Supporting Information

Mechano-responsive circularly polarized luminescence of organic solid-state chiral emitters

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I.   Syntheses

All reagents were purchased from Sigma Aldrich Chemical Co. and Alfa Aesar, depending on the supply availability, and used without further purification. Anhydrous solvents were dried and purified by passage through aluminum columns. All reactions were monitored by thin-layer chromatography (TLC) using E Merck TCL silica gel 60 F_{254}, thickness 0.2 nm, and visualized under UV 254 nm and/or 365 nm. ^1H, ^{13}C, ^{19}F, ^{11}B NMR spectra were recorded on a JEOL JMS ECS 400 MHz spectrometer (100 MHz for ^{13}C, 376.2 MHz for ^{19}F and 128.2 MHz for

^{11}B). The reference used for ^{11}B and ^{19}F NMR was a solution of BF_3OEt_2 15% in $CDCl_3$

contained in a coaxial insert, with the reference peak at 0 ppm for ^{11}B and -155 ppm for ^{19}F. High resolution mass spectroscopy was performed at the CNRS Imagif platform. Melting points were measured with a Stuart apparatus SMP10. Optical rotations were performed on a Jasco P-1010 polarimeter at 589 nm and 22°C using a 700-μL cell with a path length of 1 dm.

The synthesis of compounds **3** and **4** has already been previously reported.[1]

I.1 Synthetic procedures

*General procedure **A**: synthesis of the amide derivatives*

The acid derivative **4** (1.0 eq) and PyBOP (1.7 eq) were added in a flame-dried schlenk flask and under inert atmosphere. They were dissolved in dry DMF (C = 0.2 mol/L), the medium was cooled down to 0°C and Et_3N (3.0 eq) was added followed by the addition of the amine (1.5 eq) and the mixture was stirred at 13°C for 24 hours. The medium was then diluted with water and extracted with EtOAc. The organic moieties were washed with 5% $KHSO_4$ and brine then dried over $MgSO_4$ and evaporated under vacuum. The crude product was purified by column chromatography on silica gel to afford the desired product.

*General procedure **B**: chelation procedure*

Boron trifluorate diethyl etherate (1.1 eq) was added to a solution of diketone (1.0 eq) in anhydrous CH_2Cl_2 (C = 0.12 mol/L) under argon. The mixture was refluxed overnight; the solvent was removed *in vacuo.* The crude product was purified by column chromatography on silica gel to afford the desired product.
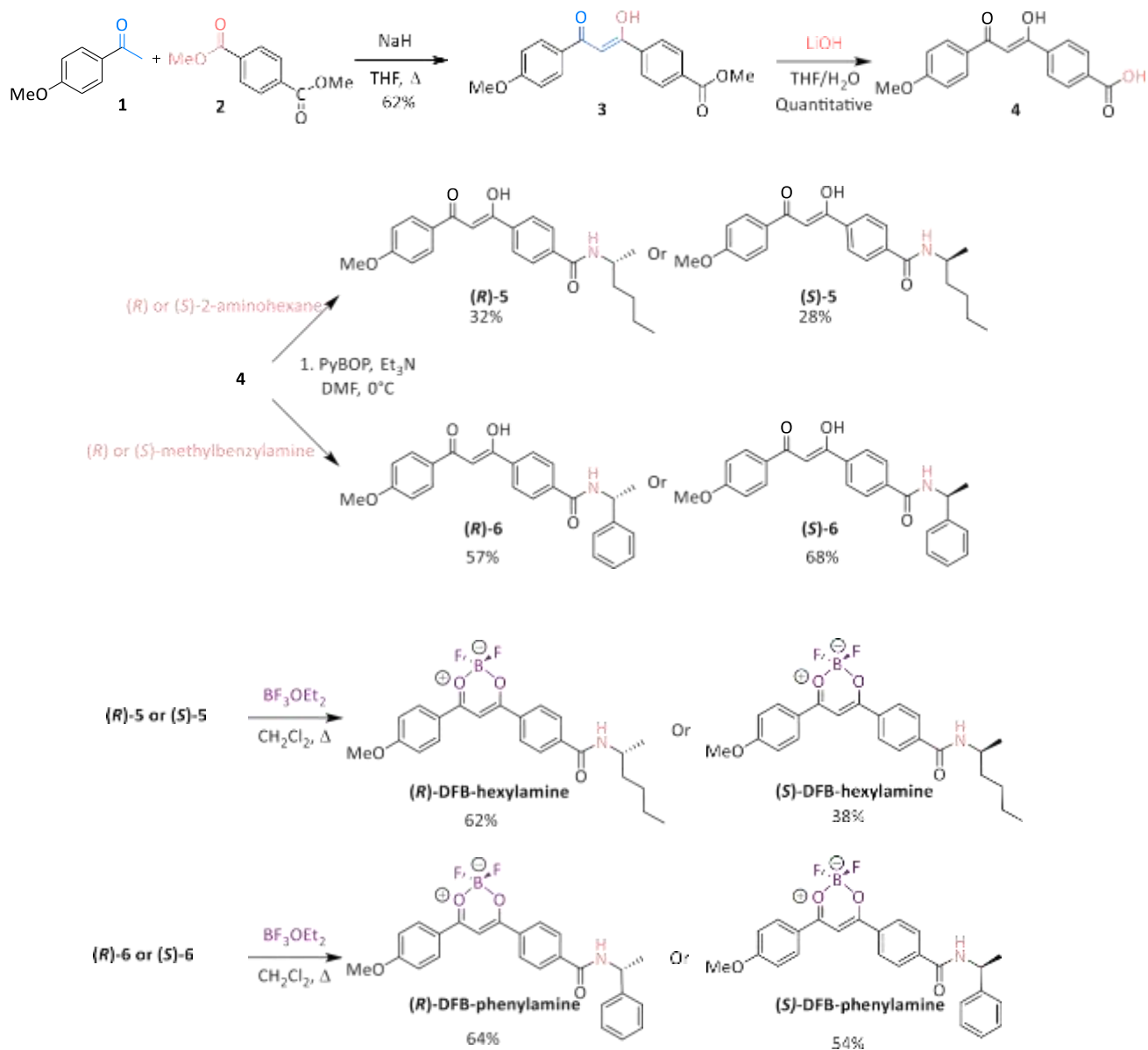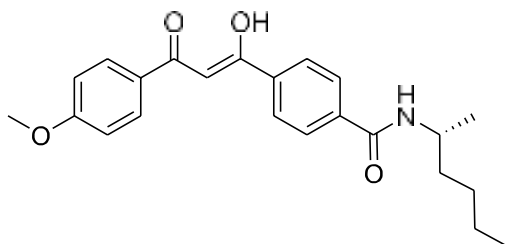
Figure S1: Synthetic route followed for the synthesis of (*R/S*)-DFB-Hex-amide and (*R/S*)-DFB-PhEt-amide derivatives

(R, Z)-N-(hexan-2-yl)-4-(1-hydroxy)-3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)benzamide).
(R)-5

Chemical formula: $C_{23}H_{27}NO_4$

Molecular weight: 381.47 g·mol^{-1}

       Compound **(R)-5** was synthesized following general procedure **A** from compound **4** (0.50 g, 1.7 mmol, 1.0 eq), PyBOP (1.50 g, 2.8 mmol, 1.7 eq), Et$_3$N (0.70 mL, 5.0 mmol, 3.0 eq) and (*R*)-2-aminohexane (0.40 mL, 2.5 mmol, 1.5 eq). The crude product was purified by column chromatography on silica gel (50/50 Petroleum Ether / EtOAc). The product was obtained as a lightly beige solid. (200 mg, 0.52 mmol, 32% yield).
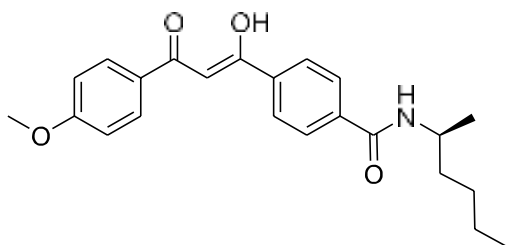The chiral amine (*R*)-2-aminohexane was purchased from Alfa Aesar.

R$_f$ (50/50 Petroleum Ether/EtOAc) = 0.82

NMR (^{1}H, 400MHz, d6-acetone) = δ (ppm) 17.33 (s, 1H); 8.16 (m, 4H); 7.99 (d, J = 8.4 Hz, 2H); 7.61 (d, J = 6.4 Hz, 1H, NH); 7.23 (s, 1H); 7.07 (d, J = 8.4Hz, 2H); 4.15 (m, 1H); 3.90 (s, 3H); 1.56 (m, 2H); 1.34 (m, 4H); 1.20 (d, J = 6.8Hz, 3H); 0.86 (t, 3H).

NMR (^{13}C, 100MHz, CDCl$_3$) = δ (ppm) 187.1; 182.3; 166.1; 163.6; 138.15; 138.11; 129.6 (2C); 128.2; 127.3; 114.2; 93.0; 56.7; 46.2; 36.9; 28.4; 23.7; 21.2; 14.3

HRMS (TOF MS ES+) = $C_{23}H_{28}NO_4$ [M+H] $^+$: m/z = 382.2026 (Calculated 382.2018)

(S, Z)-N-(hexan-2-yl)-4-(1-hydroxy)-3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)benzamide)
(S)-5

Chemical formula: $C_{23}H_{27}NO_4$

Molecular weight: 381.47 g·mol^{-1}

Compound **(S)-5** was synthesized following general procedure **A** from compound **4** (0.33 g, 1.1 mmol, 1.0 eq), PyBOP (0.98 g, 1.9 mmol, 1.7 eq), Et$_3$N (0.47 mL, 3.3 mmol, 3.0 eq) and (*S*)-2-aminohexane (0.22 mL, 1.6 mmol, 1.5 eq). The crude product was purified by column

chromatography on silica gel (50/50 Petroleum Ether / EtOAc). The product was obtained as a lightly beige solid. (120 mg, 0.31 mmol, 28% yield).

The chiral amine (*S*)-2aminohexane was purchased from Sigma Aldrich.

R$_f$ (50/50 Petroleum Ether/EtOAc) = 0.82

NMR (^{1}H, 400MHz, d6-acetone) = δ (ppm) 17.33 (s, 1H); 8.16 (m, 4H); 7.99 (d, *J* = 8.4 Hz, 2H); 7.61 (d, *J* = 6.4 Hz, 1H, NH); 7.23 (s, 1H); 7.07 (d, *J* = 8.4 Hz, 2H); 4.15 (m, 1H); 3.90 (s, 3H); 1.56 (m, 2H); 1.34 (m, 4H); 1.20 (d, *J* = 6.8Hz, 3H); 0.86 (m, 3H).

NMR (^{13}C, 100MHz, CDCl$_3$) = δ (ppm) 187.1; 182.3; 166.1; 163.6; 138.15; 138.11; 129.6 (2C); 128.2; 127.3; 114.2; 93.0; 56.7; 46.2; 36.9; 28.4; 23.7; 21.2; 14.3

HRMS (TOF MS ES+) = C$_{23}$H$_{28}$NO$_4$ [M+H] $^+$: m/z = 382.2024 (Calculated 382.2018)

(R,Z)-N-(1-phenylethyl)-4-(1-hydroxy-3(4-methoxyphenyl)-3-oxoprop-1-en-1-yl) benzamide. (R)-6
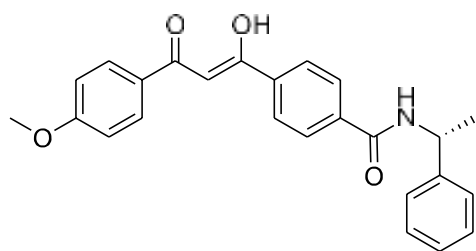
Chemical formula: C$_{25}$H$_{23}$NO$_4$

Molecular weight: 381.47 g·mol^{-1}

Compound (*R*)-6 was synthesized following general procedure **A** from compound **4** (0.50 g, 1.70 mmol, 1.0 eq), PyBOP (1.48 g, 2.9 mmol, 1.7 eq), Et$_3$N (0.70 mL, 5.0 mmol, 3.0 eq) and (*R*)-methylbenzylamine (0.33 mL, 2.50 mmol, 1.5 eq). The crude product was purified by column chromatography on silica gel (50/50 Petroleum Ether / EtOAc). The product was obtained as a lightly beige solid (360 mg, 0.96 mmol, 57% yield).
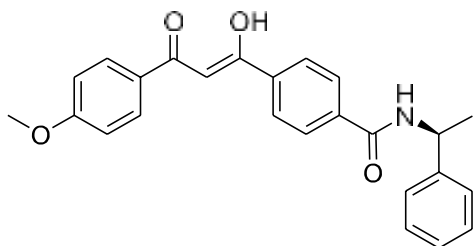
R$_f$ (50/50 Petroleum Ether/EtOAc) = 0.75

NMR (^{1}H, 400MHz, CDCl$_3$) = δ (ppm) 16.91 (s, 1H); 8.00 (m, 4H); 7.86 (d, *J* = 8.4 Hz, 2H); 7.39 (m, 4H); 7.30 (m, 1H); 6.99 (d, *J* = 8.8 Hz, 2H); 6.81 (s, 1H); 6.36 (d, *J* = 6.8 Hz, 1H, NH); 5.36 (m, 1H); 3.90 (s, 3H); 1.64 (d, *J* = 6.8 Hz, 3H).

NMR (^{13}C, 100MHz, CDCl$_3$) = δ (ppm) 187.1; 182.1; 165.8; 163.6; 142.9; 138.3; 137.6; 129.6; 129.0; 128.2; 127.8; 127.4; 127.3; 126.4; 114.2; 93.0; 55.6; 49.6; 21.8

HRMS (TOF MS ES+) = C$_{25}$H$_{24}$NO$_4$ [M+H] $^+$: m/z = 402.1702 (Calculated 402.1705)

(S,Z)-N-(hexan-2-yl)-4-(1-hydroxy-3(4-methoxyphenyl)-3-oxoprop-1-en-1-yl) benzamide.
(S)-6

Chemical formula: $C_{25}H_{23}NO_4$

Molecular weight: $401.46\ g \cdot mol^{-1}$

Compound **(S)-6** was synthesized following general procedure **A** from compound **4** (0.33 g, 1.1 mmol, 1 eq), PyBOP (0.97 g, 1.8 mmol, 1.70 eq), Et_3N (0.46 ml, 3.3 mmol, 3 eq) and (S)-methylbenzylamine (0.21 mL, 1.6 mmol, 1.5 eq). The crude product was purified by column chromatography on silica gel (50/50 petroleum ether / EtOAc). The product was obtained as a lightly beige solid (300 mg, 0.74 mmol, 68% yield).

R_f **(50/50 Petroleum Ether/EtOAc)** = 0.75

NMR (^{1}H, 400MHz, CDCl$_3$) = δ (ppm) 16.91 (s, 1H); 8.00 (m, 4H); 7.86 (d, J = 8.4 Hz, 2H); 7.39 (m, 4H); 7.30 (m, 1H); 6.99 (d, J = 8.8 Hz, 2H); 6.81 (s, 1H); 6.36 (d, J = 6.8 Hz, 1H, NH); 5.36 (m, 1H); 3.90 (s, 3H); 1.64 (d, J = 6.8 Hz, 3H).

NMR (^{13}C, 100MHz, CDCl$_3$) = δ (ppm) 187.1; 182.1; 165.8; 163.6; 142.9; 138.3; 137.6; 129.6; 129.0; 128.2; 127.8; 127.4; 127.3; 126.4; 114.2; 93.0; 55.6; 49.6; 21.8

HRMS (TOF MS ES+) = $C_{25}H_{24}NO_4$ [M+H] $^+$: m/z = 402.1699 (Calculated 402.1705)

(R)-4-(2, 2-difluoro-6-(4-methoxyphenyl)-2H-1 λ_3,3,2 λ_4,-dioxaborinin-4-yl)-N-(hexan-2-yl)benzamide. **((R)-DFB-Hex-amide)**
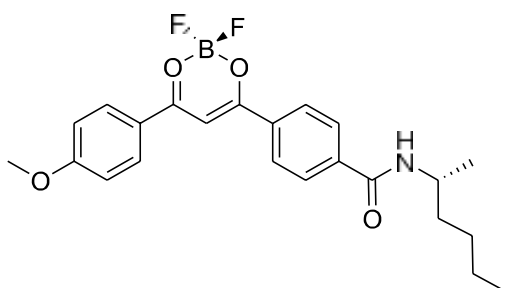
Chemical formula: $C_{23}H_{26}NO_4BF_2$

Molecular weight: $429.27 g.mol^{-1}$

(R)-DFB-Hex-amide was synthesized following procedure **B** from compound **(R)-5** (0.18 g, 0.47 mmol, 1.0 eq) and BF_3OEt_2 (0.064 mL, 0.52 mmol, 1.1 eq). The crude product was purified by column chromatography (CH_2Cl_2 then 98/2 CH_2Cl_2/EtOAc). The product was isolated as a yellow solid (125 mg, 0.29 mmol, 62%).

Rf (30/70 Petroleum Ether/EtOAc) = 0.64

NMR (^{1}H, 400MHz, CDCl$_3$): δ (ppm) 8.16 (m, 4H); 7.88 (d, $J=8.8$Hz, 2H); 7.12 (s, 1H); 7.04 (d, $J=8.8$Hz, 2H); 5.96 (d, $J=8.4$Hz, 1H, NH); 4.21 (m, 1H); 3.94 (s, 3H); 1.58 (m, 2H); 1.37 (m, 4H); 1.27 (d, $J=6.4$Hz, 3H); 0.91 (t, 3H).

NMR (^{13}C, 100MHz, CDCl$_3$): δ (ppm) 183.0; 180.0; 166.3; 165.5; 140.3; 134.8; 132.1; 128.8; 127.6; 124.0; 114.9; 93.1; 56.0; 46.3; 36.8; 28.4; 22.7; 21.1; 14.1.
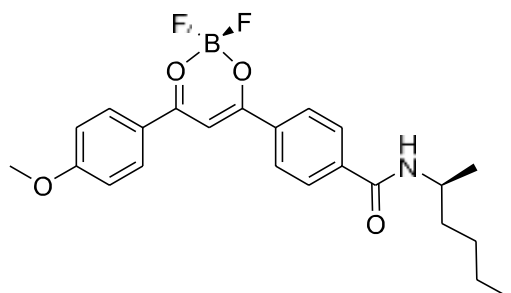
NMR (^{11}B, 128.2MHz, CDCl$_3$): -1.36 (s)

NMR (^{19}F, 376.3MHz, CDCl$_3$): -142.12 (s); -142.06 (s)

HRMS (TOF MS ES+) = $C_{23}H_{27}BF_2NO_4$ [M+H]$^+$: m/z = 430.1992 (Calculated 430.2001)

mp: 181°C

$[\square]_{\square}^{\square\square}$ = -20° ($c = 0.1$, CH$_2$Cl$_2$)

(S)-4-(2, 2-difluoro-6-(4-methoxyphenyl)-2H-1$^3\lambda$,3,2$^4\lambda$-dioxaborinin-4-yl)-N-(hexan-2-yl)benzamide. ((S)-DFB-Hex-amide)

Chemical formula: $C_{23}H_{26}NO_4BF_2$

Molecular weight: 429.27 g.mol^{-1}

(S)-DFB-Hex-amide was synthesized following procedure **B** from compound **(S)-5** (0.10 g, 0.26 mmol, 1.0 eq) and BF$_3$OEt$_2$ (0.04 mL, 0.29 mmol, 1.1 eq). The crude product was purified by column chromatography (100 CH$_2$Cl$_2$ then 98/2 CH$_2$Cl$_2$/EtOAc). The product was isolated as a yellow solid (45 mg, 0.10 mmol, 38%).

Rf (30/70 Petroleum Ether/EtOAc) = 0.64

NMR (^{1}H, 400MHz, CDCl$_3$) = δ (ppm) 8.15 (m, 4H); 7.87 (d, $J=8.4$Hz, 2H); 7.12 (s, 1H); 7.03 (d, $J=8.8$Hz, 2H); 6.04 (d, $J=8.0$Hz, 1H, NH); 4.21 (m, 1H); 3.95 (s, 3H); 1.57 (m, 2H); 1.37 (m, 4H); 1.27 (m, 3H); 0.92 (t, 3H).

NMR (^{13}C, 100MHz, CDCl$_3$) = δ (ppm) 182.9; 179.9; 166.2; 165.5; 140.3; 134.6; 132.0; 128.7; 127.5; 124.0; 114.8; 93.0; 55.9; 46.3; 36.7; 28.3; 22.6; 21.0; 14.1.
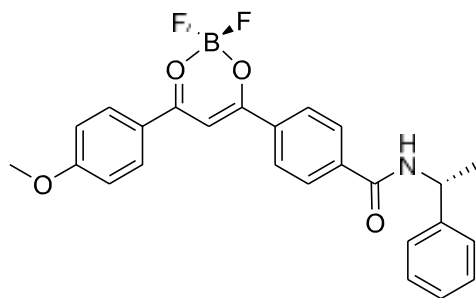
NMR (^{11}B, 128.2MHz, CDCl$_3$) = -1.36 (s)

NMR (^{19}F, 376.3MHz, CDCl$_3$) = -142.12 (s); -142.06 (s)

HRMS (TOF MS ES+) = $C_{23}H_{27}BF_2NO_4$ [M+H]$^+$: m/z = 430.2018 (Calculated 430.2001)

mp = 181°C

$[\alpha]_D^{\square}$ = +20° (c = 0.1, CH_2Cl_2)

(R)-4-(2,2-difluoro-6-(4-methoxyphenyl)-2H-1$_{\lambda^3}$,3,2$_{\lambda^4}$,dioxaborinin-4-yl)-N-(1- phenylethyl)benzamide. (**(R)-DFB-PhEt-amide**)

Chemical formula: $C_{25}H_{22}NO_4BF_2$

Molecular weight: 449.26 g.mol^{-1}

(R)-DFB-PhEt-amide was synthesized following procedure **B** from compound **(R)-6** (0.21 g, 0.55 mmol, 1.0 eq) and BF$_3$OEt$_2$ (0.07 mL, 0.61 mmol, 1.1 eq). The crude product was purified by column chromatography on silica (30/70 Petroleum Ether/EtOAc). The product was isolated as a yellow solid (150 mg, 0.34 mmol, 64% yield).

Rf (30/70 Petroleum Ether/EtOAc) = 0.60

NMR (^{1}H, 400MHz, CDCl$_3$) = δ (ppm) 8.15 (m, 4H); 7.90 (d, J = 8.4 Hz, 2H); 7.40 (m, 4H); 7.30 (m, 1H); 7.11 (s, 1H); 7.03 (d, J = 9.2 Hz, 2H); 6.40 (d, J = 7.6 Hz, 1H, NH); 5.35 (m, 1H); 3.94 (s, 3H); 1.65 (d, J = 7.6 Hz, 3H).

NMR (^{13}C, 100MHz, CDCl$_3$) = δ (ppm) 183.0; 179.8; 166.3; 165.3; 142.8; 139.8; 134.8; 132.8; 129.0; 128.7; 127.8; 127.7; 126.4; 123.9; 114.9; 93.1; 67.2; 56.0; 49.8; 21.8.
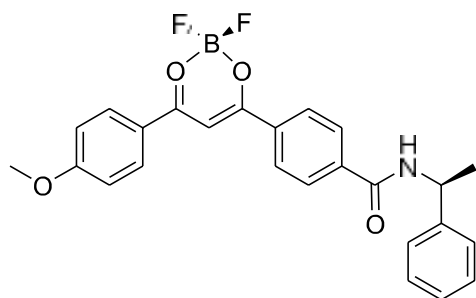
NMR (^{11}B, 128.2MHz, CDCl$_3$) = -1.75 (s)
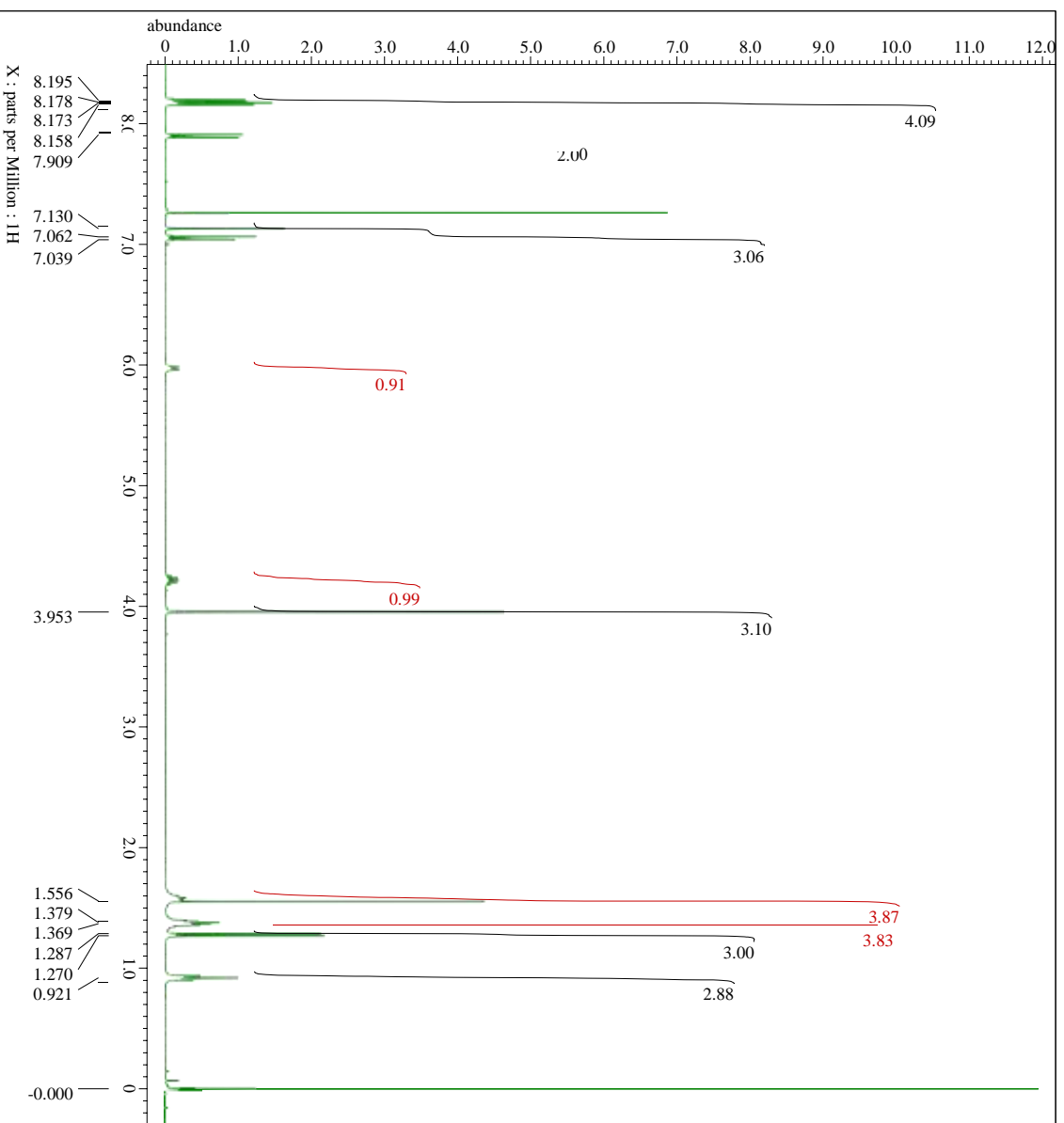
NMR (^{19}F, 376.3MHz, CDCl$_3$) = -141.43 (s); -141.56 (s)

HRMS (TOF MS ES+) = $C_{25}H_{23}BF_2NO_4$ [M+H]$^+$: m/z = 450.1690 (Calculated 450.1688)

mp = 209°C

$[\alpha]_D^{\square}$ = -45° (c = 0.1, CH_2Cl_2)

(S)-4-(2, 2-difluoro-6-(4-methoxyphenyl)-2H-1$_\lambda^3$,3,2$_\lambda^4$,-dioxaborinin-4-yl)-N-(1-phenylethyl)benzamide. ***((S)-DFB-PhEt-amide)***

Chemical formula: $C_{25}H_{22}NO_4BF_2$

Molecular weight: 449.26 g.mol^{-1}

(*S*)-DFB-PhEt-amide was synthesized following procedure **B** from compound **(*S*)-6** (0.20 g, 0.50 mmol, 1.0 eq) and BF$_3$OEt$_2$ (68µL, 0.55 mmol, 1.1eq). The crude was purified by column chromatography (30/70 Petroleum Ether/EtOAc). The product was isolated as a yellow solid (120 mg, 0.27 mmol, 54% yield).

Rf (30/70 Petroleum Ether/EtOAc) = 0.60

NMR (^{1}H, 400MHz, CDCl$_3$) = δ (ppm) 8.14 (m, 4H); 7.88 (d, *J* = 8.4Hz, 2H); 7.40 (m, 4H); 7.30 (m, 1H); 7.10 (s, 1H); 7.02 (d, *J* = 9.2Hz, 2H); 6.46 (d, *J* = 7.2Hz, 1H, NH); 5.35 (m, 1H); 3.94 (s, 3H); 1.64 (d, *J* = 7.2Hz, 3H).

NMR (^{13}C, 100MHz, CDCl$_3$) = δ (ppm) 183.0; 179.8; 166.3; 165.3; 142.8; 139.8; 134.8; 132.8; 129.0; 128.7; 127.8; 127.7; 126.4; 123.9; 114.9; 93.1; 67.2; 56.0; 49.8; 21.8.

NMR (^{11}B, 128.2MHz, CDCl$_3$) = -1.75 (s)

NMR (^{19}F, 376.3MHz, CDCl$_3$) = -141.43 (s); -141.56 (s)

HRMS (TOF MS ES+) = $C_{25}H_{23}BF_2NO_4$ [M+H]$^+$: m/z = 450.1690 (Calculated 450.1688)

mp = 209°C

$[α]_D^{□□}$ = +45° (*c* = 0.1, CH$_2$Cl$_2$)

I.2 NMR spectra

^1H

DFB-Hex-amide

X : parts per Million : 1H

8.195
8.178
8.173
8.158
7.909

7.130
7.062
7.039

3.953

1.556
1.379
1.369
1.287
1.270
0.921

-0.000

abundance

4.09

2.00

3.06

0.91

0.99

3.10

3.87

3.83

3.00

2.88

¹³C

X : parts per Million : 13C
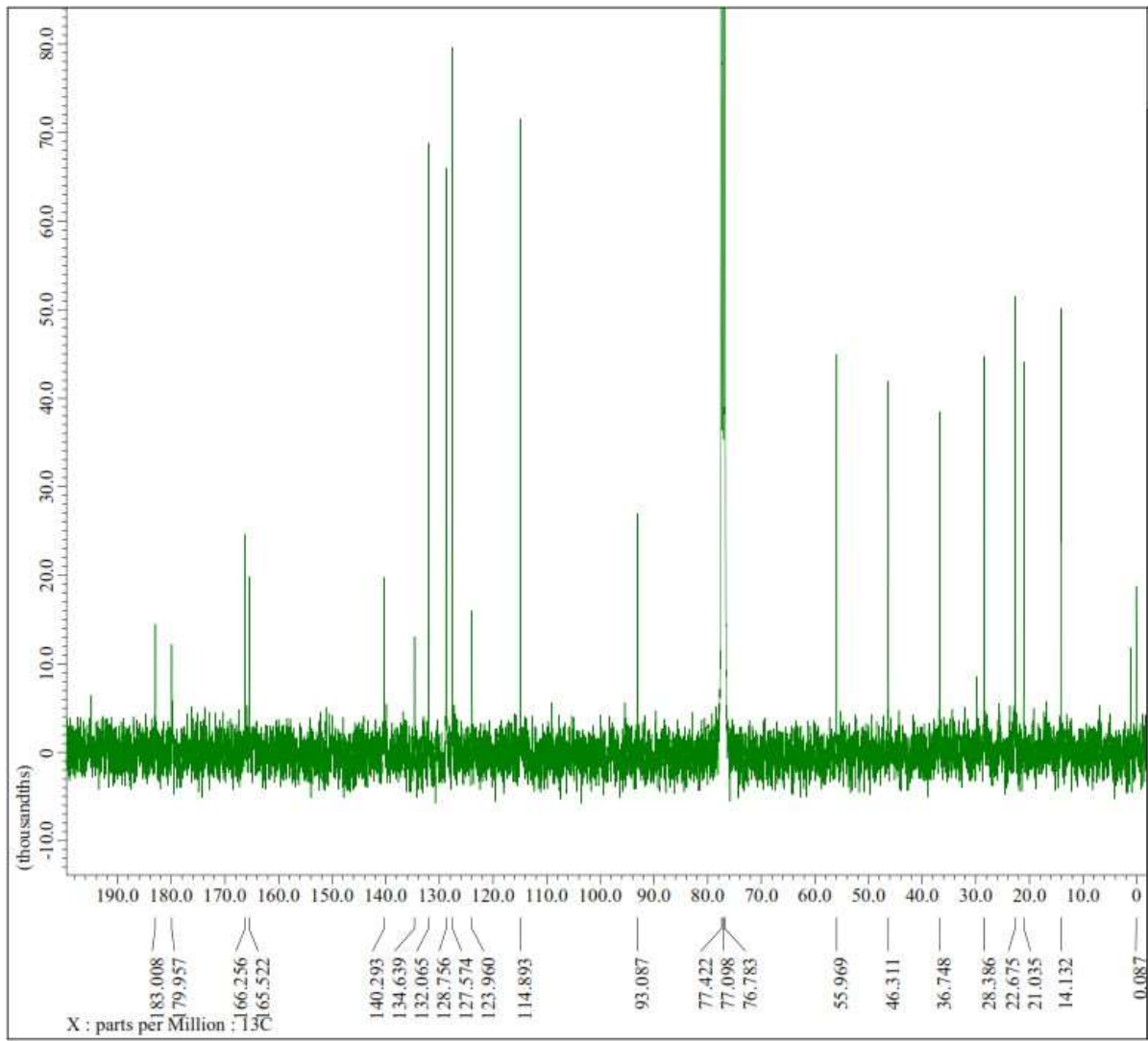
DFB-Ph-Et-amide

^1H

13C
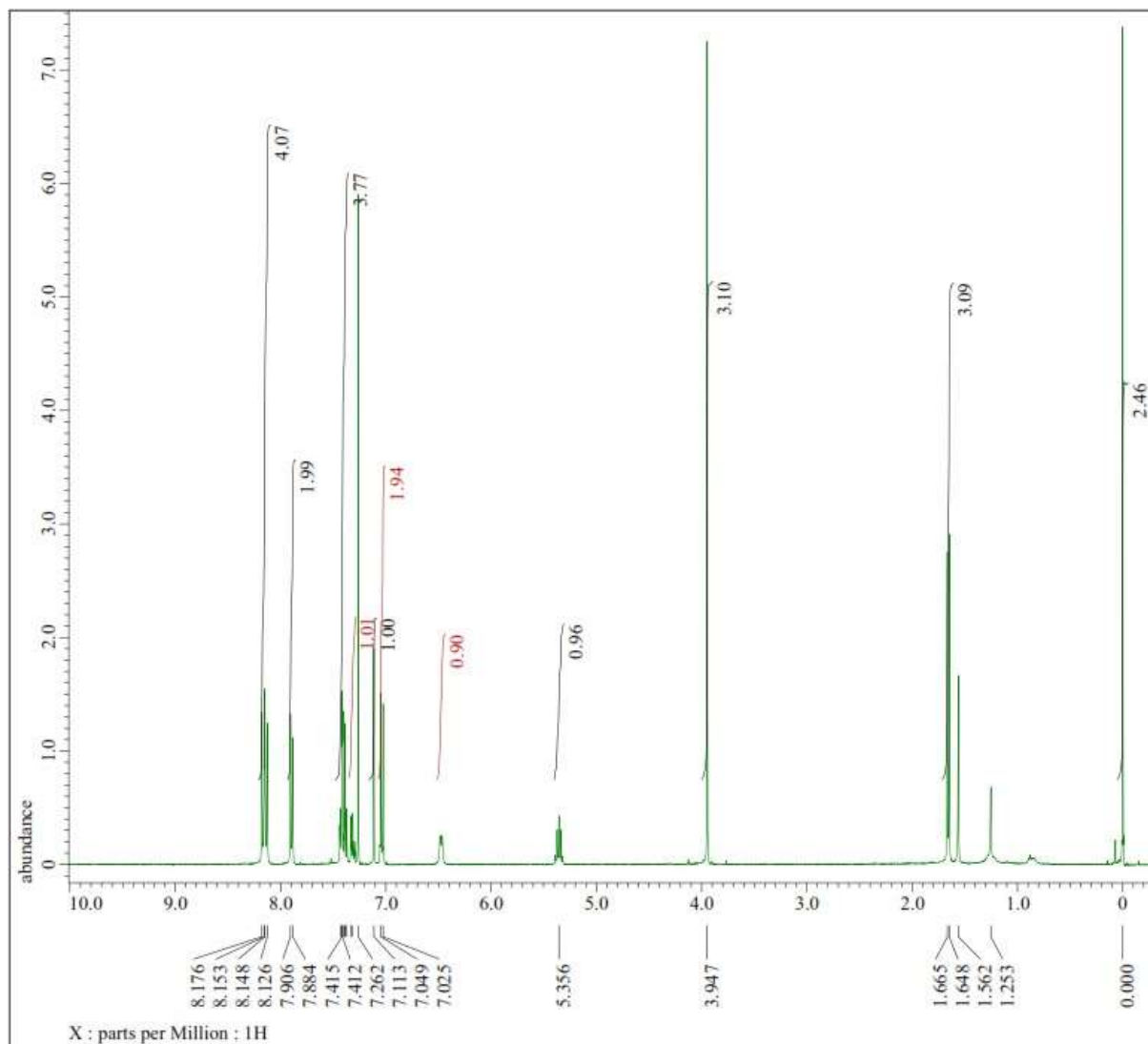
X : parts per Million : 13C
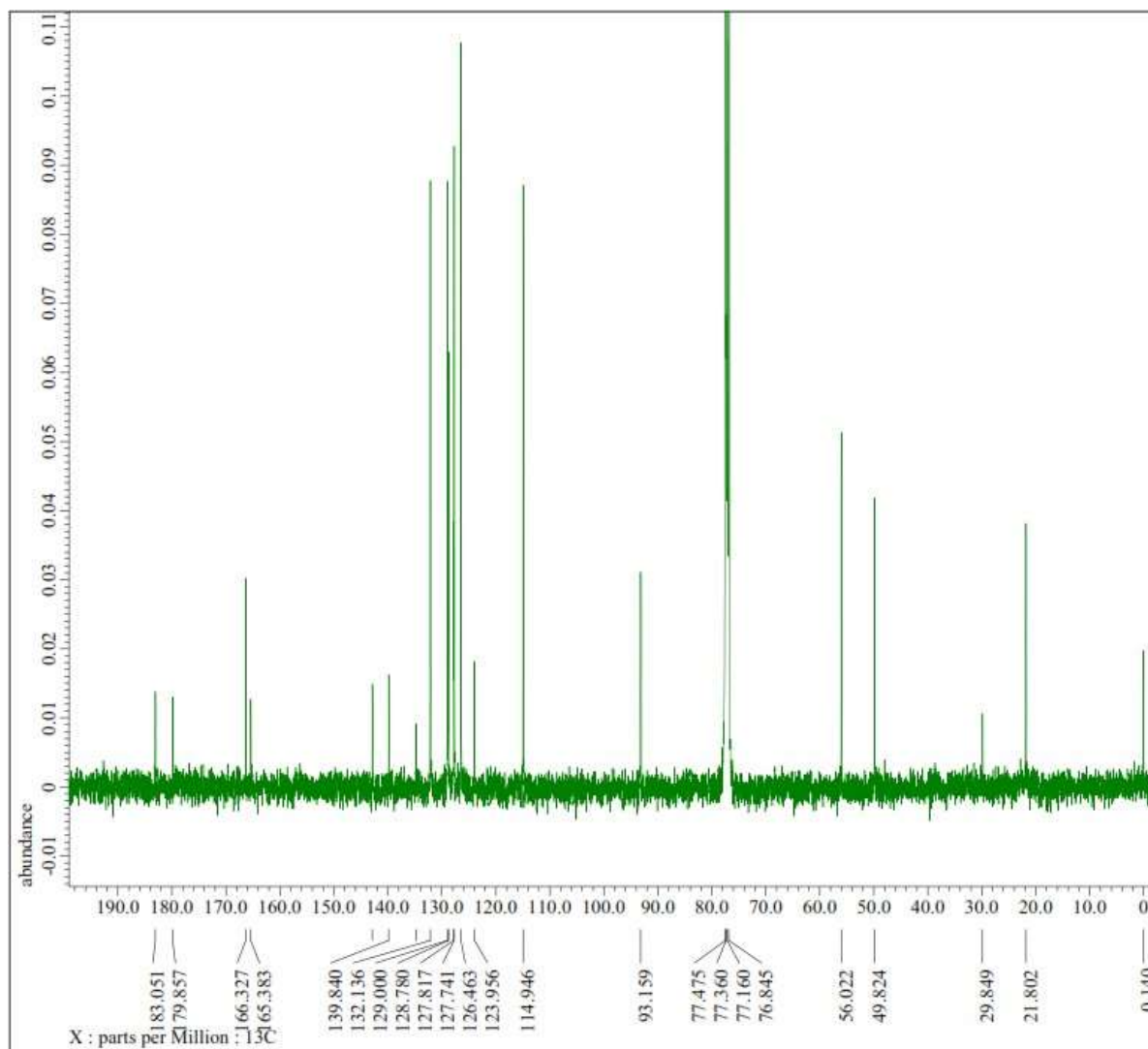
II. Photophysical study and characterizations

II.1. Equipment

Steady-state spectroscopy. The absorption spectra UV/Vis were recorded on double beam spectrometers Cary 100 or Cary 4000 equipped with deuterated/halogen lamps. The emission spectra were recorded on the Horiba Jobin-Yvon spectrofluorometers Fluoromax- FM3 or Fluorolog FL3-221 with xenon light source. Powders and thin films fluorescence quantum yields were obtained by using the integration sphere of the Fluorolog FL3-221 with a Horiba Jobin-Yvon acquisition and analysis software.

Time-resolved fluorescence. Fluorescence decay curves were obtained by the time-correlated single photon counting (TCSPC) method with femtosecond laser excitation composed of a Titanium-Sapphire laser (Tsunami, Spectra-Physics) pumped by a doubled Nd:YVO laser (Millennia Xs, Spectra-Physics). Light pulses at 780 nm from the oscillator were selected by an acousto-optic crystal at a repetition rate of 4 MHz, and then doubled at 390 nm by a nonlinear crystal. Fluorescence photons were detected at 90° through a monochromator and a polarizer at the magic angle by means of a Hamamatsu MCP R3809U photomultiplier, connected to a SPC-630 TCSPC module from Becker &Hickl. The fluorescence data were analyzed using the Globals software package developed at the Laboratory for Fluorescence Dynamics at the University of Illinois at Urbana–Champaign, which includes reconvolution analysis and global nonlinear least-squares minimization method.

CPL measurements: we used a home-build CPL measurement system, which is composed of a 375 nm CW excitation laser (5mW), a photoelastic modulator with 50kHz of modulation frequency, a monochromator (10cm, single grating) and a high speed photomultiplier tube detector with a signal amplifier. The light intensity signal was corrected with a lock-in amplifier and 50kHz Ac component was treated as the ΔI component of CPL. The dissymmetry factor was evaluated based on the ΔI component and the total light intensity, which was evaluated from the DC component of signal after correction with 2ω component for suppressing the linearly polarized light component. Detailed procedure, conditions and mathematical expression have already been discussed in a previous manuscript.[2] As the present optical system is composed of a dichroic mirror, we carried out CPL measurement with the optics based on the illumination and correction on the same direction. We have already reported reliable CPL profiles of samples in colloid, gels and powders on KBr pellet .[3] [4]

II.2 Photophysical studies in solution

Absorption and fluorescence emission in THF solution were compared with those of the achiral parent **DFB-Bu-amide** compound, for which the amide is substituted with a butyl chain.[1] Table S1 shows that all the compounds display blue fluorescence in THF (λ_{max}(em) = 442±1 nm) with high quantum yields (ϕ_F = 0.87±0.07) and monoexponential fluorescence decays (τ = 2.09±0.01 ns).

Compound	λ_{max}(abs) / nm	λ_{max}(em) / nm	ε / L mol^{-1} cm^{-1}[a]	ϕ_F[b]	τ[c]
(*R/S*)-DFB-Hex-amide	390	441	48000	0.80	2.08
(*R/S*)-DFB-PhEt-amide	390	443	47000	0.94	2.09
DFB-Bu-amide	390	442	42800	0.86	2.09

[a] Determined at λ_{max}(abs), [b] with quinine sulphate standard in H_2SO_4 0.5N, [c] λ_{exc} = 390 nm.

Table S1: Photophysical properties in THF solution

II.3 Mechanofluorochromic properties studied on the (R) enantiomers
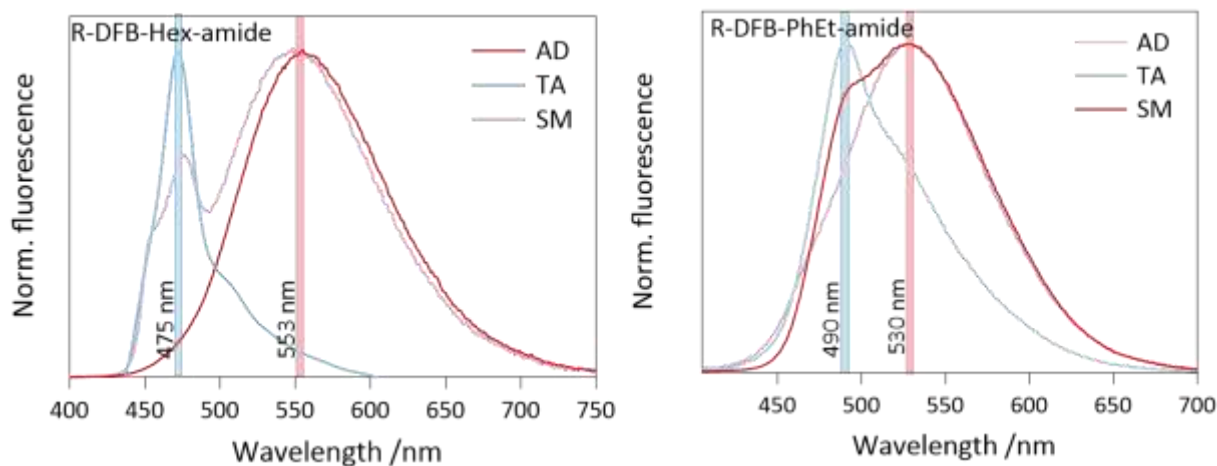
Figure S2: Fluorescence spectra of (*R*)-DFB-Hex-amide (A) and (*R*)-DFB-PhEt-amide (B) after obtention of the thin films (AD), after thermal annealing (TA) and after smearing (SM). λ_{exc}=390 nm.

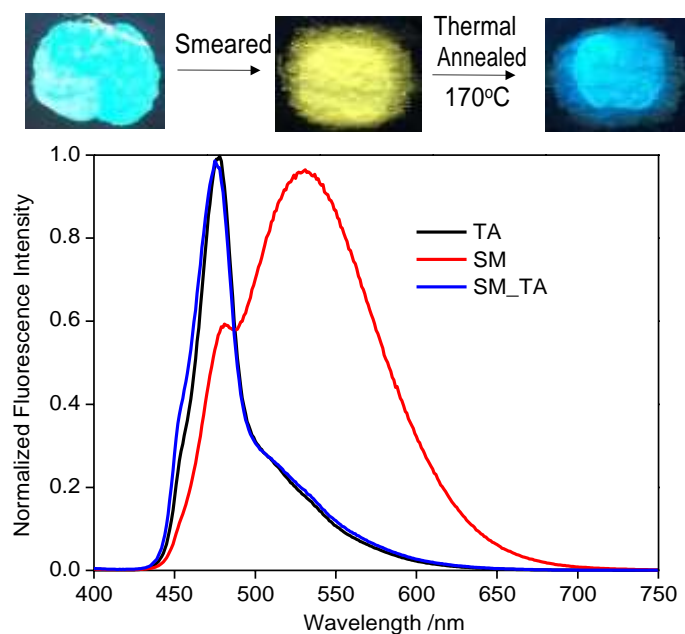## II.4 Reversibility of thermal annealing process

Figure S3: Photographs of emission of TA state of (*R*)-DFB-Hex-amide from SM sample with reversibility under UV illumination (top) and emission spectra of thermally annealed (TA), smeared (SM) and thermally annealed of smeared samples (SM_TA) (bottom).
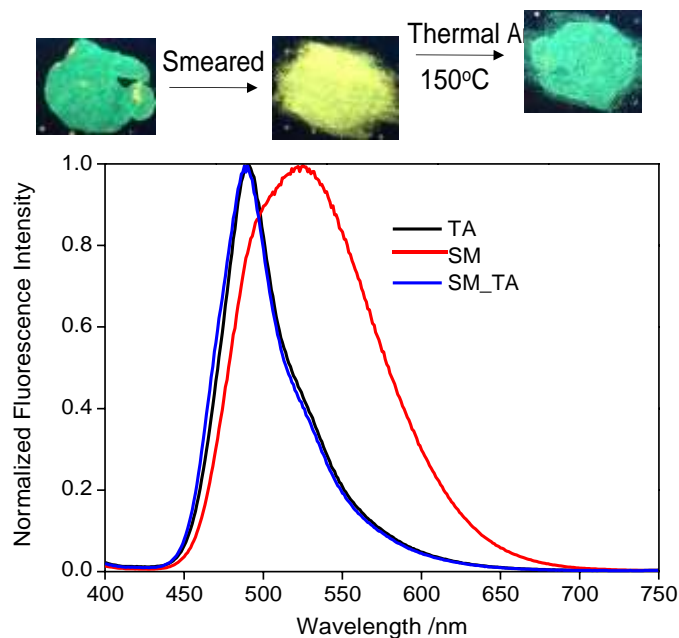

Figure S4: Photographs of emission of TA state of (*R*)-DFB-PhEt-amide from SM sample with reversibility under UV illumination (top) and emission spectra of thermal annealed (TA), smeared (SM) and thermal annealed of Smeared samples (SM_TA) (bottom).

II.5 Stability of the amorphous phases

The stability of the amorphous phases was monitored by fluorescence spectroscopy. For each enantiomer, one spectrum was recorded every 5 minutes after application of mechanical strains for 1 hour.
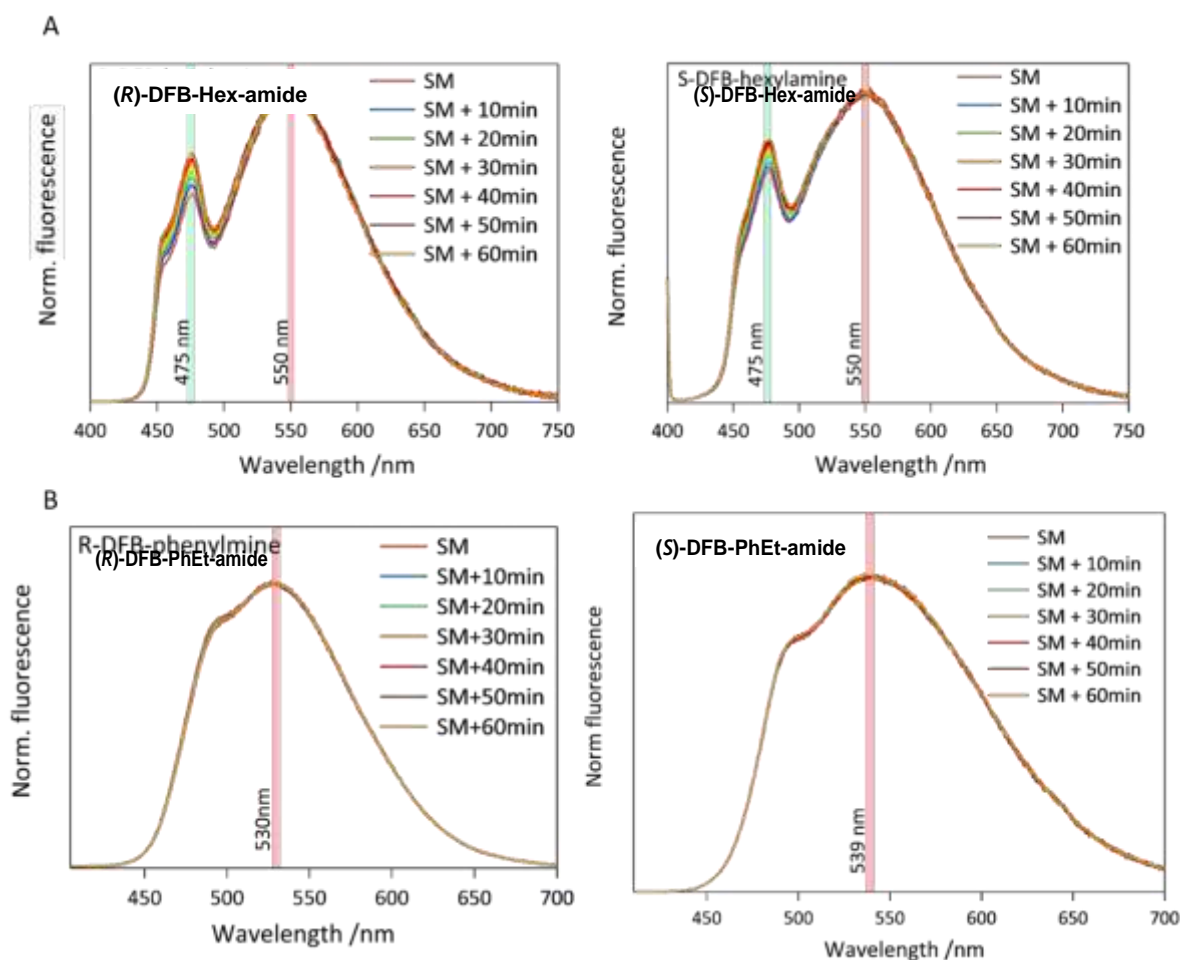
Figure S5: Fluorescence spectra of the amorphous (SM) phase recorded at different times (0min to 60min) after the shearing of the crystalline phase (TA) with the help of a spatula. λ_{exc}=390 nm.

II.6 Samples preparation for CPL measurement

0.1 M conc. of the sample in chloroform was deposited on the paper (Medical paper white paraffin light soy, http://www.monotaro.sg/g/01297128/) as a thin film and allowed it to dry to obtain thin film by slow evaporation. Thermal treatment was done in a preheated oven. **DFB-Hex-amide** was annealed at 170°C for 5 min to have a crystalline state while **DFB- PhEt-amide** was annealed for 2h at 150°C. Then mechanofluorochromism effect was checked by smearing the thermal annealed samples with a metal spatula.
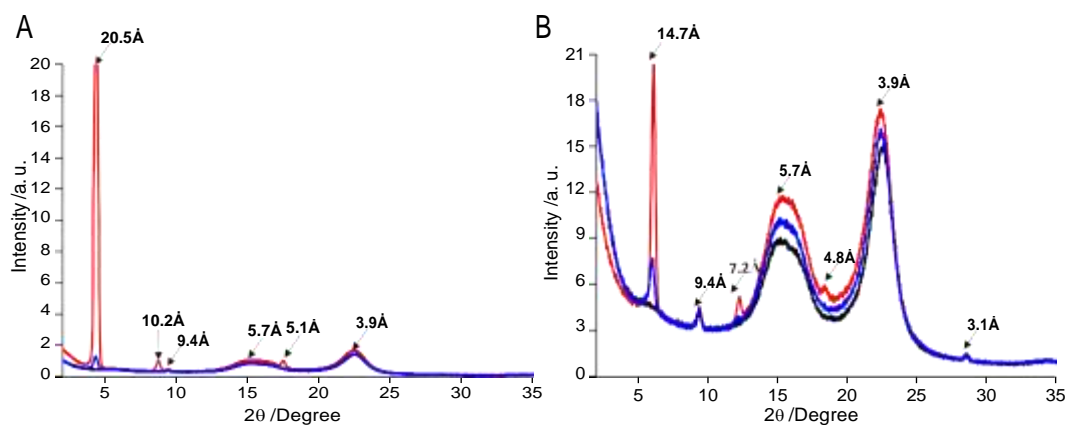
II.7 PXRD measurements

Figure S6: Powder XRD pattern of (*R*)-DFB-Hex-amide (A) and (*R*)-DFB-PhEt-amide (B) for samples blank paper in black lines, after thermal annealing (TA) in Red lines and after smearing (SM) in blue lines.
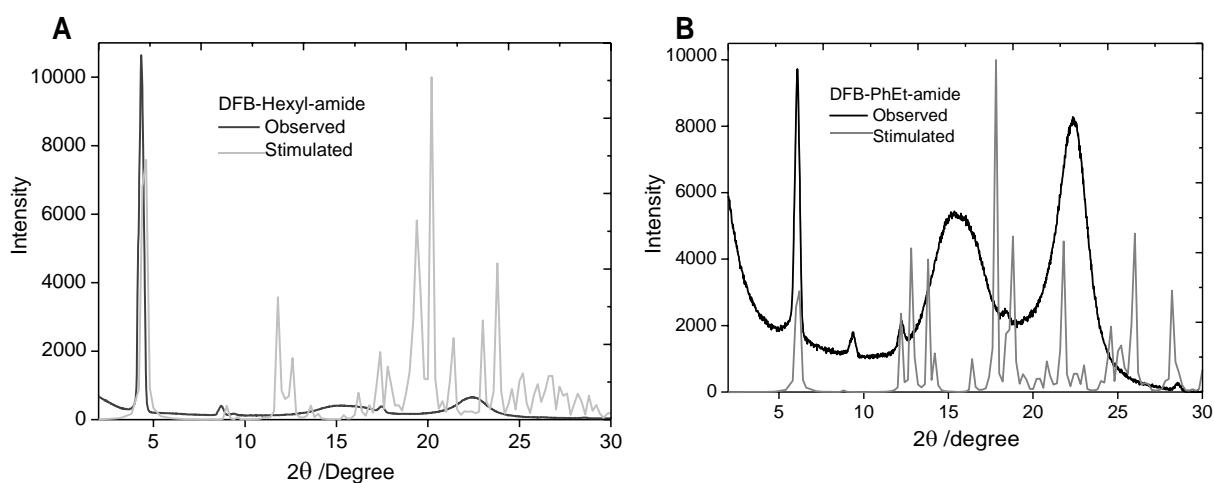

Figure S7: comparison of stimulated and observed Powder XRD pattern of (*R*)-DFB-Hex-amide (A) and (*R*)-DFB-PhEt-amide (B). (Stimulated PXRD is calculated PXRD pattern from CIF file of the respective single crystals)
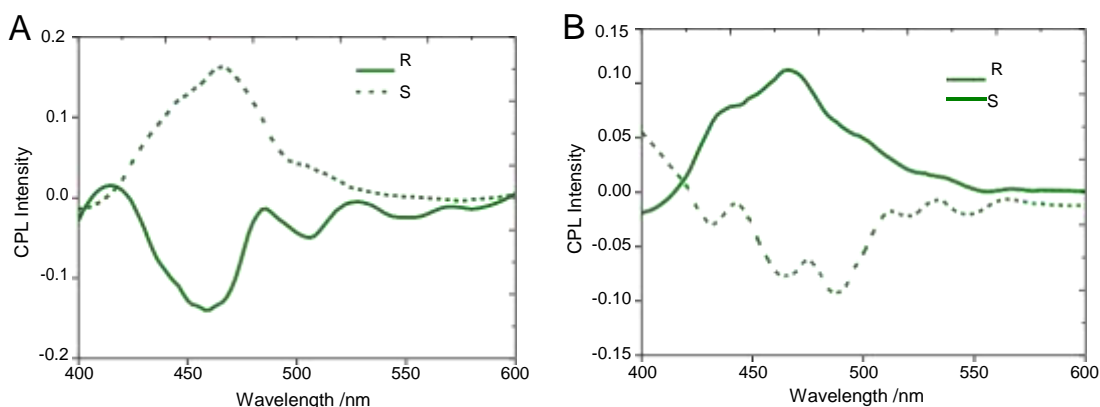
II.8 CPL Measurements in Solution State

Figure S8: CPL spectra of (*R/S*)-DFB-Hex-amide (A) and (*R/S*)-DFB-PhEt-amide (B) in chloroform with apparent g_{lum} values as 8×10^{-4} and 9×10^{-4} respectively.(conc.= 1×10^{-5} M) The accuracy in g_{um} is about 0.1×10^{-3} in our measurement system and we expect 10% probable error in these g_{lum} values. These CPL activities are thus considered to be similar in dissymmetry.

II.9 CPL Measurement in Solid State
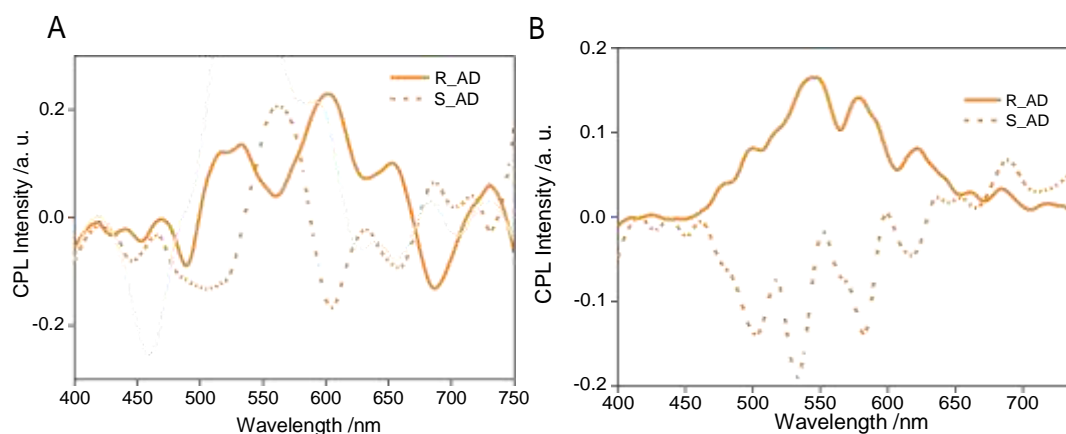
Figure S9: CPL spectra of as deposited (AD) samples of (R/S)-DFB-Hex-amide (A) and (R/S)-DFB-PhEt-amide (B) in with apparent glum values as 1.5×10^{-3} and 1.4×10^{-4} respectively.
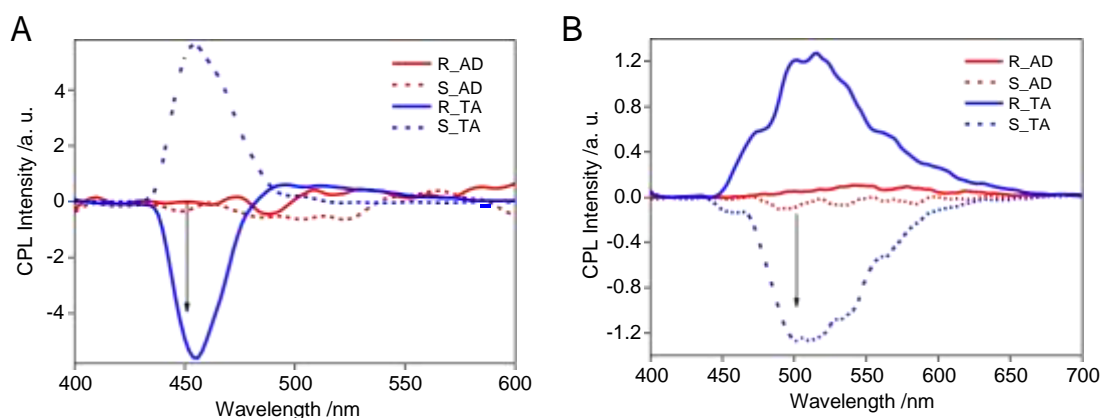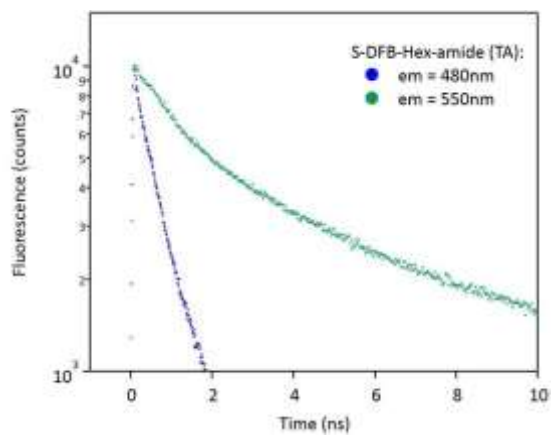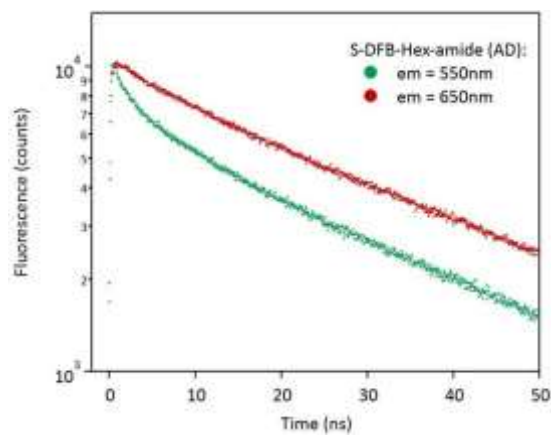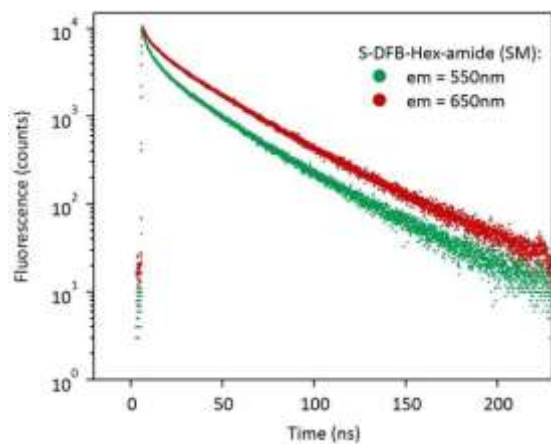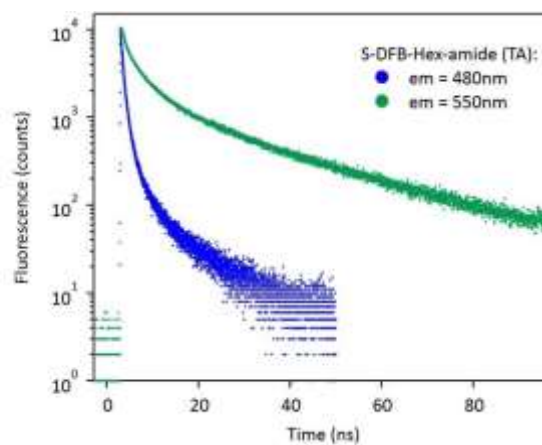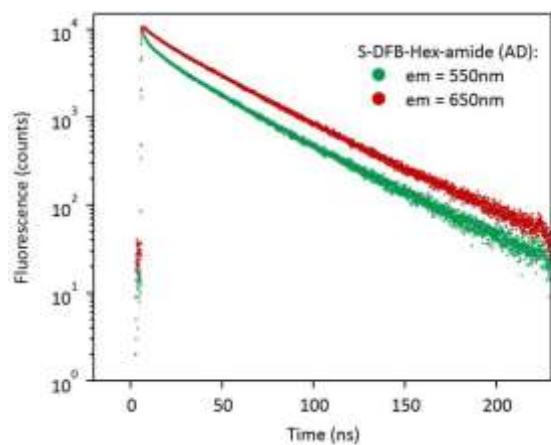

Figure S10: Comparison of CPL spectra of as deposited (AD) and thermally annealed (TA) samples of (*R/S*)-DFB-Hex-amide (A) and (*R/S*)-DFB-PhEt-amide (B) respectively.
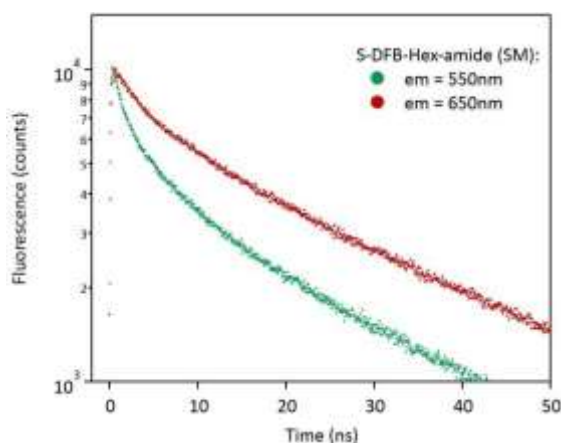
II.10 Time-resolved fluorescence

Figure S11: Fluorescence decay curves of (S)-DFB-Hex-amide in AD, TA and SM states, recorded at different emission wavelengths: $\lambda_{em} = 480$ nm (blue curves), $\lambda_{em} = 550$ nm (green curves), and $\lambda_{em} = 650$ nm (red curves). Zoomed regions at short timescales are displayed. $\lambda_{exc} = 390$ nm.

II.11 DFT and TD-DFT calculations

The geometry of compound *(S)*-**DFB-Hex-amide** and *(S)*-**DFB-PhEt-amide** have been fully optimized by the DFT (Density Functional Theory) method using the hybrid B3LYP functional with 6-31G(d,p) basis set, as implemented in Gaussian 09 software package.[5] Frequencies calculations were performed to confirm that the geometries obtained correspond to energy minima. Frank-Condon energy transitions were calculated by the time- dependent DFT formalism (TD-DFT) with the same functional and basis set. This level of theory was considered adequate for the geometry optimizations, energy calculations, molecular orbitals and electronic transitions of aromatic compounds such as difluoroboron-

β-diketones derivatives. In case of molecules in the crystal, TD-DFT calculations were

performed directly on the group of molecules, as determined by the experimental X-Ray structure: packing of 4 (resp. 2) molecules for *(S)*-**DFB-Hex-amide** (resp. *(S)*-**DFB-PhEt- amide**). For more precise simulation of the crystalline state, use of more sophisticated theoretical methods are required.[1] Absorption and CD spectra have been simulated with gaussian functions for each electronic transition, with 0.33 eV half width at half height.
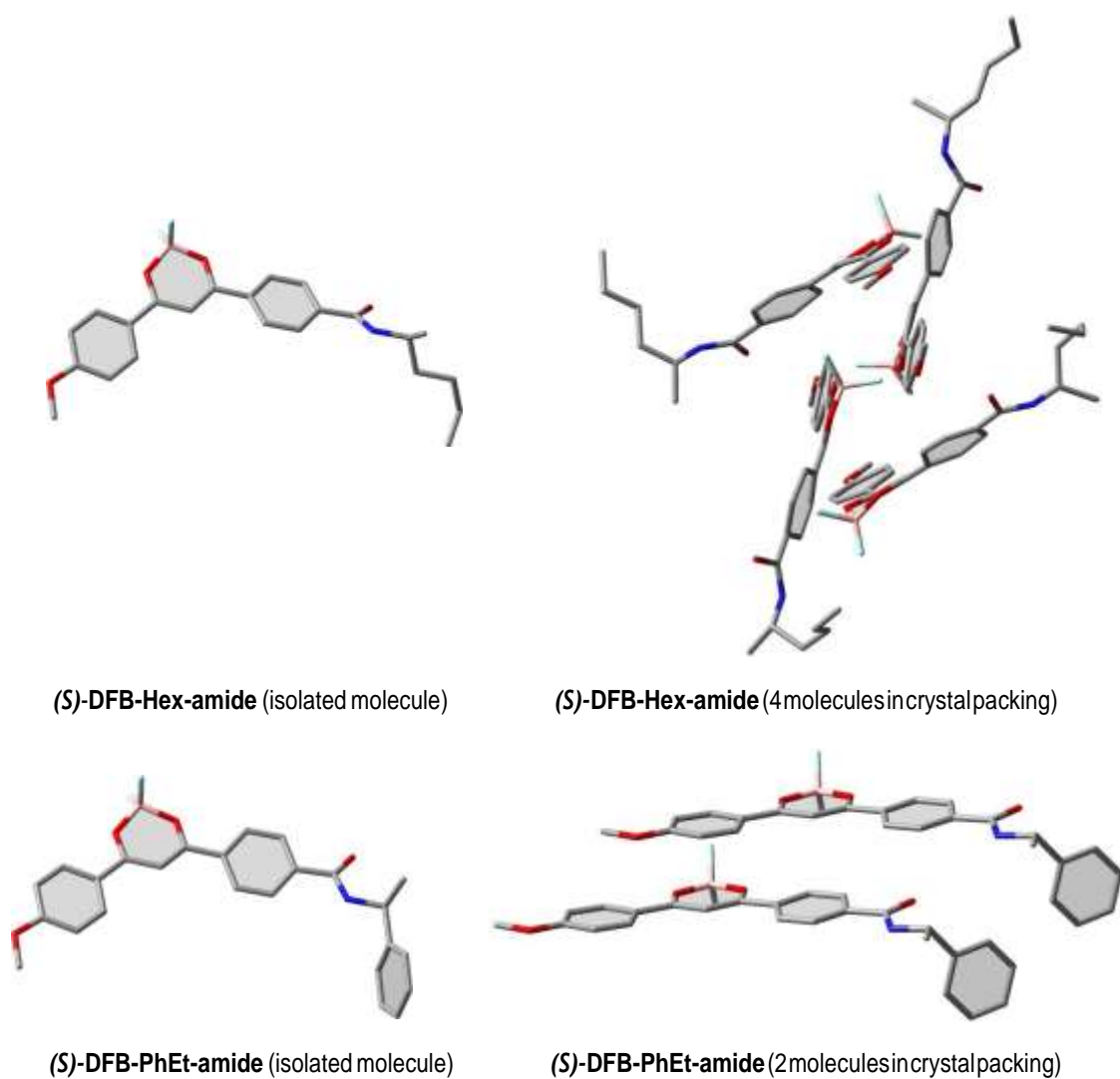
(S)-**DFB-Hex-amide** (isolated molecule)　　　　*(S)*-**DFB-Hex-amide** (4 molecules in crystal packing)

(S)-**DFB-PhEt-amide** (isolated molecule)　　　　*(S)*-**DFB-PhEt-amide** (2 molecules in crystal packing)

Figure S12: (Left) Optimized geometries of (*S*)-DFB-Hex-amide and *(S)*-DFB-PhEt-amide isolated molecule, obtained by DFT calculations at the B3LYP/6-31g(d,p) level with Gaussian 09.[5] (Right) Crystal packing from DRX measurements involving 4 and 2 molecules, respectively, used for the TD-DFT calculations.
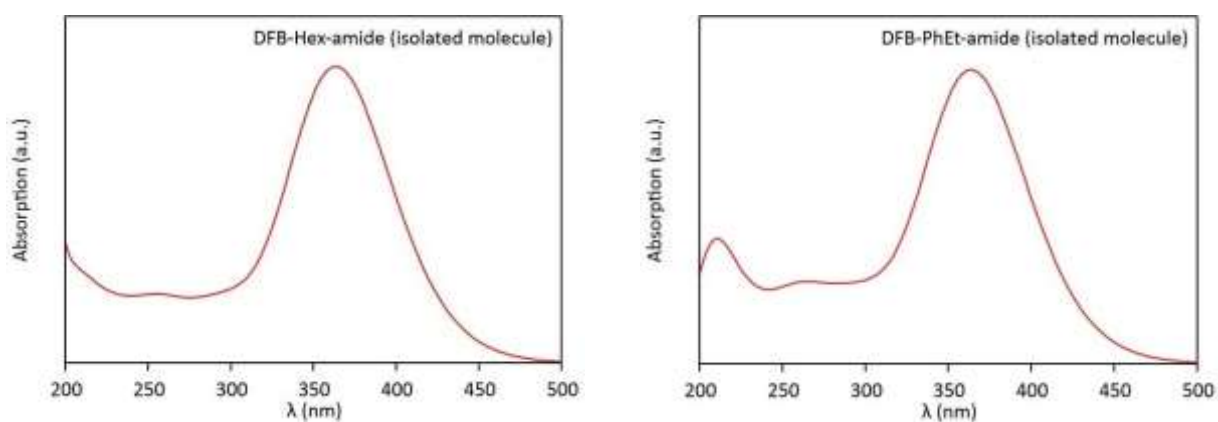

Figure S13: Calculated absorption spectra by TD-DFT (B3LYP/6-31g(d,p)) for (left) *(S)*-DFB-Hex-amide and (right) *(S)*-DFB-PhEt-amide as isolated molecule.
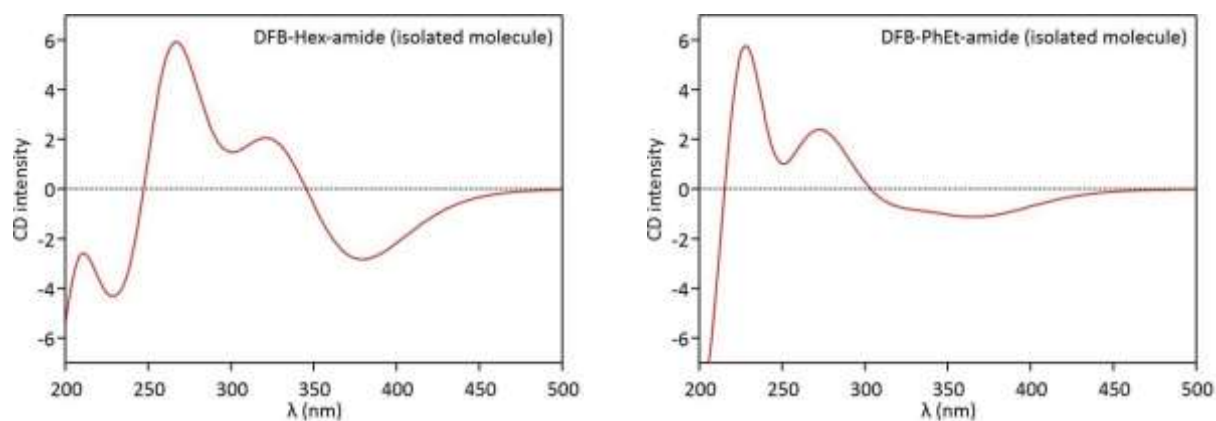
Figure S14: Calculated CD spectra by TD-DFT (B3LYP/6-31g(d,p)) for (left) *(S)*-DFB-Hex-amide and (right) *(S)*-DFB-PhEt-amide as isolated molecule.
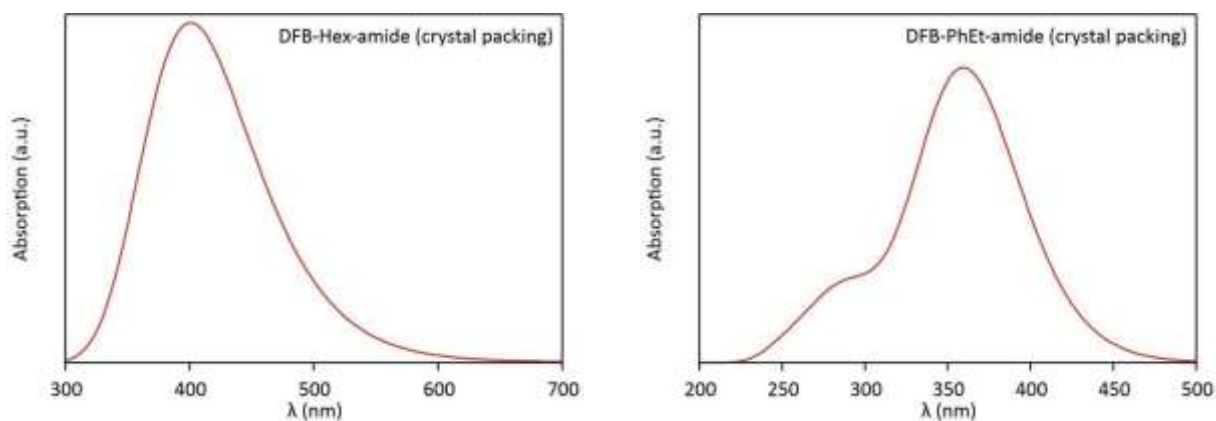

Figure S15: Calculated absorption spectra by TD-DFT (B3LYP/6-31g(d,p)) for (left) *(S)*-DFB-Hex-amide and (right) *(S)*-DFB-PhEt-amide as packing of 4 (resp. 2) molecules in the crystal structure determined experimentally.
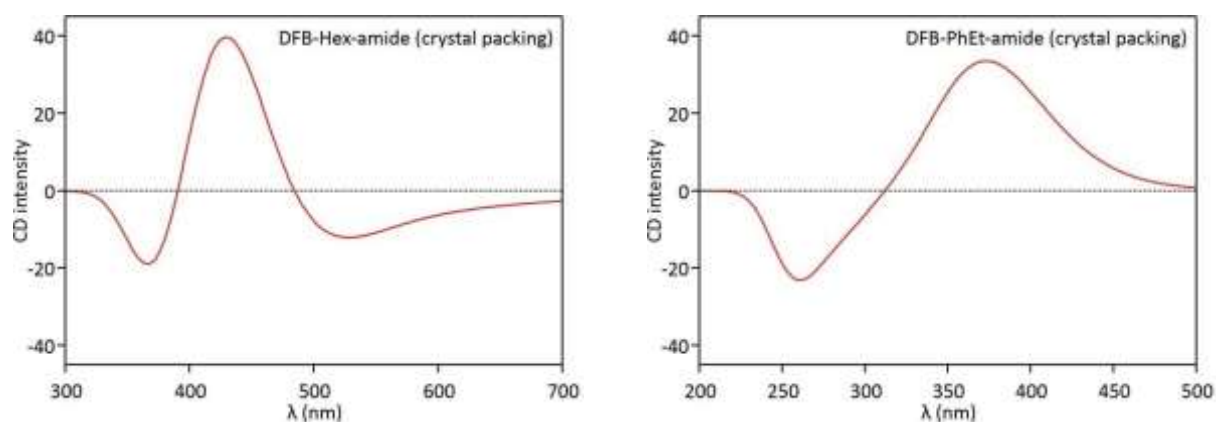

Figure S16: Calculated CD spectra by TD-DFT (B3LYP/6-31g(d,p)) for (left) *(S)*-DFB-Hex-amide and (right) *(S)*-DFB-PhEt-amide as packing of 4 (resp. 2) molecules in the crystal structure determined experimentally.

II.12 XRD data

X-ray diffraction data for compound **(*S*)-DFB-PhEt-amide** were collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IuS source Mo Ka radiation. Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as a cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value by means of an N-Helix series Cryostream cooling device within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[6] and refined against F2 by fullmatrix least-squares techniques using SHELXL-2017[7] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[8] The crystallographic analysis revealed the absolute structure of compound **(*S*)-DFB-PhEt-amide** with a Flack parameter[9] of 0.02(7) in the monoclinic *P* 2_1 space group. The crystal data collection and refinement parameters are given in Table S2. CCDC 1850803 and 1817892 contains the supplementary crystallographic data for this paper.

	(S)-DFB-Hex-amide	(S)-DFB-PhEt-amide
Formula	$C_{23}H_{26}BF_2NO_4$	$C_{25}H_{22}BF_2NO_4$
Formula weight	429.27	449.24
Crystal system	triclinic	monoclinic
Space group	P1 (#1)	$P2_1$
a (Å)	10.235(2)	5.388(3)
b (Å)	10.796(2)	13.755(8)
c (Å)	20.224(5)	14.471(8)
α (deg)	93	90
β (deg)	104	91
γ (deg)	91	90
Z value	4	2
V ($Å^3$)	2166.0(8)	1072.3(10)
ρ (g/cm^3)	1.316	1.391
T (K)	123	100
Reflection measured	29063	4884
Reflection calculated	14731	2560
R_1(I> 2σ(I))	0.1338	0.0288
wR_2 (all data)	0.3931	0.0725
CCDC No.	1850803	1817892

Table S2: crystal data collection and refinement parameters for compounds (S)-DFB-Hex-amide and (S)-DFB-PhEt-amide

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