

**Cyclometallated Platinum(II) Complexes Incorporating Ethynyl-Flavone  
Ligands: Switching Between Triplet and Singlet Emission  
Induced by Selective Binding of Pb<sup>2+</sup> Ions**

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**Electronic Supplementary Information**

**Experimental**

**General Procedure.** All manipulations were performed using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. NMR spectra were recorded on Bruker DPX-200, AV 300 or AV 500 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C chemical shifts are given versus SiMe<sub>4</sub> and were determined by reference to residual <sup>1</sup>H and <sup>13</sup>C solvent signals. Assignments of carbon atoms were based on HMBC, HMQC and COSY experiments. High resolution mass spectra (HRMS) were performed on a MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. Elemental analyses were performed by Muriel Escadeillas at the CRMPO. UV/vis absorption spectra were recorded using a UVIKON 9413 or Biotek Instruments XS spectrophotometer using quartz cuvettes of 1 cm pathlength. The flavone-based alkynes **1a-c** were prepared in good yields by alkylation of 2-(4-ethynylphenyl)-3-hydroxy-4H-chromen-4-one.<sup>1</sup>

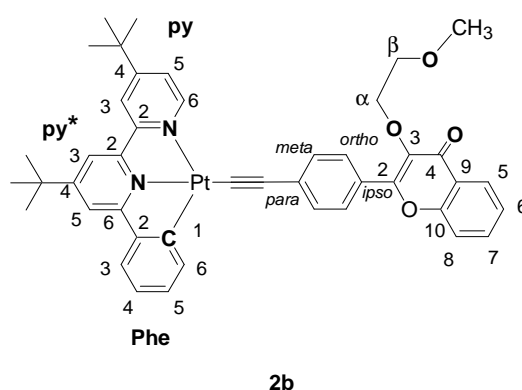
Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 or Tau-3 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube. The spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. The 77K spectra were acquired using an Oxford Instruments Cryostat model DN1704. Cryostat model DN1704. Luminescence quantum yields were determined using the method of continuous dilution, using [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as the standard ( $\phi = 0.028$  in air-equilibrated aqueous solution<sup>2</sup>) and correcting for the refractive index. Fluorescence and phosphorescence lifetimes < 10  $\mu$ s were

measured by time-correlated single-photon counting (TCSPC) following excitation at 374.0 nm with an EPL-375 pulsed diode laser. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator. Phosphorescence lifetimes in excess of 10  $\mu$ s were obtained by multichannel scaling following excitation by a pulsed xenon lamp.

The stoichiometry and complexation constants were determined by global analysis of the evolution of all absorption and fluorescence spectra by using Specfit Global analysis system V3.0 for 32-bit Windows system.<sup>3</sup>

**Caution!** Perchlorate salts are potentially explosive and should be handled with care.

### Numbering



**Synthesis of  $(C^{\wedge}N^{\wedge}N-(t\text{-Bu})_2\text{-phbpy})\text{Pt}(-\text{C}\equiv\text{C-FLV-3-OR})$ , **2** (a, R = Me; b, R =  $\text{CH}_2\text{CH}_2\text{OMe}$ ; c, R =  $(\text{CH}_2\text{CH}_2\text{O})_2\text{Me}$ )**

To a  $\text{CH}_2\text{Cl}_2$  solution of  $(C^{\wedge}N^{\wedge}N-t\text{Bu}_2\text{-pbpy})\text{PtCl}$  (179 mg, 0.31 mmol) and the appropriate acetylide-flavone derivative **1** (0.78 mmol) were added distilled of  $i\text{Pr}_2\text{NH}$  (10mL) and CuI (2.97 mg, 15.5  $\mu$ mol). The reaction mixture was refluxed for 48 h. After evaporation of the solvents, the residue was purified by column chromatography over silica gel using as eluant  $\text{CH}_2\text{Cl}_2 : \text{Et}_2\text{O} : 7/3$ . Recrystallization in a  $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  mixture afforded compounds **2** as orange microcrystals.

**2a** (61 % yield, orange powder).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 9.12 (dd,  $^3J = 6.3$  Hz,  $^3J_{\text{Pt-H}} = 14.6$  Hz, 1H,  $\text{Py}^6$ ), 8.29 (dd,  $^3J = 8$  Hz,  $^4J = 1.5$  Hz, 1H,  $\text{H}^5$ ), 8.12 (d,  $^3J = 8.6$  Hz, 2H, Ph *ortho*), 7.96 (dd,  $^3J = 6.8$  Hz,  $^3J_{\text{Pt-H}} = 64$  Hz, 1H,  $\text{Phe}^6$ ), 7.84 (d,  $^4J = 1.6$  Hz, 1H,  $\text{Py}^3$ ), 7.70 (m, 3H, Ph *meta* and  $\text{H}^7$ ), 7.56 (m, 4H,  $\text{Py}^{*3}$ ,  $\text{Py}^{*5}$ ,  $\text{Py}^5$  and  $\text{H}^8$ ), 7.41 (m, 2H,  $\text{Phe}^3$  and  $\text{H}^6$ ), 7.19 (t, 1H,  $^3J = 6.3$  Hz,  $\text{Phe}^5$ ), 7.09 (t, 1H,  $^3J = 8.5$  Hz,  $\text{Phe}^4$ ), 3.95 (s, 3H, OMe), 1.48 (s, 9H, *t*-Bu), 1.46 (s, 9H, *t*-Bu).  $^{13}\text{C}$  [ $^1\text{H}$ ] NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ): 175.07 ( $\text{C}^4$ ), 165.14 ( $\text{Py}^{*6}$ ), 163.62, 163.55 ( $\text{Py}^{*4}$ ,  $\text{Py}^4$ ), 158.13 ( $\text{Py}^2$ ), 156.03 ( $\text{C}^2$ ), 155.23 ( $\text{C}^{10}$ ), 154.42 ( $\text{Py}^{*2}$ ), 151.55 ( $\text{Py}^6$ ), 147.12 ( $\text{Phe}^2$ ), 142.19 ( $\text{Phe}^1$ ), 141.27 ( $\text{C}^3$ ), 138.52 ( $\text{Phe}^6$ ), 133.25 ( $\text{C}^7$ ), 131.84 (Ph *para*,

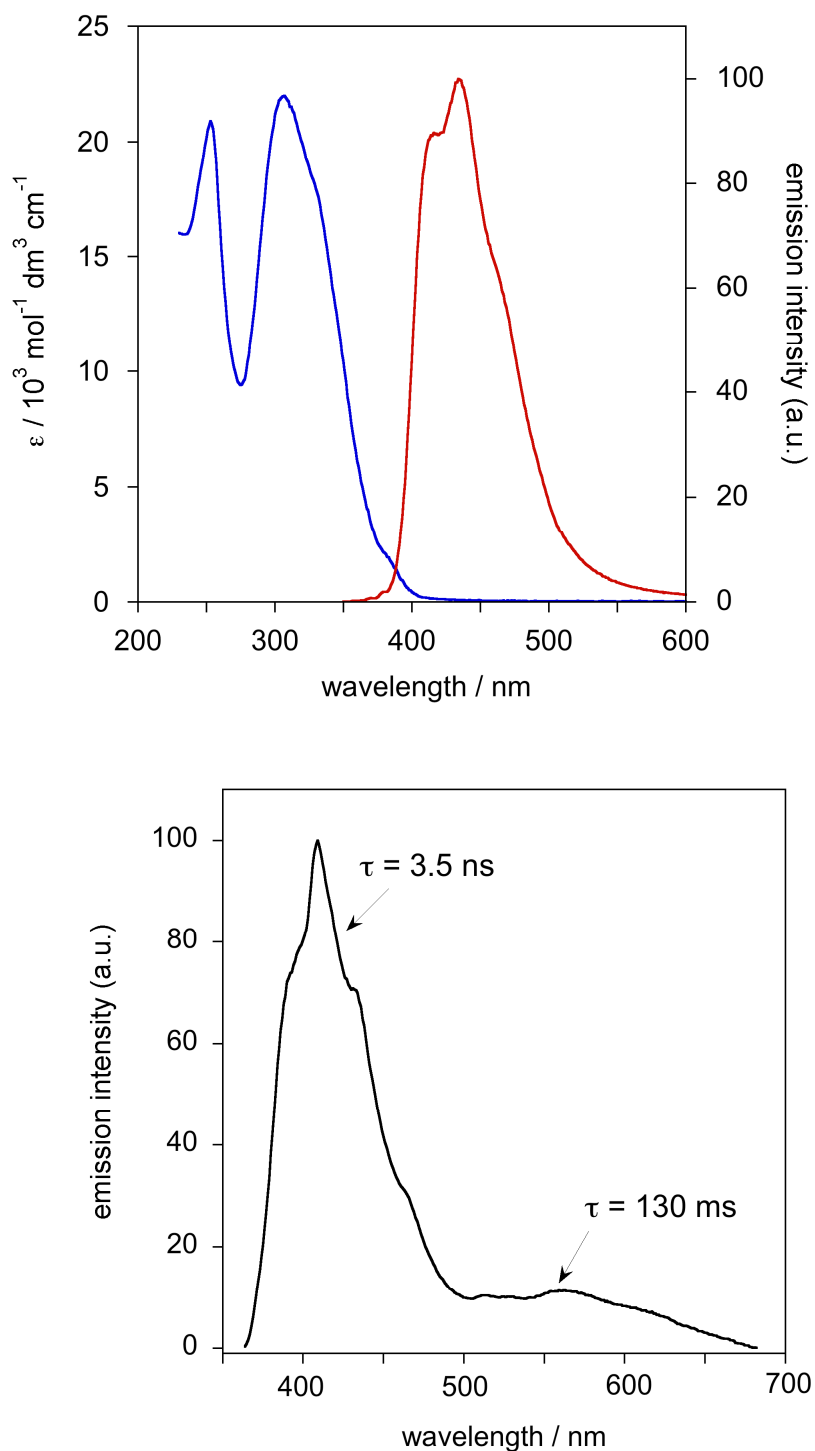
Ph *meta*), 131.28 (Phe<sup>5</sup>), 128.07 (Ph *ortho*), 126.85 (Ph *ipso*), 125.75 (C<sup>5</sup>), 124.55, 124.49, 124.27, 124.17 (Py<sup>5</sup>, C<sup>6</sup>, C<sup>9</sup>, Phe<sup>3</sup>), 123.60 (Phe<sup>4</sup>), 119.16 (Py<sup>3</sup>), 117.99 (C<sup>8</sup>), 115.53 (Py\*<sup>5</sup>), 114.50 (Py\*<sup>3</sup>), 111.62 (C≡), 106.44 (C≡), 59.99 (OMe), 35.99 (*t*-Bu), 35.72 (*t*-Bu), 30.57 (*t*-Bu); 30.35 (*t*-Bu). Anal. Calcd. for C<sub>42</sub>H<sub>38</sub>N<sub>2</sub>O<sub>3</sub>Pt: C, 61.98; H, 4.71; N, 3.44. Found: C, 61.85; H, 4.71; N, 3.49.

**2b.** (60 % yield, orange powder). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 9.13 (d, <sup>3</sup>J = 5.7 Hz, <sup>3</sup>J<sub>Pt-H</sub> = 12 Hz, 1H, Py<sup>6</sup>), 8.28 (d, <sup>3</sup>J = 8 Hz, 1H, H<sup>5</sup>), 8.18 (d, <sup>3</sup>J = 8 Hz, 2H, Ph *ortho*), 7.98 (dd, <sup>3</sup>J = 7.4 Hz, <sup>3</sup>J<sub>Pt-H</sub> = 65.6 Hz, 1H, Phe<sup>6</sup>), 7.85 (s, 1H, Py<sup>3</sup>), 7.69 (m, 2H, Ph *meta* and H<sup>7</sup>), 7.59 (m, 4H, Py\*<sup>3</sup>, Py\*<sup>5</sup>, Py<sup>5</sup> and H<sup>8</sup>), 7.42 (m, 2H, H<sup>6</sup> and Phe<sup>3</sup>), 7.20 (t, 1H, <sup>3</sup>J = 7.3 Hz, Phe<sup>5</sup>), 7.10 (t, 1H, <sup>3</sup>J = 7.3 Hz, Phe<sup>4</sup>), 4.32 (m, 2H, CH<sub>2</sub>), 3.72 (m, 2H, CH<sub>2</sub>), 3.36 (s, 3H, OMe), 1.49 (s, 9H, *t*-Bu), 1.47 (s, 9H, *t*-Bu). <sup>13</sup>C [<sup>1</sup>H] NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 174.98 (C<sup>4</sup>), 165.18 (Py\*<sup>6</sup>), 163.64 (Py\*<sup>4</sup>), 163.58 (Py<sup>4</sup>), 158.12 (Py<sup>2</sup>), 156.19 (C<sup>2</sup>), 155.42 (C<sup>10</sup>), 154.41 (Py\*<sup>2</sup>), 151.56 (Py<sup>6</sup>), 147.10 (Phe<sup>2</sup>), 142.19 (Phe<sup>1</sup>), 140.22 (C<sup>3</sup>), 138.55 (Phe<sup>6</sup>), 133.22 (C<sup>7</sup>), 131.93 (Ph *para*), 131.70 (Ph *meta*), 131.32 (Phe<sup>5</sup>), 128.37 (Ph *ortho*), 126.92 (Ph *ipso*), 125.72 (C<sup>5</sup>), 124.60 (Py<sup>5</sup>), 124.48 (C<sup>6</sup>), 124.22 (Phe<sup>3</sup>), 124.19 (C<sup>9</sup>), 123.62 (Phe<sup>4</sup>); 119.15 (Py<sup>3</sup>), 117.99 (C<sup>8</sup>), 115.54 (Py\*<sup>5</sup>), 114.49 (Py\*<sup>3</sup>), 111.15 (C≡), 106.59 (C≡), 71.81 (CH<sub>2</sub>), 71.27 (CH<sub>2</sub>), 58.80 (OMe), 36.00 (*t*-Bu), 35.73 (*t*-Bu), 30.57 (*t*-Bu), 30.56 (*t*-Bu). Anal. Calcd. for C<sub>44</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>Pt: C, 61.60; H, 4.93; N, 3.27. Found: C, 61.26; H, 5.02; N, 3.23.

**2c.** (73 % yield, orange powder). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 9.11 (dd, <sup>3</sup>J = 5.7 Hz, 1H, Py<sup>6</sup>), 8.25 (dd, <sup>3</sup>J = 8 Hz, <sup>4</sup>J = 1.4 Hz, 1H, H<sup>5</sup>), 8.16 (d, <sup>3</sup>J = 8.7 Hz, 2H, Ph *ortho*), 7.96 (dd, <sup>3</sup>J = 7.5 Hz, <sup>4</sup>J = 1 Hz, 1H, Phe<sup>6</sup>), 7.83 (d, <sup>4</sup>J = 1.7 Hz, 1H, Py<sup>3</sup>), 7.67 (m, 3H, Ph *meta* and H<sup>7</sup>), 7.56 (m, 4H, Py\*<sup>3</sup>, Py\*<sup>5</sup>, Py<sup>5</sup> and H<sup>8</sup>), 7.40 (m, 2H, Phe<sup>3</sup> and H<sup>6</sup>), 7.17 (t, 1H, <sup>3</sup>J = 6.3 Hz, Phe<sup>5</sup>), 7.08 (t, 1H, <sup>3</sup>J = 8.5 Hz, Phe<sup>4</sup>), 4.34 (m, 2H, CH<sub>2</sub>), 3.79 (m, 2H, CH<sub>2</sub>), 3.58 (m, 2H, CH<sub>2</sub>), 3.51 (m, 2H, CH<sub>2</sub>), 3.38 (s, 3H, OMe), 1.46 (s, 9H, *t*-Bu), 1.44 (s, 9H, *t*-Bu).

<sup>13</sup>C [<sup>1</sup>H] NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 175.01 (C<sup>4</sup>), 165.19 (Py\*<sup>6</sup>), 163.67, 163.62 (Py\*<sup>4</sup>, Py<sup>4</sup>), 158.12 (Py<sup>2</sup>), 156.13 (C<sup>2</sup>), 155.20 (C<sup>10</sup>), 154.41 (Py\*<sup>2</sup>), 151.53 (Py<sup>6</sup>), 147.12 (Phe<sup>2</sup>), 142.17 (Phe<sup>1</sup>), 140.13 (C<sup>3</sup>), 138.53 (Phe<sup>6</sup>), 133.21 (C<sup>7</sup>), 131.92 (Ph *para*), 131.66 (Ph *meta*), 131.30 (Phe<sup>5</sup>), 128.42 (Ph *ortho*), 126.96 (Ph *ipso*), 125.70 (C<sup>5</sup>), 124.60, 124.47, 124.20 (Py<sup>5</sup>, C<sup>6</sup>, C<sup>9</sup>, Phe<sup>3</sup>), 123.64 (Phe<sup>4</sup>), 119.16 (Py<sup>3</sup>), 117.97 (C<sup>8</sup>), 115.55 (Py\*<sup>5</sup>), 114.50 (Py\*<sup>3</sup>), 111.13 (C≡), 106.58 (C≡), 71.95 (CH<sub>2</sub>), 71.33 (CH<sub>2</sub>), 70.46 (CH<sub>2</sub>), 70.35 (CH<sub>2</sub>), 59.10 (OMe), 36.00 (*t*-Bu), 35.73 (*t*-Bu), 30.56 (*t*-Bu); 30.35 (*t*-Bu). Anal. Calcd. for C<sub>46</sub>H<sub>46</sub>N<sub>2</sub>O<sub>5</sub>Pt: C, 61.26; H, 5.14; N, 3.11. Found: C, 61.55; H, 5.49; N, 3.33.

**Figure S1.** *Upper:* Absorption and emission spectra of **1b** ( $10^{-5}$  M) in  $\text{CH}_3\text{CN}$ , 298K,  $\lambda_{\text{ex}} = 360$  nm. *Lower:* Emission spectrum of **1b** in EPA glass at 77K ( $\lambda_{\text{ex}} = 350$  nm), displaying fluorescence and phosphorescence bands. The lifetimes indicated were registered at 420 nm and 550 nm ( $\lambda_{\text{ex}} = 374$  nm).



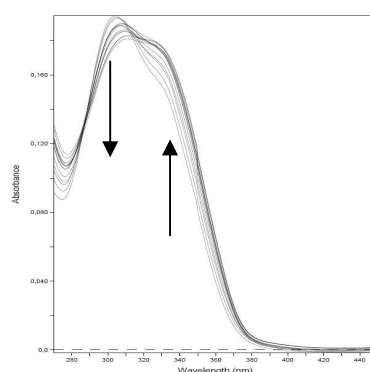
**Table S1. Photophysical (absorption and emission) data of 1b (CH<sub>3</sub>CN, 298 K)**

compound	$\lambda_{\text{abs}}/\text{nm}$ ( $\epsilon/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ )	$\lambda_{\text{em}}/\text{nm}^a$ ( $\tau$ )	$\Phi_{\text{em}}^b$
<b>1b</b>	307 (27000)	437(298 K) 414 <sup>c</sup> (77 K) (3.5 ns)	0.01

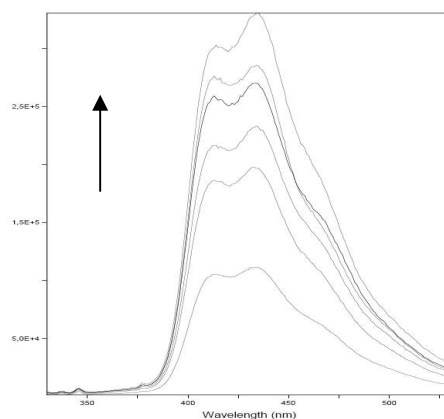
<sup>a</sup>  $\lambda_{\text{exc}} = 314$  nm. <sup>b</sup> Emission quantum yields were determined using quinine sulfate as the standard. <sup>c</sup> EPA

### Optical responses and titration of Pb<sup>2+</sup> with 1b

**Figure S2.** UV-vis absorption spectral changes of **1b** (conc = 10<sup>-5</sup> M) in CH<sub>3</sub>CN upon addition of Pb(ClO<sub>4</sub>)<sub>2</sub>.



**Figure S3.** Luminescence spectral changes of **1b** (conc = 10<sup>-5</sup> M) in CH<sub>3</sub>CN upon addition of Pb(ClO<sub>4</sub>)<sub>2</sub>. ( $\lambda_{\text{exc}} = 314$  nm)

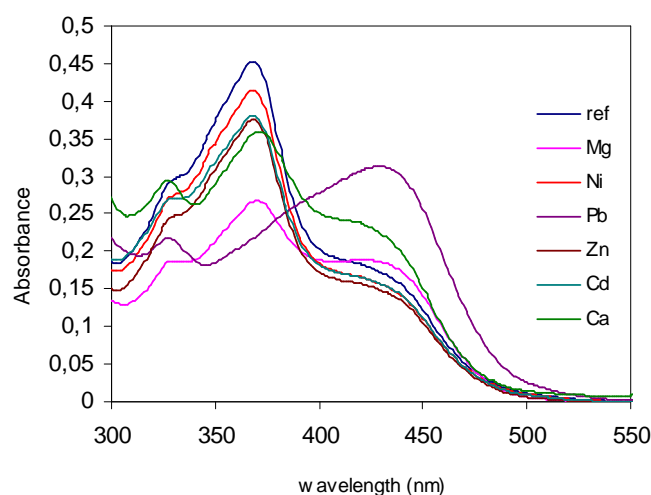


**Table S2.** Emission data for complexes **2**<sup>a</sup>

complex	medium (T/K)	$\lambda_{em}/nm$	$\tau/\mu s$	$\Phi_{em}^c$
<b>2a</b>	CH <sub>3</sub> CN (298)	565	12	0.024
	Glass <sup>b</sup> (77)	560, 605	40	-
<b>2b</b>	CH <sub>3</sub> CN (298)	567	17.5	0.027
	Glass <sup>b</sup> (77)	561, 601	20	-
<b>2c</b>	CH <sub>3</sub> CN (298)	570	21	0.032
	Glass <sup>b</sup> (77)	555,600	68	-

<sup>a</sup> Data for deoxygenated solutions. <sup>b</sup>EPA = (diethylether/isopentane/ethanol, 2/2/1 v/v). <sup>c</sup> reference: [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in air-equilibrated water

**Figure S4.** Absorption responses of **2c** (conc = 10<sup>-5</sup> M) with various metal cations (100 eq.) in CH<sub>3</sub>CN



Pb<sup>2+</sup> (log *K* = 5.0 ± 0.1), Cd<sup>2+</sup> (log *K* = 2.6 ± 0.01), Ca<sup>2+</sup> (log *K* = 3.8 ± 0.1)

**X-ray Crystallography.** Single crystals for X-ray diffraction studies were grown by slow diffusion of pentane in a CH<sub>2</sub>Cl<sub>2</sub> solution of complex **2b** at 20°C. The sample was studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized MoK $\alpha$  radiation. The data collection and refinement parameters are presented in Table S2. The structure was solved with SIR-97<sup>4</sup> which reveals the non-hydrogen atoms of the molecules. The whole structure was refined by full-matrix least-square techniques on *F*<sup>2</sup>, with hydrogens refined using the Riding mode. Structures were solved by direct methods. The structure was completed by subsequent difference Fourier techniques and refined by full-

matrix least squares on  $F^2$  (SHELXL-97) with initial isotropic parameters.<sup>5</sup> The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-651812. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [of from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ; Fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

**Table S3.** Crystallographic Data for **2b**.

	<b>2b</b>
formula	C <sub>45</sub> H <sub>44</sub> N <sub>2</sub> O <sub>4</sub> Pt.CH <sub>2</sub> Cl <sub>2</sub>
FW	942.81
Cryst syst	Triclinic
Space group	P-1
<i>a</i> , Å	11.4614(8)
<i>b</i> , Å	13.0906(9)
<i>c</i> , Å	13.8985(7)
$\alpha$ , deg	72.550(5)
$\beta$ , deg	78.944(5)
$\gamma$ , deg	81.274(6)
<i>V</i> , Å <sup>3</sup>	1942.5(2)
<i>Z</i>	2
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.612
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	3.796
Temp K	110(1)
<i>F</i> (000)	944
cryst. dimens, mm	0.24 x 0.20 x 0.20
$\theta$ rang, deg	2.91 – 27.00
Index ranges	-14 ≤ <i>h</i> ≤ 9 -16 ≤ <i>k</i> ≤ 16 -17 ≤ <i>l</i> ≤ 16
no. reflns colld	13552
no. of indep reflns/ R int.	7910/0.0444
GOF ( $F^2$ )	1.095
R1 ( <i>F</i> ) ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0502
R1 (all data)	0.0589
wR2 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.1392
wR2 (all data)	0.1464
largest diff peak/hole e/Å <sup>3</sup>	5.772/-3.901

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