Terahertz time-domain absorption spectra of Cu (I) complexes bearing tetraphosphine ligands: the bridge between C-H···π, π···π interactions and photoluminescence properties

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Contents

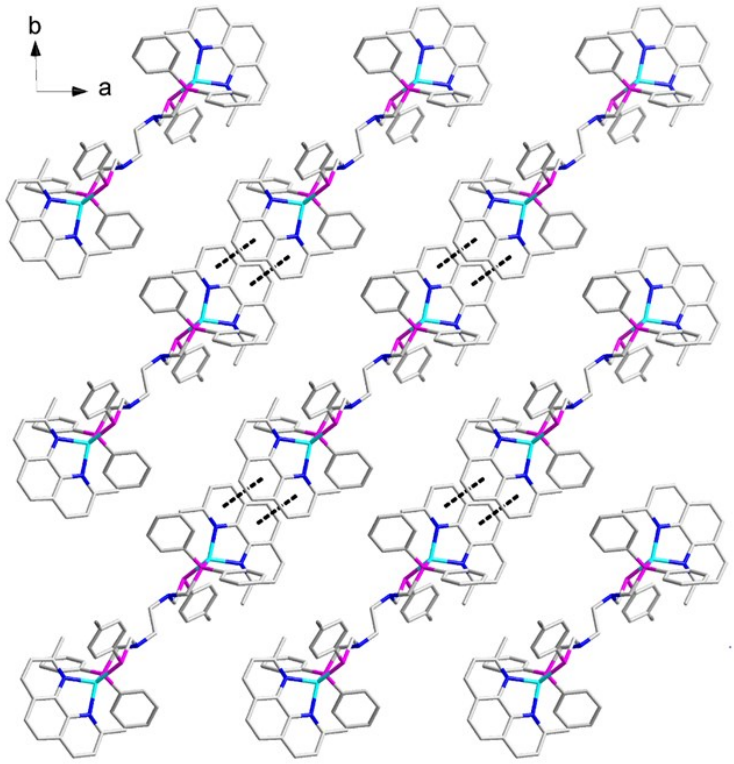


Fig. S1 The 2D mesh structure through a pair of π···π interaction along the diagonal direction of the ab axes for complex **2** (A layer).

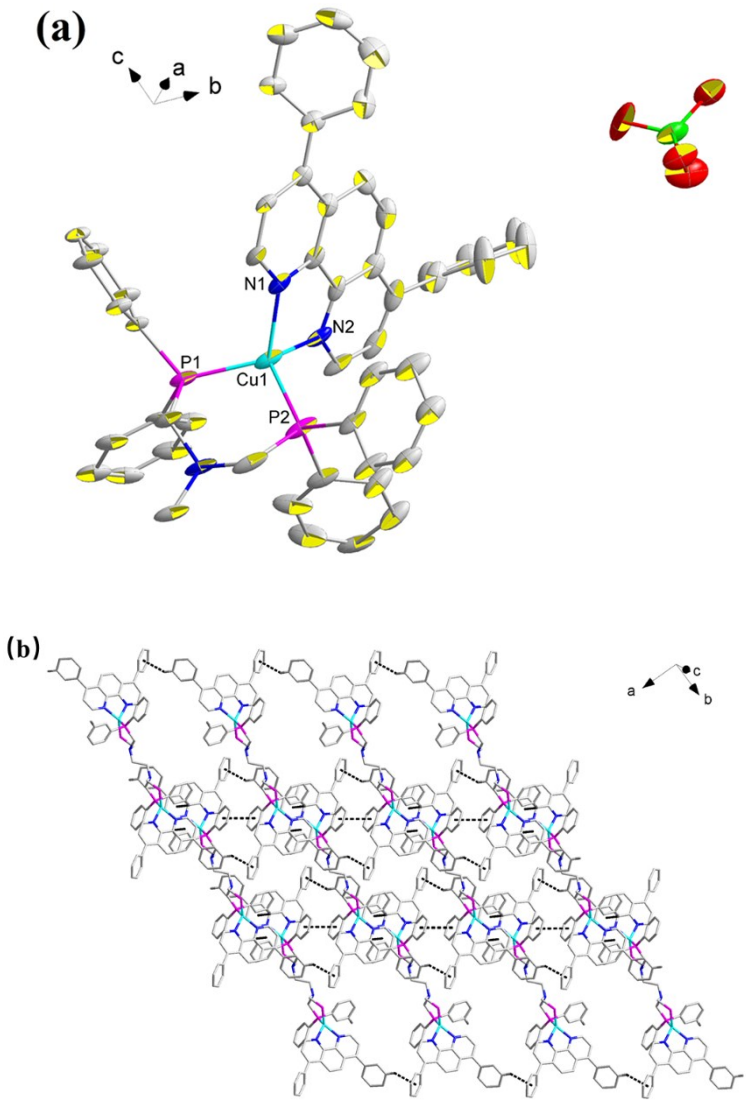


Fig. S2 Structure of complex **3**: (a) coordination environment of Cu (I). Thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms and solvent molecules are omitted for clarity. (d) The 2D mesh-like stacked structure of complex **3**. Some hydrogen atoms and benzenes are omitted for clarity.

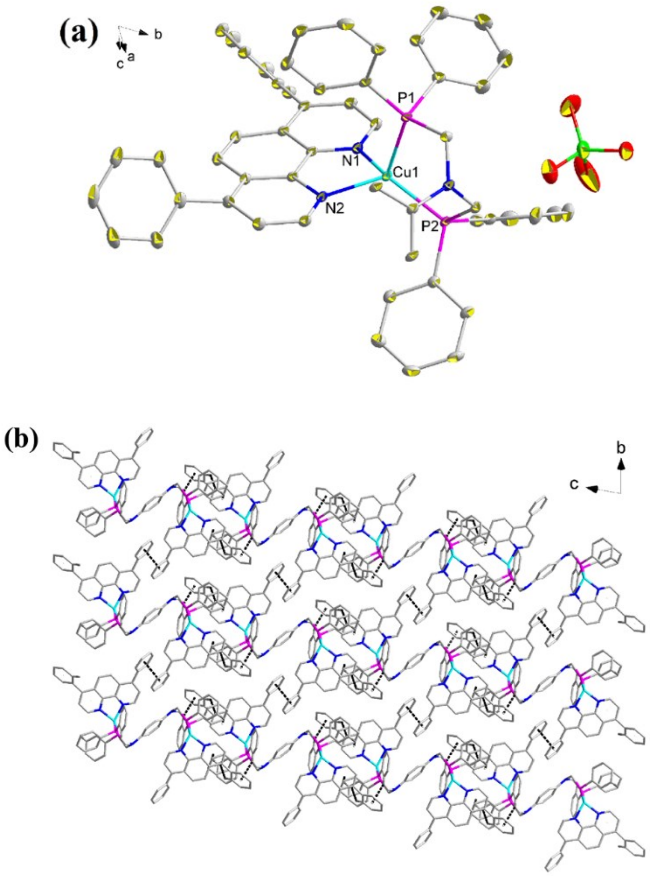
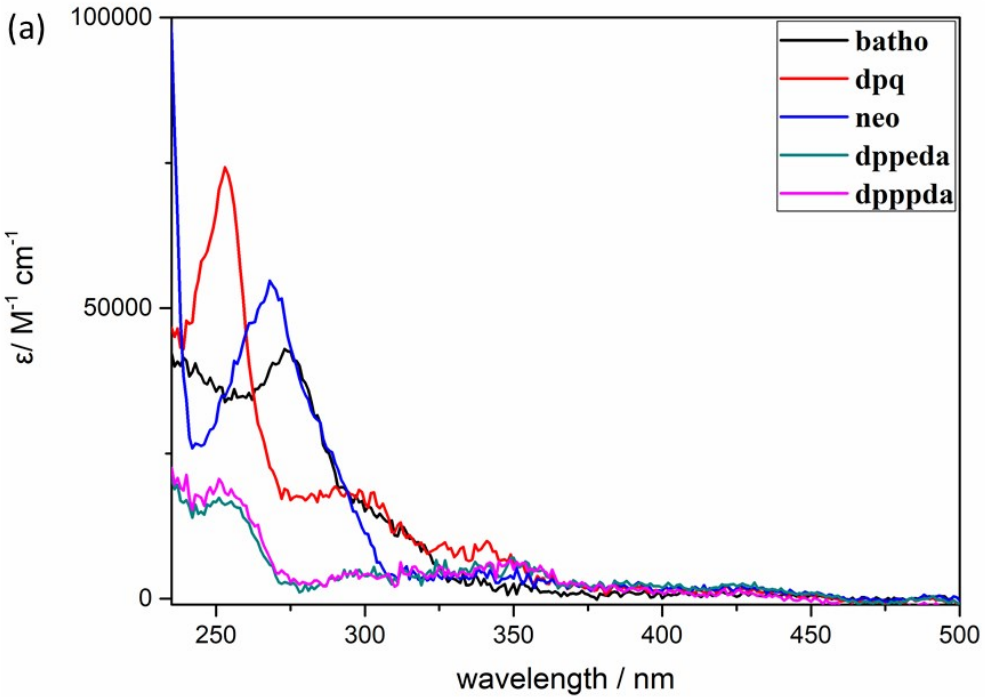


Fig. S3 Structure of complex **4**: (a) coordination environment of Cu (I). Thermal ellipsoids drawn at the 30% probability level. (d) The 3D structure of complex 4. Some hydrogen atoms and benzenes are omitted for clarity.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neo
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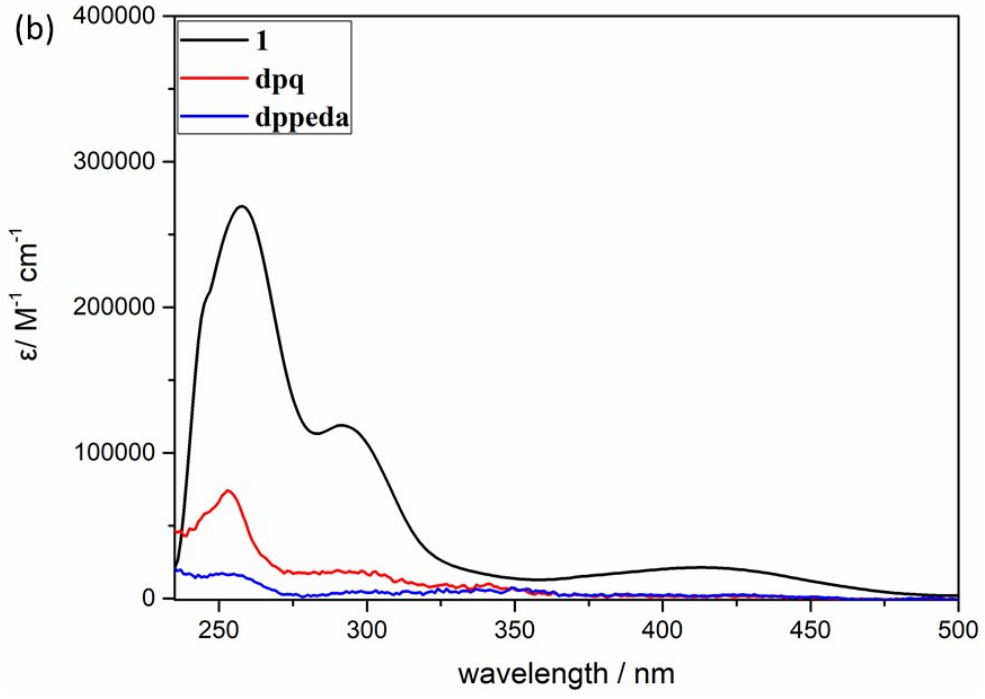
dpppda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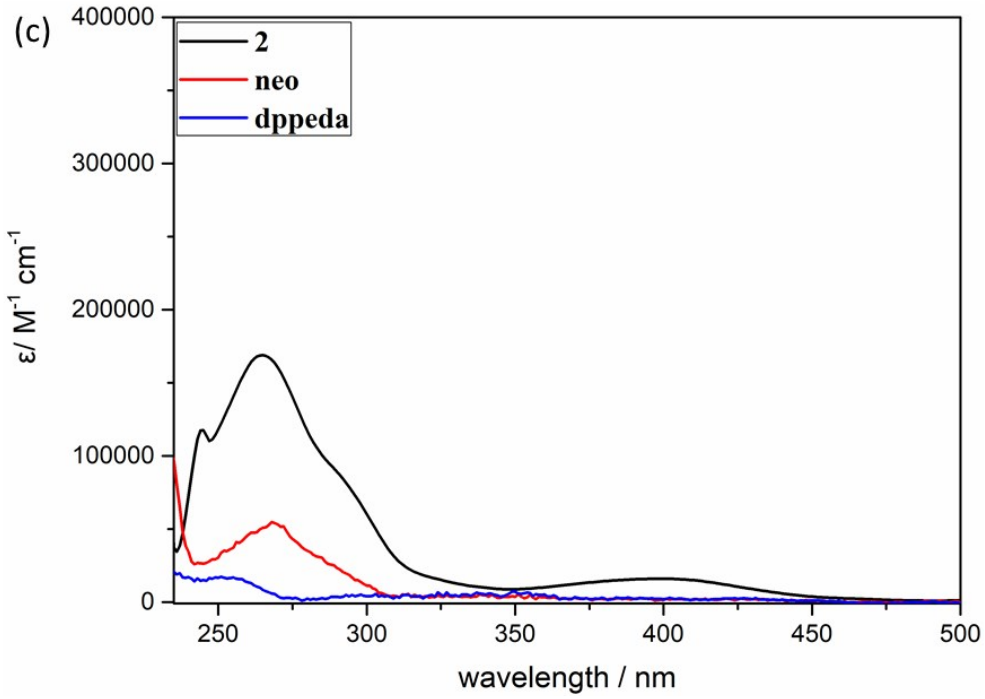
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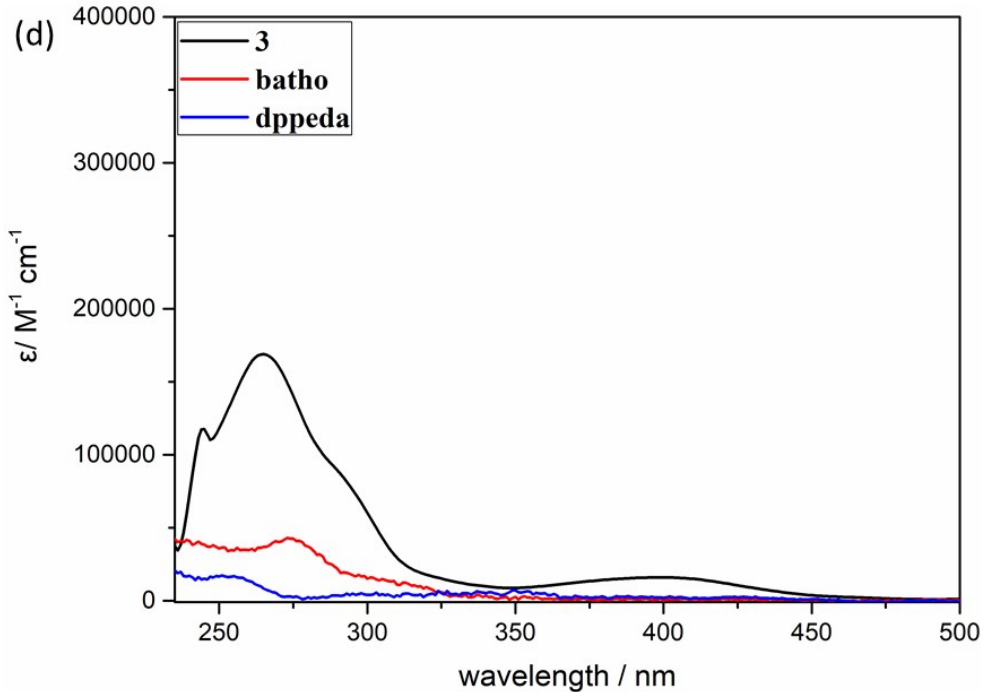
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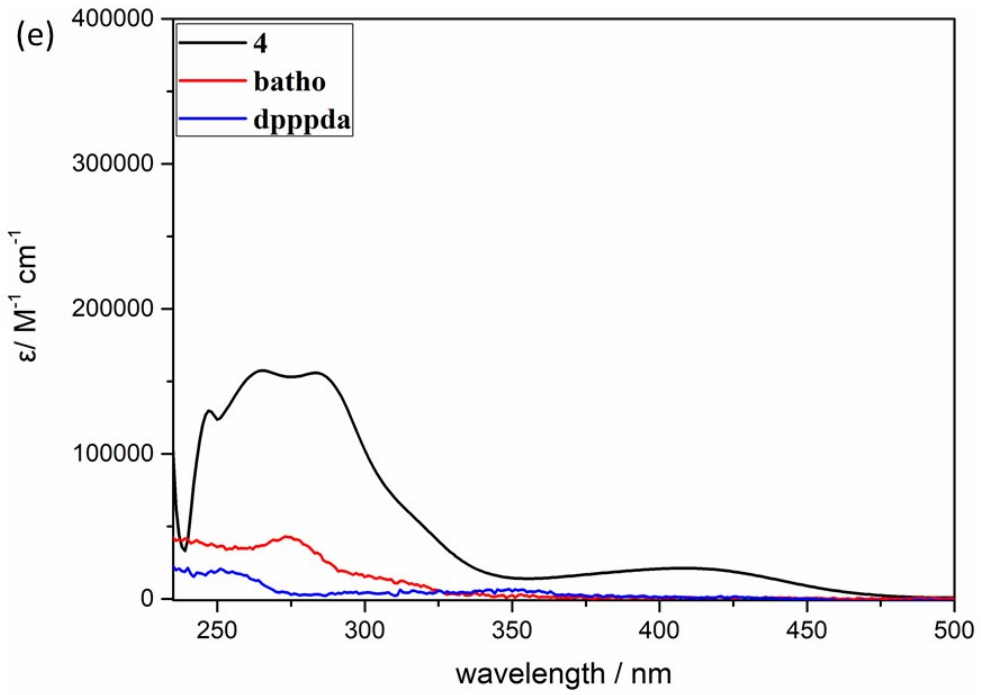


Fig. S4 (a) The UV-vis spectra of all ligands used in synthesizing complexes. (b) complex **1** and its ligands. (c) complex **2** and its ligands. (d) complex **3** and its ligands. (e) complex **4** and its ligands.

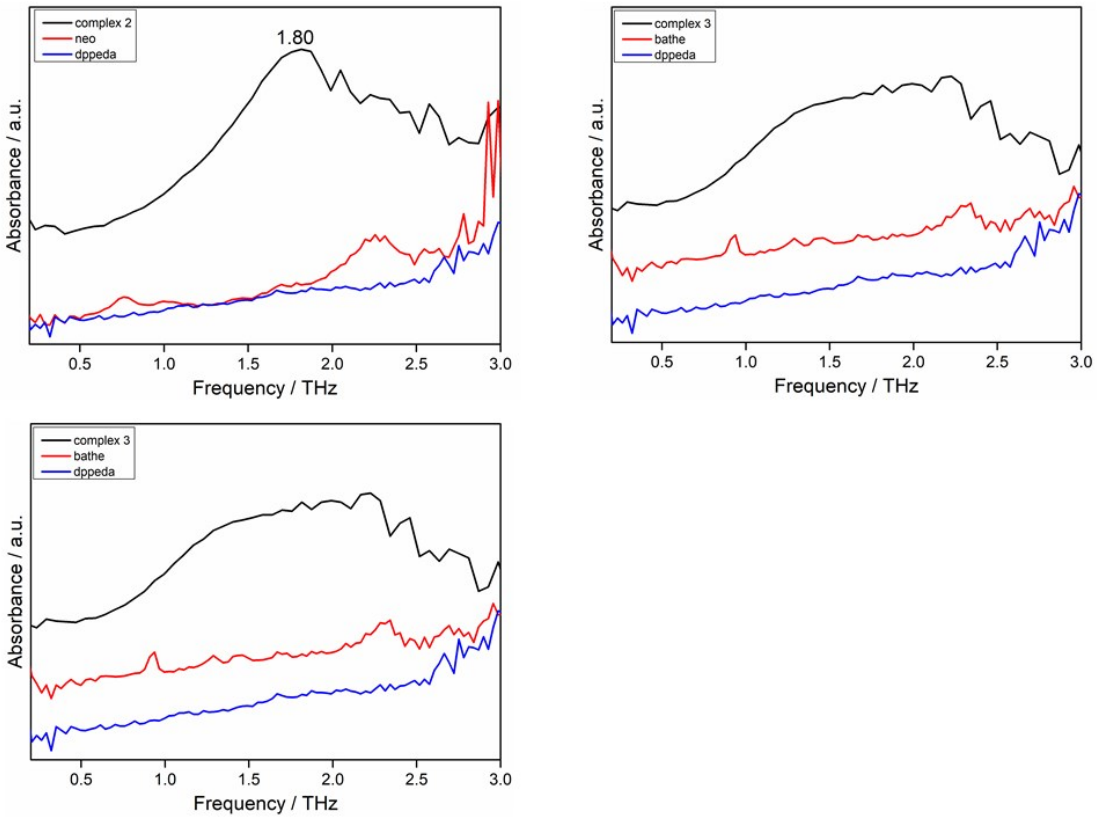
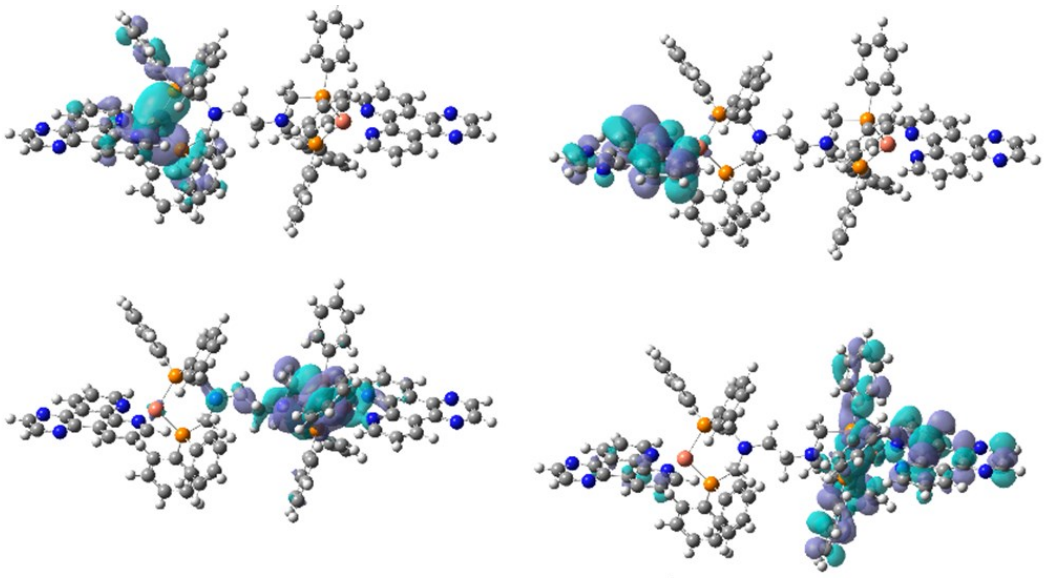
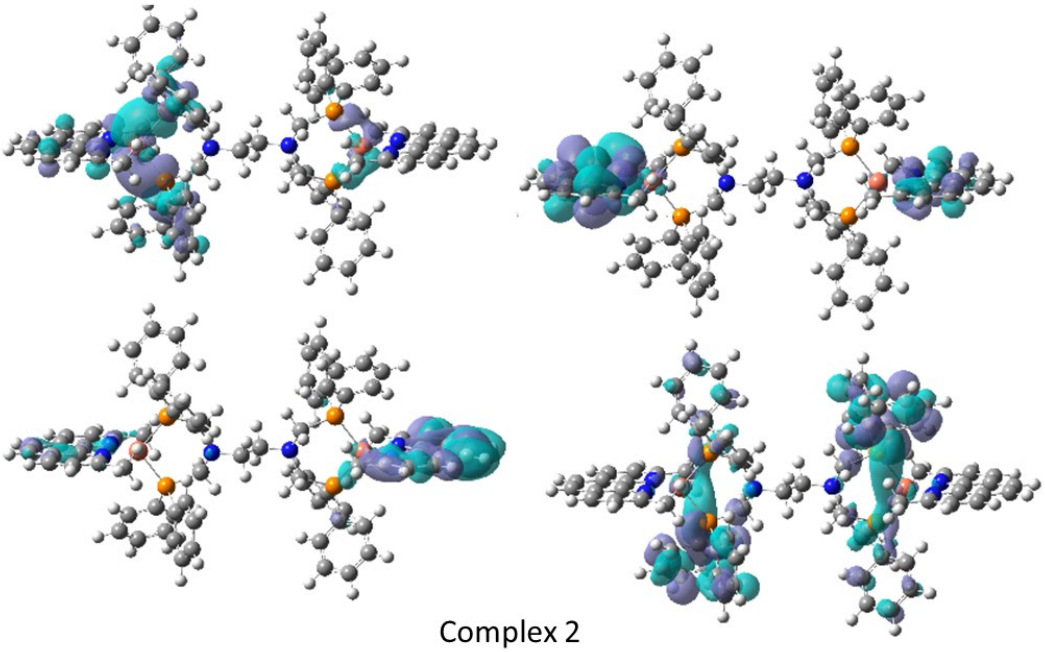


Fig. S5 The THz absorption spectra of complexes **2-4** at ambient temperature with their ligands



Complex 1



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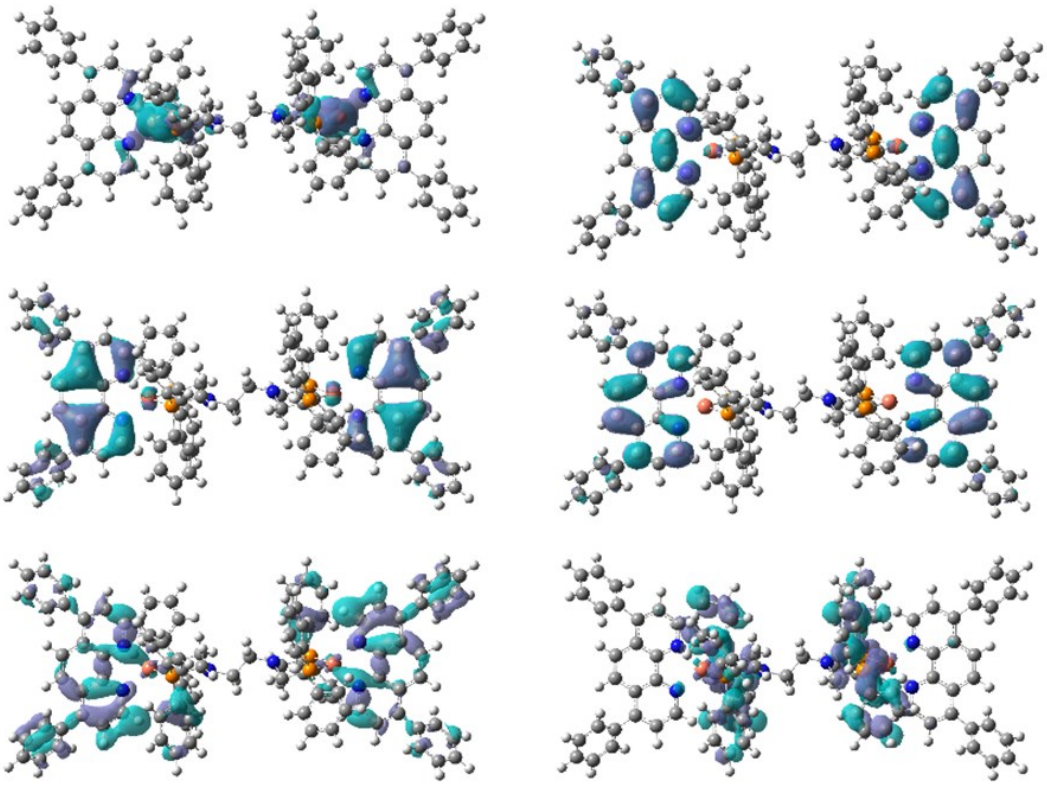


Complex 3

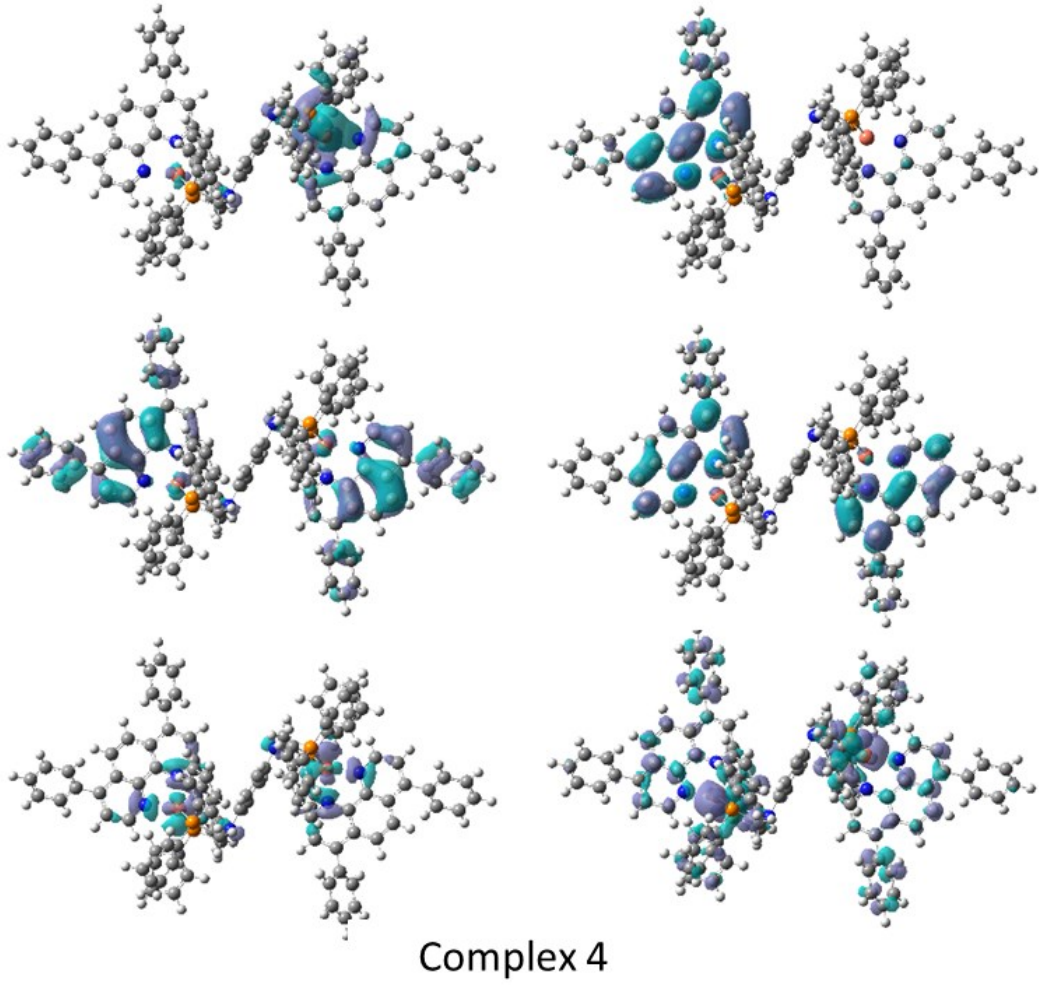
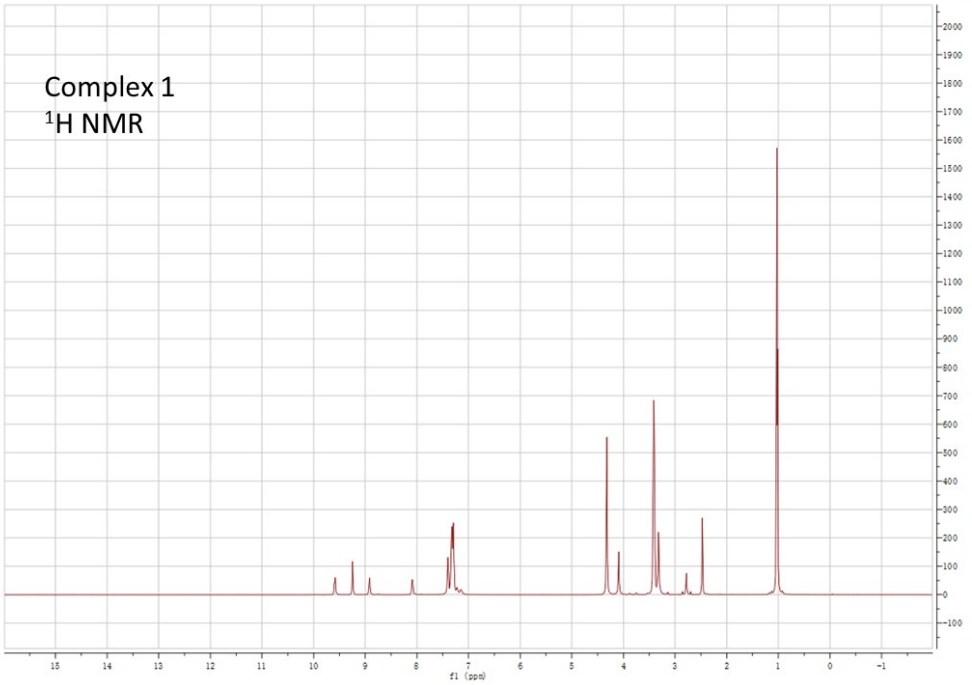
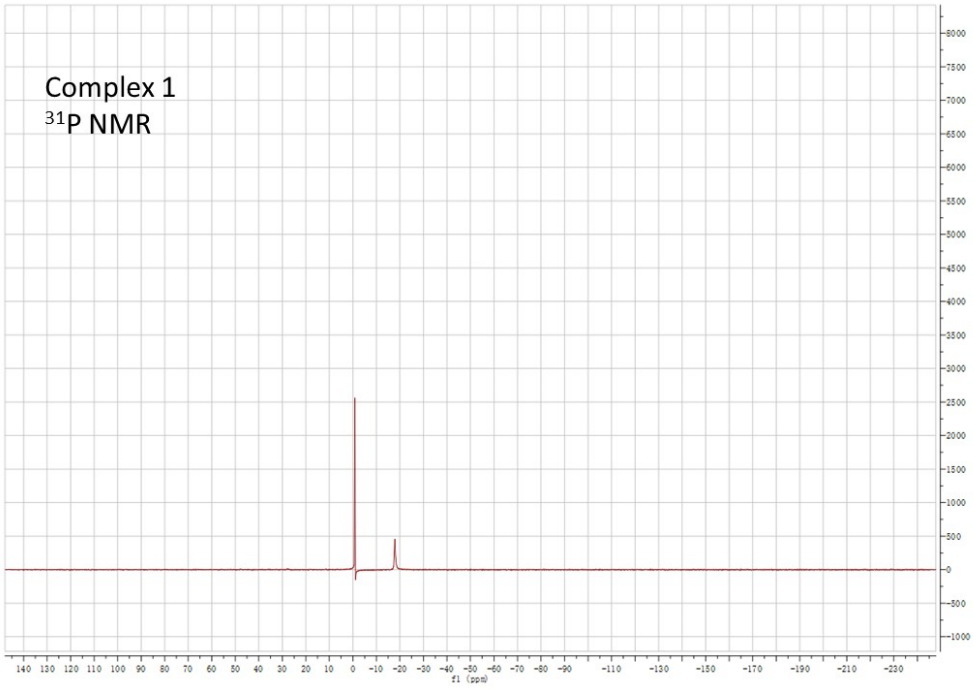


Fig. S6 Fig. S6 Natural transition orbitals for the ten absorptions in Table S4 (isovalue = 0.02). Left is for occupied and right is for unoccupied orbitals. Since each contribution is not dominant, natural transition orbitals were calculated so that the absorption can be attributed to one transition.

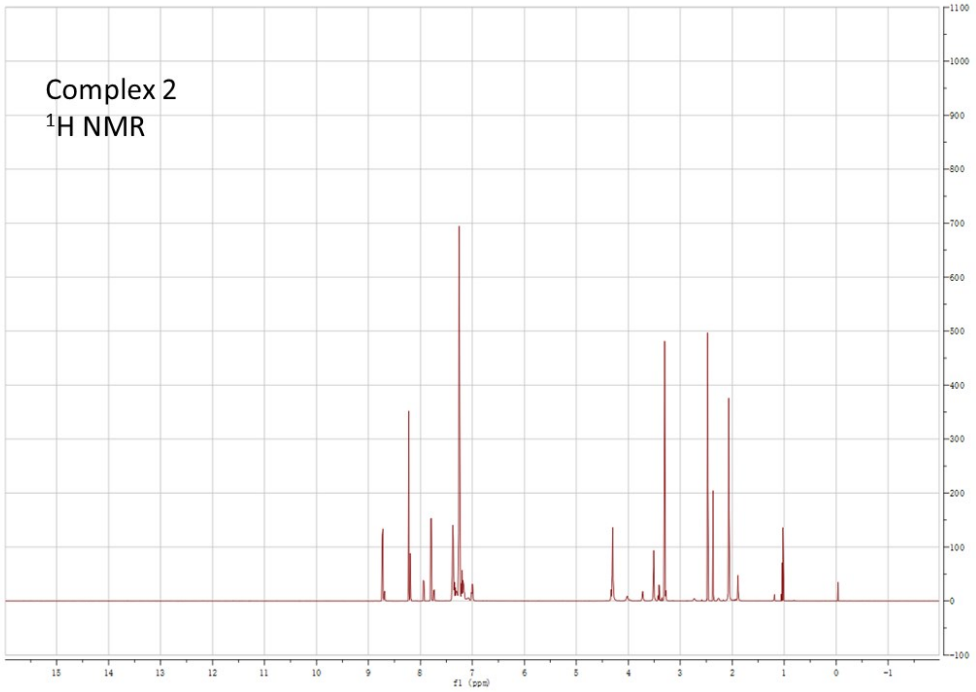
Complex 1
^{1}H NMR



Complex 1
^{31}P NMR



Complex 2
^{1}H NMR



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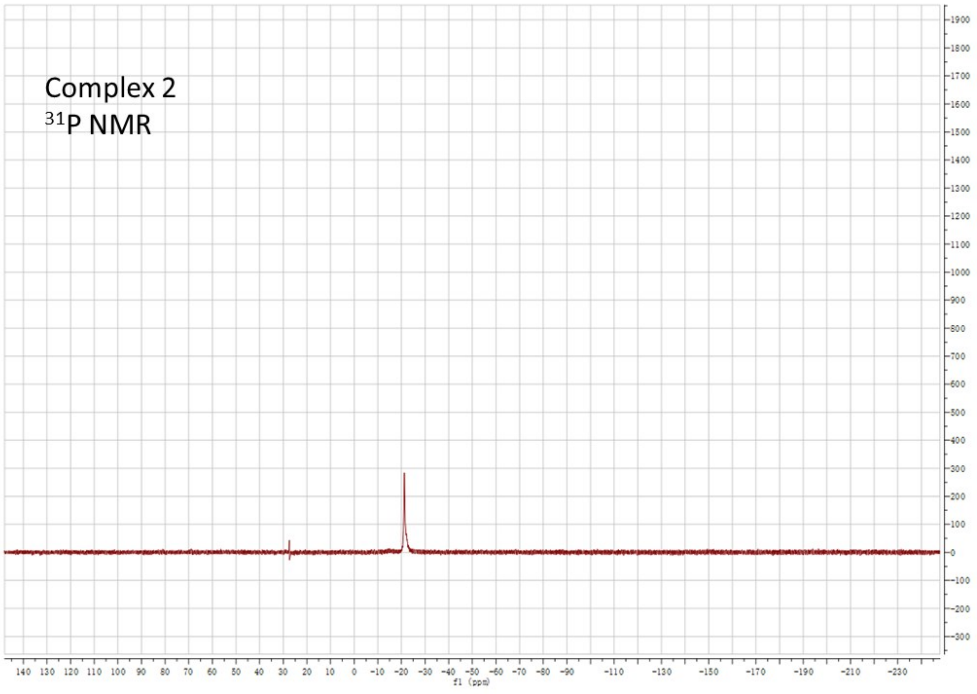
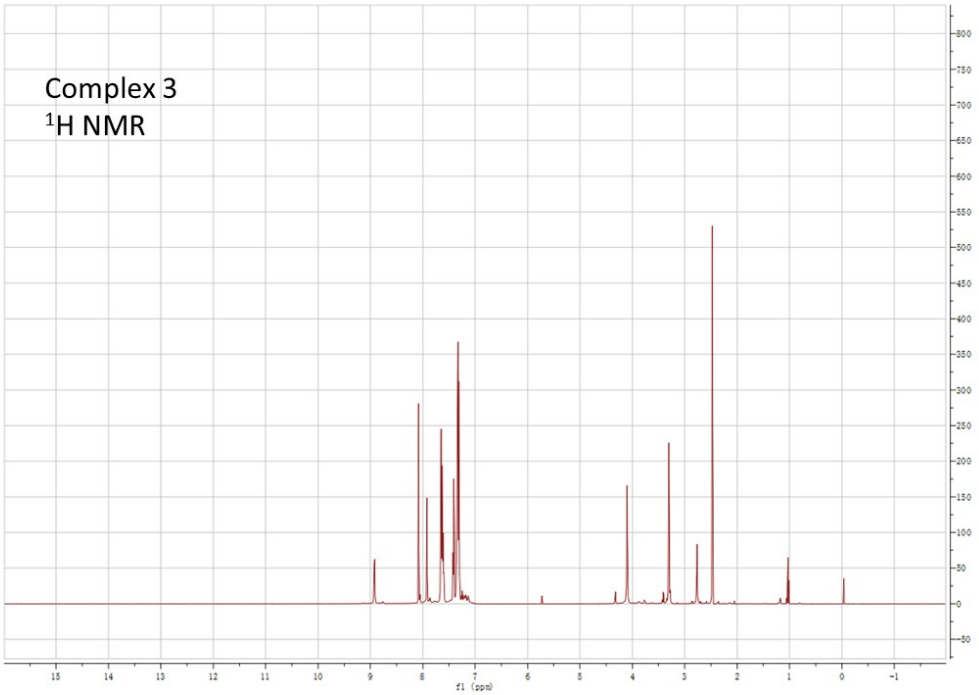
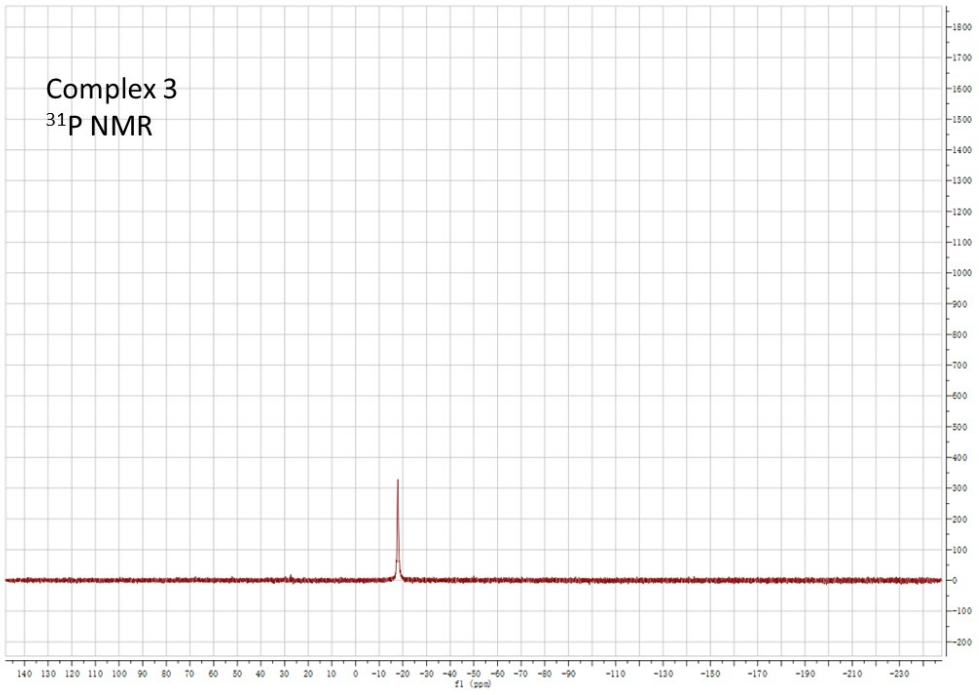
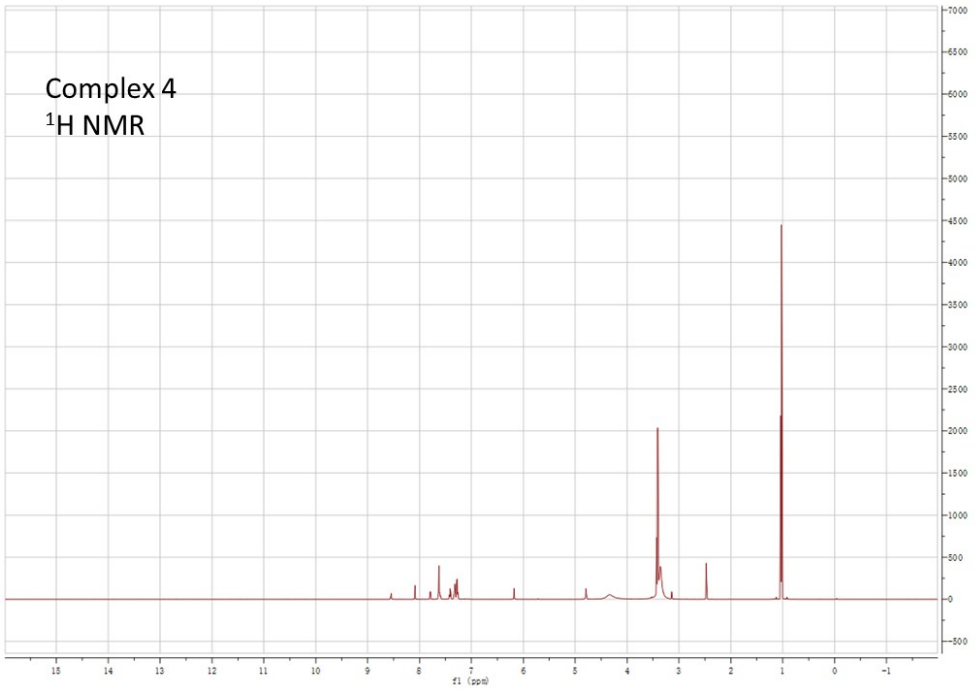


Complex 3
^{1}H NMR



Complex 3
^{31}P NMR





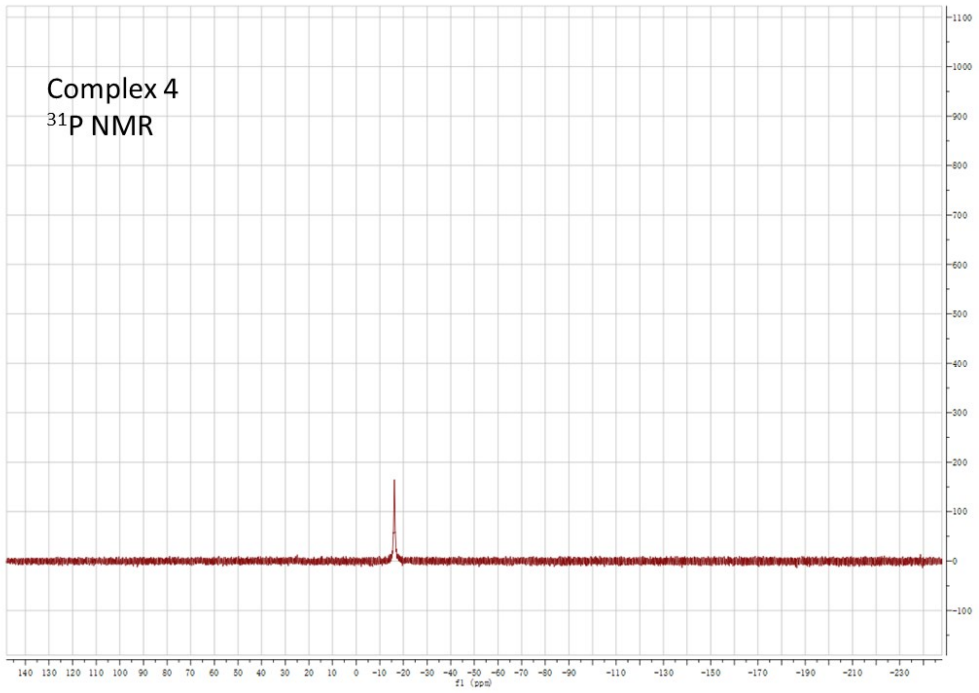


Fig. S7 The NMR spectra of all complexes.

Table S1 Selected bond length (Å) and angles (°) for complexes **1-4**

Complex **1**			
bond length (Å)		bond angle (°)	
Cu(1)-N(1)	2.105(3)	N(2)-Cu(1)-N(1)	80.84(13)
Cu(1)-N(2)	2.039(3)	N(2)-Cu(1)-P(2)	120.65(9)
Cu(1)-P(1)	2.2543(11)	N(1)-Cu(1)-P(2)	131.48(9)
Cu(1)-P(2)	2.2325(11)	N(2)-Cu(1)-P(1)	111.37(10)
Cu(2)- N(5)	2.071(3)	N(1)-Cu(1)-P(1)	107.68(10)
Cu(2)- N(6)	2.057(3)	P(2)-Cu(1)-P(1)	103.34(4)
Cu(2)- P(3)	2.2359(11)	N(6)-Cu(2)-N(5)	81.14(13)
Cu(2)- P(4)	2.2332(11)	N(5)-Cu(2)-P(4)	123.92(10)
		N(5)-Cu(2)-P(3)	111.63(10)
		N(6)-Cu(2)-P(4)	115.68(10)
		N(6)-Cu(2)-P(3)	120.13(10)
		P(4)-Cu(2)-P(3)	104.30(4)
Complex **2**			
bond length (Å)		bond angle (°)	
Cu(1)-N(1)	2.058(4)	N(2)-Cu(1)-N(1)	81.82(15)
Cu(1)-N(2)	2.065(4)	N(2)-Cu(1)-P(2)	118.77(10)
Cu(1)-P(1)	2.2376(12)	N(1)-Cu(1)-P(2)	119.30(10)
Cu(1)-P(2)	2.2316(12)	N(2)-Cu(1)-P(1)	113.45(11)
		N(1)-Cu(1)-P(1)	121.70(10)
		P(2)-Cu(1)-P(1)	102.07(4)
Complex **3**			
bond length (Å)		bond angle (°)	
Cu(1)-N(1)	2.034(6)	N(2)-Cu(1)-N(1)	
Cu(1)-N(2)	2.053(8)	N(2)-Cu(1)-P(2)	109.97(2)
Cu(1)-P(1)	2.222(3)	N(1)-Cu(1)-P(2)	123.17(2)
Cu(1)-P(2)	2.226(2)	N(2)-Cu(1)-P(1)	129.2(2)
		N(1)-Cu(1)-P(1)	111.4(2)
		P(2)-Cu(1)-P(1)	102.55(1)
Complex **4**			
bond length (Å)		bond angle (°)	
Cu(1)-N(1)	2.0621(17)	N(2)-Cu(1)-N(1)	80.70(7)
Cu(1)-N(2)	2.0482(17)	N(2)-Cu(1)-P(2)	122.92(5)
Cu(1)-P(1)	2.2583(6)	N(1)-Cu(1)-P(2)	129.43(5)
Cu(1)-P(2)	2.2132(5)	N(2)-Cu(1)-P(1)	113.31(5)
		N(1)-Cu(1)-P(1)	106.10(5)
		P(2)-Cu(1)-P(1)	103.15(2)

Table. S2 Detailed information about five and six-membered rings in complexes.

Complex 1	Cg(1)	Cu(1) --> N(1) --> C(6) --> C(5) --> N(2)
	Cg(2)	Cu(2) --> N(5) --> C(20) --> C(19) --> N(6)
	Cg(3)	Cu(1) --> P(1) --> C(41) --> N(9) --> C(54) --> P(2)
	Cg(4)	Cu(2) --> P(3) --> C(82) --> N(10) --> C(81) --> P(4)
	Cg(5)	N(1) --> C(6) --> C(7) --> C(8) --> C(9) --> C(10)
	Cg(6)	N(2) --> C(1) --> C(2) --> C(3) --> C(4) --> C(5)
	Cg(7)	N(3) --> C(11) --> C(12) --> N(4) --> C(13) --> C(14)
	Cg(8)	N(5) --> C(20) --> C(21) --> C(22) --> C(23) --> C(24)
	Cg(9)	N(6) --> C(15) --> C(16) --> C(17) --> C(18) --> C(19)
	Cg(10)	N(7) --> C(26) --> C(25) --> N(8) --> C(28) --> C(27)
	Cg(11)	C(4) --> C(5) --> C(6) --> C(7) --> C(11) --> C(12)
	Cg(12)	C(18) --> C(19) --> C(20) --> C(21) --> C(26) --> C(25)
	Cg(13)	C(29) --> C(33) --> C(32) --> C(31) --> C(30) --> C(34)
	Cg(14)	C(35) --> C(36) --> C(37) --> C(38) --> C(39) --> C(40)
	Cg(15)	C(42) --> C(43) --> C(44) --> C(45) --> C(46) --> C(47)
	Cg(16)	C(48) --> C(49) --> C(50) --> C(51) --> C(52) --> C(53)
	Cg(17)	C(57) --> C(58) --> C(59) --> C(60) --> C(61) --> C(62)
	Cg(18)	C(63) --> C(64) --> C(65) --> C(66) --> C(67) --> C(68)
	Cg(19)	C(69) --> C(70) --> C(71) --> C(72) --> C(73) --> C(74)
	Cg(20)	C(75) --> C(76) --> C(77) --> C(78) --> C(79) --> C(80)
Complex 2	Cg(1)	Cu(1) --> N(1) --> C(5) --> C(6) --> N(2)
	Cg(2)	Cu(1) --> P(1) --> C(27) --> N(3) --> C(29) --> P(2)
	Cg(3)	N(1) --> C(1) --> C(2) --> C(3) --> C(4) --> C(5)
	Cg(4)	N(2) --> C(6) --> C(7) --> C(8) --> C(9) --> C(10)
	Cg(5)	C(4) --> C(5) --> C(6) --> C(7) --> C(12) --> C(11)
	Cg(6)	C(15) --> C(16) --> C(17) --> C(18) --> C(19) --> C(20)
	Cg(7)	C(21) --> C(22) --> C(23) --> C(24) --> C(25) --> C(26)
	Cg(8)	C(30) --> C(31) --> C(32) --> C(33) --> C(34) --> C(35)
	Cg(9)	C(36) --> C(37) --> C(38) --> C(39) --> C(40) --> C(41)
	Cg(10)	Cu(2) --> N(4) --> C(47) --> C(46) --> N(5)
	Cg(11)	Cu(2) --> P(3) --> C(68) --> N(6) --> C(70) --> P(4)
	Cg(12)	N(4) --> C(47) --> C(48) --> C(49) --> C(50) --> C(51)
	Cg(13)	N(5) --> C(42) --> C(43) --> C(44) --> C(45) --> C(46)
Complex 3	Cg(1)	Cu(1) --> N(1) --> C(6) --> C(5) --> N(2)
	Cg(2)	Cu(1) --> P(1) --> C(33) --> N(3) --> C(31) --> P(2)
	Cg(3)	N(1) --> C(6) --> C(7) --> C(8) --> C(9) --> C(10)
	Cg(4)	N(2) --> C(1) --> C(2) --> C(3) --> C(4) --> C(5)
	Cg(5)	C(4) --> C(5) --> C(6) --> C(7) --> C(12) --> C(11)
	Cg(6)	C(13) --> C(14) --> C(15) --> C(16) --> C(17) --> C(18)
	Cg(7)	C(19) --> C(20) --> C(21) --> C(22) --> C(23) --> C(24)
	Cg(8)	C(25) --> C(26) --> C(27) --> C(28) --> C(29) --> C(30)
	Cg(9)	C(34) --> C(35) --> C(36) --> C(37) --> C(38) --> C(39)

	Cg(10)	C(40) --> C(41) --> C(42) --> C(43) --> C(44) --> C(45)
	Cg(11)	C(46) --> C(47) --> C(48) --> C(49) --> C(50) --> C(51)
Complex 4	Cg(1)	Cu(1) --> N(1) --> C(5) --> C(9) --> N(2)
	Cg(2)	Cu(1) --> P(1) --> C(25) --> N(3) -->C(38)-->P(2)
	Cg(3)	N(1) --> C(1) --> C(2) --> C(3) --> C(4) --> C(5)
	Cg(4)	N(2) --> C(9) --> C(8) --> C(10) --> C(11) --> C(12)
	Cg(5)	C(4) --> C(5) --> C(9) --> C(8) --> C(7) --> C(6)
	Cg(6)	C(13) --> C(14) --> C(15) --> C(16) --> C(17) --> C(18)
	Cg(7)	C(19) --> C(20) --> C(21) --> C(22) --> C(23) --> C(24)
	Cg(8)	C(26) --> C(27) --> C(28) --> C(29) --> C(30) --> C(31)
	Cg(9)	C(32) --> C(33) --> C(34) --> C(35) --> C(36) --> C(37)
	Cg(10)	C(39) --> C(40) --> C(41) --> C(42) --> C(43) --> C(44)
	Cg(11)	C(45) --> C(46) --> C(47) --> C(48) --> C(49) --> C(50)
	Cg(12)	C(51) --> C(52) --> C(53)a --> C(51)a --> C(52)a --> C(53)

Table S3 The excitation and emission data of the related ligands in the solid state at ambient temperature

Ligands		Excitation (nm)	Emission (nm)
P^P	dppeda	381	454
	dpppda	373	452
	dppBz	355	460
	bdppmapy	380	433
N^N	Dpq	382	419
	neo	388	415
	batho	365	405

Table S4 Energy, oscillator strength and major contribution of the calculated transitions for complexes **1-4**.

Excited state	Energy / eV (/ nm)	Oscillator strength	Major contribution (%)	
1 absorption	2.6580 (466.46)	0.1905	HOMO-1 → LUMO+1	14.55
			HOMO → LUMO	**79.30**
1 absorption	4.9127 (252.37)	0.4040	HOMO-33 → LUMO+3	2.50
			HOMO-28 → LUMO+2	3.11
			HOMO-28 → LUMO+5	**24.93**
			HOMO-26 → LUMO+3	3.32
			HOMO-25 → LUMO+3	4.69
			HOMO-4 → LUMO+17	2.09
			HOMO-3→ LUMO+17	4.16
			HOMO-2 → LUMO+17	10.94
1 emission	2.6626 (465.64)	0.0921	LUMO → HOMO-7	25.22
			LUMO → HOMO-6	2.87
			LUMO+1→ HOMO-1	**63.01**
2 absorption	2.8112 (441.03)	0.2192	HOMO-1→ LUMO+1	48.56
			HOMO → LUMO	**49.40**
2 absorption	4.7709 (259.88)	0.3485	HOMO-28→ LUMO	3.35
			HOMO-27 → LUMO+1	3.28
			HOMO-25 → LUMO	3.19
			HOMO-24 → LUMO+1	3.43
			HOMO-8 → LUMO+3	2.67
			HOMO-7 → LUMO+2	2.56
			HOMO-6 → LUMO+5	9.79
			HOMO-5 → LUMO+4	**28.06**
			HOMO-3 → LUMO+4	5.14
			HOMO-2 → LUMO+5	4.32
2 emission	2.8167 (440.17)	0.1073	**LUMO+1 → HOMO-1**	**97.96**
3 absorption	2.7287 (454.38)	0.3621	HOMO-4 → LUMO	3.35
			HOMO-3 →LUMO+1	4.39
			HOMO-1 →LUMO+1	43.28
			HOMO → LUMO	**46.32**
3 absorption	3.9350 (315.08)	0.6520	HOMO-10→ LUMO+2	32.99
			HOMO-9 → LUMO+3	**34.00**
			HOMO-7 → LUMO+1	3.83
			HOMO-6 → LUMO	3.79
			HOMO-1 → LUMO+6	5.57
			HOMO → LUMO+7	4.95
3 absorption	4.7517 (260.93)	0.3419	HOMO-37 →LUMO	4.18
			HOMO-36 → LUMO+1	4.63
			HOMO-35 →LUMO+1	5.18

			HOMO-34 →LUMO	5.21
			HOMO-25 →LUMO+3	3.71
			HOMO-24 →LUMO+2	3.25
			HOMO-8 → LUMO+5	4.16
			HOMO-8 → LUMO+7	2.10
			HOMO-5 →LUMO+4	**12.04**
			HOMO-4 →LUMO+12	2.57
			HOMO-3 →LUMO+4	5.14
3	2.7360	0.1982	LUMO+1 → HOMO-4	7.53
emission	(453.15)		**LUMO+1 → HOMO-1**	**88.42**
4	2.7635	0.2133	HOMO-4 → LUMO+1	14.70
absorption	(448.64)		HOMO-3 → LUMO+0	14.86
			HOMO-2 → LUMO+0	31.88
			HOMO-1 → LUMO+1	**34.21**
4	3.7991	0.4596	**HOMO-8 → LUMO+2**	**44.51**
absorption	(326.35)		HOMO-7 → LUMO+3	44.19
4	5.0280	0.2154	HOMO-38 → LUMO+2	2.37
absorption	(246.59)		HOMO-37 → LUMO+3	4.41
			HOMO-10 → LUMO+7	9.41
			HOMO-9 → LUMO+8	7.42
			HOMO-8 → LUMO+7	**20.15**
			HOMO-7 → LUMO+6	2.41
			HOMO-7 → LUMO+8	17.21
			HOMO-4 → LUMO+11	4.41
			HOMO-4 → LUMO+21	2.04
			HOMO-3 → LUMO+18	2.67
4	2.7881	0.2548	**LUMO+1 → HOMO-1**	**87.09**
emission	(444.69)		LUMO+4 → HOMO	9.65

Table S5 THz data for starting materials and complexes **1-4**

Materials and complexes	Terahertz	spectra	peak (THz)											
$Cu(CH_3CN)ClO_4$	0.30	1.30	1.47	1.82	2.05	2.17	2.28							
Dpq	0.30	0.39	1.00	1.25	1.32	1.52	1.71	1.78	2.02	2.14	2.34	2.48	2.55	2.64
neo	0.23	0.35	0.53	0.76	0.98	1.41	1.52	1.76	1.98	2.22	2.40	2.69		
batho	0.23	0.41	0.53	0.64	0.76	0.93	1.29	1.47	2.34	2.57	2.69			
dppeda	0.29	0.41	0.52	0.64	0.76	0.88	1.00	1.23	1.40	1.58	1.82	1.99	2.11	2.22
dpppda	0.26	0.35	0.44	0.61	0.70	0.82	1.07	1.16	1.70	2.08	2.28	2.48	2.54	2.64
1	0.29	1.81	2.05	2.22	2.46	2.58	2.75							
2	0.24	1.46	1.71	1.87	2.06	2.17	2.28	2.46	2.70					
3	0.29	1.70	1.82	1.93	2.17	2.22	2.46	2.58	2.69					
4	0.24	1.05	1.70	1.82	1.93	2.05	2.17	2.28	2.46	2.70				