Electronic Supplementary Information (ESI)

Investigating Structure-Fluorescence Properties of Imidazole Fused Tetraphenylethylene AIEgens: Reversible Mechanofluorochromism and Polymer Matrix Controlled Fluorescence Tuning

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1. Materials and Methods

All solvents and chemicals were purchased from commercial suppliers (Aldrich, Alfa Aesar, Merck and HiMedia) and was used as received. Solvents were purified using appropriate drying agents when necessary. Air and moisture sensitive reactions were carried out under N_2 atmosphere. Fourier transformed infrared (FT-IR) measurements were carried out with Shimadzu IR Affinity-1S spectrophotometer with KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 MHz spectrometer equipped with a 5 mm BBFO probe. The UV−Vis absorption spectra were recorded with UV-Vis spectrophotometer (Jasco V-770) with $BaSO_4$ as reference, equipped with a diffuse reflectance accessory. Fluorescence spectra and absolute quantum yield for all compounds in the solid state were recorded using Jasco fluorescence spectrometer-FP-8300 instruments equipped with integrating sphere and calibrated light source. Mass spectra were recorded on Micromass ESI-Q-TOF mass spectrometer. Single crystal X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer using graphite monochromated MoKa (λ= 0.7107 Å) radiation at 290(2) K and the intensities were measured using ω scan with a scan width of 0.3°. A total of 606 frames per set were collected in different settings of ϕ keeping the sample to detector distance of 6.054 cm. Crystal data were reduced by SAINTPLUS, and an empirical absorption correction was applied using the package SADABS available in the Bruker software package. All the crystal structures were solved by direct methods using SHELXS-97[1] and refined by full-matrix least squares method using SHELXL-97[2] present in the program suite WinGX (Version 1.7.0).

2. FT-IR Analysis

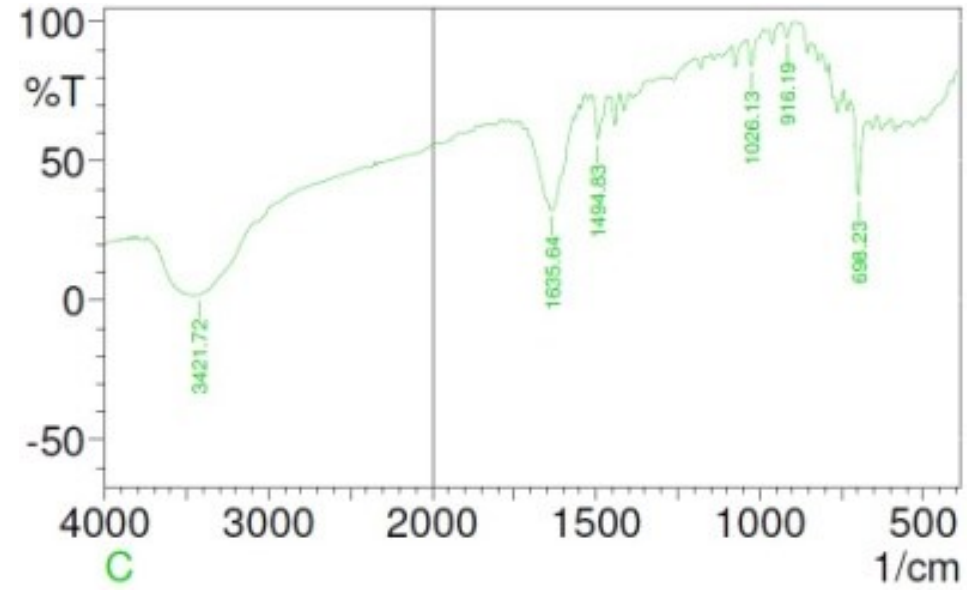


Fig. S1 FT-IR spectrum of **1**.

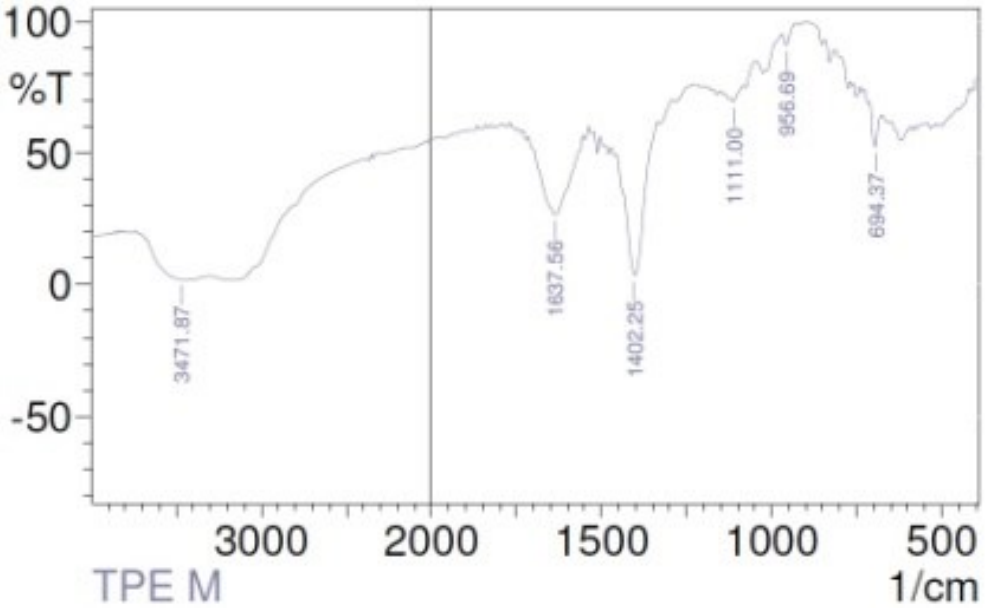


Fig. S2 FT-IR spectrum of **2**.

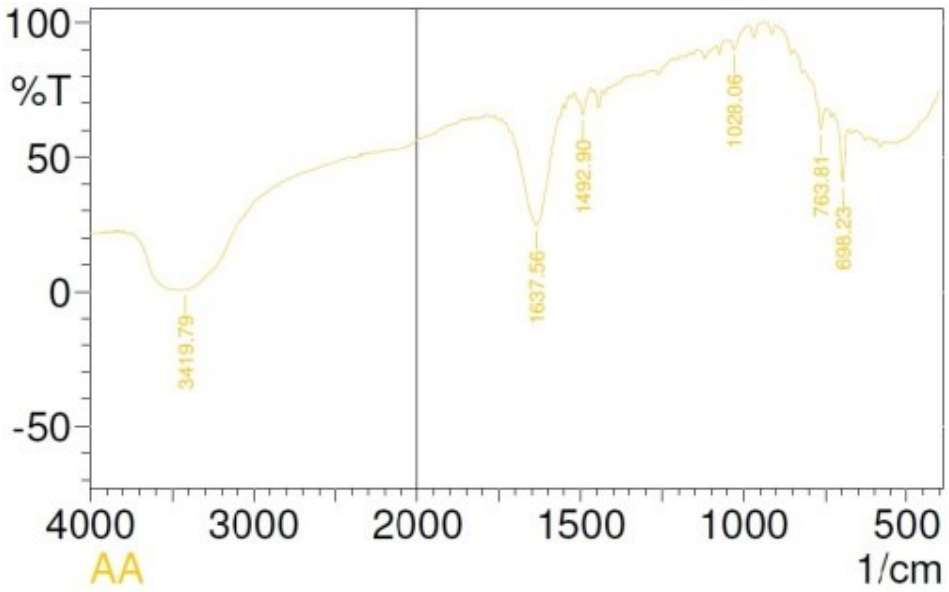


Fig. S3 FT-IR spectrum of **3**.

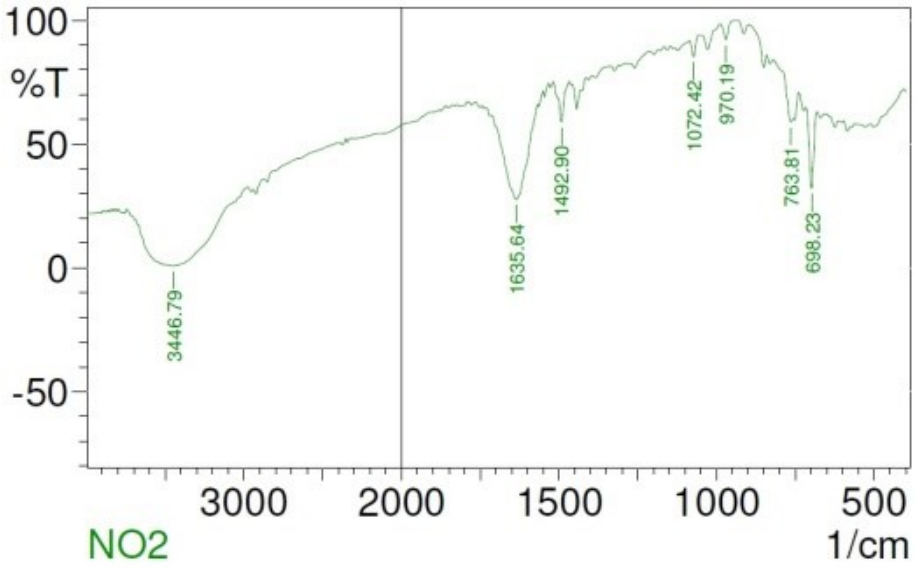


Fig. S4 FT-IR spectrum of **4**.

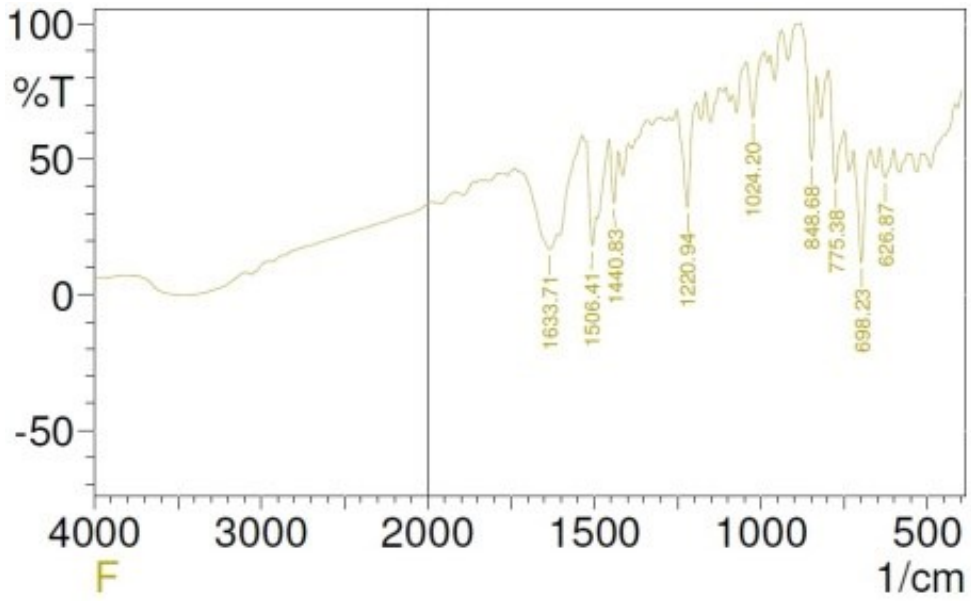


Fig. S5 FT-IR spectrum of **5**.

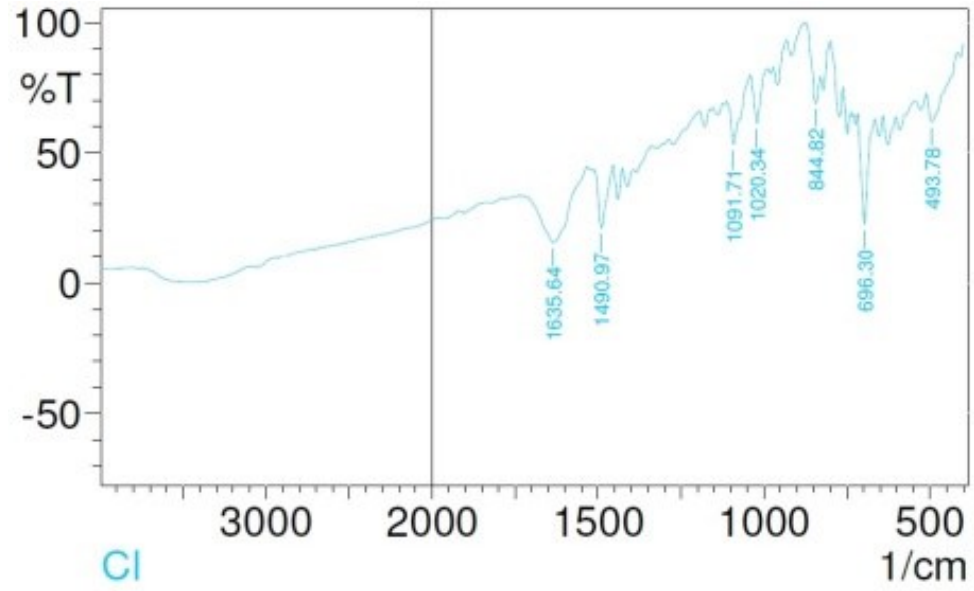


Fig. S6 FT-IR spectrum of **6**.

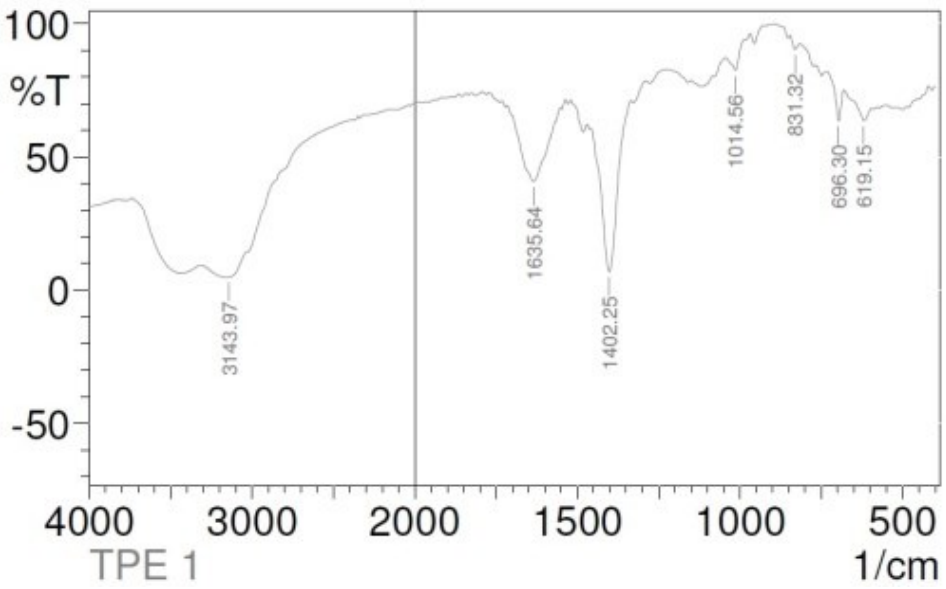


Fig. S7 FT-IR spectrum of **7**.

3. NMR Studies

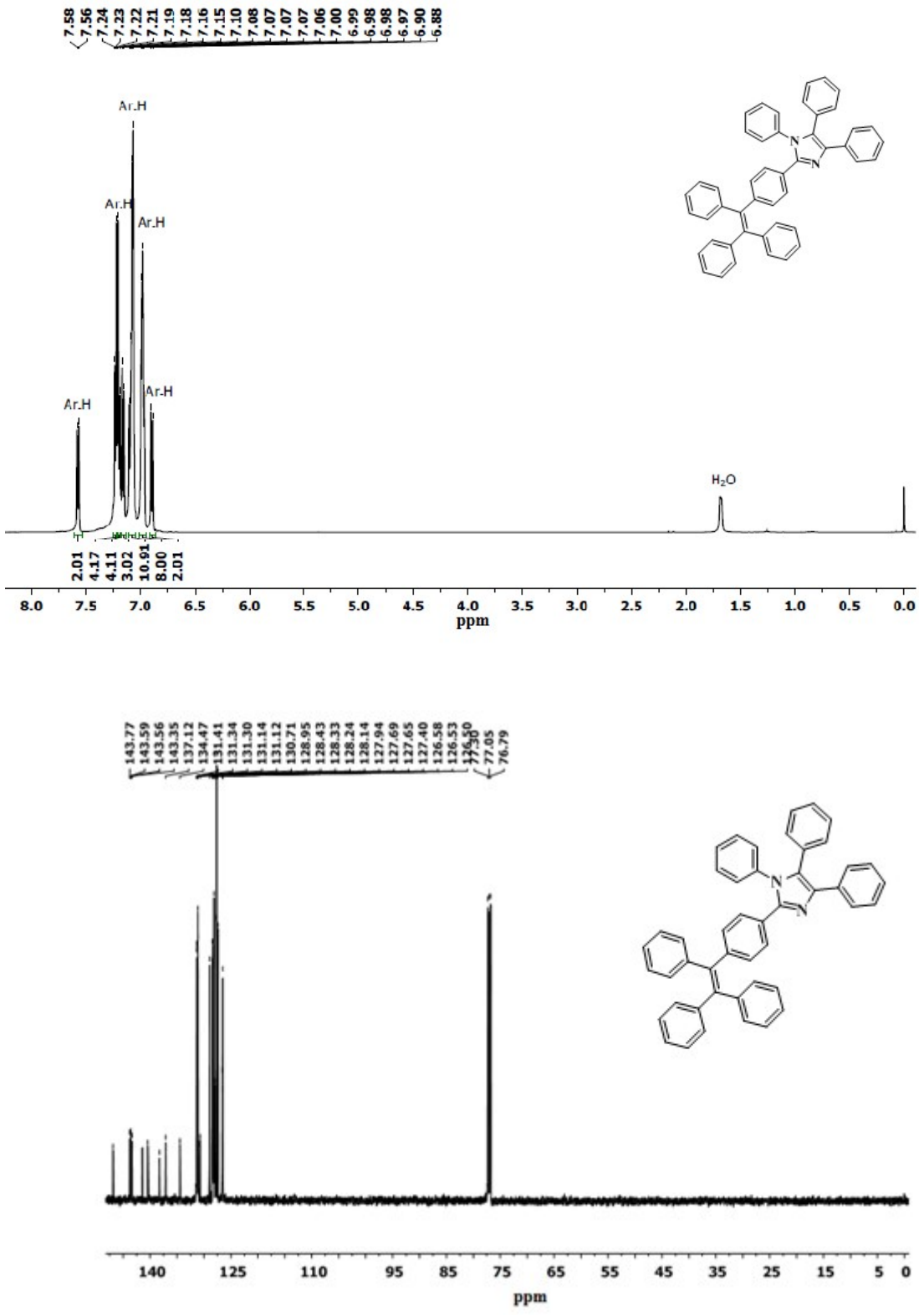
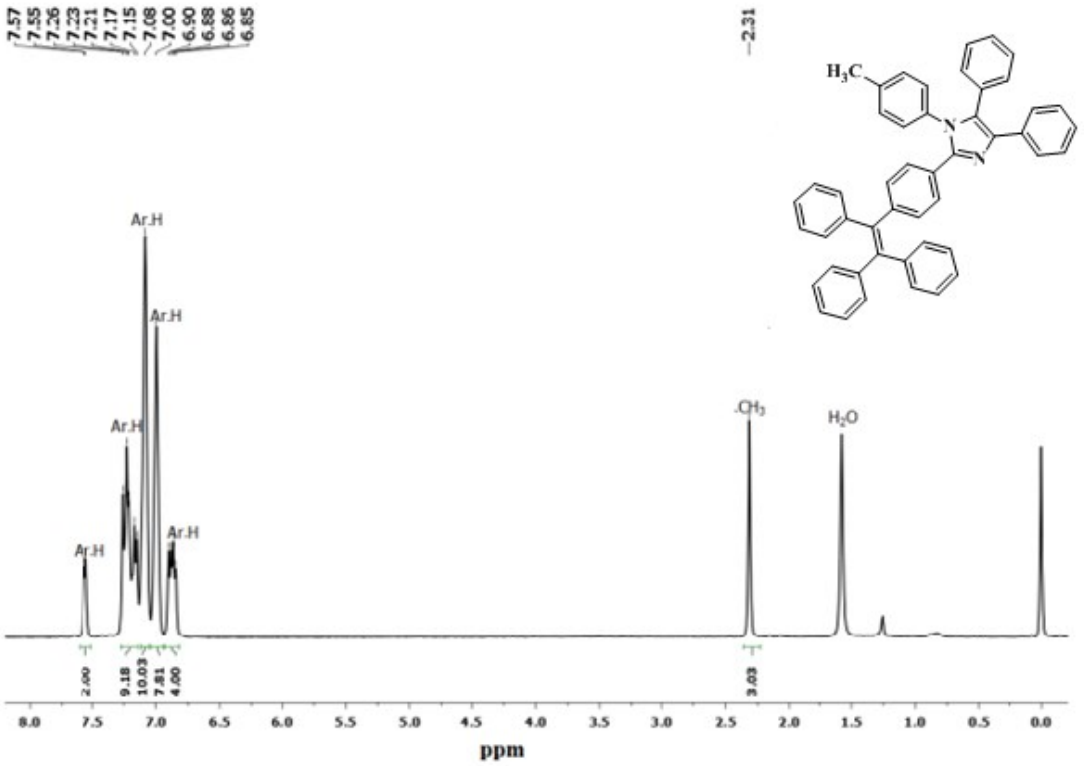


Fig. S8 ^{1}H and ^{13}C NMR spectrum of **1**.



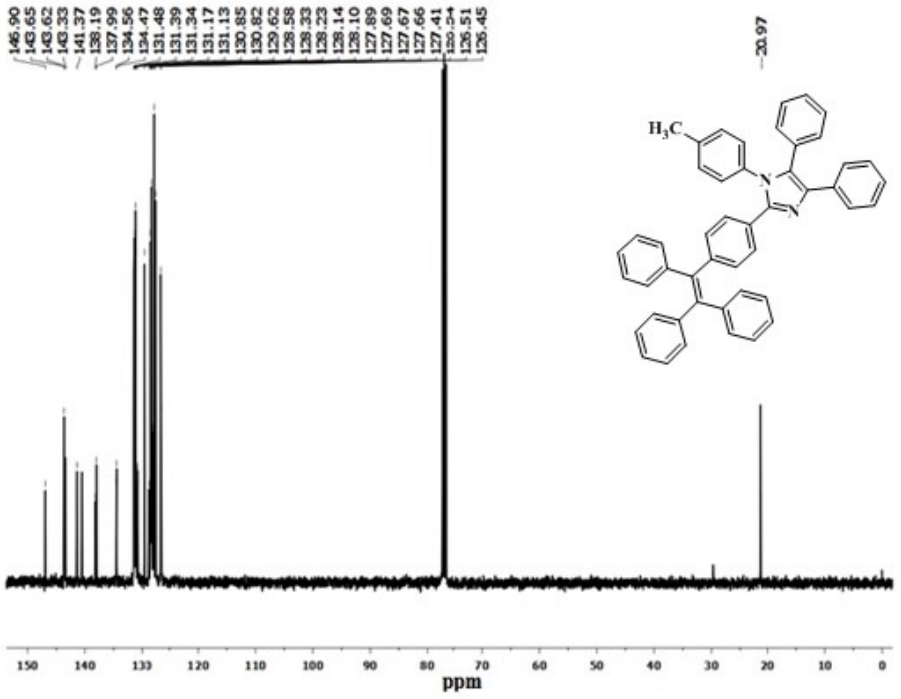


Fig. S9 ^{1}H and ^{13}C NMR spectrum of **2**.

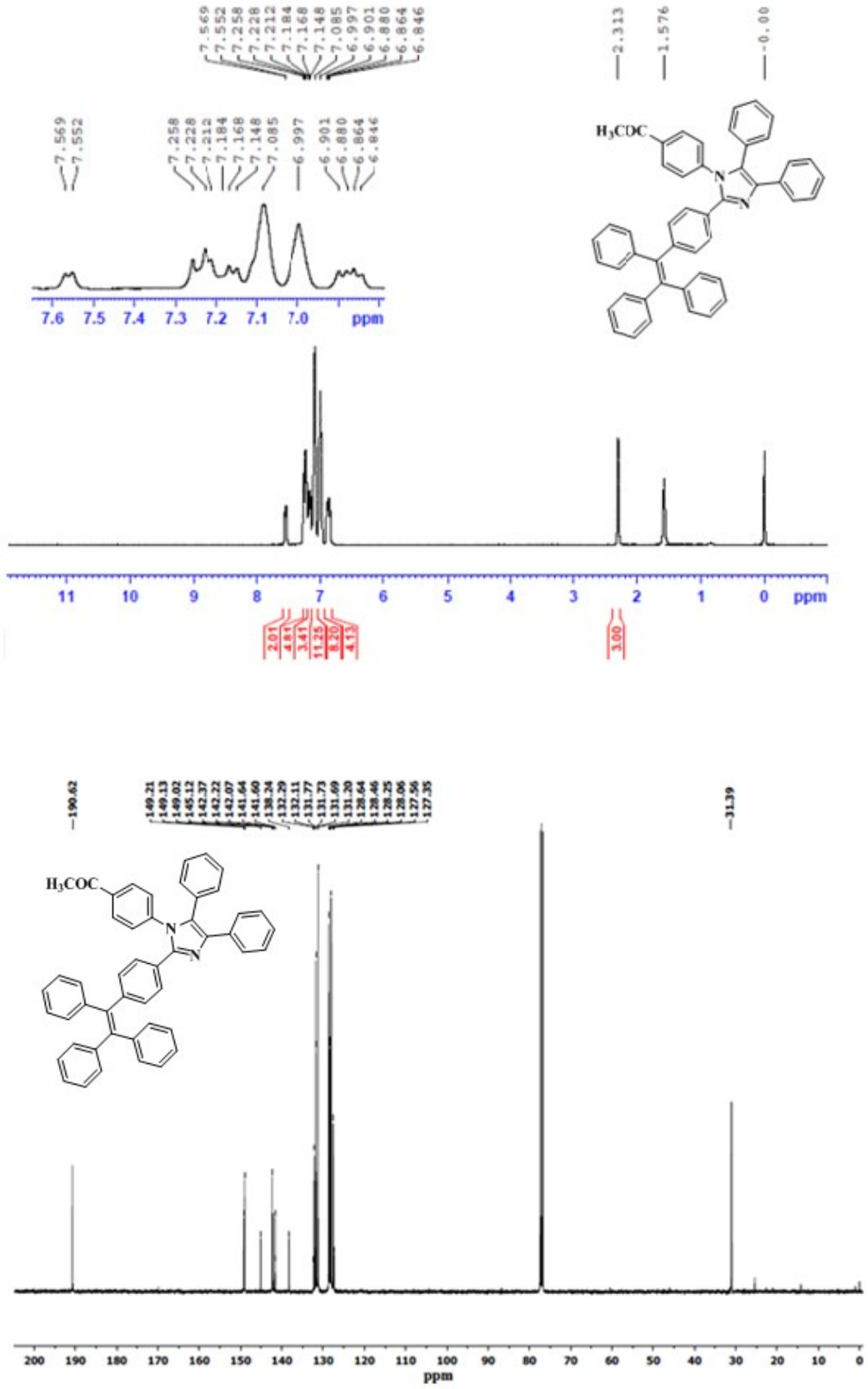


Fig. S10 ^{1}H and ^{13}C NMR spectrum of **3**.

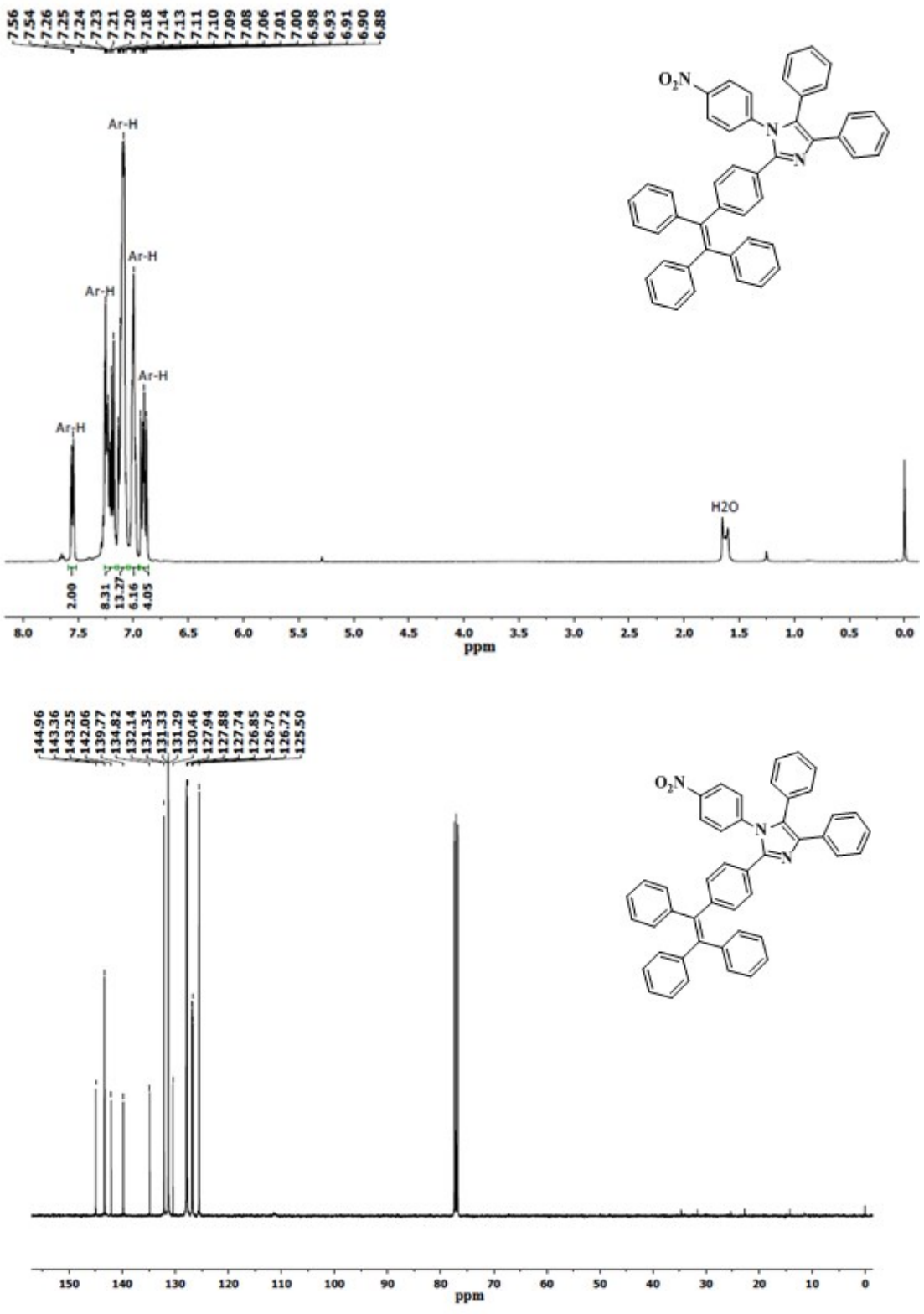


Fig. S11 ^{1}H and ^{13}C NMR spectrum of **4**.

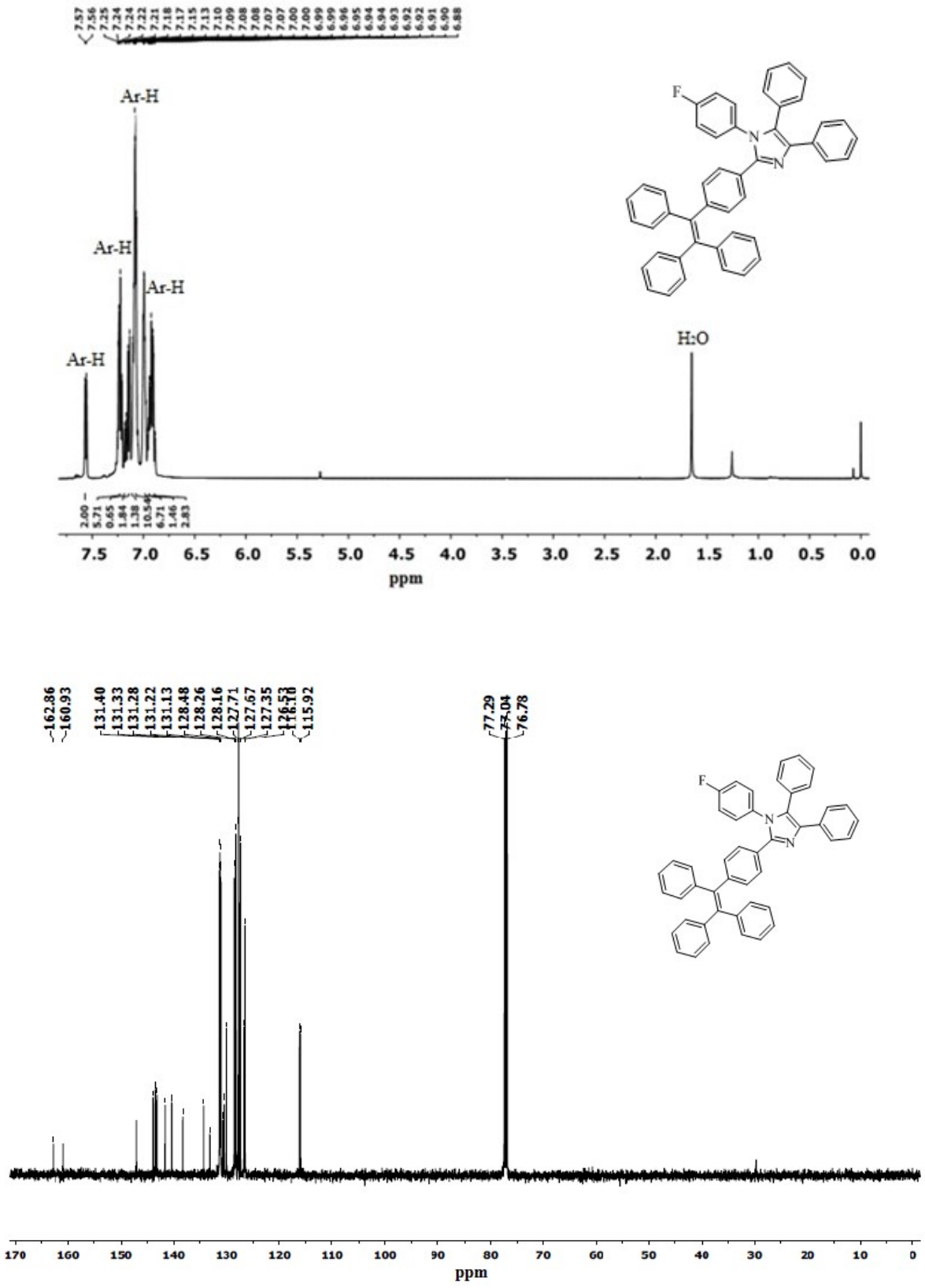


Fig. S12 ^{1}H and ^{13}C NMR spectrum of **5**.

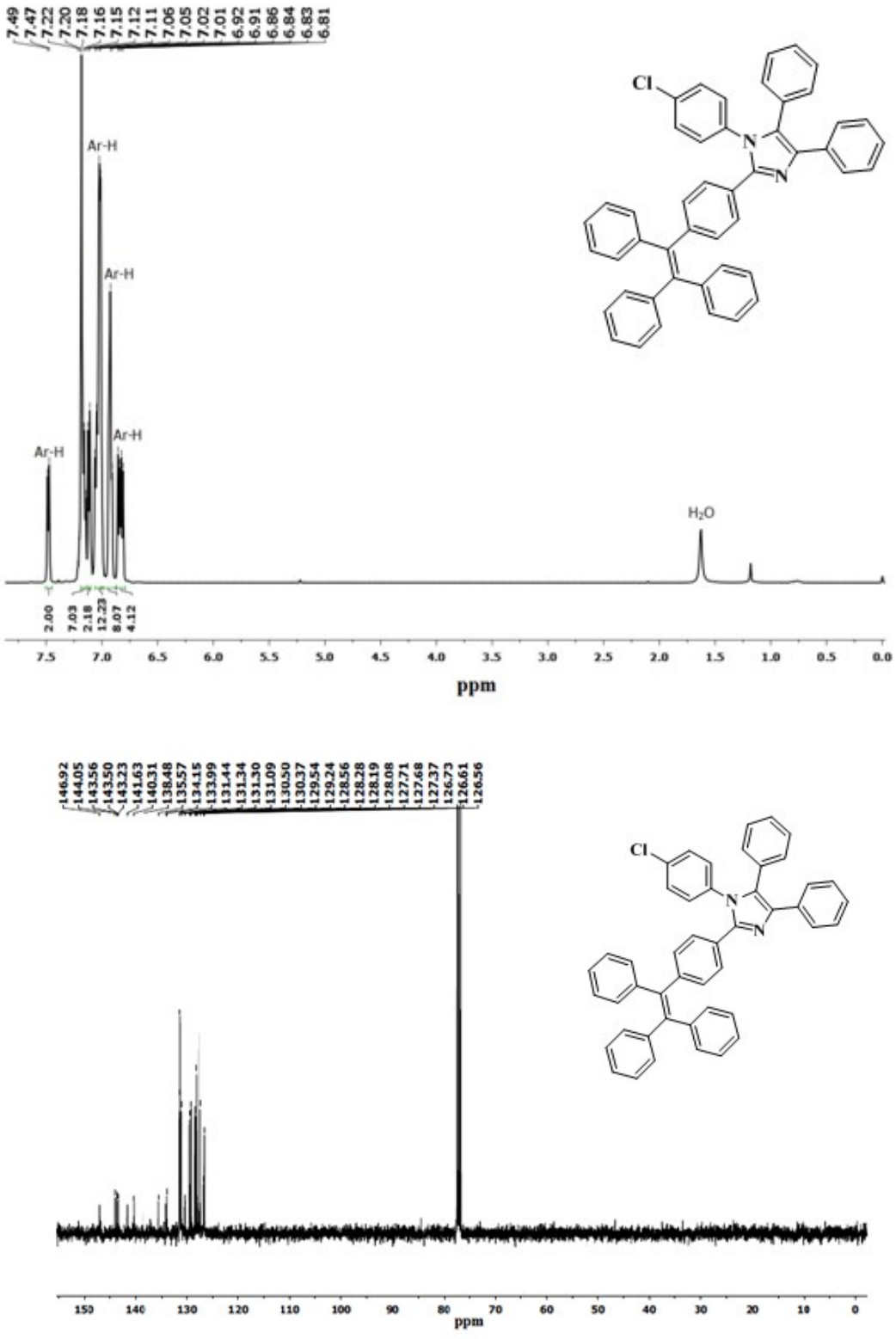


Fig. S13 ^{1}H and ^{13}C NMR spectrum of **6**.

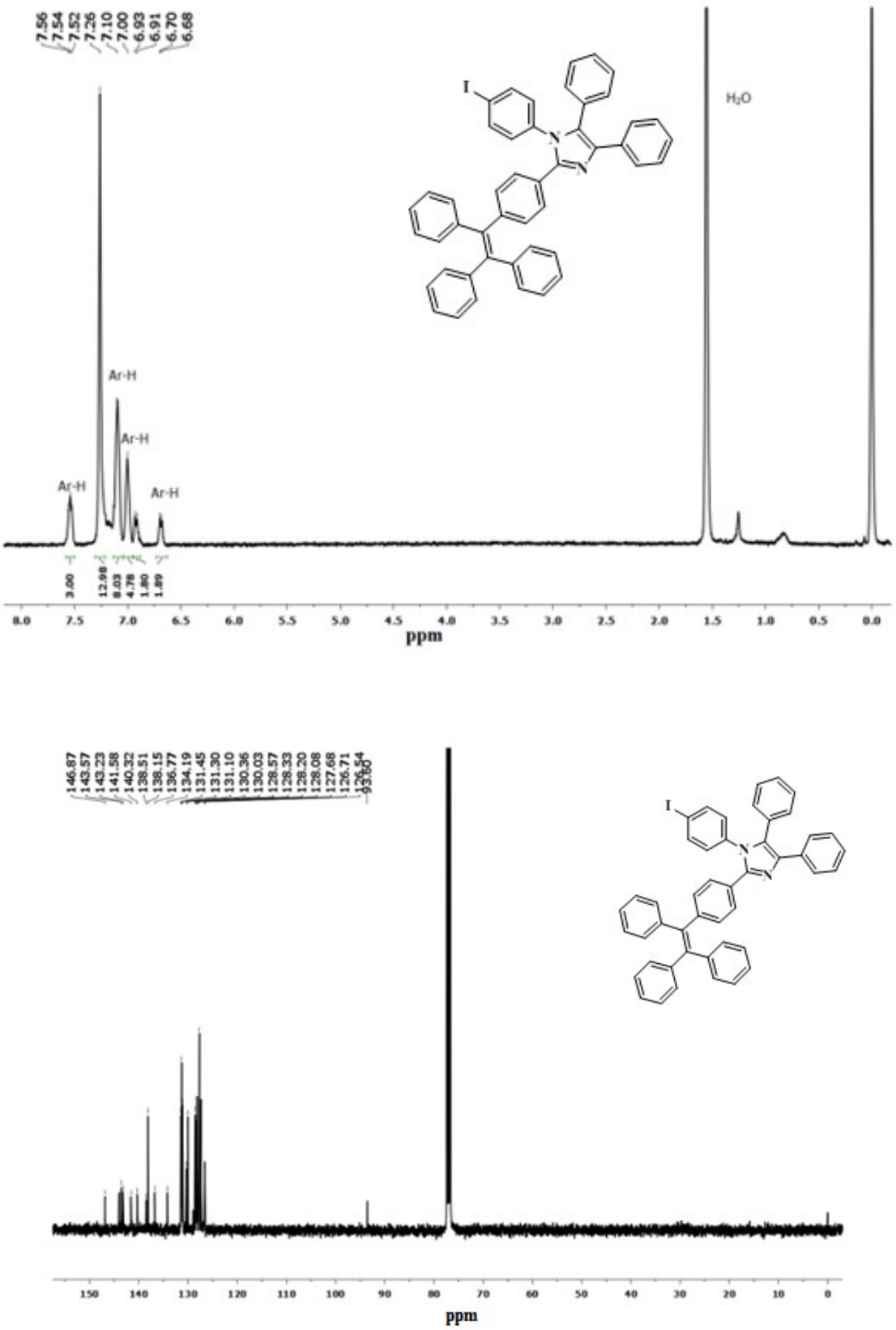


Fig. S14 ^{1}H and ^{13}C NMR spectrum of **7**.

4. Mass Analysis

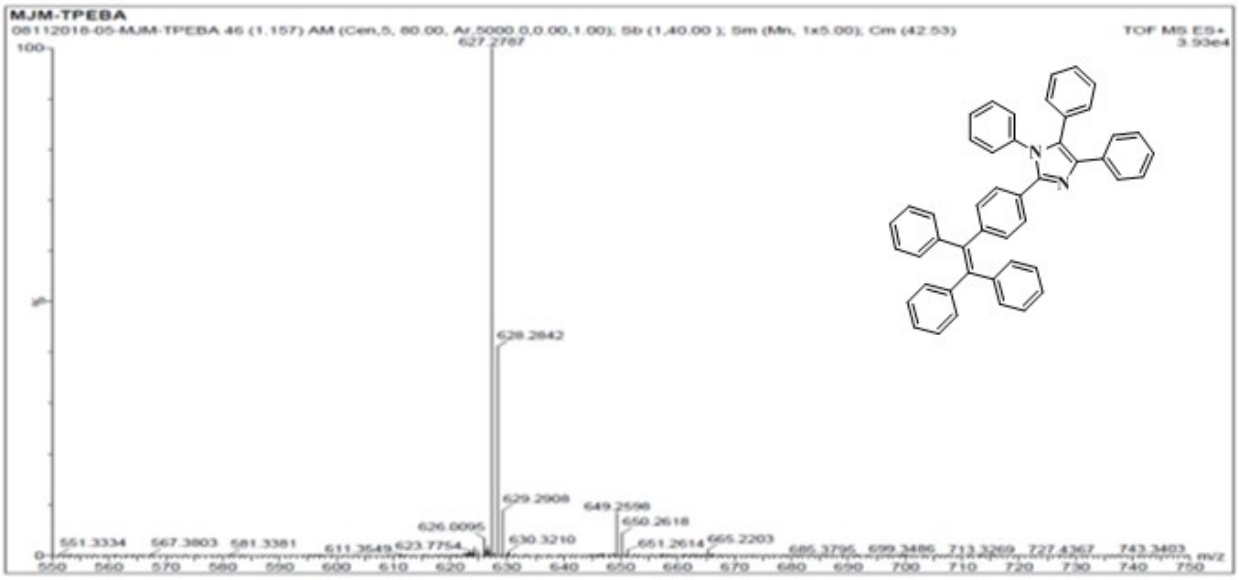


Fig. S15 Mass spectrum for **1**

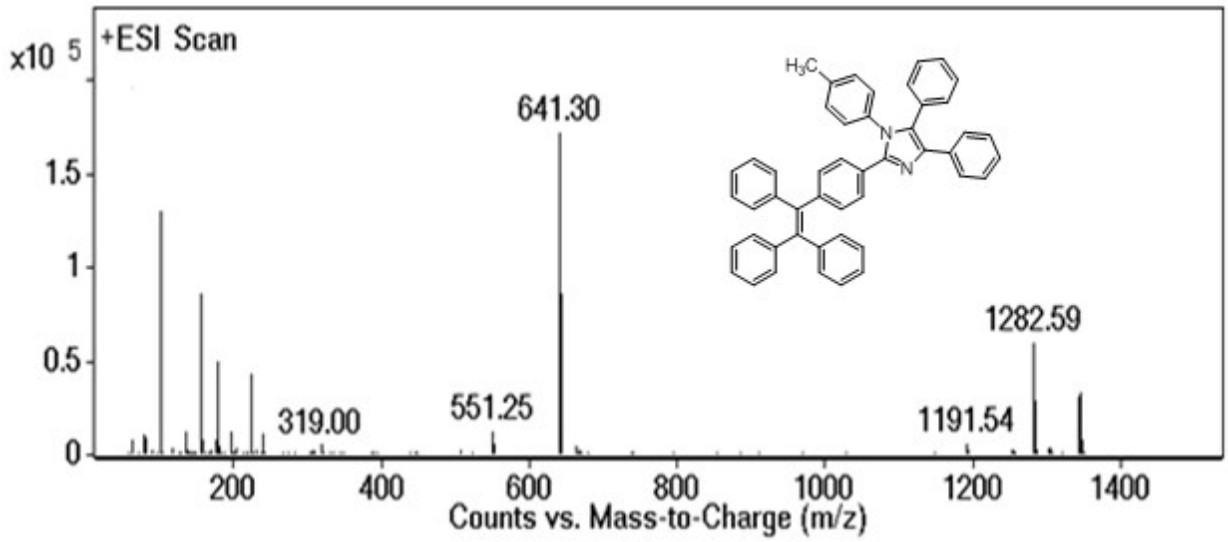


Fig. S16 Mass spectrum for **2**

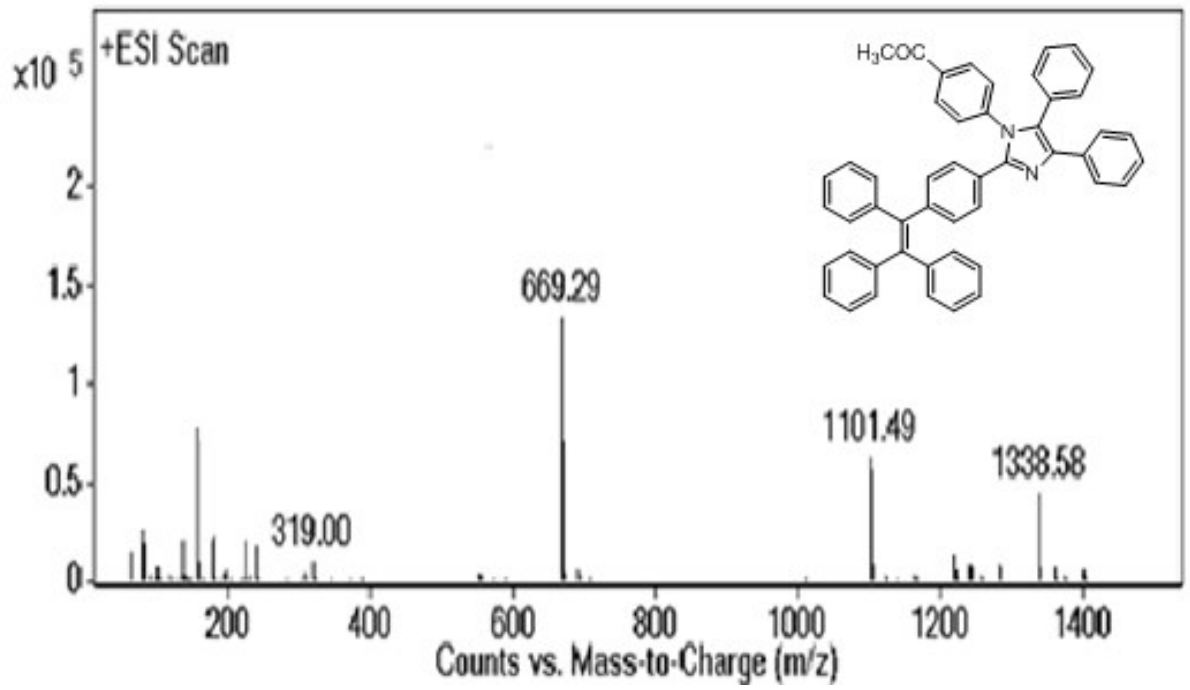


Fig. S17 Mass spectrum for **3**

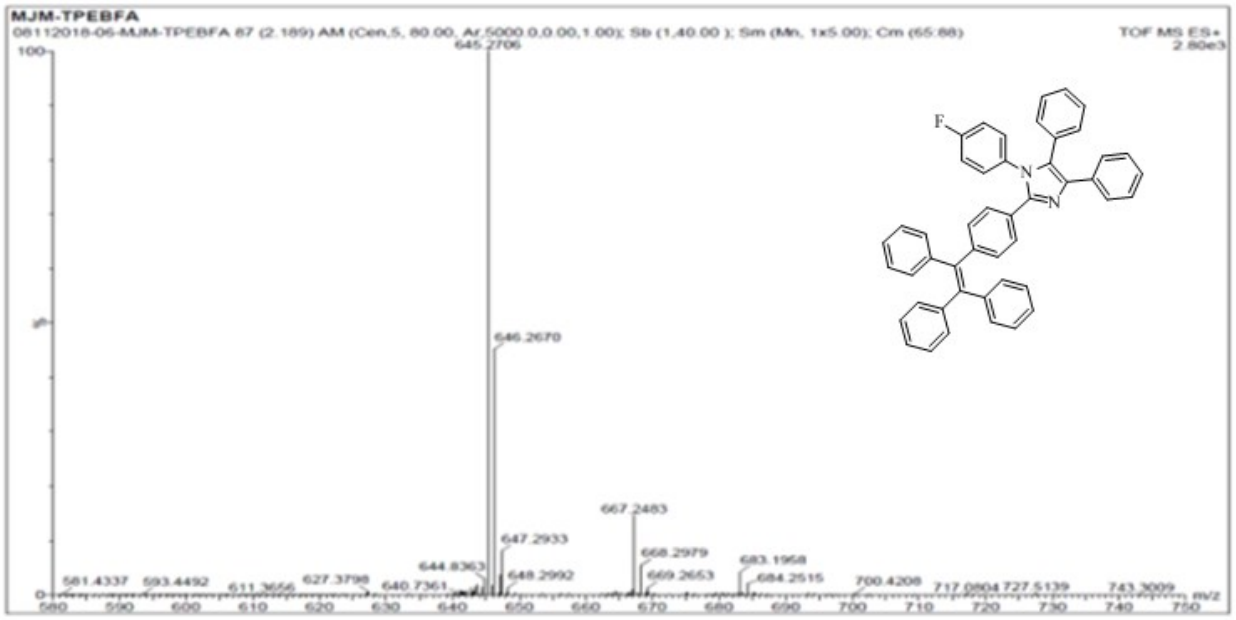


Fig. S18 Mass spectrum for **5**

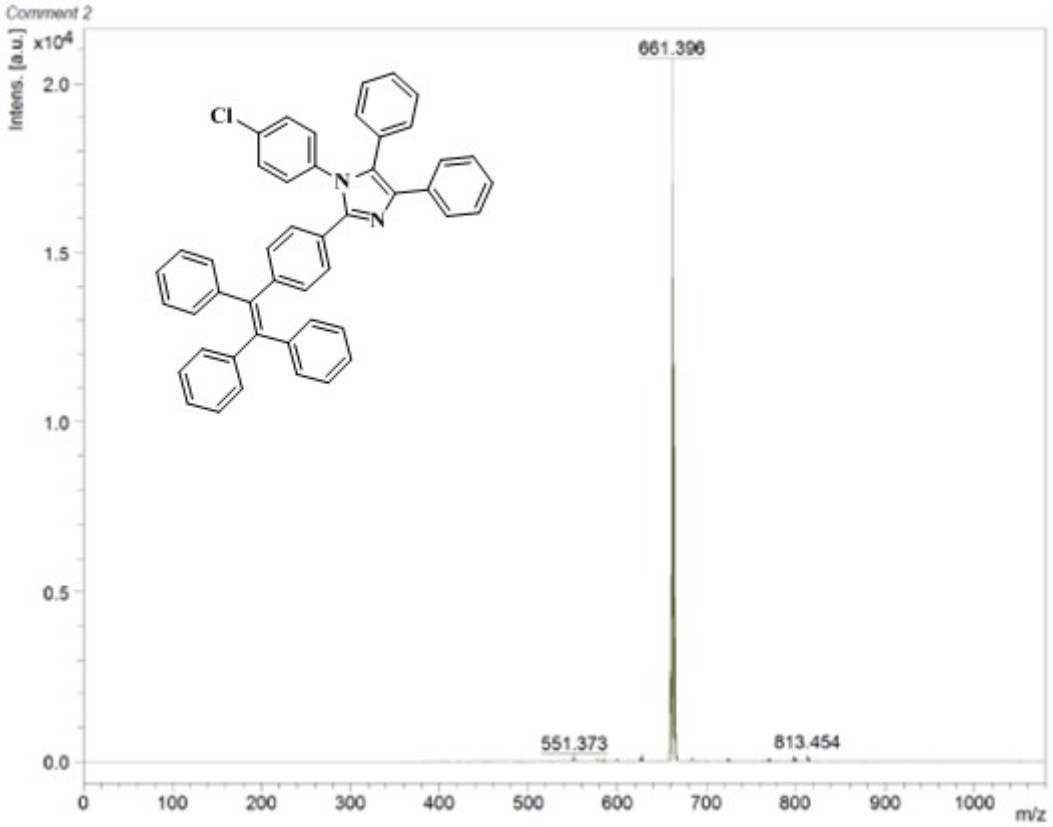


Fig. S19 Mass spectrum for **6**

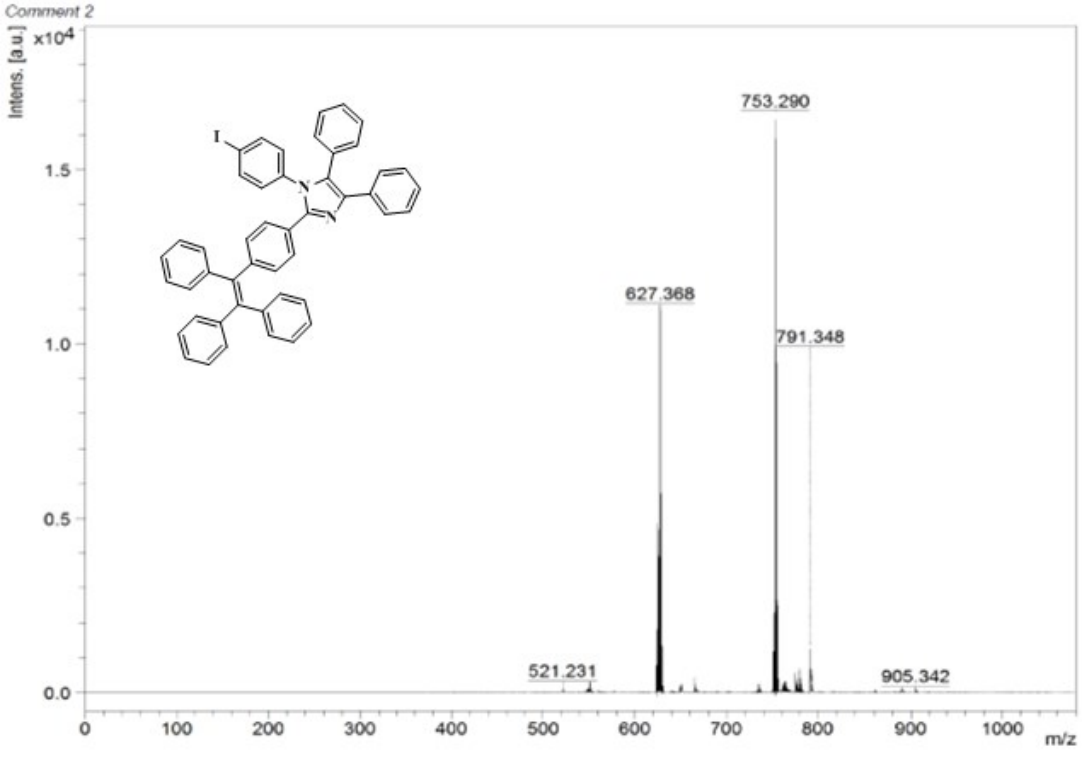


Fig. S20 Mass spectrum for **7**

5. Photophysical Properties

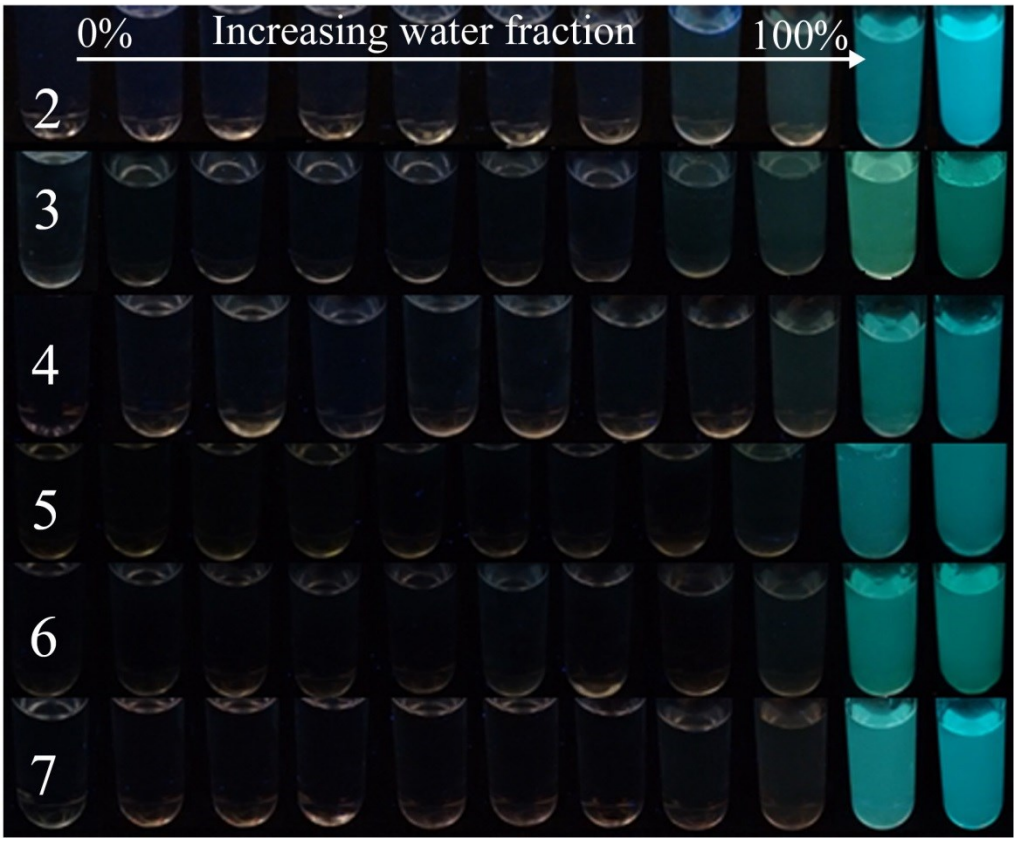


Fig. S21 Fluorescent images of **2-7** in DMF:water mixtures with different fractions of water (top) under UV light (365 nm).

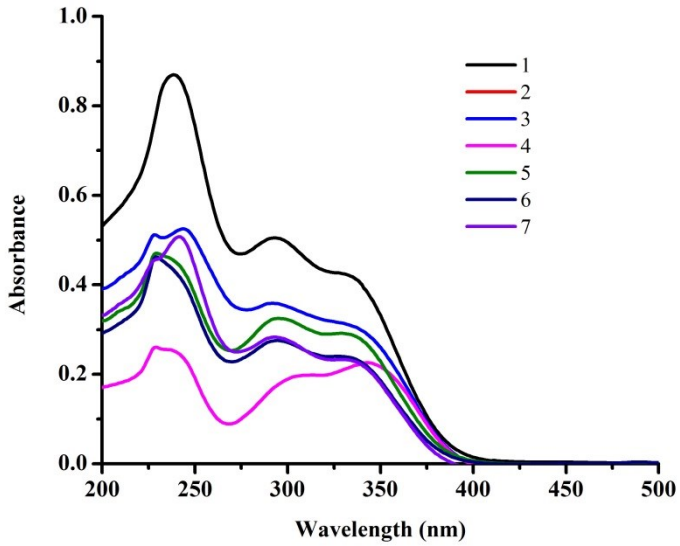


Fig. S22 Solid state UV-Vis spectrum of **1-7**

6. Thermogravimetric Analysis (TGA)

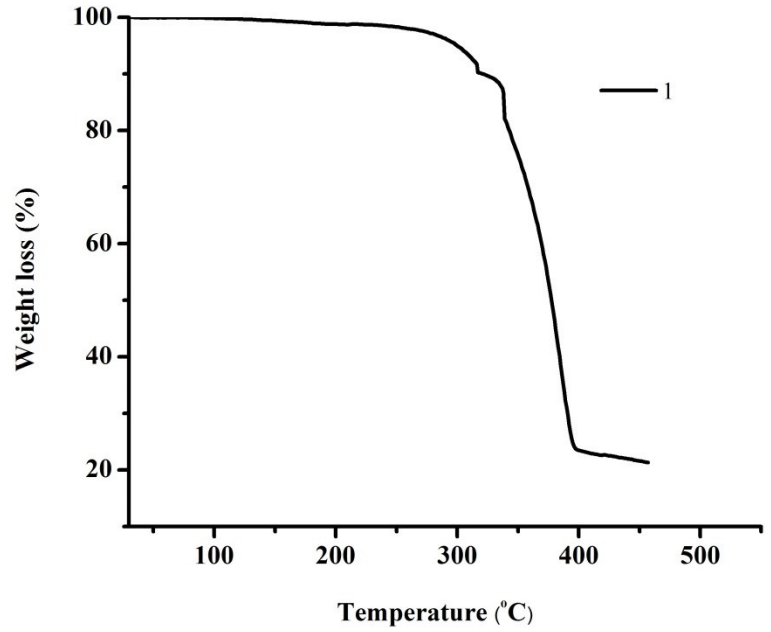


Fig. S23 Thermogravimetric analysis (TGA) curve of **1**

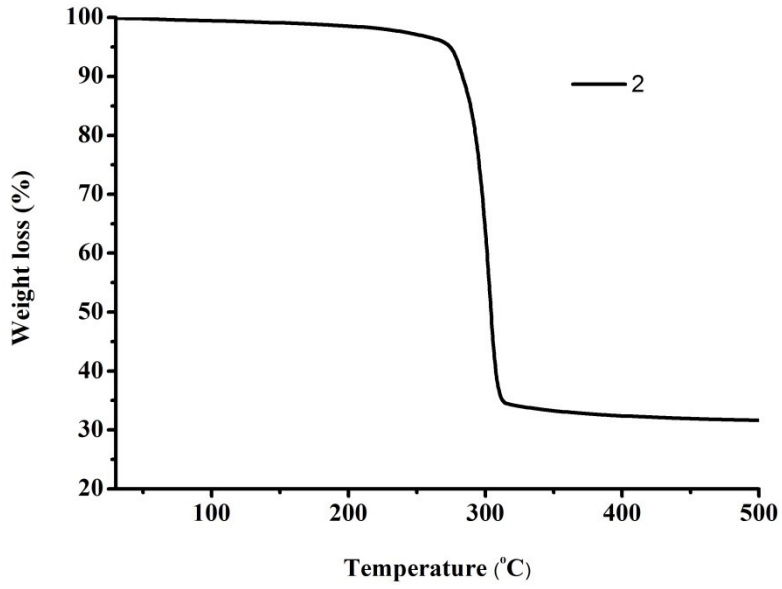


Fig. S24 Thermogravimetric analysis (TGA) curve of **2**

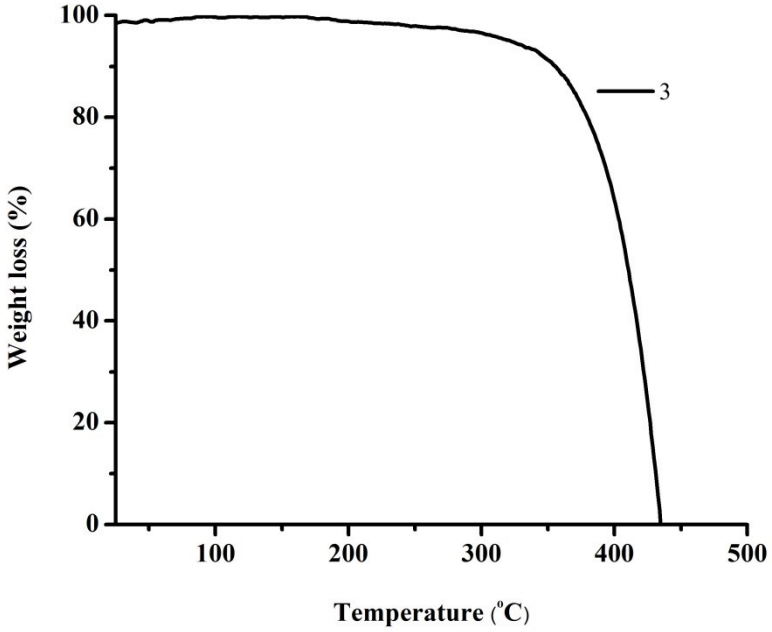


Fig. S25 Thermogravimetric analysis (TGA) crve of **3**

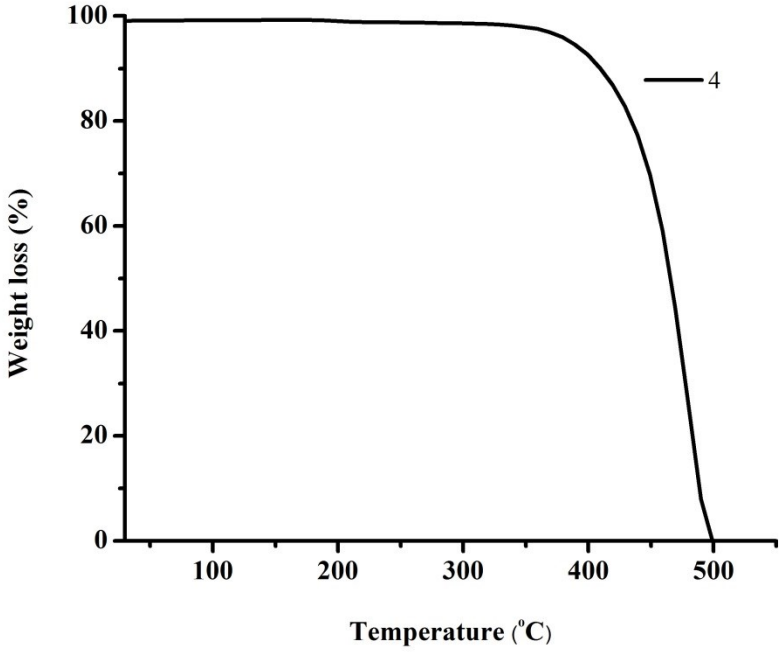


Fig. S26 Thermogravimetric analysis (TGA) curve of **4.**

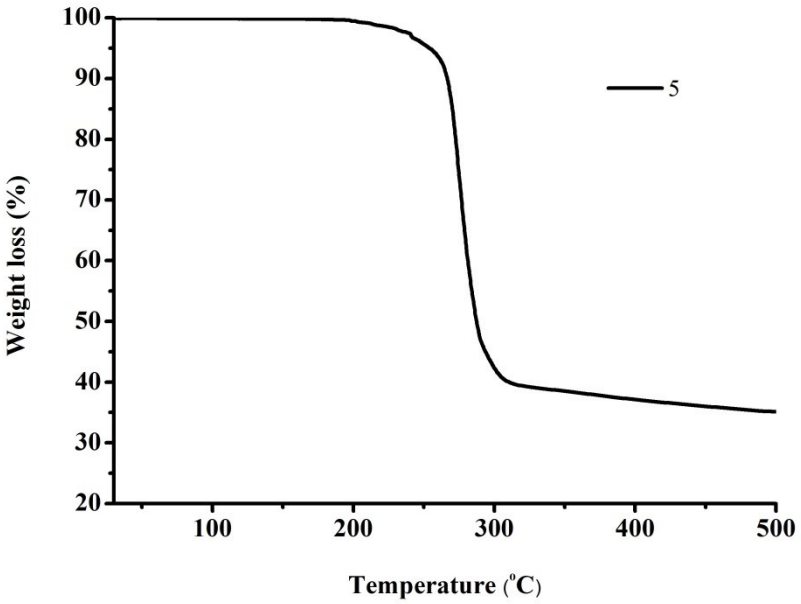


Fig. S27 Thermogravimetric analysis (TGA) curve of **5.**

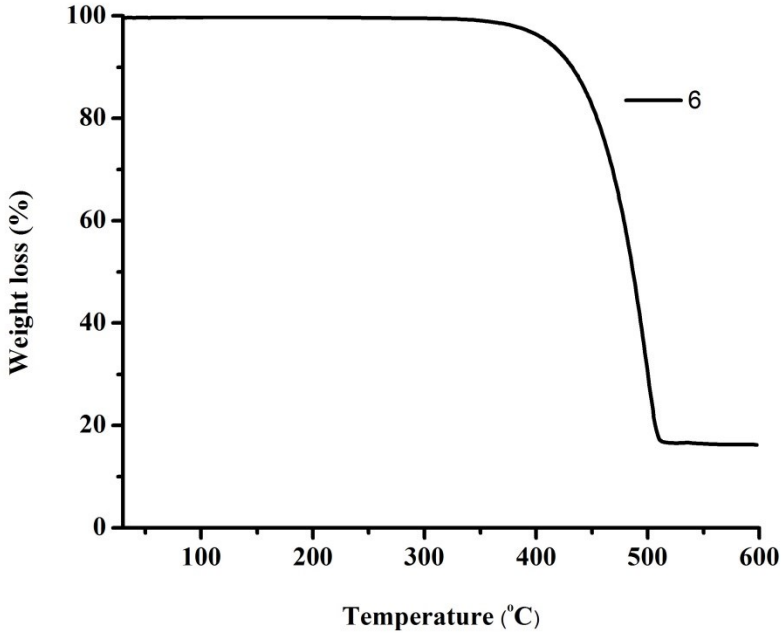


Fig. S28 Thermogravimetric analysis (TGA) curve of **6.**

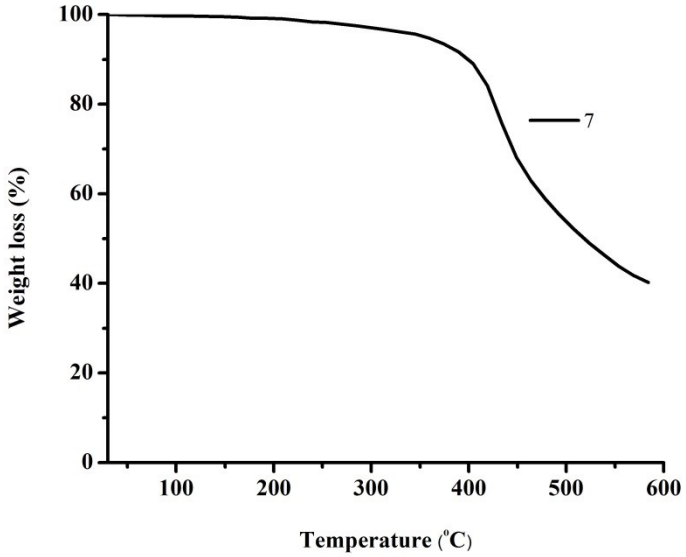


Fig. S29 Thermogravimetric analysis (TGA) curve of **7**.

7. Single Crystal X-ray Crystallography Studies

Table S1. Crystal data and structure refinement for 1, 5 and 6

Compound	1	5	6
Empirical formula	$C_{47}H_{34}N_2$	$C_{47}H_{33}N_2F$	$C_{47}H_{33}N_2Cl$
Formula weight	626.76	644.75	661.20
T [K]	273.15	273.15	273.15
Crystal system	triclinic	triclinic	triclinic
Space group	*P-1*	*P-1*	*P-1*
a, Å	9.3970(14)	9.3263(10)	9.4495(3)
b, Å	10.5684(15)	10.8791(12)	11.2688(3)
c, Å	19.829(3)	19.822(2)	18.2721(6)
α, deg	100.913(3)	98.441(4)	73.3150(10)
β, deg	91.886(4)	94.465(3)	82.2680(10)
γ, deg	113.365(3)	114.358(3)	74.3530(10)
Volume ($Å^3$)	1762.3(5)	1790.8(3)	1791.27(10)
Z	2	2	2
d_{calc} (mg/cm^3)	1.181	1.196	1.226
μ (mm^{-1})	0.068	0.073	0.143
F(000)	660.0	676.0	692.0
Crystal size/mm^3	0.42 × 0.38 × 0.28	0.33 × 0.18 × 0.1	0.38 × 0.22 × 0.2
2Θ range for data collection/°	4.214 to 56.66	4.852 to 50.564	4.926 to 50.78
Reflections collected	36182	45852	19562
Data/restraints/parameters	8792/0/443	6481/0/452	6488/0/451
Goodness-of-fit on F^2	0.967	1.085	1.046
R [I>2σ (I)]	R_1 = 0.0801 wR_2 = 0.1794	R_1 = 0.1461 wR_2 = 0.4138	R_1 = 0.0511 wR_2 = 0.1242
R [all data]	R_1 = 0.2186 wR_2 = 0.2475	R_1 = 0.1720 wR_2 = 0.4278	R_1 = 0.0603 wR_2 = 0.1303
Largest diff. Peak/hole [e $Å^{-3}$]	0.23/-0.21	0.51/-0.38	0.26/-0.45

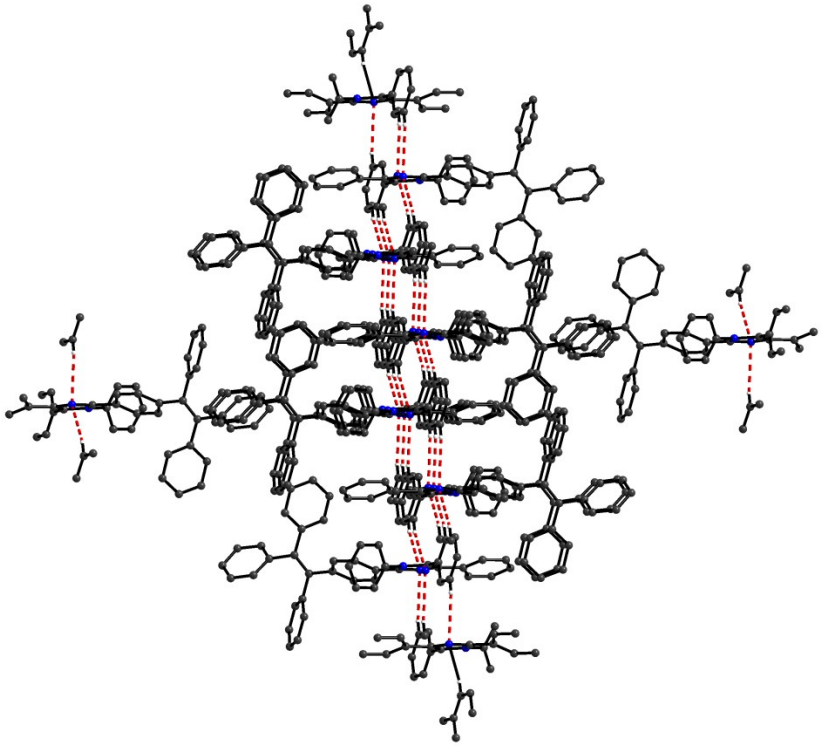


Fig. S30 The single crystal packing diagram of **1**. N···H intermolecular hydrogen bonding occurring in the crystal structure shown in dashed lines. Only H atoms participating in hydrogen bonds are shown.

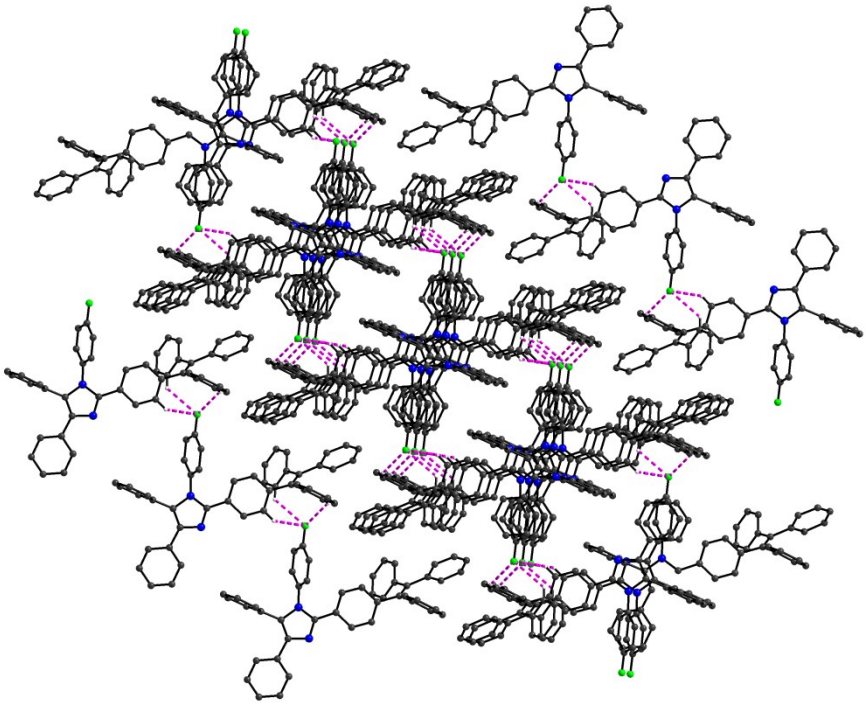


Fig. S31 The single crystal packing diagram of **5**. F···H intermolecular hydrogen bonding occurring in the crystal structure shown in dashed lines. Only H atoms participating in hydrogen bonds are shown.

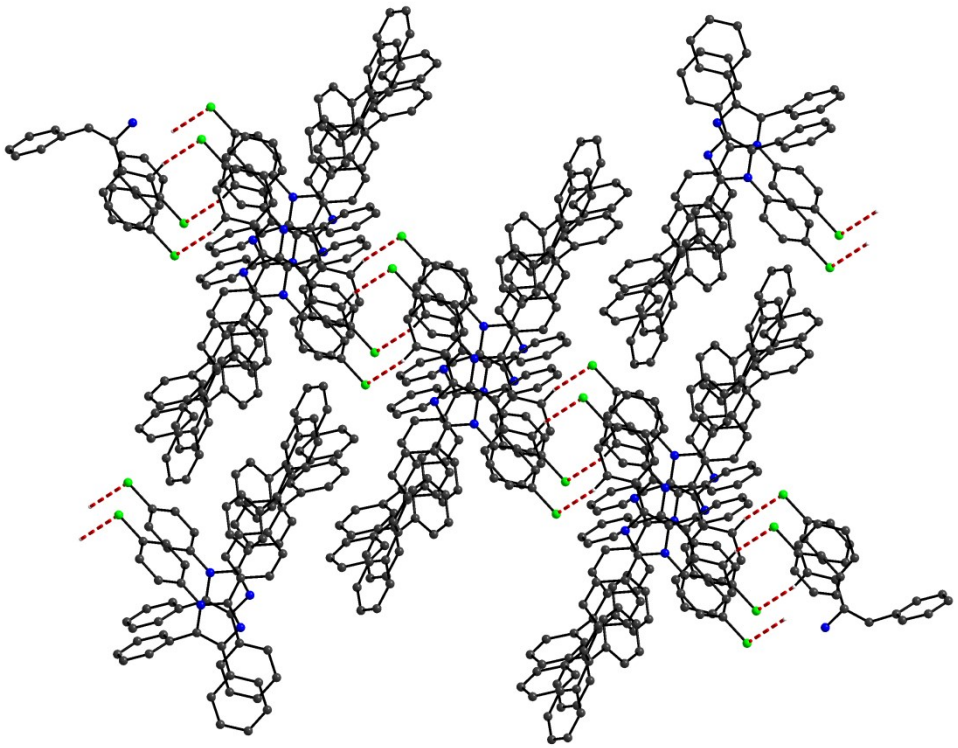


Fig. S32 The single crystal packing diagram of **6**. Cl···H intermolecular hydrogen bonding occurring in the crystal structure shown in dashed lines. Only H atoms participating in hydrogen bonds are shown.

8. Mechanofluorochromism Studies

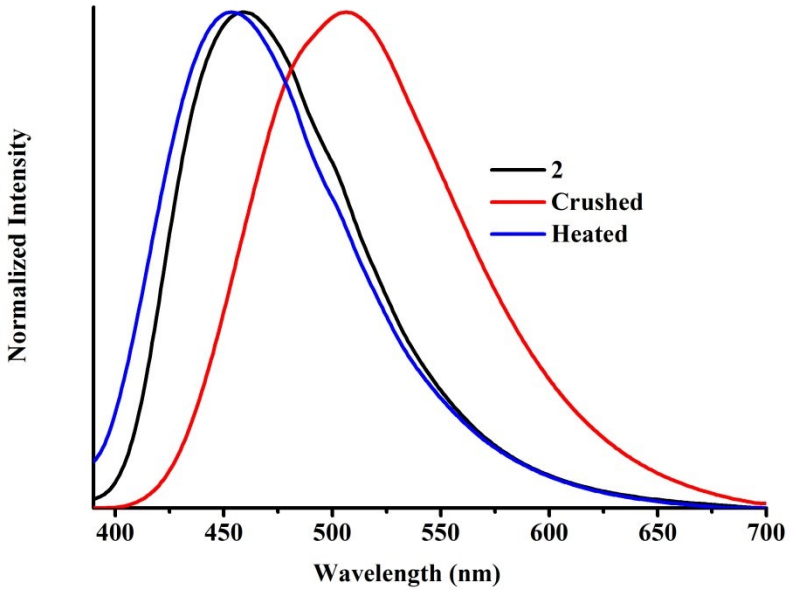


Fig. S33 Mechanofluorochromism of 2. Crushed sample heated at 120 °C.

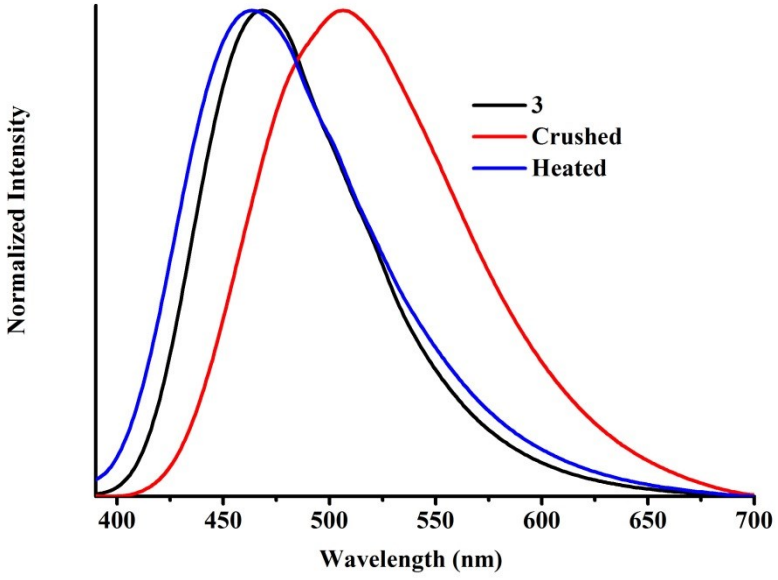


Fig. S34 Mechanofluorochromism of 3. Crushed sample heated at 120 °C.

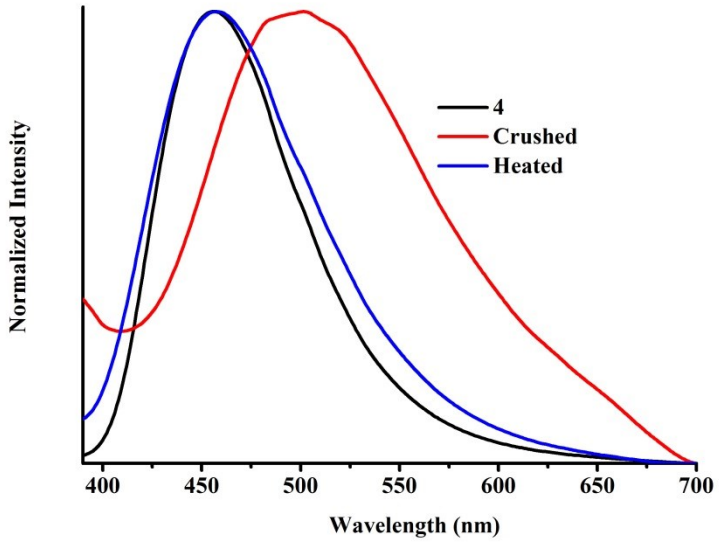


Fig. S35 Mechanofluorochromism of 4. Crushed sample heated at 120 °C.

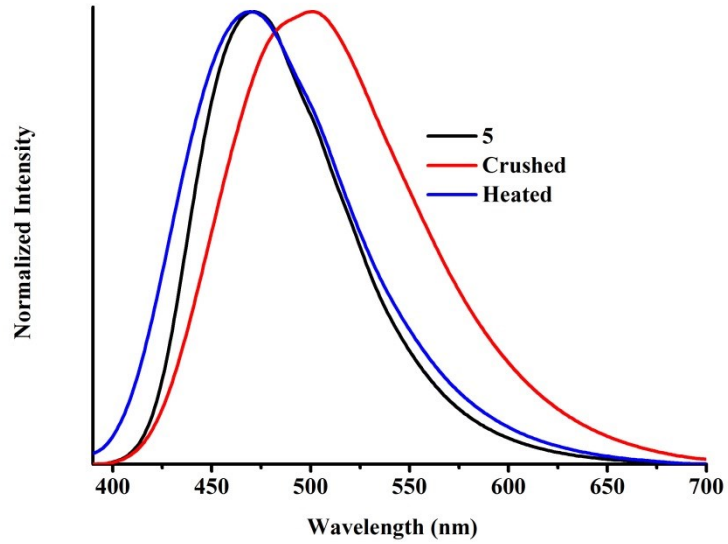


Fig. S36 Mechanofluorochromism of 5. Crushed sample heated at 120 °C.

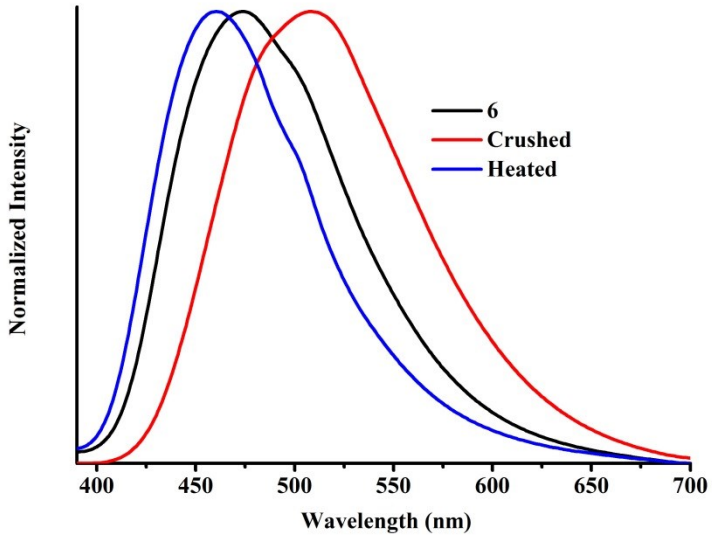


Fig. S37 Mechanofluorochromism of 6. Crushed sample heated at 120 °C.

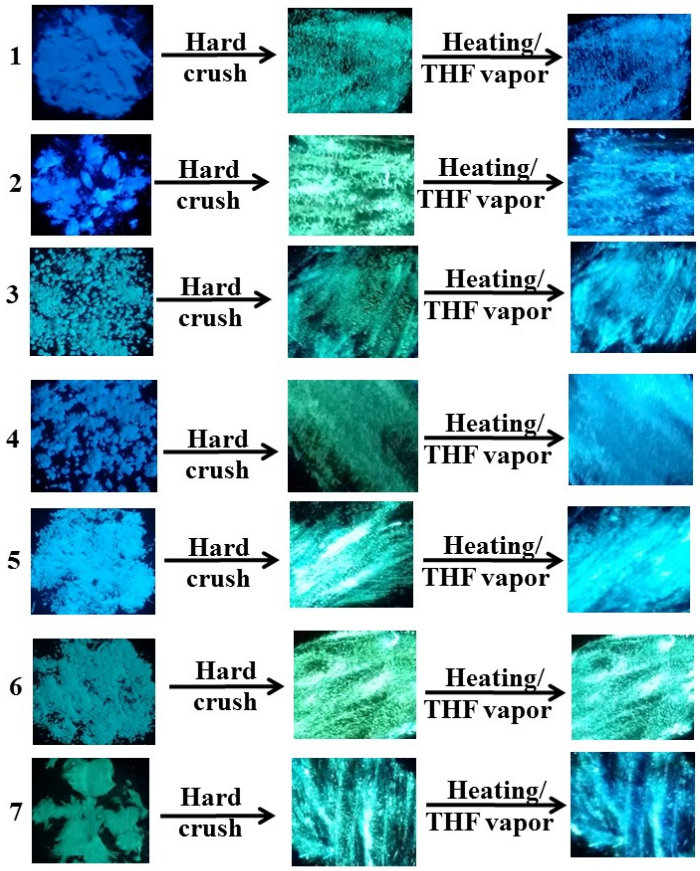


Fig. S38 Mechanofluorochromism of 1-7 upon crushing and heating/solvent exposure. Digital fluorescent images under in 365 nm of light.

9. Powder X-ray Diffraction (PXRD) Studies

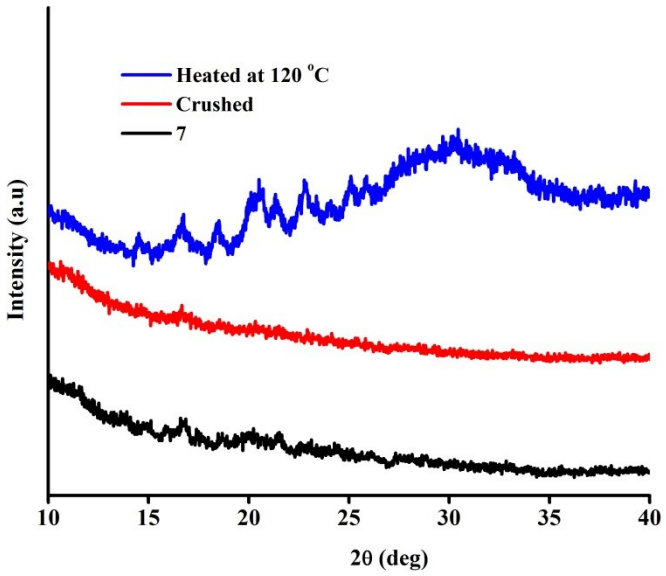


Fig. S39 PXRD pattern of **7**.

10. Acid-Responsive Fluorescence Studies

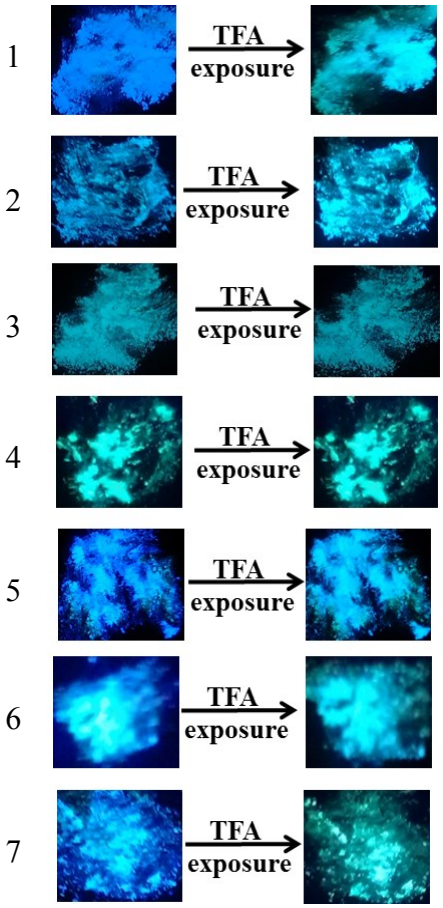


Fig. S40 Solid state fluorescent images of **1-7** before and after TFA exposure. Digital fluorescent images were taken under UV-light of 365 nm.

10. References

1. G. M. Sheldrick, SHELXS-97: *A Program for Structure Solution*, University of Göttingen, Germany, 1997.
2. G. M. Sheldrick, SHELXL-97: *A Program for Structure Refinement*, University of Göttingen, Germany, 1997.