Glass-Forming Liquid Platinum Acetylides

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There has been considerable interest in the synthesis, spectroscopy, nonlinear optics, and structure−property relationships of platinum acetylides.[1−8] Platinum acetylides are square planar molecules having the molecular formula *trans*-$Pt(PR_3)_2(C{\equiv}CR')_2$. The R′ group is typically an aromatic substituent. Common R groups include methyl, ethyl, butyl, and phenyl, which all give crystallinity. A platinum acetylide complex with interesting photophysics is *trans*-$Pt(PBu_3)_2(C{\equiv}CC_6H_4C{\equiv}CC_6H_5)_2$ (abbreviated as PE2).[9] PE2 is a crystalline compound with a melting point of 137 °C.[9] To date, all spectroscopic measurements have been performed on dilute solutions of PE2. High concentrations are necessary for the study of phenomena like triplet−triplet annihilation, exciton migration, and nonlinear optical properties. Solubility problems have prevented the study of high-concentration solutions of PE2 and related chromophores.

To increase chromophore density, we have prepared a series of PE2 derivatives that formed a liquid phase at room temperature and converted to glasses upon cooling. We designed the compounds by using the basic relation between melting point and thermodynamic parameters,[10]

$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

where ΔH_m and ΔS_m are the enthalpy and entropy of melting. We increased the entropy of melting by introducing bulky, flexible ligands and side chains. We synthesized a series of platinum acetylides having R = *n*-C_8H_{17} and variable R′ (Figure 1, Table 1). The oily products were dissolved in CH_2Cl_2 and purified on alumina. To eliminate trace amounts of solvent, the purified liquids were gently warmed under a vacuum. The measured %C and %H from combustion elemental analysis of compounds **1**−**5** and **7** were within 0.4% of the calculated values, showing they were analytically pure. To give similar agreement with compound **6**, it was necessary to assume 0.33 mol of CH_2Cl_2/mol of compound. Compound **6** had bulky *tert*-butyl groups attached to the phenyl rings. In **6**, trace amounts of the solvent molecules remained tenaciously bound despite prolonged heating under vacuum. We found the liquids could be easily pipetted into a cuvette or DSC pan, making further experimental study feasible. We made sufficient quantities of compound **3** to estimate the chromophore number density in the neat liquid. From a measured density of 1.15 g/mL, we estimated the chromophore density to be 0.86 mol of chromophore/L of **3**. The solubility limit of PE2 has been determined to be 0.08 M,[9] so use of trioctylphosphine instead of tributylphosphine as the phosphine ligand increased the chromophore number density by a factor of 10.

To investigate phase transitions of these compounds, we collected DSC thermograms. All of the compounds formed glasses upon cooling. Upon heating from the glass, some of the compounds crystallized and then melted to the liquid. An example of this behavior is shown in the thermogram of compound **2** (Figure 2). It converted to a glass at −90.5 °C. Upon heating, it converted back to a liquid. At −47.3 °C, an exotherm resulting from crystallization appeared. With continued heating, an endotherm resulting from crystal melting appeared at −5.9 °C with no other phase changes at higher temperature. The phase behavior suggested that upon cooling the high viscosity inhibited crystal growth. Upon heating, crystal growth occurred, followed by melting to the liquid phase. Similar behavior has been observed in the intensively studied glass-forming liquid triphenyl phosphite.[11] In contrast to compound **2**, the thermogram for **3** showed no evidence of crystallization from the glass upon heating (Figure 3). It converted into a glass at −82 °C and reverted back into a liquid upon heating. The glass transition, crystallization, and melting temperatures for all the compounds are summarized in Table 1. Compounds **1**, **2**, and **5** formed glasses upon cooling and crystallized followed by melting upon heating. Compounds **3**, **4**, **6**, and **7** only formed glasses and did not crystallize. There appears to be a correlation between ligand size and crystallization behavior. In all the compounds the presence of the trioctylphosphine ligands inhibited crystallization during cooling. The

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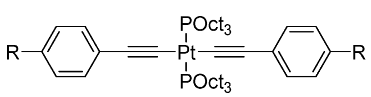

Figure 1. Chemical formula of the platinum acetylide complexes. The R groups for compounds **2**−**7** are listed in Table 1. Compound **1** is the starting material *trans*-Pt(POct$_3$)$_2$Cl$_2$.

Table 1. Thermal Transitions Observed in Differential Scanning Calorimetry Experiments

compound	no.	T_g[a]	T_{exo}[b]	T_{endo}[c]
$PtCl_2(POct_3)_2$	**1**	−70.2	−26.7	4.0
$Pt(C{\equiv}C\ C_6H_5)_2(POct_3)_2$	**2**	−90.5	−47.3	−5.9
$Pt(C{\equiv}CC_6H_4C{\equiv}C\ C_6H_5)_2(POct_3)_2$	**3**	−82.2	N/A	N/A
$Pt(C{\equiv}CC_6H_4\ C_6H_5)_2(POct_3)_2$	**4**	−81.0	N/A	N/A
$Pt(C{\equiv}CC_6H_4Br)_2(POct_3)_2$	**5**	−88.2	−33.1	7.9
$Pt(C{\equiv}CC_6H_4C{\equiv}CC_6H_4C(CH_3)_3)_2(POct_3)_2$	**6**	−78.0	N/A	N/A
$Pt(C{\equiv}CC_6H_4C{\equiv}CH)_2(POct_3)_2$	**7**	−67.0	N/A	N/A

[a] DSC measurements were performed by equilibrating a weighed sample placed in a sealed aluminum pan at 15 °C and cooling at 4 °C/min to −120 °C, followed by equilibration at −120 °C and heating at 4 °C/min to 20 °C. The glass transition temperature in °C was measured from the overshoot peak temperature of the heating portion of the thermogram. [b] No thermal transitions resulting from crystallization were observed during cooling. However, during heating, some of the compounds showed an exotherm resulting from crystallization from the supercooled liquid. The listed T_{exo} in °C is the temperature of maximum heat released during the transition. [c] For those compounds having an exotherm resulting from crystallization during heating, an endotherm resulting from melting the crystals was observed. The listed T_{endo} in °C is the temperature of maximum heat uptake during the transition.

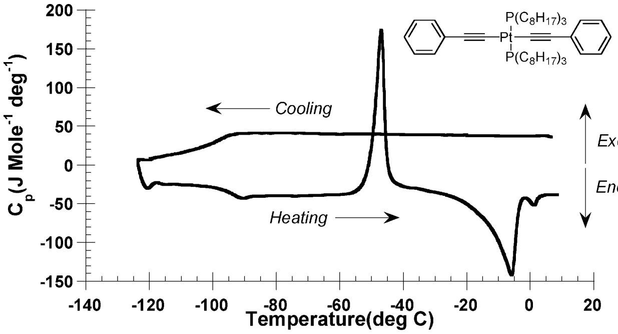

Figure 2. DSC thermogram of compound **2**.

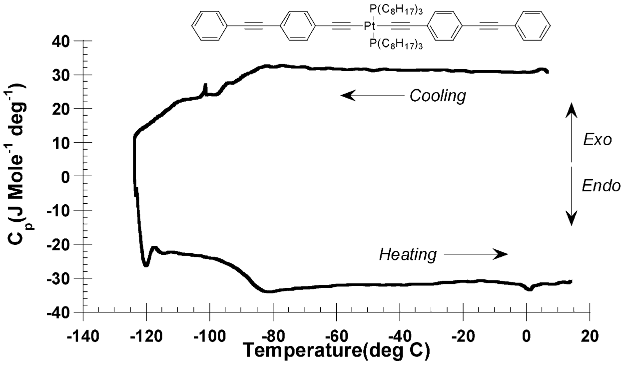

Figure 3. DSC plot for compound **3**.

presence of smaller side chains in compounds **1**, **2**, and **5** promoted crystallization during heating. The larger side chains in compounds **3**, **4**, **6**, and **7** inhibited crystallization during heating. Literature results have shown a phthalocyanine glass has a glass transition temperature of 65 °C.[12] Recently, a two-photon absorber was shown to be a glass at room temperature, converting to a fluid upon heating to 70−80 °C.[13]

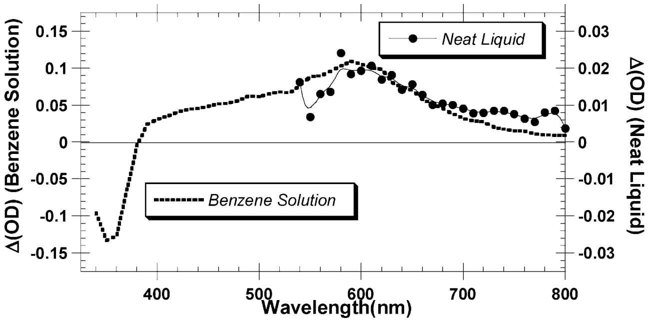

Figure 4. Triplet-state absorption spectra of compound **3**. The chromophore was diluted in benzene to an OD(355 nm) = 0.43, degassed by freeze−pump−thaw and then excited at 355 nm. The triplet-state spectrum of the solution was calculated from fitting the decay data and extrapolating to $t = 0$ s. The neat liquid **3** was air-saturated and excited at 520 nm. The data shown were collected 0.603 μs after excitation.

Glasses have been classified as either "strong" or "fragile".[14] Materials with networks of covalent bonds, like silica, show a small decrease in heat capacity (10−20%) during the glass transition and are classified as "strong" glasses. Materials where weak intermolecular forces (hydrogen bonding, van der Waals, and electrostatic) predominate show a large (~2-fold) drop in heat capacity during the glass transition and are classified as "fragile" glasses. In our compounds there was an approximately 2-fold drop in heat capacity as the compounds converted to glass, suggesting that they were "fragile" glasses.

To begin investigation of the excited-state properties of these liquids, we performed a flash photolysis experiment on compound **3**. Compound **3** is closely related to PE2. Upon optical excitation, PE2 undergoes a mixed $\pi\pi^*$-metal-to-ligand charge-transfer transition to an S_1 excited state localized on the aromatic ligand. The heavy-atom effect of the platinum promotes rapid conversion to the triplet state. The transient absorption spectrum has been shown to be that of the triplet state.[1] The ground-state absorption spectrum of dilute **3** and the triplet-state absorption spectrum were identical to the spectra of a dilute solution of PE2 (Figures S10 and S11, Supporting Information), showing substituting the ligand trioctylphosphine for tributylphosphine had no effect on **3**'s conversion to the triplet state in dilute solution. We compared the excited-state behavior of dilute **3** vs the neat liquid (Figure 4). The triplet state of degassed, dilute **3** showed single-exponential decay with a lifetime of 83 μs, in good agreement with the 42-μs lifetime of degassed, dilute PE2.[1] The triplet state of air-saturated, neat **3** showed biexponential decay with a fast lifetime of 26 ns and a slow lifetime of 1.2 μs. The fast decay may have resulted from oxygen quenching or triplet−triplet annhilation. The slow lifetime was longer than the lifetime of air-saturated, dilute PE2 (240 ns), resulting from the higher viscosity of **3**.

In this paper we have described a series of platinum acetylide complexes that are liquids at room tempera-

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ture and form glasses upon cooling. We have shown a 10-fold increase in chromophore density in compound **3** compared to that of a saturated solution of PE2. By increasing the number density, it is possible to increase the magnitude of the nonlinear coefficient $\chi^{(3)}$. Because of the high concentration, it is feasible to measure nonlinear optical properties such as two-photon absorption spectra.[15] We will present detailed investigations of the excited-state behavior of these liquids and their glasses in a future publication.

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Supporting Information Available: Complete synthesis details, purification procedures, analytical data, mass spectra, ^{1}H, ^{13}C, and ^{31}P NMR data, DSC thermograms, phosphorescence from the glass, and other spectroscopy data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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