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Chiral DPP Thin Films: Unlocking Circularly Polarized Light for Next-Gen Optoelectronics †

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Abstract

We report the synthesis and characterization of the two enantiomeric forms of a thienyl-substituted diketopyrrolopyrrole (DPP) derivative bearing chiral alkyl chains. Thin films were prepared either by spin-coating and drop-casting and analyzed by UV–Vis absorption, electronic circular dichroism (ECD), and circularly polarized luminescence (CPL). ECD spectra confirmed the opposite chirality of the (R) and (S) isomers, while CPL measurements of the S enantiomer demonstrated solid-state chiroptical activity. Preliminary device tests showed promising optoelectronic behavior, highlighting these chiral DPP materials as potential candidates for circularly polarized OLED applications, combining strong chiroptical response with good film quality.

Keywords: chiral diketopyrrolopyrrole (DPP); circularly polarized luminescence (CPL); organic optoelectronics

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1. Introduction

Chirality in organic semiconductors offers a powerful strategy to expand the functionality of π-conjugated materials by enabling selective interactions with circularly polarized light. This unique characteristic introduces optical phenomena such as electronic circular dichroism (ECD) and circularly polarized luminescence (CPL), which are key to next-generation technologies including circularly polarized photodetectors capable of distinguishing left- and right-handed light, and circularly polarized organic light-emitting diodes (CP-OLEDs) [1] that can enhance display efficiency and reduce energy losses by eliminating external polarizers. Beyond light–matter interactions, chiral semiconductors can also promote spin—selective charge transport, opening pathways toward organic spintronic devices where control over electron spin is essential. Chirality plays a pivotal role in modern science, influencing fields as diverse as pharmacology, materials chemistry, and photonics [2]. In organic electronics, the incorporation of chirality into π-conjugated systems has opened new avenues for the development of advanced functional materials capable of interacting with circularly polarized (CP) light. These chiral materials

are not only of fundamental interest due to their unique supramolecular organization and optical activity, but they also hold promise for technological applications such as CP light-emitting diodes (CP-OLEDs), chiral photodetectors, spin filters, and optical data storage devices.

The emergence of supramolecular chirality [3,4] in thin films of organic dyes is particularly intriguing. Unlike molecular chirality, which arises from stereogenic centers, supramolecular chirality results from the collective arrangement of molecules into chiral aggregates. This phenomenon can be modulated by molecular design, deposition techniques, and environmental conditions, and is often revealed through electronic circular dichroism (ECD) and circularly polarized (CP) luminescence (CPL) measurements. The ability to control and exploit such chiroptical properties is essential for the rational design of next-generation optoelectronic devices.

In this context, the study of new chiral organic materials is of paramount importance. π-conjugated systems, especially [5] those based on small molecules and oligomers, offer several advantages over polymers, including well-defined structures, tuneable properties, and easier purification. Among these, diketopyrrolopyrrole (DPP) derivatives have attracted considerable attention due to their exceptional thermal and photochemical stability, strong absorption in the visible region, and high fluorescence quantum yields (ϕ_{PL}). The DPP core is a planar, electron-deficient moiety that can be readily functionalized at multiple positions, making it a versatile building block for the synthesis of advanced organic semiconductors.

Recent studies have demonstrated the potential of DPP-based materials [6] in organic photovoltaics [7],field-effect transistors [8], organic light-emitting diodes (OLEDs) [9],and bioimaging [10]. However, their application in chiral optoelectronics is still in its infancy. While several works have explored the chiroptical properties of DPP derivatives [11] bearing chiral side chains or helicene units [12], only a few have systematically compared the behaviour of the two enantiomeric forms of a given chiral DPP molecule. Such comparative studies are crucial to understand the relationship between molecular chirality, supramolecular organization, and macroscopic optical activity.

In this work, we synthesized and characterized the two enantiomeric forms of a chiral conjugated molecule based on the DPP core and (*S*)- and (*R*)-3,7-dimethyloctyl alkyl chains (hereafter indicated as *S*-DPP and *R*-DPP). Thin films were produced using both drop-casting and spin-coating techniques, allowing us to investigate the influence of deposition method on the chiroptical properties. Electronic absorption, ECD, and CPL measurements were performed to evaluate the optical activity of the materials in films.

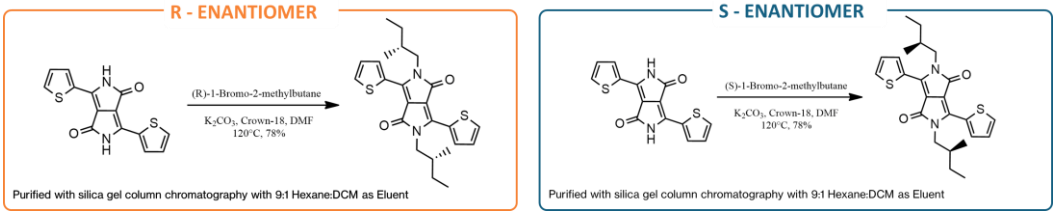
Furthermore, preliminary devices incorporating the *R*-DPP enantiomer were fabricated, demonstrating its potential as an active layer in CP-emitting OLEDs (CP-OLEDs).

2. Materials and Methods

General Information for synthesis. All reagents were purchased from commercial sources and used without further purification. All solvents have been distilled prior to use. The ^{1}H-NMR spectra were recorded with a Bruker ARX 400 MHz spectrometer (Karlsruhe, Germany).

Synthesis of S-DPP (Scheme 1a)*:* 3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1 eq, 700 mg, 2.33 mmol), K_2CO_3 (3.3 eq, 1.06 g, 7.69 mmol) and a catalytic amount of 18-crown-6 (8 mg) were added in a Schlenk tube and suspended with 10 mL of DMF. The reaction was stirred at 120 °C for 20 min and then (S)-1-bromo-2-mehylbutane (3.3 eq, 1.16 g, 7.69 mmol) was added dropwise with 1 mL of DMF. The reaction mixture was let at reflux overnight. The next day the reaction was allowed to cool to room temperature, the reaction was diluted with $CHCl_3$ washed with brine two times, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The

concentrated solution then was precipitated in methanol and filtered. The next day the reaction was allowed to cool to room temperature, the reaction was diluted with $CHCl_3$ washed with brine two times, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The concentrated solution then was precipitated in methanol and filtered. The precipitated dark red solid was purified by flash chromatography on silica gel using 9: 1 Petroleum Ether (PE)/Ethyl Acetate (EtOAC) as eluent. The desired product was obtained with 34% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.96–8.95 (dd, 2H, Ar-H), 7.62–7.61 (dd, 2H, Ar-H), 7.27–7.25 (dd, 2H, Ar-H), 4.02–3.92 (m, 4H, -NCH_2-), 1.94–1.87 (m, 2H), 1.52–1.44 (m, 2H), 1.25–1.16 (m, 2H), 0.91-0.88 (m, 12H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ = 161.90, 140.50, 136.05, 131.13, 130.56, 128.93, 108.07, 47.98, 35.79, 27.33, 16.98, 11.38. Anal. calcd for $C_{24}H_{28}N_2O_2S_2$:C,65.42;H, 6.41; N, 6.36; S, 14.55; found: C, 66.03; H, 6.93; N, 6.41; S, 15.54.



Scheme 1. Synthesis of *S*-DPP and *R*-DPP enantiomers.

Synthesis of R-DPP (Scheme 1b)*:* The reaction was carried out as reported for S-*DPP*, using the (R)-enantiomer (R)-1-bromo-2-mehylbutane as the alkyl halide. The results of the chemical analyses are comparable3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione(1 eq, 3.33mmol).

Films preparation and characterization. Drop-casted films were prepared by depositing dropwise on a glass slide 100 μL of a 5.0 10^{-3} M solution of of each chiral DPP dye in $CHCl_3$, followed by evaporation of the solvent in ambient condition. Thin film samples were prepared by spin-coating 100 μL of a 25 mg/mL solution of each chiral DPP dye in $CHCl_3$ on a glass slide, at 2000 rpm for 60 s. Neither solvent nor thermal annealing processes were performed on the films.

Chiroptical characterization. Electronic absorption spectra were carried out on a Perkin-Elmer Lambda 900 UV-VIS-NIR Spectrometer. ECD spectra were recorded with a Jasco J-1000 spectropolarimeter. Steady-state PL spectra were recorded on a modified Jobin-Yvon Horiba Fluorolog spectrofluorimeter. ϕ_{PL} have been obtained with a home-made integrating sphere [13]. CPL and CPEL activities were evaluated by means of a fixed linear polarizer and a rotating quarter wave plate placed in front of the CCD detector, as previously described [2].

Devices. Indium thin oxide (ITO) was used as anode. After sequential cleaning of 2.5 cm × 2.5 cm sized ITO-coated glasses in acetone and isopropanol in a sonicator, they were treated with a nitrogen plasma. poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) VPI 4083 was spin-coated to form a 35 nm thick film. Polyvinylcarbazole (PVK, 35 nm) film was deposited on top of PEDOT:PSS from a 10 mg/mL chlorobenzene solution. Solutions of DPP 25 mg/mL in toluene were spin-coated on top of the glass/ITO/PEDOT:PSS/PVK substrate. Finally, 1.5 nm of LiF and 100 nm of Al were thermo-sublimated inside the high vacuum 10^{-7} mbar evaporator to achieve a mirror cathode. Photons emitted in forward direction through the glass substrate were collected by a calibrated photodiode. Current density-irradiance-voltage (J-E-V) curves were recorded by dual-channel Keithley 2602 apparatus.

3. Results and Discussion

The fundamental step in the synthesis of the chiral alkyl DPP derivatives was the N-alkylation of the parent DPP scaffold. This transformation is inherently challenging due to several factors: (i) the poor solubility of the DPP core in most common organic solvents, arising from the strong intermolecular hydrogen bonding between the lactam N–H and the carbonyl groups; (ii) the competitive side reactions of the alkyl bromides at elevated temperatures, such as dehydrohalogenation and oxidation; and (iii) the propensity of the deprotonated DPP anion to undergo undesired O-alkylation, leading to N,O- or O,O-alkylated byproducts[14].

Although tosylates are generally considered superior leaving groups compared to halides, literature reports low yields (<20%) in this context, with our *S*-DPP enantiomer specifically giving a yield of only 12% [12], likely due to the ambident reactivity of the DPP anion, where the negative charge is delocalized between nitrogen and oxygen atoms, resulting in the formation of undesired N,O- and O,O-alkylated by-products, as previously described [14]. Therefore, we opted for commercially available alkyl bromides to improve reproducibility and simplify the procedure.

Under optimized conditions (using 3.3 equivalents of alkyl bromide and K_2CO_3 as base in dry DMF at 125 °C, with a catalytic amount of 18-crown-6 to enhance solubility and ion pairing) the reaction afforded the desired N-alkylated DPP enantiomers in a significantly improved isolated yield of 34% after purification by silica gel column chromatography. This protocol proved robust and reproducible for both *R*- and *S*-enantiomers, enabling further investigation of their chiroptical and morphological properties in thin films. The ^{1}H-NMR (400 MHz, $CDCl_3$) of *S*-DPP is reported in Figure 1.

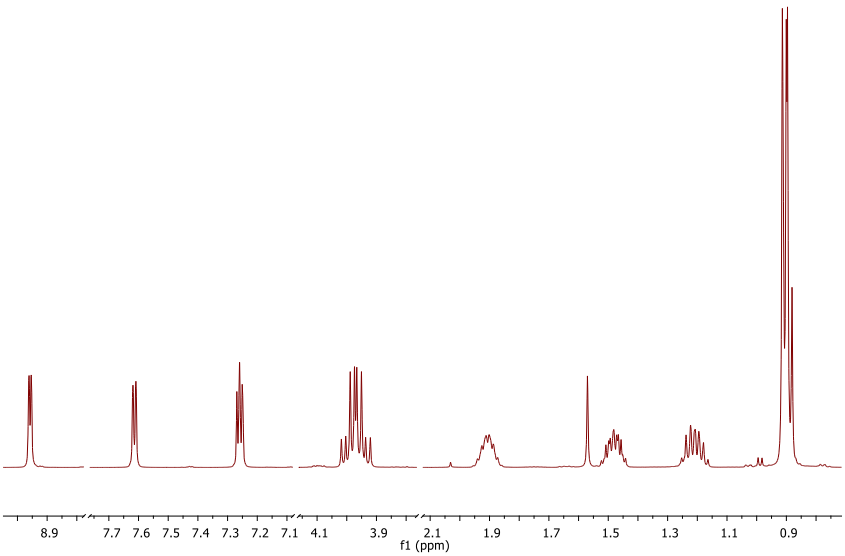


Figure 1. ^{1}H-NMR spectrum of *S*-DPP.

Enantiomers exhibit good solubility in chlorinated solvents like chloroform, but show limited solubility in highly polar solvents, especially methanol. A comparative analysis was conducted on thin films prepared by drop-casting and spin-coating, as solid-state organization in thin films can be influenced by the deposition technique used. The films were characterized by UV-Visible absorption and photoluminescence (PL) spectroscopy, confocal fluorescence microscopy, electronic circular dichroism (ECD) and circularly polarized (CP) PL (CP-PL) measurements.

Like other DPP derivatives, drop-casting the solution resulted in dark purple thick but not homogeneous films. Absorption spectra are similar with a main peak at 510 nm attributed to a $\pi \rightarrow \pi^*$ transition localized on the DPP moiety, accompanied by a second weaker peak at around 565 nm most likely due to molecular aggregation. A second band at higher energy with a double peak at 344 nm and 357 nm was observed[12].

ECD spectra of the two enantiomers exhibited mirror-image spectral bands. For the *R*-DPP film, a positive band was detected at 459 nm and a negative band at 510 nm, whereas the *S*-DPP enantiomer showed a similar spectrum with opposite signs (consistently with previous reports) [12]. Confocal fluorescence microscopy revealed the presence of large and organized crystallites (Figure 2c), which likely facilitate an optimal molecular arrangement, allowing each enantiomer to express its chiroptical properties more effectively.

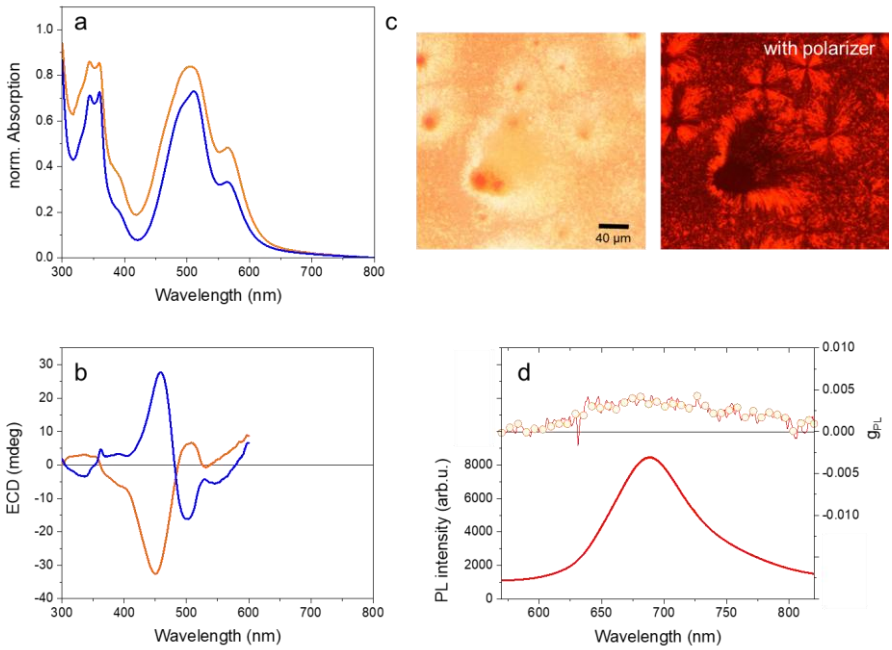


Figure 2. (**a**) Norm. absortion and (**b**) ECD of drop-casted films of *S*-DPP and *R*-DPP; (**c**) fluorescence microscopy image of *R*-DPP drop-casted film with and without polarization filter and (**d**) PL and g_{PL} spectra of *S*-DPP.

Drop-cast film of *S*-DPP showed PL emission with maximum at 564 nm. The PL dissymmetry factor (g_{PL}) for this band is 0.005 (Figure 2d).

The observed CPL emission in the red region of the spectrum is particularly promising for applications in deep-red and near-infrared optoelectronics, where efficient chiral emitters are still scarce. Although the chiroptical performance seems favourable, high-quality homogeneous films remain crucial for organic optoelectronic devices. Spin-coating was employed to enhance film quality control.

S-DPP films, prepared by spin-coating a $CHCl_3$ solution, were indeed homogeneous (Figure 3c). Corresponding absorption spectrum spans 450–600 nm, with main peaks at 522 nm and 565 nm (Figure 3a), the latter possibly assigned to the presence of aggregates.

ECD spectra (Figure 3a) of *S*-DPP show a positive ECD couplet between 400 and 600 nm, with main peaks at 466, 520 and 566 nm, corresponding to $\pi \rightarrow \pi^*$ transition band in the absorption spectrum. A second positive ECD couplet between 300 and 400 nm (in correspondence with the absorption band centered at around 350 nm).

PL emission of *S*-DPP film displayed two peak at 635 and 688 nm, with ϕ_{PL} of 0.11, accompanied by a g_{PL} of ~0.004 (Figure 3d).

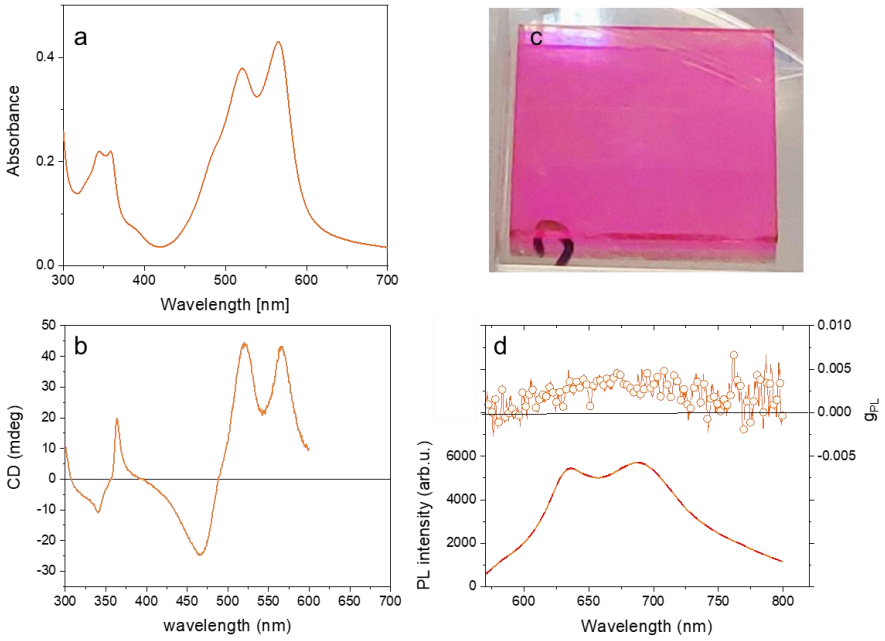


Figure 3. (**a**) Absorption and (**b**) ECD spectra of *S*-DPP spin film; (**c**) image of *S*-DPP spin film and corresponding PL spectra and g_{PL}.

We focused on the *S*-DPP enantiomer to assess its potential as an emitter in an OLED device with the following architecture ITO/PEDOT:PSS/PVK/S-DPP/LiF/Al (sketched in Figure 4a). The active layer is prepared by spin-coating the S-DPP from $CHCl_3$. Preliminary test show that the OLEDs turn on at ~6 V, exhibiting an irradiance (E) of 2.5 μW/cm² and achieving an external quantum efficiency (EQE) of 0.015% (Figure 4b). The red electroluminescence (EL) spectrum displays an emission maximum at 678 nm with a shoulder around 600 nm (Figure 4c). The measurement of the EL dissymmetry factor, which serves as the EL equivalent to the g_{PL}, is currently being conducted to assess the polarization ratio of emitted photons.

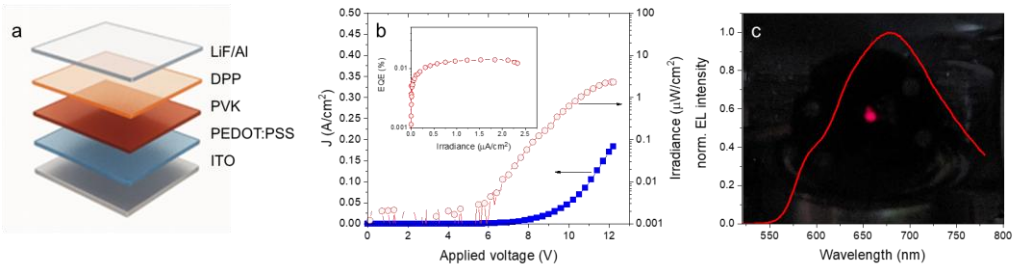


Figure 4. (**a**) DPP-based OLED architecture; (**b**) representative J-E-V curve, and corresponding EQE versus E, of ITO/PEDOT:PSS/PVK/*S*-DPP/LiF/Al device together with EL spectrum (**c**). A real image of the working pixel is embedded as plot background.

4. Conclusions

DPP derivatives stand out as one of the most promising molecular platforms for optoelectronic applications. Their planar, strongly conjugated cores combine intense light

absorption, excellent charge mobility, and exceptional chemical and thermal stability, making them ideal candidates for high-performance organic solar cells, field-effect transistors, and light-emitting devices. Introducing chirality into the DPP scaffold further enriches its functionality, enabling precise tuning of chiroptical responses and providing an opportunity to couple molecular design with advanced device architectures. By comparing the two enantiomers and analysing their behaviour under different processing conditions, this study provides new insights into the structure–property relationships governing chiroptical activity in DPP-based materials. It also highlights the importance of integrating chirality into the design of organic semiconductors, not only to enhance their performance but also to enable novel functionalities that are inaccessible to achiral systems.

These initial findings demonstrate the potential of chiral DPP derivatives as an emissive material for OLED applications. The relatively low turn-on voltage and the observed emission suggest that *S*-DPP could be suitable for use in red-emitting OLED devices. However, the EQE remains modest, indicating that further optimization of both the molecule deposition protocol and the device architecture is necessary to enhance performance. Additional studies, including the ongoing measurement of the EL dissymmetry factor, will provide deeper insights into the chiroptical properties of the device and its suitability for applications requiring CP light emission. These results lay the groundwork for future investigations aimed at improving the efficiency and functionality of DPP-based OLEDs but also other advanced optoelectronic applications.

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Conflicts of Interest:

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