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# Lanthanide-Based Single-Chain Nanoparticles as “Visual” Pass/Fail Sensors of Maximum Permissible Concentration of Cu<sup>2+</sup> Ions in Drinking Water

Jokin Pinacho-Olaciregui, Ester Verde-Sesto, Daniel Taton, and José A. Pomposo\*

The maximum permissible concentration (m.p.c.) of Cu<sup>2+</sup> ions in drinking water, as set by the World Health Organization (WHO) is m.p.c. (Cu<sup>2+</sup>)<sub>WHO</sub> = 30 × 10<sup>-6</sup> M, whereas the US Environmental Protection Agency (EPA) establishes a more restrictive value of m.p.c. (Cu<sup>2+</sup>)<sub>EPA</sub> = 20 × 10<sup>-6</sup> M. Herein, for the first time ever, a family of m.p.c. (Cu<sup>2+</sup>) “visual” pass/fail sensors is developed based on water-soluble lanthanide-containing single-chain nanoparticles (SCNPs) exhibiting an average hydrodynamic diameter less than 10 nm. Both europium (Eu)- and terbium (Tb)-based SCNPs allow excessive Cu<sup>2+</sup> to be readily detected in water, as indicated by the red-to-transparent and green-to-transparent changes, respectively, under UV light irradiation, occurring at 30 × 10<sup>-6</sup> M Cu<sup>2+</sup> in both cases. Complementary, dysprosium (Dy)-based SCNPs show a yellow color-to-transparent transition under UV light irradiation at ≈15 × 10<sup>-6</sup> M Cu<sup>2+</sup>. Eu-, Tb-, and Dy-containing SCNPs prove to be selective for Cu<sup>2+</sup> ions as they do not respond against other metal ions, such as Fe<sup>2+</sup>, Ag<sup>+</sup>, Co<sup>2+</sup>, Ba<sup>2+</sup>, Ni<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, or Cr<sup>3+</sup>. These new m.p.c. (Cu<sup>2+</sup>) “visual” pass/fail sensors are thoroughly characterized by a combination of techniques, including size exclusion chromatography, dynamic light scattering, inductively coupled plasma-mass spectrometry, as well as infrared, UV, and fluorescence spectroscopy.

in biological system – is involved as cofactor of numerous metalloenzymes.<sup>[2,3]</sup> Cu<sup>2+</sup> ions are also essential for the human body and defect of this crucial micronutrient can impart cytopenia (a reduction in the number of mature blood cells) and profound neurological deficits.<sup>[4,5]</sup> On the contrary, an excessive Cu<sup>2+</sup> intake from occupational exposure or contaminated water can cause gastrointestinal problems, liver and kidney damage, hemolytic anemia and impaired immune function, among other effects.<sup>[6,7]</sup> Thus, Cu<sup>2+</sup> ions act as one of the environment pollutants to control due to their increased use at several levels (home, industrial, and agricultural operations), as well as environmental persistency.<sup>[8]</sup>

Different regulatory Organisms have established the maximum permissible concentration (m.p.c.) of Cu<sup>2+</sup> ions in drinking water. The m.p.c. of Cu<sup>2+</sup> ions in drinking water by the World Health Organization (WHO) is m.p.c. (Cu<sup>2+</sup>)<sub>WHO</sub> = 30 × 10<sup>-6</sup> M, whereas the US Environmental Protection Agency (EPA) establishes a more restrictive value of m.p.c. (Cu<sup>2+</sup>)<sub>EPA</sub> = 20 × 10<sup>-6</sup> M.<sup>[9,10]</sup>

Although different analytical techniques are available to accurately determine the concentration of Cu<sup>2+</sup> ions in drinking water (e.g., atomic absorption spectroscopy, ion chromatography, inductively coupled plasma mass spectrometry), these techniques often involve sophisticated instrumentation

## 1. Introduction

Copper is an essential trace element for animals and plants.<sup>[1]</sup> In fact, Cu<sup>2+</sup> – the 3th most important metal ion present

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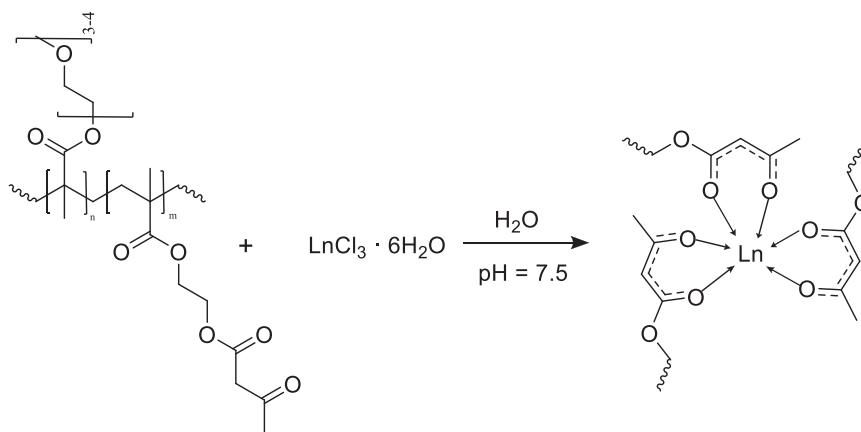
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**Scheme 1.** Schematic illustration of the synthesis of lanthanide (Ln)-based single-chain polymer nanoparticles (SCNPs) using an amphiphilic random copolymer decorated with *beta*-ketoester functional groups, namely, poly(OEGMA-*co*-AEMA) (see text).

and require skilled users. Consequently, alternative methods based on “visual” pass/fail sensors providing operational simplicity, sensitivity, and selectivity are highly desirable. To tackle that challenge, we envisioned to design single-chain polymer nanoparticles (SCNPs) incorporating lanthanide metal ions as a versatile platform towards a new generation of m.p.c. ( $\text{Cu}^{2+}$ ) “visual” pass/fail sensors. SCNPs are individual polymeric chains intramolecularly folded through intrachain interactions.<sup>[11]</sup> The folding of discrete synthetic polymer chains into SCNPs attempts to mimic the natural folding of biomacromolecules, such as proteins.<sup>[12]</sup> The chain folding process leads to locally compact domains within SCNPs, which can be of practical use to bind active species (e.g., metal ions,<sup>[13]</sup> luminophores,<sup>[14]</sup> drugs.<sup>[15]</sup>). Consequently, SCNPs offer interesting opportunities for the development of improved sensors,<sup>[16]</sup> innovative drug delivery vehicles,<sup>[17]</sup> and biomimetic catalysts,<sup>[18]</sup> including bimetallic Eu(III)/Pt(II)-SCNPs with both luminescent properties and catalytic activity.<sup>[19]</sup> On the other hand, a variety of complexes based on lanthanide ions,<sup>[20–23]</sup> have been investigated as fluorescent “turn-off” sensors of  $\text{Cu}^{2+}$  ions. However, most of these molecular sensors are not directly operative in water, but instead, in organic solvent/water mixtures.

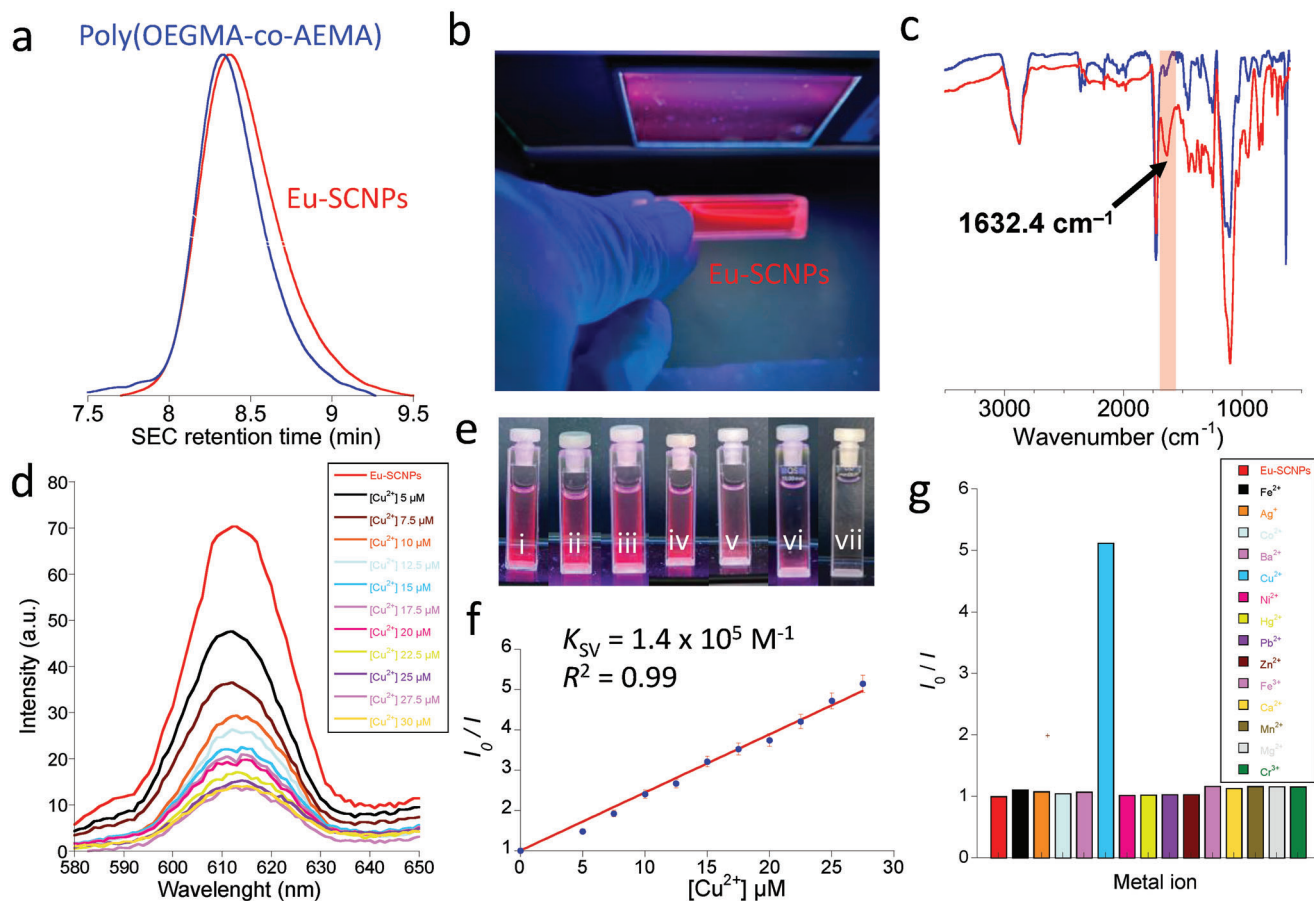
We hypothesized that, by using an amphiphilic random copolymer featuring *beta*-ketoester functional groups able to complex with lanthanide ions, water-soluble lanthanide-containing SCNPs could be achieved via intrachain *beta*-ketoester/lanthanide complexation. The resulting lanthanide-based SCNPs were thus employed as innovative m.p.c. ( $\text{Cu}^{2+}$ ) “visual” pass/fail sensors in drinking water. Here we report the synthesis of europium (Eu)-, terbium (Tb)-, and dysprosium (Dy)-based SCNPs, as well as their use—for the first time ever—as efficient “visual” pass/fail sensors of maximum permissible concentration of  $\text{Cu}^{2+}$  ions in water.

## 2. Results and Discussion

### 2.1. Eu-SCNPs as m.p.c. ( $\text{Cu}^{2+}$ ) “Visual” Pass/Fail Sensors

Europium-based single-chain nanoparticles (Eu-SCNPs) were prepared at a concentration of  $1 \text{ mg mL}^{-1}$ , following the proce-

dure depicted in **Scheme 1**. A linear amphiphilic random copolymer, namely, poly(OEGMA-*co*-AEMA) was first synthesized by RAFT copolymerization of the hydrophilic monomer OEGMA and the hydrophobic monomer AEMA. Poly(OEGMA-*co*-AEMA) was found to contain 35 mol% of *beta*-ketoester functional groups, as determined by  $^1\text{H}$  NMR spectroscopy (see Figure S1 in the Supporting Information). Poly(OEGMA-*co*-AEMA) showed a weight-average molecular weight of  $M_w = 80.7 \text{ kDa}$  and relatively low dispersity,  $D = 1.11$  (Table S1, Supporting Information). Eu-SCNPs resulted from the complexation of  $\text{Eu}^{3+}$  ions in solution by *beta*-ketoester functional groups of poly(OEGMA-*co*-AEMA) (see Scheme 1). The formation of  $\text{Ln}^{3+}$ /*beta*-ketoester complexes involving low molecular weight organic compounds is well documented.<sup>[24–26]</sup> To the best of our knowledge, however, there are no precedents of single-chain polymer nanoparticle formation via intrachain lanthanide/*beta*-ketoester complex formation. Successful preparation of Eu-SCNPs was confirmed by a combination of structural and size characterization techniques. Hence, SEC results confirmed a shift of the SEC elution time at peak maximum towards longer retention time and, hence, smaller hydrodynamic size for Eu-SCNPs when compared to the parent poly(OEGMA-*co*-AEMA) (see Figure 1a). Eu-SCNPs showed  $M_w = 85.0 \text{ kDa}$  and  $D = 1.12$ , suggesting the folding of individual copolymer chains and the absence of multichain aggregates by intermolecular crosslinking.<sup>[11]</sup> Complementary, DLS measurements showed a decrease of the average hydrodynamic diameter from 8.3 to 7.3 nm upon formation of Eu-SCNPs via intrachain  $\text{Eu}^{3+}$ /*beta*-ketoester complexation (see Figure S2 in the Supporting Information). The Eu-SCNPs were found to exhibit fluorescent properties under UV irradiation ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ), in a range of pH between 7.5 and 11 (see Figure 1b; Figures S3–S5, Supporting Information) even if the precursor Eu(III) salt was not fluorescent in water. Thus, at low pH value the Ln/*beta*-ketoester interactions were disrupted, whereas high pH caused the aggregation of the Eu-SCNPs, which ultimately led to their macroscopic precipitation from the solution. FTIR spectroscopy provided further evidence of the presence of  $\text{Eu}^{3+}$ /*beta*-ketoester complexes in Eu-SCNPs. As illustrated in Figure 1c, an intense band located at  $1632.4 \text{ cm}^{-1}$  indeed appeared in the FTIR spectrum of the



**Figure 1.** Europium-based single-chain nanoparticles (Eu-SCNPs) as “visual” pass/fail sensors of maximum permissible concentration (m.p.c.) of  $\text{Cu}^{2+}$  ions in water: a) SEC traces of the precursor, poly(OEGMA-co-AEMA), and the Eu-SCNPs, b) illustration of the reddish fluorescent Eu-SCNPs under UV light irradiation ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ), c) FTIR spectra of poly(OEGMA-co-AEMA) (blue color) and Eu-SCNPs (red color), d) PL spectra of Eu-SCNPs in water in the presence of increasing amounts of  $\text{Cu}^{2+}$  ions, e) demonstration of the utility of Eu-SCNPs as “visual” pass/fail sensors of m.p.c. of  $\text{Cu}^{2+}$  ions in water according to the WHO criterion ((i):  $5 \times 10^{-6} \text{ M}$ , (ii):  $10 \times 10^{-6} \text{ M}$ , (iii):  $15 \times 10^{-6} \text{ M}$ , (iv):  $22.5 \times 10^{-6} \text{ M}$ , (v):  $25 \times 10^{-6} \text{ M}$ , (vi):  $27.5 \times 10^{-6} \text{ M}$ , and (vii):  $30 \times 10^{-6} \text{ M}$ ), f) Stern–Volmer plot ( $I_0/I = 1 + K_{\text{SV}} [\text{Cu}^{2+}]$ ) of Eu-SCNPs (error bars estimated from triple measurements) and g) selectivity of Eu-SCNPs for  $\text{Cu}^{2+}$  ions against other metal ions.

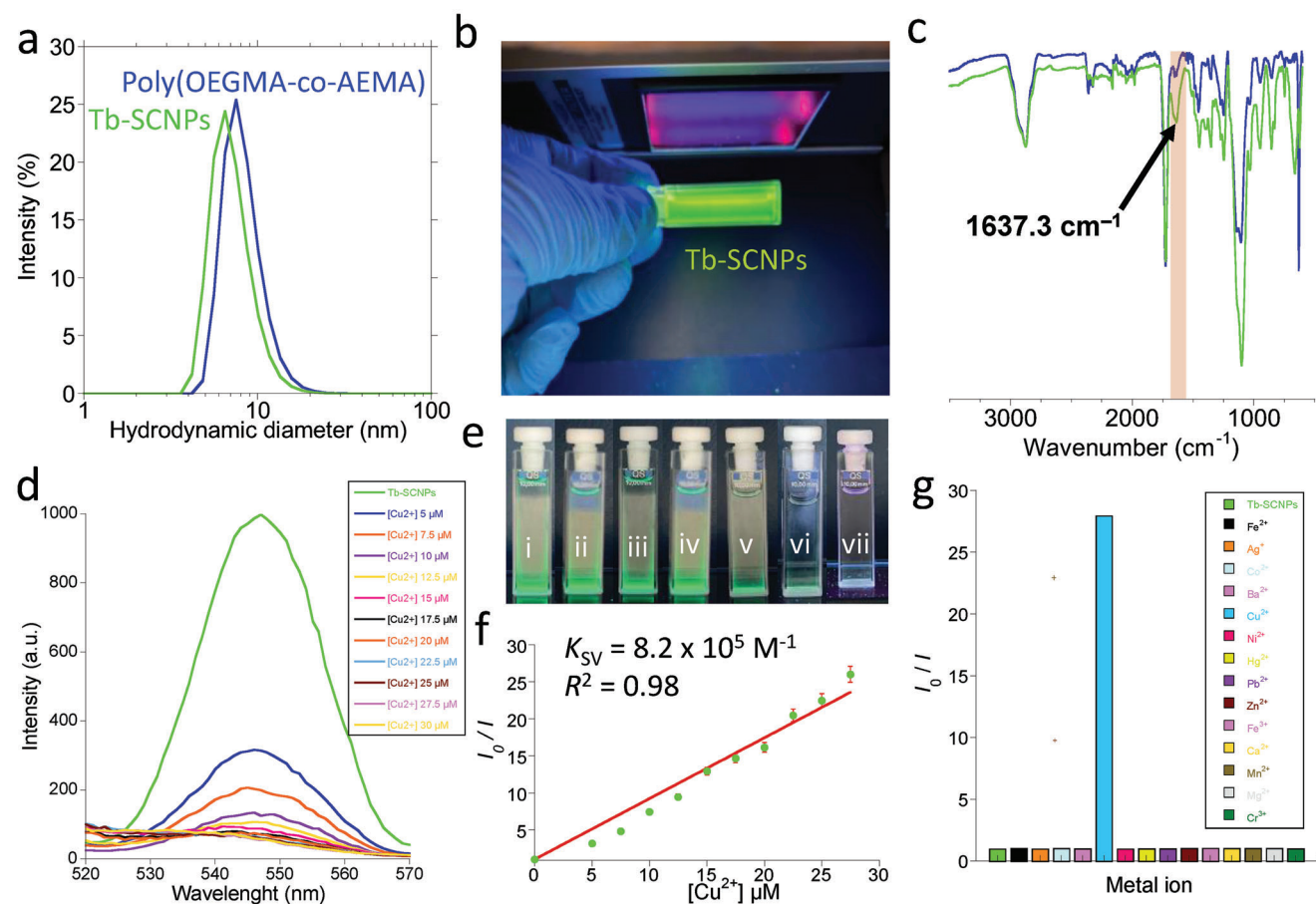
Eu-SCNPs, which could be assigned to the stretching vibration of the enol tautomer of the beta-ketoester groups bonded to  $\text{Eu}^{3+}$ . Figure 1d shows the PL spectra of Eu-SCNPs in water in the presence of increasing amounts of  $\text{Cu}^{2+}$  ions ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ). As shown in Figure 1e, Eu-SCNPs can be used as “visual” pass/fail sensors of m.p.c. of  $\text{Cu}^{2+}$  ions in water, according to the WHO criterion (m.p.c.  $(\text{Cu}^{2+})_{\text{WHO}} = 30 \times 10^{-6} \text{ M}$ ).<sup>[9]</sup> A clear red color-to-transparent change under UV light ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ) is indeed observed in Figure 1e on passing from  $[\text{Cu}^{2+}] \leq 27.5 \times 10^{-6} \text{ M}$  to  $[\text{Cu}^{2+}] = 30 \times 10^{-6} \text{ M}$  (or above, data not shown). Analysis of the data in Figure 1d using the Stern–Volmer equation.<sup>[27]</sup> ( $I_0/I = 1 + K_{\text{SV}} [\text{Cu}^{2+}]$ ) provided a value of  $K_{\text{SV}} = 1.4 \times 10^5 \text{ M}^{-1}$  and a squared coefficient of linear regression of  $R^2 = 0.99$  (see Figure 1f). Remarkably, Eu-SCNPs proved highly selective for  $\text{Cu}^{2+}$  ions against other metal ions, such as  $\text{Fe}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cr}^{3+}$  (Figure 1g).  $\text{Eu}^{3+}$  emission quenching is due to energy transfer to  $\text{Cu}^{2+}$  and, then, nonradiative relaxation to the ground state of  $\text{Cu}^{2+}$ .<sup>[28,29]</sup> Additional characterization data of the Eu-SCNPs can

be found in the Supporting Information (Figures S6–S8, Supporting Information).

## 2.2. Tb-SCNPs as m.p.c. ( $\text{Cu}^{2+}$ ) “Visual” Pass/Fail Sensors

Tb-SCNPs were obtained from the complexation of  $\text{Tb}^{3+}$  ions in solution by beta-ketoester functional groups of poly(OEGMA-co-AEMA), as displayed in Scheme 1. The average hydrodynamic diameter of the Tb-SCNPs was 7.2 nm (Figure 2a), a value smaller than that of the poly(OEGMA-co-AEMA) precursor (8.3 nm). The SEC trace of Tb-SCNPs ( $M_w = 88.9 \text{ kDa}$ ,  $D = 1.36$ , see Table S1 in the Supporting Information) confirmed the absence of multi-chain aggregates, in accordance with DLS results shown in Figure 2a. The Tb-based SCNPs were visualized as greenish fluorescent nanomaterials under UV light irradiation ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ) in a range of pH between 7.5 and 9 (see Figure 2b; Figures S9–S11, Supporting Information). Under strong acidic conditions the fluorescence disappeared due to the disruption





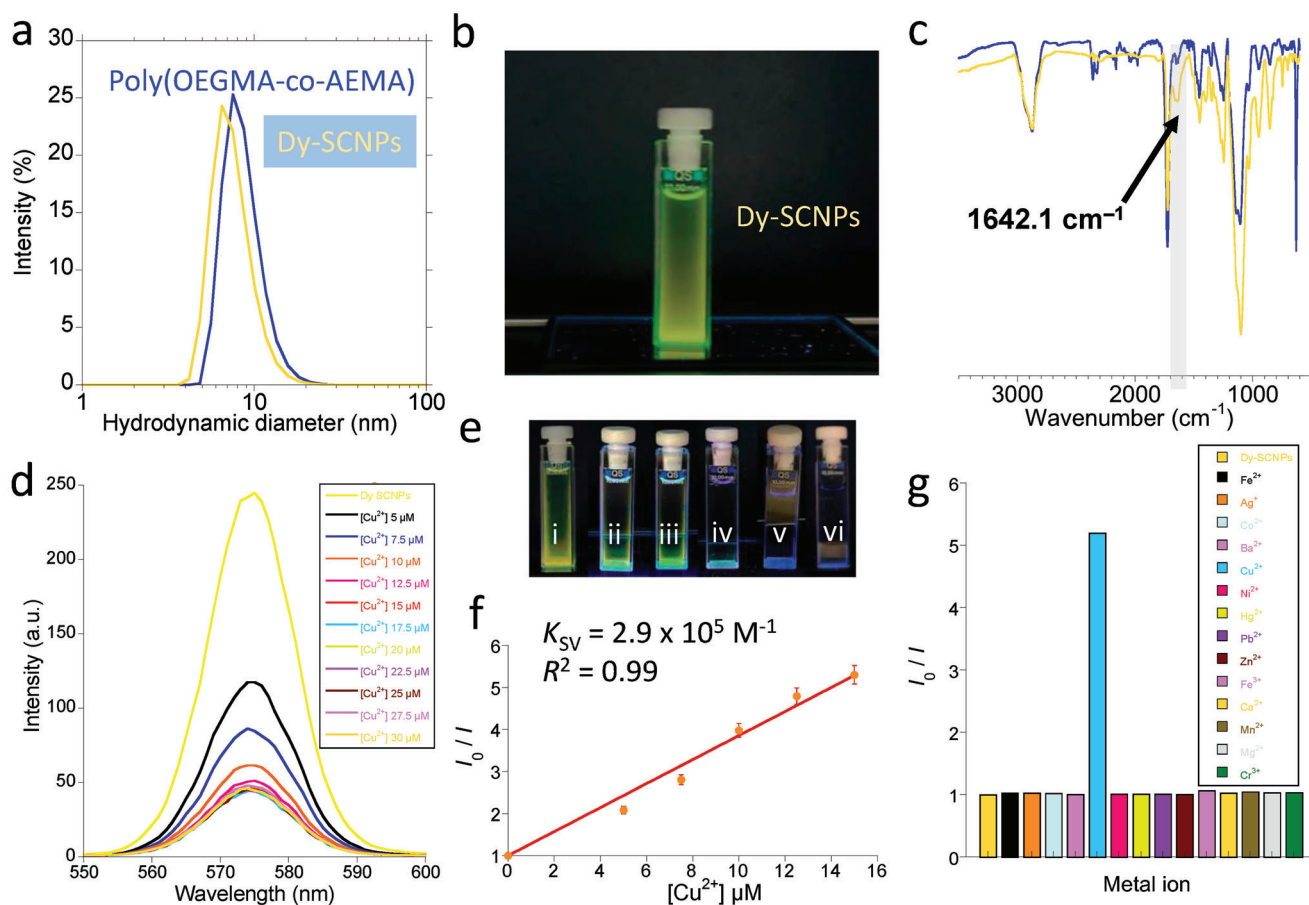
**Figure 2.** Terbium-based single-chain polymer nanoparticles (Tb-SCNPs) as “visual” pass/fail sensors of maximum permissible concentration (m.p.c.) of  $\text{Cu}^{2+}$  ions in water: a) DLS size distribution of the precursor, poly(OEGMA-co-AEMA), and the Tb-SCNPs, b) illustration of the greenish fluorescent Tb-SCNPs under UV light irradiation ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ), c) FTIR spectra of poly(OEGMA-co-AEMA) (blue color) and Tb-SCNPs (green color), d) PL spectra of Tb-SCNPs in water in the presence of increasing amounts of  $\text{Cu}^{2+}$  ions, e) demonstration of the utility of Tb-SCNPs as “visual” pass/fail sensors of m.p.c. of  $\text{Cu}^{2+}$  ions in water according to the WHO criterion ((i):  $2.5 \times 10^{-6} \text{ M}$ , (ii):  $5 \times 10^{-6} \text{ M}$ , (iii):  $15 \times 10^{-6} \text{ M}$ , (iv):  $22.5 \times 10^{-6} \text{ M}$ , (v):  $25 \times 10^{-6} \text{ M}$ , (vi):  $27.5 \times 10^{-6} \text{ M}$ , and (vii):  $30 \times 10^{-6} \text{ M}$ ), f) Stern–Volmer plot of Tb-SCNPs (error bars estimated from triple measurements), and g) selectivity of Tb-SCNPs for  $\text{Cu}^{2+}$  ions against other metal ions.

of  $\text{Tb}^{3+}$ / $\beta$ -ketoester complexes, whereas under high basic pH a decrease in fluorescence was noted, as a consequence of aggregation of the Tb-SCNPs. The stretching vibration of the enol tautomer of the  $\beta$ -ketoester groups bonded to  $\text{Tb}^{3+}$  was observed at  $1637.3 \text{ cm}^{-1}$  in the FTIR spectrum of Tb-SCNPs (Figure 2c). PL spectra of Tb-SCNPs in water in the presence of increasing amounts of  $\text{Cu}^{2+}$  ions ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ) are given in Figure 2d. A clear green color-to-transparent change under UV light ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ) was thus observed by the naked-eye, on passing from  $[\text{Cu}^{2+}] \leq 27.5 \times 10^{-6} \text{ M}$  to  $[\text{Cu}^{2+}] = 30 \times 10^{-6} \text{ M}$  or above (Figure 2e). In other words, Tb-SCNPs proved very useful as “visual” pass/fail sensors of m.p.c. of  $\text{Cu}^{2+}$  ions in water, according to the WHO criterion (m.p.c. ( $\text{Cu}^{2+}$ )<sub>WHO} =  $30 \times 10^{-6} \text{ M}$ ).<sup>[9]</sup> Analysis of the data in Figure 2d using the Stern–Volmer equation provided  $K_{\text{SV}} = 8.2 \times 10^5 \text{ M}^{-1}$  and  $R^2 = 0.98$  (see Figure 2f). The higher value of  $K_{\text{SV}}$  for Tb-SCNPs relatively to Eu-SCNPs indicates a strong sensing ability of Tb-SCNPs when compared to Eu-SCNPs. Moreover, Tb-based SCNPs display high selectivity for  $\text{Cu}^{2+}$  ions against a variety of other metal ions (Figure 2g).</sub>

Additional data of Tb-SCNPs are available in the Supporting Information (Figures S12–S14, Supporting Information).

### 2.3. Dy-SCNPs as m.p.c. ( $\text{Cu}^{2+}$ ) “Visual” Pass/Fail Sensors

Dy-SCNPs synthesized via complexation of  $\text{Dy}^{3+}$  ions in solution by  $\beta$ -ketoester functional groups of poly(OEGMA-co-AEMA) showed an average hydrodynamic diameter of 7.6 nm, a value smaller than that of the poly(OEGMA-co-AEMA) precursor (Figure 3a). Dy-SCNPs displayed yellowish fluorescence under UV light irradiation ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ) in a pH range between 7.5 and 9. Similar to the case of Eu-SCNPs and Tb-SCNPs, the fluorescence of Dy-based SCNPs could be switched-off at very low pH, owing to rupture of  $\text{Dy}^{3+}$ / $\beta$ -ketoester complexes or high pH (because of the appearance of aggregation and precipitation phenomena). Dy-based SCNPs were found to display yellowish fluorescence by the naked eye under UV light irradiation at  $\lambda_{\text{exc}} = 254 \text{ nm}$  (Figure 3b). In the FTIR spectrum of the Dy-based



**Figure 3.** Dysprosium-based single-chain polymer nanoparticles (Dy-SCNPs) as “visual” pass/fail sensors of maximum permissible concentration (m.p.c.) of  $\text{Cu}^{2+}$  ions in water: a) DLS size distribution of the precursor, poly(OEGMA-co-AEMA), and the Dy-SCNPs, b) illustration of the yellowish fluorescent Dy-SCNPs under UV light irradiation ( $\lambda_{\text{exc}} = 254 \text{ nm}$ ), c) FTIR spectra of poly(OEGMA-co-AEMA) (blue color) and Dy-SCNPs (green color), d) PL spectra of Dy-SCNPs in water in the presence of increasing amounts of  $\text{Cu}^{2+}$  ions, e) demonstration of the utility of Dy-SCNPs as “visual” pass/fail sensors of m.p.c. of  $\text{Cu}^{2+}$  ions in water according to the EPA criterion ((i):  $1 \times 10^{-6} \text{ M}$ , (ii):  $2.5 \times 10^{-6} \text{ M}$ , (iii):  $10 \times 10^{-6} \text{ M}$ , (iv):  $15 \times 10^{-6} \text{ M}$ , (v):  $20 \times 10^{-6} \text{ M}$ , and (vi):  $30 \times 10^{-6} \text{ M}$ ), f) Stern–Volmer plot of Dy-SCNPs (error bars estimated from triple measurements), and g) selectivity of Dy-SCNPs for  $\text{Cu}^{2+}$  ions against other metal ions.

SCNPs, the stretching vibration of the enol tautomer of the beta-ketoester groups bonded to  $\text{Dy}^{3+}$  was observed at  $1642.1 \text{ cm}^{-1}$  (Figure 3c). Interestingly, Dy-SCNPs show a yellow color-to-transparent transition under UV light irradiation at  $\approx 15 \times 10^{-6} \text{ M}$  of  $\text{Cu}^{2+}$  ions (Figure 3d,e) – very close to the US-EPA criterion (m.p.c.  $(\text{Cu}^{2+})_{\text{EPA}} = 20 \times 10^{-6} \text{ M}$ ) – making these Dy-based SCNPs practical “visual” pass/fail sensors of m.p.c. of  $\text{Cu}^{2+}$  ions in water according to the EPA regulation. A Stern–Volmer plot for Dy-SCNPs provided  $K_{\text{SV}} = 2.9 \times 10^5 \text{ M}^{-1}$  and  $R^2 = 0.99$  (see Figure 3f). Similarly to Eu-based and Tb-based SCNPs, Dy-based SCNPs proved selective for  $\text{Cu}^{2+}$  ions against other metal ions in solution. Additional data of Dy-SCNPs are available in the Supporting Information (Figures S15–S19, Supporting Information).

### 3. Conclusion

We introduced a new generation of m.p.c. ( $\text{Cu}^{2+}$ ) “visual” pass/fail sensors based on water-soluble lanthanide (Eu, Tb,

or Dy)-containing SCNPs of sub-10 nm size range. Under UV light irradiation at  $\lambda_{\text{exc}} = 254 \text{ nm}$ , Eu-SCNPs and Tb-SCNPs showed naked-eye red color-to-transparent and green color-to-transparent transitions, respectively, near  $[\text{Cu}^{2+}] = 30 \times 10^{-6} \text{ M}$  in water at  $\text{pH} = 7.5$ . As for Dy-based SCNPs, they displayed a yellow color-to-transparent transition at approximately  $[\text{Cu}^{2+}] = 15 \times 10^{-6} \text{ M}$ . The characteristic FTIR stretching vibration of the enol tautomer of the beta-ketoester groups bonded to  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Dy}^{3+}$  ions in Eu-SCNPs, Tb-SCNPs, and Dy-SCNPs was located at  $1632.4$ ,  $1637.3$ , and  $1642.1 \text{ cm}^{-1}$ , respectively. These “visual” pass/fail sensors show high selectivity towards  $\text{Cu}^{2+}$  ions against a variety of other metal ions ( $\text{Fe}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cr}^{3+}$ ). Consequently, Eu-SCNPs and Tb-SCNPs can be used as “visual” pass/fail sensors of m.p.c. of  $\text{Cu}^{2+}$  ions in water according to the WHO criterion (m.p.c.  $(\text{Cu}^{2+})_{\text{WHO}} = 30 \times 10^{-6} \text{ M}$ ). Complementary, Dy-SCNPs can be useful as “visual” pass/fail sensors of m.p.c. of  $\text{Cu}^{2+}$  ions in water according to the EPA regulation (m.p.c.  $(\text{Cu}^{2+})_{\text{EPA}} = 20 \times 10^{-6} \text{ M}$ ).

## 4. Experimental Section

**Materials:** Oligo(ethylene glycol) methyl ether methacrylate (OEGMA) (average  $M_n \approx 300 \text{ g mol}^{-1}$ ), (2-acetoacetoxy)ethyl methacrylate (AEMA) (95%), 2,2-azobis(2-methylpropionitrile) (AIBN) ( $\geq 98\%$ ), triethylamine (Et<sub>3</sub>N) ( $>99\%$ ), methyl acetoacetate 99%, 1,4-dioxane (anhydrous, 99.8%), *n*-hexane (anhydrous, 95%), 4-cyano-4-(thiobenzoylthio)pentanoic acid ( $\geq 97\%$ ), europium trichloride hexahydrate (EuCl<sub>3</sub>·6 H<sub>2</sub>O) (99.99% trace metals basis), terbium trichloride hexahydrate (TbCl<sub>3</sub>·6 H<sub>2</sub>O) (99.99% trace metals basis), dysprosium trichloride hexahydrate (DyCl<sub>3</sub>·6 H<sub>2</sub>O) (99.99% trace metals basis), copper (II) acetate (98%), iron (II) acetate (95%), cobalt (II) acetate tetrahydrate (99%), barium acetate (99%), nickel (II) acetate tetrahydrate (99%), mercury (II) acetate ( $\geq 98.0\%$ ), lead (II) acetate tetrahydrate (99%) zinc (II) acetate dehydrate (99%), iron (III) acetylacetonate (97%), calcium acetate monohydrate (99%), manganese (II) acetylacetonate (98%), magnesium chloride (98%), and chromium(III) acetate (98%) were supplied by Merk (Sigma-Aldrich). Potassium hydroxide (KOH) ( $\geq 85\%$ , pellets) was supplied by PanReac AppliChem (ITW Reagents). Silver (I) acetate (99%) was supplied by ITW Reagents (Acros Organics). Deionized water was obtained from a Thermo Scientific apparatus (Barnstead TII Pure Water System). Tetrahydrofuran (THF) was supplied by Scharlab. Deuterated chloroform (CDCl<sub>3</sub>) (99.8 atom % D) was supplied by Merk.

**Techniques:** <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were obtained at room temperature (r.t.) using a Bruker spectrometer operating at 400 MHz with CDCl<sub>3</sub> as the solvent. Size exclusion chromatography (SEC) measurements were conducted at 30 °C in an Agilent 1200 system that was equipped with PLgel 5 μm Guard and PLgel 5 μm MIXED-C columns. The measurements employed a triple detection system, which included a differential refractive index detector (Optilab Rex, Wyatt), a multi-angle laser light scattering (MALLS) detector (MiniDawn Treos, Wyatt), and a viscosimetric (VIS) detector (ViscoStar-II, Wyatt). SEC data were analyzed using Wyatt's ASTRA Software (version 6.1). Tetrahydrofuran (THF) was used as the eluent with a flow rate of 1 mL min<sup>-1</sup>. For both the precursor and the single-chain nanoparticles, a value of  $dn/dc = 0.1150$  was applied. Dynamic light scattering (DLS) measurements were carried out at r.t. on a Malvern Zetasizer Nano ZS apparatus. Metal content in the single-chain nanoparticles was determined by inductively coupled plasma mass spectrometry (ICP-MS). Fourier transform infrared (FTIR) spectra were recorded at r.t. on a JASCO 3600 FTIR spectrometer. UV spectroscopy was carried out in an Agilent 8453A spectrometer. Photoluminescence (PL) spectra were recorded at r.t. on an Agilent Cary Eclipse spectrometer. Horiba Laquatwin-pH-33 compact pH-meter was used for pH measurements.

**Methods—Synthesis of Amphiphilic Random Copolymer Featuring Beta-Ketoester Functional Groups:** OEGMA (1.54 mL, 5.6 mmol), AEMA (0.26 mL, 1.38 mmol), 4-cyano-4-(thiobenzoylthio)pentanoic acid (18.3 mg, 0.065 mmol), and AIBN (2.15 mg, 0.013 mmol) were dissolved at r.t. in 1,4-dioxane (3 mL). The resulting mixture was degassed by purging with argon for 15 min. Then, the mixture was subjected to reversible addition fragmentation chain-transfer (RAFT) copolymerization at 70 °C for 24 h. The resulting poly(OEGMA-*co*-AEMA) copolymer, a pink oil, was isolated by precipitation in hexane. Subsequently, the product was dissolved in a minimal amount of THF and added to an excess of hexane (twice). After removal of volatile organic solvents, further drying was carried out at r.t. under vacuum.

**Synthesis of Lanthanide-Based Single-Chain Polymer Nanoparticles (SC-NPs):** Poly(OEGMA-*co*-AEMA) (15 mg, 0.03 mmol) and the corresponding lanthanide trichloride hexahydrate (LnCl<sub>3</sub>·6 H<sub>2</sub>O; Ln = Eu, Tb, Dy) ( $30 \times 10^{-6} \text{ M}$ ) were dissolved in water (15 mL) at r.t. and pH = 7.5 for 24 h. The resulting lanthanide-containing SCNPs were purified by dialysis against deionized water. ICP-MS data about the lanthanide content in the SCNPs are provided in the ESI. Successful formation of SCNPs was confirmed by SEC and DLS measurements, according to well-established literature procedures.<sup>[11]</sup> To mitigate possible interference from molecular oxygen, all lanthanide-based SCNPs were subjected to an extensive degassing (N<sub>2</sub>) process before performing the fluorescence measurements.

## 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.

## Keywords

environmental sensors, Cu<sup>2+</sup> ions, lanthanide complexes, single-chain nanoparticles (SCNPs)

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