Communicating Particles: Identification Taggant and Temperature Recorder in One Single Supraparticle

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"Communicating particles" are reported that combine an identification (ID) taggant and a temperature recorder in one single entity—a micron-sized supraparticle. The optical information carriers within the hybrid inorganic-organic supraparticles are three different types of luminescent nanoparticles, which can be read-out using single-wavelength excitation. These three nanoparticle types are assembled into a core-satellite structure via a two-step droplet evaporation technique. The core is built-up from Tb\(^{3+}\) and Eu\(^{3+}\)-doped nanophosphors, providing an environmentally stable ID that is easily tunable through ratiometric spectral coding. This core is surrounded by organic, dye-doped polymer nanoparticle satellites, acting as thermal-history-recorders of their environment. Exposed to a threshold temperature, the luminescence of the utilized 7-diethylamino-4-methylcoumarin-doped polymer nanoparticles is irreversibly quenched. This “turn-off” signal response is attributed to conformational changes in the dyes’ excited state and an alteration of their molecular environment, respectively, triggered by the polymer nanoparticles’ glass transition. Thus, the sensitivity of the temperature recorder can be configured over a wide temperature range by varying the dye-hosting polymer. At the same time, the ID of the particle, stemming from its inorganic building blocks, stays unaffected, thus stable against thermal changes. The idea of communicating particles introduces a promising concept for smart additives.

1. Introduction

The transition of our complex world into an age of sustainability demands the implementation of innovative concepts such as Industry 4.0 and Circular Economy. These concepts require a technology transformation of passive items into smart systems to introduce a “materials world,” in which intelligent, communicating materials are the core item, and simultaneously, the solution to succeeding in both endeavors.

To achieve smart materials, we envision a flexibly applicable additive that can equip any random object with intelligence. One approach towards this is to create “communicating particles”, enabling for instance an information exchange between materials that carry these particles and machines. These particles should be capable of being identifiable, and moreover, being able to deliver information on their elapsed life cycle by recording the exposure to specific environmental influences in a memory function that requires no constant power supply.

To give a practical example, we envision a particle that enables easy, fast and resource efficient repair measures of a complex-structured electronic device through localization and identification of the defect source, e.g., a microelectronic element, caused by local overheating.

Thus, such an object should carry a unique identification (ID) signal and a recorder functionality.

In the field of ID taggants, on the macroscopic scale of a final product, barcodes, radio-frequency identification (RFID) and near-field communication (NFC) tags were introduced as a versatile and accurate technique to identify an object in a simple and fast manner. In recent years, their benefits triggered tremendous research efforts to miniaturize ID taggants, and thereby, enable novel applications. To date, various techniques to label micron- or even nano-scaled objects with markers, carrying a unique ID signal, were established. These include magnetic particles and wires, DNA segments, SERS-encoded metal nanoparticles and luminescent markers all having their own merits and shortcomings.

For practical applications, like plastic recycling, luminescent particles have come to the forefront due to their excellent spatial resolution, often unmatched sensitivity, and ability to be readable-out noninvasively, fast, and contactless. Furthermore, ratiometric intensity measurements of luminescent species, using an internal reference, provide a reliable signal response, independent from external factors, such as analyte concentration or measurement setup.

To create unique and easily adjustable luminescent ID signals, ratiometric spectral coding is a versatile and straightforward approach. This strategy utilizes the combination of spectrally distinguishable luminescent species, e.g., green and red-emitting particles, in adjustable weight ratios resulting...
in altering relative emission spectra, hence, leading to different ID signals. Unlike most other taggant systems, luminescent particles enable simultaneous read-out of multiple functionalities by making use of luminophores whose signals can be differentiated by spectral and/or temporal resolution.\textsuperscript{[14,15,18]}

All in all, luminescent taggants turn out to be an ideal platform to further increase the information storage capacity of ID markers by adding a second stimuli-responsive functionality. Herein, we focus on a first proof-of-principle for the environmental trigger “temperature.”

While the field of reported luminescent temperature sensing systems,\textsuperscript{[16,19]} even down to the scale of a single living cell (luminescence nanothermometry),\textsuperscript{[20]} is enormous in its variety, the field of luminescent temperature recorders, reacting with an irreversible signal response to specific temperature influence, is more narrow. Reversible luminescent temperature probes, i.e., sensors, typically utilize the omnipresent temperature dependence of the specific electronic band structure of materials.\textsuperscript{[16]} Luminescent temperature recorders, however, rely on irreversible thermally induced (maximum temperature, duration of temperature exposure) material changes, affecting the structure or local environment of luminophores. These changes include phase transitions,\textsuperscript{[21,22]} polymer backbone rearrangements,\textsuperscript{[23–25]} excimer formation or dissolution,\textsuperscript{[26–30]} chemical reactions,\textsuperscript{[31,32]} quantum confinement,\textsuperscript{[33]} or partial decomposition.\textsuperscript{[34]} Based on these effects, versatile thermal history recorders in the form of films,\textsuperscript{[24,25,28,32]} as well as micro- and nanoparticles,\textsuperscript{[22,30,33]} were established to indicate cold-chain breaches,\textsuperscript{[25]} heating events like explosions\textsuperscript{[25]} and thermal damages of products.\textsuperscript{[24,32]}

To achieve the goal of bringing together highly sophisticated ID and temperature recorder developments, an entity, uniting both, has to be created.

Supraparticles are a modular approach to fulfill this desire. Supraparticles have recently been introduced as a concept to unite different nanoparticle building blocks in one single particle of higher hierarchical order, enabling the combination of unusual properties, thus achieving novel functionalities.\textsuperscript{[36]} In particular, forced assembly strategies are interesting as they allow for a pretty “chemistry-independent,” flexible combination of very different types of building blocks.\textsuperscript{[17,38]}

The herein introduced concept to achieve a single supraparticle, carrying a unique ID and being at the same time equipped with a recorder functionality (herein: towards temperature), i.e., a communicating supraparticle (CP), was envisioned by us as follows (Scheme 1).

Two types of inorganic lanthanide-doped nanoparticle building blocks with an environmentally inert luminescence in the green and red wavelength area, respectively, were intended to act as coding elements.

A third building block, capable of recording the surrounding’s temperature, was envisaged to come in form of an organic, dye-doped polymer nanoparticle with blue luminescence emission. To accomplish the ultimate functionality of an indestructible ID and a sensitive temperature recorder in one particle, the concept foresaw to force the assembly of the three nanoparticle building blocks in desired ratios into a core-satellite supraparticle via a dedicated two-step droplet evaporation process. The modular design of the supraparticles would then allow for individual adjustment of both functionalities to obtain a huge variety of ID signals and temperature recording with tunable sensitivity.

Due to their inorganic-organic and overall complementary nature, ratiometric read-out of both functionalities should be ultimately achievable with single-wavelength excitation.

![Scheme 1](image-url)
2. Results and Discussion

2.1. Selection and Synthesis of Luminescent Nanoparticle Building Blocks

The first step to produce the envisioned CPs was the careful selection and synthesis of their nanoparticle building blocks. As described in more detail in a previous study, CaF₂ nanophosphors, doped with trivalent lanthanide ions, unite many beneficial properties for ratiometric spectral coding, and therefore, outperform many other nanoparticles candidates, e.g., organic dyes or quantum dots. Briefly summarized, they reveal high photostability, good resistance against environmental influences, e.g., temperature, a large stokes shift, enabling single-wavelength excitation, narrow emission lines and a high encoding capacity. Trivalent lanthanide ions are known for their ion-specific emission by intra-4f-transitions, yielding different luminescence colors, e.g., green for terbium (Tb³⁺) and red for europium ions (Eu³⁺). Herein, polymer nanoparticles derived from commercially available polymeric materials (e.g., polystyrene (PS)) were doped with C₁ via a modified reaction-free emulsion-solvent-evaporation-method (schematically depicted in Figure S3 in the Supporting Information) to aim at achieving a system that can act as temperature recorder. In this synthesis surfactant molecules, in this case sodium dodecyl sulfate (SDS), are utilized to stabilize organic droplets in an aqueous environment after the emulsification step. These droplets contain polymer and dye molecules dissolved in an organic solvent. In the following solvent evaporation step, the surfactant-stabilized droplets serve as templates to form dye-doped polymer nanoparticles. TEM and DLS analysis corroborated the formation of PS:C₁ nanoparticles.

To achieve a very simple and versatile later applicability of the finally envisaged CPs, data acquisition and accuracy in

Figure 1. Morphology and luminescent properties of the nanoparticle building blocks utilized for the CP. 1) TEM micrographs, 2) normalized absorption spectra, 3) normalized fluorescence emission spectra, and digital photographs of dried powders as well as dispersion under UV light excitation (3, insets, λ<sub>exc</sub> = 365 nm, scalebar represents 5 mm) of a) CaF₂:Tb³⁺, b) CaF₂:Eu³⁺, c) PS:C₁ nanoparticles.
fluorescence detection should be optimal and simultaneous read-out of both functionalities in a ratiometric manner should be facilitated, using single-wavelength excitation. Therefore, excitation spectra for the nanoparticles were recorded, monitoring their specific green (541 nm), red (613 nm), and blue (409 nm) luminescence emission in order to identify an ideal single excitation wavelength, eventually (Figure 1a2, b2, c2).

The excitation spectra exhibit a good spectral overlap of the three luminophores to enable single-wavelength excitation for simultaneous monitoring of their combined system. This useful feature was made possible by the combination of lanthanide-doped inorganic nanophosphors, exhibiting a large Stokes shift, with organic dye-doped polymer nanoparticles, with a narrow Stokes shift. As an ideal read-out single excitation wavelength for the combined luminescence system, an excitation wavelength of 365 nm was identified and subsequently selected as standard (Figure 1a2, b2, c2 dashed line). This wavelength is used in most commercially available ultraviolet (UV) lamps and displays an intersection of the relative excitation spectra of the two coding elements, CaF2:Tb3+ and CaF2:Eu3+, which is beneficial for the ratiometric spectral coding. Additionally, the fluorescence emission of Cl is more resistant to photobleaching when excited with a wavelength of 365 nm compared to 254 nm (Figure S4, Supporting Information). Excited with the read-out wavelength of 365 nm, for CaF2:Tb3+ nanoparticles the characteristic transitions of the Tb3+ ions were evident as four bands at 488, 541, 586, and 622 nm related to the 5D4 → 7Fn (n = 6–3) transitions (Figure 1a3).

The emission of CaF2:Eu3+ consisted of the transitions 5D0 → 7Fnm (n = 0–4) resulting in emission bands at 576, 590, 613, 650, 690 nm (Figure 1b3). Both characteristic emissions for CaF2:Tb3+ and CaF2:Eu3+ are of low line width and result in strong green and red light emission, respectively.

In contrast to the previously introduced dye-doped polymer temperature recorders by Lopez et al. that are based on initial dye exchanger formation at high dye concentrations (2 wt%), for our approach, a low dye concentration of 0.01 wt% was used. PS nanoparticles doped with 0.01 wt% Cl (PS:Cl) showed an intense blue luminescence with their emission maximum located at 409 nm (Figure 1c3). The emission maximum of PS:Cl nanoparticles was significantly hypsochromically shifted compared to its typical appearance around 450 nm which is often reported. This shift may be attributed to the dual-band emission of Cl at 405 – 420 nm and 450 nm, as revealed from laser studies. With increasing solvent polarity or use of solvents that enable hydrogen bonding due to a functional group (e.g., alcohols), an intense bathochromic shift of the fluorescence emission maximum was observed. Thus, the observed hypsochromic shift may be attributed to the absence of an interaction between the PS chains and Cl, which enables a good spectral separation of the three herein used luminophores.

It is evident that the emission characteristics of the three luminophores revealed only a small spectral overlap. Signal separation can therefore be easily enabled by means of spectral separation using different optical emission filters. Hence, PS:Cl, CaF2:Tb3+, and CaF2:Eu3+ are a suitable combination for a dual-functional luminescent tagant. To find such a combination is in practice a high challenge, and this specific combination has – to the best of the authors' knowledge – never been used before. It is noteworthy that the emission intensity of all nanoparticle building blocks can be easily adjusted by varying the content of the encapsulated luminophores (Figure S5, Supporting Information). In the case of PS:Cl, this lead to a bathochromic shift of the emission maximum from 409 to 413 nm, when the Cl concentration exceeded 0.1 wt%, which is associated with excimer formation.

2.2. Synthesis of Communicating Supraparticles

To unite the three individual luminescent nanoparticle types to one supraparticle with a core-satellite structure, a forced droplet evaporation approach was used, practically conducted by two consecutive steps using the process tool “spray-drying.” Briefly described, in a spray-drying process, small droplets from (nano)particle dispersions are generated and introduced into a hot chamber. Through the subsequent solvent evaporation, the remaining particles in the droplets are forced together to assemble to a supraparticle.

The ID core was built up from the first forced assembly step (first spray-drying step) to unite the coding elements, i.e., the CaF2:Tb3+ and CaF2:Eu3+ nanoparticles, in tunable desired ratios (Figure 2a1). At an equal-weight ratio (1:1), a white powder with a green luminescence was obtained. Scanning electron microscopy (SEM) revealed that the powder consists of spherical and doughnut-shaped nanostructured supraparticles (Figure 2a2; for SEM overview micrographs: see Figure S6a in the Supporting Information). The particle size ranges from 2.1 – 10.8 µm (d0.1 and d0.9) with a d0.5-value of 5.3 µm (laser diffraction measurements, Figure S7, Supporting Information). Excited at 365 nm, the luminescence spectrum was found to be mainly dominated by the CaF2:Tb3+ nanoparticles in accordance with the observed green luminescence color (Figure 2a3). In contrast, the CaF2:Eu3+ luminescence is very low in intensity. Following the forced assembly via spray-drying, the ID had to be further activated in a calcination process to enhance the luminescence and thereby rendering the ID functionality inert towards temperature changes (Figure 2b1).

This subsequent process comes with complex solid-state evolutions that need to be considered. Exhaustive details are discussed thoroughly in the Supporting Information section for interested readers. However, a deeper discussion at this point is avoided to not distract the reader’s focus too much with these details in this main body of the article.

Most importantly, no major changes of the supraparticles size or morphology were detected after calcination (SEM, Figure 2b2; Figure S6b, Supporting Information), however, the CaF2 primary particles increased in size (XRD, Scherrer’s formula Figure S8 in the Supporting Information). While the CaF2:Eu3+ luminescence was significantly enhanced after calcination, the CaF2:Tb3+ emission was slightly quenched, leading to the observed color shift from green to orange (Figure 2b3). As previously reported elsewhere, indication for an energy transfer from Tb3+ to Eu3+ was found, matching the recorded luminescence changes (Figure S9, Supporting Information).
Notwithstanding after the ID activation, CaF\textsubscript{2}:Tb\textsuperscript{3+} and CaF\textsubscript{2}:Eu\textsuperscript{3+} emissions are easily detectable and can be utilized as signal elements for ratiometric spectral coding. Due to the spectral overlap of the dominant emission band located at 590 nm, resulting from the \( 5\text{D}_4 \rightarrow 7\text{F}_4 \) transition of Tb\textsuperscript{3+} (586 nm) and the \( 5\text{D}_0 \rightarrow 7\text{F}_1 \) (590 nm) of Eu\textsuperscript{3+} (Figures 1a3,b3 and 2b3), to generate the spectral ID signal, the distinguishable emission peaks at 541 nm (CaF\textsubscript{2}:Tb\textsuperscript{3+}, \( 5\text{D}_4 \rightarrow 7\text{F}_5 \)) and 613 nm (CaF\textsubscript{2}:Eu\textsuperscript{3+}, \( 5\text{D}_0 \rightarrow 7\text{F}_2 \)) were assigned. When built-up from an equal-weight ratio of CaF\textsubscript{2}:Tb\textsuperscript{3+} and CaF\textsubscript{2}:Eu\textsuperscript{3+} nanoparticles, and doped with an appropriate concentration of the respective lanthanide ions, in this case 5 mol\% for CaF\textsubscript{2}:Tb\textsuperscript{3+} and 3 mol\% for CaF\textsubscript{2}:Eu\textsuperscript{3+}, these peaks leveled up to an almost equal intensity (Figure 2b3).

To combine the activated ID supraparticles with the C1-doped polymer nanoparticles, i.e., PS:C1, to the final CPs, a subsequent forced assembly of the ID supraparticles with the T-recorder nanoparticles was conducted by carrying-out a second spray-drying round (Figure 2c1).

A white powder with a strong violet luminescence was obtained. SEM micrographs show that the resulting particles possess a core-satellite structure, where the polymer nanoparticles are directly attached to the CaF\textsubscript{2} supraparticles surface (Figure 2c2). No indication for isolated polymer nanoparticles, nor other particle structures besides the core-satellite structure, was found (SEM overview images, Figure S6c, Supporting Information; laser diffraction measurements, Figure S7, Supporting Information). Besides forcing assembly of the building blocks by the evaporating liquid environment during spray-drying, which leaves the particles no other option than to unite, another assembly-aid was employed: The formation of the observed core-satellite structure was further promoted by the oppositely charged surfaces of CaF\textsubscript{2} ID supraparticles (\( +32 \text{ mV} \), zeta-potential measurements, Table S10, Supporting Information) and polymer nanoparticles (\( -43 \text{ mV} \)). The positive surface charge of the CaF\textsubscript{2} particles arises mainly from the dissociation of fluoride ions from the crystal surface.\cite{55} The negative surface charge of the polymer nanoparticles resulted from the used surfactant SDS and yielded attractive forces between ID supraparticles and polymer nanoparticles, which is known for self-limited self-assembly principles.\cite{56} Therefore, this charge-assisted forced assembly process caused exclusive

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**Figure 2.** Steps toward the fabrication of the CP. 1) Schemes of the different CP synthesis steps; 2) SEM micrographs (insets: magnified sections), 3) fluorescence emission spectra (\( \lambda_{\text{exc}} = 365 \text{ nm} \)), and digital photographs under UV light excitation (inset, \( \lambda_{\text{exc}} = 365 \text{ nm} \), scalebar represents 5 mm) of a) a pristine ID core supraparticle, b) a calcinated ID core supraparticle, and c) a final CP (the arrows in c3 indicate the emission bands used for the read-out of CPs’ functionalities; blue: C1, green: CaF\textsubscript{2}:Tb\textsuperscript{3+}, red: CaF\textsubscript{2}:Eu\textsuperscript{3+}).
formation of core-satellite supraparticles, thus crucially contributed to the overall goal of having all three luminescent components united in one particle entity.

The luminescence spectrum of the core-satellite supraparticles exhibited the addition of an intense, broad blue emission band to the ID spectrum, peaking at 409 nm (Figure 2c3). This emission band of PS:C1 overlapped with the $^{5}D_{4} \rightarrow ^{7}F_{6}$ emission from CaF$_2$:Tb$^{3+}$ nanoparticles at 488 nm. However, no significant interference with intense Tb$^{3+}$ emission band at 541 nm $^{5}D_{4} \rightarrow ^{7}F_{5}$, as well as with the Eu$^{3+}$ emission was observed. This enables an independent read-out of the different functionalities of the CPs, namely the T-recorder (C1, Figure 2c3 blue arrow) at 409 nm, and the ID at 541 nm (Tb$^{3+}$, Figure 2c3 green arrow), and 613 nm for (Eu$^{3+}$, Figure 2c3 red arrow). Thereby, a large spectral separation of more than 70 nm in wavelength between the different optical signals of the CPs was obtained, which contributes to their applicability and coding capacity.

### 2.3. Operation Principle of the Communicating Supraparticles

The ratiometric read-out of the CP functionalities was realized using single-wavelength excitation with 365 nm. The signal responses of the ID signal (ID) and the temperature recorder ($T_{\text{recorder}}$) are obtained from Equation 1 and Equation 2 respectively, utilizing relative emission intensity $I_1/I_2$ ratios of the luminophores' characteristic wavelength

\[
ID = \frac{I_{613 \text{ nm}}}{I_{541 \text{ nm}}} 
\]

\[
T_{\text{recorder}} = \frac{I_{409 \text{ nm}}}{I_{541 \text{ nm}}} 
\]

To explore the viability of the CPs, they were exposed to different selected, increasing temperatures, ranging from 40 to 180 $^\circ$C for 1 h. Afterward, the system was allowed to cool down to room temperature (RT). To investigate, whether the thermal history could be recorded, the system was subsequently studied with fluorescence spectroscopy.

The obtained emission spectra were normalized to the emission of CaF$_2$:Tb$^{3+}$ (541 nm) to facilitate the comparison of pristine and heated particles (Figure 3a). While the luminescence signal in the green and red wavelength area remained nearly constant upon exposure to elevated temperatures, significant changes were observed in the blue wavelength area. The temperature dependent alteration of the PS:C1 emission band was divided into three segments (represented with dashed lines). Only a slight intensity decrease was recorded upon an exposure to temperatures below 70 $^\circ$C (segment 1), before the emission dropped monotonously until 100 $^\circ$C without structural changes of the emission band (segment 2). A further temperature increase lead to a bathochromic shift of the maximum emission of C1 from 409 to 450 nm (segment 3) that initially also contributed to an intensity decrease at 409 nm. Afterward, no significant changes of the C1 emission intensity were detected.

![Figure 3. Operating principle of the CP. Normalized fluorescence emission spectra ($\lambda_{\text{exc}} = 365$ nm, normalized to 541 nm) recorded at RT after heating the CP for 1 h at different temperatures (a, red arrows indicate an increase in exposed temperature), calculated signal responses for the CP’s ID and T-recorder functionalities (b, error bars represent standard deviation of three averaged measurements of randomly picked powder samples, lines are a guide for the eye), and SEM micrographs from the CPs surface (c) after different temperature treatment (1: 80 $^\circ$C, 1 h, 2: 100 $^\circ$C, 1 h, 3: 120 $^\circ$C, 1 h).](image-url)
until 180 °C. Using Equation 1 and Equation 2, the recorded spectral information was transferred into signal responses of the supraparticles ID and temperature recorder functionalities, respectively (Figure 3b). While it is evident that the ID signal remained constant (+4.5%) upon temperature treatment, the \( T_{\text{recorder}} \) signal exhibited a plateau region until around 60 °C, before showing a monotonous irreversible signal decrease with increasing temperatures up to 120 °C. These results indicate a proof-of-principle for the proposed smart CPs, possessing an environmentally inert ID signal and at the same time a temperature recording functionality.

In order to elucidate the mechanism behind the observed temperature (in)dependent luminescence signal characteristics of the supraparticles, XRD, SEM, dynamic scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were employed. XRD pattern of pristine and temperature treated supraparticles remained almost unchanged, matching the constant ID signal stemming from the lanthanide-doped CaF₂ nanophosphors (Figure S11, Supporting Information). SEM micrographs of the supraparticles show an almost unchanged core-satellite structure after temperature exposure up to 100 °C (Figure 3c1, c2). Exposed to 120 °C, however, they reveal a softening of the spherical polymer nanoparticles on the supraparticle surface that results in the formation of irregular shaped clusters stemming from multiple individual nanoparticles (Figure 3c3). DSC analysis indicated that this structural change is in well accordance to the determined glass transition \( T_g \) of PS:C1 nanoparticles around 105 °C (Figure S12, Supporting Information). Thermal analysis of C1 revealed a melting process with an onset around 70 °C and a peak summit at 78 °C, however, no evidence of recrystallization was found (DSC, Figure S13a, Supporting Information). Decomposition of C1 was measured at temperatures between 200 and 300 °C (TGA, Figure S13b, Supporting Information).

Linking these data with the observed spectral changes of the PS:C1 luminescence emission (Figure 3a, we hypothesize two effects to be mainly accounting for the observed “turn-off” signal response of the temperature recorder. The monotonous decrease between 60 and 100 °C (Figure 3b, segment 2) is mainly attributed to irreversible conformal changes of C1 dye, triggered by the melting process around 70 °C inside the polymer nanoparticles. C1 is known to undergo intramolecular charge transfer upon excitation.\(^{[45]}\) Due to melting of C1 without recrystallisation afterward, radiationless deactivation from the dye’s excited state may be promoted due to an increasing transition from a fluorescent planar intramolecular charge transfer state to a partially nonfluorescent twisted charge transfer state (Figure S14, Supporting Information).\(^{[51]}\) In the excited twisted charge transfer state, radiationless relaxation is made possible by the rotation of the attached diethylamino-group at position 7. Thereby, the lifetime of the dyes excited state was reduced, resulting in a quenched emission intensity.

At temperatures higher than 100 °C, a bathochromic shift of the C1 emission is observed which is attributed to a second effect within the PS:C1 particles (Figure 3b, segment 3). When the temperature exceeds the glass transition of PS around 105 °C, the polymer softens leading to increased mobility of the polymeric chains. This softening enables a movement of the C1 molecules, resulting in an alteration of their direct environment.

As the bathochromic shift indicates the interaction of C1 with functional groups that are capable of forming intramolecular hydrogen bonding, we assume a movement of C1 to the particle surface.\(^{[44,45,51]}\) This enables an interaction of C1 molecules with their surrounding species, to form H-bonded excited state dye complexes with a reduced fluorescence quantum yield. This results in the observed bathochromically shifted and simultaneously quenched luminescence emission. To support our hypothesis for the “turn-off” signal response of the temperature recorder, the polymer type for the C1-hosting polymer nanoparticle matrix, and thereby the \( T_g \), was altered. Similar behavior was observed for these temperature recorder satellites, which will be discussed in more detail in the next chapter.

To elucidate the kinetics behind of the detected \( T_{\text{recorder}} \) signal degradation, CPs equipped with PS:C1 were heated at 120 °C for varying duration, ranging from 10 min to 8 h. After cooling down to RT, emission spectra were recorded (Figure S15a, Supporting Information). The irreversible conformal changes of C1 were fast, happening within the first 10 min, clearly visible from an intense signal decrease without major changes in the wavelength of the emission maximum. The movement of the C1 molecules due to the softening of PS, indicated by the bathochromic shift of the C1 emission maximum, was detected to start immediately after 10 min and reached a steady state after 60 min. The associated signal response of the ID functionality confirms a temperature stable ID signal (+3%) of the CPs (Figure S15b, Supporting Information). The \( T_{\text{recorder}} \) signal approached its final value within 30 min, before indicating a specific threshold temperature after 60 min without significant changes for longer temperature exposures.

### 2.4. Tunability of ID and Temperature Recorder Functionalities

For practical applications, it is desirable to be able to render ID and temperature recorder functionalities of the CPs tunable, leading to a huge code variety and defined signal response upon specific temperature exposure, respectively. Thereby, one would have a smart taggant at hand that enables simultaneous monitoring of the identity and the thermal history of different goods, ultimately identifying counterfeits or unintended temperature abuse.

To achieve both endeavors, we used the modular toolbox-like design of the introduced CPs. For creating supraparticles with different ID signals, the weight ratios of CaF₂:Tb\(^{3+}\) and CaF₂:Eu\(^{3+}\) in the initial spray-drying step were adjusted. To yield a proof-of-concept, ten weight ratios, ranging from 10:1 to 1:8 (CaF₂:Tb\(^{3+}\):CaF₂:Eu\(^{3+}\)), were investigated, leading to ten different emission characteristics (Figure 4). The applied optical encoding principle of ratiometric spectral coding becomes clearly evident by comparing normalized emission spectra of the differently encoded supraparticles (relative emission variation of PS:C1 are observed due to normalization to the varying CaF₂:Tb\(^{3+}\) share contained in the supraparticles). Starting form an equal weight ratio, with increasing share of CaF₂:Eu\(^{3+}\), the emission intensity at 613 nm raised monotonously (Figure 4a), while it decreased for rising proportions of CaF₂:Tb\(^{3+}\) (Figure 4b). Using Equation 1, the ID signal information of the
produced CPs is determined (Figure 4c,d). The obtained ID signals reveal that the variation of the CaF$_2$:Tb$^{3+}$ : CaF$_2$:Eu$^{3+}$ weight ratio yields CPs with a clearly distinguishable ID signal. The respective ID signal results from the colocalization of multiple luminescent signal building blocks into one single particulate entity that afterward carries the combined signal information in its emission characteristic. The nonlinear behavior of the ID signal with altering weight ratios in the calcinated supraparticles may be attributed to the previously introduced energy transfer from Tb$^{3+}$ to Eu$^{3+}$. However, this effect is hampering neither the coding principle nor the supraparticles coding capacity. The resulting ID signals can be even distinguished from one another with bare eyes (Figure 4e).

To verify that a single CP carries a unique luminescent ID signal that does not differ from other CPs produced within one batch, energy-dispersive X-ray (EDX) analysis was exemplarily performed on three randomly selected CPs with an equal weight ratio of CaF$_2$:Tb$^{3+}$ (5 mol%) and CaF$_2$:Eu$^{3+}$ (3 mol%) (Figure S16, Supporting Information). The comparison of the elemental mapping of Ca, F, as the main elements, of the CaF$_2$ nanoparticles as well as the mapping of C, as the main element of the PS:C1 particles, illustrates the core-satellites structure of the CP. The elemental mapping of Tb and Eu within one CP corroborates a homogenous distribution for both elements. The determined mass contents of the different elements within one CP reveals that the relative mass ratio of Eu and Tb is nearly constant (Table S17, Supporting Information). This matches the small deviation of the CPs luminescent ID signals of less than 3% during their fabrication (Figure 3b). Therefore, with ratiometric spectral coding, using two coding elements, already a huge coding variety can be established. Recently, it was shown that this encoding capacity can be substantially enhanced using more luminescent coding elements$^{[10,11]}$ or designing luminescent labels, e.g., QR-codes.$^{[57]}$

Based on the hypothesized temperature recorder mechanism, to adjust the sensitivity of the CPs temperature recorder functionality, the C1-hosting nanoparticle’s polymeric material was altered. We assumed that C1-doped polymer nanoparticles, owing a lower $T_g$, already show a distinct irreversible “turn-off” signal response at lower temperatures, while the signal decrease of temperature recorder nanoparticles with a higher $T_g$ is shifted toward higher temperatures. Therefore, various standard commercially available polymeric materials, possessing lower, poly(lactic acid) (PLA), and higher $T_g$ (polymethyl methacrylate (PMMA) and polysulfone (PSU)), respectively, were utilized to synthesize temperature
Due to the low g of PLA, the two hypothesized effects, T and a bathochromic shift of the C1 emission band triggered by their Tg around 58 °C (Figure S20a, Supporting Information). The CPs, using different polymer:C1 satellites, however, yielded significantly altered temperature recorder signal responses. These results support the hypothesized temperature recording mechanism based on polymer:C1 nanoparticle satellites of the herein introduced CPs. Furthermore, the variation of the polymeric material, used to produce the polymer:C1 nanoparticle satellites, grants for an adjustable sensitivity of the CPs’ temperature recorder functionality. Due to the varying glass transition of the utilized polymeric materials, the bathochromic shift of the C1 emission is initiated at different specific temperatures. This bathochromic shift results from the altered molecular environment of the dye after migrating to the particle surface. This dye movement is enabled by the mobility of the polymeric chains when the temperature exceeds the glass transition of polymer matrix. As this effect is significantly contributing to the temperature recorders “turn-off” signal, the choice of the polymeric material is key to yield an easily adjustable temperature recorder functionality of the CPs over a wide temperature range. Ultimately, also the use of plasticizers, copolymers and blends that alter the glass transition of a polymeric material can be considered for further adjustment of the temperature recorders sensitivity.[30] Based on these findings, the temperature recorder functionality of CPs can be tailored toward individual limitations of various goods, enabling recording of specific unintended temperature abuse.

3. Conclusion

In this work, nanostructured core-satellite supraparticles that expand the variety of nowadays smart additives by combining identification and temperature recorder functionalities in one communicating particle were developed. Key to unite the two functionalities and enable their simultaneous read-out, using single-wavelength excitation, is the hybrid inorganic-organic nature of the CPs. The supraparticles are fabricated...
in scalable spray-drying processes, employing three different spectrally distinguishable nanoparticle types. Charge-assisted forced assembly of the different particles yields exclusively the desired core-satellite structure. The ID functionality in the supraparticle core, based on CaF₂: Tb³⁺ and CaF₂: Eu³⁺ nanoparticles, is demonstrated to be inert towards temperature changes. C1-doped polymer nanoparticles, acting as the CPs temperature recorder satellites, show an intense blue luminescence that is irreversibly quenched upon exposure to temperatures exceeding a specific threshold. Thus, the combined signal response of the CPs allows for simultaneous monitoring of the particles identity and elapsed thermal history. Additionally, the applied ratiometric detection of both functionalities provides reliable information even at low analyte concentrations, rendering them attractive additives for various applications.

Furthermore, the CPs toolbox-like design enables the readily adjustment of both functionalities. Altering the weight ratio of the two coding elements leads to a huge variety of unique ID signals. The sensitivity of the temperature recorder satellites can be tailored toward specific applications over a wide temperature range, including barely reported high temperatures (140–180 °C), by simply varying the Cl-hosting polymeric material. In summary, the herein presented CPs and their underlying conceptual design give rise to an entire new family of hierarchical structured, multi-functional, and stimuli-responsive particles, applicable as smart additives to foster materials’ intelligence.

### 4. Experimental Section

**Materials and Reagents:** Ammonium fluoride (NH₄F, ≥98%) was purchased from Merck Millipore. Calcium chloride (CaCl₂, anhydrous, 90%) was received from Supelco. Sodium dodecyl sulfate (SDS, ≥98%) was bought from Acros Organics. Polylactic acid (PLA, Ingeo 4060D) was received from NatureWorks. Dichloromethane (DCM, ≥99.5%) was bought from Carl Roth. Poly(methyl methacrylate) (PMMA, Mₜ = 120,000). Polysulfone (PSU, Mₜ = 200,000), polystyrene (PS, Mₜ = 192,000), and 7-diethylamino-2-methylcoumarin (coumarin 1, C1, C₁₄H₁₇NO₂, 99%) were purchased from Sigma Aldrich. Terbium and europium chloride hexahydrates (TbCl₃ · 6 H₂O, EuCl₃ · 6 H₂O, ≥99%) were bought from Changsha Easchem Co. China and heated for 15 min at 100 °C in an oven before use. All chemicals were used without further purification. Water was deionized before use.

**Synthesis of Lanthanide-Doped Calcium Fluoride Nanoparticles:** Lanthanide-doped CaF₂ nanoparticles were synthesized in a precipitation reaction according to a previously reported procedure.(8) To obtain CaF₂ nanoparticles doped with 5 mol% Tb³⁺, 24.87 g CaCl₂ (224.3 mmol) and 4.34 g TbCl₃ · 6 H₂O (11.8 mmol) were dissolved in 240 ml deionized water in a beaker. In a second beaker, a NH₄F solution was prepared from Merck Millipore. Calcium chloride (CaCl₂, anhydrous, 90%) was received from Supelco. Sodium dodecyl sulfate (SDS, ≥98%) was bought from Acros Organics. Polylactic acid (PLA, Ingeo 4060D) was received from NatureWorks. Dichloromethane (DCM, ≥99.5%) was bought from Carl Roth. Poly(methyl methacrylate) (PMMA, Mₜ = 120,000). Polysulfone (PSU, Mₜ = 200,000), polystyrene (PS, Mₜ = 192,000), and 7-diethylamino-2-methylcoumarin (coumarin 1, C1, C₁₄H₁₇NO₂, 99%) were purchased from Sigma Aldrich. Terbium and europium chloride hexahydrates (TbCl₃ · 6 H₂O, EuCl₃ · 6 H₂O, ≥99%) were bought from Changsha Easchem Co. China and heated for 15 min at 100 °C in an oven before use. All chemicals were used without further purification. Water was deionized before use.

**Synthesis of Coumarin 1 Doped Polymer Nanoparticles:** C1-doped polymer nanoparticles were synthesized via an emulsion–solvent-evaporation-method (Figure S3, Supporting Information), modified from a previous study,(9) initially, stock solutions of C1 (0.5 mg/ml) in DCM and SDS (0.5 wt%) in deionized water were prepared. For polymer nanoparticles doped with 0.01 wt% of C1, 2 μl of the C1 stock solution (0.1 mg, 0.43 μmol) and 8 ml DCM was added to 1 g of the polymer of interest (PLA, PS, PMMA, PSU). The polymer was dissolved upon magnetic stirring for at least 1 h. Subsequently, 20 ml of the aqueous SDS stock solution (100 mg, 34.7 mmol) was added, leading to a clearly visible phase separation. The obtained mixture was emulsified via sonication for 120 s (Branson Ultrasonic Sonifier, output: 20, constant duty cycle) using an ice bath for cooling. A milky nanoemulsion was obtained. From this emulsion, the organic solvent was evaporated under vigorous stirring at RT overnight, inducing the template-assisted precipitation of polymer, ultimately resulting in an encapsulation of C1 dye in nanoparticle dispersions. The obtained aqueous polymer nanoparticle dispersion was further purified via dialysis against 4 L deionized water (five water exchanges in 48 h).

**Synthesis of Communicating Supraparticles:** Communicating supraparticles were prepared via two consecutive spray-drying processes. To create the ID core supraparticles, CaF₂:Tb³⁺ and CaF₂:Eu³⁺ dispersions were mixed in desired weight ratios (e.g., 1:1) upon magnetic stirring and adjusted to a particle concentration of 10 wt% with deionized water. The obtained mixture was spray-dried using a lab-scale spray dryer (Buchi Labortechnik AG, B290 mini connected to a dehumidifier B-296). The spray-drying parameters were kept constant for all experiments (inlet temperature: 85 °C, pump rate: 0.2 l · h⁻¹, aspirator power: 85%, N₂ gas flow: 40 l · h⁻¹, outlet temperature: 47 °C). The obtained powder was calcinated in a muffle furnace (L9/S, Nabertherm) at 430 °C (heating rate: 10 K · min⁻¹) for 4 h in order to activate the ID supraparticles. Subsequently, CPs were synthesized in a second spray-drying process from an aqueous dispersion of ID supraparticles and polymer:C1 nanoparticles in a weight ratio of 50:1 (10 wt% particles in dispersion) using the same spray-drying parameters. The prepared CPs were dried in a vacuum drying chamber (VO29, Memmert) at RT and 40 mbar for 4 h.

**Characterization:** Transmission electron microscopy (TEM) analysis was carried out with a JEM-2010 (JEOL) using an acceleration voltage of 200 kV. Carbon coated copper TEM grids were used for the sample preparation. For morphological analysis of the produced supraparticles, the powder was prepared on a carbon pad and imaged via scanning electron microscopy (SEM) using a Gemini 500 (Zeiss) with an acceleration voltage of 2 kV and a secondary electron detector (SE2). Energy dispersive x-ray (EDX) analysis was conducted with a JSM-F100 (JEOL) using an acceleration voltage of 15 kV. X-ray diffraction (XRD) analysis was performed on a D8 Advance diffractometer (Bruker) equipped with a Lynxeye XE-T detector employing Cu Kα radiation. The crystallite size of the CaF₂ particles was calculated with the Scherrer’s formula for the reflex (111) at 28.3° from the measured X-ray patterns. Particle size distributions and zeta potential were determined from diluted nanoparticle dispersion by dynamic light scattering (DLS) using a Zetasizer Nano (Malvern Panalytical) after a sonication step. Particle size distributions of the produced supraparticles were obtained from laser diffraction measurements using a Mastersizer 2000 and a Hydro 2000S (Malvern Panalytical). Supraparticles were dispersed in water under mechanical stirring and sonication.

Fluorescence emission spectra were recorded with a FP-8500 spectrofluorometer (Jasco). Excitation and emission bandwidth were set to 5 and 2.5 nm, respectively. All spectra were corrected with a blank sample and a calibrated WL light source ESC-842 (Jasco). Digital photographs were taken with an iPhone SE 2020 under UV illumination with a VL-215-LC UV lamp (Vilber Lourmat).

Glass transitions of polymers and the melting point of C1 were characterized by differential scanning calorimetry (DSC) with a DSC 214 Polyma (Netzsch) at a heating rate of 10 K · min⁻¹ in the temperature range from 20 to 200 °C followed by cooling to 20 °C at 10 K · min⁻¹. The decomposition of C1 was determined using thermogravimetric analysis (TGA). TGA was carried out in synthetic air atmosphere (10 ml · min⁻¹ O₂, 40 ml · min⁻¹ N₂) with a heating rate of 10 K · min⁻¹ in the temperature range from 30 to 1000 °C using a TG 209 F1 Libra (Netzsch).

Thermal investigation of the communicating supraparticles was carried out in a drying chamber (VO29, Memmert) by exposing the samples to 85 °C, pump rate: 0.2 l · h⁻¹, aspirator power: 85%, N₂ gas flow: 40 l · h⁻¹, outlet temperature: 47 °C.

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10–20 mg particles in a glass vial to elevated temperatures ranging from 40 to 180 °C for 1 h. For the kinetic study, the exposure time at 120 °C was varied between 10 to 480 min.

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

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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