ADVANCED MATERIALS

Supporting Information

Systematic Control of the Orientation of Organic Phosphorescent Pt Complexes in Thin Films for Increased Optical Outcoupling

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Supplementary Information

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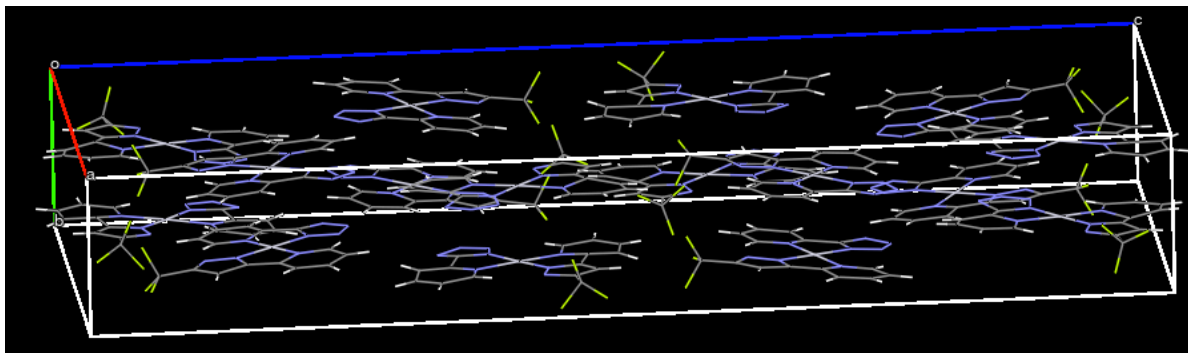*[3] Department of Chemistry, University of Northern Texas, Denson, TX, USA*

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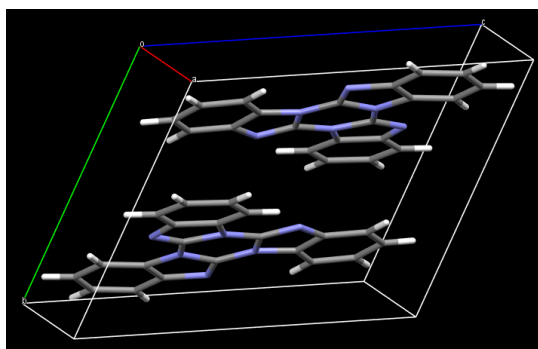[a]email: stevefor@umich.edu

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Crystal structure of PtD, Tint and (dbx)Pt(dpm)

Material	Space Group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Cell Volume (Å³)
PtD	P b c a	20.9	6.7	45.0	90	90	90	6294.1

Figure S1 | Measured single crystal structure and cell parameters of PtD based on single crystal XRD are shown. Details are included in the '.cif' file (CCDC-1919335).
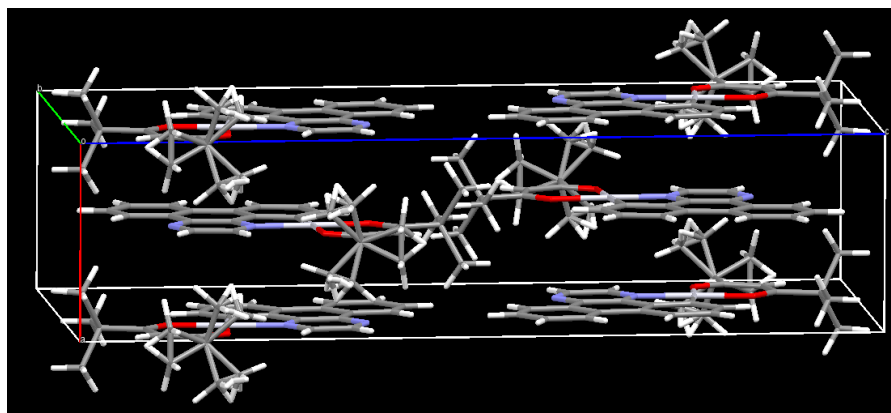

Material	Space Group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Cell Volume (Å³)
Tint	P-1	8.1	9.1	11.6	109.3	101.9	100.8	750.91

Figure S2 | Measured single crystal structure and cell parameters of Tint based on single crystal XRD. Details are included in the '.cif' file (CCDC-1919336).

The X-ray crystal structure of (dbx)Pt(dpm) crystal grown from the sublimation is shown in Fig. S4. The unit cell contains four formula units and molecules are packed favoring d-π interaction

between Pt d orbitals and π-orbitals of the dbx ligand along the z-axis of the square-planar Pt molecule.

Material	Space Group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Cell Volume (Å^3)
(dbx)Pt(dpm)	P m n a	6.7	12.9	27.3	90	90	90	2366.23

Figure S3 | Measured single crystal structure and cell parameters of (dbx)Pt(dpm) based on single crystal XRD. Details are included in the '.cif' file (CCDC-1919337).

Variable Angle Spectroscopic Ellipsometry measurement of templated NTCDA film
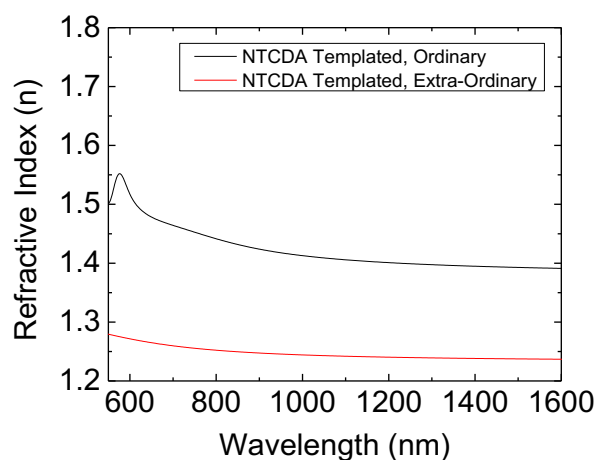
Figure S4 | The ordinary refractive index is larger than the extraordinary refractive index from the NTCDA film, showing the horizontal alignment of NTCDA molecules deposited on the PTCDA template[1]. This enables the monolayer thick NTCDA layer (1.5nm) to transfer the templated structure to the subsequently deposited molecules.

Bragg-Brentano x-ray diffraction patterns of PtD thin film on different substrates
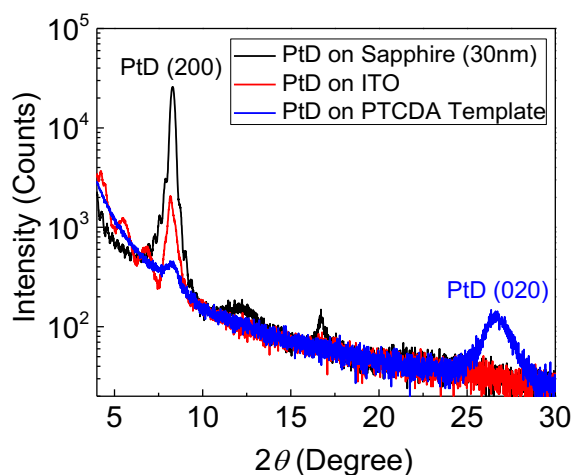

Figure S5 | Bragg-Brentano x-ray diffraction pattern of the PtD film on different substrates. The 30nm thick film of PtD deposited on sapphire substrate exhibits intense (200) diffraction, which is also observed in a film deposited on a 15 nm thick ITO surface. However, the film deposited on a 1.5 nm thick PTCDA template layer shows significantly reduced (200) peak, whereas (020) peak appears at $2\theta=26.6°$ due to the varied morphology of PtD molecules. The x-ray pole figure data are provided in Fig. 6.

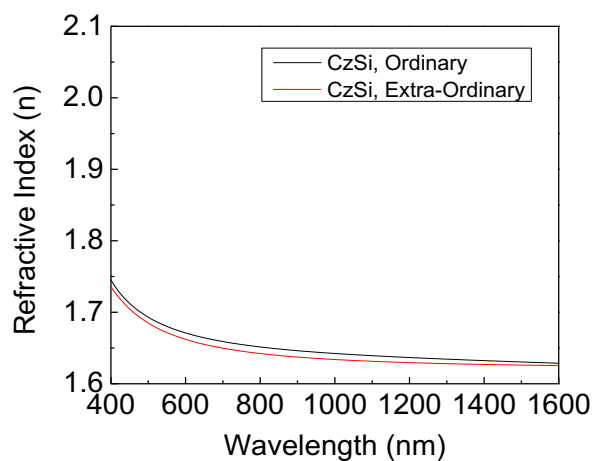# Variable Angle Spectroscopic Ellipsometry measurement of neat CzSi film

Figure S6 | The CzSi ordinary and extraordinary refractive indices are nearly identical at all wavelengths, indicating the isotropic alignment of the transition dipole moment[2]. The random orientation of this molecule stems from its bulky molecular structure[3].

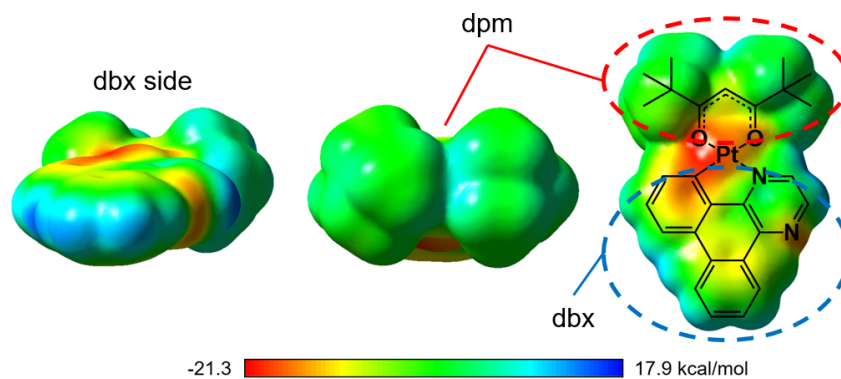# Electrostatic potential calculation of the Pt dopant

Figure S7 | Calculated electrostatic potential surface of a (dpm)Pt(dbx) molecule via DFT geometry optimization. The dpm shows almost neutral potential (3 kcal/mol) whereas the dbx ligand shows highly positive charge of 12.3 kcal/mol with the peak value of 17.9 kcal/mol near the nitrogen atoms.

Density Functional Theory Calculations

a

PtD   PtOEP

b

PtD (Monomer)   PtD (Excimer)   PtOEP

c
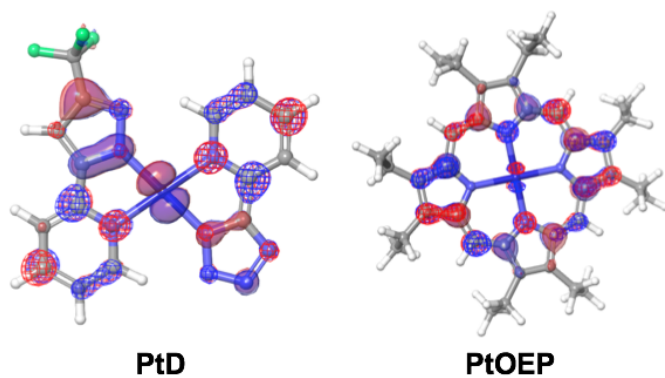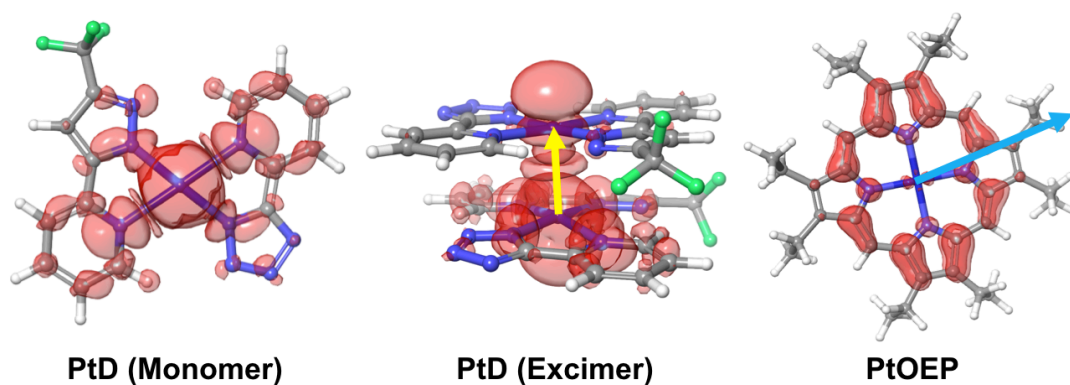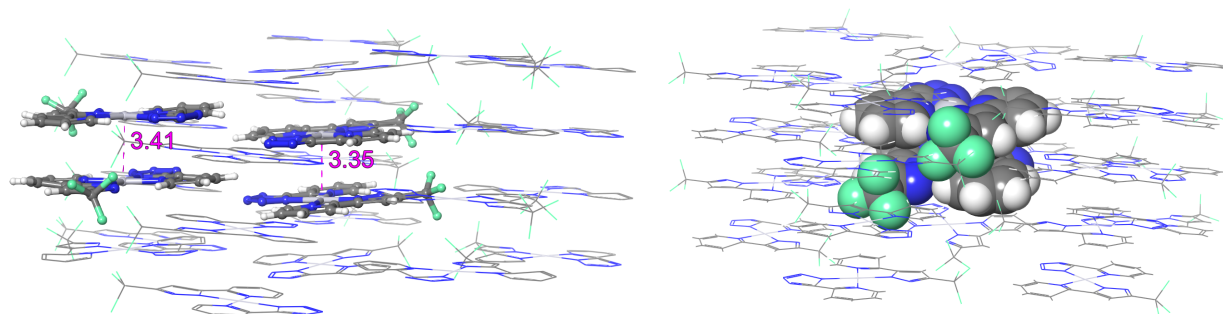
	3.35-dimer (PtD)		3.41-dimer (PtD)		PtOEP	
	Energy	f	**Energy**	f	**Energy**	f
T_1 **(I)**	2.2515 (550.67)	0.25×10^{-5}	2.2682 (546.61)	0.17×10^{-5}	1.9197 (645.86)	0.85×10^{-7}

T_1 (II)	2.2519 (550.57)	0.16×10^{-4}	2.2689 (546.45)	0.85×10^{-4}	1.9197 (645.85)	0.72×10^{-7}
T_1 (III)	2.2533 (550.22)	0.15×10^{-3}	2.2698 (546.24)	0.75×10^{-4}	1.9204 (645.62)	0.11×10^{-4}

Figure S8 | a. Frontier molecular orbital plots for the Pt complexes computed for the S_0 optimized geometries. The solid surface denotes the HOMO while the LUMO is indicated by the meshed surface in each case. **b.** Spin density plots computed using the T_1 optimized geometries. **c.** The two different dimer configurations of PtD complexes derived from the single crystal packing data (left) and an illustration of the molecular clusters used for the ONIOM calculations (right) with the central dimer (QM region) shown as a space-filling structure while the surrounding molecular shell (MM region) is indicated by a wire-frame structure. **d.** Table showing the calculated energies in eV (nm) and oscillator strengths (*f*) of the 3 T_1 sublevels for the complexes.

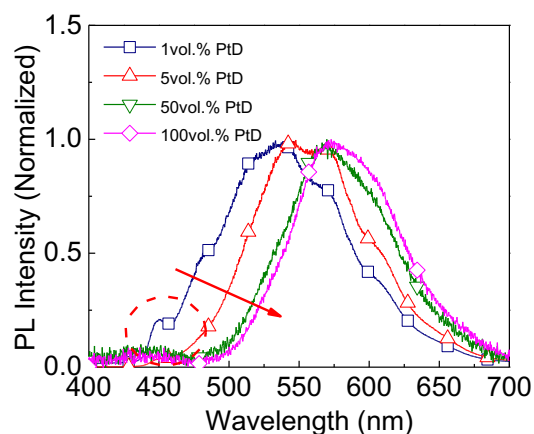## Spectrum of CzSi:PtD vs. doping concentration

Figure S9 | Spectrum vs. doping concentration of PtD in CzSi. Bathochromic shifts follow the concentration of PtD due to the lattice strain relaxation. This results in a varied d-spacing between molecules as shown in Table 1. The DFT calculations of CzSi and PtD show similar permanent dipole moments (μ = 2.6 vs. 2.2 Debye). Thus, the Bathochromic shift as a function of PtD doping concentration is mainly due to the strain relaxation of the PtD crystal domains. The monomer peak (green circle) appears at 450 nm wavelength by diluting PtD.

Time Resolved Photoluminescence of CzSi:PtD by varied doping concentration
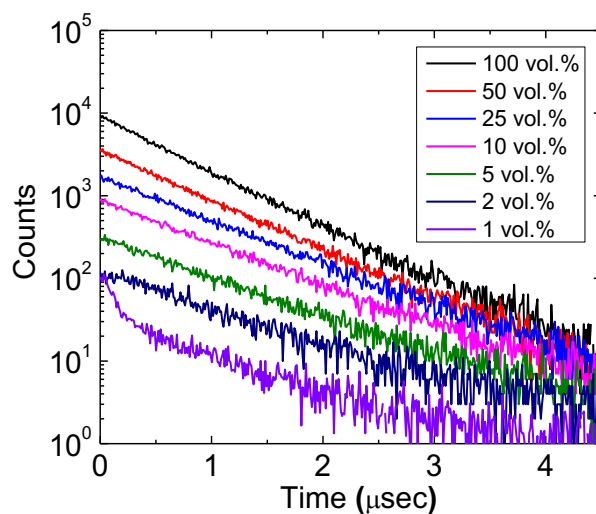
Lifetime (μsec)	100 vol.%	50 vol.%	25 vol.%	10 vol.%	5 vol.%	2 vol.%	1 vol.%
Dimer	0.64 ± 0.01	0.72 ± 0.01	0.82 ± 0.01	0.84 ± 0.01	0.90 ± 0.01	0.89 ± 0.03	0.88 ± 0.12
Monomer	-	-	-	-	-	-	0.10 ± 0.01

Figure S10 | Time resolved photoluminescence of CzSi:PtD by varied doping concentration. The non-radiative rate of the excitons within the film was assumed to be neglibible.

Synthesis of Pt complexes

The synthesis and photophysical characterization of (dbx)Pt(dpm) and (ppy)Pt(dpm) have been reported previously[4–6]. The (dbx)Pt(ppy) has similar photophysical property as their dpm analogue (dbx)Pt(dpm). The synthesis of complex (dbx)Pt(dmes) was done in a similar fashion as all the other cyclometalated Pt complexes and the (dbx)Pt system is illustrated as the archetypal in Fig. S11.
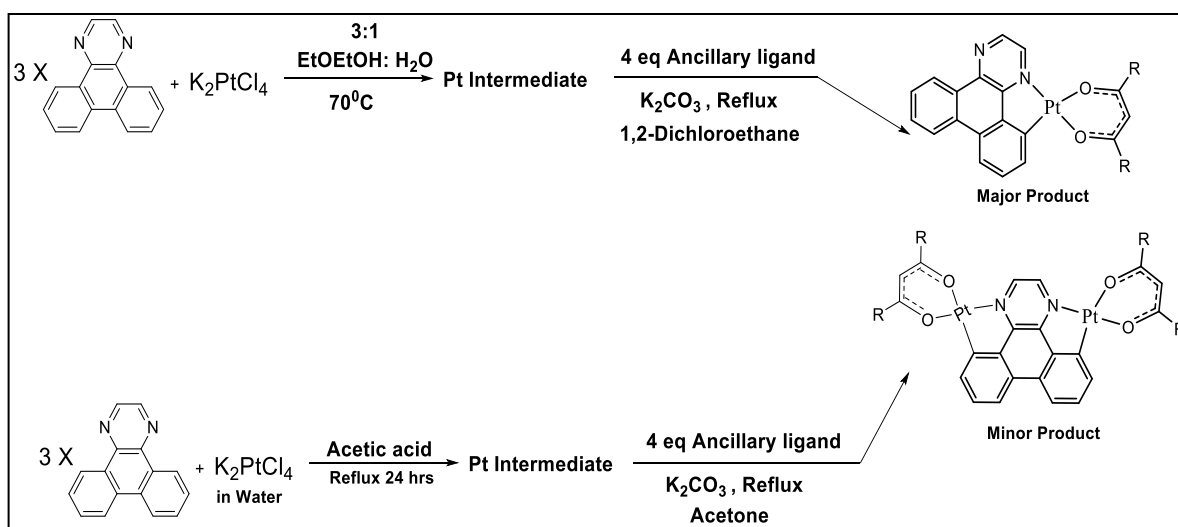

Figure S11. Two routes for the synthesis of Pt cyclometalated complexes. Conventional Nonoyama synthesis (top), modified synthesis (bottom).

The synthesis of dbx ligand was done according to the literature reported procedure[5]. The ancillary ligand 1,3-dimesityl-propane-1,3-dione (dmes) was synthesized via a stable intermediate (its aluminum complex) from malonyl dichloride and mesitylene by Friedel-Craft reaction using anhydrous aluminum chloride as the catalyst. The resultant aluminum intermediate complex was isolated, which then decomposed upon reflux in concentrate hydrochloric acid to give the dmes ligand as reported[7]. The cyclometalating ligand (ppy) for (dpm)Pt(ppy) is commercially available.

(dbx)Pt(dmes)- A 3-neck flask was charged with dbx (0.18 mL, 1.3 mmol), potassium tetrachloroplatinate(II) (230 mg, 0.55 mmol) and 60 mL of 3:1 mixture of 2-ethoxyethanol:water. The mixture was degassed and heated to 70 °C for 16 hrs. The reaction was cooled to ambient temperature and the brown solid was precipitated into water and isolated by vacuum filtration. This solid was then placed in a new 3-neck flask charged with potassium carbonate (180 mg, 1.3 mmol), ancillary ligand 1,3-dimesityl-propane-1,3-dione and charged with 30 mL of degassed 1,2-dichloroethane. The condenser was attached and the mixture was heated to 75 °C for 16 hrs. The reaction was then cooled to ambient temperature and the solvent was removed under vacuum. The resultant solid was subjected to column chromatography on silica gel 1:1 CH_2Cl_2: hexanes gradient to give a orange solid 145 mg (51%) ^{1}H NMR (500 MHz, $CDCl_3$, δ) 9.12 (d, $J = 7.87$ Hz, 1H), 9.07 (d, $J = 2.63$ Hz, 1H), 8.68 (d, $J = 2.63$ Hz, 1H), 8.60 (d, $J = 8.06$ Hz 1H), 8.19 (d, $J = 7.97$ Hz, 1H), 7.82 (t, $J = 7.31$ Hz, 1H), 7.74 (t, $J = 6.80$ Hz, 2H), 7.59 (t, $J = 7.57$ Hz, 1H), 6.89 (d, $J = 8.14$ Hz, 4H), 5.77 (s, 1H), 2.40 (d, $J = 6.55$ Hz, 12H), 2.32 (d, $J = 6.08$ Hz, 6H).
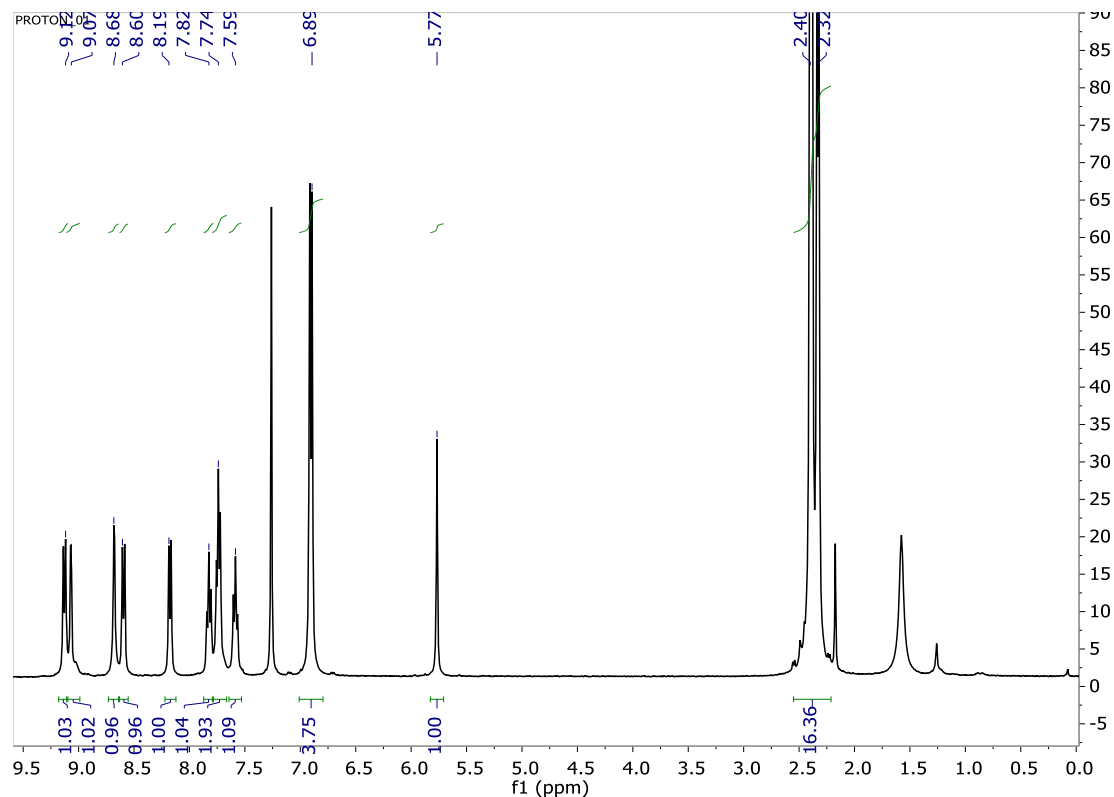
Figure S12. ^{1}H NMR spectrum of (dbx)Pt(Dmes) in CDCl$_3$.

PtD - Synthesis of [3-(trifluoromethyl))(5-(pyridyl)-pyrazolato][5-pyridyl-tetrazolato]platinum(II) (PtD) entailed the addition of 2-(5-(trifluoromethyl)-1H-pyrazol-3-yl)pyridine (ppf$_3$H, 1.2 mmol, 0.26 g)[8] and K$_2$[PtCl$_4$] (1.2 mmol, 0.50 g) to a 30-mL solution of 3.0 M HCl in water followed by heating the resulting reaction mixture to 80 °C for 12 h. The yellow precipitate, identified as Pt(ppf$_3$H)Cl$_2$, was extracted by gravity filtration, and subsequently washed with water and acetone followed by drying under vacuum. Pt(ppf$_3$H)Cl$_2$ (1.2 mmol, 0.57 g) and 2-(1H-tetrazol-5-yl)pyridine (ttzpH, 1.22 mmol, 0.18 g)[9] were added to a solution containing 15 mL of pyridine and 5 mL of deionized water then the resulting mixture was heated at 80 °C for 48 h. The solid yellow precipitate was then collected, washed with water, acetone, diethyl ether, and dried under vacuum at 100 °C. The product was purified under vacuum sublimation at (300 °C, 300 mTorr),

yielding PtD as a solid yellow powder; reaction yield: 55%. Anal. Calcd for PtD: C, 32.56; H, 1.64; F, 10.30; N, 20.25. Found: C, 32.16; H, 1.38; F, 9.70; N, 19.54.

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