Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic supporting information for

BINOLated aminostyryl BODIPY: A workable organic molecular platform for NIR circularly polarized luminescence

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1. 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 or alumina plates, and the chromatograms were visualized by using UV light (λ = 254 or 365 nm). Flash column chromatography was performed using silica gel (230-400 mesh) or activated neutral alumina (activity degree 1, 70-290 mesh ASTM). Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 20 ºC unless otherwise indicated. NMR chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the residual signals of $CDCl_3$ (δ = 7.260 and 77.03 ppm, respectively). Data are presented as follows ^{1}H NMR: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, b = broad), coupling constants, *J*, in hertz (Hz), integration ^{13}C NMR: chemical shift and type of carbon (CH_3, CH_2, CH or C). The type of carbon was assigned by DEPT-135 spectra. FTIR spectra were obtained from neat samples using the attenuated total reflection (ATR) technique. High-resolution mass spectrometry (HRMS) was performed using the EI technique. Specific optical rotations, in chloroform solution, at a given dye concentration, *c*, between 2.5×10^{-3} and 3.6×10^{-3} g/100 mL, unless otherwise indicated, were recorded at 293 K on an Anton Paar MCP 100 polarimeter using 10 mm cell. Photophysical signatures were recorded using diluted dye solutions (*ca.* 2×10^{-6} M) prepared from a concentrated stock solution (*ca.* 10^{-3} M) in acetone (except for dye **6**, whose stock solution was done in ethanol due to solubility reasons) after vacuum evaporation of the solvent from a certain amount of sample, and ulterior 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_F) were determined from corrected spectra (detector sensibility to the wavelength) by the optically dilute relative method and by the use of the following equation (Eq. 1), where I_{exc} is the luminescent intensity at the excitation wavelength, A_{exc} is the absorbance at the excitation wavelength, $\int I d\lambda$ 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. Zinc phtalocyanine in toluene with 1% (v/v) of pyridine (ϕ_F = 0.30)[2] was used as the reference.

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

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). ECD spectra were recorded on a Jasco (model J-715) spectropolarimeter using standard quartz cells of 1-cm optical-path length in chloroform solution at a dye concentration of *ca.* 3.5×10^{-5} M, unless otherwise indicated. Circularly polarized luminescence (CPL) and total luminescence spectra were recorded at 295 K in degassed chloroform solution (nitrogen was bubbled into the solution), unless otherwise indicated, at a dye concentration of *ca.* 1.0×10^{-3} M and upon excitation at *ca.* 570 nm (BODIPY chromophore excitation) on an instrument described previously,[3] 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,[4] 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. The polynomial fit tool implemented in OriginPro 9 was used to fit CPL data points to the corresponding continuous-curve CPL spectrum (5th. order polynomials were used).

2. Synthetic procedure and characterization data

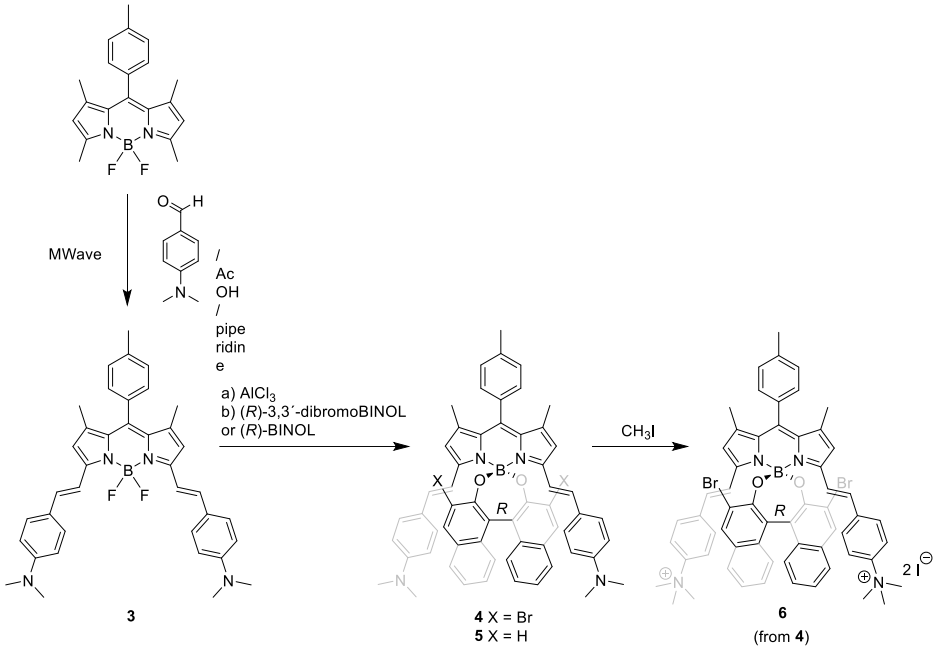


Figure S1. Synthesis of BINOLAted BODIPYs (exemplified for (*R*)-BINOLated **4-6**).

Synthesis of 3. A mixture of 1,3,5,7-tetramethyl-8-(4-methylphenyl)BODIPY[5] (70 mg, 0.21 mmol, 1 mol equiv.), 4-(dimethylamino)benzaldehyde (93 mg, 0.63 mmol, 3 mol. equiv.), acetic acid (63 mg, 1.05 mmol, 5 mol. equiv.) and piperidine (89 mg, 1.05 mmol, 5 mol. equiv.) in dry DMF (1 mL) was submitted to microwave irradiation for 40 min at 120 ºC. Then, the mixture was diluted with ethyl acetate (20 mL), washed with water (5×20 mL) and dried over anhydrous Na_2SO_4. After filtration and solvent evaporation under reduced pressure, the obtained residue was submitted to flash chromatography (silica gel; hexane/ethyl acetate 1:1) to obtain **3** (74 mg, 60%) as a black solid. R_F = 0.25 (silica gel; hexane/ethyl acetate 7:3). ^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.56 (d, *J* = 16.3 Hz, 4H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 16.3 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 4H), 6.59 (s, 2H), 3.03 (s, 12H), 2.44 (s, 3H), 1.44 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 176 MHz) δ 152.8 (C), 150.9 (C), 141.2 (C), 138.6 (C), 136.9 (C), 136.3 (CH), 133.3 (C), 132.7 (C), 129.7 (CH), 129.2 (CH), 128.7 (CH), 125.3 (C), 117.2 (CH), 115.2 (CH), 112.2 (CH), 40.4 (CH_3), 21.6 (CH_3), 14.8 (CH_3) ppm. FTIR ν 1592, 1528, 1484, 1364, 1294, 1164, 990 cm^{-1}. HRMS (ESI$^+$) *m*/z: [M]$^+$ Calcd. for $C_{38}H_{39}BF_2N_4$: 600.3236; Found 600.3224.

Synthesis of 4. The reaction was performed in a flame-dried flask. A mixture of *F*-BOPIPY **3** (30 mg, 0.05 mmol, 1 mol. equiv.) and aluminium chloride (20 mg, 0.15 mmol, 3 mol. equiv.) in dry CH_2Cl_2 (5 mL) was refluxed under argon atmosphere until disappearance of the starting material (reaction monitored by TLC). The mixture was cooled down to room temperature and then, a solution of (*R*)-3,3'-dibromoBINOL (44 mg, 0.10 mmol, 2 mol. equiv.) in dry acetonitrile (1 mL) was added dropwise. The resulting mixture was stirred at r.t. for additional 18 h, the solvent removed by distillation under reduced pressure, and the resulting residue purified by flash chromatography (neutral alumina; CH_2Cl_2) to obtain **4** (35 mg, 70%) as a black solid. R_F = 0.45 (silica gel; hexane/CH_2Cl_2 1:1). $[\alpha]_D^{20}$ +17834 (*c* 0.0036, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.99 (s, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.32-7.24 (m, 4H), 7.11-7.01 (m, 4H), 6.80 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 2H), 6.71 (br d, *J* = 16.0 Hz, 2H), 6.56 (br d, *J* = 15.9 Hz, 2H), 6.42 (br s, 2H), 6.38 (d, *J* = 8.6 Hz, 4H), 6.14 (d, *J* = 8.7 Hz, 4H), 2.88 (br s, 12H), 2.46 (s, 3H), 1.46 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 176 MHz) δ 151.4 (C), 138.4 (C), 133.1 (C), 132.2 (CH), 130.5 (C), 129.6 (CH), 128.4 (C), 127.8 (CH), 126.9 (CH), 125.0 (CH), 124.3 (CH), 123.2 (C), 119.9 (C), 111.9 (CH), 21.6 (CH_3), 15.1 (CH_3) ppm. FTIR ν 1589, 1547, 1523, 1485, 1360, 1287, 1159, 1098, 1015 cm^{-1}. HRMS (ESI^+) *m*/*z*: $[M]^+$ Calcd. for $C_{58}H_{49}BBr_2N_4O_2$: 1002.2315; Found 1002.2324.

Synthesis of ent-4. The preparation of ent-**4** (enantiomer of **4**), 69% yield, was done following just the same procedure described for **4**, but using (*S*)- instead of (*R*)-3,3´-dibromoBINOL. $[\alpha]_D^{20}$ –20734 (*c* 0.0034, $CHCl_3$). ^{1}H NMR, ^{13}C NMR, FTIR and HRMS are identical to those registered for **4** (see above).

Synthesis of 5. Following a similar procedure to that used for **4**, *F*-BODIPY **3** (25 mg, 0.04 mmol, 1 mol. equiv.) was reacted with (*R*)-BINOL ((*R*)-1,1'-binaphth-2-ol, 24 mg, 0.08 mmol). The reaction crude was purified using flash chromatography (neutral alumina; CH_2Cl_2) to obtain **5** (24 mg, 67%) as a black solid. R_F = 0.40 (silica gel; hexane/CH_2Cl_2 3:7). $[\alpha]_D^{20}$ +20023 (c 0.0029, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.28 (m, 4H), 7.27-7.23 (m, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.10 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 2H), 6.88 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 2H), 6.49-5.91 (br m, 10H), 2.89 (br s, 12H), 2.46 (s, 3H), 1.44 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 176 MHz, 50 ºC) δ 155.2 (C), 154.7 (C), 150.2 (C), 140.7 (C), 138.6 (C), 134.8 (CH), 134.1 (two C), 133.5 (C), 130.6 (C), 129.6 (CH), 129.5 (CH), 129.3 (CH), 128.6 (CH), 128.2 (CH), 127.9 (CH), 124.7 (CH), 124.6 (CH), 123.3 (CH), 122.0 (C), 118.9 (CH), 116.4 (CH), 112.3 (CH), 40.5 (CH_3), 21.5 (CH_3), 15.0 (CH_3) ppm. FTIR ν 1589, 1522,

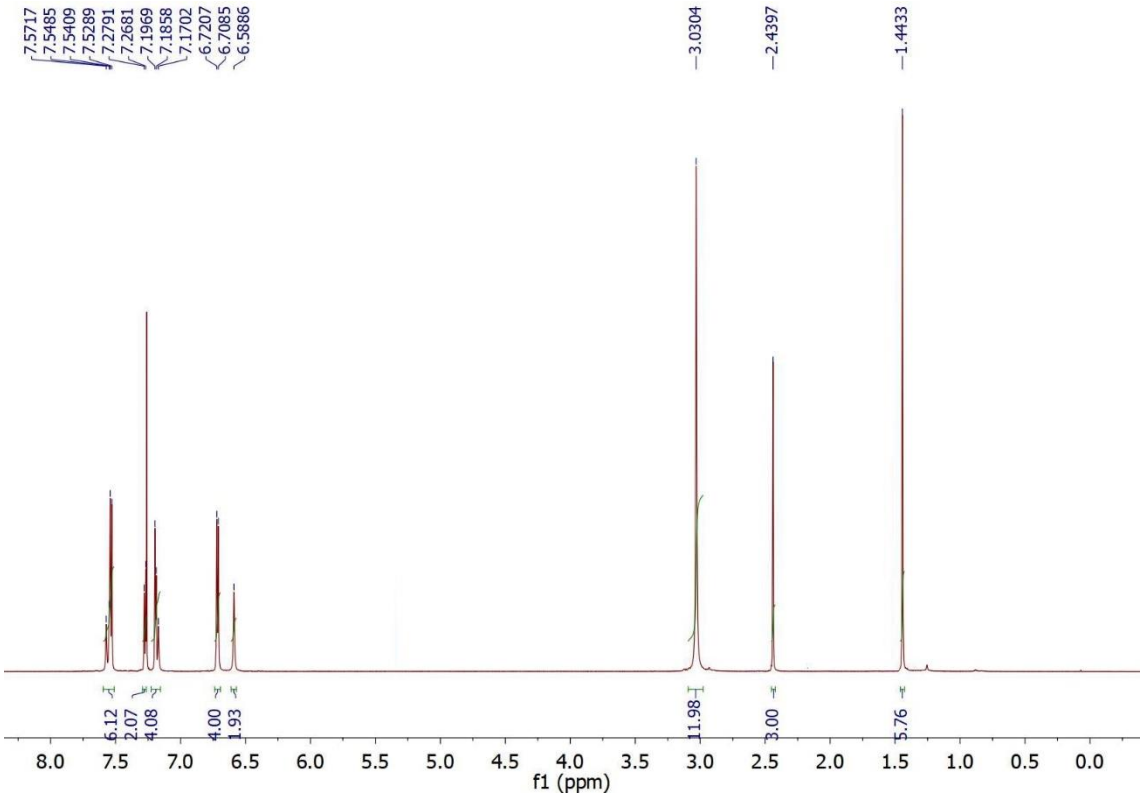
1487, 1363, 1288, 1158 cm^{-1}. HRMS (ESI^+) *m*/*z*: $[M]^+$ Calcd. for $C_{58}H_{51}BN_4O_2$: 846.4105; Found: 846.4114.

Synthesis of 6. Iodomethane (1 mL) was added to a solution of **4** (15 mg, 0.015 mmol, 1 mol equiv.) in acetonitrile (1 mL). The resulting mixture was stirred under argon for 72 h. The solvent was removed under reduced pressure and the residue purified by flash chromatography (neutral alumina; acetonitrile/water 9:1) to obtain **6** (14 mg, 73%) as a blue solid. R_F = 0.14 (neutral alumina; CH_3CN/H_2O 9:1). $[\alpha]_D^{20}$ +2242 (*c* 0.0034, H_2O). ^1H NMR (CD_3OD, 700 MHz) δ 8.04 (s, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.9 Hz, 4H), 7.17 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.04 (d, *J* = 16.2 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.95 (dd, *J* = 8.5, 6.5 Hz, 2H), 6.83 (d, *J* = 16.2 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 4H), 6.71 (s, 2H), 3.56 (s, 18H), 2.49 (s, 3H), 1.55 (s, 6H) ppm. ^{13}C NMR (CD_3OD, 176 MHz) δ 155.0 (C), 152.1 (C), 146.8 (C), 144.1 (C), 142.4 (C), 140.8 (C), 139.4 (C), 136.6 (C), 134.0 (C), 133.7 (CH), 133.5 (C), 132.5 (CH), 132.3 (C), 131.2 (CH), 129.6 (CH), 129.2 (CH), 128.5 (CH), 128.4 (CH), 126.7 (CH), 125.9 (CH), 124.4 (C), 122.3 (CH), 121.6 (CH), 120.78 (CH), 120.75 (C), 57.6 (CH_3), 21.5 (CH_3), 15.1 (CH_3) ppm. FTIR ν 1546, 1490, 1159, 1097, 990 cm^{-1}.HRMS (ESI^+) *m*/*z*: $[M+HCOO]^+$ Calcd. For $C_{61}H_{56}BBr_2N_4O_4$: 1077.2761; Found 1077.2770. HRMS (ESI^-) *m*/*z*: $[M]^-$ Calcd. for I: 126.9045; Found: 126.9046.

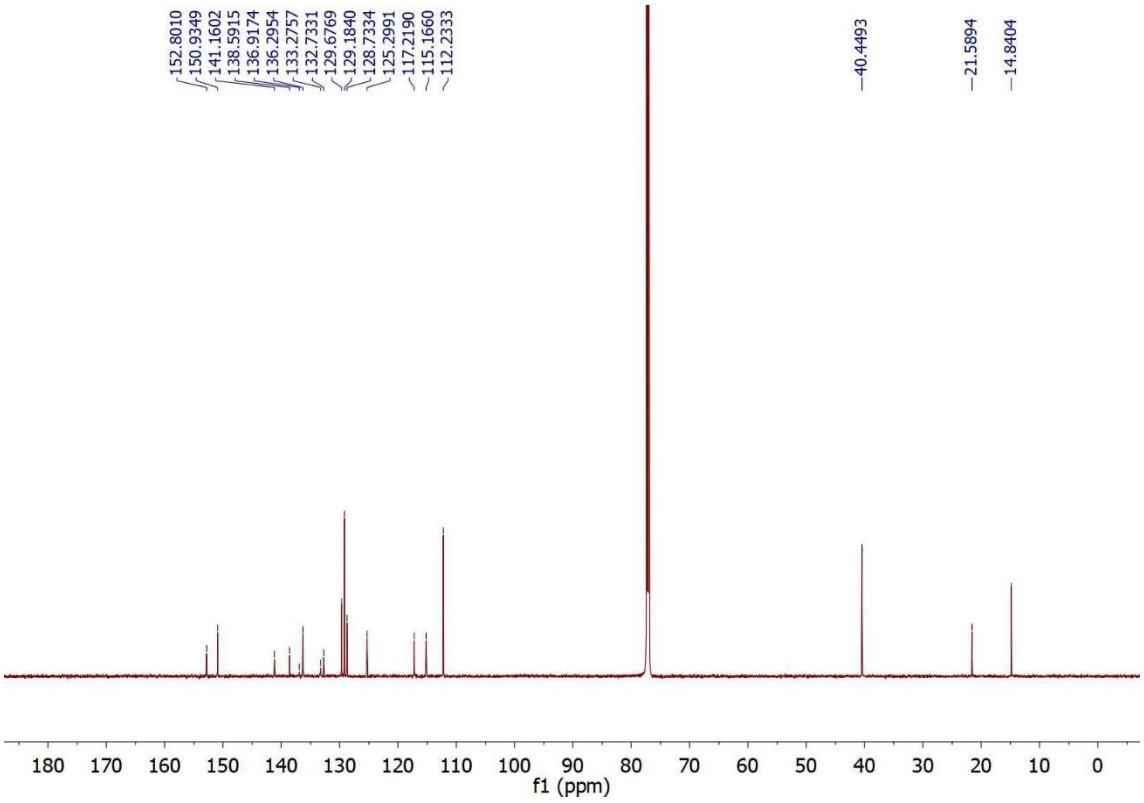
Synthesis of ent-6. The preparation of ent-**6** (enantiomer of **6**), 73% yield, was done following just the same procedure described for **6**, but starting from ent-**4** instead of **4**. $[\alpha]_D^{20}$ –2047 (*c* 0.0034, H_2O). ^1H NMR, ^{13}C NMR, FTIR and HRMS are identical to those registered for **6** (see above).

2. ^{1}H- and ^{13}C-NMR spectra

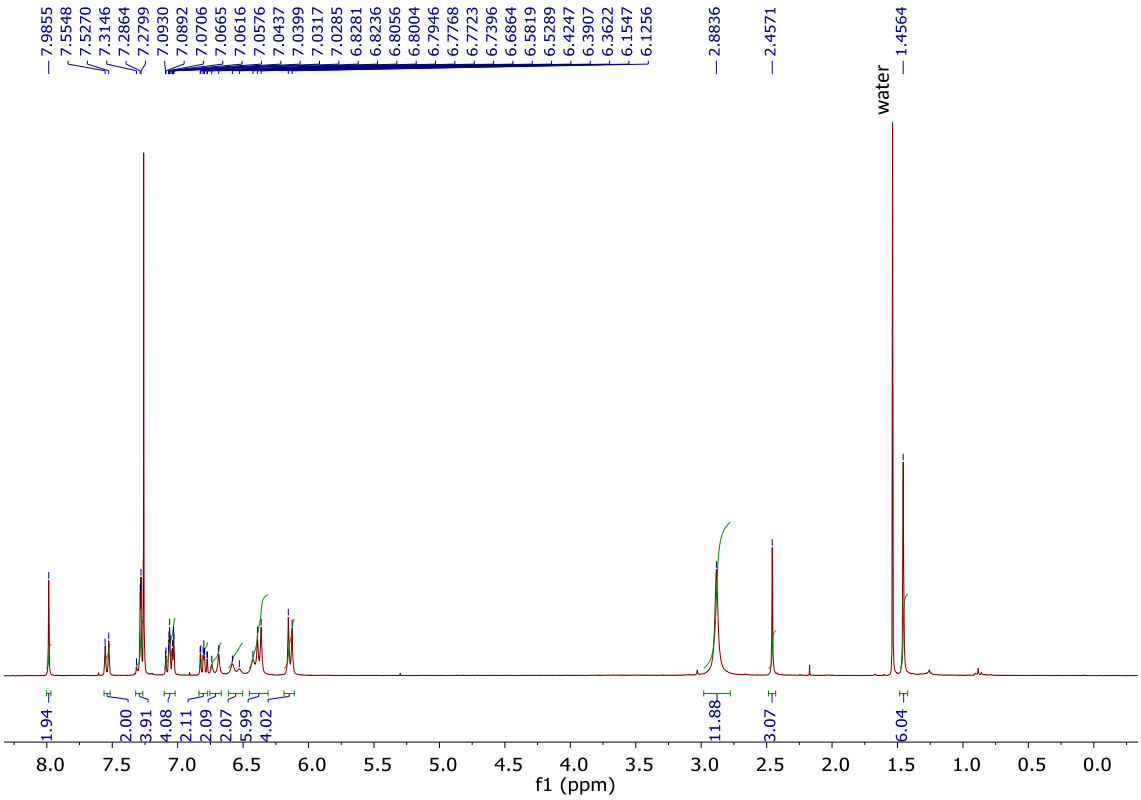
^{1}H NMR ($CDCl_3$, 700 MHz) spectrum of 3



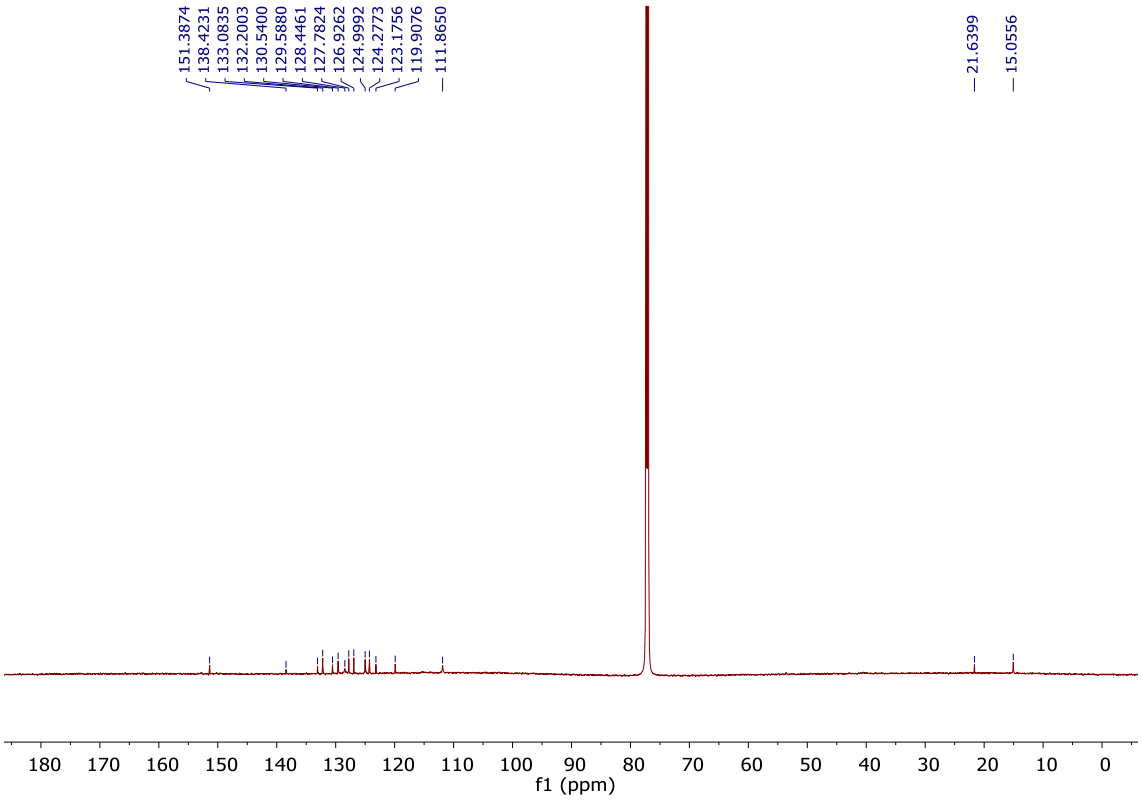
^{13}C NMR ($CDCl_3$, 176 MHz) spectrum of 3



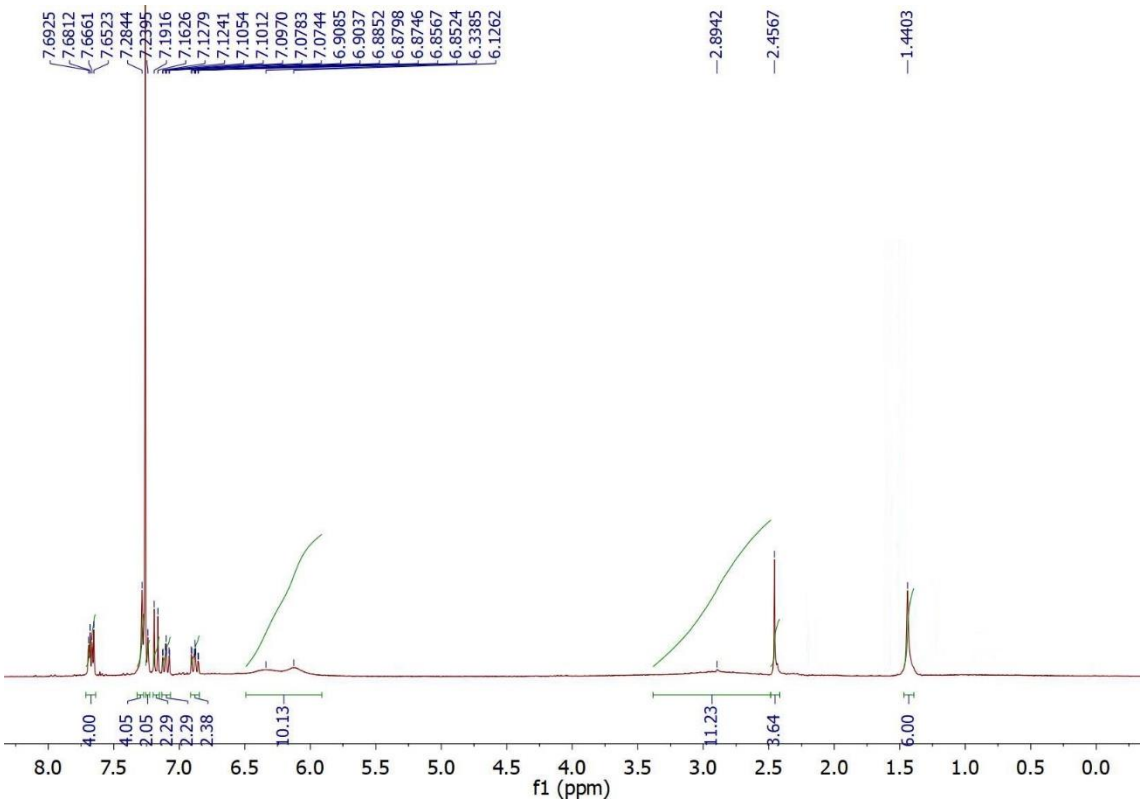
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of 4



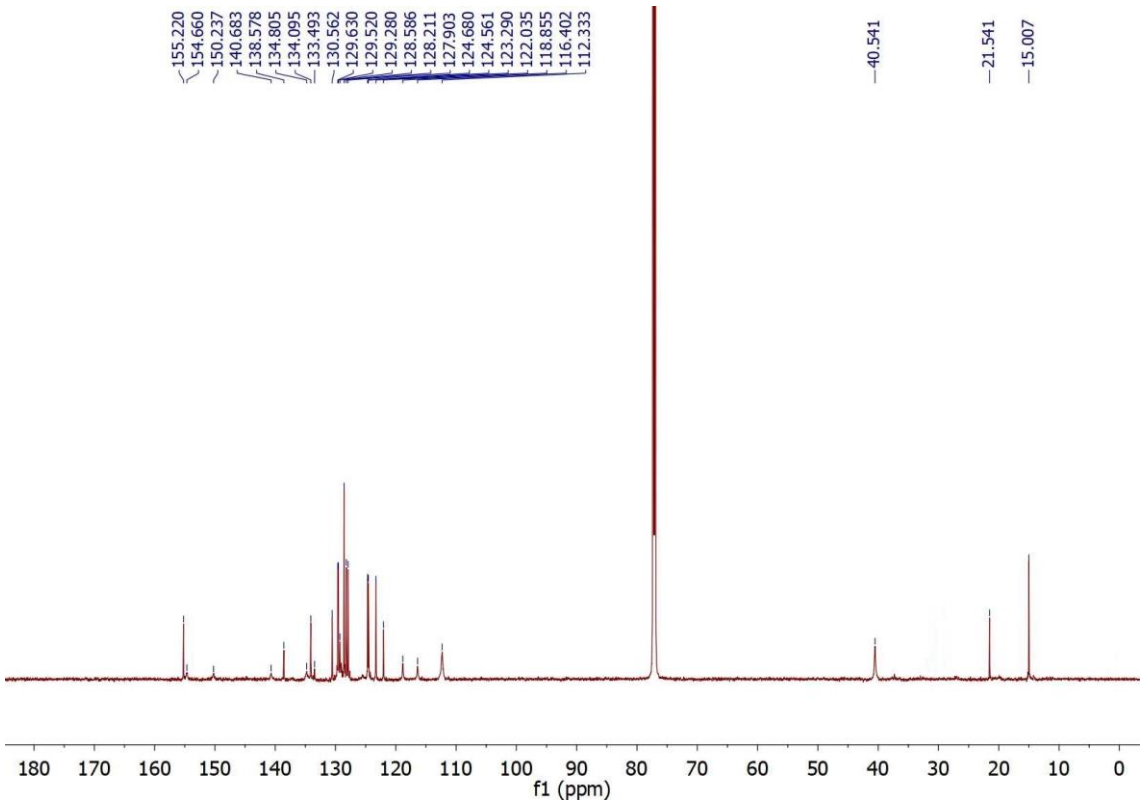
^{13}C NMR ($CDCl_3$, 176 MHz) spectrum of 4



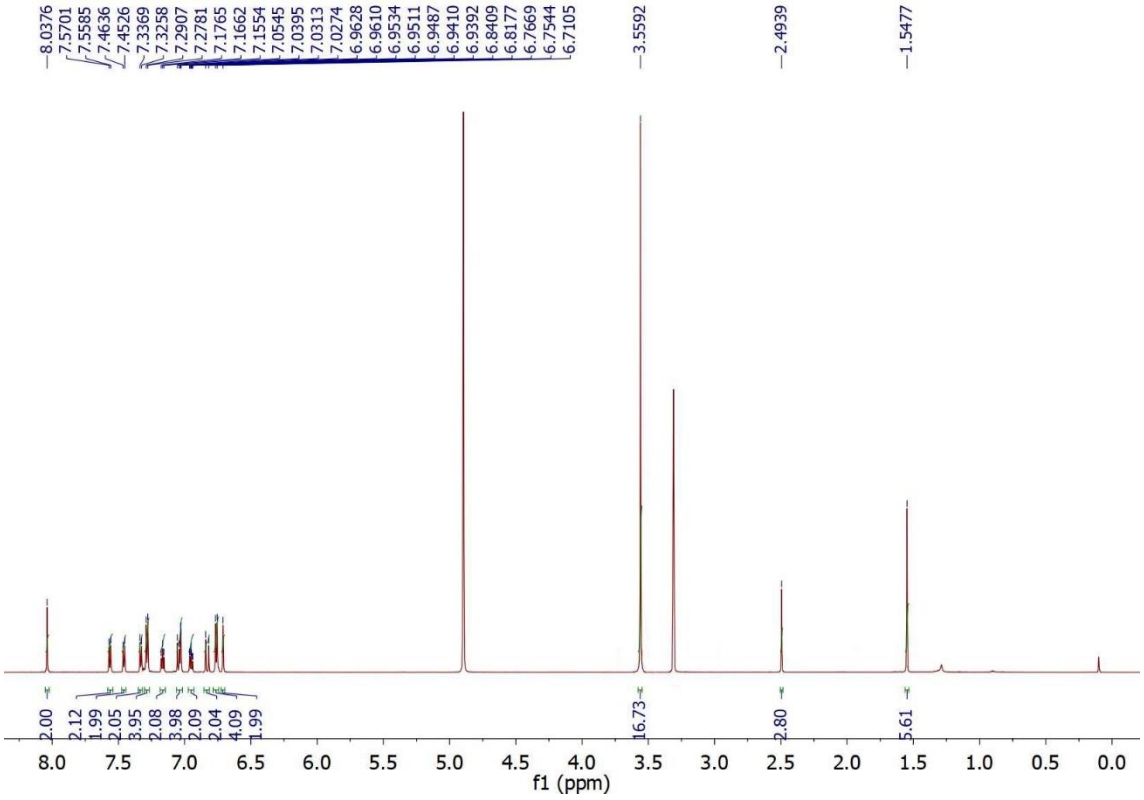
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of 5



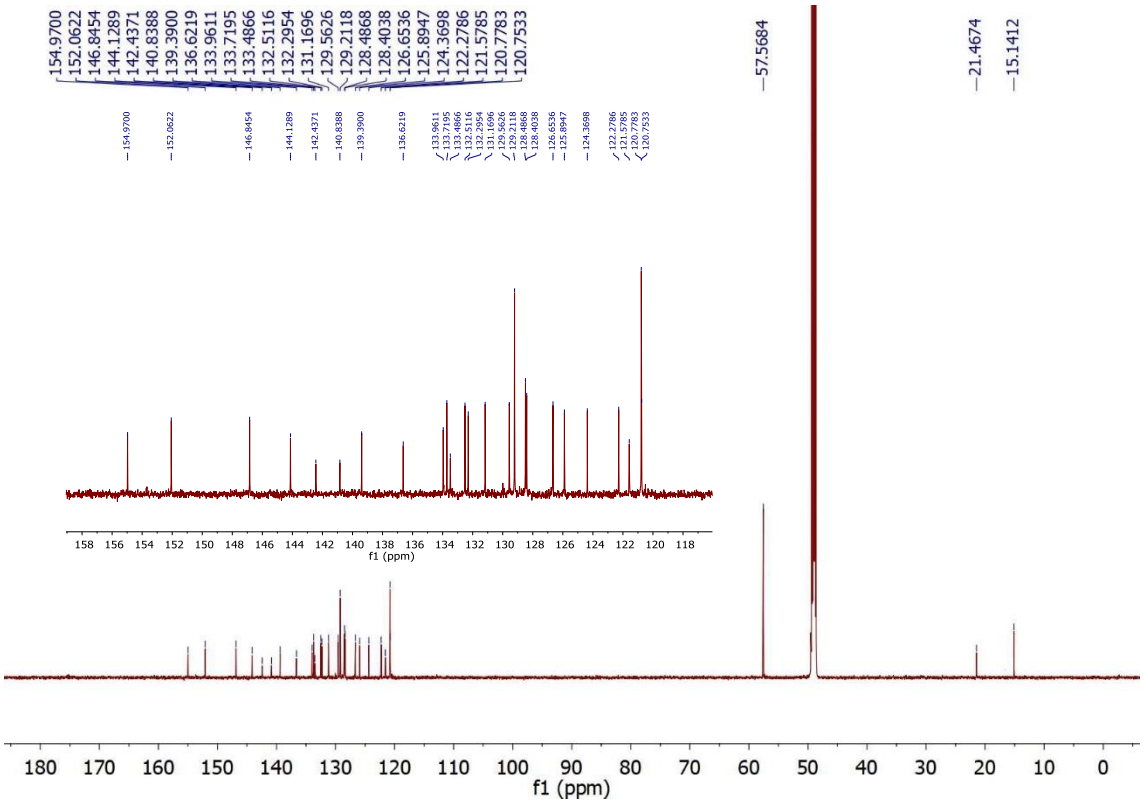
^{13}C NMR ($CDCl_3$, 176 MHz, 50 ºC) spectrum of 5



^{1}H NMR (CD_3OD, 700) spectrum of 6



^{13}C NMR (CD_3OD, 176) spectrum of 6



4. Photophysical properties

Table S1. Fluorescence signatures of BODIPYs **2**-**6** in different selected solvents allowing comparisons.

	Solvent	λ_{ab} [a] (nm)	$\varepsilon_{max}\times10^{-4}$ [b] (M^{-1} cm^{-1})	λ_F [c] (nm)	ϕ_F [d]
2 [e]	$CHCl_3$	652.0	7.4	678.0	0.69
3	$CHCl_3$	695.0	8.1	740.0	0.40
4	cyclohexane	704.0	6.8	720.9	0.46
	$CHCl_3$	701.0	8.1	742.0	0.38
	EtOH	698.0	6.1	758.5	0.15
	CH_3CN	704.0	7.5	773.5	0.12
5	$CHCl_3$	699.0	4.3	747.5	0.24
6	EtOH	629.0	3.7	648.0	0.40
	EtOH/H_2O (1:9 v/v)	627.0	1.7	644.0	0.15
	H_2O	633.0	1.1	646.0	0.07

[a]Absorption wavelength. [b]Molar absorption. [c]Fluorescence wavelength. [d]Fluorescence quantum yield. [e]Data from ref. 6.

Table S2. Chiroptical signatures of BINOLated BODIPYs **2**-**5** in chloroform, and BINOLated BODIPY **6** in water. Chiroptical signatures of ent-**4** and ent-**6** are almost similar to those exhibited by **4** and **6** respectively, in the same experimental conditions.

	Solvent	$[\alpha]_D^{20}$ [a]	$g_{abs}\times10^3$ [b]	$g_{lum}\times10^3$ [c]	B_{CPL} [d] ($M^{-1}cm^{-1}$)
2 [e]	$CHCl_3$	+14333 (*c* 0.0008)	–1.3 (656 nm)	–0.6 (741 nm)	15
4	$CHCl_3$	+18034 (*c* 0.0036)	–2.5 (707 nm)	+1.6 (780 nm) –0.6 (810 nm)	25
5	$CHCl_3$	+20023 (*c* 0.0029)	–1.4 (700 nm)	+0.9 (780 nm) –1.0 (810 nm)	5
6	H_2O	+2242 (*c* 0.0034)	–3.3 (629 nm)	+1.5 (660 nm) –1.0 (700 nm)	1

[a]Specific optical rotation (*c* within parentheses). [b]Maximum absorbance dissymmetry ratio (wavelength within parentheses). [c]Maximun luminescence dissymmetry factor (wavelength within parentheses). [d]Zinna´s CPL brightness ($B_{CPL} = \varepsilon\cdot\phi_F\cdot|g_{lum}|/2$; see ref. 7) was estimated from the dated maximum g_{lum} values and the referable ϕ_F and ε from Table S1). [e]Data from ref. 6.

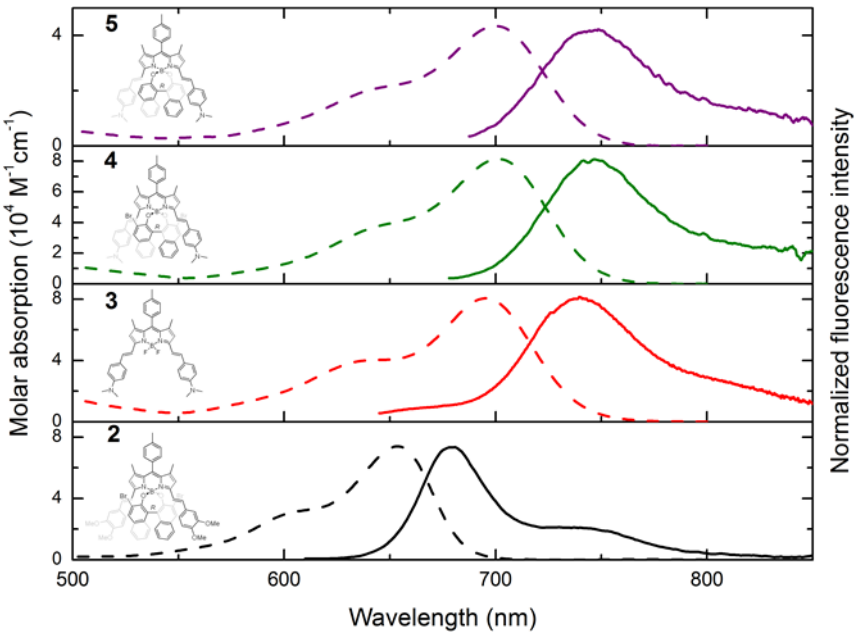


Figure S2. Visible absorption (dashed lines) and normalized fluorescence (solid lines) spectra of aminostyryl-based BODIPYs **3**-**5** in diluted solutions of chloroform. The corresponding spectra of the 3,3´-dibromoBINOLated analogue with dimethoxystyryl groups (**2**) are included for comparison.

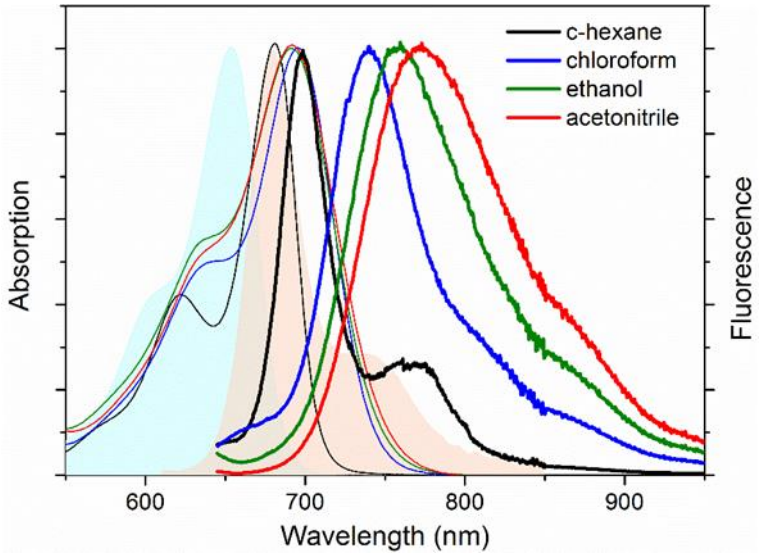


Figure S3. Normalized visible absorption (thin lines) and fluorescence (thick lines) spectra of aminostyryl-based BODIPY **4** in different solvents. Spectra of related dimethoxystyryl-based **2** in chloroform (coloured) are included for comparison.

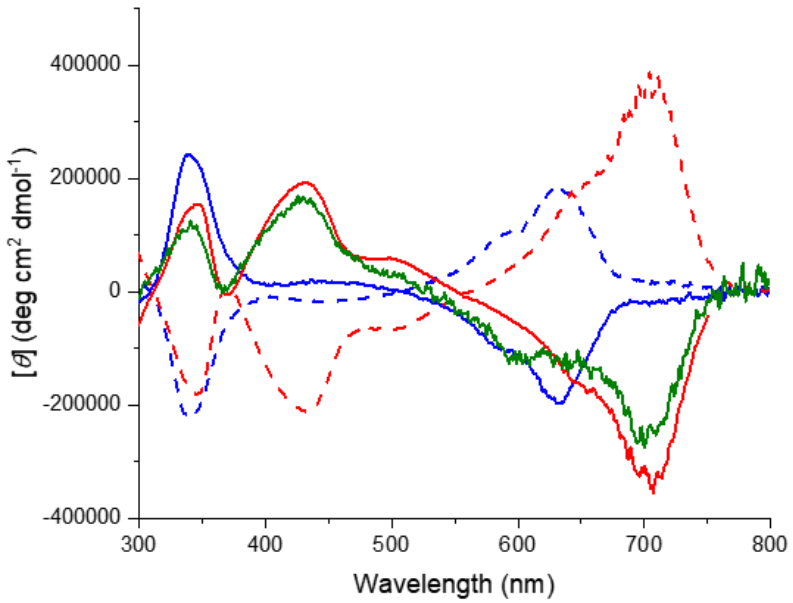


Figure S4. ECD spectra recorded from **4** (red), ent-**4** (red; dashed) and **5** (green) in chloroform, and from **6** (blue) and ent-**6** (blue; dashed) in water. Concentration *ca*. 3.5×10^{-6} M, instead of 3.5×10^{-5} M, was used for recording the spectrum of **5**.

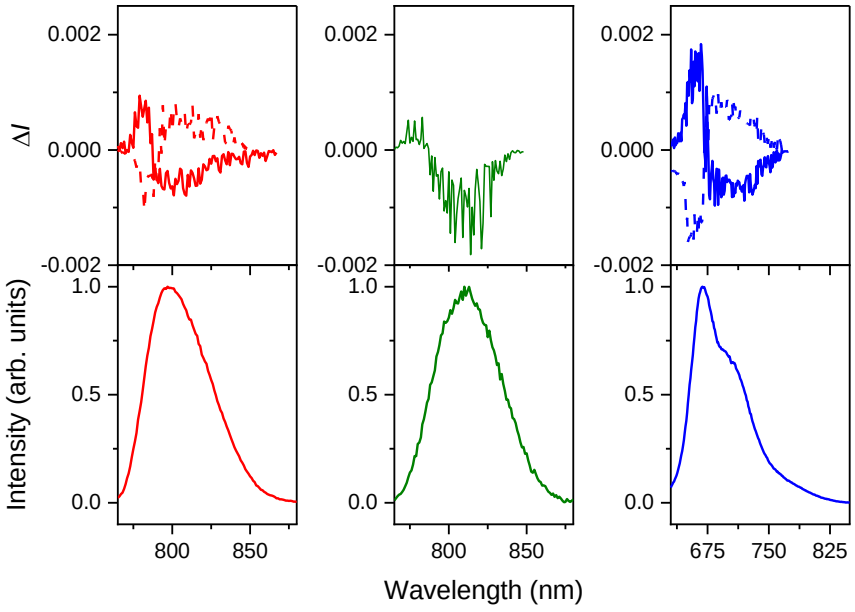


Figure S5. Visible CPL (top) and total luminescence spectra (down) recorded from **4** (red), ent-**4** (red, dashed) and **5** (green) in chloroform, and from **6** (blue) and ent-**6** (blue, dashed) in water (*ca.* 1.0×10^{-3} M).

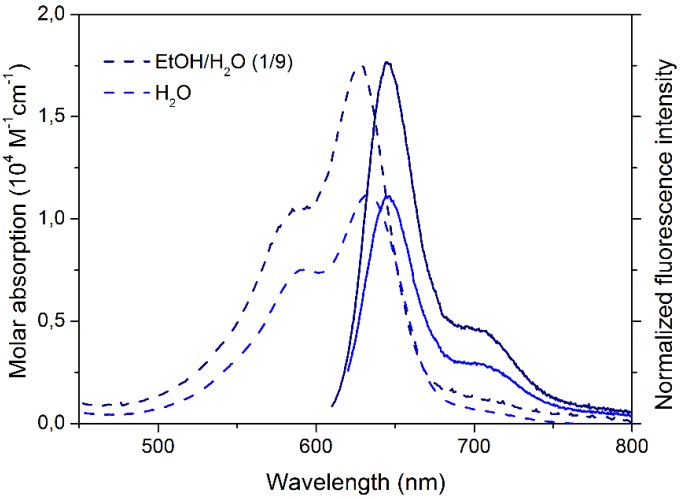


Figure S6. Visible absorption (dashed lines) and normalized fluorescence (solid lines) spectra of water-soluble BINOLated BODIPY **6** in diluted solutions of water and water-rich aqueous ethanol (ethanol 10% v/v).

5. References

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