COMMUNICATION

Molecular Ordering-Enhanced Circularly Polarized Luminescence of Chiral 1,10-Phenanthroline Derivatives

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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2,9-Bis(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanoxy)-1,10-phenanthroline [2,9-di-*L*-menthoxy-1,10-phenanthroline] (Men2Phen) and 2,9-bis(2-(*S*)-methylbutoxy)-1,10-phenanthroline (MB2Phen) were synthesized as chiral derivatives of 1,10-phenanthroline (Phen). Differences in rigidity and bulkiness of the chiral substituents at the 2- and 9-positions of Phen backbone led to distinctive molecular dissymmetry in the ground state resulting in remarkable differences in circular dichroism. Men2Phen exhibited efficient circularly polarized luminescence (CPLm) at anisotropy factor of 10^{-2} in the solid state order based on molecular ordering disclosed by X-ray crystal analysis while it showed much lower anisotropy factor in solution. MB2Phen which was rather amorphous and did not afford good crystal showed only negligible CPLm both in the solid state and in solution.

Chirality plays important roles in life as well as in functions of synthetic materials. While asymmetric catalysis and molecular recognition have been focused in chirality sciences for a long while, a rather newer aspect is circularly polarized luminescence (CPLm). Circularly polarized light (CPL) is composed of the wave of electromagnetic field rotating in a plane perpendicular to the wave direction, and the rotation can be right or left handed, which may be connected to chirality of molecules emitting CPL. In the development of CPLm materials, high efficiency as well as controlled colors is a main target of research. In order to increase CPLm efficiency, various molecules and macromolecules in addition to their hybrids have been studied so far.[1-3] In many cases, highly rigid and ordered chiral structures resulted in high anisotropy factor (g_{lum}) ($g_{lum} = 2(I_L - I_R)/(I_L + I_R)$ where I_L and I_R are intensities of left-handed and right-handed CPL): noticeable examples include helicenes and derivatives[4-7] and systems with intermolecular ordering.[8,9] In a sharp contrast, even unregulated, amorphous polymers and those combined with small molecules have been reported to lead to highly efficient CPLm.[10,11]

However, exact reasons of efficient CPLm have not been unambiguously presented in the literature. One reason for this situation is that at direct comparison of the same molecule in different states, *i.e.*, ordered and disordered intermolecular structures from a view of CPLm efficiency is not necessarily feasible. In this context, herein we report the synthesis of the two chiral 1,10-phenanthroline (**Phen**) derivatives, 2,9-bis(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanoxy)-1,10-phenanthroline [2,9-di-(1*R*,2*S*,5*R*)-menthoxy-1,10-phenanthroline] (**Men2Phen**) and 2,9-bis(2-(*S*)-methylbutoxy)-1,10-phenanthroline (**MB2Phen**) and their CPLm in solution and in the solid state (crystal or amorphous) (Fig. 1). It was found that crystal formation remarkably enhances CPLm efficiency in the case of **Men2Phen**. While Phen and derivative have been studied mainly from a view of chelating ligands for asymmetric catalysis,[12-16] emission properties have also been investigated. Though Phen shows rather weak emission,[17] structural modification has been reported to enhance emission efficiency.[18]

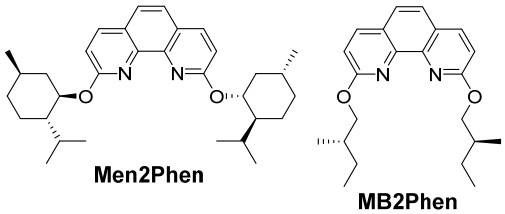

Fig. 1 Chiral Phen derivatives.

The synthesis was straightforward where Phen was first modified into the quaternary salt of 1,3-dibromopropane which was oxidized and then chlorinated at the 2- and 9-positions (Scheme 1). 2,9-Dichloro-1,10-phenanthroline was reacted with sodium (1*R*,2*S*,5*R*)-menthoxide and sodium 2-(*S*)-methylbutoxide derived from the

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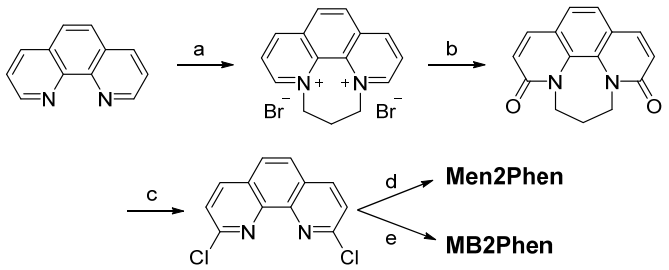
Electronic Supplementary Information (ESI) available: Experimental procedures and supplementary figures. See DOI: 10.1039/x0xx00000x

corresponding alcohols as chirality source modified to result in **Men2Phen** and **MB2Phen**, respectively. The synthetic and analytical details are found in electronic supplementary information (ESI). Because the last step of the synthesis is simple ether formation, this synthetic methodology would be applicable to the production of a wider variety of chiral Phen derivatives starting from different alcohols.



Scheme 1 Synthesis of **Men2Phen** and **MB2Phen**. [a]1,3-dibromopropane, nitrobenzene, 130 °C. [b]*t*BuOK, O_2, tBuOH, 40 °C, 20 h, 84%. [c]PCl_5, $POCl_3$, 135-140 °C. [d]NaH, (-)-(1*R*,2*S*,5*R*)-menthol, DMF, 100 °C, 12 h, 48%. [e]NaH, (S)-(-)-2-methylbutanol, DMF, r.t..

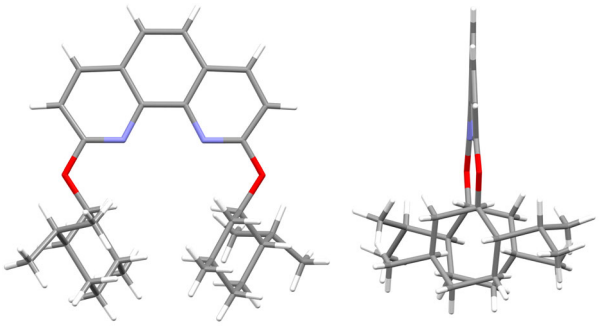


Fig. 2 Crystal structure of **Men2Phen**: views orthogonal to each other.

The structures of the two Phen derivatives were identified by NMR spectroscopy and mass spectrometry. The structure of **Men2Phen** was further confirmed by X-ray crystal analysis (Fig. 2). **Men2Phen** has a C2 symmetric conformation in crystal in which the Phen backbone and the two cyclohexyl rings are arranged roughly orthogonal to each other, creating a chiral space surrounded by the Phen backbone and two menthoxy groups. Attempts to obtain crystals of **MB2Phen** suited for X-ray analysis have so far been unsuccessful. **MB2Phen** appeared rather amorphous.

Chirality of **Men2Phen** and **MB2Phen** was studied by circular dichroism (CD) spectra in EtOH solution and in the solid state (cast film) (Fig. 3). Both **Men2Phen** and **MB2Phen** showed CD signals based on aromatic electronic transitions in EtOH, indicating that the Phen backbone is given dissymmetry by menthoxy and 2-methylbutoxy groups at the 2- and 9-positions (Fig. 3 A-D). It is notable that **MB2Phen** showed less intense CD responses than **Men2Phen** (Fig. 3 A) while the two Phen derivatives exhibited similar molar absorption coefficients in the UV spectra. These observations suggest that 2-methylbutoxy group is less efficient than menthoxyl group in inducing chirality to the Phen backbone.

The two Phen derivatives showed CD responses also in the solid state (cast film) (Fig. 3 E,F). The film CD spectra are the products of averaging four independent spectra taken at four orientations of the samples differing in angle by 90 degrees to minimize the effects of linear dichroism. As well as in solution, **Men2Phen** showed greater g_{CD} values than **MB2Phen** in the solid state ($g_{CD} = 2(\varepsilon_L - \varepsilon_R)/(\varepsilon_L + \varepsilon_R)$ where ε_L and ε_R are molar absorptivity toward L- and R-CPL). CD effects in the solid state may arise from molecular dissymmetry also in the solid state.

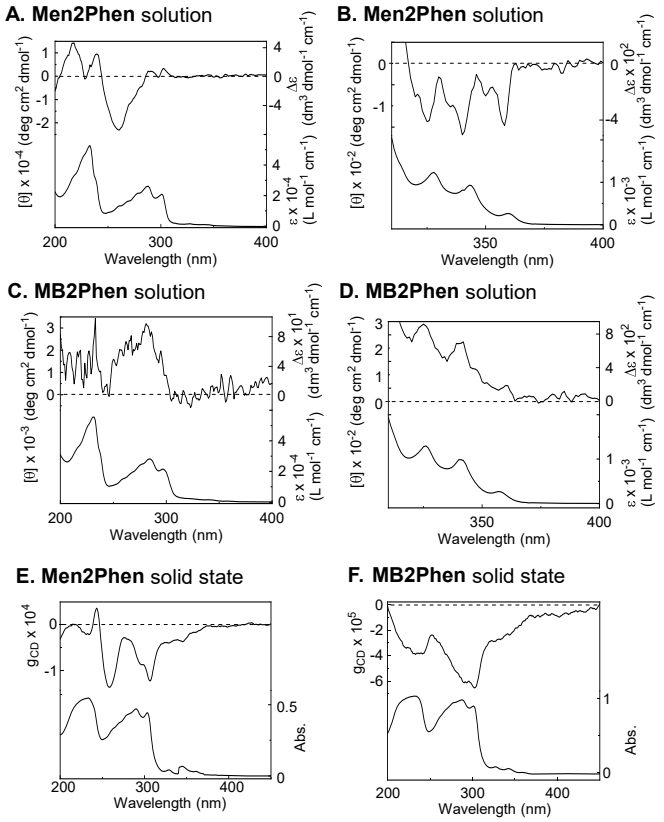


Fig. 3 CD-UV spectra of **Men2Phen** at 3.0 x 10^{-4} M in 1-mm cell (A) and at 6.0 x 10^{-4} M in 10-mm cell (B) in EtOH solution, those of **MB2Phen** at 3.0 x 10-4 M in 1-mm cell (C) and at 6.0 x 10^{-4} M in 10-mm cell (D) in EtOH solution, and those of **Men2Phen** (E) and **MB2Phen** (F) in cast film on quartz glass (solid state). The spectra in E and F were obtained by averaging spectra measured at four orientations of films differing in angle by 90 degrees (Fig. S2, S3 in ESI).

In order to understand the remarkable differences between the CD spectra of **Men2Phen** and **MB2Phen**, the structures of the two derivatives as well as that of Phen were optimized by DFT calculations, and the optimized conformations were examined in terms of selected internal dihedral angles (Fig. 4), which were indicated through simulation workflows to highly affect the chiral conformation.[19] All the examined dihedral angles of unsubstituted Phen were 180 degrees, indicating that this molecule has a completely flat conformation (Fig. 4 C). In a sharp contrast, the conformation of **Men2Phen** is slightly but clearly deviated from flatness characterized by the dihedral angles of around 176-178 degrees, resulting in a slightly dissymmetric conformation (Fig. 4 A). On the other hand, the examined dihedral angles of **MB2Phen** were closer to 180 degrees, indicating that the Phen backbone of **MB2Phen** is far less dissymmetric than that of **Men2Phen** (Fig. 4 B). The dissymmetry of **Men2Phen** appears to arise from steric repulsion between the two menthoxy groups while the two 2-methybutoxy groups of **MB2Phen** seem to have no steric interactions with each other.

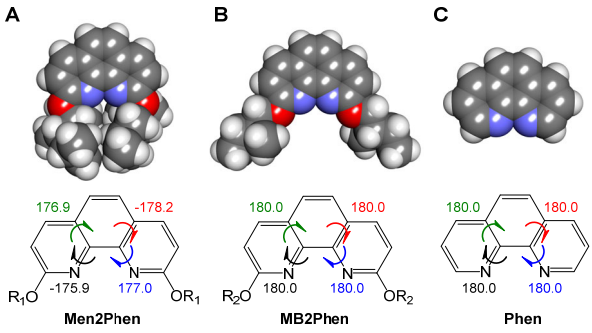


Fig. 4 Selected dihedral angles (degree) in the DFT-optimized structures of **Men2Phen**, **MB2Phen**, and **Phen**. [DFT conditions: WB97XD/6-31G(d); R_1 = *L*-menthyl, R_2 = 2-(*S*)-methylbutyl]

Next, CPLm properties of the two Phen derivatives were examined in film (solid state) and in solution. **Men2Phen** exhibited highly efficient, negative CPLm in the range of 350-460 nm with a remarkably high g_{lum} value of the order of 10^{-2} in film (Fig. 5 A). **Men2Phen** also showed negative CPLm in solution, but the g_{lum} value was much lower than in film (Fig. 5 B). This suggests that the efficient CPL may arise from molecular ordering in the solid state. On the other hand, **MB2Phen** showed CPLm of positive sign whose g_{lum} value was much lower than that of **Men2Phen** in film (Fig. 5 C), and **MB2Phen** showed only negligible CPLm in solution (Fig. 5D).

Emission lifetime (τ) was estimated to be 3.5 ns and 3.8 ns for Men2Phen and MB2Phen, respectively, in EtOH solution and 3.9 ns and 4.3 ns for Men2Phen and MB2Phen, respectively, in film (Fig. S10 in ESI). Also, quantum yield of emission was determined to be 19% for both Men2Phen and MB2Phen, respectively, in EtOH solution and 18% for both Men2Phen and MB2Phen, respectively, in film (Fig. S11 in ESI). The fact that the four τ values and the four emission quantum yields are rather similar may mean that the emission mechanism is similar in all cases in Fig. 5 apart from chirality.

In addition, the antipode of **Men2Phen** synthesized from 2,9-dichloro-1,10-phenanthroline and sodium (1*S*,2*R*,5*S*)-menthoxide showed CD and CPL spectra which were virtually mirror images of those of **Men2Phen** (Figs. S6, S8 and S9 in ESI). These results confirm that the chiroptical properties discussed so far are reliable.

To understand why **Men2Phen** showed the remarkable CPLm in film, spectral properties of this compound were calculated in excited states and in the ground state[20] for the unit cell of single crystal including an ensemble of four molecules. (Fig. 6 A). The molecular ordering of the unitary cell well describes the 2_1 helix pitch of the crystal, essential for accurate chiroptical properties predictions. Calculation methodology details are found in ESI. The simulated CD spectrum indicated negative signals in the range of around 350-380nm which roughly coincide with the experimental CD spectrum in film (Fig. 3 E and Fig. 6 B), supporting that the film CD may arise from dissymmetry of the molecular arrangement.

However, the exact molecular order responsible for the CD and CPLm spectra could differ from those in crystal because full structural details of the film samples are not yet clear including whether it is partially crystalline at the present time.

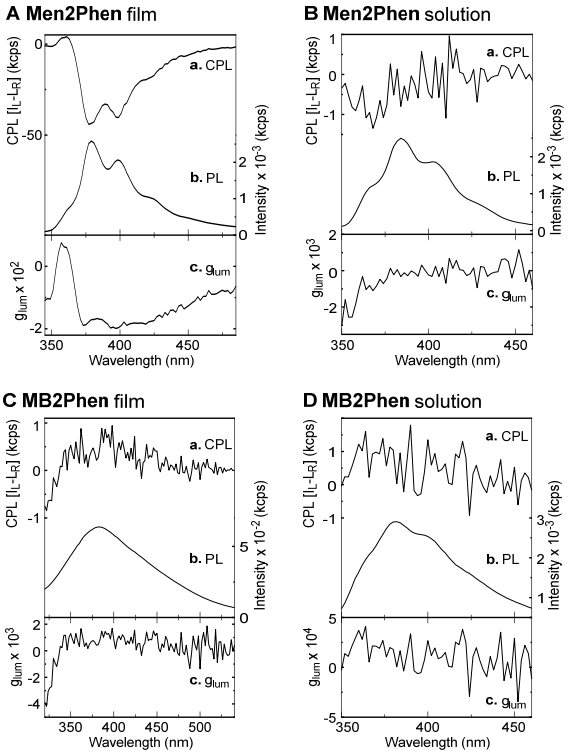


Fig. 5 CPLm (a), total emission (PL) (b), and g_{lum} (c) spectra of **Men2Phen** (A) and **MB2Phen** (C) in thin film, and those of **Men2Phen** (B) and **MB2Phen** (D) in dioxane solution at 7.0 x 10^{-4} M in 10-mm cell. The spectra in A and C were obtained by averaging spectra measured at two orientations of films differing in angle by 90 degrees (Fig. S4, S5 in ESI). [λ_{ex} 260 nm]

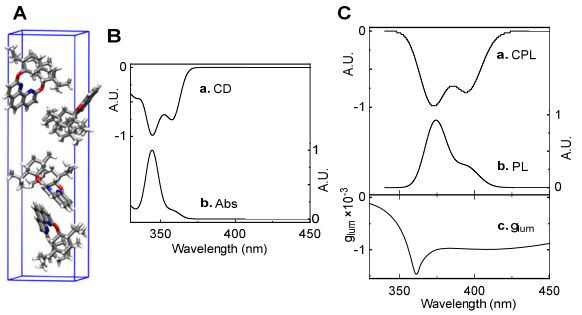


Fig. 6 Unit cell structure including four **Men2Phen** molecules (**A**) and theoretical CD (a) and absorbance (b) spectra (**B**) and theoretical CPLm (a), total emission (PL) (b), and g_{lum} (c) spectra (**C**) calculated for the ensemble of the four **Men2Phen** molecules.

In addition, the simulated PL spectrum has peaks in the range of 400-350 nm, which is in line with the experimental PL spectrum (Fig. 5 A b and Fig. 6.C b). Further, the intense CPL and glum spectra whose shape and position agree with the experimental CPL and glum spectra were reproduced for the excited-state four-molecule ensemble (Fig. 5 A a, c and Fig. 6 C a, c).

These results indicate that the observed intense CPLm of **Men2Phen** arise mainly from molecular ordering while single molecule of this compound is not a very efficient CPL emitter as evidenced by the solution CPLm properties in Fig. 5 B. This aspect is supported by the simulated CPLm spectrum of Men2Phen as single molecule showing much lower intensities than the unit cell model (Fig. S12 in ESI). Though the reason why **MB2Phen** showed only moderate CPLm even in film is not yet clear, this compound as single molecule may not have a sufficiently dissymmetric structure as suggested by the DFT calculations (Fig. 4). In addition, molecular arrangements of **MB2Phen** in film may not be sufficiently ordered, which may have a connection with the fact that this molecule has not resulted in good crystals for X-ray analysis.

In conclusion, the two chiral **Phen** derivatives were synthesized, and their chiroptical properties were studied in the ground state and excited states. The rigid, cyclic, and bulky menthoxy groups of **Men2Phen** appear to play a role in inducing a dissymmetric conformation to the **Phen** backbone in the ground state leading the CD spectra with higher intensity that those of **MB2Phen** having the more flexible chiral groups. **Men2Phen** exhibited CPLm with a remarkably high g_{lum} of the order of 10^{-2} on the basis of molecular ordering in the solid state, not of the single molecular chirality while it showed much lower g_{lum} value of emission in solution. On the other hand, **MB2Phen** appearing amorphous showed low g_{CD} values both in solution and in the solid state, supporting the importance of molecular ordering in enhancing CLPm. **Men2Phen** may fall into the category of CPLm materials whose high g_{lum} values arise from molecular ordering, not from single molecular structure.[21] Although identifying exact molecular arrangements responsible for CPLm is not necessarily feasible by experiments, it was conducted by high-precision simulations of molecular cluster in the present work.

Acknowledgements

We thank Prof. T. Nakamura of Hokkaido University for allowing access to the Rigaku XtaLAB P200 diffractometer and Hamamatsu Photonics is acknowledged for the emission lifetime measurements. Technical Division of Institute for Catalysis, Hokkaido University is acknowledged for general technical support. This work was supported by the MEXT/JSPS KAKENHI for Grant Numbers JP 24K01534 and JP 19H02759, MEXT Joint Usage/Research Center for Catalysis, the MEXT program of the Integrated Research Consortium on Chemical Sciences (IRCCS), the Italian Ministry for University and Research (MUR) and University ''Magna Græcia'' of Catanzaro under PON ''RICERCA E INNOVAZIONE'' 2014–2020, ASSE IV ''ISTRUZIONE E RICERCA PER IL RECUP- ERO'' AZIONE IV.4 ''DOTTORATI E CONTRATTI DI RICERCA SU TEMATICHE DELL0INNOVAZIONE'' D.M. 1062/2021 program, the research program PRIN 20228PH3JX, and the CINECA award under the ISCRA initiative for the availability of high-performance computing resources and support.

Data availability

The data supporting this article have been included as part of the ESI.

Conflicts of interest

There are no conflicts to declare.

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