BODIPY in matrices: brief review

A.V. Bobrov¹, M.V. Kishalova², D.A. Merkushev¹, Yu.S. Marfin¹

¹Department of Inorganic Chemistry, Ivanovo State University of Chemistry and Technology, Sheremetevsky Str., 10, 153000 Ivanovo, Russia
²Department of Chemistry and Technology of High-Molecular Compounds, Ivanovo State University of Chemistry and Technology, Sheremetevsky Str., 10, 153000 Ivanovo, Russia

bobrovalexanderv@gmail.com

Abstract. Hybrid materials with dipyrrin based luminophores are of major interest in different areas of material chemistry, sensors and photovoltaics. Vast variety of the materials with BODIPY motif were synthesized and investigated up to date. Modern trend in the material chemistry is the aimed functionalization of them by immobilizing in their structure an active components. Based on interactions between matrix and dye we can control spectral and photophysical characteristics of hybrid material for tuning practically valuable properties for specific tasks. Presented paper summarize the results of our research group, working in the field of hybrid materials with BODIPY dyes: synthesis, spectral characteristics evaluation and possibilities of practical application investigation. Discussion is focused on the methods of synthesis of materials and practical application of them as sensors for pH, polarity and in OLED devices.

1. Introduction
Nowadays hybrid materials with matrix-immobilized dyes are of great interest. They find application in photovoltaics [1,2], OLED’s [3,4], sensorics on pH [5–7], polarity [8,9], ions [10,11] and molecules [12,13] and in biological approach for delivering drugs [14–17]. Solid materials are more convenient for practical use than solutions. That’s why there is a vast variety of matrices used for immobilizing active components, as well as active components themselves. One of such components is a family of BODIPY dyes. These dyes are excellent fluorophores, and more importantly, their structure may be completely modified by functionally active substituents. Despite the high number of related works, there is still the open question in understanding the influence of matrix nature on spectral properties and stability of BODIPY dyes and on their sensing activity.

A brief review of existing data and some applications of BODIPY dyes in hybrid materials, will shed some light on this problem.

2. Synthesis of matrices
Active components may be immobilized in a variety of polymer matrices. Commonly used organic polymers are poly(methyl methacrylate) (PMMA), polysulfone (PSU), polyvinyl chloride (PVC) and ethyl cellulose. Particularly noteworthy are SiO₂ materials (pure and modified) due to the combination of high achievable optical transparency, chemical inertness, thermal stability and ease of precise
alteration of morphological characteristics. Every matrix has its own methods of preparation and requirements for immobilized dyes.

2.1. Inorganic matrices
One of the commonly used methods to obtain thin-film materials from inorganic polymers is the sol-gel method. In our previous work [18] we analyzed the influence of various synthetic factors on the final materials. It was found that the amount of solvent has a significant effect on film uniformity. With the significant increase of solvent volume the film cracks upon drying. However, complete abandonment of the solvent also leads to film inhomogeneity, caused in this case by poor homogenisation of reactants in the reaction mixture.

The coating method also influences the quality of obtaining hybrid materials. Applying the sol onto a substrate by spin coating results in a significantly thicker film, and, as a result, a way less cracks in the material. Thinner film also better contact with the substrate, in comparison with dripping method. The higher homogeneity of spin-coated films was proved by the AFM images (Figure 1). On the figure 1 (a) we may see that the average inhomogeneity depth for dripping method is 1 nm, while the inhomogeneity depth for dripping method (Figure 1 b) is twice as low and is 0.5 nm. Moreover 1 μm pores in films obtained by dripping method may be seen, and most likely they are caused by the air bubbles in the reaction mixture.

![AFM images and the surface sections of the film surfaces of hybrid materials obtained by the method of dripping a and spin coating b. Reprinted from [18].](image)

This work resulted in an optimized method for obtaining of thin-film materials by the sol-gel method. The best results show mixtures with molar ratios of reagents n(precursor): n(C2H5OH) : n(H2O) : n(HCl) = 1:4:2:0.001 at 25 °C. The solution should be stirred for one hour. Then the appropriate BODIPY powder should be added to the reaction mixture to achieve dye concentration of 10⁻⁴ M. After full dye dissolving the material should be deposited to a clean glass slide by spin-coating at 3500 rpm for 15 s. Then the films should be aged for 24 h at 25 °C.

2.2. Organic matrices
The obtaining of organic polymer matrices is much easier to conduct due to the absence of cracking process. The best results show the following method: a solid polymer should be dissolved in organic solvent, then the dye powder should be added to reach the dye concentration of 10⁻⁴ M. The resulting mixture should be dripped to a clean glass and left drying for 3 hours [19]. However, this method may be modified. In work [20], the film was prepared by spin coating method and vacuum dried at 80°C.
3. Effect of immobilization on optical properties of BODIPY

One of the interesting dye immobilization effects is solvatochromism, which leads to changes in absorption and fluorescence peaks positions. Moreover, the nature of the matrix also influences the dye response to various environmental factors, such as pH, polarity.

In order to study this effect several gel hybrid materials of different nature were obtained, mixed with BODIPY 1 and measured (Figure 2) [21]. SiO2 based hybrids were chosen to compare the influence of organic moiety on dye molecules and hybrid films morphology. Spectra of all hybrid materials differ from the dye spectra in ethanol (Table 1 of [21]) In comparison with dye solutions where 8–9 nm bathochromic shifts and decrease in quantum yields in all SiO2 hybrids. Intense dye–dye interactions in the matrix were observed and confirmed by comparing spectra of materials with spectra of the individual dyes films [21] and ethanolic solutions. And taking into account negative solvatochromic effect of the BODIPY dyes [22], peak shifts could be attributed to changes in polarity in the transition from ethanol to matrix.

![Fig. 2](image)

The specific interactions between dye and different organic parts of the polymeric matrix strongly influence the photophysical characteristics of the BODIPY. In order to reveal specific interactions taking place between the matrix and the dyes the FTIR spectra of hybrid materials were measured (Figure 3). The intermolecular interactions of the BODIPY with the matrix were determined by the changes in position and intensity of the peaks on the FTIR dyes spectra.

![Fig. 3](image)
According to FTIR spectra, \( \pi-\pi \) stacking between the phenyl ring of the matrix and phenyl moiety of the dye is clearly seen for all of the studied BODIPYs in PhTEOS hybrid materials.

Further, in materials with BODIPY 2 and PhSiO\(_2\), the hydrogen bond was found. It was formed between the lone pair of the dye amino nitrogen and matrix hydroxyl group’s hydrogen’s. A similar binding was found for the BODIPY1@NH\(_2\)SiO\(_2\) hybrid material. In this case, the hydrogen bond was formed between matrix amino group nitrogen and the dye carboxyl group hydrogen. The schematic representation of the above-mentioned interactions is presented on figure 4.

Fig. 4. Graphical representations of the interactions between the matrix and BODIPY (a - \( \pi-\pi \) stacking in the BODIPY3@PhSiO\(_2\) hybrid, b - hydrogen bond in the BODIPY2@PhSiO\(_2\) hybrid, 2 hydrogen bonds in the BODIPY1@NH\(_2\)SiO\(_2\) hybrid).

4. Application of the obtained materials
The next step of our work was the investigation of practical use of hybrid materials in sensing media pH and polarity and OLED devices.

The pH sensory activity was studied in water solutions by using hybrid materials with different chemically modified matrices. It was found that matrix nature significantly changes the fluorescent response of hybrid material on pH change (Figure 5). The dependence of relative fluorescence intensity on pH of the solution for the TEOS-derived materials (dyes a and c [19]) is mostly linear: fluorescence intensity grows with an increase of the solution alkalinity. But for the APTMOS - based hybrid with the same dyes dependence is way more pronounced and, it is important to note, reversed.

Fig. 5. Changes in fluorescence spectra of materials upon pH variation. Reprinted from [19].
For TEOS-derived (b) hybrid material the dependence is also linear and reversed (Figure 6) making it suitable for pH sensoring. At the same time materials obtained from APTMOS with BODIPY (b) and BODIPY (d) show no accountable dependencies. All investigated dyes were found to destruct at pH < 2, forming the of non-fluorescent products. To sum it up, we may say that the obtained materials may be used for effective pH measurement in the range of 2 to 12.

![Graph](image1.png)

**Fig. 6.** Dependence of fluorescence intensity for BODIPY (b) @ SiO2 material from the pH of the medium. Reprinted from [19].

The dependencies observed for PSU and PVC hybrid materials are linear. That indicates the possibility of practical application of these hybrids (Figure 7) as acidity sensors in the full pH range.

![Graph](image2.png)

**Fig. 7.** Dependence of the relative fluorescence intensity from the medium pH for hybrids (a- BODIPY(b)@PVC; b- BODIPY (b)@PSU). Reprinted from [19].

The origin of changes in spectral response is the specific interactions between the sensor molecule and the electron-donating atoms of the polymeric matrix. The type of these interactions alters upon pH variation.

Just as for liquid solutions, the relation between the fluorescence intensity and polarity was investigated for the hybrid materials. Figure 8 illustrates the drop of the fluorescence intensity taking place upon shift to vapors of the solvents with a higher dielectric constant values for compound b.

![Graph](image3.png)
Displacement of the monomer-associate equilibrium in the hybrid materials with poly (methyl methacrylate) and polyvinylcarbazole was exploited for directional tuning of their emission. The fabricated OLED devices were found to demonstrate moderate electroluminescence efficiency. Both self-absorption and aggregation induced emission effects cause desirable emission colour changes but decrease efficiency of the active layer (Figure 9) [20].

5. Conclusion
Our group has developed a technique for the synthesis of hybrid thin-film materials by the sol-gel method. The dependence of the properties of the material on the type of matrix and the type of interaction between it and the active substance was shown. The possibility of using hybrid materials with BODIPY as sensors on pH, polarity and OLED devices has been proven.
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