

Rational Design of Optical Chemosensor Materials

V.A. Sazhnikov, M.V. Alfimov
Photochemistry Center, Russian Academy of Sciences
7a, ul. Novatorov, 119421, Moscow, Russia

A rational approach to the design of optical chemosensor materials based on consideration of intermolecular interactions between analytes, indicators and matrices is discussed. In a general case, all types of interactions between these components must be taken into account. The results of an experimental study of the fluorescence spectra of a relatively simple acridinic dye, 2,7-dimethyl-9-(ditolylamino)acridine, immobilized in polystyrene, PMMA and ethylcellulose matrices in the presence of such VOCs as toluene, acetone and ethanol are presented.

1. Introduction

The concept of cross-reactive sensor arrays has led to important developments, particularly in the analysis of gaseous analytes [Dickinson et al., 1996; Rakov and Suslick, 2000]. The ultimate goal of this work is to obtain a chemosensor with quantitative, real-time optical response and exceptional selectivity for a particular analyte or class of analytes.

As well known, the analytical methods based on fluorescent sensors offer advantages in terms of sensitivity, selectivity, response time, remote sensing, etc. Therefore, the detection of analytes utilizing the fluorescence response of molecular indicators is a growing area of academic and industrial research and considerable efforts are being made to develop selective fluorescent sensors for detection of different classes of analytes (Basabe-Desmonts et al., 2007).

Preferred indicators are known to be dyes that change their fluorescence on interaction with an analyte. As a rule, each dye molecule is a complicated system containing several heteroatoms and substituent groups. Therefore, it may be involved in a considerable number of different intermolecular interactions [Plotnikov et al., 2007]. Sensor materials are usually obtained by immobilizing dyes in corresponding polymer matrices. It is evident, however, that chemical functional groups of polymers may compete with analytes for the same binding sites of immobilized dyes. As a consequence, the fluorescence response peculiar, for example, to solvent vapor may differ considerably from those characteristic of neat solvent.

As a rule, the selection of polymers for sensors based on fluorescent dyes in polymer matrices is largely empirical. It is evident that a rational approach to the selection of dyes for a given analyte and polymer matrices for the dyes must be based on consideration of all possible interactions between analytes, indicators, and matrices.

Such an approach allows one to maximize the response of sensing molecules and to select a minimal set of indicators, which are able to generate a unique signature for each analyte. Corresponding sensor arrays would be more cost-effective and they would be easier to train than larger arrays.

In this paper, we have used, as an example, the relatively simple dye, 2,7-dimethyl-9-(ditolylamino)acridine (DTAA, Fig. 1), to study some effects of intermolecular interactions between dyes, matrices, and analytes. It was found previously that incorporation of such fluorescent indicator into a polymer matrix allows for fluorescence detection of a wide variety of volatile chemical compounds. In particular, DTAA may be used as a sensing molecule in fluorescent sensors for the selective detection of VOCs.

2. Experimental

Polystyrene (PS), poly(methyl methacrylate) (PMMA), ethylcellulose (EC), spectroscopic grade toluene, acetone, and other organic solvents used in our experiments were commercial products purchased from Aldrich. They were used without further purification. DTAA was synthesized as described previously [Sazhnikov et al., 2007]. For the preparation of the sensor films, DTAA was dissolved in a solution of 5–10% polymer in toluene or acetone at a concentration of 2–55 mM. Films were cast by pouring the film forming solution onto a horizontal quartz plate. The solvents were allowed to evaporate by air drying at room temperature (20°C). The film thickness was in the range of 10–30 μm .

Emission fluorescence spectra were recorded in the range from 450 to 700 nm with an Ocean Optics fiber-optic spectrofluorimeter equipped with a reflection/backscattering probe RP200-7. The light source was a UV LED with an emission maximum at 375 nm (in the region of the DTAA second absorption maximum). To obtain saturated vapor of a solvent, it was poured into a rectangular cuvette and then a polymer-coated quartz plate was used as a cuvette cover. Accordingly, the fluorescence spectra were taken from the back side of polymer films. Upon exposure to analyte vapor, the film's fluorescence is reversibly quenched. After the cuvette was capped, the fluorescence signal was recorded as a function of time with an interval of 10–30 s. All experiments were carried out at room temperature.

3. Results and Discussion

As can be seen from Fig. 1, DTAA is a fluorescent dye of the family of nitrogen heterocyclic bases. Planar tricyclic ring system of DTAA contains a nitrogen atom with a lone electron pair in the middle ring. As we stated earlier, DTAA is a solvatochromic dye which exhibits large wavelength shifts in its emission peak with changes in the polarity of the dye environment [Sazhnikov et al., 2007]. The estimated dipole moments of DTAA is about 2 and 12 D in the ground and excited states, respectively. Owing to

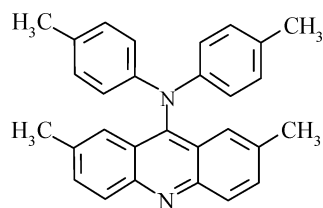


Fig. 1. Chemical structure of DTAA.

the presence of the endocyclic nitrogen lone pair and the electron-donating diphenylamino group at the 9-position, DTAA can also participate in the electron-transfer, proton-transfer, and hydrogen-bonding interactions.

Fig. 2 shows the fluorescence emission spectra of DTAA in hexane, toluene and acetone. It is seen that a pronounced change in position of the DTAA fluorescence band maximum is observed with increasing the medium polarity. The broad emission band centered at 499 nm in nonpolar hexane is red shifted to 537 nm in toluene and to 590 nm in more polar acetone. It should be pointed out that the shift from 500 to around 540 nm characteristic of toluene is also observed in benzene.

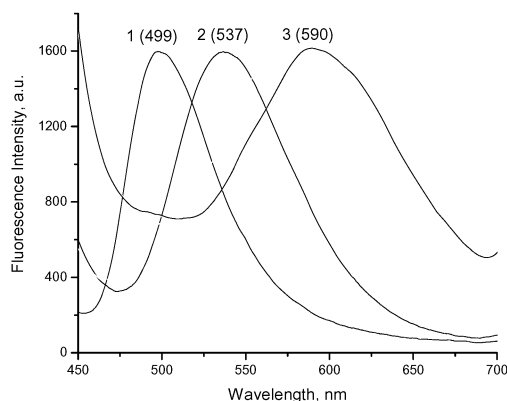


Fig. 2. Fluorescence emission spectra of DTAA ($\lambda_{ex} = 375$ nm) in different solvents: (1) hexane, (2) toluene and (3) acetone. Room temperature, $c = 10^{-3}$ M/l. The positions of fluorescent maxima are indicated in brackets.

It was also stated that the DTAA fluorescence intensity falls in the solvents of larger polarity. In going to alcohols, the maximum shifts in the 615–630 nm region and the fluorescence intensity decreases significantly.

The observed pronounced bathochromic shifts of DTAA fluorescence band in toluene, acetone, and ethanol as compared to nonpolar hexane suggests that DTAA can be used, in particular, as a toluene-, acetone, or ethanol-sensitive fluorescent indicator upon immobilization in corresponding polymer matrices. DTAA was found to be a hydrophobic dye insoluble in water. Therefore, it must be used as a fluorescent indicator by immobilization in such hydrophobic polymers as, for example, PS, PMMA or EC. Some obtained experimental results are presented below.

First of all, it should be noted that, in the absence of analytes, the fluorescence maxima of DTAA in these polymer matrices are centered within the same region (about 515–525 nm). This is in general agreement with the fact that the solvation shells of dyes in polymer matrices must consist of a small number of characteristic functional groups as compared to corresponding solutions. Diffusion of analyte molecules into a polymer matrix doped with DTAA results in changes of the dye solvation shells and, as a consequence, in progressive bathochromic shifts of fluorescence maximum and quenching or enhancement of DTAA fluorescence.

Because both PMAA and acetone contain polar carbonyl groups it can be supposed that the diffusion of acetone vapor into DTAA-doped PMMA must result in a considerable red shift of the DTAA fluorescence band. As shown in Fig. 3, such a shift is really observed, although the effect is somewhat smaller than can be expected.

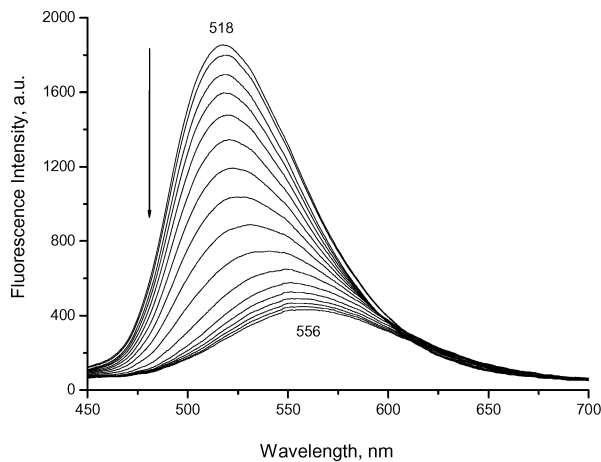


Fig. 3. Fluorescence spectrum change of a DTAA/PMMA film upon exposure to saturated acetone vapor.

Because acetone has a large dipole moment, it appears that the dipole-dipole interaction between DTAA and acetone must be considerably strong in such low-polar matrices as PS or EC. The observed changes in the fluorescence spectra of DTAA embedded in PS and FC matrices are shown in Figs. 4–5. As can be seen, in these matrices the fluorescence changes are similar to that obtained for the PMMA matrix.

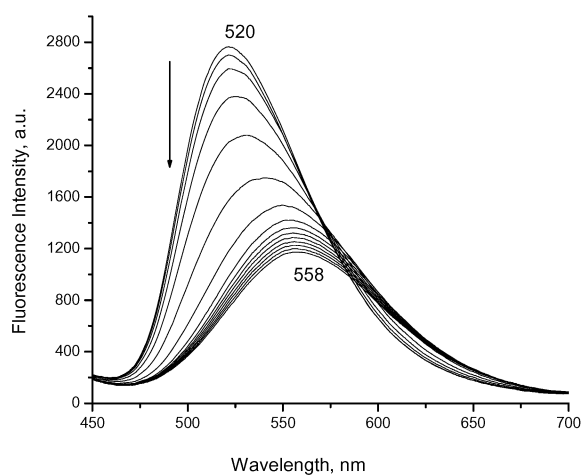


Fig. 4. Fluorescence spectrum change of a DTAA/PS film upon exposure to saturated acetone vapor.

Thus, upon exposure to saturated acetone vapor of PMMA, PS or EC films doped with DTAA, the DTAA fluorescence maximum is shifted from 518-525 nm to the region of 556-563 nm. Therefore, each of these matrices may be used as a suitable matrix for DTAA used as an indicator for acetone. It seems that the reason for this is that the dipole-dipole interaction of DTAA with acetone is stronger in comparison with the interaction of DTAA with each above matrix.

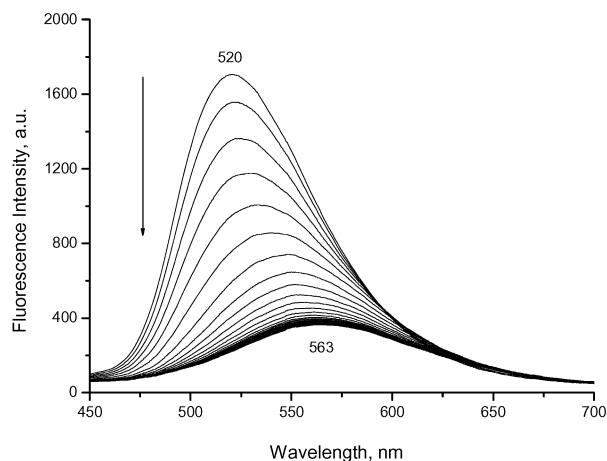


Fig. 5. Fluorescence spectrum change of a DTAA/EC film upon exposure to saturated acetone vapor.

The observed changes in the fluorescence spectrum of a DTAA/PS film upon exposure to saturated toluene vapor are shown in Fig. 6. As can be seen, the fluorescence maximum of a DTAA/PS film centered at 517 nm is shifted to 537 nm that coincides with its position in liquid toluene. It is evident that observed fluorescence changes correspond to going from a particular to full solvation shell of DTAA similar to that in toluene solution.

As mentioned above, similar red shifts of the DTAA fluorescence bands were found for solutions of DTAA both in low-polar toluene and in non-polar benzene. The same effect was observed for toluene and benzene vapor for DTAA/PS films. This suggests that quadrupole-quadrupole interactions can play a crucial role in this case.

A similar but more pronounced red shift in the presence of toluene vapor was observed for EC matrix (Fig. 7). This appears to be a consequence of the combined action of dispersion and hydrogen-bonding interactions.

In contrast, no significant change in the fluorescence spectrum of the DTAA/PMMA films was observed in the presence of toluene vapours. It should be supposed that it is due to the fact that dipole-dipole interaction of polar PMMA with DTAA is stronger than dispersion interaction between toluene and DTAA.

Thus, the DTAA/EC combination is the most effective for determination of toluene with DTAA, the DTAA/PS combination is less effective, whereas the DTAA/PMMA combination is ineffective.

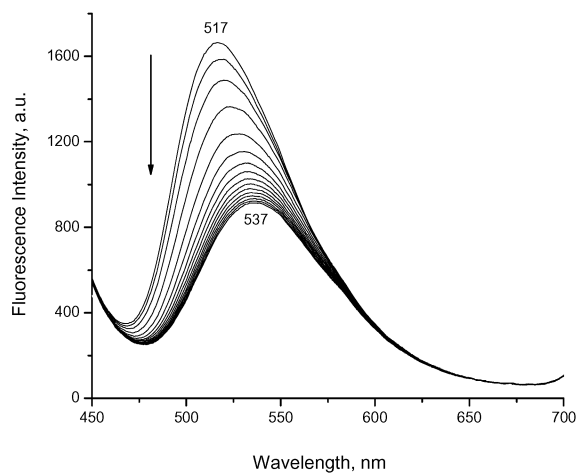


Fig. 6. Changes in the fluorescence spectrum of a DTAA/PS film in the presence of saturated vapour of toluene.

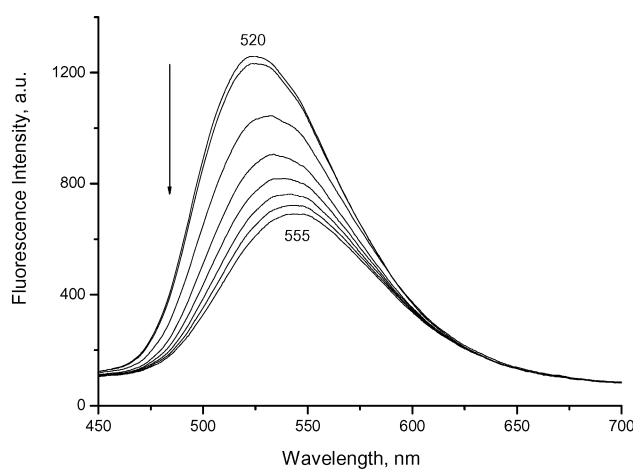


Fig. 7. Fluorescence spectrum change of a DTAA/EC film upon exposure to saturated toluene vapor.

It should be noted that DTAA/PMMA films also show no spectral change upon exposure to ethanol vapor. Therefore, it is probable that dipole-dipole interaction between DTAA and PMMA is also stronger than hydrogen bond between the PMMA carbonyl group and OH group of ethanol.

In contrast to this, relatively great red shifts were obtained for DTAA/EC films exposed to saturated ethanol vapor (Fig. 8).

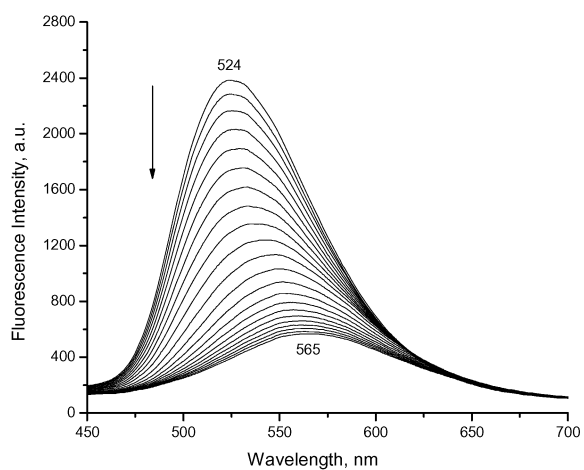


Fig. 8. Fluorescence spectrum change of a DTAA/EC film upon exposure to saturated ethanol vapor.

For DTAA/PS films the observed shifts were significantly less (Fig. 9).

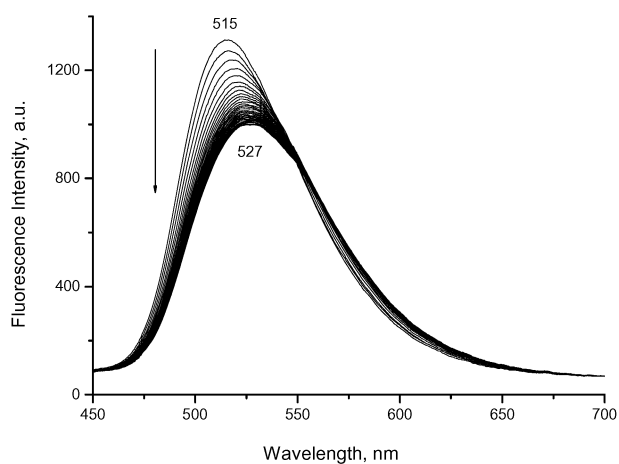


Fig. 9. Fluorescence spectrum change of a DTAA/PS film upon exposure to saturated ethanol vapor.

Thus, it seems that the DTAA/EC combination is the best for determination of ethanol with DTAA. Upon exposure to ethanol vapor, a comparatively weak hydrogen bond between nitrogen atom of DTAA and ethylcellulose OH group appears to be substituted by more stronger hydrogen bond including nitrogen atom and ethanol OH group.

4. Conclusions

The results presented above show that the rational approach to the design of sensor materials must include consideration of all possible interactions not only between a given analyte and corresponding indicator but also between the indicator and selected matrices. It is the indicator/matrix supramolecular complex that determines the fluorescence response of sensing molecule on the appearance of an analyte.

It was shown, for example, that interaction of DTAA with polar PMMA is relatively strong that leads to very small changes in the fluorescence of DTAA/PMMA films in the presence of toluene and ethanol molecules. By contrast, DTAA/EC films exhibit considerable changes in their fluorescence characteristics in the presence of toluene and ethanol that seems to be a consequence of a relatively weak intermolecular interaction between DTAA and functional groups of ethylcellulose.

Further studies to obtain more evidence on the role of intermolecular interactions for the design of sensor materials are currently under investigation in our laboratory.

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