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14. ABSTRACT A series of (cholesteryl) 2,5-dibromobenzoate dendrons consisting of a first generation (G1=1 (cholesteryl) 4-benzoate), second generation (G2=2 (cholesteryl)s 4-benzoates) and third eneration (G3=4 (cholesteryl)s 4-benzoates) were synthesized step-bystep by the convergence approach. The 2,5-dibromo G1, G2 and G3 synthesized dendrons were subjected to co-polymerization with (butyl) 2,5-diethynyl benzoate by the Sonogashira cross-coupling reaction to afford rigid rod-like vermicular dendrimers of the phenyleneethynylene type, which resulted be very soluble in non-polar solvents such as CHCl3, THF, toluene. Their chemical structures were analyzed by 1H, APT, DEPT-135, 13C NMR, however for their correct proton-carbon assignation, it was necessary to carry out 2D-HETCOR correlations. The thermal properties studied by DSC, TGA and Polarized light microscopy showed that all of the (cholesteryl) 2,5-dibromobenzoate dendrons exhibited a mesomorphic behavior: Crystal↔Smectic C (or Nematic)↔Isotropic transitions, where mesophases are presented in a very short temperature range. In what concerns to the copolymers, in spite of that they do not exhibit any know texture reported in the literature, however they seem to exhibit Smectic C and/or Nematic mesophases, nonetheless the study of X-ray at small angle is necessary in order to better determine their real supramolecular order of the mesophase(s).

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Liquid Crystals of Dendron-like Pt Complexes Processable into Nanofilms Extension (I and II)

Final Report to AFOSR - Latin American Initiative

Polymer Chemistry – Dr. Charles Y-C Lee

Proponent:

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Abstract

A series of (cholesteryl) 2,5-dibromobenzoate dendrons consisting of a first generation (G1=1 (cholesteryl) 4-benzoate), second generation (G2=2 (cholesteryl)s 4-benzoates) and third eneration (G3=4 (cholesteryl)s 4-benzoates) were synthesized step-bystep by the convergence approach. The 2,5-dibromo G1, G2 and G3 synthesized dendrons were subjected to co-polymerization with (butyl) 2,5-diethynyl benzoate by the Sonogashira cross-coupling reaction to afford rigid rod-like vermicular dendrimers of the phenyleneethynylene type, which resulted be very soluble in non-polar solvents such as CHCl3, THF, toluene. Their chemical structures were analyzed by 1H, APT, DEPT-135, 13C NMR, however for their correct proton-carbon assignation, it was necessary to carry out 2D-HETCOR correlations. The thermal properties studied by DSC, TGA and Polarized light microscopy showed that all of the (cholesteryl) 2,5-dibromobenzoate dendrons exhibited a mesomorphic behavior: Crystal↔Smectic C (or Nematic)↔Isotropic transitions, where mesophases are presented in a very short temperature range. In what concerns to the copolymers, in spite of that they do not exhibit any know texture reported in the literature, however they seem to exhibit Smectic C and/or Nematic mesophases, nonetheless the study of X-ray at small angle is necessary in order to better determine their real supramolecular order of the mesophase(s); work that is currently in progress. All the polymers absorb in solution in the UV-blue region and emit at around 430 nm with modest fluorescence quantum yield due to the presence of a lot of oxygens in the cholesteryl substituents that act as quenchers, however intersystem crossing to triplet excited state is also possible. Phosphorescence studies are in progress in order to determine their possible application in phosphorescent light emitting diodes**.**

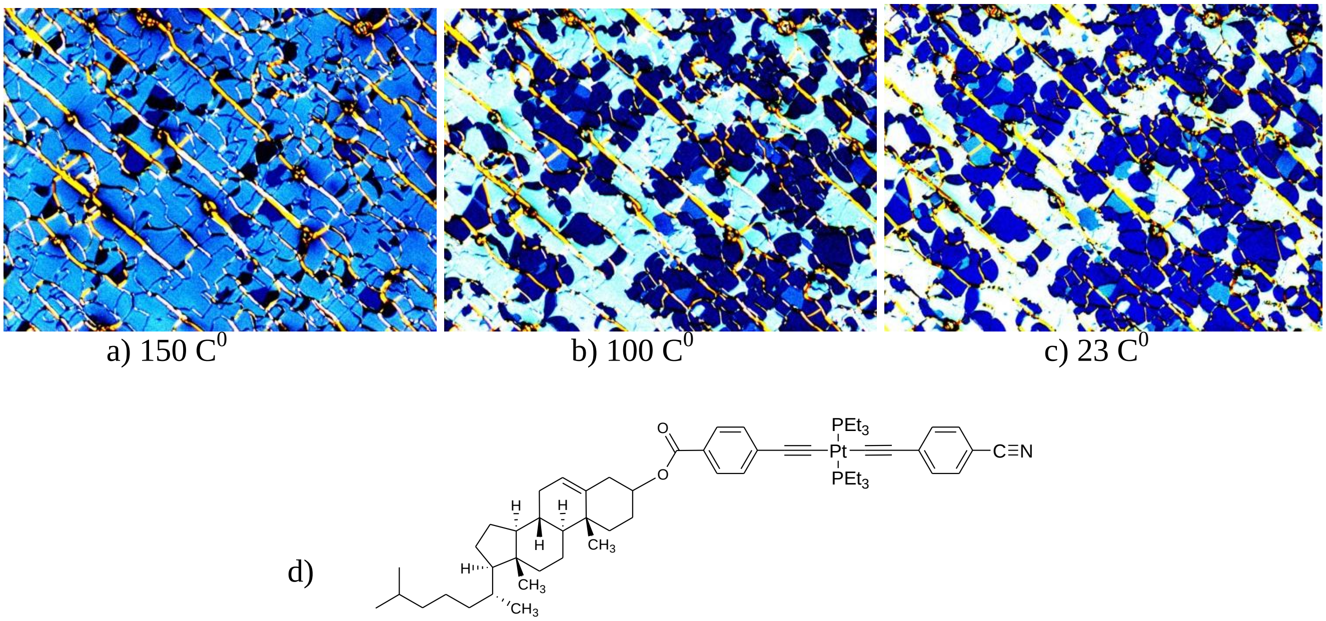
Overview

The Air Force has a requirement for materials that have a strong nonlinear response to laser radiation and use non complex, low cost processing techniques. In particular, the AFRL has performed extensive structure-property studies of platinum acetylide complexes and demonstrated strong two-photon absorption [1]. CIQA has synthesized new conjugated monomers, oligomers and polymers as ligands in such complexes to affect AFRL needed materials [2] and processing issues.

The actual challenge concerns the development and processability of these materials to hybridize their nonlinear absorption behavior with liquid crystal optics, to develop the materials into easily processable thin films, and to incorporate the systems into solid hosts. At the molecular level, our immediate focus is on modifying the current cholesterol LC system, which has a high transition temperature, to functional systems having lower transition temperatures, down to room temperature or below. CIQA has extensive experience and expertise in the synthesis of phenyleneethynylene oligomers and related materials and in effective liquid crystal substituents such as cholesterol benzoate oligomers for AFRL [3,4].

The present proposal focuses on the design, synthesis, physicochemical characterization and thin film elaboration of push-pull phenyleneethynylene oligomers for NLO technology. Oligomers bearing cholesteryl as a mesogen exhibit interesting thermotropic mesophases combined with improved NLO response due to the increased conjugation and push-pull effect accomplished by the presence of platinum, which is a strong electron donor group, and two electron withdrawing groups (CN and cholesteryl benzoate). The dendronic architecture, as well as the biphenyls, should also improve the processability of homogeneous films that could be easily prepared from solution using low cost techniques such as spin or spray coating or self-assembly.

From a complete series of oligomers bearing cholesterol as a mesogen group that has been studied, at least two of the oligomers showed thermotropic mesophases evidenced by the classical optical textures observed under polarized light microscopy (POM). Furthermore a typical cell constructed with configuration: Glass/ITO/Rubbed polyimide/Material/Rubbed polyimide/ITO/Glass allowed determining the Cholesteric pitch by using a Cano-Grandjean wedge. Two plates with planar boundary conditions were assembled to form a wedge with an opening angle β (this angle was measured independently and was 1 mrad). The cholesteric helix was perpendicular to the wedge substrates due to the planar boundary conditions. When the cell gap increased continuously along the wedge, the integer number of half pitches increased in a discontinuous way through disclination lines (observed experimentally), Fig 1. Since S was a distance between two disclination lines, then the following expressions was used to calculate the pitch P: $\frac{P}{2 \cdot S} = \tan\beta$, which was of 1.1-1.2 μm. These results are important for the design and construction of LC devices with conjugated molecules having nonlinear optical properties.



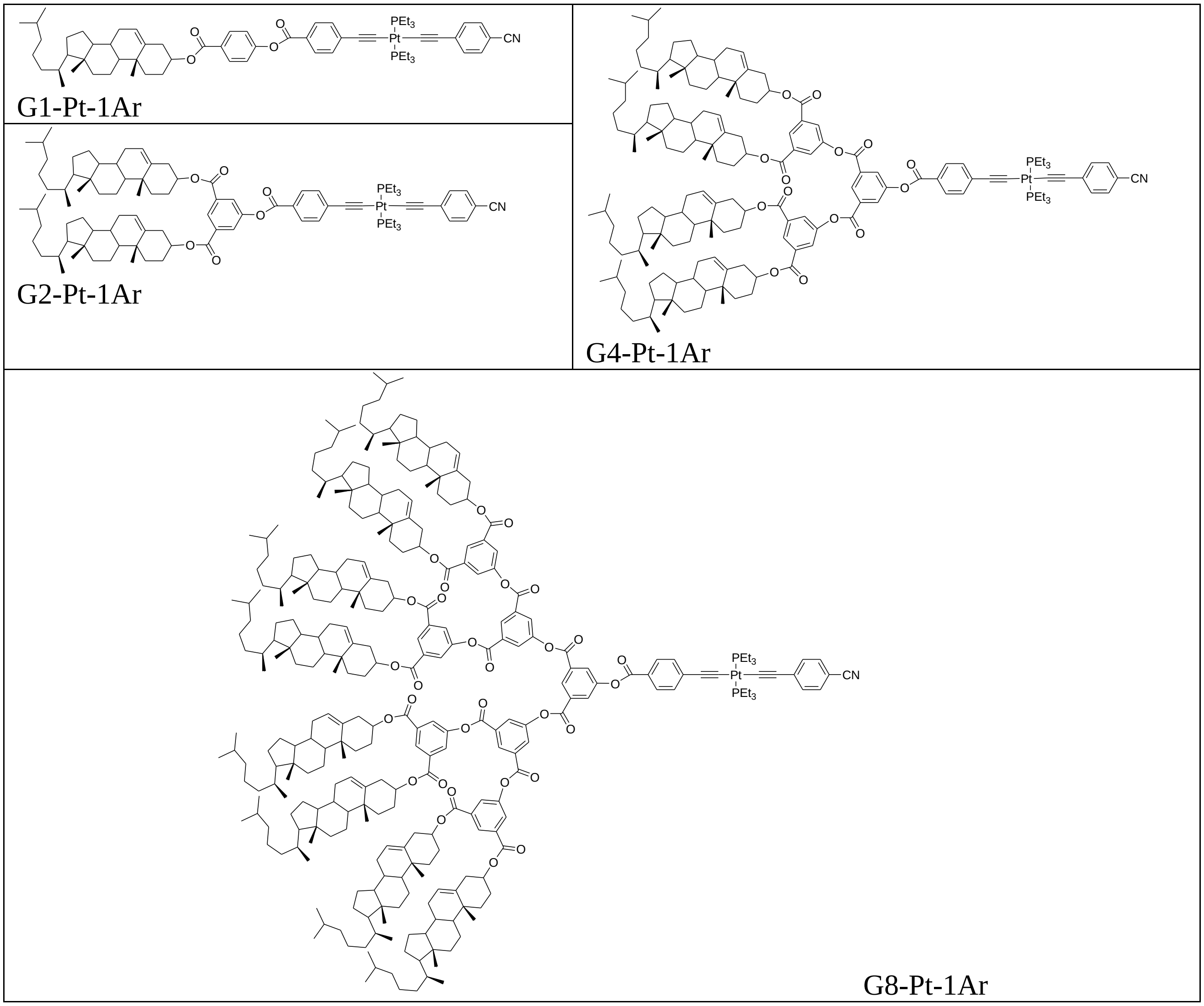
a) 150 C^0 b) 100 C^0 c) 23 C^0

d)

Fig. 1. Micrographs of the cell filled with material (d) at different temperatures, a, b and c (under cooling). Field of view is ~900 µm x 1200 µm.

However, for practical application, this oligomer presents several drawbacks: 1) at room temperature, the films are not homogeneous because of microcrystal growth, which gives rise to low optical quality samples; 2) to develop the mesophase, heating to 190°C is necessary even if the mesophase is then maintained at room temperature after sample cooling; 3) the oligomer is not conjugated enough to absorb light in the red region.

With respect to the above drawbacks, and, in order to optimize the use of oPE as a possible NLO material, we are making two chemical modifications of oPE, which should 1) decrease the temperature at which the mesophase appears and 2) improve the processability of the films. In the first case, we are introducing an additional phenyl to the cholesterylbenzoate mesogen that will help increase the molar volume (see G1, Fig. 2), and, to increase the number of cholesteryls to 2, 4 and 8, hereinafter named dendrons G1-Pt-1Ar, G2-Pt-1Ar, G4-Pt-1Ar and G8-Pt-1Ar, respectively (Fig. 2).


G1-Pt-1Ar

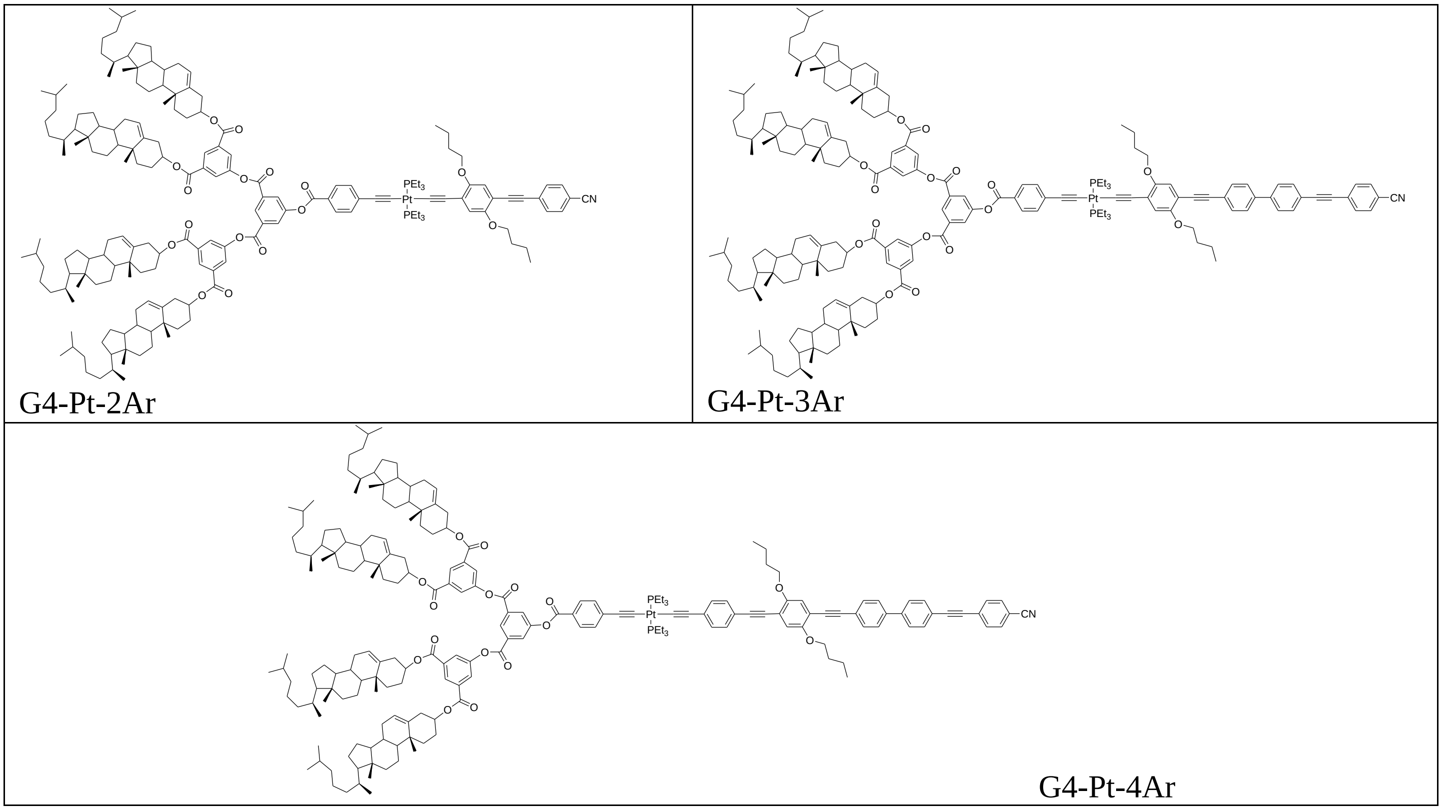
G2-Pt-1Ar

G4-Pt-1Ar

G8-Pt-1Ar

Fig. 2. Dendrons series attached to the Pt-p-cyanophenyl that might decrease the mesophase temperature of the G1-Pt-1Ar oligomer, which exhibits a cholesteric mesophase at ca. 190°C.

We performed thermal and optical characterization on the ligands to determine their liquid crystalline behavior. Platinum complexes were prepared from suitable candidates. Once we obtain the dendron-like oligomer G1-Pt-1Ar, G2-Pt-1Ar, G4-Pt-1Ar or G8-Pt-1Ar that possesses a suitable cholesteric mesophase at about 80-100°C and good optical quality nanofilms on glass substrates, we proceeded, in the second modification, to increase the oPE conjugation by introducing a different number of aryls to the unsymmetrical platinum oligomer. In this respect, as an example, and, hypothetizising that it is the dendron bearing 4 cholesteryls G4-Pt-1Ar that gives the cholesteric mesophase between 80-100°C, then the oligomers G4-Pt-2Ar, G4-Pt-3Ar and G4-Pt-4Ar would be synthesized, Fig. 3. In this respect we consider that the presence of biphenyls is a good alternative to using only phenylenethynylenes sequences because intramolecular π-π interaction can be avoided by the twist between phenyls [4]. Moreover biphenylenes are also considered as mesogens that can exhibit smectic or nematic phases depending on the molecular architecture [5].


G4-Pt-2Ar

G4-Pt-3Ar

G4-Pt-4Ar

Fig. 3. Proposed Pt-dendron like oligomers bearing 4 cholesteryls as mesogens and coupled to different conjugated chain lengths that would be synthesized in this work.

As well, and as an extension to the original FA9550-11-1-0169 project, we propose for the 24 month period encompassing 2012 and 2013, to synthesize the same above dendron like oligomers but without the platinum atom in order to give, for example, the dendrimers depicted in Fig. 4 (G4-1Ar to G4-4Ar). The latter was studied in parallel with the Pt complexes to compare all thermal and spectroscopic behavior. Thin films were prepared for all of the materials by both spin coating and self-assembly and in different solvents and concentrations and on different substrates, as we previously found that the deposition technique and parameters can affect the supramolecular organization of conjugated molecules and therein their optical properties. Particular attention was devoted to the physicochemical characterization by performing SAXS, DSC and HRTEM on the dendrons and oligo- dendrimers as well as optical studies, including UV-Vis, fluorescence, time resolved fluorescence and two photon absorption in both solutions and films. Films morphology was particularly analyzed by Scanning Tunneling Microscopy AFM and laser scanning confocal microscopy.

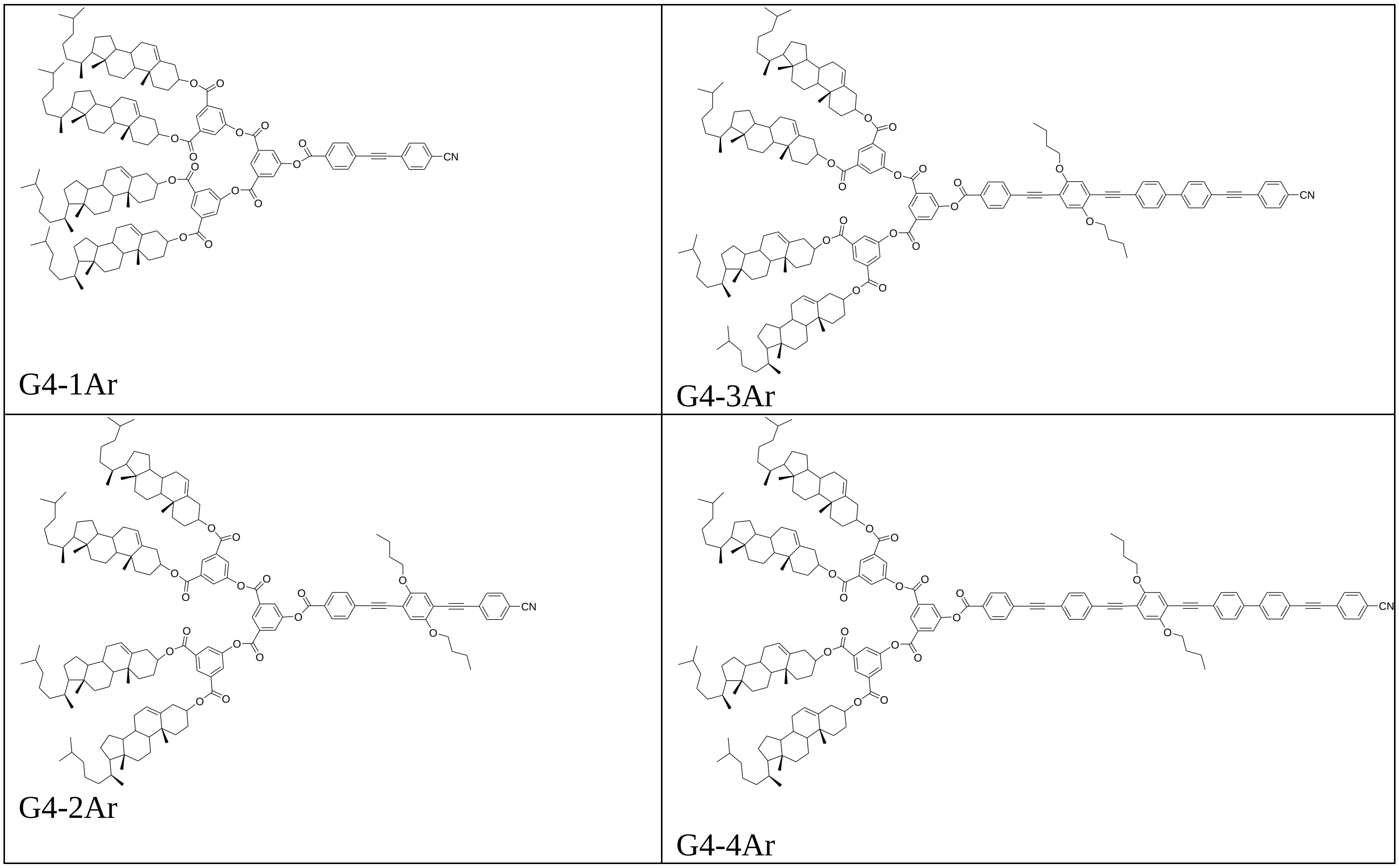


Fig. 4. Unsymmetrical dendron like oligomers with different chain length and bearing cholesteryls as mesogens as molecular models to understand their homologues bearing platinum atoms.

CIQA Resources

CIQA is an advanced research center for polymer and advanced materials design, synthesis, characterization, processing and manufacturing. It supports a fully equipped pilot plant with >100 kg capability in bulk and film materials. Available equipment for use in the proposed work includes: a fully equipped Anton Paar SAXS mc^2 small angle X-ray scattering system; state-of-the-art FEI Titan TEM microscope; TopCon, SM-510 SEM; Field Effect Jeol SEM; FEI Dual Beam Focused Ion Beam V series microscope – 3D microscopy, nanomanipulation; Varian 500 MHz NMR with micro probe and high-spin solid state probe; Digital Instruments Nanoscope Multidimension 3100 AFM with tunneling, magnetic mode, nanoindentation and electrical nanoconductive mode; Olympus Optical Microscope coupled with polarizers and heating plate; Laser Scanning Confocal Microscope Zeiss Pascal 5 with Ar and He-Ne lasers; Nicolet FTIR spectrometer, coupled to Spectra-Tech Optical Microscopy and Image Analyzer; Du Pont 1090 DSC, TGA and TMA; Instron DMA (tensile, impact, heat deflection temperatura, etc.); Capillary & Oscillatory Rheometers; Siemens PCD-4H WA X-Ray Diffractometer; Several Plasma Reactors for Surface Modification; Newport integrating sphere and spectrometer; UV-Vis Shimadzu 2401 with thin film mounting cell and polarizers (190-900 nm); Perkin Elmer LS50B spectrofluorimeter coupled with thin film mounting cell and polarizers; Dektak Profilometer; coating technology including spin and draw bar coating apparatus, LB capability and self assembly techniques. Software includes: ChemDraw and Dmol3**,** Materials Studio Modeling 3.1 package from Accelrys, Inc**.**

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Cholesteric liquid crystal glass platinum acetylides

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KEYWORDS Platinum acetylide, liquid crystal, cholesteric liquid crystal

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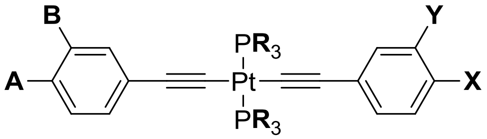
ABSTRACT: To prepare cholesteric liquid crystals with ability to be vitrified on cooling and form long time stability cholesteric glasses at room temperature, a series of platinum acetylide complexes having the chemical formula

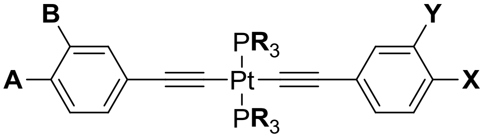


has been synthesized, where **A** = H, COO-Cholesterol or $COOC_5H_{10}$-Cholesterol; **B** = H or COO-Cholesterol, **R** = C_2H_5, C_4H_9 or C_8H_{17}; **X** = H, CN, F, OCH_3 and **Y** = H or COOCholesterol. A cholesteric liquid crystal phase was observed in the complexes **A**=COO-Cholesterol, **B** = H; **R** = C_2H_5, **Y** = H and **X** = F, OCH_3 and CN but not in any of the other complexes. When **X** = CN, a cholesteric glass was observed at room temperature which remained stable up to 130°C, then converted to a mixed crystalline/cholesteric phase and completely melted to an isotropic phase at 230°C. When **X** = F or OCH_3 the complexes were crystalline at room temperature with conversion to the cholesteric phase upon heating to 190 and 230 °C, respectively. In the series **X** = CN, OCH3, F the cholesteric pitch was determined to be 1.7, 3.4 and 9.0 μm, respectively.

Platinum acetylides are nonlinear optical materials with high linear transmission, broadband triplet state spectra and efficient conversion to the triplet state.[1] We have been investigating the relation between chemical structure and spectroscopic properties of platinum acetylide complexes having the molecular formula *trans*-$Pt(PBu_3)_2L_2$. We have processes these chromophores into solid state optical elements[2] and glass-forming liquids.[3] Cholesteric glasses are useful as large area non-absorbing polarizers,[4] optical notch filters and reflectors,[5] optically-switchable notch filters[6] and polarizing fluorescent films[7] and one-dimensional photonic band-gap for circularly polarized lasing.[8] In this Communication we describe the liquid crystal behavior of a series of cholesterol-containing platinum acetylides.

Table 1 lists the compounds we synthesized. The structure variations explored the effect of the length of the **R** group, meta- or para- cholesterol ester substitution(**A**,**B** and **Y**) and the effect of a para substituent(**X**). The method of thermal polarizing microscopy was used in order to characterize these materials [9]. We found a combination of **R**, **A**, **B**, **X** and **Y** which yielded a stable cholesteric glassy liquid crystal platinum acetylide. The necessary conditions for cholesteric phase are **R** = Et, **A** = COO-Cholesterol, **B** = **H**, X = polar group and **Y** = **H**

Table 1. List of complexes synthesized



Compound	A	B	R	X	Y
I	H	COOChol[1]	Bu	H	COOChol
II	H	COOChol	Bu	H	H
III	H	COOChol	Bu	CN	H
IV	COOChol	H	Et	H	H
V	COOChol	H	Et	F	H
VI	COOChol	H	Et	CN	H
VII	COOChol	H	Et	OCH$_3$	H
VIII	H	COOChol	Oct	H	COOChol
IX	COOC$_5$H$_{10}$COOChol	H	Et	COOC$_5$H$_{10}$COOChol	H
X	H	COOChol	Et	CN	H
XI	COOChol	H	Bu	CN	H
XII	COOC$_5$H$_{10}$COOChol	H	Et	CN	H

[1] Cholesterol

Material **I** is a crystalline solid which melts to an isotropic phase at 231.2 °C. Material **II** has asymmetry with one meta-cholesterol ester and is a crystalline solid which melts to an isotropic phase at 121.6 °C. We added a polar **CN** group in material **III.** It exhibits polycrystalline phase at room temperature (Fig. S1(a)). The polycrystalline structure melts at ~ 170 C^0 (Fig. S1(b)) to isotropic liquid at 180 C^0 Fig. S1(c)). On cooling to room temperature it shows isotropic texture (Fig. S1(d-f),Fig 1D). Material **IV** has **R = Et** and is a crystalline solid which melts to an isotropic phase 120-200 °C.

Material **V**, **X = F**, exhibits a room temperature polycrystalline phase(Fig. S2a). The polycrystalline structure melts at ~ 175-220 °C (Fig. S2(b-h)). On cooling, a cholesteric phase appears in the temperature range 188.2 °C-160 °C (Fig. S3a-h), Fig 1A). At 160 °C crystallization takes place(Fig. S3(i-p)).

Material **VI**, **X = CN**, exhibits a cholesteric phase at room temperature (Fig. S4(a-d)). In the range 130-140 °C' polycrystalline structure appears (Fig. S4(e-j)) co-existing with cholesteric phase in the temperature range ~130 – 220 °C. At 228-235 °C, is a transition to isotropic liquid occurs (Fig. S4(k-n)). MDSC measurements show crystallization and melting at 162-210 °C and a glass transition at 162-187 °C(Figure S12). A cholesteric phase appears at ~240 °C down to room temperature (Fig. S5(a-g), Fig. 1B, Fig. 2). MDSC measurements on cooling show no crystallization signal(Figure S13).

The polycrystalline Material **VII, X=OCH$_3$,** melts at ~235 °C (Fig. S6(g)), and the melting process to isotropic liquid is completed at 240 °C (Fig. S6(h)). On cooling, cholesteric phase appears at ~229 °C (Fig. S7(a)) and the sample exhibits cholesteric phase in the temperature range 229 °C-188.8 °C (Fig. S7(b-d), Fig 1C). At 188.8 °C crystallization takes place(Fig. S7(e-h)).

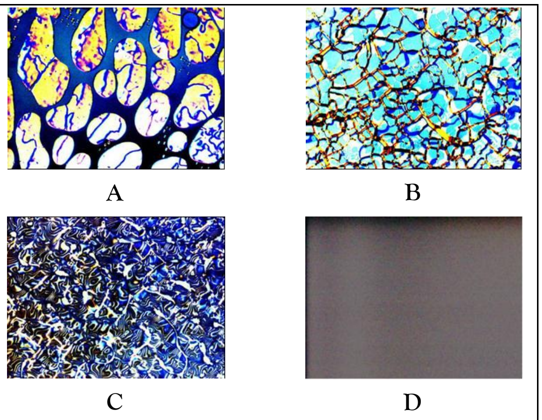

A
B
C
D

Figure 1. Selected photographs from thermal polarizing microscopy A: Material **V**, 175 °C, cooling, field of view: 500 x 750 μm; B: Material **VI**, 25 °C, cooling, field of view: 500 x 750 μm; C: Material **VII**, 200 °C, cooling, field of view 500 x 750 μm; D: Material **X**, 22 °C, cooling, field of view: 900 x 1200 μm.

Materials **VIII** and **IX** are isotropic liquids at room temperature. Material **X** exhibits a polycrystalline phase at room temperature (Fig. S8(a)). When temperature is increased (Fig. S8(b-d)), polycrystalline structure melts at ~160 °C (Fig. S8(d-e)). On cooling to room temperature, the sample under study shows isotropic texture (Fig. S8(f), 1D). Material **XI** exhibits a polycrystalline phase at room temperature (Fig. S9(a)). When the temperature is increased (Fig. S9(b,c)), the polycrystalline structure melts at ~ 175-180 °C (Fig. S9(c,d)). On cooling to room temperature the sample shows isotropic texture up to 60 °C (Fig. S9e), and crystallization takes place at reaching 50 °C (Fig.S9(f, g)). Material **XII** is an isotropic liquid at room temperature.

The cholesteric pitch *P* follows the substituent trend **X=F**(9.0 μ) > **OCH$_3$**(3.5 μ) > **CN**(1.7 μ)(Table SII).

In summary, we have synthesized a series of platinum acetylide cholesterol esters which exhibit cholesteric liquid crystal behavior. In particular, compound **VI** forms a cholesteric glass at room temperature which remains stable up to 130 °C. We are currently investigating chiral platinum acetylides with higher helical twisting power.

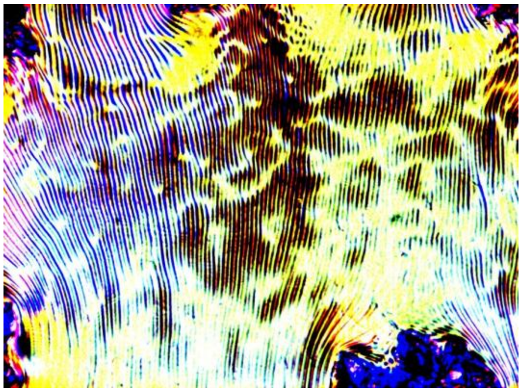


Figure 2. Cholesteric fingerprint texture observed in glassy thin film prepared from compound **VI**. Field of view 260 x 340 μm

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

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Supporting Information. Synthesis, NMR data, thermal polarizing microscopy photographs, Grandjean wedge data, DSC data, X-Ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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