Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Butterfly wing type new push-pull A-π-D-π-A organic fluorophore: Synthesis, photophysical, DFT and nonlinear optical property studies

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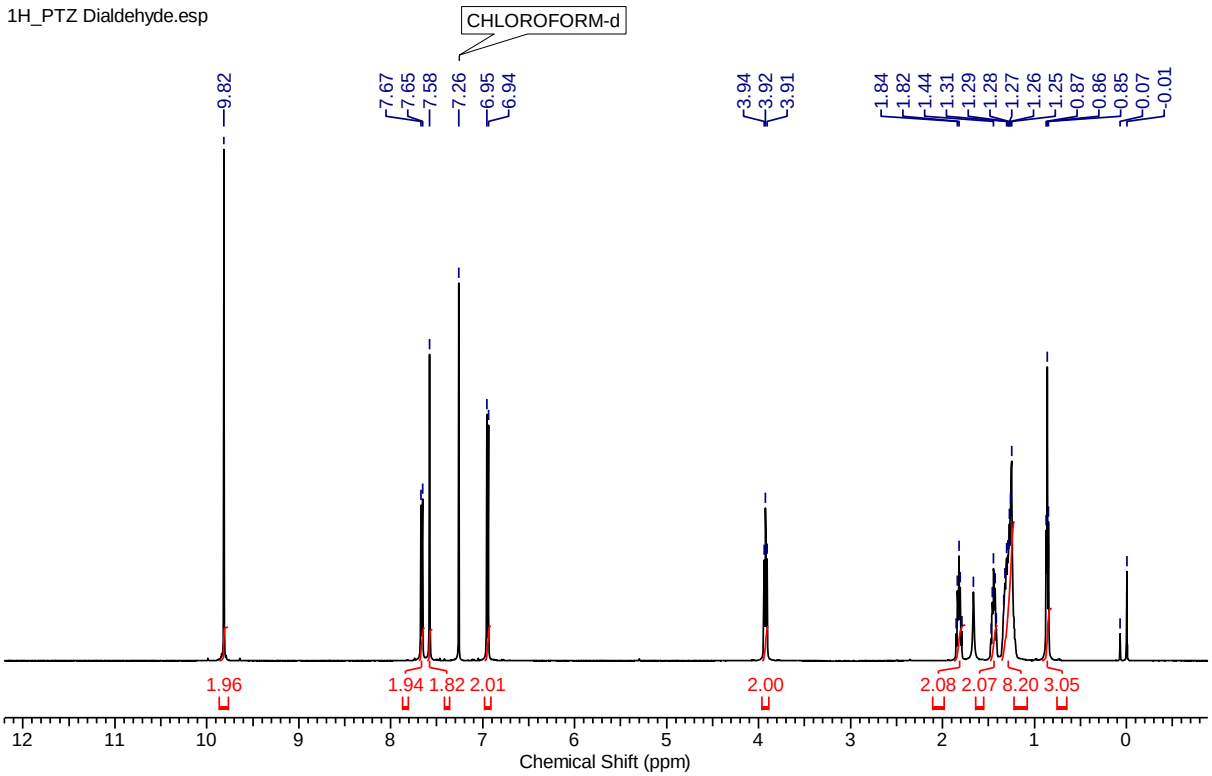

Fig. S1: ^{1}H-NMR data of compound 3

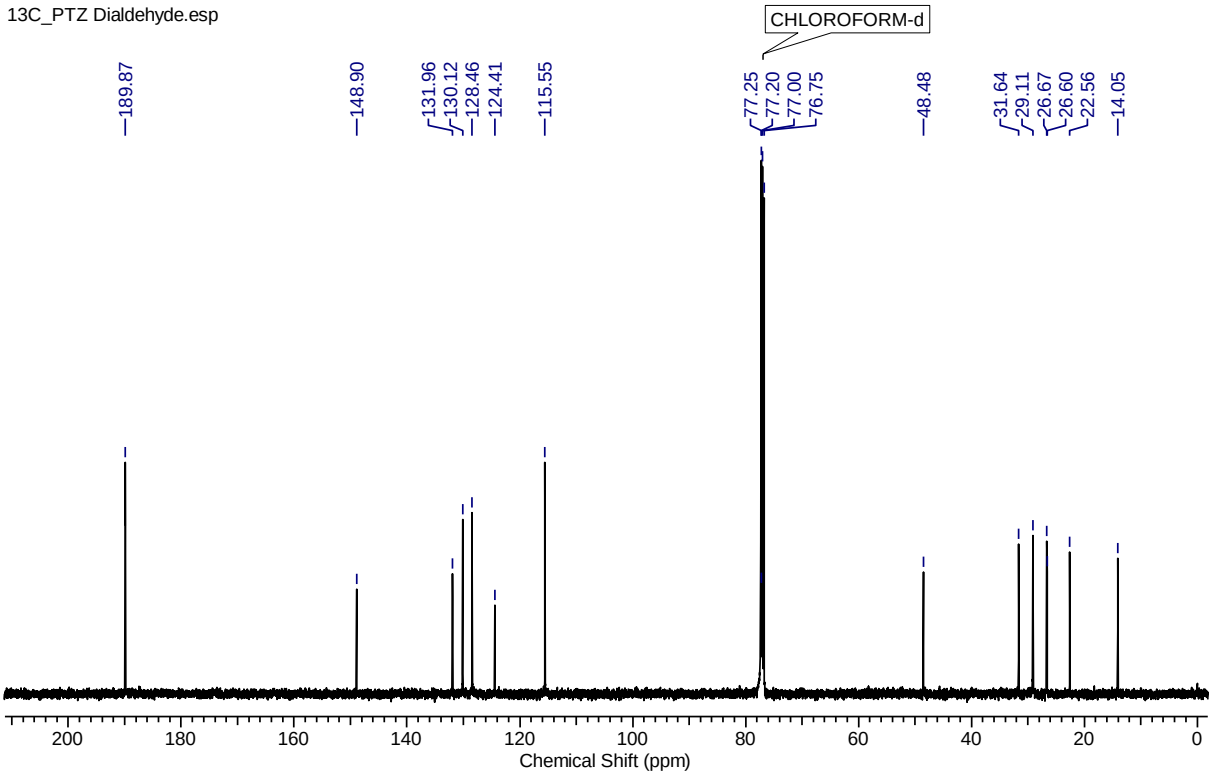

Fig. S2: ^{13}C-NMR data of compound 3

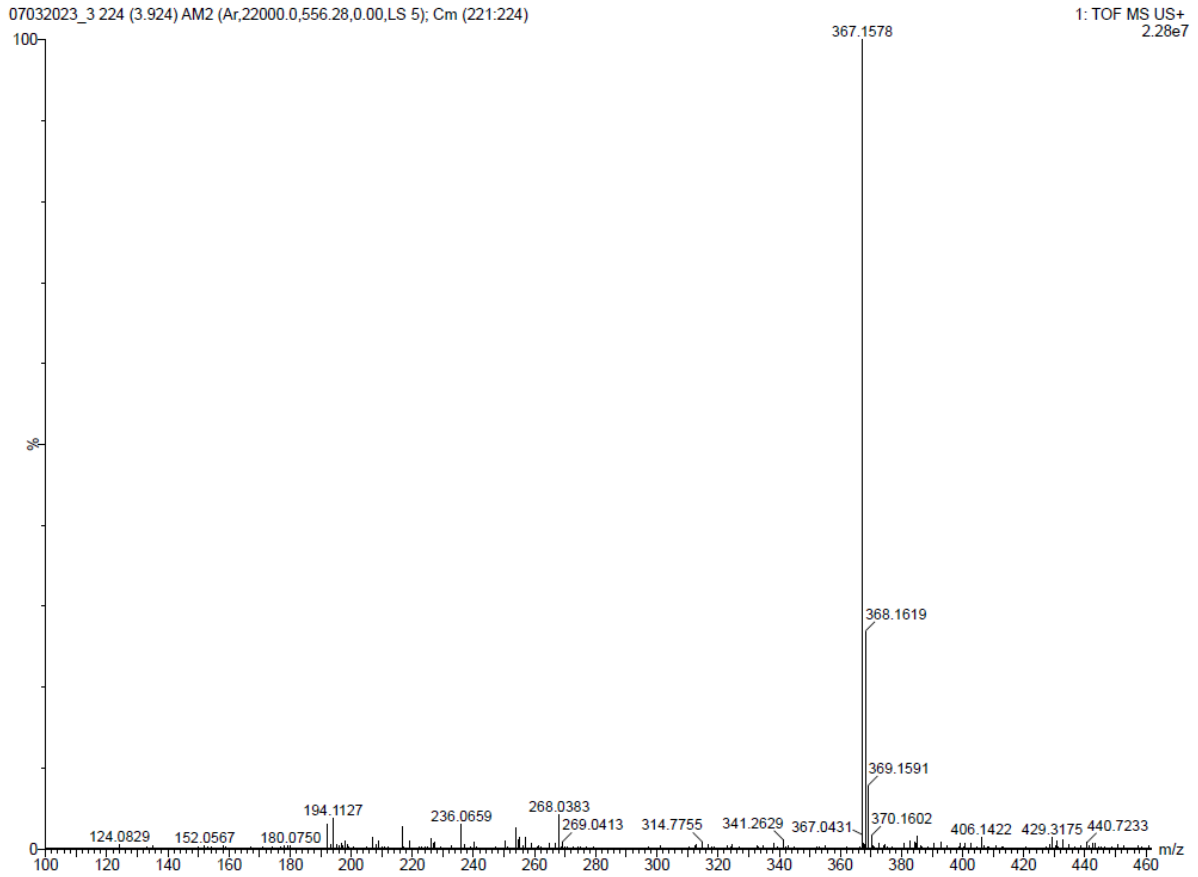

Fig. S3: MALDI-TOF of compound 3

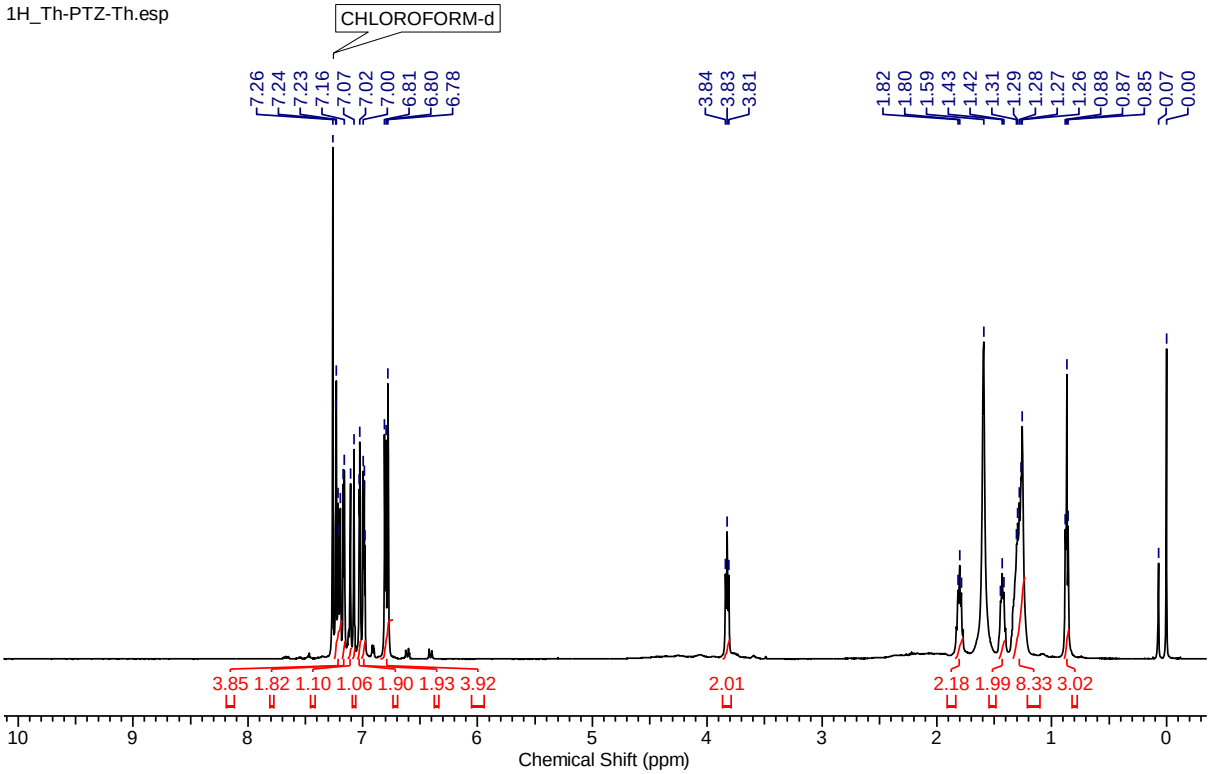

Fig. S4:[1]H-NMR data of compound 4

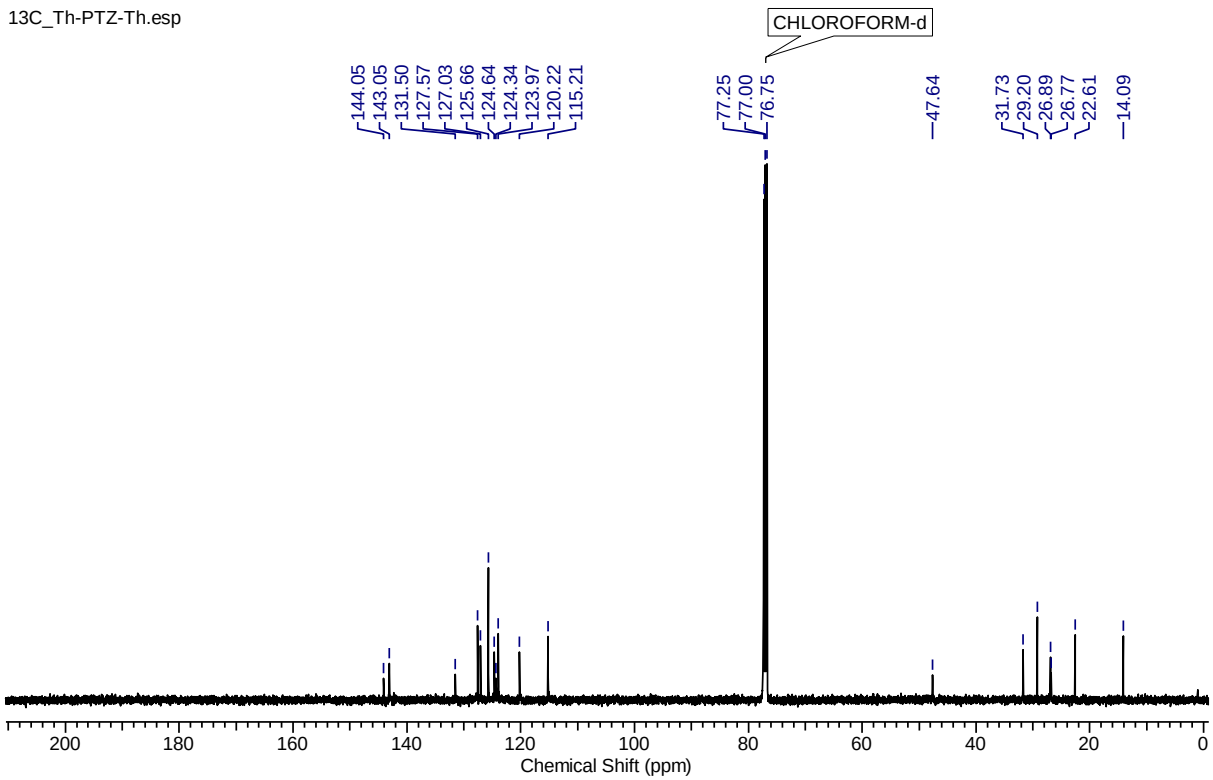

Fig. S5:^{13}C-NMR data of compound 4

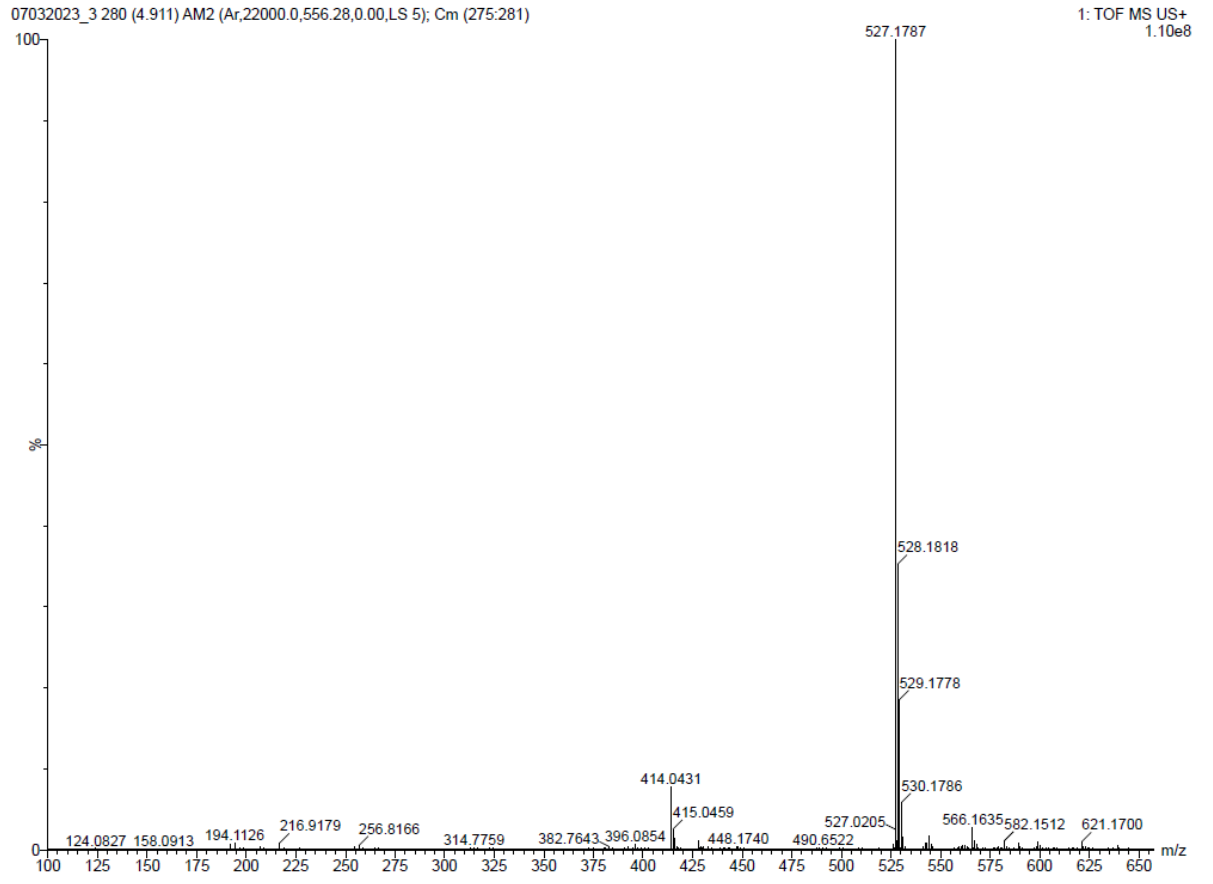

Fig. S6: MALDI-TOF data of compound 4

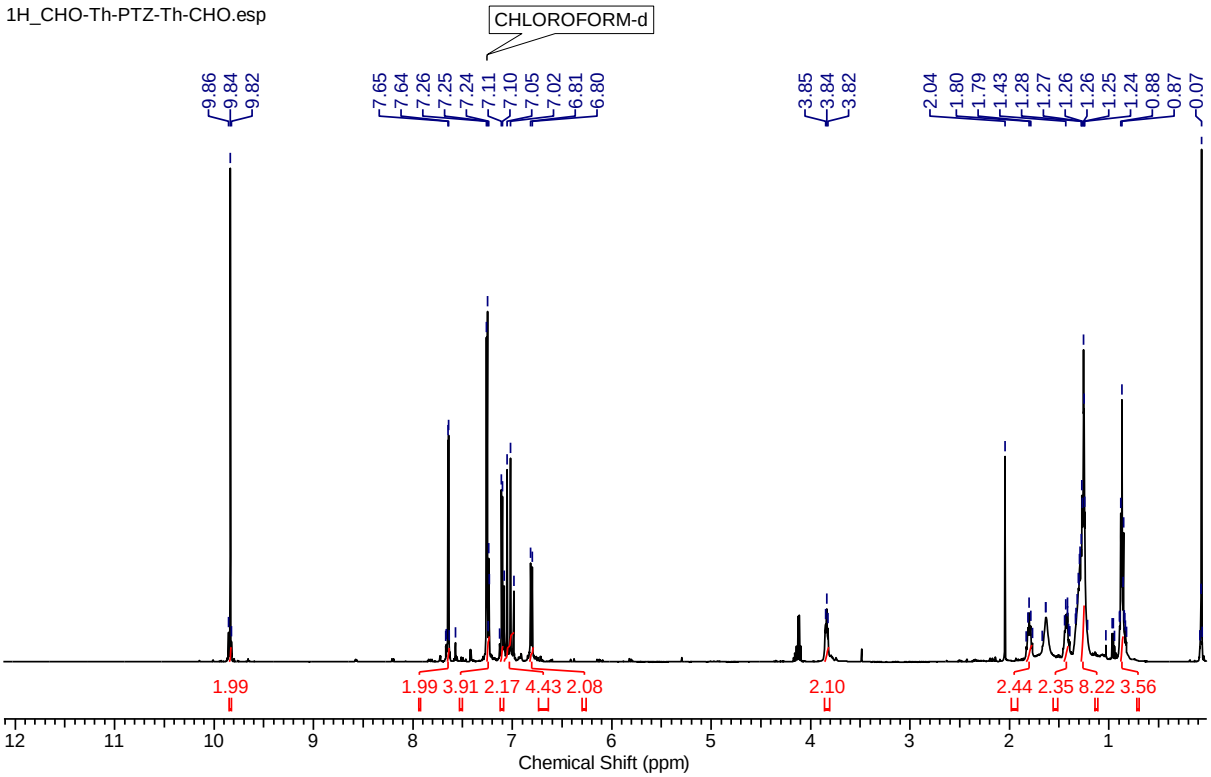

Fig. S7:[1]H-NMR data of compound 5

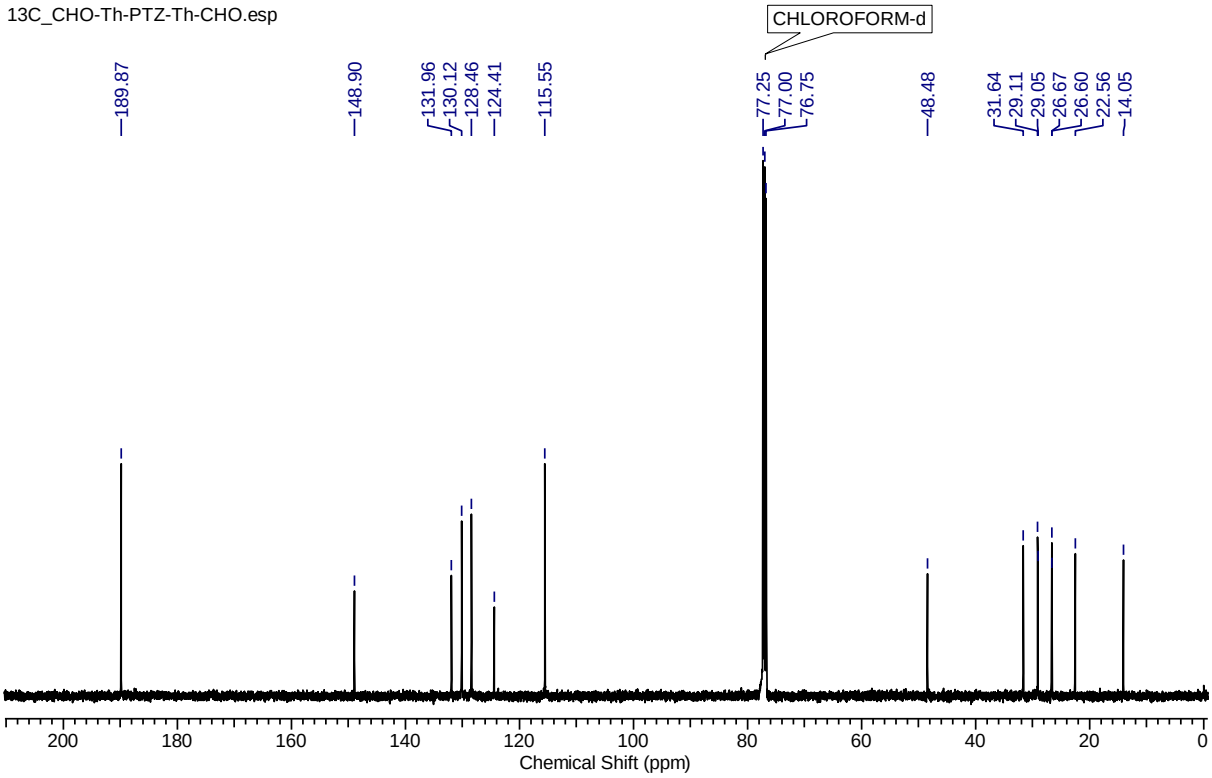

Fig. S8:[13]C-NMR data of compound 5

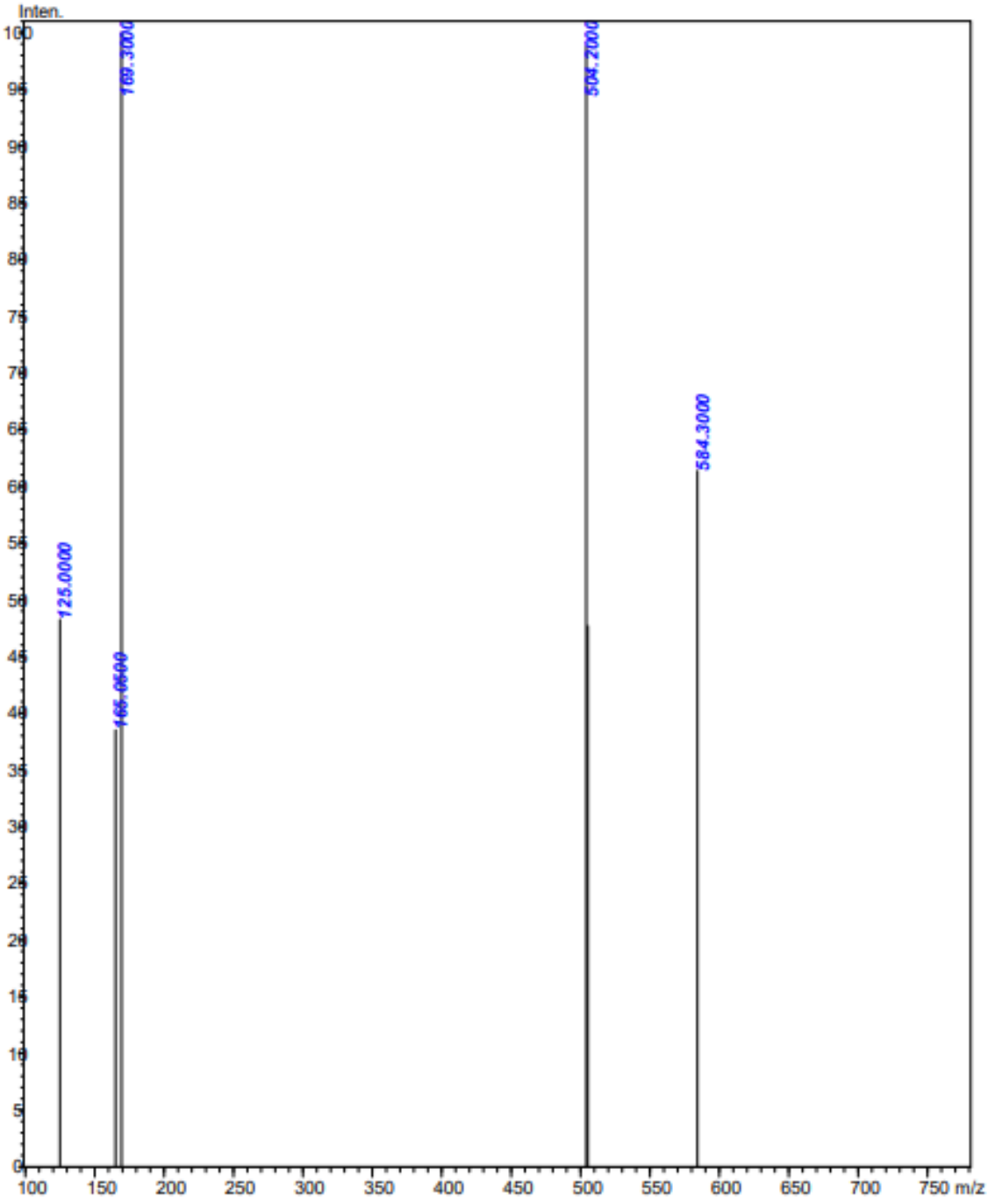

Fig. S9: HPLC-MS data of compound 5

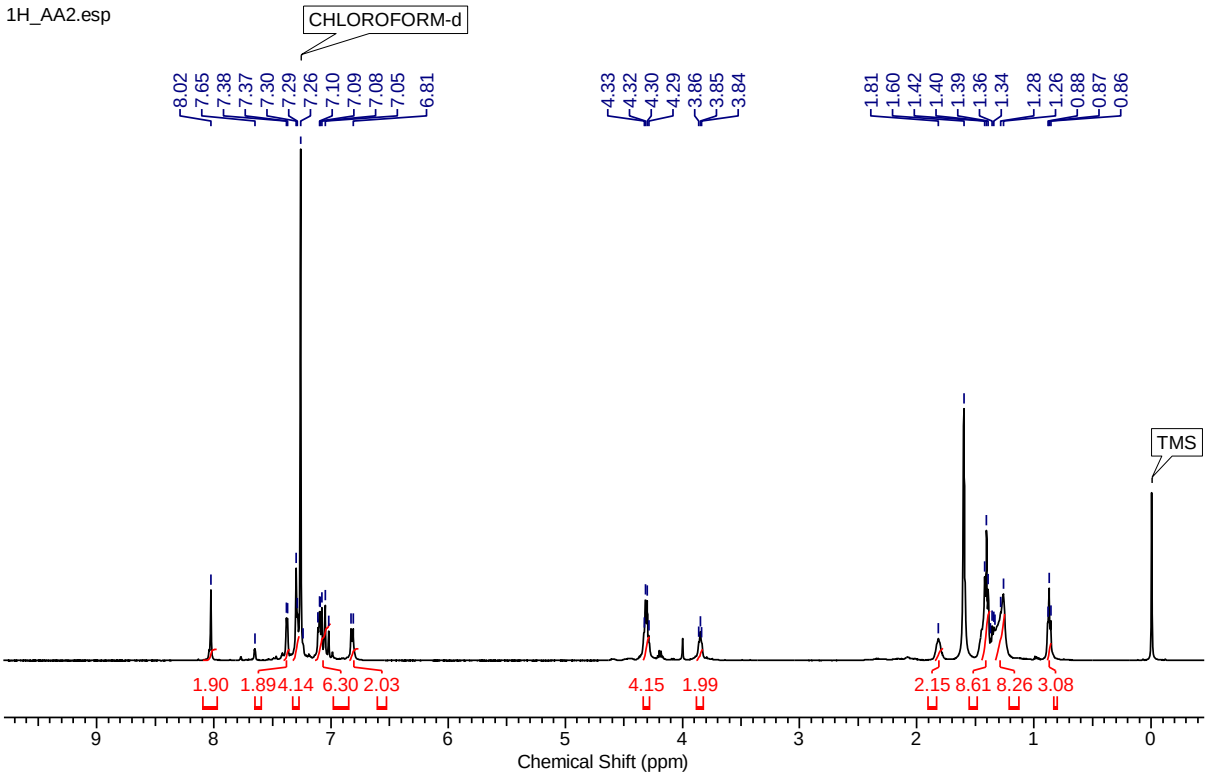

Fig. S10:[1]H-NMR data of compound AA2

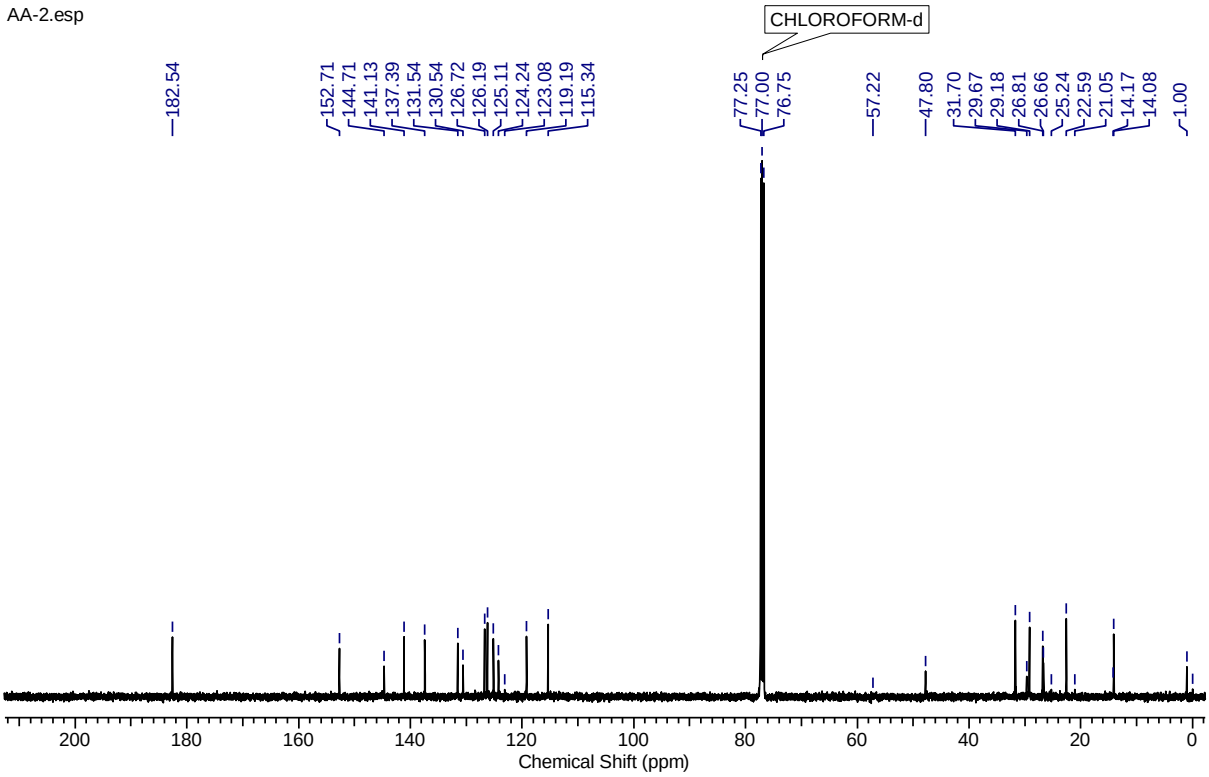

Fig. S11:[13]C-NMR data of compound AA2

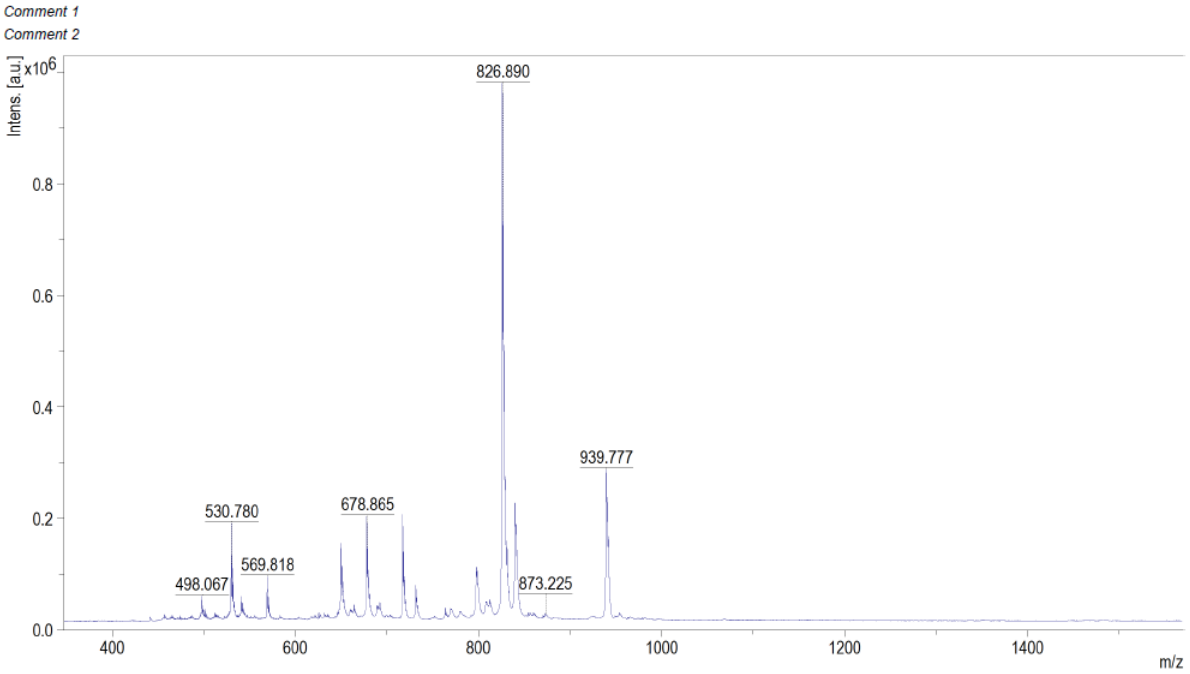

Fig. S12: MALDI-TOF data of compound AA2

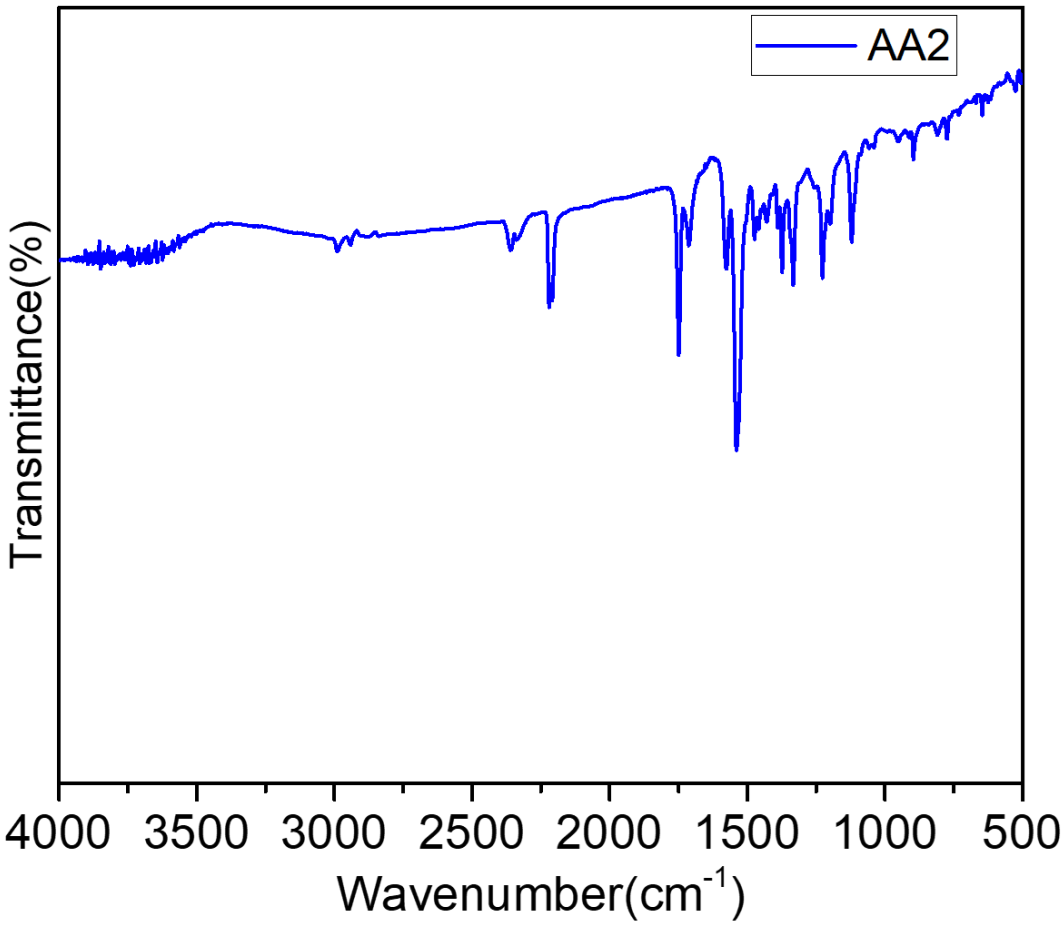

Fig. S13. FT-IR data of compound AA2

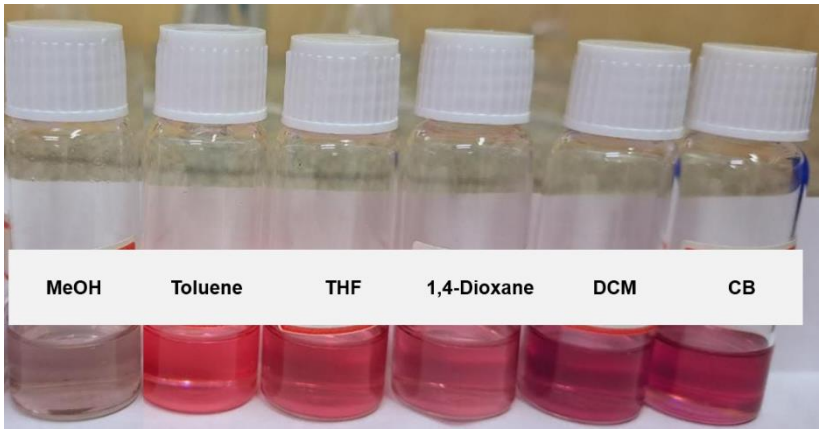

Fig. S14. Digital photograph of AA2 molecule dissolved in different solvents.

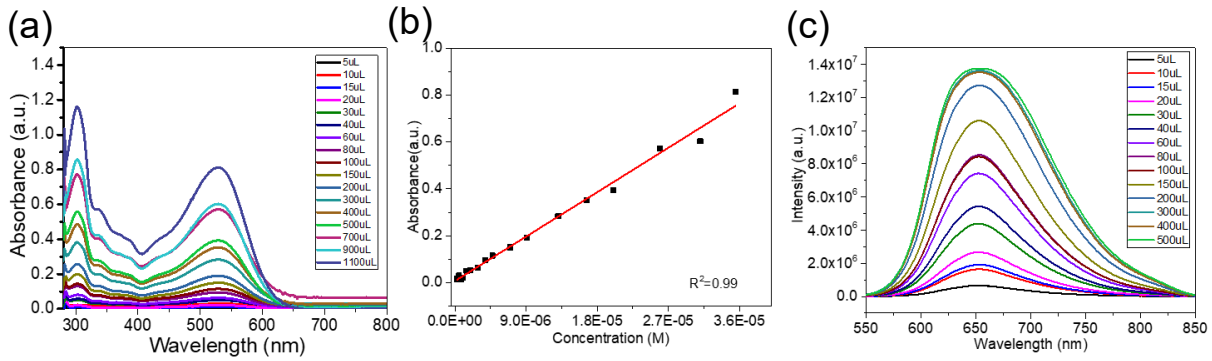

Fig. S15. AA2 molecule in toluene at various concentrations ranging from 10^{-5} to 10^{-7} M at room temperature. (a) UV-vis absorption spectra, (b) corresponding linear graph and (c) PL emission spectra.

Relative fluorescence quantum yield of the compound AA2

The relative fluorescence quantum yield of the compound AA2 in different solvents was studied in this context. To identify the relative fluorescence quantum yield of AA2, Nile blue (NB) was chosen as the standard reference with fluorescence quantum yield of 0.27 at excitation wavelength of 540 nm in the medium of methanol. Based on the equation shown below, we calculated the quantum yield.

$$\Phi_S = \Phi_R \times \frac{A_R}{A_S} \times \frac{I_S}{I_R} \times \frac{\eta_S^2}{\eta_R^2}$$

Where, Φ_S denoted as sample quantum yield, Φ_R mentiond as reference quantum yield, A_R referred as absorbance of the reference, A_S as the absorbance of sample, I_S as the area under the fluorescence curve of the sample, I_R as the area under the fluorescence curve of the reference, η_S as the solvent refractive index of the sample and η_R as the solvent refractive index of the reference.

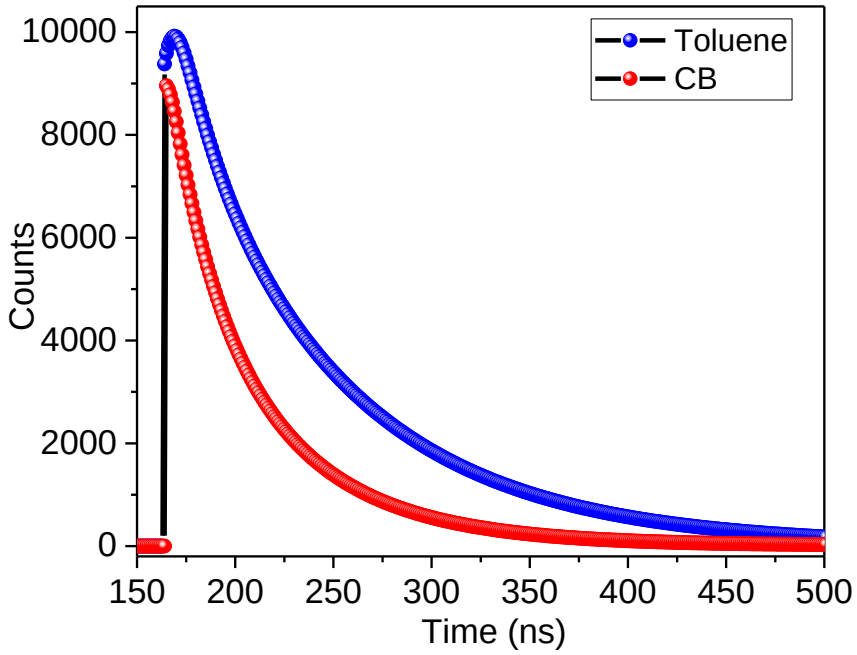

Fig. S16. Time-resolved photoluminescence (TRPL) profile of AA2 in different solvents

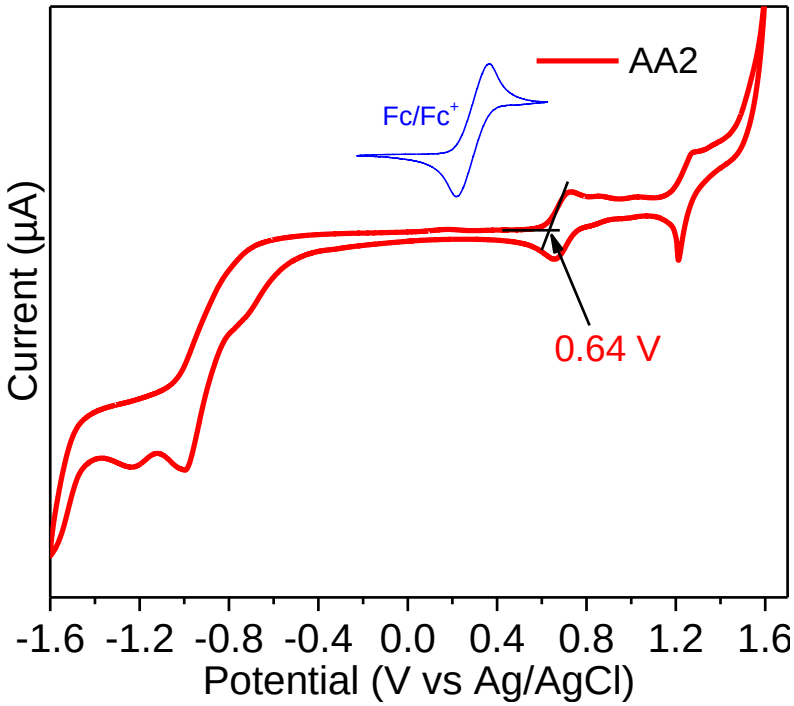

Fig. S17. Cyclic voltammetry of AA2 in dry DCM using the supporting electrolyte of n-butylammonium hexafluorophosphate (0.1 M NBu_4PF_6).

Table S1 Comparison of simulated absorption and emission wavelengths (nm) and HOMO-LUMO gap (eV) for AA2 molecule using different methods

Methods	λ_{max} (absorption) (nm)	λ_{max} (emission) (nm)	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap
B3LYP/6-31G**	1005	1222	-5.02	-2.93	2.09
CAM-B3LYP/6-31G**	495	642	-6.17	-1.83	4.33
ωB97XD/6-31G**	423	596	-6.77	-1.36	5.41
B3LYP/6-31+G*	1105	1317	-5.24	-3.22	2.01
CAM-B3LYP/6-31+G*	508	663	-6.37	-2.12	4.25
B3LYP/6-311G	712	1126	-5.34	-3.31	2.03
CAM-B3LYP/6-311G	505	639	-6.47	-2.20	4.27

Cartesian coordinates for the optimized geometries of AA2 in ground (S_0) and excited (S_1) states at CAM-B3LYP/6-31+G* level of theory using $CHCl_3$ as solvent:

AA2 (S_0)

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 107

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 C                  3.65189000    2.48191400   -0.82758300
 C                  3.78179500    1.10154000   -1.01408300
 C                  2.63919500    0.40662300   -1.42758400
 C                  1.43326100    1.05150300   -1.66105200
 H                  2.39872200    4.18996400   -0.83620400
 H                  4.50174700    3.07812000   -0.51248200
 H                  2.69866100   -0.66498300   -1.59886300
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 C                 -1.25568300    1.01807700   -1.71620200
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AA2 (S_1)

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H	16.52903500	-3.00197500	-0.84320200
H	16.36473900	-1.23634600	-0.71708600

H	-11.54563400	0.25599600	0.13812500
C	-12.09134600	-1.75961000	0.20115900
C	-11.97307400	-3.19024300	0.21427800
S	-13.77515900	-1.29324800	0.38532000
O	-10.96313200	-3.89056800	0.12308900
N	-13.25552500	-3.79400600	0.35558300
C	-13.32643800	-5.26035300	0.40245700
C	-13.27795300	-5.79743000	1.82669800
H	-12.46318100	-5.60849900	-0.16446200
H	-14.22516400	-5.57940300	-0.12251300
H	-13.32884700	-6.89009900	1.80354900
H	-12.34404200	-5.50650800	2.31539300
H	-14.11700200	-5.43422600	2.42600400
C	-14.30179600	-2.94975100	0.46984300
C	-15.66035400	-3.24115500	0.63367300
C	-16.23389100	-4.53294800	0.73866100
N	-16.76004400	-5.56409500	0.83375900
C	-16.57542300	-2.15800700	0.71611400
N	-17.31208200	-1.26265300	0.78215400

Table S2 Comparison of Inorganic & Nanostructured based Optical limiters under Nanosecond pulse Excitation[1]

S.No	Molecule name/ configuration	Concentration/ Solvent	Linear Transmittance (LT) / Laser Wavelength / Pulse-width	Optical Limiting Threshold & *undesirable LT* "⊗"
1.	SWNT-Carbon Nanotubes	$CHCl_3$	13% 532 nm/ 5 ns	0.04 J/cm^2 ⊗
2.	PbPc(β-CP)4	$CHCl_3$	62% 532 nm/ 8 ns	0.07 J/cm^2 ⊗
3.	SWNT-Carbon Nanotubes	H_2O	24% 532 nm/ 5 ns	0.15 J/cm^2 ⊗
4.	Aq GO	-	70 % 532 nm/ 35 ns	0.2 J/cm^2
5.	Fullerene - C_{60}	Toluene	65 % 532 nm/ 5 ns	0.2 J/cm^2 ⊗
6.	Gold Nanoparticles	H_2O	532 nm/ 14 ns	0.2 J/cm^2
7.	Mentho-C_{60}-Benzoyl	Toluene	70 % 532 nm/ 5 ns	0.35 J/cm^2
8.	Ag Nps/ rGO	-	80 % 532 nm/ 10 ns	0.38 J/cm^2

9	CBS	H_2O	40 % 532 nm/ 20 ns	1 J/cm^2 ⊗
10	Gold NWs	-	70% 532 nm/ 7 ns	1.56 J/cm^2
11	WSe_2	-	55.1 % 532 nm/ 6 ns	7.2 J/cm^2 ⊗
12	Graphite	-	79.7 % 532 nm/ 6 ns	15.15 J/cm^2
13	**AA2** **A-π-D-π-A**	**0.5 mM** **Toluene**	**75 %** **532 nm/** **20 ns**	**0.98 J/cm^2**

References

1 R. Gadhwal and A. Devi, *Opt. Laser Technol.*, 2021, **141**, 107144.