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Enantioselective Synthesis of a Chiral Coordination Polymer with Circularly Polarized Visible Laser[**]

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Abstract: *Circular dichroism is known to be the feature of a chiral agent which has inspired scientist to study the interesting phenomena of circularly polarized light (CPL) modulated molecular chirality. Although several organic molecules or assemblies have been found to be CPL-responsive, the influence of CPL on the assembly of chiral coordination compounds remains unknown. Herein, a chiral coordination polymer, which is constructed from achiral agents, was used to study the CPL-induced enantioselective synthesis. By irradiation with either left-handed or right-handed CPL during the reaction and crystallization, enantiomeric excesses of the crystalline product were obtained. Left-handed CPL resulted in crystals with a left-handed helical structure, and right-handed CPL led to crystals with a right-handed helical structure. It is exciting that the absolute asymmetric synthesis of a chiral coordination polymer could be enantioselective when using CPL, and provides a strategy for the control of the chirality of chiral coordination polymers.*

Modulation of molecular chirality is an important topic for biochemistry, pharmaceutical chemistry, environmental chemistry, agricultural chemistry, supramolecular chemistry, etc.[1] The study of enzymatic mechanisms has inspired scientists to modulate molecular chirality by adopting a homochiral agent.[2] Considering the limited species of natural homochiral agents and high cost of artificial homochiral agents, several physical strategies have been investigated, including photoinduction (polarized or unpolarized light),[3] vortex stirring,[4] sonic wave modulation,[5] etc. Circularly polarized light (CPL) has been investigated for the control of chirality in azobenzene-containing compounds,[6] amino-acid derivatives,[7] π-conjugated polyfluorene or thioxanthene derivatives,[8] and helical polymers with a ketone-containing group.[9] In early studies, investigations focused on the CPL-responsive behavior of small organic molecules in solution.[6k,7c–e,8b,10] Recently, polymer films,[6a–f,7a,8a,9a] liquid crystals,[6g–i,9b] and nanoparticles[6j] have shown CPL-responsive activity, and gave rise to the development of optical switching, optical storage, and light-driven devices. The successful modulation by CPL in the enantioselective synthesis and switching of chirality in these organic assemblies suggests the potential for the similar modulation of chiral coordination polymers (CCPs).

CCPs have attracted much attention because of their potential applications in asymmetric catalysis,[11] chiral resolution,[12] ferroelectric,[13] nonlinear optical effects,[14] etc. Scientists have constructed a number of CCPs from achiral starting materials in the absence of any chiral agents.[15] However, the enantioselective synthesis of these CCPs is challenging, and the prediction for the absolute configuration of these CCPs is impossible.[16] We started thinking about the possibility of the enantioselective synthesis or chirality switching for CCPs through using CPL. The high degree of polymerization and crystallinity for a CCP might make the chirality switch, by using CPL, in crystalline phase difficult. In contrast, there are some reports about CPL-induced resolution of chiral chromium(III) systems in solution, and suggests the possibility of enantioselective resolution for simple chiral coordination compounds in the liquid state by using CPL.[17] In 2009, Vlieg et al. reported a solid-liquid mixture containing an amino-acid derivative which was CPL-responsive during crystallization process,[7b] and thus motivated us to study the enantioselective behavior of CCPs during a reaction and crystallization under CPL irradiation.

A reported chiral copper(II) CCP,[16,18] $[\{P/M\text{-Cu(succinate)(4,4'-bipyridine)}\}_n]\cdot(4\,H_2O)_n$ was chosen because of its interesting crystallization process. This CCP adopts a three-dimensional network structure which includes a $[\text{Cu(succinate)}]_n$ helical configuration. In 2007, Long, Zheng et al. studied spontaneous resolution during the crystallization, thus showing either an optically inactive conglomerate after fast crystallization (one day) or homochiral crystal clusters after slow crystallization (2–7 weeks).[16] The specific handedness of the crystal was not predictable because of the lack of systematic bias in favor of one particular enantiomer over the other.

Circular dichroism (CD) spectra (Figure 1a) for the pair of enantiomers $[\{P\text{-Cu(succinate)(4,4'-bipyridine)}\}_n]\cdot(4\,H_2O)_n$ and $[\{M\text{-Cu(succinate)(4,4'-bipyridine)}\}_n]\cdot(4\,H_2O)_n$ were taken,[19] thus revealing two sets of Cotton effects in the

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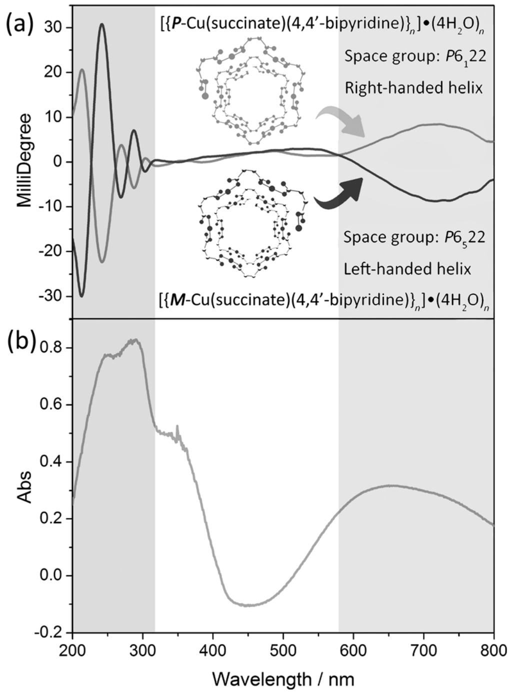

Figure 1. Solid-state CD spectra (a) and UV/Vis spectra (b) of [{*P*/*M*-Cu(succinate)(4,4′-bipyridine)}$_n$]·(4 H_2O)$_n$. Inset graph: the representation of [Cu(succinate)]$_n$ helical configuration for the title compound. The crystal structural data adopted were obtained from CCDC-653396 and 653413 in the Cambridge Crystallographic Data Centre.

ranges of $\lambda = 200$–320 nm and 580–800 nm, effects which could be attributed to the π–π* transition of 4,4′-bipyridine and d–d transition of copper(II). Compared with the corresponding UV/Vis spectra (Figure 1 b), the charge-transfer absorption band at about $\lambda = 350$ nm is missing in the CD spectrum, and indicates there is little difference in absorbance between L- or R-CPL at this wavelength. The wavelength of the CPL used would thus be chosen to be that between UV light ($\lambda = 200$–320 nm) and visible light ($\lambda = 580$–800 nm). In the early stage of crystallization, mass spectra (see Figures S1 and S2 in the Supporting Information) for the reacting solution was taken to study the coordination assembly process. The major species in solution are H-succinates (*m*/*z* cal. 117.0188, ESI (−), 117.0182), 4,4′-bipyridine (*m*/*z* cal. 156.0687, ESI (+), 157.0764), and $[Cu(succinate)(H_2O)_2(NH_3)(OH)]^-$ (*m*/*z* cal. 248.9910, ESI (−), 248.8937), which provide a clue that the self-assembly of the title compound begins with the coordination of copper(II) and succinate. A minor species at *m*/*z* 295.9601 is attributed to $[Cu(succinate)(H\text{-}succinate)]^-$ (cal. *m*/*z* 295.9588), which supports the conjecture. In contrast, the 4,4′-bipyridine ligand serves as a bridged linker in the structure, and connects the [Cu(succinate)]$_n$ helical chains to form a three-dimensional network. The role of 4,4′-bipyridine is assumed to direct the assembly process along with the phase transformation, but not influence the chirality of assembly. In this context, CPL within the visible-light region may function as a chiral modulator.

Considering the reaction and crystallization of the title compound takes some time, the light source needed to be a device which offers stable light at a certain wavelength. A diode laser device ($\lambda = 635$ nm, 200 mW) was chosen as the light source, and was run continuously for four days. L- and R-CPL were generated by using a polarizer and a quarter-wave plate. In a typical run, a solution containing $[Cu(NH_3)_4]^{2+}$ (0.5 mmol), succinate (1.5 mmol), 4,4′-bipyridine (0.5 mmol), water (10 mL), and ethanol (10 mL) was prepared and kept in cuvettes at a pH of about 9.2. Either the L- or R-CPL beam was set to transmit through the lower portion of the cuvette. Blue crystals of the title compound were obtained in three to four days. The crystalline phase and purity were characterized by X-ray powder diffraction (see Figure S3). To discuss the response efficiency, zones with and without direct CPL irradiation were identified and the crystals were harvested from each zone (Figure 2). The crystals were separated into 1) those grown in the light zone, indicating that they were bathed in the CPL irradiation (labelled *Light-L* and *Light-R* for zones irradiated by L-CPL and R-CPL, respectively), and 2) those grown in the dark zone which lies beyond the direct CPL irradiation (labelled *Dark-L* or *Dark-R*).

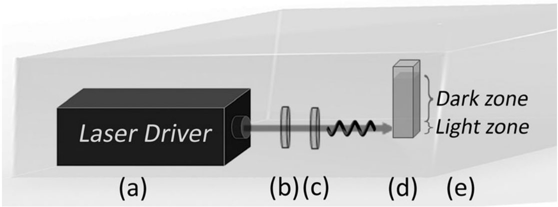

Figure 2. CPL irradiation apparatus: a) $\lambda = 635$ nm red diode laser driver, b) polarizer, c) quarter wave plate, d) cuvette as reaction container, e) dark room.

To exclude errors (cuvette leak during crystallization, or green by-product contaminated sample), 92 samples were harvested and analyzed by solid-state CD spectroscopy using a KCl disk and a wavelength range of $\lambda = 500$–800 nm. As shown in Figure 3, most of the samples exhibit distinguishable CD signals, which indicate the enantiomeric excess feature of the samples. Compared with the study in the previous report, little enantiomeric excess phenomena was observed for the fast crystallization process in the absence of either CPL or any other chiral induction.[16] Thus the CPL irradiation seems to influence the fast crystallization to deliver an enantiomeric excess.

Furthermore, the influence of CPL chirality on the handedness of the resulting crystals was studied. Because the signal intensity of the solid-state CD spectra greatly depends on the preparation of the sample disk, only the positive, negative, or silent CD signals are discussed. For Figure 3, 15 out of 19 *Light-L* samples exhibit negative CD signals (Figure 3 a), while 18 out of 20 *Light-R* samples exhibit positive CD signals (Figure 3 b). The opposing Cotton effects shown by *Light-L* and *Light-R* suggest the correlation between CPL chirality and crystals' handedness. A similar correlation was observed in the CD spectra of *Dark-L* and *Dark-R* samples, but with more dissonance. Table 1 summarizes the statistical distribution for the CD signals of the 92 CD spectra, thus revealing L-CPL irradiation always leads to

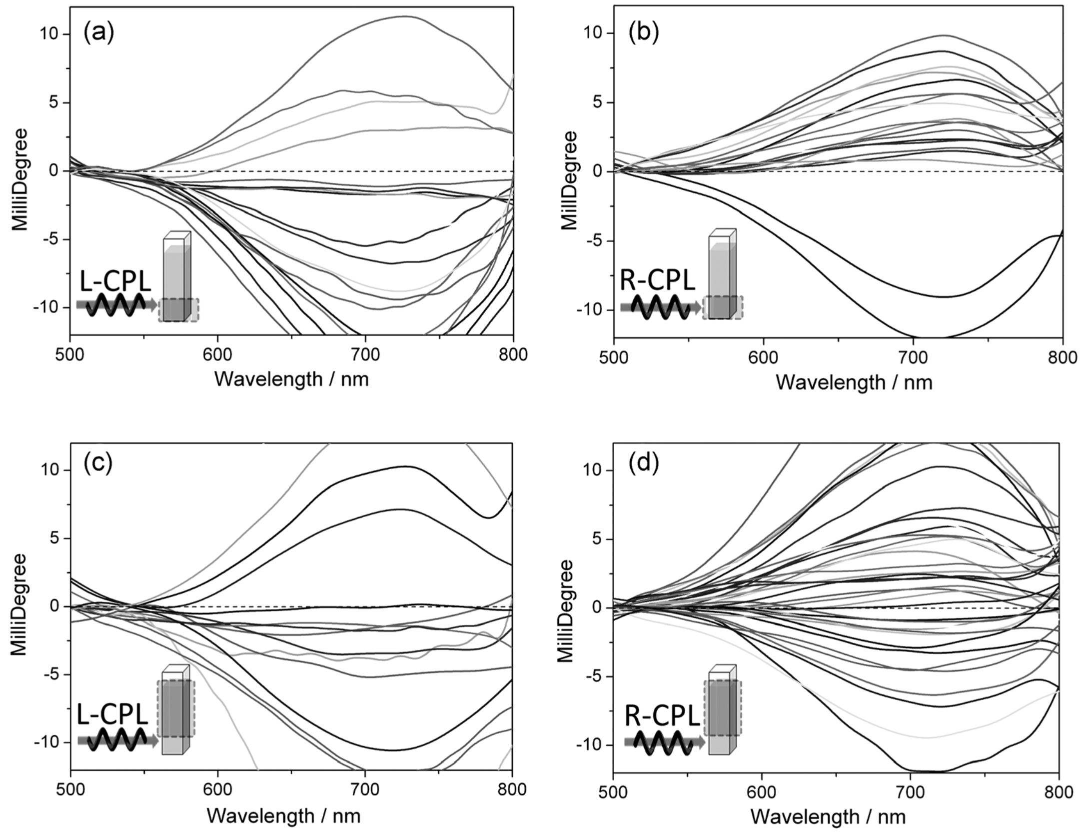

Figure 3. Solid-state CD spectra for a) *Light-L*, b) *Light-R*, c) *Dark-L*, and d) *Dark-R* samples.

Table 1: Statistical distribution for CD signals of samples.

Entry	Total number	(+) CD	CD (silent)	(−) CD	η value [%]
Light-L	19	4	0	15	58
Light-R	20	18	0	2	80
Dark-L	15	4	1	10	40
Dark-R	38	23	1	14	24

negative CD signals, while R-CPL irradiation favors positive signals. As shown in Figure 1, positive and negative CD signals represent *P* and *M* configurations, respectively, for the title compounds which feature the corresponding right-handed or left-handed helical structure. As a result, the CPL irradiation shows significant influence on the enantioselective synthesis of the title compounds. The specific correlation is that R-CPL irradiation leads to crystals with a right-handed helical structure and L-CPL irradiation leads to crystals with a left-handed helical structure.

The enantioselectivity of each entry is considered by imitating the concept of enantiomeric excesses (*ee*). An η value is calculated by dividing the difference value by the sum value. Take the first entry *Light-L*, for example, where the difference value is equal to 15 minus 4, and the sum value is 15 plus 4. Consequently, the η value for *Light-L* is 58%. As shown in the last column of Table 1, the η values for four entries are all higher than zero, which indicates enantioselectivity. However, all η values are less than 100%, especially for the *Dark-L* and *Dark-R* samples, for which crystals are grown beyond the CPL irradiation.

Based on the above finding, an impact mechanism of CPL on the enantioselective synthesis of the title compound is proposed. According to the mass spectrum study, the reaction substrates first assemble to form the precursor $[Cu(succinate)(H_2O)_2(NH_3)(OH)]^-$. When the ammonia evaporates gradually, the excessive succinate anions coordinate with the precursor, thus generating $[Cu(succinate)(H\text{-}succinate)]^-$, which was observed in the mass spectrum. The small amount of this species indicates it might be an intermediate for the next assembly step. Since $[Cu(succinate)(H\text{-}succinate)]^-$ is negatively charged, it is possible to coordinate with the cupric cations into fragments $[Cu(succinate)]_x$. The fragments may be highly reactive with 4,4′-bipyridine, and would result in the three-dimensional structure and immediate phase transformation. In previous studies, this assembly procedure occurred with spontaneous resolution, thus leaving the racemic mixture in the fast crystallization sample.[16] In this study, enantioselective results exist under CPL irradiation. Since crystallographic analysis revealed that the crystal structure of the title compound includes the $[Cu(succinate)]_n$ helical configuration, there is a good chance that the fragment $[Cu(succinate)]_x$ is helical and chiral. Perhaps, the CPL irradiation excites the chiral helical fragment $[Cu(succinate)]_x$ into a preferential configuration, which directs the enantioselective assembly.

However, we note that the circular dichroism effect of a chiral compound is always small, which means the different extents for the absorption of two types of CPL by an enantiomer is not large. In this context, the CPL irradiation could be absorbed by both enantiomeric precursors in the reaction, but to different extents. As shown in Figure 1, the Cotton effect of the title compound in the visible-light region is weaker than that in the UV-light region. As a consequence, it is exciting to observe the enantioselective results by adopting a circularly polarized visible light. The various magnitudes of the CD spectra in Figure 3 remind us that partial racemization may occur. Although the magnitudes of the CD spectra are the comprehensive contribution of the sampling process and the optical purity, those weak magnitudes, such as those at less than 5 MilliDegree, might be the result of partial racemization. The major reason may be the weak circular dichroism effect in the visible-light region, which could also explain why the η values for *Light-L* and *Light-R* samples are lower than 100%. Another reason may be the size mismatch between the laser spot (diameter ca. 3 mm) and the cuvette (diameter 10 mm). *Dark-L* and *Dark-R* samples present some enantioselectivity, which may be the result of sharing a common cuvette with the Light-zone.

In summary, the enantioselective synthesis of a CCP by the involvement of CPL in the visible-light region was achieved, with at most 80% enantioselectivity. In general, R-CPL irradiation induces the growth of crystals with a right-handed helical structure, while the L-CPL irradiation leads to crystals with left-handed helical structure. This work provides a good avenue to study the enantioselective synthesis of CCPs without using any chiral agents.

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