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Thermal equilibria between conformers enable highly reliable single-fluorophore ratiometric thermometers†

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Fluorescent thermometers based on organic dyes play an important role in the visualization of dynamic temperature topography with high resolution. Many molecular thermometers contain two fluorophores with different temperature responses to achieve ratiometric temperature detection. However, the stability and reliability of such ratiometric thermometers are highly dependent on the susceptibility of the fluorophores towards photobleaching. Despite the use of single-fluorophore ratiometric thermometers in previous reports, the difficulty and complexity in their molecular design and synthesis severely hinder their widespread applicability. In this work, we have investigated the use of commercially available dyes (*i.e.*, **BD140** and **LD688**) with conformational isomers as ratiometric thermometers. Each of these dyes consists of a mixture of conformers with distinct UV-vis absorption and emission spectra. The thermal equilibrium of these conformers successfully enabled the development of ratiometric thermometers with good stability and reliability.

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Introduction

The accuracy of temperature measurement is of vital importance in many research and industrial applications.^{1–9} Owing to the correlations between temperature and luminescence lifetime/intensity, various fluorescent thermometers based on organic dyes had been designed and synthesized for mapping temperature with high temporal and spatial resolutions. Such molecular thermometers possessed low cost, fast response, high sensitivity, remote monitoring, and non-contact operations, and have been attracting increasing research interest.^{10–14} However, developing molecular thermometers with excellent reliability and ready availability remains a significant challenge.

To date, since fluorescence lifetime measurement requires high instrument cost, most molecular thermometers employ fluorescence intensity to detect temperature variations.^{14–17} In almost all fluorophores, emission intensity is inversely correlated with temperature, as high temperature accelerates non-radiative decays of fluorophores.^{18–21} Accordingly, monitoring the intensity fluctuations of temperature-sensitive dyes, such

as Rhodamine B and analogs, provide a convenient route to track temperature variations.^{22–24} Nonetheless, as the fluorescence intensity is also affected by many other parameters, such as dye concentrations and incident laser intensity, single-emission molecular thermometers require careful calibrations and suffer from poor reproducibility in many practical applications. To circumvent these problems, both a temperature-sensitive (probe) dye and a temperature-insensitive (reference) dye are often collectively utilized to construct ratiometric fluorescent thermometers.^{25–32} In these ratiometric thermometers, the fluorescence intensity ratios from distinct wavelengths of both the probe and the reference dyes could eliminate these external effects (such as dye concentrations and laser intensities), thus affording accurate and reliable temperature detections. For example, Tian's group encapsulated a novel thermosensitive luminogen (TBB), with Rhodamine 110 (R110) in a polymer and achieved a ratiometric fluorescent thermometer with a good sensitivity of 2.37%/°C over a wide temperature sensing range between 25 and 65 °C.²⁵ This thermometer also exhibited good temperature-sensitive reversibility in the emission spectra. Yet, the long-term reliability of such dual-fluorophore systems remains a concern, due to different photobleaching rates of the two fluorophores. As a result, the concentration ratio of the probe and the reference fluorophores inevitably deviates over time and compromises the reliability of the molecular thermometers. A simple strategy to overcome this challenge would be to develop a single-fluorophore ratiometric thermometer.^{16,33–35} Such a thermometer would

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require the use of a dye that can co-exist as two or more conformational isomers. Each isomer must have a distinct emission spectrum, and the thermal equilibrium between these isomers allows ratiometric temperature detections. Notably, in a landmark study, utilizing the conformers of a “pseudo-rigid” dye (DPTB), the Yang group successfully realized ratiometric temperature sensing.¹⁶ Liu and co-workers further analyzed the working mechanism of DPTB and showed that conformational changes in the ground state play an important role in endowing DPTB with the ratiometric temperature sensing capability.³⁵ Unfortunately, DPTB and other customized dyes often require complex synthesis and their limited availability prevents widespread applications.

In contrast, many widely available fluorophores possess multiple isomers, *i.e.*, *via cis-trans* isomerism or other conformational rotations (Scheme 1a). The resulted isomers could exhibit distinct UV-vis absorption and emission spectra, molar extinction coefficients, and quantum yields. The conversion between these isomers can be easily achieved *via* thermal equilibria in the ground state, leading to significant spectral changes as a function of temperature. Moreover, based on their relative stability (Gibbs free energy), the interconversion of these isomers could be achieved at different temperature ranges, thus affording thermometers with specific measurement ranges. Finally, many of these fluorophores are commercially available at a low cost. These fluorophores have promis-

ing potentials as highly reliable and readily accessible single-fluorophore ratiometric thermometers.

In this work, we successfully demonstrated this design method of molecular thermometers, using two representative commercial compounds, **BD140** (a non-polar compound) and **LD688** (a polar compound). Both **BD140** and **LD688** exhibited temperature-dependent spectral shifts, which not only validate the thermal equilibrium of isomers but also enable ratiometric temperature sensing with superior reliability and stability (Scheme 1b). These experimental observations were further rationalized by quantum chemical calculations.

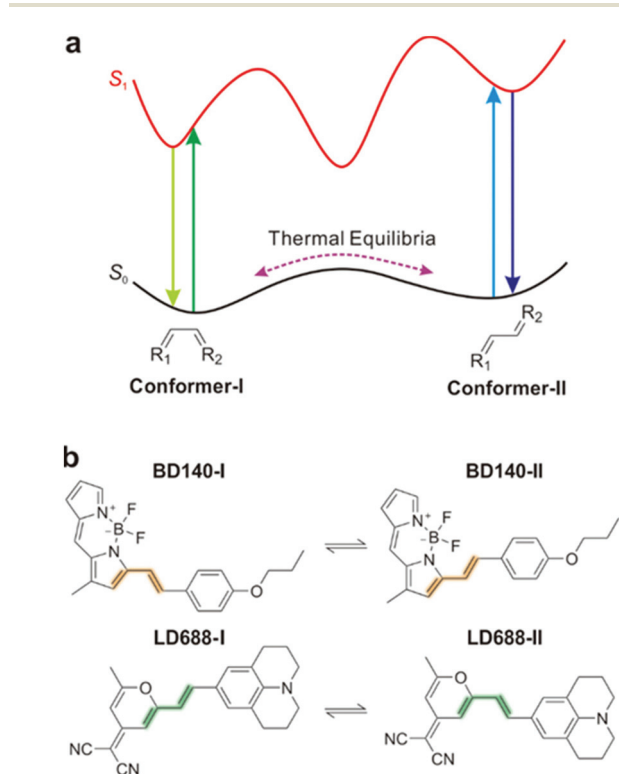
Results and discussion

We hypothesized that organic dyes with flexible conjugated chains may experience isomerism (due to bond rotations), and the UV-vis absorption and emission spectral properties of these isomers may significantly be different from each other. Provided that the interconversion of these isomers is substantial, these fluorophores could enable a single-fluorophore ratiometric molecular thermometer based on the thermal equilibria of conformers. Moreover, in consideration of their availability, we only investigated commercial products of organic dyes that are readily distributed by major suppliers in our study. These factors narrowed our focus to two candidates, namely **BD140** and **LD688**, which possess a flexible π -bridge and could experience *cis-trans* isomerism.

We thus purchased **BD140** (from Tokyo Chemical Industry Co. Ltd) and **LD688** (from Luxottica Exciton) to evaluate their potentials as molecular thermometers in various solvents (Scheme 1b). It is important to note that **BD140** and **LD688** are representative non-polar and polar fluorophores, respectively. Other related chemicals used in our experiments were shown in Table S1.†

Presence of an isoemissive point enables the construction of ratiometric thermometers based on **BD140**

The interconversion between two conformers of **BD140** is clearly shown *via* the temperature-dependent changes in the UV-vis absorption and emission spectra in methycyclohexane (MCH, dielectric constant $\epsilon = 2.204$) within the temperature range of 20 to 80 °C (Fig. 1a). In MCH, the main UV-vis absorption band of **BD140** expands from 500 to 610 nm, with a peak wavelength (λ_{abs}) at ~560 nm. As the temperature increases, it was observed that λ_{abs} exhibits a small but consistent blue shift by ~3 nm and is accompanied by a noticeable decline in absorbance. Furthermore, the UV-vis absorption and emission spectra exhibited several isosbestic points and became intensified between ~540 and ~560 nm, alluding to the fact that a conformational isomerism reaction had occurred resulting in two different isomers of **BD140**. In stark contrast, the UV-vis absorption spectra of reference compounds (without conformational isomers), Rhodamine B and Acid Red 52, did not experience a notable shift in λ_{abs} as temperature increased (Fig. S1†).



Scheme 1 (a) Structural conversion between isomers of a single fluorophore induced by thermal equilibria; (b) molecular structures for the conformational isomers of **BD140** and **LD688**.

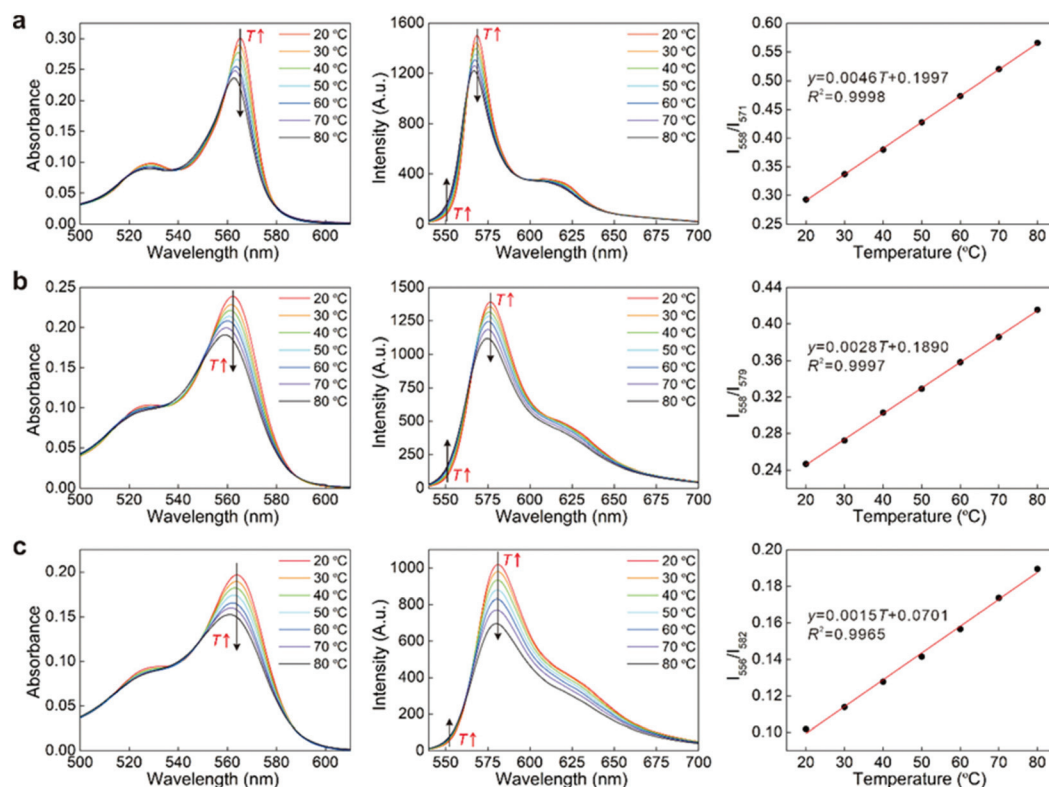


Fig. 1 The UV-vis absorption (left), emission (middle) spectra, and temperature-dependence of fluorescence intensity ratios with corresponding linear fits (right) of **BD140** in (a) MCH (the ratio of fluorescence intensities at 558 nm and 571 nm); (b) DMF (the ratio of fluorescence intensities at 558 nm and 579 nm); and (c) FM (the ratio of fluorescence intensities at 556 nm and 582 nm). The insets in the right panels show the equations of the best linear fits. All the emission spectra were excited at 532 nm.

Similarly, the emission spectra also exhibited one isoemissive point, corroborating that a conformational isomerism reaction had occurred in **BD140**. Like most fluorophores, the long-wavelength (~ 570 nm) fluorescence intensity of **BD140** decreases as the temperature increases (after the isoemissive point). In contrast, the fluorescence intensity of short-wavelength (~ 560 nm) even increases as temperature rises (before the isoemissive point), as the less stable conformers become increasingly populated at high temperatures.

Subsequently, we measured the temperature-dependent UV-vis absorption and emission spectra in several other solvents (Fig. 1b, c, and S2†), including 1,4-dioxane (Diox, $\epsilon = 2.2099$), dimethylformamide (DMF, $\epsilon = 37.219$), dimethyl sulfoxide (DMSO, $\epsilon = 46.826$) and formamide (FM, $\epsilon = 108.94$). All these solvents displayed a similar trend with high quantum yields (>68%, Table S2†).

Thermal equilibria of conformers and their different emission wavelengths allow for the creation of a ratiometric thermometer using **BD140**. An emission wavelength at each side of the isoemissive point was used to establish the ratios of fluorescence intensities (Fig. 1a–c, right panel; Fig. S2†). The intensity ratio-temperature calibration curves in all solvents demonstrated a great goodness-of-fit, indicating that the ratio of fluorescence intensities has an excellent linear relationship with temperature. Noticeably, we found that the slope of the

linear equation decreases as the solvent polarity increases, which suggests that the interconversion between the two conformers is less efficient in polar solvents.

Next, to rationalize these experimental observations, we performed geometrical optimizations of **BD140**. By comprehensive analysis of the isomers (as a result of different bond rotations), our calculations yielded four stable isomers of **BD140** in MCH (Fig. 2). Among these four isomers, **BD140-I** and **BD140-II**, which are generated by a rotation along the single-bond as highlighted in Scheme 1, are the most stable two conformations. By comparing their relative Gibbs free energies at the ground state ($\Delta G = G_x - G_1$), we noted **BD140-I** is slightly more thermodynamically favored compared to **BD140-II**. Moreover, ΔG is generally comparable to thermal energy, indicating the feasibility of thermal equilibrium between these conformational isomers in the ground state. Thus, increasing the temperature can induce the interconversion between the two isomers, which leads to the spectral changes of **BD140**. Finally, we noted that ΔG increases with the increased solvent polarity, indicating that the conversion between these two isomers becomes more and more difficult with increasing solvent polarity (Fig. S3†). This is in good agreement with the declining slopes of the intensity ratio-temperature calibration curve in Fig. 1.

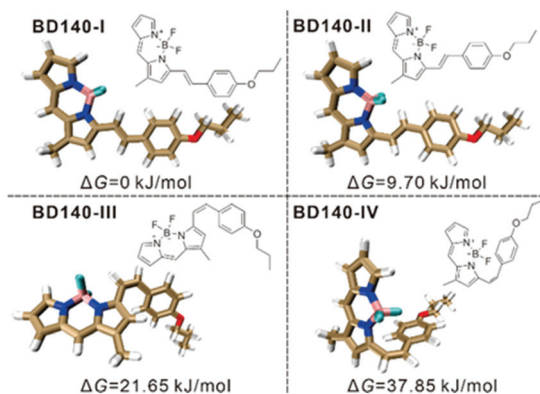


Fig. 2 The optimized molecular structures of **BD140-I**, **BD140-II**, **BD140-III**, and **BD140-IV** with their relative Gibbs free energy ($\Delta G = G_x - G_1$) at the ground state in MCH.

The increased ΔG could be attributed to different polarities of the two isomers (*i.e.* different dipole moments, 4.46 Debye for **BD140-I**, and 3.22 Debye for **BD140-II** in DMF). Due to different polarities, these isomers experience varied degrees of solvent–solute interactions and stabilization effects. These effects are amplified in high polarity solvents, thus enlarging ΔG .

Hypsochromic shifts in the emission spectra enable the ratiometric thermometers using **LD688**

Next, we explored a polar dye **LD688** with different conformers (Scheme 1b). Our initial experiments involved measuring the UV-vis absorption and emission spectra of **LD688** in 1,4-dioxane (Diox, $\epsilon = 2.204$) within the same temperature range of 20 to 80 °C (Fig. 3a).

To our delight, the λ_{abs} of **LD688** is blue-shifted from 483 nm at 20 °C to 472 nm at 80 °C in Diox (Fig. 3a and S3a†). For the emission spectra, the λ_{em} of **LD688** is blue-shifted from 586 nm at 20 °C to 578 nm at 80 °C (Fig. 3b and S4a†). Similar to **BD140**, hypsochromic shifts in both UV-vis absorption and emission spectra revealed an interconversion of different conformers with the increasing temperature. In this case, it seems that both conformers of **LD688** possess partially overlapped spectra. Hence, we only observed a gradual shift in the spectra, but not the appearance of new absorption/emission bands.

Similar observations are also noted in other solvents, including ethanol (EtOH, $\epsilon = 24.852$), acetonitrile (ACN, $\epsilon = 35.688$), and dimethyl sulfoxide (DMSO, $\epsilon = 46.826$), corroborating the existence of thermal isomerism equilibria in different solvents (Fig. 3b, S4b, and S5; Tables S3 and S4†). Yet, the degree of isomer conversion seems to decrease as solvent polarity increases. For example, the hypsochromic shifts the UV-vis absorption/emission spectra (6 nm/4 nm) in DMSO is not as large as that in Diox (11 nm/8 nm) over the same temperature range from 20 to 80 °C. This trend is again similar to that in **BD140**. Next, we selected the ratio of fluorescence intensities at a shorter wavelength (minus 15 nm for the λ_{em} at 80 °C) and a longer wavelength (plus 15 nm for the λ_{em} at 20 °C) to establish the intensity ratio-temperature calibration curves in Diox and DMSO. Similarly, the slope of the linear equation drops from 0.0046/°C in Diox to 0.0021/°C in DMSO.

To further investigate the conformational isomerism at the ground state of **LD688** and its dependence on solvent polarity, we computationally optimized four conformational isomers of **LD688**, from which the two most stable conformers of **LD688** were identified (Fig. 4). We also calculated the relative Gibbs free energy ($\Delta G = G_x - G_1$) between these two conformers at

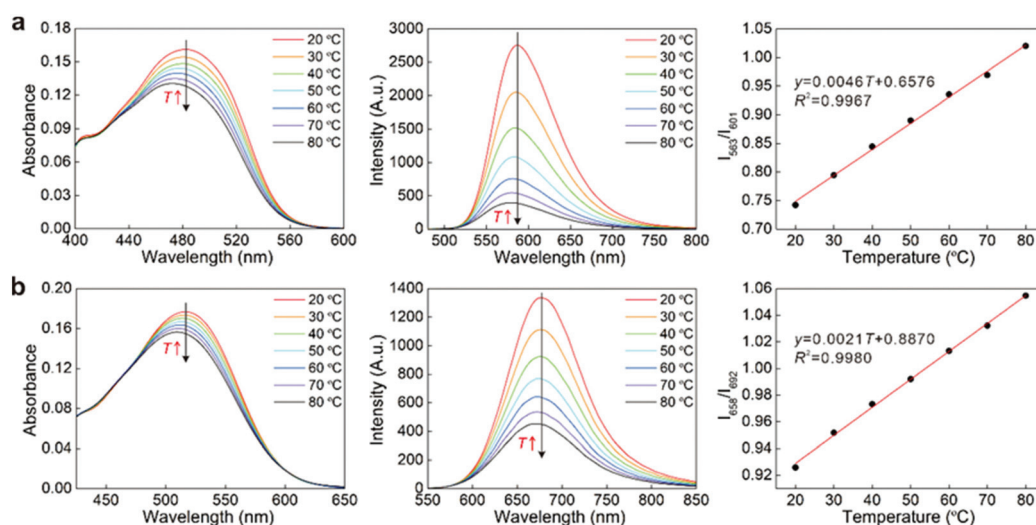


Fig. 3 The UV-vis absorption (left), emission (middle) spectra and temperature-dependence of fluorescence intensity ratios with corresponding linear fitting equations (right) of **LD688** in (a) Diox (the emission spectrum was excited at 472 nm, the ratio of fluorescence intensities at 563 nm and 601 nm); (b) DMSO (the emission spectrum was excited at 510 nm, the ratio of fluorescence intensities at 658 nm and 692 nm). The insets in the right panels show the equations of the best linear fits.

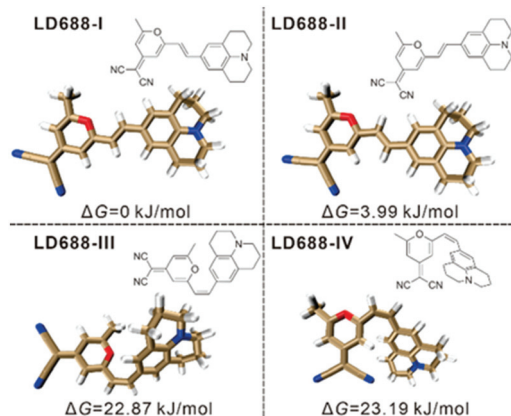


Fig. 4 The optimized molecular structures of LD688-I, LD688-II, LD688-III, and LD688-IV and their relative Gibbs free energy ($\Delta G = G_x - G_1$) at the ground state in Diox.

the ground state in Diox and DMSO, respectively (Fig. S6†). The ΔG with a positive value demonstrates LD688-I (dipole moment = 20.47 Debye in Diox) is more stable than LD688-II (dipole moment = 19.45 Debye in Diox) in both Diox and DMSO. Yet, the small value of ΔG also suggests that heating can induce the conversion between them at the ground state. Meanwhile, our calculation shows that the ΔG increases from 3.99 kJ mol⁻¹ in Diox to 6.66 kJ mol⁻¹ in DMSO, indicating increasing difficulties for isomer interconversion (Fig. S6†). This is in excellent agreement with the decreasing slope of the temperature calibration curve in DMSO in comparison to that in Diox.

Next, we calculated the λ_{abs} and λ_{em} of LD688 in Diox and DMSO, respectively (Fig. S7†). Our results show that LD688-II with a slightly higher Gibbs free energy exhibits a hypsochromic shift in both λ_{abs} and λ_{em} , in comparison to those of LD688-I. Hence, as increasing temperature led to the transformation of LD688-I to LD688-II, the UV-vis absorption and emission spectra of LD688 experienced a blue shift. These computational results are again in good agreement with experimental observations.

Finally, another similar compound, DCM, was also investigated (Fig. S8 and Table S5†). Similar temperature dependence trends observed for DCM further highlights the general applicability of our strategy in building ratiometric thermometers based on the thermal equilibrium of conformers.

Reliability comparison between one-fluorophore intensity-based molecular thermometers and ratiometric thermometers

To demonstrate the reliability of the one-fluorophore ratiometric thermometers, we prepared BD140 solution of four different concentrations (from 0.200 to 0.275 μM) to simulate the photobleaching process, which reduces the dye concentration over time (Fig. 5a, S9, and S10†). We then calculated the temperature calibration curves of all four samples in MCH, by taking the intensity ratios between 558 nm and 571 nm at various temperatures. To our delight, the linear regression equation remains almost unchanged at different dye concen-

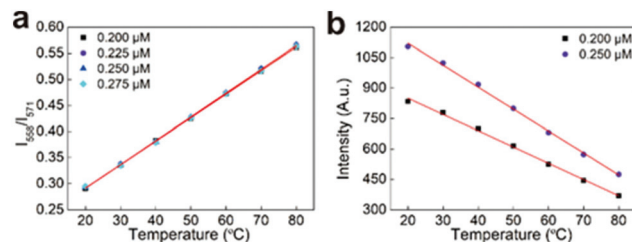


Fig. 5 (a) The temperature-dependence of fluorescence intensity ratios for BD140 at different concentrations in MCH (the ratio of fluorescence intensities at 558 nm and 571 nm); (b) the temperature-dependence of fluorescence intensities at λ_{em} for Rhodamine B at two concentrations in ethylene glycol (EG) with corresponding linear fits.

trations, demonstrating the reliability of this thermometry system (Fig. 5a and S9†).

In contrast, when conventional Rhodamine B was used, the temperature calibration curve (based on the linear relationship between the peak fluorescence intensity and temperature) is greatly affected by dye concentrations, resulting in large deviations (Fig. 5b and S11†). In comparison to these traditional molecular thermometers, the intensity ratio-temperature correlation using BD140 has the clear advantage of dye concentration independence. This concentration independence could effectively reduce the errors caused by concentration fluctuations during sample preparations as well as photobleaching, thus ensuring high reliability and stability for long-lasting temperature measurements.

We also noted that the temperature calibration curves of both BD140 and LD688 depend on solvent polarity, indicating such single-fluorophore ratiometric fluorescent thermometers are best suited for use in homogenous media. Moreover, the temperature sensitivity of both BD140 and LD688 is moderate, *i.e.*, the changes in the intensity ratios over the studied temperature range are relatively small. Exploring temperature-sensitive conformers with large wavelength and intensity differences will be the subject of our future work. To this end, two important factors require special attention: (1) the selected dyes should possess two or more isomers with small ΔG to facilitate the thermal equilibria of these conformers; (2) differences between the optical gaps of these conformers should be large to induce substantial spectral shifts. Also, it is noteworthy to mention that conformational changes could take place both in the ground state and the excited state of fluorophores. However, as excited-state molecular motions generally quench fluorescence,^{36–41} the temperature-dependent variations in emission spectra should be dominantly contributed by ground-state conformers. Thus, we only focused our discussion on the ground-state conformational changes.

Conclusions

We have demonstrated the development of highly reliable ratiometric fluorescent thermometers based on readily avail-

able fluorophores. Such fluorophores possessed multiple stable conformations, which exhibits distinct spectral properties. The conformational isomerization between these isomers could induce significant UV-vis absorption and emission spectral shifts. Specifically, **BD140** exhibited an isoemissive point in the emission spectrum in various solvents as temperature increases. Fluorescence intensities on both sides of the isoemissive point changed differently with varying temperatures, enabling its use as a ratiometric thermometer. Similarly, conversion between the isomers of **LD688** induces a hypsochromic shift at both λ_{abs} and λ_{em} . This is in stark contrast with the conventional dyes (*i.e.*, Rhodamine B) whose λ_{em} is not shifted with temperature. Additionally, we also discovered that the spectral changes of **BD140** and **LD688** displayed a higher temperature sensitivity in non-polar solvents. These single-fluorophore ratiometric thermometers overcome innate measurement inaccuracy caused by dye concentration variations and afforded outstanding stability for long-lasting temperature measurements. We believe that our work would inspire the reexamination of the current library of readily available fluorophores that can be further applied to construct single-fluorophore ratiometric thermometers with excellent sensitivities and reliability.

Author contributions

Tianruo Shen: conceptualization, methodology, investigation, formal analysis, visualization, writing – original draft. Xia Wu: methodology, investigation. Davin Tan: formal analysis, writing – review & editing. Zhaochao Xu: writing – review & editing, funding acquisition. Xiaogang Liu: project administration, funding acquisition, conceptualization, formal analysis, supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 D. Cauzzi, R. Pattacini, M. Delferro, F. Dini, C. Di Natale, R. Paolesse, S. Bonacchi, M. Montalti, N. Zaccheroni, M. Calvaresi, F. Zerbetto and L. Prodi, *Angew. Chem., Int. Ed.*, 2012, **51**, 9662–9665.
- 2 R. Fu, B. Xu and D. Li, *Int. J. Therm. Sci.*, 2006, **45**, 841–847.
- 3 Z. Chen, K. Y. Zhang, X. Tong, Y. Liu, C. Hu, S. Liu, Q. Yu, Q. Zhao and W. Huang, *Adv. Funct. Mater.*, 2016, **26**, 4386–4396.
- 4 Z. B. Sun, J. K. Liu, D. F. Yuan, Z. H. Zhao, X. Z. Zhu, D. H. Liu, Q. Peng and C. H. Zhao, *Angew. Chem., Int. Ed.*, 2019, **58**, 4840–4846.
- 5 B. Bardi, I. Tosi, F. Faroldi, L. Baldini, F. Sansone, C. Sissa and F. Terenziani, *Chem. Commun.*, 2019, **55**, 8098–8101.
- 6 S. Arai, S.-C. Lee, D. Zhai, M. Suzuki and Y.-T. Chang, *Sci. Rep.*, 2014, **4**, 6701.
- 7 S. Arai, M. Suzuki, S.-J. Park, J. S. Yoo, L. Wang, N.-Y. Kang, H.-H. Ha and Y.-T. Chang, *Chem. Commun.*, 2015, **51**, 8044–8047.
- 8 Z. Huang, N. Li, X. Zhang and Y. Xiao, *Anal. Chem.*, 2021, **93**, 5081–5088.
- 9 T. Xia, J. Wang, K. Jiang, Y. Cui, Y. Yang and G. Qian, *Chin. Chem. Lett.*, 2018, **29**, 861–864.
- 10 H. M. Xie, S. J. Li, P. Y. Zhang, J. Feng, S. Li and G. Yang, *J. Phys. Chem. A*, 2020, **124**, 889–897.
- 11 F. Yao, M. Kong, B. Yan, Y. Li, Q. Guo, J. Li, S. Wang, X. Guo, R. Hu, Y. Qian, Q. Fan and G. Yang, *Adv. Mater. Technol.*, 2020, **5**, 1901035.
- 12 F. Ye, C. Wu, Y. Jin, Y. H. Chan, X. Zhang and D. T. Chiu, *J. Am. Chem. Soc.*, 2011, **133**, 8146–8149.
- 13 Y. Cui, W. Zou, R. Song, J. Yu, W. Zhang, Y. Yang and G. Qian, *Chem. Commun.*, 2014, **50**, 719–721.
- 14 X. D. Wang, O. S. Wolfbeis and R. J. Meier, *Chem. Soc. Rev.*, 2013, **42**, 7834–7869.
- 15 Y. Cui, H. Xu, Y. Yue, Z. Guo, J. Yu, Z. Chen, J. Gao, Y. Yang, G. Qian and B. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 3979–3982.
- 16 J. Feng, K. Tian, D. Hu, S. Wang, S. Li, Y. Zeng, Y. Li and G. Yang, *Angew. Chem., Int. Ed.*, 2011, **50**, 8072–8076.
- 17 C. Cao, X. Liu, Q. Qiao, M. Zhao, W. Yin, D. Mao, H. Zhang and Z. Xu, *Chem. Commun.*, 2014, **50**, 15811–15814.
- 18 J. P. Claude and T. J. Meyer, *J. Phys. Chem.*, 1995, **99**, 51–54.
- 19 A. van Dijken, E. A. Meulenkaamp, D. Vanmaekelbergh and A. Meijerink, *J. Phys. Chem. B*, 2000, **104**, 1715–1723.
- 20 M. Weber, *Solid State Commun.*, 1973, **12**, 741–744.
- 21 O. S. Wolfbeis, *Anal. Chem.*, 2006, **78**, 3859–3874.
- 22 Y. Shiraishi, R. Miyamoto, X. Zhang and T. Hirai, *Org. Lett.*, 2007, **9**, 3921–3924.
- 23 Y. Zhou, D. Zhang, J. Zeng, N. Gan and J. Cuan, *Talanta*, 2018, **181**, 410–415.
- 24 J. J. Shah, M. Gaitan and J. Geist, *Anal. Chem.*, 2009, **81**, 8260–8263.
- 25 L. Meng, S. Jiang, M. Song, F. Yan, W. Zhang, B. Xu and W. Tian, *ACS Appl. Mater. Interfaces*, 2020, **12**, 26842–26851.

- 26 M. M. A. Mazza, F. Cardano, J. Cusido, J. D. Baker, S. Giordani and F. M. Raymo, *Chem. Commun.*, 2019, **55**, 1112–1115.
- 27 J. Liu, X. Guo, R. Hu, J. Xu, S. Wang, S. Li, Y. Li and G. Yang, *Anal. Chem.*, 2015, **87**, 3694–3698.
- 28 L. Shi, C. Yan, Z. Guo, W. Chi, J. Wei, W. Liu, X. Liu, H. Tian and W. H. Zhu, *Nat. Commun.*, 2020, **11**, 793.
- 29 Y. Zhou and B. Yan, *J. Mater. Chem. C*, 2015, **3**, 9353–9358.
- 30 Y. Wan, Y. Cui, Y. Yang and G. Qian, *Chin. Chem. Lett.*, 2021, **32**, 1511–1514.
- 31 S. Uchiyama, T. Tsuji, K. Ikado, A. Yoshida, K. Kawamoto, T. Hayashi and N. Inada, *Analyst*, 2015, **140**, 4498–4506.
- 32 D. Mao, X. Liu, Q. Qiao, W. Yin, M. Zhao, J. M. Cole, J. Cui and Z. Xu, *Analyst*, 2015, **140**, 1008–1013.
- 33 L. Shi, W. Song, C. Lian, W. Chen, J. Mei, J. Su, H. Liu and H. Tian, *Adv. Opt. Mater.*, 2018, **6**, 1800190.
- 34 W. Song, W. Ye, L. Shi, J. Huang, Z. Zhang, J. Mei, J. Su and H. Tian, *Mater. Horiz.*, 2020, **7**, 615–623.
- 35 W. Chi, W. Yin, Q. Qi, Q. Qiao, Y. Lin, Z. Zhu, S. Vijayan, M. Hashimoto, G. Udayakumar, Z. Xu and X. Liu, *Mater. Chem. Front.*, 2017, **1**, 2383–2390.
- 36 D. Su, C. L. Teoh, L. Wang, X. Liu and Y.-T. Chang, *Chem. Soc. Rev.*, 2017, **46**, 4833–4844.
- 37 W. Chi, Q. Qiao, R. Lee, W. Liu, Y. S. Teo, D. Gu, M. J. Lang, Y.-T. Chang, Z. Xu and X. Liu, *Angew. Chem., Int. Ed.*, 2019, **58**, 7073–7077.
- 38 W. Chi, J. Chen, W. Liu, C. Wang, Q. Qi, Q. Qiao, T. M. Tan, K. Xiong, X. Liu, K. Kang, Y.-T. Chang, Z. Xu and X. Liu, *J. Am. Chem. Soc.*, 2020, **142**, 6777–6785.
- 39 C. Wang, Q. Qiao, W. Chi, J. Chen, W. Liu, D. Tan, S. McKechnie, D. Lyu, X.-F. Jiang, W. Zhou, N. Xu, Q. Zhang, Z. Xu and X. Liu, *Angew. Chem.*, 2020, **59**, 10160–10172.
- 40 W. Chi, C. Wang and X. Liu, *Chem. Res. Chin. Univ.*, 2021, **37**, 157–161.
- 41 J. Mei, N. L. Leung, R. T. Kwok, J. W. Lam and B. Z. Tang, *Chem. Rev.*, 2015, **115**, 11718–11940.