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Isopinocampheyl-based *C*-BODIPYs: A model strategy to construct cost-effective boron-chelate emitters of circularly polarized light

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S1. General methods, instrumentation and techniques

Anhydrous solvents were prepared by distillation over standard drying agents according to common methods. All other solvents were of HPLC grade and were used as provided. Starting chemical substrates and reagents were used as commercially provided unless otherwise indicated. Thin-layer chromatography (TLC) was performed on silica gel plates, and the chromatograms were visualized using UV light (λ = 254 or 365 nm). Flash column chromatography was performed using silica gel (230-400 mesh). ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded in $CDCl_3$ solution at 20 ºC. NMR chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the corresponding residual signals of the deuterated solvent, acetone-d_6, for ^{1}H NMR (δ = 2.05) and ^{13}C NMR (δ = 29.84 ppm), and to $BF_3{\cdot}OEt_3$ (15% in $CDCl_3$) for ^{11}B NMR (δ = 0.00 ppm). Multiplicity is indicated as follows: s = singlet; d = doublet; t = triplet; q = quadruplet, m = multiplet and/or multiple resonances; br = broad. Coupling constants (*J*) are dated in hertz (Hz). The type of carbon (C, CH, CH_2 or CH_3) was assigned by DEPT-135 NMR experiments. Additionally, complex spin-system signals were simulated by using MestRe-C (Cobas, C.; Cruces, J.; Sardina, J., MestRe-C program version 2.3). FTIR spectra were obtained from neat samples using the attenuated total reflection (ATR) technique. High-resolution mass spectrometry (HRMS) was performed using electrospray ionization (ESI) and ion tramp (positive mode) for the detection.

Spectroscopic signatures were recorded using diluted dye solutions (*ca.* 2×10^{-6} M) prepared from a concentrated stock solution in acetone (*ca.* 10^{-3} M), after solvent evaporation under reduced pressure, and subsequent dilution with the desired solvent of spectroscopic grade, UV-vis absorption and fluorescence spectra were recorded on a Varian (model CARY 4E) spectrophotometer and an Edinburgh Instrument spectrofluorometer (model FLSP 920), respectively. Fluorescence quantum yields (ϕ) were determined from corrected spectra (detector sensibility to the wavelength) by the optically dilute relative method and by using Eq. 1, where I_{exc} is the luminescent intensity at the excitation wavelength, A_{exc} is the absorbance at the excitation wavelength, $\int I \mathrm{d}\lambda$ is the numerically integrated intensity from the luminescence spectra, and n is the index of refraction of the solution. The subscripts *R* and *S* denote reference and sample, respectively. PM546 in ethanol (ϕ_F = 0.85)[1] was used as the reference.

$$\phi_S/\phi_R = (\int I_S \mathrm{d}\lambda / \int I_R \mathrm{d}\lambda)\,(A_{R,\text{exc}} / A_{S,\text{exc}})\,(n_S / n_R)^2 \qquad \text{Eq. 1}$$

The aforementioned spectrofluorometer is also equipped with a wavelength-tunable pulsed Fianium laser. Thus, the Time Correlated Single-Photon Counting (TCSPC) technique was used to record the fluorescence decay curves. Fluorescence emission was monitored at the maximum emission

wavelength after excitation by the said Fianium at the maximum absorption wavelength. The fluorescence lifetime (τ) was obtained from the slope of the exponential fit of the decay curve, after the deconvolution of the instrumental response signal (recorded by means of a ludox scattering suspension) by means of an iterative method. The goodness of the exponential fit was controlled by statistical parameters (chi-square and the analysis of the residuals).

Optical rotations were recorded on a Perkin-Elmer (model 241) polarimeter (*c* are expressed in g / 100 mL). ECD spectra were recorded on a Jasco (model J-715) spectropolarimeter using standard quartz cells of 1 cm optical-path length in chloroform solution, unless otherwise indicated, at a dye concentration of *ca.* 5×10^{-6} M. Circularly polarized luminescence (CPL) and total luminescence spectra were recorded at 295 K in degassed cyclohexane (nitrogen was bubbled into the solution), at a dye concentration of *ca.* 2×10^{-3} M, upon excitation at *ca.* 515 nm on an instrument described previously,[2] operating in a differential photon-counting mode. The light source for excitation was a continuous wave 1000 W xenon arc lamp from a Spex Fluorolog-2 spectrofluorometer, equipped with excitation and emission monochromators with dispersion of 4 nm/mm (SPEX, 1681B). The excitation energy was selected by excitation-fluorescence spectroscopy. To prevent artefacts associated with the presence of linear polarization in the emission,[3] a high-quality linear polarizer was placed in the sample compartment, and aligned so that the excitation beam was linearly polarized in the direction of emission detection (z-axis). The key feature of this geometry is that it ensures that the molecules that have been excited and that are subsequently emitting are isotropically distributed in the plane (x,y) perpendicular to the direction of emission detection. The optical system detection consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emitted light was detected by a cooled EMI-9558B photomultiplier tube operating in photo-counting mode.

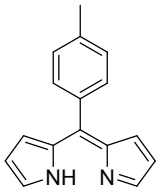
Dye photostability was evaluated by monitoring the decrease in its fluorescence emission induced upon laser excitation. To this aim, dye solution in cyclohexane (10^{-4} M) was transversely pumped with 5 mJ, 8 ns FWHM pulses from the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Lotis TII 2134) at a repetition rate of 10 Hz. The exciting pulses were line-focused onto the cell using a combination of positive and negative cylindrical lenses (f = 15 cm and f = –15 cm, respectively) perpendicularly arranged. Spectroscopic quartz cuvettes with 0.1 cm optical were used to allow for the minimum solution volume (40 μL) being excited. The lateral faces were grounded, whereupon no laser oscillation was obtained. The fluorescence emission was monitored perpendicular to the exciting beam, collected by an optical fiber, and imaged onto a spectrometer (Acton Research corporation) and detected with a charge-coupled device (CCD) (SpectruMM:GS128B). The fluorescence emission was recorded by feeding the signal to the boxcar (Stanford Research, model

250) to be integrated before being digitized and processed by a computer. The estimated error in the photostability measurements was 10%.

Quantum mechanical calculations were performed in Gaussian 16, using the "arina" computational resources provided by the UPV-EHU. Ground state energy minimizations were performed using hybrid B3LYP functional, within the Density Functional Theory (DFT), together with the double valence basis set with a diffuse function (6-31+g). The first singlet excited state was optimized with the Time Dependent (TD-DFT) method using the same calculation level and basis set. The optimized geometries were taken as a true energy minimum using frequency calculations (no negative frequencies).

S2. Synthetic procedures and characterization data

S2.1. Synthesis of 4a.

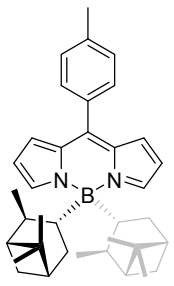


4a

4-Methylbenzaldehyde (0.50 g, 4.17 mmol) was added over a 0.18 M HCl solution in water. Then, pyrrole (0.83 g, 12.50 mmol) was added. After stirring for 3 h at rt, the precipitate was filtered, washed with water (10 mL) and hexane (10 mL), redissolved in ethyl acetate and dried over Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure. The crude was purified by column chromatography (silica gel, hexane / ethyl acetate 9:1). 5-(4-Methylphenyl)dipyrromethane: 0.80 g (81%). Brown solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (br s, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 6.69 (m, 2H), 6.21 (d, J = 2.8 Hz, 2H), 5.96 (m, 2H), 5.45 (s, 1H), 2.40 (s, 3H) ppm. The spectroscopic data match with those previously reported.[4]

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 96 mg, 0.42 mmol) was added over a solution of 5-(4-methylphenyl)dipyrromethane (100 mg, 0.42 mmol) in dry DCM. After stirring the reaction mixture for 1 h at rt, the solvent was evaporated under reduced pressure. The crude was purified by column chromatography (silica gel, hexane / ethyl acetate 8:2). 5-(4-Methylphenyl)dipyrromethene (**4a**): 62 mg (63%). Yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65 (s, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 6.64 (dd, J = 4.2, 1.1 Hz, 2H), 6.40 (dd, J = 4.2, 1.5 Hz, 2H), 2.45 (s, 3H) ppm. The spectroscopic data match with those previously reported.[4]

S2.2. Synthesis of 5a.

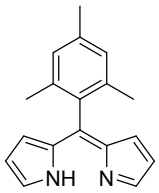


5a

A solution of **4a** (22 mg, 0.094 mmol), triethylamine (47 mg, 0.47 mmol) and (–)-(*R*)-chloro(diisopinocampheyl)borane ((–)-(*R*)-Ipc_2BCl) (151 mg, 0.47 mmol) in CH_2Cl_2 (5 mL) under argon, was reacted at room temperature for 24 h. Then, water (10 mL) was added, the phases were

separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were washed with water (5 mL), dried over Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure. The crude was purified by column chromatography (silica gel, hexane). **5a**: 31 mg (63%). Orange solid. M.p. > 85 °C (decomposes). R_f = 0.51 (hexane). $[\alpha]^D_{20}$ +402.0 (*c* 0.10 $CHCl_3$). ^{1}H NMR (acetone-d_6, 300 MHz) δ 8.18 (s, 2H); 7.52 (d, *J* = 8. 2 Hz, 2H); 7.42 (d, *J* = 7.8 Hz, 2H); 6.94 (dd, *J* = 4.3, 1.2 Hz, 2H); 6.64 (dd, *J* = 4.3, 1.8 Hz, 2H); 2.47 (s, 3H); 2.39 (m, 2H); 2.27 (ddd, *J* = 14.0, 7.4, 2.7 Hz, 2H); 2.01 (m, 2H); 1.92 (m, 2H); 1.55 (m, 2H); 1.38 (td, *J* = 5.9, 2.0 Hz, 2H); 1.26 (td, *J* = 7.3, 2.0 Hz, 2H); 1.13 (s, 6H); 1.12 (s, 6H); 0.45 (d, *J* = 9.1 Hz, 2H); 0.33 (d, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (acetone-d_6, 75 MHz) δ 148.5 (C); 144.0 (CH); 141.3 (C); 135.5 (C); 133.0 (C); 131.2 (CH); 129.8 (CH); 128.4 (CH); 117.7 (CH); 50.9 (CH); 43.1 (CH); 40.2 (C); 40.0 (CH); 33.8 (CH_2); 32.0 (CH_2); 28.7 (CH_3); 23.9 (CH_3); 23.0 (CH_3); 21.4 (CH_3) ppm. ^{11}B NMR ($CDCl_3$, 160 MHz) δ 2.25 ppm. FTIR ν 2891, 1553, 1412, 1384, 1358, 1254, 1061, 1027 cm^{-1}. HRMS (ESI^+) *m/z* calcd. for $C_{16}H_{15}N_2$ ($[M - C_{20}H_{32}B]^{+\cdot}$) 235.1235; found 235.1238.

S2.3. Synthesis of 4b.

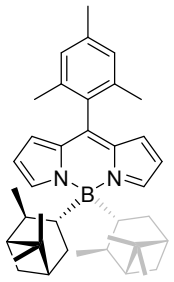


4b

Following a similar procedure to that used for the synthesis of 5-(4-methylphenyl)dipyrromethane (section S2.1), mesityl aldehyde (2,4,6-trimethylbenzaldehyde, 0.50 g, 3.38 mmol) was reacted with pyrrole (0.68 g, 10.14 mmol). 5-Mesityldipyrromethane: 0.71 g (79%). Brown solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (br s, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.69 (m, 2H), 6.21 (d, *J* = 2.8 Hz, 2H), 5.96 (m, 2H), 5.45 (s, 1H), 2.40 (s, 3H) ppm. The spectroscopic data match with those previously reported.[4]

Following a similar procedure to that used for the synthesis of **4a** (section S2.1), 5-mesityldipyrromethane (0.71 g, 2.68 mmol) was reacted with DDQ (61 mg, 2.68 mmol). 5-Mesityldipyrromethene (**4b**): 0.55 g (78%). Greenish yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62 (t, *J* = 1.3 Hz, 2H), 6.92 (m, 2H), 6.40 dd, *J* = 4.2, 1.2 Hz, 2H), 6.33 dd, *J* = 4.2, 1.5 Hz, 2H), 2.36 (s, 3H), 2.09 (s, 6H) ppm. The spectroscopic data match with those previously reported.[5]

S2.4. Synthesis of 5b.

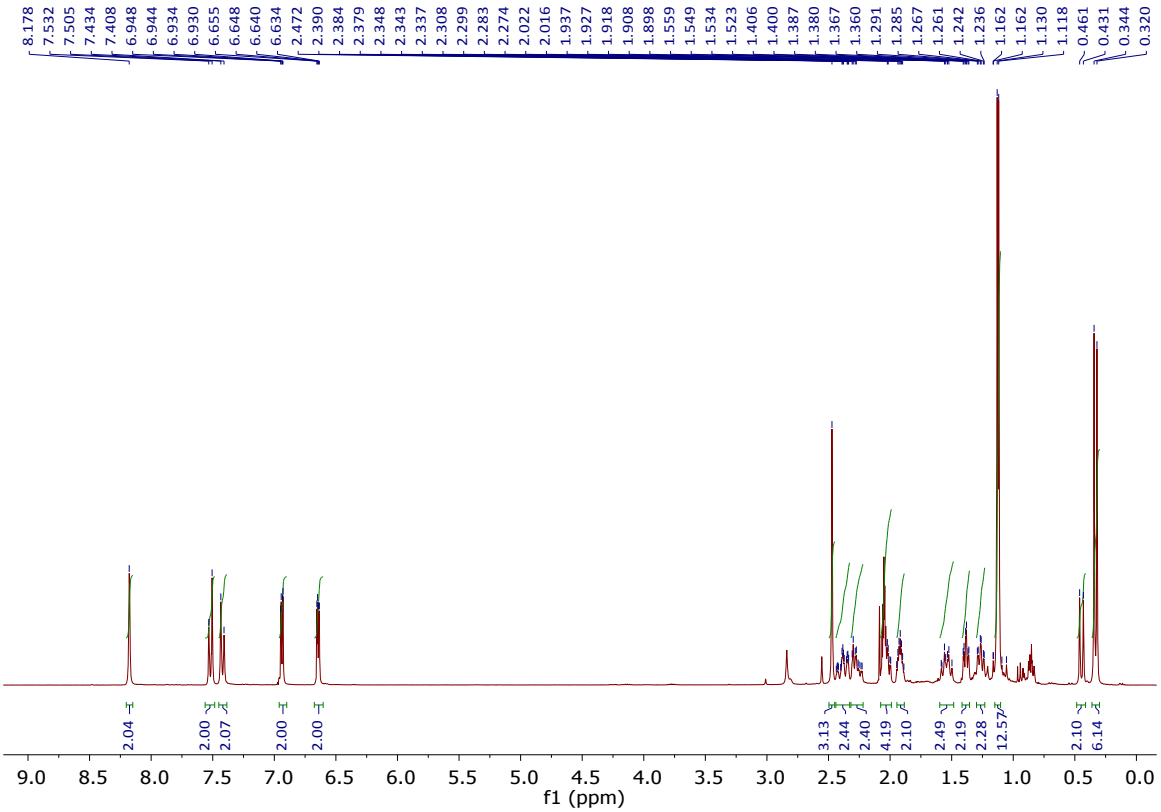


5b

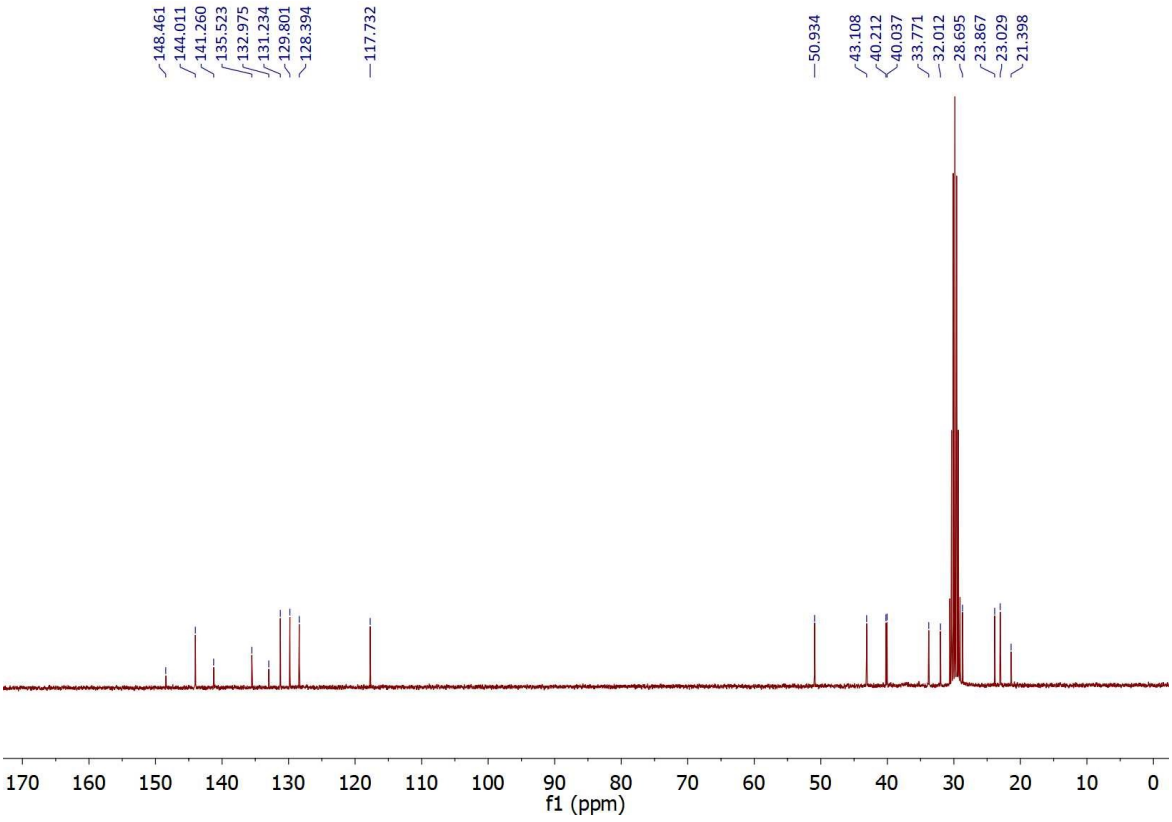
Following a similar procedure to that used for the synthesis of **5a** (section S2.2), **4b** (250 mg, 0.95 mmol) was reacted with (–)-(*R*)-Ipc_2BCl (1.53 g, 4.78 mmol). The reaction crude was purified by flash chromatography (silica gel, hexane). **5b**: 367 mg (70 %). Orange solid. M.p. > 89 °C (decomposes). R_f = 0.56 (hexane). $[\alpha]_D^{20}$ +390.7 (*c* 0.10 $CHCl_3$). ^1H NMR (acetone-d_6, 300 MHz) δ 8.17 (t, *J* = 1.5 Hz, 2H), 7.04 (m, 2H), 6.63 (dd, *J* = 4.3, 1.3 Hz, 2H), 6.59 (dd, *J* = 4.3, 1.8 Hz, 2H), 2.41 (ddd, *J* = 12.4, 3.4, 1.9 Hz, 2H), 2.36 (s, 3H), 2.29 (ddd, *J* = 14.0, 7.4, 2.6 Hz, 2H), 2.09 (s, 6H), 2.07-2.00 (m, 2H), 1.93 (m, 2H), 1.57 (m, 2H), 1.39 (td, *J* = 5.9, 2.0 Hz, 2H), 1.33 (td, *J* = 7.3, 2.0 Hz, 2H), 1.14 (s, 6H), 1.13 (s, 6H), 0.49 (d, *J* = 9.1 Hz, 2H), 0.36 (d, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (acetone-d_6, 75 MHz) δ 147.7 (C), 144.2 (CH), 139.2 (C), 136.7 (C), 135.7 (C), 132.1 (C), 128.9 (CH), 126.9 (CH), 118.0 (CH), 50.9 (CH), 43.1 (CH), 40.3 (CH), 40.1 (C), 33.8 (CH_2), 32.1 (CH_2), 28.7 (CH_3), 23.9 (CH_3), 23.0 (CH_3), 21.2 (CH_3), 19.7 (CH_3) ppm. ^{11}B NMR ($CDCl_3$, 160 MHz) δ 2.40 ppm. FTIR ν 2885, 1558, 1413, 1382, 1357, 1254, 1054, 1022 cm^{-1}. HRMS (ESI^+) *m/z* calcd. for $C_{18}H_{19}N_2$ ($[M - C_{20}H_{32}B]^{+\cdot}$) 263.1548; found 263.1549.

S3. NMR spectra

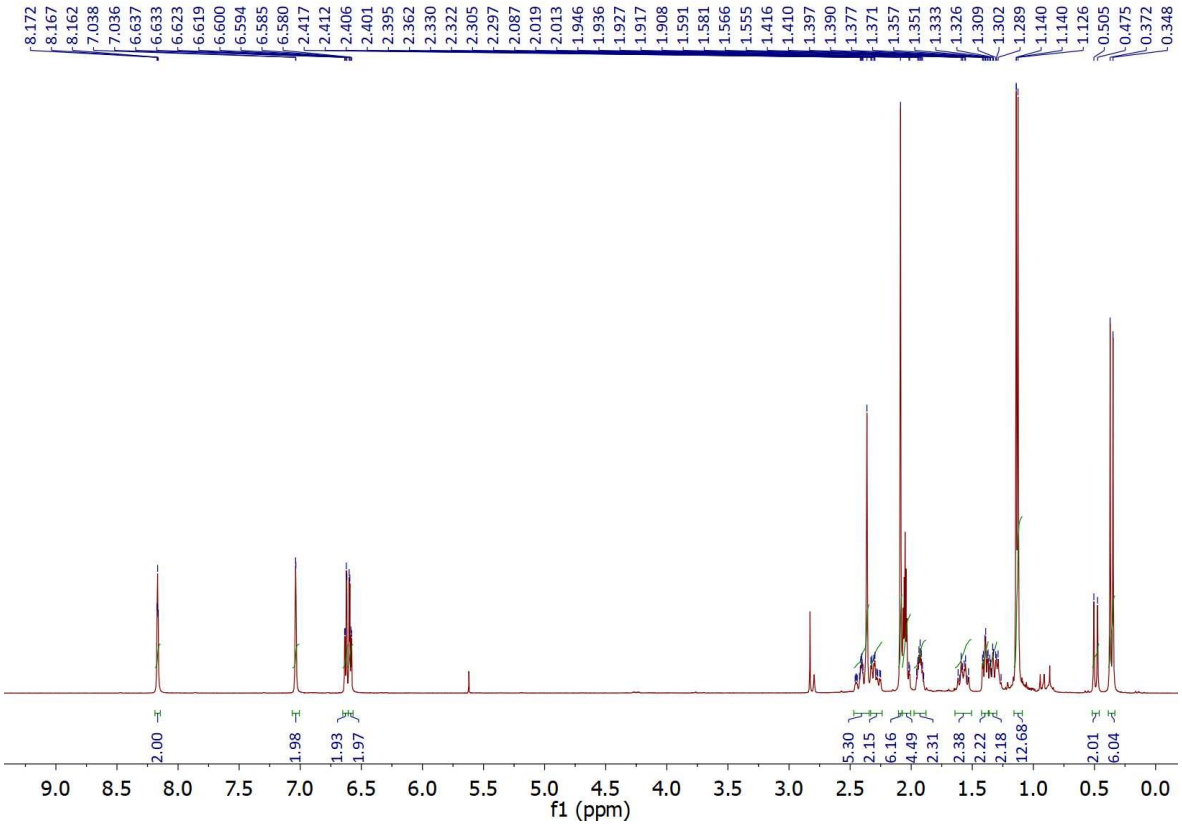
^{1}H NMR of 5a (300 MHz, acetone-d_6)



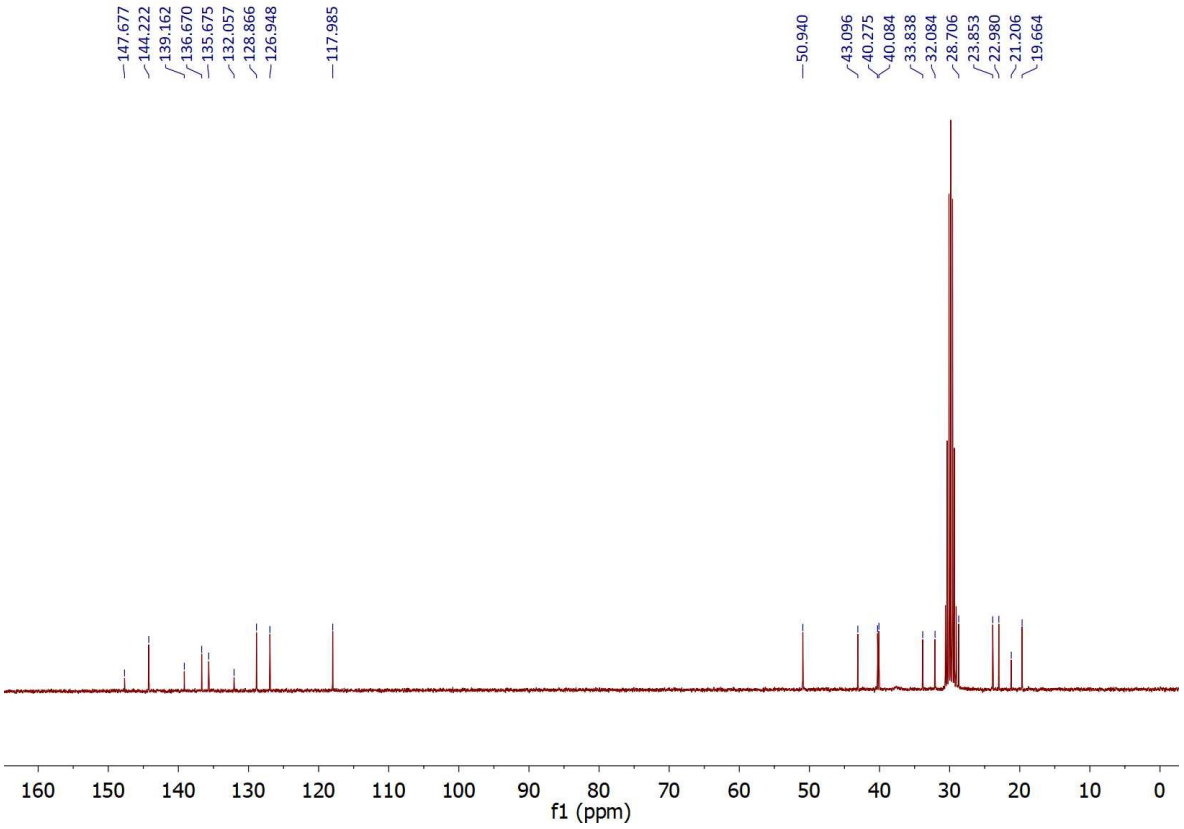
^{13}C NMR of 5a (75 MHz, acetone-d_6)



^{1}H NMR of 5b (300 MHz, acetone-d_6)



^{13}C NMR of 5b (75 MHz, acetone-d_6)



S4. Tables

Table S1. Spectroscopic signatures of *C*-BODIPYs **5a** and **5b** in diluted solution of different solvents (see section S1 for experimental details).

	λ_{ab}[a] (nm)	ε_{max}[b] × 10^{-4} ($M^{-1}cm^{-1}$)	λ_{fl}[c] (nm)	ϕ[d]	τ[e] (ns)
5a					
acetonitrile	496.5	1.9	516.5	0.013	0.15 (73%) - 0.64 (22%) - 3.18 (4%)
methanol	496.0	2.3	515.5	0.037	0.37 (65%) - 0.93 (31%) - 4.43 (4%)
chloroform	498.5	2.9	521.0	0.044	0.56 (61%) - 1.51 (34%) - 4.77 (5%)
ethyl acetate	495.5	3.0	517.0	0.010	0.14 (78%) - 0.63 (19%) - 3.06 (2%)
cyclohexane	502.5	1.3	519.5	0.030	0.17 (71%) - 0.67 (25%)-3.70 (4%)
5b					
acetonitrile	495.0	3.6	511.0	0.35	0.91 (10%) - 6.79 (90%)
methanol	495.0	4.4	511.0	0.30	1.70 (25%) - 7.20 (75%)
chloroform	501.5	4.7	515.0	0.51	5.97
ethyl acetate	497.5	5.3	512.0	0.44	1.02 (28%) - 6.31 (72%)
cyclohexane	500.5	2.5	513.5	0.57	6.01

[a]Absorption wavelength, [b]molar absorption at the maximum, [c]fluorescence wavelength, [d]fluorescence quantum yield; [e]lifetime.

Table S2. Maximum g_{abs} and g_{lum}, as well as B_{CPL} of *C*-BODIPYs **5a** and **5b** in cyclohexane (see section S1 for experimental details).

	g_{abs}[a] × 10^3 (λ)	g_{lum}[b] × 10^3 (λ)	B_{CPL}[c] ($M^{-1}cm^{-1}$)
5a	+0.3 (494 nm)	–0.7 (550 nm)	0.1
5b	+0.3 (494 nm)	–1.1 (550 nm)	7.8

[a]Kunh´s dissymmetry ratio, [b]luminescence dissymmetry factor, [c]CPL brightness ($\varepsilon \times \phi \times |g_{lum}|/2$).

Table S3. Optimized Cartesian coordinates (xyz) and energies (in hartrees) of *C*-BODIPYs **5a** and **5b** in ground (B3LYP/6-31g*) and first excited (TD-B3LYP/6-31g*) states.

	S_0				S_1			
5a	N	0.19158700	-0.26936400	1.40981000	N	-0.02847600	-0.70367500	1.35946000
	C	1.57102600	-0.47547400	1.31588800	C	1.32253900	-1.01153900	1.32195500
	C	2.21053500	-0.54945500	0.06789500	C	2.00767800	-1.15771300	0.07085000
	C	1.45647100	-0.43647500	-1.11297500	C	1.22155800	-1.04847600	-1.12585000
	N	0.07359400	-0.21532100	-1.08591600	N	-0.11268200	-0.66712200	-1.09271800
	C	1.85548700	-0.62060600	-2.46466700	C	1.53497200	-1.39085800	-2.45116400
	C	0.71620300	-0.50408800	-3.24549900	C	0.37269000	-1.20089800	-3.23667200
	C	-0.35382200	-0.25643100	-2.36068400	C	-0.61025700	-0.75689800	-2.37508100
	C	-0.11680000	-0.25087300	2.71598800	C	-0.41500400	-0.63710500	2.68113200
	C	1.03504400	-0.43769400	3.50842200	C	0.66282400	-0.89543300	3.50417200
	C	2.10178900	-0.56771300	2.63198100	C	1.77266400	-1.10909200	2.65283400
	B	-0.80838800	0.05466200	0.20274400	B	-0.84234400	-0.18000500	0.16139400
	C	-1.99742600	-1.10918800	0.38787700	C	-2.43469500	-0.57743600	0.35914100
	C	-1.23810200	1.69978100	0.30331500	C	-0.62305100	1.78416100	0.20077700
	C	-3.31695800	-1.06462100	-0.46802000	C	-3.57262000	-0.03937000	-0.59196400
	C	-3.79262200	-2.47060300	-0.90131800	C	-4.60905300	-1.13696600	-0.93194300
	C	-3.68117400	-3.58978100	0.20486000	C	-5.03859500	-2.05396800	0.27878700
	C	-2.17968600	-3.65672600	-0.22881000	C	-3.72109600	-2.83397600	-0.04057800
	C	-1.33981300	-2.54379200	0.41774200	C	-2.48302600	-2.14957200	0.55640700
	C	-0.23827100	2.52208800	1.21290800	C	0.22133900	2.21528800	1.41531700
	C	0.03203200	3.96748200	0.76861400	C	1.09591900	3.46066500	1.14400900
	C	-1.26178400	4.71286100	0.30628500	C	0.36136400	4.54058200	0.28228900
	C	-1.04182900	3.92831100	-1.04099100	C	0.75549900	3.61896000	-0.93136500
	C	-1.54848000	2.46602500	-1.04531800	C	-0.17896800	2.39200500	-1.14987200
	C	-4.44552100	-0.29432500	0.24060700	C	-4.28043800	1.21497000	-0.04464700
	C	-2.61876900	-3.17524200	-1.63425900	C	-3.86559500	-2.37197400	-1.51095900
	C	-3.02368400	2.42224400	-1.47887100	C	-1.35134000	2.73521900	-2.08150300
	C	0.47453200	3.91807200	-0.71485800	C	1.97264400	3.14735800	-0.09403000
	C	-4.46480000	-4.85040300	-0.20861300	C	-6.29833800	-2.86929000	-0.07209500
	C	-4.01122600	-3.32210100	1.67861300	C	-5.24578800	-1.50299600	1.69526600
	C	-1.02657200	6.22326000	0.11295600	C	1.13828400	5.87210500	0.24149500
	C	-2.54312500	4.56089100	1.13497400	C	-1.09876600	4.88387200	0.59539100
	C	3.67535800	-0.76622800	-0.01056200	C	3.43924400	-1.45337500	-0.00380800
	C	4.28540100	-1.84448500	0.65035400	C	4.06195600	-2.38803100	0.85301500
	C	5.66316900	-2.04183400	0.56529500	C	5.42784700	-2.64896900	0.77123600
	C	6.47935400	-1.16955500	-0.16620900	C	6.24428500	-1.99933100	-0.16448800
	C	5.86607200	-0.08963500	-0.82038000	C	5.63122200	-1.07314200	-1.02432000
	C	4.49006900	0.10754000	-0.75361600	C	4.26885700	-0.80685400	-0.95155300
	C	7.97154300	-1.38087400	-0.25820800	C	7.72382100	-2.28592400	-0.25740100
	H	2.86100300	-0.83741700	-2.79521300	H	2.48477600	-1.78227100	-2.78774000
	H	0.63778800	-0.59286700	-4.32047900	H	0.26500100	-1.37081800	-4.29915300
	H	-1.39733600	-0.12222600	-2.60283900	H	-1.62787000	-0.48041100	-2.59379800
	H	-1.13309100	-0.08384200	3.04566500	H	-1.42801800	-0.37864200	2.95028800
	H	1.06034000	-0.46472800	4.58937600	H	0.65520800	-0.91746200	4.58525500
	H	3.14311300	-0.71350800	2.88011700	H	2.78447500	-1.32639800	2.96308100
	H	-2.34583600	-0.92520600	1.41388500	H	-2.68355500	-0.14462100	1.33507600
	H	-2.18589300	1.69087000	0.85588300	H	-1.67433700	1.99914300	0.38381200
	H	-3.12378500	-0.54200800	-1.41467400	H	-3.14591800	0.25386400	-1.55937500
	H	-4.75513700	-2.39878300	-1.42669900	H	-5.42390700	-0.70681700	-1.52927000
	H	-1.67428400	-4.62901400	-0.14541300	H	-3.70632000	-3.91199200	0.17082400
	H	-1.11057700	-2.81414700	1.45651700	H	-2.41295200	-2.36697500	1.62979500
	H	-0.37429600	-2.53294600	-0.10488500	H	-1.60132300	-2.61897300	0.10212300
	H	0.74389000	2.03840000	1.25223400	H	0.92536900	1.43458400	1.73021300
	H	-0.61032100	2.51664900	2.24575800	H	-0.44652300	2.37478100	2.27245000
	H	0.68072900	4.48142100	1.49183600	H	1.58715500	3.78810600	2.06965500
	H	-1.36236600	4.43676100	-1.96082000	H	0.94558600	4.11242300	-1.89354000
	H	-0.97653100	1.99769700	-1.85752800	H	0.45451600	1.66939500	-1.68249100
	H	-5.31829500	-0.18670600	-0.41688200	H	-5.06658900	1.53899400	-0.73817300
	H	-4.12667400	0.70970200	0.53412900	H	-3.59467200	2.05796800	0.08013900
	H	-4.77552300	-0.81306500	1.14627900	H	-4.75058500	1.02707300	0.92555200
	H	-2.93446300	-3.98286600	-2.29904000	H	-4.50368700	-3.02096900	-2.11471800
	H	-1.91665900	-2.53238200	-2.17659000	H	-2.93905200	-2.18749800	-2.06293100
	H	-3.37185800	1.40309800	-1.66112000	H	-1.96537400	1.85721600	-2.30260800
	H	-3.15868500	2.98415400	-2.41241900	H	-0.97589700	3.12076500	-3.03713000
	H	-3.68606800	2.86733800	-0.72882000	H	-2.00613100	3.49884700	-1.64914200
	H	1.00756500	4.81047400	-1.05185800	H	2.84879800	3.79254200	-0.18944100
	H	1.03796100	3.03142000	-1.03013200	H	2.28814900	2.10614500	-0.22485600
	H	-4.17771800	-5.70343900	0.42024900	H	-6.43925700	-3.68446600	0.64943900
	H	-5.54279100	-4.69080600	-0.07441700	H	-7.18977200	-2.23036600	-0.02596300
	H	-4.30392400	-5.14073200	-1.25081600	H	-6.26558200	-3.31464000	-1.07035400
	H	-3.47440800	-2.47244200	2.10245600	H	-4.39305900	-0.94364900	2.08277100

	H	-5.08557400	-3.14212900	1.81382600	H	-6.12357700	-0.84563700	1.73558500
	H	-3.75625100	-4.20562800	2.27991200	H	-5.43435500	-2.33353100	2.38891700
	H	-1.88128700	6.67997000	-0.40328400	H	0.71789500	6.53311800	-0.52711900
	H	-0.92450500	6.72305600	1.08531000	H	1.05487200	6.39097100	1.20496000
	H	-0.13044800	6.45286700	-0.47076600	H	2.20273200	5.74955300	0.02359400
	H	-2.78989900	3.52598100	1.37512900	H	-1.74482900	4.00870900	0.68622300
	H	-2.43801300	5.10391600	2.08432800	H	-1.15760600	5.43410600	1.54392800
	H	-3.40262800	4.99747200	0.60974100	H	-1.52231000	5.53290700	-0.18155700
	H	3.67518700	-2.54530100	1.21142400	H	3.45898800	-2.94631200	1.56158100
	H	6.11000400	-2.89165000	1.07508000	H	5.86640900	-3.38539500	1.44109400
	H	6.47577100	0.60876900	-1.38867000	H	6.23619000	-0.54216500	-1.75650400
	H	4.04175200	0.95784400	-1.25825700	H	3.83535700	-0.06329400	-1.61302700
	H	8.29596800	-2.21921500	0.36524100	H	8.04833500	-2.97017200	0.53265900
	H	8.27856600	-1.59057500	-1.29042600	H	7.98374100	-2.74172000	-1.22156500
	H	8.51944300	-0.48685000	0.06239700	H	8.31586600	-1.36638600	-0.17141100
	E = -1534.481306				E= -1534.399580			
5b	N	0.03899000	-0.13869000	1.40406400	N	0.03086500	-0.30694900	1.36125800
	C	1.42962100	-0.24554700	1.30336100	C	1.40946200	-0.42532500	1.29479400
	C	2.06881500	-0.29927200	0.06026300	C	2.08661800	-0.51548100	0.04969100
	C	1.31207800	-0.26870700	-1.11719100	C	1.29852200	-0.48442100	-1.13734600
	N	-0.08644200	-0.17080300	-1.09674100	N	-0.08187200	-0.30036000	-1.10068900
	C	1.73899800	-0.39268700	-2.46607800	C	1.67433600	-0.67804100	-2.47430800
	C	0.59940100	-0.38077100	-3.25434200	C	0.50134800	-0.60876000	-3.26779700
	C	-0.49704700	-0.24146100	-2.37515800	C	-0.54658100	-0.37925200	-2.39845600
	C	-0.26044500	-0.15289200	2.71166200	C	-0.32901700	-0.29376600	2.69068400
	C	0.90809000	-0.26766800	3.49685900	C	0.79774100	-0.39658600	3.48983900
	C	1.97492100	-0.32400800	2.61329000	C	1.90321200	-0.47333100	2.61550700
	B	-0.99110700	0.04199900	0.19137100	B	-0.91801400	-0.07873100	0.16396600
	C	-2.04826700	-1.23747700	0.40865000	C	-2.25294300	-1.05894500	0.38234500
	C	-1.61239500	1.62809400	0.25204500	C	-1.43763100	1.79198700	0.24181900
	C	-3.34513300	-1.36664500	-0.47354000	C	-3.52775000	-0.98062800	-0.53403600
	C	-3.65531500	-2.82983400	-0.86558100	C	-4.05086400	-2.38265100	-0.92608600
	C	-3.44842900	-3.89213400	0.28142900	C	-4.05748800	-3.44752700	0.23745500
	C	-1.93906400	-3.80888100	-0.12079500	C	-2.54352600	-3.61846800	-0.11338100
	C	-1.24001100	-2.58984500	0.50114300	C	-1.67479600	-2.52673800	0.52714800
	C	-0.77319500	2.56835700	1.20639400	C	-0.52106600	2.50050600	1.26766200
	C	-0.69132900	4.04322700	0.78308100	C	-0.21786300	3.97379600	0.92087700
	C	-2.05260900	4.60345700	0.25566000	C	-1.46299300	4.72883500	0.34912300
	C	-1.65493300	3.87102400	-1.08062600	C	-1.08211000	4.01308400	-0.99915500
	C	-1.94369800	2.35041500	-1.11437100	C	-1.56325100	2.53455200	-1.11888000
	C	-4.56861000	-0.69898100	0.17933200	C	-4.65292000	-0.12899500	0.08166200
	C	-2.39522500	-3.42493100	-1.55074100	C	-2.88136000	-3.18377400	-1.56110300
	C	-3.36837000	2.09736600	-1.63555600	C	-2.96194000	2.46752200	-1.75033500
	C	-0.17171000	4.07415900	-0.67580900	C	0.38614600	3.99880900	-0.50415600
	C	-4.08053200	-5.24420600	-0.10113100	C	-4.89000800	-4.68320500	-0.15497700
	C	-3.84001900	-3.61124700	1.73751800	C	-4.44194700	-3.08654000	1.67753700
	C	-2.02195200	6.13392800	0.07823100	C	-1.22283500	6.24932000	0.25653000
	C	-3.34230600	4.26826300	1.01471400	C	-2.83158000	4.53098100	1.00936200
	C	3.55990300	-0.42210900	-0.01131200	C	3.56312300	-0.71134900	-0.01555200
	C	4.15743400	-1.70034000	-0.02881900	C	4.12087200	-1.99148300	0.21013100
	C	5.55229100	-1.78947900	-0.09170800	C	5.50956400	-2.15506800	0.14750300
	C	6.36680100	-0.65404300	-0.14055900	C	6.36909400	-1.08993700	-0.13781500
	C	5.74855300	0.59987100	-0.11724300	C	5.80091000	0.16866000	-0.35785600
	C	4.35799600	0.74043500	-0.05468400	C	4.41823400	0.37683600	-0.30397300
	C	7.86935900	-0.77850000	-0.24003500	C	7.86323300	-1.29756500	-0.23192500
	C	3.74244600	2.12173800	-0.03119700	C	3.86273900	1.76378500	-0.53780500
	C	3.32558900	-2.96276700	0.02149500	C	3.24340700	-3.18775400	0.50670700
	H	2.76739400	-0.49225500	-2.78490700	H	2.68170100	-0.88098500	-2.81280800
	H	0.53585900	-0.46146700	-4.33095100	H	0.42931700	-0.71303300	-4.34182700
	H	-1.54568400	-0.19553400	-2.62795700	H	-1.59289100	-0.24051600	-2.61979100
	H	-1.28429100	-0.07048900	3.05011700	H	-1.36312800	-0.18712300	2.98439500
	H	0.93953700	-0.30616800	4.57731400	H	0.81407800	-0.41415300	4.57109200
	H	3.02662500	-0.42215700	2.84473900	H	2.94526200	-0.58498800	2.88522600
	H	-2.43478200	-1.05473300	1.42143600	H	-2.61456000	-0.77636600	1.37774500
	H	-2.57970300	1.50576500	0.75341500	H	-2.42721700	1.64488400	0.67548500
	H	-3.18657600	-0.86059200	-1.43538000	H	-3.26808800	-0.50983100	-1.48979500
	H	-4.60757100	-2.88068600	-1.41163200	H	-4.97949600	-2.28583500	-1.50435700
	H	-1.33286700	-4.71656100	0.00688000	H	-2.09521900	-4.60903000	0.04506100
	H	-1.00435600	-2.79915300	1.55250300	H	-1.52540500	-2.73435800	1.59457900
	H	-0.27086800	-2.49139600	-0.00535000	H	-0.68026900	-2.59747300	0.06981600
	H	0.26448900	2.22459700	1.28175000	H	0.45706600	2.01178500	1.35395300
	H	-1.18049100	2.49742700	2.22358200	H	-0.97797100	2.40953300	2.26211100
	H	-0.16006400	4.63620900	1.54068600	H	0.34018200	4.44608700	1.74018600
	H	-1.99759200	4.33709500	-2.01478900	H	-1.31121600	4.54678000	-1.93070200

	H	-1.26103300	1.97453500	-1.88841600	H	-0.86394400	2.09163600	-1.83695900
	H	-5.43351400	-0.72447200	-0.49659200	H	-5.49995100	-0.05365400	-0.61194900
	H	-4.37393400	0.34820200	0.42687200	H	-4.32231600	0.88943500	0.30391200
	H	-4.85656800	-1.20825100	1.10458500	H	-5.02527200	-0.56453000	1.01381500
	H	-2.60537400	-4.28361100	-2.19288000	H	-3.21020100	-4.00622300	-2.20030500
	H	-1.75563800	-2.72587700	-2.10137900	H	-2.11814800	-2.60943500	-2.09645300
	H	-3.56290500	1.03731600	-1.81633000	H	-3.27160800	1.44063800	-1.96014500
	H	-3.52165500	2.62394500	-2.58659800	H	-2.96781900	3.01144300	-2.70271400
	H	-4.13035100	2.45536400	-0.93499800	H	-3.72389800	2.91928900	-1.10686300
	H	0.24536300	5.03669600	-0.98143900	H	0.93898400	4.91180100	-0.73594100
	H	0.52736500	3.28010400	-0.96516000	H	0.99523900	3.13629600	-0.79692500
	H	-3.71711800	-6.03889500	0.56366500	H	-4.68253200	-5.51689700	0.52836400
	H	-5.17231800	-5.19914400	0.00619100	H	-5.96206900	-4.45792600	-0.08445200
	H	-3.86485300	-5.55027200	-1.12886200	H	-4.69479900	-5.03415700	-1.17226000
	H	-3.40794000	-2.69411200	2.13995100	H	-3.87988800	-2.24585700	2.08751100
	H	-4.93041500	-3.54408900	1.84445500	H	-5.50955200	-2.84287300	1.74943200
	H	-3.50577800	-4.44045800	2.37615100	H	-4.26451700	-3.94965200	2.33340400
	H	-2.90463700	6.47101500	-0.48104500	H	-2.01523600	6.72307700	-0.33678600
	H	-2.04172400	6.63340400	1.05585500	H	-1.24537300	6.69945200	1.25718800
	H	-1.13824700	6.49303400	-0.45695600	H	-0.26598400	6.51254500	-0.20247900
	H	-3.45646500	3.20751200	1.24037600	H	-3.09934500	3.48358500	1.15919700
	H	-3.36366500	4.81265300	1.96881400	H	-2.84494800	5.01711900	1.99394500
	H	-4.22480200	4.58667700	0.44457200	H	-3.62408400	4.99532000	0.40885300
	H	6.01250300	-2.77532500	-0.10147200	H	5.92927200	-3.14420100	0.32162200
	H	6.36337700	1.49703500	-0.14709000	H	6.45096900	1.01509000	-0.57192800
	H	8.22755800	-1.69564700	0.23899600	H	8.19536500	-2.11772300	0.41336300
	H	8.19444700	-0.81128400	-1.28847600	H	8.16570400	-1.54930200	-1.25740400
	H	8.37338900	0.07311300	0.22866200	H	8.41195800	-0.39373400	0.05358900
	H	4.51717100	2.89282900	-0.06904700	H	4.66959800	2.49450000	-0.65071400
	H	3.07008900	2.27735000	-0.88313200	H	3.24404300	1.80226900	-1.44221000
	H	3.14935200	2.28346800	0.87649100	H	3.22591100	2.08516800	0.29444000
	H	2.64489500	-3.03046700	-0.83526400	H	2.44619400	-3.29281300	-0.23804300
	H	3.96590200	-3.84938100	0.01316900	H	3.83144500	-4.11069000	0.50975600
	H	2.70596400	-3.00182600	0.92485400	H	2.75321700	-3.09804300	1.48336800
	E = -1613.112664				E = -1613.027434			

Table S4. Optimized Cartesian coordinates (xyz) and energies (in hartrees) of the corresponding *F*-BODIPY counterparts (**5a´** and **5b´**) of dyes **5a** and **5b** in ground (B3LYP/6-31g*) and first excited (TD-B3LYP/6-31g*) states.

	S_0				S_1			
5a´	N	-2.03776550	-1.23728621	0.00446564	N	2.07684300	1.17723400	-0.06379400
	C	-0.64394998	-1.21978297	0.03404895	C	0.66478900	1.24956400	-0.08734600
	C	0.06747190	-0.00648497	-0.01075209	C	-0.11063400	0.08440100	-0.06263100
	C	-0.63112764	1.21306384	-0.08177671	C	0.62280000	-1.19996300	-0.20316500
	N	-2.02436557	1.24663110	-0.07384189	N	2.02722400	-1.25836300	-0.07733900
	C	-0.16541184	2.54470489	-0.25510058	C	0.20588200	-2.41510200	-0.63489100
	C	-1.28411104	3.36343212	-0.33823984	C	1.41577300	-3.27897700	-0.75898800
	C	-2.40909986	2.52201843	-0.22661656	C	2.49193600	-2.49510600	-0.42115900
	C	-2.43700765	-2.51601163	0.06465896	C	2.57075000	2.43084000	-0.16729900
	C	-1.32244006	-3.37515639	0.13733496	C	1.51621300	3.35490200	-0.23330500
	C	-0.19456485	-2.56480842	0.12909509	C	0.32621700	2.63364300	-0.16363200
	B	-2.98032027	0.01420448	0.07546395	B	2.90078900	-0.04108100	0.39264700
	C	1.54891644	-0.00874946	0.00125545	C	-1.56598100	0.05637100	-0.00898400
	C	2.27981784	-0.78434112	-0.91440055	C	-2.37047000	0.99135700	-0.70133600
	C	3.67218279	-0.77720665	-0.89815770	C	-3.75751700	0.95195600	-0.61929200
	C	4.38510173	-0.00917258	0.03234647	C	-4.42191300	-0.01606800	0.14728900
	C	3.65228372	0.75610770	0.94963654	C	-3.63113400	-0.95287900	0.82974900
	C	2.25998017	0.76632973	0.93303494	C	-2.24434300	-0.92761000	0.75108400
	C	5.89485913	0.01325666	0.03019328	C	-5.92887000	-0.07011600	0.21022200
	H	0.87134654	2.83971744	-0.33042930	H	-0.80488500	-2.70808300	-0.87816400
	H	-1.30655362	4.43553224	-0.47708093	H	1.42480100	-4.32097900	-1.04812900
	H	-3.46027321	2.77592565	-0.25839798	H	3.54808900	-2.71206200	-0.38527500
	H	-3.49098665	-2.76027911	0.06536259	H	3.63814500	2.59979600	-0.14423100
	H	-1.35717831	-4.45433555	0.19517396	H	1.62206400	4.42893500	-0.30871900
	H	0.83784465	-2.87711963	0.19206707	H	-0.67429800	3.03721300	-0.16741000
	H	1.75048023	-1.37467225	-1.65587693	H	-1.89887900	1.72243600	-1.34860900
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	H	4.17938945	1.34985524	1.69279461	H	-4.11272900	-1.70936200	1.44601200

	H	1.71398907	1.35352131	1.66497019	H	-1.66656600	-1.64665900	1.32330600
	H	6.30973616	-0.92940591	-0.34149128	H	-6.37346200	0.91477800	0.03232500
	H	6.27683504	0.81440128	-0.61664006	H	-6.33805100	-0.75262400	-0.54763800
	H	6.29464355	0.18886162	1.03433478	H	-6.27687500	-0.42716300	1.18582100
	F	-3.88885407	-0.00716255	-0.96535700	F	4.12751600	-0.08468300	-0.23910900
	F	-3.61509395	0.04892414	1.30407695	F	3.01913100	-0.10622900	1.77071300
	E = -951.750800				E = -951.644888			
5b´	N	-2.17647321	-1.24282035	-0.03277047	N	-2.15648400	-1.24230600	-0.07220300
	C	-0.78198454	-1.21299342	-0.02191260	C	-0.77102200	-1.23594900	-0.07940700
	C	-0.07902439	-0.00006910	-0.00932663	C	-0.07547600	-0.00013500	-0.04801300
	C	-0.77925472	1.21441171	-0.02104515	C	-0.77070500	1.23586000	-0.07952700
	N	-2.17371212	1.24738597	-0.03189107	N	-2.15616500	1.24257900	-0.07234400
	C	-0.30786208	2.55383206	-0.05700919	C	-0.32257700	2.57616800	-0.16175500
	C	-1.42426975	3.37861316	-0.09224018	C	-1.47119300	3.38810600	-0.21048600
	C	-2.55318037	2.53196800	-0.07469629	C	-2.57253200	2.53783200	-0.15334700
	C	-2.55883837	-2.52655978	-0.07649045	C	-2.57318700	-2.53745600	-0.15312600
	C	-1.43183007	-3.37567588	-0.09467784	C	-1.47206800	-3.38801600	-0.21028400
	C	-0.31355303	-2.55341358	-0.05890906	C	-0.32324100	-2.57638000	-0.16150000
	B	-3.12641819	0.00324245	0.06634742	B	-3.06985100	0.00026700	0.15687600
	C	1.41735708	-0.00150634	0.00210988	C	1.40401900	-0.00023300	-0.01622400
	C	2.12818773	-0.00362438	-1.21610590	C	2.16096600	-0.00036200	-1.23227400
	C	3.52608131	-0.00860145	-1.17650025	C	3.53671800	-0.00024900	-1.14901200
	C	4.23376494	-0.00871608	0.02858792	C	4.22743600	-0.00002500	0.11246600
	C	3.50353644	-0.01066858	1.22023504	C	3.48251100	-0.00004900	1.30281100
	C	2.10529501	-0.00571961	1.23346858	C	2.09903200	-0.00017900	1.27264900
	C	5.74433906	0.01802834	0.04292964	C	5.71943800	0.00027700	0.12211200
	C	1.36165379	-0.00916798	2.55057007	C	1.28837100	-0.00017900	2.52605900
	C	1.41037149	-0.00489213	-2.54756254	C	1.44848400	-0.00056200	-2.55669900
	H	0.73341467	2.84556727	-0.06288823	H	0.70766600	2.90645500	-0.20214800
	H	-1.44540293	4.45905717	-0.12986633	H	-1.50366600	4.46689000	-0.28740600
	H	-3.60315380	2.79295607	-0.08991344	H	-3.62863600	2.76682700	-0.16167900
	H	-3.60940170	-2.78513706	-0.09188051	H	-3.62934900	-2.76617700	-0.16144000
	H	-1.45530434	-4.45604398	-0.13307279	H	-1.50482000	-4.46679300	-0.28717700
	H	0.72705909	-2.84755048	-0.06506136	H	0.70692100	-2.90693400	-0.20180800
	H	4.07498037	-0.01375512	-2.11606069	H	4.13360000	-0.00032700	-2.05723500
	H	4.03461573	-0.01745512	2.16997418	H	4.00406900	0.00007100	2.25497800
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	H	6.12264390	1.04900087	0.05420156	H	6.10473100	0.87785000	-0.41565300
	H	6.14594342	-0.48402295	0.92948544	H	6.12882100	0.00028000	1.13411200
	H	2.06101954	-0.00982968	3.39168090	H	1.92206600	-0.00060800	3.41604800
	H	0.71445797	0.86988105	2.65059207	H	0.62631400	0.87328700	2.54478500
	H	0.71635971	-0.88997459	2.64754352	H	0.62558100	-0.87308100	2.54440400
	H	0.76585900	0.87471977	-2.65914578	H	0.80100600	0.87772300	-2.63854600
	H	2.12622566	-0.00468209	-3.37469301	H	2.15914700	-0.00124500	-3.38780900
	H	0.76696708	-0.88541255	-2.65854316	H	0.80005200	-0.87819000	-2.63783500
	F	-3.77483781	0.00357770	1.28770947	F	-3.55548100	0.00040700	1.46492400
	F	-4.02073966	0.00464715	-0.98624458	F	-4.12348600	0.00035300	-0.74924900
	E = -1030.382654				E = -1030.277358			

S5. Figures

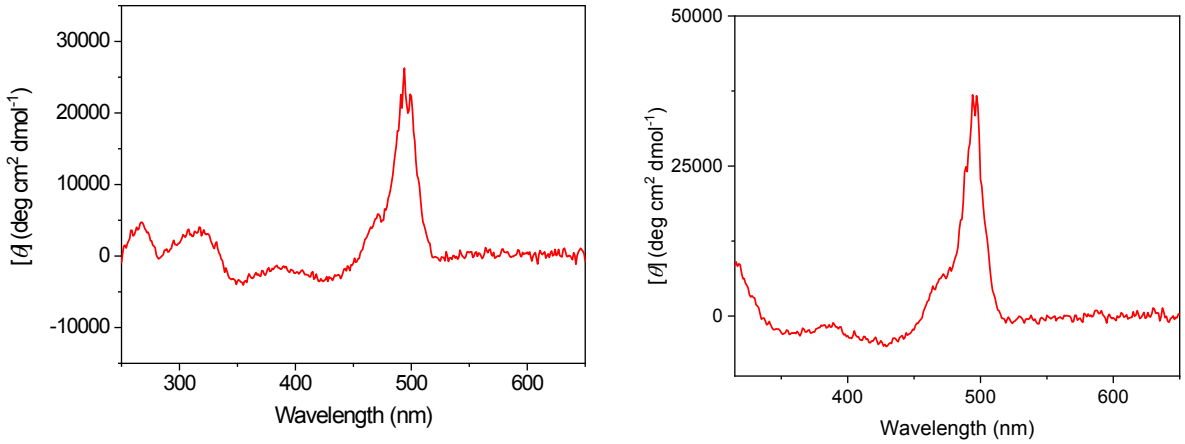

Fig. S1. ECD spectra of *C*-BODIPYs **5a** (left) and **5b** (right) in chloroform (see section S1 for experimental details).

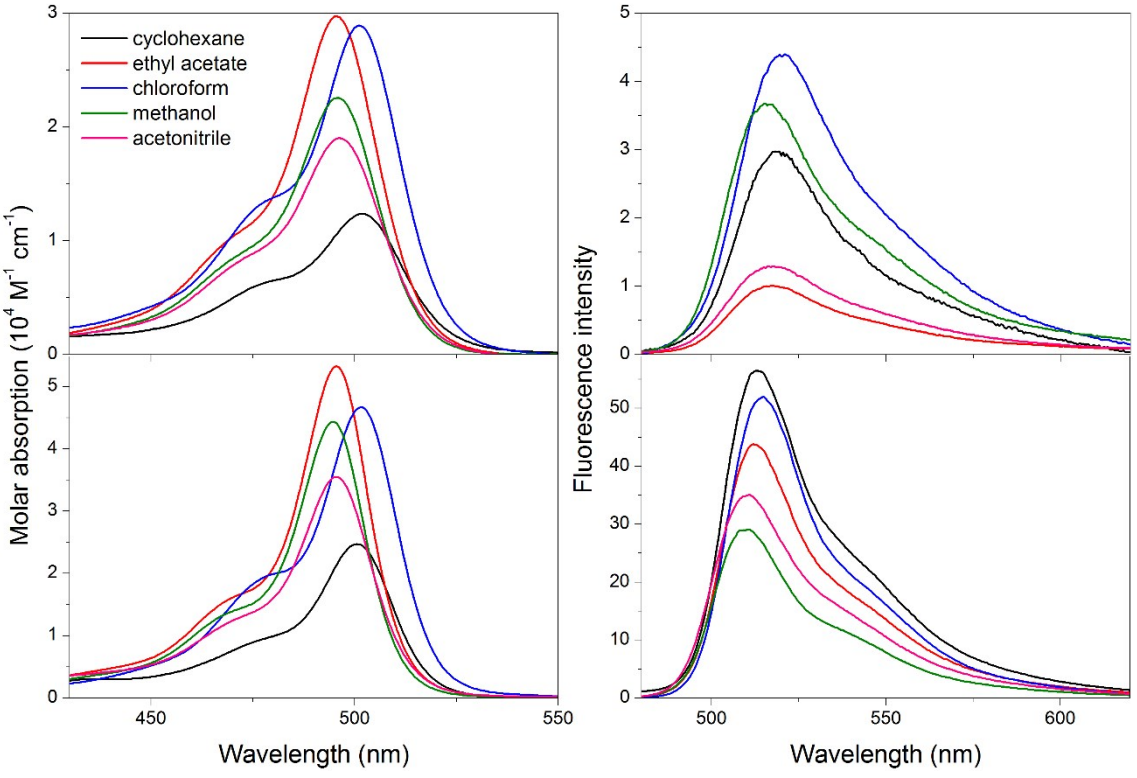

Fig. S2. Absorption and fluorescence spectra (scaled by their efficiency) of **5a** (top) and **5b** (bottom) in different solvents (see section S1 for experimental details).

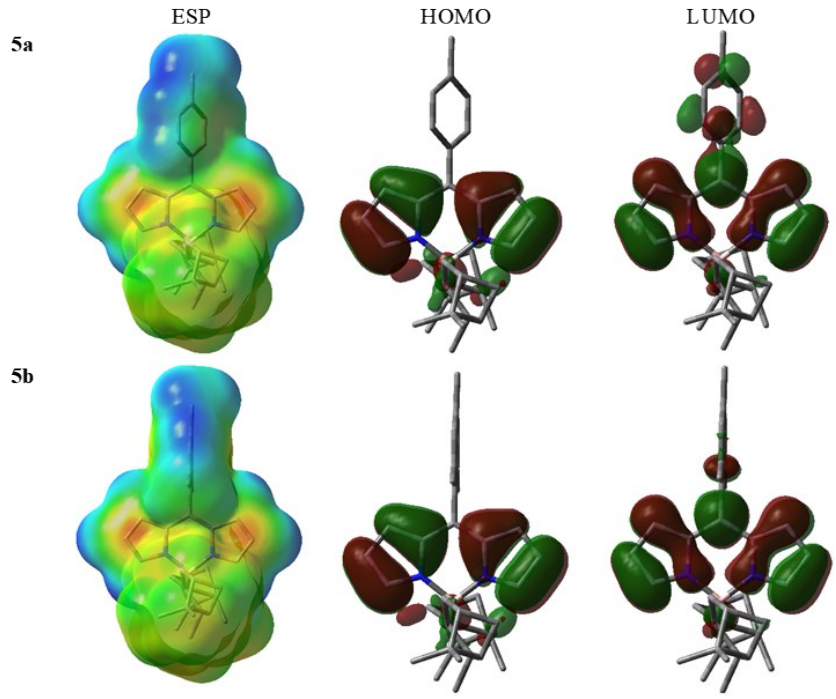

Fig. S3. Electrostatic surface potential (ESP) mapped onto the electronic density (negative charge in red and positive in blue) and contour maps of the molecular orbitals involved in the main electronic transition (HOMO and LUMO) computed for *C*-BODIPYs **5a** and **5b** (DFT-optimized ground-state geometries).

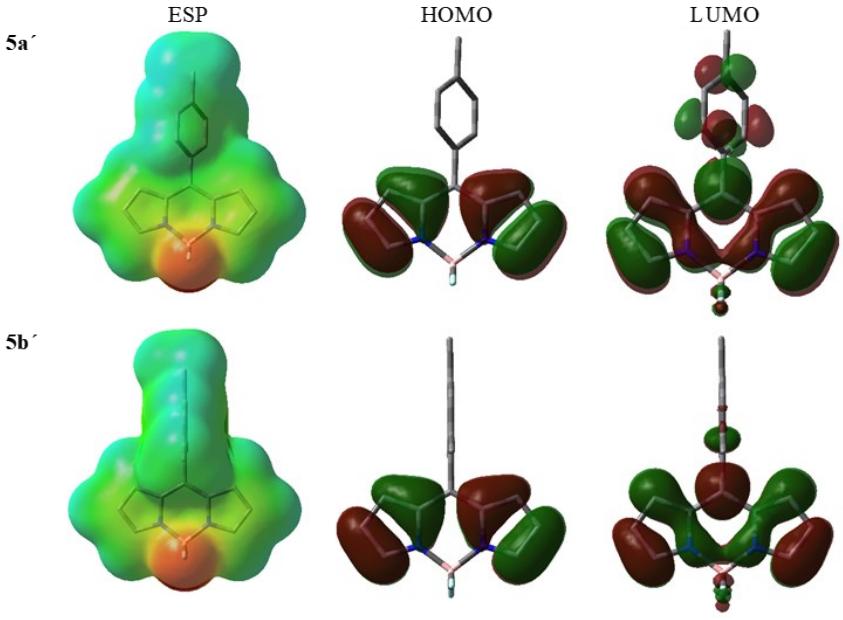

Fig. S4. Electrostatic surface potential (ESP) mapped onto the electronic density (negative charge in red and positive in blue) and contour maps of the molecular orbitals involved in the main electronic transition (HOMO and LUMO) computed for the *F*-BODIPY counterparts of **5a** and **5b** (**5a´** and **5b´**; DFT-optimized ground-state geometries).

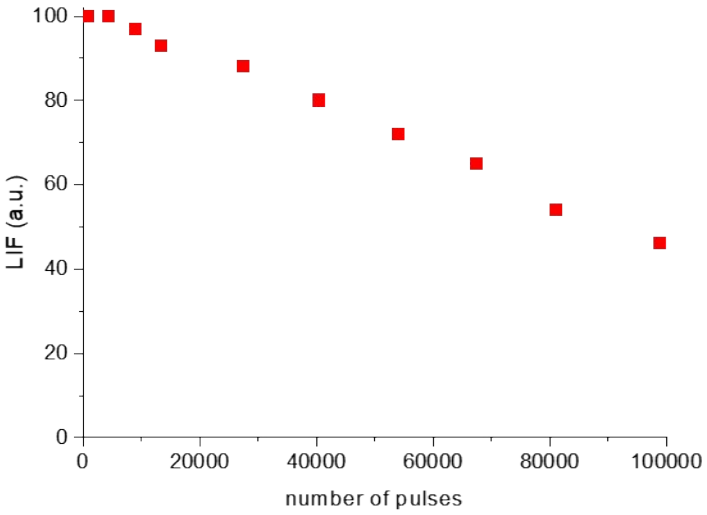

Fig. S5. LIF intensity evolution of **5b** in cyclohexane upon laser pumping (see section S1 for experimental details).

S6. References

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