Electronic Supplementary Material (ESI) for CrystEngComm.

Solid-state and solution photoluminescence of platinum(II) complexes with 4'-substituted terpirydine ligands - structural, spectroscopic and electrochemical studies.

ELECTRONIC SUPLEMENTARY INFORMATION

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Experimental data of compounds (**1**) – (**3**)

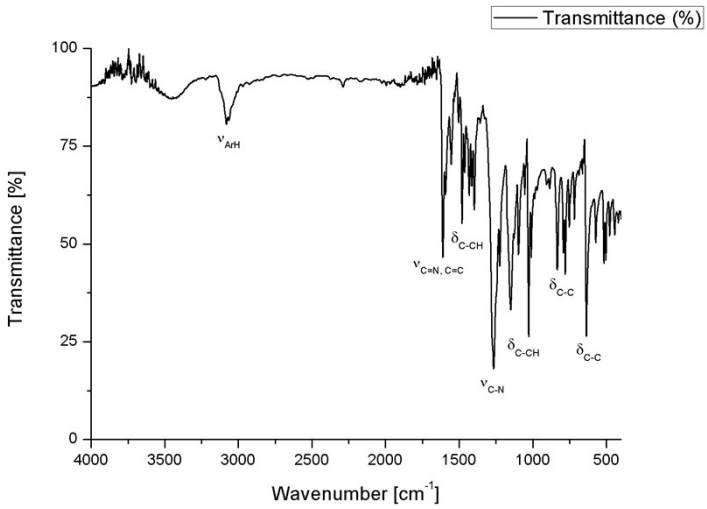
(**1**) [PtCl(L_1)]OTf: Yield 70%. $C_{21}H_{14}Cl_2N_3Pt$, CF_3O_3S. Anal. calc: C 36.53% H 1.95% N 5.81%. Anal. found: C 36.45% H 1.98% N 5.78%.

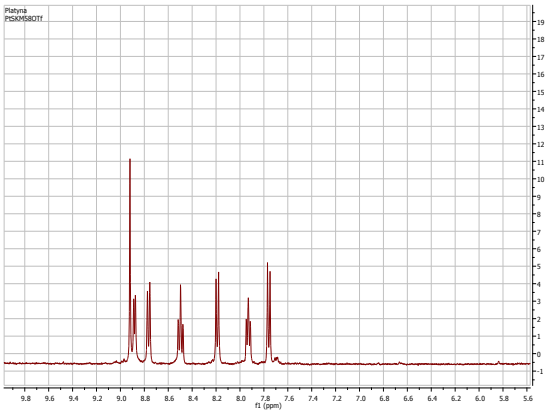
IR (KBr; cm^{-1}): 3082 $\nu_{(ArH)}$; 1610, 1554 $\nu_{(C=N,\ C=C)}$; 1480, 1397 $\delta_{(C–CH\ out\ of\ the\ plane)}$; 1265 $\nu_{(C–N)}$; 1149, 1027 $\delta_{(C–CH\ in\ the\ plane)}$; 833, 779, 751, 717 $\delta_{(C–C\ out\ of\ the\ plane)}$; 636 $\delta_{(C–C\ in\ the\ plane)}$.

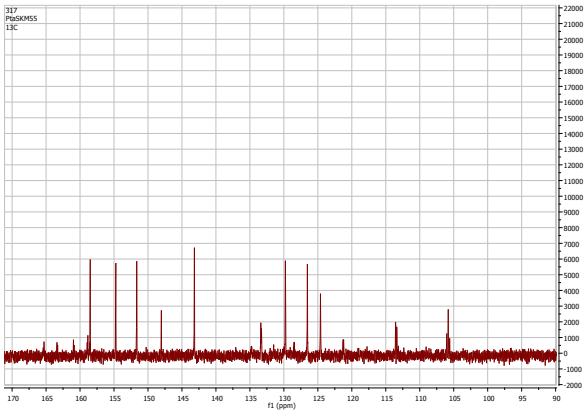
^{1}H NMR (400 MHz, DMSO) δ 8.92 (s, 2H), 8.88 (d, *J* = 5.3 Hz, 2H), 8.75 (t, *J* = 11.4 Hz, 2H), 8.54 – 8.43 (m, 2H), 8.18 (t, *J* = 10.3 Hz, 2H), 7.96 – 7.87 (m, 2H), 7.75 (t, *J* = 9.0 Hz, 2H).

^{13}C NMR (126 MHz, DMSO) δ 158.52, 154.92, 151.76, 143.02, 135.91, 133.65, 130.14, 130.00, 129.66, 126.45, 121.83.

UV-Vis (ACN, nm, (ε)): 404.5 (36000), 385.0 (30400), 352.4 (34800), 333.6 (107800), 307.3 (120400), 281.8 (155800), 260.1 (156200); (solid, nm (Abs)): 512.6(0.929), 426.4 (1.055), 346.6 (0.923), 252.5 (0.751).







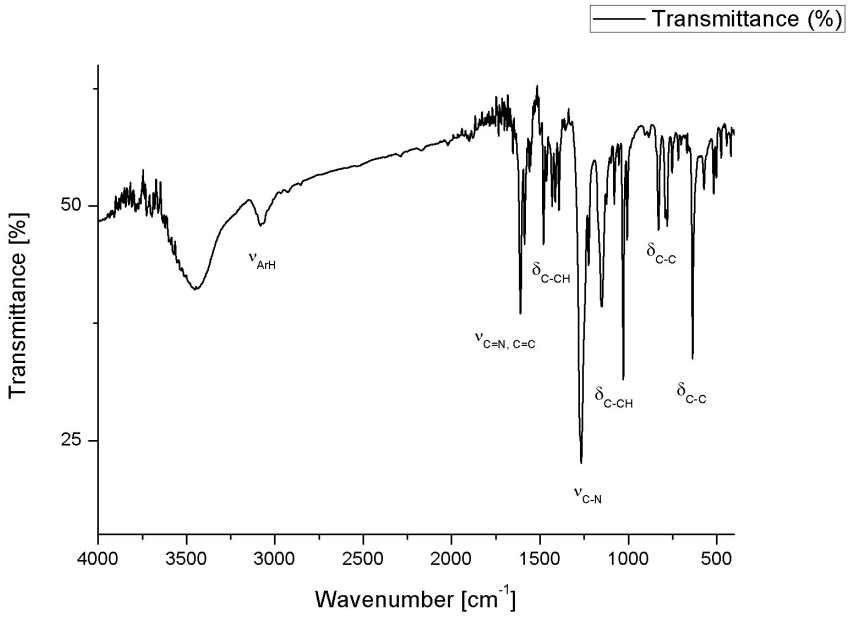
(**2**) [PtCl(L_2)]OTf: Yield 70%. $C_{21}H_{14}ClBrN_3Pt$, CF_3O_3S. Anal. calc: C 34.41% H 1.84% N 5.47%. Anal. found: C 34.50% H 1.80% N 5.43%.

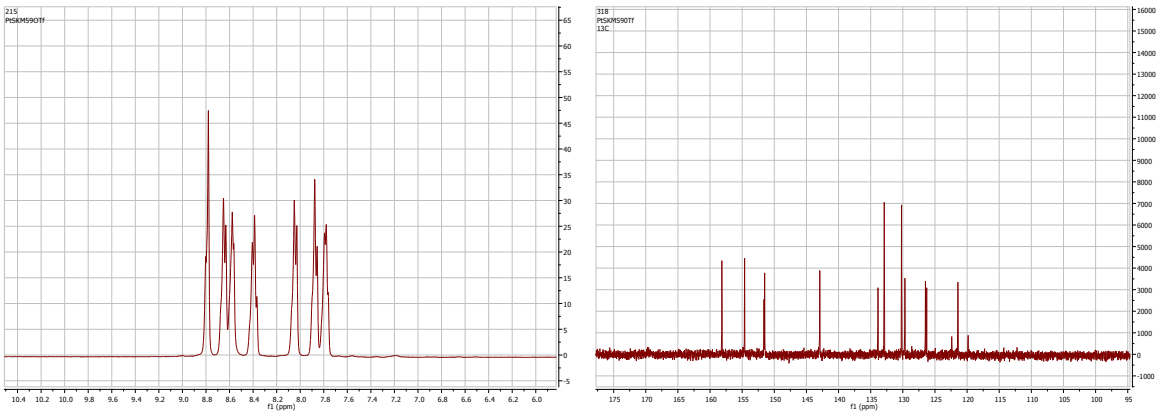
IR (KBr; cm^{-1}): 3082 $\nu_{(ArH)}$; 1611, 1587 $\nu_{(C=N,\ C=C)}$; 1479, 1414 $\delta_{(C–CH\ out\ of\ the\ plane)}$; 1247, 1224 $\nu_{(C–N)}$; 1149, 1029 $\delta_{(C–CH\ in\ the\ plane)}$; 829, 780, $\delta_{(C–C\ out\ of\ the\ plane)}$; 636 $\delta_{(C–C\ in\ the\ plane)}$.

^{1}H NMR (400 MHz, DMSO) δ 8.79 (d, *J* = 9.4 Hz, 2H), 8.61 (dd, *J* = 28.4, 6.3 Hz, 4H), 8.39 (t, *J* = 7.7 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.84 – 7.75 (m, 2H).

^{13}C NMR (126 MHz, DMSO) δ 158.16, 154.62, 151.61, 151.50, 142.92, 133.87, 132.89, 130.20, 129.67, 126.48, 126.28, 122.49, 121.43, 119.83.

UV-Vis (ACN, nm, (ε)): 404.2 (20800), 384.6 (17000), 331.9 (64800), 308.6 (68000), 281.6 (91000), 260.2 (88800); (solid, nm (Abs)): 513.6 (0.825), 422.8 (1.018), 343.7 (0.889), 252.8 (0.701).





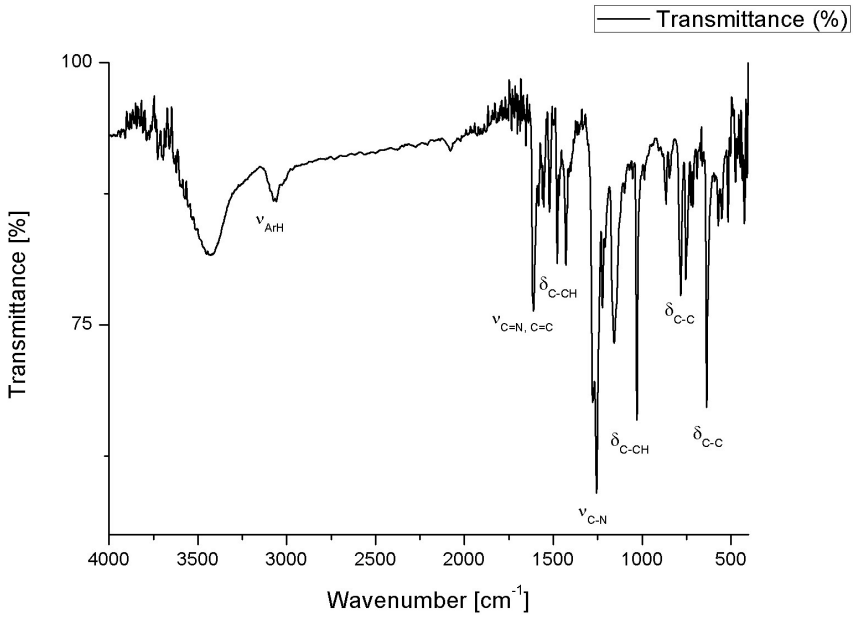
(**3**) [PtCl(L_3)]OTf: Yield 78%. $C_{23}H_{15}ClN_3PtS$, CF_3O_3S. Anal. calc: C 38.69% H 2.03% N 5.64%. Anal. found: C 38.75% H 2.12% N 5.58%.

IR (KBr; cm^{-1}): 3059 $\nu_{(ArH)}$; 1611, 1554 $\nu_{(C=N,\ C=C)}$; 1478, 1429 $\delta_{(C–CH\ out\ of\ the\ plane)}$; 1256, 1223 $\nu_{(C–N)}$; 1157, 1029 $\delta_{(C–CH\ in\ the\ plane)}$; 782, 754 $\delta_{(C–C\ out\ of\ the\ plane)}$; 637 $\delta_{(C–C\ in\ the\ plane)}$.

^{1}H NMR (400 MHz, DMSO) δ 8.63 (s, 2H), 8.43 (s, 2H), 8.35 (t, J = 7.5 Hz, 2H), 8.03 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 7.77 (s, 1H), 7.50 (dt, J = 14.7, 7.1 Hz, 4H).

^{13}C NMR (126 MHz, DMSO) δ 157.87, 154.56, 151.48, 146.37, 142.71, 141.11, 139.76, 138.29, 129.65, 128.39, 127.81, 126.45, 126.18, 125.71, 123.33, 122.48, 120.07.

UV-Vis (ACN, nm, (ε)): 423.3 (48000), 401.0 (34200), 323.4 (53600), 283.4 (81800), 255.0 (65600), 228.2 (67400), 207.5 (88000); (solid, nm (nm (Abs)): 592.1(0.774), 546.6 (0.889), 473.8 (1.135), 444.1 (1.147), 419.2 (1.140), 356.3 (1.059), 272.8 (0.943).



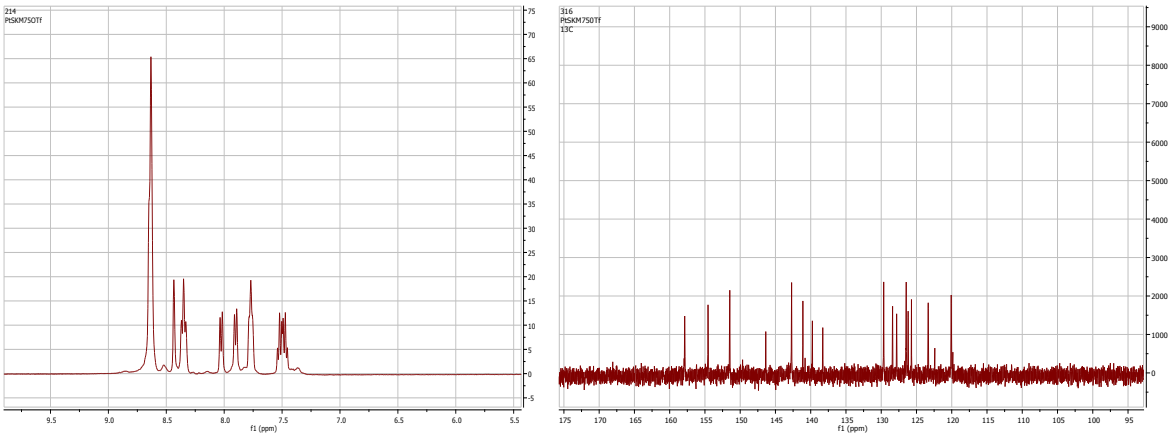


Table S1. Hydrogen bond for complex (**3**).

D-H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
		3		
C(2)-H(2)…O(3)	0.93	2.46	3.209(8)	137.7
C(4)-H(4)…O(2) #1	0.93	2.54	3.219(7)	130.1
C(7)-H(7)…S(1)	0.93	2.73	3.127(5)	106.5
C(9)-H(9)…O(1) #2	0.93	2.28	3.205(6)	174.5
C(12)-H(12)…O(1) #2	0.93	2.38	3.307(7)	172.2
C(17)-H(17)…O(1) #2	0.93	2.37	3.278(7)	166.0

Symmetry transformations used to generate equivalent atoms: #1: ½-x ,-½+y,½-z; #2: 1-x,1-y,-z

Table S2. Stacking interactions in complexes (**1**)-(**3**).

A. Short π–π interactions.

Cg(I)•••Cg(J)	Cg(I)•••Cg(J) [Å]	α[°]	β[°]	γ [°]	Cg(I)-Perp [Å]	Cg(J)-Perp [Å]
1: Cg(3): N(1)-C(1)-C(2)-C(3)-C(4)-C(5); Cg(5): N(3)-C(11)-C(12)-C(13)-C(14)-C(15); Cg(6):C(16)-C(17)-C(18)-C(19)-C(20)-C(21)						
Cg(3)•••Cg(5)[a]	3.929(3)	3.4(2)	31.80	28.47	-3.454(2)	-3.339(2)
Cg(3)•••Cg(6)[b]	3.688(3)	11.2(2)	15.31	17.89	-3.510(2)	3.557(2)
Cg(6)•••Cg(6)[c]	3.802(3)	0	14.58	14.58	3.680(2)	3.679(2)
2: Cg(3): N(1)-C(1)-C(2)-C(3)-C(4)-C(5); Cg(5): N(3)-C(11)-C(12)-C(13)-C(14)-C(15); Cg(6):C(16)-C(17)-C(18)-C(19)-C(20)-C(21)						
Cg(3)•••Cg(5)[d]	3.895(5)	3.2(5)	31.22	28.07	3.438(4)	3.331(4)
Cg(3)•••Cg(6)[e]	3.659(5)	10.4(5)	14.35	16.28	3.512(4)	-3.545(4)
Cg(6)•••Cg(6)[f]	3.846(6)	0	16.88	16.88	-3.681(4)	-3.681(4)
3: Cg(3): S(1)-C(16)-C(17)-C(18)-C(23); Cg(6): N(2)-C(6)-C(7)-C(8)-C(9)-C(10); Cg(6): N(3)-C(11)-C(12)-C(13)-C(14)-C(15); Cg(7):C(18)-C(19)-C(20)-C(21)-C(22)-C(23)						
Cg(3)•••Cg(5)[g]	3.572(3)	1.2(2)	16.06	16.89	3.4181(18)	3.4325(17)
Cg(5)•••Cg(7)[g]	3.967(3)	0.8(2)	30.88	30.29	3.4258(17)	3.405(2)
Cg(6)•••Cg(7)[g]	3.695(3)	1.7(3)	21.11	19.47	-3.483(2)	-3.447(2)

α = dihedral angle between *Cg*(I) and *Cg*(J); *Cg*(I)-Perp = Perpendicular distance of *Cg*(I) on ring J; *Cg*(J)-Perp = perpendicular distance of *Cg*(J) on ring I; β = angle *Cg*(I)→*Cg*(J) vector and normal to ring I; γ = angle *Cg*(I) →*Cg*(J) vector and normal to plane J;
Symmetry codes: (a) = -x, 1-y, -z; (b) = 1+x, y, z; (c) = -1-x, 1-y, 1-z; (d) = 1-x, 1-y, 2-z; (e) = -1+x, y, z; (f) = 2-x, 1-y, 1-z; (g) = 1-x, -y, -z.

B. C—X•••Cg(J) (π-ring) interactions for **1** and **2**.

Y-X(I)•••Cg(J)	X(I)•••Cg(J) [Å]	X-Perp [Å]	γ [°]	Y-X(I)•••Cg(J) [°]
1:Cg(4): N(2)-C(6)-C(7)-C(8)-C(9)-C(10); Cg(5): N(3)-C(11)-C(12)-C(13)-C(14)-C(15)				
Pt(1)-Cl(1)•••Cg(4)[a]	3.836(2)	-3.352	29.09	109.50(5)
C(22)-F(2)•••Cg(5)	3.253(6)	3.147	14.67	128.6(5)
2:Cg(4): N(2)-C(6)-C(7)-C(8)-C(9)-C(10); Cg(5): N(3)-C(11)-C(12)-C(13)-C(14)-C(15)				
Pt(1)-Cl(1)•••Cg(4)[b]	3.820(4)	3.364	28.32	108.40(10)
C(22)-F(2)•••Cg(5)	3.194(11)	-3.101	13.82	129.9(9)

γ = angle X(I)→Cg(J) vector and normal to plane J.
Symmetry codes: (a) = -x, 1-y, -z; (b) = 1-x, 1-y, 2-z

C. Ring-metal interactions for **1** and **2**.

Cg(I)•••Me(J)	Cg(I)•••Me(J) [Å]	MeJ-Perp [Å]	β [°]
3: Cg(7):C(18)-C(19)-C(20)-C(21)-C(22)-C(23)			
Cg(7)•••Pt(1)[a]	3.695	3.370	24.22

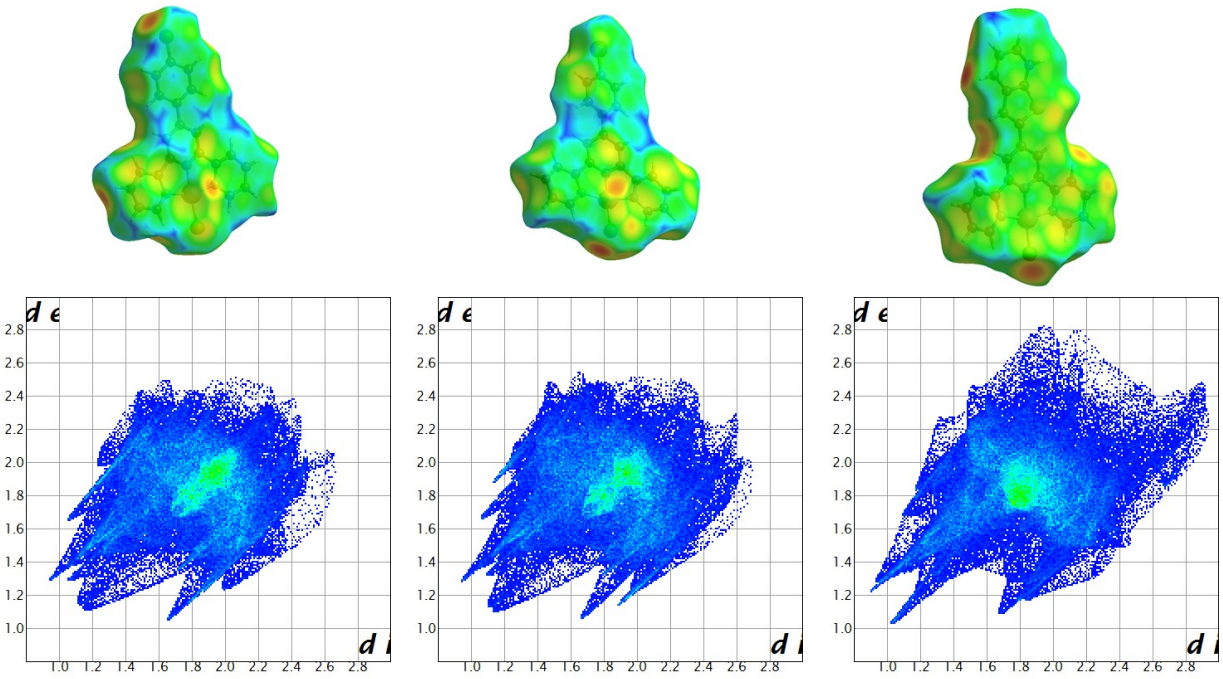
Symmetry codes: (a) = 1-x, 1-y, -z.

Table S3. Composition of selected LUMOs and HOMOs of $[PtCl(L)]^+$ cations.

	eV	R	terpy	Pt	Cl	eV	R	terpy	Pt	Cl	eV	R	terpy	Pt	Cl
	(**1**)					(**2**)					(**3**)				
L+10	-2.08	1	2	97	0	-2.02	1	2	97	0	-1.88	5	3	91	0
L+9	-2.27	97	2	1	0	-2.65	94	5	0	0	-2.65	73	27	1	0
L+8	-2.88	63	36	1	0	-2.85	62	37	1	0	-2.78	55	44	0	0
L+7	-3.0	3	97	0	0	-2.95	7	93	0	0	-2.83	57	42	1	0
L+6	-3.39	96	4	0	0	-3.34	96	4	0	0	-2.89	65	35	0	0
L+5	-4.29	22	77	1	0	-4.24	23	77	1	0	-4.27	17	83	0	0
L+4	-4.65	0	98	2	0	-4.6	0	97	2	0	-4.45	0	37	52	12
L+3	-4.72	0	36	52	12	-4.66	0	36	52	12	-4.46	0	97	3	0
L+2	-4.78	8	91	1	0	-4.74	9	90	1	0	-4.73	23	76	1	0
L+1	-5.76	1	98	1	0	-5.71	1	98	1	0	-5.55	1	98	1	0
LUMO	-6.15	6	87	6	1	-6.1	6	87	6	1	-5.99	12	81	6	1
HOMO	-9.36	39	11	20	31	-9.2	64	9	12	15	-8.72	86	6	4	3
H-1	-9.73	50	8	8	33	-9.55	29	8	17	47	-9.02	68	7	11	14
H-2	-9.81	0	5	18	77	-9.75	0	5	18	77	-9.42	31	9	14	46
H-3	-10.15	99	1	0	0	-10.09	99	1	1	0	-9.56	0	5	18	77
H-4	-10.25	0	3	95	2	-10.17	0	3	95	2	-9.95	0	3	95	2
H-5	-10.29	1	61	39	0	-10.22	100	0	0	0	-10.05	1	52	47	0
H-6	-10.62	0	72	28	0	-10.23	1	59	40	0	-10.41	4	75	21	0
H-7	-11.04	32	35	15	17	-10.57	0	73	27	0	-10.57	86	8	2	3
H-8	-11.06	77	13	5	5	-10.83	49	23	11	17	-10.83	16	40	22	21
H-9	-11.33	24	68	6	2	-11.12	20	69	5	5	-11.14	21	71	6	2
H-10	-11.52	0	20	13	66	-11.46	0	20	13	66	-11.26	1	20	13	66

Table S4. Selected calculated transitions for complexes (**1**) – (**3**)

λ_{calc} [nm]	*f*	Transition	Character	λ_{exp} [nm]
			[Pt(L$_1$)Cl]$^+$	
422.0	*0.1765*	*HOMO→LUMO (93%)*	*π_R (39%) + π_{Cl} (31%) + d_{Pt} (20%) + π_{core} (11%)→ π^*_{core} (87%) ILCT/XLCT/MLCT*	
401.1	0.0059	H-2→LUMO (99%)	π_{Cl} (77%) + d_{Pt} (18%) → π^*_{core} (87%)	404.2
376.7	0.0130	HOMO→L+1 (94%)	π_R (39%) + π_{Cl} (31%) + d_{Pt} (20%) + π_{core} (11%) → π^*_{core} (98%)	384.6
343.4	0.2075	H-4→LUMO (93%)	d_{Pt} (95%) → π^*_{core} (87%)	331.9
327.3	0.0265	H-1→L+5 (64%), H-2→L+1 (26%)	π_R (50%) + π_{Cl} (33%) → π^*_{core} (77%) + π^*_R (22%) π_{Cl} (77%) + d_{Pt} (18%) → π^*_{core} (93%)	331.9
320.3	0.3312	H-5→LUMO (81%)	π_{core} (61%) + d_{Pt} (39%)→ π^*_{core} (87%)	308.6
294.7	0.1414	HOMO→L+2 (91%)	π_R (39%) + π_{Cl} (31%) + d_{Pt} (20%) + π_{core} (11%) → π^*_{core} (91%)	
274.9	0.4123	H-5→L+1 (61%), H-6→L+1 (16%)	π_{core} (61%) + d_{Pt} (39%)→ π^*_{core} (93%) π_{core} (72%) + d_{Pt} (28%)→ π^*_{core} (93%)	281.6
265.3	0.2981	H-2→L+2 (85%)	π_{Cl} (77%) + d_{Pt} (18%) → π^*_{core} (91%)	
261.5	0.1528	HOMO→L+4 (92%)	π_R (39%) + π_{Cl} (31%) + d_{Pt} (20%) + π_{core} (11%)→ π^*_{core} (98%)	260.2
			[Pt(L$_2$)Cl]$^+$	
423.4	0.1999	HOMO→LUMO (92%)	π_R (64%) + π_{Cl} (15%) + d_{Pt} (12%) + π_{core} (9%)→ π^*_{core} (87%)	
401.0	0.0059	H-2→LUMO (99%)	π_{Cl} (77%) + d_{Pt} (18%) → π^*_{core} (87%)	404.5
377.7	*0.0124*	*HOMO→L+1 (93%)*	*π_R (64%) + π_{Cl} (15%) + d_{Pt} (12%) + π_{core} (9%)→ π^*_{core} (98%) ILCT/XLCT/MLCT*	385.0
352.6	0.1871	H-3→LUMO (92%)	π_R (99%) → π^*_{core} (87%)	352.4
327.3	0.0311	H-1→L+5 (66%), H-2→L+1 (25%)	π_{Cl} (47%) + π_R (29%) + d_{Pt} (17%) + π_{core} (8%)→ π^*_{core} (77%) + π^*_R (23%) π_{Cl} (77%) + d_{Pt} (18%) → π^*_{core} (98%)	333.6
315.1	0.0184	H-5→LUMO (71%), H-6→LUMO (26%)	π_R (100%) → π^*_{core} (87%) π_{core} (59%) + d_{Pt} (12%) → π^*_{core} (87%)	
306.6	0.0	HOMO→L+5 (82%)	π_R (64%) + π_{Cl} (15%) + d_{Pt} (12%) + π_{core} (9%)→ π^*_{core} (77%) + π^*_R (23%)	307.3
295.6	0.1694	HOMO→L+2 (91%)	π_R (64%) + π_{Cl} (15%) + d_{Pt} (12%) + π_{core} (9%)→ π^*_{core} (90%)	
275.3	0.436	H-6→L+1 (67%)	π_{core} (59%) + d_{Pt} (12%) → π^*_{core} (98%)	281.8
257.3	0.2535	H-9→LUMO (68%), H-3→L+2 (23%)	π_{core} (69%) + π_R (20%)→ π^*_{core} (87%) π_R (99%)→ π^*_{core} (90%)	260.1
			[Pt(L$_3$)Cl]$^+$	
466.1	*0.3595*	*HOMO→LUMO (97%)*	*π_R (86%) → π^*_{core} (81%) ILCT*	
426.3	0.0797	H-1→LUMO (93%)	π_R (68%) + π_{Cl} (14%) + d_{Pt} (11%) → π^*_{core} (81%)	423.3
409.8	0.0172	HOMO→L+1 (82%), H-4→LUMO (11%)	π_R (86%) → π^*_{core} (98%) d_{Pt} (95%) → π^*_{core} (81%)	401.0
324.0	0.4521	HOMO→L+2 (76%), H-2→L+5 (12%)	π_R (86%) → π^*_{core} (76%) + π^*_R (23%) π_{Cl} (46%) + π_R (31%) + d_{Pt} (11%) → π^*_{core} (83%) + π^*_R (17%)	323.4
288.4	0.1932	HOMO→L+4 (69%), H-5→L+5 (13%)	π_R (86%) → d_{Pt} (52%) + π^*_{core} (37%) π_{core} (52%) + d_{Pt} (47%) → π^*_{core} (83%) + π^*_R (17%)	283.4
254.6	0.1082	H-9→LUMO (76%)	π_{core} (71%) + π_R (21%)→ π^*_{core} (81%)	255.0
231.1	0.0358	H-9→L+1 (79%)	π_{core} (71%) + π_R (21%)→ π^*_{core} (98%)	228.2
225.8	0.0001	H-6→L+5 (92%)	π_{core} (75%) + d_{Pt} (21%)→ π^*_{core} (83%)	
209.7	0.2414	H-1→L+6 (37%), H-1→L+7 (26%)	π_R (68%) + π_{Cl} (14%) + d_{Pt} (11%) → π^*_R (65%) +π^*_{core} (35%) π_R (68%) + π_{Cl} (14%) + d_{Pt} (11%) → π^*_R (57%) +π^*_{core} (42%)	207.5



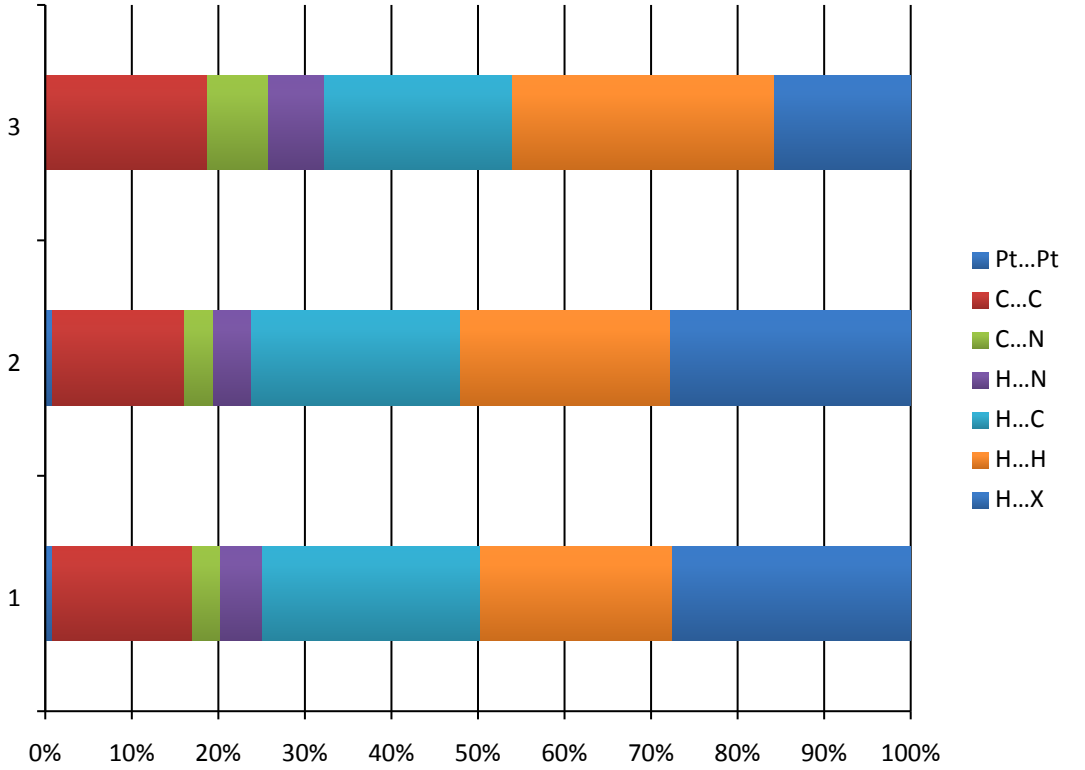


Figure S1. 2D Fingerprint plots, coordination cations Hirshfeld surfaces and percentage contributions to the surface area for the various close intermolecular contacts for molecules of (**1**), (**2**) and (**3**) complexes. Percentages are given on the histogram only for the major atom-type/atom-type contacts.

Figure S2. Density of states diagrams calculated for cationic forms of compounds (**1**)–(**3**)

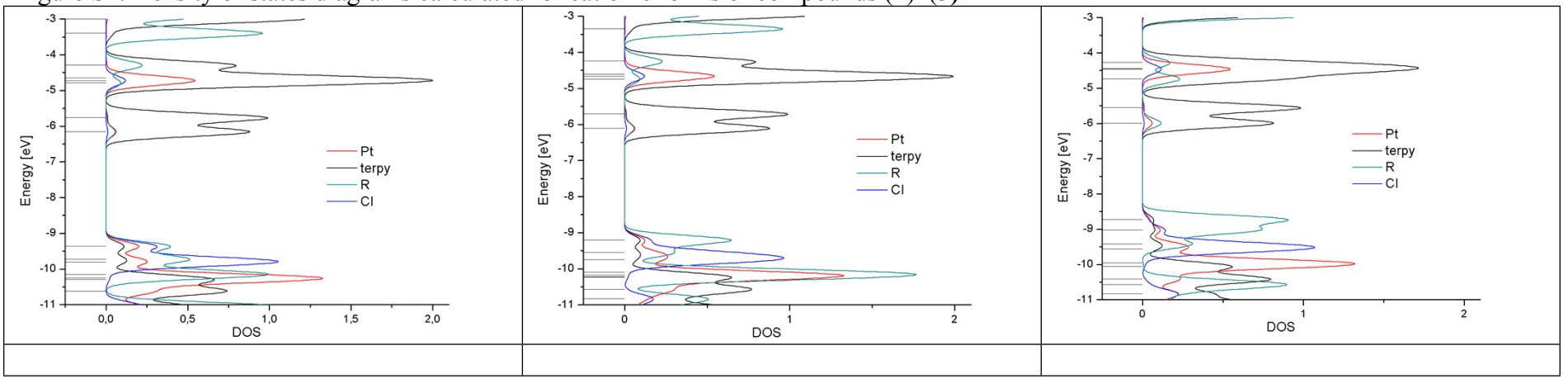


Figure S3. Excitation and emission spectra in the form normalized intensity vs. wavelength of compounds (**1**)–(**3**)

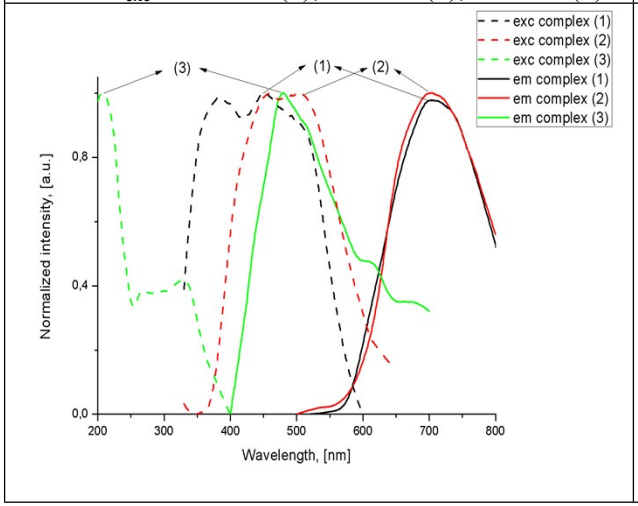
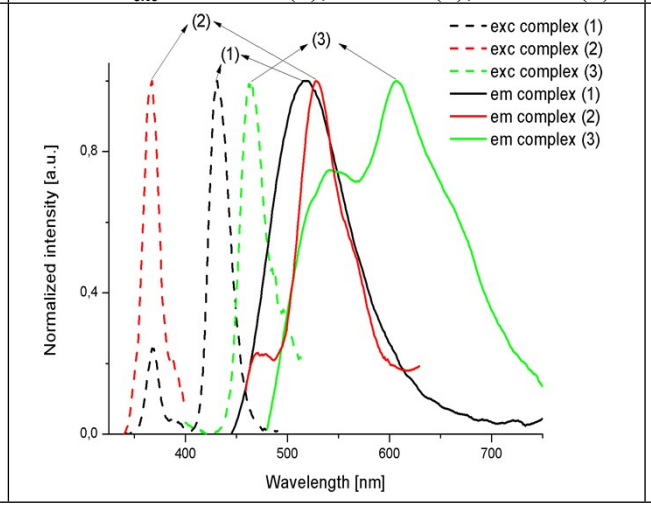
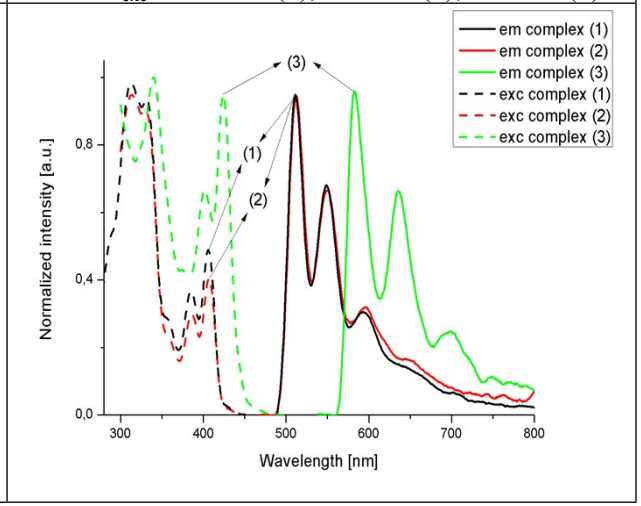
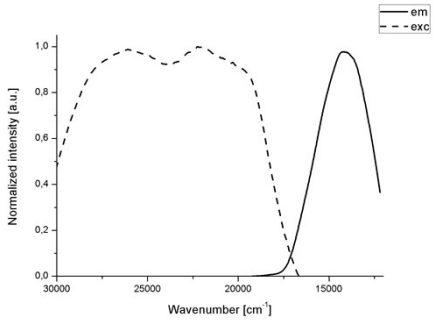
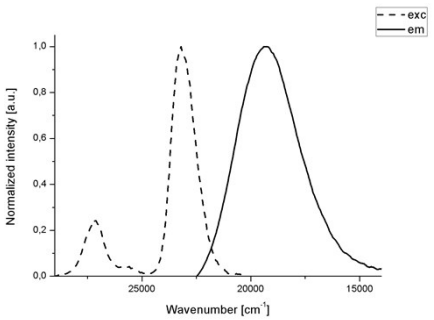
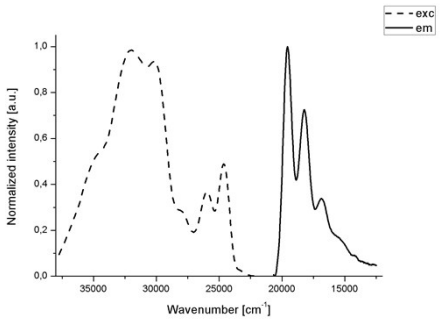
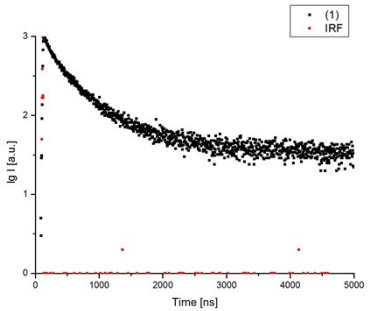
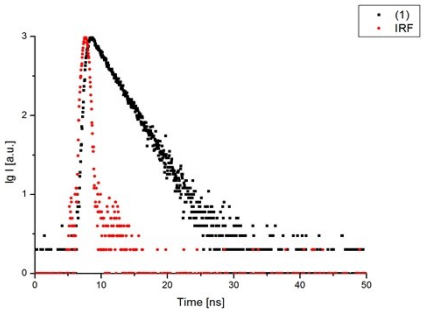
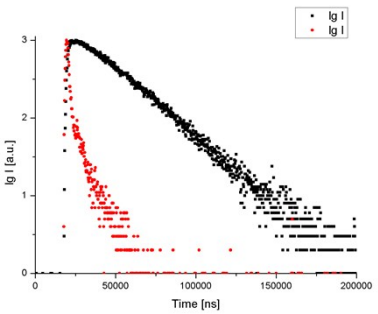
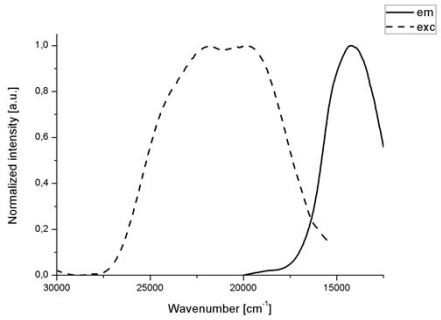
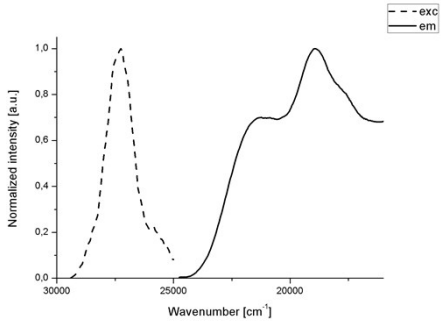
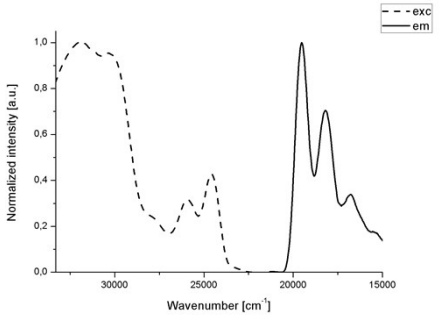
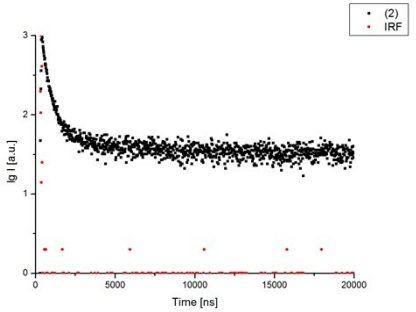
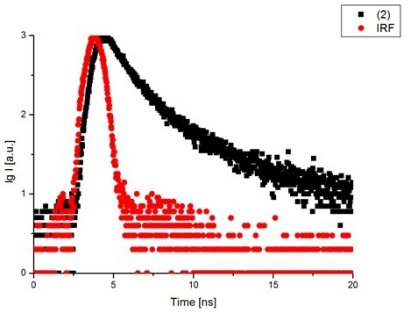
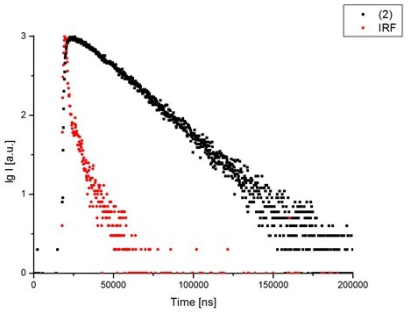
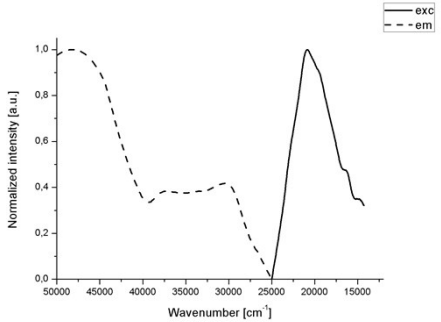
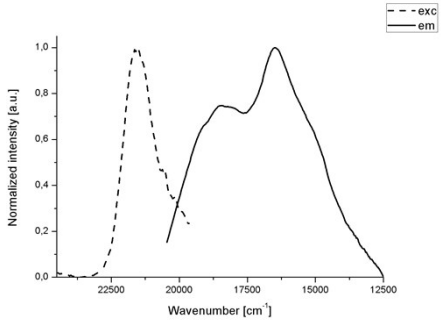
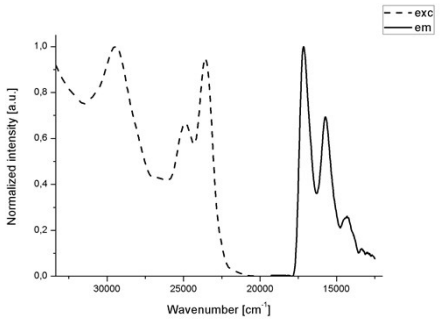
Solid: λ_{exc} = 480 nm (**1**); 500 nm (**2**); 330 nm (**3**)	ACN: λ_{exc} = 430 nm (**1**); 365 nm (**2**); 465 nm (**3**)	77K: λ_{exc} = 405 nm (**1**); 405 nm (**2**); 425 nm (**3**)
		

Figure S4. Excitation and emission spectra with decay curves for compounds.

Complex	solid	ACN	77K
(1)			
			
	τ_1 = 188.18 [ns] (29.99%), τ_2 = 628.31 [ns] (70.01%); χ^2 = 1.045	τ_1 = 3.01 [ns] (100%); χ^2 = 1.095	τ_1 = 23693.0 [ns] (100%); χ^2 = 1.057

(2)			
			
	τ_1 = 16.36 [ns] (6.40%), τ_1 = 296.31 [ns] (64.72%), τ_2 = 2177.15 [ns] (28.89%); χ^2 = 1.046	τ_1 = 1.05 [ns] (64.68%), τ_2 = 3.01 [ns] (35.32%); χ^2 = 0.997	τ_1 = 23389.4 [ns] (100%); χ^2 = 1.024
(3)			

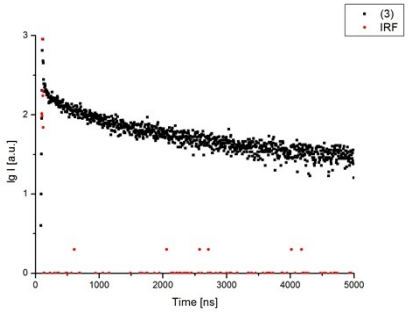
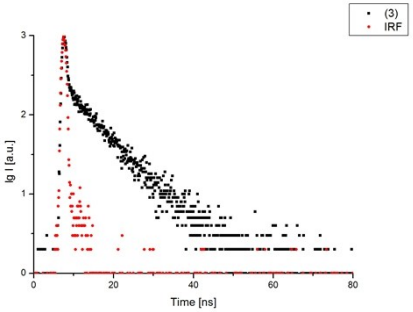
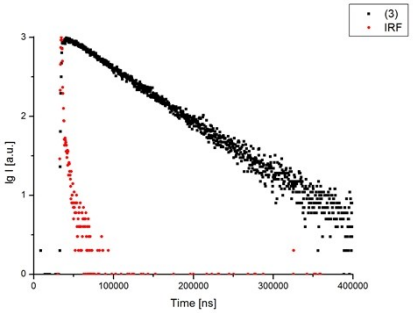
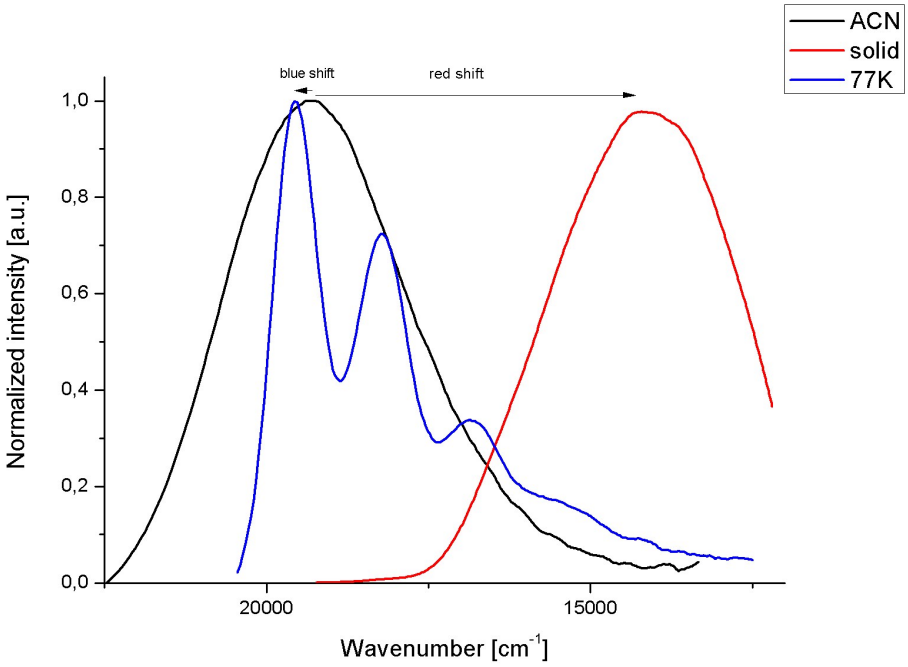
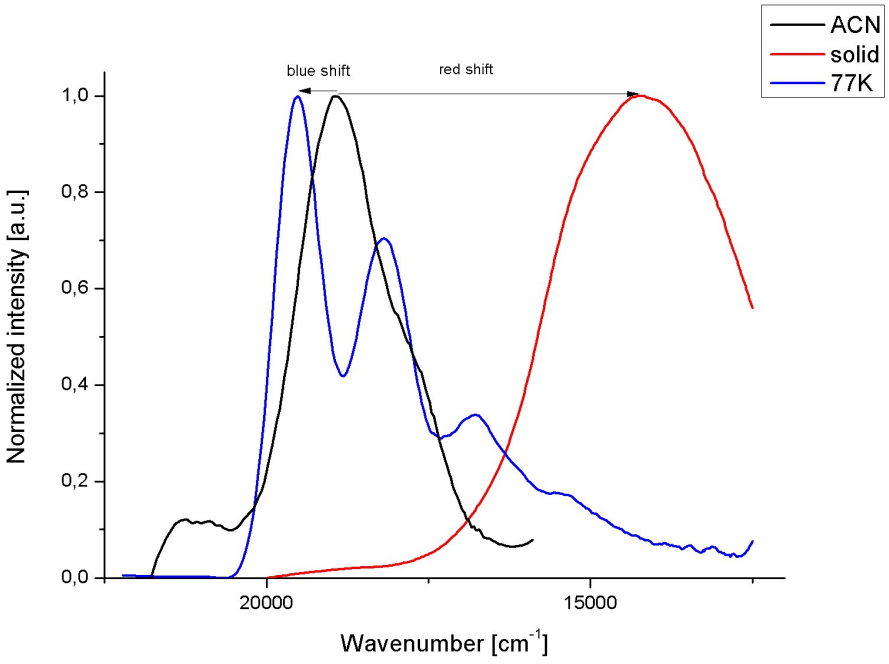
			
	τ_1 = 14.57 [ns] (20.11%), τ_1 = 267.86 [ns] (8.06%), τ_2 = 1624.00 [ns] (71.83%); χ^2 = 1.092	τ_1 = 0.09 [ns] (35.77%); τ_2 = 7.65 [ns] (64.23%) χ^2 = 1.051	τ_2 = 62434.3 [ns] (100%); χ^2 = 1.116

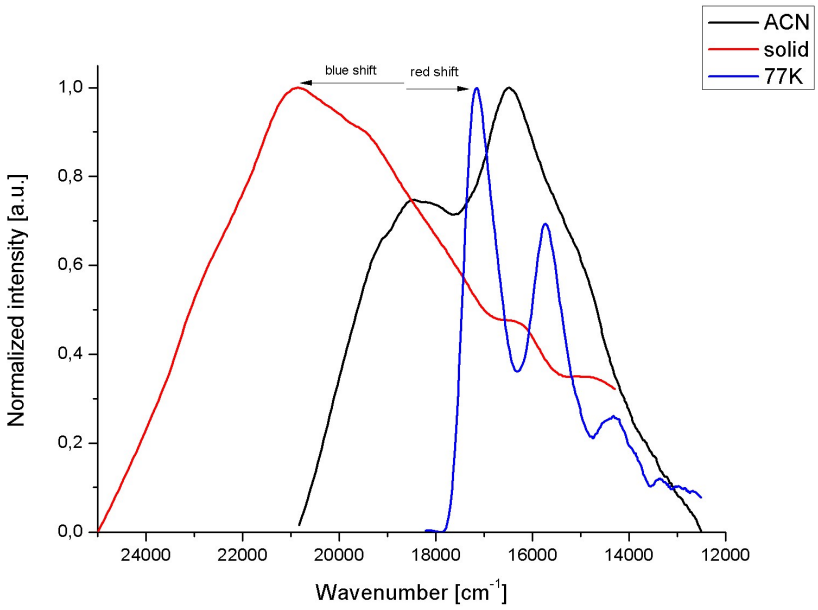
Figure S5. Comparison of emission spectra of complexes at different conditions (acetonitrile solution - black line, solid (powder)- red line, 77K –blue line)



(1)



(2)


ACN
solid
77K
blue shift
red shift
Normalized intensity [a.u.]
1,0
0,8
0,6
0,4
0,2
0,0
24000
22000
20000
18000
16000
14000
12000
Wavenumber [cm-1]

(3)