Supporting Information

Enhanced luminescence of tris(carboxylato)uranyl(VI) complexes and energy transfer to Eu(III) : A combined spectroscopic and theoretical investigation

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Experimental details:

Fluorescence quantum yield of uranyl complexes was determined in acetonitrile using optically matching solutions of Rhodamine-6G (ϕ= 0.95) using following equation-

$$\phi_F = \phi_r \, (A_r F_s / A_s F_r)(\eta_s^2/\eta_r^2)$$

where A_s and A_r are the absorbances of the sample and reference solutions, respectively at the same excitation wavelength, F_s and F_r are the corresponding relative integrated fluorescence intensities and η is the refractive index of the solvent used. To avoid re-absorption, the concentrations of the solutions were used such that the absorbance was less than 0.1.

Figure S1 Absorption spectra of uranyl at different uranyl(1×10^{-3} M) to benzoate ratio.

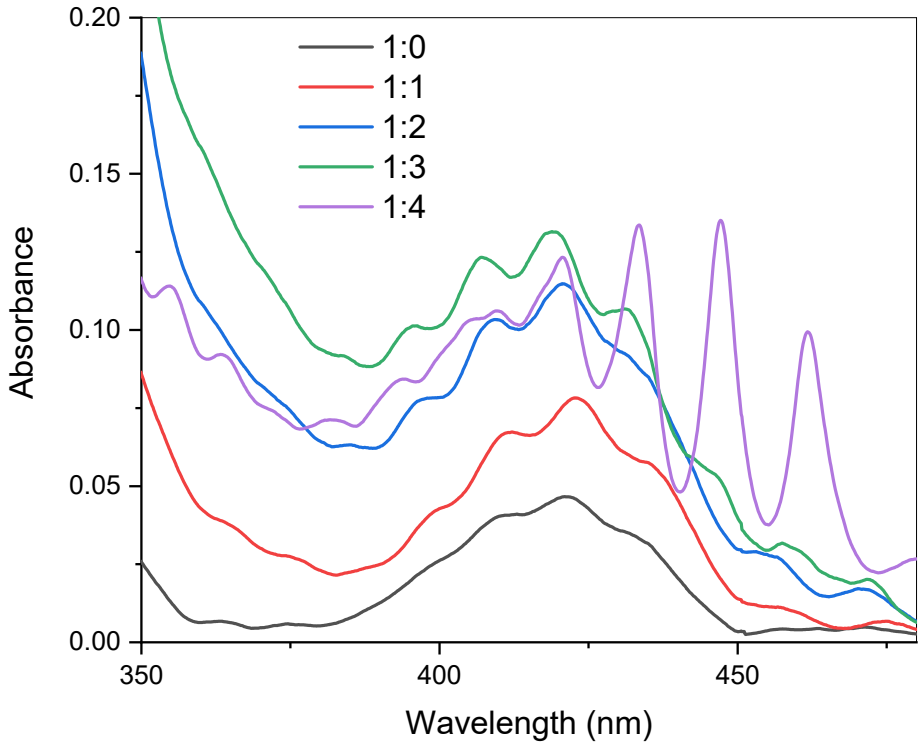

Figure S2 UV-vis titration of uranyl with a gradual increment (8×10^{-6} M) of nicotinate in acetonitrile.Uranyl- 2×10^{-5} M. I =0.1 M Bu_4N^+ ClO_4^-.

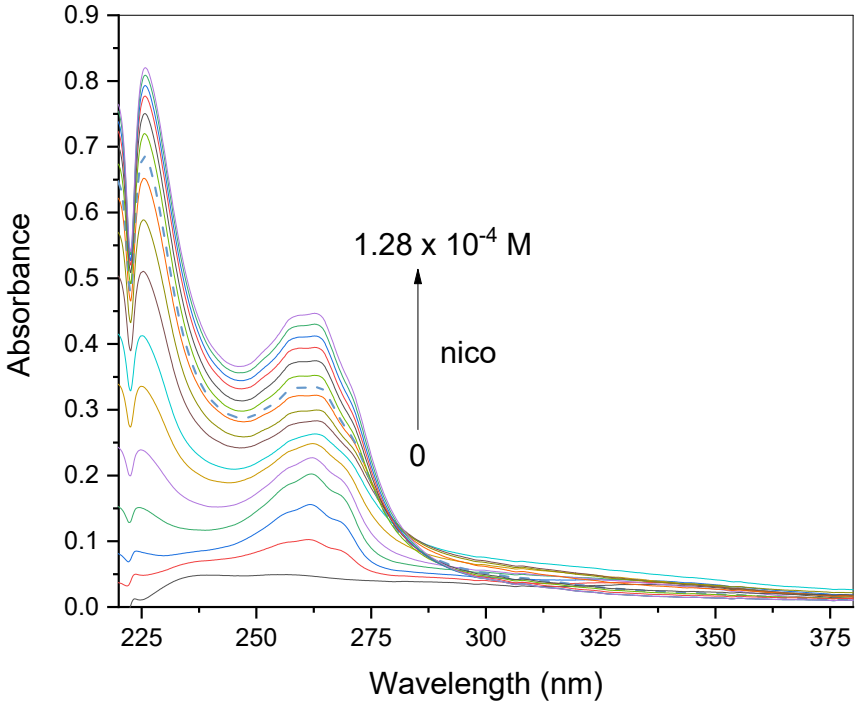

Figure S3 UV-vis titration of uranyl with a gradual increment (8×10^{-6} M) of isonicotinate in acetonitrile. Uranyl- 2×10^{-5} M. I =0.1 M Bu_4N^+ ClO_4^-.

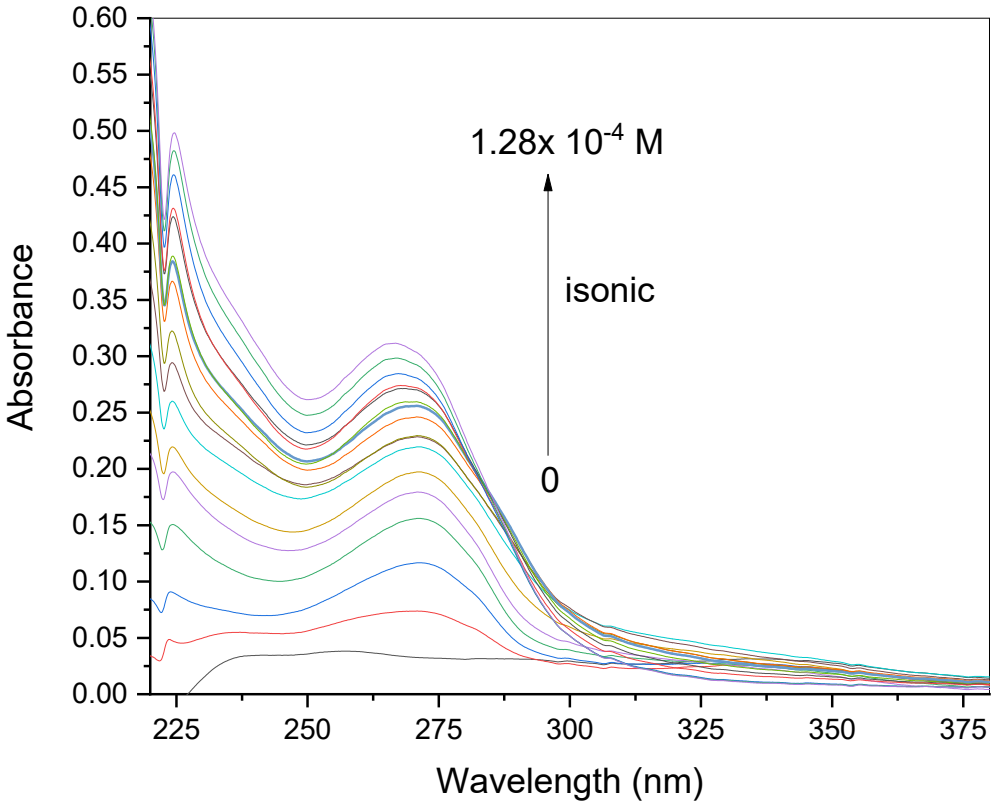

Figure S4 Absorption spectra of (a) uranyl (1×10^{-4} M) (b) ben, (c) nico and (d) isonico. Concentration of each ligand is 1×10^{-4} M.

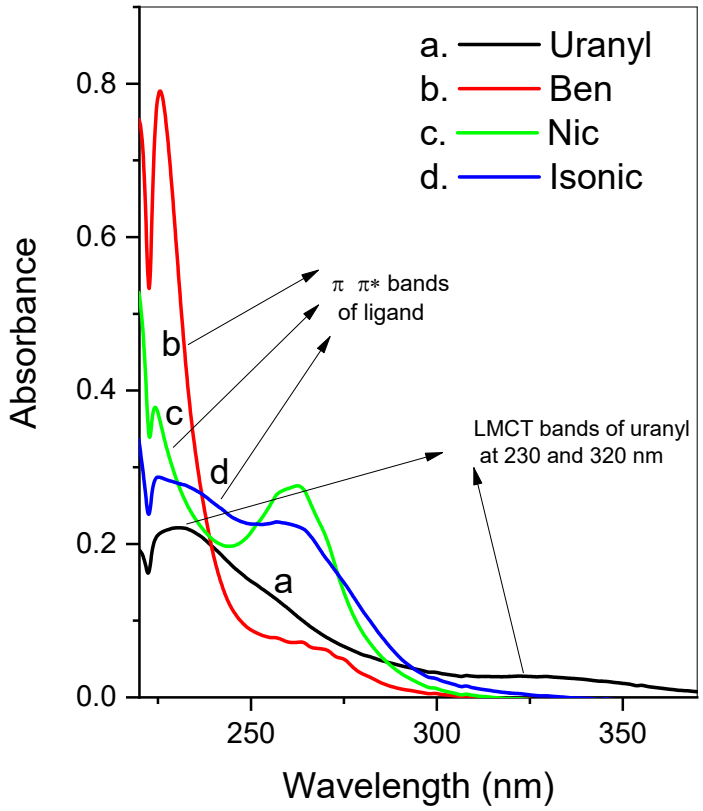

Figure S5 Emission spectra of $[UO_2(ben)_3]^-$ with the addition of Eu(III). The excitation wavelength is 416 nm for all the cases. $[UO_2(ben)_3]^-$ - 1×10^{-5} M.

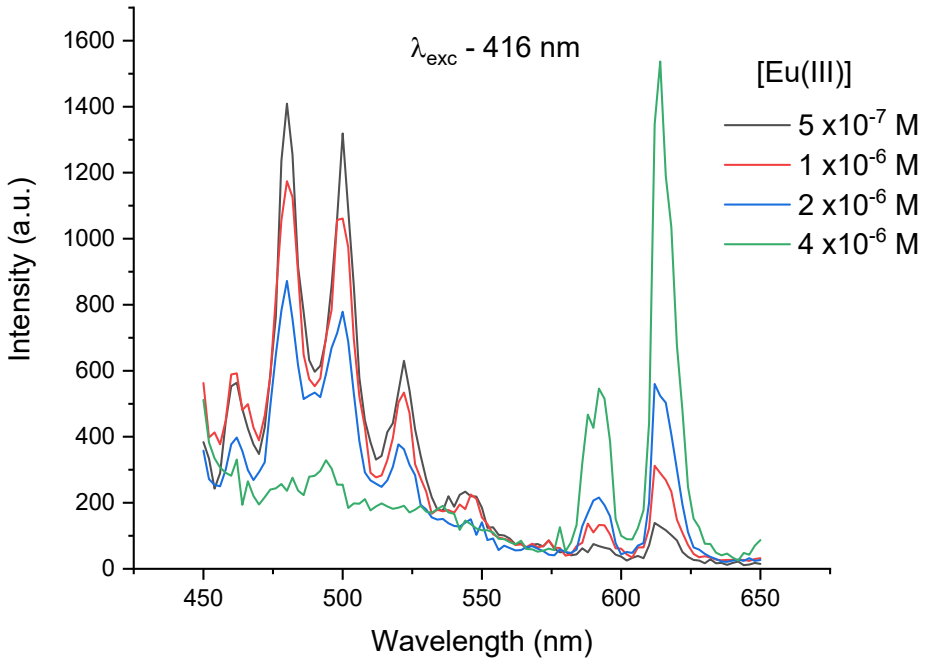

Figure S6 Emission spectra of $[UO_2(nic)_3]^-$ and $[UO_2(isonic)_3]^-$ with the addition of Eu(III). The excitation wavelength is 320 nm for all the cases. $[UO_2(L)_3]^-$ - 1×10^{-5} M.

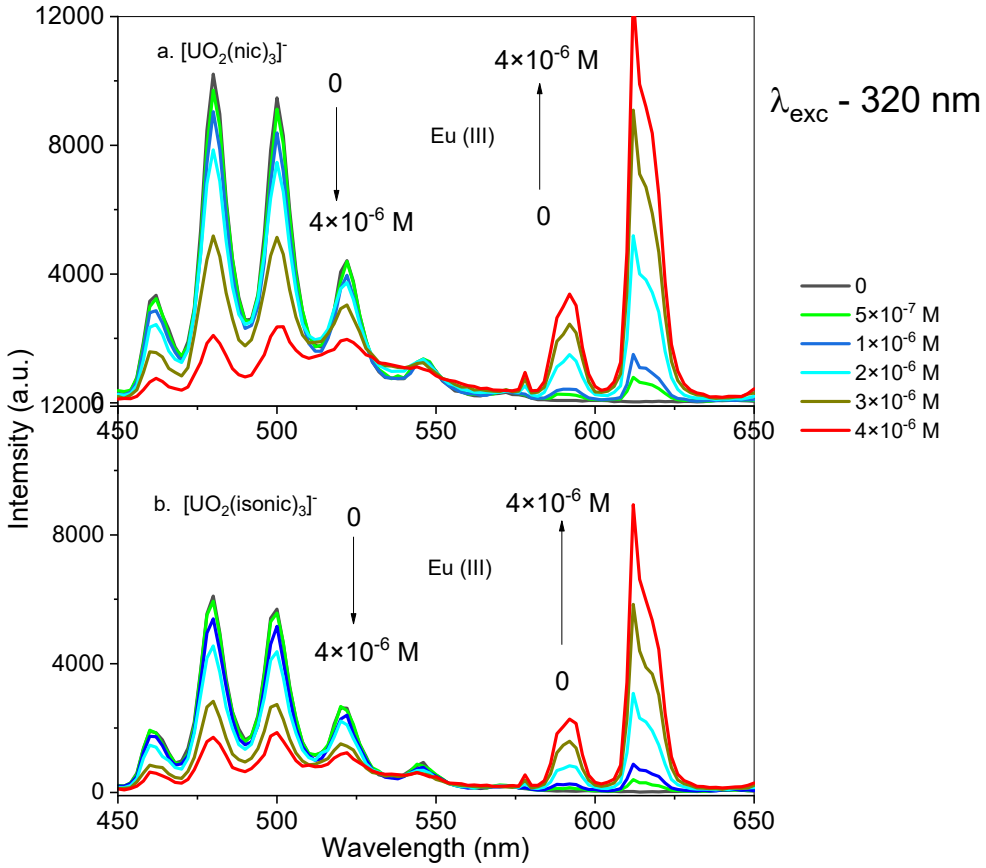

Figure S7 Bar graph showing the maximum reduction of the luminescence intensity of different $[UO_2(L)_3]^-$(1×10^{-5} M) in presence of Eu(III) (4×10^{-6} M).

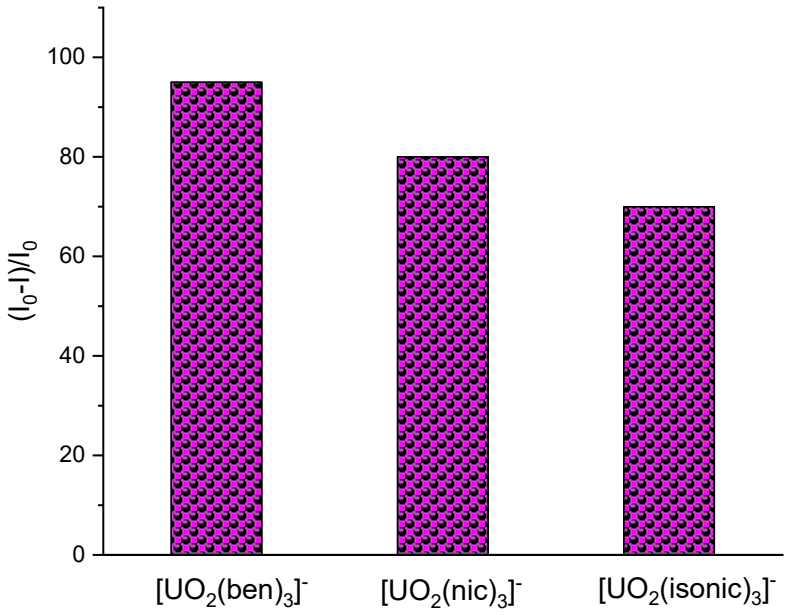

Figure S8 Lifetime of uranyl&Eu(III) in $[UO_2(ben)_3]^-$ solution (1×10^{-5} M)(a) and asymmetry ratio of Eu(III) (b) as a function of Eu(III)

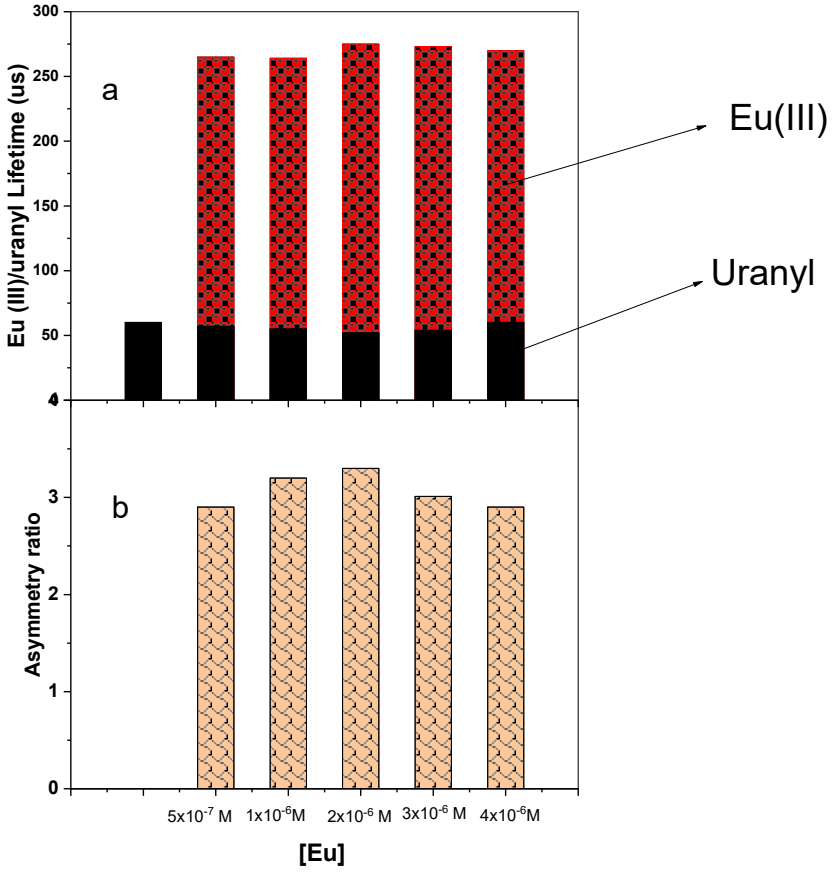

Figure S9 Time resolved spectra of $[UO_2(ben)_3]^-$ in acetonitrile.

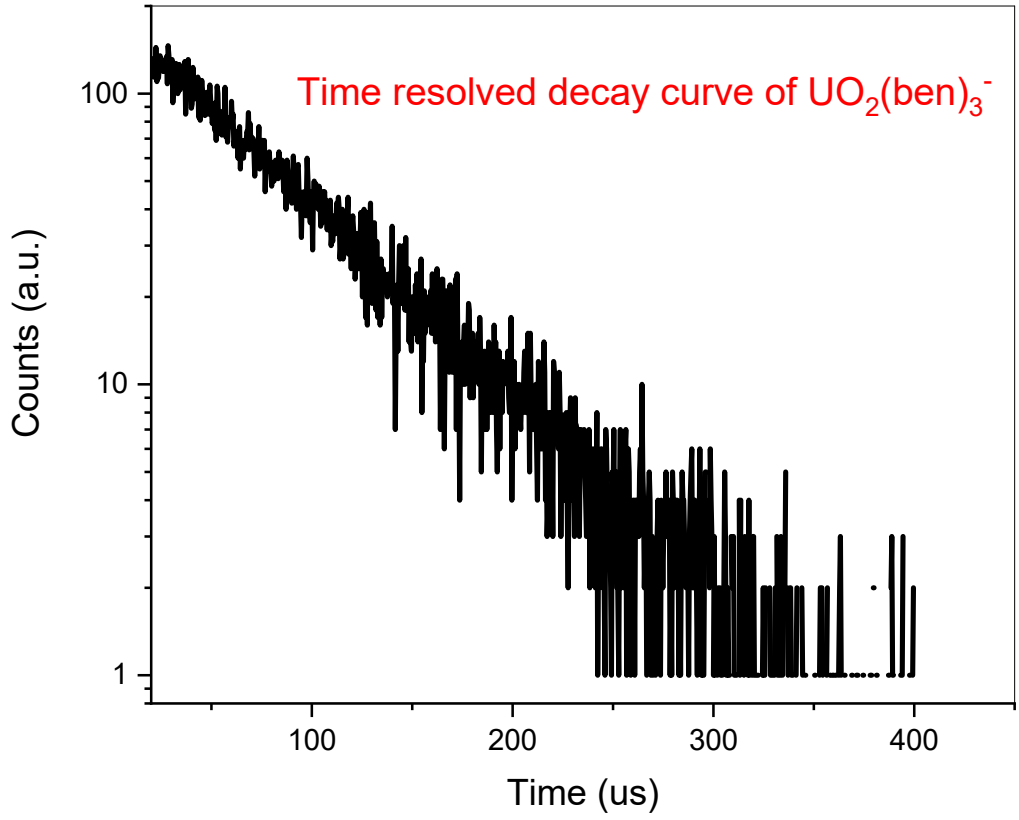

Figure S10 Excitation and emission spectra of Eu(III) (2×10^{-4} M) at different Eu(III) to benzoate ratio along with free Eu(III) (1×10^{-2} M).

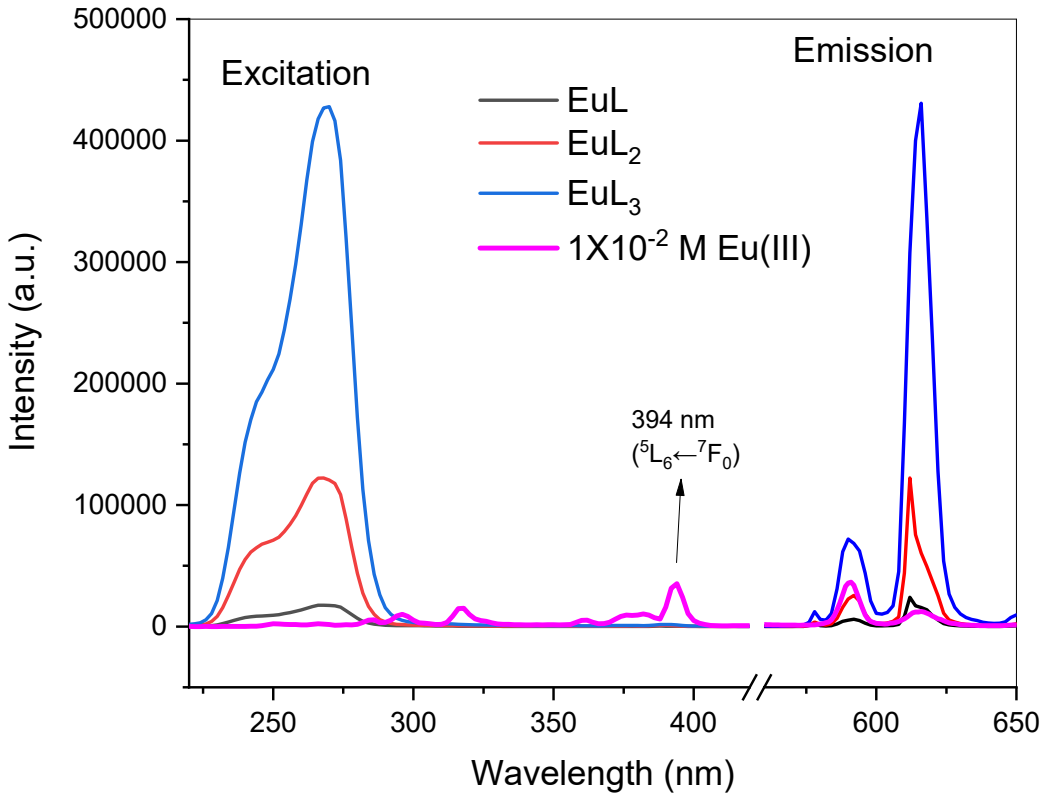

Figure S11 Asymmetry ratio and life time of Eu(III)-ben complexes (Eu(III)-2×10^{-4} M) at different Eu(III) to benzoate ratio.

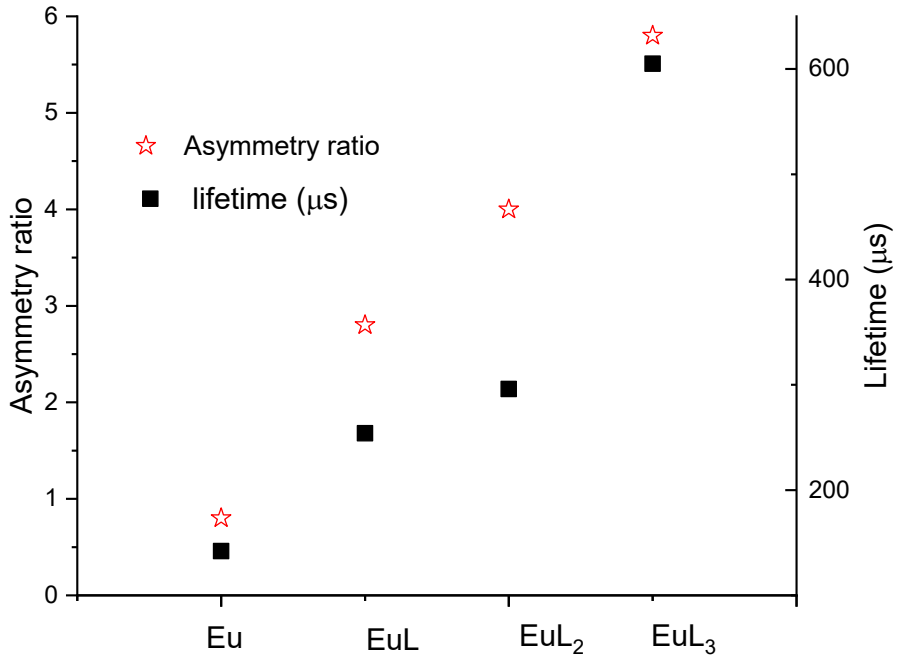

Figure S12 Emission spectra of $[UO_2(ben)_3]^-$ with the addition of Eu(III). The excitation wavelength is 316 nm for all the cases. $[UO_2(ben)_3]^-$ - 1×10^{-4} M.

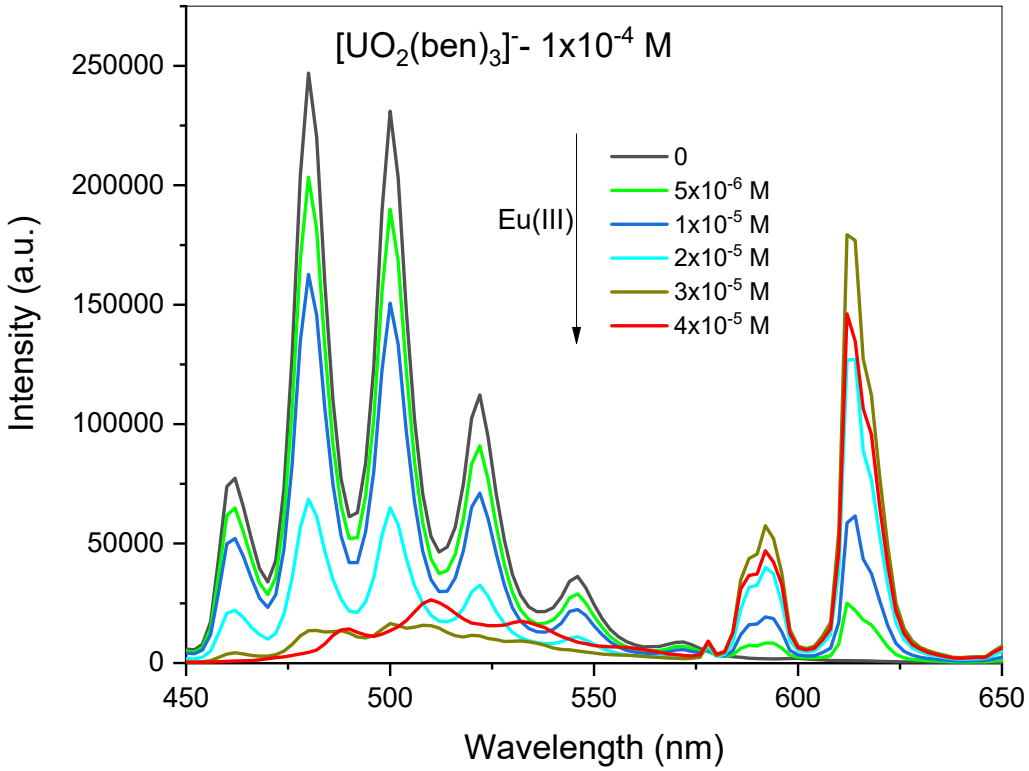

Figure S13 Emission spectra of $[UO_2(ben)_3]^-$ with the addition of Eu(III). The excitation wavelength is 316 nm for all the cases. $[UO_2(ben)_3]^-$ - 2×10^{-6} M.

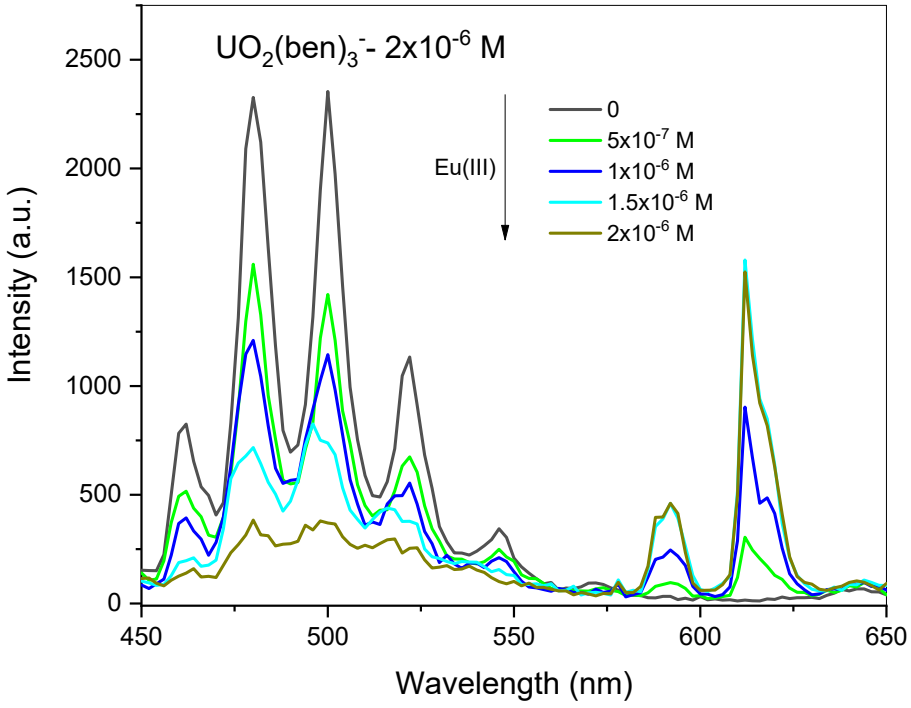

Figure S14 A linear regression analysis of the addition of Eu(III) to uranylbenzoate tris complex using 320 nm as an excitation wavelength.

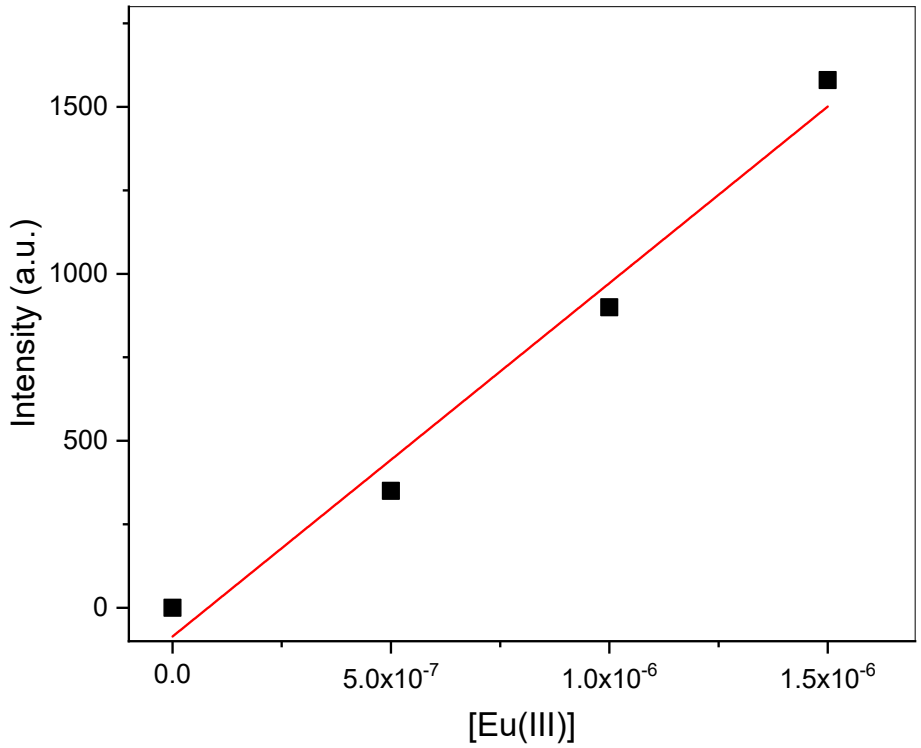

Table S1 Optimized Coordinates of various uranyl complexes at BP86/ZORA-def2-TZVP/SARC-ZORA-TZVP level of theory

A. Gaseous phase.

Input File:

```
%pal nproc 4
    end
! RKS BP86 def2-TZVP def2-TZVP/J TightOpt D3BJ ZORA RIJCOSX
! TightSCF Grid7 NoFinalGrid KDIIS GridX9
%scf
  MaxIter 200
end
%geom
  MaxIter 200
end
%basis newgto 92 "sarc-zora-tzvp" end
```

$[UO_2(H_2O)_5]^{2+}$

92	-0.191693000	0.158473000	-0.129645000
8	-0.821113000	0.451845000	1.495657000
8	0.442457000	-0.047989000	-1.766429000
8	1.826808000	1.342225000	0.680995000
1	1.927214000	1.734421000	1.569875000
1	2.658733000	1.513844000	0.199063000
8	1.521922000	-1.580598000	0.360416000
1	1.738600000	-2.013386000	1.208630000
1	2.124449000	-1.954288000	-0.311320000
8	-1.370936000	-2.009510000	0.228281000
1	-1.871700000	-2.225104000	1.038616000
1	-1.440519000	-2.783495000	-0.363162000
8	-2.377093000	0.301351000	-1.294684000
1	-2.490537000	0.263651000	-2.264059000

1	-3.267750000	0.407333000	-0.908355000
8	-0.569236000	2.556072000	-0.600279000
1	-0.407103000	3.020127000	-1.444254000
1	-0.910351000	3.220798000	0.028806000

FINAL SINGLE POINT ENERGY -29950.287022573546 Hartree

$[UO_2(ben)_3]^-$

92	0.150186000	0.102540000	0.002398000
8	0.152235000	0.103159000	1.802269000
8	0.148554000	0.101995000	-1.797474000
8	-2.357266000	0.073101000	0.004177000
6	-2.440998000	1.342985000	0.002590000
8	-1.398910000	2.073584000	0.002559000
8	1.378437000	2.288082000	0.000770000
6	2.520255000	1.725977000	0.000415000
8	2.632308000	0.458276000	0.000203000
8	1.429013000	-2.054332000	0.000852000
6	0.371107000	-2.761761000	0.002070000
8	-0.782613000	-2.224526000	0.004319000
6	0.486172000	-4.258026000	0.000730000
6	-3.794354000	1.991434000	0.000525000
6	3.758181000	2.574276000	0.000336000
6	1.747864000	-4.865710000	-0.001640000
6	1.854560000	-6.256911000	-0.002910000
6	0.700678000	-7.047691000	-0.001824000
6	-0.560534000	-6.442618000	0.000537000

18

6	-0.667784000	-5.051460000	0.001813000
1	2.628402000	-4.222509000	-0.002462000
1	2.839102000	-6.728836000	-0.004759000
1	0.784396000	-8.136439000	-0.002826000
1	-1.461358000	-7.059509000	0.001371000
1	-1.636307000	-4.550451000	0.003648000
6	3.653048000	3.970734000	0.000651000
6	4.804205000	4.759192000	0.000598000
6	6.066219000	4.155791000	0.000229000
6	6.173373000	2.761052000	-0.000084000
6	5.022533000	1.972137000	-0.000030000
1	2.655577000	4.411306000	0.000945000
1	4.720199000	5.847761000	0.000851000
1	6.967003000	4.773019000	0.000191000
1	7.158222000	2.289764000	-0.000365000
1	5.073323000	0.882883000	-0.000256000
6	-4.951444000	1.202576000	0.000451000
6	-6.209625000	1.805731000	-0.001513000
6	-6.317566000	3.200409000	-0.003420000
6	-5.162979000	3.990157000	-0.003359000
6	-3.904557000	3.387503000	-0.001392000
1	-4.834632000	0.118415000	0.001936000
1	-7.110582000	1.189033000	-0.001578000
1	-7.302326000	3.672244000	-0.004967000
1	-5.246854000	5.078736000	-0.004865000

19

1 -2.986419000 3.975784000 -0.001317000

FINAL SINGLE POINT ENERGY -30830.566998760711 Hartree

$[UO_2(nico)_3]^-$

92 0.151481000 0.102097000 0.002261000

8 0.154087000 0.102530000 1.800823000

8 0.150057000 0.101789000 -1.796306000

8 -2.353832000 0.059577000 0.004215000

6 -2.444059000 1.328724000 0.002715000

8 -1.410506000 2.068982000 0.002744000

8 1.366807000 2.291471000 0.000820000

6 2.511750000 1.736292000 0.000315000

8 2.637442000 0.471335000 -0.000110000

8 1.440295000 -2.045958000 0.000237000

6 0.386438000 -2.758890000 0.001474000

8 -0.771473000 -2.234070000 0.004004000

6 0.520742000 -4.251794000 -0.000194000

6 -3.804006000 1.959119000 0.000642000

6 3.736490000 2.600510000 0.000333000

6 1.782105000 -4.853362000 -0.002230000

6 1.857189000 -6.244681000 -0.003746000

6 0.667245000 -6.977430000 -0.003206000

7 -0.555425000 -6.420349000 -0.001295000

6 -0.610775000 -5.078503000 0.000186000

1 2.667522000 -4.216562000 -0.002598000

1 2.819446000 -6.759463000 -0.005336000

20

1	0.693683000	-8.072029000	-0.004375000
1	-1.601269000	-4.617837000	0.001756000
6	3.625185000	3.993544000	0.000987000
6	4.791713000	4.755543000	0.001004000
6	6.022024000	4.092826000	0.000357000
7	6.152445000	2.755567000	-0.000281000
6	5.018855000	2.035433000	-0.000278000
1	2.630507000	4.440847000	0.001471000
1	4.755125000	5.846235000	0.001512000
1	6.956083000	4.664122000	0.000350000
1	5.116408000	0.947414000	-0.000779000
6	-4.955766000	1.167655000	0.000382000
6	-6.198135000	1.798434000	-0.001632000
6	-6.237586000	3.195342000	-0.003297000
7	-5.143722000	3.975538000	-0.003089000
6	-3.954043000	3.352400000	-0.001149000
1	-4.847052000	0.082458000	0.001735000
1	-7.125190000	1.222661000	-0.001929000
1	-7.198708000	3.719829000	-0.004895000
1	-3.059797000	3.979792000	-0.000998000

FINAL SINGLE POINT ENERGY -30878.783485082848 Hartree

$[UO_2(isonic)_3]^-$

92	0.149087000	0.102707000	0.000131000
8	0.148940000	0.102887000	1.798049000
8	0.149205000	0.102545000	-1.797790000

21

8	-2.357534000	0.075327000	-0.000485000
6	-2.436864000	1.344035000	-0.000622000
8	-1.399367000	2.078122000	-0.000769000
8	1.378411000	2.288463000	0.000414000
6	2.516564000	1.722515000	0.000691000
8	2.633122000	0.456868000	0.001019000
8	1.428255000	-2.054242000	0.000438000
6	0.369428000	-2.757488000	0.000299000
8	-0.785265000	-2.226309000	0.000287000
6	0.485972000	-4.255674000	0.000114000
6	-3.792525000	1.992328000	-0.000566000
6	3.756232000	2.571824000	0.000589000
6	1.737557000	-4.877409000	0.000171000
6	1.790655000	-6.271335000	-0.000014000
7	0.704302000	-7.063496000	-0.000250000
6	-0.491448000	-6.448791000	-0.000305000
6	-0.654457000	-5.063415000	-0.000129000
1	2.639592000	-4.265326000	0.000354000
1	2.756245000	-6.786548000	0.000027000
1	-1.365792000	-7.107073000	-0.000500000
1	-1.640265000	-4.598123000	-0.000180000
6	3.669671000	3.966644000	0.000159000
6	4.850724000	4.708914000	0.000062000
7	6.079617000	4.163477000	0.000361000
6	6.144374000	2.820536000	0.000773000

22

6	5.025632000	1.987319000	0.000901000
1	2.688846000	4.442349000	-0.000094000
1	4.814745000	5.802767000	-0.000274000
1	7.151390000	2.391898000	0.001011000
1	5.114959000	0.900886000	0.001231000
6	-4.956873000	1.219471000	-0.000397000
6	-6.190493000	1.870652000	-0.000333000
7	-6.333134000	3.207562000	-0.000424000
6	-5.202792000	3.935583000	-0.000583000
6	-3.921608000	3.383861000	-0.000660000
1	-4.878001000	0.132232000	-0.000314000
1	-7.119567000	1.292180000	-0.000201000
1	-5.335540000	5.021948000	-0.000652000
1	-3.025643000	4.004799000	-0.000786000

FINAL SINGLE POINT ENERGY -30878.785999300642 Hartree

B. Acetonitrile phase.

$[UO_2(H_2O)_5]^{2+}$

92	-0.225284000	0.102617000	-0.165780000
8	-0.840158000	0.315602000	1.490700000
8	0.306168000	-0.159027000	-1.844145000
8	1.882260000	1.317459000	0.346671000
1	1.866690000	2.275604000	0.527894000
1	2.546155000	0.921095000	0.941133000
8	1.545086000	-1.360559000	0.666384000
1	1.531180000	-1.781749000	1.546207000

23

1 2.099793000 -1.926089000 0.097002000

8 -1.186798000 -2.113579000 -0.176684000

1 -1.703027000 -2.523285000 0.541491000

1 -1.182826000 -2.743645000 -0.920562000

8 -2.470737000 0.449939000 -0.986854000

1 -2.753645000 0.420268000 -1.919215000

1 -3.269710000 0.606882000 -0.450956000

8 -0.392450000 2.508183000 -0.547924000

1 -0.312345000 2.930978000 -1.423288000

1 -0.918201000 3.115076000 0.006078000

FINAL SINGLE POINT ENERGY -29950.588763562198 Hartree

$[UO_2(ben)_3]^-$

92 0.149942000 0.102736000 0.002355000

8 0.151679000 0.103293000 1.815367000

8 0.148382000 0.102201000 -1.810648000

8 -2.331001000 0.067146000 0.003963000

6 -2.439023000 1.342269000 0.002474000

8 -1.377796000 2.057426000 0.002506000

8 1.359833000 2.268783000 0.000851000

6 2.518149000 1.724783000 0.000540000

8 2.606894000 0.448171000 0.000375000

8 1.421037000 -2.028168000 0.000959000

6 0.370747000 -2.759254000 0.002051000

8 -0.779178000 -2.197745000 0.004140000

6 0.485032000 -4.242425000 0.000765000

24

6	-3.780623000	1.984889000	0.000517000
6	3.745440000	2.565398000	0.000420000
6	1.749993000	-4.849850000	-0.001072000
6	1.855717000	-6.240772000	-0.002373000
6	0.699852000	-7.030268000	-0.001830000
6	-0.563318000	-6.427176000	0.000014000
6	-0.671938000	-5.036475000	0.001309000
1	2.641155000	-4.222042000	-0.001390000
1	2.839361000	-6.712206000	-0.003800000
1	0.783666000	-8.118110000	-0.002862000
1	-1.463136000	-7.043725000	0.000430000
1	-1.648759000	-4.552608000	0.002639000
6	3.638975000	3.964598000	0.001066000
6	4.790673000	4.751641000	0.000904000
6	6.052342000	4.145411000	0.000109000
6	6.161666000	2.749928000	-0.000531000
6	5.011609000	1.960488000	-0.000377000
1	2.649689000	4.422445000	0.001775000
1	4.707104000	5.839218000	0.001411000
1	6.952520000	4.761937000	-0.000026000
1	7.145535000	2.278961000	-0.001150000
1	5.081006000	0.872603000	-0.000970000
6	-4.939168000	1.193140000	0.000828000
6	-6.196585000	1.797075000	-0.001106000
6	-6.302344000	3.192832000	-0.003343000

25

6	-5.148446000	3.985198000	-0.003651000
6	-3.889773000	3.383882000	-0.001726000
1	-4.841078000	0.107466000	0.002665000
1	-7.096698000	1.180955000	-0.000863000
1	-7.286339000	3.664190000	-0.004866000
1	-5.232456000	5.072739000	-0.005400000
1	-2.982304000	3.987876000	-0.002053000

FINAL SINGLE POINT ENERGY -30830.657743182845 Hartree

$[UO_2(nic)_3]^-$

92	0.151206000	0.102541000	0.001679000
8	0.153230000	0.102892000	1.811768000
8	0.149576000	0.102250000	-1.808417000
8	-2.333635000	0.042733000	0.003458000
6	-2.448616000	1.315246000	0.002221000
8	-1.399074000	2.044352000	0.002354000
8	1.341657000	2.283925000	0.000281000
6	2.501395000	1.747640000	0.000006000
8	2.608498000	0.474230000	-0.000345000
8	1.445117000	-2.019390000	-0.000262000
6	0.400574000	-2.755243000	0.001035000
8	-0.755603000	-2.210840000	0.003456000
6	0.532454000	-4.237081000	-0.000328000
6	-3.797871000	1.941967000	0.000496000
6	3.718406000	2.603303000	0.000258000
6	1.791661000	-4.848813000	-0.002853000

6	1.856080000	-6.239541000	-0.004012000
6	0.661440000	-6.964683000	-0.002499000
7	-0.558848000	-6.393831000	-0.000061000
6	-0.607794000	-5.052782000	0.000931000
1	2.693235000	-4.236079000	-0.003884000
1	2.813243000	-6.760728000	-0.006013000
1	0.681176000	-8.057549000	-0.003319000
1	-1.599083000	-4.594062000	0.002863000
6	3.617970000	3.999631000	0.000396000
6	4.789837000	4.751302000	0.000718000
6	6.015444000	4.079827000	0.001000000
7	6.131805000	2.737650000	0.000892000
6	4.995206000	2.024236000	0.000467000
1	2.636336000	4.473626000	0.000244000
1	4.762135000	5.840814000	0.000831000
1	6.951778000	4.643764000	0.001292000
1	5.094072000	0.936435000	0.000355000
6	-4.957241000	1.157311000	-0.000240000
6	-6.193864000	1.796868000	-0.001842000
6	-6.224555000	3.194028000	-0.002518000
7	-5.120051000	3.965419000	-0.001798000
6	-3.934185000	3.337298000	-0.000362000
1	-4.877358000	0.070161000	0.000418000
1	-7.123807000	1.228529000	-0.002495000
1	-7.180882000	3.723351000	-0.003707000

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1 -3.041283000 3.966432000 0.000135000

FINAL SINGLE POINT ENERGY -30878.872408500552 Hartree

$[UO_2(isonic)_3]^-$

92 0.149376000 0.102677000 0.000233000

8 0.149008000 0.102821000 1.808958000

8 0.149696000 0.102453000 -1.808500000

8 -2.336165000 0.069477000 -0.000379000

6 -2.435335000 1.341892000 -0.000465000

8 -1.381991000 2.062350000 -0.000539000

8 1.363308000 2.272309000 0.000434000

6 2.514776000 1.721949000 0.000725000

8 2.611947000 0.449470000 0.001054000

8 1.421951000 -2.033089000 0.000449000

6 0.369813000 -2.755421000 0.000383000

8 -0.780963000 -2.203725000 0.000433000

6 0.485228000 -4.245022000 0.000178000

6 -3.782927000 1.987026000 -0.000484000

6 3.747371000 2.566302000 0.000616000

6 1.739406000 -4.863909000 -0.000162000

6 1.794082000 -6.257719000 -0.000403000

7 0.702141000 -7.044849000 -0.000359000

6 -0.498003000 -6.435287000 -0.000033000

6 -0.658669000 -5.049687000 0.000264000

1 2.651220000 -4.267714000 -0.000241000

1 2.759565000 -6.769752000 -0.000699000

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1	-1.373120000	-7.089889000	0.000002000
1	-1.651418000	-4.601015000	0.000529000
6	3.656716000	3.961926000	-0.000054000
6	4.836703000	4.705788000	-0.000185000
7	6.064163000	4.153295000	0.000268000
6	6.135893000	2.809135000	0.000908000
6	5.015985000	1.977568000	0.001128000
1	2.684656000	4.453811000	-0.000468000
1	4.797761000	5.797951000	-0.000732000
1	7.140210000	2.378227000	0.001274000
1	5.123440000	0.893451000	0.001657000
6	-4.946176000	1.210602000	-0.000681000
6	-6.180428000	1.860465000	-0.000727000
7	-6.315802000	3.199711000	-0.000622000
6	-5.187654000	3.934010000	-0.000435000
6	-3.907495000	3.380034000	-0.000338000
1	-4.886041000	0.122837000	-0.000799000
1	-7.106746000	1.280578000	-0.000907000
1	-5.316729000	5.019216000	-0.000346000
1	-3.022400000	4.015223000	-0.000178000

FINAL SINGLE POINT ENERGY -30878.869653847738 Hartree

Table S2 Calculated value of complexation energy (kcal/mol) of free uranyl with L in gas and acetonitrile phase.

$$UO_2^{2+} + nL \rightarrow UO_2(L)_n \quad (n= 5 \text{ for } H_2O \text{ and } 3 \text{ for other ligands})$$

Uranyl complex	**Complexation energy(kcal/mol)**	
	Gas phase	**Acetonitrile**
$[UO_2(H_2O)_5]^{2+}$	- 260.9	-135.6
$[UO_2(ben)_3]^-$	-616.4	-207.6
$[UO_2(nic)_3]^-$	-608.7	-202.3
$[UO_2(isonic)_3]^-$	-605.8	-200.1

Table S3 Calculated value of binding energy of ion pair (kcal/mol) in gaseous and solution phase, $Me_4N^+L^- \rightarrow Me_4N^+ + L^-$

Reaction	**Phase**	**Energy of $Me_4N^+L^-$ (Hartree)**	**Energy of Me_4N^+ (Hartree)**	**Energy of ligand (Hartree)**	**Dissociation energy (kcal/mol)**
$Me_4N^+ben^- \rightarrow Me_4N^+ + ben^-$	Gas phase	-635.386	-214.402	-420.826	99.7
	Acetonitrile	-635.424	-214.488	-420.926	6.7
$Me_4N^+nico^- \rightarrow Me_4N^+ + nico^-$	Gas phase	-651.458	-214.402	-436.902	97.1
	Acetonitrile	-651.498	-214.488	-437	6.5
$Me_4N^+isonic^- \rightarrow Me_4N^+ + isonic^-$	Gas phase	-651.459	-214.402	-436.905	95.8
	Acetonitrile	-651.499	-214.488	-437	6.4