Isosteric Cl↔CH_3 Substitution in Cyclometallated Pt(II) Thiocyanate–Isocyanide Complexes: Polymorphism, Solvatomorphism and Supramolecular Organisation

Elina V. Antonova, Maria V. Kashina, Mikhail A. Kinzhalov*

Saint Petersburg State University, Universitetskaya Nab. 7−9, Saint Petersburg, 199034 Russian Federation

m.kinzhalov@spbu.ru

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S1. NMR, IR and HR-MS ESI$^+$ spectra

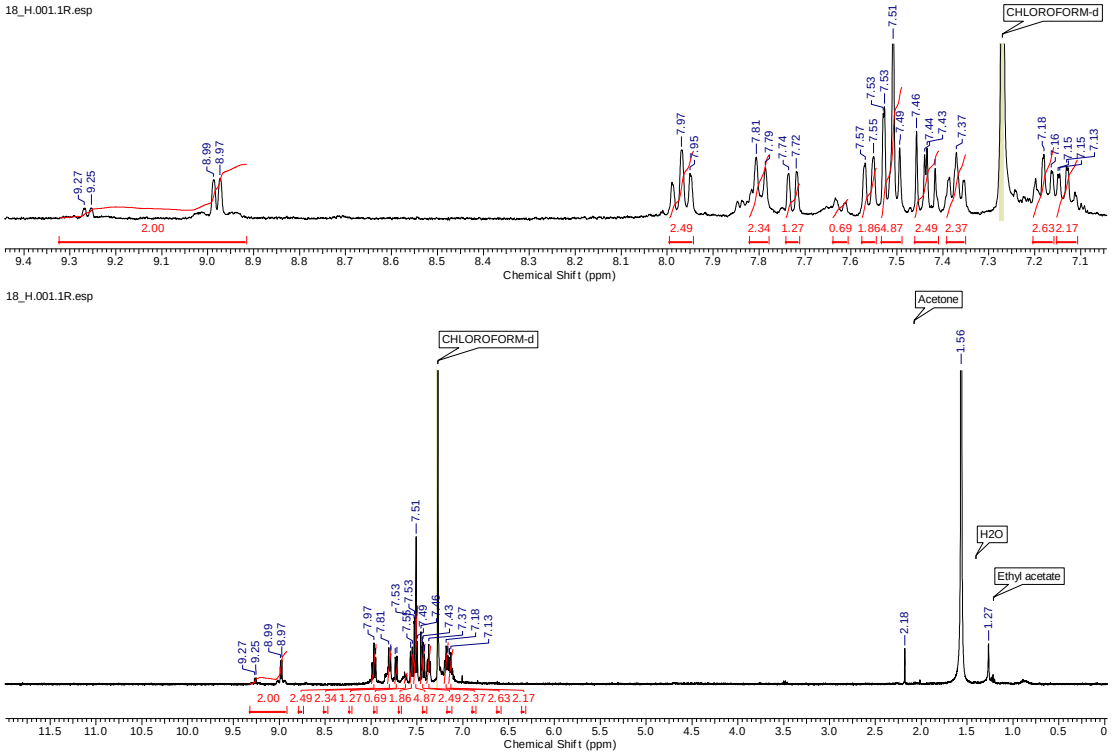

Figure S1. ^{1}H NMR spectrum of **1** (CDCl$_3$, 400 MHz).

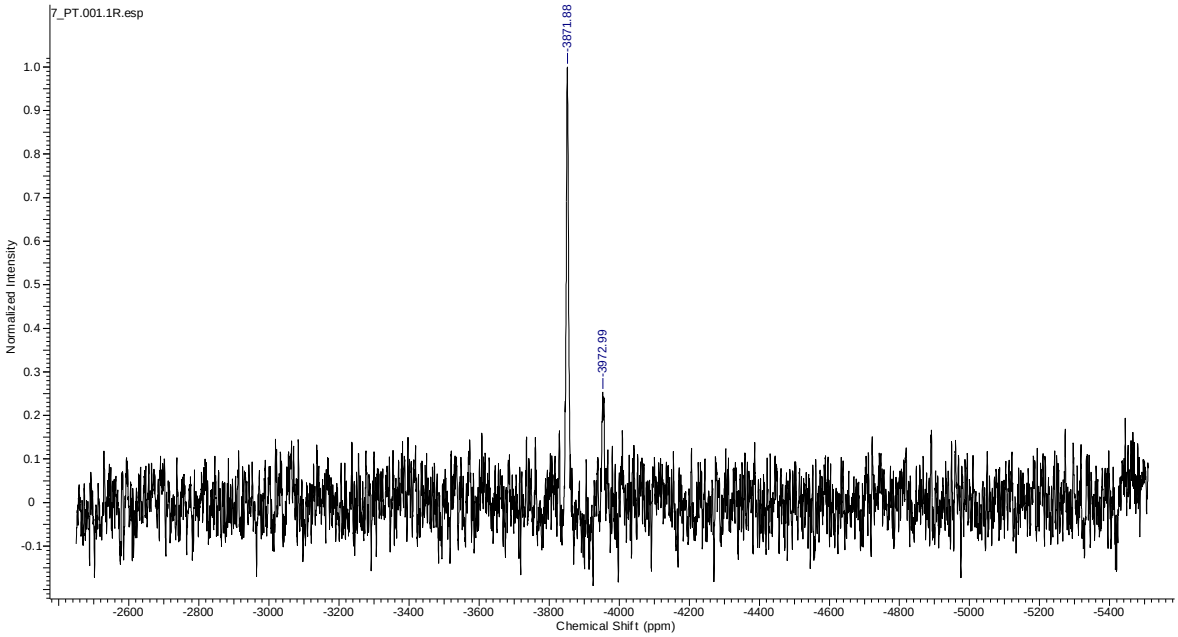

Figure S2. ^{195}Pt{^{1}H} NMR spectrum of **1** (CDCl$_3$, 86.02 MHz).

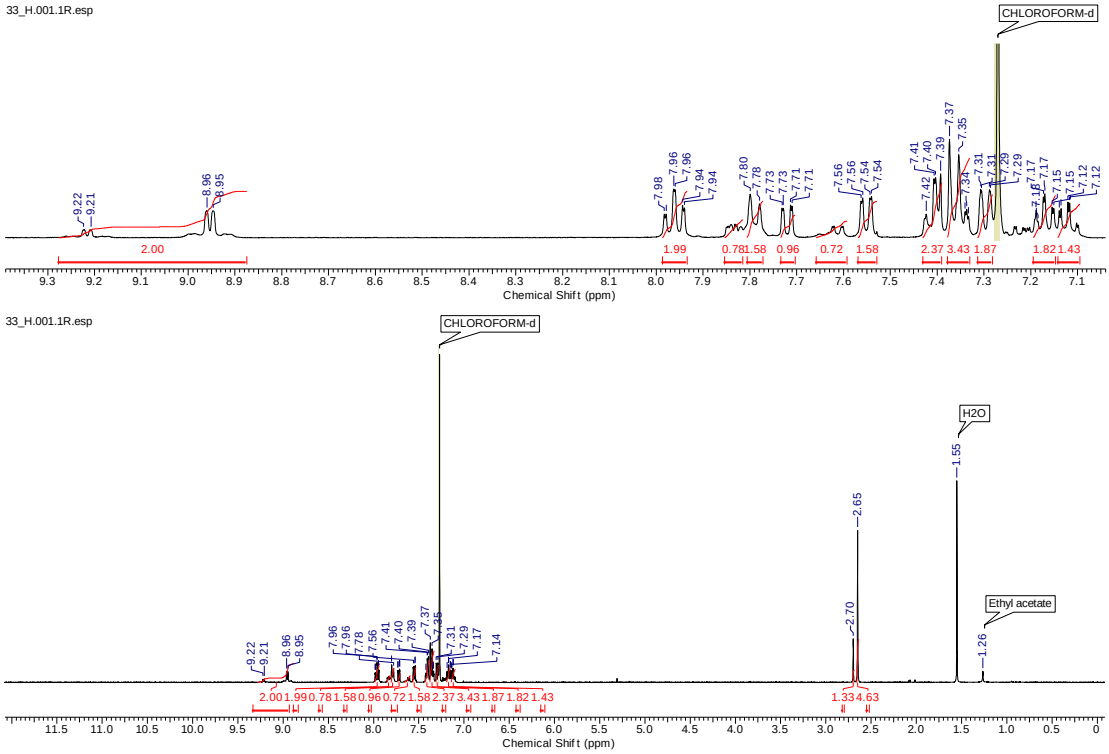

Figure S3. ^{1}H spectrum of **2** ($CDCl_3$, 400 MHz).

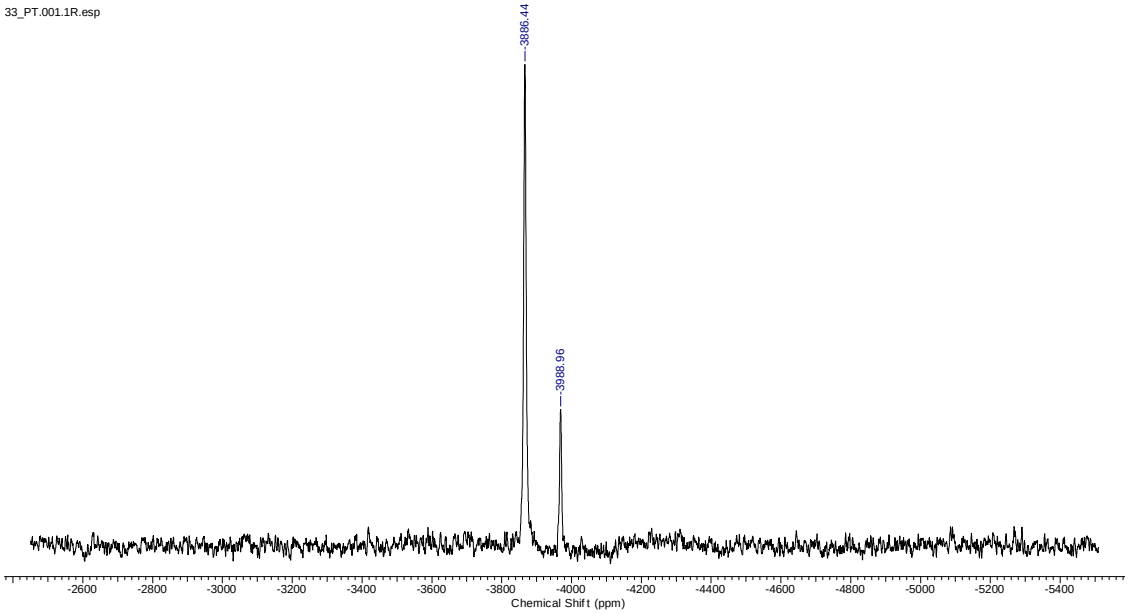

Figure S4. ^{195}Pt{^{1}H} NMR spectrum of **2** ($CDCl_3$, 86.02 MHz).

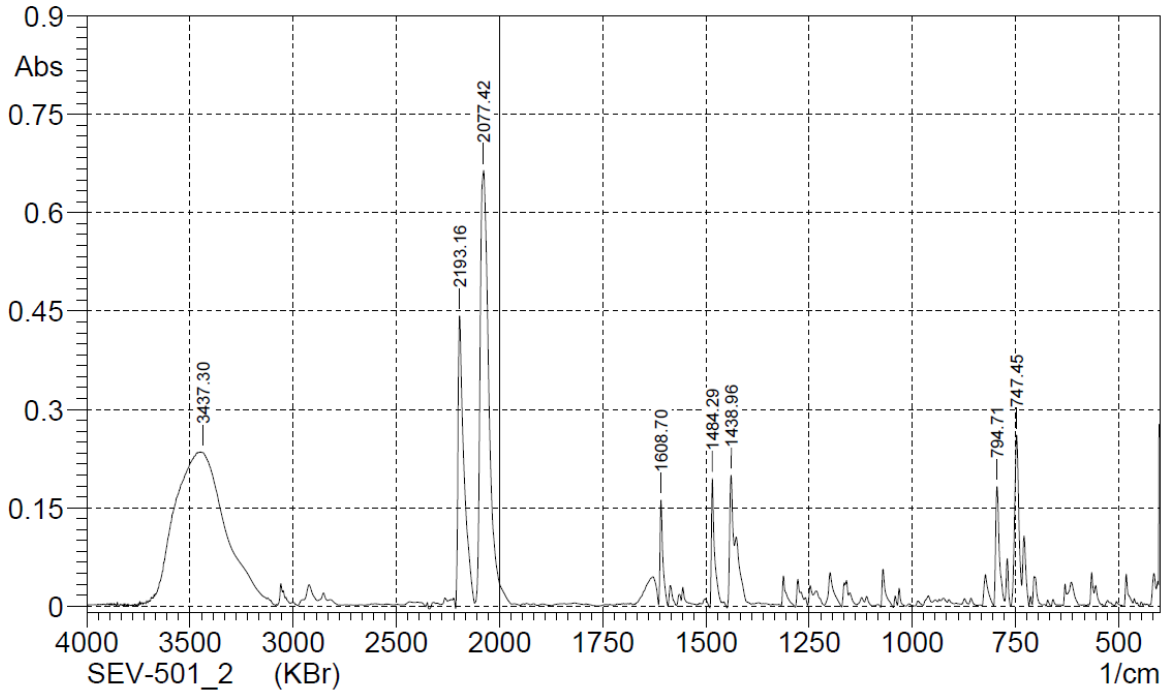

Figure S5. IR spectrum of compound **1**^{I} in a KBr pellet.

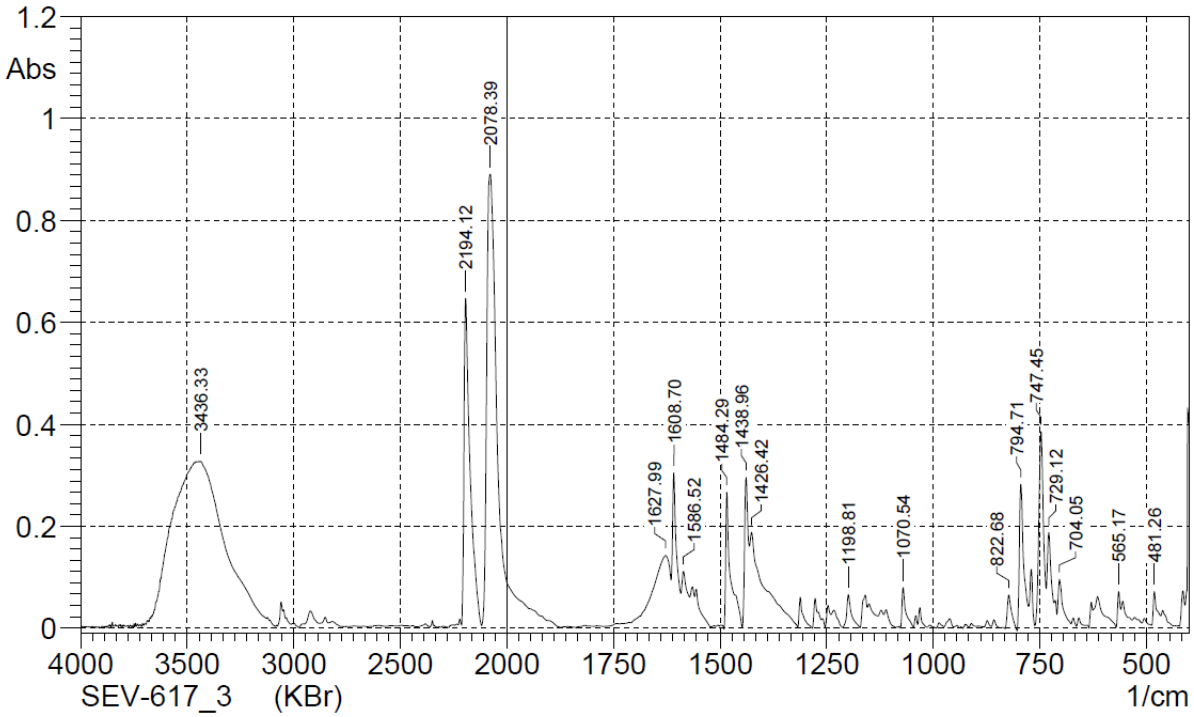

Figure S6. IR spectrum of compound **1**^{II} in a KBr pellet.

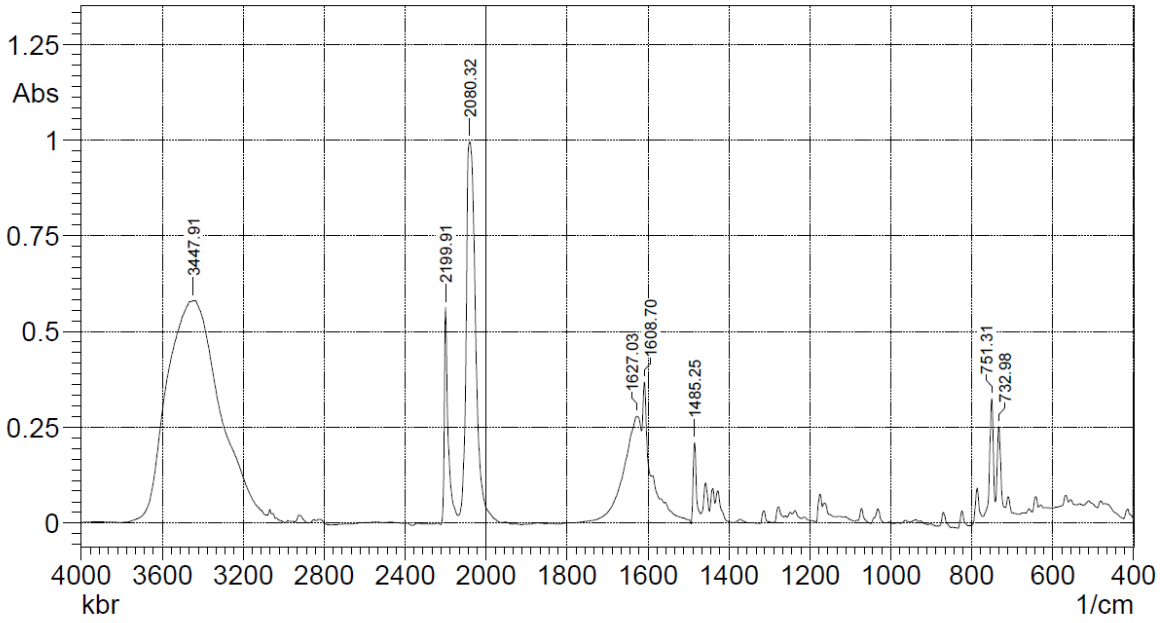

Figure S7. IR spectrum of compound **2** in a KBr pellet.

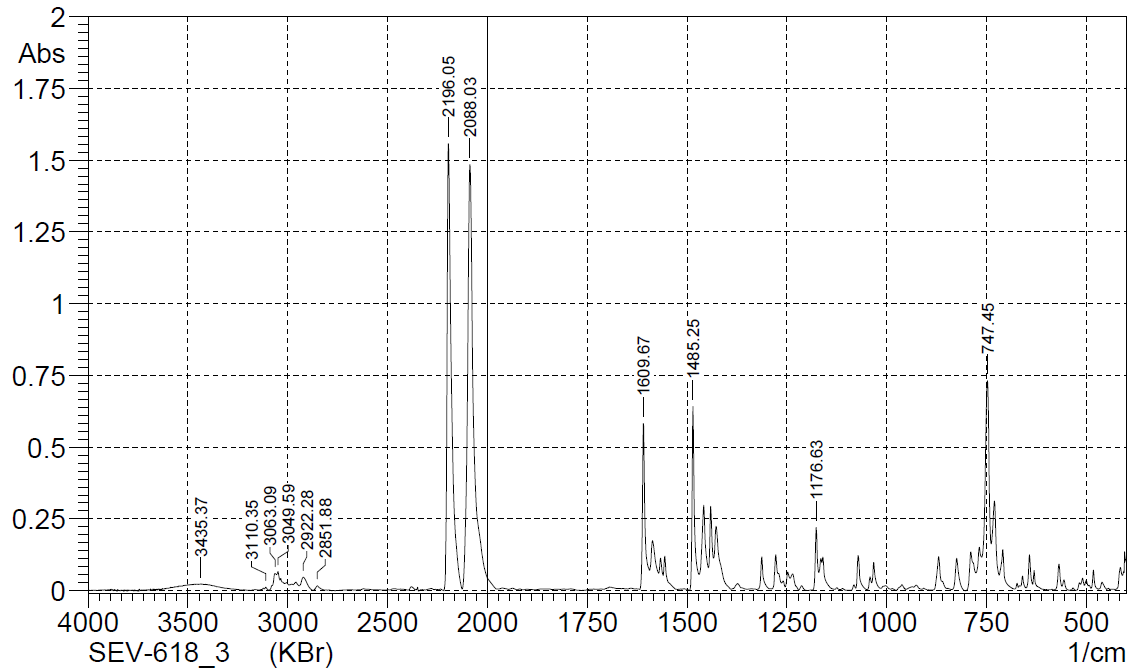

Figure S8. IR spectrum of compound **2**·$CHCl_3$ in a KBr pellet.

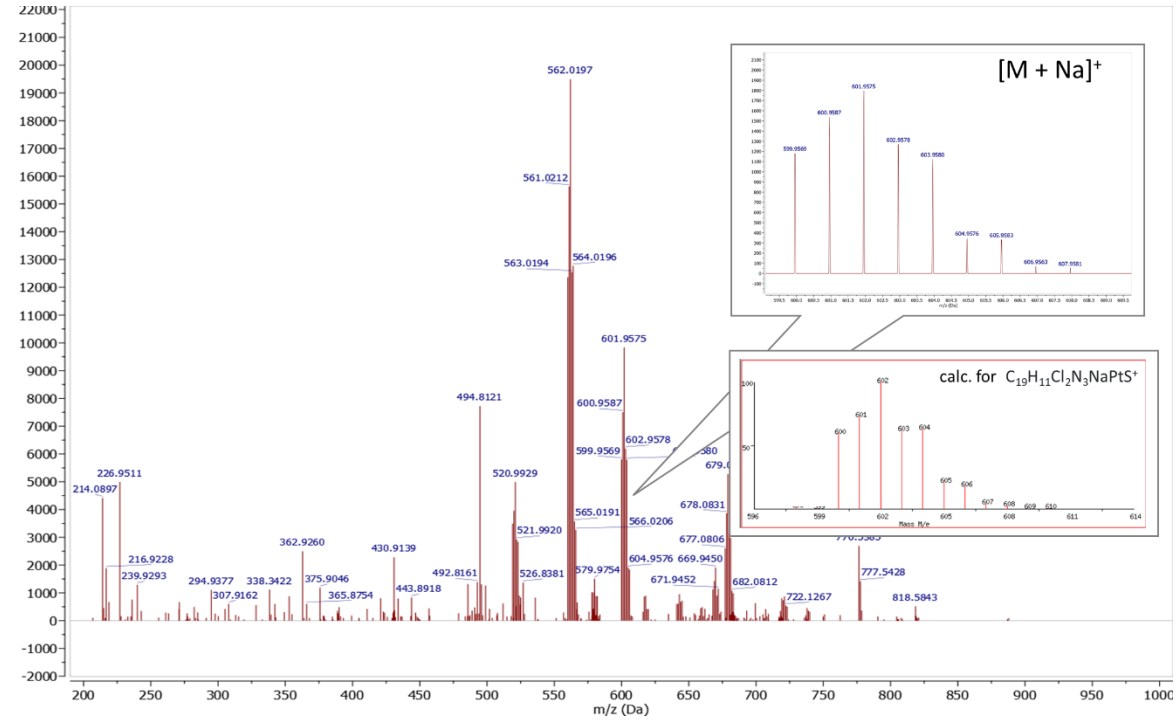

Figure S9. Fragment of HRESI$^+$-MS of **1** with [M + Na]$^+$ peak.

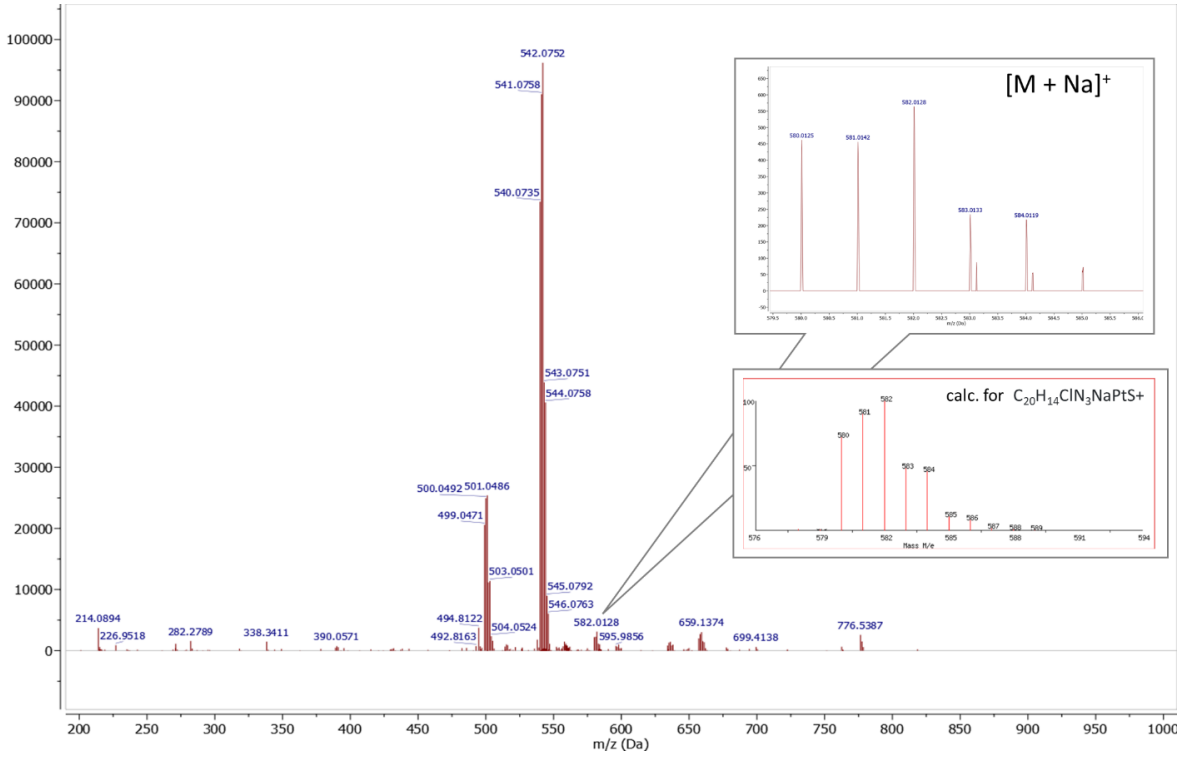

Figure S10. Fragment of HRESI$^+$-MS of **2** with [M + Na]$^+$ peak

S2. Photophysical data

Table S1. Photophysical data in solution (CH_2Cl_2, 1×10^{-5} M) and for crystalline samples.

Nos	CH_2Cl_2, $1\cdot10^{-5}$ M (298 K)			Nos	Solid state (298 K)		
	$\lambda_{abs\ solv}$/nm (10^{-3} ε/$M^{-1}cm^{-1}$)	$\lambda_{em\ solv}$/nm	Φ		$\lambda_{em\ solid}$/nm	τ/μs	Φ, %
1	246 (1.9), 300 (1.0), 318 (0.8), 333 (0.6), 383 (0.2)	482, 514, 551sh[a]	<0.1	**1^{I}**	506, 527, 555sh[b]	1.3	4
				1^{II}	526, 557sh[b]	0.9	7
2	244 (1.5), 264 (1.3), 300 (0.7), 318 (0.5), 333 (0.4), 380 (0.1)	480, 513, 552sh[a]	1.3	**2·$CHCl_3$**	496, 525, 586sh[b]	1.0	5
				2	525, 562sh[b]	1.4	5

[a]λ_{ex} = 330 nm. [b]λ_{ex} = 448 nm.

S3. X-Ray data

Table S2. Selected bond lengths (Å) and angles (deg) for **1^{I}** and **2**.

	1^{I}	**2**
Pt1–N$_{ppy}$	2.052(4)	2.048(5)
Pt2–N$_{ppy}$	2.056(4)	2.059(5)
Pt1–C$_{ppy}$	1.997(5)	1.995(6)
Pt2–C$_{ppy}$	1.986(5)	2.004(6)
Pt1–C$_{CNR}$	1.905(5)	1.894(6)
Pt2–C$_{CNR}$	1.898(5)	1.915(5)
Pt1–N$_{SCN}$	2.079(4)	2.086(5)
Pt2–N$_{SCN}$	2.079(4)	2.072(5)
C$_{ppy}$–Pt1–N$_{ppy}$	81.21(19)	81.4(2)
C$_{ppy}$–Pt2–N$_{ppy}$	89.43(18)	81.3(2)
C$_{ppy}$–Pt1–C$_{CNR}$	95.0(2)	94.5(2)
C$_{CNR}$–Pt2–C$_{ppy}$	81.2(2)	94.8(2)
C$_{CNR}$–Pt1–N$_{SCN}$	88.88(19)	89.3(2)
C$_{CNR}$–Pt2–N$_{SCN}$	94.4(2)	89.0(2)
N$_{ppy}$–Pt1–N$_{SCN}$	94.88(17)	94.83(19)
N$_{ppy}$–Pt2–N$_{SCN}$	94.94(17)	94.8(2)
Pt1–C$_{CNR}$–N$_{CNR}$	178.6(4)	177.7(5)
Pt2–C$_{CNR}$–N$_{CNR}$	178.5(4)	177.5(5)
Pt1–N$_{SCN}$–C$_{SCN}$	158.3(4)	160.7(5)
Pt2–N$_{SCN}$–C$_{SCN}$	159.3(4)	159.6(5)

Table S3. Selected bond lengths (Å) and angles (deg) for **1^{II}** and **2·CHCl$_3$**.

	1^{II}	**2·CHCl$_3$**
Pt1–N$_{ppy}$	2.049(4)	2.056(3)
Pt1–C$_{ppy}$	1.998(4)	1.994(4)
Pt1–C$_{CNR}$	1.900(4)	1.900(4)
Pt1–N$_{SCN}$	2.079(4)	2.080(4)
C$_{ppy}$–Pt1–N$_{ppy}$	81.37(15)	81.52(16)
C$_{ppy}$–Pt1–C$_{CNR}$	95.06(16)	94.85(17)
C$_{CNR}$–Pt1–N$_{SCN}$	88.74(14)	89.25(15)

N_{ppy}–Pt1–N_{SCN}	94.82(13)	1.994(4)
Pt1–C_{CNR}–N_{CNR}	177.0(4)	177.1(4)
Pt1–N_{SCN}–C_{SCN}	161.8(3)	163.2(3)