Supporting Information for

Cyclometalated Platinum(II) Cyanometallates: Luminescent Blocks for Coordination Self-Assembly

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Table S1. Crystal data and structure refinement for **1**–**8**.

Identification code	**1**[b]	**2**[b]	**3**	**3´**	**4**
Empirical formula	$C_{98}H_{76}Cu_2N_6P_4Pt_2$	$C_{98}H_{76}Ag_2N_6P_4Pt_2$	$C_{63}H_{48}Ag_2Cl_2N_6P_2Pt_2$	$C_{64}H_{50}Ag_2Cl_4N_6P_2Pt_2$	$C_{100}H_{80}Cu_2N_6P_4Pt_2$
Formula weight	1978.78	2067.44	1627.83	1712.76	2006.84
Temperature (K)			150(2)		
Wavelength (Å)			0.71073		
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions					
a (Å)	11.4119(3)	11.2565(2)	9.2122(5)	9.6064(9)	12.1032(9)
b (Å)	12.5448(3)	12.6777(2)	19.3491(10)	12.0144(11)	12.6537(10)
c (Å)	16.9820(4)	17.0873(3)	17.0238(9)	13.8676(13)	16.1583(12)
a (°)	98.9770(10)	98.1960(10)	90	83.922(2)	69.171(2)
β (°)	99.1600(10)	97.9310(10)	93.100(2)	77.016(2)	75.388(2)
γ (°)	114.7450	114.1070(10)	90	71.732(2)	65.969(1)
Volume ($Å^3$)	2111.46(9)	2150.48(7)	3030.0(3)	1479.9(2)	2095.6(3)
Z	1	1	2	1	1
ρ_{calc} (Mg/m^3)	1.556	1.596	1.784	1.922	1.590
μ (mm^{-1})	3.926	3.816	5.424	5.645	3.957
F(000)	980	1016	1564	824	996
Crystal size (mm^3)	0.370 × 0.324 × 0.144	0.198 × 0.107 × 0.102	0.703 × 0.280 × 0.216	0.333 × 0.318 × 0.247	0.13 × 0.28 × 0.32
θ range for data collection (°)	1.254 to 34.996	1.233 to 30.021	2.396 to 27.000	2.978 to 31.184	2.581 to 28.344
Index ranges	-18<=h<=18, -20<=k<=20, -27<=l<=27	-15<=h<=15, -17<=k<=17, -24<=l<=24	-11<=h<=11, -24<=k<=22, -21<=l<=21	-13<=h<=13, -17<=k<=17, -19<=l<=20	-16<=h<=16, -16<=k<=16z -19<=l<=21

Reflections collected	109141	78967	33414	30000	32081
Independent reflections	18586 [R(int) = 0.0324]	12555 [R(int) = 0.0418]	6598 [R(int) = 0.0224]	9167 [R(int) = 0.0190]	9975 [R(int) = 0.0217]
Completeness to θ= 25.24°	100.0 %	100.0 %	99.6 %	99.7 %	99.8 %
Absorption correction	Numerical	Numerical	Numerical	Numerical	Numerical
Max. and min. transmission	0.568 and 0.255	0.678 and 0.465	0.310 and 0.176	0.248 and 0.176	0.629 and 0.364
Data/ restrains/ parameters	18586 / 36 / 579	12555 / 6 / 476	6598 / 12 / 389	9167 / 0 / 361	9975/0/515
GOOF on F^2	1.031	1.013	1.076	1.029	1.020
Final R indices $[I>2\sigma(I)]^a$	R1 = 0.0247, wR2 = 0.0496	R1 = 0.0247, wR2 = 0.0454	R1 = 0.0250, wR2 = 0.0707	R1 = 0.0181, wR2 = 0.0417	R1 = 0.0209, wR2 = 0.0425
R indices (all data)	R1 = 0.0338, wR2 = 0.0521	R1 = 0.0344, wR2 = 0.0481	R1 = 0.0280, wR2 = 0.0725	R1 = 0.0206, wR2 = 0.0426	R1 = 0.0256, wR2 = 0.0437
Largest diff. peak and hole ($e.Å^{-3}$)	1.686 and -1.097	1.508 and -0.818	1.692 and -0.377	1.068 and -0.827	1.14/-0.53

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma [w(F_o^2 - Fc^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$

Table S1. Continued.

Identification code	**5**	**6**	**7**[b]	**8**[b]
Empirical formula	$C_{100}H_{80}Ag_2N_6P_4Pt_2$	$C_{64}H_{50}Ag_2N_6P_2Pt_2$	$C_{98}H_{72}Cu_2F_4N_6P_4Pt_2$	$C_{98}H_{72}Ag_2F_4N_6P_4Pt_2$
Formula weight	2095.50	1570.96	2050.75	2139.41
Temperature (K)		150(2)		
Wavelength (Å)		0.71073		
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$

Unit cell dimensions				
a (Å)	11.7210(8)	9.8020(2)	11.409(2)	11.2906(4)
b (Å)	12.9305(10)	14.8584(4)	12.648(3)	12.7098(5)
c (Å)	16.4457(12)	19.2882(5)	17.201(4)	17.2980(6)
a (^{o})	70.328(3)	90	99.160(6)	98.394(2)
β (^{o})	76.378(3)	104.0340(10)	99.009(6)	97.515(2)
γ (^{o})	66.472(3)	90	115.008(6)	114.462(2)
Volume (Å^3)	2137.1(3)	2725.32(12)	2150.1(8)	2184.27(14)
Z	1	2	1	1
ρ_{calc} (Mg/m^3)	1.628	1.914	1.584	1.626
μ (mm^{-1})	3.841	5.931	3.865	3.766
F(000)	1032	1512.0	1012	1048
Crystal size (mm^3)	0.083 × 0.045 × 0.04	0.259 × 0.215 × 0.11	0.149 × 0.069 × 0.034	0.117 × 0.107 × 0.056
θ range for data collection (^{o})	1.324 to 25.997	2.117 to 30.000	1.238 to 31.999	1.218 to 35.002
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -27 ≤ l ≤ 27	-17<=h<=17, -18<=k<=18, -25<=l<=25	-18<=h<=18, -20<=k<=20, -27<=l<=27
Reflections collected	67034	57735	115537	226439
Independent reflections	8296 [R(int) = 0.0618]	7939 [R(int) = 0.0375]	14925 [R(int) = 0.0494]	19160 [R(int) = 0.0439]
Completeness to θ= 25.24^o	98.9 %	99.9 %	100.0 %	99.9 %
Absorption correction	Numerical	Muti-scan	Numerical	Numerical
Max. and min. transmission	0.862 and 0.741	0.562 and 0.309	0.877 and 0.557	0.810 and 0.650
Data/ restrains/ parameters	8296 / 0 / 515	7939/0/344	14925 / 40 / 555	19160 / 7 / 555

GOOF on F^2	1.022	1.037	1.028	1.046
Final R indices $[I>2\sigma(I)]^a$	R_1 = 0.0261, wR_2 = 0.0393	R1 = 0.0218, wR2 = 0.0432	R1 = 0.0260, wR2 = 0.0525	R1 = 0.0244, wR2 = 0.0566
R indices (all data)	R_1 = 0.0362, wR_2 = 0.0406	R1 = 0.0309, wR2 = 0.0456	R1 = 0.0365, wR2 = 0.0552	R1 = 0.0322, wR2 = 0.0591
Largest diff. peak and hole ($e.Å^{-3}$)	1.04/-0.71	1.10/-0.59	0.941 and -0.749	1.956 and -0.952

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma [w(F_o^2 - Fc^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$. [b] The contribution of the missing solvent was taken into account by using a *SQUEEZE* routine of *PLATON*.

Table S2. Selected bond lengths (Å) and angles (deg.) for complexes **1**–**8**.

	1	**2**	**3** $P2_1/c$	**3′** $P\bar{1}$	**4**	**5**	**6**	**7**	**8**
				Bond lengths, Å					
C(1)-Pt(1)	1.9963(16)	2.011(2)	2.014(4)	1.999(2)	2.019(2)	2.0243)	2.026(3)	1.995(2)	2.001(2)
C(2)-Pt(1)	1.9590(16)	1.944(2)	1.941(4)	1.952(2)	1.933(2)	1.931(3)	1.934(3)	1.962(2)	1.947(2)
C(3)-Pt(1)	2.0320(14)	2.021(2)	2.021(4)	2.0320(19)	2.022(2)	2.013(3)	2.038(3)	2.015(2)	2.0194(17)
N(3)-Pt(1)	2.0473(14)	2.0517(19)	2.059(3)	2.0501(17)	2.0581(19)	2.05(2)	2.061(2)	2.054(2)	2.0554(16)
N(1)-Cu(1)	2.0161(14)				2.0180(18)			2.0192(18)	
N(2)-Cu(1)	2.0030(14)				1.9935(19)			2.015(2)	
N(1)-Ag(1)		2.299(2)	2.197(4)	2.2695(19)		2.308(2)			2.2983(18)
N(2)-Ag(1)		2.265(2)	2.209(3)	2.1606(18)		2.266(2)	2.185(2)		2.2814(18)
P(1)-Cu(1)	2.2581(4)				2.2749(6)			2.2637(7)	
P(2)-Cu(1)-	2.3044(4)				2.2509(6)			2.3073(7)	
P(1)-Ag(1)		2.4735(6)	2.3712(10)	2.3698(5)		2.4427(8)	2.3991(6)		2.4358(4)
P(2)-Ag(1)		2.4366(6)				2.4408(8)			2.4824(5)
C(1)-N(1)	1.157(2)	1.147(3)	1.150(5)	1.152(3)	1.155(3)	1.144(4)	1.149(3)	1.152(3)	1.149(3)
C(2)-N(2)	1.154(2)	1.147(3)	1.142(5)	1.155(3)	1.150(3)	1.147(3)	1.149(3)	1.158(3)	1.152(3)
Pt(1)-Ag(1)							2.9507(2)		
Ag(1)-C(3)							2.482(2)		

Bond angles, ^{o}									
C(2)-Pt(1)-C(1)	91.84(6)	91.65(9)	89.24(15)	90.20(8)	89.80(8)	89.31(11)	90.17(10)	91.93(8)	91.32(8)
C(2)-Pt(1)-C(3)	92.73(6)	93.04(9)	94.77(16)	93.54(8)	92.53(9)	93.43(11)	94.34(10)	92.36(9)	93.06(7)
C(1)-Pt(1)-C(3)	175.23(6)	173.79(10)	175.95(16)	176.23(8)	177.54(9)	176.77(11)	175.48(10)	175.46(9)	174.43(8)
C(2)-Pt(1)-N(3)	172.90(6)	173.36(9)	174.10(15)	173.19(7)	173.36(8)	173.62(10)	174.75(9)	173.38(8)	173.86(7)
C(1)-Pt(1)-N(3)	95.24(6)	94.93(9)	95.43(14)	95.84(8)	96.79(8)	96.55(10)	94.98(9)	94.63(8)	94.74(7)
C(3)-Pt(1)-N(3)	80.20(6)	80.46(9)	80.53(16)	80.41(8)	80.87(9)	80.79(10)	80.51(9)	81.11(8)	80.94(7)
N(1)-C(1)-Pt(1)	178.79(14)	175.8(2)	177.6(4)	177.5(2)	174.39(19)	177.1(2)	179.3(2)	178.8(2)	176.7(2)
N(2)-C(2)-Pt(1)	176.28(14)	177.6(2)	177.6(3)	177.25(19)	178.21(19)	178.3(3)	177.5(2)	176.06(19)	176.89(18)
C(1)-N(1)-Cu(1)	160.36(14)				160.8(2)			162.45(18)	
C(2)-N(2)-Cu(1)	164.04(15)				162.4(2)			164.37(19)	
C(1)-N(1)-Ag(1)		152.0(2)	155.4(3)	173.6(2)		151.0(2)			156.23(18)
C(2)-N(2)-Ag(1)		154.6(2)	175.4(3)	157.49(18)		147.5(2)	162.7(2)		156.33(18)
N(2)-Cu(1)-N(1)					103.50(8)			100.66(8)	
N(2)-Cu(1)-P(2)					110.92(6)			102.55(6)	
N(2)-Ag(1)-N(1)		100.32(8)	108.12(13)	100.32(7)		101.96(9)			98.83(7)
N(2)-Ag(1)-P(2)		114.16(6)				109.26(7)			103.72(5)

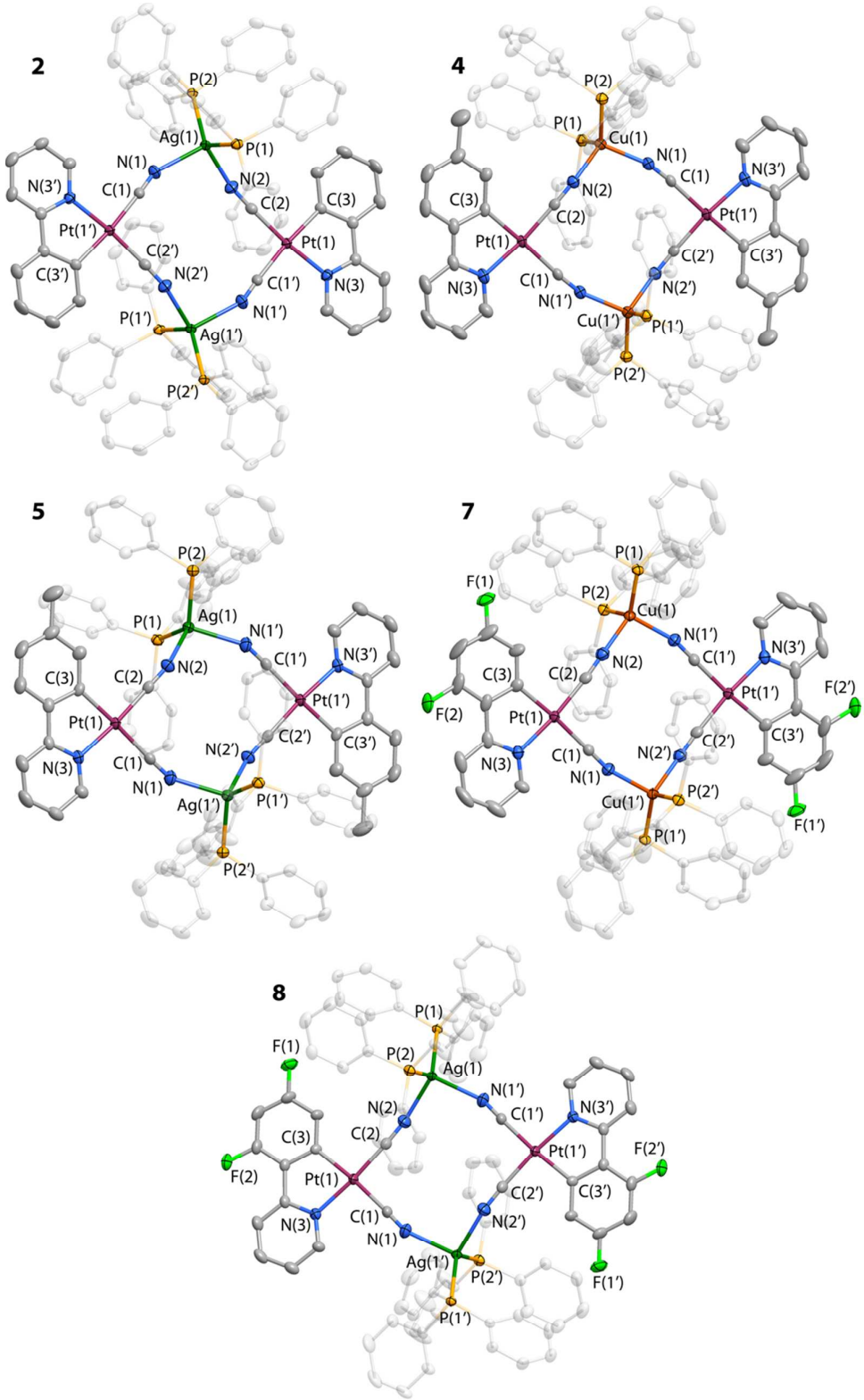

Figure S1. Molecular views of complexes **2**, **4**, **5**, **7** and **8**. Thermal ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms (′): in **2**, –x, 1–y, 1–z; in **4**, 1–x, 1–y, 1–z; in **5**, 1–x, 1–y, 1–z; in **7**, –x, 2–y, –z; in **8**, 1–x, –y, 1–z.

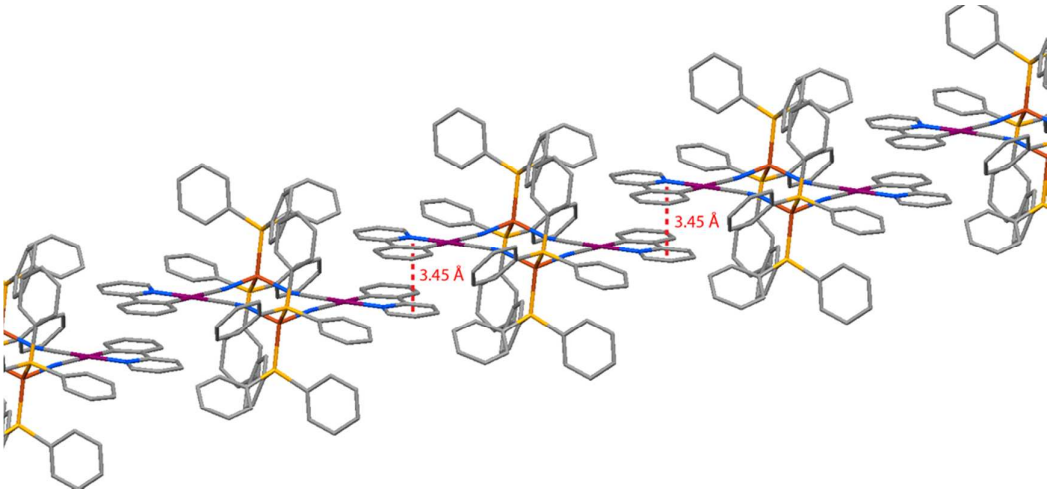

Figure S2. Solid state packing of complex **1**.

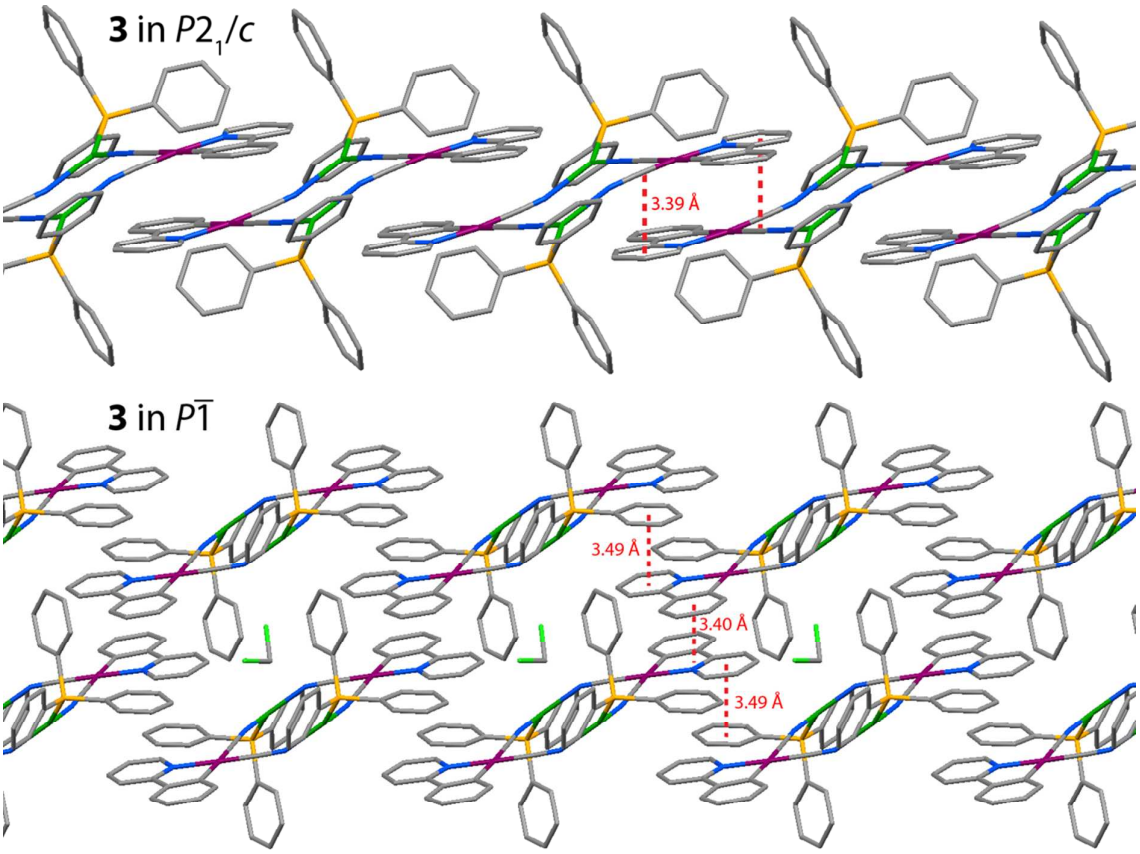

Figure S3. Solid state packing of two polymorphs of complex **3**.

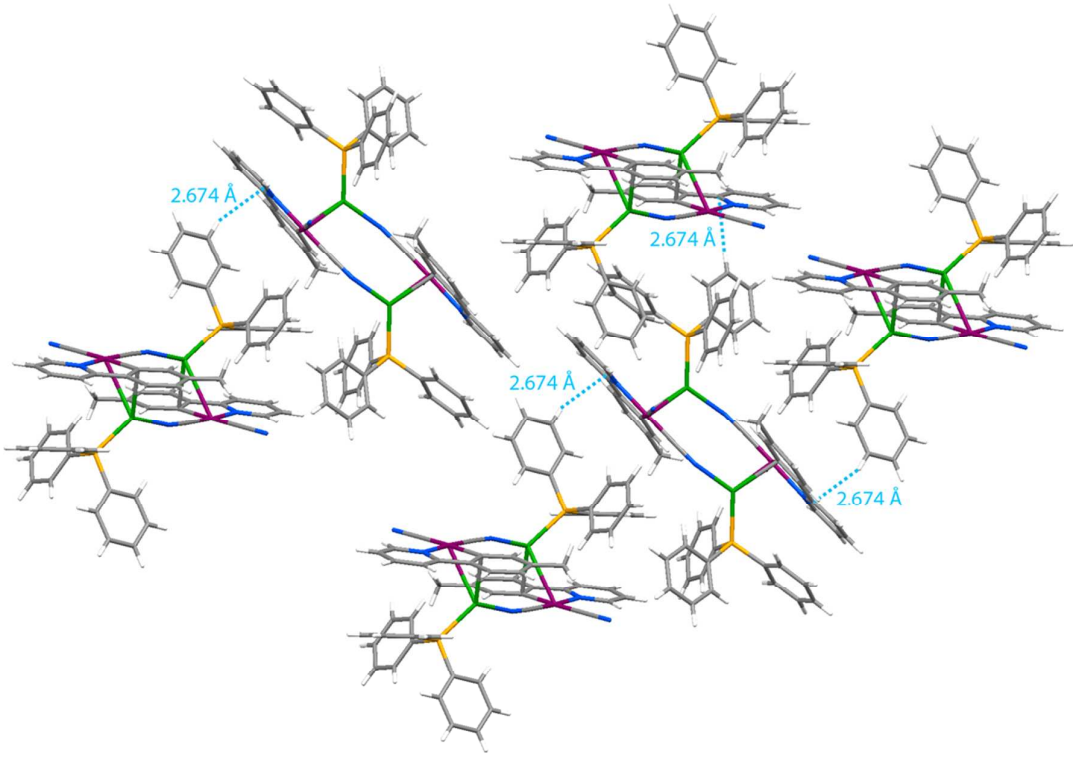

Figure S4. Solid state packing of complex **6** featuring shortest CH_{Ph}–$\pi_{C^{\wedge}N}$ contacts.

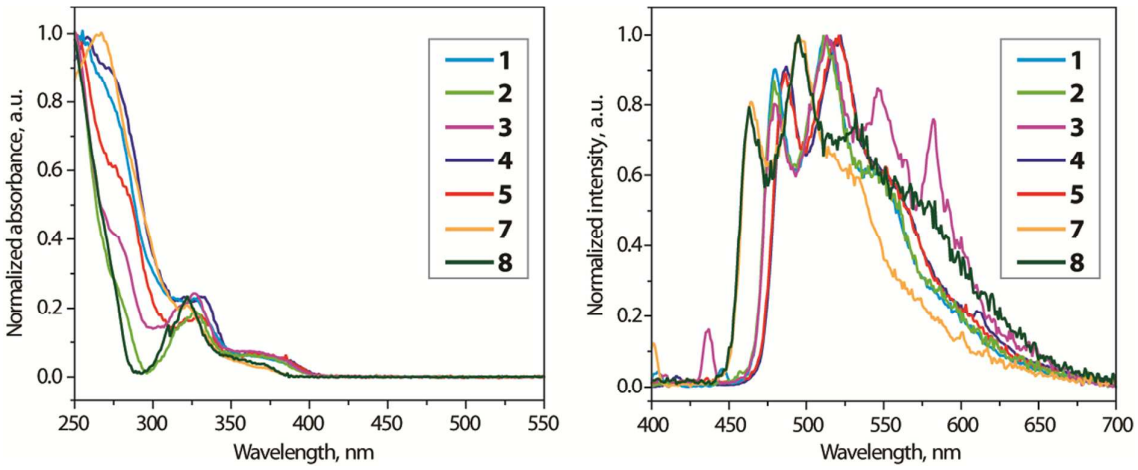

Figure S5. Normalized absorption (left) and emission (right) spectra of complexes **1**–**5**, **7**, **8** (CH_2Cl_2, 298 K).

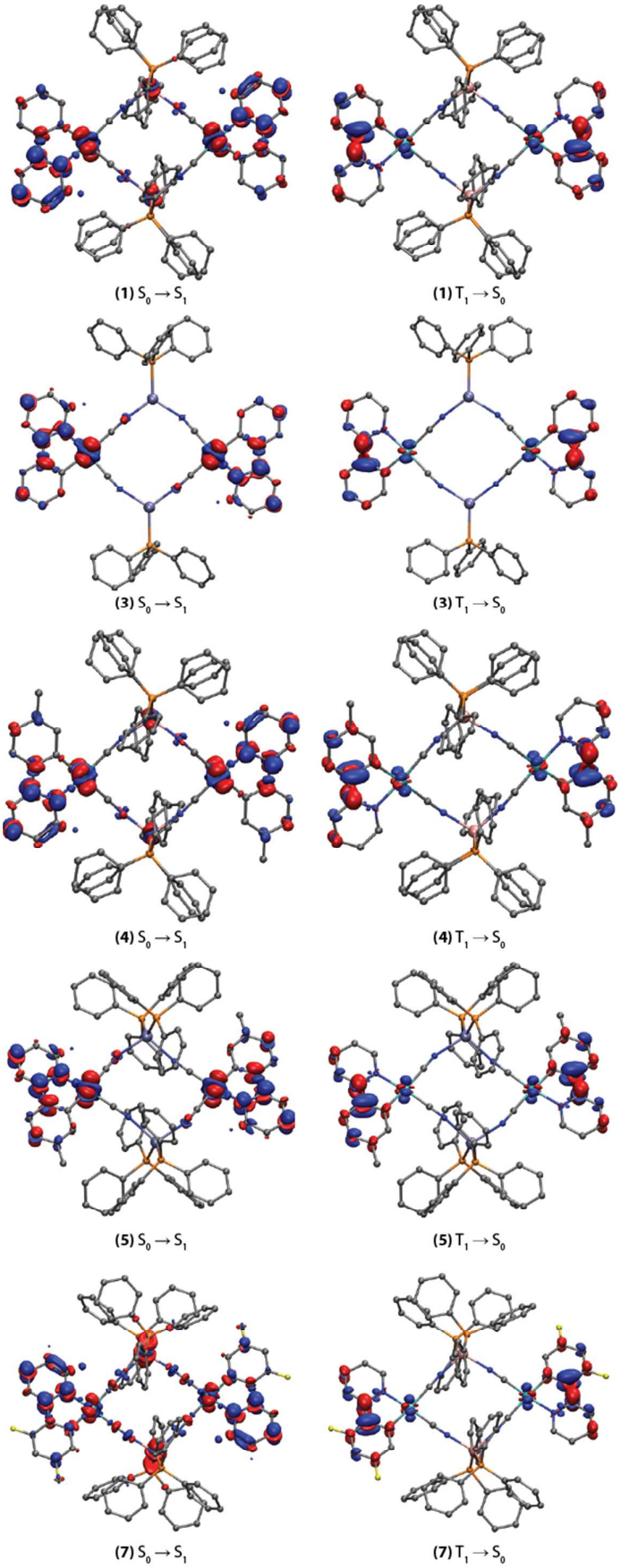

Figure S6. Electron density difference plots for the lowest energy singlet excitation ($S_0 \rightarrow S_1$) and the lowest energy triplet emission ($T_1 \rightarrow S_0$) of the complexes **1**, **3**–**5**, and **7** (isovalue 0.002 a.u.). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. Hydrogen atoms are omitted for clarity.

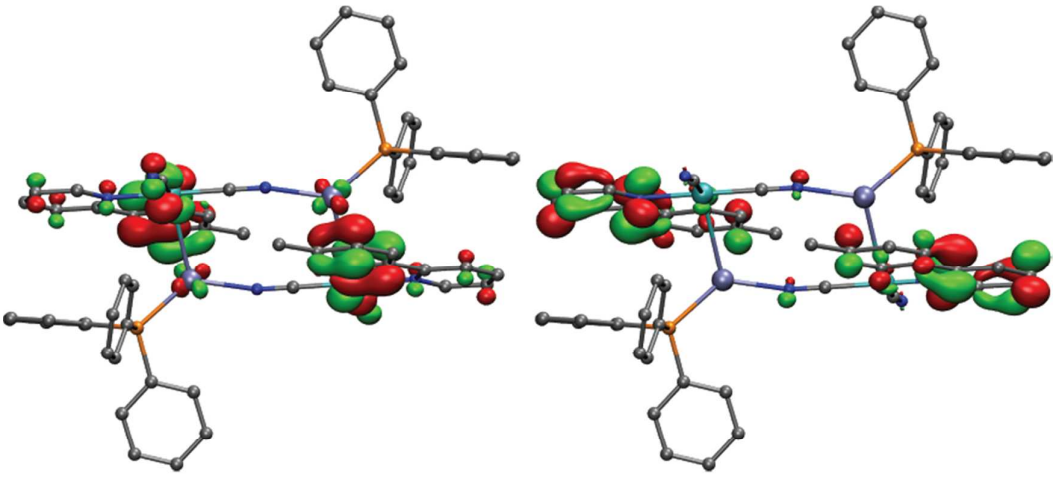

Figure S7. Frontier molecular orbitals of the complex **6** (isovalue 0.04 a.u.). Hydrogen atoms are omitted for clarity.