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Synthesis and Photophysical Properties of Difluoroboron Complexes of Curcuminoid Derivatives Bearing Different Terminal Aromatic Units and a *meso*-Aryl Ring

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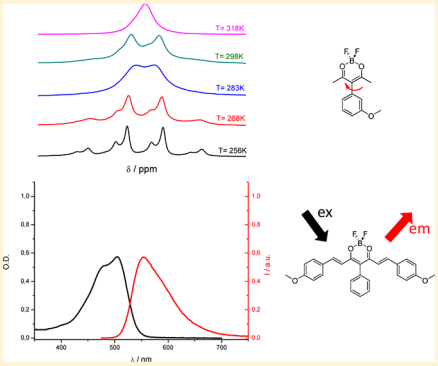
Supporting Information

ABSTRACT: The synthesis of nine curcuminoids and their difluoroboron complexes is described, with seven of them containing a *meso*-phenyl ring. Dynamic ^{19}F NMR confirmed the fact that rotation of that *meso*-aryl fragment is restricted in the latter systems at room temperature and become allowed at higher temperature (>45 °C). The molecular structure of a *meso*-substituted derivative in the solid state showed that the phenyl ring lies in a highly twisted plane with respect to the mean curcuminoid plane. The photophysical properties of the nine compounds were investigated in solvents of different polarity. *Meso*-substitution with a phenyl ring has little influence on fluorescence emission properties in solution, radiative and nonradiative kinetic constants being similar for *meso*- and nonsubstituted compounds, which is in contrast to the case of BODIPY derivatives. However, introduction of an electron donor *p*-methoxy group at the *meso*-phenyl ring leads to small perturbation of the curcuminoid π-system fluorescence emission. We also report the influence of the *meso*-phenyl group on the emission properties of the aggregated solids.



INTRODUCTION

Since the first report on boron coordination compounds with acetylacetonate (acacH),[1] there has been a long-standing interest in the spectroscopic properties of β-diketoboronates.[2−4] Currently, boron difluoride-containing molecules represent a topical class of fluorophores that encompasses a broad variety of chemical structures such as anils,[5] 2-(2′-hydroxyphenyl)benzoxazole,[6] quino[7,8-*h*]quinoline,[7] anilidopyridine,[8] chalcones,[9] and 3-hydroxyflavones,[10] with BODIPY[11] and aza-BODIPY[12] derivatives representing the most popular dyes. These materials display outstanding electronic and optical properties[3,4] with applications in nonlinear optics,[13] mechanochromism,[3e] organic photovoltaics,[14] lasing,[15] OLED display,[3a,16] sensing,[3f,17] photodynamic therapy,[18] and cell imaging.[19]

Curcuminoids are natural compounds featuring a π-conjugated system and a central β-diketone unit.[20] Their optical properties[21] and those of their metal complexes[22] have been investigated extensively. With boric acid, curcumin, the main curcuminoid, has long been known to form a highly colored dicurcuminatoboronium salt, the so-called rosocyanine, that has been used for the colorimetric determination of boron.[23] Despite that work, the fluorescence emission properties and excited-state behavior of difluoroboron complexes of natural and abiotic curcuminoids have far less been investigated. Recently, Moore and co-workers reported the application of the BF_2 complex of 1,5-bis(*N*,*N*-dimethylaminostyryl)acacH as an amyloid-β plaque-specific fluorescent probe providing a promising near-infrared fluorescent dye for in vivo biological studies.[24] Nevertheless, this study did not contain an in-depth photophysical investigation of that compound.

In line with our ongoing work on hydroxychalcone−BF_2 complexes,[9] we decided to extend our investigation toward the curcuminoid−BF_2 counterparts. In particular, we wanted to evaluate the influence of different aromatic groups placed at the terminal positions or connected at the central carbon atom (called *meso* in this paper) of the acac-BF_2 moiety on solution and solid-state optical properties. In the BODIPY series, the fact that the *meso*-phenyl ring is either constrained or free to rotate largely determines the efficiency of internal conversion and in turn of fluorescence emission.[25] To our knowledge, while few examples of *meso*-aryl-substituted acacH derivatives have been reported recently,[26] there is no report in the literature on *meso*-functionalized curcuminoids. Moreover, it occurred to us that the presence of a *meso*-aryl substituent could endow the flat, extended π-conjugated structures of curcuminoids with enhanced solubility in organic solvents as compared to the nonsubstituted analogues.

We present therein the synthesis of compounds **1**−**4** (Chart 1) and their electronic absorption and fluorescence emission properties in organic solvents at room temperature. The data are compared to those obtained for a series of model compounds **M1**−**M4** (Chart 2). The presence of the two fluorine atoms allows dynamic ^{19}F NMR studies with compounds **M1** and **M2**, which provides insight into the dynamics around the aryl-acac single C−C bond in the ground

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Chart 1. Structure of the Compounds Investigated in This Study

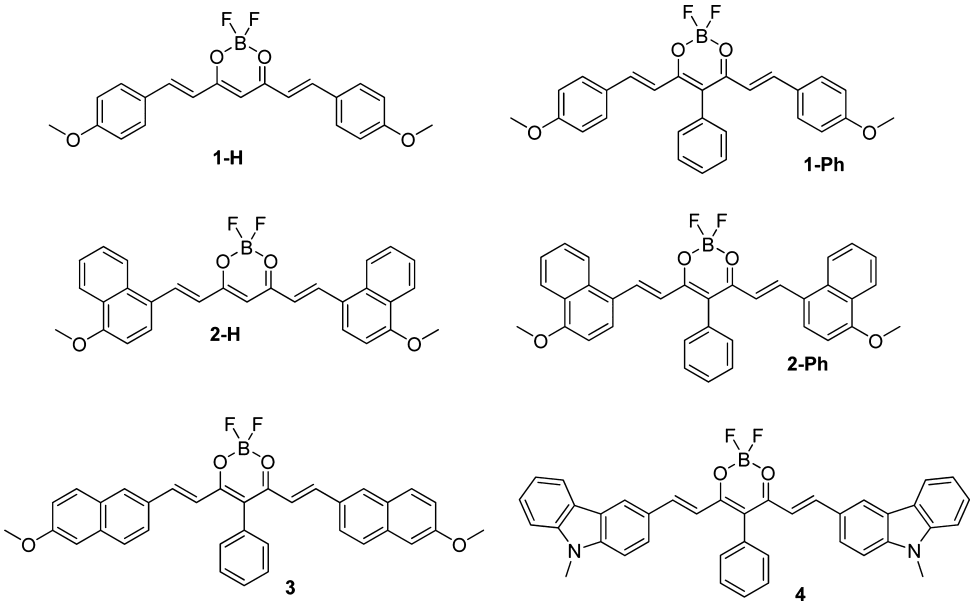
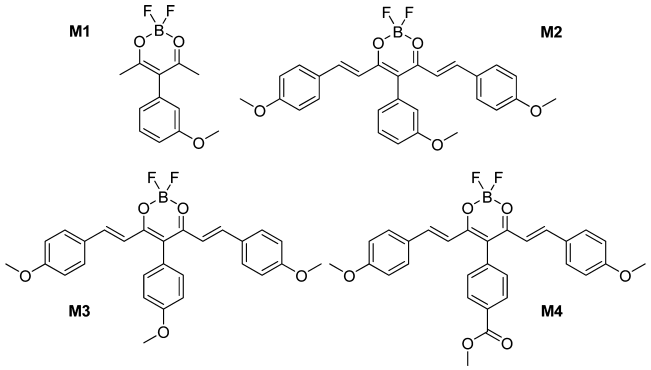


Chart 2. Formulae of the Model Compounds

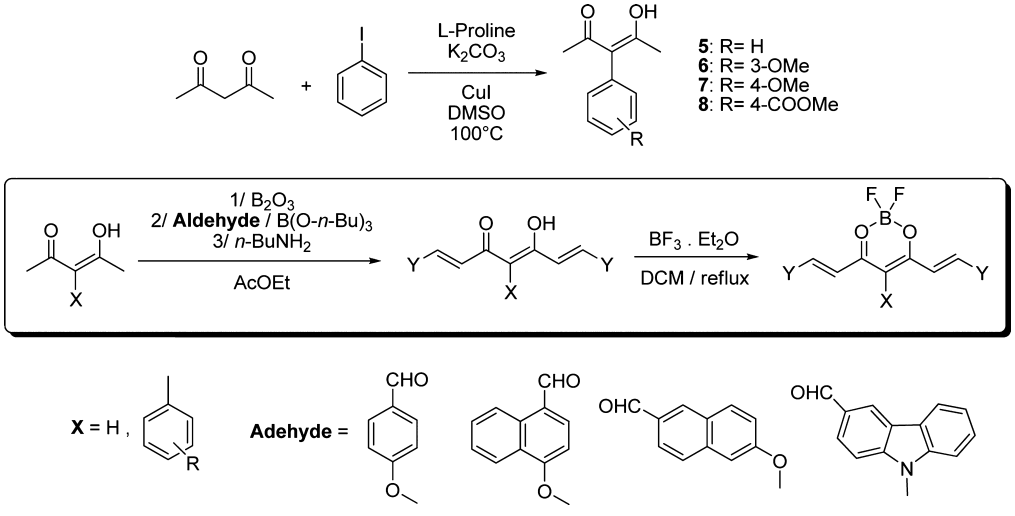


state. The molecular structure of compound **M4** in the solid state is described which represents the first example of an X-ray structure determination of a curcuminoid borondifluoride complex. Furthermore, we report the influence of the *meso*-phenyl group on the emission properties of the aggregated solids.

RESULTS AND DISCUSSION

Synthesis. The acacH ligand served as the main starting building block toward compounds **1**−**4** and **M1**−**M4** (Scheme 1). It is a very cheap and versatile compound that can easily be substituted laterally (at the methyl carbon atoms) or centrally (at the 3- or *meso* position). *Meso* substitution of acacH with different aryl groups was performed straightforwardly by CuI-catalyzed arylation of acetylacetone using the corresponding iodoaryl precursors, as previously published.[27] Lateral symmetric extension of π-conjugation leading to the introduction of donor moieties was carried by an aldol-type condensation reaction using the corresponding aldehydes (Scheme 1) and a boronium intermediate obtained by the action of boric anhydride on the acacH precursor.[28] 1,3-Diketodifluoroboronate species were produced smoothly from the free ligands by the action of boron trifluoride etherate in dichloromethane

Scheme 1. Synthetic Route to the 1,5-Distyrylacetylacetone Ligands and Their Boron Difluoride Complexes



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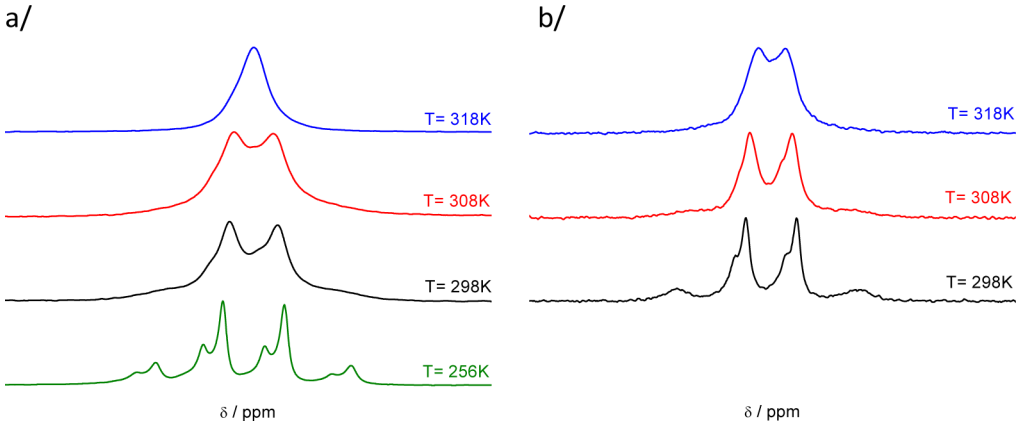

Figure 1. ^{19}F NMR spectra of compounds (a) **M1** and (b) **M2** in $CDCl_3$ at different temperatures.

(DCM) at reflux. Analytically pure samples of curcuminoids containing the flat, extended aromatic units 2-methoxynaphth-6-yl and *N*-methylcarbazol-4-yl were particularly difficult to obtain because of the poor solubility of their BF_2 complexes, and they are not presented here. In contrast, the *meso*-phenyl analogues **3** and **4** were quite soluble in organic solvents and could be obtained with the high purity grade requested for spectroscopic measurements. All compounds were found chemically and photochemically stable in solution and in the solid state. In particular, BF_2 de-coordination was not observed in all solvents used here, even in the presence of protic solvents.[9]

NMR Study. Except for **M1** and **M2**, room-temperature ^{19}F NMR spectra in $CDCl_3$ solution show a single resonance peak accompanied by a down-shielded satellite resonance due to the isotope shift effect of the 18.8% naturally abundant ^{10}B isotope. As observed previously with diketonates,[29] B-F coupling is not observed. The *m*-methoxyphenyl-substituted compounds **M1** and **M2** give rise to a broadened multiplet in $CDCl_3$ with a line shape that is highly dependent on temperature (Figure 1). In the high-temperature regime, above 320 K, a single resonance line is observed for **M1**,[30] while at low temperature, below 280 K, a well-resolved quadruplet clearly emerges along with the down-shielded similar pattern stemming from ^{10}B isotope effect (Figure 1a). At 256 K, the spectrum clearly resembled that of an AB spin system. This behavior reflects the dynamics of internal rotation around the aryl-acac orthogonal C−C bond. In the low-temperature regime, rotation is slowed down and because of the presence of the *m*-methoxy group, the plane containing the π-conjugated curcuminoid skeleton and the boron atom is no longer a symmetry plane in **M1**. At low temperature, the molecule belongs to the C_s symmetry point group. As a result, the two fluorine atoms are chemically nonequivalent. Assuming an AB spin pattern, $\Delta\nu$ was found to be 127 Hz and J_{AB} (= J_{F-F}) = 77 Hz, using 376.5 MHz ^{19}F NMR. At high temperature, rotation becomes allowed, NMR peak coalescence is observed at 310 K, and on the NMR time scale, **M1** has the average C_{2v} symmetry. Taking this value and that of $\Delta\nu$, we obtain 282 s^{-1} and ca. 60 kJ mol^{-1} for the rate constant and the activation barrier, respectively, for internal rotation in **M1** at 310 K in $CDCl_3$. This value of the energy barrier is in agreement with that determined experimentally for biphenyl compounds.[31] The ^{19}F NMR spectrum of compound **M2** in $CDCl_3$ exhibits a similar temperature dependence, but coalescence is not observed below 318 K (Figure 1b) and is believed to occur at higher temperature. This is an indication of a higher steric hindrance around the orthogonal C−C bond when the phenyl ring is connected to the π-conjugated curcuminoid skeleton. A consequence of the twisted geometry for the *meso*-aryl substituent is a significant downfield shift ($\Delta\delta$ = −0.20 ppm in **1-Ph** vs **1-H**) of the resonance of the olefinic protons at positions α (C2 and C12, see Figure 2 for atom numbering) to the acac C−O groups. This effect is consistent with the location of these protons in the shielding cone of the orthogonal aromatic group.

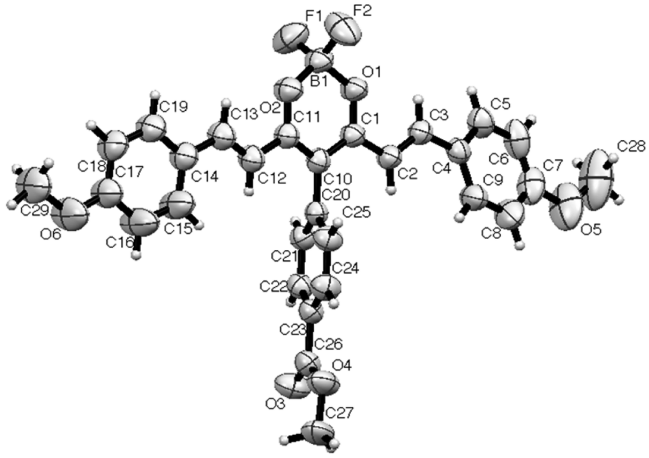

Figure 2. Molecular structure (ORTEP) of compound **M4** with displacement ellipsoids drawn at the 50% probability level.

Single-Crystal X-ray Analysis. X-ray quality crystals of **M4** were grown by slow evaporation from ethyl acetate. A single crystal was mounted on a glass fiber, and diffraction data were acquired using a Mo Kα radiation source (λ = 0.71073 Å). Detailed crystallographic parameters are included in Table 1.[32] Figure 2 shows the molecular structure of **M4** with the displacement thermal ellipsoids drawn at the 50% probability level. Compound **M4** (*P*-1, *Z* = 2) crystallizes in a triclinic crystal system with two independent molecules in the asymmetric unit.

BF_2 complexes of acacH have a large ground-state dipole moment of about 6.7 D[33] and thus behave like dipolar chromophores in the crystal.[34] Indeed, compound **M4** exists as stacks along the crystallographic *a*-axis (Figure 3) in which face-to-face, antiparallel superimposition of π-conjugated systems forms dimers with a short interplanar distance (3.65 Å). The distance between adjacent molecules of two neighboring dimers

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Table 1. Selected Crystal Data for Compound M4

compound **M4**			
formula	$C_{29}H_{25}BF_2O_6$	λ(Mo/Kα)/Å	0.71073
M/g	518.3	T/K	293(2)
Size/mm^3	0.30 × 0.26 × 0.2	Dc/g.cm^{-3}	1.284
crystal system	triclinic	θ range/deg	1.49−28.55
space group	P-1	hkl ranges	0, 11 −15, 15 −18, 17
a (Å)	8.448(1)	variable	346
b (Å)	11.579(3)	refln measured	6349
c (Å)	14.093(4)	refln $I > 2\sigma(I)$	3188
α (deg)	94.74(1)	R1 $I > 2\sigma(I)$	0.0831
β (deg)	102.62(2)	R1 all data	0.1687
γ (deg)	90.301(5)	wR2 $I > 2\sigma(I)$	0.2305
V (Å^3)	1340.3(5)	wR2 all data	0.309
Z	2	$\Delta\rho$ (±)/eÅ^{-3}	0.667/−0.659

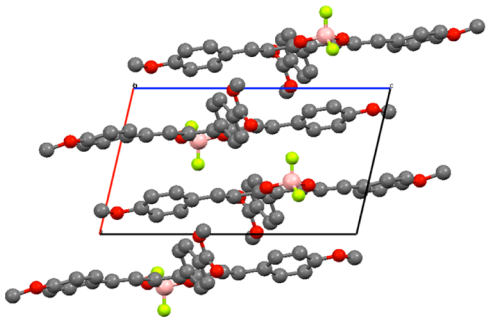

Figure 3. Crystal packing diagram of **M4** down the b-axis direction, illustrating $\pi-\pi$ stacking interactions.

is significantly increased (4.15 Å). A torsion angle of 66.4° is found between the planes of the *meso*-phenyl and dioxaborine cycles, consistent with NMR data. We further observe that one of the terminal anisole moiety is slightly twisted with respect to the rest of the distyrylacetylacetone backbone. A torsion angle of about 18° is measured between that phenyl ring and the mean molecular plane.

Spectroscopic Properties. The electronic absorption and fluorescence emission spectra were recorded in DCM (Figure 4), and the spectroscopic data are collected in Table 2. All curcuminoids exhibit a strong absorption (ε > 50000 M^{-1} cm^{-1}) with a similar band shape in the 500−570 nm range. This band is rather narrow (ca. 80 nm, i.e., 3000 cm^{-1} at half-width for **1-Ph** in DCM) and can be attributed to a $\pi-\pi^*$ transition. The spectrum of **1-Ph** is red-shifted as compared to that of **1-H**, the bathochromic shift being nearly constant irrespective of solvent nature (mean $\Delta\lambda$ = +16 nm). The same effect is also observed when passing from **2-H** to **2-Ph**, but the mean bathochromic shift is larger (ca. $\Delta\lambda$ = +20 nm in DCM). This effect might stem from an increased planarity of the 1,5-distyrylacetylacetone skeleton upon *meso*-functionalization with the aryl group. The BF_2 complexes of the curcuminoids are fluorescent in the 540−650 nm region with fluorescence quantum yields ranging from 40 to 60% in DCM. It is worth noting that the highest value of 60% is obtained with the carbazole-containing compound, giving a good brightness value of ca. 42000 M^{-1} cm^{-1}.

The solvent dependence of absorption and emission properties was examined with the two series of compounds **1-H**, **1-Ph** and **2-H**, **2-Ph** in order to get better insight into the influence of the *meso*-phenyl ring (Tables 3 and 4). Both electronic absorption and fluorescence emission spectra of these compounds show positive solvatochromism and lose their vibronic structure in the more polar solvents (Figure 5). The solvent-induced bathochromic shift of the absorption band reaches 600 cm^{-1} within both series. The observation of a positive solvatochromic effect allows to infer that vertical absorption transition led to Franck−Condon S_1 state that is more polar than the ground state (vide supra).

Plotting Stokes shift values for **1-H**, **1-Ph** and **2-H**, **2-Ph** versus the polarity function $\Delta f'$ of the solvent gave linear plots with positive slopes (Figures S36 and S37, Supporting Information),[35] which confirms the relaxation toward a solvent-equilibrated singlet excited state with a charge-transfer character and having an excited-state dipole moment larger than that in the ground state. This behavior is in agreement with that reported for diaroyl(methanato)boron difluoride compounds[4] and is related to the strong electron withdrawing effect of the difluorodioxaborine chelate.[3g] The Stokes shift values are observed to be smaller for the *meso*-substituted compounds relative to the nonsubstituted ones. It is also worth noting that solvatochromic shifts of the emission maximum are smaller for curcuminoids than for diaroyl(methanato)boron difluoride complexes.[4] From these observations, one can infer that the BF_2-containing curcuminoid backbone undergoes a limited nuclear reorganization accompanying excited-state relaxation prior to emission because it can adopt a more planar geometry in both ground and excited states,[35] especially in the case of dyes with the *meso*-phenyl ring as mentioned in

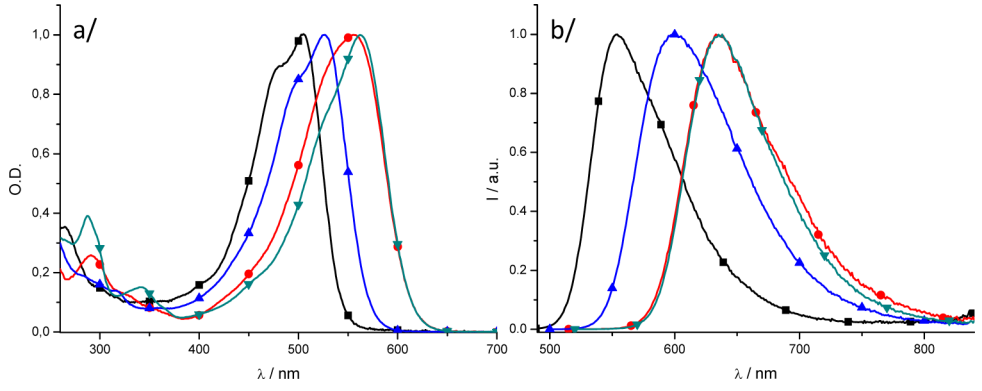

Figure 4. a/Electronic absorption spectra (conc ≈ 10^{-5} M) and corrected fluorescence emission spectra (conc ≈ 10^{-6} M, λ_{exc} at the absorption maximum) of **1-Ph** (black —, ■), **2-Ph** (blue —, ▲), **3** (red —, ●), and **4** (green —, ▼) in DCM at room temperature. All spectra are normalized.

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Table 2. Spectroscopic Data and Photophysical Properties of Compounds 1-H, 1-Ph, 2-H, 2-Ph, 3, and 4 in DCM at Room Temperature[a]

	UV−vis		fluorescence						
compd	λ_{abs}	ε_{max}	λ_{em}	$\Delta\nu_{ST}$	Φ_f	Φ_f x ε	τ_f	k_f	k_{nr}
1-H	488	75480	538	1904	0.44	33211	1.30	3.4	4.3
1-Ph	505	78230	554	1751	0.41	32074	1.35	3.0	4.4
2-H	536	54470	616	2423	0.39	21243	1.96	2.0	3.1
2-Ph	556	57080	633	2188	0.37	21120	1.91	1.9	3.3
3	526	72120	600	2344	0.51	36781	1.86	2.7	2.6
4	565	69670	636	1976	0.60	41802	2.15	2.8	1.9
M2	504	73200	556	1856	0.41	30012	1.32	3.2	4.5
M3	506	74100	571	2250	0.39	28899	1.31	3.0	4.7
M4	507	74770	557	1771	0.43	32151	1.34	3.4	4.3

[a]Absorption maximum wavelengths λ_{abs} (nm), molar absorption coefficients ε_{max} (M^{-1} cm^{-1}), fluorescence maximum wavelengths λ_{em} (nm), Stokes shifts $\Delta\nu_{ST}$ (cm^{-1}), fluorescence quantum yields Φ_f, brightness $\Phi_f \times \varepsilon$ (M^{-1} cm^{-1}), fluorescence lifetimes τ_f (ns), radiative k_f (10^8 s^{-1}) and nonradiative $k_{nr} = (1 - \Phi_f)/\tau_f$ (10^8 s^{-1}) rate constants.

Table 3. Spectroscopic Data and Photophysical Properties of Compounds 1-H and 1-Ph in Solvents of Different Polarity at Room Temperature[a]

	1-H							1-Ph						
solvent	λ_{abs}	λ_{em}	$\Delta\nu_{ST}$	Φ_f	τ_f	k_f	k_{nr}	λ_{abs}	λ_{em}	$\Delta\nu_{ST}$	Φ_f	τ_f	k_f	k_{nr}
CCl_4	477	492	639	0.20	0.50	4.0	16	493	515	870	0.24	0.70	3.4	11
Et_2O	475	497	930	0.24	0.70	3.5	11	491	520	1135	0.27	0.90	3.1	8.1
AcOEt	480	515	1415	0.35	0.88	3.9	7.4	496	534	1435	0.34	1.18	2.8	5.6
DCM	488	538	1905	0.44	1.30	3.4	4.3	505	554	1751	0.41	1.35	3.0	4.4
acetone	483	534	1980	0.45	1.49	3.0	3.7	500	549	1785	0.41	1.43	2.8	4.2
ACN	483	549	2490	0.51	1.55	3.3	3.2	500	564	2270	0.42	1.50	2.8	3.9

[a]Absorption maximum wavelengths λ_{abs} (nm), fluorescence maximum wavelengths λ_{em} (nm), Stokes shifts $\Delta\nu_{ST}$ (cm^{-1}), fluorescence quantum yields Φ_f, fluorescence lifetimes τ_f (ns), radiative k_f (10^8 s^{-1}) and nonradiative $k_{nr} = (1 - \Phi_f)/\tau_f$ (10^8 s^{-1}) rate constants; Et_2O, ethylic ether; AcOEt, ethyl acetate; DCM, dichloromethane; ACN, acetonitrile.

Table 4. Spectroscopic Data and Photophysical Properties of Compounds 2-H and 2-Ph in Solvents of Different Polarity at Room Temperature[a]

	2-H							2-Ph						
solvent	λ_{abs}	λ_{em}	$\Delta\nu_{ST}$	Φ_f	τ_f	k_f	k_{nr}	λ_{abs}	λ_{em}	$\Delta\nu_{ST}$	Φ_f	τ_f	k_f	k_{nr}
CCl_4	523	561	1295	0.23	1.18	2.0	6.5	542	577	1120	0.23	0.94	2.4	8.3
Et_2O	516	587	2344	0.29	1.34	2.1	5.3	540	583	1365	0.29	1.12	2.6	6.3
AcOEt	524	590	2135	0.31	1.51	2.1	4.5	542	603	1865	0.32	1.28	2.5	5.3
DCM	536	616	2423	0.39	1.96	2.0	3.1	556	633	2190	0.37	1.91	1.9	3.3
Acetone	532	622	2720	0.21	1.03	2.1	7.7	549	631	2370	0.22	1.02	2.2	7.6
ACN	530	651	3507	0.12	0.65	1.9	13	550	649	2775	0.12	0.63	1.8	14

[a]Absorption maximum wavelengths λ_{abs} (nm), fluorescence maximum wavelengths λ_{em} (nm), Stokes shifts $\Delta\nu_{ST}$ (cm^{-1}), fluorescence quantum yields Φ_f, fluorescence lifetimes τ_f (ns), radiative k_f (10^8 s^{-1}) and nonradiative $k_{nr} = (1 - \Phi_f)/\tau_f$ (10^8 s^{-1}) rate constants; Et_2O, ethylic ether; AcOEt, ethyl acetate; DCM, dichloromethane; ACN, acetonitrile.

the NMR study. Compared to **1-H** and **1-Ph**, compounds with the strong electron-donor aromatic groups, such as **2-H**, **2-Ph**, **3**, and **4**, give larger Stokes shift values.

Kinetic constants were determined for radiative and nonradiative deactivation pathways and are collected in Tables 2−4. Overall, k_f values are in the same order of magnitude for nonsubstituted and *meso*-substituted compounds, which indicates that the emission probability is not significantly affected by the presence of the *meso*-aryl group. The same observation holds for k_{nr} values, showing that there is no significant energy loss from the excited state via thermal deactivation pathways that would arise from rotational motions of the phenyl substituent. Such nonradiative deactivation due to *meso*-substitution is classical in BODIPY derivatives.[25] The radiative constants k_f are found to be insensitive to solvent polarity. This observation indicates that there is no increase of fluorescence transition moment with increasing polarity. This feature is consistent with a limited nuclear reorganization in the relaxed emitting state with respect to the Franck−Condon excited state.[36] The continuous decrease of k_{nr} values of **1-H** and **1-Ph** with increasing solvent polarity indicates that nonradiative processes are less efficient in polar solvents. In the case of **2-H** and **2-Ph**, the decrease in k_{nr} was followed by an increase of that parameter in highly polar solvents such as acetone and acetonitrile. This effect might be associated to a change in rotamer distribution associated with the terminal naphthalene chromophores.

Model compounds **M2** and **M4**, with a *meso*-aryl group containing an *m*-methoxy or *p*-carboxymethyl group, displayed identical absorption and fluorescence emission spectra and

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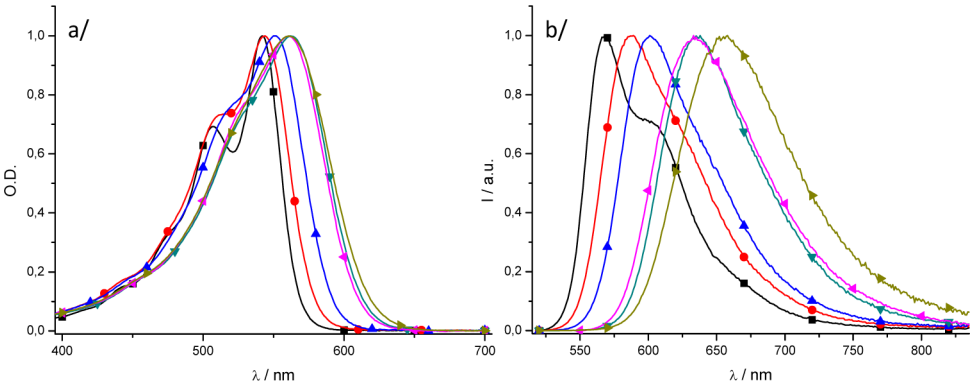

Figure 5. Electronic absorption (a) and fluorescence emission (b) spectra of compound **4** in solvents of different polarity at room temperature (λ_{exc} = 510 nm; carbon tetrachloride (—, ■), ethylic ether (red —, •), ethyl acetate (blue —, ▲), dichloromethane (green —, ▼), acetone (pink —, left-pointing triangle), and acetonitrile (gray —, right-pointing triangle)).

photophysical properties (Table 2) with respect to compound **1-Ph**. The presence of a *meso*-*p*-methoxyphenyl unit in **M3**, however, affects significantly the fluorescence emission, but not the electronic absorption properties. We notice a bathochromic shift of the emission maximum wavelength ($\Delta\lambda$ = +17 nm, i.e., $\Delta\nu$ = 537 cm^{-1}) with respect to **1-Ph** along with a loss of the vibronic structure that is already observable in weakly polar solvents (Figure 6). The amplitude of the fluorescence

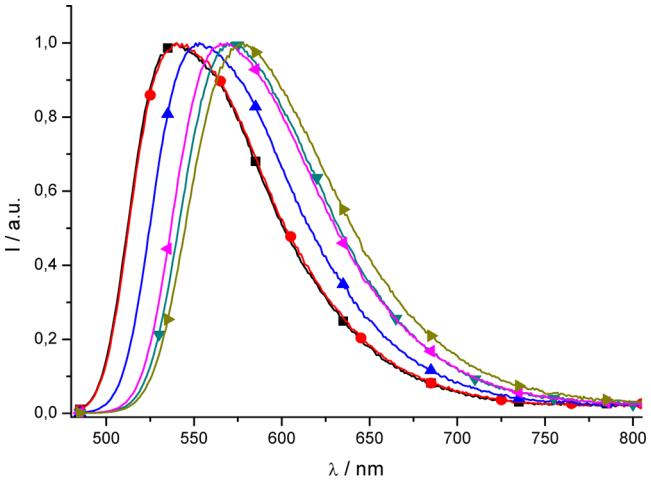

Figure 6. Normalized corrected fluorescence emission of compound **M3** (λ_{exc} = 480 nm) in solvents of different polarity at room temperature (carbon tetrachloride (black —, ■), ethylic ether (red —, •), ethyl acetate (blue —, ▲), dichloromethane (green —, ▼), acetone (pink —, left-pointing triangle), and acetonitrile (gray —, right-pointing triangle)).

solvatochromic shift is also larger than for **1-Ph** (Figures S36 and S37, Supporting Information). All together, these features are indicative of the occurrence of a more polar excited π–π state for the curcuminoid chromophore bearing the electron-donor *meso* group. Although one may expect a rather weak electronic communication between the *meso*-aryl ring and the dioxaborine chelate, because of the large twist angle noticed between these units in solution and the crystal, these observations hint at some perturbation of the curcuminoid excited-state properties by the *meso*-substituent in the case of **M3**.

By quick dilution of concentrated THF solutions of dyes **1-H**, **1-Ph**, **2-H**, and **2-Ph** in water, we obtained stable colloids suspension that allowed recording fluorescence emission spectra of the aggregated species (Figure 7).[9] The four compounds show solid-state emission spectra in the red to near-infrared range, with the *meso*-phenyl-substituted dyes exhibiting blue-shifted spectra relative to the *meso*-H analogues (711 nm vs 679 nm for **1-H** and **1-Ph**, respectively, and 823 nm vs 702 nm for **2-H** and **2-Ph**, respectively). This trend, opposite to that noticed in solution, is consistent with the sterical encumbrance of the *meso*-phenyl ring that tends to reduce the interchromophoric π contact area in the solid state (Figure 3). It is noteworthy that dynamic light scattering results indicate that particle size distributions are very sensitive to the nature of the donor group and to the presence of the *meso* aryl ring.[37] Indeed, the latter leads to smaller size (Figures S38–S41, Supporting Information), which correlates with the higher solubility observed for the *meso*-phenyl-containing analogues.

■ CONCLUSION

We have synthesized BF_2 complexes of a series of curcuminoids. Within this series, those analogues that contain a *meso*-aryl substituent are to date unprecedented structures. The experimental observations obtained by dynamic ^{19}F NMR confirm the fact that rotation of the *meso*-aryl fragment is restricted in the functionalized curcuminoids at room temperature and become allowed at higher temperature (>45 °C). All compounds give efficient fluorescence emission in solution. Except for **M3**, *meso*- and nonsubstituted compounds exhibit very close photophysical behavior showing no significant influence of the *meso*-phenyl ring on S_1 state dynamics, which is in contrast with the behavior of BODIPY dyes. As a consequence, the introduction of the axial phenyl group can be exploited for endowing the curcuminoid unit with further interesting features, such as enhanced solubility in common organic solvents and modulated π–π stacking interaction, without impeding fluorescence performance.

■ EXPERIMENTAL SECTION

General Experimental Methods. All solvents for synthesis were of analytical grade. Spectroscopy measurements were carried out with spectroscopic grade solvents. NMR spectra (^1H, ^{13}C, ^{19}F) were recorded at room temperature at 250, 62.5, and 235 MHz for ^1H, ^{13}C, and ^{19}F, respectively. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (^1H and ^{13}C); residual solvent peaks of the deuterated solvents were used as an internal standard. High-resolution mass spectra were recorded in positive electrospray ionization mode using TOF analyzer.

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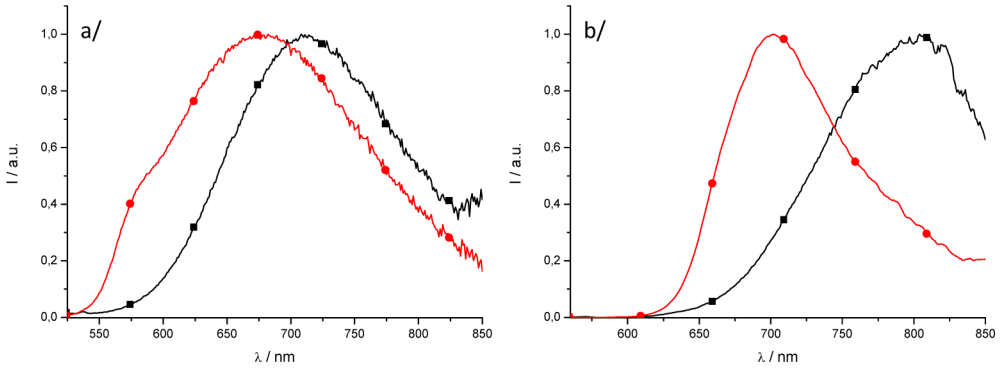

Figure 7. Normalized corrected fluorescence emission of aggregated particles in water of compound (a) **1-H** (black —, ■) and **1-Ph** (red —, ●) (λ_{exc} = 500 nm) and (b) **2-H** (black —, ■) and **2-Ph** (red —, ●) (λ_{exc} = 550 nm).

Syntheses. We used the following general procedure for the synthesis of the compounds. In a 50 mL round-bottom flask, the acetylacetonate derivative (1 molar equiv) and B_2O_3 (0.5 molar equiv) were mixed in 15 mL of ethyl acetate and stirred at 60 °C for 30 min. A solution of the appropriate aldehyde (2 molar equiv) and *n*-tributylborane (2 molar equiv) in 10 mL of ethyl acetate was added, and the mixture was stirred for 30 min at 60 °C. A catalytic amount of butylamine (0.4 molar equiv) was then added to the solution, and the reaction mixture was refluxed overnight. After the mixture was cooled to 60 °C, 30 mL of 0.4 M HCl was added, and the resulting mixture was stirred for 30 min. After cooling, the precipitate was filtered off and dried in vacuo to yield ligands **M4**, **1-H**, **2-H**, and **3**. The other derivatives were further subjected to column chromatograhy on silica. The free ligands were reacted with boron difluoride etherate to produce the corresponding BF_2 complexes as follows. In a 50 mL round-bottom flask, the ligand (1 molar equiv) was solubilized in dichloromethane (20 mL), and boron trifluoride etherate (1.3 molar equiv) was added to this solution. The reaction mixture was refluxed overnight. After being cooled to room temperature, the solvent was evaporated and the resulting solid was suspended into diethyl ether. The precipitate was filtered off, and the crude complex was purified by column chromatography using silica gel when needed. In the latter case, the chromatography conditions are specified for the compound.

(*Z*)-4-(Difluoroboryloxy)-3-(3-methoxyphenyl)pent-3-en-2-one (M1). The free ligand (175 mg, 0.85 mmol) was reacted with boron trifluoride etherate to afford the crude complex **M1** that was purified on silica using cyclohexane/DCM (3/1) as eluent. Slightly yellow solid (198 mg, 92%): mp = 116−118 °C, ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.39 (d, ^3J = 7.8 Hz, 1H), 6.97 (m, 1H), 6.75 (m, 2H), 3.85 (s, 3H), 2.14 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 191.0, 160.3, 134.2, 130.6, 122.7, 116.3, 114.1, 55.3, 23.6; ^{19}F NMR (235 MHz, $CDCl_3$) δ = −138.14 (^{10}B-F, 0.2F), −138.19 (^{11}B-F, 0.8F), −138.30 (^{10}B-F, 0.2F), −138.34(^{11}B-F, 0.8F); LRMS (EI) (positive mode) *m*/*z* 272.1 $[M + NH_4]^+$, 277.0 $[M + Na]^+$, (negative mode) 253.0 $[M - H]^-$. Anal. Calcd for $C_{12}H_{13}BF_2O_3$: C, 56.74; H, 5.16. Found: C, 57.03; H, 5.08.

(1*E*,4*Z*,6*E*)-5-(Ddifluoroboryloxy)-4-(3-methoxyphenyl)-1,7-bis(4-methoxyphenyl)hepta-1,4,6-trien-3-one (M2). The free ligand was obtained as a yellow solid from *meso*-(*m*-methoxyphenyl)-acacH (253 mg, 1.23 mmol) and *p*-methoxybenzaldehyde (334 mg, 2.45 mmol) and was purified by column chromatography on silica using cyclohexane/AcOEt (7/3 v/v) as eluent (76 mg, 14%): mp = 147 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.64 (d, ^3J = 15.7 Hz, 2H), 7.36 (d, ^3J = 8.0 Hz, 1H), 7.29 (d, ^3J = 8.8 Hz, 4H), 6.96 (dd, ^3J = 8.2 Hz, ^4J = 2.5 Hz, 1H), 6.85 (m, 6H), 6.37 (d, ^3J = 15.7 Hz, 2H), 3.83 (s, 3H), 3.78 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 182.4, 161.1, 140.6, 129.9, 129.5, 128.1, 124.8, 120.0, 117.5, 115.7, 114.2, 113.4, 55.3, 55.3; LRMS (EI) (positive mode) *m*/*z* 443.3 $[M + H]^+$, (negative mode) 441.4 [M − H]. Anal. Calcd for $C_{29}H_{26}O_6$: C, 76.00; H, 5.89. Found: C, 75.73; H, 5.60. This compound (38 mg, 0.086 mmol) was reacted with boron trifluoride etherate to afford the boron complex **M2** as a red solid (42 mg, quantitative): mp = 260−261 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.03 (d, ^3J = 15.5 Hz, 2H), 7.41 (m, 5H), 7.03 (dd, ^3J = 8.3 Hz, ^4J = 2.0 Hz, 1H), 6.85 (m, 6H), 6.39 (d, ^3J = 15.5 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 177.6, 162.7, 160.0, 147.1, 134.1, 131.3, 130.1, 127.3, 124.3, 117.8, 117.2, 117.0, 114.6, 114.5, 55.5; ^{19}F NMR (235 MHz, $CDCl_3$) δ = −141.13 (^{10}B-F, d, ^2J = 152.7 Hz, 0.2F), −141.18 (^{11}B-F, d, ^2J = 152.7 Hz, 0.8F), −141.41 (^{10}B-F, d, ^2J = 152.9 Hz, 0.2F), −141.45 (^{11}B-F, d, ^2J = 152.9 Hz, 0.8F); LRMS (EI) (positive mode) *m*/*z* 513.1 $[M + Na]^+$, 529.1 $[M + K]^+$; HRMS (ESI+) $[M + Na]^+$ calcd for $C_{28}H_{25}O_5BF_2Na^+$ 513.1660, found 513.1660.

(1*E*,4*Z*,6*E*)-5-(Difluoroboryloxy)-1,4,7-tris(4-methoxyphenyl)hepta-1,4,6-trien-3-one (M3). The free ligand was obtained as a yellow solid from *meso*-(*p*-methoxyphenyl)-acacH (314 mg, 1.52 mmol) and *p*-methoxybenzaldehyde (415 mg, 3.04 mmol) and was filtered from ethyl acetate (350 mg, 52%): mp = 166−167 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.63 (d, ^3J = 15.7 Hz, 2H), 7.30 (d, ^3J = 8.6 Hz, 4H), 7.18 (d, ^3J = 8.4 Hz, 2H), 6.97 (d, ^3J = 8.4 Hz, 2H), 6.81 (d, ^3J = 8.6 Hz, 4H), 6.38 (d, ^3J = 15.7 Hz, 2H), 3.89 (s, 3H), 3.78 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 182.7, 161.1, 159.0, 140.4, 133.4, 129.8, 128,2, 127.7, 120.1, 115.3, 114.2, 113.9, 55.3; LRMS (EI) (positive mode) *m*/*z* 443.1 $[M + H]^+$, 441.3 $[M + Na]^+$. Anal. Calcd for $C_{29}H_{26}O_6$: C, 76.00; H, 5.99. Found: C, 75.68; H, 5.60. This compound (135 mg, 0.31 mmol) was reacted with boron trifluoride etherate to afford the boron complex **M3** as a red solid (150 mg, quantitative): mp = 222−223 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.01 (d, ^3J = 15.4 Hz, 2H), 7.37 (d, ^3J = 8.6 Hz, 4H), 7.19 (d, ^3J = 8.2 Hz, 2H), 7.02. (d, ^3J = 8.2 Hz, 2H), 6.85 (d, ^3J = 8.6 Hz, 4H), 6.39 (d, ^3J = 15.4 Hz, 2H), 3.91 (s, 3H), 3.81 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 178.0, 162.7, 159.7, 147.0, 133.1, 131.3, 127.4, 124.7, 117.1, 115.1, 114.6, 114.5, 55.6; ^{19}F NMR (235 MHz, $CDCl_3$) δ = −141.27 (^{10}B-F, 0.2F), −141.33 (^{11}B-F, 0.8F); LRMS (EI) (positive mode) *m*/*z* 508.2 $[M + NH_4]^+$, 513.1 $[M + Na]^+$; HRMS (ESI+) $[M + Na]^+$ calcd for $C_{28}H_{25}O_5BF_2Na^+$ 513.1660, found 513.1660.

Methyl 4-((1E,3Z,6E)-3-(difluoroboryloxy)-1,7-bis(4-methoxyphenyl)-5-oxohepta-1,3,6-trien-4-yl)benzoate (M4). The free ligand was obtained as a yellow solid from *meso*-(*p*-methylbenzoate)-acacH (142 mg, 0.61 mmol) and *p*-methoxybenzaldehyde (165 mg, 1.21 mmol) and was filtered from ethyl acetate (117 mg, 41%): mp = 158−160 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.12 (d, ^3J = 8.5 Hz, 2H), 7.66 (d, ^3J = 15.7 Hz, 2H), 7.38 (d, ^3J = 8.3 Hz, 2H), 7.27 (d, ^3J = 8.8 Hz, 2H), 6.80 (d, ^3J = 8.8 Hz, 2H), 6.28 (d, ^3J = 15.5 Hz, 2H), 3.98 (s, 3H), 3.78 (6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 182.2, 166.9, 161.3, 141.2, 140.9, 132.5, 129.9, 129.7, 129.4, 127.9, 119.5, 114.8, 114.3, 55.3, 52.2; LRMS (EI) (positive mode) *m*/*z* 471.3 $[M + H]^+$, 493.2 $[M + Na]^+$. Anal. Calcd for $C_{29}H_{26}O_6$: C, 74.03; H, 5.57. Found: C, 74.16; H, 5.60. This compound (77 mg, 0.16 mmol) was reacted with boron trifluoride etherate to afford the boron complex **M4** as a red solid (85 mg, quantitative): mp = 229−230 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.18 (d, ^3J = 8.5 Hz, 2H), 8.04 (d, ^3J = 15.3 Hz, 2H), 7.40 (d, ^3J = 8.5 Hz, 2H), 7.34 (d, ^3J = 8.8 Hz, 2H), 6.84 (d, ^3J = 8.8 Hz, 2H), 6.28 (d, ^3J = 15.3 Hz, 2H), 3.99 (s, 3H), 3.81 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 177.4, 166.6, 162.9, 147.8, 137.9,

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132.2, 131.6, 130.6, 130.2, 127.1, 116.4, 114.7, 55.5, 52.40; ^{19}F NMR (235 MHz, $CDCl_3$) δ = −141.31 (^{10}B-F, 0.2F), −141.37 (^{11}B-F, 0.8F); LRMS (EI) (positive mode) m/z 541.2 $[M + Na]^+$, 557.2 $[M + K]^+$. Anal. Calcd for $C_{29}H_{25}BF_2O_6 \cdot {}^1/_3CH_2Cl_2$: C, 64.45; H, 4.73. Found: C, 64.09; H, 4.38.

(1*E*,4*Z*,6*E*)-5-(Difluoroboryloxy)-1,7-bis(4-methoxyphenyl)-hepta-1,4,6-trien-3-one (1-H). The free compound[38] (149 mg, 0.44 mmol) was reacted with boron trifluoride etherate to afford the crude complex **1-H** that was purified by column chromatography on silica using Et_2O/cyclohexane (1/1) as eluent. Red solid (170 mg, 74%): mp = 247−249 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.98 (d, ^3J = 15.4 Hz, 2H), 7.55 (d, ^3J = 8.8 Hz, 4H), 6.92 (d, ^3J = 8.8 Hz, 4H), 6.56 (d, ^3J = 15.4 Hz, 2H), 5.98 (s, 1H), 3.84 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 179.5, 162.8, 146.9, 131.2, 127.0, 119.1, 114.8, 101.6, 55.2; ^{19}F NMR (235 MHz, $CDCl_3$) δ = 140.96 (^{10}B-F, 0.2F), −141.08 (^{11}B-F, 0.8F); LRMS (EI) (positive mode) m/z 407.1 $[M + Na]^+$, 423 $[M + K]^+$; HRMS (ESI+) $[M + Na]^+$ calcd for $C_{21}H_{19}O_4BF_2Na^+$ 407.1241, found 407.1238.

(1*E*,4*Z*,6*E*)-5-(Difluoroboryloxy)-1,7-bis(4-methoxyphenyl)-4-phenylhepta-1,4,6-trien-3-one (1-Ph). The free ligand was obtained as a yellow solid from *meso*-(phenyl)-acacH (350 mg, 1.99 mmol) and *p*-methoxybenzaldehyde (542 mg, 3.98 mmol) and was purified by column chromatography on silica using cyclohexane/AcOEt (1/9 v:v) as eluent (205 mg, 25%): mp = 171−172 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.64 (d, ^3J = 15.6 Hz, 2H), 7.43 (m, 3H), 7.27 (m, 6H), 6.80 (d, ^3J = 8.8 Hz, 4H), 6.35 (d, ^3J = 15.6 Hz, 1H), 3.78 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 182.5, 161.2, 140.6, 135.6, 132.3, 129.8, 128.5, 128.1, 127.6, 120.1, 115.9, 114.2, 55.3; LRMS (EI) (positive mode) m/z 413.2 $[M + H]^+$, 435.2 $[M + Na]^+$, (negative mode): 411.3 $[M - H]^-$. Anal. Calcd for $C_{27}H_{24}O_4$: C, 78.62; H, 5.86. Found: C, 78.27; H, 5.91.This compound (200 mg, 0.48 mmol) was reacted with boron trifluoride etherate to afford the boron complex **1-Ph** as a red solid (223 mg, quantitative): mp = 227−229 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.02 (d, ^3J = 15.3 Hz, 2H), 7.50 (m, 3H), 7.35 (d, ^3J = 9.0 Hz, 4H), 7.28 (m, 1H), 6.84 (d, ^3J = 9.0 Hz, 4H), 6.35 (d, ^3J = 15.3 Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 177.7, 162.7, 147.2, 132.8, 132.0, 131.3, 129.1, 128.7, 127.3, 117.0, 114.6, 55.5; ^{19}F NMR (235 MHz, $CDCl_3$) δ = −141.25 (^{10}B-F, 0.2F), −141.31 (^{11}B-F, 0.8F); LRMS (EI) (positive mode) m/z 483.1 $[M + Na]^+$, 499.0 $[M + K]^+$; HRMS (ESI+) $[M + Na]^+$ calcd for $C_{27}H_{23}O_4BF_2Na^+$ 483.1555, found 483.1555.

(1*E*,4*Z*,6*E*)-5-(Difluoroboryloxy)-1,7-bis(4-methoxynaphthalen-1-yl)hepta-1,4,6-trien-3-one (2-H). The free ligand was obtained as an orange solid from acacH (305 mg, 3.05 mmol) and 4-methoxy-1-naphthaldehyde (1.14 g, 6.11 mmol) and was filtered from ethyl acetate (813 mg, 61%): mp = 233−234 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.48 (d, ^3J = 15.5 Hz, 2H), 8.32 (dd, ^3J = 8.3 Hz, ^4J = 1.0 Hz, 2H), 8.24 (d, ^3J = 8.3 Hz, 2H), 7.79 (d, ^3J = 8.2 Hz, 2H), 7.57 (m, 4H), 6.85 (d, ^3J = 8.0 Hz, 2H), 6.66 (d, ^3J = 15.5 Hz, 2H), 5.98 (s, 1H), 4.04 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 183.4, 157.4, 137.2, 132.6, 127.4, 125.8, 125.6, 125.6, 124.8, 124.2, 123.2, 122.6, 103.9, 101.7, 55.7; LRMS (EI): (positive mode) m/z 437.1 $[M + H]^+$, 459.1 $[M + Na]^+$, 478.1 $[M + K]^+$. Anal. Calcd for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54. Found: C, 79.79; H, 5.53. This compound (110 mg, 0.25 mmol) was reacted with boron trifluoride etherate to afford the crude boron complex **2-H** as a black solid that was purified by column chromatography on silica using cyclohexane/DCM (2/3) as eluent (63 mg, 52%): mp = 309−311 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.88 (d, ^3J = 15.3 Hz, 2H), 8.32 (m, 4H), 7.94 (d, ^3J = 8.3 Hz, 2H), 7.60 (m, 4H), 6.90 (d, ^3J = 8.5 Hz, 2H), 6.79 (d, ^3J = 15.5 Hz, 2H), 6.12 (s, 1H), 4.08 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): Because of the poor solubility of **2-H**, a satisfactory ^{13}C NMR spectrum could not be obtained; ^{19}F NMR (235 MHz, $CDCl_3$) δ = −140.84 (^{10}B-F, 0.2), −140.90 (^{11}B-F, 0.8); LRMS (EI) (positive mode) m/z 485.1 $[M + H]^+$, 507.1 $[M + Na]^+$, 523.1 $[M + K]^+$, 502.2 $[M + NH_4]^+$. Anal. Calcd for $C_{29}H_{23}BF_2O_4$: C, 71.92; H, 4.79. Found: C, 72.12; H, 4.76.

(1*E*,4*Z*,6*E*)-5-(Difluoroboryloxy)-1,7-bis(4-methoxynaphthalen-1-yl)-4-phenylhepta-1,4,6-trien-3-one (2-Ph). The free ligand was obtained as an orange solid from *meso*-(phenyl)-acacH (249 mg, 1.41 mmol) and 4-methoxy-1-naphthaldehyde (527 mg, 2.83 mmol) and was filtered from ethyl acetate (319 mg, 44%): mp = 234−235 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.50 (d, ^3J = 15.4 Hz, 2H), 8.26 (d, ^3J = 8.3 Hz, 2H), 8.20 (d, ^3J = 8.3 Hz, 2H), 7.47 (m, 10H), 6.72 (d, ^3J = 8.3 Hz, 2H), 6.53 (d, ^3J = 15.4 Hz, 2H), 3.97 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 182.5, 157.3, 137.6, 135.8, 132.6, 132.4, 128.6, 127.6, 127.4, 125.9, 125.5, 125.1, 123.2, 122.5, 122.4, 116.0, 103.8, 55.6; LRMS (EI) (positive mode) m/z 513.1 $[M + H]^+$, (negative mode) 511.2 $[M - H]^-$. Anal. Calcd for $C_{35}H_{28}O_4$: C, 82.01; H, 5.51. Found: C, 81.83; H, 5.67. This compound (150 mg, 0.29 mmol) was reacted with boron trifluoride etherate to afford the boron complex **2-Ph** as a red solid (164 mg, quantitative): mp = 299−301 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.88 (d, ^3J = 15.2 Hz, 2H), 8.25 (m, 4H), 7.56 (m, 9H), 7.37 (m, 2H), 6.76 (d, ^3J = 8.4 Hz, 2H), 6.56 (d, ^3J = 15.2 Hz, 2H), 4.00 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 177.4, 159.1, 143.6, 133.1, 132.9, 132.1, 129.1, 128.6, 128.2, 127.9, 129.0, 125.5, 124.1, 123.1, 122.7, 118.8, 104.0, 55.8; ^{19}F NMR (235 MHz, $CDCl_3$) δ = −141.17 (^{10}B-F, 0.2), −141.11 (^{11}B-F, 0.8); LRMS (EI) (positive mode) m/z 583.2 $[M + Na]^+$, 599.2 $[M + K]^+$; HR-MS (ESI+) $[M + Na]^+$ calcd for $C_{35}H_{27}O_4BF_2Na^+$ 583.1869, found 583.1868.

(1*E*,4*Z*,6*E*)-5-(Difluoroboryloxy)-1,7-bis(6-methoxynaphthalen-2-yl)-4-phenylhepta-1,4,6-trien-3-one (3). The free ligand was obtained as a yellow solid from *meso*-(phenyl)-acacH (224 mg, 1.27 mmol) and 6-methoxy-2-naphthaldehyde (474 mg, 2.54 mmol) and was filtered from ethyl acetate (450 mg, 69%): mp = 278−279 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.83 (d, ^3J = 15.6 Hz, 2H), 7.74 (s, 2H), 7.69 (d, ^3J = 8.9 Hz, 2H), 7.58 (d, ^3J = 8.6 Hz, 2H), 7.48 (m, 3H), 7.34 (m, 4H), 7.11 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 2H), 7.05 (d, ^4J = 2.4 Hz, 2H), 6.56 (d, ^3J = 15.6 Hz, 2H), 3.90 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 182.5, 158.8, 141.3, 135.5, 132.4, 130.7, 130.1, 129.9, 128.7, 128.6, 127.7, 127.3, 124.3, 121.4, 119.3, 116.3, 106.0, 55.4; LRMS (EI) (positive mode) m/z 513.1 $[M + H]^+$, (negative mode) 511.2 $[M - H]^-$. Anal. Calcd for $C_{35}H_{28}O_4$: C, 82.01; H, 5.51. Found: C, 82.23; H, 5.60. This compound (118 mg, 0.23 mmol) was reacted with boron trifluoride etherate to afford the boron complex **3** as a red solid (129 mg, quantitative): mp = 239−241 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.20 (d, ^3J = 15.4 Hz, 2H), 7.83 (d, ^4J = 1.1 Hz, 2H), 7.72 (d, ^3J = 9.0 Hz, 2H), 7.60 (d, ^3J = 8.7 Hz, 2H), 7.55 (m, 3H), 7.35 (m, 4H), 7.14 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 2H), 7.04 (d, ^4J = 2.3 Hz, 2H), 6.57 (d, ^3J = 15.4 Hz, 2H), 3.90 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 177.9, 159.7, 147.9, 136.5, 132.7, 132.3, 132.1, 130.7, 129.9, 129.2, 128.8, 128.6, 127.6, 124.3, 119.7, 118.4, 116.0, 106.2, 55.4; ^{19}F NMR (235 MHz, $CDCl_3$) δ = 140.95 (^{10}B-F, 0.2), 141.01 (^{11}B-F, 0.8); LRMS (EI) (positive mode) m/z 583.2 $[M + Na]^+$, 599.2 $[M + K]^+$. Anal. Calcd for $C_{35}H_{28}BF_2O_4 \cdot {}^1/_5CH_2Cl_2$: C, 73.22; H, 4.78. Found: C, 73.59; H, 4.77.

(1*E*,4*Z*,6*E*)-5-(Difluoroboryloxy)-1,7-bis(9-methyl-9*H*-carbazol-3-yl)-4-phenylhepta-1,4,6-trien-3-one (4). The free ligand was obtained as an orange-red solid from *meso*-(phenyl)-acacH (200 mg, 1.13 mmol) and *N*-methylcarbazole-3-carboxaldehyde (475 mg, 2.27 mmol) and was filtered from ethyl acetate (266 mg, 42%): mp = 256−258 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.07 (d, ^4J = 1.3 Hz, 2H), 8.03 (d, ^3J = 8.0 Hz, 2H), 7.93 (d, ^3J = 15.5 Hz, 2H), 7.44 (m, 12H), 7.27 (m, 3H), 6.55 (d, ^3J = 15.7 Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 182.6, 142.2, 142.0, 141.4, 136.0, 132.6, 128.5, 127.5, 126.6, 126.2, 125.9, 123.2, 122.7, 121.3, 120.5, 119.6, 119.5, 115.8, 108.8, 108.7, 29.2; LRMS (EI) (positive mode) m/z 559.2 $[M + H]^+$, (negative mode) 557.3 $[M - H]^-$. Anal. Calcd for $C_{39}H_{30}N_2O_2$: C, 83.85; H, 5.41; N, 5.01. Found: C, 84.07; H, 5.38; N, 4.86. This compound (111 mg, 0.20 mmol) was reacted with boron trifluoride etherate to afford the boron complex **4** as a red solid (121 mg, quantitative): mp = 309−311 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.29 (d, ^3J = 15.4 Hz, 2H), 8.13 (d, ^4J = 1.1 Hz, 2H), 8.05 (d, ^3J = 9.0 Hz, 2H), 7.60 (m, 3H), 7.51 (m, 4H), 7.41 (m, 4H), 7.30 (d, ^3J = 8.3 Hz, 4H), 6.54 (d, ^3J = 15.4 Hz, 2H), 3.90 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 177.1, 148.7, 143.1, 141.3, 133.3, 132.3, 129.1, 128.6, 127.1, 126.6, 125.8, 123.4, 122.9, 122.6, 120.6, 120.2, 116.2, 113.5, 109.1, 109.0, 29.3; ^{19}F NMR (235 MHz, $CDCl_3$) δ = −140.95 (^{10}B-F, 0.2), −141.01 (^{11}B-F, 0.8); LRMS (EI) (positive mode) m/z 629.2 $[M + Na]^+$, 645.2 $[M + K]^+$. Anal. Calcd for

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$C_{39}H_{29}BF_2N_2O_2 \cdot {}^1/_{10}CH_2Cl_2$: C, 76.37; H, 4.79; N, 4.56. Found: C, 76.72; H, 4.65; N, 4.56.

Spectroscopy. Solid-state spectra were measured and corrected for scattered light background by drop-casting the compound in dry dichloromethane (DCM) on a quartz plate. Luminescence quantum yields Φ_f were measured in diluted solution with an absorbance lower than 0.1 at the excitation wavelength using the following equation $\Phi_{fx}/\Phi_{fr} = [A_r(\lambda)/A_x(\lambda)][D_x/D_r]$ where A is the absorbance at the excitation wavelength (λ), and D the integrated luminescence intensity. Subscripts "r" and "x" stand for reference and sample, respectively. The luminescence quantum yields were not corrected by the refractive indices. We used ruthenium trisbipyridine bischloride in water (Φ_{fr} = 0.021) as reference compound. The luminescence quantum yields were double-checked using chalcone boron difluoride compounds previously reported.[9] Luminescence lifetimes were determined by a method adapted for time-correlated single-photon counting. For these measurements, pulsed LEDs with the appropriate wavelength were used. Emission was monitored perpendicular to the excitation pulse.

X-ray Crystallography. The intensity data for the single-crystal X-ray diffraction analysis of **M4** were collected at room temperature on diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data collection was performed with COLLECT,[39] cell refinement and data reduction with DENZO/SCALEPACK.[40] The structure was solved with SIR92[41] and SHELXL-97[42] was used for full matrix least-squares refinement. The H-atoms were then introduced at idealized positions and constrained to their parent atom during the last refinements. Graphics were generated with MERCURY 2.4.

■ ASSOCIATED CONTENT

Supporting Information

Proton and carbon NMR spectra of reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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