# A Metallosupramolecular Coordination Polymer for the 'Turn-on' Fluorescence Detection of Hydrogen Sulfide

Joydev Hatai,* Christoph Hirschhäuser, Carsten Schmuck[+], and Jochen Niemeyer*[a]

*Dedicated to the memory of Prof. Dr. Carsten Schmuck*

**A coumarin based** probe for the efficient detection of hydrogen sulfide in aqueous medium is reported. The investigated coumarine-based derivative forms spherical nanoparticles in aqueous media. In presence of $Pd^{2+}$, a metallosupramolecular coordination polymer is formed, which is accompanied by quenching of the coumarin emission at 390 nm. Its $Pd^{2+}$ complex could be used as a probe for chemoselective detection of monohydrogensulfide ($HS^-$). Presence of $HS^-$ leads to a'turn-on' fluorescence signal, resulting from decomplexation of $Pd^{2+}$ from the metallosupramolecular probe. The probe was successfully applied for qualitative and quantitative detection of $HS^-$ in different sources of water directly collected from sea, river, tap and laboratory drain water, as well as in growth media for aquatic species.

## 1. Introduction

An exposure to high level of hydrogen sulfide ($H_2S$) can cause several health problems such as headache, nausea, diabetes, Alzheimer's disease, and even death.[1] At pH 7.4 about two-thirds of $H_2S$ exist as monohydrogensulfide ($HS^-$) and the remaining one-third mostly as undissociated hydrogen sulfide ($H_2S$).[2] Release of $H_2S$ into the environment occurs through geothermal activity (e.g. volcanoes and hot springs) as well as industrial processes, or microbial reduction of sulfate by anaerobic bacteria.[3] In the environment the concentration of sulfide varies from μg $L^{-1}$ to mg $L^{-1}$ and its toxic effects depend on its concentration and exposure time.[4] $H_2S$ has a characteristic odor, which, however, is not a reliable indicator. Exposure to high levels (>150 ppm) of sulfide instantly triggers the smelling sensation.

Several analytical methods such as capillary electrophoresis, sulfide precipitation, chromatography, or polarographic analysis have been reported for the detection of $H_2S$.[5] Although some of these techniques are suitable for measurements of low concentrations of $H_2S$, they suffer from a lack of real-time response, high cost of instrumentation or require complicated sample preparation and thus employment of dedicated experts. Therefore, designing a fluorescent probe for $H_2S$ has attracted significant attention due to its simplicity, compatibility, sensitivity and capacity for real time detection. A variety of fluorescent probes for the detection of $H_2S$ were developed based on various strategies such as reduction of azides,[6] reduction of nitroso- or nitro-compounds,[7] reduction of selenoxides[8] and nucleophilic addition.[9]

Recently, $H_2S$ sensing based on displacement of metal ions from a non-fluorescent ligand-metal ensembles has attracted great attention.[10,11] Such systems have several advantages such as water solubility, straightforward synthesis, and wide applicability.[12] However, to date, only a limited number of $H_2S$ selective systems based on metal sequestering were reported in aqueous medium.[13] Copper complexes are among the most prominent receptors for detection of $H_2S$ due to the low solubility of CuS ($K_{sp} = 6.36 \times 10^{-36}$ $M^2$). For example, the Chang group has reported a dipicolylamine copper complex linked to fluorescein, which was used for selective sensing of sulfide in aqueous media.[13] Martínez-Máñez and coworkers have prepared silica nanoparticles functionalized with Cu(II)-macrocycles for detection of $HS^-$ anions.[14] There are also reports of a few Zn,[15] Hg,[16] and Cd[17] complexes as $H_2S$ probes. However, Pd-complexes were not explored for detection of $H_2S$ in aqueous media so far (to the best of our knowledge).

Herein, we report that the combination of the coumarin-based compound **1** and $Pd^{2+}$-ions results in a highly selective probe for the detection of hydrogen-sulfide. Compound **1** forms spherical nanoparticles in aqueous media. In presence of $Pd^{2+}$, a metallosupramolecular coordination polymer is formed, which is accompanied by quenching of the coumarin emission at 390 nm. The $\mathbf{1}\cdot Pd^{2+}$ complex could be used as a probe for selective detection of monohydrogensulfide ($HS^-$). Presence of $HS^-$ leads to a'turn-on' fluorescence signal, resulting from decomplexation of $Pd^{2+}$ from the metallosupramolecular probe. The probe was successfully applied for the qualitative and quantitative detection of $HS^-$ in different sources of water

[a] *Dr. J. Hatai, Dr. C. Hirschhäuser, Prof. Dr. C. Schmuck,[+] Dr. J. Niemeyer*
*Faculty of Chemistry (Organic Chemistry) and Center for Nanointegration Duisburg- Essen (CENIDE)*
*University of Duisburg-Essen*
*Universitätsstrasse 7*
*45141 Essen (Germany)*
*E-mail: joydev.hatai@uni-due.de*
*jochen.niemeyer@uni-due.de*

[+] *The authors deeply regret the loss of Prof. Dr. Carsten Schmuck, who was a revered scientist, teacher, mentor and friend. Prof. Schmuck was the original supervisor of the project, but as he passed away before it could be finished, Dr. Niemeyer took over supervision.*

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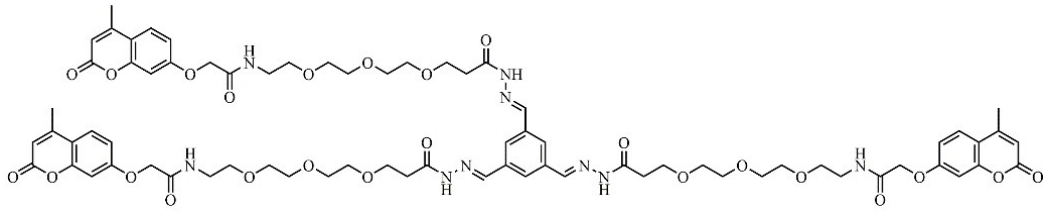

**Figure 1.** Chemical structure of compound **1**.

directly collected from sea, river, tap and laboratory drain water, as well as in growth media for aquatic species.

## 2. Results and Discussion

Probe **1** (see Figure 1) was synthesized according to our previously described procedure.[18] Compound **1** consists of coumarin fluorophores, which can aggregate in aqueous media through π-π stacking of individual coumarin units with each other as well as with the central benzene moiety.[18,19] The three-armed hydrazone linkage was chosen for metal ion induced formation of a network structure.

First, we investigated the metal binding of probe **1** in phosphate buffer (0.5 mM) at pH 7.4. The free probe showed an emission maximum at 490 nm (Quantum yield, $\Phi = 0.235$) when excited at 310 nm. The metal-sensing ability of compound **1** (10 μM) was investigated based on its fluorescence response in the presence of $Al^{3+}$, $Hg^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Ni^{2+}$, $Ag^{+}$, $Cr^{3+}$, $Cs^{+}$, $Fe^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Pt^{3+}$, $Sb^{3+}$, $Pb^{2+}$, $Na^{+}$, $Ca^{2+}$, $K^{+}$ and $Pd^{2+}$ (40 μM) ions (chloride or nitrate salt). As shown in Figure 2 (Table S1) strong fluorescence quenching of **1** was observed by the $Pd^{2+}$ ion ($\Phi = 0.02$). Among the other metal ions, $Cu^{2+}$ and $Hg^{2+}$ also quench the fluorescence of **1** to a smaller extent.

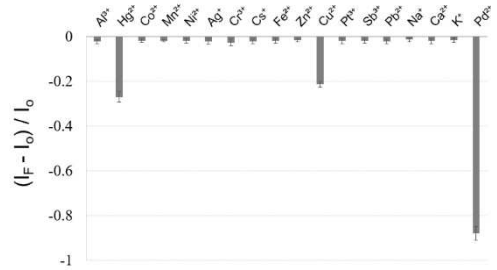


**Figure 2.** Quenching of fluorescence intensity of **1** (10 μM) after addition of different metal salts (40 μM) in aqueous phosphate buffered media (1 < % DMSO as a cosolvent) at 25 °C.

To gain better insight into the interaction of **1** by $Pd^{2+}$, we performed fluorescence and UV/Vis-titrations in aqueous media. In the fluorescence titration (10 μM **1**, 0–10 eq of $Pd^{2+}$, Figure 3), a sharp decrease in the emission intensity of **1** at 390 nm was observed up to an addition of one equivalent of $Pd^{2+}$ (Figure 3, *inset*) with a ~5 nm red shift of the emission band. At higher concentration of $Pd^{2+}$, the fluorescence intensity of **1** was further quenched and underwent a blue shift from 390 nm to 380 nm with a shoulder emission band at 363 nm (Figure 3). The Stern-Volmer constant ($K_{sv}$) for quenching of emission of **1** by $Pd^{2+}$, calculated from the linear part (0–5 μM $Pd^{2+}$) of the titration data (Figure 3), was determined as $1.8 \times 10^5\ M^{-1}$ in aqueous media (Figure S1). The analytical detection limit from the titration of **1** with $Pd^{2+}$ was found to be 37 ppb (Figure S2).[20]

In the UV/Vis, the initial absorption spectrum of **1** (15 μm) showed a strong absorption peak at 293 nm and shoulder band at 309 nm (Figure 4). Titration with increasing concentration of $Pd^{2+}$ (0–2.5 eq) revealed a continuous decrease in the main absorption peak at 295 nm and the shoulder band accompanied by a 12-nm red shift from 309 nm to 321 nm. We attribute

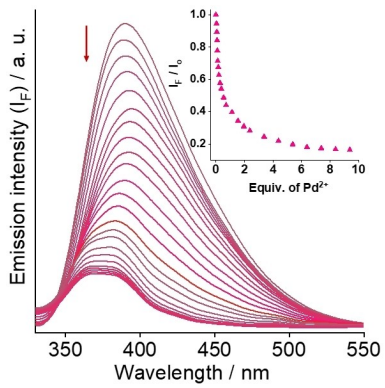


**Figure 3.** Changes in the emission of **1** (10 μM) with increasing concentration of $Pd^{2+}$ (0 to 100 μM) in aqueous phosphate buffered media (1 < % DMSO as a cosolvent) at 25 °C. *Inset:* $Pd^{2+}$ titration profile at 390 nm.

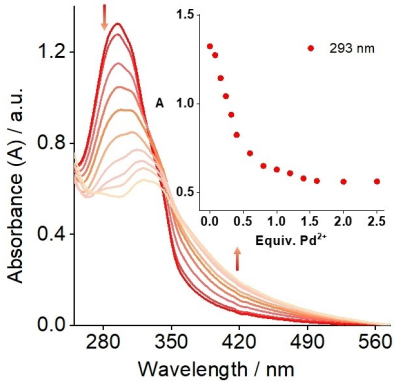


**Figure 4.** Changes in the absorption spectra of **1** (15 μM) with increasing concentration of $Pd^{2+}$ (0 to 37.5 μM) in aqueous phosphate buffered media (1 < % DMSO as a cosolvent) at 25 °C. Inset: $Pd^{2+}$ titration profile at 293 nm.


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both the decreased fluorescence and the increasing absorption of low energy bands with increasing concentration of $Pd^{2+}$ to the formation of the $\mathbf{1}\cdot Pd^{2+}$ complex.[21]

To further investigate the supramolecular interaction of **1** with $Pd^{2+}$, DLS and AFM data of **1** were recorded in the absence and presence of $Pd^{2+}$ ions (Figure 5 and Figure S3). Coumarin is prone to aggregate in aqueous media via π–π stacking interactions and indeed, dynamic light scattering (DLS) experiments agreed well with this expectation. A dispersion of **1** (10 μM) in aqueous media gave an average hydrodynamic radius (Z) of 105 nm (PDI = 0.091), thus indicating aggregation of **1** in aqueous media. Interestingly, upon addition of $Pd^{2+}$ (20 μM) the average diameter of the solution significantly increased to 1603 nm (PDI = 0.302). This is in line with the formation of a metallosupramolecular polymer due to the multidentate nature of **1** in combination with an expected coordination of $Pd^{2+}$ by two hydrazone-ligands.[22]

The transition of nanoparticles (**1** only) to a metallosupramolecular polymer ($\mathbf{1} + Pd^{2+}$) was confirmed by atomic force microscopy (AFM). As shown in Figure 5, compound **1** (10 μM) in absence of $Pd^{2+}$ ions form small spherical nanoparticles with an average lateral diameter of 85 nm, which is close to the diameter observed by DLS (105 nm). Interestingly, in presence of $Pd^{2+}$ (20 μM) a network structure was observed. Based on our finding and hydrazone-$Pd^{2+}$ complexes reported in literature a putative binding model is depicted in Figure 6.

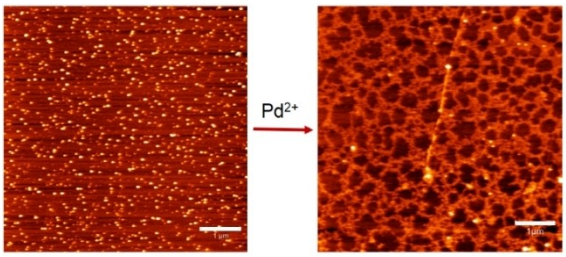


**Figure 5.** AFM measurements of probe **1** (10 μM) in absence and presence of $Pd^{2+}$ (20 μM) (scale bar 1 μm).

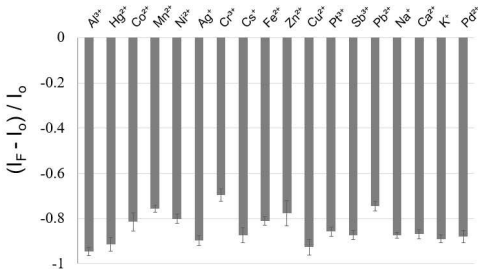


**Figure 7.** Quenching of emission of **1** by $Pd^{2+}$ in the presence of other metal ions in aqueous media. The emission from a solution of **1** (10 μM) mixed with specified metal ions (40 μM) followed by addition of $Pd^{2+}$ (40 μM) were recorded.

To test the selectivity of fluorescence quenching of probe **1** in presence of $Pd^{2+}$, competitive experiments were carried out for ternary mixtures of compound **1** (10 μM) individually mixed with selected metal ions (40 μM) and followed by addition of $Pd^{2+}$ (40 μM). We found that among the metal ions investigated here ($Al^{3+}$, $Hg^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Ni^{2+}$, $Ag^{+}$, $Cr^{3+}$, $Cs^{+}$, $Fe^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Pt^{3+}$, $Sb^{3+}$, $Pb^{2+}$, $Na^{+}$, $Ca^{2+}$ and $K^{+}$), only a minor influence was observed on the $Pd^{2+}$-induced fluorescence quenching of probe **1** (Figure 7, Table S2).

Moreover, to test the sensitivity of the $\mathbf{1}\cdot Pd^{2+}$ complex to other species that might be present in real-life samples, the fluorescence quenching was investigated in different water samples directly collected from the Adriatic Sea (Venice, Italy), the river Rhein (Düsseldorf, Germany), a laboratory drain, the Ganga river (Kolkata, India), growth media for aquatic species and a laboratory tap, using milli-Q water as a comparison. As shown in Figure 8, the response of **1** (10 μM) to $Pd^{2+}$ (12 μM) was not affected significantly by the presence of interfering ions and other species present in the real-life samples. Thus, the $\mathbf{1}\cdot Pd^{2+}$ complex can be applied in presence of various impurities.

For an application of the $\mathbf{1}\cdot Pd^{2+}$ complex, we anticipated that the presence of anions could lead to decomplexation of $Pd^{2+}$ ions from the $\mathbf{1}\cdot Pd^{2+}$ ensemble. This would restore the

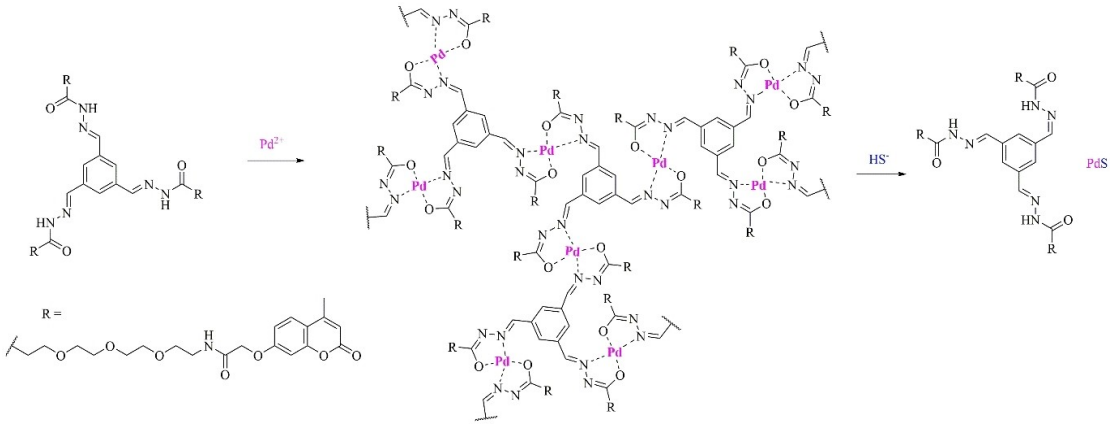


**Figure 6.** Putative complexation mode[22] of the $Pd^{2+}$ ion for formation of coordination polymers of **1** followed by decomplexation of $Pd^{2+}$ by $HS^{-}$ in aqueous media.


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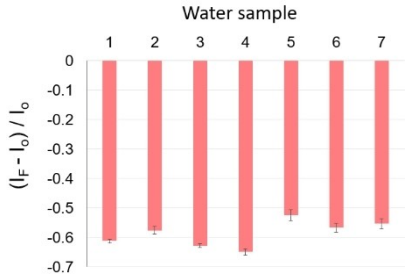


**Figure 8.** Changes in emission of **1** (10 μM) upon addition of $Pd^{2+}$ (12 μM) dissolved in different water samples directly collected from (1) water purification system (milli-Q water), (2) laboratory tap, (3) Ganga river (Kolkata, India), (4) laboratory drain, (5) Rhein river (Dusseldorf, Germany), (6) Adriatic Sea (Venice, Italy), (7) growth media for aquatic species. Low concentration of $Pd^{2+}$ was added to see whether the probe **1** is suitable to detect almost equimolar amount of $Pd^{2+}$.

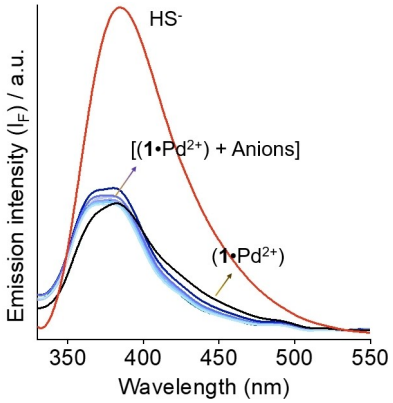


**Figure 9.** Changes in fluorescence intensity of [**1**·$Pd^{2+}$] ensemble consisting of **1** (10 μM) and $Pd^{2+}$ (30 μM) upon addition of sodium salts of various anions (120 μM) in aqueous media buffered with phosphate (0.5 mM).

fluorescence of the ligand and allow for the use of our metallosupramolecular polymer as a'turn-on' fluorescent probe for analytical purposes.

Thus, mixtures of **1** (10 μM) and $Pd^{2+}$ (30 μM) were individually mixed with fluoride, chloride, bromide, iodide, monohydrogensulfide, carbonate, acetate, sulfate, sulfite, thiocyanate, thiosulfate anions (120 μM) in phosphate buffer at pH 7.4. Among these anions, monohydrogensulfide ($HS^-$) distinctly triggered emission (Figure 9). The restoration of the emission intensity is proportional to the concentration of $HS^-$ present in the solution ($\Phi = 0.22$, meaning that 95% of the emission is recovered, Figure 10). Most likely the selective response of the **1**·$Pd^{2+}$ ensemble to $HS^-$ is due to the formation of PdS, which has a low solubility ($K_{sp}$ of PdS = $2.03 \times 10^{-58}$ $M^2$). From a titration of **1**·$Pd^{2+}$ with $HS^-$ in phosphate buffer, the limit of detection (LOD) was calculated as 15 μmol $L^{-1}$ (Figure S4).[23]

To test our assumption if addition of $HS^-$ leads to a decomplexation of $Pd^{2+}$, we followed the process by DLS and AFM measurements. Upon addition of $HS^-$ (120 μM) to **1**·$Pd^{2+}$ (10 μM of **1** and 20 μM $Pd^{2+}$), DLS showed that the overall hydrodynamic radius of the Pd-complex (1603 nm, PDI = 0.302) significantly decreased (103 nm, PDI = 0.131) (Figure S3), thus resembling the size of **1** alone (105 nm, PDI = 0.091). AFM (Figure 11) also showed that the coordination polymers are broken up by addition of $HS^-$, resulting in spherical nanoparticles with an average diameter of 80 nm. These observations suggest $HS^-$ induced decomplexation of $Pd^{2+}$ from the palladium-based coordination polymers, leading to release of compound **1** and restoring of the fluorescence signal (see Figure 6 for the putative model for $HS^-$ induced release of $Pd^{2+}$ from the **1**·$Pd^{2+}$ ensemble).

To test the application of the **1**·$Pd^{2+}$ ensemble for the detection of hydrogen sulfide, competitive experiments were carried out to investigate the effect of various anions for selective detection of $HS^-$. Thus, the recovery of emission of **1** from an **1**·$Pd^{2+}$ ensemble (10 μM of **1** and 30 μM of $Pd^{2+}$) by addition of $HS^-$ (195 μM) was recorded in presence of a mixture of other anions (fluoride, chloride, bromide, iodide, carbonate, acetate, sulfate, sulfite, thiocyanate, thiosulfate). For this, we

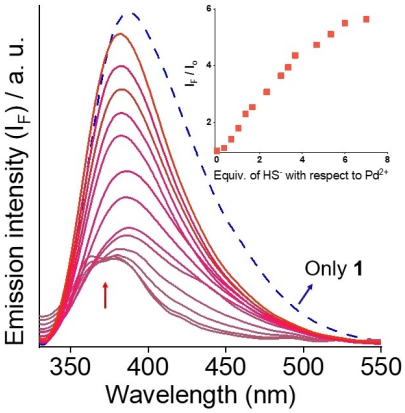


**Figure 10.** Changes in the fluorescence intensity of a **1**·$Pd^{2+}$ ensemble (10 μM of **1** and 30 μM of $Pd^{2+}$) upon addition of different equivalents of $HS^-$ in aqueous media buffered with phosphate (0.5 mM). Inset: Titration profile for recovery of emission of **1** from a **1**·$Pd^{2+}$ ensemble in the presence of $HS^-$ ions at 410 nm.

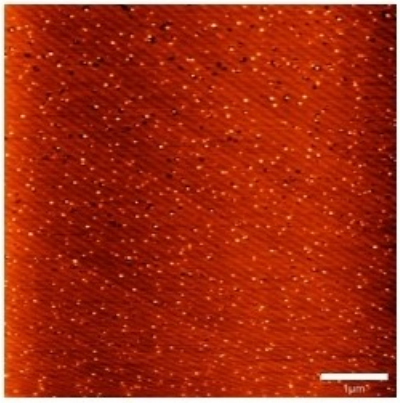

**Figure 11.** AFM measurement of **1**·$Pd^{2+}$ (10 μM of **1** and 20 μM of $Pd^{2+}$) ensemble upon addition of $HS^-$ (120 μM) in aqueous media at 25 °C (scale bar 1 μm).

used different concentrations (200 μM of each ion or 350 μM of each ion) to check their interreferences with the $HS^-$ detection.


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As shown in Figure 12 (Table S4), an 82% (for 200 μM competing ions) and 72% (for 350 μM competing ions) recovery of the emission signal (compared to fluorescence in absence of any interfering anions) was observed upon addition of $HS^-$. Thus, the presence of coexisting anions slightly altered the recovery of emission from the **1**·$Pd^{2+}$ ensemble by addition of $HS^-$, but still allowed for its use as a'turn-on' probe. We also verified that presence of $Hg^{2+}$ and $Cu^{2+}$, which showed a small degree of fluorescence quenching of compound **1**, does not interfere with the detection of hydrogen-sulfide with the **1**·$Pd^{2+}$ ensemble (Figure S5).

To mimic a practical application, the detection of hydrogen sulfide was also conducted with different water samples directly collected from a water purification system (milli-Q water), a laboratory drain, the Ganga river (Kolkata, India), the Adriatic Sea (Venice, Italy), a laboratory tap, growth media for aquatic species, and the river Rhein (Düsseldorf, Germany). As shown in Figure 13, the fluorescence recovery did not vary significantly compared to the signal obtained in milli-Q water.

Inspired by the above results, we also investigated the possibility to quantify hydrogen sulfide in water from different sources. For this, we first generated an external calibration curve using Milli-Q water as a solvent (Figure S6).[24] Then different water samples (drinking water (1), water from the Adriatic Sea (Venice, Italy) (2), water from the river Rhein (Düsseldorf, Germany) (3) and water from a laboratory drain (4)) were spiked with known concentrations of hydrogen-sulfide (18, 30 and 52 μM, respectively).

Upon application of our **1**·$Pd^{2+}$ ensemble to these samples, we could show that the hydrogen sulfide concentrations could be accurately quantified by a simple fluorescence measurement (Table 1 and Table S6). Especially for water samples 1–3, the recovery was excellent (96.7% to 100.2%), only for sample 4 the recovery was slightly worse (82.9% to 94.5%). These result points towards the suitability of our probe for practical application in the analysis of real samples without interference from competitive ions or other components present in real-life samples.

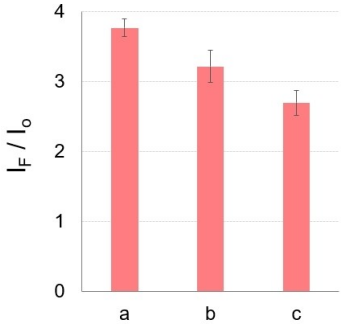


**Figure 12.** Comparison of fluorescence recovery of **1** from **1**·$Pd^{2+}$ (10 μM of **1** and 30 μM of $Pd^{2+}$) ensembles upon $HS^-$ (195 μM) addition in the presence of a mixture of (a) 0 μM, (b) 200 μM, (c) 350 μM of various anions. $I_o$ corresponds to the emission of the **1**·$Pd^{2+}$ ensemble (see supporting information).

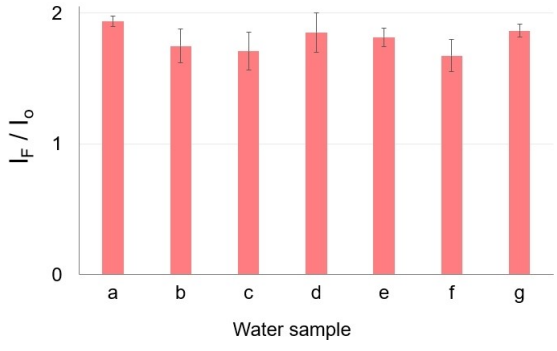


**Figure 13.** Comparison of fluorescent revival of **1**·$Pd^{2+}$ (10 μM of **1** and 5 μM of $Pd^{2+}$) ensembles by monohydrogensulfide (30 μM) dissolved in different water samples directly collected from (a) water purification system (milli-Q water), (b) laboratory drain, (c) Ganga river (Kolkata, India), (d) Adriatic Sea (Venice, Italy), (e) laboratory tap, (f) growth media for aquatic species, (g) Rhein river (Dusseldorf, Germany). $I_o$ corresponds to the emission of the **1**·$Pd^{2+}$ ensemble.

## 3. Conclusions

In summary, this study reports a novel supramolecular coordination polymer, which can be applied as a turn-on fluorescent probe for the detection of hydrogen-sulfide. The molecular interaction of the coumarin based compound **1** with $Pd^{2+}$ ions (leading to supramolecular polymerization and fluorescence quenching) and the subsequent interaction with hydrogen-sulfide (leading to Pd-decomplexation, depolymerization and fluorescence recovery) were investigated in detail. The **1**·$Pd^{2+}$ ensemble could be used for the quantitative detection of monohydrogensulfide and no significant interference of other anions or cations was observed. This we could accurately quantify hydrogen-sulfide concentrations in different real-life water samples collected from a water purification system, the Adriatic Sea, the river Rhein and a laboratory drain. Thus, our system allows for the simple and straightforward quantification of hydrogen-sulfide levels in water samples based on a simple fluorescence measurements with a low detection limit (15 μM).

**Table 1.** Results of quantitively detection of hydrogen sulfide in different water samples.[25]

| Water sample | Added NaHS [μM] | Found NaHS [μM][a]±[b] | Recovery [%] |
|---|---|---|---|
| 1 | 18 | 17.95 ± 0.2 | 99.7 |
| | 30 | 30.00 ± 0.2 | 100.0 |
| | 52 | 51.99 ± 0.5 | 99.9 |
| 2 | 18 | 17.45 ± 0.4 | 96.9 |
| | 30 | 30.06 ± 0.3 | 100.2 |
| | 52 | 52.10 ± 0.6 | 100.2 |
| 3 | 18 | 17.42 ± 0.1 | 96.7 |
| | 30 | 29.52 ± 0.6 | 98.4 |
| | 52 | 51.62 ± 0.3 | 99.2 |
| 4 | 18 | 14.93 ± 0.5 | 82.9 |
| | 30 | 28.08 ± 0.2 | 93.6 |
| | 52 | 49.12 ± 0.7 | 94.5 |

Water sample: 1. Drinking water; 2. The Adriatic Sea (Venice, Italy); 3. The river Rhein (Düsseldorf, Germany); 4. Laboratory drain. [a] Mean value of three experiments. [b] Standard deviation.


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## Experimental Section

### Materials and Equipment

A TKA MicroPure ultrapure water system was used for purified water. Determination of pH values was carried out with a pH-Meter 766 Calimatic from Knick.

### Synthesis of Probe 1

Probe **1** was synthesized based to our previously described procedure.[18]

### General Procedure for UV/Vis and Fluorescence Studies

The UV/Vis spectra were recorded on a JASCO V-660 spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse spectrofluorometer. All measurements were performed in quartz cuvettes and the total volume of the solution was 400 μl. For absorption and emission spectra, stock solutions of the metal salts (1 mM, 5.0 mM and 15 mM) and the free chemosensor **1** (5 mM) were prepared in DMSO. The stock solutions of anions (1 mM, 5.0 mM and 15 mM) were prepared in milli-Q water. The UV spectra were recoded over the range of 230–750 nm. The emission of **1** was recoded over a range of 330–600 nm in aqueous media with $<1\%$ DMSO (with respect to total volume of solution in cuvette) as a cosolvent. Excitation was performed at 310 nm with an excitation and emission slit widths at 10 nm unless otherwise indicated. The phosphate buffer (0.5 mM, pH 7.4) was used for all experiments.

### Stern–Volmer Plot

To calculate the Stern-Volmer ($K_{sv}$) quenching constant a fluorescence titration was performed between **1** (10 μM) and varying concentrations of $Pd^{2+}$ (0 to 30 μM) in aqueous media at 25 °C. The $K_{sv}$ was calculated from the slope of the following equation $I_o/I_F = 1 + K_{sv}[Pd^{2+}]$. $I_o$ is the emission intensity of **1** in absence of $Pd^{2+}$ and $I_F$ corresponds to the emission of **1** upon addition of different concentrations of $Pd^{2+}$. The Stern-Volmer constant ($K_{sv}$) for emission quenching of **1** by $Pd^{2+}$ was calculated from the linear part (0–5 μM $Pd^{2+}$) of the titration data and determined as $1.8\times10^5\ M^{-1}$ in aqueous media.

### Competitive Experiments

To study the selective detection of $Pd^{2+}$ by **1**, competitive experiments were performed. The emission was recorded after individually mixing fixed solutions of $Pd^{2+}$(40 μM) and **1** (10 μM) with selected metal ions [40 μM of aluminium nitrate ($Al(NO_3)_3$), mercury (II) nitrate ($Hg(NO_3)_2$), cobalt(II) chloride hexahydrate ($COCl_2{\cdot}6H_2O$), manganese(II) chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$), nickel(II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), silver nitrate ($AgNO_3$), chromium(III) chloride hexahydrate ($CrCl_3{\cdot}6H_2O$), caesium chloride (CsCl), iron(II) chloride ($FeCl_2$), iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), copper (II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$), antimony trichloride ($SbCl_3$), platinum(II) chloride ($PtCl_2$), lead(II) chloride ($PbCl_2$), sodium chloride (NaCl), calcium chloride ($CaCl_2$), potasium chloride (KCl) or palladium(II) chloride ($PdCl_2$)].

Interferences for the detection of $HS^-$ were investigated in the presence of a mixture of all anions [potassium fluoride (KF), sodium chloride (NaCl), potassium bromide (KBr), potassium iodide (KI), sodium hydrogen sulfide (NaHS), sodium carbonate ($Na_2CO_3$), sodium sulfate ($Na_2SO_4$), sodium sulfite ($NaHSO_3$), sodium acetate (NaOAc), sodium thiosulfate ($Na_2S_2O_3$) and sodium thiocyanate (NaSCN)]. The emission was recorded after individually mixing fixed solutions of $HS^-$(195 μM) and solutions of (a) $\mathbf{1}\cdot Pd^{2+}$ (10 μM of **1** and 30 μM of $Pd^{2+}$) + 0 μM mixture of all anions; (b) $\mathbf{1}\cdot Pd^{2+}$ (10 μM of **1** and 30 μM of $Pd^{2+}$) + 200 μM mixture of all anions; (c) $\mathbf{1}\cdot Pd^{2+}$ (10 μM of **1** and 30 μM of $Pd^{2+}$) + 350 μM mixture of all anions.

### Detection Limit

The detection limit for the ions was calculated from the titration experiments following the reported method.[20a,26] For $Pd^{2+}$ ions in aqueous media, the quenching of the emission intensity at 390 nm was normalized between the emission intensities recorded at zero and ten equivalents (maximum quenching) of $Pd^{2+}$. A linear curve from the plot of $(F_i\text{–}F_o)/(F_o\text{–}F_{max})$ *vs* Log $[HS^-]$ was obtained from these normalized fluorescence intensity data and the intercept on the x- axis was considered as the detection limit ($F_o$, $F_i$ and $F_{max}$ corresponds to emission intensity of **1** in absence of any $Pd^{2+}$, in presence of different concentrations of $Pd^{2+}$ and upon addition of the maximum concentration of $Pd^{2+}$). Thus the value obtained for $Pd^{2+}$ was found to be 37 ppb.

To calculate the detection limit for $HS^-$ the recovery of emission intensity data at 410 nm was normalized between the fluorescence intensity found at zero and seven (maximum recovery) equivalents of $HS^-$ added. A linear curve from the plot of $(F_o\text{–}F_i)/(F_{max}\text{–}F_o)$ *vs* Log $[HS^-]$ was obtained from these normalized fluorescence intensity data and the detection limit was obtained by the extrapolation of the straight line on the x-axis ($F_o$, $F_i$ and $F_{max}$ corresponds to the emission intensity of $\mathbf{1\cdot Pd^{2+}}$ complex in absence of $HS^-$, in presence of different concentrations of $HS^-$ and upon addition of the maximum concentration of $HS^-$). Thus the value obtained for the $HS^-$ was found to be $1.52\times10^{-5}$ M.

### Dynamic Light Scattering studies

The particle size of the aggregates was measured by dynamic light scattering (DLS) experiments on a Malvern Zetasizer Nano ZS instrument equipped with a 4.0 mW He–Ne laser operating at a wavelength of 633 nm. The samples and the background were measured at room temperature (25 °C) at a scattering angle of 173°. DLS experiments were carried out with an optically clear solution of **1** alone and with ions in aqueous media. The solution was equilibrated before taking the measurements.

### Atomic Force Microscopy (AFM) Studies

The overall morphology of **1** was investigated in tapping mode using a NanoDrive Controller with an Innova Scanning Probe Microscope (Veeco Germany, Mannheim) and a N-type silicon cantilever (AC 160TS OLYMPUS). The AFM sample was prepared in water by drop casting onto a freshly cleaved mica surface (Plano GmbH) and drying properly before analysis.

### Real Sample Analysis

In order to evaluate the practical applicability of probe **1** for detection of $Pd^{2+}$ and hydrogen sulfide, we conducted sensing in different sources of water directly collected from a water purification system (milli-Q water), the Adriatic Sea (Venice, Italy, collected on 10.04.2019), the river Rhein (Düsseldorf, Germany, collected on 31.09.2019), a laboratory drain, the Ganga river (Kolkata, India, collected on 07.08.2019), growth media for aquatic species, and a laboratory tap. The water samples were filtered to remove insoluble substances. A stock solution of **1** (5 mM) and $Pd^{2+}$ (2 mM) is prepared in DMSO. For qualitative measurement a stock


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solution of probe **1** (final concentration 10 μM) was added to the respective water sample, which contains a fixed concentration of $Pd^{2+}$ (12 μM) at 25 °C. Emission of coumarin was recorded (within 30 minutes) from the three different sets of the above solution and the mean value is presented.

For sensing of hydrogen sulfide in different sources of water stock solutions of **1** (5 mM) and $Pd^{2+}$ (1 mM) in DMSO and NaHS (6 mM) in respective water samples were prepared. First, probe **1** (final concentration 10 μM) then $Pd^{2+}$ (5 μM) were added to the respective water samples in order to form the $\mathbf{1}\cdot Pd^{2+}$ complex. Afterwards a fixed concentration of NaHS (30 μM) was added at 25 °C and the solution was thoroughly mixed. Emission of coumarin was recorded (within 30 minutes) from three different sets and mean value was calculated.

For quantitative detection of hydrogen sulfide, stock solutions of NaHS (2 mM, 10 mM and 20 mM in milli-Q water) were added to a solution of $\mathbf{1}\cdot Pd^{2+}$(15 μM of **1** and 45 μM of $Pd^{2+}$, stock solution in DMSO) in milli-Q water. From the titration data $I_f/I_o$ (at 410 nm) was plotted against the concentration of $HS^-$ (μM) and a calibration curve was constructed ($Y = 0.0199X + 0.9274$, $R^2 = 0.9955$). To study the recovery of NaHS a stock solution (10 mM and 20 mM) of NaHS was prepared in respective water samples (e.g. drinking water, the Adriatic Sea, the river Rhein, a laboratory drains). Then, a fixed concentration (Table S6) of $HS^-$ was added to a solution of $\mathbf{1}\cdot Pd^{2+}$ complex. The emission of coumarin was recorded within 30 minutes from the three different sets of solutions and the mean value was calculated. The recovery of NaHS in respective water samples was analyzed using the calibration curve described above

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## Conflict of Interest

The authors declare no conflict of interest.

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