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Standardizing the characterization of circularly polarized luminescence of chiral materials

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Supplementary Information

Standardizing the characterization of circularly polarized luminescence of chiral materials

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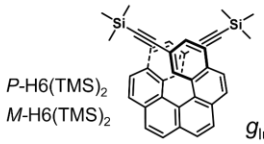
Providing precise guidelines for CPL measurements is inherently challenging, as the optimal conditions depend greatly on the specific molecular material under investigation. Achieving luminescence spectra with a satisfactory signal-to-noise ratio (S/N) often requires trade-offs—either prolonged signal accumulation (through high integration times or multiple scans) or the use of a broader experimental bandwidth (EBW) by increasing the detection slit width, which can reduce spectral resolution. This balance becomes particularly critical when analyzing emissions that are very narrow, such as those typically observed in lanthanide complexes, or emissions with vibronic structures arising from locally excited-state transitions in molecular emitters. Narrowing the slit width improves spectral resolution but simultaneously decreases signal intensity, thereby reducing the S/N ratio. At lower spectral resolutions (e.g., using a wider emission bandwidth), overlapping signals may distort the CPL signal, affecting the determination of the g_{lum}. This overlap can result in inaccurate quantification and may help explain discrepancies frequently reported in the literature. Unlike in conventional spectroscopy, an apparent improvement in spectral resolution does not necessarily result in a more accurate CPL measurement. A critical criterion for reliable interpretation is that the CPL signal should exhibit a zero slope at the zero-crossing point of the CPL curve, indicating that no overlapping transitions are present. If residual overlap persists, considerable caution must be considered: observed CPL peaks may not accurately represent the true molecular transitions in terms of position or intensity. In some cases, peaks may even be masked or exhibit inverted signs.

To mitigate this, one should optimize the spectrometer resolution by progressively decreasing the slit width until the recorded spectra—both emission and CPL—stabilize and no longer change with further narrowing. Further details and visual examples illustrating this key issue are available in refs16 and 23.

This aspect has been investigated for lanthanide complexes in ref. 23 and we further illustrate it below by recording the CPL and total luminescence spectra of one enantiomer of the [6]helicene derivative represented in Figure 1 with different slit withs at both the excitation and the emission sides while keeping the other parameters similar (data will be available in the supporting information of the comment). We finally modified the HT voltage at the detector to afford the best signal/noise ratio, while keeping in mind the experiment time.



P-H6(TMS)$_2$
M-H6(TMS)$_2$

g_{lum} = 1.8 × 10^{-2}

Measured with a commercial CPL 300

D.I.T.	1 sec
CD scale	10000 mdeg/1.0 dOD
Scanning speed	100 nm/min
Accumulations	1