# Fluorescent Temperature Sensing using Triarylboron Compounds and Microcapsules for Detection of a Wide Temperature Range on the Micro- and Macroscale

Jiao Feng, Lei Xiong, Shuangqing Wang, Shayu Li,\* Yi Li,\* and Guoqiang Yang\*

Fluorescent temperature sensing has received increasing interest in a wide range of fields, including fluid dynamics, micromechanics, and molecular cell biology. Here, a novel series of triarylboron compounds with significant thermosensitive hue transformation and high fluorescent quantum efficiency in wide temperature range is described. It is then demonstrated that fluorescent core/shell microcapsules based on one of the compounds exhibit outstanding temperature response. The microcapsules, dispersed in different liquid or solid media, can serve as highly robust, reliable, and sensitive fluorescent temperature sensors. The sensors are the first example containing a single organic luminophor with a self-reference feature that can detect on the micro-and macroscale from -30 to 140 °C. This finding may open a new avenue to the development of novel fluorescent temperature sensors.

# 1. Introduction

Temperature is a basic physical parameter that can be measured quantitatively with thermometers based on various kinds of temperature-dependent physical properties, such as volume, electric conductance and resistance, etc.<sup>[1]</sup> Currently, in situ characterizations for temperature become continuing trend in analysis and diagnostics fields because of their apparent advantages.<sup>[2]</sup> From a practical point of view, these in situ observation should have little impact on its analytes. This criterion poses a serious challenge to classical intrusive thermometers, such as measurements in microelectromechanical systems (MEMS),<sup>[3]</sup> marine research,<sup>[4]</sup> and shipbuilding and aircraft industries.<sup>[5]</sup>

J. Feng, L. Xiong, Dr. S. Q. Wang, Dr. S. Y. Li, Prof. G. Q. Yang Beijing National Laboratory for Molecular Sciences Key Laboratory of Photochemistry Institute of Chemistry Chinese Academy of Sciences Beijing 100190, China E-mail: shayuli@iccas.ac.cn; gqyang@iccas.ac.cn Prof. Y. Li Key Laboratory of Photochemical Conversion and Optoelectronic Materials Technical Institute of Physics and Chemistry Chinese Academy of Sciences Beijing 100190, China E-mail: yili@mail.ipc.ac.cn



optical methods have been developed to limit the impact of measurement.<sup>[6]</sup> Infrared (IR) and thermochromic liquid crystals (TLC) are the most used techniques for optical thermosensors.<sup>[2b,7]</sup> The IR measurement is fairly rapid but can only probe the temperature at the surface, and the transparent media which could absorb the radiation would cause errors in the measurements. TLC is capable to give high precision measurement results, but one kind of liquid crystal can only be used in a comparatively narrow temperature range.

Luminescence is one of the most sensitive and easy-observable detection signals. Some temperature-sensitive luminescence

materials, such as organic dyes, nanotube-based systems, quantum dots, inorganic phosphors and organic-inorganic hybrid materials, have been used to measure temperature in a relatively wide range.<sup>[8]</sup> Most of the approaches detected the luminescence intensity to calculate the temperature, which is so-called ratiometric fluorescence thermometry (RFT).<sup>[9]</sup> By addition of a temperature-insensitive luminescent material as reference into a temperature-dependent luminophore, the RFT method could provide a good accuracy for the measurement of the temperature.<sup>[8h,10]</sup> However, no common luminescence system could be used in both organic and aqueous system due to the solubility of the probes. Meanwhile, for the combination system, it required careful calibration because of the different physicochemical features between two or more luminophores, especially in a wide temperature range.<sup>[11]</sup> There exists a need for developing novel luminophore systems which are suitable for the temperature measurement in diverse situations.

In general, the performance of a luminescent material is also affected by its microenvironments other than temperature.<sup>[12]</sup> To avoid the disturbance from the surroundings, an appropriate approach involving microencapsulation technology has been proved to be effective.<sup>[13]</sup> Acting as barrier walls of liquids, microcapsules can protect the inside substances from external affected factors, such as oxidization, acidity, alkalinity, moisture and evaporation, which makes liquid materials possibly used in various environments with high performance.<sup>[14]</sup> Herein, we describe a novel luminescent microcapsule containing one kind of temperature sensitive dye with self-reference characteristic, which can be dispersed in different media (e.g., organic solvents, water and

#### DOI: 10.1002/adfm.201201712



Scheme 1. Structures of a) DPTB, b) MPTB, and c) TBBD.

polymers). The microcapsules can be used as a luminescent thermosensors in broad applied fields with a wide temperature range from -30 to 140 °C.

Luminescent dye is the core component of the microcapsule for temperature measurement. Although numerous dyes have been reported with intense luminescence, few of them present high quantum yield at the temperature over 100 °C because of the inevitable thermal activation of radiationless processes.<sup>[15]</sup> The requirements of temperature sensitivity and self reference cause further difficulties for luminescent molecular design. Recently, we proposed a novel strategy involved triarylboron compound, dipyren-1-yl(2,4,6-triisopropylphenyl)borane (DPTB), to circumvent the challenge.<sup>[16]</sup> The strategy exploited the intense luminescence of triarylboron compounds and temperature-sensitive population of luminescent excited states with different conformations. The triarylboron compound shows an intrinsic dual fluorescence originated from two luminescent excited states, local excited state (LE) and twisted intramolecular charge-transfer (TICT) state. Generally, microenvironment with higher polarity and lower viscosity leads to larger population of TICT state.<sup>[17]</sup> To obtain significant thermosensitive hue transformation, the reported system unfortunately must be used in polar organic solvents, e.g., 2-methoxyethyl ether (MOE), which is difficult to form microcapsules.<sup>[13,18]</sup> Taking the advantage for the attractive temperature-dependent luminescent color change, the introduction of an electron-donating group in the pyrene groups should render the luminescence with stronger intramolecular charge-transfer characteristic, which would reduce the requirement of solvent polarity.<sup>[19]</sup> This should get easier way to fabricate microcapsules. Following this idea, two new luminescent triarylboron molecules, di-6-methoxylpyren-1-yl-(2,4,6triisopropylphenyl)borane (MPTB) and 1,1'-(6,6'-((2,4,6-triisopropylphenyl)boranediyl)bis(pyrene-6,1-diyl))dipyrrolidine (TBBD) (shown in Scheme 1 with DPTB), were designed and synthesized.

# 2. Results and Discussion

For MPTB, two methoxy groups are as the electron-donating groups and the characteristics of intramolecular charge transfer are enhanced. The absorption and fluorescence spectra in different solvents are shown in Figure S1 (Supporting Information). It can be seen that both the absorption and fluorescence maximum are located at longer wavelength, compared to DPTB. When the MPTB molecules were dissolved in MOE, significant temperature effects were observed from -50 to 100 °C, similar with the results of DPTB (see Figure S2a, Supporting Information). However, when the MPTB molecules were dissolved in a solvent with low polarity, 1,2,3,4-tetrahydronaphthalene (THN), the fluorescence maximum was slightly shifted only 10 nm, from 494 nm to 484 nm, when the temperature was from -30to 100 °C (see Figure S2b, Supporting Information). It indicates that more polar molecules are needed for the reliable fluorescence shift with the temperature changing in the low polarity solvent.

The TBBD is a more polar molecule and two pyrrolidine groups are as the electron-donating groups. The THN with 5 wt% polystyrene (THN-PS), was chosen as the solvent to dissolve TBBD for its low polarity and relatively wide temperature range of liquid phase. Polystyrene is added into the system to increase the viscosity of the solvent for the fabrication of the microcapsule. As expected, TBBD shows a temperaturedependent color changing luminescence from orange-red to green-yellow in THN-PS with high quantum yields over a wide temperature range (Table 1). The absorption spectra and corrected emission spectra of TBBD in THN-PS at various temperatures are shown in Figure S3 (Supporting Information). In accord with previous results, the absorbance is temperatureinsensitive while the emission band shows a significant hypsochromic shift with increasing temperature. To fabricate the microcapsules, cross-linked poly(urea-formaldehyde) (PUF)

**Table 1.** Fluorescence quantum yield  $\Phi$  of TBBD in THN-PS at different temperatures.

T [°C]	-30	-20	-10	0	10	20	30	40	50
$\Phi$	0.30	0.34	0.39	0.41	0.44	0.46	0.5	0.53	0.56
T [°C]	60	70	80	90	100	110	120	130	140
Φ	0.59	0.60	0.62	0.63	0.64	0.65	0.65	0.64	0.60

*Adv. Funct. Mater.* **2012**, DOI: 10.1002/adfm.201201712



www.MaterialsViews.com



Figure 1. Corrected emission spectra of TBBD in THN-PS microcapsules recorded from -30 to 140 °C. Excitation wavelength: 365 nm.

was chosen as shell material to coat the THN-PS solution of TBBD. This is the first attempt to coat low polarity solvent with PUF and only nonpolar solvents (e.g., paraffin) were coated by PUF before. The procedures of encapsulation are similar to those of Fan et al. and provided in the supporting information.<sup>[20]</sup>

The microcapsules were characterized by fluorescence spectroscopy (FL), scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS) and fluorescent microscopy (FM). The corrected emission spectra of the microcapsules are very close to that of TBBD in THN-PS solution (slight difference at shorter wavelength edge), indicative of a very low scattering of the microcapsules, as shown in **Figure 1**. Meanwhile, the apparently luminescent difference (Figure S4, Supporting Information) between microcapsules and the neat TBBD suggests that the microcapsules possess liquid-core/solid-shell structure. The surface of these microcapsules is fairly smooth and integrated, revealing that the PUF fraction is dense without pores

(see Figure 2a). The transmission view indicates that the microspheres are hollow and indeed are microcapsules (Figure 2b). The diameter of the microcapsules is about 3  $\pm$  $1 \ \mu m$  from the observations of the electron microscopy, which is consistent with the DLS result (Figure S5, Supporting Information). Furthermore, the coating formation efficiency (or coating formation rate) of the encapsulation is determined by counting the number of emissive microcapsules in FM image, which is as high as  $\approx 70\%$  using our fabrication conditions (Figure S6, Supporting Information). The intense and widerange thermosensitive emission suggests the easy-prepared microcapsule to be an excellent candidate for a novel reliable and absolute luminescent temperature sensor.

The microcapsules can be dispersed in water and common organic media. No significant change on the morphology is observed after long time soaking, indicative of a great mechanical stability of the microcapsules. The normalized luminescent spectra of the microcapsules and TBBD in several common solvents are provided in Figure S7 (Supporting Information). All spectra of the microcapsules in different solvents show perfect matching regardless of whether water or organic, nonpolar or high polar solvents, which is entirely different from those of TBBD in homogeneous solutions. The results indicate that the THN-PS solution of TBBD with temperature sensitivity is encapsulated by the microcapsules. The excellent characters of the microcapsules on dispersion and solvent-insensitive luminescence fulfill the requirement of widespread use for in situ thermosensors.

Two kinds of data processing based on intensity and color are executed on luminescence spectra to determine the calibration curve. For the intensity-based procedure, the function of temperature versus the fluorescence intensity ratio of 530/650 nm is depicted (Figure 3a), which can be fitted by a fifth-order polynomial (solid curve; the inset of Figure 3a). The slope of calibration curve gives temperature sensitivities dI/dT ranging from 0.011 °C<sup>-1</sup> at T = -30 °C<sup>-1</sup> to 0.059 °C<sup>-1</sup> at T = 140 °C, suggesting the outstanding sensitivity in such wide temperature range.<sup>[8n]</sup> The microcapsule was used to measure the melt points of ice and 1-octadecanol to test its practical applicability. The intensity ratios were 0.6818 and 3.303, respectively, which corresponded to 0.3 °C and 58.4 °C that compared well with the reported results.<sup>[21]</sup> For color-based procedure, the temperature-dependent spectra are transformed to the Commission Internationale de l'Eclairage (CIE) 1931 coordinates (Figure 3b). The color-based approach is suitable for direct observation of temperature gradient with the naked eye while it is not sensitive as ratiometric method because the spectral transformation lost intensity information. Both processes eliminate the errors due to non-uniform excitation and fluctuation of excitation power, which guarantee a high-precision measurement for temperature, while the accuracies are strongly instrument dependent.

Because this is a one-to-one correspondence between temperature and luminescence, the accuracy and the precision



Figure 2. a) SEM and b) TEM images of microcapsules.



**Figure 3.** a) Temperature dependence of the ratio of fluorescence intensity ( $I = I_{530nm}/I_{650nm}$ ) of TBBD-THN-PS microcapsules. b) CIE chromaticity diagram showing the temperature dependence of the (x,y) color coordinates of TBBD-THN-PS microcapsules.

(repeatability) of the microcapsule thermometry will be determined by the quality of the observation equipments and the stability of the microcapsules. The shell of cross-linked PUF is dense and greatly chemically inert with high resistance against swelling, dissolution and degradation, therefore, a high stability of the microcapsules is expected. The heating and irradiation tests were conducted to evaluate the luminescent stability within the microcapsules. The luminescence spectra are changeless before and after heating at 140 °C for 30 min (Figure S8, Supporting Information). Additional thermogravimetric analysis reveals that TBBD does not dissociate upon heating to 320 °C (Figure S9, Supporting Information). In irradiation test, a 1000 W medium pressure mercury lamp was placed 50 mm distant from the microcapsule dispersed solution, and a filter was used to cut-off the light below 340 nm. The shape of the emission spectrum of the microcapsules exhibits exactly same and only 5% decrease of intensity after 10 min irradiation (Figure S10, Supporting Information).

Moreover, response speed to the changes in temperature and spatial resolution must be considered for evaluating the luminescence thermosensor systems. Considering that the conformation reversal between LE state and TICT state is in a time range of pico- or nanoseconds, the probe response time is determined just by the thermal diffusion distance and the coefficient of the conductive media (e.g., PUF and THN). The thermal diffusion distance is the radius of the microcapsules which is about 1 to 2 µm. The thermal diffusion coefficient of the media is assumed as  $\approx 100 \ \mu m^2/ms$ , just like other organic polymers (e.g., nylon 90  $\mu$ m<sup>2</sup>/ms, rubber 130  $\mu$ m<sup>2</sup>/ms). Hence, the response time is estimated less than 1 ms, which can be considered as a real-time measurement. The spatial resolution of the approach is limited by the size of microcapsules. With these microcapsules, the spatial resolution is as high as 4  $\mu$ m. The excellent thermo- and photostability, fast response and high spatial resolution provide possible applications of the microcapsules as high performance thermometer for in situ microarea and large-area temperature measurement.

As mentioned earlier, determining transient temperature of the fast flowing system is very important in MEMS and other fluid dynamics research fields. To demonstrate the availability of the microcapsules in these fields, a fast flowing system was



simulated and measured. The hot and cold salt aqueous solutions containing 5% (w/w) microcapsules were injected into two end ports of a T-shaped square tube with width 1 mm, respectively, and then outflowed from the third port. Upon irradiation of the tube, a color pattern of the temperature gradient was observed in the fast moving fluid. The orange-red and green-yellow are corresponding to cold fluid and hot fluid, respectively. It is interesting that two flows in opposite directions do not interfere with each other until they outflow from the third exit (Figure 4a). When one of the injecting ports was exchanged with the outflowing one, the luminescent pattern showed a different feature, and an instantaneous of flow is clearly

observed (Figure 4b). The cold and hot flows met in a T-shaped junction perpendicularly to generate turbulence, resulting in a half-moon distribution. This visualized observation provides an approach to map real-time temperature distribution of a dynamic fluid system conveniently.

The microcapsules can also be used in macrosize systems. The amphiphilic PUF shell makes the microcapsules to be easily sprayed on the surface of objects or placed in polymer as temperature sensitive paints (TSP) for aerodynamics mechanics and heat transfer experiments. To simulate TSP for mapping the full-field temperature distributions of the large surface, the CH<sub>2</sub>Cl<sub>2</sub> solution of 10% polystyrene containing 20% (w/w) microcapsules were sprayed on a square aluminum plate. When the center of the surface was cooled by a stream of cold nitrogen gas, a color changing pattern of the temperature gradient was observed upon irradiation (Figure 5). The temperature distribution can be readily estimated or measured by comparing with the temperature dependent CIE chromaticity diagram. This simulation result demonstrates the feasibility of using the microcapsules to map the surface temperature distribution of macroscale objects.

#### 3. Conclusions

Two new triarylboron compounds were synthesized and the temperature sensitivity behaviors of the compounds were



**Figure 4.** Fluorescence microscopy images of fluids with different temperature. Fluid flow a) in opposite directions and b) in perpendicular directions.

www.afm-iournal.de





www.MaterialsViews.com



Figure 5. Fluorescence photograph of TSP.

studied. Based on the luminescent properties of the compounds, a novel thermosensitive microcapsule has been developed by encapsulation of the TNH-PS solution of TBBD into an cross-linked poly(urea–formaldehyde) microshell. This luminescent microcapsule can map transient temperature in fast flowing systems and gradient temperatures of objects with large areas, and works under a wide range of -30 to 140 °C with high stability and a 4  $\mu$ m spatial resolution. The temperature values are transformed to the luminescence spectra or the luminescence color, which can be observed directly by the naked eye or with a camera. This thermosensitive microcapsule can serve a wide variety of temperature monitoring functions in industries and scientific researches.

# 4. Experimental Section

General: All chemicals and reagents were used as received from commercial sources. Solvents for chemical synthesis were purified or freshly distilled prior to use according to standard procedures. All chemical reactions were carried out under an inert atmosphere. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 spectrometer. MALDI-TOF-MS spectra were measured by a Bruker BIFLEX III spectrometer. El mass spectra were recorded on a Waters Micromass GCT mass spectrometer. UV-vis absorption spectra were recorded on a Hitachi U-3010 spectrophotometer. Photoluminescence spectra were carried out on a Hitachi F-4500 spectrophotometer. Elemental analyses were performed by a Carlo Erba 1106. Fluorescence microscopy images were taken using an Olympus IX81 fluorescence microscope. The microscopic images were captured by transmission electron microscopy (TEM, JEOL JEM-1011) and field emission scanning electron microscopy (FE-SEM, Hitachi-S4300). Thermogravimetric analysis (TGA) was carried out with a Seiko TG/DTA 6300 instrument.

Synthesis of the 1-Bromo-6-methoxypyrene/1-Bromo-8-methoxypyrene: Bromine (1.6 g, 10 mmol) at 0 °C was gradually added to a  $CH_2CI_2$  (25 mL) solution of 1-methoxypyrene (2.32 g, 10 mmol). After 30 min, the temperature was allowed to naturally rise to room temperature. Stirring was then continued for a further 3 h. All the solvents were removed under reduced pressure. The residue was extracted with ethyl acetate. The crude product obtained after evaporation of solvent. Recrystallization from ethanol gave 1-bromo-6-methoxypyrene/1-bromo-8-methoxypyrene mixture products as colorless solid (2.76 g, yield 89%). The mixture products were used without further purification.

Synthesis of the Di-6-methoxylpyren-1-yl-(2,4,6-triisopropylphenyl)borane (MPTB): n-BuLi (4.4 mmol, 1.60 M solution in n-hexane) was added at -78 °C to a Et<sub>2</sub>O (30 mL) solution of the mixture of 1-bromo-6methoxypyrene/1-bromo-8-methoxypyrene (1.24 g, 4.0 mmol): after one hour, the temperature was allowed to naturally rise to room temperature. Stirring was then continued for an additional hour. The mixture was then cooled again to -78 °C and 2,4,6-triisopropylphenylboronate<sup>[21]</sup> (0.56 g, 2.0 mmol) in Et<sub>2</sub>O (5 mL) was added by injection, then was stirred for 1 h at this temperature, allowed slowly to reach room temperature, and stirred overnight. All the solvents were removed under reduced pressure. The residue was hydrolyzed and the product was extracted with ethyl acetate. The crude product obtained after evaporation of solvent was purified by column chromatography (silica gel, eluent: 15% dichloromethane in petroleum ether), followed by crystallization from ethanol to obtain MPTB as a yellow powder (0.35 g, yield 26%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.55 (d, J = 9.1 Hz, 2H; Ar H), 8.19 (d, J = 9.7 Hz, 2H; Ar H), 8.09 (dd, J = 8.7 Hz, 4H; Ar H), 7.95 (d, J = 8.4 Hz, 2H; Ar H), 7.84 (d, J = 9.2 Hz, 2H; Ar H), 7.50 (dd, J = 8.9 Hz, 4H; Ar H), 7.07 (s, 2H, Ar H), 4.16 (s, 6H, CH<sub>3</sub>), 2.98-2.87(m, 3H, CH), 1.36 (d, J = 9.0 Hz, 6H; CH<sub>3</sub>), 0.93 (d, J = 8.2 Hz, 6H; CH<sub>3</sub>), 0.79 (d, J = 8.0 Hz, 6H; CH<sub>3</sub>); MALDI-TOF m/z (%): 676.5 [M<sup>+</sup>]; Anal. calcd for C<sub>49</sub>H<sub>45</sub>BO<sub>2</sub>: C 86.97, H 6.70; found: C 87.03, H 6.90.

Synthesis of the 1-(6-Bromopyren-1-yl)pyrrolidine: Tris(dibenzylideneacetone)dipalladium-chloroform adduct (Pd2(dba)3•CHCl3) (100 mg, 0.1 mmol), sodium t-butoxide (NaOtBu) (1.5 g, 15.6 mmol), and (R)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) (120 mg, 0.2 mmol) were placed in a three-neck round-bottom flask equipped with a reflux condenser under argon atmosphere. Degassed toluene (50 mL) was added to the flask, and stirred for 15 min. Then, 1,6-dibromopyrene (1.80 g, 5 mmol) was added and stirred for 15 min. Pyrrolidine (0.5 mL, 6 mmol) was added and the mixture was slowly heated to 90 °C over 1.5 h. After stirring for a further 3 h at 90  $^\circ$ C, the hot mixture was filtered though Celite. The Celite layer was washed with hot toluene (ca. 50 mL). The combined filtrate was concentrated. The residual mixture was separated by column chromatography (silica gel, eluent: 50% dichloromethane in petroleum ether). Recrystallization from ethanol gave 1-(6-bromopyren-1-yl)pyrrolidine as yellow crystals (910 mg, yield 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.41 (d, J = 9.1 Hz, 1H; Ar H), 8.19 (d, / = 9.1 Hz, 1H; Ar H), 8.14 (d, / = 8.2 Hz, 1H; Ar H), 8.07 (d, / = 8.4 Hz, 1H; Ar H), 8.02 (d, J = 9.1 Hz, 1H; Ar H), 7.88 (t, J = 9.6 Hz, 2H), 7.60 (d, J = 8.3 Hz, 1H; Ar H), 3.60 (s, 4H, CH<sub>2</sub>), 2.07 (s, 4H, CH<sub>2</sub>); EIMS m/z (%): 351(100) [M<sup>+</sup>], 350(33) [M<sup>+</sup>], 349(100) [M<sup>+</sup>], 200(45) [C16H8+]; Anal. calcd for C20H16BrN: C 68.58, H 4.60, N 4.00; found: C 68.47, H 4.55, N 3.96.

1, 1'-(6, 6'-((2, 4, 6-triisopropylphenyl)boranediyl)-Svnthesis of the bis(pyrene-6,1-diyl))dipyrrolidine (TBBD): n-BuLi (2.2 mmol, 1.60 M solution in *n*-hexane) was added at -78 °C to a Et<sub>2</sub>O (20 mL) solution of 1-(6-bromopyren-1-yl)pyrrolidine (700 mg, 2.0 mmol); after one hour, the temperature was allowed to naturally rise to room temperature. Stirring was then continued for an additional hour. The mixture was then cooled again to -78 °C and 2,4,6-triisopropylphenylboronate (278 mg, 1.0 mmol) in Et<sub>2</sub>O (5 mL) was added by injection, then was stirred for 1 h at this temperature, allowed slowly to reach room temperature, and stirred overnight. All the solvents were removed under reduced pressure. The residue was hydrolyzed and the product was extracted with ethyl acetate. The crude product obtained after evaporation of solvent was purified by column chromatography (silica gel, eluent: 30% dichloromethane in petroleum ether), followed by crystallization from THF to obtain TBBD as a red powder (500 mg, Yield 66%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.50 (d, J = 9.1 Hz, 2H; Ar H), 8.14 (d, J = 6.8 Hz, 2H; Ar H), 8.00 (t, J = 8.0 Hz, 4H; Ar H), 7.85 (q, J = 8.3 Hz, 4H; Ar H), 7.56 (s, 2H, Ar H), 7.43 (d, J = 8.5 Hz, 2H; Ar H), 7.06 (s, 2H, Ar H), 3.61 (s, 8H, CH<sub>2</sub>), 2.98 (t, J = 6.7 Hz, 1H; CH), 2.91 (t, J = 5.7 Hz, 2H; CH), 2.11 (s, 8H, CH<sub>2</sub>), 1.35 (d, J = 6.8 Hz, 6H; CH<sub>3</sub>), 0.94 (d, J = 5.9 Hz, 6H; CH<sub>3</sub>), 0.78 (d, J = 6.0 Hz, 6H; CH3); MALDI-TOF m/z (%): 754.5 [M+]; Anal. calcd for C<sub>55</sub>H<sub>55</sub>BN<sub>2</sub>: C 87.51, H 7.34, N 3.71; found: C 87.10, H 7.26, N 3.57.



Fabrication of Microcapsules: Water (30 mL), urea (0.5 g), resorcinol (0.05 g), ammonium chloride (0.05 g), sodium chloride (1.00 g), sodium dodecylbenzene sulfuric (0.038 g), gum Arabic (0.035 g), 37 wt% formalin solution (1.5 mL), and 2  $\times$  10<sup>-5</sup> M 1,2,3,4-tetrahydronaphthalene (containing 5 wt% polystyrene) solution of 1,1'-(6,6'-((2,4,6-triisopropylphenyl)boranediyl)bis(pyrene-6,1-diyl)) dipyrrolidine) (TBBD) (0.8 mL) were mixed in a beaker. O/W emulsions were formed using a high-speed homogeniser at the rotation speed of 10000 rpm for 10 min. O/W emulsions were transferred to a three-neck round-bottom flask equipped with mechanical agitation. Stirring at the rotation speed of 1000 rpm for 4 min and the emulsions were slowly and carefully adjusted to pH = 3.5 using diluted aqueous citric acid solutions. Then, stirring speed was reduced to 300 rpm and the emulsions were heated at a rate of 2 °C min<sup>-1</sup> to 60 °C. After 4 h, the reaction was ended. The microcapsules that formed were separated from aqueous solution with suction filtration and the microcapsules were collected.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

### Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (Grant Nos. 21073206, 20733007, 20873165, 50973118) and the National Basic Research Program (2007CB808004, 2009CB930802) and Chinese Academy of Sciences.

Received: June 24, 2012 Published online:

- a) P. R. N. Childs, J. R. Greenwood, C. A. Long, *Rev. Sci. Instrum.* 2000, 71, 2959; b) I. Suzuki, *Rev. Sci. Instrum.* 1983, 54, 868; c) J. Seyedyagoobi, *Rev. Sci. Instrum.* 1991, 62, 249.
- [2] a) A. Mesli, L. Dobaczewski, K. B. Nielsen, V. Kolkovsky,
  M. C. Petersen, A. N. Larsen, *Phys. Rev. B* 2008, 78;
  b) K. T. V. Grattan, A. W. Palmer, *Rev. Sci. Instrum.* 1985, 56, 1784; c) T. W. Lee, N. Hegde, *Combust. Flame* 2005, 142, 314;
  d) S. Uchiyama, A. P. de Silva, K. Iwai, *J. Chem. Educ.* 2006, 83, 720.
- [3] a) K. D. Benkstein, B. Raman, C. B. Montgomery, C. J. Martinez, S. Semancik, *IEEE Sens. J.* 2010, 10, 137; b) T. Sato, Y. Koizumi, H. Ohtake, *J. Heat Transfer* 2008, 130; c) S. Youssef, J. Podlecki, R. Al Asmar, B. Sorli, O. Cyril, A. Foucaran, *J. Microelec-tromech. Syst.* 2009, 18, 414.
- [4] a) L. Mata, J. Silva, A. Schuenhoff, R. Santos, *Aquaculture* 2006, 252, 12; b) J. S. Earl, J. M. Dulieu-Barton, R. A. Shenoi, *Compos. Sci. Technol.* 2003, *63*, 211.
- [5] a) O. S. Wolfbeis, Adv. Mater. 2008, 20, 3759; b) J. J. Lee, J. C. Dutton, A. M. Jacobi, J. Mech. Sci. Technol. 2007, 21, 1253.
- [6] D. Ross, M. Gaitan, L. E. Locascio, Anal. Chem. 2001, 73, 4117.
- [7] a) E. F. J. Ring, *Infrared Phys. Technol.* 2007, *49*, 297; b) M. Seredyuk,
  A. B. Gaspar, V. Ksenofontov, S. Reiman, Y. Galyametdinov,
  W. Haase, E. Rentschler, P. Gutlich, *Chem. Mater.* 2006, *18*, 2513;
  c) C. R. Smith, D. R. Sabatino, T. J. Praisner, *Exp. Fluids* 2001, *30*, 190; d) D. Dabiri, *Exp. Fluids* 2009, *46*, 191.



- [8] a) H. S. Peng, M. I. J. Stich, J. B. Yu, L. N. Sun, L. H. Fischer, O. S. Wolfbeis, Adv. Mater. 2010, 22, 716; b) J. B. Yu, L. N. Sun, H. S. Peng, M. I. J. Stich, J. Mater. Chem. 2010, 20, 6975; c) A. J. Qin, L. Tang, J. W. Y. Lam, C. K. W. Jim, Y. Yu, H. Zhao, J. Z. Sun, B. Z. Tang, Adv. Funct. Mater. 2009, 19, 1891; d) A. Mills, C. Tommons, R. T. Bailey, M. C. Tedford, P. J. Crilly, Analyst 2006, 131, 495; e) F. H. C. Wong, D. S. Banks, A. Abu-Arish, C. Fradin, J. Am. Chem. Soc. 2007, 129, 10302; f) G. S. Vasylevska, S. M. Borisov, C. Krause, O. S. Wolfbeis, Chem. Mater. 2006, 18, 4609; g) C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millán, V. S. Amaral, F. Palacio, L. D. Carlos, New J. Chem. 2011, 35, 1177; h) C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millán, V. S. Amaral, F. Palacio, L. D. Carlos, Adv. Mater. 2010, 22, 4499; i) S. J. Lee, J. E. Lee, J. Seo, I. Y. Jeong, S. S. Lee, J. H. Jung, Adv. Funct. Mater. 2007, 17, 3441; j) L. M. Maestro, E. M. Rodríguez, F. S. Rodríguez, M. C. Lglesias-dela Cruz, A. Juarranz, R. Naccache, F. Vetrone, D. Jaque, J. A. Capobianco, J. G. Solé, Nano Lett. 2010, 10, 5109; k) R. Contreras-Caceres, I. Pastoriza-Santos, J. Pérez-Juste, J. Pacifico, A. Fernández-Barbero, L. M. Liz-Marzán, Adv. Funct. Mater. 2009, 19, 3070; I) F. Vetrone, R. Naccache, A. Zamarron, A. J. de la Fuente, F. Sanz-Rodriguez, L. M. Maestro, E. M. Rodríguez, D. Jaque, J. G. Solé, J. A. Capobianco, ACS Nano 2010, 4, 3254; m) L. H. Fischer, G. S. Harms, O. S. Wolfbeis, Angew. Chem. Int. Ed. 2011, 50, 4546; n) S. M. Borisov, A. S. Vasylevska, C. Krause, O. S. Wolfbeis, Adv. Funct. Mater. 2006, 16, 1536.
- [9] a) C. E. Estrada-Pérez, Y. A. Hassan, S. Tan, *Rev. Sci. Instrum.* 2011, 82, 074901; b) E. J. McLaurin, V. A. Vlaskin, D. R. Gamelin, *J. Am. Chem. Soc.* 2011, 133, 14978.
- [10] a) D. Ross, C. F. Ivory, L. E. Locascio, K. E. Van Cott, *Electrophoresis* 2004, 25, 3694; b) C. Rogers, J. Coppeta, L. Racz, A. Philipossian, F. B. Kaufman, D. Bramono, *J. Electron. Mater.* 1998, 27, 1082; c) J. Sakakibara, R. J. Adrian, *Exp. Fluids* 2004, 37, 331; d) P. Kujawa, V. Aseyev, H. Tenhu, F. M. Winnik, *Macromolecules* 2006, 39, 7686.
- [11] T. Barilero, T. Le Saux, C. Gosse, L. Jullien, Anal. Chem. 2009, 81, 7988.
- [12] a) S. Draxler, M. E. Lippitsch, Anal. Chem. 1996, 68, 753;
  b) J. L. Gao, Acc. Chem. Res. 1996, 29, 298; c) M. S. Díaz,
  M. L. Freile, M. I. Gutiérrez, Photochem. Photobiol. Sci. 2009, 8, 970;
  d) R. T. Williams, J. W. Bridges, J. Clin. Pathol. 1964, 17, 371; e) J. Lin,
  TrAC-Trends Anal. Chem. 2000, 19, 541; f) G. Oster, Y. Nishijima,
  J. Am. Chem. Soc. 1956, 78, 1581.
- [13] K. Landfester, Angew. Chem. Int. Ed. 2009, 48, 4488.
- [14] G. Nelson, Rev. Prog. Color Relate. Top. 2008, 31, 57.
- [15] C. Baleizão, S. Nagl, S. M. Borisov, M. Schäferling, O. S. Wolfbeis, M. N. Berberan-Santos, *Chem. Eur. J.* 2007, 13, 3643.
- [16] J. Feng, K. J. Tian, D. H. Hu, S. Q. Wang, S. Y. Li, Y. Zeng, Y. Li, G. Q. Yang, Angew. Chem. Int. Ed. 2011, 50, 8072.
- [17] M. A. Haidekker, T. P. Brady, D. Lichlyter, E. A. Theodorakis, *Bioorg. Chem.* 2005, 33, 415.
- [18] M. M. Ali, H. D. H. Stöver, ACS Symp. Ser. 2003, 854, 299.
- [19] a) K. Shirai, M. Matsuoka, K. Fukunishi, Dyes Pigments 2000, 47, 107; b) Y. Chen, P. F. Wang, S. K. Wu, Acta Chim. Sin. 1996, 54, 119; c) E. H. Ellison, D. Moodley, J. Hime, J. Phys. Chem. B 2006, 110, 4772.
- [20] C. J. Fan, X. D. Zhou, Polym. Bull. 2011, 67, 15.
- [21] J. A. Dean, Lange's Handbook of Chemistry, 15th ed., McGraw-Hill, London 1999.