Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Competition between the Heavy Atom Effect and Vibronic Coupling in Donor-Bridge-Acceptor Organometallics: Supporting Information.

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S1 Experimental Data

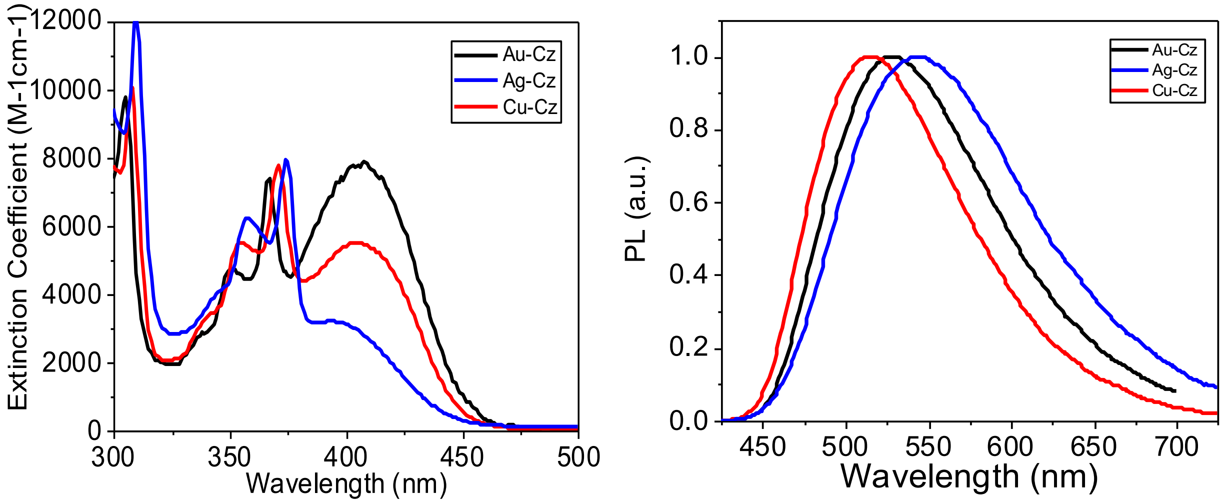

Figure S1: Experimental absorption (left) and normalised luminescence spectra of 0.5mg/ml of **Au-Cz** (blue), **Ag-Cz** (black) and **Cu-Cz** (red) recorded in toluene solution at 300 K.

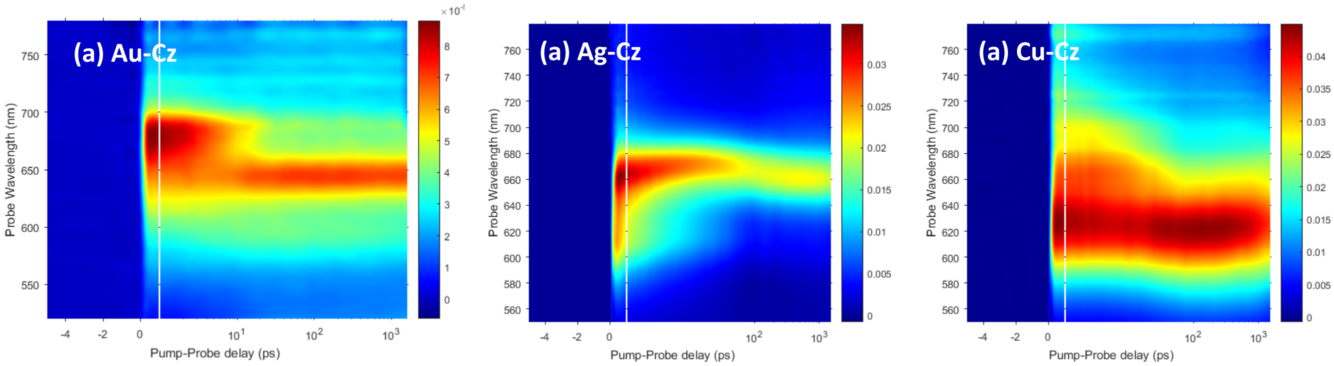

Figure S2: Transient Absorption of **Au-Cz** (left), **Ag-Cz** (middle) and **Cu-Cz** (right) in toluene on picosecond-microsecond time scales. The initial excited state absorption associated with the singlet is at centred around 680 nm for **Au-Cz**, 670 nm for **Ag-Cz**, 640 nm for **Cu-Cz**. Method as described in ref.[1]. The ISC is evidenced by the growth a new PIA spectrum, whose peak is red-shifted versus the singlet PIA, and the loss of the original singlet PIA feature. Excitation at 400nm, corresponding to direct excitation of the charge-transfer absorption band.

S2 Ag-Cz coordinates

S1 GS – Co-planar

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	3.260	-3.528	1.095	H	-0.805	-1.893	5.807	H	-0.422	-4.714	3.409
C	1.915	-3.857	1.200	H	-0.167	-2.925	4.513	H	-0.309	-5.518	1.832
C	0.982	-2.965	1.740	H	-1.582	-1.882	4.208	H	-1.866	-4.876	2.380
C	1.460	-1.721	2.208	H	-1.049	3.034	4.995	H	4.474	-0.550	4.133
C	2.812	-1.338	2.049	H	-1.208	4.377	3.863	H	4.871	1.071	3.508
C	3.693	-2.271	1.495	H	0.457	1.290	4.818	H	5.457	-0.369	2.665
N	0.219	0.127	-1.951	H	-1.069	0.553	5.317	H	2.656	0.916	0.455
C	-0.090	0.132	2.173	H	0.419	2.726	2.976	H	4.335	0.342	0.432
C	-0.885	0.995	3.139	H	-2.632	-0.329	3.098	H	3.927	1.855	1.279
C	-0.320	0.570	4.516	H	2.330	-0.141	4.905	C	1.061	-0.684	-2.673
C	0.326	-0.805	4.336	H	2.116	-1.914	4.908	C	0.896	-0.483	-4.076
C	-2.422	0.747	2.979	H	1.393	-0.922	6.194	C	-0.124	0.526	-4.203
C	-3.188	1.539	4.047	H	-2.431	0.633	0.796	C	-0.499	0.858	-2.867
Ag	0.058	0.184	0.100	H	-4.000	0.984	1.526	C	-1.489	1.826	-2.636
C	-2.919	3.038	3.880	H	-3.258	4.567	2.372	C	-0.743	1.161	-5.286
C	-1.413	3.301	3.990	H	-4.507	3.312	2.422	C	1.665	-1.217	-4.986
C	-0.663	2.519	2.901	H	1.572	-4.825	0.830	C	1.996	-1.620	-2.201
C	-3.420	3.484	2.504	H	-0.983	4.065	1.433	C	2.747	-2.336	-3.125
C	-2.675	2.704	1.417	H	-0.624	2.495	0.717	H	2.129	-1.781	-1.127
C	-1.176	2.984	1.536	H	2.555	0.601	2.912	H	3.478	-3.067	-2.767
C	-2.921	1.203	1.601	H	-0.808	-2.415	-0.279	C	-2.089	2.443	-3.726
N	0.557	-0.788	2.844	H	-2.064	-3.583	0.206	H	-1.782	2.086	-1.615
C	-0.615	-1.945	4.725	H	-0.472	-4.154	-0.345	H	-2.862	3.198	-3.556
C	1.624	-0.953	5.119	H	4.741	-1.995	1.358	C	2.588	-2.140	-4.509
C	-0.489	-3.344	1.688	H	-4.266	1.335	3.932	H	1.542	-1.065	-6.063
C	-0.782	-4.682	2.370	H	-2.924	1.209	5.065	H	3.195	-2.719	-5.211
C	3.333	0.058	2.355	H	-3.449	3.596	4.670	C	-1.723	2.118	-5.045
C	3.574	0.835	1.057	H	-3.033	3.015	0.422	H	-0.459	0.908	-6.311
C	4.598	0.045	3.216	H	-1.060	-2.563	2.209	H	-2.213	2.621	-5.882
C	-0.983	-3.372	0.237	H	3.967	-4.242	0.668				

Table S1: Cartesian coordinates of the ground state co-planar minimum of **Ag-Cz**.

S2 S_1 – perpendicular

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	3.153	-3.839	1.379	H	-1.962	-1.592	5.301	H	-0.708	-4.795	3.413
C	1.805	-4.129	1.321	H	-1.384	-2.869	4.233	H	-0.462	-5.726	1.939
C	0.848	-3.221	1.768	H	-2.230	-1.469	3.556	H	-2.053	-5.050	2.292
C	1.268	-1.994	2.313	H	-0.324	2.982	5.032	H	3.965	-1.194	4.713
C	2.643	-1.682	2.348	H	0.104	4.352	4.019	H	4.525	0.445	4.342
C	3.561	-2.615	1.880	H	0.530	0.873	4.816	H	5.183	-0.932	3.465
N	0.000	0.000	-2.166	H	-1.185	0.650	5.120	H	2.824	0.721	1.023
C	-0.060	0.054	2.054	H	1.154	2.288	3.136	H	4.461	0.037	1.166
C	-0.641	1.096	3.010	H	-2.715	0.486	2.751	H	4.017	1.482	2.088
C	-0.393	0.457	4.397	H	1.742	-1.094	5.186	C	1.038	0.298	-2.995
C	-0.188	-1.044	4.187	H	0.997	-2.686	4.971	C	0.656	0.234	-4.364
C	-2.145	1.421	2.744	H	0.373	-1.574	6.194	C	-0.747	-0.137	-4.344
C	-2.713	2.374	3.801	H	-1.978	1.430	0.587	C	-1.074	-0.260	-2.966
Ag	0.000	0.000	0.000	H	-3.392	2.277	1.207	C	-2.365	-0.602	-2.561
C	-1.942	3.692	3.782	H	-1.571	5.309	2.393	C	-1.704	-0.360	-5.304
C	-0.461	3.412	4.035	H	-3.164	4.569	2.228	C	1.574	0.501	-5.351
C	0.088	2.469	2.956	H	1.482	-5.080	0.913	C	2.344	0.627	-2.627
C	-2.106	4.352	2.416	H	0.480	4.091	1.590	C	3.256	0.896	-3.634
C	-1.561	3.418	1.338	H	0.339	2.518	0.811	H	2.625	0.664	-1.582
C	-0.081	3.148	1.602	H	2.328	0.160	3.336	H	4.276	1.154	-3.379
C	-2.325	2.096	1.382	H	-0.754	-2.809	-0.424	C	-3.318	-0.826	-3.542
N	0.325	-1.053	2.807	H	-2.045	-3.940	0.014	H	-2.605	-0.683	-1.509
C	-1.521	-1.791	4.320	H	-0.425	-4.543	-0.352	H	-4.328	-1.093	-3.257
C	0.795	-1.634	5.188	H	4.620	-2.382	1.915	C	2.881	0.835	-4.973
C	-0.612	-3.583	1.599	H	-3.772	2.561	3.586	H	1.305	0.457	-6.400
C	-0.978	-4.857	2.357	H	-2.678	1.931	4.800	H	3.615	1.048	-5.741
C	3.165	-0.357	2.865	H	-2.330	4.357	4.563	C	-2.997	-0.708	-4.891
C	3.647	0.523	1.713	H	-1.684	3.881	0.352	H	-1.477	-0.272	-6.360
C	4.270	-0.525	3.905	H	-1.199	-2.756	1.997	H	-3.761	-0.886	-5.637
C	-0.977	-3.727	0.123	H	3.885	-4.559	1.030				

Table S2: Cartesian coordinates of the S_1 perpendicular minimum of **Ag-Cz**.

S3 T$_1$ – Co-planar

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	2.717	-4.075	1.204	H	-1.735	-1.491	5.519	H	-1.132	-4.666	3.374
C	1.343	-4.210	1.218	H	-1.302	-2.772	4.389	H	-1.099	-5.543	1.847
C	0.520	-3.200	1.712	H	-2.196	-1.354	3.819	H	-2.558	-4.681	2.328
C	1.108	-2.034	2.237	H	-0.172	3.065	5.045	H	3.982	-1.453	4.491
C	2.509	-1.872	2.181	H	0.157	4.438	4.000	H	4.745	0.066	3.998
C	3.288	-2.904	1.669	H	0.730	0.938	4.764	H	5.154	-1.435	3.175
N	0.221	0.106	-2.130	H	-0.954	0.752	5.217	H	2.935	0.430	0.750
C	-0.047	0.128	2.079	H	1.188	2.394	3.054	H	4.493	-0.408	0.887
C	-0.584	1.164	3.062	H	-2.659	0.503	2.956	H	4.220	1.102	1.766
C	-0.233	0.536	4.429	H	1.919	-1.037	5.065	C	1.007	-0.702	-2.893
C	-0.084	-0.971	4.224	H	1.144	-2.623	4.919	C	0.797	-0.480	-4.282
C	-2.112	1.449	2.903	H	0.631	-1.499	6.181	C	-0.211	0.561	-4.348
C	-2.627	2.400	3.988	H	-2.079	1.428	0.747	C	-0.511	0.866	-2.992
Ag	0.093	0.120	0.024	H	-3.477	2.252	1.437	C	-1.457	1.839	-2.664
C	-1.886	3.733	3.908	H	-1.665	5.347	2.478	C	-0.860	1.223	-5.364
C	-0.385	3.486	4.057	H	-3.242	4.560	2.440	C	1.498	-1.211	-5.211
C	0.109	2.550	2.949	H	0.892	-5.117	0.828	C	1.919	-1.660	-2.444
C	-2.167	4.375	2.551	H	0.357	4.180	1.558	C	2.617	-2.387	-3.395
C	-1.675	3.445	1.445	H	0.213	2.604	0.789	H	2.063	-1.827	-1.383
C	-0.173	3.221	1.607	H	2.462	0.027	3.118	H	3.329	-3.138	-3.075
C	-2.397	2.103	1.549	H	-1.118	-2.514	-0.374	C	-2.101	2.496	-3.701
N	0.306	-1.008	2.804	H	-2.514	-3.499	0.086	H	-1.674	2.066	-1.629
C	-1.409	-1.691	4.494	H	-0.997	-4.280	-0.376	H	-2.841	3.254	-3.476
C	0.971	-1.568	5.144	H	4.366	-2.788	1.641	C	2.414	-2.168	-4.755
C	-0.979	-3.383	1.610	H	-3.701	2.566	3.841	H	1.354	-1.062	-6.275
C	-1.466	-4.636	2.335	H	-2.521	1.968	4.987	H	2.972	-2.752	-5.476
C	3.208	-0.606	2.634	H	-2.232	4.397	4.709	C	-1.810	2.195	-5.028
C	3.746	0.174	1.435	H	-1.878	3.901	0.469	H	-0.649	1.005	-6.405
C	4.332	-0.877	3.632	H	-1.443	-2.510	2.067	H	-2.329	2.724	-5.819
C	-1.425	-3.422	0.150	H	3.342	-4.877	0.825				

Table S3: Cartesian coordinates of the T$_1$ co-planar minimum of **Ag-Cz**.

S4 T_1 – perpendicular

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	3.025	-3.916	1.314	H	-1.696	-1.569	5.494	H	-0.828	-4.735	3.428
C	1.664	-4.144	1.301	H	-1.159	-2.837	4.394	H	-0.658	-5.641	1.927
C	0.762	-3.190	1.768	H	-2.123	-1.484	3.781	H	-2.206	-4.900	2.331
C	1.256	-1.979	2.288	H	-0.395	3.046	4.995	H	4.032	-1.183	4.602
C	2.644	-1.725	2.265	H	-0.132	4.431	3.945	H	4.698	0.383	4.110
C	3.504	-2.706	1.782	H	0.634	0.998	4.742	H	5.228	-1.094	3.311
N	0.143	0.065	-2.147	H	-1.039	0.713	5.182	H	2.926	0.603	0.839
C	-0.050	0.095	2.065	H	1.030	2.443	3.026	H	4.534	-0.143	0.986
C	-0.667	1.113	3.023	H	-2.697	0.330	2.885	H	4.165	1.353	1.858
C	-0.297	0.529	4.406	H	1.933	-0.895	5.117	C	1.206	0.278	-2.972
C	-0.050	-0.967	4.228	H	1.261	-2.528	4.982	C	0.833	0.209	-4.343
C	-2.205	1.307	2.834	H	0.649	-1.416	6.210	C	-0.590	-0.076	-4.330
C	-2.791	2.232	3.907	H	-2.125	1.290	0.677	C	-0.937	-0.148	-2.954
Ag	0.091	0.082	0.012	H	-3.591	2.017	1.339	C	-2.250	-0.409	-2.557
C	-2.129	3.605	3.832	H	-1.977	5.224	2.399	C	-1.549	-0.266	-5.296
C	-0.618	3.450	4.002	H	-3.509	4.352	2.341	C	1.774	0.398	-5.326
C	-0.056	2.536	2.906	H	1.286	-5.082	0.909	C	2.527	0.531	-2.599
C	-2.427	4.226	2.469	H	0.122	4.168	1.506	C	3.463	0.720	-3.602
C	-1.867	3.322	1.374	H	0.067	2.580	0.747	H	2.804	0.571	-1.553
C	-0.358	3.182	1.556	H	2.442	0.172	3.177	H	4.495	0.919	-3.341
C	-2.505	1.939	1.473	H	-0.867	-2.674	-0.370	C	-3.204	-0.599	-3.543
N	0.373	-1.001	2.818	H	-2.206	-3.740	0.087	H	-2.502	-0.461	-1.505
C	-1.334	-1.764	4.480	H	-0.631	-4.425	-0.328	H	-4.230	-0.804	-3.263
C	1.017	-1.482	5.183	H	4.572	-2.518	1.776	C	3.096	0.657	-4.943
C	-0.716	-3.485	1.639	H	-3.871	2.335	3.743	H	1.511	0.350	-6.376
C	-1.123	-4.759	2.377	H	-2.675	1.810	4.909	H	3.849	0.808	-5.708
C	3.243	-0.410	2.719	H	-2.525	4.249	4.625	C	-2.863	-0.530	-4.890
C	3.750	0.397	1.526	H	-2.082	3.756	0.391	H	-1.307	-0.215	-6.352
C	4.360	-0.591	3.744	H	-1.256	-2.643	2.068	H	-3.629	-0.682	-5.641
C	-1.126	-3.586	0.170	H	3.711	-4.673	0.951				

Table S4: Cartesian coordinates of the T_1 perpendicular minimum of **Ag-Cz**.

S3 Cu-Cz coordinates

S1 GS – Co-planar

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	3.666	-3.246	1.135	H	-0.695	-2.117	5.629	H	-0.010	-4.915	3.067
C	2.356	-3.705	1.151	H	0.070	-3.036	4.318	H	0.221	-5.564	1.430
C	1.310	-2.909	1.632	H	-1.438	-2.128	4.014	H	-1.397	-5.088	1.963
C	1.635	-1.628	2.123	H	-1.344	2.896	4.823	H	4.568	-0.071	4.062
C	2.948	-1.111	2.043	H	-1.478	4.220	3.665	H	4.696	1.584	3.411
C	3.951	-1.951	1.553	H	0.183	1.207	4.798	H	5.452	0.237	2.551
N	0.199	0.108	-1.757	H	-1.279	0.275	5.121	H	2.346	1.035	0.497
C	-0.094	0.051	2.045	H	0.271	2.621	2.917	H	4.098	0.787	0.366
C	-0.977	0.843	2.991	H	-2.660	-0.548	2.857	H	3.467	2.212	1.236
C	-0.472	0.420	4.391	H	2.237	0.007	4.873	C	-0.616	0.664	-2.716
C	0.340	-0.867	4.214	H	2.222	-1.777	4.855	C	-0.135	0.389	-4.030
C	-2.487	0.536	2.739	H	1.340	-0.886	6.114	C	1.059	-0.395	-3.847
C	-3.350	1.306	3.746	H	-2.312	0.407	0.572	C	1.207	-0.537	-2.437
Cu	0.032	0.138	0.134	H	-3.958	0.688	1.161	C	2.281	-1.269	-1.910
C	-3.131	2.813	3.579	H	-3.420	4.315	2.035	C	1.993	-0.976	-4.713
C	-1.649	3.137	3.791	H	-4.621	3.015	2.011	C	-0.828	0.865	-5.149
C	-0.795	2.374	2.768	H	2.130	-4.700	0.761	C	-1.790	1.412	-2.544
C	-3.550	3.228	2.168	H	-1.051	3.882	1.242	C	-2.464	1.874	-3.668
C	-2.702	2.468	1.145	H	-0.605	2.296	0.599	H	-2.165	1.621	-1.540
C	-1.224	2.799	1.362	H	2.454	0.752	2.952	H	-3.381	2.456	-3.542
C	-2.901	0.959	1.324	H	-0.436	-2.270	-0.360	C	3.195	-1.838	-2.789
N	0.621	-0.803	2.735	H	-1.596	-3.604	-0.108	H	2.389	-1.389	-0.830
C	-0.479	-2.113	4.550	H	0.073	-3.949	-0.633	H	4.036	-2.411	-2.388
C	1.615	-0.880	5.049	H	4.974	-1.576	1.480	C	-1.991	1.606	-4.964
C	-0.119	-3.403	1.479	H	-4.411	1.056	3.571	H	-0.462	0.654	-6.157
C	-0.332	-4.816	2.019	H	-3.132	0.998	4.782	H	-2.542	1.981	-5.830
C	3.275	0.342	2.345	H	-3.736	3.357	4.324	C	3.058	-1.694	-4.182
C	3.300	1.141	1.038	H	-3.000	2.762	0.126	H	1.885	-0.867	-5.796
C	4.567	0.526	3.137	H	-0.772	-2.725	2.045	H	3.794	-2.152	-4.847
C	-0.543	-3.302	0.011	H	4.466	-3.888	0.760				

Table S5: Cartesian coordinates of the ground state co-planar minimum of **Cu-Cz**.

S2 GS – Perpendicular

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	3.897	-3.237	1.502	H	-1.009	-2.054	5.538	H	0.077	-4.943	3.159
C	2.602	-3.726	1.408	H	-0.135	-3.027	4.339	H	0.501	-5.640	1.582
C	1.499	-2.955	1.793	H	-1.552	-2.060	3.845	H	-1.177	-5.190	1.918
C	1.749	-1.666	2.303	H	-1.373	2.950	4.602	H	4.511	-0.081	4.495
C	3.054	-1.125	2.353	H	-1.407	4.235	3.395	H	4.639	1.588	3.879
C	4.115	-1.940	1.952	H	0.160	1.228	4.728	H	5.484	0.273	3.050
N	0.180	0.128	-1.795	H	-1.359	0.377	5.017	H	2.486	1.026	0.822
C	0.019	-0.006	2.027	H	0.356	2.587	2.814	H	4.252	0.841	0.792
C	-0.921	0.828	2.881	H	-2.617	-0.542	2.701	H	3.521	2.228	1.644
C	-0.511	0.451	4.325	H	2.104	-0.092	5.100	C	1.072	0.753	-2.635
C	0.248	-0.876	4.244	H	2.008	-1.874	5.066	C	0.664	0.650	-3.998
C	-2.416	0.532	2.548	H	1.042	-0.947	6.235	C	-0.568	-0.093	-3.976
C	-3.331	1.356	3.465	H	-2.121	0.319	0.393	C	-0.813	-0.380	-2.599
Cu	0.205	0.059	0.113	H	-3.789	0.643	0.878	C	-1.964	-1.098	-2.233
C	-3.078	2.852	3.250	H	-3.245	4.292	1.629	C	-1.467	-0.523	-4.958
C	-1.606	3.161	3.545	H	-4.464	3.010	1.583	C	1.435	1.229	-5.013
C	-0.703	2.348	2.608	H	2.434	-4.727	1.005	C	2.251	1.444	-2.311
C	-3.401	3.213	1.798	H	-0.854	3.805	1.021	C	3.000	2.012	-3.334
C	-2.503	2.399	0.864	H	-0.379	2.202	0.451	H	2.573	1.535	-1.272
C	-1.039	2.727	1.163	H	2.455	0.710	3.264	H	3.918	2.552	-3.088
C	-2.739	0.903	1.095	H	-0.039	-2.420	-0.378	C	-2.843	-1.514	-3.225
N	0.671	-0.843	2.794	H	-1.191	-3.771	-0.216	H	-2.165	-1.330	-1.184
C	-0.665	-2.077	4.493	H	0.529	-4.095	-0.544	H	-3.740	-2.073	-2.945
C	1.428	-0.950	5.205	H	5.132	-1.545	1.979	C	2.601	1.908	-4.679
C	0.105	-3.488	1.516	H	-4.380	1.111	3.229	H	1.121	1.150	-6.058
C	-0.131	-4.888	2.080	H	-3.188	1.089	4.524	H	3.211	2.366	-5.462
C	3.322	0.329	2.704	H	-3.719	3.435	3.932	C	-2.602	-1.232	-4.581
C	3.403	1.156	1.419	H	-2.728	2.645	-0.186	H	-1.279	-0.301	-6.013
C	4.555	0.531	3.581	H	-0.620	-2.810	1.987	H	-3.311	-1.572	-5.340
C	-0.165	-3.443	0.009	H	4.741	-3.860	1.196				

Table S6: Cartesian coordinates of the ground state perpendicular minimum of **Cu-Cz**.

S3 S_1 – Perpendicular

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	4.079	-2.870	1.307	H	-1.522	-2.091	5.109	H	0.564	-4.834	3.229
C	2.858	-3.504	1.210	H	-0.597	-3.153	4.050	H	1.077	-5.652	1.756
C	1.683	-2.887	1.633	H	-1.784	-2.033	3.360	H	-0.643	-5.421	2.076
C	1.749	-1.598	2.192	H	-1.167	2.800	4.809	H	4.116	-0.126	4.651
C	2.993	-0.935	2.269	H	-1.067	4.217	3.777	H	4.205	1.607	4.297
C	4.136	-1.588	1.825	H	0.186	0.971	4.676	H	5.223	0.474	3.417
N	0.000	0.000	-1.922	H	-1.409	0.280	4.912	H	2.502	1.437	0.976
C	-0.082	0.003	1.883	H	0.502	2.472	2.975	H	4.265	1.226	1.109
C	-0.929	0.864	2.822	H	-2.768	-0.259	2.526	H	3.446	2.486	2.047
C	-0.566	0.317	4.222	H	1.898	-0.591	5.078	C	0.909	0.582	-2.759
C	0.052	-1.069	4.030	H	1.620	-2.325	4.854	C	0.555	0.406	-4.123
C	-2.456	0.790	2.510	H	0.685	-1.426	6.053	C	-0.683	-0.351	-4.097
C	-3.279	1.585	3.528	H	-2.212	0.801	0.363	C	-0.960	-0.561	-2.721
Cu	0.000	0.000	0.000	H	-3.822	1.270	0.909	C	-2.098	-1.256	-2.313
C	-2.870	3.055	3.496	H	-2.870	4.688	2.076	C	-1.539	-0.839	-5.057
C	-1.375	3.165	3.798	H	-4.218	3.567	1.884	C	1.354	0.918	-5.117
C	-0.569	2.375	2.760	H	2.807	-4.503	0.789	C	2.070	1.268	-2.399
C	-3.147	3.628	2.108	H	-0.546	4.012	1.353	C	2.863	1.780	-3.413
C	-2.347	2.843	1.070	H	-0.266	2.431	0.626	H	2.336	1.386	-1.357
C	-0.856	2.960	1.383	H	2.179	0.737	3.272	H	3.769	2.318	-3.164
C	-2.752	1.372	1.127	H	0.082	-2.882	-0.593	C	-2.948	-1.744	-3.293
N	0.581	-0.940	2.661	H	-0.874	-4.321	-0.199	H	-2.301	-1.401	-1.260
C	-1.026	-2.154	4.137	H	0.855	-4.468	-0.526	H	-3.839	-2.289	-3.005
C	1.133	-1.368	5.058	H	5.095	-1.085	1.893	C	2.514	1.610	-4.750
C	0.376	-3.619	1.425	H	-4.345	1.489	3.286	H	1.103	0.794	-6.165
C	0.342	-4.954	2.167	H	-3.160	1.183	4.538	H	3.154	2.019	-5.523
C	3.128	0.475	2.803	H	-3.440	3.614	4.247	C	-2.676	-1.541	-4.643
C	3.352	1.466	1.662	H	-2.549	3.243	0.070	H	-1.347	-0.689	-6.113
C	4.230	0.609	3.851	H	-0.418	-2.982	1.814	H	-3.360	-1.931	-5.387
C	0.096	-3.835	-0.060	H	4.984	-3.368	0.976				

Table S7: Cartesian coordinates of the S_1 perpendicular minimum of **Cu-Cz**.

S4 T$_1$ – Co-planar

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	-1.892	-2.401	-4.644	C	-3.827	-2.521	0.820	H	2.113	0.762	0.676
C	-1.024	-1.369	-5.046	C	-3.394	-3.806	0.520	H	0.658	-2.999	2.426
C	-0.394	-0.619	-4.069	C	-2.095	-4.184	0.844	H	-2.483	0.542	-0.108
C	-0.630	-0.901	-2.690	C	-1.229	-3.309	1.510	H	-3.786	1.608	0.473
C	-1.496	-1.931	-2.293	C	-3.480	-0.184	1.678	H	-4.192	0.095	-0.377
C	-2.122	-2.673	-3.291	C	-3.490	0.555	0.338	H	-1.741	-5.181	0.571
N	0.076	-0.061	-1.875	C	0.215	-3.725	1.730	H	0.702	3.703	4.435
C	0.777	0.783	-2.691	C	0.363	-5.122	2.329	H	0.842	2.187	5.325
C	0.540	0.498	-4.070	C	-2.022	-0.355	4.700	H	3.096	3.140	4.934
C	1.166	1.246	-5.051	C	-0.823	-2.514	4.736	H	2.339	3.272	0.702
C	2.031	2.282	-4.657	C	-4.845	-0.096	2.359	H	-2.740	0.324	2.309
C	2.260	2.563	-3.306	C	1.000	-3.598	0.422	H	-4.062	-4.509	0.015
C	1.639	1.820	-2.305	H	-1.920	-0.291	5.795	H	-4.860	-0.633	3.319
Cu	0.057	-0.144	0.080	H	-2.968	-0.874	4.486	H	-5.645	-0.519	1.731
C	0.017	-0.286	1.987	H	-2.092	0.670	4.310	H	-5.109	0.955	2.555
N	-0.862	-1.159	2.630	H	2.887	0.655	4.907	H	-0.216	-5.234	3.259
C	-0.833	-1.121	4.105	H	4.139	1.181	3.778	H	1.420	-5.328	2.561
C	0.495	-0.384	4.333	H	1.298	-1.132	4.440	H	0.029	-5.907	1.632
C	0.787	0.459	3.070	H	0.475	0.195	5.267	H	0.944	-2.560	0.056
C	2.317	0.511	2.804	H	2.672	-0.529	2.699	H	0.600	-4.268	-0.357
C	3.050	1.200	3.963	H	-0.757	1.979	3.388	H	2.062	-3.847	0.575
C	2.571	2.650	4.095	H	0.052	-3.098	4.423	H	1.807	2.030	-1.249
C	1.062	2.662	4.355	H	-1.730	-3.080	4.473	H	2.935	3.376	-3.032
C	0.331	1.952	3.208	H	-0.792	-2.426	5.833	H	-1.667	-2.134	-1.235
C	2.621	1.274	1.514	H	0.095	2.221	1.075	H	-2.801	-3.481	-3.010
C	2.133	2.721	1.637	H	0.245	3.744	1.984	H	0.999	1.043	-6.111
C	0.627	2.711	1.909	H	3.953	3.419	2.603	H	2.532	2.879	-5.422
C	2.866	3.404	2.795	H	2.541	4.455	2.885	H	-0.858	-1.172	-6.108
C	-1.703	-2.027	1.885	H	-4.832	-2.208	0.526	H	-2.396	-3.000	-5.406
C	-2.996	-1.611	1.486	H	3.704	1.246	1.303				

Table S8: Cartesian coordinates of the T$_1$ co-planar minimum of **Cu-Cz**.

S5 T_1 – Perpendicular

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	3.966	-3.122	1.361	H	-1.232	-1.990	5.447	H	0.324	-4.970	3.225
C	2.693	-3.672	1.311	H	-0.338	-3.062	4.349	H	0.704	-5.693	1.649
C	1.572	-2.956	1.749	H	-1.651	-2.035	3.718	H	-0.979	-5.319	2.064
C	1.752	-1.656	2.276	H	-1.265	2.969	4.651	H	4.393	-0.089	4.517
C	3.043	-1.071	2.281	H	-1.303	4.273	3.461	H	4.517	1.604	3.978
C	4.131	-1.823	1.830	H	0.273	1.159	4.640	H	5.414	0.336	3.128
N	0.142	0.083	-1.907	H	-1.286	0.422	5.025	H	2.454	1.161	0.865
C	-0.056	-0.029	1.955	H	0.381	2.561	2.794	H	4.244	1.005	0.848
C	-0.932	0.838	2.859	H	-2.694	-0.452	2.767	H	3.467	2.330	1.758
C	-0.476	0.432	4.282	H	2.077	-0.301	5.091	C	1.062	0.689	-2.717
C	0.196	-0.946	4.176	H	1.864	-2.067	5.031	C	0.700	0.587	-4.095
C	-2.461	0.617	2.624	H	0.940	-1.097	6.200	C	-0.556	-0.150	-4.101
C	-3.314	1.460	3.581	H	-2.229	0.404	0.490	C	-0.831	-0.421	-2.728
Cu	0.111	0.011	0.054	H	-3.894	0.782	0.997	C	-1.986	-1.120	-2.348
C	-3.023	2.948	3.369	H	-3.201	4.410	1.768	C	-1.432	-0.576	-5.084
C	-1.530	3.202	3.606	H	-4.464	3.167	1.757	C	1.507	1.144	-5.070
C	-0.693	2.362	2.631	H	2.558	-4.681	0.910	C	2.236	1.351	-2.328
C	-3.387	3.334	1.933	H	-0.839	3.837	1.047	C	3.036	1.908	-3.322
C	-2.553	2.498	0.958	H	-0.447	2.197	0.491	H	2.507	1.419	-1.274
C	-1.067	2.768	1.205	H	2.359	0.694	3.235	H	3.955	2.429	-3.044
C	-2.831	1.009	1.190	H	-0.136	-2.533	-0.319	C	-2.857	-1.542	-3.349
N	0.652	-0.911	2.775	H	-1.182	-3.962	-0.091	H	-2.186	-1.320	-1.295
C	-0.816	-2.074	4.431	H	0.533	-4.175	-0.528	H	-3.763	-2.088	-3.079
C	1.339	-1.110	5.175	H	5.131	-1.381	1.845	C	2.681	1.808	-4.671
C	0.195	-3.563	1.551	H	-4.384	1.255	3.397	H	1.246	1.077	-6.129
C	0.058	-4.959	2.157	H	-3.127	1.182	4.631	H	3.327	2.253	-5.431
C	3.263	0.373	2.700	H	-3.619	3.549	4.077	C	-2.587	-1.276	-4.696
C	3.370	1.271	1.467	H	-2.815	2.768	-0.079	H	-1.239	-0.375	-6.141
C	4.460	0.560	3.631	H	-0.526	-2.899	2.044	H	-3.288	-1.616	-5.461
C	-0.166	-3.564	0.065	H	4.830	-3.699	1.021				

Table S9: Cartesian coordinates of the T_1 perpendicular minimum of **Cu-Cz**.

S6 T$_2$ – Co-planar

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	-1.967	-2.287	-4.509	C	-3.837	-2.545	0.853	H	1.978	0.641	0.653
C	-1.069	-1.299	-4.894	C	-3.395	-3.825	0.542	H	0.675	-3.008	2.411
C	-0.394	-0.567	-3.909	C	-2.089	-4.196	0.841	H	-2.252	0.496	0.005
C	-0.629	-0.837	-2.532	C	-1.223	-3.324	1.508	H	-3.556	1.614	0.467
C	-1.537	-1.837	-2.152	C	-3.465	-0.196	1.686	H	-3.924	0.120	-0.438
C	-2.195	-2.551	-3.146	C	-3.297	0.549	0.358	H	-1.728	-5.181	0.536
N	0.127	-0.015	-1.725	C	0.239	-3.699	1.675	H	0.683	3.735	4.359
C	0.857	0.794	-2.567	C	0.454	-5.125	2.179	H	0.876	2.253	5.295
C	0.577	0.496	-3.933	C	-2.055	-0.440	4.756	H	3.101	3.225	4.771
C	1.219	1.202	-4.957	C	-0.782	-2.566	4.768	H	2.172	3.150	0.571
C	2.133	2.195	-4.628	C	-4.889	-0.057	2.218	H	-2.787	0.283	2.403
C	2.407	2.488	-3.281	C	0.982	-3.460	0.358	H	-4.058	-4.524	0.027
C	1.781	1.800	-2.249	H	-1.969	-0.409	5.854	H	-5.026	-0.592	3.170
Cu	0.075	-0.133	0.197	H	-2.988	-0.968	4.509	H	-5.634	-0.445	1.506
C	-0.021	-0.320	2.084	H	-2.134	0.595	4.397	H	-5.131	1.004	2.389
N	-0.887	-1.200	2.683	H	2.925	0.734	4.867	H	-0.091	-5.313	3.117
C	-0.842	-1.166	4.162	H	4.124	1.224	3.667	H	1.524	-5.306	2.365
C	0.467	-0.382	4.390	H	1.291	-1.102	4.525	H	0.125	-5.876	1.444
C	0.760	0.454	3.121	H	0.414	0.223	5.306	H	0.892	-2.406	0.041
C	2.274	0.494	2.801	H	2.633	-0.547	2.733	H	0.579	-4.077	-0.460
C	3.045	1.243	3.896	H	-0.796	1.953	3.442	H	2.056	-3.683	0.464
C	2.550	2.690	3.979	H	0.100	-3.123	4.424	H	2.004	2.046	-1.209
C	1.054	2.697	4.301	H	-1.681	-3.149	4.514	H	3.128	3.274	-3.039
C	0.283	1.937	3.214	H	-0.730	-2.495	5.865	H	-1.724	-2.055	-1.098
C	2.505	1.198	1.465	H	-0.048	2.119	1.071	H	-2.903	-3.333	-2.860
C	2.009	2.643	1.536	H	0.126	3.667	1.905	H	1.003	0.973	-6.004
C	0.519	2.637	1.873	H	3.861	3.396	2.393	H	2.643	2.754	-5.417
C	2.784	3.381	2.634	H	2.455	4.433	2.683	H	-0.892	-1.094	-5.953
C	-1.718	-2.059	1.911	H	-4.842	-2.237	0.555	H	-2.501	-2.865	-5.267
C	-3.010	-1.635	1.520	H	3.571	1.160	1.183				

Table S10: Cartesian coordinates of the T$_1$ co-planar minimum of **Cu-Cz**.

S7 T$_2$ – Perpendicular

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
C	3.985	-3.091	1.316	H	-1.207	-2.023	5.475	H	0.334	-5.011	3.084
C	2.707	-3.628	1.242	H	-0.291	-3.069	4.368	H	0.706	-5.640	1.465
C	1.595	-2.926	1.720	H	-1.619	-2.055	3.745	H	-0.973	-5.281	1.904
C	1.799	-1.657	2.309	H	-1.296	3.054	4.535	H	4.450	-0.182	4.603
C	3.092	-1.077	2.337	H	-1.256	4.293	3.279	H	4.585	1.528	4.120
C	4.169	-1.819	1.846	H	0.227	1.172	4.698	H	5.471	0.284	3.226
N	-0.028	0.101	-1.764	H	-1.332	0.400	5.016	H	2.530	1.216	0.978
C	-0.025	-0.065	2.041	H	0.436	2.526	2.800	H	4.302	1.034	0.968
C	-0.913	0.835	2.876	H	-2.671	-0.452	2.778	H	3.544	2.334	1.925
C	-0.489	0.428	4.311	H	2.062	-0.261	5.179	C	0.905	0.717	-2.569
C	0.211	-0.946	4.231	H	1.887	-2.032	5.103	C	0.560	0.591	-3.944
C	-2.424	0.604	2.580	H	0.923	-1.091	6.262	C	-0.672	-0.157	-3.968
C	-3.307	1.510	3.449	H	-2.105	0.254	0.456	C	-0.983	-0.429	-2.604
Cu	0.025	-0.017	0.150	H	-3.759	0.688	0.860	C	-2.144	-1.148	-2.278
C	-2.985	2.978	3.164	H	-3.058	4.343	1.469	C	-1.522	-0.603	-4.986
C	-1.507	3.235	3.468	H	-4.333	3.116	1.461	C	1.378	1.154	-4.930
C	-0.629	2.334	2.588	H	2.562	-4.611	0.788	C	2.065	1.411	-2.195
C	-3.266	3.283	1.690	H	-0.665	3.703	0.896	C	2.863	1.962	-3.190
C	-2.394	2.382	0.806	H	-0.267	2.055	0.447	H	2.342	1.518	-1.143
C	-0.924	2.654	1.121	H	2.422	0.660	3.355	H	3.770	2.504	-2.909
C	-2.711	0.919	1.111	H	-0.140	-2.368	-0.333	C	-2.972	-1.581	-3.307
N	0.703	-0.917	2.835	H	-1.192	-3.788	-0.149	H	-2.397	-1.366	-1.237
C	-0.785	-2.090	4.460	H	0.514	-3.989	-0.621	H	-3.879	-2.142	-3.062
C	1.341	-1.087	5.244	H	5.172	-1.387	1.868	C	2.528	1.837	-4.550
C	0.210	-3.505	1.500	H	-4.369	1.303	3.232	H	1.116	1.058	-5.987
C	0.066	-4.935	2.019	H	-3.166	1.288	4.519	H	3.176	2.281	-5.309
C	3.321	0.350	2.804	H	-3.612	3.626	3.801	C	-2.669	-1.314	-4.653
C	3.435	1.287	1.600	H	-2.593	2.593	-0.257	H	-1.286	-0.393	-6.033
C	4.520	0.497	3.739	H	-0.502	-2.874	2.048	H	-3.341	-1.666	-5.439
C	-0.171	-3.413	0.021	H	4.840	-3.657	0.939				

Table S11: Cartesian coordinates of the T$_1$ perpendicular minimum of **Cu-Cz**.

S4 Spin-vibronic Hamiltonian and Quantum Dynamics

To study the excited state dynamics of the **Ag-Cz** and **Cu-Cz**, we adopt a 2-dimensional model spin-vibronic Hamiltonian[2–4]. The model spin-vibronic Hamiltonian for **Au-Cz** is described in ref.[5]. It include the three lowest triplet states (T_1, T_2 and T_3) as well as either the lowest or the two lowest singlet states (S_1 and S_2) for **Ag-Cz** and **Au-Cz**, respectively. Each of the three M_s components of the triplet states are considered. The Hamiltonian contains therefore 10 or 11 electronic states, for **Ag-Cz** and **Au-Cz**, respectively.
The two degrees of freedom are φ and $r_{\mathrm{M-N_2}}$ discussed in the main text.
The Hamiltonian operator is expressed as:

$$\mathcal{H} = \mathbf{T_N} + \mathbf{W} \tag{1}$$

where $\mathbf{T_N}$ and $\mathbf{W}$ are the kinetic and potential energy operators, respectively, and are defined in sections S1 and S2.

S1 The kinetic energy operator

In this work, we adopt a kinetic energy operator (KEO) expressed as a sum of two uncoupled mono-dimensional KEOs,

$$\mathbf{T_N} = -\frac{1}{2I}\frac{\partial^2}{\partial\varphi^2} - \frac{1}{2\mu}\frac{\partial^2}{\partial r^2_{\mathrm{M-N_2}}}. \tag{2}$$

The first term is the KEO of the rotation of a solid top, where I is the moment of inertia,

$$I = \sum_i m_i r_i^2 \tag{3}$$

where i denotes all atoms of the rotating carbazole ligand, m_i denotes their mass, and r_i denotes their distance to the rotation axis. The second term is the KEO associated to $r_{\mathrm{M-N_2}}$, with μ being the reduced mass of the system,

$$\mu = \frac{\left(\sum_A m_A\right)\left(\sum_B m_B\right)}{\sum_A m_A + \sum_B m_B} \tag{4}$$

where A and B denote the atoms of the Cz and CAAC (including the metal) moieties, respectively, and m_A and m_B denote their respective mass. The parameters I and μ are reported in table S12.

	I / amu.a$_0^2$	μ / amu
Cu-Cz	5927.01	130.08
Ag-Cz	5887.63	133.85

Table S12: Moment of intertia I and reduced mass μ for **Cu-Cz** and **Ag-Cz**.

S2 The potential energy

The potential energy component of the Hamiltonian, $\mathbf{W}$, is expressed as the sum:

$$\mathbf{W} = \mathbf{W^{vib}} + \mathbf{W^{SOC}}, \tag{5}$$

where $\mathbf{W^{vib}}$ contains the diabatic electronic states and the coupling between them, described in sections S1 for **Ag-Cz** and S2 for **Cu-Cz**. $\mathbf{W^{SOC}}$ contains the spin-orbit coupling matrix elements (SOCMEs) in the diabatic picture. They are obtained by transformation of the computed SOCME between the so-called electronic adiabatic states ($\mathbf{V^{SOC}}$). Let $\mathcal{R}$ be the adiabatic to diabatic rotation matrice that transforms the adiabatic electronic states $\mathbf{V}$ into the diabatic electronic states matrix $\mathbf{W^{vib}}$ through the transformation:

$$\mathbf{W^{vib}} = \mathcal{R}^{-1}\mathbf{V}\mathcal{R}. \tag{6}$$

$\mathbf{W^{soc}}$ is then obtained thourgh the same rotation:

$$\mathbf{W^{soc}} = \mathcal{R}^{-1}\mathbf{V^{soc}}\mathcal{R}. \tag{7}$$

$\mathbf{W^{soc}}$ and $\mathbf{V^{soc}}$ are reported, for **Ag-Cz** and **Cu-Cz** in tables S15 and S17, respectively, and the rotation matrices for **Ag-Cz** and **Cu-Cz** in tables S16 and S18, respectively.

The vibronic coupling occurs between electronic states of same spin multiplicity, $\mathbf{W^{vib}}$ can therefore be written:

$$\mathbf{W^{vib}} = \begin{pmatrix} \mathbf{E_{T_1}} & \lambda^{\mathbf{T1,T2}} & \lambda^{\mathbf{T1,T3}} & 0 \\ \lambda^{\mathbf{T1,T2}} & \mathbf{E_{T_2}} & \lambda^{\mathbf{T2,T3}} & 0 \\ \lambda^{\mathbf{T1,T3}} & \lambda^{\mathbf{T2,T3}} & \mathbf{E_{T_3}} & 0 \\ 0 & 0 & 0 & \mathbf{E_{S_1}} \end{pmatrix} \tag{8}$$

E_{T_n} and E_{S_1} being the diabatic potential energy for the triplet and S$_1$ states, and $\lambda^{Tn,Tm}$ is the vibronic coupling between the T$_n$ and T$_m$ states. $\mathbf{W^{soc}}$ is written:

$$\mathbf{W^{soc}} = \begin{pmatrix} 0 & \eta^{\mathbf{T1,T2}} & \eta^{\mathbf{T_1,T_3}} & \eta^{\mathbf{T_1,S_1}} \\ \eta^{*\,\mathbf{T_1,T_2}} & 0 & \eta^{\mathbf{T_2,T_3}} & \eta^{\mathbf{T_2,S_1}} \\ \eta^{*\,\mathbf{T_1,T_3}} & \eta^{*\,\mathbf{T_2,T_3}} & 0 & \eta^{\mathbf{T_3,S_1}} \\ \eta^{*\,\mathbf{T_1,S_1}} & \eta^{*\,\mathbf{T_2,S_1}} & \eta^{*\,\mathbf{T_3,S_1}} & 0 \end{pmatrix} \tag{9}$$

with

$$\eta^{\mathbf{T_n,T_m}} = \begin{pmatrix} \mathcal{I}(\eta') & -\mathcal{R}(\eta)+\mathcal{I}(\eta) & 0 \\ -\mathcal{R}(\eta)+\mathcal{I}(\eta) & 0 & \mathcal{R}(\eta)+\mathcal{I}(\eta) \\ 0 & \mathcal{R}(\eta)+\mathcal{I}(\eta) & \mathcal{I}(\eta') \end{pmatrix} \tag{10}$$

and

$$\eta^{\mathbf{T_n,S_1}} = \begin{pmatrix} \mathcal{R}(\eta)+\mathcal{I}(\eta) \\ \mathcal{I}(\eta') \\ \mathcal{R}(\eta)-\mathcal{I}(\eta) \end{pmatrix} \tag{11}$$

$\mathcal{R}(\eta)$ and $\mathcal{I}(\eta)$ are the real and imaginary part of the SOCMEs. In the present model we consider them as constant, taking their value at the minimum of S$_1$ excited state. The 3×3 matrix in Equation 8 represents the the coupling between each of the M$_s$ components of the triplet states.

$\mathbf{W^{vib}}$ is constructed by a fit to the diabatic electronic states along the $\mathrm{r_{Au-N_2}}$ stretch and torsion, φ. The diabatic electronic states and coupling are computed using the diabatisation scheme[6] implemented within Q-chem. The details of the fit of the diabatic states and coupling for **Ag-Cz** and **Cu-Cz** are described in sections S1 and S2.

S3 Wavepacket Dynamics

As for ref.[5] The quantum dynamics were performed using the multi-configurational time-dependent Hartree (MCTDH) method as implemented within the Quantics quantum dynamics package.[7] The 2-dimensional model spin-vibronic Hamiltonian was represented on a Fast Fourier Transform (FFT) grid of

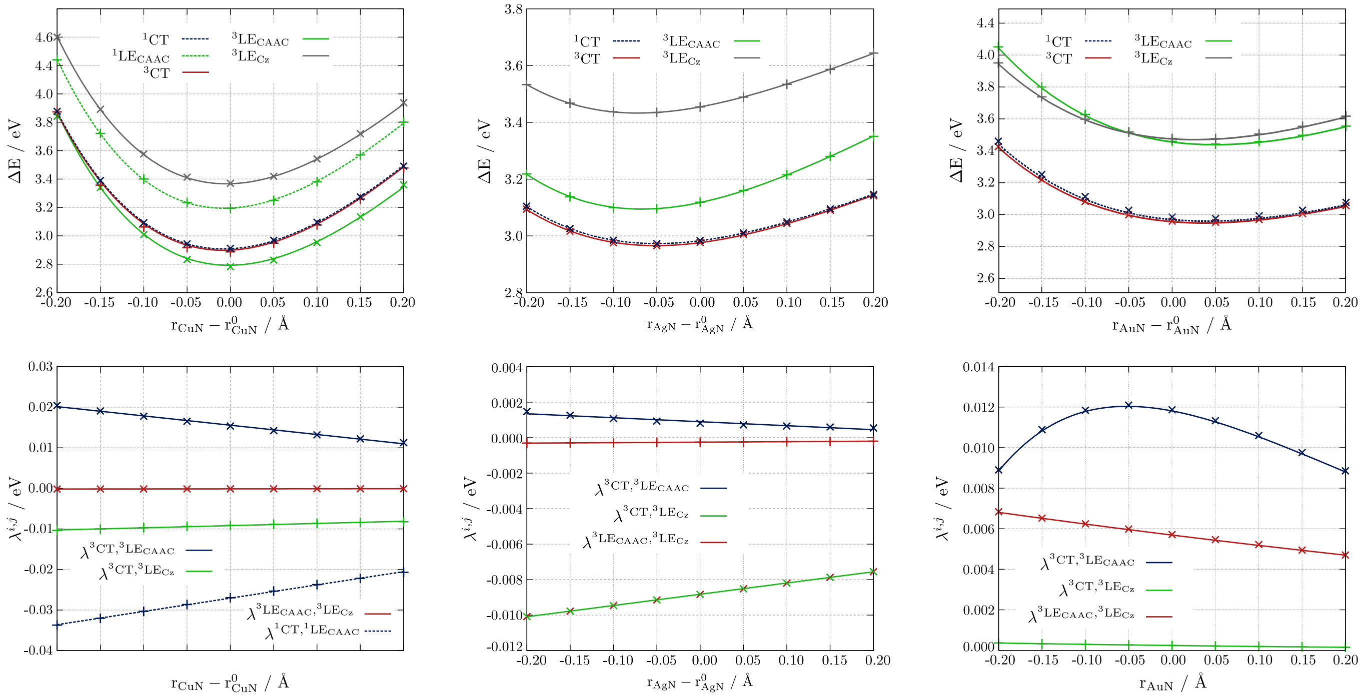

Figure S3: Diabatic potential energy curves (top) and vibronic coupling (bottom) for **Cu-Cz** (left), **Ag-Cz** (center), and **Au-Cz** (right) along $\mathrm{r_{M-N_2}}$.

1001×801 grid points for the torsion and the stretching modes, respectively. The torsional mode was set with periodic boundary conditions ranging from -$\pi \rightarrow \pi$. The multi-set formalism was adopted, and 10 single particle functions (SPFs) were used for each mode on the S$_1$ and T$_1$ states and 2 SPFs were used for each mode on the T$_2$ and T$_3$ states. The evolution of the A-vector was calculated with the constant mean field integration scheme, and the SPFs were propagated with the Runge-Kutta integrator to eighth order (RK8). One initial wavepacket used in the simulations was obtained from a relaxation of a guessed wavepacket upon the ground state surface along the stretching motion, vertically projected onto the S$_1$ surface. The width and position of the initial wavepacket along the torsion was adopted to better represent the distribution of φ associated with the flat nature of the potential along this motion.

S5 Potential Energy Surfaces

S1 The potential Ag-Cz

The diabatic potential energy surface for state i as a function of φ and r (E$_i$) can be decomposed as

$$E_i\left(\varphi, r\right) = E_i\left(\varphi\right) + E_i\left(r\right) \tag{12}$$

where $E_i\left(\varphi\right)$ and $E_i\left(r\right)$ are the diabatic energies along each coordinate. The analytical expressions fitted to the calculation diabatic energies take the form:

$$E_i(\varphi) = \beta_i \cos(2(\varphi - \tau_i)) + \gamma_i \cos(0.5(\varphi - \psi_i))^{64} + \delta_i \cos(0.5(\varphi - \theta_i))^{64}. \tag{13}$$

along the torsion φ, and is a Morse potential along the stretch coordinate r:

$$E_i(\mathrm{r_{Ag-N_2}}) = D_i \left(\exp\left(-\alpha_i(\mathrm{r_{Ag-N_2}} - \mathrm{r^0_{Ag-N_2}}) - 1\right)^2 \right). \tag{14}$$

where D_i is the dissociation energy, α describes the width of the potential, and $\mathrm{r}^0_{\mathrm{Ag-N_2}}$ is the bond length at the minimum of energy. The fit parameters are reported in Tab.S13.
The vibronic coupling is decomposed in a similar fashion:

$$\lambda^{i,j}(\varphi, r) = \lambda^{i,j}(\varphi) + \lambda^{i,j}(r) \tag{15}$$

where the analytical expressions of $\lambda^{i,j}(\varphi)$ and $\lambda^{i,j}(r)$ fitted to the computed coupling take the form:

$$\lambda^{Tn,Tm}(\varphi) = \epsilon_1 \sin(1(\varphi - \nu_1)) + \epsilon_2 \sin(0.5(\varphi - \nu_2))^6 + \epsilon_3 \sin(0.5(\varphi - \nu_3))^6. \tag{16}$$

along the torsion φ, and: Vibronic coupling along the stretch are fitted using a second order polynomial expression:

$$\lambda^{T_n,T_m}(\mathrm{r_{Ag-N_2}}) = a\mathrm{r_{Ag-N_2}}^2 + b\mathrm{r_{Ag-N_2}} + \lambda^{T_n,T_m}(\varphi_0)\,. \tag{17}$$

along the stretch coordinate r. All fit parameters for the vibronic coupling are reported in Tab.S13.

PES along φ | Vibr. coupling along φ

Parameter	T_1	T_2	T_3	S_1	Parameter	$T_1 - T_2$	$T_1 - T_3$	$T_2 - T_3$
β/eV	-0.004	-0.013	-0.006	-0.036	β/eV	-0.112	-0.090	0.000
γ/eV	0.834	0.878	0.860	0.832	γ/eV	0.126	0.111	0.000
δ/eV	0.666	0.704	0.687	0.664	δ/eV	-0.132	-0.113	0.000
$\tau/°$	-210.3	-181.3	-197.0	-176.7	$\tau/°$	-105.6	-80.4	-
$\psi/°$	60.4	60.4	60.4	60.4	$\psi/°$	-206.8	-204.5	-
$\theta/°$	-119.4	-119.4	-119.4	-119.4	$\theta/°$	-26.6	-24.1	-

PES along r | Vibr. coupling along r

Parameter	$\mathrm{T_1}$	$\mathrm{T_2}$	$\mathrm{T_3}$	$\mathrm{S_1}$	Parameter	$\mathrm{T_1}$-$\mathrm{T_2}$	$\mathrm{T_1}$-$\mathrm{T_3}$	$\mathrm{T_2}$-$\mathrm{T_3}$
$\mathrm{D_i}$ / eV	1.278	2.012	1.357	1.171	a/eV.Å^{-2}	0.0045	0.0002	0.0001
α / Å^{-1}	1.770	1.628	1.924	1.854	b/eV.Å^{-1}	0.0020	-0.0061	-0.0003
$\mathrm{r}^0_{\mathrm{Ag-N}}$ / Å	-0.051	-0.067	-0.072	-0.050				
ϵ_i / eV	2.96	3.00	3.43	3.10				

Table S13: Fitted parameters of the diabatic states (left) and vibronic coupling (right) along the torsion φ (top) and the stretch r (bottom) for the **Ag-Cz** complex. Do the stretch part

S2 The potential Cu-Cz

Due to the bent C-Cu-N angle, the analytical expressions for both the diabatic energies and the coupling need to be more complex to assess the asymmetry. The diabatic energy along φ for the singlet states is

$$\begin{aligned} S_i(\varphi) =& a_1 \cos\left(2\left(\varphi-\tau_1\right)\right)+a_2 \cos\left(0.5\left(\varphi-\tau_2\right)\right)^{64}+a_3 \cos\left(0.5\left(\varphi-\tau_3\right)\right)^{64} \\ &+a_4 \cos\left(0.5\left(\varphi-\tau_4\right)\right)^{\beta_i}+a_5 \cos\left(0.5\left(\varphi-\tau_5\right)\right)^{\beta_i}+\varepsilon_i \end{aligned} \tag{18}$$

analytical expression and for the triplet states by

$$\begin{aligned} T_i(\varphi) =& a_1 \cos\left(2\left(\varphi-\tau_1\right)\right)+a_2 \cos\left(0.5\left(\varphi-\tau_2\right)\right)^{64}+a_3 \cos\left(0.5\left(\varphi-\tau_3\right)\right)^{64} \\ &+a_4 \cos\left(4\left(\varphi-\tau_4\right)\right)+a_5 \cos\left(0.5\left(\varphi-\tau_5\right)\right)^{64}+\varepsilon_i \end{aligned} \tag{19}$$

analytical expression. The energy along the stretch coordinate takes the form of a Morse potential:

$$E_i(\mathrm{r_{Cu-N}}) = D_i\left(\exp\left(-\alpha_i(\mathrm{r_{Cu-N}}-\mathrm{r^0_{Cu-N}})-1\right)^2\right). \tag{20}$$

The vibronic coupling along φ is fitted by:

$$\begin{aligned} \mathrm{T_1-T_2}(\varphi) &= a_1 \sin\left(x-b1_1\right)+a_2 \sin\left(x-b1_2\right)^3+s1 \\ \mathrm{T_1-T_3}(\varphi) &= a_1 \sin\left(2\left(x-b_1\right)\right)+s2 \\ \mathrm{T_2-T_3}(\varphi) &= a_1 \cos\left(x-b_1\right)+a_2 \cos\left(0.5\left(x-b3_2\right)\right)^{36}+a_3 \cos\left(0.5\left(x-b_3\right)\right)^{36} \\ \mathrm{S_1-S_2}(\varphi) &= a_1 \sin\left(x-b_1\right)^3+a_2 \sin\left(x-b_2\right)^3+s4 \end{aligned} \tag{21}$$

And along r_{Cu-N} by a linear function:

$$\lambda_{i,j}\left(r_{Cu-N}\right) = a r_{Cu-N}+b. \tag{22}$$

All fit parameters are reported in Tab.S14.

PES along φ

Parameter	T_1	T_2	S_1	S_2	T_3
a_1 / eV	-0.033	0.000	-0.100	0.041	-0.027
a_2 / eV	2.721	2.721	2.720	2.721	2.721
a_3 / eV	3.674	3.674	3.674	3.674	3.674
a_4 / eV	-0.024	-0.024	0.054	0.090	-0.027
a_5 / eV	0.046	0.014	0.016	0.046	0.041
$\tau_1/^\circ$	-174.5	168.8	183.1	82.9	168.8
$\tau_2/^\circ$	118.6	118.6	118.6	118.6	118.6
$\tau_3/^\circ$	-59.0	-59.0	-59.0	-59.0	-59.0
$\tau_4/^\circ$	-168.8	-168.8	57.3	57.3	-168.8
$\tau_5/^\circ$	52.8	55.6	-116.3	-122.0	55.6
b^i	-	-	64	30	-

Vibr. coupling along φ

Parameter	T_1-T_2	T_1-T_3	T_2-T_3	S_1-S_2
a_1 / eV	-0.019	0.001	0.071	0.038
a_2 / eV	-0.048	-	0.036	0.011
a_3 / eV	-	-	-0.035	-
$\tau/^\circ$	-297.5	54.6	-84.4	-53.3
$\tau/^\circ$	-55.9	-	92.3	-180.5
$\tau/^\circ$	-	-	-87.2	-
s_1 / eV	-0.005	0.001	-	0.008

PES along r

Parameter	T_1	T_2	T_3	S_1	S_2
$\mathrm{D_i}$ / eV	6.149	7.060	6.092	7.050	6.316
α / Å^{-1}	1.763	1.639	1.769	1.639	1.775
$\mathrm{r}^0_{\mathrm{Cu-N}}$ / Å	-0.002	-0.008	-0.005	-0.008	-0.007
ϵ_i / eV	2.793	2.898	3.367	2.908	3.195

Vibr. coupling along r

Parameter	T_1-T_2	T_1-T_3	T_2-T_3	S_1-S_2
a/eV.Å^{-1}	-0.023	0.000	0.005	0.033
b/eV	0.016	-0.000	-0.009	-0.027

Table S14: Fitted parameters of the diabatic states (left) and vibronic coupling (right) along the torsion φ (top) and the stretch r (bottom) for the **Cu-Cz** complex.

S6 The Spin-Orbit Coupling Matrix Elements

S1 SOC in Ag-Cz

Adiabatic SOC				
	^{3}CT	^{3}LE$_{\mathrm{CAAC}}$	^{3}LE$_{\mathrm{Cz}}$	^{1}CT
^{3}CT	0.00	295.20	26.68	1.92
^{3}LE$_{\mathrm{CAAC}}$	295.21	0.00	3.97	142.81
^{3}LE$_{\mathrm{Cz}}$	26.68	3.97	0.00	13.33
^{1}CT	1.92	142.81	13.33	0.00
Diabatic SOC				
	^{3}CT	^{3}LE$_{\mathrm{CAAC}}$	^{3}LE$_{\mathrm{Cz}}$	^{1}CT
^{3}CT	0.00	295.31	27.83	2.58
^{3}LE$_{\mathrm{CAAC}}$	295.31	0.00	1.80	142.76
^{3}LE$_{\mathrm{Cz}}$	27.83	1.80	0.00	12.84
^{1}CT	2.58	142.76	12.84	0.00

Table S15: Adiabatic (top) and Diabatic (bottom) SOC (in cm^{-1}) between the considered states for **Ag-Cz**

$$\begin{array}{c} & \mathsf{T}_1 & \mathsf{T}_2 & \mathsf{T}_3 & \mathsf{S}_1 \\ \begin{array}{c}\mathsf{T}_1\\ \mathsf{T}_2\\ \mathsf{T}_3\\ \mathsf{S}_1\end{array} & \multicolumn{4}{c}{\left(\begin{array}{cccc} 1.000 & 0.006 & 0.019 & 0.000 \\ -0.006 & 1.000 & -0.001 & 0.000 \\ -0.009 & 0.001 & 1.000 & 0.000 \\ 0.019 & 0.000 & 0.000 & 1.000 \end{array}\right)} \end{array}$$

Table S16: Adiabatic to diabatic matrice rotation for **Ag-Cz**

S2 SOC in Cu-Cz

Adiabatic SOC					
	^{3}LE$_{\mathrm{CAAC}}$	^{3}CT	^{3}LE$_{\mathrm{Cz}}$	^{1}CT	^{1}LE$_{\mathrm{CAAC}}$
^{3}LE$_{\mathrm{CAAC}}$	0.00	517.27	10.24	240.83	41.67
^{3}CT	517.27	0.00	9.78	13.81	289.88
^{3}LE$_{\mathrm{Cz}}$	10.24	9.72	0.00	4.27	5.87
^{1}CT	240.83	13.82	4.27	0.00	0.00
^{1}LE$_{\mathrm{CAAC}}$	41.67	289.88	5.87	0.00	0.00
Diabatic SOC					
	^{3}LE$_{\mathrm{CAAC}}$	^{3}CT	^{3}LE$_{\mathrm{Cz}}$	^{1}CT	^{1}LE$_{\mathrm{CAAC}}$
^{3}LE$_{\mathrm{CAAC}}$	0.00	517.16	11.55	242.23	27.76
^{3}CT	517.16	0.00	12.03	19.76	289.84
^{3}LE$_{\mathrm{Cz}}$	11.55	12.03	0.00	5.94	4.80
^{1}CT	242.23	19.76	5.91	0.00	0.00
^{1}LE$_{\mathrm{CAAC}}$	27.76	289.84	4.80	0.00	0.00

Table S17: Adiabatic (top) and Diabatic (bottom) SOC (in cm^{-1}) between the considered states for **Cu-Cz**

$$\begin{array}{c} & \mathsf{T}_1 & \mathsf{T}_2 & \mathsf{T}_3 & \mathsf{S}_1 & \mathsf{S}_2 \\ \begin{array}{c}\mathsf{T}_1\\ \mathsf{T}_2\\ \mathsf{T}_3\\ \mathsf{S}_1\\ \mathsf{S}_2\end{array} & \multicolumn{5}{c}{\left(\begin{array}{ccccc} 0.990 & 0.142 & -0.001 & 0.000 & 0.000 \\ -0.142 & 0.990 & -0.019 & 0.000 & 0.000 \\ -0.002 & 0.019 & 1.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.996 & 0.094 \\ 0.000 & 0.000 & 0.000 & -0.094 & 0.996 \end{array}\right)} \end{array}$$

Table S18: Adiabatic to diabatic matrice rotation for **Cu-Cz**

S7 Supplementary Dynamics

S1 Dynamics Ag-Cz

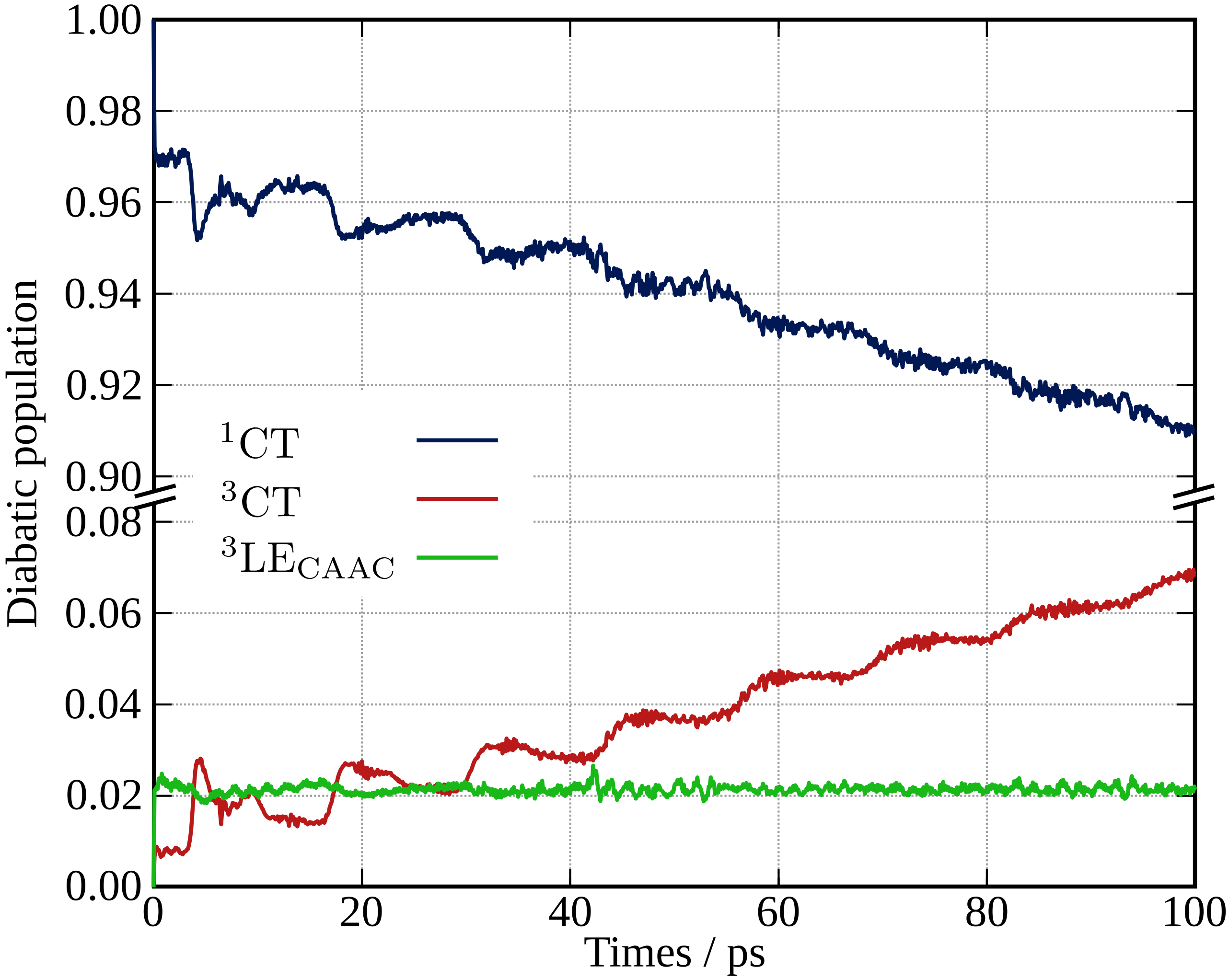

Figure S4: Evolution of the diabatic population along time for **Ag-Cz** with the Hamiltonian without ^{3}LE(Cz)

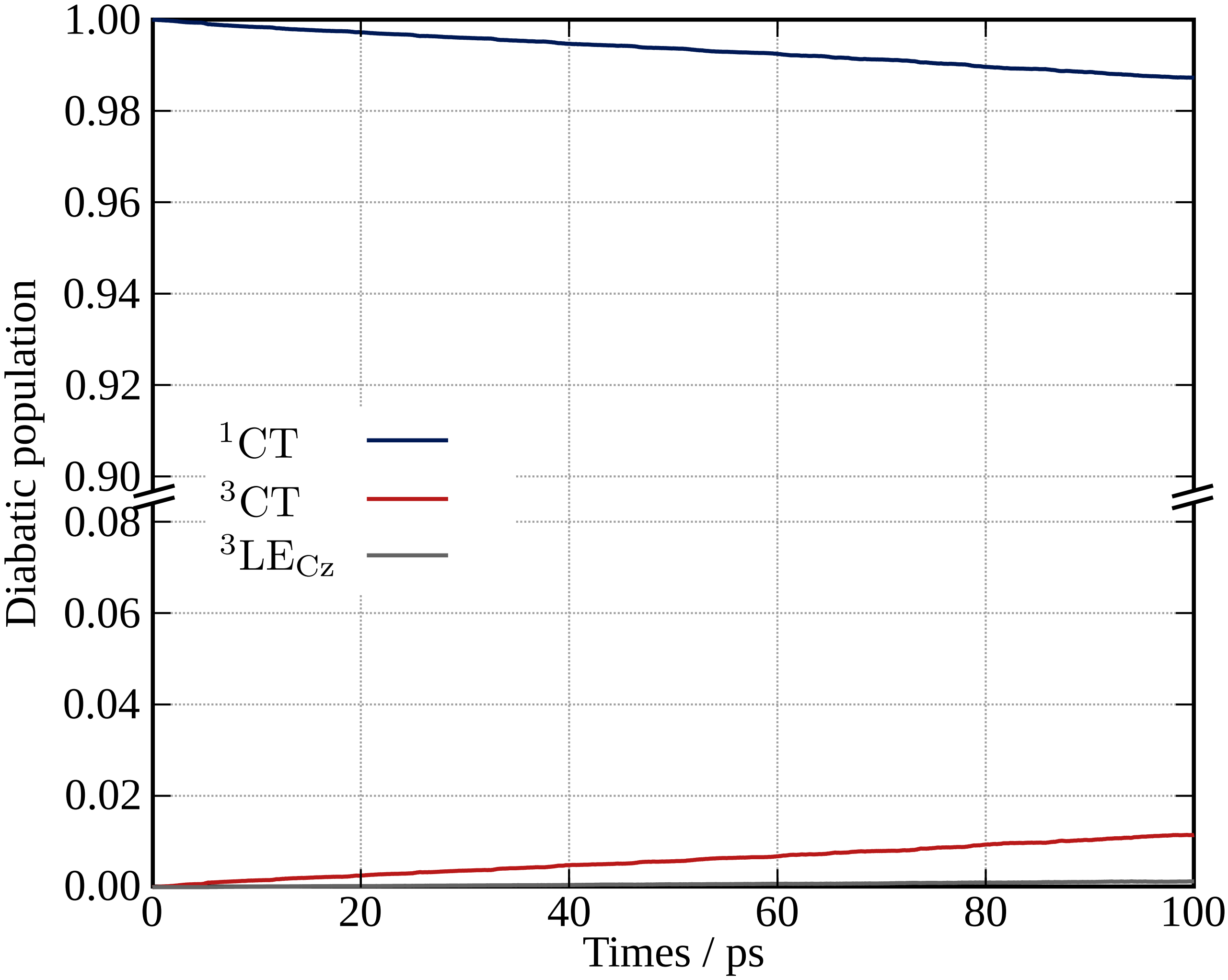

Figure S5: Evolution of the diabatic population along time for **Ag-Cz** with the Hamiltonian without ^{3}LE(CAAC)

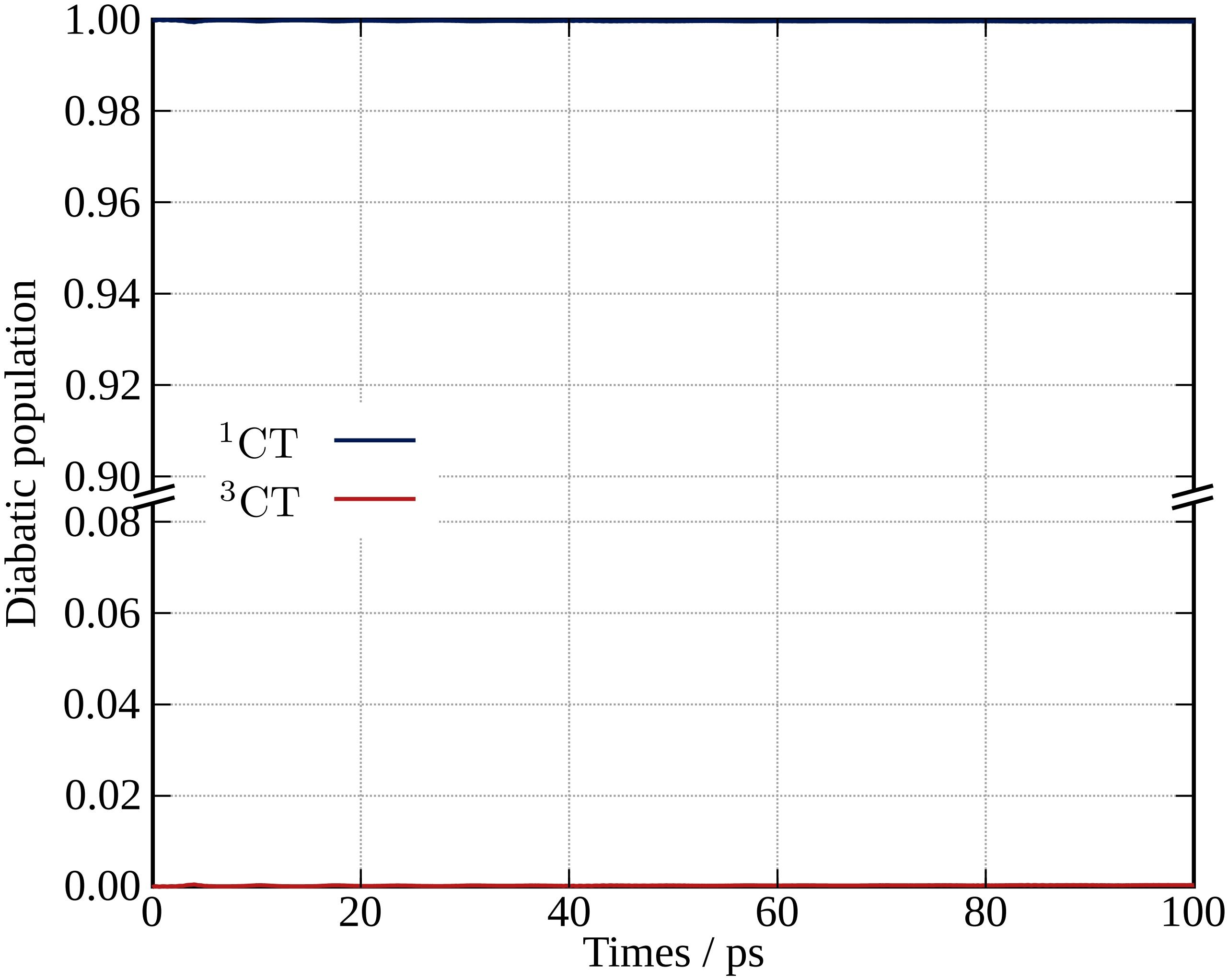

Figure S6: Evolution of the diabatic population along time for **Ag-Cz** with the Hamiltonian without ^{3}LE(Cz) and ^{3}LE(CAAC).

S2 Dynamics Cu-Cz

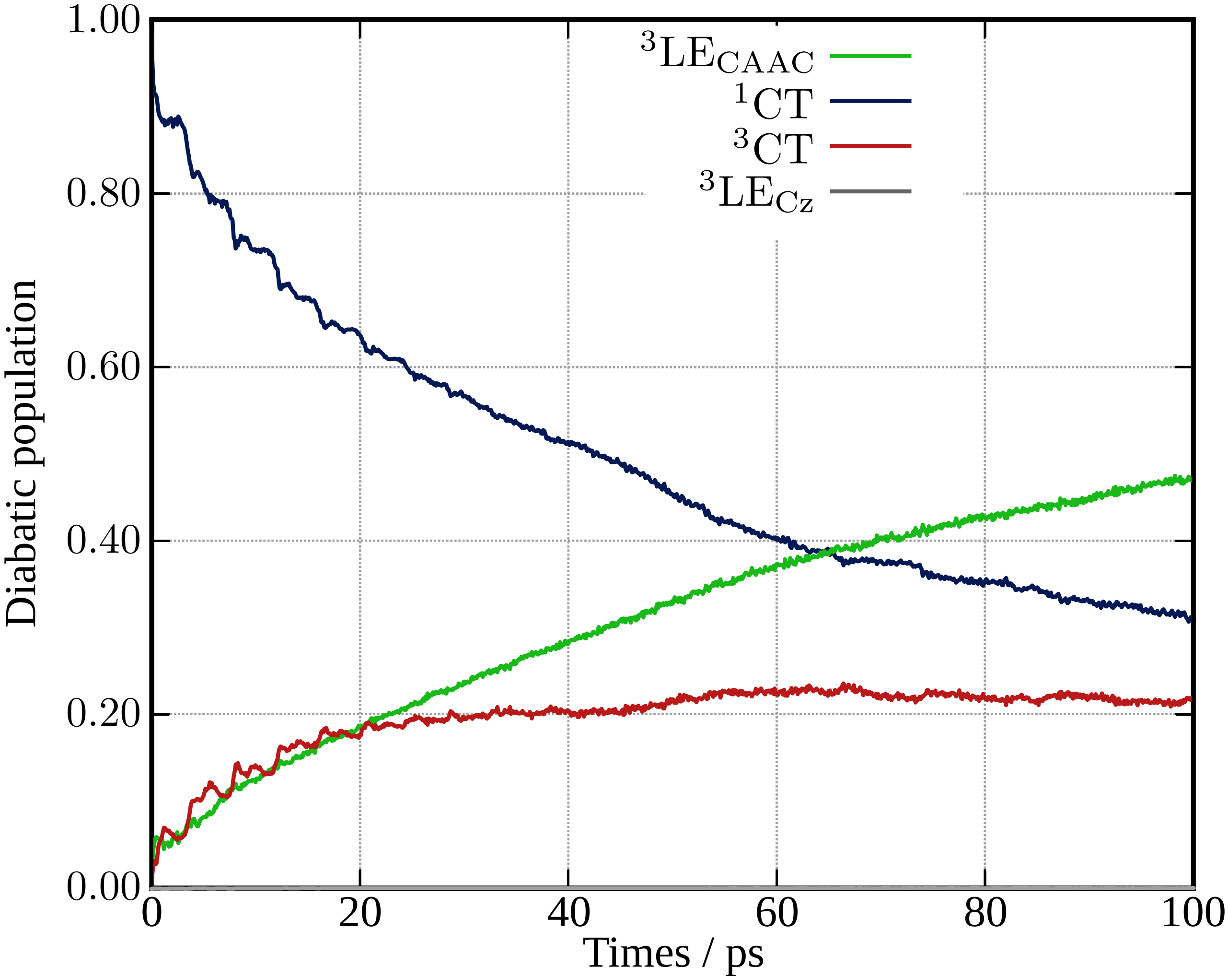

Figure S7: Evolution of the diabatic population along time for **Cu-Cz** with the Hamiltonian without ^{1}LE(CAAC).

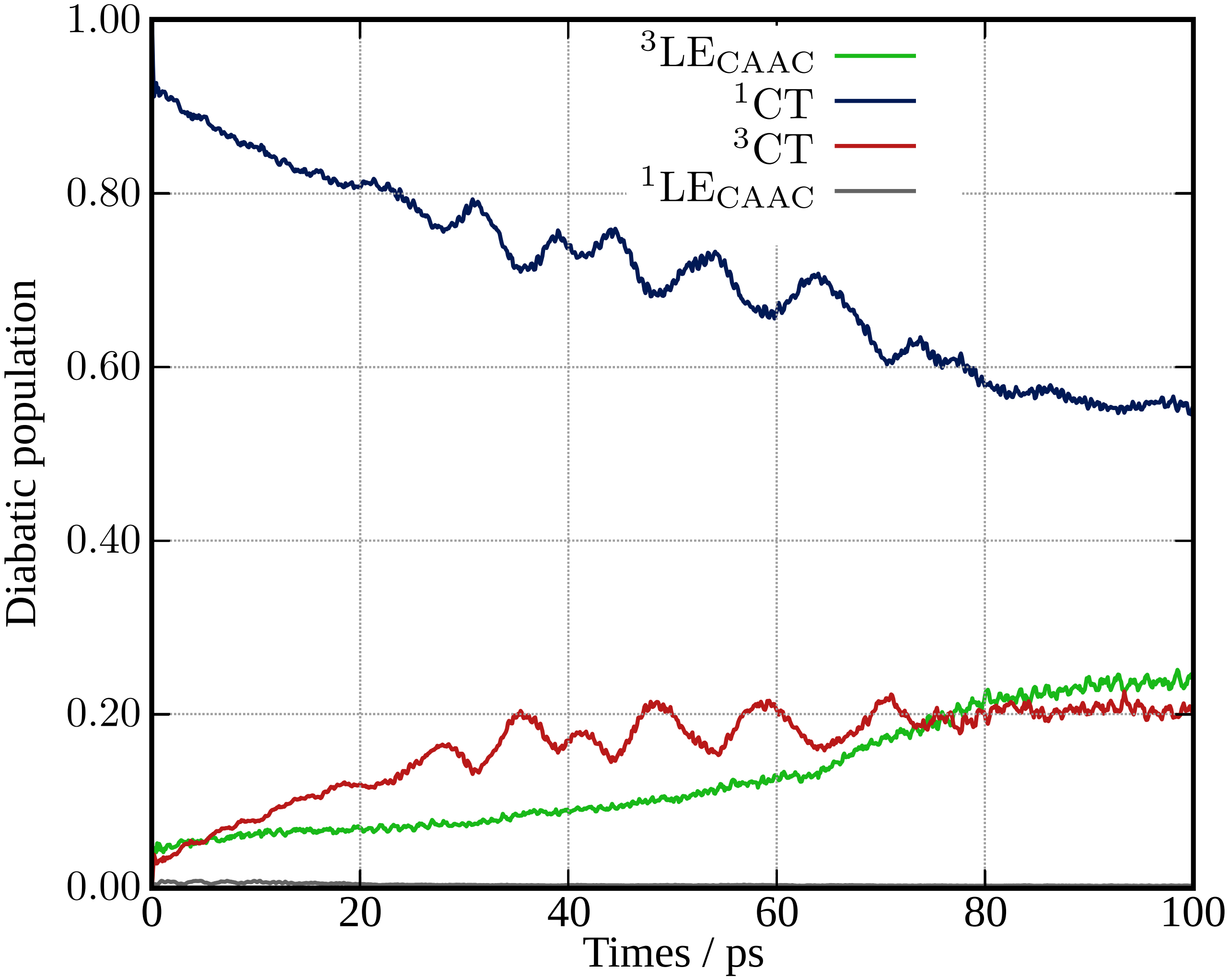

Figure S8: Evolution of the diabatic population along time for **Cu-Cz** with the Hamiltonian without ^{3}LE(Cz).

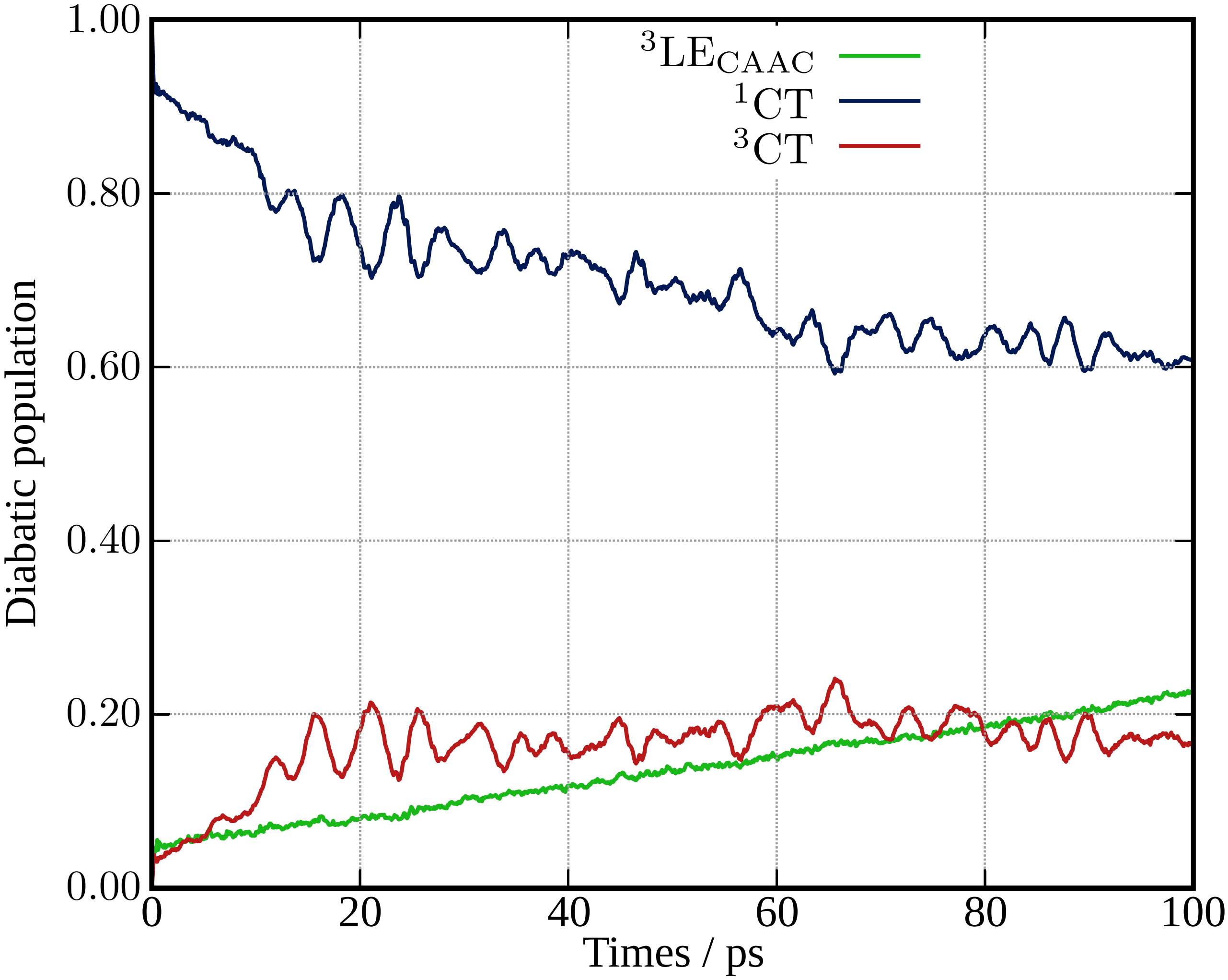

Figure S9: Evolution of the diabatic population along time for **Cu-Cz** with the Hamiltonian without ^{3}LE(Cz) and ^{1}LE(CAAC).

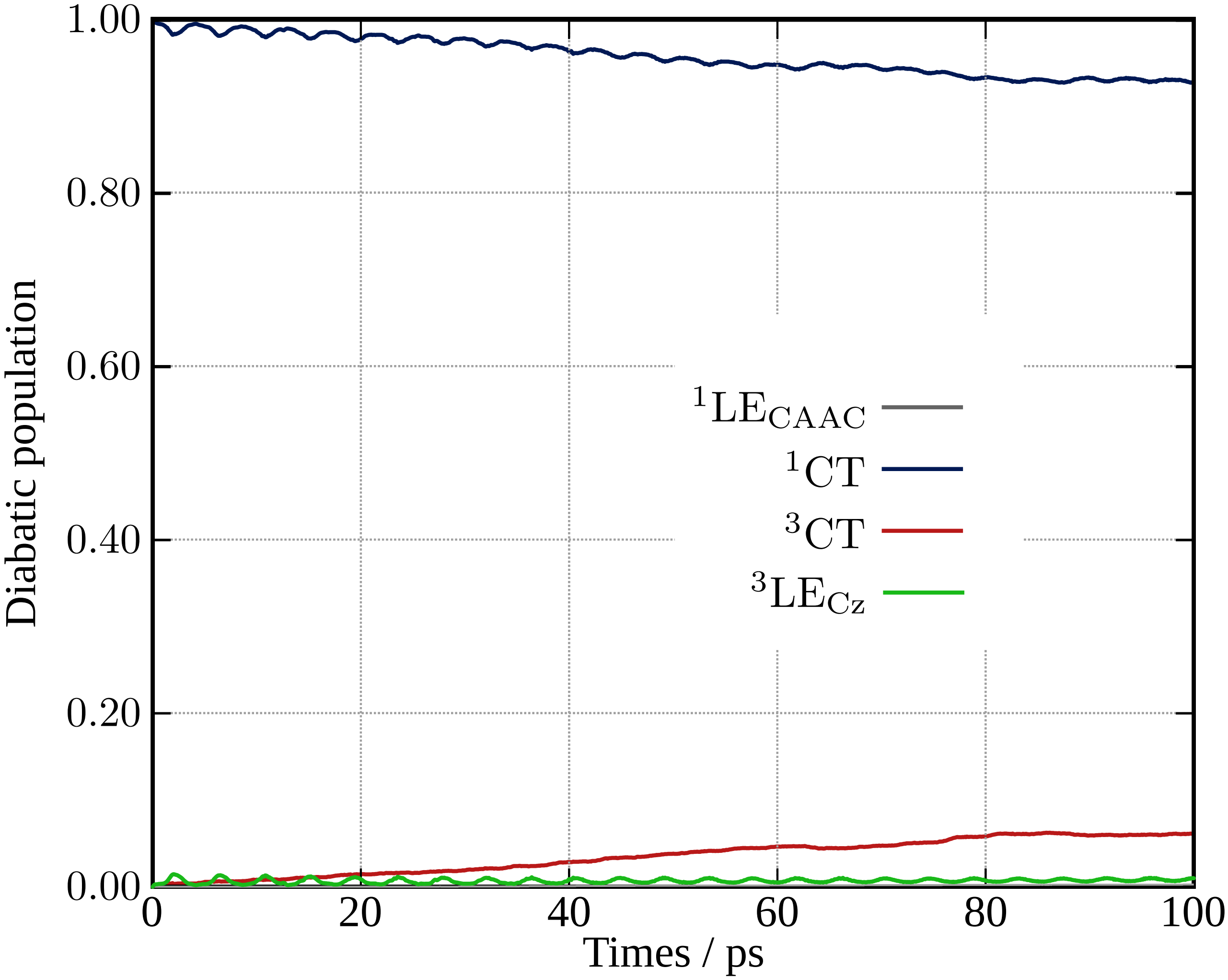

Figure S10: Evolution of the diabatic population along time for **Cu-Cz** with the Hamiltonian without ^{3}LE(CAAC).

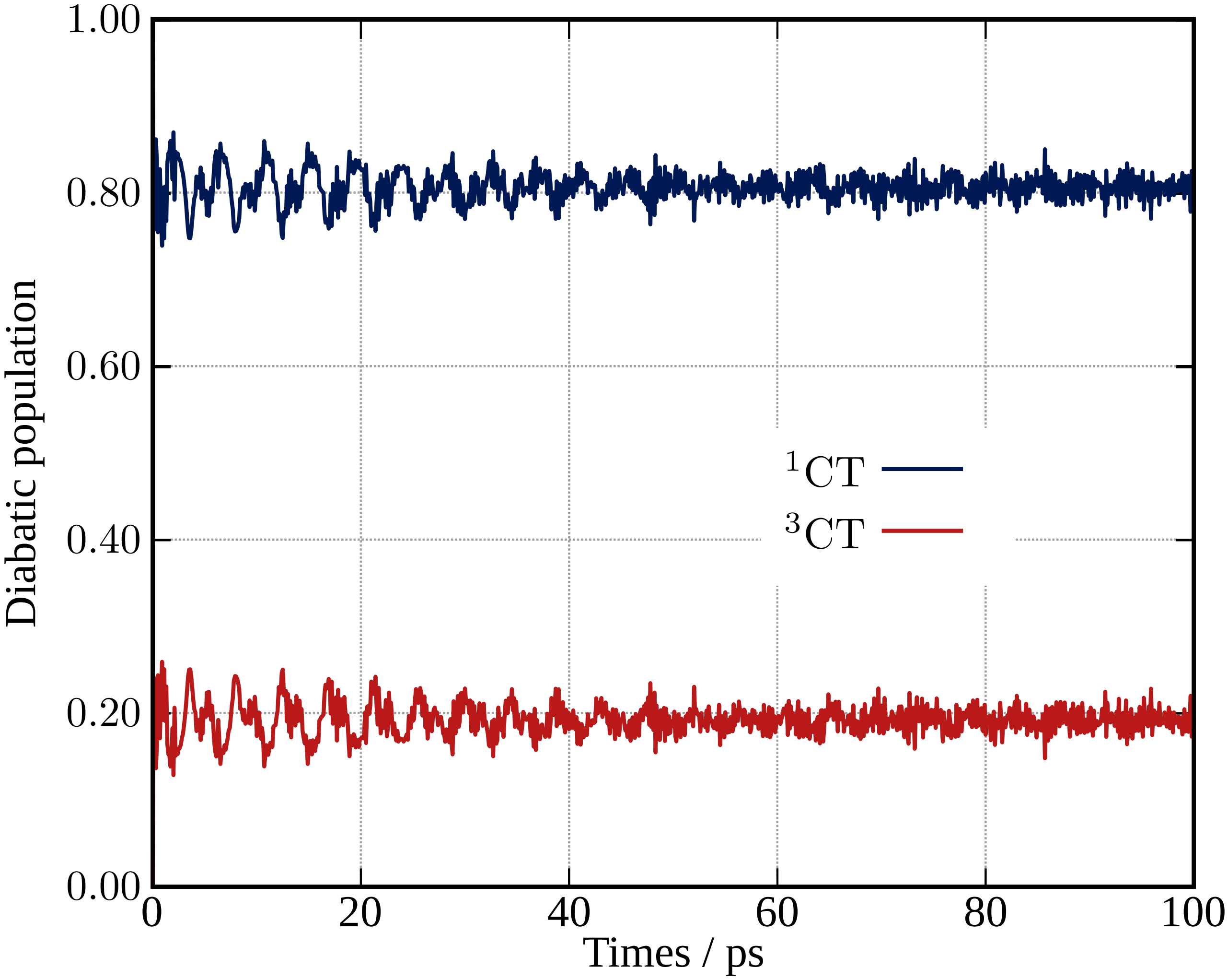

Figure S11: Evolution of the diabatic population along time for **Cu-Cz** with the Hamiltonian without ^{3}LE(Cz), ^{3}LE(CAAC) and ^{1}LE(CAAC).

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