Sensing of Ce(III) using di-naphthoylated oxacalix[4]arene via realistic simulations and experimental studies

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Contents

1. **Significant change in λmax of dinaphthoylated oxacalix[4]arene (DNOC) (4×10^{-5} M) upon the addition of various metal ions (4×10^{-5} M) in acetonitrile**

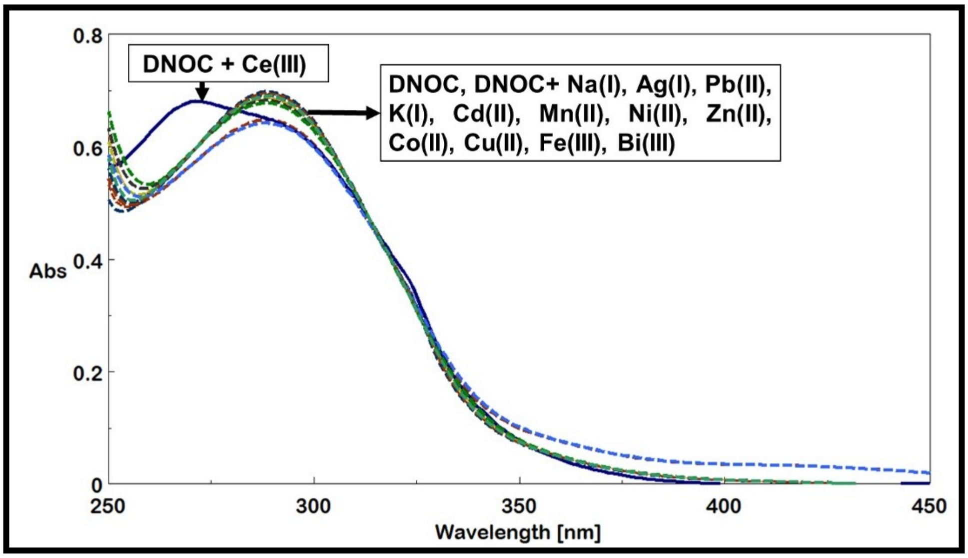
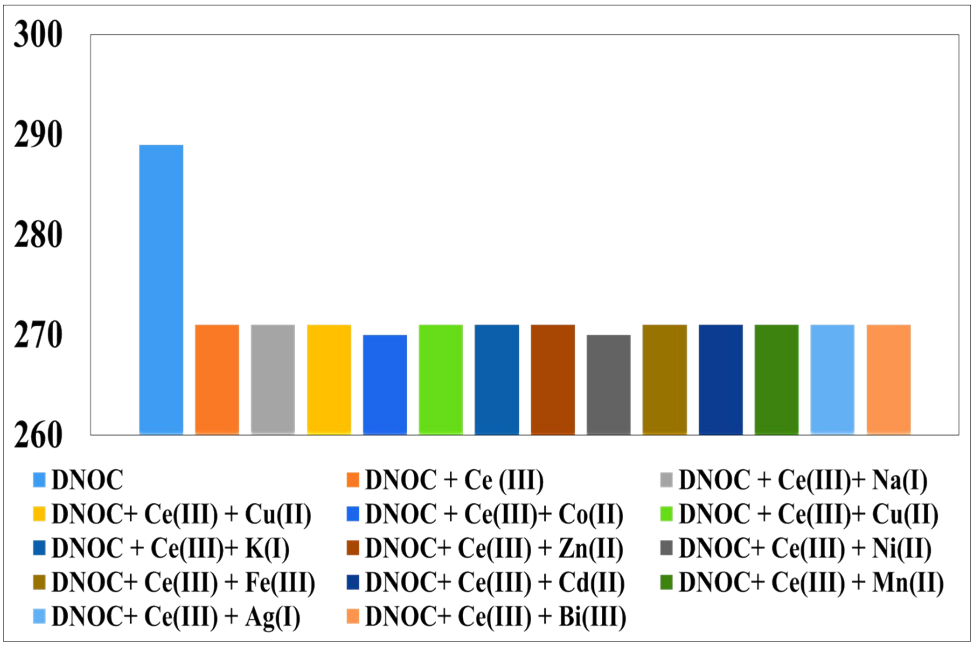


Fig. S1

2. **Competitive absorption spectra of DNOC ligand with Ce(III) complex with other metal ions**



3. **Procedure for determination of binding constant**

The binding constant is a special case of the equilibrium constant (K) and is associated with the binding and unbinding reaction of the receptor (R) and ligand (L) molecules, which is formalized as follows:

$$R + L = RL$$

Here, Ce(III) showed considerably change in the emission intensity; therefore, its emission titration was used to assess its binding constant with DNOC using the procedure in ref [37, 38].

$$\frac{(F_0 - F)}{(F - F_1)} = [M] \Big/ (K_{diss})^n$$

4. Determination of Quantum yield

The quantum yield was determined by the comparative method:

$$\Phi = \Phi_{std} \frac{(F \times A_{std} \times \eta)}{(F_{std} \times A \times \eta_{std})}$$

Here, F and F_{std} are the areas under the fluorescence emission curves of the Ce(III) complex with DNOC and the standard DNOC, respectively. η and η_{std} are the refractive indices of acetonitrile used for the sample and standard, respectively. A and A_{std} are the relative absorbance of the sample and standard at the absorption wavelength, respectively. The sample and the standard both were excited at the same relevant wavelength. Using emission spectra of NC (standard fluorophore) the quantum yield of DNOC (fluoroionophore) was determined.

5. Table S1

Real sample analysis

Sample	Spiked Ce(III) Concentration (M)	Conc. (in M) of Ce(III) obtained from (N=4, Mean ± SD), fig.2a	% Recovery	Found by ICP-AES
Waste Water Sample 1	----	$1.28\times 10^{-9} \pm 0.58$	---	1.35×10^{-9}
Waste Water Sample 2	100×10^{-9}	$101.35 \times 10^{-9} \pm 0.63$	101.6	101.37×10^{-9}
Waste Water Sample 3	200×10^{-9}	$201.22 \times 10^{-9} \pm 0.21$	98.6	201.24×10^{-9}
Waste Water Sample 4	300×10^{-9}	$301.45 \times 10^{-9} \pm 0.39$	102.3	301.56×10^{-9}
		$101.48\times 10^{-9} \pm 0.21$		100.11×10^{-9}
Synthesized Ce(III)-polluted water 1	100×10^{-9}	$199.26\times 10^{-9} \pm 0.47$	97.6	200.27×10^{-9}
Synthesized Ce(III)-polluted water 2	200×10^{-9}	$301.78 \times 10^{-9} \pm 0.27$	102.8	301.52×10^{-9}

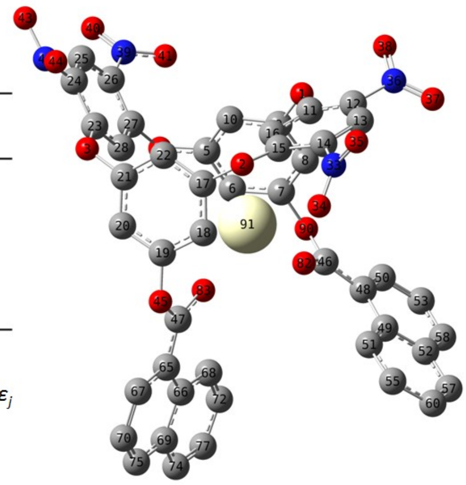
Synthesized Ce(III)-polluted water 3	300×10^{-9}	$401.68 \times 10^{-9} \pm 0.65$	101.6	401.32×10^{-9}

6. **Stabilising interactions the oxygen centres (napthoyl groups) and calix ring carbons (C6,C7,C46,C47)**

Donor(i)-Acceptor(j)	$E_{(2)}$ (Kcal/mol)	$\varepsilon_j-\varepsilon_i$ (a.u.)
$n_{O82} \rightarrow n^*_{Ce91}$	37.20	0.79
$n_{O83} \rightarrow n^*_{Ce91}$	41.67	0.88
$\sigma_{C47\text{-}O83} \rightarrow n^*_{Ce91}$	8.50	1.26
$\sigma_{C46\text{-}O82} \rightarrow n^*_{Ce91}$	6.78	1.19
$\sigma_{C6\text{-}C7} \rightarrow n^*_{Ce91}$	5.47	0.46

$$E_{(2)} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

Where E(2) charge transfer second-order interaction energies and $\varepsilon_i/\varepsilon_j$ are diagonal elements.



7. **Optimized Coordinates of the inclusion complex:**

```
91
Title Card Required  0.000000
O -3.3686 -2.6979  0.3768
O  0.4148 -1.8226  3.5482
O  3.3285 -2.7413 -0.3752
O -0.4440 -1.8272 -3.5488
C -1.3149 -1.3888 -2.4880
C -1.8313 -0.0811 -2.6122
C -2.8188  0.3774 -1.6952
C -3.2829 -0.4783 -0.6603
C -2.7495 -1.7845 -0.5682
C -1.7732 -2.2655 -1.4686
C -2.6319 -2.9039  1.5642
C -3.2024 -3.8099  2.5214
C -2.5710 -4.0433  3.7497
C -1.3630 -3.4004  4.0612
C -0.7551 -2.5063  3.1234
C -1.4053 -2.2626  1.8842
C  1.2922 -1.3991  2.4868
C  1.8280 -0.0991  2.6099
C  2.8228  0.3437  1.6931
C  3.2746 -0.5200  0.6593
C  2.7217 -1.8181  0.5683
C  1.7377 -2.2836  1.4685
C  2.5884 -2.9420 -1.5614
C  3.1468 -3.8586 -2.5156
C  2.5126 -4.0874 -3.7432
C  1.3133 -3.4295 -4.0570
C  0.7172 -2.5246 -3.1221
C  1.3704 -2.2855 -1.8835
H -1.4830  0.5747 -3.4202
H -4.0500 -0.1063  0.0301
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H	1.4893	0.5627	3.4171
H	4.0473	-0.1607	-0.0314
N	-0.7249	-3.7180	5.4422
O	0.3945	-3.0995	5.7750
O	-1.3671	-4.6018	6.1897
N	-4.5356	-4.5629	2.2548
O	-4.9794	-5.3272	3.2403
O	-5.1257	-4.3989	1.0837
N	0.6714	-3.7429	-5.4372
O	1.3019	-4.6377	-6.1816
O	-0.4395	-3.1105	-5.7724
N	4.4695	-4.6290	-2.2462
O	4.9052	-5.3991	-3.2306
O	5.0591	-4.4729	-1.0738
O	3.2717	1.6732	1.9460
C	-4.2428	2.3090	-1.0675
C	4.2750	2.2536	1.0637
C	-4.5378	3.7229	-1.5748
C	-5.4820	4.5737	-0.8644
C	-3.8991	4.1982	-2.7241
C	-6.1777	4.1480	0.3220
C	-5.7305	5.9049	-1.3749
C	-4.1526	5.5125	-3.2205
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C	-7.0679	4.9950	0.9653
H	-5.9673	3.1296	0.6805
C	-6.6619	6.7571	-0.6792
C	-5.0456	6.3469	-2.5624
H	-3.6345	5.8544	-4.1264
C	-7.3134	6.3137	0.4614
H	-7.5933	4.6583	1.8696
H	-6.8449	7.7661	-1.0732
H	-5.2450	7.3600	-2.9394
H	-8.0221	6.9695	0.9851
C	4.5932	3.6623	1.5714
C	5.5483	4.4990	0.8591
C	3.9652	4.1463	2.7231
C	6.2339	4.0635	-0.3297
C	5.8187	5.8258	1.3697
C	4.2404	5.4560	3.2198
H	3.2494	3.4998	3.2483
C	7.1350	4.8973	-0.9751
H	6.0069	3.0487	-0.6882
C	6.7610	6.6641	0.6720
C	5.1442	6.2772	2.5597
H	3.7304	5.8051	4.1275
C	7.4022	6.2116	-0.4709
H	7.6526	4.5532	-1.8812
H	6.9608	7.6699	1.0662
H	5.3603	7.2868	2.9370
H	8.1194	6.8569	-0.9963
O	-4.7424	1.7331	-0.0708
O	4.7638	1.6704	0.0658
H	2.9580	-4.7907	-4.4666
H	-3.0254	-4.7385	4.4753
H	-0.9636	-1.5563	1.1730

```
H   0.9381 -1.5710 -1.1748
H   1.3464 -3.3056  1.3942
H  -1.3971 -3.2932 -1.3934
O  -3.2473  1.7135 -1.9486
Ce  0.1393  0.5288  0.2694
```

8. Energy versus geometry cycle: Cerium optimization clip is also given as supplementary video file