Supplementary Information

1. NMR Spectroscopy

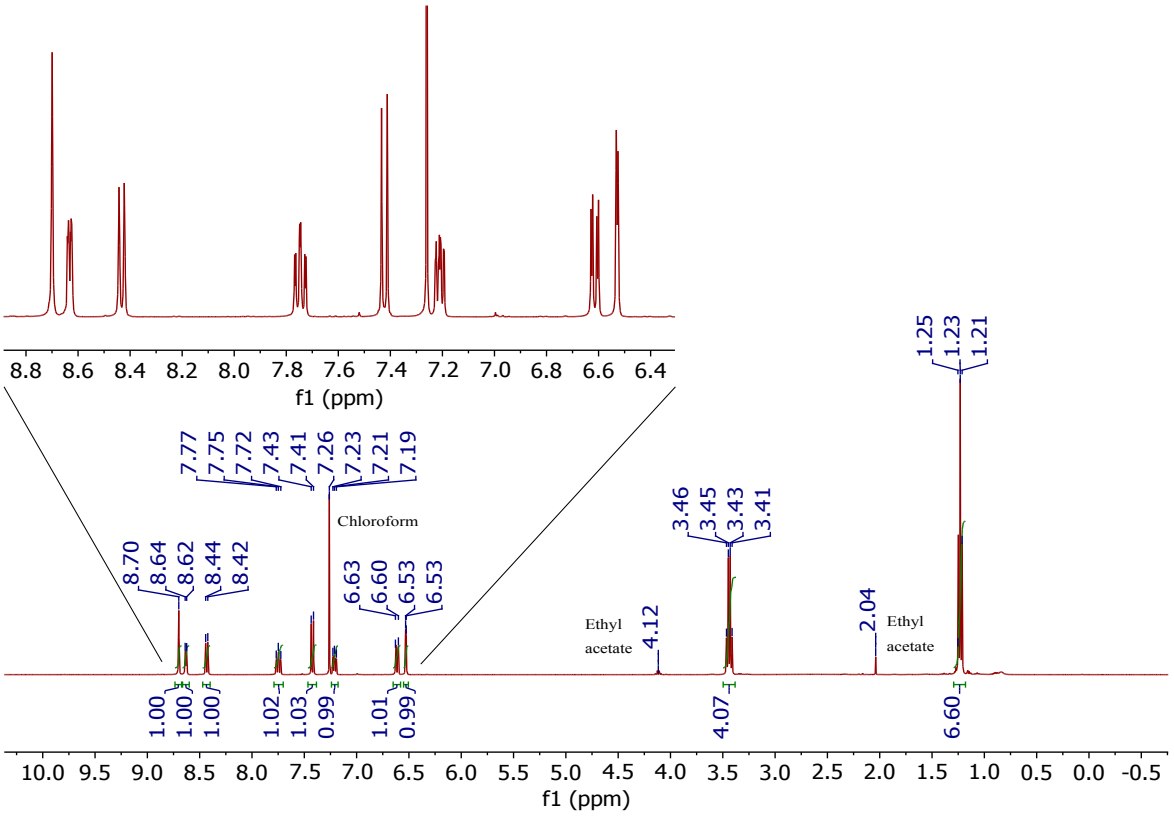

Figure S1. ^{1}H-NMR spectrum of ligand **L1** in $CDCl_3$.

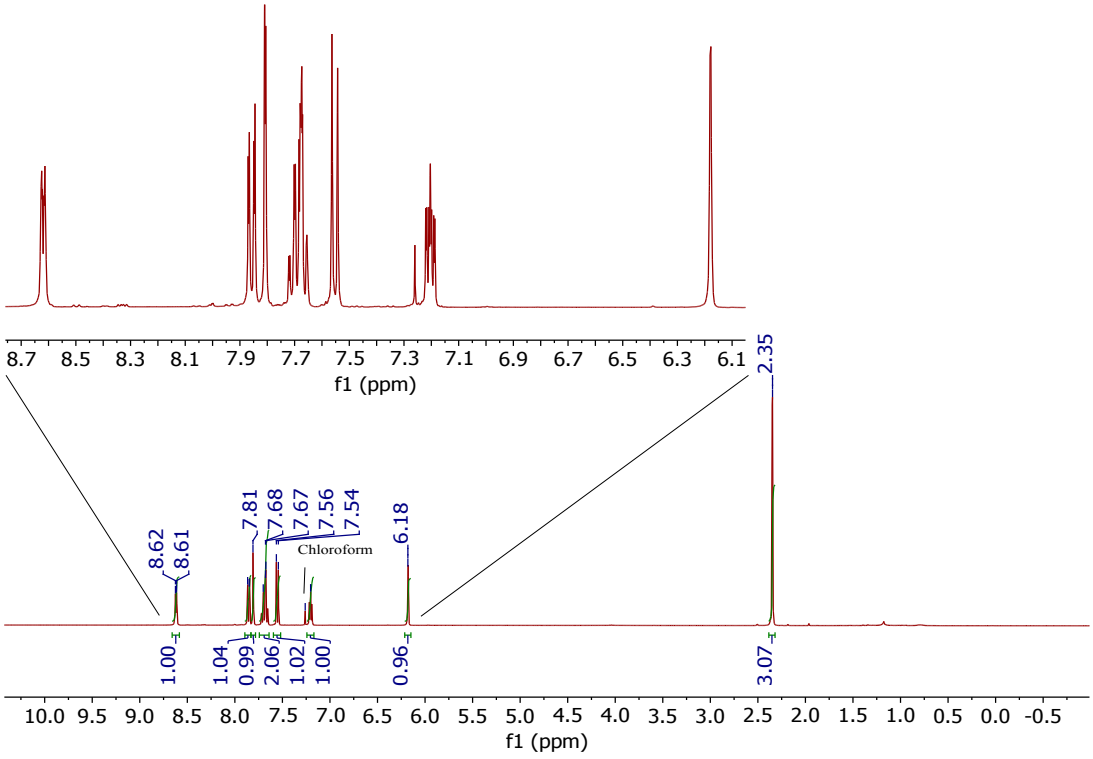

Figure S2. ^{1}H-NMR spectrum of ligand **L2** in $CDCl_3$.

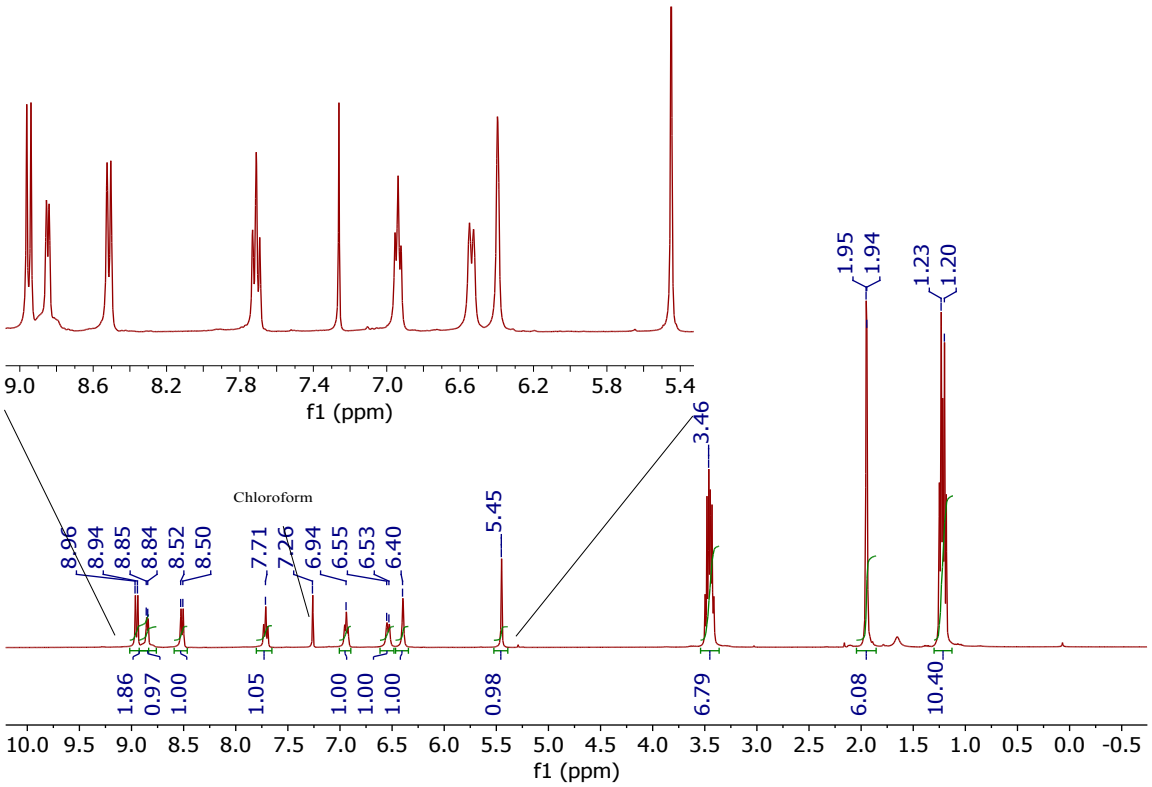

Figure S3. ^{1}H-NMR spectrum of complex **1** in $CDCl_3$.

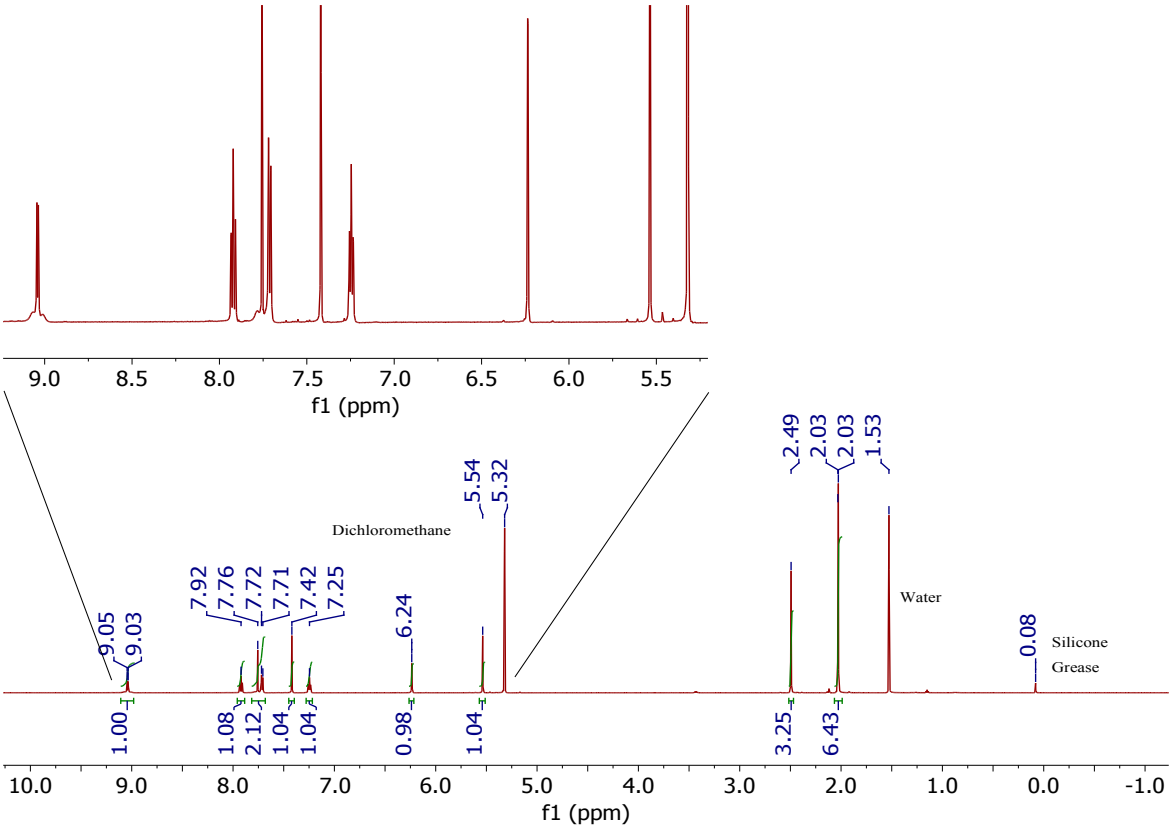

Figure S4. ^{1}H-NMR spectrum of complex **2** in CD_2Cl_2.

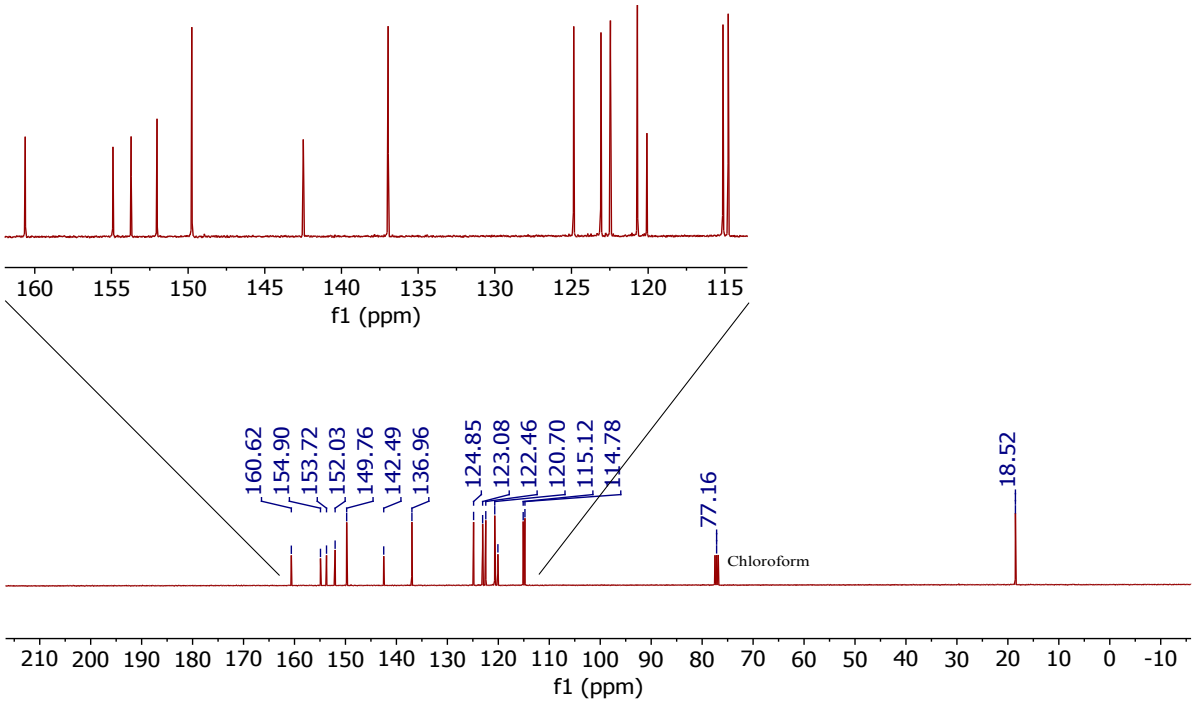

Figure S5. ^{13}C-NMR spectrum of ligand **L2** in $CDCl_3$.

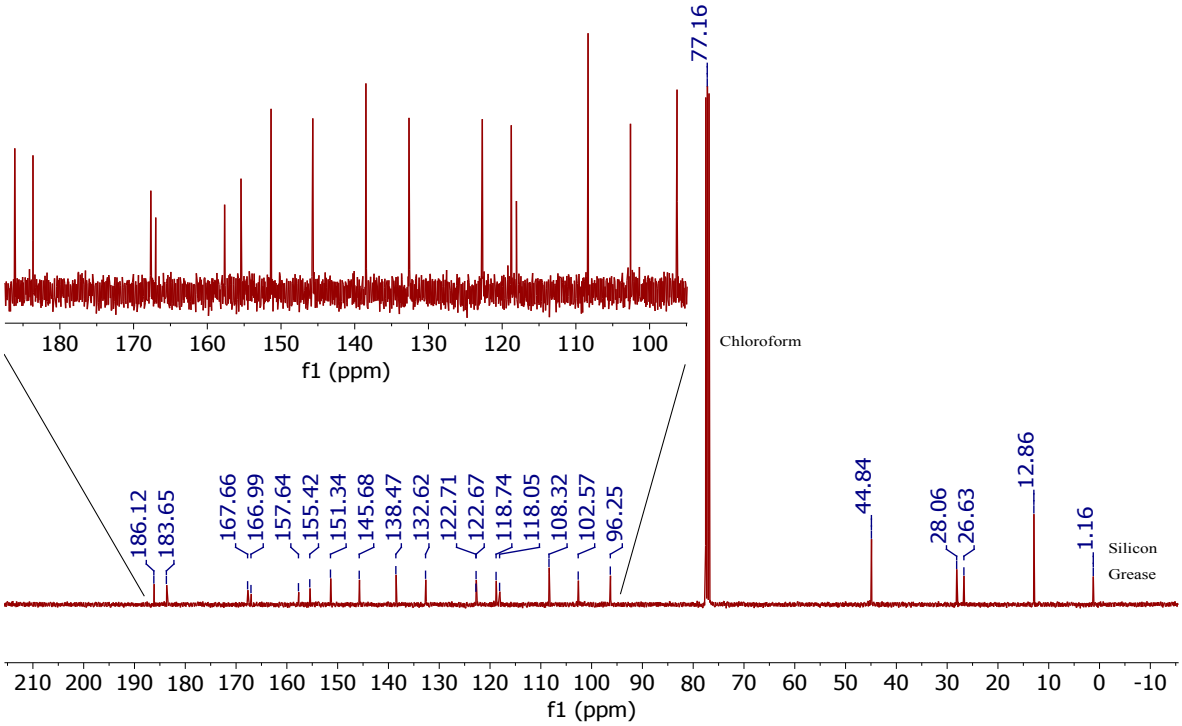

Figure S6. ^{13}C-NMR spectrum of complex 1 in $CDCl_3$.

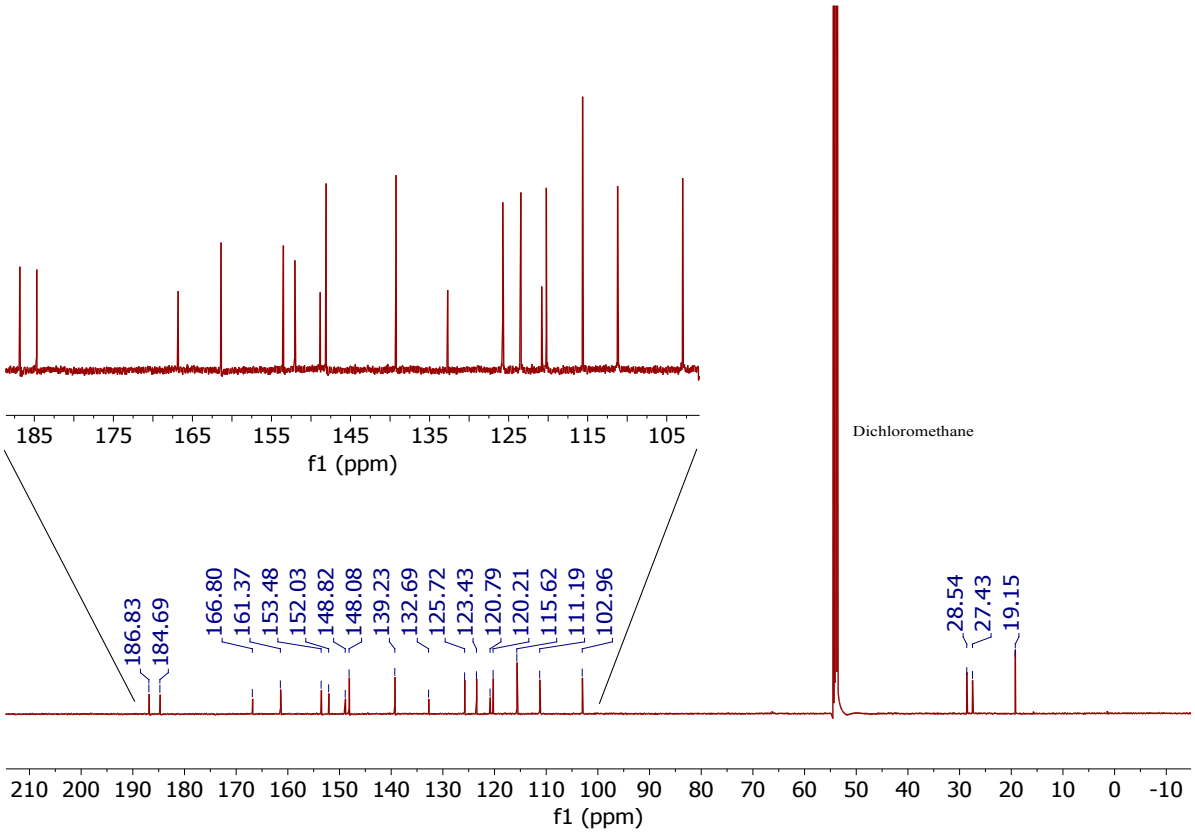

Figure S7. ^{13}C-NMR spectrum of complex **2** in CD_2Cl_2.

2. Crystallographic Data

Table S1. Crystal data and structure refinement for complexes 1 and 2.

	Complex 1	**Complex 2**
Empirical formula	$C_{23}H_{24}N_2O_4Pt$	$C_{20}H_{17}NO_4Pt$
Formula weight	587.53	530.44
Crystal size	0.3 x 0.4 x 0.5 mm	0.4 x 0.3 x 0.2 mm
Color	red	orange
Habit	plate	block
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/c$
Unit cell dimensions [Å], [°]	a = 7.6251(15), α = 80.47(3)	a = 8.2099(16), α = 90
	b = 11.565(2), β = 76.46(3)	b = 11.547(2), β = 111.91(3)
	c = 11.953(2), γ = 86.57(3)	c = 19.235(5), γ = 90
Volume [Å^3]	1010.4(3)	1691.8(6)
Formula units per cell Z	2	4
Calculated density [g/cm^3]	1.931	2.083
Absorption coefficient [mm^{-1}]	6.977	8.320
F(000)	572	1016

Table S1. *Cont.*

	Complex 1	**Complex 2**
Temperature [K]	99 (2)	100 (2)
Wavelength Mo K_α λ [Å]	0.71073	0.71073
Effective range for data collection θ [°]	1.77 to 26.74	2.10 to 26.92
Completeness to θ [%]	99.1	98.3
Limiting indices	$-9 \le h \le 9$, $-14 \le k \le 14$, $-15 \le l \le 15$	$-10 \le h \le 10$, $-14 \le k \le 14$, $-24 \le l \le 24$
Collected reflections	13661	24804
Unique reflections	4254 [R(int) = 0.0928]	3602 [R(int) = 0.1516]
Data with $I > 2/\sigma(I)$		
Max. and min. transmission	0.5853 and 0.3701	0.6133 and 0.3000
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4254 / 0 / 273	3602 / 0 / 238
Goodness-of-fit on F^2	1.120	1.096
Final R indices [$I > 2/\sigma(I)$]	$R_1 = 0.0382$, $wR_2 = 0.0848$	$R_1 = 0.0645$, $wR_2 = 0.1457$
R indices (all data)	$R_1 = 0.0432$, $wR_2 = 0.0865$	$R_1 = 0.0824$, $wR_2 = 0.1646$
Absorption correction	Integration	Integration
Largest diff. peak and hole [e / Å^3]	3.860 and -3.615	5.702 and -3.545

Table S2. List of bond lengths and bond angles of complex 1.

Bond lengths [Å]		**Angles [°]**	
Pt(1)-N(2)	1.974(5)	N(2)-Pt(1)-C(7)	81.3(2)
Pt(1)-C(7)	1.978(6)	N(2)-Pt(1)-O(3)	176.67(16)
Pt(1)-O(3)	2.013(4)	C(7)-Pt(1)-O(3)	98.98(19)
Pt(1)-O(4)	2.072(4)	N(2)-Pt(1)-O(4)	89.64(18)
O(1)-C(13)	1.379(7)	C(7)-Pt(1)-O(4)	170.40(18)
O(1)-C(14)	1.382(7)	O(3)-Pt(1)-O(4)	89.91(16)
N(1)-C(11)	1.366(7)	C(13)-O(1)-C(14)	121.2(4)
N(1)-C(17)	1.453(7)	C(11)-N(1)-C(17)	121.9(5)
N(1)-C(15)	1.461(7)	C(11)-N(1)-C(15)	121.6(5)
C(1)-N(2)	1.332(8)	C(17)-N(1)-C(15)	116.2(5)
C(1)-C(2)	1.383(8)	N(2)-C(1)-C(2)	123.4(5)
O(2)-C(14)	1.221(7)	C(1)-N(2)-C(5)	119.9(5)
N(2)-C(5)	1.379(7)	C(1)-N(2)-Pt(1)	123.9(4)
C(2)-C(3)	1.392(8)	C(5)-N(2)-Pt(1)	116.3(4)
O(3)-C(20)	1.292(7)	C(1)-C(2)-C(3)	118.2(5)
C(3)-C(4)	1.396(8)	C(20)-O(3)-Pt(1)	125.4(4)
O(4)-C(22)	1.279(7)	C(2)-C(3)-C(4)	119.4(5)
C(4)-C(5)	1.408(8)	C(22)-O(4)-Pt(1)	126.1(4)
C(5)-C(6)	1.449(8)	C(3)-C(4)-C(5)	119.8(5)
C(6)-C(7)	1.372(8)	N(2)-C(5)-C(4)	119.3(5)
C(6)-C(14)	1.446(7)	N(2)-C(5)-C(6)	112.0(4)
C(7)-C(8)	1.465(7)	C(4)-C(5)-C(6)	128.7(5)
C(8)-C(9)	1.396(8)	C(7)-C(6)-C(14)	124.2(5)
C(8)-C(13)	1.416(7)	C(7)-C(6)-C(5)	116.3(5)
C(9)-C(10)	1.380(8)	C(14)-C(6)-C(5)	119.4(5)
C(10)-C(11)	1.428(7)	C(6)-C(7)-C(8)	116.8(5)

Table S2. *Cont.*

Bond lengths [Å]		Angles [°]	
C(11)-C(12)	1.408(8)	C(6)-C(7)-Pt(1)	114.0(4)
C(12)-C(13)	1.382(8)	C(8)-C(7)-Pt(1)	129.2(4)
C(15)-C(16)	1.519(9)	C(9)-C(8)-C(13)	115.4(5)
C(17)-C(18)	1.535(8)	C(9)-C(8)-C(7)	126.4(5)
C(19)-C(20)	1.509(8)	C(13)-C(8)-C(7)	118.3(5)
C(20)-C(21)	1.387(8)	C(10)-C(9)-C(8)	122.8(5)
C(21)-C(22)	1.393(8)	C(9)-C(10)-C(11)	121.3(5)
C(22)-C(23)	1.499(8)	N(1)-C(11)-C(12)	122.2(5)
		N(1)-C(11)-C(10)	121.3(5)
		C(12)-C(11)-C(10)	116.5(5)
		C(13)-C(12)-C(11)	120.8(5)
		O(1)-C(13)-C(12)	114.6(5)
		O(1)-C(13)-C(8)	122.2(5)
		C(12)-C(13)-C(8)	123.2(5)
		O(2)-C(14)-O(1)	114.7(5)
		O(2)-C(14)-C(6)	128.3(5)
		O(1)-C(14)-C(6)	117.1(5)
		N(1)-C(15)-C(16)	112.8(5)
		N(1)-C(17)-C(18)	113.3(5)
		O(3)-C(20)-C(21)	127.6(5)
		O(3)-C(20)-C(19)	113.0(5)
		C(21)-C(20)-C(19)	119.4(5)
		C(20)-C(21)-C(22)	125.5(5)
		O(4)-C(22)-C(21)	125.4(5)
		O(4)-C(22)-C(23)	114.7(5)
		C(21)-C(22)-C(23)	119.9(5)

Table S3. List of bond lengths and bond angles of complex **2**.

Bond lengths [Å]		Angles [°]	
Pt(1)-C(7)	1.965(11)	C(7)-Pt(1)-N(1)	82.4(4)
Pt(1)-N(1)	1.983(9)	C(7)-Pt(1)-O(3)	91.2(4)
Pt(1)-O(3)	2.010(9)	N(1)-Pt(1)-O(3)	173.6(3)
Pt(1)-O(4)	2.089(8)	C(7)-Pt(1)-O(4)	175.9(4)
O(1)-C(14)	1.371(13)	N(1)-Pt(1)-O(4)	93.5(3)
O(1)-C(10)	1.395(11)	O(3)-Pt(1)-O(4)	92.9(3)
O(2)-C(14)	1.241(14)	C(14)-O(1)-C(10)	120.2(9)
O(3)-C(17)	1.284(13)	C(17)-O(3)-Pt(1)	124.0(8)
O(4)-C(19)	1.283(14)	C(19)-O(4)-Pt(1)	123.3(7)
N(1)-C(1)	1.303(15)	C(1)-N(1)-C(5)	120.1(10)
N(1)-C(5)	1.380(12)	C(1)-N(1)-Pt(1)	123.2(8)
C(1)-C(2)	1.407(16)	C(5)-N(1)-Pt(1)	116.7(7)
C(2)-C(3)	1.403(15)	N(1)-C(1)-C(2)	122.2(11)
C(3)-C(4)	1.395(15)	C(3)-C(2)-C(1)	119.0(10)
C(4)-C(5)	1.384(16)	C(4)-C(3)-C(2)	118.1(11)
C(5)-C(6)	1.461(15)	C(5)-C(4)-C(3)	119.9(10)
C(6)-C(11)	1.409(14)	N(1)-C(5)-C(4)	120.7(10)
C(6)-C(7)	1.444(16)	N(1)-C(5)-C(6)	112.5(10)
C(7)-C(8)	1.373(16)	C(4)-C(5)-C(6)	126.8(9)
C(8)-C(9)	1.426(14)	C(11)-C(6)-C(7)	120.3(10)
C(9)-C(10)	1.391(15)	C(11)-C(6)-C(5)	124.7(10)
C(9)-C(12)	1.450(16)	C(7)-C(6)-C(5)	115.1(9)
C(10)-C(11)	1.385(15)	C(8)-C(7)-C(6)	119.0(10)
C(12)-C(13)	1.343(15)	C(8)-C(7)-Pt(1)	127.7(9)
C(12)-C(15)	1.496(16)	C(6)-C(7)-Pt(1)	113.3(8)
C(13)-C(14)	1.435(15)	C(7)-C(8)-C(9)	121.0(10)
C(16)-C(17)	1.518(17)	C(10)-C(9)-C(8)	118.6(10)
C(17)-C(18)	1.418(15)	C(10)-C(9)-C(12)	119.0(10)
C(18)-C(19)	1.400(15)	C(8)-C(9)-C(12)	122.4(10)

Table S3. *Cont.*

Bond lengths [Å]		Angles [°]	
C(19)-C(20)	1.508(14)	C(11)-C(10)-C(9)	122.6(9)
		C(11)-C(10)-O(1)	116.1(10)
		C(9)-C(10)-O(1)	121.3(10)
		C(10)-C(11)-C(6)	118.6(10)
		C(13)-C(12)-C(9)	118.0(11)
		C(13)-C(12)-C(15)	121.6(11)
		C(9)-C(12)-C(15)	120.4(9)
		C(12)-C(13)-C(14)	123.0(11)
		O(2)-C(14)-O(1)	116.3(10)
		O(2)-C(14)-C(13)	125.3(11)
		O(1)-C(14)-C(13)	118.4(10)
		O(3)-C(17)-C(18)	126.5(12)
		O(3)-C(17)-C(16)	113.0(10)
		C(18)-C(17)-C(16)	120.5(10)
		C(19)-C(18)-C(17)	127.9(10)
		O(4)-C(19)-C(18)	125.3(10)
		O(4)-C(19)-C(20)	116.7(10)
		C(18)-C(19)-C(20)	118.0(10)

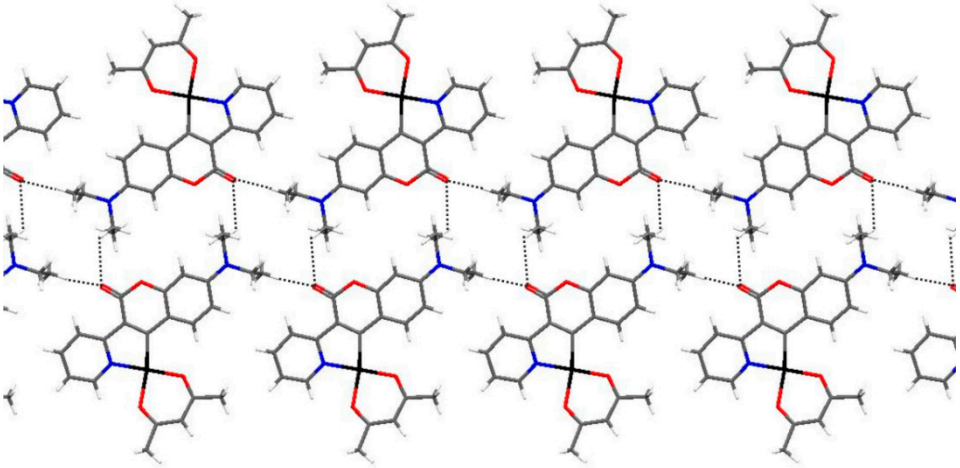

Figure S8. Hydrogen bonds between individual molecules of complex **1**, indicated by dashed lines.

(a)

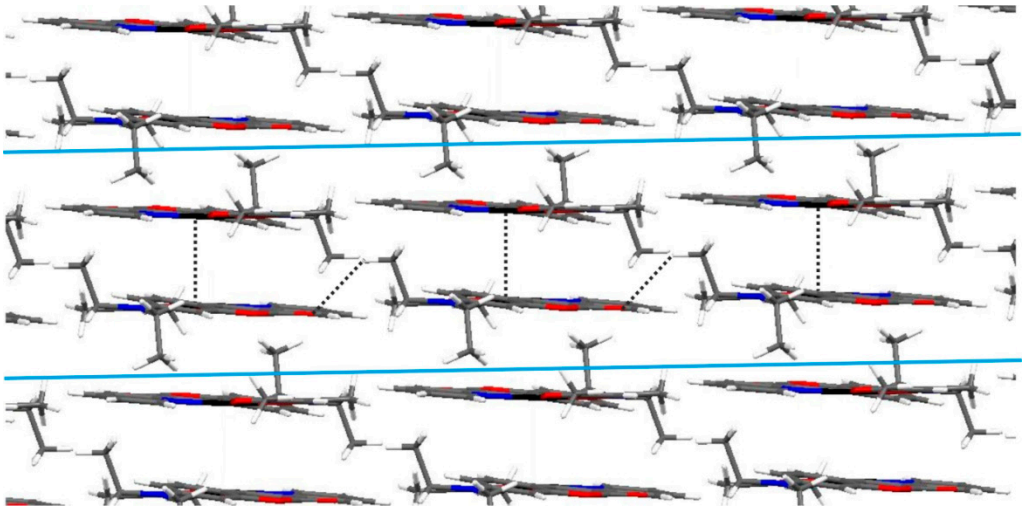

Figure S9. *Cont.*

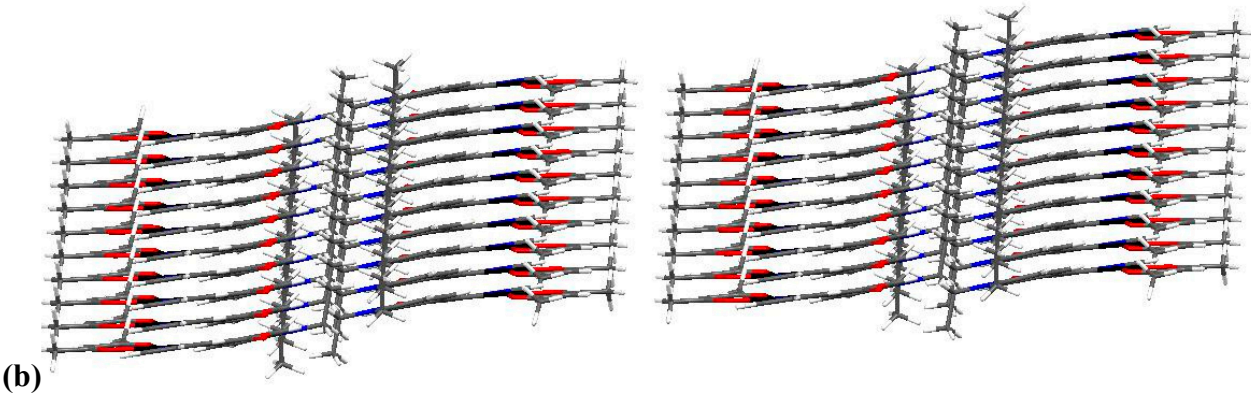

Figure S9. Two-dimensional cuts from the crystal structure of complex **1** showing the stacking arrangement. Hydrogen bonds and d^8-d^8-interactions of individual molecules are indicated by dashed lines.

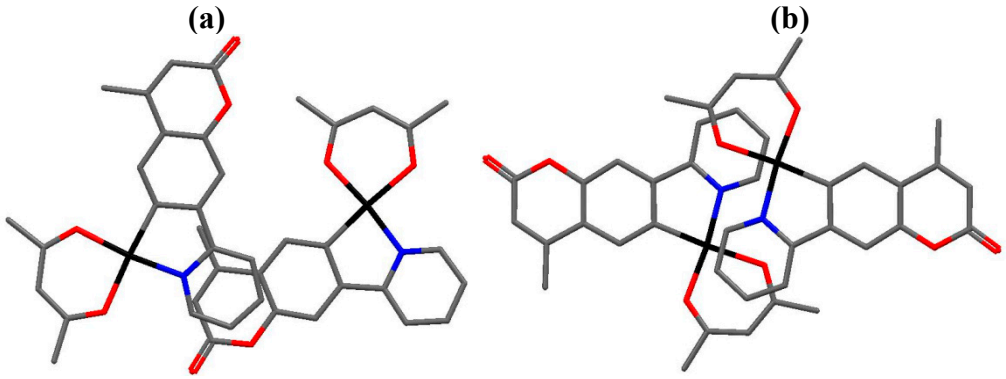

Figure S10. π-Stacking of individual molecules of **2** by overlapping of (**a**) pyridyl and pyranonyl units over 3.278 Å and (**b**) pyridyl and acac units over 3.377 Å. Hydrogen atoms are omitted for clarity.

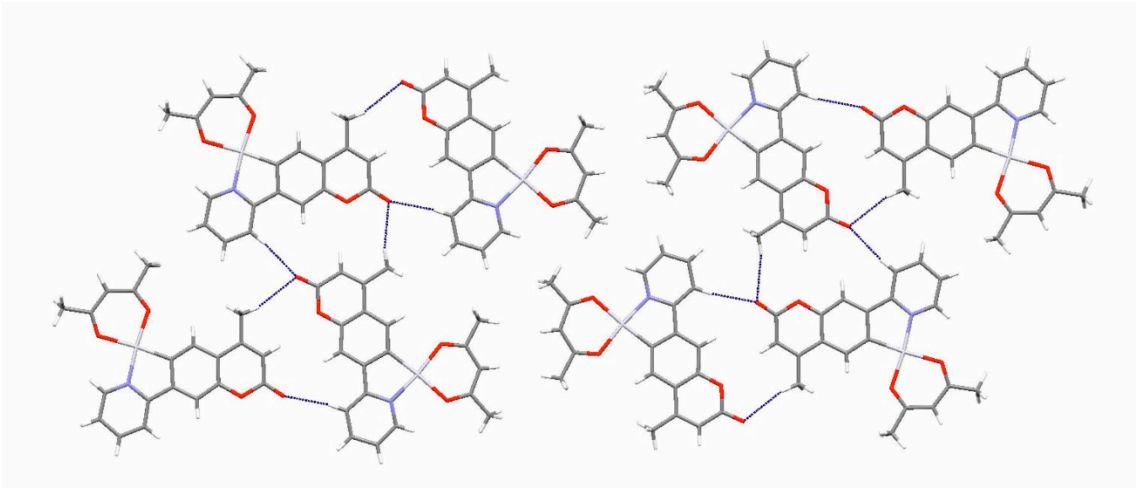

Figure S11. Sheetlike arrangement of individual molecules of complex **2** showing hydrogen bonds involving the exocyclic carbonyl oxygen atom, indicated by dark blue dashed lines.

3. IR Spectroscopy

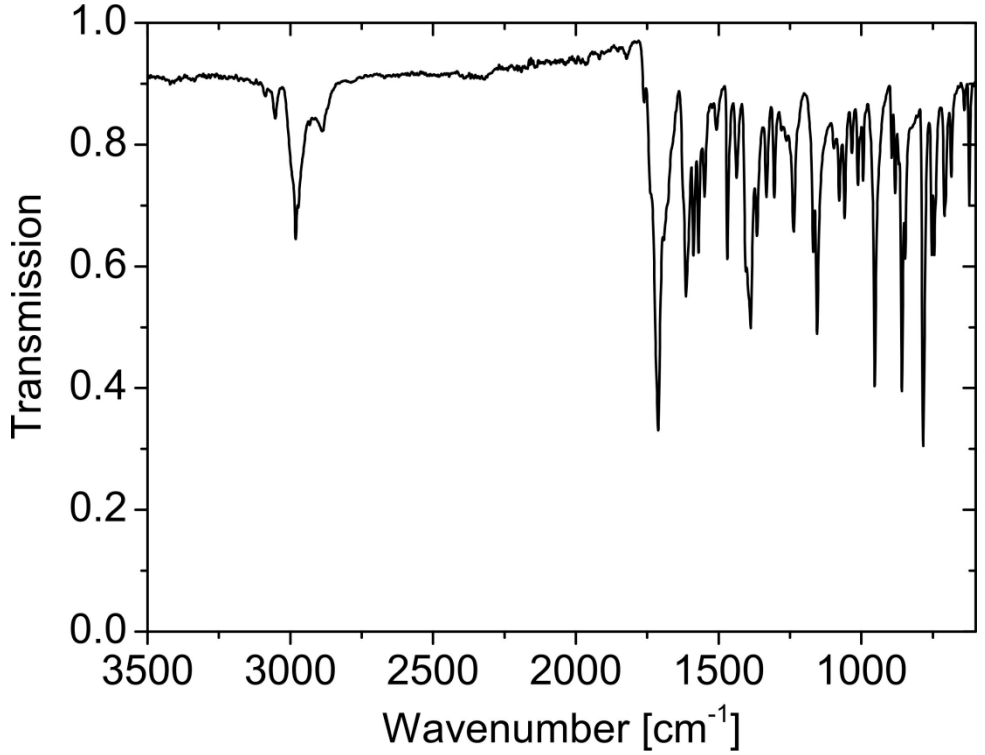

Figure S12. IR spectrum of ligand **L2**.

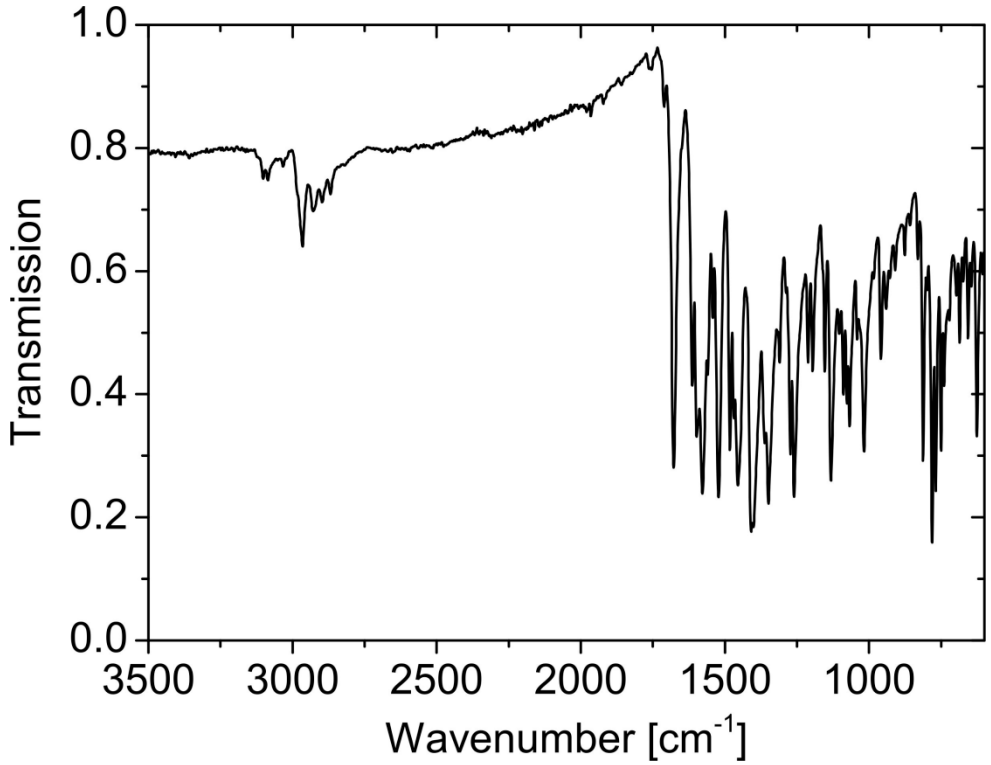

Figure S13. IR spectrum of complex **1**.

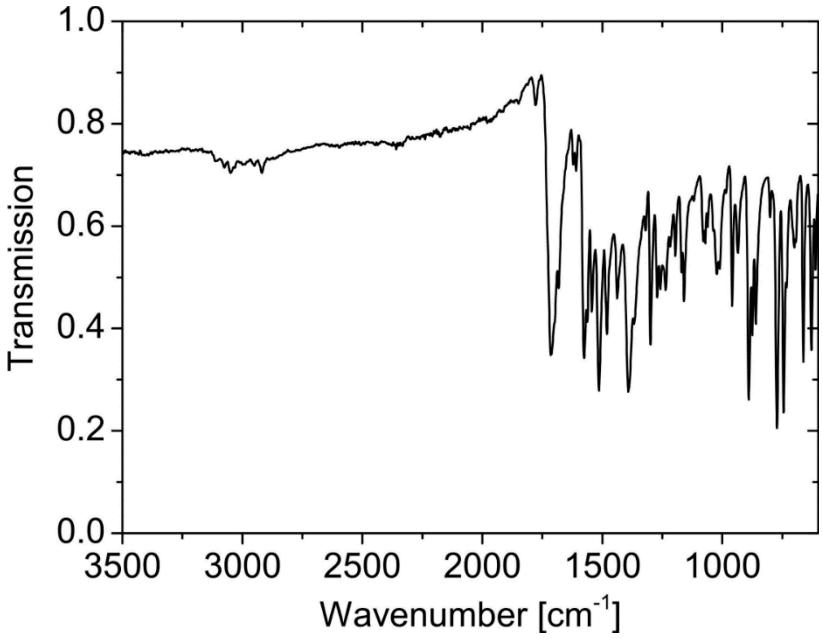

Figure S14. IR spectrum of complex **2**.

4. Electrochemistry

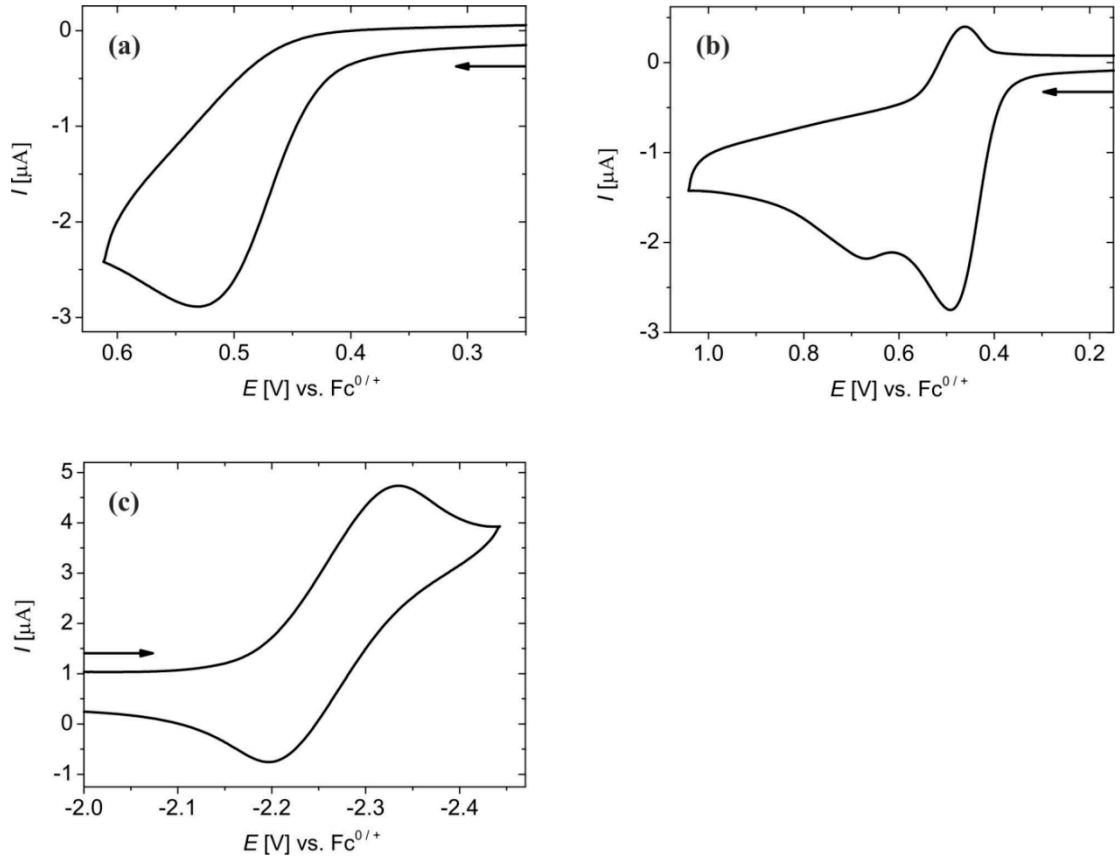

Figure S15. (**a**) The first; (**b**) the first and the second oxidations of **1** in the 0.1 M NBu_4PF_6 solution in dichloromethane and (c) the first reduction of **1** in the 0.1 M NBu_4PF_6 solution in THF at a sweep rate $\nu = 100$ mV s^{-1} at ambient conditions.

Table S4. Electrochemical data for complexes **1** and **2**.

	E_{pf} [V] (r)	$E_{1/2}$ [V] (r)
1	0.53 (irr), 0.67 (irr)	- 2.27 (1)
2	0.65 (irr), 0.93 (irr)	- 2.09 (1), - 2.40 (0.67)

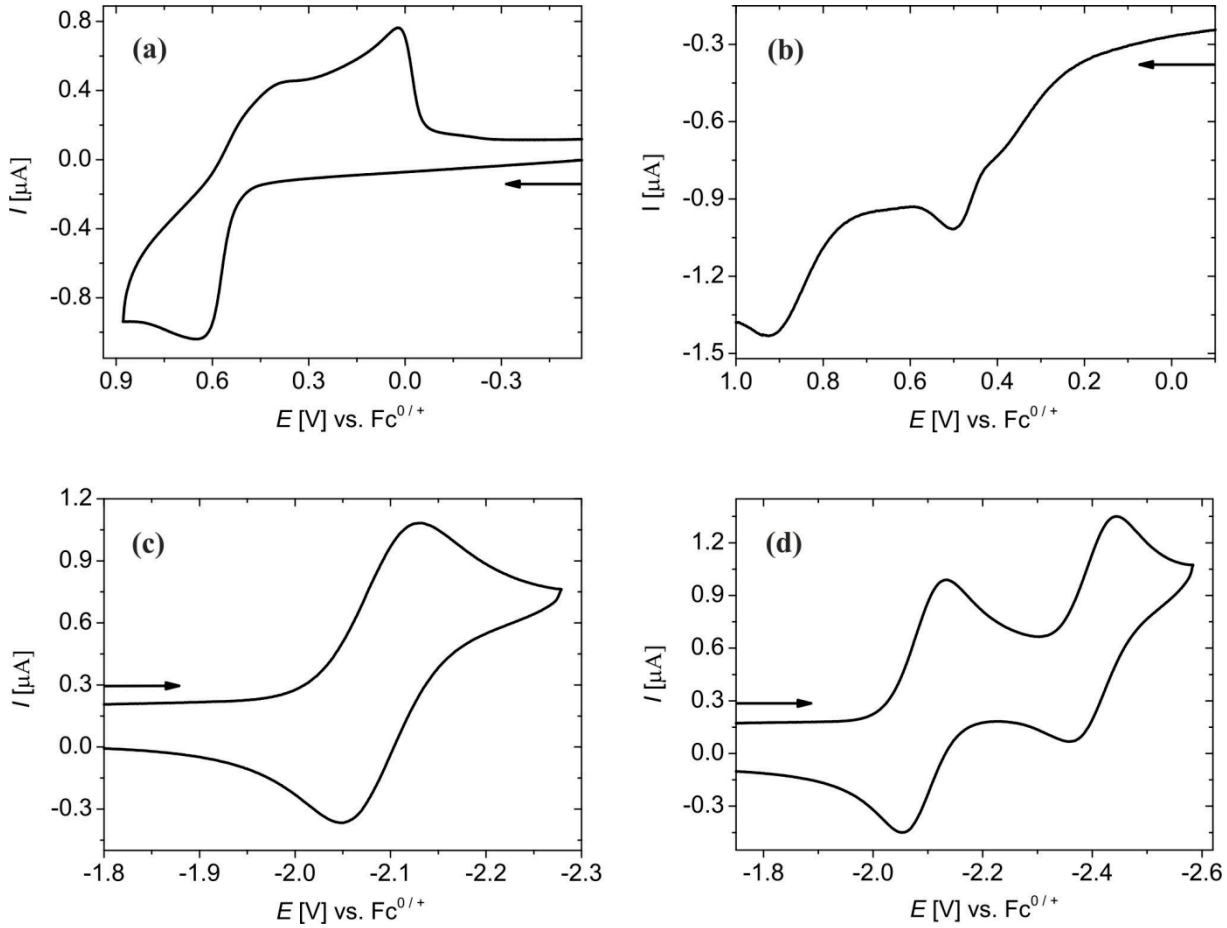

Figure S16. (**a**) The first; (**b**) the first and the second oxidations of **2** in the 0.1-M NBu_4PF_6 solution in dichloromethane. (**c**) The first; (**d**) the first and the second reductions of **2** in the 0.1-M NBu_4PF_6 solution in THF. The measurements were performed at ambient conditions at a sweep rate $\nu = 100$ mV s^{-1}.

Table S5. Peak positions of different redox states of **2** in IR in the 0.2 M NBu_4PF_6 THF solution.

	Wavenumber [cm^{-1}]										
2	1777	1729	-	1679	1652	1641	-	1577	1564	1545	1522
$\mathbf{2}^{\bullet-}$	1777	1726	1692	1673	1647	1644	1604	1577	-	1545	1519
$\mathbf{2}^{2-}$	-	1723	-	-	-	-	1604	1577	-	-	1519

5. Time-Resolved Luminescence Spectroscopy

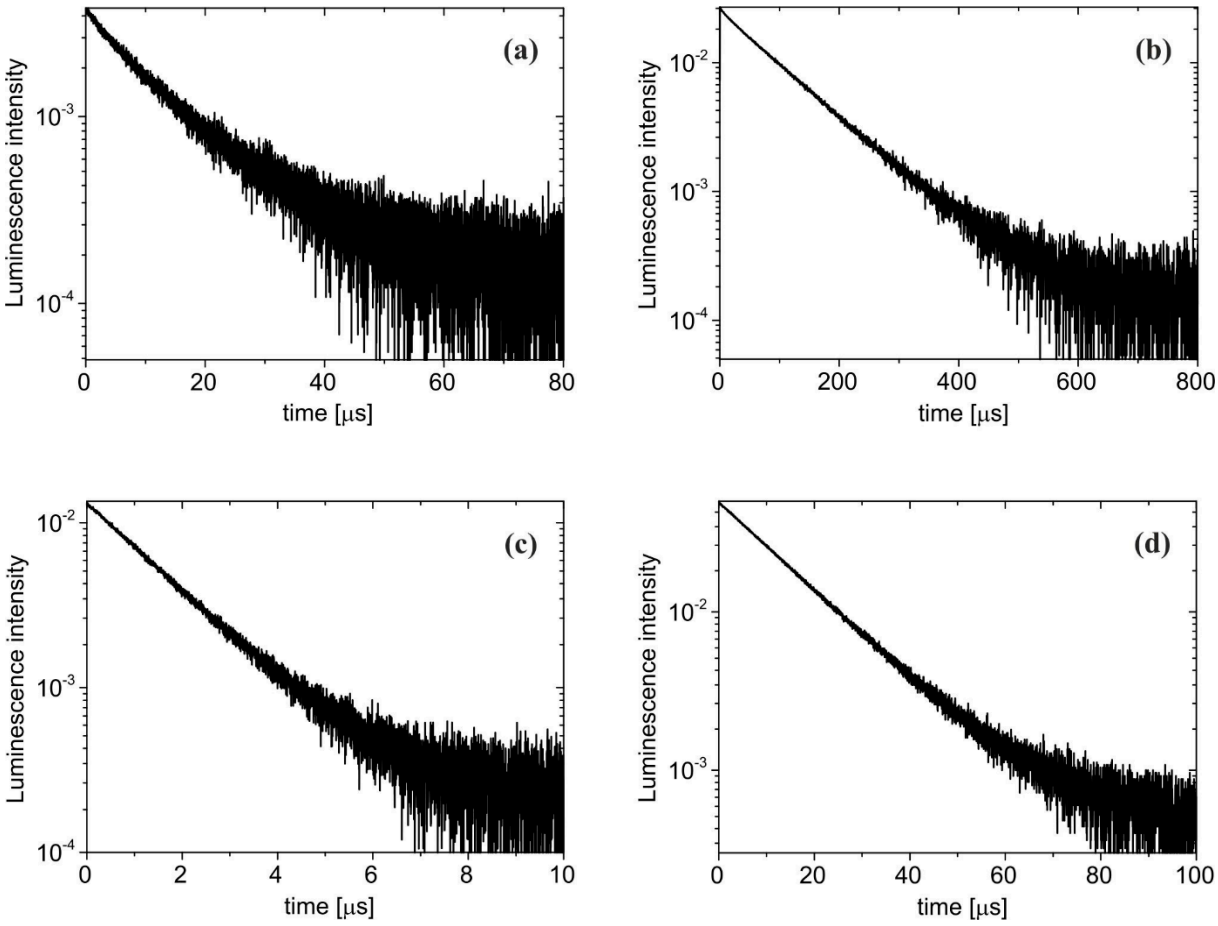

Figure S17. Temporal evolution of the luminescence signal of complex **1**: (**a**) at ambient conditions, detected at 566 nm; (**b**) at 77 K, detected at 558 nm; of complex **2**: (**c**) at r.t., detected at 550 nm; (**d**) at 77 K, detected at 540 nm after pulsed excitation at 355 nm with pulse width of 10 ns in deoxygenated 2-MeTHF.

6. Quantum Chemical Calculations

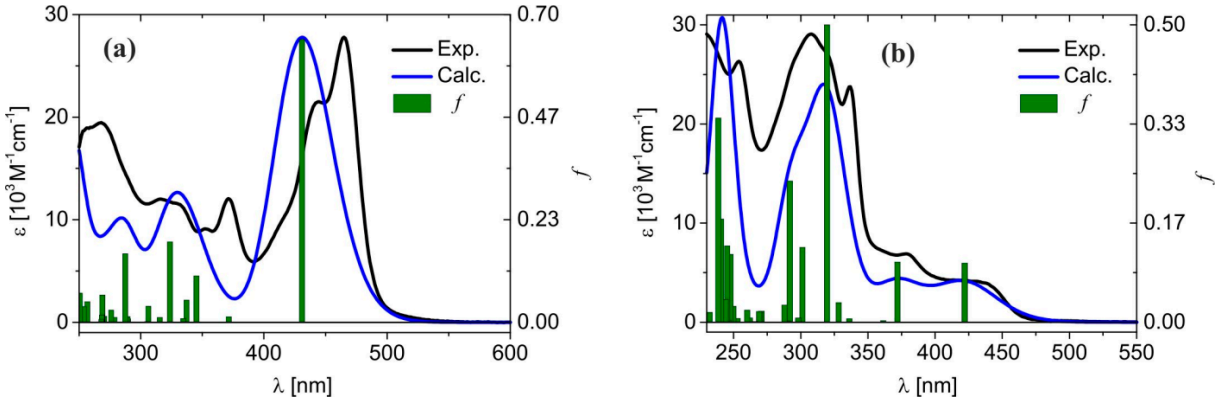

Figure S18. Scaled TD-DFT (B3LYP) calculated and experimental absorption spectra of complexes **1** (a) and **2** (b) in CH_2Cl_2 (exp.) or 1,2-dichloroethane (calcd.).

Table S6. Major contributions to the TD-DFT transitions of complex **1**.

ῡ [cm^{-1}]	λ [nm]	Osc. strength	Major contributions
23201	431	0.651	HOMO → LUMO (96%)
28974	345	0.107	H-1 → LUMO (87%)
30884	324	0.185	HOMO → L+2 (85%)
34793	287	0.158	H-2 → L+1 (80%)
41018	244	0.106	H-1 → L+3 (83%)
41271	242	0.096	H-3 → L+2 (64%), HOMO → L+7 (19%)

Table S7. Major contributions to the TD-DFT transitions of complex 2.

ῡ [cm^{-1}]	λ [nm]	Osc. strength	Major contributions
23698	422	0.100	HOMO → LUMO (95%)
26884	372	0.102	H-1 → LUMO (93%)
31295	320	0.503	H-3 → LUMO (77%)
33197	301	0.127	H-4 → LUMO (17%), H-1 → L+1 (64%)
34272	292	0.239	H-1 → L+2 (61%), HOMO → L+3 (25%)
40368	248	0.115	H-5 → L+4 (11%), H-4 → L+2 (19%), HOMO → L+5 (40%)
40778	245	0.129	H-9 → LUMO (30%), H-5 → L+4 (11%), H-4 → L+1 (12%), HOMO → L+5 (16%)
41557	241	0.175	H-4 → L+2 (50%), H-3 → L+3 (10%), HOMO → L+5 (10%)
41906	239	0.345	H-3 → L+3 (47%), HOMO → L+5 (14%)

Table S8. Fragment population analysis for frontier molecular orbitals of complexes 1 and 2.

		1						**2**			
MO	**eV**	**coum**	**py**	**acac**	**Pt**	**MO**	**eV**	**coum**	**py**	**acac**	**Pt**
L+7	0.31	51	6	2	41	L+7	0.56	39	20	1	40
L+6	0.01	45	5	2	48	L+6	0.03	11	4	7	78
L+5	0.01	27	3	2	68	L+5	-0.13	74	5	2	19
L+4	-0.45	16	15	13	57	L+4	-0.24	8	9	9	74
L+3	-0.47	48	47	1	4	L+3	-0.86	44	50	3	3
L+2	-0.93	19	70	9	2	L+2	-1.3	11	13	72	4
L+1	-1.43	2	8	88	2	L+1	-1.43	18	56	23	3
LUMO	-1.93	53	36	1	10	LUMO	-2.24	58	38	1	3
HOMO	-5.22	89	11	0	1	HOMO	-5.76	53	5	14	27
H-1	-6.13	19	9	46	26	H-1	-6.16	19	9	44	28
H-2	-6.37	37	14	19	30	H-2	-6.46	3	1	3	93
H-3	-6.52	92	1	1	6	H-3	-6.59	66	13	6	15
H-4	-6.59	8	1	4	87	H-4	-6.98	17	8	36	39
H-5	-7.06	15	20	26	40	H-5	-7.19	6	2	25	68
H-6	-7.18	46	4	29	21	H-6	-7.41	21	2	68	10
H-7	-7.23	28	2	22	48	H-7	-7.43	46	22	9	23
H-8	-7.5	19	14	19	48	H-8	-7.55	99	0	1	0
H-9	-7.71	40	4	49	7	H-9	-7.82	36	32	5	28

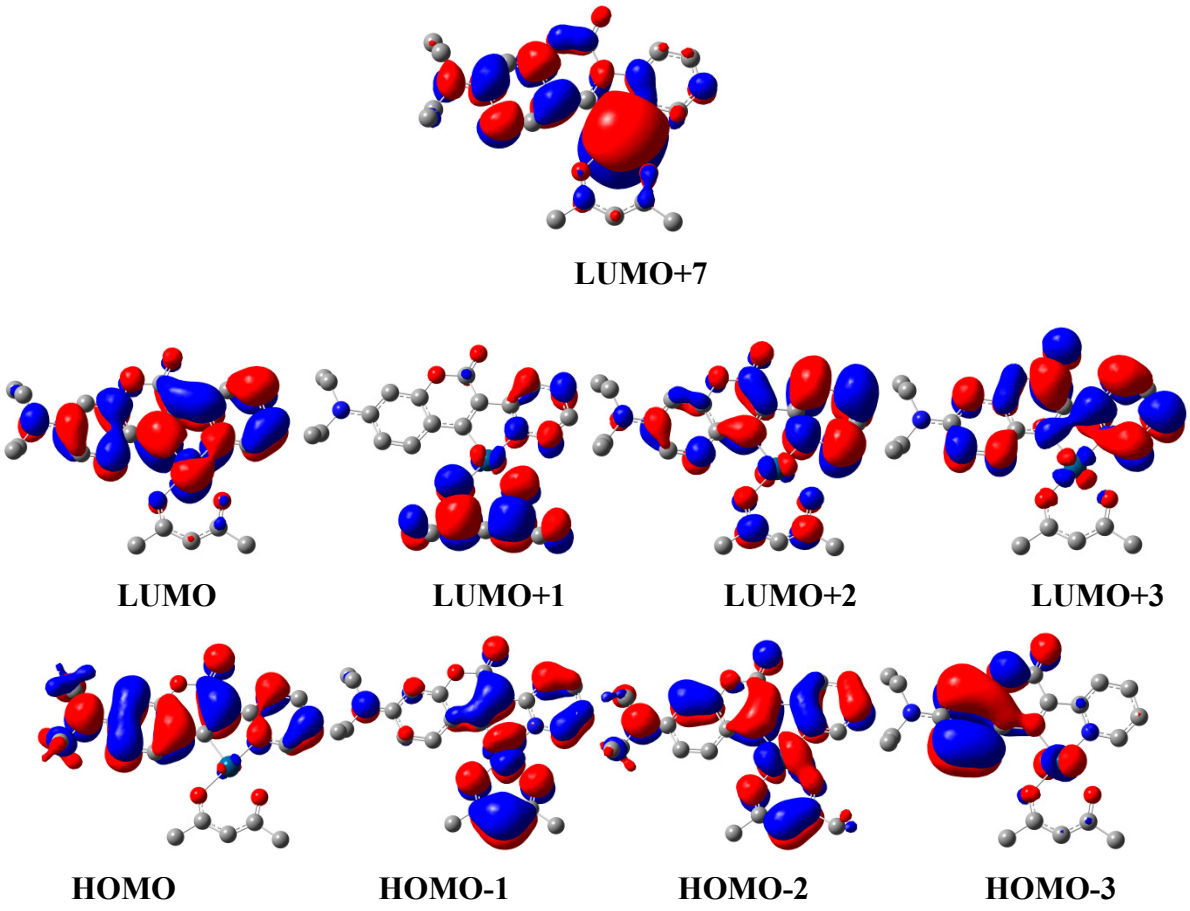

Figure S19. Selected molecular orbitals of complex **1**. Hydrogen atoms are omitted for reasons of clarity.

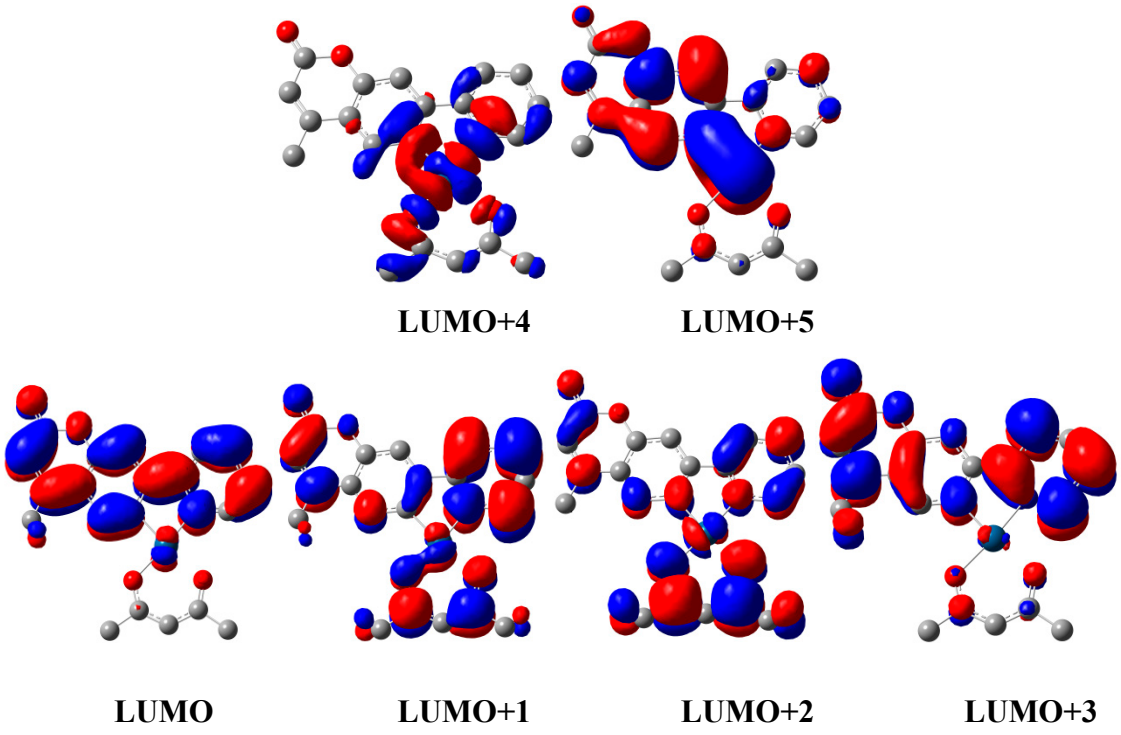

Figure S20. *Cont.*

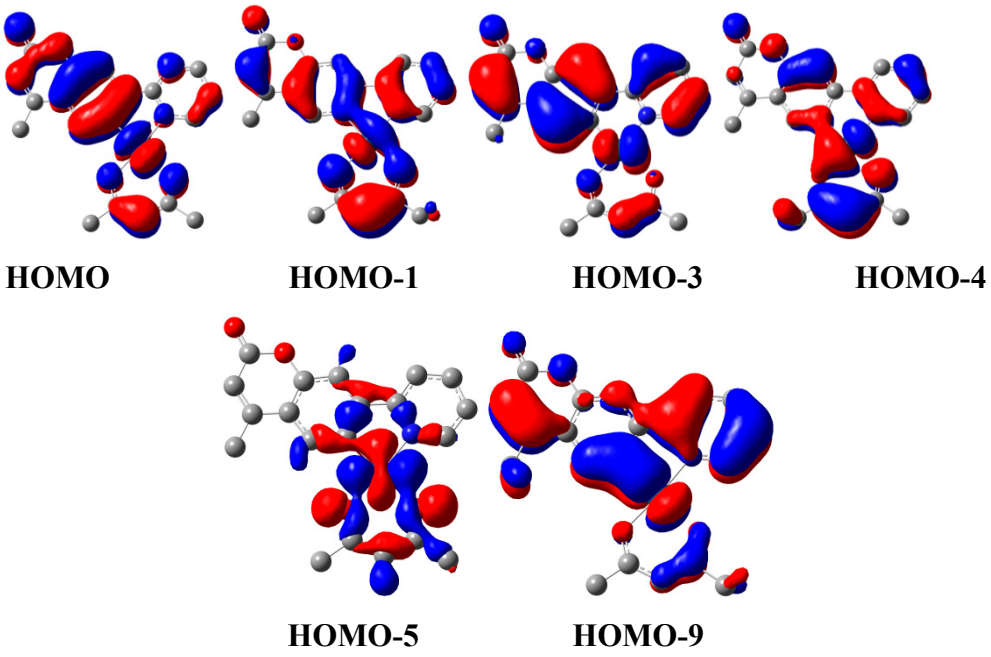

Figure S20. Selected molecular orbitals of complex **2**. Hydrogen atoms are omitted for reasons of clarity.

Table S9. List of calculated bond lengths and bond angles for optimized singlet ground state geometry of **1** in a dichloroethane medium.

(a) Calculated with the PBE0 functional.

Bond lengths [Å]		Angles [°]	
Pt(1)-O(3)	2.0339	O(3)-Pt(1)-O(4)	88.78
Pt(1)-O(4)	2.0960	O(3)-Pt(1)-N(2)	179.48
Pt(1)-N(2)	2.0039	O(3)-Pt(1)-C(7)	99.22
Pt(1)-C(7)	1.9946	O(4)-Pt(1)-N(2)	90.78
O(1)-C(13)	1.3576	O(4)-Pt(1)-C(7)	171.99
O(1)-C(14)	1.3717	N(2)-Pt(1)-C(7)	81.22
O(2)-C(14)	1.2196	C(13)-O(1)-C(14)	122.79
O(3)-C(20)	1.2826	Pt(1)-O(3)-C(20)	126.67
O(4)-C(22)	1.2744	Pt(1)-O(4)-C(22)	126.49
N(1)-C(11)	1.3623	C(11)-N(1)-C(15)	122.09
N(1)-C(15)	1.4558	C(11)-N(1)-C(17)	121.76
N(1)-C(17)	1.4554	C(15)-N(1)-C(17)	116.16
N(2)-C(1)	1.3426	Pt(1)-N(2)-C(1)	122.77
N(2)-C(5)	1.3621	Pt(1)-N(2)-C(5)	116.25
C(1)-C(2)	1.3826	C(1)-N(2)-C(5)	120.98
C(2)-C(3)	1.3948	N(2)-C(1)-C(2)	121.9
C(3)-C(4)	1.3853	C(1)-C(2)-C(3)	118.34
C(4)-C(5)	1.4017	C(2)-C(3)-C(4)	119.73
C(5)-C(6)	1.4455	C(3)-C(4)-C(5)	119.84
C(6)-C(7)	1.4028	N(2)-C(5)-C(4)	119.21
C(6)-C(14)	1.4435	N(2)-C(5)-C(6)	113.05
C(7)-C(8)	1.4345	C(4)-C(5)-C(6)	127.73
C(8)-C(9)	1.4143	C(5)-C(6)-C(7)	116.4
C(8)-C(13)	1.4147	C(5)-C(6)-C(14)	120.45
C(9)-C(10)	1.3746	C(7)-C(6)-C(14)	123.15
C(10)-C(11)	1.4237	Pt(1)-C(7)-C(6)	113.07
C(11)-C(12)	1.4092	Pt(1)-C(7)-C(8)	130.13

Table S9. Cont.

Bond lengths [Å]		Angles [°]	
C(12)-C(13)	1.3832	C(6)-C(7)-C(8)	116.8
C(15)-C(16)	1.5236	C(7)-C(8)-C(9)	125.92
C(17)-C(18)	1.5247	C(7)-C(8)-C(13)	119.20
C(19)-C(20)	1.503	C(9)-C(8)-C(13)	114.89
C(20)-C(21)	1.3953	C(8)-C(9)-C(10)	122.77
C(21)-C(22)	1.4008	C(9)-C(10)-C(11)	121.43
C(22)-C(23)	1.5034	N(1)-C(11)-C(10)	121.61
		N(1)-C(11)-C(12)	121.61
		C(10)-C(11)-C(12)	116.77
		C(11)-C(12)-C(13)	120.64
		O(1)-C(13)-C(8)	121.48
		O(1)-C(13)-C(12)	115.02
		C(8)-C(13)-C(12)	123.51
		O(1)-C(14)-O(2)	115.62
		O(1)-C(14)-C(6)	116.59
		O(2)-C(14)-C(6)	127.79
		N(1)-C(15)-C(16)	113.41
		N(1)-C(17)-C(18)	113.39
		O(3)-C(20)-C(19)	113.59
		O(3)-C(20)-C(21)	126.98
		C(19)-C(20)-C(21)	119.43
		C(20)-C(21)-C(22)	125.69
		O(4)-C(22)-C(21)	125.39
		O(4)-C(22)-C(23)	115.04
		C(21)-C(22)-C(23)	119.57

(b) Calculated with the B3LYP functional.

Bond lengths [Å]		Angles [°]	
Pt(1)-O(3)	2.0538	O(3)-Pt(1)-O(4)	88.49
Pt(1)-O(4)	2.1187	O(3)-Pt(1)-N(2)	178.69
Pt(1)-N(2)	2.0247	O(3)-Pt(1)-C(7)	99.48
Pt(1)-C(7)	2.0157	O(4)-Pt(1)-N(2)	91.02
O(1)-C(13)	1.3663	O(4)-Pt(1)-C(7)	172.04
O(1)-C(14)	1.3836	N(2)-Pt(1)-C(7)	81.02
O(2)-C(14)	1.2238	C(13)-O(1)-C(14)	122.74
O(3)-C(20)	1.2889	Pt(1)-O(3)-C(20)	126.64
O(4)-C(22)	1.2802	Pt(1)-O(4)-C(22)	126.40
N(1)-C(11)	1.3706	C(11)-N(1)-C(15)	122.11
N(1)-C(15)	1.4664	C(11)-N(1)-C(17)	121.84
N(1)-C(17)	1.4660	C(15)-N(1)-C(17)	116.06
N(2)-C(1)	1.3481	Pt(1)-N(2)-C(1)	122.90
N(2)-C(5)	1.3687	Pt(1)-N(2)-C(5)	116.06
C(1)-C(2)	1.3863	C(1)-N(2)-C(5)	121.03
C(2)-C(3)	1.3984	N(2)-C(1)-C(2)	121.84
C(3)-C(4)	1.3888	C(1)-C(2)-C(3)	118.35
C(4)-C(5)	1.4057	C(2)-C(3)-C(4)	119.81
C(5)-C(6)	1.4527	C(3)-C(4)-C(5)	119.91
C(6)-C(7)	1.4070	N(2)-C(5)-C(4)	119.06
C(6)-C(14)	1.4480	N(2)-C(5)-C(6)	113.23
C(7)-C(8)	1.4377	C(4)-C(5)-C(6)	127.71
C(8)-C(9)	1.4191	C(5)-C(6)-C(7)	116.7
C(8)-C(13)	1.4183	C(5)-C(6)-C(14)	120.35
C(9)-C(10)	1.3777	C(7)-C(6)-C(14)	122.95
C(10)-C(11)	1.4284	Pt(1)-C(7)-C(6)	112.92
C(11)-C(12)	1.4139	Pt(1)-C(7)-C(8)	129.89
C(12)-C(13)	1.3868	C(6)-C(7)-C(8)	117.18
C(15)-C(16)	1.5334	C(7)-C(8)-C(9)	125.97
C(17)-C(18)	1.5335	C(7)-C(8)-C(13)	119.24
C(19)-C(20)	1.5119	C(9)-C(8)-C(13)	114.79
C(20)-C(21)	1.3989	C(8)-C(9)-C(10)	122.77
C(21)-C(22)	1.4050	C(9)-C(10)-C(11)	121.53

Table 9S. *Cont.*

Bond lengths [Å]		Angles [°]	
C(22)-C(23)	1.5116	N(1)-C(11)-C(10)	121.70
		N(1)-C(11)-C(12)	121.64
		C(10)-C(11)-C(12)	116.66
		C(11)-C(12)-C(13)	120.61
		O(1)-C(13)-C(8)	121.31
		O(1)-C(13)-C(12)	115.04
		C(8)-C(13)-C(12)	123.64
		O(1)-C(14)-O(2)	115.44
		O(1)-C(14)-C(6)	116.54
		O(2)-C(14)-C(6)	128.02
		N(1)-C(15)-C(16)	113.67
		N(1)-C(17)-C(18)	113.67
		O(3)-C(20)-C(19)	113.57
		O(3)-C(20)-C(21)	126.99
		C(19)-C(20)-C(21)	119.43
		C(20)-C(21)-C(22)	126.07
		O(4)-C(22)-C(21)	125.41
		O(4)-C(22)-C(23)	115.05
		C(21)-C(22)-C(23)	119.53

Table S10. List of calculated bond lengths and bond angles for optimized singlet ground state geometry of 2 in a dichloroethane medium.

(a) Calculated with the PBE0 functional.

Bond lengths [Å]		Angles [°]	
Pt(1)-O(3)	2.0209	O(3)-Pt(1)-O(4)	91.33
Pt(1)-O(4)	2.1055	O(3)-Pt(1)-N(1)	174.97
Pt(1)-N(1)	2.0092	O(3)-Pt(1)-C(7)	93.64
Pt(1)-C(7)	1.9731	O(4)-Pt(1)-N(1)	93.7
O(3)-C(17)	1.2837	O(4)-Pt(1)-C(7)	175.03
O(4)-C(19)	1.274	N(1)-Pt(1)-C(7)	81.33
O(1)-C(10)	1.3635	Pt(1)-O(3)-C(17)	124.8
O(1)-C(14)	1.3726	Pt(1)-O(4)-C(19)	123.89
O(2)-C(14)	1.214	C(10)-O(1)-C(14)	122.14
N(1)-C(1)	1.3403	Pt(1)-N(1)-C(1)	123.36
N(1)-C(5)	1.3622	Pt(1)-N(1)-C(5)	116.18
C(1)-C(2)	1.3861	C(1)-N(1)-C(5)	120.46
C(2)-C(3)	1.3928	N(1)-C(1)-C(2)	121.88
C(3)-C(4)	1.3884	C(1)-C(2)-C(3)	118.67
C(4)-C(5)	1.3943	C(2)-C(3)-C(4)	119.29
C(5)-C(6)	1.4606	C(3)-C(4)-C(5)	119.81
C(6)-C(7)	1.4214	N(1)-C(5)-C(4)	119.89
C(6)-C(11)	1.3930	N(1)-C(5)-C(6)	113.51
C(7)-C(8)	1.3903	C(4)-C(5)-C(6)	126.6
C(8)-C(9)	1.4061	C(5)-C(6)-C(7)	114.56
C(12)-C(9)	1.4512	C(5)-C(6)-C(11)	123.96
C(12)-C(13)	1.357	C(7)-C(6)-C(11)	121.48
C(12)-C(15)	1.4947	Pt(1)-C(7)-C(6)	114.41
C(9)-C(10)	1.4054	Pt(1)-C(7)-C(8)	127.63
C(11)-C(10)	1.3878	C(6)-C(7)-C(8)	117.95
C(13)-C(14)	1.447	C(7)-C(8)-C(9)	121.71
C(16)-C(17)	1.5025	C(9)-C(12)-C(13)	118.38
C(17)-C(18)	1.3974	C(9)-C(12)-C(15)	120.21
C(18)-C(19)	1.4047	C(13)-C(12)-C(15)	121.41
C(19)-C(20)	1.5045	C(8)-C(9)-C(12)	123.82

Table S10. *Cont.*

Bond lengths [Å]		Angles [°]	
		C(8)-C(9)-C(10)	118.41
		C(12)-C(9)-C(10)	117.77
		C(6)-C(11)-C(10)	118.9
		O(3)-C(17)-C(16)	113.54
		O(3)-C(17)-C(18)	127.14
		C(16)-C(17)-C(18)	119.32
		C(17)-C(18)-C(19)	127.04
		O(4)-C(19)-C(18)	125.8
		O(4)-C(19)-C(20)	115.05
		C(18)-C(19)-C(20)	119.15
		O(1)-C(10)-C(9)	121.93
		O(1)-C(10)-C(11)	116.53
		C(9)-C(10)-C(11)	121.54
		C(12)-C(13)-C(14)	123.07
		O(1)-C(14)-O(2)	117.44
		O(1)-C(14)-C(13)	116.7
		O(2)-C(14)-C(13)	125.86

(b) Calculated with the B3LYP functional.

Bond lengths [Å]		Angles [°]	
Pt(1)-O(3)	2.0404	O(3)-Pt(1)-O(4)	90.71
Pt(1)-O(4)	2.1297	O(3)-Pt(1)-N(1)	175.05
Pt(1)-N(1)	2.0334	O(3)-Pt(1)-C(7)	93.97
Pt(1)-C(7)	1.9915	O(4)-Pt(1)-N(1)	94.24
O(3)-C(17)	1.29	O(4)-Pt(1)-C(7)	175.31
O(4)-C(19)	1.2788	N(1)-Pt(1)-C(7)	81.08
O(1)-C(10)	1.3722	Pt(1)-O(3)-C(17)	125.02
O(1)-C(14)	1.3841	Pt(1)-O(4)-C(19)	124.04
O(2)-C(14)	1.2175	C(10)-O(1)-C(14)	122.09
N(1)-C(1)	1.3462	Pt(1)-N(1)-C(1)	123.6
N(1)-C(5)	1.3691	Pt(1)-N(1)-C(5)	115.93
C(1)-C(2)	1.3893	C(1)-N(1)-C(5)	120.47
C(2)-C(3)	1.3963	N(1)-C(1)-C(2)	121.82
C(3)-C(4)	1.3916	C(1)-C(2)-C(3)	118.71
C(4)-C(5)	1.3979	C(2)-C(3)-C(4)	119.33
C(5)-C(6)	1.4657	C(3)-C(4)-C(5)	119.94
C(6)-C(7)	1.4258	N(1)-C(5)-C(4)	119.73
C(6)-C(11)	1.3972	N(1)-C(5)-C(6)	113.71
C(7)-C(8)	1.3931	C(4)-C(5)-C(6)	126.56
C(8)-C(9)	1.4113	C(5)-C(6)-C(7)	114.87
C(12)-C(9)	1.4551	C(5)-C(6)-C(11)	123.87
C(12)-C(13)	1.3601	C(7)-C(6)-C(11)	121.26
C(12)-C(15)	1.5039	Pt(1)-C(7)-C(6)	114.41
C(9)-C(10)	1.4097	Pt(1)-C(7)-C(8)	127.48
C(11)-C(10)	1.3915	C(6)-C(7)-C(8)	118.10
C(13)-C(14)	1.4510	C(7)-C(8)-C(9)	121.79
C(16)-C(17)	1.5120	C(9)-C(12)-C(13)	118.56
C(17)-C(18)	1.4004	C(9)-C(12)-C(15)	120.29
C(18)-C(19)	1.4091	C(13)-C(12)-C(15)	121.16
C(19)-C(20)	1.5129	C(8)-C(9)-C(12)	123.95

Table S10. *Cont.*

Bond lengths [Å]	Angles [°]	
	C(8)-C(9)-C(10)	118.2
	C(12)-C(9)-C(10)	117.86
	C(6)-C(11)-C(10)	119.01
	O(3)-C(17)-C(16)	113.46
	O(3)-C(17)-C(18)	127.19
	C(16)-C(17)-C(18)	119.35
	C(17)-C(18)-C(19)	127.21
	O(4)-C(19)-C(18)	125.82
	O(4)-C(19)-C(20)	115.03
	C(18)-C(19)-C(20)	119.15
	O(1)-C(10)-C(9)	121.8
	O(1)-C(10)-C(11)	116.56
	C(9)-C(10)-C(11)	121.64
	C(12)-C(13)-C(14)	123.18
	O(1)-C(14)-O(2)	117.39
	O(1)-C(14)-C(13)	116.53
	O(2)-C(14)-C(13)	126.08

The calculated emissions of **1** and **2** (B3LYP) are located at 457 and 484 nm, respectively.