Supporting information for:

New discovery in crystallography: correlation of terahertz time-domain spectra with crystal structures, and photoluminescence properties of mononuclear/ binuclear diimine-Cu (I)-phosphine complexes

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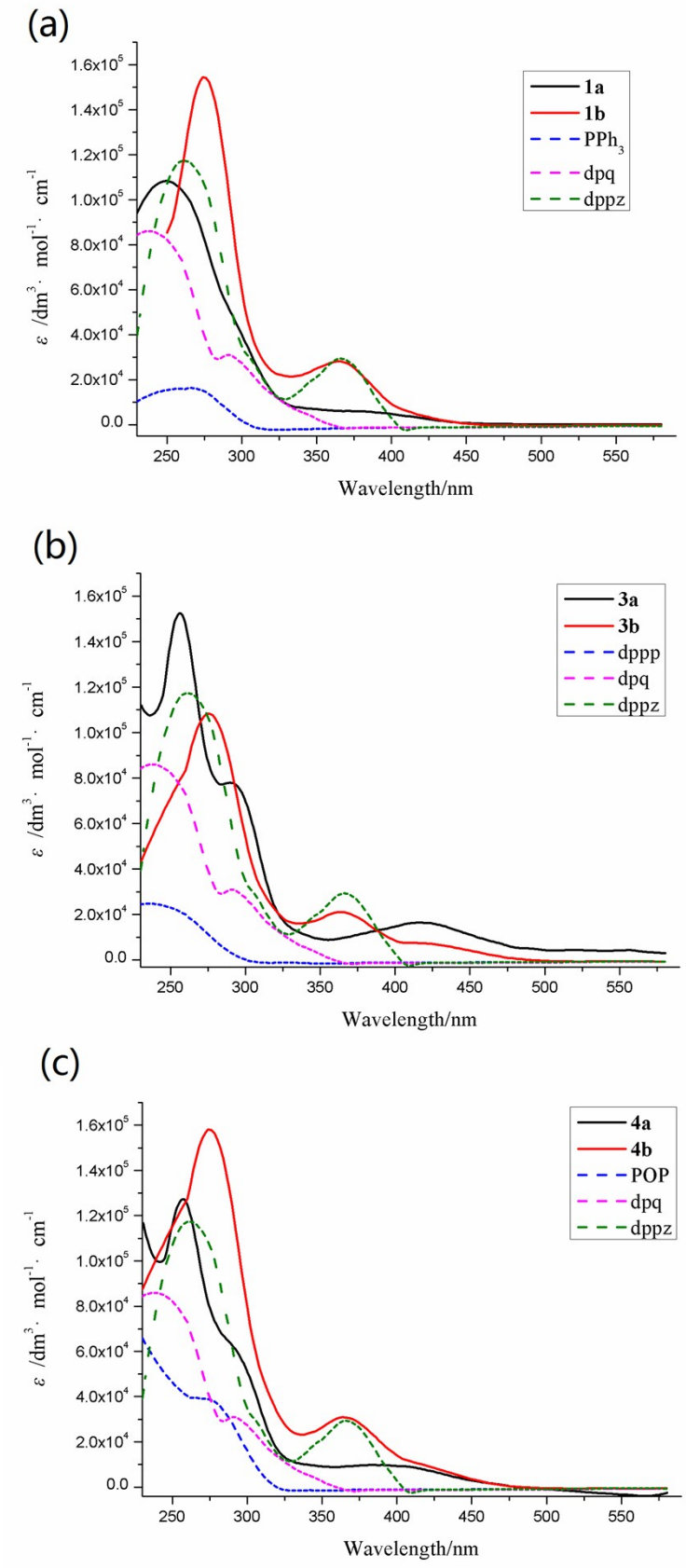

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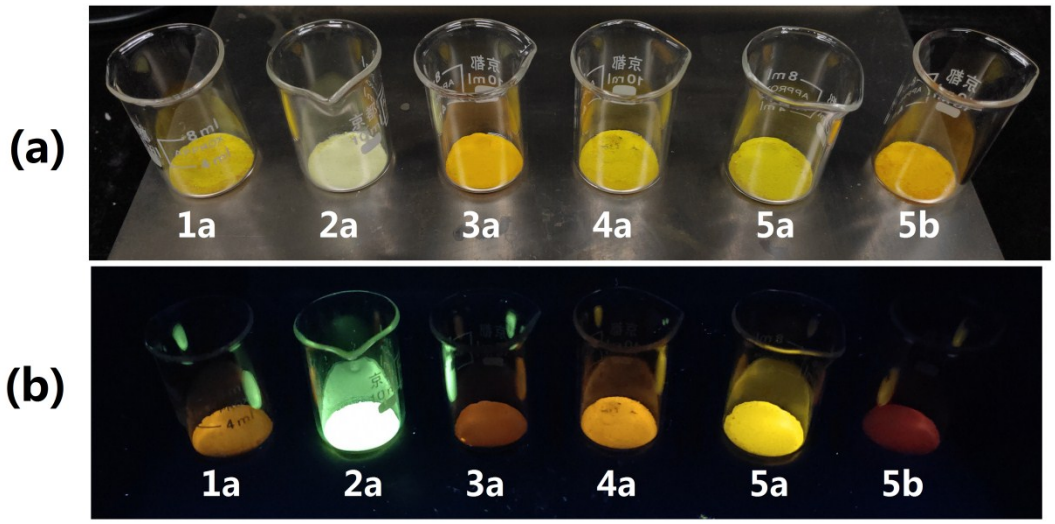

Fig. S2 Images of **1a-5a**, **5b** (a) before and (b) after under 365 nm UV-light irradiation.

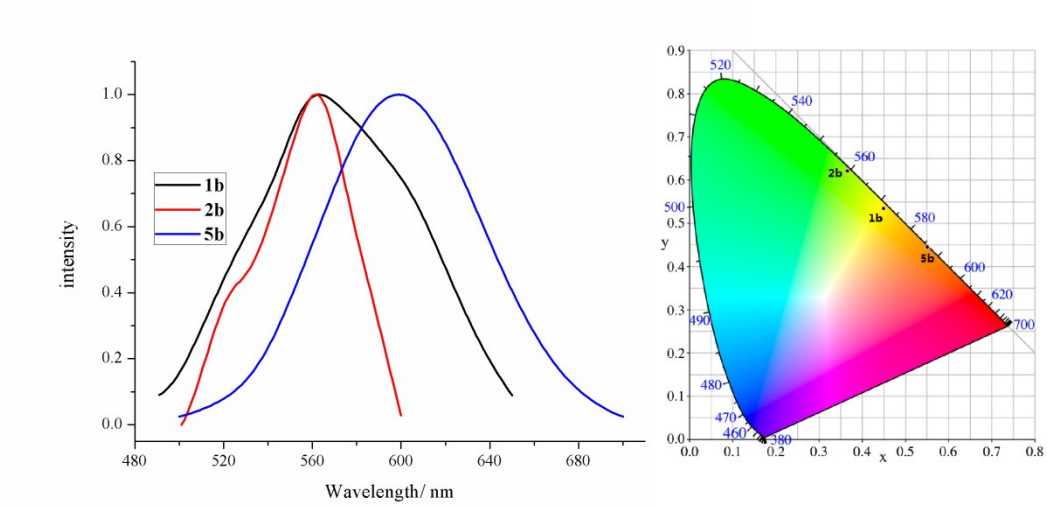

Fig. S3 Emission spectra of complexes **1b**, **2b** and **5b** in the solid states at ambient temperature.

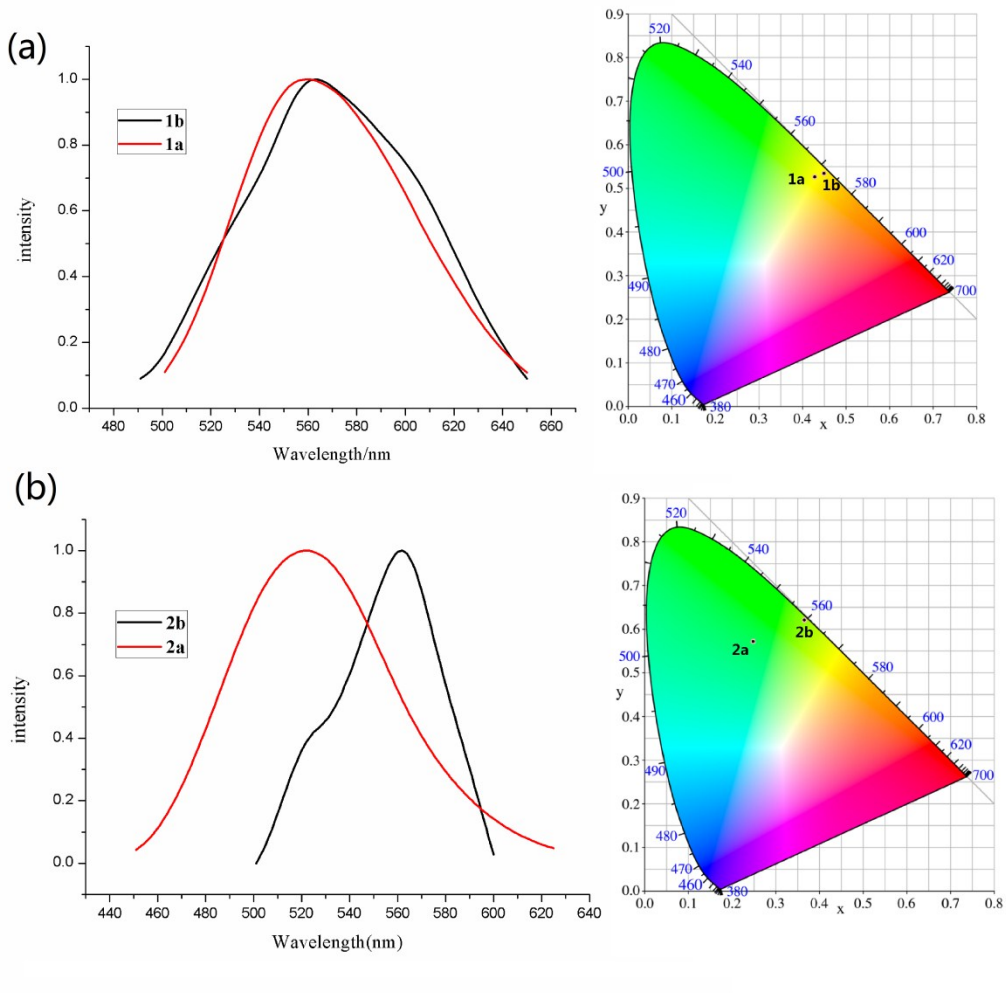

Fig. S4 Emission spectra of (a) **1a**, **1b**, (b) **2a, 2b** in the solid states at ambient temperature.

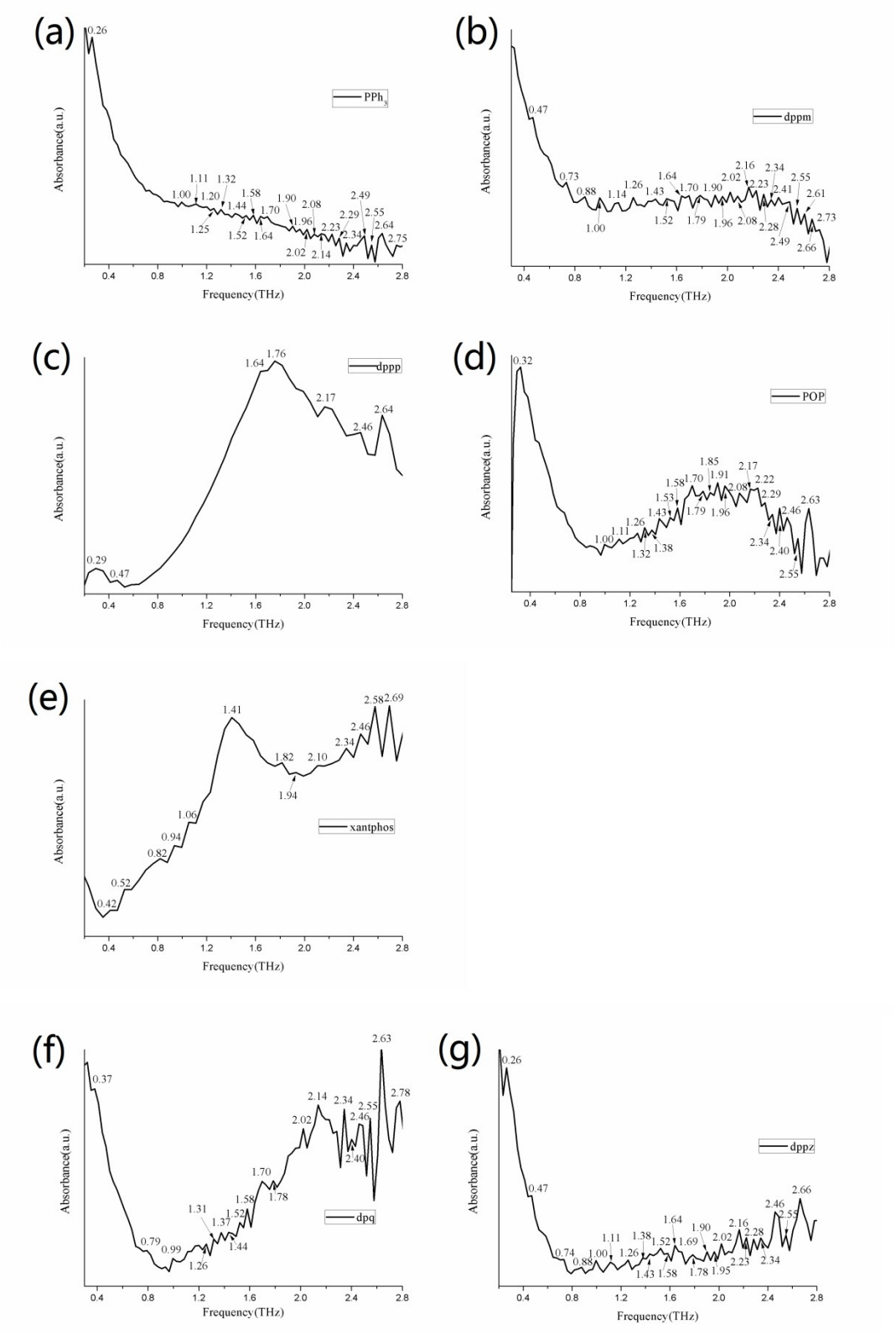

Fig. S5 THz absorption spectra of the corresponding ligands: (a) PPh_3, (b) dppm, (c) dppp, (d) POP , (e)xantphos; (f) dpq, (g) dppz at ambient temperature.

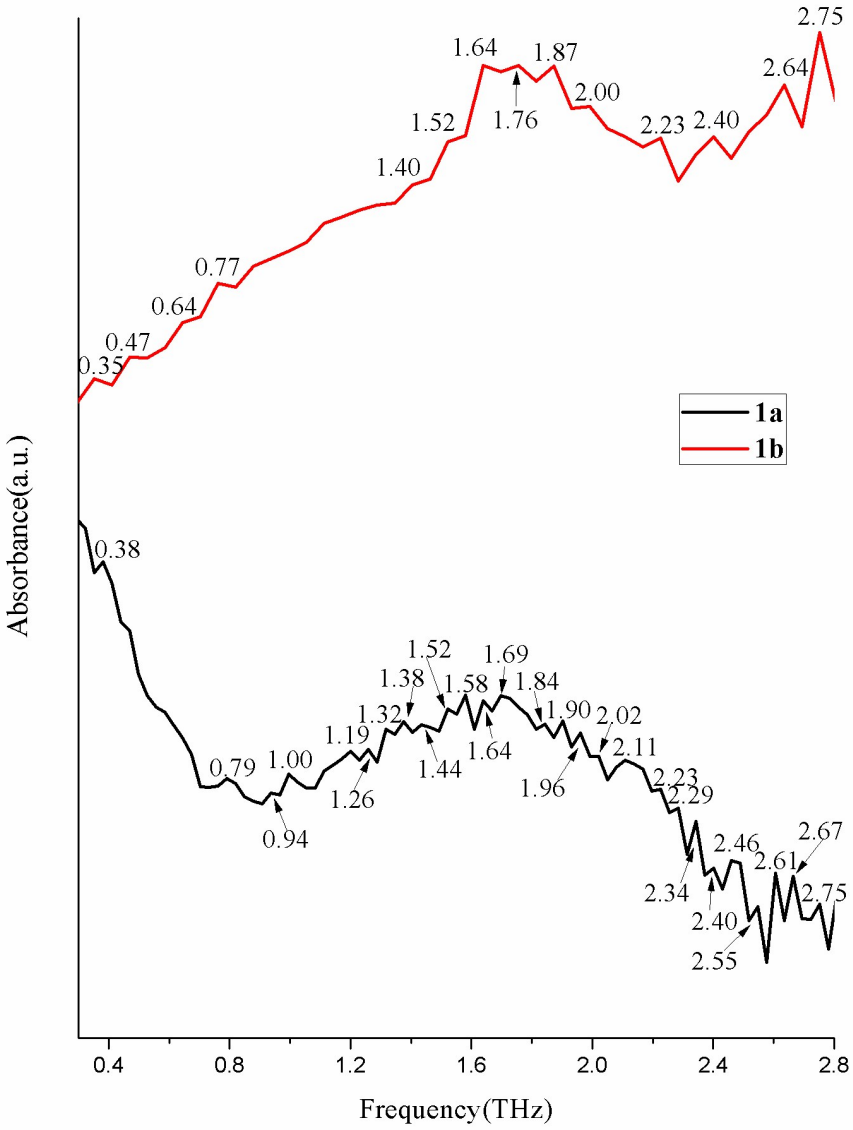

Fig. S6 THz absorption spectra of complex **1a** and **1b** at ambient temperature.

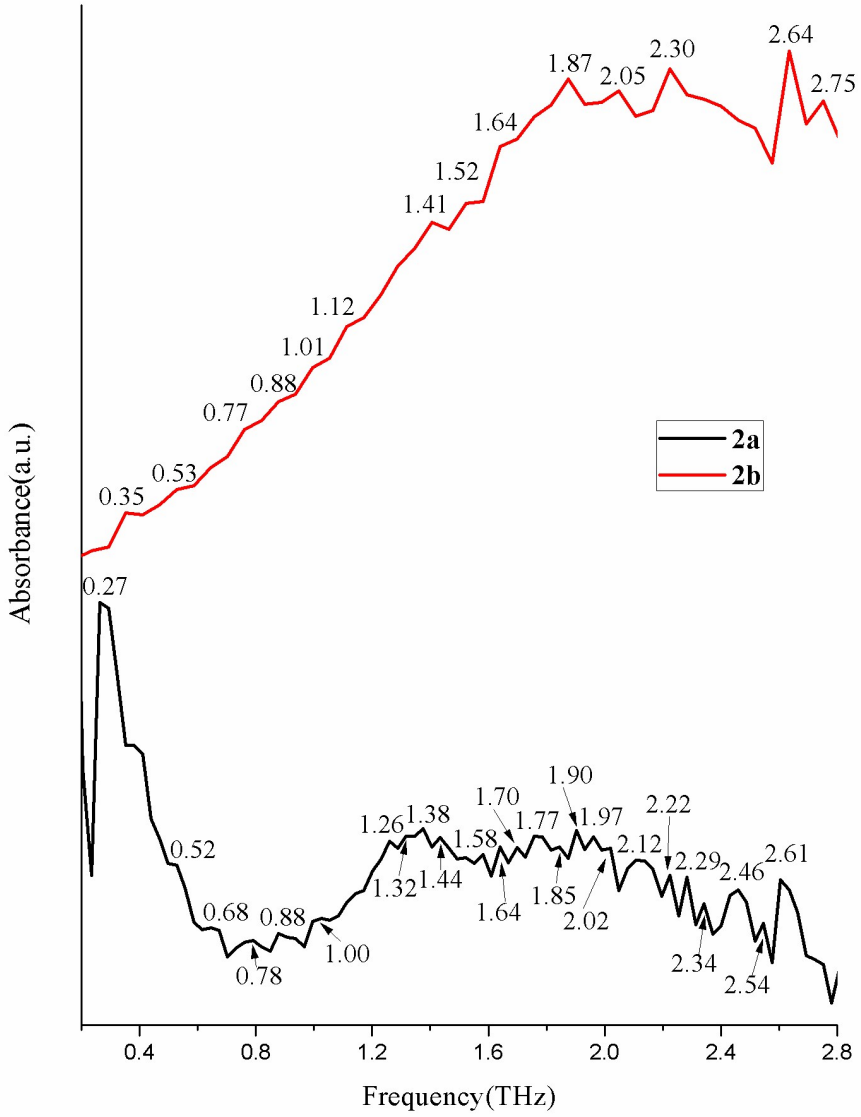

Fig. S7 THz absorption spectra of complex **2a** and **2b** at ambient temperature.

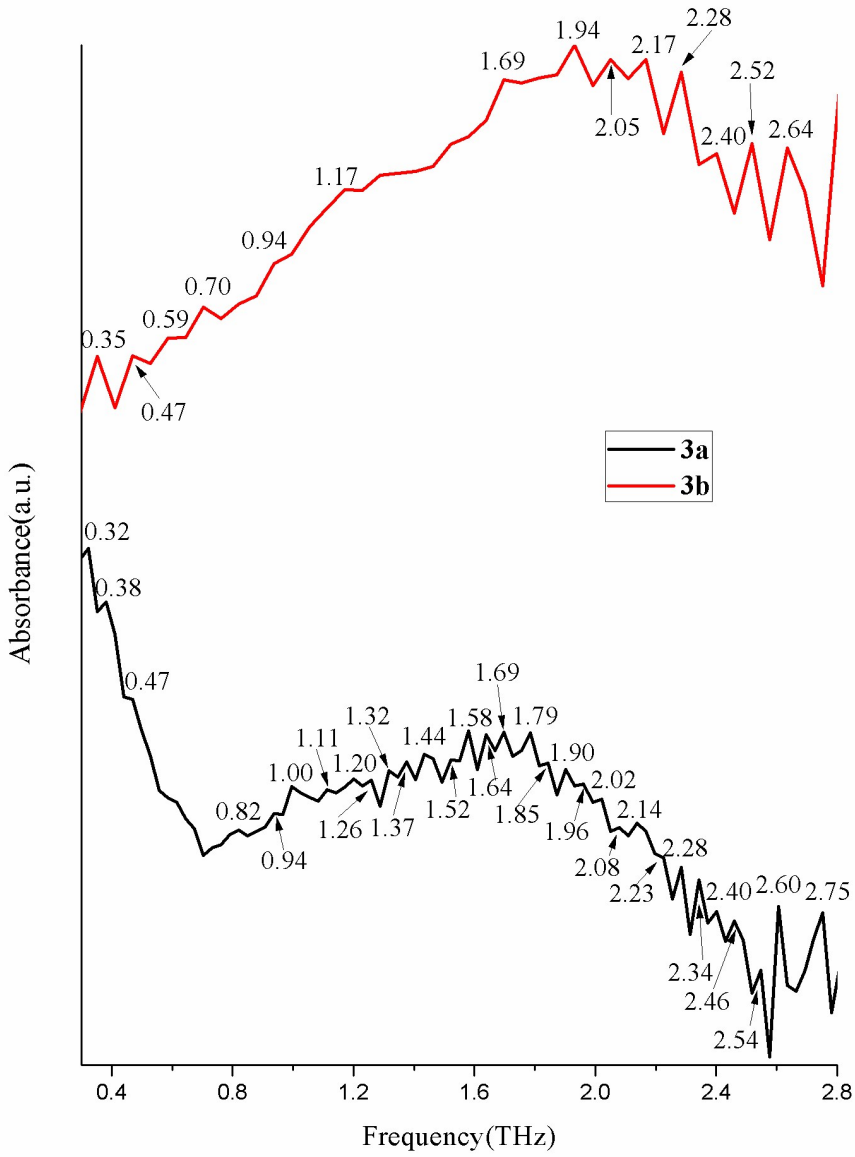

Fig. S8 THz absorption spectra of complex **3a** and **3b** at ambient temperature.

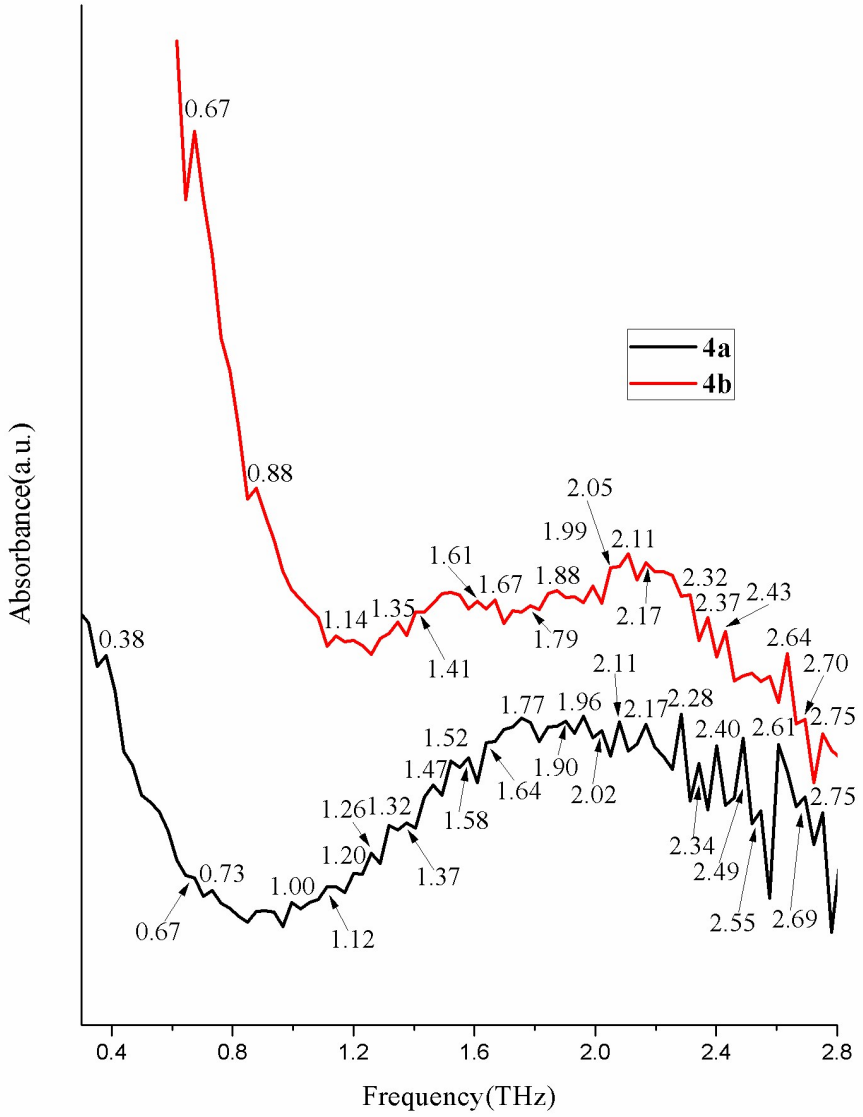

Fig. S9 THz absorption spectra of complex **4a** and **4b** at ambient temperature.

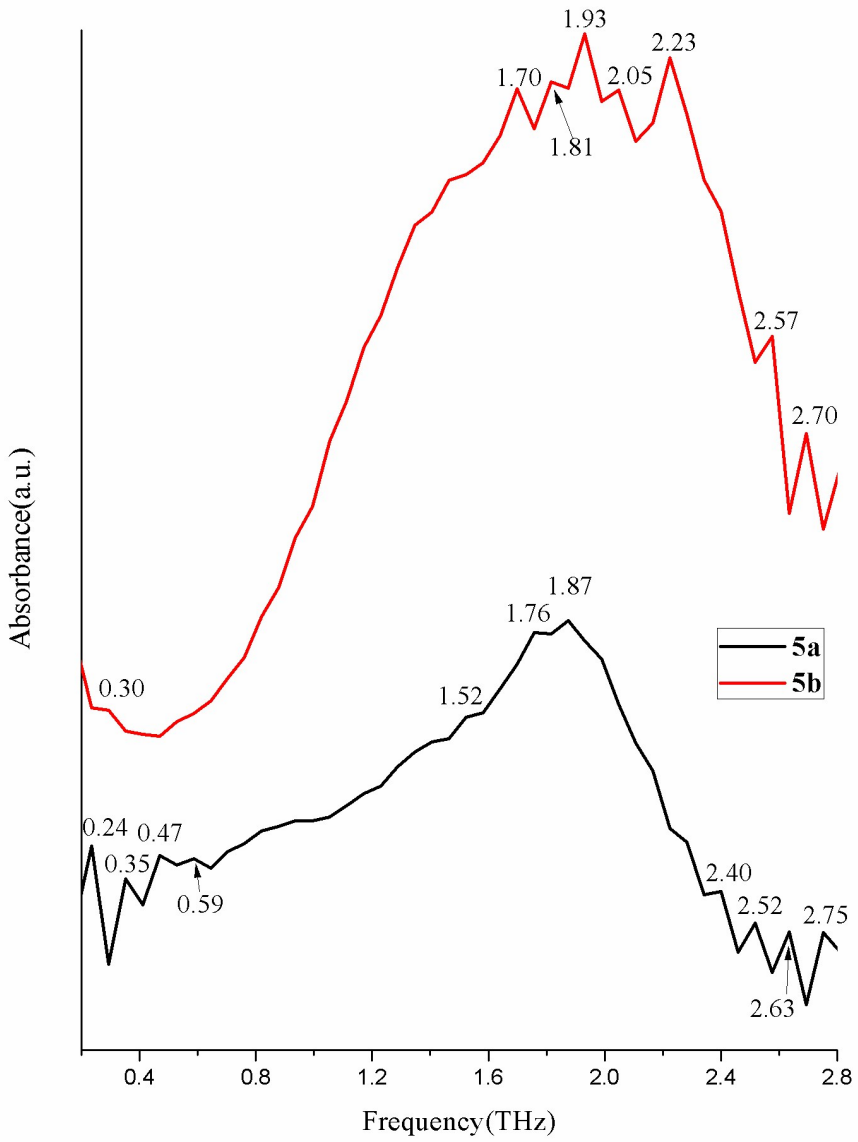

Fig. S10 THz absorption spectra of complex **5a** and **5b** at ambient temperature.

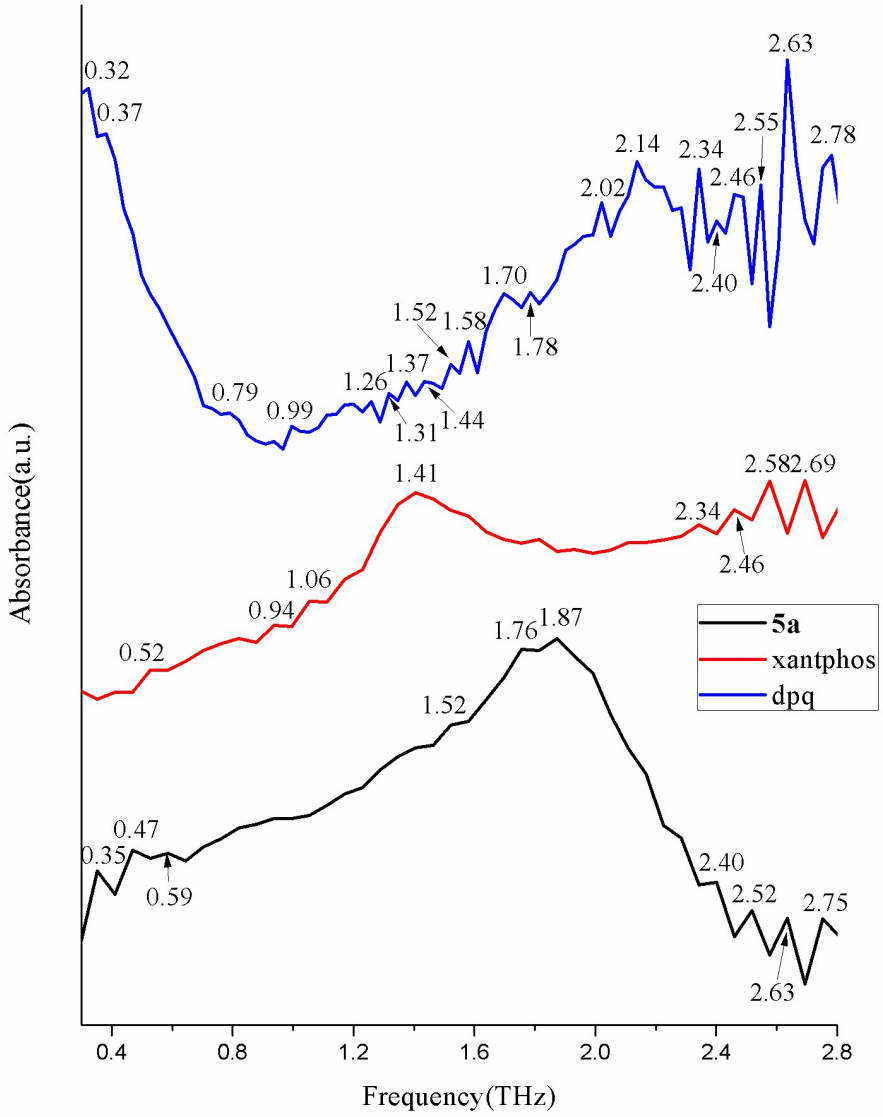

Fig. S11 THz absorption spectra of complex **5a** and the corresponding ligands at ambient temperature.

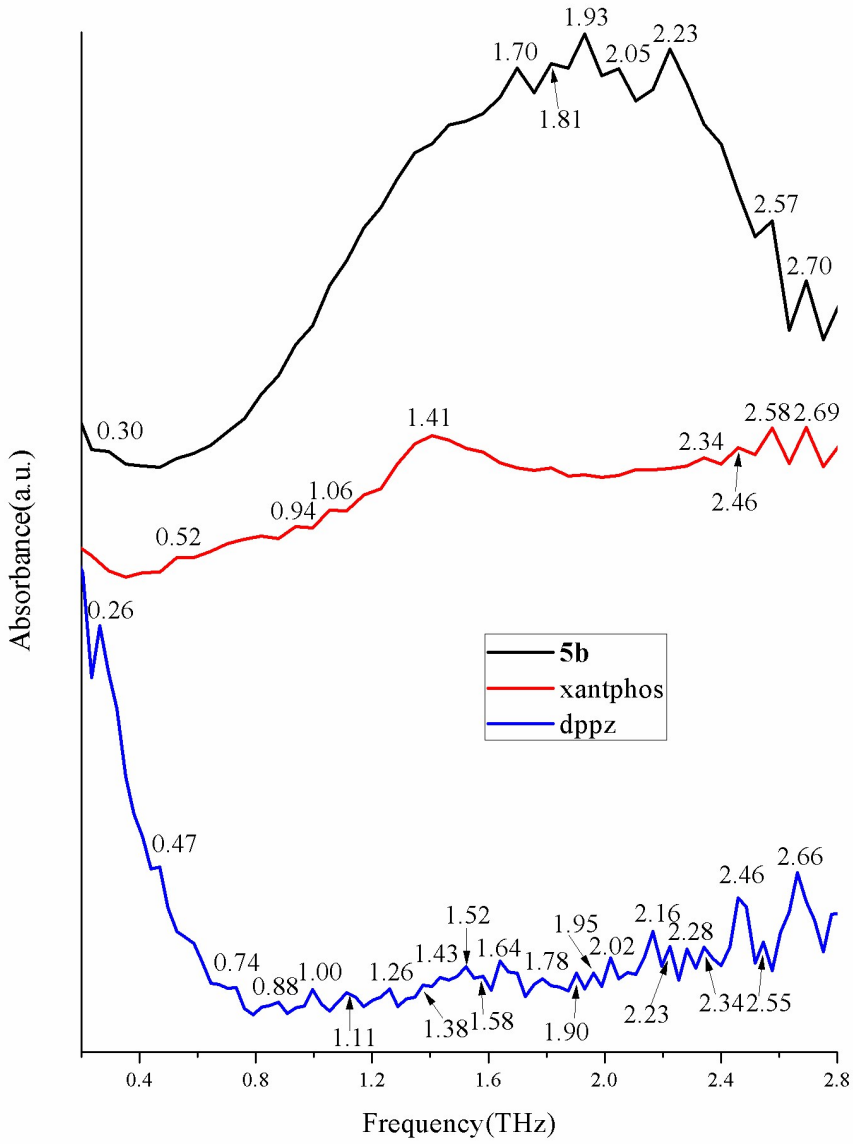

Fig. S12 THz absorption spectra of complex **5b** and the corresponding ligands at ambient temperature.

Table S1 Selected bond length (Å) and angles (°) for complexes **1a**, **b**-**5a**, **b**

Complex **1a**			
Cu(1)-P(1)	2.2624(15)	P(2)-Cu(1)-P(1)	116.10(6)
Cu(1)-P(2)	2.2531(15)	N(2)-Cu(1)-P(1)	118.89(12)
Cu(1)-N(1)	2.123(4)	N(2)-Cu(1)-P(2)	116.06(13)
Cu(1)-N(2)	2.056(4)	N(2)-Cu(1)-N(1)	79.78(17)
		N(1)-Cu(1)-P(1)	108.54(12)
		N(1)-Cu(1)-P(2)	110.87(12)
Complex **1b**			
Cu(1)-P(1)	2.2562(5)	P(1)-Cu(1)-P(2)	127.11(2)
Cu(1)-P(2)	2.2709(5)	N(1)-Cu(1)-P(1)	114.96(4)
Cu(1)-N(1)	2.0914(15)	N(1)-Cu(1)-P(2)	105.97(4)
Cu(1)-N(2)	2.0951(15)	N(1)-Cu(1)-N(2)	80.06(6)
		N(2)-Cu(1)-P(1)	111.22(4)
		N(2)-Cu(1)-P(2)	107.48(4)
Complex **2a**			
Cu(1)-N(1)	2.088(4)	N(1)-Cu(1)-N(2)	79.25(14)
Cu(1)-N(2)	2.112(4)	N(1)-Cu(1)-P(2)	119.71(11)
Cu(1)-P(1)	2.2655(13)	N(2)-Cu(1)-P(2)	106.94(10)
Cu(1)-P(2)	2.2269(13)	N(1)-Cu(1)-P(1)	102.44(11)
		N(2)-Cu(1)-P(1)	97.22(11)
		P(2)-Cu(1)-P(1)	134.20(5)
Complex **2b**			
Cu(1)-N(1)	2.175(12)	N(2)-Cu(1)-N(1)	77.0(5)
Cu(1)-N(2)	2.121(12)	N(2)-Cu(1)-P(3)	122.7(4)
Cu(1)-P(1)	2.317(4)	N(1)-Cu(1)-P(3)	109.3(4)
Cu(1)-P(3)	2.263(5)	N(2)-Cu(1)-P(1)	101.4(4)
Cu(2)-N(5)	2.199(12)	N(1)-Cu(1)-P(1)	97.7(3)
Cu(2)-N(6)	2.089(13)	P(3)-Cu(1)-P(1)	131.88(16)
Cu(2)-P(2)	2.252(5)	N(6)-Cu(2)-N(5)	79.6(5)
Cu(2)-P(4)	2.304(5)	N(6)-Cu(2)-P(2)	122.0(4)
		N(5)-Cu(2)-P(2)	106.1(4)
		N(6)-Cu(2)-P(4)	102.5(4)
		N(5)-Cu(2)-P(4)	99.7(3)
		P(2)-Cu(2)-P4)	131.43(17)
Complex **3a**			
Cu(1)-N(1)	2.048(3)	N(1)-Cu(1)-N(2)	80.33(12)
Cu(1)-N(2)	2.081(3)	N(1)-Cu(1)-P(2)	116.60(8)
Cu(1)-P(1)	2.2497(11)	N(2)-Cu(1)-P(2)	127.26(8)
Cu(1)-P(2)	2.2346(10)	N(1)-Cu(1)-P(1)	116.79(8)
		N(2)-Cu(1)-P(1)	113.78(9)
		P(2)-Cu(1)-P(1)	102.20(4)
Complex **3b**			

Cu(1)-P(1)	2.239(2)	P(1)-Cu(1)-P(2)	104.54(11)
Cu(1)-P(2)	2.239(2)	N(2)-Cu(1)-P(1)	119.06(18)
Cu(1)-N(1)	2.060(6)	N(2)-Cu(1)-P(2)	110.00(19)
Cu(1)-N(2)	2.088(6)	N(2)-Cu(1)-N(1)	80.5(2)
		N(1)-Cu(1)-P(1)	124.2(2)
		N(1)-Cu(1)-P(2)	117.0(2)
Complex **4a**			
Cu(1)-P(1)	2.2654(9)	P(2)-Cu(1)-P(1)	113.32(3)
Cu(1)-P(2)	2.2405(9)	N(1)-Cu(1)-P(2)	125.34(8)
Cu(1)-N(1)	2.062(3)	N(1)-Cu(1)-P(1)	111.83(8)
Cu(1)-N(2)	2.092(3)	N(1)-Cu(1)-N(2)	80.41(12)
		N(2)-Cu(1)-P(2)	112.66(9)
		N(2)-Cu(1)-P(1)	107.56(9)
Complex **4b**			
Cu(1)-P(1)	2.2885(7)	P(2)-Cu(1)-P(1)	113.40(3)
Cu(1)-P(2)	2.2308(7)	N(1)-Cu(1)-P(1)	110.83(6)
Cu(1)-N(1)	2.063(2)	N(1)-Cu(1)-P(2)	125.87(6)
Cu(1)-N(2)	2.093(2)	N(1)-Cu(1)-N(2)	80.44(8)
		N(2)-Cu(1)-P(1)	100.76(6)
		N(2)-Cu(1)-P(2)	118.96(6)
Complex **5a**			
Cu(1)-P(1)	2.2384(11)	P(1)-Cu(1)-P(2)	120.01(4)
Cu(1)-P(2)	2.2611(11)	N(1)-Cu(1)-P(1)	109.22(10)
Cu(1)-N(1)	2.086(3)	N(1)-Cu(1)-P(2)	109.63(10)
Cu(1)-N(2)	2.059(3)	N(2)-Cu(1)-P(1)	120.68(10)
		N(2)-Cu(1)-P(2)	109.03(10)
		N(2)-Cu(1)-N(1)	81.10(14)
Complex **5b**			
Cu(1)-N(1)	2.062(2)	N(1)-Cu(1)-N(2)	80.19(16)
Cu(1)-N(2)	2.081(4)	N(1)-Cu(1)-P(2)	112.92(11)
Cu(1)-P(1)	2.2793(15)	N(2)-Cu(1)-P(2)	125.87(12)
Cu(1)-P(2)	2.2217(14)	N(1)-Cu(1)-P(1)	103.92(11)
		N(2)-Cu(1)-P(1)	101.12(12)
		P(2)-Cu(1)-P(1)	123.28(6)

Table S2 The excitation and emission data of the related ligands in the solid state at ambient temperature

Ligands		Excitation (nm)	Emission (nm)
P or P^P	PPh_3	363	423
	dppm	341	382
	dppp	356	421
	POP	322	431
	xantphos	387	445
N^N	dpq	382	419
	dppz	370	458

Table S3 Energy, oscillator strength and major contribution of the calculated transitions for complexes **2a**, **b** and **5a**, **b**

Excited state	Energy / eV (/ nm)	Oscillator strength	Major contribution (%)
2a absorption	4.9264 (251.68)	0.3125	**HOMO-31→LUMO+3 (18.50)** HOMO-2 → LUMO+2 (3.94) HOMO-2 → LUMO+3 (4.11) HOMO-2 → LUMO+5 (2.70) HOMO-2 → LUMO+3 (3.82) HOMO-2 → LUMO+4 (10.89) HOMO-23 → LUMO+4 (3.54) HOMO-4 → LUMO+12 (2.36) HOMO-2 → LUMO+18 (2.15) HOMO-1 → LUMO+20 (5.15) HOMO → LUMO+21 (6.13)
2a emission	2.7541 (450.18)	0.1703	HOMO-5 → LUMO+1 (8.41) HOMO-4 → LUMO (19.16) HOMO-3 → LUMO+1 (27.04) **HOMO-2 → LUMO (35.42)** HOMO-1 → LUMO+1 (5.43)
2b absorption	4.1981 (295.34)	0.5710	HOMO-20 → LUMO+3 (2.47) HOMO-18 → LUMO (2.66) HOMO-17 → LUMO (2.27) HOMO-15 → LUMO+2 (5.92) HOMO-13 → LUMO+1 (9.09) HOMO-13 → LUMO+3 (7.96) HOMO-12 → LUMO+1 (2.24) HOMO-11 → LUMO (2.15) HOMO-9 → LUMO (3.83) HOMO-9 → LUMO+2 (11.16) HOMO-8 → LUMO+1 (2.82) HOMO-8 → LUMO+3 (5.28) HOMO-6 → LUMO+4 (2.20) **HOMO-5 → LUMO+5 (11.80)** HOMO-2 → LUMO+6 (5.72) HOMO-1 → LUMO+7 (3.21)
2b absorption	3.6112 (343.33)	0.0740	**HOMO-9 → LUMO (18.79)** HOMO-8 → LUMO+1 (18.77) HOMO-7 → LUMO+3 (2.68) HOMO-6 → LUMO+2 (4.90) HOMO-6 → LUMO+4 (12.38) HOMO-5 → LUMO+3 (2.87) HOMO-5 → LUMO+5 (17.95)

			HOMO-4 → LUMO+4 (10.62) HOMO-3 → LUMO+5 (2.07) HOMO → LUMO+4 (2.95)
2b emission	2.5973 (477.35)	0.1017	HOMO-4 → LUMO (13.87) HOMO-3 → LUMO (24.18) HOMO-2 → LUMO (16.43) **HOMO-1 → LUMO (32.37)** HOMO → LUMO+2 (3.37)
5a absorption	4.8713 (254.52)	0.3510	HOMO-19 → LUMO (23.96) HOMO-19 → LUMO+1 (4.57) HOMO-19 → LUMO+2 (6.69) HOMO-18 → LUMO (3.53) **HOMO-18 → LUMO+2 (30.73)** HOMO-1 → LUMO+11 (2.09) HOMO → LUMO+8 (2.12) HOMO → LUMO+14 (2.56)
5a emission	2.5011 (495.72)	0.0858	HOMO-4 → LUMO (2.56) **HOMO-2 → LUMO (88.80)** HOMO → LUMO (2.61)
5b absorption	4.3565 (284.60)	0.5869	HOMO-16 → LUMO+1 (9.13) HOMO-15 → LUMO (7.71) HOMO-12 → LUMO (5.67) HOMO-10 → LUMO+2 (5.71) HOMO-8 → LUMO+2 (3.92) **HOMO-4 → LUMO+2 (33.98)** HOMO-1 → LUMO+5 (12.51) HOMO → LUMO+9 (5.03)
5b absorption	3.6451 (340.14)	0.0765	HOMO-15 → LUMO (5.26) HOMO-13 → LUMO (3.92) **HOMO-12 → LUMO (32.81)** HOMO-10 → LUMO (20.80) HOMO-8 → LUMO (5.17) HOMO-4 → LUMO+2 (27.06)
5b emission	2.8059 (441.87)	0.0514	HOMO-4 → LUMO (13.42) HOMO-4 → LUMO+1 (7.14) HOMO-2 → LUMO (6.63) **HOMO-2 → LUMO+1 (64.83)** HOMO → LUMO+1 (2.69)
5b emission	2.4397 (508.20)	0.0302	**HOMO-2 → LUMO (88.88)** HOMO-2 → LUMO+1 (7.77)

Table S4 THz spectral data for ligands at ambient temperature

Ligands	Terahertz spectra peaks (THz)											
PPh_3	0.26	1.00	1.11	1.20	1.25	1.32	1.44	1.52	1.58	1.64	1.70	1.90
	1.96	2.02	2.08	2.14	2.23	2.29	2.34	2.49	2.55	2.64	2.75	
dppm	0.47	0.73	0.88	1.00	1.14	1.26	1.43	1.52	1.64	1.70	1.79	1.90
	1.96	2.02	2.08	2.16	2.23	2.28	2.34	2.41	2.49	2.55	2.61	2.66
	2.73											
dppp	0.29	0.47	1.64	1.76	2.17	2.46	2.64					
POP	0.32	1.00	1.11	1.26	1.32	1.38	1.43	1.53	1.58	1.70	1.79	1.85
	1.91	1.96	2.08	2.17	2.22	2.29	2.34	2.40	2.46	2.55	2.63	
xantphos	0.42	0.52	0.82	0.94	1.06	1.41	1.82	1.94	2.10	2.34	2.46	2.58
	2.69											
dpq	0.37	0.79	0.99	1.26	1.31	1.37	1.44	1.52	1.58	1.70	1.78	2.02
	2.14	2.34	2.40	2.46	2.55	2.63	2.78					
dppz	0.26	0.47	0.74	0.88	1.00	1.11	1.26	1.38	1.43	1.52	1.58	1.64
	1.69	1.78	1.90	1.95	2.02	2.16	2.23	2.28	2.34	2.46	2.55	2.66

Table S5 THz spectral data for complexes **1a**, **b**-**5a**, **b** at ambient temperature

Complexes	Terahertz spectra peaks (THz)											
1a	0.38	0.79	0.94	1.00	1.19	1.26	1.32	1.38	1.44	1.52	1.58	1.64
	1.69	1.84	1.90	1.96	2.02	2.11	2.23	2.29	2.34	2.40	2.46	2.55
	2.61	2.67	2.75									
1b	0.35	0.47	0.64	0.77	1.40	1.52	1.64	1.76	1.87	2.00	2.23	2.40
	2.64	2.75										
2a	0.27	0.39	0.52	0.68	0.78	0.88	1.00	1.26	1.32	1.38	1.44	1.58
	1.64	1.70	1.77	1.85	1.90	1.97	2.02	2.12	2.22	2.29	2.34	2.46
	2.54	2.61										
2b	0.35	0.53	0.77	0.88	1.01	1.12	1.41	1.52	1.64	1.87	2.05	2.30
	2.64	2.75										
3a	0.32	0.38	0.47	0.82	0.94	1.00	1.11	1.20	1.26	1.32	1.37	1.44
	1.52	1.58	1.64	1.69	1.79	1.85	1.90	1.96	2.02	2.08	2.14	2.23
	2.28	2.34	2.40	2.46	2.54	2.60	2.75					
3b	0.24	0.35	0.47	0.59	0.70	0.94	1.17	1.69	1.94	2.05	2.17	2.28
	2.40	2.52	2.64									
4a	0.38	0.67	0.73	1.00	1.12	1.20	1.26	1.32	1.37	1.47	1.52	1.58
	1.64	1.77	1.90	1.96	2.02	2.11	2.17	2.28	2.34	2.40	2.49	2.55
	2.61	2.69	2.75									
4b	0.67	0.88	1.14	1.35	1.41	1.61	1.67	1.79	1.88	1.99	2.05	2.11
	2.17	2.32	2.37	2.43	2.51	2.58	2.64	2.70	2.75			
5a	0.24	0.35	0.47	0.59	1.52	1.76	1.87	2.40	2.52	2.63	2.75	
5b	0.30	1.70	1.81	1.93	2.05	2.23	2.57	2.70				