Supplementary Information

X/Y Platinum(II) complexes: some features of supramolecular assembly *via* halogen bonding

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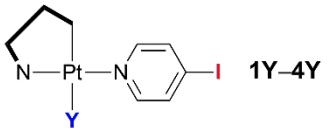
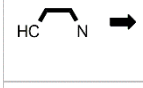
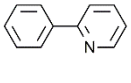
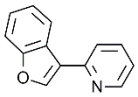
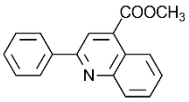
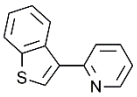
Content



1Y–4Y

	1Y	**2Y**	**3Y**	**4Y**
				
Y = Cl	**1Cl**	**2Cl**	**3Cl**	**4Cl**
Br	**1Br**	**2Br**	**3Br**	**4Br**
I	**1I**	**2I**	**3I**	**4I**

Scheme S1. Numeration of Pt(II) complexes **1Y**−**4Y** (Y = Cl, Br, I).

X-Ray structure determination

The crystal structures of **1Cl**, **1I**, **2Cl**, **2Br**, **3I**, **4Cl** and **4Br** were determined by the means of single crystal X-ray diffraction analysis. Crystals were fixed on a micro mounts and the diffraction data have been collected on the Rigaku Oxford Diffraction diffractometers at a temperature of 100K. The molecular structures of **1Br** and **3Cl** in the crystal were determined by means of single-crystal X-ray diffraction using Bruker APEX-II CCD for the data collection at a temperature of T = 150 K and T = 296 K respectively. Crystals of **1Cl**, **1I**, **2Cl**, **2Br**, **3I**, **4Cl** were placed on the Xcalibur, Eos diffractometer and measured using monochromated MoKα radiation. Crystals of **1Br** and **3Cl** were placed on the Bruker APEX-II CCD diffractometer and measured using monochromated MoKα radiation. Crystal of **4Br** was placed on the XtaLAB Synergy, HyPix diffractometer and measured using monochromated CuKα radiation. Data were integrated and corrected for background, Lorentz, and polarization effects. An empirical absorption correction based on spherical harmonics implemented in the SCALE3 ABSPACK algorithm was applied in CrysAlisPro[1] or SADABS[2] programs. The unit-cell parameters (Tables S1 and S2) were refined by the least-squares techniques. The structures were solved by dual-space algorithm and refined using the SHELX programs[3,4] incorporated in the OLEX2 program package.[5] The final models included coordinates and anisotropic displacement parameters for all non-H atoms. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the 'riding' model approximation, Uiso(H) set to 1.5Ueq(C) and C–H 0.96 Å for the CH3 groups, Uiso(H) set to 1.2Ueq(C) and C–H 0.97 Å for the CH2 groups, Uiso(H) set to 1.2Ueq(C) and C–H 0.93 Å for the CH groups. Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (CCDC 2254744−2254747, 2254749, 2254751, 2254752, 2254791, 2256851) and can be obtained free of charge *via* www.ccdc.cam.ac.uk/structures/.

Table S1. Crystallographic data for compounds **1Cl**, **1Br**, **2Br**, **3I** and **4Cl**.

Compound	**1Cl**	**1Br**	**2Br**	**3I**	**4Cl**
Formula	$C_{16}H_{12}ClIN_2Pt$	$C_{16}H_{12}BrIN_2Pt$	$C_{18}H_{12}BrIN_2OPt$	$C_{22}H_{16}I_2N_2O_2Pt$	$C_{18}H_{12}ClIN_2PtS$
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
a (Å)	11.6368(5)	20.7756(17)	7.34450(10)	13.6171(4)	16.2664(3)
b (Å)	15.3999(12)	23.3714(19)	11.2531(2)	12.2009(3)	9.3324(2)
c (Å)	8.9903(7)	10.0722(8)	21.0064(4)	13.7764(4)	23.3511(5)
α (°)	90	90	90	90	90
β (°)	94.531(5)	90	98.666(2)	106.076(3)	90
γ (°)	90	90	90	90	90
V ($Å^3$)	1606.08(19)	4890.6(7)	1716.32(5)	2199.30(11)	3544.80(13)
Molecular weight	589.72	634.18	674.20	789.26	645.80
Space group	$P2_1/c$ (14)	Pnma (62)	$P2_1/n$ (14)	$P2_1/c$ (14)	Pbca (61)
μ (mm^{-1})	10.819	12.946	12.309	9.208	9.929
Temperature (K)	100(2)	150(2)	100(2)	100(2)	100(2)
Z	4	12	4	4	8
D_{calc} (g/cm^3)	2.439	2.584	2.609	2.384	2.420
Crystal size (mm^3)	0.3 × 0.2 × 0.03	0.3 × 0.2 × 0.2	0.05 × 0.04 × 0.02	0.2 × 0.14 × 0.06	0.2 × 0.15 × 0.05
Diffractometer	Xcalibur, Eos	Bruker APEX-II CCD	Xcalibur, Eos	Xcalibur, Eos	Xcalibur, Eos
Radiation	MoKα	MoKα	MoKα	MoKα	MoKα
Total reflection	7429	23265	7707	14802	38676
Unique reflection	3146	4860	3354	4320	3470
Angle range 2θ (°)	6.12 to 51.99	6.63 to 51.99	5.66 to 51.98	6.08 to 51.99	5.33 to 51.996
Reflections with $\|F_o\| \geq 4\sigma_F$	2818	4683	3014	3971	3279
R_{int}	0.0282	0.0283	0.0213	0.0301	0.0368

R_σ	0.0380	0.0229	0.0286	0.0281	0.0153
R_1 ($\|F_o\| \geq 4\sigma_F$)	0.0281	0.0271	0.0212	0.0198	0.0173
wR2 ($\|F_o\| \geq 4\sigma_F$)	0.0547	0.0557	0.0434	0.0453	0.0372
R1 (all data)	0.0338	0.0286	0.0258	0.0232	0.0193
wR2 (all data)	0.0574	0.0562	0.0450	0.0467	0.0379
S	1.042	1.210	1.064	1.063	1.148
ρ_{max}, ρ_{min} (e/Å^3)	1.21/−1.80	1.50/−1.26	0.74/−0.81	0.92/−0.60	0.93/−0.41
CCDC	2254745	2254744	2254746	2254747	2254749

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters.

Table S2. Crystallographic data for compounds **1I**, **2Cl**, **3Cl** and **4Br**.

Compound	**1I**	**2Cl**	**3Cl**	**4Br**
Formula	$C_{16}H_{12}I_2N_2Pt$	$C_{18}H_{12}ClIN_2OPt$	$C_{22}H_{16}ClIN_2O_2Pt$	$C_{18}H_{12}BrIN_2PtS$
Crystal system	orthorhombic	monoclinic	triclinic	orthorhombic
a (Å)	10.2865(2)	20.9097(8)	9.2830(6)	23.48680(10)
b (Å)	23.5155(7)	11.5922(3)	12.6518(8)	18.57310(10)
c (Å)	20.9909(4)	31.8136(9)	21.0436(15)	16.48480(10)
α (°)	90	90	90	90
β (°)	90	107.886(4)	90	90
γ (°)	90	90	99.172(3)	90
V (Å^3)	5077.5(2)	7338.6(4)	2439.9(3)	7191.04(7)
Molecular weight	681.17	629.74	697.81	690.26
Space group	Pcmn (62)	P2/c (13)	P-1 (2)	$Pna2_1$ (33)
μ (mm^{-1})	11.933	9.483	7.144	31.782
Temperature (K)	100(2)	100(2)	297(2)	100(2)
Z	12	16	4	16

D_{calc} (g/cm^3)	2.673	2.280	1.900	2.550
Crystal size (mm^3)	0.18 × 0.12 × 0.09	0.33 × 0.20 × 0.13	0.78 × 0.56 × 0.35	0.24 × 0.2 × 0.08
Diffractometer	Xcalibur, Eos	Xcalibur, Eos	Bruker APEX-II CCD	XtaLAB Synergy, HyPix
Radiation	MoKα	MoKα	MoKα	CuKα
Total reflection	132557	36261	16511	128082
Unique reflection	7533	14235	5166	12891
Angle range 2θ (°)	5.20 to 59.996	5.14 to 52.00	4.85 to 55.00	6.07 to 134.98
Reflections with $\|F_o\| \geq 4\sigma_F$	7331	12252	4327	12810
R_{int}	0.0507	0.0454	0.0322	0.1178
R_σ	0.0177	0.0513	0.0428	0.0368
R_1 ($\|F_o\| \geq 4\sigma_F$)	0.0740	0.0797	0.0524	0.0781
wR2 ($\|F_o\| \geq 4\sigma_F$)	0.1674	0.1893	0.1386	0.1730
R1 (all data)	0.0753	0.0906	0.0612	0.0783
wR2 (all data)	0.1680	0.1968	0.1447	0.1731
S	1.399	1.098	1.013	1.056
ρ_{max}, ρ_{min} (e/Å^3)	3.26/−4.52	13.68/−2.22	3.66/−1.20	5.57/−7.07
CCDC	2256851	2254751	2254752	2254791

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters.

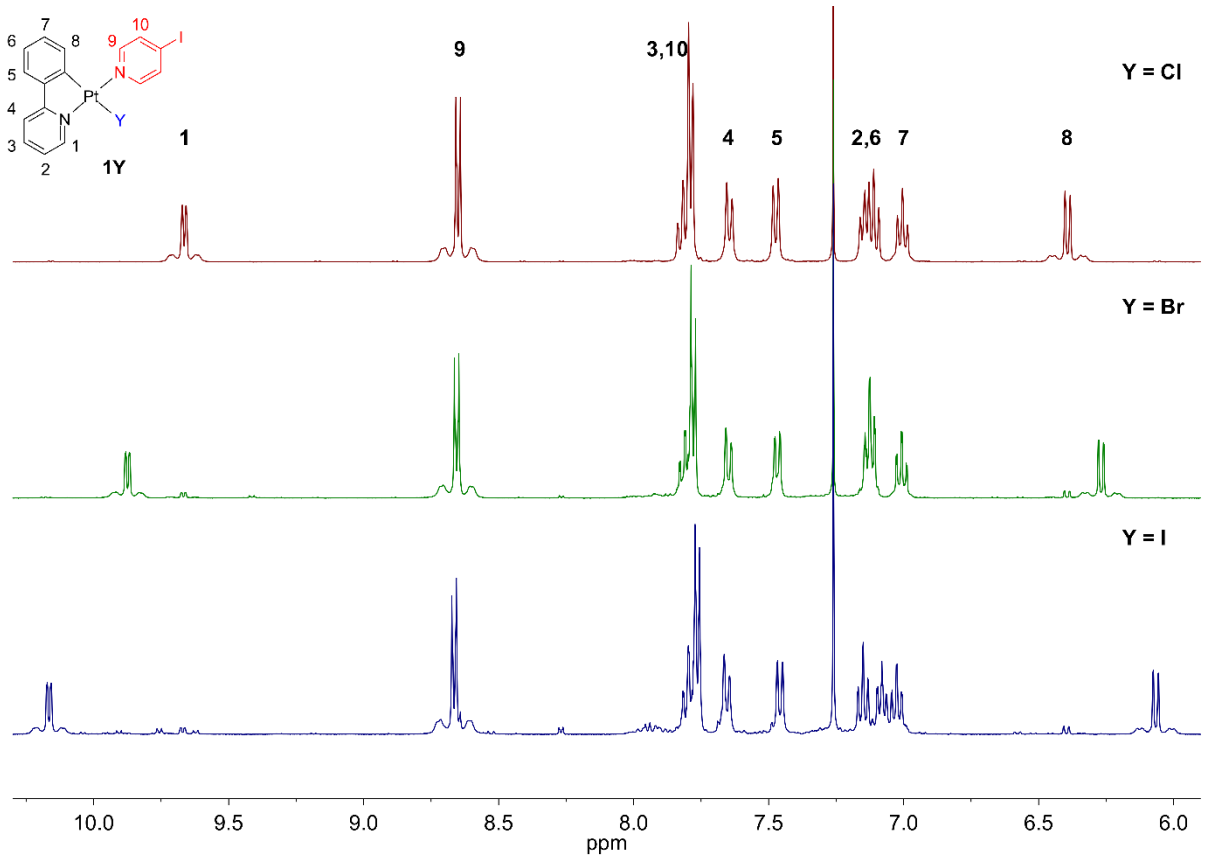


Figure S1. ^{1}H NMR spectra of complexes **1Y**, d_1-chloroform, r.t.

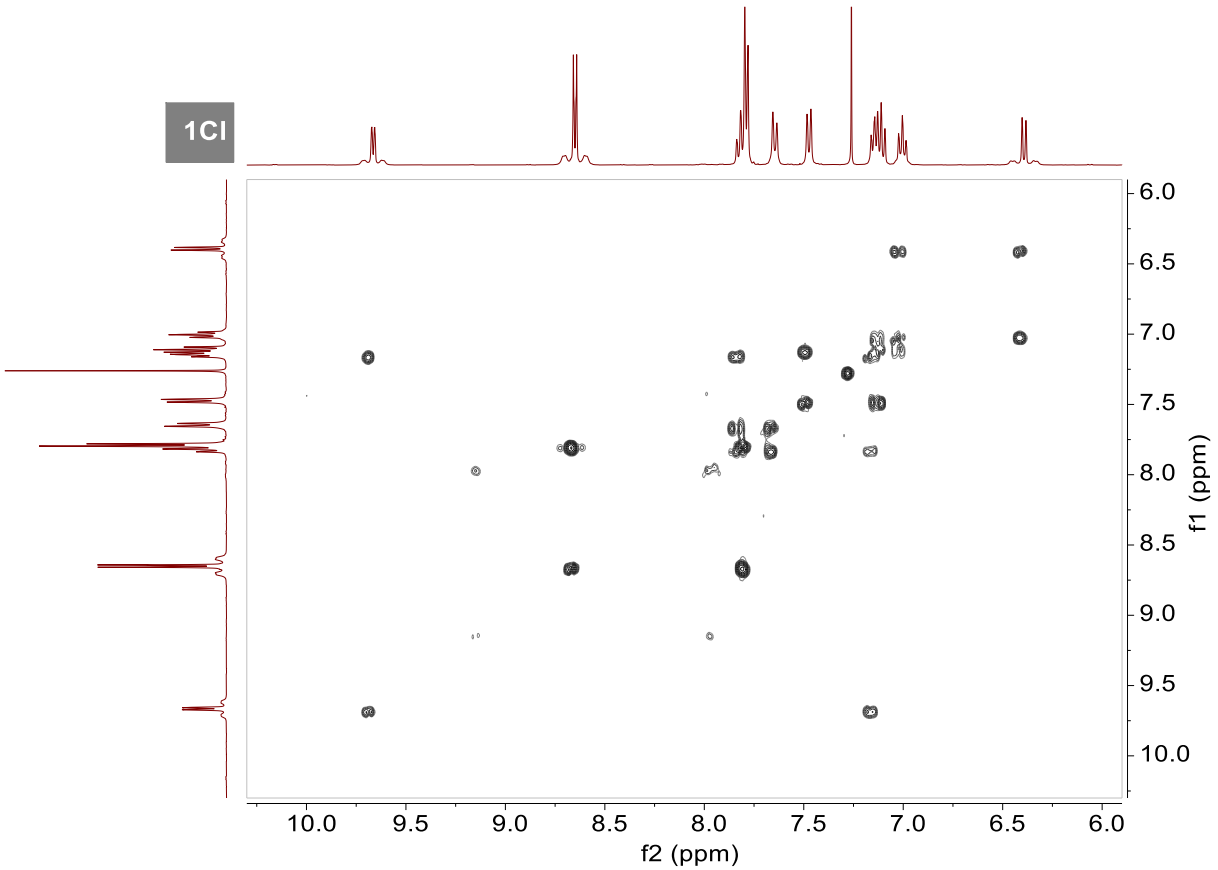


Figure S2. ^{1}H^{1}H COSY NMR spectrum of complex **1Cl**, d_1-chloroform, r.t.

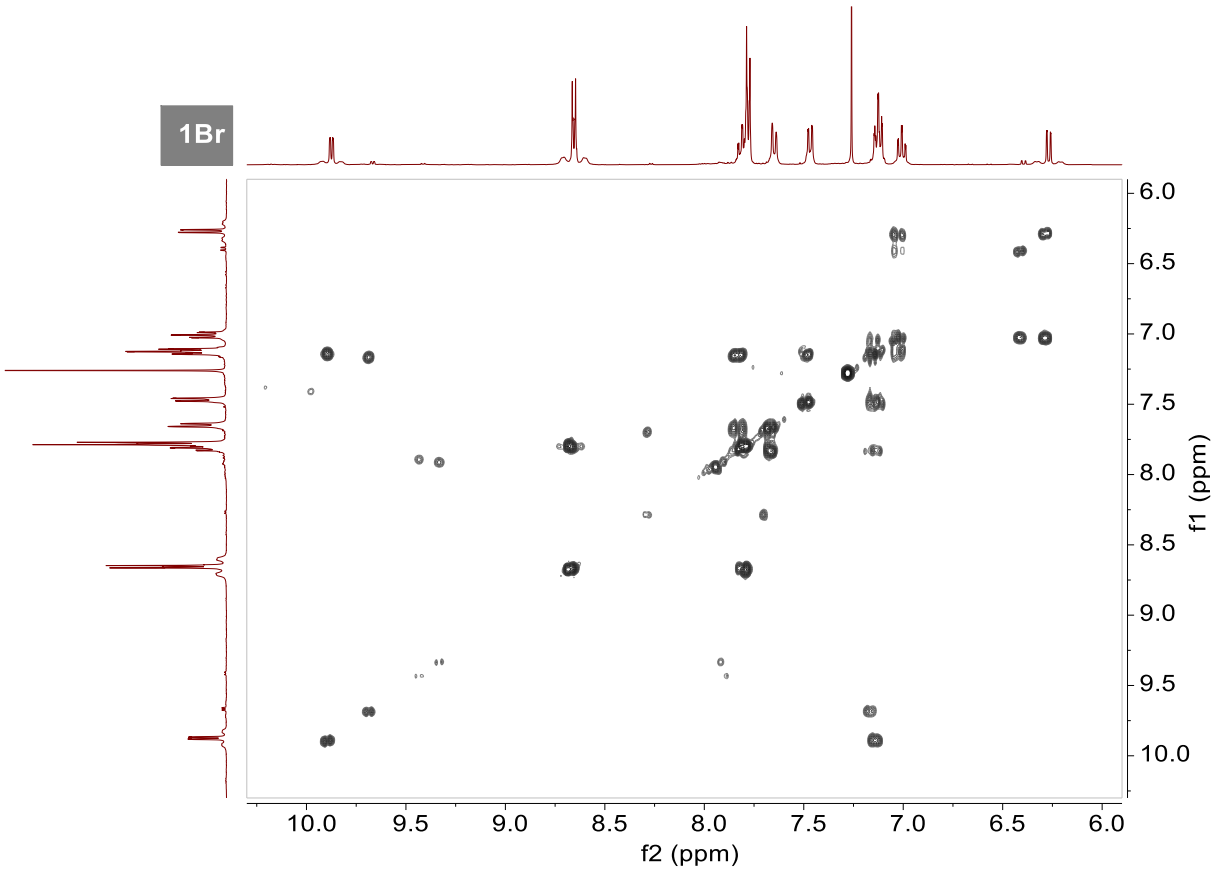


Figure S3. $^{1}H^{1}H$ COSY NMR spectrum of complex **1Br**, d_1-chloroform, r.t.

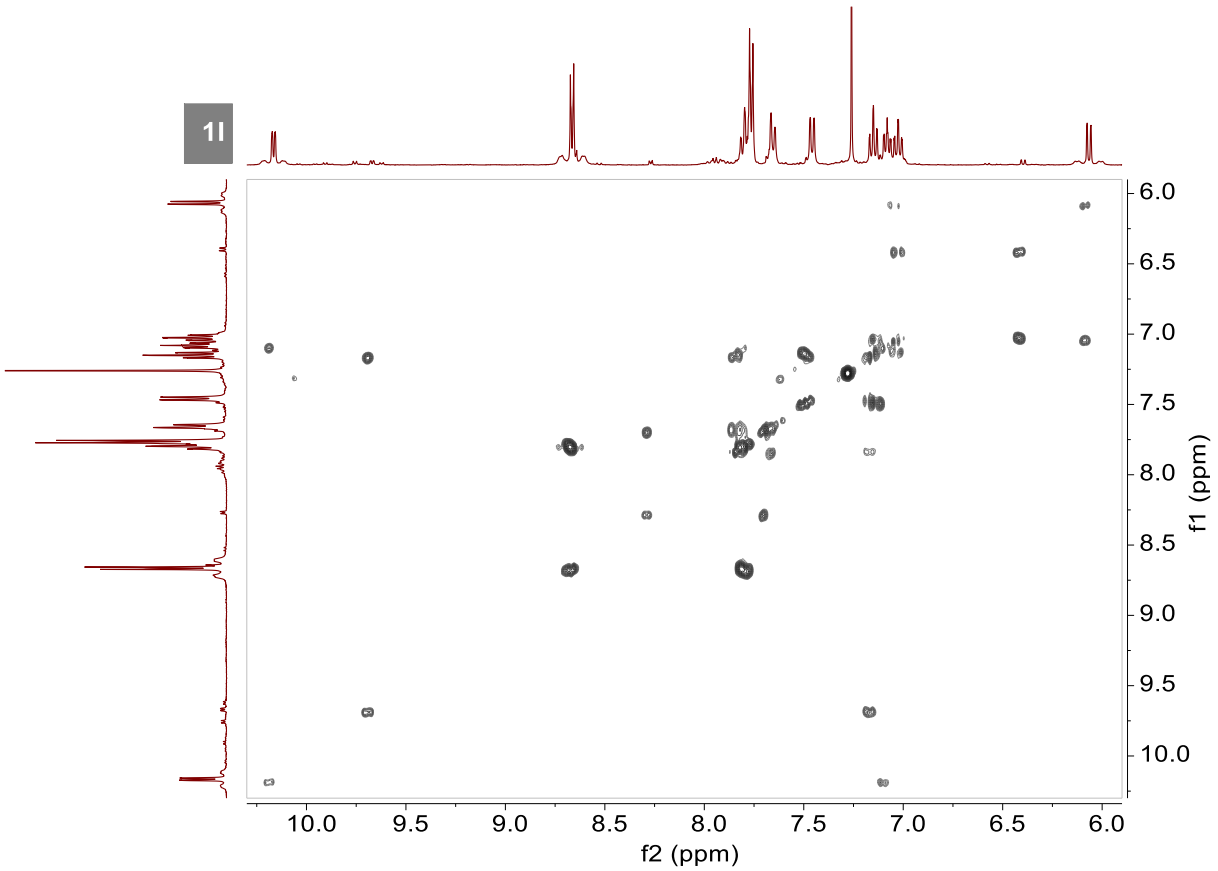


Figure S4. $^{1}H^{1}H$ COSY NMR spectrum of complex **1I**, d_1-chloroform, r.t.

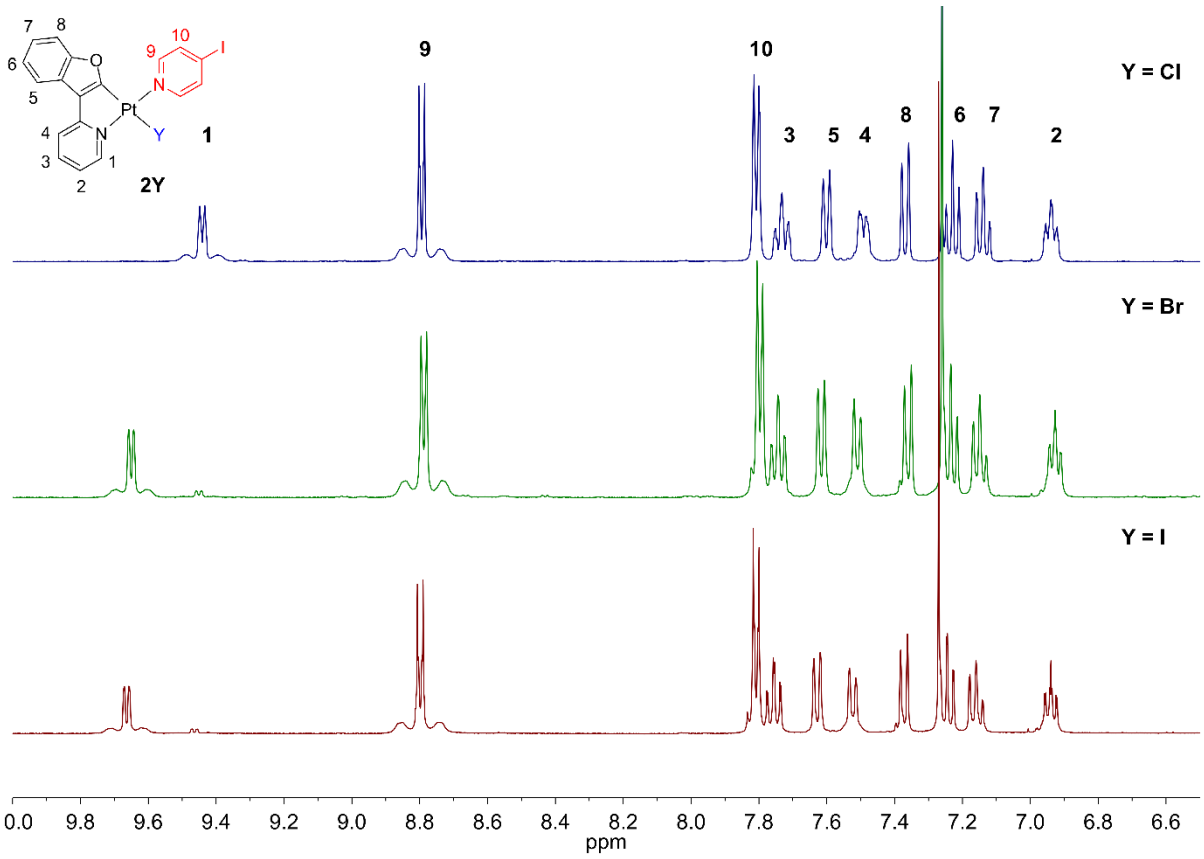


Figure S5. ^{1}H NMR spectra of complexes **2Y**, d_1-chloroform, r.t.

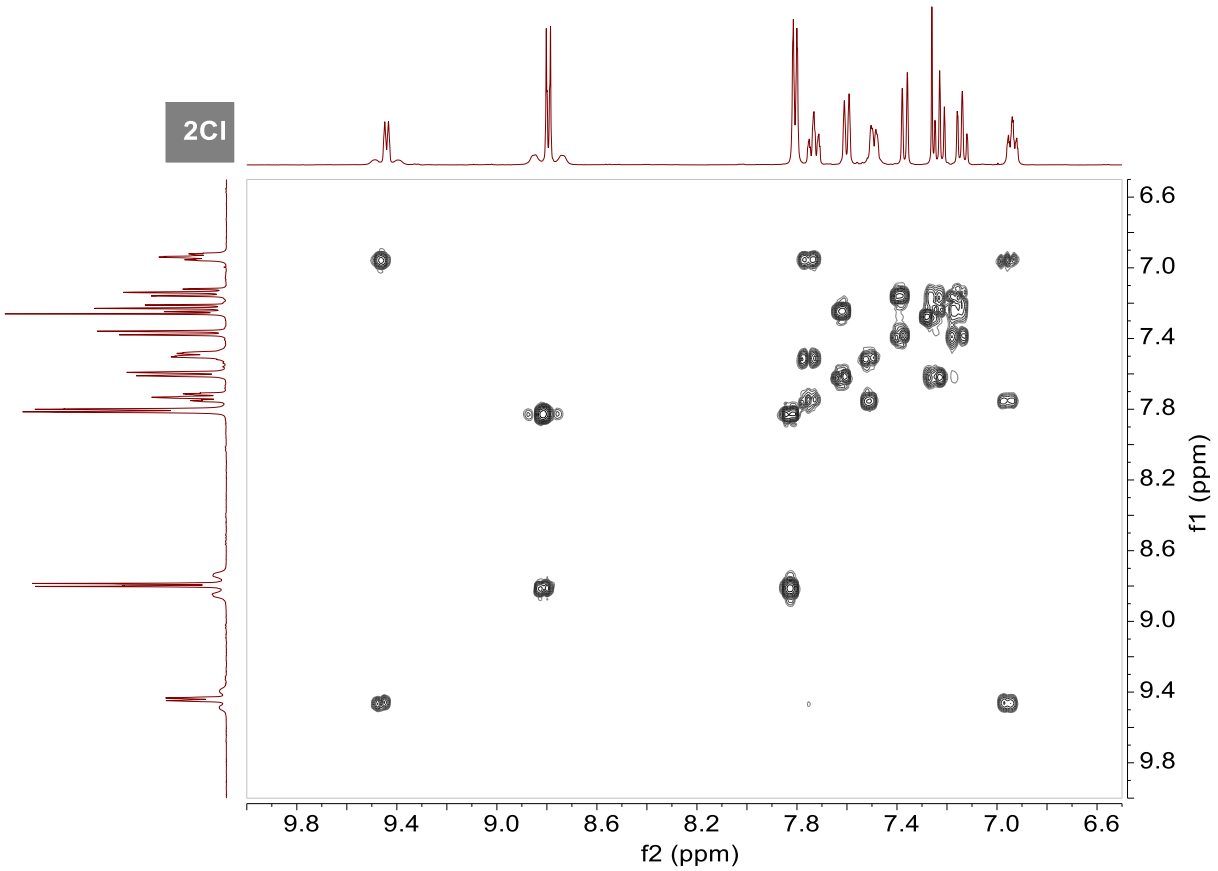


Figure S6. ^{1}H^{1}H COSY NMR spectrum of complex **2Cl**, d_1-chloroform, r.t.

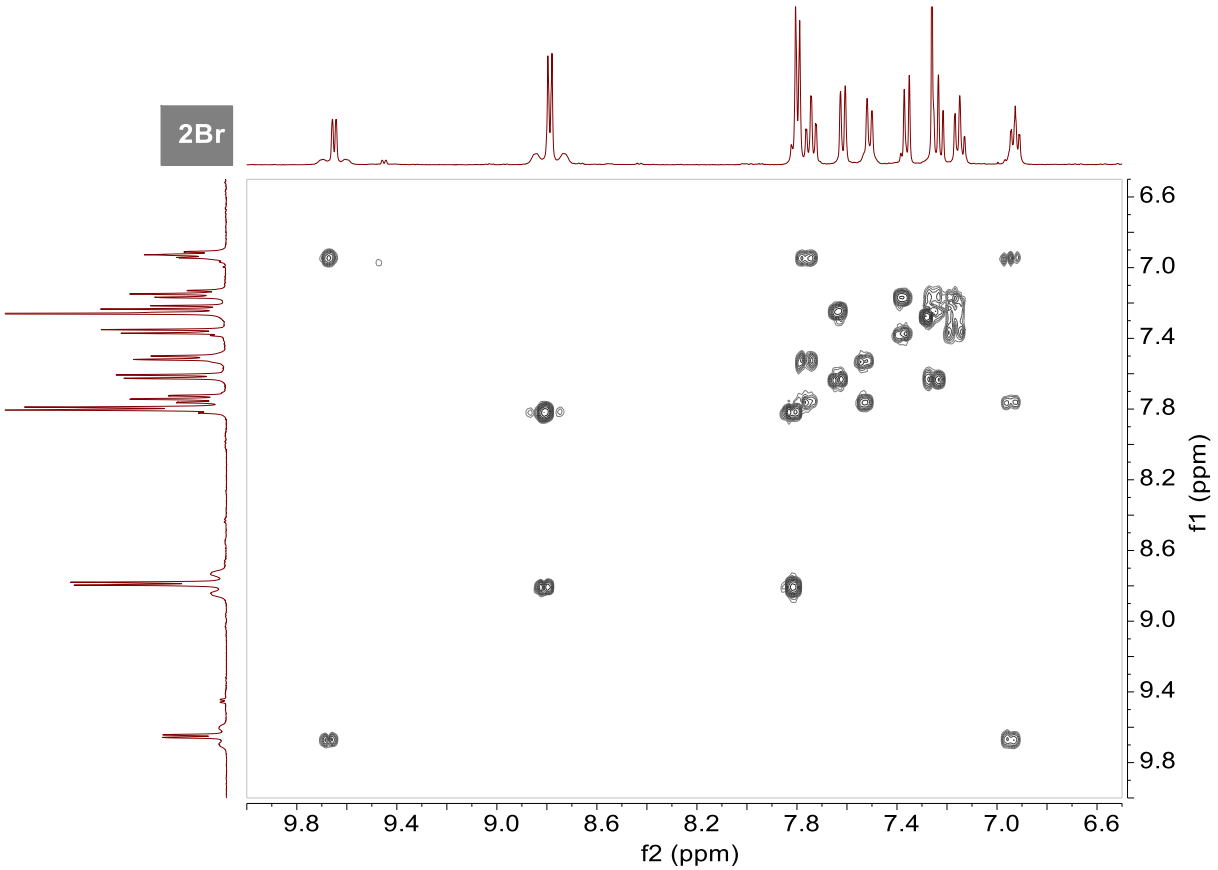


Figure S7. $^{1}H^{1}H$ COSY NMR spectrum of complex **2Br**, d_1-chloroform, r.t.

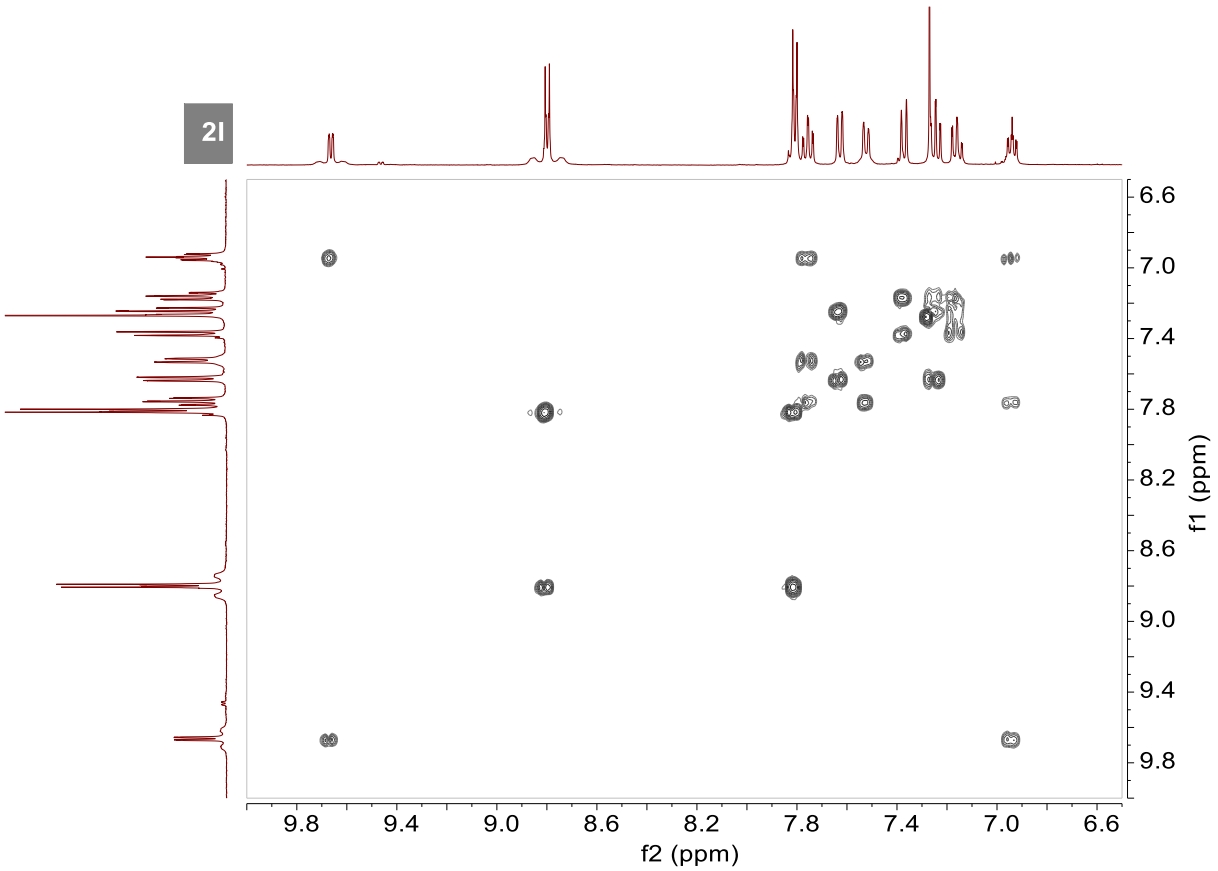


Figure S8. $^{1}H^{1}H$ COSY NMR spectrum of complex **2I**, d_1-chloroform, r.t.

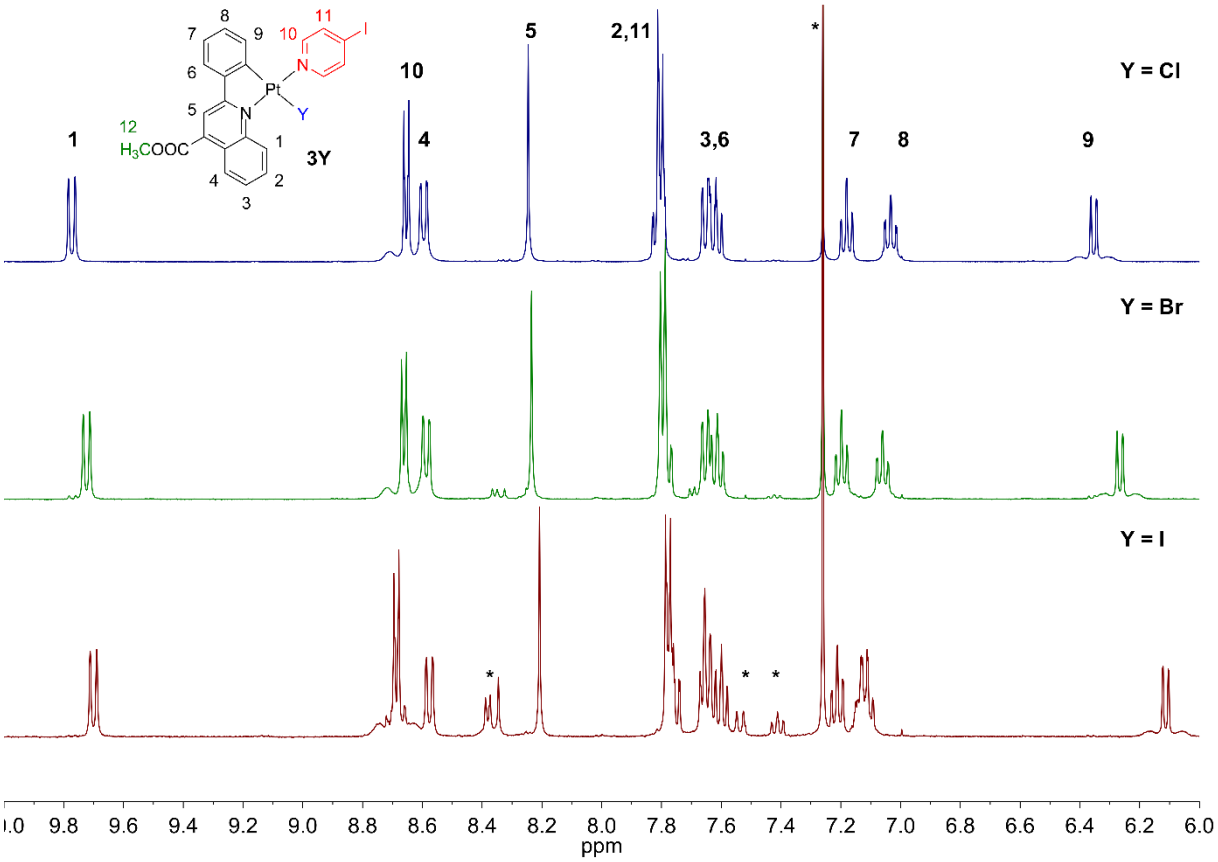


Figure S9. ^{1}H NMR spectra of complexes **3Y**, d_1-chloroform, r.t.

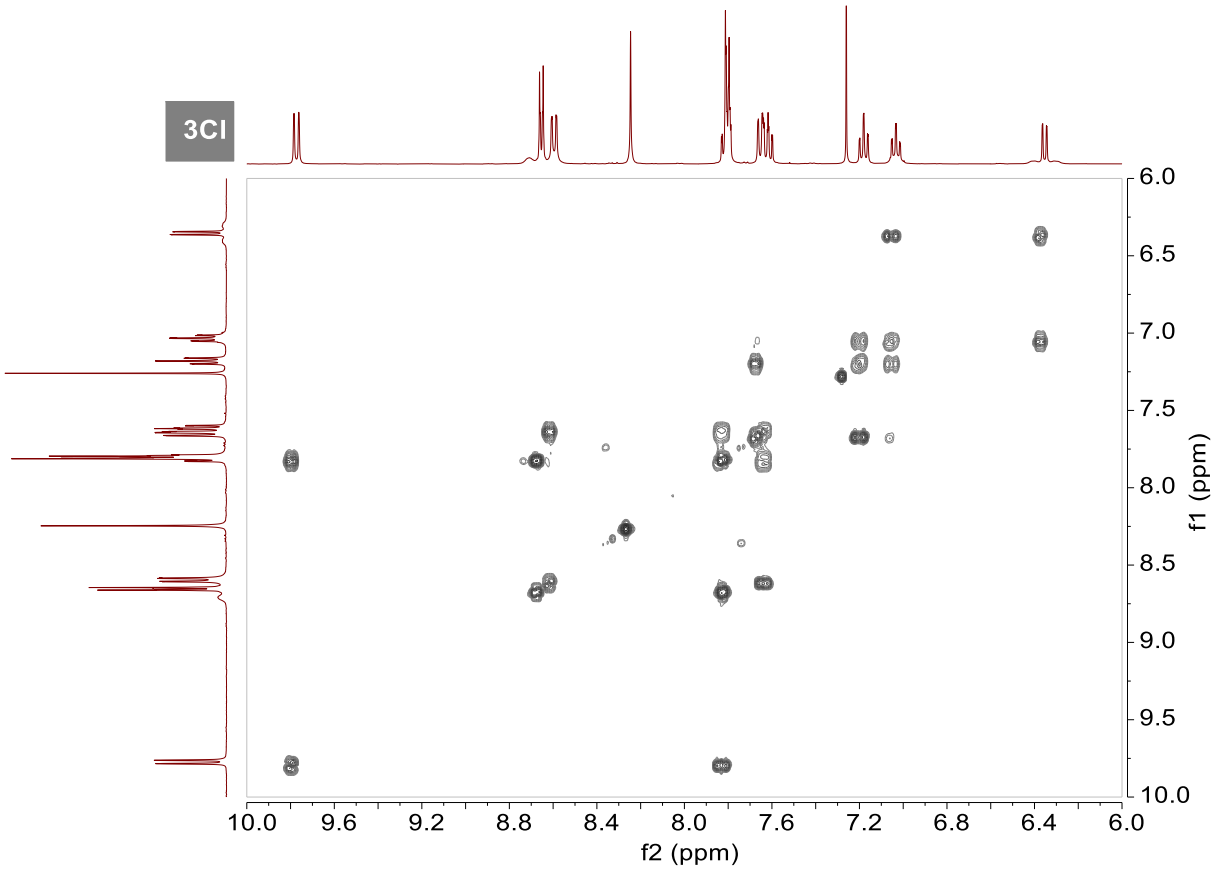


Figure S10. ^{1}H^{1}H COSY NMR spectrum of complex **3Cl**, d_1-chloroform, r.t.

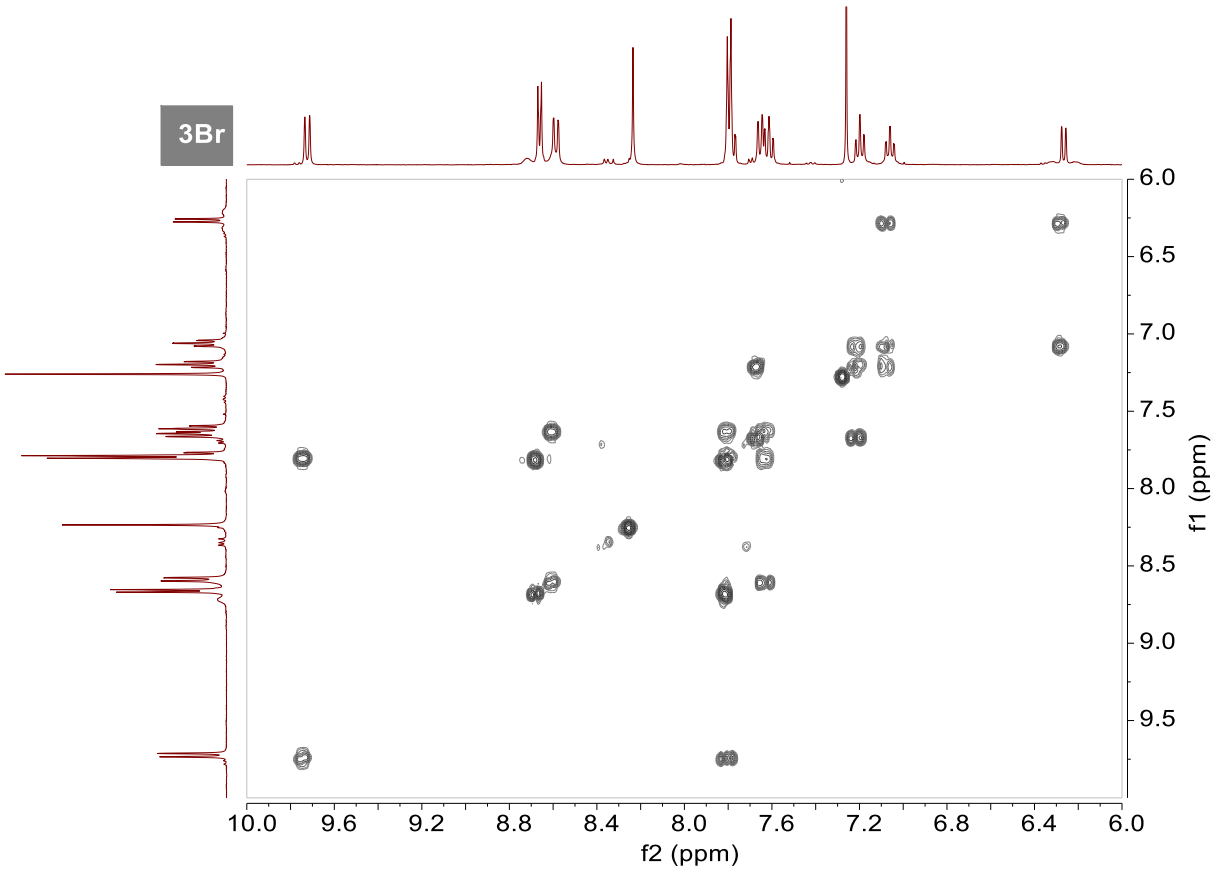


Figure S11. $^{1}H^{1}H$ COSY NMR spectrum of complex **3Br**, d_1-chloroform, r.t.

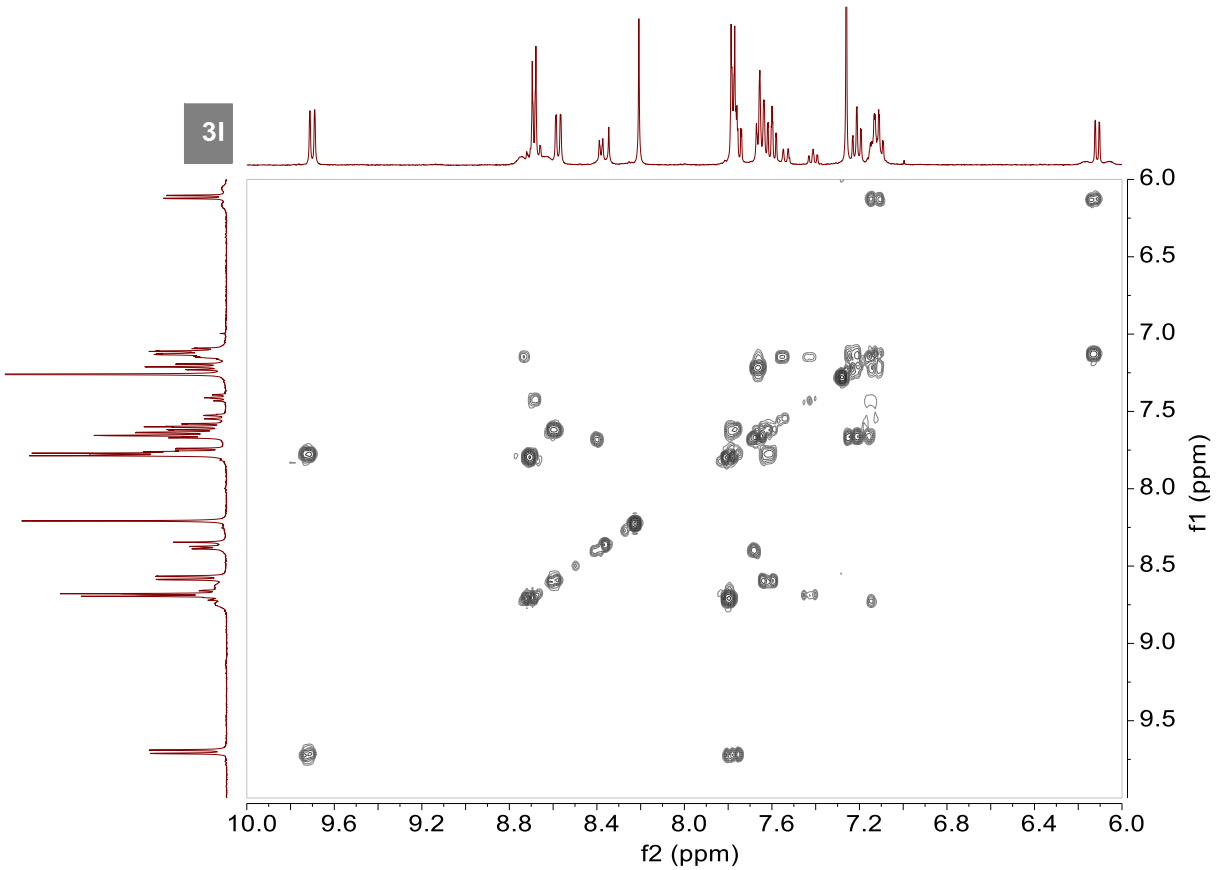


Figure S12. $^{1}H^{1}H$ COSY NMR spectrum of complex **3I**, d_1-chloroform, r.t.

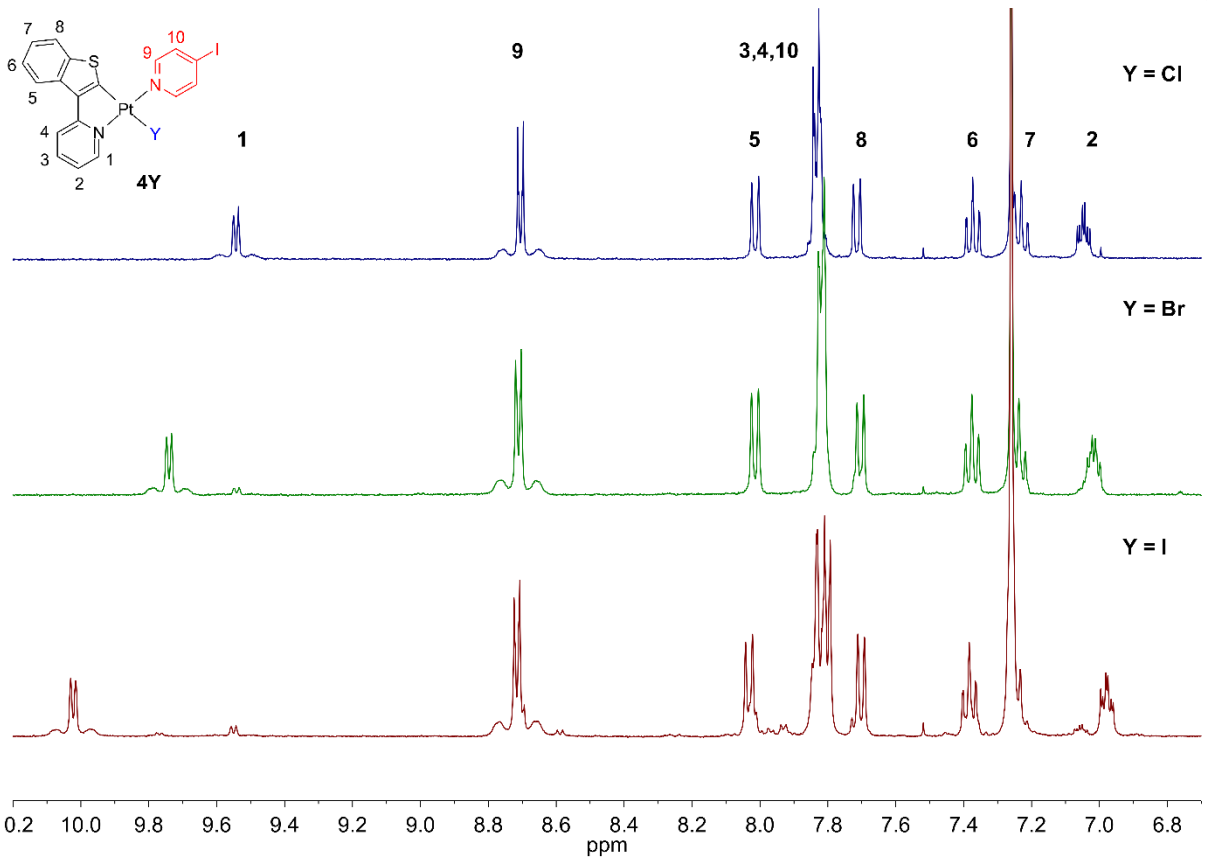


Figure S13. ^{1}H NMR spectra of complexes **4Y**, d_1-chloroform, r.t.

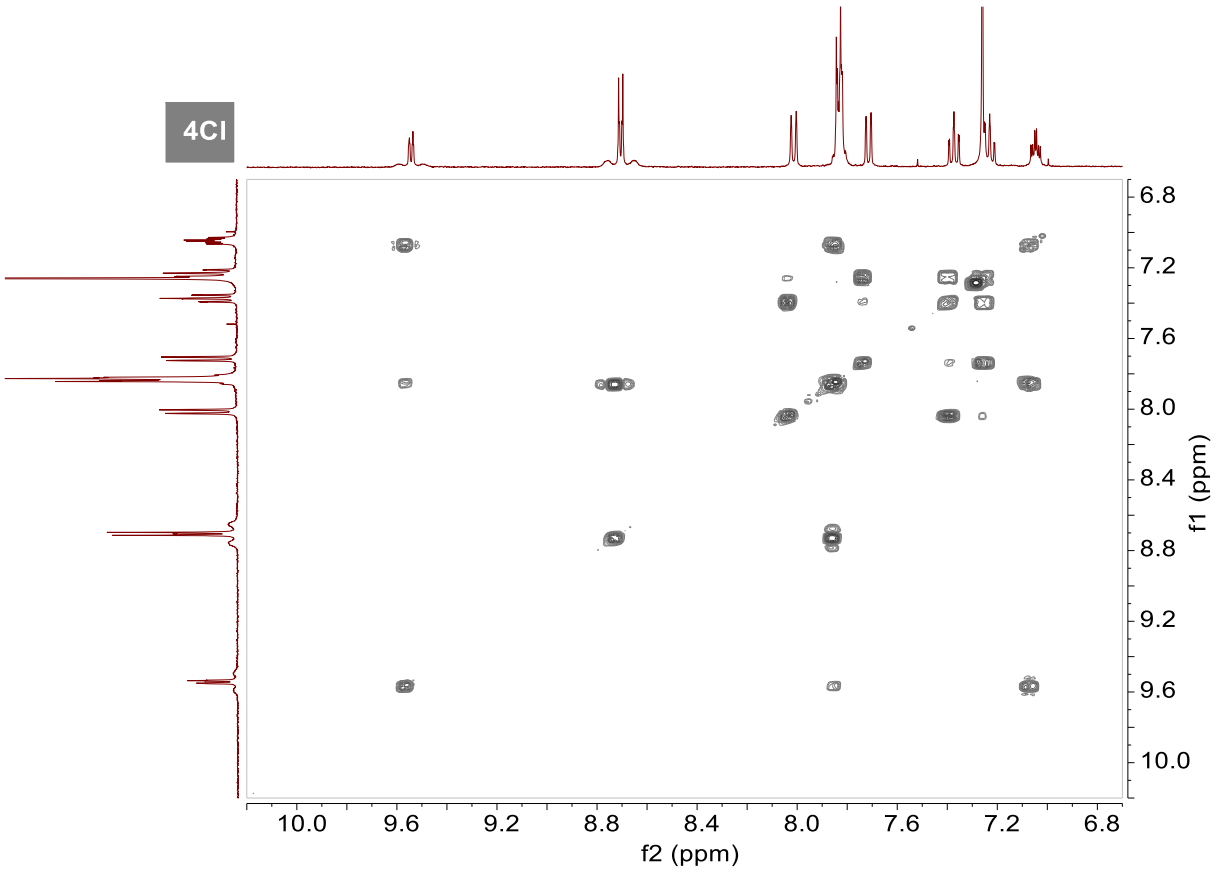


Figure S14. ^{1}H^{1}H COSY NMR spectrum of complex **4Cl**, d_1-chloroform, r.t.

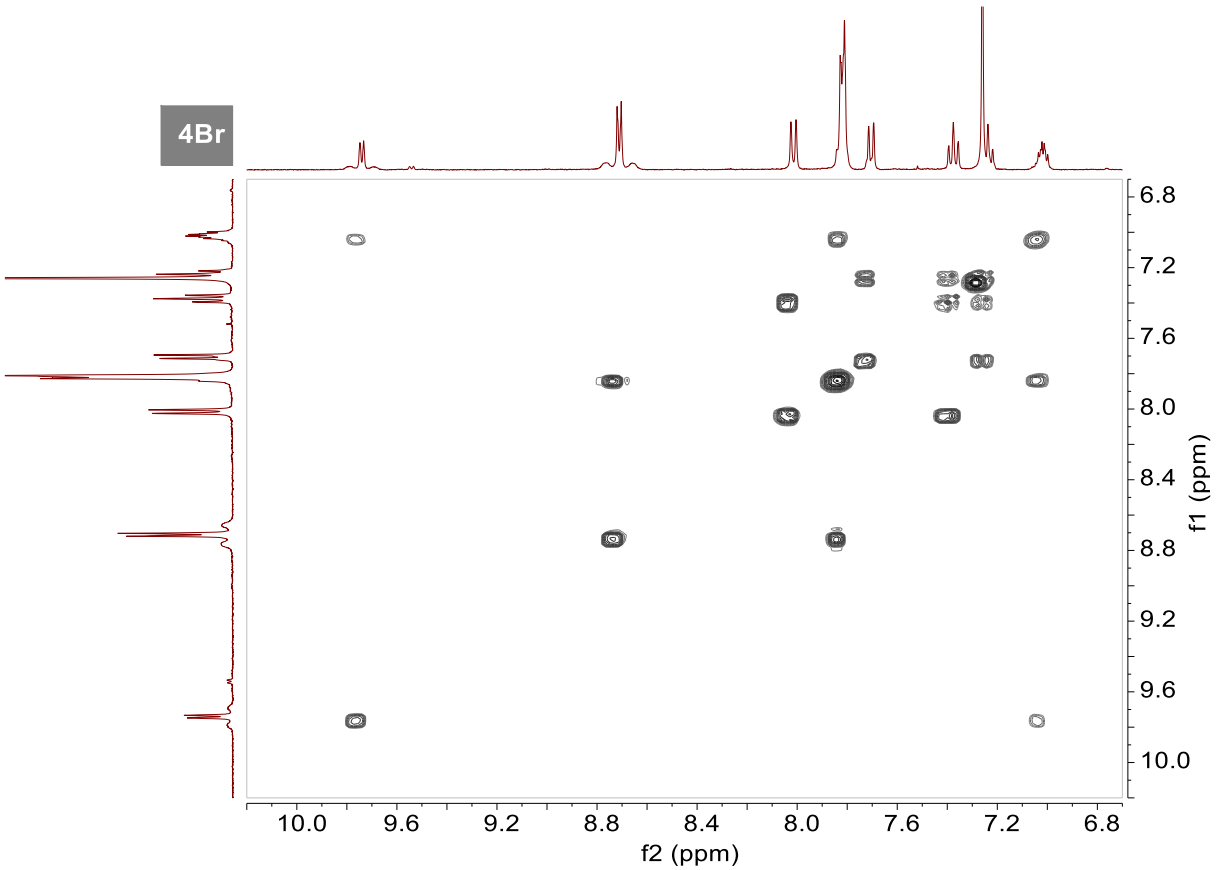


Figure S15. $^{1}H^{1}H$ COSY NMR spectrum of complex **4Br**, d_1-chloroform, r.t.

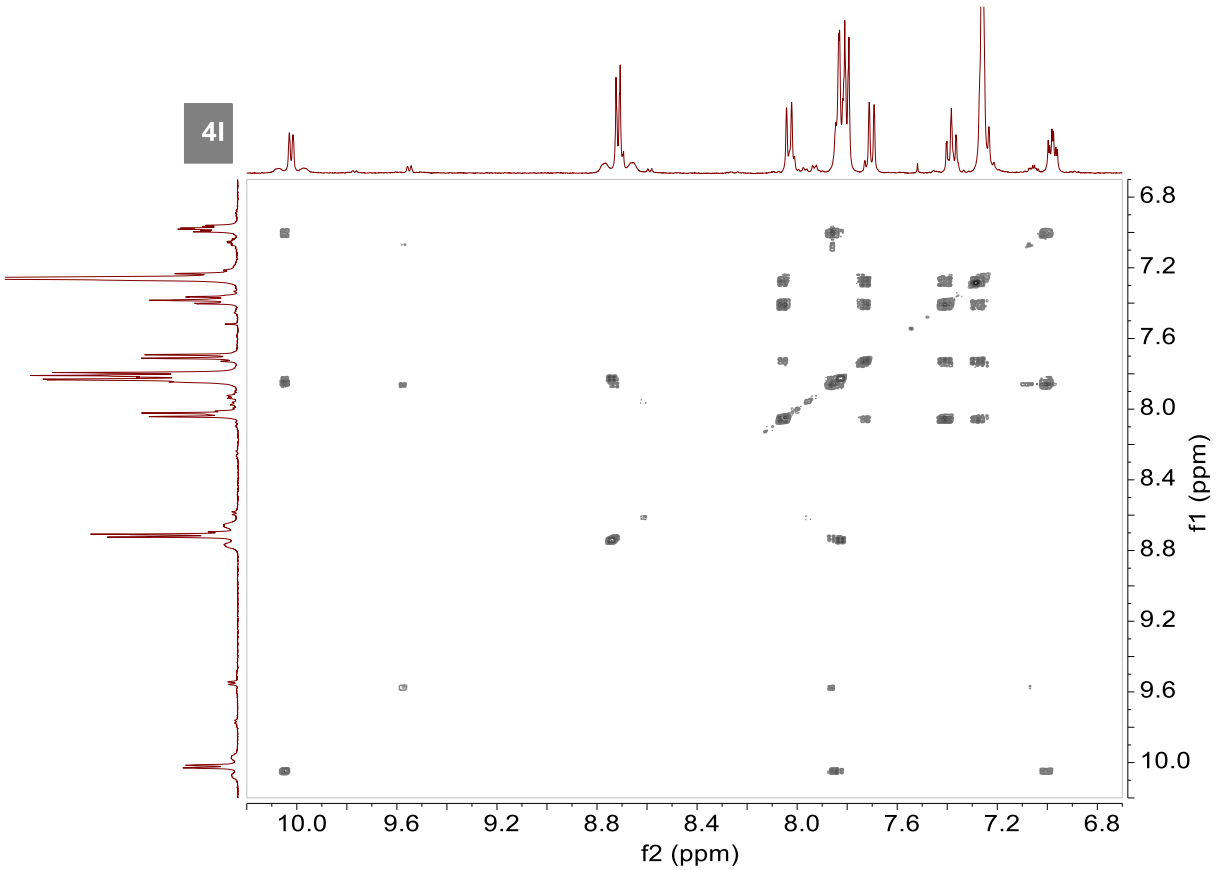


Figure S16. $^{1}H^{1}H$ COSY NMR spectrum of complex **4I**, d_1-chloroform, r.t.

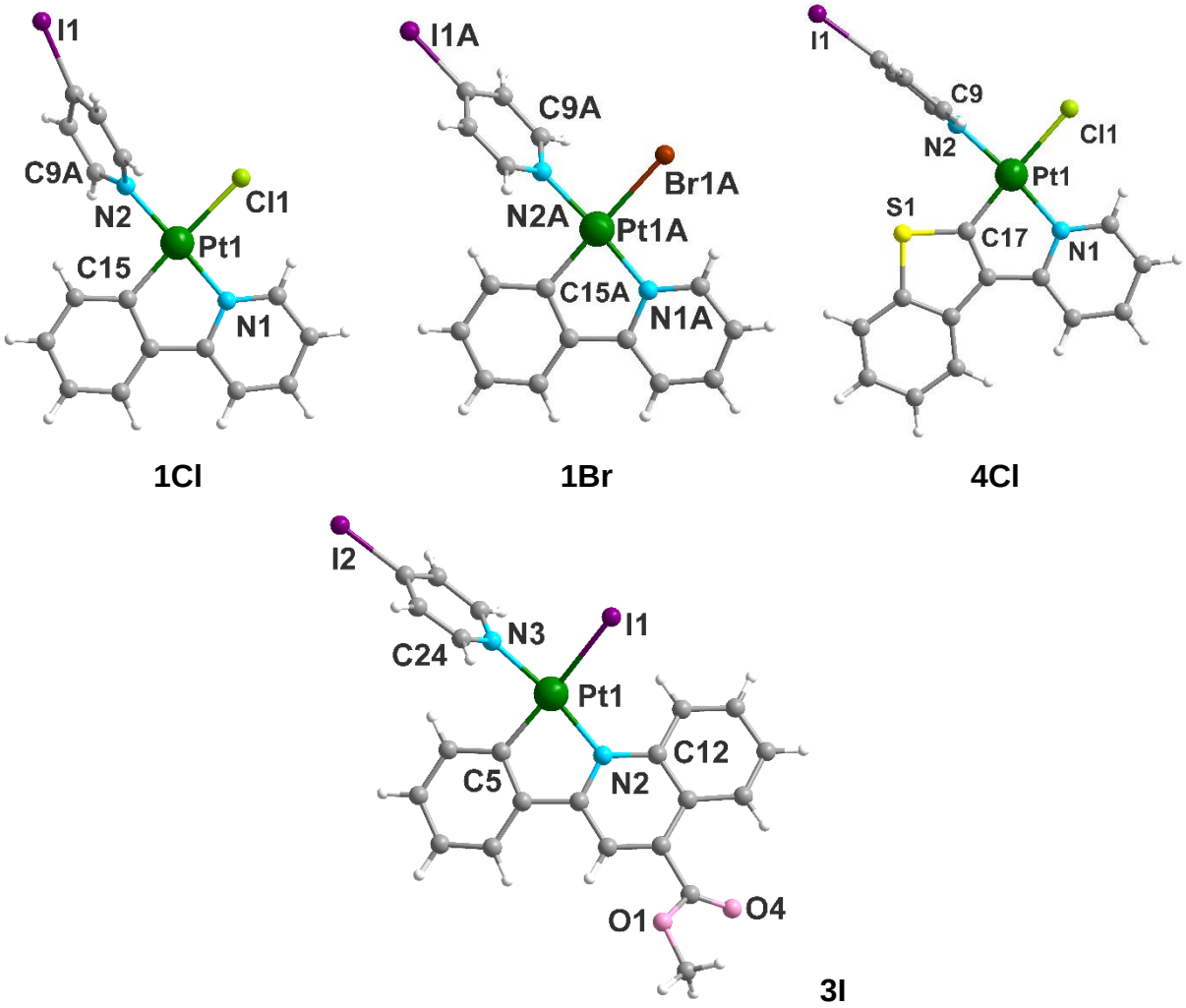


Figure S17. Molecular structure of **1Cl**, **1Br**, **3I** and **4Cl**.

Table S3. Selected structure parameters of **1Cl**, **1Br**, **2Br**, **3I** and **4Cl**.

	Distance, Å		Angle, °		Torsion, °	
1Cl	Pt1−N2	2.027(5)	N2−Pt1−C15	96.4(2)	C9A−N2−Pt1−Cl1	110.9(7)
	Pt1−N1	2.006(5)	C15−Pt1−N1	82.1(2)		
	Pt1−C15	1.980(6)	N1−Pt1−Cl1	95.1(1)		
	Pt1−Cl1	2.397(2)	Cl1−Pt1−N2	86.4(1)		
1Br	Pt1A−N1A	2.018(4)	Br1A−Pt1A−N2A	86.6(1)	C9A−N2A−Pt1A−Br1A	64.6(4)
	Pt1A−N2A	2.015(4)	N2A−Pt1A−C15A	94.7(2)		
	Pt1A−C15A	1.993(6)	C15A−Pt1A−N1A	81.1(2)		
	Pt1A−Br1A	2.5438(6)	N1A−Pt1A−Br1A	97.5(1)		
2Br	Pt1−N1	2.046(3)	N1−Pt1−Br1	96.46(9)	C9−N2−Pt1−Br1	136.6(3)
	Pt1−N2	2.034(3)	Br1−Pt1−N2	89.18(9)		
	Pt1−C17	1.941(4)	N2−Pt1−C17	95.9(2)		
	Pt1−Br1	2.5091(5)	C17−Pt1−N1	78.5(2)		
3I	Pt1−N3	2.022(2)	C5−Pt1−N3	91.4(1)	C24−N3−Pt1−C5	77.5(3)
	Pt1−I1	2.7208(4)	N3−Pt1−I1	86.00(8)	C12−N2−Pt1−I1	−30.0(3)
	Pt1−N2	2.051(2)	I1−Pt1−N2	101.44(7)		
	Pt1−C5	1.989(4)	N2−Pt1−C5	80.4(1)		
4Cl	Pt1−N2	2.018(3)	N2−Pt1−C17	94.5(1)	C9−N2−Pt1−Cl1	−88.6(2)
	Pt1−N1	2.022(3)	C17−Pt1−N1	79.7(1)		
	Pt1−C17	1.949(4)	N1−Pt1−Cl1	97.20(8)		
	Pt1−Cl1	2.3738(9)	Cl1−Pt1−N2	88.68(8)		

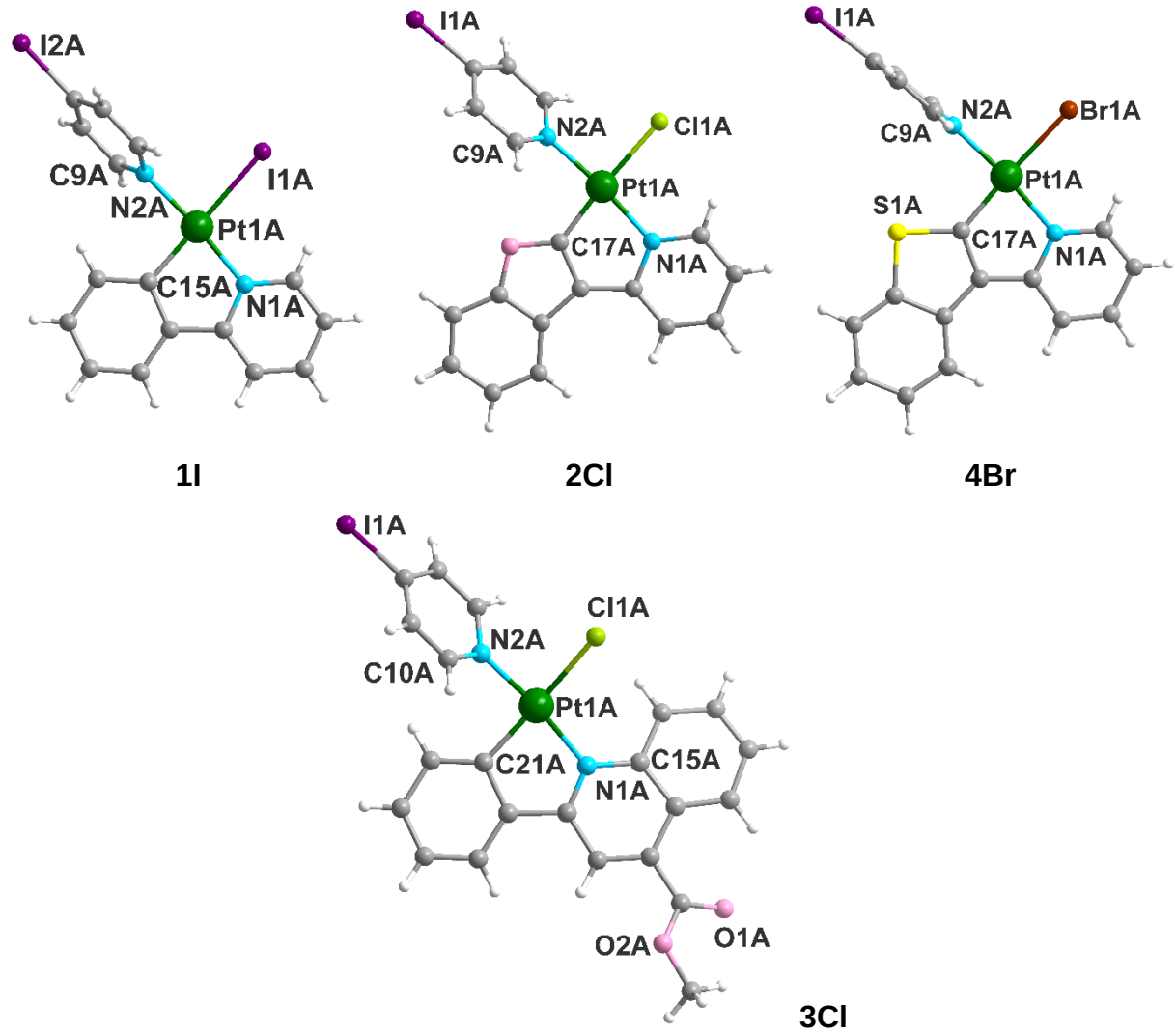


Figure S18. Molecular structure of **1I**, **2Cl**, **3Cl** and **4Br**.

Table S4. Selected structure parameters of **1I**, **2Cl**, **3Cl** and **4Br**.

	Distance, Å		Angle, °		Torsion, °	
1I	I1A−Pt1A	2.699(1)	N1A−Pt1A−C15A	80.9(6)	C9A−N2A−Pt1A−I1A	108(1)
	Pt1A−N1A	2.02(1)	C15A−Pt1A−N2A	94.1(5)		
	Pt1A−C15A	1.99(2)	N2A−Pt1A−I1A	85.5(3)		
	Pt1A−N2A	2.02(1)	I1A−Pt1A−N1A	99.5(4)		
2Cl	N2A−Pt1A	2.02(1)	N2A−Pt1A−Cl1A	89.5(4)	C9A−N2A−Pt1A−Cl1A	−124(1)
	Pt1A−Cl1A	2.369(5)	Cl1A−Pt1A−N1A	96.1(5)		
	Pt1A−N1A	2.03(1)	N1A−Pt1A−C17A	79.6(7)		
	Pt1A−C17A	1.92(2)	C17A−Pt1A−N2A	94.8(7)		
3Cl	Cl1A−Pt1A	2.431(3)	Cl1A−Pt1A−N1A	102.2(3)	C15A−N1A−Pt1A−Cl1A	−25(1)
	Pt1A−N1A	2.03(1)	N1A−Pt1A−C21A	81.8(5)	C10A−N2A−Pt1A−Cl1A	−110(1)
	Pt1A−C21A	1.97(1)	C21A−Pt1A−N2A	91.6(5)		
	Pt1A−N2A	1.99(1)	N2A−Pt1A−Cl1A	83.5(3)		
4Br	Br1A−Pt1A	2.492(4)	Br1A−Pt1A−N2A	89.6(7)	C9A−N2A−Pt1A−Br1A	−89(2)
	Pt1A−N1A	2.05(3)	N2A−Pt1A−C17A	94(1)		
	Pt1A−C17A	1.93(3)	C17A−Pt1A−N1A	80(1)		
	Pt1A−N2A	2.02(3)	N1A−Pt1A−Br1A	97.0(7)		

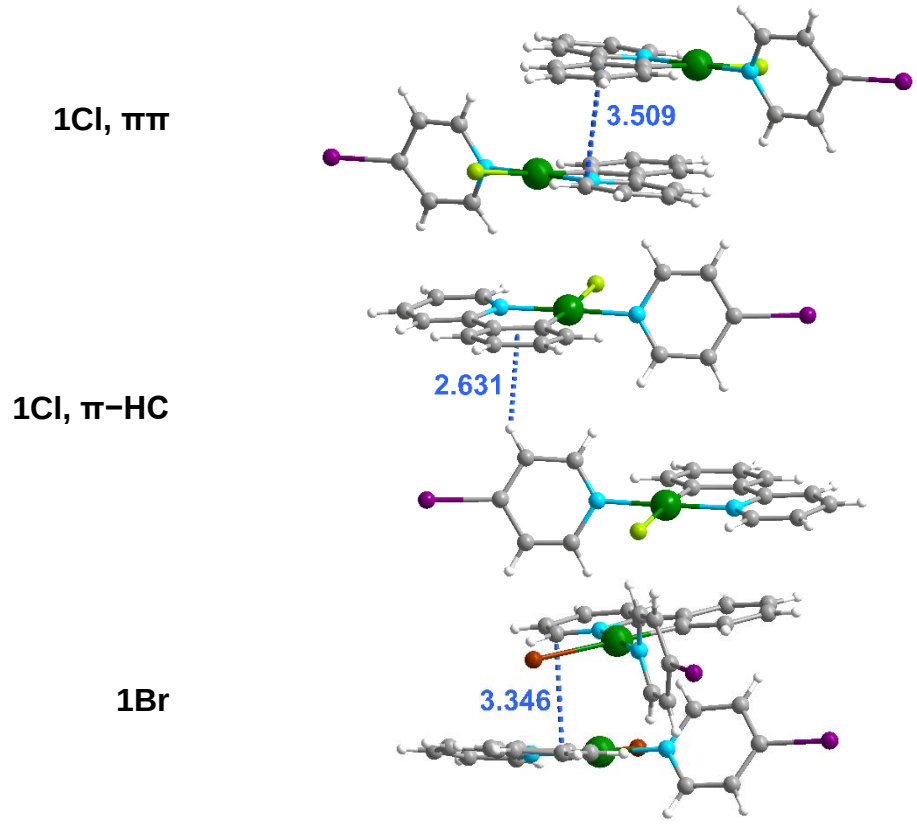


Figure S19. Fragment of molecular packing of **1Y** (Y = Cl, Br). The intermolecular ππ distance was measured between the closest atoms, distances are given in Å.

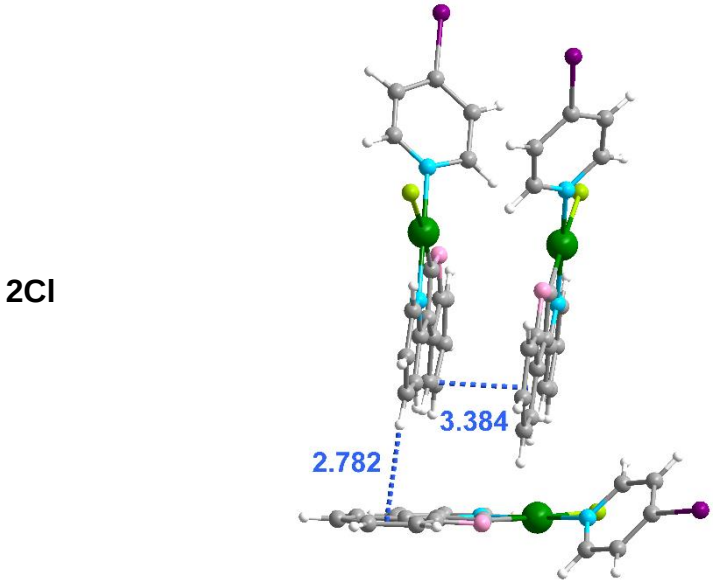


Figure S20. Fragment of molecular packing of **2Cl**. The intermolecular ππ distance was measured between the closest atoms, distances are given in Å.

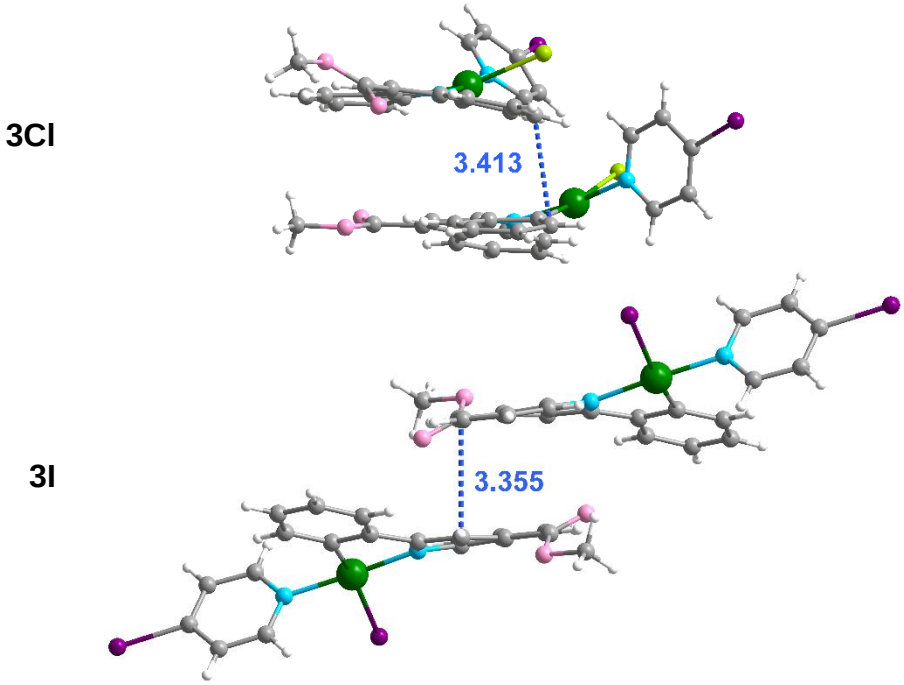


Figure S21. Fragment of molecular packing of **3Y** (Y = Cl, I). The intermolecular ππ distance was measured between the closest atoms, distances are given in Å.

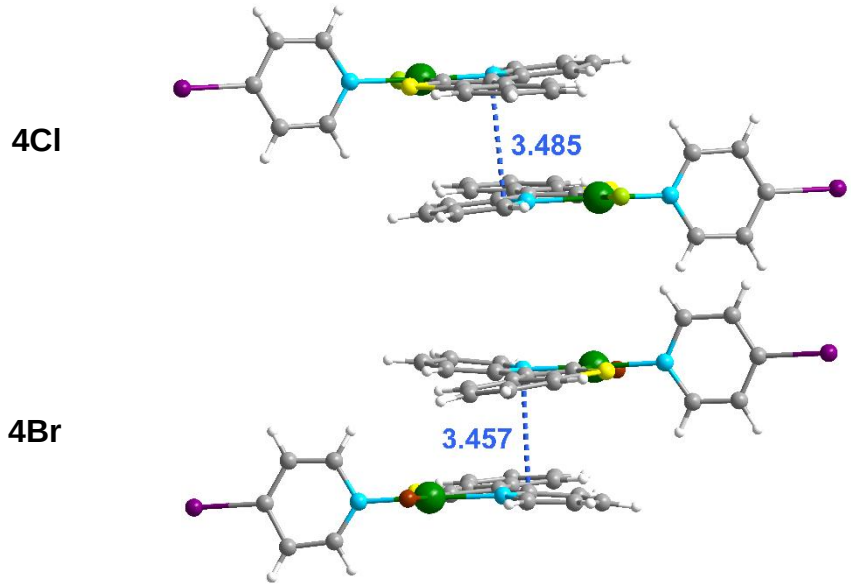


Figure S22. Fragment of molecular packing of **4Y** (Y = Cl, Br). The intermolecular ππ distance was measured between the closest atoms, distances are given in Å.

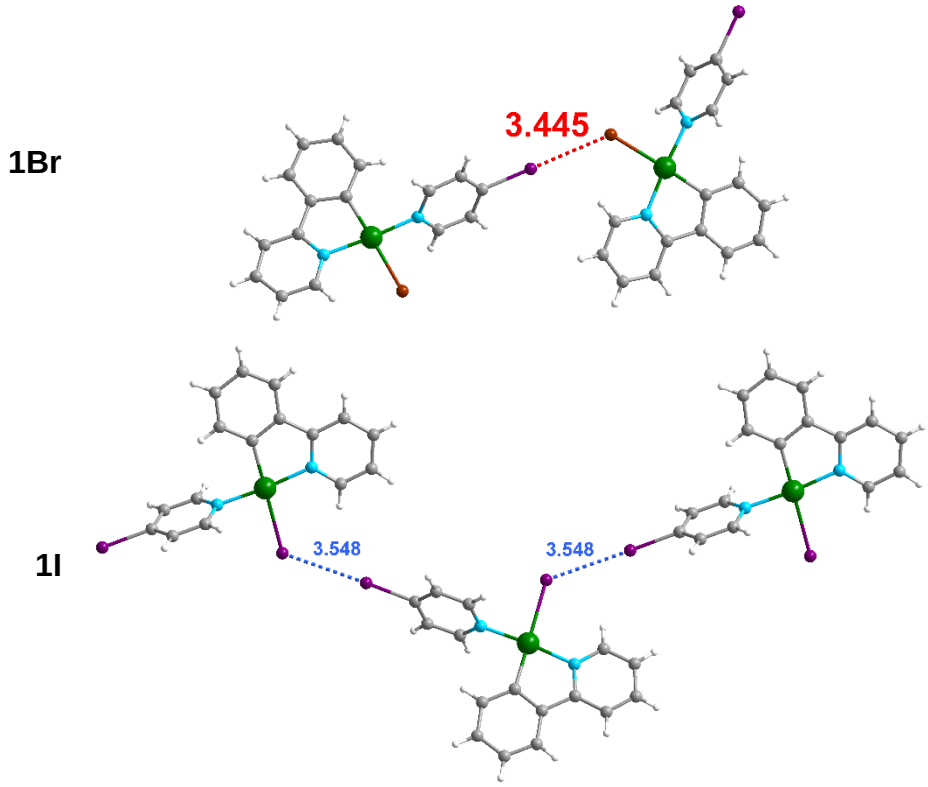


Figure S23. Fragments of molecular packing of **1Y** (Y = Br, I) with XB visualization, distances are given in Å.

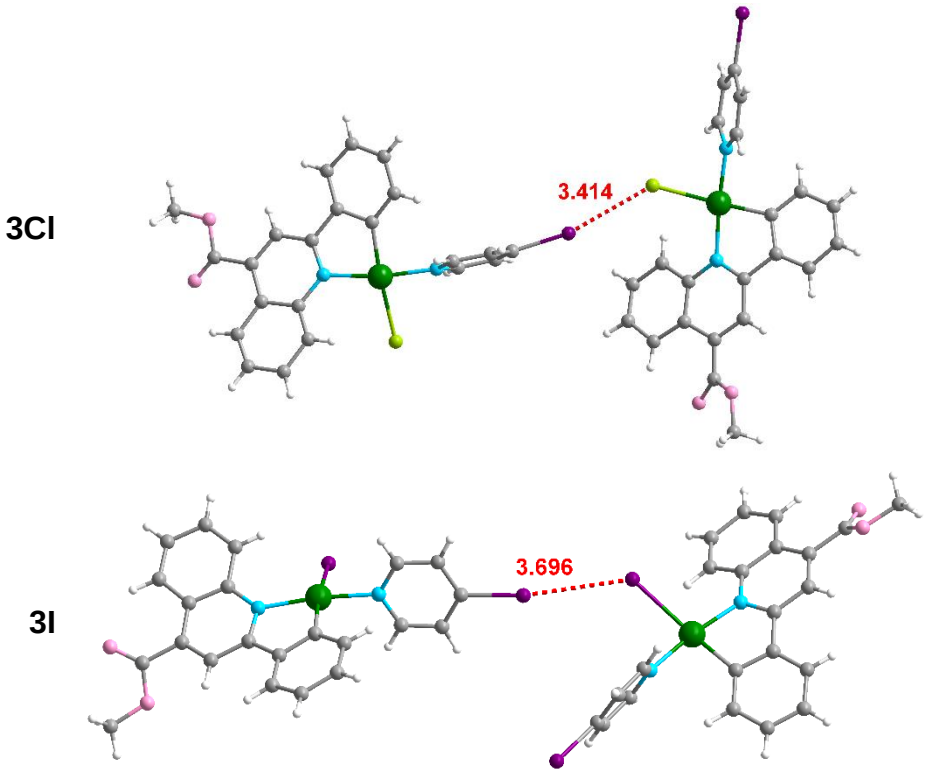


Figure S24. Fragments of molecular packing of **3Y** (Y = Cl, I) with XB visualization, distances are given in Å.

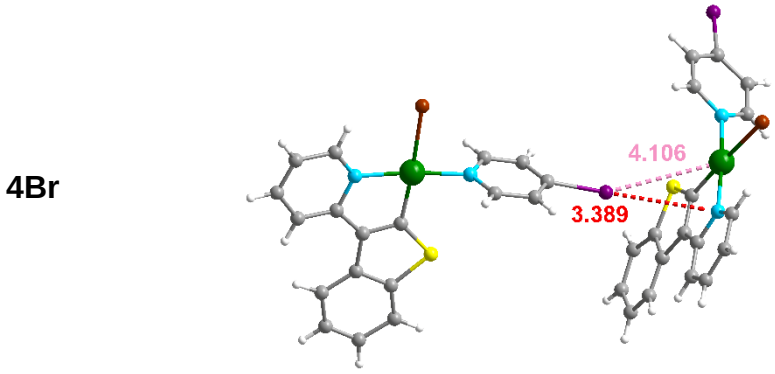


Figure S25. Fragments of molecular packing of **4Br** with XB visualization, distances are given in Å.

Table S5. Structural parameters of XBs of **1I**, **2Cl**, **3Cl** and **4Br**.

	Y	*d*(I···Y), Å	R_{IY}*[6]	C–I···Y, °	Pt–Y···I, °
1I	I	3.5476	0.896	177.67	122.93
2Cl	Cl	3.8607	1.035	147.91	119.09
3Cl	Cl	3.4141	0.915	167.34	135.11
4Br	Ce**	3.389	–	171.11	–

* $R_{IY} = d_{I–Y}/(r_I + r_Y)$, r_I and r_Y are van der Waals radii.[7]

** Ce is centroid of metallocycle {$PtNC_3$}.

Table S6. Realization of non-covalent interactions in crystal structure of **1Y**−**4Y**.

	ππ	**π···H−C**	**C−I···Y**	**C−I···Pt**	**C−I···Ce***
1Cl	■	■		■	
1Br	■		■		
1I			■		
2Cl	■	■			
2Br	■		■		
3Cl	■		■		
3I	■		■		
4Cl	■				■
4Br	■				■

* Ce is centroid of metallocycle {$PtNC_3$}.

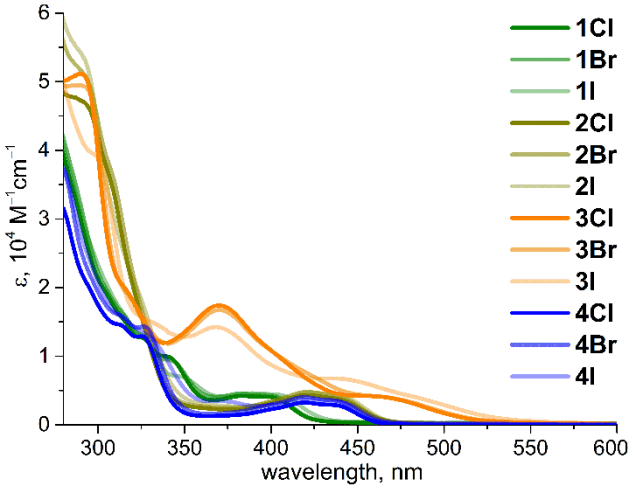


Figure S26. UV-vis spectra of Pt(II) complexes **1Y**−**4Y** (Y = Cl, Br, I), DCE solution 10^{-5} M, r.t.

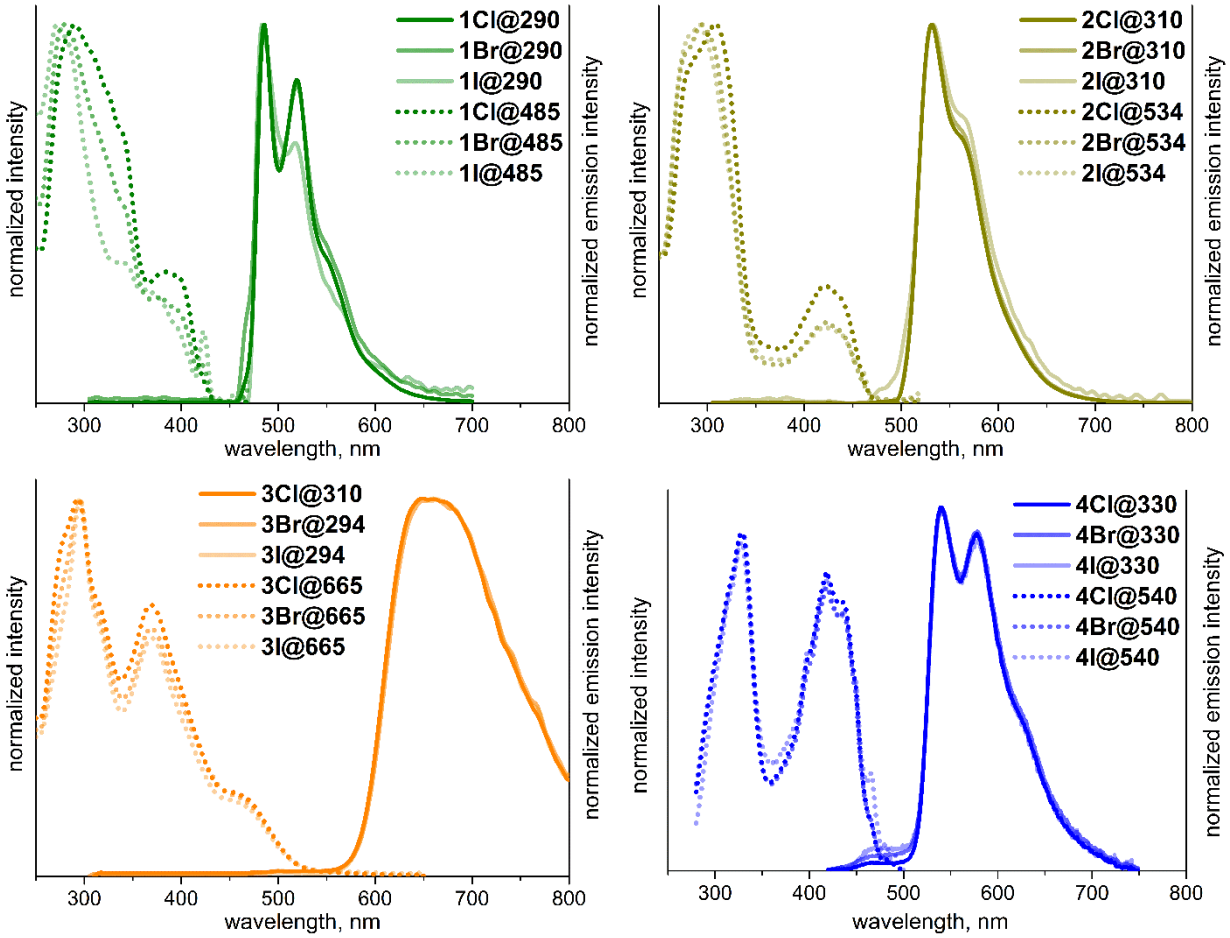


Figure S27. Normalized excitation (dot line) and normalized emission (solid line) spectra of Pt(II) complexes **1Y**−**4Y** (Y = Cl, Br, I); DCE solution 10^{-5} M, r.t., registration and excitation wavelengths are indicated on diagram.

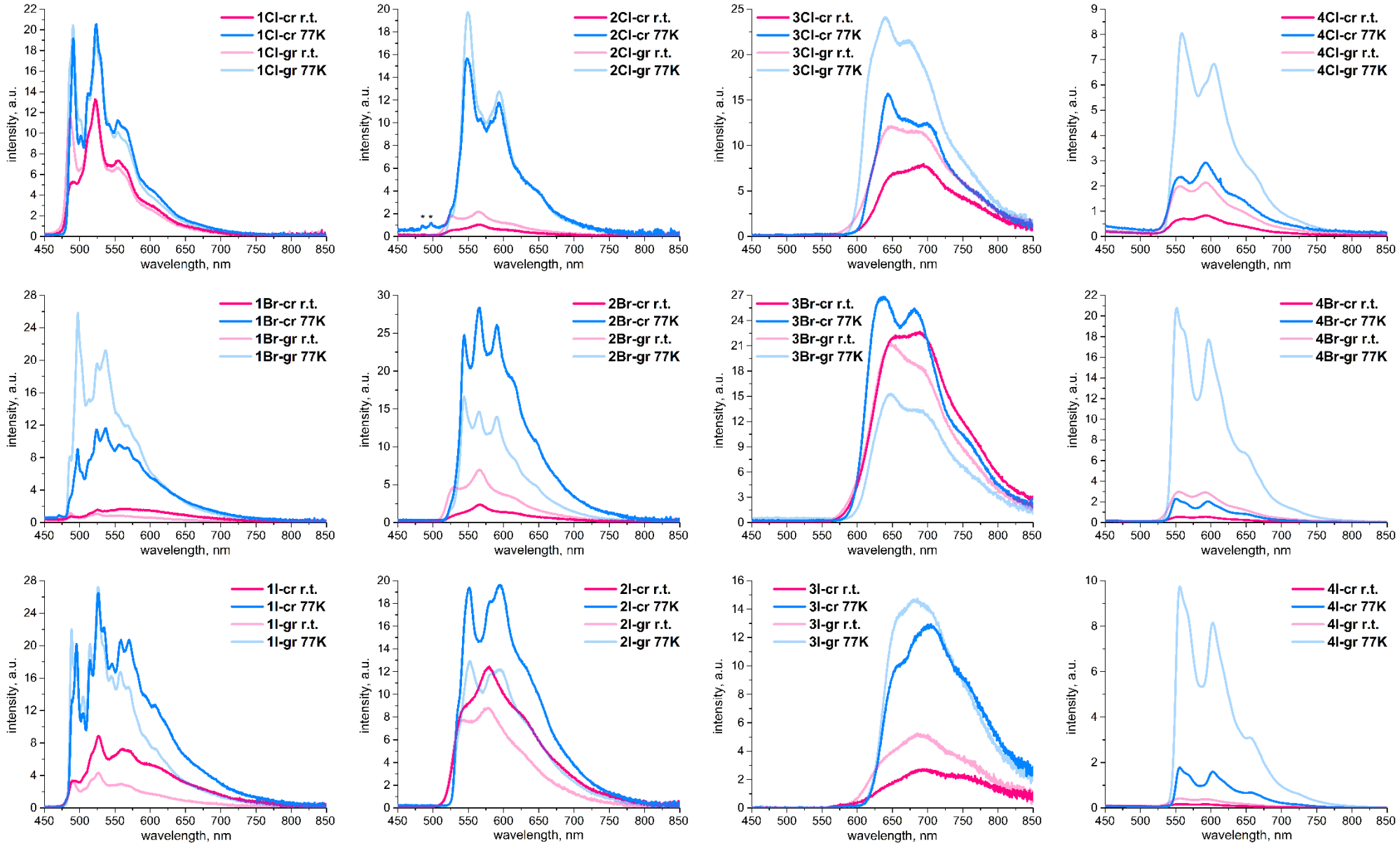


Figure S28. Variable temperature solid-state emission spectra of complexes **1Y**–**4Y** (Y = Cl, Br, I); λ_{ext} 351 nm (**1Y**–**3Y**) and 365 nm (**4Y**); cr = crystals, gr = ground powder.

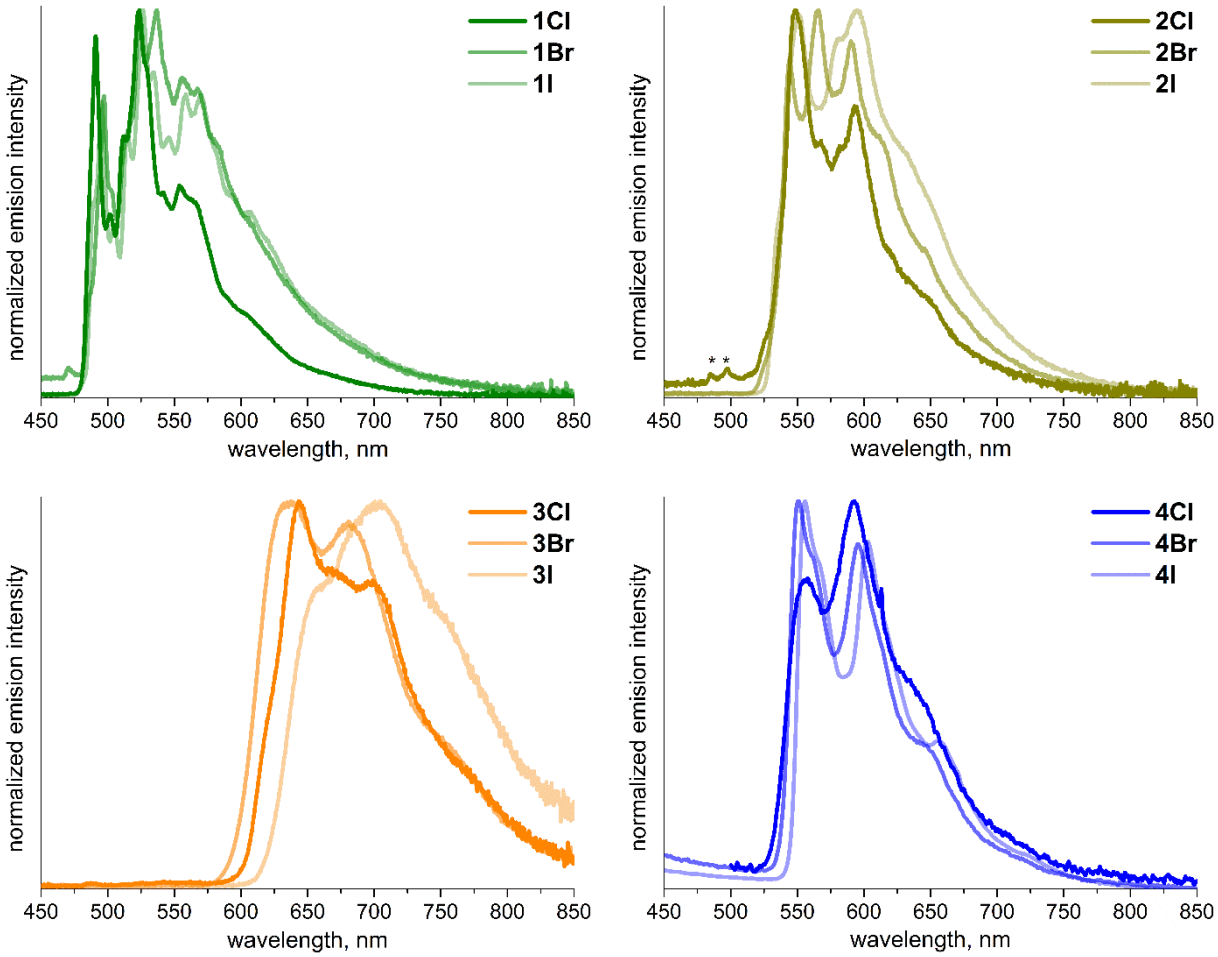


Figure S29. Normalized emission spectra of complexes **1Y**−**4Y** (Y = Cl, Br, I) in solid-state, crystalline samples, 77K.

Table S7. Photophysical properties of complexes **1Y**−**4Y** (Y = Cl, Br, I) in solid state, crystalline samples, λ_{exct} 351 nm.

Complex	λ_{em}, nm		τ_{av},[#] ns	
	298 K	77 K	298 K	77 K
1Cl	490, 523, 557, 604[sh]	480, 523, 554, 608[sh]	740	5328
1Br	489, 526, 566	498, 524, 536, 557	1211	6840
1I	491, 526, 561, 608[sh]	496, 526, 559, 570, 607[sh]	341	3795
2Cl	528, 565, 611	548, 593, 646[sh]	488	10820
2Br	535[sh], 566, 613[sh]	544, 566, 590, 611[sh], 646[sh]	347	11450
2I	544[sh], 580, 623[sh]	551, 595, 629[sh]	363	10465
3Cl	650[sh], 694, 761[sh]	643, 699, 769[sh]	715	3290
3Br	655, 688, 760[sh]	638, 682, 753[sh]	781	3905
3I	642[sh], 692, 754[sh]	657[sh], 700, 754[sh]	120	2698
4Cl	558[sh], 595, 642[sh]	555, 593, 640[sh]	2752	15062
4Br	554, 593, 643[sh]	551, 596, 648[sh]	6345	12722
4I	557, 594, 641[sh]	556, 603, 658	1764	10224

[#] Amplitude average lifetime $\tau_{aver} = \sum A_i\tau_i$ was calculated according to published method.[8]

Table S8. Photophysical properties of complexes **1Y**−**4Y** (Y = Cl, Br, I) in solid state, ground powder, λ_{exct} 351 nm.

Complex	λ_{em}, nm		τ_{av},[#] ns		Φ[**], %
	298 K	77 K	298 K	77 K	
1Cl	486, 522, 553. 601[sh]	491, 523, 554, 604[sh]	781	7137	1.7
1Br	487, 525, 557	497, 537, 569[sh]	1163	7406	1.15
1I	489, 527, 560, 609[sh]	489, 526, 559, 608[sh]	439	4488	0.15
2Cl	526, 566, 612[sh]	550, 594, 545[sh]	410	10870	0.47
2Br	529, 567, 612[sh]	544, 566, 591, 614[sh], 644[sh]	340	11920	0.57
2I	540, 578, 620[sh]	552, 595, 632[sh]	216	7265	0.19
3Cl	646, 689, 753[sh]	639, 674, 751[sh]	671	3096	1.22
3Br	646, 692[sh], 757[sh]	647, 694[sh], 758[sh]	562	2988	1.06
3I	642[sh], 685, 753[sh]	659[sh], 683, 746[sh]	104	2074	n/a
4Cl	555, 593, 645[sh]	559, 605, 659[sh]	5468	16072	6.0
4Br	555, 592, 642[sh]	552, 597, 650[sh]	6737	12992	2.8
4I	556, 596, 630[sh]	557, 603, 657	1598	10209	1.54

[#] Amplitude average lifetime $\tau_{aver} = \sum A_i\tau_i$ was calculated according to published method.[8] [**] 298 K

Table S9. Observed lifetime (ns) of complexes **1Y**−**4Y** (Y = Cl, Br, I) in the solid-state (cr = crystalline samples, gr = ground powder).

	298 K						**77 K**					
	τ_1	A_1	τ_2	A_2	τ_3	A_3	τ_1	A_1	τ_2	A_2	τ_3	A_3
1Cl_cr	136	0.11	463	0.56	1435	0.33	893	0.03	3298	0.46	8826	0.45
1Cl_gr	187	0.13	603	0.69	1931	0.18	1642	0.13	5167	0.59	13911	0.28
1Br_cr	47.9	0.30	312	0.27	2570	0.43	516	0.15	3747	0.47	12997	0.38
1Br_gr	80.3	0.40	512	0.24	2808	0.36	805	0.12	4741	0.57	14765	0.31
1I_cr	30.8	0.51	157	0.24	1159	0.25	360	0.23	1191	0.47	9368	0.30
1I_gr	33.5	0.33	128	0.37	1235	0.30	416	0.23	2198	0.45	10614	0.32
2Cl_cr	143	0.43	487	0.49	2211	0.08	1103	0.04	7509	0.56	16328	0.40
2Cl_gr	73	0.14	284	0.59	878	0.27	3949	0.14	10661	0.80	28104	0.06
2Br_cr	104	0.23	357	0.63	883	0.14	721	0.05	7339	0.43	15923	0.52
2Br_gr	86	0.18	309	0.63	680	0.19	1444	0.09	10640	0.79	27941	0.12
2I_cr	21.5	0.02	161	0.34	483	0.64	1604	0.07	7013	0.41	14271	0.52
2I_gr	93	0.49	264	0.47	1176	0.04	722	0.11	3901	0.43	11960	0.46
3Cl_cr	107	0.16	453	0.49	1349	0.35	454	0.04	2226	0.38	4187	0.58
3Cl_gr	110	0.12	455	0.51	1156	0.37	386	0.05	1956	0.39	4111	0.56
3Br_cr	57	0.10	355	0.44	1342	0.46	408	0.04	2288	0.32	4911	0.65
3Br_gr	64	0.16	327	0.51	1168	0.39	207	0.05	1516	0.36	4104	0.59
3I_cr	23	0.51	111	0.32	435	0.17	172	0.08	1243	0.32	3813	0.60
3I_gr	23	0.55	108	0.36	591	0.09	155	0.12	1022	0.40	3435	0.48
4Cl_cr	340	0.05	1286	0.34	3780	0.61	4355	0.07	15885	0.93	–	–
4Cl_gr	1688	0.16	6166	0.84	–	–	6582	0.09	17028	0.91	–	–
4Br_cr	1201	0.07	3797	0.39	8778	0.55	4524	0.09	13570	0.91	–	–
4Br_gr	639	0.02	2992	0.26	8279	0.72	3451	0.08	13778	0.92	–	–
4I_cr	306	0.09	970	0.41	2673	0.50	2244	0.05	10601	0.95	–	–
4I_gr	136	0.03	748	0.35	2171	0.61	935	0.02	5755	0.30	12454	0.68

Table S10. Selected parameters of the **1Cl**−**4Cl** optimized geometries (in dichloroethane solution). The corresponding experimental parameters in crystal are given in parentheses.

Complex	Distance, Å		Angle, °	
1Cl	Pt1−N2	2.025 (2.027)	N2−Pt1−C15	95.6 (96.4)
	Pt1−N1	2.018 (2.006)	C15−Pt1−N1	81.1 (82.1)
	Pt1−C15	1.981 (1.980)	N1−Pt1−Cl1	96.1 (95.1)
	Pt1−Cl1	2.427 (2.397)	Cl1−Pt1−N2	87.1 (86.4)
2Cl	N2A−Pt1A	2.026 (2.02)	N2A−Pt1A−Cl1A	88.8 (89.5)
	Pt1A−Cl1A	2.399 (2.369)	Cl1A−Pt1A−N1A	95.7 (96.1)
	Pt1A−N1A	2.046 (2.03)	N1A−Pt1A−C17A	79.0 (79.6)
	Pt1A−C17A	1.937 (1.92)	C17A−Pt1A−N2A	96.4 (94.8)
3Cl	Cl1A−Pt1A	2.441 (2.431)	Cl1A−Pt1A−N1A	102.0 (102.2)
	Pt1A−N1A	2.057 (2.03)	N1A−Pt1A−C21A	80.7 (81.8)
	Pt1A−C21A	1.971 (1.97)	C21A−Pt1A−N2A	93.5 (91.6)
	Pt1A−N2A	2.021 (1.99)	N2A−Pt1A−Cl1A	83.4 (83.5)
4Cl	Pt1−N2	2.028 (2.018)	N2−Pt1−C17	96.2 (94.5)
	Pt1−N1	2.030 (2.022)	C17−Pt1−N1	79.4 (79.7)
	Pt1−C17	1.953 (1.949)	N1−Pt1−Cl1	96.3 (97.20)
	Pt1−Cl1	2.397 (2.3738)	Cl1−Pt1−N2	88.2 (88.68)

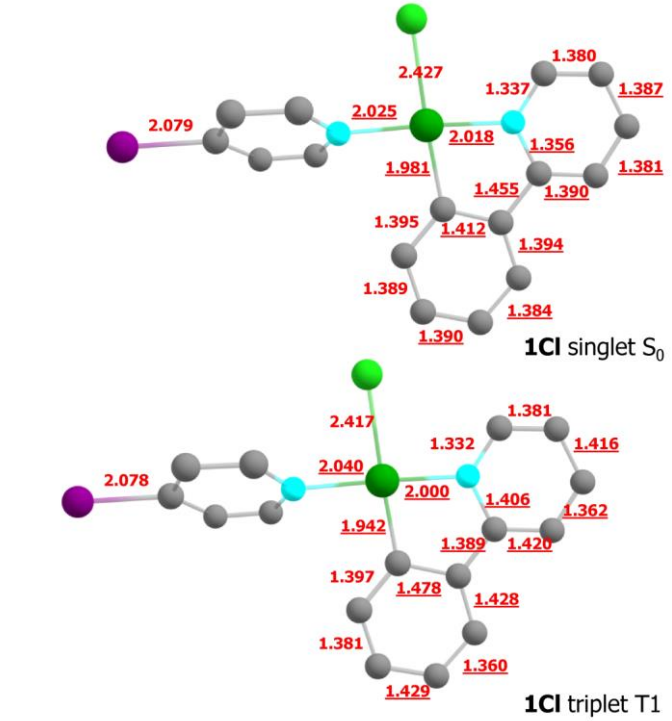


Figure S30. Selected bond lengths (Å) in the S_0 (top) and T_1 (bottom) optimized structures of **1Cl**. The distances changing by more than 0.01 **Å** on going from S_0 to T_1 are underlined.

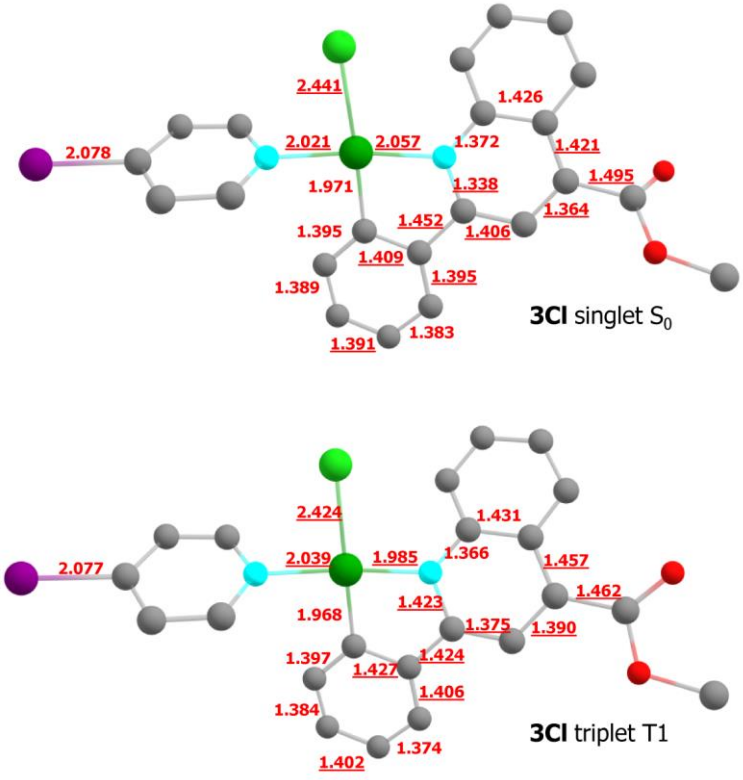


Figure S31. Selected bond lengths (Å) in the S_0 (top) and T_1 (bottom) optimized structures of **3Cl**. The distances changing by more than 0.01 **Å** on going from S_0 to T_1 are underlined.

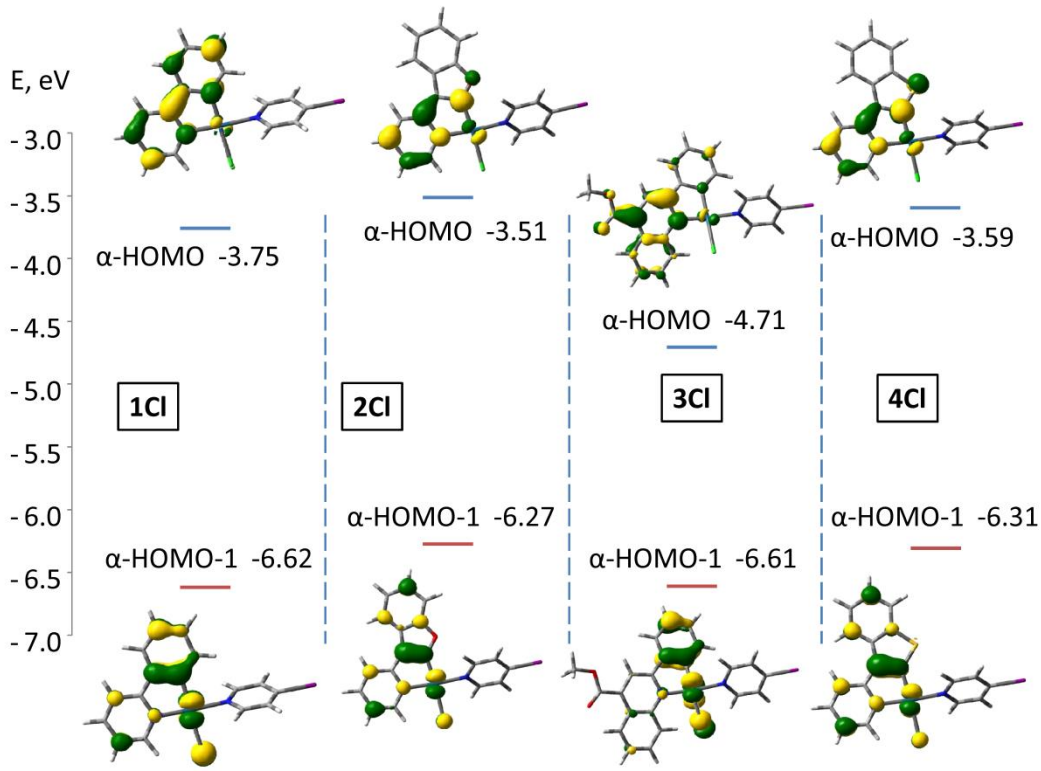


Figure S32. Isosurfaces (0.05) and energies (eV) of the **1Cl**−**4Cl** α-HOMO and α-HOMO−1 in the T_1 state.

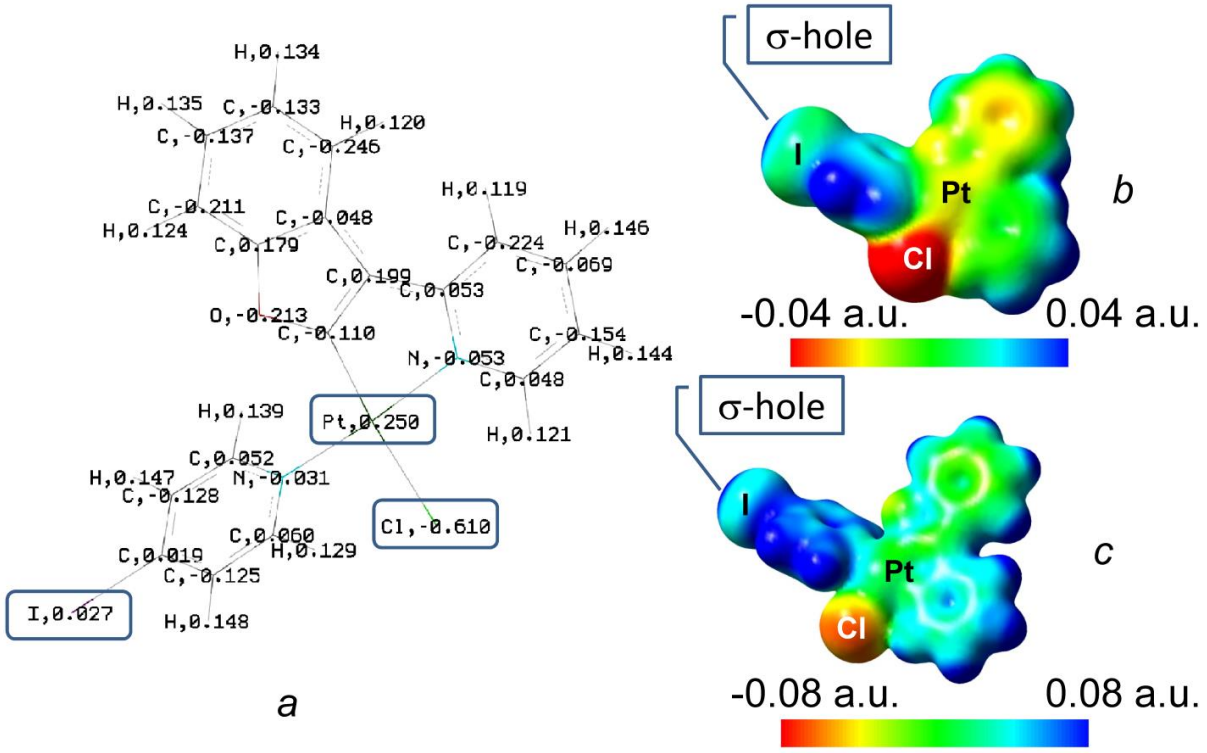


Figure S33. Mulliken charge distribution (a) and ESP mapped on the ED isosurface (b, c) in the **2Cl** molecule in dichloroethane solution. The ED isovalue is 0.001 a.u. (a) and 0.01 a.u. (b).

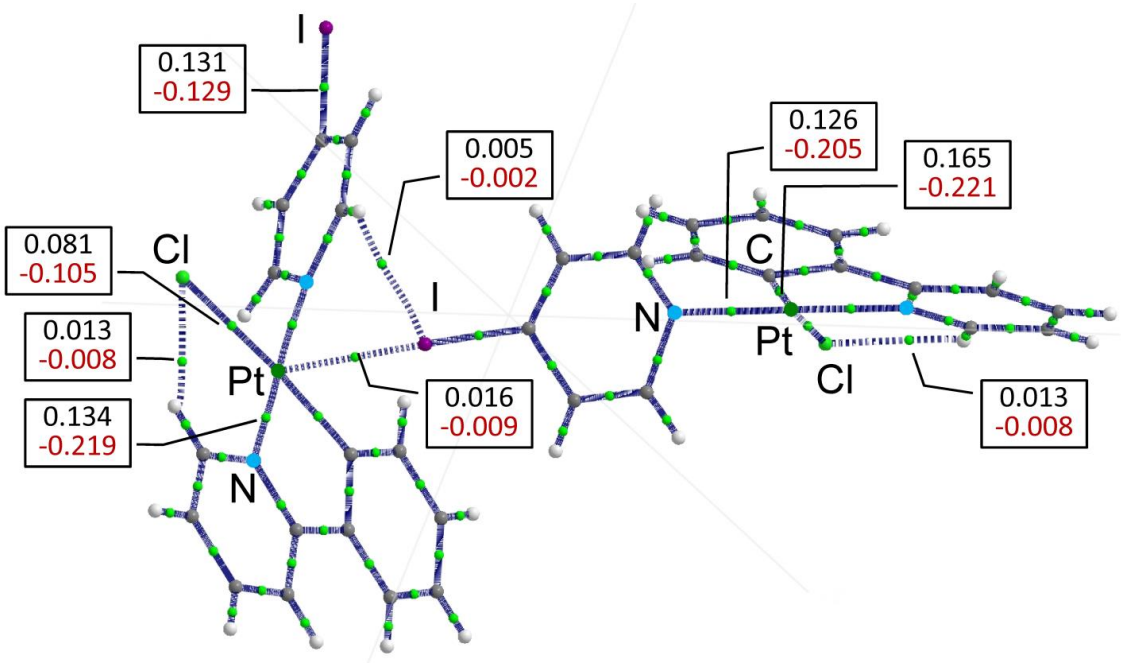


Figure S34. Molecular graph of the **1Cl** dimer obtained from analysis of the electron density topology. Bonding critical points (3,−1) are presented as small green spheres. Electron densities (a.u., black) and potential energy densities (a.u., red) are given for selected critical points.

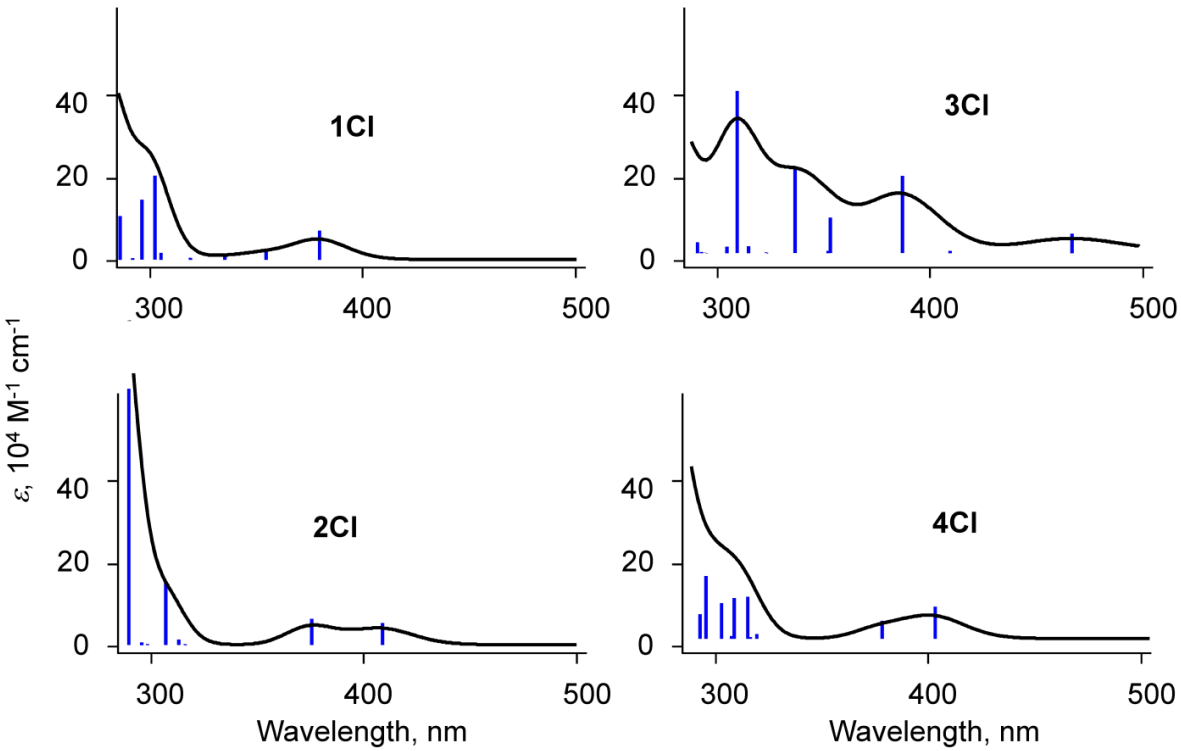


Figure S35. Calculated electronic absorption spectra of **1Cl**–**4Cl** in dichloroethane.

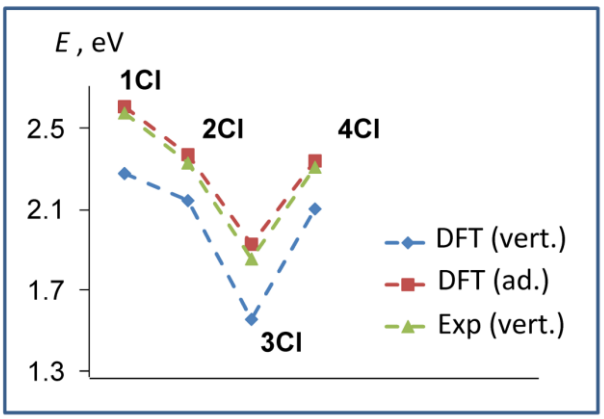


Figure S36. Calculated adiabatic and vertical energies of the $T_1 \rightarrow S_0$ emission in **1Cl**–**4Cl** (dichloroethane solution). The experimental vertical energies are given for comparison.

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