Zn(II)-bisthienylethynylbipyridine complex: preparation, characterization and vapochromic behaviour in polymer films

Irina Platonova,^a Alberto Brandi,^a Marco Lessi,^a Giacomo Ruggeri,^{a,b} Fabio Bellina,^{a,}
Andrea Pucci^{a,b,c*}*

^aDipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy

^bINSTM, Unità di Ricerca di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

^cIstituto per i Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche (IPCF-CNR),
Via G. Moruzzi 1, I-56124 Pisa, Italy

Corresponding authors:

Dr. Andrea Pucci, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via
Risorgimento 35, 56126 Pisa, Italy

Tel: +39 050 2219270

Fax: +39 050 2219260

e-mail: andrea.pucci@unipi.it

Prof. Fabio Bellina, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via
Risorgimento 35, 56126 Pisa, Italy

Tel: +39 050 2219282

Fax: +39 050 2219260

e-mail: fabio.bellina@unipi.it

Abstract

In the present work, we report the vapochromic behaviour of PMMA films doped with small amounts of **1a**:Zn fluorophore, a Zn^{2+} adduct of the bithienylethynylbipyridine ligand.

1a:Zn exhibited polarity-dependent changes in the fluorescence spectral properties when dissolved in solvents with different polarity index, indicating that its fluorescence states are of intramolecular charge transfer character. When **1a**:Zn was dispersed in the PMMA matrix, its emission resulted barely influenced by the polymer environment. By contrast, **1a**:Zn/PMMA films showed a significant variation of its emission with a 40 nm red-shift when exposed to a saturated atmosphere of dichloromethane. This vapochromic behaviour was much less evident when progressive amounts of methanol were added to dichloromethane due to both lower vapour pressure and limited interaction of the former with PMMA. The experiments revealed also that the rate constants associated with the vapochromic behaviour were affected by solvent composition and easily determined by luminescent experiments.

Keywords

bipyridyl derivatives, zinc adducts, solvatochromism, dye dispersion, smart materials, vapochromic materials

1. Introduction

In the last decade, significant interest has been addressed to the design of luminescent materials for various promising applications in diverse fields, ranging from solar energy conversion,^[1] to optoelectronic devices^[2] and chromogenic materials.^[3-6] Chromogenic systems are capable to respond to various stimuli (e.g. light, heat, mechanical stress and chemical stimuli) through a macroscopic optical output.^[5, 7, 8] The energy of the stimulus is properly transduced into optical variations (i.e., absorption, emission, refractive index) as a function of external interference. This mechanism allows the preparation of “smart” devices for many different applications, such as anti-counterfeiting systems, attoreactor sensors and informational displays.^[9-11] Recently, vapochromic materials,^[12-14] which display colour changes upon exposure to vapours of volatile organic compounds (VOCs), have been also rapidly evolved due to their applications for chemical vapour detection. Such chemical sensors are of great interest as environmental monitoring devices, as safety systems at workplaces and for defence and security applications.

Soft intelligent materials are based on the assembly of different units performing specific functions; for example, organic or inorganic chromophores constitute the basis of the sensor mechanism since they confer to the material a variation of the opto-electronic features as a consequence of a stimulus.

Recently, heteroaromatic backbones have been reported as very promising building blocks to prepare diverse classes of strongly emissive smart materials.^[15, 16] Among various molecular backbones, N-heterobiaryl compounds are advantageous to employ due to their easy derivatization with an assorted class of donor end-capping functionalities to tune their optical properties as a function of the desired application.^[17-20] Their opto-electronic properties can be effectively tuned via complexation of metal cations at their chelating sites.^[21, 22] For example, in the case of bipyridyl derivatives, metal binding leads to a red shift in absorption

and emission maxima due to the extension of the effective conjugation length provided by the planarization of the bipyridyl units. Bipyridyl derivatives are the most-employed ligands in coordination chemistry due to their robust redox stability, ease of functionalization and ability to bind a wide collection of d- and f-block elements.^[23] Although many transition metals induce such a response, Zn^{2+} is the most investigated cation since its closed-shell d^{10} configuration permits the metal-ligand fluorophores to remain emissive.^[24, 25] Recently, Zn^{2+} adducts of bipyridine-based system with methyl- and methoxy-phenyleneethynylene at the 4,4' positions has been proposed as conjugate molecular systems which possess chromogenic properties as a function of substituents and solvent polarity.^[21] Large variations of the emission properties were found as a function of both solvent polarity and electron donating ability of the substituents on the phenyleneethynylene moiety, thus suggesting a charge-transfer character of the lowest electronic transition.

Starting from these observations, we have herein targeted similar chromogenic Zn^{2+} adducts employing the easily-derivatised thienyleneethynylene at the 6,6' positions of the bipyridine ligand to enforce the 1:1 ligand to metal ratio desired for chemosensor applications. The major advantages of using thienyleneethynylene moieties may be attributed to a couple of reasons. First, it is well reported that the cylindrical symmetry of the acetylene unit maintains the π -electron conjugation at any degree of rotation;^[26-28] second, the heteroaromatic rings are not coplanar, and this helps in keeping low the intermolecular interactions based on π -stacking.^[29]

Bisthienylethynylbipyridines **1a** and **1b** bearing a 5-methyl and a 5-methoxy group on their thienyl moieties, respectively, were easily prepared using a rapid and convenient procedure having as key step a double Sila-Sonogashira cross-coupling reaction involving 6,6'-bis(trimethylsilylethynyl)-2,2'-bipyridine (**2**) and 5-substituted 2-bromothiophenes **3a-b** (Scheme 1).

<Scheme 1 near here>

The photophysical properties of AB dyes were investigated as a function of the addition of Zn^{2+} ions and solvent polarity, showing tuneable luminescent properties, thereby making them suitable candidates for the preparation of materials with chromogenic properties. Eventually, the target Zn^{2+} adduct was dispersed in a poly(methyl methacrylate) (PMMA) matrix, and optical properties of the resulting vapochromic material were investigated.

2. Material and method

2.1 Materials

All reactions were performed under argon, by standard syringe, cannula and septa techniques. Unless otherwise stated, commercially available materials were used as received.

6,6'-Bis((trimethylsilyl)ethynyl)-2,2'-bipyridine (**2**) and 2-bromo-5-methoxythiophene (**3b**) were prepared according to published procedures^[30, 31]

Poly(methyl methacrylate) (PMMA, Aldrich) with number average molecular weight of 350,000 g/mol (SEC), a Tg of about 105 °C (DSC) and an acid number <1 mg KOH/g was purified by reprecipitation from a dichloromethane solution poured into 95 % methanol, subsequently drying to constant mass at room temperature under vacuum.

6,6'-Bis((5-methylthiophen-2-yl)ethynyl)-2,2'-bipyridine (1a).

According to our previously published procedure,^[32] to a mixture of 6,6'-bis((trimethylsilyl)ethynyl)-2,2'-bipyridine (**2**) (0.26 g, 0.75 mmol), 5-bromo-2-methylthiophene (**3a**) (0.19 mL, 0.29 g, 1.65 mmol), $\text{PdCl}_2(\text{PhCN})_2$ (28.8 mg, 0.075 mmol), $t\text{Bu}_3\text{PHBF}_4$ (43.5 mg, 0.15 mmol), CuI (28.6 mg, 0.15 mmol), $\text{Bn}(n\text{Bu})_3\text{NCl}$ (93.6 mg, 0.3 mmol) in toluene (8 mL) was added a 2.5N aqueous solution of NaOH (8 mL), and the resulting biphasic mixture was stirred under argon at 40 °C for 19 h. After being cooled to room temperature, the reaction mixture was diluted with AcOEt (15 mL) and poured into a

saturated aqueous NH₄Cl solution (30 mL), and the resulting mixture was stirred in the open air for 0.5 h and then extracted with AcOEt (4 × 10 mL). The organic extract was washed with water (2 × 5 mL), dried and concentrated under reduced pressure. The crude reaction mixture was dissolved in CH₂Cl₂ (4 mL) and purified by flash chromatography on silica gel using toluene as eluent to give **1a** (0.23 g, 76%) as a light pink solid: m.p. 172-174 °C. ¹H NMR (CDCl₃, 200 MHz) δ 8.43 (2H, d, *J* = 8.1 Hz, Py ring), 7.80 (2H, dd, *J* = 8.1 and 7.8 Hz, H₃ Py ring), 7.53 (2H, d, *J* = 7.8 Hz, Py ring), 7.22 (2H, d, *J* = 3.3 Hz, Thio ring), 6.70 (2H, d, *J* = 3.3 Hz, Thio ring), 2.51 ppm (6H, s, CH₃). ¹³C NMR (CDCl₃, 50.3 MHz) δ 155.9, 143.4, 142.7, 137.0, 133.7, 127.2, 125.6, 120.6, 119.7, 91.9, 83.1, 15.6 ppm. ESI-MS: *m/z* [M+H]⁺ = 397. Anal. Calcd. for C₂₄H₁₆N₂S₂: C, 72.7; H, 4.1; N, 7.1. Found C, 73.1; H, 4.2; N, 7.0.

6,6'-Bis((5-methoxythiophen-2-yl)ethynyl)-2,2'-bipyridine (1b).

According to our previously published procedure,^[32] to a mixture of 6,6'-bis((trimethylsilyl)ethynyl)-2,2'-bipyridine (**2**) (0.35 g, 1.0 mmol), 5-bromo-2-methoxythiophene (**3b**) (0.26 mL, 0.42 g, 2.2 mmol), PdCl₂(PhCN)₂ (38.4 mg, 0.1 mmol), *t*Bu₃PHBF₄ (58.0 mg, 0.2 mmol), CuI (38.0 mg, 0.2 mmol), Bn(*n*Bu)₃NCl (0.13 g, 0.4 mmol) in toluene (10 mL) was added a 2.5N aqueous solution of NaOH (10 mL), and the resulting biphasic mixture was stirred under argon at 40 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with AcOEt (15 mL) and poured into a saturated aqueous NH₄Cl solution (30 mL), and the resulting mixture was stirred in the open air for 0.5 h and then extracted with AcOEt (4 × 10 mL) and CH₂Cl₂ (2 × 10 mL). The organic extract was washed with brine (4 × 5 mL), dried and concentrated under reduced pressure. The crude reaction mixture was dissolved in CH₂Cl₂ (10 mL) and purified by flash chromatography on silica gel using a mixture of CH₂Cl₂ and AcOEt (80:20) as eluent to give **1b** (0.12 g, 28%) as a light brown solid: m.p. 173-175 °C. ¹H NMR (CDCl₃, 200 MHz) δ

8.40 (2H, d, $J = 7.8$ Hz, Py ring), 7.79 (2H, dd, $J = 7.8$ and 7.4 Hz, H₃ Py ring), 7.49 (2H, d, $J = 7.4$ Hz, Py ring), 7.10 (2H, d, $J = 4.3$ Hz, Thio ring), 6.14 (2H, d, $J = 4.3$ Hz, Thio ring), 3.93 ppm (6H, s, OCH₃). ¹³C NMR (CDCl₃, 50.3 MHz) δ 168.0, 155.9, 142.8, 137.0, 132.5, 127.1, 120.5, 108.4, 104.3, 90.8, 83.6, 60.3 ppm. ESI-MS: m/z [M+H]⁺ = 429. Anal. Calcd. for C₂₄H₁₆N₂O₂S₂: C, 67.3; H, 3.8; N, 6.5. Found C, 67.0; H, 3.7; N, 6.9.

Preparation of 1a:Zn

Zn(OAc)₂·2 H₂O (11 mg, 0.048 mmol) was added to an anhydrous acetonitrile solution (40 mL) of **1a** (19 mg, 0.048 mmol). The reaction mixture was stirred for 4 h at room temperature. The solvent was then evaporated and crystallization of the residue in a CH₂Cl₂/pentane mixture afforded a yellow powder (0.020 mg, 70%).

FTIR (KBr disk, cm⁻¹): 2210 (stretching C≡C), 1580 (stretching C=C and C=N of bipyridine ring), 1412 (stretching + H bending of bipyridine ring).

¹H NMR (CDCl₃, 600 MHz) δ 8.40 (2H, d, $J = 8.1$ Hz, Py ring), 7.70 (2H, dd, $J = 8.1$ and 7.8 Hz, H₃ Py ring), 7.50 (2H, d, $J = 7.8$ Hz, Py ring), 7.19 (2H, d, $J = 3.3$ Hz, Thio ring), 6.67 (2H, d, $J = 3.3$ Hz, Thio ring), 2.50 ppm (6H, s, CH₃), 2.05 ppm (6H, s, CH₃).

Anal. Calcd. for C₂₈H₂₂N₂O₄S₂Zn, 2 H₂O: C, 58.0; H, 3.8; N, 4.8. Found C, 58.5; H, 3.4; N, 4.9.

Preparation of PMMA films containing 1a:Zn

1a:Zn/PMMA films were prepared by dissolving 0.300 g of polymer and the 0.05-1 wt.% of **1a:Zn** in CHCl₃. The solution is then cast on a cold glass and slowly evaporated at room temperature.

Methods

Melting points were recorded on a hot-stage microscope (Reichert Thermovar). Fluka precoated 60 F254 aluminium silica gel sheets were used for TLC analyses.

GLC analyses were performed using two types of capillary columns: an Alltech AT-35 bonded FSOT column (30 m x 0.25 mm i.d.) and an Alltech AT-1 bonded FSOT column (30 m x 0.25 mm i.d.). Purifications by flash-chromatography were performed using silica gel Merck 60 (particle size 0.040–0.063 mm).

ESI-MS analyses were carried out using a Perkin-Elmer/Sciex API 365 instrument with Turbo Ion Spray as Ion source, in flow injection analysis positive ions.

Infrared spectra were recorded by a Fourier transform infrared spectrometer (Spectrum One, PerkinElmer) on KBr windows.

NMR spectra were recorded at room temperature, unless otherwise stated, with a Varian Unity Inova at 600 MHz (^1H) or with a Varian Gemini at 200 MHz (^1H) and 50.3 MHz (^{13}C) and were referred to TMS or to the residual protons of deuterated solvents.

UV-Vis spectra of THF solutions were recorded at room temperature in isotropic conditions with the help of a Perkin Elmer Lambda 650.

The absorption responses of **1a** or **1b** to Zn^{2+} excess were determined by placing 1 mL aliquot of the ligand (10 μM in acetonitrile) in a cuvette, and an initial UV-vis spectrum was collected. Microliter aliquots of a 1 mM solution of $\text{Zn}(\text{OAc})_2 \cdot 2 \text{H}_2\text{O}$ in acetonitrile were then added, and the cell was capped. The cuvette was shaken gently several times to affect mixing and placed in the spectrophotometer. The association constant of the Zn^{2+} adducts were determined by the Benesi-Hildebrand method.^[33]

Fluorescence spectra of solutions were recorded at room temperature with the help of a Horiba Jobin-Yvon Fluorolog[®]-3 spectrofluorometer.

The fluorescence quantum yield (Φ_f) in THF was determined at room temperature relative to quinine sulphate ($\Phi_f^s = 0.54$ in 0.1 M H_2SO_4) using the following relation:

$$\Phi_x = \Phi_{\text{ST}} \left(\frac{\text{Grad}_x}{\text{Grad}_{\text{ST}}} \right) \left(\frac{\eta_x^2}{\eta_{\text{ST}}^2} \right)$$

Where the subscripts ST and X are standard and dye respectively, Grad the gradient from the plot of integrated fluorescence intensity vs absorbance for different solutions of standard and dyes. In order to minimise re-absorption effects, absorbances never exceed 0.1 in correspondence and above the excitation wavelength. η is the refractive index of the solvent, i.e. 1.405 for THF and 1.333 for water.

The fluorescence responses of **1a** or **1b** to excess Zn^{2+} were determined by placing 1 mL aliquot of the ligand (10 μM in acetonitrile) in a cuvette, and an initial emission spectrum was collected. Microliter aliquots of 1 mM solution of $\text{Zn}(\text{OAc})_2 \cdot 2 \text{H}_2\text{O}$ in acetonitrile was then added, and the cell was capped. After the cuvette was shaken gently several times to affect mixing, another emission spectrum was acquired until the end of the titration. The association constants of the Zn^{2+} adducts were determined by the Benesi-Hildebrand method.^[34]

The fluorescence of polymer composites were recorded by using the F-3000 Fiber Optic Mount apparatus coupled with fiber-optic bundles. Light is focused from the excitation spectrometer into the fiber-optic bundle, and then directed to the sample. Fluorescence emission from the sample is directed back through the bundle and into the front-face collection port in the sample compartment.

The fluorescence variation of the composite films was tested by subjecting the film to CH_2Cl_2 or MeOH vapours at room temperature. The film was attached to an aluminium foil which covers a closed container as shown in Figure 1.

<Figure 1 near here>

3. Results and discussion

The reaction of the known 6,6'-bis((trimethylsilyl)ethynyl)-2,2'-bipyridine (**2**)^[30] with 2.2 equiv of 5-substituted 2-bromothiophenes **3a-b** was carried out in a mixture of toluene and NaOH_{aq} at 40 °C in the presence of 10 mol.% PdCl₂(PhCN)₂, 20 mol.% *t*Bu₃PHBF₄, 20 mol.% CuI and 40 mol.% *n*Bu₃BnNCl as phase-transfer catalyst, according to our recent protocol for the Pd- and Cu-catalyzed Sila-Sonogashira cross-coupling under phase-transfer conditions^[32]. The reaction gave the required bipyridines **1a-b** in 76 and 28% isolated yields, respectively (Scheme 2).

<Scheme 2 near here>

The bipyridines **1a-b** are indefinitely stable towards light and air, and were fully characterized by ¹H and ¹³C NMR, ESI-MS spectrometry, as well by satisfactory elemental analyses.

All the optical features of **1a** and **1b** in THF and acetonitrile (ACN) solutions are summarized in Table 1.

<Table 1 near here>

The UV-vis spectra of the dyes are mostly unstructured with absorption bands between 340 and 350 nm (Figure S1), which are tentatively assigned to combinations of the intraligand $\pi \rightarrow \pi^*$ transitions of the bipyridyl moieties with the $\pi \rightarrow \pi^*$ transitions of the thienyleneethynylene units. The bathochromic shift and the corresponding increase in the extinction coefficient of **1b** with respect to **1a** is possibly due to the greater electron donating ability of the methoxy group with respect to the methyl functionality at the thiophene nucleus. The absorption profile and the maximum appear moderately affected by varying the solvent polarity on passing from THF to ACN. The mild negative solvatochromism can be attributed to the more polar ground state with respect to the excited state, which is stabilized by solvents of lower polarity.^[35-37]

The emission spectra of both ligands are mostly unstructured as well (Figure S2) with very

low quantum yield values (< 0.1 %). Notably, the effect of solvent polarity on the emission property of the dyes was found to be pronounced as compared to the absorption spectra (Table 1).

The absorption and emission spectral responses of **1a** and **1b** to excess Zn^{2+} ions was then investigated and reported in Figure 2.

<Figure 2 near here>

Upon increasing the concentration of Zn^{2+} in ACN solution, a decrease in the intensity of the UV absorption bands was observed for both dyes, flanked by the emergence of new bands at longer wavelengths attributed to the charge transfer character of the lowest-energy $\pi \rightarrow \pi^*$ transition. The changes of the absorption spectra are characterized by the presence of a single isosbestic point at 345 nm and 360 nm for **1a** and **1b**, respectively.

The emission spectra variations of **1a** and **1b** to excess Zn^{2+} ions was recorded by exciting at the respective isosbestic points (Figure 2c and 2d), and for both cases new red-shifted emission bands are observed at 503 ($\Delta\lambda = 120$ nm) and 490 nm ($\Delta\lambda = 88$ nm), respectively. **1a** shows larger red-shift which is also associated with a great increase of the emitted light. By contrast, the emission of **1b** decreased to a certain extent upon the addition of Zn^{2+} ions, suggesting a partial inhibition of the charge transfer singlet state of the free ligand.^[21]

Titration with Zn^{2+} ions also determined the association constants of the adducts on the basis of Benesi-Hildebrand analyses (Figure S3).^[33, 34] For example, **1a** exhibited absorption ($K_f = 0.59 \cdot 10^4 \text{ M}^{-1}$) and fluorescence ($K_f = 0.58 \cdot 10^4 \text{ M}^{-1}$) binding constants that are about 10-20 times lower than those of phenyleneethynylene bipyridyl-based ligands.^[24] This behaviour can be addressed to the significant degree of steric hindrance provided by the 6,6'-bisthiénylethynyl functionalization at the pyridine atoms, which are involved less effectively in the binding interactions.^[38]

Anyway, looking at the emissions, compound **1a**:Zn displays both the largest luminescence

variation in wavelength (120 nm) and especially in intensity, thereby making it suitable as a possible candidate for the preparation of chromogenic materials.

Moreover, **1a**:Zn shows polarity-dependent changes in the fluorescence spectral properties when dissolved in solvents with different polarity index (Table 2 and Figure S4).

<Table 2 near here>

The fluorescence peaks red-shifted of about 40 nm from toluene to ACN solutions, thus indicating that the fluorescent states of **1a**:Zn are of intramolecular charge transfer (ICT) character.^[37]

1a:Zn was then dispersed in poly(methyl methacrylate) (PMMA) films by solution-casting at different concentration in the range between 0.05-1 wt.%.

All **1a**:Zn/PMMA films show absorption features identical in their form, with absorption bands centred at 340 and 380 nm, as analogously recorded in solution of ACN. By contrast, compared with the emission spectra of **1a**:Zn in solution, the emission spectra of **1a**:Zn/PMMA films are blue-shifted of more than 25 nm.

<Figure 3 near here>

This phenomenon can be addressed to the ICT character of the **1a**:Zn emission, which results barely influenced by the polymer environment of the PMMA repeating units.

Noteworthy, no emission bands attributed to the generation of supramolecular chromophoric aggregates are detected in the range of concentration investigated. Only a red-shift of about 5 nm occurs with concentration, probably due to self-absorption phenomena.^[39] The emitted photons at highest energy can be actually re-absorbed by the **1a**:Zn molecule at high concentration.

Considering the significant influence of the **1a**:Zn fluorescence properties towards solvation environment, the **1a**:Zn/PMMA films have been exposed to vapours of organic solvents. The vapochromic behaviour has been determined by placing the films in contact with an

aluminium plate which covers a recipient containing the target solvent (Figure 1). The fluorescence emitted by the films is collected by optical fibres connected to a spectrofluorimeter, and the variation of the emission monitored with the exposition time.

Notably, the **1a**:Zn/PMMA film shows a significant variation of its emission when exposed to a saturated atmosphere of dichloromethane (Figure 4a).

<Figure 4 near here>

The wavelength of the emission peak shifts from 435 nm to a maximum of 472 nm (i.e., 37 nm red-shifted) just after 390 seconds (i.e., 6 min and half) of exposition (Figure 4b). This solvent dependence can be again addressed to the ICT character of the **1a**:Zn emission and resides in the reorganization energy of the transition with increasing polarity.^[37]

PMMA matrix is in the glassy state and contains free volume in the form of a number of channels and holes of molecular dimensions. As soon as the dichloromethane vapours fill these empty spaces the diffusion process and the swelling of the polymer layer start. The swollen layer contains the polymer material in a rubber-like state, thus allowing the **1a**:Zn dye to be effectively solvated. This solvation besides decreasing the energy gap between the electronic states of dye,^[37] promotes the electron transfer rate thus leading to a faster and higher amplitude relaxation to a permanently quenched state.^[40] This phenomenon is possibly responsible of the decreasing of the emission intensity of **1a**:Zn along with its shift to higher wavelengths.

The **1a**:Zn/PMMA film shows a red-shift variation of its emission of only 19 nm when exposed to a saturated atmosphere of methanol (Figure 5a).

<Figure 5 near here>

The wavelength shift was reduced by half in extent and significantly slower of about 310 seconds than that shown in dichloromethane (Figure 5b). This behaviour can be addressed to a combination of effects: the first resides on the lower vapour pressure of methanol (i.e., 16.9

kPa for methanol against 58.2 kPa for dichloromethane, at 25 °C)^[41] which can delay the solvent absorption by the film, and the second consists on the limited interaction between methanol and the PMMA macromolecules of the matrix. This feeble interaction hampers methanol uptake by the polymer, thus making the phenomenon less effective than in dichloromethane. By contrast, dichloromethane is reported as one of the best interacting solvents for PMMA.

1a:Zn/PMMA films have been then exposed to dichloromethane/methanol mixtures in order to determine whether the system is sensitive and/or selective to vapours of different composition (Figure 6). Methanol can be actually utilized as a sort of diluent for dichloromethane.

<Figure 6 near here>

Comparing the wavelength variations collected by exposing the **1a**:Zn/PMMA films at solvent mixtures of 100 vol.% (Figure 4b), 50 vol.%, 30 vol.% and 20 vol.% of dichloromethane (Figure 6), the red-shift of the emission becomes progressively smaller in extent, according to the decreasing amount of dichloromethane in the vapour composition.

Notably, the rate constants associated with the vapochromic behaviour is affected by solvent composition as well (Figure 7).

<Figure 7 near here>

More specifically, by plotting the natural logarithm of the rate constant τ , obtained from the mono-exponential fits, against the inverse of the dichloromethane concentration (vol.%) a linear Arrhenius^[42] type behaviour appears evident. The same behaviour was also attained by considering the composition of the vapour phase as determined from literature data collected at 25 °C under saturated conditions (Figure S8).^[43]

This indicates that the vapochromic behaviour of **1a**:Zn might be predicted when dispersed in PMMA films and the derived parameters can be easily determined by means of luminescent

experiments.

4. Conclusions

We have demonstrated that a bipyridine Zinc complex with intramolecular charge transfer (ICT) character of its luminescence can be utilized as an effective chromogenic dye for the preparation of plastic films with vapochromic characteristics. The Zn^{2+} adduct was prepared starting from the easily-derivatised thienyleneethynylene at the 6,6' positions of the bipyridine ligand and it exhibited polarity-dependent emission properties when dissolved in solvents with different polarity. This solvatochromic behaviour was also retained in the solid state when the luminescent dye was dispersed at low loadings (<1 wt.%) in a PMMA matrix. When exposed to a saturated atmosphere of dichloromethane the plastic films showed a significant variation of its emission with a red-shift of about 40 nm due to the effective solvation of the dye by the absorbed solvent. By contrast, the films appeared much less responsive when methanol, a solvent barely interacting with PMMA, was used. This characteristic response made plastic films able to discern vapours of different composition. Actually, the rate constant associated with the vapochromic behaviour was found to be affected by solvent composition and easily determined by luminescent experiments. These findings could be exploited quite reliably for the realization of vapochromic plastic materials and further study is extended to different classes of solvents in order to validate the discovered method as a new tool to detect vapours of volatile organic compounds (VOCs).

Acknowledgements

This work was supported by the Fondazione Pisa under “POLOPTEL” project no. 167/09 and by MIUR-FIRB (RBFR122HFZ).

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Table 1. Spectroscopic properties of fluorophores AB12 and AB15 dissolved in THF and ACN.

	λ_{abs} [nm]		ε [$\text{M}^{-1}\text{cm}^{-1}$]		λ_{em} [nm]		$\Phi_{\text{f}}^{[\text{a}]}$
	THF	ACN	THF	ACN	THF	ACN	THF
1a	340	336	30,800	34,500	390	383	0.009
1b	349	347	48,100	55,300	416	402	0.004

[a] Fluorescence quantum yield (Φ) was determined relative to quinine sulphate in 0.1M H_2SO_4 ($\Phi = 0.54$).

Table 2. Emission maxima of **1a**:Zn in different solvents. The polarity index^[44] (PI) is reported in parentheses.

	Toluene (PI = 2.4)	Dichloromethane (PI = 3.1)	Ethyl Acetate (PI = 4.4)	Acetonitrile (PI = 5.8)
Emission _{MAX} (nm)	460	474	485	503

Caption to figures

Scheme 1. Retrosynthesis of compounds **1a-b**

Scheme 2. Synthesis of compounds **1a-b**

Figure 1. Apparatus used to study the vapochromic behaviour

Figure 2. Progressive changes in the absorption (up) and fluorescence (down) of 10^{-5} M ACN solutions of **1a** (left, (a) and (c)) and of **1b** (right, (b) and (c)) observed upon the addition of 10^{-3} M $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ in ACN. The excitation wavelength for the emission spectra of AB12 was 345 nm, whereas for AB15 was 360 nm.

Figure 3. Emission spectra ($\lambda_{\text{exc.}} = 380$ nm) of **1a**:Zn/PMMA films as a function of **1a**:Zn concentration (wt.%).

Figure 4. (a) Progressive changes in the fluorescence of the 0.5 wt.% **1a**:Zn/PMMA film as a function of the exposition to dichloromethane vapours. The spectra were collected in succession over a range of 500 s with 30 s data interval. **Inset: wavelength shift reported with exposition time and mono-exponential growth fitting function.**

Figure 5. (a) Progressive changes in the fluorescence of the 0.5 wt.% **1a**:Zn/PMMA film as a function of the exposition to methanol vapours. The spectra were collected in succession over a range of 500 s with 30 s data interval. **Inset: wavelength shift reported with exposition time.**

Figure 6. Wavelength shift of the 0.5 wt.% **1a**:Zn/PMMA film reported with exposition time to vapours of dichloromethane/methanol (a) 50:50 v/v, (b) 30:70 v/v, and (c) 20:80 v/v mixtures and mono-exponential growth fitting functions.

Figure 7. Natural logarithm of the constant rates τ , obtained from the mono-exponential fits of data reported in Figure 6 against the inverse of dichloromethane volume % in the liquid mixture (X) and in the vapour phase (Y) as determined by extrapolation of literature data.^[43]

Scheme 1

Scheme 2

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

(a)

(b)

(c)

Figure 7

Graphical abstract

Supporting information

Figure S1. Absorption spectra of 1E-5 M **1a** and **1b** (a) THF and (b) acetonitrile (ACN) solutions

Figure S2. Emission spectra of 10^{-5} M **1a** and **1b** THF solutions ($\lambda_{\text{exc.}} = 330$ nm)

Figure S3. Benesi-Hildebrand^[33, 34] plot used to determine the association constants, derived from titration of **1a** with Zn^{2+} in ACN in absorption (up) and in emission (down), respectively.

Figure S4. Emission spectra of 10^{-5} M **1a**:Zn solutions of different solvents

Figure S5. (a) Progressive changes in the fluorescence of the 0.5 wt.% **1a**:Zn/PMMA film as a function of the exposition to vapours of dichloromethane/methanol mixtures 50:50 v/v. The spectra were collected in succession over a range of 500 s with 30 s data interval.

Figure S6. Progressive changes in the fluorescence of the 0.5 wt.% **1a**:Zn/PMMA film as a function of the exposition to vapours of dichloromethane/methanol mixtures 30:70 v/v. The spectra were collected in succession over a range of 500 s with 30 s data interval.

Figure S7. Progressive changes in the fluorescence of the 0.5 wt.% **1a**:Zn/PMMA film as a function of the exposition to vapours of dichloromethane/methanol mixtures 20:80 v/v. The spectra were collected in succession over a range of 500 s with 30 s data interval.

Figure S8. Equilibrium data of the binary systems of dichloromethane with methanol at 25 °C^[43]