

Figure S1 : Optimized structures of the Ca^{2+} complexes with **psq** and **ptsq**

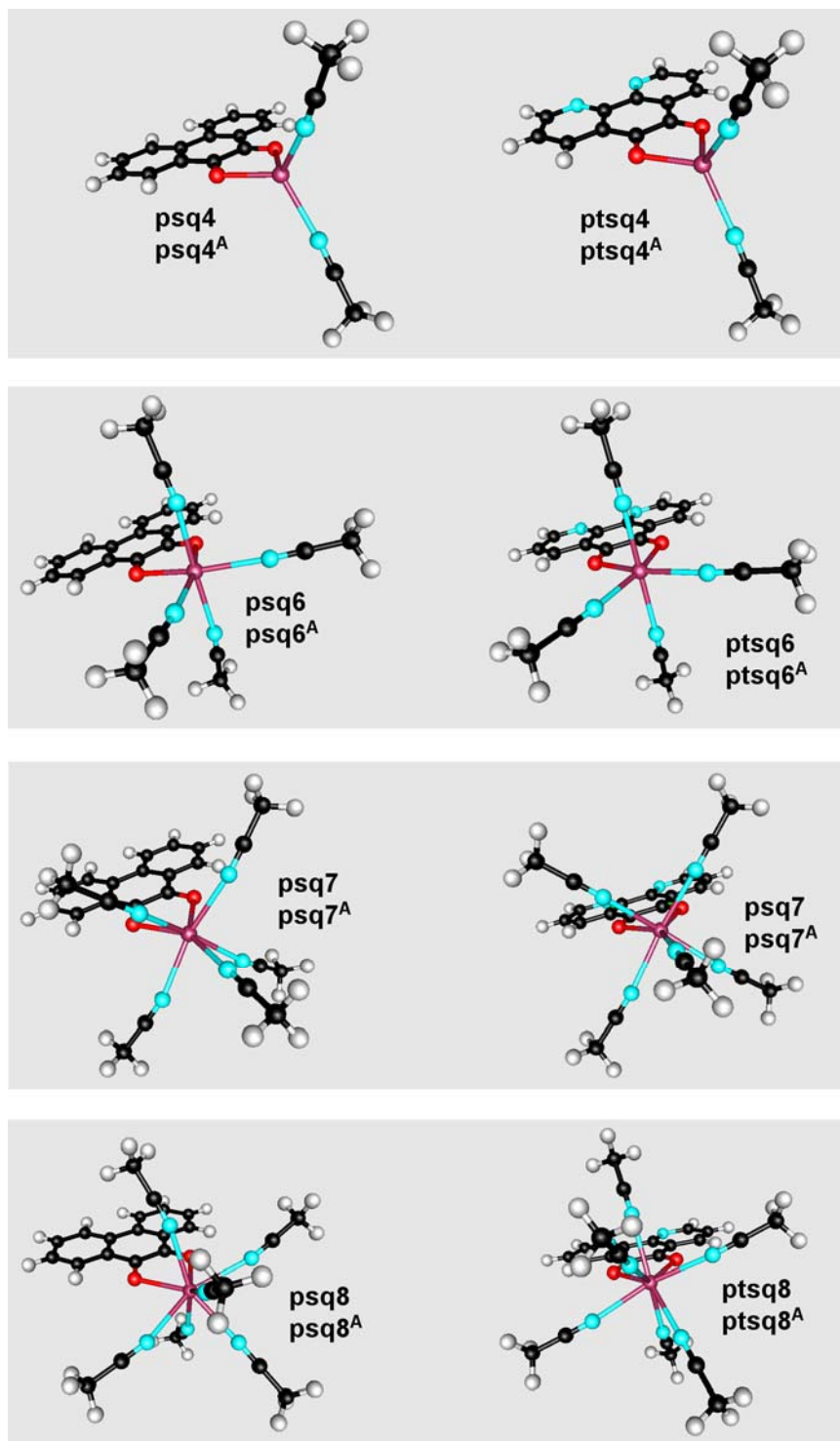


Table S1: Lengths of the C–O and O–Ca bonds (in Å) as well as Löwdin spin populations (ρ); all computed at the UB3LYP/TZVP theory level.

	R_{C1-O1}	R_{C2-O2}	R_{O1-M}	R_{O2-M}	ρ_{C1}	ρ_{C2}	ρ_{O1}	ρ_{O2}	ρ_M
sq	1.252	1.252	n/a	n/a	0.060	0.060	0.253	0.253	n/a
sq ^A	1.265	1.265	n/a	n/a	0.104	0.104	0.243	0.243	n/a
psq	1.249	1.249	n/a	n/a	0.146	0.146	0.230	0.230	n/a
psq ^A	1.263	1.263	n/a	n/a	0.148	0.148	0.230	0.230	n/a
ptsq	1.249	1.249	n/a	n/a	0.097	0.097	0.248	0.248	n/a
ptsq ^A	1.259	1.259	n/a	n/a	0.140	0.140	0.237	0.237	n/a
Ca²⁺ Complexes									
sq4	1.285	1.285	2.320	2.320	0.183	0.183	0.196	0.188	0.008
sq4 ^A	1.274	1.273	2.489	2.486	0.149	0.149	0.212	0.213	0.003
sq6	1.277	1.277	2.381	2.381	0.149	0.149	0.215	0.215	0.003
sq6 ^A	1.273	1.273	2.498	2.496	0.144	0.144	0.217	0.217	0.002
sq7	1.274	1.274	2.441	2.441	0.139	0.139	0.219	0.219	0.003
sq7 ^A	1.271	1.271	2.488	2.487	0.135	0.135	0.222	0.221	0.002
sq8	1.271	1.271	2.465	2.465	0.128	0.129	0.226	0.226	0.000
sq8 ^A	1.271	1.270	2.551	2.551	0.127	0.126	0.228	0.228	0.000
psq4	1.288	1.288	2.310	2.310	0.206	0.206	0.167	0.167	0.011
psq4 ^A	1.274	1.274	2.458	2.445	0.188	0.188	0.192	0.191	0.006
psq6	1.279	1.279	2.373	2.372	0.188	0.188	0.193	0.193	0.003
psq6 ^A	1.273	1.273	2.485	2.485	0.181	0.181	0.200	0.200	0.002
psq7	1.275	1.275	2.430	2.430	0.179	0.179	0.199	0.199	0.002
psq7 ^A	1.272	1.272	2.484	2.485	0.171	0.172	0.207	0.207	0.002
psq8	1.271	1.271	2.461	2.461	0.168	0.168	0.211	0.211	0.001
psq8 ^A	1.272	1.272	2.484	2.485	0.163	0.165	0.215	0.214	0.000
ptsq4	1.860	1.286	2.318	2.318	0.207	0.207	0.175	0.175	0.010
ptsq4 ^A	1.270	1.270	2.484	2.479	0.183	0.183	0.202	0.202	0.006
ptsq6	1.278	1.278	2.382	2.382	0.188	0.188	0.199	0.199	0.003
ptsq6 ^A	1.270	1.270	2.501	2.501	0.177	0.177	0.209	0.209	0.002
ptsq7	1.274	1.274	2.439	2.439	0.178	0.178	0.205	0.205	0.002
ptsq7 ^A	1.269	1.268	2.491	2.502	0.166	0.165	0.217	0.216	0.002
ptsq8	1.270	1.270	2.469	2.469	0.168	0.168	0.217	0.217	0.001
ptsq8 ^A	1.267	1.267	2.516	2.516	0.157	0.160	0.224	0.223	0.000

Table S2: Spin populations on Ca computed with different basis set.

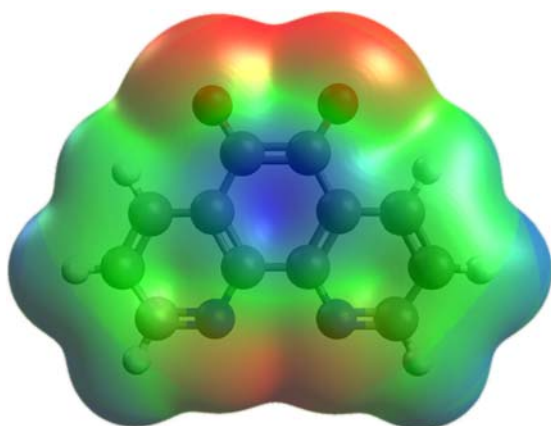
	UB3LYP				UBP86			
	SVP	TZVP	TZVPPP	QZVP	SVP	TZVP	TZVPPP	QZVP
sq4	0.013	0.008	0.000	0.014	0.017	0.014	0.000	0.021
sq4^A	0.006	0.003	-0.001	0.006	0.008	0.007	0.000	0.015
sq6	0.005	0.003	-0.001	0.009	0.008	0.005	0.000	0.015
sq6^A	0.003	0.002	-0.001	0.005	0.005	0.004	0.000	0.010
sq7	0.002	0.003	-0.001	0.006	0.006	0.004	0.000	0.007
sq7^A	0.001	0.002	-0.001	0.002	0.002	0.003	0.000	0.004
sq8	0.001	0.000	-0.001	0.004	0.003	0.002	0.000	0.005
sq8^A	0.000	0.000	-0.001	0.001	0.002	0.001	0.000	0.002

The semiquinone radical derived from 1,10-phenanthroline-5,6-dione (**ptsq**) is an ambidentate ligand and therefore the alternative binding of metal ions via nitrogen atoms might occur. The influence of the interaction between Mg^{2+} and the N-donors of **ptsq** on the g tensor was investigated by us previously (J. Phys. Chem. B 2011, 115, 3172) and a similar analysis for Ca^{2+} is presented in Table S3. First we focus on the relative stability of the N,N- and O,O-chelating **ptsq** complexes with Ca^{2+} ions. The stability is evaluated by comparing the relative energies of the N,N- and O,O-complexes. The relative energies for the complexes with N,N-chelation were predicted to be significantly greater than for O,O-chelation by 17-25 kcal/mol depending on the coordination sphere and PCM inclusion (see Table S2). This observation is in agreement with the experimental results suggesting the coordination through the oxygen donors to be the most likely (J. Yuasa, T. Suenobu, S. Fukuzumi *ChemPhysChem* 7 (2006) 942.).

To understand the higher stability of the O,O- complexes one has to take a closer look at the interaction between Ca^{2+} and an o-semiquinone which is mainly of electrostatic nature. Since the metal ion is positively charged, hence its interaction with the donor atoms on which the more negative charge is located will be energetically beneficial. The UB3LYP/TZVP calculations on **ptsq** revealed that significantly larger negative charge is located on the hydroxyl oxygens (see the electrostatic potential below) and therefore the O,O- complexes with Ca^{2+} are energetically more beneficial. This finding stays in accordance with the Pearson hard and soft acid and base concept (HSAB). **ptsq** is a Lewis base involving a harder (O) and softer (N) basic center. Ca^{2+} , being a hard acid, in terms of HSAB should form coordination compound via the O donors of **ptsq**.

Table S2: Comparison of the relative energy between the N,N- and O,O- complexes; structures of the former are shown in Figure S2.

	O,O-chelation				N,N-chelation		
	E^0 [a.u.]	ZPVE [kcal/mol]	ΔE^0 [kcal/mol]		E^0 [a.u.]	ZPVE [kcal/mol]	ΔE^0 [kcal/mol]
ptsq4	-1664.234439	156.01	0	N,N-ptsq4	-1664.194050	155.24	24.6
ptsq4^A	-1664.386408	153.99	0	N,N-ptsq4A	-1664.351137	154.13	22.3
ptsq6	-1929.911331	213.97	0	N,N-ptsq6	-1929.877383	213.21	20.5
ptsq6^A	-1930.016591	211.03	0	N,N-ptsq6A	-1929.990110	212.01	17.6
ptsq7	-2062.730852	242.93	0	N,N-ptsq7	-2062.697362	242.34	20.4
ptsq7^A	-2062.835586	240.91	0	N,N-ptsq7A	-2062.806480	241.11	18.5
ptsq8	-2195.713682	261.81	0	N,N-ptsq8	-2195.673023	260.81	24.5
ptsq8^A	-2195.827886	259.99	0	N,N-ptsq8A	-2195.790284	258.29	21.9



Electrostatic potential calculated at the UB3LYP/TZVP theory level for the **ptsq** radical anion; red color indicates negative charge.

Figure S2: Optimized structures of the complexes with Ca^{2+} coordinated to ptsq via the nitrogen atoms

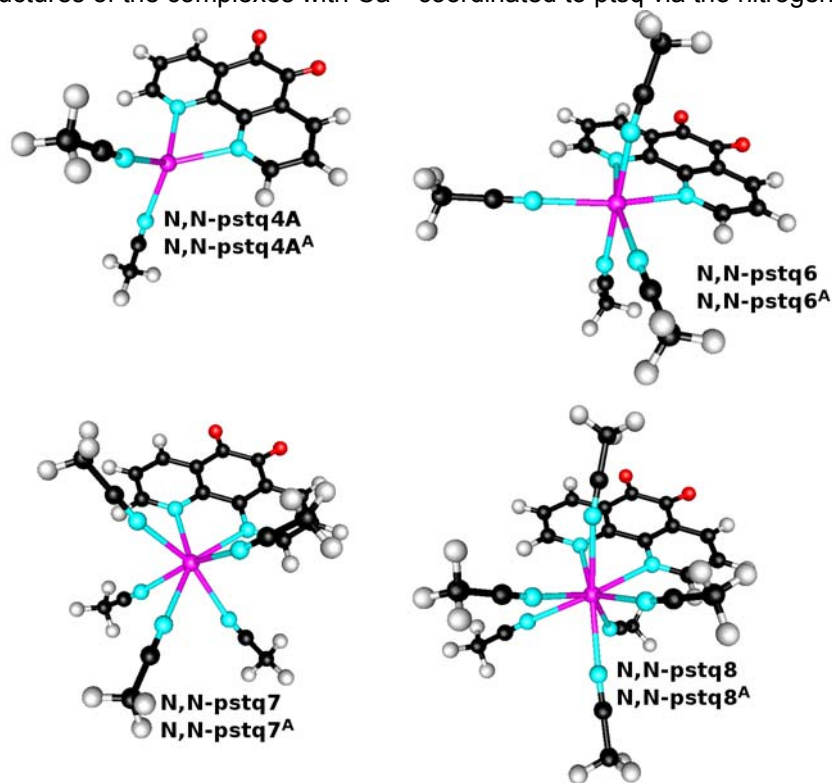


Table S3: Δg Tensors (in ppm) calculated for the ptsq complexes with Ca^{2+} coordinated via nitrogen atoms; the optimized structures are shown in Figure S2

	UB3LYP/TZVP				UBP86/TZVP			
	Δg_{xx}	Δg_{yy}	Δg_{zz}	Δg_{iso}	Δg_{xx}	Δg_{yy}	Δg_{zz}	Δg_{iso}
N,N-ptsq4	4191	4090	-20	2754	3757	3702	-44	2472
N,N-ptsq4 ^A	4368	4319	2	2896	4106	3935	15	2686
N,N-ptsq6	4470	4468	30	2989	4066	4043	40	2717
N,N-ptsq6 ^A	4416	4350	44	2937	4096	4025	59	2727
N,N-ptsq7	4629	4524	55	3069	4213	4096	70	2793
N,N-ptsq7 ^A	4526	4333	66	2975	4133	4086	88	2769
N,N-ptsq8	4704	4591	75	3123	4278	4158	89	2842
N,N-ptsq8 ^A	4513	4316	103	2977	4133	4075	114	2774