Supporting Information

Reactivity of ZrO(MFP) and ZrO(RP) Nanoparticles with LnCl₃ for Solvatochromic Luminescence Modification and pH-Dependent Optical Sensing**

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Supporting Information

1. Characterization of $[\text{ZrO}]^{2+}[\text{MFP}]^{2-}$ and $[\text{ZrO}]^{2+}[\text{RP}]^{2-}$ IOH-NPs

Synthesis and characterization of $[\text{ZrO}]^{2+}[\text{MFP}]^{2-}$ and $[\text{ZrO}]^{2+}[\text{RP}]^{2-}$ IOH-NPs were published in a previous study.$^{[S1]}$ The analytical data of both nanoparticles are here summarized as Supporting Information to characterize $[\text{ZrO}]^{2+}[\text{MFP}]^{2-}$ and $[\text{ZrO}]^{2+}[\text{RP}]^{2-}$, which serve as starting materials in the present study.

Analytical tools

*Dynamic light scattering (DLS).* DLS measurements were performed to obtain particle diameter and particle size distribution of the as-prepared IOH-NP suspensions. This was conducted with a Malvern Instruments Nanosizer ZS (Malvern, United Kingdom), equipped with a He-Ne laser (detection via non-invasive back-scattering at an angle of 173 °; 256 detector channels). Suspensions of $[\text{ZrO}]^{2+}[\text{MFP}]^{2-}$ and $[\text{ZrO}]^{2+}[\text{RP}]^{2-}$ IOH-NPs were investigated in water at room temperature in glass cuvettes.

*Scanning electron microscopy (SEM)* was carried out with a Zeiss Supra 40 VP microscope (Zeiss, Germany), equipped with a Schottky field emitter (2.0 nm resolution). To this concern, diluted suspensions of the as-prepared nanoparticles in ethanol or isopropanol were deposited on silicon wafers and evaporated. The acceleration voltage was in the range of 5-10 kV and the working distance was 3 mm. Average particle diameters were calculated by statistical evaluation of at least 150 nanoparticles (Scandium 5.0 software package, Soft Imaging Systems).

*Fourier-transform infrared spectroscopy (FT-IR)* was performed on a Bruker Vertex 70 FT-IR spectrometer (Bruker, Germany). The nanoparticles were pesteled and diluted with KBr (1 mg of sample per 300 mg of KBr) and pressed to pellets.
Fluorescence spectroscopy (FL). Excitation and emission spectra of fluorescent IOH-NPs were recorded using a photoluminescence spectrometer Horiba Jobin Yvon Spex Fluorolog 3 (Horiba Jobin Yvon, France), equipped with a 450 W Xenon lamp, double monochromators, Ulbricht sphere and photomultiplier as detector (90 ° angle between excitation source and detector).

Energy-dispersive X-ray (EDX) analysis. EDX was performed with an Ametek EDAX (Ametek, U.S.), device mounted on the above described Zeiss SEM Supra 40 VP scanning electron microscope. For this purpose, the IOH-NPs were pressed to dense pellets in order to guarantee a smooth surface and a quasi-infinite layer thickness. These pellets were fixed with conductive carbon pads on aluminum sample holders. EDX was only used to validate the presence and ratio of zirconium and phosphorus in [ZrO]^{2+}[MFP]^{2-} and [ZrO]^{2+}[RP]^{2-} IOH-NPs. The lighter elements (C/N/O/H) cannot be reliably quantified via the method.

Thermogravimetry (TG) was performed with a Netzsch STA 449 F3 (Netzsch, Germany) applying α-Al_{2}O_{3} as crucible material and reference sample. The IOH-NP samples were heated under air flow to 800 °C or 1400 °C with a heating rate of 1 K min\(^{-1}\). Such slow heating is essential for complete combustion of the functional organic anion. Note that the thermal decomposition of the IOH-NPs is complicated by the encapsulation of the organics content in the metal phosphates that are formed during thermal decomposition of the IOH-NPs. In fact, many typical fire retarding materials are phosphates, showing the effect of phosphate films encapsulating organic material, and thereby increasing the ignition temperature \(^1\). For thermal analysis of the IOH-NPs, therefore, slow heating rates to high temperatures are required to guarantee complete combustion. This situation, however, explains the partly lower experimental C/H/N contents in comparison to the calculated values (Tables S1,S2).

Elementary analysis (C/H/N) was performed with an Elementar Vario EL device (Elementar, Germany). In this regard, it needs to be noticed that the combustion analysis of the IOH-NPs is hampered by the encapsulation of the organics content in the metal phosphate that is formed during thermal decomposition of the IOH-NPs. Note that many typical fire retarding materials are phosphates, showing the effect of phosphate films encapsulating organic material, and thereby increasing the ignition temperature.\(^{[S2]}\) For combustion analysis of the IOH-NPs, therefore, slow heating to high temperatures is required to guarantee complete combustion. This situation,
however, explains the partly lower experimental C/H/N contents in comparison to the calculated values (Tables S1,S2).

Synthesis of $[\text{ZrO}]^{2+}[\text{MFP}]^{2-}$ and $[\text{ZrO}]^{2+}[\text{RP}]^{2-}$-IOH-NPs

The following starting materials were used: $\text{ZrOCl}_2\times8\text{H}_2\text{O}$ (>99%, Aldrich, Germany), cyclohexylammonium methylfluorescein phosphate (~95%, Sigma-Aldrich, Germany), resorufin phosphorous acid was prepared according to the literature.[S3] $[\text{ZrO}]^{2+}[\text{MFP}]^{2-}$ and $[\text{ZrO}]^{2+}[\text{RP}]^{2-}$-IOH-NPs were prepared by admixing a solution of $\text{ZrOCl}_2\times8\text{H}_2\text{O}$ (10 mg) in $\text{H}_2\text{O}$ (5 mL) to a solution of cyclohexylammonium methylfluorescein phosphate ($\text{H}_2(\text{MFP})\times\text{C}_6\text{H}_{11}\text{NH}_2$, 24 mg) or resorufin phosphorous acid ($\text{H}_2(\text{RP})$, 15 mg) in $\text{H}_2\text{O}$ (50 mL) at room temperature. Admixing was performed under vigorous stirring. Immediately after mixing, transparent suspensions were formed as can be derived from the occurrence of a Tyndall cone. After 2 min of stirring, the nanoparticles were separated by centrifugation (15 min, 25,000 r.p.m.). For washing, the nanoparticles were twice resuspended in and centrifuged from $\text{H}_2\text{O}$ to remove all remaining salts. Finally, stable suspensions were obtained by resuspending the nanoparticles in water. Stable suspensions in ethanol or diethylene glycol (DEG) are also feasible.

Characterization of $[\text{ZrO}]^{2+}[\text{MFP}]^{2-}$ and $[\text{ZrO}]^{2+}[\text{RP}]^{2-}$-IOH-NPs

Particle diameter

Mean particle diameters were determined by statistical evaluation of at least 150 nanoparticles from SEM overview images (Table S1). Figure S1 shows overview SEM images of $[\text{ZrO}]^{2-}[\text{MFP}]^{2-}$ and $[\text{ZrO}]^{2-}[\text{RP}]^{2-}$-IOH-NPs.
Table S1. Particle diameter and molar weight of \([\text{ZrO}]^{2+}[\text{MFP}]^{2-}\) and \([\text{ZrO}]^{2+}[\text{RP}]^{2-}\) IOH-NPs.

| Compound          | Molar weight (g mol\(^{-1}\)) | Load of fluorescent organic anion \([R_{dye}\text{OPO}_3]^{2-}\) (wt-%) | Particle diameter (from SEM) (nm) |
|-------------------|-------------------------------|---------------------------------------------------------------|----------------------------------|
| \([\text{ZrO}]^{2+}[\text{MFP}]^{2-}\) | 533                           | 80.0                                                          | 26(6)                            |
| \([\text{ZrO}]^{2+}[\text{RP}]^{2-}\) | 386                           | 72.3                                                          | 27(8)                            |

Figure S1. Electron microscopy of \([\text{ZrO}]^{2+}[\text{MFP}]^{2-}\) and \([\text{ZrO}]^{2+}[\text{RP}]^{2-}\) IOH-NPs.

Apart from SEM, the particle size of the as-prepared IOH-NPs is shown in water (Figure S2). However, the DLS analysis should not be overestimated as the IOH-NPs are currently not stabilized by any specific surface-active agent. Therefore, agglomeration in water (as a highly polar solvent with very high surface tension) is to be expected. If the nanoparticles were dispersed in more stabilizing solvents such as diethylene glycol, the particle size turned out as significantly smaller and the particle size distribution is much narrower.\(^{[S4,S5]}\) This finding indicates that the IOH-NPs do not form hard agglomerates (as they can be deagglomerated just by choosing a more stabilizing solvent).
**Infrared spectra (FT-IR)**

Infrared spectroscopy (FT-IR) confirms the presence of the dye anions in \([\text{ZrO}]^{2+}[\text{MFP}]^{2-}\) and \([\text{ZrO}]^{2+}[\text{RP}]^{2-}\) IOH-NPs by comparing the spectra with the starting materials of the organic functional anions (Figures S3). All characteristic vibrations of the relevant functional organic anions are visible for the IOH-NPs. In general, the IOH-NPs exhibit broader and less structured vibrations in comparison to the much sharper and partly fine-splitted vibrations of the starting materials. This finding and difference is related to the non-crystallinity of the IOH-NPs and in contrast to the highly crystalline starting materials.

**Thermogravimetry (TG)**

The TG data of the \([\text{ZrO}]^{2+}[\text{MFP}]^{2-}\) and \([\text{ZrO}]^{2+}[\text{RP}]^{2-}\) IOH-NPs show one to three decomposition steps that are significantly overlapping each other (Figures S4). Thermal decomposition starts at about 100 °C and is mainly finished at 600 °C. At even higher temperature (800-1000 °C), an additional minor weight loss is sometimes
observed and can be attributed to the oxidation of remaining carbon fragments. In general, the decomposition of \([\text{ZrO}]^{2+}[\text{R}^\text{dye}O\text{PO}_3]^{2−}\) nanoparticles can be rationalized based on the following equation:

\[
4[\text{ZrO}]^{2+}[\text{R}^\text{dye}O\text{PO}_3]^{2−} \rightarrow \text{ZrO}_2 + \text{Zr}_3(\text{PO}_4)_4 + (\text{CO}_2, \text{N}_2, \text{H}_2\text{O})↑
\]

Herein, the organic part \(R\) function is thermally completely decomposed in air under formation of gaseous \(\text{CO}_2\), \(\text{N}_2\) and \(\text{H}_2\text{O}\). \(\text{ZrO}_2\) and \(\text{Zr}_3(\text{PO}_4)_4\) were identified as the thermal remnant via X-ray powder diffraction. A comparison of the calculated weight loss (according to the above equation) and the experimentally observed weight loss is given in Table S2. Similar to elemental analysis, the thermal decomposition of the IOH-NPs is complicated by the encapsulation of the organics content in the metal phosphate that is formed during thermal decomposition of the IOH-NPs. In fact, many typical fire retarding materials are phosphates, showing the effect of phosphate films encapsulating organic material, and thereby increasing the ignition temperature.[S2] For thermal analysis of the IOH-NPs, therefore, slow heating rates to high temperatures are required to guarantee complete combustion. This situation, however, explains the partly lower experimental C/H/N contents in comparison to the calculated values (Table S2).

**Figure S4.** Thermogravimetry of the as-prepared \([\text{ZrO}]^{2+}[\text{MFP}]^{2−}\) and \([\text{ZrO}]^{2+}[\text{RP}]^{2−}\) IOH-NPs. Measurements were performed with a total sample weight of 20-30 mg in air and with a heating rate of 1 K min⁻¹.

**Chemical composition**

The chemical composition of the \([\text{ZrO}]^{2+}[\text{MFP}]^{2−}\) and \([\text{ZrO}]^{2+}[\text{RP}]^{2−}\) IOH-NPs was derived from different independent analytical methods, including Fourier-transform infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDX), thermogravimetry (TG), and elemental analysis/combustion analysis (EA). Hereof, FT-IR evidences the presence of the relevant functional organic anions \([\text{MFP}]^{2−}\) and \([\text{RP}]^{2−}\)
The presence and function of the fluorescent organic anion is furthermore proven by fluorescence spectroscopy (Figure S5). The presence of zirconium as the inorganic cation is validated by EDX (Table S2). Note furthermore that no nanoparticles are formed if the inorganic anion or the functional organic anion were not present.

Table S2. Chemical composition of the \([\text{ZrO}]^2+\text{[MFP]}^2−\) and \([\text{ZrO}]^2+\text{[RP]}^2−\) IOH-NPs (calculated values in brackets).

| Compound            | Zr : P ratio (EDX) | Weight loss (TG) /wt% | C content (EA) /wt% | H content (EA) /wt% | N content (EA) /wt% |
|---------------------|--------------------|------------------------|---------------------|---------------------|---------------------|
| \([\text{ZrO}]^2+\text{[RP]}^2−\) | 1.2:1 (1:1)        | 43 (48)                | 26 (34)             | 2.8 (1.6)           | 2.5 (3.6)           |
| \([\text{ZrO}]^2+\text{[MFP]}^2−\) | 1.1:1 (1:1)        | 62 (64)                | 42 (47)             | 3.6 (2.8)           | 0.2 (0)             |

The ratio of inorganic cation and functional organic anion in the IOH-NPs was determined by EDX (based on the Zr : P ratio, Table S2) for the \([\text{ZrO}]^2+\text{[MFP]}^2−\) and \([\text{ZrO}]^2+\text{[RP]}^2−\) IOH-NPs. In the case of the EDX analysis of the Zr : P ratio, bulk-Zr$_3$(PO$_4$)$_4$ was used as a reference sample. Moreover, the ratio of inorganic cation and functional organic anion was independently obtained from the weight loss as determined by TG. Here, the fluorescent organic anion is completely oxidized in air under formation of CO$_2$, N$_2$ and H$_2$O (Figure S4), whereas ZrO$_2$ and Zr$_3$(PO$_4$)$_4$ were observed via X-ray powder diffraction as thermal remnants. Finally, the contents of carbon, hydrogen and nitrogen were determined by elemental analysis/combustion analysis (EA) (Table S2). In sum, the chemical composition is consistently determined based on different independent analytical methods.

Fluorescence spectroscopy

Fluorescence spectra of the \([\text{ZrO}]^2+\text{[MFP]}^2−\) and \([\text{ZrO}]^2+\text{[RP]}^2−\) IOH-NPs are shown in Figure S5. Accordingly, the excitation can be performed for \([\text{ZrO}]^2+\text{[MFP]}^2−<500\text{ nm (λ}_{\text{max}} = 475\text{ nm})\) and for \([\text{ZrO}]^2+\text{[RP]}^2−<600\text{ nm (λ}_{\text{max}} = 580\text{ nm})\). Emission spectra indicate green (460-700 nm, \(\lambda_{\text{max}} = 518\text{ nm})\) and red (550-700 nm, \(\lambda_{\text{max}} = 584\text{ nm})\) emission of \([\text{ZrO}]^2+\text{[MFP]}^2−\) and \([\text{ZrO}]^2+\text{[RP]}^2−\), respectively (Figure S5). Due to the quasi-infinite number of fluorescence centers, the IOH-NPs show intense spot-light emission in aqueous suspension at typical concentrations of 1-5 wt%.
Figure S5. Excitation and emission spectra of \([\text{ZrO}^2+]\text{[MFP]}^2^-\) (green) and \([\text{ZrO}^2+]\text{[RP]}^2^-\) (red).

2. Characterization of Reaction Products

Dynamic Light Scattering and Electron Microscopy, EDX

Figure S6. Particle size determined by dynamic light scattering (DLS, a) in pyridine and electron microscopy (b) of YCl₃@ZrO(RP) composite particles (4).
Tab. S3 Exemplary EDX studies of $\text{YCl}_3@\text{ZrO(RP)}$ (4). The sample contains additional amounts of Si caused by the sample holder (not listed below).

| Element | At% |
|---------|-----|
| C K     | 42.28 |
| O K     | 18.85 |
| Y L     | 3.90  |
| Cl K    | 6.33  |
| P K     | 0.00  |
| Zr L    | 0.00  |

Photoluminescence and IR Spectroscopy

Figure S7. Excitation and emission spectra of ZrO(RP) composite particles (4) as dispersions in pyridine for different reaction temperatures and storage conditions (left). Photographs at daylight and upon excitation via UV light ($\lambda_{\text{Exc}} = 365$ nm) (right).
Figure S8. Infrared spectra of $\text{YCl}_3@\text{ZrO(RP)}$ composite particles (4) in comparison to unmodified $\text{ZrO(RP)}$ nanoparticles dried from a suspension in pyridine.
References

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