Experimental section

Materials, Method and Instrumentation.

All solvents for synthesis were of analytic grade. Spectroscopy measurements were carried out with spectroscopic grade solvents. NMR spectra (¹H, ¹³C) were recorded at room temperature on JEOL JNM ECS 400 operating at 400 and 100 MHz for ¹H and ¹³C, respectively. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (¹H and ¹³C); residual solvent peaks of the deuterated solvents were used as spectra were realized in internal standards. Mass Spectropole de Marseille (http://www.spectropole.fr/). Thin films spectra and fluorescence quantum yields were measured using an integrating sphere. UV-Vis-absorption spectra were measured on a Varian Cary 5000. Emission spectra were measured on a Horiba-JobinYvon Fluorolog-3 spectrofluorimeter that was equipped with a three-slit double-grating excitation and a spectrograph emission monochromator with dispersions of 2.1 nm.mm⁻¹ (1200 grooves.mm⁻ ¹). Steady-state luminescence excitation was done using unpolarized light from a 450W xenon CW lamp and detected at an angle of 90° for dilute-solution measurements (10 mm quartz cell) and with a red-sensitive Hamamatsu R928 photomultiplier tube. Special care was taken to correct emission spectra that were obtained with the latter device. The detector was corrected according to the procedure described by Parker et al.¹ The observed photomultiplier output A_1 was recorded at a wavelength λ , which corresponds to the apparent emission spectrum. A_1 is given by $A_1 = (F_1)(S_1)/\lambda^2$, where F_1 and S_1 are, respectively, the corrected emission spectrum and the spectroscopic sensitivity factor of the monochromatorphotomultiplier setup. To calculate S_1 , we used 4-N,N-dimethylamino-4'-nitrostilbene (DMANS) as a standard fluorophore for which its corrected emission spectrum has been precisely determined.² Luminescence quantum yields (Φ_f) were measured in dilute DCM solutions with an absorbance below 0.1 using $\Phi_{fx}/\Phi_{fr} = [OD_r(\lambda)/OD_x(\lambda)][I_x/I_r][n_x/n_r]$. where $OD(\lambda)$ is the absorbance at the excitation wavelength (λ), n the refractive index, and I the integrated luminescence intensity. The "r" and "x" subscripts stand for reference and sample, respectively. The luminescence quantum yields were not corrected by the refractive indices. We used as reference ruthenium trisbipyridine bischloride ($\Phi_{\rm fr} = 0.021$ in water).³

<u>Time-resolved fluorescence measurements</u> were carried out using a Noncolinear Optical Parametric Amplifier (NOPA) pumped by a fiber femtosecond laser (Amplitude Systemes Tangerine), and a streak camera (Hamamatsu PLP system) with a time resolution of about 10 ps. The pulse duration was 100 fs and the repetition rate was 10 kHz. The pumping intensity was controlled using a set of neutral densities. The PL was collected at the magic angle between the polarization of the excitation light and the polarization of the detected polarized light in order to avoid any polarization anisotropy effect; the reported τ values are given with an estimated uncertainty of about 10%.

<u>Cyclic voltammetric</u> (CV) data were acquired using a BAS 100 Potentiostat (Bioanalytical Systems) and a PC computer containing BAS100W software (v2.3). A three-electrode system with a Pt working electrode (diameter 1.6 mm), a Pt counter electrode and an Ag/AgCl (with 3M NaCl filling solution) reference electrode was used. [$(n-Bu)_4N$]PF₆ (0.1 M in dichloromethane) served as an inert electrolyte. Cyclic voltammograms were recorded at a scan rate of 100 mV.s⁻¹. Ferrocene was used as internal standard.⁴

The values of half-waves potentials of each redox process are extracted using a deconvolution process incorporated in the BAS100W software (v2.3). The difference between the half-peak

 E_p E_1 value $\frac{1}{2}$ and the half-wave value $\frac{1}{2}$ (considered as equal to E⁰ because the concentrations of the oxidant and of the reducer are supposed to be equal at the electrode) is typically of 28 mV.

For example considering an oxidation process and using a positive scan, these two values are linked by :

$$E_{\frac{1}{2}} = E_{\frac{p}{2}} + 1.09 \frac{RT}{nF} \approx E_{\frac{p}{2}} + \frac{0.028}{n}$$

For example considering a reductive process and using a negative scan, these two values are linked by :

$$E_{\frac{1}{2}} = E_{\frac{p}{2}} - 1.09 \frac{RT}{nF} \approx E_{\frac{p}{2}} - \frac{0.028}{n}$$

Herein, all the half-wave potential values were calibrated using the one corresponding to the oxidation of ferrocene (Fc \rightarrow Fc⁺ + e⁻) by scanning in a positive (forward) direction (this value is considered to be equal to 0.46 V vs. SCE.)

HOMO-LUMO calculation:

The HOMO was found by measuring its workfunction using photoelectron spectroscopy (Riken Keiki, AC-3). In addition, it was calculated by using the method published by Gritzner and Kuta⁵:

 $E^{HOMO} = - (E^{ox} (vs. Fc/Fc+) + 5.13) eV = - (0.63 + 5.13) = -5.76 eV$

Ground state calculation (Bilot-Kawski)^{6,7}:

$$\nu_a - \nu_f = m^{(1)} f(\mathcal{E}, n) + cste \tag{1}$$

$$\nu_a + \nu_f = -m^{(2)} [f(\xi, n) + 2g(n)] + cste$$
⁽²⁾

Where v_a is the absorption maximum and v_f is the fluorescence maximum, both in wavenumber. ε is the permittivity and n is the refractive index. $m^{(1)}$ and $m^{(2)}$ represent the slope plotting relation (1) and (2) using Bakshiev polarity function $f(\varepsilon,n)$ and Kawski-Chamma-Viallet polarity function g(n):

$$f(\mathfrak{E},n) = \frac{2n^2 + 1}{n^2 + 1} \left(\frac{\mathfrak{E} - 1}{\mathfrak{E} + 2} - \frac{n^2 - 1}{n^2 + 2}\right)$$
(3)

$$g(n) = \frac{3}{2} \left(\frac{n^4 - 1}{\left(n^2 + 2\right)^2} \right)$$
(4)

Following Onsager theory, $m^{(1)}$ and $m^{(2)}$ can be expressed as following:

$$m^{(1)} = \frac{2(\mu_e - \mu_g)^2}{hca^3}$$
(5)

$$m^{(2)} = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{6}$$

Where h is Planck constant ($h = 6.63 \times 10^{-34}$ Js), c the velocity of light in vacuum ($c = 3 \times 10^8$ m.s⁻¹) and *a* is the Onsager radius with μ_g , the ground state dipole moment and μ_e , the excited state dipole moment.

Therefore the ground state dipole moment can be found by using the following equation (7)

$$\mu_g = \frac{m^{(2)} - m^{(1)}}{2} \left(\frac{hca^3}{2m^{(1)}}\right)^{1/2} \tag{7}$$

In this equation, as in the case of Lippert-Mataga, the Onsager radius is calculated using equation (8).

$$a = \left(\frac{3M}{4\Pi\delta N_A}\right)^{1/3} \tag{8}$$

Where δ is the density of the considered dye (taken as 1.3), M is the molecular weight of the dye and N_A is the Avogadro's number.

Here, it can be noted that similar value of radius (*i.e.* 5.22×10^{-8} cm) can be found by looking the X-Ray crystal structures of similar dyes.⁸

Excited state calculation (Lippert-Mataga)^{9, 10}:

The Lippert-Mataga equation can be expressed as following:

$$\Delta v = v_a - v_f = \frac{2}{hc} \Delta f' \frac{(\mu_e - \mu_g)^2}{a^3} + cste$$

With $\Delta f'$ defined as following:

$$\Delta f' = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{22n^2 + 1}\right)$$

Preparation of OLED samples:

PEDOT:PSS films were spin coated on precleaned ITO glass substrates and annealed at 180°C for 30 min (thickness: 45 nm). Subsequently, the blend of CBP and dye in chloroform solution was spin coated on top of the PEDOT:PSS (thickness: 80 nm). DPEPO and TPBi films were then thermally evaporated on the active layer, respectively yielding thickness of 10 and 55 nm. Finally, LiF/Al electrodes were thermally evaporated through a shadow mask. The active area of the OLEDs was 4 mm². To avoid degradation and emission quenching because of oxygen and moisture, the OLEDs were encapsulated in a glove box prior to the device characterization.

OLED measurements:

The current density (J) – voltage (V) – luminance (L) characteristics were obtained using a source meter (Keithley 2400, Keithley Instruments Inc.) and an absolute external quantum efficiency measurement system (C9920-12, Hamamatsu Photonics). Electroluminescence spectra were measured using an optical fiber connected to a spectrometer (PMA-12, Hamamatsu Photonics).

Preparation of ASE samples:

The blend of the dye and CBP was made in chloroform solution and spin coated on fused silica substrate (thickness measurements: 200 nm).

ASE measurements:

The spin-coated thin films were photo-excited by a nitrogen laser (excitation wavelength of 337 nm, repetition rate of 8 Hz and pulse width of 800 ps). The intensity of the pump beam was controlled using a set of neutral density filters. The pump beam was focused into a 0.5 cm \times 0.08 cm stripe. An optical fiber connected to a charge-coupled device spectrometer (PMA-11, Hamamatsu Photonics) was used to measure the emission spectra from the edge of the organic layers.

Synthesis

In a 50 mL flask, the mixture of benzoylacetone (475 mg, 2.926 mmol, 1 eq) and BF₃:Et₂O (398 μ L, 3.219 mmol, 1.1 eq) in 3mL ethyl acetate was heated for 30min at 50-60°C in air. Dissolved 4-(N,N-Diphenylamino)-benzaldehyde (1 g, 3.658 mmol, 1.25 eq) and B(n-OBu)₃ (0.987 mL, 3.658 mmol, 1.25 eq) into 12mL ethyl acetate, then the solution was injected into the first mixture. The reaction was stirred at 50-60°C for another 30 min. First portion of BuNH₂ (58 μ L, 0.585mmol, 0.4eq) was added dropwise into the reaction. After 6 h heating, second portion of BuNH₂ (29 μ L, 0.293mmol, 0.2eq) was added, and the reaction was kept heating at 50-60°C overnight. All the solvents were evaporated. The crude product could be obtained by flash column chromatography (silica, CH₂Cl₂) mixed with few ligand and aldehyde. The further purification was done by precipitating three times from CH₂Cl₂/petroleum ether, giving dark red powder (997 mg, 73% yield).

¹H NMR (400 MHz, DMSO-*d6*, ppm): 8.10 (m, 3H), 7.70 (m, 3H), 7.59 (t, ${}^{3}J=$ 8.0 Hz, ${}^{3}J=$ 7.6Hz, 2H), 7.38 (t, ${}^{3}J=$ 8.0 Hz, 4H), 7.29 (s, 1H), 7.17 (m, 6H), 6.95 (d, ${}^{3}J=$ 15.6 Hz, 1H), 6.82 (d, ${}^{3}J=$ 8.8 Hz, 2H); ¹³C NMR (400 MHz, DMSO-*d6*, ppm): 182.02, 179.14, 152.03, 148.98, 145.70, 132.45, 132.35, 132.21, 130.57, 129.93, 128.88, 126.87, 126.44, 126.06, 119.43; 117.85; 97.82. HRMS (ESI+) [M + Na]⁺ calcd for C₂₉H₂₂NO₂BF₂Na⁺ m/z= 488.1609, found m/z= 488.1607.



Figure NMR1. ¹H NMR spectrum of (E)-4-(4-(diphenylamino)styryl)-2,2-difluoro-6-phenyl-2H-1,3,2-dioxaborinin-1-ium-2-uide in DMSO-*d6*



Figure NMR2. ¹³C NMR spectrum of (E)-4-(4-(diphenylamino)styryl)-2,2-difluoro-6-phenyl-2H-1,3,2-dioxaborinin-1-ium-2-uide in DMSO-*d6*





Figure S1. Thermogravimetric analysis of the hemicurcuminoid borondifluoride (heating rate: 10 °C/min) a/ in vacuum (1Pa) and b/ under nitrogen. c/ DSC trace of the hemicurcuminoid borondifluoride recorded at a heating rate of 10 °C/min, which indicates a glass transition temperature T_g of 98.3 °C.



Figure S2. a/ Cyclic voltammogram of a) the hemicurcuminoid boron difluoride complex (1mM) in DCM solution containing 0.1M [(ⁿBu₄N)PF₆] (Scan rate of 100 mV/s); b) the same



solution after the addition of an aliquot of Ferrocene.





Figure S4. Electronic absorption and steady-state fluorescence spectra of the hemicurcuminoid boron difluoride complex in solvents of different polarity at room temperature ($\lambda_{exc} = 480$ nm).



Figure S5. Bakshiev (a/) and Kawski-Chamma-Viallet (b/) plots for the hemicurcuminoid boron difluoride dye where Bakshiev polarity function is : $[(2n^2 + 1)/(n^2 + 2)][(\varepsilon - 1)/(\varepsilon + 2) - (n^2 - 1)/(n^2 + 2)]$ and Kawski-Chamma-Viallet polarity function is: $[(2n^2 + 1)/(n^2 + 2)][(\varepsilon - 1)/(\varepsilon + 2) - (n^2 - 1)/(n^2 + 2)]+1.5[(n^4 - 1)/(n^2 + 2)^2].^{6,7}$



Figure S6. Lippert-Mataga plot for the hemicurcuminoid boron difluoride dye where $\Delta f' = [(\epsilon - 1)/(2\epsilon + 1)] - 0.5 [(n^2 - 1)/(2n^2 + 1)].^{9, 10}$



Figure S7. Overlap of the fluorescence spectrum of a thin film of pure CBP (—) with the hemicurcuminoid boron difluoride electronic absorption spectrum of 40wt.% in CBP (—) illustrating the good overlap for an efficientFörster type energy transfer.



Figure S8. Electronic absorption spectra of the hemicurcuminoid boron difluoride dye in 15wt.% CBP blend film (—), in cyclohexane (—) and in acetonitrile (—), and fluorescence spectra in 15wt.% CBP blend film (---), in cyclohexane (---) and in acetonitrile (---).



Figure S9. Steady-state fluorescence spectrum of the hemicurcuminoid boron difluoride in 2wt/% (—), 4wt.% (—) and 6wt.% (—) CBP blend film (λ^{exc} = 325nm), a/ whole spectrum and b/ residual emission of the CBP moiety.



Figure S10. Variation of the Stokes shift of the monomeric (\blacksquare) and dimeric (\bullet) structures as function of the dye concentration in CBP.



Figure S11. a/ HOMO-LUMO of the hemicurcuminoid boron difluoride and CBP. b/ Energylevel diagram of the OLED devices.



Figure S12. Current density-voltage (J-V) curves of the OLEDs



Figure S13. Emission spectra of the CBP blend films (a/ 2wt.%; b/ 15wt.%; c/ 40wt.% and d/ 60wt.%) at different excitation densities.



Figure S14. Output intensity emitted from the edge of the CBP blend films as a function of the pumping intensity for the doping concentrations of a/ 2wt.%, b/ 15wt.%, c/ 40wt.% and d/ 60wt.%.



Figure S15. Full emission (—), emission of the monomeric (—) and dimeric (—) structures with the ASE signal (—) for the doping concentration in CBP of a/ 2wt.%, b/ 15wt.%, c/ 40wt.% and d/ 60wt.%. The full emission was measured by steady state measurements, the dimeric emission (long lived) was measured by streak camera removing the monomeric emission (short lived, τ_1) by taking the emission after 8 x τ_1 , the monomeric emission was deconvoluted from the full emission and the long live emission.

solvent	λ_{abs}	λ_{em}	Δv_{ST}	$arPsi_{ m f}$	$ au_{ m f}$	$k_{ m f}$	$k_{ m nr}$
CycloH	514	541.5	988	0.296	2.35	1.3	3.0
Bu ₂ O	513	598	2771	0.409	3.26	1.3	1.8
Et ₂ O	511	630	3696	0.353	3.35	1.1	1.9
Chloroform	533	691	4290	0.165	n.d.	n.d.	n.d.
AcOEt	515	685	4819	0.033	0.45	0.75	21.7
DCM	535	736	5105	0.028	0.24	1.2	40.2
Acetone	520	742	5754	0.001	n.d.	n.d.	n.d.
ACN	524	787	6377	0.0003	n.d.	n.d.	n.d.

Table S1. Spectroscopic data and photophysical properties of the dye in solvents of different polarity at room temperature^{*a*}

^{*a*} Absorption maximum wavelengths λ_{abs} (nm). fluorescence maximum wavelengths λ_{em} (nm). Stokes shifts Δv_{ST} (cm⁻¹). fluorescence quantum yields Φ_{f} . fluorescence lifetimes τ_{f} (ns). radiative k_{f} (10⁸ s⁻¹) and nonradiative $k_{nr} = (1 - \Phi_{f})/\tau_{f}$ (10⁸ s⁻¹) rate constants; CycloH: cyclohexane, Bu₂O: n-dibutylether, Et₂O: ethylic ether, AcOEt: ethyl acetate, DCM: dichloromethane, ACN: acetonitrile.

Table S2. Spectroscopic data and photophysical properties in CBP matrix with different concentration

Hemicurcuminoid boron difluoride										
	λ^{abs}/nm	FWHM / cm ⁻¹	λ^{em}/nm	Φ_{f}^*	Φ _f **	λ^{em1} / nm	λ^{em2}/nm	τ / ns	Φ _f	
2wt.%	543	3275	626	0.76	0.955	625	684	0.80, 4.22	9 x 10 ⁻³	
4wt.%	543	3335	652	0.62	0.825	n.d.	n.d.	n.d.	3 x 10 ⁻³	
6wt.%	544	3285	665	0.51	0.745	n.d.	n.d.	n.d.	_ a	
15wt.%	540	3482	686	0.295	0.38	659	692	0.64, 3.90	_ a	
40wt.%	539	3762	712	0.145	0.19	684	719	0.52, 3.21	_ a	
60wt.%	534	3962	716	0.095	0.12	697	726	0.47, 3.04	_ a	

*: excitation at 520 nm measuring the emission of Hemicurcuminoid boron difluoride; **: excitation at 340nm in CBP measuring the emission of Hemicurcuminoid boron difluoride, ^a : too low to be measured. The last column (CBP, Φ_f) represent the photoluminescence quantum yield of the residual emission of CBP in the blends.

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