Supporting Information

Simultaneous Detection ofCircularly Polarized Luminescence and Raman Optical Activity in an Organic Molecular Lemniscate

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## Supporting Information

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Spectroscopic Measurements

Raman and ROA spectra were recorded simultaneously in a BioTools ChiralRAMAN © spectrometer (BioTools Inc, Jupiter FL, USA). Raman Optical Activity (ROA) was measured as the intensity difference between the scattered radiation right and left circularly polarized (SCP-ROA). Spectra were recorded at the room temperature from 100 μl of saturated solutions in deuterated dichloromethane, CD₂Cl₂. Excitation wavelength at 532 nm was used as generated by a Nd:VO₄ laser operating at 20 mw. Only radiation scattered in the backward direction with respect to the incident laser was led to the detector. Spectral resolution was always better than 7 cm⁻¹, and the standard acquisition times were greater than 24 h. Each spectrum was confirmed by at least two different Raman/ROA experiments recorded from independently prepared samples.

Electronic absorption and Electronic Circular Dichroism (ECD) spectra were recorded on a Jasco 815 spectrometer working at the room temperature and continuously purged with dry N₂ gas. Spectra in the 300-700 nm range were achieved from 200 μl of solutions 0.05 mol/l in CH₂Cl₂ placed in a 0.1 cm path cell. The recording parameters were time constant of 1 second, scan rate of 100 nm/min, bandwidth of 1 nm and blank correction over a pure CH₂Cl₂ solution. Final spectra were obtained as the average of a minimum of three scans after a blank correction.
Computational Methods

Density Functional Theory (DFT) quantum chemical calculations were performed with the Gaussian’16 suite of programs\textsuperscript{51}. The hybrid exchange–correlation functional B3LYP was used in combination with the Becke (B3) gradient-corrected exchange functional, with the Lee-Yang-Parr (LYP) non-local correlations and the Tawada\textsuperscript{52,53} long-range corrections, and the Dunning’s correlation consistent basis set CC-PVDZ,\textsuperscript{54,55} which includes polarization functions for hydrogen and heavy atoms. Raman and ROA spectra were obtained from the calculated DFT intensities and vibrational wavenumbers uniformly scaled by 0.977.\textsuperscript{56} Every band was represented by a Gaussian function of 10 cm\textsuperscript{-1} half-height width. Electronic excitation energies were obtained by using the time-dependent DFT (TDDFT) formalism\textsuperscript{57,58} for which up to the twenty low-lying energy states were considered.

A sharp vibrational analysis was carried out with the Pyvib2 program,\textsuperscript{59} developed by M. Fedorovsky. This implements a vibrational correlation interface able to compare the nuclear motions of vibrations of different molecules. It also uses the molecular decomposition method, proposed by W. Hug,\textsuperscript{60} in order to obtain a topological and more friendly description of the Raman and ROA intensities. In this method, the three invariants which determine the circular difference differential scattering cross section of a normal mode, namely $aG'$, $\beta_G^2$ and $\beta_A^2$,\textsuperscript{29} are dissected into additive quasi-atomic terms. Then, the atomic contributions of a specific molecular fragment to any vibrational eigenvalue can be added up to obtain a topological and more friendly description of its whole ROA activity.
Figure S1. (a) Experimental Raman spectrum of CPPL in dichloromethane solution. (b) Calculated Raman spectrum (scaled by a uniform factor of 0.977) of CPPL.
Figure S2. Calculated eigenvectors of selected ν(C=C/C-C) modes of (M)-CPPL. The scaled (0.977) wavenumbers are inserted. The colours represent the phase of the atomic vibrations, whereas the volume of each sphere is proportional to the vibrational amplitude.
**Figure S3.** Group coupling matrices (GCM) obtained for selected \(v(C=C/C-C)\) modes of \((M)\)-CPPL Groups in GCM are defined in the Fig. S4. The circle and sphere sizes are normalized to the maximum value obtained for the 1607 cm\(^{-1}\) vibration.
Figure S4. Molecular fragments for the GCM analysis of (M)-CPPL. A (green): the bicarbazole group; B (blue) and C (pink): the two equivalent oligophenyl groups; D (light blue): the hydrogens.
Figure S5. Calculated absorption UV-vis and ECD spectra of \((P-)\) and \((N-)\) enantiomers of CPPL in dichloromethane solution.
Table S1. Ground to excited state transition electric (ETDM) dipole moments (atomic units) calculated for the 25 lowest energy excited states of \((M)\)-CPPL. TD-DFT calculations were performed at the B3LYP/CC-PVDZ level of theory.

| state | X        | Y        | Z         | Dip. S. | Osc. |
|-------|----------|----------|-----------|---------|------|
| 1     | -0.4991  | 0.7251   | 0.0001    | 0.7749  | 0.0554 |
| 2     | -0.0008  | -0.0000  | -0.9640   | 0.9293  | 0.0691 |
| 3     | -4.9753  | -0.0043  | 0.0001    | 24.7536 | 1.9791 |
| 4     | -3.7989  | -0.1557  | 0.0001    | 14.4560 | 1.1655 |
| 5     | 0.0006   | -0.0001  | 0.1574    | 0.0248  | 0.0020 |
| 6     | 0.0174   | -0.9968  | -0.0001   | 0.9939  | 0.0814 |
| 7     | 0.0000   | -0.0002  | 0.0695    | 0.0048  | 0.0004 |
| 8     | 0.5696   | -2.0098  | -0.0000   | 4.3637  | 0.3737 |
| 9     | 0.0004   | 0.0001   | -0.3295   | 0.1086  | 0.0094 |
| 10    | -0.0008  | 0.0039   | 0.0229    | 0.0005  | 0.0000 |
| 11    | -0.0836  | 0.4100   | -0.0001   | 0.1751  | 0.0154 |
| 12    | 0.1043   | 3.1074   | 0.0002    | 9.6668  | 0.8602 |
| 13    | 0.0008   | 0.0007   | -0.3285   | 0.1079  | 0.0098 |
| 14    | -0.0012  | -0.0008  | -0.1220   | 0.0149  | 0.0014 |
| 15    | -0.0144  | -0.0078  | -0.7032   | 0.4948  | 0.0450 |
| 16    | 0.5745   | 0.3181   | -0.0178   | 0.4316  | 0.0393 |
| 17    | -0.0003  | -0.0002  | 0.0741    | 0.0055  | 0.0005 |
| 18    | -0.0002  | 0.0001   | 0.4764    | 0.2269  | 0.0210 |
| 19    | -0.0001  | 0.0004   | -0.3071   | 0.0943  | 0.0088 |
| 20    | 2.8426   | 0.0162   | 0.0002    | 8.0807  | 0.7564 |
| 21    | 0.4575   | 0.1347   | -0.0000   | 0.2275  | 0.0216 |
| 22    | -0.9434  | 0.1348   | -0.0001   | 0.9081  | 0.0866 |
| 23    | 0.0008   | 0.0002   | -0.1049   | 0.0110  | 0.0011 |
| 24    | -0.0009  | 0.0002   | -0.0808   | 0.0065  | 0.0006 |
| 25    | 1.8069   | -0.1330  | -0.0000   | 3.2827  | 0.3167 |
Table S2. Ground to excited state transition magnetic (MTDM) dipole moments (atomic units) calculated for the 25 lowest energy excited states of $(M)$-CPPL. TD-DFT calculations were performed at the B3LYP/CC-PVDZ level of theory.

| state | X    | Y    | Z    |
|-------|------|------|------|
| 1     | -1.0625 | -4.5538 | 0.0003 |
| 2     | 0.0002  | 0.0006 | -12.0128 |
| 3     | 1.3504  | 0.8395 | 0.0010 |
| 4     | 1.2083  | 1.3559 | 0.0018 |
| 5     | -0.0002 | -0.0002 | 1.9901 |
| 6     | 0.5920  | 2.0352 | 0.0001 |
| 7     | 0.0001  | 0.0006 | -0.6618 |
| 8     | -0.2165 | -1.0107 | -0.0006 |
| 9     | -0.0002 | -0.0006 | 0.0196 |
| 10    | 0.0007  | 0.0035 | 0.4556 |
| 11    | 0.0962  | 0.4084 | -0.0032 |
| 12    | -0.1746 | 0.5789 | -0.0001 |
| 13    | -0.0006 | -0.0005 | 2.6292 |
| 14    | 0.0007  | 0.0007 | -2.1392 |
| 15    | 0.0065  | 0.0062 | -4.5128 |
| 16    | -0.2615 | -0.2410 | -0.1249 |
| 17    | 0.0000  | -0.0003 | 3.2315 |
| 18    | -0.0001 | -0.0000 | 1.0290 |
| 19    | -0.0001 | -0.0000 | 0.6026 |
| 20    | -1.0834 | -0.6240 | 0.0005 |
| 21    | -0.3480 | -0.0782 | -0.0003 |
| 22    | 0.3505  | 0.2177 | 0.0000 |
| 23    | -0.0005 | -0.0002 | 0.1504 |
| 24    | -0.0002 | 0.0005 | 0.2059 |
| 25    | 0.0461  | -0.6286 | -0.0000 |
**Figure S6.** ETDM \((10^{-18} \text{ esu cm, blue vectors})\) and MTDM \((10^{-21} \text{ erg G}^{-1}, \text{ red vectors})\) of the D4 and D6 electronic transitions calculated for \((P)\)-CPPL.

Table S3. Assignment of the D2 and D3 electronic transitions of \((M)\)-CPPL. TD-DFT calculations were performed at the B3LYP/CC-PVDZ level of theory.

Transition D2: \[2.9623 \text{ eV} \quad 418.54 \text{ nm} \quad f=0.0681 \quad <S^{**2}> = 0.000\]

- homo-1 → lumo \[0.52949\]
- homo → lumo+1 \[-0.44832\]

Transition D3: \[3.1994 \text{ eV} \quad 387.52 \text{ nm} \quad f=1.8934 \quad <S^{**2}> = 0.000\]

- homo-2 → lumo \[0.10277\]
- homo → lumo+2 \[0.68353\]
Figure S7. Topological representation of the molecular orbitals involved in the D2 and D3 electronic transitions of (M)-CPPL.
Figure S8. Comparison between the ROA spectra of CPPL in dichloromethane and decalin.
Supporting References

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