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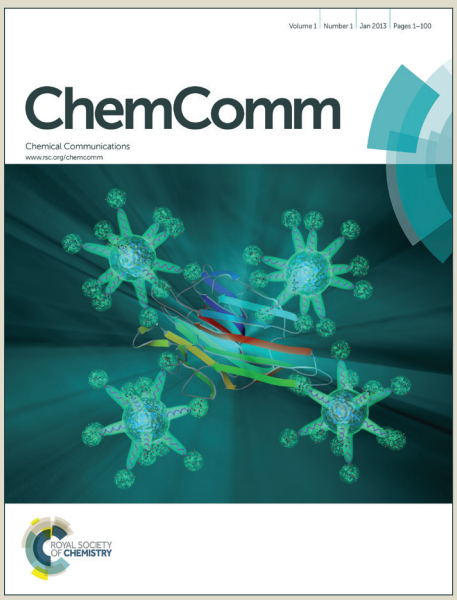

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COMMUNICATION

A Triarylboron-Based Fluorescent Temperature Indicator: Sensitive both in Solid Polymers and in Liquid Solvents

Xuan Liu[a], Shayu Li[a], Jiao Feng[a], Yi Li*[b] and Guoqiang Yang*[a]

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A novel triarylboron compound MPB with reversible thermochromic dual-fluorescence in solid-state polymers and in liquid solvents was designed and synthesized. The fluorescent solid-state polymer with MPB can serve as a highly sensitive self-reference temperature indicator with a concentration independent feature.

Thermochromic luminescent polymer systems in the solid state have received great interest in recent years[1]. Besides the general advantages of polymer systems, such as stability, easy processing and low cost, these systems allow sensitive and accurate temperature detection for the following reasons: a) luminescence is one of the most sensitive and easy-observable detection signals; b) self-reference feature of the thermochromic luminescence could provide a good accuracy for the measurement of the temperature, especially in opaque polymer systems[2]. The thermally responsive luminescent polymer systems are usually obtained by dispersing fluorophore in bulk polymers. Above certain temperature, e.g. glass transition point, the monodispersed fluorosphore in the host polymers would be able to move and aggregate to stacking structures with different fluorescence, or the aggregates could be broken up by heating[3]. The change of the ratio of the monodispersed fluorosphore and the aggregates responds to the temperature and could be used as thermochromic sensors. However, in these cases, the thermochromism processes are concentration dependent and irreversible with only a few exceptions[4].

Molecular rotors respond to free volume changes of media, which have also been applied to study polymer glass transition points, relaxation, physical aging effects and so on[5, 6]. However, the responsive character of the molecular rotors is usually only the intensity change of their luminescence, which is not an absolute measure and can be affected by many factors.

Recently, we reported special triarylboron compounds with intense thermochromic dual-fluorescence in a wide temperature range[7]. The variation of the temperature induces the population change of their two distinct excited-state conformations, demonstrating different fluorescence colors. However, as mentioned in our previous paper[7], the compounds can only be used as temperature indicators in liquid solvents, but not in solid-state polymers because their high viscosity hinders the conformation change, which restricts the formation of their twisted intramolecular charge transfer excited states (TICT). Along with our continuing efforts in the exploration of fluorescent thermometer, we herein report a novel intramolecular charge transfer (ICT) triarylboron compound, tris(2,3,5,6-tetramethyl-4-morpholinophenyl)borane (MPB). MPB was designed with less bulky substituents than previous compounds, thus the exchange of its excited-state conformations would require smaller free volume. Consequently, MPB can respond to the change of free volume in solid polymers[6, 8], making it an excellent and rare candidate for real-time and reversible temperature indicator with a concentration independent feature.

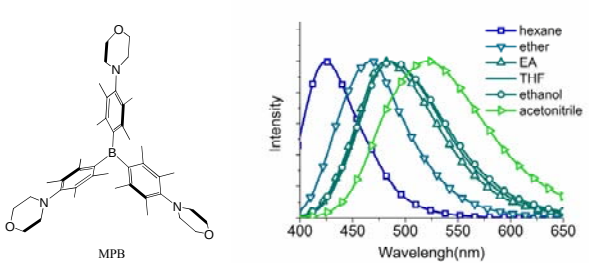

Figure 1. Left: Structure of MPB; Right: Normalized emission spectra of MPB recorded in hexane, ether, ethyl acetate (EA), THF, ethanol and acetonitrile (λ_{ex} = 335 nm).

In common liquid solvents, the photophysical properties of MPB are similar to those of the triarylboron compounds we investigated previously[7]. The electronic absorption and normalized emission spectra of MPB in different solvents are shown in Figure S1 (supporting information) and Figure 1. The absorption spectra are almost independent of the polarity of solvents. In contrast, the intense fluorescence of MPB displays significant bathochromic shifts with increasing solvent polarity, indicating typical ICT characters. The dual-fluorescence feature of MPB in all six solvents was identified by double-exponential decays (Table S1). The ratio of the shorter lifetime species to the longer lifetime species decreases with increasing emission wavelength, therefore, the shorter and longer lifetime species could be assigned to the ICT excited state and the TICT excited state of MPB, respectively.

The population of the two excited states of MPB should be affected by the temperature according to our previous research[7]. The temperature effect on the two excited states of MPB was studied by the time-resolved fluorescence measurements in the liquid solvent 2-methoxyethyl ether (MOE) at various temperatures. The decay curves at all emission wavelengths could be fitted by double-exponentials with acceptable χ^2. The lifetime

data at 470, 520 and 570 nm between -50°C and 30°C were summarized in Table S2. The contribution of the TICT excited state emission at lower temperature is more than that at higher temperature, which clearly demonstrates that the dynamic equilibrium between the ICT excited state and the TICT excited state is evidently influenced by the temperature.

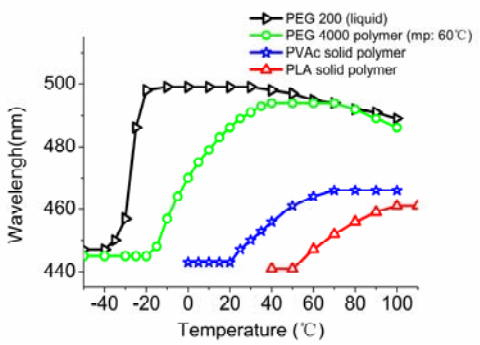

Figure 2. Temperature dependence of the emission maximum of MPB in PEG 200 and solid polymers (PEG 4000, PVAc and PLA) (λ_{ex} = 335 nm).

Besides temperature, the equilibrium between the two excited states should also be affected by free volume of its media，because the conformation change between the two excited states requires extra space. Therefore, the thermochromic property of MPB in high viscosity liquid solvent polyethylene glycol 200 (PEG 200, with glass transition point at -50°C) was evaluated (Figure 2). When the temperature is in the range of 100~30°C, the free volume of PEG 200 is larger than 10.5% based on Doolittle Equation[9] and it is large enough for the conformation changing freely between the two excited states. Thus, the temperature effect on the population of the two excited states of MPB is similar to those in normal liquid solvents. A red shift of the fluorescence maximum was observed with temperature decreasing because of the increased contribution of the TICT emission at longer wavelength. Interestingly, when the temperature decreases from -20°C to -40°C, the free volume of the liquid solvent PEG 200 changes from 5.3% to 3.3%, the TICT emission disappears gradually accompanying with an abnormal 52 nm blue shift of the fluorescence maximum. It indicates that the conformation change starts to be hindered at -20°C and is suppressed at -40°C. From 30°C to -20°C, the fluorescence maximum is almost the same, which can be ascribed to the combination effect of temperature and free volume. The fluorescence quantum yields remain higher than 0.19 in the whole temperature range of -50°C to 100°C (Table S6), and all the thermochromic processes are reversible.

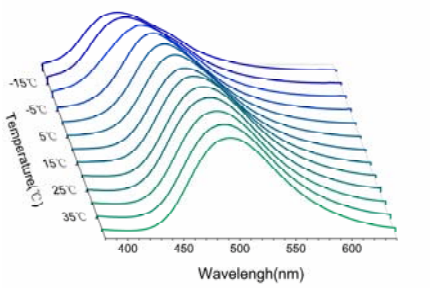

Figure 3. Corrected emission spectra of MPB recorded in PEG 4000 solid-state polymer between -20°C and 40°C (λ_{ex} = 335 nm).

Based on the small free volume responsive property of MPB observed in the PEG 200 liquid, the capability of MPB as a temperature indicator monodispersed in rubbery state polymeric systems was estimated. In the solid-state polymer polyethylene glycol 4000 (PEG 4000, with glass transition point at -22°C and melting point at 60°C), the fluorescence color of MPB changes from green at 40°C to blue at -20°C (Figure 2 and Figure 3). Within this temperature drop, the free volume of the PEG 4000 solid-state polymer system decreases from 5.3% to 2.6% based on Doolittle Equation[9], which is similar to that of the PEG 200 liquid from -20°C to -40°C . Above the melting point of PEG 4000, the free volume is large enough for conformation changes freely, therefore the fluorescence of MPB blue shifted with temperature rise from 70°C to 100°C (Figure S7). In the PEG 4000 system, although the accurate fluorescence quantum yields could not obtained due to the opacity of the polymer, the experiment results indicated that the emission was intense enough to be recorded veraciously. Similar phenomenon was also observed in some other solid-state polymeric systems such as polyvinyl acetate (PVAc) and polylactic acid (PLA). A 23 nm and a 20 nm hypsochromic shifts of the fluorescence maximum of MPB were observed from 70°C to 20°C in PVAc and from 100°C to 50°C in PLA, respectively (Figure 2). The relationship between the maximum of spectra and the temperature is nonlinear; however, the changing processes are gradual, reversible (Figure S8), and concentration independent (Figure S9). Considering the excited-state conformation changes in a time range of pico- or nanoseconds, the response speed is very fast; rendering MPB an excellent real-time temperature indicator in the solid polymers.

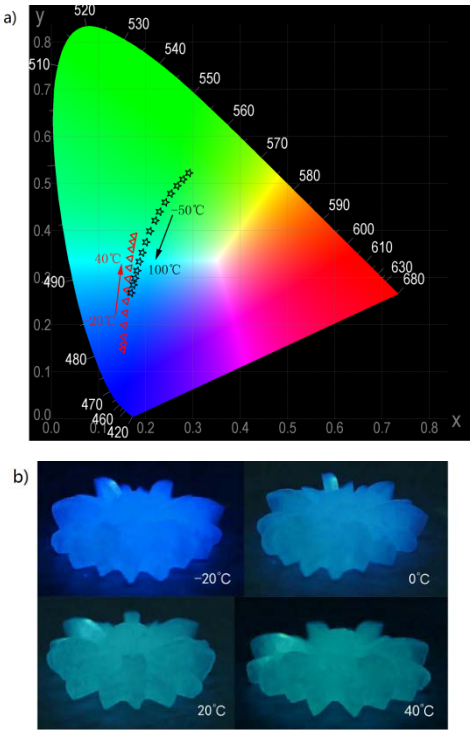

Figure 4. a) CIE chromaticity diagram showing the temperature dependence of the (x, y) color coordinates of MPB in PEG 4000 solid-state polymeric system (△) and in MOE liquid solvent (☆). b) Fluorescence images of the flower shape MPB-PEG 4000 polymer (2.5×2.5×0.5 cm^3) at different temperatures (λ_{ex} = 335 nm).

Two kinds of data processing methods can be used to determine temperature quantificationally based on fluorescence, and the PEG 4000 polymer system was taken as an example. For the intensity-based procedure, taking the ratio of fluorescence intensity of 530 nm to 430 nm as a function of temperature gives a calibration curve as depicted in Figure S10, which can be fitted by a third-order polynomial. The slope of the curve gives temperature sensitivities dI/dT ranging from 0.016°C^{-1} at -20°C to 0.14°C^{-1} at 10°C, indicative of a very high sensitivity within a wide temperature range. With the spectrometer employed, the ratiometric response shows reversibility within 0.5% for all samples studied; therefore the temperature resolution is better than 0.5°C. For color-based procedure, the temperature dependent spectra are transformed to the Commission Internationale de L'Eclairage (CIE) 1931 coordinates (Figure 4a). Although the colorimetric method is not as sensitive as the intensity ratiometric method, it advantages the direct observation, such as by the naked eyes or a CCD camera. The sensitivity of the methods is highly dependent on the equipments and software; it could be improved by the development of technology.

To visualize the applicability of MPB as a temperature indicator in the solid-state polymeric systems, a flower shape device model was manufactured by cooling the melting MPB-PEG 4000 dispersion in a silicone mold. The color of the polymeric flower changes from blue to green when the temperature increases from -20°C to 40°C (Figure 4b), demonstrating the reality of MPB as a temperature indicator in atactic shape polymeric solids within a certain temperature range.

Conclusions

In summary, a novel luminescent thermometer has been developed by using a triarylboron compound MPB, which has reasonable fluorescence quantum yields over a wide temperature range and exhibits reversible thermochromic processes. The fluorescence of MPB shows not only temperature dependence but also free volume dependence. This thermometer can be applied over a temperature range of -50 to +100°C with high stability and reversibility in liquid solvent MOE (Figure S4 and Figure S5). More importantly, the extraordinary property of free volume dependence of MPB expands application fields of the fluorescent thermometer into solid-state polymers. In PEG 4000, it is perfectly suitable for monitoring the temperature in the range of -20°C to 40°C with fluorescent color change. By using this thermometer, the luminescence spectra or the luminescence color can be correlated to the temperature values. With the self-reference feature, the former gives a better accuracy; and the latter advantages the direct observation by the naked eyes or a camera. The present study provides a new strategy for developing highly sensitive thermometers capable of being used in a wide variety of temperature monitoring functions in industries and scientific researches.

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Notes and references

[a] *Beijing National Laboratory for Molecular Sciences, Key laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190 (China) . Fax:* +86-10-82617315*; Tel:* +86-10-*82617263; E-mail: gqyang@iccas.ac.cn*

[b] *Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190 (China) . Fax:* +86-10-82543518*; Tel:* +86-10-82543518*; E-mail: yili@mail.ipc.ac.cn*

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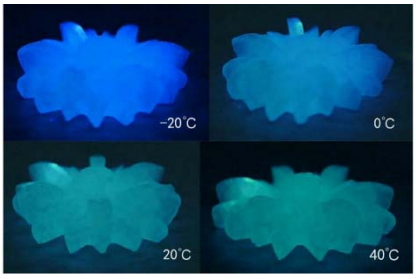

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