## 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) $\mathbf{1}\left(50-500 \mathrm{mV} / \mathrm{sec}, n-\mathrm{Bu}_{4} \mathrm{NClO}_{4}, \mathrm{~N}_{2}\right)$ b) $\mathbf{2}$ ( $50-500 \mathrm{mV} / \mathrm{sec}, n-\mathrm{Bu}_{4} \mathrm{NPF}_{6}, \mathrm{~N}_{2}$ ), and c) $\mathbf{3}\left(50-500 \mathrm{mV} / \mathrm{sec}, n-\mathrm{Bu}_{4} \mathrm{NPF}_{6}, \mathrm{~N}_{2}\right)$.

Figure S2. Polarized optical microscope images of $\mathbf{1}$.
Figure S3. Polarized optical microscope images of $\mathbf{2}$.
Figure S4. Polarized optical microscope images of $\mathbf{3}$.
Figure S5. Variable temperature XRD patterns of 1 at a) 210, b) 40 , c) -30 , and d) $-70^{\circ} \mathrm{C}$.
Figure S6. Variable temperature XRD patterns of 2 at a) 220, b) 35, c) -40 , d) - 55, and e) $-70^{\circ} \mathrm{C}$.

Figure S7. Variable temperature XRD patterns of $\mathbf{3}$ at a) 215 , b) 35 , c) -50 , and d) $-70^{\circ} \mathrm{C}$.
Figure S8. DSC curves of a) $\mathbf{2}(5 \mathrm{~K} / \mathrm{min})$ and b) $\mathbf{3}(5 \mathrm{~K} / \mathrm{min})$.
Figure S9. Plots of CT band energy vs. $[\mathrm{Pt}(\mathrm{NN})(\mathrm{SS})]$ solvent parameter (a, c, and e) and $E_{\mathrm{T}}$ solvent scale (b, d, f) for $\mathbf{1}$ (a and b), 2 (c and d), and $\mathbf{3}$ (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) $\mathbf{3}$ in the solvents (from
left; acetone, dichloromethane, chloroform, THF, and benzene).
a)

b)


Fig. S1
c)



Fig. S2


Fig. S3
a)

c)

e)

$$
\mathrm{G} \text { at }-70^{\circ} \mathrm{C}
$$

b)

d)


Fig. S4


Fig. S5
a)

b)
c)


Fig. S6
d)

e)


a)

b)

c)


Fig. S7
d)

d)

b)


Fig. S8


Fig. S9 Plots of CT band energy vs. $[\mathrm{Pt}(\mathrm{NN})(\mathrm{SS})]$ solvent parameter (a, c, and e) and $E_{\mathrm{T}}$ solvent scale (b, d, f) for $\mathbf{1}$ (a and b), $\mathbf{2}$ (c and d), and $\mathbf{3}$ (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 $E_{\mathrm{T}}$ solvent scale and the solvent parameter for the $[\mathrm{Pt}(\mathrm{NN})(\mathrm{SS})]$ 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 benzene. Other solvent scales such as Kamlet's $\pi^{*}$ scale gave considerably weaker correlations. The obtained slopes, which reflects a magnitude of a dipole moment of each complex, clearly show the similarity of Cat $\left(\mathbf{1}\right.$, slope $=304\left(E_{\mathrm{T}}\right)$ and $4039([\mathrm{Pt}(\mathrm{NN})(\mathrm{SS})])$ and Bdt (3, slope $=306\left(E_{\mathrm{T}}\right)$ and $4068([\operatorname{Pt}(\mathrm{NN})(\mathrm{SS})])$ complexes, while those of $\mathbf{2}$ are found to be $244\left(E_{\mathrm{T}}\right)$ and $4039([\mathrm{Pt}(\mathrm{NN})(\mathrm{SS})])$, much smaller than those of $\mathbf{1}$ and 3. These trends are identical with that for the clearing points, $\mathbf{2}<\mathbf{1 \sim 3}$, at which the $\mathrm{Col}_{\text {ho }}$ phases transform to isotropic liquids. In general, a phase transition temperature ( $T_{\mathrm{c}}$ ) of a condensed phase is an index of thermodynamic stability of the phase that exits at lower temperature than the $T_{\mathrm{c}}$. Therefore, the lowest clearing point of 2 among 1-3 suggests weaker intermolecular interactions within the column of the $\mathrm{Col}_{\text {ho }}$ phase of $\mathbf{2}$ compared with those in $\mathbf{1}$ and $\mathbf{3}$.
a)

b)

c)


Fig. S10

