Luminescent liquid crystal materials based on unsymmetrical boron difluoride β-diketonate adducts†

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A strategic design based on the use of asymmetrically 1,3-alkyloxyphenyl substituted β-diketonate ligands towards the BF_2 group allowed us to find unsymmetrical compounds that, in addition to a high photoluminescent quantum yield, possess a liquid crystal behaviour, which is related to the presence of the banana-shaped liquid crystal mesophases B_1.

Introduction

In recent years a wide range of emissive materials have been reported for use in electroluminescent devices due to their possible applications in modern technologies such as molecular recognition, fluorescence probes and microscopy imaging, electroluminescent materials, electro-optical sensors, lighting and organic light-emitting diodes (OLEDs), among many others.[1–5]

As an extension of these materials, the luminescent liquid crystals are a class of materials which are especially interesting because the molecular self-organization can be exploited to improve device performance in order to achieve linear polarized electroluminescence.[6] Other interest in these materials proceeds from their carrier high charge mobility as well as their ability to develop defect-free layers.[7]

Therefore achieving liquid crystal and luminescence properties combined in the same material led to intrinsically luminescent mesogens, which constitute a realistic challenge in flat-panel technology.[8]

On the other hand, the research of photophysical and photochemical properties of boron difluoride β-diketonate derivatives permanently increases because they exhibit high emission quantum yields in the visible range, being potentially used as components of light emitting devices. As an interesting consideration, it is observed that the intensity of luminescence of those compounds is dependent on their geometry and electronic structure.[9]

In a previous paper we described the preparation and a preliminary description of the photoluminescent behaviour of a family of related boron derivatives containing β-diketonates with alkyloxyphenyl substituents of the type $[BF_2(OO^{2R(n,n)})]$ ($OO^{2R(n,n)}$ = 1,3-di(4-*n*-alkyloxyphenyl)propane-1,3-dionate).[10] New studies have also been recently reported to provide evidence of the lack of excimer formation being their low tendency to self-aggregation an interesting result for developing applications based on highly concentrated solutions of the dye or in the solid phase (OLEDs, fluorescent sensors, solid laser dyes, *etc.*).[11]

However, our previous results on the symmetrically substituted compounds confirmed that, although all of them were highly luminescent materials, none of them exhibited liquid crystal behaviour.[10,11]

At this point we have to take into account that in designing thermotropic liquid crystals, anisometric rod-like or disk-like molecules exhibit the common prerequisite to perform this behaviour. However, liquid crystals based on a molecular banana shape with a bent-core[12] are not extensively reported, especially for those based on non-organic molecules.[13] This kind of material is growing in importance since the discovery of polar switching and their potential application in display technology.[14]

In the previous paper we also reported the crystal structure of the compound $[BF_2(OO^{2R(4,4)})]$ which can be considered as having a molecular banana shape with a bent-core (Fig. 1) related to that observed in several organic compounds.

On this basis we decided to explore the thermal behaviour of unsymmetrical adducts of the type $[BF_2(OO^{2R(12,n)})]$ ($OO^{2R(12,n)}$ = 1-(4-*n*-dodecyloxyphenyl)-3-(4-*n*-alkyloxyphenyl)-propane-1,3-dionate), related to those symmetrical ones previously described by us.[10,11] These were built by the simple introduction of different alkyl chain lengths in the 1,3

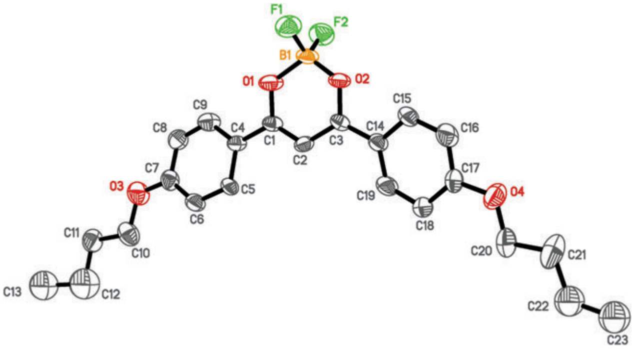

Fig. 1 ORTEP plot of the symmetrical adduct $[BF_2(OO^{2R(4,4)})]$.[10]

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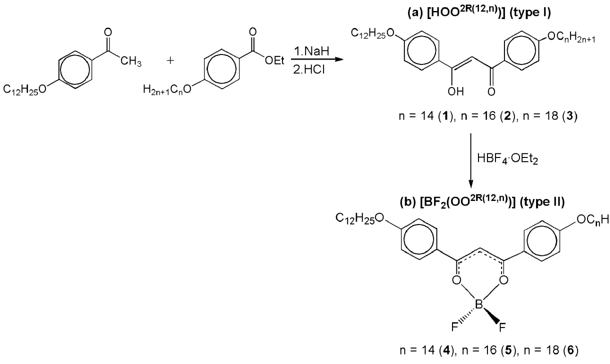

Scheme 1

substituents of the β-diketonate ligands. We consider that the asymmetry of those bent-core molecules should play an important role in the steric packing of the molecular self-organization at the mesophase.

In this work we report the mesomorphic behaviour and luminescent properties of the unsymmetrical bent-core compounds of the type [BF$_2$(OO$^{2R(12,n)}$)] (type **II**) (Scheme 1b) as well as the liquid crystal behaviour of the precursors β-diketones ligand (Scheme 1a; type **I**). All the compounds were designed with two unsymmetrical arms at the 1, 3 positions of the β-diketonate ligand. In particular different alkyl chain with 14, 16 or 18 carbon atoms at one of these positions (1 or 3) were used to elongate one of the arms, while the other arm at the other position is maintained with the same alkyl length with 12 carbon atoms.

Results and discussion

Synthesis and characterisation

The β-diketone ligands (**1–3**) and the boron difluoride adducts (**4–6**) were prepared according to Scheme 1 and unambiguously characterized by elemental analysis, IR and ^{1}H-NMR spectroscopies.

The CDCl$_3$ solution ^{1}H-NMR spectra of the ligands **1–3** show well defined signals for the β-diketone core and the alkyloxyphenyl substituents. The presence of a singlet at *ca.* 6.7 ppm corresponding to the C(2)H group of the β-diketone core, a signal at *ca.* 14.8 ppm from the OH group and a singlet at *ca.* 4.5 ppm confirms the existence in solution of keto and enol tautomers. From the ^{1}H-NMR data it is deduced that the enol is the major form but the NMR time scale do not allow to distinguish between the two possible enol forms a and b (Fig. 2).

In the aromatic region duplicated doublets at *ca.* 8.0, 7.9 and 7.0, 6.9 ppm corresponding to the *ortho* and *meta* protons of the phenyl rings of the two tautomeric keto and enol forms are observed.

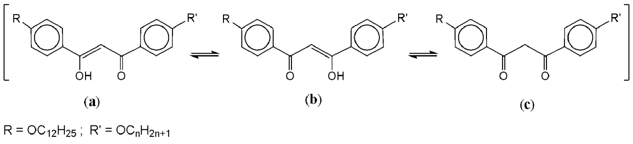

Fig. 2 Keto-enol equilibrium.

The IR spectra in CH$_2$Cl$_2$ solution shows two bands at 1711 and 1683 cm^{-1} corresponding to the ν(CO) absorption in agreement with the presence of the keto and enol forms respectively. On the other hand the IR spectra in KBr show three bands at 1676, 1607 and 3450 cm^{-1} assigned to the ν(CO), ν(C=C)$_\varnothing$ and ν(OH) absorptions confirming the sole presence of the enol form in the solid state.

The ^{1}H-NMR spectra of the compounds of the type **II** (**4–6**) in CDCl$_3$ at room temperature show the characteristic signals of the ligand β-diketonate bearing alkyloxyphenyl substituents.

The proton of the central C(2)H group of the diketonate core appears as a singlet at *ca.* 7.0 ppm consistent with the coordination of the ligand as enolate form. The spectra also show two doublets at *ca.* 8.1 and 7.0 ppm for the *ortho* and *meta* aromatic protons of the phenyl ring respectively.

The IR spectra in solid state display the characteristic bands of the carbonyl groups of the β-diketonate ligands at *ca.* 1562 cm^{-1} bathochromically shifted with respect to the free β-diketone ligand (*ca.* 1676 cm^{-1}). The lack of the ν(OH) absorption bands (from the enol tautomer of the β-diketone) and the presence of the ν(BO) band at *ca.* 1376 cm^{-1} demonstrate the coordination of the carbonyl groups of the ligand in the β-diketonate form to the boron atom.

Thermal studies

The thermal behaviour of the starting β-diketones (**1–3**) was studied by polarized-light optical microscopy (POM) and differential scanning calorimetry (DSC) (Table 1). The three compounds exhibit enantiotropic mesomorphism showing a SmC mesophase established on the basis of their characteristic *schlieren* texture observed by POM (Fig. 3).

The DSC thermograms show three or four endothermic peaks on heating (Table 1). The first peaks (one or two depending on the diketone) are assigned to solid–solid phase transitions. The last two peaks were related to the melting and clearing processes respectively, these results being consistent with the polymorphic nature of this type of compounds.[15] No significant differences in the mesophases range (*ca.* 7 °C) of compounds **1–3** can be established. By contrast, the melting and clearing points increase with the length of the alkylic chain (that is, with the increase of the asymmetry from **1** to **3**).

Temperature-dependent powder X-ray diffraction (XRD) studies for the β-diketones (**1–3**) gave rise to characteristic patterns of smectic phases in agreement with the SmC mesophases assigned by POM (Table 2). The XRD patterns show two or three sharp maxima in the low-angle region with a reciprocal spacing ratio of 1 : 2 : 3 corresponding to the (0 0 1), (0 0 2) and (0 0 3) reflections of a lamellar mesophase. The diffuse halo due to the liquid-like arrangement of the aliphatic chains also appears at *ca.* 4.5 Å.

The indubitable evidence of mesomorphic behaviour of β-diketones **1–3** was in contrast with the suggested no liquid crystal nature reported in the literature[16] for the compound namely as our β-diketone **1**. However the results obtained for all compounds of the type **I** allow us to establish the absolute identity of those as liquid crystal materials.

Table 1 Phase behaviour of compounds **1–6** determined by DSC

n		Transition	T/°C	ΔH/kJmol^{-1}
14	**1**	Cr → Cr′	72	9.9
		Cr′ → SmC	80	26.5
		SmC → I	87	1.1
		I → SmC	81	−1.0
		SmC → Cr	72	−31.7
16	**2**	Cr → Cr′	71	10.1
		Cr′ → Cr″	81	24.3
		Cr″ → SmC	97	29.7
		SmC → I	103	1.5
		I → SmC	91	−1.8
		SmC → Cr	75	−25.3
18	**3**	Cr → Cr′	76	6.6
		Cr′ → Cr″	83	18.9
		Cr″ → SmC	100	28.1
		SmC → I	114	3.2
		I → SmC	113	−4.4
		SmC → Cr′	80	−24.8
		Cr′ → Cr″	74	−15.3
14	**4**	Cr → Cr′	135	18.6
		Cr′ → B1	141[a]	26.3
		B1 → I		
		I → B1	138[a]	−27.2
		B1 → Cr′		
		Cr′ → Cr	96	−15.6
16	**5**	Cr → Cr′	125	26.6
		Cr′ → B1	139[a]	23.0
		B1 → I		
		I → B1	136[a]	−21.4
		B1 → Cr′		
		Cr′ → Cr	87	−19.0
18	**6**	Cr → Cr′	128	27.4
		Cr′ → B1	139[a]	26.1
		B1 → I		
		I → B1	136[a]	−26.2
		B1 → Cr′		
		Cr′ → Cr	84	−23.6

[a] Overlapped processes.

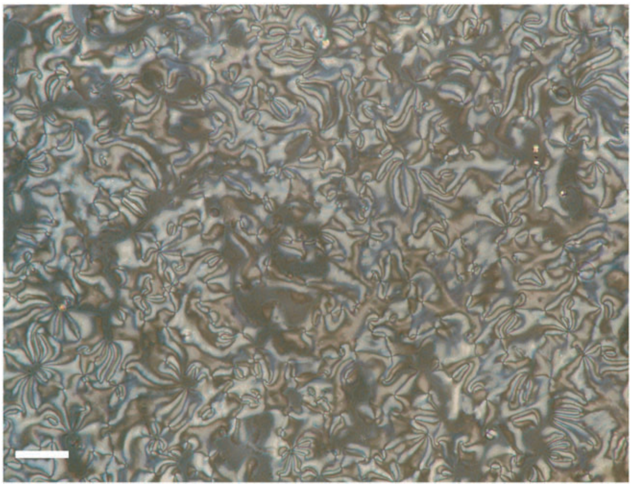

Fig. 3 Texture observed by POM of SmC phase for **2** at 100 °C on heating (the white bar indicates 100 μm).

Thermal behaviour of the boron difluoride adducts **4–6** (type **II**, Table 1) exhibits similar features. The range of the existence of the mesophase found for those adducts is very narrow and the melting temperatures are close to the clearing points. So, we observe the presence of crystal, liquid crystal and isotropic liquid phases partially overlapping, this feature makes it difficult to completely identify the mesophase. However by a careful and precise control of the temperature (each 0.1 °C) we were able to observe of the formation of the mesophase without the presence of crystals or the quick appearance of the isotropic liquid (140.2, 139.8 and 139.6 °C for **4**, **5** and **6** respectively).

In this way the mesophase for the three compounds, was characterized as a mesophase B_1 which seems to exhibit a fluid smectic structure in agreement with the literature data.[17]

The assignment is supported by the mosaic texture and the dendritic growth[17–19] (Fig. 4) observed by POM as well as by XRD studies which will be later discussed. The establishment of that bent-core liquid crystal phase agrees with that expected for the designed bent-core adducts $[BF_2(OO^{2R(12,n)})]$.

The DSC thermograms of compounds **4–6** exhibit similar features. In all cases the DSC thermograms show on heating two endothermic peaks. The first one in the 125–135 °C range is related to a solid-solid phase transition in agreement with X-ray results. The second peak at higher temperatures (*ca.* 140 °C) is assigned to an overlapping of the melting and clearing processes above mentioned.

In order to establish a complete identification of the mesophase and following the above mentioned temperature requirements to be detected, the X-ray diffractograms were registered in different stage at temperatures close to the clearing process being maintained the temperature each stage for several minutes. Several registers were taken for each stage at sequential times. In particular, for compound **6** diffractograms were taken for each stage at 138 and 141 °C on heating and at 141 and 138 °C on cooling. Only on cooling from the isotropic liquid (150 °C) until the appearance of the solid phase (138 °C) we were able to obtain a diffractogram at 141 °C which allow us to establish the presence of a B_1 phase. The two reflection peaks, in the small angle region, indexed as (1 0 1) and (0 0 2), indicate the rectangular columnar arrangement (Table 2).

Once again it was remarkable that in the previous paper above mentioned[16] the authors described the liquid crystal behaviour of a compound considered to be like **4** of our work. However neither the mesomorphic behaviour nor the luminescent properties described for that compound respond to our current data. The absolute characterization of our compounds as well as the regular mesomorphic behaviour found for those allow us undoubtedly to establish their identity. From the best of our knowledge the unsymmetrical compounds $[BF_2(OO^{2R(12,n)})]$ described in this work can be considered between the first materials of these type which exhibit both liquid crystal and luminescence properties.

Luminescence studies

Luminescence studies were carried out both in dichloromethane solution and in the solid state for compounds of the type **II** (**4–6**)

Solution studies. The UV-Vis absorption spectra of dilute solutions (4.45×10^{-6} M) in dichloromethane of all compounds exhibit two absorption bands, the strongest one

Table 2 X-Ray diffraction data for mesomorphic compounds **1–3** (type **I**) and **6** (type **II**)

	T/°C	Phase	Position (°)/2θ	d-spacing/Å	Miller indices (h k l)	Lattice parameters/Å
1	88	SmC	3.3	26.5	0 0 1	c = 26.4
			6.7	13.2	0 0 2	
			19.0	4.7	[a]	
2	90	SmC	3.0	29.0	0 0 1	c = 29.0
			6.1	14.5	0 0 2	
			9.1	9.7	0 0 3	
			19.8	4.5	[a]	
3	105	SmC	2.7	32.2	0 0 1	c = 32.0
			5.5	16.0	0 0 2	
			8.3	10.6	0 0 3	
			19.7	4.5	[a]	
6	141	B_1	2.4	36.5	1 0 1	a = 52.3
			3.5	3.5	0 0 2	c = 51.0

[a] Halo of the molten alkyloxy chains.

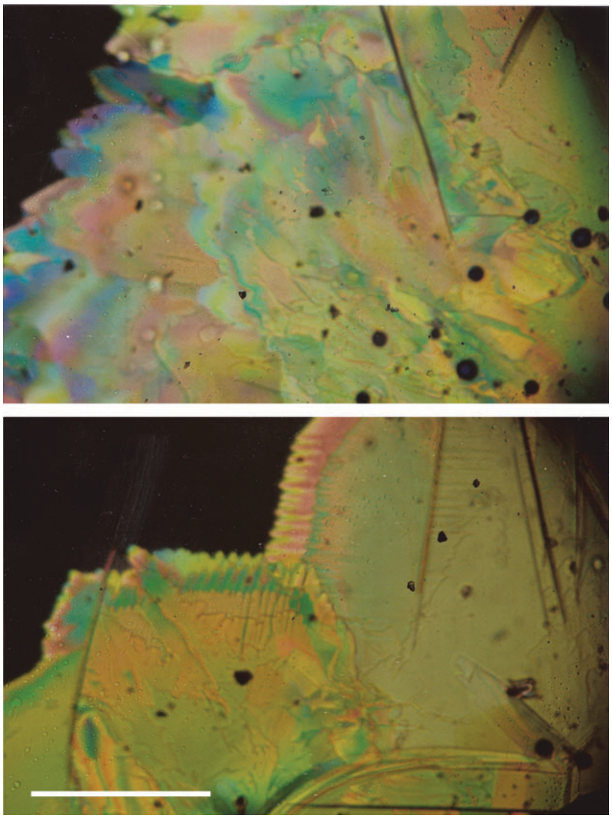

Fig. 4 Textures observed by POM of B_1 mesophase for **4** at 140.2 °C on cooling (the white bar indicates 100 μm).

centered at *ca.* 414 nm (Table 3, Fig. 5). This absorption is characteristic of the electronic π–π* transition of chelating β-diketonate ligands.[20]

The fluorescence spectra display an unresolved vibronic substructure in the blue region with a maximum at *ca.* 440 nm with an excellent photoluminescence relative quantum yield (Φ = 0.95, estimated error of ±5%) using a solution of acridine yellow as standard (Φ = 0.47).[21] The emissive nature of these compounds was markedly higher than that reported for several boron difluoride arylsubstituted-β-diketonates.[9,11] The high quantum yield close to the unity, in addition to the observed absorption in the yellow region and emission in the blue-violet range, makes this compound to be a good candidate as fluorescent biological probes.

Table 3 Absorption (λ_{abs}^{max}) and emission (λ_{em}^{max}) maxima in nm, molar absorption coefficients (ε) in $Lmol^{-1}cm^{-1}$ and fluorescence quantum yields (Φ_F) of the compounds of the type **II** in aerated 4.45×10^{-6} M in dichloromethane solution and in the solid state at room temperature

	n	λ_{abs}^{max} solution[a]	$\varepsilon/10^4$	λ_{em}^{max} solution[b]	Φ_F[c]	λ_{em}^{max} solid[d]
4	14	414	4.3	440	0.95	484
5	16	411	6.8	437	0.95	486
6	18	414	5.6	440	0.95	493

[a] Estimated error: ±1 nm. [b] λ_{ex} = 414 nm; estimated error: ±1 nm. [c] λ_{ex} = 414 nm; estimated error: ±5%. [d] λ_{ex} = 414 nm; estimated error: ±1 nm.

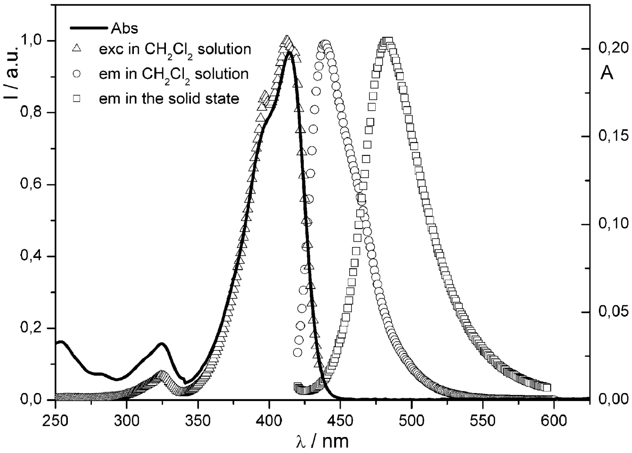

Fig. 5 UV-vis and normalized excitation and fluorescence spectra of adduct **4** in dichloromethane solution and in the solid state at room temperature.

Solid state studies. The emission spectra of the adducts **4–6** exhibit a similar pattern consistent with a broad band peaked at *ca.* 490 nm, bathochromically shifted with respect to the solution emission (Table 3; Fig. 5).

Variable-temperature studies. In order to prove the luminescent behaviour of compounds in the liquid crystal

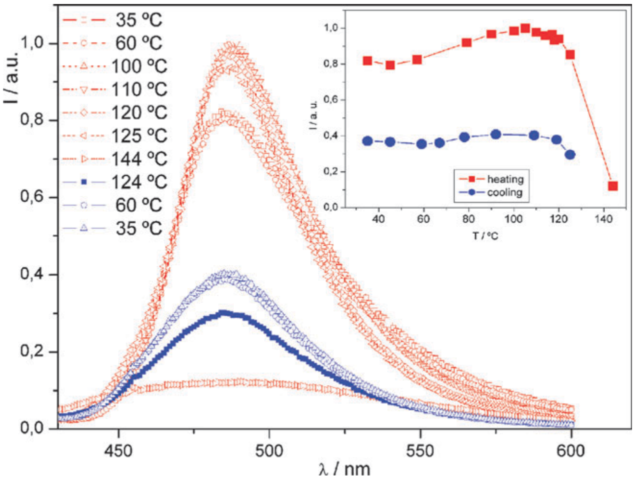

Fig. 6 Fluorescence spectra of compound **4** in solid state as a function of temperature.

state, the emission spectra of the adducts **4–6** were studied at different temperatures from the solid state to the isotropic liquid. The fluorescence spectra were also registered on cooling from the isotropic liquid until the solidification temperature (Fig. 6) all of them exhibiting a similar pattern.

In general terms the behaviour of the emission band on heating shows that the intensity of the fluorescence is maintained until 127 °C and it decreased on increasing the temperature, almost disappearing at *ca.* 145 °C. The pattern of the band is maintained in all temperature range used so much on heating and on cooling (Fig. 6). The above results allow us to establish that the liquid crystal state does not quench the emission.

On cooling, the emission is reversible and increases the intensity when the temperature decreases being the total fluorescence emission rescued until *ca.* 40%. It is noticeable that the emission maximum is maintained in the heating/cooling cycle indicating that the excited state is not modified.

Experimental

Materials and physical measurements

All commercial reagents were used as supplied. The synthetic route to unsymmetrical alkyloxyphenyl-disubstituted β-diketones (type **I**) was carried out following similar procedures to that used for the related symmetrical derivatives.[10,11,15] Commercial solvents were dried prior to use.

Elemental analyses for carbon, hydrogen and nitrogen were carried out by the Microanalytical Service of Complutense University. IR spectra were recorded on a FTIR Thermo Nicolet 200 spectrophotometer with samples as KBr pellets in the 4000–400 cm^{-1} region: vs (very strong), s (strong), m (medium), w (weak).

^{1}H-NMR spectra were performed at room temperature on a Bruker DPX-300 spectrophotometer (NMR Service of Complutense University) from solutions in $CDCl_3$. Chemical shifts δ are listed relative to Me_4Si using the signal of the deuterated solvent as reference (7.26 ppm), and coupling constants J are in hertz. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), m (multiplet). The ^{1}H chemical shifts and coupling constants are accurate to ±0.01 ppm and ±0.3 Hz, respectively.

Phase studies were carried out by optical microscopy using an Olympus BX50 microscope equipped with a Linkam THMS 600 heating stage. The temperatures were assigned on the basis of optic observations with polarised light.

Measurements of the transition temperatures were made using a Perkin Elmer Pyris 1 differential scanning calorimeter with the sample (1–4 mg) sealed hermetically in aluminium pans and with a heating or cooling rate of 5–10 K min^{-1}.

The X-ray diffractograms at variable temperature were recorded on a Panalytical X'Pert PRO MPD diffractometer in a θ–θ configuration equipped with a Anton Paar HTK1200 heating stage (X-ray Diffraction Service of Complutense University).

Absorption spectra were recorded on a JASCO 650 UV spectrophotometer and fluorescence emission on a Horiba-Jobin-Yvon SPEX Fluoromax 4 spectrofluorimeter equipped with a JULABO 32 bath. The linearity of the fluorescence emission *vs.* concentration was checked in the concentration range used (10^{-4}–10^{-6} M). A correction for the absorbed light was performed when necessary. All spectrofluorimetric studies were performed as follows: the stock solutions of the ligands (*ca.* 10^{-3} M) were prepared by dissolving an appropriate amount of the ligand in a 50 mL volumetric flask and diluting to the mark with dichloromethane HPLC or UVA-sol grades. The relative fluorescence quantum yields were determinate by comparison with a standard solution of acridine yellow (AY) in absolute ethanol ($\Phi = 0.47$).[21] In order to avoid the inner filter effects, in all the experiments the absorbance of both compounds was kept below 0.1. The excitation wavelength chosen was the wavelength where both absorption spectra cross it. The emission spectra were performed using the same excitation wavelength for both compounds, and the area of both emission spectra was calculated using the Origin Program. The equation used was:

$$\phi = \phi \times \frac{I}{I_{st}} \times \frac{n^2}{n^2_{st}}$$

where ϕ = unknown fluorescence quantum yield, ϕ_{st} = standard fluorescence quantum yield, n = unknown solvent refraction index, n_{st} = standard solvent refraction index, I and I_{st} = integrated emission spectra.

Fluorescence spectra of solid samples were recorded on the spectrofluorimeter exciting the solid compounds at appropriate λ (nm) using a fiber-optics devices connected to the spectrofluorimeter. The emission spectra as a function of the temperature were recorded in the 300–800 nm range, using a fiber optic system connected to the spectrofluorimeter and the solid samples were heated over a hotplate with an external temperature control provided with a XS intrument digital thermo par.

Preparation of the compounds of the type I: [HOO$^{2R(12,n)}$] (1–3)

The compounds were obtained by Claysen synthesis. To a solution of 0.04 mol of 4-*n*-dodecyloxyacetophenone and 0.1 mol of NaH (60 wt% dispersion in mineral oil) dissolved in dimethoxyethane (300 mL) was added 0.06 mol of the corresponding ethyl 4-*n*-alkyloxybenzoate. The solution was refluxed for 24 h to give a suspension of sodium salts that was left to cool to room temperature, and then a hydrochloric acid solution (*spec. grav.* 1.19) was added to obtain a brown precipitate. The mixture was stirred for 24 h at room temperature. The brown precipitate was filtered off and washed repeatedly with hexane and dried *in vacuo*.

Preparation of the compounds of the type II: $[BF_2(OO^{2R(12,n)})]$ (4–6)

To a solution in dichloromethane (20 mL) of the corresponding β-diketone (0.20 mmol) or sodium β-diketonate (prepared *in situ* from the β-diketone and 0.22 mmol of NaH 60% dispersion in mineral oil), 0.60 mmol of $HBF_4{\cdot}OEt_2$ was added. The mixture was stirred at room temperature for 24 h. The deep-yellow solid formed was filtered off and purified by chromatography using dichloromethane as eluent.

Spectroscopic IR and ^{1}H-NMR data are given for **2** and **5** as selected representative examples of each type of compounds. Data for the other homologues are essentially identical. Yields and elemental analysis are collected in supporting information (ESI†).

$[HOO^{2R(12,16)}]$ (**2**). ν_{max}(KBr)/cm^{-1} 3450w (OH), 1676s (C=O enol form) and 1607s $(C{=}C)_{\varnothing}$. $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1711m (C=O keto form), 1683w (C=O enol form) and 1604m $(C{=}C)_{\varnothing}$. δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (t, ^3J 6.8, CH_3), 1.26 (m, CH_2), 1.80 (m, CH_2), 4.02 (t, ^3J 6.4, OCH_2), 4.52 (s, $C(2)H_2$ keto form), 6.73 (s, C(2)H enol form), 6.92 (d, ^3J 8.9, H_m), 6.97 (d, ^3J 8.5, $H_{m'}$) 7.94 (d, ^3J 8.5, $H_{o'}$), 8.03 (d, ^3J 8.9, H_o), 14.84 (s, OH).

$[BF_2(OO^{2R(12,16)})]$ (**5**). ν_{max}(KBr)/cm^{-1} 1562vs (C=O), 1376m (BO) and 1038s (BF). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (6 H, t, ^3J 6.4, CH_3), 1.26 (44 H, m, CH_2), 1.83 (4 H, m, CH_2), 4.07 (4 H, t, ^3J 6.4, OCH_2), 7.00 (s, C(2)H), 7.00 (4 H, d, ^3J 9.0, H_m), 8.11 (4 H, d, ^3J 9.0, H_o).

Conclusions

In previous studies we reported that compounds $[BF_2(OO^{2R(n,n)})]$ with a banana-molecular shape and identical alkyloxyphenyl substituents possess a strong luminescence in the solid state and in solution, but they were not liquid crystal materials. The strategic introduction of asymmetry in this type of compounds by using substituents of different chain length in the rigid BF_2-diketonate core appears to provide a lateral dipole so favouring the mesomorphic properties. This kind of compound opens the study of new boron difluoride β-diketonates unsymmetrically substituted looking for excellent photoluminescent materials with liquid crystal properties.

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