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CHOLESTERIC LIQUID CRYSTAL GLASS PLATINUM ACETYLIDES (POSTPRINT)

Thomas M. Cooper, Aaron R. Burke, and Douglas M. Krein
AFRL/RXAP

Ronald F. Ziolo, Eduardo Arias, and Ivana Moggio
2Centro de Investigacion en Quimica Aplicada(CIQA)

Albert Fratini
University of Dayton

Yuriy Garbovskiy and Anatoliy V.Glushchenko
University of Colorado at Colorado Springs

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//Signature//

THOMAS M. COOPER
Photonic Materials Branch
Functional Materials Division

//Signature//

CHRISTOPHER D. BREWER, Chief
Photonic Materials Branch
Functional Materials Division

//Signature//

TIMOTHY J. BUNNING, Chief
Functional Materials Division
Materials and Manufacturing Directorate

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14. ABSTRACT
To prepare cholesteric liquid crystalline nonlinear optical materials with ability to be vitrified on cooling and form long time stability cholesteric glasses at room temperature, a series of platinum acetylide complexes modified with cholesterol has been synthesized. The materials synthesized have the formula *trans*-Pt(PR_3)(cholesterol (3 or 4)-ethynyl benzoate)(1-ethynyl-4-X-benzene), where R = Et, Bu or Oct and X = H, F, OCH_3 and CN. A cholesteric liquid crystal phase was observed in the complexes R = Et, and X = F, OCH3 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, OCH_3 and F, the cholesteric pitch was determined to be 1.7, 3.4 and 9.0 μ, respectively.

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6. AUTHOR(S)

Thomas M. Cooper, Aaron R. Burke, and Douglas M. Krein - Materials and Manufacturing Directorate, Air Force Research Laboratory, Functional Materials Division

Ronald F. Ziolo, Eduardo Arias, and Ivana Moggio - Centro de Investigacion en Quimica Aplicada(CIQA), Boulevard Enrique Reyna

Albert Fratini - Department of Chemistry, University of Dayton

Yuriy Garbovskiy and Anatoliy V.Glushchenko - Department of Physics, University of Colorado at Colorado Springs

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

AFRL/RXAP
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750

Centro de Investigacion en Quimica Aplicada(CIQA)
Boulevard Enrique Reyna 140,25294
Saltillo, Coahuila, Mexico

Department of Chemistry
University of Dayton
Dayton, OH 45469

Department of Physics
University of Colorado at Colorado Springs
Colorado Springs, CO 80933

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Cholesteric liquid crystal glass platinum acetylides

Thomas M. Cooper,[1] Aaron R. Burke,[1] Douglas M. Krein,[1] Ronald F. Ziolo,[2] Eduardo Arias,[2] Ivana Moggio,[2] Albert Fratini,[3] Yuriy Garbovskiy,[4] Anatoliy V.Glushchenko[4]

[1]Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH, 45433
[2]Centro de Investigacion en Quimica Aplicada(CIQA), Boulevard Enrique Reyna 140,25294 Saltillo, Coahuila, Mexico
[3]Department of Chemistry, University of Dayton, Dayton, OH 45469
[4]Department of Physics, University of Colorado at Colorado Springs, Colorado Springs, CO 80933

ABSTRACT

To prepare cholesteric liquid crystalline nonlinear optical materials with ability to be vitrified on cooling and form long time stability cholesteric glasses at room temperature, a series of platinum acetylide complexes modified with cholesterol has been synthesized. The materials synthesized have the formula *trans*-Pt(P**R**$_3$)(cholesterol (3 or 4)-ethynyl benzoate)(1-ethynyl-4-**X**-benzene), where **R** = **Et**, **Bu** or **Oct** and **X** = **H**, **F**, **OCH$_3$** and **CN**. A cholesteric liquid crystal phase was observed in the complexes **R** = **Et**, 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 ^{o}C, then converted to a mixed crystalline/cholesteric phase and completely melted to an isotropic phase at 230 ^{o}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 ^{o}C, respectively. In the series **X** = **CN**, **OCH$_3$** and **F**, the cholesteric pitch was determined to be 1.7, 3.4 and 9.0 μ, respectively.

INTRODUCTION

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$_3$)$_2$L$_2$ including two photon spectroscopy. We have processed these chromophores into solid state optical elements[2] and glass-forming liquids[3]. To increase our understanding of the excited state behavior in a chiral environment, we synthesized platinum acetylides having a cholesteric liquid crystal phase. 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 proceeding we describe the liquid crystal behavior of a series of cholesterol-containing platinum acetylides having the general formula shown in Table 1. 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**.

EXPERIMENT

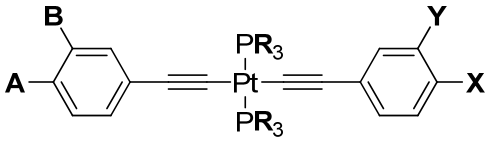
Table 1 lists the compounds we synthesized. The structure variations explored the effect of the length of the **R** group, *meta*- or *para*- cholesterol ester substitution(**A**,**B** and **Y**) and the effect of a para substituent(**X**). The method of thermal polarizing microscopy was used in order to characterize these materials[9]. ITO-glasses were covered with polyimide by spin-coating (20 s; 2,000 rpm), pre-baked (~80 ^{o}C, ~3-5 min) and baked (~180 ^{o}C, 1 hr). Polyimide layers were rubbed in anti-parallel directions with velvet cloth, then fiber spacers (3-5 μ) were sputtered over the surface of the one (bottom) of two substrates. Second (top) and the bottom substrates were clamped, and sealed with UV-glue (NOA65). An empty cell with powders of material on one of its edges was placed on the hot stage. The hot stage was heated above the melting temperature of the material under study until powders were melted, and the cell was filled due to capillary forces. The time required to fill empty cell was about 10-30 min.

Cholesteric pitch was determined 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 about 1 mrad. The cholesteric helix is perpendicular to the wedge substrates due to planar boundary conditions. When the cell gap increases continuously along the wedge, the integer number of half pitches increases in a discontinuous way through disclination lines. These lines can be observed experimentally. If S is a distance between two disclination lines, then the following expressions is used to calculate the pitch P:

$$\frac{P}{2 \cdot S} = \tan \beta$$

The main challenge of the experiments was to create alignment for all three liquid crystals as the process of their orientation requires usage of high temperatures. Common materials used in liquid crystal technologies fail at around 200 ^{o}C. To align these three liquid crystals we needed to warm our samples till approximately 250 ^{o}C and then cool them down slowly to induce the necessary planar alignment. To prepare high temperature cells, we sputtered inorganic SiO_x on a glass surface at oblique incidence. This inorganic material withstood higher temperature than those normally used in these experiments.

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	COOQ[2]	H	Et	COOQ	H
X	H	COOChol	Et	CN	H
XI	COOChol	H	Bu	CN	H
XII	COOQ	H	Et	CN	H

[1]Chol = Cholesterol [2]Q = $C_5H_{11}COOChol$

DISCUSSION

Phase behavior

Material **I** is a crystalline solid which melts to an isotropic phase at 231.2 ^{o}C. Material **II** has asymmetry with one meta-cholesterol ester and is a crystalline solid which melts to an isotropic phase at 121.6 ^{o}C. We added a polar **CN** group in material **III.** It exhibits polycrystalline phase at room temperature. The polycrystalline structure melts at ~ 170 ^{o}C to isotropic liquid at 180 C^{0} . On cooling to room temperature it shows isotropic texture. Material **IV** has **R** = **Et** and is a crystalline solid which melts to an isotropic phase 120-200 ^{0}C. Material **V**, **X** = **F**, exhibits a room temperature polycrystalline phase. The polycrystalline structure melts at ~ 175-220 ^{o}C . On cooling, a cholesteric phase appears in the temperature range 188.2 ^{o}C-160 ^{o}C (Fig 1A). At 160 ^{o}C crystallization takes place. Material **VI**, **X** = **CN**, exhibits a cholesteric phase at room temperature. In the range 130-140 ^{o}C, polycrystalline structure appears co-existing with cholesteric phase in the temperature range ~130 – 220 ^{o}C. At 228-235 ^{o}C, a transition to isotropic liquid occurs. MDSC measurements show crystallization and melting at 162-210 ^{o}C and a glass transition at 162-187 ^{o}C. A cholesteric phase appears at ~240 ^{o}C down to room temperature(Fig. 1B, Fig. 2). MDSC measurements on cooling show no crystallization signal. The polycrystalline Material **VII, X** = **OCH_3,** melts at ~235 ^{o}C, and the melting process to isotropic liquid is completed at 240 ^{o}C. On cooling, cholesteric phase appears at ~229 ^{o}C and the sample exhibits cholesteric phase in the temperature range 229 ^{o}C-188.8 ^{o}C (Fig 1C). At 188.8 ^{o}C crystallization takes place over 20-30 min.

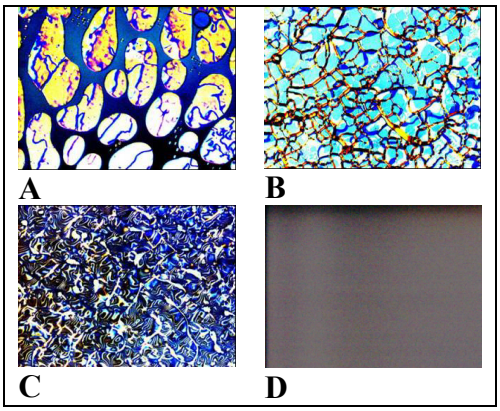


Figure 1. Selected photographs from thermal polarizing microscopy A: Material **V**, 175 ^{o}C, cooling, field of view: 500 x 750 µm; B: Material **VI**, 25 ^{o}C, cooling, field of view: 500 x 750

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.

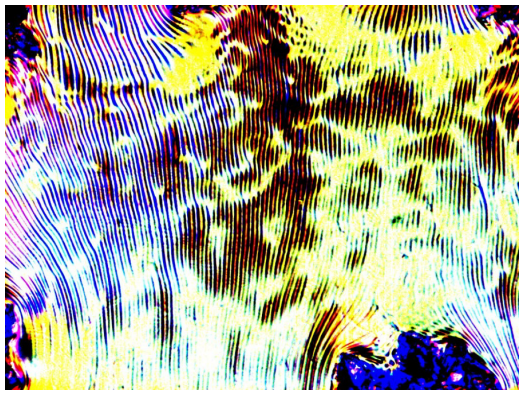


Figure 2. Cholesteric fingerprint texture observed in glassy thin film prepared from compound **VI**, field of view 260 x 340 μm.

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

Measurement of cholesteric pitch

Figure 3 shows photograph of samples used for cholesteric pitch determination. The optical microscope was used to measure the width of Cano - Grandjean stripes for material **VI**. In the case of materials **V** and **VII**, the optical microscope was not used in order to determine cholesteric pitch *P* due to the large values of *P*. In this instance, the wedge cell was heated on the hot stage, then it was taken out, placed between two crossed polarizers, and snapshots were taken. The cholesteric pitch *P* follows the substituent trend **X=F**(9.0 μ) > **OCH_3**(3.5 μ) > **CN(**1.7 μ). Cholesteric phase of material **VI** was characterized at high temperature (~150 °C) and at room temperature as the cholesteric phase was preserved at low temperatures as an overcooled state. In both cases the pitch was 1.7 μ. We performed Gaussian 09 DFT calculations(B3LYP/LANL2DZ) on methyl ester analogues of these compounds and found a calculated dipole moment trend **X=CN**(4.6 D) > **OCH_3**(3.2 D) > **F**(1.8 D) which is consistent with the observed cholesteric pitch trend.

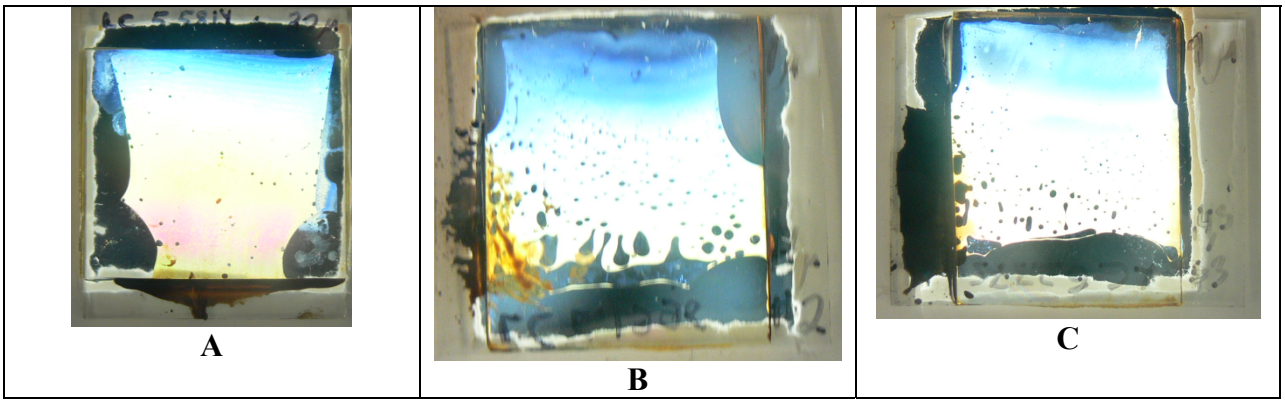


Figure 3. **A**: Photograph of wedge cell (β = 1.45 mrad) filled with material **VI** cooled to ~22 ^{o}C. **B**: wedge cell (β = 1.1 mrad) filled with material **VII**; colorful horizontal stripes are seen in the upper part of the picture(T=230 ^{o}C -190 ^{o}C). **C**: Wedge cell (β = 1.0 mrad) filled with material **V** on cooling(T=190 ^{o}C -160 ^{o}C); colorful horizontal stripes are seen in the upper part of the picture.

CONCLUSIONS

Figure 4 summarizes the phase behavior of these compounds. When **X** = **H**, no cholesteric phase is observed, but when **X** = polar group(**F**, **OCH$_3$** or **CN**), a cholesteric phase appears. When **R** = **Bu** or **Oct**, no cholesteric phase appears, but is observed with **R** = **Et**. Even though **X** = **CN** and **R** = **Et** in compound **X**, its bent geometry gives no cholesteric phase, while the linear geometry of compound **VI** gives a cholesteric phase. The substituent effects on phase behavior are consistent with cholesteric phase appearing in compounds that are chiral, have linear shape, good ability to pack and also the presence of a polar group.

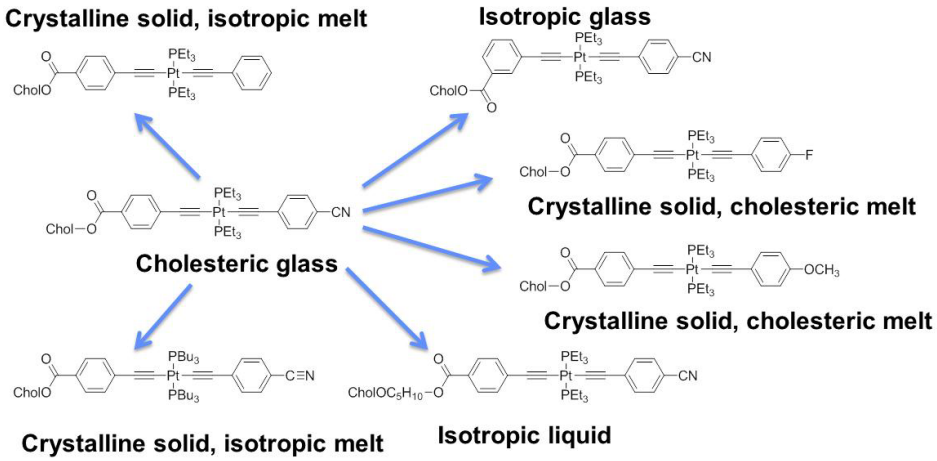


Figure 4. Summary of phase behavior

Materials **V**, **VI** and **VII** are monotropic: they form cholesteric mesophase only under cooling. In particular, compound **VI** forms an overcooled cholesteric glass at room temperature which remains stable up to 130 ^{o}C. Materials **V** and **VII** form a polycrystalline phase at room temperature. We are currently investigating chiral platinum acetylides with higher helical twisting power.

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REFERENCES

1. (a) J.E. Rogers, J.E. Slagle, D.M. Krein, A.R. Burke, B.C. Hall, A. Fratini, P.A. Fleitz, T.M. Cooper, M. Drobizhev, N.S. Makarov, A. Rebane, K.-Y. Kim, R. Farley and K.S. Schanze Inorg. Chem. 46, 6483 (2007); (b)J.E. Haley, D.M. Krein, J.L. Monahan, A.R. Burke, D.G. McLean, J.E. Slagle, A. Fratini and T.M. Cooper J. Phys. Chem. A 115, 265 (2011); (c) A. Rebane, M. Drobizhev, N.S. Makarov, E. Beuerman, J.E. Haley, D.M. Krein, A.R. Burke, J.L. Flikkema and T.M. Cooper J. Phys. Chem. A 115, 4255 (2011); (d) T.M. Cooper, D.M. Krein, A.R. Burke, D.G. McLean, J.E. Haley, J. Slagle, J. Monahan and A. Fratini, J. Phys. Chem. A 116, 139 (2012).
2. C. Liao, A.H. Shelton, K.-Y. Kim and K.S. Schanze ACS Appl. Mater. Interfaces, 3, 3225 (2011).
3. J.E. Slagle, T.M. Cooper, D.M. Krein, J.E. Rogers, D.G. McLean and A.M. Urbas Chem. Phys. Lett., 447, 65 (2007).
4. (a)T.J. Bunning, P.T. Mather, W. Barnes and P.J. Hood Liq. Cryst, 26, 557 (1999); (b) S.H. Chen, J.C. Mastrangelo and R. J. Jin Adv. Matl.,11, 1135 (1999).
5. H. Chen, D. Katsis, J. Mastrangelo, S. Chen, S. Jacob and P.J. Hood Adv. Matls. 12, 1283 (2000).
6. N.S. Kumar, S. Abraham, K. Ratheesh, N. Tamaoki, S. Furumi and S. Das J. Photochem. Photobiol. A: Chemistry 73, 207 (2009).
7. N. Tamaoki N. Adv. Matl. 13, 1135 (2001).
8. S. Furumi, Chem. Rec. 10, 394 (2010).
9. I. Dierking, I., *Textures of Liquid Crystals*, (Wiley-VCH Verlag Gmbh & Co., Weinheim, 2003)