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## Frustrated Excited State Intramolecular Proton Transfer (ESIPT) in 10-Hydroxy-11*H*-benzo[*b*]fluoren-11-one: synthesis and photophysics

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#### Abstract

A new hydroxybenzofluorenone has been designed and synthesized in order to investigate the origin of excited state intramolecular proton transfer reactions in this familiy of compounds. 10-Hydroxy-11*H*-benzo[*b*]fluoren-11-one (10-HHBF) does not show dual fluorescence in contrast to its well known analogue 1-hydroxy-11*H*-benzo[*b*]fluoren-11-one (1-HHBF). It is suggested that in 10-HHBF ESIPT is not occuring. The origin of the difference between these isomers is likely to be found in the increased donor-acceptor distance in 10-HHBF and in the lower stability of its excited state tautomer. This streses the large impact in the photophysics of this class of materials of subtle structural changes which must be taken into account for the desingn of single-molecule white light emitters.

**Keywords:** excited state intramolecular proton transfer, white light fluorescence, hydroxybenzofluorenone, Fries rearrangement, regioselectivity, spontaneous cyclization

#### 1. Introduction

The search of molecules emitting white light has been attracting much attention for already several decades. They are intended to substitute combinations of multiple emitters in applications like white organic light emitting diodes (WOLEDs) [1]. There are however not many examples of single white light emitters reported in the literature [2], moreover, molecules with high emission quantum yields are still lacking, except for some heteroaromatics [3].

In single white light emitters two emissive states of relatively close energies are connected through an excited state intramolecular reaction, usually electron or proton transfer. Whether the final emission will arise from only one or both of the states is difficult to predict as the phenomenon depends not only on the states energies, but also on the kinetic rates of their intrinsic decays with respect to those of the reaction connecting them [4]. Even more difficult is to make predictions based on the compounds chemical structures. Therefore, more examples are required to help rationalizing the occurrence of white light emission.

Of the several candidates showing excited-state intramolecular proton transfer (ESIPT), 1hydroxy-11*H*-benzo[*b*]fluoren-11-one (1-HHBF, Chart 1) got our attention: its simple structure with a relatively straightforward synthesis, consists of a benzofluorenone core and a hydroxyl group attached to the benzene ring and exhibits broadband emission (CIE 1931 chromaticity coordinates: (0.30 0.27)) [2c]. This emission consists of two bands originating from two energetically close excited states (normal and tautomeric forms) after the excitation of one dominant ground state tautomer.

The work on molecules structurally related to 1-HHBF has to be tracked back to the findings of ESIPT in 7-hydroxy-1-indanone (I, Chart 1) [5]. By expanding the ring to 1-hydroxy-9*H*-fluoren-9-one (II, Chart 1) the ESIPT seems to be hindered, though contradicting reports can be found in the literature about the occurrence of the tautomeric emission [2c,6]. Finally, in 2011 the group of Chou extended the conjugated system of hydroxyfluorenone (II) from the benzene ring side, leading to white light emission in 1-HHBF [2c].



Chart 1 10-HHBF and molecules structurally related to it.

Recently, the study of this family has been expanded to tert-butyl substituted 1-HHBF molecules [7, 8, 9]. In ref. 7 it was experimentally demonstrated the high sensitivity of the ESIPT to the inductive–resonance effects of the substituents. The yield of the ESIPT reaction was correlated with the distance between the oxygen atoms of the donor and acceptor groups in the enol form, in line with the theoretical predictions by Siskos et al [10]. This adds interest to the study of the structural modifications of these molecules as their sensitivity to them is relatively large.

There are two different explanations given to the occurrence of ESIPT in this family of compounds in the literature: the first one reasons that the changes in conjugation and aromaticity upon ESIPT tune the energy of the tautomeric form [2c, 11], while the second one relies on the amount of charge that the keto oxygen acquires after excitation of the dominant enolic form in the ground state [12, 13].

We have synthesised a structural isomer of 1-HHBF, placing the additional benzene ring fused to that containing the OH group in hydroxyfluorenone: 10-HHBF (Chart 1). The two above explanations for the occurrence of ESIPT lead to contradicting predictions for this new molecule: according to the first, it is possible that 10-HHBF does not show ESIPT, while in agreement with the second the behaviour should be very similar to that of 1-HHBF. A recent theoretical paper has not found major differences between these two isomers [14].

In this work we present a new synthesis method for 1- and 10-HHBF, their photophysics in a collection of organic solvents and quantum mechanical calculations.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> The quantum-mechanical calculations are done following the methods tested and recommended for this class of compounds by previous authors [15, 12, 2c] and are used as a guidance although they are not the major target of the present work.

#### 2. Experimental

#### 2.1 Materials and methods

The starting materials, 2-naphthoyl chloride, phenol, benzoyl chloride, 1-naphthol and AlCl<sub>3</sub>, as well as hydrogen chloride solution (2.0 M) in diethyl ether were purchased from Aldrich. The reactions were carried out under Argon (< 1 ppm H<sub>2</sub>O). TLC analyses were carried out using aluminium plates coated with Silica gel 60 F254 from Merck. Column chromatography was carried out on silica gel 70–230 mesh. Tetrahydrofuran (THF) was dried by distillation from LiAlH<sub>4</sub> and stored with molecular sieves A3. NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts ( $\delta$  ppm) were determined with TMS as the internal reference, J values are given in Hz.

The solvents used for spectroscopic measurements, cyclohexane (CHEX), amyl ether (AE), ethyl ether (EE), toluene (TOL), butyl acetate (BA), tetrahydrofuran (THF), acetonitrile (ACN), methanol (MeOH), were of spectroscopic quality and further dried with molecular sieves when needed.

Absorption spectra were recorded with a Shimadzu UV 3100 spectrophotometer. Extinction coefficients were measured for four independently prepared samples by precise weighting. The measurements of emission spectra were carried out using a Fluorolog-3 Horiba spectrofluorimeter. The luminescence spectra were subsequently corrected by subtraction of the background due to the solvent (e.g., Raman lines, and second order of the Rayleigh scattering) and for the sensitivity of the detection. Luminescence quantum yields were determined using quinine sulfate in 0.1 N H<sub>2</sub>SO<sub>4</sub> as a standard ( $\Phi_F$ =0.54) and corrected for the refractive index of the solvent [16]. For quantum yield determinations, optical density of both the sample and the standard were around 0.05 at the excitation wavelengths. The quantum yields were determined exciting at wavelengths between 385 and 396 nm, and at shorter wavelengths to check the independency of the result on the position of the excitation. Lifetime measurements were performed with a home-made setup equipped with a Time Harp 100 TCSPC card and a 379 nm pulsed excitation laser from PicoQuant. Fluorescence decay curves were measured at narrow emission wavelengths after passing through a monochromator from Spectral Product CM110 by a PMT from Becker&Hickl. The FWHM for IRF was 0.39 ns. The crystal structure was solved by direct methods SHELXS-2014 [17] and refined with full-matrix least-squares calculations on F2 using SHELX-20144. All nonhydrogen atoms were refined anisotropically. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms. The infrared (IR) spectroscopy measurements by ATR (Attenuated total reflectance) technique on ZnSe crystals

were performed on a FTIR SHIMADZU IRTracer-100 spectrometer. Electrospray ionization high-resolution mass spectra (ESI-HR) were recorded with MALDISynapt G2-S HDMS (Waters Inc.) mass spectrometer equipped with an electrospray ion source and q-TOF type mass analyser. ESI-MS spectra were recorded in the negative ion mode.

#### 2.2 Synthesis and characterization

#### 2.2.1 2-(2-Hydroxybenzoyl)-naphthalene (2) [18]

A Schlenk tube was charged with phenyl 2-naphthoate (**1**, 100 mg, 0.40 mmol) and a 10 times the quantity of equimolar mixture of NaCl and AlCl<sub>3</sub> in argon atmosphere. The sealed tube was placed in oil bath preheated to 215°C and melted together while stirring. After 4 hours water was added to hot reaction mixture and the product was extracted with AcOEt (3x). Combined organic layers were washed with diluted NH<sub>4</sub>Cl and saturated NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, then filtered. The filtrate was concentrated and purified by flash chromatography, hexane : dichloromethane (9:1) to afford the product as yellowish powder, 66 mg (66%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.03 (s, 1H), 8.17 (s, 1H), 7.88 - 8.00 (m, 3H), 7.77 (dd, J = 8.5, 1.6 Hz, 1H), 7.67 (dd, J = 8.0, 1.5 Hz, 1H), 7.49 - 7.64 (m, 3H), 7.10 (dd, J = 8.4, 0.8 Hz, 1H), 6.92 – 6.85 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  201.4, 163.2, 136.3, 135.1, 134.9, 133.6, 132.2, 130.4, 129.2, 128.3, 128.2, 127.8, 127.0, 125.3, 119.4, 118.7, 118.4.

#### 2.2.2 2-(4-Hydroxybenzoyl)-naphthalene (3) [19]

A Schlenk tube was charged with phenyl 2-naphthoate (**1**, 104 mg, 0.42 mmol) and a 10 times the quantity of equimolar mixture of NaCl and AlCl<sub>3</sub> in air atmosphere. The open tube was placed in oil bath preheated to 215°C and melted together with stirring. After 4 hours water was added to the hot reaction mixture and products were extracted with AcOEt (3x). Combined organic layers were washed with diluted NH<sub>4</sub>Cl and saturated NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, then filtered. The filtrate was concentrated and purified by flash chromatography on silica gel 70-230 Mesh, hexane : ethyl acetate (95:5 (**2**) and 8:2 (**3**)). Product **3** was obtained as whitish powder, 34 mg (36%) and product **2** as yellowish powder 38 mg (40%). <sup>1</sup>H NMR (400 MHz, Acetone-d6)  $\delta$  9.25 (s, 1H), 8.27 (s, 1H), 7.97 - 8.09 (m, 3H), 7.86 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.54 - 7.69 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, Acetone-d6)  $\delta$  195.3, 162.6, 136.8, 135.9, 133.5, 133.4, 131.4, 130.4, 130.2, 129.0, 128.9, 128.7, 127.7, 126.6, 116.1.

#### **2.2.3** <u>1-Hydroxy-11*H*-benzo[*b*]fluoren-11-one (**1-HHBF**) [2c]</u>

Pd(II)-catalyzed dehydrogenative cyclization. Under air atmosphere, Pd(TFA)<sub>2</sub> (0.0075 mmol, 2.48 mg, 5 mol%), Ag<sub>2</sub>O (0.22 mmol, 51.8 mg, 1.5 eq), K<sub>2</sub>CO<sub>3</sub> (0.37 mmol, 51.5 mg, 2.5 eq) and the 2-(2-hydroxybenzoyl)-naphthalene (4) (0.15 mmol, 37 mg) were added into a dry Schlenk tube. The tube was stopped and vacuumed and filled with Argon for three times. Then trifluoroacetic acid (TFA), (0.4 mL) was added by syringe. The mixture was stirred under Argon atmosphere at 140°C for 48 h. Then the mixture was cooled down to room temperature and evaporated in vacuum and further purified by flash chromatography on silica gel with mixture hexane : dichloromethane (95:5) contaminated with 2.0 M hydrogen chloride solution in diethyl ether (approximately 5 drop in 100 ml of eluent) to give the product 1-HHBF (6.6 mg, 18%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.67 (s, 1H), 8.12 (s, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.83 (s, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.55 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 7.47 (ddd, J = 8.1, 7.0, 1.3 Hz, 1H), 7.42 (dd, J = 8.4, 7.2 Hz, 1H), 7.19 (dd, J = 7.3, 0.5 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.5, 157.7, 144.3, 138.1, 137.8, 136.8, 133.5, 132.8, 130.8, 129.1, 128.9, 127.1, 125.6, 120.22, 120.0, 117.4, 113.0, 77.3, 77.0, 76.7; HRMS (ESI-TOF): calcd m/z  $C_{17}H_{11}O_2^+$  ([M + H]<sup>+</sup>) 247.0759 found 247.0755; IR (neet):  $v_{max}$  /cm<sup>-1</sup>= 3347, 3049, 1676, 802.

#### 2.2.4 <u>10-Hydroxy-11H-benzo[b]fluoren-11-one (10-HHBF)</u>

The Schlenk tube was charged with 1-naphthyl benzoate (**8**, 107 mg, 0.43 mmol) and a 10 times the quantity of equimolar mixture of NaCl and AlCl<sub>3</sub> in argon atmosphere. The open tube was placed into preheated to 215 °C oil bath and melted together with steering. After 4 hours water was added to hot reaction mixture and products were extracted with AcOEt (3x). Combined organic layers were washed with diluted NH<sub>4</sub>Cl and saturated NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, then filtered. The filtrate was concentrated and purified by flash chromatography on silica gel with mixture hexane: dichloromethane (95:5) contaminated with HCl in Et<sub>2</sub>O to give the product **10-HHBF** (56 mg, 56%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.48 (s, 1H), 8.22 (d, J = 8.2 Hz, 1H), 7.70 (t, J = 7.3 Hz, 2H), 7.65 (d, J = 7.6 Hz, 1H), 7.48 – 7.57 (m, 2H), 7.44 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.36 (s, 1H), 7.32 (td, J = 7.5, 0.9 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  195.4, 155.9, 144.4, 138.8, 136.9, 136.3, 134.6, 130.1, 129.0, 128.9, 126.4, 126.1, 124.4, 124.0, 121.5, 112.7, 112.5. HRMS (ESI-TOF): calcd m/z C<sub>17</sub>H<sub>9</sub>O<sub>2</sub><sup>-</sup> ([M - H]) 245.0603 found 245.0603; IR (neet): v<sub>max</sub> /cm<sup>-1</sup> = 3321, 3053, 1676, 978.

#### 2.3 Computational Methodology

The calculations were performed with the Gaussian 09 program [20]. Geometry optimization for both states, the ground state and the first singlet excited state, of molecules (for both tautomers) was carried out using density functional theory (DFT) and time-dependent density functional theory (TDDFT) respectively, with CAM-B3LYP hybrid function and the 6-311+G(2d,2p) basis sets. The solvent, cyclohexane, was modelled with IEFPCM within the SCRF method. No constrains for symmetry, bonds, angles, or dihedral angles were employed in the geometry optimization calculations. The oscillator strengths are taken from the calculation of the relaxed excited states.





We planned to access 1-HHBF and 10-HHBF in one pot reaction, through a sequence of Fries rearrangement of appropriate esters followed by oxidative cyclization. To the best of our knowledge, such a straightforward and atom-economical strategy was reported only once for the synthesis of 1-hydroxybenzanthrone directly from 2-naphtyl benzoate, employing 10-fold excess of the mixture of NaCl and AlCl<sub>3</sub> (1:1) in presence of oxygen [21, 22]. A molten mixture of AlCl<sub>3</sub> and NaCl (2.2 : 1) was also used in cyclization of aryl vinyl ketones to indanones [23]. Moreover, one example of sequential Fries rearrangement and cyclization of quinol dicrotonate yielding 4,7-dihydroxy-3-methylindan-1-one was shown to proceed under

similar conditions [23]. Conversely, phenyl benzoate underwent only Fries rearrangement, without any sign of nascent cyclization [23]. Furthermore, two examples of AlCl<sub>3</sub>-mediated oxidative coupling of diaryl ketones have been reported so far: (3-hydroxy-2-naphthyl) phenylmethanone to 6-hydroxy-7*H*-benzo[*c*]fluoren-7-one [24], and 2-duroylresorcinol to 1,2,3,4-tetramethyl-8-hydroxyfluorenone [25]. Notably, in both cases starting ketones were substituted by free OH group.

The synthesis of 1-HHBF (Scheme 1) starts by obtaining phenyl 2-naphthoate (1) according to the reported procedure [26]. Then, ester 1 was subjected to conditions reported by Kranzlein et al. [21], however the reaction required a higher temperature (215°C) and argon atmosphere to provide complete selectivity towards ketone 2. (Table 1, Entry 1). Moreover, only ketone 2 resulting from Fries rearrangement was formed, without even a sign of nascent oxidative cyclization. Under air conditions at 215°C (Table 1, Entry 2) or at a lower temperature (180°C) (Table 1, Entry 3) formation of the mixture of isomers (2 and 3) was observed.

Table 1	Fries Rearrangement	of phenyl 2-naphthoa	te (1) – evaluation	of the reaction conditions.
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Entry	NaCI/AICI <sub>3</sub>	Atmosphere	θ [°C]	t [h]	Yield [%] <sup>[a]</sup>
	(1:1) (eq)				(Product)
1	10	Argon	215	4	66 ( <b>2</b> )
2	10	Air	215	4	40 ( <b>2</b> ), 36 ( <b>3</b> )
3	10	Argon	180	4	30 ( <b>2</b> ), 36 ( <b>3</b> )
<sup>[a]</sup> icol	atad wialda				

<sup>[a]</sup> isolated yields

To complete the synthesis of the desired 1-HHBF, we envisioned oxidative cyclization of ketone **2** based on the palladium-catalyzed protocol developed by Shi for synthesis of fluorenones from benzophenones [20]. Although we observed a high conversion of ketone **2** under these conditions, the desired 1-HHBF was isolated in low 10% yield (Table 2, Entry 1). Extension of the reaction time to 48h only slightly improved the yield to 13% (Table 2, Entry 2). We have tested various combinations of Pd- catalysts and bases (Table 2, Entries 1-6) of which Pd(OAc)<sub>2</sub>/Cs<sub>2</sub>CO<sub>3</sub> or Pd(TFA)<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub> performed the best, enabling the isolation of 1-HHBF in 18% yield (Table 2, Entries 4-5).

Interestingly, decreasing the reaction temperature by only 10°C almost completely shuts down the reactivity, resulting in negligible conversions and yields (Table 2, Entries 7-8). The relatively low yields of the desired product (accompanied by high conversion of **2**) could be attributed to its decomposition under the conditions of oxidative coupling. It is worth mentioning that severe drop in yield was also observed by Shi for cyclization leading to hydroxy-substitued fluorenone [27].

Entry	Catalyst	Base	θ[°C]	t [h]	Yield [%] <sup>[b]</sup>	Conv. [%]
1 <sup>[c]</sup>	Pd(OAc) <sub>2</sub>	$K_2CO_3$	140	24	10	71
2	Pd(OAc) <sub>2</sub>	$K_2CO_3$	140	48	13	77
3	Pd(OAc) <sub>2</sub>	$Cs_2CO_3$	140	24	7	33
4	Pd(OAc) <sub>2</sub>	$Cs_2CO_3$	140	44	18	75
5	Pd(TFA) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	140	48	18	75
6	Pd(TFA) <sub>2</sub>	$Cs_2CO_3$	140	48	12	73
7	Pd(TFA) <sub>2</sub>	$K_2CO_3$	130	21	Trace	small
8	Pd(TFA) <sub>2</sub>	$Cs_2CO_3$	130	21	1.5	small

 Table 2
 Pd-catalyzed dehydrogenative cyclization – evaluation of the reaction conditions.<sup>[a]</sup>

<sup>[a]</sup> reactions were conducted with **1**, catalyst (5 mol %), Ag<sub>2</sub>O (1.5 eq), base (2.5 eq), TFA (0.5 ml), Argon atmosphere; <sup>[b]</sup> isolated yields; <sup>[c]</sup> original conditions proposed by Shi [27].

As for the synthesis of 10-HHBF (Scheme 1), 1-Naphthyl benzoate **4** was obtained in analogous way as phenyl naphtoate **1**. Fortunately, in contrast to Fries rearrangement of **1** leading to ketone **2**, ester **4** underwent the expected sequence of rearrangements followed by spontaneous cyclization providing exclusively 10-HHBF in good yield (55%) (Table 3, Entry 1). The regioselectivity is independent of the atmosphere and temperature (Table 3, Entry 2-3). Interestingly when ester **4** was treated with pure AlCl<sub>3</sub> in chlorobenzene corresponding ketone resulting from Fires rearrangement was formed as the sole product [28].

 Table 3
 One-pot reaction from 1-naphthyl benzoate (4) to 10-HHBF – evaluation of reaction conditions.

Entry	$NaCl/AlCl_3$ (1:1) (eq)	Atmosphere	θ [°C]	t [h]	Yield [%] <sup>[a]</sup>
1	10	Argon	215	4	55
2	10	Air	215	4	53
3	10	Argon	180	4	42
<sup>[a]</sup> isola	ated yields				

#### **3.2 Spectroscopic Properties**

The molecular geometry of 1-HHBF and of 10-HHBF enables the occurrence of intramolecular hydrogen bonding between the hydroxyl and keto groups. It is to be expected that in both cases the proton may be transferred from the donor to the acceptor only in the excited state.

In the case of 1-HHBF, the ESIPT reaction happens in a six-membered ring, and a broadband dual emission is observed because of the quickly established equilibrium between the excited states of normal and tautomer forms. The latter form emits with a large Stokes shift. So far the emission of 1-HHBF has been measured in cyclohexane ( $\Phi_F = 0.020 + 0.006$ ) and in the solid state ( $\Phi_F \approx 0.1$ ) [2c]. We have further characterized the photophysics of 1-HHBF in other solvents.

The position of absorption spectra for 1-HHBF is independent of solvent polarity (Fig. 1, c), although the structure of the band changes. In some solvents an additional band between 450 and 500 nm appears, most likely due to water impurities as its intensity depends on the dryness of the solvent [ESI section 7]. In other words from the absorption spectra it seems that only one tautomeric form is present in the ground state. In cyclohexane the extinction coefficients at the absorption maxima amounts to  $2635 \pm 170 \text{ M}^{-1}\text{cm}^{-1}$ . This value is at odds with the reported in the past (1300 M<sup>-1</sup> cm<sup>-1</sup>) though it fits better to the series published in there [7].



**Fig. 1** Absorption spectra of 10-HHBF (a), and of 1-HHBF (c), fluorescence emission spectra of 10-HHBF (b) and of 1-HHBF (d) in eight solvents: CHEX (cyclohexane, black lines), AE (amyl ether, dark blue lines), EE (ethyl ether, light blue lines), TOL (toluene, red lines), BA (butyl acetate, light green lines), THF (tetrahydrofuran, dark green lines), ACN (acetonitrile, grey lines), MeOH (methanol, pink lines). None of the solvents in these measurements were further dried. The absorption spectra are scaled arbitrarily for a clearer presentation, while the fluorescence is normalized to the maximum of the blue band. See ESI for a representation in wavenumbers scale Fig. A.8.

In aprotic solvents dual fluorescence in 1-HHBF is observed independently of the polarity and mostly the ratio between the bands is affected, with the contribution of the tautomeric form emission larger the lower the solvent polarity (Fig.1, d). In more polar solvents, like acetonitrile, this second band is barely visible, and a bathochromic shift of the

normal form emission is noticeable, indicative of a larger dipole moment in the excited state of the normal form. In protic methanol just one emission band occurs with a maximum strongly red-shifted with respect to that of the normal form in acetonitrile.

The total quantum yield of fluorescence for 1-HHBF is in the range of 3% in all solvents except MeOH (6%) (Table 4) and it slightly increases with polarity. The fluorescence time decay is about 0.5 ns in cyclohexane and also grows together with the polarity of the solvent to 2.44 ns in acetonitrile, and 3.1 ns in MeOH. These decay time constants are independent of the wavelength of emission. We do not observe shorter components due to the limited time resolution of our set-up (0.39 ns) indicating that the ESIPT rate constants are in the range of times shorter than that, as measured in the past [2c].

**Table 4** Fluorescence experimental data for 1-HHBF and 10-HHBF:  $\Phi_F$  - total fluorescence quantum yield,  $\mathbb{P}_F \mathbb{P}$ time decay constant of fluorescence, apparent radiative,  $k_R$ , and non-radiative,  $k_{NR}$ , rate constants.

Solvent	$\Phi_{ extsf{F}}{}^{[a]}$	$ au_{ extsf{F}}$ / ns ( $\lambda_{ extsf{em}}$ [b] / nm)	$k_R / ns^{-1}$	k <sub>NR</sub> / ns⁻¹				
	1-HHBF							
CHEX	0.023	0.54(447), 0.53(447)	0.042	1.809				
AE	0.025	0.75(458), 0.67(578)	0.035	1.373				
EE	0.024	0.84(461), 0.81(576)	0.029	1.190				
TOL	0.029	0.95(470), 0.92(587)	0.031	1.044				
BA	0.029	1.14(470), 1.13(582)	0.025	0.851				
THF	0.033	1.21(470), 1.17(582)	0.027	0.812				
ACN	0.043	2.46(493), 2.42(585)	0.017	0.392				
MeOH	0.063	3.10(545)	0.017	0.252				
	10-HHBF							
CHEX	0.062	1.22(445)	0.050	0.768				
AE	0.063	1.50(453)	0.042	0.624				
EE	0.073	1.96(462)	0.037	0.473				
TOL	0.094	1.91(464)	0.049	0.474				
BA	0.104	1.94(461)	0.053	0.461				
THF	0.104	1.93(464)	0.053	0.464				
ACN	0.095	2.95(475)	0.032	0.306				
MeOH	0.162	4.46(505) <sup>[c]</sup>	0.080	0.414				

<sup>[a]</sup>  $\Phi_{\rm F}$  measured with  $\lambda_{\rm ex}$  385 - 396 nm depending on the solvent; <sup>[b]</sup> detection wavelength; <sup>[c]</sup> weighted lifetime average from bi-exponential decay (2.02 ns (0.4) and 6.09 ns (0.6) ).

For the excitation spectra of 1-HHBF we find a good agreement with the absorption spectra, independently of the emission wavelength in most of the solvents [ESI Fig. A.7a-h]. For THF an additional band appears with an intensity dependent on the emission wavelength (ESI Fig. A.7f). This change becomes stronger when setting the emission at wavelengths above 480 nm, that is, for the range corresponding to the second emission band.

The absorption spectra of 10-HHBF are very similar in position to those of 1-HHBF. The major difference is that the extinction coefficient of 10-HHBF is close to three times larger (6470  $\pm$  52 M<sup>-1</sup> cm<sup>-1</sup>) than that of 1-HHBF (2635 $\pm$  170 M<sup>-1</sup>cm<sup>-1</sup>) (Fig. 1, a vs c). An additional band is observed in several solvents, except cyclohexane and toluene, if water traces are present (ESI section 7).

Dual fluorescence for 10-HHBF is not observed at any solvent polarity (b, Fig.1). Moreover, the fluorescence emission appears to be from the normal form what is not characteristic for most of the ESIPT molecules in which a large Stokes shift is expected (emission from tautomeric form) [1c]. Such lack of ESIPT was found only in few examples [29].

The quantum yield of emission for 10-HHBF (around 7% in low polar solvents) is larger than that of 1-HHBF (3%), and the time decay constants are longer by a factor of two (Table 4). Both the quantum yield and the lifetime increase with the polarity of the solvent.

In the fluorescence excitation spectra [ESI Fig. A.6a-h] we observed an additional band, associated with a second species, in all solvents, even for CHEX when placing the emission wavelength at 555 nm (the red edge of the emission band). When recorded at emission wavelengths closer to the blue edge of the fluorescence band, we did not observe additional bands in the fluorescence excitation spectra.

#### 3.3 Computational Results

The calculated energies for the excited states of both tautomers of 1-HHBF in cyclohexane are not the same as in reference 2c, due to the different DFT method used in here which is a long-range-corrected version of B3LYP, CAM-B3LYP (Tables 5 and 6). When using B3LYP as in ref. 2c we have obtained very similar results (ESI Table A.2). Once this checking has been performed we proceeded to calculate also 10-HHBF. The results in cyclohexane are collected in Table 5. The main result of interest for the occurrence of ESIPT is the difference in energy between both tautomers in the excited state. According to this calculation in none of the cases the reaction is thermodynamically favoured. Moreover, the ESIPT reaction should be easier for 10-HHBF than for 1-HHBF. A slightly different picture arises from the B3LYP calculation without correction, as performed in ref. 2c: both energy differences between N\* and T\* are more similar (3.37 and 4.46 kcal/mol for 10- and 1-HHBF respectively, see ESI Table A.2).

Both transition energies and oscillator strengths are similar also for 1- and 10-HHBF. In both cases the oscillator strength for the N form transition is smaller than for that of the T form.

Therefore, according to these calculations, if just the energy difference between the excited states is to be corrected, in the manner it was performed in ref. 2c, 10-HHBF should

experience a tautomerization reaction in the excited state leading to a strong emission from the T\* state.

**Table 5** Calculated energy in relaxed state (E) and oscillator strength (f) for 1-HHBF and 10-HHBF with CAM-B3LYP in cyclohexane.

	1-HHBF			10-HHBF		
	E/kcal mol <sup>-1</sup>	$\Delta E/kcal mol^{-1}$	λ/nm (f)	E/kcal mol <sup>-1</sup>	$\Delta E/kcal mol^{-1}$	λ/nm (f)
N1*	N* 72.92	4.79	460 (0.053)	72.96	1.04	448 (0.088)
IN <sup>1</sup>			363 (0.178)			379 (0.190)
T* 77.70	77 70		520 (0.314)	74.00		517 (0.175)
	//./0		447 (0.117)			446 (0.324)
Ν	1.06			0		
Т	16.02			8.95		(

Additional information can be obtained from the calculated structures. In Table 6 the distance between the oxygen atoms of the donor and acceptor groups for all the states relevant to the ESIPT reaction are collected. The experimental distance in the solid state, obtained from X-ray dispersion, is also provided in the table. Interestingly, the discrepancy between the experimental and the calculated value is the largest for 10-HHBF. The calculated distances are quite similar in both excited states, being the largest difference for the excited tautomers. Again, according to the calculations, if the kinetics of the ESIPT reaction are controlled by the distance between these groups in the N\* state, both molecules should be reactive.

Table 6Calculated distance between donor and acceptor oxygen atoms D-A [Å] for optimized geometricstructures in the ground state for normal (N) and tautomer (T) forms and first singlet excited state for normal $(N^*)$  and tautomer (T\*) forms.

	1-HHBF	10-HHBF				
Ν	2.86 (2.88) <sup>(a)</sup>	2.84 (3.00) <sup>[b]</sup>				
N*	2.78	2.80				
T*	2.76	2.69				
Т	2.63	2.73				
<sup>[a]</sup> reference [30] <sup>(b)</sup> X-Ray measurements						

The frontier orbitals for both molecules are represented in the (ESI Fig. A.15). Taking into account the different position of the OH group, state by state the structures of 1- and 10-HHBF are also very similar: in both cases a large increase of the charge density is expected to happen upon excitation of the N form.

#### 3.4 Discussion

The major question rising from the photophysical properties of 1-HHBF and 10-HHBF is why there is a dual fluorescence in the former and not in the latter. Two possible explanations, not mutually exclusive, are that either the T\* form in 10-HHBF has a very small radiative rate constant, or that the forward ESIPT rate constant to form it is much smaller than the decay rate constant of the N\* state. Comparing the collected properties for both molecules might help clarifying this thrilling mystery.

The X-ray data provide with an important clue regarding the strength of the intramolecular H-bond: in 10-HHBF the distance between the enol O and the keto O is larger than in 1-HHBF -3.00 vs 2.88 Å (Table 6). This leaves 10-HHBF out of range (2.713-2.919 Å) in the Table 2 of reference [7] for the compounds of the same family showing ESIPT. However, there is a fundamental difference in these structures: in 10-HHBF a trimer linked by intermolecular H-bonds is deduced (ESI Fig. A.14a,b).

The <sup>1</sup>H-NMR data are not congruent with the trends observed for the *tert*-butyl derivatives [7] of the chemical shift of the enol H with the strength of the intramolecular H-bond: for 10-HHBF this corresponds to 9.48 ppm (broad signal) (ESI Fig. A.1a,b <sup>1</sup>H NMR), while for 1-HHBF we found 8.67 ppm (narrow signal) (ESI Fig. A.2a,b <sup>1</sup>H NMR). The same is true for the position in the infrared (IR) spectrum of the OH stretching transition: it is placed at similar wavenumbers for both molecules within the range typically attributed to the H bonded OH (ESI Fig. A.3-4). IR experiments, performed in the solid state and with a large packing of the molecules, probe the H atom and suggest that in both molecules it is involved in a H-bond, though don't allow to discern between intra- and intermolecular classes.

Regarding the structure of the electronic absorption spectra, in apolar solvents it is much more pronounced for 10-HHBF than for 1-HHBF suggesting a weaker H-bonding for the former. In polar solvents the structure becomes less pronounced in both molecules. Adding water to THF has the same effect (ESI Section7).

The extinction coefficient of the least energetic absorption transition is larger by a factor 2.5 for 10-HHBF than for 1-HHBF in CHEX. On the contrary, the next transition has similar extinction coefficient in both molecules. This points to a quite important effect of the H-bonding also in this quantity and being this bond weaker in 10-HHBF than in 1-HHBF.

The sensitivity to water impurities, as shown in the ESI (Fig. A.9-10), in an experiment in which water was added in a controlled manner to dry THF, is much larger in the case of 10-HHBF than in that of 1-HHBF. This also points towards a more accessible H-bonding site for

the solvent in the former molecule, and therefore to a weaker intramolecular H-bond. This fact could explain the observations in IR and <sup>1</sup>H-NMR if we admit small traces of water in these samples, despite being the <sup>1</sup>H-NMR probe for 10-HHBF much drier than for 1-HHBF (see the region around 1.5 ppm in the <sup>1</sup>H-NMR spectra collected in the ESI Fig. A.1a and Fig. A.2a).

The emission spectra of the normal form shifts to the red in both cases with the solvent polarity. On the contrary, in 1-HHBF the emission band of the tautomer doesn't shift and simply gets weaker with the same change of medium. The former observed shift indicates that the excited state of the normal form has a larger dipole moment than its ground Franck-Condon state, while the tautomer dipole moments are similar in both states. The absolute values of the N\* and T\* dipole moments cannot be accessed from these measurements, although a smaller dipole moment for T\* in 1-HHBF would be congruent with the decrease of its emission intensity. This is because its relative energy would then increase in polar media with respect to the more stabilized N\* due to its larger polarity. However, this speculation is purely based on the relative energies of the states and do not take into account the polarity effects on the energy barrier for the ESIPT, which could also be important.

In both molecules the quantum yields of fluorescence are quite modest, as it is usually the case for keto containing chromophores subject to large intersystem crossing to the triplet state (ISC), in agreement with the El-Sayed rules [31,5]. The quantum yield of 10-HHBF is larger by a factor of 3 than that of 1-HHBF in all solvents of polarity below that of ACN. The lifetimes are larger by a factor of 2. From the extinction coefficient in CHEX, the radiative rate constant of 10-HHB is expected to be larger in its normal form than that of 1-HHBF. Although it is difficult to access this quantity for 1-HHBF because of the presence of excited state reaction, we can make a comparison using a solvent in which most of the emission appears to be from the N\* state: ACN. Even in this solvent the ratio  $\phi_F/\tau_F$  is about 2 times larger in 10-HHBF, in line with the mentioned difference in extinction coefficients (Table 4). Then, the drop in the lifetime and quantum yield of 10-HHBF with reducing the polarity of the medium can be attributed to the accessibility to the triplet  $n\pi^*$  state and a larger ISC. This would explain this variation without needing to invoke ESIPT. In summary, the observed behaviour of the fluorescence of 10-HHBF can be explained assuming a complete lack of ESIPT, rather than a small radiative rate constant of the tautomer.

The intermolecular H-bonding deserves a discussion apart. We have already mentioned the effects on the absorption spectra, quite simple to interpret in terms of formation of a complex, or even total abstraction of the proton of the enol group; the difference between both molecules, according to the experiment in THF with added water, (ESI section 7) relies on the better availability of 10-HHBF to intermolecular H-bonding. The

comparison of the emission spectra in THF and MeOH leads us to think that MeOH binds preferentially to the keto group of 1-HHBF or that the H-bonding to this group affects more strongly the photophysics of the molecule. This argument is based on the similarity of the Kamlett-Taft parameters for THF and MeOH, which differ significantly only in the H-bond donating ability of the solvent (parameter alfa) [32]. On the other hand, the emission bands in MeOH could be attributed to deprotonated forms of the HHBF molecules (see ESI section 7 for further discussion). The similarities in 1-HHBF and 10-HHBF spectra in this solvent would be indicative of similar basicities of their keto groups. Therefore, the differences in ESIPT cannot be attributed to the increased charging of this atom upon excitation of the normal forms, as suggested in [12,13,15]. It is clear in any case that such an increase in charge density is rather a necessary condition for the ESIPT to happen. Finally, a representation of the spectra in the wavenumber scale shows a congruent and continuous shift of the emission spectra explainable by dipolar solvation and the discussed specific interaction in MeOH (ESI Fig. A.8).

In summary most of the data point towards a lack of ESIPT in 10-HHBF rather than to a very low quantum yield of the tautomeric form. Apparently, the O-O distance is larger than in the 1-HHBF ground state, hindering kinetically the ESIPT reaction. Additionally, it is quite likely that the reason is a higher energetic cost of the tautomer formation in this molecule from the normal precursor. This may be explained considering that the structure of 10-HHBF plays against the ESIPT: such a reaction would lead to an important decrease of the aromaticity in both the benzene and the naphthol rings (Scheme 2). [2c, 11]. Unfortunately, the performed TDDFT calculations do not help in this case as they fail to reproduce the correct energies of the tautomers. This deficiency has been observed in the past with many different methods [2c,12, 15]. Nevertheless, if the error in the energy of the tautomeric forms is systematic, and thus correctable by constant factor, the trend obtained from the TDDFT calculations is an increase of the ESIPT reaction on going from 1- to 10-HHBF. If this is the case, the explanation for the lack of reaction in the latter molecule should be found in a larger kinetic barrier than in the former. This would be in agreement with the larger distance between donor and acceptor groups found in the X-ray measurement, although not in the calculation.



**Scheme 2** Representative resonant tautomer structures of 10-HHBF and 1-HHBF. 1-HHBF retains the aromaticity of the naphthalene moiety, 10-HHBF doesn't. The opposite is true for the benzene moiety, although in 1-HHBF it is compensated by the extended pi-conjugation with the keto group and the 5-carbon ring.

#### 4. Conclusions

We have presented a comparative study of two structural isomers: the known 1-HHBF and the newly designed 10-HHBF, fluorophores with appropriate structures for ESIPT.

We have found a straightforward and selective method for the synthesis of 10-HHBF, based on the sequence of Fries rearrangement of 1-naphthyl benzoate followed by spontaneous cyclization. Conversely, under the same conditions, phenyl 2-naphthoate doesn't provide the expected 1-HHBF, but undergoes only Fries rearrangement, still however with complete *ortho*-regioselectivity.

Both compounds are highly sensitive to water and possibly to other proton donating agents, as we have observed in absorption and, even more pronouncedly, in emission and excitation spectra.

10-HHBF does not show dual emission, in contrast to 1-HHBF. There are two possible explanations for this: either there is no ESIPT or the tautomer has a very small fluorescence quantum yield. From the comparison between the spectroscopic data collected for both compounds we conclude that the ESIPT reaction in 10-HHBF is not occurring.

The possible reasons for this change of behaviour with the position of the hydroxyl group would be a larger separation between the donor and the acceptor groups in 10-HHBF and a less stable excited state tautomer due to a drastic decrease of its aromaticity. Very small molecular details may control the appearance of secondary emission bands from

excited tautomers and much care must be taken when designing new molecules intended as single emitters for WOLED applications.

#### Acknowledgements

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#### Appendix A: Supplementary data

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## Appendix A

## **Supporting Information for**

## Frustrated Excited State Intramolecular Proton Transfer in 10-Hydroxy-11*H*-benzo[*b*]fluoren-11-one: synthesis and photophysics

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## 1. Synthesis

O-acylation of phenol in diluted TfOH according to the known procedure [1].

Phenyl 2-naphthoate (1) [2]



Phenol (263 mg, 2.8 mmol) and 2-naphthoyl chloride (1.07 g, 5.6 mmol, 2 eq.) were dissolved in 1% TfOH/CH<sub>3</sub>CN (10 ml). The reaction mixture was stirred at room temperature for an hour, then poured into cold water and extracted with ethyl acetate. The organic layer was washed with 1 M HCl, saturated NaHCO<sub>3</sub>, and saturated NaCl, and dried over Na<sub>2</sub>SO<sub>4</sub>, then filtered. The filtrate was concentrated and chromatographed SiO<sub>2</sub> 70-230 Mesh, hexane : ethyl acetate (95:9) to afford O-acylated products (**1**) as a white powder, 686 mg (99%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.79 (s, 1H), 8.20 (dd, J = 8.6, 1.7 Hz, 1H), 8.00 (dd, J = 8.0, 0.6 Hz, 1H), 7.93 (dd, J = 8.5, 11.4 Hz, 2H), 7.53 - 7.67 (m, 2H), 7.41 - 7.49 (m, 2H), 7.25 - 7.32 (m, 3H); 13C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.3, 151.1, 135.8, 132.5, 131.9, 129.5, 129.5, 128.6, 128.4, 127.8, 126.8, 125.9, 125.5, 121.8.

1-naphthyl benzoate (4) [1]



1-Naphthol (500 mg, 3.47 mmol) and benzoyl chloride (1.2 ml, 10.4 mmol, 3 eq.) were dissolved in 1% TfOH/CH<sub>3</sub>CN (10 ml). The reaction mixture was stirred at room temperature for an hour, then poured into cold water and extracted with ethyl acetate. The organic layer was washed with 1 M HCl, saturated NaHCO<sub>3</sub>, and saturated NaCl, and dried over Na<sub>2</sub>SO<sub>4</sub>, then filtered. The filtrate was concentrated and purified by flash chromatography on silica gel 70-230 Mesh with hexane: ethyl acetate (95:5) to afford O-acylated product **4** as a colorless oil 766 mg (89 %).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.29 - 8.41 (m, 1H), 7.92 - 7.98 (m, 1H), 7.89 (dd, *J* = 6.9, 2.5 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.64 - 7.71 (m, 1H), 7.45 - 7.58 (m, 3H), 7.38 (dd, *J* = 7.5, 1.0 Hz, 1H).













605.65-

Fig. A.3 IR (neet) of 1-HHBF

600 cm-1



## 4. Crystallographic data

Crystallographic data for the 10-HHBF reported in this paper have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, 129 Cambridge CB21EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 1853657.

Cry	stal data for 10 -HHBF
Chemical formula	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub>
Formula weight [g/mol]	246.25
Crystal appearance	Yellow plate
Crystal size [mm]	0.065 x 0.118 x 0.743
Crystal system	orthorhombic
Space group	P 21 21 21
	Init cell parameters
a [Å]	5.2992(2)
<i>b</i> [Å]	11.5774(5)
<i>c</i> [Å]	19.0917(8)
α [°]	90
в [°]	90
γ [°]	90
<i>V</i> [Å <sup>3</sup> ]	1171.29(8)
Z	4
D <sub>calc.</sub> [g/cm <sup>3</sup> ]	1.396
F(000)	512
θ range [°]	4.47 to 68.12°
Absorption coefficient	0.732

u [mm <sup>-1</sup> ]	
Absorption correction	numerical
Max. and min. transmission	0.9540 and 0.6120
	-5<=h<=6,
Index ranges	-13<=k<=13,
	-22<=l<=22
No. of measured reflections	18666
No. of independent reflections	2136 [R <sub>int</sub> = 0.0686]
Completeness	99.8%
Refinement st	atistic
Final R indices: R <sub>1</sub> , wR <sub>2</sub>	0.0345, 0.0653
Goodness-of-fit on F <sup>2</sup>	1.094
Data/restraints/parameters	2136 / 0 / 213
R indices (all data):R <sub>1</sub> , wR <sub>2</sub>	0.0508, 0.0703
Absolute structure parameter	0.3(4)
Largest diff peak and hole [eÅ <sup>-3</sup> ]	0.091 and -0.098

Table A.1 Crystal data and structure refinement for compound 10-HHBF.



Fig. A.5 Ellipsoid representation of 10-HHBF. The ellipsoids are drawn at the 50% probability level.

## 5. Absorption spectra vs excitation spectra in different solvents

Absorption spectra are the same as those presented in the main text, and the excitation spectra from the same samples as those used for the emission spectra presented in the main text in eight solvents: CHEX (cyclohexane), AE (amyl ether), EE (ethyl ether), TOL (toluene), BA (butyl acetate), THF (tetrahydrofuran), ACN (acetonitrile), MeOH (methanol).

In some spectra the Rayleigh dispersion and Raman lines have not been removed.



**Fig. A.6a** The absorption spectrum for 10-HHBF in CHEX (cyclohexane, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 445 nm (cyan line),  $\lambda_{em}$  = 555 nm (pink line).



**Fig. A.6b** The absorption spectrum for 10-HHBF in AE (amyl ether, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 453 nm (cyan line) with band from Rayleigh dispersion (453 nm),  $\lambda_{em}$  = 522 nm (pink line).



**Fig. A.6c** The absorption spectrum for 10-HHBF in EE (ethyl ether, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 462 nm (cyan line) with band from Rayleigh dispersion (462 nm) ,  $\lambda_{em}$  = 482 nm (pink line).



**Fig. A.6d** The absorption spectrum for 10-HHBF in TOL (toluene, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 464 nm (cyan line) with band from Rayleigh dispersion (464 nm),  $\lambda_{em}$  = 534 nm (pink line).



**Fig. A.6e** The absorption spectrum for 10-HHBF in BA (butyl acetate, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 461 nm (cyan line) with band from Rayleigh dispersion (461 nm),  $\lambda_{em}$  = 526 nm (pink line).



**Fig. A.6f** The absorption spectrum for 10-HHBF in commercial THF (tetrahydrofuran, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em} = 464$  nm (cyan line),  $\lambda_{em} = 524$  nm (pink line).



**Fig. A.6g** The absorption spectrum for 10-HHBF in ACN (acetonitrile, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 482 nm (cyan line),  $\lambda_{em}$  = 498 nm (pink line).



**Fig. A.6h** The absorption spectrum for 10-HHBF in MeOH (methanol, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 505 nm (cyan line),  $\lambda_{em}$  = 524 nm (pink line).



**Fig. A.7a** The absorption spectrum for 1-HHBF in CHEX (cyclohexane, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em} = 447$  nm (cyan line) with band from Rayleigh dispersion (447 nm) and Raman (396 nm);  $\lambda_{em} = 572$  nm (pink line).



**Fig. A.7b** The absorption spectrum for 1-HHBF in AE (amyl ether, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 482 nm (cyan line) with band from Raman (422 nm);  $\lambda_{em}$  = 578 nm (pink line).



**Fig. A.7c** The absorption spectrum for 1-HHBF in EE (ethyl ether, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em} = 458$  nm (cyan line) with band from from Rayleigh dispersion (458 nm) and Raman (405 nm);  $\lambda_{em} = 580$  nm (pink line).



**Fig. A.7d** The absorption spectrum for 1-HHBF in TOL (toluene, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 470 nm (cyan line) with band from Rayleigh dispersion (470 nm) and Raman (412 nm);  $\lambda_{em}$  = 587 nm (pink line).



**Fig. A.7e** The absorption spectrum for 1-HHBF in BA (butyl acetate, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 470 nm (cyan line) with band from Rayleigh dispersion (470 nm) and Raman (413 nm);  $\lambda_{em}$  = 582 nm (pink line).



**Fig. A.7f** The absorption spectrum for 1-HHBF in commercial THF (tetrahydrofuran, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em} = 471$  nm (cyan line) with band from Rayleigh dispersion (471 nm) and Raman (414 nm);  $\lambda_{em} = 495$  nm (brown line) with band from Rayleigh dispersion (495 nm) and Raman (431 nm);  $\lambda_{em} = 582$  nm (pink line);  $\lambda_{em} = 632$  nm (grey line).



**Fig. A.7g** The absorption spectrum for 1-HHBF in dried ACN (dry acetonitrile, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 498 nm (cyan line) and  $\lambda_{em}$  = 550 nm (pink line).



**Fig. A.7h** The absorption spectrum for 1-HHBF in MeOH (methanol, black line) compared with the normalized fluorescence excitation spectra:  $\lambda_{em}$  = 545 nm (pink line).

#### 6. Absorption and emission spectra in another representation



**Fig. A.8** Absorption spectra of 10-HHBF (b), and of 1-HHBF (d), fluorescence emission spectra of 10-HHBF (a) and of 1-HHBF (c) in eight solvents: CHEX (cyclohexane, black lines), AE (amyl ether, dark blue lines), EE (ethyl ether, light blue lines), TOL (toluene, red lines), BA (butyl acetate, light green lines), THF (tetrahydrofuran, dark green lines), ACN (acetonitrile, grey lines), MeOH (methanol, pink lines). These spectra are represented according to the recommendations of ref. [3]

# 7. Additional data and discussion about the influence of water and base in the spectroscopic measurements

The origin of the additional band in the absorption spectra in 1-HHBF and 10-HHBF was not straightforwardly understandable, but certainly was not connected to any contamination of the compound or to a second tautomer in ground state. Moreover, we observed that the shape of the emission band of both compounds often depends on the excitation wavelength, and such effect is more pronounced on moving to lower energies. This should not be the case for none of the molecules as it was assumed that there is no tauromerism in the ground state. We suggest that the additional band could appear as a result of external hydrogen bonding or of proton transfer, generated with water or other appropriate species. To prove our hypothesis we performed additional experiments.



**Fig. A.9** Influence of water in the absorption spectrum of 10-HHBF in THF. Thick black line: THF dried over A3 molecular sieve. Black and grey lines: from 0 to 140  $\mu$ l of water added to 3 ml of THF; Orange line: 190  $\mu$ l; pink line: 290  $\mu$ l; blue line 390  $\mu$ l. From 0 to 90  $\mu$ l the amount of water increases by 10  $\mu$ l; from 90 to 190  $\mu$ l the amount of water increases by 50  $\mu$ l. The spectra have been corrected for the dilution factor. The equilibrium constant of the reaction for 10-HHBF with H<sub>2</sub>O in THF can be estimated to be about 1 M<sup>-1</sup>



**Fig. A.10** Influence of water in the absorption spectra of 1-HHBF in THF: dry THF– black line; 50  $\mu$ l of water in 3 ml of THF – cyan line; 100  $\mu$ l of water in 3 ml of THF – pink line.

All former measurements were done in commercially available solvents of spectroscopic grade, which in principle contain very small traces of water.

In fact, after having dried further THF, we noticed that in absorption an additional band appears depending on the added amount of water to the solvent, and the effect is much stronger for compound 10-HHBF (Fig. A.9) than for 1-HHBF (Fig. A.10).

Also, in dry THF the emission band of 1-HHBF became almost independent of the excitation wavelength (although when exciting in the red edge it still changes despite the invariance of the shape of the absorption band) (Fig. A.11).



**Fig. A.11** The registered fluorescence intensity for 1-HHBF in dry THF (dried over A3 sieves) - influence of water on the emission spectra: dry THF,  $\lambda_{ex}$  = 360 nm – grey line; dry THF,  $\lambda_{ex}$  = 460 nm, registered fluorescence intensity multiplied by 10 – black line; 50 µl of water in 3 ml of THF – cyan line; 100 µl of water in 3 ml of THF – pink line.

Thus, we suggest that a second species is produced by the creation of an external hydrogen bond between the compound and water, or by proton transfer. In compound 1-HHBF the dual emission is destroyed by this effect (Fig. A.11), and in 10-HHBF the emission band is broader and shifted to the red respect to the N band (Fig. A.12); in both cases the final position of the new band is quite similar (not identical). In fact, the band(s) observed in THF with added water, is very similar to the band(s) observed in MeOH.



**Fig. A.12** The registered fluorescence for 10-HHBF in dry THF (dried over A3 sieves) - influence of water on the emission spectra: dry THF – black line and 290  $\mu$ l of water in 3 ml of THF – pink line.

The sensitivity to water of compound 10-HHBF seems to be much larger than for 1-HHBF. It is still necessary to determine if the water influence is due to just H-boning or proton transfer. In the second case the produced species would be the anion of the HHBFs. We have

performed experiments adding increasing amounts of the base sodium bis(trimethylsilyl)amide (NaHMDS) in which presence the proton transfer to the base is the only possibility. As it can be seen in Fig. A.13, the changes in the spectra of absorption and emission are not like in the presence of water (Fig. A.9): in absorption the effect of the added base doesn't saturate at the level it does with water. In fluorescence the change is quite drastic and it seems to lead to a species with a larger emission quantum yield and with a spectrum much more structured than that seen in presence of water.



**Fig. A.13** Influence of base (NaHMDS) in the absorption and emission spectra ( $\lambda$ ex 385 nm) of 10-HHBF in THF: dry THF- blue line; 27 increments of the concentration of the base from 3E-7 to 3E-5 M in absorption and 13 in fluorescence -red lines; from 4.7E-5 to 3E-4 M of base –grey lines. In all the measurements the 10-HHBF concentration was kept at a constant value of 2.1E-5 M.

We conclude thus that the origin of the effect produced by adding water, or of the spectral position in methanol is different than the observed when adding a strong base, and is coherent with H-bonding and not with the formation of the anion. Moreover, the H-bonding is most likely from the solvent (added water or MeOH) to the keto group of the HHBF, rather than the other way around: in the latter case it wouldn't be understandable the differences observed in the spectra between dry THF nad MeOH.

Also the sensitivity for homo-intermolecular interactions seems to be stronger. This effect is clearly observed in X-Ray measurements. In the crystal structure of 1-HHBF oxygen atoms engage in intramolecular hydrogen bonding and almost do not take part in intermolecular bonds (Fig. A.14a). A different situation is observed for 10-HHBF, whose molecules are organized in groups of three connected by intermolecular hydrogen bonds between the keto oxygen and the hydroxyl group of a second molecule, and between hydroxyl group and a keto oxygen of a third one (Fig. A.1b).



Fig. A.14a View of intermolecular interactions in crystal structure of compound 1-HHBF.



Fig. A.14b View of Intermolecular interactions in crystal structure of compound 10-HHBF [4].

The influence of water could be also observed in the NMR spectra. Some minor shifts of the signals for 1-HHBF are observed with respect to the literature data, what can be connected with different amounts of water in CDCl<sub>3</sub>. For 10-HHBF the signal from H-OH is much broader than for 1-HHBF what abounds in the stronger intermolecular hydrogen bonding with the environment in this case.

### 8. Computational Data

The theoretical calculations were performed with the Gaussian 09 program [5]. Geometry optimization for the ground state and first singlet excited state of molecules (for both tautomers) was carried out using density functional theory (DFT) and time-dependent density functional theory (TDDFT) respectively, with CAM-B3LYP and B3LYP hybrid function and the 6-311+G(2d,2p) basis sets. The solvent, cyclohexane, was modelled with IEFPCM within the SCRF method. No constrains for symmetry, bonds, angles, or dihedral angles were employed in the geometry optimization calculations. All the local minima were confirmed by the absence of an imaginary mode in vibrational analysis calculations.



**10-HHBF** 

Fig. A.15 Calculated frontier molecular orbitals (HOMO and LUMO) of 10-HHBF and 1-HHBF in the ground state for normal (N) and tautomer (T) form and first singlet excited state for normal (N\*) and tautomer (T\*) form.

-							
	1-HHBF		10-HHBF				
	E/kcal mol <sup>-1</sup>	λ/nm, f	E/kcal mol <sup>-1</sup>	λ/nm, f			
N*	72.918	460, 0.053	72.957	448, 0.088	CAM-B3LYP cyclohexane		
		363, 0.178		379, 0.190			
	62.935	512, 0.063		495, 0.101	B3LYP cyclohexane		
		402, 0.116	63.220	409, 0.106			
Т*	77.705	520, 0.314	73.999	517, 0.175	CAM-B3LYP cyclohexane		
		447, 0.117		446, 0.324			
	67.396	603, 0.177	66.589	546, 0.113	B3LYP cyclohexane		
		491, 0.168		481, 0.252			
Ν	1.057		0		CAM-B3LYP cyclohexane		
	0.848		0		B3LYP cyclohexane		
Т	16.017		8.951		CAM-B3LYP cyclohexane		
	14.307		8.118		B3LYP cyclohexane		

**Table A.2** Calculated energy in the relaxed state (E) and oscillator strength (f) for 1-HHBF and 10-HHBF: CAM-B3LYP cyclohexane vs B3LYP cyclohexane.

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## Highlights:

- 1. Comparative study of two structural isomers of hydroxybenzofluorenone
- 2. Dual band white light vs single band emission of positional isomers
- 3. Frustrated ESIPT as origin of the observed difference
- 4. Straightforward and selective synthesis of 10-Hydroxy-11H-benzo[b]fluoren-11-one