Preparation and Characterization of Luminescent SCS and NCN Pincer Platinum Complexes Derived from 3,5-Bis(anilinothiocarbonyl)toluene

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Supplementary Information

General Procedures. All solvents were dried and distilled prior to use, and the reactions were carried out under N_2. NMR spectra were recorded on a JEOL JNM-EX-400 NMR spectrometer. Elemental analyses were carried out with a Yanaco CHN Corder MT-5 and a Yanaco SX-Elements Micro Analyzer YS-10. UV-visible absorption spectra and emission spectra were recorded on a Shimadzu UV-2550 UV-visible spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Samples for time-resolved measurements were excited at 400 nm using the second harmonic of an amplified mode-locked Ti:Sapphire laser and the luminescence was detected with a photomultiplier tube (Hamamatsu R928) and recorded using a digital storage oscilloscope, before transfer to a PC for analysis. TG analyses were carried out with a Shimadzu TGA-50 at a heating rate of 10 ºC min^{-1} under N_2. Cyclic voltammetry was carried out with a Hokuto Denko HSV-100 standard voltammetry tool. A conventional three-electrodes configuration was used, with glassy carbon working electrode, platinum wire auxiliary electlode, and Ag^+/Ag reference electrode. The voltammograms were adjusted to a ferrocene-ferrocenium couple (Cp_2Fe^+/Cp_2Fe) as the standard ($E_{1/2}$ = +0.18 V *vs*. Ag^+/Ag).

X-ray Crystallographic Study. The diffraction data were collected with a Rigaku Saturn CCD area detector with graphite monochromated MoKα (λ = 0.71070 Å) at –160 ºC. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods (SIR 92) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. In the refinement all hydrogen atoms were included using the riding model with temperature parameter factors.

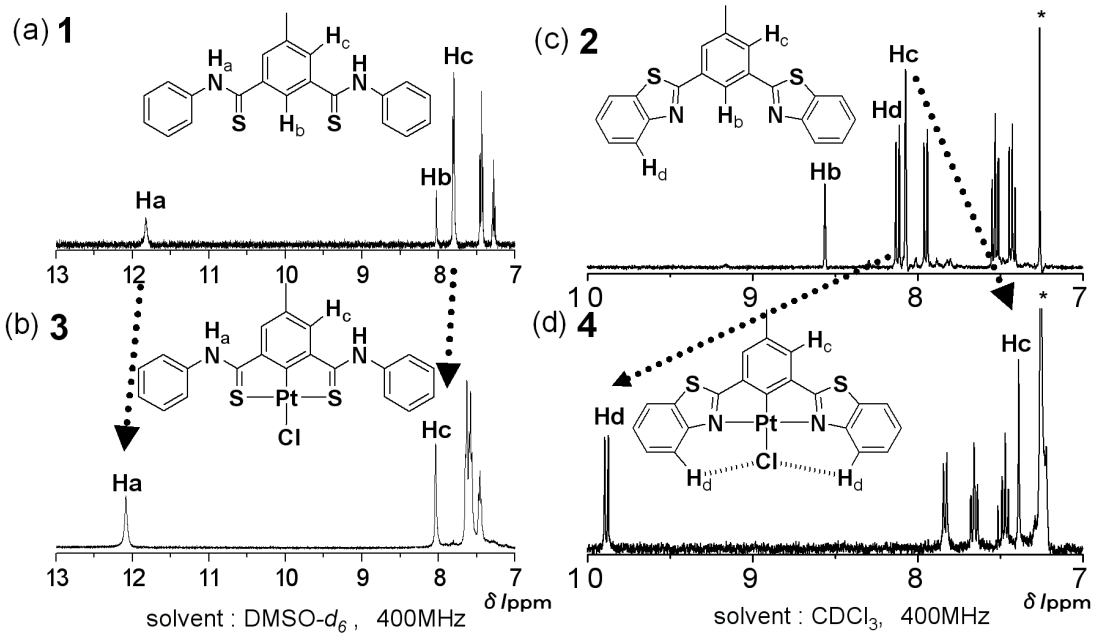

Figure S1. ^{1}H NMR spectra of (a) **1** and (b) **3** in DMSO-d_6 and (c) **2** and (d) **4** in $CDCl_3$ at room temperature. H_d in figures S1(c) and S1(d) is denoted as H(4') in the text.

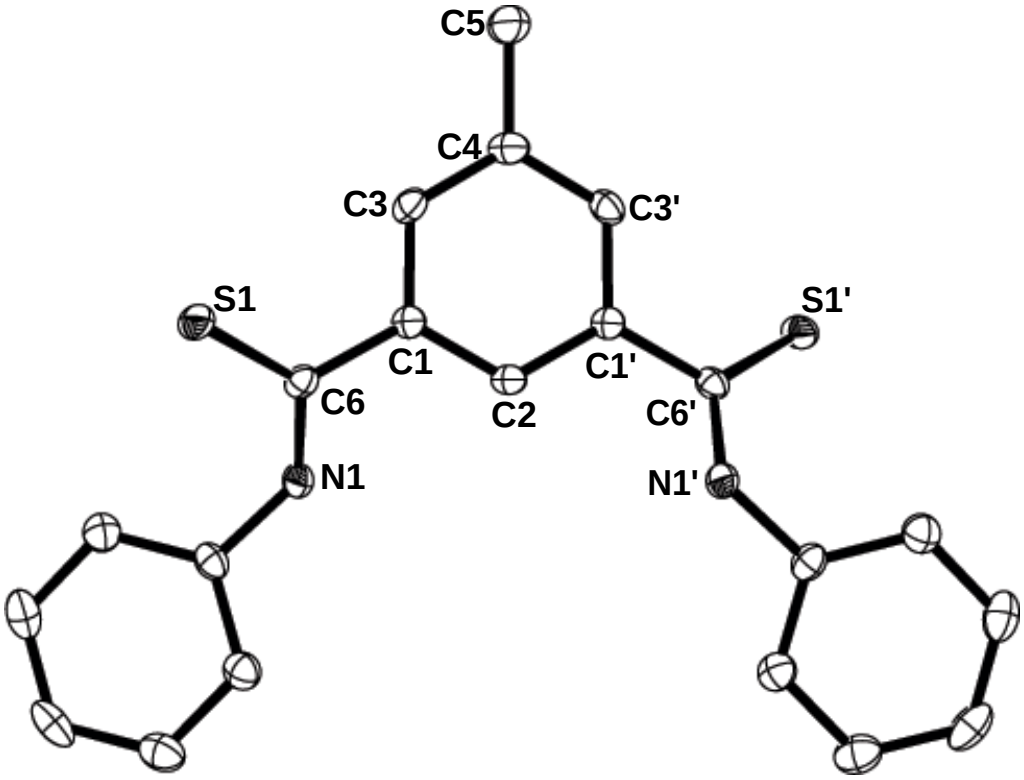

Figure S2. X-ray crystal structure of **1** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for simplicity.

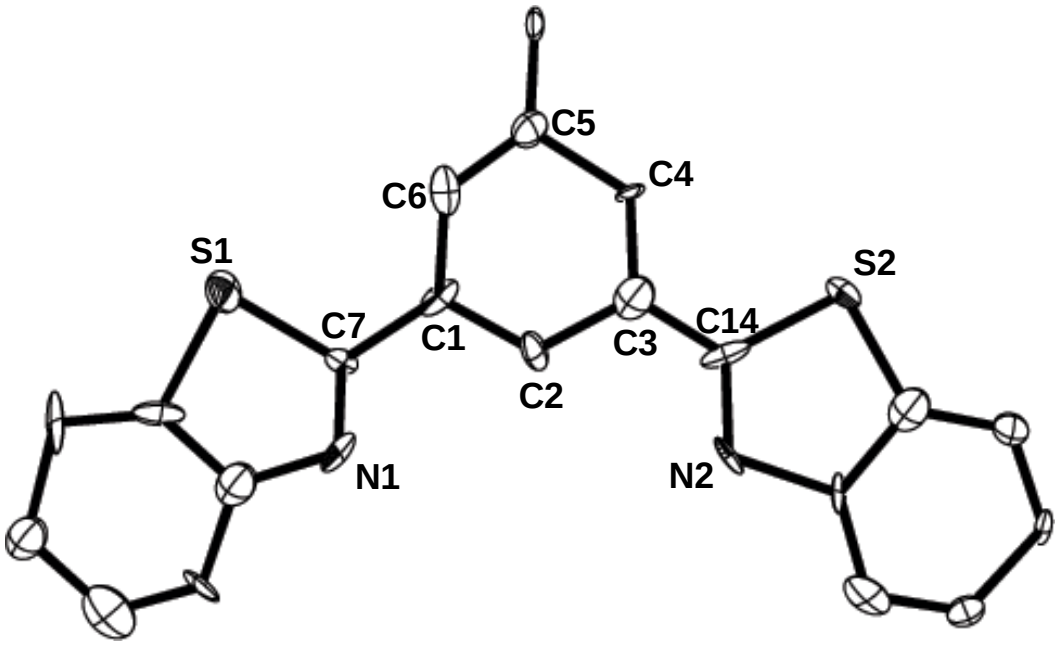

Figure S3. X-ray crystal structure of **2** with thermal ellipsoids drawn at the 50% probability level. One of the two crystallographically independent molecules of **2** is shown. Hydrogen atoms are omitted for simplicity.

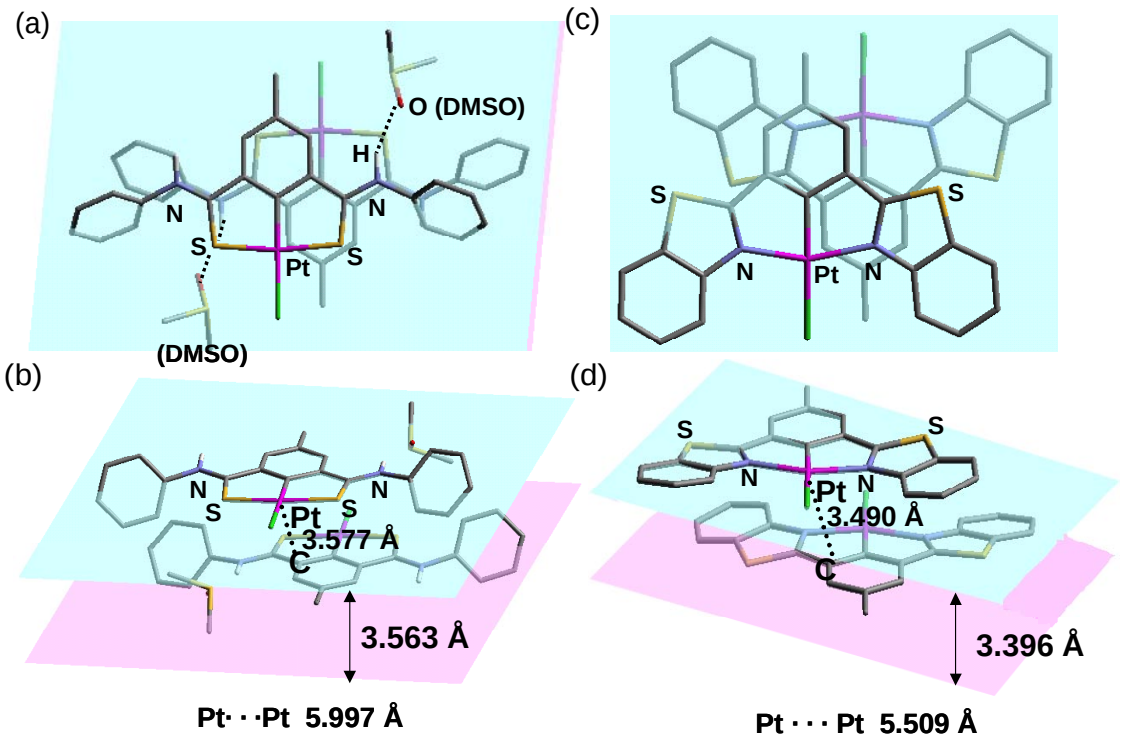

Figure S4. Views of the molecular packing; (a) top view and (b) side view of **3** and (c) top view and (d) side view of **4**.

Table S1. Solvatochromism Data for **3**

solvent	absorption λ_{max}/nm	
	π-π*	MLCT
MeOH	286	435
EtOH	286	445
CH_2Cl_2-THF(3:2)	292	465
acetone	–	468
THF	290	475

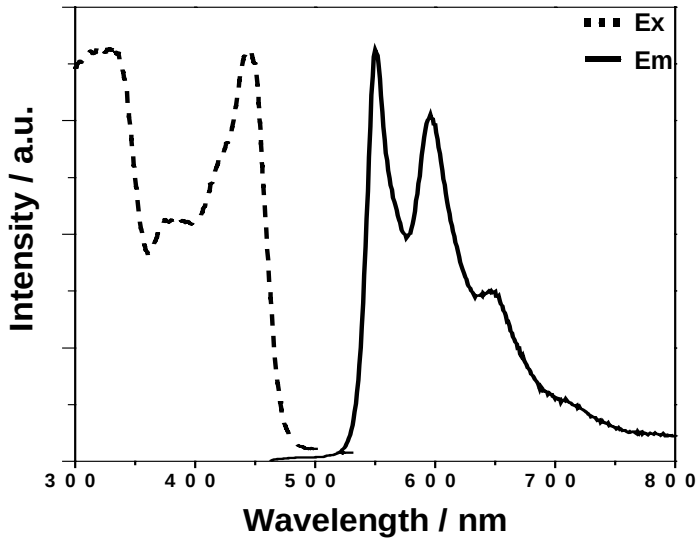

Figure S5. Emission and excitation spectra of **4** in a 3:2 mixture of CH_2Cl_2 and THF at room temperature.

Table S2. Crystal data and details of the structure refinements for **1**, **2**, **3**, and **4**.

	1	**2**	**3**·2DMSO	**4**
Formula	$C_{21}H_{18}N_2S_2$	$C_{42}H_{28}N_4S_4$	$C_{25}H_{29}ClN_2O_2S_4Pt$	$C_{21}H_{13}ClN_2S_2Pt$
Formula Weight	362.51	716.95	748.30	588.01
Crystal Color	yellow	pale yellow	red	orange
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Lattice Parameters				
a/Å	11.239(12)	7.5508(16)	11.157(6)	7.964(4)
b/Å	17.766(17)	14.336(3)	17.573(8)	15.430(7)
c/Å	9.630(10)	15.891(4)	14.538(7)	14.702(7)
β/^{o}	113.112(13)	103.788(3)	100.779(8)	96.796(8)
V/ Å^3	1768(3)	1670.7(6)	2800(2)	1794.0(14)
Space Group	C2/c (#15)	$P2_1$ (#4)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
Z value	4	2	4	4
No. Reflections				
Measured				
Total	6571	12566	19566	12764
Unique	1941	5956	6282	4067
Observations	1551	4388	5396	3408
(I>2.00σ(I))				
D_{calc}/g cm^{-3}	1.361	1.425	1.775	2.177
Structure Solution	Direct Methods	Direct Methods	Direct Methods	Direct Methods
	(SIR92)	(SIR92)	(SIR92)	(SIR92)
Reflection/Parameter	11.93	9.16	15.64	13.26
Ratio				
R (I>2.00σ (I))	0.0359	0.0805	0.0568	0.0308
Rw (I>2.00σ (I))	0.0515	0.1455	0.0741	0.0413
Goodness of Fit	1.011	1.000	0.995	1.002
Indicator				