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Circularly polarized luminescence: a themed collection

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Circularly polarized luminescence (CPL), a fascinating property discovered in the 1970s,[1] has recently received great attention thanks to (i) the very recent availability of commercial CPL apparatus operating from the far-UV to the infrared domains and (ii) the availability of a diversity of molecules exhibiting both chirality and emission properties.

CPL intensity is determined by the dissymmetry factor g_{lum}, which represents the degree of circular polarization of emitted light and is defined as

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Jeanne Crassous

Dr Jeanne Crassous (born Costante) received her PhD in 1996 under the supervision of Prof. André Collet (ENS Lyon, France), focussing on the absolute configuration of bromochlorofluoromethane. After a one-year postdoctoral period studying the chirality of fullerenes in Prof. François Diederich's group (ETH Zurich, Switzerland), she received in 1998 a CNRS researcher position at the ENS Lyon. In 2005, she joined the Institut des Sciences Chimiques de Rennes (University of Rennes, France) where she is currently CNRS Director of Research. Her group is dealing with many fields related to chirality: organometallic and heteroatomic helicenes, fundamental aspects of chirality such as parity violation effects, chiroptical activity such as electronic and vibrational circular dichroism, or circularly polarized luminescence, magnetochirality and spintronics. In 2020, she received the National Prize of the Organic Chemistry Division of the French Chemical Society (DCO-SCF). She was elected Member of the European Academy of Science (EurASc) in 2021 and Fellow of Chemistry Europe in 2022. In 2023, she was awarded the CNRS Silver Medal.

Lorenzo Di Bari

Lorenzo Di Bari is Professor of Organic Chemistry at the University of Pisa, where from 2018 to 2022 he was the head of the Department of Chemistry and Industrial Chemistry. He received his PhD in Chemistry at the Scuola Normale Superiore in 1992 with a thesis on NMR methods for stereochemical determinations. He started working on chiroptical spectroscopies in 1997 and his current research focuses on the development of experimental methods for the stereochemistry of organic and inorganic compounds and on scouting new applications of chiroptical properties.

$2\Delta I/I = 2(I_\mathrm{L} - I_\mathrm{R})/(I_\mathrm{L} + I_\mathrm{R})$, where I_L and I_R denote the left- and right-handed circularly polarized emission intensities, respectively. From a theoretical point of view, the g_lum dissymmetry factor varies like $\frac{|\mu||m|\cos\theta}{(|\mu| + |m|)^2} \cong \frac{|m|}{|\mu|}\cos\theta$, where m and μ are the magnetic and electric transition moments, respectively, and θ is the angle between them. The approximate equality holds when $|\mu| \gg |m|$, which is a common situation, and thus magnetically-allowed and electrically-forbidden transitions with well-aligned directions are sought. In an analogy with the brightness of fluorescent emitters, which takes into account the chromophore extinction coefficient, ε, and the emission quantum yield, ϕ, the CPL brightness $B_\mathrm{CPL} = \varepsilon \times \Phi \times g_\mathrm{lum}/2$ was recently proposed as a good figure of merit.[2]

Extreme g_lum values of $g_\mathrm{lum} = \pm 2$ arise when either pure left- or right-polarized light is emitted after standard excitation, although for the majority of cases g_lum spans 10^{-4}–10^{-1} and rarely exceeds 1. All types of stereogenic elements (central, planar, axial, helical, or inherent chirality) are currently being introduced into efficient emitters and structure–property relationships are progressively being established.[3] Typical examples are biarylic systems, paracyclophanes, or helicenes. At least in the form of isolated molecules, these organic fluorescent molecules are known to display g_lum values on the order of 10^{-4}–10^{-2} in the wavelength domains from the far-UV to the infrared. Introducing donor and acceptor units enables one to tune the emission wavelength and reach challenging domains of great interest, such as deep-blue and infrared chiral emitters, while open-shell systems may contribute to an increase in the magnetic contribution. Furthermore, the combination of CPL properties with other phenomena, such as Förster energy transfer, exciplex formation, triplet–triplet annihilation (TTA), thermally-activated delayed fluorescence (TADF), phosphorescence, aggregation-induced emission, chiral-induced spin selectivity, or implementation into strongly chiral media, are currently closely examined.

The present dedicated issue spans a large variety of topics, witnessing the diverse directions of a fertile research area.

On a dimensional order, we can start with several instances of small organic molecules, composed by one twisted chromophore, or by systems with strongly interacting chromophores, held together by stereodefined frameworks. In these cases, the inequality $|\mu| \gg |m|$ holds, and considerable CPL arises from the combined effect of large $|m|$ and $\cos\theta$ (*i.e.* small θ). Helicenes can be excellent examples of this strategy: the distribution of aromatic rings along a well-defined arch determines a considerable rotation of charge during an electronic transition, which means large $|m|$ perpendicular to the helicene pseudo-plane. Along the same direction ($\theta \approx 0$), there is also a significant charge displacement. Going one step further, X.-Y. Wang *et al.* developed push–pull systems from aza[7]helicene as the chiral donor and triazine as the acceptor and showed that the well-engineered dihedral angle between the two units can give amplified CPL activity (**https://doi.org/10.1039/D2TC04848E**). Paracyclophanes represent the extreme case of another interesting strategy: bringing two more or less identical chromophores into very close proximity, to the point that there is a very strong orbital interaction between them. Here the approximation of dealing with two (or sometimes more) isolated systems must be released and, at least to some extent, one must switch to a diffuse chromophore description, reminiscent of that for exciplexes (see the review on compact chiral paracyclophanes by

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Wai-Yeung Wong

Professor Wai-Yeung Wong obtained his BSc (Hons.) and PhD degrees from the University of Hong Kong. After postdoctoral work at Texas A&M University (with Prof. F. A. Cotton) and the University of Cambridge (with Profs. The Lord Lewis and P. R. Raithby), he joined Hong Kong Baptist University from 1998 to 2016 and now works at the Hong Kong Polytechnic University as the Dean of Faculty of Science and Chair Professor of Chemical Technology. Among his awards are the RSC Chemistry of the Transition Metals Award, FACS Distinguished Young Chemist Award, State Natural Science Award from China and RGC Senior Research Fellow Award. His research focuses on synthetic inorganic/organometallic chemistry, aiming at developing photofunctional metal–organic molecules and polymers for optoelectronic and energy-related applications.

You-Xuan Zheng

Prof. You-Xuan Zheng received his PhD degree in Chemistry from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, in 2002. Then, he worked at the Technische Universität Dresden in Germany (2002–2004), Istituto per la Sintesi Organica e la Fotoreattivit in Italy (2005) and Queen Mary University of London in UK (2006) as a postdoctoral fellow. In 2006 he joined the School of Chemistry and Chemical Engineering in Nanjing University. His current research interests include the synthesis of fluorescent and thermally activated delayed fluorescent materials, lanthanide and phosphorescent metal complexes, chiral luminescent materials, and their application in organic light-emitting diodes.

E. Benedetti *et al.*, **https://doi.org/10.1039/D2TC04885J**). Interestingly, heteroatoms can be widely integrated into organic scaffolds, and generate a rich diversity of original architectures with tuned chiroptical activities.

Going one step further, purely organic molecules have been integrated with a variety of transition metals. These coordination compounds join the pliancy of organic frameworks with the spectroscopic properties of transition metals. Firstly, these compounds take advantage of long-lived emission from triplet states, *i.e.* phosphorescence, thanks to the strong spin–orbit coupling of the heavy metal. Secondly, they take advantage of low energy (vis-NIR) electronic transition with considerable magnetic-dipole character and, finally, they display very low propensity to photobleaching. A particular case that deserves a separate mention is provided by lanthanide systems. Their peculiarity resides in the poor covalency of the bonds they establish, which ensures that f → f transitions maintain most of their intraconfigurational character: they exhibit sharp, pure-color emission lines, often with extraordinarily high g_{lum} values. Interestingly, all these organometallic systems span a very wide range of emission wavelengths (**https://doi.org/10.1039/D3TC00034F**) and are amenable to two-photon excitation (**https://doi.org/10.1039/D2TC05362D**).

Chiral organic polymers have also revealed appealing CPL activity. In the polymeric systems described herein (see for instance the advances and perspectives reviewed by Z.-Q. Wu *et al.*; **https://doi.org/10.1039/D2TC04715B**), the backbone can be helical, thus ensuring a long-range chiral environment. Thanks to the ordered repetition of chiral elements, g_{lum} can attain values often above 0.1, *i.e.* much larger than for discrete molecules. When the helical backbone itself is a conjugated chain, it must be considered an intrinsically chiral fluorophore, which may be responsible for the observed chiroptical properties. Interestingly, these conditions can be associated with applications in optoelectronic devices, thanks to the possibility that these systems act as (semi)conductors.

At a still further level of complexity, we find aggregated systems endowed with supramolecular chiral order. This can give rise to liquid-crystalline phases, like chiral nematic, where molecules gather in domains characterized by high local order (see the work of H.-L. Xie *et al.* on the circularly polarized (CP) organic room-temperature phosphorescence activated by liquid-crystalline polymer networks; **https://doi.org/10.1039/D2TC04829A**). In the absence of external stimuli, these domains remain uncorrelated, which ensures that, overall, the local linear anisotropies average to 0. Still, if the chiral order remains the same for each domain, common chiroptical features appear. Mesogens can be either small molecules or even polymeric systems. The interesting feature of liquid-crystalline phases arises from their dynamical behaviour, which may react to external stimuli of various types. In these systems, CPL provides a very sensitive readout of the functional responses. In general, molecular aggregates can give rise to conspicuous natural and magnetic CPL (**https://doi.org/10.1039/D2TC05006D** and **https://doi.org/10.1039/D2TC04841H**).

We next consider more rigid organizations, like in gels or in completely solid (thin) films. Here, the chiroptical properties can report the pathway through which aggregation is achieved. With proper transduction technologies, where circular polarization of light is exploited, these systems may find applications in the development of sensors. Furthermore, we should not forget that in the vast majority of applications in devices, one must deal with solid-state films of suitable materials. As a result, CP emitters have been incorporated into optoelectronic devices (such as in white CP OLEDs described by W.-Y. Wong *et al.*; **https://doi.org/10.1039/D2TC04802G**), in biological or other imaging techniques, or in cryptography and counterfeiting systems.

A special mention must be made of chiral perovskites (**https://doi.org/10.1039/D2TC04825F** and **https://doi.org/10.1039/D2TC03810B**). The excellent emitting properties of these intrinsically hybrid systems and the possibility to incorporate chiral molecules, in particular chiral cations, has drawn considerable interest, which is likely to grow in the near future.

Finally, we would note the successful modulation of CPL though the control of geometrical parameters, achieved, for example, in the works of de la Moya (**https://doi.org/10.1039/D2TC04793D**) and Ono (**https://doi.org/10.1039/D2TC04636A**).

In conclusion, this themed collection gives an effective, integrated and multidisciplinary representation of the state of the art of CPL investigation.

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