Liquid Crystals

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Supramolecular Polymers and Chromonic Mesophases Self-Organized from Phosphorescent Cationic Organoplatinum(II) Complexes in Water**

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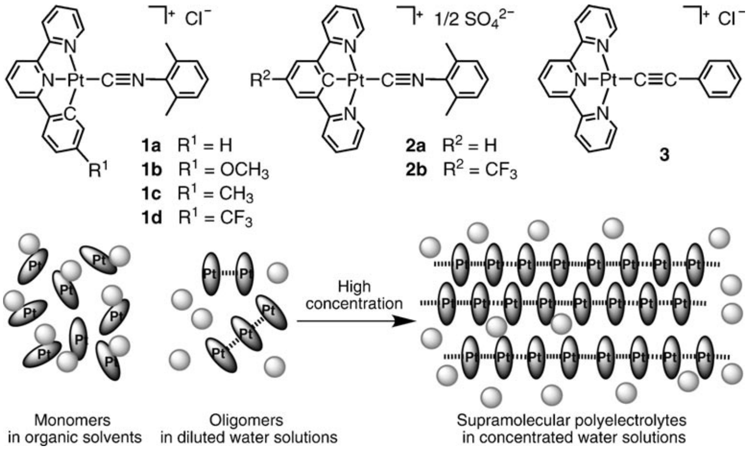
Self-assembly of π-conjugated organic or organometallic molecules through weak noncovalent interactions provides an entry into new classes of supramolecular materials with tunable structures and multiple functionalities.[1] The self-organization of phosphorescent platinum(II) complexes containing π-conjugated ligands through extended Pt^{II}···Pt^{II} or ligand–ligand interactions has recently been adopted as an efficient bottom-up approach to construct superstructures and to develop novel molecular materials on the nanoscale or sub-microscale.[2] As a representative example, Ziessel and co-workers reported a thermotropic liquid crystal and organogelator harnessing Pt^{II}···Pt^{II} and solvatophobic interactions.[2c] In this context, a pivotal challenge is to develop a solution-processible protocol to orient the Pt^{II} complexes in architectures such as aligned films and discrete one-dimensional nano- or microstructures. Recent studies have demonstrated that custom fabrication of prototype microdevices can be achieved by direct drawing of single microfibers from polymer solutions.[3] It is known that controlling the molecular organization in mesophases and polymeric materials is essential to improving their charge-transport properties and mechanical processiblity.[4] Herein we describe the preparation of supramolecular polymers with chromonic liquid crystallinity[5] by self-organization of cationic organoplatinum(II) complexes in water through extended Pt^{II}···Pt^{II} and hydrophobic interactions. Aligned films and discrete uniaxial microfibers with cofacial molecular orientations can be readily produced with these phosphorescent viscoelastic mesophases.

The organoplatinum(II) salts in the present study, namely [5''-R^1-(C^N^N)PtC≡N(C$_6$H$_3$-2,6-Me$_2$)]Cl (HC^N^N = 6-phenyl-2,2'-bipyridyl, **1a–d**), [4-R^2-(N^C^N)PtC≡N(C$_6$H$_3$-2,6-Me$_2$)]$_2$(SO$_4$) (N^CH^N = 1,5-bis(2'-pyridyl)benzene, **2a,b**),[6] and [(terpy)PtC≡CC$_6$H$_5$]Cl (terpy = terpyridyl, **3**), consist of a planar arrow-shaped cation with a chloride or sulfate anion (Scheme 1). It has been noted that the recently reported tridentate cyclometalated terpyridyl Pt^{II} complexes, which form thermotropic liquid crystals, bear peripheral long alkyl substituents.[2c,7] Although the spectroscopic properties of luminescent platinum(II) complexes containing π-conjugated oligopyridyl cyclometalated ligands in organic solvents and in the solid state and the effects of Pt^{II}···Pt^{II} and π–π stacking interactions on these properties have been well-documented,[8] the related aggregation behavior in aqueous solutions and the consequent emission properties have seldom been explored. This aspect could be an important subject of investigation, as unexpected phenomena may result from aligning hydrophobic π-conjugated cations to form a flexible, liquid-crystalline polyelectrolyte in water (a solvent having extensive polar intermolecular H-bonding interactions and a medium for biomolecular self-organization).



Scheme 1.

We chose chloride and sulfate anions because they have the largest ionic polarizability in the Hofmeister anion

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series,[9] which is crucial for both the cationic platinum(II) complexes to be dissolved and to stabilize the dispersion of the resultant polycations in water. Indeed, we experienced no problems in preparing transparent aqueous solutions of the chloride and sulfate salts of complexes **1a**–**d**, **2a**, **2b**, and **3** with concentrations up to 20 wt%. In contrast, the nitrate salts of these organoplatinum(II) complexes start to precipitate at concentrations higher than approximately 1 wt% in water, whereas the hexafluorophosphate and perchlorate salts are barely water-soluble.

Spectroscopic measurements revealed that complexes **1a**–**d** and **2a**,**b** oligomerize in water at 298 K even at a dilution of 2.0×10^{-5} mol dm^{-1} (ca. 0.0013 wt%). As depicted in Figure 1, aqueous solutions of both **1a** and **2a** show distinct absorption bands at around 500 nm and structureless red emission with peak maxima at 677 and 655 nm, respectively. In contrast, methanolic solutions of **1a** and **2a** at the same concentration show no significant absorbance beyond 400 nm; concomitantly, vibronically structured high-energy emissions with peak maxima at 525 and 480 nm, respectively, are observed. According to previous studies,[8] we assign the high-energy emission from methanolic solutions to a mixture of triplet metal-to-ligand charge-transfer and triplet intraligand charge-transfer (^{3}MLCT/^{3}ILCT) excited states and the low-energy emission from aqueous solutions to a metal-metal-to-ligand charge-transfer (^{3}MMLCT) excited state. Formation of molecular aggregates through Pt^{II}···Pt^{II} interactions is involved in the latter case. Complex **3** is not emissive in water at 298 K.

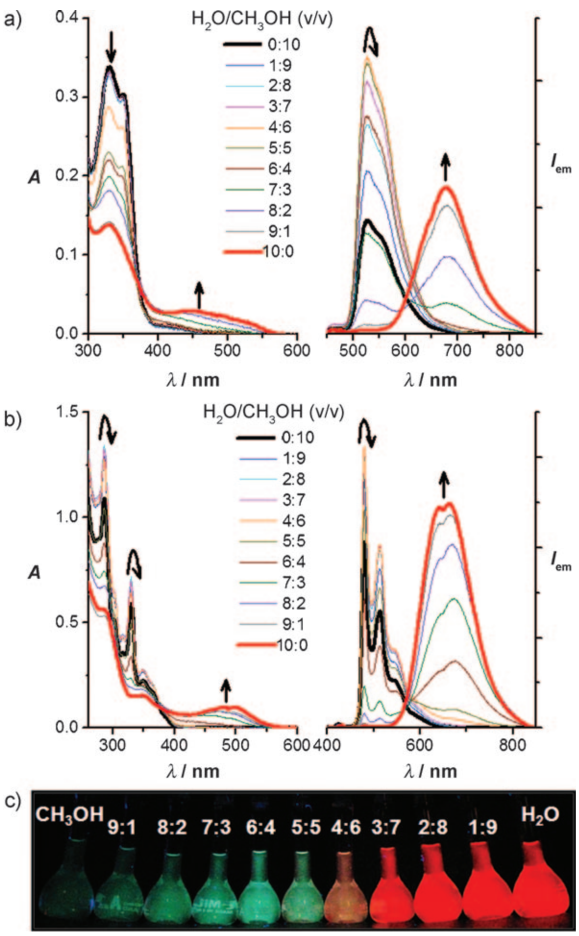

Figure 1. UV/Vis absorption and emission ($\lambda_{ex}=370$ nm) traces at 298 K for a) **1a** and b) **2a** in aerated H$_2$O/CH$_3$OH mixtures upon increasing the water percentage from 0 to 100% (concentration is maintained at 2.0×10^{-5} mol dm^{-3}). The sample series of **2a** under a 365 nm UV lamp is shown in (c).

Further increasing the concentration of Pt^{II} complex in water led to the formation of lyotropic chromonic mesophases, which have been investigated by ^{2}H NMR spectroscopy and polarized optical microscopy. As shown in Figure 2a, the ^{2}H NMR spectra of **1a** (2.0 wt% in ^{2}H$_2$O) at temperatures below 31 °C show two sharp peaks, indicating that the ^{2}H nucleus is in an anisotropic environment, that is, an aligned chromonic nematic (N) phase upon exposure to the NMR magnetic field.[10] When the sample was allowed to warm up from 31 to 35 °C, a singlet in the middle of the doublet peaks gradually emerged at the expense of the doublet intensity. At 35 °C, only the singlet signal remained. These changes are indicative of a transition from the N phase to the isotopic (I) phase. Similar N-to-I phase transition has also been detected by ^{2}H NMR spectroscopy with a 2.0 wt% solution of **2a** in ^{2}H$_2$O at 16–24 °C (Figure 2b). At 25 °C, polarized optical micrographs of aqueous solutions of **1a** (1.0 wt%), **2a** (5.0 wt%), and **3** (10 wt%) exhibit birefringent droplet texture for a I + N two-phase mixture (Figure 2c), grainy texture for a chromonic M phase (Figure 2d), and reticulated texture for a I + N two-phase mixture (Figure 2e), respectively. The critical concentrations for mesophase formation at 25 °C were estimated to be around 1.5, 3.0, and 10 wt% for **1a**–**c**, **2a**,**b**, and **3**, respectively.

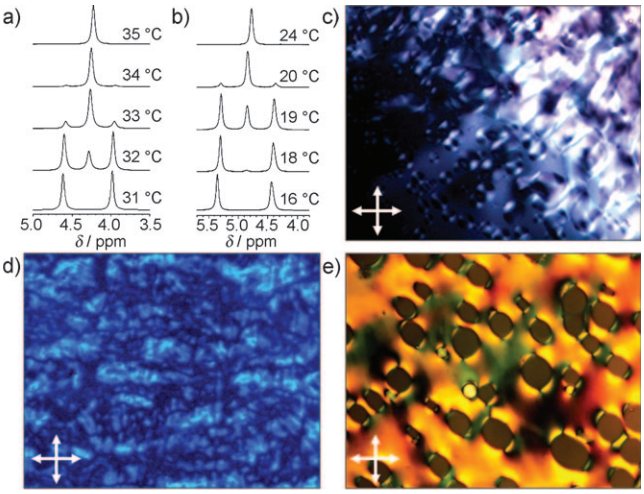

Figure 2. Variable-temperature ^{2}H NMR spectra of a ^{2}H$_2$O solution of a) **1a** (2.0 wt%) and b) **2a** (2.0 wt%). Optical micrographs of aqueous solutions of c) **1a** (1.0 wt%, during peripheral evaporation), d) **2a** (5.0 wt%), and e) **3** (10 wt%) between two crossed polarizers. The double arrows indicate the configurations of the polarizers.

Complexes **1a**–**1c** and **2a**,**b** form supramolecular polyelectrolytes in water with high solution viscosity and fiber-forming capability.[11] As shown in Figure 3a, the log–log plot of specific viscosity of aqueous solutions of **1a** versus

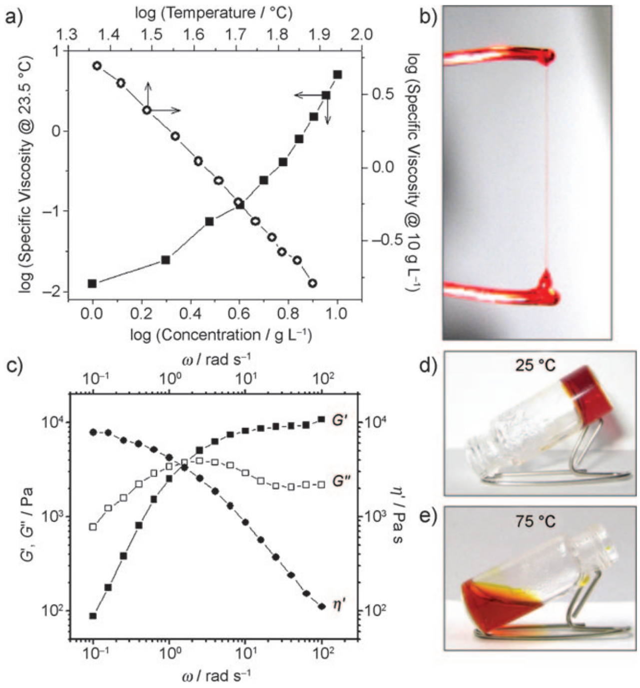

Figure 3. a) Log–log plots of concentration- and temperature-dependent viscosity of the aqueous solution of **1a**, measured in an Ubbelohde viscometer. b) A single fiber pulled out from a 10 wt% aqueous solution of **1a**. c) Variation of storage modulus (G', ■), loss modulus (G'', □), and complex viscosity (η', ●) as a function of oscillatory shear frequency (ω) of a viscoelastic fluid formed by 3.0 wt% **1d** in water at 25 °C. An aqueous sample of **1d** (3.0 wt%) at d) 25 °C and e) 75 °C.

concentration shows a critical concentration at around 3 $\mathrm{g\,L^{-1}}$, above which the viscosity increased much more significantly than below. This behavior is typical for a solution of polymeric species on transition from a dilute to a semi-dilute concentration regime in which entanglement of individual polymer chains occurs. The viscosity of this aqueous solution is temperature-dependent. A log–log plot of the specific viscosity versus temperature is linear for **1a** in water with a concentration of 10 $\mathrm{g\,L^{-1}}$ (Figure 3 a). Aqueous solutions of **1a–c** and **2a,b** with concentrations higher than 10 $\mathrm{g\,L^{-1}}$ are too viscous to flow through the Ubbelohde viscometer at 25 °C. Instead, microfibers can be easily pulled out from these solutions (Figure 3 b), indicating an exceptionally high extensional viscosity.

The substituent groups on the cyclometalated ligand affect both the liquid crystallinity and viscosity of the polymeric solutions. For example, aqueous solutions of **1c** (with 5″-CH_3) at concentrations up to 20 wt% exhibited chromonic, fiber-forming, and fluid-like properties, whereas aqueous solutions of **1d** (with 5″-CF_3) at concentrations higher than 3.0 wt% formed gel-like semi-solids (Figure 3 d) showing no birefringence texture under a polarized microscope. As shown in Figure 3 c, the viscoelastic response of a semi-solid formed by 3.0 wt% **1d** in water at 25 °C exhibited a viscous response at lower shear frequencies ($G'' > G'$); above the crossing point (higher shear frequencies, $G'' < G'$), an elastic response of a transient entangled network was observed. This rheological behavior is typical for weak gels of polyelectrolytes and elongated micelles.[12] The gel-like semi-solid of **1d** becomes fluidic at 75 °C (Figure 3 e), and this thermal phase transition is reversible. Notably, a weak hydrogel can be formed from these cationic organometallic complexes that contain neither hydrogen-bonding motifs to form one-dimensional aggregates nor long alkyl chains to segregate the nanodomains.

The microfibers directly pulled out from concentrated solutions of complexes **1a–c** and **2a,b** were semi-crystalline, optically uniaxial, and strongly luminescent. The diameters of the microfibers were in the sub-micrometer to several micrometer range, and the lengths were up to 50 cm, leading to aspect ratios up to 10^5. The diameter was uniform along a single microfiber and the surface was smooth down to nanoscale, as depicted in the scanning electron micrographs (Figure 4 a, b). A selected area electron diffraction (SAED) pattern of a single fiber (Figure 4 c) reveals a *d* spacing of 3.43 Å along the fiber long axis, indicating $\mathrm{Pt^{II}\cdots Pt^{II}}$ or ligand–ligand π–π stacking interactions along the stretching direction of the microfiber.[2b–e] No distinct diffraction spots were observed in the lateral directions, suggesting a less ordered molecular packing perpendicular to the fiber-drawing direction. Polarized micrographs of the microfibers confirmed their optical uniaxiality. Figure 4 d, e shows the respective bright and dark (under crossed polarization) field images of a manually deposited microfiber pattern of **1b**. Only the microfibers 45° to the direction of both the polarizers have the maximized anisotropy birefringence, whereas the ones parallel to either of the polarizers have the minimal birefrin-

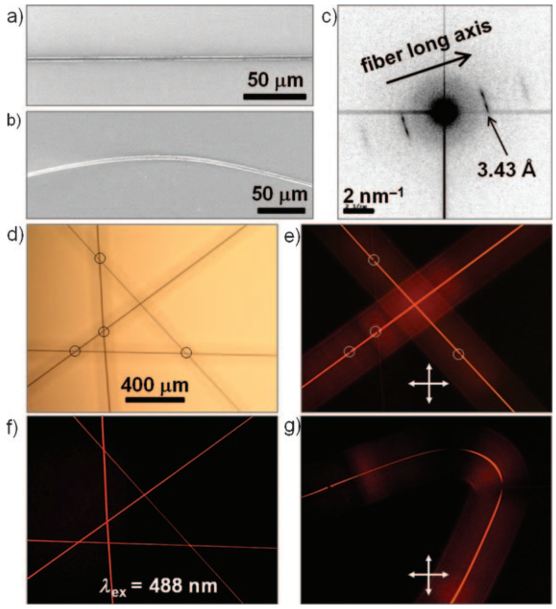

Figure 4. Scanning electron micrographs of single fibers of **1a** (a) and **2a** (b) and selected area electron diffraction pattern (c) of a fiber of **1a**. Bright field (d), polarized optical (e, g), and fluorescence (f) micrographs of patterns fabricated with microfibers of **1b**. The double arrows indicate the configurations of the polarizers, and the circles in (d) and (e) were added to guide the eyes.

gence. This result is consistent with the optical axis of the microfibers being along the direction of $Pt^{II}\cdots Pt^{II}$ or ligand–ligand π–π stacking interactions and perpendicular to the cation planes. These microfibers are remarkably flexible and can be bent into curved shapes without sacrificing their optical uniaxiality,[13] as depicted in Figure 4g for a bent fiber of **1b** with a diameter around 10 µm. Furthermore, these microfibers exhibited an intense red emission upon excitation at 488 nm under a fluorescence microscope, as depicted in Figure 4f for the manually deposited microfiber pattern of **1b**.

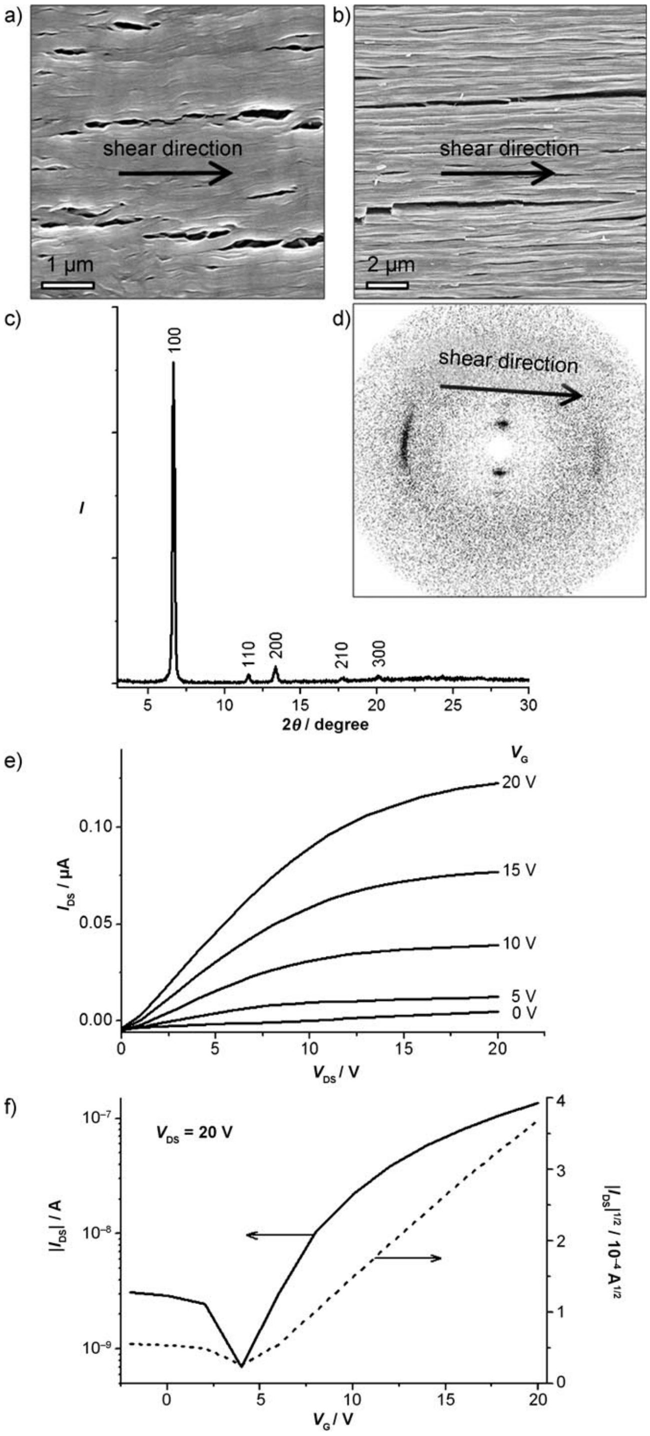

Figure 5. Scanning electron micrographs of dry films of a) **1a** and b) **2a** aligned with shear force. c) Powder X-ray diffraction pattern showing the out-of-plane scattering signals from the dry film of **1a**. d) 2D wide-angle X-ray scattering image recorded when an incident X-ray beam transmits through the shear-aligned film of **1a** mounted on a thin glass slide. e) Output (I_{DS} vs. V_{DS}) and f) transfer (I_{DS} vs. V_G) characteristics of a bottom-contact FET device with an aligned film of **1a** as semiconducting material.

Aligned films can be obtained by applying a shear force on concentrated solutions of complexes **1a–c** and **2a,b** and allowing the residual water to evaporate. Observation at high magnification by SEM revealed uniformly aligned fibrillar structures with an in-plane orientation, as depicted in Figure 5a,b for **1a** and **2a**, respectively. Powder X-ray diffraction (XRD) and 2D wide-angle X-ray scattering (WAXS) patterns measured with the shear-aligned dry film of **1a** are shown in Figure 5c,d. Five out-of-plane XRD peaks were indexed to give a primitive hexagonal 2D lattice with $a = 15.2$ Å, comparable to the longest dimension of the cation of **1a**. Furthermore, the 2D WAXS image of **1a** displayed two sharp diffraction spots at $2\theta \approx 6.5°$ (ca. 13.6 Å) in the meridional planes of the image and a pair of diffuse arc-like signals at $2\theta \approx 26°$ (ca. 3.4 Å) along the equator of the image. The former are attributed to lateral interactions of the molecules, while the latter are indicative of weak intermolecular $Pt^{II}\cdots Pt^{II}$ or ligand–ligand π–π stacking interactions that are essentially parallel to the shear direction. X-ray studies consistently revealed that the planes of the cations are roughly aligned in a face-to-face fashion perpendicular to the shear direction.

We studied the charge-transport properties of a shear-aligned film of **1a** using a bottom-contact field-effect transistor (FET) configuration with shear direction perpendicular to the source and drain electrodes. The output (Figure 5e) and transfer (Figure 5f) characteristics of this FET device revealed that the aligned film behaves as an n-type, electron-transporting semiconductor. The threshold voltage, field-effect electron mobility (μ_e), and on/off ratio of this device were calculated to be 2 V, 2×10^{-3} $cm^2V^{-1}s^{-1}$, and 10^3, respectively. Channel current was observed even at zero gate ($V_G = 0$ V) while the drain-source voltage was swept higher than 15 V. However, at elevated gate voltages, saturation in the channel current was observed, as shown in Figure 5e. A transient measurement with this FET device at $V_{DS} = V_G = 20$ V revealed charge accumulation in the initial several seconds during operation (see the Supporting Information). All these characteristics are typical for FET devices using ionic materials as semiconductors.[14]

In summary, weak $Pt^{II}\cdots Pt^{II}$ and hydrophobic interactions have been harnessed to manipulate cationic organoplatinum(II) complexes in a bottom-up then top-down approach. Chromonic properties confer these organometallic compounds long-range order, whereas their polymeric nature renders the self-organized materials viscoelastic and mechanically processible. These novel materials may be used as active components in miniature sensors, FETs, and light-emitting diodes.

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