Supporting Information

Syntheses, Structures and Luminescence of multinuclear Silver(I) pyrazolate adducts with 1, 10-Phenanthroline derivatives

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Table S1. **Experimental details and refinement parameters of complexes** 2 - 4**.**

datablock	3	2	4
Formula moiety	$C_{48}H_{28}Ag_4F_{24}N_{12}$	$C_{32}H_{12}Ag_4F_{24}N_{10}$	$C_{52}H_{40}AgN_4$,$C_{30}H_6Ag_5F_{36}N_{12}$
Brutto formula	$C_{48}H_{28}Ag_4F_{24}N_{12}$	$C_{32}H_{12}Ag_4F_{24}N_{10}$	$C_{82}H_{46}Ag_6F_{36}N_{16}$
Formula weight	1660.30	1424.00	2586.57
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD	Bruker APEX-II CCD
Scan mode	ω and ϕ scans	ϕ and ω scans	ϕ and ω scans
Anode [Wavelength, Å]	MoKα [0.71073]	MoKα [0.71073]	MoKα [0.71073]
Crystal Dimensions, mm	0.1 × 0.14 × 0.3	0.17 × 0.22 × 0.27	0.18 × 0.25 × 0.28
Crystal color	colourless	colourless	orange
Crystal system	triclinic	triclinic	triclinic
a, Å	10.762(2)	12.2023(5)	14.3696(5)
b, Å	11.734(2)	12.9913(5)	16.7297(6)
c, Å	12.469(2)	16.1279(7)	38.1790(13)
α, °	65.492(3)	79.2640(10)	79.6540(10)
β, °	85.582(3)	70.2820(10)	81.7590(10)
γ, °	70.097(3)	68.3560(10)	87.1010(10)
Volume, Å³	1343.4(4)	2231.46(16)	8932.8(5)
Density, gcm⁻³	2.052	2.119	1.923
Temperature, K	120	120	120
T_{min}/T_{max}	0.6065/0.7458	0.5088/0.7461	0.6104/0.7461
μ, mm⁻¹	1.569	1.869	1.419
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	1	2	4
F(000)	804	1356	5024
Reflections collected	20802	34754	138385
Independent reflections	7207	8760	55006
Reflections (I>2σ(I))	5890	7724	38738
Parameters	399	631	2529
R_{int}	0.0345	0.0264	0.0443
$2\theta_{min}$ - $2\theta_{max}$, °	3.600 - 58.304	3.382 - 51.998	2.864 - 61.318
wR_2 (all reflections)	0.0767	0.0613	0.0984
R_1(I>σ(I))	0.0305	0.0251	0.0438
GOF	1.028	1.051	1.012

ρ_{min}/ρ_{max}, eÅ^{-3}	-0.762/1.018	-0.996/1.329	-1.254/1.951

Table S2. Selected bonds lengths for two independent crystallographic adducts A and B of complex 3.

adduct **A**			adduct **B**		
Ag1A	N1A	2.342(2)	Ag1B	N1B	2.299(2)
Ag1A	N2A	2.280(3)	Ag1B	N2B	2.315(3)
Ag1A	N3A	2.339(2)	Ag1B	N3B	2.270(3)
Ag1A	N4A	2.275(3)	Ag1B	N4B	2.361(2)
N1A	C1A	1.332(4)	N1B	C1B	1.328(4)
N1A	C11A	1.366(4)	N1B	C11B	1.361(4)
N2A	C10A	1.334(4)	N2B	C10B	1.330(4)
N2A	C12A	1.357(4)	N2B	C12B	1.365(4)
N3A	C27A	1.332(4)	N3B	C27B	1.333(5)
N3A	C37A	1.363(4)	N3B	C37B	1.363(4)
N4A	C36A	1.332(4)	N4B	C36B	1.334(4)
N4A	C38A	1.362(4)	N4B	C38B	1.364(4)
Ag2A	Ag3A	3.221(1)	Ag2B	N5B	2.205(3)
Ag2A	N5A	2.195(3)	Ag2B	N7B	2.178(3)
Ag2A	N7A	2.282(3)	Ag2B	N9B	2.266(3)
Ag2A	N9A	2.176(3)	Ag3B	N6B	2.076(3)
Ag3A	Ag4A	3.1996(5)	Ag3B	N11B	2.081(3)
Ag3A	N6A	2.085(3)	Ag4B	N12B	2.192(3)
Ag3A	N11A	2.086(3)	Ag4B	N13B	2.166(3)
Ag4A	N12A	2.195(3)	Ag4B	N15B	2.359(3)
Ag4A	N13A	2.210(3)	Ag5B	N8B	2.096(3)
Ag4A	N15A	2.282(3)	Ag5B	N14B	2.097(3)
Ag5A	N8A	2.079(3)	Ag6B	N10B	2.085(3)
Ag5A	N14A	2.083(3)	Ag6B	N16B	2.086(3)
Ag6A	N10A	2.088(3)	N5B	N6B	1.360(4)
Ag6A	N16A	2.090(3)	N5B	C53B	1.342(4)
N5A	N6A	1.359(4)	N6B	C55B	1.343(4)
N5A	C53A	1.339(5)	N7B	N8B	1.356(4)
N6A	C55A	1.343(4)	N7B	C56B	1.335(5)
N7A	N8A	1.355(4)	N8B	C58B	1.340(5)
N7A	C56A	1.346(4)	N9B	N10B	1.351(5)
N8A	C58A	1.348(4)	N9B	C59B	1.340(4)
N9A	N10A	1.363(4)	N10B	C61B	1.345(5)
N9A	C59A	1.344(4)	N11B	N12B	1.359(4)
N10A	C61A	1.346(4)	N11B	C62B	1.344(5)
N11A	N12A	1.360(4)	N12B	C64B	1.345(4)
N11A	C62A	1.347(5)	N13B	N14B	1.363(4)
N12A	C64A	1.348(4)	N13B	C65B	1.330(4)
N13A	N14A	1.358(4)	N14B	C67B	1.342(4)
N13A	C65A	1.337(4)	N15B	N16B	1.360(4)
N14A	C67A	1.346(4)	N15B	C68B	1.341(4)
N15A	N16A	1.358(4)	N16B	C70B	1.343(4)
N15A	C68A	1.338(4)			
N16A	C70A	1.339(5)			

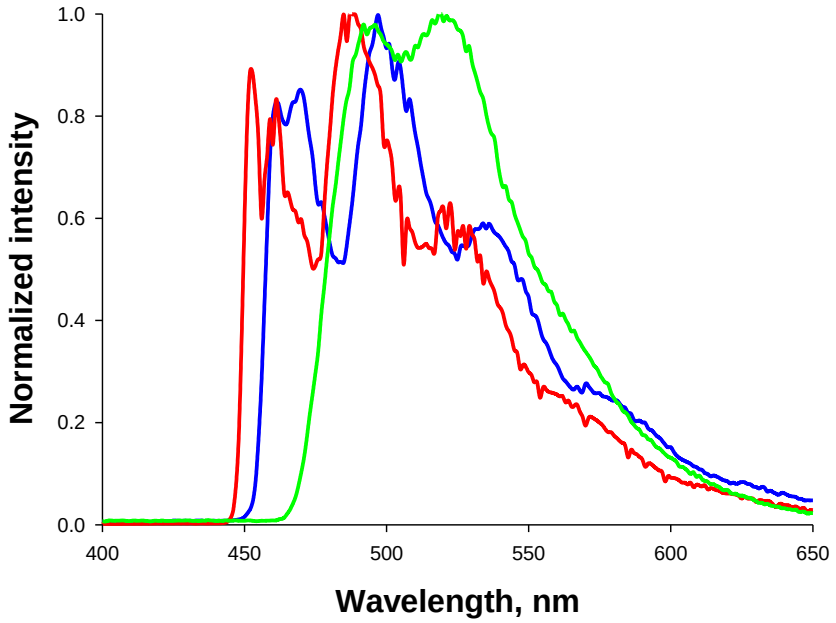


Figure S1. Normalized emission (λ_{exc} = 340 nm) spectra of complexes 2 (blue), 3 (red) and 4 (green) in solid state at 77 K.

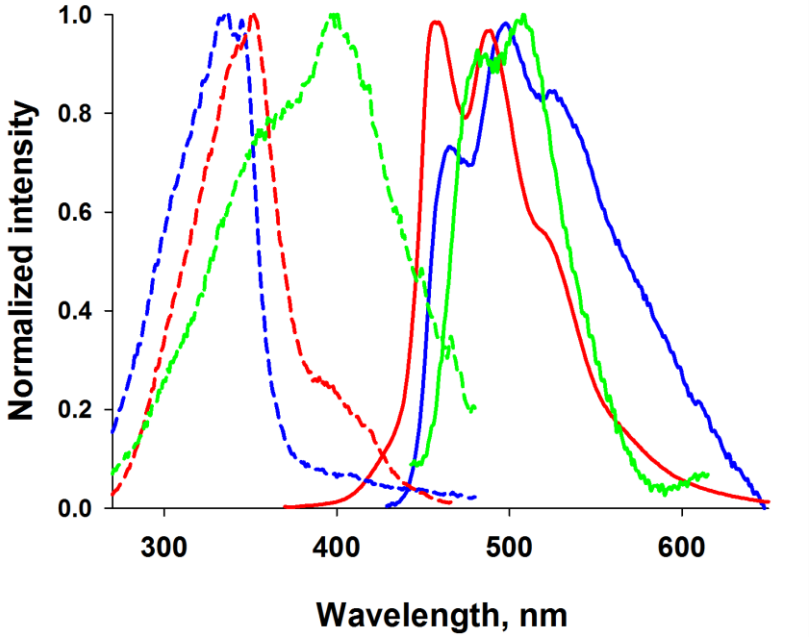


Figure S2. Normalized emission (solid, λ_{exc} = 340 nm) and excitation (dashed) spectra of complexes 2 (blue), 3 (red) and 4 (green) in solid state at 298K.

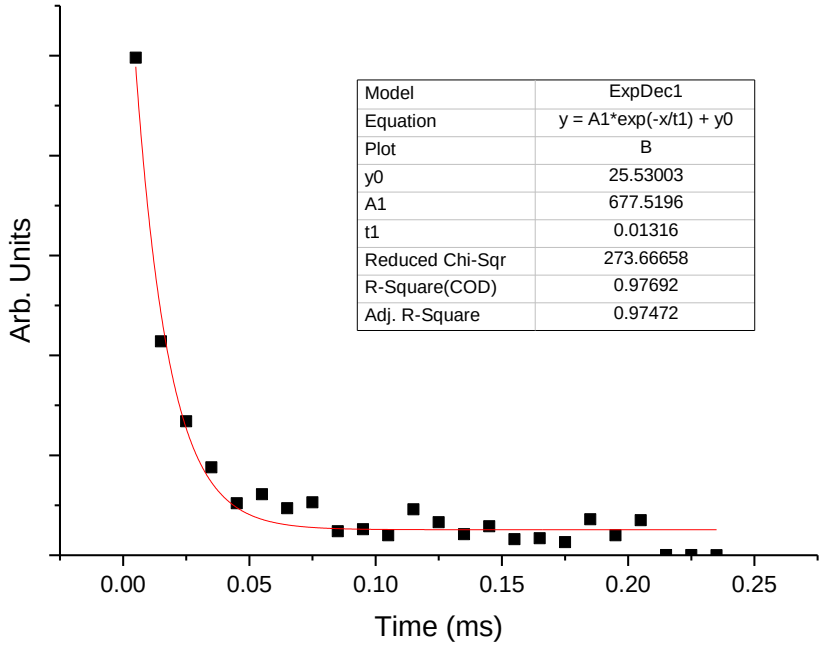


Figure S3. Phosphorescence decay by delay of complex 2 at RT.

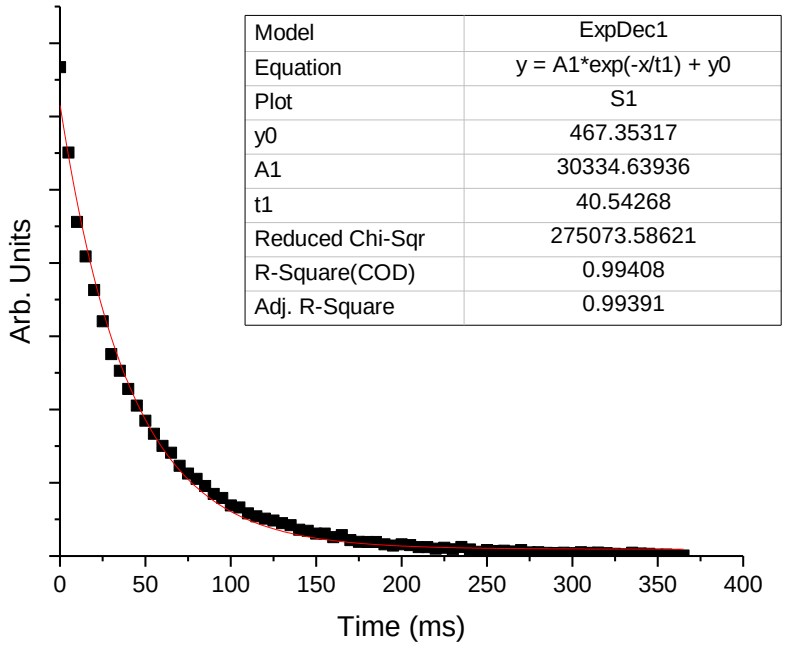


Figure S4. Phosphorescence decay by delay of complex 2 at 77 K.

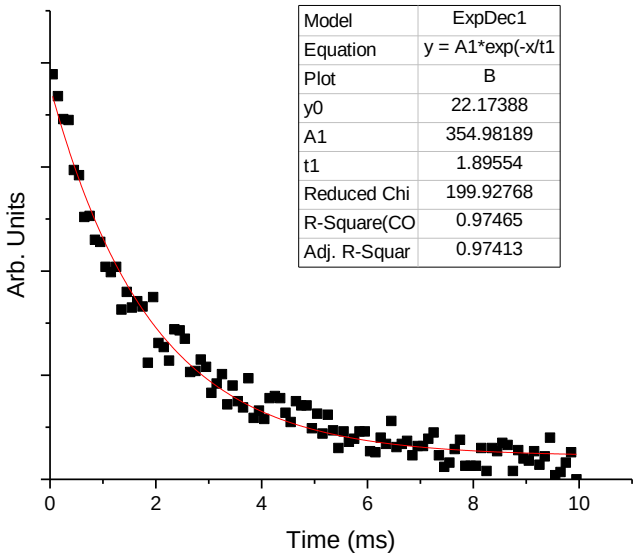


Figure S5. Phosphorescence decay by delay of complex 3 at RT.

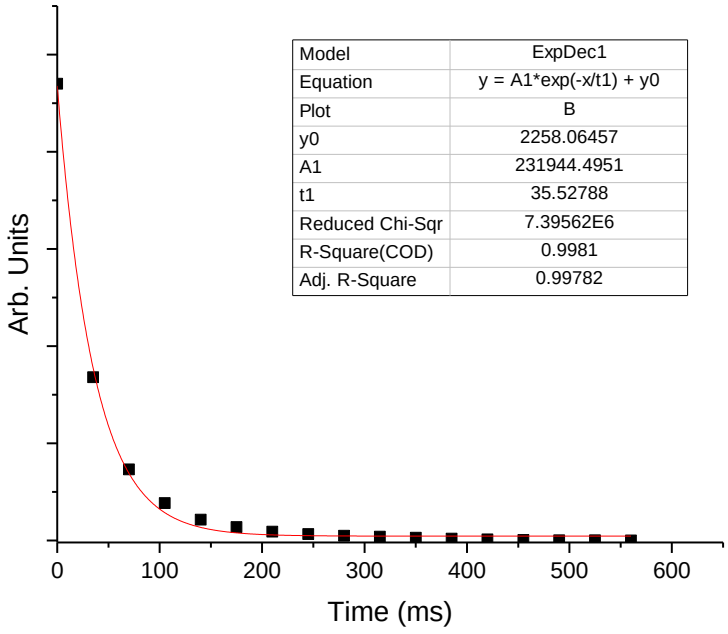


Figure S6. Phosphorescence decay by delay of complex 3 at 77K.

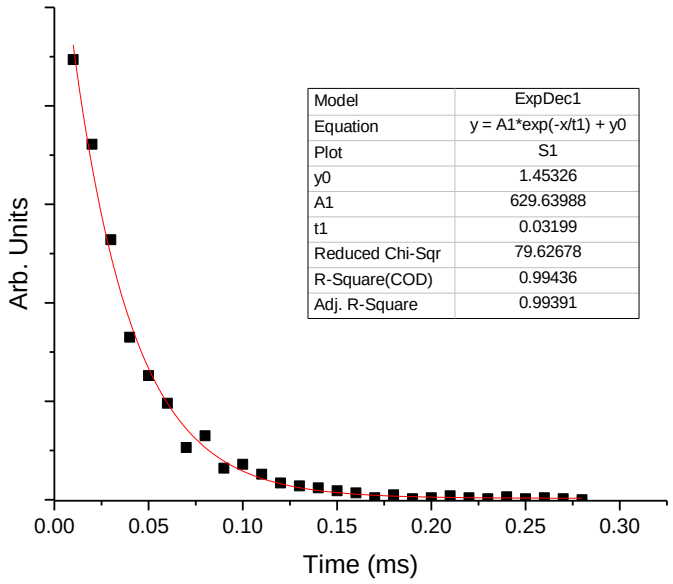


Figure S7. Phosphorescence decay by delay of complex 4 at RT.

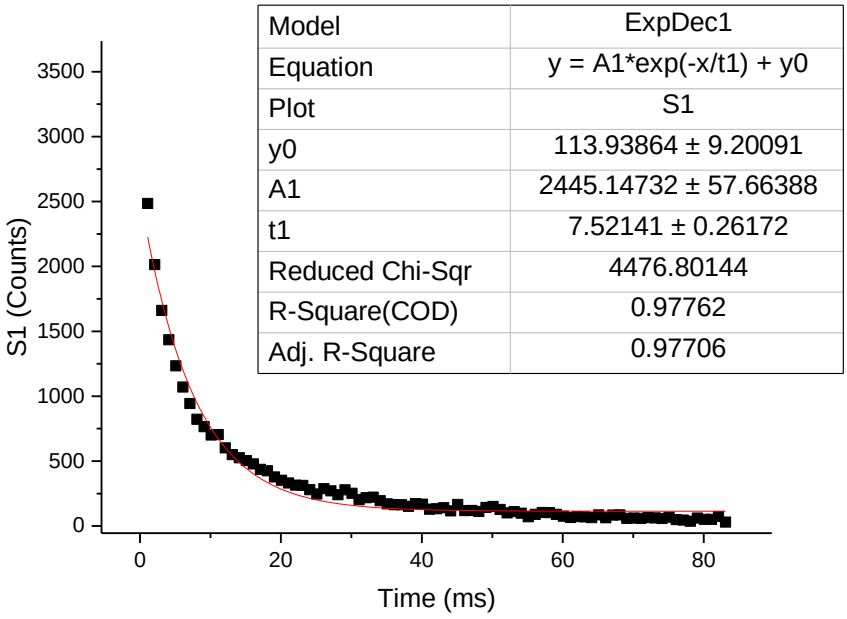


Figure S8. Phosphorescence decay by delay of complex 4 at 77 K.

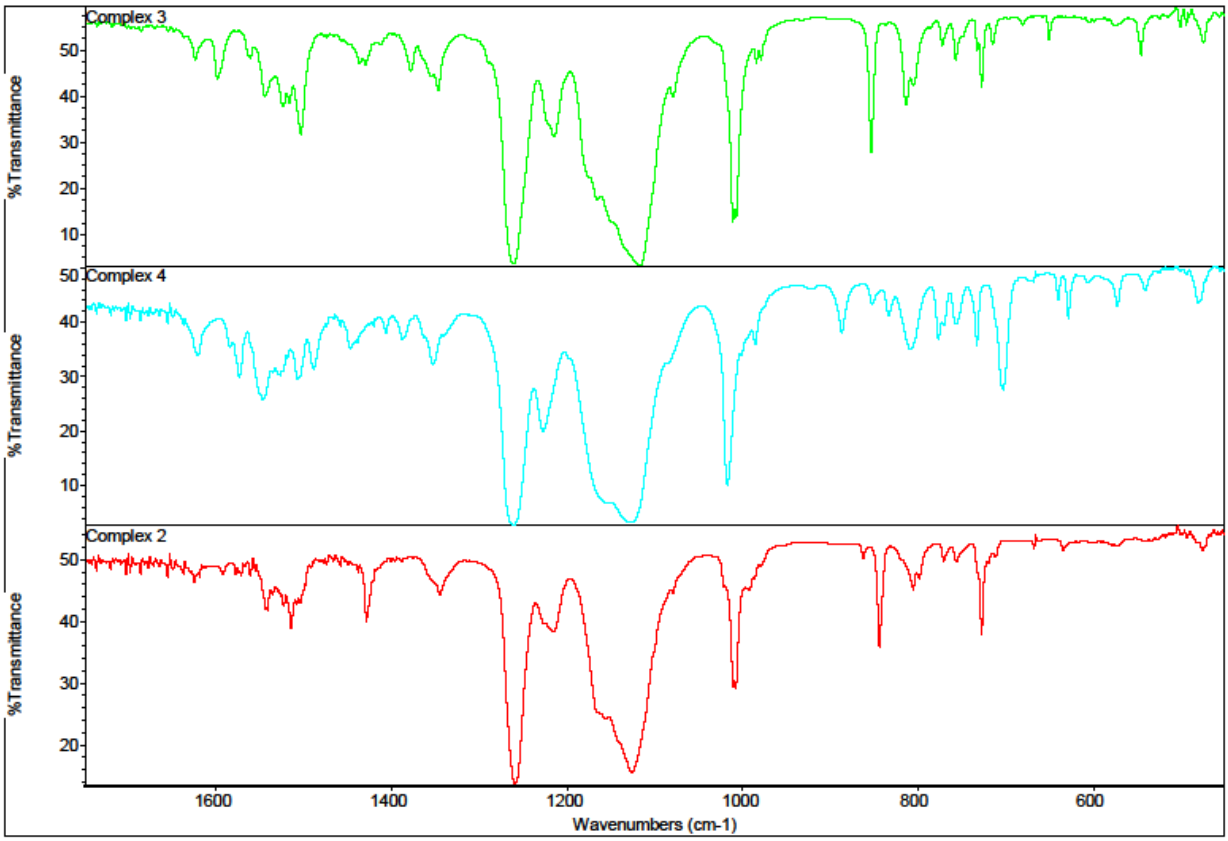


Figure S9. IR spectra of complexes in KBr pellets in the fingerprint region.

Table S3. Computed characteristics of the excited states of **2**.

#	E, eV	f	Composition of hole	Similarity of T to S1
S1	4.076	0.0012	N^N(84.7%) Ag4(8.8%) Pz4(6.5%)	
T1	2.773	-	N^N(99.7%) Ag4(0.3%)	s_H = 0.84; s_E = 0.63
T2	3.371	-	N^N(98.5%) Ag4(1.1%) Pz4(0.4%)	s_H = 0.79; s_E = 0.89

Table S4. Natural transition orbitals of singlet and triplet excited states of **2** as isosurfaces at 0.04 a.u., occupancies of NTOs (in parentheses) and their principal symmetry.

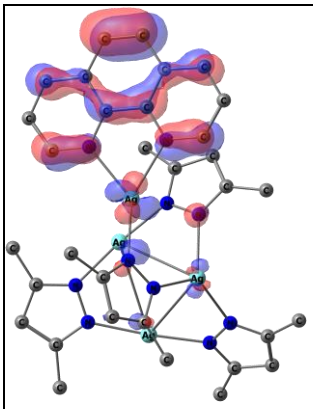
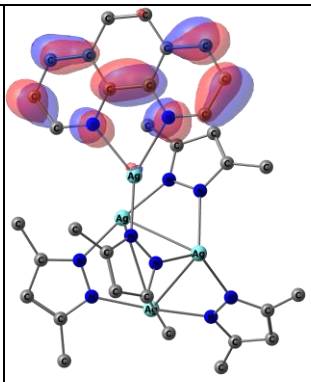
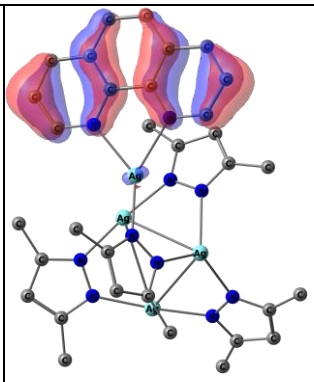
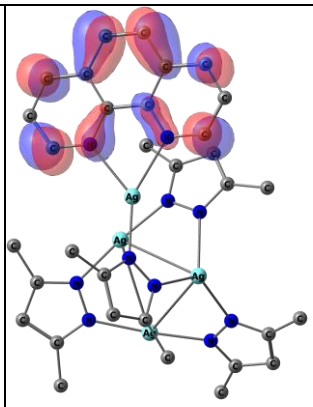
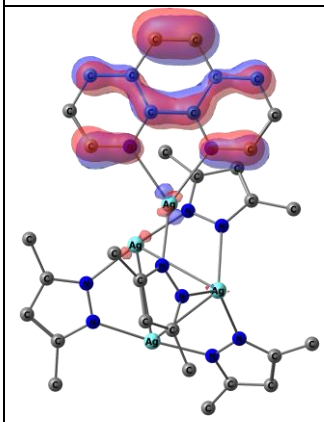
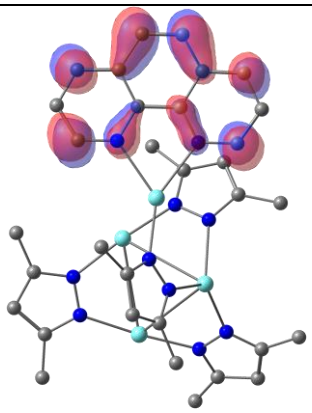
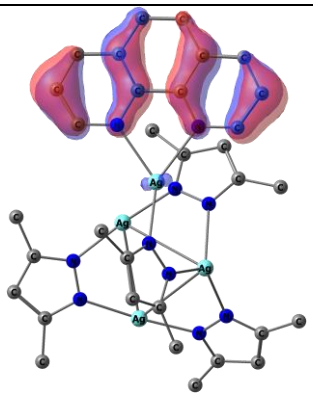
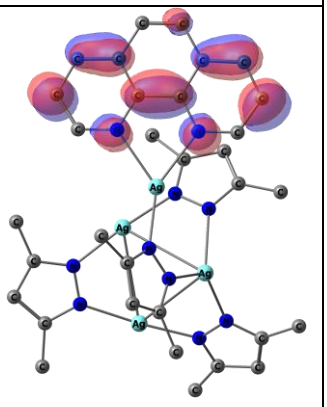
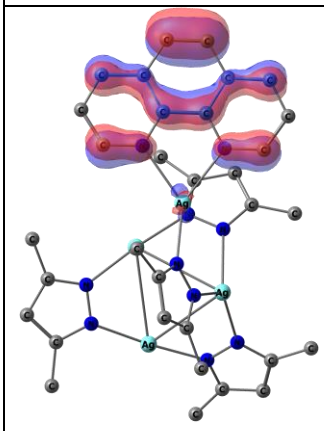
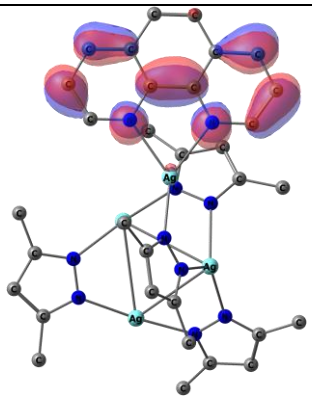
			
S1 HONTO (0.85), B_2	S1 LUNTO, B_2	S1 HONTO-1 (0.14), A_2	S1 LUNTO+1, A_2
			
T1 HONTO (0.74), B_2	T1 LUNTO, A_2	T1 HONTO-1 (0.21), A_2	T1 LUNTO+1, B_2
			
T2 HONTO (0.92) B_2	T2 LUNTO, B_2		

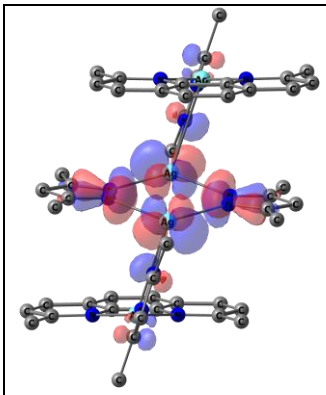
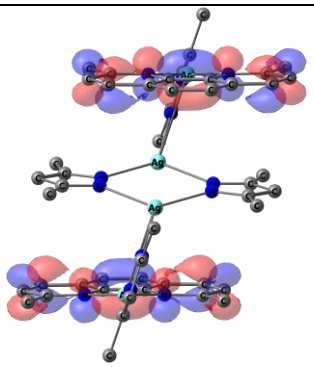
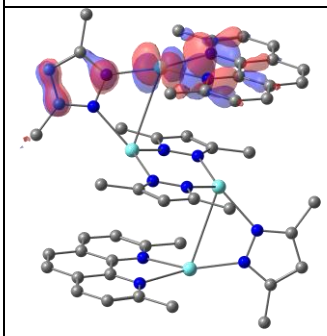
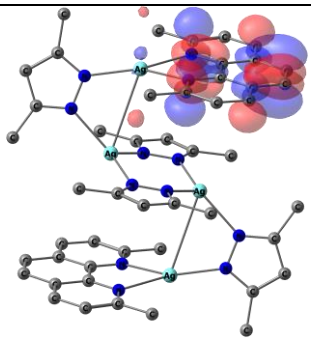
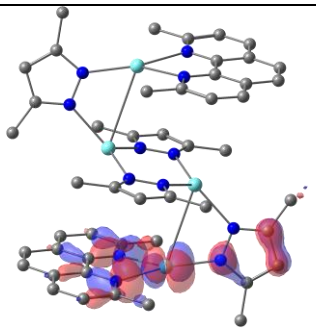
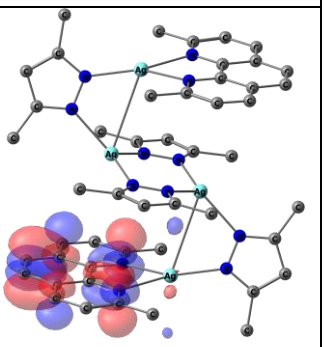
Table S5. Computed characteristics of the excited states of **3**.

#	E, eV	f	Composition of hole	Similarity of T to S4[b]
S1	3.651	0.0001	N^N(0.3%) Ag4(47.9%) Pz4(51.8%)	
S2	3.812	0.0011	N^N(45.5%) Ag4(38.4%) Pz4(16.1%)	
S3	3.890	0.0027	N^N(11.1%) Ag4(48.0%) Pz4(40.9%)	
S4	3.931	0.0111	N^N(85.0%) Ag4(8.0%) Pz4(7.0%)	
T1[a]	2.774	-	N^N(100%)	$s_H = 0.82$; $s_E = 0.61$
T3[a]	3.183	-	N^N(67.4%) Ag4(26.0%) Pz4(6.6%)	$s_H = 0.44$; $s_E = 0.91$
T5[a]	3.197	-	N^N(84.5%) Ag4(13.0%) Pz4(2.5%)	$s_H = 0.71$; $s_E = 0.92$
T7[a]	3.494	-	N^N(100%)	$s_H = 0.62$; $s_E = 0.93$

[a] Only even triplets are given in the table due to double degeneracy of the lowest triplet states.

[b] Due to degeneracy of triplet states the average of atomic contributions to the T_n and T_{n+1} was taken for calculating similarity of T_n (e.g. $(a_i^{T3}+a_i^{T4})/2$ for the T3-S4 similarity)

Table S6. Natural transition orbitals of singlet excited states of **3** as isosurfaces at 0.04 a.u., occupancies of NTOs (in parentheses) and their principal symmetry.

			
S1 HONTO, B_g	S1 LUNTO, B_u		
			
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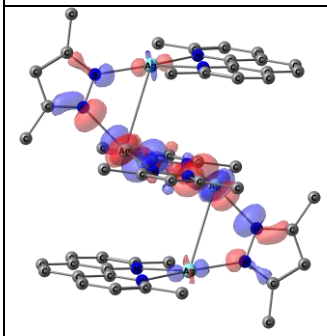
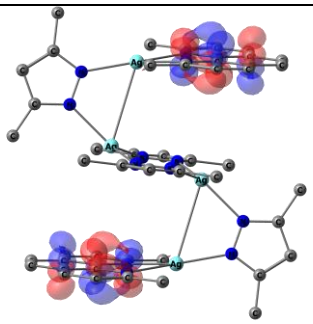
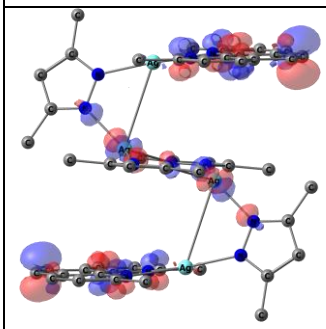
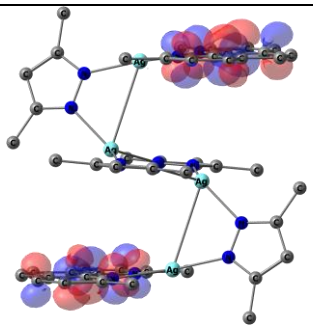
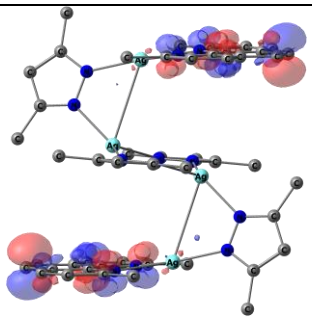
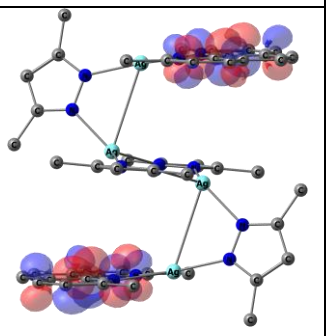
			
S3 HONTO (0.90), B_u	S3 LUNTO, A_g		
			
S4 HONTO (0.49), B_u	S4 LUNTO, A_g	S4, HONTO+1 (0.39), A_g	S4 LUNTO+1, B_u

Table S7. Natural transition orbitals of triplet excited states of **3** as isosurfaces at 0.04 a.u., occupancies of NTOs (in parentheses) and their principal symmetry.

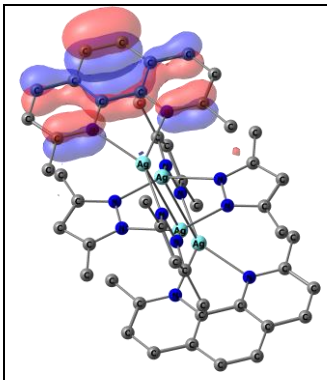
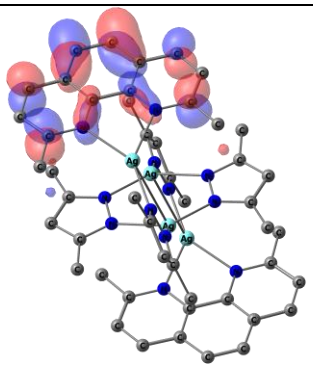
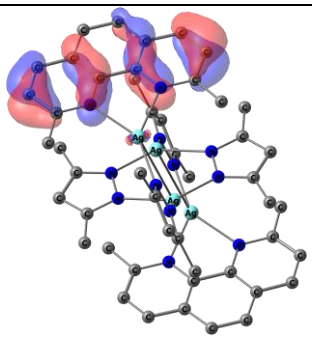
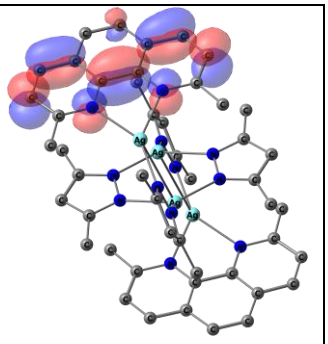
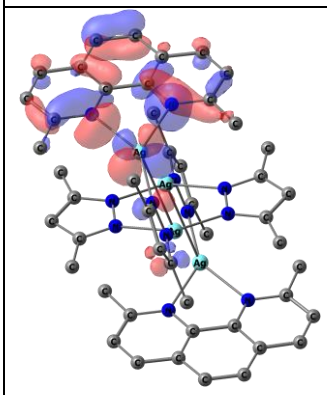
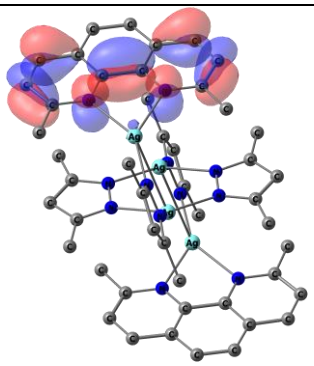
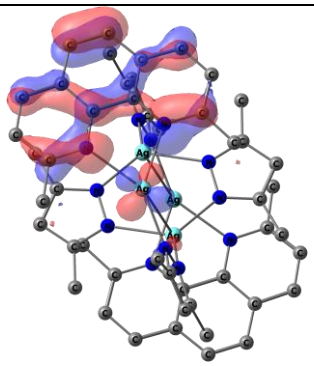
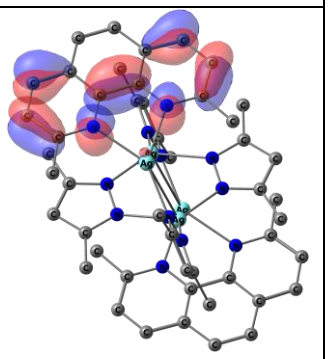
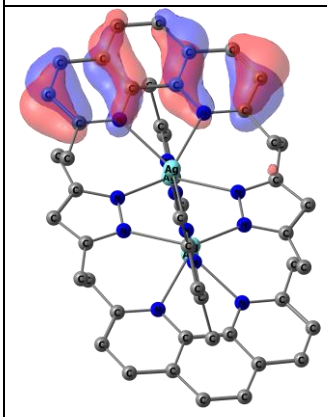
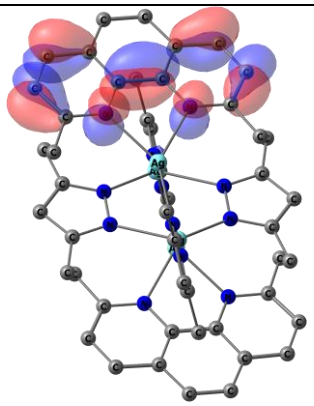
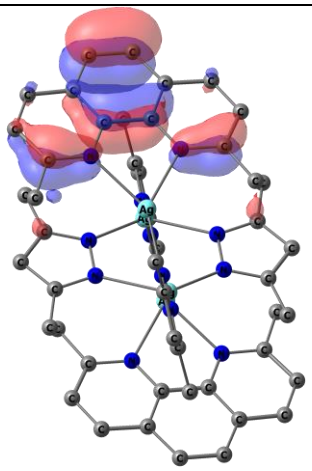
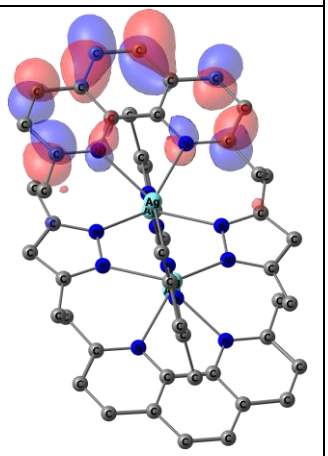
			
T1 HONTO (0.71), B_2	T1 LUNTO, A_2	T1 HONTO-1 (0.21), A_2	T1 LUNTO+1, B_2
			
T3 HONTO (0.97), A	T3 LUNTO, B_2	T5 HONTO (0.93), A	T5 LUNTO, B_2
			
T7 HONTO (0.68), A_2	T7 LUNTO, B_2	T7 HONTO-1 (0.20), B_2	T7 LUNTO+1, A_2

Table S8. XYZ coordinates of PBE0/def2-TZVP optimized complexes.

2

47	-0.913607031	-1.515668132	0.640498050
47	2.502251267	-0.021894101	1.384739108
47	-3.066499141	0.738632092	-0.758108053
47	0.194393116	1.108980039	-1.249319094
7	0.761691144	0.355985969	2.558775198

7	-0.413755962	-0.255993050	2.401247185
6	0.688157155	1.137256032	3.644970282
6	-0.565028944	1.040489051	4.223874328
6	-1.218926016	0.145185000	3.392858260
6	1.846100261	1.959143068	4.087765314
6	-2.622196133	-0.343010004	3.509729273
1	-0.938536958	1.534957098	5.103817394
9	2.235382312	2.838987124	3.146132241
9	1.547657257	2.656210128	5.184177399
9	2.927648328	1.211079984	4.367824335
9	-3.166961166	0.066133041	4.658992358
9	-3.403020183	0.115215050	2.516303194
9	-2.700750173	-1.678258102	3.475644268
7	0.791252091	-1.787049197	-0.928104069
7	1.145235147	-0.705686120	-1.628463120
6	1.438426119	-2.830416289	-1.448791109
6	2.236171189	-2.436348279	-2.516653191
6	2.008980203	-1.075276168	-2.587376196
6	1.235575070	-4.209997390	-0.923713068
6	2.581033271	-0.089332108	-3.544351266
1	2.872695223	-3.040821339	-3.139852236
9	1.121743058	-4.227623390	0.412959035
9	0.137850971	-4.788351409	-1.416573104
9	2.274583128	-4.995354473	-1.246733095
9	1.634529211	0.525899961	-4.266276322
9	3.271313348	0.882512952	-2.920160221
9	3.417426319	-0.685154175	-4.397137331
7	-3.693401235	-1.243511046	-0.701107048
7	-2.928093202	-2.161174136	-0.105431005
6	-3.608345279	-3.308041207	-0.091531004
6	-4.849518340	-1.818497063	-1.064055076
6	-4.850028372	-3.148990164	-0.696054051
6	-3.049735266	-4.559105316	0.495319041
6	-5.912007385	-1.044744980	-1.763132131
1	-5.627831423	-3.879838201	-0.837626063
9	-1.944179178	-4.331232327	1.212891093
9	-3.938744350	-5.153810340	1.301700101
9	-2.731329262	-5.456212415	-0.449452031
9	-5.500930380	-0.591513953	-2.958452222
9	-6.992821488	-1.798902010	-1.970076150
9	-6.296139425	0.032984113	-1.061783080
7	-2.270144035	2.676498218	-0.787090059
7	-0.950142931	2.833095201	-0.931135070
6	-1.848743951	4.867659378	-0.726539053
6	-2.823542049	3.886356326	-0.662216050
6	-0.681275877	4.143005291	-0.898742066
6	-4.297184157	4.050460372	-0.491415035
6	0.712118243	4.657279300	-0.993542075
1	-1.970953933	5.934994474	-0.662280049
9	-4.746878206	3.414453333	0.596766048
9	-4.977271222	3.561994353	-1.536108112
9	-4.612366149	5.341399473	-0.368879025
9	1.426170279	4.020576235	-1.933008146
9	1.385942288	4.504173272	0.161944015
9	0.723027274	5.958072423	-1.283483095
7	4.159965359	-1.527344254	0.788977063
7	4.218493426	1.165033948	0.302341026
6	4.241691456	2.462683049	0.080881009
6	5.277277553	3.097054073	-0.613772043
6	6.317223593	2.337898990	-1.081268079
6	6.322234584	0.952844884	-0.851593061
6	7.376073666	0.104842792	-1.303787097
6	7.350006606	-1.224818309	-1.059212077
6	6.266930535	-1.816211329	-0.343710024

6	6.208500476	-3.191400434	-0.067615002
6	5.140896378	-3.697691444	0.625645050
6	4.132376322	-2.820851352	1.037455082
6	5.202843449	-1.013085242	0.113197012
6	5.232672483	0.406462866	-0.145429008
1	3.407060409	3.037133111	0.466375039
1	5.239643573	4.167177156	-0.772030056
1	7.138358673	2.790366001	-1.626831122
1	8.200702691	0.550879808	-1.848671136
1	8.153303650	-1.866735379	-1.403423103
1	7.010363502	-3.837682502	-0.408275028
1	5.059132349	-4.752755523	0.852674070
1	3.271583249	-3.193338360	1.580890123

3

47	-1.381207459	1.189337281	-0.059921556
47	-3.698894883	-1.201555841	-0.673347325
9	-1.825411288	2.880332669	-3.249906869
9	-0.507170732	3.935542864	-1.916985929
9	-0.059071003	3.840112325	-4.027958501
9	3.783262702	-0.615087053	-2.984557838
9	2.216603457	-2.087393079	-3.065270910
9	-7.047612289	-0.432822697	0.313986427
9	2.631876224	-0.852689586	-4.788002840
9	-6.737873732	-0.269756504	-1.806266687
9	-2.368930325	4.082791567	0.751014548
9	-7.955521642	1.189826426	-0.779272423
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7	-2.412801278	-2.488671584	-2.131804666
7	0.955437265	0.095214198	-1.798933592
7	0.152114570	1.155644577	-1.677777476
7	-3.551682853	1.775438101	-0.188470991
9	-4.314068690	4.981012822	1.030139513
9	-3.424071235	4.925923947	-0.925537406
6	-5.605609948	2.669918581	-0.193956919
1	-6.421929620	3.369253235	-0.133045202
6	-5.654786707	1.310273831	-0.442797219
6	-2.006127107	-3.662060723	-1.615727031
6	-2.527638514	-4.078769000	-0.335236735
6	-4.246055009	2.907043674	-0.039334431
6	-1.971887820	-2.091787118	-3.313200960
6	-3.907293404	-3.644960117	1.470608441
6	0.262925835	1.893848606	-2.791278112
6	-2.652845905	-5.688610817	1.437733929
1	-2.352433605	-6.629230098	1.886842199
6	-3.545492664	-4.865451127	2.067255519
1	-3.974578550	-5.136376336	3.023697438
6	-0.625830526	-4.063610347	-3.535262774
1	0.085928454	-4.674719977	-4.079621943
6	-1.098063832	-4.501356092	-2.287881437
6	-2.114644845	-5.315016230	0.197392753
6	-0.532846321	3.135385011	-2.990493222
6	1.558247152	0.169431091	-2.992438266
6	2.542748017	-0.849283076	-3.448571554
6	1.153438008	1.307409257	-3.675916335
1	1.450915591	1.647442671	-4.653384323
6	-1.063628448	-2.874733106	-4.048318336
1	-0.711232395	-2.518740531	-5.008301715
6	-4.876441376	-2.723454882	2.131584137
1	-4.392487996	-1.776383301	2.381278316
1	-5.278138164	-3.158742302	3.046263524
1	-5.705097546	-2.492652246	1.458481095
6	-6.846129586	0.454720464	-0.679007680

6	-0.691801027	-5.736446324	-1.705564605
1	0.024507549	-6.349701794	-2.240415412
6	-2.445198895	-0.777441655	-3.835356736
1	-3.496037161	-0.618834623	-3.588142959
1	-2.315831240	-0.709180118	-4.915552231
1	-1.874274499	0.035294834	-3.377121905
6	-1.183181299	-6.129199826	-0.508875179
1	-0.871560343	-7.066097562	-0.061087945
6	-3.583305152	4.217310366	0.203836329
47	1.381108979	-1.189298546	0.060039718
47	3.698940922	1.201491657	0.673272293
9	1.825383522	-2.880201253	3.250055980
9	0.507094473	-3.935444194	1.917208803
9	0.059061573	-3.839944306	4.028191831
9	-3.783261649	0.615277054	2.984778806
9	-2.216572649	2.087556674	3.065395483
9	7.047592498	0.432528867	-0.314097696
9	-2.631809310	0.852912708	4.788178394
9	6.737896858	0.269577897	1.806169969
9	2.368644463	-4.082850893	-0.750783330
9	7.955439726	-1.190119194	0.779213912
7	3.397322934	3.277523047	-0.306779083
7	4.418077483	-0.793314581	0.432801182
7	2.412778666	2.488697810	2.131588190
7	-0.955488637	-0.095110732	1.799079407
7	-0.152174497	-1.155548213	1.677934309
7	3.551553961	-1.775514921	0.188547148
9	4.313725032	-4.981193584	-1.029925255
9	3.423791835	-4.925956740	0.925777759
6	5.605431562	-2.670110154	0.194023230
1	6.421710964	-3.369492301	0.133125224
6	5.654689920	-1.310456471	0.442800593
6	2.006233720	3.662110069	1.615462611
6	2.527901055	4.078774582	0.335019711
6	4.245858864	-2.907165850	0.039447215
6	1.971712054	2.091845328	3.312937906
6	3.907699198	3.644856779	-1.470689664
6	-0.262960513	-1.893716847	2.791459123
6	2.653385248	5.688591290	-1.437953606
1	2.353076815	6.629225864	-1.887101062
6	3.546036362	4.865367157	-2.067382554
1	3.975230994	5.136253874	-3.023787255
6	0.625761056	4.063759660	3.534850994
1	-0.086015548	4.674917461	4.079131126
6	1.098154612	4.501467896	2.287516543
6	2.115039013	5.315043324	-0.197660981
6	0.532809416	-3.135252294	2.990690541
6	-1.558258471	-0.169279962	2.992607592
6	-2.542726061	0.849464250	3.448744162
6	-1.153441876	-1.307242666	3.676106865
1	-1.450889651	-1.647241726	4.653595544
6	1.063425736	2.874854044	4.047955982
1	0.710902908	2.518887314	5.007902139
6	4.876846657	2.723279185	-2.131564091
1	4.392851736	1.776237502	-2.381293403
1	5.278660377	3.158529404	-3.046209141
1	5.705423678	2.492425806	-1.458379885
6	6.846085347	-0.454956838	0.678941687
6	0.692032346	5.736582005	1.705150567
1	-0.024291297	6.349887165	2.239924071
6	2.444876230	0.777468257	3.835146584
1	3.495730651	0.618788886	3.588046405
1	2.315386827	0.709215896	4.915327612
1	1.873946065	-0.035230178	3.376848659

6	1.183558592	6.129293702	0.508507555
1	0.872043947	7.066208318	0.060681870
6	3.583029498	-4.217408502	-0.203636997