Photo-physical and Structural Impact of Phosphorylated Anions Associated to Lanthanide Complexes in Water

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Supplementary Information (13 pages including this one)

Full reference 43 : Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., *Gaussian 98; Revision A.5 ed.; Gaussian, Inc.: Pittsburgh PA.* **1998.**

Synthesis of Ligand L_C.

Bis-[(6'-carboxy-2,2'-bipyridine-6-yl)]phenylphosphine oxide L_C : Bis-[(6'-carboethoxy-2,2'-bipyridine-6-yl)]phenylphosphine oxide (180 mg, 0.31 mmol) and NaOH (50 mg, 1.25 mmol) were dissolved in a mixture of EtOH (15 mL) and H_2O (10 mL) and heated at 72 °C during 14 h. After the mixture had cooled to r.t., the solvents were evaporated under reduced pressure. The solid was dissolved in H_2O, precipitated with dil. HCl (2N) and centrifugated to give $\mathbf{L_C}$·2HCl·H_2O (147 mg, 77%) as a yellow cristalline solid. ^{1}H-NMR (300MHz, CD_3OD): δ = 7.59-7.70 (m, 3H), 7.97 (t, 2H, ^{3}J=8.0 Hz), 8.13-8.21 (m, 8H), 8.42 (d, 2H, ^{3}J=8.0 Hz), 8.79-8.83 (m, 2H); ^{13}C{^{1}H}-NMR (75MHz, CD_3OD): δ = 124.9 (CH), 125.5 (CH), 126.6 (CH), 129.5 (CH, d, J_{PC}=11Hz), 129.8 (CH), 130.7 ($C_{quat.}$, d, J_{PC}= 104Hz), 133.6 (CH, J_{PC}=9Hz), 134.0 (CH), 139.1 (CH, d, J_{PC}=9Hz), 139.8 (CH), 149.1 ($C_{quat.}$), 156.4 ($C_{quat.}$),

156.7, 156.8, 157.1 ($2C_{quat.}$), 167.9 ($C_{C=O}$); ^{31}P-NMR (CD_3OD): δ = 21.45; IR (KBr, cm^{-1}): 2922 (w), 1763 (w), 1717 (s, ν_{CO}), 1577 (m, $\nu_{C=C}$,$\nu_{C=N}$), 1557 (w), 1430 (s, $\nu_{C=C}$), 1379 (m), 1353 (m), 1238 (m, $\nu_{P=O}$), 1135 (m), 1103 (m), 1077 (s), 766 (s); MS (FAB^+): 523.3 ($[M+H]^+$, 100%); Anal. Calcd for $C_{28}H_{19}N_4PO_5.2HCl.H_2O$: C 54.83, H 3.78, N 9.13. Found: C 54.64, H 3.65, N 8.96.

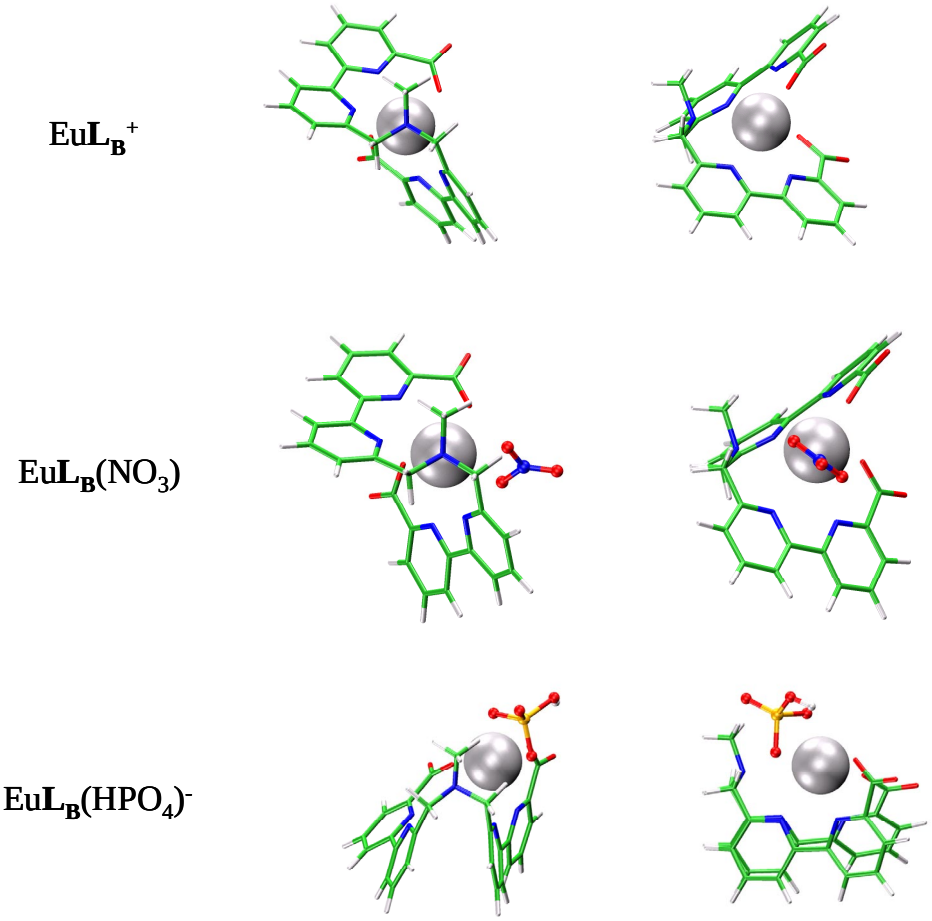


Figure S1 : Orthogonal views of the $[EuL_B]^+$ complex and its adducts with nitrate and HPO_4^{2-} after a B3LYP/6-31G* optimization.

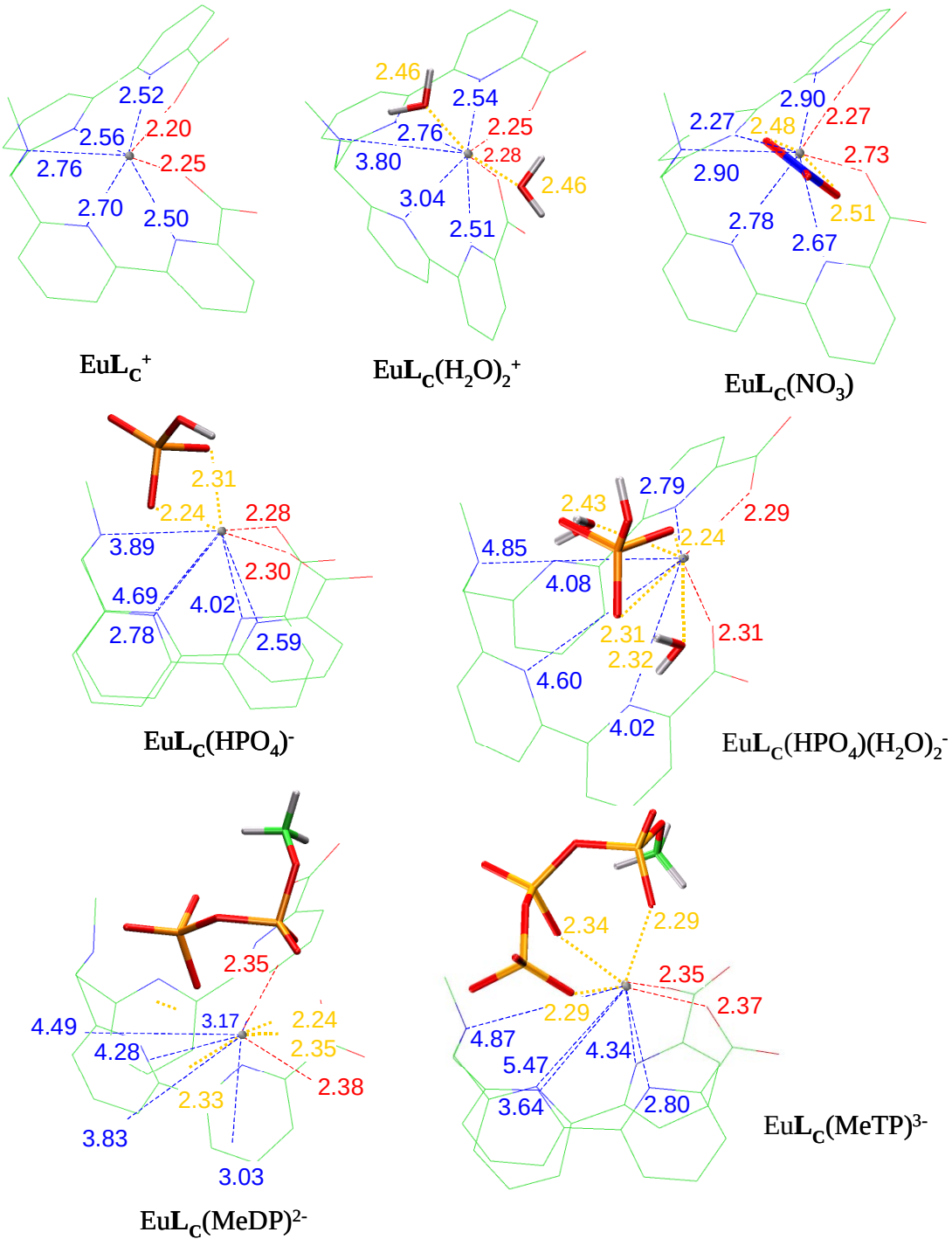


Figure S2 : Typical bond distances (in Å).

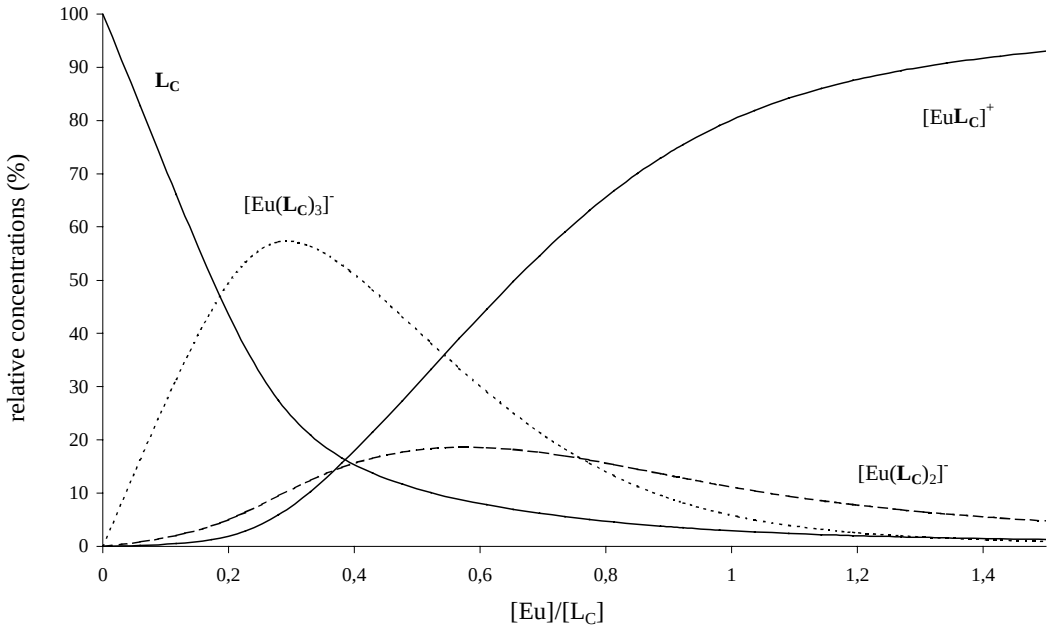


Figure S3 : Evolution of the relative concentrations of the species formed upon titration of $\mathbf{L_C}$ with $EuCl_3.6H_2O$ in water (0.01 M TRIS/HCl, pH = 7.0).

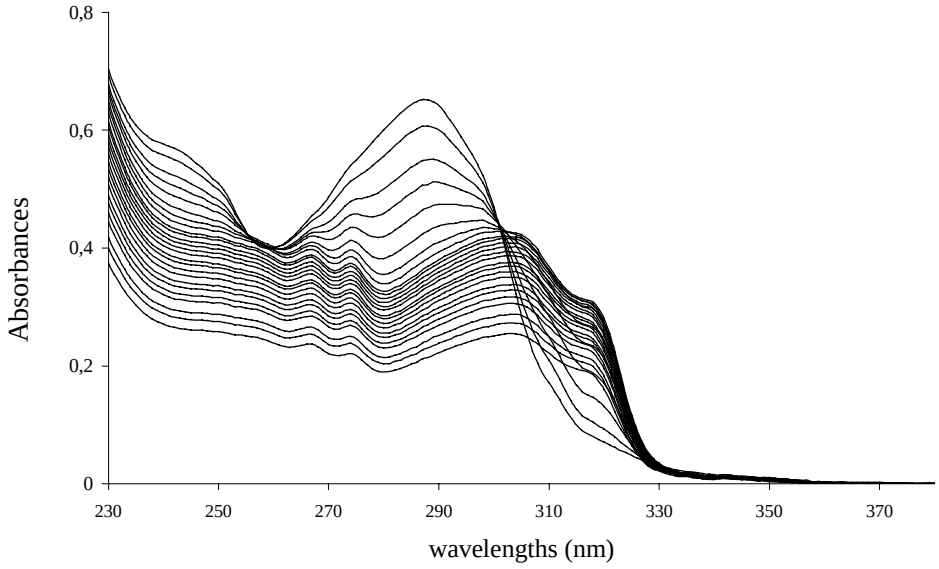


Figure S4 : Evolution of the UV-Vis absorption spectra of a solution of $\mathbf{L_C}$ upon addition of $EuCl_3.6H_2O$ in water, 0.01 M TRIS/$HClO_4$, pH = 7.0 (uncorrected for dilution).

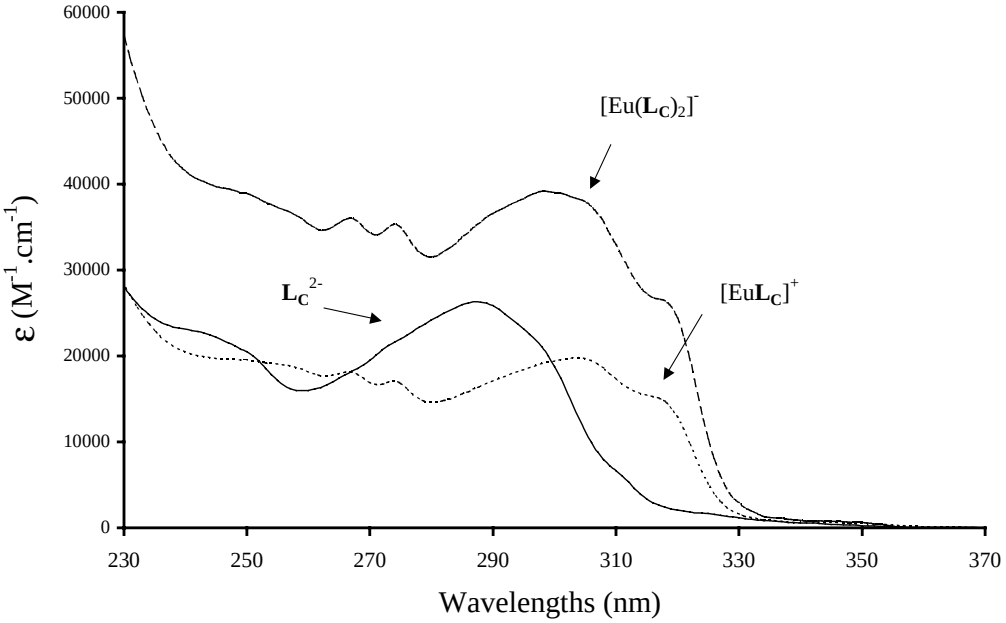


Figure S5 : Calculated UV-Vis absorption spectra of the species formed upon titration of $\mathbf{L_C}$ by $EuCl_3.6H_2O$ in water at pH = 7.0, 0.01 M TRIS/$HClO_4$.

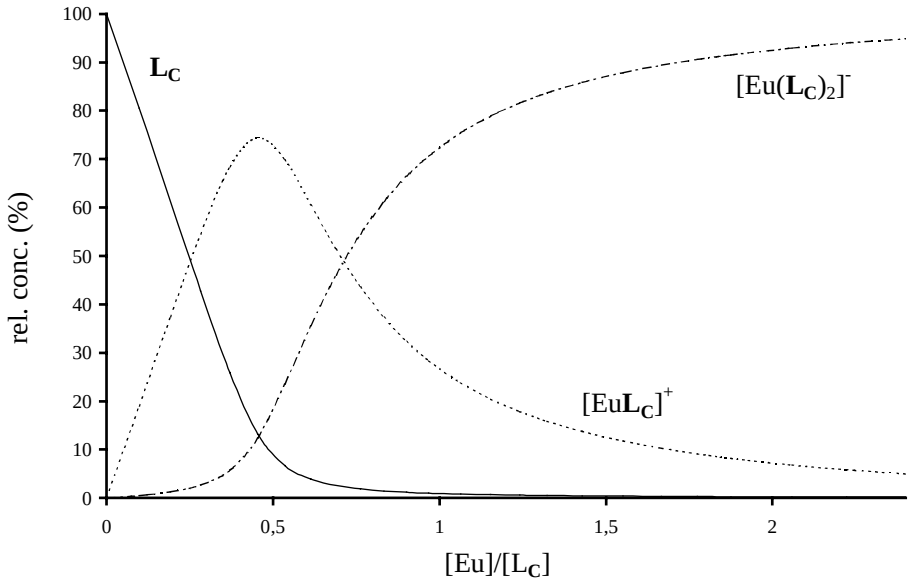


Figure S6 : Evolution of the relative concentrations of the species formed upon titration of $\mathbf{L_C}$ by $EuCl_3.6H_2O$ in water at pH = 7.0, 0.01 M TRIS/$HClO_4$.

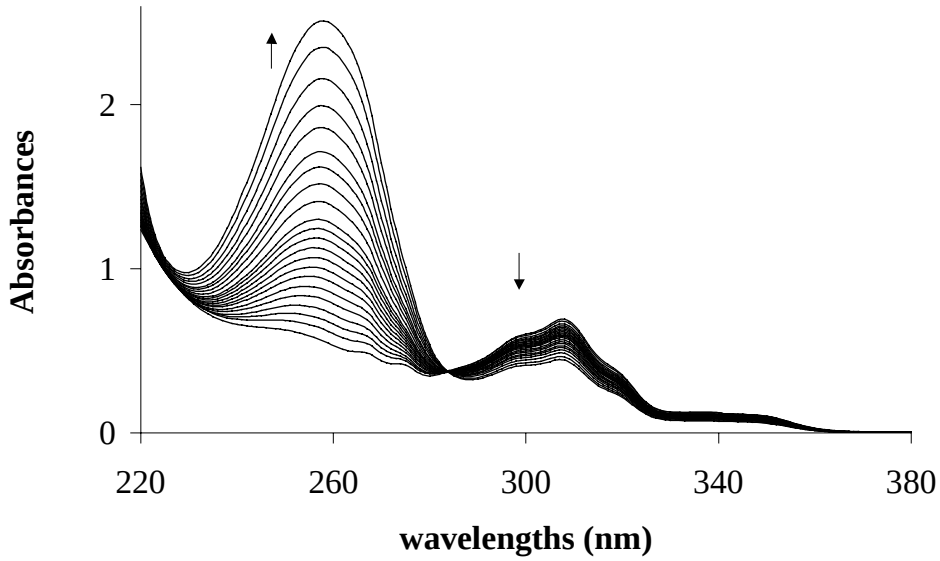


Figure S7 : Evolution of the UV-Vis absorption spectra of a solution of $[Eu\mathbf{L_C}]^{+}$ upon addition of ADP^{3-} in water, 0.01 M TRIS/HCl pH = 7.0 (uncorrected for dilution).

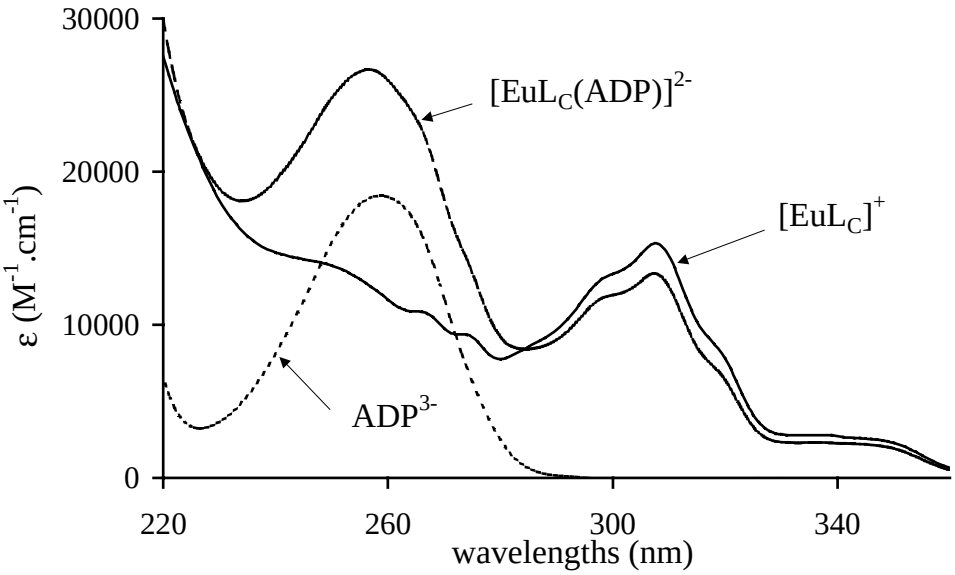


Figure S8 : Calculated UV-Vis absorption spectra of the species formed upon addition of ADP^{3-} in water, 0.01 M TRIS/HCl, pH = 7.0.

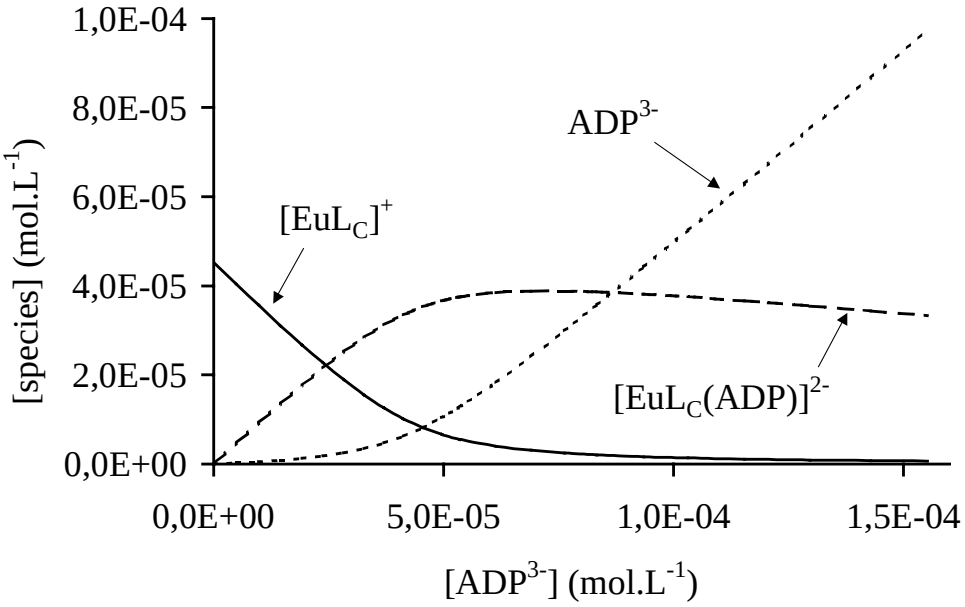


Figure S9 : Evolution of the concentrations of the species formed upon titration of $[Eu\mathbf{L_C}]^+$ (5×10^{-5} M) by ADP^{3-} in water at pH = 7.0, 0.01 M TRIS/HCl, pH = 7.0.

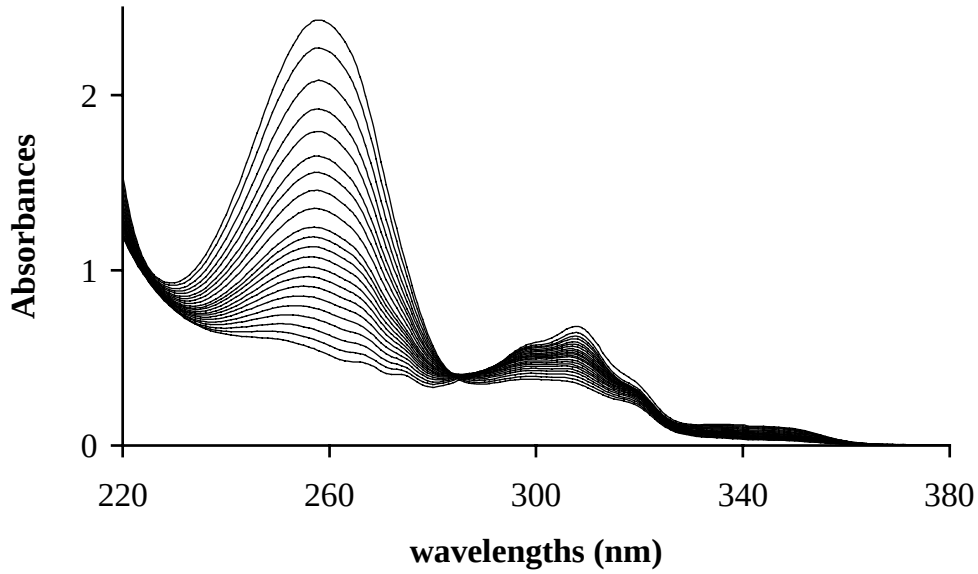


Figure S10 : Evolution of the aborption spectra of a solution of $[Eu\mathbf{L_C}]^+$ upon addition of ATP^{3-} in water, 0.01 M TRIS/HCl, pH = 7.0 (uncorrected for dilution).

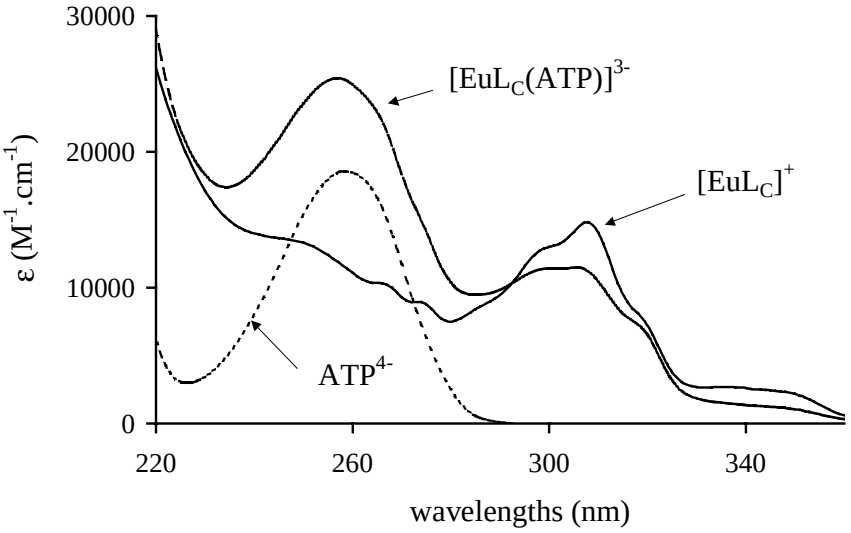


Figure S11 : Calculated UV-Vis absorption spectra of the species formed upon addition of ATP^{4-} in water, 0.01 M TRIS/HCl, pH = 7.0.

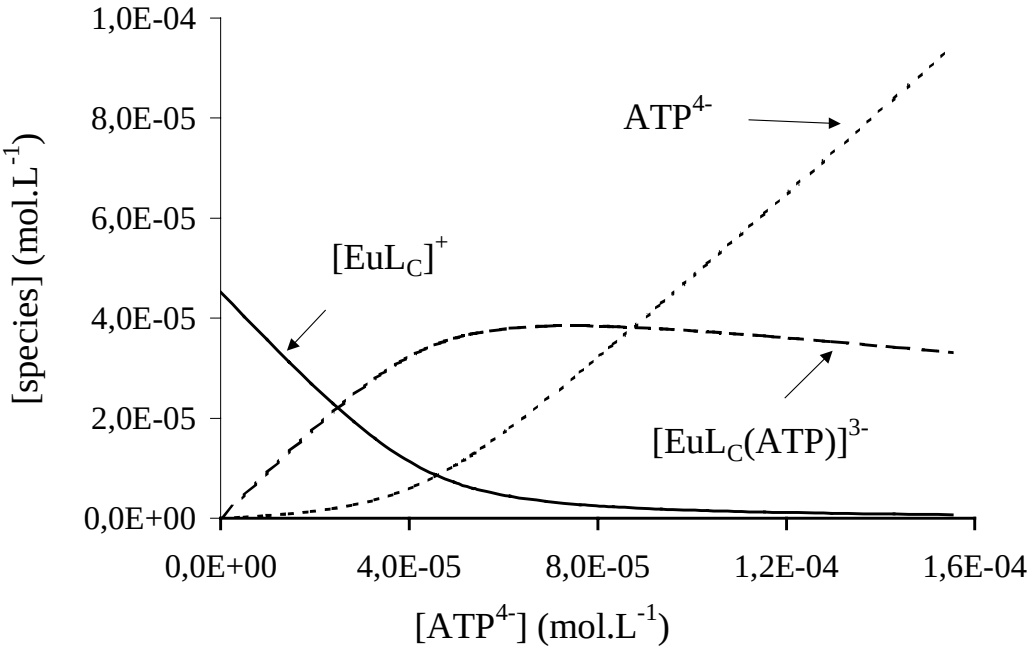


Figure S12 : Evolution of the concentrations of the species formed upon titration of $[Eu\mathbf{L_C}]^+$ (5×10^{-5} M) by ATP^{4-} in water, 0.01 M TRIS/HCl, pH = 7.0.

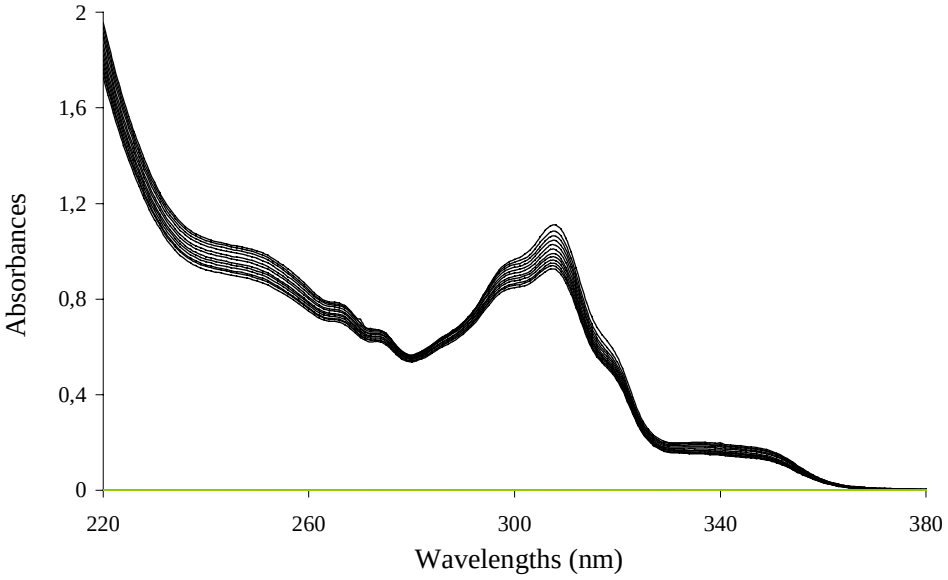


Figure S13 : Evolution of the aborption spectra of a solution of $[Eu\mathbf{L_C}]^+$ upon addition of HPO_4^{2-} in water, 0.01 M TRIS/HCl, pH = 7.0 (uncorrected for dilution).

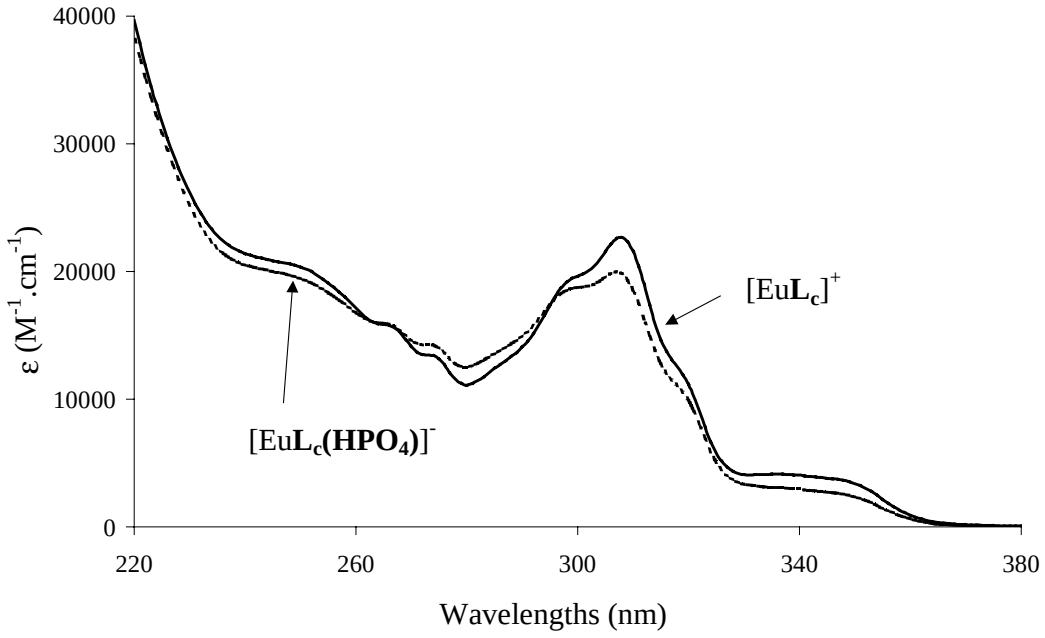


Figure S14 : Calculated UV-Vis absorption spectra of the species formed upon addition of HPO_4^{2-} in water, 0.01 M TRIS/HCl, pH = 7.0.

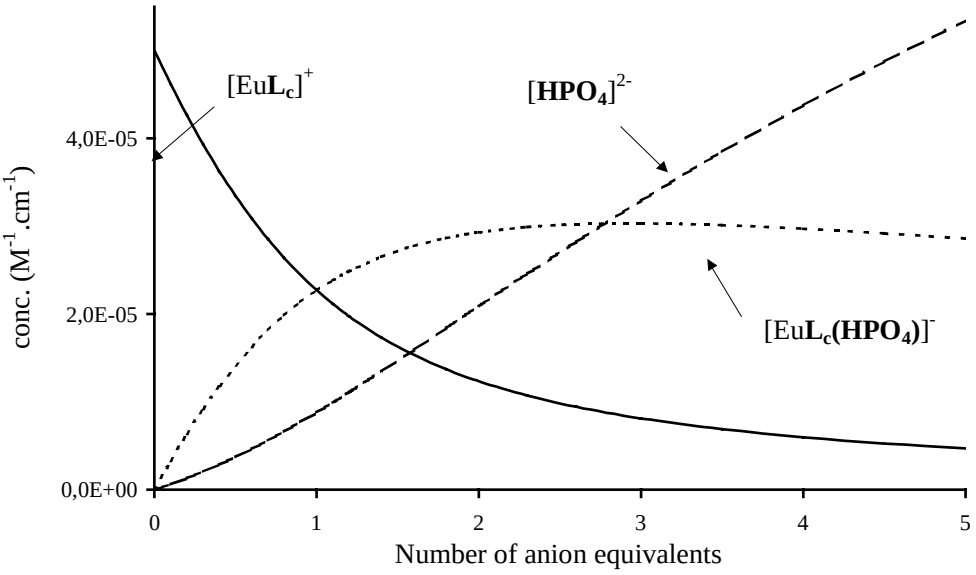


Figure S15 : Evolution of the concentrations of the species formed upon titration of [Eu**L$_C$**]$^+$ (5×10^{-5} M) by HPO_4^{2-} in water, 0.01 M TRIS/HCl, pH = 7.0.

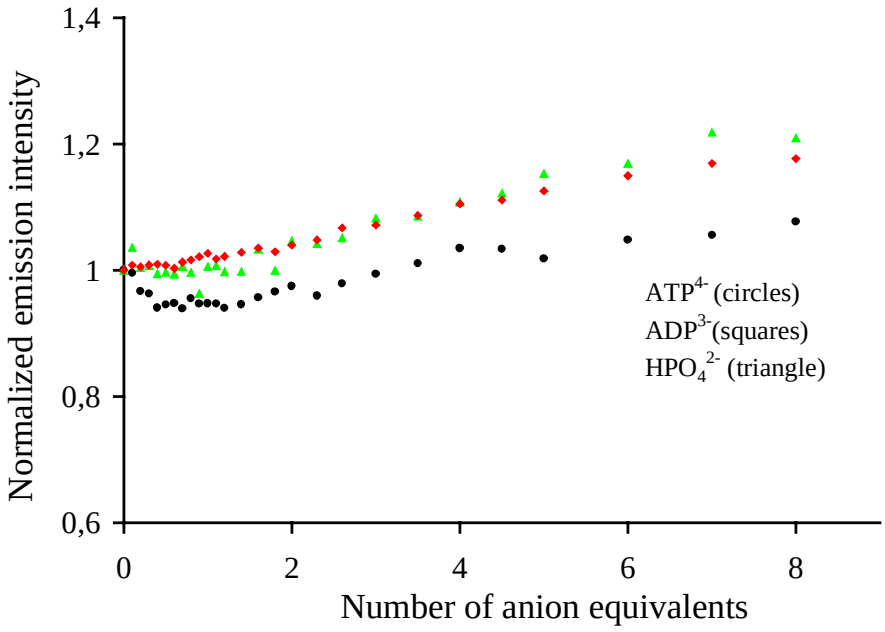
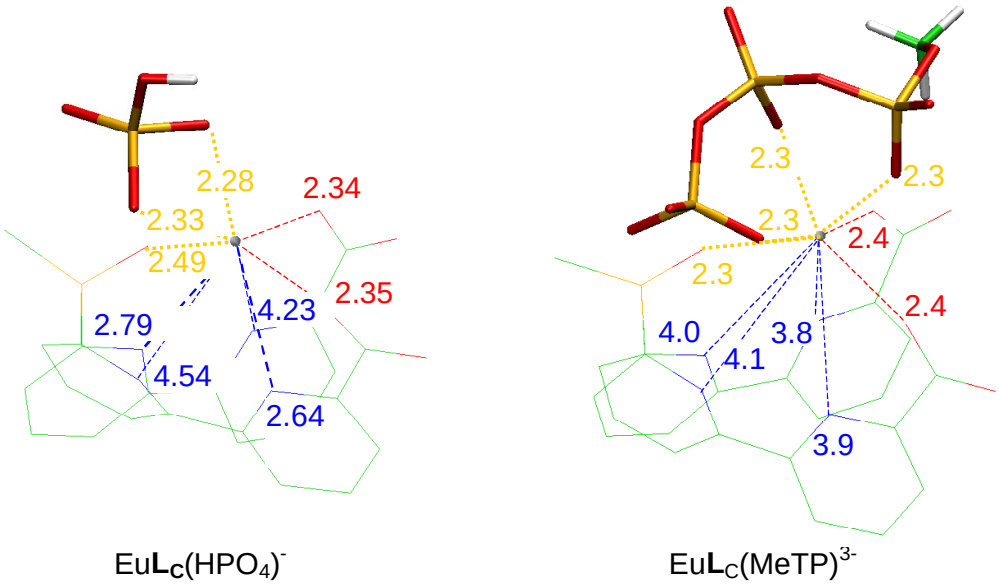


Figure S16 : Evolution of the normalized emission intensity of $[Eu\mathbf{L_C}]^{+}$ (λ_{exc} = 300 nm; λ_{em} = 615 nm for HPO_4^{2-}, 600 nm for the others with a 350 nm cut-off filter) as a function of added equivalents of anion in water, 0.01 M TRIS/HCl, pH = 7.0.



$Eu\mathbf{L_C}(HPO_4)^{-}$ $Eu\mathbf{L_C}(MeTP)^{3-}$

Figure S17 : Typical bond distances (in Å) in the modeled structure of $[Eu\mathbf{L_C}(HPO_4)]^{-}$ and $[Eu\mathbf{L_C}(MeTP)]^{3-}$ complexes.

Table T1 : Evolution of the europium based luminescence lifetime at varying concentration of added NO_3^- in water, 0.01 M TRIS/HCl, pH = 7.0.

equiv. NO_3^-	0	1	2	3	4	5	6	7
Luminescence lifetimes (μs)	743	767	742	792	778	756	748	760

Table T2 : Evolution of the europium based luminescence lifetime at varying concentration of added ADP^{3-} in water, 0.01 M TRIS/HCl, pH = 7.0.

equiv. ADP^{3-}	0	1	2	3	4	5	6	7
Luminescence lifetimes (μs)	808	944	1009	1019	1045	1017	1086	1075

Table T3 : Evolution of the europium based luminescence lifetime at varying concentration of added ATP^{4-} in water, 0.01 M TRIS/HCl, pH = 7.0.

equiv. ATP^{4-}	0	1	2	3	4	5	6	7
Luminescence lifetimes (μs)	739	976	931	1014	1003	1069	1007	1001

Table T4 : Evolution of the europium based luminescence lifetime at varying concentration of added HPO_4^{2-} in water, 0.01 M TRIS/HCl, pH = 7.0.

equiv. HPO_4^{2-}	0	1	2	3	4	5	6	7
Luminescence lifetimes (μs)	780	818	840	865	815	886	865	839

In all cases, luminescence lifetimes were fitted according to single mono-exponential functions.