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COMMUNICATION

A calixarene-based fluorescent ratiometric temperature probe

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We report the first macrocycle-based ratiometric molecular thermometer exploiting the conformational thermosensitivity of a calixarene functionalized with two different fluorophores. Thanks to the dependence on temperature of the efficiency of excitation energy transfer between the organic fluorophores, the thermometer works over a 60 °C-wide temperature range with a sensitivity of 4% °C⁻¹.

Temperature is a fundamental parameter affecting the behavior of most chemical, physical and biological systems. Sensors offering sub-micrometric resolution are in special need whenever the control of temperature is required at the nanometer scale, as in the case of microelectronics or microfluidics or in nanoconfined environments, including living cells.^{1,2}

In non-contact thermometry strategies, typically based on optical techniques, fluorescence is the preferred process, thanks to its high sensitivity and simple readout.³ The emission properties of organic fluorophores are affected by temperature in terms of either intensity^{4–6} or lifetime^{5,7,8} or spectral position^{9–11} or anisotropy.¹² Nonetheless, the fluorescence of organic molecules is strongly affected by many solvent/environment characteristics, such as the dielectric properties, viscosity or ionic strength, also influenced by temperature and, at the same time, the absolute fluorescence intensity is highly sensitive to instrumental variables. To cancel out these external effects, ratiometric approaches, that compare the intensity of emission at two different wavelengths, are preferable.^{3,13,14} Ratiometric fluorescent thermometers exploit either the change of the emission bandshape with temperature or the presence of at least two emission bands,¹⁵ whose relative intensity is sensitive to temperature. Contrary to

lanthanides, whose emission is characterized by multiple bands,¹⁶ organic fluorophores typically have one single emission band (according to the so-called Kasha rule).¹⁷ Dual emission in organic fluorophores occurs when the Kasha rule is violated or excimers or different isomers are present, or (reverse) intersystem crossing takes place: this (rare) phenomenon can be exploited for a ratiometric readout.^{9,18–26} Otherwise, ratiometric temperature probes based on organic fluorophores should contain at least two different emitting dyes.^{27–32}

The confinement of a pair of chromophores in a space of nanometric size sets the conditions for the occurrence of fluorescence resonance energy transfer (FRET),^{17,33} provided that the spectral overlap between the emission of one dye and the absorption of the other is non-negligible.¹⁷ Limiting our attention to purely organic systems,³⁴ a few fluorescence-based ratiometric temperature sensors exploiting FRET have been reported. These are based on the thermal responsivity of polymers^{28–30} or of DNA structures^{31,32} functionalized with different dyes capable of FRET. In both cases, the polymer and the DNA change their conformation according to the temperature, thus modulating the distance and, consequently, the FRET efficiency between the fluorophores.

To the best of our knowledge, however, FRET-based ratiometric temperature sensors exploiting non-polymeric structures have not been reported so far. We envisaged that a simple system constituted by two different dyes linked to a conformationally thermoresponsive molecular scaffold could provide a well-controllable and easy to handle molecular thermometer. In particular, we present a calix[4]arene derivative (**1**, Scheme 1) functionalized with a pair of FRET donor and acceptor fluorophores (Coumarin 343 and NBD, respectively) working as a ratiometric temperature probe on a 60 °C-wide range. In solution, calix[4]arenes, when blocked in the *cone* structure by appropriate alkylation of the lower rim, rapidly interconvert between two equivalent *flattened* (or *pinched*) *cone* conformations (Figure S1).³⁵ In the *flattened* structure, two opposite aromatic rings are parallel, while the other two are tilted outwards. If two substituents are introduced on the distal

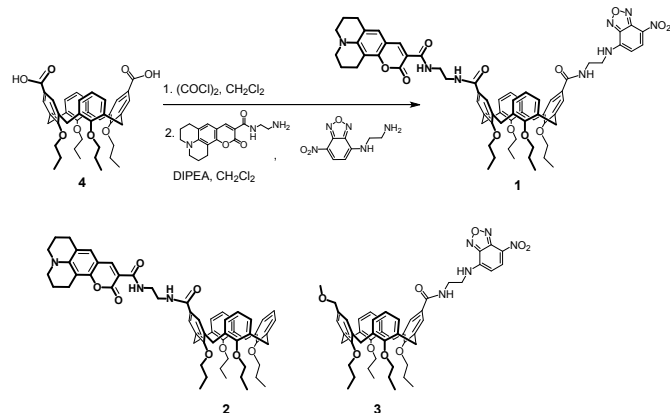
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positions of the upper rim, the two *flattened cone* conformations lose their equivalence.³⁶ Most commonly, the structure where the substituted rings point outwards, called *open flattened cone* conformation, is favored, due to the minimization of the steric repulsions between the substituents. However, in case of attractive interactions between the substituents (such as H-bonds or π -stacking interactions), the *closed flattened cone* structure, with the substituted rings in a parallel arrangement, may be stabilized (Figure S2).^{36–38} Due to the non-covalent nature of the interactions between the substituents, external stimuli can induce a switch between the *open* and *closed* conformations. Previous works^{39–41} demonstrated that a reversible *closed*→*open* interconversion can be triggered by an increase of the solvent polarity. Relevantly to our aims, the conformational variation results in a modification of the distance (and orientation) between the substituents. Herein we report that also a temperature variation can influence the conformational behavior of the calix[4]arene and, in consequence, modulate the efficiency of the FRET between the fluorophores.

Calix[4]arene **1** was synthesized following a mixed condensation strategy^{40,42} consisting of the reaction of the bis-carboxylic acid **4**,⁴³ activated as acyl chloride, with an equimolar mixture of the two dyes linked to an aminoethyl spacer (Scheme 1). The resulting amide functionalities, in appropriate conditions, can be involved in an intramolecular hydrogen bond that may function as a “stud” to bring the two chromophores close together.^{38,40} The monochromophoric reference compounds **2** and **3**⁴⁰ (Scheme 1 and ESI) were also obtained.



Scheme 1. Synthesis of **1** and structure of the reference compounds **2** and **3**.

A conformational analysis of compound **1** was performed via ¹H NMR spectroscopy. As expected, the conformation of **1** in solution depends on the solvent. As evidenced by the relative position of the signals of the aromatic rings (see ESI for a detailed description), in CDCl₃ the amide groups are involved in an intramolecular hydrogen bond that forces the calixarene in a *closed* flattened cone conformation. On the contrary, in DMSO-*d*₆ the intramolecular H-bond is hindered by the interactions of the amide NH groups with the solvent and the calixarene scaffold adopts an *open* structure (Figure S3). A variable-temperature ¹H NMR study in CDCl₃ revealed that the calixarene conformation also depends on temperature. In particular, the

signals of the aromatic protons *ortho* to the amide groups are shifted downfield when the temperature is increased and upfield upon cooling the solution, while the signals of the non-substituted aromatic rings move in the opposite direction. This behavior is consistent with an “opening” of the calixarene scaffold when the temperature is increased and a “closure” when the solution is cooled down (Figure 1) in consequence of a loosening or strengthening of the intramolecular hydrogen bond, respectively. Additional NMR experiments confirmed that this behavior is peculiar of the bichromophoric compound and ruled out aggregation phenomena at the investigated concentration (Figure S4 and S5).

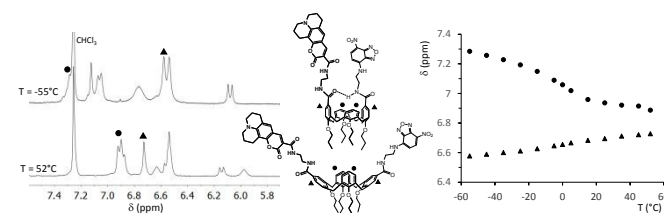


Figure 1. Left: portions of ¹H NMR spectra of compound **1** (10⁻³ M) in CDCl₃ at different temperatures. Middle: schematic representation of the variation of conformation. Right: chemical shift of aromatic protons (see molecular structures in the middle for the assignment) as a function of temperature.

Absorption, fluorescence emission and excitation spectra of **1**, **2** and **3** in CHCl₃ at different temperatures were measured, for solutions with a concentration of ~10⁻⁵ mol L⁻¹ (absorption) and ~10⁻⁶ mol L⁻¹ (emission). The main spectral properties at room temperature are summarized in Table 1 (corresponding spectra in Figure S6). Compound **2** absorbs in the 375–450 nm region and has a very intense emission ($\phi \cong 1$) in the 450–550 nm region. Compound **3** absorbs in the 400–500 nm region and has a broad intense emission in the 475–650 nm region.⁴⁰ The good overlap between the absorption spectrum of **3** and the emission spectrum of **2** (Figure S7) should grant good FRET from Coumarin343 to NBD in compound **1**.

Table 1. Experimental spectroscopic data collected in CHCl₃. Data of **3** are taken from Ref. ⁴⁰.

	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$	$\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{max}}^{\text{fluo}}/\text{nm}$	ϕ^a
2 (D)	438	17500	462	1
3 (A)	454	11700	522	0.62
1 (D-A)	438	40700	514	0.23 ^b ; 0.22 ^c

^a Fluorescence quantum yield; standard: Fluorescein in NaOH 0.1 M ($\phi = 0.9$). ^b Excitation wavelength: 470 nm. ^c Excitation wavelength: 438 nm.

At all the investigated temperatures, the absorption spectrum of the bichromophoric compound **1** is roughly the superposition of the absorption of **2** and **3** (Figure S8). The validity of the Lambert-Beer law for compound **1** was checked for concentrations in between 10⁻⁶ and 5×10⁻⁴ mol L⁻¹ (see Figure S9 and S10), thus ruling out any aggregation effect in this range of concentrations.

Emission spectra of **1** collected exciting at the maximum of absorption (corresponding to the maximum of absorption of the energy donor) show two bands (Figure 2), corresponding to the emission of Coumarin343 and of NBD (see Figure S11 for emission spectra of the reference compounds). At any

temperature, the emission of Coumarin343 is strongly quenched in the bichromophore, signaling the occurrence of FRET. The emission of **1** is strongly affected by temperature (Figure 2, left panel): in particular, the ratio between the fluorescence intensity at the maximum of emission of NBD (515 nm) and the fluorescence intensity at the maximum of emission of Coumarin343 (465 nm) in **1** strongly increases when the temperature is decreased (Figure 2, right panel). This makes the calixarene-based bichromophore **1** a ratiometric temperature sensor, with a sensitivity of 4% °C⁻¹.

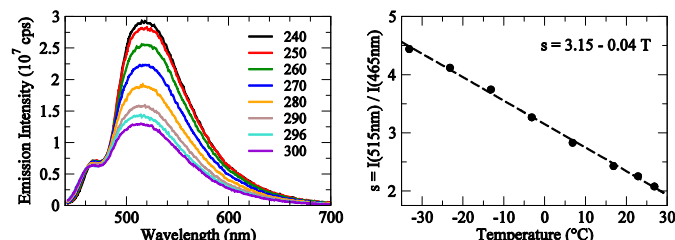


Figure 2. Left: emission spectrum of **1** in CHCl₃ as a function of temperature (λ_{exc} = 438 nm). Right: temperature dependence of the ratio between the emission intensity at 515 nm and the emission intensity at 465 nm (dots: experimental data; dashed line: linear fit), with corresponding equation in the legend.

This result is interesting in and of itself; however, we were interested in understanding the mechanism governing the temperature dependence of fluorescence in compound **1**. Even if the two reference fluorophores **2** and **3** have emission efficiencies that differently depend on temperature (Table S1), the slope of their emission ratio vs. temperature is almost flat (see Figure S12). Notably, the thermal responsiveness of compound **1** could therefore be ascribed to a dependence of the efficiency of FRET itself on temperature.

To prove that, for all the investigated temperatures we estimated the FRET efficiency in **1**. Two different methods were adopted, one (method A) involving the FRET-induced increase of the acceptor emission in **1**, the other (method B) relying on the comparison between the absorption spectrum of **1** and its excitation spectrum measured while collecting the emission of the sole acceptor (details are reported as ESI).

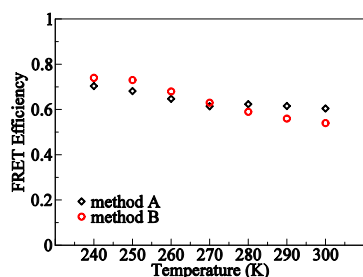


Figure 3. FRET efficiency as a function of temperature, estimated via two different methods.

The two methods gave consistent results (Figure 3), demonstrating that the FRET efficiency increases when the temperature is decreased. This proves that the ratiometric thermal responsivity of compound **1** is not related to a “trivial” temperature-induced variation of the intrinsic emission efficiencies of the two fluorophores, but involves a more subtle and elegant mechanism related to the temperature-dependence of the FRET efficiency.

Many reasons could be responsible for the temperature

dependence of the FRET efficiency, among which the temperature dependence of the spectral overlap between the emission of the donor and the absorption of the acceptor, the different solvent screening at the different temperatures, the temperature-dependence of the interchromophore distance/orientation in **1**. To discriminate between these possibilities, we evaluated the Förster distance for the Coumarin343-NBD pair in the whole temperature range, based on experimental data collected for **2** and **3**.

At a given temperature, the Förster distance R_0 (at which the FRET efficiency amounts to 50%) is defined as:

$$R_0 = 0.211 \sqrt[6]{\frac{k^2 \phi_D}{n^4 J}} \quad (1)$$

where k is the orientational factor, n is the refractive index of the solvent, ϕ_D the fluorescence quantum yield of the isolated donor **2** and J the overlap integral (see ESI). The refractive index of the solvent increases when the temperature is decreased (see Table S2). The quantum yield of **2** was found to be constant ($\phi_D = 1$) with temperature. The overlap integral J slightly depends on temperature (increase of 20% from 300 K to 240 K, see Table S3). The most difficult parameter to evaluate is the orientational factor: for this reason, we define an effective Förster distance, R_k , which incorporates the orientational factor: $R_k = R_0 / \sqrt[6]{k^2}$. Since the temperature dependences of J and n^4 compensate each other in eq. 1, R_k is found to be roughly constant with temperature for the Coumarin343-NBD pair (Table S3).

The FRET efficiency is related to the Förster distance and the interchromophoric distance r as follows:

$$\phi_{FRET} = \frac{R_k^6}{R_k^6 + r_k^6} \quad (2)$$

where $r_k = r / \sqrt[6]{k^2}$ is the effective interchromophoric distance (incorporating the orientational factor). Having demonstrated that R_k is roughly constant with temperature, it follows that ϕ_{FRET} depends on temperature because of the temperature-dependence of the effective interchromophoric distance. In particular, r_k significantly decreases as the temperature is decreased (from 41 to 36 Å, see Table S3), consistently with the temperature-dependent conformational change evidenced by the NMR study. This variation, that could seem small, is actually big if compared to the dimension of the calix (the distance between two opposite carbon atoms in the upper rim ranges from ~5 to ~10 Å)⁴⁴ and has a great effect on the FRET efficiency since the interchromophore distance enters at the sixth power. The ability of **1** to work as a temperature probe in other solvents was tested (results in Figure S14). In a non-H-bonding solvent as toluene, the probe works with the same sensitivity as in chloroform. In H-bonding solvents, instead, the sensitivity of the probe is decreased, according to the H-bonding ability of the specific solvent. Namely, in acetone (a H-bond acceptor) the sensitivity is reduced to 1% °C⁻¹; in ethanol (a H-bond donor and acceptor) the sensitivity is even lower, amounting to 0.05% °C⁻¹. These data further confirm that the working mechanism of **1** as a temperature probe is related to the conformational change of the calix[4]arene mediated by the loosening or strengthening of the intramolecular hydrogen bond.

In conclusion, we synthesised a new calix[4]arene scaffold

functionalized at the upper rim with an appropriate pair of fluorophores chosen as to perform FRET transfer and linked to the macrocycle through spacers containing an amide group. The amide groups can form an intramolecular H-bond that stabilizes the *closed* conformation of the scaffold, bringing the chromophores at short distance. The strength of this intramolecular interaction depends on the solvent ability to compete in forming H-bonds. Moreover, a variation in temperature modulates the intramolecular H-bond strength, inducing a variation of the interfluorophore distance/orientation, affecting in turn the efficiency of the FRET process. This induces a temperature dependence of the relative emission intensity of the two fluorophores in the bichromophoric system, making compound **1** a ratiometric temperature probe over a 60 °C-wide temperature range. The response to the change in temperature is completely reversible and repeatable, being the system very robust in the investigated temperature range (see Figure S15). Compound **1** constitutes the first example of FRET-based molecular probes for temperature exploiting the thermosensitive conformational variation of a macrocycle. This prototype is meant to work best in non-H-bonding organic solvents, with a sensitivity that decreases in H-bonding solvents.

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Conflicts of interest

There are no conflicts to declare.

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