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Tetraphenylpyrazine-triphenylamine (TPP-TPA) was used to detect water traces in organic solvents by monitoring the shift of the fluorescence peak wavelength. This wavelength based method avoids intrinsic problems of fluorescence intensity change based methods. The use of optical fibres for the detection provides remote and field-deployable sensing ability.

1. Introduction

The determination of water traces in organic solvents is of great significance in diverse scientific and industrial fields requiring precise control of water content.

For instance, in the pharmaceutical and chemical industries, the presence of water inhibits not only the production of chemicals and drugs, but also the efficiency and usefulness of products.[1] Especially in organometallic chemistry, the presence of water leads to quenching of reactive organometallic compounds, such as organolithium and Grignard reagents, and inhibits the reaction or lowers the product yields. Moreover, due to the high reactivity of the organometallic reagents, under certain circumstances such as fire and explosions, the presence of water can lead to disastrous failures.[2] Furthermore, water is a contaminant in refined gasoline. It affects the stability of fuel combustion, corrodes storage tanks and is strongly associated with unexpected microorganism proliferation.[3] More importantly, when the temperature is low enough, emulsification and phase separation may occur, causing clogged fuel ducts and leading to engine damage and failure.[2] Therefore, developing a simple, stable and accurate sensor to detect water in organic solvents is important and useful.

The Karl Fischer titration is the most widely used traditional method for the determination of water in liquid and solid samples over a large dynamic range.[4, 5] This method is based on the simultaneous reaction of iodine and water with a premade alkyl sulfite reagent.[2] The consumption of a known amount of iodine, detected by either a volumetric (for relatively high contents of water, over 0.1 v/v%) or a coulometric approach (for relatively low contents of water, less than 0.1 v/v%), can thus be correlated with the content of water introduced into a system.[2] However, such approaches have several unavoidable disadvantages, such as the need for specialized instruments and water-free titration cells, and the fact that they can only be performed by trained personnel and are easily disturbed by interfering compounds.[5] Furthermore, such approaches require *ex situ* analysis, indicating their incapacity for real-time monitoring.[2]

Recent research has focussed on developing highly sensitive fluorescent probes that can be made using simple synthesis, and have potential applications in remote and *in situ* monitoring.[2]

Different fluorescence dyes can be categorised by the different sensing mechanisms underlying their mode of action.[2] For chemosensors, the reversible association of water with a vital part of the fluorophores in their immediate environment can cause a change in either the intensity or the peak position (wavelength) of the fluorescence of the probes due to a variety of mechanisms, such as photo-induced electron transfer (PET),[6] intramolecular charge transfer (ICT),[7] excited state intramolecular proton transfer and water as a competitive ligand.[8, 9] We have summarized several florescence dyes in this field to provide a brief overview (Table 1).

Firstly, most of the reported fluorescent methods, shown in Table 1, are based on the change of fluorescence intensity as a function of water content.[10-13] However, the change of fluorescence intensity can be caused by a range of factors in practical measurements, not only the change of water content. For the optical fibre-based detection, the power instability of the excitation source (i.e. laser) and the inconsistency of the optical alignment, i.e. the vibrations of optical components (mirrors, lenses and mounts) or drift in the laser beam or changes in

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environmental conditions such as temperature can lead to fluorescence intensity change.[14] Furthermore, the fluorescence intensity is prone to be affected by the background noise from the scattering light of impurities, other ions and the luminescence of optical components.[3] Thus, a fluorescence intensity measurement requires costly, stable laser source, consistency of the optical alignment and pure samples to diminish any possible background noise to gain high sensitivity and accuracy. These ideal conditions can hardly be achieved in practical measurements. In addition, for quantitative analysis, fluorescence intensity change-based methods require high photo-stability of the fluorescence molecules, i.e. consistency of fluorescence intensity of fluorophores over a long period, and the concentration of fluorophores must be precisely controlled in each sample. All these limitations can clearly affect the signal stability, sensitivity and reproducibility of fluorescence intensity change-based methods.

In contrast, the fluorescence peak wavelength is a unique characteristic of a particular molecule during the fluorescence process and it is not easily affected by other factors. Although previous fluorescence dyes with a twisted intramolecular charge transfer (TICT) effect, TPEM and TPEBM, developed by Yu et al., were found to shift the fluorescence peak wavelength with water content, there was no reported limit of detection (LOD) for any organic solvent.[12]

Table 1 Comparison of different fluorescence dyes

#	Solvent	Sensing mechanism	Ref.
OF-2	1,4-Dioxane	PET	10
	THF		
	Acetonitrile		
	Ethanol		
KD-F0011 (immobilized to PEGDMA)	Diethyl ether	ICT	11
	THF		
	Ethyl acetate		
	Acetonitrile		
TPEM	THF	ICT and AEE	12
TPEBM	THF	ICT and AEE	
ECPS	Acetonitrile	Aggregation based monomer–excimer switching	13
	Ethanol		
	Methanol		
	1,4-Dioxane		

Abbreviations: [aggregation-enhanced emission (AEE)].

Secondly, laboratory-based fluorescence spectrophotometers have been used for most of the fluorescent methods, requiring transport of samples to a laboratory, making on-site and *in situ* measurement impossible. However, practical measurements in industry require fast detection and on-site analysis of water content in organic solvents for quality testing.

In this paper, we report a fluorescence dye, TPP-TPA (Fig. 1a), with aggregation-enhanced emission (AEE) and solvatochromic luminescence properties, for the detection of water traces by measuring the shift of the fluorescence peak wavelength to overcome the aforementioned limitations of the fluorescence intensity change-based methods.[15] The detection range of our method is fairly large, from 0 to 60 v/v% in THF/water mixtures with a LOD of 0.04 v/v%. In addition, we used optical fibres and a portable spectrometer to achieve remote and *in situ* sensing ability.

2. Experimental

In this study, all the water detection experiments were conducted using an optical fibre connected to a hand-held portable Ocean Optics QE65000 spectrometer instead of a laboratory-based fluorescence spectrophotometer (Fig. 1b). We used two UV-vis transparent optical fibres with 200 μm core diameter (Ocean Optics), which were arranged at 90° for fluorescence excitation and collection. The 405 nm laser (iBeam smart-S), with its wavelength being close to the absorption peak wavelength of TPP-TPA at 363 nm,[15] was coupled into one fibre to guide the excitation beam to the sample. The maximum transmitted power was used as an indicator of optimised coupling efficiency to the core.[14] The absorption profiles of TPP-TPA is virtually free from the influence of solvent polarity.[15] The other fibre collected the fluorescence from the sample and guided it to the spectrometer.

Water detection measurements were conducted in 2 mL bulk solutions with constant TPP-TPA concentration of 10 μM. THF is completely miscible with water. The initial concentration of TPP-TPA in THF was 1mM. A range of water concentrations was prepared by adding the initial TPP-TPA solution to water/THF mixture with a finial volume of 2 mL. Laser power of 86.4 μW and spectrometer integration time of 5.00 s were used. Each measurement comprised 3 discrete spectral scans that the device driver accumulated and averaged before the operating software (OceanView) received a spectrum. An optical shutter was synchronised with the data acquisition of the Ocean Optics spectrometer to minimise photo−bleaching (Fig. 1b). Considering that THF can dissolve PMMA, borosilicate glass tubes (Kimble) were used as containers rather than PMMA cuvettes during the experiments.

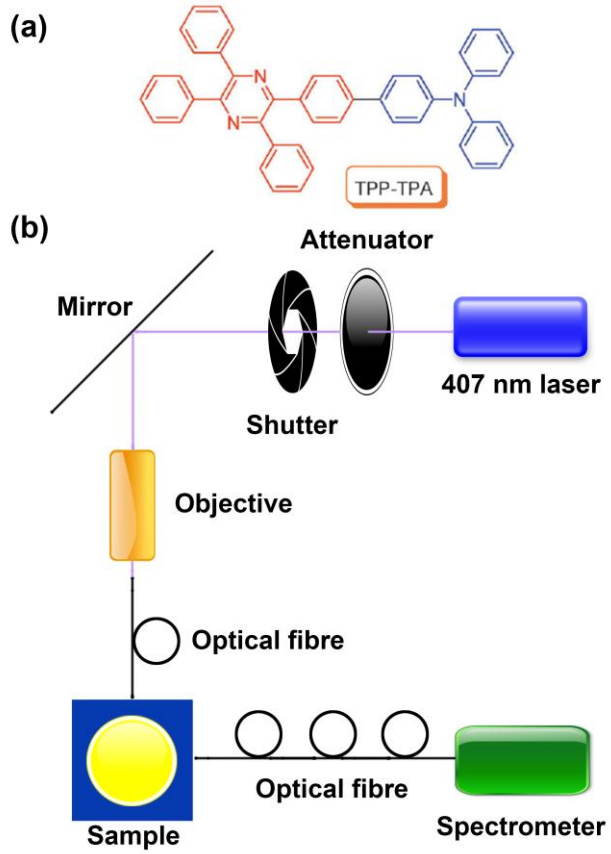

Fig. 1 (a) Molecular structure of TPP-TPA.[15] (b) Setup of the optical fibre platform.

3. Results and discussion

The sensing mechanism of TPP-TPA is solvatochromic luminescence, where the dipole strength of the donor–acceptor couple of the molecule is altered in the presence of water with high polarity, influencing the bonding at the electron acceptor region and causing changes in both the fluorescence intensity and the fluorescence peak wavelength.[2]

Fig. 2 shows that the fluorescence peak wavelength of TPP-TPA in THF with 0 v/v% water content increases linearly with time. Although during the experiments care was taken to prevent water absorption from the environment by sealing the glass tubes with a stopper, storing freshly dried THF in a flask with molecular sieves, using a nitrogen balloon and using the THF immediately after being decanted out, fluorescence red-shifting of TPP-TPA occurred, indicating absorption of water vapour by THF from the experiment atmosphere. The effect of THF water vapor absorption on the fluorescence peak wavelength was observed to begin after 30 seconds at the second measurement continuously. The standard deviation of all the slopes of the linear growth relationships between fluorescence peak wavelength and time for different water content samples from 0 to 40 v/v% was 0.00256 nm/s, which indicated the ultra-sensitivity of TPP-TPA to the presence of water in the THF. Due to the unavoidable water absorption property of THF and the ultra-sensitivity of TPP-TPA to the presence of water, each data point is the result of the first measurement for quantitative analysis. Compared to a method using laboratory-based fluorescence spectrophotometers where samples are liable to changes in the water content during the transport to a laboratory, our method using optical fibres and portable spectrometers with quick response allows measuring the continuously changing water content in realtime.

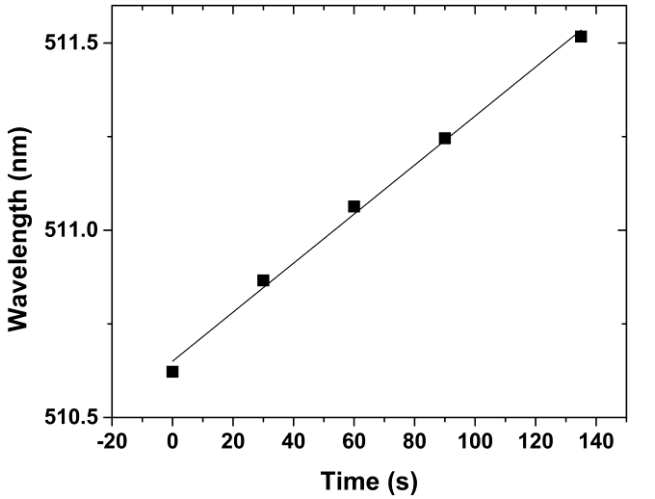

Fig. 2 The relationship between the fluorescence peak wavelength of TPP-TPA in THF with 0 v/v% water content and time using portable spectrometer. Each data point is the result of the first measurement. The linear equation is as follows: y=0.0065x + 510.65 (R^2 = 0.9959) (y is the fluorescence peak wavelength; x is time).

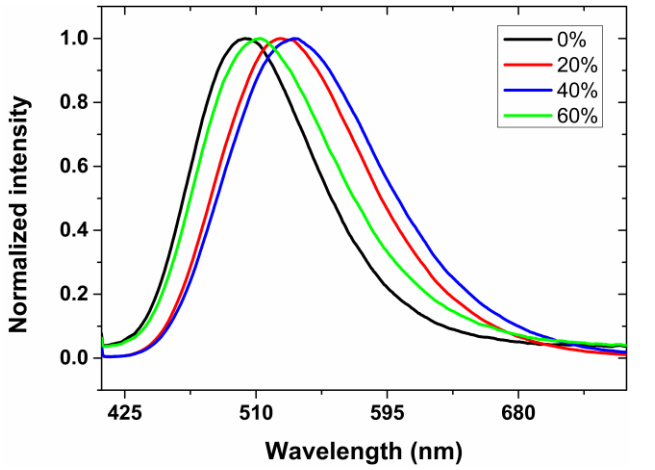

Fig. 3 Fluorescence spectrum of TPP-TPA with normalized intensity in THF with different water content, 0, 20, 40, 60 v/v%. Each curve is the result of the first measurement. Measured by a portable Ocean Optics spectrometer.

Fig. 3 shows the fluorescence spectrum of TPP-TPA in THF with different water content, 0, 20, 40, 60 v/v% and using the portable Ocean Optics QE65000 spectrometer. In order to observe peak wavelength shifting with changed water content, the fluorescence intensity of each raw spectrum obtained from OceanView was normalized to the range 0 to 1 without using any smoothing algorithm. The fluorescence peak wavelength of TPP-TPA shows a continuous increase until the water content reaches 40 v/v%. When the water content exceeds 40 v/v%, it decreases dramatically. The red-shifting of the peak is due to the solvatochromic luminescence property of TPP–TPA in THF/water mixtures, which is induced by the gradually in-

creased fraction of polar water.[15, 16] The blue-shifted peak that occurred after 40 v/v% is attributed to aggregate formation due to the decreasing solvating power of the THF/water mixture towards the fluorophore as a result of reduced association of water with TPP–TPA (Fig. 4).[15] Concurrently, the rotation of the phenyl rings of TPP-TPA was greatly restricted in the aggregate state, and thus the unique AEE occurred.[15] In addition, it is worth mentioning that the fluorescence of 0 v/v% and 30 v/v% water-in-THF solutions can be easily observed and distinguished by the naked eyes, as shown in Fig. 4.

The relationship between the fluorescence peak wavelength and water content up to 60 v/v% can be fitted with a quartic polynomial regression, which can be used to quantitatively determine the water content. The following equation was obtained by fitting the experimental data of the first measurement (y is the fluorescence peak wavelength; x is the water content):

$$y = 512.331 + 3.172x - 0.167x^2 + 0.004x^3 - 3.762 \times 10^{-5}x^4 \ (R = 0.9863)$$

The limit of detection (LOD) is defined as the lowest concentration at which an analyte can be sensed over the noise with a high degree of certainty of generally three times the standard deviation of the blank.[2] The standard deviation for the first measurement data of the 10 blank samples is 0.087 nm, thus the LOD of TPP-TPA in THF is 0.08 v/v%.

An issue for quantitative analysis is that there is overlap between the fluorescence peak wavelength range of TPP-TPA before and after 40 v/v% water content. One approach to overcome this issue is to add extra water to the test samples and monitor the wavelength shifting. If red-shifting of the wavelength is observed, the authentic water content of the test sample is under 40 v/v% or vice versa. However, for most applications, the aim is to detect trace amounts of water. For such applications, the quartic polynomial regression between the fluorescence peak wavelength and water content over the range from 0 to 10 v/v% results in a lower LOD of 0.04 v/v%.

To determine the consistency of the fluorescence peak wavelength for different fluorophore concentrations, the fluorescence peak wavelength of TPP-TPA was measured in THF solutions with 1.00 v/v% water content (Fig. 5), using the same optical setup but a laboratory-based Horiba iHR320 spectrometer to gain higher sensitivity than portable Ocean Optics spectrometer for rigorous comparison. The results indicated the high signal stability of fluorescence peak wavelength for practical application regardless of fluorescence intensity change. The results also demonstrated the reduced requirements for sample preparation and measuring environment of TPP-TPA, e.g. the laser power, the position of the container and the fluorophore concentration, which do not need to be precisely controlled each time.

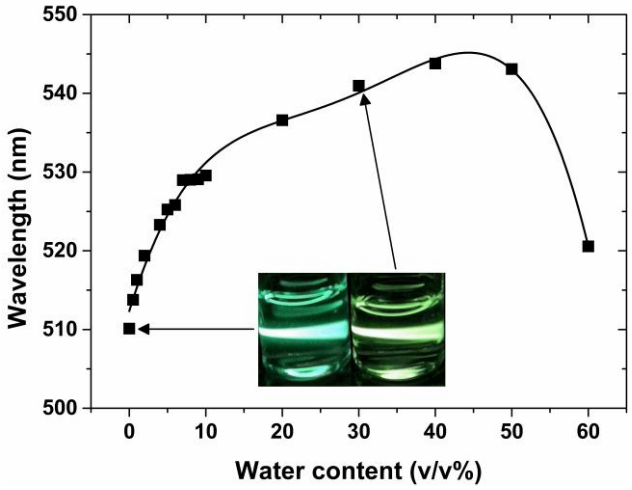

Fig. 4 The quartic polynomial regression between the fluorescence peak wavelength of TPP-TPA and water content from 0 to 60 v/v% in THF using portable spectrometer. Each data point is the result of the first measurement. The inset shows the fluorescence of 0 v/v% and 30 v/v% samples from left to right.

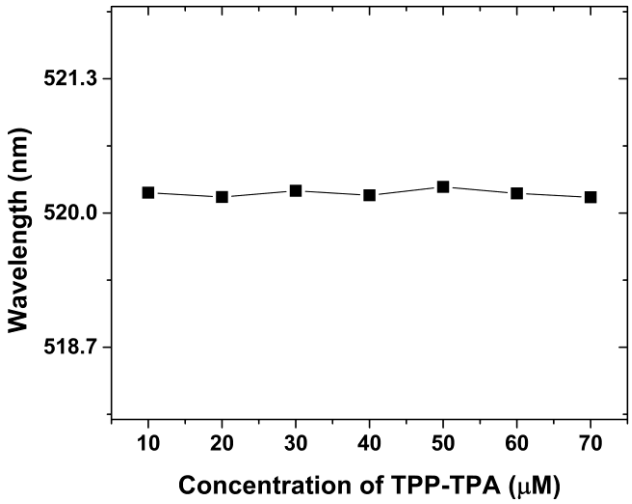

Fig. 5 The consistency of the fluorescence peak wavelength of TPP-TPA at different concentrations of TPP-TPA in THF with consistent 1.00 v/v% water content, measured by a laboratory-based Horiba iHR320 spectrometer. Each data point is the result of the first measurement. The standard deviation for all the data points was 0.033.

Furthermore, the photo-stability of TPP-TPA was investigated by a laboratory-based Horiba iHR320 spectrometer. The TPP-TPA sample was contained in a glass tube sealed with stopper and exposed to continuously high-power 405 nm laser over 5 mins (Fig. 6). The results showed that the fluorescence intensity change $\Delta I/I$ was 1.34% and the peak wavelength change $\Delta\lambda/\lambda$ was 0.06%, which indicated that the effect of photo-bleaching was negligible when it was used for measurements within 5 mins.

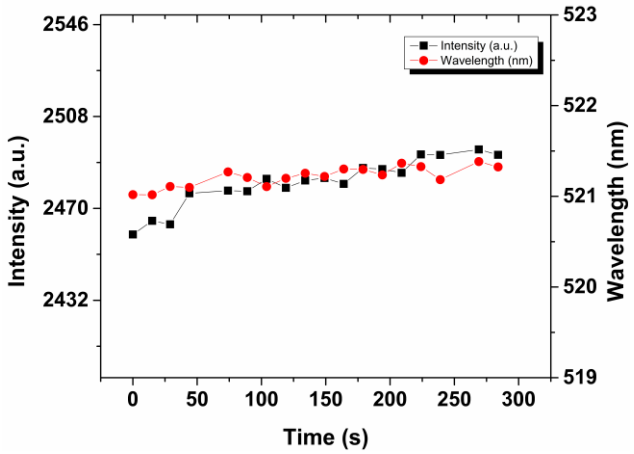

Fig. 6 The fluorescence intensity and peak wavelength of TPP-TPA in THF during photo stability test. 1 mL TPP-TPA (10 μM) sample was contained in a glass tube and sealed with stopper and exposed to continuously 405 nm laser (120 μW) over 5 mins. Measured by a laboratory-based Horiba iHR320 spectrometer.

Conclusions

In summary, we report for the first time the use of the solvatochromic luminescence property of TPP-TPA to detect water traces in organic solvents based on the fluorescence peak wavelength shifting with a fairly large detection range from 0 to 60 v/v% and a LOD for THF of 0.04 v/v%. Such a large measurement range cannot be achieved with most of the fluorophores based on fluorescence intensity change or peak wavelength shifting. Furthermore, our method overcomes the aforementioned limitations of methods based on changes in fluorescence intensity.[10-13] The concentration of molecules, laser power and container position do not need to be precisely controlled for quantitative analysis in each measurement. In addition, compared to other fluorescent molecules,[13] TPP-TPA has a much simpler structure and synthesis process, features which contribute to its low-cost and importance for industrial analysis.[15] Moreover, the high resistance to photo-bleaching due to its intrinsic aromatic conjugated structure, is important for repeating measurements over a long period.

In a commercial fluorescence spectrophotometer, the light for excitation and the fluorescence are propagating through free space in the large sample compartment before reaching the test sample and detector. However, in our optical fibre platform, a test sample is located closer to the tip of optical fibres for excitation along with the collection of fluorescence from fluorophores. Moreover, the laser source and fluorescence can be guided by optical fibres with high thermal, mechanical and corrosion stability, a feature which dramatically improves sensitivity and accuracy in harsh industrial environments and strong magnetic fields.[17] More importantly, the setup used in our experiments can be easily assembled into a hand-held device if an optical circulator or fibre coupler is used instead of separate mirrors, lenses and filters to allow on-site and *in situ* measurements in the field.[18] Furthermore, our optical fibre platform can be generally applied to other fluorophores to realize remote sensing ability in real time over long distances at inaccessible sites and thus opens up possibility for new applications.[17]

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