

Structure and Emission Studies of Dimorphic Crystals of [PtBr₂(5,5'-bis(CF₃CH₂OCH₂)-2,2'-bpy)](1)[†]

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1.

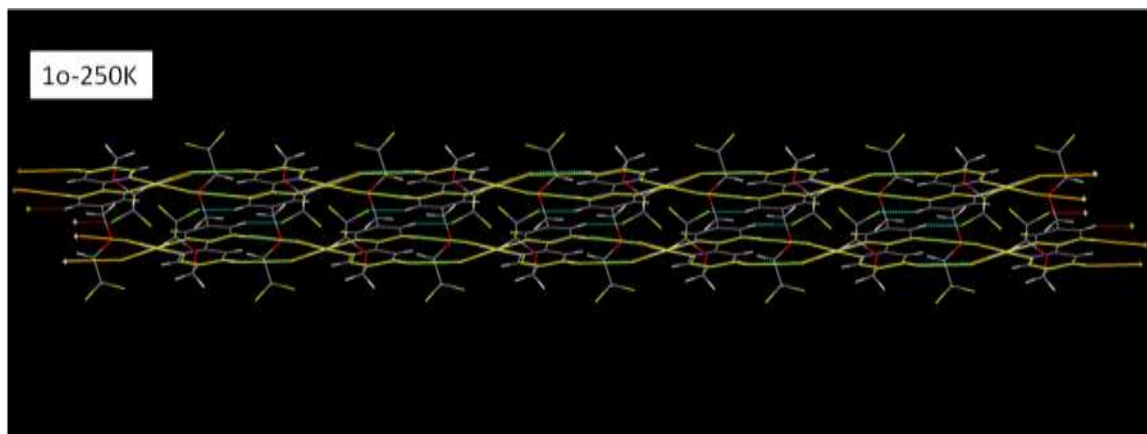
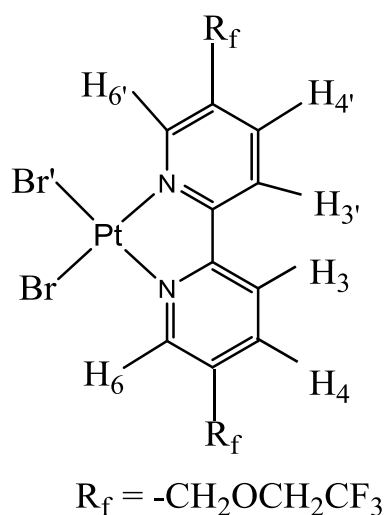


Figure S1. A better pictorial view of a double belt, which is highlighted by a yellow line, for **1o** at 250K; A closely packed pair of **1o** exhibiting Br, Br'...H3, H4' short contacts to molecules next on the belt and H4...F-C short contacts to molecules next on the opposite belt; [Note: Pt: purple; O: red; C: gray; H: white; F: yellow; Br: brown; Schematic drawing of complex **1** with labeling was shown in scheme A.]



Scheme A schematic drawing of complex **1** (either **1o** or **1y**); [corresponding to the molecule located at the lower left corner and at the upper left corner in Figure S1 and Figure S2 (below), respectively.]

2.

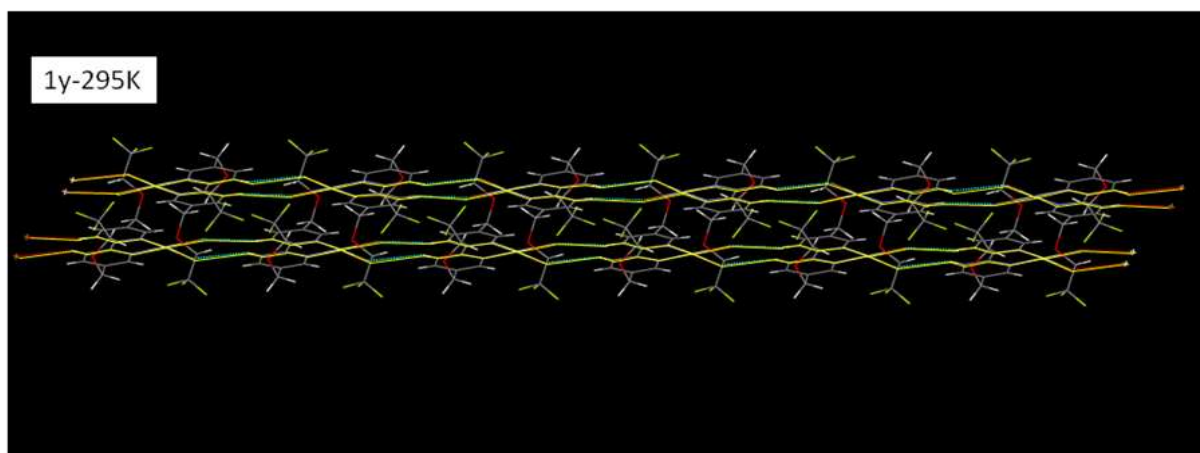


Figure S2. A pictorial view of a double belt, which is highlighted by a yellow line, for **1y** at 295K. A dimeric pair of **1y** exhibiting Br, Br'...H₃, H₃' short contacts to molecules next on the belt. [Note: Pt: purple; O: red; C: gray; H: white; F: yellow; Br: brown. The schematic drawing of the molecule located at the upper left corner is also shown in Scheme A.]

3.

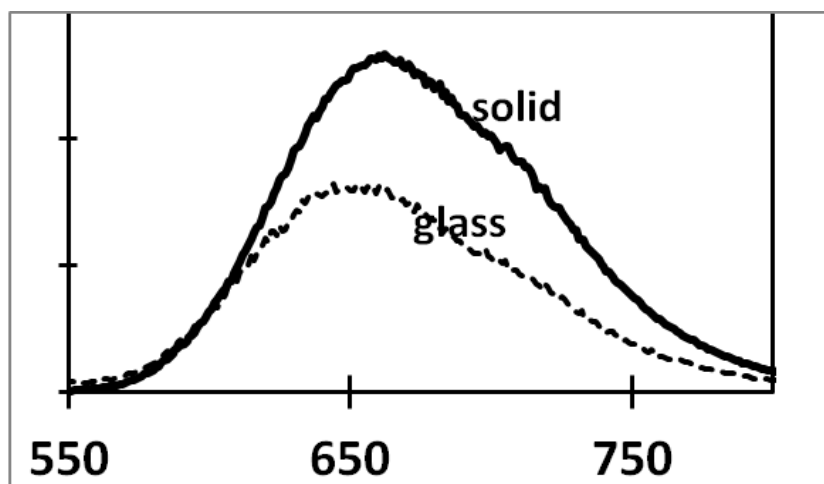


Figure S3. Emission spectra of [PtBr₂bpy] in the solid state at 90 K (—) and glassy matrix in 1:1 DCM/toluene at 77K (---).

4.

Table S1. Dependence of unit cell parameters of the **1o** dimorph on temperature. The temperature was maintained at ± 0.1 K.

Temp. (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg.)	β (deg.)	γ (deg.)	Volume (Å ³)
295	7.1492(2)	9.2419(2)	15.9759(4)	95.290(1)	102.563(1)	93.596(1)	1022.17(4)
250	7.1269(2)	9.2336(2)	15.9319(5)	95.597(1)	102.619(1)	94.175(1)	1013.42(5)

Note: Full cif information of **1o** deposited at CDCC for both 295 and 250 K data.

5.

Table S2. Dependence of unit cell parameters of the **1y** dimorph on temperature. The temperature was maintained at ± 0.1 K.

Temp. (K)	a (Å)	b (Å)	c (Å)	alpha (deg.)	beta (deg.)	gamma (deg.)	volume (Å ³)
295	7.6147(2)	9.2829(2)	15.1696(3)	94.413(1)	99.808(1)	107.229(1)	999.91(4)
200	7.5650(2)	9.2677(2)	15.0434(4)	93.945(1)	100.345(1)	107.144(1)	983.10(4)
150	7.5396(2)	9.2604(3)	14.9961(4)	93.703(1)	100.584(1)	107.011(1)	976.35(5)
125	7.5261(2)	9.2596(3)	14.9759(5)	93.591(1)	100.702(1)	106.922(1)	973.51(5)
100	7.5185(3)	9.2611(3)	14.9578(5)	93.465(2)	100.823(1)	106.817(1)	971.91(6)

Note: Full cif information of **1y** deposited at CDCC for temperatures ranging from 295 to 100 K.

6. Table S3. The Pt...Pt structural parameters at different temperatures for **1y** and **1o**

Polymorph	Temp. (K)	Pt(up)-Pt (Å)	Pt-Pt(down) (Å)	Pt(up)-Pt-Pt(down) (deg.)
1y	295	3.5258(2)	4.7690(2)	132.72(1)
	200	3.5013(2)	4.7604(2)	132.01(1)
	150	3.4900(2)	4.7563(2)	131.60(1)
	125	3.4838(2)	4.7548(2)	131.37(1)
	100	3.4798(2)	4.7574(2)	131.15(1)
1o	295	3.5903(2)	3.6186(2)	165.25(1)
	250	3.5792(4)	3.6110(4)	164.78(1)