

Emissive Exciplexes of Surface-Immobilized Dybenzoylmethanoboron Difluoride with Gaseous Benzene, Toluene and Xylenes

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Abstract:

Core-shell silica nanoparticles consisting of a SiO₂ core and a shell with covalently attached alkoxy-silyl derivative of dibenzoylmethanoboron difluoride (DBMBF₂) were synthesized. It was found that the nanoparticles may be used as the basis of selective sensor materials suitable for detecting benzene, toluene and xylene vapors. The DBMBF₂ fluorescence quenching followed by the appearance of the DBMBF₂/analyte exciplex fluorescence is observed upon adsorption of benzene or its methyl derivatives on the nanoparticle surface. The position of the isoemissive point is characteristic of each analyte and can be used for its identification.

Key words: BTX, exciplex, fluorescence, nanoparticle, isoemissive point.

Introduction

Benzene, toluene and xylenes (BTX) are VOCs of great environmental significance. But the greatest health risk from exposure to BTX is known to be due to benzene. The OSHA's permissible exposure levels for benzene is 1 ppm as compared to 100 ppm for toluene and xylenes. Therefore, the development of materials exhibiting both high sensitivity and good selectivity towards the individual BTX components is one of the most interesting and difficult challenges.

It is known that formation of exciplexes between dibenzoylmethanoboron difluoride (DBMBF₂) and benzene or methyl-substituted benzenes in solutions is one of the most characteristic properties of the fluorophore [1-3]. The fluorescence characteristics of these exciplexes depend on the methylbenzene nature. In principle, this fact can be used for the development of new selective sensor materials. Recently, it was shown that DBMBF₂ immobilized on silica gel can also form fluorescent exciplexes with toluene and m-xylene adsorbed from the vapor phase [4, 5]. In this work, an alkoxy-silyl derivative of DBMBF₂ was synthesized and then covalently grafted onto the surface of synthesized silica nanoparticles (SNP). The goal was to study the spectral features of exciplexes formed between

DBMBF₂ covalently linked to the nanoparticle surface and vapor-phase adsorbed benzene, toluene and xylenes.

Experimental

¹H and ¹³C NMR and ¹⁹F NMR spectra were measured on a Bruker Avance II 300 spectrometer. IR spectra were recorded with a Bruker Equinox 55/S spectrometer. TEM photographs were taken on a Leo 912 AB Omega (Germany) transmission electron microscope. Fluorescence responses to the vapour exposure were obtained in a closed box (volume 1.7 L) where a definite pressure of BTX vapors were created by evaporating a certain amount of an alkylbenzene (0.05-0.15 mL). A small electrical fan was used to obtain uniform vapour distribution over the box volume. The samples were prepared by drop-casting a SNP dispersion onto the surface of a TLC plate (Sorbfil, silica gel sorbent layer of 110-120 μm thickness, sorbent size 5-17 μm). Changes in the fluorescence spectra were registered using an R400-7 UV/VIS fiber-optic fluorescent probe inserted into the box and attached to a D-2000 Ocean Optic fiber-optic spectrofluorimeter. A LED (375 nm) was used as a light source. The fluorescence responses of the samples at low analyte concentrations (10-50 ppm) were studied using a special experimental system designed for this purpose [6].

Results and Discussion

Monodisperse silica nanoparticles with diameters ranging from 90 to 100 nm were obtained by hydrolytic polycondensation of tetraethoxysilane in mixtures of ethanol, water and ammonia. The synthesis of alkoxysilyl derivative of DBMBF₂ involved several stages shown in Fig.1.

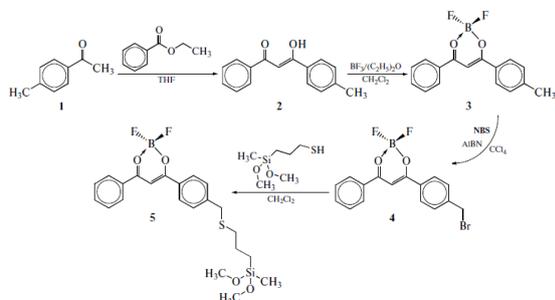


Fig. 1. Schema of four-step synthesis of an alkoxysilyl derivative of DBMBF₂.

Schematic representation of the synthesis of DBMBF₂ grafted SNP is given in Fig. 2.

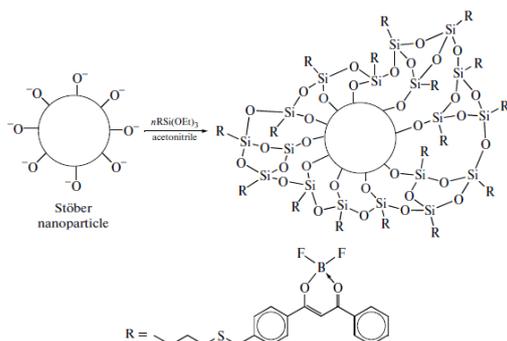


Fig. 2. Schematic of the synthesis of silica nanoparticles with covalently linked DBMBF₂.

The TEM microphotographs show that the shell thickness is about 2-4 nm.

Figs. 3-6 show the time evolution of the fluorescence emission spectra of TLC-plate samples containing dispersed SiO₂ nanoparticles with covalently grafted DBMBF₂ during exposure to saturated BTX vapors (front-face configuration, $\lambda_{\text{ex}} = 375$ nm, room temperature). The values of the fluorescence maxima and isoemissive points are shown. Spectra were obtained at every 4 s from the beginning of exposure to vapors. Surface-immobilized DBMBF₂ exhibits a single fluorescence band centered at 425 nm. Upon exposure to BTX vapors, the intensity of this band is decreased (except benzene) and broad red-shifted fluorescence bands peaked at 480-500 nm appear. As can be seen, the observed spectra exhibit the isoemissive points whose location is dependent on the nature of an analyte.

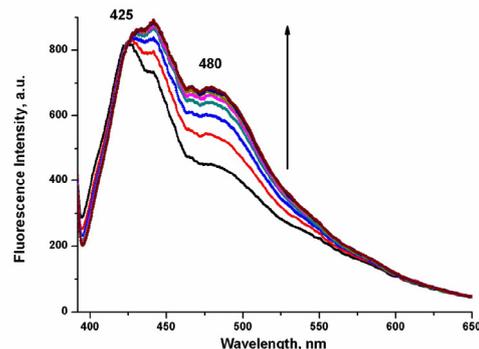


Fig. 3. Time-dependent fluorescence spectra of DBMBF₂-grafted SNP upon exposure to saturated benzene vapor (one measurement every 4 s).

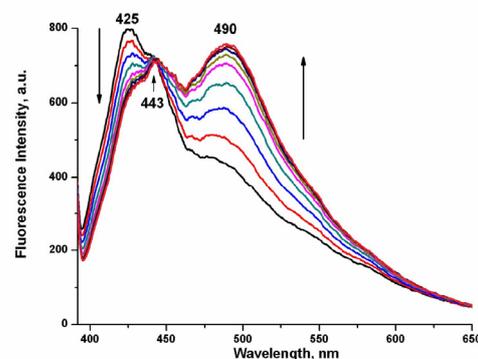


Fig. 4. Time-dependent fluorescence spectra of DBMBF₂-grafted SNP upon exposure to saturated toluene vapor (one measurement every 4 s).

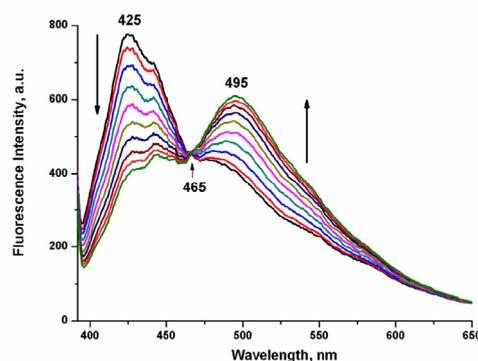


Fig. 5. Time-dependent fluorescence spectra of DBMBF₂-grafted SNP upon exposure to saturated *m*-xylene vapor (one measurement every 4 s).

Such a behavior is analogous to that observed for DBMBF₂ in solutions containing benzene or methyl-substituted benzenes [1-3] and must be related to formation of DBMBF₂/analyte exciplexes similar to exciplexes formed by

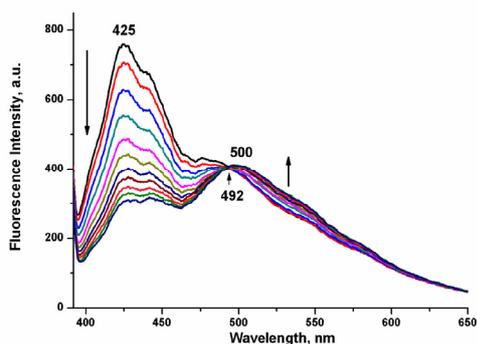


Fig. 6. Time-dependent fluorescence spectra of DBMBF₂-grafted SNP upon exposure to saturated *p*-xylene vapor (one measurement every 4 s).

pyrene and dimethylaniline on the SiO₂ surface [7]. Note that the positions of the exciplex fluorescence maxima and isoemissive points are considerable red-shifted in comparison with solutions. For example, the position of the isoemissive point of the DBMBF₂/toluene exciplex is comparable with the position of the isoemissive point of the DBMBF₂/1,2,3,4-tetramethylbenzene exciplex in cyclohexane solution [1]. This may be a consequence of the presence of polar silanol groups in the vicinity of formed exciplexes.

It can be seen that the isoemissive point for benzene is located in the neighborhood of the *c* fluorescence maximum (425 nm), whereas for toluene the point is shifted to 443 nm. Going from toluene to meta-xylene results in the shift to 465 nm. It is worth noting that the spectral changes for *ortho*-xylene having the same ionization potential as *meta*-xylene are practically identical with those for *meta*-xylene (fluorescence maximum and isoemissive point are located at 497 and 467 nm, respectively, as compared to 495 and 465 nm for meta-xylene). However, a further bathochromic shift to 492 nm is observed for *para*-xylene. Thus, the position of the isoemissive point differs markedly in the benzene-toluene-xylenes family and therefore it can be used for a decisive identification of an individual analyte.

From the results presented in Figs. 3-6 it is apparent that at a high concentration an analyte can be detected either by a decrease in the DBMBF₂ fluorescence intensity or by an increase in the fluorescence intensity of corresponding exciplex. For the samples studied, the response times were equal to several tens of seconds. It is evident that the response time may depend on a number of factors, in particular, on the diffusion rate of analytes within a sensor layer and can be

varied within wide limits by changing the composition and structure of the layer.

To test the possibility of detecting low concentrations of BTX, the fluorescence response to the presence of 12 ppm *ortho*-xylene was measured. The results are presented in Fig. 7.

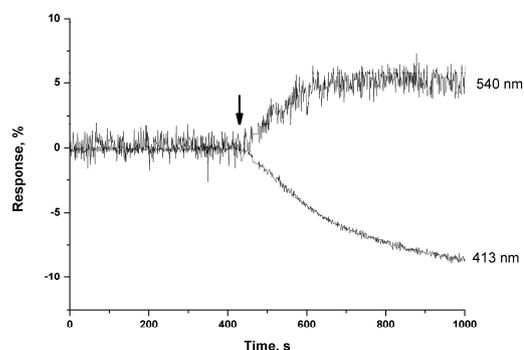


Fig. 7. Fluorescence response upon exposure to *o*-xylene vapor ($c = 12$ ppm) at two wavelengths. The arrow indicates the moment when *o*-xylene vapor was admitted.

As can be seen, the observed changes in the fluorescence intensity at both wavelengths corresponding to the fluorescence of DBMBF₂ (413 nm) and its exciplex with *o*-xylene (540 nm) are sufficient for a reliable registration of *o*-xylene vapour even at such a low concentration.

The process of exciplex formation on the SNP surface may be suggested as follows. When a DBMBF₂ molecule is electronically excited, its interaction with one of adsorbed analyte molecules leads to formation of a fluorescent DBMBF₂/analyte exciplex. It should be pointed out that an analyte molecule can form weak complex with a DBMBF₂ molecule already in its ground electronic state. It may be inferred from the fact that the vapor exposure in the dark results in the same fluorescence response as exposure under continuous excitation.

Conclusions

Thus, core-shell silica nanoparticles with a shell consisting of covalently linked alkoxy-silyl derivative of DBMBF₂ were synthesized and investigated as sensitive and selective components of a sensor material suitable for detection of gaseous BTX. It was shown that the occurrence of the characteristic isoemissive points can be used for unique identification of a BTX analyte. This may offer new opportunities for qualitative and quantitative analysis of BTX mixtures.

Acknowledgements

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