This paper must be cited as:
Martínez, E. D., Brites, C. D. S., Carlos, L. D., García-Flores, A. F., Urbano, R. R., Rettori, C., Adv. Funct. Mater. 2019, 29, 1807758.
https://doi.org/10.1002/adfm.201807758
Electrochromic Switch Devices Mixing Small- and Large-Sized Upconverting Nanocrystals

Eduardo D. Martínez*, Carlos D. S. Brites, Luís D. Carlos, Alí F. García-Flores, Ricardo R. Urbano and Carlos Rettori

Dr. Eduardo D. Martínez, Dr. Alí F. García-Flores, Prof. Ricardo R. Urbano, Prof. Carlos Rettori
“Gleb Wataghin” Institute of Physics (IFGW), University of Campinas (UNICAMP), 13083-859, Campinas, SP, Brazil

Dr. Carlos D. S. Brites, Prof. Luís D. Carlos
Physics Department and CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal.

Prof. Carlos Rettori
Federal University of ABC (UFABC), 09210-580, Santo André, SP, Brazil.

E-mail: edmartin@ifi.unicamp.br

Keywords: optoelectronic devices, upconversion nanoparticles, electrothermal control, silver nanowires, high thermal sensitivity

The hasty progress in smart, portable, flexible, and transparent integrated electronics and optoelectronics is currently one of the driving forces in nanoscience and nanotechnology. A promising approach is the combination of transparent conducting electrode materials (e.g., silver nanowires, AgNWs) and luminescent nanoparticles. Here, tunable electrochromic transparent devices covering a broad range of the chromatic diagram are fabricated by combining the electrical control of the heat dissipation in AgNWs networks with size-dependent thermal properties of upconverting nanoparticles (UCNPs). The electrochromic devices are based on transparent nanocomposite films of poly(methyl methacrylate) and AgNWs covered by UCNPs of different sizes and compositions. As illustrative examples, devices mixing large-sized (>70 nm) β-NaYF₄:Yb,Ln and small-sized (<15 nm) NaGdF₄:Yb,Ln@NaYF₄ core@shell UCNPs (Ln=Tm, Er, Ce/Ho) are presented. The temperature-dependent emission of the
particles is monitored by the intensity ratio of the Er	extsuperscript{3+} \( ^{2}H_{11/2} \) and \( ^{4}S_{3/2} \rightarrow ^{4}I_{15/2} \) emission lines, while externally controlling the current flow in the AgNWs network. Moreover, by defining a new thermometric parameter involving the intensity ratio of transitions from large- and small-sized UCNPs, a relative thermal sensitivity of 5.88 % K\(^{-1}\) (at 339 K) is obtained; a 6-fold improvement over the values reported so far.

1. Introduction

Lanthanide-doped upconversion nanoparticles (UCNPs) are host-guest systems in which a dielectric host lattice, such as sodium yttrium (or gadolinium) fluoride (NaY(Gd)F\(_{4}\)), is doped with trivalent lanthanide ions (Ln\(^{3+}\)) enabling anti-Stokes emissions under near infrared (NIR) excitation.\(^{[1-5]}\) Typically, Yb\(^{3+}\) ions are incorporated as sensitizers (due to its large absorption cross section in the NIR spectral range) and erbium (Er\(^{3+}\)), holmium (Ho\(^{3+}\)) or thulium (Tm\(^{3+}\)) as activator ions (due to their long lifetime and ladder-like arranged energy levels). When illuminated with NIR radiation, incident low-energy photons are primarily absorbed by the Yb\(^{3+}\) sensitizers and then the energy is non-radiatively transferred to adjacent activators generating visible or ultraviolet upconversion emissions. Recent advances have enabled a precise control over the particles’ crystallographic structure, morphology, size, composition, core@shell architecture and specific surface functionalization.\(^{[6-10]}\) Hence, UCNPs are promising candidates for a wide range of applications, spanning bioimaging\(^{[11, 12]}\) and therapeutics,\(^{[8, 9]}\) thermal sensing,\(^{[13, 1]}\) photovoltaics,\(^{[14, 4]}\) anticounterfeiting,\(^{[15, 16]}\) full-color volumetric three-dimensional display technology\(^{[17, 18]}\) and single-particle tracking.\(^{[19]}\)

In recent years, the thermal effects on the light emission of UCNPs were found to be a size-dependent phenomenon. Although several hypotheses have been formulated to explain this intriguing thermal effect, the matter remains an open question.\(^{[20-25]}\) Systematic studies on UCNPs emission intensity controlled by a thermal field have already been performed by Li et
al.\cite{20,21} and Shao et al.\cite{22,23} These authors showed that the emission intensity is enhanced with the increase of temperature for UCNPs smaller than a critical size of 20-30 nm, whereas emission quenching occurs for larger particles. These effects were used to control the nanoparticles’ emission color via modulation of the irradiation laser power, which obviously affected the total intensity of the emissions, or by directly varying the temperature through complex heating systems, involving a copper sample cell and a ceramic plate controlled by a proportional–integral–derivative (PID) regulator.\cite{20, 21, 23} Both approaches, however, seem unpractical for the direct application of the thermal peculiarities of UCNPs in actual optoelectronic devices.

Here, we demonstrate that nanocomposite transparent films combining a poly(methyl methacrylate) (PMMA) matrix and a percolating network of silver nanowires (AgNWs)\cite{26, 27} are excellent platforms to electrically control the local temperature and therefore to fine-tune the emission intensity of UCNPs. AgNWs are being intensively studied as transparent electrodes to replace traditional materials, such as indium tin oxide, for the next-generation of flexible electronics,\cite{28, 29} including flexible solar-cells\cite{30, 31} and wearable electronics.\cite{32, 33} The heat dissipation produced by the flow of an electrical current through the AgNWs network has enabled their use as nanoheater films.\cite{34, 33} In a recent work we have explored the application of these nanostructures as a tool for thermally-controlled experiments.\cite{35} Here, we show that combining UCNPs’ with different thermal sensitivity we can easily control the emission color through the heat dissipation in the AgNWs/PMMA layer by simply applying different DC voltages. We analyzed the changes in the intensity of the emission lines of \(\text{Er}^{3+}\), \(\text{Tm}^{3+}\) and \(\text{Ho}^{3+}\) ions in UCNPs of different sizes as well as the reversibility after several cycles. As a proof of concept, electrochromic devices combining small- and large-size UCNPs with different emitting dopants were constructed displaying unprecedented high relative thermal sensitivity values.
The approach we show in this work provides a route to fabricate innovative and versatile multichromatic upconversion nanostructures in the form of thin semitransparent films, whose spectral emission can be externally adjusted. Such approach constitutes a step forward in optoelectronics, where the remarkable utility of AgNWs networks for temperature-controlled experiments is combined with the temperature dependence of the light emission of UCNPs, which varies with the particle size, an intriguing and barely understood nanoscale phenomenon.

2. Results

2.1. Electrothermal devices

Transparent electrothermal devices were fabricated by spin coating the AgNWs/PMMA ink over a glass substrate, as described in the Supporting Information.

Figure 1a and 1b illustrate the resulting devices. Scanning electron microscopy (SEM) images of the AgNWs show a random arrangement of the nanowires with no preferential orientation in a percolating network (Figure 1c and 1d). The statistical analysis of the SEM images indicates a Gaussian size distribution with length (60±30) μm and diameter (115±30) nm (Supporting Information Figure S1). The transmission electron microscopy (TEM) images of individual nanowires show the reminiscent polyvinylpyrrolidone (PVP) coating layer (ca. 1-3 nm thick, Figure 1e). Atomic force microscopy (AFM, Supporting Information Figure S2) analysis to the AgNWs/PMMA film shows a rough surface with heights up to ±100 nm and a film thickness of (1.1±0.1) μm. The AgNWs/PMMA film presents a sheet resistance of (2.0±0.1) Ω sq⁻¹ (determined by 4-probe measurements) and an optical transmittance of 67% at 600 nm (determined by UV-visible spectrophotometry, Supporting Information Figure S3).

UCNPs were deposited over the AgNWs/PMMA composite film by drop casting the cyclohexane particles’ suspensions and further evaporation of the solvent. The particles’ morphology and size are shown in Figure 2, Table 1 displays the nomenclature adopted in this
work, the particles’ nominal composition and size. TEM and SEM images show hexagonal plate-like shapes for the large-sized $\beta$-NaYF$_4$:Yb,Ln particles and spherical shape for the small-sized NaGdF$_4$:Yb,Ln@NaYF$_4$ core@shell ones (Ln=Tm, Er, Ce/Ho). The corresponding XRD patterns (Supporting Information Figure S4a) show that all samples crystalize in the pure hexagonal $\beta$-phase. Dynamical light scattering (DLS) performed on small-size UCNPs (Supporting Information Figure S4b-d) show mean particle sizes in accordance with TEM images and estimations from XRD peak widths. For large-sized UCNPs, particle aggregation prevented conclusive results by DLS, so TEM was used for size analysis instead.

Dark-field optical microscopy images under white-light illumination of an electrothermal device, fabricated depositing 2L UCNPs (Table 1) over the AgNWs/PMMA layer, show a set of nanoparticles dispersed within the AgNWs network (Figure 1f). When the device is illuminated by 976 nm radiation, the image displays bright green spots, (average diameter ca. 5 µm), well-suited with the light scattering by nanoparticle clusters and emission color compatible with the well-known upconversion emission profile of Er$^{3+}$ ions (Figure 1g).

The unique design of the electrothermal devices reported here allows the control of the local temperature through the heat dissipation in the AgNWs/PMMA conductive layer, by simply applying different DC voltages, as mentioned above. This permits to track in real-time the temperature dependence of the upconversion emission features of distinct UCNPs deposited over the transparent electrically conductive layer, on the top of the device. The UCNPs’ local temperature was precisely measured illuminating the assembled device with a NIR laser (976 nm, $50\times10^4$ W m$^{-2}$) and recording the upconversion emission spectra of Er$^{3+}$ ions in the UCNPs (using a cost-effective portable spectrometer, see Methods). Four electrothermal devices incorporating small- and large-sized UCNPs were prepared. Two devices contain simultaneously Tm$^{3+}$- and Er$^{3+}$- doped UCNPs (1L/2L and 1S/2S) and the other two encompass Ce$^{3+}$/Ho$^{3+}$ co-doped UCNPs (3L and 3S).
2.2. Upconversion primary thermometry

Recently, a straightforward method to predict the temperature calibration curve of any upconverting thermometer based on two thermally-coupled electronic levels was reported. It demonstrates that these systems are intrinsically luminescent primary thermometers, thus avoiding time-consuming calibration procedures.\cite{36,37} A seminal example is the Er\textsuperscript{3+} emission in which the \textsuperscript{2}H\textsubscript{11/2}→\textsuperscript{4}I\textsubscript{15/2} (\(I_H\)) and \textsuperscript{4}S\textsubscript{3/2}→\textsuperscript{4}I\textsubscript{15/2} (\(I_S\)) emission bands (Supporting Information Figure S8a) allow to calculate the absolute temperature \(T\) by:\cite{37}

\[
\frac{1}{T} = \frac{1}{T_0} - \frac{k_B}{\delta E} \ln \left( \frac{\Delta}{\Delta_0} \right)
\]

where \(k_B\) is the Boltzmann constant, \(\delta E\) is the energy gap between the barycenters of the \textsuperscript{2}H\textsubscript{11/2} and \textsuperscript{4}S\textsubscript{3/2} levels and \(\Delta=I_H/I_S\) is the thermometric parameter with \(\Delta_0\) the value at room temperature \(T_0\) (see Supporting Information for the calculus of \(\delta E\) and Figure. S8a and S9a).

To attest the validity of Equation 1 for our UCNPs, we prepared a glass slide covered with 2S nanoparticles (as an illustrative example) positioned in thermal contact with a Peltier element (controlled by an Arduino board; Supporting Information). The temperature was calibrated by measuring the emission spectra of the UCNPs under laser excitation firstly at room temperature (\(T_0=297\) K, corresponding to \(\Delta_0=0.2898\)) and, then, in the 280–390 K range. Figure S8b in Supporting Information compares the temperature readout of the thermocouple placed in contact with the 2S nanoparticles with that calculated using Equation 1, giving an excellent agreement between both values. The same procedure was repeated for 2L UCNPs, as presented in Figure S9 in Supporting Information. For 2S nanoparticles the maximum relative thermal sensitivity and minimum temperature uncertainty at 297 K are 1.13 % K\(^{-1}\) and 0.45 K,
respectively, and its repeatability between 318 and 373 K is 99.8% (Figure S8c and S8d and details of the calculus in Supporting Information). These values are analogous to the highest ones reported for Yb\(^{3+}\)/Er\(^{3+}\)-co-doped UCNPs.\(^{[36]}\)

### 2.3. Electrothermal control of the up-conversion emission

The electrothermal devices described above are appropriate platforms to perform real-time temperature control experiments. By applying a continuous power supply to the AgNWs layer of the devices, the heat released via Joule effect was controlled inducing an increase of the local temperature, which could be measured through the emission spectra of the UCNPs.

For the large-sized particles, the increase of temperature produced a systematic decrease of the emission intensity (Figure 3a-c and Figure S10a in Supporting Information for 1L/2L and 3L UCNPs, respectively). A detailed analysis of the total intensity of Tm\(^{3+}\), Er\(^{3+}\), and Ho\(^{3+}\) transitions shows that all of them suffer thermal quenching upon temperature increase, although in distinct extents. In the visible spectral range, the total intensity of the \(^{1}I_6\rightarrow^{3}F_{4}\), \(^{1}D_2\rightarrow^{1}G_4\), \(^{3}H_4\rightarrow^{3}H_6\) (Tm\(^{3+}\)), \(^{5}S_2\rightarrow^{5}F_5\rightarrow^{5}I_8\) (Ho\(^{3+}\)), and \(^{2}H_{9/2,11/2}\rightarrow^{4}I_{15/2}\) (Er\(^{3+}\)) transitions decreases by a factor \(I(T)/I(T_0)\) ranging from 0.9 to 0.1 (Table 2) for an applied electrical power of 1.3 W. Here \(T\) and \(T_0\) indicate the maximum and initial temperatures of the experiments, respectively. The thermal quenching on micro-sized particles and bulk upconversion materials has been frequently attributed to multi-phonon non-radiative relaxation mechanisms, resulting in higher decay probabilities; so, the observed trends are expected.\(^{[38,39]}\) However, and intriguingly, an emission enhancement occurs for small-sized UCNPs when increasing the temperature (Figure 3d-f and Figure S10c and S10d in Supporting Information for 1S/2S and 3S UCNPs, respectively). For all tested small-sized particles, the total intensity of the Tm\(^{3+}\), Er\(^{3+}\), and Ho\(^{3+}\) transitions present a remarkable thermal enhancement, although to a different extent (Table 2). In the visible spectral range, the total intensity of the \(^{1}D_2\rightarrow^{3}F_4\), \(^{1}G_4\), \(^{3}H_4\rightarrow^{3}H_6\)
\( \text{Tm}^{3+} \), \( ^5\text{S}_2/\text{F}_4,^5\text{F}_5 \rightarrow ^5\text{I}_8 \) (Ho\(^{3+}\)) and \( ^2\text{H}_{11/2},^4\text{S}_{3/2},^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2} \) (Er\(^{3+}\)) transitions increases by a factor ranging from 1.3 to 8.3 (for an applied electrical power of 1.3 W).

The total enhancement depends on several factors, besides the applied electrical power \((i.e., \text{the heat dissipated})\) and the size of UCNPs. Both factors will be discussed in the following sections. We recall that the value of \( \Delta \) always increases with temperature, independently of the size of the sample, which confirms the validity of Equation 1.

For both small- and large-sized particles, when the electrical power was turned off and the heat dissipation by the Joule effect was suppressed, the emission spectra recovered the values recorded at the beginning of the experiment, indicating reversibility. In fact, it is remarkable that the emission spectra present reversible changes upon several temperature cycling, independently of particle size and Ln\(^{3+}\) composition (Figure 4). Moreover, an initial increase of temperature of the small-size nanoparticles \((ca. 11 \text{ K})\) was measured before turning on the electrical power supply, due to the heating produced by the incident laser irradiation (power density of \(ca. 50 \times 10^4 \text{ W m}^{-2}\)) (Figure 4c and 4d). The laser heating effect is less noticeable in large-size UCNPs as the larger volume of the crystals enables a faster energy dissipation, acting as a heat sink in this case.

Interestingly, in some experiments a clear difference was observed in the first cycle compared to the following ones. It was noticed that the initial emission intensity was not completely recovered (Figure S10 and S12 in Supporting Information), indicating a non-reversible process acting at the beginning of the experiments. We suspect that the organic capping may be irreversibly damaged affecting the emission intensity, although further research is required to clarify this point. Also, we have observed a gradual increase of the emission intensity of the small-sized UCNPs when submitted to the electrothermal cycling immediately after the deposition. The modification of the oleic acid capping ligand and thermal desorption of solvent residues may be responsible for this observation. To prevent spurious effects, a thermal pre-
treatment at 140 °C for at least 30 minutes is recommended (Figure S13 in Supporting Information).

The thermal enhancement of the upconversion emission intensity in small-sized nanoparticles displayed an upper critical temperature, as already observed by Zhou et al. Relative to the initial values at 297 K, the emission intensity of the \( ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2} \), \( ^1\text{G}_4 \rightarrow ^3\text{H}_6 \) and \( ^3\text{H}_4 \rightarrow ^3\text{H}_6 \) transitions increased by a maximum factor of 3 (at 0.7 W), 13 (at 0.9 W) and 8 (at 1.4 W), respectively. The corresponding critical temperatures \( T_c \) were different for each transition as shown in Figure 5. The subsequent increase of the temperature above \( T_c \) induced the quenching of the \( ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2} \) transition above \( \approx 390 \) K and of the \( ^1\text{G}_4 \rightarrow ^3\text{H}_6 \) transition above 415 K, whereas the intensity of the \( ^3\text{H}_4 \rightarrow ^3\text{H}_6 \) one remained barely constant in the 415–475 K range, decreasing for higher temperatures (Figure 5). Finally, thermal cycling induced by supplying different electrical powers was tested indicating a thermal failure of the devices for electrical powers higher than 1.89 W (Figure S11 in Supporting Information). The failure is due to the breakdown of AgNWs at high current densities and it can be noticed as an abrupt drop in current, or a large increase in the resistance. It was observed that the AgNWs network is damaged at the edge of the bottom gold contacts, opening the circuit. Whether small or large UCNPs are used, the failure is the same. Figure S11 in Supporting Information shows the optical effect on 2L UCNPs where the electrical failure is also detected optically as a sudden change in the emission intensity.

2.4. Electrochromic devices

The electrothermal devices present excellent transparency and a controlled heating that can be used to perform fundamental thermal studies or to construct functional systems. Here, we exploited the different thermal effects of small- and large-sized UCNPs to produce electrochromic devices. To get a fine-control of the upconversion emissions, two sets of
nanoparticles were deposited over the AgNWs/PMMA nanocomposite film following the above-mentioned drop casting method. Then, as examples, we fabricated two electrochromic devices (A and B) combining small- and large-sized UCNPs (Figure 6).

Device A (2L and 1S UCNPs) was submitted to the electrothermal control of the emission color by supplying 1.3 W. Under these conditions, and as predictable from the characterization performed on isolated particles, the Er\(^{3+}\) green emission \(\left( ^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2} \text{ and } ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2} \right)\) of the large-sized 2L particles was thermally quenched while the Tm\(^{3+}\) blue emission \(\left( ^1\text{G}_4 \rightarrow ^3\text{H}_6 \right)\) of the small-sized 1S particles was thermally enhanced (Figure 6c). Increasing the temperature via Joule effect, the observable emitted color shifted from green to blue, as seen from the trajectory depicted in the Commission Internationale de L'Éclairage (CIE) 1931 chromatic diagram (Figure 6a). For device B (2L and 3S nanoparticles), on the other hand, when the electrothermal action was switched on at 1.3 W the red emissions were thermally enhanced (Figure 6d) while the overall green emissions were thermally quenched, corresponding to a shift from green to yellow (Figure 6a) in the emitted color. Note that the green emission in the device B is composed by the sum of the \(^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}\) and \(^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}\) Er\(^{3+}\) transitions (generated by the 2L large-sized particles) and the \(^5\text{S}_2, ^5\text{F}_4 \rightarrow ^5\text{I}_8\) Ho\(^{3+}\) ones (generated by the 3S small-sized particles).

Then, when temperature is increased, the Er\(^{3+}\) emission is thermally quenched while the Ho\(^{3+}\) red and green emissions are thermally enhanced (Figure 6d). The fine-tune of the upconversion emission color is reversible, allowing the fabrication of transparent displays by smart design of the heating elements (AgNWs/PMMA layer) and accurate deposition of the Ln\(^{3+}\)-doped nanoparticles of controlled size. Indeed, virtually any color (controlled by the UCNPs doping ions) and any trajectory in the CIE 1931 chromatic diagram (controlled by the UCNPs size) can be achieved within the shadowed area in Figure 6a, marking the color coordinates of each Ln\(^{3+}\) ion separately, simply by combining distinct UCNPs.
2.5. Designing high thermal sensitivity devices

The combination of large and small UCNPs in a single device also permits the design of ratiometric and self-calibrated thermometers with relative thermal sensitivity values much higher than those reported so far for single UCNPs.\cite{36} For this, and to the best of our knowledge, we define for the first time a new thermometric parameter as the intensity ratio between one transition of small particles, whose intensity rises with increasing temperature, (e.g., the $^1G_4 \rightarrow ^3H_6$ transition in 1S, namely $I_G$), and other of larger particles, whose intensity is thermally quenched (e.g., the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition in 2L, $I_S$). In other words, defining a new thermometric parameter as the ratio between the emission intensities of thermally enhanced and thermally quenched transitions yields to a stepper temperature change, and thus, to an increased sensitivity in comparison with the conventional approach, that uses emissions with similar thermal behavior. In an exploratory experiment, we simply record the time evolution of the emission spectrum of device A (a proof-of-concept example) when a heating current is employed to the AgNWs. We kept a 10 s delay between measurements to ensure thermal equilibrium between the 1S and 2L nanoparticles. First, we use the emission spectra of 2L particles to calculate the device’s temperature through Equation 1 (Figure 7a). We observe a change of the thermometric parameter $\Delta' = \frac{I_G}{I_S}$ (involving transitions of 1S and 2L UCNPs) with $\Delta$ (Figure 7b). As $\Delta$ is a direct measurement of the device’s temperature, we calibrated $\Delta'$ using the temperature calculated trough $\Delta$ and Equation 1 (Figure 7c). This methodology of using an inner temperature reference allows the system to be self-calibrated, circumventing tedious calibration procedures. For device A we observe that $\Delta'$ increases with temperature (calculated through 2L emissions) resulting in a maximum relative thermal sensitivity of $S_r=5.88 \% \text{ K}^{-1}$ at 339 K. This is more than a 6-fold improvement relatively to the value calculated at the same temperature using the conventional thermometric parameter defined by the ratio between the $I_H$ and $I_S$ Er$^{3+}$ emission bands (Figure 7d).
3. Discussion

3.1. Rationalizing the temperature and size dependent up-conversion emission

The thermal effect on the emission intensity cannot be ascribed to eventual particle coalescence\textsuperscript{40} or to a modification of the surface induced by thermal damage of the capping ligands since both effects would produce irreversible changes in the UCNPs’ emission profiles. Although the thermal emission quenching effects of large nanocrystals and bulk upconverting materials are well known, only recently the anomalous behavior of small-sized UCNPs was demonstrated in a set of systematic studies performed by Jiang’s group.\textsuperscript{[20-23]} Initially, these authors suggested that the phonon density of states is modified by quantum confinement reducing the number of available low-energy modes. Then, a temperature increase would produce a higher population of low energy phonons favoring the energy transfer from the sensitizers (Yb\textsuperscript{3+}) to the activators (Er\textsuperscript{3+}, Tm\textsuperscript{3+}, Ho\textsuperscript{3+}), inducing the concomitant increase on the emission intensity.\textsuperscript{[20]} Afterward, the same group proposed that the adsorption of water molecules could be responsible for a partial quenching of the emission intensity and, then, thermal desorption of water should increase the emission intensity.\textsuperscript{[23]} A recent study by Zhou et al.\textsuperscript{[25]} proposed a thermal-assisted energy transfer mechanism mediated by the chelation of surface Yb\textsuperscript{3+} ions by the carboxylic groups of the capping molecules. This seems to settle the controversy. The vibrational modes of the \([\text{Yb/Y/Tm} \cdots \text{O}]\) coordination, with energies in the 450–650 cm\(^{-1}\) range, generate surface phonons that, upon thermal activation, assist the energy transfer to the emitting ions (Er\textsuperscript{3+}, Tm\textsuperscript{3+} and Ho\textsuperscript{3+}). A layer of such surface phonons, referred as “dark layer”, constitutes a considerable fraction of the total nanocrystal volume, e.g. 70\% for a 10 nm diameter UCNP. Nevertheless, a physical mechanism that fully explains this surface phonon-assisted energy transfer mechanism still remains inconclusive.\textsuperscript{[24]}
Here, we observed a thermal enhancement of the Ln$^{3+}$ emission intensity (Ln=Tm, Er, Ho) in small-sized core@shell UCNPs containing an optically active Yb$^{3+}$-doped NaGdF$_4$ thin shell (Figure S12 in Supporting Information). Moreover, this same thermal enhancement effect is also observed in analogous small-sized core@shell UCNPs with an optically inert NaYF$_4$ or NaGdF$_4$ thin shells, Figure 3d and 3e, Figure 4c and Figure S12 in Supporting Information, contrary to the previous report by Shao et al.$^{[23]}$ who showed that only optically active shells present a thermal enhancement effect. Here, we estimated the thickness of the shell layer by comparing the particle size distribution (determined by DLS and TEM) before and after the growing process of the shell layers (Figures S5, S6 and S7 in Supporting Information). Albeit Zhou et al.$^{[25]}$ reported that β-NaYF$_4$:Tm and β-NaYF$_4$ shells with an average thickness of ~7.5 nm should prevent the formation of the “dark layer”, here we observed a thermal enhancement of the Ln$^{3+}$ emission intensity (Ln=Tm, Er, Ho) in small-sized core@shell nanoparticles with a thinner shell (~1-2 nm) (either optically active or optically inert). This intriguing effect may be due to an incomplete coverage of the surface of the core-UCNPs or to a migration of Yb$^{3+}$ ions through the thin shell layer (facilitated by the temperature increase$^{[41-43]}$). Clearly, although outside the scope of the present manuscript, a systematic and detailed study of the effect of the shell thickness and composition on the thermal enhancement is required.

4. Perspectives

In previous sections we have shown as a proof of concept the possibilities resulting from the combination of UCNPs with different thermal behaviors and the electrothermal control provided by AgNWs networks. Improvements to the design and construction process are under development. For example, the homogeneity in the distribution of UCNPs can be improved by formulating polymer-based nanocomposites. We have successfully tested the incorporation of UCNPs in chloroform solutions of either PMMA or poly(lactic acid) (PLA) that can be
deposited by spin coating on glass, or even on flexible substrates (Figure 8a,b), showing excellent homogeneity and transparency. A second improvement is the construction of flexible electrochromic devices. With this in mind, we assembled an electrothermal device on a flexible cellulose acetate sheet (Figure 8c) depositing 3S and 2L UCNPs by the standard method of drop-casting. The color change of the emissions could be triggered electrically, although a material with a better heat resistance would be preferred. Finally, we have successfully tested the encapsulation of the device in poly(dimethylsiloxane) (PDMS) to provide mechanical stability and isolation from the environment. Furthermore, we have used a PDMS spacer for the construction of an electrothermal cell[44] to study the thermal behavior of UCNPs in liquid suspensions (Figure 8d,e). As an example, Figure 8f shows the emission spectra of 2L UCNPs dispersed in water during the electrothermal heating. Experimental details are described in the Supporting Information.

5. Conclusions

In summary, we fabricated and characterized electrothermal devices based on transparent conductive nanocomposite films containing AgNWs in PMMA for local temperature control. The developed devices present excellent transparency and electrical control properties that can be employed as a tool for fundamental studies or to build functional optoelectronic systems. As an illustrative application, we used the devices to control the temperature dependent emissions of $\beta$-NaY(Gd)F$_4$:Yb$^{3+}$/Ln$^{3+}$ (Ln=Tm, Er, Ce/Ho) UCNPs of different sizes. Independent of the nanoparticle composition and structure, we observed that in particles with a mean size below 15 nm, increasing temperature between 300 and 415 K results in an enhancement of the Ln$^{3+}$ upconversion emission intensity. On the contrary, for large-sized nanoparticles the effect is the opposite and thermal quenching occurs. We realized that the emission intensity is reversibly controlled by applying different DC voltages to the AgNWs network, being the instantaneous
temperature optically measured through the intensity ratio of the \( ^2H_{11/2} \rightarrow ^4I_{15/2} \) and \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) Er\(^{3+}\) transitions. Our results are consistent with the surface phonon-assisted energy transfer mechanism for the enhancement of small-sized UCNPs, which is mediated by the chemical coordination of exposed Ln\(^{3+}\) ions. A quenching effect originated by thermally activated multi-phonon relaxation mechanism dominates at higher temperatures and for large-sized UCNPs.

Smart design permits to fabricate transparent and flexible electrochromic devices covering virtually any color (controlled by the doping Ln\(^{3+}\) ions) and any temperature dependence (controlled by the size of UCNPs) in the CIE chromaticity diagram with a thermal sensitivity \( S_r = 5.88\% \, K^{-1} \) (at 339 K), a 6-fold improvement relatively to the values reported so far for single UCNPs. Such devices may certainly contribute to shed new light on the thermal studies of photonic nanomaterials and may find applications in solar-cells assisted by upconversion, displays, bioimaging, anticounterfeiting devices, and luminescent nanothermometers.

6. Experimental Section

**Materials and Synthesis:** The materials and the syntheses methods are detailed in the Supporting Information. Briefly, AgNWs were synthesized by adapting the polyol method described by Jiu et al.\(^ {45}\)

For the preparation of the AgNWs/PMMA film, 2 mL of the AgNWs colloid in isopropyl alcohol were centrifuged at 1000 rpm and the supernatant was discarded. Then, 200 mL of a PMMA solution, 7% wt. in chlorobenzene, was added followed by vortex agitation to homogenize the mixture. The as-obtained AgNWs-ink was used to form a film over a glass substrate by spin coating at 3000 rpm. We notice that it could also be applied as a conductive ink that cures at room temperature.\(^ {27, 35}\)

Large-sized (> 70 nm) hexagonal (β) NaYF\(_4\):Yb,Ln (Ln=Tm, Er, Ce/Ho) UCNPs were synthesized by the well-established thermal decomposition method of fluoroacetates, as described by Ye et al.\(^ {44}\) whereas small-sized (<15 nm) β-NaGdF\(_4\):Yb,Ln (Ln=Tm, Er, Ce/Ho) UCNPs were synthesized by the co-precipitation route,\(^ {46, 47}\) using rare-earth acetates as the
main precursors (Figure S2 and S3 in Supporting Information). As the quantum yield of the upconversion process is reduced for small-sized nanoparticles,[48] a thin inert shell of undoped NaYF$_4$ or NaGdF$_4$ was grown on the surface of the prepared core-small-sized UCNPs following Liu et al.[47] Additional core@shell UCNPs with a NaGdF$_4$:Yb,Er core and shells formed by undoped NaGdF$_4$ or Yb-doped NaGdF$_4$ were prepared by the co-precipitation route.[46] For both types of core@shell small-sized UCNPs, the thicknesses of the shell layer were estimated from DLS and TEM measurements performed before and after the application of the shell growth protocol (Figures S5-S7 in Supporting Information). The shell’s thickness is a critical factor in the temperature dependence of the UCNPs’ emission, as the upconversion intensity is not enhanced when the Yb$^{3+}$ ions are isolated from the surface of the nanoparticle with an inert shell of ~7.5 nm.[25] Therefore, thinner shells were used here.

**Electron and Optical Microscopy:** Electron microscopy was performed at LNNano, CNPEM, Campinas, Brazil. SEM images were acquired in a FEI Quanta 650 FEG microscope operated at 20 kV. TEM images were obtained with a JEM 2100 equipped with a LaB$_6$ filament and operated at 200 kV. For optical imaging, a NIR CW laser (976 nm) was coupled to a Nikon SMZ 1000 microscope set in dark field mode using an 8× objective lens.

**Upconverting Thermometry:** Upconversion was recorded using a collimated BL976-PAG900 FBG-stabilized laser (ThorLabs) as excitation. All measurements were performed at a nominal power of 500 mW except indicated otherwise. The emission was analyzed with a QEPro spectrometer (Ocean Optics) coupled to a 600 μm diameter optical fiber. A short-pass optical filter was used to avoid the spectrometer saturation by the 976 nm laser. The electrical power ($P$) in the electrothermal device (Figure 6) was calculated through the applied voltage ($V$), controlled manually or using an Arduino board, at the device’s terminals and the current ($i$) flowing across it. To calibrate the UCNPs, a glass substrate covered with the UCNPs was placed in contact with a Peltier plate, whose temperature was controlled using an Arduino board. The
upconversion emission spectra were acquired using the QEPro spectrometer and converted in
temperature using Equation 1. For comparison, a thermocouple was placed in thermal contact
with the glass substrate.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
Authors are grateful to Prof. G. J. A. A. Soler-Illia for his help in establishing this international
 collaboration and to Prof. Daniel Jaque for helpful discussions. This work was supported and performed
under the auspices of the Brazilian agencies CAPES, CNPq and Fundação de Amparo à Pesquisa do
Estado de São Paulo (FAPESP) through Grants #2011/19924-2, #2012/04870-7, #2012/05903-6,
#2015/21290-2, and #2015/21289-4. Work was partially developed in the scope of the project CICECO
– Aveiro Institute of Materials (Ref. FCT UID/CTM/50011/2013), financed by Portuguese funds through
the Fundação para a Ciência e a Tecnologia/Ministério da Educação e Ciência (FCT/MEC) and when
applicable co-financed by FEDER under the PT2020 Partnership Agreement. Financial support of FCT
(PTDC/CTM-NAN/4647/2014 and POCI-01-0145-FEDER-016687) is also acknowledged and the project
has received funding from the European Union’s Horizon 2020 FET Open programme under grant
agreement Nº 801305. EDM acknowledge, respectively, the post-doctoral FAPESP fellowship
#2015/23822-4 and BEPE #2018/12489-8. CDSB acknowledge the grant financed by the
SusPhotoSolutions project CENTRO-01-0145-FEDER-000005. The SEM, TEM and AFM data were
acquired at LNNano, Centro Nacional de Pesquisa em Energia e Materiais (CNPEM) in Campinas, SP,
Brazil.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))
References

[1] M. Bettinelli, L. D. Carlos, X. Liu, *Phys. Today* **2015**, 68, 38.
[2] G. Y. Chen, H. Agren, T. Y. Ohulchanskyy, P. N. Prasad, *Chem. Soc. Rev.* **2015**, 44, 1680.
[3] B. Zhou, B. Shi, D. Jin, X. Liu, *Nat. Nanotechn.* **2015**, 10, 924.
[4] J. Zhou, Q. Liu, W. Feng, Y. Sun, F. Li, *Chem. Rev.* **2015**, 115, 395.
[5] A. Nadort, J. B. Zhao, E. M. Goldys, *Nanoscale* **2016**, 8, 13099.
[6] J. H. Zeng, J. Su, Z. H. Li, R. X. Yan, Y. D. Li, *Adv. Mater.* **2005**, 17, 2119.
[7] F. Wang, Y. Han, C. S. Lim, Y. H. Lu, J. Wang, J. Xu, H. Y. Chen, C. Zhang, M. H. Hong, X. G. Liu, *Nature* **2010**, 463, 1061.
[8] G. Y. Chen, H. L. Qu, P. N. Prasad, X. Y. Chen, *Chem. Rev.* **2014**, 114, 5161.
[9] A. Gnach, T. Lipinski, A. Bednarkiewicz, J. Rybka, J. A. Capobianco, *Chem. Soc. Rev.* **2015**, 44, 1561.
[10] C. S. Ma, X. X. Xu, F. Wang, Z. G. Zhou, D. M. Liu, J. B. Zhao, M. Guan, C. I. Lang, D. Y. Jin, *Nano Lett.* **2017**, 17, 2858.
[11] A. Hilderbrand, F. W. Shao, C. Salthouse, U. Mahmood, R. Weissleder, *Chem. Commun.* **2009**, 28, 4188.
[12] Z. H. Li, H. Yuan, W. Yuan, Q. Q. Su, F. Y. Li, *Coord. Chem. Rev.* **2018**, 354, 155.
[13] F. Vetrone, R. Naccache, A. Zamarron, Á. J. de la Fuente, F. Sanz-Rodriguez, L. M. Maestro, E. M. Rodriguez, D. Jaque, J. G. Solé, J. A. Capobianco, *ACS Nano* **2010**, 4, 3254.
[14] X. Huang, S. Han, W. Huang, X. Liu, *Chem. Soc. Rev.* **2013**, 42, 173.
[15] Y. Q. Lu, J. B. Zhao, R. Zhang, Y. J. Liu, D. M. Liu, E. M. Goldys, X. S. Yang, P. Xi, A. Sunna, J. Lu, Y. Shi, R. C. Leif, Y. J. Huo, J. Shen, J. A. Piper, J. P. Robinson, D. Y. Jin, *Nat. Photonics* **2014**, 8, 33.
[16] Y. D. Han, H. Y. Li, Y. B. Wang, Y. Pan, L. Huang, F. Song, W. Huang, *Sci. Rep.* **2017**, 7, 1320.
[17] E. Downing, L. Hesselink, J. Ralston, R. Macfarlane, *Science* **1996**, 273, 1185.
[18] R. Deng, F. Qin, R. Chen, W. Huang, M. Hong, X. Liu, *Nat. Nanotechn.* **2015**, 10, 237.
[19] Y. J. Liu, Y. Q. Lu, X. S. Yang, X. L. Zheng, S. H. Wen, F. Wang, X. Vidal, J. B. Zhao, D. M. Liu, Z. G. Zhou, C. S. Ma, J. J. Zhou, J. A. Piper, P. Xi, D. Y. Jin, *Nature* **2017**, 543, 229.
[20] D. D. Li, Q. Y. Shao, Y. Dong, J. Q. Jiang, *J. Phys. Chem. C* **2014**, 118, 22807.
[21] D. D. Li, Q. Y. Shao, Y. Dong, F. Fang, J. Q. Jiang, *Part. Part. Syst. Char.* **2015**, 32, 728.
[22] Q. Y. Shao, L. L. Ouyang, L. F. Jin, J. Q. Jiang, *Opt. Express* **2015**, 23, 30057.
[23] Q. Y. Shao, G. T. Zhang, L. L. Ouyang, Y. Q. Hu, Y. Dong, J. Q. Jiang, *Nanoscale* **2017**, 9, 12132.
[24] L. L. Liang, X. G. Liu, *Nat. Photonics* **2018**, 12, 124.
[25] J. Zhou, S. Wen, J. Liao, C. Clarke, S. A. Tawfik, W. Ren, C. Mi, F. Wang, D. Jin, *Nat. Photonics* **2018**, 12, 154.
[26] X. He, A. L. Liu, X. Y. Hu, M. X. Song, F. Duan, Q. M. Lan, J. D. Xiao, J. Y. Liu, M. Zhang, Y. Q. Chen, Q. G. Zeng, *Nanotechnology* **2016**, 27, 475709.
[27] E. D. Martinez, J. H. Lohr, M. Sirena, R. D. Sanchez, H. Pastoriza, *Flex. Print. Electron.* **2016**, 1, 035003.
[28] A. R. Madaria, A. Kumar, F. N. Ishikawa, C. W. Zhou, *Nano Res.* **2010**, 3, 564.
[29] D. A. Dinh, K. N. Hui, K. Hui, P. Kumar, J. Singh, *Rev. Adv. Sci. Eng.* **2013**, 2, 1.
[30] D. P. Langley, M. Lagrange, G. Giusti, C. Jimenez, Y. Brechet, N. D. Nguyen, D. Bellet, *Nanoscale* **2014**, 6, 13535.
[31] Y. Jin, Y. Sun, K. Wang, Y. Chen, Z. Liang, Y. Xu, F. Xiao, *Nano Res.* **2018**, 11, 1.
[32] A. C. Myers, H. Huang, Y. Zhu, *RSC Adv.* **2015**, 5, 11627.
J. G. Lee, J. H. Lee, S. An, D. Y. Kim, T. G. Kim, S. S. Al-Deyab, A. L. Yarin, S. S. Yoon, *J. Mater. Chem. A* **2017**, *5*, 6677.

T. Kim, Y. W. Kim, H. S. Lee, H. Kim, W. S. Yang, K. S. Suh, *Adv. Funct. Mater.* **2013**, *23*, 1250.

E. D. Martínez, A. F. García Flores, H. Pastoriza, R. R. Urbano, C. Rettori, *Sens. Act. B* **2018**, *259*, 475.

C. D. S. Brites, A. Millán, L. D. Carlos, in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 49 (Eds: J.-C. G. Bünzli, V. K. Pecharsky), Elsevier Science, B. V., Amsterdam 2016, 339.

S. Balabhadra, M. L. Debasu, C. D. S. Brites, R. A. S. Ferreira, L. D. Carlos, *J. Phys. Chem. C* **2017**, *121*, 13962.

X. A. Shen, Q. H. Nie, T. F. Xu, S. X. Dai, X. S. Wang, *J. Lumin.* **2010**, *130*, 1353.

D. C. Yu, J. Ballato, R. E. Riman, *J. Phys. Chem. C* **2016**, *120*, 9958.

A. Bednarkiewicz, D. Wawrzynczyk, A. Gagor, L. Kepinski, M. Kurnatowska, L. Krajczyk, M. Nyk, M. Samoc, W. Strek, *Nanotechnology* **2012**, *23*, 45705.

B. Chen, D. F. Peng, X. Chen, X. S. Qiao, X. P. Fan, F. Wang, *Angew. Chem. Int. Edit.* **2015**, *54*, 12788.

S. Duhnen, M. Haase, *Chem. Mater.* **2015**, *27*, 8375.

D. Hudry, D. Busko, R. Popescu, D. Gerthsen, A. M. M. Abeykoon, C. Kubel, T. Bergfeldt, B. S. Richards, *Chem. Mater.* **2017**, *29*, 9238.

X. C. Ye, J. E. Collins, Y. J. Kang, J. Chen, D. T. N. Chen, A. G. Yodh, C. B. Murray, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 22430.

J. Jiu, T. Araki, J. Wang, M. Nogi, T. Sugahara, S. Nagao, H. Koga, K. Suganuma, E. Nakazawa, M. Hara, H. Uchida, K. Shinozaki, *J. Mater. Chem. A* **2014**, *2*, 6326.

F. Wang, R. R. Deng, X. G. Liu, *Nat. Protoc.* **2014**, *9*, 1634.

J. Liu, G. Y. Chen, S. W. Hao, C. H. Yang, *Nanoscale* **2017**, *9*, 91.

J. C. Boyer, F. C. J. M. van Veggel, *Nanoscale* **2010**, *2*, 1417.
Figure 1. Electrothermal devices. (a) Exploded view and (b) schematic of an assembled electrothermal device. (c,d) SEM and (e) TEM images of the device showing (c) a general view of the AgNWs percolation network, (d) a magnification of a selected group of AgNWs and (e) a representative individual AgNW. Dark field images of the electrothermal device under (f) white-light and (g) 976 nm illumination. The green dots are ascribed to the Er$^{3+}$ upconversion emission of nanoparticles’ clusters.
Figure 2. Electron microscopy characterization. (a,b) SEM photographs of 2L UCNPs. TEM photographs of (c,d) 1L, (e-g) 3L, (h) 1S, (i,j) 2S, and (k) 3S. The planes indicated in (b), (d), and (f) correspond to the exposed face while distances represented in (d), (g), and (j) correspond to (10\bar{1}0) planes with inter-plane distances of 4.90, 4.91 and 5.00 Å, respectively.
Figure 3. Response of small- and large-sized nanoparticles to the heat. Temperature-dependent emission spectra of (a) 1L/2L and (d) 1S/2S UCNPs deposited over the AgNWs/PMMA film. Relative change in the sum of the integrated areas of the Er$^{3+}$ and Tm$^{3+}$ transitions with the temperature in (b) 1L/2L and (e) 1S/2S particles (lines are guides to the eyes). Thermal calibration (c) of the 1L/2L and (f) 1S/2S UCNPs using Equation 1.
Figure 4. Effect of cycling the electrical power on the upconversion intensity and thermometric parameter. Sum of the integrated areas of the Er$^{3+}$ (green squares) and Tm$^{3+}$ (blue circles) transitions in a set of on-off electrical power cycles performed in electrothermal devices with (a) 1L/2L UCNPs (1.36 W) and (c) 1S/2S UCNPs (1.30 W). Changes on the thermometric parameter $\Delta=I_H/I_S$ in a set of on-off electrical power cycles for (b) 1L/2L and (d) 1S/2S UCNPs.
**Figure 5.** Stepping the electrical power supplied to the AgNWs/PMMA composite film covered by 1S/2S UCNPs. (a) Temperature calculated from the emission spectra of 2S nanoparticles, according to Equation 1. (b) Integrated intensities of representative emission lines of 1S/2S nanoparticles deposited over the electrothermal device. (c) Supplied electrical power. In the first 10 minutes the increase of the integrated intensity of all transitions is due to the laser-induced heating (no supplied electrical power, inset of a). The vertical lines mark the critical power values (c) and the temperatures corresponding to the maximum of the integrated intensities of the three transitions (a).
Figure 6. Electrochromic devices. (a) CIE 1931 (x,y) chromaticity diagram presenting the chromatic trajectories followed by device A (2L/1S) and device B (2L/3S) upon electrothermal control. The shadowed area marks the color region that can be covered combining the distinct UCNPs. The color coordinates are calculated using the ColorCalculator 7.15 (OSRAM SYLVANIA) software (Supporting Information). (b) Design principle of the electrochromic devices. Temporal evolution of the Ln$^{3+}$ emission integrated areas (Ln=Tm, Er, Ho) recorded.
for (c) device A and (d) device B in the blue (400–500 nm, circles), green (500–600 nm, squares), and red (600–720 nm, diamonds) spectral ranges. The inserts present the initial and final emission spectra and the corresponding emission colors. The color bars represent the color of the devices upon electrothermal control.

Figure 7. (a) Temperature dependence of $\Delta$ measured for 2L nanoparticles. The line corresponds to Eq.1. (b) Thermometric parameter $\Delta'$ as a function of $\Delta$ recorded in a temperature ramp. The temperature to calibrate $\Delta'$ can be calculated using Eq.1. (c) Thermometric parameter $\Delta'$ as a function of temperature. The line is the best fit to experimental data using an empirical sigmoidal curve, Equation S5 in Supporting Information. The fitting parameters are presented Table S2 in Supporting
Relative thermal sensitivity calculated for $\Delta'$. The corresponding value for $\Delta$ (plotted also in Figure S9c, Supporting Information) is presented for comparison.
Figure 8. (a) Emission intensity map in a 5 x 5 mm of a 2S-UCNPs/PMMA nanocomposite prepared by spin coating on a glass substrate. (b) Pictures of 2L-UCNPs/PLA nanocomposite deposited on cellulose acetate flexible slides under laboratory light and 976 nm excitation. The inset presents a photograph under 976 nm excitation. (c) Photograph of the electrothermal device made on a flexible cellulose acetate film covered by 3L and 2S UCNPs by regular drop-casting from cyclohexane colloids under laboratory light illumination. The insets present photographs under 976 nm excitation when the heating is off or on. (d) Scheme and (e) photograph of the electrothermal cell device for the study of thermo-optical properties of nanofluids based on UCNPs (magenta lines). (f) Emission spectra collected from the electrothermal cell device filled with 2L-UCNPs in water suspension. The inset photograph presents the device with 2L-UCNPs water suspension under 976 nm irradiation.
Table 1. Nomenclature, nominal composition and particle size ± standard deviation (determined using the TEM/SEM images) of the UCNPs employed to fabricate the electrochromic devices.

| Sample | Composition | Size (nm) | Obs. |
|--------|-------------|-----------|------|
| 1S     | NaGd_{0.695}Yb_{0.300}Tm_{0.005}F_4@NaYF_4 | 6.6±0.8   |      |
| 2S     | NaGd_{0.78}Yb_{0.20}Er_{0.02}F_4@NaYF_4 | 9.0±2.0   | Small |
| 3S     | NaGd_{0.63}Yb_{0.20}Ce_{0.15}Ho_{0.02}F_4@NaYF_4 | 9.0±2.0   |      |

| Sample | Composition | Size (nm) |
|--------|-------------|-----------|
| 1L     | NaY_{0.695}Yb_{0.300}Tm_{0.005}F_4 | (128±5)×(55±4) |
| 2L     | NaY_{0.78}Yb_{0.20}Er_{0.02}F_4 | (300±8)×(160±6) |
| 3L     | NaY_{0.63}Yb_{0.20}Ce_{0.15}Ho_{0.02}F_4 | (85±5)×(40±3) |

Table 2. Maximum relative change $I(T)/I(T_0)$ of the integrated intensities ($I$) of some Ln$^{3+}$ transitions upon 976 nm excitation in small- and large-sized UCNPs. $T$ and $T_0$ indicate the maximum and initial temperatures of the experiments, respectively, at a constant electrical power of 1.30 W (small-sized) and 1.36 W (large-sized). Values for the transitions indicated as N/A could not be determined due to low signal-to-noise ratio.

| Transition | Peak wavelength (nm) | Emitting center | $\frac{I(T)}{I(T_0)}$ |
|------------|----------------------|-----------------|-----------------------|
|            |                      |                 | Small | Large |
| $^1$I_6→^3$F_4$ | 344                  |                 | N/A   | 0.5   |
| $^1$D_2→^3$H_6$ | 360                  |                 | N/A   | 0.6   |
| $^1$D_2→^3$F_4$ | 450                  | Tm$^{3+}$       | 1.3   | 0.6   |
| $^1$G_4→^3$H_6$ | 476                  |                 | 8.3   | 0.7   |
| $^3$H_4→^3$H_6$ | 798                  |                 | 4.2   | 0.7   |
| $^2$H_9/2→^4$I_{15/2}$ | 407                   |                 | N/A   | 0.1   |
| $^2$H_{11/2}→^4$I_{15/2}$ | 525                | Er$^{3+}$      | 4.0   | 0.8   |
| $^4$S_{3/2}→^4$I_{15/2}$ | 545                |                 | 2.1   | 0.3   |
| $^4$F_{9/2}→^4$I_{15/2}$ | 657                |                 | 3.8   | 0.4   |
| $^5$S_{2/5}F_4→^5$I_8$ | 540                  | Ho$^{3+}$       | 1.9   | 0.5   |
| $^5$F_5→^5$I_8$ | 644                  |                 | 2.0   | 0.9   |
