# Electronic Supplementary Information (ESI)

## Oxacalix[4]arene Derived Dual Sensing Fluorescence Probe for the Detection of As (V) and Cr (VI) Oxyanions in Aqueous Media

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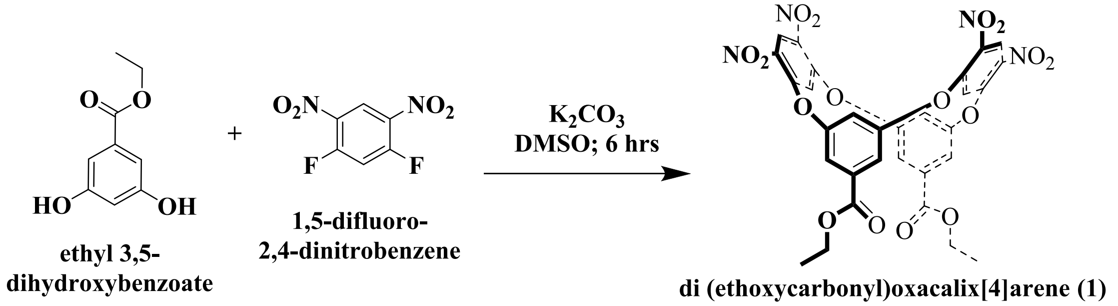
## S1. Synthesis of di(ethoxycarbonyl)oxacalix[4]arene (1):



**Scheme 1** Synthesis scheme for the preparation of di(ethoxycarbonyl)oxacalix[4]arene (**1**)

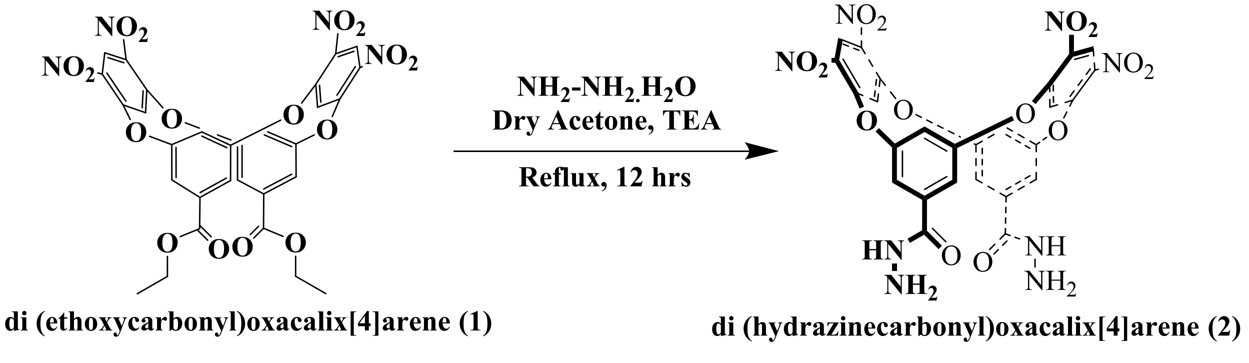
Compound **1** was synthesized following the reported synthetic procedure[1]. Typically, to a mixture of ethyl 3,5-dihydroxybenzoate (1.0 g, 5.49 mmol) and $K_2CO_3$ (1.89 g, 13.7 mmol) in DMSO, 1,5-difluoro2,4-dinitrobenzene (1.12 g, 5.49 mmol) was added, and the mixture was stirred for 6 hours at room temperature. The Progress of the reaction was monitored through TLC. After completion of the reaction, the organic layer was extracted with ethyl acetate, dried over $Na_2SO_4$ and evaporated under reduced pressure to obtain yellow powder of di(ethoxycarbonyl)oxacalix[4]arene (**1**) with 85% yield. Further the crude was purified through column chromatography using a mixture of ethyl acetate and hexane as eluent, maintaining the ratio of 2:8.

MS (ESI): m/z for $C_{30}H_{20}N_4O_{16}$ Calcd: 692.50 [M], Found 692.10. (Figure S1)

$^1$H-NMR (500 MHz, $CDCl_3$) δ= 1.37 (t, 6H), 4.34 (q, 4H), 6.15 (s, 2H), 6.99 (t, 2H), 7.73 (s, 4H), 8.74 (s, 2H) (Figure S2).

$^{13}$C NMR (125 MHz, DMSO *d*$_6$) δ=14.46, 62.24, 111.40, 114.18, 118.05, 125.11, 134.51, 135.61, 154.35, 156.23, 164.44 (Figure S3)

## S2. Synthesis of di(hydrazinecarbonyl)oxacalix[4]arene (2):



**Scheme 2** Synthesis scheme for the preparation of di(hydrazinecarbonyl)oxacalix[4]arene (**2**)

The compound **2** was prepared according to the previous reported synthesis procedure by our group[2]. To a mixture of **1** (1.0 g, 1.44 mmol) and triethylamine (0.5 ml, 3.61 mmol) in dry acetone, hydrazine hydrate (0.2 ml, 3.61 mmol) was added dropwise at room temperature. Then the mixture was refluxed for 24 hours. Color of the solution turns from yellow to orange. The completion of the reaction was monitored through TLC. After completion, the organic layer was extracted through ethyl acetate, dried over $Na_2SO_4$, and evaporated under reduced pressure to obtain the desired product with 78% yield. The crude was further purified through recrystallization in methanol.

MS (ESI): m/z for $C_{26}H_{16}N_8O_{14}$ Calcd: 664.46 [M], Found 664.5 (Figure S4)
$^1$H-NMR (500 MHz, DMSO *d₆*) δ= 4.24 (dd, 4H), 6.23 (s, 2H), 6.82 (s, 4H), 7.20 (s, 2H), 8.89 (s, 2H), 9.62 (s, 2H) (Figure S5).
$^{13}$C NMR (125 MHz, DMSO *d₆*) δ= 107.50, 109.61, 120.81, 129.11, 131.95, 132.03, 158.97, 160.24, 166.19 (Figure S6)

## S3. Optimization of reaction conditions

Initially the structural and fluorescent stability of the receptor **L** was investigated in aqueous medium. For this purpose, emission spectra of the receptor **(L)** was recorded for 60 hours with an interval of 12 hours and the results indicate no significant change in fluorescent maxima (Figure S10). Moreover, sensitivity of the fluorescent probe **L-Ce(III)** could be influenced by two major factors, such as incubation time and pH dependence. To enhance sensitivity and reproducibility, the fluorescent responses of **L-Ce(III)** towards chromate and arsenate were investigated with different time interval. The time dependence sensing process was investigated by fluorescence studies with three different concentration of both the oxyanions and plotted as a function of incubation time. It was observed that 2 minutes of incubation time is enough with no noticeable change in $\Delta I_{375}$ afterwards. Control experiments were also performed at different pH values ranging from 4.0-10.0 and the quenching of emission maxima $\Delta I_{375}$ was noted. Maximum quenching in fluorescent intensity was observed within the range of pH 6.0-7.0 (Figure S11). Therefore, the optimum conditions to carry out the experiments were set at pH 7.0 with 2 min incubation time.

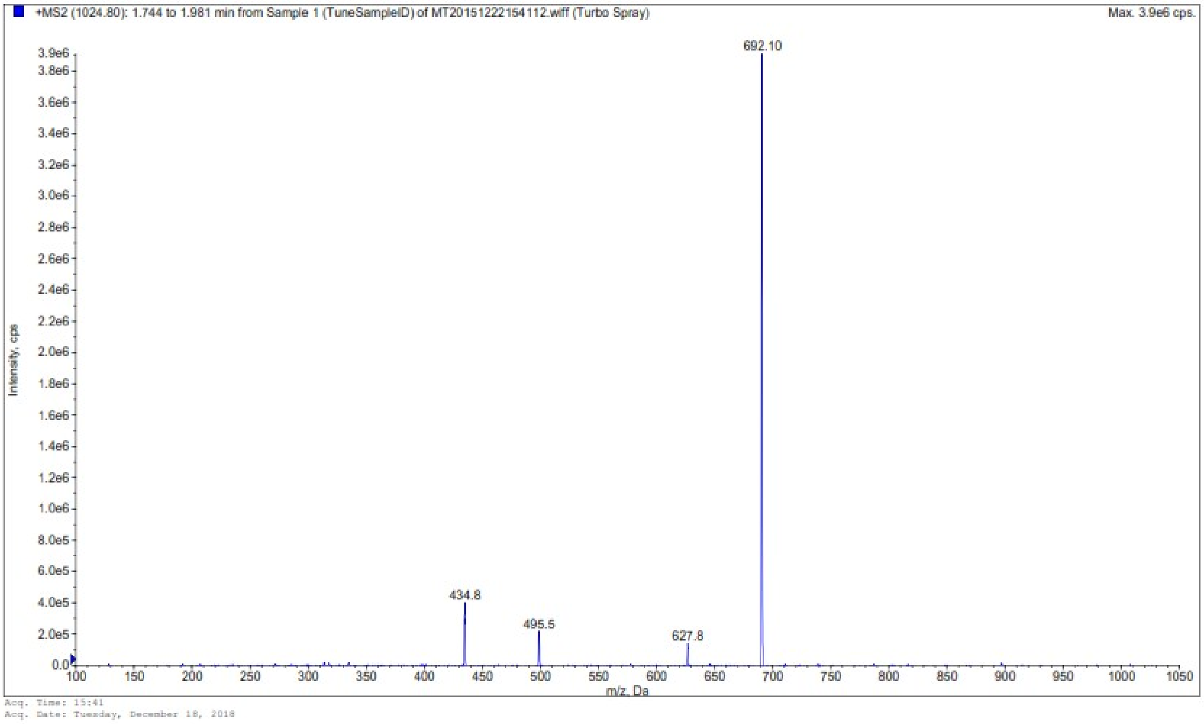


**Figure S1** ESI-MS spectrum of compound **1**

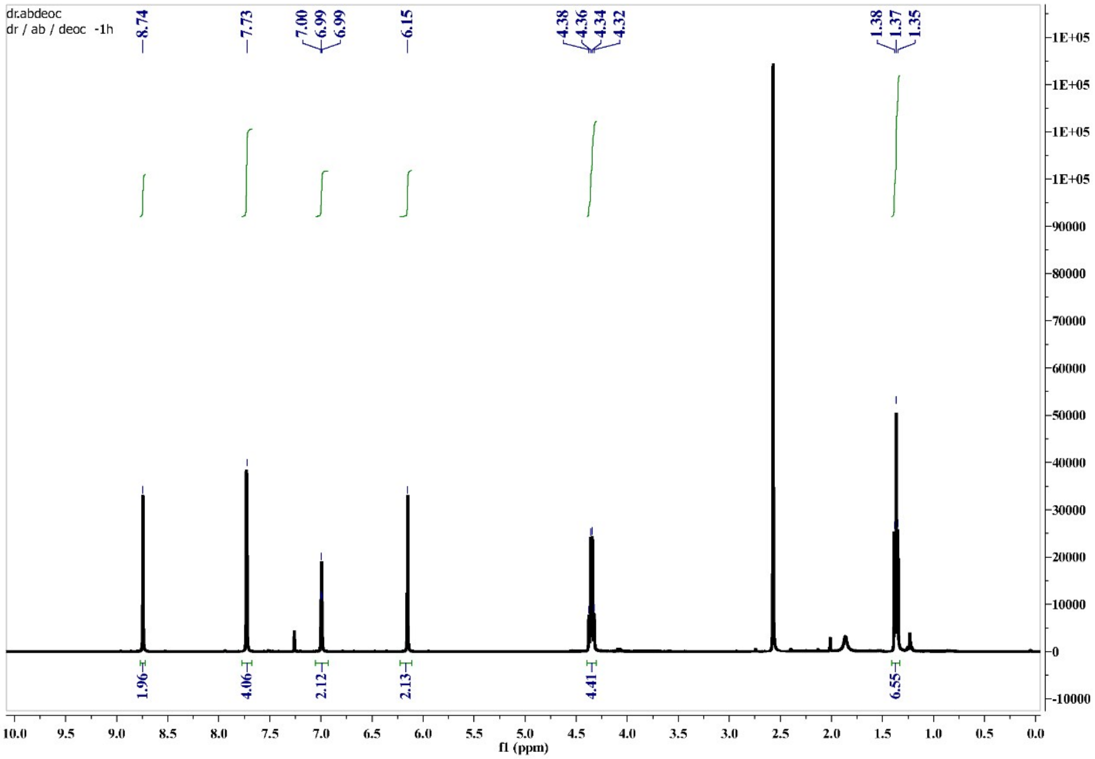


**Figure S2** $^1$H-NMR spectrum of compound **1**

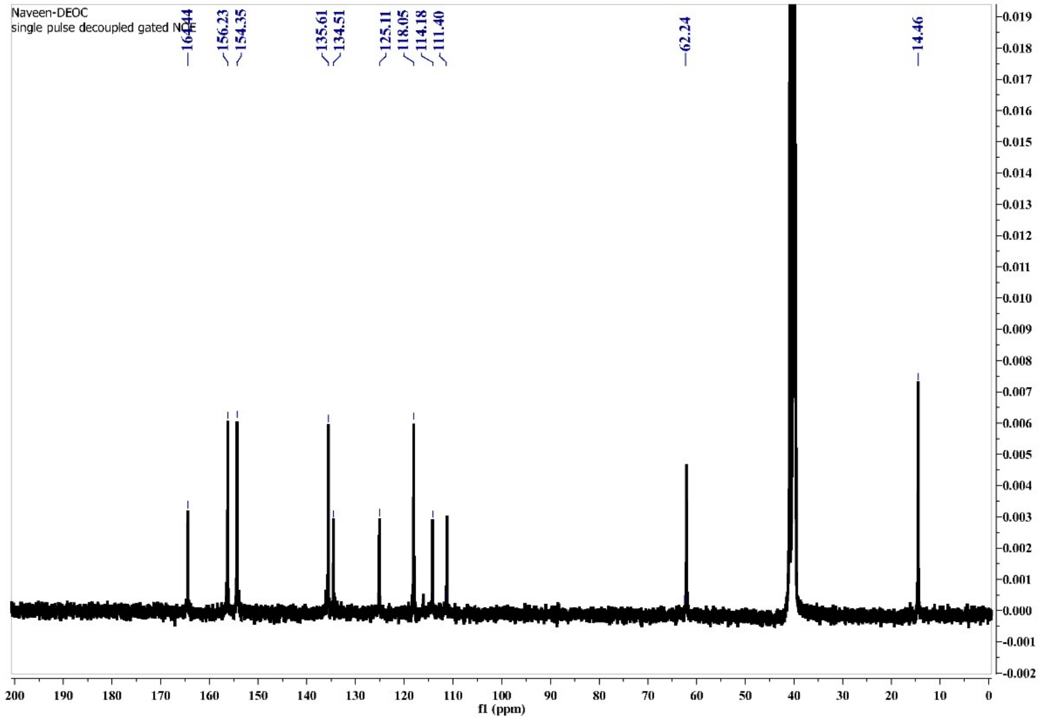


**Figure S3**. $^{13}$C-NMR spectrum of compound **1**

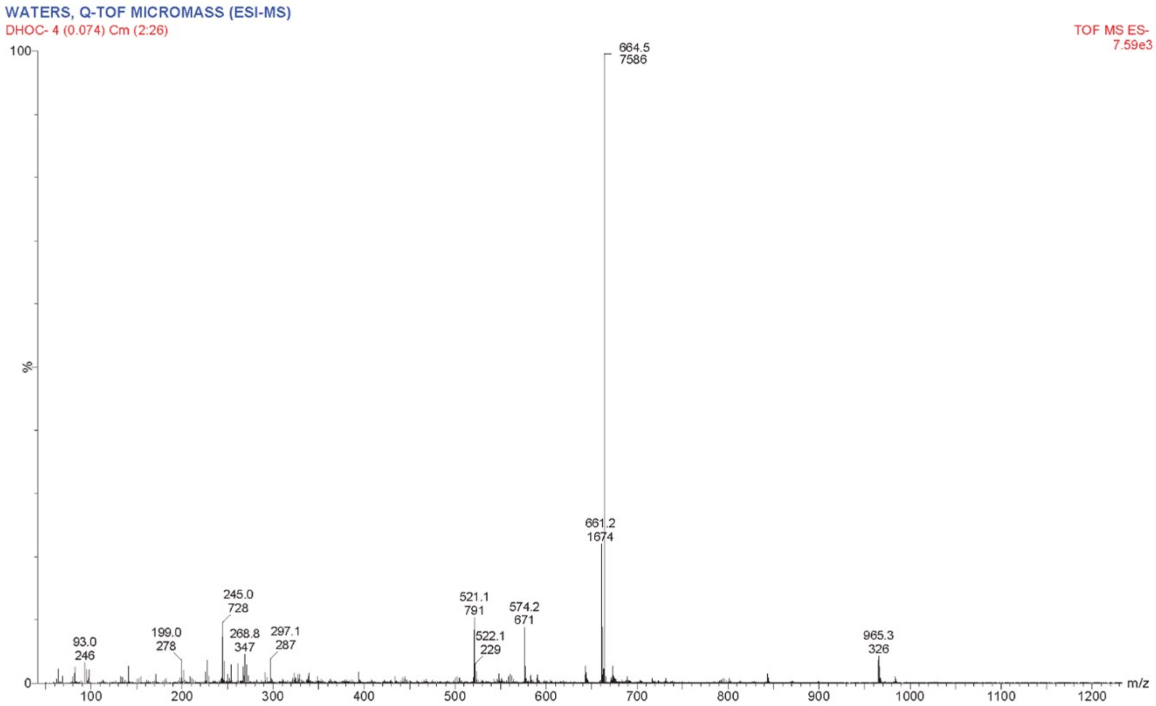


**Figure S4** ESI-MS spectrum of compound **2**

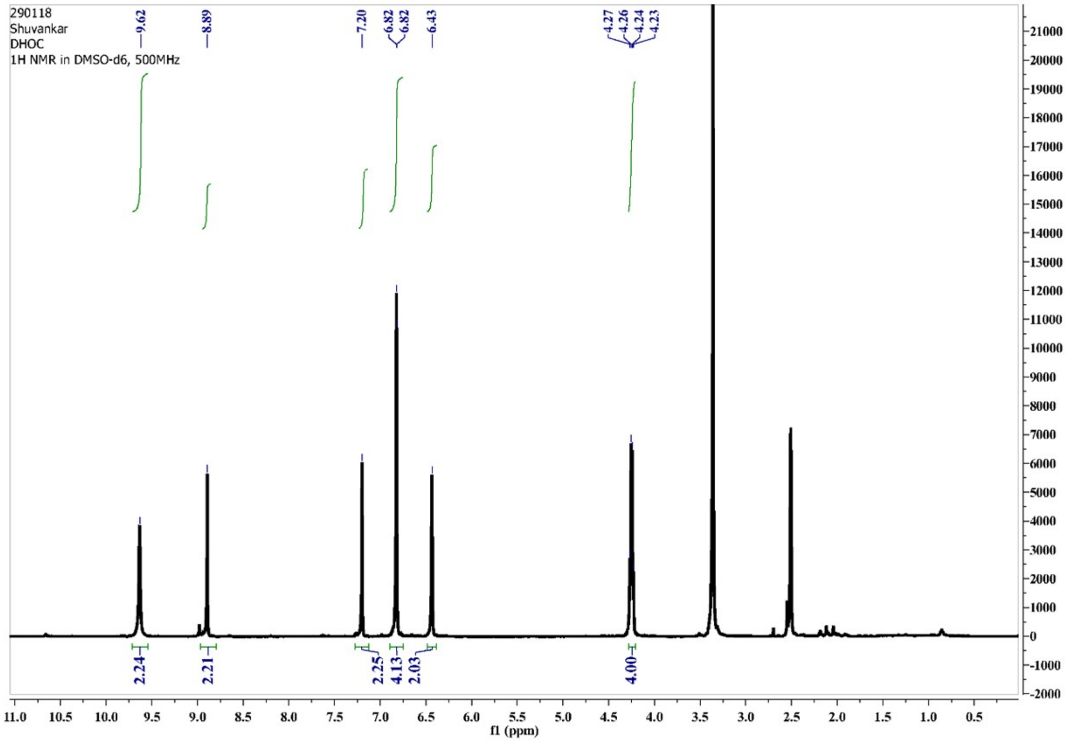


Figure S5 $^{1}$H-NMR spectrum of compound **2**

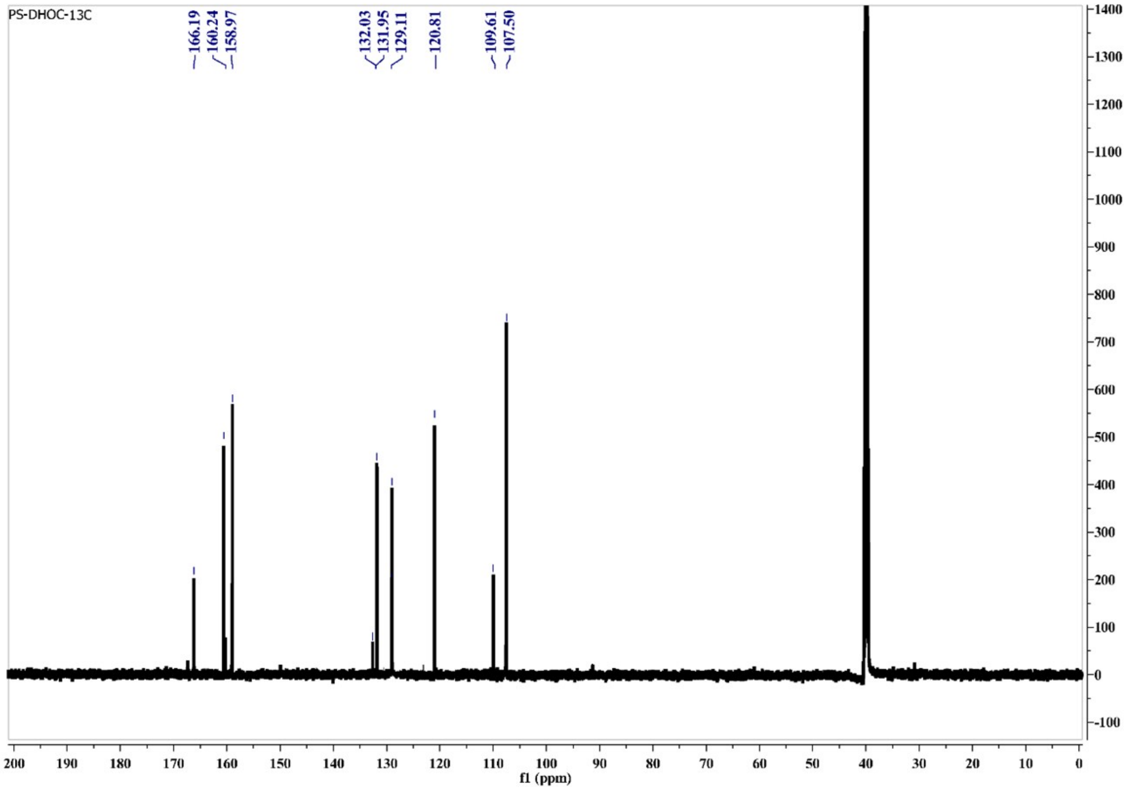


Figure S6 $^{13}$C-NMR spectrum of compound **2**

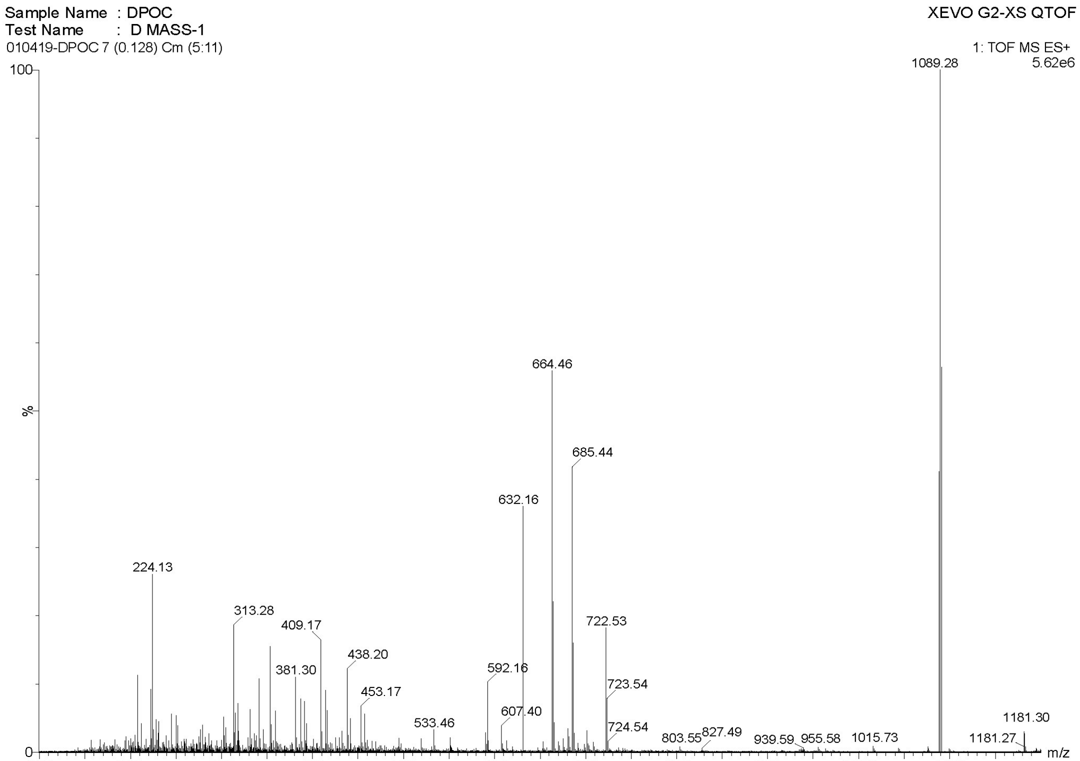


**Figure S7** ESI-MS spectrum of **L**

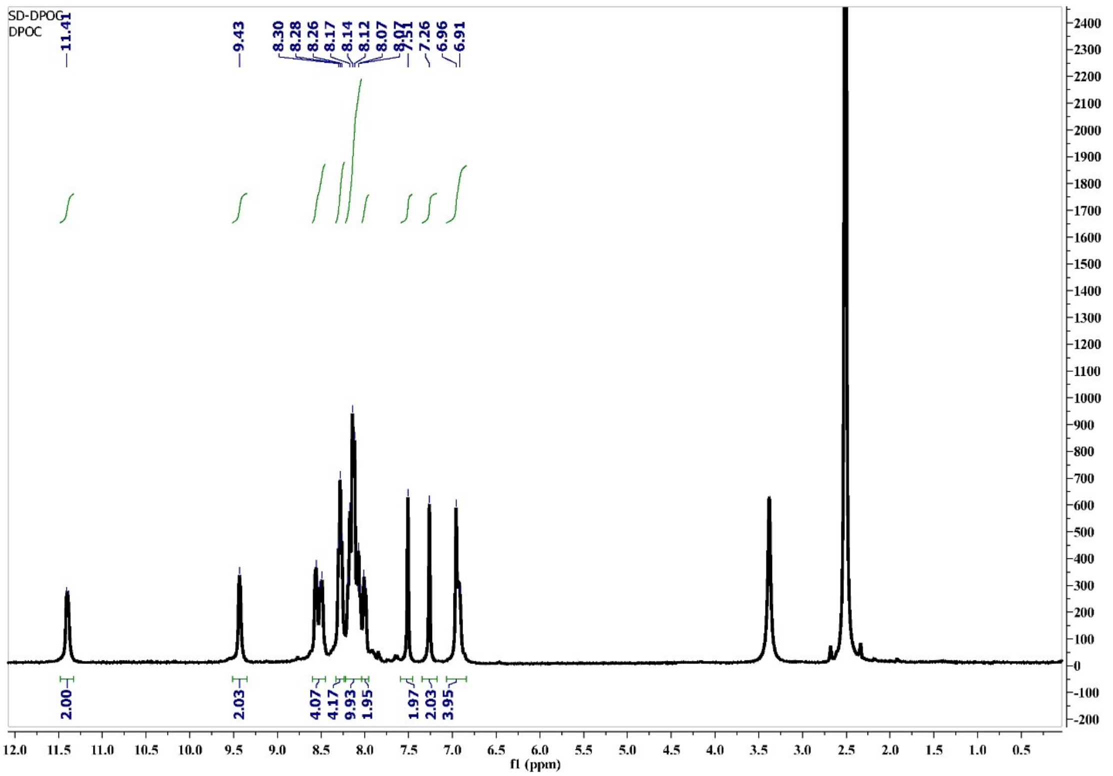


**Figure S8** $^1$H-NMR spectrum of **L**

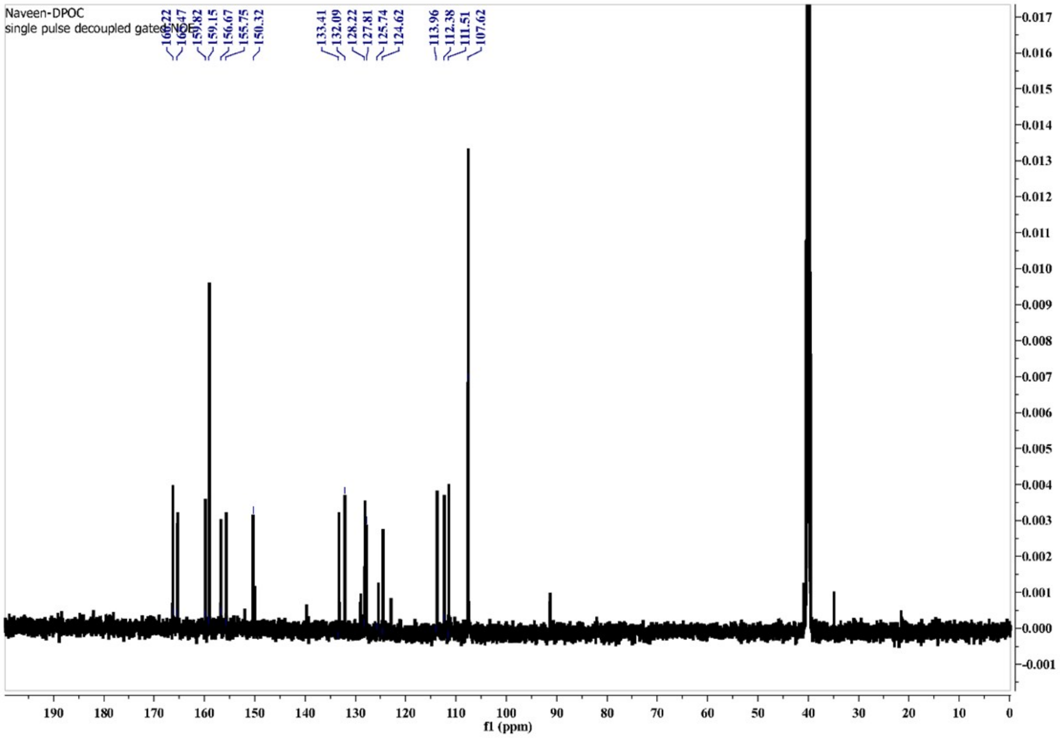


**Figure S9** $^{13}$C-NMR spectrum of **L**

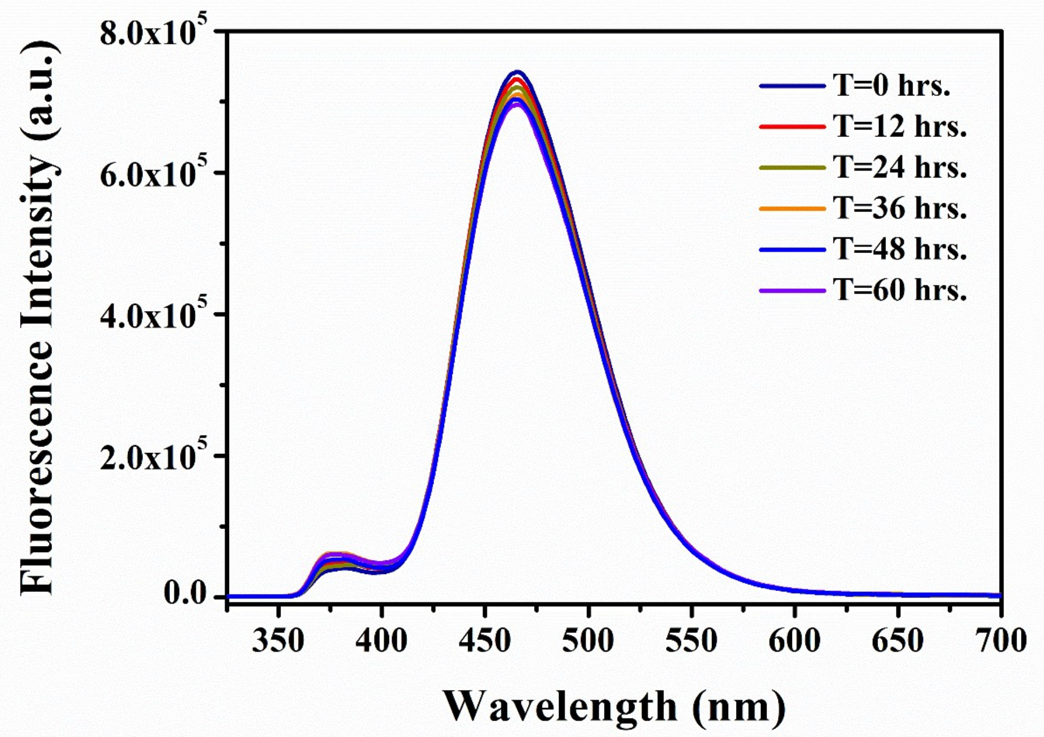


**Figure S10** Variation in emission maxima of **L** with a regular interval of 12 hrs.

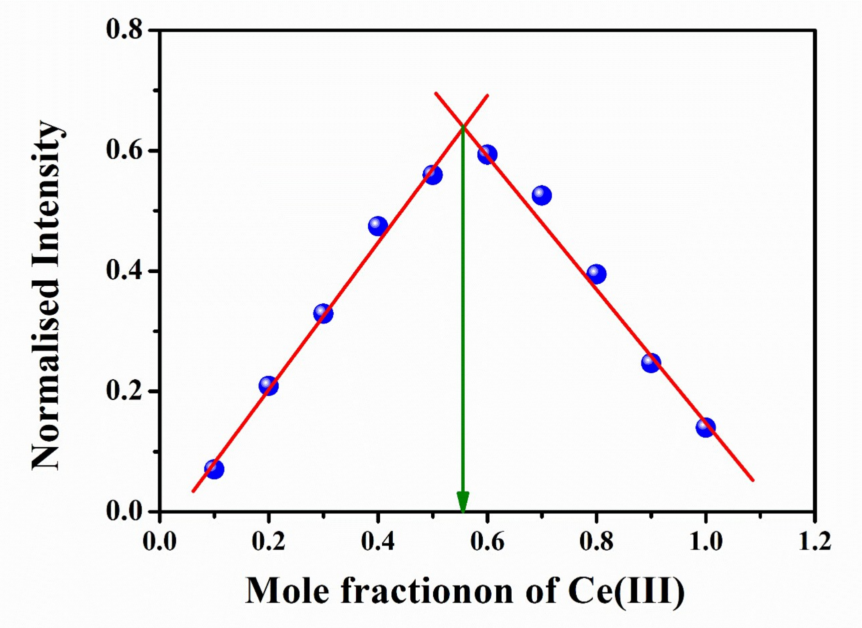


**Figure S11** Jobs plot analysis for receptor L and Ce (III)Complexation

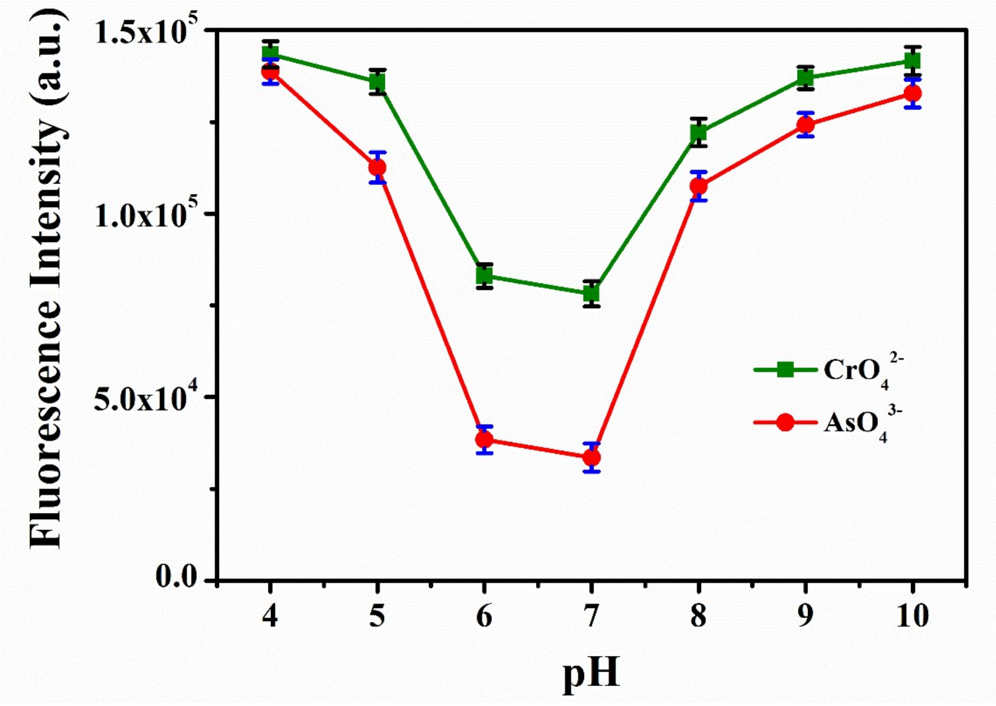


**Figure S12** Quenching in fluorescence intensity of **L-Ce(III)** upon addition of $CrO_4^{2-}$ and $AsO_4^{3-}$ with varying pH

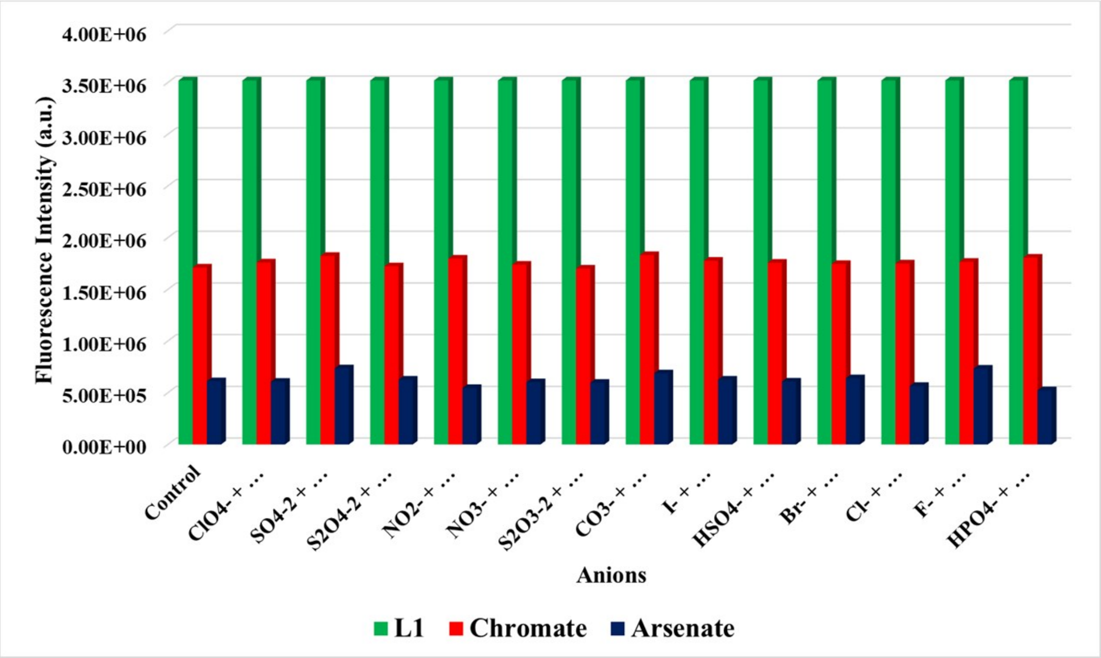


**Figure S13** Fluorescent selectivity of **L-Ce(III)** towards chromate ($CrO_4^{2-}$) and arsenate ($AsO_4^{3-}$) over other competitive anions

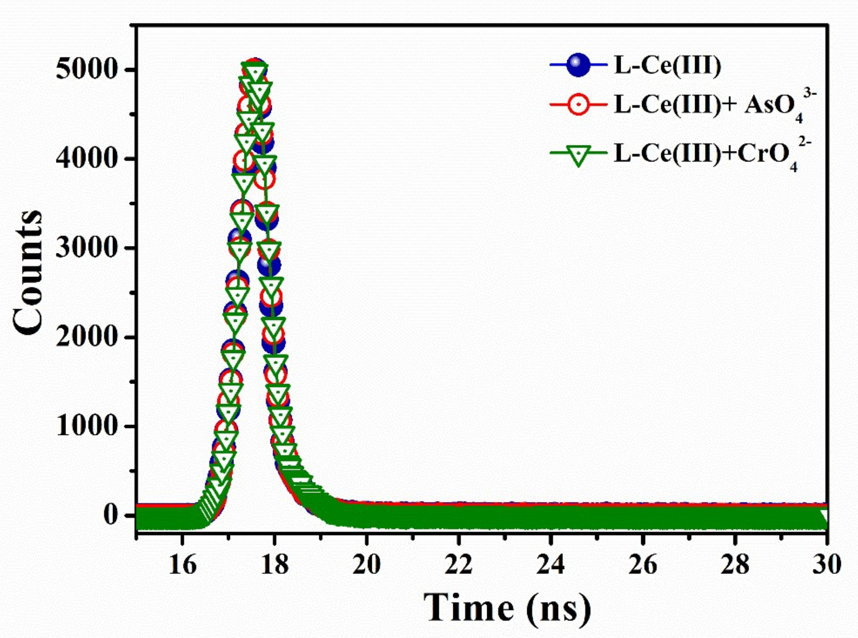


**Figure S14** Fluorescence decay profile of **L-Ce(III)** in the absence and presence of $AsO_4^{3-}$, $CrO_4^{2-}$

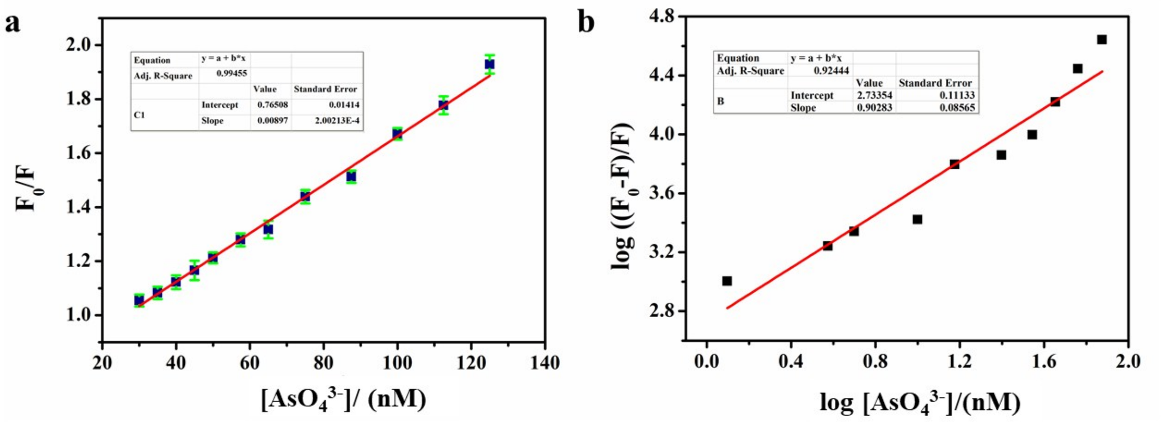


**Figure S15** (a) Stern-Volmer plot for **L-Ce(III)**-$AsO_4^{3-}$ system. (b) Plot of $log\frac{(F_0 - F)}{F}$ vs log [$AsO_4^{3-}$] system

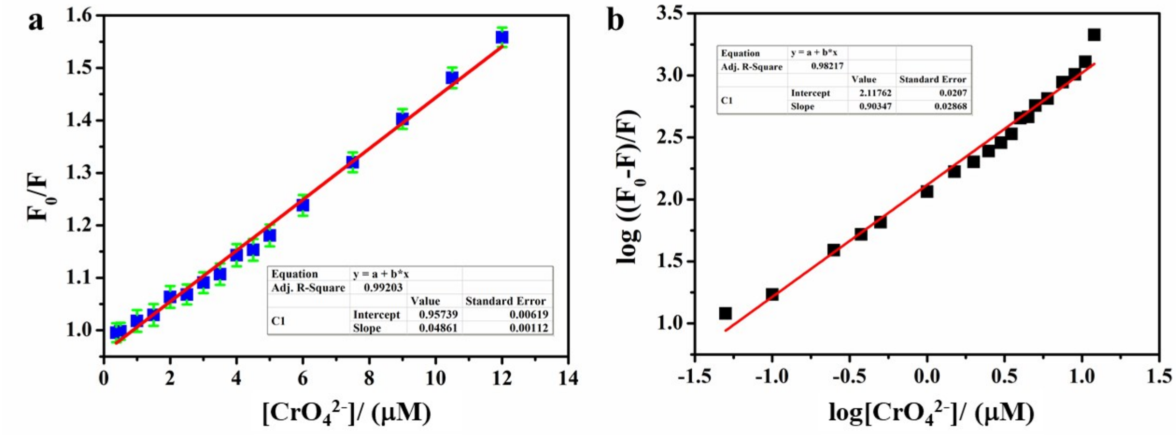


**Figure S16** (a) Stern-Volmer plot for **L-Ce(III)**-$CrO_4^{2-}$ system. (b) Plot of $log\frac{(F_0 - F)}{F}$ vs log [$CrO_4^{2-}$] system

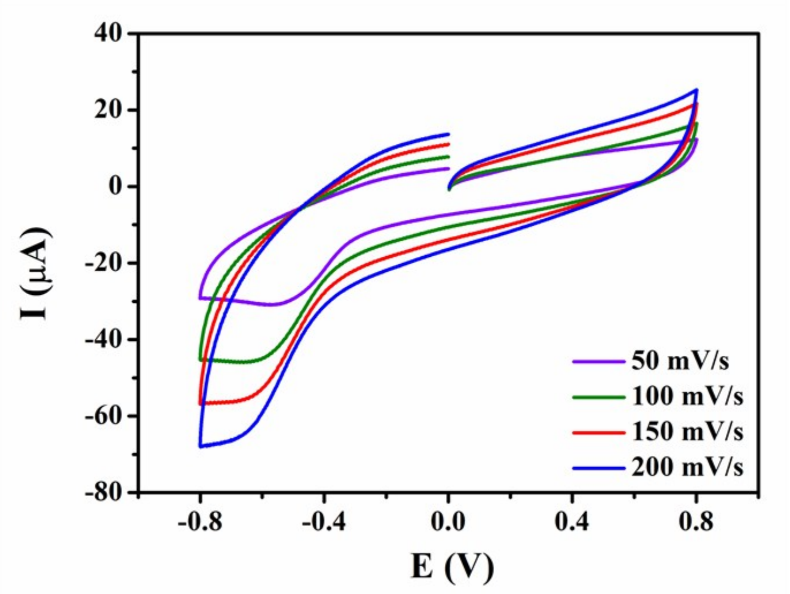


**Figure S17** Cyclic voltammogram of 50 μM **L-Ce(III)** in 0.1 M phosphate buffer (pH 7) at various scan rates (50-200 mV/s)

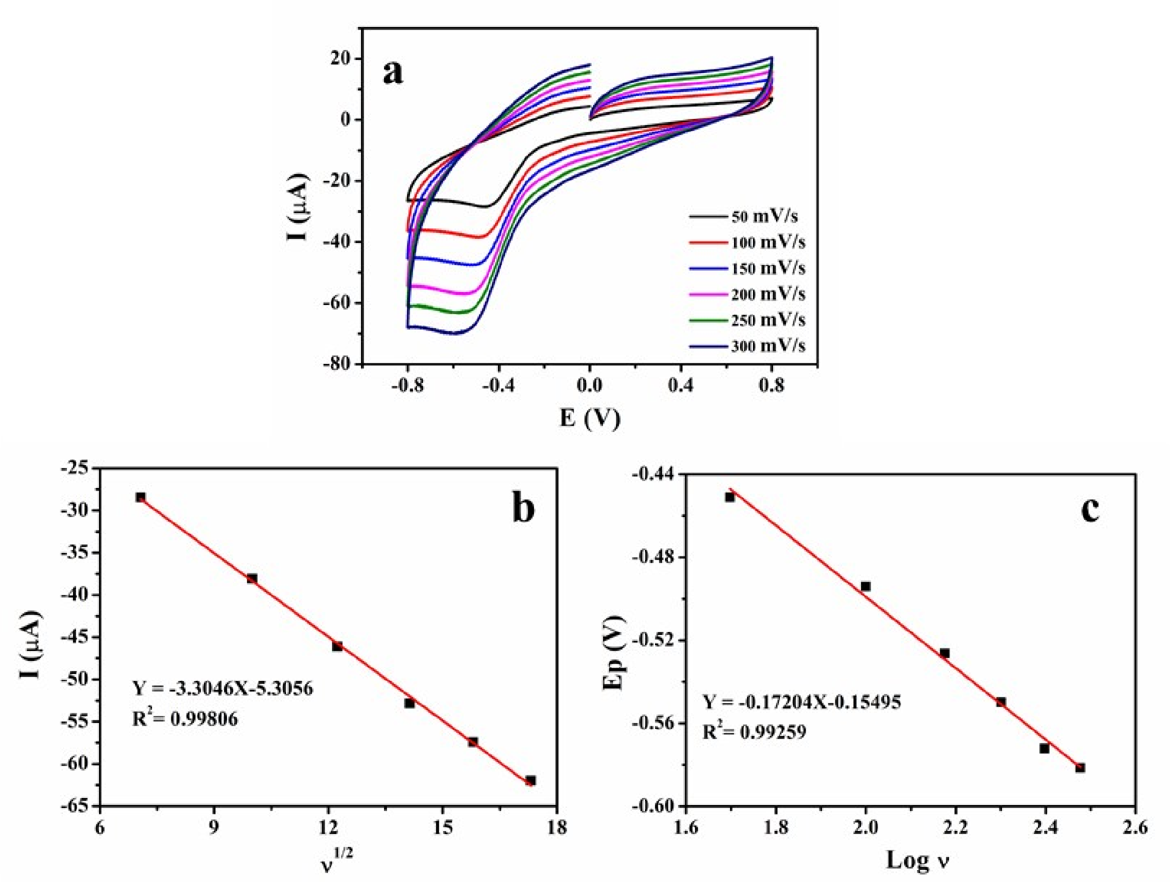


**Figure S18** (a) Cyclic voltammogram of 50 μM **L-Ce(III)** in 0.1 M phosphate buffer (pH 7) at various scan rates (50-300 mV/s) in presence of $AsO_4^{3-}$, (b) Plot of Ip vs ν $^{½}$, (c) Plot of Ep vs log ν

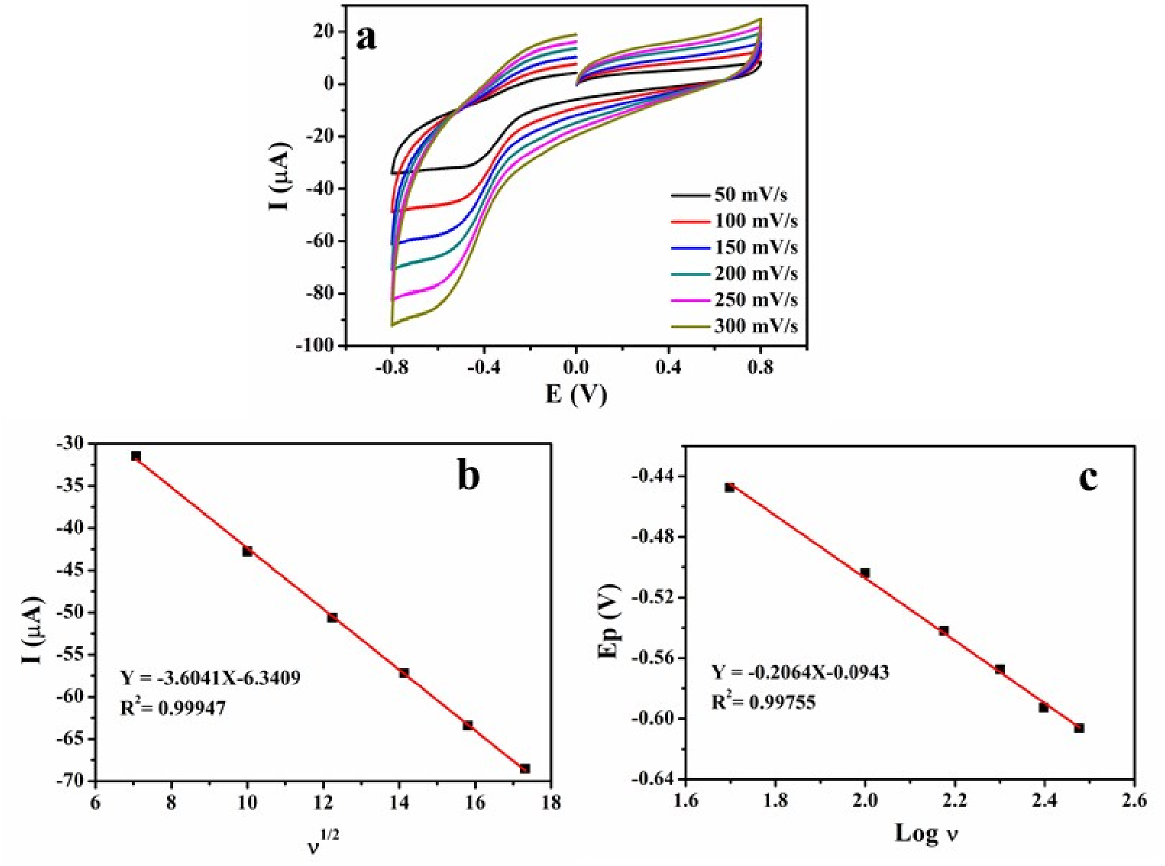


**Figure S19** (a) Cyclic voltammogram of 50 μM **L-Ce(III)** in 0.1 M phosphate buffer (pH 7) at various scan rates (50-300 mV/s) in presence of $CrO_4^{2-}$, (b) Plot of Ip vs ν ½, (c) Plot of Ep vs log ν

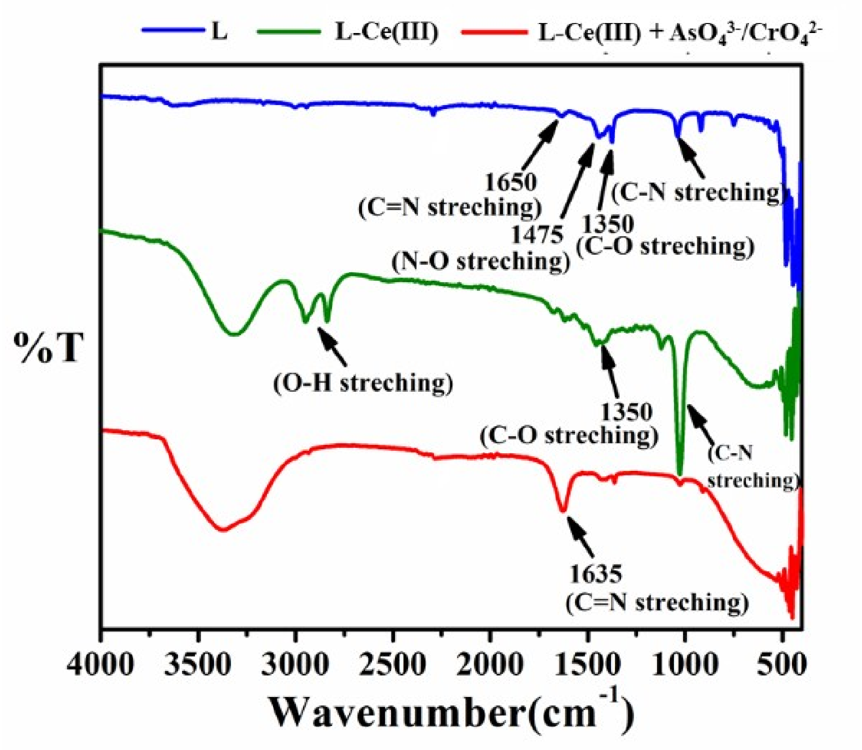


**Figure S20** Comparison of IR spectra between receptor (L), L-Ce (III) and L-Ce (III) + $AsO_4^{3-}/CrO_4^{2-}$

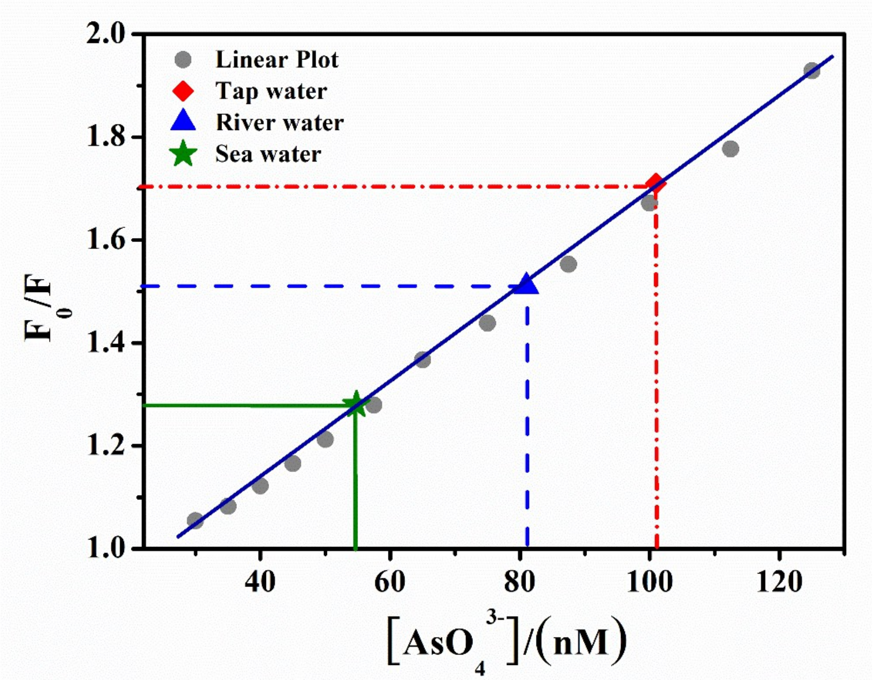


**Figure S21** Determination of unknown concentration of arsenate via spectrofluorometric method

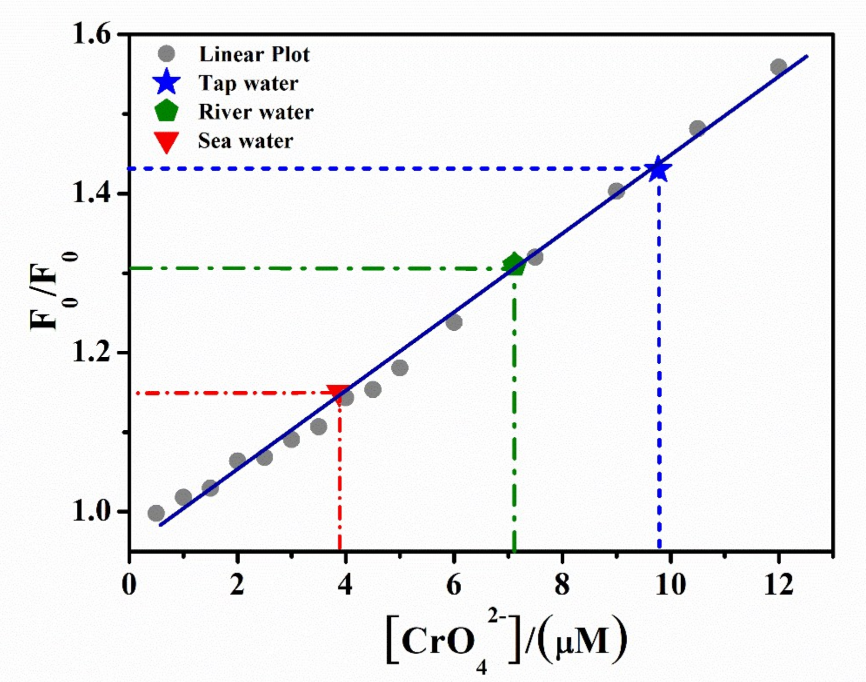


**Figure S22** Determination of unknown concentration of chromate via spectrofluorometric method

**Table S1** Crystallography and refinement details

| DATA | **Compound 1** |
|---|---|
| Moiety formula | $C_{30}H_{20}N_4O_{16}$ |
| CCDC | 1979411 |
| Solvent | Methanol + Hexane (1:1) |
| Formula weight | 1385.00 |
| Temperature (K) | 140(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group, Z, Z' | *P-1*, 4, 2 |
| a(Å) | 13.4320(4) |
| b(Å) | 14.8221(5) |
| c(Å) | 15.7791(5) |
| α (˚), β (˚), γ (˚) | 90.092(2), 101.455(2), 91.416(2) |
| Volume ($Å^3$), Density ($g/cm^3$) | 3077.88(17), 1.494 |
| F (000), μ($mm^{-1}$) | 1424, 0.124 |
| Θ (min, max) | 1.317, 27.876 |
| $h_{min, max}$, $k_{min, max}$, $l_{min, max}$ | (-17, 17), (-19, 18), (-20, 20) |
| Treatment of Hydrogens | Fixed |
| No. unique ref./ obs. Ref. | 14527/4924 |
| No of parameters | 925 |
| R_all, R_obs | 0.2316, 0.0789 |
| $wR_2$_all, $wR_2$_obs | 0.2483, 0.1867 |
| $\Delta\rho_{min, max}$($eÅ^{-3}$) | -0.576, 1.362 |
| G.o.F | 0.914 |

**Table S2** Results of recovery experiments for detecting chromate and arsenate in real samples (n=3)

| Determination of arsenate ($AsO_4^{3-}$) | | | | |
|---|---|---|---|---|
| Sample | Spiked Amount (nM) | Detected using linear plot (nM) | Result using ICP-OES (nM) | Recovery (%) |
| Tap water | 100.0 | 100.92 ± 0.12 | 100.25 | 101 |
| River water | 80.0 | 81.12 ± 0.07 | 80.04 | 101 |
| Sea water | 55.0 | 54.69 ± 0.29 | 55.32 | 99 |

| Determination of chromate ($CrO_4^{2-}$) | | | | |
|---|---|---|---|---|
| Sample | Spiked Amount (μM) | Detected using linear plot (μM) | Result using ICP-OES (μM) | Recovery (%) |
| Tap water | 10.0 | 9.78 ± 0.23 | 10.15 | 98 |
| River water | 7.0 | 7.11 ± 0.15 | 7.06 | 101 |
| Sea water | 4.0 | 3.88 ± 0.35 | 4.14 | 97 |

**References:**

1 J. L. Katz, M. B. Feldman, R. R. Conry, C. College and M. Hill, 2005, 2567–2570.

2 V. Mehta, M. Panchal, A. Kongor, U. Panchal and V. K. Jain, *Catal. Letters*, 2016, **146**, 1581–1590.