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学位論文題名	Synthetic Studies of Pyrene Oligomers and Their Functionalization Aiming at Circularly Polarized Luminescence ピレン多量体の合成と官能基化、および円偏光発光挙動に関する研究 (英文)
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【論文の内容の要旨】

Circularly polarized luminescence (CPL), is the differential emission of right- and left circularly polarized light of chiral molecules in the excited state. A variety of applications have been proposed for CPL and/or CPL active materials including three-dimensional displays, quantum computers, fluorescence sensors, and so on. Because of its designability, axially chiral 1,1'-Bi-2-naphthol (BINOL) has been used widely in CPL science; however, its poor physical properties, low quantum yield, and small anisotropy factors ($|g_{em}|$); have hindered the development of this science. To enhance the properties of BINOLs, our group expanded the π -system of BINOLs and reported pyrene-based axially chiral molecules, 1,1'-bi-2-pyrenols (bipyrenols). The quantum yield of bipyrenol was much enhanced, $\Phi_f = 0.57$, comparing with that of BINOL, $\Phi_f = 0.04$. Therefore, bipyrenol showed clear CPL spectrum. This thesis aims at obtaining some CPL active molecules having large anisotropy factors, i.e., large ($|g_{em}|$) value. In this thesis, I designed and prepared the optically pure pyrene tetramers from optically pure bipyrenyl menthyl ester which proceeded stereoselectively. These tetramer had more intense CD bands and higher quantum yield (0.79) and $|g_{em}|$ (1.3×10^{-3}) than those of bipyrenol (0.57 and 3.6×10^{-4} , respectively). To further improve the chiroptical properties including CPL, I performed the oligomerization of optically pure bipyrenol, which afforded the tetramer, hexamer and octamer of pyrene incredibly, diastereoselectively. The synthesized hexamer and octamer have more enhanced CPL properties and will make them suitable candidate for CPL active material.

The second chapter describes the revised work on previous bipyrenol configuration. From the beginning of my thesis work I faced some problem with the previous stereochemistry of bipyrenol. So I revised the previous work. In case of previous bipyrenyl chemistry, rac-bipyrenol was converted into the corresponding menthylcarbonate by treatment with (-)-menthyl chloroformate. The separation of dia-menthylcarbonate were achieved by conventional SiO₂ chromatography to afford two fractions, the first fraction having R_f = 0.38 (F1) and the second fraction having R_f = 0.27 (F2). Here the first fraction was assigned as (*R*) configuration and the second fraction as (*S*) configuration. The revised work was done by comparing of ¹H NMR and HPLC analysis of F1-Bi-Py-Ment with previous (*R*) Bi-Py-Ment, comparing of CD spectra F1 and F2-Bi-Py-Ment with previous (*R*) and (*S*) -Bi-Py-Ment and finally studying Single Crystal X-ray diffraction analysis of F1-Bi-Py-OH with previous (*R*) Bi-Py. The revised result was also done by making Mosher esters of optically pure bipyrenols and from their Single Crystal X-ray diffraction analysis. From the ¹H NMR, HPLC and CD spectra it can be said that (*R*)- Bipyrenol and my F1-Bi-Py-OH are the same compound. Single crystal analysis of my F1-Bi-Py-OH, showed that it was (*S*)-configuration. Using this (*S*)-configuration we can explain further dimerization of my tetramer chemistry as well my imine chemistry and Mosher's acid chloride chemistry, which is not possible by using the previous configuration. So it can be concluded that some errors were occurred in the handling of the samples for the measurement of previous X-ray samples.

Chapter three illustrates an alternative synthesis of bipyrenol. Chiral 1,1'-bi-2-pyrenols (bipyrenols) which showed clear circularly polarized luminescence (CPL) compare to BINOL, was synthesized by classical method, *i.e.*, the oxidative coupling reaction of 2-pyrenol with FeCl₃ in ethanol. However, this method requires the skill of organic synthesis because of the instability of hydroxypyrene. Then menthyl carbonate was introduced to separate the *R* and *S* bipyrenol. Considering the wide application of bipyrenol, I developed a simple and high-yield alternative synthesis in this chapter. My revision is simple, just switch the reaction order. Unstable hydroxypyrene is protected with menthyl carbonate, first, then oxidative coupling is carried out to afford the corresponding pyrene dimer. In marked contrast to our previous method, *i.e.*, the oxidation of 2-hydroxypyrene, the revised method was a clean and high yield reaction. By optimizing the reaction conditions, the yield of the alternative synthesis was increased to 88% in this chapter. My revised synthetic method could contribute to the application of bipyrenol in various fields of chemistry, including asymmetric synthesis, molecular recognition, and advanced materials, and could be used in the synthesis of new π -expanded axially chiral molecules.

In chapter four the functionalization of 1,1'-bi-2-pyrenol (bipyrenol) was carried out. For the

application of bipyrenol in advanced materials chemistry such as bio-imaging fluorophore, its absorption and emission should be occurred in visible region to avoid the deterioration caused by UV-ray. Considering these context, functionalizations of bipyrenol were examined. I focused on the introduction of imine via aldehyde on the 3- and 3'-positions of bipyrenol, because this functional group is quite effective to induce bathochromic shift for dyes and fluorophores. Then corresponding imines were produced by reacting with aniline, *p*-nitroaniline and *p*-anisidine respectively. Using the reaction condition estimated for racemic compound, the corresponding optically pure compounds were synthesized. The structure of (*R*)-phenyl imine bipyrenol was determined by X-ray diffraction studies. Then absorption and emission spectra were measured for these imine compounds. Both absorption and emission spectra were red shifted compare to bipyrenol. Substituents also induced the shift of the bands, for example, the bands of methoxy and nitro compounds were observed at 416 and 431 nm compare to unsubstituted one (404 nm) respectively. As the substituents are attached the terminal of these molecules, these significant shifts seem to be strange. To understand the electronic structure of my imines, theoretical studies were carried out. The calculation showed that the energy levels of the frontier orbitals are changed depending on the substituents, that is, electron donating methoxy group unstabilizes and electron withdrawing nitro group stabilizes the orbitals. The CD and CPL properties of these imine compounds were also measured. They have low quantum yield and for this reason the corresponding $|g_{\text{abs}}|$ and $|g_{\text{em}}|$ were not so enhanced.

Chapter five deals with the design, synthesis and chiroptical properties of optically pure bipyrenyl carboxylic acids. At first the esters derivatives were prepared by the reaction of methylbromoacetate with optically pure bipyrenol. Then performed hydrolysis and got the corresponding carboxylic acid derivatives. The ester and the corresponding carboxylic acid compounds have been characterized by the $^1\text{H-NMR}$ and mass spectra. The optically pure bipyrenyl carboxylic acid showed strong cotton effect on CD spectra and also showed intense CPL signal with mirror image relationship. The band-shapes and absorption energies of carboxylic acids measured in CHCl_3 and dimethylformamide (DMF) were different at low concentration. This behavior suggests that electronic interaction occurred between DMF solvent and carboxylic acid, which is absent in CHCl_3 . At low concentration reverse phase is found in CPL spectra which is very important in security tags system.

The last chapter represents the design, syntheses and chiroptical properties of optically pure tetramer, hexamer and octmer of Pyrene. The quantum yield of bipyrenol was much enhanced, $\Phi_f = 0.57$, comparing with that of BINOL, $\Phi_f = 0.04$. So I further expand the π system to enhance the chiroptical properties. In this chapter the target compounds were synthesized by three different pathways. In the first attempt, I designed and prepared the optically pure pyrene tetramers having menthyl ester. The synthesis was carried out by the dimerization of the optically pure dimers by

$\text{Cu}(\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$. Surprisingly, this dimerization proceeded stereoselectivity, *i.e.*, (*S*)-bipyrenyl menthyl ester afforded (*S,S,S*) tetramer- and (*R*)- bipyrenyl menthyl ester afforded (*R,R,R*) tetramer. Menthyl carbonate groups were removed to afford Tetrapyrenol. Because of the instability of hydroxyl group under ambient condition, the corresponding ethyl ether derivatives were prepared and used for physical and chiroptical properties measurements. The structures of tetramer were unambiguously determined by X-ray diffraction studies. These tetramer had more intense CD bands and higher quantum yield (0.79) and $|\text{g}_{\text{em}}|$ (1.3×10^{-3}) than those of bipyrenol (0.57 and 3.6×10^{-4} , respectively). In the second attempt, the starting was the optically pure mono-substituted bipyrenyl menthyl ester, which on dimerization by $\text{Cu}(\text{OTf})_2$ produced optically pure tetramer, hexamer and octamer of pyrenyl mono menthyl ester. On hydrolysis they produced optically pure tetrapyrenol, hexapyrenol and octapyrenol. By Williamson ether synthesis the corresponding ether were produced. In the third attempt, I performed the oligomerization of optically pure bipyrenol by $\text{Cu}(\text{OTf})_2$, which also afforded the tetramer, hexamer and octamer of pyrene incredibly, diastereoselectively. The synthesized hexamer and octamer have more enhanced CPL properties which will make them suitable for application in this area.

In conclusion the revised work absolutely determined the proper configuration of bipyrenol. The alternative synthetic method of bipyrenol was easy and gave higher yield. Then functionalization of bipyrenol were carried out by imine formation via Duff formylation as well as making carboxylic acid of bipyrenol. Finally, I carried out further oligomerization of bipyrenol, which proceeded stereoselectively and produced tetramer, hexamer and octamer, which have increased chiroptical properties compare to that of bipyrenol.