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Tuning the photophysical and chiroptical properties of [4]helicene-diketopyrrolopyrroles

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Abstract

Synthesis and functionalization of diketopyrrolo[3,4-*c*]pyrrole (DPP) derivatives containing chiral groups able to induce a strong chiral perturbation of the DPP core is still a challenging task. We report in this work the straightforward preparation of four bis([4]helicene)-DPP and bis([4]thiahelicene)-DPP dyes upon the condensation of 2-CN-[4](thia)helicene precursors, followed by their N-alkylation by nucleophilic substitution (compounds **9**-**11**) or by a Mitsunobu type strategy (compound **12**). The compound **12**, which contains *sec*-phenylethyl groups attached to the nitrogen atoms, has been obtained as (***R,R***) and (***S,S***) enantiomers. The four DPP-helicenes are luminescent in solution, while the N-benzyl (**10**) and *N*-*sec*-phenethyl (**12**) are emissive in the solid state as well. The chiroptical properties of compound **12** in solution and in the solid state indicate a strong chiral perturbation provided by the α-stereogenic centres, in spite of the stereodynamic nature of the [4]helicene flanking units.

KEYWORDS: chirality, diketopyrrolopyrrole, (thia)helicenes, circular dichroism, photophysics

1. INTRODUCTION

The 3,6-diaryl derivatives of the 2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione, commonly described as diketopyrrolopyrroles (DPPs), are known as outstanding fluorescent dyes and brilliant pigments.[1] The planar, rigid, and conjugated bilactam core of DPPs bridging two aromatic units accounts for remarkable optoelectronic properties such as intense UV-visible absorption with high fluorescence quantum yields, as well as a strong tendency to solid-state organization through π-stacking interactions.[2-7] Owing to these features different DPP derivatives have been employed as active materials in a number of optoelectronic applications such as semiconducting layers in transistors,[8,9] energy harvesting[10,11] and storage,[12,13] fluorescent probes,[14,15] bioimaging[16-18] and theranostics.[19]

A recent trend in the development of new DPP dyes consists in the introduction of elements of chirality into the molecular structure, in order to enrich the optoelectronic properties with chiroptical activity.[20,21] For instance, chiral DPP have recently received increasing attention as circularly polarized luminescence (CPL) emitters, an emerging class of luminophores with possible application into future innovative technologies ranging from cryptography, quantum photonics, three-dimensional imaging, chiral probes, stereoscopic and/or anti-glare displays with enhanced external efficiency.[22-26]

The synthesis of DPP derivatives typically relies on a double condensation reaction between aromatic nitriles and succinic esters in the presence of tertiary alkoxides, that results in the formation of the conjugated bicyclic bilactam scaffold flanked by aromatic units, with different electron-rich character.[1] Unhindered and/or electron poor aromatic nitriles generally give DPPs with higher yields, yet a great variety of bis-aryl DPP are known, including phenyl, thienyl, furyl, pyridyl, and benzofuryls derivatives.[27,28]
The DPP lactam functions obtained through the succinic method are of secondary type and susceptible to establishing extensive hydrogen bonding which prevents solubility in most of the solvents. For this reason, DPPs are thereafter often subjected to *N*-functionalization, in order to ensure satisfactory solubility for processing or further functionalization reactions. For this purpose, *N*-alkyl chains are commonly introduced *via* a bimolecular nucleophilic substitution reaction between the corresponding alkyl halide and the deprotonated lactams.[29] Recently, other types of *N*-derivatization have also been developed, allowing for the introduction of aryl,[30,31] cleavable *tert*-butoxycarbonyl,[32-34] and, especially, chiral α-branched benzyl-type groups.[35]
In order to develop chiral DPP derivatives, stereogenic functions can thus either be introduced at the *N*-position as chiral substituents, or by carefully choosing stereogenic aromatic flanking groups. Accordingly, DPPs *N*-functionalized with chiral chains such as dihydrocitronellyl[36] and caproamides of chiral amines[37] have been reported and described as CD (circular dichroism) active upon aggregation, which indicates adoption of preferential chiral conformations and increased chiral supramolecular organization. However, these derivatives seem to be non-emissive under aggregation, so that CD activity is not accompanied by measurable CPL. Conversely, stereogenic features can be introduced at the flanking positions as aromatic groups endowed with axial chirality or decorated with functions containing elements of point chirality.[20,21,38] Enantiopure binaphthyl groups, for instance, have been used as peripheral substituents on a bis(thien-2-yl) DPP derivative resulting in a CPL active fluorophore reaching g_{lum} dissymmetry factors of $5.8*10^{-4}$ in dichloromethane solutions.[21] Similar g_{lum} dissymmetry factors (up to $9*10^{-4}$ in dichloromethane solutions) have been obtained thanks to a mechanism of chiral exciton coupling for a dyad of achiral diketopyrrolopyrrole (DPP) fluorophores covalently bonded through ethynyl bridges to an enantiopure [6]carbohelicene.[20] However, in both these latter two cases the stereogenic motifs (binaphthyls and helicenes) are likely too distant from the DPP core to contribute directly with their chiral sets of π-electrons to the chiroptical properties of the overall chromophores, but only by means of through-space chiral perturbation (in binaphtyl-DPP derivatives) or by inducing reciprocal chromophore arrangement (in DPP dyads).
Under this premise, we speculate that the capabilities of helicenes as strong chiroptical inducers, remain underexplored in the domain of DPP-based CPL emitters. For these reasons, in our work we have the purpose to investigate the synthetic viability of the direct connection of helicenes with the DPP core through sp^2-sp^2 bonds, and the chiroptical properties of the resulting compounds. In order to do so, we attempted the direct synthesis of the DPP scaffold through classical condensation reactions between succinic esters and aromatic nitriles, but with the unprecedented use of cyano-helicenes as nitrile derivatives.[1] All the while, we considered also the use of bulky *N*-substituents with the goal of reducing the extent of the aggregation caused quenching (ACQ). In particular, *N*-functionalization with chiral *sec*-phenethyl groups turned out to be beneficial towards enhanced chiroptical properties in the presence of stereodynamic and non-resolvable [4]helicenes[39] as aromatic flanking groups.

2. MATERIALS AND METHODS

2.1 General

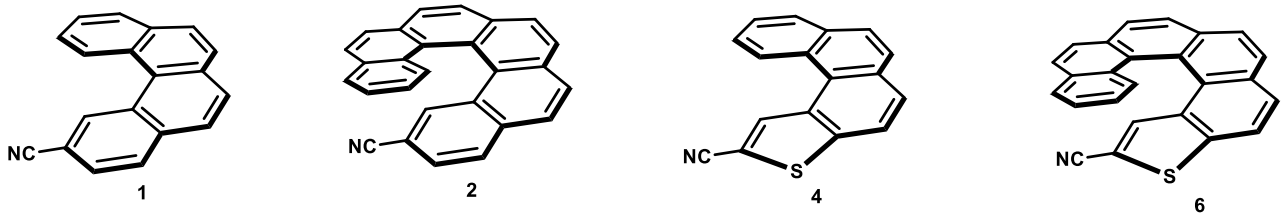


Chart 1: Molecular structure of the cyano-helicenes employed in this work.

All commercially available reagents and solvents were used as received unless otherwise noted. Dry tetrahydrofuran was directly used from the purification machines. Chromatography purifications were performed on silica gel Sorbent Technologies Silica Gel (60 Å, 65 x 250 mesh) and thin layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel 60 (EMD 40–60 mm, 230–400 mesh with 254 nm dye). All reactions were carried out in Schlenk tubes under argon atmosphere. NMR spectra were acquired on a Bruker Avance DRX 300 and 500 spectrometers operating at 300 and 500 MHz for ^{1}H and 75 and 125 MHz for ^{13}C, respectively, at room temperature in $CDCl_3$ solutions. ^{1}H and ^{13}C NMR spectra were referenced to the residual protonated solvent (^{1}H) or the solvent itself (^{13}C). All chemical shifts are expressed in parts per million (ppm) downfield from external tetramethylsilane (TMS), using the solvent residual signal as an internal standard and the coupling constant values (J) are reported in Hertz (Hz). The following abbreviations have been used: s, singlet; d, doublet; dd, doublet of doublets; dd, doublet of doublets of doublets; t, triplet; m, multiplet (Figures S1-S17). Mass spectrometry MALDI–TOF MS and HRMS analyses were recorded on JEOL JMS3000 (MALDI/TOF-TOF) spectrometer. In all cases the used matrix was DCTB trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile.

2.2 Experimental procedures

*Synthesis of 5-(2-(naphthalen-2-yl)vinyl)thiophene-2-carbonitrile (**3**)*

In a Schlenk tube filled with argon, (naphthalen-2-ylmethyl)triphenylphosphonium bromide[40] (1.000 g, 2.1 mmol) was dissolved in dry THF (50 mL). While stirring at -78 °C, *n*-BuLi (1.6 M in hexane, 1.36 mL, 2.17 mmol) was added dropwise to the solution, which was then let to reach rt over 30 min. The deep red/orange solution was cooled again at -78 °C and the 5-formylthiophene-2-carbonitrile (0.284 g, 2.1 mmol) was added. The mixture was stirred overnight eventually reaching rt.
The mixture was passed through a pad of celite and the solvent evaporated. The crude mixture was purified by column chromatography on silica gel with petroleum ether / dichloromethane 7:3 as the eluent, affording 0.520 g (98% yield) of **3** as white crystals of both *E* and *Z* isomers.

Z isomer:
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94 – 7.82 (m, 4H), 7.61 – 7.53 (m, 2H), 7.42 (dd, J = 8.4, 1.7 Hz, 1H), 7.40 (d, J = 3.9 Hz, 1H), 6.98 (d, J = 11.0 Hz, 1H), 6.97 (d, J = 4.4 Hz, 1H), 6.78 (d, J = 11.9 Hz, 1H) ppm.
^{13}C NMR (76 MHz, $CDCl_3$) δ = 146.93, 136.79, 133.54, 133.52, 133.40, 133.17, 128.82, 128.38, 128.13, 127.97, 127.93, 126.73, 126.59, 125.98, 122.31, 114.45, 108.63 ppm.
E isomer:
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.88 – 7.79 (m, 4H), 7.67 (dd, J = 8.7, 1.6 Hz, 1H), 7.53 (d, J = 3.9 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.30 (d, J = 16.2 Hz, 1H), 7.21 (d, J = 16.1 Hz, 1H), 7.07 (d, J = 3.9 Hz, 1H) ppm.
^{13}C NMR (76 MHz, $CDCl_3$) δ = 150.16, 138.26, 133.67, 133.29, 132.86, 128.82, 128.34, 127.93, 127.92, 126.84, 126.80, 125.67, 123.13, 120.23, 114.67, 107.33 ppm.

*Synthesis of phenanthro[3,4-*b*]thiophene-2-carbonitrile (**4**)*

In a 1L photochemical reactor, ***3*** (0.450 g, 1.72 mmol) was dissolved in toluene (650 mL) and argon was bubbled through the mixture for about 10 min. Iodine (0.437 g, 1.72 mmol) and propylene oxide (6.0 mL, 86.1 mmol) were added, and the mixture was stirred overnight under irradiation from a 150W UV lamp. The mixture was then concentrated under vacuum, washed with a saturated aqueous solution of NaS_2O_3, dried over $MgSO_4$, and finally the solvent removed under reduced pressure. The resulting crude was purified by column chromatography on silica gel with petroleum ether / dichloromethane 9:1 as the eluent, affording 0.440 g (99% yield) of **4** as a white solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.95 (s, 1H), 8.80 – 8.75 (m, 1H), 7.98 (dd, J = 7.2, 2.2 Hz, 1H), 7.90 (s, 2H), 7.84 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 8.7 Hz, 1H), 7.75 – 7.63 (m, 2H) ppm.
^{13}C NMR (76 MHz, $CDCl_3$) δ = 142.53, 136.38, 133.26, 133.12, 130.85, 129.71, 129.62, 129.14, 127.80, 127.22, 127.02, 127.01, 126.89, 125.91, 120.64, 115.00, 109.15 ppm.

HRMS (DCTB, M+) calcd for $C_{17}H_9NS^+$ 259.04510; found 259.04502.

*Synthesis of 5-(2-(benzo[c]phenanthren-2-yl)vinyl)thiophene-2-carbonitrile (**5**)*

In a Schlenk tube filled with argon, (benzo[c]phenanthren-2-ylmethyl)triphenylphosphonium bromide[41] (1.300 g, 2.23 mmol) was dissolved in dry THF (50 mL). While stirring at -78 °C, *n*-BuLi (1.6M in hexane, 1.39 mL, 2.23 mmol) was added dropwise to the solution, which was then let to reach rt over 30 min. The deep red/orange solution was cooled again at -78 °C and the 5-formylthiophene-2-carbonitrile (0.306 g, 2.23 mmol) was added. The mixture was stirred overnight eventually reaching rt.
The mixture was passed through a pad of celite and the solvent evaporated. The crude mixture was purified by column chromatography on silica gel with 5% ethyl acetate in petroleum ether as the eluent, affording 0.788 g (98% yield) of **5** as white crystals of both *E* and *Z* isomers.

Z isomer
^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.04 (s, 1H), 8.84 (d, J = 8.4 Hz, 1H), 8.09 – 7.99 (m, 2H), 7.95 – 7.80 (m, 4H), 7.63 – 7.55 (m, 3H), 7.40 (d, J = 2.5 Hz, 1H), 7.09 (d, J = 11.6 Hz, 1H), 7.00 (d, J = 2.5 Hz, 1H), 6.78 (s, J = 12.0 Hz, 1H) ppm.

E isomer
^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.09 (s, 1H), 9.08 (d, J = 8.1 Hz, 1H), 8.05 (dd, J = 7.9, 1.5 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 15.5 Hz, 1H), 7.83 (d, J = 15.6 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.78 (dd, J = 8.4, 1.5 Hz, 1H), 7.75 (ddd, J = 8.5, 6.9, 1.6 Hz, 1H), 7.67 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 7.53 (d, J = 3.9 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.08 (d, J = 3.9 Hz, 1H) ppm.
^{13}C NMR (76 MHz, $CDCl_3$) δ = 150.16, 138.26, 133.77, 133.74, 133.55, 133.32, 131.55, 130.66, 130.31, 129.36, 128.86, 128.17, 127.98, 127.79, 127.49, 127.18, 126.95, 126.58, 126.23, 125.69, 122.99, 120.26, 114.70, 107.28 ppm.

HRMS (DCTB, M+) calcd for $C_{25}H_{15}NS^+$ 361.09274; found 361.09197.

*Synthesis of naphtho[1',2':5,6]phenanthro[3,4-b]thiophene-2-carbonitrile (**6**)*

In a 1L photochemical reactor, ***5*** (0.300 g, 0.83 mmol) was dissolved in toluene (650mL) and argon was bubbled through the mixture for about 10 min. Iodine (0.211 g, 0.83 mmol) and

propylene oxide (2.9 mL, 41.5 mmol) were added, and the mixture was stirred overnight under irradiation from a 150W UV lamp. The mixture was then concentrated under vacuum, washed with a saturated aqueous solution of NaS_2O_3, dried over $MgSO_4$, and finally the solvent removed under reduced pressure. The resulting crude was purified by column chromatography on silica gel with petroleum ether / ethyl acetate 95:5 as the eluent, affording 0.198 g (67% yield) of ***6*** as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.06 (d, J = 8.6 Hz, 1H), 8.02 – 7.91 (m, 7H), 7.70 (d, J = 8.5 Hz, 1H), 7.41 (ddd, J = 7.8, 6.9, 1.0 Hz, 1H), 7.38 (dd, J = 7.0, 1.3 Hz, 1H), 7.11 (d, J = 0.4 Hz, 1H), 6.92 (ddd, J = 8.4, 7.0, 1.3 Hz, 1H) ppm.
^{13}C NMR (76 MHz, $CDCl_3$) δ = 140.45, 137.27, 133.99, 133.19, 132.28, 132.03, 130.91, 129.80, 128.97, 128.58, 128.57, 128.34, 127.50, 127.41, 127.18, 127.07, 126.94, 126.47, 126.20, 125.52, 124.15, 120.90, 114.60, 106.34 ppm.

*Synthesis of 3,6-bis(benzo[c]phenanthren-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**7**)*

In a three-neck flask, sodium metal (0.171 g, 7.42 mmol) was dissolved under argon atmosphere in refluxing *tert*-amyl alcohol (8 mL) with the help of few grains of $FeCl_3$. Once all the sodium was completely dissolved, the temperature was lowered to 50 °C and ***1*** (0.470g, 1.86 mmol) dissolved in 4 mL of toluene was added to the stirred mixture. The temperature was raised to 130°C and di-*tert*-amyl succinate (0.959 g, 3.71 mmol) dissolved in *tert*-amyl alcohol (4 mL) was added dropwise over 18 h, letting the reaction to proceed overnight. The temperature was then lowered to 65 °C, 1 mL acetic acid was injected, and the mixture brought to reflux for 5 min before being finally cooled to rt. The resulting mixture was poured into 100 mL of MeOH. The precipitate was collected by filtration, washed with MeOH and Et_2O, affording 0.192 g (35% yield) of ***7*** as a dark red powder which was used without further purification.

*Synthesis of 3,6-bis(phenanthro[3,4-b]thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**8**)*

In a three-neck flask, sodium metal (0.237 g, 10.32 mmol) was dissolved under argon atmosphere in refluxing *tert*-amyl alcohol (10 mL) with the help of few grains of $FeCl_3$. Once all the sodium was completely dissolved, the temperature was lowered to 50 °C and ***4*** (0.670 g, 2.58 mmol) dissolved in 5 mL of toluene was added to the stirred mixture. The temperature was raised to 130°C and di-*tert*-amyl succinate[42] (1.335 g, 5.17 mmol) dissolved in *tert*-amyl alcohol (5 mL) was added dropwise over 18 h, letting the reaction to proceed overnight. The temperature was then lowered to 65 °C, 1 mL acetic acid was injected, and the mixture brought to reflux for 5 min before being finally cooled to rt. The resulting mixture was poured into 150 mL of MeOH. The precipitate was collected by filtration, washed with MeOH and Et_2O, affording 0.400 g (52% yield) of ***8*** as a dark purple powder which was used without further purification.

*Synthesis of 3,6-bis(benzo[c]phenanthren-2-yl)-2,5-dimethyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**9**)*

Under argon atmosphere, ***7*** (0.160 g, 0.3 mmol) was dissolved in dry DMF (15 mL) with K_2CO_3 (0.188 g, 1.1 mmol), and stirred at 100°C for 30 min. The temperature was lowered to 60 °C, iodomethane (70 µL, 1.1 mmol) was injected, and the mixture stirred for 3h at 100°C. Once cooled back to rt, the mixture was poured into 150 mL of water, and the resulting precipitate was collected by filtration and washed with few mL of cold MeOH.
The compound was purified by column chromatography on silica gel with dichloromethane as the eluent, affording 0.160 g (95% yield) of ***9*** as a dark red solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.54 (s, 2H), 9.34 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 0.9 Hz, 4H), 8.01 (dd, J = 7.9, 1.3 Hz, 2H), 7.93 (s, 4H), 7.93 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 8.5 Hz, 2H), 7.78 (ddd, J = 8.3, 7.0, 1.3 Hz, 2H), 7.65 (ddd, J = 7.9, 7.0, 1.0 Hz, 2H), 3.50 (s, 6H) ppm.
^{13}C NMR (76 MHz, $CDCl_3$) δ = 162.97, 149.06, 134.79, 133.66, 131.51, 130.12, 130.09, 129.49, 129.19, 129.17, 129.14, 128.60, 128.57, 128.30, 127.92, 127.10, 126.72, 126.47, 125.87, 125.77, 110.06, 29.89 ppm.

HRMS (DCTB, M+) calcd for $C_{44}H_{28}N_2O_2^+$ 616.21344; found 616.21453.

*Synthesis of 3,6-bis(benzo[c]phenanthren-2-yl)-2,5-dibenzyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**10**)*

Under argon atmosphere, **7** (0.070 g, 0.12 mmol) was dissolved in dry DMF (5 mL) with K_2CO_3 (0.164 g, 1.2 mmol), and stirred at 100 °C for 30 min. The temperature was lowered to 60 °C, benzyl bromide 140 µL, 1.2 mmol) was injected, and the mixture stirred for 3h at 100 °C. Once cooled back to rt, the mixture was poured into 50 mL of water, and the resulting precipitate was collected by filtration and washed with few mL of cold MeOH.
The compound was purified by column chromatography on silica gel with dichloromethane as the eluent, affording 0.055 g (60% yield) of **10** as a dark red solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.53 (s, 2H), 9.26 (d, J = 9.0 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 9.3 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.94 (s, 4H), 7.84 (d, J = 8.6 Hz, 4H), 7.59 (ddd, J = 7.2, 1.4 Hz, 4H), 7.53 (ddd, J = 8.4, 7.1, 1.6 Hz, 2H), 7.23 – 7.17 (m, 10H), 5.04 (s, 4H) ppm.

HRMS (DCTB, M+) calcd for $C_{56}H_{36}N_2O_2^+$ 768.27757; found 768.27713.

*Synthesis of 2,5-dibutyl-3,6-bis(phenanthro[3,4-b]thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**11**)*

Under argon atmosphere, **8** (0.03 g, 0.05mmol) was dissolved in dry DMSO (5.0 mL) with K_2CO_3 (0.028 g, 0.2 mmol), and stirred at 140 °C for 45 min. The temperature was lowered to 60 °C, 1-bromobutane (30 µL, 0.3 mmol) was injected, and the mixture refluxed for 5 h. Once cooled back to rt, the mixture was poured into 50 mL of water, and the resulting precipitate was collected by filtration and washed with few mL of cold MeOH.
The compound was purified by column chromatography on silica gel with dichloromethane as the eluent, affording 0.008 g (22 % yield) of **11** as a dark purple solid.

^{1}H NMR (499 MHz, $CDCl_3$) δ = 10.52 (s, 2H), 9.69 (d, J = 8.5 Hz, 2H), 8.07 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.96 – 7.92 (m, 4H), 7.90 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 8.7 Hz, 2H), 7.72 (dd, J = 7.3 Hz, 2H), 4.37 – 4.32 (m, 4H), 1.94 (tt, J = 7.5 Hz, 4H), 1.63 – 1.54 (m, 4H), 0.88 (t, J = 7.5 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.93, 145.93, 143.88, 137.02, 134.24, 132.24, 132.23, 131.96, 131.89, 131.74, 131.42, 130.75, 130.54, 130.50, 130.34, 130.11, 129.94, 123.88, 102.90, 49.14, 32.79, 24.75, 16.88 ppm.

HRMS (DCTB, M+) calcd for $C_{46}H_{36}N_2O_2S_2^+$ 712.22217; found 712.22127.

*Synthesis of 3,6-bis(benzo[c]phenanthren-2-yl)-2,5-bis(1-phenylethyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**12**)*

Under argon atmosphere, tributylphosphine (750µL, 3 mmol) was dissolved in dry THF (30mL) and the mixture cooled at 0 °C, then DIAD (600 µL, 3 mmol) was added dropwise resulting in a colourless solution. In a separate Schlenk tube, under argon atmosphere, **7** (0.010 g, 0.06 mmol) was dispersed in dry THF (3 mL) and the mixture cooled at 0 °C. 3.2 mL of the first solution containing the Bu_3P/DIAD complex were added dropwise to the second solution resulting in a bright purple solution. At this point, (*S*)-1-phenyl-ethanol (37 µL, 0.3 mmol) dissolved in THF (1mL) was injected dropwise to the mixture over 2h. The mixture was then allowed to reach rt and kept under stirring overnight.
The mixture was concentred under vacuum, diluted into CH_2Cl_2 and washed with 1M HCl, then water. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure.
The compound was purified by column chromatography on silica gel with petroleum ether / dichloromethane 2:8 as the eluent, affording 0.015 g (66% yield) of **12** as a red solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.49 (s, 2H), 9.36 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 8.01 (dd, J = 7.9, 0.7 Hz, 2H), 7.95 (d, J = 7.1 Hz, 2H), 7.94 (s, 4H), 7.84 (d, J = 8.5 Hz, 2H), 7.76 (dd, J = 8.4, 1.4 Hz, 2H), 7.60 (t, J = 7.2 Hz, 2H), 7.41 (ddd, J = 7.1, 1.2 Hz, 2H), 7.37 – 7.22 (m, 10H), 5.43 (q, J = 7.2 Hz, 2H), 1.99 (d, J = 7.1 Hz, 6H) ppm.

^{13}C NMR (76 MHz, $CDCl_3$) δ = 163.19, 149.85, 141.43, 134.72, 133.50, 131.47, 130.34, 130.12, 129.86, 129.14, 129.06, 128.84, 128.62, 128.37, 127.90, 127.28, 127.24, 127.03, 126.88, 126.63, 126.35, 125.77, 125.23, 111.22, 53.75, 18.64.

HRMS (DCTB, M+) calcd for $C_{58}H_{40}N_2O_2^+$ 796.30710; found 796.30843.

2.3 CD and UV Measurements

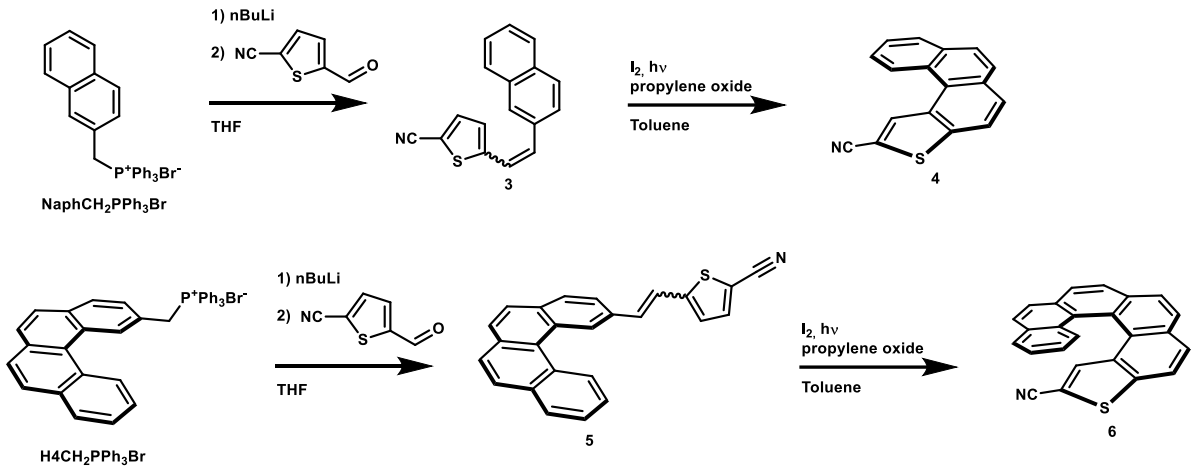
CD and UV-Vis-NIR absorption spectra were recorded on a Jasco J-1500 CD spectrophotometer equipped with standard PMT detector (for the spectral range 180-800 nm) or InGaAs detector (800-1600 nm). All spectra were recorded at 20 °C in the transmission mode.

3. RESULTS AND DISCUSSION

3.1 Synthesis of DPP-helicenes

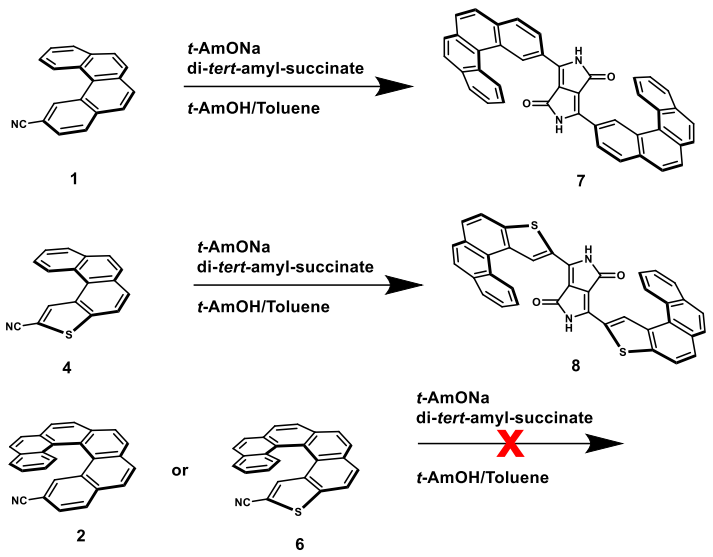
Aromatic nitriles are the key intermediates in the synthesis of DPP derivatives *via* the succinic method, with phenyl and thienyl derivatives being some of the most employed.[1] The nature of the first aromatic ring connected to the bilactam core of the DPP is known to deeply impact the morphology and the spectroscopic properties of the resulting dye. Also, due to the lower steric hindrance of five-membered rings with respect to phenyl rings, cyanothiophenes usually give higher yields in the DPP synthesis. Moving from these premises, in order to include helicene moieties directly connected to the bilactam core of DPP, a series of helicenes with a terminal benzonitrile or a thienonitrile ring, including the 2-cyano-carbo[4]helicene (**1**)[43], the 2-cyanocarbo-[6]helicene (**2**),[44] the 2-cyano-thia[4]helicene (**4**), and the 2-cyano[6]thiahelicene (**6**), were prepared *via* a well-known two-steps procedure for sequential *ortho*-annulation. The compounds ***1***,[43] and ***2***[44] were synthesized according to previously reported procedures.

Similarly, the thieno-fused compounds ***4*** and ***6*** were prepared starting from phosphonium salts: $NaphCH_2PPh_3Br$ and $H4CH_2PPh_3Br$ were first olefinated with formylthiophene-2-carbonitrile under Wittig conditions, and then the resulting mixtures of E/Z diarylethenes were subjected to oxidative photocyclization in the Mallory conditions,[40,45] yielding the cyano-thiahelicenes ***4*** and ***6***, respectively (Scheme 1).



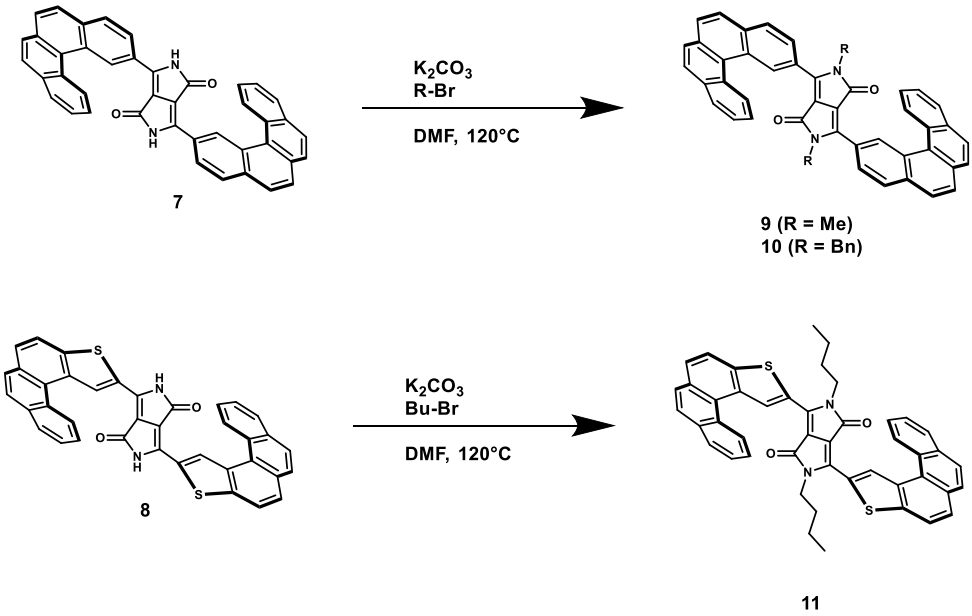
Scheme 1: Synthetic route to compounds ***4*** and ***6***, starting from (naphthalen-2-ylmethyl)triphenylphosphonium bromide ($NaphCH_2PPh_3Br$), and (benzo[c]phenanthren-2-ylmethyl)triphenylphosphonium bromide ($H4CH_2PPh_3Br$**)** respectively.

However, the subsequent condensation of these derivatives with succinic esters failed when performed in classical conditions, namely in sodium *tert*-amoxide/*tert*-amyl alcohol solutions. Indeed, this reaction tends to give lower yields as the electron-donating character and the steric hindrance increase within the aromatic reagent. Moreover, the cyano-helicenes showed poor solubility in *tert*-amyl alcohol (boiling point: 102°C). We therefore modified the protocol by dissolving the cyano-helicenes in hot toluene, and injecting the resulting solution into the hot reaction mixture, before starting the dropwise addition of the succinate ester. When cyano-helicenes ***1*** and ***4*** were used, a colour change from light brown to purple was observed few minutes after succinate addition, indicating the DPP formation. Conversely, cyano-helicenes ***2*** and ***6*** did not react, but were recovered almost quantitatively (Scheme 2). Under the assumption that toluene does not take part into the reaction mechanism due to its relatively high pka value, we presume that the increased reactivity of ***1*** and ***4*** under these conditions is to be ascribed to a better solubilization as well as to an increased reflux temperature (boiling point of toluene: 111 °C).



Scheme 2: Synthetic route to DPP-helicenes ***7*** and ***8*** *via* an optimized succinic method for DPP synthesis. The cyanohelicenes ***2*** and ***6*** did not react and were recovered almost quantitatively after work-up.

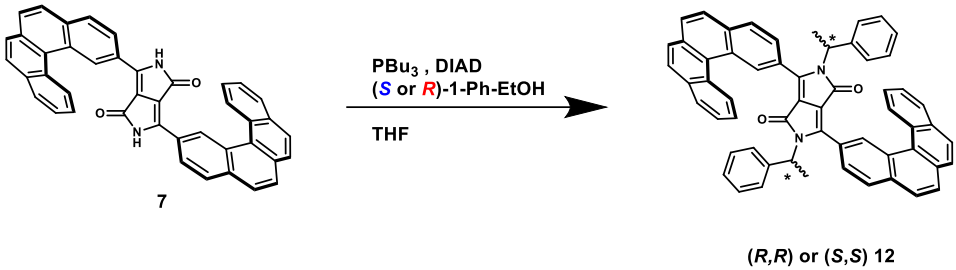
The lack of reactivity of ***2*** and ***6*** remains unexplained, and it is not clear if it has a steric or electronic origin, yet it seems to agree with the observed reduced reactivity of aromatic nitriles in reactions involving anionic nucleophiles, as the aromatic system becomes larger.[46]
Due to the stereodynamic properties of [4]-helicenes,[39] these derivatives required further modifications to become chiral. Achiral counterparts were synthesized by classical *N*-alkylation with alkyl or benzyl chains, for comparison. In details, the DPP ***7*** was alkylated with methyl groups and benzyl groups, yielding the dyes ***9*** and ***10*** respectively. Conversely, the DPP ***8*** gave the soluble derivative ***11*** upon *N*-alkylation with longer chains only, such as n-butyl chains (Scheme 3).



Scheme 3: *N*-alkylation of DPP-helicenes ***7*** and ***8*** *via* S_N2 reaction with alkyl bromides, yielding the compounds ***9***, ***10***, and ***11***.

Following our recently developed method for *N*-alkylation of DPP with chains bearing stereocenters at the *alpha*-position,[35] we modified the DPP ***7*** with stereodefined 1-phenyl-ethyl

chains, aiming at an effective chiral perturbation in compounds ***12*** (Scheme 4). The spectroscopic, chiroptical, and electrochemical properties of the resulting molecules were characterised.



Scheme 4: Enantioselective *N*-functionalization of DPP ***7*** *via* Mitsunobu reaction with enantiopure *sec*-phenethyl alcohols. As Walden inversion occurs during this type of reaction, the *R*,*R* enantiomer is obtained from (*S*)-1-phenyl-ethanol, and *vice versa*.

3.2 Photophysical and chiroptical characterization

Helicene-DPPs ***9***, ***10*** and ***12*** in 10^{-5} M chloroform solutions, show unresolved absorption bands peaking at 504 nm, 496 nm, and 494 nm, respectively. The resulting fluorescence spectra, measured under excitation at the wavelength of maximum absorption, exhibit large Stoke shifts (65 nm, 76 nm, and 58 nm respectively) and unresolved band structure. The large Stoke shifts indicate a significant flexibility of the chromophore scaffold that is able to dissipate a large part of the excitation energy *via* vibrational coupling. On the other hand, the thiahelicene-DPP ***11*** exhibited both absorption and emission spectra with evident vibronic structuration, and a relatively small Stoke shift of 15 nm, suggesting a more rigid molecular structure. Also, the intense bathochromic shift affecting the compound ***11*** compared to the carbohelicene-DPPs, of more than 100 nm, is coherent with a more planar conformation and a more efficient conjugation between the DPP core and the helicene (Figure 1).

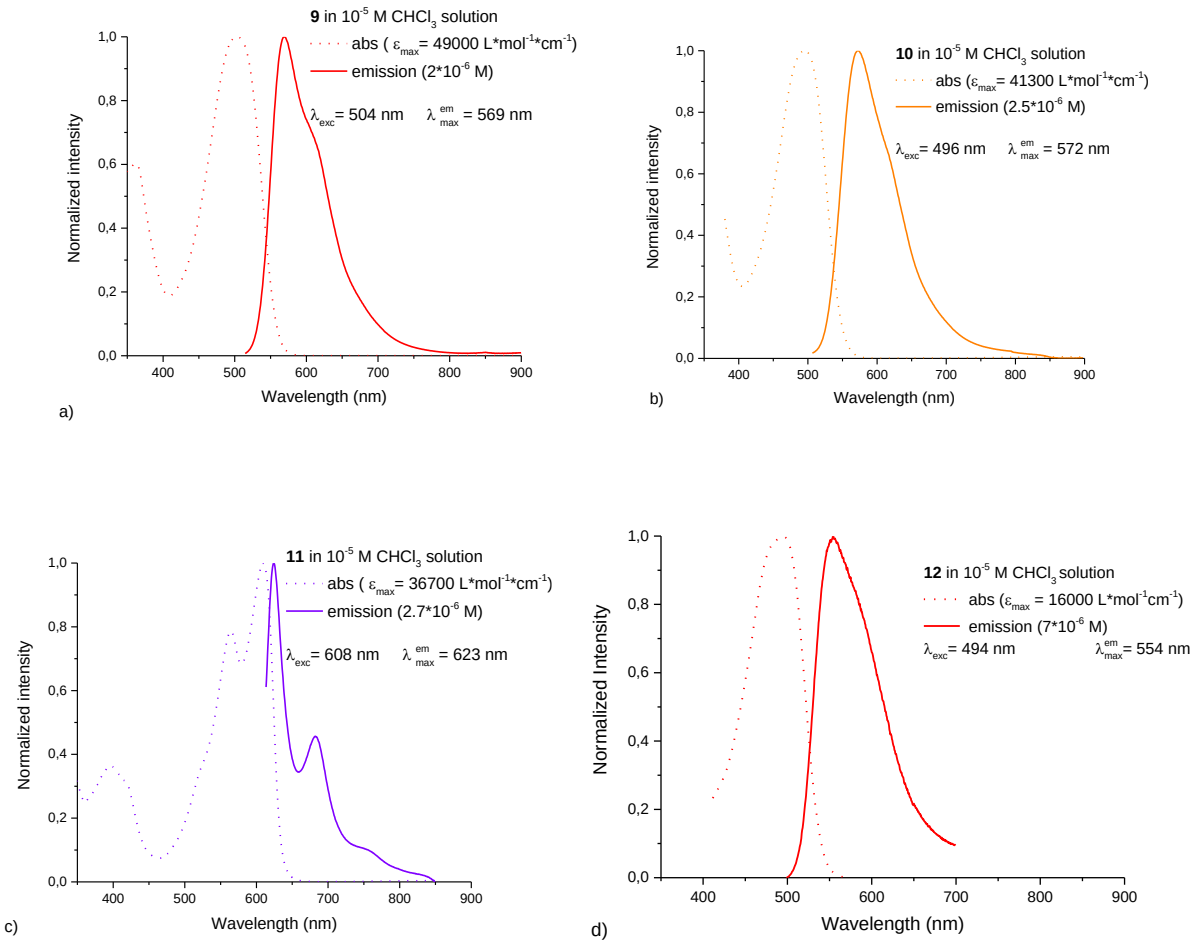


Figure 1: Normalized absorption (dotted lines) and emission (solid lines) spectra of compounds ***9*** (a), ***10*** (b), ***11*** (c), and ***12***(d), in 10^{-5} M chloroform solutions. The ε reported in each panel correspond to the molar extinction coefficient at the wavelength of maximum absorption, $\boldsymbol{\lambda_{max}^{abs}}$. The fluorescence spectra are measured under excitation at , $\boldsymbol{\lambda_{exc}}$ = , $\boldsymbol{\lambda_{max}^{abs}}$, on diluted solutions with absorbance of 0.1 in 1 cm wide cells, and the wavelength of maximum emission, $\boldsymbol{\lambda_{max}^{em}}$ is reported in each panel.

The two enantiomers **(*R*,*R*)** and **(*S*,*S*)** of the compound ***12*** in 10^{-4} M THF solutions exhibited detectable mirror image circular dichroism (CD) activity, all over the UV-visible absorption region, which indicates that the chromophore is efficiently perturbed by the presence of the α-chiral *N*-substituent. In THF, the low energy band at 475 nm corresponds to a g_{abs} of $+1.5*10^{-4}$, while the high energy bands peaking at 281 nm reach g_{abs} of $-2.5*10^{-4}$, for the ***RR*** enantiomer.
In order to assess the impact of molecular chirality on the formation of stereodefinite aggregates and/or stereodefinite conformations stabilised upon aggregation, CD spectroscopy was performed on solutions of ***12*** in a series of binary mixtures of good and bad solvents, such as THF/H_2O and $CHCl_3$/MeOH.[47,48] It resulted that while the CD signature does not significantly evolve upon changing THF with a THF/water mixture in a 1:9 ratio (a bathochromic shift of 15 nm is observed only, Figure 2a), in $CHCl_3$/MeOH mixtures, a slight evolution of the CD spectra is observed while increasing the methanol fraction: in pure chloroform the low energy band at 475 nm corresponds to a g_{abs} of $+1.7*10^{-4}$, for the ***RR*** enantiomer, and gradually increase up to $+3.3*10^{-4}$ in pure methanol, along with a slight bathochromic shift of 6 nm. Similarly, the band at 277 nm passes from a g_{abs} of $-1.1*10^{-4}$ to $-2.4*10^{-4}$, for the ***RR*** enantiomer, when the solvents changes from 100% chloroform to 100% methanol. Moreover, a signal peaking at 299 nm emerge upon increasing methanol fraction, going from negligible g_{abs} in 100% chloroform up to $-2.7*10^{-4}$ in 100% methanol, for the ***RR*** enantiomer (Figure 2b).

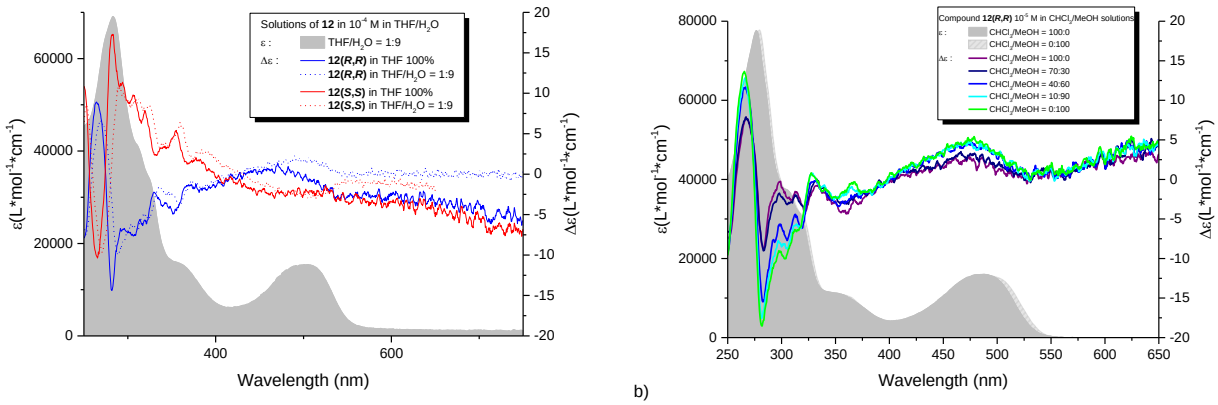


Figure 2: Circular dichroism spectra of the ***RR*** and ***SS*** enantiomers of compound ***12***, in different solutions: *a*) each enantiomer is dissolved into THF (solid lines) or a mixture of THF/water (dotted lines) at a concentration of 10^{-4} M; *b*) the ***RR*** enantiomer is dissolved at concentration of 10^{-5} M in a series of chloroform/methanol mixtures with $CHCl_3$/MeOH ratio of 10:0 (purple line), 7:3 (dark blue line), 4:6 (blue line), 1:9 (cyan line), 0:10 (green line). The average ε of the enantiomeric pair is shown in both panel as underlying gray area.

Films of **(*R,R*)-*12*** and **(*S,S*)-*12*** were prepared by spin coating 10^{-3} M THF solutions onto glass slides (0.1 mL, 1000 rpm, 90 s), in order to study the solid state chiroptical properties of the resulting materials. The maximum absorption is red-shifted of around 15 nm with respect to solutions and the corresponding CD spectra show two large bands one with positive ellipticity at low energies, and negative at high energies, for the ***RR*** enantiomer. Upon thermal annealing (1h, 165 °C) the CD signals almost doubled in intensity, and the high energy band showed a marked evolution into a structured system (Figure 3a). In all the cases, the observed ECD is dominated by the intrinsic isotropic circular dichroism of molecular/supramolecular origin, since rotations around the optical axis or 180° flips of the sample did not produce any considerable variations in the ECD response.[49,50]

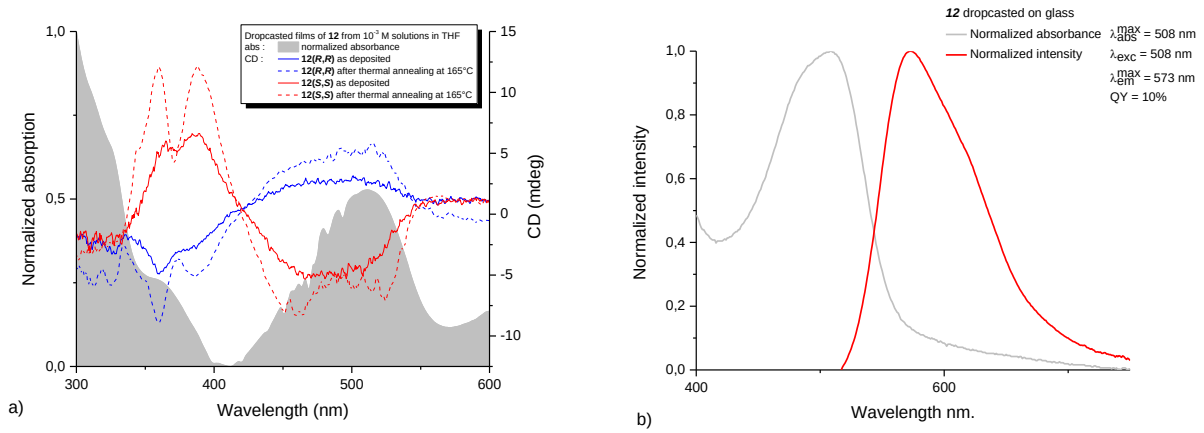


Figure 3: a) circular dichroism spectra of the ***RR*** and ***SS*** enantiomers of compound ***12***, in dropcasted films, before (solid lines) and after (dotted lines) thermal annealing at 165°C for 1h (the normalized absorbance is shown as underlying gray area); b) photoluminescence spectrum (red line) of compound ***12*** in dropcasted film on glass, under excitation at $\boldsymbol{\lambda_{exc}}$ = 508 nm (the emission has a peak at $\boldsymbol{\lambda_{max}^{em}}$= 573 nm, and the absolute fluorescence quantum yield is measured as 10%).

Interestingly, compounds **10** and **12** are emissive in the solid state as well (Fig. S18 and Fig. 3b), very likely thanks to the presence of the steric bulk benzyl and phenethyl groups which prevents the quenching due to π-π stacking between the DPP cores.

In conclusion, the synthetic strategy we adopted here for the chiral functionalization of the DPP core proves its efficiency, as the presence of stereogenic centres on the *N*-substituents in the α-position induces a chiral perturbation of the rest of the molecule, in spite of the dynamic

chirality of the [4]helicene units, which is visible in the CD spectra in solution, in aggregates and in the thin films.

4. CONCLUSION

In summary, the synthesis of DPP-helicenes, with direct covalent link between the bilactam core and the helicene units, has been attempted for a series of four 2-cyano-[4] and [6](thia)helicenes. Only the corresponding bis-[4](thia)helicene-DPP **7** and **8** could be obtained and then engaged in *N*-alkylation reactions either by classical SN2 reaction or by the Mitsunobu strategy. The latter allowed the preparation of the enantiopure compounds (***S,S***)-**12** and (***R,R***)-**12** containing α-stereogenic centers, while the former afforded the achiral compounds **9**-**11**. All the newly prepared DPP derivatives are luminescent in solution, while compounds **10** and **12** are emissive in the solid state as well. Particularly interesting are the chiroptical properties of the chiral DPP **12**, which shows strong CD activity in solution and in the solid state, demonstrating that the presence of the N-phenethyl groups ensures a chiral perturbation of the entire molecule, in spite of the stereodynamic nature of the [4]helicene units. Further endeavour in this direction is devoted to the investigations of the CPL properties of such chiral DPP derivatives and to the understanding of their CD activity.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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