

A Triarylboron-Based Fluorescent Thermometer: Sensitive Over a Wide Temperature Range**

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Temperature is one of the most frequently measured variables as it is a principal thermodynamic property.^[1] Many types of thermometers, which utilize various kinds of temperature-dependant physical properties, such as volume, electric potential, and electric conductance, have been developed for quantitative temperature measurement.^[2] Precise temperature measurements in various environments require higher thermometer performance. For instance, in situ large-area or gradient temperature measurements with high spatial resolution, which are often required in marine research, underground geochemistry, wind tunnels, and automobile and aircraft industries, present a serious challenge to traditional thermometers.^[3] A sensor with size from tens of micrometers to several millimeters is required for temperature detection in most thermometers, such as liquid-in-glass thermometers, thermocouples, and thermistors. An array of these sensors is used to achieve this goal, but has disadvantages because of complications, high cost, and low spatial resolution.

The intrinsic limitation of mechanical or electrical thermometers encourages the development of optical thermometers that operate for large-area or fluidic samples.^[4] Among the available optical methods, infrared thermometers that use the principle of blackbody radiation are flexible and easy to use, but can only measure the temperature of surfaces, thus limiting their applications.^[5] Luminescence-based temperature sensors have received more attention because of their fast response, high spatial resolution, and safety of remote handling.^[6] To date, several luminescent materials based on phosphors, dyes, or metal–ligand complexes have been

reported for temperature detection,^[4g,7] which operates by using the temperature-dependant luminescence intensity and/or decay time of these compounds.^[8] As measuring the luminescence decay requires a relatively long time, the intensity-based approach using a fast camera is more applicable for large-area or gradient temperature measurements.^[9] However, the luminescence intensity is also affected by the quantity of the luminophore, excitation power, and the sample morphology. These drawbacks reduce the accuracy and thus restrict the general utility of these techniques.^[10] To improve the performance of the luminescent thermometer, some systems based on the intensity ratio of two emissive compounds were developed.^[7j,11] In these cases, the differences of physicochemical features between two compounds might require extra calibration before data collection.^[12] Meanwhile, as a consequence of increased thermal activation of radiationless processes with increasing temperature, a significant decrease of the luminescence quantum yield is an inevitable problem, except for some materials.^[8b] Therefore, it is important to develop novel single-luminophore thermometers with high and stable luminescence quantum yield over a wide temperature range. Additionally, when aiming to facilitate fast and direct observation for temperature distribution, significant thermosensitive hue transformation is also required for these thermometers.^[13]

In general, the luminescence quantum yield of organic compounds decreases with increasing temperature. Some compounds, such as twisted intramolecular charge transfer (TICT) compounds, exhibit a total luminescence intensity maintenance or even an enhancement from lower temperature to room temperature.^[14] This process is concomitant with a luminescence colorimetric change that results from the shift of the thermal equilibrium between local excited state emission (LE) and the TICT excited state emission.^[15] However, it is difficult to apply the reported TICT compounds in thermometers. Almost all TICT compounds have only moderate luminescent quantum yields and the luminescence decreases to very low levels at higher temperatures.^[16] Recently, several arylboron compounds were found to have high luminescence quantum yields, even above room temperature.^[17] Following our interest in the design of novel highly luminescent systems,^[18] we designed a thermosensitive molecule that combined the advantages of TICT compounds with two reverse luminescence intensity changes, and arylboron compounds with high luminescence. This molecule can be used as a sensitive luminescent colorimetric thermometer for in situ large-area or gradient temperature measurements over a wide temperature range and with high spatial resolution.

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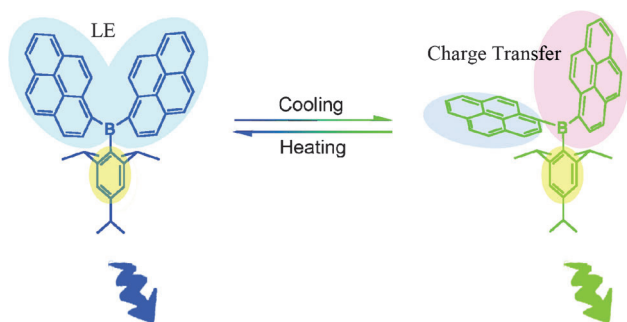
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A luminescent pyrene-containing triarylboron molecule, dipyrren-1-yl(2,4,6-triisopropylphenyl)borane (DPTB; Scheme 1) has been designed and synthesized based on the following considerations: 1) an electron-deficient boron atom with an empty p orbital is well known as a highly effective



Scheme 1. Mechanism of emission changes with temperature.

electron acceptor, and the pyrene (Py) group is known as an electron donor, so an intramolecular charge-transfer excited state should be present;^[19] 2) the contribution of these two Py groups to the luminescent excited state is possibly not equivalent because of the large steric hindrance in the compact Py–B–Py structure; 3) any substituents that may enhance radiationless decay are avoided and the rigid Py group is chosen for facilitating the high luminescence quantum yield;^[20] 4) the sterically bulky substituent 2,4,6-triisopropylphenyl (tipp) group has been proved to be an effective stabilizer for the boron compound (details of the synthesis are provided in the Supporting Information).^[21]

DPTB shows temperature-dependant green to blue luminescence with a very high quantum yield (Table 1) over a wide temperature range (–50 to +100 °C). This intense thermosensitive emission over a wide range conquers the

Table 1: Quantum yields Φ of DPTB in MOE at different temperatures.

T [°C]	–50	–30	–10	10	30	50	70	90	100
Φ	0.64	0.68	0.73	0.78	0.80	0.83	0.81	0.74	0.67

limitation that high temperatures induce a low signal/noise ratio, thus suggesting that DPTB is an excellent candidate for a reliable and absolute luminescent temperature sensor.

Figure 1 shows the absorption and corrected emission spectra of DPTB in 2-methoxyethyl ether (MOE) at various temperatures. MOE, which is a chemically stable liquid with a relatively low melting point and high boiling point, was chosen as the medium for DPTB in order to extend the testing temperature range. An absorption band that extends from 350 nm to 460 nm, with a peak around 420 nm, is observed at room temperature. The absorption band is not temperature-sensitive and only shows very few changes over the whole temperature range. In contrast, the emission profile of the compound shows completely different features. At room temperature, DPTB exhibits an abnormally wide luminescence band that is identified as dual luminescence by its decay

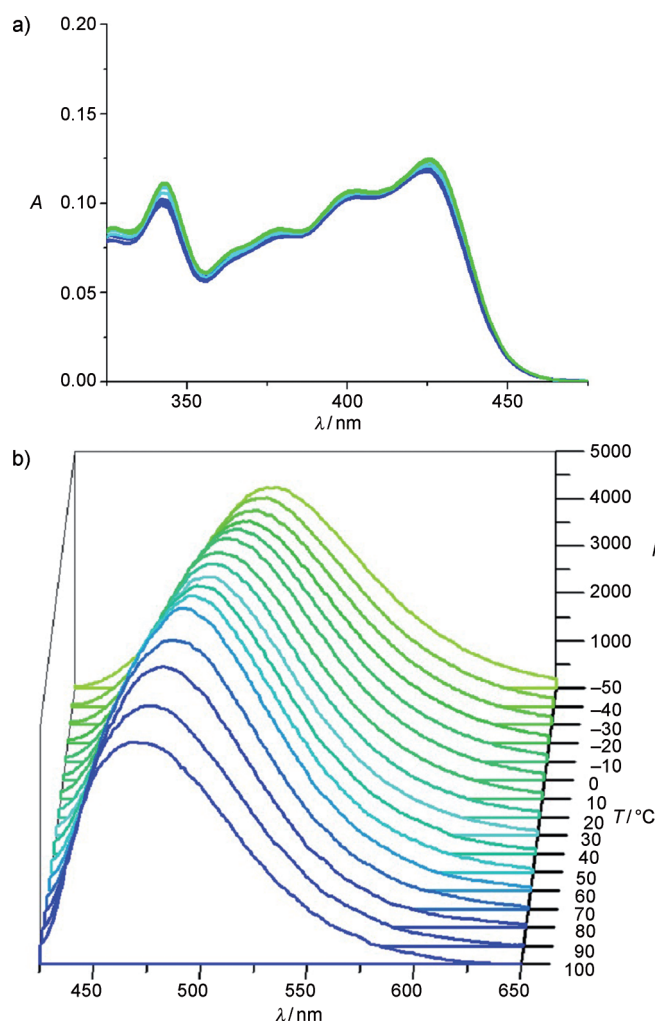


Figure 1. a) Absorption and b) corrected emission spectra of DPTB recorded between –50 and 100 °C (excitation wavelength 410 nm).

lifetime measurements (see the Supporting Information). The components with shorter- and longer-wavelength luminescence bands are assigned to the emissions from the LE and TICT states of DPTB, respectively (see the Supporting Information). Similar to the case of other dual-luminescent TICT compounds,^[15,16] the temperature strongly influenced the dynamic equilibrium between the LE and TICT excited states of DPTB. The luminescence color was determined by the population of the two distinct excited-state conformations. The lower-energy TICT excited state is preferentially occupied with decreasing temperature, and, as expected a bathochromic shift of the luminescence is observed. Upon heating the system, the molecular motion that crosses the thermal barrier between the two excited states increases the population of the LE state,^[22] thus resulting in a hypsochromic luminescence. A feasible luminescence sensing mechanism for temperature detection is shown in Scheme 1.

Accuracy is another important factor for evaluating the luminescent thermometer systems. As shown in Figure 1b, the luminescence spectrum gradually shifts to higher energy with increasing temperature. There is a good linear relation-

ship between the maximum emission wavelength and temperature (Figure 2a). This linear relationship can be fitted as a function of $T = 1673.3 - 3.34\lambda_{\max}$ with correlation coefficient 0.9988, where λ_{\max} is the maximum emission wavelength (nm),

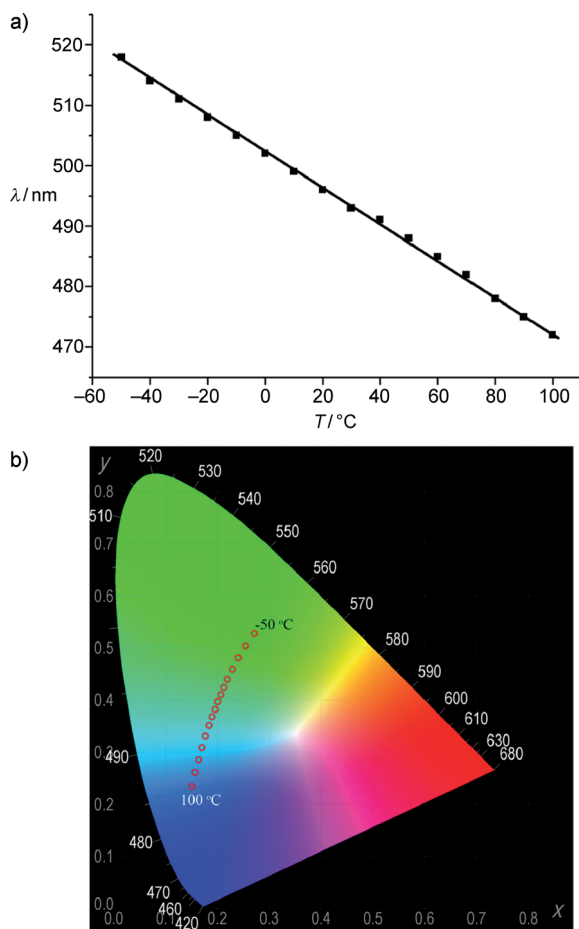


Figure 2. a) Temperature dependence of maximum emission wavelength of DPTB. b) CIE chromaticity diagram showing the temperature dependence of the (x, y) color coordinates of DPTB.

T is the temperature of the DPTB–MOE system (°C). Calculations show that the corresponding wavelength shift per degree centigrade is as large as 0.30 nm, which can be readily measured by using a modern UV/Vis fluorescence spectrometer, and is thus indicative of an accuracy better than 1 °C.

Although the thermosensitive wavelength shift method is sufficiently sensitive for practical temperature detection, the broad emission band introduces some difficulties to accurately identify the maximum. To facilitate the use of this system, the temperature-dependant spectra are transformed to the Commission Internationale de L'Éclairage (CIE) 1931 coordinates. Figure 2b shows the color change of the luminescence in the CIE (x, y) chromaticity diagram at different temperatures. The system color shifts between green and blue, which can be easily observed by the naked eye and captured by a single CCD camera. In this case, the accuracy of this approach is highly dependent on the CCD camera and the software, and is calculated to be approximately 2 °C within the

temperature range of -50 to $+100$ °C according to the resolution of current commercial colorimeters.

For further evaluation of the reversibility of the DPTB–MOE system, 30 cycles of the temperature-dependent emission were conducted between -50 °C and 100 °C with cycling rates of 30 °C s^{-1} heating and 10 °C s^{-1} cooling. The spectra at different temperatures are exactly same for each cycle, even at 100 °C (Figure S5a), and are thus indicative of the excellent reversibility of this system. Furthermore, the isothermal test of stirring and heating at 100 °C for 3 h was carried out to examine the stability of the degassed system. The luminescence spectra at 100 °C show perfect matching before and after durable heating (Figure S5b). Additional thermogravimetric analysis reveals that DPTB does not dissociate upon heating to 300 °C. In comparison with the structure of other boron compounds,^[23] we can conclude that the bulky substituent 2,4,6-triisopropylphenyl group separates the central boron atom and surrounding molecules to prevent the possible Lewis acidic/basic reaction, and contribute to better stability of DPTB. The good reversibility and stability make the DPTB–MOE system a good candidate for high-performance thermometers.

To demonstrate the usefulness of the DPTB–MOE system, we have applied it to the temperature gradient in a fluid, as this situation is often encountered in industrial, atmospheric, and marine research. A quartz tube filled with DPTB–MOE solution was heated from the top and cooled from the bottom (Figure 3a). A color-change pattern of the temperature gradient is observed in the nonconvected vertical fluid. The bottom is green and the top is blue, while the color of the middle part continuously changes from green through

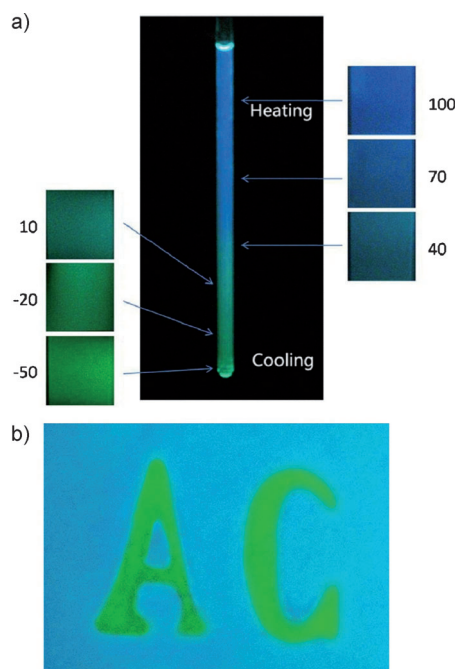


Figure 3. a) Photographs of fluorescence at different temperatures (°C) and the gradient fluorescence of DPTB solution in a quartz tube (central). b) The characters A and C were written at low temperature with DPTB solution in a polyvinyl chloride (PVC)/polypropylene (PP) sandwich structure.

cyan to blue as the temperature of the fluid increases. According to the direct color observation with the naked eye or a camera, the environmental temperature can be readily estimated or measured by comparison with the temperature-dependent CIE chromaticity diagram. This visualization technique provides a useful tool for the detection of temperature distribution.

The applicability of this luminescent thermometer for detecting the temperature distribution in a certain area, as is often required in the automobile and aircraft industries, was also examined. The DPTB–MOE solution was sealed in a sandwich structure PVC–porous PP–PVC film ($5 \times 5 \text{ cm}^2$, can be enlarged to any size). The thickness of the film is $60 \mu\text{m}$, which is flexible and easy to adhere to the surface to map the temperature distribution. As an example, Figure 3b shows the characters A and C that were cooled from the bottom of the film. The image of the characters is sharp and clear. Considering the excited-state conformation changes in a time range of pico- or nanoseconds,^[24] the edge roughness of the pattern is only determined by the thermal diffusion coefficient of the conductive media. In the DPTB–MOE system, the thermal diffusion coefficient of MOE media is about $10^{-12} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1}$.^[25] The edge roughness of the DPTB–MOE system is estimated to be $30\text{--}40 \mu\text{m}$ when the image capture time is set to 10 ms, indicative of a high spatial resolution. Therefore, the thin-film system containing DPTB–MOE can be used as a thermometer for in situ large-area temperature measurement.

In some cases, such as industrial painting applications, fluorescent dyes need to be placed in a polymer rather than in a sandwich structure. High viscosity and low polarity hinder the formation of the TICT state. No notable fluorescence color changes are observed when DPTB is placed in low-polarity polymers such as poly(decyl methacrylate) (Figure S6). It has been found that DPTB shows an apparent temperature-dependant wavelength shift in polyurethane with a low glass transition temperature. Further experiments are needed to clarify this phenomenon, and the results will be reported elsewhere.

In summary, a novel luminescent thermometer has been developed by using a triarylboron compound, which has a high luminescence quantum yield over a wide temperature range and exhibits temperature-dependant luminescence. This thermometer can be applied over a temperature range of -50 to $+100^\circ\text{C}$ with high stability and reversibility. By using this thermometer, the luminescence spectra or the luminescence color can be correlated to the temperature values. The accuracy of former is better than 1°C , and the latter can be observed directly by naked eye or camera, thus facilitating in situ large-area or gradient temperature measurements with the accuracy of 2°C . The liquid thermometer can be fabricated in various forms and can thus be adapted for use in different research areas.

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