Temperature sensing with a bichromophoric macrocyle through fluorescence energy transfer

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We report the first macrocycle-based ratiometric molecular thermometer exploiting the conformational thermosensitivity of a calixarene functionalized with two different chromophores performing fluorescence energy transfer.
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1. Introduction

Sensing and measuring temperature in nanometer-size environments is of paramount importance for innumerous scientific studies and technological applications in different fields, ranging from (opto)electronic and photonic devices to micro/nanofluidics and nanomedicine [1]. The research in the field of nanothermometry is dominated by the exploitation of luminescent probes, because of the intrinsic high sensitivity of the technique and the ease in the readout [2].
In this paper, we present a new approach to non-contact nanothermometry with a ratiometric luminescence readout, exploiting the conformational thermosensitivity of a macrocycle functionalized with a pair of chromophores capable of fluorescence resonance energy transfer (FRET).

2. Results

We synthesized a calix[4]arene derivative, **1**, functionalized with a pair of FRET donor and acceptor fluorophores (Coumarin343 and NBD, respectively). A variable-temperature ^1H NMR study in $CDCl_3$ revealed that the calixarene conformation depends on temperature, with an "opening" of the calixarene scaffold when the temperature is increased and a "closure" when the solution is cooled down (Fig. 1) in consequence of a loosening or strengthening of the intramolecular hydrogen bond, respectively.

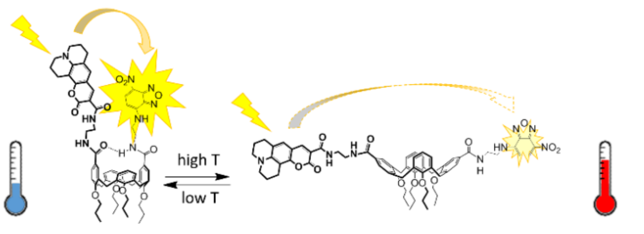

Fig. 1 Working mechanism of the calix[4]arene-based nanothermometer.

The emission of **1** is strongly affected by temperature (Fig. 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 (Fig. 2, right panel). This makes the calixarene-based bichromophore **1** a ratiometric temperature sensor, with a sensitivity of 4% $°C^{-1}$.

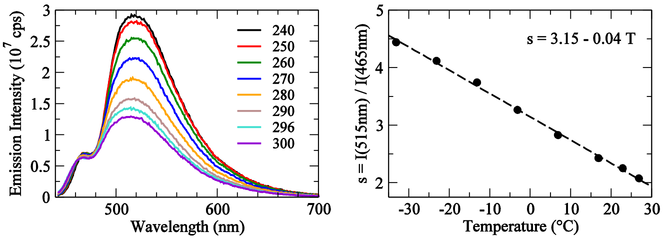

Fig. 2 Left: Emission spectrum of **1** in $CHCl_3$ as a function of temperature. Right: Temperature dependence of the ratio between the emission intensity at 515 nm and the emission intensity at 465 nm.

Notably, we demonstrated that the thermal responsiveness of compound **1** is ascribed to a dependence of the efficiency of FRET itself on temperature. In particular, the efficiency depends on temperature because of the temperature-dependence of the effective interchromophoric distance.
Compound **1** constitutes the first example of FRET-based molecular probe for temperature exploiting the thermosensitive conformational variation of a macrocycle [3].

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