## **Supporting Information for**

## Where Does the Density Localize? Convergent Behavior for Global Hybrids, Range Separation, and DFT+U

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**Table S1.** List of pseudopotentials used in this work with filenames as obtained from the
 Quantum-ESPRESSO website (.UPF file extension is omitted).

Element	Pseudopotential name
Ti	Ti.pbe-sp-van ak
Fe	Fe.pbe-sp-van
Ni	Ni.pbe-nd-rrkjus
Н	H.pbe-rrkjus
С	C.pbe-rrkjus
Ν	N.pbe-rrkjus
0	O.pbe-rrkjus
Al	Al.pbe-sp-van
Р	P.pbe-n-rrkjus_psl.0.1
S	S.pbe-n-rrkjus_psl.0.1
Cl	Cl.pbe-n-rrkjus psl.0.1
Se	Se.pbe-n-rrkjus_psl.0.2
Те	Te.pbe-dn-rrkjus psl.0.2.2

**Table S2.** List of all complexes studied in this work together with the box dimensions used in

 Quantum-ESPRESSO simulations (all distances are in units of Angstroms). The charge refers to

 the overall charge of the complex. Coordinate files of all geometries are uploaded separately.

S/N	Metal	Ligand	Geometry	Spin mult.	Charge	Q-E box dim	M-L dist	Remarks
1	Fe	OH2	Octahedral	5	+2	8	1.7	Squeezed
2	Fe	OH2	Octahedral	5	+2	8	1.9	Squeezed
3	Fe	OH2	Octahedral	5	+2	8	2.0	Squeezed
4	Fe	OH2	Octahedral	5	+2	8	2.1	Equilibrium
5	Fe	OH2	Octahedral	5	+2	8	2.2	Stretched
6	Fe	OH2	Octahedral	5	+2	10	2.3	Stretched
7	Fe	OH2	Octahedral	5	+2	10	2.5	Stretched
8	Fe	OH2	Octahedral	5	+2	10	2.7	Stretched
9	Fe	OH2	Octahedral	5	+2	10	3.1	Stretched
10	Fe	SH2	Octahedral	5	+2	8	2.6	Equilibrium
11	Fe	SeH2	Octahedral	5	+2	8	2.8	Equilibrium
12	Fe	TeH2	Octahedral	5	+2	10	3.1	Equilibrium
13	Fe	AlH3	Octahedral	5	+2	10	2.7	Constructed
14	Fe	NH3	Octahedral	5	+2	8	2.3	Equilibrium
15	Fe	PH3	Octahedral	5	+2	10	2.7	Equilibrium
16	Fe	CO	Octahedral	5	+2	10	1.8	Squeezed
17	Fe	CO	Octahedral	5	+2	10	2.0	Squeezed
18	Fe	CO	Octahedral	5	+2	10	2.3	Equilibrium
19	Fe	CO	Octahedral	5	+2	12	2.7	Stretched
20	Fe	CO	Octahedral	5	+2	12	3.0	Stretched
21	Fe	CO	Octahedral	5	+2	12	3.5	Stretched
22	Fe	Cl	Octahedral	5	-4	10	2.7	Equilibrium
23	Fe	O4	Dist. Tetrahedral	5	-2	8	2.0	Equilibrium
24	Fe	S4	Dist. Tetrahedral	5	-2	12	2.4	Equilibrium
25	Fe	Se4	Dist. Tetrahedral	5	-2	12	2.6	Equilibrium
26	Fe	OH2	Octahedral	1	+2	8	2.1	Equilibrium
27	Ni	OH2	Octahedral	3	+2	8	2.1	Equilibrium
28	Ni	NH3	Octahedral	3	+2	8	2.2	Equilibrium
29	Ni	CO	Octahedral	3	+2	10	2.2	Equilibrium
30	Ti	OH2	Octahedral	3	+2	8	2.2	Equilibrium
31	Ti	NH3	Octahedral	3	+2	8	2.3	Equilibrium
32	Ti	CO	Octahedral	3	+2	10	2.3	Equilibrium

Method	HFX	U	omega	CASPT2
q(Fe) GGA	1.52	1.49	1.52	1.49
Sp	0.33	0.013	0.25	-

**Table S3.** Comparison of CASPT2- and DFT-derived Fe Bader partial charges for the equilibrium  $[Fe(H_2O)_6]^{2+}$  (left) and  $[Fe(NH_3)_6]^{2+}$  (right) complexes.

Method	HFX	U	omega	CASPT2
q(Fe) GGA	1.37	1.31	1.38	1.62
Sp	0.38	0.013	0.30	-





**Figure S1**. Projected density of states for  $[Fe(H_2X)_6]^{2+}$  complexes (left: spin-down density, right: spin-up density, top to bottom: X = Fe to Te). In particular, we note the destabilization of the occupied ligand valence states and concomitant decreasing energetic overlap between the Fe 3*d* states and surrounding ligand valence *p* states.

S/N			a(H	IF)						U (eV	)			Omega (au)					
	0.0	0.1	0.2	0.3	0.4	Sp	0	1	2	3	4	5	Sp	0.0	0.1	0.2	0.3	0.4	Sp
1	1.449	1.465	1.481	1.495	1.508	0.148	1.526	1.524	1.525	1.527	1.528	1.531	0.0017	1.441	1.440	1.440	1.449	1.464	0.056
2	1.455	1.487	1.514	1.538	1.558	0.257	1.470	1.480	1.489	1.499	1.508	1.518	0.0095	1.455	1.457	1.471	1.496	1.523	0.170
3	1.483	1.521	1.553	1.579	1.601	0.294	1.478	1.490	1.502	1.514	1.525	1.535	0.0114	1.487	1.490	1.509	1.540	1.571	0.211
4	1.519	1.562	1.597	1.626	1.649	0.326	1.494	1.508	1.521	1.534	1.546	1.557	0.0127	1.524	1.529	1.553	1.589	1.623	0.248
5	1.550	1.598	1.637	1.667	1.692	0.354	1.514	1.529	1.543	1.556	1.568	1.578	0.0129	1.558	1.563	1.592	1.633	1.670	0.280
6	1.576	1.630	1.671	1.704	1.729	0.384	1.523	1.540	1.555	1.568	1.580	1.591	0.0135	1.586	1.592	1.626	1.672	1.711	0.314
7	1.603	1.674	1.725	1.762	1.791	0.469	1.529	1.547	1.564	1.579	1.592	1.601	0.0145	1.616	1.627	1.677	1.735	1.779	0.408
8	1.581	1.677	1.745	1.791	1.824	0.607	1.523	1.543	1.565	1.582	1.594	1.604	0.0163	1.598	1.616	1.690	1.768	1.819	0.553
9	1.417	1.538	1.679	1.782	1.834	1.042	1.508	1.534	1.562	1.586	1.601	1.606	0.0195	1.438	1.471	1.602	1.767	1.849	1.027
10	1.138	1.200	1.257	1.308	1.351	0.532	1.088	1.103	1.120	1.138	1.155	1.173	0.0169	1.147	1.160	1.215	1.285	1.347	0.501
11	0.939	1.007	1.072	1.132	1.183	0.612	1.013	1.031	1.049	1.069	1.088	1.110	0.0193	0.947	0.963	1.027	1.106	1.177	0.574
12	0.762	0.834	0.906	0.972	1.032	0.674	0.490	0.510	0.530	0.553	0.580	0.607	0.0233	0.771	0.792	0.862	0.950	1.028	0.643
13	-1.017	-0.993	-0.976	-0.969	-0.967	0.123	-1.287	-1.261	-1.240	-1.226	-1.217	-1.210	0.0156	-1.062	-1.075	-1.058	-1.004	-0.960	0.256
14	1.373	1.419	1.460	1.495	1.525	0.382	1.309	1.322	1.335	1.348	1.362	1.374	0.0131	1.379	1.384	1.412	1.457	1.500	0.303
15	1.105	1.158	1.207	1.252	1.292	0.466	0.892	0.905	0.920	0.937	0.957	0.976	0.0169	1.108	1.120	1.163	1.220	1.274	0.416
16	1.087	1.101	1.109	1.176	1.197	0.276	1.106	1.097	1.088	1.077	1.066	1.047	-0.0100	1.059	1.056	1.064	1.074	1.085	0.064
17	1.307	1.325	1.356	1.379	1.400	0.232	1.247	1.242	1.238	1.234	1.231	1.230	-0.0038	1.298	1.298	1.310	1.317	1.348	0.124
18	1.400	1.433	1.463	1.490	1.515	0.287	1.310	1.319	1.326	1.327	1.336	1.346	0.0072	1.400	1.405	1.426	1.459	1.494	0.235
19	1.433	1.499	1.557	1.603	1.638	0.513	1.366	1.380	1.396	1.408	1.422	1.447	0.0163	1.442	1.455	1.513	1.587	1.644	0.503
20	1.422	1.513	1.591	1.645	1.683	0.652	1.392	1.412	1.429	1.445	1.464	1.466	0.0179	1.441	1.464	1.546	1.643	1.704	0.659
21	1.362	1.462	1.588	1.676	1.737	0.937	1.442	1.460	1.484	1.498	1.511	1.515	0.0173	1.372	1.413	1.545	1.701	1.791	1.047
22	1.369	1.434	1.488	1.533	1.568	0.497	1.168	1.201	1.220	1.239	1.256	1.270	0.0204	1.385	1.402	1.461	1.529	1.581	0.490
23	1.265	1.339	1.403	1.455	1.498	0.584	1.194	1.217	1.238	1.259	1.280	1.300	0.0211	1.273	1.320	1.324	1.392	1.457	0.460
24	1.020	1.096	1.168	1.230	1.282	0.653	0.986	1.006	1.028	1.054	1.079	1.102	0.0233	1.033	1.049	1.116	1.204	1.280	0.617
25	0.889	0.961	1.031	1.095	1.151	0.653	0.853	0.870	0.888	0.908	0.929	0.950	0.0193	0.895	0.910	0.975	1.063	1.140	0.611
26	1.404	1.459	1.514	1.556	1.591	0.467	1.323	1.341	1.359	1.378	1.397	1.417	0.0187	1.417	1.422	1.455	1.505	1.555	0.346
27	1.425	1.479	1.526	1.563	1.595	0.425	1.392	1.403	1.415	1.426	1.439	1.452	0.0120	1.426	1.431	1.459	1.504	1.549	0.306
28	1.190	1.254	1.313	1.366	1.411	0.554	1.108	1.116	1.126	1.137	1.149	1.163	0.0110	1.191	1.197	1.233	1.291	1.353	0.405
29	1.204	1.255	1.305	1.351	1.391	0.468	1.084	1.084	1.085	1.087	1.090	1.096	0.0022	1.191	1.196	1.223	1.269	1.324	0.333
30	1.552	1.580	1.604	1.626	1.645	0.233	1.640	1.652	1.666	1.680	1.693	1.706	0.0131	1.552	1.556	1.574	1.602	1.627	0.188
31	1 4 2 6	1 4 5 1	1 4 7 8	1 506	1 5 2 4	0 246	1 505	1 513	1 5 2 5	1 530	1 5 5 2	1 566	0.0121	1 4 2 5	1 4 2 6	1 4 4 9	1 4 8 1	1 5 1 1	0.215

Table S4. List of metal partial Bader charges for all complexes at all values of tuning parameters and linearly approximated charge

sensitivities (see main text for definition). Complexes are numbered according to Table S2.



**Figure S2.** Charge sensitivity plotted against metal partial Bader charges at the GGA level of theory for full dataset (HF exchange top left, U top right,  $\omega$  bottom left). S/N 13 in Table S4 (AlH<sub>3</sub> complex) is an obvious outlier in each case and is thus omitted. Note the lack of overall correlation despite the apparent correlation among Group 16 complexes that is discussed in the main text.

**Table S5.** List of metal partial NPA charges and linearly approximated charge sensitivities. Complexes are numbered according to Table S2. NPA charges were not calculated for DFT+U simulations due to the difference in basis set formalism.

S/N			a(H	IF)			Omega (au)								
	0.0	0.1	0.2	0.3	0.4	Sp	0.0	0.1	0.2	0.3	0.4	Sp			
1	0.745	0.781	0.812	0.841	0.866	0.303	0.726	0.726	0.739	0.768	0.806	0.200			
2	1.122	1.171	1.212	1.247	1.277	0.387	1.110	1.113	1.141	1.190	1.241	0.328			
3	1.338	1.398	1.448	1.490	1.526	0.470	1.340	1.345	1.376	1.425	1.474	0.335			
4	1.406	1.469	1.521	1.564	1.600	0.485	1.412	1.418	1.453	1.506	1.557	0.363			
5	1.447	1.514	1.567	1.610	1.646	0.497	1.455	1.463	1.503	1.560	1.611	0.390			
6	1.467	1.537	1.593	1.637	1.674	0.518	1.477	1.485	1.531	1.592	1.645	0.420			
7	1.455	1.540	1.604	1.653	1.692	0.594	1.469	1.482	1.543	1.616	1.673	0.512			
8	1.401	1.508	1.588	1.646	1.690	0.724	1.419	1.439	1.523	1.616	1.681	0.657			
9	1.255	1.378	1.517	1.626	1.690	1.086	1.276	1.310	1.442	1.610	1.706	1.075			
10	0.931	1.008	1.079	1.142	1.195	0.661	0.936	0.952	1.015	1.097	1.171	0.588			
11	0.770	0.843	0.913	0.977	1.032	0.655	0.777	0.793	0.852	0.930	1.004	0.566			
12	0.581	0.652	0.720	0.784	0.840	0.648	0.591	0.608	0.667	0.743	0.816	0.563			
13	-0.152	-0.098	-0.071	-0.061	-0.058	0.235	-0.103	-0.107	-0.089	-0.055	-0.034	0.173			
14	1.330	1.390	1.442	1.487	1.525	0.487	1.334	1.341	1.378	1.433	1.488	0.386			
15	0.888	0.958	1.023	1.080	1.128	0.599	0.898	0.911	0.963	1.032	1.098	0.500			
16	0.252	0.306	0.355	0.396	0.435	0.456	0.230	0.235	0.288	0.341	0.384	0.385			
17	0.757	0.808	0.857	0.902	0.943	0.465	0.747	0.752	0.778	0.823	0.874	0.319			
18	1.057	1.120	1.175	1.221	1.261	0.508	1.058	1.065	1.104	1.165	1.226	0.421			
19	1.144	1.222	1.286	1.338	1.380	0.591	1.152	1.166	1.230	1.312	1.381	0.574			
20	1.130	1.224	1.305	1.368	1.418	0.721	1.143	1.164	1.256	1.361	1.442	0.747			
21	1.111	1.214	1.334	1.425	1.496	0.964	1.124	1.160	1.294	1.456	1.562	1.095			
22	1.110	1.221	1.312	1.385	1.443	0.832	1.144	1.188	1.299	1.400	1.474	0.825			
23	0.940	1.081	1.195	1.286	1.361	1.053	0.953	1.034	1.073	1.195	1.303	0.873			
24	0.598	0.714	0.817	0.904	0.976	0.945	0.619	0.641	0.731	0.848	0.950	0.827			
25	0.435	0.542	0.639	0.722	0.792	0.893	0.459	0.482	0.570	0.679	0.773	0.787			
26	1.197	1.279	1.360	1.424	1.478	0.703	1.221	1.229	1.276	1.350	1.424	0.506			
27	1.367	1.434	1.492	1.540	1.580	0.533	1.367	1.374	1.408	1.462	1.518	0.376			
28	1.162	1.238	1.308	1.369	1.422	0.650	1.161	1.169	1.211	1.277	1.348	0.469			
29	0.839	0.915	0.988	1.055	1.113	0.685	0.827	0.834	0.874	0.942	1.019	0.482			
30	1.156	1.205	1.248	1.287	1.321	0.413	1.149	1.153	1.183	1.228	1.273	0.311			
31	1.029	1.068	1.104	1.135	1.165	0.340	1.013	1.014	1.033	1.068	1.107	0.236			
32	0.349	0.394	0.437	0.478	0.517	0.419	0.320	0.326	0.364	0.424	0.487	0.416			



**Figure S3.** Comparison of metal GGA partial charges calculated using the NPA (y-axis) and Bader (x-axis) partitioning schemes for HF exchange (i.e., BLYP). Range-separation (i.e., PBE) yields almost identical points and is thus omitted. The problematic complexes discussed in the main text, namely compressed bonds and the  $[Ti(CO)_6]^{2+}$  complex, are indicated by red points, whereas all other complexes are indicated by blue points. The AlH<sub>3</sub> complex is also omitted due to its contrived nature. In the absence of the red points, we note that the Bader and NPA charges are strongly correlated with a slope close to 1 (the y = x line is drawn for comparison).

**Text S1.** Compressed bonds and charge sensitivity.

We consider the effect of metal-ligand bond length reduction on  $S_p$  and GGA partial charges. In both hexa-aqua and hexa-carbonyl complexes, bond length reduction leads to increased electron density on the metal center through increased hybridization, regardless of charge partitioning scheme employed (Figure 7 and NPA partial charges in Table S5). The sensitivities are reduced in a consistent manner for both complexes across all three tuning approaches to around 0.1- $0.5S_p(r_e)$ , with DFT+U showing the greatest reduction followed by HF exchange and rangeseparation (Supporting Information Table S4). If the tuning parameters required to eliminate SIE at stretched distances were applied equivalently to short distances, these reduced sensitivities would correspond to a modest 0.04-0.2 e loss from the Fe center in comparison. Negative sensitivities, i.e. further charge reduction with increasing tuning parameter, are observed only for DFT+U on hexa-carbonyl complexes (Figure 8). This divergent behavior for strong overlap at short distances in the hexa-carbonyl complexes is due to the fact that at short distances the rangeseparation parameter introduces less HF exchange, whereas the local DFT+U approach effectively applies to more molecular orbitals that have atomic 3d character. Overall, all methods show enhanced charge tuning effects for bond elongation and decreased charge tuning effects at short bond distances, which is qualitatively consistent with increased need for SIE-correction of GGA electron densities to bring them into agreement with CASPT2 as heterolytic bonds are stretched.

Text S2. Additional discussion on Bader versus NPA results.

Returning to  $[Ti(CO)_6]^{2+}$ , we observe that in this case, the charge and sensitivity with functional tuning is uniquely sensitive to the charge partitioning scheme employed. Throughout, we have applied Bader analysis, owing to the equivalence in density partitioning across all DFT

or WFT methods and basis sets studied in this work. However, we note that here and in several compressed bond cases, the NPA and Bader charge partitioning schemes diverge (see Supporting Information Table S5 and Figure S3). Namely, the NPA GGA charge of Ti is much more neutral at 0.3, whereas the Bader charge is 1.6, and NPA instead predicts positive sensitivities (see Supporting Information Table S5). Such reduced sensitivities that were observed for compressed bonds also suffer from the same charge-partitioning ambiguity (Figure 8 and Supporting Information Table S5). Although partial charges are known<sup>1-2</sup> to be sensitive to the partitioning scheme employed, with ongoing debate regarding the best scheme to choose<sup>1-4</sup>, we note that the influence of this choice on charge sensitivities only become significant here when the division between the metal and ligand atom becomes ambiguous due to strong or short bonds, i.e., Ti-C in strong-field carbonyl complexes or r < 90% of  $r_e$  in other complexes.

In general, differences in predictions of charge partitioning schemes can be attributed to differences in how the shared electron density is distributed between metal and ligand. Among the Ti(II) complexes, there is significant variability in the Ti character of the Ti-L bonding NBOs: at the GGA level of theory, the Ti-C bonding NBOs in  $[Ti(CO)_6]^{2+}$  have about 17% Ti character whereas the Ti-N and Ti-O bonding NBOs in  $[Ti(NH_3)_6]^{2+}$  and  $[Ti(H_2O)_6]^{2+}$  respectively have 8% and 6% Ti character respectively, consistent with a relatively low Ti partial charge in  $[Ti(CO)_6]^{2+}$  (0.3 versus 1.0 and 1.2 respectively). In contrast, the Bader charges show much less variability across ligands (1.6, 1.4 and 1.6). Furthermore, as the Ti character decreases with increasing tuning parameter, the difference in NPA and Bader charge sensitivity is likely a result of the charge assigned to Ti by the NBO maximum-occupancy scheme decreasing without a concomitant shift of electron density across the zero-flux surface. The effect of shifts in the zero-flux boundaries were found to be negligible as the Bader partial charges were found to be in

near-quantitative agreement to partial charges computed based on fixed Voronoi (closestdistance) cells using the Voronoi option of the BADER program.



**Figure S4.** Variation of LUMO error (au) with  $a_{HF}$  (top left), U (top right) and  $\omega$  (bottom left) for the  $[Fe(H_2S)_6]^{2+}$  complex. The best-fit curves (top left/bottom left) and lines (top right) are also shown. The  $p^*$  values that eliminate curvature (i.e, LUMO error = 0) are the smallest zero(s) of the best-fit equations and solved analytically. Some of us have previously justified the linear extrapolation of the LUMO error as a function of U (see Figure 6 of ref. <sup>5</sup>). In practice, extension of the line to larger values of U is ambiguous due to shifts in orbital ordering (as discussed in previous work<sup>5</sup>) and convergence difficulties at large U.

**Table S6.** CASPT2- and DFT-derived Fe magnetic moments (in  $\mu_B$ ) for the equilibrium  $[Fe(H_2O)_6]^{2+}$  (top left), stretched  $[Fe(H_2O)_6]^{2+}$  (top right) and equilibrium  $[Fe(NH_3)_6]^{2+}$  (bottom left) complexes. The values of *p* correspond to  $a_{HF}$  (HFX), U (fractions of 10 eV) and  $\omega$  (bohr<sup>-1</sup>) as described in the main text.

	HFX	U	omega	CASPT2
p = 0.0	3.66	3.72	3.68	
p = 0.1	3.71	3.75	3.68	
p = 0.2	3.75	3.77	3.71	
p = 0.3	3.77	3.79	3.75	3.88
p = 0.4	3.80	3.81	3.78	
p = 0.5	-	3.84	-	
Sp	0.33	0.02	0.26	

<b>T2</b>		HFX	U	omega	CASPT2
	p = 0.0	3.53	3.77	3.56	
	p = 0.1	3.64	3.84	3.59	
	p = 0.2	3.79	3.91	3.71	
3	p = 0.3	3.89	4.01	3.86	3.95
	p = 0.4	3.91	4.09	3.91	
	p = 0.5	I	4.13	-	
	Sp	0.96	0.07	0.89	

	HFX	U	omega	CASPT2
p = 0.0	3.64	3.72	3.66	
p = 0.1	3.69	3.74	3.67	
p = 0.2	3.73	3.77	3.69	
p = 0.3	3.76	3.79	3.73	3.87
p = 0.4	3.78	3.82	3.76	
p = 0.5	-	3.84	_	
Sp	0.34	0.02	0.25	

**Table S7.** Energetic components of the LUMO error for subset of 15 complexes (numbered according to Table S2). All energies are in units of Hartrees. The blank entries for S/N 11 and 16 DFT+U arise as a result of lack of 3d AO character in the LUMO as discussed in the main text. Entries in bold correspond to use of non-LUMO orbitals, i.e. LUMO+1 or LUMO+2, in the tuning procedure due to LUMO eigenvalue crossing as described in the main text.

		E(3+ LUMO)														
Param	Val	4	10	11	12	14	15	18	22	7	1	16	19	30	31	32
	0	-0.747	-0.668	-0.639	-0.588	-0.689	-0.640	-0.828	0.216	-0.729	-0.720	-0.889	-0.797	-0.675	-0.630	-0.775
	0.1	-0.738	-0.643	-0.612	-0.561	-0.663	-0.611	-0.809	0.229	-0.749	-0.696	-0.874	-0.791	-0.666	-0.614	-0.763
	0.2	-0.725	-0.623	-0.599	-0.554	-0.640	-0.584	-0.790	0.231	-0.755	-0.671	-0.859	-0.792	-0.654	-0.598	-0.750
	0.3	-0.710	-0.612	-0.592	-0.548	-0.617	-0.571	-0.773	0.235	-0.763	-0.646	-0.842	-0.792	-0.642	-0.582	-0.737
HFX (%)	0.4	-0.693	-0.603	-0.584	-0.544	-0.596	-0.559	-0.756	0.241	-0.770	-0.619	-0.825	-0.793	-0.628	-0.564	-0.723
	0	-0.744	-0.629		-0.542	-0.677	-0.630	-0.813	0.260	-0.741	-0.676		-0.797	-0.654	-0.595	-0.750
	1	-0.738	-0.616		-0.521	-0.661	-0.611	-0.797	0.266	-0.736	-0.670		-0.779	-0.648	-0.584	-0.734
U (eV)	2	-0.731	-0.600		-0.499	-0.645	-0.592	-0.780	0.271	-0.733	-0.663		-0.759	-0.643	-0.571	-0.720
	0	-0.744	-0.666	-0.636	-0.585	-0.685	-0.636	-0.823	0.215	-0.726	-0.716	-0.887	-0.792	-0.673	-0.630	-0.773
	0.1	-0.694	-0.617	-0.587	-0.535	-0.634	-0.585	-0.772	0.264	-0.677	-0.663	-0.838	-0.744	-0.623	-0.577	-0.722
	0.2	-0.664	-0.583	-0.553	-0.506	-0.596	-0.545	-0.737	0.287	-0.658	-0.622	-0.808	-0.727	-0.591	-0.542	-0.687
	0.3	-0.650	-0.564	-0.544	-0.502	-0.569	-0.514	-0.714	0.283	-0.672	-0.592	-0.789	-0.730	-0.575	-0.519	-0.665
w (au)	0.4	-0.641	-0.560	-0.543	-0.502	-0.548	-0.509	-0.698	0.278	-0.694	-0.569	-0.774	-0.738	-0.564	-0.504	-0.654
									E(3+)							r
Param	Val	4	10	11	12	14	15	18	22	7	1	16	19	30	31	32
	0	-580.867	-2518.440	-184.844	-177.822	-461.796	-2181.034	-801.975	-2884.490	-580.786	-580.619	-801.546	-801.932	-515.631	-396.528	-736.722
	0.1	-580.869	-2518.540	-184.812	-177.785	-461.811	-2181.136	-801.975	-2884.600	-580.786	-580.663	-801.534	-801.925	-515.644	-396.552	-736.729
	0.2	-580.877	-2518.644	-184.782	-177.751	-461.828	-2181.241	-801.980	-2884.715	-580.766	-580.651	-801.527	-801.923	-515.661	-396.577	-736.741
	0.3	-580.889	-2518.751	-184.755	-177.718	-461.849	-2181.349	-801.988	-2884.834	-580.766	-580.671	-801.527	-801.925	-515.681	-396.604	-736.756
HFX (%)	0.4	-580.905	-2518.860	-184.729	-177.686	-461.871	-2181.459	-802.002	-2884.956	-580.769	-580.695	-801.532	-801.932	-515.703	-396.633	-736.775
	0	-226.254	-198.235	-212.845	-774.808	-193.614	-180.585	-252.687	-228.497	-226.259	-226.101	-252.403	-252.704	-160.113	-127.737	-186.752
	1	-226.240	-198.223	-212.832	-774.799	-193.604	-180.576	-252.677	-228.482	-226.245	-226.083	-252.384	-252.695	-160.092	-127.718	-186.731
U (eV)	2	-226.227	-198.213	-212.823	-774.791	-193.595	-180.567	-252.667	-228.468	-226.233	-226.066	-252.365	-252.686	-160.071	-127.700	-186.712
	0	-580.386	-2517.515	-184.805	-177.774	-461.377	-2180.112	-801.257	-2883.486	-580.287	-580.139	-800.854	-801.208	-515.147	-396.120	-736.016
	0.1	-580.402	-2517.540	-184.831	-177.799	-461.399	-2180.142	-801.280	-2883.509	-580.311	-580.174	-800.876	-801.228	-515.164	-396.142	-736.038
	0.2	-580.454	-2517.602	-184.867	-177.823	-461.464	-2180.218	-801.342	-2883.567	-580.339	-580.220	-800.931	-801.282	-515.219	-396.208	-736.101
( )	0.3	-580.524	-2517.674	-184.885	-177.826	-461.541	-2180.304	-801.405	-2883.641	-580.392	-580.301	-800.983	-801.334	-515.291	-396.285	-736.162
w (au)	0.4	-580.595	-2517.747	-184.890	-177.815	-461.609	-2180.390	-801.444	-2883./22	-580.449	-580.383	-801.016	-801.364	-515.364	-396.352	-736.200
Damage	14-1		10		42		45	10	E(2+)	-		40	10	20	24	22
Param	vai	4	10	105 405	170.242	14	15	18	22	7 F01 422	L	16	19	30	31	32
	0 1	-301.407 E01 E02	2519.022	105.405	170.342	462.302	2101.309	-002.091 002.701	2004.190	-301.422 E01.4E2	-301.190	°02.331	-002.045	-510.109 E16 102	207.029	727 401
	0.1	-581.505	-2519.131	-105.301	-170.311	-402.383	-2181.030	-802.701	-2004.317	-581.453	-501.241	-802.322	-802.033	-516 217	-207 090	-727 /19
	0.2	-501.522	-2519.244	-105.301	-178 261	-402.410	-2101.007	-802.710	-2004.440	-501.452	-501.220	-802.317	-802.071	-516 244	-207 124	-727 /20
	0.3	-J01.J4J	2519.300	105.343	170.201	402.437	2101.921	902.734	2004.301	-J01.471	-J01.240	902.320	902.03Z	-J10.244	207 157	737.435
ΠFA (70)	0.4	-361.300	100 750	212 215	775 265	104 152	101 117	252 274	2004.717	226 906	-361.270	252 177	252 206	160 627	129 202	107 202
	1	220.035	100 750	212 209	775 255	104 146	101.117	253.374	220.141	220.090	220.032	253.177	253.390	160 612	120.205	107.393
11 (0)/)	2	-226.8/1	-198 7/12	-213 301	-775 2/10	-19/ 1/0	-181 100	-253 350	-220.135	-226.891	-226 621	-253.130	-253.392	-160 500	-128 174	-187 351
0 (61)	0	-581 002	-2518 006	-185 364	-178 201	-161 9/0	-2180 662	-801 969	-220.129	-580 921	-580 715	-801 629	-203.300	-515 684	-396 620	-736 691
	0 1	-581 022	-2518 125	-185 304	-178 321	-461.940	-2180.005	-801.908	-2882 21/	-580.921	-580 7/10	-801.662	-801 9/0	-515 702	-396 6/2	-736 705
	0.1	-581 097	-2518 201	-185 ///	-178 250	-462 020	-2180.090	-802.064	-2882 202	-581 002	-580 704	-801 724	-802 012	-515 767	-396 716	-736 770
	0.2	-581 174	-2518 299	-185 / 70	-178 376	-462.039	-2180.781	-802.000	-2883 301	-581 080	-580 891	-801 792	-802.013	-515 852	-396 802	-736 829
w (211)	0.5	-501.1/4	-2510.200	-105.479	-170.370	402.129	-2100.078	-902.143	-2003.391	-591 175	-580.064	-001.703	-902.092	-515 026	-350.003	726 994
w (au)	0.4	-201.201	-2310.3/0	-105.499	-1/0.3/8	1-402.209	-2100.974	-002.197	-2003.495	-201.1/2	-200.904	-001.020	-002.148	-212.230	-220.000	-/30.884

**Table S8.** LUMO errors and critical parameter values  $(p^*)$  for subset of 15 complexes (numbered according to Table S2). According to the sign convention we have adopted, the LUMO error starts negative and increases with tuning parameter. All energies are in units of Hartrees. The blank entries for S/N 11 and 16 DFT+U arise as a result of lack of 3*d* AO character in the LUMO as discussed in the main text. Critical parameter values were determined by fitting of the LUMO errors to linear (U)/quadratic (HFX and  $\omega$ ) functions and subsequent interpolation/extrapolation (see Figure S4 below for an illustration).

								LL	JMO err	or						
Param	Val	4	10	11	12	14	15	18	22	7	1	16	19	30	31	32
	0	-0.127	-0.086	-0.078	-0.068	-0.123	-0.085	-0.112	-0.084	-0.093	-0.142	-0.104	-0.086	-0.137	-0.129	-0.109
	0.1	-0.105	-0.052	-0.043	-0.035	-0.089	-0.051	-0.083	-0.054	-0.082	-0.118	-0.085	-0.062	-0.118	-0.108	-0.091
	0.2	-0.080	-0.023	-0.021	-0.020	-0.059	-0.018	-0.054	-0.037	-0.070	-0.094	-0.069	-0.044	-0.098	-0.085	-0.073
	0.3	-0.056	-0.003	-0.003	-0.005	-0.028	0.002	-0.027	-0.018	-0.058	-0.070	-0.049	-0.026	-0.078	-0.062	-0.054
HFX (%)	0.4	-0.031	0.016	0.015	0.010	0.000	0.021	-0.001	0.002	-0.046	-0.044	-0.031	-0.009	-0.057	-0.039	-0.034
	0	-0.143	-0.106		-0.084	-0.139	-0.099	-0.125	-0.096	-0.104	-0.124		-0.104	-0.140	-0.130	-0.109
	1	-0.130	-0.090		-0.065	-0.119	-0.080	-0.106	-0.081	-0.090	-0.116		-0.082	-0.127	-0.114	-0.094
U (eV)	2	-0.116	-0.071		-0.042	-0.100	-0.059	-0.089	-0.068	-0.077	-0.108		-0.057	-0.115	-0.098	-0.080
	0	-0.127	-0.085	-0.078	-0.067	-0.122	-0.085	-0.111	-0.084	-0.092	-0.141	-0.103	-0.085	-0.136	-0.130	-0.107
	0.1	-0.074	-0.032	-0.024	-0.013	-0.069	-0.031	-0.058	-0.031	-0.037	-0.087	-0.051	-0.032	-0.084	-0.076	-0.056
	0.2	-0.032	0.016	0.025	0.029	-0.021	0.018	-0.013	0.012	0.006	-0.045	-0.015	0.005	-0.043	-0.034	-0.017
	0.3	0.000	0.051	0.050	0.048	0.019	0.059	0.024	0.034	0.025	-0.013	0.010	0.028	-0.014	-0.001	0.011
w (au)	0.4	0.024	0.069	0.066	0.061	0.052	0.075	0.056	0.051	0.032	0.013	0.030	0.047	0.008	0.024	0.031
			-	-			-	-	р*		-				-	-
Para	m	4	10	11	12	14	15	18	22	7	1	16	19	30	31	32
HFX (9	%)	0.525	0.308	0.304	0.319	0.402	0.286	0.403	0.397	0.769	0.570	0.564	0.469	0.670	0.562	0.561
U (e\	/)	10.56	6.06		3.99	7.12	5.02	6.83	6.96	7.70	15.09		4.46	11.25	8.11	7.50
w (au	(L	0.297	0.163	0.146	0.128	0.251	0.156	0.232	0.172	0.189	0.344	0.249	0.187	0.358	0.301	0.254



**Figure S5.** Comparison of tuning parameter values that eliminate curvature (i.e, LUMO error = 0) among tuning procedures (global HF exchange, DFT+U and range separation). The left and right figures respectively show U\* (eV) vs  $a_{HF}^*$  and  $\omega$  (bohr<sup>-1</sup>) vs  $a_{HF}^*$ .



**Figure S6.** Comparison of charge loss at point of curvature elimination among tuning procedures (global HF exchange, DFT+U and range separation). A positive value indicates net loss of electrons from metal to ligands (according to the Bader partitioning scheme). The left and right figures respectively show U-tuning vs global exact exchange tuning and range separation tuning vs global exact exchange tuning. Removal of the outliers discussed in the main text (red points) results in stronger correlations.

**Table S9.** List of charge loss at point of curvature elimination for all complexes/methods in the tuning subset. Complexes are numbered according to Table S2. The blank entries for S/N 11 and 16 DFT+U arise as a result of lack of 3d AO character in the LUMO as discussed in the main text.

	e- loss for curv elim		
S/N	HFX	U	Omega
4	0.171	0.134	0.074
10	0.164	0.102	0.082
11	0.186		0.084
12	0.215	0.093	0.082
14	0.153	0.093	0.076
15	0.133	0.085	0.065
18	0.115	0.049	0.055
22	0.197	0.142	0.084
7	0.361	0.112	0.077
1	0.085	0.026	0.019
16	0.156		0.016
19	0.241	0.072	0.094
30	0.156	0.147	0.067
31	0.138	0.098	0.065
32	0.026	-0.039	-0.002

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