Synthesis, Electrochemical and Photophysical Studies of the Borondifluoride Complex of a meta-Linked Biscurcuminoid

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Supporting information
Figure NMR1. $^1$H NMR spectrum of 1 ((1E,4Z,6E)-5-(difluoroboryloxy)-1,7-bis(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in (CD$_3$)$_2$CO.

Figure NMR2. $^1$H NMR spectrum of Lig 3 ((1E,4Z,6E)-5-hydroxy-7-(4-methoxyphenyl)-1-(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in CDCl$_3$.

Figure NMR3. $^{13}$C NMR spectrum of Lig 3 ((1E,4Z,6E)-5-hydroxy-7-(4-methoxyphenyl)-1-(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in CDCl$_3$.

Figure NMR4. $^1$H NMR spectrum of 3 ((1E,4Z,6E)-5-(difluoroboryloxy)-7-(4-methoxyphenyl)-1-(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in DMSO-$d_6$.

Figure NMR5. $^1$H NMR spectrum of Lig 4 ((1E,1'E,4Z,4'Z,6E,6'E)-1,1'-(2,4,6-tris(octyloxy)-1,3-phenylene)bis(5-hydroxy-7-(4-methoxyphenyl)hepta-1,4,6-trien-3-one)) in CDCl$_3$.

Figure NMR6. $^{13}$C NMR spectrum of Lig 4 ((1E,1'E,4Z,4'Z,6E,6'E)-1,1'-(2,4,6-tris(octyloxy)-1,3-phenylene)bis(5-(difluoroboryloxy)-7-(4-methoxyphenyl)hepta-1,4,6-trien-3-one)) in CDCl$_3$.

Figure NMR7. $^1$H NMR spectrum of 4 ((1E,1'E,4Z,4'Z,6E,6'E)-1,1'-(2,4,6-tris(octyloxy)-1,3-phenylene)bis(5-(difluoroboryloxy)-7-(4-methoxyphenyl)hepta-1,4,6-trien-3-one)) in (CD$_3$)$_2$CO.

Figure S1. Cyclic voltammogram of the bis borondifluoride complex 1 (a), 2 (b) and 3 (c) in DCM solution containing 0.1M [([nBu$_4$N]PF$_6$] (Scan rate of 100 mV/s).

Figure S2. Lippert-Mataga plots for a/ 1 (■), 2 (●) and 3 (▲); b: 3 (▲) and 4 (▼).

Figure S3. Electronic absorption (a) and fluorescence emission (b) spectra of compound 1 in solvents of different polarity at room temperature ($\lambda_{exc} = 450$nm).

Figure S4. Electronic absorption (a) and fluorescence emission (b) spectra of compound 2 in solvents of different polarity at room temperature ($\lambda_{exc} = 480$nm).

Figure S5. Electronic absorption (a) and fluorescence emission (b) spectra of compound 3 in solvents of different polarity at room temperature ($\lambda_{exc} = 480$nm).

Figure S6. Electronic absorption (a) and fluorescence emission (b) spectra of compound 4 in solvents of different polarity at room temperature ($\lambda_{exc} = 480$nm).

Figure S7. Dependencies of the fluorescence intensity versus laser excitation power for 1 (■, black) in DCM.

Figure S8. Two-photon excitation in DCM: a/ dye 1 and b/ dye 2.

Table S1. Spectroscopic data and photophysical properties of compounds 1 and 2 in solvents of different polarity at room temperature.

Table S2. Spectroscopic data and photophysical properties of compounds 3 and 4 in solvents of different polarity at room temperature.
Figure NMR1. $^1$H NMR spectrum of 1 ((1E,4Z,6E)-5-(difluoroboryloxy)-1,7-bis(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in (CD$_3$)$_2$CO.

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**Figure NMR3.** $^{13}$C NMR spectrum of Lig 3 ((1E,4Z,6E)-5-hydroxy-7-(4-methoxyphenyl)-1-(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in CDCl$_3$.

**Figure NMR4.** $^1$H NMR spectrum of 3 ((1E,4Z,6E)-5-(difluoroboryloxy)-7-(4-methoxyphenyl)-1-(2,4,6-trimethoxyphenyl)hepta-1,4,6-trien-3-one) in DMSO-$d_6$. 
Figure NMR5. $^1$H NMR spectrum of Lig 4 ((1E,1'E,4Z,4'Z,6E,6'E)-1,1'-(2,4,6-tris(octyloxy)-1,3-phenylene)bis(5-hydroxy-7-(4-methoxyphenyl)hepta-1,4,6-trien-3-one)) in CDCl$_3$.

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**Figure NMR7.** $^1$H NMR spectrum of 4 ((1E,1′E,4Z,4′Z,6E,6′E)-1,1′-(2,4,6-tris(octyloxy)-1,3-phenylene)bis(5-(difluoroboryloxy)-7-(4-methoxyphenyl)hepta-1,4,6-trien-3-one)) in (CD$_3$)$_2$CO.

**Figure S1.** Cyclic voltammogram of the bis borondifluoride complex 1 (a), 2 (b) and 3 (c) in DCM solution containing 0.1M [($^t$Bu$_4$N)PF$_6$] (Scan rate of 100 mV/s).
Figure S2. Lippert-Mataga plots for a/ 1 (■), 2 (●) and 3 (▲); b: 3 (▲) and 4 (▼) where \( \Delta f' = \frac{[\varepsilon - 1]}{2\varepsilon + 1} - 0.5 \left[ \frac{n^2 - 1}{(2n^2 + 1)} \right] \).

Figure S3. Electronic absorption (a) and fluorescence emission (b) spectra of compound 1 in solvents of different polarity at room temperature (\( \lambda_{exc} = 450\text{nm} \); carbon tetrachloride (■), n-dibutylether (●), ethylic ether (▲), ethyl acetate (●), dichloromethane (■), 1,2-dichloroethane (●), acetone (●) and acetonitrile (●)).
Figure S4. Electronic absorption (a) and fluorescence emission (b) spectra of compound 2 in solvents of different polarity at room temperature ($\lambda_{\text{exc}} = 480\text{nm}$; carbon tetrachloride (●), n-dibutylether (●), ethylic ether (●), ethyl acetate (●), dichloromethane (●), 1,2-dichloroethane (●), acetone (●) and acetonitrile (●)).

Figure S5. Electronic absorption (a) and fluorescence emission (b) spectra of compound 3 in solvents of different polarity at room temperature ($\lambda_{\text{exc}} = 480\text{nm}$; carbon tetrachloride (●), n-dibutylether (●), ethylic ether (●), ethyl acetate (●), dichloromethane (●), 1,2-dichloroethane (●), acetone (●) and acetonitrile (●)).
Figure S6. Electronic absorption (a) and fluorescence emission (b) spectra of compound 4 in solvents of different polarity at room temperature ($\lambda_{\text{exc}} = 480$nm; carbon tetrachloride (●), n-dibutylether (○), ethylic ether (●), ethyl acetate (●), dichloromethane (●), 1,2-dichloroethane (○), acetone (●) and acetonitrile (ــــ)).

Figure S7. Dependencies of the fluorescence intensity versus laser excitation power for 1 (■, black) in DCM.
Figure S8. Two-photon excitation (▪, higher x-coordinate and ▬, right y-coordinate) with their error bars, OPA spectra (▬, lower x-coordinate and ▬, left y-coordinate) in DCM: a/ dye 1 and b/ dye 2.

Table S1. Spectroscopic data and photophysical properties of compounds 1 and 2 in solvents of different polarity at room temperature

<table>
<thead>
<tr>
<th>solvent</th>
<th>( \lambda_{\text{abs}} ) (nm)</th>
<th>( \lambda_{\text{em}} ) (nm)</th>
<th>( \Delta \nu_{ST} ) (cm(^{-1}))</th>
<th>( \phi_f )</th>
<th>( \tau_f ) (ns)</th>
<th>( k_f ) ((10^8 \text{ s}^{-1}))</th>
<th>( k_{nr} ) ((10^8 \text{ s}^{-1}))</th>
<th>( \lambda_{\text{abs}} ) (nm)</th>
<th>( \lambda_{\text{em}} ) (nm)</th>
<th>( \Delta \nu_{ST} ) (cm(^{-1}))</th>
<th>( \phi_f )</th>
<th>( \tau_f ) (ns)</th>
<th>( k_f ) ((10^8 \text{ s}^{-1}))</th>
<th>( k_{nr} ) ((10^8 \text{ s}^{-1}))</th>
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\( a \) Absorption maximum wavelengths \( \lambda_{\text{abs}} \) (nm). Fluorescence maximum wavelengths \( \lambda_{\text{em}} \) (nm). Stokes shifts \( \Delta \nu_{ST} \) (cm\(^{-1}\)). Fluorescence quantum yields \( \phi_f \). Fluorescence lifetimes \( \tau_f \) (ns). Radiative \( k_f \) \((10^8 \text{ s}^{-1})\) and nonradiative \( k_{nr} \) \((10^8 \text{ s}^{-1})\) rate constants; Bu\(_2\)O: n-dibutylether. Et\(_2\)O: ethylic ether. AcOEt: ethyl acetate. DCM: dichloromethane. DCE: 1,2-dichloroethane. ACN: acetonitrile.
Table S2. Spectroscopic data and photophysical properties of compounds 3 and 4 in solvents of different polarity at room temperature$^d$

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\lambda_{\text{abs}}$</th>
<th>$\lambda_{\text{em}}$</th>
<th>$\Delta\nu_{\text{ST}}$</th>
<th>$\Phi_f$</th>
<th>$\tau_f$</th>
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<th>$\lambda_{\text{em}}$</th>
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$^d$ Absorption maximum wavelengths $\lambda_{\text{abs}}$ (nm), fluorescence maximum wavelengths $\lambda_{\text{em}}$ (nm), Stokes shifts $\Delta\nu_{\text{ST}}$ (cm$^{-1}$), fluorescence quantum yields $\Phi_f$, fluorescence lifetimes $\tau_f$ (ns), radiative $k_f$ ($10^8$ s$^{-1}$) and nonradiative $k_{\text{nr}}$ = (1 - $\Phi_f$)/$\tau_f$ ($10^8$ s$^{-1}$) rate constants; Bu$_2$O: n-dibutylether, Et$_2$O: ethylic ether, AcOEt: ethyl acetate, DCM: dichloromethane, DCE: 1,2-dichloroethane, ACN: acetonitrile.