FULL PAPER

Temperature Sensors

ADVANCED FUNCTIONAL MATERIALS

www.afm-journal.de

Off/On Fluorescent Nanoparticles for Tunable High-Temperature Threshold Sensing

*Alex Julià López, Daniel Ruiz-Molina, Katharina Landfester, Markus B. Bannwarth, and Claudio Roscini**

Adv. Funct. Mater. **2018**, *28*, 1801492

A. Julià López, Dr. D. Ruiz-Molina, Dr. C. Roscini
Catalan Institute of Nanoscience and Nanotechnology (ICN2)
CSIC and The Barcelona Institute of Science and Technology (BIST)
Campus UAB, Bellaterra 08193, Barcelona, Spain
E-mail: Claudio.roscini@icn2.cat

Prof. K. Landfester, Dr. M. B. Bannwarth
Max Planck Institute for Polymer Research
Ackermannweg 10, 55128 Mainz, Germany

Jyoti Sarita Mohanty
08-09-2018

Background of the paper……

- Temperature Tunable Photonic Crystals
- Thermochromism in Polymers Based on Nanoparticles
  - Surface-Plasmon Resonance
  - Growth of Particle Size
  - Particle Agglomeration
  - Change of Particle Shape
- Quantum Dots
- Thermochromism by Self-Assembling of Dye–Dye Aggregates
- Thermochromism by Polymer–Dye Interaction

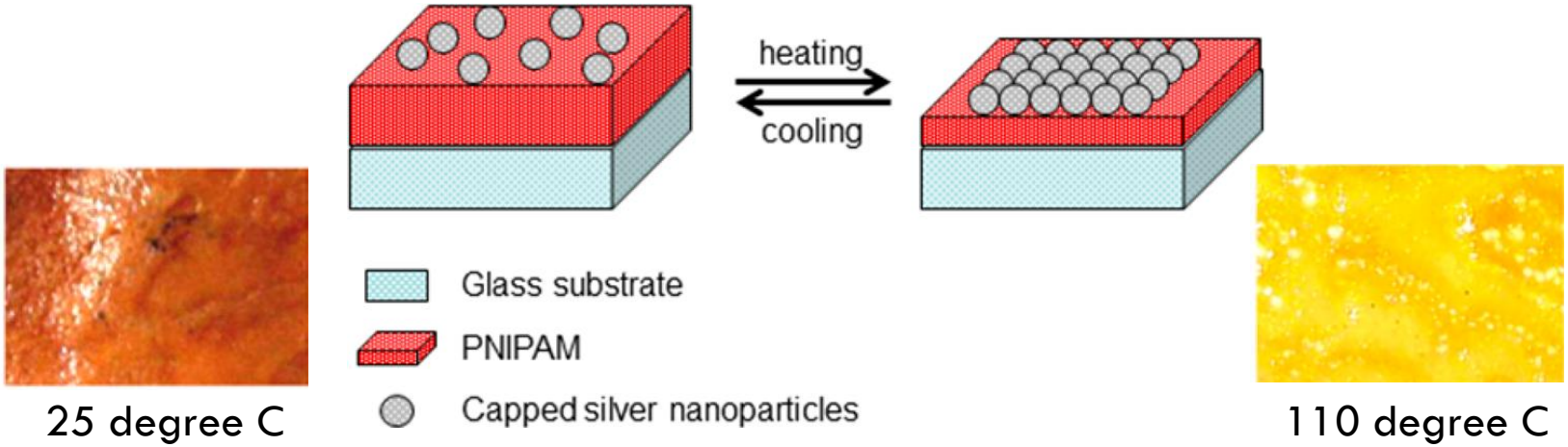
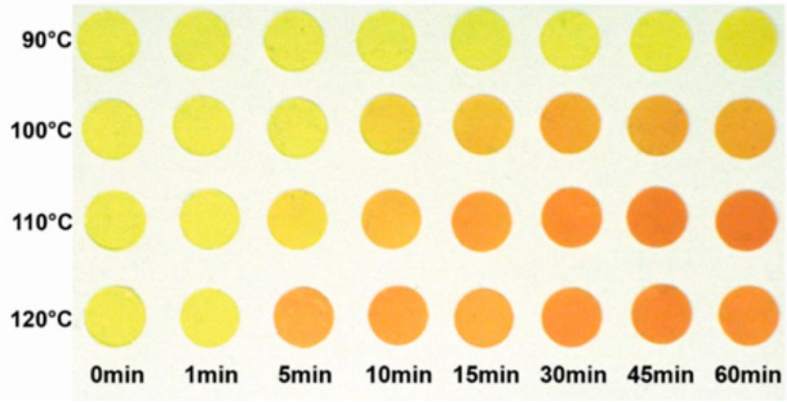
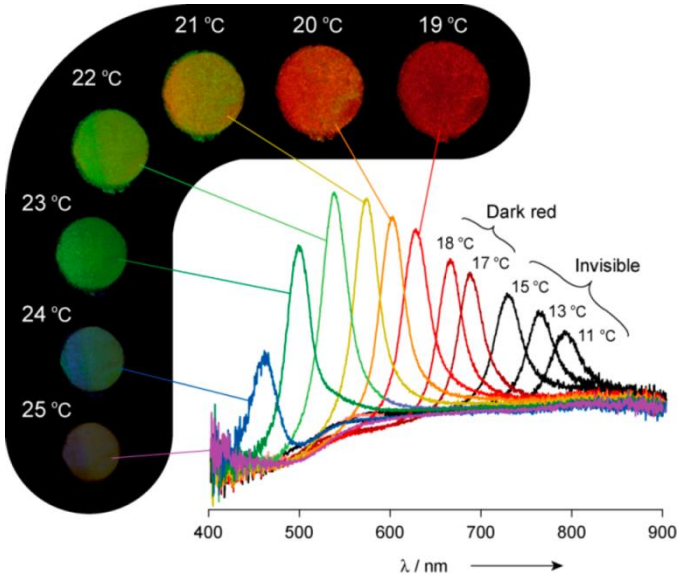


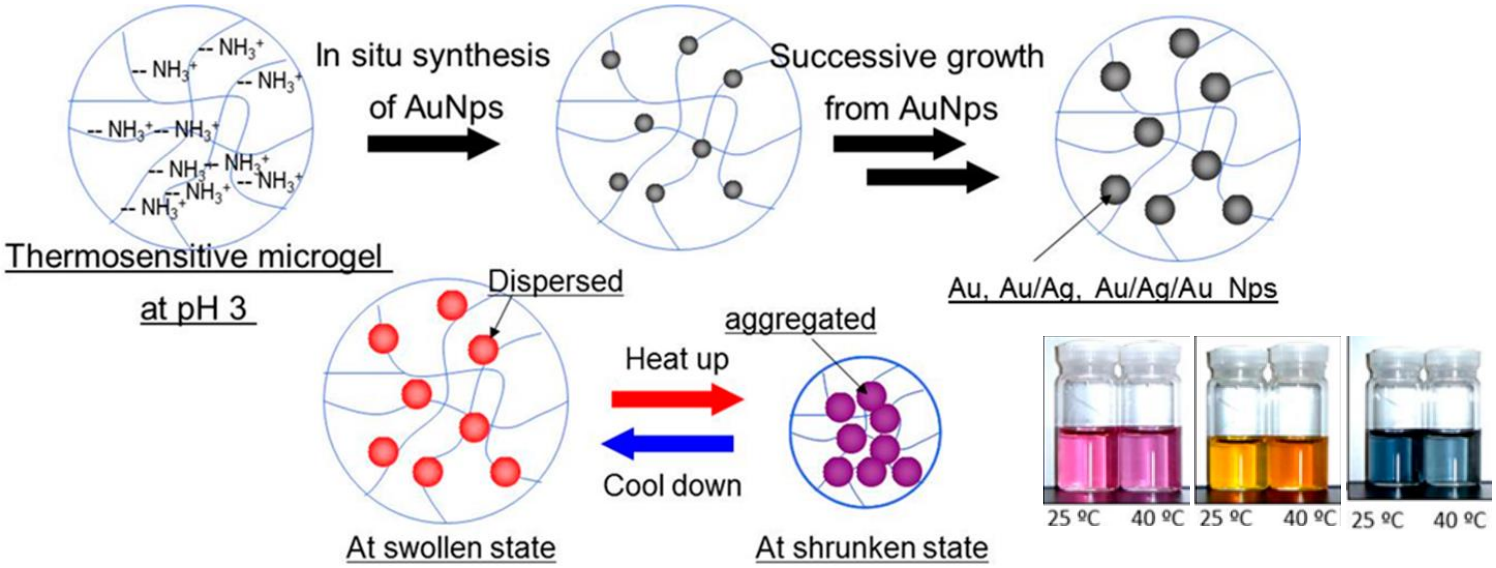
Illustration of the structural change of the silver nanoparticle monolayer due to thermoresponsive volume change of the polymer substrate layer.



1.1% w/w Cyano OPV I/poly(ethylene terephthalate glycol) blend after annealing as indicated.



Photographs and reflection spectra of the porous azobenzene/PNIPAM gel at various temperatures.



Preparation route and thermoresponsive swelling/deswelling mechanism of the investigated microgels containing gold, gold/silver or gold/ silver/gold nanoparticles.

Why this paper……

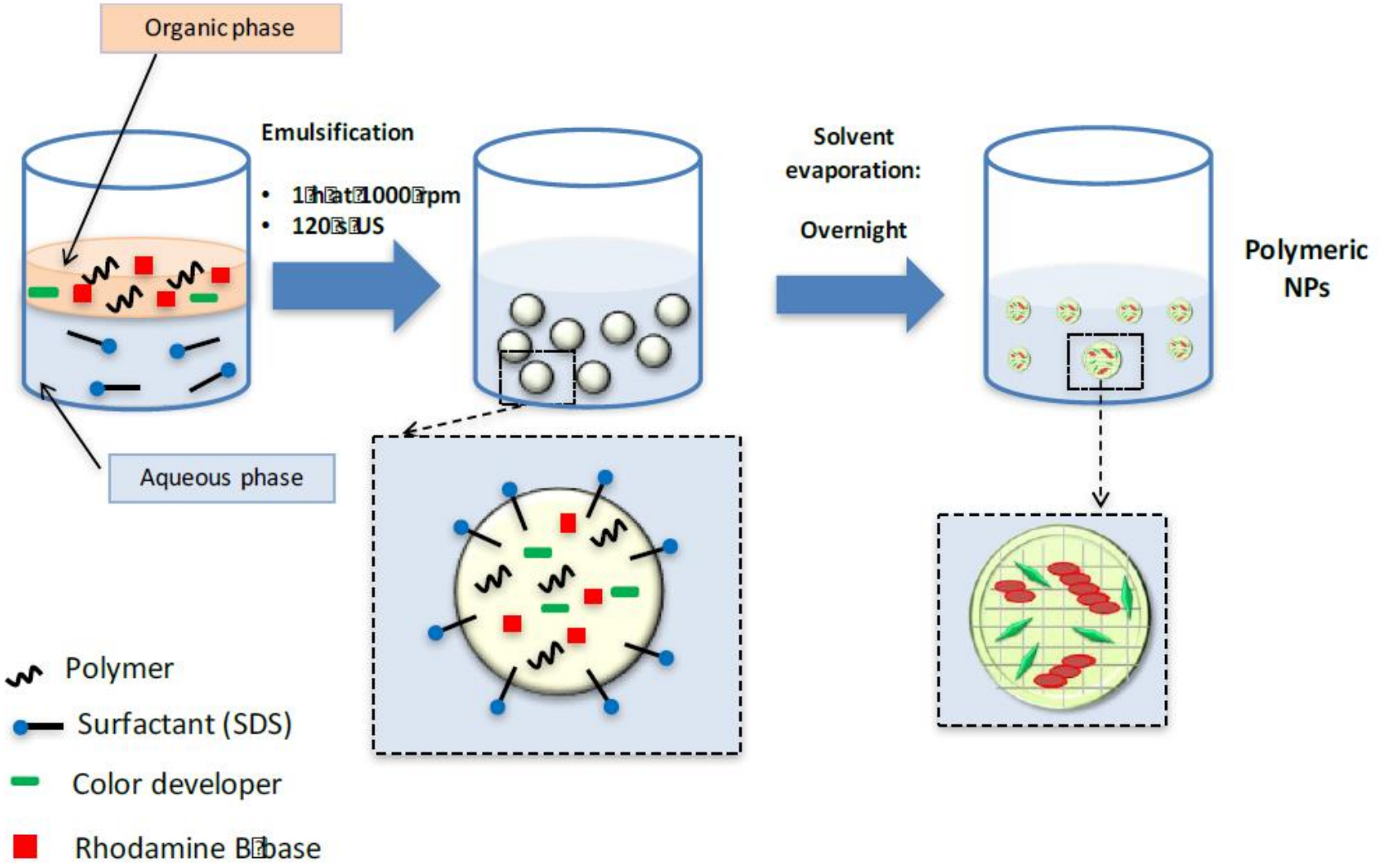
❑ This shows a simple strategy to synthesize nanoparticles from standard thermoplastic polymers, a fluorescence developer, and the commercially available widely used fluorescent dye molecule, Rhodamine B.

❑ This is the first RhB-based solid fluorescence thermometer revealing threshold temperatures as high as 200 °C.

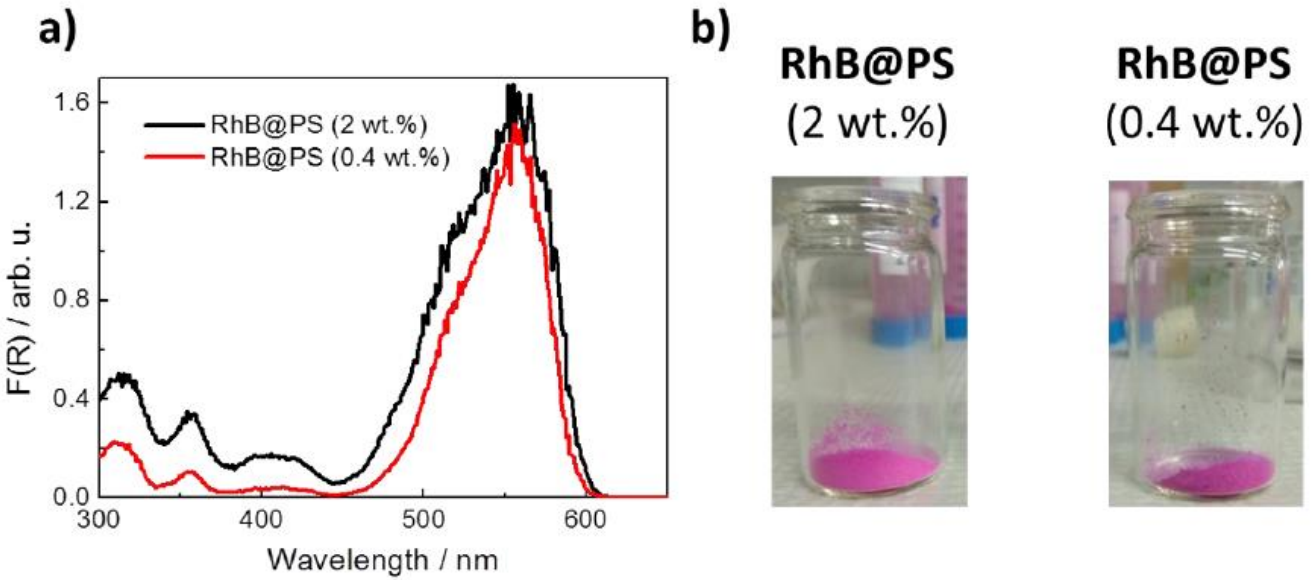
❑ It can be used as a versatile threshold temperature sensor, based on the glass transition temperature and fluorescence activation of a dye/developer duo, encapsulated in polymeric nanoparticles.

Polymer	Tg (° C)
Polysrtyrene (PS)	80-90
Polymethyl methacrylate (PMMA)	105
Poly-Bisphenol-A carbonate (PC)	150
Polyethersulfone (PES)	185
Polyetherimide (PEI)	215

Schematic:

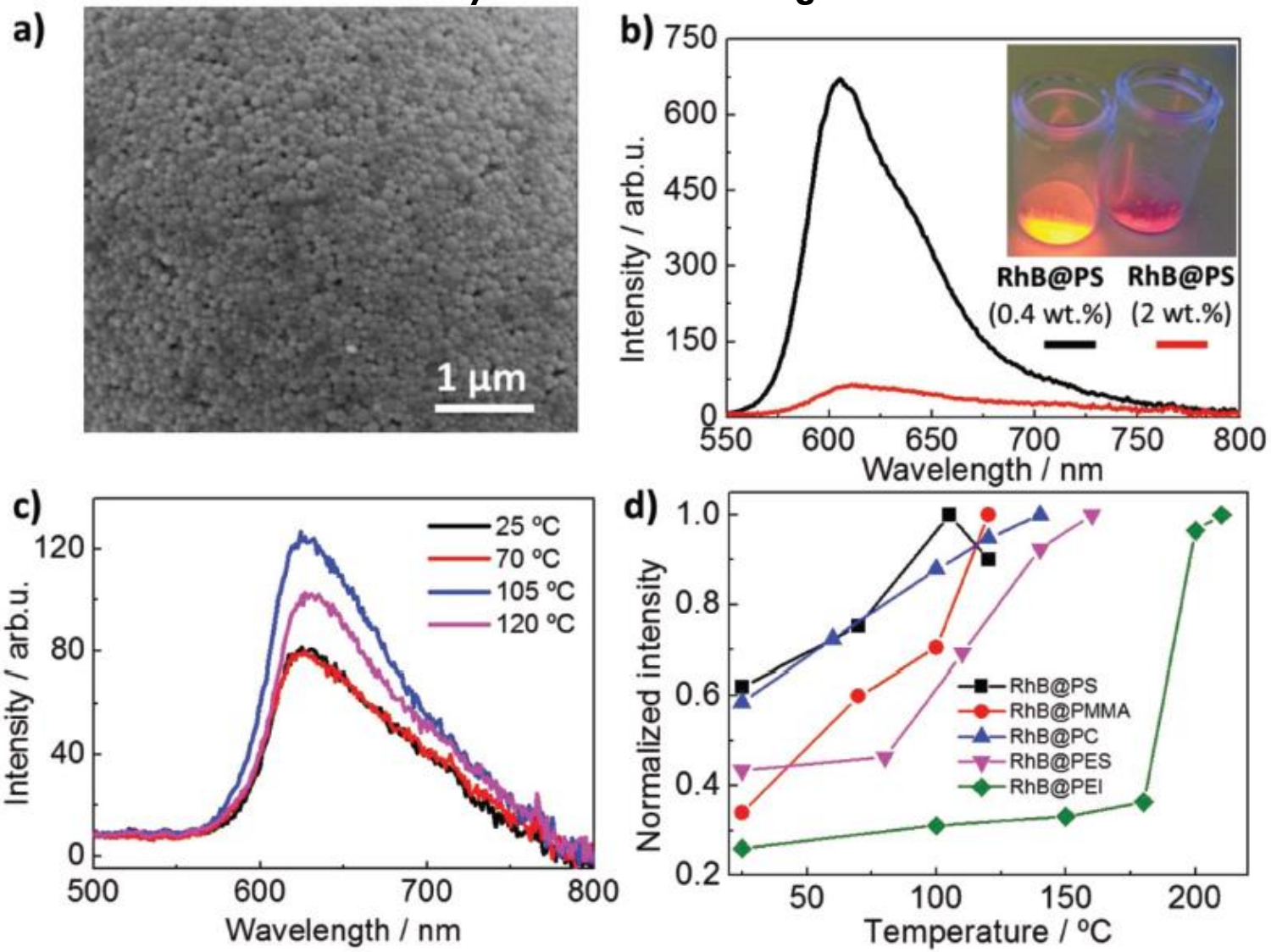


synthesis of polymeric nanoparticles containing RhB. In the color developercontaining NPs this is added in the organic phase before the emulsification. No color developer is added in the RhB@polymer NPs.



a) Absorption spectra and b) digital photos of RhB@PS NPs with two different RhB concentrations (2 wt. % and 0.4 wt. %).

Polymer NPs containing RhB



(a) SEM image of the RhB@PS NPs **(b)** fluorescence spectra (λexc = 355 nm) and digital photos (inset) in presence of UV light of the RhB@PS NPs with two different RhB concentrations (2 and 0.4 wt%) **(c)** fluorescence emission spectra (λexc = 355 nm) of the RhB@PS NPs (2 wt%), recorded at RT, after heating the NPs at different temperatures **(d)** integrated emission intensities of the NPs Vs temperature.

Reason for Coencapsulation of DA (dodecanoic acid)

- The fluorescence enhancement was not as high as desired and making these NPs not ideal to develop precise off/on threshold sensors.

Only RhB@PEI NPs exhibited a clear fluorescence enhancement within just 20 °C.

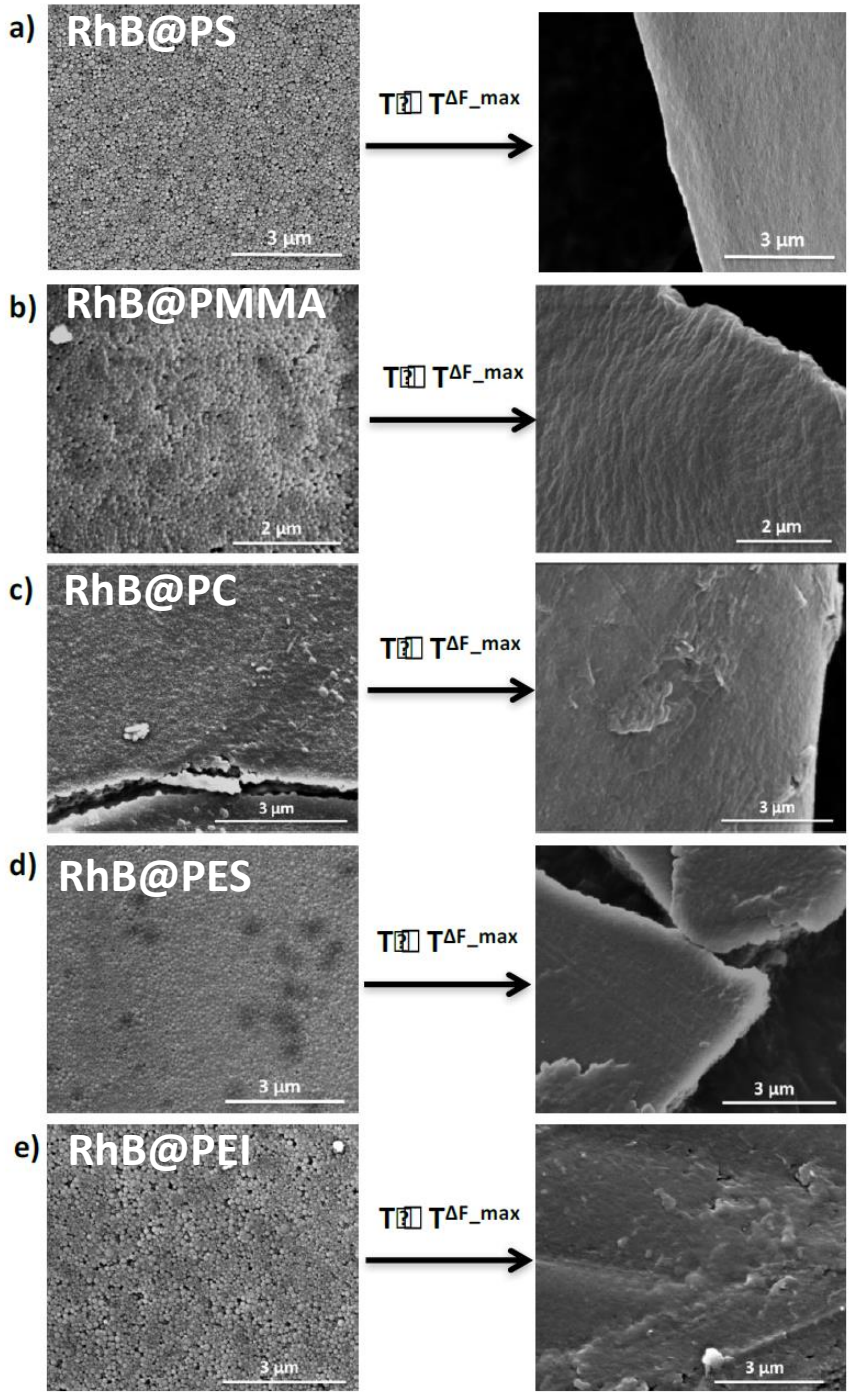
This was ascribed to: i) the high rigidity of PEI, which does not allow the dye molecules to diffuse until the polymer reaches its *Tg and*

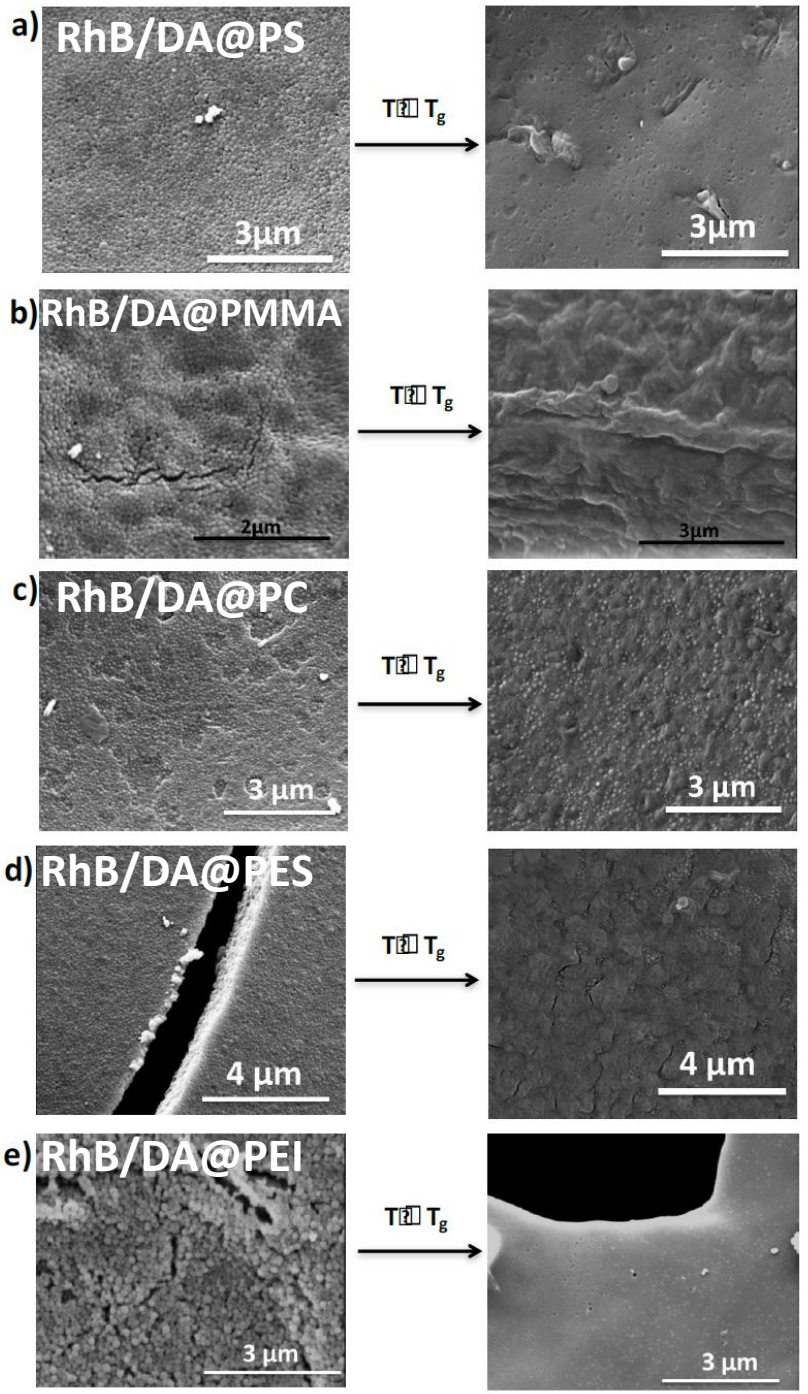
ii) the higher temperature needed to reach the *Tg*, which in turn tips the system with more energy to efficiently disaggregate the dyes.

To overcome this limitation, coencapsulation of additives favoring the diffusion and the disaggregation of RhB at higher temperatures was done.

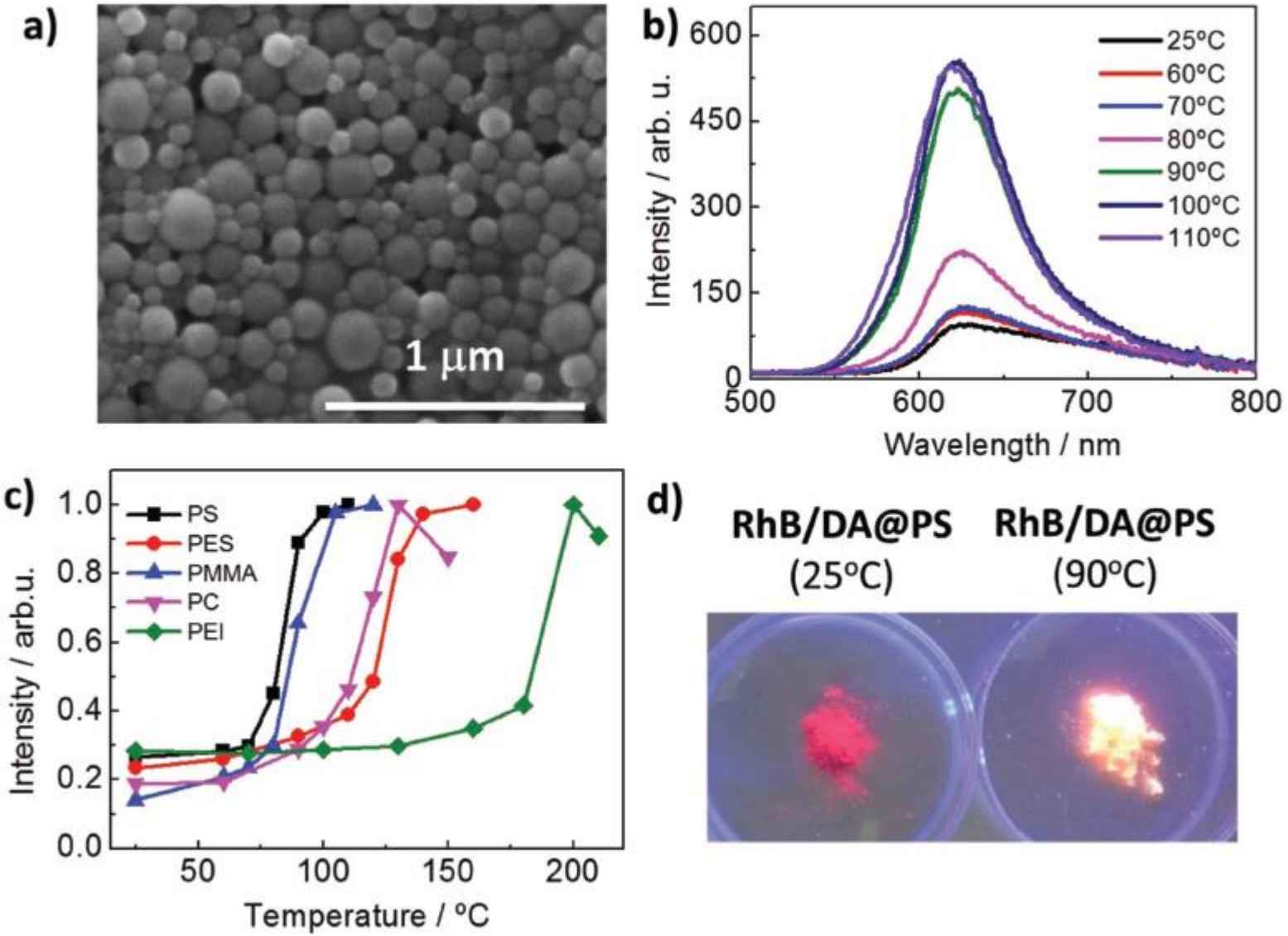
dodecanoic acid (DA), a twelve-carbon nonvolatile weak acid with melting point (*Tm) of 43.8* °C.

Above its Tm, DA is expected to act as a) plasticizer of the polymer, increasing the RhB molecules mobility, b) intercalate between the RhB molecules through the formation of H-bonding.

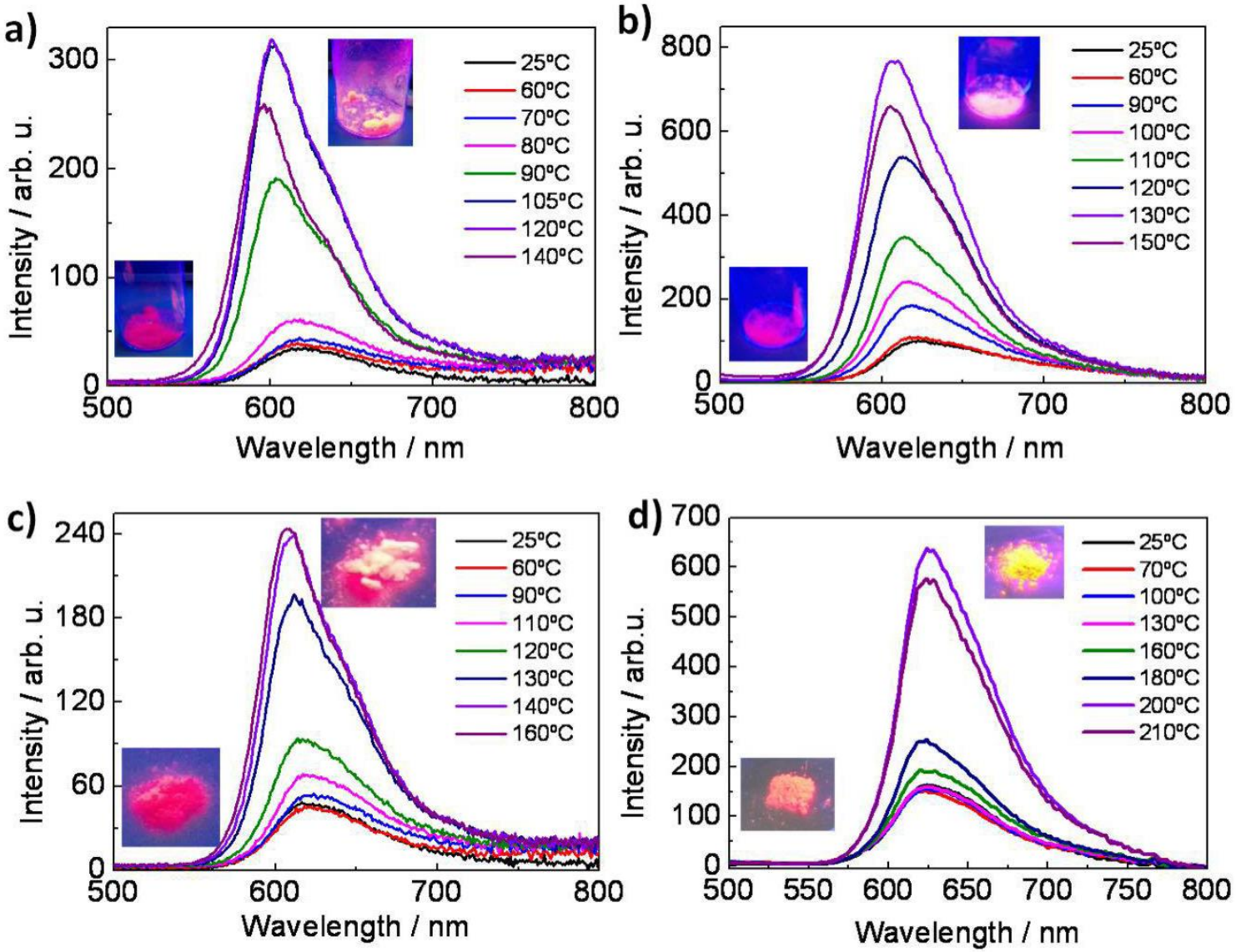

a)
RhB@PS
3 μm
T T^ΔF_max
3 μm
b)
RhB@PMMA
2 μm
T T^ΔF_max
2 μm
c)
RhB@PC
3 μm
T T^ΔF_max
3 μm
d)
RhB@PES
3 μm
T T^ΔF_max
3 μm
e)
RhB@PEI
3 μm
T T^ΔF_max
3 μm


a)
RhB/DA@PS
3μm
T T_g
3μm
b)
RhB/DA@PMMA
2μm
T T_g
3μm
c)
RhB/DA@PC
3 μm
T T_g
3 μm
d)
RhB/DA@PES
4 μm
T T_g
4 μm
e)
RhB/DA@PEI
3 μm
T T_g
3 μm

Polymer NPs containing RhB and DA.



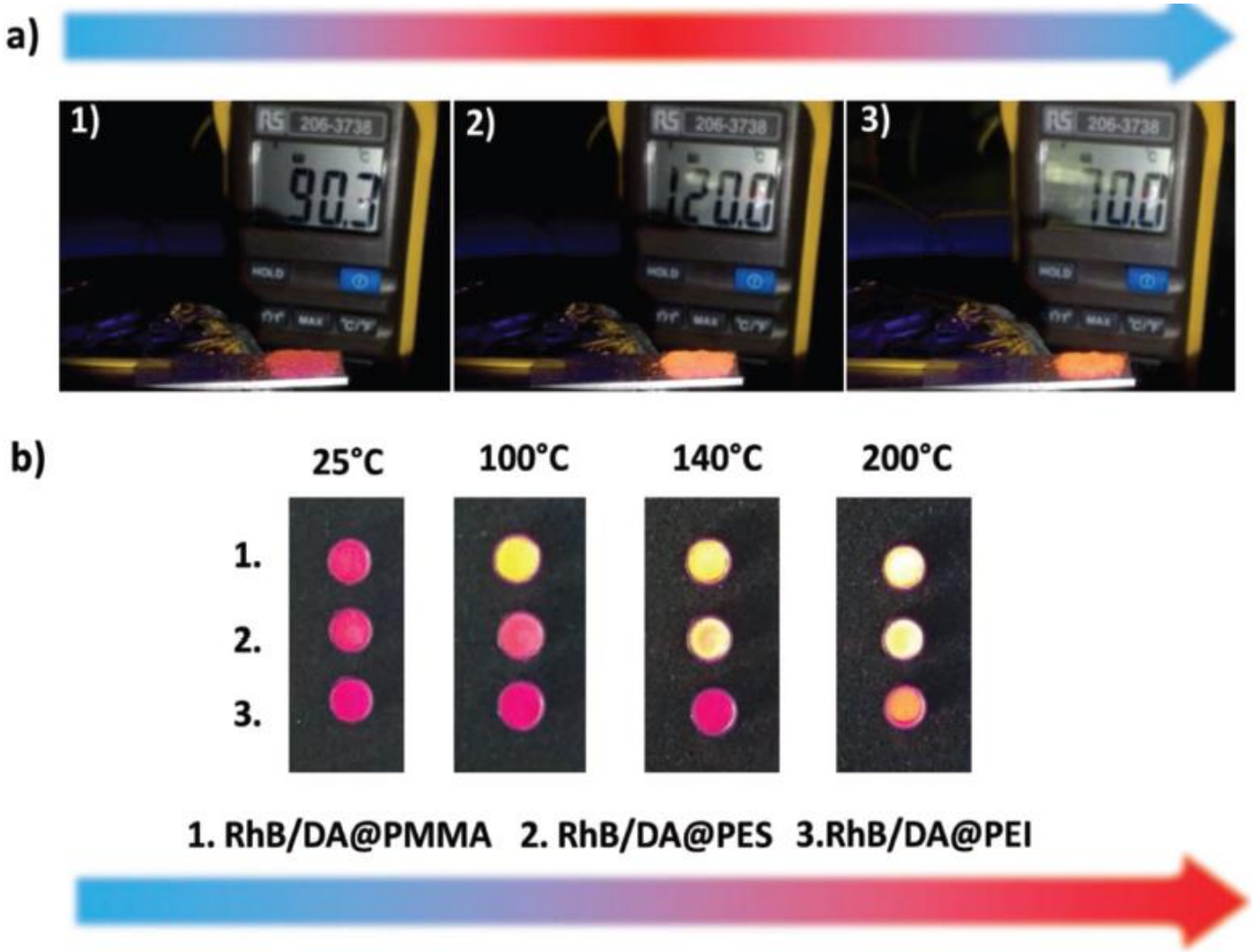
(a) SEM image of RhB/DA@PS NPs **(b)** emission spectra (λexc = 355 nm) of the RhB/DA@PS nanoparticles (2 wt%), recorded at RT after heating the NPs at different temp. **(c)** emission intensities of RhB/DA containing NPs made of different polymers **(d)** digital photographs of RhB/DA@PS taken atRT before (25 °C) and after (90 °C) heating, under UV light



Emission spectra (λexc = 355 nm) of **(a)** RhB/DA@PMMA, **(b)** RhB/DA@PC, **(c)**RhB/DA@PES and **(d)** RhB/DA@PEI NPs.

Insets: digital photos of the NPs before and after heating at the temperature yielding ΔF_{max}.

Tunable Threshold Temperature Sensors



(a) Snapshots showing the fluorescence enhancement between 90 and 125 °C and the fluorescence maintenance once back to lower temperatures (λexc = 365 nm)
(b) digital photos of the RhB/DA@PMMA, RhB/DA@PC, and RhB/DA@PES NPs in aluminum containers after being exposed to different temperatures (λexc = 365 nm).

Summary:

- A novel, general, and straightforward methodology for the development of fluorescent tunable threshold temp. sensors were able to record the thermal history of surfaces and environments over a broad range of temperatures, from 90 up to almost 200 °C is made.

- The strategy is based on the encapsulation of Rhodamine B base together with a developer within polymeric NPs, easily prepared from commercially available polymers and without requiring additional design and/or synthesis of new molecular dyes.

- It provides
  - a fast (<10 min) fluorescence enhancements around the Tg due to the developer-induced disaggregation of RhB molecules within the polymer.
  - easy tunability of the threshold fluorescence activation temp. by simply changing the constituent polymer.
  - an irreversible cooled down (to room temperature) fluorescent sensing material that allows recording the thermal history of surfaces and/or environments exposed to overheating.