Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Thermoresponsive Multicolor-Emissive Materials Based on Solid Lipid Nanoparticles

*Jaume Ramon Otaegui, Daniel Ruiz-Molina, Loredana Latterini, Jordi Hernando** *and Claudio Roscini**

J. R. Otaegui, Prof. D. Ruiz-Molina, Dr. C. Roscini
Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain
E-mail: claudio.roscini@icn2.cat

J. R. Otaegui, Dr. J. Hernando
Departament de Química, Universitat Autònoma de Barcelona, Edifici C/n, Campus UAB, 08193 Cerdanyola del Vallès, Spain
E-mail: jordi.hernando@uab.cat

Prof. L. Latterini
Department of Chemistry, Biology and Biotechnology, Perugia University, Via Elce di sotto, 8, 06123 Perugia, Italy

Table of Contents

1. Experimental Section

Materials: All the PCMs used (eicosane (EC), tetracosane (TC), octacosane (OC)) and hydrogen tetrachloroaurate (III) hydrate were purchased from Alfa Aesar. Sodium borohydride, bovine serum albumin (BSA) and (3-aminopropyl)triethoxysilane (APTES), were obtained from Sigma Aldrich. All these compounds were used as received without further purification. The PDI dye was synthesized as previously described in our group.[1]

Characterization methods: SEM images of AuNSs, SLPs and nanocomposites were registered by means of a FEI Quanta 650 ESEM microscope applying a 5 kV voltage. All the samples, except AuNSs, were metalized with a layer of about 5 nm of Pt prior to SEM imaging. The morphology of eicosane SLPs was analyzed by TEM using a JEM-1400 (120 kV) microscope. The samples were prepared by droplet evaporation of diluted samples over carbon supported onto a copper grid and stained with uranyl acetate (2 %, 8 μL). A TA-instruments Q20 differential scanning calorimeter was used to investigate the thermal properties - i.e., melting temperatures - of the samples prepared. For all the samples, a temperature ramp rate of 10 ºC min^{-1} was used. The extinction spectrum of AuNSs in aqueous suspension was measured using an Agilent Cary 60 spectrophotometer in transmission mode. For the dye solution in liquid PCM, the same equipment was used to register their absorption spectra and the temperature was controlled with a single cell Peltier. When solid, the absorption of the sample was measured at room temperature using the same spectrophotometer in diffuse reflectance mode and a remote integrating sphere connected with a fiber optic cable. In this case, the Kubelka-Munk function was used to estimate the absorption spectra. The fluorescence spectra of all the samples were recorded by means of a custom-made spectrofluorometer using a cw diode laser (λ_{exc} = 405 or 445 nm) as the excitation source. Emitted photons were detected using an Andor ICCD camera coupled to a spectrograph. All the emission spectra registered were corrected by the wavelength dependence of the spectral response of the detection system. For the dye-PCM mixtures, the temperature was controlled using a refrigerated circulator bath (Huber MPC-K6) connected to the sample holder. For the emission measurements of thermofluorochromic films at different temperatures, a custom-made heating holder was used. Absolute quantum yields of the PDI@EC@PVA films below and above the melting point of the EC-based SLPs were obtained by means of a Hamamatsu Quantum Yield fluorimeter C9920-02G, using an integrating sphere and irradiating at 445 nm. The solid film was put in the holder for solid materials and the cuvette without the film was used for the scattering reference signal. The quantum yield of the film with the liquid PDI@EC_SLPs was determined by heating the film above the melting point of eicosane just before introducing it in the sample holder. As NIR irradiation source, a cw diode laser was used (λ_{exc} = 830 nm). The confocal fluorescence images were obtained in a Leica TCS SP5 confocal microscope (λ_{exc}= 458 nm). The thermal images were acquired using a FLIR ETS320 thermal imaging system.

Preparation of bulk PDI-paraffin mixtures: The convenient volume of a stock solution of PDI in dichloromethane was added to the corresponding amount of EC or OC to obtain the concentrations indicated in the text ($c_{PDI} \sim 0.1 - 0.2$ wt%). Then, dichloromethane was evaporated under reduced pressure while heating the mixtures slightly above the PCM melting temperature. After that, the solution was cooled down to room temperature to obtain the desired solid PDI-paraffin mixture.

Preparation of solid lipid particles: SLPs were prepared via the emulsion-cooling methodology. First, 0.5 g of the desired PDI-PCM mixture ($c_{PDI} \sim 0.2$ wt%) were heated up to 10 °C above the melting temperature of the PCM; then, the resulting solution was added to 20 mL of water containing 1 wt% of PVA as stabilizer that was also heated at the same temperature. Afterwards, the mixture was emulsified first with an Ultra-Turrax ® homogenizer at 5000 rpm for 5 minutes and subsequently for 2 additional minutes using an ultrasonic homogenizer operating at 70% amplitude (Branson 450 D Sonifier, 400 W-20 kHz, equipped with disruptor horn and 13 mm flat tip). Finally, the ultrasonicated emulsion was poured onto 30 mL of precooled water (4 °C) to induce the solidification of the PCMs droplets and generate a suspension of the corresponding PDI-loaded SLPs.

Preparation of DCA-miglyol emulsion: The DCA@M812 emulsion was prepared following a methodology previously reported in our group but using DCA as trapped dye (c_{DCA} = 2.5 mM in Miglyol® 812).[2]

Gold nanoshell synthesis: AuNSs were prepared following the method described by Guan et al.[3] First, 20 µL of APTES and 9.2 mL of water were mixed under stirring (500 rpm) for 30 seconds. Then, 640 µL of a 40 mM $HAuCl_4$ aqueous solution were added, obtaining a yellow emulsion due to the poor solubility of APTES in water. The $HAuCl_4$/APTES mixture was stirred for 30 seconds followed by the addition of 800 µL of a 0.1 M aqueous suspension of $NaBH_4$. Immediately, the color of the mixture changed to deep green and 800 µL of BSA 0.1 M aqueous solution were then added to stabilize the formed AuNSs.

Preparation of thermofluorochromic and photothermofluorochromic PVA films: The PVA films with thermally- and photothermally-induced fluorescence variations were prepared using the following procedure. First, the convenient volumes of the desired PDI@PCM_SLPs and, if required, DCA@M812 suspensions were added to 4.5 g of an aqueous solution of PVA (10 wt%) and stirred until homogenous mixture. For the preparation of the NIR-responsive photothermofluorochomic films, 300 µL of a AuNSs (0.34 mg mL^{-1}) suspension were also added. Then, the mixture obtained was poured onto a polystyrene mold (2 cm x 3 cm) and the water solvent was evaporated under ambient conditions for 48 hours. After that time, the film was obtained and could be easily peeled off from the mold.

Inkjet printing of thermofluorochromic SLPs: Thermofluorchromic inks were prepared by mixing water suspensions of the PDI-loaded SLPs of interest with glycerol (8:2 v/v). The resulting mixture was stirred for 10 minutes and then added to empty cartridges of a Canon PIXMA iP4200 inkjet printer.

2. Supplementary Figures S1-S15

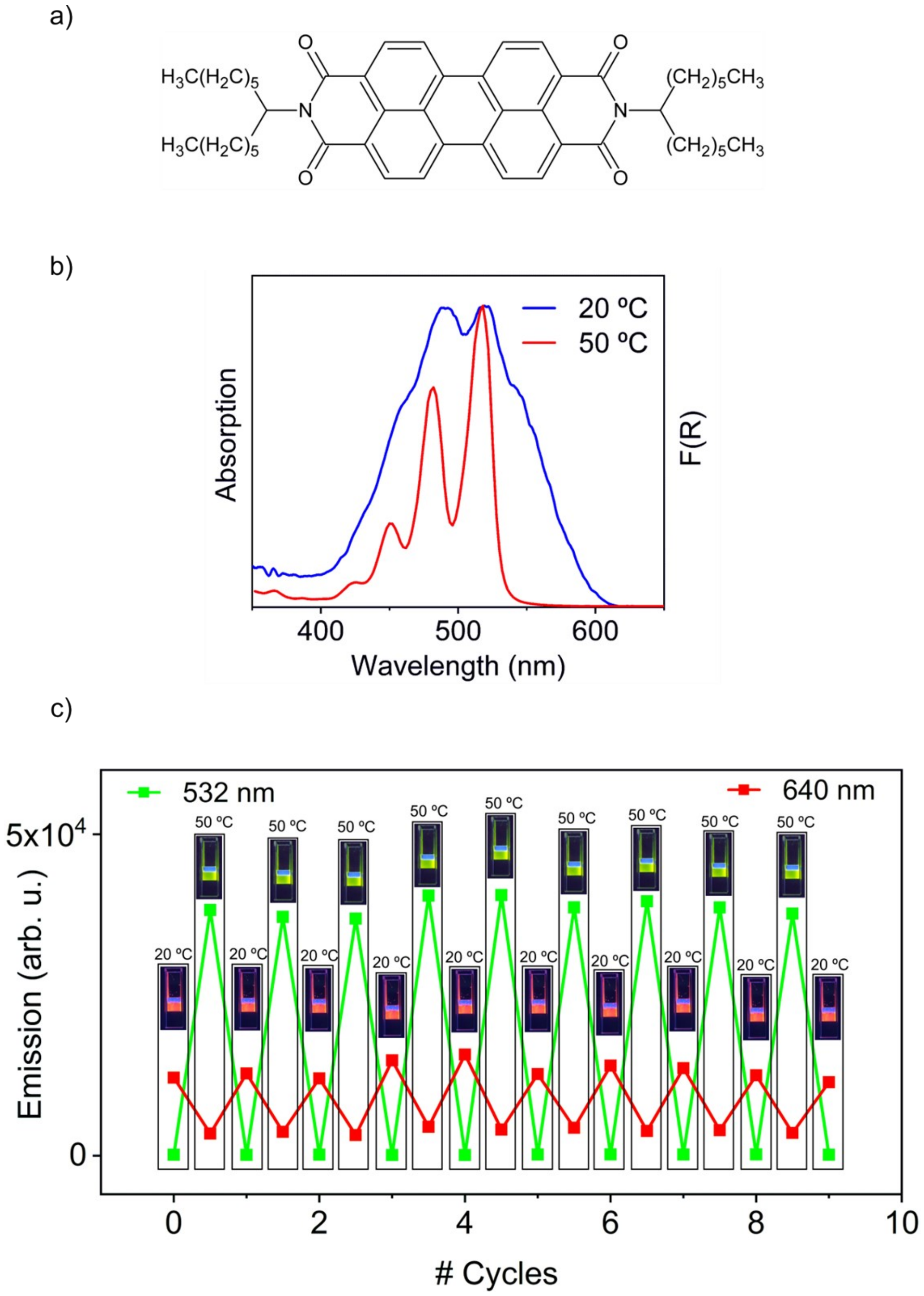


Fig. S1. a) Structure of PDI. b) Absorption spectra of PDI in solid (20 ºC) and melted (50 ºC) eicosane (c_{PDI} = 0.11 wt%). In the case of the solid sample, the Kubelka-Munk function (F(R)) determined from the diffuse reflectance spectrum is given. Both spectra are normalized to unity at their maxima in the visible region, which allows clearly observing the broadening, the variation of the relative intensity ratio of the vibronic bands and the appearance of a red-shifted tail for the absorption of PDI in solid EC. These are typical features for PDI aggregation.[1] c) Intensity variation of the excimer (red, $\lambda_{em,excimer}$ = 640 nm) and monomer (green, $\lambda_{em,monomer}$ = 532 nm) emission of PDI in eicosane (c_{PDI} = 0.11 wt%) during consecutive heating (50 ºC) and cooling (20 ºC) cycles.

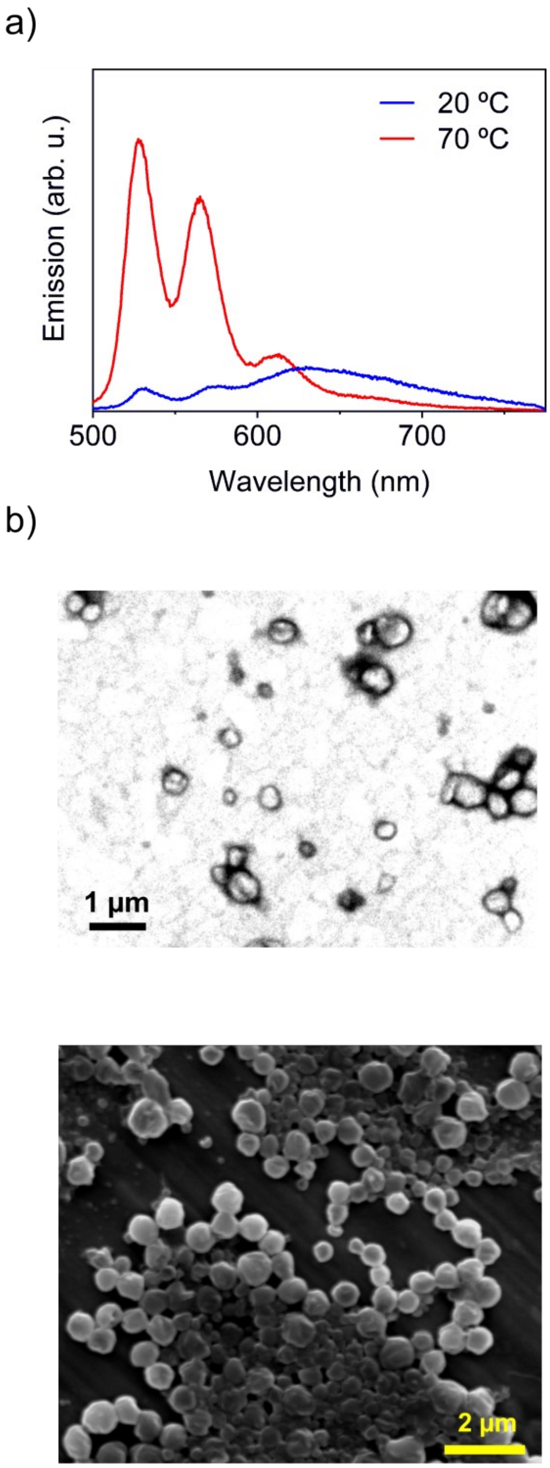


Fig. S2. a) Emission spectra of an aqueous suspension of PDI@OC_SLPs acquired below (20 ºC, blue) and above (70 ºC, red) octacosane's melting point (λ_{exc} = 405 nm). The switch from excimer to pure monomer emission upon PCM melting can be clearly observed. b) TEM image of (top) PDI@EC_SLPs (negative staining with uranyl acetate), and (bottom) SEM image of PDI@TC_SLPs.

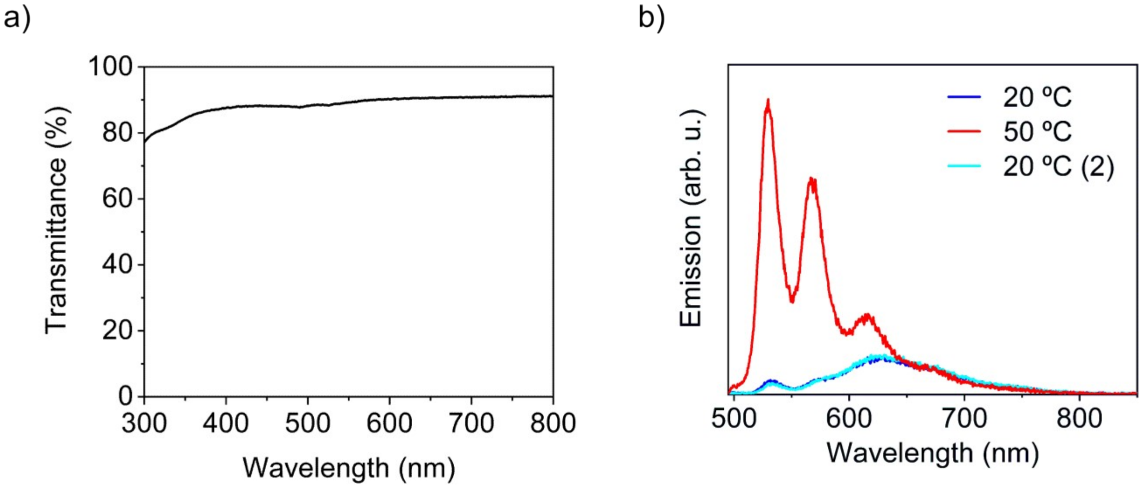


Fig. S3. a) Transmittance spectrum of a PDI@EC@PVA film (thickness ~ 100 µm), which demonstrates its high transparency to visible light. b) Emission spectra of a PDI@EC@PVA layer at 20 ºC and 50 ºC. To show the reversibility of the thermofluorochromic behavior of this sample, an additional measurement at 20 ºC (20 ºC (2)) was recorded after a full cycle of heating to 50 ºC and cooling down to room temperature.

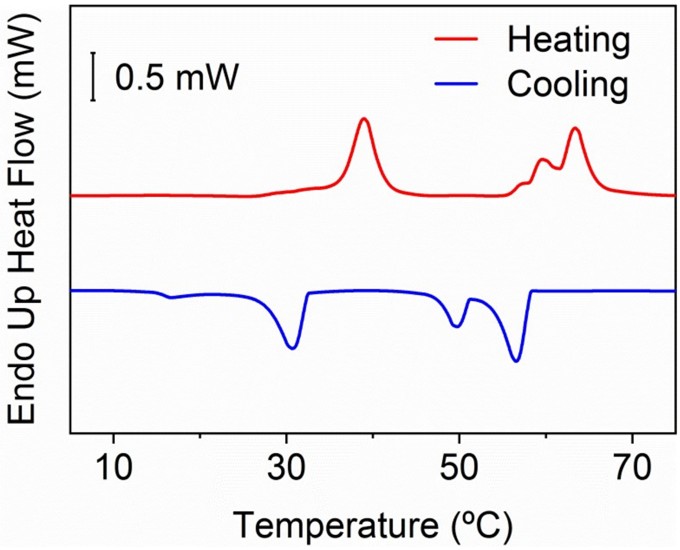


Fig. S4. DSC thermogram of a PDI@EC$_{0.5}$OC$_{0.5}$SLP@PVA film. Clearly separated endothermic peaks at T = 37 ºC and T = 61 ºC are observed that can be ascribed to the different melting processes of eicosane and octacosane. The other peaks observed at temperatures slightly below the bulk T_m values have been reported for the melting process of nanostructured alkanes and are commonly ascribed to the transition between different crystalline phases present in solid paraffins.[4,5]

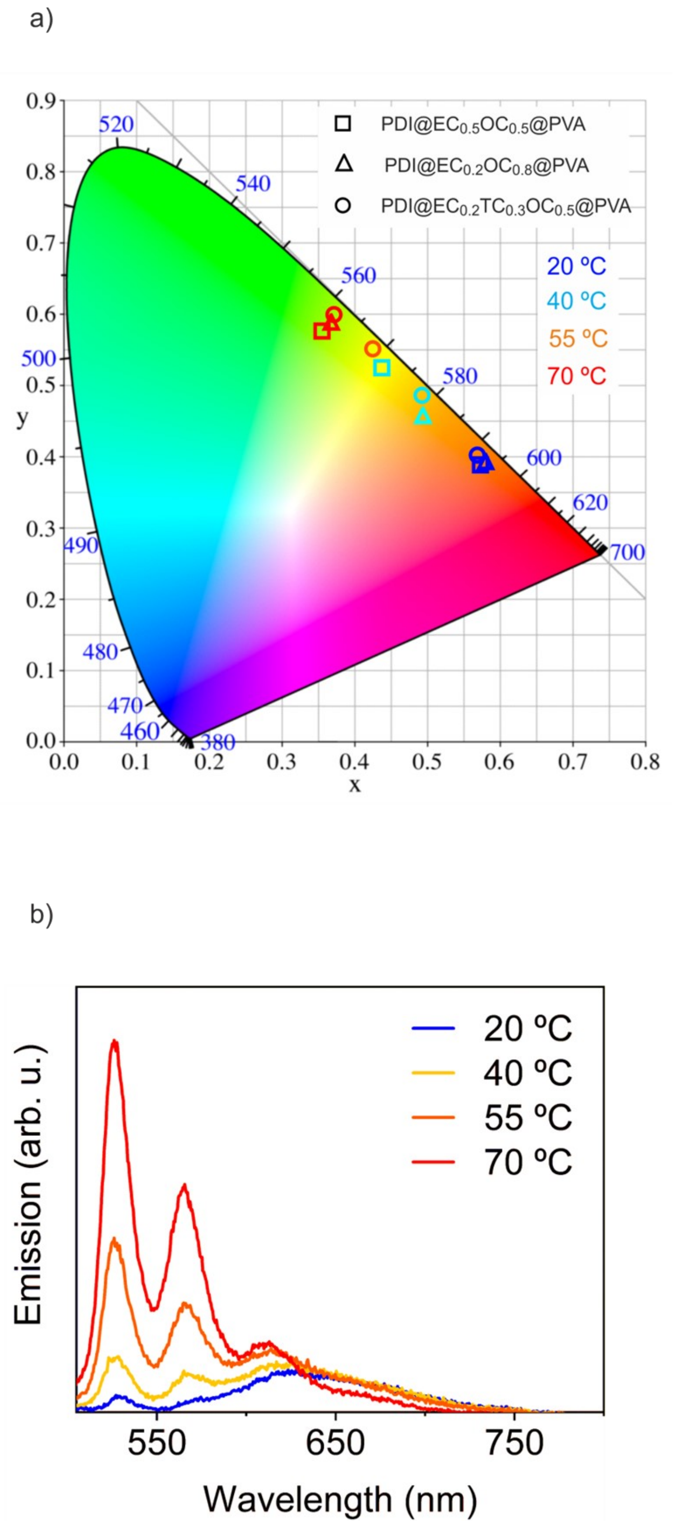


Fig. S5. (a) Temperature-dependent chromaticity coordinates of the emission of PDI@EC$_{0.5}$OC$_{0.5}$@PVA, PDI@EC$_{0.2}$OC$_{0.8}$@PVA and PDI@EC$_{0.2}$TC$_{0.3}$OC$_{0.5}$@PVA films (λ_{exc} = 445 nm). For all the samples, measurements were taken at 20 ºC, 40 ºC and 70 ºC, while additional data was registered for PDI@EC$_{0.2}$TC$_{0.3}$OC$_{0.5}$@PVA at 55 ºC. (b) Temperature-dependent emission spectra of PDI@EC$_{0.2}$TC$_{0.3}$OC$_{0.5}$@PVA (λ_{exc} = 445 nm).

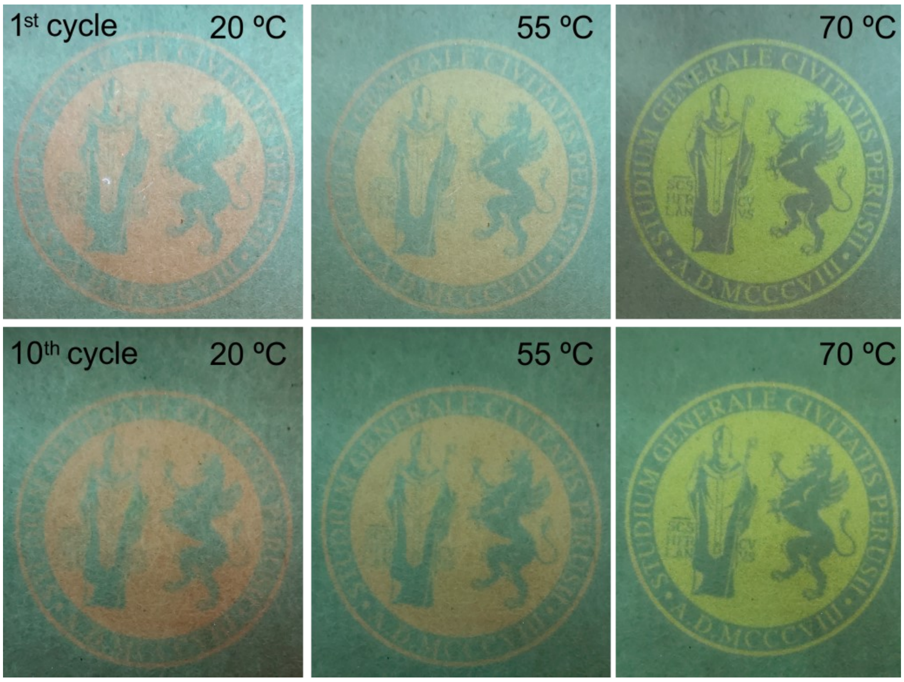
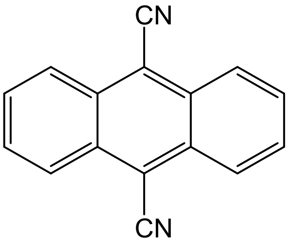


Fig. S6. Photographs of the emission from a paper inkjet-printed with a mixture of PDI@TC_SLPs and PDI@OC_SLPs. The thermofluorochromic sample was subjected to 10 consecutive heating-cooling cycles and images are shown for (top) the 1st and (bottom) 10th of these cycles. All the photographs were taken under wide field illumination with a 365 nm UV lamp.

a)



b)

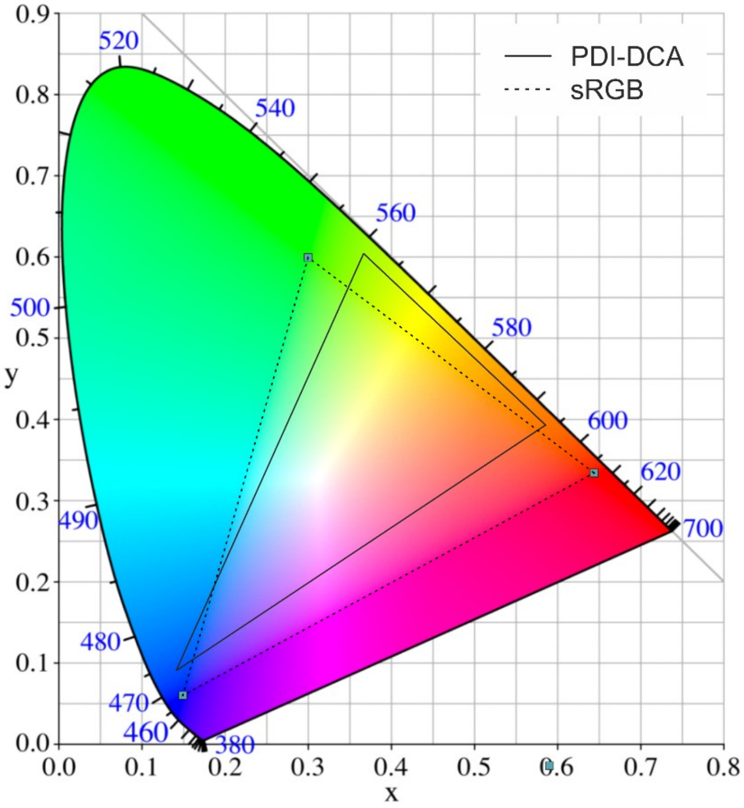


Fig. S7. a) Structure of 9,10-dicyanoanthracene (DCA). b) Comparison of the standard RGB color space (sRGB, dotted line) and the chromatic color space defined by the red excimer emission of PDI, the green monomeric emission of PDI and the blue monomeric emission of DCA (PDI-DCA, continuous line).

Fig. S8. Photographs taken (a) under ambient conditions and (b) under irradiation with a 365 nm UV lamp in the dark for two polymer films loaded with thermofluorochromic SLPs: (left) PDI/DCA@EC$_{0.25}$OC$_{0.25}$M812$_{0.5}$@PVA and (right) PDI/DCA@EC$_{0.3}$OC$_{0.6}$M812$_{0.1}$@PVA.

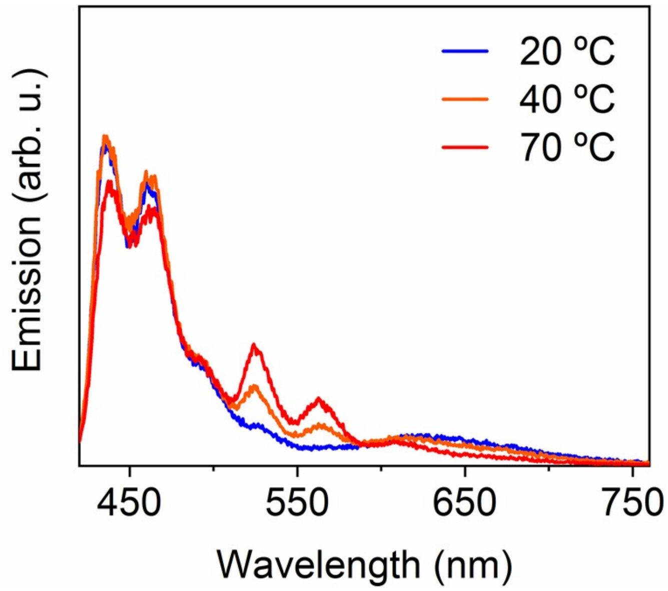


Fig. S9. Emission spectra at 20 ºC, 40 ºC and 70 ºC of the PDI/DCA@EC$_{0.25}$OC$_{0.25}$M812$_{0.5}$@PVA film (λ_{exc} = 405 nm).

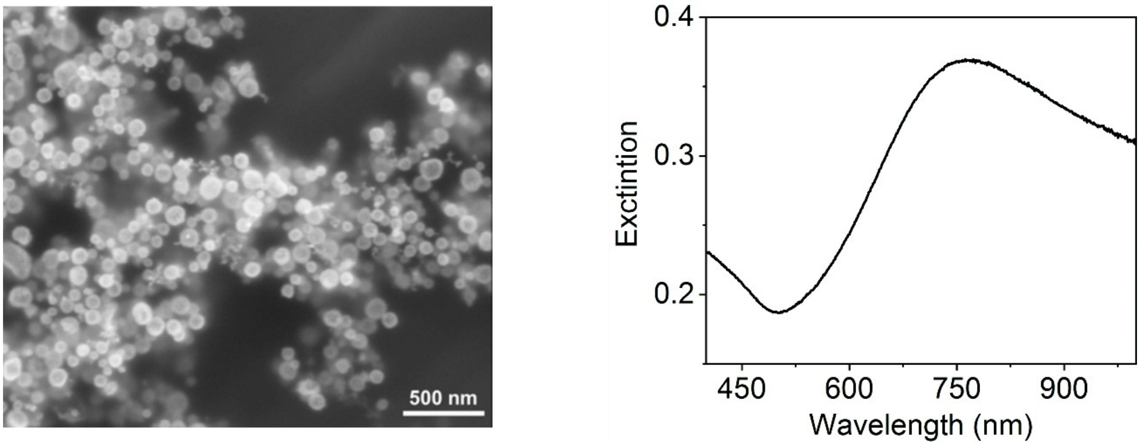


Fig. S10. SEM image and extinction spectra in water of the AuNSs (22 μg mL^{-1}) used in this work as NIR-excitable nanoheaters.

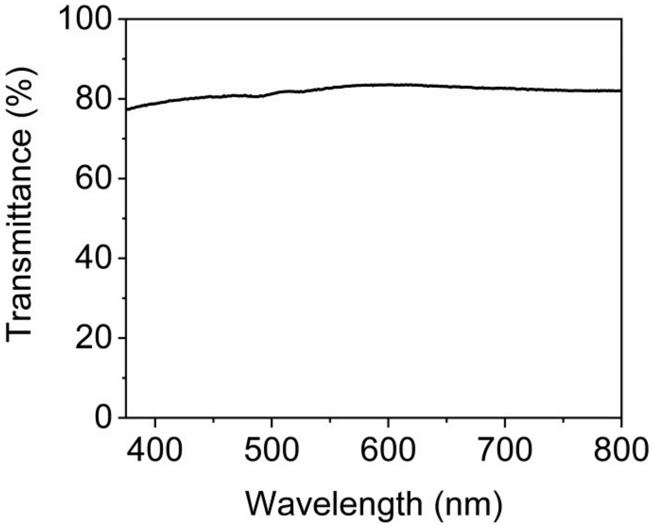
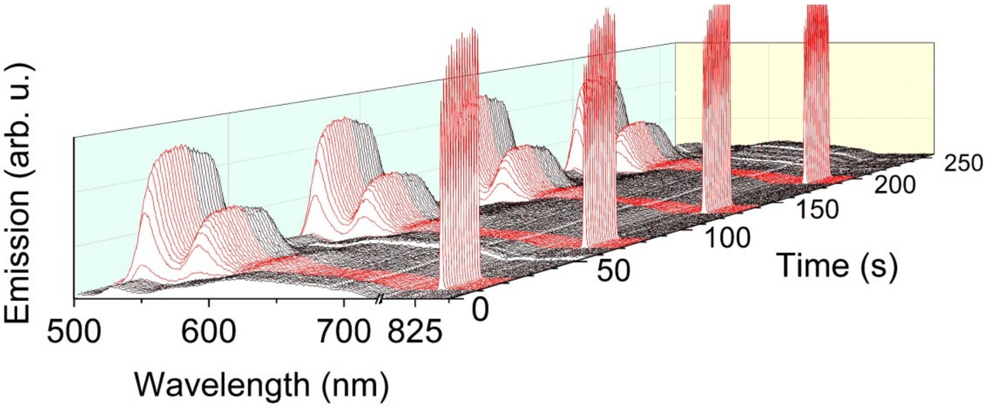


Fig. S11. Transmittance spectrum of a PDI@EC@PVA film loaded with AuNSs (0.02 wt%, thickness ~ 100 μm), which demonstrates its high transparency to visible light.



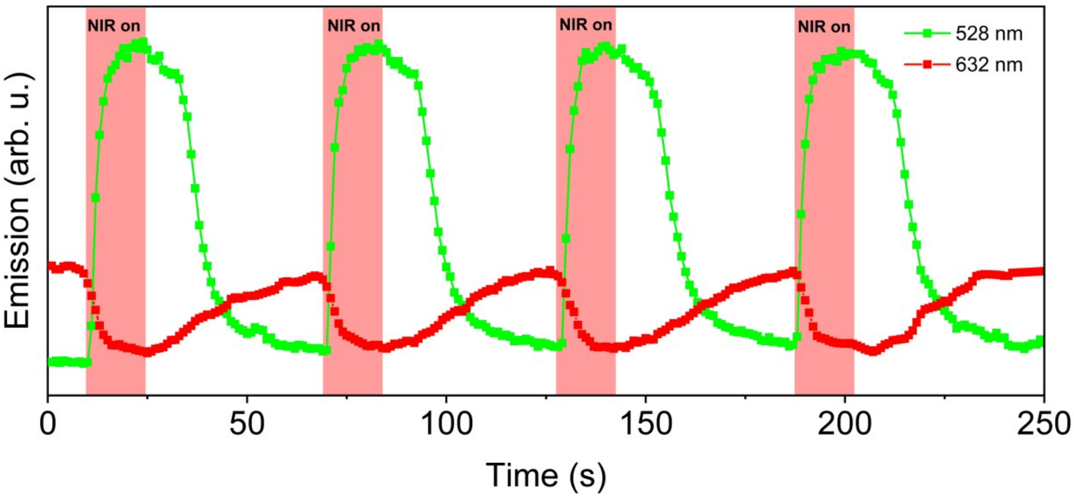


Fig. S12. (top) Variation of the emission spectra (λ_{exc} = 445 nm) of a PDI@EC@PVA film loaded with AuNSs (c_{AuNSs} = 0.02 wt%) under consecutive cycles of photothermal heating with a NIR laser (10 s, λ_{exc} = 830 nm, NIR power = 1300 mW cm^{-2}) and cooling (45 s) in the dark. The narrow intense signal at λ = 830 nm corresponds to the scattering signal of the NIR laser, which clearly correlates with the time lapses when PDI monomeric emission is registered. (bottom) 2D plot of the intensity variation of excimer (red, $\lambda_{em,excimer}$ = 632 nm) and monomer (green, $\lambda_{em,monomer}$ = 528 nm) emission during the consecutive cycles of photothermal heating of the PDI@EC@PVA film.

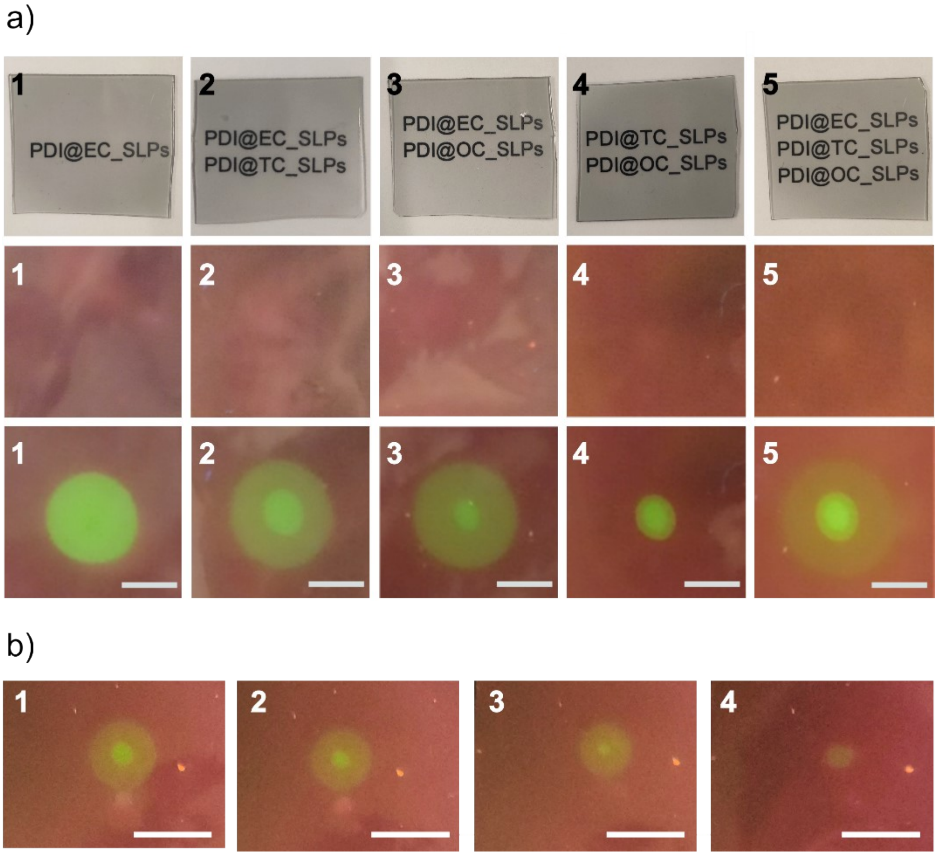


Fig. S13. a) Photographs of different PVA films loaded with PDI-based SLPs and AuNSs (0.02 wt%) under (top) ambient light, (middle) UV ($\lambda_{exc} = 365$ nm) excitation in the dark, and (bottom) UV excitation ($\lambda_{exc} = 365$ nm) together with NIR-point illumination ($\lambda_{exc} = 830$ nm, 3000 mW cm^{-2}, 2.5 mm in diameter spot) in the dark. All the measurements were conducted at 21.5 ºC. Scale bar = 2.5 mm. b) Photographs of the NIR-induced fluorescent patterns created in a PVA film loaded with AuNSs (0.034 wt%) and a 1:1 mixture of PDI@EC_SLPs and PDI@OC_SLPs when varying the NIR illumination power ($\lambda_{exc} = 830$ nm, 2.5 mm in diameter spot, 1 = 2500 mW cm^{-2}, 2 = 2020 mW cm^{-2}, 3 = 1600 mW cm^{-2}, 4 = 760 mW cm^{-2}). Scale bar = 6.0 mm.

3. References

[1] L. Parejo, M. Chaari, S. Santiago, G. Guirado, F. Teixidor, R. Núñez, J. Hernando, *Chem. – A Eur. J.* 2021, **27**, 270.

[2] Y. Guan, Z. Xue, J. Liang, Z. Huang, W. Yang, *Colloids Surf. A* 2016, **502**, 6.

[3] H. Torres-Pierna, D. Ruiz-Molina, C. Roscini, *Mater. Horizons* 2020, **7**, 2749.

[4] C. Alkan, A. Sari, A. Karaipekli, *Energy Convers. Manag*. 2011, **52**, 687.

[5] D. Sebastia-Saez, T. Ramirez, R. Silva, H. Arellano-Garcia, *Int. J. Energy Res.* 2020, **44**, 2306.