Supporting Information

Reversible photoluminescence switching behavior and luminescence thermochromism of copper (I) halide cluster coordination polymers

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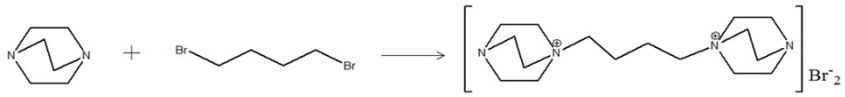
Synthesis of 4-Aza-1-azoniabicyclo[2.2.2]octane, 1,1'-(1,4-butanediyl)bis-,dibromide (L)

Ligand (**L**) is synthesized by adopting the procedure reported Asim Bhaumik et.al with slight modifications [1]. Diazobicyclo[2,2,2]octane (90.0 mmol , 10 g) was dissolved in 200 mL acetone under vigorous stirring. Then 1, 4-Dibromobutane (20.0 mmol, 4.32 g) was added dropwise and the reaction was carried out at room temperature for 36 h. at last the white solid was filtered, washed with acetone and ethyl acetate.



[1] M. Sasidharan a, A. Bhaumik, Phys. Chem. Chem. Phys, 2011, 13, 16282–16294.

Table S1. Selected bond lengths (Å) in 1 and 2 at two different temperatures (K).

Bond	1 (298K)	1 (120K)
I(1)-Cu(2)#1	2.6879(13)	2.6859(11)
I(1)-Cu(2)	2.6879(13)	2.6859(11)
I(1)-Cu(1)	2.7589(19)	2.7286(15)
I(2)-Cu(2)	2.5935(11)	2.5894(10)
I(2)-Cu(1)	2.7037(10)	2.6987(8)
I(3)-Cu(2)#2	2.6832(14)	2.6809(12)
I(3)-Cu(2)#3	2.6832(14)	2.6809(12)
I(3)-Cu(1)	2.7609(18)	2.7530(14)
Cu(1)-I(2)#1	2.7037(10)	2.6987(8)
Cu(1)-Cu(2)	2.7641(17)	2.7384(14)
Cu(1)-Cu(2)#1	2.7641(17)	2.7384(14)
Cu(2)-N(2)	2.124(5)	2.121(5)
Cu(2)-Cu(2)#1	2.5747(17)	2.5625(16)
Cu(2)-I(3)#4	2.6832(13)	2.6809(12)

Symmetry codes: #1 -x+1/2,y,z; #2 x,y-1/2,z+1/2; #3 -x+1/2,y-1/2,z+1/2; #4 x,y+1/2,z-1/2 #5 -x+1,-y+2,z ; #6 -x+1,-y+1,z

Bond	2 (298K)	2 (120K)
I(1)-Cu(2)	2.656(2)	2.6397(19)
I(1)-Cu(3)	2.730(3)	2.716(2)
I(1)-Cu(1)	2.796(3)	2.775(2)
I(2)-Cu(2)	2.615(2)	2.6180(19)
I(2)-Cu(1)	2.711(3)	2.696(2)
I(3)-Cu(3)	2.628(3)	2.628(2)
I(3)-Cu(1)	2.642(3)	2.636(2)
Br(1)-Cu(2)	2.594(3)	2.580(2)
Br(1)-Cu(1)#1	2.627(3)	2.629(2)
Br(1)-Cu(3)	2.628(3)	2.631(2)
Cu(1)-Cu(2)	2.621(3)	2.587(2)
Cu(1)-Br(1)#2	2.627(3)	2.629(2)
Cu(1)-Cu(3)	2.689(3)	2.652(2)
Cu(2)-N(2)	2.129(13)	2.111(12)
Cu(2)-Cu(3)	2.672(3)	2.654(3)
Cu(3)-N(3)	2.07(2)	2.004(12)
Symmetry codes: #1 -x+1/2,y-1/2,z ; #2 -x+1/2,y+1/2,z ; #3 -x,-y,-z		

Table S2. Comparison of bond lengths (Å) changing in the cooper (I) halide cluster of compound 1 and 2 at two different temperatures (K).

Bond	1 (298K)	1 (120K)	$\Delta_{\text{bond length}}$
I(1)-Cu(2)#1	2.6879(13)	2.6859(11)	0.002
I(1)-Cu(2)	2.6879(13)	2.6859(11)	0.002
I(1)-Cu(1)	2.7589(19)	2.7286(15)	0.0303
I(2)-Cu(2)	2.5935(11)	2.5894(10)	0.0041
I(2)-Cu(1)	2.7037(10)	2.6987(8)	0.005
I(3)-Cu(2)#2	2.6832(14)	2.6809(12)	0.0023
I(3)-Cu(2)#3	2.6832(14)	2.6809(12)	0.0023
I(3)-Cu(1)	2.7609(18)	2.7530(14)	0.0079
Cu(1)-I(2)#1	2.7037(10)	2.6987(8)	0.005
Cu(2)-I(3)#4	2.6832(13)	2.6809(12)	0.0023
Cu(1)-Cu(2)	2.7641(17)	2.7384(14)	0.0257
Cu(1)-Cu(2)#1	2.7641(17)	2.7384(14)	0.0257
Cu(2)-Cu(2)#1	2.5747(17)	2.5625(16)	0.0122
Bond	**2 (298K)**	**2 (120K)**	$\Delta_{\text{bond length}}$
I(1)-Cu(2)	2.656(2)	2.6397(19)	0.0163
I(1)-Cu(3)	2.730(3)	2.716(2)	0.014
I(1)-Cu(1)	2.796(3)	2.775(2)	0.021
I(2)-Cu(2)	2.615(2)	2.6180(19)	**-0.003**
I(2)-Cu(1)	2.711(3)	2.696(2)	0.015
I(3)-Cu(3)	2.628(3)	2.628(2)	**0**
I(3)-Cu(1)	2.642(3)	2.636(2)	0.006

Br(1)-Cu(2)	2.594(3)	2.580(2)	0.014
Br(1)-Cu(1)#1	2.627(3)	2.629(2)	**-0.002**
Br(1)-Cu(3)	2.628(3)	2.631(2)	**-0.003**
Cu(1)-Br(1)#2	2.627(3)	2.629(2)	**-0.002**
Cu(1)-Cu(2)	2.621(3)	2.587(2)	0.034
Cu(1)-Cu(3)	2.689(3)	2.652(2)	0.037

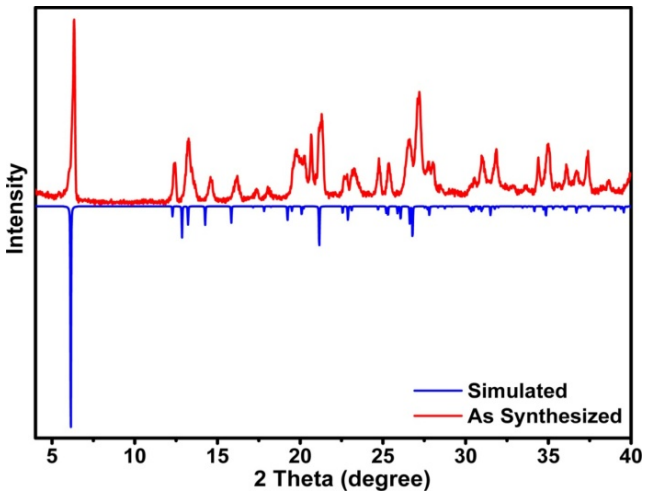


Figure S1. The XRD patterns of sample **1**.

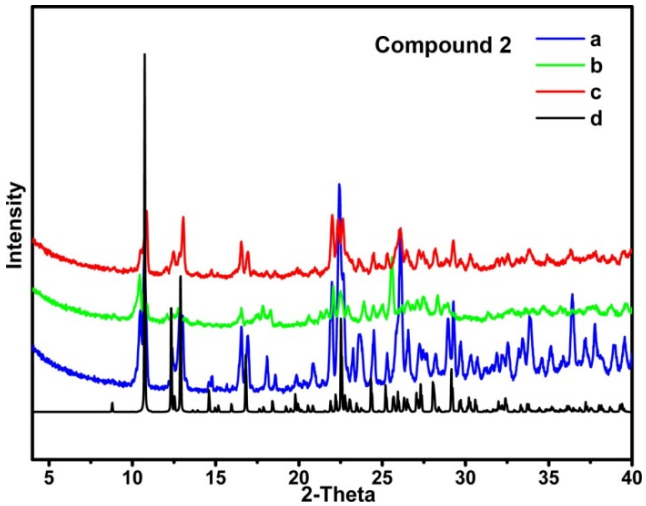


Figure S2. The XRD patterns for sample **2** and **2a**: a) sample **2**; b) sample **2a**; c) sample 2a immersed in CH_3CN for 24 h; (d) simulated

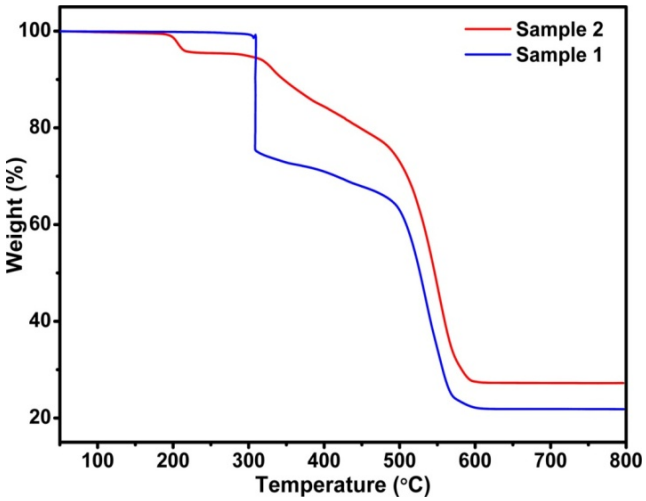


Figure S3. The TG of sample **1** and **2.** The first sharp mass loss of sample **2** is about 4.42% at 240 ºC (calc 4.93%).

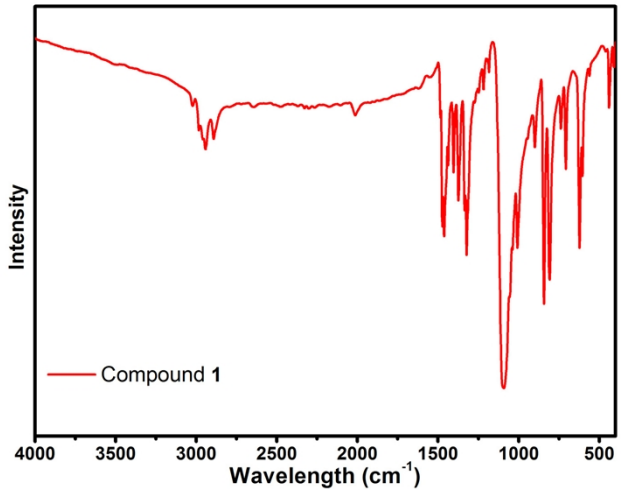


Figure S4. The IR spectra of sample **1**

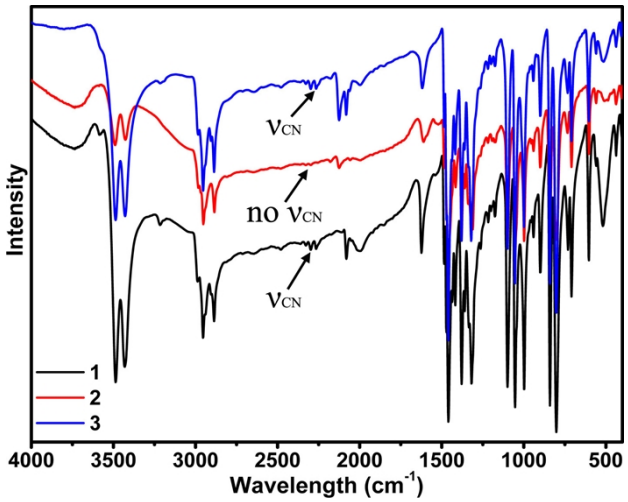


Figure S5. The IR spectra of sample **2** and **2a**; 1) sample **2**; 2) sample **2a**; 3) sample **2a** immersed in CH_3CN for 24 h.

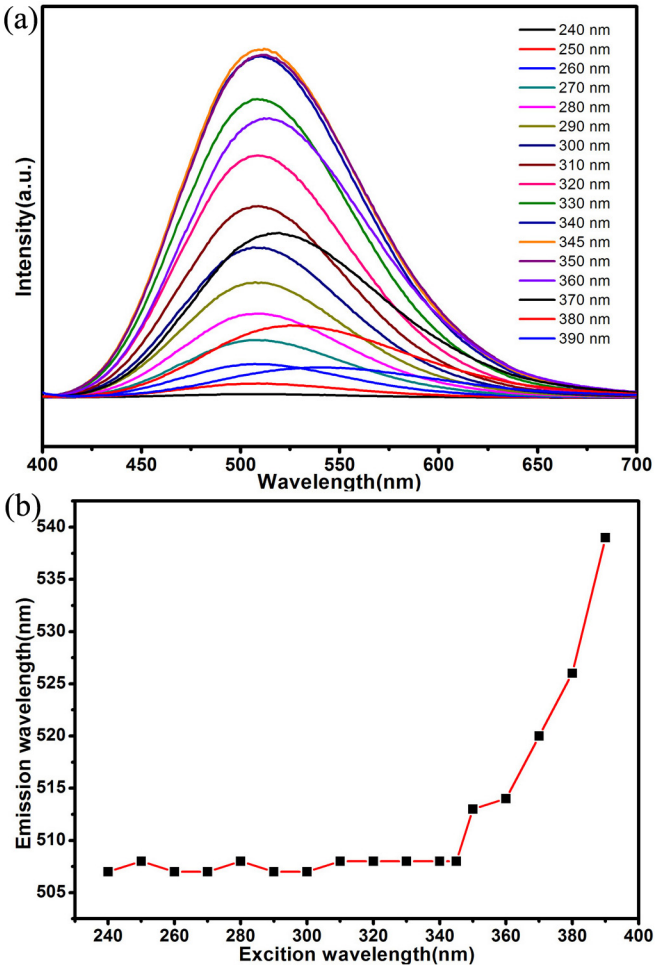


Figure S6. (a) The emission spectra of compound **1** under different excitation. (b) Corresponding emission peak position of each excitation.

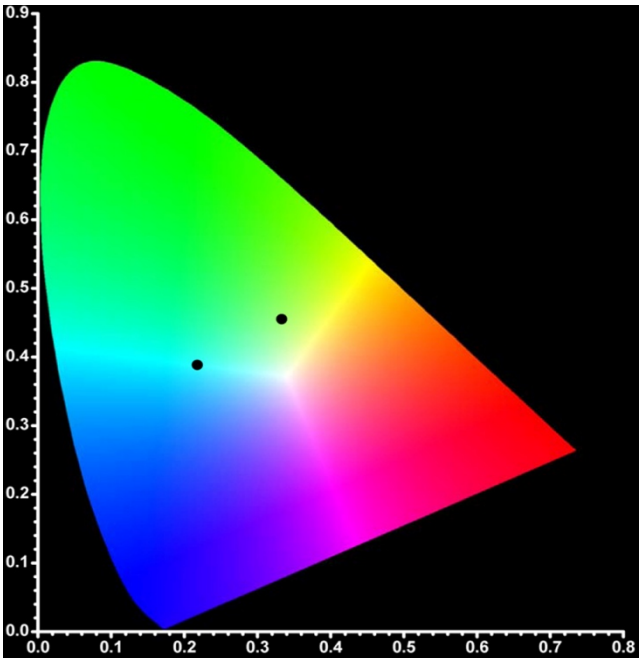


Figure S7. Corresponding calculated CIE coordinate of **2** and **2a** at room temperature.

Table S3. Pattern Indexing Results of 2a[#]

fm	fn	P	R	C	S.G.(#)	a	b	c	<α>	<β>	<γ>	Vol.
32	24	0	3	O	Pbca (61)	14.256	13.807	20.027	90.0	90.0	90.0	3942.2

@	2T(o)	(h k l)	2T(c)	Delta	d(c)	d(o)	Del-d	I%
[ ]	8.938	(0 0 2)	8.824	-0.115	10.0135	9.8851	0.1285	5.6
[ ]	-----	(1 1 1)	9.944	---	8.8880	---	---	
[ ]	10.713	(1 0 2)	10.788	0.075	8.1942	8.2513	-0.0571	32.9
[ ]	12.438	(2 0 0)	12.407	-0.031	7.1282	7.1107	0.0175	14.2
[ ]	-----	(1 1 2)	12.551	---	7.0467	---	---	
[ ]	12.815	(0 2 0)	12.812	-0.003	6.9037	6.9021	0.0016	25.5
[ ]	-----	(0 2 1)	13.556	---	6.5268	---	---	
[ ]	13.985	(2 1 0)	13.970	-0.015	6.3339	6.3272	0.0067	5.1
[ ]	-----	(2 1 1)	14.656	---	6.0391	---	---	
[ ]	-----	(1 2 1)	14.916	---	5.9344	---	---	
[ ]	-----	(2 0 2)	15.245	---	5.8071	---	---	
[ ]	-----	(0 2 2)	15.578	---	5.6838	---	---	
[ ]	-----	(1 1 3)	15.990	---	5.5381	---	---	
[ ]	16.541	(2 1 2)	16.547	0.006	5.3530	5.3547	-0.0018	27.4
[ ]	-----	(1 2 2)	16.778	---	5.2797	---	---	
[ ]	17.542	(0 0 4)	17.700	0.158	5.0068	5.0514	-0.0446	17.7
[ ]	17.840	(2 2 0)	17.871	0.032	4.9591	4.9679	-0.0088	31.2
[ ]	18.300	(2 2 1)	18.416	0.116	4.8137	4.8439	-0.0302	23.1
[ ]	-----	(0 2 3)	18.473	---	4.7990	---	---	
[ ]	18.831	(1 0 4)	18.769	-0.062	4.7239	4.7085	0.0154	5.4
[ ]	-----	(2 1 3)	19.301	---	4.5948	---	---	
[ ]	-----	(1 2 3)	19.501	---	4.5482	---	---	
[ ]	-----	(1 1 4)	19.848	---	4.4696	---	---	
[ ]	-----	(2 2 2)	19.963	---	4.4440	---	---	
[ ]	-----	(3 1 1)	20.237	---	4.3844	---	---	
[ ]	20.598	(3 0 2)	20.672	0.073	4.2932	4.3083	-0.0151	13.5
[ ]	-----	(1 3 1)	20.742	---	4.2787	---	---	
[ ]	21.642	(3 1 2)	21.659	0.017	4.0996	4.1028	-0.0032	13.8
[ ]	-----	(2 0 4)	21.673	---	4.0971	---	---	
[ ]	-----	(0 2 4)	21.911	---	4.0531	---	---	
[ ]	22.062	(1 3 2)	22.134	0.072	4.0128	4.0257	-0.0128	53.5
[ ]	-----	(2 2 3)	22.314	---	3.9809	---	---	
[ ]	22.499	(2 1 4)	22.619	0.120	3.9278	3.9485	-0.0207	46.5
[ ]	-----	(1 2 4)	22.791	---	3.8986	---	---	
[ ]	22.942	(2 3 0)	22.982	0.041	3.8665	3.8733	-0.0067	16.1
[ ]	-----	(3 2 1)	23.133	---	3.8417	---	---	
[ ]	-----	(2 3 1)	23.413	---	3.7964	---	---	
[ ]	-----	(3 1 3)	23.851	---	3.7277	---	---	
[ ]	23.900	(1 1 5)	23.940	0.040	3.7140	3.7201	-0.0061	32.9
[ ]	-----	(1 3 3)	24.285	---	3.6620	---	---	
[ ]	24.478	(3 2 2)	24.395	-0.083	3.6458	3.6335	0.0122	22.8
[ ]	-----	(2 3 2)	24.661	---	3.6070	---	---	

[ ] 25.035	(4 0 0)	24.963	-0.073	3.5641	3.5539	0.0102	22.0
[ ] -----	(2 2 4)	25.256	---	3.5234	---	---	
[ ] 25.580	(0 2 5)	25.692	0.112	3.4645	3.4794	-0.0149	100.0
[ ] -----	(0 4 0)	25.788	---	3.4518	---	---	
[ ] -----	(4 1 0)	25.795	---	3.4510	---	---	
[ ] -----	(3 0 4)	25.827	---	3.4468	---	---	
[ ] 26.175	(0 4 1)	26.175	0.001	3.4017	3.4018	-0.0001	11.0
[ ] -----	(4 1 1)	26.182	---	3.4009	---	---	
[ ] -----	(2 1 5)	26.304	---	3.3853	---	---	
[ ] -----	(3 2 3)	26.372	---	3.3767	---	---	
[ ] -----	(1 2 5)	26.453	---	3.3665	---	---	
[ ] 26.536	(4 0 2)	26.524	-0.012	3.3578	3.3563	0.0015	13.8
[ ] -----	(2 3 3)	26.620	---	3.3458	---	---	
[ ] -----	(3 1 4)	26.634	---	3.3442	---	---	
[ ] -----	(0 0 6)	26.685	---	3.3378	---	---	
[ ] -----	(1 4 1)	26.924	---	3.3088	---	---	
[ ] 27.099	(1 3 4)	27.026	-0.074	3.2965	3.2877	0.0088	21.5
[ ] -----	(0 4 2)	27.306	---	3.2634	---	---	
[ ] -----	(4 1 2)	27.312	---	3.2627	---	---	
[ ] -----	(3 3 1)	27.318	---	3.2619	---	---	
[ ] 27.461	(1 0 6)	27.421	-0.041	3.2500	3.2453	0.0047	25.6
[ ] -----	(1 4 2)	28.026	---	3.1811	---	---	
[ ] -----	(4 2 0)	28.154	---	3.1670	---	---	
[ ] -----	(1 1 6)	28.185	---	3.1635	---	---	
[ ] 28.338	(3 3 2)	28.406	0.068	3.1394	3.1468	-0.0074	32.6
[ ] -----	(4 2 1)	28.511	---	3.1281	---	---	
[ ] -----	(2 2 5)	28.624	---	3.1160	---	---	
[ ] -----	(2 4 0)	28.711	---	3.1067	---	---	
[ ] 28.939	(3 2 4)	28.929	-0.010	3.0838	3.0828	0.0010	23.9
[ ] -----	(2 4 1)	29.062	---	3.0700	---	---	
[ ] -----	(0 4 3)	29.099	---	3.0662	---	---	
[ ] -----	(4 1 3)	29.105	---	3.0656	---	---	
[ ] 29.239	(2 3 4)	29.157	-0.082	3.0602	3.0518	0.0084	7.5
[ ] -----	(2 0 6)	29.526	---	3.0229	---	---	
[ ] -----	(4 2 2)	29.559	---	3.0196	---	---	
[ ] -----	(0 2 6)	29.705	---	3.0050	---	---	
[ ] -----	(1 4 3)	29.780	---	2.9976	---	---	
[ ] -----	(3 1 5)	29.858	---	2.9900	---	---	
[ ] 30.019	(2 4 2)	30.092	0.073	2.9672	2.9743	-0.0071	5.9
[ ] -----	(3 3 3)	30.140	---	2.9627	---	---	
[ ] -----	(1 3 5)	30.211	---	2.9558	---	---	
[ ] -----	(2 1 6)	30.241	---	2.9529	---	---	
[ ] -----	(1 2 6)	30.373	---	2.9404	---	---	
[ ] -----	(4 0 4)	30.768	---	2.9036	---	---	
[ ] 31.340	(4 2 3)	31.234	-0.106	2.8613	2.8519	0.0095	12.5
[ ] -----	(0 4 4)	31.453	---	2.8419	---	---	

[ ] -----	(4 1 4)	31.458	---	2.8414	---	---	
[ ] -----	(4 3 0)	31.727	---	2.8180	---	---	
[ ] -----	(2 4 3)	31.742	---	2.8167	---	---	
[ ] 31.961	(3 2 5)	31.941	-0.019	2.7995	2.7979	0.0016	5.6
[ ] -----	(4 3 1)	32.048	---	2.7905	---	---	
[ ] -----	(1 4 4)	32.088	---	2.7871	---	---	
[ ] -----	(2 3 5)	32.150	---	2.7819	---	---	
[ ] -----	(2 2 6)	32.303	---	2.7690	---	---	
[ ] -----	(3 4 1)	32.339	---	2.7661	---	---	
[ ] -----	(5 1 1)	32.344	---	2.7656	---	---	
[ ] 32.484	(3 3 4)	32.425	-0.059	2.7589	2.7540	0.0049	8.1
[ ] -----	(1 1 7)	32.546	---	2.7489	---	---	
[ ] -----	(5 0 2)	32.627	---	2.7423	---	---	
[ ] 32.781	(3 0 6)	32.760	-0.020	2.7314	2.7297	0.0017	10.7
[ ] -----	(4 3 2)	32.994	---	2.7126	---	---	
[ ] -----	(3 4 2)	33.277	---	2.6901	---	---	
[ ] -----	(5 1 2)	33.282	---	2.6897	---	---	
[ ] -----	(1 5 1)	33.323	---	2.6866	---	---	
[ ] -----	(3 1 6)	33.414	---	2.6795	---	---	
[ ] -----	(4 2 4)	33.452	---	2.6765	---	---	
[ ] 33.624	(1 3 6)	33.733	0.110	2.6548	2.6632	-0.0084	9.8
[ ] -----	(0 2 7)	33.888	---	2.6430	---	---	
[ ] 34.035	(2 4 4)	33.931	-0.105	2.6398	2.6319	0.0079	9.1
[ ] -----	(1 5 2)	34.237	---	2.6169	---	---	
[ ] -----	(0 4 5)	34.265	---	2.6148	---	---	
[ ] -----	(4 1 5)	34.270	---	2.6144	---	---	
[ ] -----	(5 2 1)	34.292	---	2.6128	---	---	
[ ] -----	(2 1 7)	34.366	---	2.6074	---	---	
[ ] -----	(1 2 7)	34.483	---	2.5988	---	---	
[ ] -----	(4 3 3)	34.519	---	2.5961	---	---	
[ ] 34.681	(3 4 3)	34.792	0.111	2.5764	2.5844	-0.0080	14.1
[ ] -----	(5 1 3)	34.797	---	2.5761	---	---	
[ ] -----	(2 5 0)	34.812	---	2.5750	---	---	
[ ] -----	(1 4 5)	34.855	---	2.5719	---	---	
[ ] -----	(2 5 1)	35.108	---	2.5540	---	---	
[ ] -----	(3 3 5)	35.168	---	2.5497	---	---	
[ ] -----	(5 2 2)	35.184	---	2.5486	---	---	
[ ] -----	(3 2 6)	35.309	---	2.5398	---	---	
[ ] -----	(2 3 6)	35.500	---	2.5266	---	---	
[ ] 35.699	(1 5 3)	35.716	0.017	2.5118	2.5130	-0.0012	13.3
[ ] -----	(0 0 8)	35.841	---	2.5034	---	---	
[ ] 35.991	(2 5 2)	35.982	-0.008	2.4939	2.4933	0.0006	8.4
[ ] -----	(4 2 5)	36.126	---	2.4843	---	---	
[ ] -----	(4 4 0)	36.197	---	2.4796	---	---	
[ ] -----	(2 2 7)	36.218	---	2.4782	---	---	
[ ] -----	(5 0 4)	36.225	---	2.4777	---	---	

[ ] 36.417	(1 0 8)	36.408	-0.009	2.4657	2.4651	0.0006	6.3
[ ] -----	(4 4 1)	36.483	---	2.4608	---	---	
[ ] -----	(4 3 4)	36.561	---	2.4557	---	---	
[ ] -----	(2 4 5)	36.574	---	2.4549	---	---	
[ ] -----	(5 2 3)	36.630	---	2.4513	---	---	
[ ] -----	(3 4 4)	36.820	---	2.4390	---	---	
[ ] -----	(5 1 4)	36.825	---	2.4387	---	---	
[ ] 36.860	(4 0 6)	36.863	0.003	2.4363	2.4365	-0.0002	6.8
[ ] -----	(1 1 8)	37.005	---	2.4273	---	---	
[ ] -----	(3 1 7)	37.226	---	2.4134	---	---	
[ ] 37.322	(4 4 2)	37.330	0.008	2.4069	2.4074	-0.0005	10.3
[ ] -----	(5 3 1)	37.339	---	2.4063	---	---	
[ ] -----	(2 5 3)	37.401	---	2.4025	---	---	
[ ] -----	(0 4 6)	37.449	---	2.3995	---	---	
[ ] -----	(4 1 6)	37.453	---	2.3992	---	---	
[ ] -----	(1 3 7)	37.517	---	2.3953	---	---	
[ ] -----	(1 5 4)	37.701	---	2.3840	---	---	
[ ] 37.841	(6 0 0)	37.832	-0.009	2.3761	2.3755	0.0005	15.1
[ ] -----	(3 5 1)	37.919	---	2.3708	---	---	
[ ] -----	(1 4 6)	37.996	---	2.3662	---	---	
[ ] -----	(2 0 8)	38.067	---	2.3620	---	---	
[ ] -----	(5 3 2)	38.170	---	2.3558	---	---	
[ ] -----	(0 2 8)	38.210	---	2.3534	---	---	
[ ] -----	(3 3 6)	38.287	---	2.3489	---	---	
[ ] -----	(6 1 0)	38.410	---	2.3417	---	---	
[ ] -----	(5 2 4)	38.574	---	2.3320	---	---	
[ ] -----	(2 1 8)	38.641	---	2.3281	---	---	
[ ] -----	(6 1 1)	38.682	---	2.3258	---	---	
[ ] -----	(4 4 3)	38.706	---	2.3244	---	---	
[ ] -----	(3 5 2)	38.739	---	2.3225	---	---	
[ ] 38.759	(1 2 8)	38.748	-0.012	2.3220	2.3213	0.0007	16.4
[ ] -----	(6 0 2)	38.924	---	2.3119	---	---	
[ ] -----	(3 2 7)	38.960	---	2.3098	---	---	
[ ] -----	(4 3 5)	39.050	---	2.3047	---	---	
[ ] -----	(0 6 0)	39.112	---	2.3012	---	---	
[ ] -----	(2 3 7)	39.136	---	2.2999	---	---	
[ ] -----	(4 2 6)	39.179	---	2.2974	---	---	
[ ] -----	(3 4 5)	39.295	---	2.2909	---	---	
[ ] -----	(5 1 5)	39.300	---	2.2907	---	---	
[ ] -----	(2 5 4)	39.313	---	2.2899	---	---	
[ ] -----	(0 6 1)	39.380	---	2.2862	---	---	
[ ] -----	(6 1 2)	39.488	---	2.2801	---	---	
[ ] -----	(5 3 3)	39.521	---	2.2783	---	---	
[ ] 39.583	(2 4 6)	39.597	0.014	2.2741	2.2749	-0.0008	15.8
[ ] -----	(1 6 1)	39.904	---	2.2573	---	---	

#: calculated by **JADE.5**.