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

Electronic Supplementary Information (ESI)

Basic photophysical analysis of a thermally activated delayed fluorescence copper(I) complex in solid state: theoretical estimations from a polarizable continuum model (PCM)-tuned range-separated density functional approach

Lingling Lv*[a], Kun Yuan[a], Yongcheng Wang[b]

[a] *College of Chemical Engineering and Technology, Tianshui Normal University, TianShui, GanSu 741001, China. E-mail: lvling100@163.com*

[b] *College of Chemistry and Chemical Engineering, Northwest Normal University, LanZhou, GanSu 730070, China. E-mail:ycwang02@163.com*

* Corresponding author: E-mail: lvling100@163.com

Table S1. Obtained vital structural parameters for Cu(pop)(pz_2Bph_2) using the different functional methods, and compared to the experimental values.

Parameters	B3LYP	CAM-B3LYP	LC-ωBPE*	LC-BLYP*	Exp. value
	The gas state				
R(Cu1–P1)	2.4239	2.3727	2.3086	2.2832	2.2957(6)
R(Cu1–P2)	2.3197	2.2921	2.2557	2.2310	2.2203(6)
R(Cu1–N1)	2.0714	2.0532	2.0353	2.0029	2.0290(20)
R(Cu1–N3)	2.0719	2.0514	2.0352	2.0084	2.0197(18)
∠ P1–Cu1–P2	111.83	112.11	112.66	112.18	109.20(2)
∠ N1–Cu1–N3	94.72	95.17	95.67	97.09	96.45(8)
∠ P1–Cu1–N1	104.05	104.15	103.77	103.08	103.20(10)
∠ P1–Cu1–N3	104.23	104.01	104.74	104.65	107.07(6)
∠ P2–Cu1–N1	124.86	124.56	123.99	124.20	126.94(6)
∠ P2–Cu1–N3	114.32	114.04	113.38	113.06	112.11(6)
MAD[a]	0.0805	0.0450	0.0175	0.0151	
MAD[b]	2.21	2.09	1.89	1.64	
	The solution state (CH_2Cl_2)				
R(Cu1–P1)	2.4238	2.3765	2.3239	2.3524	2.2957(6)
R(Cu1–P2)	2.3267	2.2977	2.2672	2.2843	2.2203(6)
R(Cu1–N1)	2.0843	2.0628	2.0429	2.0490	2.0290(20)
R(Cu1–N3)	2.0833	2.0607	2.0429	2.0536	2.0197(18)
∠ P1–Cu1–P2	111.66	111.86	112.51	112.41	109.20(2)
∠ N1–Cu1–N3	93.66	94.37	95.35	95.64	96.45(8)
∠ P1–Cu1–N1	104.74	104.35	104.46	103.88	103.20(10)
∠ P1–Cu1–N3	104.79	104.37	104.59	104.52	107.07(6)
∠ P2–Cu1–N1	124.79	124.67	123.88	123.99	126.94(6)
∠ P2–Cu1–N3	114.42	114.06	113.38	113.63	112.11(6)
MAD[a]	0.0883	0.0577	0.0280	0.0436	
MAD[b]	2.25	2.13	2.08	1.95	
	The solid state				
R(Cu1–P1)	2.4196	2.3718	2.3178	2.3343	2.2957(6)
R(Cu1–P2)	2.3245	2.2978	2.2633	2.2721	2.2203(6)
R(Cu1–N1)	2.0812	2.0619	2.0407	2.0424	2.0290(20)
R(Cu1–N3)	2.0799	2.0606	2.0396	2.0378	2.0197(18)
∠ P1–Cu1–P2	111.71	112.20	112.59	112.53	109.20(2)
∠ N1–Cu1–N3	93.92	94.40	95.67	96.16	96.45(8)
∠ P1–Cu1–N1	104.63	104.55	104.61	103.91	103.20(10)
∠ P1–Cu1–N3	104.95	104.99	105.11	104.14	107.07(6)
∠ P2–Cu1–N1	124.64	123.90	123.78	123.89	126.94(6)
∠ P2–Cu1–N3	114.27	114.08	113.46	113.50	112.11(6)
MAD[a]	0.0851	0.0568	0.0241	0.0274	
MAD[b]	2.18	2.21	2.01	1.95	

MAD[a]: Mean absolute deviations of bond lengths; MAD[b]: Mean absolute deviations of bond angles. The MAD

values are calculated with respect to the corresponding experimental values, $MAD = 1/n \sum_1^n \left| R_{cal.} - R_{exp.} \right|$.

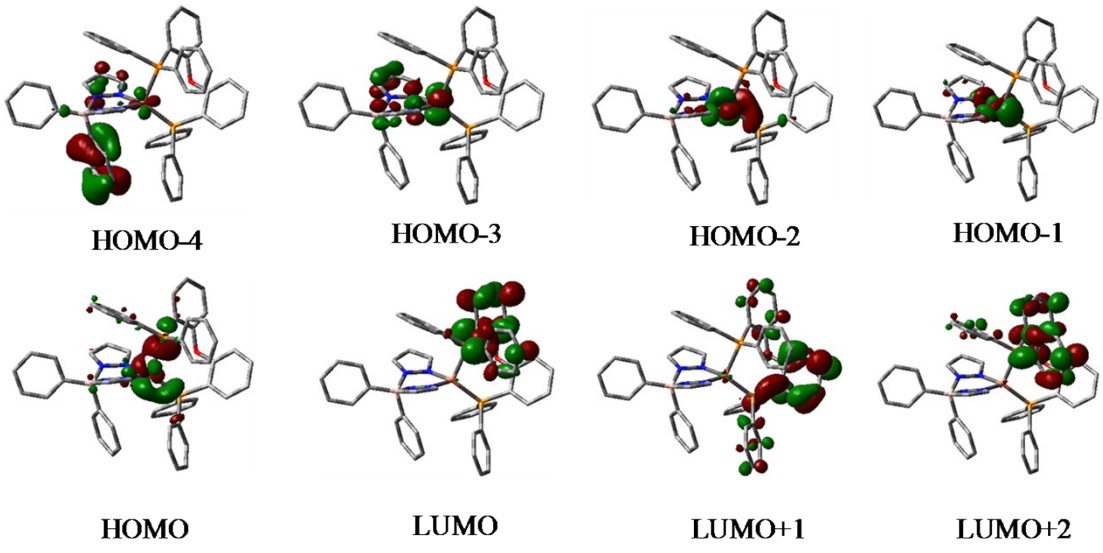
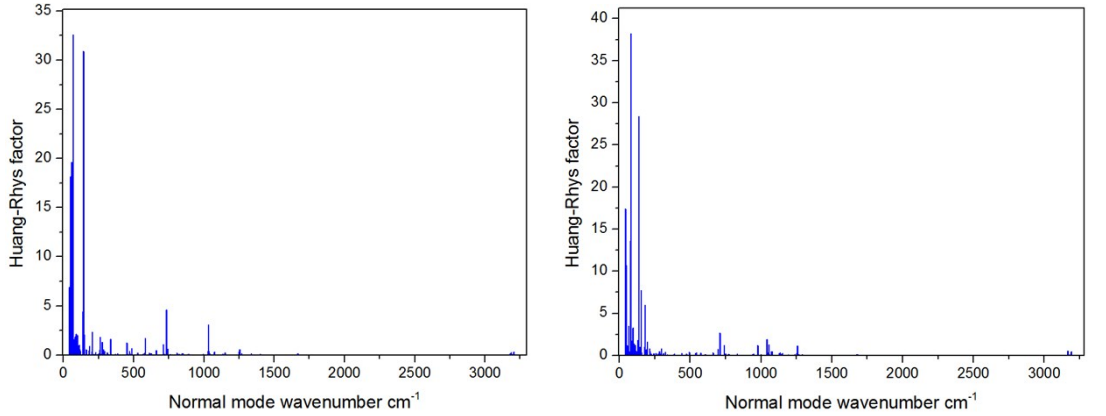
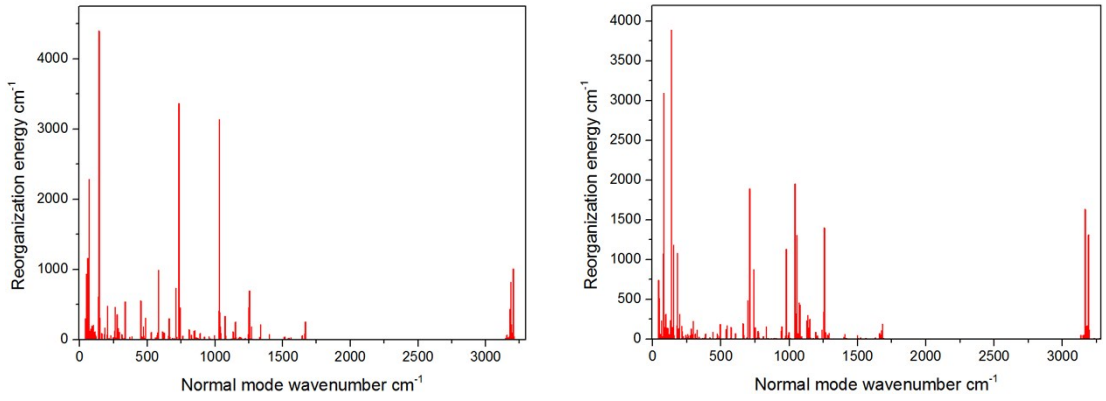


Figure S1. Active transition orbitals of the mononuclear Cu(pop)(pz_2Bph_2) complex in the triplet state.

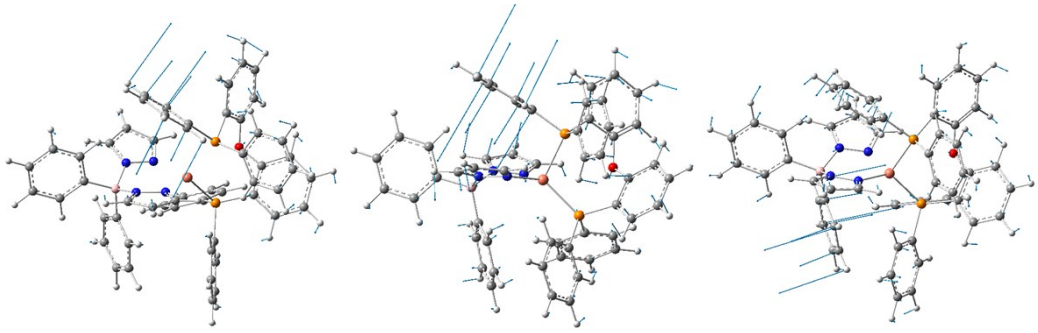


(a) (b)



(c) (d)

Figure S2. Calculated Huang-Rhys factors and reorganization energies versus the normal modes in term of the corresponding S_0 (a, c) and S_1 (b, d) potential surfaces at the PCM-tuned LC-BLYP* level .



(a) (b) (c)

Figure S3. The displacement vectors of three important vibration modes with the largest values of Huang-Rhys factor. a for T_1 state; b and c for the S_1 state.

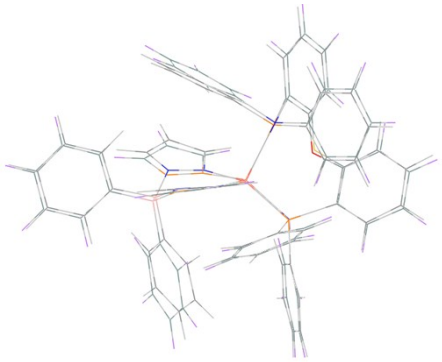


Figure S4. The geometries are intuitive pictures comparing the S_1 and T_1 geometries for the Cu(pop)(pz_2Bph_2) complex in the PCM-tuned LC-BLYP*/6-31+G(d) level.

Table S2. Cartesian coordinate of the PCM-tuned LC-BLYP* optimized ground state and TD-LC-BLYP* optimized excited state geometries using the 6-31+G(d) basis set for the mononuclear Cu(pop)(pz_2Bph_2) complex .

Cartesian coordinates for the S_0 geometry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.052373	-0.021320	-0.162963
2	15	0	1.479251	-1.889294	-0.070783
3	15	0	1.195158	1.953799	-0.057080
4	8	0	2.697070	0.225628	1.766571
5	7	0	-1.304244	-0.483069	-1.627516
6	7	0	-2.646100	-0.687822	-1.376305
7	7	0	-1.239489	-0.310057	1.407002
8	7	0	-2.573971	-0.614512	1.232734
9	6	0	0.512819	-3.459961	-0.296907
10	6	0	-0.565089	-3.711241	0.586319
11	6	0	-1.388036	-4.833705	0.405947
12	6	0	-1.163260	-5.713021	-0.670326
13	6	0	-0.106515	-5.461985	-1.560966
14	6	0	0.728063	-4.343804	-1.375835
15	6	0	2.867271	-2.050837	-1.299003
16	6	0	3.902885	-3.001559	-1.158062
17	6	0	4.919876	-3.094189	-2.122363
18	6	0	4.914544	-2.238710	-3.240179

19	6	0	3.891103	-1.286890	-3.386120
20	6	0	2.875841	-1.192128	-2.417828
21	6	0	2.350874	-2.179181	1.553344
22	6	0	2.472356	-3.453386	2.152164
23	6	0	3.086210	-3.616051	3.405742
24	6	0	3.585798	-2.498427	4.096205
25	6	0	3.476900	-1.219740	3.524637
26	6	0	2.875991	-1.074199	2.266053
27	6	0	3.579963	0.736308	0.811001
28	6	0	4.932388	0.366356	0.763004
29	6	0	5.773139	0.967685	-0.189051
30	6	0	5.263853	1.933790	-1.073363
31	6	0	3.904734	2.288983	-1.014855
32	6	0	3.034303	1.694091	-0.077543
33	6	0	0.912811	2.968061	1.473748
34	6	0	1.958156	3.528226	2.238000
35	6	0	1.670469	4.294594	3.382124
36	6	0	0.336502	4.515969	3.767934
37	6	0	-0.709660	3.959843	3.008852
38	6	0	-0.424497	3.182927	1.874145
39	6	0	0.935943	3.203708	-1.409194
40	6	0	0.390966	2.758907	-2.632723
41	6	0	0.181125	3.660179	-3.691352
42	6	0	0.501657	5.019732	-3.532361
43	6	0	1.031788	5.474826	-2.310591
44	6	0	1.247991	4.572905	-1.254982
45	6	0	-1.085832	-0.870024	-2.907039
46	6	0	-2.280525	-1.309432	-3.510173
47	6	0	-3.243040	-1.175099	-2.506335
48	6	0	-0.945084	-0.562639	2.703941
49	6	0	-2.084688	-1.024610	3.393148
50	6	0	-3.094038	-1.036873	2.425300
51	6	0	-4.841948	-0.946261	-0.013599
52	6	0	-4.906179	-2.362573	0.061284
53	6	0	-6.128737	-3.054891	0.090601
54	6	0	-7.342123	-2.341655	0.040292
55	6	0	-7.311110	-0.939083	-0.039122
56	6	0	-6.076574	-0.259545	-0.064584
57	6	0	-3.513695	1.446500	-0.083345
58	6	0	-3.287525	2.221439	-1.245076
59	6	0	-3.444700	3.621154	-1.252288
60	6	0	-3.847252	4.292275	-0.084355
61	6	0	-4.084446	3.548145	1.086740
62	6	0	-3.913596	2.152191	1.079638

63	5	0	-3.394057	-0.181957	-0.065473
64	1	0	-0.764184	-3.027160	1.416738
65	1	0	-2.210999	-5.016244	1.103267
66	1	0	-1.810743	-6.582344	-0.814569
67	1	0	0.074904	-6.135663	-2.403384
68	1	0	1.547278	-4.165276	-2.076578
69	1	0	3.920065	-3.669166	-0.291731
70	1	0	5.716414	-3.833704	-2.000356
71	1	0	5.708193	-2.310489	-3.988992
72	1	0	3.885276	-0.611060	-4.245884
73	1	0	2.093201	-0.434592	-2.521266
74	1	0	2.065207	-4.327271	1.637133
75	1	0	3.165234	-4.614557	3.843519
76	1	0	4.054365	-2.616798	5.076537
77	1	0	3.844989	-0.330511	4.042509
78	1	0	5.319596	-0.382205	1.458216
79	1	0	6.827009	0.679913	-0.231968
80	1	0	5.917360	2.405229	-1.811879
81	1	0	3.510640	3.027460	-1.717282
82	1	0	2.999275	3.367439	1.943913
83	1	0	2.490283	4.721364	3.967320
84	1	0	0.113757	5.113904	4.656181
85	1	0	-1.751441	4.121743	3.301112
86	1	0	-1.246017	2.740818	1.302961
87	1	0	0.109557	1.708334	-2.747018
88	1	0	-0.244765	3.301212	-4.632708
89	1	0	0.331548	5.723501	-4.351946
90	1	0	1.275422	6.532808	-2.177766
91	1	0	1.654925	4.937458	-0.307325
92	1	0	-0.079847	-0.827862	-3.321256
93	1	0	-2.425413	-1.679259	-4.522253
94	1	0	-4.307169	-1.391072	-2.517658
95	1	0	0.070902	-0.408190	3.063536
96	1	0	-2.167604	-1.308104	4.439610
97	1	0	-4.142115	-1.310845	2.503734
98	1	0	-3.973290	-2.937729	0.094736
99	1	0	-6.137015	-4.148135	0.150076
100	1	0	-8.297766	-2.874348	0.061226
101	1	0	-8.246347	-0.371607	-0.082090
102	1	0	-6.076221	0.833250	-0.126151
103	1	0	-2.972186	1.723675	-2.168316
104	1	0	-3.246588	4.186374	-2.169013
105	1	0	-3.969470	5.379693	-0.084035
106	1	0	-4.396432	4.055886	2.005562

107	1	0	-4.093392	1.595260	2.006940

Cartesian coordinates for the S_1 geometry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.080555	-0.071009	-0.089959
2	15	0	1.576340	-1.845210	-0.073985
3	15	0	1.219892	1.915530	0.059635
4	8	0	2.715809	0.285646	1.800626
5	7	0	-1.143470	-0.785136	-1.457645
6	7	0	-2.496928	-0.859786	-1.300078
7	7	0	-1.221815	-0.007122	1.400142
8	7	0	-2.495562	-0.472237	1.244262
9	6	0	0.369301	-3.241264	-0.079514
10	6	0	-0.496361	-3.371906	1.022487
11	6	0	-1.508456	-4.336539	1.016398
12	6	0	-1.666928	-5.181522	-0.090772
13	6	0	-0.810999	-5.052714	-1.191707
14	6	0	0.197729	-4.080843	-1.190658
15	6	0	2.638346	-2.085739	-1.508396
16	6	0	3.419268	-3.271672	-1.657846
17	6	0	4.423824	-3.340801	-2.620376
18	6	0	4.697042	-2.245658	-3.461860
19	6	0	3.941375	-1.067522	-3.318664
20	6	0	2.936218	-0.981691	-2.358025
21	6	0	2.376842	-2.095901	1.538969
22	6	0	2.725859	-3.409312	1.986692
23	6	0	3.555219	-3.601850	3.089890
24	6	0	4.080122	-2.510360	3.804547
25	6	0	3.783467	-1.204511	3.363257
26	6	0	2.979228	-1.024953	2.250064
27	6	0	3.591889	0.815773	0.872372
28	6	0	4.943910	0.468241	0.779931
29	6	0	5.742657	1.121408	-0.164197
30	6	0	5.210806	2.111632	-1.001352
31	6	0	3.851866	2.431355	-0.917869
32	6	0	3.031708	1.779854	0.015385
33	6	0	0.770583	2.930651	1.508533
34	6	0	1.714899	3.336172	2.463260
35	6	0	1.304675	4.089852	3.570424

36	6	0	-0.043034	4.439246	3.722768
37	6	0	-0.985285	4.031632	2.768409
38	6	0	-0.584303	3.272018	1.666695
39	6	0	0.804694	2.967510	-1.383043
40	6	0	0.472826	2.348630	-2.599940
41	6	0	0.181480	3.122886	-3.728384
42	6	0	0.211762	4.520614	-3.644439
43	6	0	0.532432	5.142526	-2.430343
44	6	0	0.827579	4.369794	-1.301687
45	6	0	-0.847832	-1.262485	-2.685531
46	6	0	-2.023690	-1.627890	-3.351467
47	6	0	-3.042925	-1.357131	-2.435667
48	6	0	-0.902794	-0.117130	2.706410
49	6	0	-1.987273	-0.650432	3.418212
50	6	0	-2.976822	-0.853192	2.452898
51	6	0	-4.716797	-0.958392	-0.000468
52	6	0	-4.756934	-2.359562	0.177950
53	6	0	-5.967132	-3.057356	0.258344
54	6	0	-7.182189	-2.364483	0.154917
55	6	0	-7.169358	-0.977730	-0.031016
56	6	0	-5.948951	-0.289027	-0.106703
57	6	0	-3.348797	1.400475	-0.285280
58	6	0	-2.815253	2.066165	-1.403965
59	6	0	-2.836715	3.465051	-1.513136
60	6	0	-3.419339	4.237733	-0.502136
61	6	0	-3.969923	3.599988	0.619600
62	6	0	-3.921102	2.204746	0.724137
63	5	0	-3.289166	-0.206320	-0.095670
64	1	0	-0.374704	-2.713678	1.891376
65	1	0	-2.178635	-4.422605	1.878348
66	1	0	-2.459562	-5.936781	-0.096884
67	1	0	-0.930150	-5.709039	-2.059709
68	1	0	0.857108	-3.970264	-2.057914
69	1	0	3.227732	-4.132991	-1.007698
70	1	0	5.004165	-4.264346	-2.723022
71	1	0	5.488925	-2.308960	-4.213514
72	1	0	4.141850	-0.204973	-3.963795
73	1	0	2.379338	-0.044528	-2.243638
74	1	0	2.291520	-4.276394	1.477806
75	1	0	3.779141	-4.623096	3.416118
76	1	0	4.715789	-2.665630	4.679915
77	1	0	4.172121	-0.321756	3.881760
78	1	0	5.351780	-0.310524	1.429306
79	1	0	6.798877	0.847389	-0.246941

80	1	0	5.847717	2.616774	-1.732789
81	1	0	3.414329	3.170877	-1.596567
82	1	0	2.767767	3.060532	2.343011
83	1	0	2.042393	4.404300	4.315111
84	1	0	-0.360412	5.028108	4.589144
85	1	0	-2.042430	4.294290	2.877766
86	1	0	-1.329936	2.948139	0.932029
87	1	0	0.419953	1.255608	-2.663261
88	1	0	-0.081797	2.631072	-4.669874
89	1	0	-0.022793	5.127054	-4.524865
90	1	0	0.548721	6.234482	-2.359232
91	1	0	1.062726	4.855627	-0.348739
92	1	0	0.195438	-1.344532	-2.996459
93	1	0	-2.123758	-2.049663	-4.348839
94	1	0	-4.121003	-1.485974	-2.507265
95	1	0	0.090617	0.181646	3.045048
96	1	0	-2.049149	-0.858371	4.484007
97	1	0	-3.992252	-1.235037	2.538802
98	1	0	-3.811828	-2.915523	0.248219
99	1	0	-5.964570	-4.144126	0.397485
100	1	0	-8.132563	-2.905149	0.214879
101	1	0	-8.112312	-0.427598	-0.120116
102	1	0	-5.954467	0.796653	-0.256057
103	1	0	-2.356258	1.480478	-2.210392
104	1	0	-2.382558	3.948850	-2.385441
105	1	0	-3.439129	5.329601	-0.582633
106	1	0	-4.431541	4.193220	1.417301
107	1	0	-4.332461	1.721399	1.620210

Cartesian coordinates for the T_1 geometry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.065519	-0.058091	-0.080132
2	15	0	1.576310	-1.888244	-0.069167
3	15	0	1.283300	1.914113	0.038766
4	8	0	2.893773	0.236892	1.710783
5	7	0	-1.221852	-0.652169	-1.506815
6	7	0	-2.578890	-0.796341	-1.292587
7	7	0	-1.245908	-0.122998	1.461260
8	7	0	-2.564274	-0.495272	1.294473

9	6	0	0.378463	-3.300189	-0.079592
10	6	0	-0.417462	-3.534079	1.069411
11	6	0	-1.394418	-4.540789	1.067637
12	6	0	-1.604649	-5.320148	-0.085672
13	6	0	-0.832899	-5.081173	-1.238739
14	6	0	0.143329	-4.071875	-1.240655
15	6	0	2.619592	-2.126622	-1.559771
16	6	0	3.415668	-3.308858	-1.701304
17	6	0	4.391684	-3.394956	-2.702137
18	6	0	4.615846	-2.319837	-3.590944
19	6	0	3.842644	-1.143045	-3.453753
20	6	0	2.872731	-1.042623	-2.450093
21	6	0	2.452569	-2.144490	1.517055
22	6	0	2.755781	-3.468899	2.000711
23	6	0	3.649673	-3.673303	3.055003
24	6	0	4.285197	-2.584274	3.696671
25	6	0	4.026598	-1.270721	3.226477
26	6	0	3.160875	-1.076875	2.155733
27	6	0	3.730998	0.809329	0.757109
28	6	0	5.101296	0.522369	0.641211
29	6	0	5.862459	1.215272	-0.315373
30	6	0	5.269921	2.188551	-1.139990
31	6	0	3.895205	2.455898	-1.025537
32	6	0	3.109492	1.765459	-0.079141
33	6	0	0.931424	2.906337	1.553502
34	6	0	1.952679	3.346363	2.422471
35	6	0	1.630496	4.095854	3.567252
36	6	0	0.290312	4.414725	3.850831
37	6	0	-0.730162	3.977300	2.985856
38	6	0	-0.415676	3.220279	1.847033
39	6	0	0.824808	3.042391	-1.356387
40	6	0	0.501396	2.485877	-2.613177
41	6	0	0.190357	3.317573	-3.701182
42	6	0	0.185335	4.714543	-3.540439
43	6	0	0.495114	5.275949	-2.288527
44	6	0	0.813069	4.446651	-1.199861
45	6	0	-0.967257	-1.100118	-2.762610
46	6	0	-2.154876	-1.510217	-3.388732
47	6	0	-3.148826	-1.299044	-2.424605
48	6	0	-0.956773	-0.256193	2.779441
49	6	0	-2.084772	-0.710599	3.485218
50	6	0	-3.080368	-0.842903	2.508100
51	6	0	-4.804871	-0.955227	0.037301
52	6	0	-4.854419	-2.365128	0.195629

53	6	0	-6.071026	-3.065354	0.261329
54	6	0	-7.290312	-2.367363	0.164765
55	6	0	-7.272526	-0.971689	0.002400
56	6	0	-6.044668	-0.282928	-0.059266
57	6	0	-3.480842	1.436604	-0.203131
58	6	0	-3.202590	2.118826	-1.410596
59	6	0	-3.339955	3.515911	-1.527305
60	6	0	-3.773643	4.276884	-0.428006
61	6	0	-4.062827	3.625705	0.786103
62	6	0	-3.912260	2.231489	0.889094
63	5	0	-3.366929	-0.183916	-0.046273
64	1	0	-0.266884	-2.926506	1.966280
65	1	0	-1.996501	-4.711827	1.964663
66	1	0	-2.369720	-6.101517	-0.089130
67	1	0	-0.992232	-5.680823	-2.139409
68	1	0	0.732318	-3.887213	-2.142378
69	1	0	3.257012	-4.157061	-1.028311
70	1	0	4.978988	-4.314030	-2.797826
71	1	0	5.379298	-2.394463	-4.369644
72	1	0	4.000342	-0.300326	-4.134398
73	1	0	2.306088	-0.112837	-2.343640
74	1	0	2.255659	-4.328896	1.548119
75	1	0	3.841116	-4.694788	3.398784
76	1	0	4.970692	-2.744942	4.531637
77	1	0	4.490553	-0.399710	3.698132
78	1	0	5.559486	-0.230412	1.285155
79	1	0	6.929152	0.994180	-0.408731
80	1	0	5.870556	2.730338	-1.874625
81	1	0	3.426413	3.192955	-1.682017
82	1	0	2.997857	3.110915	2.206847
83	1	0	2.429353	4.433180	4.233387
84	1	0	0.042128	4.999055	4.741036
85	1	0	-1.775799	4.218443	3.197675
86	1	0	-1.221431	2.877043	1.192084
87	1	0	0.477331	1.400681	-2.742247
88	1	0	-0.058855	2.872411	-4.668251
89	1	0	-0.065188	5.362622	-4.384612
90	1	0	0.489984	6.361321	-2.156166
91	1	0	1.051257	4.892819	-0.231097
92	1	0	0.057063	-1.121065	-3.131745
93	1	0	-2.280200	-1.910725	-4.391342
94	1	0	-4.220826	-1.467788	-2.470224
95	1	0	0.047480	-0.031500	3.135040
96	1	0	-2.170788	-0.918358	4.548755

97	1	0	-4.116750	-1.156157	2.596145
98	1	0	-3.916474	-2.928680	0.267087
99	1	0	-6.069786	-4.153060	0.385715
100	1	0	-8.241046	-2.906766	0.213860
101	1	0	-8.212852	-0.417017	-0.077560
102	1	0	-6.053818	0.804174	-0.185916
103	1	0	-2.861777	1.551760	-2.283476
104	1	0	-3.100279	4.008450	-2.475266
105	1	0	-3.880612	5.362480	-0.513238
106	1	0	-4.400416	4.204216	1.652335
107	1	0	-4.132771	1.748216	1.848232