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Excimer emission and energy transfer in cofacial boradiazaindacene (BODIPY) dimers built on a xanthene scaffold

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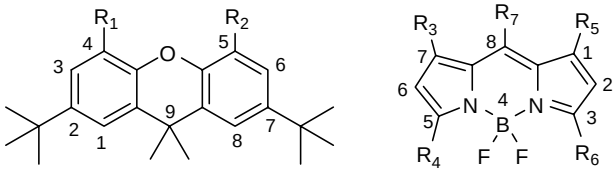
Abstract—Using a rigid xanthene scaffold, a series of boradiazaindacene derivatives were synthesized. In some of these compounds, two boradiazaindacene derivatives were placed cofacially, resulting in significant inter-chromophoric interactions, including excimer emission. A simple modification of boradiazaindacene structure leads to formation of an ICT dye, which has distinct spectral properties. Energy transfer between two BODIPY dyes was demonstrated as well. In addition, the spectral properties of ICT dye can be modulated by the addition of the acid leading to an acid switchable energy transfer cassette.

1. Introduction

Boradiazaindacenes (a.k.a, BODIPY dyes, BDPs, difluorobora-dipyrromethenes, etc.) are well known fluorescent dyes with remarkable spectral properties like high quantum yields, large extinction coefficients and narrow emission bands.[1] These properties facilitated their application in many fields, such as fluorescent labeling of biomolecules,[2] ion sensing and signaling,[3] energy transfer cassettes,[4] light harvesting systems[5] and fluorescent stains.[1] Especially considering the relative ease of derivatization, it should not be difficult to predict further diversification of applications in the near future. Dimeric boradiazaindacenes should be particularly interesting as a new subclass of these dyes. It is well known that when biomolecules are labeled with boradiazaindacene dyes at relatively large dye/protein ratios, two boradiazaindacene moieties can come very close to each other and interactions yield quenching of the emission and/or formation of a bathochromically shifted excimer band.[6] The existence of two structurally distinct dimers were proposed and based on these observations, a BODIPY dimer obtained by the labeling of diaminocyclohexane was studied.[7] However, in all of these dimeric systems, boradiazaindacene units are highly flexible and in principle can adopt a number of different excited state structures. Thus, it would be very interesting to assemble two boradiazaindacene units in a rigid cofacial arrangement on a suitable scaffold. Here, there is just one possible transition dipole, which might lead to a very clearly understandable experimental results. The xanthene unit seems to provide such a structural feature because functionalization at positions 4 and 5 looks straightforward (Fig. 1). In recent literature, there are reports of cofacially arranged porphyrin and perylenediimide dyes,[8] but no examples of cofacial boradiazaindacene dimers were found. In this paper, we present the synthesis, energy transfer and acid switching of spectral properties of novel boradiazaindacene dimers built on a xanthene scaffold.



I II

Figure 1. Structures of 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthane I and difluorobora-dipyrromethene II.

2. Results and discussion

The synthesis of the dyes **4**, **5** and **9** starts with the chloromethylation of the *t*-butylated xanthene derivative **1** (Scheme 1). Paraformaldehyde and concd HCl was used to carry out this transformation. Following a standard work-up, the product was usually obtained in satisfactory purity and

Keywords: BODIPY dyes; Energy transfer; Multichromophoric systems; Molecular switches.
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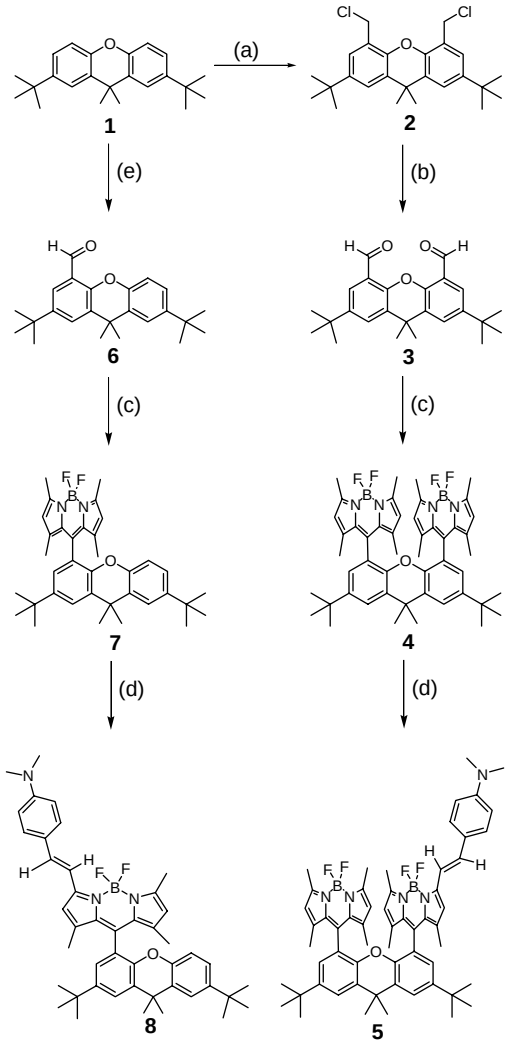
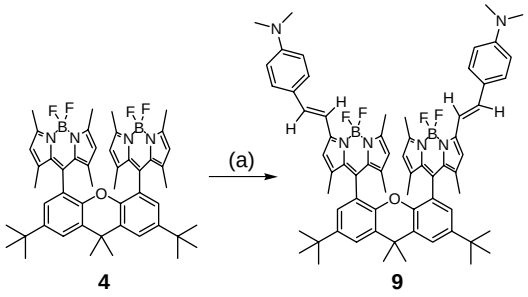


Scheme 1. Synthesis of BODIPY dyes **4**, **5**, **7** and **8**. Reagents and conditions: (a) HCl, $(CH_2O)_n$, Δ, CH_3COOH, *o*-phosphoric acid; (b) DMSO, $NaHCO_3$, Δ; (c) 2,4-dimethylpyrrole, TFA, Et_3N, BF_3:OEt_2, rt; (d) piperidine, CH_3COOH, *N*,*N*-dimethyl-4-aminobenzaldehyde; (e) HMTA, TFA, reflux.

used directly in the next step, which is the oxidation to bis-aldehyde **3** using DMSO. This aldehyde was then utilized in the construction of two boradiazaindacene units on the xanthene scaffold. This was done in analogy to the literature procedures, using 2,4-dimethylpyrrole as the source for the pyrrole unit. Following the purification steps, a bright green fluorescent dye **4** was obtained in 24% yield. Due to the acidity of the methyl groups at positions 3 and 5 of the boradiazaindacene heterocyclic system, extension of conjugation is possible by the condensation with aromatic aldehydes.[3e,9] We chose *p*-dimethylaminobenzaldehyde as the aldehyde in this reaction, because the electron donor capacity of the dialkylamino group can be modified by the protonation/deprotonation equilibrium, which could result in significant spectral changes. Thus, compounds **5** and **9** were obtained by refluxing the aldehyde together with the dye **4** in a Dean–Stark apparatus (Scheme 2). The second methyl group in each boradiazaindacene unit is presumably less reactive. In order to accurately assess the inter-chromophoric interactions including resonance energy transfer, we also synthesized xanthene derivatives carrying just one boradiazaindacene unit (compounds **7** and **8**).



Scheme 2. Synthesis of BODIPY dye **9**. Reagents and conditions: (a) piperidine, CH_3COOH, *N*,*N*-dimethyl-4-aminobenzaldehyde.

The normalized absorption spectra of compounds **4** and **7** in THF are shown in Figure 2. There are remarkable changes in the absorption spectrum. In the cofacial dimer **4**, the absorption peak is blue shifted to 478 nm with a shoulder at 504 nm. Compound **5**, as expected, shows two peaks, one for the standard boradiazaindacene absorption (455 nm) and one for the extended conjugation chromophore 575 nm. When a few drops of TFA is added, the long wavelength ICT absorption shifts to shorter wavelengths (530 nm) reflecting lower electron donor characteristics of the protonated dialkylamino groups (Fig. 3). Also, the absorption spectra of compounds **5**, **8** and **9** are shown separately in Figure 4. Extension of conjugation, as expected, results in a broad longer wavelength absorption at 571 nm. This is in accordance with the internal charge transfer (ICT) character of the dyes. The emission spectra are even more interesting: while monochromophoric **7** yields a very strong emission at 500 nm when excited at 480 nm, **4** results in highly quenched emission with two

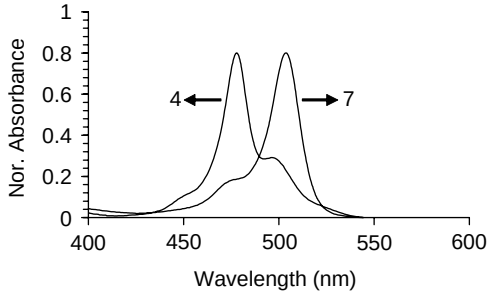


Figure 2. Normalized absorption spectra of compounds **4** and **7**. Normalized (performed at the maxima (478 and 504 nm, respectively)) to an arbitrary value of 0.8.

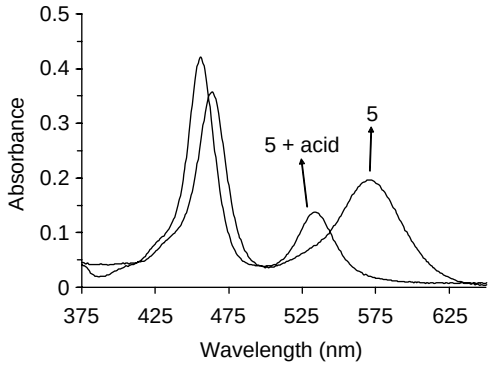


Figure 3. Absorption spectra of compound **5** and its acidified form. Upon acidification with a few drops of TFA, a significant blue shift is observed.

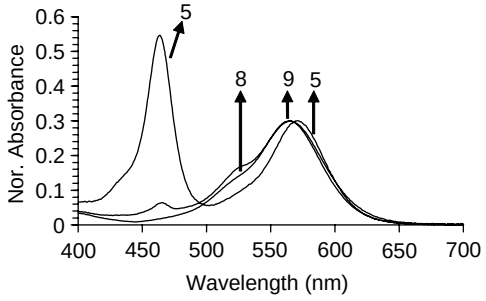


Figure 4. Normalized absorption spectra of compounds **5**, **8** and **9**. Normalization was done at the long wavelength peaks to an arbitrary value of 0.3.

peaks one at 505 nm and a broader excimer emission with a peak at 590 nm (Fig. 5). This is in accordance with the earlier observations made with less rigid boradiazaindacene dimers and organized media like micelles. In Figure 6, emission characteristics of **4**, **5** and **8** were compared. When the absorptions at the excitation wavelength (480 nm) for **4** and **5** were adjusted to 0.1, the emission spectra give more quantitative information about the quantum yields and the efficiency of the energy transfer relative emission. Very clearly, in compound **5**, the emission from the green emitting boradiazaindacene unit is further quenched, and some emission at long wavelength can be seen, this is due to energy transfer between the donor and the acceptor chromophore. The absorption of compound **8** was also adjusted at the long wavelength peak (near 550 nm) to that of compound **5**. But, since this chromophore does not absorb at 480 nm effectively, the emission is very weak. When analyzed together, it becomes obvious that in compound **5** there is efficient energy transfer. The efficiency can be

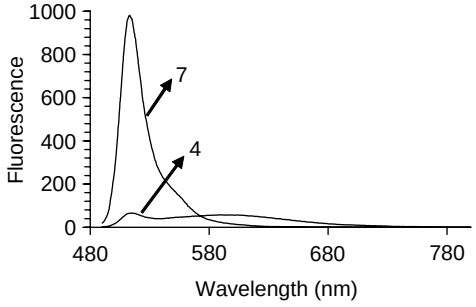


Figure 5. Emission spectra of compounds **4** and **7**. The absorption values at the excitation wavelength (480 nm) was adjusted to 0.1.

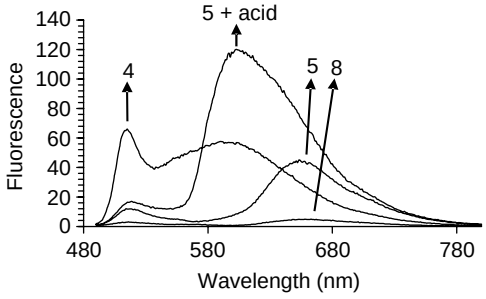


Figure 6. Emission spectrum of **4**, **5**, **8**. Absorption values of the dyes **4** and **5** were set at 0.1, whereas the absorption peaks at the long wavelength region (near 550 nm) were set to be comparable for the dyes **5** and **8**.

further improved by the protonation of the dialkylaminogroups by the addition of a few drops of TFA. The increase in intensity is probably in part due to the increased spectral overlap caused by the blue shift in the absorption spectrum of compound **5**.

3. Conclusion

We have synthesized and characterized xanthene derivatives with boradiazaindacene units attached orthogonally and in a very rigid arrangement. The cofacial chromophores were separated from each other only by a distance of approximately 4.5 Å, so both energy transfer and excimer formation can be observed in these systems. These derivatives can be excellent models to study the role of orientation of dipole moments during excitation. A careful inspection of the structure of compound **9** reveals that *syn–anti* stereoisomerism is possible. Although isolation of both isomers would be very useful in the study relative chromophore orientations in energy transfer, we were able to isolate only one isomer, most likely the *anti*-isomer. Based on our modeling studies, and considering the steric requirements of the condensation reaction, the *anti*-isomer is expected to be the major, if not the sole product.

The bichromophoric systems described here, have some potential as energy transfer cassettes, as well. In principle, these compounds can be excited at 480 nm, and the emission can be collected at 650 nm. As novel fluorophore systems, it is also likely that water soluble derivatives can be used in labeling biomolecules and in novel fluorescent chemosensors for cations or anions.

4. Experimental

4.1. General

The compounds were characterized and analyzed by nuclear magnetic resonance spectroscopy (NMR), UV/vis spectroscopy, and fluorescence spectroscopy. ^{1}H and ^{13}C nuclear magnetic resonance spectra of all compounds were recorded in $CDCl_3$ with Bruker Gmbh DPX-400, 400 MHz High Performance Digital FT-NMR Spectrometer. UV/vis spectra were recorded by Varian Bio 100 UV/vis Spectrophotometer. Fluorescence spectra were recorded using Varian Cary Eclipse Fluorescence Spectrophotometer. All solvents were distilled over $CaCl_2$ before use. 2,7-Di-*tert*-butyl-9,9-dimethyl-xanthane and 2,4-dimethylpyrrole were obtained from Aldrich. Hexamethylenetetramine was purchased from MERCK-Schuchardt. Merck Silica Gel 60 F_{254} TLC Aluminum sheets were used in monitoring reactions by thin-layer chromatography. Merck Silica Gel 60 (particle size 0.040–0.0963 mm, 230–400 mesh ASTM) used in column chromatography.

4.1.1. 2,7-Di-*tert*-butyl-4,5-bis(chloromethyl)-9,9-dimethyl-9*H*-xanthene 2. A mixture of 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene (500 mg, 1.55 mmol), *p*-formaldehyde (200 mg), orthophosphoric acid (0.14 mL), HCl (0.6 mL) and acetic acid (8.2 mL) were heated in a pressure

tube at 85 °C for overnight. The reaction mixture was then diluted with $CHCl_3$ and the solution was washed with saturated $NaHCO_3$. Then, the organic phase was dried over anhydrous Na_2SO_4 and solvent was evaporated under reduced pressure to give bis(chloromethyl)xanthene **2** as white powder (585 mg, 90%). Used in the following steps without further purification. Mp 201–202 °C. IR (KBr) ν_{max}: 3022, 1110 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 18H, $C(CH_3)_3$), 1.57 (s, 6H, $C(CH_3)_2$), 4.75 (s, 4H, CH_2), 7.17 (s, 2H, Ar-H), 7.28 (s, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.9, 32.0, 32.8, 34.9, 42.5, 123.9, 124.4, 125.9, 130.0, 146.1, 146.4.

4.1.2. 2,7-Di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene-4,5-dicarbaldehyde 3. 2,7-Di-*tert*-butyl-4,5-bis(chloromethyl)-9,9-dimethyl-9*H*-xanthene (1.2 g, 2.86 mmol) and $NaHCO_3$ (600 mg, 7.14 mmol) were heated in DMSO (200 mL) for 3 days. The reaction mixture was then diluted with $CHCl_3$, and the solution was washed with water until all the DMSO was removed. Then the mixture was dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by silica gel column chromatography (CH_3OH/$CHCl_3$ 1:99) to give **3** (324.7 mg, 30%) as a white solid. Mp 248–249 °C. IR (KBr) ν_{max}: 3031, 1721, 1128 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 18H, $C(CH_3)_3$), 1.62 (s, 6H, $C(CH_3)_2$), 7.64 (d, J_{meta}=2.38 Hz, 2H, Ar-H), 7.74 (d, J_{meta}=2.39 Hz, 2H, Ar-H), 10.6 (s, 2H, CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.7, 32.6, 32.8, 35.1, 62.4, 123.8, 124.4, 129.8, 130.9, 147.0, 149.9, 189.2. Elemental analysis: Found: C, 79.13; H, 8.05. $C_{25}H_{30}O_3$ requires C, 79.33; H, 7.99.

4.1.3. Bis-(boradiazaindacenyl)-derivatized xanthene 4. 2,4-Dimethylpyrrole (456 mg, 4.8 mmol) was added to a solution of 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene-4,5-dicarbaldehyde (400 mg, 1.05 mmol) in argon bubbled CH_2Cl_2 (750 mL). Then a drop of CF_3COOH was added and the solution was allowed to stir for 4 h at room temperature. Then tetrachloro-1,4-benzoquinone (258.3 mg, 1.05 mmol) in absolute CH_2Cl_2 (50 mL), Et_3N (4 mL) and BF_3:OEt_2 (4 mL) were added in order to the solution and stirred for overnight at at room temperature for overnight. The solution was concentrated under reduced pressure and washed with water several times and dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography (CH_3OH/$CHCl_3$ 1:99) to obtain reddish product **4** (162.9 mg, 20%). IR (KBr) ν_{max}: 3027, 1178, 1133 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.25–1.29 (overlapping singlets, 18H+12H, $C(CH_3)_3$+pyr-CH_3), 1.57 (s, 6H, $C(CH_3)_2$), 2.03 (s, 12H, pyr-CH_3), 5.21 (s, 4H, pyr-H), 7.17 (d, J_{meta}=1.96 Hz, 2H, Ar-H), 7.33 (d, J_{meta}=2.0 Hz, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 14.7, 31.5, 33.5, 34.7, 62.5, 120.1, 122.3, 123.3, 125.1, 128.7, 131.2, 136.8, 141.4, 143.8, 147.1, 155.1. Elemental analysis: Found: C, 72.14; H, 6.74; N, 6.99. $C_{49}H_{56}N_4OB_2F_4$ requires C, 72.25; H, 6.93; N, 6.88.

4.1.4. Bichromophoric xanthene derivative 5. Compound **4** (110 mg, 1.35 mmol) and *N*,*N*-dimethyl-4-aminobenzaldehyde (143.1 mg, 1.35 mmol) in a mixture of benzene (18 mL), acetic acid (510 μL) and piperidine (560 μL). Water formed during the reaction was removed azeotropically by heating in a Dean–Stark apparatus for 3 h. The solution containing the crude product was concentrated under reduced pressure and purified by silica gel column chromatography (1:4 ethylacetate/hexane) in 75% yield. IR (KBr) ν_{max}: 3093, 3036, 1172, 1095 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (unresolved singlets, 18H+12H, $C(CH_3)_3$+pyr-CH_3), 1.57 (s, 6H, $C(CH_3)_2$), 2.34 (s, 3H, pyr-CH_3), 2.39 (s, 3H, pyr-CH_3), 2.41 (s, 3H, pyr-CH_3), 3.0 (s, 6H, $N(CH_3)_2$), 5.20 (s, 1H, pyr-H), 5.51 (s, 1H, pyr-H), 5.55 (s, 1H, pyr-H), 5.65 (s, 1H, pyr-H), 6.63–6.65 (m, 2H), 6.88–7.05 (m, 4H), 7.4–7.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.4, 33.3, 33.7, 34.7, 119.8, 120.7, 112.4, 123.2, 123.3, 125.2, 125.5, 128.7, 130.9, 131.5, 136.7, 140.5, 141.8, 143.9, 144.1, 153.6, 156.9. Elemental analysis: Found: C, 73.43; H, 7.07; N, 7.29. $C_{58}H_{65}N_5OB_2F_4$ requires C, 73.66; H, 6.93; N, 7.40.

4.1.5. 2,7-Di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene-4-carbaldehyde 6. A mixture of 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene (967 mg, 3 mmol), hexamethylene–tetramine (840 mg, 6 mmol) and CF_3COOH (6 mL) were refluxed for 24 h. The acid was removed under reduced pressure and the residue was then subjected to silica gel column chromatography. (CH_3OH/$CHCl_3$ 1:99) to yield compound **6** (540 mg, 51%). Mp 158–160 °C. IR (KBr) ν_{max}: 3039, 1719, 1114 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 18H, $C(CH_3)_3$), 1.62 (s, 6H, $C(CH_3)_2$), 6.8 (d, J_{ortho}=8.5 Hz, 1H, Ar-H), 7.06 (dd, J_{ortho}=8.5 Hz, J_{meta}=2.3 Hz, 1H, Ar-H), 7.3 (d, J_{meta}=2.3 Hz, 1H, Ar-H) 7.52 (d, J_{meta}=2.2 Hz, 1H, Ar-H), 7.62 (d, J_{meta}=2.3 Hz, 1H, Ar-H), 10.5 (s, 1H, CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 31.5, 32.8, 34.7, 41.4, 62.4, 116.0, 121.6, 122.9, 123.5, 124.4, 129.8, 130.9, 136.5, 148.5, 189.2. Elemental analysis: Found: C, 82.45; H, 8.58. $C_{24}H_{30}O_2$ requires C, 82.24; H, 8.63.

4.1.6. Boradiazaindacenyl-xanthene derivative 7. 2,4-Dimethylpyrrole (540 mg, 5.14 mmol) was added to a solution of 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene-4-carbaldehyde (540 mg, 2.57 mmol) in argon bubbled CH_2Cl_2 (750 mL). Then a drop of CF_3COOH was added and the solution was allowed to stir for 4 h at room temperature. Then, tetrachloro-1,4-benzoquinone (258 mg, 2.57 mmol) in dry CH_2Cl_2 (50 mL), Et_3N (4 mL) and BF_3:OEt_2 (4 mL) were added in that order to the solution, and stirred at room temperature overnight. The solution was concentrated under reduced pressure and washed with water several times, then dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography (CH_3OH/$CHCl_3$ 1:99) to obtain reddish product **7** (350.4 mg, 24%). IR (KBr) ν_{max}: 3024, 1180, 1130 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 18H, $C(CH_3)_3$), 1.34 (s, 6H, $C(CH_3)_2$), 1.59 (s, 6H, pyr-CH_3), 2.52 (s, 6H, pyr-CH_3) 5.87 (s, 2H, pyr-H), 6.77 (d, 1H, Ar-H, J_{ortho}=8.6 Hz), 7.01 (d, 1H, Ar-H, J_{meta}=2.6 Hz), 7.06 (dd, 1H, Ar-H, J_{ortho}=8.5 Hz, J_{meta}=2.3 Hz), 7.3 (d, 1H, Ar-H, J_{meta}=2.3 Hz), 7.4 (d, 1H, Ar-H, J_{meta}=2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 31.7, 32.8, 62.4, 123.8, 124.4, 129.8, 130.9, 147.0, 149.9, 189.2. Elemental analysis: Found: C, 76.23; H, 7.81; N, 4.78. $C_{36}H_{43}N_2OBF_2$ requires C, 76.05; H, 7.62; N, 4.93.

4.1.7. Extended conjugation boradiazaindacenyl xanthene derivative 8. Compound **7** (100 mg,

0.176 mmol) and *N*,*N*-dimethyl-4-aminobenzaldehyde (25.6 mg, 0.176 mmol) in a mixture of benzene (18 mL), acetic acid (506 μL) and piperidine (557 μL). Any water formed during the reaction was removed azeotropically by heating in a Dean–Stark apparatus for 3 h. The reaction mixture was concentrated under reduced pressure and then subjected to silica gel column chromatography (1:4 ethylacetate/hexane) to yield the desired product **8** in 50% yield (61 mg). IR (KBr) ν_{max}: 3090, 3032, 1177, 1101 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 18H, $C(CH_3)_3$), 1.35 (s, 3H, pyr-CH_3), 1.39 (s, 3H, pyr-CH_3), 1.59 (s, 6H, $C(CH_3)_2$), 2.5 (s, 3H, pyr-CH_3), 3.01 (s, 6H, $N(CH_3)_2$), 5.87 (s, 1H, pyr-H), 6.49 (s, 1H, pyr-H), 6.66 (d, 2H, $J=8.7$ Hz), 7.04–7.10 (m, 4H), 7.31 (d, $J=2.3$ Hz, 1H), 7.43–7.46, (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5, 32.2, 32.4, 34.5, 34.7, 116.3, 122.1, 122.2, 123.0, 124.4, 125.2, 128.7, 129.1, 130.4, 145.8, 146.5, 148.1. Elemental analysis: Found: C, 77.45; H, 7.92; N, 5.99. $C_{47}H_{56}N_3OBF_2$ requires C, 77.57; H, 7.76; N, 5.77.

4.1.8. Extended conjugation bis-(boradiazaindacenyl)-xanthene derivative 9. Compound **4** (110 mg, 0.176 mmol) and *N*,*N*-dimethyl-4-aminobenzaldehyde (52.6 mg, 0.352 mmol) in a mixture of benzene (18 mL), acetic acid (506 μL) and piperidine (557 μL). Any water formed during the reaction was removed azeotropically by heating in a Dean–Stark apparatus for 3 h. The reaction mixture was concentrated under reduced pressure and then subjected to silica gel column chromatography (1:4 ethylacetate/hexane) to yield the desired product **8** in 40% yield (65 mg). IR (KBr) ν_{max}: 3087, 3033, 1173, 1099 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.24–1.30 (two unresolved singlets, 18H+12H), 1.59 (s, 6H), 2.55 (s, 6H), 3.01 (s, 12H, $N(CH_3)_2$) 5.85 (s, 2H), 6.50 (s, 2H), 6.64 (d, 4H, $J=8.7$ Hz), 6.78–6.82 (m, 2H), 7.02–7.25 (m, 8H), 7.35 (d, 2H). Elemental analysis: Found: C, 74.53; H, 6.92; N, 7.69. $C_{67}H_{74}N_6OB_2F_4$ requires C, 74.72; H, 6.93; N, 7.80.

Acknowledgements

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References and notes

1. *Handbook of Fluorescent Probes and Research Products*; Haugland, R. P., Ed. 9th ed.; Molecular Probes: Eugene, OR, 2003.
2. (a) Yee, M.; Fas, S. C.; Stohlmeyer, M. M.; Wandless, T. J.; Cimprich, K. A. *J. Biol. Chem.* **2005**, *280*, 29053–29059. (b) Tan, K.; Jaquinod, L.; Paolesse, R.; Nardis, S.; Di Natale, C.; Di Carlo, A.; Prodi, L.; Montalti, M.; Zaccheroni, N.; Smith, K. M. *Tetrahedron* **2004**, *60*, 1099–1106.
3. Recent examples: (a) Turfan, B.; Akkaya, E. U. *Org. Lett.* **2002**, *4*, 2857–2859. (b) Ulrich, G.; Ziessel, R. *J. Org. Chem.* **2004**, *69*, 2070–2083. (c) Gabe, Y.; Urano, Y.; Kikuchi, K.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2004**, *126*, 3357–3367. (d) Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968–969. (e) Coskun, A.; Baytekin, B. T.; Akkaya, E. U. *Tetrahedron Lett.* **2003**, *44*, 5649–5651. (f) Coskun, A.; Akkaya, E. U. *Tetrahedron Lett.* **2004**, *45*, 4947–4949. (g) Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2005**, *127*, 10464–10465.
4. (a) Burghart, A.; Thoresen, L. H.; Chen, J.; Burgess, K.; Bergström, F.; Johansson, L.B.-Å. *Chem. Commun.* **2000**, 2203–2204. (b) Wan, C.-W.; Burghart, A.; Chen, J.; Bergström, F.; Johansson, L.B.-Å.; Wolford, M. F.; Kim, T. G.; Topp, M. R.; Hochstrasser, R. M.; Burgess, K. *Chem. Eur. J.* **2003**, *9*, 4430–4441. (c) Ulrich, G.; Goze, C.; Guardigli, M.; Roda, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3694–3698.
5. Maas, H.; Calzaferri, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2284–2288.
6. Dahim, D.; Mizuno, N. K.; Li, X.-M.; Momsen, W. E.; Momsen, M. M.; Brockman, H. L. *Biophys. J.* **2002**, *83*, 1511–1524.
7. (a) Bergström, F.; Mikhalyov, I.; Hägglöf, P.; Wortmann, R.; Ny, T.; Johansson, L.B.-Å. *J. Am. Chem. Soc.* **2002**, *124*, 196–204. (b) Mikhalyov, I.; Gretskaya, N.; Bergström, F.; Johansson, L.B.-Å. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5663–5670.
8. (a) Jokic, D.; Asfari, Z.; Weiss, J. *Org. Lett.* **2002**, *4*, 2129–2132. (b) Yagi, S.; Yonekura, I.; Awakura, M.; Ezoe, M.; Takagishi, T. *Chem. Commun.* **2001**, 557–558. (c) Giaimo, J. M.; Gusev, A. V.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 8530–8531. (d) Chang, C. J.; Loh, Z. H.; Deng, Y. Q.; Nocera, D. G. *Inorg. Chem.* **2003**, *42*, 8262–8269.
9. (a) Haugland, R. P.; Kang, H. C. (Molecular Probes, Inc.). U.S. Patent 4,774,339, 1988. (b) Rurack, K.; Kollmannsberger, M.; Daub, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 385–387.