Electronic Supporting Information (ESI)

Pyrene-antipyrine based highly selective and sensitive turn-on fluorescent sensor for Th(IV)

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I. Procedure for the determination of quantum yield

The fluorescence quantum yield was determined using anthracene as a reference with a known ϕ_R of 0.27 in ethanol. The probe and the reference were excited at the same wavelength, with nearly equal absorbance and the emission spectra were recorded. The quantum yield is calculated according to the following equation:

$$\phi_S/\phi_R = [A_S/A_R] \times [(Abs)_R/(Abs)_S] \times [\eta_S^2/\eta_R^2]$$

Where, ϕ_S and ϕ_R are the fluorescence quantum yields of the sample and reference, respectively. A_S and A_R are the area under the emission spectra of the sample and reference respectively, $(Abs)_S$ and $(Abs)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation and η_S and η_R are the values of refractive index for the respective solvent used for the sample and reference.

II. Figures
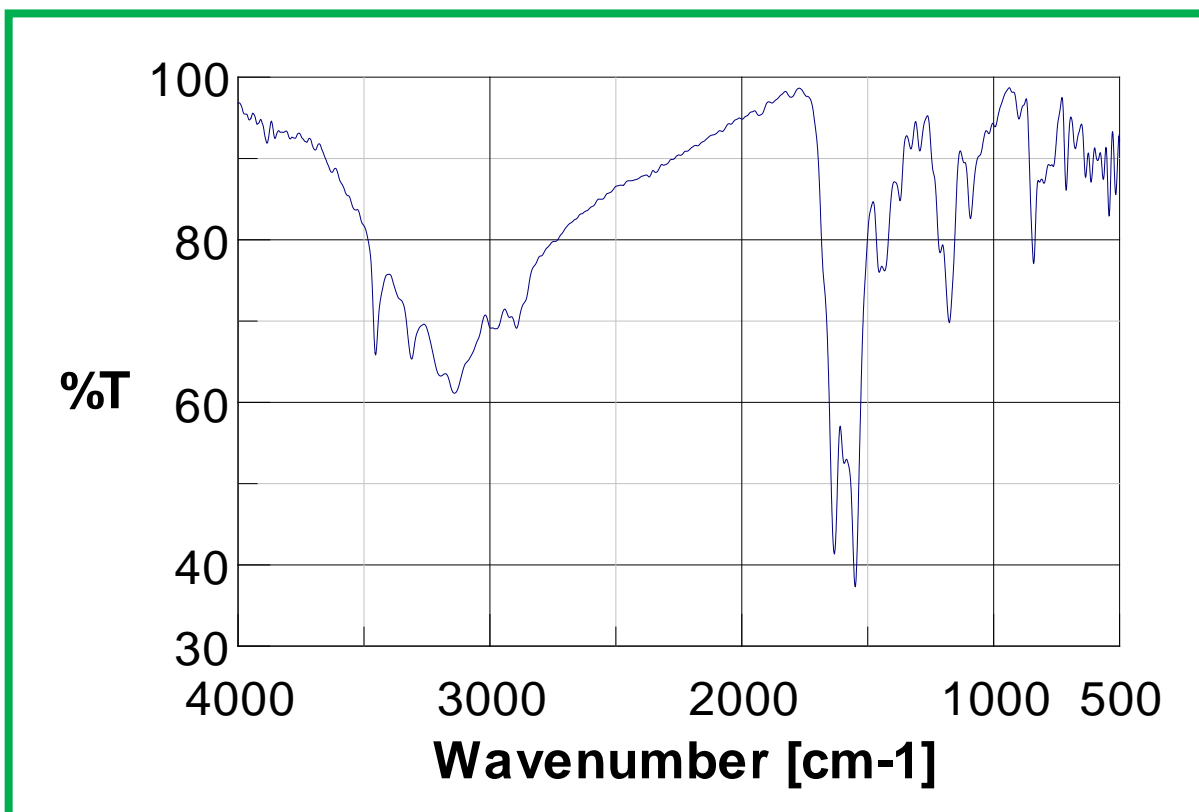
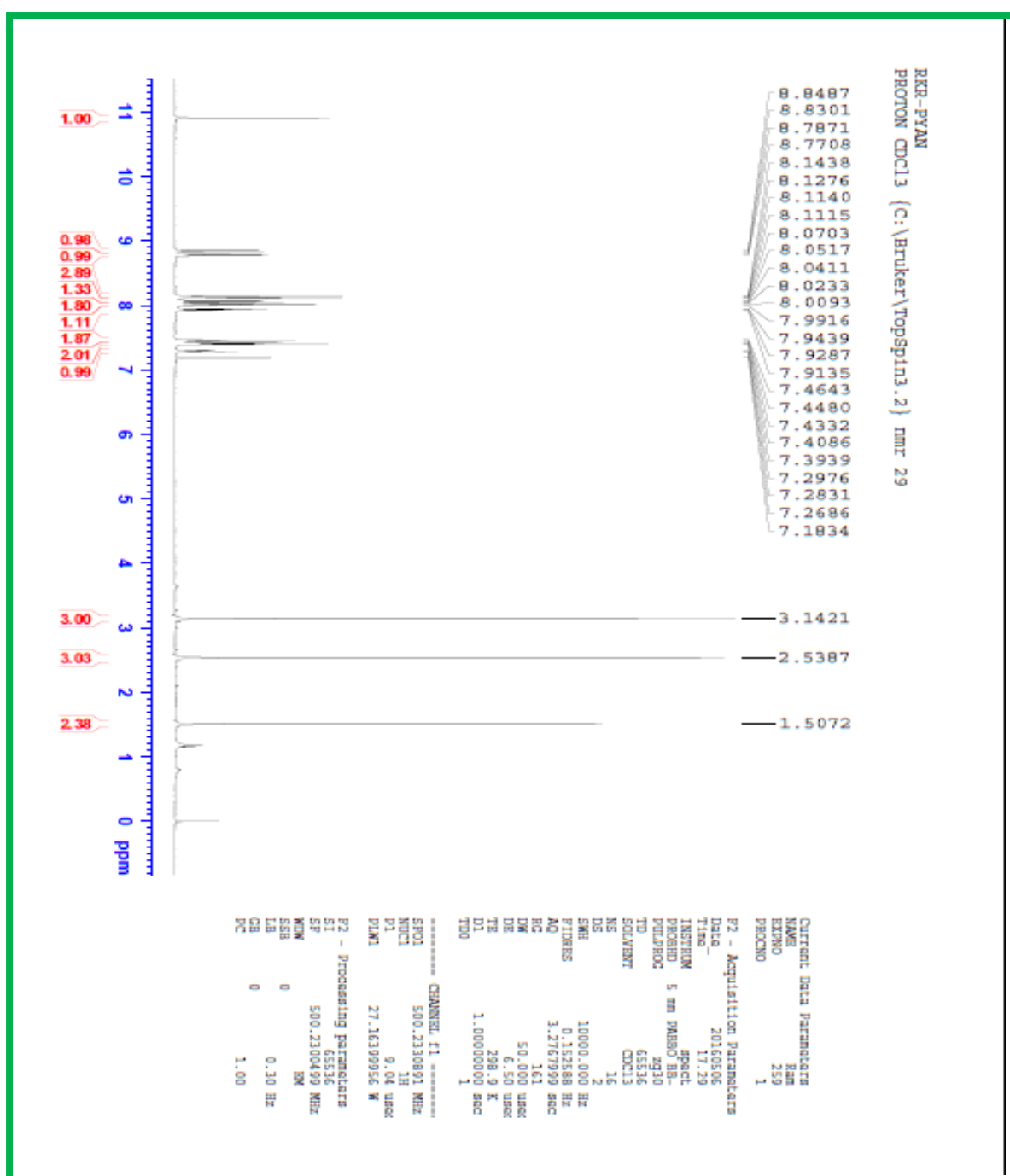**Fig. S1** FT-IR spectrum of the Probe PYAN.
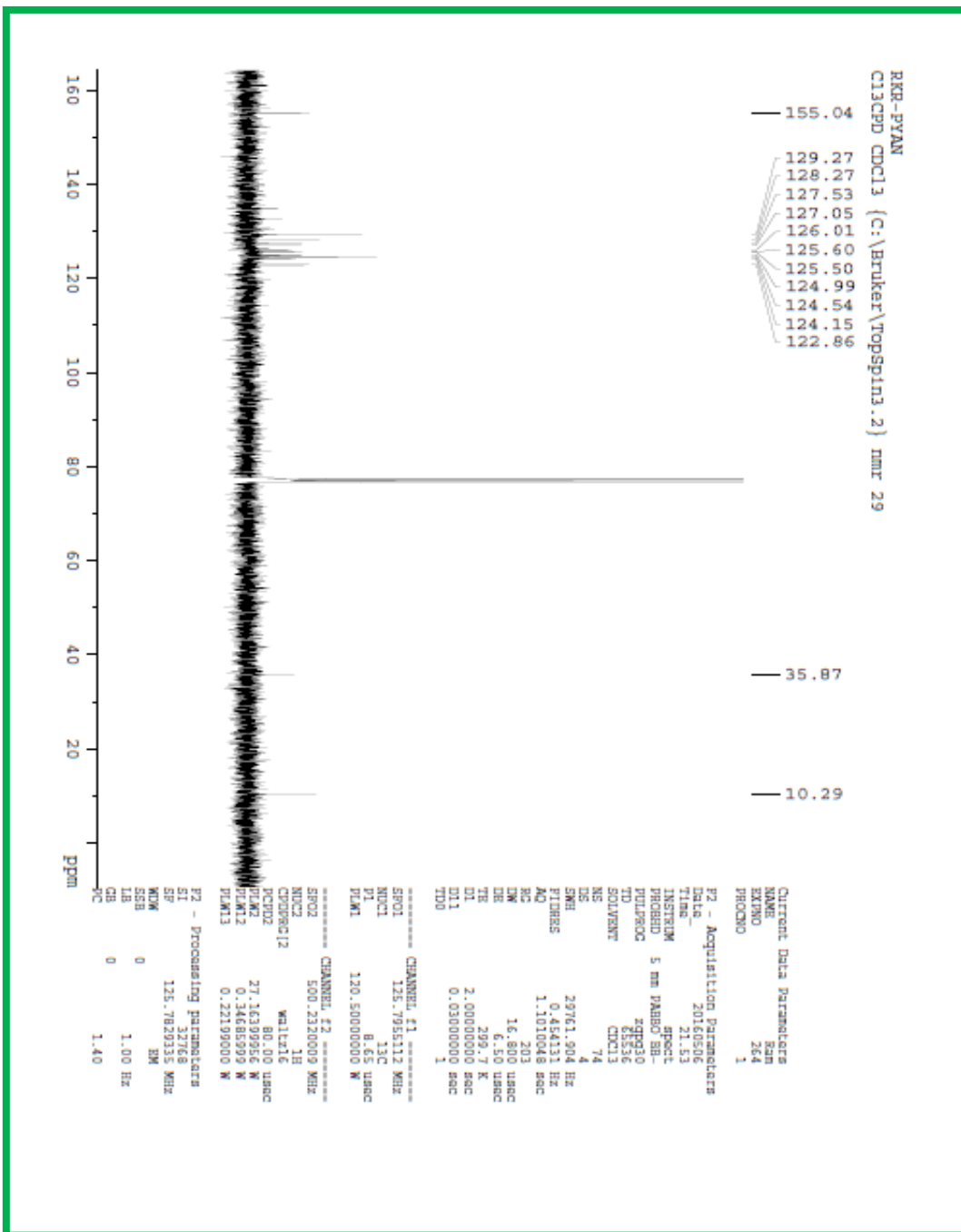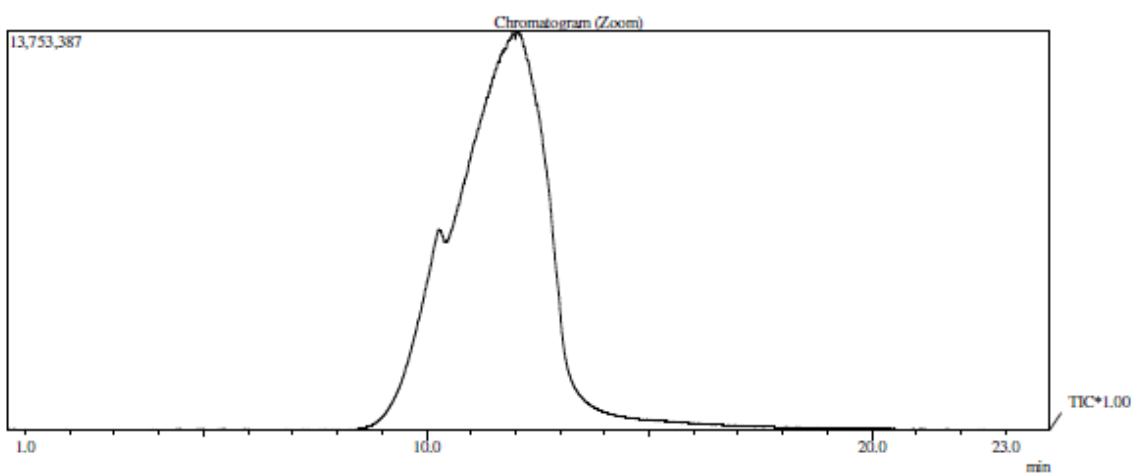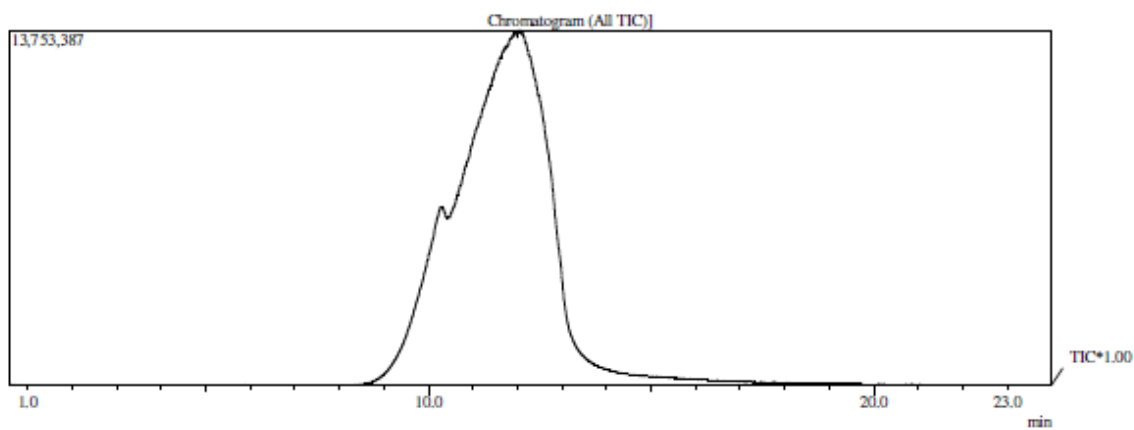
Fig. S2 ^{1}H NMR spectrum of the Probe PYAN.

Fig. S3 ^{13}C NMR spectrum of the Probe PYAN.

Chromatogram (All TIC)]

13,753,387

TIC*1.00

Chromatogram (Zoom)

13,753,387

TIC*1.00

Spectrum

Line#:1 R.Time:12.067(Scan#:1377)
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RawMode:Averaged 8.542-16.583(954-1919) BasePeak:56.05(981801)
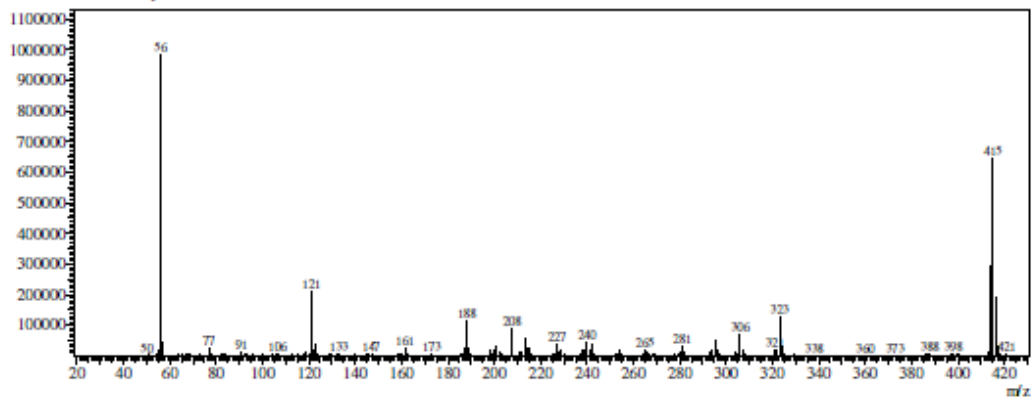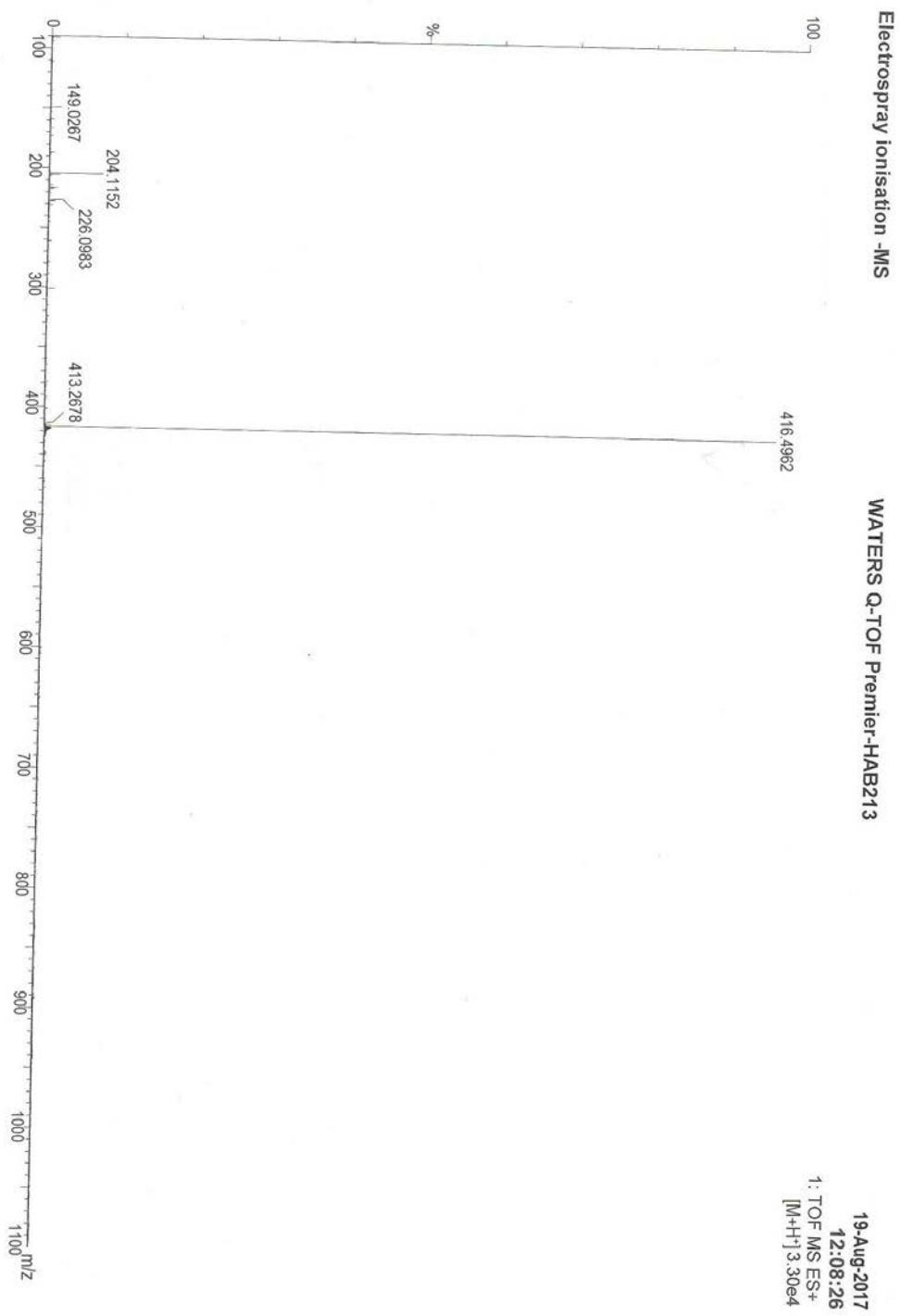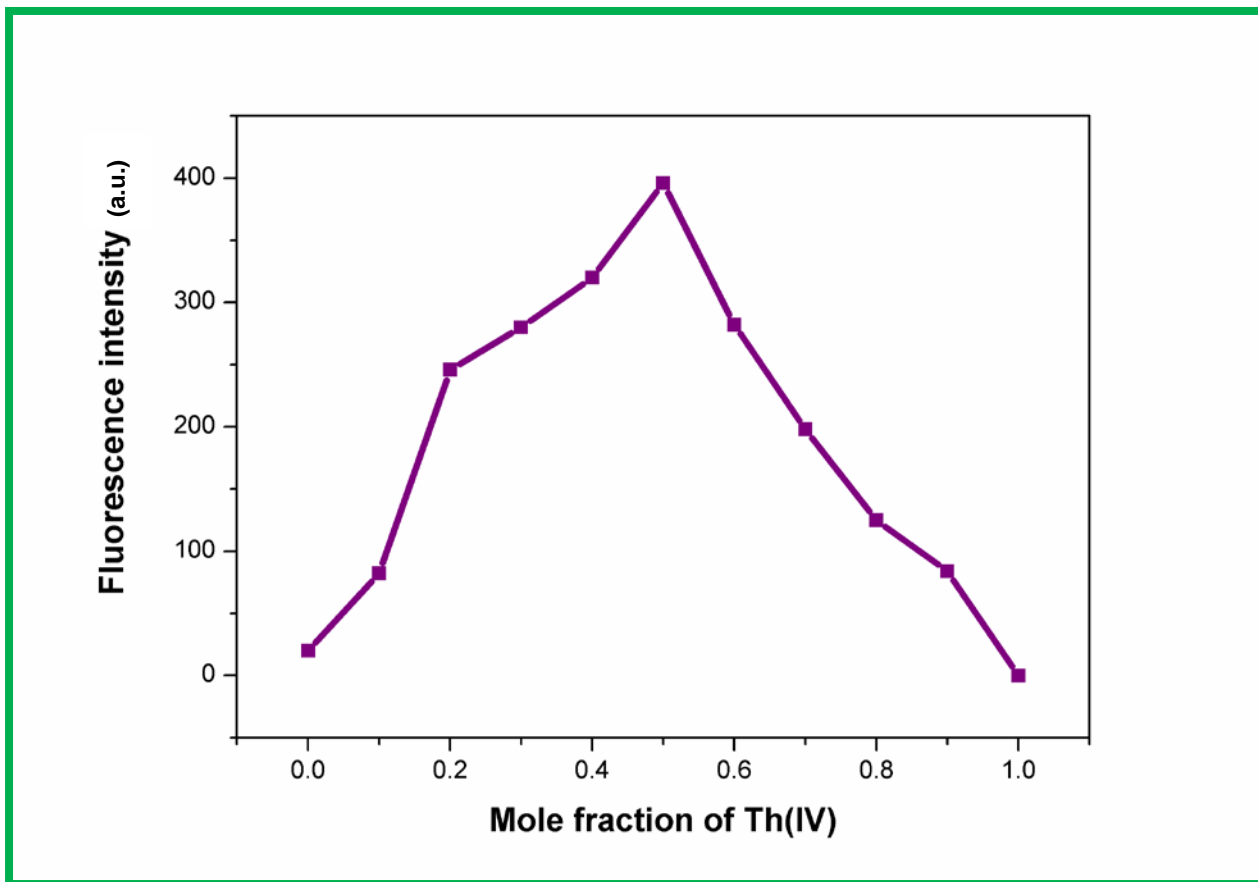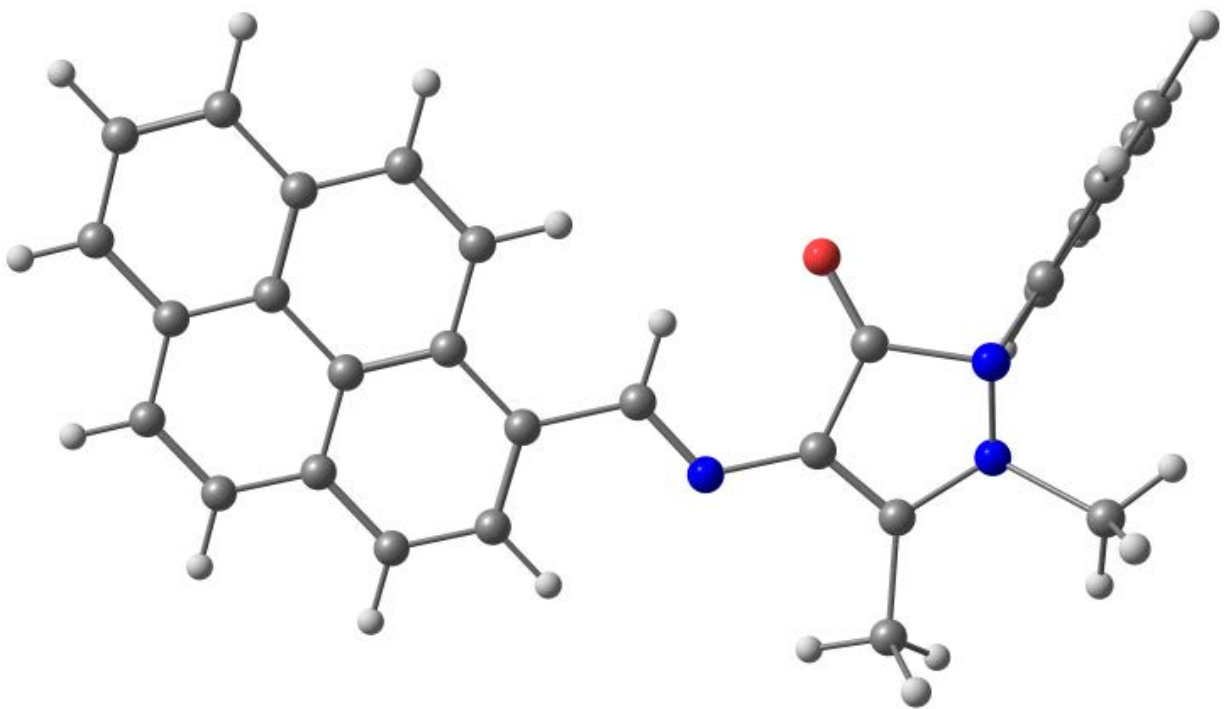BG Mode:None Group 1 - Event 1

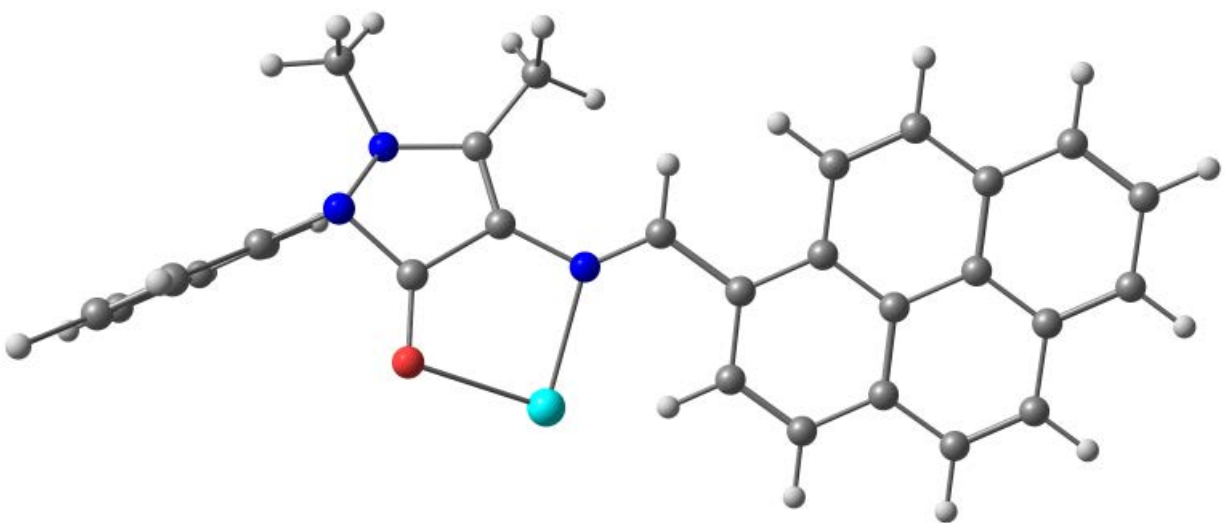**Fig. S4** Mass spectrum of the Probe PYAN (GC-MS)

Fig. S5 Mass spectrum of the Probe PYAN: MS-ESI

Fig. S6 Job's plot for emission intensity of PYAN versus mole fraction of Th(IV).
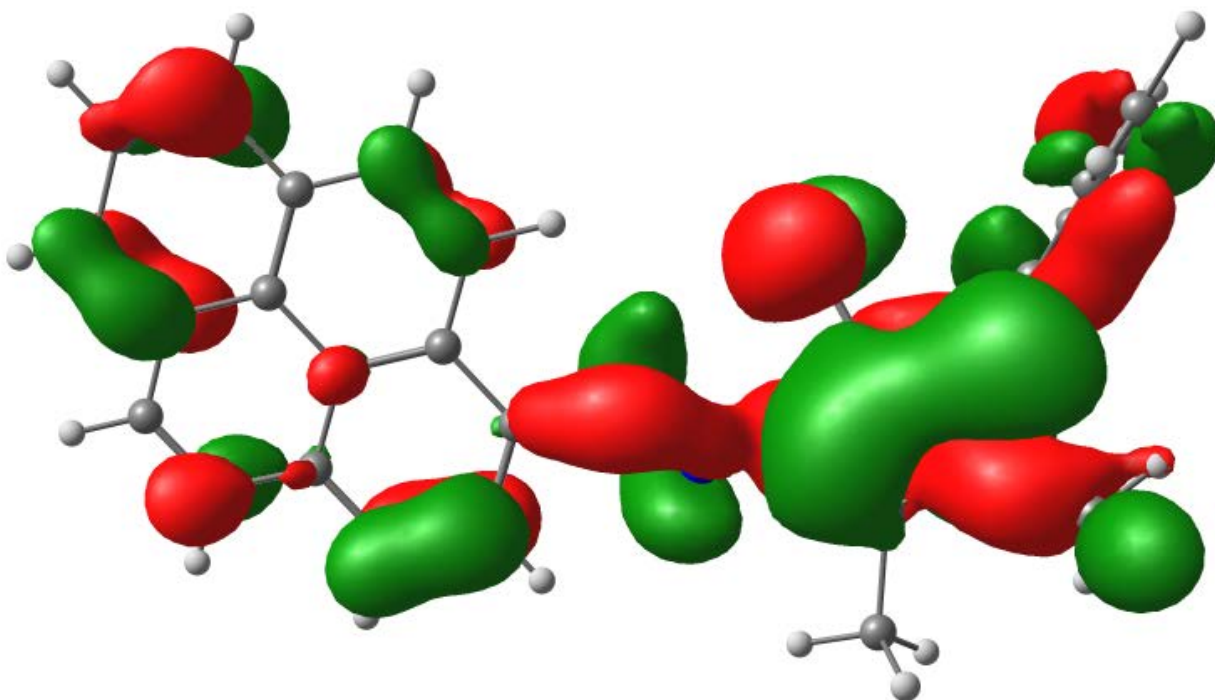
PYAN

PYAN+Th(IV)

Fig. S7 Optimized structures of PYAN and PYAN-Th(IV) using B3LYP-6-311G, B3LYP-6-311G quasi-relativistic effective core potentials(RECP) respectively.
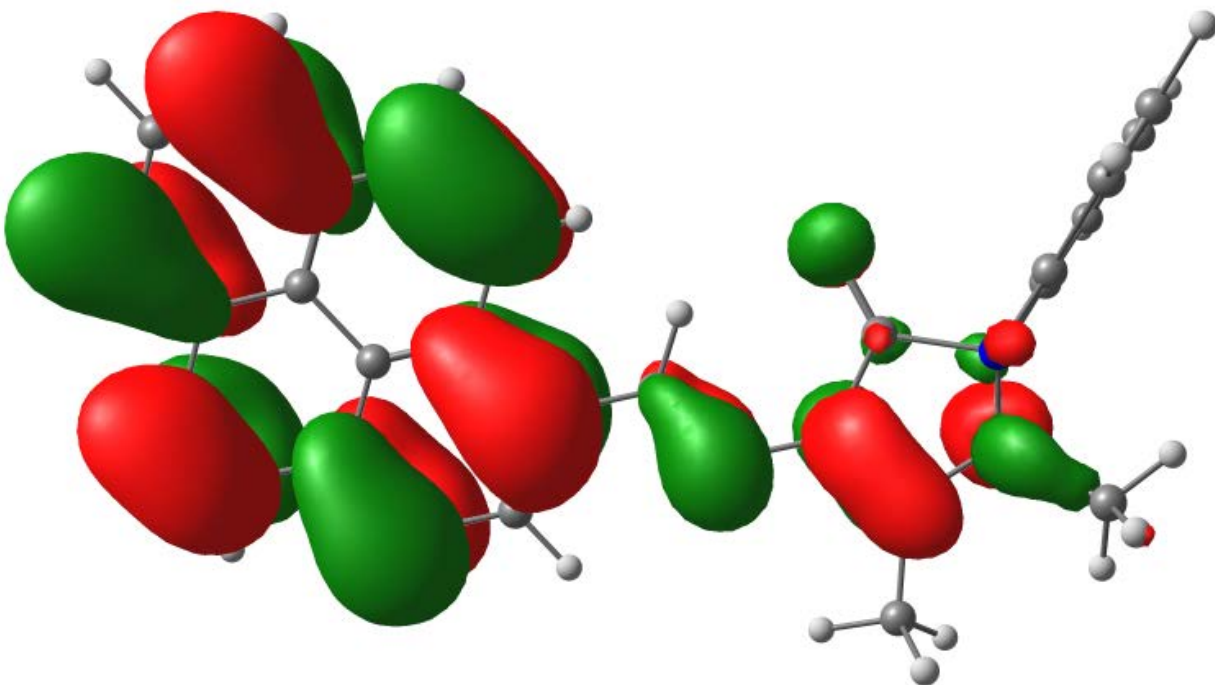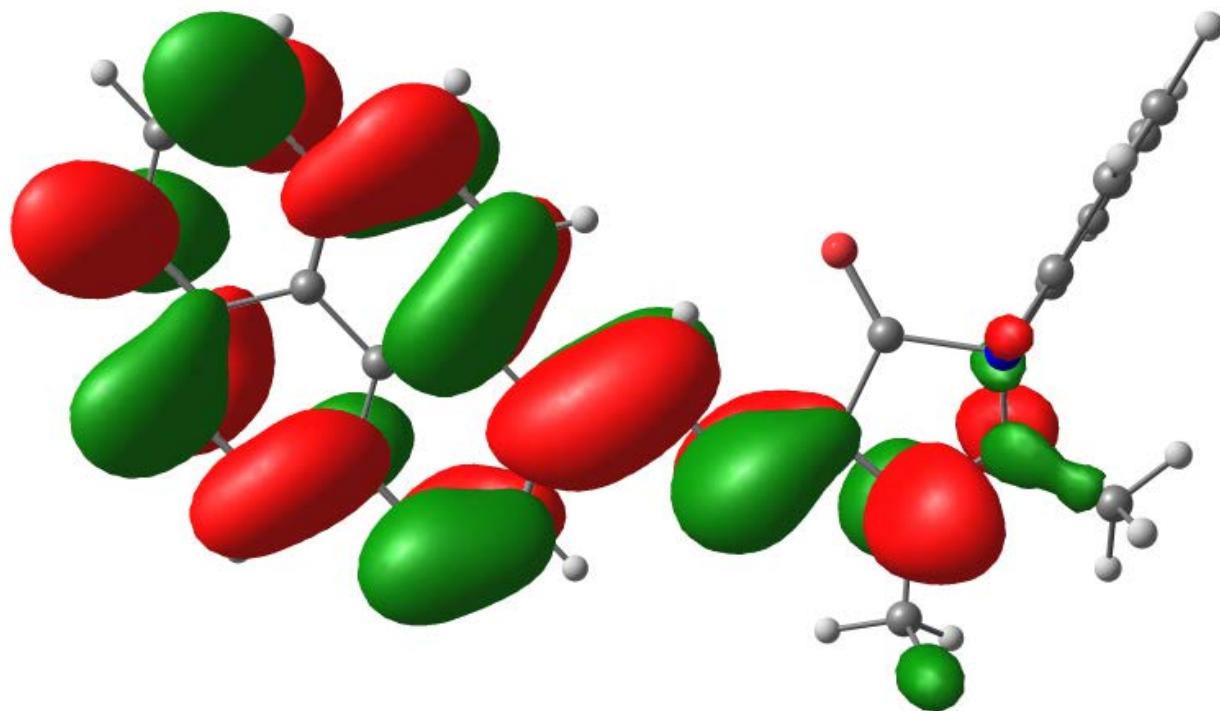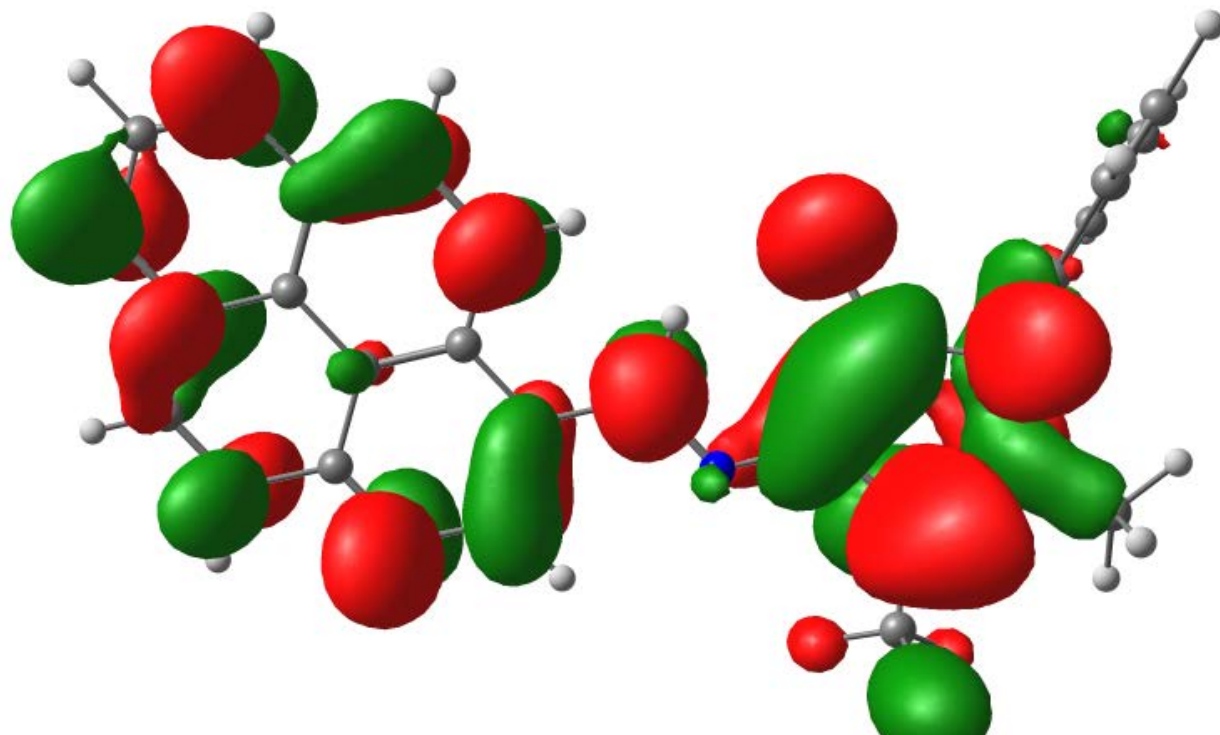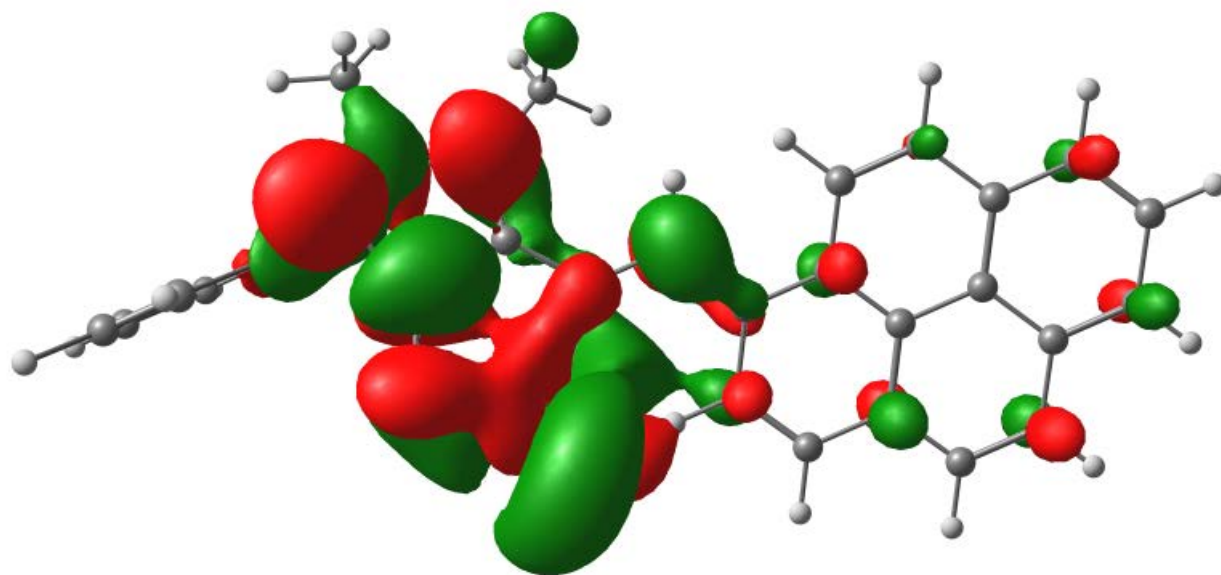
Probe: PYAN

HOMO-1

HOMO

LUMO

LUMO+1

Probe with thorium: PYAN+Th(IV)

HOMO-1

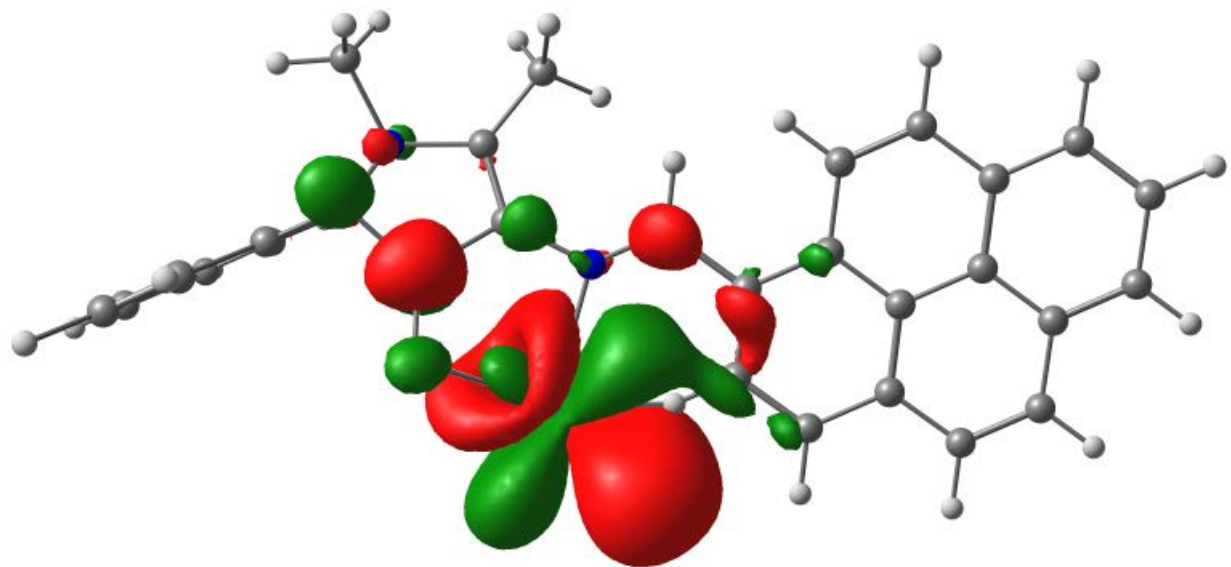**HOMO**
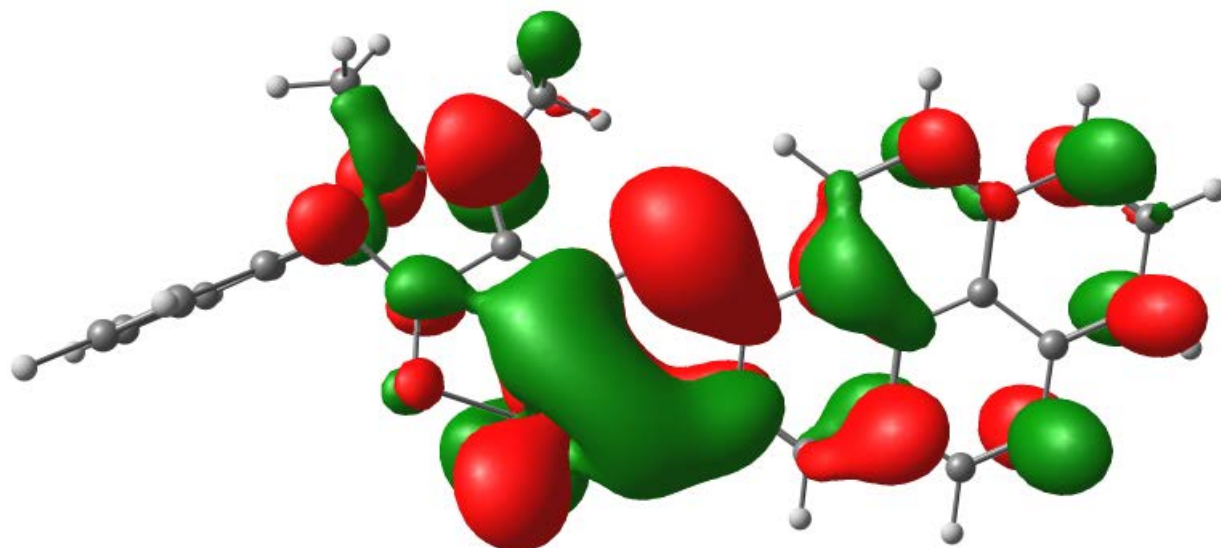
LUMO
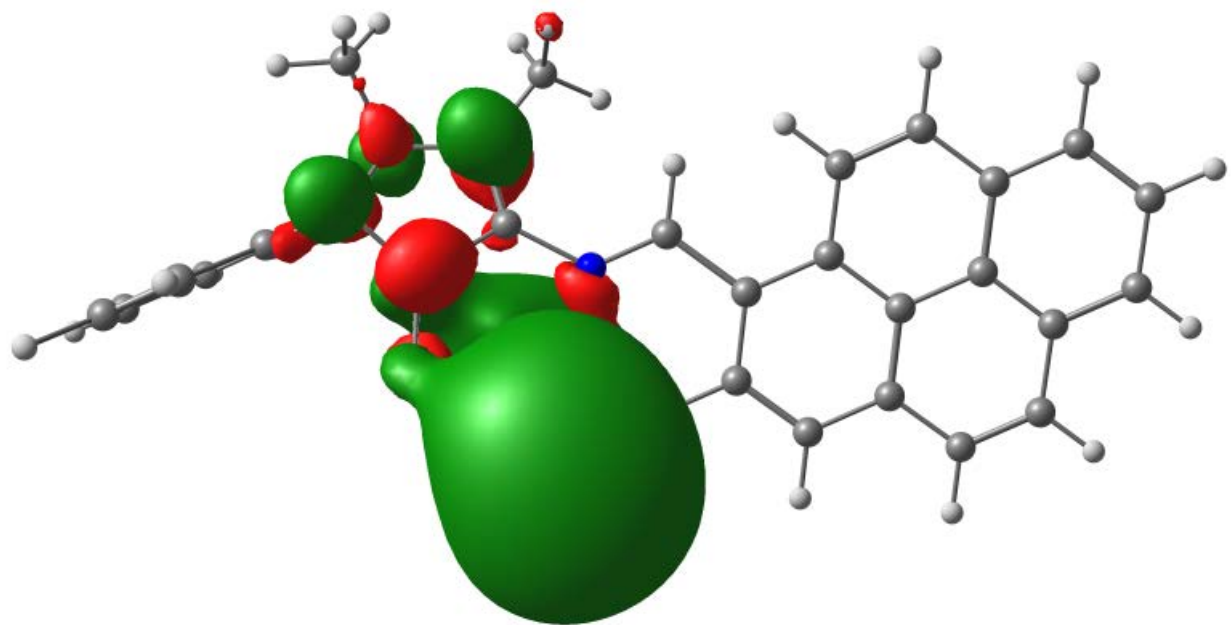
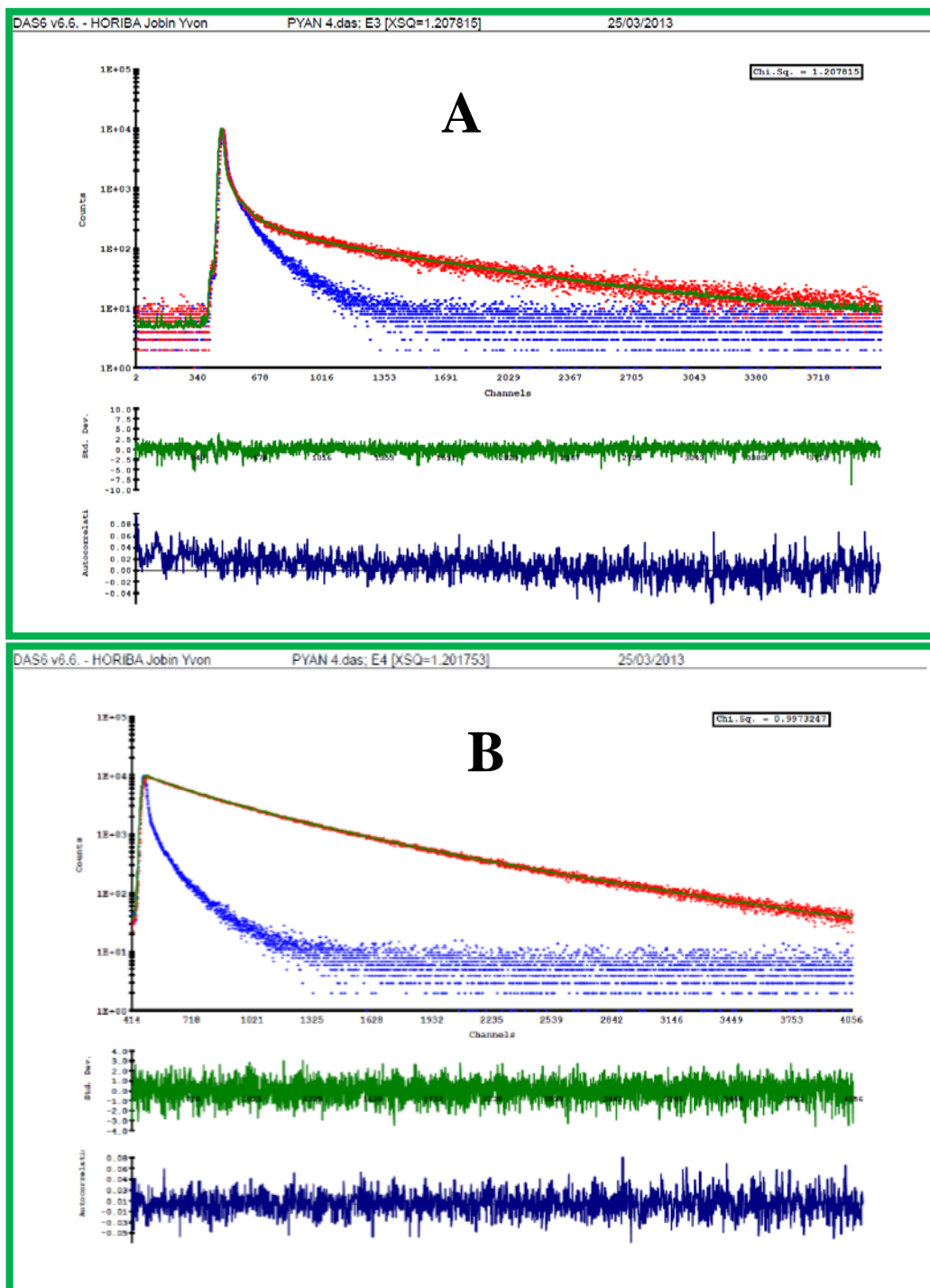**LUMO+1**

Fig. S8 Frontier molecular orbitals (FMO's) of PYAN and PYAN + Th(IV) obtained using Gaussian 09 program.

Fig. S9. Fluorescence decay profile of PYAN in ACN:H$_2$O (1:1, v/v) λ_{ex} = 341 nm; λ_{em} = 446 nm (prompt-blue, decay-red, fit-green) (a) PYAN and (b) PYAN+Th(IV).

The plot shows data points with the fit line:

$$y = 9.6E{-}07x + 0.0432$$
$$R^2 = 0.9951$$

Y-axis: $1/I{-}I_0$

X-axis: $1/[Th^{4+}]$
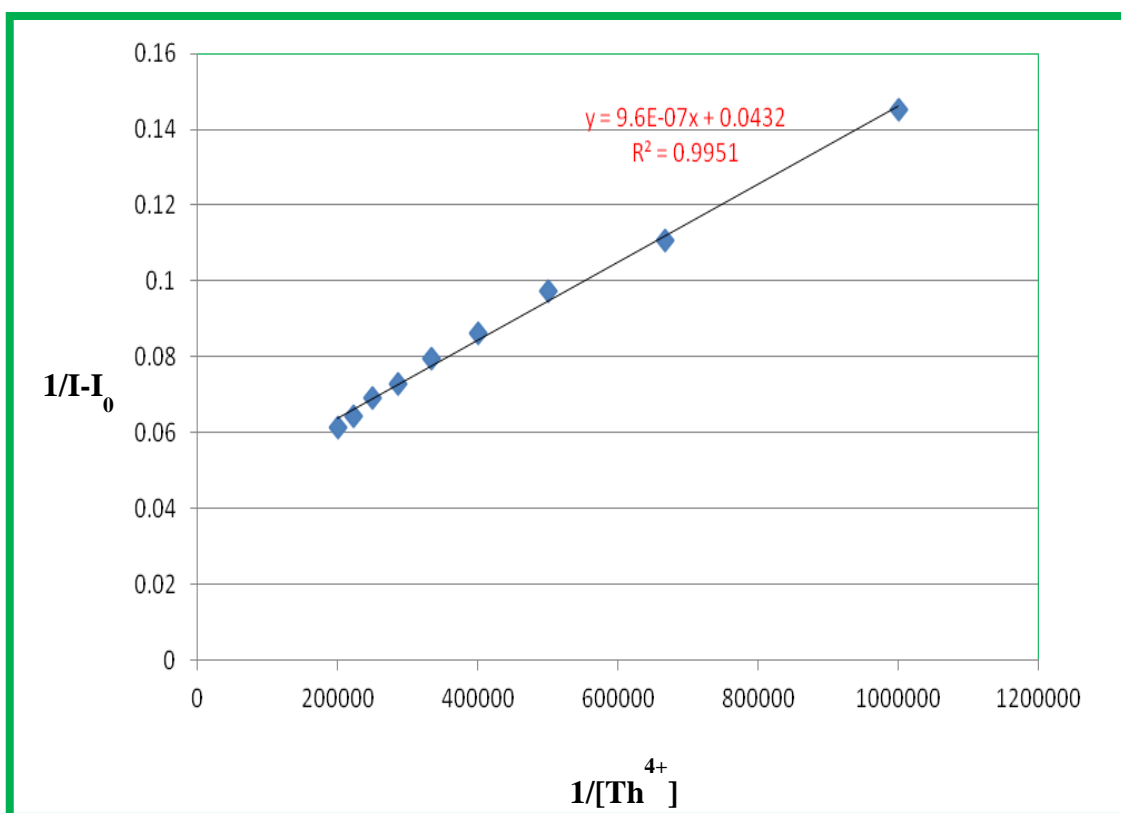
Fig. S10 Benesi-Hilderbrand plot of PYAN-Th(IV) using 5 µM of PYAN.
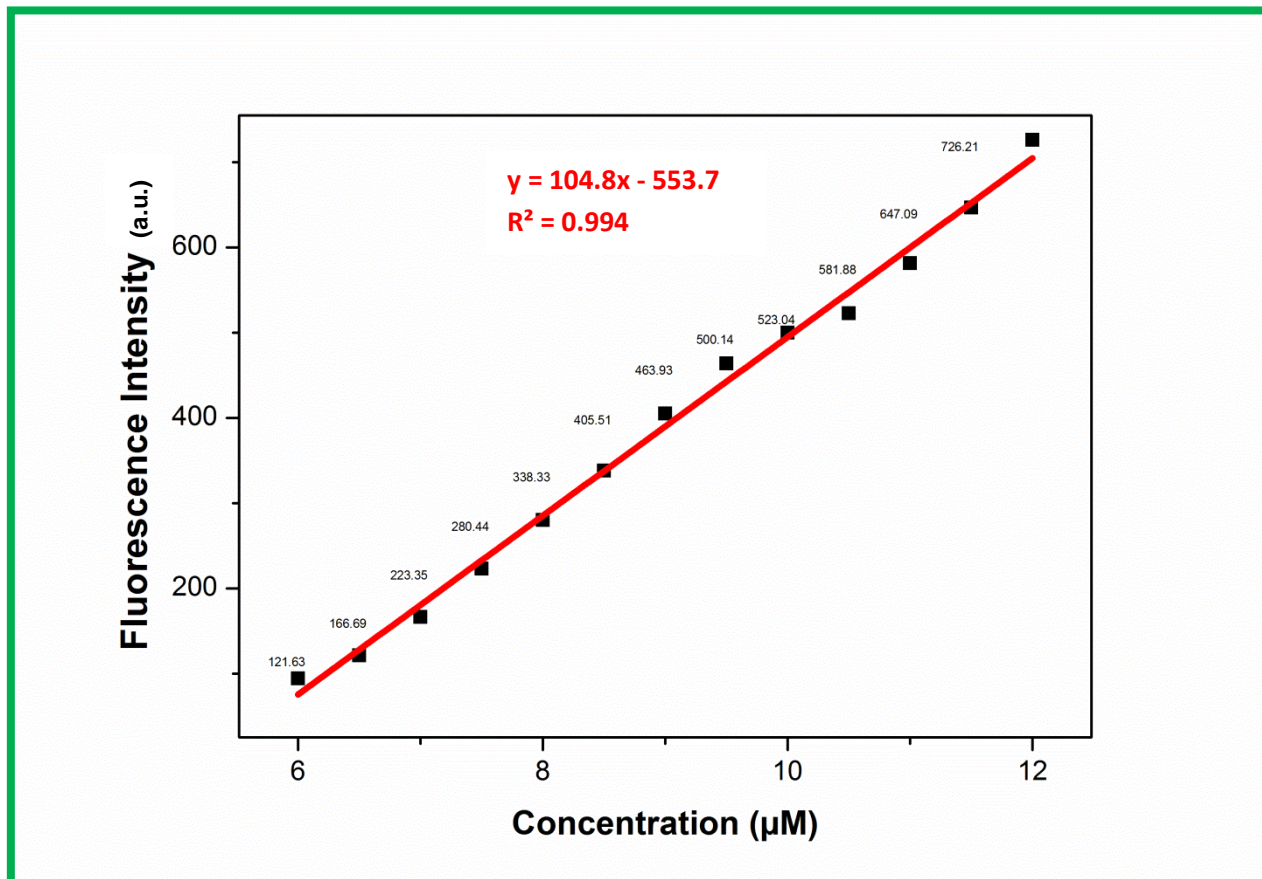
Fig. S11 Variation in fluorescence intensity with Th(IV) concentration (6 μM to 12 μM).

III. Table

Table S1. Comparison of the present fluorophore with the reported fluorophores for Th(IV) detection.

Fluorophores	Medium	Mechanism	LOD (M)	Ref
BINOL derivative	MeOH:H$_2$O [1:1]	Turn-OFF	6.00×10^{-7}	24(a)
Pillar[5]arene derivative	CH$_3$CN:H$_2$O [9:1]	Turn-OFF	5.35×10^{-7}	24(b)
Thorin	Acidic pH	Turn-ON	1.85×10^{-6}	24(c)
Malanohydrazide derivative	MeOH:H$_2$O [1:1]	Turn-ON	0.10×10^{-6}	24(d)
Tetraphenylethenes derivative	MeOH:H$_2$O [7:3]	Turn-ON	1.67×10^{-7}	24(e)
Coumarin derivative	DCM:MeOH [9:1]	Turn-ON	1.50×10^{-6}	24(f)
Pyrene-Antipyrine Schiff base	CH$_3$CN:H$_2$O [1:1]	Turn-ON	4.90×10^{-9}	Present work