Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Impact of the Lanthanide Contraction on the Activity of a Lanthanide-dependent Methanol Dehydrogenase – A Kinetic and DFT Study

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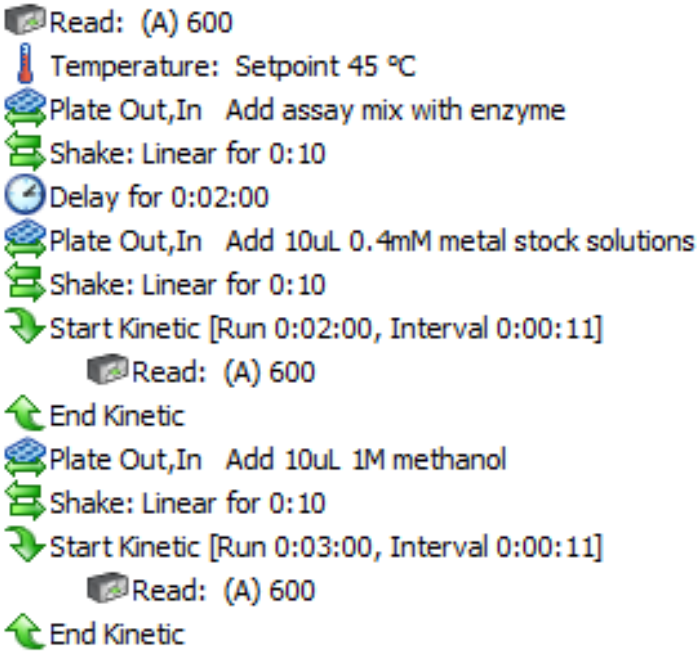

Figure S1 Typical procedure for the Epoch 2 plate-reader assay with Eu-MDH and different lanthanide ions. The plate type used was a 96 well plate. A path length correction was applied (Path length Correction: 977 / 900, Absorbance at 1 cm: 0.18)

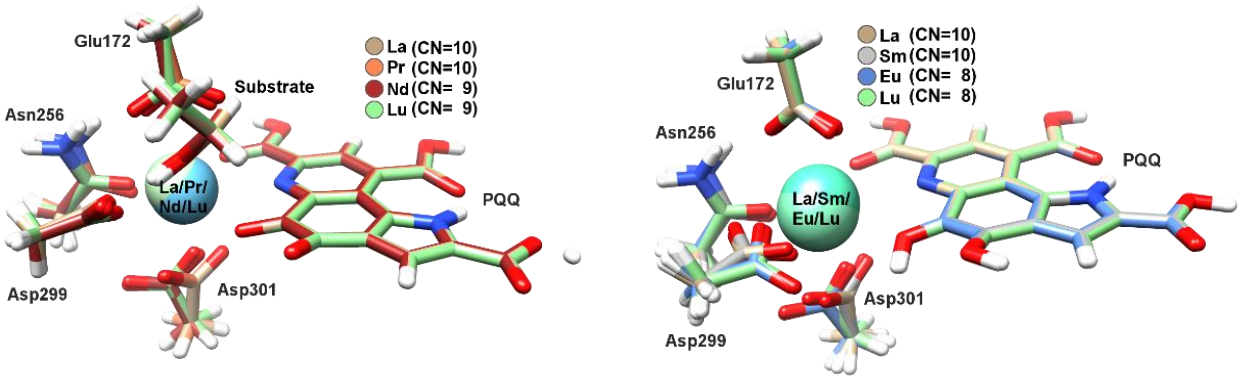

Figure S2 Left: Optimized Structures for the active center with PQQ^0, substrate and La (tan), Pr (light brown), Nd (brown) and Lu (green). **Right**: Optimized Structures for the active center with $PQQH_2$ and La (tan), Sm (grey), Eu (blue) and Lu (green) - Images generated with the UCSF Chimera package.[1] Structure optimizations were similar to a procedure described by Schelter *et al*.[2] and performed using Gaussian 09[3] and the B3LYP functional with the 6-31G(d) basis set for C, H, N, O.[4-9] Starting point was the crystal structure of the known Ce-MDH (PDB 4MAE).[10] The present amino acids in the active site were truncated and the terminal carbon atoms, as well as all of the PQQ-atoms were frozen, to mimic the sterics imposed by the protein. The present polyethylenglycol was truncated as well and used as a substrate-model. The cerium atom was then exchanged with every Ln in the series. Quasi relativistic effective core potentials (ECP) and segmented basis sets were used for the central metal: ECP-MWB46+4f^n.[11-13] Calculations were performed with 11 outer sphere electrons, as pseudo-singlets (f-electrons included in ECP) and restricted closed-shell calculations.[14] Calculations were conducted in the gas phase. For additional active site calculations, the truncated polyethylene glycol residue was manually removed, and/or the PQQ-quinone part was manually converted to the quinol. For simplification, the added quinol protons were frozen as well in their position. In case of Gd, the Harris functional was not able to form the initial guess, therefore the core Hamiltonian was used instead, using "guess=(core,always)". None of the calculations showed negative frequencies.

Figure S3 Example input for Gaussian optimizations (in this case La^{3+} PQQ with substrate). -1 denotes a frozen carbon atom.

```
%chk=57-LaIII-PQQ-with-Substrate.chk
%mem=64GB
%nprocshared=4
#p opt freq rb3lyp/gen geom=connectivity 5d 7f
pseudo=read

La(III) - PQQ – with substrate

0 1
C          -1   -4.90400000    3.34400000    3.52500000
C           0   -4.43100000    2.75000000    2.21200000
O           0   -5.31600000    2.48300000    1.32700000
O           0   -3.21300000    2.47700000    2.02300000
C          -1   -7.59200000    1.55900000   -2.75400000
C           0   -6.78400000    1.98800000   -1.55100000
O           0   -5.53400000    1.90100000   -1.57100000
N           0   -7.44100000    2.47100000   -0.49176943
C          -1   -7.57000000   -2.04200000    0.45144469
C           0   -6.14900000   -1.61500000    0.75161945
O           0   -5.81500000   -0.46701986    0.29292243
O           0   -5.39000000   -2.35900000    1.42100000
C          -1   -3.16200000   -0.96440872   -4.27600000
C           0   -3.96500000   -0.84870079   -2.97500000
O           0   -5.10800000   -1.31100000   -2.91900000
O           0   -3.34000000   -0.27056742   -1.98200000
N          -1    3.33000000   -0.81662988    1.47900000
C          -1    3.61300000   -2.05900000    1.97300000
C          -1    5.01500000   -2.49400000    2.20800000
O          -1    5.88200000   -1.54200000    1.91200000
O          -1    5.26800000   -3.61500000    2.62500000
C          -1    2.41800000   -2.74800000    2.13600000
C          -1    1.39400000   -1.87800000    1.71500000
C          -1    1.99200000   -0.65850047    1.29400000
C          -1   -0.03196565   -2.09600000    1.68300000
O          -1   -0.65585683   -3.02200000    2.17600000
C          -1   -0.80639866   -0.98447544    0.95671480
O          -1   -1.97200000   -1.16300000    0.63270177
C          -1   -0.13660882    0.31747211    0.63836618
N          -1   -0.97622754    1.23100000    0.17358237
C          -1   -0.50347008    2.43600000   -0.15877326
C          -1   -1.51600000    3.38500000   -0.69429278
O          -1   -2.68200000    3.07700000   -0.90161786
O          -1   -1.02900000    4.60100000   -0.94685640
C          -1    0.84871874    2.74100000   -0.04652754
C          -1    1.77100000    1.78600000    0.39850560
C          -1    3.21000000    2.20900000    0.35976671
O          -1    3.37200000    3.51000000    0.13590368
O          -1    4.17700000    1.46400000    0.47970217
```

C	-1	1.28200000	0.49657896	0.78449450
O	0	-3.93300000	-0.32848794	2.35300000
C	0	-3.16200000	-0.45069210	3.55200000
C	-1	-4.04600000	-0.73580415	4.76200000
H	0	-7.34200000	2.20600000	-3.60200000
H	0	-7.28400000	0.54246200	-3.01600000
H	0	-8.67000000	1.59400000	-2.58300000
H	0	-7.70800000	-2.10900000	-0.63361256
H	0	-7.80300000	-3.00600000	0.90925659
H	0	-8.26700000	-1.28200000	0.82000108
H	0	-5.67800000	4.09600000	3.34900000
H	0	-5.35100000	2.54500000	4.12900000
H	0	-4.07300000	3.78100000	4.08500000
H	0	-4.78000000	0.06458975	4.90600000
H	0	-4.58800000	-1.67900000	4.63500000
H	0	-3.43600000	-0.81454479	5.67000000
H	0	-2.63900000	0.50250317	3.66600000
H	0	-2.41400000	-1.24600000	3.43300000
H	0	-2.74100000	0.00689772	-4.55900000
H	0	-2.32100000	-1.65000000	-4.12400000
H	0	-3.79400000	-1.34200000	-5.08200000
H	-1	4.34900000	3.70100000	-0.00827955
H	-1	1.19100000	3.72400000	-0.32958075
H	-1	6.90200000	-1.87400000	1.98800000
H	-1	-1.75500000	5.14900000	-1.30300000
H	-1	4.02400000	-0.11676026	1.22800000
H	-1	2.30000000	-3.76900000	2.46200000
H	0	-8.45000000	2.47400000	-0.46268410
H	0	-6.90800000	2.66300000	0.35974909
H	0	-4.37900000	-1.19400000	2.13400000
La	0	-3.90000000	0.86148825	0.01088327

1 2 1.0 50 1.0 51 1.0 52 1.0
2 3 1.5 4 1.5
3 70 1.0
4 70 1.0
5 6 1.0 44 1.0 45 1.0 46 1.0
6 7 2.0 8 1.5
7 70 1.0
8 67 1.0 68 1.0
9 10 1.0 47 1.0 48 1.0 49 1.0
10 11 1.5 12 1.5
11 70 1.0
12
13 14 1.0 58 1.0 59 1.0 60 1.0
14 15 1.5 16 1.5
15 70 1.0
16 70 1.0
17 18 1.5 24 1.5 65 1.0
18 19 1.0 22 1.5
19 20 1.5 21 2.0
20 63 1.0
21
22 23 1.5 66 1.0
23 24 1.5 25 1.5
24 40 1.0
25 26 2.0 27 1.0
26
27 28 2.0 29 1.0
28 70 1.0
29 30 1.5 40 1.5
30 31 1.5 70 1.0
31 32 1.0 35 1.5
32 33 2.0 34 1.5
33 70 1.0
34 64 1.0
35 36 1.5 62 1.0
36 37 1.0 40 1.5
37 38 1.5 39 2.0
38 61 1.0
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41 42 1.0 69 1.0 70 1.0
42 43 1.0 56 1.0 57 1.0
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C H N O 0
6-31G(d)
****
La 0
MWB46
****

La 0
MWB46

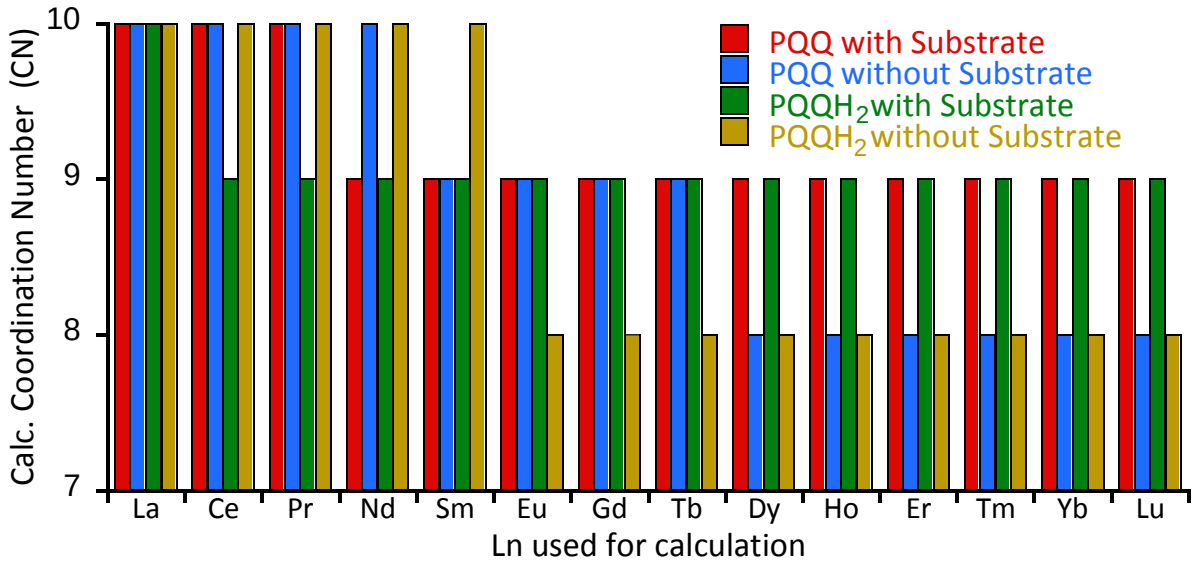

Figure S4 Calculated coordination numbers of the active site in MDH with oxidized (PQQ) or reduced ($PQQH_2$) cofactor with- and without substrate.

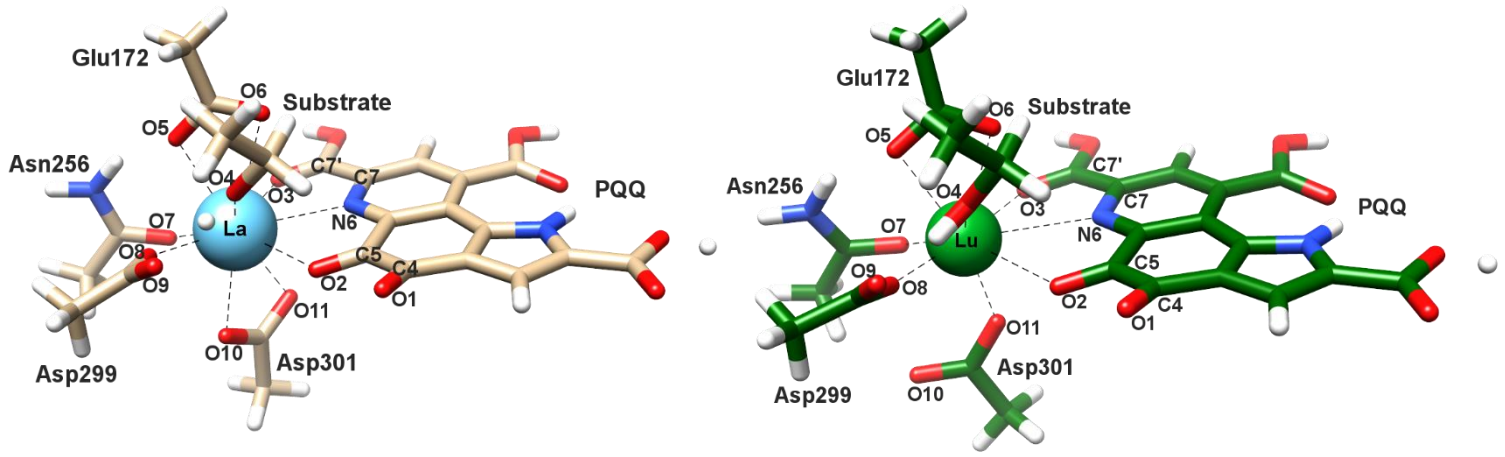

Table S1 Calculated bond lengths and angles of the structure optimizations for Ln^{3+} with PQQ^{0} and substrate as described in Figure S2. Example structures of the La^{3+} and Lu^{3+} calculations are given above.

PQQ + S	Distance Substr.-O-C5	Distance Substr.-O-M	Distance C5(O)-M	Distance N6-M	Distance C7'(CO_2)-M	Distance O10-M	Distance O11-M	Bond angle O10-M-O11	Binding mode (ASP301)	Binding mode (ASP299)	CN	Atomic number
La	3.41871	2.66856	2.77142	2.89968	2.70271	2.64509	2.69935	48.99033	bidentate	monodentate	10	57
Ce	3.41485	2.66337	2.76197	2.89762	2.70936	2.63128	2.69154	49.14706	bidentate	monodentate	10	58
Pr	3.41219	2.65857	2.75417	2.89826	2.71734	2.61729	2.68469	49.29969	bidentate	monodentate	10	59
Nd	3.41778	2.61171	2.8574	2.99031	2.73730	3.49774	2.37672	39.70468	monodentate	monodentate	9	60
Sm	3.41537	2.59286	2.86013	3.00451	2.75280	3.59349	2.34644	37.85292	monodentate	monodentate	9	62
Eu	3.41492	2.58683	2.8639	3.01475	2.76106	3.60815	2.33595	37.51399	monodentate	monodentate	9	63
Gd	3.41444	2.58184	2.8679	3.02469	2.76871	3.61594	2.32783	37.31441	monodentate	monodentate	9	64
Tb	3.41577	2.57695	2.87418	3.03645	2.77646	3.62958	2.31973	37.00105	monodentate	monodentate	9	65
Dy	3.41595	2.57284	2.88008	3.04880	2.78509	3.63383	2.3123	36.86735	monodentate	monodentate	9	66
Ho	3.41630	2.56955	2.88679	3.06206	2.79398	3.63696	2.30498	36.75500	monodentate	monodentate	9	67
Er	3.41718	2.5667	2.89434	3.07614	2.80304	3.63804	2.29817	36.68542	monodentate	monodentate	9	68
Tm	3.41814	2.56512	2.90226	3.08903	2.81036	3.63908	2.29201	36.62292	monodentate	monodentate	9	69
Yb	3.41893	2.56333	2.9108	3.10398	2.81956	3.63864	2.2857	36.58582	monodentate	monodentate	9	70
Lu	3.41938	2.56218	2.91864	3.11756	2.82784	3.63362	2.28047	36.64844	monodentate	monodentate	9	71

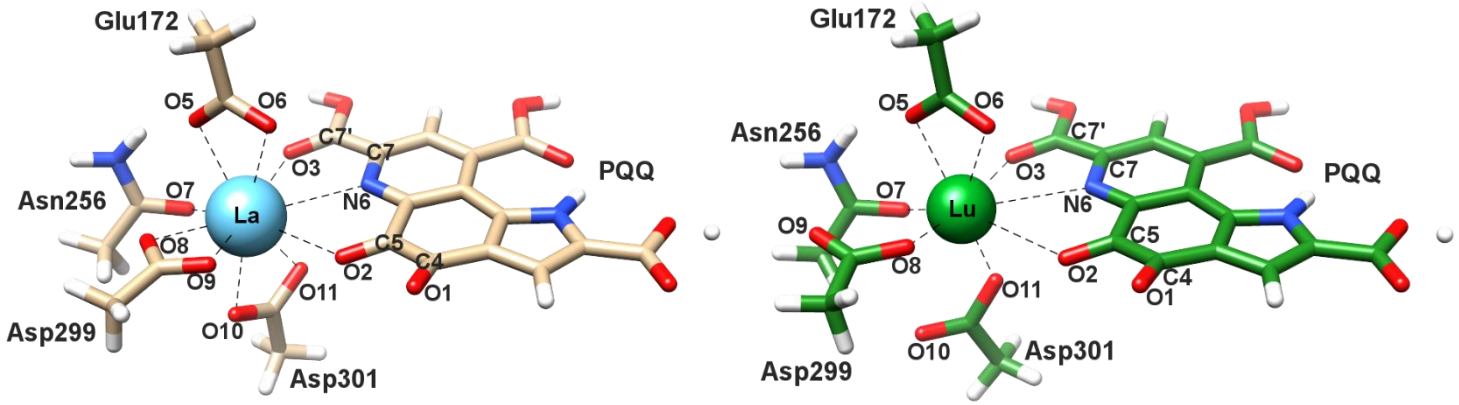

Table S2 Calculated bond lengths and angles of the structure optimizations for Ln^{3+} with PQQ^{0} and without substrate as described in Figure S2. Example structures of the La^{3+} and Lu^{3+} calculations are given above.

PQQ - S	Distance C5(O)-M	Distance N6-M	Distance C7'(CO_2)-M	Distance O10-M	Distance O11-M	Bond angle O10-M-O11	Binding mode (ASP301)	Binding mode (ASP299)	CN	Atomic number
La	2.96030	3.20725	2.86410	2.63074	2.59339	50.21016	bidentate	bidentate	10	57
Ce	2.97706	3.22575	2.86963	2.62193	2.57966	50.37921	bidentate	bidentate	10	58
Pr	2.99437	3.24509	2.87580	2.61454	2.56625	50.53544	bidentate	bidentate	10	59
Nd	3.01204	3.26478	2.88222	2.60951	2.5525	50.67674	bidentate	bidentate	10	60
Sm	2.89771	3.03707	2.71801	2.55847	2.5967	50.68474	bidentate	monodentate	9	62
Eu	2.90947	3.04857	2.71891	2.54712	2.59047	50.82384	bidentate	monodentate	9	63
Gd	2.91986	3.05875	2.71977	2.53707	2.58482	50.94776	bidentate	monodentate	9	64
Tb	2.93182	3.07068	2.72104	2.52512	2.57823	51.10283	bidentate	monodentate	9	65
Dy	3.10597	3.18576	2.69915	3.42002	2.29714	40.74210	monodentate	monodentate	8	66
Ho	3.12665	3.20178	2.69759	3.46268	2.2822	39.91409	monodentate	monodentate	8	67
Er	3.14994	3.22022	2.69600	3.48318	2.2708	39.48094	monodentate	monodentate	8	68
Tm	3.19116	3.24933	2.68576	3.42667	2.26154	40.50209	monodentate	monodentate	8	69
Yb	3.21140	3.26725	2.68713	3.44662	2.25019	40.08331	monodentate	monodentate	8	70
Lu	3.22792	3.2828	2.68946	3.45084	2.24257	39.96807	monodentate	monodentate	8	71

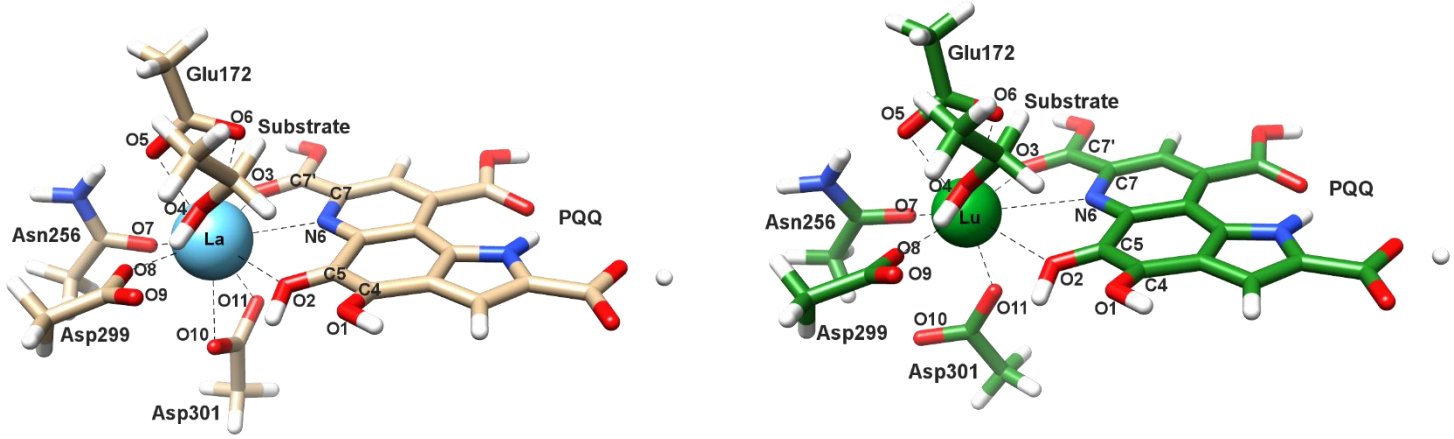

Table S3 Calculated bond lengths and angles of the structure optimizations for Ln^{3+} with reduced $PQQH_2$ and substrate as described in Figure S2. Example structures of the La^{3+} and Lu^{3+} calculations are given above.

$PQQH_2$ + S	Distance Substr.-O-C5	Distance Substr.-O-M	Distance C5(O)-M	Distance N6-M	Distance C7'(CO_2)-M	Distance O10-M	Distance O11-M	Bond angle O10-M-O11	Binding mode (ASP301)	Binding mode (ASP299)	CN	Atomic number
La	3.54092	2.70834	2.81254	2.86802	2.62451	2.71244	2.66632	48.64818	Bidentate	monodentate	10	57
Ce	3.54946	2.63521	2.91106	2.95102	2.64007	3.68944	2.40021	36.28487	Monodentate	monodentate	9	58
Pr	3.54064	2.63263	2.90953	2.95712	2.64814	3.69075	2.3828	36.19016	Monodentate	monodentate	9	59
Nd	3.5334	2.62958	2.91074	2.96688	2.65772	3.68653	2.36869	36.19823	Monodentate	monodentate	9	60
Sm	3.52661	2.62199	2.91926	2.98775	2.67306	3.69495	2.34789	35.9033	Monodentate	monodentate	9	62
Eu	3.52627	2.62008	2.92709	2.99971	2.67872	3.69484	2.33881	35.83736	Monodentate	monodentate	9	63
Gd	3.52663	2.61864	2.93476	3.01084	2.68363	3.69327	2.33143	35.81268	Monodentate	monodentate	9	64
Tb	3.52582	2.61692	2.94434	3.02416	2.68955	3.69751	2.32426	35.67653	Monodentate	monodentate	9	65
Dy	3.52649	2.61604	2.95369	3.03771	2.69576	3.69566	2.3173	35.65926	Monodentate	monodentate	9	66
Ho	3.52752	2.61594	2.96397	3.05224	2.70222	3.69367	2.31027	35.64429	Monodentate	monodentate	9	67
Er	3.52895	2.61629	2.97493	3.06762	2.70907	3.69064	2.30366	35.65323	Monodentate	monodentate	9	68
Tm	3.53062	2.61775	2.98598	3.08189	2.71457	3.68782	2.29767	35.66513	Monodentate	monodentate	9	69
Yb	3.53273	2.61924	2.99806	3.09834	2.72169	3.68425	2.29139	35.68734	Monodentate	monodentate	9	70
Lu	3.53428	2.62061	3.0085	3.11303	2.72844	3.67742	2.28598	35.78303	Monodentate	monodentate	9	71

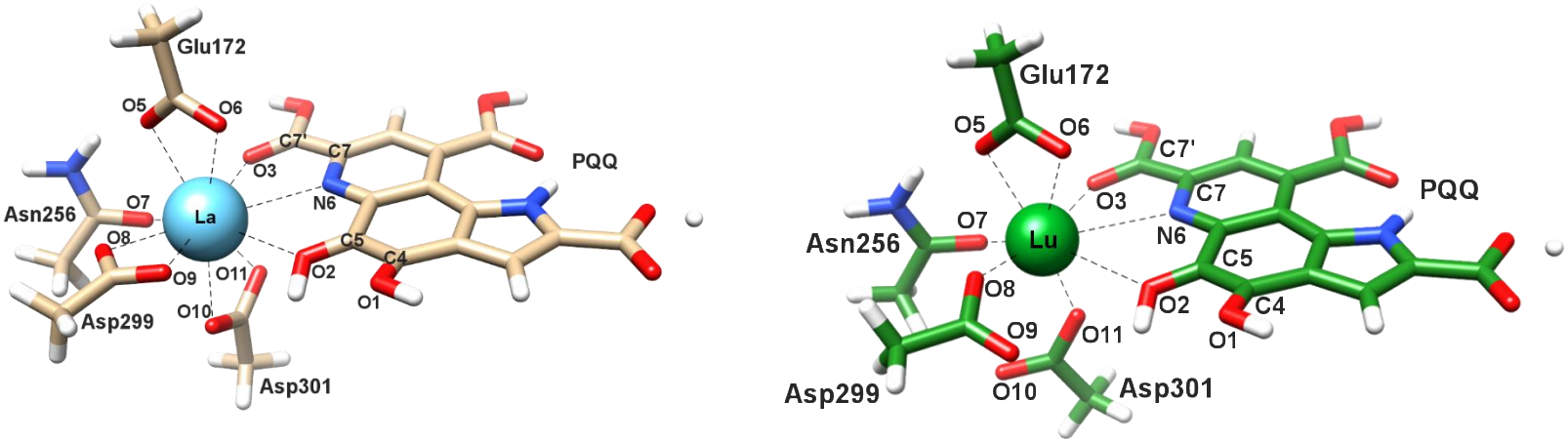

Table S4 Calculated bond lengths and angles of the structure optimizations for Ln^{3+} with reduced $PQQH_2$ and without substrate as described in Figure S2. Example structures of the La^{3+} and Lu^{3+} calculations are given above.

$PQQH_2$ - S	Distance C5(O)-M	Distance N6-M	Distance C7'(CO_2)-M	Distance O10-M	Distance O11-M	Bond angle O10-M-O11	Binding mode (ASP301)	Binding mode (ASP299)	CN	Atomic number
La	2.95742	3.13982	2.78158	2.63361	2.60395	50.02797	bidentate	bidentate	10	57
Ce	2.97215	3.15675	2.78697	2.62111	2.59302	50.20832	bidentate	bidentate	10	58
Pr	2.98586	3.17385	2.79371	2.61024	2.58227	50.37431	bidentate	bidentate	10	59
Nd	3.00095	3.19184	2.80022	2.6013	2.57175	50.52454	bidentate	bidentate	10	60
Sm	3.07479	3.2641	2.81502	2.63305	2.51598	50.66503	bidentate	bidentate	10	62
Eu	3.03114	3.09536	2.66574	3.4818	2.30303	39.60913	monodentate	monodentate	8	63
Gd	3.04624	3.10588	2.66276	3.52863	2.28762	38.66039	monodentate	monodentate	8	64
Tb	3.06665	3.12128	2.66008	3.56398	2.27436	37.90669	monodentate	monodentate	8	65
Dy	3.0875	3.13792	2.65814	3.57228	2.26438	37.68103	monodentate	monodentate	8	66
Ho	3.10862	3.15511	2.65662	3.57863	2.25469	37.49011	monodentate	monodentate	8	67
Er	3.12939	3.17266	2.65601	3.57974	2.24588	37.40832	monodentate	monodentate	8	68
Tm	3.14776	3.18799	2.65536	3.57983	2.23828	37.35706	monodentate	monodentate	8	69
Yb	3.16743	3.2055	2.65608	3.57884	2.2299	37.31814	monodentate	monodentate	8	70
Lu	3.18277	3.22011	2.6578	3.57202	2.22282	37.40757	monodentate	monodentate	8	71

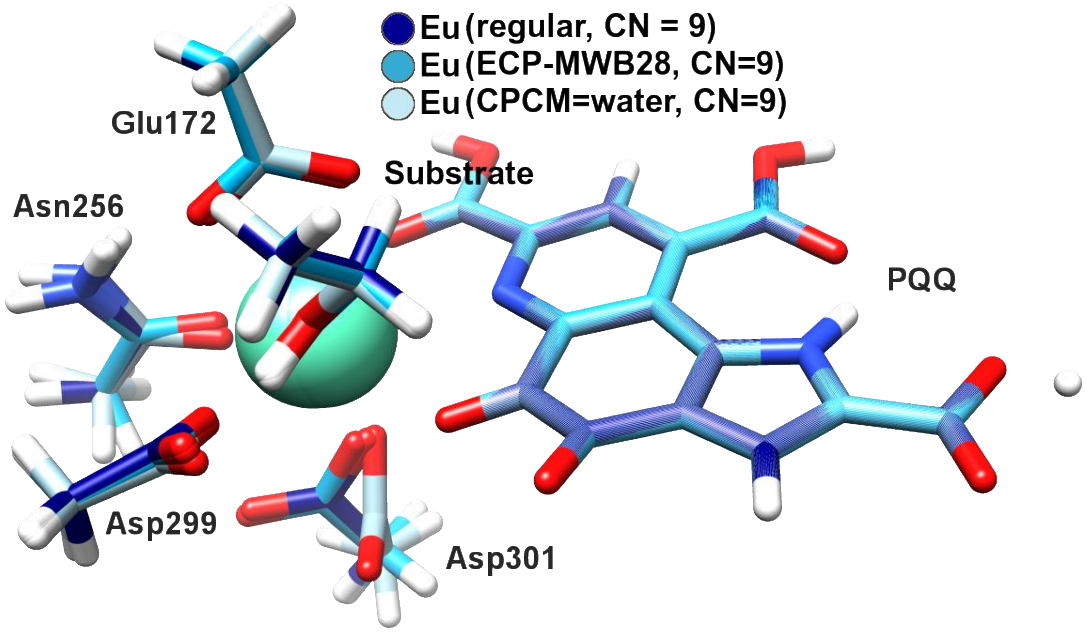

Figure S5 Optimized and superimposed structures for the active center with PQQ, substrate and Eu^{3+}. The regular calculation, as described in Figure S2-S3 is given in dark blue. An open shell calculation, using the smaller ECP-MWB28[11-13] and taking the f-electrons into account is given in blue and a calculation, taking solvent effects into account, by using the CPCM method with water, is given in light blue. Input commands for the calculations are given below. The structures received from the calculations only differ slightly, with an exception of Asp301, which is tilted away under the influence of the solvent model (light blue). Since all calculations show the same coordination number – the property of interest - the simplified, "regular" calculations described above were used for every Ln and active site configuration. None of the calculations showed negative frequencies.

Figure S6 Example inputs of the calculations described in Figure S2. **Left**: Open shell calculation, using the smaller ECP-MWB28. **Right**: Closed-shell calculation, considering solvent effects by the use of CPCM with water.

Eu (ECP-MWB28)

#p opt freq ub3lyp/gen geom=connectivity
5d 7f pseudo=read

0 7

Atomic coordinates and
geometry specifications as in Figure S3

C H N O 0
6-31G(d)
****
Eu 0
MWB28
****

Eu 0
MWB28

Eu (CPCM=water)

#p opt freq rb3lyp/gen scrf=(cpcm,solvent=water)
geom=connectivity 5d 7f pseudo=read

0 1

Atomic coordinates and
geometry specifications as in Figure S3

C H N O 0
6-31G(d)
****
Eu 0
MWB52
****

Eu 0
MWB52

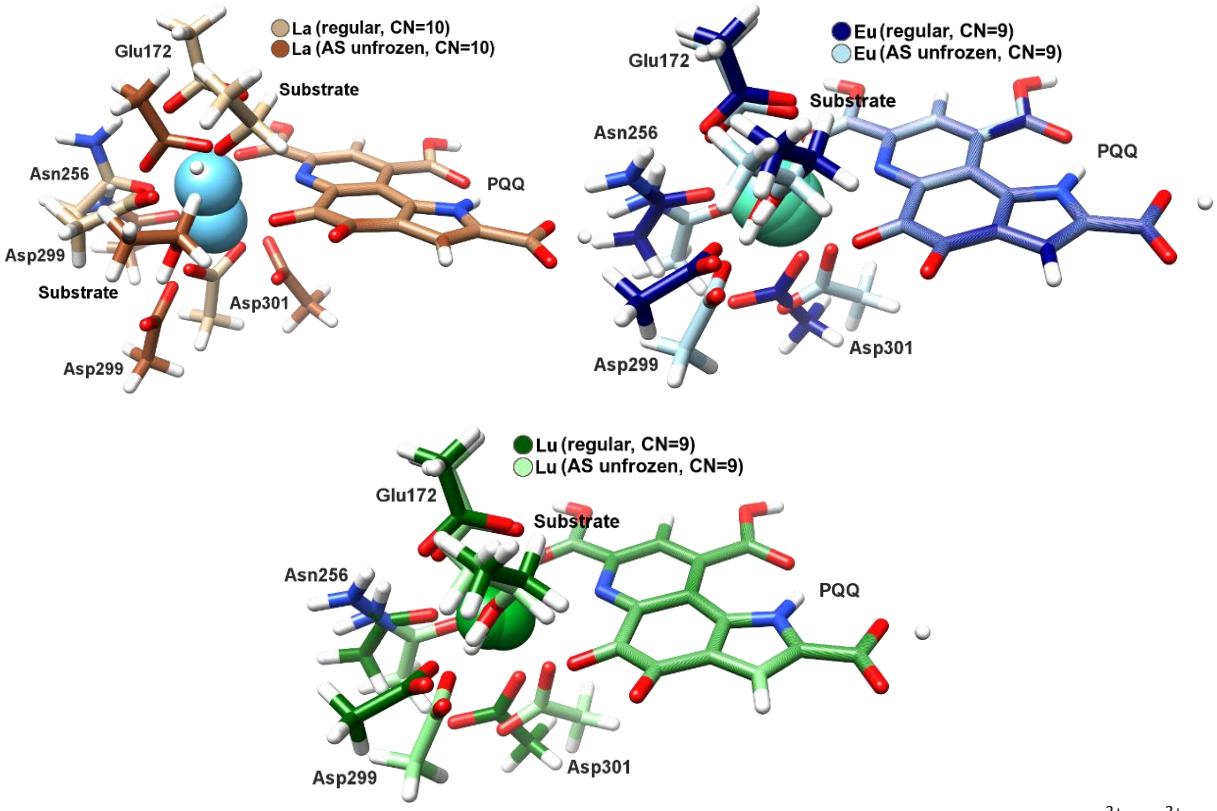

Figure S7 Optimized and superimposed structures for the active center with PQQ, substrate and La^{3+}, Eu^{3+} or Lu^{3+}. Calculations were performed exactly as the "regular" ones described in Figure S2-S3, but with all amino acid residues set to unfrozen. An example input command for the La^{3+} calculation is given below in Figure S8. Both Eu and Lu calculations only differ slightly from the regular ones. Glu172 and the substrate almost keep their position, while Asn256, Asp299 and Asp301 are shifted more significantly from their position. The unfrozen La calculation differs strongly from the regular one, with all amino acids, central metal and substrate rearranged. However, the coordination number for all three calculations does not differ from the respective regular calculation. The coordination number is therefore not forced by the frozen amino acids but only by the varying properties of the Ln. None of the calculations showed negative frequencies.

Figure S8 Example input for Gaussian optimizations with all amino acids set to unfrozen (while keeping all PQQ atoms frozen). -1 denotes a frozen carbon atom.

```
%chk=LaIII-PQQ-with-Substrate-not-frozen.chk
%mem=60GB
%nprocshared=8
#p opt freq rb3lyp/gen geom=connectivity 5d 7f pseudo=read

La(III) - PQQ - with Substrat
AS not frozen

0 1
C        0  -4.90400000   3.34400000   3.52500000
C        0  -4.43100000   2.75000000   2.21200000
O        0  -5.31600000   2.48300000   1.32700000
O        0  -3.21300000   2.47700000   2.02300000
C        0  -7.59200000   1.55900000  -2.75400000
C        0  -6.78400000   1.98800000  -1.55100000
O        0  -5.53400000   1.90100000  -1.57100000
N        0  -7.44100000   2.47100000  -0.49176943
C        0  -7.57000000  -2.04200000   0.45144469
C        0  -6.14900000  -1.61500000   0.75161945
O        0  -5.81500000  -0.46701986   0.29292243
O        0  -5.39000000  -2.35900000   1.42100000
C        0  -3.16200000  -0.96440872  -4.27600000
C        0  -3.96500000  -0.84870079  -2.97500000
O        0  -5.10800000  -1.31100000  -2.91900000
O        0  -3.34000000  -0.27056742  -1.98200000
N       -1   3.33000000  -0.81662988   1.47900000
C       -1   3.61300000  -2.05900000   1.97300000
C       -1   5.01500000  -2.49400000   2.20800000
O       -1   5.88200000  -1.54200000   1.91200000
O       -1   5.26800000  -3.61500000   2.62500000
C       -1   2.41800000  -2.74800000   2.13600000
C       -1   1.39400000  -1.87800000   1.71500000
C       -1   1.99200000  -0.65850047   1.29400000
C       -1  -0.03196565  -2.09600000   1.68300000
O       -1  -0.65585683  -3.02200000   2.17600000
C       -1  -0.80639866  -0.98447544   0.95671480
O       -1  -1.97200000  -1.16300000   0.63270177
C       -1  -0.13660882   0.31747211   0.63836618
N       -1  -0.97622754   1.23100000   0.17358237
C       -1  -0.50347008   2.43600000  -0.15877326
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O       -1  -2.68200000   3.07700000  -0.90161786
```

O	-1	-1.02900000	4.60100000	-0.94685640
C	-1	0.84871874	2.74100000	-0.04652754
C	-1	1.77100000	1.78600000	0.39850560
C	-1	3.21000000	2.20900000	0.35976671
O	-1	3.37200000	3.51000000	0.13590368
O	-1	4.17700000	1.46400000	0.47970217
C	-1	1.28200000	0.49657896	0.78449450
O	0	-3.93300000	-0.32848794	2.35300000
C	0	-3.16200000	-0.45069210	3.55200000
C	0	-4.04600000	-0.73580415	4.76200000
H	0	-7.34200000	2.20600000	-3.60200000
H	0	-7.28400000	0.54246200	-3.01600000
H	0	-8.67000000	1.59400000	-2.58300000
H	0	-7.70800000	-2.10900000	-0.63361256
H	0	-7.80300000	-3.00600000	0.90925659
H	0	-8.26700000	-1.28200000	0.82000108
H	0	-5.67800000	4.09600000	3.34900000
H	0	-5.35100000	2.54500000	4.12900000
H	0	-4.07300000	3.78100000	4.08500000
H	0	-4.78000000	0.06458975	4.90600000
H	0	-4.58800000	-1.67900000	4.63500000
H	0	-3.43600000	-0.81454479	5.67000000
H	0	-2.63900000	0.50250317	3.66600000
H	0	-2.41400000	-1.24600000	3.43300000
H	0	-2.74100000	0.00689772	-4.55900000
H	0	-2.32100000	-1.65000000	-4.12400000
H	0	-3.79400000	-1.34200000	-5.08200000
H	-1	4.34900000	3.70100000	-0.00827955
H	-1	1.19100000	3.72400000	-0.32958075
H	-1	6.90200000	-1.87400000	1.98800000
H	-1	-1.75500000	5.14900000	-1.30300000
H	-1	4.02400000	-0.11676026	1.22800000
H	-1	2.30000000	-3.76900000	2.46200000
H	0	-8.45000000	2.47400000	-0.46268410
H	0	-6.90800000	2.66300000	0.35974909
H	0	-4.37900000	-1.19400000	2.13400000
La	0	-3.90000000	0.86148825	0.01088327

1 2 1.0 50 1.0 51 1.0 52 1.0
2 3 1.5 4 1.5
3 70 1.0
4 70 1.0
5 6 1.0 44 1.0 45 1.0 46 1.0
6 7 2.0 8 1.5
7 70 1.0
8 67 1.0 68 1.0
9 10 1.0 47 1.0 48 1.0 49 1.0
10 11 1.5 12 1.5
11 70 1.0
12
13 14 1.0 58 1.0 59 1.0 60 1.0
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15 70 1.0
16 70 1.0
17 18 1.5 24 1.5 65 1.0
18 19 1.0 22 1.5
19 20 1.5 21 2.0
20 63 1.0
21
22 23 1.5 66 1.0
23 24 1.5 25 1.5
24 40 1.0
25 26 2.0 27 1.0
26
27 28 2.0 29 1.0
28 70 1.0
29 30 1.5 40 1.5
30 31 1.5 70 1.0
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6-31G(d)
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La 0
MWB46
****

La 0
MWB46

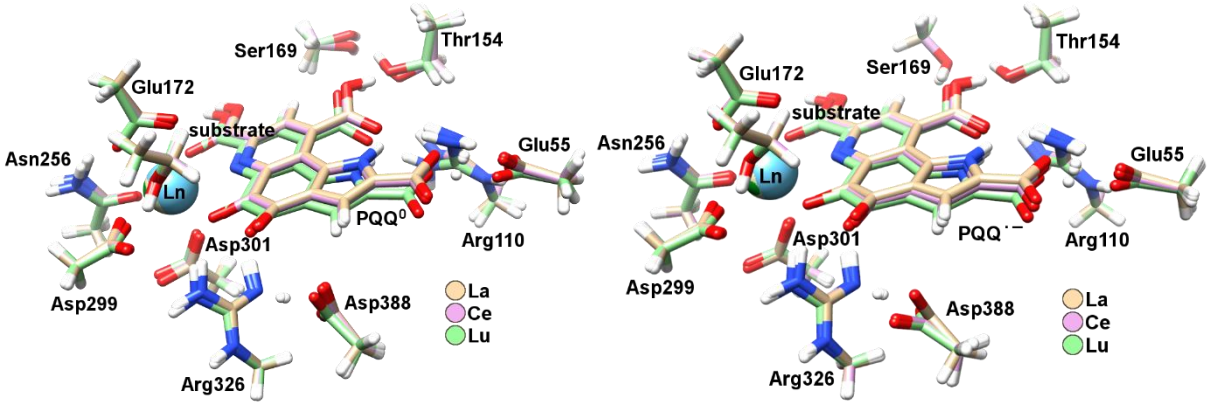

Figure S9: Optimized Structures for the extended active center with substrate and La (tan), Ce (purple) or Lu (green) with PQQ in the active quinone state (PQQ^0 – left) or the resting semiquinone state ($PQQ^{\bullet-}$ – right). Electronic-structure calculations were performed with Gaussian 09 and exactly as described by Schelter *et al*.[2] The B3LYP functional with the 6-31G(d) basis set was used for C, H, N and O. 28 electron quasi relativistic effective core potentials (ECP) and segmented basis sets were used for each central metal respectively (La, Ce, Lu): ECP-MWB28.[11-13] Starting point of the geometry optimization was the active site of the crystal structure of Ce-MDH isolated from SolV (4MAE).[10] The present amino acids in the active site were truncated and the terminal carbon atoms were frozen, to mimic the sterics imposed by the protein. The present polyethylenglycol was truncated as well and used as a substrate-model. The conductor-like polarizable continuum model (CPCM) was used for water, with the default settings for the universal force field (UFF) and a dielectric constant of 4, to reproduce the interior of the protein and the active site pocket. The charge and multiplicity for the quinone PQQ^0 state were set to "0 1" for La and Lu and to "0 2" for Ce. The additional electron for the semiquinone $PQQ^{\bullet-}$ state was taken into account, by changing the system to "−1 2" for La and Lu and to "−1 3" for Ce. None of the calculations showed negative frequencies. All structures differed only slightly, by changing the central metal or the PQQ state. The PQQ ligand moved closer to the central metal, especially in case of Lu, probably due to the decreased ionic radius. In contrast to the simplified calculations described in Figure S2-S3, Asp301 remained monodentate for all calculations and therefore the overall coordination number did not change over the exchange of La to Ce or Lu. Since the simplified system given in S2 was also calculated with a smaller ECP and solvent effects as described in Figure S5, the binding mode of Asp301 is probably influenced during the optimization by the larger hydrogen bond network due to the additional amino acids and the change of the dielectric constant to 4.

Figure S10 Example input for Gaussian optimizations (in this case La^{3+} PQQ^0). -1 denotes a frozen carbon atom.

```
%chk=C:\Users\akdaumann\Desktop\La(III)-PQQ(0).chk
%mem=128GB
%nprocshared=12
#p opt=maxcycle=999 freq rb3lyp/gen
scrf=(cpcm,solvent=water,read)
geom=connectivity pseudo=read scf=maxcycles=1024
formcheck

La(III) - PQQ(0)

0 1
C      -1  10.31100000  -2.74300000   0.91007048
C       0   8.93000000  -2.09500000   0.98227463
O       0   8.26200000  -2.29300000   2.04300000
O       0   8.55300000  -1.38000000   0.00969315
C      -1   8.18300000  -0.06179479  -3.80000000
N       0   7.90300000  -0.03453109  -2.37100000
C       0   7.07000000   0.82769766  -1.78300000
N       0   6.37600000   1.73100000  -2.50700000
N       0   6.93100000   0.79380766  -0.44848331
C       0   7.08000000   4.45200000  -0.35938247
O       0   5.73400000   4.21400000  -0.86097367
C      -1   7.09400000   5.43300000   0.80182198
C      -1   2.43900000   6.91600000  -0.75832705
O       0   3.32900000   5.98400000  -1.38600000
C      -1  -4.90400000   3.34400000   3.52500000
C       0  -4.43100000   2.75000000   2.21200000
O       0  -5.31600000   2.48300000   1.32700000
O       0  -3.21300000   2.47700000   2.02300000
C      -1  -7.59200000   1.55900000  -2.75400000
C       0  -6.78400000   1.98800000  -1.55100000
O       0  -5.53400000   1.90100000  -1.57100000
N       0  -7.44100000   2.47100000  -0.49176943
C      -1  -7.57000000  -2.04200000   0.45144469
C       0  -6.14900000  -1.61500000   0.75161945
O       0  -5.81500000  -0.46701986   0.29292243
```

O	0	-5.39000000	-2.35900000	1.42100000
C	-1	-3.16200000	-0.96440872	-4.27600000
C	0	-3.96500000	-0.84870079	-2.97500000
O	0	-5.10800000	-1.31100000	-2.91900000
O	0	-3.34000000	-0.27056742	-1.98200000
N	0	3.33000000	-0.81662988	1.47900000
C	0	3.61300000	-2.05900000	1.97300000
C	0	5.01500000	-2.49400000	2.20800000
O	0	5.88200000	-1.54200000	1.91200000
O	0	5.26800000	-3.61500000	2.62500000
C	0	2.41800000	-2.74800000	2.13600000
C	0	1.39400000	-1.87800000	1.71500000
C	0	1.99200000	-0.65850047	1.29400000
C	0	-0.03196565	-2.09600000	1.68300000
O	0	-0.65585683	-3.02200000	2.17600000
C	0	-0.80639866	-0.98447544	0.95671480
O	0	-1.97200000	-1.16300000	0.63270177
C	0	-0.13660882	0.31747211	0.63836618
N	0	-0.97622754	1.23100000	0.17358237
C	0	-0.50347008	2.43600000	-0.15877326
C	0	-1.51600000	3.38500000	-0.69429278
O	0	-2.68200000	3.07700000	-0.90161786
O	0	-1.02900000	4.60100000	-0.94685640
C	0	0.84871874	2.74100000	-0.04652754
C	0	1.77100000	1.78600000	0.39850560
C	0	3.21000000	2.20900000	0.35976671
O	0	3.37200000	3.51000000	0.13590368
O	0	4.17700000	1.46400000	0.47970217
C	0	1.28200000	0.49657896	0.78449450
O	0	-3.93300000	-0.32848794	2.35300000
C	0	-3.16200000	-0.45069210	3.55200000
C	-1	-4.04600000	-0.73580415	4.76200000
C	-1	-1.81800000	-5.63500000	-3.12600000
N	0	-2.49200000	-5.27000000	-1.87800000
C	0	-2.38200000	-4.05700000	-1.31700000
N	0	-1.38300000	-3.25400000	-1.70400000
N	0	-3.28000000	-3.66000000	-0.40296842
C	-1	2.04400000	-6.54300000	-1.24900000
C	0	1.30700000	-5.20800000	-1.01900000
O	0	0.91595122	-4.60900000	-2.08800000
O	0	1.10700000	-4.82700000	0.15045621
H	0	-7.34200000	2.20600000	-3.60200000
H	0	-7.28400000	0.54246200	-3.01600000
H	0	-8.67000000	1.59400000	-2.58300000
H	0	-7.70800000	-2.10900000	-0.63361256
H	0	-7.80300000	-3.00600000	0.90925659
H	0	-8.26700000	-1.28200000	0.82000108
H	0	-5.67800000	4.09600000	3.34900000
H	0	-5.35100000	2.54500000	4.12900000
H	0	-4.07300000	3.78100000	4.08500000
H	0	-4.78000000	0.06458975	4.90600000
H	0	-4.58800000	-1.67900000	4.63500000
H	0	-3.43600000	-0.81454479	5.67000000
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H	0	-2.41400000	-1.24600000	3.43300000
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H	0	-2.32100000	-1.65000000	-4.12400000
H	0	-3.79400000	-1.34200000	-5.08200000
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H	0	2.70200000	-6.48700000	-2.12300000
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H	0	8.60600000	0.88889236	-4.14600000
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H	0	8.11900000	5.56800000	1.16300000
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H	0	1.19100000	3.72400000	-0.32958075
H	0	6.90200000	-1.87400000	1.98800000
H	0	-1.75500000	5.14900000	-1.30300000
H	0	4.02400000	-0.11676026	1.22800000
H	0	2.30000000	-3.76900000	2.46200000
H	0	-3.08300000	-2.86900000	0.19805491
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H	0	-8.45000000	2.47400000	-0.46268410
H	0	-6.90800000	2.66300000	0.35974909
H	0	-4.37900000	-1.19400000	2.13400000
La	0	-3.90000000	0.86148825	0.01088327

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S 1 1.00
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13.9024000 1.0
P 1 1.00
4.2361000 1.0
P 1 1.00
2.2936000 1.0
P 1 1.00
1.1258000 1.0
P 1 1.00
0.5279000 1.0
P 1 1.00
0.2292000 1.0
P 1 1.00
0.0800000 1.0
D 6 1.00
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113.5768000 0.000612
33.5588000 0.007687
14.4198000 -0.076510
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3.9483000 0.421873
D 1 1.00
2.0150000 1.0
D 1 1.00
0.9581000 1.0
D 1 1.00

0.3109000 1.0
D 1 1.00
0.0954000 1.0
F 5 1.00
124.7971000 0.001150
43.9427000 0.014333
19.2668000 0.062594
8.4893000 0.164000
3.7672000 0.285863
F 1 1.00
1.5902000 1.0
F 1 1.00
0.6098000 1.0
F 1 1.00
0.1973000 1.0
G 4 1.00
19.2668000 -0.002118
8.4893000 0.026709
3.7672000 -0.029667
1.5902000 0.282785
G 1 1.00
0.6098000 1.0
G 1 1.00
0.1973000 1.0
****

La 0
ECP28MWB 5 28
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P-H
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D-H
1
2 15.128259 186.058232
F-H
1
2 23.103875 -49.433352
G-H
1
2 15.639020 -20.123020

stoichiometry=H2O1
solventname=water
eps=4.0

Figure S11 Input for the calculation of the La^{3+} $PQQ^{\bullet-}$ species.

For the semiquinone $PQQ^{\bullet-}$ species, following modification was implemented, while the rest of the input file was unchanged to figure S10:

#p opt=maxcycle=999 freq ub3lyp/gen scrf=(cpcm,solvent=water,read)
geom=connectivity formcheck pseudo=read scf=maxcycles=1024

La(III) - PQQ(-1)

-1 2

Figure S12 Input for the calculation of the Ce^{3+} and Lu^{3+} variants of the PQQ^{0} species. For the semiquinone $PQQ^{\bullet -}$ species, the input files were exactly the same, but the charge and multiplicity were changed to −1 3 for Ce^{3+} and −1 2 for Lu^{3+}.

Ce^{3+} PQQ^{0}

```
#p opt(maxcycle=999) freq ub3lyp/gen
scrf=(cpcm,solvent=water,read)
geom=connectivity scf=maxcycles=1024 pseudo=read

Ce(III) - PQQ(0)

0 2

Atomic coordinates and
geometry specifications as in Figure S10

C H N O 0
6-31G(d)
****
Ce 0
S 5 1.00
66920.6810000 0.000005
7142.4190000 0.000062
1149.2279000 0.000408
626.0474000 0.000080
137.2813000 0.003559
S 1 1.00
36.6434000 1.0
S 1 1.00
25.9742000 1.0
S 1 1.00
11.8859000 1.0
S 1 1.00
3.0284000 1.0
S 1 1.00
1.5664000 1.0
S 1 1.00
0.5937000 1.0
S 1 1.00
0.2630000 1.0
S 1 1.00
0.0490000 1.0
S 1 1.00
0.0207000 1.0
P 6 1.00
3813.8026000 0.000005
1216.9447000 0.000051
496.6641000 0.000053
212.5431000 0.000671
27.6306000 0.008805
19.6040000 0.150861
P 1 1.00
13.8918000 1.0
P 1 1.00
4.4389000 1.0
P 1 1.00
2.3374000 1.0
P 1 1.00
1.1067000 1.0
P 1 1.00
0.5287000 1.0
P 1 1.00
0.2305000 1.0
P 1 1.00
0.0800000 1.0
D 6 1.00
367.7157000 0.000120
109.8798000 0.000991
36.0211000 0.007778
14.7637000 -0.062958
7.3281000 0.180342
3.9441000 0.432529
D 1 1.00
2.0202000 1.0
D 1 1.00
0.9649000 1.0
D 1 1.00
0.3273000 1.0
D 1 1.00
0.1032000 1.0
F 5 1.00
123.4821000 0.001566
43.9881000 0.018101
19.4518000 0.076157
8.6013000 0.192683
3.8049000 0.324332
F 1 1.00
1.6176000 1.0
F 1 1.00
0.6364000 1.0
F 1 1.00
0.2164000 1.0
G 4 1.00
19.4518000 0.002199
8.6013000 0.037428
3.8049000 0.030378
1.6176000 0.355664
G 1 1.00
0.6364000 1.0
G 1 1.00
0.2164000 1.0
****

Ce 0
ECP28MWB 5 28
H-Komponente
1
2 1.000000 0.000000
S-H
1
2 20.137829 580.083457
P-H
1
2 15.998482 310.302833
D-H
1
2 14.974187 167.813944
F-H
1
2 23.402455 -49.390229
G-H
1
2 16.570553 -21.331879

stoichiometry=H2O1
solventname=water
eps=4.0
```

Lu^{3+} PQQ^{0}

```
#p opt=maxcycle=999 freq rb3lyp/gen
scrf=(cpcm,solvent=water,read) geom=connectivity
pseudo=read scf=maxcycles=1024 formcheck

Lu(III) - PQQ(0)

0 1
Atomic coordinates and
geometry specifications as in Figure S10

C H N O 0
6-31G(d)
****
Lu 0
S 5 1.00
95169.7670000 0.000022
15488.4030000 0.000145
3776.2335000 0.000651
1079.0501000 0.002038
268.9538000 0.005127
S 1 1.00
63.4679000 1.0
S 1 1.00
45.1332000 1.0
S 1 1.00
21.4568000 1.0
S 1 1.00
5.3483000 1.0
S 1 1.00
2.6778000 1.0
S 1 1.00
1.0287000 1.0
S 1 1.00
0.4408000 1.0
S 1 1.00
0.0791000 1.0
S 1 1.00
0.0313000 1.0
P 6 1.00
4043.9748000 0.000294
958.8771000 0.002353
309.1220000 0.010441
114.2203000 0.025828
37.1091000 0.085047
20.4579000 -0.200371
P 1 1.00
14.5932000 1.0
P 1 1.00
6.527500 1.0
P 1 1.00
3.2448000 1.0
P 1 1.00
1.4504000 1.0
P 1 1.00
0.6635000 1.0
P 1 1.00
0.2858000 1.0
P 1 1.00
0.080000 1.0
D 6 1.00
484.5275000 0.002286
146.6655000 0.018629
56.3779000 0.074088
23.6711000 0.161554
9.4401000 0.308091
4.3712000 0.448334
D 1 1.00
1.9580000 1.0
D 1 1.00
0.7272000 1.0
D 1 1.00
0.2460000 1.0
D 1 1.00
0.0744000 1.0
F 5 1.00
175.1559000 0.004102
62.8909000 0.039086
28.3624000 0.147044
13.2478000 0.271092
6.1440000 0.345665
F 1 1.00
2.7623000 1.0
F 1 1.00
1.1574000 1.0
F 1 1.00
0.4244000 1.0
G 4 1.00
28.3624000 0.047905
13.2478000 0.150128
6.1440000 0.322911
2.7623000 0.444494
G 1 1.00
1.1574000 1.0
G 1 1.00
0.4244000 1.0
****

Lu 0
ECP28MWB 5 28
H-Komponente
1
2 1.000000 0.000000
S-H
1
2 35.162097 989.995584
P-H
1
2 19.464402 278.865652
D-H
1
2 10.006865 71.009178
F-H
1
2 23.517932 -47.405890
G-H
1
2 29.412238 -35.557146

stoichiometry=H2O1
solventname=water
eps=4.0
```

Table S5: Location of highest electron density and energy values of the calculated molecular orbitals (MO) for the calculations given in Figure S9.

Number	Orbital	Location of highest e^--density	Additional e^--density	Energy		
				Hartrees	eV	kJ/mol
La^{3+} PQQ^0						
265	HOMO-3	Asp388	Asp301 + Arg326	-0.23192	-6.31087	-608.906
266	HOMO-2	Asp301	Asp388	-0.23137	-6.29590	-607.462
267	HOMO-1	Asp388	Arg326	-0.22645	-6.16202	-594.544
268	HOMO	Asp388	-	-0.21038	-5.72473	-552.353
269	LUMO	PQQ	-	-0.14161	-3.85341	-371.797
270	LUMO+1	PQQ	-	-0.11693	-3.18183	-307.000
La^{3+} $PQQ^{\bullet-}$						
266-a	HOMO-3	PQQ	Asp388	-0.22487	-6.11903	-590.396
266-b	HOMO-2	Asp388	Arg326 + PQQ	-0.22295	-6.06678	-585.355
267-a	HOMO-2	Asp388	Arg326	-0.22282	-6.06324	-585.014
267-b	HOMO-3	PQQ	Arg326 + Asp388	-0.22212	-6.04420	-583.176
268-a	HOMO-1	Asp388	-	-0.20769	-5.65154	-545.290
268-b	HOMO-1	Asp388	-	-0.20768	-5.65126	-545.264
269-a	HOMO	PQQ	-	-0.17401	-4.73506	-456.863
269-b	LUMO	PQQ	-	-0.10397	-2.82917	-272.973
270-a	LUMO+1	PQQ	-	-0.10276	-2.79624	-269.796
Ce^{3+} PQQ^0						
266-b	HOMO-3	Asp388	Asp301	-0.23159	-6.30189	-608.040
266-a	HOMO-3	Asp388	Asp301	-0.23158	-6.30162	-608.013
267-b	HOMO-2	Asp388	Arg326	-0.22657	-6.16529	-594.860
267-a	HOMO-2	Asp388	Arg326	-0.22657	-6.16529	-594.860
268-b	HOMO-1	Asp388	-	-0.21046	-5.72691	-552.563
268-a	HOMO-1	Asp388	-	-0.21046	-5.72691	-552.563
269-a	SOMO	Ce^{3+}	-	-0.19763	-5.37779	-518.878
269-b	LUMO	PQQ	-	-0.14155	-3.85177	-371.640
270-a	LUMO	PQQ	-	-0.14155	-3.85177	-371.640
270-b	LUMO+1	PQQ	-	-0.11667	-3.17475	-306.317
271-a	LUMO+1	PQQ	-	-0.11671	-3.17584	-306.422
Ce^{3+} $PQQ^{\bullet-}$						
266-a	HOMO-3	PQQ	-	-0.22722	-6.18297	-596.566
266-b	HOMO-3	PQQ	-	-0.22373	-6.08801	-587.403
267-a	HOMO-2	Asp388	Arg326	-0.22237	-6.05100	-583.832
267-b	HOMO-2	Asp388	Arg326	-0.22235	-6.05045	-583.780
268-a	HOMO-1	Asp388	-	-0.20890	-5.68446	-548.467
268-b	HOMO-1	Asp388	-	-0.20885	-5.68310	-548.336
269-a	SOMO	Ce^{3+}	-	-0.18258	-4.96826	-479.364
270-a	HOMO	PQQ	Ce^{3+}	-0.17564	-4.77941	-461.143
269-b	LUMO	PQQ	-	-0.10564	-2.87461	-277.358
270-b	LUMO+1	PQQ	-	-0.09881	-2.68876	-259.426
Lu^{3+} PQQ^0						
272	HOMO-3	Asp388	Arg326 + PQQ	-0.23099	-6.28556	-606.464
273	HOMO-2	Asp388	Arg326 + Asp301	-0.22661	-6.16638	-594.965
274	HOMO-1	Asp301	-	-0.22574	-6.14270	-592.680
275	HOMO	Asp388	-	-0.21016	-5.71875	-551.775
276	LUMO	PQQ	-	-0.14311	-3.89422	-375.735
277	LUMO+1	PQQ	-	-0.11684	-3.17938	-306.763
Lu^{3+} $PQQ^{\bullet-}$						
273-a	HOMO-3	Asp388	Arg326	-0.22188	-6.03767	-582.546
273-b	HOMO-3	Asp388	Arg326	-0.22187	-6.03739	-582.520
274-a	HOMO-2	Asp301	-	-0.22005	-5.98787	-577.741
274-b	HOMO-2	Asp301	-	-0.21990	-5.98379	-577.347
275-a	HOMO-1	Asp388	-	-0.20811	-5.66296	-546.393
275-b	HOMO-1	Asp388	-	-0.20806	-5.66160	-546.262
276-a	HOMO	PQQ	-	-0.17618	-4.79410	-462.561
276-b	LUMO	PQQ	-	-0.10606	-2.88604	-278.461
277-a	LUMO+1	PQQ	-	-0.10285	-2.79869	-270.033

1 Hartree ~ 27.2114 eV ~ 2625.50 $kJ \cdot mol^{-1}$.[15]

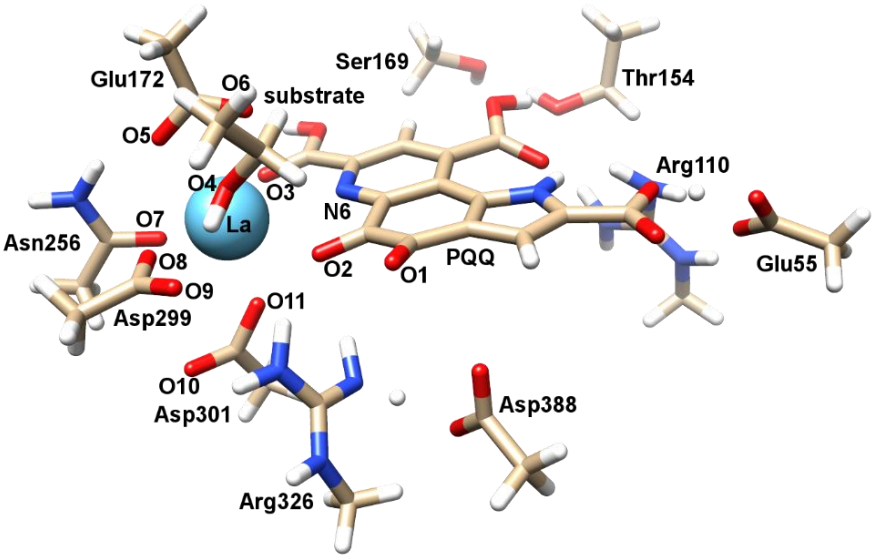
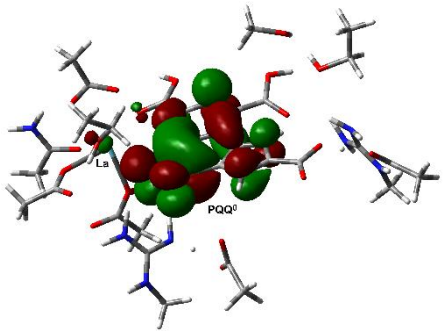
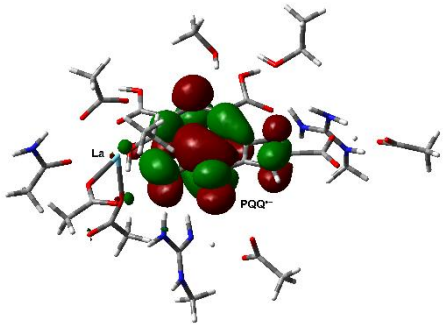
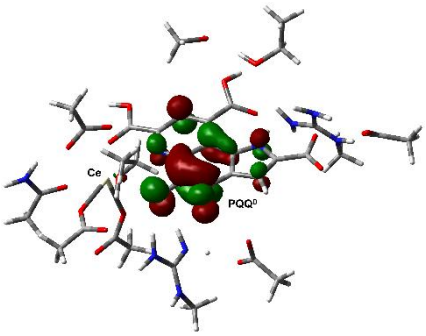
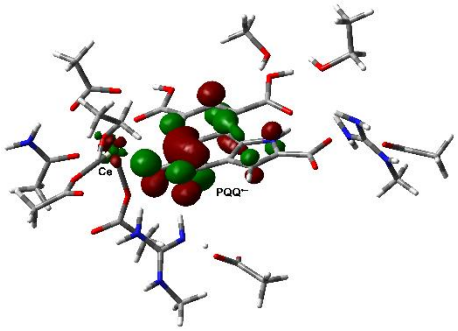
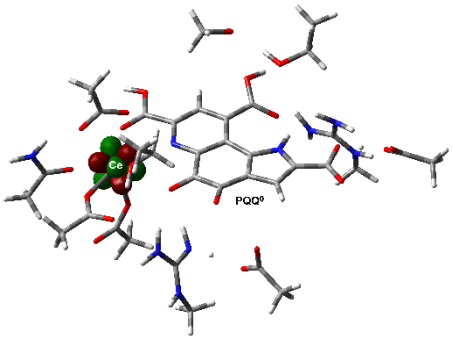
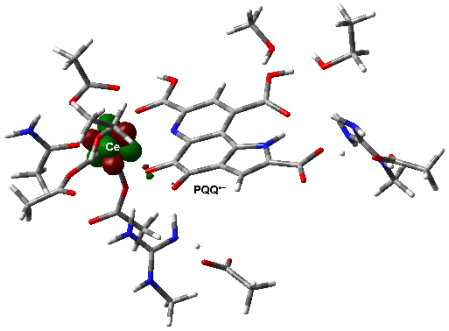
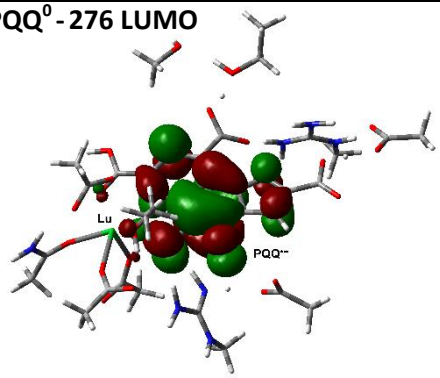
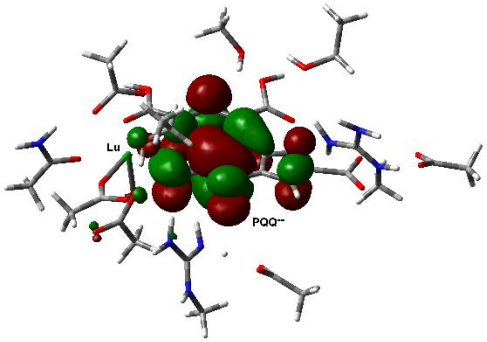


Table S6 Ln-ligand distances [Å] for the active site calculations given in Figure S9.

	La-PQQ^{0}	La-PQQ$^{\bullet-}$	Ce-PQQ^{0}	Ce-PQQ$^{\bullet-}$	Lu-PQQ^{0}	Lu-PQQ$^{\bullet-}$
PQQ O2	2.88072	2.61357	2.86311	2.59050	2.72515	2.43018
PQQ N6	2.96958	2.85159	2.94383	2.81733	2.73335	2.63617
PQQ O3	2.71471	2.76245	2.69047	2.73264	2.49334	2.55311
Substrate O4	2.63346	2.65730	2.63014	2.66181	2.59689	2.57834
Glu172 O5	2.54295	2.56530	2.52417	2.55965	2.41993	2.44482
Glu172 O6	2.67813	2.71147	2.66758	2.65592	2.55701	2.67900
Asn256 O7	2.53227	2.61032	2.50117	2.58137	2.28928	2.39758
Asp299 O8	2.39335	2.44359	2.35205	2.38363	2.17319	2.21431
Asp301 O10	3.86233	4.08612	3.84750	3.98604	3.73898	3.80749
Asp301 O11	2.38081	2.36061	2.35938	2.33516	2.30894	2.28001

Table S7 Visualization of the frontier orbitals for the calculations given in Figure S9. In all cases, the LUMO of the PQQ^0 species and the HOMO of the $PQQ^{\bullet-}$ species seem to be the same PQQ related orbital. In case of La^{3+} and Lu^{3+}, the sign of the orbital wave function changes, probably due to the change from a closed- to an open shell system.

 **La^{3+} PQQ^0 - 269 LUMO**	 **La^{3+} $PQQ^{\bullet-}$ - 269-a HOMO**
 **Ce^{3+} PQQ^0 - 270-a LUMO**	 **Ce^{3+} $PQQ^{\bullet-}$ - 270-a HOMO**
 **Ce^{3+} PQQ^0 - 269-a SOMO**	 **Ce^{3+} $PQQ^{\bullet-}$ - 269-a SOMO**
Lu^{3+} PQQ^0 - 276 LUMO 	**Lu^{3+} $PQQ^{\bullet-}$ - 276-a HOMO** 

References

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