Nanoscale Organization of a Platinum(II) Acetylide Cholesteric Liquid Crystal Molecular Glass for Photonics Applications

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The fabrication, molecular structure, and spectroscopy of a stable cholesteric liquid crystal platinum acetylide glass obtained from *trans*-Pt(PtEt₃)₂(C≡C–C₆H₅–C≡N)(C≡C–C₆H₅–COO–Cholesterol), are described and designated as PE1-CN-Chol. Polarized optical microscopy, differential scanning calorimetry, and wide-angle X-ray scattering experiments show room temperature glassy/crystalline texture with crystal formation upon heating to 165 °C. Further heating results in conversion to cholesteric phase. Cooling to room temperature leads to the formation of a cholesteric liquid crystal glass. Scanning tunneling microscopy of a PE1-CN-Chol monolayer reveals self-assembly at the solid–liquid interface with an array of two molecules arranged in pairs, oriented head-to-head through the CN groups, giving rise to a lamella arrangement. The lamella structure obtained from molecular dynamics calculations shows a clear phase separation between the conjugated platinum acetylide and the hydrophobic cholesterol moiety with the lamellae separation distance being 4.0 nm. Ultrafast transient absorption and flash photolysis spectra of the glass show intersystem crossing to the triplet state occurring within 100 ps following excitation. The triplet decay time of the film compared to aerated and deoxygenated solutions is consistent with oxygen quenching at the film surface but not within the film. The high chromophore concentration, high glass thermal stability, and long triplet lifetime in air show that these materials have potential as nonlinear absorbing materials.

1. Introduction

In photonic devices, materials with pronounced nonlinear optical (NLO) properties represent the key component and much effort is spent on the design of novel materials with large and tailored NLO responses.^[1] Molecular glasses are particularly interesting since, in comparison to crystalline solids, they offer a vast chemical space to be explored, and have numerous applications including electro-optics,^[2] nonlinear absorption (NLA),^[3] and holographic data storage.^[4]

Several strategies have emerged to tune the photophysical properties and improve the NLO behavior of molecules including varying the conjugation length, changing the conjugated bridge character, increasing chromophore planarity, increasing the π -conjugated system dimension, dendrimer, glass encapsulation, and incorporating different metals.^[5] A heavy metal center with strong spin–orbit coupling makes possible efficient intersystem crossing from the singlet to the triplet state, leading to strong excited-state absorption (ESA). In this context,

different metal centers have been used such as platinum, gold, mercury, nickel, and palladium.^[6–8] The total number of metal atoms in the system can be varied, and mixed-metal heterometallic compounds have been synthesized.^[6]

Our research focuses on the structure and photophysics of platinum(II) complexes. In a recent review,^[6] the Pt(II) acetylides were grouped into several categories according to the effects of the ligands, molecular symmetry, and with mixed-metal. It has been shown that the organic spacer ligand can be selected to improve the NLA property of materials, i.e., selection of different electron-donating and electron-withdrawing groups^[7–14] or increasing the conjugation.^[15,16] It has been shown for platinum(II) acetylides that as the conjugation length increases, the redox, optical, and electronic properties change. Smaller triplet quantum yield and the longer triplet excited-state lifetime is seen with increasing conjugation length as well as an increase of the NLA response.^[15] Good NLA performance

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Figure 1. Structure of the cholesteric platinum acetylide (PE1-CN-Chol). The 1-2-3 corresponds to the angle, mentioned in the text below, where the structure bends.

was also observed for platinum complexes with a heterocyclic nitrogen to introduce electron-withdrawing characteristics in the ligand.^[6,16] Several research groups have also studied the positioning of the heavy atom in Pt(II) acetylide complexes including terminal-end placements.^[6]

In addition to the tuning of molecular properties, the nanoscale organization must be considered in the production of successful photonic materials. In this context, highly branched molecules with globular, dendrimer-like architecture enabling a variety of applications have been synthesized and studied.^[17–20] A series of dendrimer-encapsulated Pt(II) acetylides up to the fourth generation was developed, and it was shown that they are effective NLA materials. Moreover, the NLA response was enhanced with increasing size of the dendritic substituent from the first to the fourth generation, and they all showed improved performance compared to the native complex.^[21–23] Platinum acetylides that are neat liquids at room temperature have been prepared.^[20] Silica hybrid sol–gel glass materials containing Pt(II) organic compounds as molecular hosts have been fabricated and it was demonstrated that surface-polished solids with chromophore concentrations as high as 400×10^{-3} M could be produced.^[24]

High chromophore concentration increases NLO responses in materials, although quenching mechanisms become significant.^[25] For example, platinum acetylides that are liquid at room temperature have reduced triplet state lifetimes due to triplet–triplet annihilation^[20] and triplet excimer formation.^[26] An organic molecular glass former has a polyfunctional nucleus and substituents different enough to inhibit crystallization but similar enough to inhibit phase separation.^[27–29] We decided to prepare platinum acetylide liquid crystal molecular glasses. A molecule exhibiting cholesteric liquid crystal behavior has a rod shape, permanent dipole, and chiral center.^[30] We previously explored the phase behavior of a series of platinum acetylides, *trans*-Pt(PR₃)₂(C≡C–C₆H₅–X)(C≡C–C₆H₅–COO–Cholesterol): X=H, R=CH₃, C₂H₅, C₄H₉, and C₈H₁₇. Compound R=CH₃, X=CN is crystalline and decomposes upon heating. Compounds with R=C₄H₉ or C₈H₁₇ show no liquid crystal or glassy properties. When R=C₂H₅, liquid crystal behavior is observed as X was varied. The triethyl phosphine derivatives are designated as “PE1-X-Chol,” where one phenyl acetylene ligand has a chiral *p*-substituted cholesterol ester and the other phenyl acetylene ligand has a *p*-substituted polar X unit, X=H, CN, F, and OCH₃.^[31,32] We performed polarized optical microscopy studies and found that compound X=H melts and crystallizes upon cooling, while compounds X=F and OCH₃ exhibited a

cholesteric phase above the melting temperature, but crystallized upon cooling. Compound X=CN converted to a liquid crystalline phase upon heating and retained the liquid crystal phase upon cooling to a glass. In this paper, we give a detailed study of PE1-CN-Chol (**Figure 1**). It represents the ultimate concentration limit for enhancement of optical responses. We achieve microscale organization of the chromophore by attaching it to a cholesterol unit. It is noted that cholesteryl side chains have been found to contribute positively also to optical response properties as it was shown to enhance the NLA properties of C₆₀.^[33] Also Castruita et al. have synthesized benzoate-ethynylene oligomers with a cholesterol moiety and proposed their supramolecular assembly in bilayers.^[34] Here, we describe the liquid crystalline behavior and spectroscopic properties of a cholesteric liquid crystal platinum acetylide PE1-CN-Chol. We also provide characterization and interpretation of the self-assembly studied by scanning tunneling microscopy (STM) imaging and molecular dynamics (MD) simulations.

2. Results and Discussion

2.1. Material Preparation and Characterization

2.1.1. DSC, POM, TGA, and X-Ray Analysis

The first heating and cooling cycle obtained by differential scanning calorimetry (DSC) of PE1-CN-Chol is given in **Figure 2**.^[35] On heating, a broad endothermic transition between 137 and 210 °C is observed, with one main peak at 180 °C and a shoulder at 193 °C. The high enthalpy (30 J g^{−1}) suggests that this transition could correspond to the melting of a highly crystalline material, however, according to the X-ray analyses (**Figure 3a**), and corroborated by polarizing optical microscopy (POM) analysis (**Figure 2f**), this transition is consistent with a fusion of crystals coexisting with a cholesteric phase. An isotropic phase forms in the temperature range 200–210 °C (**Figure S1h,i**, Supporting Information). In contrast, on cooling, no exothermic transition was observed. The isotropic phase remains stable up to 230 °C without any sign of crystallization, (**Figure 2a–k** and **Figure S1a–i, j–o**, Supporting Information). The X-ray scattering pattern (**Figure 3a**), as previously mentioned, confirms what was observed by POM, i.e., before heating a crystalline phase coexists with the expected cholesteric phase, seen as an halo from $2\theta = 7$ to 20° , which is maintained from room temperature, up to 170 °C. However, the cholesteric phase could be

Figure 2. a) Thermogram of the first heating and cooling scan at $5\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen of PEI-CN-Chol. The arrows and letters indicate the temperature at which the polarizing optical microscopy (POM) images were taken. Complete series of images from a to o can be found in the Supporting Information.

better identified at $180\text{--}190\text{ }^{\circ}\text{C}$, where a broad and weak peak centered at $2\theta = 2.65^{\circ}$; $d = 3.33\text{ nm}$ is observed. This is comparable to STM measurements of the platinum acetylide dimer unit length (3.70 nm) formed by CN–CN interactions (Table 1). In powder, PEI-CN-Chol does not self-assemble in lamellae as it does in a self-assembled monolayer (SAM) on highly oriented pyrolytic graphite (HOPG) (vide infra).

Observations on heating from a glassy state show that PEI-CN-Chol exhibits a glassy cholesteric phase even at room temperature (Figure S1a, Supporting Information). When the temperature increases up to $130\text{ }^{\circ}\text{C}$, a polycrystalline structure

appears (Figure S1b, Supporting Information). The polycrystalline islands and glassy cholesteric phase co-exist in the temperature range of $130\text{ }^{\circ}\text{C}$ – $185\text{ }^{\circ}\text{C}$ (Figure S1c–f, Supporting Information). It is difficult to determine the exact temperature diapason at which the glassy cholesteric phase becomes being a pure cholesteric phase. Snapshots (Figure S1e–g, Supporting Information), indicate that at $180\text{ }^{\circ}\text{C}$ – $190\text{ }^{\circ}\text{C}$, typical cholesteric textures coexist with polycrystalline and isotropic textures. Isotropic islands grow when the temperature increases (Figure S1h–i, Supporting Information), and, at reaching $T = 225\text{ }^{\circ}\text{C}$, a phase transition to an isotropic state is completely achieved.

On cooling, islands of cholesteric phase appear at $\approx 209\text{ }^{\circ}\text{C}$ (Figure S2j, Supporting Information). These cholesteric islands become bigger in size while temperature decreases (Figure S2k, Supporting Information), and a typical cholesteric texture is observed at $190\text{ }^{\circ}\text{C}$ (Figure S2l, Supporting Information).

Figure 3. a) First heating temperature dependence X-ray scattering patterns for PEI-CN-Chol powder. b) Temperature dependence X-ray scattering patterns for PEI-CN-Chol powder upon cooling from isotropic melt.

Table 1. Monolayer dimensions obtained from scanning tunneling microscopy (STM) measurements and molecular dynamics (MD) calculations.

Dimension	STM	MD
c^a	3.70 ± 0.18	3.52 ± 0.16
d^b	6.68 ± 0.25	6.66 ± 0.17
ΔL^c	1.66 ± 0.09	1.37 ± 0.15

^a) Length of platinum acetylide dimer unit parallel to cholesterol groups [nm]. Figure 4a,b depicts these dimensions; ^b) Distance between cholesterol lamellae [nm]; ^c) Distance between adjacent platinum acetylide units perpendicular to cholesterol groups [nm].

Further cooling (Figure S2m,n, Supporting Information) does not show any sign of crystallization and the cholesteric phase remains stable (as a glassy cholesteric) even at room temperature (Figure S2o, Supporting Information).

Modulated differential scanning calorimetry (MDSC) gives additional data concerning the second heat and cool cycles. On heating, crystallization and melting at 162 °C–210 °C and a glass transition at 46 °C–56 °C (Figure S3, Supporting Information) appear. On cooling, no crystallization signal (Figure S4, Supporting Information) appears. A second heating measurement (Figure S5, Supporting Information) shows a glass transition at 48 °C–53 °C but no crystallization or melting. A second cooling measurement (Figure S6, Supporting Information) also shows no melting or crystallization.

To measure thermal stability, we performed thermogravimetric analysis (TGA) on PE1-CN-Chol (Figure S7, Supporting Information). A weighed sample was heated from room temperature to 700 °C. A small (<1%) loss was observed at ≈168 °C. Upon heating to 200 °C, there was 2% loss which increased to 3% at 230 °C. There was a loss peak at 338 °C with 70% loss upon heating to 500 °C, followed by another loss peak at 600 °C with 17% loss upon heating to 700 °C.

We previously reported measurements of the cholesteric pitch of PE1-CN-Chol as well as PE1-F-Chol and PE1-OCH₃-Chol by the Cano-Grandjean wedge technique.^[31,32] The technique and results for PE1-CN-Chol are reproduced for reference in the Supporting Information. We measured PE1-CN-Chol's pitch of 1.6–1.7 μm by this technique (Figure S8, Supporting Information), compared to X=F (9 μm) and X=OCH₃ (3.5 μm), showing that the substituent X influences the helical pitch. The micron-scale pitch reflects the weak helical twisting power of the cholesterol unit.

2.1.2. Scanning Tunneling Microscopy (STM)

The supramolecular organization in a monolayer of PE1-CN-Chol on HOPG was studied by STM. In our study, 1,2,4-trichlorobenzene (TCB) was a good solvent to obtain the STM images. We found that the PE1-CN-Chol adsorbed easily on

the HOPG surface at the solid–liquid interface from 2.8×10^{-3} M solution. After depositing the solution on HOPG, we immediately applied a pulse of 2–4 V in order to induce the monolayer ordering that instantaneously appeared and looked like a “wet” surface. **Figure 4** shows a high resolution STM image of SAM of PE1-CN-Chol at the TCB–HOPG interface. In general, the molecule forms a lamellar-like pattern adopting a face-on arrangement,^[36] where the conjugated backbones are lying flat on the HOPG surface, likely due to the π – π interaction. Well-organized domains with clear boundaries are observed, where the bright stripes and dark areas cover the whole surface in the STM area. The bright parts correspond to the π -conjugated rigid backbones, which are characterized by a larger electron density, while the dark parts are related to both the cholesteryl and the triethylphosphines because of their lower electron density. The presence and interaction of both cholesteryl and triethylphosphine groups do not permit an interlocking of adjacent molecules to form linear patterns, which may explain the large distance between two adjacent stripes. According to the image (Figure 4a) and the current profiles (Figure S9, Supporting Information), three dimensions, listed in Table 1, can be determined: c = length of platinum acetylide dimer unit parallel to cholesterol groups (nm), d = distance between cholesterol lamellae (nm), and ΔL = distance between adjacent platinum acetylide units perpendicular to cholesterol groups (nm). The length of c = 3.70 nm, Figure S4 (Supporting Information), was unambiguously assigned to the conjugated backbone due to the higher tunneling current detected by the STM tip with the π electrons of about 40 pA, while the dark ones were rather related to cholesteryls and triethylphosphines because detected currents were of ≈0 pA. In addition, the conjugated length confirms that the only possible interaction between two molecules is between the two CN groups.

To support the STM data on the PE1-CN-Chol organization on HOPG, molecular dynamics (MD) simulations were performed (Figure 4b). There is a clear separation between the cholesteryl, and platinum and conjugated/benzene units of the chromophore. It forms an organized layer with overlapping cholesterol groups. The chromophore adopts a linear conformation, which is contrary to how it behaves in solution with

Figure 4. a) Uncorrected high resolution scanning tunneling microscopy (STM) image showing the lamella-like assembly pattern of PE1-CN-Chol on the HOPG–TCB (where HOPG is highly oriented pyrolytic graphite and TCB is 1,2,4-trichlorobenzene) interface obtained at a $V_{\text{bias}} = -0.80$ V, $I_{\text{set}} = 0.16$ nA superimposed with the organization obtained by molecular dynamics (MD); b) PE1-CN-Chol self-assembly, depicting the entire supramolecular organization, with average dimensions found by MD. A comparison of dimensions found by STM versus MD is shown in Table 1.

no graphite layer (Section 2.2). From DFT geometry optimization the calculated cholesterol-to-cyano length of PE1-CN-Chol is determined to be 3.76 nm. The measured distance between cholesterol lamellae, $d = 6.68$ nm, supports self-assembly into a head-to-head pair via dipole–dipole interactions between CN groups as previously observed for cholesterol on Au,^[37,38] and cholesterol esters on HOPG.^[39–41] The calculated dimensions c , d , and ΔL are in good agreement with STM results (Table 1). In summary, PE1-CN-Chol self-assembles at the solid–liquid interface on HOPG as two molecules arranged in pairs through dipole–dipole interactions between CN groups. This arrangement gives rise to a lamella or plate-like arrangement. Each molecule-pair unit orients with respect to another at a specific distance established by the triethylphosphines and the cholesterol substituents in agreement with the maximum full filling space criterion. The lamellae are oriented in a “face-on” or flat mode on the HOPG surface, likely due to the π – π interactions of the conjugated backbones with the graphite.

2.2. 3D Nanostructure Organization from MD Simulations

Unlike the MD simulations on HOPG, here we used a bottom-up approach to study the 3D organization of PE1-CN-Chol starting with a single molecule and increasing the number of molecules to identify higher order structures. Unless explicitly stated, the discussed MD simulations were performed in water solution. Starting from a linear conformation, the single cholesteric platinum acetylide quickly went to a bent form as shown in **Figure 5** with an average 1–2–3 angle of 95° . The

second chromophore was added into the simulation box in a way such that the two residues were not in contact at the beginning of the MD simulation. During the dynamics, they approached one another and locked with the cholesterol moieties being on one side and the platinum acetylide moieties on the other side (Figure 5). As consequence of the chromophores being locked, the 1–2–3 angle decreased its value to $\approx 81^\circ$. The separation of the cholesterol and platinum acetylide moieties was still observable when adding a third chromophore. We then replicated the three-chromophore system and continued the MD simulation and, after ≈ 17 ns, there was again observed a clear separation of the cholesterol and platinum acetylide moieties. We repeated the process by replication of the 6-chromophore system to arrive at a 12-chromophore system (Figure 5) for which we could observe the formation of a layered structure with the cholesteric unit organizing in a plane with the platinum acetylide moieties organizing on top and bottom of the complex aggregate.

Based on the development from a 12 chromophore system, we created a periodic layered structure composed of 768 chromophores (Figure S10, Supporting Information) that was allowed to relax and self-assemble in an *NPT*-ensemble simulation. Finally, we solvated this layer and replicated it three times in the *z*-direction (Figure S10, Supporting Information) after which we performed an evaporation of the water molecules to reach a realistic lamellar organization of the 3D cholesteric liquid crystal. The evaporation process was gradual over the course of 60 ns as shown in Figure S11 (Supporting Information) and during which the density gradually increased. The final photonic crystal displays a clear phase separation between

Figure 5. Structures of single chromophore, up to 12 chromophores as obtained with molecular dynamics (MD) simulations. Platinum atom in purple, cyclic part of cholesterol in pink (also represented by beads representation), and the chain part of cholesterol in cyan (in beads representation as well).

Figure 6. From beginning of molecular dynamics (MD) simulation (membrane-like cholesteric platinum acetylides chromophore before running MD simulation), through solvated arrangement after MD simulation, to three membrane-like layers. Profile of platinum and cholesteric moieties shows a distribution of the moieties after the evaporation process. Platinum atoms in purple. Water in red.

the conjugated platinum acetylide and the hydrophobic cholesterol moiety and the lamellae separation distance amounts to ≈ 4.0 nm as shown in the distribution plot in **Figure 6**. With respect to performance, it is noted that the chromophore concentration in the cholesteric liquid crystal amounts to 1.07 M, which is close to three times larger than what was reached with sol-gel glasses and it is expected that NLO responses are correspondingly stronger in the liquid crystal.

2.3. Spectroscopy

The ground state absorption spectrum of PE1-CN-Chol was collected in different solvents (**Figure 7A**). It presents an intense band at around 340 nm associated with the HOMO $\rightarrow$ LUMO electronic transition.^[13,14] The bandshape of the UV-Vis spectrum changes in solvents of different dielectric constant. The red shift of a few nm suggests the S_1 state has a larger dipole moment than the ground state. The relative absorbance of the band at 300 nm increases in nonpolar solvents, perhaps

associated with a solvent-dependent conformation change or dimerization via dipolar CN-CN interactions. The UV-Vis spectra do not change with concentration in the spectrophotometer detectable range of optical density (0.002–3), whatever solvent was used, excluding intermolecular aggregation. As the electronic transition from the cholesterol substituent could not be observed in solutions due to the UV cut-off of the solvents, the UV-Vis spectrum of a spun film on quartz was obtained and reported in **Figure 7B**. There are two peaks at 349 and 305 nm, which resemble those observed in solution with a slight red shift consistent with solid-state effects. Additionally, a higher energy peak at 235 nm is likely due to cholesterol. We prepared a liquid crystalline film and obtained variable temperature (77–300 K) phosphorescence spectra (**Figure 7C**) and phosphorescence lifetimes (**Figure 7D**). The phosphorescence spectra have a strong 0–0 band and a lower intensity vibronic envelope. The three vibronic bands are associated with C–C stretch, C_6H_6 “breathing” and $C\equiv C$ stretch modes.^[42] Previous studies of the triplet state of platinum acetylides have shown the triplet exciton to be confined to one ligand and the vibronic

Figure 7. A) Ground state absorption spectra of PEI-CN-Chol in various solvents. The extinction coefficient [$\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$] in THF was measured at CIQA and AFRL to be 53000 ± 3440 [95% CI, $n = 4$]. B) Ground state absorption spectra of PEI-CN-Chol deposited on a quartz slide. C) Emission spectra obtained from a liquid crystal film from room temperature to 77 K with vibronic bands [cm^{-1}]. D) Emission decay rate constant as a function of temperature. The data were fit according to Equation (1).

envelope consists of ligand ground state vibrations.^[43,44] We fit the data to Equation (1), where the temperature dependence of the emission lifetime fits to a radiative and nonradiative contribution (Figure 7D).

$$k_{\text{ph}}[\text{sec}^{-1}] = 31,700 + 1.95 \times 10^7 \exp\left(-\frac{2}{RT}\right) \quad (1)$$

From the first term, the oscillator strength can be estimated from the radiative rate constant ($k_{\text{ph}} \sim \nu_0^2 f$) to be $\approx 10^{-4}$, a low value as expected for a spin-forbidden transition. From the second term, the activation energy for radiationless decay is measured to be 2 kcal mol⁻¹, associated with conformation changes and weak coupling with the intermolecular environment. The pre-exponential factor of the second term is approximately 1000× less than the diffusion rate constants in measured in nonviscous solvents.^[45] From the Debye equation, we estimate the room temperature viscosity of the molecular glass to be 330 cP, which is $\approx 16\times$ larger than ethylene glycol and comparable to oligomeric molecular glasses.^[45,46] The high viscosity slows intermolecular collisions and minimizes quenching due to triplet–triplet annihilation and excimer formation.

The femtosecond transient absorption spectrum of PEI-CN-Chol was measured in aerated hexane, toluene, acetone, tetrahydrofuran solution, and as a liquid crystal thin film (Figure 8). All the samples were excited at 400 nm. Very high concentrations were needed as the molecule has a small

absorption cross-section at 400 nm. The spectra fit to three relaxation times. The spectra in THF show more complex features than those in other solvents. The time zero spectrum of the THF solution has no distinct maximum, but a broad, relatively flat signal from 570 to 635 nm. In the time 6–20 ps and >3750 ps spectra, the higher energy absorption peaks begin to decay as a maximum grows in at about 670 nm. A shoulder persists around 565 nm for longer times until the final spectrum at $t > 3750$ ps is observed. Three lifetimes are observed, with the first being 0.21 ps. This is likely intramolecular vibration relaxation of the singlet excited state. A second lifetime of 45.9 ps could possibly be stabilization of the S_1 state via solvent reorganization. The third lifetime of 946 ps would then be inter-system crossing to yield the triplet state observed at 6 ns. The spectrum at $t > 3750$ ps is almost assuredly the relaxed triplet state. The spectrum of the film at time zero resembles that of THF solution at around 1 ns. There is a slight shoulder around 565 nm which then decays rapidly. It seems the 0.17 ps lifetime corresponds to this change and the triplet state is formed over this fast lifetime and the long lifetime of 217 ps is just monitoring the decay of the triplet. The data on the hexane, acetone, toluene solutions and film are much simpler, with minor changes in the bandshape during decay. Table 2 summarizes the decay times. For both τ_1 and τ_2 , the decay time is larger for nonpolar solvents compared to polar solvents. The film has a short τ_1 like a polar solvent but a long τ_2 like a nonpolar solvent. The normalized spectra (Figure 8) show blue shifting in THF

Figure 8. Ultrafast transient absorption spectra of PE1-CN-Chol in various solvents, liquid crystal thin film, and time ranges.

solution and red shifting of the film at time zero up to 20 ps. The other three solvents have spectra between THF and the film. At $t > 3750$ ps, the film spectrum is red-shifted compared to the solution spectra. It is unclear why the solution and liquid crystal samples give such different data, but there are several possible reasons. The film is a much different form and also much more concentrated. Solute and solvent motion is also less restricted in solution, and the polarity could also be very different.

To measure triplet state absorption spectra and lifetimes, we performed nanosecond laser flash photolysis measurements on air-saturated, degassed toluene solution and liquid crystal thin films (Figure 9 and Table 3). The ns transient spectra of the solutions present a negative peak at almost 340 nm, corresponding to the ground state depletion, in agreement with the UV-Vis spectra. The positive absorption is peaked at 673/672 nm as found in the ultrafast spectroscopy for the long-time absorption. Similar results were found for the film where

the triplet-triplet absorption is found at 685 nm as in the femto-second experiments. The triplet state spectra shown in Figure 8 are very similar to the long-time spectra in Figure 9, demonstrating conversion to the triplet state after around 100 ps after excitation. The triplet state lifetimes show the trend τ (air saturated) $< \tau$ (degassed) $< \tau$ (liquid crystal film). These measurements show that oxygen quenching and solvent environment decreases the triplet lifetime. The liquid crystal film showed a two-component decay. The fast decay time was equal to the decay time in air-saturated toluene while the slow decay time was longer than both air-saturated and degassed toluene. The result suggests the triplet lifetimes of the films include contributions from the surface, which is exposed to atmospheric oxygen and from an oxygen-impermeable region in the center of the film. The behavior observed in the heavy atom complex PE1-CN-Chol free-standing film compares well with data obtained from heavy atom free, deuterated molecular glasses having long room temperature triplet lifetimes, strong room

Table 2. Summary of ultrafast TA spectra and relaxation times.

Solvent	$\lambda_{\text{max}}^{\text{a)}$ 0 ps	$\lambda_{\text{max}}^{\text{a)}$ 6–20 ps	$\lambda_{\text{max}}^{\text{a)}$ >3750 ps	τ_1 [ps] ^{b)}	τ_2 [ps]	τ_3 [ps]
n-Hexane	644	647	650	4.55 (0.28)	131 (5)	Long
Toluene	654	670	676	6.44 (4.07)	89.5 (25.3)	Long
Tetrahydrofuran	604/634	666	669	0.21 (0.11)	45.9 (16.4)	950(150)
Acetone	648	657	664	0.30 (0.22)	60.4 (3.9)	1750(330)
Film	675	688	684	0.17 (0.2)	217 (2)	Long

^{a)}[nm]; ^{b)}Lifetimes from triexponential fit; standard deviation in parenthesis.

Figure 9. A,B) Flash photolysis data of PE1-CN-Chol in air saturated and degassed toluene solution; C,D) liquid crystal glass.

temperature phosphorescence,^[47] NLA,^[48,49] and large refractive index increase.^[50] PE1-CN-Chol can potentially perform as both a triplet exciton donor and host for doped triplet chromophore acceptors.

3. Conclusions

In this work, we have performed detailed physical characterization, MD simulations, and measurements of spectroscopic properties of a cholesteric liquid crystal molecular glass formed from PE1-CN-Chol. PE1-CN-Chol is a special case of the general formula *trans*-Pt(PR₃)₂(C≡C–C₆H₅–X)(C≡C–C₆H₅–Y), where R controls intermolecular packing, X is a polar end group, and Y provides chirality. In previous work, we varied X and R and found liquid crystal behavior when R=C₂H₅, X=OCH₃, F, CN, and Y=COO–Cholesterol, with the best properties observed when X=CN.^[31,32] The current physical characterization studies show crystallization upon heating but formation of a stable cholesteric glass upon cooling. STM measurements of a monolayer show formation of an ordered monolayer with strong intermolecular interactions between dipolar CN groups and between

nonpolar cholesterol groups. The MD simulations predict a phase separation between the conjugated platinum acetylide and the hydrophobic cholesterol groups and the formation of lamellae. The calculated chromophore concentration in the cholesteric liquid is estimated to be ≈1 M. We were able to measure the triplet state behavior of PE1-CN-Chol both in solution and in thin film, including steady state and time-resolved spectra. The triplet state lifetime of PE1-CN-Chol is longer in the film than in deoxygenated solution, suggesting low oxygen permeability. The high chromophore concentration, high glass thermal stability, and long triplet lifetime in air show that these materials have potential as nonlinear absorbing materials. Compounds with Y having high helical twisting power would yield glasses with NLO properties and cholesteric reflection bands in the visible spectrum.

4. Experimental Section

DSC, TGA, POM, and SWAXS: PE1-CN-Chol was synthesized according to published procedures presented in the Supporting Information.^[31,32] DSC analyses were carried out on a DuPont 951 instrument under nitrogen at a heating rate of 5 °C min^{−1} and using 5–8 mg of sample. The thermal stability of PE1-CN-Chol was determined in a thermogravimetric analyzer, TGA 951 from Du Pont Instruments connected to N₂ gas, heating from 300 to 700 °C at 10° min^{−1}. MDSC measurements were performed with a TA instruments Q2000 instrument. Optical textures were captured with an Olympus BX60 polarizing optical microscope (POM) coupled with a Mettler FP84HT hot stage. Small and wide angle X-ray scattering patterns were obtained with an Anton Paar SAXSess mc² SWAXS instrument using CuKα radiation at a wavelength of 0.1542 nm, a sample holder unit (TCS 300- C), an image plate detector, and a temperature controlled TSU50.

Table 3. Summary of laser flash photolysis experiments.

Sample	λ_{max} [nm]	τ_1 [ns] ^{a)}	τ_2 [ns]
Air saturated toluene	673	–	114
Degassed toluene	672	81	192
Liquid crystal film	685	114	643

^{a)} Lifetimes obtained from biexponential fit.

XRD scattering experiment was conducted in a sealed Lendemann glass capillary having an outer diameter and a wall thickness of 1.0 and 0.01 mm, respectively.

Scanning Tunneling Microscopy (STM): STM characterizations were performed between ≈ 23 and 25°C using an AA5000 Scanning Probe Microscope (Angstrom Advanced Inc., Braintree, MA USA). The scanner tube calibration was performed by means of atomic resolution images obtained using commercial HOPG substrates from Ted Pella (Redding, CA USA) and SPI Supplies (West Chester, PA USA), grade SPI-3; samples were exfoliated before each measurement by the adhesive tape method. Pt/Ir tips were prepared by mechanically cutting 0.25 mm diameter 80/20 wire from Nanoscience, Switzerland. The solvent TCB (Sigma Aldrich, $\geq 99\%$) was used as received. The PEI-CN-Chol was dissolved in TCB (2.8×10^{-3} M), sonicated and heated to 60°C for 1 h. A droplet of the solution ($\approx 3\ \mu\text{L}$) was placed between substrate and tip to obtain a monolayer. All measurements were performed in the constant-current mode at the solid–liquid interface. Different samples and tips were used to corroborate the reproducibility of the results. The bias and current values were constantly adjusted during each scan. Details on the experiment bias and current set-point are given below each image. The raw and FFT images were processed from WsXM 5.0 software^[51] with the aim to reduce noise and normally observed drift.

Spectroscopy: To prepare liquid crystal thin films, we used a calibrated hot plate. A polyimide-coated glass slide was heated to 215°C (isotropic point) and then a small amount of PEI-CN-Chol solid was added to the middle of the slide. The solid melted very quickly as this is over the melting point. The slide was covered with another polyimide coated slide oriented perpendicular to the first slide, shear aligned, and allowed to sit in the isotropic phase at 204°C for about ten minutes while being covered with a watch glass. The slides were then removed and immediately allowed to cool on a cooling block (previously put in freezer for ≈ 20 minutes) and then allowed to return to room temperature. Temperature-dependent emission spectra were collected from thin films placed in an Oxford Instruments OptistatDN2 cryostat. Emission lifetimes were measured from time-correlated single photon counting (Edinburgh Instruments).

Room temperature ultrafast transient absorption measurements used a modified version of the femtosecond pump-probe UV–vis spectrometer described elsewhere. Briefly, 1 mJ, 150 fs pulses at 800 nm and at 1 kHz repetition rate were obtained from a diode pumped, Ti:Sapphire regenerative amplifier (Spectra Physics Hurricane). The output laser beam was split into pump and probe (85 and 15%) by a beam splitter. The pump beam was directed into a frequency doubler (CSK Super Tripler) and then was focused into the sample. The probe beam was delayed in a computer-controlled optical delay (Newport MM4000 250 mm linear positioning stage) and then was focused into a sapphire plate to generate white light continuum. The white light was combined with the pump beam in a 2 mm quartz cuvette and coupled into a CCD detector (Ocean Optics S2000 UV-VIS). Data acquisition was controlled by software developed by Ultrafast Systems LLC.

Room temperature triplet state absorption spectra and lifetimes were measured by laser flash photolysis on toluene solutions deoxygenated by three successive freeze-pump-thaw cycles. A detailed description of the laser flash photolysis apparatus has been published.^[15] Nanosecond transient absorption measurements were carried out using the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Quantel Brilliant, pulse width of ≈ 5 ns). Pulse fluences of up to $1\ \text{mJ cm}^{-2}$ at the excitation wavelength were typically used.

Molecular Dynamics Simulation Setup: Geometry optimization and electrostatic potential charges calculations were carried out using density functional theory with the B3LYP exchange–correlation functional^[52] and a combination of the 6–31G* (for carbon, nitrogen, and oxygen) and 6–31G (for hydrogen) basis sets^[53,54] The Stuttgart (SDD) relativistic effective core potential was used for platinum and phosphorus atoms.^[55,56] Calculations were performed with the Gaussian 09 software package.^[57]

All MD simulations were carried out using the Amber 14 package.^[58] Topologies and initial coordinates were created using LEaP program

with the general amber force field (GAFF).^[59] which contains parameters for almost all the organic molecules. Parameters for nonstandard atoms not included in GAFF (namely platinum) were explicitly added based on already published articles.^[58,60] The MD simulations were performed at 300 K (if not stated otherwise) using Langevin dynamics and constant pressure periodic boundary with an average pressure of 1 atm and with isotropic position scaling using Berendsen barostat.^[61] The simulations ran with a time step of 2 fs per step, the trajectories were recorded every 5000 steps, and the cut-off were set to 12 Å for nonbonded interactions. We used the cpptraj program implemented in the Amber package to calculate an average angle 1–2–3 along 300 frames corresponding to 3 ns of MD simulation.

For a membrane-like systems, we applied anisotropic pressure scaling, and periodic boundary conditions so the sheet propagates in the *xy*-plane. First, we let the sheet reorganized in the presence of water (Figure S10, Supporting Information), then we multiplied the sheet three times and performed evaporation of water molecules (Figure S11, Supporting Information). Evaporation rate was set to 36 water molecules every 40 ps with a total number of waters being equal to 52 367. The trajectories were recorded every 10000 steps. After the evaporation, we continued the MD simulation for another ≈ 25 ns using an *NPT* ensemble.

For simulations on HOPG, the HOPG was generated as four layers of graphene sheets each with side length of 12.5 nm with TCB as a solvent. First, only one PEI-CN-Chol was placed on the surface in which case the chromophore stayed in a linear conformation. Then, the second chromophore was added, and a cholesterol separation was already seen. Consequently, systems with 4, 8, 16, and 32 chromophores were ran for 11, 15, 20, and 20 ns of MD simulation, respectively. In majority of cases, the linear organization and clear separation of individual moieties were observed. In few cases, as our PEI-CN-Chol was not built periodically over the whole simulation box but only up to 32 molecules on the graphite, we observed a few single events (i.e., forming π – π stacking interaction of some of the phenyls) that broke the linear organization that we observed in the experimental image. We extracted various structure parameters and compared to the experiment (*c*, *d*, ΔL , see the main text).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cholesteric liquid crystals, molecular dynamics, molecular glass, nonlinear optics, platinum acetylide, triplet states

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