

Intramolecular Photo-Physical Processes and Spectral-Luminescence Properties of a Dye Merocyanine 540 and its Complexes with Water

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ABSTRACT

Merocyanine 540 (M540) is famous dye that used in electronics and medicine. An important feature of the dye is a significant intramolecular transfer of the electron density in the excited state. Experimentally was investigated the electronic absorption and fluorescence spectra in different solvents M540. Electronic structure, spectra and rate constants of photo-physical processes of an isolated molecule and its complexes with water molecules were calculated by INDO method with spectroscopic parameterization.

Analysis of the results allowed establishing the effect of individual fragments and hydrogen bonds with water on the electronic charge transfer between the terminal units in the state S_1 . Examination of photo-physical processes of decomposition of the fluorescent state was showed that the intramolecular processes of decay of the S_1 state are not the cause of the differences calculated and experimental fluorescence quantum yield. Consideration of *trans-cis* photo-isomerization leads to the elimination of this non-compliance.

Keywords: Merocyanine 540, photo-physical processes, complexes with water, quantum-chemical calculations, *trans-cis* photo-isomerization

1. INTRODUCTION

Merocyanine 540 (the name according to IUPAC rules is sodium 3-[(2Z)-2-[(Z)-4-(1,3-dibutyl-4,6-dioxo-2-sulfanylidene-1,3-diazinan-5-ylidene)but-2-enylidene]-1,3-benzoxazol-3-yl]propane-1-sulfonate) is a well-known organic dye that is used in different fields. Thus, in electronics it is used along with other merocyanine dyes in elements of solar cells^{1,2}. However the main usage of merocyanine 540 is in medicine. It is widely used for indicator and diagnostic purposes as fluorescent markers, in lipophilic and membrane probes³. Also, it applies for therapeutic purposes as a photo-sensitizer in photo-dynamic therapy of malignant tumors, including blood diseases^{4,6}. Moreover, merocyanine 540 is used as anti-virus agent^{7,8}, for example, its toxic activity against the virus of human immunodeficiency was shown⁹.

Merocyanine 540 (M540) is a typical representative of a class of merocyanine dyes with the significant transfer of electron density between end fragments under excitation. Especially, this feature of the merocyanine 540 along with its solvatochromic effects, determines its applications in electronics and medicine. In this connection, a comprehensive study of the effectiveness and channels of intramolecular photo-processes in this molecule is an urgent task. Many research works are dedicated to the investigation of spectral-luminescence properties of M540 in different solvents, study of the generation of singlet oxygen, of the photo-chemical transformations, isomerization, and nonstationary absorbance¹⁰⁻¹². Nevertheless, there are only a few theoretical quantum-chemical calculations of the molecules from the class of merocyanine that is connected to the complexity of such systems.

In the connection with mentioned above, the aim of the present work was to investigate the features of electronic structure, spectral-luminescence, proton-acceptor properties, and photo-physical processes of merocyanine 540 using the methods of quantum chemistry in comparison with experimental data, and the study of the change of the effectiveness of photo-processes during *trans-cis* isomerization.

2. EXPERIMENT AND CALCULATION

Experimental study of absorbance, fluorescence, and anisotropy of excitation of fluorescence (polarization spectra) was performed on Spectrofluorimeter CM 2203 (Solar) and Spectrophotometer Cary 100 (Varian) at room temperature. Quantum yield of fluorescence was measured in relation to rhodamine 6G in ethanol ($\Phi_f = 0,95$) using standard method¹².

Quantum chemical calculations of spectra and rate constants of intramolecular photo-physical processes were conducted via semi-empirical method with intermediate neglect of differential overlap (INDO) with spectroscopic parameterization using a software package developed by V.Ya. Artyukhov¹³. The average length bonds and valence angles according to¹⁴ were used for the calculation of the ground state and spectrum of absorbance. Molecule is non-planar due to excluding of the right fragment ($\varphi=45^\circ$) from the molecular plane. During calculation of the spectrum of fluorescence changes in the lengths of chemical bonds were taken into account by accounting of changes in the populations of the bonds in the excited state in relation to the ground state according to Mulliken¹⁵. Using in the calculation the molecular geometry of M540 optimized by B3LYP functional has not given the fundamental differences in the spectrum and nature of the states. But there was a significant divergence with the experimental value of energy of electronic transitions forming the absorption spectrum (more than by 3500 cm^{-1} for the long-wavelength absorption band)¹⁶.

3. EXPERIMENT AND CALCULATION

Merocyanine 540 is an ionic dye, and its electron spectrum observed in visible and UV ranges belongs to anion. That is why the calculations were performed for this part of the molecule with the charge of $q = -e$ (Figure 1). The specific feature of the molecules of M540 is that they contain atoms with high electronic density (O, S, N, Figure 1) that create proton-acceptor centers, and result in the appearance of proton-acceptor properties of the whole molecule. This feature of M540 leads to its activity in intermolecular interactions with proton-donor solvents, and monomers of the molecule can be detected in polar solvents. In non-polar solvents M540 forms dimers and more complicated aggregates of its molecules^{8,10}. That is why it is more logical to compare the results of calculations for monomer of M540 with experimental spectra of absorbance and fluorescence in proton-donor solvents, for example, in water.

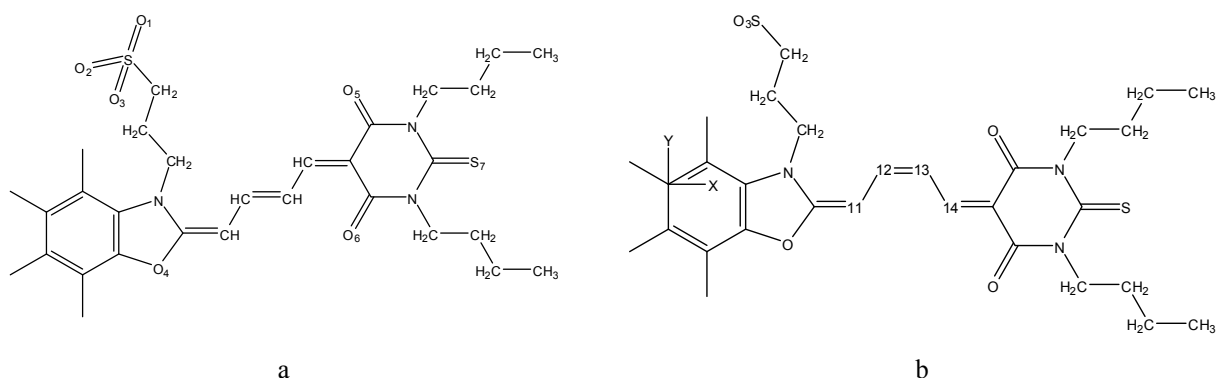


Figure 1. Structural formulas of *trans*- (a) and *cis*- (b) isomers of merocyanine 540.

In the experimental absorbance spectrum of M540 in water the most intense band of absorbance is the band at longer wavelengths with double-maxima (Figure 2).

The ratio between intensities of these maxima may differ depending on the concentration of the solution (Figure 2a, curve 1 – 10^{-4} M and curve 2 – 10^{-5} M). Some authors^{8,10} believe that the longer wavelengths maximum belongs to the monomer, and the shorter wavelengths maximum – to the dimer. On our opinion the most likely nature of these maxima is a result of the vibrational structure of the band of the single electron transfer. This is typical of many similar structure symmetrical and asymmetrical molecules with ethylene chain. The half-width of the band ($\sim 4040\text{ cm}^{-1}$) corresponds to the usual half-width of the absorption band formed by one electronic transition, and the distance between the maxima ($\Delta\nu = 1260\text{ cm}^{-1}$) – to the oscillation frequency of C-C bonds of the polymethine chain (PC). In order to approve this point of view we have calculated the spectrum of M540 dimer with "sandwich" geometry. Long molecular axes of the molecules of *trans*-dimer, which are at a distance of 3.5 \AA , are antiparallel. Calculations have shown that the transition to the state S_1 in the dimer is forbidden. The transition $S_0 \rightarrow S_2 (\pi\pi^*)$ is localized on the PC, as well as the transition $S_0 \rightarrow S_1 (\pi\pi^*)$ of the monomer, but its intensity is more than 2 times higher than the intensity of the transition $S_0 \rightarrow S_1 (\pi\pi^*)$ in the monomer. The energy of the allowed transition $S_0 \rightarrow S_2 (\pi\pi^*)$ in the dimer is 20920 cm^{-1} , the oscillator strength is -2.7 . Thus, the molar extinction coefficient of the "sandwich"-type dimer is almost an order of magnitude must be greater than the experimentally observed. And the distance between the absorption bands of the monomer and the dimer should exceed $\sim 2000\text{ cm}^{-1}$. The similar result of calculations was obtained previously for dimers of thiocarbocyanine cations¹⁷.

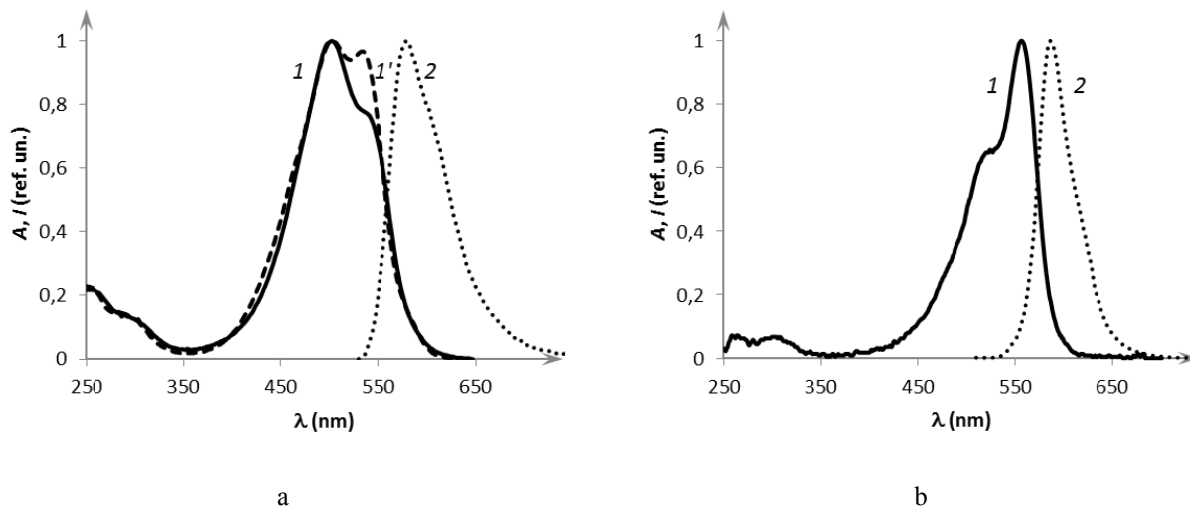


Figure 2. Absorbance spectra (1, 1') and fluorescence spectra (2) of M540 in water (a) and in glycerol (b).

Table 1. Calculated absorbance spectra for isomers of marocyanine 540.

State	E_i , cm^{-1}	f	P	State	E_i , cm^{-1}	f	P
<i>Trans-isomer</i>				<i>Cis-isomer</i>			
$S_1(\pi\pi)$	18960	1.319	X	$S_1(\pi\pi)$	18490	1.139	X
$S_2(n_{5,6}+\pi\pi)$	28790	0.102	X	$S_2(n_{5,6}+\pi\pi)$	28410	0.154	X
$S_3(n_{5,6}+\pi\pi)$	30700	0.008	X	$S_3(n_{5,6}\pi)$	30500	0.023	X
$S_4(n_7\pi)$	31100	0.004	Z	$S_4(n_{5,6}\pi)$	30750	0.007	X
$S_5(n_{5,6}\pi)$	31290	0.004	Y, Z	$S_5(\sigma_7\pi)$	31110	10^{-5}	Y
$S_6(n_{1-3}\pi)$	33120	10^{-4}	Z	$S_6(n_{1-3}\pi)$	31900	10^{-5}	Y
$S_7(\pi\pi)$	34150	0.008	X	$S_7(\sigma_7\pi)$	34010	0.009	Y
$S_9(\pi\pi)$	35330	0.119	Z	$S_8(\pi\sigma)$	34890	0.087	Y
$S_{12}(\pi\pi)$	38440	0.119	X	$S_{12}(\pi\pi)$	38210	0.122	X
$S_{13}(\pi\pi)$	40104	0.152	X	$S_{13}(\pi\pi)$	39880	0.140	X
$S_{15}(\pi\pi)$	41450	0.174	Y	$S_{16}(\pi\pi)$	41320	0.109	Y
$S_{16}(\pi\pi)$	41640	0.068	X	$S_{19}(\pi\pi)$	41700	0.217	X, Y
$S_{18}(\pi\pi)$	42430	0.140	Y	$S_{20}(\pi\pi)$	42600	0.105	Y

Analysis of the calculations showed that the intensity of the long-wavelength absorption band of M540 is formed by one-electron transition of $\pi\pi^*$ -type that is fully localized on the PC. This is typical for symmetric polymethines and merocyanines^{18,19}. In order to test and refine the above interpretation of the absorption spectrum, we obtained the spectra of anisotropy excitation of fluorescence (polarization spectra) that are sensitive to changes in the polarization of electron transitions in the two solvents - water and glycerin. A wide plateau in the polarization spectrum in the range of ~500 - 350 nm correlates with the three lower electron transitions ($S_0 \rightarrow S_1$ - S_3 , see Table 1) having the same polarization. Low-intensity transitions into the states $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$ (Table 1), which are impossible to identify in the absorbance

spectrum due to its proximity to the intense transition $S_0 \rightarrow S_1$, are detected as a minimum at 310 nm on the polarization spectrum. Maximum of the polarization spectrum at ~ 285 nm is apparently formed by the forbidden $S_0 \rightarrow S_6$ transition, and a minimum at ~ 255 nm probably relates to the electronic transitions $S_0 \rightarrow S_7$ and $S_0 \rightarrow S_9$ (Table 1).

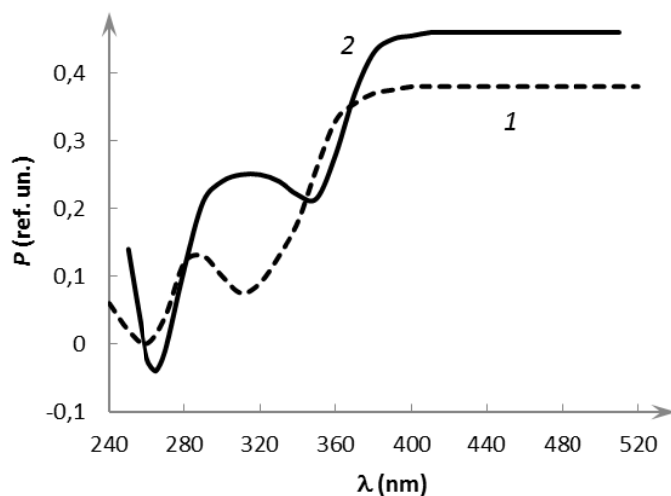


Figure 3. Polarization spectra of merocyanine 540 in water (1), and in glycerol (2).

Analysis of the electron density distribution in isolated isomers of M540 anion has shown that in the state S_0 the negative charge ($q = -1e$) is distributed substantially between the left and right end fragments (Table 2). In the left fragment the negative charge is localized on the substituent in this fragment, and in the right fragment it is localized on the heterocycle. PC carries a small positive charge. The electronic excitation of the state S_1 ($\pi\pi^*$) increases the electron density at the substituent, and the heterocycle of the left end fragment, and on the PC of *trans*-isomer due to the transfer of the electron density from the heterocycle of right end fragment (Table 2).

Table 2. Electron density distribution on the fragments of the isomers of M540 and complex of *trans*-isomer M540 +7H₂O in ground and excited states.

State	Left cycle	Substituent in the left cycle	PC	Right cycle	Substituent in the right cycle 1	Substituent in the right cycle 2
<i>Trans-isomer M540</i>						
S_0	0.230	-0.785	0.189	-0.952	0.155	0.156
$S_1(\pi\pi^*)$	0.139	-0.810	0.059	-0.714	0.157	0.159
<i>Cis-isomer M540</i>						
S_0	0.223	-0.775	0.182	-0.911	0.144	0.141
$S_1(\pi\pi^*)$	0.044	-0.768	0.016	-0.619	0.156	0.161
<i>Trans-isomer M540 +7 H₂O</i>						
S_0	0.250	-0.773	0.207	-1.022	0.170	0.166
$S_1(\pi\pi^*)$	0.188	-0.761	0.032	-0.802	0.172	0.172

Considering the whole end fragments of the isolated molecule we can say that the right end fragment of M540 acts as a donor, and the left – as an acceptor of electron density both in the ground and excited states. This situation is similar to the *cis*- and *trans*-isomers.

Proton-donor solvent the most strongly effects on the properties of the substituent of the left fragment of the molecule of *trans*-isomer in the state S_1 ($\pi\pi^*$), transforming it from the acceptor (isolated molecule) to a weak donor (a complex with water). In general, the inclusion of water molecules into the analysis in principle does not change the overall picture of the distribution of the electron charge in the ground state. However, it reduces the amount of charge transferred from the right fragment to the left one in the excited state. Thus, in the complex the electron density on the PC increases in the excited state to a greater extent due to the charge transfer from the right fragment.

In addition to the calculation of the spectrum of electronic excited states rate constants of photophysical processes were calculated. They are necessary to assess the radiative properties of the molecule. Fig. 4 shows the calculated energy of the lower electronically excited states, the rate constants of photophysical processes, and fluorescence quantum yields of isomers of M540 and complex with water. According to the calculations, the rate constant of radiative decay (k_r) in isomers and complex with water is $(3.0\div 3.5)\times 10^8 \text{ c}^{-1}$, which is close to the value of k_r obtained from the experimental data¹⁶ – $2,2\times 10^8 \text{ c}^{-1}$.

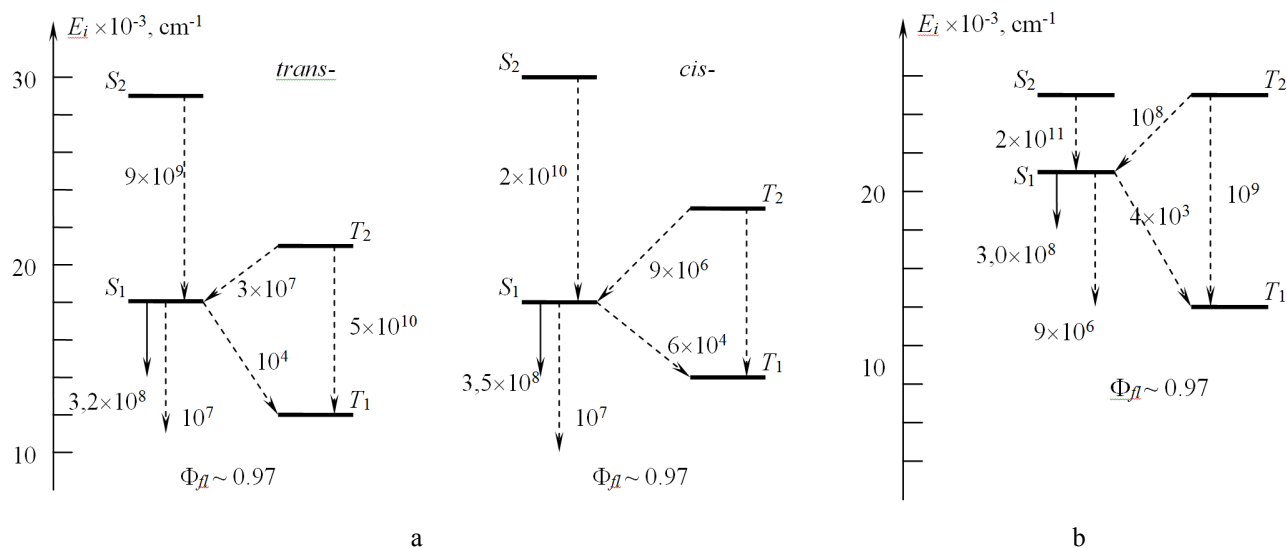


Figure 4. Energy-level diagrams of electron excited states of the isomers of the isolated molecule of M540 – a, and of the complex of *trans*-isomer M540 + 7H₂O – b.

From nonradiative intramolecular processes in the *trans*-isomer the process of internal $S_1(\pi\pi^*)\rightarrow S_0$ conversion (k_{VK}) has an advantage. Its effectiveness is several orders higher than the rate constant for intersystem crossing¹⁰.

The process of the singlet-triplet conversion (k_{ST}) in the *trans*-isomer of M540 performed in channel $S_1(\pi\pi^*)\rightarrow T_1(\pi\pi^*)$. The reason of the low value of k_{ST} constant is a large energy range between interacting singlet and triplet states (up to ~ 10000 cm⁻¹). An approval of the correctness of the calculation of k_{ST} value is an experimentally established fact^{8,10} of a small quantum yield of the population of the state of $T_1(\pi\pi^*)$ at intramolecular channel ($\Phi_T = 0.002-0.04$). Thus, according to the results of the calculation, radiative and non-radiative decay processes of fluorescent state in both isomers M540 and its complex with water have the ratio of $k_r > k_{BK} \gg k_{ST}$. And the calculated fluorescence quantum yield is close to 1 (Fig. 4). That is not consistent with the experimental data according to which it varies from 0.04 (the water) to 0.26 (toluene). For example, in an aqueous solution of M540 the quantum yield of fluorescence according to our measurements is about 7%, which is consistent with data from other authors^{10,11}.

Based on the fact that the rate constants of photo-physical processes obtained from the calculations are in accordance with the experimental data, it may be suggested that in molecule M540 there should be additional channels of deactivation of the fluorescent state. One of the most probable processes that significantly affect the fluorescence quantum yield and is not considered in the calculations described above can be *trans-cis* photo-isomerization taking place in state $S_1(\pi\pi^*)$. For example, according to the research work⁸, the reaction rate constant of *trans-cis* photo-isomerization of M540 reaches $3.6\times 10^9 \text{ c}^{-1}$, which is much superior to k_r . Thus, an adequate consideration of this process in the calculation can reduce the fluorescence quantum yield for about an order and bring it closer to the experimental value.

Preliminary analysis of the changes in the population of C-C bonds of PC at the excitation has identified the C-C bond of the PC that is the most weakened under excitation. This bond is C₁₂-C₁₃ (Fig. 1), around which the rotation is possible. The situation is similar in the case of complex *trans*-isomer with water (M540 + 7H₂O).

Table 3. The energy of S₁ state, the rate constant of the photo-physical processes, and the quantum yield of fluorescence change at *trans-cis* photo-isomerization of M540 and of the complex of *trans*-isomer with water (M540+7H₂O).

φ, °	0	40	60	80	100	120	140	160	180
M540									
S ₁ , cm ⁻¹	18520	18160	16490	12820	11500	14640	16700	17600	18210
k _r , c ⁻¹	3×10 ⁸	3×10 ⁸	2×10 ⁸	2×10 ⁷	2×10 ⁶	7×10 ⁷	2×10 ⁸	2×10 ⁸	3×10 ⁸
k _{BK} , c ⁻¹	10 ⁷	2×10 ⁷	1×10 ⁸	6×10 ⁸	4×10 ⁸	3×10 ⁸	6×10 ⁷	2×10 ⁷	1×10 ⁷
k _{ST} , c ⁻¹	4×10 ⁴	4×10 ⁵	2×10 ⁶	1×10 ⁸	3×10 ⁸	2×10 ⁸	9×10 ⁶	9×10 ⁶	3×10 ⁶
γ _{fl}	0.96	0.94	0.66	0.03	0.003	0.12	0.74	0.87	0.96
M540+7H ₂ O									
S, cm ⁻¹	19146	18830	17350	14140	13170	15840	17540	18290	18790
k _r , c ⁻¹	3×10 ⁸	3×10 ⁸	2×10 ⁸	3×10 ⁷	3×10 ⁶	8×10 ⁷	2×10 ⁸	3×10 ⁸	3×10 ⁸
k _{BK} , c ⁻¹	10 ⁷	2×10 ⁷	8×10 ⁷	3×10 ⁸	2×10 ⁸	2×10 ⁸	5×10 ⁷	2×10 ⁷	1×10 ⁷
k _{ST} , c ⁻¹	5×10 ⁴	3×10 ⁶	2×10 ⁶	2×10 ⁸	2×10 ⁸	5×10 ⁷	1×10 ⁷	1×10 ⁷	4×10 ⁶
γ _{fl}	0.97	0.93	0.69	0.06	0.007	0.19	0.77	0.89	0.95

Simulation of the reaction of *trans-cis* photo-isomerization using INDO for monomer of M540 and its complex has shown the following (Table 3). During the process of photoreaction not only lowering of the energy S₀→S₁ transition occurs, but also the change of its orbital nature takes place. As a result of the rotation in the range of angles of φ = 80-100° the fluorescence comes from a prohibited state πσ*-type. This reduces the efficiency of radiative decay by almost two orders of magnitude, while the internal conversion efficiency is increased by the order, and intersystem crossing – by two to four orders of magnitude. As a result, in this range of angles, the quantum yield decreases by 2 orders of magnitude, approaching the experimental value (Table 3). Thus, theoretical study performed suggested that *trans-cis* photo-isomerization can be the reason of the experimentally-observed low quantum yield of the fluorescence of M540.

It can be also assumed that the transfer of energy from the fluorescent state of M540 to the excited state of the singlet oxygen can make the additional contribution to the non-radiative deactivation of electronic excitation energy at deactivation of the state S₁(ππ*). A comparison of the energy of the singlet excited states of oxygen²⁰ (7870 cm⁻¹(¹Σ, v=0), 13120 cm⁻¹(¹Δ, v=0) and 14530 cm⁻¹(¹Δ, v=1)) and the energy of the fluorescent state of M540 that changes in *trans-cis* photo-isomerization (Table 3) shows that the singlet-singlet energy transfer is possible in all cases. However, this assumption requires special examination.

It should be noticed that since, according to calculations, the spectra and efficiency of photo-physical processes, including the fluorescence quantum yields, for the *trans*- and *cis*-isomers of M540 and its complex with water, are similar (Table 1, Fig. 4), the isomers should be difficult to identify in the experiment.

4. ACKNOWLEDGMENTS

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