

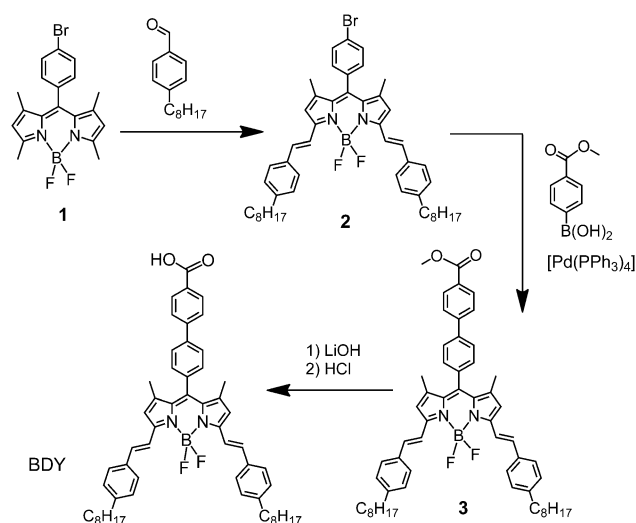
A Dual Emissive BODIPY Dye and Its Use in Functionalizing Highly Monodispersed PbS Nanoparticles**

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BODIPY (boron-dipyrromethene) dyes and derivatives are well-known to be very effective in light-harvesting and energy-transfer processes, owing to their high fluorescence quantum yields, large molar absorption coefficients, relatively long excited-state lifetimes, and excellent photochemical stability.^[1] Thus, they have frequently been used in light-harvesting molecules, as dye sensitizers, and as probes and labels for biomolecules.^[1–2] One important class of materials for various optoelectronic applications, including solar cells, is the class of semiconductor nanoparticles (NPs). The optical and energetic properties of these nanoparticles can be tuned by varying their shape, size, or surface ligands.^[3–4] Lead sulfide NPs are particularly attractive among NPs owing to their narrow band gap, large exciton Bohr radii, and their absorption and emission in the near-IR region.^[3e,5] Several recent reports have shown that PbS NPs are very promising materials for achieving high-performance photovoltaic devices.^[4e,5,6] The most commonly used surface ligand for PbS NPs is oleic acid, which can effectively protect the NPs from oxidation and can facilitate their dispersion in organic solvents.^[3,5–7] However, because they lack any interesting photophysical properties, oleic acid capping ligands do not engage in any electronic communication or interactions with the NPs and thus have little influence on the properties of the NPs and insulate NPs from each other and the surrounding medium. New surface ligands that can communicate electronically with PbS NPs and enhance their performance in optoelectronic devices are therefore in demand. Based on this consideration and the very attractive photophysical proper-

ties of BODIPY dyes, we initiated the investigation of new BODIPY dyes as potential new surface ligands for PbS NPs. Herein, we report the synthesis and photophysical properties of a new BODIPY dye (BDY) and its use in PbS NPs functionalization.

The procedure used to synthesize BDY is illustrated in Scheme 1. The bromophenyl-BODIPY starting material **1** was synthesized by using a modified literature procedure.^[8]



Scheme 1. Synthetic procedure for BDY.

The 3- and 5-methyl groups in **1** are acidic enough to undergo Knoevenagel condensation,^[9] which allowed the introduction of two *p*-octyl styryl groups to the core to produce **2**.

The octyl groups are necessary to provide the desired solubility of the functionalized NPs in organic solvents. The conjugated terminal carboxylate group was connected to the BODIPY core by using a standard Suzuki coupling method between **2** and the corresponding boronic acid to produce **3**. Replacement of the ester group by a carboxylic acid converts **3** to the final product BDY, which was fully characterized by ¹H NMR spectroscopy, HRMS, and elemental analysis. BDY has a moderate solubility in most organic solvents, including toluene and hexanes. Although we have not been able to obtain single crystals of BDY, the structure of its ester (**3**) was determined successfully by X-ray diffraction analysis.^[10] Compound **3** forms needlelike crystals that aggregate into black balls of spikes. The crystal structure of **3** is shown in Figure 1. In the crystal lattice, molecules of **3** arrange in a head-to-head and tail-to-tail fashion, with extensive intermolecular interactions involving the styryl groups, the biphenyl

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Supporting information (including synthetic procedure and characterization data of BDY, PbS nanoparticle synthesis, crystal-structure data, TD-DFT computational details, photophysical property characterization, and electrochemical data) for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201104690>.

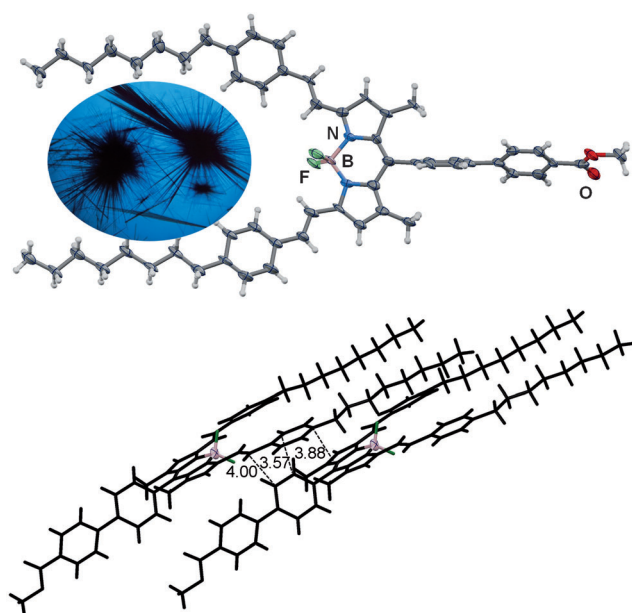


Figure 1. Top: Crystal structure of **3** and a photo showing the “spike-ball”-like crystals of **3** in hexanes. Bottom: a diagram showing intermolecular interactions of **3**; distances in Ångstrom.

group, and the BODIPY core (Figure 1; see also the Supporting Information).

The BDY molecule has an intense dark purple-blue color in solution and the solid state. Its absorption spectrum in toluene has two intense absorption bands at 580 and 636 nm and a shoulder band at approximately 520 nm (Figure 2). It is fluorescent with two emission peaks, one in the orange region $\lambda_{\text{max}} \approx 585$ nm ($\tau = 3.75(16)$ ns) and one in the red region, $\lambda_{\text{max}} \approx 655$ nm ($\tau = 4.13(10)$ ns) in toluene. The fluorescence quantum efficiency of BDY was determined to be approximately 0.24, with $\lambda_{\text{ex}} = 560$ or 510 nm, using Rhodamine B as the standard. In the solid state, BDY is a dark black solid and not emissive at all. Both absorption and emission spectra of BDY experience a hypsochromic shift with increasing solvent polarity, thus indicating that the dye has a much greater dipole in the ground state than in the excited state. Although the absorption spectrum and the fluorescence spectrum of BDY bear some resemblance to those of several reported phenyl-vinyl functionalized BODIPY molecules,^[11] the two absorption and emission peaks at 580–590 nm and 640–660 nm cannot be simply attributed to intramolecular electron transitions.

The first evidence for intermolecular electronic transitions is the concentration-dependent behavior of both absorption and emission spectra of BDY. In the absorption mode, in the low concentration range (5.0×10^{-7} M to 5.0×10^{-6} M), when the concentration of BDY increases, the intensity of the peak at 640 nm increases much faster than that of the peak at 590 nm (Figure 2). In the emission mode, the peak near 655 nm also experiences a much greater increase of intensity with concentration than the peak at 590 nm in the relatively low concentration range (5.0×10^{-7} M to 1.0×10^{-5} M). At higher concentrations, the 655 nm peak

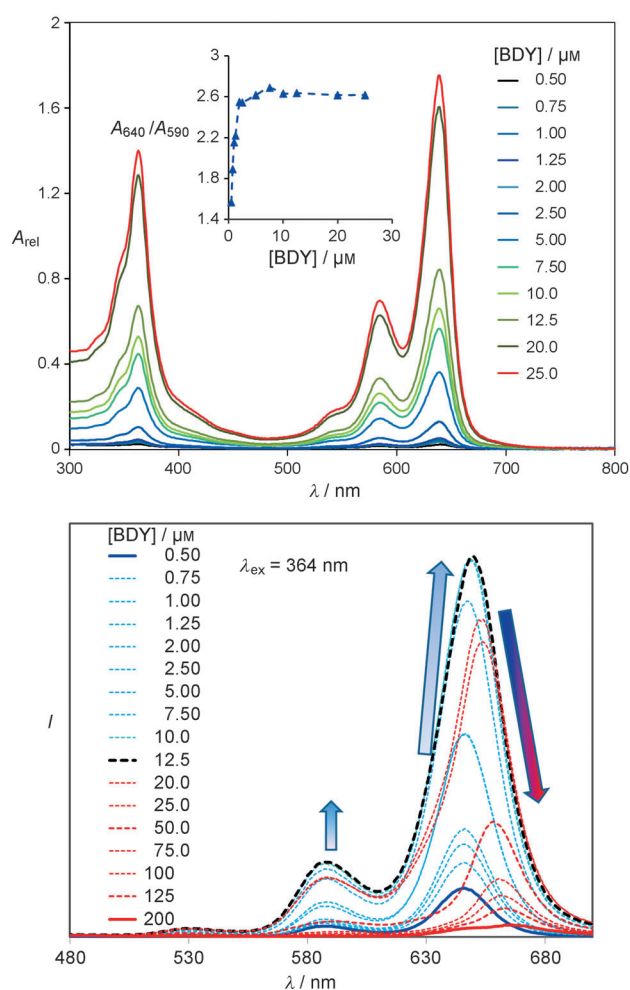


Figure 2. Absorption (top) and fluorescence (bottom) spectral changes of BDY with increasing concentration in toluene. Inset: the relative absorbance change of the peak at 640 nm vs. that at 590 nm plotted against concentration of BDY.

shows a clear red shift and a steady decrease of intensity with increasing concentration. Thus, the low-energy peak in both the absorption and the emission spectrum most likely has an intermolecular origin. Further evidence comes from the excitation-energy dependence of BDY dual emission. As shown in Figure 3, the emission peak at approximately 655 nm does not change intensity significantly with excitation energy, while the peak near 590 nm is very sensitive to excitation energy: its intensity is highest for excitation at 570 nm and becomes weaker as excitation energy increases. The distinct red or orange emission color of BDY can be observed visually with the appropriate choice of the excitation source (Figure 3). This finding strongly suggests that the two emission peaks are from two different species. This conclusion is further supported by fluorescence anisotropy measurements, which revealed that the two emission peaks have distinct anisotropies (0.0606(28) for the peak at 585 nm and 0.0249(22) for the peak at 655 nm). The anisotropic parameters indicate that the two species have either a very different shape, size, or molecular weight.^[12] NMR spectra did

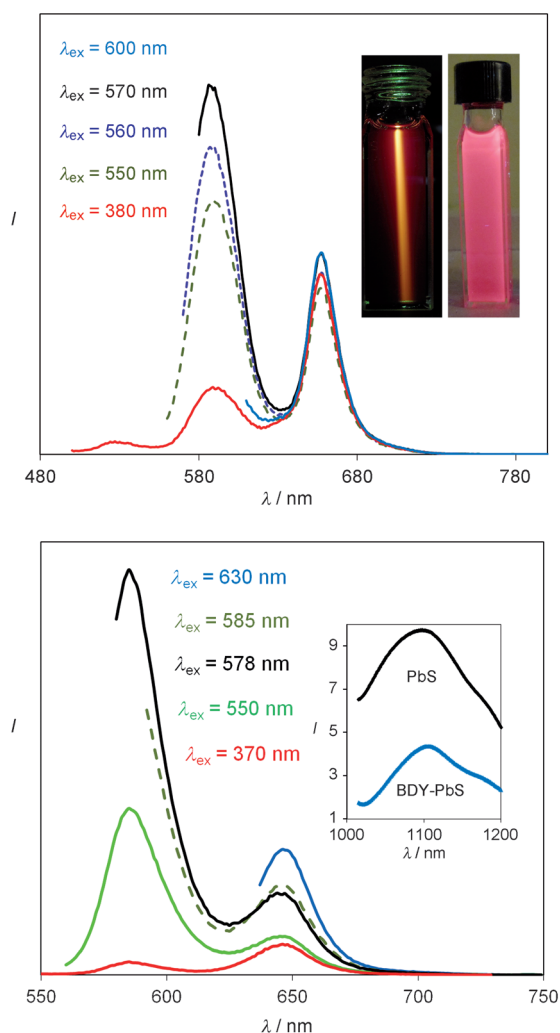


Figure 3. Top: the dependence of BDY fluorescence on excitation energy (1.0×10^{-5} M in toluene) with photos showing the orange emission color of the BDY solution upon excitation by a green laser (left) and the red emission color (right) upon irradiation by a UV lamp at 365 nm. Bottom: the dependence of BDY-PbS NP fluorescence on excitation energy in toluene, inset: the NIR emission of oleic acid capped PbS NPs and BDY-PbS NPs ($\lambda_{\text{ex}} = 578$ nm, in toluene).

not show any detectable impurities or an olefin *trans-cis* isomerization process that may be responsible for the dual emission phenomenon. Hydrogen-bonded dimers are also ruled out, because the ester molecule **3** displays similar dual absorption and emission bands (see the Supporting Information). Time-dependent density functional theory (TD-DFT) computational results for the discrete BDY molecule showed only one absorption band ($\lambda_{\text{max}} = 571$ nm) that matches well with the experimental absorption band at 580 nm, thereby supporting the conclusion that the peak at 636 nm does not have an intramolecular origin. Furthermore, TD-DFT established that the lowest energy transition is a $\pi \rightarrow \pi^*$ transition localized on the BODIPY-bis(styryl) portion of the molecule (see the Supporting Information). Hence, intermolecular interactions involving this part of the molecule will likely have an impact on the fluorescence of the molecule. Such

intermolecular interactions are indeed possible for BDY, as revealed by the crystal structure of **3** in Figure 1. We thus suggest that the low-energy absorption/emission band at approximately 640 nm is caused by molecular aggregation and intermolecular interactions. The same intermolecular interactions are likely responsible for the lack of emission of BDY in the solid state. Although many BODIPY derivatives are known in the literature,^[1–2,11] and intramolecular excimer emission involving a BODIPY dye is also known,^[11e] BDY is the first example, to our knowledge, that displays such unusual dual emission among this family of compounds.

Functionalization of PbS NPs with BDY was achieved successfully by simply mixing BDY with oleic acid capped PbS NPs^[5c,d] in toluene under nitrogen, and subsequent precipitation of the BDY-capped PbS NPs (BDY-PbS NPs) using acetone. The ligand-exchange process was monitored by ^1H NMR spectroscopy (see the Supporting Information). The best procedure is to use a tenfold excess of BDY ligand to exchange with the oleic acid on the PbS NPs at room temperature for 10 min. The aromatic-proton chemical shifts of the bound BDY in BDY-PbS NPs appear as a broad peak in the NMR spectrum that covers the entire aromatic region, attributable to the low mobility of the BDY ligand on the surface of the PbS NPs. The signals from oleic acid and unbound BDY are completely absent in the NMR spectrum of isolated BDY-PbS NPs.

The formation of new BDY-PbS NPs was further verified by TEM imaging, which shows that the BDY-PbS NPs are highly uniform with an average size of approximately 3 nm, similar to the original oleic acid capped PbS NPs (Figure 4).

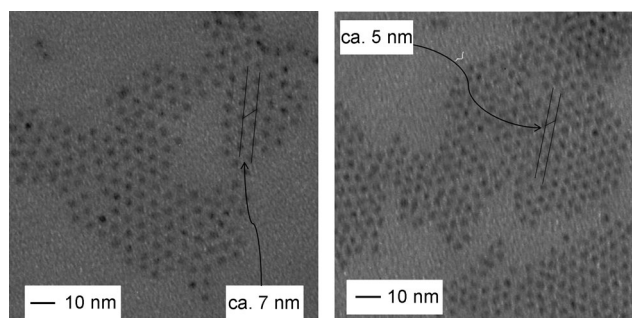


Figure 4. TEM images of BDY-PbS NPs (left) and oleic acid capped PbS NPs (right).

However, the separation distance between the NPs is much longer (ca. 7 nm) for BDY-PbS NPs than for oleic acid PbS NPs (ca. 5 nm). This result is in excellent agreement with the fact that BDY is a much longer and bigger ligand (ca. 3 nm in length) than oleic acid (ca. 2 nm). The retention of a high uniformity and of the particle size of the BDY-PbS NPs is quite remarkable, because increased NP sizes and poor uniformity were widely reported after ligand exchange of NPs.^[4,13] These results support that BDY is a highly effective ligand for PbS NPs.

The BDY-PbS NPs have a distinct turquoise color in solution (Figure 5). Upon irradiation by a UV lamp at 365 nm, the BDY-PbS NPs emit red light, which is much

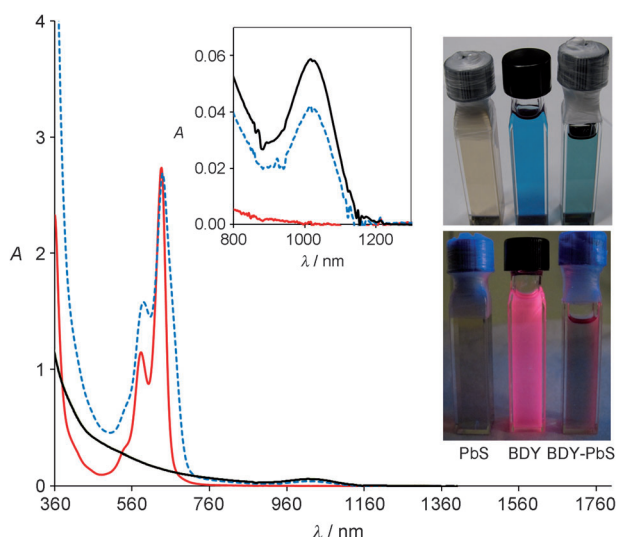


Figure 5. Absorption spectra of BDY (red), oleic acid capped PbS NPs (black), and BDY-PbS NPs (blue dashed) in toluene. Inset: The absorption spectra in the NIR region and photos showing the colors of the three samples under ambient light (top) and under UV (365 nm) irradiation (bottom).

weaker than that of free BDY in toluene. Interestingly, the BDY-PbS NPs display similar dual emission peaks in the 500–700 nm region as BDY, except that the emission peak at 645 nm is blue-shifted about 10 nm compared to free BDY at a similar concentration in toluene. Like BDY, the emission spectrum of BDY-PbS NPs is also highly sensitive to excitation energy (Figure 3), thus supporting the conclusion that interligand interactions similar to those of BDY are also present in the NPs. However, while for BDY the low energy emission band at 655 nm does not change intensity with excitation energy, the 645 nm emission band of the BDY-PbS NPs does lose intensity as the excitation energy increases; this observation is an indication of either energy transfer or charge transfer from the ligand to the NPs. Fluorescence titration experiments of BDY with oleic acid capped PbS NPs showed approximately 70 % quenching of BDY emission by the NPs. This quenching may be caused by energy transfer, because the PbS NPs have considerable absorption in the 600–700 nm region. On the other hand, cyclic voltammetry measurements indicate that the LUMO (lowest unoccupied molecular orbital) level of BDY is at approximately -3.4 eV, significantly above the electron affinity energy (ca. -4.2 eV) of the PbS NP core, while the HOMO (highest occupied molecular orbital) level of BDY is similar to the ionization potential energy of PbS NPs (ca. -5.2 eV).^[14] It is therefore conceivable that excited-state charge transfer from BDY to the NP core may occur, which can also act as an effective pathway for quenching the emission of BDY. The PbS NPs have a distinct NIR exciton peak at 1024 nm and a NIR emission band at approximately 1100 nm. The replacement of oleic acid surface ligands by BDY did not change the NIR absorption and emission energy at all, thus further supporting the conclusion that there is no surface-state change or etching of the NPs during the ligand exchange.^[4] The ligand exchange, however, did lead to approximately 50 % intensity reduction

of the NIR emission band, as confirmed by fluorescence titration experiments (see Figure 3 and the Supporting Information). Since BDY has no absorption in the NIR region, the NIR emission quenching is most likely caused by a charge-transfer process between BDY and the PbS NP core.

To illustrate the impact of BDY functionalization on the performance of PbS NPs in photovoltaic (PV) devices, we fabricated a simple PV device with the structure of indium tin oxide (ITO)/BDY-PbS NPs (100 nm)/LiF (1 nm)/Al (100 nm). The BDY-PbS NPs were deposited onto the ITO substrate by spin-coating a corresponding chloroform solution. Photocurrent production upon simulated solar irradiation was observed from this simple device with $V_{oc} = 0.37$ V, $J_{sc} = 0.10$ mA cm⁻², and a fill factor (FF) of 0.31. Although this simple PV device is not efficient at all, it is much better than the control PV device with the oleic acid capped PbS NPs as active layer; this control device did not display any detectable photocurrent at all. The improved PV performance of the BDY-PbS NPs device can be attributed to the improved electronic communications between the surface ligand and the NP core. Efforts are being taken to further understand the electronic properties of the BDY-PbS NPs and to explore their applications in PV and other optoelectronic devices.

In summary, a new BODIPY molecule BDY that possesses unusual dual-emissive properties has been synthesized. Its use as a highly effective surface ligand for achieving highly uniform and monodispersed PbS NPs has been demonstrated. The presence of electronic communication between BDY and the PbS core has been established. The enhancement in PV performance of PbS NPs by the BDY surface ligand, compared to oleic acid, has been verified by a simple PV device.

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