Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary information

Mechanoluminescence and aggregation-enhanced emission (AEE) of an In-MOF based on 9,9'-diphenyl-9*H*-fluorene tetraacid linker

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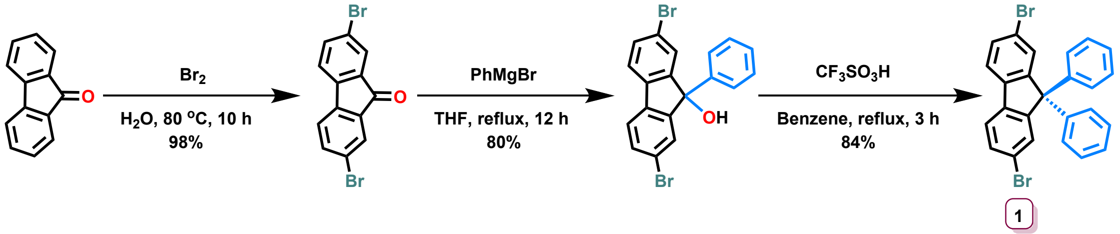
CONTENTS

General aspects

All the starting materials and reagents were procured from commercial sources. The progress of reactions was monitored by analytical thin layer chromatography (TLC) using aluminium sheets pre-coated with silica gel (Merck TLC silica gel 60F_{254}). Purification of products was carried out using column chromatography using silica gel of 100–200 mm mesh (Acme, Mumbai, India). ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL Lambda spectrometer. IR spectra were recorded with a Bruker Vector 22 FT-IR spectrophotometer. High-resolution mass spectroscopic (HRMS) analyses were carried out using Waters ESI-QTOF instrument. TGA was performed on a Mettler–Toledo apparatus under N_2 gas atmosphere with a heating rate of 10 ^{o}C/min. Powder X-ray diffractograms (PXRDs) were recorded on a Bruker D8 Advance series 2 powder X-ray diffractometer. XPS analyses were used to investigate chemical compositions of the ground MOF by using an X-ray photoelectron spectroscopy module (PHI 5000 Versa Prob II, FEI Inc.). SEM images were recorded on a Nova Nano SEM 450 FE-SEM scanning electron microscope.

Syntheses and characterization of precursors

Synthesis of 2,7-dibromo-9,9'-diphenyl-9*H*-fluorene 1



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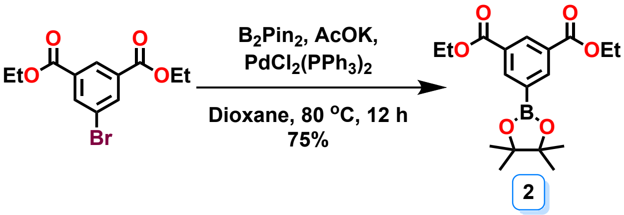
To the suspension of fluorenone (1.0 g, 5.55 mmol) in 20 mL of distilled water, bromine (4.4 g, 27.7 mmol) was added dropwise over a period of 10 min at 0 ^{o}C. Later, the temperature of the reaction mixture was slowly raised to 80 ^{o}C and stirring was continued at this temperature for a period of 10 h. After completion of the reaction as monitored by TLC analysis, the reaction mixture was cooled to rt and quenched with ice cold Na_2SO_3 solution. The resultant precipitate was filtered, washed thoroughly with water and dried. 2,7-Dibromofluorenone[1] was isolated as yellow solid by silica gel column chromatography using $CHCl_3$-pet. ether (10:90) as an eluent in 98% yield. (1.8 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 1.2 Hz, 8.4 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.76 (s, 2H).

A freshly prepared phenyl magnesium bromide, prepared from bromobenzene (1.0 g, 6.3 mmol), activated magnesium turnings (0.201 g, 8.3 mmol) and catalytic amount of 1,2-dibromoethane in THF (5 mL), was added to a solution of 2,7-dibromofluorenone (1.0 g, 2.9 mmol) in 20 mL THF at rt. Subsequently, the reaction mixture was heated at reflux for 12 h. After completion of the reaction, the reaction mixture was cooled to rt, quenched with 10% HCl, and the organic material was extracted with ethyl acetate multiple times. The combined organic extract was dried over anhyd Na_2SO_4 and concentrated over rotary evaporator. The crude product was subjected to silica-gel column chromatography using EtOAc-pet. ether (20:80) as an eluent to afford 2,7-dibromo-9-phenyl-9H-fluoren-9-ol[2] as an off-white solid in 80% yield (0.98 g). ^1H NMR (400 MHz, $CDCl_3$) δ 2.5 (s, 1H), 7.35-7.27 (m, 5H), 7.43 (bs, 2H), 7.5 (d, J = 1.2 Hz, 4H).

To a solution of 2,7-dibromo-9-phenyl-9*H*-fluoren-9-ol (1.0 g, 2.4 mmol) in 30 mL of benzene contained in a 100 mL round bottom flask was added CF_3SO_3H (0.72 g, 4.8 mmol) dropwise under N_2 atmosphere, and the reaction mixture was heated at reflux for 3 h. After completion of the reaction, the reaction mixture was cooled to rt, and the solvent was removed in vacuo. The organic material was extracted with $CHCl_3$ multiple times and the combined extract was washed thoroughly with aqueous $NaHCO_3$ to remove CF_3SO_3H. It was further dried over anhyd Na_2SO_4 and evaporated to dryness under reduced pressure. The crude product was purified by silica-gel column chromatography using hexane as the eluent to afford pure 2,7-dibromo-9,9'-diphenyl-9H-fluorene (**1**)[2] as an off-white solid in 84% yield (0.96 g). ^1H NMR (400 MHz, $CDCl_3$) δ 7.14-7.17 (m, 6H), 7.26-7.27 (m, 4H), 7.48 (d, J = 2 Hz, 2H), 7.51 (s, 2H), 7.60 (d, J = 8.8 Hz, 2H).

Synthesis of bis(3,5-ethoxycarbonyl)phenylboronate ester 2



A 100 mL two-necked round bottom flask was charged with diethyl 5-bromoisophthalate (1.0 g, 3.3 mmol), bis(pinacolato)diboron (0.93 g, 3.6 mmol), $PdCl_2(PPh_3)_2$ (0.14 g, 0.2 mmol) and AcOK (0.36 g, 3.6 mmol) in 20 mL of dioxane under N_2 atmosphere, and heated at 80 °C for 12 h. After completion of the reaction, the reaction mixture was cooled to rt and passed through a celite pad to remove the inorganic impurities, the latter was thoroughly washed with EtOAc. The filtrate was evaporated under reduced pressure to yield crude product material. Silica-gel column chromatography of the latter using EtOAc:pet. ether (30:70) as an eluent to afford the product bis(3,5-carboethoxy)phenylboronate ester **2**[3] as an off-white solid in 75% yield (0.87 g).^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 12H), 1.41 (t, *J*= 6.8 Hz, 6H), 4.41 (q, *J* = 7.2 Hz, 4H), 8.61 (d, *J* = 1.6 Hz, 2H), 8.75 (t, *J* = 2 Hz, 1H).

Single crystal X-ray structure determination

The data collection and structure refinements were done as described earlier.[4] Hydrogens were fixed geometrically and were treated as riding on their non-hydrogens. They were refined isotropically, while all non-hydrogens were subjected to anisotropic refinement. To treat the highly disordered solvent molecules within the pores of the MOF, solvent mask in OLEX2[5] was applied. Topological analysis of the 3D network, i.e., In-MOF, was carried out using ToposPro program.[6]

Table S1 Crystal data of **In-DPF**

Identification code	**In-DPF**
Empirical formula	$C_{44}H_{29}In_2NO_{12}$
Formula weight	993.32
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	11.241 (6)
b (Å)	13.279 (7)
c (Å)	18.002 (10)
α (deg)	86.46 (2)
β (deg)	75.80 (2)
γ (deg)	81.05 (2)
Volume ($Å^3$)	2572.6 (2)
Z	2
Density (calculated) (g/cm^3)	1.282
Absorption coefficient (mm^{-1})	0.948
F(000)	988.0
2θ range for data collection (°)	5.378 to 56.662°
Index ranges	$-14 \leq h \leq 15$, $-17 \leq k \leq 17$, $-23 \leq l \leq 24$
Reflections collected	40762
Independent reflections	12768 [R_{int} = 0.0551, R_{sigma}= 0.0640]
Completeness to theta (24.995°)	100%
Absorption correction	None[2]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12768/0/516
Goodness-of-fit on F^2	1.00
Final R indices [I>2sigma(I)]	R_1 = 0.0523, wR_2 = 0.1428
Final R indices (all data)	R_1 = 0.0738, wR_2 = 0.1591
Largest diff. peak and hole	1.76 and -1.05 $e/Å^3$
CCDC deposition number	1953705

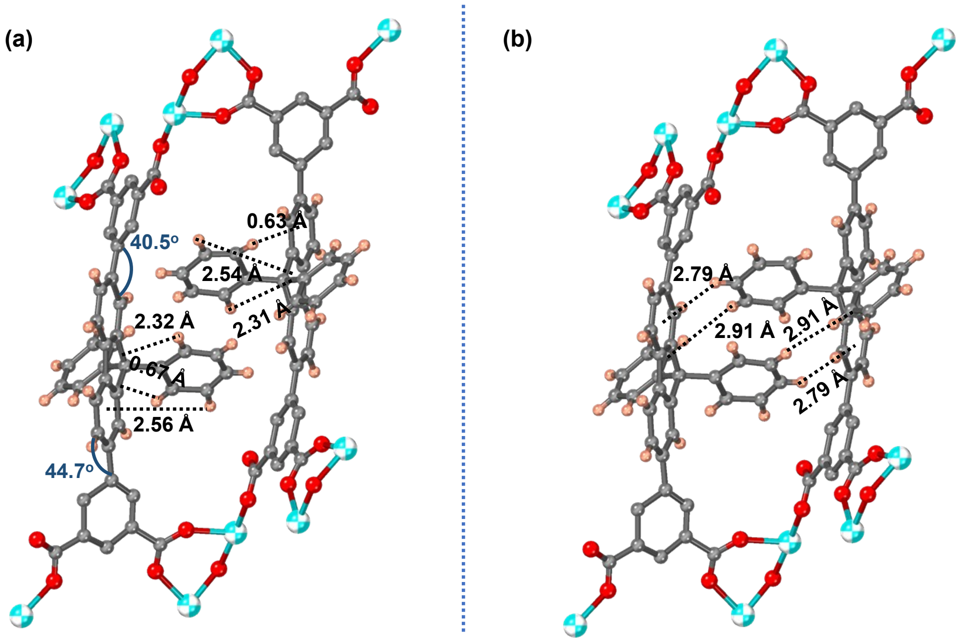


Fig. S1 A portion of the crystal structure showing dihedral angles between isophtahlate and fluorene fragments and intramolecular (a), and intermolecular (b) C-H···π interactions between phenyl rings and fluorene fragments.

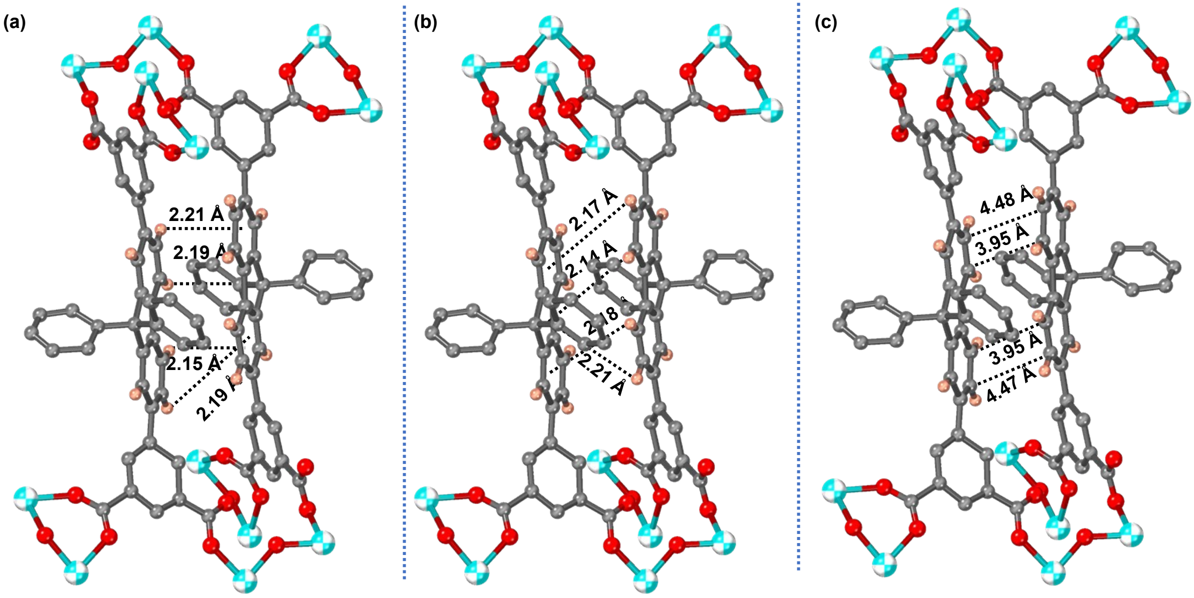


Fig. S2 Pertinent packing motifs of the crystal structure of **In-DPF** showing inter- and intramolecular C-H···π interactions between the adjacent linker moieties, (a) and (b), respectively. (c) Distance between two adjacent fluorene fragments.

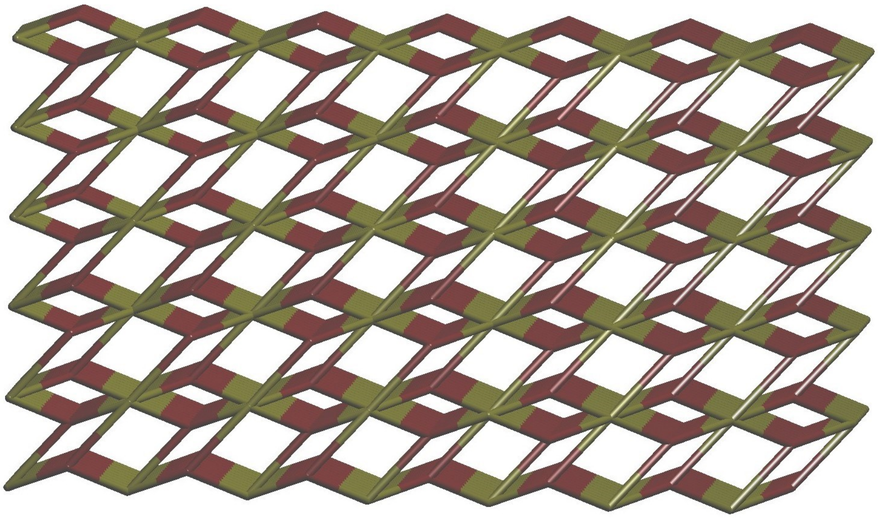


Fig. S3 Simplified topological network of **In-DPF** along (100) direction.

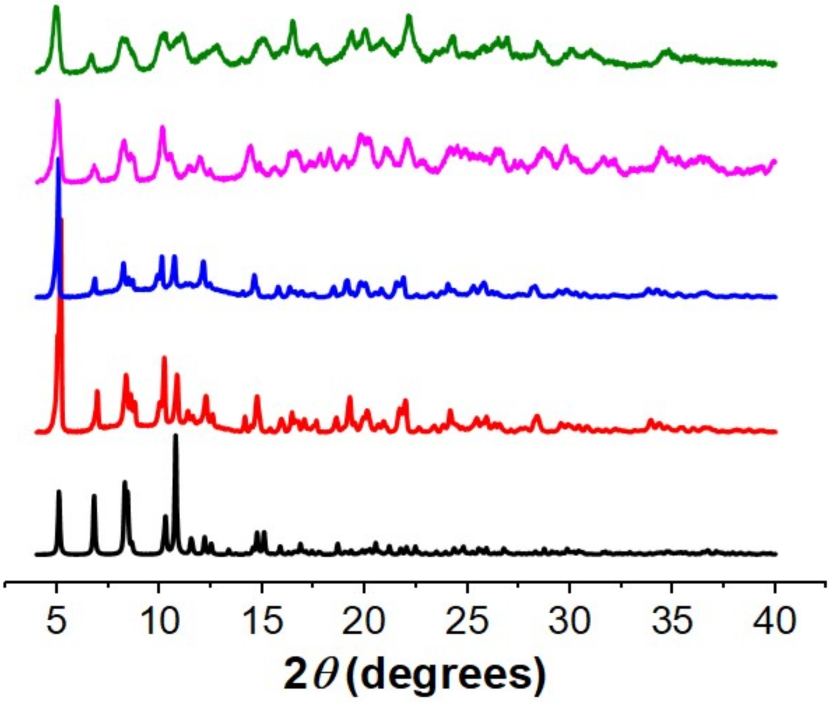


Fig. S4 PXRD profiles: simulated for the X-ray determined single crystal structure (black), pristine **In-DPF** crystals synthesized in bulk (red), MOF crystals after grinding for 300 sec (blue), MOF crystals treated with DMF-H_2O solvent mixture for 24 h (pink), and MOF crystals after soaking in aq. Al^{3+} solution for 24 h (green).

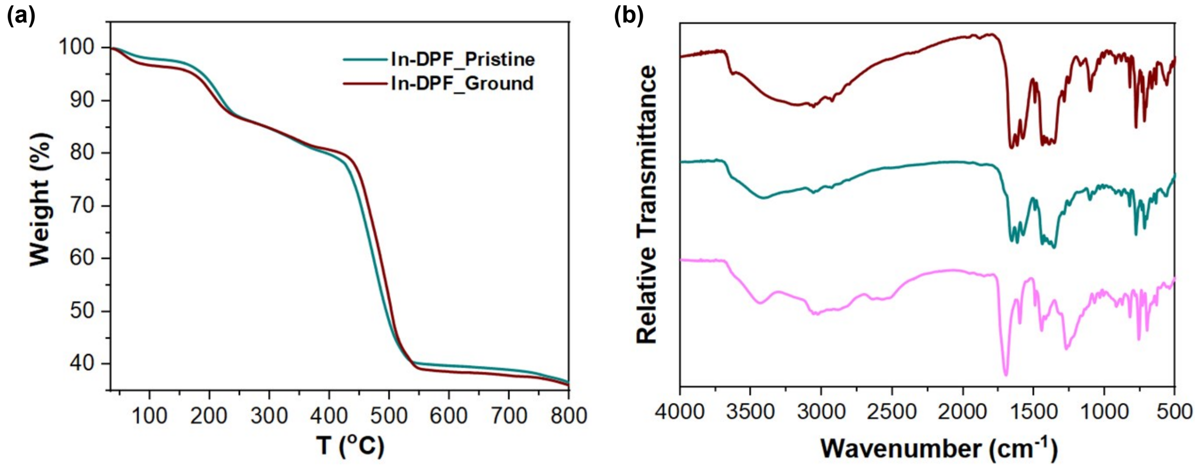


Fig. S5 (a) TGA profile of pristine (cyan) and ground **In-DPF** (wine). (b) IR (KBr) spectra of **H_4DPF** (pink), pristine (cyan) and ground **In-DPF** (wine).

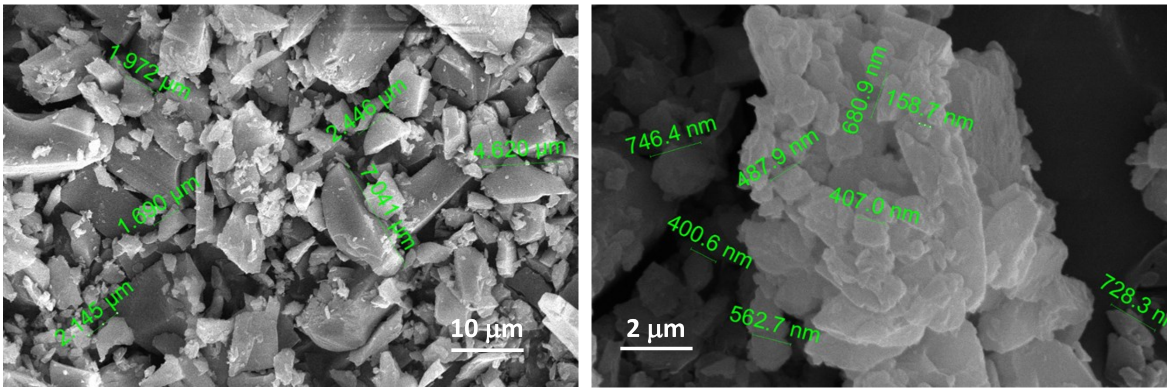


Fig. S6 SEM images of the pristine (left) and ground (300 s, right) samples of **In-DPF**.

Aggregation test for ground In-DPF in solvent-H_2O mixture

The aggregation experiments for **In-DPF** were conducted in three different organic solvent mixtures, i.e., DMF-H_2O, DMSO-H_2O and THF-H_2O with water fraction (f_w) in the range of 0-90%. Ten different stock solutions of 5 mL in DMF-H_2O, DMSO-H_2O and THF-H_2O were prepared for f_w = 0-90%. Later, 0.3 mg of **In-DPF** (0.4-0.7 µm) sample was transferred into 10 different vials, and a 3 mL solution from the stock solution was transferred to each vial. Subsequently, fluorescence experiment was performed immediately by transferring 3.0 mL of the MOF suspension into a 1 cm width quartz cuvette (λ_{ex} = 330 nm; λ_{em} = 345-580 nm).

The fluorescence spectra for aggregation studies of **H_4DPF** were performed using 1 µM solution in 5 mL of DMF-H_2O mixtures. The solution in each case was prepared by transferring 100 µL aliquot from the stock solution of 5×10^{-5} M concentration, and the rest being transferred from the stock solution of DMF-H_2O with f_w = 0-90%. Later, the fluorescence spectra was recorded by transferring 3.0 mL of the solution to a 1 cm width quartz cuvette (λ_{exc} = 330 nm).

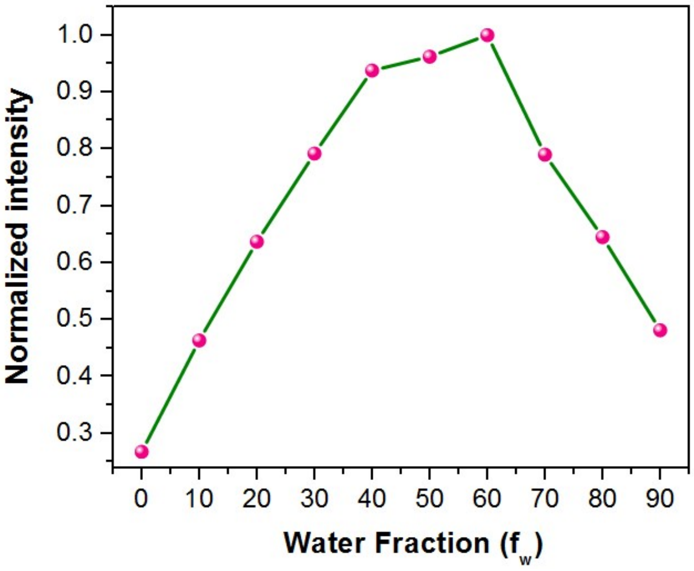


Fig. S7 Changes in the fluorescence intensity of ground **In-DPF** in DMF-H_2O mixtures for different water fractions (f_w) in the range of 0-90% (λ_{ex} = 330 nm).

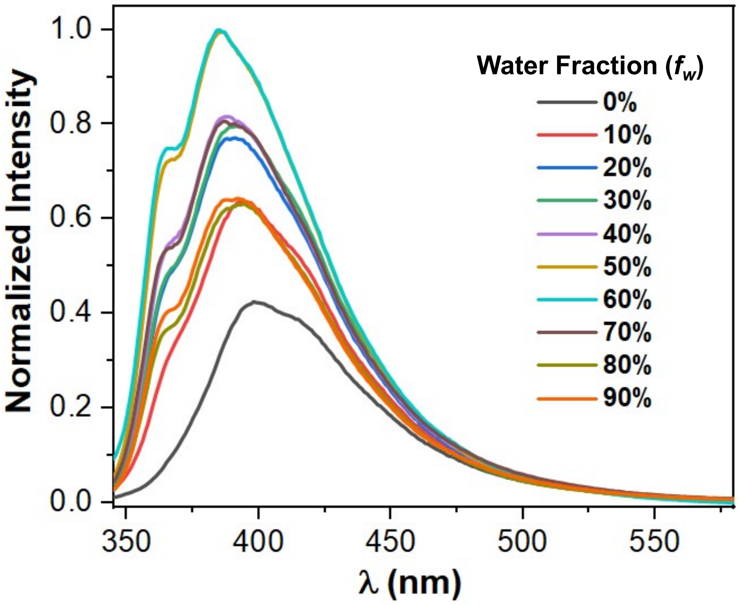


Fig. S8 Fluorescence spectra of **In-DPF** in THF-H_2O solvent mixtures for f_w = 0-90% (λ_{exc} = 330 nm).

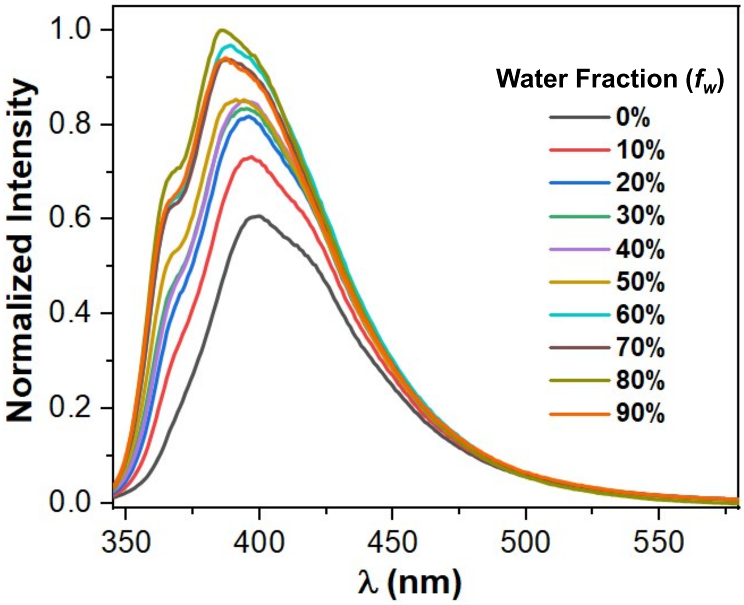


Fig. S9 Fluorescence spectra of **In-DPF** in DMSO-H_2O solvent mixtures for f_w = 0-90% (λ_{exc} = 330 nm).

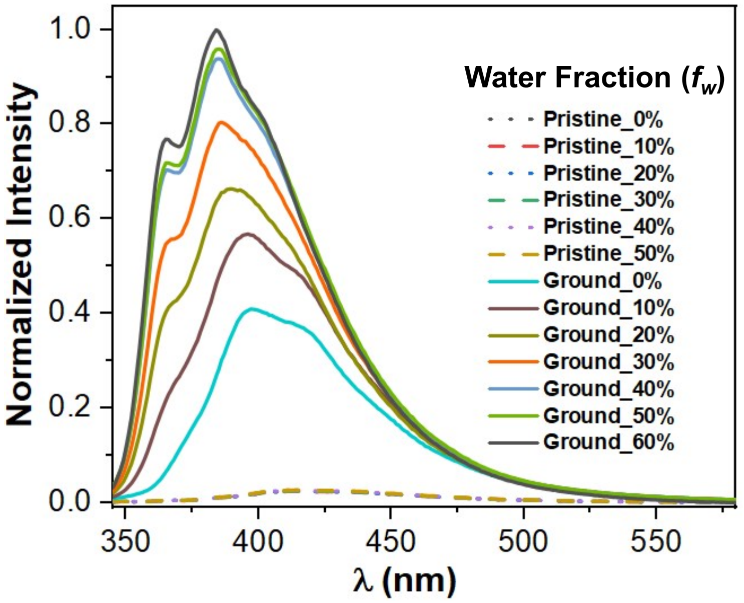


Fig. S10 Fluorescence spectra of pristine and ground **In-DPF** in DMF-H_2O solvent mixtures for f_w = 0-50% (λ_{exc} = 330 nm).

Table S2 Quantum Yield (ϕ_F) Data of **In-DPF** in DMF-H_2O Solvent Mixtures

f_w	Solvent mixture	ϕ_F (%)
0%	DMF:H_2O (100:0)	27.0
20%	DMF:H_2O (80:20)	49.8
40%	DMF:H_2O (60:40)	63.3
60%	DMF:H_2O (40:60)	64.0
80%	DMF:H_2O (20:80)	51.3

Dynamic light scattering (DLS) experiments

DLS experiments were carried out using a Malvern Zetasizer particle size analyzer at 293 K. The samples were freshly prepared by the above mentioned method using ground MOF suspensions in DMF-H_2O for f_w = 0, 20, 40, 60 and 80%, and particle size distributions of the resultant suspensions were analyzed immediately using DLS analysis.

Table S3 Particle size distributions of ground **In-DPF** in DMF-H_2O solvent mixture based on DLS analysis

f_w	Solvent mixture	Dh (nm)
0%	DMF:H_2O (100:0)	295
20%	DMF:H_2O (80:20)	1110
40%	DMF:H_2O (60:40)	2670
60%	DMF:H_2O (40:60)	5560
80%	DMF:H_2O (20:80)	459

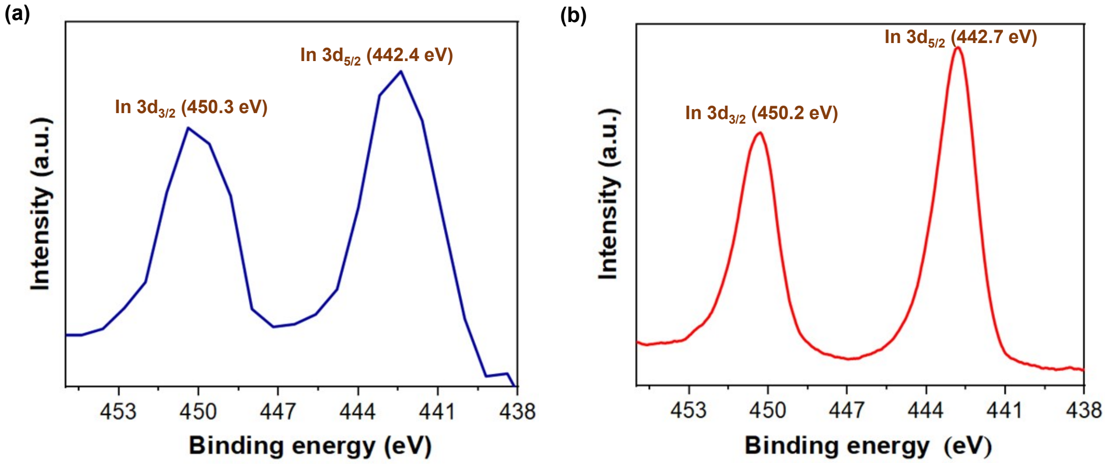


Fig. S11 XPS of (a) ground **In-DPF** MOF, and (b) after treatment with DMF-H_2O mixture.

Fluorescence sensing of metal ions with ground In-MOF suspension in aqueous medium

Fluorescence quenching experiments were performed using an aqueous suspension of the ground **In-DPF** in distilled water. The suspension was prepared by taking 5 mg of ground MOF in 10 mL of distilled water, sonicated for about 30 min, and left undisturbed for additional 30 min. Subsequently, 2.5 mL of the above-prepared MOF suspension was placed in a 1 cm width quartz cuvette, and the blank spectrum (λ_{exc} = 330 nm) was recorded. Fluorescence titrations were performed by incremental addition of 1 mM aqueous solutions of nitrate salts of Al^{3+}, Pb^{2+}, Cr^{3+}, Cu^{2+}, Na^{+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Fe^{3+}, Hg^{2+} and Ni^{2+} to the MOF suspension and to the solution of tetraester **3** (1 μM in H_2O).

Fluorescence quenching efficiency (η%) is defined by the equation as following:

$$\eta = \left[\frac{I_0 - I}{I_0}\right] \times 100\,\%$$

Table S4 Sensing of metal ions by suspension of the ground **In-DPF** in aqueous medium

Entry	M^{n+}	η%
1.	Al^{3+}	98.0%
2.	Fe^{3+}	57.0%
3.	Cr^{3+}	35.0%
4.	Pb^{2+}	35.0%
5.	Cu^{2+}	17.8%
6.	Cd^{2+}	10.0%
7.	Hg^{2+}	9.0%
8.	Ni^{2+}	7.3%
9.	Zn^{2+}	6.7%
10.	Co^{2+}	4.8%
11.	Ag^{+}	4.5%
12.	Mg^{2+}	3.5%
13.	Na^{+}	3.0%

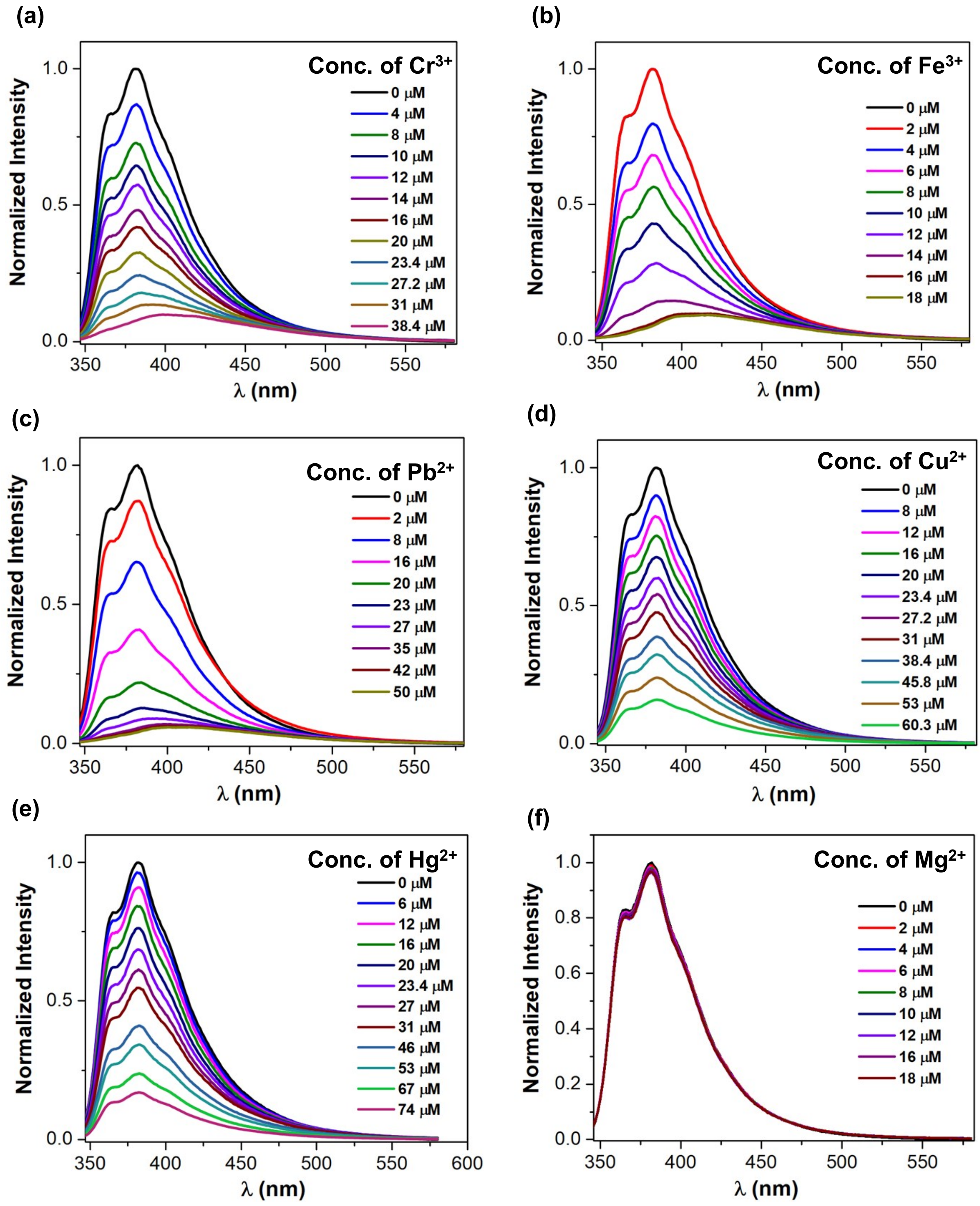


Fig. S12 Fluorescence sensing of metal ions, i.e., (a) Cr^{3+}, (b) Fe^{3+}, (c) Pb^{2+}, (d) Cu^{2+}, (e) Hg^{2+} and (f) Mg^{2+}, by **In-DPF** suspension in water (λ_{ex} = 330 nm) with the increasing concentration of each of the former.

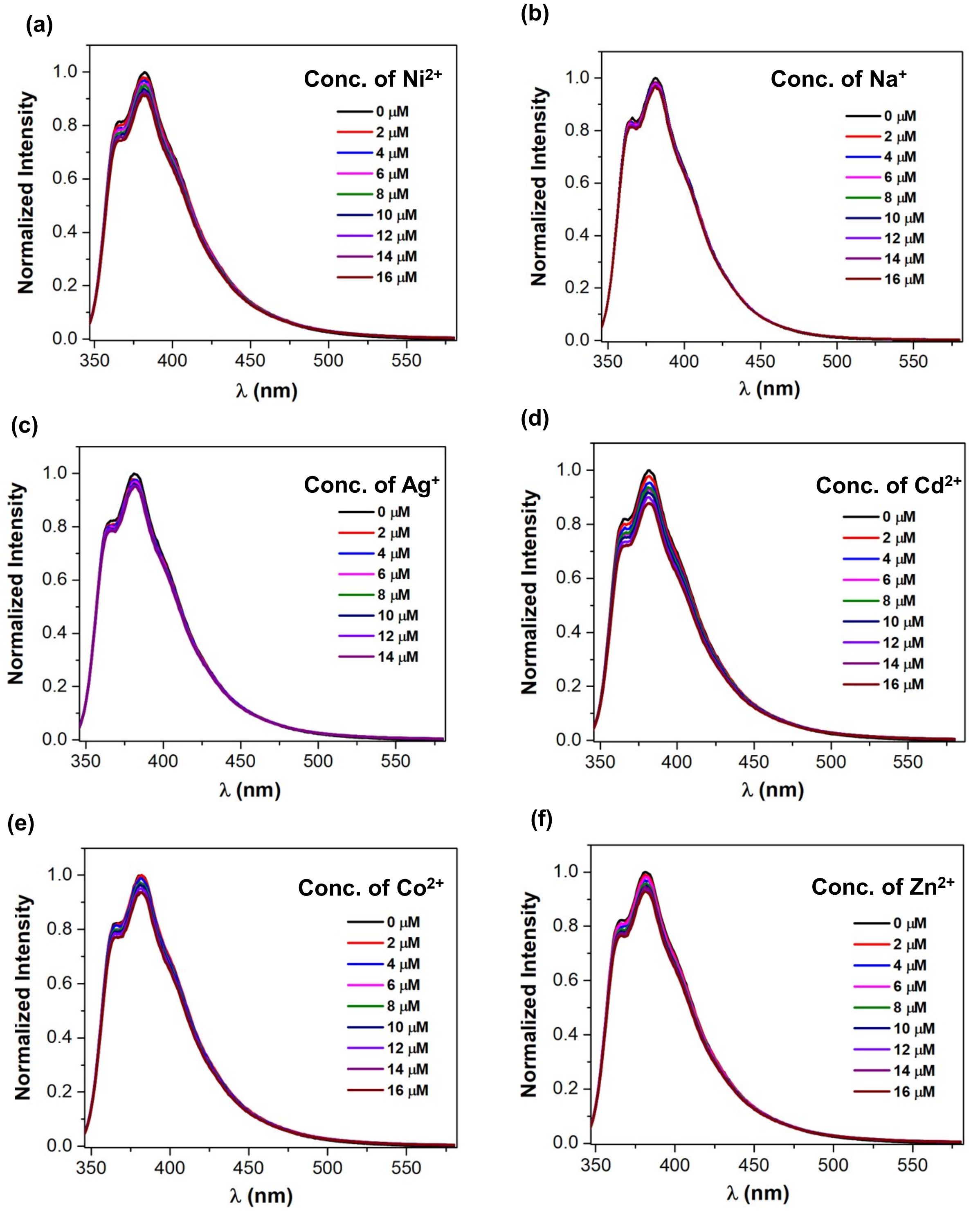


Fig. S13 Fluorescence sensing of metal ions, i.e., (a) Ni^{2+}, (b) Na^{+}, (c) Ag^{+}, (d) Cd^{2+}, (e) Co^{2+} and (f) Zn^{2+}, by **In-DPF** suspension in water (λ_{ex} = 330 nm) with the increasing concentration of each of the former.

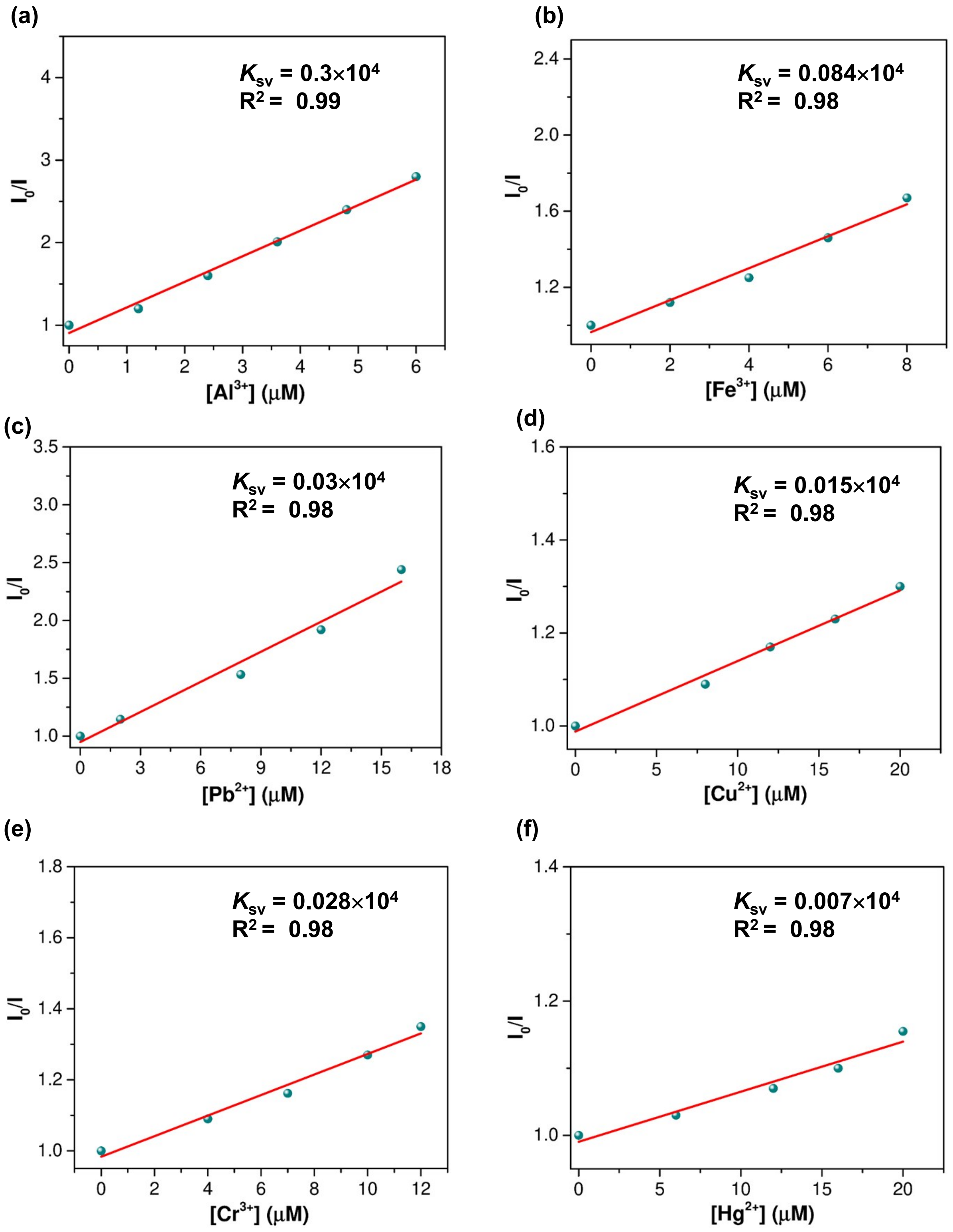


Fig. S14 Determination of Stern-Volmer constant (K_{sv}) for each of the ions, i.e., (a) Al^{3+}, (b) Fe^{3+}, (c) Pb^{2+}, (d) Cu^{2+}, (e) Cr^{3+} and (f) Hg^{2+}.

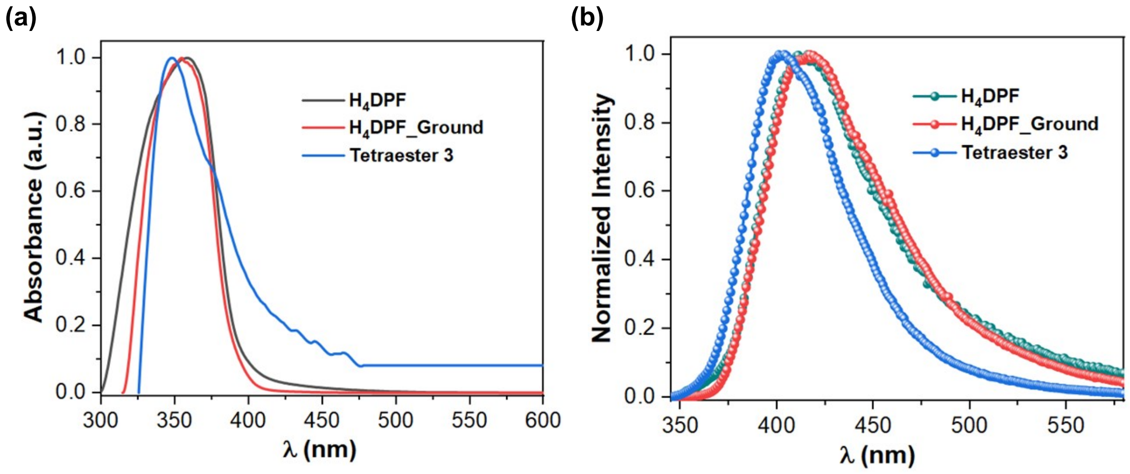


Fig. S15 Solid-state (a) UV-vis absorption spectra recorded in a diffuse reflectance mode at rt, and (b) fluorescence spectra of **H_4DPF**, ground **H_4DPF** and the tetraester **3**.

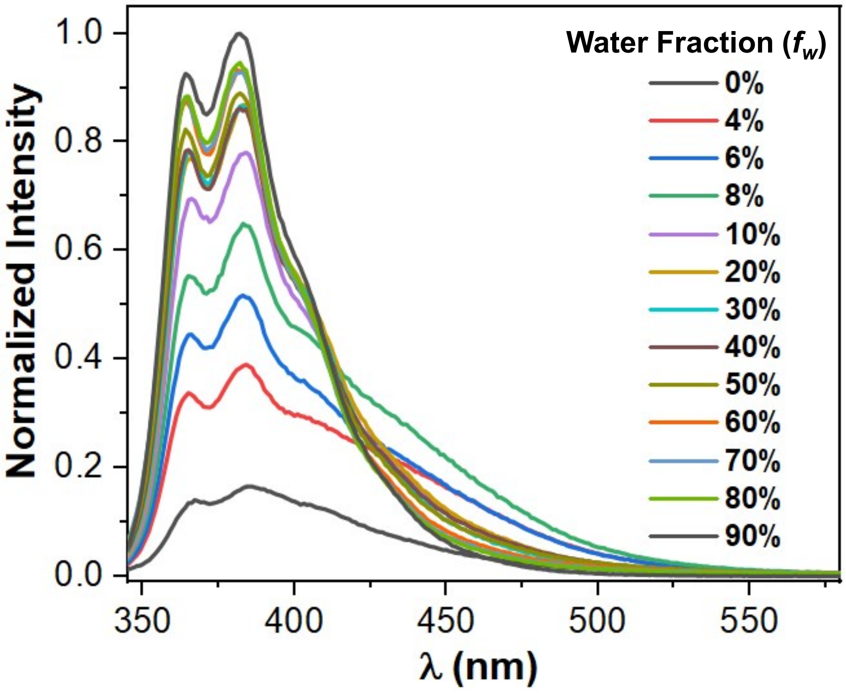


Fig. S16 Fluorescence spectra of **H_4DPF** in DMF-H_2O solvent mixture for f_w = 0-90% (λ_{exc} = 330 nm).

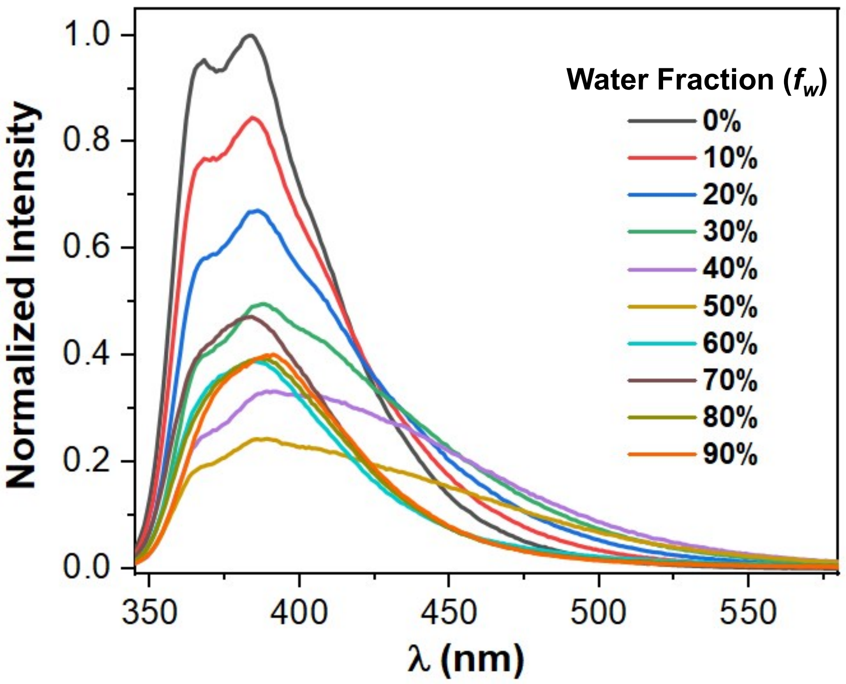


Fig. S17 Fluorescence spectra of tetraester **3** in DMF-H_2O solvent mixture for f_w = 0-90% (λ_{exc} = 330 nm).

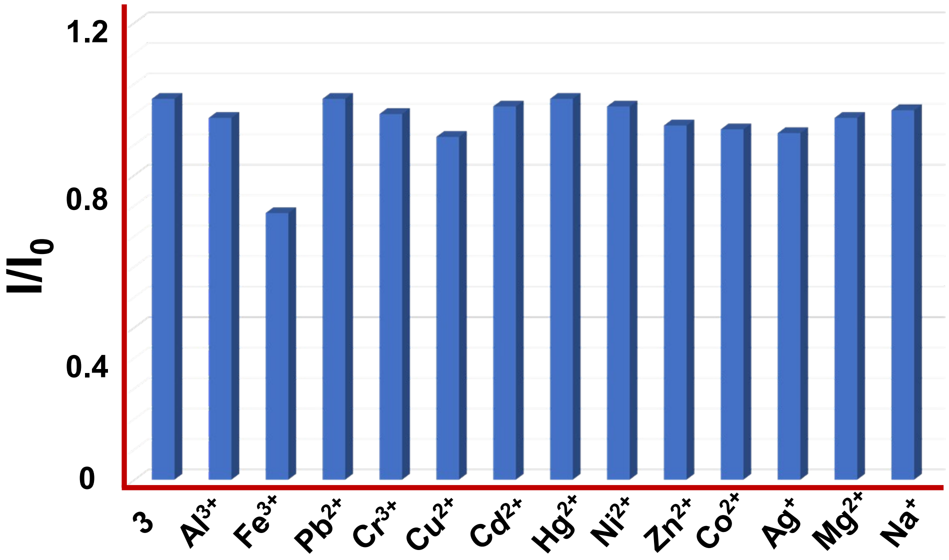


Fig. S18 Changes in the fluorescence intensity of tetraester **3** in the presence of selected metal ions (0.27 mM for each).

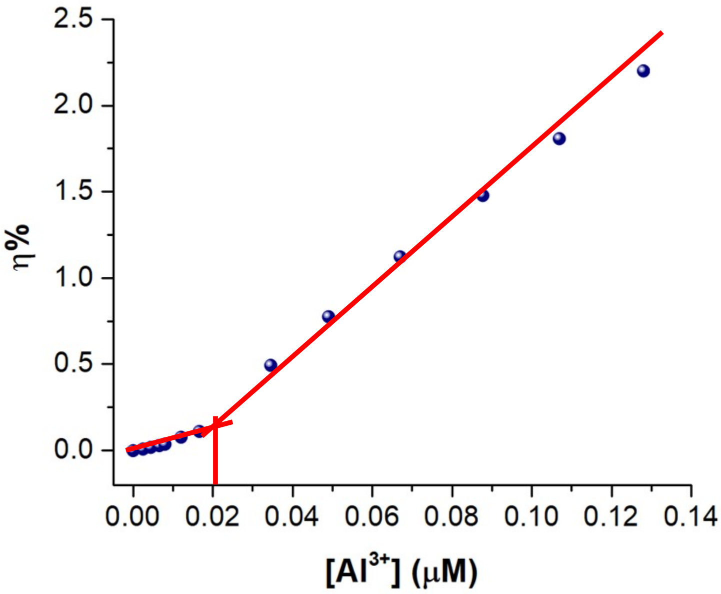


Fig. S19 Determination of the sensitivity limit of **In-DPF** MOF for detection of **Al**$^{3+}$ ion. Notice that the limiting concentration has been determined from the point of intersection of two linear fits that are colored in red.[7]

The limiting conc. thus turns out to be 0.021μM, i.e., 21 nM. The detection limit in ppb (i.e., μg/L) was calculated using the following equation:

x (in ppb) = y (in nM) × molar mass of analyte/1000. Given that the molar mass of **Al**$^{3+}$ is 26.98, the detection limit in ppb should be = (21×26.98/1000) ppb ≈ 0.57 ppb.

References

1 D. M. E. Freeman, A. J. Musser, J. M. Frost, H. L. Stern, A. K. Forster, K. J. Fallon, A. G. Rapidis, F. Cacialli, I. McCulloch, T. M. Clarke, R. H. Friend and H. Bronstein, *J. Am. Chem. Soc.*, 2017, **139**, 11073–11080.

2 R. Jagarapu and V. Parthasarathy, *Chem. - An Asian J.*, 2017, **12**, 181–189.

3 X.-H. Chang, L.-F. Ma, G. Hui and L.-Y. Wang, *Cryst. Growth Des.*, 2012, **12**, 3638–3646.

4 S. Jindal, V. K. Maka, G. Anjum and J. N. Moorthy, *ACS Appl. Nano Mater.*, 2021, **4**, 449–458.

5 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

6 V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Cryst. Growth Des.*, 2014, **14**, 3576–3586.

7 A. Mukhopadhyay, S. Jindal, G. Savitha and J. N. Moorthy, *Inorg. Chem.*, 2020, **59**, 6202–6213.

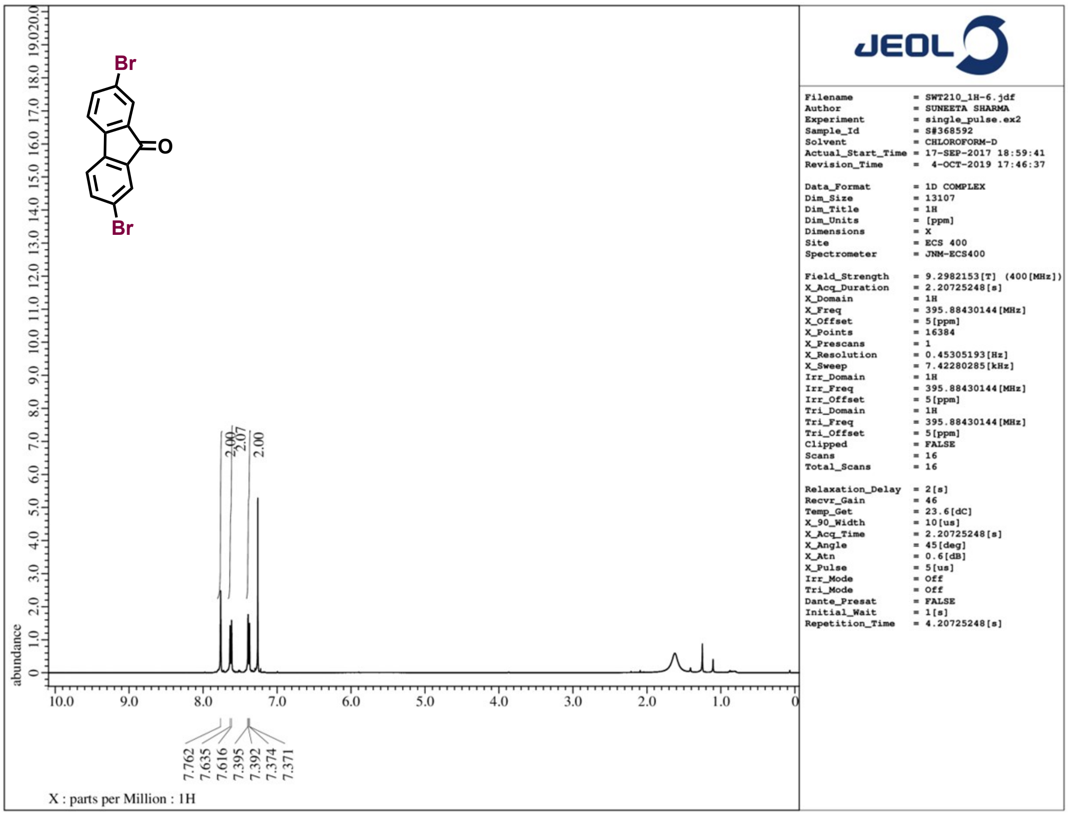


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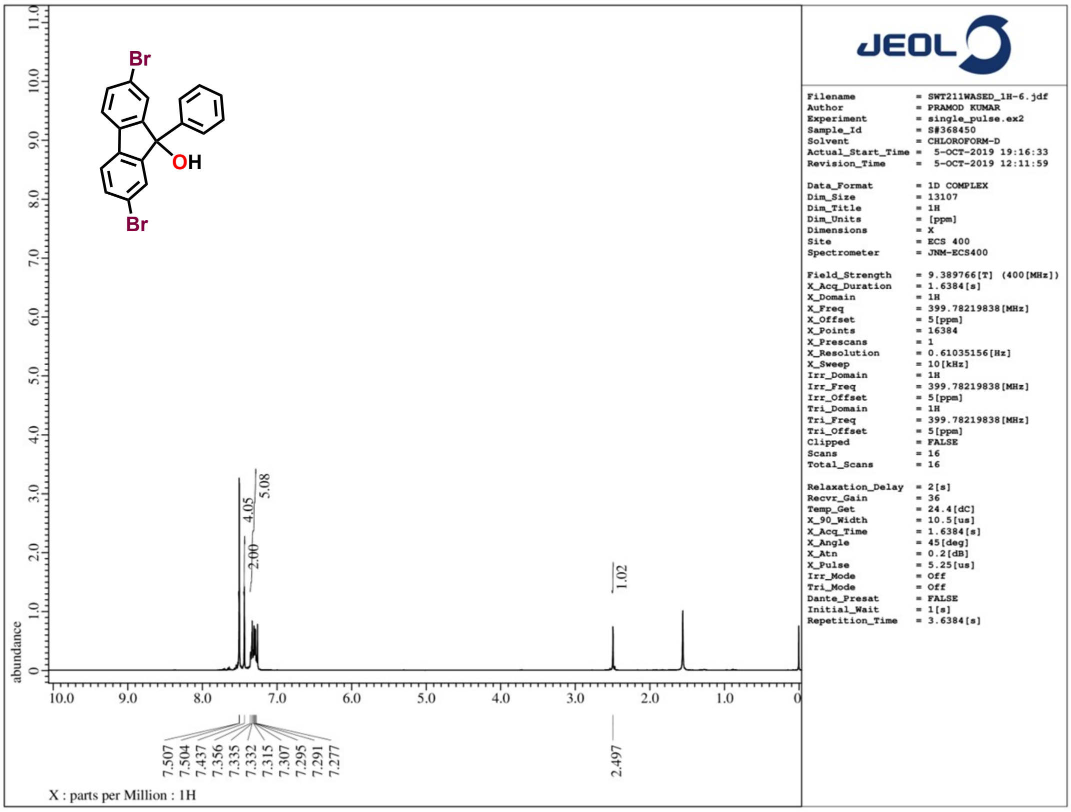
Fig. S20 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2,7-dibromofluorenone.



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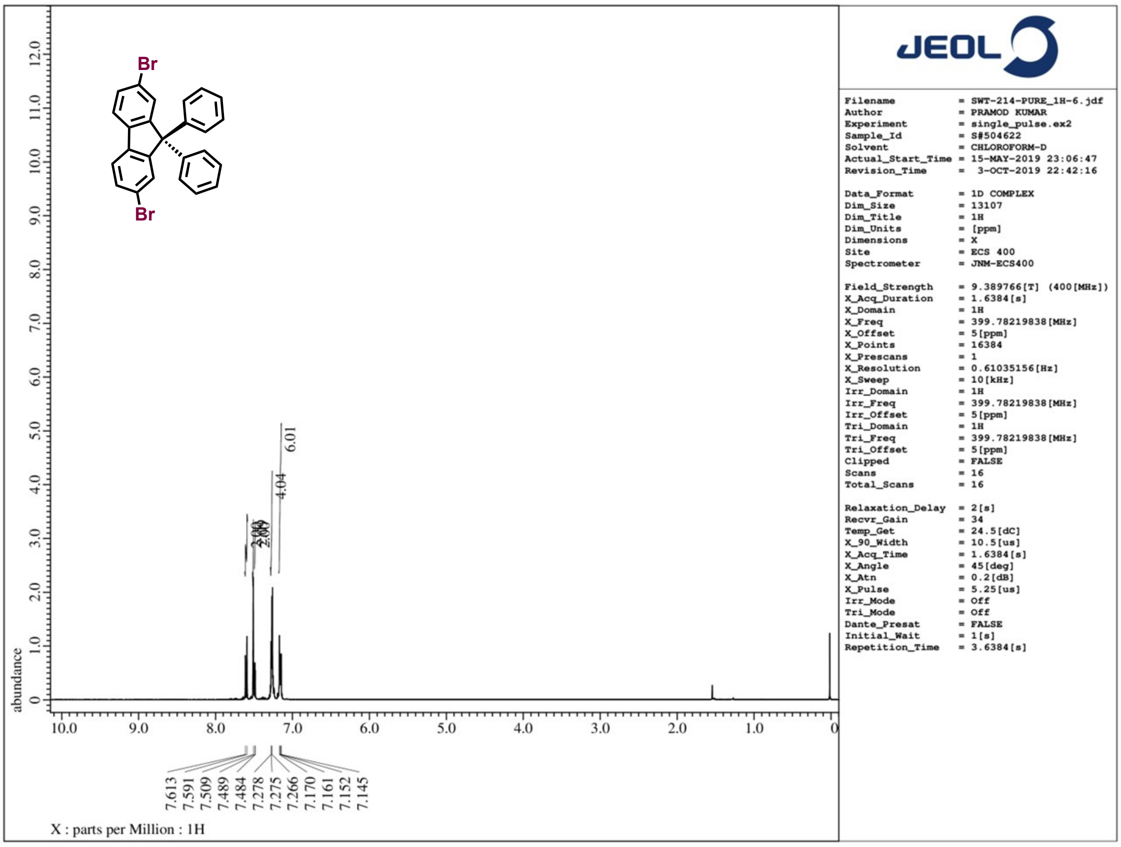
Revision_Time      =  5-OCT-2019 12:11:59

Data_Format        = 1D COMPLEX
Dim_Size           = 13107
Dim_Title          = 1H
Dim_Units          = [ppm]
Dimensions         = X
Site               = ECS 400
Spectrometer       = JNM-ECS400

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 1.6384[s]
X_Domain           = 1H
X_Freq             = 399.78219838[MHz]
X_Offset           = 5[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.61035156[Hz]
X_Sweep            = 10[kHz]
Irr_Domain         = 1H
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = 1H
Tri_Freq           = 399.78219838[MHz]
Tri_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 16
Total_Scans        = 16

Relaxation_Delay   = 2[s]
Recvr_Gain         = 36
Temp_Get           = 24.4[dC]
X_90_Width         = 10.5[us]
X_Acq_Time         = 1.6384[s]
X_Angle            = 45[deg]
X_Atn              = 0.2[dB]
X_Pulse            = 5.25[us]
Irr_Mode           = Off
Tri_Mode           = Off
Dante_Presat       = FALSE
Initial_Wait       = 1[s]
Repetition_Time    = 3.6384[s]
```

Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2,7-dibromo-9-phenyl-9H-fluoren-9-ol.



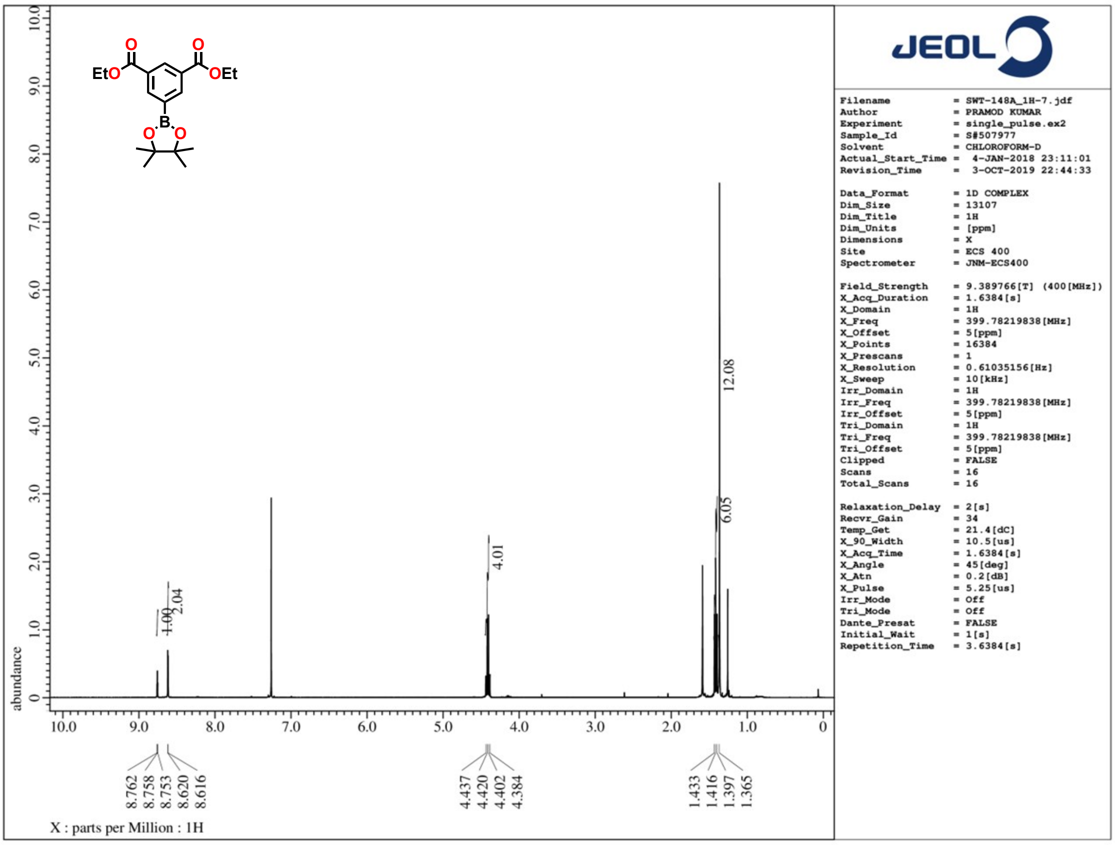
```
Filename            = SWT-214-PURE_1H-6.jdf
Author              = PRAMOD KUMAR
Experiment          = single_pulse.ex2
Sample_Id           = S#504622
Solvent             = CHLOROFORM-D
Actual_Start_Time = 15-MAY-2019 23:06:47
Revision_Time       =  3-OCT-2019 22:42:16

Data_Format         = 1D COMPLEX
Dim_Size            = 13107
Dim_Title           = 1H
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = JNM-ECS400

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.6384[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.61035156[Hz]
X_Sweep             = 10[kHz]
Irr_Domain          = 1H
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = 1H
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 16
Total_Scans         = 16

Relaxation_Delay    = 2[s]
Recvr_Gain          = 34
Temp_Get            = 24.5[dC]
X_90_Width          = 10.5[us]
X_Acq_Time          = 1.6384[s]
X_Angle             = 45[deg]
X_Atn               = 0.2[dB]
X_Pulse             = 5.25[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 3.6384[s]
```

Fig. S22 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1**.



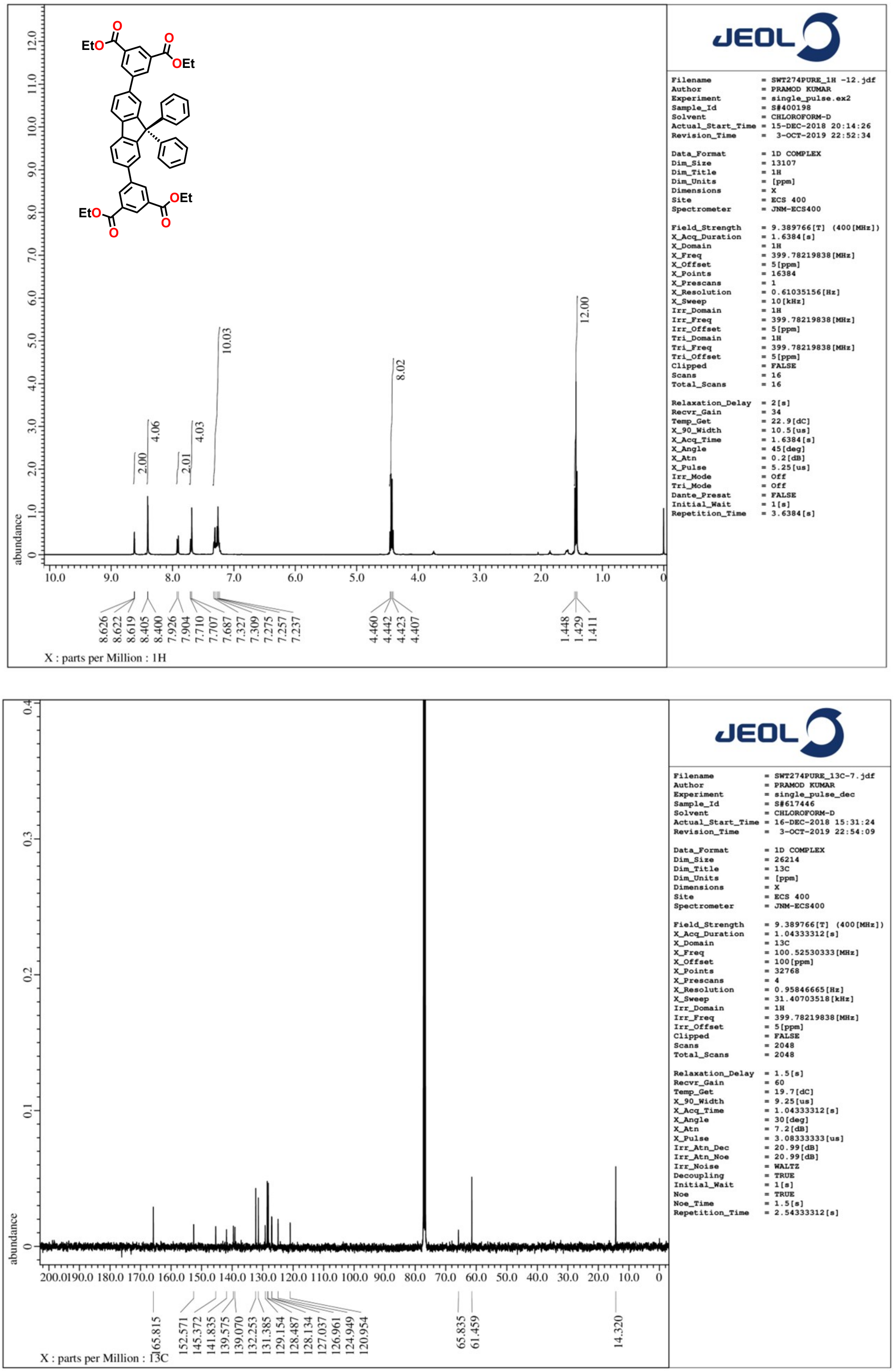
```
Filename            = SWT-148A_1H-7.jdf
Author              = PRAMOD KUMAR
Experiment          = single_pulse.ex2
Sample_Id           = S#507977
Solvent             = CHLOROFORM-D
Actual_Start_Time =  4-JAN-2018 23:11:01
Revision_Time       =  3-OCT-2019 22:44:33

Data_Format         = 1D COMPLEX
Dim_Size            = 13107
Dim_Title           = 1H
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = JNM-ECS400

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.6384[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.61035156[Hz]
X_Sweep             = 10[kHz]
Irr_Domain          = 1H
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = 1H
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 16
Total_Scans         = 16

Relaxation_Delay    = 2[s]
Recvr_Gain          = 34
Temp_Get            = 21.4[dC]
X_90_Width          = 10.5[us]
X_Acq_Time          = 1.6384[s]
X_Angle             = 45[deg]
X_Atn               = 0.2[dB]
X_Pulse             = 5.25[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 3.6384[s]
```

Fig. S23 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**.



```
Filename           = SWT274PURE_1H -12.jdf
Author             = PRAMOD KUMAR
Experiment         = single_pulse.ex2
Sample_Id          = S#400198
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 15-DEC-2018 20:14:26
Revision_Time      =  3-OCT-2019 22:52:34

Data_Format        = 1D COMPLEX
Dim_Size           = 13107
Dim_Title          = 1H
Dim_Units          = [ppm]
Dimensions         = X
Site               = ECS 400
Spectrometer       = JNM-ECS400

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 1.6384[s]
X_Domain           = 1H
X_Freq             = 399.78219838[MHz]
X_Offset           = 5[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.61035156[Hz]
X_Sweep            = 10[kHz]
Irr_Domain         = 1H
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = 1H
Tri_Freq           = 399.78219838[MHz]
Tri_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 16
Total_Scans        = 16

Relaxation_Delay   = 2[s]
Recvr_Gain         = 34
Temp_Get           = 22.9[dC]
X_90_Width         = 10.5[us]
X_Acq_Time         = 1.6384[s]
X_Angle            = 45[deg]
X_Atn              = 0.2[dB]
X_Pulse            = 5.25[us]
Irr_Mode           = Off
Tri_Mode           = Off
Dante_Presat       = FALSE
Initial_Wait       = 1[s]
Repetition_Time    = 3.6384[s]
```

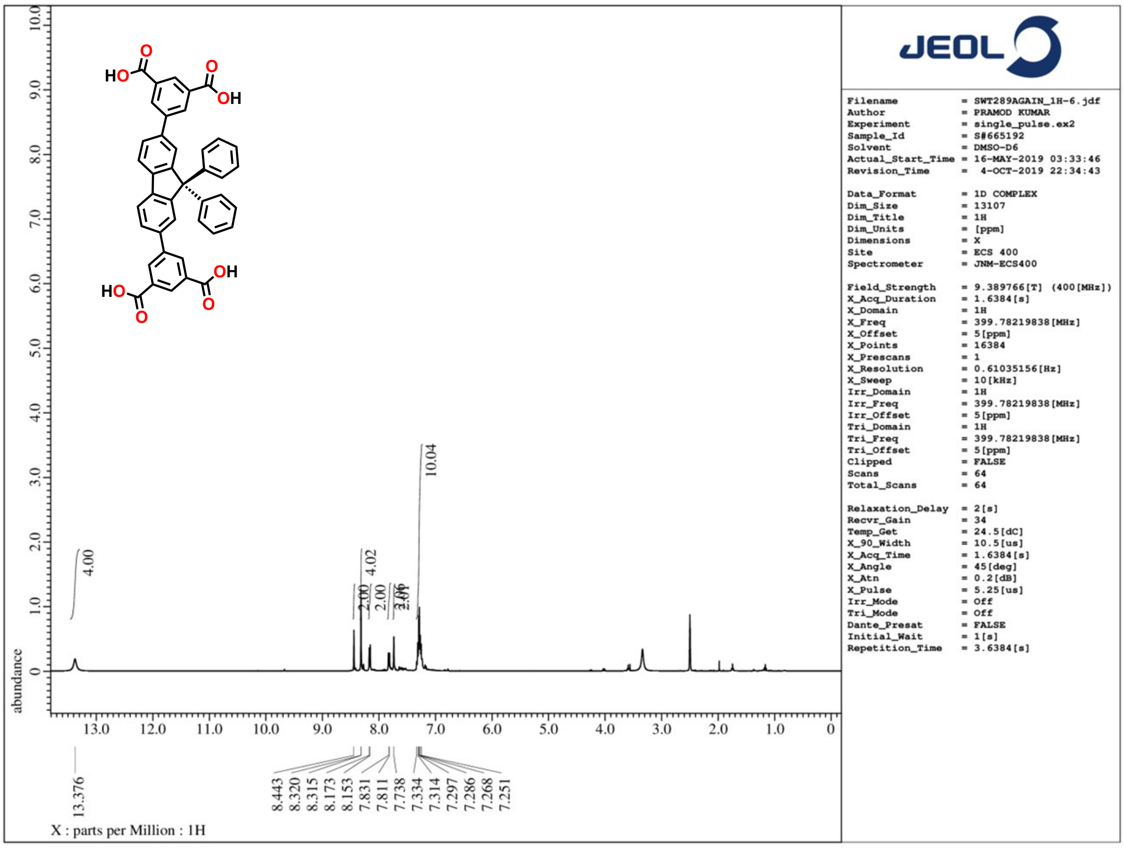
```
Filename           = SWT274PURE_13C-7.jdf
Author             = PRAMOD KUMAR
Experiment         = single_pulse_dec
Sample_Id          = S#617446
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 16-DEC-2018 15:31:24
Revision_Time      =  3-OCT-2019 22:54:09

Data_Format        = 1D COMPLEX
Dim_Size           = 26214
Dim_Title          = 13C
Dim_Units          = [ppm]
Dimensions         = X
Site               = ECS 400
Spectrometer       = JNM-ECS400

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 1.04333312[s]
X_Domain           = 13C
X_Freq             = 100.52530333[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 0.95846665[Hz]
X_Sweep            = 31.40703518[kHz]
Irr_Domain         = 1H
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 2048
Total_Scans        = 2048

Relaxation_Delay   = 1.5[s]
Recvr_Gain         = 60
Temp_Get           = 19.7[dC]
X_90_Width         = 9.25[us]
X_Acq_Time         = 1.04333312[s]
X_Angle            = 30[deg]
X_Atn              = 7.2[dB]
X_Pulse            = 3.08333333[us]
Irr_Atn_Dec        = 20.99[dB]
Irr_Atn_Noe        = 20.99[dB]
Irr_Noise          = WALTZ
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 1.5[s]
Repetition_Time    = 2.54333312[s]
```

Fig. S24 ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of tetraester **3**.

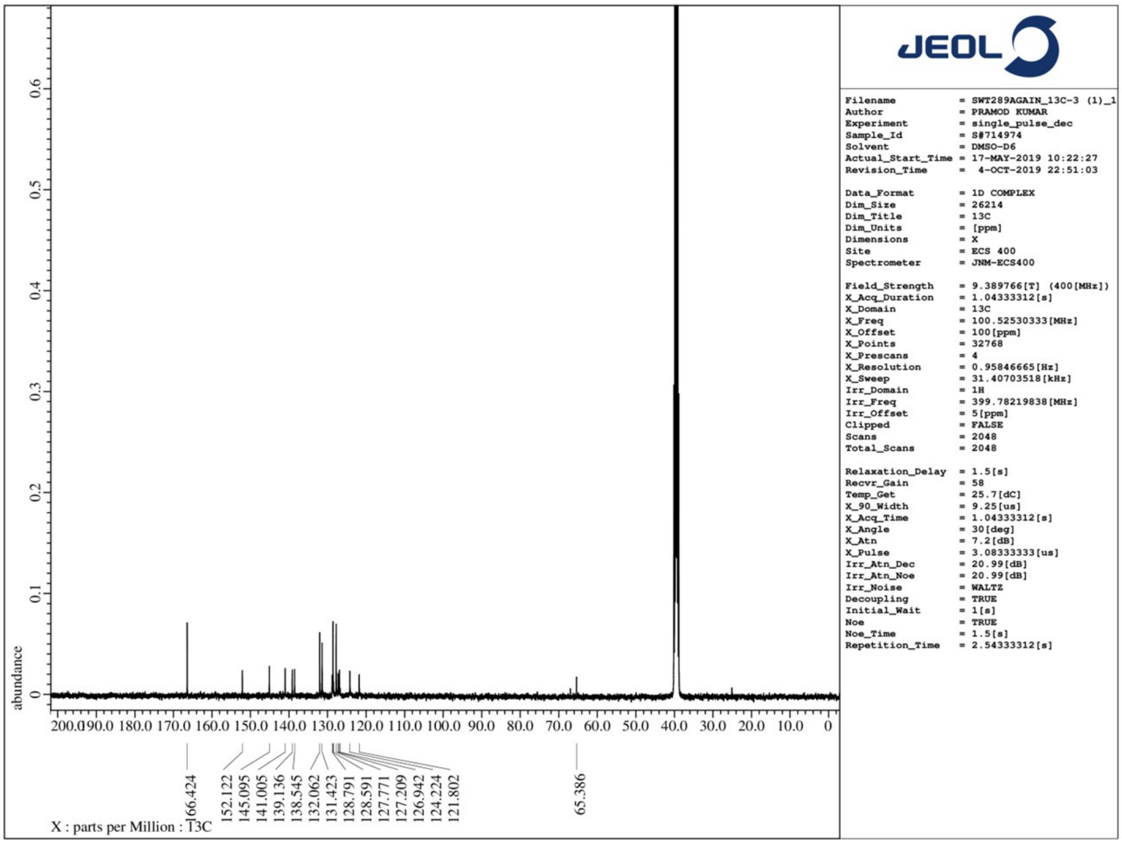


```
Filename           = SWT289AGAIN_1H-6.jdf
Author             = PRAMOD KUMAR
Experiment         = single_pulse.ex2
Sample_Id          = S#665192
Solvent            = DMSO-D6
Actual_Start_Time = 16-MAY-2019 03:33:46
Revision_Time      =  4-OCT-2019 22:34:43

Data_Format        = 1D COMPLEX
Dim_Size           = 13107
Dim_Title          = 1H
Dim_Units          = [ppm]
Dimensions         = X
Site               = ECS 400
Spectrometer       = JNM-ECS400

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 1.6384[s]
X_Domain           = 1H
X_Freq             = 399.78219838[MHz]
X_Offset           = 5[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.61035156[Hz]
X_Sweep            = 10[kHz]
Irr_Domain         = 1H
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = 1H
Tri_Freq           = 399.78219838[MHz]
Tri_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 64
Total_Scans        = 64

Relaxation_Delay   = 2[s]
Recvr_Gain         = 34
Temp_Get           = 24.5[dC]
X_90_Width         = 10.5[us]
X_Acq_Time         = 1.6384[s]
X_Angle            = 45[deg]
X_Atn              = 0.2[dB]
X_Pulse            = 5.25[us]
Irr_Mode           = Off
Tri_Mode           = Off
Dante_Presat       = FALSE
Initial_Wait       = 1[s]
Repetition_Time    = 3.6384[s]
```



```
Filename           = SWT289AGAIN_13C-3 (1)_1
Author             = PRAMOD KUMAR
Experiment         = single_pulse_dec
Sample_Id          = S#714974
Solvent            = DMSO-D6
Actual_Start_Time = 17-MAY-2019 10:22:27
Revision_Time      =  4-OCT-2019 22:51:03

Data_Format        = 1D COMPLEX
Dim_Size           = 26214
Dim_Title          = 13C
Dim_Units          = [ppm]
Dimensions         = X
Site               = ECS 400
Spectrometer       = JNM-ECS400

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 1.04333312[s]
X_Domain           = 13C
X_Freq             = 100.52530333[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 0.95846665[Hz]
X_Sweep            = 31.40703518[kHz]
Irr_Domain         = 1H
Irr_Freq           = 399.78219838[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 2048
Total_Scans        = 2048

Relaxation_Delay   = 1.5[s]
Recvr_Gain         = 58
Temp_Get           = 25.7[dC]
X_90_Width         = 9.25[us]
X_Acq_Time         = 1.04333312[s]
X_Angle            = 30[deg]
X_Atn              = 7.2[dB]
X_Pulse            = 3.08333333[us]
Irr_Atn_Dec        = 20.99[dB]
Irr_Atn_Noe        = 20.99[dB]
Irr_Noise          = WALTZ
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 1.5[s]
Repetition_Time    = 2.54333312[s]
```

Fig. S25 ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **H$_4$DPF**.