Supporting Information

A Coordination Polymer Based on Tetranuclear Tb^{3+} Clusters Exhibiting Dual Turn-on/off Fluorescence Sensing of Long- and Short-chain Polyfluoroalkyl Substances

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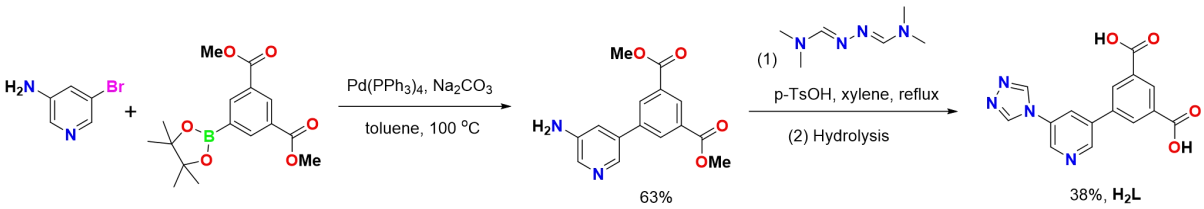


Scheme S1. Synthesis of **H_2L**.

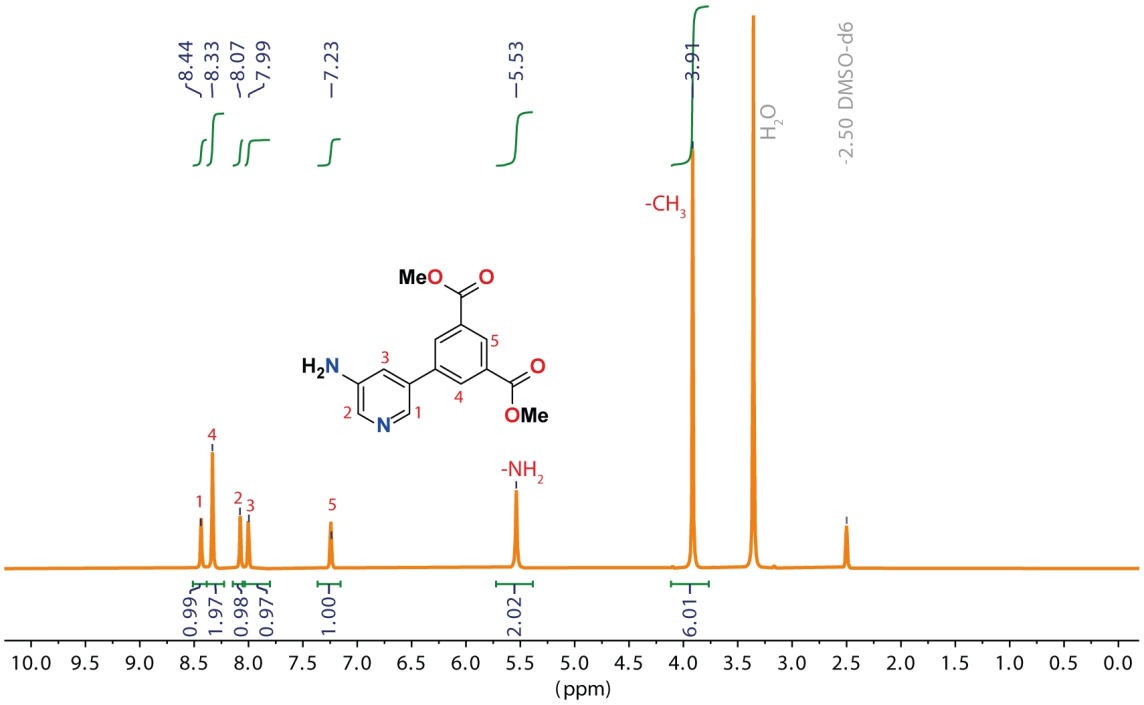
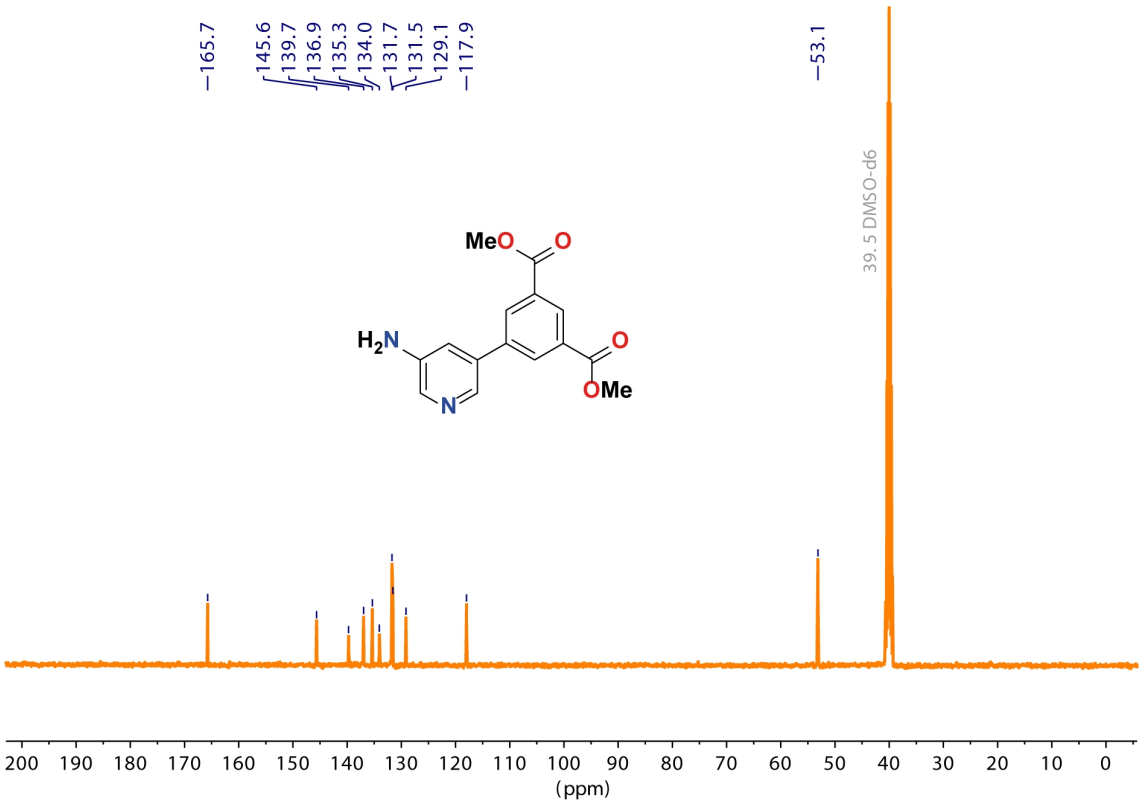


Figure S1. ^{1}H NMR of dimethyl 5-(5-aminopyridin-3-yl)isophthalate in DMSO-d_6.



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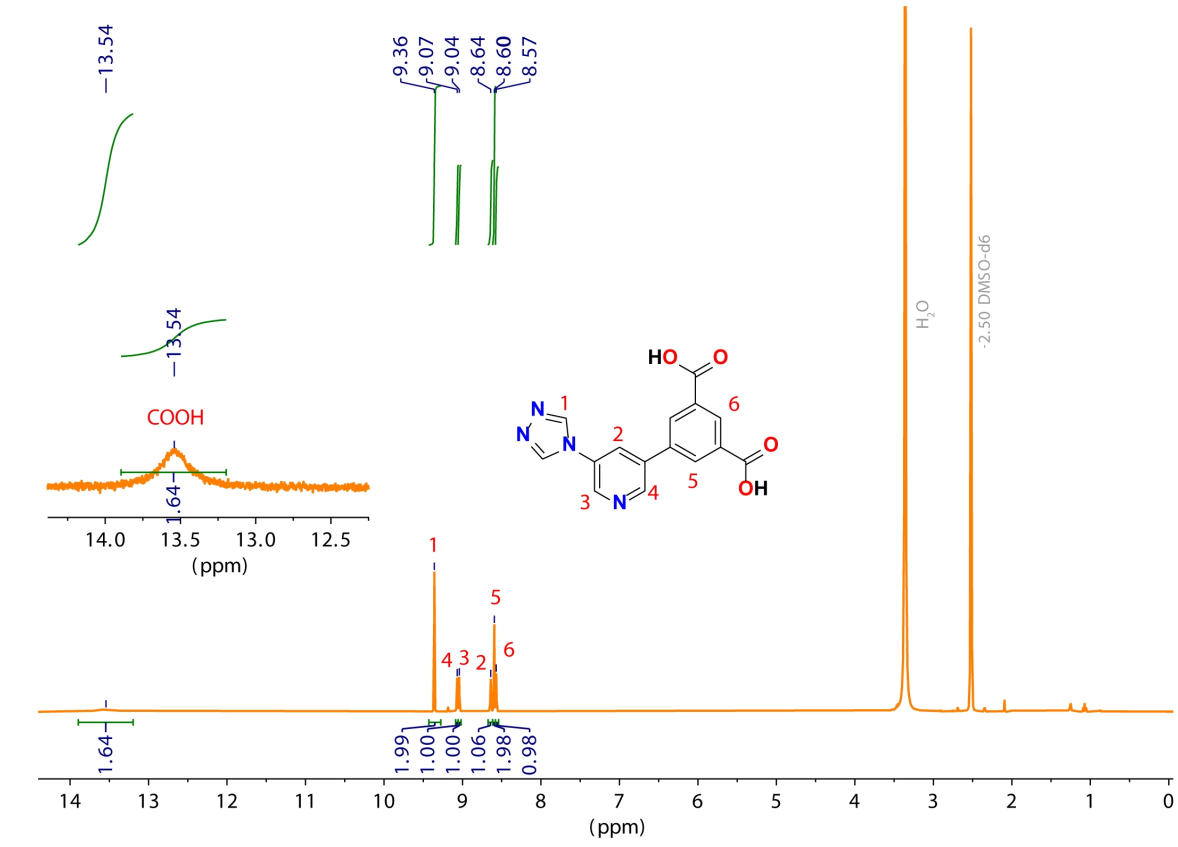


Figure S3. ^{1}H NMR of **H_2L** in DMSO-d_6.

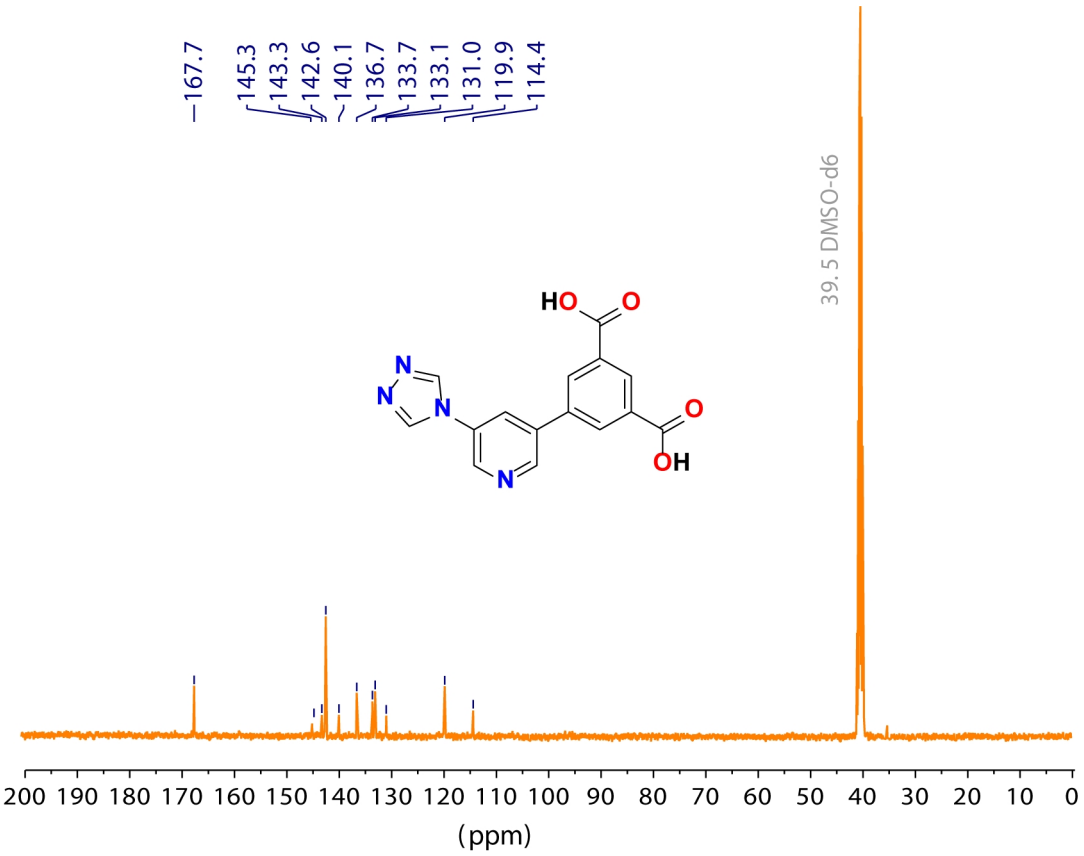


Figure S4. ^{13}C NMR of **H_2L** in DMSO-d_6.

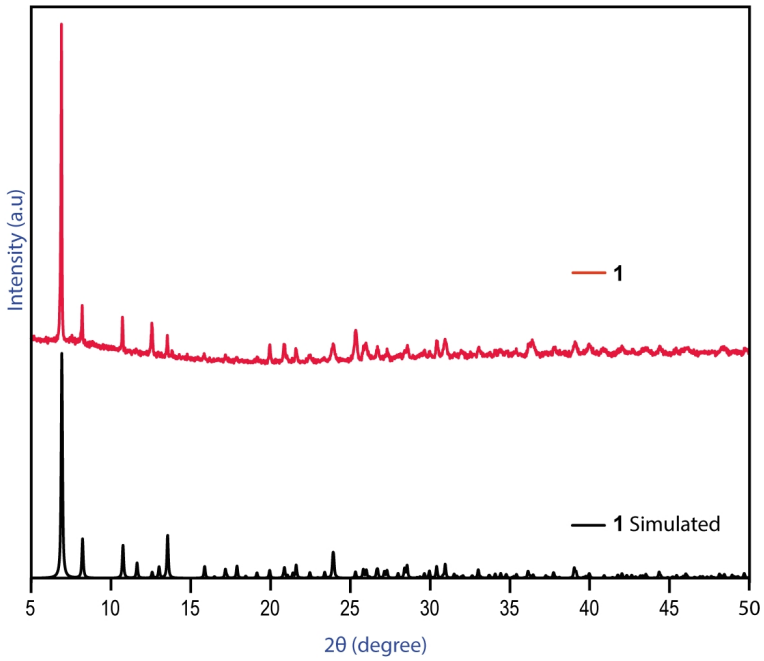
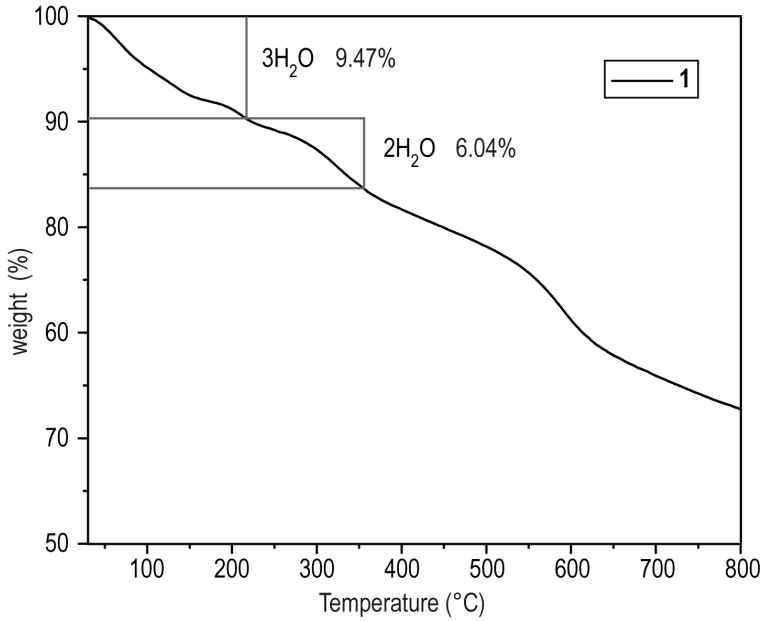


Figure S5. Comparaison of the simulated and experimental PXRD patterns of **1**.



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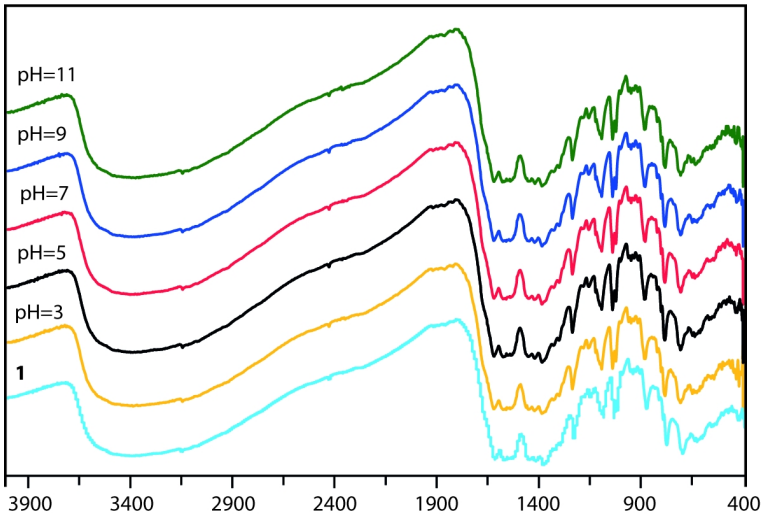

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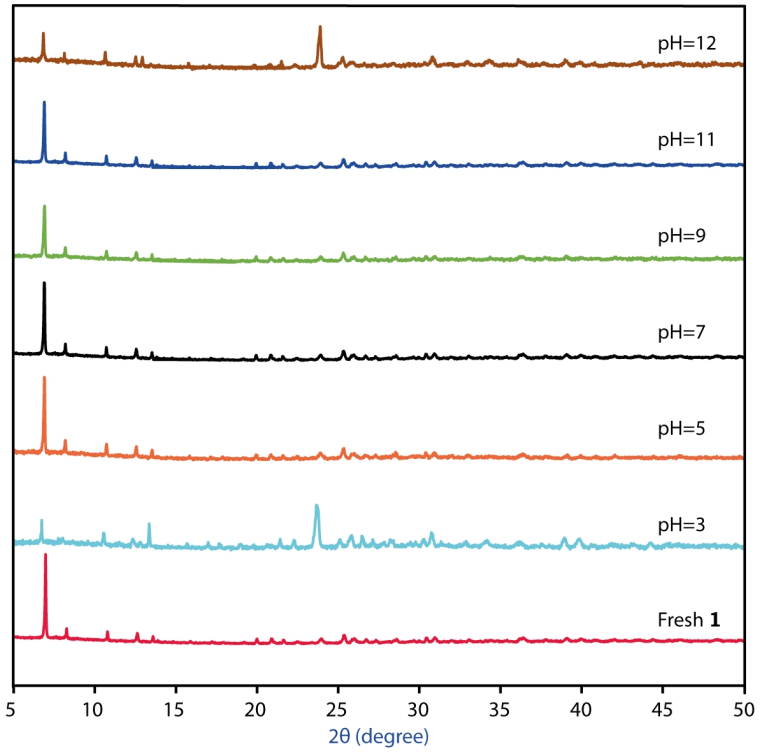

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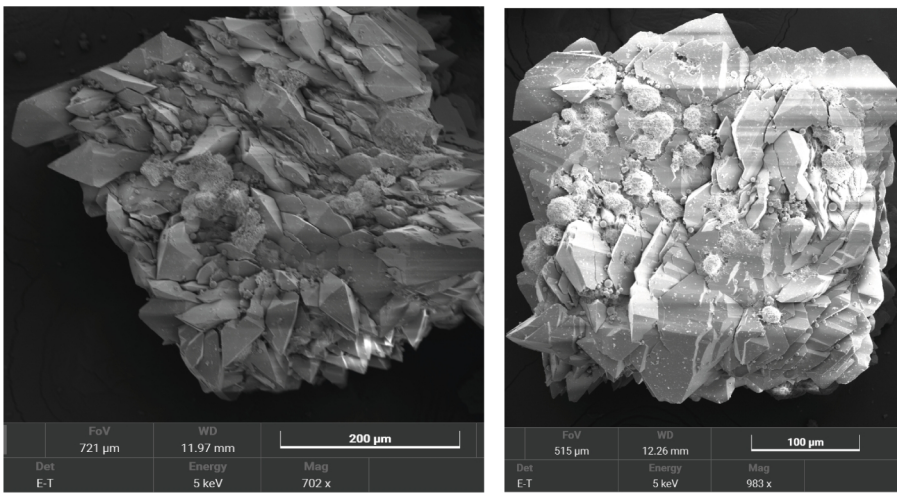

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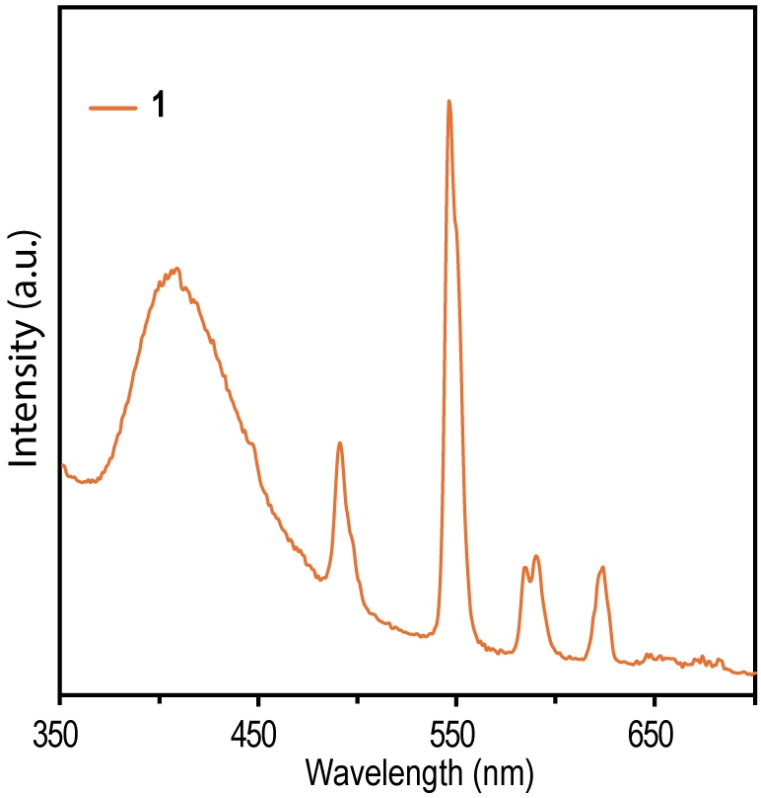

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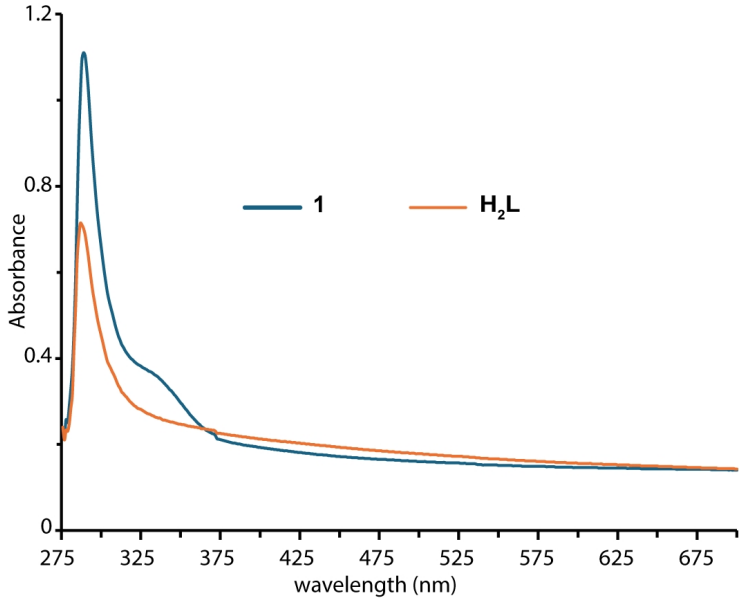

Figure S11. UV-vis spectra of **H_2L** and **1**.

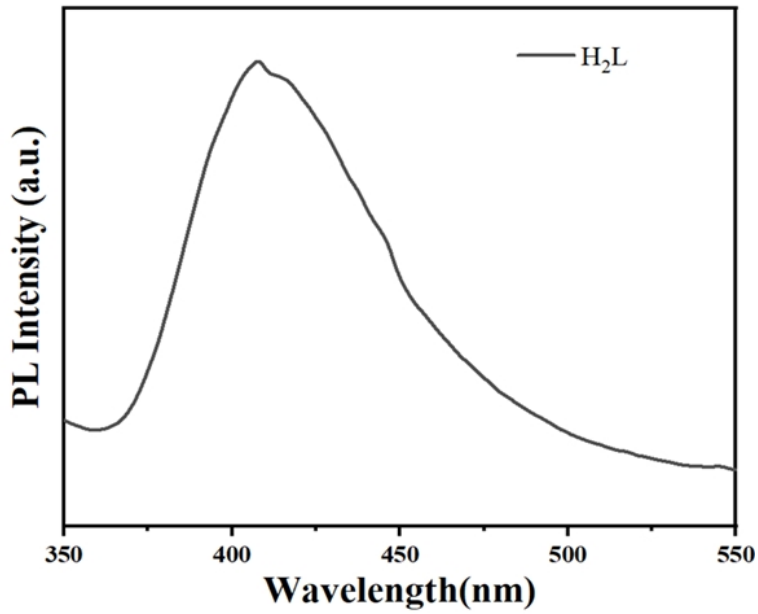

Figure S12. Fluorescence spectrum of **H_2L**.

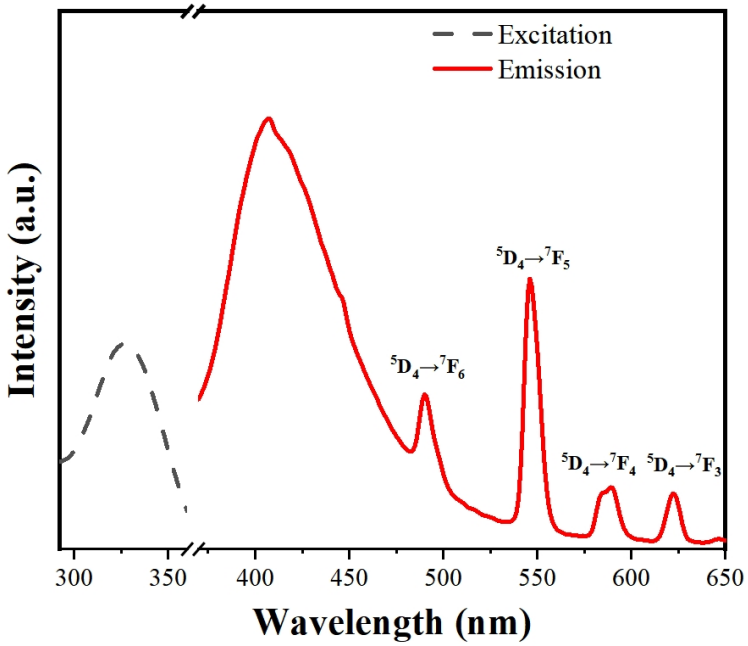

Figure S13. Excitation and Emission spectrum of **1**.

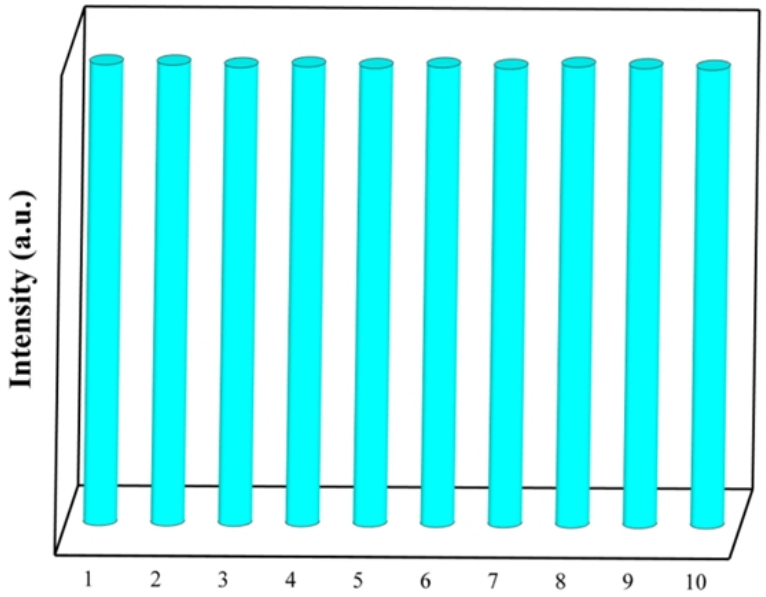

Figure S14. The fluorescence intensity of **1** at 407 nm was monitored at 6 min intervals over a period of one hour.

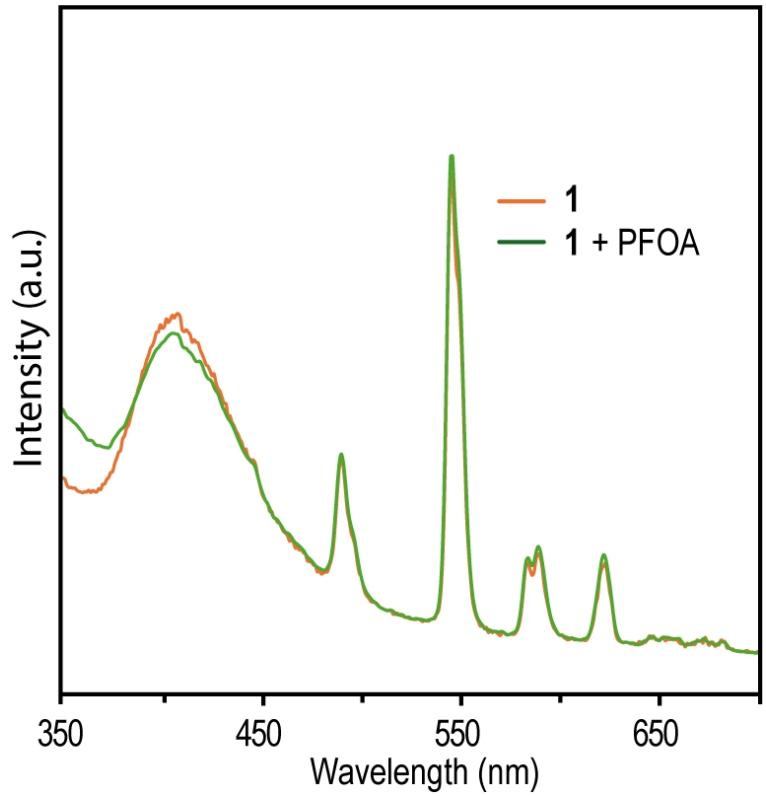

Figure S15. Solid state fluorescence Spectrum of **1,** before and after sensing of PFOA.

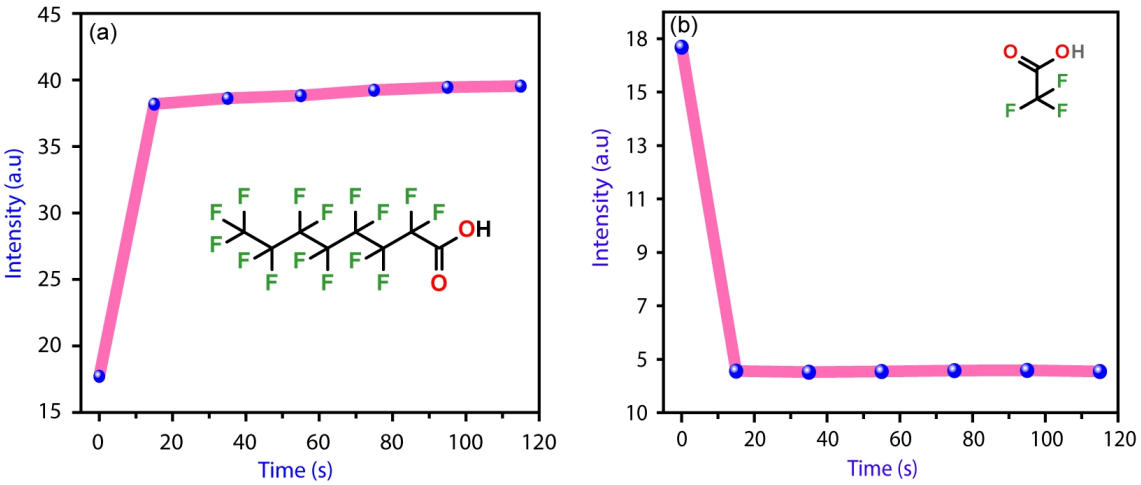

Figure S16. (a) Response time of **1** toward PFOA at various cycles and (b) response time of **1** toward TFA at various cycles in distilled water.

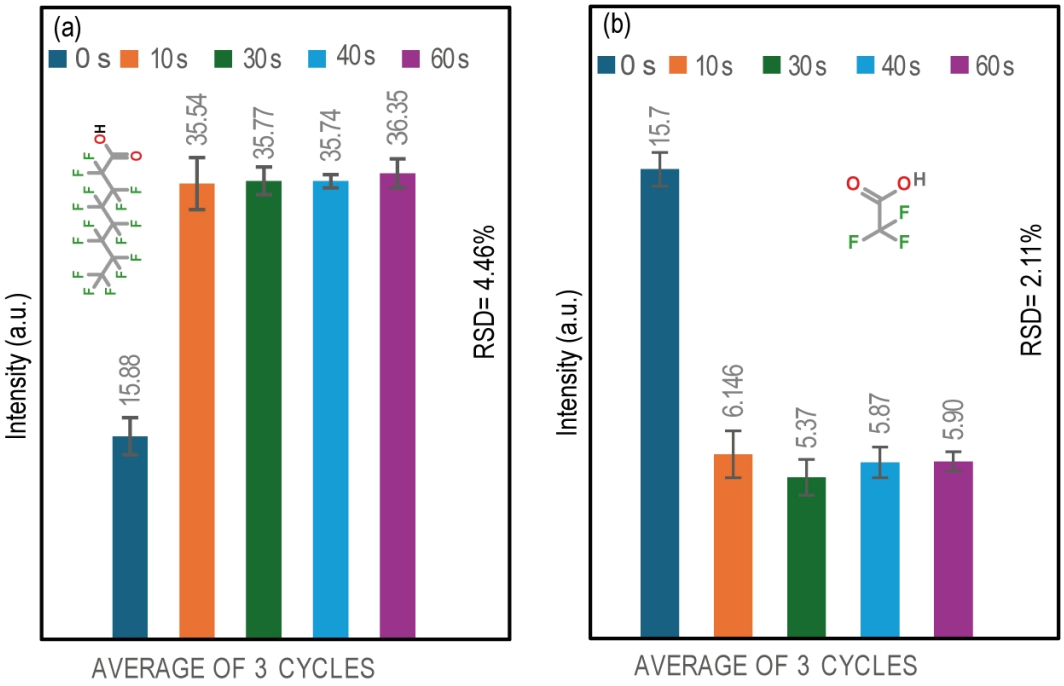

Figure S17. Response time of **1** to (a) PFOA and (b) over 3 cycles, monitored in the time span of 60 s.

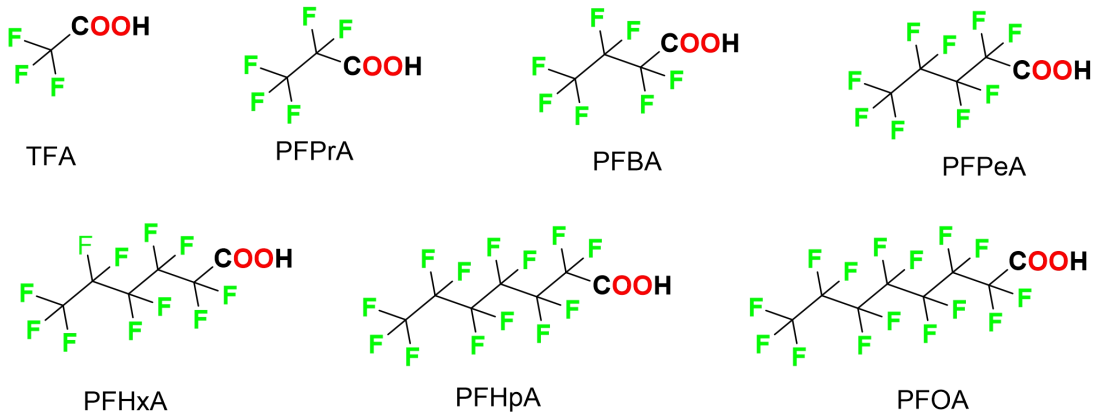

Figure S18. Structure of PFAS used for testing TFA: Trifloroacetic acid, PFPrA: Pentafluoropropanoic acid, PFBA: Perfluorobutanoic acid PFPeA: Perfluoropentanoic acid, PFHxA : Perfluorohexanoic acid, PFHpA: Perfluoroheptanoic acid, and PFOA: perfluorooctanoic acid.

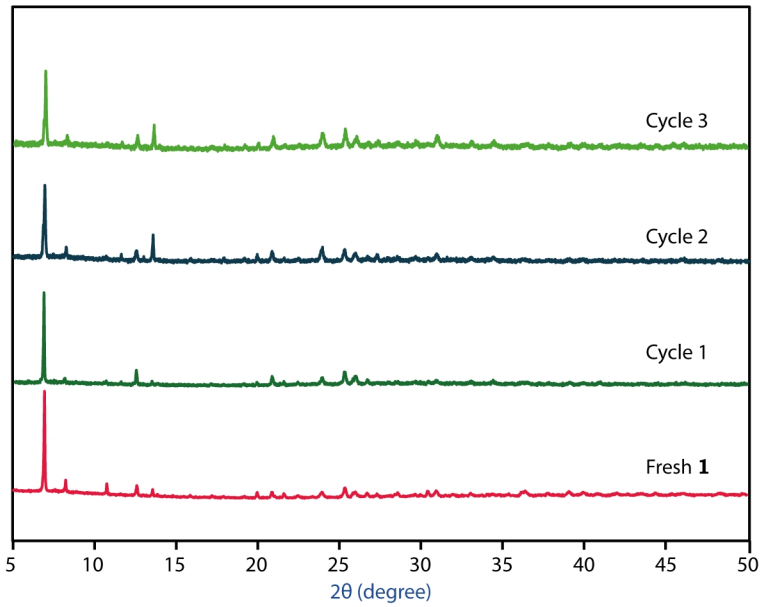

Figure S19. PXRD patterns of **1** after using three recycles of PFOA detection.

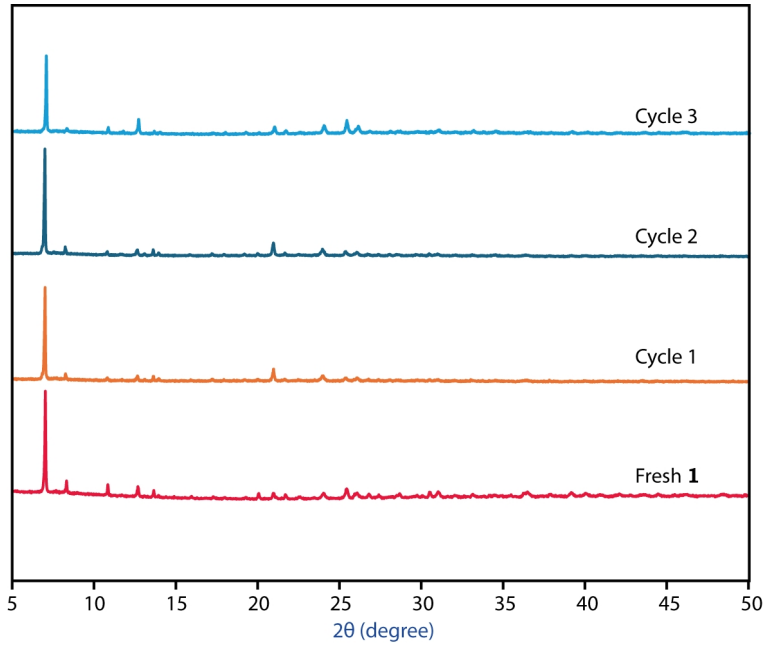

Figure S20. PXRD patterns of **1** after using three recycles of TFA detection.

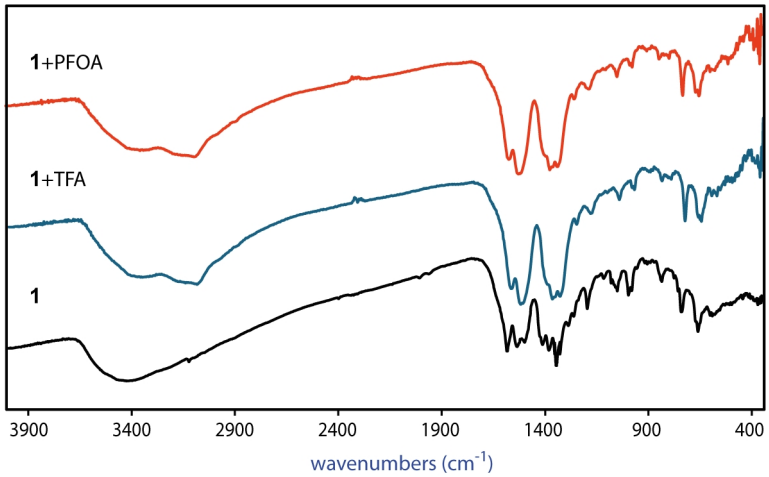

Figure S21. FT-IR spectra of **1** before and after sensing PFOA and TFA.

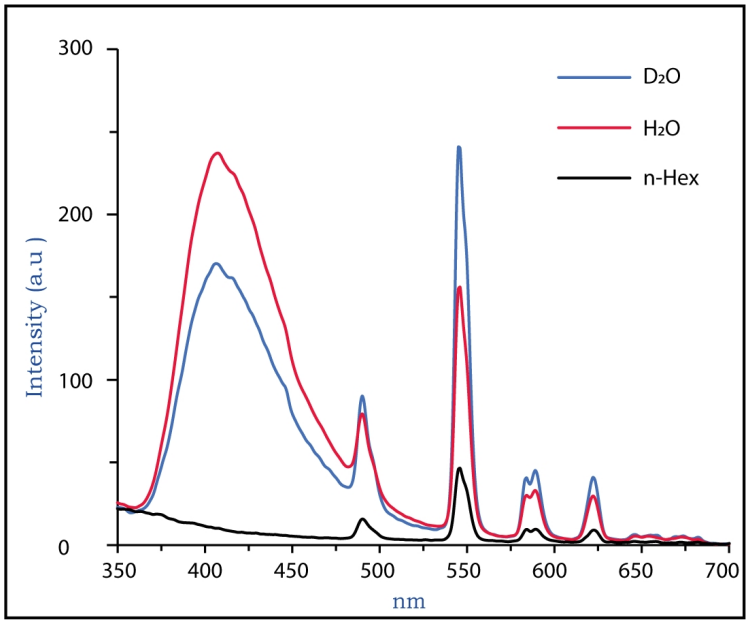

Figure S22. Emission spectra of **1** dispersed in different solvents.

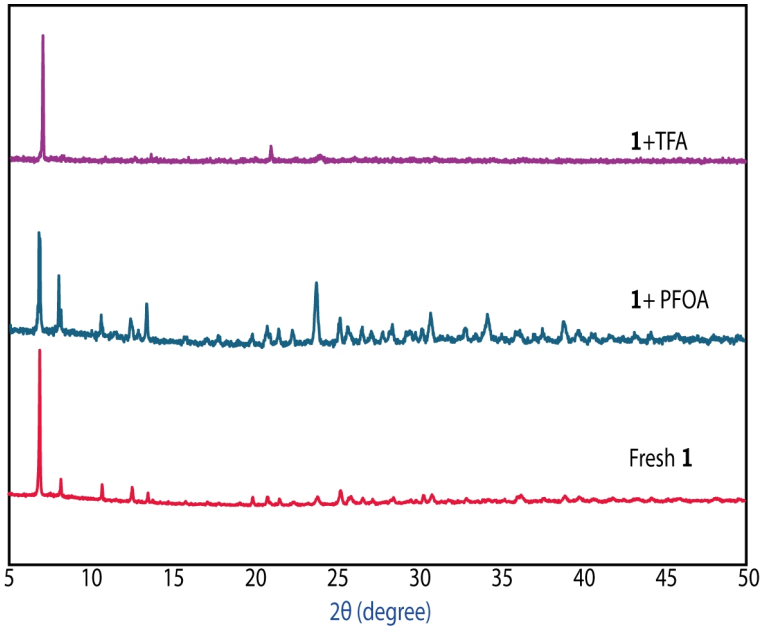

Figure S23. PXRD of **1** before and after the treatment of PFOA and TFA.

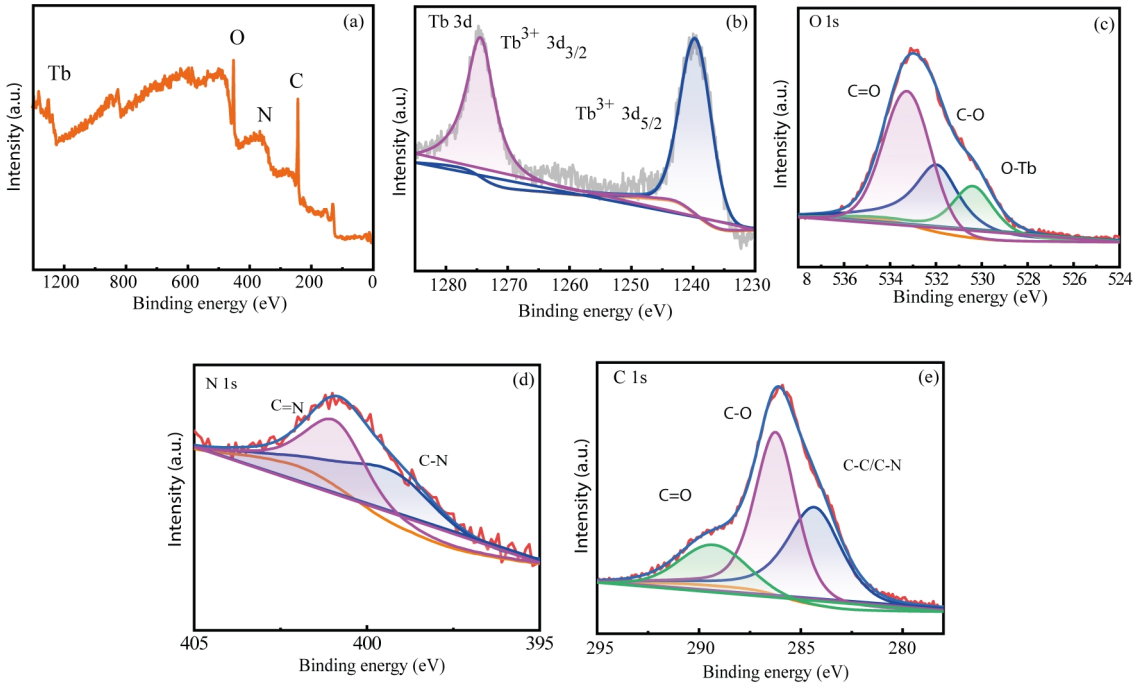

Figure S24. (a) XPS full spectrum of **1**; Narrow region scans of (b) Tb 3d (c) O 1s (d) N1s and (e) C 1s.

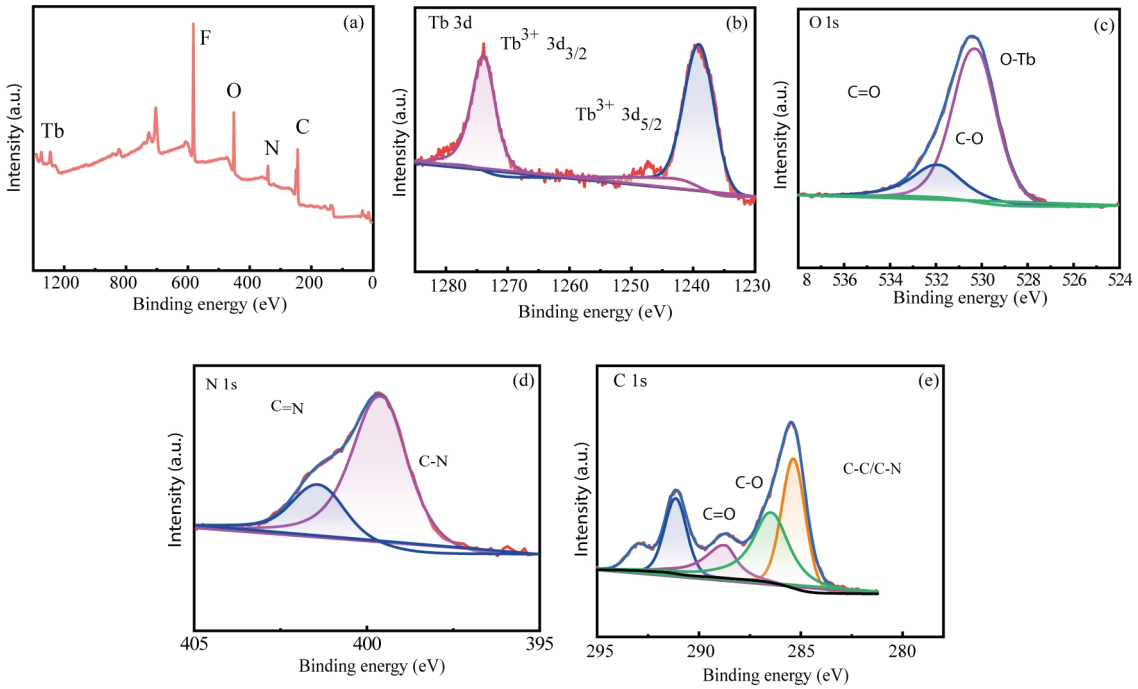

Figure S25. (a) XPS full spectrum of **1** after sensing with TFA; Narrow region scans of (b) Tb 3d (c) O 1s (d) N 1s, and (e) C 1s.

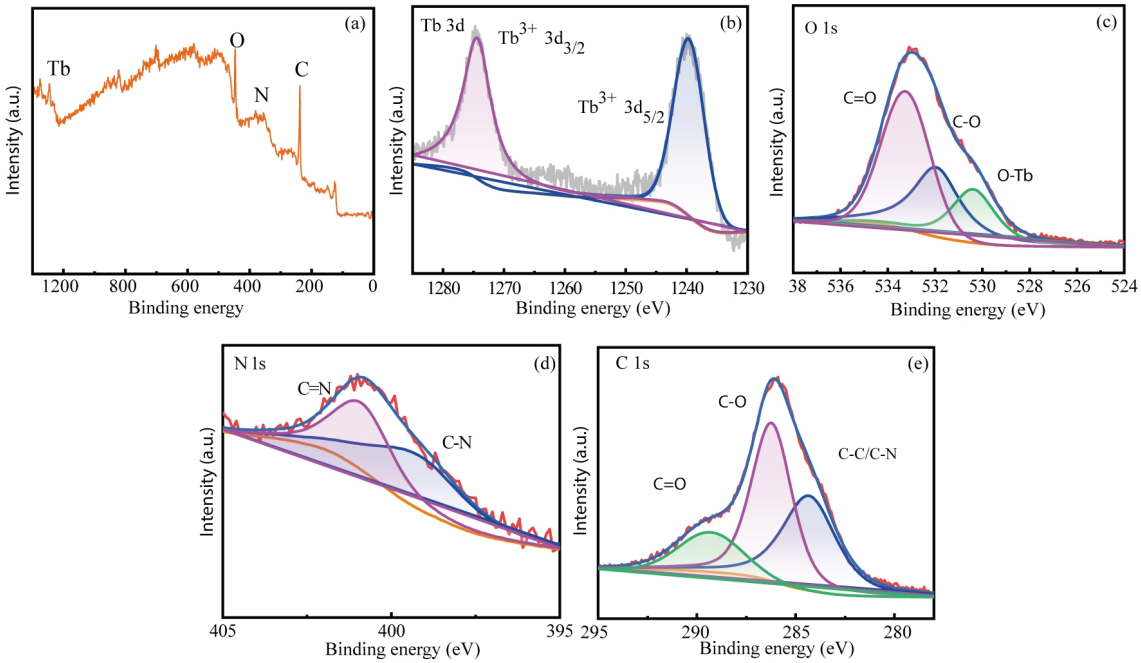

Figure S26. (a) XPS full spectrum of **1** after sensing with TFA and treatment with $NH_3 \cdot H_2O$; Narrow region scans of (b) Tb 3d, (c) O 1s, (d) N 1s, and (e) C 1s after sensing with TFA and treatment with $NH_3 \cdot H_2O$.

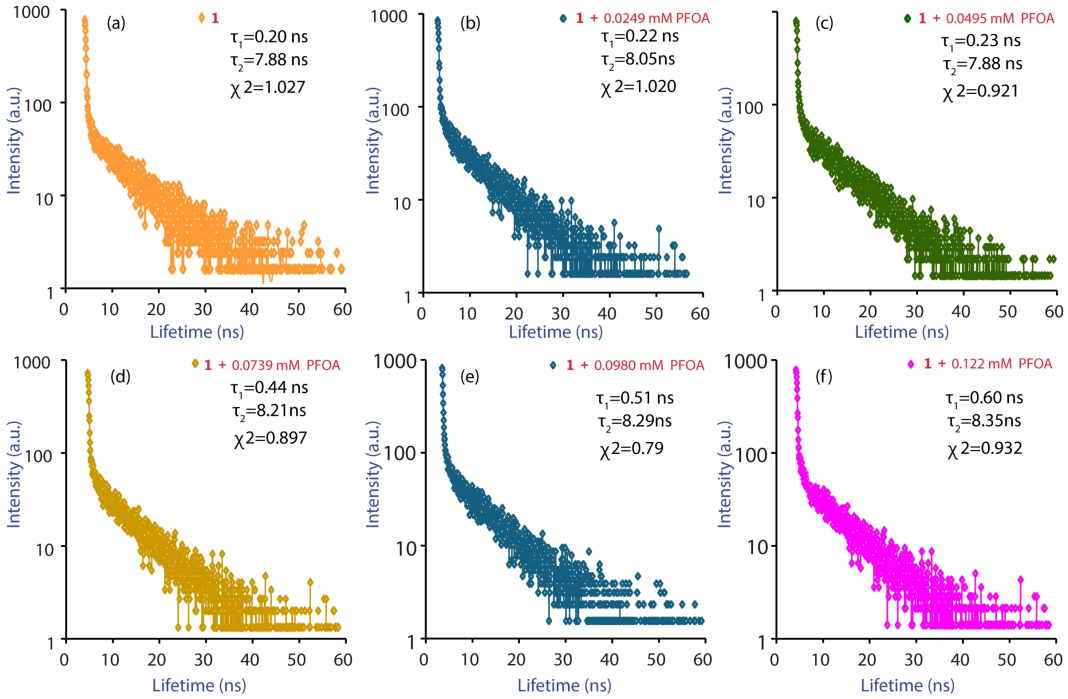

Figure S27. Fluorescence lifetimes (407 nm) of **1** suspension in the (a) absence and presence of PFOA (b) 0.0249 mM, (c) 0.0495 mM, (d) 0.0739 mM, (e) 0.0980 mM, (f) 0.122 mM PFOA in aqueous solution.

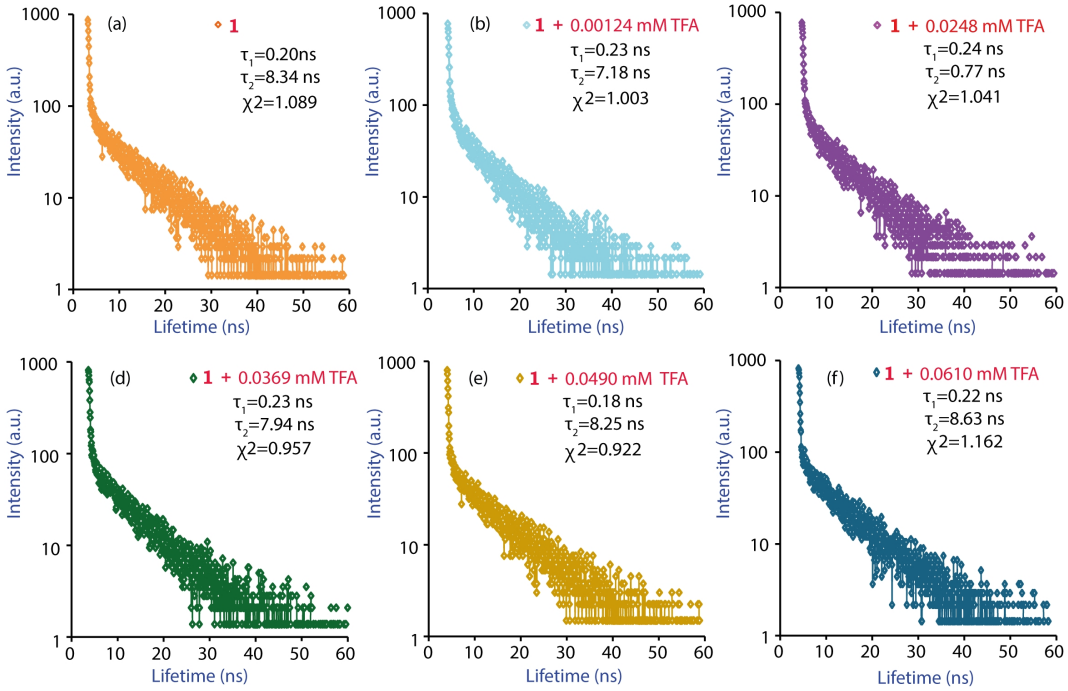

Figure S28. Fluorescence lifetimes (407 nm) of **1** suspension in the (a) absence and presence of TFA (b) 0.0124 mM, (c) 0.0248 mM, (d) 0.0369 mM, (e) 0.0490 mM, (f) 0.0610 mM TFA in aqueous solution.

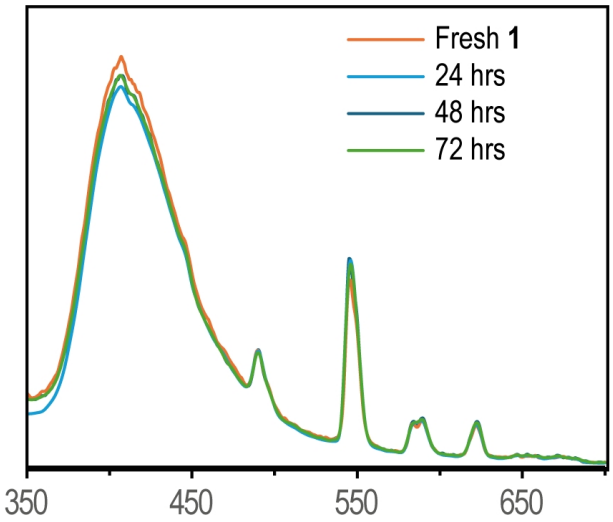

Figure S29. Fluorescence spectra of **1**, in Pearl River water dispersion, recorded in a time span of 72 h.

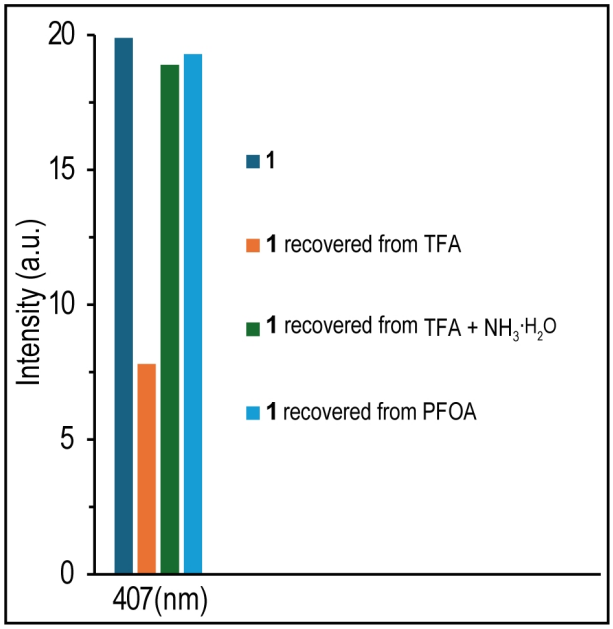

Figure S30. Emission intensity of **1**, recovered **1** from TFA, recovered **1** from TFA after treatment with $NH_3 \cdot H_2O$ and **1** recovered from PFOA sensing.

Table S1. Crystal data and structural refinement parameters for **1**.

Complexes	**1**
Empirical formula	$C_{15}H_{19}N_4O_{10}Tb$
Formula weight	574.26
Temperature/K	200.15
Crystal system	tetragonal
Space group	*I* -42*d*
a/Å	21.4514(4)
b/Å	21.4514(4)
c/Å	15.7716(7)
α/°	90
β/°	90
γ/°	90
V/Å^3	7257.5(4)
Z	16
ρ_{calc}g/cm^3	2.102
μ/mm^{-1}	19.796
F(000)	4512.0
Radiation	Cu Kα (λ = 1.54184)
Reflections collected	9766
Independent reflections	3206 [R_{int} = 0.0697, R_{sigma} = 0.0590]
GOF on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0621, wR_2 = 0.1580
Final R indexes [all data]	R_1 = 0.0704, wR_2 = 0.1651
Largest diff. peak/hole / e Å^{-3}	1.40/-0.99
Flack parameters	0.035(16)

Table S2. Selected bond lengths (Å) and angles (°) for **1**.

Tb1 O3	2.326(11)	O3 Tb1 $O2^4$	75.0(5)	$O2^4$ Tb1 O7	74.7(4)
Tb1 $O2^4$	2.357(11)	O3 Tb1 $O1^5$	143.0(4)	$O2^4$ Tb1 O6	143.0(5)
Tb1 $O1^5$	2.349(9)	O3 Tb1 O5	74.1(4)	$O1^5$ Tb1 O5	142.8(4)
Tb1 O5	2.369(9)	O3 Tb1 $O5^2$	124.6(4)	$O1^5$ Tb1 $O5^2$	79.9(3
Tb1 $O5^2$	2.364(10)	O3 Tb1 $O5^1$	132.8(4)	$O1^5$ Tb1 $O5^1$	78.5(4)
Tb1 $O5^3$	2.383(9)	O3 Tb1 O7	75.8(4)	$O1^5$ Tb1 O7	67.7(4)
Tb1 O7	2.526(11)	O3 Tb1 O6	75.0(5)	$O1^5$ Tb1 O6	89.4(5)
Tb1 O6	2.406(15)	$O2^4$ Tb1 $O5^1$	74.3(4)	$O5^1$ Tb1 $O5^2$	70.6(3)
Tb1 $Tb1^1$	3.7952(15)	$O2^4$ Tb1 $O5^2$	144.5(4)	O5 Tb1 O7	149.5(3
		$O2^4$ Tb1 O5	94.1(4)	O5 Tb1 O6	102.3(5)

Symmetry codes: [1]+X, -1/2-Y, -3/4-Z; [2]-1-Y, -1/2-X, 1/4+Z; [3]-1/2+Y, -1/2-X, -1/2-Z; [4]-1-X, -Y, +Z; [5]-1/2-Y, -1-X, -1/4+Z.

Table S3. Comparative literature survey of the present work with recently reported metal-organic compound-based PFOA and TFA sensors.

No.	Type of compounds/Metal ions	Method of detection	Limit of detection (LOD) (PFOA)	Ref
1	**Tb^{3+}-H_2L**	Fluorimetry	0.17 nM	**This work**
2	Zr^{4+}-Perylene Diimide	Fluorimetry	3.1 nM	1
3	Tb^{3+}-BDC	Mass spectrometry	1.35 nM	2
4	Zr^{4+}-(PCN-999)	^{19}F NMR	\	3
5	Ln^{3+}-TCPP	Fluorimetry	15 μM	4
6	Tb/Triazole	Fluorimetry	0.066 nM	5
	Type of compounds/Metal ions	**Method of detection**	**Limit of detection (LOD) (PFOA)**	**Ref**
7	**Tb^{3+}-H_2L**	**Fluorimetry**	**105 nM**	**This Work**
8	Tb^{3+}-Amide Ligand	Visual	/	6
9	cyclodextrin	Fluorimetry	0.25 ppm	7
10	Pd^{2+}- 1,3-di(1*H*-imidazol-1-yl) benzene	^{19}F NMR	/	8

BDC: terephthalic acid; TCPP: 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine.

Table S4. The summarizes of the K_{BH}, K_{EC} and LOD in distilled water, Pearl River water.

Analyte	Solution	K_{BH} (M^{-1})	LOD (nM)
PFOA	Distilled water	9.27×10^7	0.017
	Pearl River water	7.93×10^7	0.019
		K_{EC} (M^{-1})	LOD (nM)
TFA	Distilled water	1.48×10^4	105
	Pearl River water	1.43×10^4	109

Table S5. Luminescence lifetime of **1** with or without PFOA and TFA.

Additions[a] / mL	Lifetime[b] 407 nm / ns		Additions[c] / mL	Lifetime[b] 407 nm / ns	
	τ_1	τ_2		τ_1	τ_2
0	0.20	7.88	**0**	0.20	8.34
0.010	0.22	8.05	**0.010**	0.23	7.18
0.020	0.23	7.88	**0.020**	0.24	7.77
0.030	0.44	8.21	**0.030**	0.23	7.94
0.040	0.51	8.29	**0.040**	0.18	8.25
0.050	0.60	8.35	**0.050**	0.22	8.63

[a]5 mM PFOA was added to 2 mL of **1** Suspension in different volumes. [b]Excited at 407 nm. [c]2.5 mM TFA was added to 2 mL of **1** Suspension in different volumes.

Table S6. HOMO and LUMO energies for H_2L, PFOA, and TFA.

Compounds	HOMO (eV)	LUMO (eV)	Band Gap (eV)
H_2L	-2.636	-7.434	4.798
PFOA	-9.168	-1.941	7.227
TFA	-9.141	-1.725	7.416

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