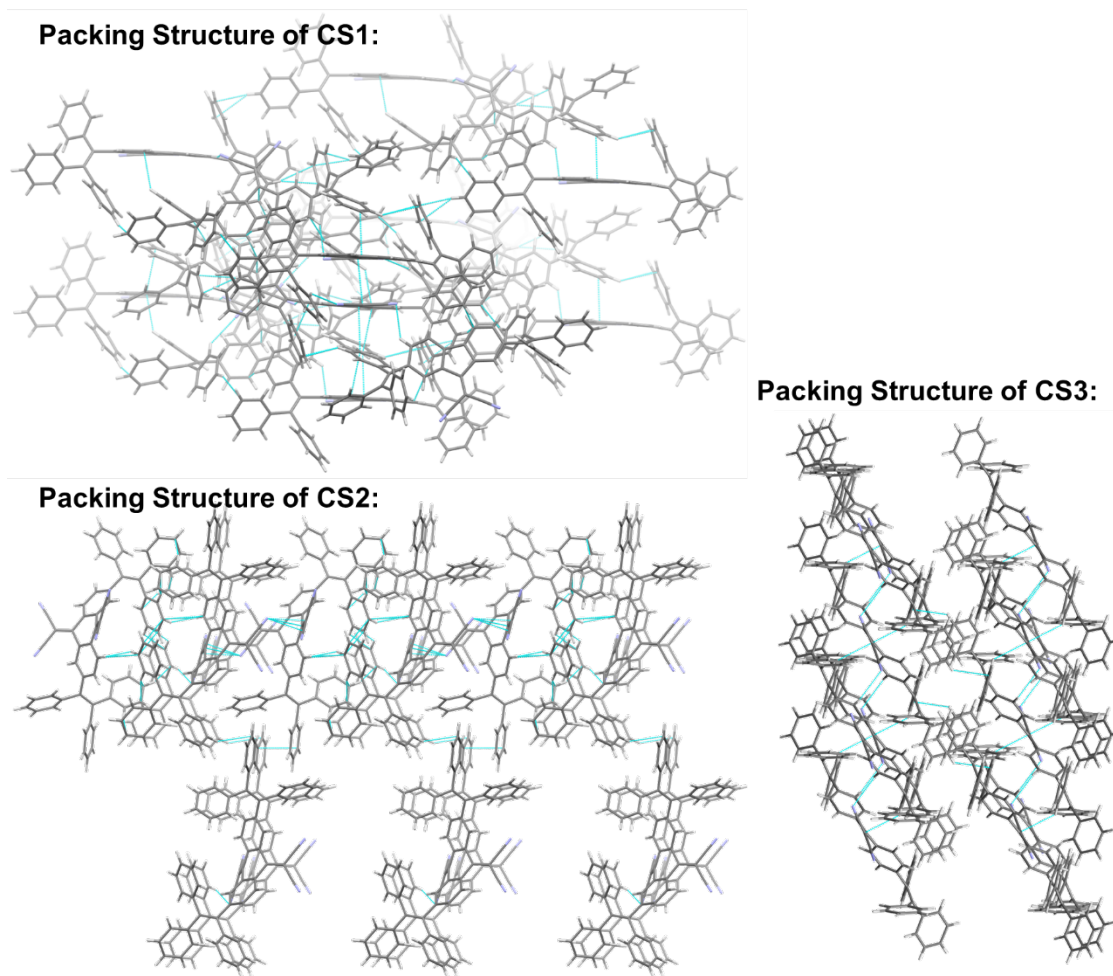


Figure S12. Packing structure of **CS1**, **CS2** and **CS3** obtained from single crystal XRD analysis.

For **CS1** – **CS3**, the 1,1-dicyanomethylidene- groups also played a crucial role in molecular packing as shown in **Figure 12**. Similar to **TPE-FLN**, **CS1** packs in an anti-parallel fashion but with adjacent 1,1-dicyanomethylidene- groups in close contact. Of the two cyano- groups for each compound **CS1**, one interacts with a fluorene-moiety proton of an adjacent molecule, and the other to a terminal phenyl ring proton of another adjacent molecules via hydrogen bonding. Molecules of **CS2** pack in a slightly different manner. In a pair of adjacent **CS2** molecules, supramolecular interactions existed between one whole 1,1-dicyanomethylidene group of the first molecule with just one cyano- group of the second molecule. That leaves one cyano- group for both molecules to interact with the phenyl ring protons of other adjacent molecules. On top of this, CH- π interactions were also observed between terminal phenyl rings that also contributed to crystal packing of **CS2**. Finally, for **CS3**, each of the two cyano- groups interact with the phenyl protons of two adjacent molecules. These two phenyl rings, however, are not terminal phenyl rings, but rather, the ones directly bonded to the 1,1-dicyanomethylidene- group. The packing structure is further

reinforced by favourable interactions between the germinal (1-)carbon of 1,1-dicyanomethylidene group with a terminal phenyl ring proton.

S3. Density Functional Theory (DFT) Calculations

Table S4. DFT (G09: B3LYP/6-31G(d,p))⁴ calculated total energy, HOMO and LUMO, dipole moment for six synthesized molecules and three detected cyanated compounds.

	chemical formula	Total energy (ha)	HOMO (eV)	LUMO (eV)	LH gap (eV)	dipole moment (Debye)	Zero Point E (ha/particle)
TPE-FLN	C ₅₃ H ₃₆ O	-2116.60752823	-5.223	-2.157	3.066	2.9449	0.721075
TPE-AQN	C ₅₄ H ₃₆ O ₂	-2229.95022441	-5.516	-2.602	2.914	0.0007	0.731784
TPE-BZP	C ₅₃ H ₃₈ O	-2117.80660942	-5.443	-1.852	3.591	3.1091	0.743183
CS1	C ₅₆ H ₃₆ N ₂	-2265.16376491	-5.319	-3.013	2.306	5.4852	0.741821
CS2	C ₆₀ H ₃₆ N ₄	-2527.01277826	-5.676	-3.545	2.130	0.0019	0.772865
CS3	C ₅₆ H ₃₈ N ₂	-2266.35626487	-5.563	-2.563	3.000	7.5657	0.763764
CS1+CN	C ₅₇ H ₃₇ N ₃	-2358.59466809	-5.406	-1.847	3.558	6.3252	0.762954
CS2+CN	C ₆₁ H ₃₇ N ₅	-2620.44774331	-5.701	-3.185	2.516	1.4733	0.793656
CS3+CN	C ₅₇ H ₃₉ N ₃	-2359.78528417	-5.570	-1.630	3.940	7.6617	0.784733

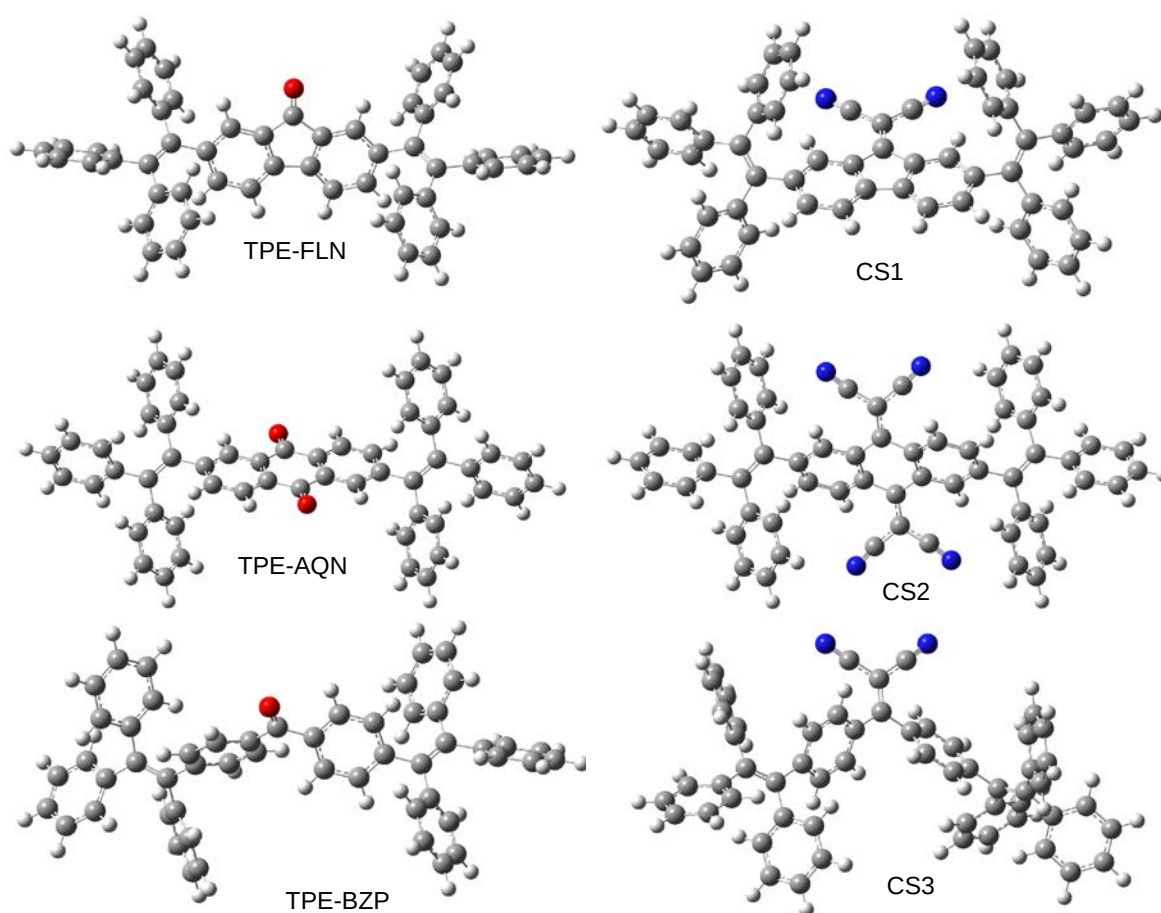


Figure S13. DFT optimized geometry structures of TPE-FLN, TPE-AQN, TPE-BZP, CS1, CS2 and CS3.

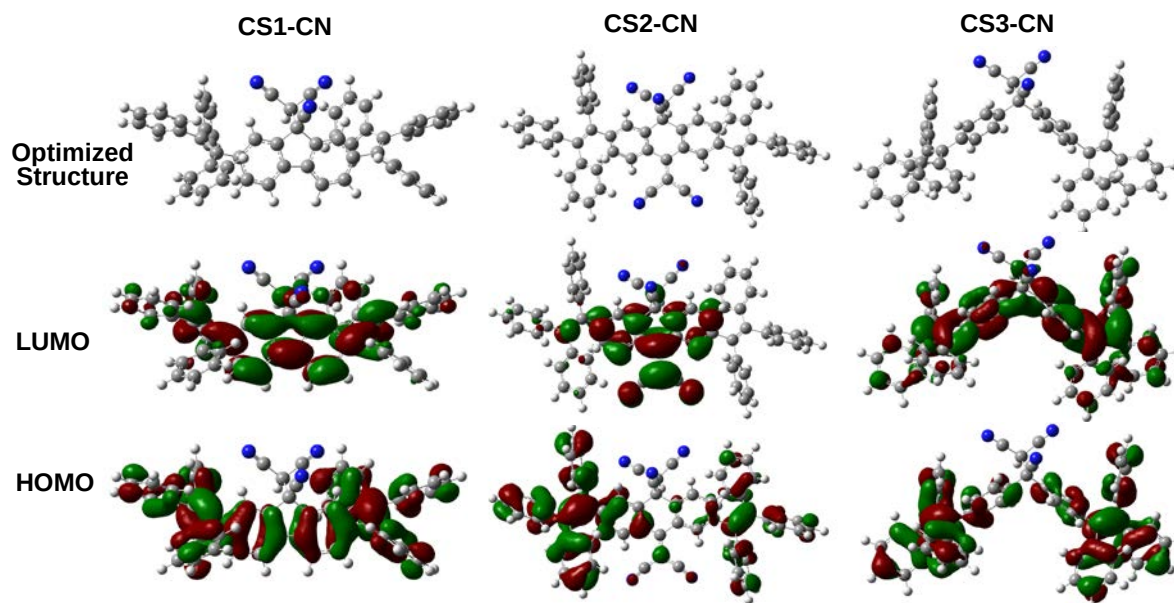


Figure S14. DFT optimized geometry structures, HOMO and LUMO molecular orbital amplitude plots of cyanated species CS1-CN, CS2-CN and CS3-CN (isovalue = 0.02)

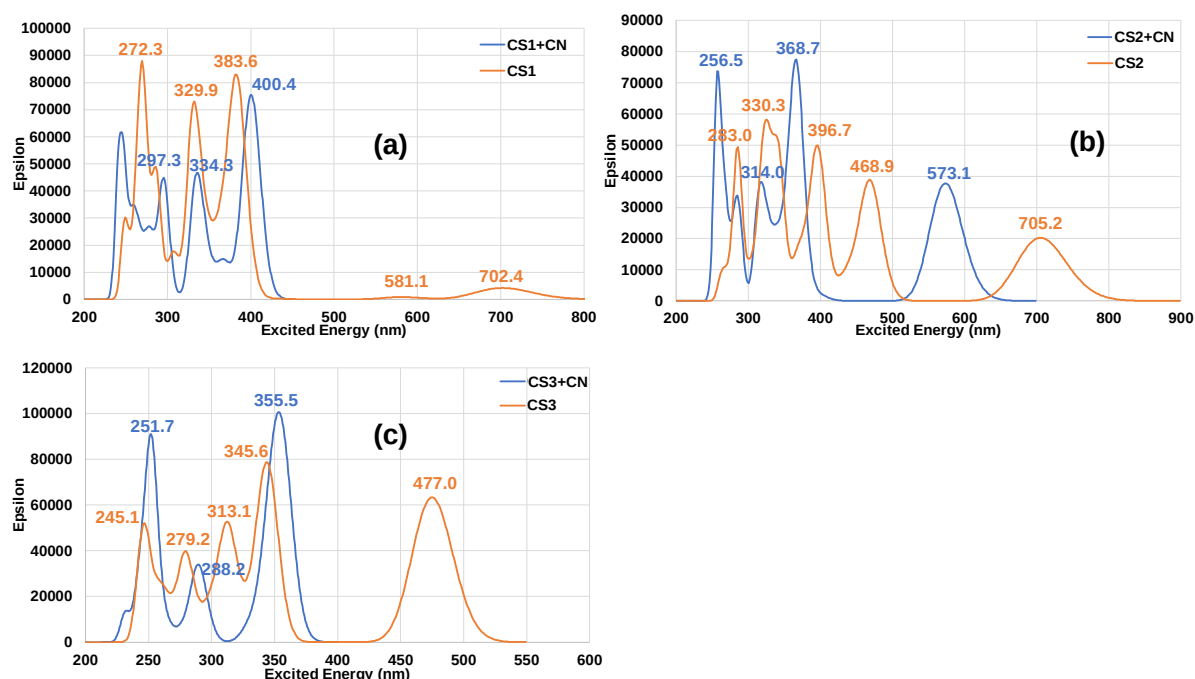
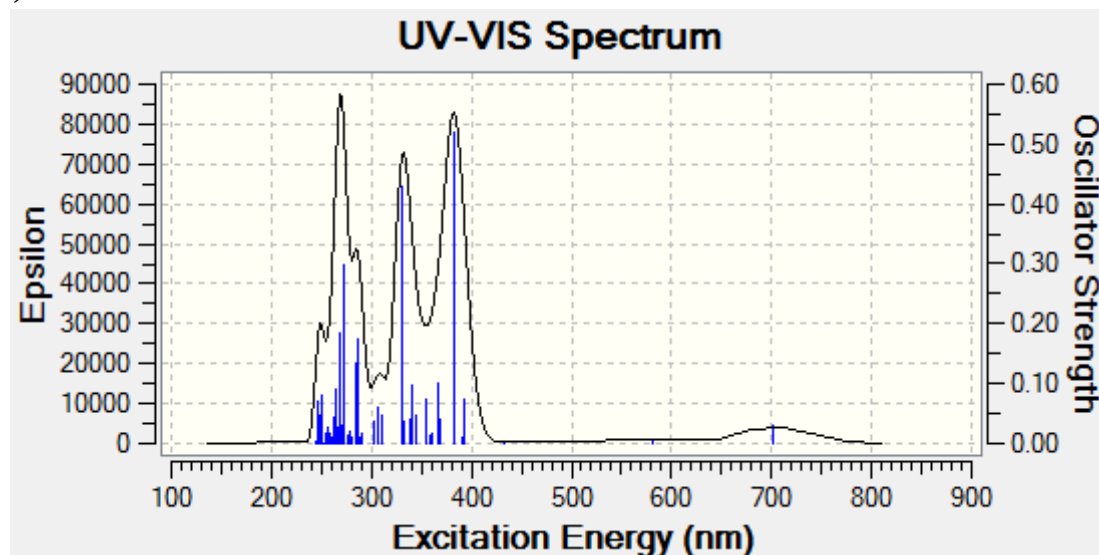


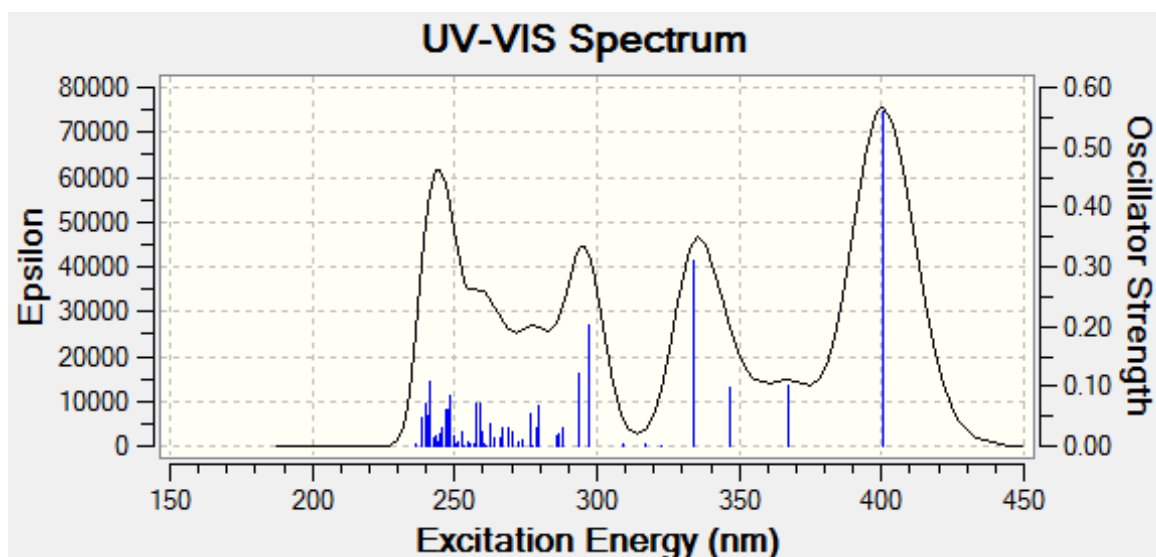
Figure S15. Comparisons of TD-DFT (B3LYP/6-31G(d,p))⁴ calculated absorption spectra between (a) CS1 and CS1-CN, (b) CS2 and CS2-CN, as well as (c) CS3 and CS3-CN.

Table S5. Selected TD-DFT (B3LYP/6-31G(d,p))⁴ calculated energies, oscillator strength and compositions of major electronic transitions of **CS1**. (In reference to attached spectra of CS1)



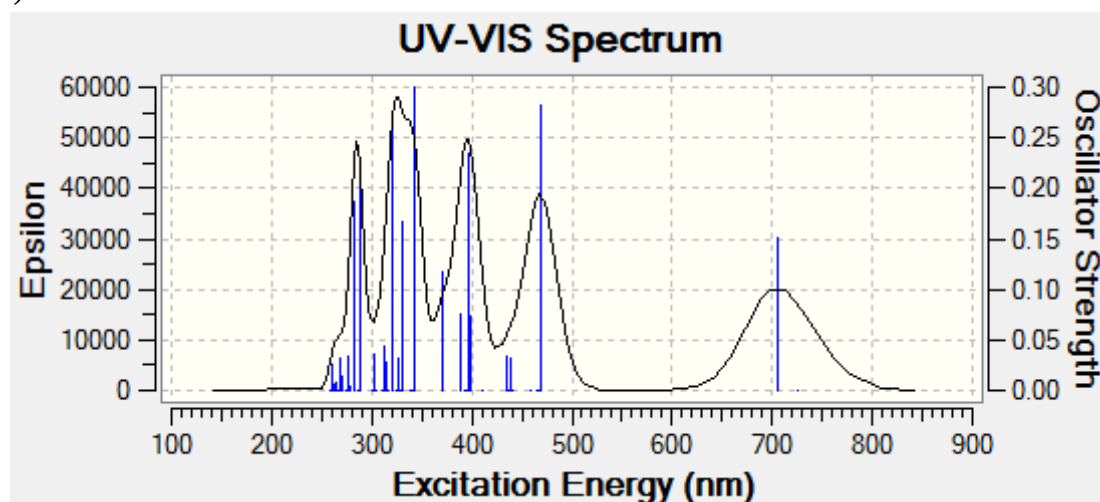
Wavelength (nm)	Osc. Strength (<i>f</i>)	Assignment (H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
702.36	0.0312	H → L (70%)
581.06	0.0063	H-1 → L+1 (70.5%)
382.63	0.5189	H-8 → L (+13%); H-7 → L (+37%); H-4 → L (+16%); H → L+1 (+53%)
329.94	0.4285	H-13 → L (+35%); H-6 → L (+21%); H-3 → L (+13%); H → L+2 (48%)

Table S6. Selected TD-DFT (B3LYP/6-31G(d,p))⁴ calculated energies, oscillator strength and compositions of major electronic transitions of **CS1-CN**. (In reference to attached spectra of CS1+CN)



Wavelength (nm)	Osc. Strength (<i>f</i>)	Assignment (H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
400.40	0.5594	H → L
334.30	0.3117	H-1 → L+3 (11%); H → L+1 (69%)
297.36	0.2012	H-2 → L (66%); H → L+3 (17%)

Table S7. Selected TD-DFT (B3LYP/6-31G(d,p))⁴ calculated energies, oscillator strength and compositions of major electronic transitions of CS₂. (In reference to attached spectra of CS₂)

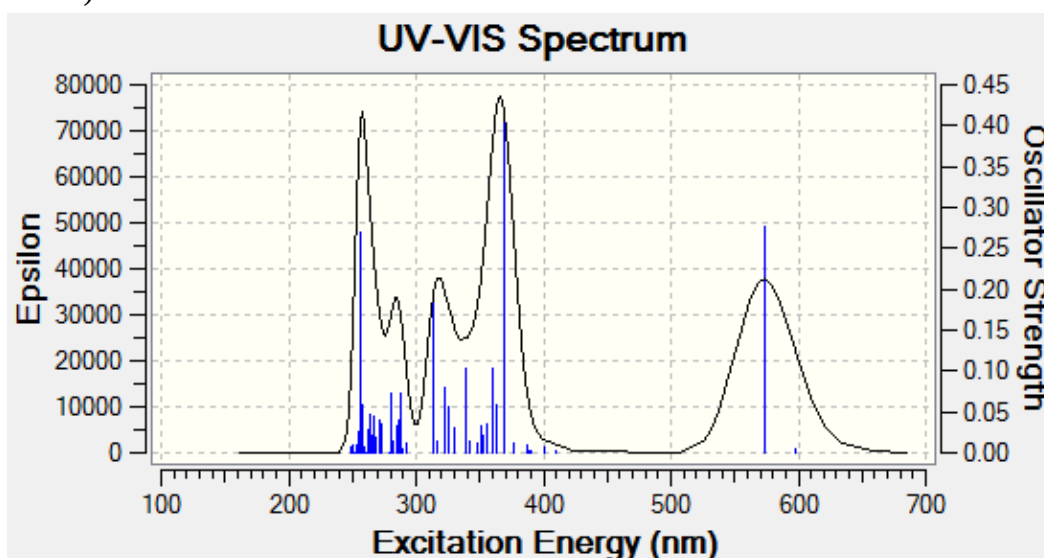


Wavelength (nm)	Osc. Strength (<i>f</i>)	Assignment (H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
705.20	0.1502	H-1 → L (70%)
468.90	0.2820	H → L+1 (70%)
396.72	0.2337	H-14 → L (+11%); H-12 → L (+22%); H-8 → L (46%); H-4 → L (18%); H-2 → L (24%)

342.87	0.2999	H $\rightarrow$ L+2 (62%)
330.33	0.1678	H-7 $\rightarrow$ L+1 (38%); H-5 $\rightarrow$ L+1 (56%)

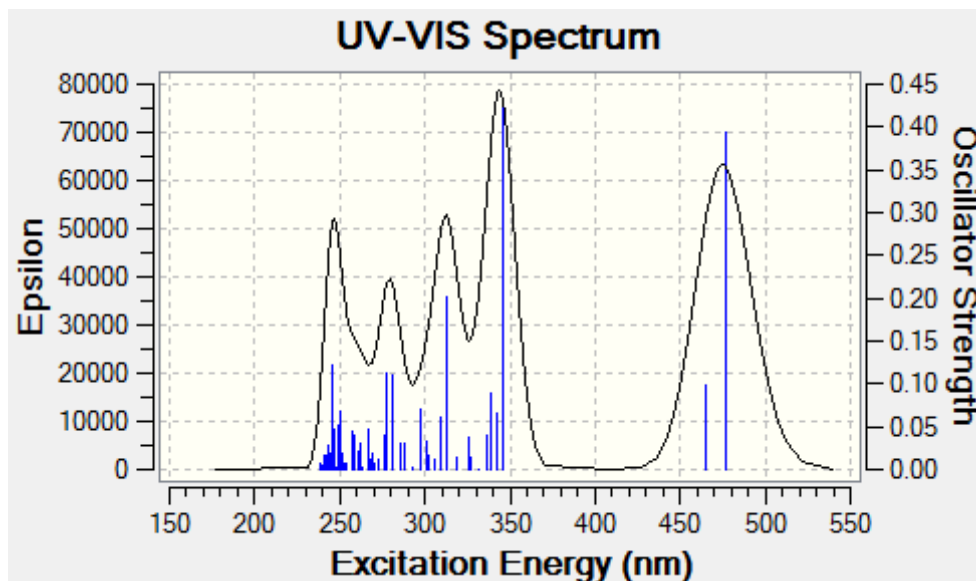
Remarks: HOMO $\rightarrow$ LUMO transition, calculated at 724.64nm, is forbidden with $f = 0.0000$

Table S8. Selected TD-DFT (B3LYP/6-31G(d,p))⁴ calculated energies, oscillator strength and compositions of major electronic transitions of CS₂-CN. (In reference to attached spectra of CS₂+CN)



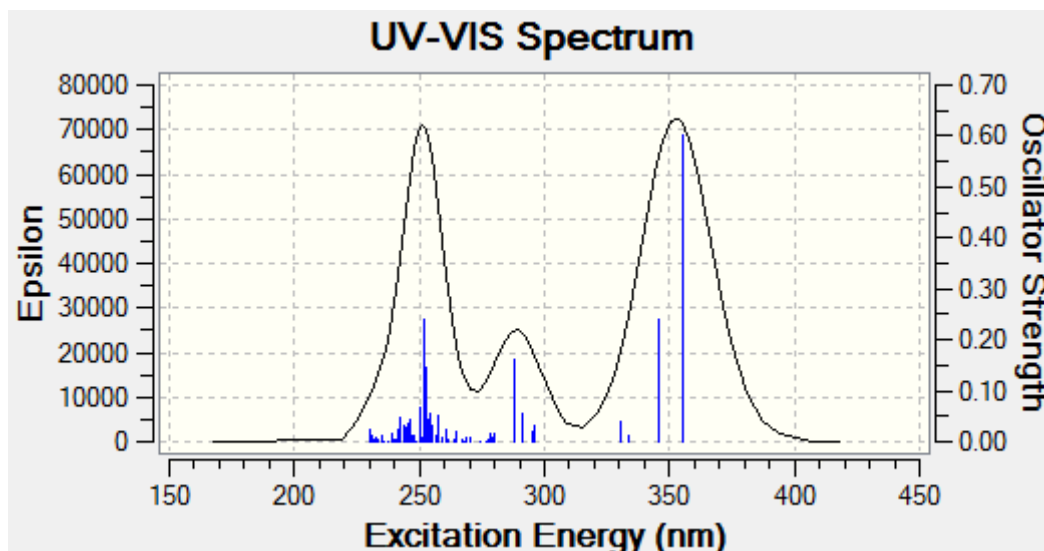
Wavelength (nm)	Osc. Strength (f)	Assignment (H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
573.06	0.2769	H-1 $\rightarrow$ L (43%); H $\rightarrow$ L (56%)
368.72	0.4093	H-1 $\rightarrow$ L+1 (+50%); H-1 $\rightarrow$ L+2 (+14%)
314.01	0.1962	H-15 $\rightarrow$ L (31%); H-1 $\rightarrow$ L+3 (55%); H $\rightarrow$ L+3 (21%)
256.46	0.2702	H-12 $\rightarrow$ L+1 (+36%); H-8 $\rightarrow$ L+2 (+17%); H-3 $\rightarrow$ L+3 (+16%); H-1 $\rightarrow$ L+8 (+14%); H-1 $\rightarrow$ L+10 (11%); H $\rightarrow$ L+8 (19%); H $\rightarrow$ L+9 (23%); H $\rightarrow$ L+10 (17%)

Table S9. Selected TD-DFT (B3LYP/6-31G(d,p))⁴ calculated energies, oscillator strength and compositions of major electronic transitions of **CS3**. (In reference to attached spectra of CS3)



Wavelength (nm)	Osc. Strength (<i>f</i>)	Assignment (H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
476.97	0.3931	H-1 → L (+65%)
465.05	0.0990	H-1 → L (27%); H → L (65%)
345.62	0.4241	H-2 → L (11%); H-1 → L+2 (12%); H → L+1 (67%)
313.32	0.2021	H-2 → L (+10.5%); H → L+2 (+54%)
280.44	0.1104	H-1 → L+6 (+15%); H → L+3 (+16%); H → L+4 (+61%)
277.96	0.1133	H-1 → L+4 (+60%); H → L+6 (+18%)
245.13	0.1216	H-18 → L (+11%); H-11 → L+1 (+45%); H-3 → L+2 (+17%)

Table S10. Selected TD-DFT (B3LYP/6-31G(d,p))⁴ calculated energies, oscillator strength and compositions of major electronic transitions of **CS3-CN**. (In reference to attached spectra of CS3+CN: Peak half width at half height 0.15 eV)



Wavelength (nm)	Osc. Strength (<i>f</i>)	Assignment (H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
355.53	0.6031	H-1 $\rightarrow$ L+1 (27%); H $\rightarrow$ L (64%)
345.87	0.2410	H-1 $\rightarrow$ L (57%); H $\rightarrow$ L+1 (41%)
288.17	0.1626	H-1 $\rightarrow$ L+2 (+45%); H-1 $\rightarrow$ L+4 (+33%); H $\rightarrow$ L+5 (+28%)
251.71	0.2392	H-11 $\rightarrow$ L (+26%); H-9 $\rightarrow$ L (+16%); H-1 $\rightarrow$ L+13 (+13%); H $\rightarrow$ L+12 (+22%)

Reference:

⁴ Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

S4. Detection of Cyanide

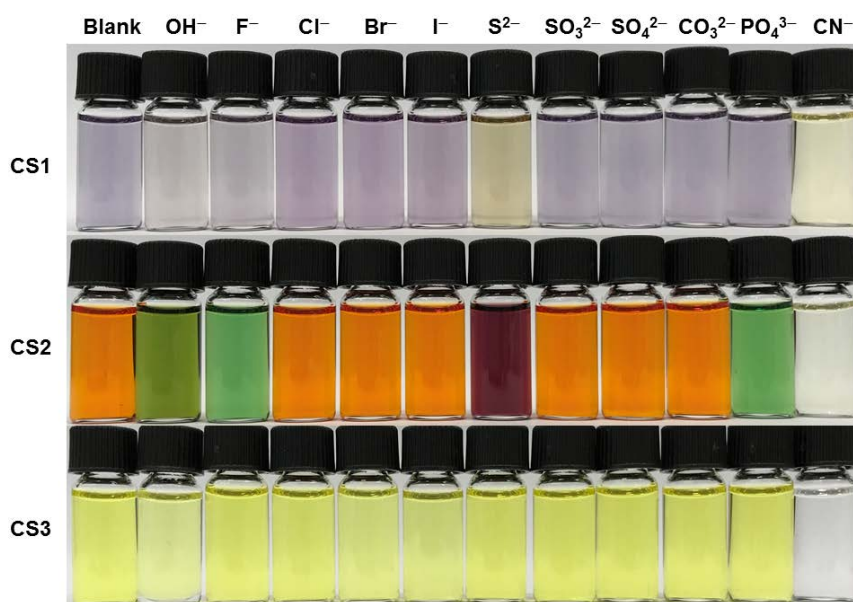


Figure S16. Selectivity test for **CS1**, **CS2** and **CS3** with common anions.

Solutions of **CS1**, **CS2** and **CS3** of 0.33 mM concentration in THF/water (2:1 v/v) were added with 10 molar equivalence of selected anions (OH^- , F^- , Cl^- , Br^- , I^- , S^{2-} , SO_3^{2-} , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} and CN^-) and the colour changes were visually observed.

The results show that all three compounds exhibit general selectivity towards CN^- . No significant colour change was observed for **CS1**, **CS2** and **CS3** in the presence of excess Cl^- , Br^- , I^- , SO_3^{2-} , SO_4^{2-} and CO_3^{2-} . **CS1** is reactive towards both S^{2-} and CN^- where purple colouration turns pale brown. **CS2** is reactive towards OH^- , F^- , S^{2-} and PO_4^{3-} on top of CN^- , where colour changes were observed. **CS3** is desirably reactive only towards CN^- where decolourisation took place.

The reactivity of **CS1** and **CS2** towards the other stated anions was, however, not further investigated in detail for they were not in the scope of this work.

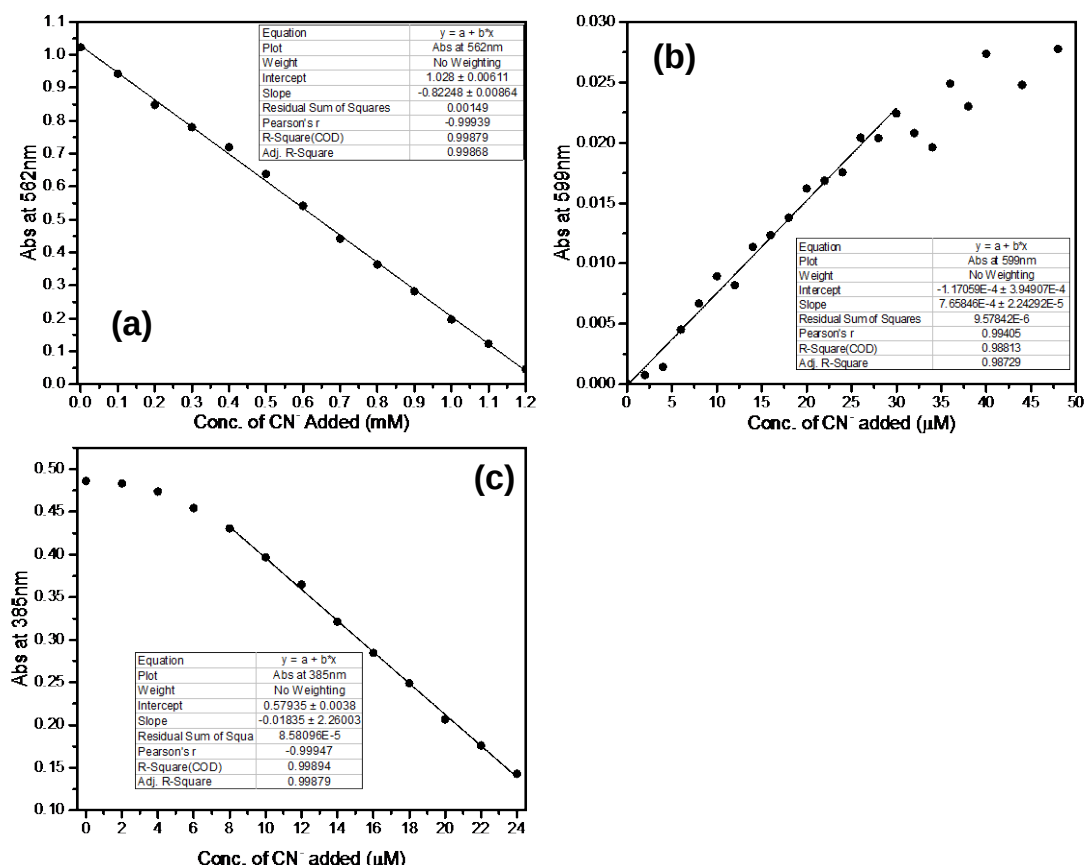


Figure S18. Changes in intensities of (a) 562 nm absorption peak of **CS1** (1 mM in THF), (b) 599 nm absorption peak of **CS2** (20 μ M in THF), and (c) 385 nm absorption peak of **CS3** (30 μ M in THF) in response to incremental addition of cyanide. The corresponding absorption profiles from spectrophotometric titration studies are shown in **Figure 4** of main manuscript.

The decrease in intensity of the charge transfer absorption band at 562 nm of **CS1** was used to monitor its reaction with cyanide anions. The decrease in peak intensities showed a linear regression relationship from 0 to 1.2 mM of cyanide added. The limit of detection (LOD) determined from the data was 2.45×10^{-5} M.

The increase in intensity of 599 nm absorption band, which arises from the formation of cyanated species, was monitored for the reaction between **CS2** and cyanide anions. A linear regression relationship can be fitted from the range of 0 to 28 μ M of cyanide added. The limit of detection (LOD) determined from the data was 1.70×10^{-6} M.

The decrease in intensity of the charge transfer absorption band at 385 nm of **CS3** was used to monitor its reaction with cyanide anions. The decrease in peak intensities started off gradual and then proceeded to show a linear regression relationship between the range of 8 to 24 μ M of cyanide added. The limit of detection (LOD) determined from the data was 5.07×10^{-6} M.

LOD were measured for **CS1** and **CS2** using the formula $LOD = 3.3\sigma/m$ where σ is the standard deviation of the y-intercept and m the slope of the linear regression fitting curve. For **CS3**, LOD was determined to be at the point of intersection between the linear fitting curve and horizontal line at the initial y-intercept value.

AIE of cyanated solutions of CS1, CS2 and CS3:

2mL of 0.1mM of CS1, CS2 and CS3 solutions in THF were added 1.2, 2.4 and 1.2 molar equivalence of cyanide anions (dissolved in water at 0.1M) respectively. The solutions were briefly shaken and an immediate colour change was observed for all three solutions, indicating reaction between the compounds and cyanide. TLC analysis was performed to confirm complete reaction of the three compounds. Each reacted solution was then aliquoted into ten smaller vials and topped off with different volume of THF and water to a concentration of 10 μ M. The emission spectra of each diluted solutions were taken immediately (to prevent further reaction upon standing) and the photos taken under UV irradiation at 365nm. The results are as shown below in **Figure 23** to **Figure 25**.

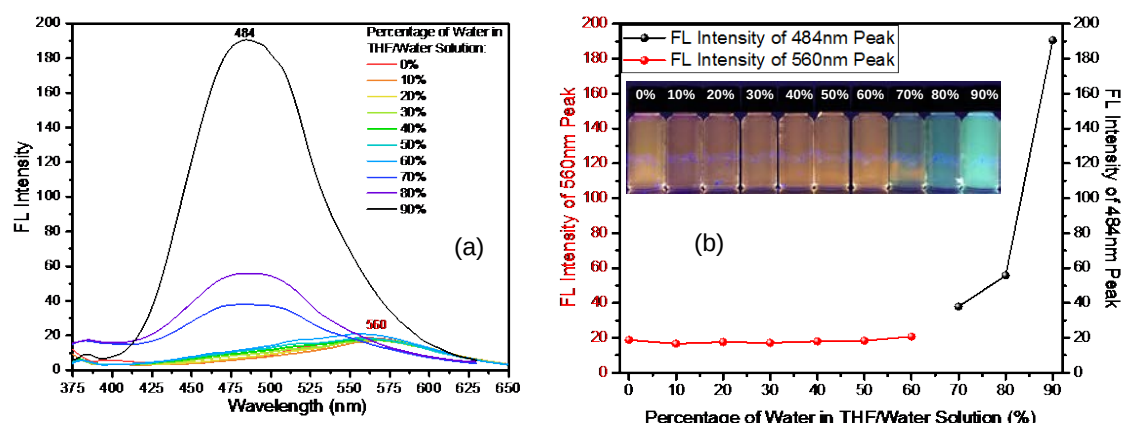


Figure S19. (a) Fluorescence spectra of CS1 solutions after reaction with 1.2 molar equivalence of cyanide, in different proportions of water and THF, at fixed concentration of 10 μ M. (b) Emission intensities trend of 560nm and 484nm emission peaks in different proportions of water and THF. Insert is photo of the solutions in different proportions of water taken under UV irradiation (365nm).

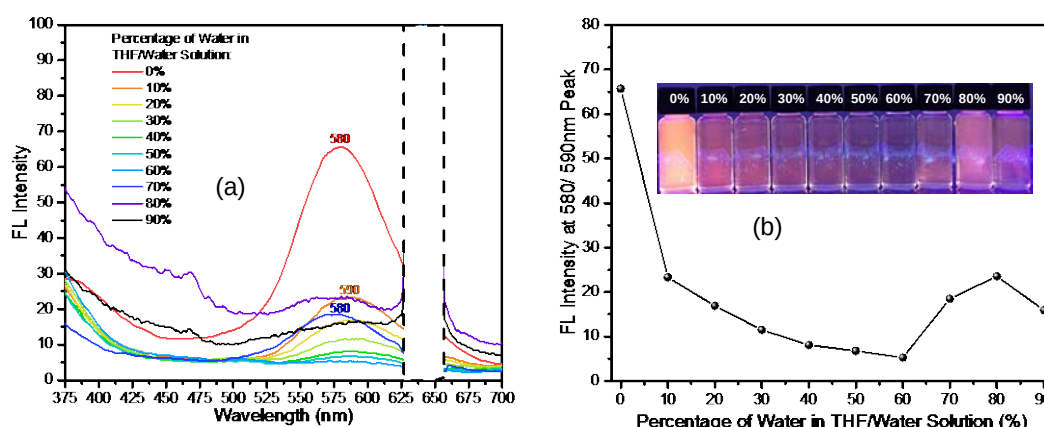


Figure S20 (a) Fluorescence spectra of CS2 solutions after reaction with 2.4 molar equivalence of cyanide, in different proportions of water and THF, at fixed concentration of 10 μ M. A portion of spectra (625nm – 660nm) was cropped off in to mask towering scattering peaks (680nm) arising from excitation source. (b) Emission intensities trend of 580nm emission peaks in different proportions of water and THF. Insert is photo of the solutions in different proportions of water taken under UV irradiation (365nm).

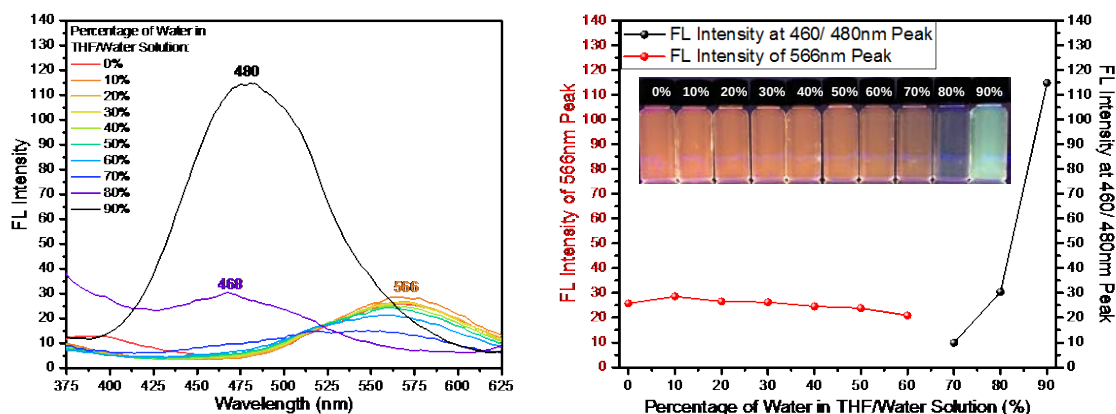


Figure S21. (a) Fluorescence spectra of CS3 solutions after reaction with 1.2 molar equivalence of cyanide, in different proportions of water and THF, at fixed concentration of 10 μ M. (b) Emission intensities trend of 566nm and 460/580nm emission peaks in different proportions of water and THF. Insert is photo of the solutions in different proportions of water taken under UV irradiation (365nm).

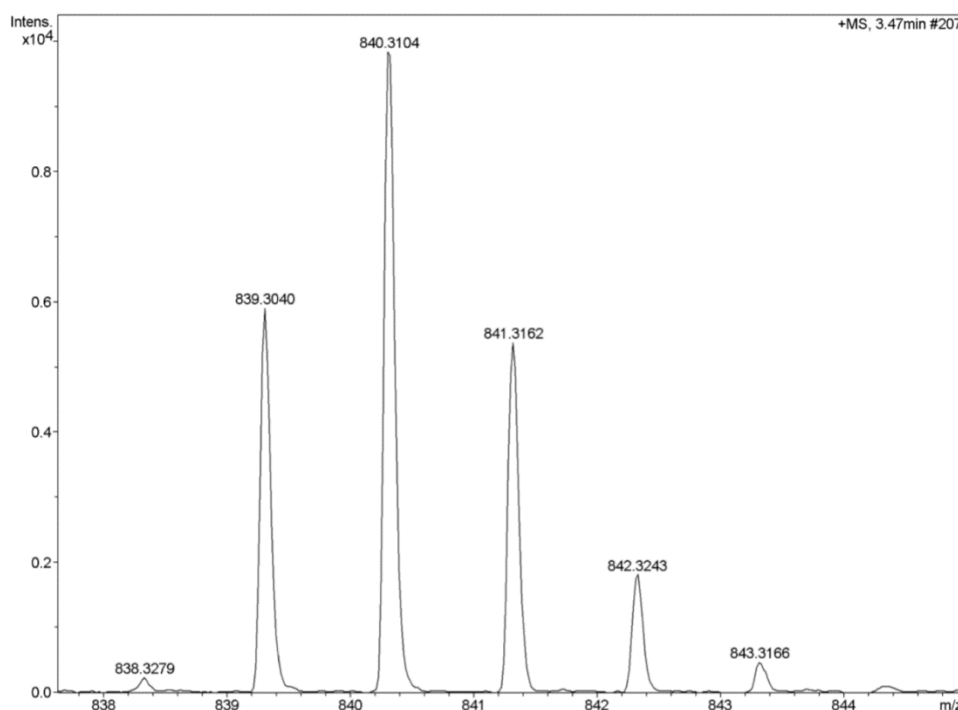


Figure S22. High resolution (APCI) mass spectra of CS2-CN recorded immediately after reaction. $[M]^+$ calculated for $C_{61}H_{38}N_5$ is 840.3122, found 840.3104.

We were unable to isolate and characterize CS2-CN due to its poor stability and ease of decomposition. HRMS was thus used to detect the presence and formation of this species between the reaction of CS2 and cyanide. CS2-2CN was, however, not detected.

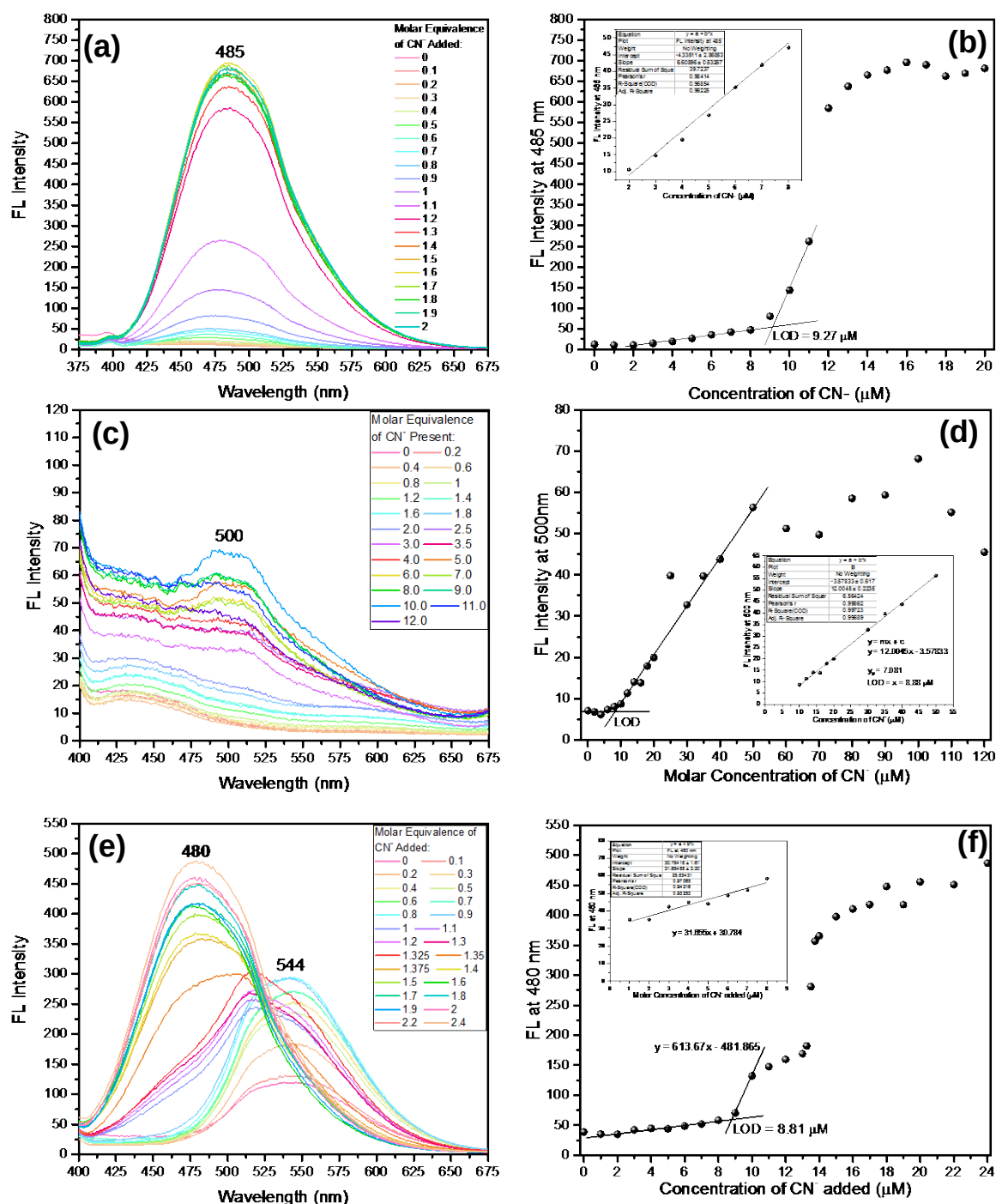


Figure S23. Fluorescence profile changes of 10 μM (a) CS1, (c) CS2, and (e) CS3 in THF/water (2:8 v/v), in the presence of increasing concentration of CN⁻. The corresponding fluorescence intensities of the compounds at 560, 500 and 480 nm, respectively, were plotted against concentration of CN⁻ in (b), (d) and (f), respectively.

The changes to fluorescence spectra of CS1, CS2 and CS3 (10 μM concentration, THF/water = 2:8 v/v) upon reaction with increasing amount of cyanide was monitored. The results are shown in **Figure S23**. The formation of CS1-CN from the reaction between CS1 and cyanide was monitored by the increase in emission intensities at 485 nm. The 485 nm peak intensity rose very gradually from the cyanide concentration range of 0 to 8 μM before picking up suddenly. The increase in peak intensity then slow down again beyond 14 μM of cyanide.

The limit of detection (LOD) was taken to be at the onset of the jump in 485 nm peak intensity, which was calculated to be 9.27×10^{-6} M.

The reaction between **CS2** and cyanide does not lead to formation of any brightly emitting species in the aggregated form, as previously shown in **Figure S20**. From the results obtained and shown in **Figure S23(c)**, no distinctive peaks were observed although an emission peak at 500 nm emerged on addition of 10 molar equivalence of cyanide. Monitoring the intensities at 500 nm across the range of cyanide concentration added, a linear regression relationship can be fitted in the concentration range between 0 to 50 μ M, of which the limit of detection (LOD) was estimated to be 8.88×10^{-6} M. This value, however, was **not exactly meaningful** or reflective given the extremely lowly emissive nature of **CS2** and its cyanated species.

CS3 is AIE-active and so it **CS3-CN**, which is formed on reaction with cyanide. As such, it would be useful to monitor the decrease in fluorescence intensities of 544 nm peaks (from the consumption of **CS3**), as well as the increase in fluorescence intensity of 480 nm peaks (from the formation of **CS3-CN**). Unexpectedly, the 544 nm emission peak was observed to increase in emission intensity on the reaction with 0 to 9 μ M of cyanide, with no signs of emergence of emission band at 480 nm. The emission profile changed at 10 μ M of cyanide added as shown in **Figure S23(e)**, which could be attributed to the superposition of two emission bands (544 and 480 nm). The 480 nm emission band becomes distinctive and prominent beyond 13.5 μ M of cyanide reacted.

Monitoring the increase in emission intensities of the 480 nm emission band, it was observed that emission intensity increased very gradually from the cyanide concentration range of 0 to 8 μ M, followed by a jump at 9 μ M. The emission intensity then increased gradually again from the cyanide concentration range of 10 to 13 μ M followed by a second jump in emission intensity between 13 to 15 μ M. Thereafter, the emission intensity at 480 nm increased gradually. The limit of detection (LOD) is thus taken at the first onset of the jump in fluorescence intensity, which is calculated to be 8.81×10^{-6} M.

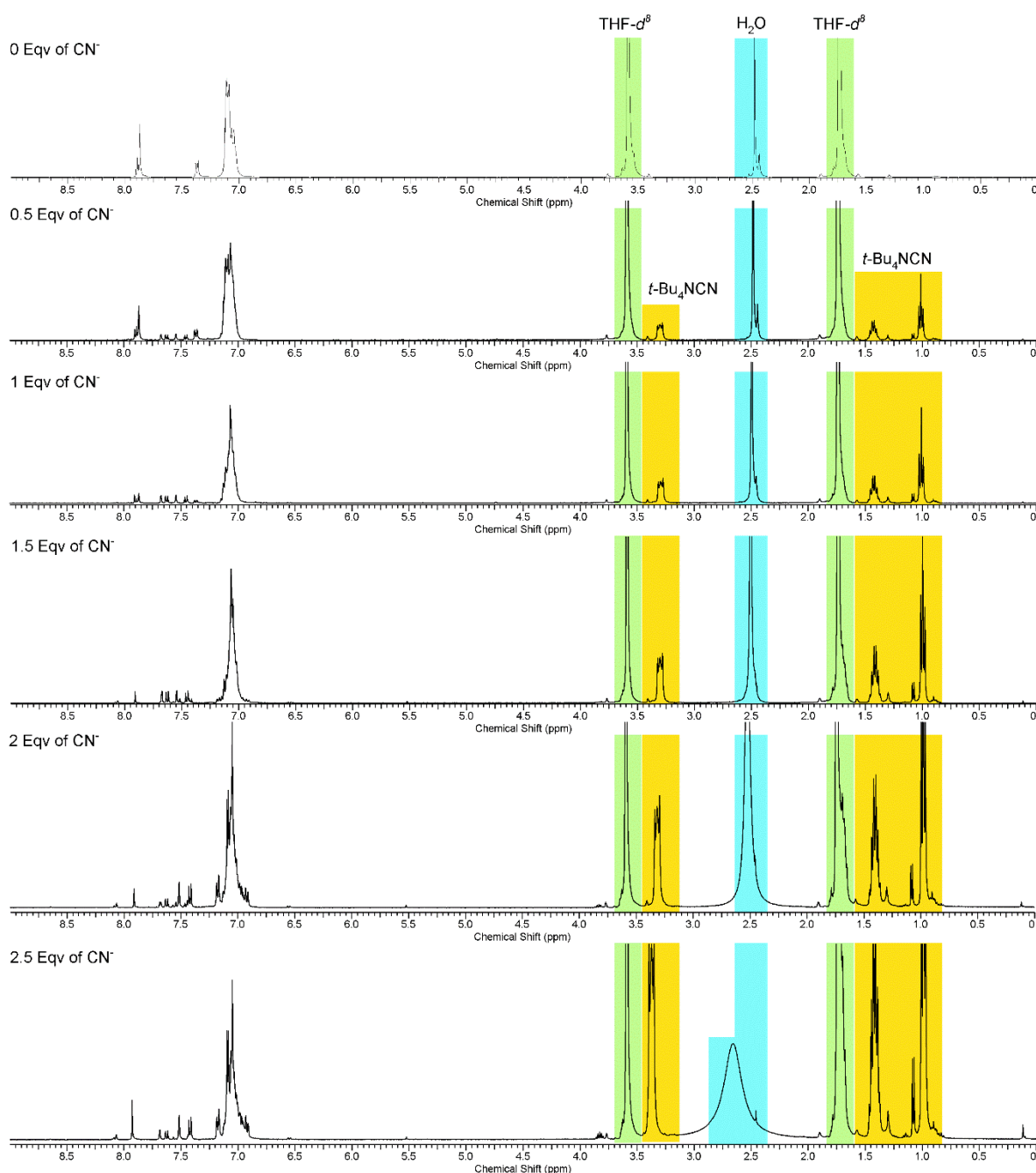
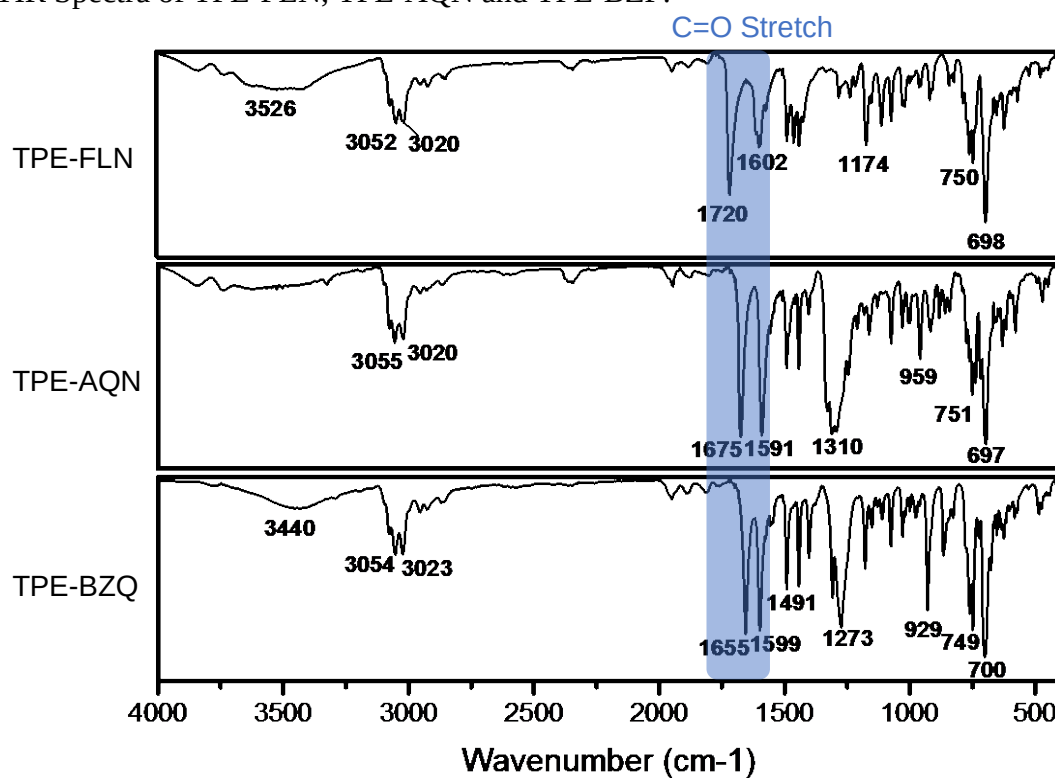


Figure S24. The limitation of detection (LOD) is one of the most important parameters for the chemosensors. This important value should be provided and discussed in this manuscript.

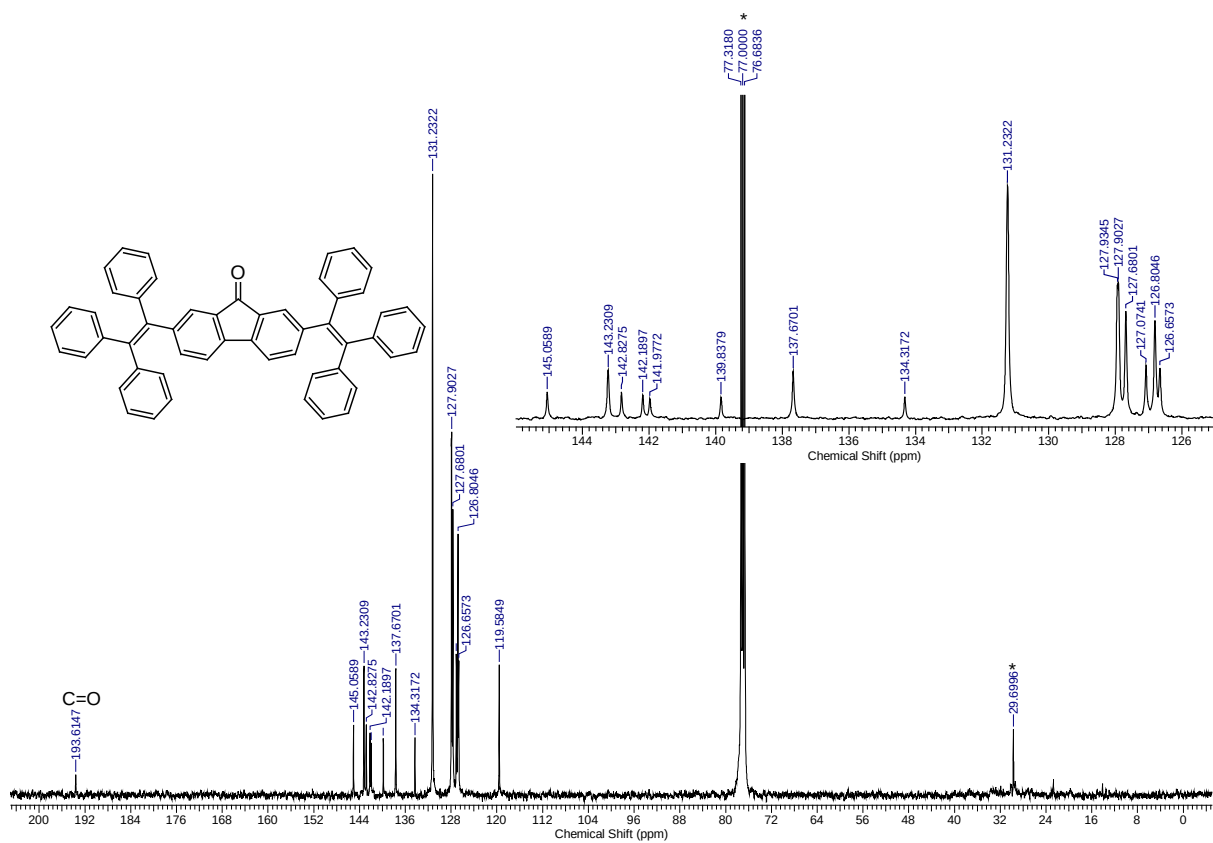
The characteristic signal ($\text{CH}(\text{CN})_2$) is however observed might be due to the spectral overlapping. Another possibility is that two species ($\text{CS}_2\text{-CN}$, $\text{CS}_2\text{-2CN}$) are not stable.

S5. Annex

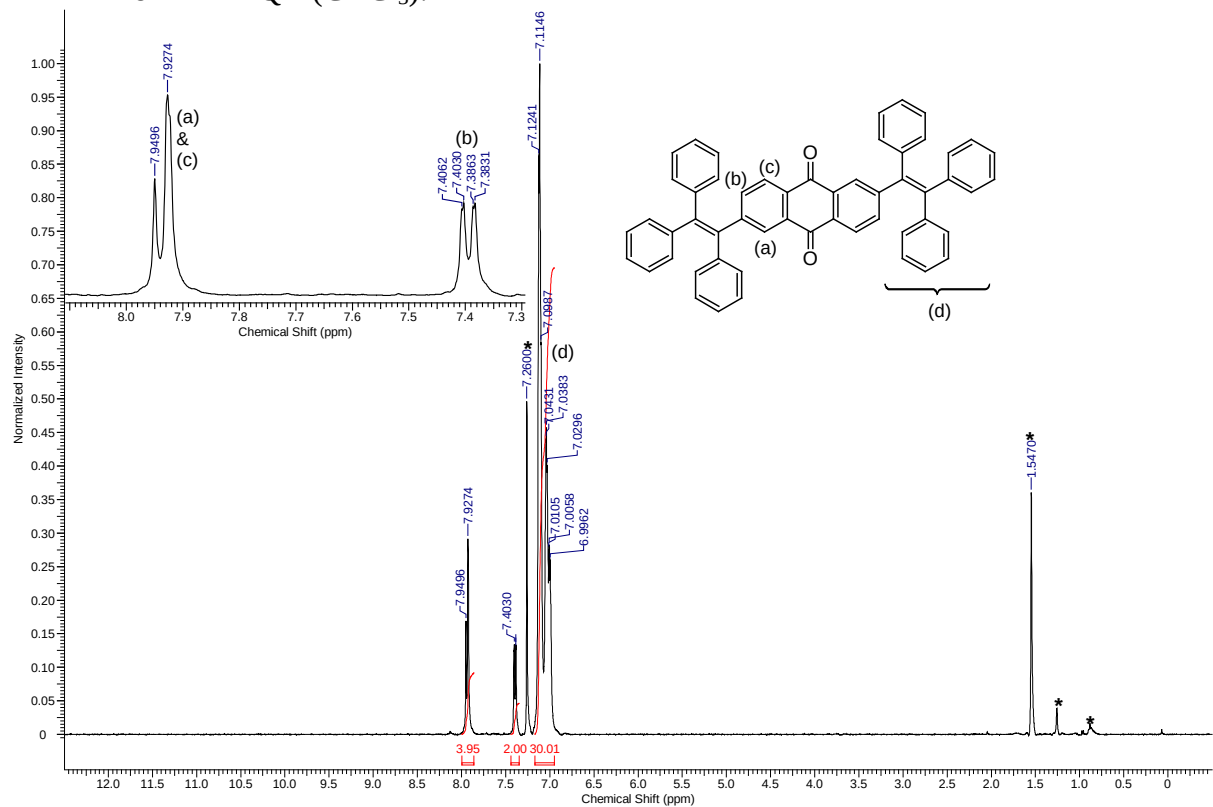
FTIR Spectra of TPE-FLN, TPE-AQN and TPE-BZP:



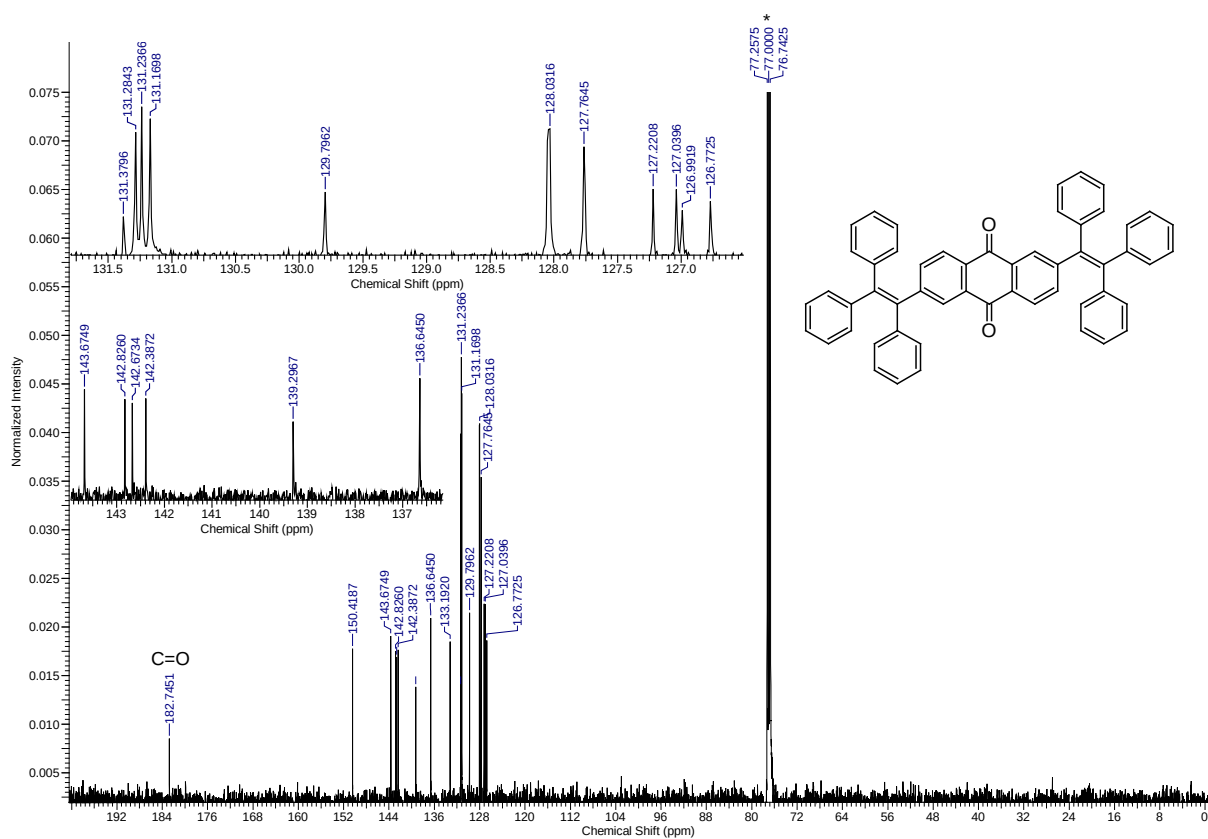
FTIR Spectra of CS1, CS2 and CS3:



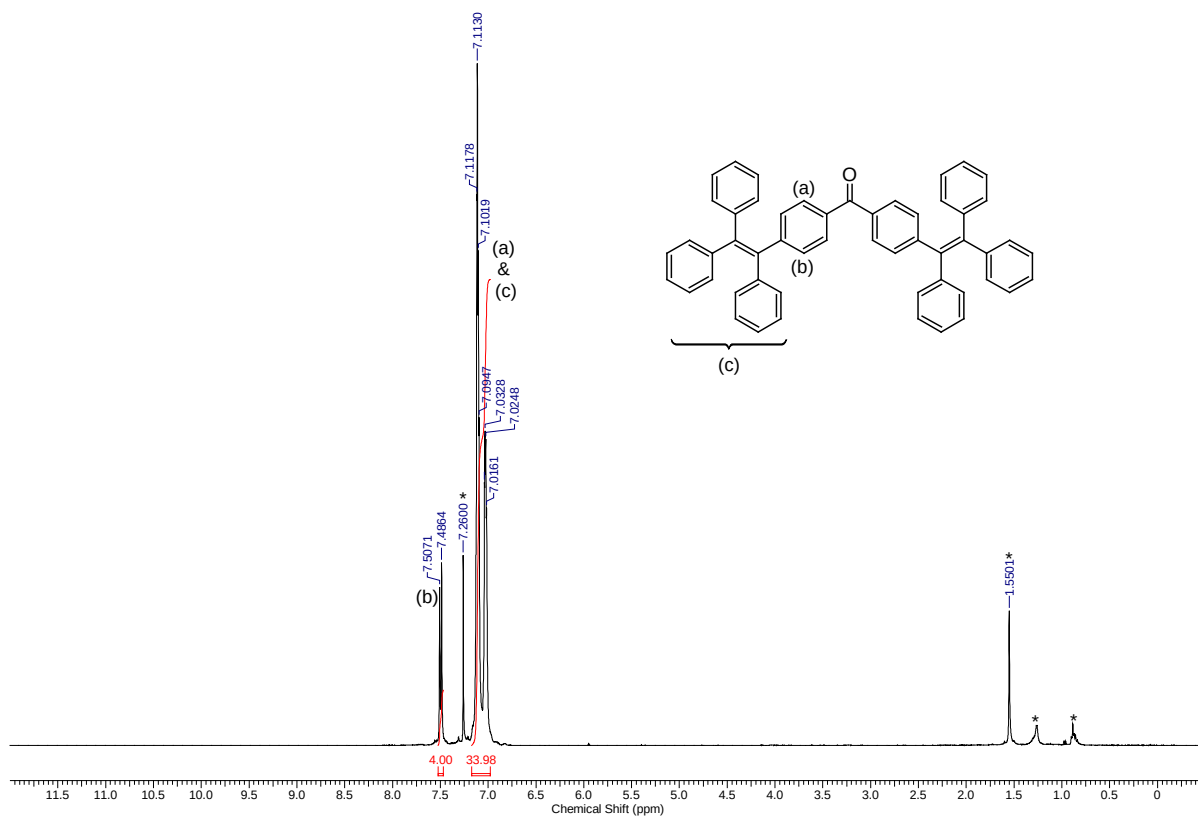
¹H NMR of TPE-AQN (CDCl₃):



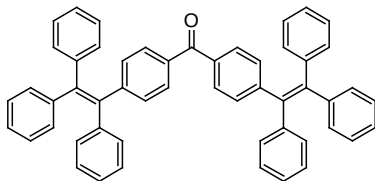
¹³C NMR of TPE-FLN (CDCl₃):



¹H NMR of TPE-BZP (CDCl₃):



¹³C NMR of TPE-BZP (CDCl₃):



Chemical structure of compound 1, a bis-indole derivative. The structure is labeled with (a) for the indole ring, (b) for the C3-C9 bond, (c) for the C2-C3 bond, and (d) for the C2-C6 bond.

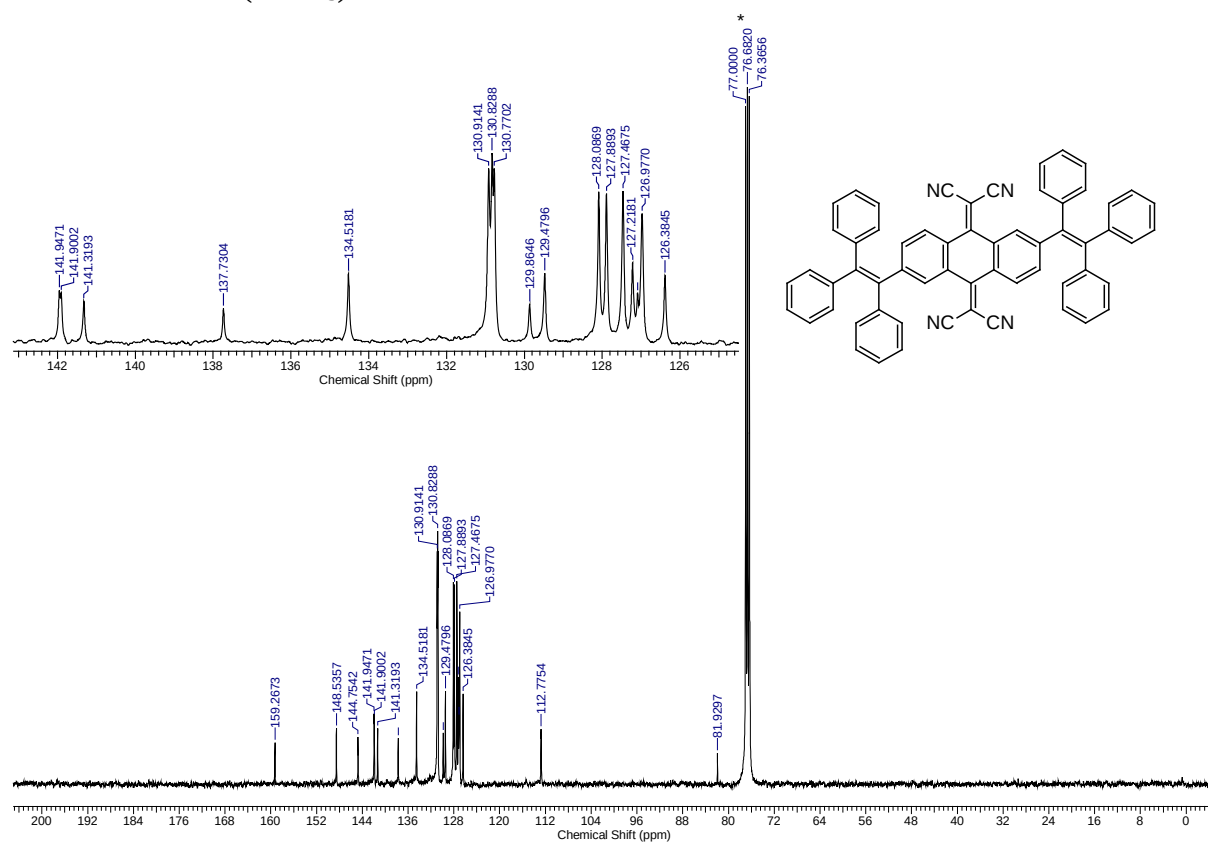


Figure 1 displays the ^{13}C NMR spectra of compound **1**. The top spectrum shows the ^{13}C NMR spectrum in CDCl_3 , with peaks labeled at 143.03, 142.94, 142.69, 142.50, 139.97, 139.44, 137.37, 134.13, 131.35, 131.14, 129.76, 128.06, 127.99, 127.66, 126.89, 126.75, 77.31, and 77.00 ppm. The bottom spectrum shows the ^{13}C NMR spectrum in $\text{DMSO}-d_6$, with peaks labeled at 160.87, 145.22, 143.03, 142.69, 142.50, 139.97, 139.44, 137.37, 134.13, 131.35, 129.76, 128.06, 127.66, 126.89, 126.75, 119.87, 112.95, and 75.60 ppm. The chemical structure of compound **1** is shown on the right, featuring a central benzene ring substituted with two phenyl groups and two cyano groups.

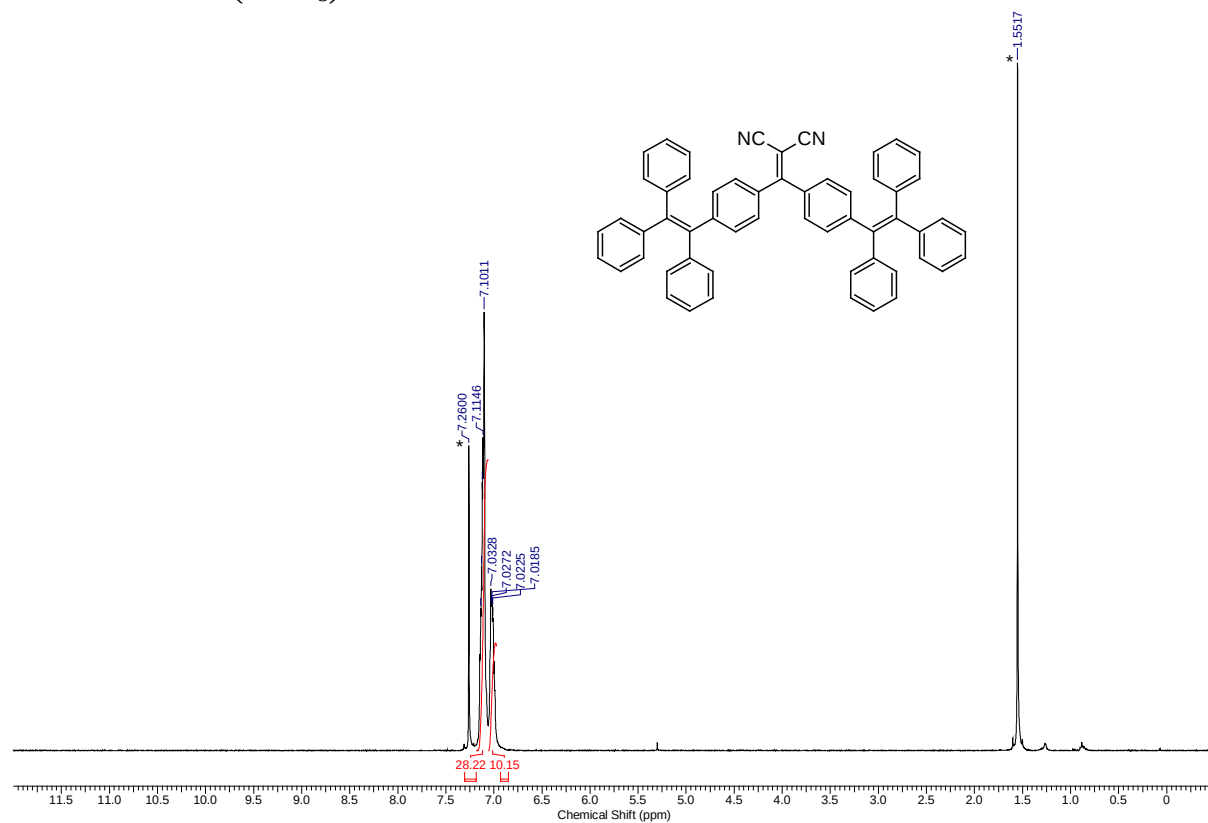
¹H NMR spectrum of compound **1** in CDCl₃. The spectrum displays peaks in the aromatic region (6.9–7.9 ppm) and aliphatic region (1.4–1.6 ppm). Integration values are provided for several peak groups. The chemical structure of compound **1** is shown below the spectrum, with protons labeled (a) through (d).

Chemical structure of compound **1** is shown below the spectrum, with protons labeled (a) through (d).

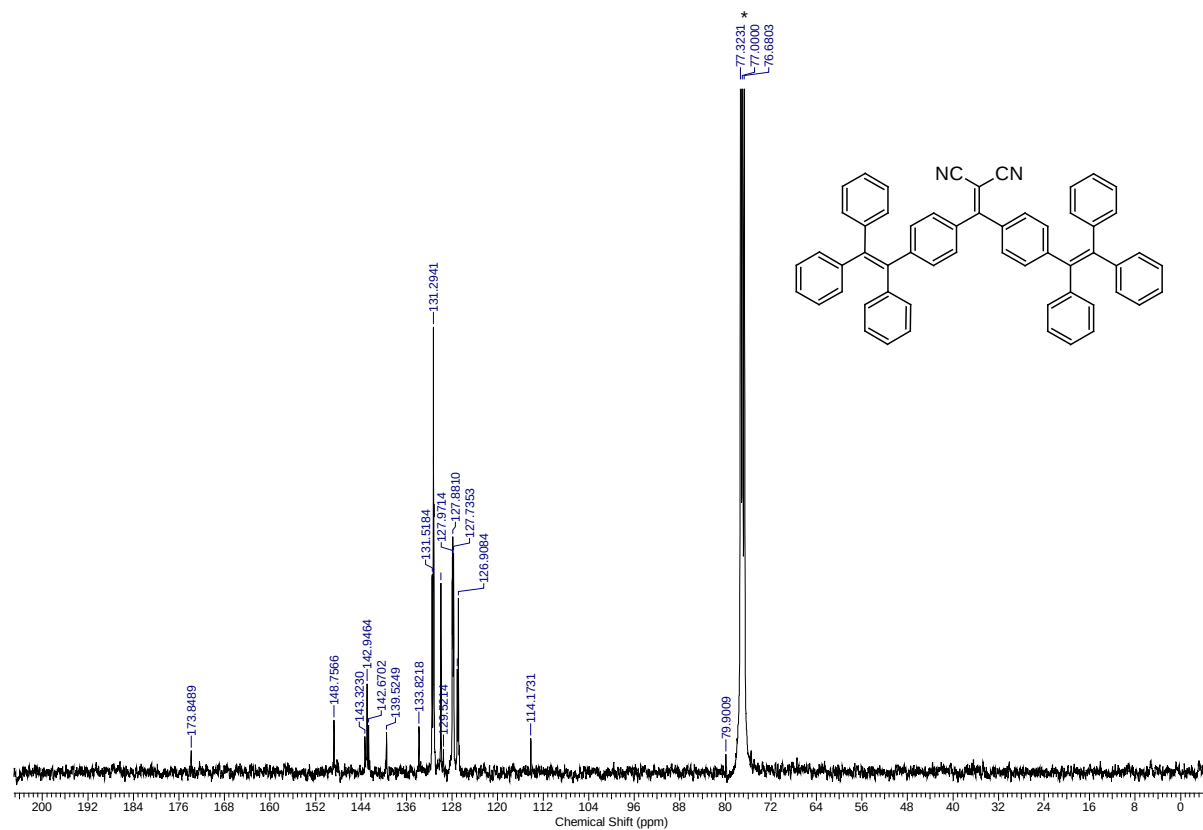
^{13}C NMR of CS2 (CDCl₃):



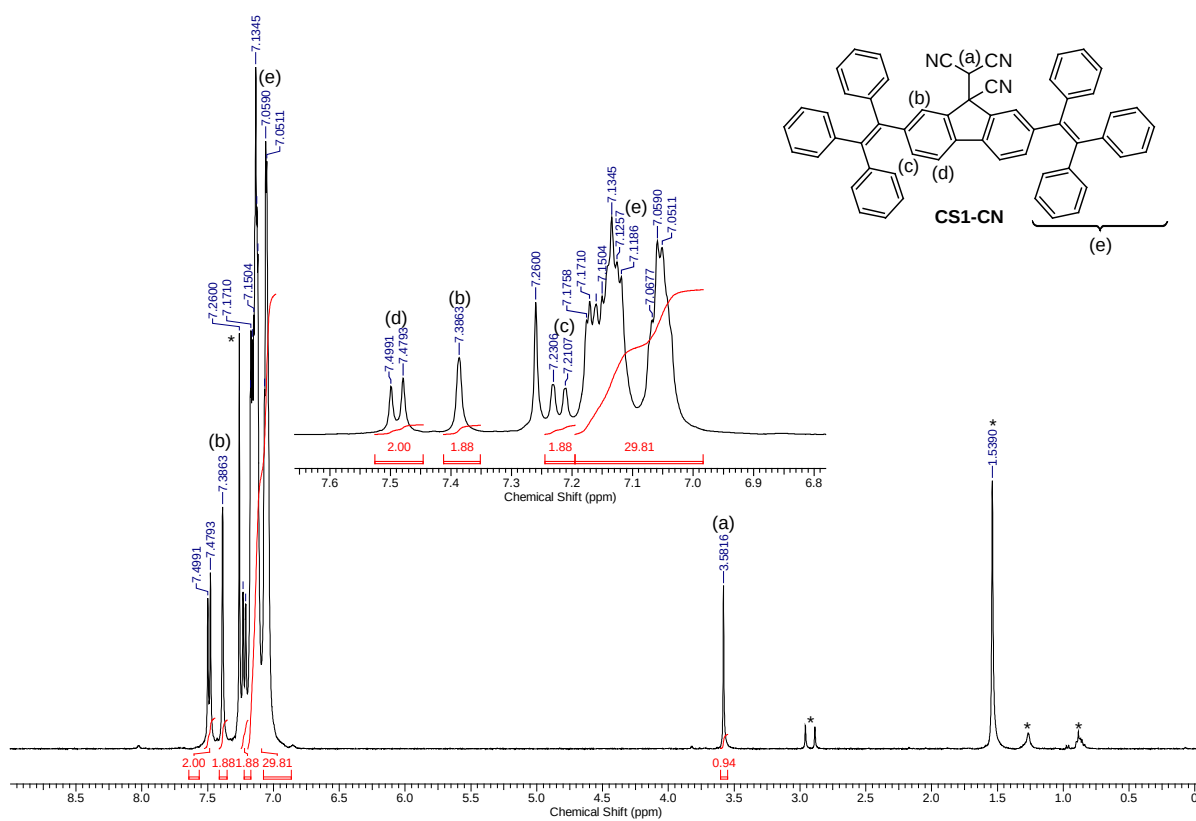
^1H NMR of CS3 (CDCl₃):



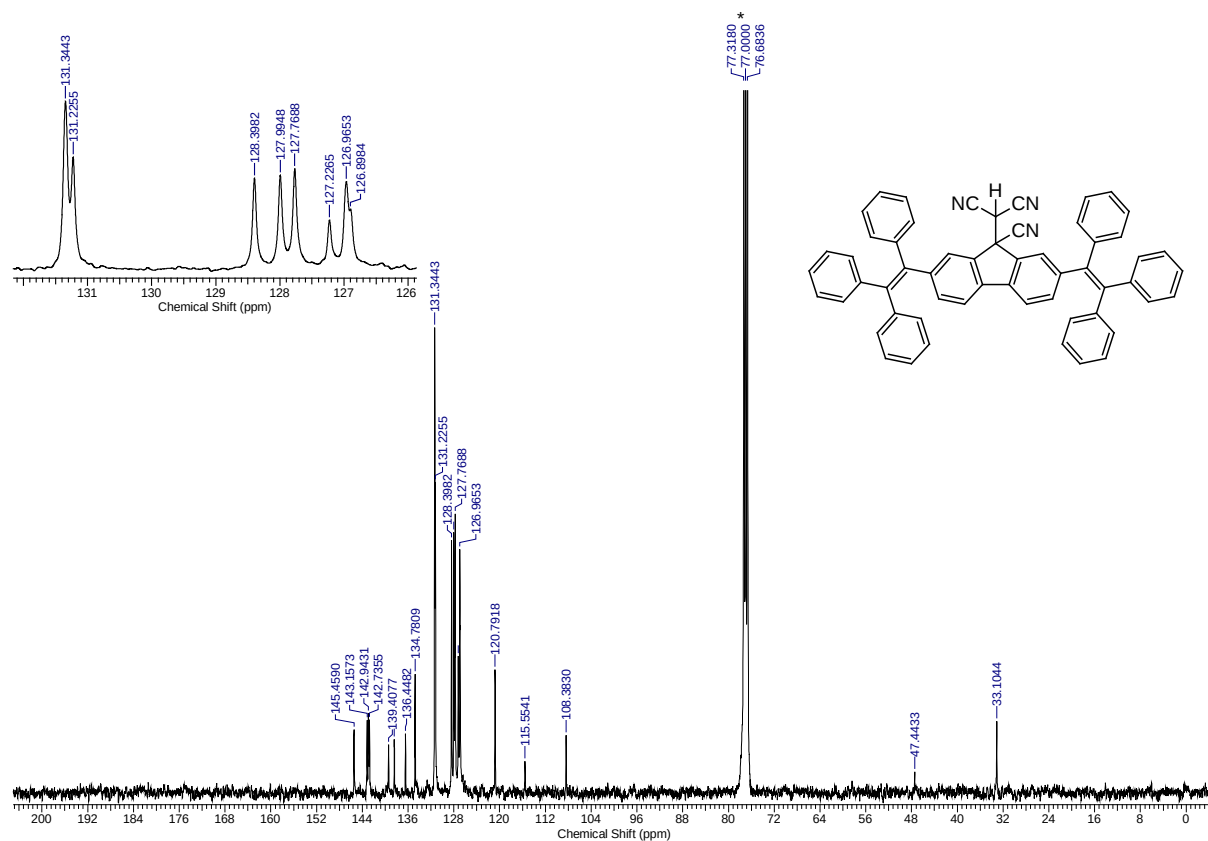
^{13}C NMR of CS3 (CDCl_3):



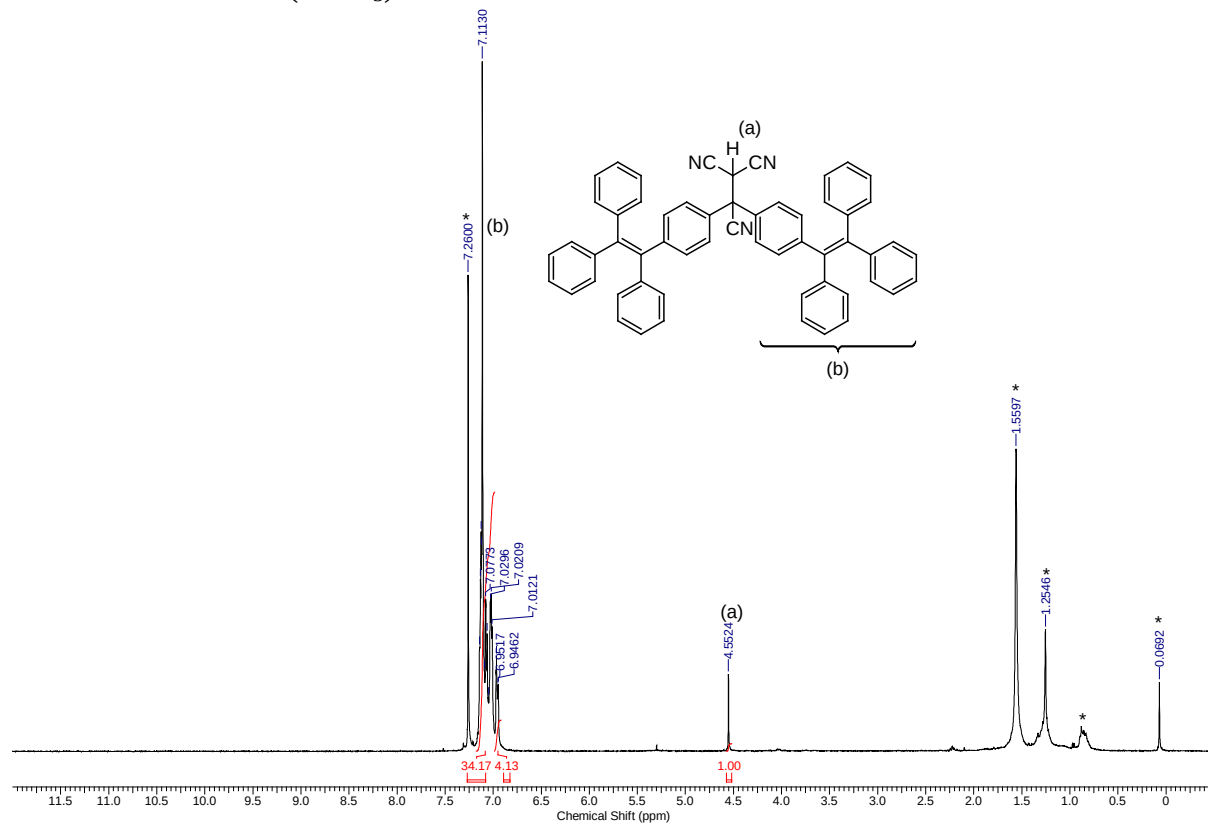
^1H NMR of CS1-CN (CDCl_3):



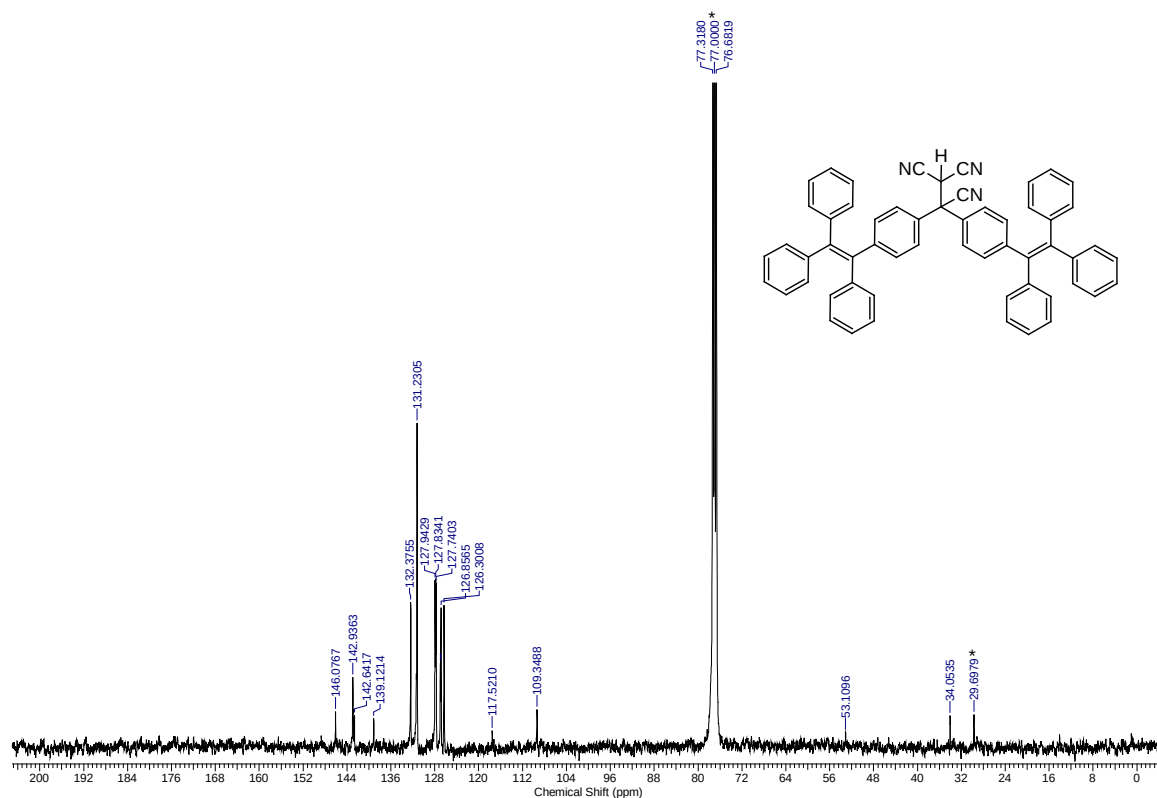
^{13}C NMR of CS1-CN (CDCl_3):



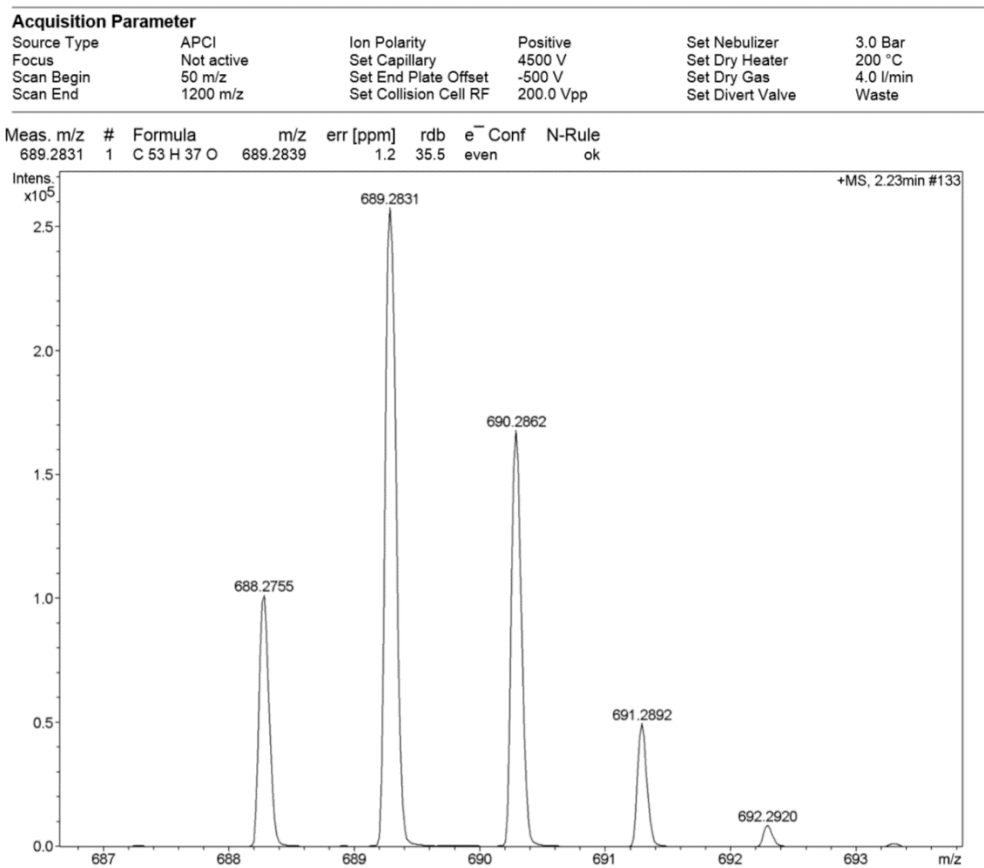
^1H NMR of CS3-CN (CDCl_3):



^{13}C NMR of CS3-CN (CDCl_3):



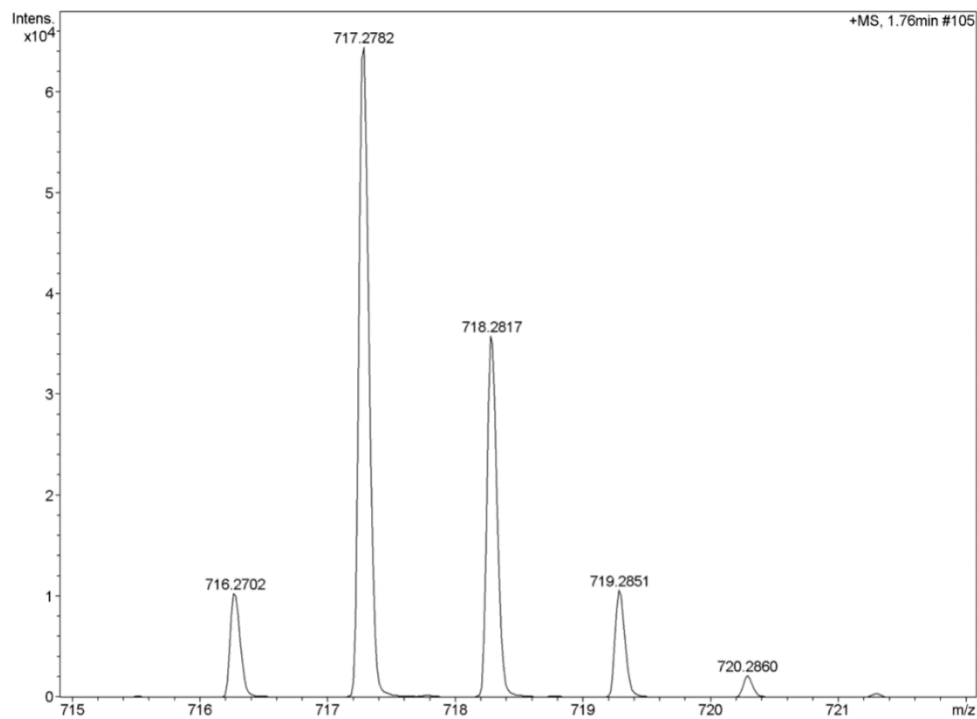
APCI-HR-MS of TPE-FLN:



APCI-HR-MS of TPE-AQN:

Acquisition Parameter					
Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

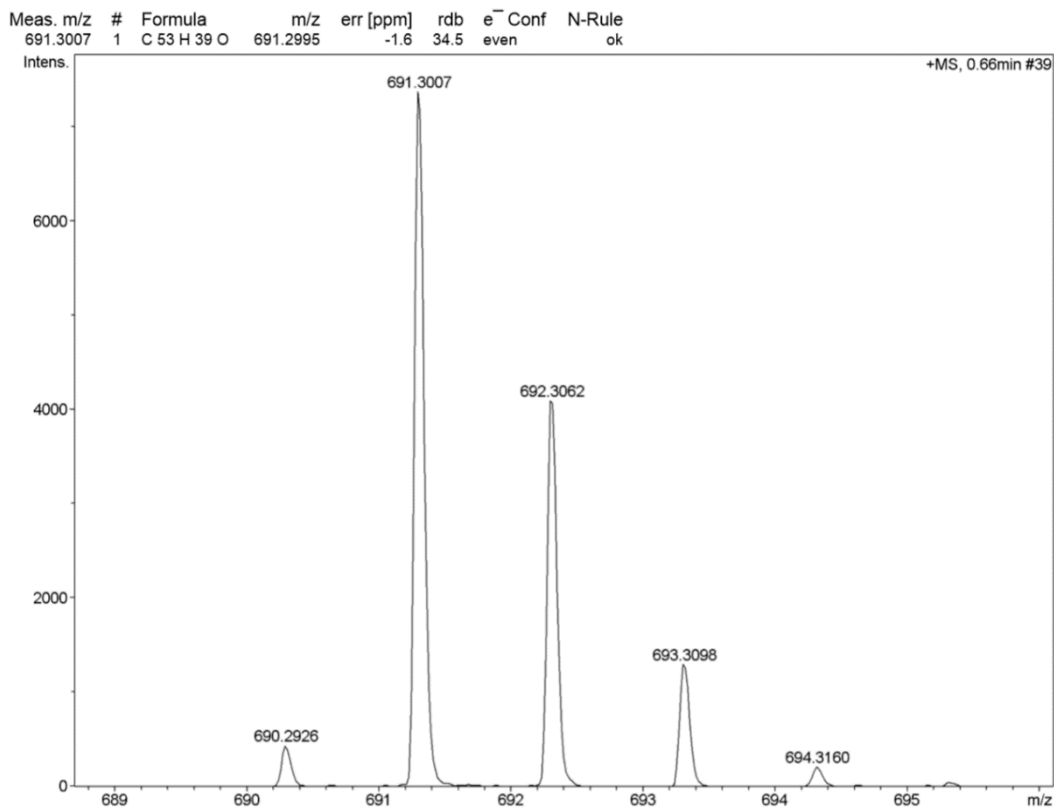
Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e ⁻ Conf	N-Rule
717.2782	1	C ₅₄ H ₃₇ O ₂	717.2788	0.9	36.5	even	ok



APCI-HR-MS of TPE-BZP:

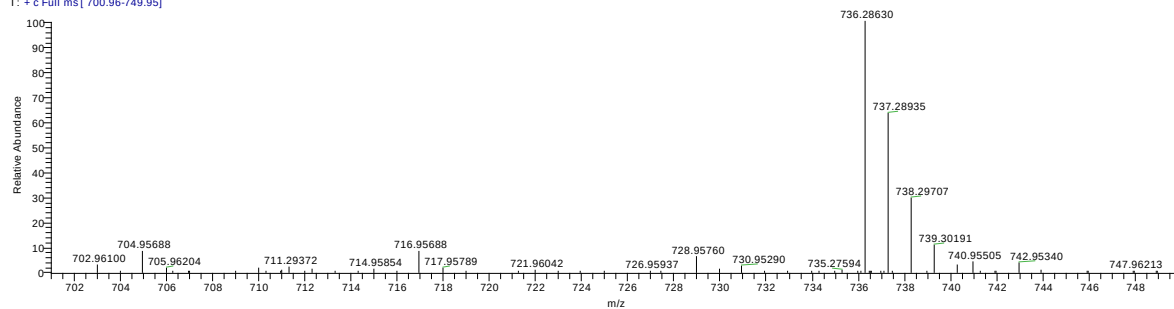
Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste



EI-HR-MS of CS1:

MH251-c1-av #1 RT: 3.60 AV: 1 NL: 1.24E6
T: + c Full ms [700.96-749.95]



MH251-c1-av#1 RT: 3.60
T: + c Full ms [700.96-749.95]
m/z = 735.69384-736.57319

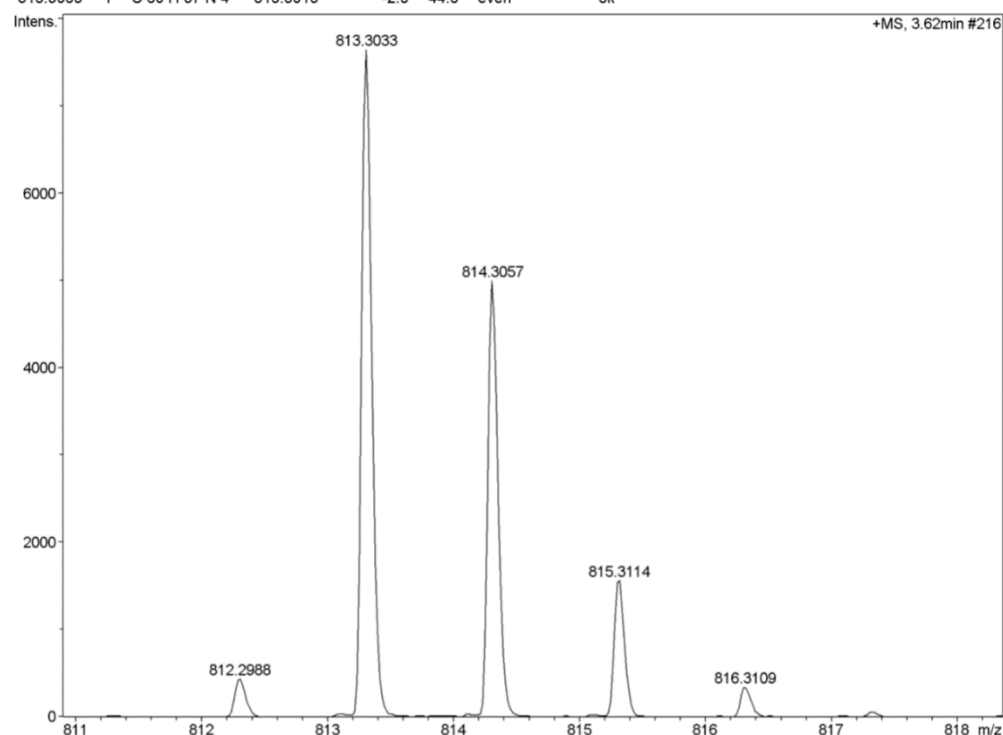
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
736.28630	1242920.0	100.00	736.28785	-2.10	40.0	C ₅₆ H ₃₆ N ₂

APCI-HR-MS of CS2:

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e ⁻ Conf	N-Rule
813.3033	1	C 60 H 37 N 4	813.3013	-2.5	44.5	even	ok

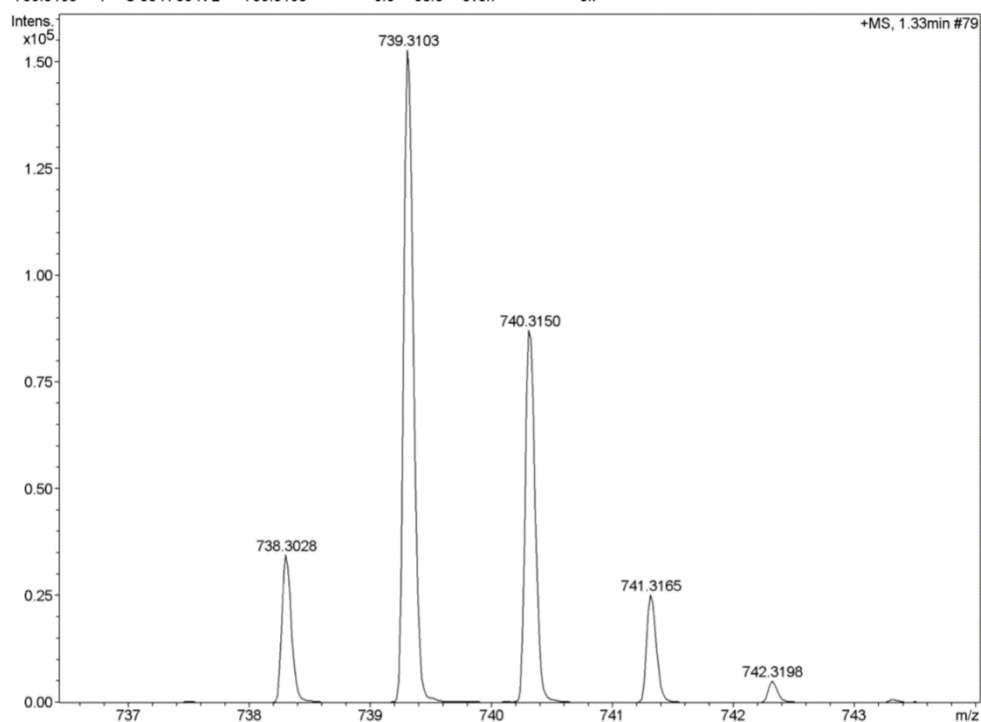


APCI-HR-MS of CS3:

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e ⁻ Conf	N-Rule
739.3103	1	C 56 H 39 N 2	739.3108	0.6	38.5	even	ok

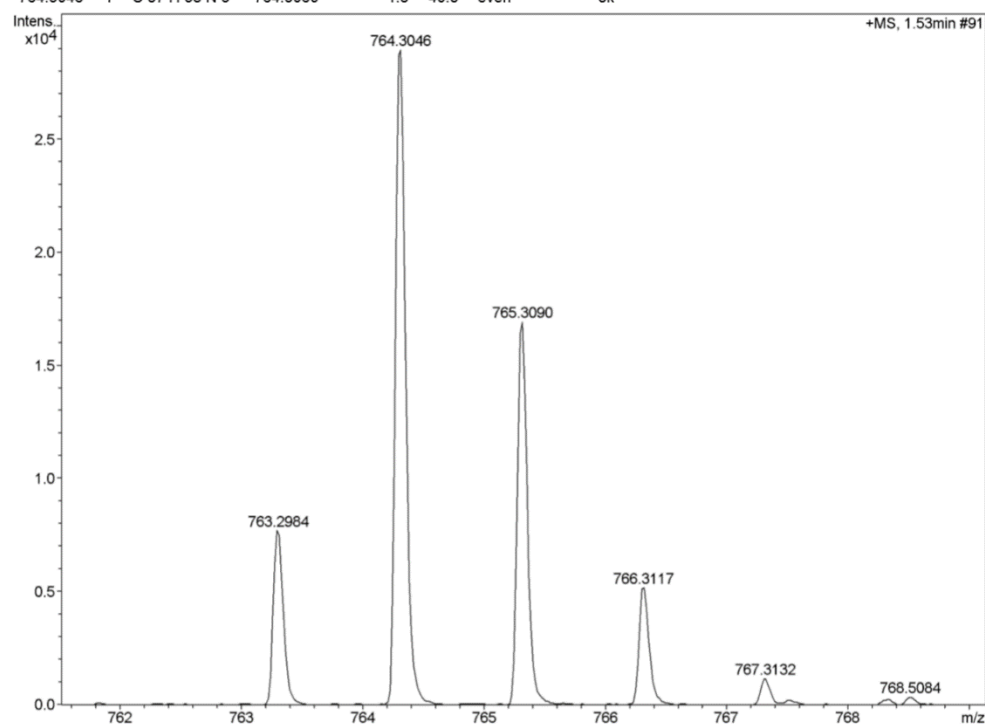


APCI-HR-MS of CS1-CN:

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e ⁻ Conf	N-Rule
764.3046	1	C 57 H 38 N 3	764.3060	1.8	40.5	even	ok

**APCI-HR-MS of CS₃-CN:****Acquisition Parameter**

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e ⁻ Conf	N-Rule
765.3133	1	C 57 H 39 N 3	765.3138	0.7	40.0	odd	ok

