Chapter 1
Frontiers of Circularly Polarized Luminescence Chemistry of Isolated Small Organic Molecules

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Abstract Lately, circularly polarized luminescence (CPL), differential left- and right-polarized emission from chiral materials, has been attracted great attention, especially that of small organic molecules (SOMs). Despite the fact that the luminescence dissymmetry factor (g_{lum}) of SOMs, a measure of degree of chirality in CPL, is typically in a range of 10^{-3} to 10^{-5}, considerably smaller than those based on materials with forbidden transition, the value of SOM-based CPL materials are progressively revised upwards. This trend is primarily due to the fact that a structural modification of SOMs is permanently rational and relatively easy, allowing a straightforward control of absorption and/or emission wavelengths as well as luminescence intensity. Biological compatibility and ease of device fabrication are additional advantages of SOM-based CPL materials. In this chapter, we outline the basics of CPL such as a definition and a quantification. Then, we briefly discuss about an information attained by the CPL measurement of SOMs. Finally, a perspective on the rapid progress of SOM-based CPL materials is provided.

1.1 Introduction

In whole of the following chapters of this book, you will soon find the recent advances of circularly polarized luminescence (CPL) behaviors of isolated small organic molecules (SOMs) and some related phenomena. Before going into individual topic in details, we briefly outline in this first chapter the basic concept and technical details of CPL. These include a definition of CPL, a quantification of CPL intensity, and an information attained by the CPL measurement. This chapter may be skipped for the specialists; however, we provide this fundamental information focusing on for those who are relatively new to this field, to facilitate a further reading. At the end of this chapter, a blight perspective on latest development of

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future CPL materials is also provided, demonstrating the rapid evolution of SOMs-based CPL chemistry in the last 5 years.

1.2 Background

Circularly polarized luminescence (CPL) represents a difference of incidental emission of left- and right-handed circularly polarized light from chiral materials (Fig. 1.1). The phenomenon can be observed, in principle, at the atomic, molecular, as well as supramolecular levels, necessarily involving chiral substances and/or surroundings. Such a polarized luminescence may be induced even for achiral systems by the external applied field (such as magnetic field), but we only focus on in this book the "*natural*" CPL that occurs through the electronic transition in the absence of external field. As a whole, emissions from both singlet and triplet (as well as other) electronically excited states are similarly treated without distinction between fluorescence and phosphorescence, unless the cases when a particular emphasis is placed. First of all, the CPL measurement is attractive and powerful means to elucidate the chiral information in their emissive excited states, complemental to its ground-state analog, circular dichroism (CD). Recently, the materials with strong CPL intensity (usually defined by a dissymmetry factor, vide infra) has been attracting great attention due to their promising applications in advanced photonic materials for chiral devices, enantioselective sensing systems, and biomedical applications, more specifically 3D displays, OLED materials, optoelectronic devices, spintronics devices, security painting, information storage, and so forth. More recently, functional CPL materials responsive to various stimuli such as pH, chemicals, temperature changes, mechanical forces, or light have been also developed as smarter chiroptical switching devices.

At the early stage of CPL chemistry, the CPL spectrum was only measured on a custom-made instrument, limiting such measurement only to the spectroscopist. This instrumental limitation unquestionably hampered the progress of CPL chemistry for a certain period. Now, the instrument becomes commercially available, facilitating to obtain reliable and reproducible CPL spectra expanding into other relevant fields

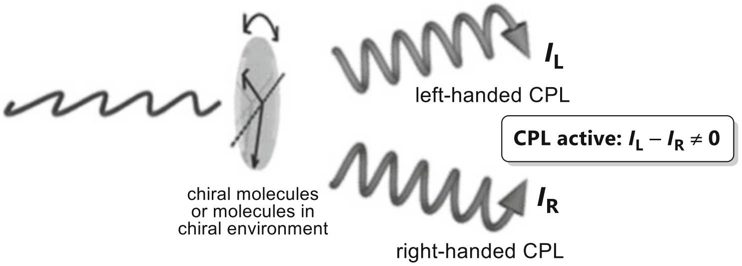

Fig. 1.1 Circularly polarized luminescence (CPL) obtained from or with chiral substances

(including organic chemistry) and to systematically attain the structure-property relationship. As a consequence, the development of new CPL emitters becomes an active field of research, particularly for the last 5 years, by rationally designing materials with improved dissymmetry factors. Amongst the CPL active compounds, lanthanide complexes, especially those based on europium or terbium, are normally reported for greater CPL responses. Recently, self-assembled materials, liquid crystals, and polymers provide more efficient CPL responses, thanks to a supramolecular chirality, typically with at least one order of magnitude improved luminescence dissymmetry factors than simple SOMs. Nevertheless, the study on the CPL responses of SOMs becomes more and more attractive, probably because SOMs have some intrinsic advantage over the other materials. Hypothetically, their fluorescence efficiency, absorption and emission wavelengths and the bandwidths, and degree of dissymmetry can be rationally controlled by logical and relatively facile structural modifications. Additional advantages may be biological compatibility for in vivo sensing and ease of fabrication and manufacturing for electronic and photonic devices. You will soon find a variety of such efforts on SOMs and related systems in the following chapters, by focusing on the nature of respective structural motifs. In recent CPL research on SOMs, special emphases are placed on the π-π^* transition of extended aromatic systems.

In addition to the materials chemistry standpoint, the CPL spectroscopy is valuable to elucidate the configurational and/or conformational information of optical active molecules in their emissive excited states, although the molecules under investigation must be reasonably luminescent. On the contrary, the information obtained through the CD spectroscopy is based on the thermally equilibrated electronic ground state. In principle, CD and CPL are mutually complementary probes for the structural features of chiral molecules in the different electronic states. When the structural differences and the vibrational contributions can be negligible, the structural information provided by the two chiroptical methods becomes similar. In practice, combination of CD and CPL spectroscopies provides a wealth of information concerning the structural differences in their ground and excited states. The CPL spectroscopy also provides information concerning the excited-state dynamics and energetics along the photophysical consequences from the initial absorption to the emission event. A necessity of fluorophore seems disadvantage at a glance, but can be beneficial for its selectivity and specificity. The CPL active emissive state may be accessible either by direct excitation, by indirect energy transfer process, or by relaxation from the higher excited state, which is in sharp contrast to the CD spectral technique, where the band overlap or small absorption may disturb the accurate analysis.

As stated by the Frank-Condon principle, electronic transition (both absorption and emission) always occurs instantly without accompanying geometrical change, represented as the vertical transition. According to the Kasha's rule, luminescence occurs from the lowest electronically excited state, typically in the S_1 state (or T_1 state in the triplet manifold). Therefore, information obtained by the CPL is responsible to S_1 to S_0 electronic transition, parallels to that of the lowest-energy CD, where

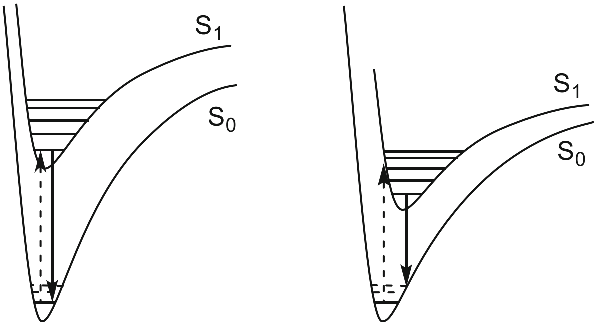

Fig. 1.2 Potential energy surfaces in the ground (S_0) and excited (S_1) states with negligible (left) and typical (right) geometry change in a rigid aromatic system, exemplified by the transverse S_1 surface displacement. Absorption (CD) and emission (CPL) processes are indicated by dashed and solid arrows, respectively

S_0 to S_1 transition is involved (Fig. 1.2). Emission in condensed phase, however, generally occurs from the vibrationally relaxed state, which is different from the Frank-Condon state. In other words, depending on the nature of the excited-state potential surface of molecules under study, the degree of relaxation (or structural change) is different to a certain degree. Nevertheless, the absorption and emission spectra are usually mirror-imaged each other with a small energy gap called the Stokes shift, particularly in the rigid π-systems (for which most of the chapters focusing on in this book). In such systems, the potential energy surfaces and the vibrational frequency and spacing are comparable between the S_1 and S_0 states. As a result, the same sign and comparable magnitudes of dissymmetry factors are anticipated in the CPL and CD spectra. Still, the measurement of CPL spectrum, in comparison with CD spectrum, characterizes the valuable structural differences between the ground and electronically excited states of the chiral molecules. Readers are directed to further discussion on this issue in "Perspective" section.

1.3 Definition

When chiral molecules or molecules in chiral environment are excited with an unpolarized light in a typical CPL spectroscopy, the observed intensity of light emission is oscillated between (I + ΔI) and (I − ΔI) by a polarizing modulator. Thus, total intensity

$$I = I_L + I_R$$

and the difference

$$\Delta I = I_L - I_R$$

are simultaneously determined, where I_L and I_R are the emission intensities of left- and right-handed circularly polarized light. Because the evaluation of absolute I and ΔI values is generally difficult, degree of chirality is generally discussed in terms of dissymmetry factor of luminescence, g_{lum}, which is defined by the difference emission divided by an averaged emission intensity, as follows:

$$g_{\mathrm{lum}} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)} = 2\frac{\Delta I}{I}$$

The index g_{lum} is occasionally called as luminescence anisotropy factor or more simply g factor. Note that the emission anisotropy is also used to quantify a linearly polarized luminescence; therefore, dissymmetry is a probably more favorable term. By definition, minimum and maximum g_{lum} factors are -2 and +2.

In most of recent studies to explore the CPL responses in molecular and supramolecular systems primarily concern the g_{lum} value, as this parameter has been always the most limiting factor, especially in small organic molecules where g_{lum} values are typically in an order of 10^{-3} to 10^{-5} range. However, in order to fully compare the overall CPL efficiency, it should be more appropriate to consider other photophysical parameters beside the polarization efficiency (i.e., dissymmetry factor), such as efficiencies of light absorption (oscillator strength, f) and emission intensity (quantum yield, Φ). The magnitude of f for an electronic transition is related to the maximum molar absorption coefficient (ε) and full width at half maximum of the absorption band ($\Delta\nu$):

$$f \quad \propto \quad \varepsilon \times \Delta\nu$$

Accordingly, a circular polarization luminosity (Λ_{CPL}) from the single chiral molecule in the excited state is described as follows, defined as an intrinsic CPL efficiency based on a single chiral molecule or matter:

$$\Lambda_{\mathrm{CPL}} = f \times \Phi \times \frac{|g_{\mathrm{lum}}|}{2} \quad \propto \quad \varepsilon \times \Phi \times |g_{\mathrm{lum}}|$$

By definition, the Λ_{CPL} values should be in the range between 0 and 1. Assuming comparable band-shape ($\Delta\nu$), Λ_{CPL} becomes proportional also to ε. The latter term, $\varepsilon \times \Phi$, is commonly referred to as molecular brightness B. In principle, the materials with larger Λ_{CPL} (or g_{lum} within the similar systems assuming the brightness is comparable) values at the desired excitation and emission wavelengths are considered as favorable chiroptical materials.

From a theoretical point of view, the emission intensities (as well as absorption intensities) f are proportional to the dipole strength D produced by the action of electromagnetic radiation on an electric dipole of substances. The value D is defined as the square of the electric transition dipole moment (etdm, $\boldsymbol{\mu}$) for the electronic transition between the emissive state j and ground state i, where $\boldsymbol{\mu}$ is a real vector:

$$D = \langle \Psi_j | \boldsymbol{\mu} | \Psi_i \rangle^2$$

As stated by Rosenfeld equation, the CPL (as well as CD) spectra are characterized by an analogous parameter, which is referred to as a rotational (or rotatory) strength R. To describe a rotation of the coordinate system, a magnetic transition dipole moment (mtdm, $\boldsymbol{m}$) is given as a purely imaginary vector. From a product of wavefunction overlap integrals, R can be expressed as follows:

$$R = \mathrm{lm}\left[\langle \Psi_j | \boldsymbol{\mu} | \Psi_i \rangle \cdot \langle \Psi_i | \boldsymbol{m} | \Psi_j \rangle\right]$$

where Im refers to an imaginary component of the scalar product between $\boldsymbol{\mu}$ and $\boldsymbol{m}$. In most situations, it can be also stated that:

$$R = |\boldsymbol{\mu}| \cdot |\boldsymbol{m}| \ \cos\theta$$

where θ is the angle between the two dipole moments. Thus, in the CPL active materials, the magnetic and electric transition dipole moments must not be orthogonal to each other. It is to note that the order of magnitude of $\boldsymbol{\mu}$ is typically Debye ($1\ \mathrm{D} = 3.3 \times 10^{-30}$ C m), while that of $\boldsymbol{m}$ is approximately Bohr magneton ($1\ \mu_B = 9.3 \times 10^{-24}\ \mathrm{J\ T^{-1}}$). In cgs unit, CPL and fluorescence bands as function of transition energy (E) in spectra can be obtained through the following equations:

$$\Delta I(E) = \frac{16\, E^3\, \rho(E)}{3\, c^3\, \hbar^4}\, R$$

$$I(E) = \frac{4\, E^3\, \rho(E)}{3\, c^3\, \hbar^4}\, D$$

where $\hbar$ is the reduced Planck's constant, c is the speed of light, and $\rho(E)$ is a Gaussian band shape. The E^3 dependence is explained as the total luminescence and CPL is measured by counting the number of photons in space.

The degree of chirality in CPL, quantified by the dissymmetry factor g_{lum}, is a function of both strengths D and R. Strictly speaking, g_{lum} values are also dependent on the ratio of shape factors of the CPL and emission spectra, refractive index of medium (solvent) n, and inverse of internal field correction factor β. In isotropic solutions, it is approximated by assuming that these factors are mutually cancelled out. The dissymmetric factor g_{lum} is consequently given by:

$$g_{\mathrm{lum}} = 4 \times \frac{R}{D} = 4 \times \frac{|\boldsymbol{m}|}{|\boldsymbol{\mu}|} \cos\theta$$

Thus, the luminescence dissymmetry factor g_{lum} is inversely proportional to the amplitude of $\boldsymbol{\mu}$ and directly proportional to that of $\boldsymbol{m}$, as well as cosine of their relative angle (θ).

The rotational and dipole strengths, and thus the dissymmetric factor, can be directly estimated by the quantum chemical calculations. The time-dependent density functional theory (TD-DFT) has been successfully employed for the evaluation of the CPL spectra of distorted chiral ketones and some π-systems. Superior theoretical methods such as coupled-cluster type theory have been also applied recently. The accuracy of predicted values, however, depends on the ansatz used in the calculations as well as the geometrical features (size, flexibility, etc.) of chiral systems under study. Compared with the calculation of the CD spectra, theoretical investigation of CPL counterparts are still in the preliminary stage, which is however most likely dissolved very soon.

1.4 Measurement

To the best of our knowledge, very first CPL was reported by Samoilov in 1948 for chiral crystals of sodium uranyl acetate at the liquid helium temperature. In 1967, the first example of CPL from small organic molecule was reported by Emeis and Oosterhof, employing cyclic chiral ketone, *trans*-β-hydrindanone (*trans*-bicyclo [4.3.0]nonan-8-one). Then for a while, the target organic molecules for SOMs-based CPL study have been restricted to optically active cyclic ketones, almost nearly until this century. This is because these intrinsically chiral ketones exhibit relatively large g_{lum} values due to the magnetically allowed electronically forbidden n-π^* transition of distorted carbonyl group, which appears as an isolated band at ~300 nm. In all these measurements, custom-built instrument has been employed, which required in-depth technical attentions in order to avoid any possible artifacts. Recently, measurements became considerably easier since a recent appearance of commercial CPL spectrofluorimeter such as JASCO CPL-300. In this decade, a rapid growth was realized in the CPL chemistry as the CPL spectra of most of chiral π-systems, typically bearing g_{lum} in an order of 10^{-3} or less, can be reliably obtained. Nevertheless, additional difficulties exist for obtaining reliable and reproducible CPL due to several experimental limitations, which are briefly described below.

In addition to the common precautions taken care of in the measurement of UV-vis, CD, fluorescence, and phosphorescence spectra such as medium/solvent and sample cell, amount of sample, temperature dependence, and light intensity (slit width), special attention should be required for the reliable CPL measurement. At first, light beam, polarizer/depolarizer, photoelastic modulator, and monochromator should be properly aligned and carefully calibrated (even for commercial instrument). This task is not trivial as the instrumental standard is not established thus far, although some suggestions are available. In practice, precautions are needed when the fluorescence and CPL is close to the absorption wavelength. In such cases, the observed CPL signals should be properly corrected, as a part of the emitted radiation may be re-absorbed in different degrees for left and right circularly polarized light. Concentration of samples may also matter in several ways. Aggregation leads to the supramolecular effect for CPL measurement, which gives signals typically at least one order of magnitude stronger in g_{lum} than the isolated molecule. Depending on the conditions, an artifact may be also obtained through the photoselection and birefringent. When scattering phenomena become important, chiral scattering may manifest itself as apparent CPL. Last but not the least, the degradation of the sample may occur during the measurement, due to an inevitable exposure to a relatively strong excitation light during the CPL measurement. It is thus important to verify the stability (and recovery) of the sample at the end of the measurement. Unfortunately, above precautions do not always appear to have been completed in the literature examples. More serious artifact can appear for the CPL spectra of solid-state samples. One should consult the literature to understand the possible sources of artifacts before attempting to measure the CPL in the solid state or in any anisotropic conditions.

1.5 Perspective

Progressively large numbers of successful examples of SOMs-based CPL-active materials have been appeared in the literature. Nevertheless, total amount of study is still limited. Therefore, it is natural that a solid structure-property (i.e., CPL) relationship has not yet been established. Recent investigations are mostly focusing on the π-π^* transition of rigid aromatic systems, as their fluorescence quantum yields are normally moderate to high. The ideal CPL-active materials are expected to simultaneously have high luminescence quantum yield and high (absolute) g_{lum} value, and if possible that also function with some desired stimuli. It is certainly a great advantage that rational modification on the structure of SOMs, particularly of aromatic systems, can effectively modulate the various physical parameters in the CPL-responsible materials, while the luminescence dissymmetry factors for SOMs still remain unsatisfactory; further progresses are certainly desired.

We have recently examined quantitative relationship between the dissymmetric factors of CPL (g_{lum}) and CD (g_{abs}) for such π-π^* transitions of extended aromatic systems. It was the first systematic investigation to experimentally elucidate the relationship between the dissymmetry factors in order to strategically design the CPL response through the rational molecular modification on the aromatic systems. Although the number of the available data was still limited to around 100 examples, they unexpectedly afforded a good empirical linear correlation as a global fit: $|g_{\mathrm{lum}}| = 0.81 \times |g_{\mathrm{abs}}|$ ($r^2 = 0.60$) (Fig. 1.3). It is also to highlight that all the CPL data used in the study have been published in 2011 or later, except for two cases,

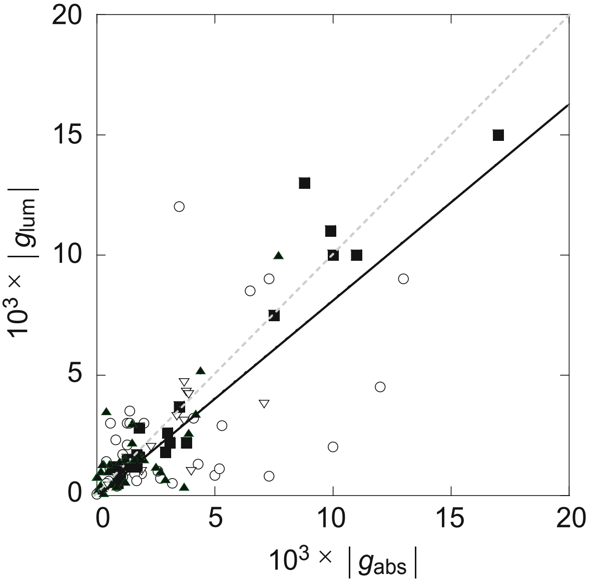

Fig. 1.3 The g_{lum}-g_{abs} correlation for of the π-π* transition in chiral aromatic molecules. Square, cyclophanes; triangle, biaryls; open circle, helicene-like molecules; open inverted triangle, BODIPY derivatives. Reproduced with permission [1]. Copyright 2018, Wiley

implying the innovative aspect of this study area. Such correlation can be easily understood as follows. In the rigid aromatic systems, minimal structural changes are expected in the S_1 state for the relaxation to the emissive state, as they always provide mirror-imaged absorption and emission spectra. Accordingly, the influence of the vibrational and structural relaxation in the excited state can be negligible, and thus the chiroptical properties obtained from the CD and CPL spectra become consistent with each other, as they originate from the upward and downward transitions between the same two states. When more carefully analyzed, distinct (but still linear) correlations are more likely, depending on the molecular structure, i.e., type of chirality, varying from 0.99 for planar chiral cyclophanes, to 0.93 for axially chiral biaryls, to 0.77 for chiral BODIPY dyes, and then to 0.61 for helicenes and related molecules. Nevertheless, the slope of ≈0.8 obtained of all the g_{lum}-g_{abs} data reported by 2017 clearly suggests that the dissymmetry of chiral extended π molecules does not significantly deteriorate on average after the structural relaxation upon the photoexcitation. Such structural considerations are of paramount importance and would make us available to more sensibly design the further advanced CPL materials in the future.

Finally, we draw attention to the recent stimulating discoveries such as the enhanced CPL response through fluorescence resonance energy transfer and for up-converted emission, as well as the CPL associated with delayed and dual fluorescence. All these possibilities show that chiral SOMs, especially those of the extended π-systems, are the most promising candidates for more innovative CPL materials that are readily accessible, theoretically predictable, rationally designable and modifiable.

Considering the nature of this chapter, we did not cite various original papers as a reference. We suggest the following review articles for a further reading for those more interested in the CPL phenomena, where you will find better and more detailed information and explanation on mathematical expression, historical view, critical issues, and additional examples [1–13]. Also note that photophysical aspect on CPL, CPL under external fields, CPL from metal complexes or polymers, and additional recent findings besides the SOMs-based CPL phenomena are all outside the scope of this book.

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