Zn(II) Schiff Bases: Bright TADF Emitters for Self-referenced Decay Time-Based Optical Temperature Sensing

Andreas Steinegger and Sergey M. Borisov*

ABSTRACT: Thermally activated delayed fluorescence (TADF) is a highly temperature-dependent process and can be used in optical thermometry. TADF-based optical thermometers reported so far show fairly high-temperature sensitivity but have poor brightness and significant oxygen cross-talk. A new class of TADF emitters, Zn(II) Schiff base complexes, possess excellent brightness and high temperature sensitivity of the decay time at ambient temperature (4.1%/K change of TADF lifetime at 25 °C), enabling a resolution better than 0.03 °C. Oxygen cross-sensitivity is eliminated by covering the sensing layer (luminophore in polystyrene) with an off-stoichiometry thiol–ene polymer as an oxygen-consuming layer, and a poly(vinylidene chloride-co-acrylonitrile) layer as an oxygen barrier. The material is stable after more than 2 months of storage at ambient air, which enables long-term temperature monitoring.

INTRODUCTION

Temperature is a fundamental parameter that is measured by a variety of methods. Although conventional temperature probes such as resistance temperature sensors are widely used offering good resolution over a broad temperature range, luminescent temperature probes represent an interesting alternative for some applications. Similar to IR thermometers, sensors based on luminescent probes offer advantages such as contactless measurement, minimal invasiveness, the possibility of imaging, and the absence of interference from electromagnetic fields. Moreover, they can be combined with optical probes for other analytes, enabling compensation of temperature cross-talk in situ, and be used on a nanoscale for studies in small objects such as microfluidic devices and cells. Luminescent probes with analytically useful temperature-dependent behavior include complexes of transition-metals and lanthanides, inorganic phosphors, polymers, nanomaterials, proteins, and organic dyes. Transition-metal complexes (most prominently Ru(II) polypyridyls) are subject to oxygen quenching because of their long lifetimes and typically feature moderate brightness. The luminescence of lanthanide chelates is much less affected by oxygen, but these complexes often suffer from low chemical stability (especially in polar solvents) and short-wavelength excitation which spans from the UV to blue part of the spectrum. In contrast, inorganic phosphors show much better chemical, thermal, and photochemical stability but their brightness is significantly lower than that for (metal)organic dyes. Moreover, the temperature coefficients are typically below 1%/K, particularly in the case of the decay time read-out. Quantum dots generally possess high quantum yields, good photostability, and strongly temperature-dependent luminescence but toxicity has been a concern. Fluorescent organic dyes such as rhodamine and derivatives display high brightness and no oxygen cross-talk but moderate temperature sensitivity. Because all the above probes show some limitations, search for alternative concepts utilizing other luminescent phenomena is still of high interest.

Thermally activated delayed fluorescence (TADF) is a highly temperature-dependent process that so far has only scarcely been used in optical thermometry. The reported TADF dyes show high temperature sensitivity which makes them attractive emitters for potential applications such as molecular thermometers. On the other hand, fluorescence brightness, a crucial parameter for sensing and imaging applications, is moderate to poor because of low molar absorption coefficients. In this contribution, we will show that a new class of TADF emitters, Zn(II) complexes with Schiff bases, combine high fluorescence brightness with highly temperature-dependent luminescence decay time and are, therefore, excellent indicators for luminescence thermometry. We will also demonstrate a simple approach to eliminate the intrinsic cross-sensitivity of such materials to oxygen by covering the sensing layer with an oxygen consuming off-stoichiometry thiol–ene polymer (OSTE) layer and, subsequently, with an gas-impermeable poly(vinylidene chloride-co-acrylonitrile) layer as an oxygen barrier. The material is stable after more than 2 months of storage at ambient air, which enables long-term temperature monitoring.
co-acrylonitrile) layer. The resulting material has a 4.1 %K\(^{-1}\) change of the TADF lifetime at 25 °C and a resolution exceeding 0.03 °C.

## RESULTS AND DISCUSSION

### TADF Indicators

Dyes with TADF have strongly temperature-sensitive luminescence that can be used for optical thermometry.\(^{44,45,50,51,59}\) This dependency is manifested in TADF intensity that is enhanced with the temperature and the TADF decay time that is decreased with temperature. Whereas the fluorescence intensity depends on numerous parameters like the intensity of the excitation light or sensitivity of the photodetector and so forth, the luminescence decay time is a self-referenced parameter free of these interferences. TADF dyes have been reported to show strong temperature dependency of the decay time varying from \(-2.0\) to \(-3.7\%/\)K for anthraquinone and dicyanobenzene emitters. Unfortunately, typical TADF emitters possess moderate to poor brightness\(^{50}\) because of low molar absorption coefficients. Another challenge to overcome is strong oxygen cross-talk because of long decay times.\(^{45}\)

Previously, we reported a series of metal complexes with a donor–acceptor Schiff base.\(^{21}\) Whereas Pd(II) and Pt(II) complexes were phosphorescent, a Zn(II) chelate possessed prompt fluorescence and TADF. Despite rather high molar absorption coefficients, the solubility of the Zn(II) complex in organic solvents and polymers was poor which prevented potential applications of the dye in sensing materials. In order to address this issue, we prepared an analogous dye Zn-1 (Figure 1) that is equipped with four 2-ethylhexyl chains ensuring excellent solubility of the dye in apolar media. The dye can be conveniently prepared in several steps (Figures S1 and S2). In order to investigate the possibility of reducing the TADF lifetime by using a stronger donor in the donor–acceptor structure of the dye,\(^{60}\) we also synthesized dye Zn-2 (Figure 1). The dye bears 3,6-di-tert-butylcarbazole that is a stronger electron donor compared to \(N,N\)-dialkylaniline. Four tert-butyl groups were expected to ensure sufficient solubility of the Zn(II) complex.

### Photophysical Properties of the Indicators

Absorption and emission spectra of the Zn(II) complexes are shown in Figure 2 and the photophysical properties are summarized in Table 1. Both dyes absorb in the violet to blue region of the electromagnetic spectrum. Zn-1 features a molar absorption coefficient of 75,000 M\(^{-1}\) cm\(^{-1}\) at 426 nm. The value is similar to the one reported for the dibutyl-substituted Zn(II) Schiff base complex.\(^{21}\) This is several times higher than for typical TADF emitters, for instance dicyanobenzenes (\(\varepsilon < 15,000\) M\(^{-1}\) cm\(^{-1}\)) and 2,6-diarylaminoanthraquinones (\(\varepsilon < 25,000\) M\(^{-1}\) cm\(^{-1}\)).\(^{50}\) The dye also shows efficient absorption at around 500 nm (\(\varepsilon \approx 45,000\) M\(^{-1}\) cm\(^{-1}\)). Such spectral properties enable excitation with a bright palette of blue and green LEDs. Zn-2 has a lower molar absorption coefficient of 39,000 M\(^{-1}\) cm\(^{-1}\) at 435 nm.

![Figure 1. Synthesis and chemical structures of Zn(II) Schiff base complexes.](image1)

![Figure 2. Absorption and emission spectra of Zn-1 and Zn-2 in toluene and photographic images of the solutions under UV-excitation (Zn-1 left, Zn-2 right).](image2)

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Table 1. Photophysical Properties of Zn(II) Schiff Bass Complexes in Toluene at 25 °C

| dye  | λ_{max,abs} [nm] | ε [M^{-1} cm^{-1}] | λ_{max,em} [nm]| ϕ_{DF} [%] | ϕ_{TP} [%] | τ_{DF} [μs] | τ_{TP} [ns] |
|------|-----------------|-------------------|---------------|------------|------------|-------------|-------------|
| Zn-1 | 426             | 75,000 ± 1,700    | 542           | 26 ± 2     | ≥5         | 1.6 ± 0.1   | ≥2.1 × 10³  |
|      | 486             | 46,000 ± 1,200    |               |            |            |             |             |
| Zn-2 | 435, 490        | 39,000 ± 600      | 547           | 27 ± 2     | 14 ± 2     | 1.8 ± 0.1   | 435 ± 1     |

"sh, shoulder. "Anoxic conditions.

The dyes show bright green to orange emissions (Figure 2) that are attributed to a combination of prompt and delayed fluorescence. The latter is completely quenched by molecular oxygen in air-saturated solutions. In the case of Zn-2 at 25 °C, the quantum yield of delayed fluorescence was estimated to be 14%, which is about 30% of the overall emission quantum yield (Table 1). For Zn-1, the quantum yield ϕ of prompt fluorescence determined under air-saturation was very similar to Zn-2 (26 and 27%, respectively). Precise determination of the contribution of TADF is difficult in these conditions because of long decay times of the delayed fluorescence (>2.1 ms) and therefore very high efficiency of oxygen quenching. Estimation with the help of oxygen-scavenging Na2SO3 solution showed that ϕ DF is at least 5% for Zn-1, however, some degree of quenching by molecular oxygen cannot be excluded. As expected, increase in the donor strength resulted in a significant decrease of the TADF lifetime (435 μs and >2.1 ms for Zn-2 and Zn-1), respectively. The decay curves have a mono-exponential form. Measurement at 77 K in a frozen glass (toluene/THF (4 + 6), v/v) reveal red phosphorescence with ~625 and ~630 nm, for Zn-1 and Zn-2, respectively. The singlet-triplet energy gap was estimated (i) from temperature dependency of the DF decay time using an Arrhenius type model that is analogous to eq 35 from ref 61 and (ii) from the emission spectra. For Zn-1, the singlet–triplet energy gap was estimated to be 2725 cm⁻¹ from the temperature calibration and 2515 cm⁻¹ from the emission spectra. For Zn-2, the values are 2450 and 2280 cm⁻¹, respectively.

**Optical Temperature Sensors.** In order to utilize TADF in optical temperature sensing, the emitters have to be immobilized into a polymeric or inorganic host. A common strategy to minimize oxygen cross-talk is immobilization into polymers with very low oxygen permeability such as poly-(acrylonitrile) or poly(vinylidene chloride-co-acrylonitrile). This strategy usually works well for the dyes with moderate decay times (~1−100 μs) but cannot ensure complete elimination of the cross-talk in the case of Zn-2 and particularly Zn-1. Moreover, we observed strong quenching of the TADF component upon immobilization of the Zn(II) Schiff base complexes into polycracylonitrile (PAN). In fact, the TADF component for PAN-immobilized Zn-2 constituted only approximately 2.5% of the overall fluorescence intensity. Therefore, PAN was not used for further investigations. Augesto et al. reported a sensor design, where C70-PS particles were dispersed in PAN by applying a pressure of 178 ton/m² for 1 h, at 120 °C. The system shows high sensitivity and no oxygen cross-talk, but requires a hydraulic heated press. Here, we present another straightforward strategy to eliminate oxygen cross-talk by covering the sensing layer with an oxygen-consuming OSTE layer (off-stoichiometry thiol–ene polymer) and, subsequently, with a gas-blocking poly(vinylidene chloride-co-acrylonitrile) (PVDCCoAN) layer used to reduce the oxygen diffusion into the OSTE layer, and hence prolong the oxygen-scavenging capability (Figure 3A). The OSTE resin is cured via a UV-initiated thiol–ene click reaction and then is subjected to further thermal curing. This step is needed to ensure attachment of the gas-blocking layer, although the oxygen-scavenging properties of the OSTE layer would be better with no thermal curing. Nevertheless, the cured resin contains an excess of unreacted thiol groups responsible for the oxygen-scavenging properties of the material so that the sensing layer underneath can be deoxygenated completely. The glass support material is completely impermeable to oxygen and shields the sensing layer from one side.

This strategy provides the possibility to use virtually any polymer as a matrix for immobilization of the TADF emitter. Polystyrene (PS) was chosen for its high chemical stability, excellent optical properties, and good compatibility with the Zn(II) complexes. As can be seen (Table 2) the dyes show both prompt and delayed fluorescence in PS, and the photophysical properties of the immobilized are generally similar to those in toluene (Figure 3B). However, the quantum yield of TADF is strongly enhanced compared to toluene, particularly for Zn-2. Moreover, the TADF decay time increased several fold compared to toluene (Tables 1 and 2), which may be due to the more rigid environment in the polymer. Additionally, the decay curves now adopt a biexponential form (Figure 4A). Hence, the delayed fluorescence decays in PS were fitted with a bi-exponential model and average decay times were calculated. Because the delayed fluorescence is almost completely quenched in air, temperature dependency of the photophysical properties of PS foil was studied under anoxic conditions. The overall fluorescence intensity remains roughly constant. The intensity of the TADF component slightly increases with temperature. Such behavior is advantageous compared to molecular...
The temperature sensitivity was 3.7 and 3.5% K−1 about twofold on going from 5 to 25 °C. The reaction products/quenchers that are formed during the curing effect is likely to be caused by some interaction between the indicator and the reaction products/quenchers that are formed during the curing steps which also maybe the reason for a shoulder in the emission spectrum at ~490 nm (Figure 3B).

The response curve shown in Figure 4 represents the average from five measurement cycles, three of which were performed in air saturated water and two in the anoxic aqueous solution. Evidently, no influence of oxygen is visible. A long equilibration (4 h) in air-saturated and anoxic water also revealed no difference in the lifetimes in these conditions within the standard deviation from the calibration.

At 25 °C, the temperature sensitivity of the Zn-1-based sensor was calculated to be 4.1% K−1 of the TADF lifetime change. To the best of our knowledge, these values are the highest reported up to date for temperature probes utilizing phosphorescence. In fact, whereas the S/N ratio for TADF emitters (25,51) and inorganic phosphors (29–31,57) (cf. Table 3), the poly(N-isopropylacrylamide)-based probes represent a notable exception showing very high sensitivity (10−27% K−1) in a very narrow range (30–35 °C).8,64 Although, the tested temperature range for most of the (metal)organic probes is typically limited to about 0–50 °C (Table 3), these probes are likely to be useful in a broader range. As can be seen from Figure 4B, the TADF-based sensor is expected to operate well below 5 °C and above 45 °C. Particularly, at elevated temperatures TADF appears to be advantageous over phosphorescence. In fact, whereas the S/N ratio of TADF probes is nearly constant or even initially improves with temperature, the phosphorescent probes show intensity decrease at elevated temperatures. Clearly, the (metal)organic probes are inferior to inorganic phosphors in respect to the temperature range. The latter feature high stability at temperatures well above 100 °C.

The resolution of the sensing material at 21.5 °C was estimated using a frequency domain measurement of the luminescence phase shift with the help of a lock-in amplifier and optical fiber. To do so, the 3σ standard deviation (obtained from 100 measurement points) was divided by the sensitivity at the same temperature (Figure 5). The resolution calculated for the PS/OSTE/PVDcoAN-sensing material is 0.03 °C. It should be considered that the resolution may be higher in reality because minor temperature fluctuations during the measurement cannot be excluded. Unfortunately, the resolution of a PT-100 resistance thermometer used as a reference is only 0.02 °C according to the specifications of the manufacturer.

The long-term stability of the Zn-1/PS/OSTE/PVDcoAN-sensing material was assessed via decay time measurements at 25 °C during storage at ambient air (Figure 6). The decay time is expected to decrease after the oxygen-scavenging capabilities of the OSTE layer are exhausted.

As can be seen, no change in the decay time could be observed over 62 days. It should be noted that the thickness of the oxygen-scavenging layer is rather high (~1.1 mm) but the concept is expected to be efficient for thinner scavenging layers. The ability to completely eliminate oxygen quenching thermometers based on phosphorescent dyes and the majority of thermographic phosphors that show a decrease of luminescence intensity with temperature and thus decrease in the S/N ratio.

The temperature dependency of the TADF lifetime of the PS-immobilized complexes is shown in Figure 4. As can be seen, both dyes show extremely strong temperature dependency of the TADF lifetime. In fact, the decay time decreases by about twofold on going from 5 to 25 °C (Table 2). At 25 °C, the temperature sensitivity was 3.7 and 3.5% K−1 of the TADF lifetime change for Zn-1 and Zn-2 in PS, respectively.

Although both Zn(II) complexes are suitable for optical temperature sensing, Zn-1 was selected for further investigation because of its significantly better solubility in PS and higher temperature coefficient. Application of additional layers of OSTE and PVDcoAN was found to only slightly affect the TADF lifetime (Figure 4B). A minor effect is likely to be caused by some interaction between the indicator and the reaction products/quenchers that are formed during the curing steps which also maybe the reason for a shoulder in the emission spectrum at ~490 nm (Figure 3B).

Table 2. Photophysical Properties of Zn(II) Schiff Base Complexes in PS

| dye | λmax abs [nm] | λmax em [nm] | τ 0 DF at 5 °C [ms] | τ 0 DF at 25 °C [ms] | Φpy at 25 °C [%] |
|-----|---------------|--------------|---------------------|---------------------|------------------|
| Zn-1 | 438           | 542          | 14.4 ± 0.5          | 7.41 ± 0.03         | 19 ± 4           |
| Zn-2 | 446           | 547          | 2.91 ± 0.11         | 1.45 ± 0.01         | 18 ± 2           |

Figure 4. (A) TADF decay of Zn-1 in different environments at 25 °C. (B) Temperature dependency of the average TADF decay time for the Zn(II) complexes embedded in PS. The decay times were measured under anoxic conditions in the case of PS foil (2 wt % aq Na2SO3 solution). For PS/OSTE/PVDcoAN, the decay times are average values from measurements under air (2 times) and in deoxygenated conditions (3 times).

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could also be useful for the design of reference materials for optical sensors based on phosphorescent dyes.

**CONCLUSIONS**

We presented highly sensitive materials for optical temperature monitoring based on the TADF-emitting Zn(II) Schiff base complexes. In contrast to common TADF emitters, the new dye class is characterized by high molar absorption coefficients resulting in excellent brightness under photoexcitation. The complexes feature unusually high temperature sensitivity of TADF lifetime exceeding 3.5%/K at 25 °C, enabling a resolution of at least 0.03 °C and benefitting from self-referenced character of the decay time read-out. Although, the carbazole-based derivative shows poor solubility in organic solvents and polymer matrices, it features about fourfold shorter decay times and higher TADF quantum yield compared to the N,N-dialkylamino derivative, which can be attractive for measurements in the frequency domain because of the higher modulation frequencies required.

Oxygen cross-talk is an intrinsic property of molecular emitters with long luminescence decay times. Above, we demonstrated a simple and efficient method to completely eliminate this cross-talk by adding a layer of the oxygen-scavenging OSTE polymer combined with a gas barrier made of PVDCcoAN. The OSTE layer retains its oxygen-scavenging capabilities for more than 60 days during storage under ambient air ensuring suitability of the new sensor for long-term temperature monitoring. The new materials are expected to be attractive for high-resolution optical temperature sensing and imaging at ambient conditions. Moreover, Zn(II) complexes with Schiff bases do not contain precious metals but abundant zinc and thus may be interesting for further investigation for potential applications in OLED technology. Zn-2 shows exceptionally high TADF quantum yield when immobilized in a polymer matrix but the energy gap is still too high. Synthetic modifications that reduce the energy gap (stronger

Table 3. Figures of Merits for Optical Thermometers Based on Decay Time Read-out

| material                         | T [K] | Ex/Em [nm] | relative sensitivity, Δr/ΔT [%/K] | τ [μs] | T range [°C] | refs  |
|----------------------------------|-------|------------|----------------------------------|-------|--------------|-------|
| Ru(phen)                         | 303   | 470/580    | −0.64                            | 3.6   | 0–60         | 15    |
| [Ru(phen)2(4-Clp)]2+             | 298   | 450/590    | −1.35                            | 2.65  | 0–40         | 20    |
| Eu(TTA)3                         | 298   | 350/615    | −2.3                             | 293   | 5–50         | 22    |
| EuDT                             | 298   | 400/616    | −2.2                             | 250   | 10–50        | 26    |
| Ir(ppy)2carbac                   | 303   | 405/519    | −0.5                             | 2.2   | 1–50         | 16    |
| Mn2+-doped magnesium fluorogermanate | 274 | 355/620–683 | −0.19                           | 3610  | 25–725       | 29    |
| ruby                             | 274   | 520 or 532/694 | −0.25                          | 3980  | 15–400       | 30    |
| spinel                           | 274   | 520 or 532/690 | −0.38                          | 9830  | 15–400       | 30    |
| Cr3+-doped yttrium aluminium borate | 274 | 422 or 600/NIR | −0.97                          | 237   | −10 to 70    | 31    |
| Y2Al2O5:Ce nanophosphor          | 298   | 337/700    | −0.48                            | 25    | 7–77         | 32    |
| sulfonaphthomide derivative      | 298   | 540/565–605 | −1.3                            | 2.8   | 5–55         | 46    |
| 1 nm CdTe quantum dots           | 298   | 405/510    | −1.7                             | 14    | 20–50        | 40    |
| arylamino-substituted anthraquinone | 298 | 465/610    | −3.7                             | 677   | 5–50         | 50    |
| carbazole-substituted anthraquinone | 298 | 470/580    | −2.7                             | 42    | 5–50         | 50    |
| carbazole-substituted dicyanobenzene | 298 | 455/530    | −2.0                             | 11    | 5–50         | 50    |
| PS-C60/PAN film                  | 293   | 470/700    | ~−0.75                           | 27.2  | −75 to 105   | 51    |
| Pd(II) Schiff base complex       | 298   | 392/613    | −2.1                             | 103   | 5–65         | 21    |
| Zn-1                             | 298   | 456/542    | −3.7 (PS)                        | 7.41  | 5–45         | this work |
|                                 |       |            | −4.1 (PS/OSTE)                  | 5.71  | (PS/OSTE)    | this work |
| Zn-2                             | 298   | 456/547    | −3.5                             | 1.45  | 5–45         | this work |

Figure 5. Time trace of the luminescence signal from the Zn-1/PS/OSTE/PVDCcoAN sensor (modulation frequency 32 Hz; black line) and the temperature as measured by a PT-100 resistance thermometer (blue line).

Figure 6. Long-term stability of the Zn-1/PS/OSTE/PVDCcoAN-sensing material assessed via decay time measurements at 25 °C. The material was stored under ambient conditions between the measurements.
donor and acceptor groups) and improve solubility in polymers appear to be necessary here and they also are expected to be beneficial for the application of the dye as a molecular thermometer.

**EXPERIMENTAL SECTION**

**Materials.** Silica gel (0.04–0.063 mm) was purchased from Acros Organics (www.acros.com); anhydrous sodium sulfate and sodium hydrogen carbonate from VWR (www.vwr.com); chloro(trimethyl)silane, Zn(OAc)₂·2H₂O, POCl₃, and BBr₃·SMc₃ from Aldrich (www.sigmaaldrich.com); and methanesulfonic acid from abc (https://www.abc.de/). Solvents were purchased from VWR (cyclohexane (CH), ethyl acetate (EA), tetrahydrofuran (THF), all deuterated solvents), Fisher Scientific (dichloromethane (DCM)), Acros Organics (1,2-dichloroethane) and Roth [chloroform, N,N-dimethylformamide (DMF), toluene]. PS, av. MW ≈ 260,000 Da, was purchased from Acros Organics, PVDCcoAN, 20 wt % acrylonitrile content, av. Mₙ ≈ 80,000 Da, av. MW ≈ 125,000 Da, was from Scientific Polymer (scientificpolymer.com). Ostemer 322 Crystal Clear (OSTE) was purchased from Merece Labs AB (https://www.ostemers.com/). Biaxially oriented polyethylene terephthalate (PET) foils (125 μm) (MELINTEX 506) were supplied by Pütz GmbH Co. Folinik KG (www.puetz-folien.com).

**Synthesis.** 3-(Bis(2-ethylhexyl)amino)phenol (P1) and 4-(3,6-di-t-butyl-9H-carbazol-9-yl)-2-methoxybenzaldehyde (P2) were prepared according to literature procedures (Figures S1 and S2).

**4-(Bis(2-ethylhexyl)amino)-2-hydroxybenzaldehyde (1).** In a flame-dried and Ar-flushed Schlenk tube, 447 mg (1.34 mmol, 1 equiv) of P1 were dissolved in 13.4 mL of dry DMF. The slightly yellow solution was cooled to −50 °C and 650 μL (6.7 mmol, 5 equiv) of POCl₃ were added under stirring. The green reaction mixture was stirred for 30 min at −50 °C and was then allowed to warm up to room temperature. After quantitative conversion monitored by TLC, the solution was warmed to 40 °C and stirred for 2 h. After quantitative conversion, water was added to the reaction mixture and the precipitate was isolated via centrifugation and washed with water. The crude product was removed under reduced pressure. The crude product was purified via precipitation from DCM with methanol/water mixture (4 + 1, v/v), the precipitation was repeated five times. Yield: 16 mg (51%), dark red solid.

**Sensor Preparation. Silanization of Glass Slides.** Microscopy glass slides were thoroughly washed with acetone and dried for 30 min at 110 °C. The slides were then immersed in a 10 wt % solution of chloro(trimethyl)silane in dry THF for 30 min. After drying at ambient air, the slides were further dried at 120 °C for 1 h. After silanization, the slides were broken to diagonally fit into 10 mm cuvettes.

**PS Sensor Foil.** Dye (1 wt % with respect to PS) and PS were dissolved in chloroform (7.5 wt % of PS in chloroform) and this “cocktail” was knife-coated (25 μm thick wet film) onto dust-free PET support foil. After evaporation of the solvent, the sensor foil was dried at 60 °C for 24 h.
OSTE Sensor Slides and Spots. Preparation of the sensing layer was performed as described above but dust-free trimethylsilyl-modified glass slides or spots (Ø 8 mm, www.hilgenberg-gmbh.de) were used as a support instead of PET. The slides or spots were then covered with an approximately 1 mm thick layer (exact thickness of 1.14 ± 0.02 mm as determined with an "Inductive Dial Comparator 2000 Extramess" from Mahr, https://www.mahr.com/) of OSTE (from two components according to instructions) and UV cured for 2 min (365 nm, 8 W, UV-handheld lamp from Herolab supplied by Carl Roth GmbH). Subsequently, the slides were thermally cured at 150 °C for 7 min. Finally, the OSTE layer was covered with a (PVDCcoAN) solution in THF (10% wt) in a dry atmosphere (glove box) and dried for 24 h. The thickness of the PVDCcoAN layer was 79 ± 2 μm.

Characterization. NMR spectra were recorded on a Bruker AVANCE III spectrometer equipped with an autosampler (300.36 MHz 1H NMR, 75.53 MHz 13C NMR). MS: mass spectrometric measurements of Zn-1 and Zn-2 were performed on a matrix-assisted laser desorption/ionization (MALDI)-TOF/TOF (time of flight) spectrometer from Bruker (www.bruker.com). Mass spectrometry of the precursors was performed on an Advion expression CMS with Bruker (www.bruker.com). Mass spectrometry of the precursors was performed on an Advion expression CMS with Bruker (www.bruker.com). Mass spectrometry of the precursors was performed on an Advion expression CMS with Bruker (www.bruker.com). Mass spectrometry of the precursors was performed on an Advion expression CMS with Bruker (www.bruker.com).

For temperature calibrations, the temperature was adjusted with a Cary SPV-1X0 Single Cell Peltier Accessory Peltier element from Varian in combination with a cryostat from Avantor, model 1150S (us.wvr.com). The PS sensor foil or the PS/OSTE/PVDCcoAN sensor slides were placed diagonally in Hellma Analytics optical glass 10 mm precision cuvettes. The cuvettes were filled with air-saturated water (OSTE sensors) or aqueous 2 wt % Na2SO3 solution (PS and OSTE sensors). After temperature adjustment, the cuvettes were thermally equilibrated for 10 min. The temperature was adjusted between 5 and 45 °C. Five decay time measurements were made at each temperature. The calibration cycle was repeated three times.

Determination of the Resolution with the Fiber Optic Setup. The fiber was immersed in a cryostat from Avantor, model 1150S (us.wvr.com). The temperature was adjusted to 15 and 35 °C. The calibration cycle was repeated three times at a modulation frequency of 32 Hz. The average phase shifts were used to determine the sensitivity of the sensor. To determine the noise, the sensor fiber was immersed in a 5 L beaker that was thermally equilibrated at room temperature and the phase shift of 100 measurement points was recorded. The resolution was calculated by dividing three times the standard deviation obtained for 100 measurements by the sensitivity. The temperature was logged with a PT-100 resistance thermometer (resolution of 0.02 °C) connected to a commercially available FireStingO2 oxygen meter (from PyroScience, www.pyroscience.com).

Long-Term Stability. For the long-term stability tests, the sensor material was stored at ambient conditions (air; temperature ~22 °C), but shielded from light. For measurements, the PS/OSTE/PVDCcoAN sensor slides were placed diagonally in cuvettes filled with air-saturated water. The temperature was adjusted to 25 °C with the same setup used for temperature calibration. The cuvettes were thermally equilibrated for 10 min and then five decay time measurements were made.

Data Analysis. An Arrhenius type model12 (eq 1) was used to fit the average decay times from the temperature calibrations

\[
\tau = (k_0 + k_1 \times e^{-\Delta E/k_B T})^{-1}
\]

where \(k_0\) is the temperature-independent decay rate for the excited-state deactivation, \(k_1\) is a pre-exponential factor, \(k_B\) is the Boltzmann constant, \(\Delta E\) is the energy necessary for the reverse ISC (corresponds to the singlet−triplet energy gap), and \(T\) is the absolute temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01062.

Reaction schemes for the synthesis of the precursors and NMR and MS spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

Sergey M. Borisov – Graz University of Technology, Institute of Analytical Chemistry and Food Chemistry 8010 Graz, Austria; orcid.org/0000-0001-9318-8273; Phone: +43 (316) 873-32516; Email: sergey.borisov@tugraz.at
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Notes
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