Electronic Supplementary Information

Luminescent ionic liquids based on cyclometalated platinum(II) complexes exhibiting thermochromic behaviour in different colour regions

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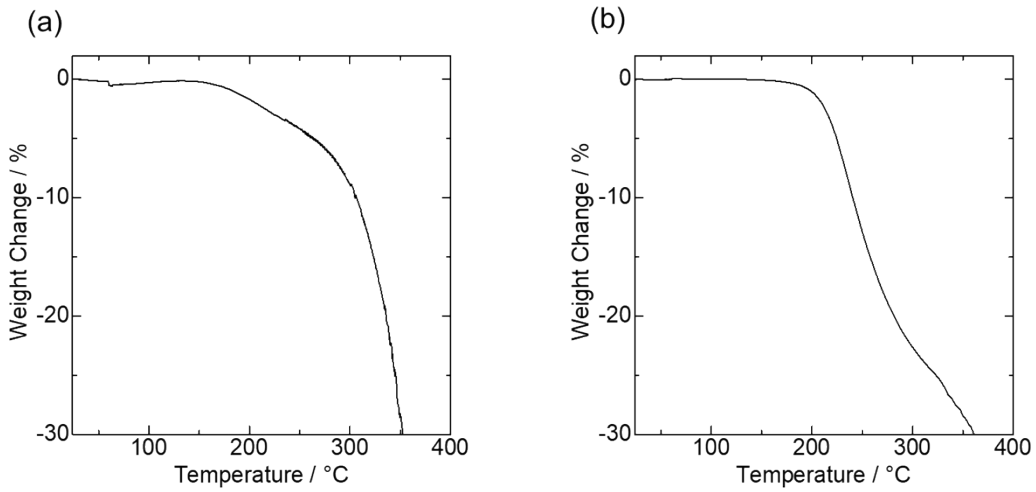

Fig. S1. TG curves of (a) **2** and (b) **3**. (The measurements were carried out under Ar atmosphere with scan rate of 5° min^{-1})

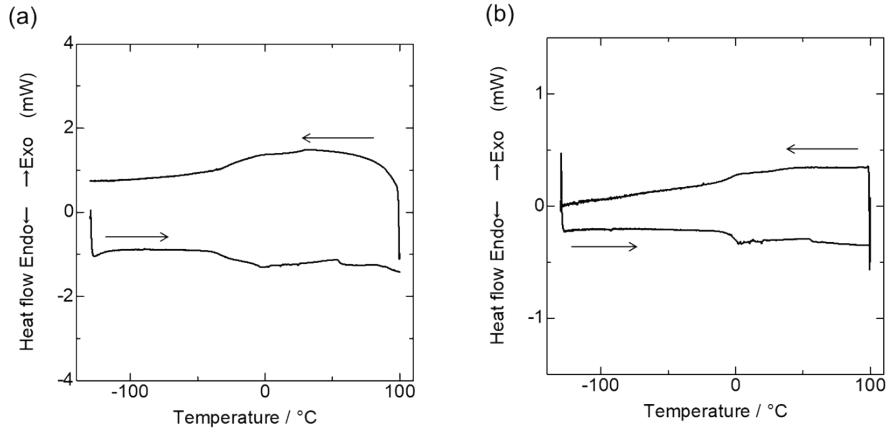

Fig. S2. DSC curves of (a) **2** and (b) **3** (first cooling scan and second heating scan, scan rate = 5° min^{-1}).

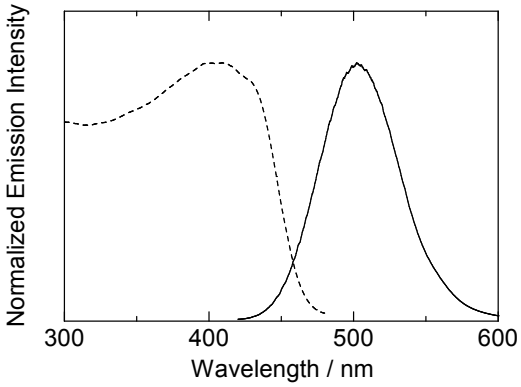

Fig. S3. Emission (solid line) and excitation (dotted line) spectra of **4** in the solid state at room temperature (λ_{ex} = 350, λ_{em} = 500 nm). Φ = 0.29, τ_{av} = 0.40 μs

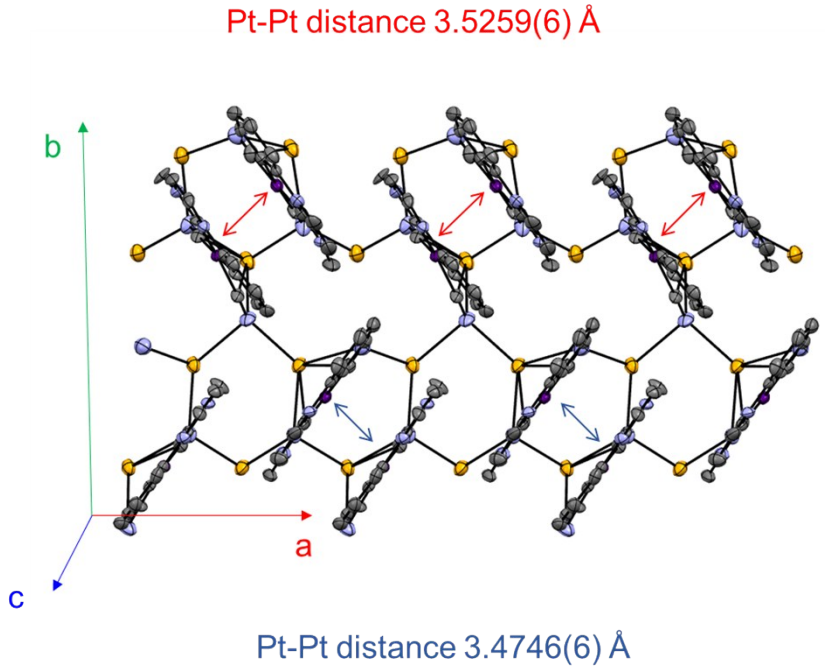

Fig. S4. ORTEP drawings showing the dimer structure of potassium salt **4**. Displacement parameters are drawn at the 50% probability level. Hydrogen atoms and water oxygen atoms are omitted for clarity. Color code: Pt, purple; C, grey; N, blue; K, orange.

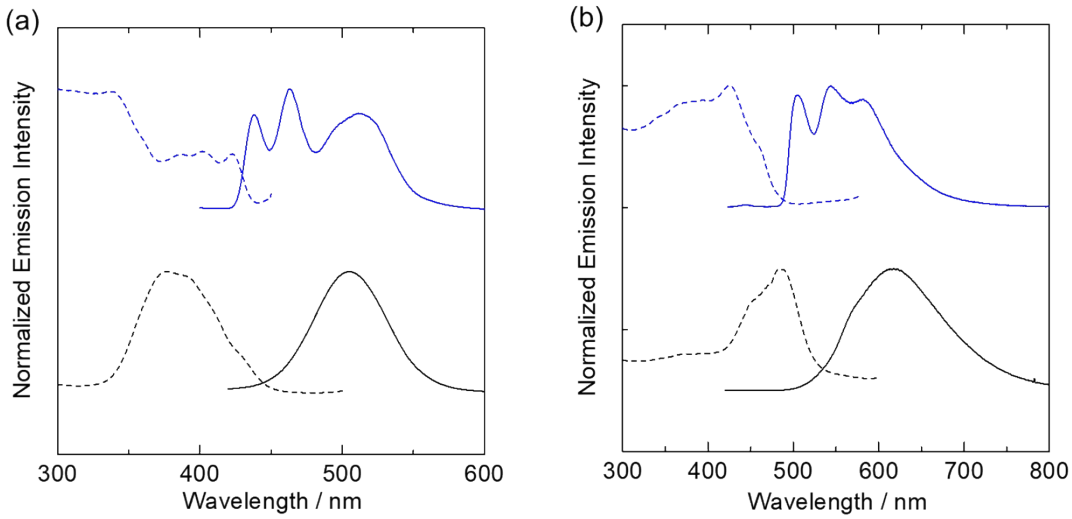

Fig. S5. Emission (solid lines) and excitation (dotted lines) spectra of neat **2** (a) (λ_{ex} = 350 nm, λ_{em} = 520 nm) and **3** (b) (λ_{ex} = 350 nm, λ_{em} = 620 nm) at 298 (black, neat liquid state) and 77 K (blue, neat glass state) under N_2 atmosphere.

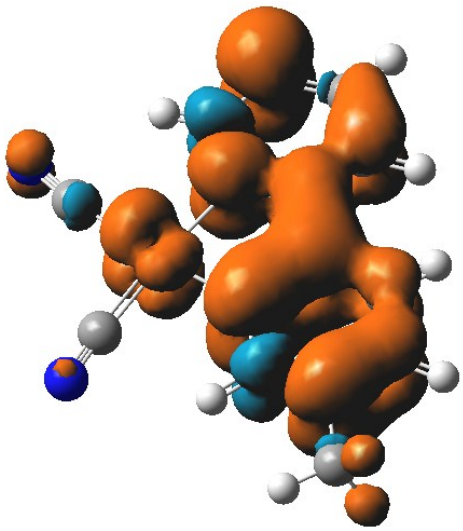

Fig. S6. Spin density of monomer **1** ($[Pt(CN)_2(ptpy)]^-$) of the S=1 state mainly delocalized on the ptpy ligand, suggesting that the two-unpaired electron are on the ptpy ligand. Therefore, S=1 state can be assigned to **^{3}LC**.

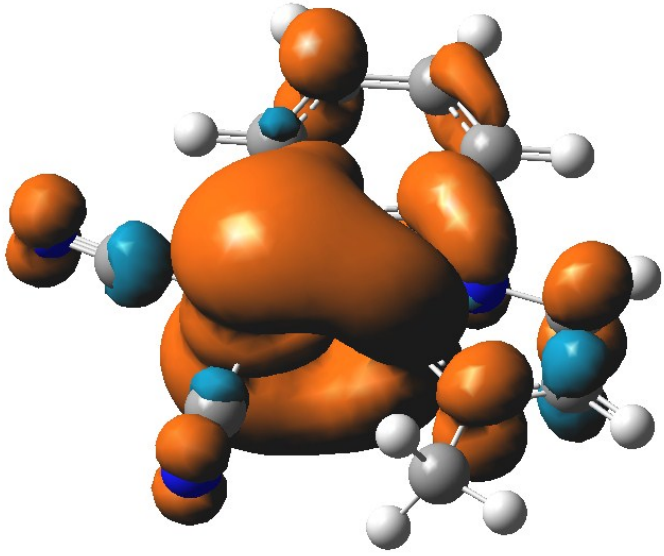

Fig. S7. Spin density of monomer **2** ($[Pt(CN)_2(mpi)]^-$) of the S=1 state is delocalized on both Pt ion and mpi ligand, suggesting that the two-unpaired electron are on Pt ion and mpi ligand. Therefore, S=1 may show both **^{3}LC** and **^{3}MLCT** mixed character.

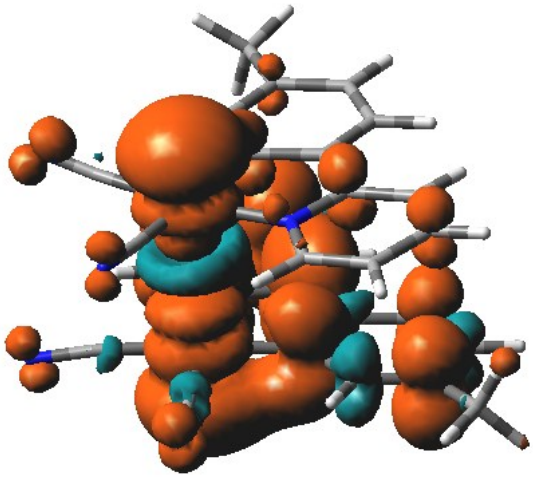

Fig. S8. Spin density of dimer **1** ($[Pt(CN)_2(ptpy)]^-$) of the S=1 state is delocalized on both Pt ions a ptpy ligand, suggesting that the two-unpaired electron are on the Pt ions and a ptpy ligand. Therefore, S=1 state can be assigned to **^{3}MMLCT**.

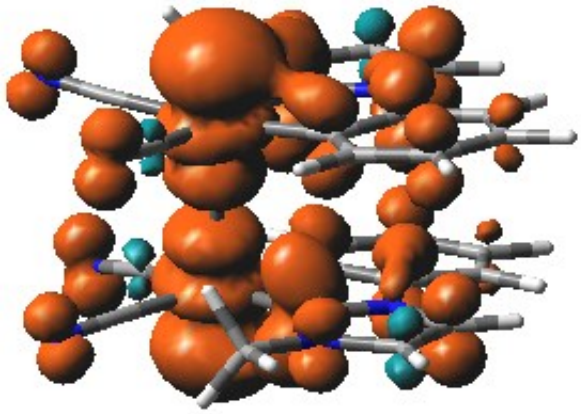

Fig. S9. Spin density of dimer **2** ($[Pt(CN)_2(mpi)]^-$) of the S=1 state is delocalized on both Pt ions a both mpi ligands, suggesting that the two-unpaired electron are on the Pt ions and mpi ligands. Therefore, S=1 state can be assigned to **^{3}MMLCT**.

Table S1. Crystal Data for complex $K[Pt(CN)_2(mpi)]$ (**4**)

	$K[Pt(CN)_2(mpi)]\cdot 0.5H_2O$ (**4**)
Formula	$C_{12}H_9KN_4O_{0.5}Pt$
Formula Weight	451.42
Crystal system	Triclinic
Space group	*P*-1
a (Å)	8.400(1)
b (Å)	16.506(3)
c (Å)	20.116(4)
α (°)	109.731(2)
β (°)	94.688(2)
γ (°)	90.344(3)
V (Å^3)	2615.0(8)
T (K)	200
Z	8
D_{calc} (g cm^{-3})	2.293
F(000)	1680.00
measured refl.	21080
unique refl.	11795
GOF on F^2	1.049
R_{int}	0.0346
R_1[a]	0.0457
wR_2[b](all data)	0.1176

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o)^2]^{1/2}$, $w = [\sigma_c^2(F_o^2) + (xP)^2 + yP]^{-1}$, $P = (F_o^2 - 2F_c^2)/3$.

Table S2. Emission spectral data of corresponding crystalline complexes of monomer and dimer structures.

Complex anion	$[Pt(CN)_2(mpi)]^-$		$[Pt(CN)_2(bzq)]^-$	
Cation	*n*-Bu_4N^+	K^+	*n*-Bu_4N^+	K^+
λ_{max} / nm	430, 455, 481	502	480, 515, 553	636
assignment	^{3}LC	^{3}MMLCT	^{3}LC	^{3}MMLCT

Table S3. Cartesian coordinates of the optimized ground state monomer structure of **1** ($[Pt(CN)_2(ptpy)]^-$).

Pt	2.545369	-0.72595	3.449749
N	0.381916	1.115905	4.752314
N	1.030105	-1.52104	0.724712
N	4.205151	-1.92257	2.827966
C	4.274058	-2.6173	1.681707
C	5.383237	-3.37689	1.336249
C	6.46267	-3.41377	2.218706
C	6.393171	-2.697	3.403284
C	5.250151	-1.94418	3.708929
C	5.056183	-1.15323	4.915588
C	6.0303	-1.06531	5.924171
C	5.801042	-0.29904	7.05567
C	4.589305	0.397512	7.203424
C	3.628904	0.302333	6.194341
C	3.817866	-0.46148	5.03147
C	4.33947	1.226386	8.42866
C	1.168561	0.414962	4.224597
C	1.487437	-1.16433	1.751141
H	3.394208	-2.53982	1.04305
H	5.392661	-3.92294	0.396091
H	7.352447	-3.99777	1.984421
H	7.224797	-2.71358	4.104172
H	6.978696	-1.59814	5.82958
H	6.562519	-0.2352	7.835408
H	2.689106	0.84504	6.312468
H	4.371759	0.618708	9.344034
H	5.097541	2.013083	8.54918
H	3.358629	1.712472	8.386905

Table S4. Cartesian coordinates of the excited triplet state monomer structure of **1** ($[Pt(CN)_2(ptpy)]^-$).

Pt	2.613655	-0.655	3.43042
N	0.477853	1.24511	4.664617
N	1.038042	-1.30837	0.689701
N	4.196094	-1.90116	2.80412
C	4.281876	-2.58837	1.671273
C	5.376897	-3.39076	1.345717
C	6.460562	-3.48352	2.266738
C	6.394094	-2.78412	3.440472
C	5.253161	-1.97076	3.740357
C	5.06748	-1.21269	4.900936
C	6.022644	-1.14542	5.977815
C	5.7557	-0.37915	7.074194
C	4.537606	0.378134	7.201077
C	3.606412	0.324326	6.170983
C	3.795841	-0.43606	5.006929
C	4.313499	1.199618	8.438446
C	1.253443	0.529268	4.170407
C	1.536062	-1.01812	1.704181
H	3.433251	-2.4876	0.999513
H	5.384929	-3.9265	0.403683
H	7.325049	-4.10009	2.039463
H	7.206496	-2.83877	4.157697
H	6.9543	-1.70081	5.923047
H	6.481801	-0.33253	7.885225
H	2.684487	0.894268	6.260878
H	5.097871	1.958404	8.563653
H	3.349453	1.713314	8.395326
H	4.326201	0.575235	9.342115

Table S5. Cartesian coordinates of the optimized ground state monomer structure of **2** ($[Pt(CN)_2(mpi)]^-$).

Pt	5.536674	-3.45997	5.402163
N	7.129699	-0.96563	4.146945
N	6.095646	-2.29246	2.801263
N	6.686796	-2.13633	8.097177
N	4.028824	-5.86153	6.853604
C	5.296465	-3.41446	2.452508
C	3.746048	-5.6159	1.944611
H	3.128403	-6.49384	1.748947
C	4.183967	-4.83084	0.878162
H	3.916053	-5.08467	-0.14731
C	4.881082	-4.17298	3.56508
C	7.677581	-0.32895	5.328071
H	8.771998	-0.31573	5.270175
H	7.309905	0.701058	5.39979
H	7.369195	-0.88619	6.21643
C	4.603326	-4.95541	6.368387
C	4.089945	-5.28989	3.260089
H	3.737183	-5.91681	4.079506
C	7.337256	-0.49066	2.861986
H	7.92728	0.395794	2.671987
C	6.240753	-2.66128	7.140103
C	4.973822	-3.70869	1.132134
H	5.324396	-3.08399	0.3085
C	6.683972	-1.32918	2.014396
H	6.592741	-1.31697	0.937417
C	6.357821	-2.08955	4.135522

Table S6. Cartesian coordinates of the optimized excited triplet state monomer structure of **2** ($[Pt(CN)_2(mpi)]^-$).

Pt	5.514582	-3.43138	5.342572
N	7.151303	-0.98965	4.138228
N	6.109269	-2.31634	2.740082
N	6.669028	-2.08171	8.035171
N	3.983233	-5.76076	6.888801
C	5.337277	-3.37482	2.409669
C	3.729474	-5.60842	1.999869
H	3.103339	-6.47385	1.804806
C	4.202302	-4.82173	0.879372
H	3.922041	-5.1133	-0.12958
C	4.876394	-4.15252	3.601884
C	7.665824	-0.39142	5.358702
H	8.263222	0.481557	5.085894
H	6.839957	-0.10031	6.010147
H	8.274571	-1.11564	5.902904
C	4.559062	-4.89124	6.36736
C	4.066759	-5.26722	3.300112
H	3.703585	-5.86828	4.12931
C	7.385273	-0.52662	2.869223
H	7.992092	0.34934	2.691969
C	6.230126	-2.60254	7.087342
C	4.992797	-3.72258	1.072492
H	5.347884	-3.13231	0.231674
C	6.745314	-1.33768	1.978022
H	6.691862	-1.29991	0.902756
C	6.360261	-2.10572	4.118869

Table S7. Cartesian coordinates of the optimized ground state dimer structure of **1** ($[Pt(CN)_2(ptpy)]^-$).

Pt	2.735372	-0.63795	3.384538
Pt	4.025582	1.845521	1.513732
N	0.365932	1.019675	4.555776
N	3.17481	0.595213	-1.214
N	1.165234	3.284635	1.49062
N	0.861988	-1.28921	0.872635
N	4.539065	2.519816	3.465825
N	4.416683	-1.62961	2.53737
C	4.470094	-2.06925	1.271082
C	5.608922	-2.66679	0.747222
C	6.730154	-2.79334	1.564973
C	6.685819	-2.30069	2.860903
C	5.515387	-1.70287	3.343392
C	5.339617	-1.11963	4.671195
C	6.357529	-1.12002	5.635798
C	6.141867	-0.55573	6.887231
C	4.900024	0.022138	7.193787
C	3.900616	0.030367	6.217725
C	4.072217	-0.52139	4.937831
C	4.655435	0.629926	8.544528
C	1.274407	0.369494	4.184533
C	1.52672	-1.00148	1.797753
C	3.669455	3.082548	4.318328
C	4.030686	3.438866	5.611008
C	5.335666	3.187296	6.030047
C	6.222492	2.571069	5.159612
C	5.809455	2.224654	3.867721
C	6.624115	1.541741	2.866204
C	7.963956	1.195215	3.09255
C	8.699246	0.546643	2.107968
C	8.102231	0.231049	0.877504
C	6.762278	0.567969	0.671703
C	5.976743	1.21941	1.636459

C	8.889218	-0.46573	-0.19431
C	3.576487	1.082438	-0.22069
C	2.19045	2.710372	1.501984
H	3.564549	-1.91274	0.683957
H	5.612467	-2.99728	-0.28938
H	7.649179	-3.24057	1.183012
H	7.567378	-2.34723	3.49743
H	7.335316	-1.55266	5.409734
H	6.942821	-0.54957	7.631101
H	2.944182	0.505979	6.452208
H	5.560503	1.107067	8.948022
H	3.86358	1.388715	8.499813
H	4.336574	-0.1216	9.282993
H	2.661461	3.226421	3.929158
H	3.288143	3.878506	6.273569
H	5.651339	3.435453	7.044531
H	7.230007	2.321559	5.486766
H	8.441121	1.421322	4.049392
H	9.74026	0.269938	2.294033
H	6.294541	0.293928	-0.27806
H	8.229053	-1.02161	-0.87258
H	9.459315	0.243622	-0.81371
H	9.616704	-1.17433	0.227811

Table S8. Cartesian coordinates of the optimized excited triplet state dimer structure of **1** ($[Pt(CN)_2(ptpy)]^-$).

Pt	2.804174	-0.40297	3.24931
Pt	3.939878	1.692682	1.60447
N	0.36598	1.019669	4.555765
N	3.174831	0.595214	-1.21395
N	1.165203	3.284652	1.490602
N	0.861949	-1.28922	0.872615
N	4.645524	2.567628	3.377295
N	4.432195	-1.60142	2.606412
C	4.475362	-2.2869	1.45402
C	5.531822	-3.12757	1.138083
C	6.589768	-3.24574	2.048752
C	6.566975	-2.48999	3.210085
C	5.467821	-1.66681	3.490857
C	5.294239	-0.86062	4.700803
C	6.258808	-0.79388	5.718285
C	6.026902	-0.02535	6.850071
C	4.822599	0.685154	6.992203
C	3.869676	0.608496	5.977355
C	4.071224	-0.14489	4.811455
C	4.59253	1.571619	8.187704
C	1.309053	0.5561	4.052815
C	1.572625	-0.91095	1.711366
C	3.93069	3.363991	4.197997
C	4.478084	3.967497	5.312021
C	5.838757	3.731242	5.615146
C	6.556621	2.871322	4.804651
C	5.963695	2.291289	3.671417
C	6.622488	1.417833	2.717871
C	7.967032	1.009213	2.833008
C	8.534536	0.185525	1.87648
C	7.780524	-0.24959	0.765819
C	6.45583	0.161844	0.655138
C	5.835542	0.984855	1.610209

C	8.389247	-1.18718	-0.24191
C	3.464589	0.950469	-0.14258
C	2.141784	2.659913	1.58298
H	3.629971	-2.13558	0.786761
H	5.52166	-3.66882	0.19793
H	7.425553	-3.91228	1.848361
H	7.39284	-2.53642	3.911846
H	7.202616	-1.32756	5.624363
H	6.784103	0.034811	7.631264
H	2.939697	1.165009	6.086732
H	5.216136	1.274813	9.039888
H	4.835286	2.612242	7.93359
H	3.543424	1.551543	8.503793
H	2.887386	3.495713	3.922686
H	3.85699	4.606018	5.931676
H	6.309357	4.19315	6.480354
H	7.592538	2.640286	5.033773
H	8.567365	1.324993	3.684828
H	9.57099	-0.13614	1.982507
H	5.87104	-0.17474	-0.20071
H	7.760521	-1.267	-1.13513
H	9.38933	-0.85747	-0.55532
H	8.49706	-2.20018	0.175082

Table S9. Cartesian coordinates of the optimized ground state dimer structure of **2** ($[Pt(CN)_2(mpi)]^-$).

Pt	3.097825	-0.61216	5.800151
Pt	5.409762	-3.32632	5.28638
N	6.609251	-0.5935	4.1613
N	2.331829	-1.22206	3.065483
N	1.641342	-2.93115	4.185916
N	5.721532	-1.95334	2.742774
N	4.674042	1.247256	7.841859
N	2.318995	-2.47778	8.285178
N	6.712558	-2.40081	8.062641
N	4.105126	-5.65083	7.010153
C	2.25377	-1.7312	4.340268
C	1.422317	-3.88082	5.264261
H	0.844148	-4.72158	4.867714
H	2.379262	-4.24281	5.658886
H	0.888057	-3.39827	6.086077
C	5.054913	-3.13849	2.348918
C	3.76917	-5.48921	1.743876
H	3.25902	-6.42704	1.510112
C	4.099567	-4.60897	0.713234
H	3.853526	-4.84555	-0.3231
C	4.035016	1.848198	4.006415
H	4.427311	2.325968	4.908274
C	4.743181	-3.99404	3.431558
C	6.987559	0.063027	5.399319
H	7.956341	0.557734	5.26428
H	6.219656	0.791676	5.683048
H	7.048955	-0.67889	6.199368
C	1.360928	-3.17157	2.853856
H	0.930835	-4.10788	2.525012
C	4.630269	-4.8414	6.337866
C	3.656544	1.928517	1.609947
H	3.743224	2.441793	0.651087
C	4.086186	-5.18068	3.072367

H	3.817933	-5.8844	3.863837
C	3.435838	0.584065	4.126782
C	4.146086	2.512275	2.778538
H	4.620044	3.495915	2.733184
C	6.65912	0.015297	2.919616
H	7.035025	1.021893	2.796253
C	6.219748	-2.70065	7.037387
C	2.948241	0.043512	2.912499
C	3.046157	0.672942	1.675815
H	2.656906	0.198985	0.771389
C	2.619911	-1.80686	7.367209
C	1.790488	-2.09406	2.14409
H	1.80066	-1.90936	1.079133
C	4.75256	-3.41175	1.018558
H	5.017175	-2.70799	0.225518
C	6.107176	-0.84253	2.022144
H	5.919916	-0.73209	0.963175
C	4.056343	0.589408	7.087111
C	6.021625	-1.81301	4.078739

Table S10. Cartesian coordinates of the optimized excited triplet state dimer structure of **2** ($[Pt(CN)_2(mpi)]^-$).

Pt	3.365817	-0.81446	5.779368
Pt	5.25692	-3.1827	5.34291
N	6.89087	-0.75085	4.189691
N	2.48655	-1.28588	3.077238
N	1.565439	-2.8774	4.220892
N	5.809682	-1.98879	2.779189
N	4.674062	1.247299	7.841921
N	2.319	-2.47776	8.285127
N	6.712508	-2.40081	8.062581
N	4.10515	-5.6509	7.010202
C	2.378153	-1.7987	4.346146
C	1.25298	-3.79207	5.307512
H	0.668413	-4.61856	4.895318
H	2.1768	-4.17298	5.752187
H	0.690263	-3.27433	6.086921
C	5.005765	-3.08112	2.412139
C	3.520587	-5.34149	1.883989
H	2.943267	-6.24181	1.679955
C	3.945978	-4.53376	0.823881
H	3.700883	-4.79379	-0.20369
C	4.543606	1.540132	4.047787
H	4.983436	1.951912	4.955132
C	4.576483	-3.85546	3.524633
C	7.334037	-0.15712	5.440819
H	7.909723	0.741427	5.204621
H	6.467157	0.105261	6.054781
H	7.944123	-0.86908	6.00006
C	1.202924	-3.0511	2.901248
H	0.608735	-3.89483	2.585481
C	4.475895	-4.72822	6.400948
C	4.13681	1.720184	1.659934
H	4.261658	2.246846	0.716195
C	3.826571	-4.99687	3.20521

H	3.48744	-5.63825	4.017688
C	3.822301	0.34073	4.140448
C	4.695385	2.22693	2.837975
H	5.256297	3.159804	2.812764
C	7.088392	-0.2172	2.93282
H	7.651174	0.692074	2.787263
C	6.151538	-2.61988	7.067383
C	3.253899	-0.11932	2.921627
C	3.405533	0.531403	1.699562
H	2.956412	0.12789	0.79359
C	2.722924	-1.89595	7.362402
C	1.768545	-2.05334	2.175516
H	1.763842	-1.8666	1.114057
C	4.698581	-3.38779	1.088747
H	5.045895	-2.75379	0.274609
C	6.42237	-0.99157	2.038662
H	6.293108	-0.88311	0.97415
C	4.252353	0.455067	7.096205
C	6.082662	-1.83726	4.115855

Table S11. Calculated emission wavelength and observed emission wavelength.

Complex anion	Structure	Wavelength (calc)	Wavelength (obs)
(**1**)[$Pt(CN)_2(ptpy)]^-$	Monomer	529	487
	Dimer	567	560
(**2**) [$Pt(CN)_2(mpi)]^-$	Monomer	444	438
	dimer	472	505

Table S12. Emission lifetime data for **2** at various temperatures.

Temperature	A_1[a]	τ_1[b] (μs)	A_2[a]	τ_2[b] (μs)
77	0.43	5.0	0.56	8.6
100	0.48	3.9	0.52	7.7
130	0.72	2.8	0.36	5.8
160	1.04	1.8	0.08	4.5
190	1.05	1.0	0.16	2.5
220	0.66	0.33	0.36	1.4
250	0.73	0.25	0.38	1.2
280	0.97	0.13	0.24	0.85
298	1.13	0.10	0.13	0.57

[a] Pre-exponential factors. [b] Emission lifetimes; Emission decays were analyzed with bi-exponential fitting: $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$.

Table S13. Emission lifetime data for **3** at various temperatures.

Temperature	A_1[a]	τ_1[b] (μs)	A_2[a]	τ_2[b] (μs)
77	0.87	10.1	0.20	147.0
100	0.88	6.6	0.17	68.3
130	0.96	6.6	0.10	43.8
160	1.09	4.3	0.04	25.0
190	1.17	3.1	0.02	21.7
220	1.16	2.4	0.02	19.4
250	1.01	1.7	0.04	7.2
280	1.00	1.1	0.04	5.6
298	0.93	0.75	0.15	2.4

[a] Pre-exponential factors. [b] Emission lifetimes; Emission decays were analyzed with bi-exponential fitting: $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$.