Fluorescent Self-Assembled Monolayers of Bis(salicylaldiminato)zinc(II) Schiff-Base Complexes

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The synthesis and fluorescence properties of novel bis(salicylaldiminato)zinc(II) Schiff-base complexes is reported. Self-assembled monolayers (SAMs) of these complexes are obtained by reaction of coupling layers, functionalized quartz substrates and a derivatized precursor complex. A comparison between the integrated emission intensity of the SAM films and that of a suitable model compound in solution indicates molecular fluorescence retention of the Zn^{II} Schiff bases on going from the solution phase to the monolayer. This is consistent with the absence of significant self-quenching processes, as expected on the basis of the relatively high estimated surface coverage.

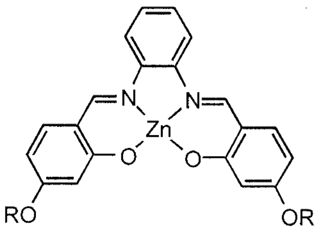
Introduction

Nanostructured functional molecular materials are attracting growing interest in the expanding field of molecular electronics and optoelectronics,[1] where molecular organization in defined assemblies and its control on a molecular scale represents one of the most interesting issues.

Molecular self-assembly is one of the most efficient methods to achieve well-defined and organized molecular architectures covalently anchored to various substrates.[2] Among various functional molecular systems, self-assembled monolayers (SAMs) of fluorescent molecules are attractive for a variety of potential applications,[3] including molecular electronics and optoelectronics.[4]

Recently, Schiff base bis(salicylaldiminato)metal complexes have been widely investigated for their properties and applications in different fields, such as catalysis[5] and materials chemistry.[6] For example, metal complexes possess distinct second-order nonlinear optical[6,7] and fluorescent[8,9] properties that are closely related to the coordinated metal centre. In fact, as far as the luminescent properties are concerned, while the free Schiff-base ligands are non-emissive, their complexes with metal ions such as Zn^{II}, Al^{III} and Mg^{II} exhibit an appreciable fluorescence.[9]

In this paper we report the synthesis and spectroscopic properties of novel bis(salicylaldiminato)zinc(II) Schiff-base complexes and related self-assembled monolayers on quartz substrates.



R = H **1**
R = CH_3 **2**

Results and Discussion

Synthesis and Spectroscopic Properties of Zn^{II} Schiff-Base Complexes

In order to compare the spectroscopic properties of the self-assembled monolayer of the complex **1** (SAM-**1**) with a suitable model compound, the 4,4′-methoxy derivative **2** was synthesized. Both the 4,4′-dihydroxy-substituted Zn^{II} Schiff-base precursor complex **1** and the model compound **2** were synthesized by standard methods.[7] The complexes were characterized by mass spectrometry, ^1H NMR spectroscopy, and satisfactory microanalysis.

Figure 1 shows the absorption and emission spectra of **2** in CH_2Cl_2 solution. The absorption is characterized by two bands at 310 and 374 nm and a shoulder at about 420 nm. The fluorescence emission exhibits an unstructured band with a maximum at 508 nm. Based on the overlap of the fluorescence emission with the lowest energy absorption

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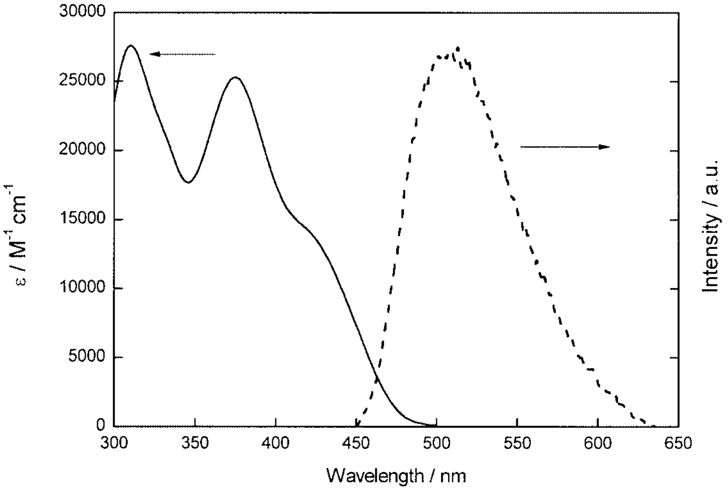


Figure 1. Absorption and fluorescence spectra of **2** in CH_2Cl_2 solution

band, the lowest excited singlet state can be experimentally located at about 260 kJ·mol^{-1}.

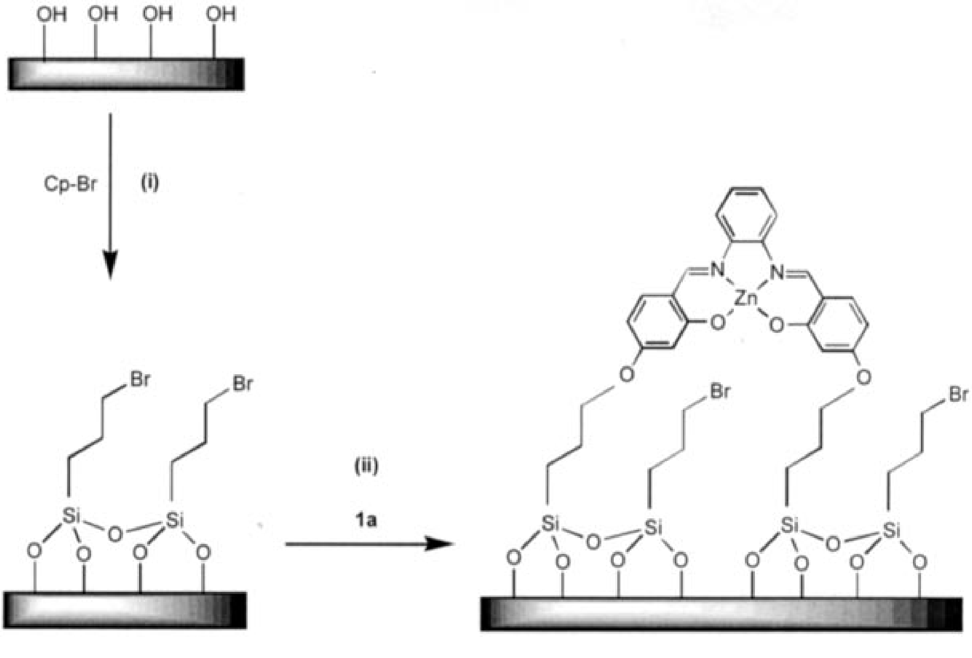
The fluorescence quantum yield, Φ_f, is found to be about 0.05 in CH_2Cl_2. This value is almost unaffected on going to more polar solvents such as THF and CH_3CN. The fluorescence lifetime in the above solvents lies in the sub-nanosecond time domain. These photophysical properties are consistent with those recently found for analogous Zn^{II} Schiff-base complexes.[8]

Preparation and characterization of SAM-1

The derivatization of the molecular precursor with appropriate end-groups represents the initial step for the self-assembly process. It should consist of an accessible and efficient chemistry so that the derivatized group can easily react with the substrate or with an appropriate derivatized substrate, the so-called coupling layer. In our case the 4,4′-dihydroxy-substituted Zn^{II} Schiff-base complex **1** was used as precursor. Actually, given their acid nature, 4-hydroxyl groups can readily be transformed into the related phenoxides **1a**, which, in turn, are nucleophilic species for a variety of substitution reactions.

SAM-**1** was obtained by a two-step approach (Scheme 1), which involves chemisorption of the $Br(CH_2)_3SiCl_3$ (CP-Br) coupling layer onto hydroxylated quartz substrates followed by grafting of **1** by a nucleophilic-substitution reaction between the alkyl bromide of the silylated surface and the derivatized salt **1a**.

The first step was carried out with standard procedures.[10] It leads to the formation of densely packed, sil-



Scheme 1. Preparation of fluorescent self-assembled monolayers of the Zn^{II} Schiff-base complex

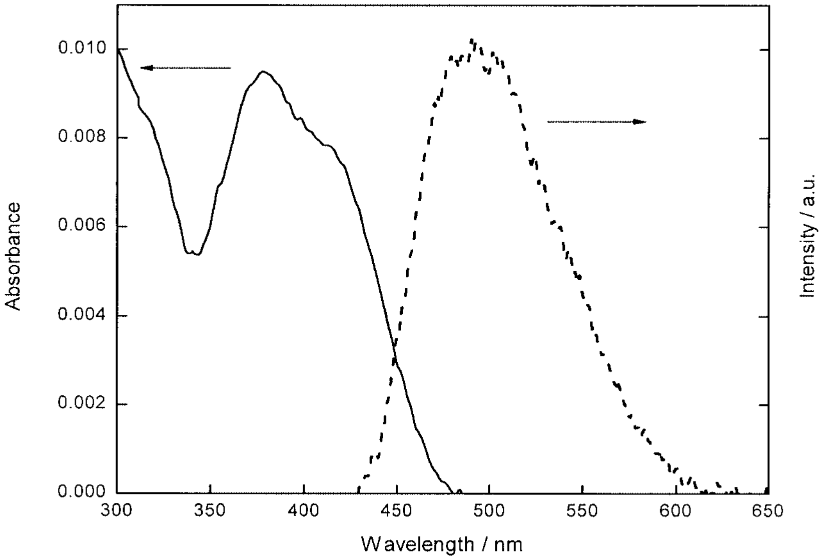


Figure 2. Absorption and fluorescence spectra of SAM-**1**

ane-based coupling layers bound to the quartz surface through a siloxane linkage. The typical advancing aqueous contact-angle (θ_a) values (ca. 68°) confirmed the complete silylation of the surface.

The second step was achieved by immersion of substrates terminated with the coupling layer in an anhydrous DMF solution of the derivatized complex **1a** for 20 h at 80 °C. The substrates were then washed and sonicated with DMF and acetone to remove any physisorbed material on the surface. Aqueous contact-angle measurements after the second step indicated that θ_a changes from 66−68° for the substrate terminated with the coupling layer to 78−80° for SAM-**1**. This is consistent with an increased surface hydrophobicity due to the relatively apolar Zn^{II} complex headgroup.[11]

SAM-**1** was characterized by UV/Vis absorption and emission spectroscopy (Figure 2). It shows an optical absorption band at 378 nm and a shoulder at about 416 nm. These features are similar to those of the model complex **2** in CH_2Cl_2 (Figure 1), except for a slight shift. It should be noted that the observed absorbance is related to two monolayers, one for each side of the quartz slide. These absorbance values allow an estimation of the surface coverage (Γ_{surf}) of the functional Zn^{II} complex by the relation $\Gamma_{surf} = A\varepsilon^{-1}$, where A is the absorbance of the SAM-**1** and ε is the molar extinction coefficient of the chemisorbed species.[12] Using the extinction coefficient of the model compound **2** (λ_{max} = 374 nm; ε_{max} = 25300 $\text{M}^{-1}\cdot\text{cm}^{-1}$ in CH_2Cl_2) and a monolayer absorbance of about 0.005, the estimated surface density of the Zn^{II} derivative is about 1.2×10^{14} molecules/cm^2 or about 1.2 molecules/100 Å^2. These surface coverage values for the bulky complex **1** are within the range commonly observed for analogous systems.[2,13]

The fluorescence spectrum of SAM-**1** (Figure 2) is characterized by a shape similar to that observed in solution for the model compound **2** (Figure 1), although the emission maximum is somewhat blue-shifted (by about 16 nm). A comparison between the integrated emission intensity of SAM-**1** and that of a solution of **2** having the same absorbance at the excitation wavelength reveals that the fluorescence efficiency of the monolayer is similar to that of the model compound **2**. This result indicates molecular fluorescence retention of the Zn^{II} Schiff base complex on going from the solution phase to the monolayer. This is consistent with the absence of significant self-quenching processes, as expected on the basis of the relatively high surface coverage estimated above. Quenching of fluorescence is actually quite common in more densely packed monolayers as a result of effective inter-chromophore interactions.[14]

In summary, we have presented a simple, efficient route to fluorescent self-assembled monolayers of novel Zn^{II} Schiff-base complexes. They may be appealing systems in the perspective of molecular optical devices.

Experimental Section

Materials and General Procedures: Zinc acetate dihydrate, 2,4-dihydroxybenzaldehyde, 2-hydroxy-4-methoxybenzaldehyde, sodium methoxide, (3-bromopropyl)trichlorosilane [$Br(CH_2)_3SiCl_3$], and anhydrous DMF (Aldrich) were used without purification. 1,2-Phenylenediamine (Aldrich) was purified by sublimation in vacuo. Pentane and heptane (Aldrich) were distilled from Na/K alloy before use. The coupling layer formation was performed in a dry box (under nitrogen atmosphere; <1 ppm O_2 and <3 ppm H_2O).

Physical Measurements: Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. ^{1}H NMR spectra were recorded on a Varian Inova 500 spectrometer, using TMS as internal standard. The absorption and fluorescence spectra were recorded with a Beckman DU 650 spectrophotometer and a Spex Fluorolog-2 (mod. F-111) spectrofluorimeter, respectively, and λ_{max} values are considered accurate to ±1 nm. The fluorescence quantum yield was obtained using quinine sulfate in 1 N H_2SO_4 as standard. The absorbance value of the samples at the excitation wavelength were lower than 0.15 for a 1-cm path length. The fluorescence lifetimes in air-equilibrated solutions were determined by means of a time-correlated single-photon counting system. A nitrogen-filled lamp was used for excitation at 337 nm. Fluorescence measurements on SAM-**1** were carried out by aligning the quartz slide sample at an angle of 60° with respect to the excitation beam. Reflection of the excitation from the sample was to the opposite side of the emission detection. ESI mass spectra were recorded on an Agilent 1100 Series ESI/MSD spectrometer. Experimental conditions were as follows: capillary voltage, 3.5 kV; fragmentor, 100 V; source temperature, 350 °C; drying gas, N_2 (10 L/min); carrier solvent, methanol (0.4 mL/min). Advanced aqueous contact angles were measured using a goniometer (KERNCO) under ambient conditions.

[1,2-Phenylenebis(iminomethyl)bis(4-hydroxy-2-phenolato]zinc(II) (1): 2,4-Dihydroxybenzaldehyde (1.106 g, 8.00 mmol) was added, whilst stirring, to a solution of 1,2-phenylenediamine (0.433 g, 4.00 mmol) in methanol (25 mL) at room temperature. Zinc acetate dihydrate (0.878 g, 4.00 mmol), dissolved in methanol (20 mL), was added to the resulting solution, and the mixture was heated at reflux for 2 h. After cooling, the precipitate was collected by filtration, washed with water, and dried. The yellow solid was crystallized from a THF/*n*-hexane mixture. Yield: 1.556 g (94%). $C_{20}H_{14}N_2O_4Zn$ (411.73): calcd. C 58.34, H 3.43, N 6.80; found C 58.05, H 3.38, N 6.90. ESI MS: *m*/*z* (%) = 433 (50) $[M + Na]^+$. ^1H NMR (500 MHz, [D$_6$]DMSO): $\delta = 6.03$ (m, 4 H, Ar*H*), 7.19 (d, $J_{ortho} = 9.0$ Hz, 2 H, Ar*H*), 7.24 (m, 2 H, Ar*H*), 7.75 (m, 2 H, Ar*H*), 8.79 (s, 2 H, C*H*=N), 9.71 (s, 2 H, O*H*) ppm. UV/Vis (DMF): $\lambda_{max} = 308, 388, 426$ (sh) nm.

Disodium Zincate 1a: Compound **1** (1.556 g, 3.78 mmol) was added, with stirring, to a solution of sodium methoxide (1.73 mL of a 25% w/w methanol solution, 7.56 mmol), and the mixture heated at 50 °C for 1 h under a nitrogen atmosphere. The solution was then concentrated under vacuum. The precipitate product was collected and washed with anhydrous THF. A yellow-brown solid was obtained (1.583 g, 92%). $C_{20}H_{12}N_2Na_2O_4Zn$ (455.69): calcd. C 52.71, H 2.65, N 6.15; found C 52.40, H 2.60, N 6.09.

Zinc(II) Complex 2: Zinc acetate dihydrate (0.094 g, 0.43 mmol) was added to a solution of *N*,*N'*-bis(4-methoxy-2,4-dihydroxybenzylidene)-1,2-phenylenediamine[7c] (0.116 g, 0.43 mmol) in methanol (30 mL). The resulting yellow solution was heated at reflux for 2 h. After cooling, the precipitate was collected by filtration, washed with water and dried. The yellow solid was crystallized from THF (1.60 g, 85%). $C_{22}H_{18}N_2O_4Zn$ (439.78): calcd. C 60.08, H 4.13, N 6.37; found C 59.62, H 4.09, N 6.43. ESI MS: *m*/*z* (%) = 461 (100) $[M + Na]^+$. ^1H NMR (500 MHz, [D$_6$]DMSO): $\delta = 3.75$ (s, 6 H, C*H*$_3$), 6.15 (dd, $J_{ortho} = 9.0$, $J_{meta} = 2.5$ Hz, 2 H, Ar*H*), 6.19 (d, $J_{meta} = 2.5$ Hz, 2 H, Ar*H*), 7.29 (m, 4 H, Ar*H*), 7.79 (m, 2 H, Ar*H*), 8.86 (s, 2 H, C*H*=N) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^4$) = 310 (2.75), 374 (2.53), 420 (sh) nm (1.40).

Preparation of SAMs

Substrate Cleaning: Substrates were cleaned by standard procedures.[15] Quartz slides (0.5 × 1 cm) were cleaned by immersion in "piranha" solution (H_2SO_4/30% H_2O_2 = 70:30 v/v) at 80 °C for 1 h (***warning****: piranha is an extremely strong oxidising reagent; it should be handled with caution because it can detonate unexpectedly*).[16] After cooling to room temperature, the substrates were repeatedly rinsed with deionized water and then cleaned with a (H_2O/30% H_2O_2/28% NH_3 = 5:1:1 v/v/v) solution, at room temperature for 40 min. The substrates were then washed with a large amount of deionized water and dried under vacuum at room temperature.

Coupling Layer Formation: Substrate silylation was performed by immersion of freshly cleaned quartz substrates in a 1:100 (v/v) solution of $Br(CH_2)_3SiCl_3$ (CP-Br) in dry heptane for 40 min, at room temperature. The substrates were first rinsed with dry heptane, then with dry pentane, sonicated in acetone for 1 min, and dried at room temperature. Advancing contact angle: CP−Br, $\theta_a(H_2O) = 68°$.

Monolayer Formation: Under a dry nitrogen atmosphere the freshly silylated substrates were immersed in a 3.0 mM solution of salt **1a** in anhydrous DMF at 80 °C for 20 h, whilst stirring. After cooling to room temperature, the substrates were rinsed with DMF, sonicated in DMF for 1 min, and washed with acetone. Advancing contact angle: SAM-**1**, $\theta_a(H_2O) = 80°$. UV/Vis: SAM-**1**, λ_{max} = 378 nm ($A = 0.095$).

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