Supplementary information

Complexes of divalent europium with dotp and dotpph

Przemysław Starynowicz

Table S1. Na-O distances (Å) in **eudotp**.

Na1—O11^{i}	2.317 (3)	Na4—O31^{vii}	2.379 (3)
Na1—O21^{i}	2.399 (3)	Na4—O32	2.286 (3)
Na1—O23	2.335 (3)	Na4—O43^{vii}	2.309 (3)
Na1—OW1^{i}	2.545 (3)	Na4—OW13^{vii}	2.341 (3)
Na1—OW8^{i}	2.371 (3)	Na5—O21	2.405 (3)
Na1—OW3	2.562 (3)	Na5—O23^{i}	2.419 (3)
Na2—OW9^{ii}	2.351 (3)	Na5—O32	2.673 (3)
Na2—OW4	2.359 (3)	Na5—OW1	2.418 (3)
Na2—OW5	2.410 (3)	Na5—OW8^{i}	2.303 (3)
Na2—OW4^{iii}	2.421 (3)	Na5—OW13^{vii}	2.318 (3)
Na2—OW6^{iv}	2.477 (3)	Na6—O11	2.483 (3)
Na2—OW11	2.579 (3)	Na6—O41	2.288 (3)
Na3—OW7^{v}	2.376 (3)	Na6—OW1	2.702 (3)
Na3—OW14	2.393 (3)	Na6—OW2^{viii}	2.399 (3)
Na3—OW17^{vi}	2.394 (4)	Na6—OW3^{i}	2.495 (3)
Na3—OW3^{iv}	2.470 (3)	Na6—OW14^{vii}	2.612 (3)
Na3—OW10	2.496 (3)		
Na3—OW2^{v}	2.500 (3)		

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) *x*−1, *y*+1, *z*; (iii) −*x*−1, −*y*+1, −*z*+1; (iv) *x*−1, *y*, *z*; (v) *x*, *y*−1, *z*; (vi) −*x*+1, −*y*, −*z*; (vii) −*x*, −*y*, −*z*+1; (viii) −*x*, −*y*+1, −*z*+1.

Table S2. Eu1-N,O distances (Å).

Eu1—O21	2.39 (3)
Eu1—O11	2.425 (10)
Eu1—N2	2.65 (2)
Eu1—N1	2.671 (15)
Eu1—O31	2.695 (18)
Eu1—O41	2.89 (3)
Eu1—N3	2.982 (19)
Eu1—N4	3.07 (2)

Table S3. Hydrogen bonds in **eudotp** (please note that OW20 and OW21 atoms are disordered).

H-bond	D-H (Å)	H···A (Å)	D···A (Å)	∠(DHA) (°)
OW1-H1W1···O33^{i}	0.86	2.25	3.086(4)	162
OW1-H2W1···O31	0.86	1.82	2.664(5)	168
OW2-H1W2···O42	0.86	2.10	2.930(5)	163
OW2···O13			2.739(4)	
OW3-H1W3···OW5^{ii}	0.86	1.88	2.733(5)	172
OW3-H1W3···O22	0.86	1.96	2.808(4)	167
OW4-H1W4···O12^{iii}	0.86	1,94	2.794(5)	171
OW4-H2W4···O43	0.86	1.84	2.691(4)	170
OW5-H1W5···O42	0.86	1.89	2.744(4)	171
OW5-H2W5···O13^{iv}	0.86	1.88	2.741(4)	179
OW6-H1W6···O43^{iv}	0.75	2.07	2.809(4)	166
OW6-H2W6···O13^{iv}	0.78	1.99	2.773(5)	175
OW7-H1W7···O42	0.86	1.92	2.754(4)	163
OW7-H2W7···OW19	0.86	1.94	2.756(6)	157
OW8-H1W8···O12	0.86	2.02	2.871(4)	170
OW8-H2W8···OW9^{v}	0.86	2.08	2.889(5)	156
OW9-H1W8···O32	0.86	1.85	2.707(3)	173
OW9-H2W9···O22	0.86	1.88	2.732(5)	177
OW10-H1W0···O23^{vi}	0.86	2.39	2.941(4)	123
OW10···O33			2.812(7)	
OW11-H1WA···OW15^{vii}	0.86	2.08	2.895(6)	158
OW11-H2WA···O42	0.86	2.05	2.893(4)	167
OW12-H1WB···OW11^{viii}	0.86	1.89	2.736(7)	167
OW12-H2WB···O12^{v}	0.86	1.98	2.837(4)	170
OW13···O33			2.694(4)	
OW14-H1WD···O33	0.86	1.96	2.778(5)	159
OW14-H2WD···OW6^{ix}	0.86	1.93	2.787(4)	174
OW15-H1WE···O22	0.86	1.82	2.680(5)	176
OW15-H2WE···OW7^{ii}	0.86	1.92	2.757(5)	164
OW16-H1WF···OW12^{x}	0.86	2.01	2.777(4)	149
OW17-H1WG···O16	0.86	1.97	2.782(6)	160
OW17···OW20			2.859(7)	
OW17···OW20			2.710(15)	
OW18-H1WH···O12	0.86	1.96	2.800(4)	164
OW18-H2WH···OW13^{viii}	0.86	1.95	2.763(5)	158
OW19···OW18^{x}			2.828(8)	
OW19···OW21^{x}			2.492(15)	
OW20···OW10^{viii}			2.999(10)	
OW20···OW15			2.908(9)	
OW21···OW10^{viii}			2.632(12)	
OW21···OW20^{xi}			2.613(13)	

Symmetry codes: (i) -x, -y, -z+1; (ii) x+1, y-1, z; (iii) x-1, y, z; (iv) -x, -y+1, -z+1; (v) -x+1, -y, -z+1; (vi) x-1, y, z; (vii) x-1, y+1, z; (viii) x+1, y, z; (ix) x, y-1, z; (x) -x+1, -y+1, -z; (xi) -x+2, -y, -z.

Table S4. Hydrogen bonds and C-H···π contacts in **eudotpph**.

H-bond	D-H (Å)	H···A (Å)	D···A (Å)	∠(DHA) (°)

OW1-H1W1···O32	0.82	1.94	2.755(4)	172
OW1-H2W1···O42	0.77	2.02	2.785(4)	170
OW2-H1W2···O22	0.85	1.92	2.764(4)	171
OW2-H2W2···O12	0.97	1.78	2.743(4)	173
N51-H51A···O42^{i}	0.86	2.07	2.833(4)	147
N51-H51B···OW2^{ii}	0.86	2.08	2.866(4)	151
N52-H52A···O21	0.86	2.10	2.925(4)	159
N52-H52B···OW2^{ii}	0.86	2.21	2.958(4)	146
N53-H53A···O31	0.86	1.95	2.796(4)	169
N53-H53B··· O42^{i}	0.86	2.19	2.930(4)	143
N61-H61A···OW1^{i}	0.86	1.98	2.804(4)	161
N61-H61B···O22^{ii}	0.86	2.19	2.932(4)	144
N62-H62B···O22^{ii}	0.86	2.13	2.897(4)	147
N63-H63A···O11	0.86	2.13	2.925(4)	153
C43-H43···X1^{iii}*	0.93	2.68	3.61	175
C23-H23···X3^{iv}**	0.93	2.58	3.50	171

Symmetry codes: (i) –x+3/2, y-1/2, -z+1/2; (ii) –x+1/2, y-1/2, -z+1/2; (iii) –x+1, -y, -z+1; (iv) –x+1, -y, -z.

* X1 – geometric centre of the ring formed by C11 through C16 atoms;

** X3 – geometric centre of the ring formed by C31 through C36 atoms.

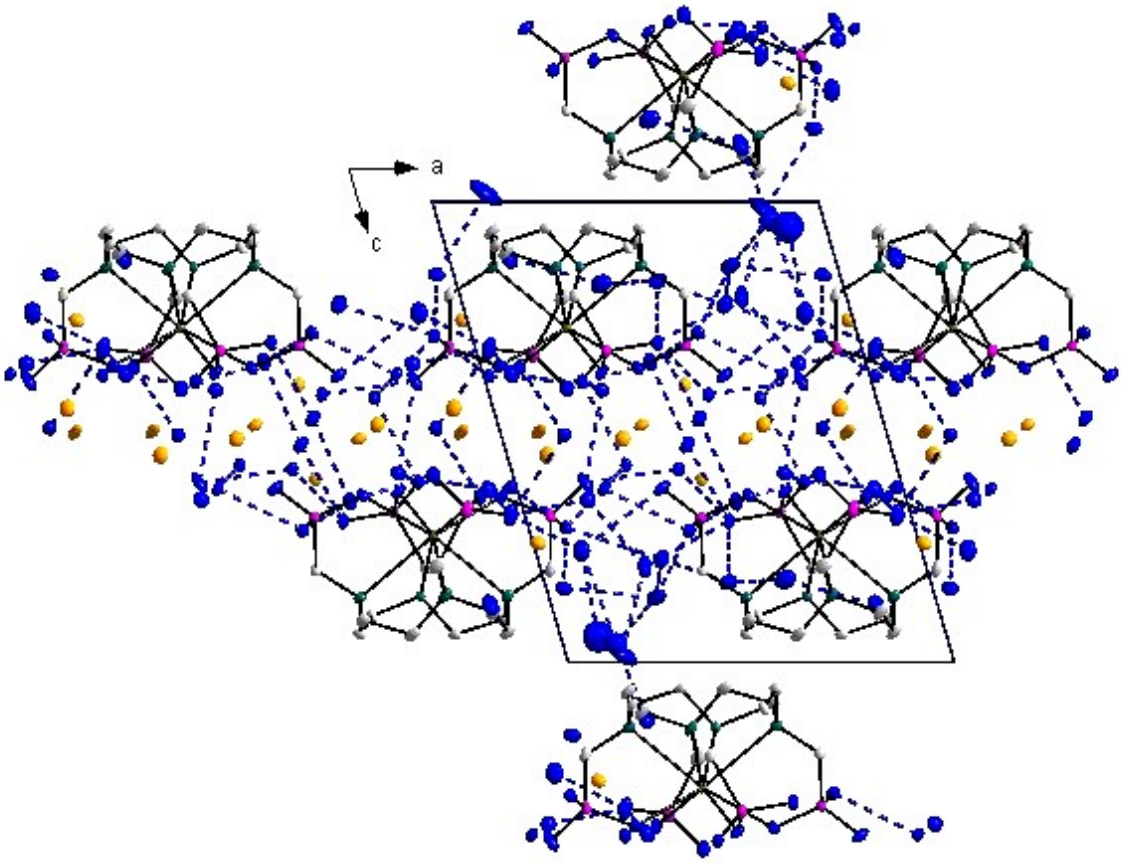

Fig. S1. Packing diagram of **eudotp**. The H atoms and Na-O bonds have been removed for clarity. The Na cations are yellow and the hydrogen bonds are shown with blue dashed lines.

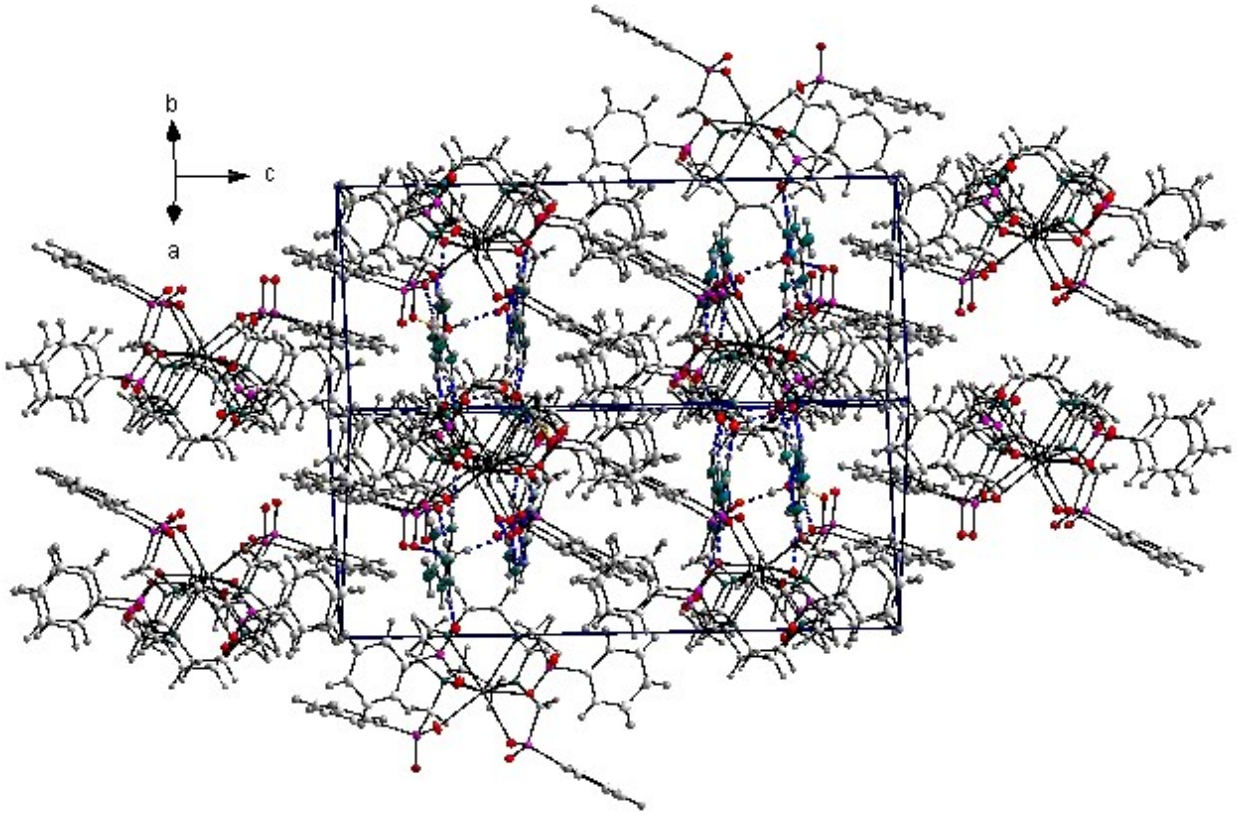

Fig. S2. Packing diagram of **eudotpph**. The Eu1 atoms have been removed for clarity; the hydrogen bonds are blue dashed.

Table S5. Results of the fitting of the polarographic curves. The current was fitted according the following relation:

$$i = \frac{i_{d(1)}}{\left(1+\exp\left[\frac{n\alpha F}{0.9163RT}(E-E_{1/2}^{(1)}\right]\right)} + i_0(+\frac{i_{d(2)}}{\left(1+\exp\left[\frac{n\alpha F}{0.9163RT}(E-E_{1/2}^{(2)}\right]\right)}),$$

where $i_{d(m)}$ and $E_{1/2}^{(m)}$ are the diffusion current and the half-wave potential of the m-th wave, i_0 is the initial residual current and other symbols are conventional or explained in the main text.

complex	pH	$E_{1/2}$	$n\alpha$
eudotp	7.15	-1.394(1)	0.608(11)
	8.47	-1.413(1)	0.555(14)
	10.08	-1.411(1)	0.498(37)
	11.83	-1.410(1)	0.504(10)
eudotpph	6.63	-1.196*)	0.395(9)
		-1.388(3)	0.337(11)
	10.80	-1.196(3)	0.434(14)
		-1.418(3)	0.463((16)

*) This parameter was taken from the fit for pH=10.80 and fixed

Relations between the Eu-O and Eu-N distances in **eudotp** and **eudotph** (taken jointly) and bond degrees and delocalization indices:

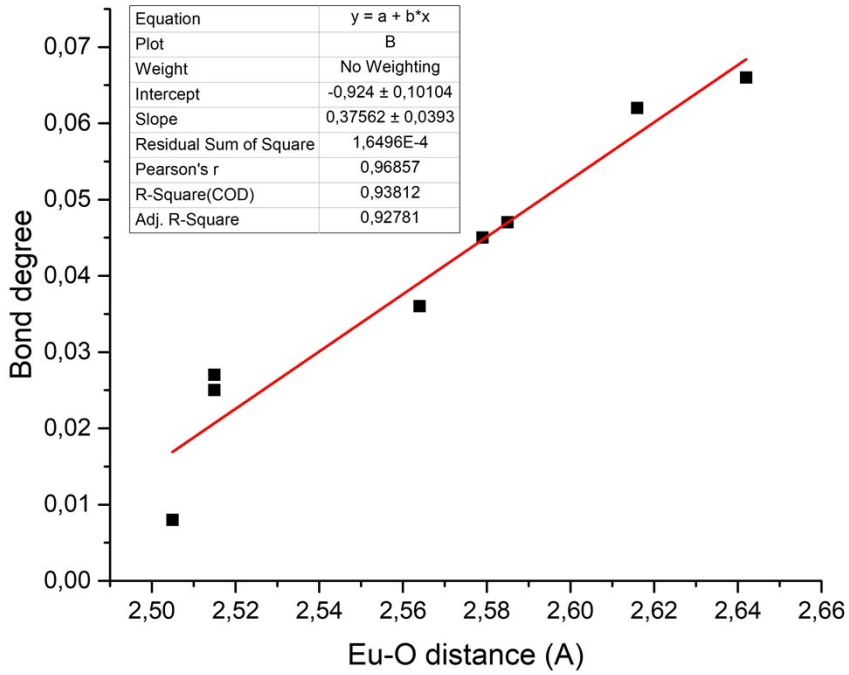

Fig. S3. Bond degree of the Eu-O bonds as a function of the Eu-O distance. The red line represents the least-squares fitted linear function.

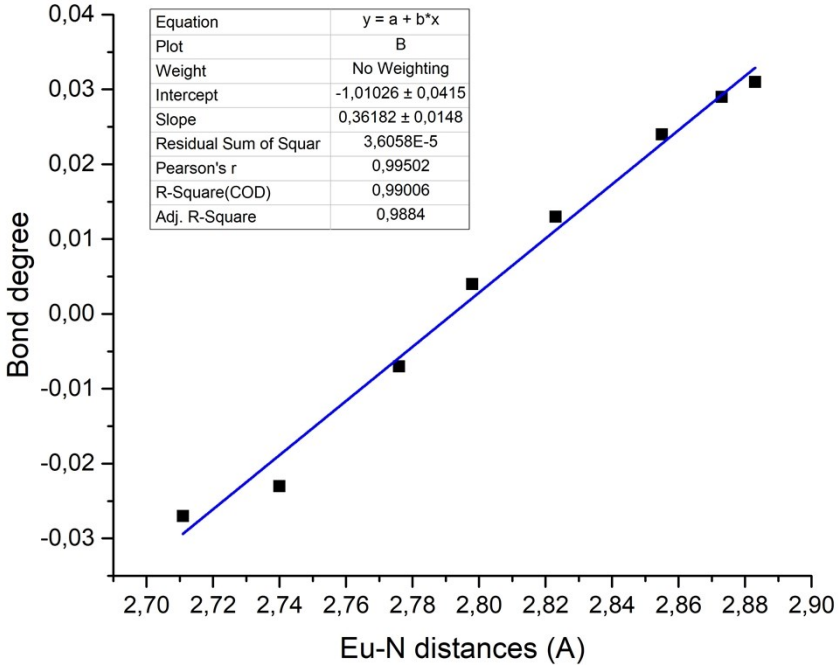

Fig. S4. Bond degree of the Eu-N bonds as a function of the Eu-N distance. The blue line represents the least-squares fitted linear function.

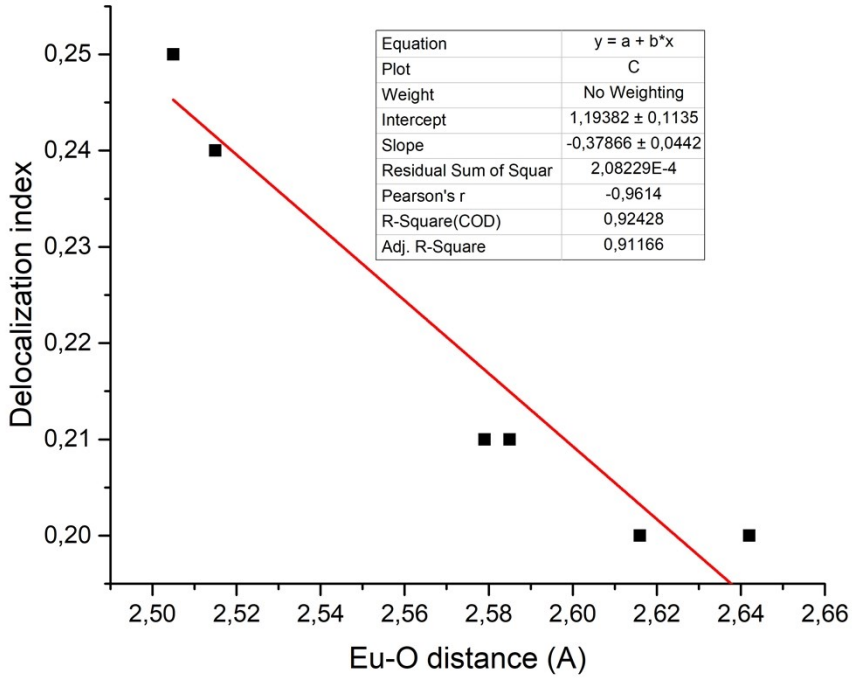

Fig. S5. Delocalization index of the Eu-O bonds as a function of the Eu-O distance. The red line represents the least-squares fitted linear function.

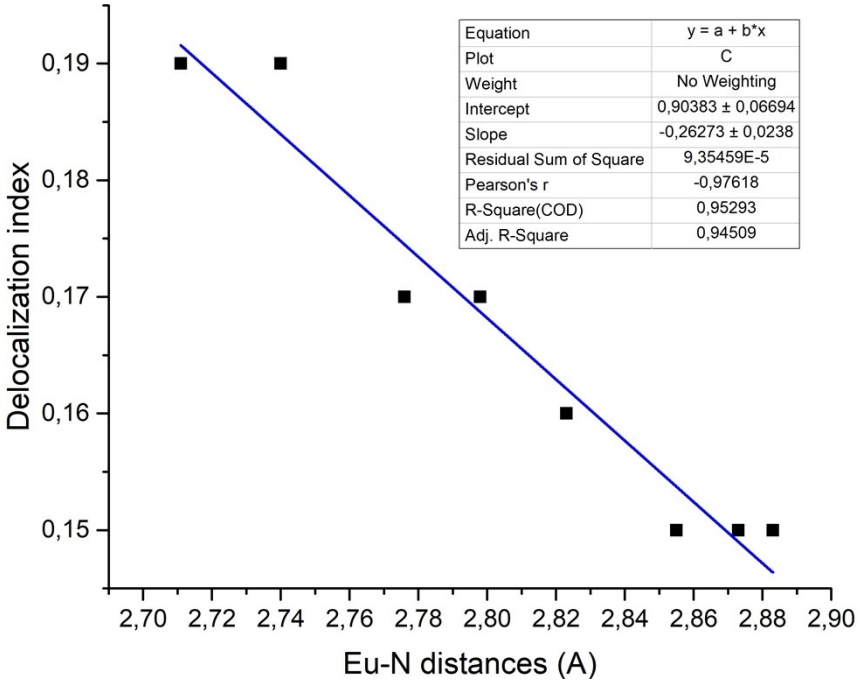

Fig. S6. Delocalization index of the Eu-N bonds as a function of the Eu-N distance. The blue line represents the least-squares fitted linear function.

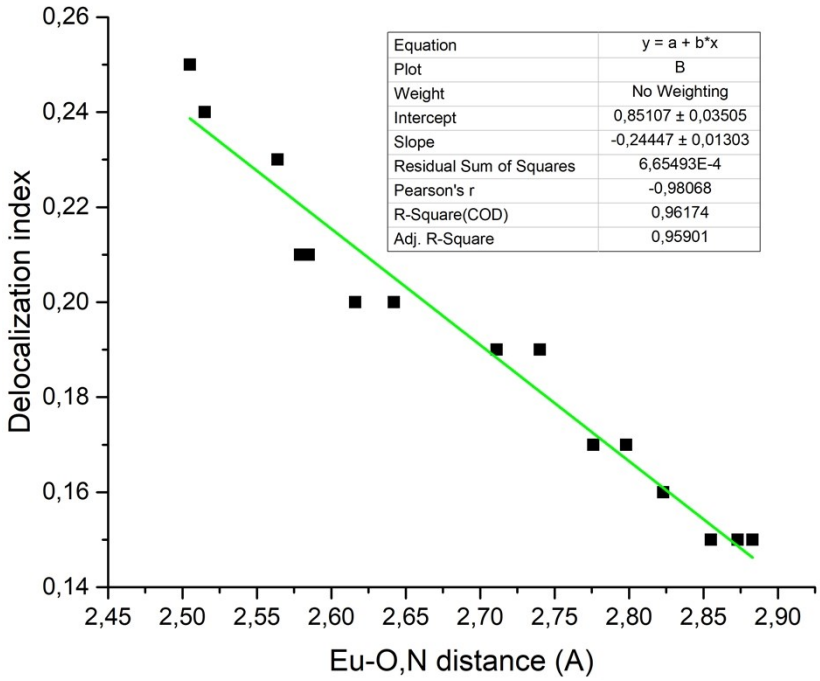

Fig. S7. Delocalization index of all the Eu-O and Eu-N bonds as a function of the Eu-ligand distance. The green line represents the least-squares fitted linear function.

Table S6. Bader charges (Q_B) for Eu, coordinated atoms and those constituting the phosphonate or phosphinate groups. The phenyl groups are given their sum charges; each such group is attached to the P atom listed above the respective group.

eudotp		**eudotpph**	
atom	Q_B	atom	Q_B
Eu	1.66	Eu	1.66
P1	3.40	P1	3.08
O11	-1.55	O11	-1.50
O12	-1.49	O12	-1.50
O13	-1.47	phen	-0.50
P2	3.42	P2	3.09
O21	-1.55	O21	-1.51
O22	-1.49	O22	-1.50
O23	-1.53	phen	-0.50
P3	3.39	P3	3.11
O31	-1.52	O31	-1.50
O32	-1.52	O32	-1.50
O33	-1.50	phen	-0.51
P4	3.41	P4	3.12
O41	-1.54	O41	-1.51
O42	-1.49	O42	-1.51
O43	-1.49	phen	-0.48
N1	-0.90	N1	-0.89
N2	-0.90	N2	-0.90
N3	-0.89	N3	-0.89
N4	-0.90	N4	-0.89

Table S7. NLM lone spinorbitals (lsp) of the coordinating O and N atoms – hybridization, admixture amount (in %) of Eu empty spinorbitals and the admixture composition.

atom	lsp1			lsp2			lsp2		
	hybridization	admixture	composition	hybridization	admixture	composition	hybridization	admixture	composition
eudotp									
spin α									
O11	$sp^{0.66}$	1.91	$sd^{2.06}$	p	0.57	d	p	0.75	d
O21	$sp^{0.65}$	1.86	$sd^{2.38}$	p	0.46	d	p	0.64	d
O31	$sp^{0.84}$	1.54	$sd^{2.85}$	p	0.48	d	p	0.64	$sd^{5.68}$
O41	$sp^{0.63}$	1.88	$sd^{2.51}$	p	0.55	d	p	0.69	d
N1	$sp^{4.10}$	2.07	$sd^{4.30}$						
N2	$sp^{4.01}$	1.95	$sd^{3.50}$						
N3	$sp^{4.13}$	1.83	$sd^{4.65}$						
N4	$sp^{4.14}$	2.14	$sd^{3.59}$						
spin β									
O11	$sp^{0.66}$	2.19	$sd^{2.17}f^{0.86}$	p	0.77	$df^{0.62}$	p	0.92	$df^{0.51}$
O21	$sp^{0.66}$	2.15	$sd^{2.21}f^{0.73}$	p	0.60	$df^{0.58}$	p	0.79	df^{038}
O31	$sp^{0.83}$	1.81	$sd^{2.79}f^{0.92}$	p	0.61	df^{072}	$sp^{9.52}$	0.83	$sd^{5.89}f^{3.07}$
O41	$sp^{0.64}$	2.17	$sd^{2.34}f^{0.73}$	p	0.67	$df^{0.64}$	p	0.92	$df^{0.46}$
N1	$sp^{4.06}$	2.33	$sd^{3.64}f^{1.39}$						
N2	$sp^{4.00}$	2.18	$sd^{3.16}f^{1.20}$						
N3	$sp^{4.09}$	2.19	$sd^{3.83}f^{1.70}$						
N4	$sp^{4.11}$	2.33	$sd^{3.25}f^{1.19}$						
eudotpph									
spin α									
O11	$sp^{0.60}$	1.35	$sd^{2.40}$	p	0.52	d	p	0.58	d
O21	$sp^{0.62}$	1.28	$sd^{2.54}$	p	0.51	d	p	0.52	d
O31	$sp^{0.59}$	1.51	$sd^{2.66}$	p	0.45	d	p	0.53	d
O41	$sp^{0.58}$	1.57	$sd^{3.00}$	p	0.60	d	p	0.58	d
N1	$sp^{3.94}$	1.49	$sd^{4.42}$						
N2	$sp^{4.04}$	1.56	$sd^{4.03}$						
N3	$sp^{3.91}$	1.53	$sd^{3.97}$						
N4	$sp^{4.03}$	1.66	$sd^{3.71}$						
spin β									
O11	$sp^{0.59}$	1.56	$sd^{2.44}f^{0.88}$	p	0.62	$df^{0.43}$	p	0.68	$df^{0.42}$
O21	$sp^{0.63}$	1.48	$sd^{2.46}f^{0.99}$	p	0.62	$df^{0.45}$	p	0.60	$df^{0.41}$
O31	$sp^{0.59}$	1.67	$sd^{2.66}f^{0.62}$	p	0.51	$df^{0.42}$	p	0.61	$df^{0.32}$
O41	$sp^{0.58}$	1.74	$sd^{2.94}f^{0.74}$	p	0.66	$df^{0.42}$	p	0.69	$df^{0.38}$
N1	$sp^{3.92}$	1.63	$sd^{3.81}f^{1.12}$						
N2	$sp^{3.97}$	1.68	$sd^{3.74}f^{1.00}$						
N3	$sp^{3.88}$	1.68	$sd^{3.54}f^{1.09}$						
N4	$sp^{3.97}$	1.75	$sd^{3.45}f^{0.91}$						

Theoretical analysis of isolated Eu^{2+} cation

The results presented below were obtained with ADF, version 2019, using Hartree-Fock approach or CAMY-B3LYP functional. The base used was QZ4P (quadruple ζ, four polarization functions), relativity was included as scalar ZORA with predefined spin polarization (35 α electrons and 28 β ones). Fig. S6 presents the calculated levels in the HOMO-LUMO region.

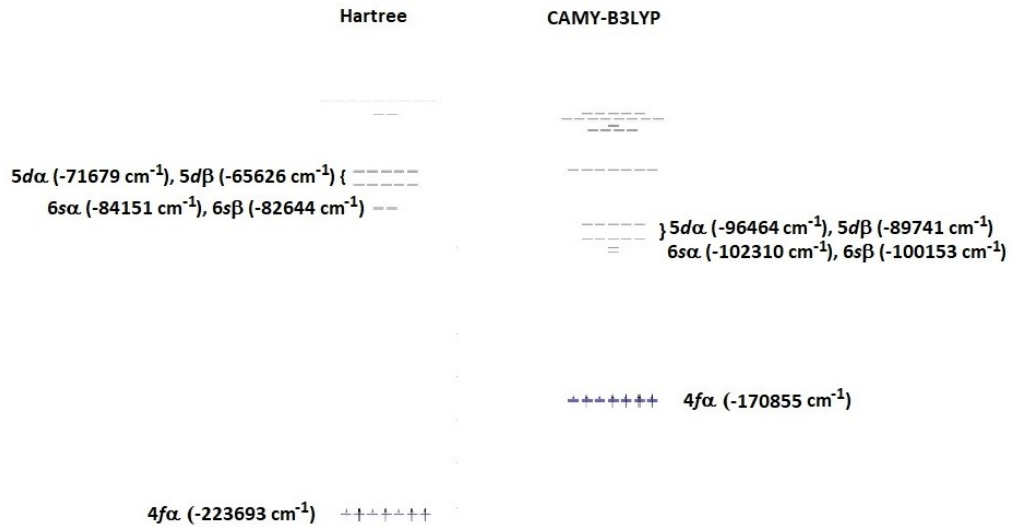

Fig. S8. Energies of selected orbitals calculated with Hartree-Fock and CAMY-B3LYP DFT approaches. The respective spins are labelled with α and β. The functions denoted as 5*d* were in fact combinations of 5*d* and 6*d*; the admixture of the latter ranged from 15% (CAMY-B3LYP) to 50 % (Hartree-Fock).

It may be noticed that the 6*s* level is located slightly below the 5*d* ones in both approaches. Fig. S7 shows energies of calculated transitions. For the need of discussion the 4*f*→6*s* and 4*f*→7*s* transitions are marked with asterisks. The Hartree-Fock results show that the 4*f*→6*s* transition is located above (that is, has higher energy) the lowest 4*f*→5*d* ones; however the calculations based on CAMY-B3LYP functional yielded the reverse outcome. As a consequence of the spherical symmetry of the system the oscillator strengths are in majority null.

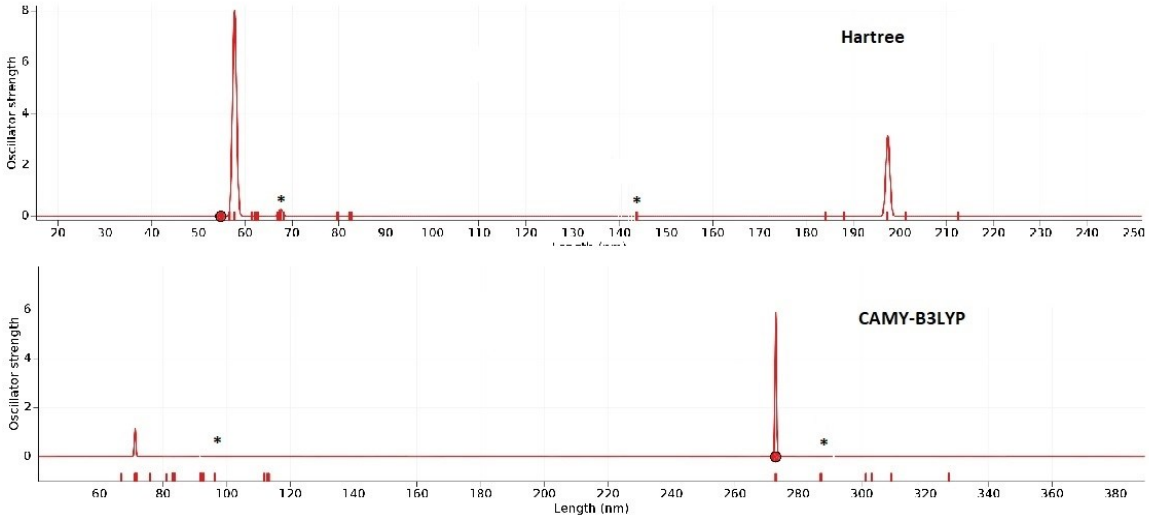

Fig. S9. Calculated spectra of Eu^{2+}. The *f*→*s* transitions are marked with asterisks.