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Porphyrin- and Bodipy-helicene conjugates: syntheses, separation of enantiomers and chiroptical properties†

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The synthesis of several new compounds containing a chromophore and a helicenic moiety is reported. The preparation, characterisation and some physico–chemical studies are detailed. In particular, the two enantiomers of several chiral molecules of this type were separated by chiral HPLC (both analytically and in a preparative way) and their racemisation rates were determined for short-lived species. Electronic circular dichroism (ECD) and circular polarised luminescence (CPL) measurements were performed for the compounds with a very long racemisation half-life. Chiral porphyrins and Bodipys both gave ECD and CPL responses over a large area of the visible spectrum.

Introduction

Helicenes are inherently chiral, π-conjugated molecules that have been the subject of numerous studies during the last twenty years after improvements of synthetic procedures for their preparation and progress in chromatographic separation of their enantiomers.[1–7] This interest was and is still due to their exceptional chiroptical properties. Future applications are expected in optoelectronics, non-linear optics, asymmetric synthesis or catalysis, chiroptical switches, and even magnetochirality.[8–13] The two enantiomers of these helicenes are stable as soon as the number of *ortho*-fused rings is equal to or higher than six.[14] However, one main drawback for optical applications is their poor absorbance in the visible area of the electronic spectrum. One way which might lead to an improvement of these optical properties, is to connect these helical aromatics to known chromophores. Porphyrins and Bodipys are poly-pyrrolic aromatics that absorb strongly in the visible area and both compounds are also good photosensitisers with emission in the visible region. To obtain compounds presenting CPL, covalent linkages of these molecules to chiral helicenes might be of interest (see Fig. 1). Several examples of helical porphyrinoids[15–27] and Bodipy-helicenes conjugates were described earlier in the literature.[28–38] Some of us have shown recently that a fused porphyrin–helicene conjugate presented interesting absorbance properties covering the full visible spectrum.[27]

During this study, the presence of electron donating groups and the positioning of these substituents on the aromatic helicene attached to the porphyrin proved to be crucial in order to fuse together the two aromatic moieties. In this report, the preparation of new porphyrin conjugates with [4] or [6]helicenic groups bearing methyl donating groups will be detailed, and the Scholl reaction attempts to fuse the aromatics with the porphyrin core is described. Bodipy-[6]helicene conjugates were also prepared, and together with several other porphyrins bearing helicenic substituents were submitted to chiral HPLC to separate the enantiomers. For the stable enantiomers, CD

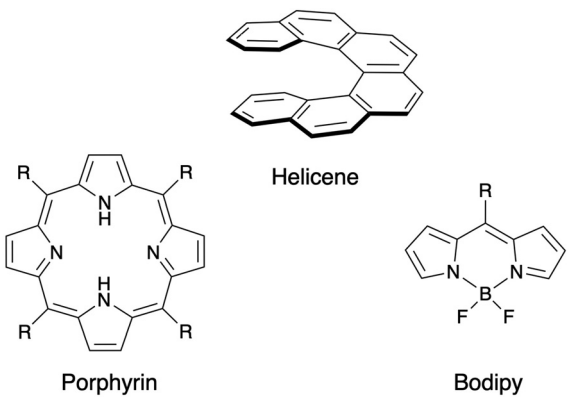

Fig. 1 Chemical structures of a helicene, a porphyrin, and a Bodipy.

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spectra were obtained and for the compounds presenting emission, CPL spectra were also recorded.

Results and discussion

Synthesis and characterisation

All helicenes were prepared following described procedures, but with (or without) different donating substituents at one terminal aromatic.[39,40] The aromatic aldehyde **3** was prepared according to the described procedure by substituting the starting aromatic phosphonate with two additional methyl groups. Even if the steric hindrance should decrease the cyclisation yield, the favourable inductive effect of the methyl groups and the limitation to only one possible cyclisation led to a rather good yield of 61% in the photocyclisation reaction compared to unsubstituted stilbene derivatives (see Scheme 1).

Following the same synthetic route, the bromo[6]helicene **4** bearing two methyl groups at the brominated terminal aromatic was prepared starting from the known benzo[*c*]phenanthrene-2-carbaldehyde (see Scheme 1, bottom).[41] Classical chemistry afforded the [6]helicene **5** bearing a pinacolborate substituent, ready for coupling reactions.

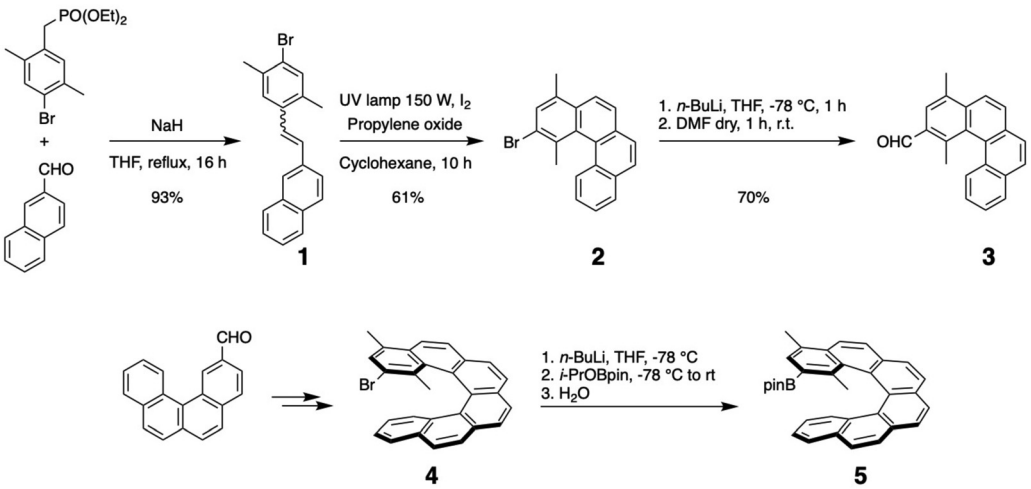
A mixture of pyrrole, aldehyde **3** and 2,6-dimethyl-4-(*tert*-butyl)-benzaldehyde was then reacted in presence of trifluoroborate etherate under classical Lindsey conditions to obtain, after chromatographic separation, porphyrin **6** in 9% yield. After quantitative metalation with nickel(II), the nickel(II) porphyrin **7** was treated with iron(III) chloride to obtain the fused compound **8** with a respectable 43% yield (see Scheme 2). The nickel(II) ion was chosen, because nickel(II) porphyrins are very stable and diamagnetic, thus avoiding complexation with iron (III) during the course of the oxidation reaction. The cyclodehydrogenative oxidation (Scholl reaction) is known to afford fused nickel(II) porphyrins with many different aryl groups bearing donating substituents.[42–49]

To obtain an analogous nickel(II) porphyrin, now bearing one [6]helicenic *meso*-group, the synthetic route was modified, because the yield of the statistical Lindsey porphyrin synthesis used previously was rather low (9%). Starting from the known triarylporphyrin base **9**, iodination and metalation with nickel (II) afforded nickel(II) porphyrin **10** in very good yield (see Scheme 3). A Suzuki–Miyaura coupling between this porphyrin and helicene **5** afforded then in 25% yield the nickel(II) porphyrin **11**. Despite many attempts to run the cyclodehydrogenative oxidation with **11**, the fused compound was never observed, in strong contrast with the previous Scholl reaction performed on porphyrin **7** to obtain fused nickel(II) porphyrin **8**. We had encountered similar failures running Scholl reactions earlier and this was attributed to the steric hindrance of the terminal aromatic phenyl group which prevented the cyclisation.[27]

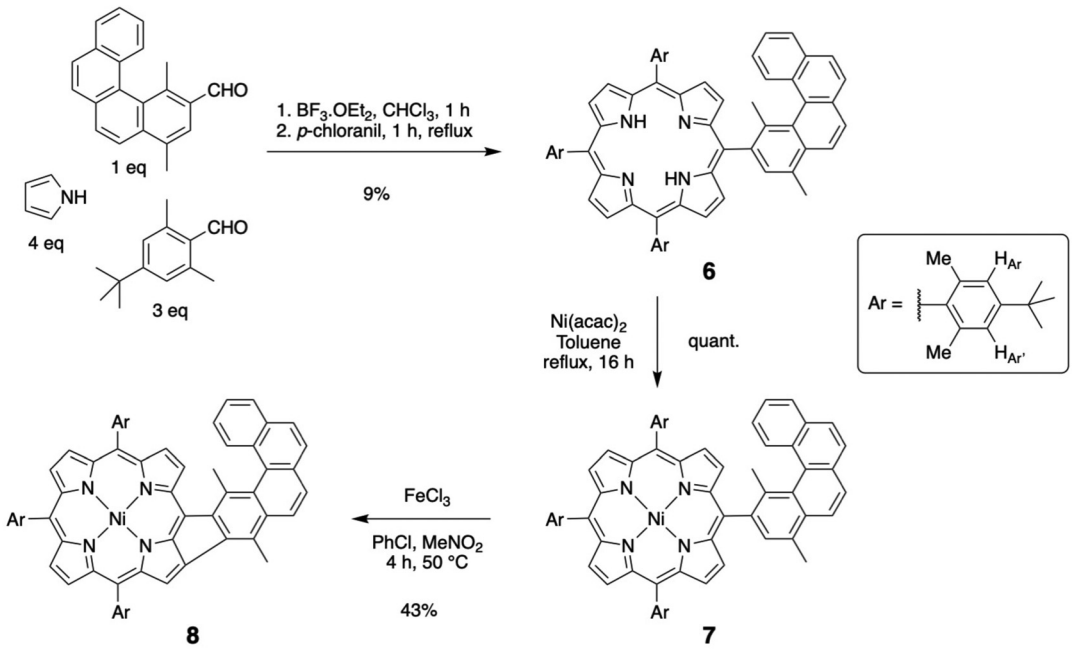
Other chromophores of importance for potential CPL applications are the sensitisers derived from the Bodipy scaffold. As mentioned earlier, a few helicenic Bodipy derivatives have been previously described, but surprisingly not the simplest one (compound **12** shown in Scheme 4). Compound **12** was obtained by a very simple one-pot procedure following a described protocol.[50]

The racemisation rate of the enantiomers of [6]helicenes is known and even when unsubstituted, the half-life is higher than a year at room temperature.[14] However, the half-life of methylated [4]helicenes are much shorter (closer to one hour) and it was necessary to check the potential stability of the enantiomers of compound **8** by variable temperature NMR, before starting a tedious preparative HPLC separation of the enantiomers.

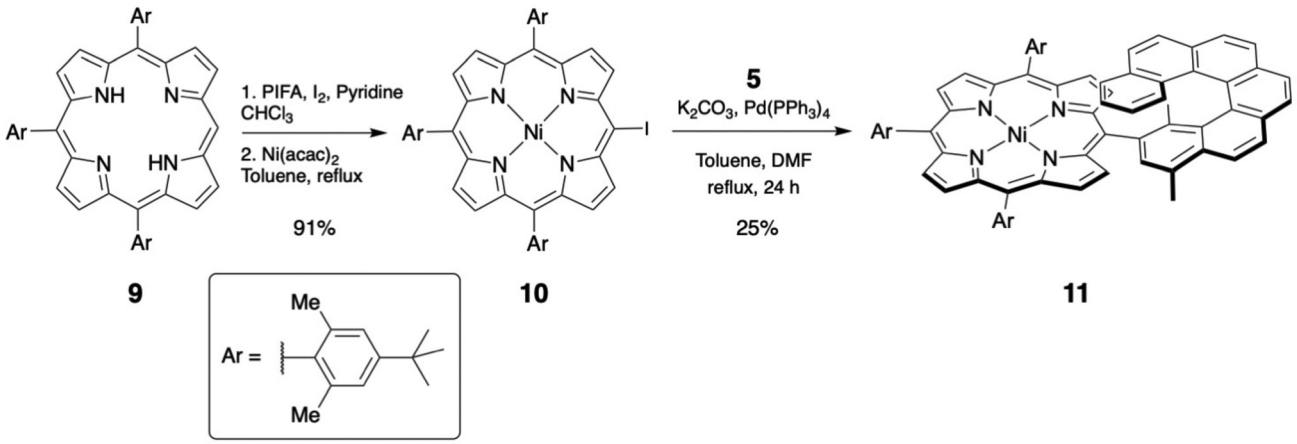
The ^{1}H NMR spectra of compound **8** were recorded at different temperatures in D_2-tetrachloroethane (from 25 °C to 100 °C, see Fig. S05 in ESI†). The two aromatic protons of each *meso*-aryl groups (noted H_{Ar} and $H_{Ar'}$), located above or below the mean plane of the porphyrin, are not equivalent because the fused dimethyl-helicene differentiates the two faces. Six



Scheme 1 Preparation of dimethylated [4] and [6]helicenes **3** and **5**.



Scheme 2 Preparation of fused nickel(II) porphyrin **8**.



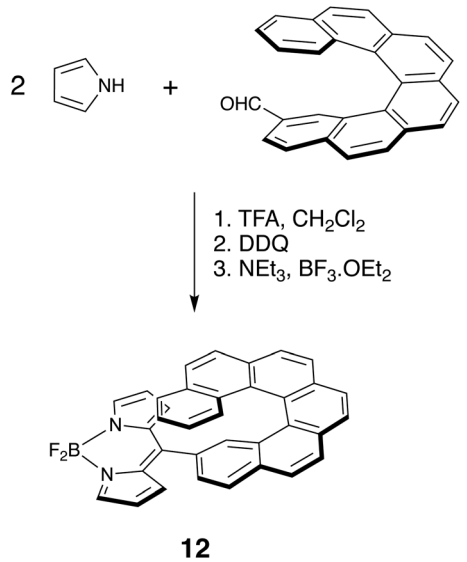
Scheme 3 Preparation of nickel(II) porphyrin **11** bearing one [6]helicenic *meso* group.

signals were observed at room temperature and even heating up to 100 °C did not modify the spectrum. By assuming a coalescence temperature of 150 °C, the enantiomerisation barrier would be approximatively 85 kJ mol^{-1}, a value close to the one reported for 1-methyl-[4]helicene.[14] After chiral HPLC separation of the enantiomers, this value was determined more precisely (*vide infra*).

Separation of the enantiomers by analytical and preparative HPLC

The newly prepared helicene-porphyrin derivatives **8** and **11**, and the helicene-bodipy product **12**, together with a series of additional compounds already reported previously[27] (compound **14** and methoxy-substituted systems **13** and **15**, see Fig. 2 for the structures) were also subjected for chiral HPLC separation.

The separation of compound **8** enantiomers was studied in detail (see ESI† for experimental conditions). Even if baseline peak separation was observed in analytical separations, it was not possible to isolate the two enantiomers in high purity, due to relatively rapid racemisation. After isolation of the almost pure enantiomers, the racemisation rate of these metastable compounds was determined by following the enantiomeric ratio as a function of time. At 25 °C and in a mixture heptane/dichloromethane 80/20, the enantiomerisation barrier was equal to 93.4 kJ mol^{-1} and a half-life of 21 minutes was determined. This half-life is still notably too short for accurate ECD measurements. The isolated enantiomers of the five other



Scheme 4 Preparation of Bodipy **12** bearing one [6]helicene.

compounds containing a [6]helicene were stable and their ECD spectra were determined; while for three of them CPL measurements were carried out. The enantiomers of the two nickel porphyrins **11** and **14** were obtained in purities close to 99% after separations using a (*S*,*S*)-Whelk-O1 HPLC column. The UV-vis and ECD spectra of these pairs of enantiomers are shown in Fig. 3.

Very similar signatures are observed in the UV-vis spectra of the Ni complexes **11** and **14**, with (i) a set of high energy bands below 400 nm ($33 \times 10^3 < \varepsilon < 70 \times 10^3$ M^{-1} cm^{-1}), corresponding to the absorption region of the helicene, (ii) the highly intense Soret band at 416–418 nm ($\varepsilon > 2 \times 10^5$ M^{-1} cm^{-1}), and (iii) two small Q bands at 528–563 nm ($\varepsilon \sim 17 \times 10^3$ and 3×10^3 M^{-1} cm^{-1} respectively). In the ECD spectra, the helicenic region displays the intense classical negative-positive signature for the *P*-enantiomers at around 250 and 330 nm, respectively, thus enabling clear assignment of the absolute configuration, while the Soret band also displays a negative–positive signature at around 390 and 420 nm, respectively, but of lower intensities compared to the helicenic ones (see Table 1 for the ECD intensities). The Q bands do not show any ECD activity. Note that nickel(II) porphyrins are non-emissive, and thus not CPL-active.

After HPLC separations (using a chiralpak IG column), the two enantiomers of bodipy **12** were isolated in very good purities (>99.5%). The enantiomers of porphyrin free bases **13** and **15** were obtained in purities higher than 99% by chiral HPLC separations (again using analytical and preparative (*S*,*S*)-Whelk-O1 HPLC columns). UV-vis and ECD spectra of all isolated compounds are shown in Fig. 4. Similarly to the Ni complexes, free porphyrin-helicenes **13** and **15** display three distinct sets of bands, corresponding to the helicenic part, the

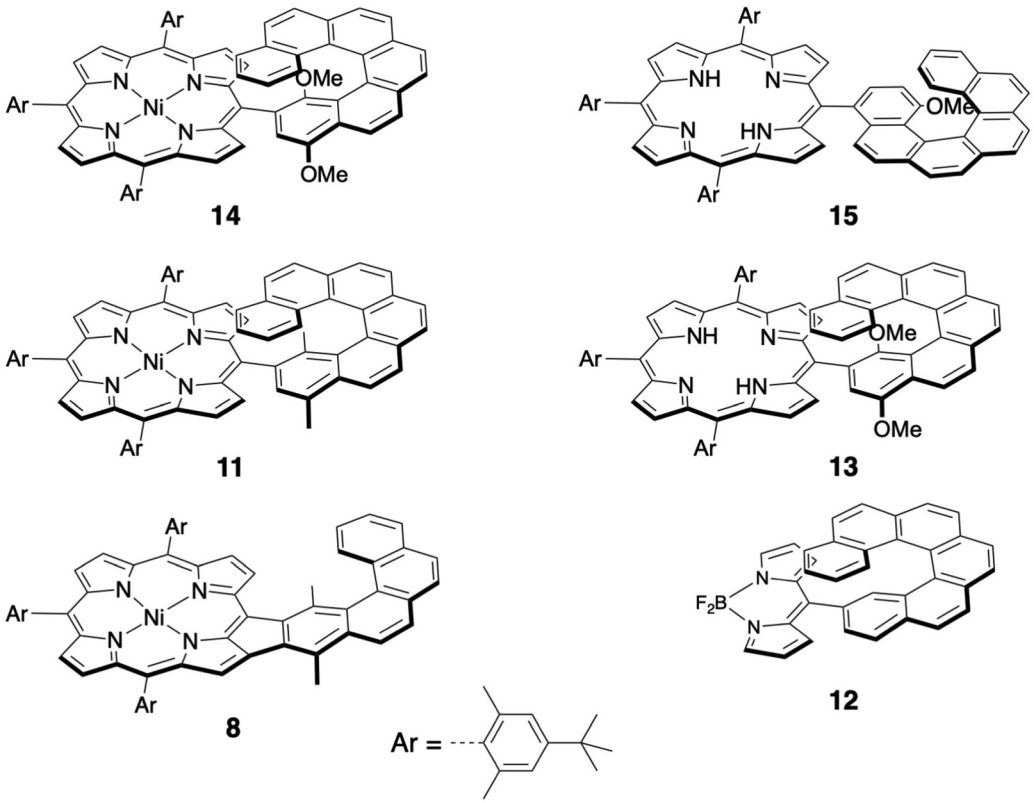


Fig. 2 Chemical formula of the compounds submitted for chiral HPLC separation. Porphyrins **13**, **14**, and **15** were described earlier.[27]

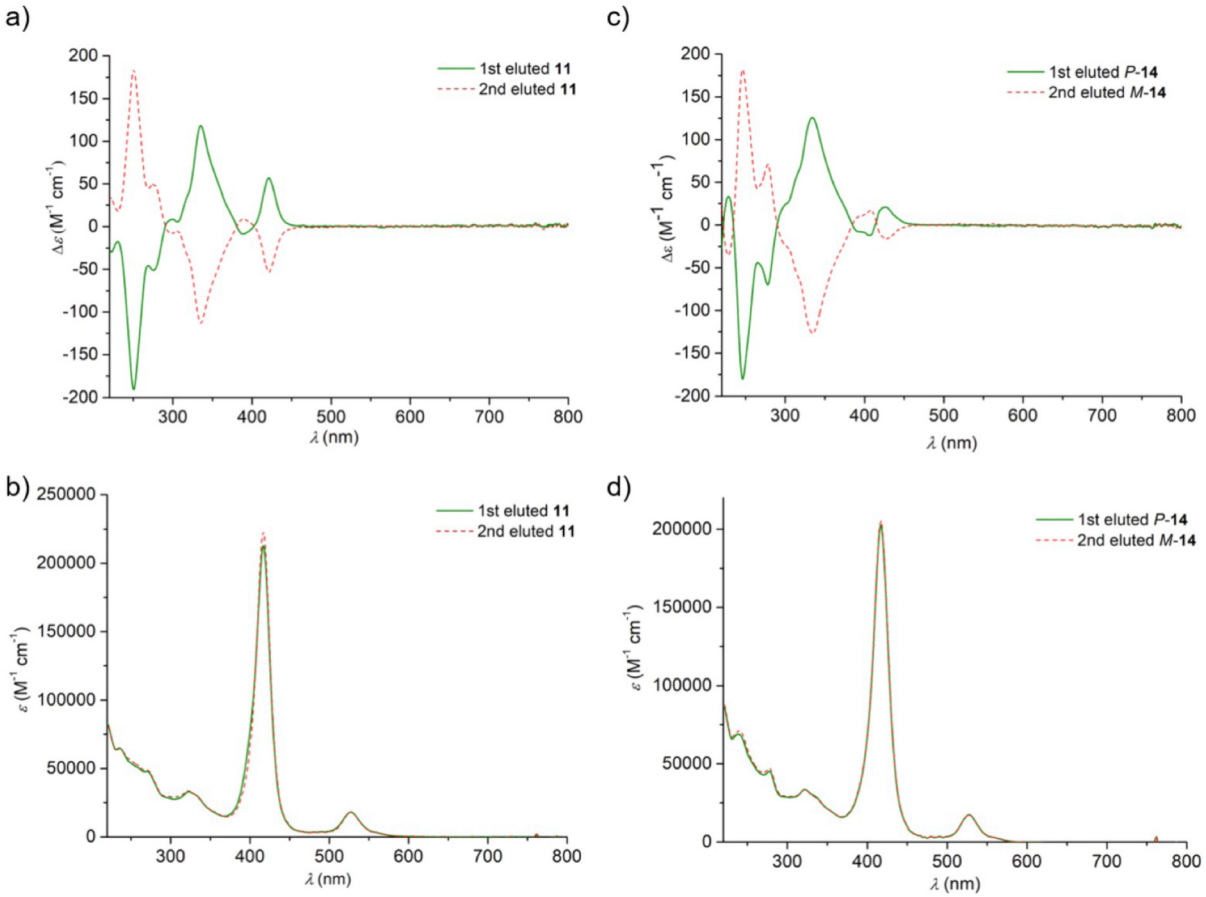


Fig. 3 UV-visible absorption (b and d) and CD (a and c) spectra of enantiomers of nickel porphyrins **11** and **14** recorded in dichloromethane.

Table 1 UV-visible absorption and ECD intensities (molar absorption coefficients) of compounds **11–15** (P enantiomers)

Compound (1st eluted)	Solvent	λ (ε) (nm/M^{-1} cm^{-1})	λ ($\Delta\varepsilon$) (nm/M^{-1} cm^{-1})
P-**11**	CH_2Cl_2	237 (64 400), 270 (48 000), 322 (33 000), 418 (212 000), 528 (17 900), 561 (3000).	222 (−29), 250 (−191), 276 (−51), 298 (+8), 318 (+36), 336 (+117), 390 (−8), 421 (+57).
P-**12**	CH_3CN	199 (39 200), 232 (43 000), 260 (45 200), 320 (26 900), 344 (15 000), 474 (17 500), 499 (37 200).	194 (+86.2), 210 (−37.4), 219 (−49), 230 (+18.6), 248 (−212.1), 308 (+54.5), 321 (+181.8), 347 (+67), 430 (+15.5), 500 (−16.5).
P-**13**	CH_2Cl_2	244 (67 000), 279 (49 200), 323 (44 300), 403 (89 300), 420 (350 000), 515 (22 800), 550 (6300), 646 (4500).	228 (+23), 246 (−202), 278 (−72.5), 294 (+28), 310 (+71.1), 333 (+162), 375 (+37.2), 398 (−15.5), 419 (−67.3), 432 (+21.6), 545 (+2.5), 646 (+4.6).
P-**14**	CH_2Cl_2	239 (69 000), 278 (45 000), 322 (33 400), 416 (202 000), 528 (17 500), 563 (2400).	230 (+32), 246 (−180), 277 (−70), 315 (+59), 333 (+125), 391 (−7), 408 (−12), 425 (+20).
P-**15**	CH_2Cl_2	250 (66 000), 275 (44 700), 326 (37 600), 405 (94 400), 422 (330 000), 518 (22 600), 550 (6800), 593 (6500), 650 (5350).	230 (+19.4), 250 (−164), 273 (−58.5), 291 (+23.8), 311 (+84.8), 330 (+218), 354 (+53.3), 403 (−41), 421 (−66.5), 518 (−6).

intense Soret band and a set of four Q bands. In the ECD spectra, the Soret band signatures appear slightly differently, *i.e.* displaying only one negative band in the case of **15**. Interestingly, in the two systems, some Q bands are slightly ECD-active (see the exact intensities in Table 1). Here again, the typical ECD signature of the helicenic part enables the assignment of the absolute configuration. Overall, compared to the nickel complexes, the free systems show similar signature, except that some of the Q bands are slightly ECD-active, while the Soret band shows slightly different features. These features also deserve to be compared to previously reported helicene-porphyrins, especially to a helicene-bis-porphyrin system displaying a strong excitonic coupling signature in the porphyrin Soret band ($\Delta\varepsilon$ −82 at 430 nm and +393 M^{-1} cm^{-1}

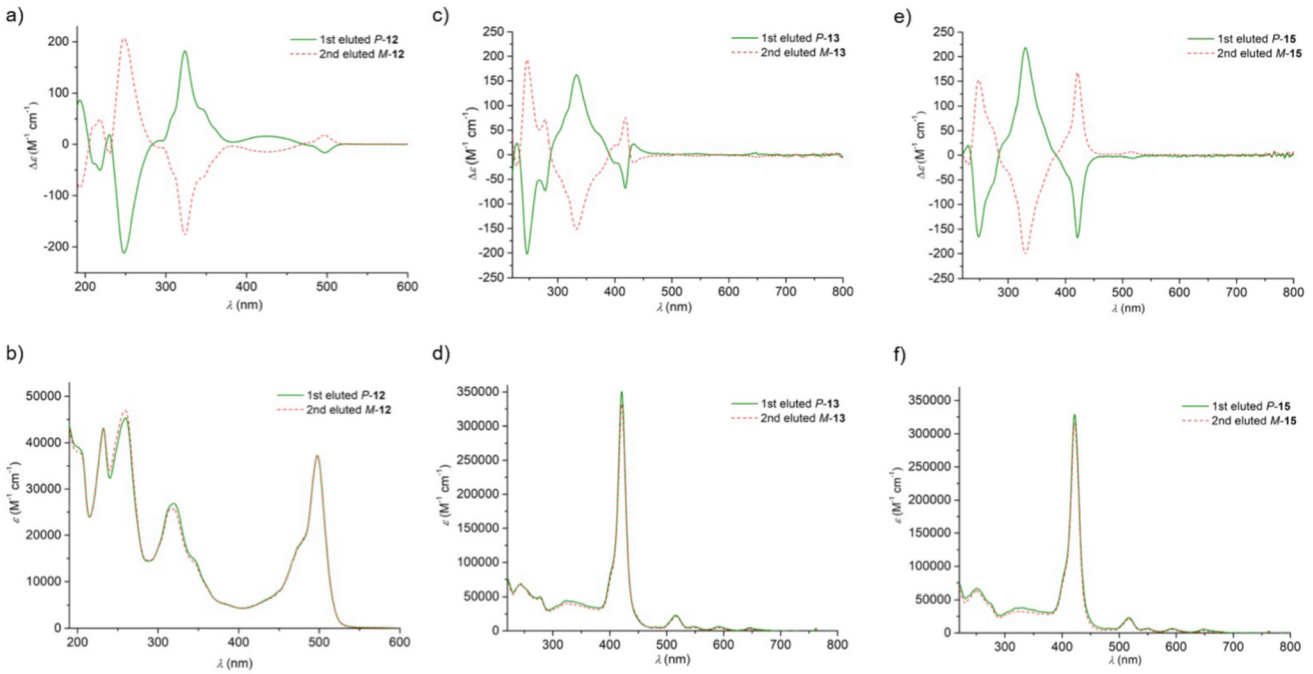


Fig. 4 UV-visible absorption (b, d and f) and ECD (a, c and e) spectra of the enantiomers of bodipy-helicene **12** (recorded in acetonitrile) and free porphyrin-helicenes **13** and **15** (recorded in dichloromethane).

at 446 nm) and ECD-active Q bands ($\Delta\varepsilon$ +18 M^{-1} cm^{-1} at 570 nm and +6 M^{-1} cm^{-1} at 654 nm) for the *P* enantiomer.[24] In the case of bodipy-helicene **12** enantiomers, aside from the classical helicenic UV-vis bands below 400 nm, a set of strong absorption bands is found in the visible region around 500 nm, typical of the Bodipy chromophore. This set of bands appears moderately ECD-active, with a positive Cotton effect at 430 nm and a negative one at 500 nm for the *P* enantiomer ($\Delta\varepsilon$ ~ 15 M^{-1} cm^{-1}, 1st eluted). In addition, the strong ECD-active helicenic bands are present (see Table 1 for the exact intensities).

Interestingly, the free helicene-porphyrin **13**, **15** and the helicene-bodipy **12** enantiomers are emissive and their circularly polarized emission can be studied. The non-polarized and circularly polarized emission properties of compounds **12**, **13** and **15** were studied in solution. In dichloromethane, 2-Bodipy-substituted [6]helicene **12** exhibits two emission bands at 525 and 608 nm (excitation wavelength λ_{exc} at 490 nm, $C \approx 10^{-5}$ M) most probably corresponding to typical fluorescence signals. A low quantum yield was found for compound **12** (2% in dichloromethane using rhodamine 6G as standard). The latter nevertheless also displayed CPL activity, with a negative signal at 525 nm and a positive one at 608 nm for the 1st eluted enantiomer (*P* enantiomer). At 608 nm, the dissymmetry factors g_{lum} were found to be $+2.3 \times 10^{-3}$ for the first eluted (*P*-**12**) and -1.9×10^{-3} for the second eluted (*M*-**12**). These values fall within the classical range for this type of Bodipy substituted [5] or [6]helicene derivatives.[32,34,35] Note however that the CPL signal found at 525 nm may be due to residual reabsorption phenomenon in the Soret band. Regarding porphyrin-helicenes **13** and **15**, they exhibit two emission bands at 652/717 nm and 654/720 nm (in dichloromethane, excitation wavelength λ_{exc} at 420 nm, C ~2.5–3 × 10^{-5} M), with respective quantum yields of 9% and 11% (with H_2TPP used as standard). Compound **13** also shows CPL activity with a positive signal for the first eluted (*P* enantiomer) and a negative one for the second eluted (*M* enantiomer) at around 655 nm, with respective emission dissymmetry factors g_{lum} of around $+1 \times 10^{-3}$ and -0.7×10^{-3} (noisy signals, see Fig. 5).

Note that the CPL signals were found noisy. In order to get reasonable signal to noise ratios, it was necessary to irradiate at the Soret band rather than the lower energy Q bands. Nevertheless, CPL-active porphyrin derivatives still remain quite rare and are thus of interest in the area of far-red CPL emitters.[24,25] Compound **15** was found to display no clear CPL activity in dichloromethane solution.

Experimental part

General information

The HRMS ESI and MALDI were obtained on a Bruker MicrOTOF. UV-vis spectra were recorded in dichloromethane with a Cary 5000 UV-Vis-NIR double-beam instrument. ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2 °C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was base-

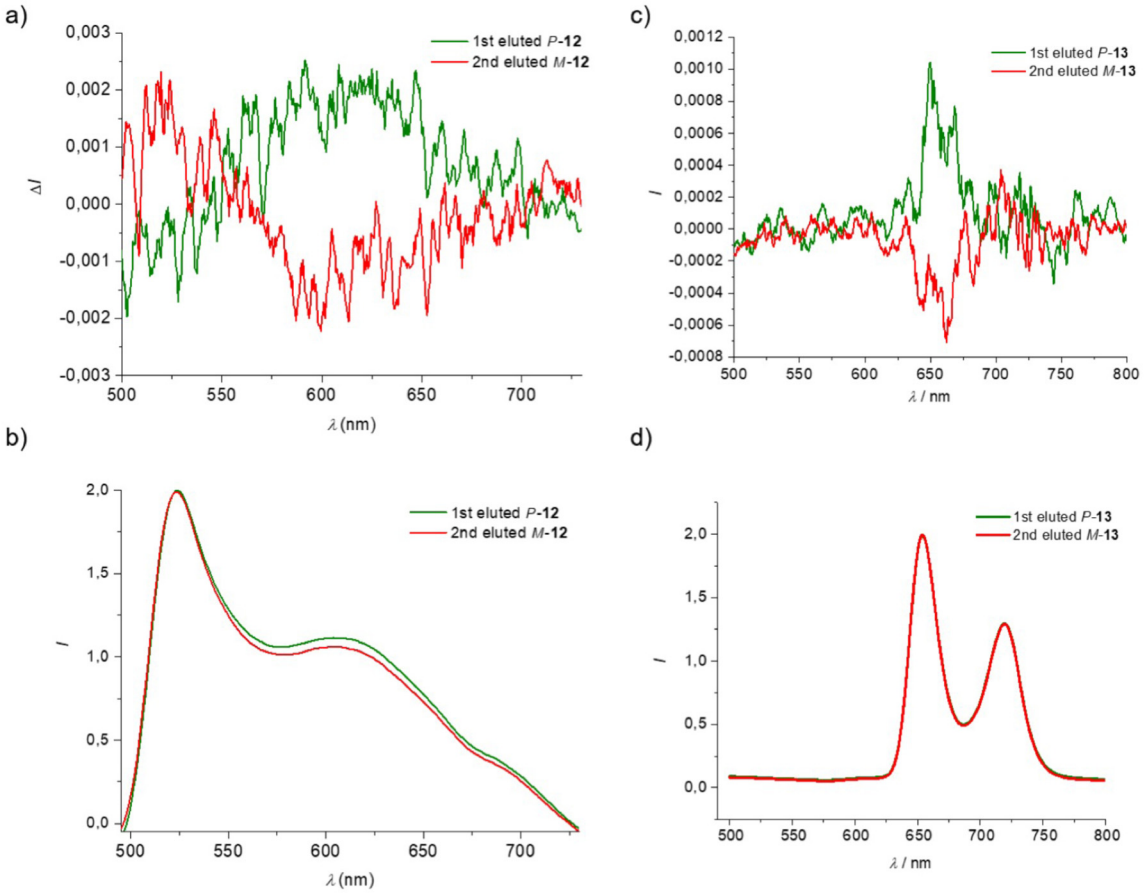


Fig. 5 Fluorescence (b and d) and CPL (a and c) spectra of compounds **12** and **13** (λ_{exc} at 490 and 420 nm, respectively, recorded in dichloromethane).

line subtracted. UV-Visible (UV-vis, in M^{-1} cm^{-1}) absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Steady-state fluorescence measurements were performed on dilute solutions (*ca.* 10^{-5} M, optical density <0.1) contained in standard 1 cm quartz cuvettes using an Edinburgh Instrument (FLS920) spectrometer in photon-counting mode. The circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter (constructed with the help of the JASCO Company). The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. The following parameters were used: emission slit width ≈10 mm, integration time = 8 s, scan speed = 50 nm min^{-1}, accumulations = 5. The concentration of all the samples was *ca.* 10^{-5} M. Chromatographic separations were performed with silica gel (Merck, 40–63 μm). Dichloromethane was distilled over calcium hydride and THF from sodium/benzophenone ketyl. NMR spectra were recorded on Bruker Avance 400 and 500 spectrometers equipped with a cryoprobe for ^{13}C. Chemical shifts are given in parts per million (ppm) by taking the solvent signals as a reference (δ = 7.26 ppm or δ = 77.16 ppm). All other solvents and reagents were used without further purification. Porphyrins **13**, **14**, and **15** were prepared as previously described.[25]

Syntheses

Compound 1. Under argon, NaH (60% in mineral oil) (237 mg, 5.92 mmol, 1.1 eq.) was added to a solution of diethyl 4-bromo-2,5-dimethylbenzylphosphonate (2.02 g, 5.49 mmol, 1.1 eq.)[51] in freshly distilled THF (50 mL). After 15 min of stirring at room temperature, a solution of 2-naphthaldehyde (0.84 g, 5.38 mmol, 1.0 eq.) in freshly distilled THF (30 mL) was added dropwise. The resulting solution was heated at 50 °C for 16 h. The solution was allowed to cool to room temperature and H_2O (50 mL) was added. The solution was concentrated under reduced pressure. The resulting solid was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with a saturated aqueous solution of NH_4Cl (3 × 20 mL), dried over $MgSO_4$, and filtered. Subsequent purification of the crude product by column chromatography afforded the desired product as a yellow solid (1.68 g, 4.98 mmol, 93%). ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 7.87–7.81 (m, 4H, H_1 + H_4 + H_5 + H_8), 7.74 (dd, J = 8.6, 1.8 Hz, 1H, H_3), 7.54–7.42 (m, 3H, H_o + H_6 + H_7), 7.38 (s, 1H, H_m), 7.34 (d, J = 16.1 Hz, 1H, H_a), 7.16 (d, J = 16.1 Hz, 1H, H_b), 2.42 (s, 3H, CH_3), 2.41 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 135.7, 135.5, 135.2, 135.1, 134.0 (CH), 133.8, 133.2, 130.5 (CH), 128.5 (CH),

128.2 (CH), 127.9 (CH), 127.6 (CH), 126.9 (CH), 126.6 (CH), 126.1 (CH), 125.9 (CH), 123.9, 123.6 (CH), 22.6 (CH_3), 19.3 (CH_3). ESI-TOF-MS (*m*/*z*): Calcd for ([$M^{\bullet+}$]) 336.0333; found 336.0349.

Compound 2. A solution of compound **1** (1.6 g, 4.74 mmol, 1 eq.) and iodine (≃0.015 eq.) in cyclohexane (400 mL) was irradiated in a photoreactor equipped with an immersion lamp (150 W) for 10 h. Sodium thiosulfate (5 g) was added and the solution was stirred overnight. The solvent was evaporated, and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 40/60) to afford compound **2** as a yellow solid (969 mg, 2.89 mmol, 61%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.04–8.00 (m, 1H, H_{12}), 8.00–7.94 (m, 3H, H_5 + $H_{7,8}$ + H_9), 7.85 (d, J = 8.5 Hz, 1H, H_6), 7.80 (d, J = 8.5 Hz, 1H, $H_{7,8}$), 7.73 (s, 1H, H_3), 7.57–7.53 (m, 2H, H_{10} + H_{11}), 2.77 (s, 3H, CH_{3out}), 2.37 (s, 3H, CH_{3in}). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 133.2, 133.0, 132.1, 131.93, 131.90, 131.2, 131.1 (CH), 130.7, 129.8 (CH), 128.0 (CH), 127.7 (CH), 127.2, 126.2 (CH), 125.81 (CH), 125.79, 125.7 (CH), 125.6 (CH), 123.3 (CH), 26.9 (CH_3), 19.4 (CH_3). ESI-TOF-HR-MS (*m*/*z*): Calcd for ([$M^{\bullet+}$]) 334.0352; found 334.0354.

Compound 3. Under argon at −78 °C, a solution of *n*-BuLi (1.6 M in hexanes) (1.21 mL, 1.94 mmol, 1.3 eq.) was added to a solution of compound **2** (500 mg, 1.49 mmol, 1.0 eq.) in distilled THF (15 mL). After 1 h of stirring at this temperature, dry DMF (0.35 mL, 4.47 mmol, 3 eq.) was added, the solution was allowed to warm to room temperature and H_2O (10 mL) was added. The solution was concentrated under reduced pressure and CH_2Cl_2 (20 mL) was added. The organic layer was washed with a saturated aqueous solution of NH_4Cl (5 × 30 mL), dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure. The desired compound was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 40/60) to give **3** as a yellow solid (295 mg, 1.04 mmol, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) 10.65 (s, 1H, CHO), 8.06–7.93 (m, 5H, H_3 + H_5 + $H_{7,8}$ + H_9 + H_{12}), 7.88 (dd, J = 8.5 Hz, 1H, H_6), 7.85 (dd, J = 8.5 Hz, 1H, $H_{7,8}$), 7.63–7.51 (m, 2H, H_{10} + H_{11}), 2.80 (s, 3H, CH_{3out}), 2.62 (s, 3H, CH_{3in}). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 193.0 (CH), 138.5, 136.1, 132.23, 132.16, 132.1, 131.7, 130.6, 130.5, 129.9 (CH), 129.0 (CH), 128.1 (CH), 127.83, 127.79 (CH), 126.7 (CH), 126.2 (CH), 125.81 (CH), 125.79 (CH), 123.1 (CH), 21.8 (CH_3), 19.6 (CH_3). ESI-TOF-HR-MS (*m*/*z*): Calcd for ([M + H^+]) 285.1274; found 285.1274.

Compound 4. Under argon, NaH (60% in mineral oil) (414 mg, 10.4 mmol, 1.2 eq.) was added to a solution of diethyl 4-bromo-2,5-dimethylbenzylphosphonate (3.15 g, 9.4 mmol, 1.1 eq.) in freshly distilled THF (50 mL). After 15 min of stirring at room temperature, a solution of benzo[*c*]phenanthrene-2-carbaldehyde (1.28 g, 4.99 mmol, 1.0 eq.)[40] in freshly distilled THF (30 mL) was added dropwise. The resulting solution was heated at 50 °C for 16 h. The solution was allowed to cool to room temperature, H_2O (50 mL) was added and the solution was concentrated under reduced pressure. The solid was dissolved in CH_2Cl_2 (50 mL) and the resulting solution was washed with a saturated aqueous solution of NH_4Cl (3 × 20 mL), dried over $MgSO_4$, and filtered. Subsequent purification of the crude product by column chromatography afforded the desired stilbene intermediate as a yellow solid (3.79 mg, 8.67 mmol, 92%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.21–9.08 (m, 2H, H_1 + H_{12}), 8.04 (dd, J = 8.0, 1.5 Hz, 1H, H_9), 8.01 (d, J = 8.4 Hz, 1H, H_{5-8}), 7.92 (d, J = 8.4 Hz, 1H, H_{5-8}), 7.88–7.84 (m, 2H, H_3 + H_{5-8}), 7.83–7.75 (m, 2H, H_4 + H_{5-8}), 7.73 (ddd, J = 8.6, 6.9, 1.5 Hz, 1H, H_{11}), 7.65 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H, H_{10}), 7.56 (s, 1H, H_o), 7.43 (d, J = 17.1 Hz, 1H, H_b), 7.40 (s, 1H, H_m), 7.28 (d, J = 17.1 Hz, 1H, H_a), 2.44 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 135.7, 135.5, 135.4, 135.2, 134.1 (CH), 133.7, 133.3, 131.5, 130.9 (CH), 130.8, 130.5, 129.1 (CH), 128.8 (CH), 127.9 (CH), 127.8 (CH), 127.52 (CH), 127.48, 127.4 (CH), 127.3 (CH), 127.1 (CH), 127.0 (CH), 126.4 (CH), 126.13 (CH), 126.11 (CH), 123.9, 123.4 (CH), 22.7 (CH_3), 19.3 (CH_3). ESI-TOF-HR-MS (*m*/*z*): Calcd for ([$M^{\bullet+}$]) 436.0821; found 436.0804.

A solution of the intermediate stilbene (1.0 g, 2.29 mmol, 1 eq.) and iodine (≃0.015 eq.) in cyclohexane (400 mL) was irradiated in a photoreactor equipped with an immersion lamp (150 W) for 10 h. Sodium thiosulfate (5 g) was added and the solution was stirred overnight. The solvent was evaporated, and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 40/60) to afford compound **4** as a yellow solid (678 mg, 1.56 mmol, 68%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.08 (d, J = 8.1 Hz, 1H, H_{7-12}), 8.07–8.02 (m, 2H, H_5 + H_{7-12}), 8.01 (d, J = 8.1 Hz, 1H, H_{7-12}), 7.97 (d, J = 8.2 Hz, 1H, H_{7-12}), 7.93 (d, J = 8.7 Hz, 1H, H_6), 7.91–7.88 (m, 2H, H_{7-12}), 7.86 (dd, J = 8.1, 1.3 Hz, 1H, H_{13}), 7.30 (s, 1H, H_3), 7.19 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H, H_{14}), 6.81 (dd, J = 8.5, 1.2 Hz, 1H, H_{16}), 6.47 (ddd, J = 8.5, 6.8, 1.3 Hz, 1H, H_{15}), 2.78 (s, 3H, CH_{3out}), 0.88 (s, 3H, CH_{3in}). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 133.3, 132.8, 132.1, 131.5, 131.0, 130.8 (CH), 130.5, 128.49, 128.48, 128.0 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 126.8 (CH), 126.4 (CH), 126.3 (CH), 125.9 (CH), 125.80, 125.77 (CH), 125.4 (CH), 124.6, 123.7 (CH), 123.5 (CH), 24.0 (CH_3), 19.4 (CH_3). ESI-TOF-HR-MS (*m*/*z*): Calcd for ([$M^{\bullet+}$]) 434.0665; found 434.0640.

Compound 5. Under argon, at −78 °C, a solution of *n*-BuLi (1.6 M in hexanes) (1.03 mL, 1.65 mmol, 1.2 eq.) was added to a solution of **4** (600 mg, 1.38 mmol, 1.0 eq.) in distilled THF (15 mL). After 1 min of stirring at this temperature, i-PrOBpin (0.33 mL, 1.79 mmol, 1.3 eq.) was added and the solution was allowed to warm to room temperature. H_2O (10 mL) was added and the solution was concentrated under reduced pressure. CH_2Cl_2 (50 mL) was added and the organic layer was washed with a saturated aqueous solution of NH_4Cl (5 × 30 mL). The solution was dried over $MgSO_4$, filtered, and the solvents were evaporated under reduced pressure. The crude product was then purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 50/50) to afford **5** as a yellow solid (454 mg, 0.94 mmol, 68%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.09 (d, J = 8.6 Hz, 1H, H_5), 8.07 (d, J = 8.0 Hz, 1H, H_{7-8}), 8.04–7.99 (m, 2H, H_{7-8} + H_{9-10}), 7.95 (d, J = 8.6 Hz, 1H, H_{9-10}), 7.92 (d, J = 8.6 Hz, 1H, H_6), 7.89 (d, J = 8.5 Hz, 1H, H_{11}), 7.84 (d, J = 8.5 Hz, 1H, H_{12}), 7.68–7.62 (dd, J = 8.0, 1.4 Hz, 1H, H_{13}), 7.46 (s, 1H,

H_3), 7.07 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H, H_{14}), 6.77 (dd, J = 8.4, 1.2 Hz, 1H, H_{16}), 6.39 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H, H_{15}), 2.79 (s, 3H, CH_{3out}), 1.22 (s, 6H, CH_{3Bpin}), 1.21 (s, 6H, CH_{3Bpin}), 1.03 (s, 3H, CH_{3in}). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 141.5, 133.3 (CH), 132.9, 131.8, 131.6, 131.5, 130.8, 129.4, 129.0, 128.6, 127.6 (CH), 127.1 (CH), 126.9 (CH), 126.83 (CH), 126.75 (CH), 126.48 (CH), 126.46 (CH), 126.36 (CH), 126.3, 126.1, 124.8 (CH), 123.8 (CH), 123.4 (CH), 83.0, 25.0 (CH_3), 24.7 (CH_3), 23.0 (CH_3), 19.5 (CH_3). ESI-TOF-HR-MS (m/z): Calcd for ([M + K^+]) 521.2049; found 521.2044.

Porphyrin free base 6. A solution of 2,6-dimethyl-4-*tert*-butylbenzaldehyde (253 mg, 1.33 mmol, 3 eq.), compound **3** (126 mg, 0.44 mmol, 1 eq.), and pyrrole (123 mL, 1.77 mmol, 4 eq.) in $CHCl_3$ (100 mL) was degassed in the dark for 30 minutes by argon bubbling. Then, $BF_3{\cdot}OEt_2$ (0.55 mL, 5.7 mM) was added and the solution was stirred under argon and in the dark for one hour. *p*-Chloranil (327 mg, 1.33 mmol, 3 eq.) was added and the solution was heated to reflux for an additional hour. After chromatographic purification (silica gel, cyclohexane to cyclohexane/dichloromethane 8/2), the desired porphyrin **6** (43 mg, 41 mmol, 9%) was isolated as a purple solid. ^{1}H NMR ($C_2D_2Cl_4$, 500 MHz, 25 °C): δ_H (ppm) = 9.30 (d, J = 4.6 Hz, 1H, H_{pyrr}), 8.96 (d, J = 4.6 Hz, 1H, H_{pyrr}), 8.70–8.61 (m, 5H, H_{pyrr}), 8.52 (d, J = 8.4 Hz, 1H, H_{12}), 8.41 (d, J = 8.8 Hz, 1H, H_5), 8.38 (d, J = 4.6 Hz, 1H, H_{pyrr}), 8.23 (s, 1H, H_3), 8.06 (d, J = 8.8 Hz, 1H, H_6), 8.03 (br s, 2H, H_7 + H_8), 8.00–7.98 (m, 1H, H_9), 7.60–7.54 (m, 1H, H_{11}), 7.53 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.53–7.48 (m, 1H, H_{10}), 7.47 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.43 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.42 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.39 (d, J = 2.1 Hz, 1H, H_{Ar}), 3.06 (s, 3H, CH_{3out}), 2.12 (s, 3H, CH_{3Ar}), 2.09 (s, 3H, CH_{3in}), 1.95 (s, 3H, CH_{3Ar}), 1.91 (br s, 6H, CH_{3Ar}), 1.90 (s, 3H, CH_{3Ar}), 1.88 (s, 3H, CH_{3Ar}), 1.61 (s, 9H, H_{tBu}), 1.57 (s, 9H, H_{tBu}), 1.55 (s, 9H, H_{tBu}), −2.47 (br s, 2H, NH). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 150.87, 150.83, 150.79, 140.9, 138.75, 138.69, 138.66, 138.61, 138.5, 137.9, 137.74, 137.71, 135.2, 133.8, 132.7, 131.83, 131.80, 130.5, 129.8, 129.5, 129.3, 127.6, 127.5, 127.4, 126.1, 126.0, 125.5, 125.2, 124.0, 123.81, 123.77, 120.2, 118.5, 118.3, 118.1, 34.51, 34.46, 34.43, 31.63 (*t*Bu), 31.59 (*t*Bu), 31.56 (*t*Bu), 25.2 (CH_3), 22.4 (CH_3), 22.22 (CH_3), 22.20 (CH_3), 22.16 (CH_3), 22.14 (CH_3), 18.8 (CH_3). ESI-TOF-HR-MS (m/z): Calcd for ([M + H^+]) 1045.6143; found 1045.6129. UV-vis (CH_2Cl_2): λ_{max} = 423 nm (ε = 197 000 L cm^{-1} mol^{-1}), 519 (17 700), 550 (6700), 592 (6100), 648 (4300).

Nickel(II) porphyrin 7. A solution of free-base porphyrin **6** (40 mg, 38 mmol, 1 eq.) and $Ni(acac)_2$ (49 mg, 0.19 mmol, 5 eq.) in toluene (20 mL) was heated to reflux overnight. Filtration of the reaction mixture through a pad of alumina, evaporation of the solvent and crystallization afforded the desired porphyrin **7** (42 mg, 38 mmol, quant.) as a red solid. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.20 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.80 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.60 (d, J = 4.9 Hz, 1H, H_{pyrr}), 8.58 (d, J = 4.9 Hz, 1H, H_{pyrr}), 8.55 (br s, 2H, H_{pyrr}), 8.48 (d, J = 4.9 Hz, 1H, H_{pyrr}), 8.39–8.37 (m, 1H, H_9), 8.36 (d, J = 8.8 Hz, 1H, H_5), 8.33 (d, J = 4.9 Hz, 1H, H_{pyrr}), 8.24 (s, 1H, H_3), 8.02 (d, J = 8.8 Hz, 1H, H_6), 7.99 (br s, 2H, H_7 + H_8), 7.97–7.93 (m, 1H, H_{12}), 7.50 (d, J = 1.9 Hz, 1H, H_{Ar}), 7.47–7.44 (m, 2H, H_{10} + H_{11}), 7.43 (d, J = 1.9 Hz, 1H, H_{Ar}), 7.40 (d, J = 1.9 Hz, 1H, H_{Ar}), 7.37 (d, J = 1.9 Hz, 1H, H_{Ar}), 7.36 (d, J = 1.9 Hz, 1H, H_{Ar}), 7.34 (d, J = 1.9 Hz, 1H, H_{Ar}), 3.04 (s, 3H, CH_{3out}), 2.16 (s, 3H, CH_{3Ar}), 2.03 (s, 3H, CH_{3Ar}), 1.93 (s, 3H, CH_{3Ar}), 1.91 (s, 3H, CH_{3in}), 1.81 (s, 3H, CH_{3Ar}), 1.78 (s, 3H, CH_{3Ar}), 1.76 (s, 3H, CH_{3Ar}), 1.59 (s, 9H, H_{tBu}), 1.56 (s, 9H, H_{tBu}), 1.53 (s, 9H, H_{tBu}). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 150.87, 150.83, 150.79, 143.3, 142.7, 142.6, 140.2, 138.84, 138.78, 138.74, 138.6, 137.5, 137.43, 137.39, 135.3, 133.3 (CH), 133.0, 132.2, 132.1, 131.9 (CH), 131.8 (CH), 131.59 (CH), 131.55 (CH), 131.5 (CH), 131.2 (CH), 130.9, 130.1 (CH), 129.9, 129.5, 127.8, 127.7 (CH), 127.6 (CH), 126.3 (CH), 126.1 (CH), 125.5 (CH), 125.3 (CH), 124.11 (CH), 124.09 (CH), 124.02 (CH), 123.98 (CH), 123.8 (CH), 118.3, 117.5, 117.4, 117.3, 34.82, 34.78, 34.7, 31.84 (*t*Bu), 31.81 (*t*Bu), 31.78 (*t*Bu), 24.9 (CH_3), 22.2 (CH_3), 22.1 (CH_3), 22.0 (CH_3), 21.93 (CH_3), 21.92 (CH_3), 19.9 (CH_3). ESI-TOF-HR-MS (m/z): Calcd for ([M + H^+]) 1101.5340; found 1101.5295. UV-vis (CH_2Cl_2): λ_{max} = 417 nm (ε = 130 000 L cm^{-1} mol^{-1}), 529 (11 000), 561 (2100).

Nickel(II) porphyrin 8. Under argon, nickel(II) porphyrin **7** (21 mg, 19 mmol, 1 eq.) was dissolved in chlorobenzene (6 mL) and degassed by argon bubbling for 30 minutes. In a second flask, anhydrous $FeCl_3$ (77 mg, 0.48 mmol, 25 eq.) was dissolved in $MeNO_2$ (1 mL) and degassed for 30 minutes by argon bubbling. The iron chloride solution was added to the porphyrin solution. The resulting solution instantly turned to dark green upon addition. The solution was heated for 4 h at 50 °C while maintaining the argon bubbling. The solution was allowed to cool to room temperature and NEt_3 (5 mL) and MeOH (5 mL) were added. The solvents were removed under reduced pressure and CH_2Cl_2 (50 mL) and H_2O (50 mL) were added. The organic layer was collected, washed thrice with H_2O (3 × 20 mL), dried over Na_2SO_4, filtered and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 1/1) to afford the desired nickel(II) porphyrin **8** (9 mg, 8.2 mmol, 43%) as a green solid. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.44 (d, J = 4.9 Hz, 1H, H_{pyrr}), 8.74 (d, J = 8.2 Hz, 1H, H_{12}), 8.55 (d, J = 4.9 Hz, 1H, H_{pyrr}), 8.23 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.21 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.19–8.16 (m, 2H, H_{pyrr}), 8.06 (d, J = 8.5 Hz, 1H, H_5), 8.03 (d, J = 8.1 Hz, 1H, H_9), 7.98 (s, 1H, H_{pyrr}), 7.91 (d, J = 8.4 Hz, 1H, H_7), 7.83 (d, J = 8.4 Hz, 1H, H_8), 7.82–7.79 (m, 1H, H_{11}), 7.78 (d, J = 8.5 Hz, 1H, H_6), 7.67 (m, 1H, H_{10}), 7.51 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.48 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.44 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.31 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.29 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.25 (d, J = 2.1 Hz, 1H, H_{Ar}), 3.02 (s, 3H, CH_{3out}), 2.81 (s, 3H, CH_{3in}), 2.41 (s, 3H, CH_{3Ar}), 2.35 (s, 3H, CH_{3Ar}), 2.28 (s, 3H, CH_{3Ar}), 1.67 (s, 3H, CH_{3Ar}), 1.58 (s, 6H, CH_{3Ar}), 1.58 (s, 9H, H_{tBu}), 1.56 (s, 9H, H_{tBu}), 1.52 (s, 9H, H_{tBu}). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 155.2, 151.1, 151.0, 149.3, 147.9, 145.6, 144.7, 144.2, 143.8, 142.9, 141.4, 138.8, 138.6, 138.4, 138.3, 138.2, 137.0, 136.7, 135.8, 135.1, 135.0, 133.7, 133.4 (CH), 132.9 (CH), 132.7, 132.1, 131.0, 130.9 (CH), 130.52 (CH), 130.50 (CH), 130.2 (CH), 129.7, 128.9, 128.5 (CH), 127.9 (CH), 127.4 (CH), 126.5, 126.3 (CH), 126.0 (CH), 125.1 (CH), 124.24 (CH), 124.20 (CH), 124.17 (CH),

124.09 (CH), 124.06 (CH), 123.6 (CH), 121.6 (CH), 121.0, 120.6, 117.9, 113.7, 34.83, 34.76, 34.7, 31.9 (*t*Bu), 31.82 (*t*Bu), 31.78 (*t*Bu), 27.0 (CH_3), 22.26 (CH_3), 22.25 (CH_3), 22.0 (CH_3), 21.84 (CH_3), 21.78 (CH_3), 21.7 (CH_3), 17.1 (CH_3). ESI-TOF-HR-MS (*m*/*z*): Calcd for ($[M^{\bullet+}]$) 1098.5105; found 1098.5088. UV-vis (CH_2Cl_2): λ_{max} = 483 nm (ε = 83 000 L cm^{-1} mol^{-1}), 584 (7900), 627 (6300), 694 (1900).

Nickel(II) porphyrin 10. Under argon and in the dark, a solution of iodine (450 mg, 1.77 mmol, 7 eq.) in $CHCl_3$ (75 mL) was added to a solution of [bis(trifluoroacetoxy)iodo]benzene (PIFA) (805 mg, 202 mmol, 8 eq.) in $CHCl_3$ (75 mL). Pyridine (0.5 mL) was added, causing the decoloration of the solution to yellow. The mixture was added dropwise over 2 h to a stirred solution of the porphyrin (200 mg, 0.25 mmol, 1 eq.) in $CHCl_3$ (300 mL). The organic phase was washed with a saturated aqueous solution of $Na_2S_2O_3$ (30 mL), dried over Na_2SO_4 and filtered. The solvents were removed under reduced pressure and the resulting crude product was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 2/8) to afford the desired porphyrin free base (211 mg, 230.1 mmol, 91%) as a purple solid. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.59 (d, *J* = 4.8 Hz, 2H, H_{pyrr}), 8.71 (d, *J* = 4.8 Hz, 2H, H_{pyrr}), 8.62–8.56 (m, 4H, H_{pyrr}), 7.45 (br s, 4H, H_{Ar}), 7.42 (s, 2H, H_{Ar}), 1.88 (s, 6H, CH_{3Ar}), 1.87 (s, 12H, CH_{3Ar}), 1.59 (s, 18H, H_{tBu}), 1.56 (s, 9H, H_{tBu}), −2.48 (s, 2H, NH). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 151.24, 151.22, 139.03, 138.97, 138.1, 137.8, 124.1 (CH), 119.3, 119.1, 34.9, 34.8, 31.9 (*t*Bu), 31.8 (*t*Bu), 22.3 (CH_3), 22.2 (CH_3). ESI-TOF-HR-MS (*m*/*z*): Calcd for ($[M + H^+]$) 917.4014; found 917.4027. UV-vis (CH_2Cl_2): λ_{max} = 423 nm (ε = 280 000 L cm^{-1} mol^{-1}), 522 (13 100), 557 (7500), 597 (4200), 654 (4000).

A solution of the porphyrin free base (80 mg, 86 mmol, 1 eq.) and $Ni(acac)_2$ (110 mg, 0.43 mmol, 5 eq.) in toluene (40 mL) were heated to reflux overnight. Filtration of the reaction mixture through a pad of alumina, evaporation of the solvent and crystallization afforded the desired porphyrin **10** (85 mg, 86 mmol, quant.) as a red solid. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) 9.49 (d, *J* = 4.9 Hz, 2H, H_{pyrr}), 8.60 (d, *J* = 4.9 Hz, 2H, H_{pyrr}), 8.51 (br s, 4H, H_{pyrr}), 7.43–7.38 (m, 6H, H_{Ar}), 1.89 (s, 12H, CH_{3Ar}), 1.88 (s, 6H, CH_{3Ar}), 1.57 (s, 9H, H_{tBu}), 1.56 (s, 18H, H_{tBu}). ^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 151.1, 144.5, 143.4, 142.8, 142.7, 138.6, 138.5 (CH), 136.8, 132.6 (CH), 132.20 (CH), 132.15 (CH), 124.1 (CH), 118.0, 117.9, 34.80, 34.75, 31.78 (*t*Bu), 31.76 (*t*Bu), 22.0 (CH_3), 21.9 (CH_3). ESI-TOF-HR-MS (*m*/*z*): Calcd for ($[M + H^+]$) 972.3132; found 972.3126. UV-vis (CH_2Cl_2): λ_{max} = 419 nm (ε = 258 000 L cm^{-1} mol^{-1}), 531 (18 500), 564 (4400).

Nickel(II) porphyrin 11. Under argon, the boronate ester **5** (51 mg, 106 mmol, 1.5 eq.) and the porphyrin **10** (65 mg, 71 mmol, 1 eq.) were dissolved in a mixture toluene/DMF (30 mL, 2/1) and the resulting solution was degassed by argon bubbling for 30 minutes. K_2CO_3 (78 mg, 0.57 mmol, 8 eq.) and $Pd(PPh_3)_4$ (41 mg, 35 mmol, 0.5 eq.) were added and the resulting mixture was refluxed for 24 h. Solvents were removed under reduced pressure. H_2O (50 mL) and CH_2Cl_2 (50 mL) were added. The organic layer was collected, washed with water (3 × 20 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 20/80 to 40/60) to afford the desired product **11** as a red solid (20 mg, 17 mmol, 25%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.52–8.47 (m, 3H, H_{pyrr} + H_5), 8.44 (d, *J* = 4.8 Hz, 1H, H_{pyrr}), 8.41 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 8.38 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 8.23 (d, *J* = 4.9 Hz, 1H, H_{pyrr}), 8.14 (d, *J* = 8.8 Hz, 1H, H_6), 8.09 (d, *J* = 8.1 Hz, 1H, H_{7-12}), 8.04 (d, *J* = 8.1 Hz, 1H, H_{7-12}), 7.99 (s, 1H, H_3), 7.97–7.92 (m, 1H, H_{13}), 7.91 (d, *J* = 8.1 Hz, 1H, H_{7-12}), 7.85 (d, *J* = 4.9 Hz, 1H, H_{pyrr}), 7.72 (d, *J* = 8.1 Hz, 1H, H_{7-12}), 7.65–7.54 (m, 4H, H_{14} + H_{Ar} + 2*H_{7-12}), 7.39 (br s, 2H, H_{Ar}), 7.32–7.27 (m, 3H, H_{Ar} + H_{16}), 7.22 (br s, 1H, H_{Ar}), 7.01–6.92 (m, 2H, H_{pyrr} + H_{15}), 3.06 (s, 3H, CH_{3out}), 2.25 (s, 3H, CH_{3Ar}), 2.06 (s, 3H, CH_{3Ar}), 1.85 (s, 3H, CH_{3Ar}), 1.64 (br s, 12H, CH_{3Ar} + H_{tBu}), 1.57 (s, 3H, CH_{3Ar}), 1.55 (s, 3H, CH_{3Ar}), 1.51 (s, 9H, H_{tBu}), 1.46 (s, 9H, H_{tBu}), 0.38 (s, 3H, CH_{3in}). ^{13}C DEPT (126 MHz, $CDCl_3$): δ_C (ppm) 133.6 (CH), 133.2 (CH), 131.3 (CH), 131.2 (CH), 131.04 (CH), 131.01 (CH), 130.8 (CH), 130.5 (CH), 128.5 (CH), 127.7 (CH), 127.1 (CH), 127.0 (CH), 126.8 (CH), 126.33 (CH), 126.26 (CH), 126.2 (CH), 125.9 (CH), 125.7 (CH), 124.49 (CH), 124.47 (CH), 123.93 (CH), 123.89 (CH), 123.8 (CH), 123.73 (CH), 31.8 (*t*Bu), 31.7 (*t*Bu), 31.6 (*t*Bu), 22.6 (CH_3), 22.1 (CH_3), 22.0 (CH_3), 21.73 (CH_3), 21.72(CH_3), 21.71 (CH_3), 21.66 (CH_3), 20.0 (CH_3). ESI-TOF-HR-MS (*m*/*z*): Calcd for ($[M + H^+]$) 1201.5653; found 1201.5653. UV-vis (CH_2Cl_2): λ_{max} = 408 nm (ε = 143 000 L cm^{-1} mol^{-1}), 523 (13 000), 553 (4100).

Bodipy 12. Under argon, two drops of trifluoroacetic acid were added to a solution of pyrrole (64 mg, 0.95 mmol, 2.25 eq.) and 2-formyl-[6]helicene (150 mg, 0.42 mmol, 1 eq.) in freshly distilled dichloromethane (40 mL). The solution was stirred at room temperature for 4 h. A solution of DDQ (96 mg, 0.42 mmol, 1 eq.) in dichloromethane (5 mL) was added, followed by the addition of NEt_3 (2 mL) and $BF_3{\cdot}OEt_2$ (2 mL) and the resulting solution was stirred at room temperature for two additional hours. The solution was washed with water (3 × 30 mL) and dried over sodium sulfate. The solid was filtered and the solvent was removed under reduced pressure. The resulting crude material was purified by column chromatography (silica gel, CH_2Cl_2/cyclohexane 2/8 to 1/1) to afford the desired product (8 mg, 17 μmol, 4%) as an orange solid.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ_H (ppm) = 8.08 (d, *J* = 8.5 Hz, 1H, H_{hel}), 7.92–8.05 (m, 5H, H_{hel}), 7.82 (d, *J* = 8.5 Hz, 1H, H_{hel}), 7.73–7.80 (m, 3H_{hel} + 2H_{pyr}), 7.72 (dd, *J* = 8.0 and 1.4 Hz, 1H, H_{hel}), 7.66 (dd, *J* = 8.5 and 1.1 Hz, 1H, H_{hel}), 7.36 (dd, *J* = 8.5 and 1.1 Hz, 1H, H_{hel}), 7.21 (ddd, *J* = 8.0, 6.8 and 1.1 Hz, 1H, H_{hel}), 6.79 (ddd, *J* = 8.5, 6.8 and 1.4 Hz, 1H, H_{hel}), 6.30 (br s, 2H, H_{pyr}), 5.85 (br s, 2H, H_{pyr}). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ_C (ppm) = 156.2, 154.9, 147.2, 143.7, 144.9, 133.5, 132.7, 132.6, 131.8, 131.7, 130.7, 130.1, 129.8 (CH), 129.4, 128.41, 128.40 (CH), 128.38 (CH), 128.37 (CH), 128.21, 128.19 (CH), 127.84, 127.79 (CH), 127.7, 127.5 (CH), 127.44 (CH), 127.43 (CH), 127.2 (CH), 126.9 (CH), 126.7 (CH), 126.1 (CH), 124.9 (CH), 123.8, 118.1 (CH), 114.5 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = −145.3 ppm. UV-Vis (CH_2Cl_2): λ_{max} = 261 nm (ε = 45 000 L cm^{-1} mol^{-1}), 321 (27 000), 345 (14 700), 497

(82 300), 475 (17 700), 498 nm (37 100 M^{-1} cm^{-1}). MS, EI: m/z = 518.3 Calcd for ($M^{\cdot+}$): 518.1766.

Conclusions

Several nickel and free base porphyrins bearing helicene *meso*-groups were synthesized and their enantiomers separated by preparative chiral HPLC. CPL measurements for the free base porphyrins and one Bodipy derivative were realized and these new compounds showed g_{lum} values in the range of the previously described porphyrinoids. Since porphyrins presenting CPL activities are still quite rare, synthetic efforts to obtain new chiral extended porphyrins with absorbances reaching the NIR region are in progress.

Conflicts of interest

There are no conflicts to declare.

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