Hybrid Inorganic–Organic Luminescent Supraparticle Taggants with Switchable Dual-Level ID

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1. Introduction

Smart (sub)micrometer-scaled particles, which could be incorporated in a highly flexible manner into any raw material or product component and equip these with encoded information, bear great potential to contribute to a sustainable future.[1] In particular, the use of identification (ID) taggants as smart additives could enable automatic identification, tracking, and tracing of materials, thus aiding the implementation of sustainable concepts, such as Circular Economy.[2–6] Additionally, developments in the digitalization of manufacturing could be fostered by the realization of the Internet of Things, thanks to programmable ID taggants.[7–9] Moreover, ID taggants could contribute to the establishment of transparent global trading networks and prevent product counterfeiting, thereby improving quality assurance.[10–12]

Established marking technologies such as radio-frequency identification (RFID) chips are suitable for superficially marking macroscale end products.[14] However, tagging of micrometer-sized product (sub) components or raw materials, which are often further processed under harsh conditions, remains a major challenge.

In addition, RFID chips offer little to no readout protection.[11,16] Sensitive data, such as product-specific information, can therefore leak out unnoticed and uncontrollably and thereby, enabling misusage and product counterfeiting on a large scale.

Micrometer-sized additives, bearing intrinsic physicochemical ID signatures, are advantageous, since they can be flexibly applied to even the smallest product components.[14] In a large number of scientific works, spectrally encoded composite materials have been created by combining nanoparticles (NPs) or molecules as encoding elements that possess distinctive physical, hence code-carrying signal properties, such as photoluminescence (PL)[17–23] or magnetism.[24–27]

Luminescent taggants are particularly attractive due to their high sensitivity, ease of visualization of their codes, and the possibility of utilizing additional coding parameters, such as spatially resolved arrangement of chromophores (Quick-Response (QR) code-like patterns)[28–30] and luminescence kinetics, including fluorophore lifetime and phase angle.[31–33]

To achieve a high coding capacity, spectral luminescent encoding has come to the forefront. More precisely, spectral optical coding relies on relative intensity ratios of spectrally distinguishable emission bands, provided by different luminescent coding elements combined in one taggant.[37,38] The resulting ratiometric luminescent ID signature can thus be easily transferred into a numerical code and digitized.

A promising approach for the realization of ratiometrically encoded additives is the assembly of nanosized building blocks, yielding hierarchically structured, micrometer-sized entities. These units can be termed supraparticles (SPs).[35]
Due to their characteristic colocalization functionality, these SPs can be equipped with a luminescent ID fingerprint, which is precisely defined by the intrinsic luminescence properties of the utilized nanosized coding elements and their quantity-weighted ratios. Exemplarily, wisely chosen combinations of rare-earth-doped CaF$_2$:RE$^{3+}$ NPs, with narrow clearly distinguishable emission bands, resulted in luminescent ID SPs, as shown in our previous works.$^{[36,37]}$

As a tool to assemble SPs, spray-drying, in particular, has proven to be advantageous due to its scalability, flexibility, and ability to freely combine all kinds of nanomaterials, even with repulsive properties.$^{[35]}$ Spray-drying is thus not only restricted to either the world of inorganics or organics, but a versatile tool that opens up possibilities to bridge both worlds.

As demonstrated by us recently, spectrally encoded, thermally stable inorganic ID SPs can be entangled with temperature-sensitive organic NP building blocks. Ultimately, a particle with an ID and a temperature indicator in one entity resulted.$^{[38]}$

Another interesting approach in which the divergent nature of organic and inorganic materials was crucial, involved equipping ID SPs with an ID readout indication function.$^{[37]}$ Thermally stable inorganic luminescent encoding elements were combined in the presence of a temperature-sensitive, bright stealth fluorophore, resulting in SPs that bear an initially concealed ID. Thermal energy input irreversibly activated the inorganic ID and enabled its readout. Since ID activation cannot be reversed, the ID status of the SPs indicates whether sensitive, encrypted data may have been accessed. Like a seal of approval, these hidden ID SPs indicate data originality, paving the way for advanced marking technologies with enhanced security features.

Refining the concept of SPs with an activatable ID, based on hybrid encoding elements, the next step toward advanced taggants would be to generate ID SPs, which have not only one but several switchable luminescent ID-levels and thus, possess a higher coding capacity.

Hybrid inorganic–organic SPs are an interesting approach to circumvent the limitations of ratiometric luminescent coding: the coding capacity of ratiometric luminescent ID fingerprints is reduced due to spectral overlap of respective emission peaks and thus, limited by their spectral width. By contrast, hybrid SPs with multiple spectral ID-levels that are irreversibly switched upon specific energy input, achieve a higher coding capacity than the aforementioned ID SPs systems developed by us.$^{[36–38]}$ In previous works, we succeeded in equipping ID SPs with a single or with a hidden, activatable ID signature, or realized SPs which possess an ID functionality and a temperature indicator simultaneously.$^{[36–38]}$ However, two spectrally superimposed ID signatures within one SP, whose interplay results in temperature-dependent distinct ID signals, have not yet been developed. In particular, the assembly of different organic fluorophore-containing and inorganic nanobuilding blocks to SPs, as well as their distance-dependent interactions, have not been analyzed yet. While marker particles that switch their ID state reversibly$^{[39–44]}$ or irreversibly$^{[45–48]}$ have been introduced, to the best of our knowledge, there is no comparable work that considers the versatility of a hierarchically structured SP design to realize flexibly adjustable multilevel ID taggants with stimuli-triggered switchable ID signature.

This approach might open up the perspective of monitoring the product history even after the end of the product life and could therefore be interesting to identify recycled raw materials and refurbished or reused product components. For example, such hybrid SP ID taggants could be added to polymers during their synthesis or could be applied onto products to label them initially with an organic ID signature. Once the product is broken down into its components, the organic ID could be vanished by energy input and reveal the inorganic ID, which irreversibly activates the object as already used. Moreover, if plastics are recycled, the elevated temperatures during processing should cause a degradation of the organic ID signatures either gradually or completely, revealing the temperaturerelated inorganic ID. It is conceivable that this approach not only enables to easily distinguish between virgin polymer and recycle but also indicates how many times a material has already been recycled, which is valuable information in terms of quality assurance for manufacturing processes in a well-functioning circular economy.$^{[49–51]}$

2. Strategy toward Multiply Encoded, Switchable Luminescent ID SPs

UV or IR excitation is required to detect luminescent ID signatures throughout the visible wavelength range. As shown in numerous studies, upconverting NPs are suitable as nanothermometers to sense thermal changes and display them utilizing a ratiometric luminescent ID since relative intensity ratios of respective emission bands vary in a temperature-dependent manner.$^{[52–55]}$ However, ID changes especially below 200 °C, are usually reversible and thus cannot reliably record a past thermal event. Organic fluorophores, on the other hand, gradually decompose thermally even at moderate temperatures, enabling irreversible ID changes, making them more promising candidates for indicating a product’s history. Therefore, organic fluorophores are selected as thermally sensitive components and combined with thermally stable inorganic nanoparticles. Since visible-light-emitting organic dyes are usually not excitable with IR light but with photons of higher energy, the combination of these with downconverting inorganic nanoparticles is preferred over upconverting ones to be able to ensure simultaneous ID detection by UV excitation. Hence, four differently doped luminescent CaF$_2$:RE$^{3+}$ NPs were combined with three signal-covering organic fluorescent encoding elements, yielding SP taggants, equipped with two switchable ID-levels (organic and inorganic ID). Initially, only the organic ID is displayed, which is visible to everyone and thus, can be used for tracking and tracing a product or raw material, i.e., at the beginning of a product’s lifetime. For the organic ID, fluorescent dye-hosting sodium dodecyl sulfate (SDS)-stabilized polystyrene (PS) NPs, as previously published elsewhere,$^{[56]}$ were utilized, that are prone to thermal degradation. They are suitable for ratiometric coding due to defined emission bands in the blue (PS:coumarin 1, PS:Cl NPs), green (PS:coumarin 6, PS:C6 NPs), and red (PS:rhodamine B, PS:RhB NPs) wavelength area. By using CaF$_2$:RE$^{3+}$ (CaF$_2$:Tm$^{3+}$ 0.4 mol%, CaF$_2$:Tb$^{3+}$ 0.4 mol%, CaF$_2$:Dy$^{3+}$ 1.0 mol%, CaF$_2$:Sm$^{3+}$ 1.0 mol% NPs), more precisely described in our previous work,$^{[36]}$ a second, temperature-stable...
ratiometric code could be realized. After thermal treatment, the concealing organic ID-level is quenched irreversibly and the inorganic ID revealed. This functionality originates from the thermal decomposition of organic substances while RE$^{3+}$-doped nano phosphors enhance their fluorescence due to crystallization and diffusion processes.$^{[37,38]}

What seems simple in the first place, in fact is a challenging task, since between the closely packed NPs numerous undesirable coupling effects occur within the micrometer-sized SP entities before, during, and after the thermally induced ID switch.

Due to the versatility of the spray-drying process, it is possible to precisely tune the architecture of the SPs. Thus, the aforementioned problems can be circumvented by adjusting spray-drying process parameters and the choice of nanobuilding blocks according to their physicochemical properties.$^{[59,60]}$

Thus, this work not only focused on overcoming these challenges, but also on using beneficial coupling effects within the SPs to optimize the resulting ID taggant system by precise, intelligent SP architecture design. The overall subject of this work is summarized and visualized in Scheme 1. Scheme 1a gives an overview of the employed coding elements. Scheme 1b schematically represents the systematic development and optimization of the targeted SP design. Scheme 1c shows the herein established finally selected SP architecture for the temperature-triggered switchable ID taggants. Scheme 1d depicts the two previously mentioned potential use cases for the developed ID SPs.

3. Optical Properties of Single Encoding Elements

To create an easy-to-read, flexible dual-ID SP system, it is necessary to ensure that both ID signatures can be detected with only one readout method. In order to achieve simultaneous detection of all seven luminescent organic and inorganic encoding elements, thus the overall ID signature, UV light excitation was chosen. Previous studies have shown that excitation at $\lambda_{\text{exc.}} = 357$ nm (Tm$^{3+}$ absorption $^3H_4 \rightarrow ^1D_2$)$^{[61]}$ leads to approximately equal emission intensities of the respective assembled and annealed (430 °C, 4 h) RE$^{3+}$-doped CaF$_2$ NPs, which is advantageous in terms of the coding application.$^{[61]}$ Therefore, this wavelength was selected for detecting the dual-ID system. The single emission bands of the respective RE$^{3+}$ dopants can be observed in PL spectra of CaF$_2$ SPs, consisting only of one type of CaF$_2$:RE$^{3+}$ NPs, each (Figure S1, Supporting Information and described in detail elsewhere$^{[36]}$).

Due to their luminescence properties, RE$^{3+}$-doped materials are predestined as building blocks for ID SPs.$^{[62,63]}$ Since the 4f orbitals are shielded by the electrons of the 5s and 5p shells, they are only marginally affected by their environment and f–f transitions result in line-like emission bands.$^{[84]}$ Thus, undesired coupling effects within an RE$^{3+}$-doped SP are only weakly present, and spectral overlap is minimized. The large Stokes shift of RE$^{3+}$-based materials makes single wavelength excitation easily feasible.$^{[62]}

To generate hybrid dual-ID SPs, the inorganic luminescent encoding elements are to be combined with organic ones. Commercially available and economically feasible dyes with a sufficient photostability that emit light in the blue (C1), green (C6), and red (RhB) wavelength area respectively have been chosen. However, it must be taken into account that the luminescence mechanism of fluorescent dyes fundamentally differs from that of lanthanides and poses some challenges with respect to the desired application: organic fluorescent dyes usually possess a narrow Stokes shift and rather broad excitation and emission bands.$^{[65]}$ Therefore, if the particle design is unfortunate, undesired cross-coupling effects in form of reabsorption effects between C1 (donor), C6 (donor, acceptor), and RhB (acceptor) or self-quenching can occur and disrupt the ratiometry of the coding system.$^{[66,67]}$

To counteract these phenomena, the three utilized dyes were incorporated into SDS-stabilized PS NPs, yielding organic water-soluble coding elements that could thus be combined with the hydrophilic CaF$_2$:RE$^{3+}$ NPs. In the PS:dye NPs, the polymer host matrix creates spatial separation between the luminophores and thereby, reduces cross-coupling.

Furthermore, their fluorescence is based on delocalized π-electron systems, which are strongly dependent on the molecular environment. Since C6 has a large transitional dipole moment, its emission is bathochromically shifted when interacting with polar groups, which is disadvantageous for the envisioned coding functionality due to C6-RhB spectral emission and absorption overlap.$^{[68,69]}$ Furthermore, concerning the application, it is important that the host matrix is transparent and can withstand the temperatures prevailing during the spray-drying process, yet decomposes easily and preferably residue-free at higher temperatures to reveal the inorganic ID. Thus, the polymer-matrix material was chosen wisely. Nonpolar PS, has proven to be a suitable matrix material for this purpose. Nevertheless, it can be said that, due to the aforementioned reasons, coupling effects are to be expected and taken into account in the SP design when assembling dye-containing NPs.

Due to their small Stokes shift the fluorophores show varying excitability by UV light. Therefore, organic dye concentrations within the PS NPs were adjusted so that all organic encoding elements emit light within the same intensity range when excited with $\lambda_{\text{exc.}} = 357$ nm. Furthermore, the organic ID components should illuminate as brightly as possible to sufficient initial coverage of the inorganic ID. At the same time, a low overall PS to CaF$_2$ ratio is desired, since the polymers leave voids after thermal decomposition and thus, do not exhibit a stabilizing function in the particle composite. The usage of PS NPs with dye concentrations of PS:C1 (0.06 wt%), PS:C6 (0.5 wt%), and PS:RhB (0.06 wt%) have proven to meet the aforementioned requirements. The optical properties of the respective organic NPs are depicted in Figure S2a,b (Supporting Information). The hydrodynamic particle size distributions and zeta potential measurements obtained from dynamic light scattering (DLS) are shown in Figure S3 (Supporting Information).

4. Evaluation of SP Architecture: Intermixed versus Core–Shell SPs

The straightforward approach to achieve a dual-level hybrid ID system would be the co-spray-drying of all four inorganic and three organic NP dispersions, yielding an intermixed SP
system (intermixed CaF$_2$:RE$^{3+}$(Tm$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Sm$^{3+}$)-doped CaF$_2$ NPs) and thermally sensitive (PS:dye (C1, C6, RhB)) encoding elements and their respective emission bands. b) Schematic representation of the synthesis route of hybrid inorganic–organic dual-level ID SPs: a) illustration of thermally stable (RE$^{3+}$(Tm$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Sm$^{3+}$)-doped CaF$_2$ NPs) and thermally sensitive (PS:dye (C1, C6, RhB)) encoding elements and their respective emission bands. b) Schematic representation of the evaluation and development of the SP architecture to gain the desired dual-ID functionality: b1) a core (inorganic) shell (organic) SP design was favored over an intermixed one and selected as the target design, b2) the optical and morphological properties of the core were precisely adjusted by addition of SiO$_2$ NPs, resulting in a CaF$_2$ to SiO$_2$ NP mass ratio of 30:1 being eventually selected, b3) by variation of RE$^{3+}$-doped CaF$_2$ NPs ratios, exemplarily four inorganic ID SP cores were prepared, and b4) subsequently the cores were equipped with varying amounts of PS:dye NP to form an organic ID SP shell, a core to shell mass ratio of 50:1 was finally chosen. c) Schematic depiction of the evaluated final SP ID system and its working principle. d) Schematic depiction of two specific use cases of the established dual-ID SP system: d1) ID taggants with readout indication and d2) ID taggants that monitor the materials history within recycling processes.

A defined energy input of 430 °C for 4 h is required to activate the second inorganic ID.[36] Upon this treatment, as especially due to high C6 concentrations within the PS:C6 NPs, excimer formation is likely. These molecular interactions of C6–C6/C1–C1 molecules result in the appearance of two emission peaks in close proximity and therefore an overall broadening of emission bands which is well described in literature.[70–72]
Figure 1. Choice of SP architecture: a1) schematic drawing of intermixed SPs, generated by simultaneously assembling CaF$_2$ NPs and PS NPs via one co-spray-drying process and a2) of assembled and preannealed (430 °C, 4 h) CaF$_2$ SP cores, subsequently coated with organic PS:dye NPs via a second spray-drying step, forming a core–shell SP architecture; absolute (b1,c1) and relative PL spectra (b2,c2) of respective samples (λ$_{exc}$ = 357 nm) b) as prepared and c) thermally treated at 430 °C for 4 h. Insets show digital photographs of the respective illuminated (λ$_{exc}$ = 357 nm) powder samples (scale bar = 0.5 cm). d) Scanning electron microscopy (SEM) images of intermixed (d1) and core–shell SPs (d2) as prepared and thermally treated, respectively. Red circles in inset SEM images highlight PS:dye NPs.
shown in Figure 1c, the organic luminophores are quenched, and the characteristic RE\(^{3+}\) signals are revealed as desired (see Figure S4, Supporting Information, for inorganic ID). Thermogravimetical analysis (TGA) measurements indicate the complete thermal decomposition of PS:dye NPs at temperatures beyond 400 °C (Figure S5, Supporting Information). However, in the case of co-spray-dried intermixed samples, the presence of organic components within the inorganic SP compound after the heat treatment has a strong impact on the optical properties that negatively affect the ID functionality. Although the peaks are detectable at the expected wavelengths, they are significantly attenuated, as a broad white luminescence of the sample appeared (Figure 1c, inset photographs). It is known that this luminescence emission phenomena can arise from energy levels induced by carbon interstitial defects within crystalline lattices.[73–75] Some of the decomposed PS:dye NPs escape from the SP system as volatile gases during the annealing process. However, a large proportion of carbon impurities probably remains trapped within the particle composite and the limited accessibility of carbon could therefore result in carbon defects in the CaF\(_2\):RE\(^{3+}\) SP crystal lattice.

This issue could successfully be overcome by implementing a core (CaF\(_2\):RE\(^{3+}\) NPs)–shell (PS:dye NPs) SP architecture (core \{CaF\(_2\):RE\(^{3+}\)\{1:1:1\}] 50@shell [PS:dye \{1:1:1\}] 1). To achieve this, equally mass-weighted CaF\(_2\):RE\(^{3+}\) NPs were first assembled via spray-drying and annealed at 430 °C for 4 h. Subsequently, the calcined inorganic CaF\(_2\):RE\(^{3+}\{1:1:1\}\) SPs, which exhibited sufficient mechanical stability, were transferred to an equally mass-weighted \{1:1:1\} PS:dye NPs dispersion and the mixture was spray-dried once again. Upon droplet evaporation in the spray-drying process, the smaller PS:dye NPs deposit as a shell on the SPs. A precondition to achieve this is that the quantity ratios of core and shell material are chosen wisely.[76–78] The equally mass-weighted ratios of differently colored PS:dye NPs (1:1:1) and the ratio of organic to inorganic components (core:shell, 50:1) were kept equal to the priorly co-spray-dried intermixed SP sample.

As it can be seen from PL spectra, the RE\(^{3+}\) signals are also completely covered, initially, for the core–shell system. Interestingly, the relative emission intensity ratio of the three fluorescent dyes changed quite strongly compared to the intermixed system, although the same quantitative ratios prevailed. It seems likely that the PS:dye NPs are spatially packed closer together due to the core–shell architecture and not spatially separated by CaF\(_2\):RE\(^{3+}\) NPs, acting as spacers. This could enhance emission-reabsorption events between the PS:dye NPs (Figure S2, Supporting Information). Due to spectral overlap, the blue (C1) and/or green (C6) emissions are likely to be reabsorbed by C6 and RhB, respectively, which leads to a relative increase in the corresponding emission bands. Especially the high dye concentrations within the PS:C6 NPs besides the occurrence of spectral overlap render cross-coupling effects likely. However, no homogeneous shell has formed on the core SPs, but rather an irregular core–satellite structure (Figure 1d2, scanning electron microscopy (SEM) images) what makes distant dependent intra-SP interactions due to the spatial separation rather unlikely. Since not only one SP but a volume element of a powder is analyzed, inter-SP interactions between several core–shell SPs nearby seem likely and will be discussed in more detail at a later stage. SEM images also indicated that due to the overall low PS NP to CaF\(_2\):RE\(^{3+}\) NP mass ratio and the opposite charge of CaF\(_2\):RE\(^{3+}\) and SDS-stabilized PS:dye NPs (zeta-potential measurements, Figure S3, Supporting Information), no pure PS:dye SPs as side products were formed. The core–shell SP architecture permits oxygen access and thus, renders the volatilization of the organic material more likely. Furthermore, preannealing of the core SP prior to coating with PS:dye NPs might reduce interactions between them and the already crystallized inorganic core material. Thus, fewer crystal defects occur, which is why the characteristic Tm\(^{3+}\), Tb\(^{3+}\), Dy\(^{3+}\), and Sm\(^{3+}\) ID signals appear much more intense when compared to the intermixed sample. X-ray diffra- tograms (Figure S5, Supporting Information) indicate that, due to the preannealing step, the core–shell SPs possess a higher CaF\(_2\) crystallinity. However, in both cases, i.e., for core–shell as well as intermixed SPs, no other crystalline structure besides CaF\(_2\) was formed.

Overall, it was found that a core–shell SP architecture is crucial and a prerequisite for the implementation of a functional dual-ID SP taggant system.

5. Optimization and Characterization of the Inorganic ID Core SPs

According to the SEM images (Figure 1d), the CaF\(_2\) NPs do not form spherical, but rather malformed, buckled SPs when spray-dried. Therefore, the CaF\(_2\) ID SPs, described in previous work,[16] are not suitable as a core material to be coated with a homogeneously distributed PS:dye NP shell, since the reproducibility and adjustability of the organic ID and consequently the functionality of the dual-ID taggant system would be impaired.

Interestingly, the co-spray-drying of oppositely charged RE\(^{3+}\)-doped CaF\(_2\) NPs (d = 20–50 nm, positively charged) and smaller SiO\(_2\) NPs (d = 10 nm, negatively charged) (zeta-potential measurements, Figure S3, Supporting Information) had a beneficial effect on the core sphericity of the SPs as it can be seen in SEM images in Figure 2a. Ultrasonic treatment of the binary dispersion before spray-drying induces agglomeration due to attractive electrostatic interactions between the oppositely charged NP building blocks. The degree of agglomeration depends on NP charges, size-, and number ratios as described elsewhere.[79] The number-weighted hydrodynamic particle size distributions of ultrasonically treated CaF\(_2\):RE\(^{3+}\) and SiO\(_2\) dispersions, as well as the binary mixed system (mass ratio CaF\(_2\):SiO\(_2\) = 30:1) clearly indicate the colloidal destabilization of the binary colloidal dispersion (DLS measurements, Figure S7a, Supporting Information). Furthermore, the increasing dispersion turbidity associated with agglomeration can be observed in the corresponding photograph (Figure S7b, Supporting Information).

Controlled agglomeration of the mixed NP dispersion prior to spray-drying, influences the droplet drying process, which mainly controls the morphology of the resulting SP.[80] The droplets that result from atomization of a colloidal dispersion, initially shrink isotropically during the drying process. Under common spray-drying conditions, the diffusion process of colloidal NPs is much slower than the drying time (Péclet number...
Pe > 1). Hence, a viscoelastic shell, consisting of densely packed NPs, forms at the droplet–air interface, driven by solvent flow during drying. Consequently, capillary pressure is built up and leads to shell-buckling, which results in misshaped SPs.[81,82] Lintingre et al.[83] have shown that the key parameter to avoid buckling is to increase the permeability of the built-up NP shell at the droplet–air interface. The destabilization of the colloidal dispersion before the spray-drying process leads to a rather loose packing of fractal agglomerates with a large permeability during the shell formation. Consequently, the so-called Darcy stress remains small enough for the droplets to shrink isotropically without buckling. Therefore, the binary mixture of oppositely charged SiO$_2$ to CaF$_2$:RE$^{3+}$ NPs forms larger subunits among themselves within an SP unit, their calcination process is disturbed and slowed down due to the spatial separation by amorphous SiO$_2$ NPs. Hence, the microscale

![Figure 2. Design of SP core: a1) schematic drawings of the synthesis approach and SEM images of CaF$_2$:RE$^{3+}$(1:1:1:1) SPs (CaF$_2$:Tm$^{3+}$, CaF$_2$:Tb$^{3+}$, CaF$_2$:Dy$^{3+}$, CaF$_2$:Sm$^{3+}$) NP mass ratio = 1:1:1:1) and a2) of [CaF$_2$:RE$^{3+}$(1:1:1:1)] 30/[SiO$_2$] 1 SPs (CaF$_2$:RE$^{3+}$(1:1:1:1) SPs, containing ~10 nm sized SiO$_2$ NPs with a mass ratio CaF$_2$:SiO$_2$ of 30:1) as prepared, thermally treated at 430 and at 600 °C, respectively, for 4 h. Absolute (b1,c1) and relative PL spectra (b2,c2) of b) CaF$_2$:RE$^{3+}$(1:1:1:1) SPs and c) [CaF$_2$:RE$^{3+}$(1:1:1:1)] 30/[SiO$_2$] 1 (~$\lambda_{ex}$ = 357 nm) and d) X-ray diffractograms of the respective samples.](image-url)
spherical shape of [CaF$_2$:RE$^{3+}$ (1:1:1)] 30/[SiO$_2$] 1 SPs is maintained. By contrast, annealing at 600 °C for 4 h leads to sintering of CaF$_2$:RE$^{3+}$ (1:1:1) SPs to a macroscopic CaF$_2$ bulk material with enhanced crystallinity. X-ray diffractograms in Figure 2c show exclusively characteristic reflexes of the cubic CaF$_2$ crystalline phase for pure CaF$_2$:RE$^{3+}$ as well as for CaF$_2$:RE$^{3+}$-SiO$_2$ composite SPs. This indicates that no side phases were formed in the presence of SiO$_2$ upon annealing, however, the increased width of the reflexes indicates lower crystallinity of the sample. Other studies also confirm the preferential coordination of fluorine to calcium over silicon,	extsuperscript{84,85} which is consistent with the aforementioned results.

However, the relative intensity of different emission peaks, which is determined by the probability of the respective f-f transitions, seems to depend strongly on the SP composition and thus, also on the surrounding matrix of RE$^{3+}$ ions. To investigate the influence of the SiO$_2$ environment on the respective RE$^{3+}$ emission bands further, SPs were prepared, consisting of one-quarter singly doped and three-quarter undoped CaF$_2$ NPs. The samples were prepared in each case with and without SiO$_2$ content and annealed at 430 and 600 °C, respectively, for 4 h. Their normalized emission spectra are depicted in Figures S8–S10 (Supporting Information). It can be seen that the incorporation of SiO$_2$ NPs not only has a positive influence on the SP morphology but also regarding the ID functionality, as the luminescent ID fingerprint is influenced beneficially in terms of ratiometric coding. In the presence of SiO$_2$, the RE$^{3+}$ emission bands, which result from various electron dipole (ED) and magnetic dipole (MD) transitions of different encoding elements are shifted in a way, so that undesired spectral overlap is reduced. This can be explained by the fact, that ED transitions are, in contrast to MD transitions, especially sensitive to changes in the surrounding RE$^{3+}$ environment.	extsuperscript{86,87} An exhaustive discussion on this can be found in the Supporting Information.

Furthermore, the presence of SiO$_2$ leads to a relative intensity alignment of all relevant coding emissions bands (Tm$^{3+}$ 458 nm ED, Tb$^{3+}$ 542 nm MD, Dy$^{3+}$ 577 nm ED, and Sm$^{3+}$ 604 nm ED + MD), which is also evident from the comparison of the excitation spectra, depicted in Figure S9 (Supporting Information), of SiO$_2$ containing and pure CaF$_2$ samples. The excitation spectra of the respective coding wavelengths cross approximately at the excitation wavelength of 357 nm after the addition of SiO$_2$ NPs, which is advantageous with respect to the coding application.

As depicted in Figure S11a (Supporting Information), a further increase in SiO$_2$ NP content within the SPs leads to a further decrease in ED/MD ratio. Since CaF$_2$:RE$^{3+}$ crystals possess a periodic structure, characterized by well-defined low-symmetry C$_{4v}$ substitution sites, while amorphous glass materials allow a varying local crystal structure,	extsuperscript{88,89} the relative ED/MD emission intensity ratio is much lower in doped glass samples than in doped crystals. X-ray diffractograms of annealed SPs with different amounts of SiO$_2$ NPs, illustrated in Figure S11b (Supporting Information), show a broadening of the reflections and thus, decreasing crystallinity of the samples with increasing SiO$_2$ NP content. This trend can also be observed from the SEM images in Figure S11c (Supporting Information), as the primary CaF$_2$:RE$^{3+}$ NPs of the 600 °C annealed SPs have coalesced less into larger subunits with decreasing SiO$_2$ NP content.

It is known from literature that changing the crystal field environment of RE$^{3+}$ ions also influences the Stark splitting of the respective f-f transitions.	extsuperscript{90} A splitting of the $^4S_3/2$ levels into a multitude of crystal field levels detectable as well-resolved Stark emission lines are common in crystalline materials.	extsuperscript{91,92} By contrast, well-resolved Stark lines are known to diminish in RE$^{3+}$-doped amorphous glass samples as the surroundings for RE$^{3+}$ ions varies in the glass host.	extsuperscript{93} The introduction of amorphous SiO$_2$ NPs to the crystalline CaF$_2$:RE$^{3+}$ SPs leads to RE$^{3+}$ ions being located in different crystal environments due to enhanced crystal defects. Therefore, Stark splitting of all transitions was reduced and led to less spectral overlap, especially of Sm$^{3+}$ ($^{4}G_{5/2} \rightarrow ^{4}H_{15/2}$, $^{4}G_{5/2} \rightarrow ^{4}H_{17/2}$) and Dy$^{3+}$ ($^{4}F_{9/2} \rightarrow ^{6}H_{31/2}$) transitions, which is highly advantageous in terms of coding (Figure S8, Supporting Information). SPs with a desired mass ratio of 30:1 (CaF$_2$:RE$^{3+}$:SiO$_2$ NP) ([CaF$_2$:RE$^{3+}$ (1:1:1)] 30/[SiO$_2$] 1) were chosen as the inorganic ID core architecture, corresponding to an estimated number ratio of 1:2:1 (CaF$_2$ NPs:SiO$_2$ NPs).

Assembling the four different types of CaF$_2$:RE$^{3+}$ NPs in different mass ratios while keeping the SiO$_2$ NP fraction constant leads to SPs ([CaF$_2$:RE$^{3+}$ (w:w:w:z)] 30/[SiO$_2$] 1) that reproducibly exhibit distinguishable luminescent ID signatures after a 4 h thermal treatment at 600 °C (error bars represent measurements from three independently produced batches). Annealing of [CaF$_2$:RE$^{3+}$ (1:1:1:1)] 30/[SiO$_2$] 1 cores prior to organic ID shell application is necessary, to ensure their mechanical stability during the subsequent spray-drying process to yield core–shell SPs. Normalized relative PL emission spectra of the respective samples are depicted in Figure 3a1 and the resulting numerical codes are visualized in Figure 3a2.

Energy-dispersive X-ray spectroscopy (EDS) analyses of single SPs (SEM image, Figure 3b), exemplified here for [CaF$_2$:RE$^{3+}$ (1:1:1)] 30/[SiO$_2$] 1 and [CaF$_2$:RE$^{3+}$ (1:1:2:4)] 30/[SiO$_2$] 1 show characteristic X-ray emissions of the respective RE$^{3+}$ dopants (Figure 3c). The relative intensity ratios of the element-specific Lα X-rays vary, depending on the SPs composition, which suggests that indeed a micrometer-scaled particle carries all relevant coding elements and thus, could serve as an ID-taggant additive to mark even the smallest product components.

6. Development of Organic Temperature Labile ID

In the next step, the inorganic ID SP core is equipped with a second, organic ID as a shell. Hence, CaF$_2$:RE$^{3+}$ ID SPs, previously annealed at 600 °C, 4 h, were spray-dried a second time in the presence of PS:dye NPs. Due to the size differences and opposite surface charges of SPs and NPs, respectively (zeta-potential measurements, Figure S3, Supporting Information), a core–shell PS architecture (core [CaF$_2$:RE$^{3+}$ (1:1:1)] X@shell [PS:dye (1:1:1)]) was achieved by a wisely selected mass ratio.	extsuperscript{66,72} Figure 4a shows PI absolute emission spectra (a1) and normalized at C1 emission peak (a2) of CaF$_2$:RE$^{3+}$ core–PS shell SPs that were spray-dried with varying core-to-shell material ratios.

It becomes evident that in all cases it was possible to completely cover the RE$^{3+}$-derived inorganic ID. Although the
mass ratios of the PS:dye NPs, were kept constant and equally weighted (PS:C1, PS:C6, PS:RhB = 1:1:1), there is not only an increase in absolute intensity but also, interestingly, a steady relative increase in the intensity ratio of the red to green to blue emission band with increasing PS:dye to CaF$_2$:RE$^{3+}$ mass ratio. This blue-to-red shift in chromaticity can be observed even by the naked eye when the sample is excited at 357 nm in a dark chamber (photographs, Figure 4a, insets). The increased PS:dye NP concentration on the SP surface seems to benefit cross-coupling of the dye molecules, more precisely reabsorption events of C1 and/or C6 emissions by C6 and/or RhB, respectively. Also, the broadening and the bathochromic shift of C6 emission bands with increasing PS:dye NP content indicates excimer formation of the C6 molecules (C6–C6 molecule interaction), presumably at PS:dye NP interfaces.\[70] Furthermore, the C1 emission band shifts hypsochromically with increasing PS:dye content and narrows. Possibly, the emission of excited C1 molecules is reabsorbed more efficiently by C6 and/or RhB molecules due to spectral overlap rather than leading to the formation of C1–C1 excimers, which is why the emission band narrows and shifts hypsochromically with increasing PS:dye content on the SP-shell.

The luminescence excitation and emission spectra of as-prepared core–shell SPs, shown in Figure S12 (Supporting Information), each equipped with only one shell coding element (1/3 coding element, 2/3 pure PS), support the assumption of interacting luminescent shell components when assembled. Comparing their emission spectra with those of SPs containing an equal amount of the three PS:dye NPs (1/3 each, black line), one can see that the absolute intensity of the two coumarin bands is found to decrease, while the RhB band increases as soon as several encoding elements are combined.

The increasing coating fraction of inorganic core ID SPs with PS:dye NPs becomes apparent in SEM images, depicted in Figure 4b, of the respective samples. Instead of forming a densely packed shell around the cores, it can be seen that the SPs architecture resembles more a core–satellite structure. Since there are only a few PS:dye NPs in close proximity to each other, intra-SP cross-coupling effects between the shell building blocks are rather unlikely. However, since a volume element of SP powder is measured spectrally, it is more likely that inter-SP cross-coupling effects occur between several core–shell SPs interfaces rather than that intra-SP interactions lead to the observed phenomena.
To investigate this further, core–shell SPs (ratio 1:5) were gradually mixed with nonluminescent, SiO$_2$ SPs acting as spacer between the ID taggant SPs and PL measurements of the resulting powder mixtures were performed. In addition to the absolute intensity of the sample, the emission intensities of RhB and C6 also decreased relative to the C1 emission band upon inter-SP spacing, as depicted in Figure S13 (Supporting Information). Thereby, inter-SP cross-coupling between ID taggant SPs is prevented. The aforementioned characteristic wavelength shifts of the respective emission bands (bathochromic shift of C1, hypsochromic shift of C6 and RhB) due to SiO$_2$ spacing indicate a reduced inter-SP interaction as well.

Subsequently, it was to be clarified to what extent the core-to-shell quantity ratio affects the exposure of underlying hidden inorganic ID of the SPs by thermal energy input. Figure S14 (Supporting Information) shows PL emission spectra of previously annealed ID core SPs with high (turquoise line), low (green line), and no shell mass fraction (red line), which were subjected to varying heat treatments. Emission spectra of bare and previously annealed ID SPs cores (yellow line) serve as reference. As shown in Figure S14a (Supporting Information), thermal treatment of the dual-ID taggant SPs at 430 °C for 4 h leads to the residue-free revelation of the characteristic RE$^{3+}$-based ID core emission signature, as desired. No significant difference can be observed according to the PS:dye shell amount. This is probably because the encoded ID core has already been previously annealed at 600 °C for 4 h and crystallized. Thus, the milder post-heat-treatment only leads to the decomposition of organic substances but has no significant influence on the luminescent properties of the core SPs. The effect of a more intense thermal treatment at 600 °C for 4 h on the optical and morphological properties of ID SPs is explained in detail in the Supporting Information.

The fact that the inorganic ID signature is very sensitive to thermal input shows that it is not sufficient to simply heat the sample to reveal a specific ID. A characteristic energy input, well known to the end-user, is necessary for this, which on the one hand significantly increases the readout security of the system. Furthermore, this finding opens up the possibility of encoding multiple data at different temperature levels. The XRD data of the samples exposed to a milder temperature treatment (430 °C, 4 h) (Figure S15, Supporting Information) do not show any crystalline minor phases, and also in the SEM images, the SPs all appear to have the same surface structure, which supports the hypothesis that under these conditions, no significantly detectable further crystallization of the SPs takes place. As a reference, all building blocks, including SiO$_2$ NPs, were co-spray-dried at once (in analogy to the experiment in Section 3; Figure S18 blue line, Supporting Information). Again, these results indicate that the core–shell SP architecture is crucial for the desired working principle of the system (see Supporting Information for detailed discussion).

7. Optimized ID SP Architecture

In terms of application, the multiple phenomena that have occurred in SP fabrication must be taken into account to obtain the best performing dual-ID taggant system.
As shown earlier, a core (inorganic)–shell (organic) SP structure is advantageous to ensure polymer-independent annealing of crystalline CaF$_2$:RE$^{3+}$ to obtain the characteristic RE$^{3+}$ ID signatures.

1) Inorganic ID core design:
- The assembly of code-carrying CaF$_2$:RE$^{3+}$ NPs with ≈10 nm sized SiO$_2$ NPs in a 30:1 mass ratio results, after an annealing step at 600 °C for 4 h, in spherical self-contained microscale taggants bearing an inorganic, luminescent ID signature.

2) Organic ID shell design:
- Sufficient PS:dye NPs concentrations, must be targeted to ensure the complete coverage of the inorganic ID signature.
- However, at elevated PS:dye concentrations, cross-coupling effects occur due to reabsorption–emission events between the polymer building blocks. Concerning the application, these dependencies between the coding elements are disadvantageous due to a reduced SPs’ coding capacity and should be minimized. Furthermore, complete exposure of the inorganic RE$^{3+}$ ID signature by decomposition of the organic components has to be fulfilled, whereby a PS:dye concentration as low as possible is advantageous.
- Furthermore, concerning ratiometric coding, it is desired that equally weighted PS:dye NP quantity ratios result in equally weighted relative intensities. To meet all the aforementioned criteria, a core-to-shell ratio of 50:1 was selected.

8. Hybrid Inorganic–Organic Dual-Level ID SPs: Proof of Concept

To demonstrate the working principle of the dual-level ID SPs, the different preannealed ID cores were covered with different quantity-weighted fractions of blue, green, and red luminescent NP signal elements by spray-drying. The core-to-shell mass ratio was set to 50:1 for all samples. Figure 5 depicts the emission spectra of the respective ID SPs before and after a thermal energy input of 430 °C for 4 h.

All ID signatures of inorganic and organic nature and the numerical codes based on relative emission intensity ratios can be reproducibly and unambiguously distinguished from each other. It can be observed that the C6 emission band is hypsochromically shifted with increasing PS:RhB to PS:C6 amount, which again is a clear sign for emission–reabsorption events between the PS:dye NPs. As shown in the digital photographs on the right, a luminescence hue change of the respective excited samples after thermal treatment can even be seen with the naked eye. This also opens up the possibility, to combine precisely switchable spatially resolved with spectral coding strategies presented herein, by arranging the SPs as additives in certain switchable multicolor patterns, as shown in a previous work.[37]

Milder thermal treatments, mimicking, e.g., polymer recycling conditions, at 200 °C, 4 h (Figure S19a, Supporting
Information), alter the first ID levels of the ID SPs but are not sufficient to entirely quench the organic ID and thus, to expose the inorganic one completely. The coumarin emission bands are still recognizable and strongly bathochromically shifted by excimer and/or exciplex formation. The aggregation of dye molecules was made possible by exceeding the temperature over the glass transition of PS:dye NPs (around 100 °C). Additionally, TGA measurements in Figure S5 (Supporting Information) confirm that higher temperatures are required to completely decompose the PS:dye NPs. However, the organic luminescent ID-signature relatively changes upon exposure of the taggant to milder thermal conditions. As depicted in Figure S19b (Supporting Information), the relative ID signals differ upon multiple exposures to the mentioned thermal treatment. Thus, the developed ID SPs could in principle be suitable for displaying the material history in recycling processes (i.e., indication, how often a material was recycled) if further process optimizations are applied.

9. Conclusion

In this work, a strategy for the generation of multiple spectrally luminescent encoded SPs that switch their ID signature selectively and precisely upon exposure to energy input, e.g., temperature, was presented. These smart additives are hierarchically composed of individual code-carrying luminescent nanosized building blocks, which are either vulnerable or resistant to heat. The ID signature is based on relative emission intensity ratios of temperature-sensitive fluorescent dye-labeled PS:dye NPs and inorganic thermally stable RE3+-doped CaF2:RE3+ NPs, which can be excited simultaneously. Initially, the bright emission of the organic luminophores conceals all RE3+ signals. When these hybrid SPs are applied to a product or raw material, they can be tagged uniquely, utilizing the organic ID-level. Once the SPs are exposed to heat, depending on the thermal treatment, the organic ID is altered or entirely quenched to reveal the underlying RE3+-based inorganic ID-level. This has been demonstrated that the development of a well-considered, precisely tailored SP architecture is mandatory to prevent undesired cross-coupling effects between the different building blocks. Moreover, beneficial cross-coupling effects were exploited in a targeted manner, concerning the application. Due to the flexibility of the manufacturing process via spray-drying, it was possible to realize an inorganic core–organic shell SP structure, which was of decisive importance with regard to the functional principle of the SPs. The assembly of inorganic CaF2:RE3+ core SPs with the organic building blocks within a second spray-drying step then provided the final dual spectrally luminescent encoded SPs whose ID could be precisely and irreversibly switched gradually (200 °C for 4 h) or entirely (430 °C for 4 h).

The initially hidden inorganic ID-level can be used to hide secret, encrypted information. At the same time, the developed taggant is envisioned to be able to record product or material histories in a Circular Economy: for example, marked virgin polymers could be distinguished from those that have already been recycled once or possibly even several times. A gradual or complete ID change would be initiated by exposing the marked plastic to higher temperatures during the recycling process. The irreversible nature of the ID change of the SPs is the key factor for the indication of the material history. Especially for products from the pharmaceutical industry, the use of virgin polymers and thus, clear differentiation of these material classes within a closed-loop recycling economy is of great importance and again underlines the relevance of the functional material presented here.

10. Experimental Section

See the Supporting Information for the Experimental Section.

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

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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coupling effects, ID taggants, luminescent nanoparticles, marker particles, rare-earth-doped particles, smart additives, supraparticles

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