

## Supporting Information

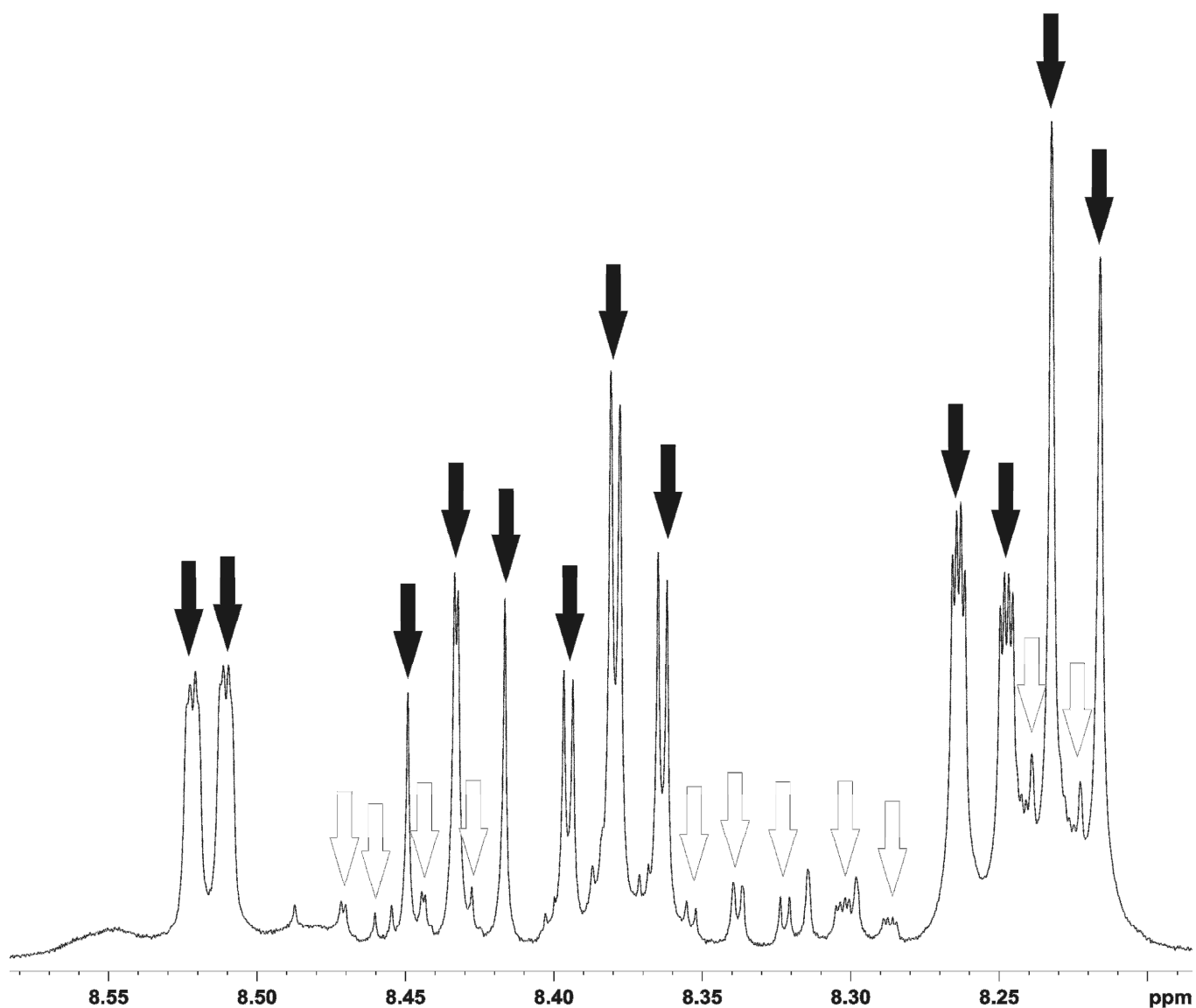
### **Speciation in solution, solid state spectroscopy and vapochromism of [Pt(trpy)(NCS)]SbF<sub>6</sub> where trpy = 2,2':6',2''-terpyridine**

**John S. Field,\* Craig D. Grimmer, Orde Q. Munro and Bradley P. Waldron**

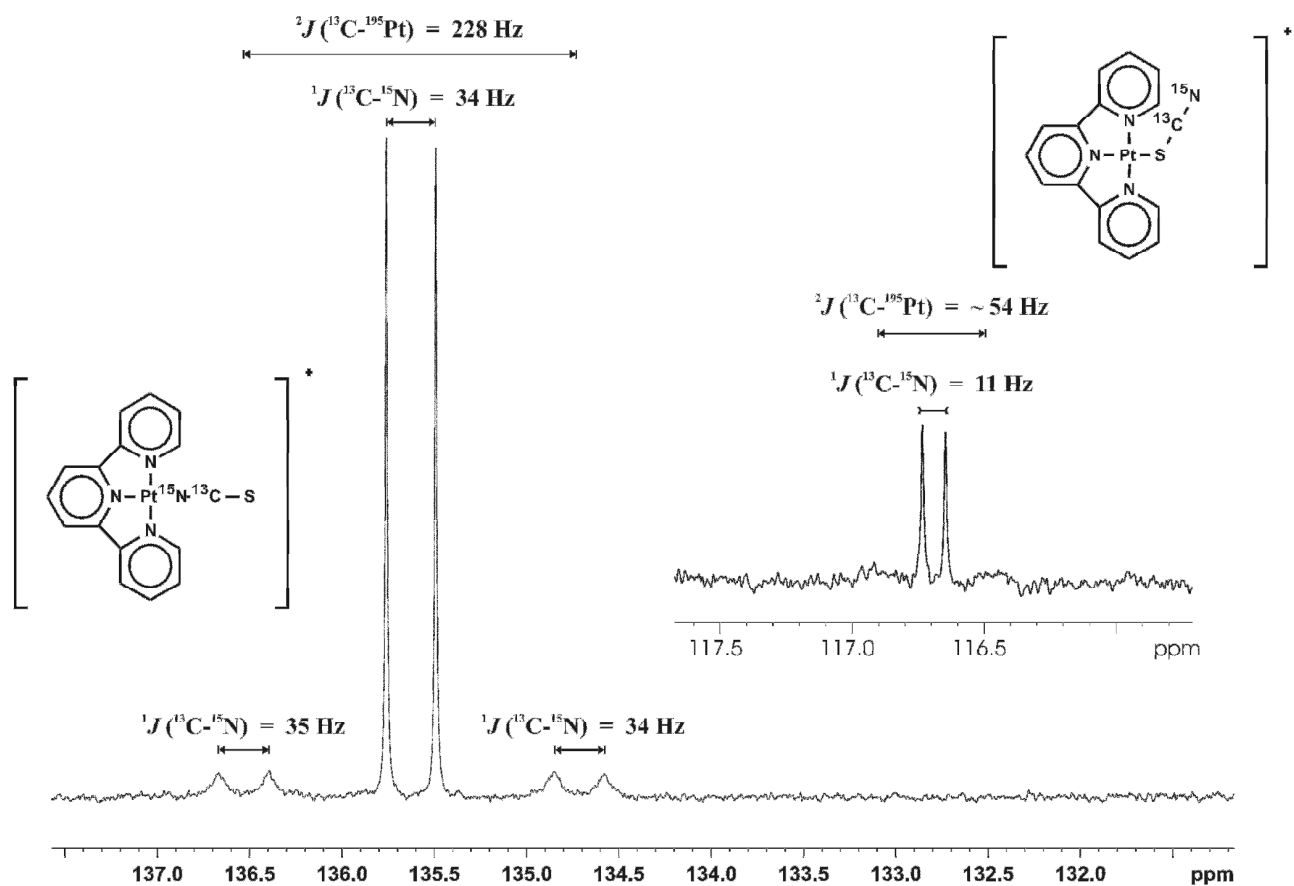
*School of Chemistry, University of KwaZulu-Natal, Private Bag X01, Pietermaritzburg,  
3201, South Africa*

## Supporting Information Table of Contents

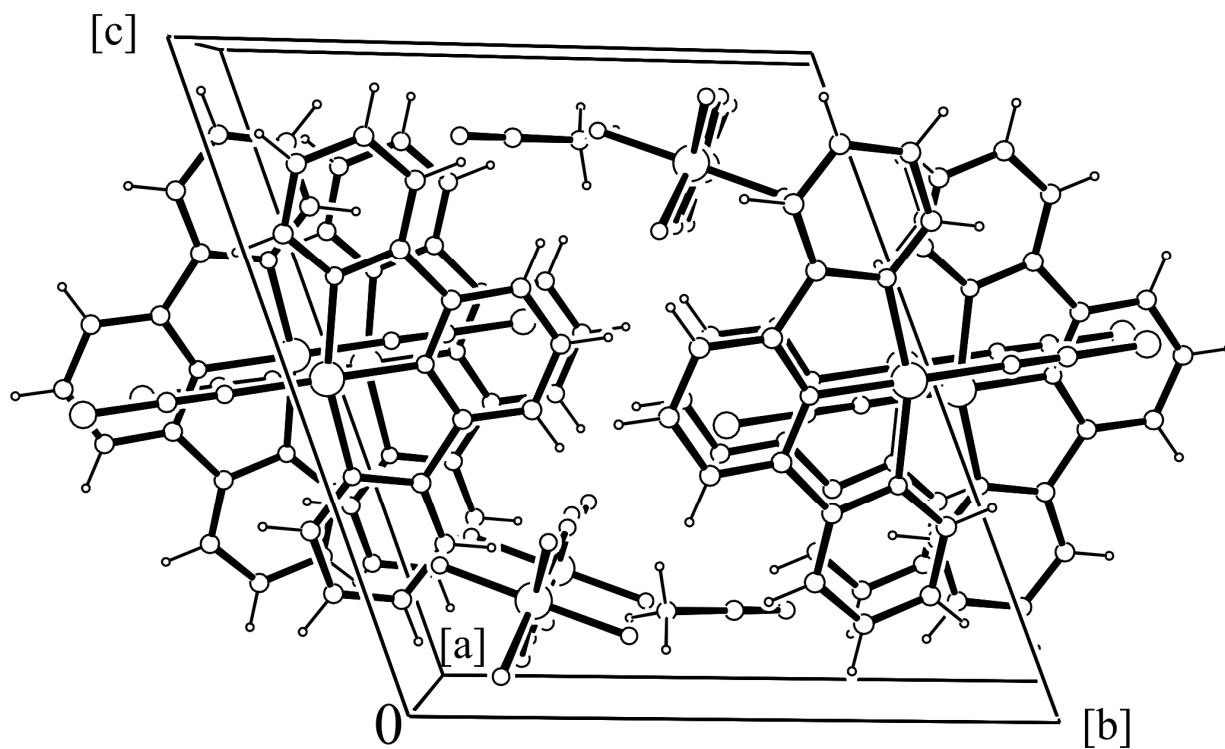
<b>Title</b>		S1
<b>Table of contents</b>		S2
<b>Figure S1</b>	<sup>1</sup> H NMR spectrum of [Pt(trpy)(NCS)]SbF <sub>6</sub> ( <b>1</b> ) recorded at 303 K in CD <sub>3</sub> CN. The signals due to the major (N-bound) isomer are marked with a solid arrow; signals due to the S-bound isomer are indicated with an un-shaded arrow.	S3
<b>Figure S2</b>	<sup>13</sup> C NMR spectrum of the “Pt <sup>15</sup> N <sup>13</sup> CS” unit in [Pt(trpy)( <sup>15</sup> N <sup>13</sup> CS)]SbF <sub>6</sub> recorded at 303 K in CD <sub>3</sub> CN.	S4
<b>Figure S3</b>	View down the [a]-axis of the unit cell contents that illustrates the cation, anion and solvent columns in [Pt(trpy)(NCS)]SbF <sub>6</sub> ·CH <sub>3</sub> CN ( <b>1</b> ·CH <sub>3</sub> CN).	S5
<b>Figure S4</b>	View parallel to the cation planes in [Pt(trpy)(NCS)]SbF <sub>6</sub> ·CH <sub>3</sub> CN ( <b>1</b> ·CH <sub>3</sub> CN) showing that the cations of adjacent stacks are not co-planar; in fact displaced by about one-third along a perpendicular line joining the cation planes. In (A) the anions and solvent molecules are included; in (B) the solvent molecules have been artificially removed. The dotted purple lines represent S···H <sup>⋙</sup> -C <sup>⋙</sup> (trpy) non-bonded contacts. The dotted red lines represent Pt···Pt distances less than 3.5 Å. The arrows in (B) indicate how, when solvent is lost, adjacent dimers might slide into new positions that results in the extended chain structure shown in (C).	S6
<b>Figure S5</b>	Comparison of the 295 K powder XRD spectrum measured for <b>1</b> with that calculated for <b>1</b> ·CH <sub>3</sub> CN (using a 295 K intensity dataset: see <b>1MeCN295K.cif</b> in the Supplementary Information) in the 2θ range of (A) 5 to 23° and (B) 23 to 40°.	S7
<b>Table S1</b>	Vapochromic response times for <b>1</b> .	S8



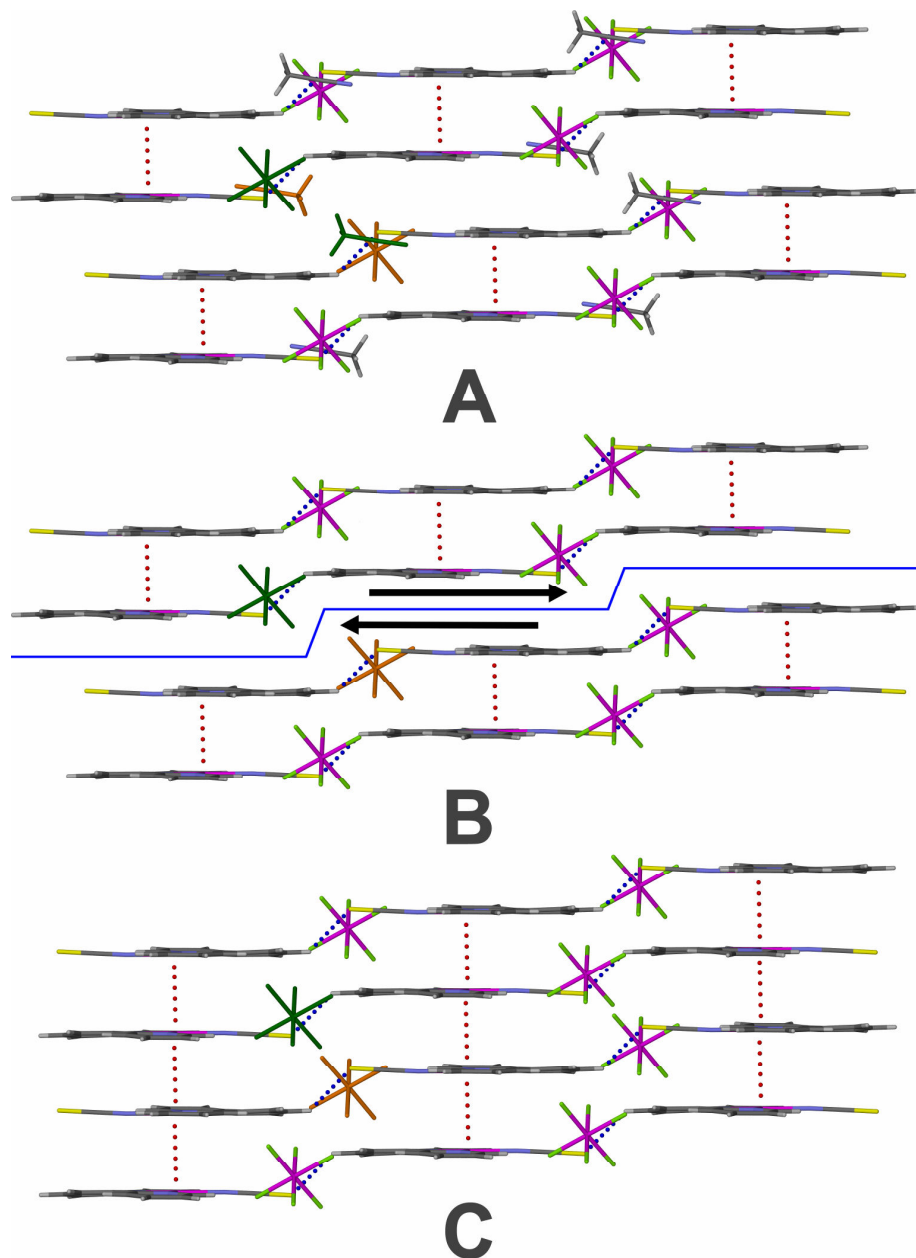
**Figure S1**  $^1\text{H}$  NMR spectrum of  $[\text{Pt}(\text{trpy})(\text{NCS})]\text{SbF}_6$  (**1**) recorded at 303 K in  $\text{CD}_3\text{CN}$ . The signals due to the major (N-bound) isomer are marked with a solid arrow; signals due to the S-bound isomer are indicated with an un-shaded arrow.



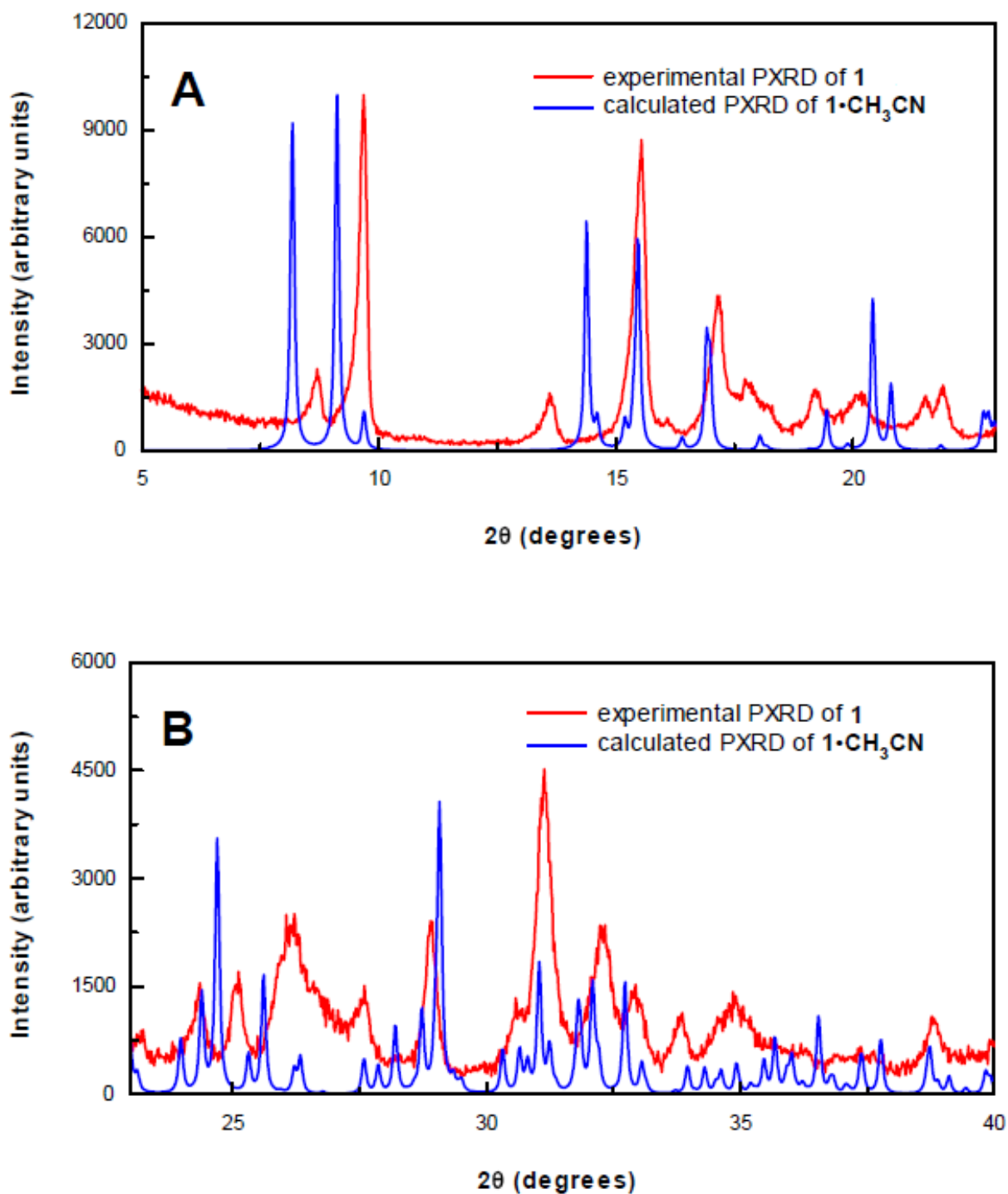
**Figure S2**  ${}^{13}\text{C}$  NMR spectrum of the “ $\text{Pt}^{15}\text{N}^{13}\text{CS}$ ” unit in  $[\text{Pt}(\text{trpy})({}^{15}\text{N}^{13}\text{CS})]\text{SbF}_6$  recorded at 303 K in  $\text{CD}_3\text{CN}$ .



**Figure S3** View down the [a]-axis of the unit cell contents that illustrates the cation, anion and solvent columns in [Pt(trpy)(NCS)]SbF<sub>6</sub>·CH<sub>3</sub>CN (**1**·CH<sub>3</sub>CN).



**Figure S4** View parallel to the cation planes in  $[\text{Pt}(\text{trpy})(\text{NCS})]\text{SbF}_6 \cdot \text{CH}_3\text{CN}$  ( $1 \cdot \text{CH}_3\text{CN}$ ) showing that the cations of adjacent stacks are not co-planar; in fact displaced by about one-third along a perpendicular line joining the cation planes. In (A) the anions and solvent molecules are included; in (B) the solvent molecules have been artificially removed. The dotted purple lines represent  $\text{S} \cdots \text{H} \cdots \text{C}(\text{trpy})$  non-bonded contacts. The dotted red lines represent  $\text{Pt} \cdots \text{Pt}$  distances less than  $3.5 \text{ \AA}$ . The arrows in (B) indicate how, when solvent is lost, adjacent dimers might slide into new positions that results in the extended chain structure shown in (C).



**Figure S5** Comparison of the 295 K powder XRD spectrum measured for **1** with that calculated for **1·CH<sub>3</sub>CN** (using a 295 K intensity dataset: see **1MeCN295K.cif** in the Supplementary Information) in the 2θ range of (A) 5 to 23° and (B) 23 to 40°.

**Table S1** Vapochromic response times for **1**

VOC	Response time	Time to de-solvate <sup>a</sup>	Vapour pressure at 298 K (torr) <sup>b</sup>
CH <sub>3</sub> CN	< 10 seconds	< 1 minute	88.47
DMF	< 10 seconds	7 days (2 days)	3.70
pyridine	< 10 seconds	15 days (4 days)	20.68

<sup>a</sup> This is the time taken when the solvated species is exposed to ambient conditions of temperature and pressure. If the sample of the solvate is gently heated under vacuum the times are reduced: see the values in brackets. <sup>b</sup> Taken from S. Ohe, in *Computer-aided Data book of Vapor Pressure*, Elsevier, New York, 1976.