

Electronic Supporting Information

Soft salts based on platinum(II) complexes with high emission quantum efficiencies in the near infrared region for *in vivo* imaging

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Experimental section

General

All the chemicals and solvents were purchased from commercial suppliers and were used without any further purification. ^1H and ^{13}C NMR spectra were obtained on a Bruker Ultrashield 400 MHz FT-NMR spectrometer in CDCl_3 or $\text{DMSO-}d_6$ with tetramethylsilane (TMS) as an internal standard. Infrared spectra were collected on Nicolet Magna 550 Series II FTIR spectrometer using KBr pellets for solid state measurements. Mass spectra were measured on a Bruker Autoflex matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS). X-Ray diffraction (XRD) data were collected using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker APEX DUO diffractometer at 293 K. UV-visible absorption spectra were recorded with a Cary 100 UV-Vis spectrophotometer. Photoluminescence spectra of the solution were obtained on the LS50B fluorescence spectrophotometer. The solid-state photophysical properties including emission, lifetime and quantum efficiency were recorded on a HORIBA/Fluorolog-3 combined fluorescence lifetime and steady state spectrometer.

Synthesis of the anionic Pt(II) complexes:

The corresponding Pt-dimer was refluxed with 10 equivalents of tetrabutylammonium cyanide for 6 hours with stirring.¹ After cooling down to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in 20 mL DCM and was washed with water (20 mL x 3) to obtain the crude products, which were further purified by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give the corresponding anionic Pt(II) complexes in quantitative yields.

A1: Yellow-green solid. Yield 38%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.45 (d, 1H, Ar), 8.07 (d, 1H, Ar), 7.84 (t, 1H, Ar), 7.71 (dd, 1H, Ar), 7.11 (t, 1 H, Ar), 6.49 (ddd, 1H, Ar), 3.27-3.33 (m, 8H, CH_2), 1.56-1.72 (m, 8H, CH_2), 1.41 (q, 8H, CH_2), 0.94 (t, 12H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.62, 161.36, 160.92, 157.89, 152.30, 143.23, 138.21, 128.91, 121.75, 121.43, 119.58, 115.99, 98.86, 57.76, 23.01, 18.61, 12.63. Negative ESI-MS: $m/z = 436.2$

(calc. $C_{18}H_6F_2N_3Pt = 437.1$), positive ESI-MS: $m/z = 242.7$ (calc. $C_{16}H_{36}N = 242.2$).

IR (cm^{-1}): 2131, 2119 for $C\equiv N$ stretching.

A2: Orange solid. Yield 47%. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.30-9.32 (d, 1H, Ar), 8.76-8.78 (d, 1H, Ar), 8.24-8.26 (d, 1H, Ar), 7.96-7.98 (d, 1H, Ar), 7.82-7.84 (d, 1H, Ar), 7.76-7.78 (t, 1H, Ar), 7.65 (t, 1H, Ar), 7.40-7.41 (d, 1H, Ar), 7.13-7.17 (m, 2H, Ar), 3.23-3.27 (m, 8H, CH_2), 1.53-1.60 (m, 8H, CH_2), 1.31-1.36 (q, 8H, CH_2), 0.85-0.89 (t, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 183.76, 169.59, 158.75, 148.22, 144.93, 138.97, 137.54, 130.53, 129.24, 128.23, 127.49, 125.45, 123.29, 120.58, 118.18, 58.73, 23.99, 19.61, 13.64. Negative ESI-MS: $m/z = 451.1$ (calc. $C_{17}H_{10}N_3Pt = 451.1$), positive ESI-MS: $m/z = 242.2$ (calc. $C_{16}H_{36}N = 242.2$). IR (cm^{-1}): 2108, 2127 for $C\equiv N$ stretching.

Synthesis of the cationic Pt(II) complexes:

The corresponding Pt-dimer and 3 equivalents of ethane-1, 2- diamine were added in 20 mL dichloromethane under an argon flow and the mixture was stirred for 30 minutes at room temperature to obtain the corresponding cationic Pt(II) complexes as yellow or orange precipitates.² The resulting powder was washed with ether and DCM to give quantitative yield of the corresponding cationic Pt(II) complexes.

C1: Orange solid. Yield 79%. 1H NMR (400 MHz, $DMSO-d_6$): δ (ppm) 8.50-8.51 (d, 1H, Ar), 7.92-7.96 (m, 1H, Ar), 7.65-7.66 (d, 1H, Ar), 7.52-7.54 (d, 1H, Ar), 7.12-7.16 (m, 1H, Ar), 7.04-7.05 (d, 1H, Ar), 6.22 (s, 2H, NH_2), 5.52 (s, 2H, NH_2), 2.60 (s, 4H, CH_2CH_2). ^{13}C NMR (100 MHz, $DMSO-d_6$): δ (ppm) 162.37, 151.84, 149.63, 140.99, 140.52, 133.62, 129.65, 121.23, 118.04, 119.86, 48.83, 43.78. Positive ESI-MS: $m/z = 415.0$ (calc. $C_{11}H_{14}N_3PtS = 415.0$).

C2: Light yellow solid. Yield 47%. 1H NMR (400 MHz, $DMSO-d_6$): δ (ppm) 8.71-8.72 (d, 1H, Ar), 8.10-8.14 (dd, 1H, Ar), 7.95-7.97 (d, 1H, Ar), 7.36-7.39 (dd, 1H, Ar), 6.91-6.96 (m, 2H, Ar), 6.22 (s, 2H, NH_2), 5.59 (s, 2H, NH_2), 2.65 (s, 4H, CH_2CH_2). ^{13}C NMR (100 MHz, $DMSO-d_6$): δ (ppm) 162.35, 161.16, 161.05,

158.13, 151.64, 149.18, 128.29, 122.29, 121.10, 116.36, 47.73, 43.64. Positive ESI-MS: $m/z = 445.1$ (calc. $C_{13}H_{14}F_2N_3Pt = 445.1$).

Synthesis of the soft salts:

The Pt(II) based soft salts were synthesized through simple metathesis reactions according to the modified procedures in the literature.³ To a 5 mL ethanol solution, 1 equivalent of the anionic Pt(II) complexes and 1.1 equivalents of the cationic Pt(II) complexes were added to obtain a yellow solution. Then the mixed solution was treated under ultrasonic bath for 10 min, the yellow solution became red immediately and red precipitates were formed. Then the solution was poured into 35 mL D.I water followed by another 30 min sonication. After removing the solvent by centrifugation, the residues were washed with 10 mL D.I water and 10 mL DCM to acquire the products as red solids.

S1: Red solid. Yield 87%. 1H NMR (400 MHz, $DMSO-d_6$): δ (ppm) 9.31-9.32 (t, 1H, Ar), 8.47-8.48 (d, 1H, Ar), 8.08-8.18(m, 3H, Ar), 7.96-8.01 (dt, 1H, Ar), 7.46-7.71 (m, 3H, Ar), 7.18-7.21 (t, 1H, Ar), 7.05-7.06 (d, 1H, Ar), 6.87-6.93 (m, 1H, Ar), 6.17 (s, 2H, NH_2), 5.42 (s, 2H, NH_2), 2.64 (s, 4H, CH_2CH_2). ^{13}C NMR (100 MHz, $DMSO-d_6$): δ (ppm) 163.12 162.84, 158.74, 151.19, 148.88, 141.76, 140.59, 140.32, 140.10, 132.96, 129.71, 129.27, 124.00, 122.52, 122.32, 120.78, 119.69, 119.53, 117.64, 114.73, 99.63, 48.34, 43.33. Negative ESI-MS: $m/z = 436.2$ (calc. $C_{18}H_6F_2N_3Pt = 437.1$), positive ESI-MS: $m/z = 415.0$ (calc. $C_{11}H_{14}N_3PtS = 415.0$).

S2: Red solid. Yield 85%. 1H NMR (400 MHz, $DMSO-d_6$): δ (ppm) 9.12-9.14 (d, 1H, Ar), 8.79-8.81 (d, 1H, Ar), 8.62-8.64 (d, 1H, Ar), 8.13-8.17 (t, 1H, Ar), 8.01-8.06 (m, 4H, Ar), 7.88-7.92 (t, 1H, Ar), 7.79 (s, 2H, Ar), 7.41-7.44 (t, 1H, Ar), 7.14-7.15 (d, 2H, Ar), 6.95-7.14 (t, 2H, Ar), 6.90-6.92 (d, 2H, Ar), 6.11 (s, 2H, NH_2), 5.40 (s, 2H, NH_2), 2.66 (s, 4H, CH_2CH_2).

^{13}C NMR (100 MHz, $DMSO-d_6$): δ (ppm) 168.93, 159.90, 151.94, 149.27, 148.20, 145.33, 144.41, 141.14, 138.63, 137.53, 132.43, 130.55, 129.63, 128.03,

127.53, 125.22, 124.04, 123.52, 122.96, 121.68, 116.76, 100.38, 100.11, 99.85, 79.77, 79.44, 79.11, 48.23, 44.19. Negative ESI-MS: $m/z = 451.1$ (calc. $C_{17}H_{10}N_3Pt = 451.1$), positive ESI-MS: $m/z = 445.1$ (calc. $C_{13}H_{14}F_2N_3Pt = 445.1$).

***In vivo* imaging**

Animal experiments were conducted according to the guidelines of the Institutional Animal Care and Use Committee. Male BALB/c mice (~20 g) was purchased from Jiangsu KeyGEN BioTECH Corp., Ltd. The mouse was subcutaneously injected with **S2** (1×10^{-4} M in 200 μ L of 1 : 99 = DMSO : PBS). As a control, the same mouse was also subcutaneously injected with DMSO/PBS solution. The mouse was then imaged (30 min after the injection) by using IVIS Lumina XR Series III MS *in vivo* imaging system, with an excitation filter of 440 nm and an emission filter of 690–740 nm.

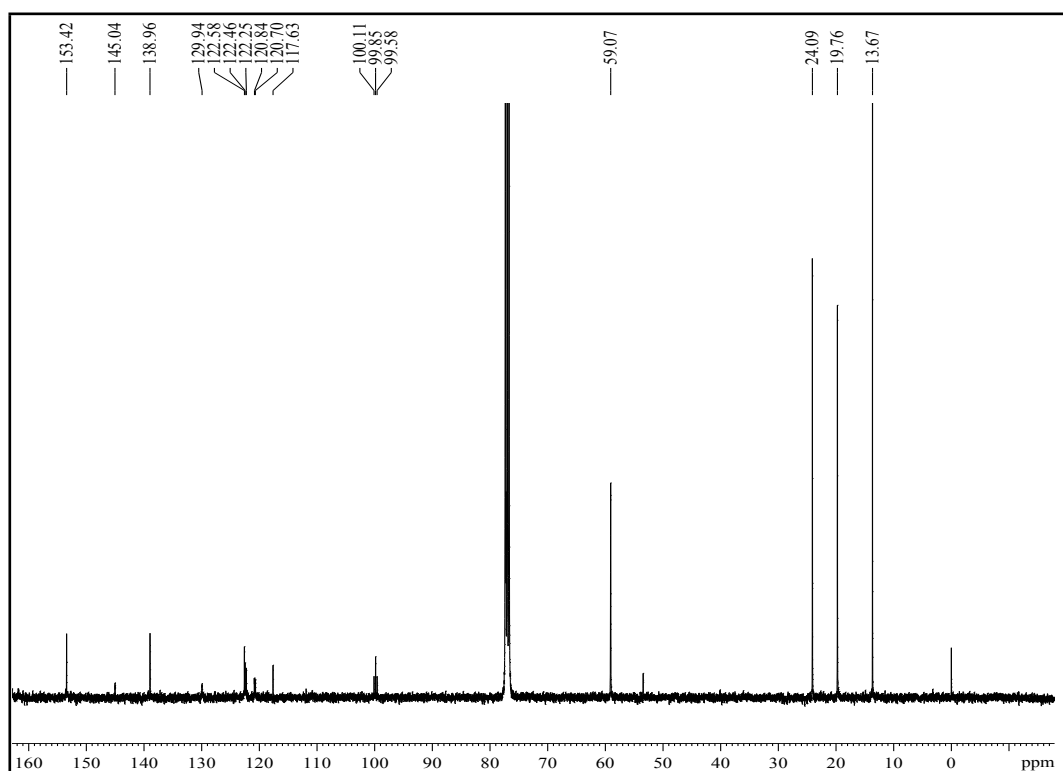
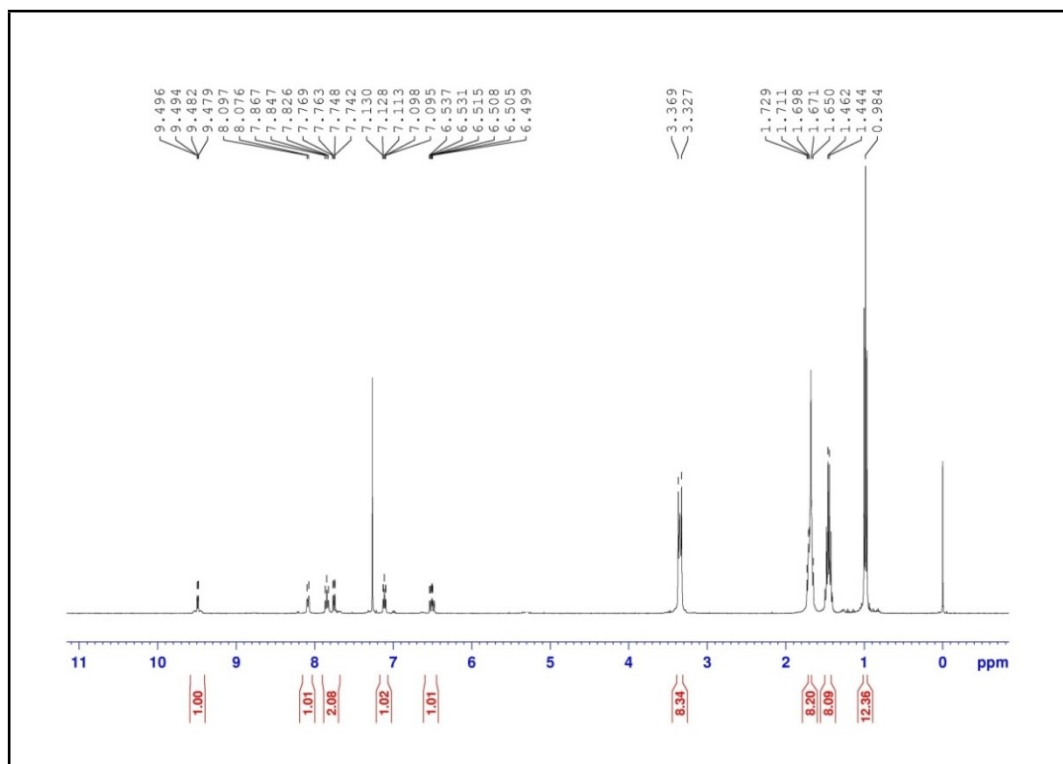


Fig. S1 ¹H NMR (top) and ¹³C NMR (bottom) spectra of A1 in CDCl₃

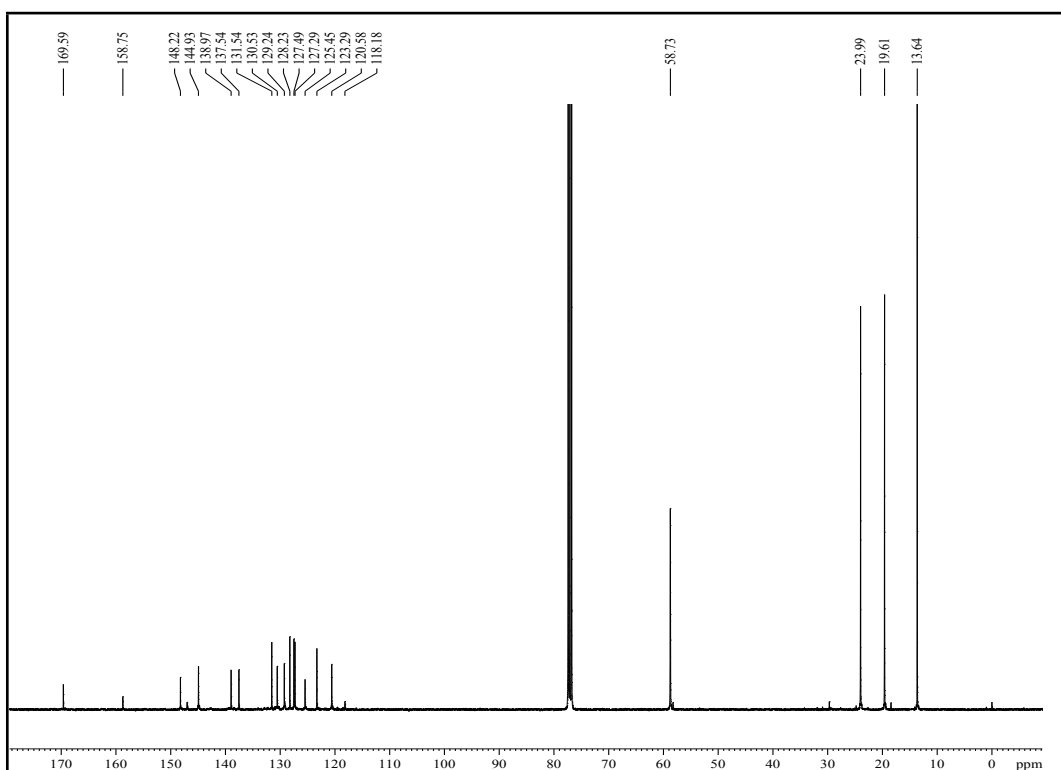
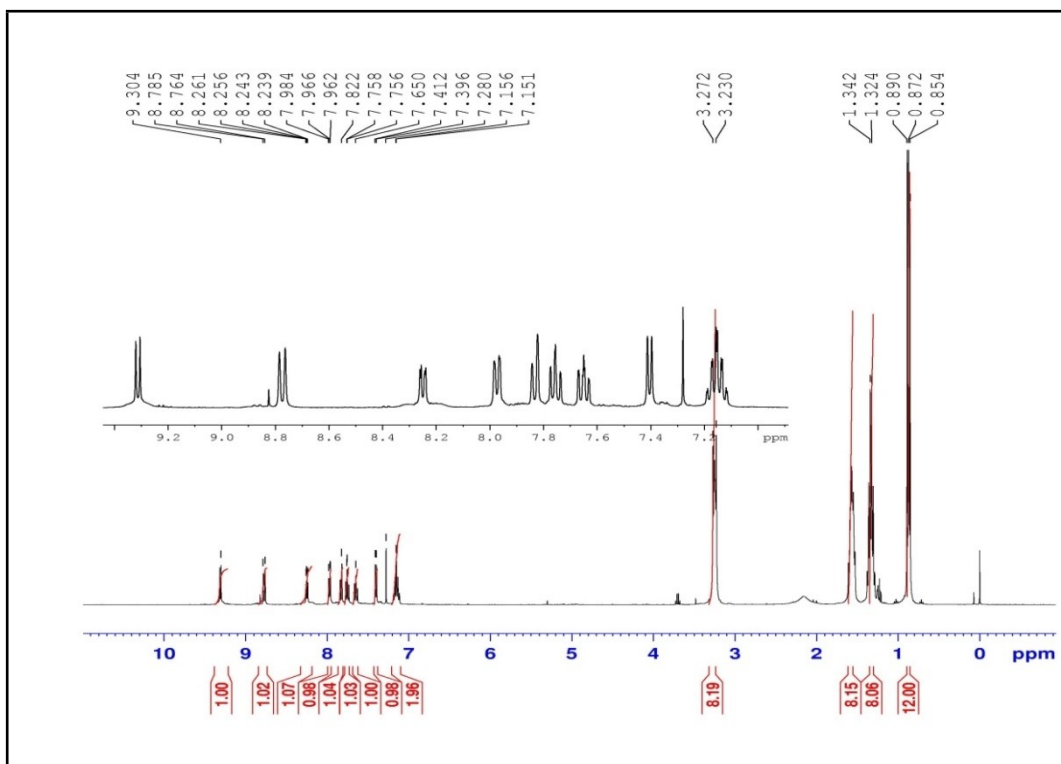


Fig. S2 ¹H NMR (top) and ¹³C NMR (bottom) spectra of **A2** in CDCl₃

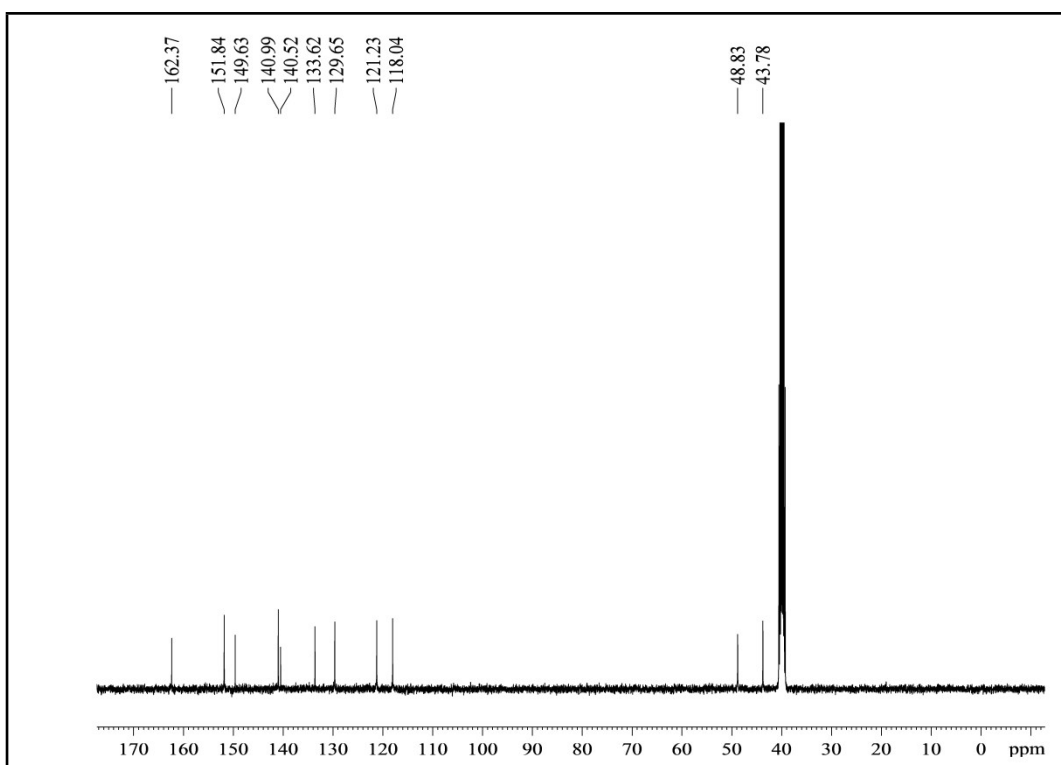
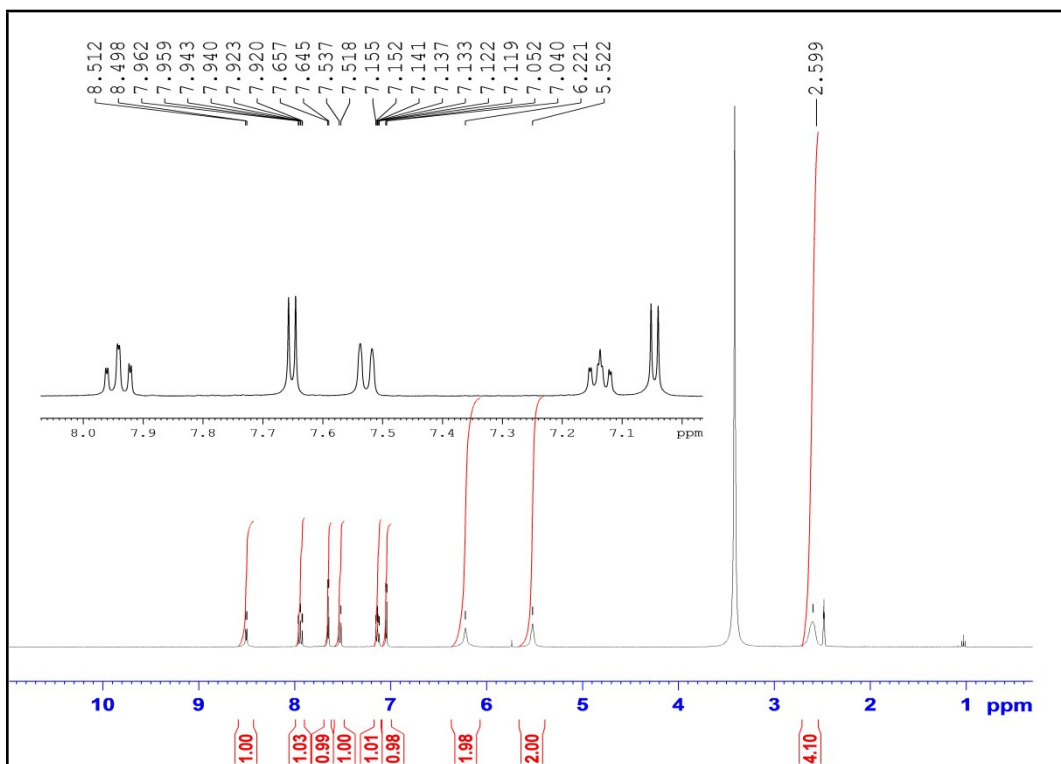


Fig. S3 ^1H NMR (top) and ^{13}C NMR (bottom) spectra of complexes C1 in $\text{DMSO-}d_6$

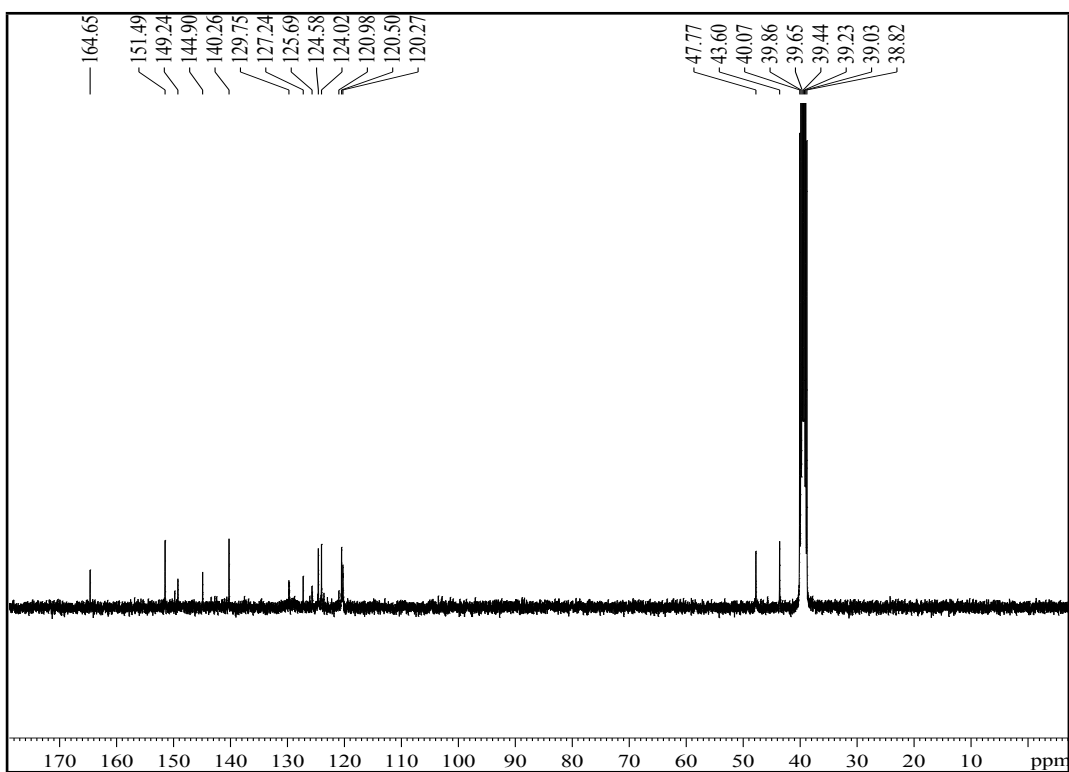
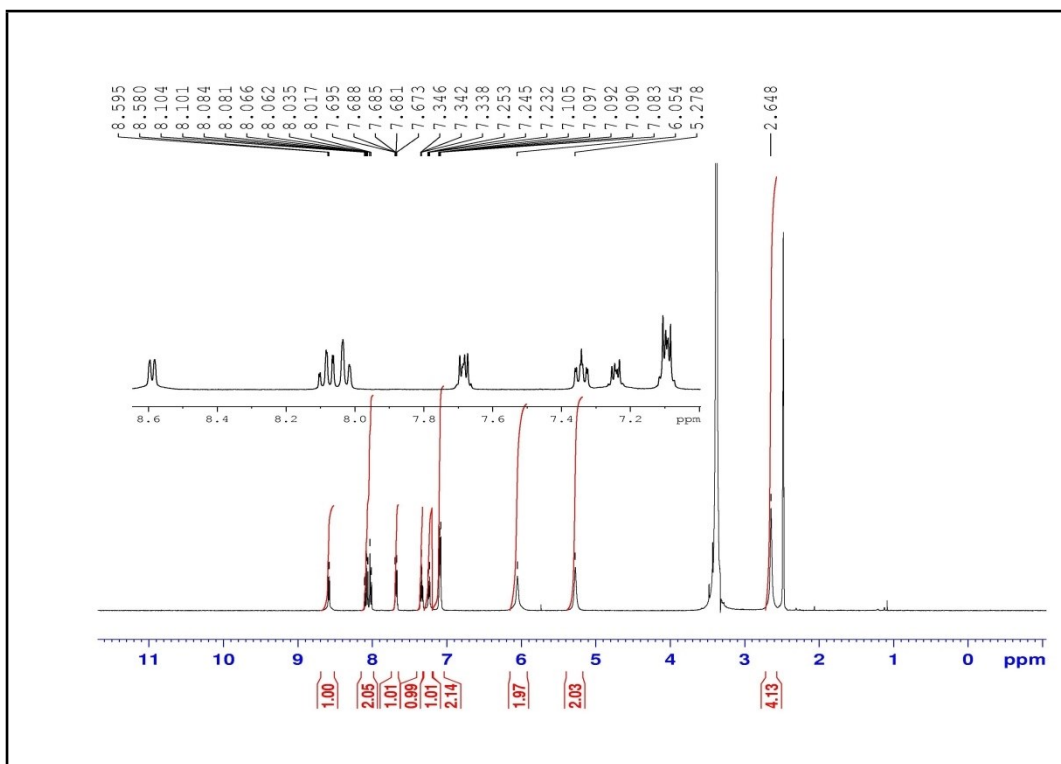


Fig. S4 ^1H NMR (top) and ^{13}C NMR (bottom) spectra of complexes C2 in $\text{DMSO-}d_6$

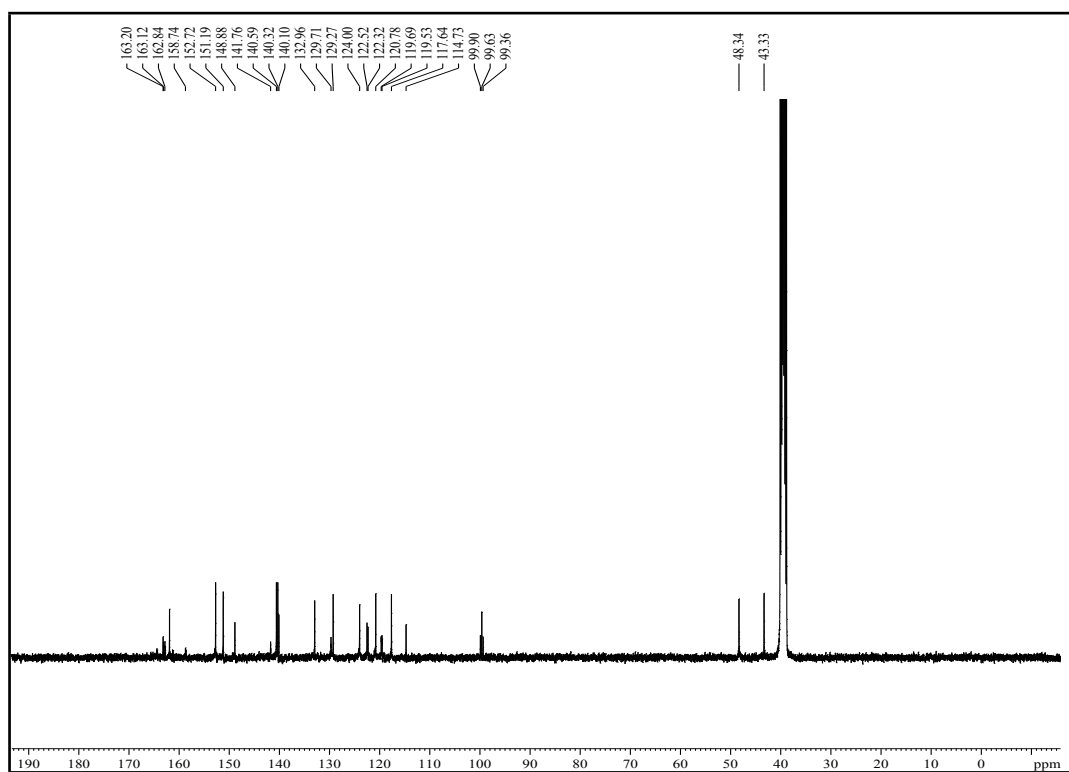
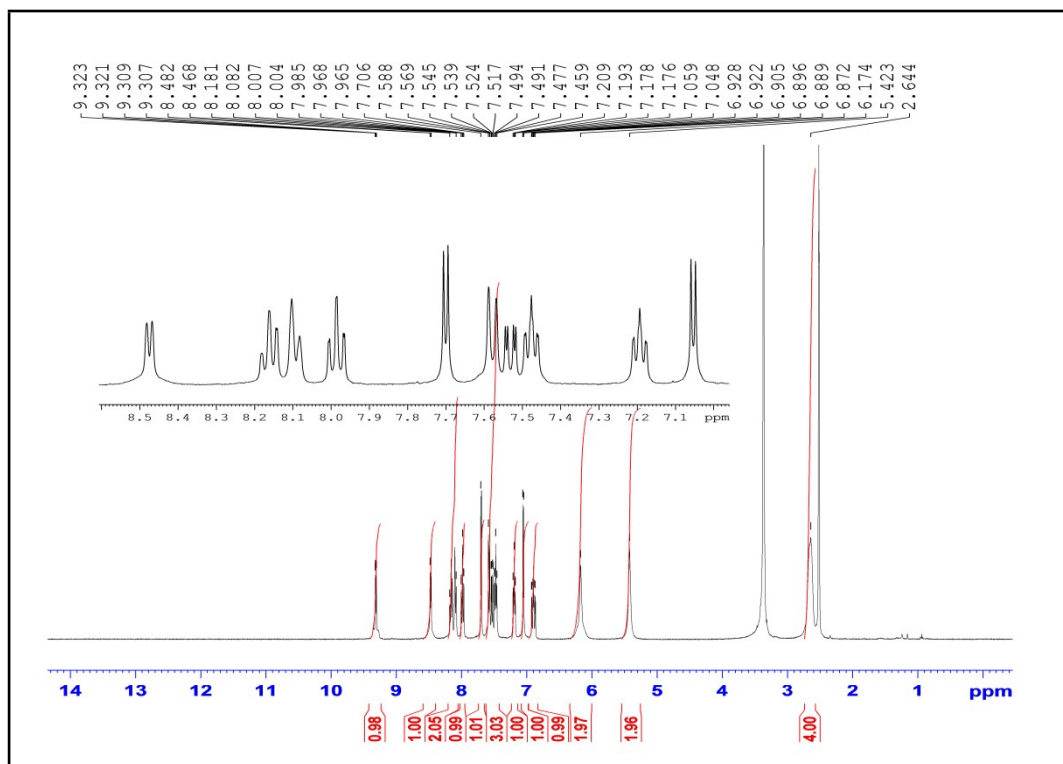


Fig. S5 ¹H NMR (top) and ¹³C NMR (bottom) spectra of complexes **S1** in DMSO-*d*₆

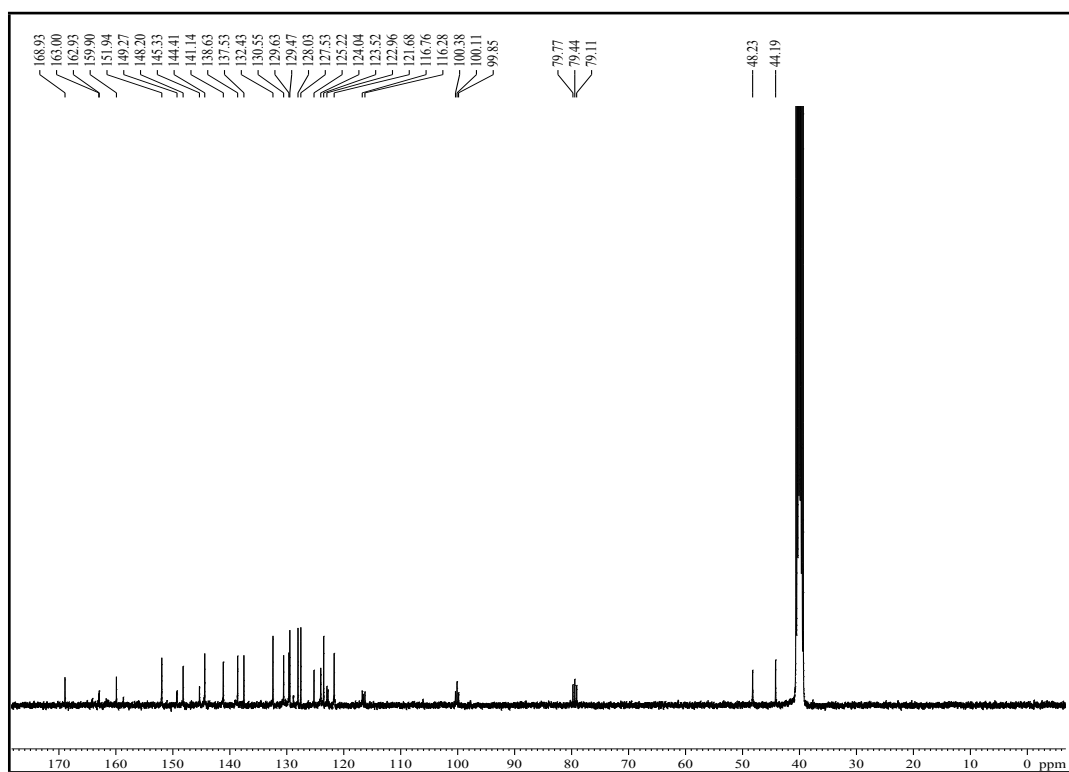
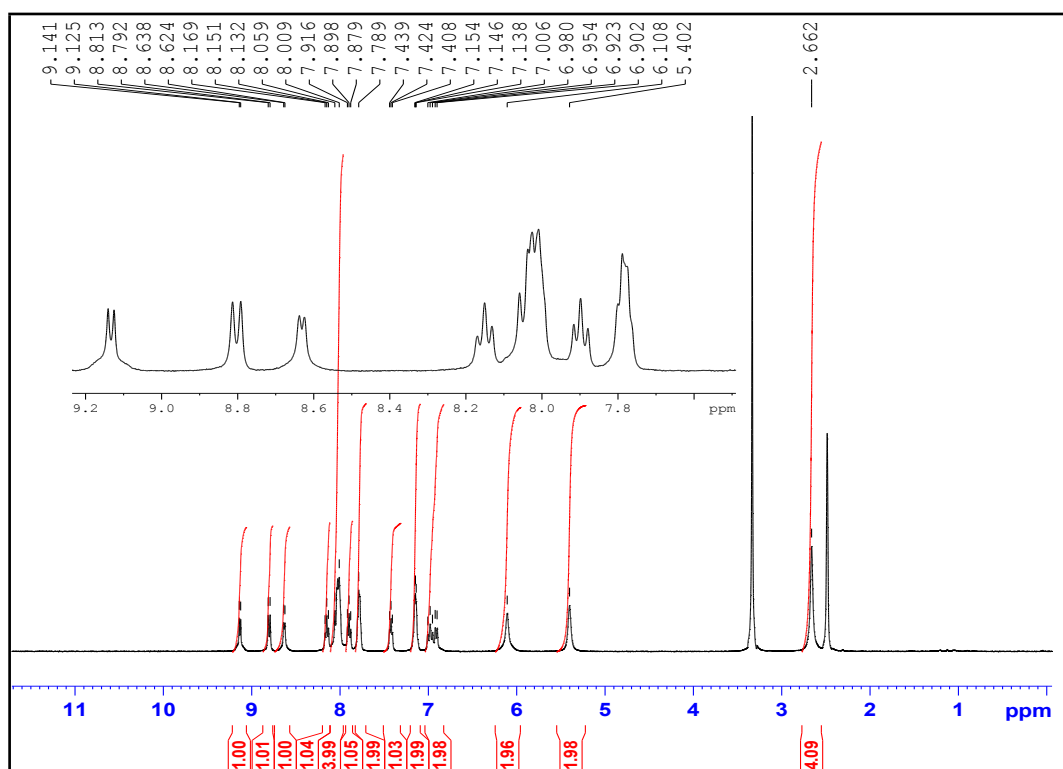


Fig. S6 ¹H NMR (top) and ¹³C NMR (bottom) spectra of complexes S2 in DMSO-*d*₆

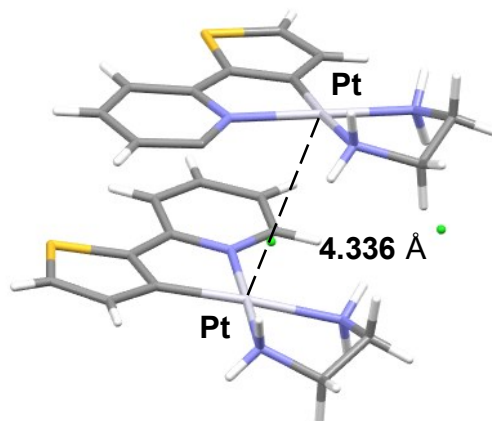


Fig. S7 Single crystal of **C1** and its packing diagram, showing the absence of Pt···Pt interaction.

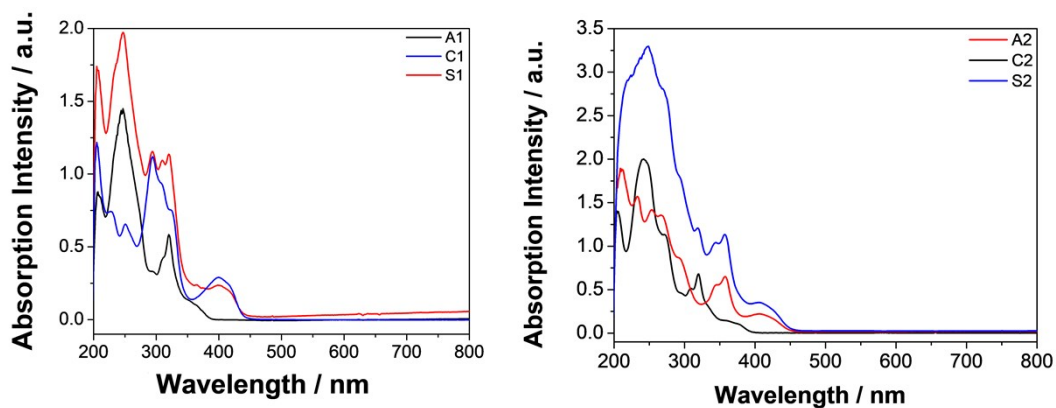


Fig. S8 UV-Vis spectra of **A1**, **C1**, **S1** and **A2**, **C2**, **S2** in MeOH (1×10^{-4} M).

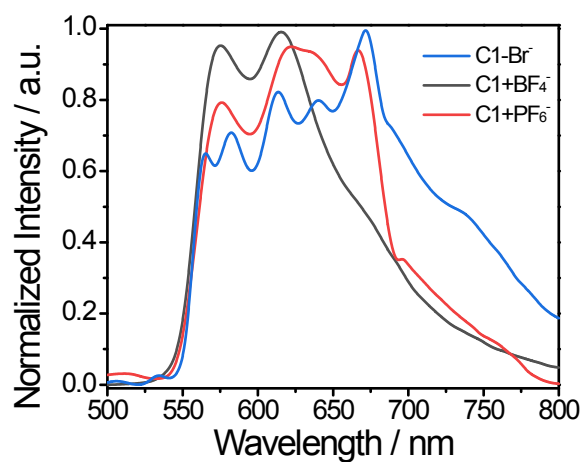


Fig. S9 PL spectra of cationic complex **C1** with different counterions in the solid state.

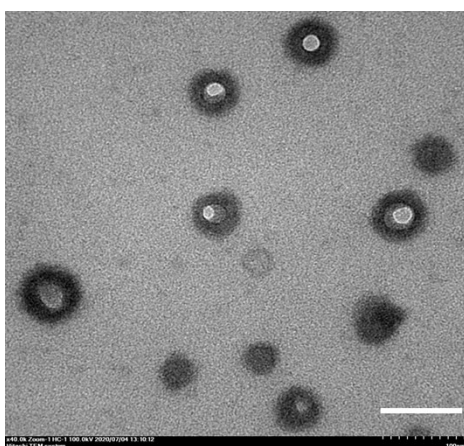


Fig. S10 TEM image of **S2** dispersed in DMSO/PBS mixture, scale bar = 100 nm.

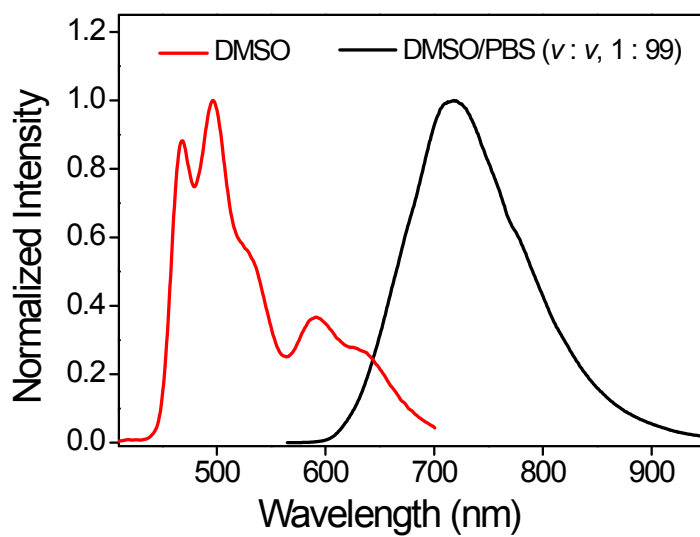
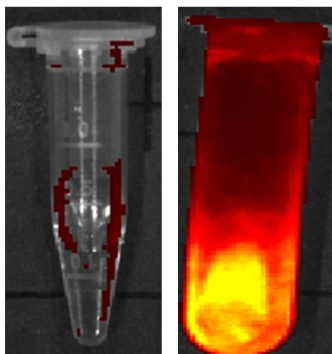


Fig. S11 PL spectra of **S2** in DMSO and DMSO/PBS (QY = 16.6%) mixture (v : v, 1 : 99).

S2



DMSO DMSO : PBS
1 : 99

Fig. S12 PL images of S2 in DMSO and DMSO/PBS mixture ($v : v$, 1 : 99).

Table S1 Selected parameters in S1 crystal

Selected bond	Bond length / Å	Selected angle	Bond angle / °
Pt(1)-C(13)	1.85(5)	C(13)-Pt(1)-C(1)	93.8(16)
Pt(1)-C(1)	2.04(3)	C(13)-Pt(1)-N(3)	174.3(15)
Pt(1)-N(3)	2.04(2)	C(1)-Pt(1)-N(3)	80.6(9)
Pt(1)-C(12)	2.10(4)	C(13)-Pt(1)-C(12)	92.5(18)
Pt(2)-C(20)	1.99(2)	C(1)-Pt(1)-C(12)	173.8(14)
Pt(2)-N(4)	2.063(16)	N(3)-Pt(1)-C(12)	93.2(13)
Pt(2)-N(6)	2.093(18)	C(20)-Pt(2)-N(4)	80.6(7)
Pt(2)-N(5)	2.171(18)	C(20)-Pt(2)-N(6)	97.1(8)
N(1)-C(12)	1.03(4)	N(4)-Pt(2)-N(6)	177.6(8)
N(2)-C(13)	1.24(6)	C(20)-Pt(2)-N(5)	179.2(8)
		N(4)-Pt(2)-N(5)	99.1(7)
		N(6)-Pt(2)-N(5)	83.2(8)
		C(22)-S(1)-C(19)	90.0(11)

Table S2 Distance of selected atoms to the dfppy plane (anionic complexes)

Selected atoms	Distance	Selected atoms	Distance
N4	3.346	C18	3.384
S1	3.349	C19	3.347
C14	3.434	C20	3.337
C15	3.384	C21	3.325
C16	3.412	C22	3.300
C17	3.345	C23	3.349
\bar{d}	3.360		

Table S3 Common NIR probes for *in vivo* imaging

Probe	Emission wavelength	Quantum yield	Selected reference
S1/S2	674/718 nm	20.3/17%	This work
Methylene blue	665/686 nm	9.6%	Q. R. J. G. Tummers <i>et al. Surgery</i> 2015, 158 , 1323–1330
Quaternary ammonium cyanine dyes	666/692 nm	9.7%	H. Hyun <i>et al. Angew. Chem. Int. Ed.</i> 2015, 54 , 8648–8652
TPE-TPA-FN	671 nm	12.5%	D. Ding <i>et al. Adv. Health. Mater.</i> 2013, 2 , 500–507
AIE dot			
Quantum dots	700-900 nm	8-17%	B. Del Rosal <i>et al. Adv. Funct. Mater.</i> 2016 26 , 6060–6068
Metal nanoclusters	810 nm	0.7%	M. X. Yu <i>et al. Angew. Chem. Int. Ed.</i> 2016, 55 , 2787– 2791
Infrared fluorescent proteins	711 nm	8.0%	J. Chu <i>et al. Nat. Methods</i> 2014, 11 , 572–578
Zwitterionic cyanine dyes	772 nm	15%	H. S. Choi <i>et al. Nat. Biotechnol.</i> 2013, 31 , 148–153
IR-PEG nanoparticles	808 nm	1.8%	X. N. Dang <i>et al. Proc. Natl Acad. Sci. USA</i> 2016, 113 5179–5184
Non-sulfonated cyanine dyes	747 nm	28%	M. J. Page, <i>et al. Nat. Commun.</i> 2015, 6 , 8448
IRDye800CW	774 nm	12%	L. J. Cruz <i>et al. Nano Res.</i> 2016, 9 , 1276–1289
Indocyanine green	807 nm	9.3%	P. E. Burrows <i>et al. Proc. Natl Acad. Sci. USA</i> 2013, 110 8621–8626

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