

Circularly polarized light at the mirror: caveats and opportunities

Abstract: moving from the simple concept that reflection onto a mirror surface changes the handedness of circularly polarized light, we describe what happens to the emergent polarization in two different cases after reflection on a back mirror. In the first case, a regular emitter is taken into account, where reflection has the effect to destroy the emergent polarization.

In the second case we show what could happen when a hypothetical apparently non-reciprocal emitting material undergoes a similar experiment. These simple concepts have important implications in the design of efficient circularly polarized emitting devices.

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In honor and memory of Prof. Koji Nakanishi

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Introduction

It is a well-known fact that a mirror produces an image of any dissymmetric object which is not superimposable to the original object. Circularly polarized light can be regarded as a chiral entity and therefore, upon reflection upon a mirror surface, it undergoes handedness reversal. A common and simple educational experiment to grab the concept is to observe a mirror by wearing spectacles mounting opposite circular polarizers on the two eyes, now by closing one eye, only that eye would be visible in the mirror, while the open one will be concealed by the dark polarizer. The same principle is applied in most LED displays to reduce glaring from ambient light.¹ In this case, a circular polarizer (say R-polarizing) is placed in front of the LED panel, each LED having a reflective cathode. In this way, one polarization (say L) is immediately blocked by the polarizer, while the other one (R) can pass through and be reflected by the LED reflective cathode, changing its handedness (now L) and therefore being rejected by the polarizer. In this way it is possible to produce almost completely black screen, at the cost that even half of the light emitted by the (O)-LEDs (organic light emitting diodes) in the display will be blocked by means of the same mechanism. In other words, around 50% of the light produced by a screen of this type is lost. In this context, it becomes clear that an (O)-LED emitting preferentially one circular polarization (hence circularly polarized or CP-OLEDs) could in principle increase the efficiency of LED displays.¹⁻⁷

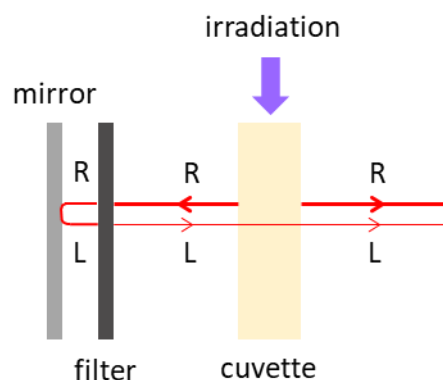
For these reasons, understanding the fate of polarized light inside a device is key in the design of new chiral and optically active materials as well as devices for chiral electronics.

In this brief contribution we aim at giving the scientists interested in the field some "food for thought" and ideas for discussions, maybe useful in the recently blossoming field of chiral organic photonics.

Discussion

We shall start taking into account the simple case of a chiral molecular (i.e. non-aggregated) emitter in solution which is also CPL (circularly polarized luminescence) active. With a simple

experiment, we can study how the emergent circular polarization changes upon variation of back reflection of the emitted light. The experimental set-up used consisted of a quartz cuvette containing the luminescent chiral molecule in solution, irradiated with UV light in the usual 90° geometry, with a glass mirror on the back. Between the mirror and the cuvette, neutral density filters with different transmittance are inserted in order to vary the extent of back reflected light (figure 1). Both the glass mirror and the filters are placed very close to the cuvette in order to collect only the light propagating straight with respect to the cuvette-mirror system (figure 1). Circularly polarized light is collected and analyzed from the front of the cuvette. We chose CsEu(hfbc)₄ (hfbc = heptafluorobutylcamphorate)^{4, 8-9} as the chiral emitter, since it displays characteristic sharp bands with high dissymmetry factor in the red region. In particular, the CPL signal at 612 nm was used for detection for its high emission dissymmetry factor (*g*) value (0.23, see figure 2) combined with intense emission.



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FIGURE 1. Depiction on how a circularly polarized component (R) emitted by CsEu(hfbc)₄ is affected upon reflection onto a back mirror.

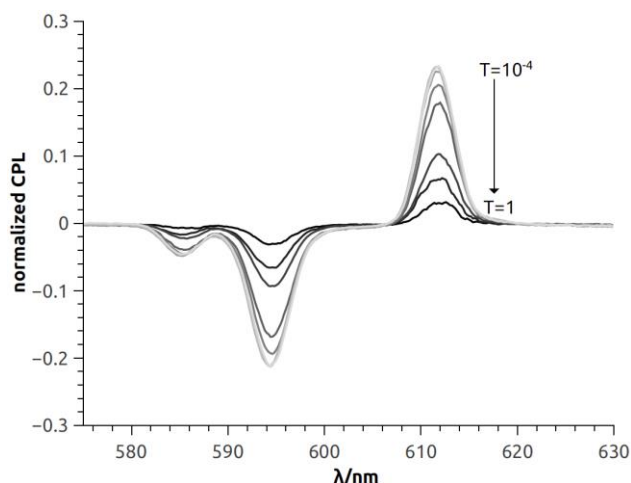


FIGURE 2. Spectra of CsEu(-)-hfbc₄, recorded in the set-up depicted in figure 1, upon variation of transmittance of the back neutral density filter.

In a simple interpretation of the experiment we may consider only the light emitted forward and backward by the sample.⁴ The intensity is evenly distributed on such components (half forward and half backward). The forward component leaves the cuvette with no change in polarization, while the backward component is (partially) reflected by the mirror with ensuing handedness change (e.g. from R to L, figure 1). This contribution decreases the overall emergent circular polarization of the exiting emitted light, quantified by the emergent dissymmetry factor (g_{em} , figure 3). The presence of the neutral density filter attenuates the back component, and therefore it has an impact on the emergent circular polarization (figure 2). For these reasons, maximum polarization is obtained for a filter with $T=0$ (no light reaches the mirror), while minimum polarization ($g_{em}=0$, according to our model in the case of a perfectly reflecting mirror) is expected when $T=1$.

Mathematically the emergent dissymmetry factor will be (see Appendix for derivation):

$$g_{em} = g_0 \frac{(1-RT^2)}{(1+RT^2)} \quad (1)$$

where g_0 is the intrinsic dissymmetry factor of the emitter, R is the reflectance of the mirror and T the transmittance of the filter, and the square factor takes into account that back-emitted light is attenuated both before and after the reflection. In figure 3, we show the experimental g_{em} plotted against T and the line fitting the experimental points through eq. 1. As the plot shows, the mathematical model, despite its simplicity, is perfectly able to reproduce the experimental trend. In such model, light emitted sideways is neglected, since it does not reach the detector. We may note that in an actual OLED, the device thickness is usually very small compared to the front area.

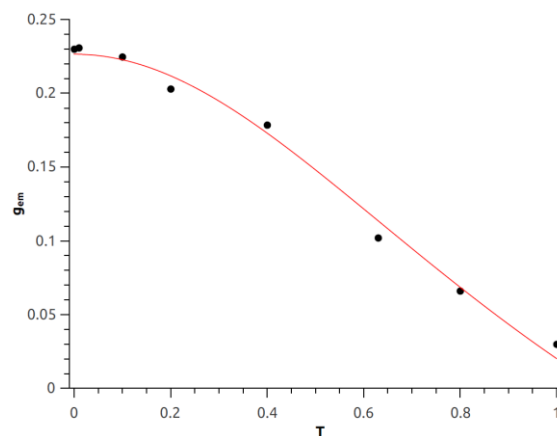


FIGURE 3. Experimental g_{em} points measured at $\lambda=612$ nm from the CPL spectra of CsEu(-)-hfbc₄ (figure 2) and fitted curve according to eq. 1 ($g_0=0.23$, $R=0.84$; $r^2=0.992$).

This model reproduces in a controlled and simplified way what happens in a CP-OLED in which the active layer is made of single molecule chiral emitters.⁴⁻⁵ The standard construction of OLEDs consists of a reflective back electrode (cathode), an organic active layer, and a (semi-)transparent electrode (anode). Indeed, in such cases a reflecting back electrode has the drawback to reduce the total circular polarization of the electroluminescence exiting the device. In order to rationalize such detrimental effect, recently we proposed a model which is able to rationalize the dependence of the electroluminescence dissymmetry factor inside a CP-OLED as a function of the position of the recombination zone, the transmittance of the active layer and the reflectance of the cathode:⁵

$$g_{em} = g_0 \frac{(1-Re^{-2\alpha(d-x)})}{(1+Re^{-2\alpha(d-x)})} \quad (2)$$

where x is the distance between the recombination zone of the device (that is where light is actually generated within the active layer) and front electrode, d the distance between anode and cathode and α being the attenuation coefficient of the active layer. From eq. 2, it is clear that in this case, the best polarization performances are obtained when the recombination zone is as close as possible to the front transparent electrode (anode).⁵

We can see that eq. 2 is a generalization of eq. 1, in the particular case in which the absorbing material is concentrated only between the mirror surface and the emitter. The qualitative or semiquantitative validity of such equation has been demonstrated for CP-OLEDs, at least in the case of single molecule emitters by changing the key parameters (R, x). In particular, R can be tuned by modulating cathode thickness (thin cathodes are semitransparent)^{4,5} or, in principle, by using a black back electrode. The position of the recombination zone can be varied as well by employing electrode interlayers modulating charge injection/extraction.⁵

On the other hand, considering again the experimental set-up in figure 1, we might modify the set-up by adding a quarter wave plate between the mirror and the cuvette. In this way, the backward emitted circularly polarized light will be transformed into linearly polarized light before being reflected by the mirror. As the mirror does not change linearly polarized light states, such component, after reflection, is transformed back into circularly polarized light with the original handedness by the quarter wave plate. Thus, in principle, one can recover the back component with no polarization loss. In a CP-OLED device, this scenario could be achieved by depositing a cathode interlayer formed by a suitably aligned polymer film or through other plasmonic structures acting

as a quarter wave plate. However, it must be borne in mind that the layers constituting an efficient device must meet stringent requirements such as charge mobility, HOMO and LUMO position, which limits considerably the freedom to choose the material.

At this point we must observe that our conclusions are strictly valid only when dealing with materials with negligible absorption-emission overlap and scattering. The situation can be very different in devices in which the polarization is produced taking advantage of different principles other than single molecule emitters,^{3, 10-12} such as oriented liquid crystal or cholesteric phases displaying (at least partially) circular Bragg phenomenon (i.e. reflection of CP light of one handedness and transmittance of light with opposite handedness) or differential scattering.¹² When this happens, completely different factors are at play and eq. 1 and 2 are no longer able to predict the behavior of polarized light in the device.

Now let us consider a different type of emitters.

There are many examples of (meta)materials displaying apparent non-reciprocal contributions to circular extinction¹³⁻¹⁴ due to the coupling of linear anisotropies (linear dichroism and linear birefringence).¹⁵ That is, materials showing different transmittance for L and R circularly polarized light changing by reversing the direction of the wavevector, that is by flipping the sample and irradiating it from the front or the back. Recently, such phenomenon has been demonstrated in thin films of chiral small semi-conducting organic molecules, with almost complete reversal of the emergent circular dichroism signal upon sample flipping.¹⁶⁻¹⁸

In principle, the same phenomenon could occur in emission as well, thanks to a coupling between linear birefringence and fluorescence linear anisotropy,¹⁹ although, to the best of our knowledge no organic material of such kind has been reported so far. So, let us consider what the outcome would be if such a material were to be employed in an active layer of a CP-OLED with fully reflective back electrode (figure 4).

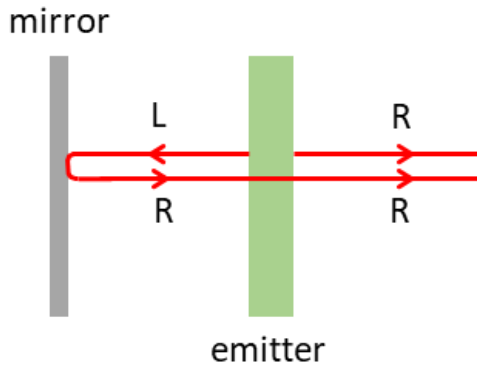


FIGURE 4. Depiction on how circularly polarized components emitted by an apparently non-reciprocal material are affected upon reflection onto a back mirror.

In such case, the emergent dissymmetry factor would be described by (see Appendix for derivation):

$$g_{em} = \frac{(g^f - g^b RT^2)}{(1 + RT^2)} \quad (3)$$

Where g^f and g^b are the dissymmetry factors of the front and backward emitted light respectively. We can rewrite eq. 3 defining $g^f = \alpha g^b$ with α ranging from -1 to 1 :

$$g_{em} = g^f \frac{(1 - \alpha RT^2)}{(1 + RT^2)} \text{ or } g_{em} = g^f \gamma(\alpha; T) \quad (4)$$

Now, the most favorable case for maximization of g_{em} is when $\alpha = -1$ ($g^b = -g^f$), and $g_{em} = g^f$. In this way no polarization is lost due to reflection on the back electrode, allowing one to fully take advantage of the backward emission component without any detrimental effect on the emergent circular polarization of light. Note that, for $\alpha = 1$, $g^b = g^f$ and eq. 4 is reduced to eq. 1. Figure 5 displays the plots of $\gamma(\alpha; T)$ (eq. 4) for $-1 < \alpha < 1$.

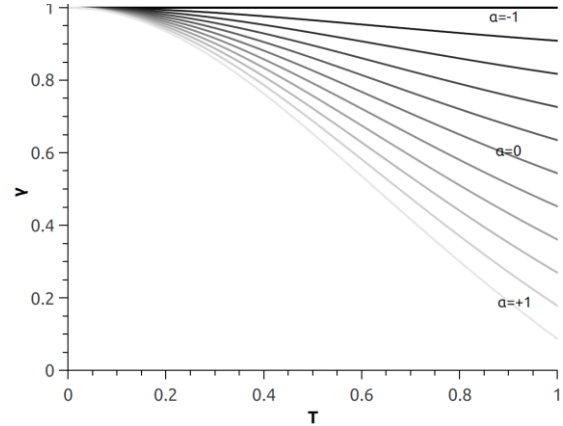


FIGURE 5. Plot of eq. 4 for various values of α .

Conclusion

In conclusion, different emitters behave completely differently when placed in a situation in which reflection on a back electrode is expected, such as a CP-OLED. In particular, a hypothetical apparently non-reciprocal emitting material could substantially benefit CP-OLEDs performances. In any case a general understanding and careful design of the system at play is necessary for the improvement of CP-OLED technology.

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Appendix

Eq. 1 is worked out as follows: considering the situation depicted in figure 1, the two polarized components exiting the cuvette (I'_L and I'_R) are:

$$I'_L = 1/2 (I_L^0 + I_R^0 RT^2) \quad (S1)$$

$$I'_R = 1/2 (I_R^0 + I_L^0 RT^2) \quad (S2)$$

Where I_L^0 and I_R^0 are the intrinsic polarization components emitted by the chiral molecule. The attenuation term RT^2 arises from one reflection from the mirror with reflectance R and two transmissions through the sample with transmittance T . By definition of emission dissymmetry factor we have:

$$g_{em} = 2 \frac{I'_L - I'_R}{I'_L + I'_R} \quad (S3)$$

Combining eq. S1 and S2 with eq. S3:

$$g_{em} = 2 \frac{(I_L^0 - I_R^0)(1 - RT^2)}{(I_L^0 + I_R^0)(1 + RT^2)} \quad (S4)$$

Now noting that $g_0 = 2 \frac{(I_L^0 - I_R^0)}{(I_L^0 + I_R^0)}$, we get eq. 1:

$$g_{em} = g_0 \frac{(1 - RT^2)}{(1 + RT^2)} \quad (1)$$

Eq. 3 is worked out as follows: considering the situation depicted in figure 3, the two polarized components exiting the material from the front (I_L^f and I_R^f) and the back (I_L^b and I_R^b) side are:

$$I_L^f = I_L^i + I_R^i RT^2 \quad (S5)$$

$$I_R^f = I_R^i + I_L^i RT^2 \quad (S6)$$

Combining eq. S5 with eq. S6 with the definition of dissymmetry factor (eq. S3), we have:

$$g_{em} = 2 \frac{(I_L^f - I_R^f) - RT^2(I_L^b - I_R^b)}{(I_L^f + I_R^f) + RT^2(I_L^b + I_R^b)} \quad (S7)$$

Now, noting that:

$$I_L^f + I_R^f = I_0^f \text{ and } I_L^b + I_R^b = I_0^b \quad (S8)$$

and

$$I_L^f - I_R^f = 1/2 I_0^f g^f \text{ and } I_L^b - I_R^b = 1/2 I_0^b g^b \quad (S9)$$

We get eq. 3:

$$g_{em} = \frac{(g^f - g^b RT^2)}{(1 + RT^2)} \quad (3)$$

References

- Brandt JR, Wang X, Yang Y, Campbell AJ, Fuchter MJ, Circularly polarized phosphorescent electroluminescence with a high dissymmetry factor from PHOLEDs based on a platinahelicene, *J Am Chem Soc* **2016**;138:9743-9746.
- Peeters E, Christiaans MP, Janssen RA, Schoo HF, Dekkers HP, Meijer E, Circularly polarized electroluminescence from a polymer light-emitting diode, *J Am Chem Soc* **1997**;119:9909-9910.
- Yang Y, da Costa RC, Smilgies DM, Campbell AJ, Fuchter MJ, Induction of circularly polarized electroluminescence from an achiral light-emitting polymer via a chiral small-molecule dopant, *Adv Mater* **2013**;25:2624-2628.
- Zinna F, Giovanella U, Di Bari L, Highly circularly polarized electroluminescence from a chiral europium complex, *Ad Mater* **2015**;27:1791-1795.
- Zinna F, Pasini M, Galeotti F, Botta C, Di Bari L, Giovanella U, Design of lanthanide-based OLEDs with remarkable circularly polarized electroluminescence, *Adv Funct Mater* **2017**;27:1603719.
- Han J, Guo S, Lu H, Liu S, Zhao Q, Huang W, Recent progress on circularly polarized luminescent materials for organic optoelectronic devices, *Adv Optical Mater* **2018**;6:1800538.
- Brandt JR, Salerno F, Fuchter MJ, The added value of small-molecule chirality in technological applications, *Nat Rev Chem* **2017**;1:0045.
- Lunkley JL, Shirotni D, Yamanari K, Kaizaki S, Muller G, Extraordinary circularly polarized luminescence activity exhibited by cesium tetrakis (3-heptafluoro-butylryl-(+)-camphorato) Eu (III) complexes in EtOH and CHCl₃ Solutions, *J Am Chem Soc* **2008**;130:13814-13815.
- Lunkley JL, Shirotni D, Yamanari K, Kaizaki S, Muller G, Chiroptical spectra of a series of tetrakis ((+)-3-heptafluorobutylrylcamphorato) lanthanide (III) with an encapsulated alkali metal ion: circularly polarized luminescence and absolute chiral structures for the Eu (III) and Sm (III) complexes, *Inorg Chem* **2011**;50:12724-12732.
- Lee DM, Song JW, Lee YJ, Yu CJ, Kim JH, Control of circularly polarized electroluminescence in induced twist structure of conjugate polymer, *Adv Mater* **2017**;29:1700907.
- Di Nuzzo D, Kulkarni C, Zhao B, Smolinsky E, Tassinari F, Meskers SC, Naaman R, Meijer E, Friend RH, High circular polarization of electroluminescence achieved via self-assembly of a light-emitting chiral conjugated polymer into multidomain cholesteric films, *ACS nano* **2017**;11:12713-12722.
- Wan L, Wade J, Salerno F, Arteaga O, Laidlaw B, Wang X, Penfold T, Fuchter MJ, Campbell AJ, Inverting the Handedness of Circularly Polarized Luminescence from Light Emitting Polymers Using Film Thickness, *ACS nano* **2019**;13:8099-8105
- Kahr B, Freudenthal J, Gunn E, Crystals in light, *Accounts Chem Res.* **2010**;43:684-692.
- Arteaga O, Maoz BM, Nichols S, Markovich G, Kahr B, Complete polarimetry on the asymmetric transmission through subwavelength hole arrays, *Opt express* **2014**;22:13719-13732.
- Shindo Y, Kani K, Horinaka J, Kuroda R, Harada T, The application of polarization modulation method to investigate the optical homogeneity of polymer films, *J Plast Film Sheet* **2001**; 17:164-183.
- Albano G, Górecki M, Pescitelli G, Di Bari L, Jávorfí T, Hussain R, Siligardi G, Electronic circular dichroism imaging (CDi) maps local aggregation modes in thin films of chiral oligothiophenes, *New J Chem* **2019**;43:14584-14593.
- Albano G, Salerno F, Portus L, Porzio W, Aronica LA, Di Bari L, Outstanding Chiroptical Features of Thin Films of Chiral Oligothiophenes, *ChemNanoMat* **2018**;4:1059-1070.
- von Weber A, Hooper DC, Jakob M, Valev VK, Kartouzian A, Heiz U, Circular Dichroism and Isotropy – Polarity Reversal of Ellipticity in Molecular Films of 1,1'-Bi-2-Naphtol, *ChemPhysChem* **2019**;20:62-69.
- Shindo Y, Oda Y, Mueller matrix approach to fluorescence spectroscopy. Part I: Mueller matrix expressions for fluorescent samples and their application to problems of circularly polarized emission spectroscopy, *Appl Spectrosc* **1992**;46:1251-1259.

Graphical Abstract

