

Highly Birefringent Materials Designed Using Coordination Polymer Synthetic Methodology**

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Dedicated to Professor Clifford C. Leznoff on the occasion of his 67th birthday

Materials with a large degree of anisotropy, both molecular and crystallographic, show a wide range of properties, such as piezoelectricity,^[1] ferroelectricity,^[2] nonlinear optics (NLO),^[3] and birefringence^[4,5] (the non-zero difference in the refractive index of a crystal in two perpendicular directions). Birefringence is exploited in many optical applications in which the isotropic equivalent would be more mechanically cumbersome. For example, birefringent crystals have been used to make lenses with two focal points and an improved depth of field relative to their isotropic counterparts.^[6] These lenses can be adapted for different frequency responses^[7] and are used in a variety of applications, such as common-path profilometry systems^[8] and compact-disk readers.^[9] Similarly, current NLO materials such as Si and GaAs (both of which belong to the cubic crystal class and show no birefringence), which are used in the communication industry to generate coherent light at frequencies where lasers are unavailable, suffer from low nonlinear coefficients and dephasing problems.^[10] Introducing birefringence into these systems has greatly increased the nonlinear coefficient and the coherence length, owing to phase matching.^[10–12]

The modular nature of coordination-polymer synthesis has been heavily utilized to target materials with useful magnetic,^[13–15] gas storage,^[16–18] sensor,^[19,20] and optoelectronic^[21] properties. Surprisingly, the rational design and synthesis of highly birefringent coordination polymers has not received much attention. The ability to judiciously choose a metal center, a chelating ligand, and a bridging ligand to tailor the overall physical and optical properties of the resulting polymer affords an exceptional design freedom in materials science.^[22,23] For example, we have shown that incorporating highly polarizable units such as mercury(II) into the 2D layer structure $[\text{Cu}(\text{tmeda})\{\text{Hg}(\text{CN})_2\}_2\{\text{HgCl}_4\}]$ ^[24] (tmeda = N,N,N',N'-tetramethylethylenediamine) and lead(II) into the $[\text{Au}(\text{CN})_2]^-$ -based coordination polymer $[\text{Pb}(\text{H}_2\text{O})\{\text{Au}(\text{CN})_2\}_2]$ ^[25] results in large birefringence values of $\Delta n = 0.0638$ and 0.070 , respectively. The only other birefringence value reported for a coordination polymer is $\Delta n = 0.105$ for $[\text{Ag}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}]$.^[26] Although these Δn values are very large in comparison with most solid materials (liquid crystals can have very large Δn values^[4]),^[27] they remain lower than the $\Delta n = 0.172$ for commercially utilized calcite. One design principle by which a more highly birefringent coordination polymer could be synthesized would be to modify the $[\text{Pb}(\text{H}_2\text{O})\{\text{Au}(\text{CN})_2\}_2]$ system by substituting the water molecule with a ligand having a high structural or polarization anisotropy, thereby forcing the polarizability or density (or both) of the resulting material to be strongly directionally dependent, which is a key for high optical anisotropy according to the Lorentz–Lorenz equation.^[28] In this light, the terpy ligand (2,2',6'2''-terpyridine) offers two important features. It contains three pyridine groups, which exhibit both a large polarization and large structural anisotropy.^[29] Furthermore, terpy is a tridentate, meridional capping ligand, which may afford a $[\text{Au}(\text{CN})_2]^-$ -based coordination polymer in which all neighboring terpy molecules are aligned face-to-face,^[30–32] this arrangement is not observed in the free ligand.^[33,34] As for Pb^{II} , its use in the design of functional coordination polymers is driven primarily by the many materials dependent on the presence of such a highly polarizable cation.^[35–38] Having delineated these design principles targeting high birefringence, we report the synthesis and structures of a series of coordination polymers of the form $[\text{M}(\text{terpy})\{\text{M}'(\text{CN})_2\}_2 \cdot (\text{H}_2\text{O})_x]$ ($\text{M} = \text{Pb}^{\text{II}}, \text{Mn}^{\text{II}}; \text{M}' = \text{Ag}^{\text{I}}, \text{Au}^{\text{I}}; x = 0-1/2$). By examining this series of structurally similar polymers, the effect of the metal centers and of a stereochemically active lone pair^[39–43] on the optical and structural anisotropy was determined. Overall, these polymers are extremely birefringent, with Δn values exceeding twice that of calcite.

The reaction of $\text{Pb}(\text{ClO}_4)_2$ with terpy and $\text{K}[\text{Au}(\text{CN})_2]$ in water/methanol (1:1) produced large plates of $[\text{Pb}(\text{terpy})\{\text{Au}(\text{CN})_2\}_2]$ (**1**), which grow perpendicular to the *b* axis.^[44] The structure consists of a Pb^{II} center in a distorted pentagonal-biprismatic geometry (Figure 1a), with a terpy ligand occupying three of the meridional sites with bond lengths of 2.495(13) and 2.539(8) Å. The remaining four coordination sites around the Pb^{II} center are taken up by cyano N donors from the linear cyanometalate, with axial and equatorial bond lengths of 2.623(9) and 3.016(15) Å, respectively. The large span of the bond lengths in **1** is attributed to

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[**] We are grateful to NSERC of Canada and Simon Fraser University for financial support. M.J.K. thanks Natural Resources Canada for an Internship. CFI and BCKDF funded the acquisition of the SEM instrument.

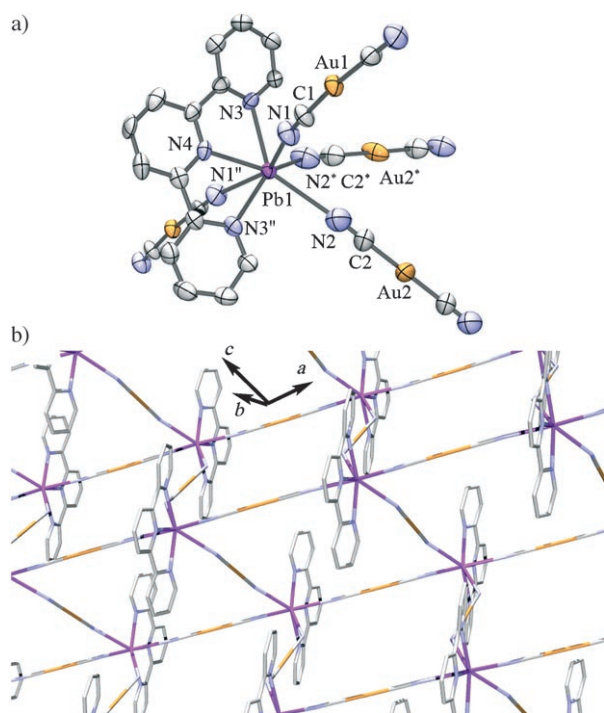


Figure 1. a) Local geometry of Pb^{II} in **1**; thermal ellipsoids are set at the 50% probability level. b) A 2D corrugated sheet of **1** showing all the terpy molecules aligned face-to-face. Water molecule removed for clarity. Selected bond lengths [Å]: Pb1–N1/1'' 2.623(9), Pb1–N2/2* 3.016(15), Pb1–N3/3'' 2.539(8), Pb1–N4 2.495(13).

the stereochemically active lone pair of s electrons on the Pb^{II} ion.^[39,40,45–47]

The {Pb(terpy)}²⁺ units are linked through the axial bonds to the cyano N donors, forming a 1D chain. These chains further link through the longer bonds to the equatorial cyanide ligands, thus forming the overall corrugated 2D (4,4) network (Figure 1b).^[48–50] The sheets stack through π – π interactions of approximately 3.27 Å.^[22] The metrical parameters for the isostructural [Ag(CN)₂][–] analogue **2** are comparable to those in **1**. Importantly, the terpy ligands are all aligned face-to-face in the crystal.

To probe the effect of the stereochemically active lone pair on both the structure and the birefringence, the Pb^{II} cation was replaced with Mn^{II}. Synthesized under similar reaction conditions, [Mn(terpy){Au(CN)₂}]₂·½ H₂O (**3**) consists of an octahedral Mn^{II} center having one terpy ligand and three N-bound [Au(CN)₂][–] groups in meridional geometries (Figure 2). Unlike the large range of bond lengths observed for **1** and **2**, those in **3** span only 2.179(17)–2.276(15) Å, owing to the lack of the extra lone pair on the isotropic high-spin d⁵ Mn^{II} center versus the d¹⁰s² Pb^{II} center. The axial [Au(CN)₂][–] units, which are perpendicular to the face of the terpy ligand, connect adjacent Mn^{II} ions to form an overall 1D chain. The major structural difference upon substitution of Mn^{II} for Pb^{II} is in the coordination number around the central metal ion (six vs. seven), which impacts the final dimensionalities in that **1** and **2** form 2D sheets while **3** remains 1D, forming a ladder through hydrogen bonds. Despite these differences, the key

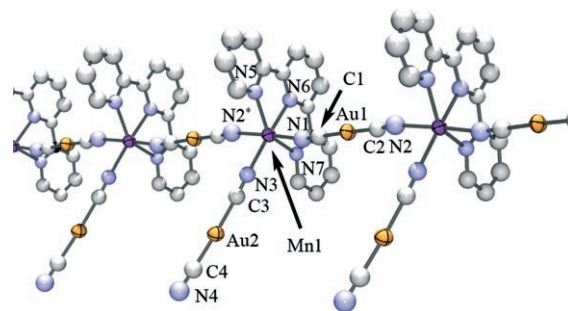


Figure 2. 1D chain of **3** showing the face-to-face alignment of terpy molecules; thermal ellipsoids for metal atoms are set at the 50% probability level. Neighboring chains are aligned parallel to that shown. Selected bond lengths [Å]: Mn1–N1 2.179(17), Mn1–N2* 2.217(17), Mn1–N3 2.186(15), Mn1–N5 2.276(15), Mn1–N6 2.231(14), Mn1–N7 2.247(14).

structural feature of terpy molecules aligned face-to-face, as found in **1** and **2**, is preserved in **3**.

The polymers **1–3** all crystallize in the monoclinic crystal class^[44] and are therefore biaxial, having three refractive indices that define the indicatrix (the ellipsoid defining the directional dependence of the refractive index). Since the *b* axis is the only axis of symmetry, one of the primary components of the indicatrix must coincide with the crystallographic *b* axis.^[51] The observed birefringence in the *ac* plane represents the difference between the remaining two primary components of the indicatrix. Accordingly, the birefringence of **1–3**, measured at 546 nm by means of polarized-light microscopy, yields values of $\Delta n = 0.396(8)$ for **1**, 0.43(4) for **2**, and 0.388(8) for **3**. Not only are these values larger than those reported for Hg^{II}- and Pb^{II}-based coordination polymers,^[24,25] they are significantly larger than that of the majority of inorganic compounds, including commercially utilized calcite ($\Delta n = 0.172$).^[27]

Viewed down the *b* axis, the Pb^{II} and Mn^{II} coordination polymers show similar features; all three materials are structurally anisotropic, having all of the terpy molecules aligned face-to-face in the *ac* plane (normal to the crystal-growth direction). In contrast, the two reported crystal structures of terpy do not have neighboring molecules aligned in such a manner.^[33,34] Ideally, the optical properties of **1–3** would be compared to the birefringence observed for terpy. However, terpy forms very low-quality crystals,^[33] and to date, to our knowledge, no birefringence measurements have been reported. However, the phenyl-based biphenyl and phenanthrene molecules show a polarization anisotropy comparable to pyridine, and Δn values of 0.384 and 0.372, respectively, have been reported.^[28] Furthermore, these compounds show similar structural features to terpy, in that neighboring molecules of both biphenyl and phenanthrene do not align face-to-face. While these organic moieties show optical anisotropies that are comparable to the polymers reported herein, their birefringence would theoretically be significantly higher if the molecular polarizabilities were aligned, as occurs in polymers **1–3**.^[29]

Substitution of the Pb^{II} center, with its stereochemically active lone pair, for the isotropic Mn^{II} ion elicited no

significant change in the birefringence. This finding is attributed to the location of the lone pair with respect to the measured birefringence direction. The lone pair is located along the *b* axis of the crystal, as evidenced by the bond lengths around the Pb^{II} centers in **1** and **2**.^[39] Thus, the anisotropy of the polarization around the Pb^{II} ion in the *ac* plane of crystals of **1** and **2** is primarily influenced by the terpy and cyanometalate moieties, which, in comparison with the Mn^{II} structure **3**, are relatively unchanged in the *ac* plane. The birefringence along the other pairs of the optical indicatrix may indeed be different in the Pb^{II} structures versus the Mn^{II} system, but the crystal-growth direction precluded measurements to clarify this point. However, on the basis of the indicatrix of biphenyl and phenanthrene and its relationship to the molecular polarizabilities, the remaining two birefringence values are expected to be lower.

Substituting Au^I with Ag^I also generated no significant change in the observed birefringence. However, long-term exposure of **2** to light photodegraded the polymer, thus indicating that [Ag(CN)₂][−] incorporation is actually detrimental. Although calculations for silver show a higher static polarizability than for gold, additional calculations on AgBr and AuBr suggest that the polarizability anisotropy is larger for AuBr;^[52] the observation that there is no difference in the optical anisotropy between **1** and **2** suggests that the optical anisotropies of gold and silver dicyanide are quite similar. That said, the use of the highly structurally anisotropic linear cyanometalates and their alignment in the crystal is vital to forming birefringent materials, as more commonly utilized hexacyanometalates would have isotropic polarizabilities.^[30]

In summary, a class of highly birefringent coordination polymers incorporating linear anionic cyanometalates and the terpy ligand were designed and prepared; the Δn values exceed twice that of calcite. The polarizability of the metal cation appears not to be a key factor, although the appropriate use of a metal cation as a platform to control ligand orientation and alignment is essential. Overall, the combination of the face-to-face alignment of the terpy molecules, aligned by the [M(CN)₂][−] units by incorporation into a highly ordered coordination polymer network, in concert with the inherently high optical anisotropy of both the pyridine-based ligand and the linear cyanometalate, produces the high birefringence of these coordination polymers. In addition, using the modular nature of coordination-polymer synthesis, hybrid multifunctional birefringent materials should also be readily attainable by judicious choice of the metal and the ancillary ligand. This work demonstrates that coordination polymers can be used to produce highly ordered systems that have extremely large birefringence values.

Experimental Section

General procedures: All manipulations were performed in air. All reagents were obtained from commercial sources and used as received. Infrared spectra were recorded as KBr pressed pellets on a Thermo Nicolet Nexus 670 FT-IR spectrometer. Microanalyses (C, H, N) were performed at Simon Fraser University by Mr. Miki Yang.

Caution: Although we have experienced no difficulties, perchlorate salts are potentially explosive and should only be used in small quantities and handled with care.

1: A methanol solution (5 mL) of 2,2',6'2''-terpyridine (terpy, 23 mg, 0.099 mmol) was added to a methanol/water solution (15 mL, 1:2) containing Pb(ClO₄)₂·3 H₂O (42 mg, 0.091 mmol). A methanol/water solution (20 mL, 1:1) of K[Au(CN)₂] (57 mg, 0.199 mmol) was added to the resulting pale yellow solution. After 24 h, single crystals of **1** had formed. The solution was allowed to evaporate slowly for one week, after which it was filtered, yielding pale yellow X-ray quality crystals. Yield: 47 mg (55 %). Elemental analysis (%) calcd for C₁₉H_{11.32}N₇Au₂PbO_{0.16}: C 24.21, H 1.21, N 10.41; found: C 23.94, H 1.28, N 10.36. IR (KBr): $\tilde{\nu}$ = 3110 (w), 3084 (w), 3017 (w), 2153 (s), 2137 (s), 2113 (w), 2097 (w), 1592 (br,m), 1579 (m), 1572 (m), 1565 (w), 1563 (m), 1479 (m), 1454 (w), 1449 (m), 1446 (m), 1433 (m), 1429 (w), 1396 (w), 1372 (w), 1363 (w), 1309 (m), 1295 (w), 1269 (w), 1242 (m), 1193 (w), 1168 (m), 1156 (m), 1113 (w), 1092 (w), 1074 (w), 1054 (w), 1040 (w), 1012 (m), 1007 (m), 978 (w), 899 (w), 825 (w), 802 (w), 777 (s), 737 (w), 723 (w), 667 (w), 655 (m), 649 (m), 635 (m), 522 (w), 501 (w), 427 cm^{−1} (w). Hydrothermal recrystallization generates very large single-crystal plates (8 × 2 × 0.5 mm³).

2: A methanol solution (5 mL) of terpy (23 mg, 0.099 mmol) was added to a methanol/water solution (15 mL, 1:2) containing Pb(ClO₄)₂·x H₂O (42 mg, 0.091 mmol). A methanol/water solution (20 mL, 1:1) of K[Ag(CN)₂] (43 mg, 0.216 mmol) was added to the resulting pale yellow solution. After 24 h, single crystals of **2** had formed. The solution was allowed to slowly evaporate for one week, after which it was filtered, yielding pale yellow X-ray quality crystals. Yield: 49 mg (71 %). Elemental analysis (%) calcd for C₁₉H₁₁N₇Ag₂Pb: C 30.02, H 1.46, N 12.90; found: C 30.21, H 1.55, N 12.65. IR (KBr): $\tilde{\nu}$ = 3105 (w), 3082 (w), 3073 (w), 3015 (w), 2140 (s), 2131 (m), 1593 (br,m), 1579 (m), 1573 (m), 1566 (w), 1562 (m), 1482 (m), 1480 (m), 1464 (w), 1454 (w), 1449 (m), 1447 (m), 1430 (m), 1428 (w), 1394 (w), 1307 (m), 1293 (w), 1270 (w), 1260 (w), 1242 (m), 1192 (m), 1166 (m), 1155 (w), 1113 (w), 1091 (m), 1074 (w), 1053 (w), 1047 (w), 1006 (m), 978 (w), 902 (w), 833 (w), 825 (w), 802 (m), 776 (s), 737 (w), 727 (w), 722 (w), 667 (w), 655 (m), 650 (m), 635 (m), 523 (w), 501 cm^{−1} (w).

3: A methanol/water solution (5 mL, 1:1) of terpy (23 mg, 0.099 mmol) was added to a methanol/water solution (5 mL, 1:1) containing MnCl₂·4 H₂O (20 mg, 0.101 mmol). A methanol/water solution (10 mL, 1:1) of K[Au(CN)₂] (57 mg, 0.199 mmol) was added to the resulting yellow solution. After 3 h, thin needles of **3** had formed. Larger X-ray quality single crystals of **3** were produced hydrothermally. Yield: 38 mg (48 %). Elemental analysis (%) calcd for C₁₉H₁₂N₇Au₂MnO_{0.5}: C 28.68, H 1.52, N 12.33; found: C 29.05, H 1.51, N 12.29. IR (KBr): $\tilde{\nu}$ = 3520 (br,s), 3437 (br,s), 3112 (w), 3105 (w), 3087 (w), 3074 (w), 3064 (w), 2170 (s), 2158 (m), 2151 (m), 1630 (w), 1593 (br,m), 1578 (m), 1571 (m), 1477 (m), 1475 (m), 1460 (w), 1450 (m), 1447 (m), 1438 (w), 1434 (m), 1338 (w), 1315 (m), 1297 (w), 1254 (w), 1247 (m), 1232 (w), 1186 (m), 1165 (m), 1158 (m), 1099 (w), 1093 (w), 1073 (w), 1051 (w), 1043 (w), 1020 (m), 1014 (m), 890 (m), 830 (w), 797 (w), 768 (w), 741 (w), 731 (w), 661 (m), 651 (m), 639 (m), 472 cm^{−1} (m).

The birefringence was measured on plate-shaped single crystals of **1**, **2**, and **3** by means of polarized-light microscopy utilizing an Olympus BX60 microscope. The optical retardation was measured using a tilting Berek compensator (3λ for **1**, 20λ for **2** and **3**) at the wavelength of λ = 546.1 nm at room temperature. The birefringence was calculated by dividing the measured retardation by the crystal thickness of 4.85(10) μm for **1**, 28(2) μm for **2**, and 32.7(7) μm for **3**. (The larger error in **2** is due to a larger variation in crystal thickness relative to **1** and **3**.) Crystal thicknesses were measured on an FEI 235 dual-beam SEM instrument.

Received: June 29, 2007

Published online: October 29, 2007

Keywords: birefringence · cyanides · gold · materials science · supramolecular chemistry

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- [44] Crystallographic data: **1** $C_{19}H_{11.32}N_7Au_0.16Pb_1$, $M_r = 941.9$, $0.22 \times 0.21 \times 0.04 \text{ mm}^3$, monoclinic, space group $C2/c$, $a = 11.2566(15)$, $b = 16.306(4)$, $c = 12.052(2) \text{ \AA}$, $\beta = 107.268(14)^\circ$, $V = 2112.4(7)$, $Z = 4$, $\rho_{\text{calcd}} = 2.960 \text{ g cm}^{-3}$, $\mu = 21.827 \text{ mm}^{-1}$, $\lambda = 0.70930$, $T = 293$, $2\theta_{\text{max}} = 55$, 2529 reflections were collected, of which 1657 were significant ($I > 2.5\sigma(I)$), $R = 0.0317$, $wR = 0.0393$, min/max residual electron density: $-1.36/0.97 \text{ \AA}^{-3}$. **2** $C_{19}H_{11}N_7Ag_2Pb_1$, $M_r = 760.3$, $0.23 \times 0.19 \times 0.18 \text{ mm}^3$, monoclinic, space group $C2/c$, $a = 11.3836(14)$, $b = 16.413(3)$, $c = 11.867(2) \text{ \AA}$, $\beta = 106.294(11)^\circ$, $V = 2128.0(6)$, $Z = 4$, $\rho_{\text{calcd}} = 2.373 \text{ g cm}^{-3}$, $\mu = 9.733 \text{ mm}^{-1}$, $\lambda = 0.70930$, $T = 293$, $2\theta_{\text{max}} = 55$, 2556 reflections were collected, of which 1564 were significant ($I > 2.5\sigma(I)$), $R = 0.0369$, $wR = 0.0335$, min/max residual electron density: $-0.71/0.83 \text{ \AA}^{-3}$. **3** $C_{19}H_{11.67}N_7Au_0.5Pb_1$, $M_r = 794.9$, $0.28 \times 0.14 \times 0.06 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 10.567(2)$, $b = 17.521(3)$, $c = 12.336(2) \text{ \AA}$, $\beta = 110.333(15)^\circ$, $V = 2141.6(7)$, $Z = 4$, $\rho_{\text{calcd}} = 2.465 \text{ g cm}^{-3}$, $\mu = 14.269 \text{ mm}^{-1}$, $\lambda = 0.70930$, $T = 293$, $2\theta_{\text{max}} = 48$, 3519 reflections were collected, of which 1809 were significant ($I > 2.5\sigma(I)$), $R = 0.0442$, $wR = 0.0399$, min/max residual electron density: $-0.88/1.23 \text{ \AA}^{-3}$. All crystal structures were collected on an Enraf Nonius Cad4 diffractometer. The structures were solved using direct methods and refined by least-squares procedures in CRYSTALS.^[53] CCDC-650152 (**1**), 650153 (**2**), and 650154 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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