Supporting Information of

Chromic Behaviors of Hexagonal Columnar Liquid Crystalline Platinum

Complexes with Catecholato, 2-Thiophenolato, and Benzenedithiolato

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Contents

Figure S1. Scan rate dependency of CVs of a) **1** (50-500 mV/sec, n-Bu₄NClO₄, N₂) b) **2** (50-500 mV/sec, n-Bu₄NPF₆, N₂), and c) **3** (50-500 mV/sec, n-Bu₄NPF₆, N₂).

Figure S2. Polarized optical microscope images of 1.

Figure S3. Polarized optical microscope images of 2.

Figure S4. Polarized optical microscope images of 3.

Figure S5. Variable temperature XRD patterns of 1 at a) 210, b) 40, c) –30, and d) –70 °C.

Figure S6. Variable temperature XRD patterns of **2** at a) 220, b) 35, c) -40, d) -55, and e) -70 °C.

Figure S7. Variable temperature XRD patterns of 3 at a) 215, b) 35, c) –50, and d) –70 °C.

Figure S8. DSC curves of a) 2 (5 K/min) and b) 3 (5 K/min).

Figure S9. Plots of CT band energy vs. [Pt(NN)(SS)] solvent parameter (a, c, and e) and $E_{\rm T}$ solvent scale (b, d, f) for **1** (a and b), **2** (c and d), and **3** (e and f) with a linear least-squares fit to the data. The fitting results are included in each figure.

Figure S10. The pictures show solvatochromism of a) 1, b) 2, and c) 3 in the solvents (from

left; acetone, dichloromethane, chloroform, THF, and benzene).











Fig. S2



Fig. S3



Fig. S4



Fig. S5









Fig. S8



Fig. S9 Plots of CT band energy vs. [Pt(NN)(SS)] solvent parameter (a, c, and e) and $E_{\rm T}$ solvent scale (b, d, f) for **1** (a and b), **2** (c and d), and **3** (e and f) with a linear least-squares fit to the data. The fitting results are included in each figure.

The experimental estimation of the dipole moments would be very informative to rationalize the observed tendency in the clearing points of 1-3. In fact, plots of the energies of the CT bands vs. solvent polarity parameters shown below gave excellent linear correlations using $E_{\rm T}$ solvent scale and the solvent parameter for the [Pt(NN)(SS)] used in the literature (Eisenberg et al., J. Am. Chem. Soc., 1996, 118, 1949.). The fitted curves in the figures demonstrate excellent linear correlations, where the lower CT maxima were used for Other solvent scales such as Kamlet's π^* scale gave considerably weaker benzene. correlations. The obtained slopes, which reflects a magnitude of a dipole moment of each complex, clearly show the similarity of Cat (1, slope = $304 (E_T)$ and 4039 ([Pt(NN)(SS)]) and Bdt (3, slope = 306 (E_T) and 4068 ([Pt(NN)(SS)]) complexes, while those of 2 are found to be 244 ($E_{\rm T}$) and 4039 ([Pt(NN)(SS)]), much smaller than those of 1 and 3. These trends are identical with that for the clearing points, $2 < 1 \sim 3$, at which the Col_{ho} phases transform to isotropic liquids. In general, a phase transition temperature (T_c) of a condensed phase is an index of thermodynamic stability of the phase that exits at lower temperature than the T_c . Therefore, the lowest clearing point of 2 among 1-3 suggests weaker intermolecular interactions within the column of the Col_{ho} phase of 2 compared with those in 1 and 3.



Fig. S10