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Fluorescence solvato and vapochromism of a dimethylaminostyryl terpyridine derivative

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Abstract

The luminescence of dimethylaminostyryl terpyridine derivative (**MNpvpt**) is highly solvatochromic, ranging from blue emission in hexane ($\lambda_{em} = 450$ nm) to red emission in DMSO ($\lambda_{em} = 630$ nm). When the molecule is incorporated as a guest in polymer host (polystyrene or PMMA) matrices, it exhibits rapid and reversible changes in the luminescence maximum upon exposure to vapors of a variety of solvents.

Keywords: Luminescence solvatochromism; Phenylene vinylene; Vapochromism; Flouorescence sensing

1. Introduction

Phenylene–vinylene-derivatized terpyridine ligands represent a new category of highly luminescent chromophores with chelating functions [1]. Studies of excited state behavior of these ligands can be applied to the development of fluorescent sensors [2] and highly luminescent materials for organic light emitting devices (OLEDs) [3,4]. These systems are solvatochromic and such molecules have been used in chemical sensing [5] and may be potentially used to detect volatile organic compounds (VOCs). Several groups are working toward synthesizing metal complexes for this purpose and examples include platinum polypyridine complexes [6], Pt(II) double salts [7–14] and thallium–gold(I) complexes [15]. These compounds are particularly interesting because of their demonstrated ability to detect trace amounts of vapors of organic solvents and particular organic materials such as DNT and TNT. The sensitivity and selectivity of these substances is generally attained through a specific analyte–chromophore interaction.

By contrast, vapochromism of organic systems toward VOCs involve a variety of mechanisms and various solid supports [16–20]. In one report, Cao and Chen report luminescence quenching of luminescence from 1-methyl-1,2,3,4,5-pentaphenylsilole thin films upon exposure to a variety of organic vapors [18]; the response time was in excess of 1 min in this system. Changes in fluorescence have also been observed following H-bonding interactions between various N donor analytes and poly(phenylene ethynylene)s with pendant hexafluoro-2-propanol moieties [19]. These thin film polymer systems are sensitive, selective and have rapid response times. Recent work by An et al. illustrates vapor sensing by what they refer to as aggregation induced enhanced emission in which the chromopore, a bis-vinylbiphenyl stilbene derivative, exhibits solvent induced emission changes when adsorbed on silica TLC plates. The emission change results from aggregation of the chromophores in the presence of the solvent vapor. The changes observed are rapid and reversible and involve quenching along with a spectral shift [20]. Finally, and perhaps most significantly, thin films of fluorescent conjugated polymers (i.e. MEH-PPV) have been shown to exhibit fluorescence quenching in the presence of nitroaromatics, in particular DNT and TNT, presumably by electron transfer [21]. The extreme sensitivity of these systems (low ppb range) is linked to the fact that excitons migrating in the polymer chains may be quenched at any point along the chain.

In this paper, we report the photophysical properties of a dimethylaminostyryl terpyridine derivative [22], **MNpvpt**, that shows large emission solvatochromism. The chromophore was introduced as a guest in polystyrene (PS) and polymethyl methacrylate host matrices and thin films of these polymer/chromophore complexes were coated on quartz. Films

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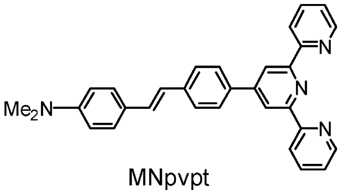
containing the chromophore exhibit rapid and reversible luminescence vapochromism.



MNpvpt

2. Experimental

Solvents were obtained from Aldrich Chemical Co. and were used without further purification unless otherwise noted. All absorption spectra were taken using a Hewlett Packard 8452 Diode Array Spectrophotometer. Emission spectra were obtained using a Spex Fluorolog Fluorimeter equipped with a CCD detector. Spectra were not corrected for detector wavelength response.

2.1. Syntheses

The ligand **MNpvpt** was prepared from 4′-(*p*-methylphenyl)-2,2′,6′,2″-terpyridine (Aldrich) as described below.

*2.2. 4′-(p-Bromomethylphenyl)-2,2′:6′,2″-terpyridine (**2**)*

A solution of 4′-(*p*-tolyl)-2,2′:6′,2″-terpyridine 1 (1.00 g, 3.09 mmol), NBS (0.56 g, 3.09 mmol) and benzoyl peroxide (0.025 g, 0.10 mmol) in CCl_4(20 ml) was heated at reflux for 5 h under N_2 protection, then cooled down to room temperature. The precipitate was removed through filtration, and the precipitate was washed with chloroform (50 ml). The combined solutions were dried to obtain the solid product by rotary evaporation. The solid obtained was recrystallized from 20 ml of mixture of ethanol and acetone (3/1, v/v). The product solid was obtained by filtration and rinsing with cold ethanol. The weight, after drying under vacuum, was 0.52 g (42% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.49 (s, 2H, CH_2Br), 7.27–7.30 (m, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.79–7.83 (m, 4H), 8.60 (d, $J = 8.0$ Hz, 2H), 8.70–8.72 (m, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm): 33.24, 119.08, 121.69, 124.19, 128.00, 129.88, 137.34, 138.67, 138.86, 149.22, 149.73, 156.02, 156.2.

*2.3. [4′-(p-Triphenylphosphoniummethylphenyl)-2,2′:6′,2″-terpyridine bromide] (**3**)*

A mixture of 4′-(*p*-bromomethylphenyl)-2,2′:6′,2″-terpyridine (**2**) (0.372 g, 0.926 mmol) and triphenylphosphine (0.606 g, 2.31 mmol) in toluene (25 ml) was heated at reflux for 12 h. The white precipitate was filtered off while the suspension was cooled down to room temperature. The collected solid was washed with toluene and dried under vacuum.

This afforded the phosphonium salt (**3**) as a white solid (0.56 g, 90% yield). This was used for the synthesis of **4** without further analysis.

*2.4. Dimethyl-{4-[2-(4-[2,2′;6′,2″]terpyridin-4′-yl-phenyl)-vinyl]-phenyl}-amine (**4**) (**MNpvpt**)*

To a solution of compounds **3** (0.111 g, 0.16 mmol) and 4-(dimethylamino)benzaldehyde (0.025 g, 0.16 mmol) in methylene chloride (20 ml) was added *t*-BuOK solution (0.17 ml, 1.0 M solution in THF) dropwise via a syringe under N_2. The resulting mixture was allowed to stir at room temperature for 24 h. After removal of most of solvent, methanol (100 ml) was added into the remaining residue. The solid was collected and washed with methanol, giving a yellow fluorescent ligand **MNpvpt** (0.034 g, 45%). ^{1}H NMR spectral data indicate that the product is exclusively *trans* (i.e. *J* value of olefinic protons is 16.4 Hz, typical of *trans*-stilbene derivatives) isomer. ^{1}H NMR (CDCl) δ (ppm): 2.99 (s, 6H), 6.76 (d, $J = 6.4$ Hz, 2H), 6.97 (d, $J = 16.40$ Hz, 1H, vinyl), 7.64 (d, $J = 16.40$ Hz, 1H, vinyl), 7.35 (t, $J = 6.0$ Hz, 2H), 7.45 (d, $J = 6.0$ Hz, 2H), 7.59 (d, $J = 6.0$ Hz, 2H), 7.85–7.91 (m, 4H), 8.67 (d, $J = 7.6$ Hz, 2H), 8.73 (d, $J = 4.8$ Hz, 2H), 8.76 (s, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 40.89, 112.89, 118.72, 121.67, 124.08, 126.73, 128.00, 129.84, 136.51, 137.24, 139.26, 149.25, 150.07, 155.99, 156.4. Combustion analysis yielded the following: Calc. (found) for $C_{31}H_{26}N_4$, C, 81.91 (79.46); H, 5.76 (5.63); N, 12.32 (11.78). All three values are below the calculated percentages by an average of 3%, indicating the presence of a small amount of a non-carbon containing impurity. However, the ^{1}H NMR spectrum is completely free of impurity peaks, and, given the signal to noise for the experiment, a purity in excess of 99% is insured; the spectrum is included as supporting information.

2.5. Thin film fabrication

Thin films are prepared from CH_3Cl solution containing **MNpvpt** (10^{-6} M) and PMMA or PS in the ratio of 1:25 (w/w). The quartz slide (1 cm × 4 cm) was mounted on a stepping motor-driven dipper and the solution was coated on 1.5 cm of the length of the slide in a single dip cycle. It yielded uniform films and the thickness measured using profilometry. The surface morphology was examined using atomic force microscopy (AFM).

2.6. Results and discussion

MNpvpt shows a small solvent dependence of the absorption maximum ($\lambda_{max} \sim 282$ and 384 nm) but, upon excitation at 384 nm, large solvent effects on the emission maximum were observed, as is clearly evident (Fig. 1 and Table 1). The luminescence ranges from blue emission ($\lambda_{em} = 450$ nm) in hexane to red emission in DMSO ($\lambda_{em} = 630$ nm); the luminescence lifetime was measured by TCSPC in $CHCl_3$ at room temperature and was found to be less than 2 ns, near the limit of detection of our apparatus. In addition, the emission quantum yield in most solvents was high (Table 1). In non-polar solvents, the emission exhibits vibrational structure, but appears as a single broad maximum in more polar solvents. Since the chromophore has an electron-donating Me_2N-group at one end and an electron accepting

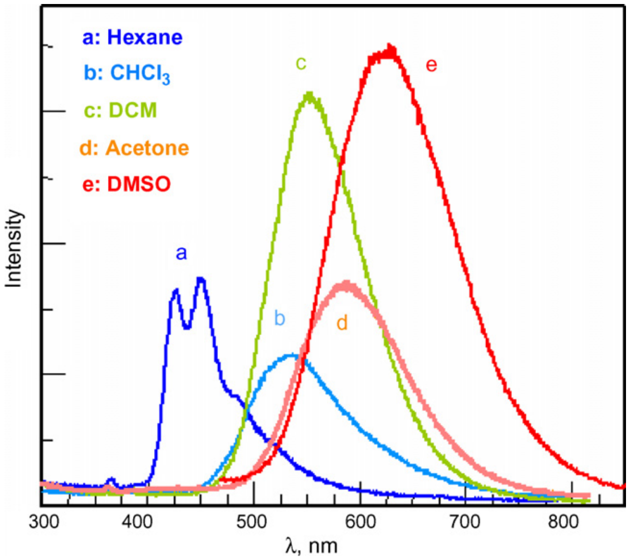


Fig. 1. Emission spectra of **MNpvpt** in different solvents.

terpyridine at other, the excited state may be described as a π–π* state with significant contributions from intraligand charge transfer (ICT) in more polar solvents [23]. These ICT contributions result in lowering of the HOMO–LUMO gap and hence bathochromic shifts of fluorescence. The structured emission observed in hexane and toluene suggests that the luminescence originates from the more localized π–π* state.

Such solvatochromic behavior has been quantitatively treated using a dielectric continuum model, resulting in what is now known as the Lippert–Mataga equation [24,25]. In Eq. (1), ν_{CT}, $\nu_{CT}(0)$ and $\Delta\mu$ denote the energy of the charge transfer (CT) fluorescence maximum observed, the wavenumber of the gas-phase CT fluorescence maximum and the difference in dipole moment:

$$\nu_{CT} = \frac{\nu_{CT}(0) - 2(\Delta\mu)^2 \Delta f}{hc\rho^3}; \qquad \Delta f = \frac{(D-1)-(n^2-1)}{(2D+1)(4n^2+2)} \tag{1}$$

between the ground state and fluorescent state, respectively. ρ represents the radius of the spherical solvent cavity in which the molecule fits. D and n are the solvent dielectric constant and refractive index. For an elongated molecule such as **MNpvpt**, ρ is usually estimated as 40% of the longest axis assuming an ellipsoidal solvent cavity [23]. The ρ value for **MNpvpt** is calculated to be 490 pm. Emission energies for **MNpvpt** determined in various solvents fit the Lippert–Mataga model (Fig. 2) reasonably well for solvents ranging from hexane ($\Delta f = 0.07$) to DMSO ($\Delta f = 0.37$). From the slope, the difference between ground and excited state dipoles is estimated [23] to be 12.2D. Similar analysis for dimethylamino stilbene [24] and *p*-(dimethylamino)-*p*'-cyanostilbene [25] yield $\Delta\mu$ values of 9.4 and 15.3D, respectively. This suggests that the terpyridyl substituent behaves as an electron withdrawing substituent in **MNpvpt**.

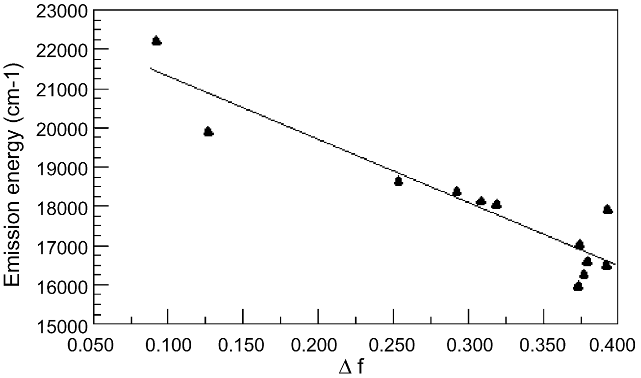


Fig. 2. Lippert–Mataga plot of **MNpvpt** in various solvents.

Table 1
Photophysical properties of **MNpvpt** in solution and polymer matrices

Solvent (Δf)	λ_{em}[a] (nm)	Φ_{em}[a]	λ_{em}, PS	λ_{em}, PMMA
DMSO (0.373)	626	0.52	–	–
DMF (0.377)	614	0.77	–	–
CH_3CN (0.392)	606	0.60	540	581
EtOH (0.379)	602	0.11	502	548
Acetone (0.374)	587	0.85	553	576
DCM (0.318)	554	0.79	552	552
THF (0.308)	551	0.88	548	547
EtOAc (0.292)	544	0.64	544	544
$CHCl_3$ (0.253)	536	0.60	536	537
Toluene (0.126)	502	0.32	503	508
Hexane (0.091)	450	0.25	452	450
Air	–	–	461	462

[a] In solution.

The Lippert–Mataga model can also be applied to binary solvent mixtures. In this case, the solvent polarity factor, Δf, is determined from averages of the dielectric constant and refractive index weighted for the mole fraction of each solvent in the mixture. For **MNpvpt** in toluene/acetone mixtures, a good linear relationship between mixed solvent polarity (Δf) and emission energy (Fig. 3) is observed. The calculated dipole moment of **MNpvpt** determined in this way is 11.8D. Thus, the observed emission energy serves as a reasonable gauge of the microenvironment of the chromophore.

MNpvpt was incorporated into thin film polymer matrices of polystyrene (PS) and polymethylmethacrylate (PMMA) following dip coating from $CHCl_3$ (10^{-6} M **MNpvpt**) solutions. Films prepared by this method were typically 420 ± 10 nm thick in the

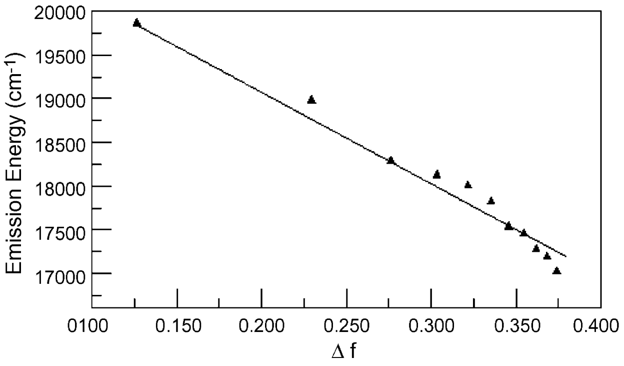


Fig. 3. Lippert–Mataga plot of **MNpvpt** in a binary solvent mixture of acetone and toluene.

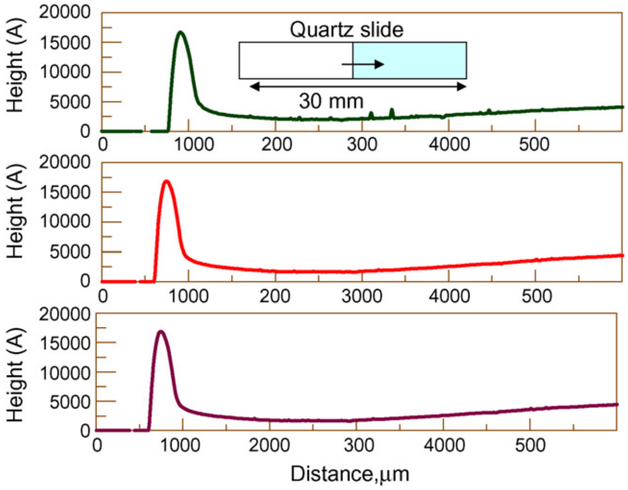


Fig. 4. Profilometry scans for three different quartz slides coated with a film of polystyrene containing **MNpvpt**.

mid portion of the film as assessed by profilometry. Fig. 4 shows profilometry images of three films prepared in this manner. As can be seen, the dip coating procedure is highly reproducible, and while it also results in formation of a thick region of the film at the bottom of the glass slide, this region is small and well away from the area subjected to luminescence interrogation.

The films were placed in fluorescence cells saturated with the vapors of different solvents by simply injecting 20 ml of the solvent into a small piece (2 mm diameter on average) of cotton gauze placed in the cell. The extreme vapochromic sensitivity of the ligand toward the solvent vapors, even when immobilized in a solid polymer matrix (PMMA), is clearly evident (Fig. 5, Table 1). There is a nearly instantaneous (<2 s) change in emission as the quartz slide coated with the polymer-encapsulated chromophore is introduced into the cell saturated with organic vapor. The original spectrum is immediately restored following removal from the vapor source. This is reversible and can be repeated for many cycles.

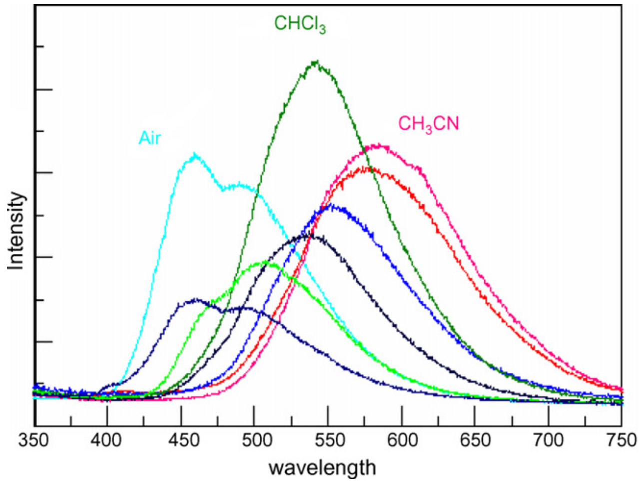


Fig. 5. Emission spectra of **MNpvpt**–PMMA film exposed to vapors of a variety of solvents (air = film in air with no vapor).

As can be seen from Table 1, solvents that have very low vapor pressures at room temperature (DMF and DMSO) did not affect the emission behavior of the chromophore in the polymer; however, even toluene, with a vapor pressure of 30 mmHg at room temperature, induces a distinct change in the emission of **MNpvpt** in both matrices.

Table 1 also illustrates that the response of **MNpvpt** to various solvents differs in the two host matrices. Of particular interest is the fact that the more hydrophilic PMMA microenvironment results in larger vapochromic shifts with more polar solvents. In addition, while very little emission change is observed when films of **MNpvpt** in PS are exposed to ethanol vapor, a large vapochromic shift is observed for the chromophore in PMMA. Thus, the polymer host clearly limits which volatile solvents permeate the film. The role of the host matrix in determining the magnitude of the vapochromic shift is clearly more complex but appears to be related to both the relative dielectric characteristics of the polymer matrix and vapor and the degree of permeation of the matrix by the vapor.

Clearly, the **MNpvpt** embedded in the polymer matrices can be solvated to some extent by vapor, which diffuses into the polymer. It is interesting to note that for all solvents less polar than acetone (in terms of Δf) the emission maximum in the polymer matrix (for both polymers) is nearly the same as that in the corresponding pure solvent. Based on mixed solvent results for correlating emission maxima and relative solvent polarity, the implication is that the polymer-encapsulated chromophore appears to be completely solvated by the vapor for all the volatile less polar solvents. It may be that the excited state solvation is influenced by the relative dielectric relaxation rate constants for the vapor and the polymer. Dielectric relaxation rate constants are a strong function of viscosity for solvents [26]. The polymer film, being many orders of magnitude more viscous than the solvent molecules adsorbed into the film from the vapor, may be incapable of solvating the excited state of the **MNpvpt** to any significant extent during its excited state lifetime (<2 ns).

This system may find use as a sensory material since its mode of detection does not rely on quenching luminescence but rather on changes in emission energy. In addition, the synthesis and fabrication are simple and direct. We are in the process of evaluating the relative sensitivity of these thin film sensors and we are also examining other potential candidate chromophores that have charge transfer excited states with large dipole moment changes between ground and excited states.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2006.10.017.

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