

Petro O. Kondratenko, Yuriy M. Lopatkin, Vita V. Solomko, and Anna G. Malashenko.
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Journal of Sensors

Volume 2017 (2017), Article ID 1320717, 5 pages

<https://doi.org/10.1155/2017/1320717>

Research Article

Polymethine Dye as Sensors of NH₃ and CO

Petro O. Kondratenko,¹ Yuriy M. Lopatkin,² Vita V. Solomko,² and Anna G. Malashenko²

¹Department of Theoretical and Applied Physics, Aerospace Institute, National Aviation University, 1 Cosmonaut Komarov Avenue, Kyiv 03680, Ukraine

²Department of General and Theoretical Physics, Sumy State University, 2 Rimsky-Korsakov Street, Sumy 40007, Ukraine

Correspondence should be addressed to Anna G. Malashenko

Received 28 October 2016; Revised 12 December 2016; Accepted 20 December 2016; Published 10 January 2017

Academic Editor: Kalisadhan Mukherjee

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Abstract

We have investigated the properties of polymethine dyes (PMD) and the purpose of using them as sensors of hazardous gases presence. Research indicates that in case of utilizing PMD as a sensor of hazardous gases we need to use the monochromatic light which wavelength corresponds to the inflection point of the long-wave absorption edge of PMD. Such sensor of hazardous gases can detect changes in the optical density of the sensor layer or the light intensity transmitted through the layer.

1. Introduction

The wide use of polymethine dyes is caused by their properties. The stability of these dyes while being exposed to sunlight provides their utilization in the fabric dyeing industry. In addition, they can be used in dye lasers construction due to their stability against laser emission and the possibility of the emission spectrum restructuring. There is a possibility of adjusting the spectrum over a wide frequency range from the near UV to near IR region.

Unique properties of PMD provide their use for sensitization of light-sensitive materials based on silver halide in the predetermined spectral region, as well as for the multipurpose compact discs production [1–3].

The restructuring of the dye molecule during the interaction with other molecules leads to a change in its properties that are essential for using the dye as a core element of sensor devices [4–11].

In this paper we propose to expand the use of PMD, exploring the sensitivity of these molecules to the presence of hazardous gases.

2. The Object and Method of Investigation

Certain initial conditions must be met in order to create a harmful gas sensor. Primarily, the sensor must respond quickly to the presence of hazardous gas and relax rapidly to initial state after removing gas from the space.

The first requirement is easily implemented for thin polymer layers, which contain the PMD. The characteristic time of gas molecules diffusion into a layer is proportional to the ratio of the squared layer thickness and gas diffusion coefficient in the layer. If the diffusion coefficient is set 10^{-9} cm²/s [12] and the layer thickness is 1 micrometer, the characteristic time will be 10 seconds.

To implement the second requirement, namely, the possibility of relaxing rapidly to initial state at removing gas from the space, it is necessary that the interaction between the gas molecules and the PMD is quite weak. The formation of hydrogen bonds between these molecules can satisfy this requirement. This, in turn, imposes restrictions on the nature of the gas, which presence we are going to register. Certainly, we can detect the presence of ammonia and carbon monoxide (CO). Water vapor will also be registered but since it is not a harmful substance we should protect our sensor against it.

As the model object for research we use one of the easiest types of the trimethine cyanine dye (Figure 1).

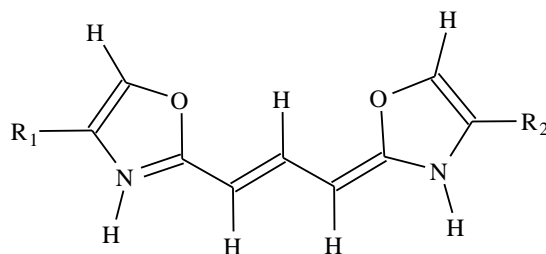


Figure 1

In Figure 1 this molecule we will vary two substituents: R1 and R2. If both substituents form single bonds with an oxazole rings, the total number of electrons in the neutral molecule will be odd. Consequently, we will get a radical, that is, an unstable structure. Typically, such molecules are converted to the cationic state by introducing an anion into the systems. Thus, in this case we use R1 = H, and R2 will vary within OCF₃, OCCl₃, COOH, and NO₂.

We will choose R1 = O, in case we want to conduct research with neutral PMD molecules.

We will conduct the study of the system using quantum-chemical calculations. The main methods of research in this work are AM1 and DFT, which allow us to obtain reliable results of the absorption spectrum view and the energy changes.

3. The Results of the Conducted Research and Their Discussion

Molecules investigated in this study are presented in Table 1.

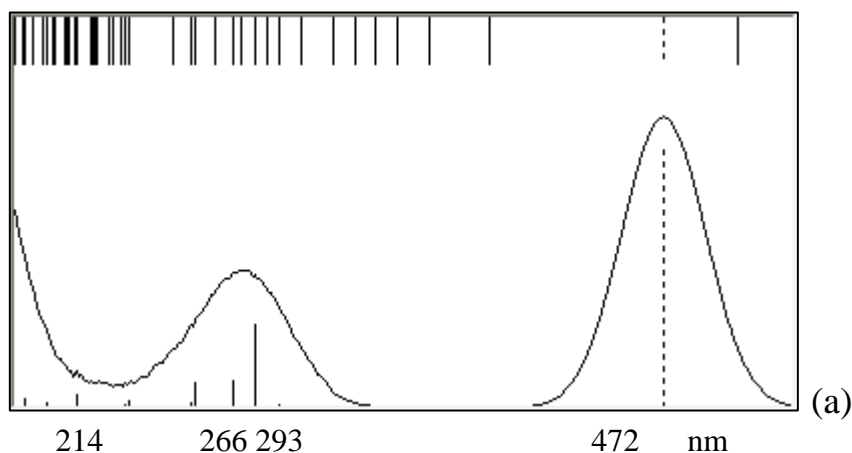
Table 1: The calculated parameters of the molecules PMD.

| Designations | R ₂ -substituent in the PMD molecule | The long-wavelength absorption band, λ, nm | The oscillator strength |
|--|---|--|-------------------------|
| PMDcations(R ₁ = H) | | | |
| PMD-I | OCF ₃ | 472.52 | 0.973 |
| PMD-II | OCCl ₃ | 464.16 | 1.010 |
| PMD-III | COOH | 471.03 | 1.001 |
| PMD-IV | NO ₂ | 464.80 | 1.050 |
| Neutral PMD molecules (R ₁ = O) | | | |
| PMD-V | OCF ₃ | 535.18 | 0.810 |
| PMD-VI | OCCl ₃ | 528.24 | 0.854 |
| PMD-VII | COOH | 535.36 | 0.840 |
| PMD-VIII | NO ₂ | 536.23 | 0.875 |

The structural changes of the molecule have led to the energy change of the various isomers ground state. The isomer depicted in Figure 1 has the lowest energy of the ground state. Assuming that different isomers in solution remain in thermodynamic equilibrium, it is easy to find the equilibrium concentration of each of them. We have found out that 64% of all molecules in the solution are presented by major isomer, while the other isomers have small contributions. Due to this fact, we conduct research with only major isomer PMD varying the nature of R1 and R2 substituents.

PMD and PMD-III-VII molecules containing substituent COOH are among the investigated PMD molecules. This substituent has the ability to dissociate into a proton and a carboxylic acid, that is, an anion, in alkaline aqueous media. We do not consider this case investigate because the sensors of harmful gases are made on the polymer water insoluble base. Consequently, the medium cannot be in the alkaline condition.

The absorption spectrum of the investigated molecule contains one broadband in the visible region of the spectrum (Figure 2). All other quantum transitions provide the molecular absorption in the UV region of the spectrum.



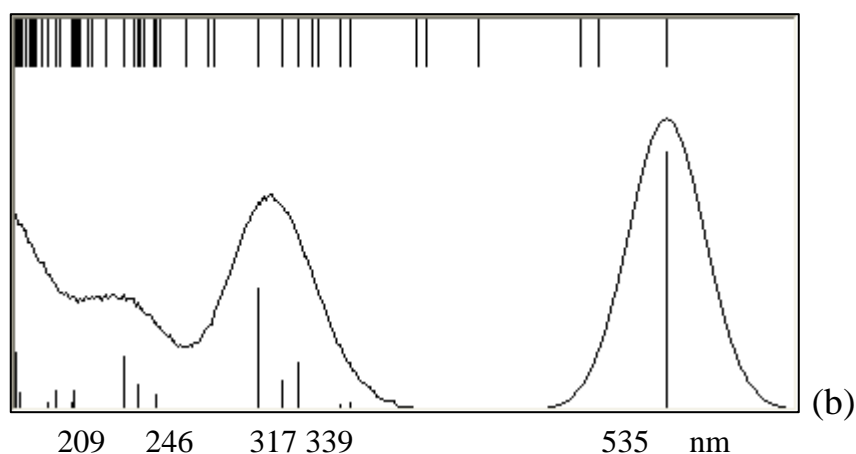


Figure 2: (a) The calculated absorption spectrum of the PMD-I dye. (b) Calculated absorption spectrum of the PMD-V dye.

In Figures 2(a) and 2(b) the calculated position of the quantum transitions that form the absorption spectrum are marked by vertical lines from below. The position of the singlet and triplet quantum transitions is shown above the figures, regardless of the oscillator strength value.

The absorption spectra of other PMD qualitatively resemble the spectrum shown on Figure 2.

Usually, such type of absorption spectrum belongs to the dye solution in the liquid solvent with the concentration of about 10–5 moles/liter in the 1 cm cuvette. If we perform the transition to the polymeric film with thickness of 1 micron, the concentration of PMD is expected to grow about 4 orders.

Now we introduce the molecule of ammonia into the interaction with PMD. Typically, such interaction leads to the short-wavelength shift of the absorption band (Table 2). However, introduction of the second or third ammonia molecule into the interaction does not cause further appreciable shift of the absorption band. Thus, we notice that our gas sensor will operate in a range of ammonia concentrations not exceeding PMD concentration in the polymer layer.

Table 2: The spectral position of the long-wavelength absorption band of PMD complex with ammonia molecule.

| PMD molecule | λ_1 ($\Delta\lambda$), first position of NH_3 | λ_2 ($\Delta\lambda$), second position of NH_3 | The oscillator strength in the second case |
|--------------|--|---|--|
| PMD -I | 472.54 (+0.02) | 466.44 (-6.08) | 0.959 |
| PMD -II | 460.07 (-4.09) | 455.47 (-8.69) | 0.992 |
| PMD -III | 470.65 (-0.38) | 465.76 (-5.27) | 0.983 |
| PMD -IV | 468.15 (+3.35) | 455.34 (-9.46) | 1.020 |
| PMD -V | 535.40 (+0.22) | 530.61 (-4.57) | 0.800 |
| PMD -VI | 529.00 (+0.76) | 523.70 (-4.54) | 0.864 |
| PMD -VII | 535.10 (-0.26) | 529.58 (-5.78) | 0.838 |
| PMD -VIII | 536.43 (+0.20) | 531.42 (-4.81) | 0.882 |

To find the optimal structure of the PMD complex with ammonia molecule we set different initial orientations of NH₃ relatively to the PMD molecule. However, the calculation procedure of the complex geometric structure optimization has transferred the ammonia molecule to the hydrogen atom bound with the nitrogen atom. There are two such positions. The first position is associated with the NH group near R2 substituent and the second one with the NH group near R1. The structure of the complex testifies that the complex has been formed through the hydrogen bonding between the components. Comparison study results for selected PMD molecules revealed that the best effect can be obtained only for the second position of the ammonia molecule. The binding energy of NH₃ with PMD in the second position is larger by 0.5 kcal/mol compared to the first one. This makes it possible to estimate the type-II complex and type-I complex concentrations ratio that occurred equal to 2.4. Therefore, in a dynamic equilibrium state, 70% of the complexes are presented by the type-II complex. The calculation results of the spectral position of the long-wavelength absorption band for two cases of the ammonia molecule location are given in Table 2.

As shown in Table 2, the spectral shift is usually negligible in the first position of the ammonia molecule in the associate. Exceptions are PMD-II and PMD-IV that show the significant shift of the absorption spectrum. The detailed consideration of these cases has shown that the ammonia molecule interacts with PMD not only due to the hydrogen bond between the hydrogen atom of the NH group and the nitrogen atom of ammonia molecule but also due to one between the ammonia hydrogen atom and the oxygen atom of R2-substituent. It distinguishes the results found for the PMD-II and PMD-IV from the results for the other PMD.

In the second position of the ammonia molecule relatively to the first four PMD the hydrogen bond appears in pure form. In this case, the best results for the PMD sensitivity to the presence of ammonia are shown by PMD-II and PMD-IV. Investigation of the binding energy value of ammonia molecules with PMD cations has shown that it is about 0.33 eV (Table 3). At such value of the binding energy, the ratio of free ammonia molecules to the molecules bound in associate with PMD is $1.8 \cdot 10^{-6}$. Consequently, almost all ammonia molecules are associated with PMD cations.

Table 3: The binding energy of the NH₃ and CO molecules in the associate with the PMD molecule (position 2).

| PMD molecule | Binding energy of the NH ₃ , eV | Binding energy of the CO, eV |
|--------------|--|------------------------------|
| PMD -I | 0.33 | 0.14 |
| PMD -II | 0.32 | 0.13 |
| PMD -III | 0.34 | 0.14 |
| PMD -IV | 0.35 | 0.14 |
| PMD -V | 0.23 | 0.09 |
| PMD -VI | 0.23 | 0.11 |
| PMD -VII | 0.23 | 0.11 |
| PMD -VIII | 0.24 | 0.11 |

The binding energy of the ammonia molecules with the neutral molecule is somewhat smaller. However, in this case almost all the ammonia molecules are associated (the proportion of free molecules of ammonia is only $1 \cdot 10^{-4}$). As shown in Table 3, the binding energy of the ammonia molecules with PMD molecules exceeds twice the binding energy of CO molecules with the same PMD molecules. However, the detailed research of the NH₃ and CO associates with neutral PMD

molecules configurations showed that the hydrogen binding energy and are almost identical (0.13 eV and 0.11 eV, resp.).

The increase of the binding energy of NH₃ with the neutral PMD molecule occurs due to the structure of associate in which the N-H bond of the ammonia molecule closes the six-membered ring with the OCNH group of the oxazine ring. At the same time the interaction is added, which leads to the increase of the binding energy of NH₃ with the neutral PMD molecule.

There is no correlation between the hydrogen bond energy and the value of the absorption band shift because the absorption band is formed by π -electron system, and hydrogen bond is formed by the σ -electron system. Binding energy of NH₃ and CO in the associate is significantly different. However, the absorption band shift caused by the association of these molecules has the same value for a number of associates.

The results of research of the effect of the PMD association with the CO molecule are shown in Table 4.

Table 4: Results of calculation spectral position of the long-wavelength absorption band PMD complex with a molecule of CO.

| PMD molecule | First position CO, λ_1 , nm | Second position CO, λ_2 ($\Delta\lambda$), nm | Oscillator strength in the second case |
|-----------------|--|--|---|
| PMD-I 472.52 | 466.97 (-5.55) | 463.89 (-8.63) | 0.980 |
| PMD-II 464.16 | 463.02 (-1.14) | 463.55 (-0.61) | 1.001 |
| PMD-III 471.03 | 463.49 (-7.54) | 462.24 (-8.79) | 1.003 |
| PMD-IV 464.80 | 465.97 (+1.17) | 462.54 (-2.26) | 1.038 |
| PMD-V 535.18 | 531.74 (-3.44) | 530.67 (-4.51) | 0.832 |
| PMD-VI 528.24 | 520.86 (-7.38) | 518.93 (-9.31) | 0.893 |
| PMD-VII 535.36 | 531.70 (-3.66) | 528.77 (-6.59) | 0.861 |
| PMD-VIII 536.23 | 527.71 (-8.52) | 526.39 (-9.84) | 0.922 |

These results indicate that the absorption spectrum shift in two different molecule positions does not differ essentially. If it is large for the position 2, it has great value for the position 1 too. In particular, there is a significant result for PMD-I and PMD-III cations and for neutral PMD-VI and PMD-VIII molecules. Herewith the R₂ substituents which cause the activity of PMD molecules are different (mutually exclusive) from substituents that cause activity of PMD cations.

The associate of phosgene with PMD we investigate along with the associates of PMD with ammonia and carbon monoxide. The resulting value of electronegativity is quite substantial and is 3.3. The hydrogen bond forms and we observe the spectrum shift of this associate (21 nm) as in the previous case. The similar experimentally observed shift at the formation of associates has been described in [13].

Molecular spectra in solution, usually, have the half-width substantially greater than 10 nm at the long-wavelength edge of the first absorption band. Shortwave edge contains the oscillatory repetition, not shown in Figure 2, since the quantum-chemical calculation operates only pure electronic transitions. These oscillatory repetitions significantly extend the shortwave edge of absorption band and often appear in the form of oscillatory structure of the absorption band.

In the presence of associate PMD/gas molecule at the arbitrary wavelength of the optical density of the polymer film with the thickness depends on the concentration of PMD (C_0) and the associate (C_1), according to the expression

$$D = d \cdot [(C_0 - C_1) \cdot \varepsilon_0 + C_1 \cdot \varepsilon_1] = d \cdot [C_0 \cdot \varepsilon_0 + C_1 \cdot (\varepsilon_1 - \varepsilon_0)] = D_0 + C_1 d \cdot (\varepsilon_1 - \varepsilon_0) \quad (1)$$

Here ε_0 and ε_1 are the extinction coefficients in absorption bands of the PMD and the associate, respectively, at the particular wavelength. Weak associates which we deal with (the shift of the absorption band is less than 10 nm) change the shape of the absorption band slightly only shifting it to shorter wavelengths. If we tune into the long-wavelength wing of the PMD absorption band then $\Delta\lambda$ is less than λ . This can be written in the certain approximation: $\varepsilon_1(\lambda) - \varepsilon_0(\lambda) = \frac{d\varepsilon_0}{d\lambda} \cdot \Delta\lambda$. In this case,

$$\varepsilon_1(\lambda) - \varepsilon_0(\lambda) = \varepsilon_0(\lambda + \Delta\lambda) - \varepsilon_0(\lambda) = \frac{d\varepsilon_0}{d\lambda} \cdot \Delta\lambda \quad (2)$$

The derivative of the extinction coefficient reaches the maximum value in the inflection at the long-wavelength edge of the absorption band. We take the value of $\Delta\lambda$ from Tables 2 and 3. The resulting formula will look like

$$D(\lambda) = d \cdot [C_0 \cdot \varepsilon_0 + C_1 \cdot (\varepsilon_1 - \varepsilon_0)] = D_0 + C_1 d \cdot \frac{d\varepsilon_0}{d\lambda} \cdot \Delta\lambda \quad (3)$$

Consequently, the greater the value of $\Delta\lambda$ the greater the sensitivity of the polymer layer with the PMD to the presence of the hazardous gas. Sensitivity to the presence of the gas is defined by the formula

$$\gamma = \frac{dD}{dC_1} = d \cdot \frac{d\varepsilon_0}{d\lambda} \cdot \Delta\lambda \quad (4)$$

that is, it is determined by the value of $\Delta\lambda$ and the slope of extinction coefficient on the long-wavelength edge of the absorption band of PMD.

If we want to detect the presence of hazardous gas by changing the intensity of the light transmitted through the film then the value of the intensity is determined by the formula

$$I = I_0 \cdot \exp -D = I_0 \cdot \exp -D_0 - C_1 d \cdot \frac{d\varepsilon_0}{d\lambda} \cdot \Delta\lambda \quad (5)$$

This formula can be simplified for small changes of $\Delta\lambda$

$$I = I_0 \cdot \left(1 - C_1 d \cdot \frac{d\varepsilon_0}{d\lambda} \cdot \Delta\lambda \right) \cdot \exp -D_0 \quad (6)$$

Since the optical density at the long-wavelength edge of the absorption band decreases with wavelength increasing, will increase. This will cause the change of the point of extremum of the sensor sensitivity to the presence of hazardous molecules.

4. Conclusions

Based on the conducted research of the influence of hazardous gases (ammonia and carbon monoxide) on the absorption spectra of PMD of cationic and neutral types, we can make the following conclusions.

- (1) NH₃ and CO molecules create associates with the trimethine cyanine molecules due to the formation of hydrogen bonds between the hydrogen atom of the NH group of the PMD molecule and atoms of nitrogen or oxygen of the studied gas. The hydrogen bond almost completely transforms free PMD molecules into associates.
- (2) The shift of the PMD absorption band mainly occurs in the short-wavelength region of the spectrum. The shift value depends on the nature of the substituent in the oxazine fragment.

Among four tested substituents only two (OCF₃ and COOH) provided maximum sensitivity of the PMD cation, while the other two substituents (OCCl₃ and NO₂) provided maximum sensitivity of the neutral PMD molecule to carbon monoxide.

- (3) If PMD is used as a sensor of the hazardous gases the device needs to be tuned for registration of monochromatic light of which wavelength corresponds to the inflection point of the long-wavelength absorption edge of the PMD. The magnitude of the effect is proportional to the shift value of the absorption band $\Delta\lambda$.
- (4) The hazardous gas sensor can detect the change in optical density of the layer or the intensity of light transmitted through the sensor layer. In both cases it is necessary to use a monochromatic light tuned to the maximum change in optical density or light intensity.

Competing Interests

The authors declare that they have no competing interests.

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