Borondipyrromethene Dyes with Pentane-2,4-dione Anchors

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ABSTRACT
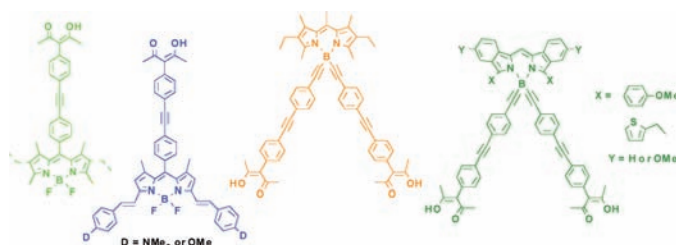
New, acetylacetone-linked borondipyrromethene (BODIPY) dyes were readily obtained from BODIPY cores by various protocols involving direct grafting with acetylacetone or cross-coupling from a preorganized phenylacacH derivative bearing either an iodo or an ethynyl function. Facile anchoring on TiO₂ powder is obtained and scrutinized by FT-IR spectroscopy.

Acetylacetonate anion (acac⁻) and its derivatives and analogues are versatile ligands for a wide variety of metal ions.[1] They possess several advantages over phosphine or oligopyridine ligands due to their ease of synthesis, their anionic nature, and the ready formation of their complexes. The various functionalizations provide a means to control the electronic properties of their complexes as well as their physical characteristics (e.g., solubility, volatility). Particular examples are provided by their use in dendrimers to anchor a phosphorescent label[2] and as intermediates in the synthesis of liquid crystalline materials.[3] Nonetheless, very few hybrid acac ligands combining electroactive,[4] photoactive, or additional chelating fragments have been described up to now.[5] In part, this reflects the dominance of the interest in acacH (= acetylacetone = 2,4-pentanedione) and

related species as extremely useful precursors for the synthesis of numerous heterocycles, amino alcohols, and amino acids.[6] It is known, however, that copper salts promote the arylation of activated methylene groups such as those of malononitrile, ethylcyanoacetate, and acetylacetone,[7] and the recent discovery that a Cu(I)/ʟ-proline mixture[8] efficiently catalyzes the arylation of acetylacetone prompted us to attempt the substitution of borondipyrromethene dyes (BODIPYs) with acacH fragments. The objective of the present work was therefore to develop procedures as part of a battery of methods for introducing acacH residues onto these fluorescent dyes to link them to transition metals or inorganic semiconductor particles or surfaces.

To this end, we first explored the synthesis of **2** by a conventional route (Scheme 1). Arylation of acetylacetone with

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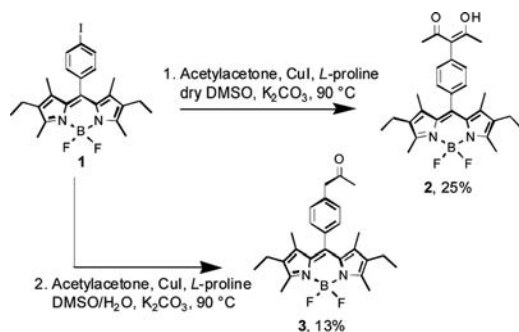(5) McNamara, W. R.; Snoeberger, R. C., III; Li, G.; Schleicher, J. M.; Cady, C. W.; Poyatos, M.; Schmuttenmaer, C. A.; Crabtree, R. H.; Brudvig, G. W.; Batista, V. S. *J. Am. Chem. Soc.* **2008**, *130*, 14329–14338.
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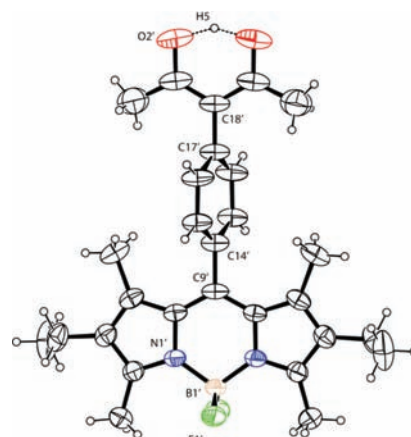(8) Jiang, Y.; Wu, N.; Wu, H.; He, M. *Synlett* **2005**, 2731–2734.

Figure 1. ORTEP view of **2** with displacement ellipsoids shown at the 30% probability level.

the phenyliodo-substituted BODIPY **1** under anhydrous conditions provided the target ligand **2** in moderate yield. In the presence of water, **2** was not isolated, but the ketone **3** was obtained in low yield. Compound **2** appears stable in ordinary daylight and is highly fluorescent in solution (*discussed below*). This compound was also structurally characterized by single-crystal X-ray diffraction. It crystallizes in the space group *C2/c*, the molecules lying in stacked columns down *a* such that the BODIPY core planes are parallel (though remote, with an interplanar spacing >4 Å). Down *a*, each consecutive molecule within a column is rotated by 120° relative to the preceding, placing the acetylacetone unit of every third molecule on a site of 2-fold symmetry. Thus, there are two inequivalent molecules present in the latttice, though the differences between them dimensionally are slight.

Within both acetylacetone units, the dimensions and planarity are consistent with their adoption of a delocalized, enol form (Figure 1), in keeping with that of related aromatic derivatives.[9−11] Thus, bond lengths within the OCCCO units are (molecule 1) C(17)−O(3) 1.306(8), C(17)−C(16) 1.399(9), C(16)−C(19) 1.393(8), C(19)−O(2) 1.317(8) (molecule 2, 2-fold symmetric), C(19′)−O(2′) 1.306(6), C(19′)−C(18′) 1.392(7) Å. The acetylacetone segments are nearly coplanar (dihedral angle, molecule 1, 11.9°, molecule 2, 2.5°) with their linked Bopdipy cores, though the phenyl linker is nearly orthogonal (dihedral angle molecule 1, 78.1°, molecule 2, 70.8°) to the BODIPY unit. The O···O separations are 2.409(7) Å (molecule 1) and 2.450(6) Å (molecule 2 in Figure 1), consistent with (symmetrical) bridging by the enolic proton.
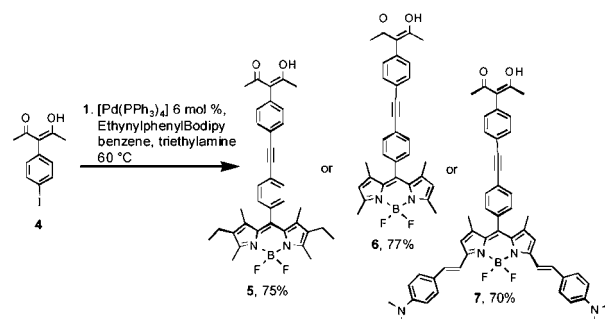
Unfortunately, the cross-coupling of acacH modules to more electron-rich BODIPYs having an extended dipyrromethene core provided by two styryl fragments in the 3,5-substitution positions failed under various experimental conditions. Thus, a new strategy based on the cross-coupling of the acacH-linked phenyliodo derivative **4** was devised. Substitution of one iodo group of 1,4-di-iodobenzene by an acacH unit proved facile, yielding **4** in 65% yield under the experimental conditions of Scheme 1. Cross-coupling of **4** with an ethynyl-substituted BODIPY was found not to be limited to simple BODIPY species (yellow and green emitters **5** and **6**, respectively) but

was successful also with the NIR emitter **7**. The isolated yields are acceptable in all cases (Scheme 2). It is worth noting that conventional Pd catalysts are not deactivated by the acac residues despite the basic conditions.

We have previously noted that some particular ethynyl-substituted BODIPY derivatives could not be fully purified owing to their high reactivity and tendency to polymerize rapidly.[12] This limits the cross-coupling strategy of Scheme 2 to stable ethynyl-grafted BODIPYs.

Our next objective was the synthesis of an acacH building block bearing a reactive terminal alkyne. This scenario would help to prepare many various dyes by shortcutting the synthesis of the BODIPY alkyne derivatives. TMS-acetylene reacts under standard conditions to afford the protected compound **8**. Unfortunately, this compound appears to be relatively unstable, and its deprotection was unsuccessful probably because of the presence of fluoride or water (Scheme 3). In situ deprotection of the trimethylsilyl group enabled the cross-coupling to iodophenyl BODIPYs, but the reaction product was the keto derivative **9**. Attempts to deprotonate the methylene group and to acylate it with an ester failed in all cases providing an intractable mixture of compounds (Scheme 3).
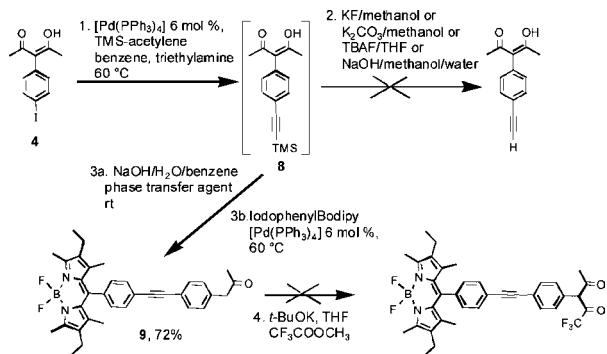
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Thus, an alternative strategy investigated was the substitution of the iodo group in **4** with acetylene (used to degass the reaction mixture), followed by a one-pot cross-coupling reaction with iodophenyl-BODIPY dyes after removing all residual acetylene from the reaction mixture. Dyes **6** and **10** with an acetylenic linker were successfully isolated in good yields by this one-pot protocol (Scheme 4).

Scheme 4. Synthesis of the acacH BODIPYs **6** and **10**
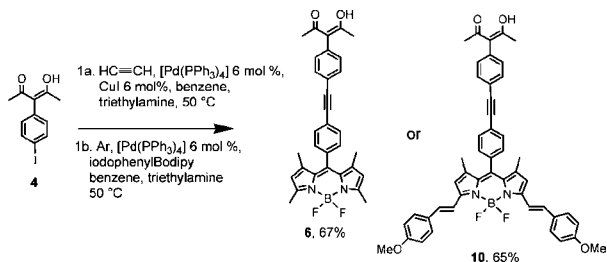
In extension of this one-pot reaction, we performed more sophisticated syntheses in which two sites were functionalized (Scheme 5). While the ethynyl derivatives of dyes **11−13** are too unstable to be used in coupling reactions to **4**, the procedure defined in Scheme 4 enabled isolation of compounds **14−16** in appreciable yields.

The absorption spectra of **14−16** in dilute dichloromethane solutions showed two main absorption peaks. That at 300 nm is common to the whole series, while the lower-energy absorption varies with the BODIPY core (Figure 2a). The absorption bands located at higher energies are assigned to $\pi-\pi^*$ transitions localized on the acacH fragment, and its intensity is proportional to the number of units. The absorption bands localized at 515, 643, and 709 nm, respectively, for **14**, **15**, and **16** are safely assigned, in light of previous data, to $S_0{\rightarrow}S_1$ transitions.[13–15] Interestingly, the weak absorption in the 360−400 nm range, probably due to $S_0{\rightarrow}S_2$ transitions, showed, in contrast, only a weak dependence on an increase in the core delocalization of the BODIPY unit. Excitation in the low-energy absorption bands of **14**, **15**, and **16** led to strong emissions at 533, 672, and 749 nm, respectively, with quantum yields in the range 50−70% (Table 1 and Figure
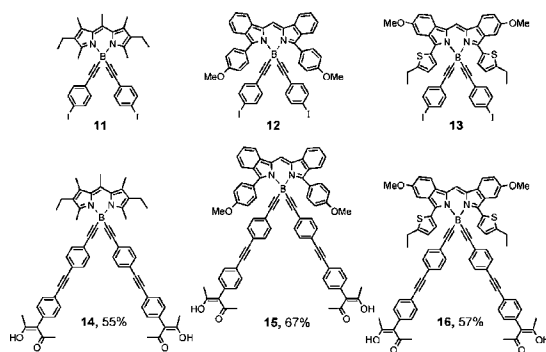
2b). The fluorescence spectra showed relatively good mirror symmetry with respect to the lowest-energy absorption transitions, confirming that the same optical transitions are involved in both absorption and emission processes. These transitions were weakly polarized, as is typical for S_1 emitters. Furthermore, the fluorescence decay profiles fitted a single exponential, with fluorescence lifetimes in the 3−15 ns range. The fact that the radiative rate constant (about 1 $\times\ 10^8\ s^{-1}$) is much greater than the nonradiative rate constant (about $5 \times 10^7\ s^{-1}$) shows that the molecular excited state preferentially deactivates radiatively. The small Stokes shift observed may be explained by the substantial invariance of the molecular geometric structure in the ground (S_0) and the first excited (S_1) states, while the perfect match between the excitation and absorption spectra points to the efficient radiative deactivation of the excited electronic state.

Finally, after some experimentation, we succeeded in linking in a covalent fashion dyes **2** (orange), **10** (blue), and **7** (green) to TiO_2 powder (Degussa, P-25). By mixing a dichloromethane solution of the dye with TiO_2 dispersed in a small volume of isopropanol at 60 °C, the powder progressively took on the color of the solution. After 2 h, the color of the solution had diminished in intensity by about 50%. After vigorous washing of the colored powder under sonication, the dried samples were orange, blue, and green, demonstrating efficient linking of the BODIPY dyes (Figure 3). Treatment of TiO_2 powders with dyes carrying an iodo function in place of the acacH fragment does not provide colored powders, excluding possible adsorption of the dyes on the particle surface (Figure 3, left-hand side). FT-IR spectra of the powders were also in keeping with complexation of 1,3-diketonate units to Ti centers, with a carbonyl region absorption ($\nu_{acac} = 1599\ cm^{-1}$) very close to that of soluble Ti−acac complexes (Figure 4) but absent in genuine TiO_2.[17] It is well established that grafting dyes to inorganic surfaces by pincer type of anchors is more efficient than single tethers like carboxylates or phosphonates. The binding energies of *acac*

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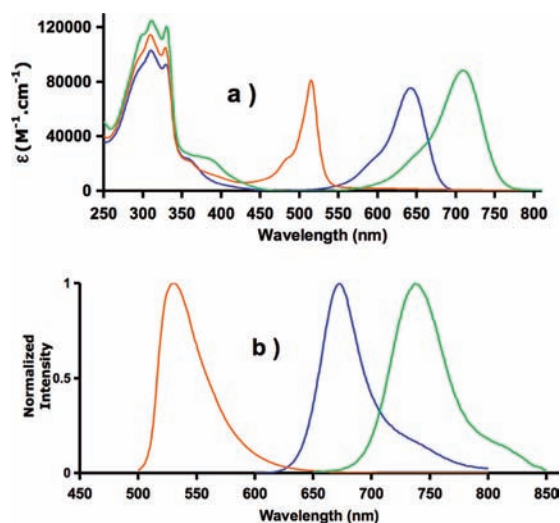
Figure 2. Data measured in dichloromethane at rt for dyes **14** (orange), **15** (blue), and **16** (green). (a) Absorption at $c \approx 10^{-5}$ M. (b) Emission at $c \approx 10^{-6}$ M, excitation wavelength 480 nm for **14**, 595 nm for **15**, and 630 nm for **16**.

Table 1. Optical Data Measured in Dichloromethane Solution

	λ_{abs} (nm)	ε M^1.cm^{-1}	λ_F (nm)	$\Phi_F{}^a$	τ_F (ns)	$k_r{}^b$ 10^8 s^{-1}	$k_{nr}{}^b$ 10^8 s^{-1}
2	525	70,000	540	0.90	8.0	1.12	0.13
3	525	71,300	539	0.91	9.0	1.01	0.10
5	524	75,000	541	0.60	8.0	0.75	0.50
6	502	76,000	514	0.53	3.0	1.77	1.57
7	705	103,000	764	0.25	3.0	0.83	2.5
9	526	68,000	541	0.63	7.0	0.90	0.53
10	645	132,000	662	0.55	9.0	0.61	0.50
14	515	73,000	533	0.70	15.0	0.47	0.20
15	643	75,000	672	0.66	13.0	0.51	0.26
16	709	88,000	749	0.50	9.0	0.56	0.56

^{a} Determined at rt, using Rhodamine 6G as reference ($\Phi_F = 0.78$ in water, $\lambda_{exc} = 488$ nm).[16] All Φ_F are corrected for changes in refractive index. ^{b} Calculated using the following equations: $k_r = \Phi_F/\tau_F$, $k_{nr} = (1 - \Phi_F)/\tau_F$, assuming that the emitting state is produced with unit quantum efficiency.

fragments to oxygen vacancy sites of TiO_2 is by far more suitable than carboxylates.[5] Furthermore, we believe that *acac* derivatives will be less prone to hydrolysis versus surface Ti(IV)-carboxylate esters and should provide more robust solar cells.

In conclusion, we have developed a new series of 1,3-diketone-substituted BODIPYs based either on direct substitution with Cu(I)−L proline catalysts or on Pd(0)-promoted cross-coupling reactions either with ethynyl-substituted BODIPYs or with ethynyl-substituted acacH compounds. The chemical scope of these pentadione compounds could be enlarged by reaction with functionalized aldehyde to provide novel energy transfer cassettes and third-order nonlinearities.[18] The introduction of acacH fragments does not, as expected, significantly perturb the optical properties of the dyes which remain highly fluores-

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Figure 3. TiO_2 powders labeled with dyes **2**, **10**, and **7** and their dichloromethane solution. Solution **A** is an equimolar solution of the phenyliodo BODIPYs **11**, **12**, and **13**. Solutions **B**, **C**, and **D** are micromolar solutions of the acacH dyes **2**, **10**, and **7**. The bottom glass slides contain the dry powders of TiO_2 which have been treated from left to right with solutions **A**, **B**, **C**, and **D**, respectively, highlighting the covalent linking of the dye to the semiconductor.
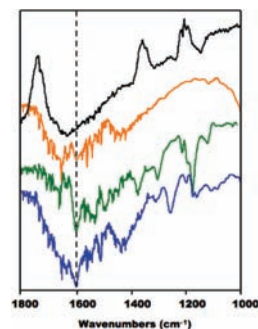
Figure 4. FT-IR of the TiO_2 powders grafted with the acacH-dyes dispersed in KBr pellets: genuine TiO_2 (black); TiO_2 + dye **2** (orange); TiO_2 + dye **7** (green); TiO_2 + dye **10** (blue).

cent and stable under various conditions. Anchoring these novel dyes to TiO_2 nanoparticles is facile, leading to highly colored powders which may find interesting applications in solar cells or related energy conversion devices. The fluorescence of the dyes linked to the semiconductor is completely quenched which is a good indication of electron injection in the conduction band of the semiconductor. We are currently using these dyes in electrochemical solar cells.

Supporting Information Available: Synthetic procedures and analytical data reported herein. CIF file deposited at Cambridge Crystallographic Data Centre under the number 740694. This material is available free of charge via the Internet at http://pubs.acs.org.

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