Boron Dipyrromethene Dyes Bearing Ancillary 2,2′:6′,2′′-Terpyridine Coordination Sites

Anthony Harriman,*[a] Laura J. Mallon,[a] Beverly Stewart,[a] Gilles Ulrich,[b] and Raymond Ziessel*[b]

Two new boron-dipyrromethene dyes have been synthesised and their photophysical properties have been investigated by steady-state and time-resolved fluorescence spectroscopy. These dyes are equipped with ancillary 2,2′:6′,2′′-terpyridine (terpy) residues, attached either at the B centre or at the *meso* position of the organic framework; in this latter case two ethynylated pyrene units are bound to the B atom. Under most experimental conditions, the absorption and emission spectral properties are typical of this class of dye. Complexation of zinc(II) cations to the terpy units attached at the B centre causes complete extinction of the fluorescence due to intramolecular electron transfer from the excited state dye to the resultant zinc(II) bis-terpy complex. Similar behaviour is noted when the terpy is attached at the *meso* site, although the rate of electron transfer is slower due to the weaker driving force. A most unusual feature of the pyrene-substituted dye is its facile self association in acetonitrile solution. This results in the reversible formation of a fluorescent associate, believed to be a symmetric dimer, that absorbs and emits to the red of the monomer. Self association is considered to be driven by a solvophobic effect in which the pyrene units seek to minimize surface contact with the surrounding solvent molecules.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

The discovery of new molecular materials with improved luminescence, electrochemical, and charge transport properties is a thriving subject undergoing rapid development. This widespread interest stems from their use as light-emitting films,[1] electro-luminescent materials[2] and molecular probes.[3] Recently, for example, multi-component arrays based on new luminescent materials have been employed as the key components in supramolecular devices capable both of performing photochemical light-energy conversion and of the storage of information at the molecular level.[4–6] Usually, the properties of the final device depend on both the particular structures of the active chemical centres and on the manner in which different centres are linked together. The latter point is of particular importance and considerable attention is now been paid to finding improved ways in which to self-associate preformed modules into an ordered array. Here, we are concerned with the preparation of highly fluorescent building blocks equipped with the nec-essary functionality to associate in solution into new structures. Emission is provided by using a carefully selected fluorophore as the central unit.

The applicability of fluorescent dyes depends upon their photostability, solvatochromism, molar absorptivity, luminescence quantum yield, solubility and processability. Difluoro-boradiaza-*s*-indacenes, commonly named boron-dipyrromethene dyes (F-Bodipy),[7] are effective fluorescent probes/sensors and the facile modification of their structure provides new opportunities to vary their properties and to provide recognition sites for a variety of analytes. These dyes combine high molar absorption coefficients and high fluorescence quantum yields, excellent chemical and photochemical stability in solution and in the solid state, and valuable charge-transfer properties. Furthermore, their optical properties are sensitive to modifications around the pyrrole core,[8] the central *meso* position[9,10] and the boron atom.[11] Their current uses include those as chromogenic probes,[12] fluorescent switches,[13] electro-chemiluminescent materials,[14,15] laser dyes,[16] sensitizers for solar cells,[17] fluorescent labels for biomolecules,[11] drug delivery agents,[18] and as electron-transfer probes for radical ion pairs generated by local electric fields.[19]

The well-defined molecular structure of bodipy makes it relatively easy to establish firm structure-reactivity relationships. Up to now, major efforts have been devoted to the engineering of classical bodipy structures and the investigation of their salient physical and spectroscopic proper-

[a] Molecular Photonics Laboratory, School of Natural Sciences, Bedson Building, University of Newcastle,
Newcastle upon Tyne, NE1 7RU, United Kingdom
Fax: +44-191-222-8660
E-mail: Anthony.harriman@ncl.ac.uk
[b] Laboratoire de Chimie Moléculaire, Ecole Européenne de Chimie, Polymères et Matériaux, Université Louis Pasteur,
25 rue Becquerel, 67087 Strasbourg Cedex 02, France
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

ties.[20] The recent availability of more advanced bodipy dyes, however, offers the potential to tackle specific problems linked to: (i) sensing of protons[21] or various cations[22,23] by opto-electronic switching, (ii) light-harvesting in porphyrin-based arrays,[24] or other sophisticated architectures,[25,26] and (iii) Stokes' shift enhancement based on molecular cassettes.[27–29] In certain cases, adequate tailoring could induce special sensing properties,[9,30] including fluorescence amplification,[31] and such neutral dyes might also be suitable for the preparation of well-organized thin films, liquid crystals or organo-gelators,[32] which could find application as light-emitting diodes or transistors.[1,14,15] Nevertheless, relatively few hybrid derivatives engineered from a bodipy core and bearing ancillary chelating fragments are known, due to difficulties in synthesising the requisite starting materials and to the onset of intramolecular electron-transfer processes that quench the bright green fluorescence of the bodipy dye.[9,30,33] Interestingly, when a strong electron-donating group (such as dimethylaminophenyl or phenylaza crown) is attached at the pseudo meso position of a F-bodipy, a weakly emissive, charge-

transfer state is apparent[34] and can be utilized to detect alkali and alkaline-earth metal ions.[22] Along the same lines, substitution of the 3 position with ethenyl phenyl donor groups also perturbs the fluorescence properties because of internal charge-transfer effects.[35–37]

Herein, we describe two additional bodipy derivatives in which electron-withdrawing 2,2′:6′,2′′-terpyridine units are linked to either the boron centre or to the meso position. In the latter case, the usual fluorine substituents are replaced with ethynylpyrene subunits, which serve as diagnostic probes of the electronic state of the molecule. Both molecules are constructed from a Kryptopyrrole (3-ethyl-2,4-dimethylpyrrole) precursor, Scheme 1.[38]

Results and Discussion

Synthesis

The preparation of **1** is realized at low temperature by reacting 4-lithioethynyl-2,2′:6′,6′′-terpyridine with the corresponding F-bodipy. Similarly, **2** was prepared by treating 1-lithio-ethynylpyrene with 4′-{ethynylphenyl-4′′′-[4′′′′,4′′′′-difluoro-8′′′′-(1′′′′,3′′′′,5′′′′,7′′′′-tetramethyl-2′′′′,6′′′′-diethyl-4′′′′-bora-3′′′′a,-4′′′′a-diaza-s-indacene)]}-2:2′;6′:2′′-terpyridine.[39] All compounds were purified by classical procedures, including chromatographic separation, and were unambiguously characterised by standard spectroscopic techniques.

Electrochemical Properties

For the E-bodipy compounds **1** and **2**, the first oxidation process remains reversible and anodically shifted by 90 and 120 mV, respectively, relative to the corresponding process found for the reference compound **A**, while the reductions are cathodically shifted by 40 mV. There is no indication for oxidation to the dication or reduction to the dianion within the given electrochemical window. However, the additional two-electron processes observed for compounds **1** and **2** are assigned with respect to reference compounds to the reduction of the ethynyl-terpyridine subunits (Table 1). Interestingly, for the hybrid dye **2** an additional oxidation wave can be attributed to the irreversible oxidation of the ethyn-
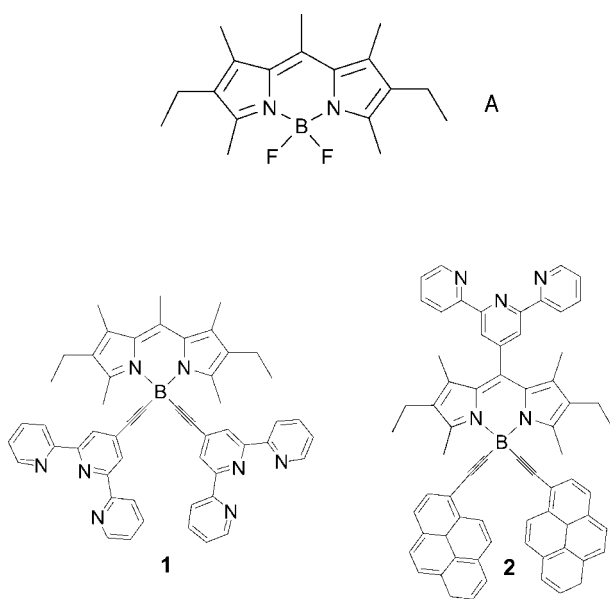
Scheme 1. Molecular formulas of the new bodipy dyes and reference compound studied herein.

Table 1. Electrochemical properties measured for the bodipy-based dyes in solution at room temperature.[a]

Compound	Aryl[+]/aryl[b]	Bodipy[+]/bodipy	Bodipy/bodipy[·]	Aryl/aryl[−]
A	–	0.95 (70)	−1.43 (60)	–
1	–	0.88 (60)	−1.48 (60)	−1.87 (80)
1-Zn[c]	–	0.94 (60)	−1.46 (65)	−1.16 (60)
				−1.32 (60)
2	1.30[d]	0.83 (60)	−1.47 (70)	1.72 (80)
2-Zn[e]	1.36[d]	0.90 (70)	−1.46 (70)	−1.45[d]
				−1.92[d]

[a] Potentials determined by cyclic voltammetry in a mixture of deoxygenated CH_2Cl_2/MeCN (2:1) containing 0.1 M $TBAPF_6$, at a solute concentration of ca. 0.5 mM. Potentials were standardised vs. ferrocene (E_{ox} = 0.38 V vs. SCE) as internal reference and converted to SCE. Error in the quoted half-wave potentials is ±15 mV. For fully reversible processes, the peak separation in mV is given in parenthesis. [b] Aryl refers to the aromatic substituent (terpy or pyrene) and bodipy refers to the dye core. [c] Addition of 4 equiv. of zinc(II) triflate. [d] Irreversible peak (I_c/I_a = 0.4). [e] Addition of 2 equiv. of zinc(II) triflate.

ylpyrene fragments.[28] Finally, replacing the ethynyl-boron substituent of the terpy subunits in **1** by a bodipy fragment in **2** results in an anodic shift of the terpyridine reduction by 150 mV, suggesting to us that the bodipy subunit is more electron-withdrawing that is an ethynylene function (Table 1).

Photophysical Properties of 1

The absorption and fluorescence spectra recorded for **1** in various solvents remain as expected for a bodipy dye (Figure 1). For example, in 2-methyltetrahydrofuran (MTHF) solution at room temperature the absorption maximum is at 517 nm whilst the fluorescence maximum occurs at 532 nm. The rather small Stokes' shift of 545 cm^{-1} is typical of this class of dye. The fluorescence quantum yield (Φ_F) and excited-singlet state lifetime (τ_S) measured in deoxygenated solution are 0.72 and 6.5 ns, respectively. Again, these values are in line with those recorded previously for related bodipy dyes,[40] indicating that the attached terpy group does not perturb the photophysical properties. It is notable that the terpy substituents are located at the B centre rather than linked through the organic framework. Changes in solvent polarity have marginal effect on these values. In each case, the corrected excitation spectrum matches well with the absorption spectrum and the higher-energy transition ($S_0 - S_2$) can be seen clearly at around 340–400 nm. At higher energies, π,π^* transitions localised on the terpy unit can be recognized at around 280 nm.
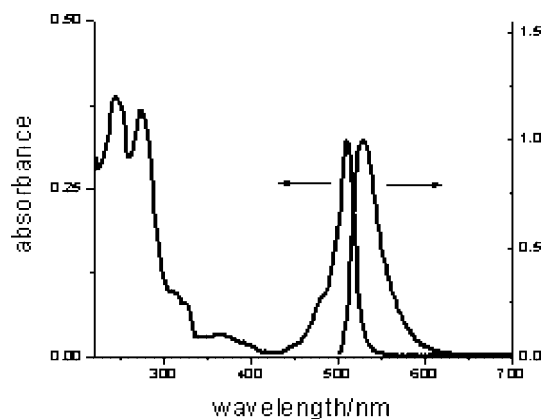

Figure 1. Absorption and fluorescence (λ_{EXT} = 480 nm) spectra recorded for **1** in MTHF at room temperature.

Addition of [Zn(ClO$_4$)$_2$]·6H$_2$O to **1** in MTHF results in the appearance of an absorption band around 330 nm, that is attributed to the formation of the corresponding [Zn(terpy)$_2$]$^{2+}$ complex,[41] and a slight red shift for the characteristic bodipy S$_0$–S$_1$ transition at 517 nm (see supporting information; for supporting information see also the footnote on the first page of this paper). In the presence of excess cation, the lowest-energy absorption band is centred at 520 nm. Addition of [Zn(ClO$_4$)$_2$]·6H$_2$O also affects the fluorescence spectrum recorded in MTHF (Figure 2). Indeed, the fluorescence intensity decreases pro-

gressively with increasing concentration of cation, the concentration required to extinguish 50% of the initial fluorescence signal being 6.2 µM. At very high concentrations of cation, the fluorescence signal is difficult to resolve from the baseline and there is no real indication of a spectral shift. We can suppose that the added cation coordinates to the vacant terpy units so as to form a dinuclear complex. As such, the reported absorption maximum must correspond to the bodipy unit present within the complex. The red shift is a natural consequence of attaching the cation close to the chromophore. On increasing the concentration of cation there is no further change in the fluorescence properties and, under these conditions, Φ_F has fallen to <0.001. Time-resolved fluorescence records measured in the presence of excess cation show only the presence of a component with τ_S = 6 ns, which can be assigned to free **1** remaining in solution.
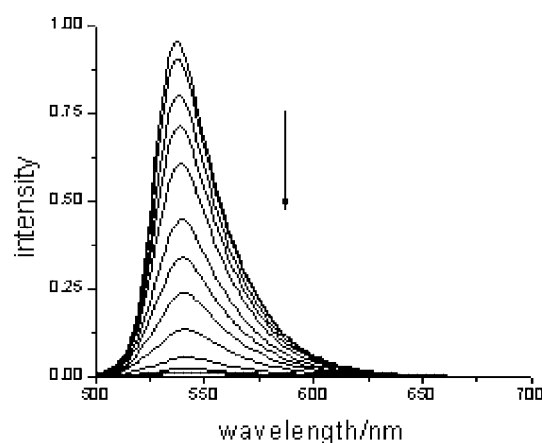

Figure 2. Effect of increasing concentration of Zn(ClO$_4$)$_2$ on the fluorescence spectrum (λ_{EXT} = 480 nm) of **1** in MTHF at room temperature.

The decreased Φ_F and τ_S values found for the complex could be explained in terms of increased spin-orbit coupling due to the heavy-atom effect[42] and/or intramolecular electron transfer.[43] However, the coordinated cation might be considered to reside too far from the bodipy fluorophore to effectively catalyze intersystem crossing and this route is unlikely to be responsible for complete extinction of the fluorescence. In contrast, cyclic voltammetry shows that the addition of 4 equiv. of zinc(II) triflate shifts the reduction potential for the terpy moiety from –1.87 V vs. SCE to –1.16 V vs. SCE. A second terpy-based reduction process is seen at –1.32 V vs. SCE (see Supporting Information). Both these reduction steps are reversible under the conditions used (Table 1). The coordinated cation has a modest effect on the oxidation potential of the bodipy unit, shifting it from 0.88 V vs. SCE to 0.94 V vs. SCE but the reduction potential for the bodipy residue is hardly affected by the presence of the zinc cation. Taking the excitation energy to be 2.43 eV, this being the crossover point between normalised absorption and fluorescence spectra, together with the above electrochemical results indicates that there is a modest thermodynamic driving force (ΔG^0 = –0.33 eV) for light-

induced electron transfer from the bodipy dye to the coordinated terpy unit. As such, the most likely cause of the observed fluorescence quenching is intramolecular electron transfer, as has been observed in somewhat related structures.[43]

The geometry of the resultant zinc(II) complex is unknown and could range from a zigzag polymer to a molecular square, although there is no reason to suppose that a single species predominates. Fitting the fluorescence spectral titration data to various models shows that the best fit, solely in mathematical terms, involves a 1:1 overall stoichiometry with an average binding constant of 8×10^5 M^{-1}. This analysis also implies that the complex is essentially non-fluorescent.

Photophysical Properties of 2

Compound **2** has the terpy function moved from the B centre to the *meso* position of the bodipy unit and possesses ethynylated pyrene fragments at the B unit. It should also be noted that the terpy residue now lacks the bridging ethynylene group. The absorption spectrum recorded for **2** in most organic solvents (e.g., MTHF, benzene, CH_2Cl_2, ethyl acetate) was as expected for a B-substituted bodipy dye (Figure 3). For example, in MTHF solution the absorption maximum occurs at 524 nm and the spectral profile closely resembles that found for **1** under the same conditions. Fluorescence is observed in these solvents and again the properties are far from unusual. In MTHF, for example, Φ_F is 0.76 whilst the decay profile is mono-exponential with τ_S being 5.6 ns. The Stokes shift in MTHF is 560 cm^{-1} and remains comparable to that recorded for **1**. The radiative rate constant calculated from the Strickler–Berg expression[44] ($k_{RAD} = 1.3 \times 10^8$ s^{-1}) agrees very well with that found by experiment ($k_{RAD} = \Phi_F/\tau_S = 1.4 \times 10^8$). In agreement with earlier work, the corrected excitation spectra recorded for **2** in MTHF agree well with the absorption spectrum over the entire spectral range. It is clear that photons absorbed by the pyrene units are transferred rapidly to the bodipy residue, probably via the S_2 state.[45] There is only a small amount of residual emission from the pyrene unit. Similar behaviour was found in benzene solution ($\Phi_F = 0.68$; $\tau_S = 5.2$ ns).

Addition of excess $Zn(ClO_4)_2$ to a solution of **2** in MTHF causes the absorption maximum to undergo a red shift of 5 nm and also introduces the characteristic absorption spectral features of the Zn^{II} bis-terpy complex. As noted above for **1**, it can be assumed that the cation coordinates to the vacant terpy unit under these conditions. Complexation can be followed by fluorescence spectroscopy. Here, successive addition of the salt induces a progressive decrease in the fluorescence yield. Unlike the situation found for **1**, the fluorescence yield does not decrease to zero but reaches a plateau value corresponding to a fivefold reduction in the yield (Figure 4). This is accompanied by a 15 nm red shift for the emission maximum. Time-resolved fluorescence studies carried out in the presence of excess
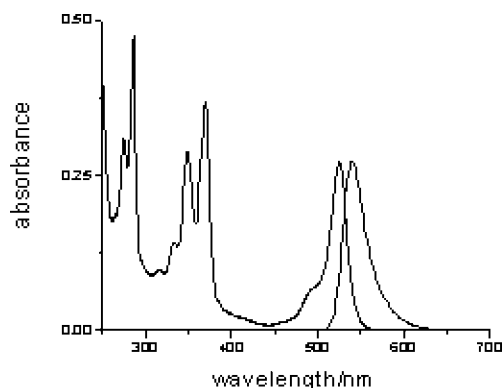

Figure 3. Absorption and fluorescence ($\lambda_{EXT} = 490$ nm) spectra recorded for **2** in MTHF at room temperature.

$Zn(ClO_4)_2$ show the presence of two fluorescent species. One component retains a lifetime comparable to that of free **2** and is clearly the uncomplexed dye remaining in solution. The second component corresponds to a lifetime of 0.86 ns and can be attributed to the bodipy dye bearing a coordinated zinc(II) cation. This situation is fully consistent with the incomplete fluorescence quenching seen from the steady-state studies. Under the conditions used, the complex is most likely the bis-terpy species formed on binding two molecules of **2** to a single cation (see below).
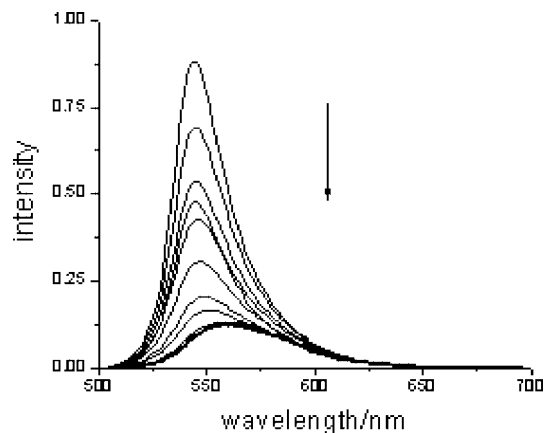

Figure 4. Effect of increasing concentration of $Zn(ClO_4)_2$ on the fluorescence spectrum of **2** in MTHF at room temperature.

Again, the most likely mechanism responsible for the observed decrease in fluorescence yield involves electron transfer from the singlet-excited state of the bodipy dye to the nearby bis-terpy Zn^{II} complex, although catalysed intersystem crossing cannot be ruled out entirely. The rate constant (k_{ET}) for light-induced electron transfer in MTHF can be calculated from the respective lifetimes as being 9.7×10^8 s^{-1}. This is much lower than the corresponding value estimated for **1** ($k_{ET} > 10^{10}$ s^{-1}) under identical conditions. This disparity in rate is easily explained in terms of the respective thermodynamic driving forces for electron transfer. Thus, cyclic voltammetry studies made for **2** in the presence of a small excess of zinc(II) salt show that the coordinated terpy unit is reduced at about the same potential as the bodipy unit, although the process is poorly reversible

(Table 1). Oxidation of the bodipy core is made slightly more difficult on complexation, probably due to an electrostatic effect, such that the driving force for light-induced electron transfer becomes negligible. In part, this effect is offset by the shorter separation distance but it has to be emphasised that the acetylenic connector is an excellent conduit for electron tunneling.[46]

The fluorescence spectral titration data collected for successive addition of $Zn(ClO_4)_2$ to **2** in MTHF could be analysed in terms of stepwise formation of both 1:1 and 1:2 (metal:ligand) complexes (Figure 4). At low concentrations of cation, the 1:2 complex predominates and the binding constant for this species is 7×10^{10} M^{-2}. At very high cation concentrations, the 1:2 complex dissociates in favour of the corresponding 1:1 complex, for which the binding constant is computed to be 4.4×10^5 M^{-1}. The two complexes show similar fluorescence profiles and yields. The derived binding constants are comparable to those reported previously with related structures,[43] where formation of the terpy-based 1:2 complexes was confirmed by X-ray crystallography.

Self Association of 2

In certain solvents, notably acetonitrile (MeCN) and ethanol, the absorption spectrum recorded for **2** cannot be regarded as being typical of a bodipy dye. In dilute MeCN solution, for example, the low-energy region comprises two sets of transitions; the higher-energy side resembles that reported for **2** in MTHF but there is also a lower-energy series that is red shifted by some 58 nm from the expected transitions. Progressive dilution with MTHF (Figure 5), or increasing the temperature, favours the normal absorption profile, although it is clear that two distinct species are present in equilibrium (Figure 6). One of these species is the usual monomer while the other is presumed to be a higher-order associate. Fluorescence is observed from both the monomer and the associated form, although in the latter case the emission peak is shifted to 585 nm. For the associate, τ_S is reduced somewhat to 1.9 ns while Φ_F is decreased substantially to 0.01 in MeCN. Replacing MeCN with other nitriles (propionitrile, butyronitrile, acrylonitrile, benzonitrile, pentanenitrile or octanenitrile) restores the normal monomer absorption and fluorescence spectral profiles. The behaviour noted in MeCN, however, is fully reversible and reproducible. Furthermore, the spectra do not change with aging. Assuming equivalent molar absorption coefficients, the equilibrium is shifted in favour of the monomer in ethanol and cyclohexane relative to MeCN.

Addition of $Zn(ClO_4)_2$ to a solution of **2** in MeCN had little effect. Thus, in the presence of excess salt the fluorescence yield falls by ca. 35%, but the absorption spectrum does not change. This behaviour suggests that the cation does not break-up the associate under these conditions, presumably because it does not coordinate to the vacant terpy site. Various structures can be considered for the associate that might help to explain these observations. Earlier work has concluded that the pyrene unit seeks to minimize its
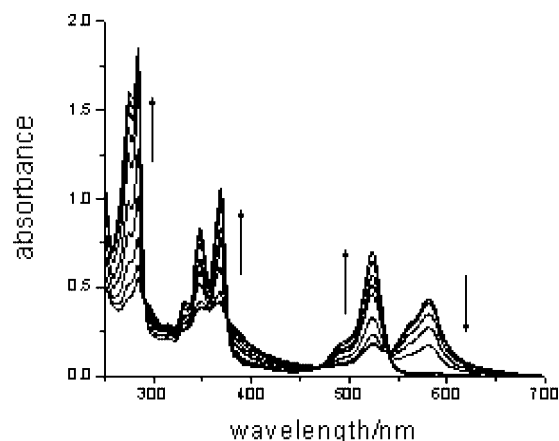

Figure 5. Effect on the absorption spectrum of adding increasing amounts of MTHF to a solution of **2** in MeCN at room temperature.
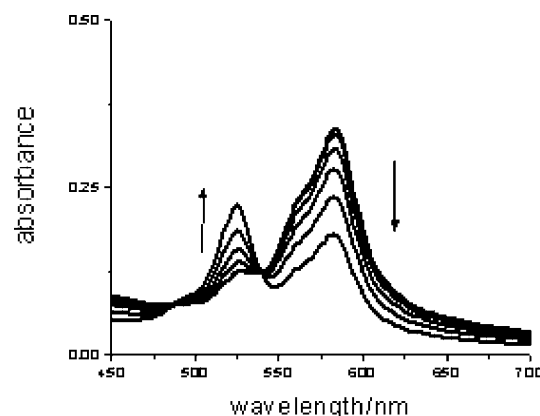

Figure 6. Effect of increasing temperature of the absorption spectrum of **2** in MeCN at room temperature.

surface exposure to certain solvents[47] while the shift in the bodipy absorption bands indicates that this unit lies in a different electronic environment in MeCN relative to better solvents like MTHF or benzene. Indeed, the absorption spectral changes are inconsistent with formation of a J aggregate[48] or with the introduction of excitonic coupling[49] between nearby bodipy units. This suggests that the bodipy residues do not associate into a π stack. Deconvolution of the absorption spectrum recorded for **2** in MTHF shows that the entire profile can be well explained in terms of four vibrational bands each having a half-width of 695 cm^{-1} and being separated by 670 cm^{-1}. The lowest-energy Gaussian-shaped component lies at 19060 cm^{-1}. A similar analysis made for **2** in MeCN locates the lowest-energy vibronic transition at 17180 cm^{-1} but retains the same spacing of 670 cm^{-1}. Each vibrational band is broadened slightly to 750 cm^{-1}. The oscillator strength calculated for the S_0–S_1 transition changes from 0.32 in MTHF to 0.075 in MeCN. The Stokes' shift for the dimer is reduced to only 90 cm^{-1}, indicating negligible structural change upon excitation.

Self-association of **2** in MeCN causes serious perturbation of the absorption bands due to the pyrene units. The oscillator strengths for these transitions are decreased sig-

nificantly with respect to MTHF and there is a small red shift (Figure 5). The pyrene units appear to be undergoing exciton coupling in MeCN. Computer modelling of the dimer that might arise from close interaction between two molecules of **2**, with due allowance for the above realisations, leads us to the centro-symmetric structure shown as Figure 7 (see supporting information for further views of the computed structure). Here, the four pyrene residues form two closely-spaced pairs, where the closest contacts are within 3.6 Å. This type of π-stacking would serve to reduce surface contact with MeCN molecules. The two bodipy units align to form a skewed face-to-face arrangement where the closest contact is ca. 6 Å. This interaction should suffice to cause the observed shift in the absorption spectrum. The two B centres lie some 7.8 Å apart. The terpy units play a subtle role in self association in that they do not participate directly in π-stacking but the corresponding bodipy dye lacking the *meso*-sited terpy residue does not self associate in MeCN. Thus, the terpy unit in **2** is considered to exert a small but critical effect on the solubility.
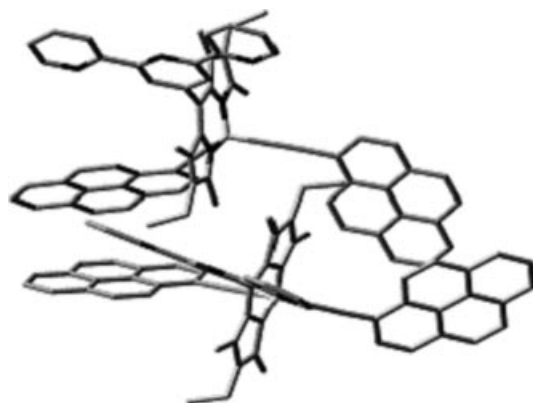

Figure 7. Computed structure for the dimer believed to form when **2** is dissolved in MeCN. Note the H atoms have been omitted for clarity.

Dimerisation of bodipy dyes is rare but there is a report of the red-shifted fluorescence from a bodipy dimer formed in the plasma membrane.[50] Here, the dimer emits at 620 nm compared to the monomer fluorescence at 515 nm. As might be expected, dimer fluorescence is broad and featureless. For **2** in MeCN, very weak fluorescence is observed with an unusually small Stokes' shift but the spectral profile is comparable to that observed in MTHF. In part, the low emission probability arises from the reduced oscillator strength and lower excitation energy,[51] which also enhances nonradiative decay.[52] The photophysical properties measured for the dimer appear to be fully consistent with its proposed structure.

Conclusions

Two new bodipy-based dyes are reported that bear ancillary terpy ligands able to bind adventitious cations from solution. In both cases, the corresponding bis-terpy zinc(II) complexes function as electron acceptors for the excited singlet state of the bodipy dye and quench its fluorescence. The degree of fluorescence quenching depends on the reduction potential of the metal complex, this being set by the nature of the linker. Because the bodipy unit is strongly fluorescent in the absent of cation, the dyes could be used as fluorescent sensors for a wide range of cations, including protons, and might be built into a suitable device. This is an attractive possibility because, especially in the case of **1**, the dye is easily attached to a surface or macroreticular support by way of the *meso* site. This positions the terpy units so as to trap cations from a passing effluent stream. In principle, the terpy unit could be replaced with a wide range of ancillary complexation units in order to introduce selective binding of preferred cations from a mixture.

Self-association of **2** has been noted in MeCN and alcohol solvents. This behaviour is believed to arise from the solvophobic effect in which the pyrene residues attempt to minimize surface contact with the surrounding solvent. This is a remarkable effect, not seen previously for any bodipy dye, and results in formation of a fluorescent associate, believed to be a dimer or higher-order aggregate. The computed structure for the dimer places the pyrene units in a position suitable for π stacking but keeps the two bodipy units reasonably well apart. Presumably, the close proximity of the pyrene units is responsible for the red shifted absorption and emission spectra for the bodipy unit.

Experimental Section

General Methods: The 200.1 (^{1}H), 300.1 (^{1}H), 50.3 (^{13}C), and 75.46 (^{13}C) MHz NMR spectra were recorded at room temperature using perdeuterated solvents, with residual protiated solvent signals providing internal references. The 128.4 ([11]B) MHz NMR spectra were recorded at room temperature using glass residual B_2O_3 as reference. A fast-atom bombardment ZAB-HF-VB analytical apparatus in positive mode was used with *m*-nitrobenzyl alcohol (*m*NBA) as matrix. FT-IR spectra were recorded on the neat liquids or as thin films, prepared with a drop of dichloromethane and the solvents evaporated to dryness on KBr pellets. Melting points were obtained with a capillary melting point apparatus in open-ended capillaries and are uncorrected. Chromatographic purification was conducted using standard aluminium oxide 90. Thin-layer chromatography (TLC) was performed on aluminium oxide plates coated with fluorescent indicator. All mixtures of solvents are given in v/v ratio.

Electrochemical studies employed cyclic voltammetry with a conventional 3-electrode system using a BAS CV-50W voltammetric analyser equipped with a Pt microdisk (2 m²) working electrode and a silver wire counter-electrode. Ferrocene was used as an internal standard and was calibrated against a saturated calomel reference electrode (SSCE) separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electro-active substrate in deoxygenated and anhydrous dichloromethane or acetonitrile containing doubly recrystallised tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The quoted half-wave potentials were reproducible within ≈ 10 mV.

Materials: CH_2Cl_2 was distilled from P_2O_5. Kryptopyrrole, methyl iodide, DDQ, $BF_3 \cdot Et_2O$, 4-formylpyridine, Et_3N and $BF_3 \cdot Et_2O$ were used as purchased. All reactions were carried out under dry argon by using Schlenk-tube techniques.

General Procedure for the Substitution of Fluoride by Acetylide: In a Schlenk flask, *n*-butyllithium (2.2 equiv.) was added at –78 °C to a stirred degassed solution of the acetylenic compound (2.2 equiv.) in anhydrous THF or diethyl ether. The mixture was stirred at –78 °C for 1 h and at room temperature for 30 min. The resulting anion was then transferred via cannula to a degassed solution of the precursor difluoroboradiazaindacene (1 equiv.) in anhydrous THF (or diethyl ether). The solution was stirred at room temperature until complete consumption of the starting material was observed by TLC. Water was added, and the solution was extracted with CH_2Cl_2. After evaporation, the organic layer was purified by column chromatography.

2,6-Diethyl-1,3,5,7,8-pentamethyl-4,4-bis[2-(2,2′:6′,2′′-terpyridin-4′-yl)ethynyl]-4-bora-3a,4a-diaza-*s*-indacene (1): Prepared according the general procedure with 4′-ethynyl-2,2′:6′,2′′-terpyridine (0.162 g, 0.63 mmol) in 10 mL of THF, 0.44 mL of *n*-butyllithium (1.55 M in *n*-hexane), and **A** (0.1 g, 0.31 mmol) in 20 mL of THF. Complete consumption of the starting material was observed after 10 min. The chromatography was performed on alumina (CH_2Cl_2/cyclohexane, 20:80), and recrystallisation in hot acetonitrile gave 0.032 g of **3** (13% yield). ^1H NMR (CDCl$_3$ 300 MHz): δ = 8.68 (m, 4 H), 8.57 (d, ^3J = 7.9 Hz, 4 H), 8.42 (s, 4 H), 7.83 (dt, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 4 H), 7.32 (dd, ^3J = 4.7 Hz, ^4J = 1.1 Hz, 2 H), 7.29 (dd, ^3J = 4.8 Hz, ^4J = 1.3 Hz, 2 H), 2.84 (s, 6 H), 2.69 (s, 3 H), 2.49 (q, ^3J = 7.5 Hz, 4 H), 2.41 (s, 6 H), 1.11 (t, ^3J = 7.5 Hz, 6 H) ppm. $^{13}C\{^1H\}$ NMR (CDCl$_3$, 75 MHz): δ = 156.3, 155.3, 152.2, 149.2, 136.9, 135.6, 134.9, 132.8, 130.3, 123.8, 123.4, 121.3, 17.6, 17.4, 15.2, 14.8, 14.4 ppm. $^{11}B\{^1H\}$ NMR (CDCl$_3$, 128 MHz): δ = –9.88 (s) ppm. UV/Vis (CH_2Cl_2): λ (ε, M^{-1} cm^{-1}) = 517 (129500), 376 (13000), 278 (129500), 251 nm (134500). IR (KBr): $\tilde{v}$ = 2867 (s), 1581 (s), 1185 (s), 978 (m), 791 (s) cm^{-1}. FAB$^+$ *m/z* (nature of peak, relative intensity): 793.2 ([M]$^+$, 100). $C_{52}H_{45}BN_8$ (792.78): calcd. C 78.78, H 5.72, N 14.13; found C 78.46, H 5.49, N 13.82.

2,4-Diethyl-1,3,5,7-tetramethyl-4,4-bis[2-(pyren-1-yl)ethynyl]-8-(2,2′:6′,2′′-terpyridin-4′-yl)-4-bora-3a,4a-diaza-*s*-indacene (2): Prepared according the general procedure with 1-ethynylpyrene (0.041 g, 0.179 mmol) in 5 mL of THF, 0.15 mL of *n*-butyllithium (1.55 M in *n*-hexane) (formation of a dark green anion), and 4′-{ethynylphenyl-4′′′-[4′′′′,4′′′′-difluoro-8′′′′-(1′′′′,3′′′′,5′′′′,7′′′′-tetramethyl-2′′′′,6′′′′-diethyl-4′′′′-bora-3a′′′′,4a′′′′-diaza-*s*-indacene)]}-2:2′;6′:2′′-terpyridine (0.048 g, 0.089 mmol) in 10 mL of THF. Complete consumption of the starting material was observed after 10 min. The chromatography was performed on alumina (CH_2Cl_2/cyclohexane, 20:80), and recrystallisation gave 0.025 g of **2** (30% yield). ^1H NMR (CDCl$_3$ 400 MHz): δ = 8.82 (d, ^3J = 9.0 Hz, 2 H), 8.75–8.69 (m, 6 H), 8.22–7.98 (m, 16 H), 7.91 (dt, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 2 H), 7.37 (m, 2 H), 3.15 (s, 6 H), 2.45 (q, ^3J = 7.6 Hz, 4 H), 1.57 (s, 6 H), 1.09 (t, ^3J = 7.5 Hz, 6 H) ppm. $^{13}C\{^1H\}$ NMR (CDCl$_3$, 75 MHz): δ = 156.4, 155.7, 154.6, 149.5, 147.1, 137.0, 136.3, 133.6, 132.3, 131.5, 131.4, 130.5, 129.9, 128.6, 128.0, 127.6, 127.5, 126.5, 126.1, 125.3, 125.2, 124.75, 124.70, 124.6, 124.3, 121.5, 121.3, 120.8, 17.2, 15.0, 14.7, 12.9 ppm. $^{11}B\{^1H\}$ NMR (CDCl$_3$, 128 MHz): δ = –8.92 (s) ppm. UV/Vis (CH_2Cl_2) λ nm (ε, M^{-1} cm^{-1}) = 526 (70000), 370 (103000), 358 (78000), 285 (111400), 275 (74400), 248 (106000). IR (KBr): $\tilde{v}$ = 2961 (s), 2164 (m), 1582 (s), 1402 (s), 1178 (s), 978 (s), 845 (s) cm^{-1}. FAB$^+$ *m/z* (nature of peak, relative intensity): 948.2 (100) [M + H]$^+$, 722.2 (20) [M – (pyr–≡–)]$^+$. $C_{68}H_{50}BN_5$ (947.97): calcd. C 86.16, H 5.32, N 7.39; found C 85.95, H 5.12, N 7.27.

Photophysical Studies: Absorption and fluorescence spectra were recorded using a Hitachi U3310 spectrophotometer and a Hitachi F4500 spectrofluorimeter, respectively. Emission quantum yields were measured in N$_2$-purged solution relative to A.[43] Fluorescence lifetimes were recorded using the phase modulation method on an Yvon-Jobin Fluorolog Tau-3 Lifetime System with the instrumental response function being measured against a solution of Ludox in distilled water. Fluorescence titrations were made by addition of small aliquots of a Zn(ClO$_4$)$_2$ solution (1 mM) to dilute solutions (ca. 5 μM) of the free ligand. A minimum of 30 additions was made for each titration and measurements were repeated at least twice. Data analysis was made with SPECFIT. Molecular modelling of the self-associated form of **2** was made with SPARTAN on the understanding that a dimer was involved. A wide variety of starting geometries were used.

Supporting Information (see also the footnote on the first page of this article): Included is a typical cyclic voltammogram recorded for **1** in the presence of Zn^{II} triflate, an absorption spectrum of **1** in the presence of excess zinc(II) salt and additional views of the structure computed for the dimer of **2** in MeCN.

[1] a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151–154; b) J. H. Schon, A. Dodabalapur, C. Kloc, B. Batlogg, *Science* **2000**, *290*, 963–965; c) Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, S. R. Forrest, *Nature* **2006**, *440*, 908–910.

[2] J. H. Burroughes, D. D. C. Bradley, H. R. Brown, R. N. Marks, K. Mackay, R. H. Freind, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539–541.

[3] a) M. Hissler, A. El-ghayoury, A. Harriman, R. Ziessel, *Angew. Chem. Int. Ed.* **1998**, *37*, 1717–1720; b) M. Hissler, A. Harriman, P. Jost, G. Wipff, R. Ziessel, *Angew. Chem. Int. Ed.* **1998**, *37*, 3249–3252; c) A. Harriman, M. Hissler, P. Jost, G. Wipff, R. Ziessel, *J. Am. Chem. Soc.* **1999**, *121*, 14–27; d) H. Miyaji, W. Sato, J. L. Sessler, *Angew. Chem. Int. Ed.* **2000**, *39*, 1777–1780; e) P. Anzenbacher Jr, K. Jursikova, J. L. Sessler, *J. Am. Chem. Soc.* **2000**, *122*, 9350–9351; f) P. Zhang, T. Beck, W. Tan, *Angew. Chem. Int. Ed.* **2001**, *40*, 402–405; g) T. D. James, S. Shinkai, *Top. Curr. Chem.* **2002**, *218*, 159–200; h) L. J. Charbonnière, R. Ziessel, M. Montalti, L. Prodi, N. Zaccheroni, C. Boehme, G. Wipff, *J. Am. Chem. Soc.* **2002**, *124*, 7779–7788; i) F. Sancenon, R. Martinez-Manez, J. Soto, *Angew. Chem. Int. Ed.* **2002**, *41*, 1416–1419.

[4] F. Loiseau, C. Di Pietro, S. Serroni, S. Campagna, A. Licciardello, A. Manfredi, G. Pozzi, S. Quici, *Inorg. Chem.* **2001**, *40*, 6901–6909.

[5] A. P. De Silva, H. Q. N. Gunaratne, T. M. Gunnlaugsson, A. J. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566.

[6] *Chemosensors of Ion and Molecular Recognition*, (Eds: J.-P. Desverne, A. W. Czarnik), NATO Advanced Study Institute Series C492, Kluwer, Dordrecht, **1997**.

[7] R. P. Haugland, in *Handbook of Molecular Probes and Research Products*, 9th ed., Molecular Probes Inc., Eugene, OR, **2002**.

[8] a) R. P. Haugland, H. C. Kang, *US Patent*, US 4,774,339, **1998**; b) L. H. Thoresen, H. Kim, M. B. Welch, A. Burghart, K. Burgess, *Synlett* **1998**, 1276–1279.

[9] C. Goze, G. Ulrich, L. Charbonnière, R. Ziessel, *Chem. Eur. J.* **2003**, *9*, 3748–3755.

[10] W. Qin, M. Baruah, M. van der Auweraer, F. C. DeSchryver, N. Boens, *J. Phys. Chem. A* **2005**, *109*, 7371–7384.

[11] G. Ulrich, C. Goze, M. Guardigli, A. Roda, R. Ziessel, *Angew. Chem. Int. Ed.* **2005**, *44*, 3694–3698.

[12] a) R. W. Wagner, J. S. Lindsey, *Pure Appl. Chem.* **1996**, *68*, 1373–1380; b) G. Beer, K. Rurack, J. Daub, *Chem. Commun.* **2001**, 1138–1139; c) G. Beer, C. Niederalt, S. Grimme, J. Daub, *Angew. Chem. Int. Ed.* **2000**, *39*, 3252–3255; d) M. Kollmannsberger, K. Rurack, U. Resch-Genger, W. Rettig, J. Daub, *Chem. Phys. Lett.* **2000**, *329*, 363–369; e) F. Sancenon, R. Martinez-Manez, J. Soto, *Angew. Chem. Int. Ed.* **2002**, *41*, 1416–1419; f) Y. Gabe, Y. Urano, K. Kikuchi, H. Kojima, T. Nagano, *J. Am. Chem. Soc.* **2004**, *126*, 3357–3367.

[13] T. A. Golovkova, D. V. Kozlov, D. C. Neckers, *J. Org. Chem.* **2005**, *70*, 5545–5549.

[14] R. Y. Lai, A. J. Bard, *J. Phys. Chem. B* **2003**, *107*, 5036–5042.

[15] a) J. M. Brom Jr, J. L. Langer, *J. Alloys Compd.* **2002**, *338*, 112–115; b) A. Hepp, G. Ulrich, R. Schmechel, H. von Seggern, R. Ziessel, *Synth. Met.* **2004**, *146*, 11–15.

[16] a) T. Chen, J. H. Boyer, M. L. Trudell, *Heteroat. Chem.* **1997**, *8*, 51–54; b) G. Sathyamoorthi, L. T. Wolford, A. M. Haag, J. H. Boyer, *Heteroat. Chem.* **1994**, *5*, 245–249.

[17] S. Hattori, K. Ohkubo, Y. Urano, H. Sunahara, T. Nagano, Y. Wada, N. V. Tkchanko, H. Lemmetyinen, S. Fukuzumi, *J. Phys. Chem. B* **2005**, *109*, 15368–15375.

[18] C. McCusker, J. B. Carroll, V. M. Rotello, *Chem. Commun.* **2005**, 996–997.

[19] M. P. Debreczeny, W. A. Svec, M. R. Wasielewski, *Science* **1996**, *274*, 584–587.

[20] a) A. Burghart, H. Kim, M. B. Wech, L. H. Thorensen, J. Reibenspies, K. Burgess, *J. Org. Chem.* **1999**, *64*, 7813–7819; b) H. Kim, A. Burghart, M. B. Welch, J. Reibenspies, K. Burgess, *Chem. Commun.* **1999**, 1889–1890; c) J. Chen, J. Reibenspies, A. Derecskei-Kovacs, K. Burgess, *Chem. Commun.* **1999**, 2501–2502; d) K. Rurack, M. Kollmannsberger, J. Daub, *New J. Chem.* **2001**, *25*, 289–292; e) K. Rurack, M. Kollmannsberger, J. Daub, *Angew. Chem. Int. Ed.* **2001**, *40*, 385–387.

[21] T. Gareis, C. Huber, O. S. Wolfbeis, J. Daub, *Chem. Commun.* **1997**, 1717–1718.

[22] M. Kollmannsberger, K. Rurack, U. Resch-Genger, J. Daub, *J. Phys. Chem. A* **1998**, *102*, 10211–10220.

[23] a) K. Rurack, M. Kollmannsberger, U. Resch-Genger, J. Daub, *J. Am. Chem. Soc.* **2000**, *122*, 968–969; b) S. Y. Moon, N. R. Cha, Y. H. Kim, S.-K. Chang, *J. Org. Chem.* **2004**, *69*, 181–183.

[24] a) F. Li, S. I. Yang, Y. Ciringh, J. Seth, C. H. Martin III, D. L. Singh, D. Kim, R. R. Birge, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Am. Chem. Soc.* **1998**, *120*, 10001–10017; b) R. K. Lammi, A. Amboise, T. Balasubramanian, R. W. Wagner, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Am. Chem. Soc.* **2000**, *122*, 7579–7591; c) A. Amboise, C. Kirmaier, R. W. Wagner, R. S. Loewe, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Org. Chem.* **2002**, *67*, 3811–3826.

[25] I. V. Sazanovich, C. Kirmaier, E. Hindin, L. Yu, D. F. Bocian, J. S. Lindsey, D. Holten, *J. Am. Chem. Soc.* **2004**, *126*, 2664–2665.

[26] M. D. Yilmaz, O. A. Bozdemir, E. U. Akkaya, *Org. Lett.* **2006**, *8*, 2871–2873.

[27] a) A. Burghart, L. H. Thorese, J. Che, K. Burgess, F. Bergström, L. B.-Å. Johansson, *Chem. Commun.* **2000**, 2203–2204; b) C.-W. Wan, A. Burghart, J. Chen, F. Bergström, L. B.-Å. Johansson, M. F. Wolford, T. G. Kim, M. R. Topp, R. M. Hochstrasser, K. Burgess, *Chem. Eur. J.* **2003**, *9*, 4430–4441.

[28] R. Ziessel, C. Goze, G. Ulrich, M. Césario, P. Retailleau, A. Harriman, J. P. Rostron, *Chem. Eur. J.* **2005**, *11*, 7366–7378.

[29] Z. Shen, H. Röhr, K. Rurack, H. Uno, M. Spieles, B. Schulz, G. Reck, N. Ono, *Chem. Eur. J.* **2004**, *10*, 4853–4871.

[30] B. Turfan, E. U. Akkaya, *Org. Lett.* **2002**, *4*, 2857–2859.

[31] J. L. Bricks, A. Kovalchuk, C. Trieflinger, M. Nofz, M. Büschel, A. I. Tolmachev, J. Daub, K. Rurack, *J. Am. Chem. Soc.* **2005**, *127*, 13522–13529.

[32] F. Camerel, L. Bonardi, M. Schmutz, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 4548–4549.

[33] R. Ziessel, L. Bonardi, P. Retailleau, G. Ulrich, *J. Org. Chem.* **2006**, *71*, 3093–3102.

[34] K. Rurack, M. Kollmannsberger, U. Resch-Genger, J. Daub, *J. Am. Chem. Soc.* **2000**, *122*, 968–969.

[35] K. Rurack, M. Kollmannsberger, J. Daub, *Angew. Chem.* **2001**, *40*, 385–387.

[36] a) A. Coskun, E. Deniz, E. U. Akkaya, *Org. Lett.* **2005**, *7*, 5187–5189; b) A. Coskun, E. U. Akkaya, *J. Am. Chem. Soc.* **2005**, *127*, 10464–10465.

[37] M. Baruah, W. Qin, C. Flors, J. Hofkens, R. A. L. Vallée, D. Beljonne, M. van der Auweraer, W. M. De Borggraeve, N. Boens, *J. Phys. Chem. A* **2006**, *110*, 5998–6009.

[38] H. Fischer, P. Halbig, B. Walach, *Justus Liebigs Ann. Chem.* **1927**, *452*, 268–272.

[39] a) G. Ulrich, R. Ziessel, *Synlett* **2004**, 439–444; b) G. Ulrich, R. Ziessel, *J. Org. Chem.* **2004**, *69*, 2070–2083; c) G. Ulrich, R. Ziessel, *Tetrahedron Lett.* **2004**, *45*, 1949–1953.

[40] a) F. Bergström, I. Mikhalyov, P. Hägglöf, R. Wortmann, T. Ny, L. B. Johansson, *J. Am. Chem. Soc.* **2002**, *124*, 196–204; b) K. Rurack, M. Kollmannsberger, U. Resch-Genger, J. Daub, *J. Am. Chem. Soc.* **2000**, *122*, 968–969; M. Kollmannsberger, K. Rurack, U. Resch-Genger, J. Daub, *J. Phys. Chem. A* **1998**, *102*, 10211–10220; c) F. Lopez Arbeloa, P. Banuelos Prieto, V. Martinez Martinez, T. Arbeloa Lopez, I. Lopez Arbeloa, *ChemPhysChem* **2004**, *5*, 1762–1771; d) W. Qin, M. Baruah, M. Van der Auweraer, F. C. de Schryver, N. Boens, *J. Phys. Chem. A* **2005**, *109*, 7371–7384.

[41] J. P. Rostron, G. Ulrich, G. Retailleau, A. Harriman, R. Ziessel, *New J. Chem.* **2005**, *29*, 1241–1244.

[42] S. P. McGlynn, T. Azumi, M. Kinoshiya, *Molecular Spectroscopy of the Triplet State*, Prentic-Hall, Englewood Cliffs, NJ, **1969**.

[43] A. Harriman, J. P. Rostron, M. Cesario, G. Ulrich, R. Ziessel, *J. Phys. Chem. A* **2006**, *110*, 7994–8002.

[44] S. J. Strickler, R. A. Berg, *J. Chem. Phys.* **1962**, *37*, 814–822.

[45] A. Harriman, G. Izzet, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 10868–10875.

[46] a) A. Benniston, A. Harriman, V. Grosshenny, R. Ziessel, *New J. Chem.* **1997**, *21*, 405–408; b) V. Grosshenny, A. Harriman, R. Ziessel, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1100–1102.

[47] C. Goze, G. Ulrich, L. J. Mallon, B. D. Allen, A. Harriman, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 10231–10239.

[48] H. Tachibana, Y. Yamanaka, H. Sakai, M. Abe, M. Matsumoto, *J. Lumin.* **2000**, *87*, 800–802.

[49] A. Chowdhury, L. Yu, I. Raheem, L. Peteanu, L. A. Liu, D. J. Yarin, *J. Phys. Chem. A* **2003**, *107*, 3351–3362.

[50] R. E. Pagano, O. C. Martin, H. C. Kang, R. P. Haugland, *J. Cell Biol.* **1991**, *113*, 1267–1279.

[51] M. Bixon, J. Jortner, J. W. Verhoeven, *J. Phys. Chem.* **1994**, *116*, 7349–7355.

[52] a) R. Englman, J. Jortner, *Mol. Phys.* **1970**, *18*, 145–154; b) M. Bixon, J. Jortner, J. Cortes, H. Heitele, M. E. Michel-Beyerle, *J. Phys. Chem.* **1994**, *98*, 7289–7299.