

Columnar Liquid Crystallinity and Mechanochromism in Cationic Platinum(II) Complexes

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S Supporting Information

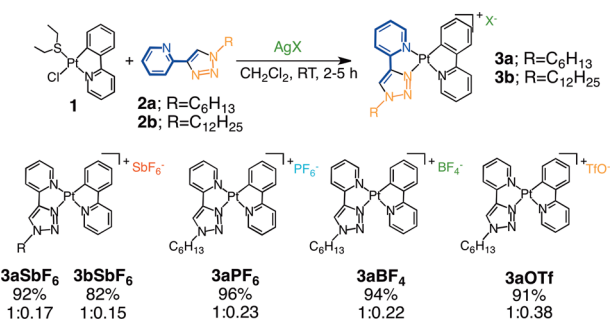
ABSTRACT: Cationic square planar Pt(II) complexes are reported with high degrees of intermolecular association. These complexes display thermotropic columnar liquid crystalline behavior in spite of having only a single side chain. Crystals undergo mechanochromic transformations that can be reversed with solvent.

The directed assembly of molecules offers opportunities for the design of advanced materials using an expanding diversity of molecular shapes, intermolecular potentials, and dispersive forces.¹ A widely successful application of molecular assembly has been the use of liquid crystalline molecules in the displays of common electronics (i.e., LCDs).² Although the success of liquid crystal technology in displays is unquestioned, its use in the creation of optimized high-performance electronic materials is largely unrealized.³ Natural candidate structures for these applications are planar organometallic complexes that can assemble into columnar phases generating extended intermetallic interactions.⁴ As part of our ongoing interest in developing electronically active metal organic materials,⁵ we designed novel cationic square planar platinum complexes and explored their intermolecular associations. We report herein that these compounds display environmentally sensitive Pt···Pt intermolecular interactions, which facilitate the formation of thermotropic columnar liquid crystalline phases as well as unique mechanochromic behavior in the crystal phase.

A common design principle for columnar thermotropic liquid crystals is to position side chains at locations such that in the melt these chains fill the space surrounding the columns.⁶ Implementation of this principle often requires multiple long alkyl chains attached to a single core;⁷ however, in materials having complementary shapes, dynamic correlations between nearest-neighbor mesogens can also facilitate liquid crystallinity.^{8,9} Here, we have found that Pt···Pt interactions can act as the dominant attractive force in the formation of columnar hexagonal liquid crystals, resulting in discotic liquid crystalline compounds with only one short ($-C_6H_{13}$) alkyl chain. These Pt(II) complexes are one of only a few mesogens with a single side chain to exhibit robust liquid crystal formation.¹⁰ Furthermore, reports of thermotropic columnar liquid crystals with less than three side chains are rare.⁷

The series of cationic platinum complexes **3** were prepared from Pt(II) precursor Pt(2-phenyl-pyridine)Cl(Et₂S)¹¹ **1** and pyridyl triazole ligand **2** (Scheme 1). Ligand **2** is readily prepared from an azide and alkyne and allowed for modulation of the single side chain. The synthesis of the cationic Pt(II)

Scheme 1. Synthesis and Stereoisomer Ratios (*trans:cis*)



complexes was facilitated by silver salts, where the Ag(I) assisted in ligand exchange and also allowed for isolation of series **3** with varying counteranions. We hypothesized that the degree of coordination and hydrogen-bonding properties of these ions would affect the intermolecular Pt···Pt interactions. To further characterize the behavior of the Pt(II) core, we performed 2D NMR analysis on **3aSbF₆**. We found that all **3a** compounds exist as a mixture of stereoisomers, and ROESY analysis (see Figure S1 as an example) revealed that the dominant isomers are those shown in Scheme 1 with the C–Pt bond *trans* to the triazole nitrogen. The stereoisomer composition is dynamic and can vary with solvent (Figures S2–5). At 25 °C, the stereoisomer ratios (*trans:cis*) for **3aSbF₆** were found to be 1:0.17, 1:0.42, and 1:0.91 when dissolved in CH₂Cl₂, acetone, and DMSO, respectively.

We were able to grow X-ray quality crystals of **3aBF₄**, and the resulting structure is shown in Figure 1A. **3aBF₄**'s space group is *P2₁/c*. The crystal structure shows that the cationic Pt(II) complexes favor an alternating dimer packing (Figure 1B), with a Pt···Pt distance of 3.64 Å. The BF₄[−] counteranions reside between columns of Pt(II) cations and exhibit hydrogen-bonding interactions with four different aryl protons from adjacent molecules (Figures S22–24, Tables S1–3). Notably, the square planar structure is distorted with a 25° torsion angle between the different ligand planes, suggesting that these compounds have enhanced conformational flexibility thereby enhancing the dispersive forces compared to other more planar organometallic complexes,¹² an important aspect for metallomesogens.

Differential scanning calorimetry (DSC) revealed traces suggesting liquid crystalline behavior in several of the compounds. Specifically, series **3a** displayed low-enthalpy

Received: November 9, 2013

Published: February 17, 2014

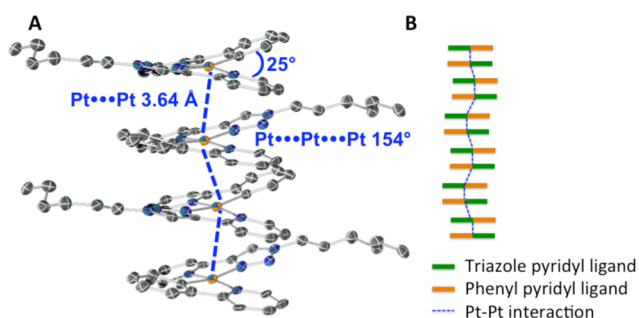


Figure 1. Single crystal X-ray structure of **3aBF₄**. (A) Crystal structure packing. (B) Representation of stacking orientation by the green and orange colors representing a set of ligands on the molecule and dotted lines representing Pt...Pt interactions.

clearing transitions and modest supercooling.¹³ Through DSC analysis, we were able to gain insight on the role of the counteranion (Table 1). The clearing temperatures decrease in

Table 1. Phase Transitions of Complexes **3**^{a,b}

Compound	Phase	T(°C)(ΔH(kJ/mol))	Phase
3aSbF₆	K	173 (8.0)	Col _h
		110 (3.3)	
3aPF₆	Col _h (glass)	115 (-6.6)	Col _h
		c	
3aBF₄	K	164 (13.4)	Col _h
		132 (3.7)	
3aOTf	Col _h (glass)	c	Col _h
		c	
3aSbF₆	K	220 (7.5)	I
		182 (5.7)	

^aPhase nomenclature: K = crystal, Col_h = columnar hexagonal mesophase, and I = isotropic liquid. ^bScan rate for all runs was 10 °C/min, and phase transitions represent peak maxima and second/third runs. ^cWe do not observe a clear transition by DSC for a glass transition to a solid form.

the order of **3aSbF₆** (219 °C) > **3aPF₆** (203 °C) > **3aBF₄** (164 °C) = **3aOTf** (164 °C). This trend corresponds well with the solubilities of the compounds with **3aOTf** being qualitatively the most soluble, suggesting that the strength of the intermolecular interactions is responsible for this trend as the counteranion is bulkier and allows for weaker intermolecular interactions.¹⁴ Aside from the clearing transition temperatures, we observed significant differences in the DSC traces of the series **3a** with each counteranion. Compound **3aSbF₆** exhibits the most liquid crystalline behavior containing well-defined transitions. In other cases, DSC traces displayed similar clearing temperatures and small enthalpy transitions with cooling suggesting liquid crystallinity. In all cases, our characterization of phases as liquid crystalline is based on a combined analysis of DSC, Polarized Optical Microscopy (POM), and X-ray Diffraction (XRD) data.

Using the DSC isotropic temperatures as a guide, we observed that the series **3a** exhibited birefringence and surface textures characteristic of liquid crystals via polarized optical microscopy. We found that all compounds (**3a**) displayed temperature-dependent surface anisotropy and classic textures of hexagonal columnar phases (Col_h) (Figure 2). These

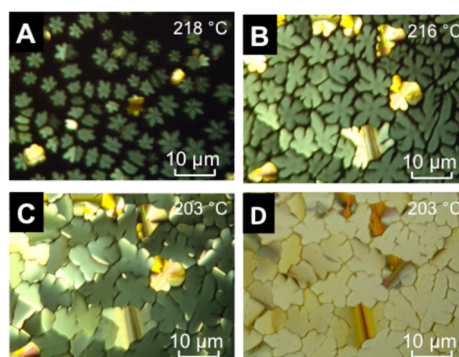


Figure 2. Polarized optical microscopy images of the Col_h phase of **3aSbF₆**. (A–C) 90° polarized and (D) nonpolarized generated by cooling from the isotropic phase (2 °C/min) between glass substrates.

textures include six-fold symmetry of the domains and rectilinear defects. As with the DSC traces, the **3aSbF₆** complex displayed the most robust liquid crystalline behavior.

In agreement with the microscopy data above, variable-temperature X-ray diffractograms show patterns characteristic of a Col_h phase (Figure 3). Most notably, the dominant low-angle features have a 1:1/√3:1/2 ratio in their *d*-spacing.¹⁵ The peak at 25.0° corresponds to diffuse scattering centered at 3.6 Å, which is consistent with the intermolecular spacing between neighboring platinum complexes within each column. This correlates well with the Pt...Pt distance in the crystal structure of 3.64 Å. We also see other diffuse wide-angle scattering that is likely from the loose ordering of the aryl ligands along the column's axis. The weak, broad nature of this peak is consistent with the presence of only a single alkyl chain. Additionally, the value *a* that is geometrically derived from the packing (Figure S44) can approximate the intercolumnar distance (13.3 Å), which is in agreement with the single crystal structure (13.6 Å). X-ray diffraction studies on all four complexes show columnar spacings in the mesophase that are largely unaffected by the counteranions indicating that all compounds (**3a**) are liquid crystalline.

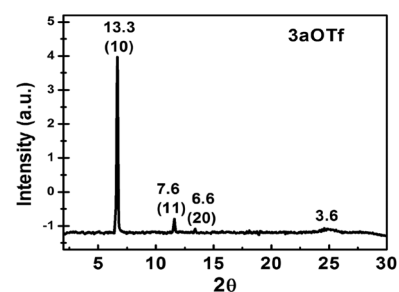


Figure 3. X-ray diffractogram of **3aOTf** at 170 °C. The distances (in Å) are above the peaks and *hk* plane designations are in parentheses.

Given that robust liquid crystalline behavior was observed with a short $-C_6H_{13}$ chain, we were interested to see if a longer chain would enhance the liquid crystallinity. Complex **3bSbF₆** with a $-C_{12}H_{25}$ alkyl chain was prepared in a manner analogous to **3aSbF₆** (Scheme 1). Upon analysis of the DSC, polarized optical microscopy, and X-ray diffraction, we found that the $-C_{12}H_{25}$ chain drastically decreased the compound's liquid crystallinity, which is rare but not unprecedented.¹⁶ Further effects of the contribution of the ligand and alkyl side chains on liquid crystallinity remain to be explored.

This series **3a** exhibits solid-state phosphorescence¹⁷ as well as distinct color and luminescence changes upon heating or processing (Figure S48–49). We predicted that, as with the liquid crystalline behavior, these unique photophysical properties are due to the permutable Pt···Pt intermolecular interactions.¹⁸ Supporting this hypothesis, the **3aSbF₆** complex displayed both the most robust liquid crystallinity and the most drastic optical changes. Figure 4 shows the mechanochromic

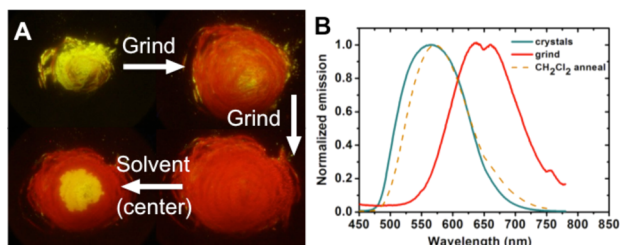


Figure 4. Reversible mechanochromism of **3aSbF₆**. (A) Yellow crystals of **3aSbF₆** (upper left) were ground; the yellow emission was restored with a drop of CH₂Cl₂ (lower left). All images were obtained under UV radiation (365 nm). (B) Solid-state emission spectra of yellow crystals (green), ground solid (red), and solid annealed after grinding (orange) ($\lambda_{\text{ex}} = 400$ nm).

response of **3aSbF₆**. The yellow form (polymorph A) represents **3aSbF₆** recrystallized from CH₂Cl₂/hexanes, which can be readily converted into an orange-red form (polymorph B) by grinding with a pestle. The yellow form can be recovered by the addition of CH₂Cl₂ or heat (Figure 4A, Figure S50, Video S1). **3aSbF₆** in its ground red polymorph B can be transformed to yellow polymorph A upon initial heating and then back to polymorph B after complete melting, which is retained with cooling. Additionally, direct formation of the red polymorph B can be achieved by rapid precipitation from acetone.

More quantitative photophysical characterization revealed that **3aSbF₆** is more emissive in the solid than in solution state. The yellow crystals of polymorph A exhibited broad and featureless emission ($\lambda_{\text{em}} = 565$ nm) in the range of 480–700 nm (Figure 4B). This turn-on of luminescence in the solid state is introduced by the self-assembly of **3aSbF₆** and is attributed to the excited triplet metal–metal-to-ligand charge transfer (³MMLCT) states. The solid-state quantum yield of **3aSbF₆** reached up to 86%, which is on par with the best solid-state Pt(II) emitters reported.¹⁹ The red-colored polymorph B displayed bright red emission from 550–800 nm. We propose this emission is a combination of the *trans* and *cis* isomers, which exhibit different emission maxima at 635 and 660 nm due to aggregation in the solid state (see features in the red “grind” trace in Figure 4B). The reversibility is confirmed by the spectral overlap of the initial crystals and CH₂Cl₂-annealed sample (Figure 4B green and orange dashed traces). **3aSbF₆** is not visibly emissive in its liquid crystalline state, presumably as a result of thermally activated nonradiative pathways.

To further probe the Pt···Pt intermolecular interactions of **3aSbF₆**, we doped this complex into different polymer matrixes (6–8% w/w relative to the polymer). Films of polystyrene (PS), polyethylene oxide (PEO), poly(methyl methacrylate) (PMMA), and poly(4-vinylpyridine) (P4VP) were prepared by spin-coating a solution of the polymer and **3aSbF₆**. The photoluminescence spectra and images of the resulting films are depicted in Figure 5. **3aSbF₆** exhibits red emission in both PS

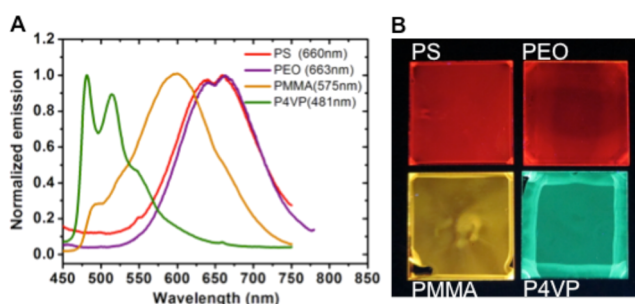


Figure 5. Polymer films doped with **3aSbF₆**. (A) Solid-state emission spectra of **3aSbF₆** in polymer matrixes: PS (red), PEO (magenta), PMMA (orange), and P4VP (green). (B) Film color contrasts observed under UV radiation (365 nm).

and PEO, which are inert hosts. The composites with PMMA display **3aSbF₆**-dependent responses, varying from yellow to orange as the concentration of the Pt complex increases. The PMMA/**3aSbF₆** films also contain a small 490 nm emission shoulder, which matches the monomer emission of **3aSbF₆** observed in fluid solutions, suggesting incomplete aggregation. In contrast with the other polymer matrixes, the P4VP films exhibit primarily green emission ($\lambda_{\text{em}} = 481$ nm) and well-defined vibrational splitting patterns indicating the presence of monomeric **3aSbF₆**.

The lack of aggregation in this latter composite can be attributed to the pyridyl groups of P4VP coordinating to the metal centers, thereby impeding intermolecular interactions. These results are consistent with our hypothesis that the unique properties of the series **3a** are dependent on changes in the Pt···Pt interactions, which are readily affected by the degree of aggregation.

In summary, we have found that platinum complexes with cationic cores encourage strong intermolecular associations, which promote liquid crystalline and mechanochromic behavior. Despite the absence of multiple alkyl side chains, complexes of the **3a** series formed discotic liquid crystals with columnar hexagonal packing. We attribute the liquid crystallinity to significant intermolecular Pt···Pt interactions and enhanced dispersive forces due to distortions from square planarity. In the crystal form, we identified two distinct polymorphs of **3aSbF₆**, which can be interconverted by mechanical force, melting, or solvent exposure. We expect that other cationic organometallic structures will display similarly strong intermolecular interactions and that this approach will have utility in creating other materials that are mechanically, thermally, and chemically responsive.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details of experimental procedures and additional characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Peter Mueller for his help solving the single crystal X-ray structure, Ellen Sletten for her help editing the manuscript, Phil Reusswig for his direction in using the integrating sphere setup, Baltasar Bonillo Fernandez for his help with the video, Dorte Ravnsbaek for her assistance with powder diffraction data analysis, and Lionel Moh for his help with DSC measurements. This work was supported by the National Science Foundation DMR-1005810 and the Department of Defense NDSEG Fellowship Program 2291100.

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