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Emission of boron dipyrromethene dyes through energy transfer to their S_2 state from polysilane S_1 state

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ABSTRACT

Irradiation of a mixture of a poly(methylphenyl)silane containing a Boron dipyrromethene dye was found to induce green color emission from the BODIPY dye via energy transfer from the polysilane S_1 state to the S_2 state of the BODIPY in the solid state, whereas in the solid the BODIPY dyes themselves are nonfluorescent due to aggregation and self-quenching.

1. Introduction

Polysilanes are well known as a new type of σ-conjugated polymers having Si backbone with high oscillator strength and conductivity [1,2]. They exhibit unique characteristics such as one-dimensional semiconduction, photo conductivity with high hole mobility, large non-linear optical effects and effective light emission in the near ultraviolet region due to one-dimensional excitonic states [3–7]. The ultraviolet emission of polysilanes is unsuitable for their application in electroluminescene and optical devices. In previous studies, it has been demonstrated that the luminescence wavelength could be controlled by introducing dyes as the luminescence centers in linear polysilanes [8–11]. Shifting the absorption and emission wavelengths of polysilanes to the visible and even to the NIR region by structural modifications is difficult, because of synthetic limitations [12,13]. Highly efficient energy transfer could be realized by mixing dyes into the polysilane, the combination of polysilanes and dyes, Actually, perylene, coumarin, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) and Zinc tetra-phenylporphyrin (ZnTPP) have been reported to induce electroluminescene (EL) in the visible region through energy transfer to S_1 level of dyes from polysilane S_1 states [14,15]. Considering the high oscillator strength and the conductivity by the σ-conjugated one-dimensional configuration of polysilanes, design and synthesis of new dye-polysilane systems for electoluminescene devices is highly desirable [15].

As a new type dye for a variety of applications, boron dipyrromethene (BODIPY) is attractive, because they feature narrow.and intense absorption and fluorescence bands, high fluorescencequantum yields, negligible triplet-state formation, and high stability [16,17]. We notice that there is strong spectral overlap of fluorescence bands of a polysilane with the higher energy absorption ($S_0 \rightarrow S_2$) band of a BODIPY molecule, while no overlap with the BODIPY $S_0 \rightarrow S_1$ band. Energy transfer would effectively occur from excited polysilanes to the S_2 state of BODIPY dyes. Spectral overlap is an essential requirements for Foerster type energy transfer. However, less information is available for the energy transfer to upper-lying excited states of the acceptor, while several such cases have been described including that from the pyrene S_1 state to the BODIPY S_2 state [18,19].

We report herein that when a mixture of BODIPY with a polysilane is irradiated in the solid state, intense green fluorescence of the BODIPY is observed via efficient energy transfer from singlet-

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excited state of the polysilane to the S_2 state of the BODIPY. BODIPYs are highly promising as an acceptor to modify the color of polysilane-based electroluminescence and related optoelectronic devices.

2. Materials and methods

2.1. Instrument and reagents

^{1}H NMR spectra were recorded on a Bruker DPX400 spectrometer and referenced to the residual proton signals of the solvent. Mass spectra were measured on Thermo Finnigan LCQ Advantage Spectrometer. UV–Vis absorption spectra were recorded on a Shimadzu UV-2550 UV–Vis Spectrophotometer. Fluorescence spectra were measured on a Hitachi F-4600 FL Spectrophotometer (the path-length of the quartz cell is 1 cm) with a xenon arc lamp as the light source. All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. All air and moisture-sensitive reactions were carried out under nitrogen atmosphere. Dichloromethane was distilled over calcium hydride. Triethylamine was obtained by simple distillation. Toluene was dried over sodium metal and fresh distilled before to use.

2.2. Synthesis

2.2.1. Synthesis of BODIPY **1** and **2**

4-Hydroxybenzaldehyde (2 mmol) and 2,4-dimethylpyrrole (380 mg, 4 mmol) were dissolved in dry CH_2Cl_2 (100 mL) under nitrogen. One drop of trifluoroacetic acid (TFA) was added, and the solution was stirred for 4 h at ambient temperature in the dark. 2,3-Dichloro-5,6-dicyanoquinone (DDQ, 442 mg, 2.0 mmol) was added to the mixture and then stirred for additional 20 min. The reaction mixture was then treated with triethylamine (3 mL) for 5 min and boron trifluoride etherate (3.2 mL) for another 40 min. The dark brown solution was washed with water (2 × 20 mL) and brine (30 mL), dried over anhydrous magnesium sulfate, and concentrated at reduced pressure. The crude product was purified by silica-gel flash column chromatography (elution with 10% EtOAc/petroleum ether) followed by recrystallization from $CHCl_3$/hexane to yield **1** as red crystal (yield 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, $J = 8.4$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 2H), 2.55 (s, 6H), 1.45 (s, 6H), ESI-MS: m/z 341.31 $[M + H]^+$, 321.47 $[M - F]^+$; HRMS-ESI: m/z: calcd for $C_{19}H_{19}BF_2N_2ONa^+$: 363.1451 $[M + Na]^+$, found: 363.1465; IR (KBr pellet, cm^{-1}): 3419, 1543, 1509, 1307, 1197, 1157. A similar procedure using benzaldehyde instead of 4-hydroxybenzaldehyde afforded **2** as red crystal (yield 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 3H), 7.29 (d, 2H), 2.55 (s, 6H), 1.37 (s, 6H); ESI-MS: m/z 325.27 $[M + H]^+$, 305.35 $[M - F]^+$, HRMS-ESI: m/z: calcd for $C_{19}H_{19}BF_2N_2Na^+$: 347.1502 $[M + Na]^+$, found: 347.1513; IR (KBr pellet, cm^{-1}): 1543, 1509, 1305, 1183, 1155.

2.2.2. Synthesis of polysilanes

Dry toluene (50 mL) containing sodium metal (2.7 g, 117.4 mmol) was stirred at reflux in an argon atmosphere. Dichloromethylphenylsilane (9.5 g, 50 mmol), was added dropwise into the mixture. After the addition was complete, the reaction mixture was stirred for 5 h. It was cooled down to room temperature, and ethanol (10 mL) was added to remove the sodium metal and to terminate the end groups. The mixture was washed with water (2 × 20 mL) and brine (30 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo to give the crude product. Pure poly(methylphenyl)silane (**PMPS**, see Fig. 1) was obtained as a white powder by reprecipitation using a toluene-methanol system, in the yield of 4.8 g (60%). The molecular weight of the polymer was determined by gel permeation chromatography (GPC) calibrated by polystyrene standards with chloroform as the eluent. **PMPS**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.3–7.2 (br, 4H), −0.9–0.1(br, 3H); UV $\lambda_{max}(\log\varepsilon)$(THF) = 334 nm; $M_n = 7{,}000$, $M_w = 19{,}950$, $M_w/M_n = 2.85$.

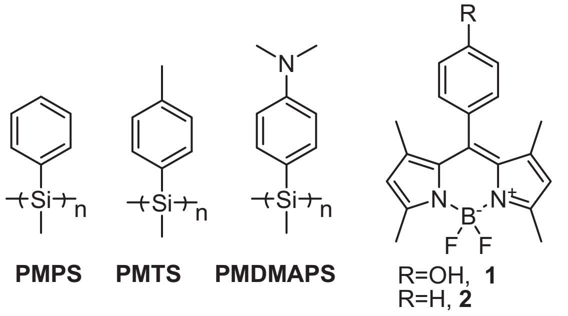


Fig. 1. Structural formula of poly(methylphenyl)silane (**PMPS**), poly(methyl-4- tolyl) silane (**PMTS**), poly[methyl-(4-dimethylaminophenyl)]silane (**PMDMAPS**), BODIPY **1** and **2**.

Similarly, polysilanes **PMTS** and **PMDMAPS** shown in Fig. 1 were obtained using dichloromethyl-4-tolylsilane and dichloro methyl-(4-dimethylaminophenyl)silane as the substrates, the corresponding **PMTS** and **PMDMAPS** were obtained in 35% and 30% isolated yields, respectively. **PMTS**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.1–6.8 (br, 4H), 2.2 (br, 3H), −0.9–0.2(3H); UV $\lambda_{max}(\log\varepsilon)$(THF) = 342 nm; $M_n = 5{,}100$, $M_w = 10{,}965$, $M_w/M_n = 2.15$. **PMDMAPS**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.7–7.7 (br, 4H), 2.9 (br, 6H), 0.1–0.6 (br, 3H); UV $\lambda_{max}(\log\varepsilon)$ (THF) = 350 nm, $M_n = 1400$, $M_w = 2{,}016$, $M_w/M_n = 1.44$.

3. Results and discussion

Poly(methylphenyl)silane (**PMPS**), poly(methyltolyl)silane (**PMTS**), and poly[methyl-(4-dimethylaminophenyl)]silane (**PMDMAPS**) were prepared as suitable candidates of the energy donors, by Wurtz-type condensation with sodium metal according to the method of Miller and Michl [6]. BODIPY dyes (4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a, 4a-diaza-s-indacene), **1** and **2**, were prepared through TFA-catalyzed condensation of 2,4-dimethylpyrrole with benzaldehyde and 4-hydroxybenzaldehyde, respectively, in a one–pot reaction [20,21]. All compounds were identified by H^1 NMR, MS and GPC.

The absorption spectra of **1** show a narrow spectral band at 497 nm with a shoulder at 475 nm, which is attributed to the strong

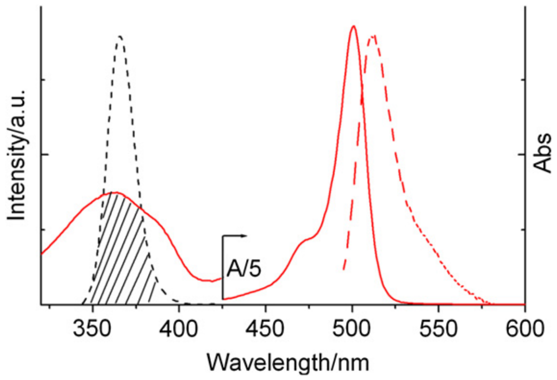


Fig. 2. Fluorescence spectra of **PMPS** (black dash line) and **1** (red dash line), absorption spectra of **1** (red line) in THF solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

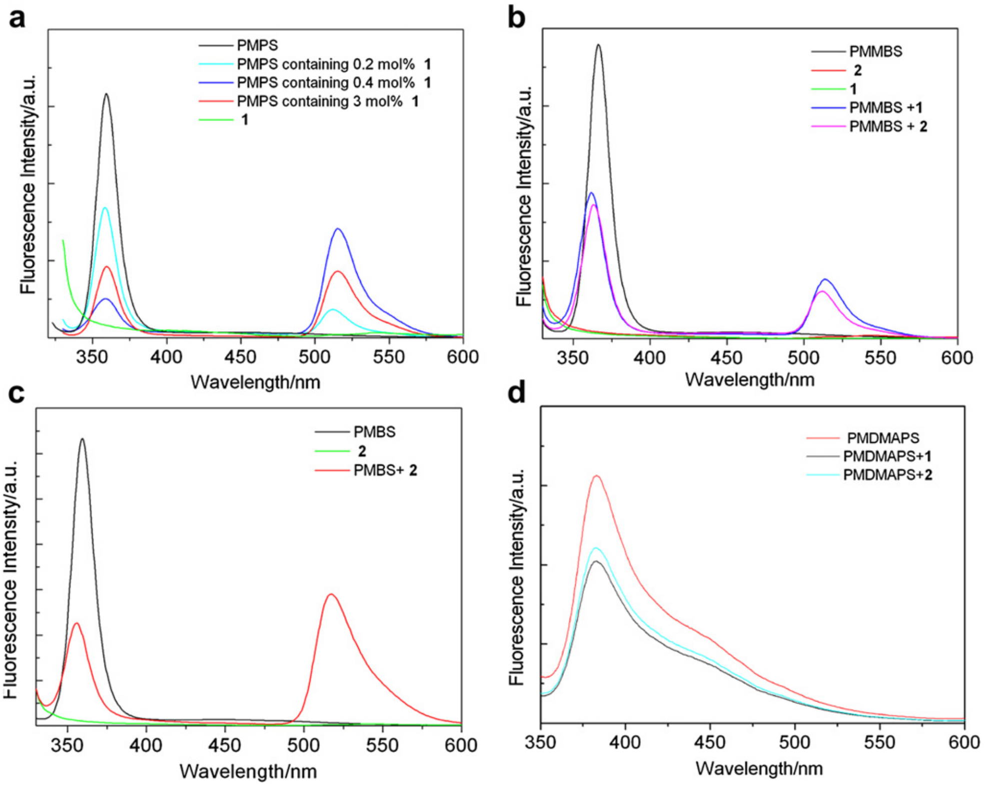
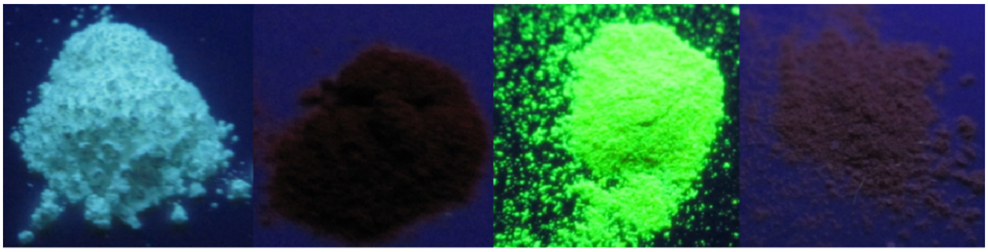


Fig. 3. Fluorescent spectra of films of polysilane-BODIPY mixed systems. (a) **PMPS/1**, (b) **PMTS/1** and **2**, (c) **PMPS/2**, and (d) **PMDMAPS/1** and **2** systems.

S_0–S_1 transition, in addition to a broader and weaker absorption band in the 330–380 nm range assigned to the second lowest-energy (S_0–S_2) transitions [22] (Fig. 2). The absorption spectra of **2** is almost identical to that of **1**, indicating the absence of interactions between meso-position and indacene plane in the ground state, which is obviously due to the sterically demanding methyl groups that force the molecule into a twisted conformation [23]. As reported, the fluorescent bands of polysilanes **PMPS** and **PMTS** appear at 360 ± 5 nm, which are attributed to a fluorescence from their lowest σ–σ^* excited state [24]. The polysilane fluorescent bands overlap strongly with the absorption bands of the BODIPY-based S_2 state, but do not with the S_1 state as shown in Fig. 2. In contrast, the fluorescence of **PMDMAPS** occurs at around 385 nm with weak spectra overlap with BODIPY-based S_2 absorption, because of the strong electron donor substituent effects of a *p*-dimethylaminophenyl group on a Si atom.

Fluorescent spectra of solid BODIPY-polysilane mixed systems are shown in Fig. 3. Usually, emission of BODIPYs is never observed in the solid state, because the emission is completely quenched by π–π interaction in aggregation and self-quenching. As expected, no emission was observed for pure BODIPY films as shown in Fig. 3 [25]. The fluorescent spectra of spin-coated **PMPS** and **PMTS** without BODIPY show maxima at 358 nm and 360 nm with a narrow and intense band, as expected. A film of a mixture of a polysilane and a BODIPY was prepared typically as follows: a dye is added to a THF solution of a polysilane and then spin-coated on a quartz plate, which is utilized to measure the electronic spectra. As shown in Fig. 3(a), a **PMPS** film doped with increasing amounts of **1** shows a broad emission from the S_1 state of **1** (Fl_B) at around 526 nm, in addition to a PMPS fluorescent band (Fl_S) at 360 nm; the **1** band is a little broader than that in solution probably due to significant intermolecular interaction in the solid state. Energy transfer from the polysilane S_1 state to the S_2 state of the BODIPY dye in the solid state is the responsible for the emission. The relative intensity of Fl_B to Fl_S depends on the concentration of **1**. Thus, the Fl_B/Fl_S value is consistent with the amount of BODIPY at lower concentration of the dye than 3 mol % but decreases at the higher concentration, probably due to the enhanced aggregation of **1**. In contrast, no emission of BODIPY dyes was observed for **PMDMAPS** systems doped with 1 % **1** and **2**, as shown in Fig. 3 (d). The



PMPS **1** **PMPS +1%wt 1** **PMDMAPS+ 1% wt 1**

Fig. 4. The color of polysilane powders with and without 1%wt **1** (excited at 365 nm using a high-pressure Hg arc lamp).

characteristics are not only in good accord with the negligible spectral overlap between **PMDMAPS** fluorescence with the BODIPY $S_0 \rightarrow S_2$ absorption but also confirm that the appearance of BODIPY emission of the mixed film originates from the energy transfer of polysilane S_1 to BODIPY S_2 states and not from the change of the aggregation of BODIPY in the solid. Compared to **PMPS** and **PMTS**, the spectra of **PMDMAPS** become broaden, which can be attributed the charge transfer or branching defects in PMDMAPS by the introduction of the strong electron donor of a *p*-dimethylaminophenyl group [26].

Fig. 4 shows the color of polysilane powders with and without **1** under irradiation at 365 nm light. While no photoluminescence is observed for neat **1** and **PMDMAPS**/**1** system, **PMPS**/**1** powder exhibits strong green photoluminescence under the irradiation, whereas alone the of BODIPY dyes are nonfluorescent in powder.

Although not much is known about the S_2 states of BODIPYs, it has been shown that the internal conversion from S_2 to S_1 is extremely fast (i.e., 100–250 fs) [27]. Because polysilanes are transparent in the visible region, BODIPY-polysilane mixed systems may have advantages in controlling the color of dye-doped photoluminescent systems.

4. Conclusion

We have investigated the emission of BODIPY-doped polysilane systems for the first time. **PMPS** and **PMTS** films with less than 3 mol% of **1** or **2** in the solid state were found to show intense green fluorescence of BODIPYs through efficient energy transfer from polysilane S_1 to the upper-lying singlet-excited state (S_2) of the BODIPY acceptor, while no such energy transfer was observed for energy miss-matching BODIPY-**PMDMAPS** systems. Because polysilanes are usually transparent in the visible region and their fluorescence appears at near UV region, the color of photoluminescence of dye-doped systems is expected to be similar to that of dye itself. BODIPY-doped polysilane systems are expected to provide new types of polysilane-based electroluminescence and related optoelectronic devices.

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