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Phase Transition and Vapochromism in Molecular Assemblies of a Polymorphic Zinc(II) Schiff-Base Complex

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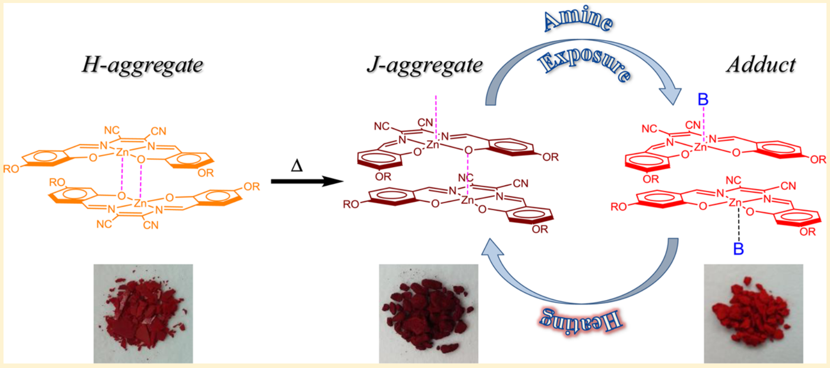
Supporting Information



ABSTRACT: This paper reports for the first time the irreversible thermally induced phase transition, accompanied by color change, and the vapochromic behavior of an amphiphilic, Lewis acidic Zn^{II} Schiff-base complex, through detailed X-ray diffraction, thermogravimetric analysis and differential scanning calorimetry, and optical absorption studies. The unprecedented irreversible phase transition for such kind of complexes is associated with a thermal, lamellar-to-hexagonal columnar structural transition, which involves a different arrangement of each molecular unit within the assembled structure, H- and J-type aggregates, respectively, responsible for the thermochromic behavior. The vapochromism, investigated either in powder samples or in thermally annealed cast films, is related to the formation of 1:1 adducts upon exposure to vapors of strong Lewis bases and implies dramatic optical absorption variations and naked-eye observation of the change in color from red-brown to red. The chemisorption process is fast, completely reversible, reproducible, and selective for amines. The reversible switching of the chemisorption−desorption process in cast films is demonstrated by successive cycles, amine exposure and subsequent heating, by monitoring the substantial optical absorption changes in the visible region. Vapochromism of this material can potentially be used to detect vapors of volatile amines.

■ INTRODUCTION

Vapochromism, the reversible color or luminescence change of a solid compound upon exposure to volatile organic compounds, in recent years has attracted much attention because it provides the basis for the development of various chemosensors.[1] It essentially involves transition metal complexes and invariably results in the sorption of the volatile compound into the solid to produce a change in its structure.[2]

Although the color change in these vapochromic complexes can be related to a variety of different mechanisms, this phenomenon in most cases can be ascribed to one of the following interactions: type I, change in intermolecular metallophilic,[3] $\pi-\pi$, or hydrogen bonding interactions; type II, change in the coordination environment. Type I interactions are the most common and mainly involve organometallic and coordination complexes of Pt^{II} and Au^{I}.[2,4] To vapochromic materials with type II interactions, in addition to Pt and Au complexes, belong coordination complexes mainly of Co^{II}, Ni^{II}, and Cu^{I}, as well as some coordination polymers of Cu^{I} and Cu^{II}.[2a,b,5]

In this context, zinc(II) Schiff-base coordination complexes are potential candidates as type II vapochromic materials. Actually, these complexes are Lewis acidic species,[6] which in the absence of Lewis bases form molecular aggregates via intermolecular Zn···O interactions[7] and in the presence of Lewis bases are stabilized as monomeric adducts.[8,9] The switching from the molecular aggregate to the monomeric adducts is accompanied by relevant changes in optical absorption,[6,10,11] second-order nonlinear optical,[12] and fluorescent properties.[6,10−13] Moreover, the Lewis acidic properties of these Zn^{II} complexes allowed the achievement of a variety of supramolecular structures.[14]

In this paper, we report the thermally induced phase transition, involving thermochromic behavior, and the vapochromic properties of a dimorphic amphiphilic bis(salicylaldiminato)Zn^{II} Schiff-base complex, **1**. To the best of our knowledge, it represents the first example of polymorphism

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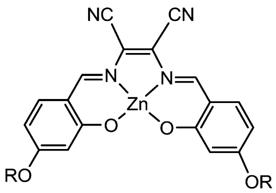
in a Schiff-base zinc(II) complex exhibiting thermochromic behavior and type II vapochromism. In fact, in the literature, there is only one case of a Schiff-base zinc(II) complex exhibiting type I vapochromism.[15] Moreover, only a few more examples of vapochromic materials involving Zn^{II} complexes[16,17] or $Zn[Au(CN)_2]_2$[18] and Pt/Zn-based[19] coordination polymers have been reported.



$R = C_{11}H_{21}$; **1**

RESULTS AND DISCUSSION

Vapochromic Properties. The idea to investigate the vapochromic properties of **1** was suggested by the observed dramatic color change of the complex solid, obtained by crystallization from methanol in the workup procedure,[10b] upon its subsequent drying (120 °C, 10^{-2} Torr). Actually, with the change from the crystallized complex to the dried one, its color changes from orange-red to red-brown (Figure 1).

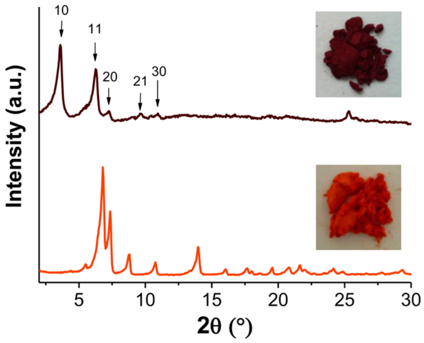


Figure 1. XRD patterns of complex **1** crystallized from methanol before (bottom) and after (top) drying. The insets are photographic images of the sample before and after drying.

Because such complexes crystallized from solutions of coordinating solvents always form adducts with the solvent axially coordinated to the Zn^{II} metal center,[8,9] the observed color change upon drying is likely related to the desorption of the coordinated solvent. In fact, thermogravimetric analysis (TGA) (see Figure S1 of the Supporting Information) of solid **1** crystallized from methanol shows a weight loss at ~100 °C (4.4% loss), consistent with the methanol content of the **1**·methanol adduct (4.28%). Moreover, powder X-ray diffraction (XRD) diffractograms (Figure 1) indicate that while the **1**·methanol adduct is characterized by a rich pattern with sharp peaks, typical of a crystalline species, after drying the XRD pattern is very different, with the appearance of a sharp peak at smaller angles consistent with the formation of an assembled structure. In particular, the diffraction pattern of the dried sample shows a set of diffraction peaks at 2θ values of 3.60°, 6.27°, 7.24°, 9.63°, and 10.95°, corresponding to d values of 24.54, 14.09, 12.21, 9.18, and 8.08 Å, respectively, in a $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}:1/\sqrt{9}$ ratio, in agreement with Miller indices of 10, 11, 20, 21, and 30, respectively, for a hexagonal columnar structure with a lattice constant a of 28.34 Å. It is well-known that analogous Zn^{II} Schiff-base complexes self-assemble into nanostructures through intermolecular Zn···O interactions from solutions of various coordinating solvents, by being drop cast or by complete solvent evaporation, upon solvent desorption.[20]

On the basis of these results, we ask the following question. Is it possible to obtain a reversible color change of the dried solid **1** upon exposure to vapors of a Lewis base? In other words, does dried solid **1** have sufficient Lewis acidic character to form adducts with volatile Lewis bases? The answer is affirmative. Actually, after exposure (5 min, 20 °C) of dried solid **1** to saturated vapors of isopropylamine, a highly volatile (bp 33 °C), strong Lewis base,[10a] an evident color change, from red-brown to red, which is restored by subsequent heating (10 min at 140 °C) (see Figure S2 of the Supporting Information), is observed.

The XRD pattern of the solid after amine exposure, except for the first intense peak that is shifted at 2θ = 3.93°, corresponding to d = 22.48 Å, is very different from that of the started dried complex, with the appearance of new relatively intense peaks at larger angles (Figure 2A). In particular, the low-intensity peak at 2θ = 7.90°, corresponding to d = 11.19 Å, can be related to the high-order reflection of the 10 peak observed at 2θ = 3.93°, while the peak at 9.21° can be associated with the 11 reflection of a rectangular columnar arrangement with a and b parameters of 22.48 and 10.62 Å, respectively. Therefore, these data indicate the existence of a lower-symmetry, assembled structure upon coordination of the amine to complex **1**. Thermogravimetric analysis (Figure 2B) of solid **1** after exposure to isopropylamine vapors shows a weight loss at ~140 °C (7.5% loss), consistent with the isopropylamine content for the **1**·isopropylamine adduct (7.62%), thus suggesting a stoichiometric chemisorption of the amine to the

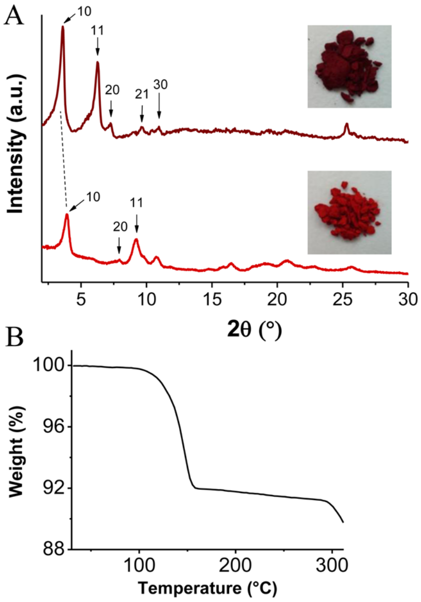


Figure 2. Vapochromism of **1**. (A) XRD patterns of dried solid **1** before (top) and after (bottom) exposure to isopropylamine vapors. The insets are photographic images of the sample before and after amine exposure. (B) Thermogravimetric analysis (scan rate of 5 °C min^{-1}) of dried solid **1** after exposure to isopropylamine vapors.

complex. The different color observed for the two adducts, orange-red for the **1**·methanol adduct crystallized from methanol and red for the **1**·isopropylamine adduct obtained by chemisorption from dried solid **1**, may originate either from their different structures or from the different Lewis-base coordinating atoms. As expected, the XRD pattern upon heating the solid exposed to isopropylamine vapors is identical to that of the initial dried solid, thus confirming its complete restoration. Therefore, Zn^{II} complex **1** possesses all features of a vapochromic material.

Polymorphism and Thermochromic Behavior. To exploit this complex as vapochromic material, we can consider various approaches. For example, using complex **1** in films or powders, the former were obtained by casting onto a transparent substrate the solution of dried solid **1** dissolved in a noncoordinating, volatile solvent. However, with a starting point of a dichloromethane (DCM) solution of **1**, either cast films or powder samples, the latter obtained by complete evaporation of the solvent, give colors and XRD patterns (see Figure 3A and Figure S3 of the Supporting Information) very different from those observed for the samples crystallized from methanol or after drying (Figure 1). In particular, the XRD pattern of the powder sample (Figure 3A) shows a sharp diffraction peak at $2\theta = 3.15°$ and a low-intensity peak at $2\theta = 6.39°$, corresponding to d values of 28.05 and 13.83 Å, respectively, in a 1:0.5 ratio, consistent with a lamellar organization. Moreover, a series of relatively sharp peaks are observed at larger angles (2θ values of 21.13°, 23.40°, 26.39°, and 30.18°, corresponding to d values of 4.20, 3.80, 3.38, and 2.96 Å, respectively), presumably related to the $\pi-\pi$ stacking and interdigitated hydrophobic interactions of the assembled structure.

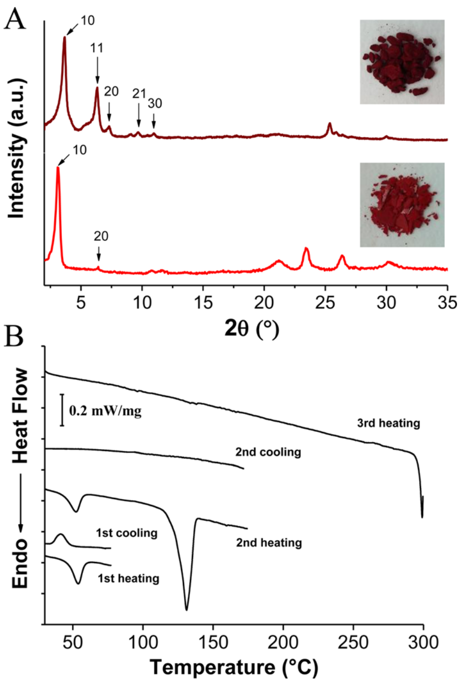


Figure 3. Irreversible phase transition of **1**. (A) XRD patterns of a powder sample of **1**, obtained from a DCM solution by complete evaporation of the solvent, before (bottom) and after (top) heating at 140 °C. The insets are photographic images of the sample before and after heating. (B) DSC thermograms (scan rate of 5 °C min^{-1}) of a powder sample of **1**.

Cast or powder samples obtained from DCM solutions of **1** exhibit an interesting thermal behavior. Actually, after these cast or powder samples had been heated (10 min at 140 °C), an XRD pattern almost identical to that obtained for **1** crystallized from methanol after drying is observed, showing the observed typical brown color described above (Figure 3A). The thermal properties of these powder samples were thus investigated by TGA and differential scanning calorimetry (DSC). TGA indicates that **1** is stable up to 300 °C (see Figure S4 of the Supporting Information). DSC analysis shows the presence of a reversible endothermic transition at 53 °C and an irreversible endothermic transition at 131 °C, as verified by successive heating–cooling cycles (Figure 3B). Melting occurs at 300 °C with concurrent decomposition. The weaker reversible transition at 53 °C (ΔH = 9.8 kJ mol^{-1}) can be likely related to structural rearrangements of the side chains, followed by the strong irreversible phase transition at 131 °C (ΔH = 48 kJ mol^{-1}). The latter is an unusual thermal behavior for such complexes, as analogous amphiphilic Zn^{II} Schiff bases generally exhibit mesomorphic transitions.[21]

In summary, the overall data indicate the existence of an irreversible thermally induced, lamellar-to-hexagonal, phase transition of the self-assembled structure of **1** in the solid state, accompanied by a color change, i.e., of an "irreversible thermochromism".[22] In this regard, it represents the first example of thermochromic behavior involving a Zn^{II} Schiff-base complex, as the other few cases of solid-state thermochromism of Schiff-base complexes reported in the literature refer to an oxovanadium(IV),[23] and some nickel(II) and copper(II)[22,24] complexes.

The color change of solid **1** upon the irreversible phase transition can be better evaluated considering optical absorption spectra of films of **1** obtained by casting from a DCM solution onto a transparent substrate, before and after thermal annealing at 140 °C. In fact, while as-cast films exhibit a orange-yellow color and are characterized by a broad absorption band centered at 440 nm, after annealing a hypochromism of the shorter wavelength feature between 300 and 400 nm is observed along with the appearance of a new band centered at 565 nm, which can be referenced to the evolution of the longer wavelength feature observed before heating, responsible for the observed red-brown color (Figure 4).

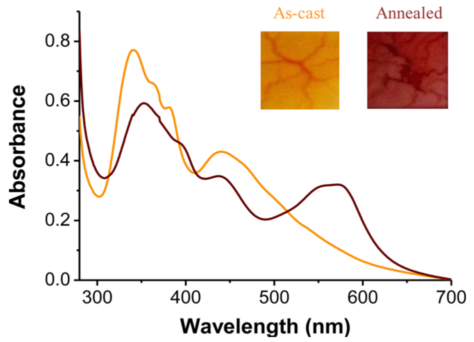
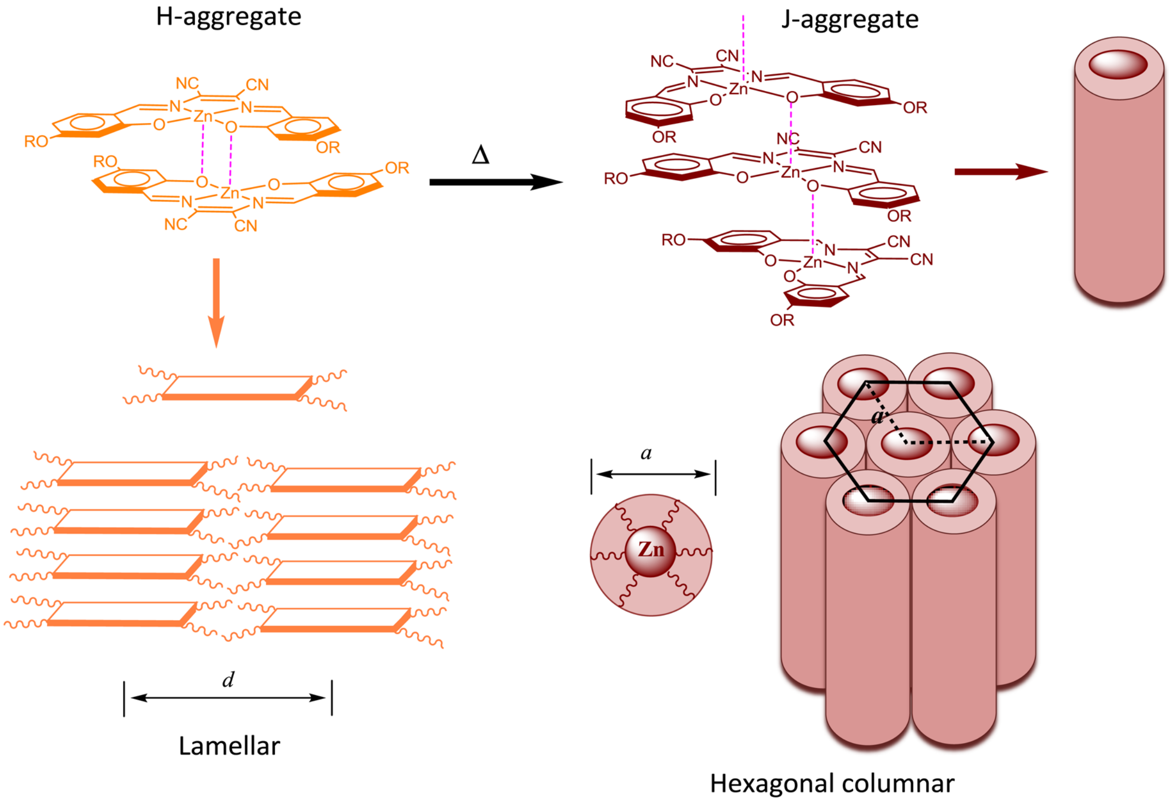


Figure 4. UV–vis absorption spectra of **1** deposited by casting onto a glass substrate from a 1.0×10^{-3} M DCM solution, before (orange-yellow line) and after (red-brown line) heating. The insets are photographic images of the as-cast and annealed films.

Scheme 1. Representation of the Lamellar Structure of 1 and the Hexagonal Columnar Structure upon the Thermal Structural Transition



These optical absorption features are consistent with a different arrangement of each molecular unit of aggregate complex **1** upon the phase transition. In particular, while the optical absorption spectrum of the as-cast samples is in agreement with the formation of H-aggregates, the appearance of the longer wavelength feature upon heating can be related to J-like aggregates.[25] As pictorially depicted in Scheme 1, the formation of J-like aggregates is promoted by thermal treatment of H-aggregates and involves a phase transition from lamellar to hexagonal structure.

Vapochromic Performance of Cast Films. To explore the optical absorption changes associated with the vapochromic behavior of **1**, in view of the observed color change upon the phase transition described above, thermally annealed cast films deposited from solutions of **1** in DCM were considered. The exposure to isopropylamine vapors implies dramatic optical absorption variations and naked-eye observation of the change in color from red-brown to red. The optical absorption spectra of an annealed cast film of **1** before and after exposure to saturated vapors of isopropylamine (5 min) and subsequent heating (10 min at 120 °C) are reported in Figure 5.

The optical absorption spectrum upon chemisorption of isopropylamine clearly shows the formation of a new band envelope between 450 and 500 nm, with two maxima at λ = 459 and 504 nm, responsible for the observed red color upon exposure, and the partial disappearance of the band centered at 565 nm. After subsequent heating, the optical absorption spectrum is almost indistinguishable from that of the starting annealed film, thus confirming its complete restoration. It is noteworthy that the λ_{max} at 504 nm of the exposed film almost corresponds to the minimal absorption for the annealed film. Therefore, this "window" of the optical absorption spectrum can be used to assess the vapochromic performance of cast films of **1**. The reversible switching of the chemisorption–desorption process is thus demonstrated by successive cycles of amine exposure and subsequent heating by monitoring the substantial optical absorption changes at λ = 504 nm [Δ absorbance up to 0.27 (see Figure 5)]. It results in the complete restoration–disappearance of this optical absorption band for many cycles, without a loss of absorbance.[26] Moreover, the process is repeatable and reproducible even upon discontinuous exposure–heating cycles conducted within several weeks. These findings provide clear and direct evidence that a reversible switching of the chemisorption–desorption process, accompanied by significant changes of the optical properties of the annealed film, occurs upon the exposure–heating treatment.

Analogous results are observed even from annealed cast films prepared from DCM solutions of **1** at different concentrations. In fact, the diagram of the absorbance at 504 nm versus $\Delta_{absorbance}$ at 504 nm, after exposure to saturated vapors of isopropylamine for various annealed films, indicates an almost linear relationship (see Figure S5 of the Supporting Information). This further suggests that the chemisorption of the amine to complex **1** is likely quantitative.

To check whether the same structural transformations occur in both powder samples and cast films, XRD patterns were recorded for annealed cast films of **1** before and after exposure to isopropylamine vapors and compared with related XRD patterns of the dried solid (see Figure S6 of the Supporting Information). XRD patterns are comparable in both powder samples and cast films, especially as far as the relevant diffraction peaks at smaller angles are concerned. This suggests that analogous structural transformations occur upon the

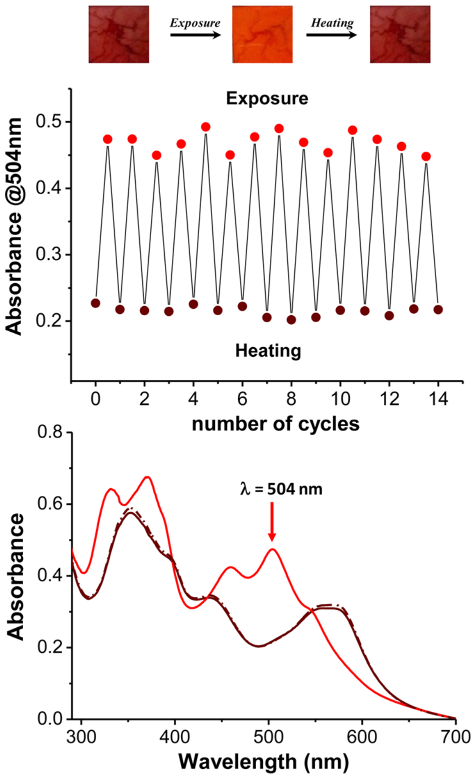


Figure 5. Vapochromism of annealed cast films of **1**: (bottom) UV−vis absorption spectra of an annealed cast film of **1** deposited onto a glass substrate from a 1.0×10^{-3} M DCM solution, before (red-brown line) and after (red-line) exposure to isopropylamine vapors and after heating (dotted lines); and (top) switching of the optical absorption band at $\lambda = 504$ nm of the annealed cast film of **1** upon successive cycles of isopropylamine exposure and subsequent heating. The insets are photographic images of an annealed film before and after exposure to isopropylamine vapors and after successive heating.

thermally induced phase transition and chemisorption in both powder samples and cast films.

Chemisorption to complex **1** is observed even using other volatile amines. Thus, analogous results, in terms of optical absorption spectral changes, are obtained upon exposure of annealed films of **1** to saturated vapors of diethylamine (bp 55 °C) and triethylamine (bp 89 °C) also characterized by a strong Lewis basicity[10a] (Figure 6). In contrast, exposure of annealed films of **1** to air saturated with vapors of other volatile species, e.g., methanol (bp 65 °C) and tetrahydrofuran (bp 66 °C), gives different optical absorption spectra. In fact, in comparison to those of films exposed to amines, in these cases optical absorption spectra lack the band at 504 nm, while the band at shorter wavelengths, 445 nm for tetrahydrofuran and 461 nm for methanol, is less pronounced (Figure 6). Finally, acetone (bp 56 °C), having the lowest Lewis basicity among these involved volatile Lewis bases,[10a] does not show any appreciable vapochromism (Figure 6). Therefore, because annealed films of **1** show a distinct vapochromism with the diverse volatile Lewis bases, these results suggest that it is possible to discriminate volatile amines from the other volatile Lewis bases.

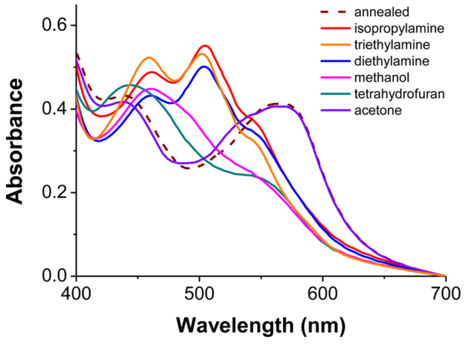


Figure 6. Vis absorption spectra of annealed cast films of **1**, deposited onto a glass substrate from a 1.0×10^{-3} M DCM solution, after exposure to saturated vapors of different volatile Lewis bases. The optical absorption spectrum of an annealed cast film (---) is reported for comparison.

It is also interesting to investigate the vapochromic behavior of the as-cast films of **1**. Comparison of optical absorption spectra of an as-cast film of **1** from DCM solutions before and after exposure to saturated vapors of isopropylamine is reported in Figure 7. In this case, exposure to isopropylamine vapors results in minor variations in the optical absorption spectrum in the visible region, with an incipient appearance of the new features between 450 and 550 nm observed in the case of exposure of annealed films. Moreover, the optical absorption spectrum remains unchanged even after exposure to isopropylamine vapors for several hours. Therefore, these data suggest that as-cast films of **1** are less prone to forming adducts with volatile Lewis bases than annealed films. In other words, H-type aggregates exhibit a Lewis acidity weaker than that of J-type aggregates. Obviously, after the first cycle of exposure and subsequent desorption by the heating treatment, the as-cast films behave as annealed films.

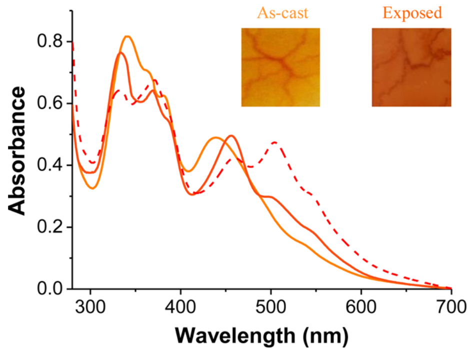


Figure 7. UV−vis absorption spectra of an as-cast film of **1**, deposited onto a glass substrate from a 1.0×10^{-3} M DCM solution, before (orange-yellow line) and after (orange-red line) exposure to isopropylamine vapors. The optical absorption spectrum of an annealed film, after simultaneous exposure with the as-cast film to isopropylamine vapors (dotted red line), is reported for comparison. The insets are photographic images of the as-cast and exposed films.

■ CONCLUSIONS

This paper demonstrates for the first time that an amphiphilic Zn^{II} Schiff-base complex is involved in an irreversible thermally induced phase transition, accompanied by a color change, and exhibits type II vapochromic behavior, with formation of adducts upon exposure to vapors of strong Lewis bases.

The observed unprecedented irreversible phase transition for such complexes is associated with a thermal, lamellar-to-hexagonal columnar structural transition, which involves a different arrangement of each molecular unit within the assembled structure, H- and J-type aggregates, respectively, responsible for the thermochromic behavior. Therefore, higher-symmetry structures, i.e., J-type aggregates, can easily be obtained by thermal annealing of cast films or powder samples obtained from DCM solutions of the complex.

The dimorph having a hexagonal columnar structure quantitatively reacts, either in powder or in cast films, with vapors of amines to form 1:1 adducts. Favorable optical absorption spectral changes are observed on switching to the annealed desorbed films. Thus, the reversible switching of the chemisorption−desorption process in cast films is demonstrated by successive cycles of amine exposure and subsequent heating by monitoring the substantial optical absorption changes in the visible region. Moreover, the process is reproducible even upon discontinuous exposure−heating cycles conducted within several weeks. Chemisorption is observed even with other volatile Lewis bases, accompanied by different optical absorption spectral changes. Therefore, it is possible to discriminate volatile amines with respect to the other volatile Lewis-base species.

In summary, we have discovered and studied the unique thermochromic and vapochromic characteristics of an amphiphilic, Lewis acidic Zn^{II} Schiff-base complex. It could represent a prototype of a new family of vapochromic materials whose color change is related to the formation of Lewis acid−base adducts. Vapochromism of this material, in addition to its rapidity and simplicity, also enjoys the advantages of complete reversibility and reproducibility. Therefore, it can potentially be applied as a simple and cheap sensing component to detect vapors of strong Lewis bases such as volatile amines.

EXPERIMENTAL SECTION

Materials. Zinc acetate dihydrate, 2,4-dihydroxybenzaldehyde, and 11-bromo-1-undecene (Aldrich) were used without purification. Diaminomaleonitrile (Aldrich) was purified by recrystallization from an ethanol solution. Dichloromethane (Aldrich) stabilized with amylene was used to prepare solutions of **1**. All other reagents and solvents (Aldrich) employed here were used as received.

Synthesis. The synthesis of the complex [2,3-bis[[2-hydroxy-4-(undec-10-enyloxy)benzylidene]amino]-2-butenedinitrilato]Zn^{II} (**1**) was previously reported.[10b] Orange-red solid crystallized from methanol: $C_{40}H_{50}N_4O_4Zn{\cdot}CH_3OH$ (748.30). Anal. Calcd: C, 65.81; H, 7.27; N, 7.49. Found: C, 66.20; H, 7.23; N, 7.38. Red-brown powder obtained after drying (120 °C, 10^{-2} Torr): $C_{40}H_{50}N_4O_4Zn$ (716.26). Anal. Calcd: C, 67.08; H, 7.04; N, 7.82. Found: C, 67.48; H, 6.97; N, 7.93.

Physical Measurements. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Optical absorption spectra were recorded at room temperature with a JASCO V-650 spectrophotometer. TGA measurements were performed on a Mettler Toledo TGA/SDTA851^e instrument under a nitrogen atmosphere. DSC measurements were performed on a Mettler Toledo DSC12E instrument under a nitrogen atmosphere. $\theta-2\theta$ X-ray diffraction patterns were determined on a Bruker-AXS D5005 $\theta-\theta$ X-ray diffractometer, using a Göebel mirror to parallel Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV and 30 mA. X-ray patterns were recorded in grazing incidence mode (0.5°) for the cast films and in Bragg−Brentano mode for the powders.

Vapochromic Studies. Powder samples were obtained from DCM solutions of **1** by complete evaporation of the solvent at room temperature and dried under vacuum. DCM solutions of **1** were prepared using the dried red-brown complex **1**, the latter obtained from the complex crystallized from methanol and dried under vacuum at 120 °C. Films were prepared by casting DCM solutions of **1** into cleaned glass substrates. The solvent was allowed to evaporate at room temperature. Annealed films were obtained by heating the samples for 10 min in an oven at 140 °C. Upon exposure to vapors of volatile species, films were restored using an analogous heating treatment (10 min at 120 °C for amines and 10 min at 140 °C for the other volatile solvents). Vapochromic studies were conducted using a sealed glass vapor chamber (a 500 mL vessel equipped with a screw cap) in which the volatile liquid (5 mL into a flat-bottom vessel) and the films were placed inside. Films were exposed for 5 min in the case of isopropylamine and 15 min in the case of all the other investigated species.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional TGA, XRD, and optical absorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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