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Highly phosphorescent platinum(II) complexes supported by (2-(1H-benzimidazole)-phenyl)diphosphine oxide ancillary ligands

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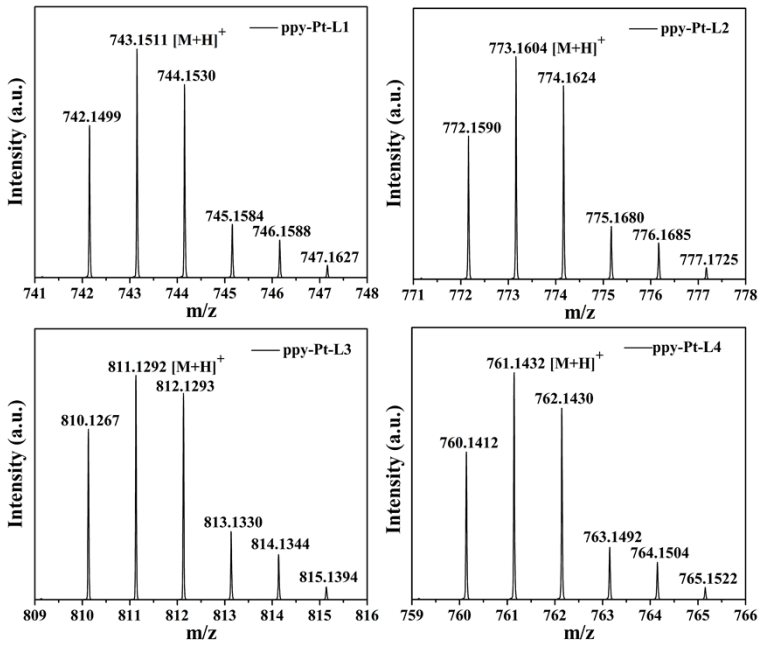

Fig. S1 High-resolution mass spectrometry (HRMS) of ppy-Pt-L complexes.

Table S1. Crystal data and details of data collection and refinement of **ppy-Pt-L1** and **ppy-Pt-L2** complexes.

Compound reference	**ppy-Pt-L1**	**ppy-Pt-L2**
Empirical formula	$C_{38}H_{28}Cl_6N_3OPPt$	$C_{41}H_{36}N_3O4PPt$
Formula weight	981.39	860.79
Temperature/K	291.15	293(2)
Crystal system	triclinic	monoclinic
Space group	P-1	P21/n
a/Å	12.0268(4)	10.2624(3)
b/Å	12.3029(3)	17.1500(5)
c/Å	13.5666(5)	20.1248(4)
α/°	80.235(3)	90
β/°	77.228(3)	95.063(2)

γ/°	89.628(2)	90
Volume/Å^3	1928.34(11)	3528.16(16)
Z	2	4
ρ_{calc}g/cm^3	1.690	1.621
μ/mm^{-1}	11.303	4.069
F(000)	960.0	1712.0
Crystal size/mm^3	0.22 × 0.2 × 0.18	0.2 × 0.2 × 0.15
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.782 to 133.194	4.63 to 54.954
Reflections collected	13895	18629
Independent reflections	6817 [R_{int} = 0.0363, R_{sigma} = 0.0460]	7808 [R_{int} = 0.0587, R_{sigma} = 0.0778]
Data/restraints/parameters	6817/0/451	7808/1/424
Goodness-of-fit on F^2	1.021	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0346, wR_2 = 0.0888	R_1 = 0.0447, wR_2 = 0.0912
Final R indexes [all data]	R_1 = 0.0389, wR_2 = 0.0918	R_1 = 0.0696, wR_2 = 0.1026
CCDC number	2032296	2032297

Table S2. Crystal data and details of data collection and refinement of **ppy-Pt-L3** and **ppy-Pt-L4** complexes.

Compound reference	**ppy-Pt-L3**	**ppy-Pt-L4**
Empirical formula	$C_{38}H_{26}Cl_3F_3N_3OPPt$	$C_{37}H_{27}Cl_2FN_3OPPt$
Formula weight	930.03	845.57
Temperature/K	293(2)	291.15
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.1541(10)	11.8502(5)
b/Å	13.0636(9)	11.9267(5)
c/Å	13.5513(11)	13.1295(5)
α/°	88.629(7)	77.794(3)
β/°	63.523(8)	75.159(4)
γ/°	72.753(7)	68.373(4)
Volume/Å^3	1824.5(3)	1653.27(13)
Z	2	2
ρ_{calc}g/cm^3	1.693	1.699
μ/mm^{-1}	4.159	4.494
F(000)	908.0	828.0
Crystal size/mm^3	0.16 × 0.12 × 0.1	0.2 × 0.16 × 0.13
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.29 to 58.942	3.236 to 53.466

Reflections collected	16816	14538
Independent reflections	8393 [R_{int} = 0.0578, R_{sigma} = 0.0725]	6972 [R_{int}= 0.0656, R_{sigma} = 0.0711]
Data/restraints/parameters	8393/42/451	6972/6/415
Goodness-of-fit on F^2	1.056	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.1081	R_1 = 0.0370, wR_2 = 0.0735
Final R indexes [all data]	R_1 = 0.0638, wR_2 = 0.1194	R_1 = 0.0517, wR_2 = 0.0796
CCDC number	2032298	2032299

Table S3. Selected bond lengths (Å) and angles (deg) for the complexes obtained from experimental data.

Complex		Length/Å		Angle/°
ppy-Pt-L1	Pt1-O1	2.130(3)	N1-Pt1-O1	90.93(15)
	Pt1-N1	2.015(4)	N2-Pt1-O1	90.25(14)
	Pt1-N2	2.031(4)	N2-Pt1-N1	176.71(14)
	Pt1-C1	1.962(4)	C1-Pt1-O1	172.94(16)
			C1-Pt1-N1	82.04(19)
			C1-Pt1-N2	96.80(18)
ppy-Pt-L2	Pt1-O1	2.172(4)	N1-Pt1-O1	92.58(16)
	Pt1-N1	2.024(4)	N2-Pt1-O1	89.91(16)
	Pt1-N2	2.023(4)	N2-Pt1-N1	175.65(17)
	Pt1-C1	1.984(5)	C1-Pt1-O1	173.86(17)
			C1-Pt1-N1	81.66(19)
			C1-Pt1-N2	95.97(19)
ppy-Pt-L3	Pt1-O1	2.152(4)	N1-Pt1-O1	92.69(18)
	Pt1-N1	2.010(5)	N2-Pt1-O1	88.82(17)
	Pt1-N2	2.021(5)	N2-Pt1-N1	177.51(17)
	Pt1-C1	1.964(6)	C1-Pt1-O1	173.72(19)
			C1-Pt1-N1	81.3(2)
			C1-Pt1-N2	97.3(2)
ppy-Pt-L4	Pt1-O1	2.150(3)	N1-Pt1-O1	93.02(14)
	Pt1-N1	2.015(4)	N2-Pt1-O1	89.32(14)
	Pt1-N2	2.020(4)	N2-Pt1-N1	176.93(14)
	Pt1-C1	1.965(5)	C1-Pt1-O1	174.48(15)
			C1-Pt1-N1	81.68(18)
			C1-Pt1-N2	96.04(18)

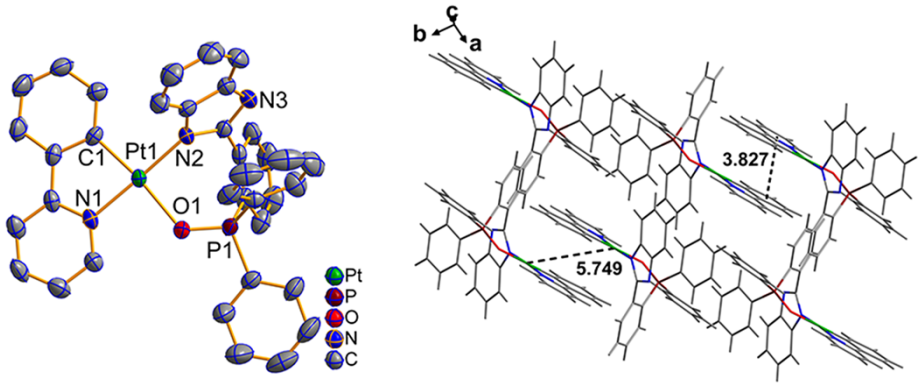

Fig. S2 Molecular structure (left) and Packing diagram of the **ppy-Pt-L1** (right). Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

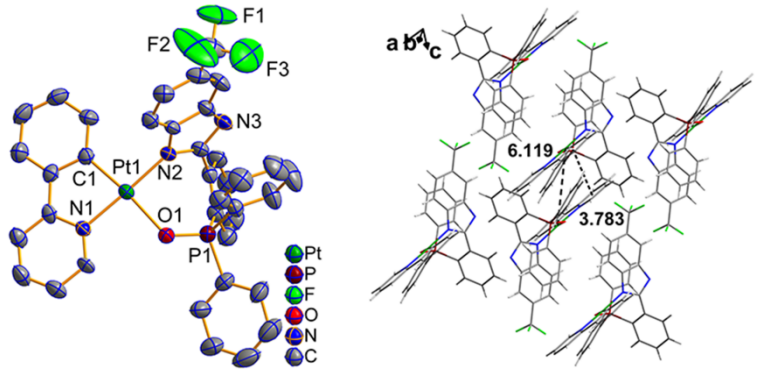

Fig. S3 Molecular structure (left) and packing diagram of the **ppy-Pt-L3** (right). Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

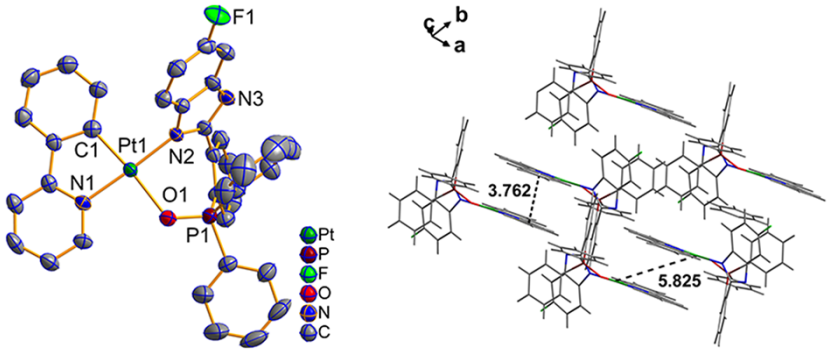

Fig. S4 Molecular structure (left) and packing diagram of the **ppy-Pt-L4** (right). Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

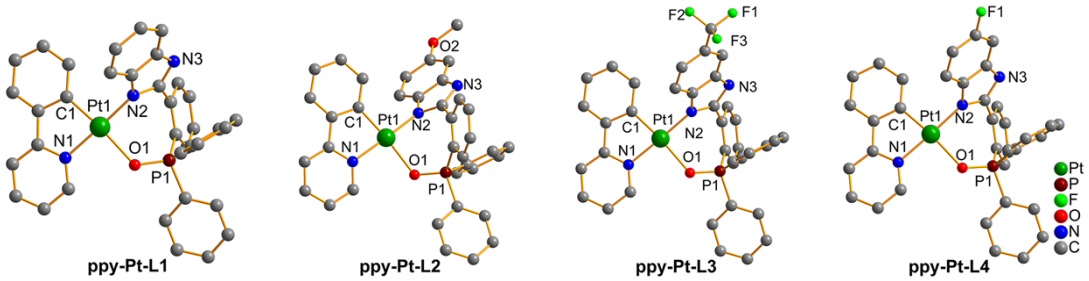

Fig. S5 The optimized structure of the complexes in the ground state (S_0). Hydrogen atoms are omitted for clarity.

Table S4. Selected bond lengths (Å) and angles (deg) for the complexes in the ground state (S_0).

Complex		Length/Å		Angle/°
ppy-Pt-L1	Pt1-O1	2.243(0)	N1-Pt1-O1	92.87(8)
	Pt1-N1	2.054(4)	N2-Pt1-O1	88.68(0)
	Pt1-N2	2.051(0)	N2-Pt1-N1	177.32(0)
	Pt1-C1	1.984(9)	C1-Pt1-O1	172.94(7)
			C1-Pt1-N1	80.94(4)
			C1-Pt1-N2	97.62(3)
ppy-Pt-L2	Pt1-O1	2.239(7)	N1-Pt1-O1	92.79(7)
	Pt1-N1	2.055(6)	N2-Pt1-O1	88.73(6)
	Pt1-N2	2.049(9)	N2-Pt1-N1	177.06(0)
	Pt1-C1	1.985(0)	C1-Pt1-O1	172.86(0)
			C1-Pt1-N1	80.97(3)
			C1-Pt1-N2	97.64(3)
ppy-Pt-L3	Pt1-O1	2.240(0)	N1-Pt1-O1	92.64(8)
	Pt1-N1	2.052(2)	N2-Pt1-O1	88.73(9)
	Pt1-N2	2.052(4)	N2-Pt1-N1	177.51(2)
	Pt1-C1	1.985(0)	C1-Pt1-O1	172.86(0)
			C1-Pt1-N1	81.02(2)
			C1-Pt1-N2	97.70(9)
ppy-Pt-L4	Pt1-O1	2.246(5)	N1-Pt1-O1	92.82(2)
	Pt1-N1	2.053(2)	N2-Pt1-O1	88.67(4)
	Pt1-N2	2.054(0)	N2-Pt1-N1	177.14(4)
	Pt1-C1	1.984(7)	C1-Pt1-O1	172.93(8)
			C1-Pt1-N1	81.00(1)
			C1-Pt1-N2	97.64(5)

Table S5. Cartesian coordinates for optimized ground state structure of the complexes by theoretical calculations.

Complex	Atom	x	y	z	Complex	Atom	x	y	z
ppy-Pt-L1	Pt	-1.16061	-0.44981	-0.19479	**ppy-Pt-L2**	Pt	-0.52887	-1.22936	-0.19835
	N	-3.06991	-0.01635	0.31996		P	2.20225	0.64458	-0.07569
	N	-0.29067	1.51203	0.18372		O	1.4884	-0.49216	-0.83357

	C	3.31215	-1.79742	-0.17991		O	-4.98559	4.20065	-1.21422
	C	-3.97329	-1.03886	0.17706		N	-0.12086	-3.15664	-0.78559
	C	-2.00589	-2.21383	-0.60075		N	-1.01754	0.69253	0.32096
	C	2.64902	0.93191	-0.94834		N	-1.2235	2.59572	1.568
	C	1.86887	-0.09202	1.73151		C	-2.20729	-2.10068	0.40476
	C	-1.45921	2.897	-1.59473		C	-3.28607	-1.50975	1.0781
	H	-1.82806	2.0644	-2.18698		H	-3.26935	-0.4473	1.29326
	C	-0.69539	2.67799	-0.43699		C	-4.39172	-2.2698	1.47082
	N	0.51123	3.27961	1.41134		H	-5.21612	-1.78727	1.98971
	C	2.89142	2.03486	-3.08954		C	-4.44785	-3.64155	1.20282
	H	2.67341	2.08172	-4.15225		H	-5.30974	-4.22672	1.50887
	C	5.62917	-2.49266	-0.33053		C	-3.38635	-4.2551	0.54311
	H	6.6842	-2.23886	-0.37334		H	-3.42829	-5.32164	0.34122
	C	-3.3999	-2.27416	-0.35047		C	-2.27197	-3.4989	0.14811
	C	0.4355	1.95586	1.26076		C	-1.10502	-4.06793	-0.52924
	C	4.67716	-1.47838	-0.23084		C	-0.92833	-5.40236	-0.91362
	H	4.9966	-0.44115	-0.20519		H	-1.70692	-6.12811	-0.71148
	C H	-3.46427 -2.69519	1.17026 1.92569	0.82102 0.90433		C H	0.2428 0.38165	-5.79005 -6.8239	-1.55563 -1.85542
	C	-1.38291	-3.35553	-1.12051		C	1.23241	-4.83817	-1.8127
	H	-0.32024	-3.32461	-1.34093		H	2.1566	-5.09954	-2.31477
	C	2.51909	-0.90868	2.67456		C	1.01092	-3.52729	-1.41139
	H	3.06521	-1.78503	2.34469		H	1.72868	-2.73339	-1.58123
	C	-0.19965	3.76591	0.33903		C	-2.0574	1.43377	-0.21314
	C	2.37839	0.98952	-2.32411		C	-2.91502	1.20462	-1.29972
	H	1.75526	0.2273	-2.78108		H	-2.83212	0.30422	-1.90024
	C	-4.13386	-3.44376	-0.60268		C	-3.87188	2.16705	-1.58351
	H	-5.20269	-3.48332	-0.40918		H	-4.55728	2.04116	-2.41581
	C	2.91144	-3.14089	-0.2385		C	-3.9895	3.34711	-0.80349
	H	1.85464	-3.38393	-0.2125		C	-3.14731	3.58472	0.27854
	C	-4.77855	1.41414	1.19562		H	-3.21924	4.4792	0.88546
	H	-5.0482	2.38717	1.5896		C	-2.17293	2.60928	0.57168
	C	3.93573	2.97458	-1.1192		C	-0.56218	1.45067	1.36668
	H	4.52593	3.75419	-0.64738		C	0.58135	1.07014	2.22217
	C	3.67268	3.02491	-2.48897		C	0.41097	1.15332	3.61249
	H	4.06613	3.84213	-3.08646		H	-0.55253	1.47578	3.99198
	C	-5.30999	-0.83373	0.53933		C	1.44099	0.82298	4.49059
	H	-6.01975	-1.6442	0.42235		H	1.27683	0.88554	5.56221

	C	3.42572	1.93146	-0.34528		C	2.6761	0.40797	3.99171
	H	3.61243	1.91203	0.72355		H	3.48329	0.14284	4.66722
	C	-5.71798	0.39266	1.04845		C	2.87769	0.34934	2.6136
	H	-6.7549	0.54968	1.32987		H	3.84934	0.05358	2.23506
	C	-2.11482	-4.51837	-1.37149		C	1.84956	0.68341	1.71582
	H	-1.61444	-5.39479	-1.77679		C	-5.16998	5.40363	-0.48305
	C	5.22616	-3.82889	-0.3837		H	-5.99745	5.92877	-0.96317
	H	5.96933	-4.61692	-0.4649		H	-4.27431	6.03735	-0.51291
	C	1.16946	1.36494	3.54095		H	-5.42805	5.20509	0.56513
	H	0.65271	2.26432	3.85712		C	1.81731	2.27686	-0.77616
	C	1.15105	1.0496	2.17248		C	1.47752	2.3407	-2.13663
	C	1.82345	0.55206	4.46068		H	1.38691	1.42485	-2.71186
	H	1.81085	0.81298	5.51521		C	1.24717	3.57628	-2.74093
	C	2.48835	-0.59897	4.03141		H	0.97997	3.62072	-3.7923
	H	2.99259	-1.24392	4.74455		C	1.35571	4.75184	-1.99335
	C	-3.48953	-4.56733	-1.11092		H	1.17575	5.71318	-2.46527
	H	-4.05286	-5.47456	-1.30838		C	1.68619	4.69194	-0.63766
	C	3.86837	-4.15133	-0.339		H	1.75882	5.60366	-0.05278
	H	3.55228	-5.18922	-0.38676		C	1.91427	3.45838	-0.0259
	C	-0.46582	5.09074	-0.04652		H	2.15524	3.41939	1.03161
	H	-0.08503	5.91966	0.54304		C	3.99817	0.40061	-0.28023
	C	-1.22161	5.29922	-1.19323		C	4.48017	-0.90593	-0.45894
	H	-1.44167	6.31385	-1.51456		H	3.78489	-1.73819	-0.47986
	C	-1.71104	4.21532	-1.95826		C	5.84806	-1.13277	-0.61427
	H	-2.29235	4.41964	-2.85351		H	6.21394	-2.14542	-0.75392
	P	2.02908	-0.50791	-0.03362		C	6.74206	-0.05968	-0.59413
	O	0.76544	-1.12075	-0.68892		H	7.80619	-0.23737	-0.71764
						C	6.26756	1.24278	-0.42005
						H	6.95987	2.07902	-0.41038
						C	4.90071	1.47514	-0.26483
						H	4.54064	2.49139	-0.14166
ppy-Pt-L3	Pt	-0.42835	-1.36857	-0.17611	**ppy-Pt-L4**	Pt	1.11013	-0.642	-0.2035
	P	-1.8529	1.64263	-0.09877		P	-2.20084	-0.37138	-0.07063

	F	7.10957	0.1237	-0.68671		F	2.20045	6.27463	-1.2433
	F	6.45392	1.81142	-1.87686		O	-1.01747	-1.00757	-0.82517
	F	6.83142	2.06987	0.25		N	1.70294	-2.52803	-0.75776
	O	-1.74357	0.30927	-0.86343		N	0.58624	1.28283	0.28583
	N	-1.72426	-2.79767	-0.87583		N	-0.18977	3.04987	1.50967
	N	0.93205	0.02419	0.4737		C	3.00255	-0.55925	0.38897
	N	1.95174	1.5757	1.80664		C	3.65158	0.49776	1.04261
	C	0.53092	-2.99048	0.4509		H	3.11411	1.41677	1.24664
	C	1.71811	-3.05284	1.19421		C	4.98997	0.38913	1.43175
	H	2.23486	-2.13907	1.46511		H	5.47033	1.22388	1.93582
	C	2.25506	-4.2817	1.58971		C	5.71498	-0.78005	1.1796
	H	3.17786	-4.30277	2.16379		H	6.75449	-0.85869	1.48308
	C	1.61802	-5.48082	1.25491		C	5.09205	-1.84823	0.53966
	H	2.03985	-6.43236	1.5639		H	5.65408	-2.75852	0.35125
	C	0.43293	-5.44697	0.52472		C	3.7482	-1.74725	0.14843
	H	-0.06438	-6.37883	0.27133		C	3.01091	-2.82945	-0.50671
	C	-0.11241	-4.21727	0.1253		C	3.51449	-4.08206	-0.87653
	C	-1.36247	-4.09072	-0.62663		H	4.55203	-4.32423	-0.68005
	C	-2.17322	-5.1356	-1.08515		C	2.68328	-5.00777	-1.49799
	H	-1.88894	-6.16269	-0.89032		H	3.07181	-5.97923	-1.78654
	C	-3.33717	-4.85175	-1.79127		C	1.35032	-4.6739	-1.74953
	H	-3.96679	-5.66029	-2.14873		H	0.67244	-5.36563	-2.23575
	C	-3.68395	-3.52117	-2.03735		C	0.89755	-3.41903	-1.36396
	H	-4.58059	-3.25908	-2.58671		H	-0.12003	-3.08596	-1.53109
	C	-2.84772	-2.51962	-1.56211		C	-1.89827	-0.13451	1.71552
	H	-3.0485	-1.4661	-1.71698		C	-2.61487	-0.92216	2.63186
	C	-1.65477	1.46646	1.70954		H	-3.31815	-1.66371	2.27111
	C	-2.76771	1.68574	2.53795		C	-2.44886	-0.75693	4.00634
	H	-3.72456	1.94374	2.09904		H	-3.0103	-1.37894	4.69629
	C	-2.66131	1.5911	3.92519		C	-1.57276	0.21816	4.4828
	H	-3.5353	1.76122	4.54594		H	-1.44552	0.3647	5.55116
	C	-1.42829	1.29224	4.50386		C	-0.85373	1.00569	3.58573
	H	-1.33119	1.228	5.5834		H	-0.17099	1.76657	3.94783
	C	-0.31502	1.07216	3.69452		C	-0.98125	0.83467	2.19942
	H	0.64806	0.84206	4.13698		C	-0.18735	1.72592	1.3253

	C	-0.40669	1.1336	2.29668		C	1.11407	2.43527	-0.26754
	C	0.83387	0.90777	1.52112		C	1.96972	2.64034	-1.35829
	C	2.22968	0.15969	0.03019		H	2.34396	1.80568	-1.94203
	C	2.93118	-0.46217	-1.01449		C	2.32293	3.94974	-1.66939
	H	2.45292	-1.20151	-1.64828		H	2.97875	4.17349	-2.50398
	C	4.25546	-0.09742	-1.20688		C	1.82489	5.01234	-0.89529
	H	4.82869	-0.55676	-2.00608		C	0.98179	4.84555	0.1875
	C	4.87901	0.86581	-0.37524		H	0.62103	5.69698	0.75429
	C	4.19203	1.48511	0.66423		C	0.62285	3.52354	0.50667
	H	4.67303	2.2221	1.2973		C	-3.63201	-1.48714	-0.24939
	C	2.85298	1.12474	0.86888		C	-4.95236	-1.01153	-0.2629
	C	6.30556	1.21958	-0.66122		H	-5.15342	0.05114	-0.17469
	C	-0.64919	2.86773	-0.69184		C	-6.01518	-1.90453	-0.4031
	C	-0.1857	2.74803	-2.01143		H	-7.03408	-1.52994	-0.41676
	H	-0.50567	1.90891	-2.62077		C	-5.76871	-3.27347	-0.53339
	C	0.69302	3.6989	-2.52996		H	-6.59799	-3.96544	-0.64602
	H	1.05359	3.60059	-3.54927		C	-4.45637	-3.75208	-0.52445
	C	1.11051	4.77156	-1.73786		H	-4.26216	-4.81502	-0.63037
	H	1.79574	5.51018	-2.14293		C	-3.38991	-2.86372	-0.38411
	C	0.65469	4.89173	-0.42301		H	-2.37004	-3.23313	-0.38325
	H	0.98686	5.71899	0.1965		C	-2.68898	1.2244	-0.78924
	C	-0.22118	3.94153	0.10369		C	-2.41899	1.44079	-2.14964
	H	-0.55896	4.03166	1.13124		H	-1.87725	0.6904	-2.7165
	C	-3.51193	2.3275	-0.41351		C	-2.8359	2.62163	-2.76365
	C	-3.75259	3.70937	-0.45483		H	-2.62068	2.78771	-3.81476
	H	-2.93912	4.41243	-0.30846		C	-3.52372	3.58892	-2.02634
	C	-5.04097	4.18748	-0.69662		H	-3.84627	4.50831	-2.50581
	H	-5.21966	5.25775	-0.73075		C	-3.79015	3.37923	-0.67138
	C	-6.09426	3.29295	-0.90049		H	-4.31519	4.13463	-0.09498
	H	-7.09529	3.66817	-1.0911		C	-3.37252	2.2015	-0.04977
	C	-5.85986	1.9162	-0.86432		H	-3.56984	2.05231	1.00708
	H	-6.67606	1.21901	-1.02706					
	C	-4.57386	1.43255	-0.6231					
	H	-4.39067	0.36357	-0.60039					

Table S6. UV/Vis absorption data of the compounds in CH_2Cl_2 solution (1.0×10^{-5} M).

compound	λ_{abs}/nm ($\varepsilon \times 10^4/M^{-1}\ cm^{-1}$)
HL1	229 / 5.07, 316 / 3.03
HL2	231 / 5.21, 335 / 3.55
HL3	230 / 4.88, 311 / 3.26
HL4	230 / 4.62, 317 / 3.43
ppy-Pt-L1	229 / 4.76, 256 / 3.36, 282 / 2.39, 319 / 1.50, 410 / 0.34
ppy-Pt-L2	229 / 4.37, 257 / 3.12, 283 / 2.06, 330 / 1.28, 409 / 0.40
ppy-Pt-L3	229 / 4.45, 249 / 3.14, 283 / 1.91, 315 / 1.38, 408 / 0.31
ppy-Pt-L4	230 / 4.40, 256 / 3.22, 282 / 2.23, 319 / 1.49, 411 / 0.35

Table S7. Calculated energies (eV) and energy gaps of HOMO and LUMO orbitals of complexes.

complex	**ppy-Pt-L1**	**ppy-Pt-L2**	**ppy-Pt-L3**	**ppy-Pt-L4**
HOMO	-4.994	-5.096	-5.684	-5.459
LUMO	-1.561	-1.679	-1.719	-1.703
ΔE	3.433	3.417	3.965	3.756

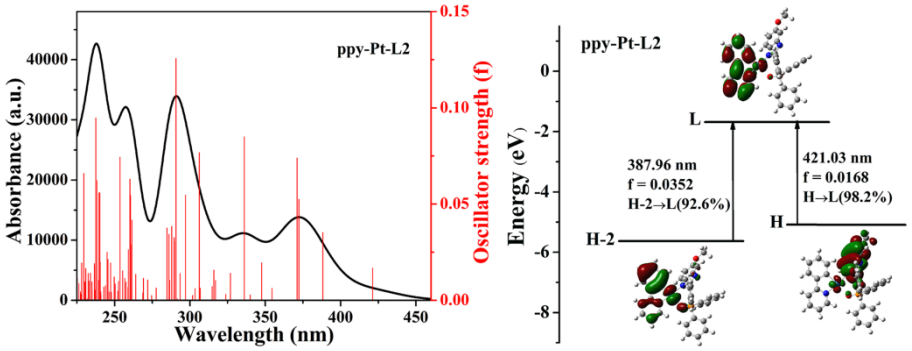

Fig. S6 The simulated absorption spectra of the **ppy-Pt-L2** (left). The calculated low-energy transitions for the **ppy-Pt-L2** and the relative frontier molecular orbitals (contributions > 25%) (right).

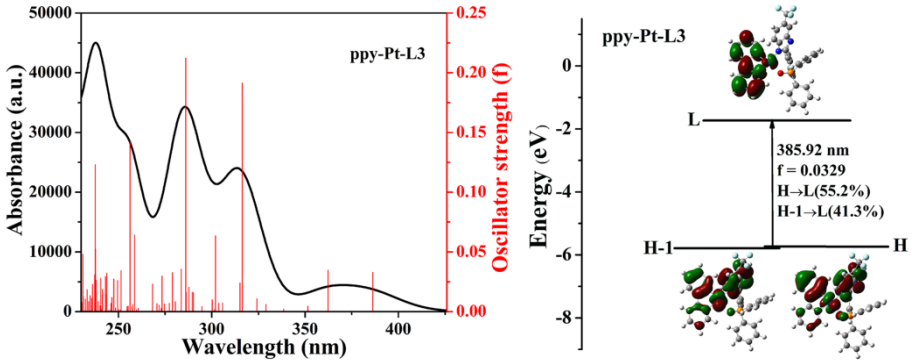

Fig. S7 The simulated absorption spectra of the **ppy-Pt-L3** (left). The calculated low-energy transitions for the **ppy-Pt-L3** and the relative frontier molecular orbitals (contributions > 25%) (right).

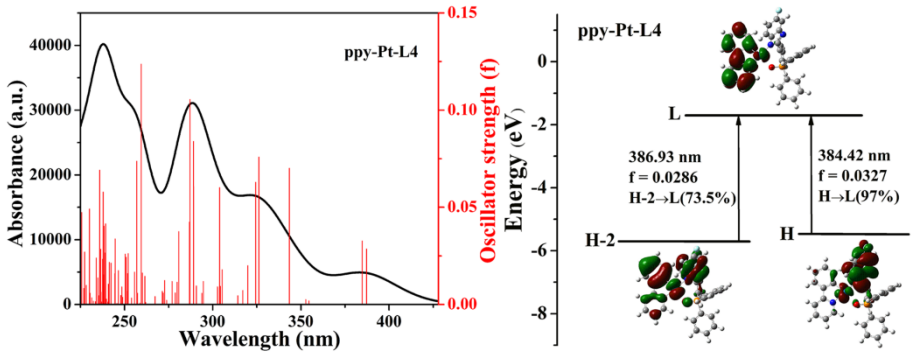

Fig. S8 The simulated absorption spectra of the **ppy-Pt-L4** (left). The calculated low-energy transitions for the **ppy-Pt-L4** and the relative frontier molecular orbitals (contributions > 25%) (right).

Table S8. Calculated low-energy (>375 nm) transitions for the complexes (λ (wavelengths) and f (Oscillator Strengths)) [a].

Complex	λ (nm)	f [a]	Contribution [b]	Assignment
ppy-Pt-L1	394.07 nm	0.0303	H→L (95.9%)	MLCT, LLCT
	391.56 nm	0.0266	H-2→L (96.4%)	MLCT, ILCT
ppy-Pt-L2	421.03 nm	0.0168	H→L (98.2%)	LLCT
	387.96 nm	0.0352	H-2→L (92.6%)	MLCT, ILCT
ppy-Pt-L3	385.92 nm	0.0329	H-1→L (41.3%), H→L(55.2%)	MLCT, ILCT, LLCT
ppy-Pt-L4	386.93 nm	0.0286	H-2→L (73.5%)	MLCT, ILCT
	384.42 nm	0.0327	H→L (97%)	MLCT, LLCT

[a] Only calculated excitation with oscillator strength f > 0.015. [b] Singly excited configurations contributing more than 25% are listed.

Table S9. Compositions of the frontier molecular orbitals involved in the low-energy (>375 nm) transitions for the complexes based on the calculations.

Complex	Moieties	HOMO-2	HOMO-1	HOMO	LUMO
ppy-Pt-L1	Pt (%)	51.0	1.4	15.5	5.9
	ppy (%)	42.8	-	2.8	91.0
	L (%)	3.3	94.5	73.7	0.6
ppy-Pt-L2	Pt (%)	50.1	8.7	5.6	5.9
	ppy (%)	44.9	1.9	-	90.7
	L (%)	1.3	97.3	93.6	-
ppy-Pt-L3	Pt (%)	3.8	34.7	37.3	5.9
	ppy (%)	-	17.7	28.9	71.8
	L (%)	93.2	42.8	31.0	0.7
ppy-Pt-L4	Pt (%)	41.0	14.7	13.5	5.9
	ppy (%)	34.4	1.6	2.3	72.9
	L (%)	22.8	71.3	69.1	-

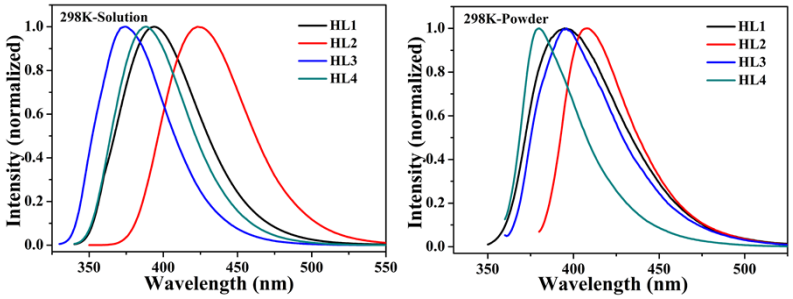

Fig. S9 Normalized emission spectra of ligands HL1-HL4 in CH_2Cl_2 solution (left) and in powder (right).

Table S10. Luminescence quantum efficiency of ligands HL1-HL4 in CH_2Cl_2 (1×10^{-5} M) solution and in powder at 298 K.

Ligand	Solution state			Solid state	
	λ_{em}/nm	τ/ns	Φ[a]	λ_{em}/nm	Φ[b]
HL1	394	1.8	30.4	395	51.3
HL2	423	3.0	45.6	408	69.4
HL3	375	1.7	26.9	396	59.4
HL4	389	1.7	36.9	380	58.1

[a] Quantum yields are measured in CH_2Cl_2 solution relative to a standard of $H_2Qn{\cdot}SO_4$ in 0.1 M aqueous H_2SO_4 (Φ = 55%).[1] [b] The Φ is measured using calibrated integrating sphere.

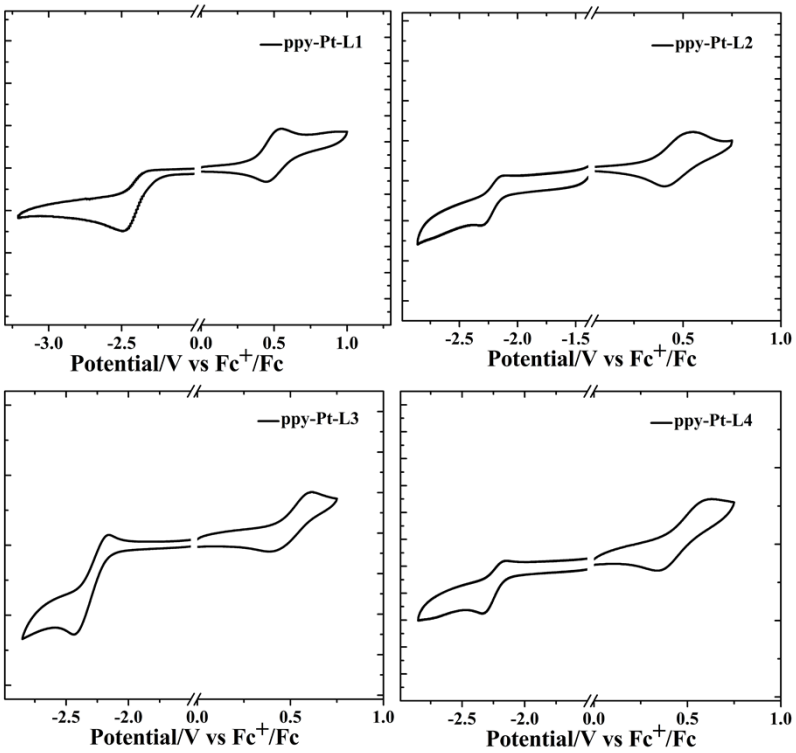

Fig. S10 Cyclic voltammograms of ppy-Pt-L complexes in CH_2Cl_2 solution in the presence of $[Bu_4N][PF_6]$ (0.1 M) at 298K.

Table S11. The characteristics of OLED devices based on **ppy-Pt-L3** and **ppy-Pt-L4**.

Dopant	Dopant level (wt%)	λ_{em} (nm)	V_{on}[a] (V)	CE_{max} (cd A^{-1})	L_{max} (cd m^{-2})	EQE_{max}(%)	CIE (x, y)[b]
ppy-Pt-L3	5	491,526,560	4.0	64.4	21220	21.1	(0.242,0.609)
ppy-Pt-L4	5	489,523,559	3.8	55.2	8788	16.8	(0.242,0.576)

[a] V_{on} = turn-on voltage. [b] Commission Internationale de L'Eclairage coordinates measured. CE, current efficiency. EQE, external quantum efficiency.

Table S12. EL performance of representative OLEDs using heteroleptic platinum(II) complexes based on ppy derivatives.

Device	λ_{EL} (nm)	EQE_{max}	CE_{max} (cd A^{-1})	L_{max} (cd m^{-2})	Reference
ppy-Pt-L3	491,526,560	21.1	64.4	21220	This work[c]
(dfppy-DC)Pt(acac)	488	17.79	58.31	5463	2[b]
Pt1	495,523	18.0	55.6	31494	3[c]
1	584	18.6	50.0	28295	4[c]
Pt-BppyA	~530	20.9	64.8	-[a]	5[c]
(4tfmppy)Pt(dptp)	~506	26.9	88.5	39871	6[c]

[a] Not reported. [b] Solution-processed device. [c] Vacuum-deposited device.

Notes and references

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