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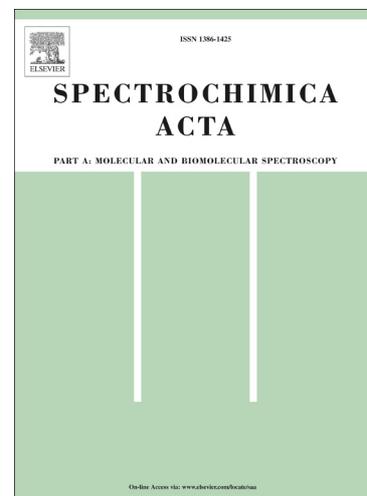
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**The computational and experimental investigations of photophysical and spectroscopic properties of BF<sub>2</sub> dipyrromethene complexes**

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**Abstract**

The electronic excited states of BF<sub>2</sub> dipyrromethene (2BrDPM, DPMI, DPMII, PM567 and 4PhDPM) complexes were investigated using the extended multi-configuration quasi-degenerate at the second order of perturbation theory (XMCQDPT2) and the second-order approximate coupled-cluster (CC2) methods. The excitation energies calculated by CC2 are significantly overestimated by 0.42-0.59 eV because of the substantial contributions of double excitation levels to excited states (>10%). However, the calculated XMCQDPT2 excitation energies agree well with experimental ones within the accuracy 0.11-0.20 eV. The very low lasing efficiency (7.8%-8.4%) of 4PhDPM compound was explained by the T<sub>1</sub>→T<sub>4</sub> and T<sub>1</sub>→T<sub>5</sub> reabsorptions at XMCQDPT2 level of theory. The molecular photonics of pyrrromethenes are studied using a combination of the first-principle and semi-empirical calculations. The main mechanism for the deactivation of the energy of the first singlet excited electronic state is the radiative electronic transition for DPMI, DPMII, PM567 and 4PhDPM compounds. Also, the main mechanism for the quenching of fluorescence in considered complexes (except DPMII compound) is the internal conversion. The processes of the internal conversion and intersystem crossing compete with each other in DPMII compound. The measured and calculated fluorescence quantum yields agree well for all considered molecules.

**Keywords:** internal conversion, intersystem crossing, photophysics, quantum yields

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## 1. Introduction

BF<sub>2</sub> dipyrromethenes are the class of compounds which have wide application in laser technology because they have specific spectroscopic and photophysical properties [1-6]. The high photostability, thermal and chemical stability and the fluorescence from green to red parts of spectrum and high fluorescence quantum yield are the main characteristics of dipyrromethene compounds [7-12]. It is obviously, they rival with rhodamine dyes, which are often used in dye lasers. Therefore, the new derivatives of dipyrromethenes are intensively synthesized and investigated using both experimental and theoretical methods.

Theoretical investigation of photophysical properties of molecules implies the calculation of the energies of electronic excitation levels and the rate constants of electronic transitions in molecules. The knowledge of the values of the rate constants of electronic transitions allows to estimate the probabilities of deactivation processes of excited electronic energies through the different relaxation channels and to calculate the fluorescence and phosphorescence quantum yields.

At present time, the theoretical investigations of spectroscopic properties of big molecules (more than 38 atoms) usually use the time-dependent density functional theory (TDDFT)[13], multi-configuration second-order perturbation theory (CASPT2)[14] and the second-order approximate coupled-cluster (CC2)[15-18]. However, the calculated characteristics of absorption and excitation spectra using TDDFT and CC2 methods agree not well with experimental data when the excited states have substantial contributions from double excitations [15,19]. Besides, the calculation at TDDFT level of theory leads to the underestimation of the energy of charge transfer (CT) transitions [20,21]. Therefore, the choice of the method for the calculation depends on the specific system which is investigated. It should be noted that the most of the theoretical works, where the photophysical properties are studied, are only devoted to the estimation of the values of the rate constants of the intersystem crossing (IS) and the radiative rate constants of the phosphorescence [22-26]. However, the rate constants of the internal conversion (IC) are also required for the fluorescence quantum yield

calculations. The process of internal conversion is a radiationless transition between different electronic and vibrational states within the same spin multiplicity. Calculation of the IC rate constants is very expensive in computational cost and is not trivial when *ab initio* methods are used. These difficulties appear because the matrix elements of non-adiabatic operator (NACME) must be calculated [27,28]. In this case the computation efforts are concerned with the *ab initio* calculations of the derivatives of wave function on coordinates [27]. To avoid this problem, the use of semi-empirical methods for calculation of NACME can be applied to reduce the cost of such calculations [29,30]. In the recent work of Valiev et al. [19] the rate constants of IC and IS for porphyrins molecules were calculated using both *ab initio* and semi-empirical methods. These calculations show that the estimations of fluorescence and phosphorescence quantum yields obtained by this way agree well with experimental ones. Therefore, the algorithm in Ref. [19] can be applied to other organic molecules.

The aim of the work is to investigate the spectroscopic and photophysical properties of the 4,4-difluoro-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (DPMI), 4,4-difluoro-1,3,5,7-tetramethyl-2,6-diethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (DPMII), 4,4-difluoro-1,3,5,7,8-pentamethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (PM567), 4,4-difluoro-1,3,5,7-tetra phenyl-4-bora-3a,4a-diaza-s-indacene (4PhDPM) and 4,4-difluoro-2,6-dibromo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (2BrDPM) compounds using experimental and theoretical methods. These molecules are of interest because they have the high fluorescence quantum yields (> 90%) under excitation of the  $S_0 \rightarrow S_1$  transition (except 2BrDPM) and are widely applied for lasing [5,6,9,11,12]. Therefore, their spectroscopic and photophysical properties are very interest for scientific society.

## 2. Calculation and experimental details

### 2.1. Synthesis

In this work, the synthesis of the DPMI, DPMII, PM567 compounds was performed according to methods which are described in Ref. [31]. The 2BrDPM compound was synthesized using the algorithm described in Ref. [32]. The 4PhDPM compound was synthesized according the scheme

which is shown in fig. 1. The 3,5 diphenylpyrrol (0.44 g. and 2.02 mM) and 2-formyl-3,5-diphenylpyrrol (0.5 g. and 2.02 mM) were dissolved in a mixture of acetic acid (10 ml.) and acetic anhydride (2.5 ml.) and then boiled within an hour. As a result, the solution became crimson and then turn to a precipitate. Thereafter, the precipitate was filtered and washed with methanol and then was dried. The acetic acid solution was poured into 200 ml of water, the precipitate was filtered off, dried and chromatographed with the use the silica gel. The yield of the product is 0.7 g (77%).

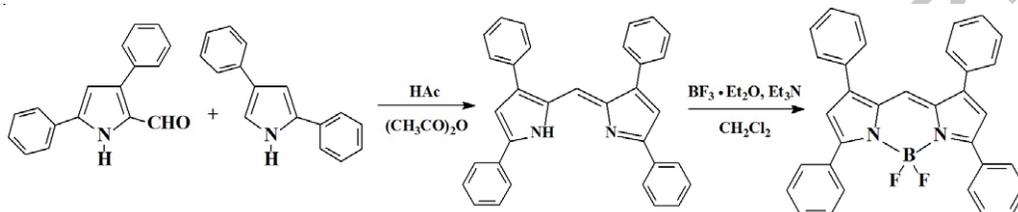


Fig. 1. The synthetic scheme of 4PhDPM compound.

## 2.2. Electronic absorption and fluorescence spectra measurements

Absorption spectra and luminescent characteristics were measured on the SM2203 spectrometer (SOLAR, Belarus). The cyclohexan was used solvent for all measurements. The fluorescence quantum yield was measured in respect to the rhodamine 6G with an error of 10% and the concentration of the investigated compounds was  $10^{-5}$ - $10^{-6}$  M. The long-lived (ms) emission in frozen solutions (at 77 K) was investigated using the Cary Eclipse spectrofluorimeter with an Optistat DN cryostat (Oxford).

## 2.3. Calculations

The equilibrium geometries of electronic ground state of investigated complexes were optimized at DFT level of theory using the Becke's three-parameter functional in combination with the Lee-Yang-Parr correlation functional (B3LYP) [33,34] and the def2-TZVP basis set [35] in the framework of the Turbomole 6.3 package [36]. The excitation energies were calculated at extended multi-configuration quasi-degenerate at the second order of perturbation theory (XMCQDPT2) [37] in Firefly [38] and at the CC2 level using the resolution of the identity approximation (RI) in Turbomole 6.3 package [36].

The rate constants of IC and IS were estimated using method which is described in details in the works of Valiev et al. [19] and Plotnikov [30]. Note that the XMCQDPT2 excitation energies and the received equilibrium geometries of the electronic ground states at DFT level of theory were used because the Stokes shift of fluorescence for these molecules is small ( $<1000\text{ cm}^{-1}$ ). The NACME and matrix elements of spin-orbital operator were computed at the INDO level using a set of fitting parameters, chosen with respect to the solvent effects, for considered molecules [39].

The fluorescence quantum yields ( $\varphi_{fl}$ ) for all compounds were estimated as

$$\varphi_{fl} = \frac{k_r}{k_r + k_{IC} + k_{S_iT_i}}$$

where  $k_r$  is the radiative rate constant of fluorescence,  $k_{IC}$  is the rate constant of IC and  $k_{S_iT_i}$  is the rate constant of the IS between the first excited singlet state ( $S_1$ ) and the  $i$ -th excited triplet state ( $T_i$ ).

### 3. Results and discussions

#### 3.1. Molecular structures

The equilibrium geometries of the electronic ground states of all considered complexes are shown in Fig. 2. The cartesian coordinates are given as supplementary material. Note that the equilibrium geometries of the electronic ground state agree well with X-ray data [40-43]. The frequencies analysis has confirmed that the obtained geometries of the considered compounds are really equilibrium.

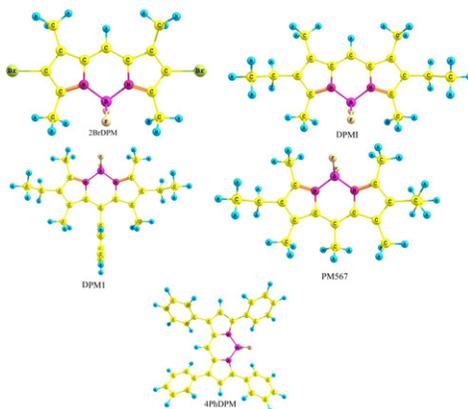


Fig. 2. The equilibrium structures of the considered complexes in the ground electronic state.

### 3.1. Vertical excitation energies

The calculated vertical excitation energies and oscillator strengths ( $f$ ), the peak positions of bands of experimental electronic absorption spectra and the experimental estimation of oscillator strengths for all investigated compounds are given in Tables 1-5. Note that the experimental excitation energies of the first triplet state for 2BrDPM, DPMII compounds were taken from the phosphorescence spectra from Ref. [32].

#### 3.1.1. 2BrDPM

The complete active space self consistent field (CASSCF) calculation is required before to compute XMCQDPT2 excitation energies. Therefore, Hartree-Fock (HF) molecular orbitals (MO) were chosen for the calculations with the CASSCF method. The HOMO, HOMO- $n$  (where  $n=1..8$ ) and LUMO, LUMO+1 were used in the CASSCF calculation. Note that these MO were chosen in accordance with that the electronic transitions, formed by these MO, in the configuration interaction (CI) expansion of the first four electronic excited singlet states at CIS level of theory for 2BrDPM compound have the maximum weights ( $\geq 0.2$ ).

The optimized MO at the CASSCF level of theory are given in supplementary material for 2BrDPM complex and other compounds. Contributions of the most relevant transitions of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies, oscillator strengths of 2BrDPM compound are given in Table 1. As it is visible from Table 1, the discrepancy between the theoretical and experimental excitation energies is 0.16 eV for the first excited singlet state. The second band of electronic absorption spectrum of 2BrDPM is located in the range from 410 to 340 nm (see supplementary material). The position of the peak of the second band is 3.24 eV. However, in order to determine accurately the energies of electronic transitions which form this absorption band the femtosecond fluorescence upconversion study is required [44]. One can consider that the second band is formed only by the 2-4 electronic transitions. Note that the using XMCQDPT2 method leads to the good agreement of the calculated and observed energy of the first triplet state.

Table 1. Contributions of the most relevant configuration state functions (the weights are given in parentless) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first four electronic excited states of 2BrDPM compound.

State	CASSCF		XMCQDPT2	Experiment
	single	double	E(f)	E(f)
S <sub>1</sub>	H→L (0.61)	H→L;H-2→L (-0.17)	2.14(0.19)	2.3(0.2)
	H-1→L (-0.21)			
S <sub>2</sub>	H→L (0.59)	H→L;H-1→L (0.23)	2.85(0.04)	3.24(0.03)
		H→L;H→L (-0.20)		
S <sub>3</sub>	H-1→L (0.60)		2.90(0.02)	
	H→L (-0.24)			
S <sub>4</sub>	H-3→L (-0.37)	H→L;H→L (-0.68)	4.11(0.01)	
	H-4→L (-0.30)			
T <sub>1</sub>			1.70	1.56 <sup>a</sup>
T <sub>2</sub>			2.27	

<sup>a</sup>Measured in ethanol [32].

The results of CASSCF calculation shows that the 1-th, 2-th and 4-th excited singlets have the substantial contributions ( $\geq 0.2$ ) from the double excitations. It is expected that the TDDFT and CIS methods lead to an overestimation of these energies because the TDDFT and CIS methods do not include double excitations. It should be noted also that there is a good agreement (within the order) between the calculated and experimental oscillator strengths of S<sub>0</sub>→S<sub>1</sub> transition.

### 3.1.2. DPMI

The HOMO, HOMO-n (n=1..3) and LUMO, LUMO+1 were chosen for the CASSCF calculation. The criterion of the selection of MO is the same as in the case of 2BrDPM compound. This criterion will be also applied for other considered compounds. The results of the calculations are given in Table 2. As seen from the Table 2, the using of the XMCQDPT2 method leads to small underestimation of the S<sub>1</sub> energy (0.1 eV). Also, there are significant contribution ( $\geq 0.2$ ) of double

excitations in  $S_1$  and  $S_2$  states. It should be noted the energetic gap between  $T_2$  and  $S_1$  energy levels is 0.02 eV ( $161 \text{ cm}^{-1}$ ).

### 3.1.3. DPMII

The molecular orbitals were used in the CASSCF calculations are given in supplementary material. The experimental and theoretical results are given in Table 3. The discrepancy between the XMCQDPT2 calculated and experimental excitation energies of  $S_1$  level is 0.27 eV. Also, the calculation at CASSCF level of theory shows that there are substantial double excitations ( $\geq 0.2$ ) in the  $S_1$ - $S_4$  excited states. Therefore, the TDDFT method leads to the significant overestimation of the excitation energy of  $S_1$  state by 1.1 eV (see Table 3). Also, the discrepancy between the calculated and experimental excitation energies of  $T_1$  state is 0.1 eV.

Table 2 Contributions of the most relevant configuration state functions (the weights are given in parenthesis) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first two electronic excited states of DPMI compound.

State	CASSCF		XMCQDPT2	Experiment
	single	double	E(f)	E(f)
$S_1$	H $\rightarrow$ L (-0.63)	H-3 $\rightarrow$ L;H $\rightarrow$ L (-0.19)	2.23(0.22)	2.33(0.30)
$S_2$	H-1 $\rightarrow$ L (0.53) H-2 $\rightarrow$ L (0.33)	H $\rightarrow$ L;H-1 $\rightarrow$ L (0.19)	2.98(0.02)	
$T_1$			1.52	
$T_2$			2.25	

### 3.1.4. PM567

HOMO, HOMO-n ( $n=1..3$ ) and LUMO, LUMO+m ( $m=1..5$ ) have to be included in CASSCF calculations for PM567 complex. The results of the calculations of excitation energies, oscillator strengths at XMCQDPT2 level of theory together with experimental ones are given in Table 4. It is seen from Table 4 that the calculated and experimental excitation energies of the  $S_1$  state agree well (the discrepancy is 0.22 eV). It should be noted that the using CASSCF method gives the substantial

contributions of double excitations ( $\geq 0.2$ ) to all singlet excited states. Therefore, the calculations of excitation energies using TDDFT method leads to the significant overestimation of them.

Table 3. Contributions of the most relevant configuration state functions (the weights are given in parentheses) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first four electronic excited states of DPMII compound.

State	CASSCF		XMCQDPT2	B3LYP/6-31G(d,p) [45]	Experiment
	single	double	E(f)	E	E(f)
S <sub>1</sub>	H→L (-0.59)	H→L;H-2→L (-0.16)	2.03(0.17)	3.40	2.30(0.20)
	H-1→L (-0.27)				
S <sub>2</sub>	H-1→L (-0.55)	H→L;H-2→L (-0.24)	2.68(0.01)		3.26(0.02)
	H→L (0.29)				
S <sub>3</sub>	H-2→L (0.59)	H→L;H-2→L (0.31)	2.85(0.01)		
S <sub>4</sub>	H-5→L (0.39)	H→L;H→L (0.71)	4.05(0.03)		
		H-5→L;H-5→L (0.27)			
T <sub>1</sub>			1.71		1.70 <sup>a</sup>
T <sub>2</sub>			2.29		

<sup>a</sup>Measured in ethanol [32].

### 3.1.5. 4PhDPM

In this case, the HF HOMO, HOMO-n (n=1..5) and LUMO were chosen for CASSCF calculations. The calculation results obtained in the framework of XMCQDPT2 level of theory together with the observed results are given in Table 5. This table shows a good agreement of the calculated and observed both excitation energies of S<sub>1</sub> state (0.17 eV) and oscillator strength of S<sub>0</sub>→S<sub>1</sub> transition (the discrepancy doesn't exceeded one order of magnitude). At that the calculated and observed excitation energies of T<sub>1</sub> state can not be compared because the phosphorescence of 4PhDPM compound is absent. Also, there is the problem concerned with the very low lasing efficiency ( $\eta$ ) of 4PhDPM complex in polar and nonpolar solvents. In this case,  $\eta$  equals to 7.8%-8.4% when the fluorescence quantum yield is 0.9 and excitation energy is 2.33 eV (18800 cm<sup>-1</sup>). The most likely the reason of the low value of  $\eta$  is the reabsorption of the laser emission at the wavenumber 16500 cm<sup>-1</sup> on

the  $S_1 \rightarrow S_i$  and/or  $T_1 \rightarrow T_i$  transitions. In order to confirm this conclusion the calculations of excitation energies and the oscillator strengths for  $S_1 \rightarrow S_i$  and  $T_1 \rightarrow T_i$  electronic transitions were carried out. The results of the calculations are given in Table 6. It is visible from this table that  $T_1 \rightarrow T_4$  and  $T_1 \rightarrow T_5$  electronic transitions give the large contribution to the formation of T-T reabsorption at the wavelength of laser emission because T-T energies are close to laser wavenumber and the oscillator strengths of these transitions are large.

Table 4. Contributions of the most relevant configuration state functions (the weights are given in parenthesis) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first four electronic excited states of PM567 compound.

State	CASSCF		XMCQDPT2	B3LYP/6-31G(d,p) [45]	Experiment
	single	double	E(f)	E	E(f)
$S_1$	H $\rightarrow$ L (0.6)		2.08(0.17)	3.40	2.30(0.20)
	H-1 $\rightarrow$ L (-0.22)	H $\rightarrow$ L;H-2 $\rightarrow$ L (-0.19)			
$S_2$	H-2 $\rightarrow$ L (-0.45)	H $\rightarrow$ L;H $\rightarrow$ L (-0.44)	3.45(0.01)		3.30(0.03)
		H $\rightarrow$ L;H-1 $\rightarrow$ L (0.18)			
$S_3$	H-1 $\rightarrow$ L (0.53)	H $\rightarrow$ L;H-3 $\rightarrow$ L (0.24)	3.55(0.01)		
$S_4$	H-3 $\rightarrow$ L (-0.29)				
	H-2 $\rightarrow$ L (-0.28)	H $\rightarrow$ L;H $\rightarrow$ L (-0.48)	4.11(0.03)		
$T_1$			1.71		
$T_2$			2.29		

### 3.2. The CC2 calculation

The calculations of excitation energies and oscillator strengths, the single and double contributions of excitation levels are given in Table 7. Note, the D1 diagnostics is 0.07 for all calculations. Therefore, the electronic ground states of considered molecules are not the multiconfigurational character [36]. As seen from Table 7, the calculated excitation energies of  $S_1$  state are overestimated by 0.42-0.59 eV for all considered compounds. The reason of the overestimation is the substantial contributions of double excitation levels (> 10%) [19,46]. Therefore, the CC2

calculation explains the bad agreement of the TDDFT excitation energies with experimental ones. Note that only one triplet state ( $T_1$ ) is lower than the  $S_1$  state according to the results of CC2 calculations for all considered complexes. Therefore, the  $S_1$  energy can be deactivated by the internal conversion ( $S_1 \rightarrow S_0$ )

Table 5. Contributions of the most relevant configuration state functions (the weights are given in parentless) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first four electronic excited states of 4PhDPM compound.

State	CASSCF		XMCQDPT2	Experiment
	single	double	E(f)	E(f)
$S_1$	H $\rightarrow$ L (-0.64)	H $\rightarrow$ L;H-4 $\rightarrow$ L (0.20)	2.01(0.19)	2.18(0.20)
$S_2$	H-2 $\rightarrow$ L (-0.62)	H-2 $\rightarrow$ L;H $\rightarrow$ L (-0.26)	2.55(0.01)	3.30
$S_3$	H-2 $\rightarrow$ L (0.62)	H-2 $\rightarrow$ L;H $\rightarrow$ L (0.30)	2.72(0.01)	
$S_4$	H-3 $\rightarrow$ L (-0.37) H-5 $\rightarrow$ L (0.20)	H $\rightarrow$ L;H $\rightarrow$ L (-0.75)	3.45(0.001)	
$T_1$			1.47	
$T_2$			2.20	

Table 6. The excitation energies (cm<sup>-1</sup>) and oscillator strengths (f) for the  $S_1 \rightarrow S_i$  and  $T_1 \rightarrow T_i$  electronic transitions of 4PhDPM compound calculated by XMCQDPT2 level of theory.

Type	E(f)	Type	E(f)
$S_1 \rightarrow S_2$	4370(0.0)	$T_1 \rightarrow T_3$	6950(0.09)
$S_1 \rightarrow S_3$	5700(0.012)	$T_1 \rightarrow T_4$	15000(0.6)
$S_1 \rightarrow S_4$	11600(0.001)	$T_1 \rightarrow T_5$	18500(0.1)
$T_1 \rightarrow T_2$	5700(0.04)		

and the intersystem crossing ( $S_1 \rightarrow T_1$ ) or by the photon emission (the radiative electronic transition) for considered compounds.

### 3.3. The rate constants of electronic transitions

The calculation of excitation energies of the first singlet and triplet states for considered compounds using XMCQDPT2 method lead to the good agreement with the experimental ones (the discrepancy is less than 0.25 eV). Therefore, the XMCQDPT2 excitation energies were used to calculate the IC and IS rate constants and to estimate the quantum fluorescence yields ( $\phi_f$ ) for considered complexes. Also, the equilibrium geometries of the ground electronic states were used for the modeling of the geometries for the first excited states for all considered molecules. This modeling is possible because the Stokes shifts are  $< 800 \text{ cm}^{-1}$ . The results of the calculations of the rate constants of the intersystem crossing ( $k_{S,T_1}$ ), the internal conversion ( $k_{IC}$ ) and the radiation rate constants ( $k_r$ ) are given in Table 8 for the studied compounds. It should be noted that the measurements of the fluorescence spectra and the fluorescence quantum yields were carried out at very small concentrations ( $10^{-5}$ - $10^{-6}$  M) of the complexes. Therefore, the intermolecular mechanisms of the quenching of fluorescence can be neglected.

The results show that the main mechanism of the deactivation of the excited electronic energy is the radiative electron transition for DPMI, DPMII, PM567 and 4PhDPM compounds. The probability of the radiationless electronic transitions is significantly less than the probability of the radiative electron transitions for DPMI, DPMII, PM567 and 4PhDPM compounds whereby these compounds have the high fluorescence quantum yields ( $>0.9$ ). Note that the presence of the heavy atom of bromine in 2BrDPM compound leads to the competition between the processes of the intersystem crossing and the photon emission. In this case, the quenching of fluorescence is caused mainly by the intersystem crossing process. Therefore, the fluorescence quantum yield of 2BrDPM complex is substantially less than it for DPMI, DPMII, PM567 and 4PhDPM compounds. It should be also noted that the main mechanism for the quenching of fluorescence in DPMI, PM567 and 4PhDPM molecules is the internal conversion. As to DPMII compound, the processes of the internal conversion and the intersystem crossing compete each with other for this compound.

Table 7. The excitation energies (in eV) and oscillator strengths (f), the single and double contributions of the excitation levels to excited states are calculated with using CC2 level of theory.

2BrDPM				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.72(0.6)	2.3(0.2)	88	12
T <sub>1</sub>	1.95	1.7	90	10
T <sub>2</sub>	2.95		89	11
DPMI				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.73(0.6)	2.33(0.3)	88	12
T <sub>1</sub>	1.95		97	3.0
T <sub>2</sub>	2.95		97	3.0
DPMII				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.75(0.6)	2.30(0.3)	88	12
T <sub>1</sub>	1.96	1.61	91	8.0
T <sub>2</sub>	2.95		89	11
PM567				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.77(0.6)	2.18(0.3)	88	12
T <sub>1</sub>	2.02		91	8.0
T <sub>2</sub>	3.02		89	11
4PhDPM				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.54(0.6)	2.18(0.2)	86	14
T <sub>1</sub>	1.98		91	8.0
T <sub>2</sub>	2.95		87	13

The validity of the obtained results is confirmed by the very good agreement of the calculated fluorescence quantum yields with the experimental ones.

Table 8. The calculated rate constants (in  $s^{-1}$ ) for the photophysical processes of the 2BrDPM, DPMI, DPMII, PM567 and 4PhDPM compounds are given. The obtained fluorescence quantum yields are compared to experimental values.

	2BrDPM	DPMI	DPMII	PM567	4PhDPM
$k_r$	$4.0 \cdot 10^7$	$2.7 \cdot 10^7$	$3.2 \cdot 10^7$	$3.7 \cdot 10^7$	$3.5 \cdot 10^7$
$k_{IC}$	$1.1 \cdot 10^6$	$5.3 \cdot 10^6$	$4.2 \cdot 10^6$	$5.5 \cdot 10^6$	$2.7 \cdot 10^6$
$k_{S_1T_1}$	$4.3 \cdot 10^7$	$4.9 \cdot 10^4$	$2.4 \cdot 10^6$	$4.9 \cdot 10^5$	$2.0 \cdot 10^6$
$\phi_f$	0.47	0.87	0.83	0.87	0.92
$\phi_f$ (exp)	0.45	0.90	0.90	0.90-1.00	0.90

#### 4. Conclusion

The equilibrium molecular structures of the electronic ground states of 2BrDPM, DPMII, PM567 and 4PhDPM compounds were obtained at DFT level of theory using B3LYP functional and TZVP basis set. The electronic absorption and fluorescence spectra of the considered complexes were observed. The all compounds have almost the same position of the maximums of the first absorption band and the close values of intensity. The electronic structures of the electronic excited states were investigated using XMCQDPT2 and CC2 methods. The application of both methods have shown the substantial contributions of double excitation levels to excited states (>10%) of all considered compounds. Therefore, the calculation of the excitation energies of the considered compounds leads to the overestimation of them by 0.42-0.59 eV when the CC2 level of theory is used. In contrast, the calculated XMCQDPT2 excitation energies agree well with experimental values (the discrepancy is 0.11-0.20 eV). Also, in this work the low efficiency of the laser emission of 4PhDPM complex was explained by the  $T_1 \rightarrow T_4$  and  $T_1 \rightarrow T_5$  reabsorption.

The rate constants of the internal conversion and the intersystem crossing, the radiative rate constants were calculated. The measured and estimated fluorescence quantum yields of the considered compounds largely agree. The main mechanism of the deactivation of the electronic energy of the  $S_1$

state for DPMI, DPMII, PM567 and 4PhDPM complexes is the radiative electron transitions. Also, the main mechanism of the quenching of fluorescence in the DPMI, PM567 and 4PhDPM complexes is the internal conversion. The processes of internal conversion and intersystem crossing compete each with other in DPMII compound. As to the 2BrDPM compound, the quenching of fluorescence is caused mainly by the intersystem crossing process.

### Acknowledgements

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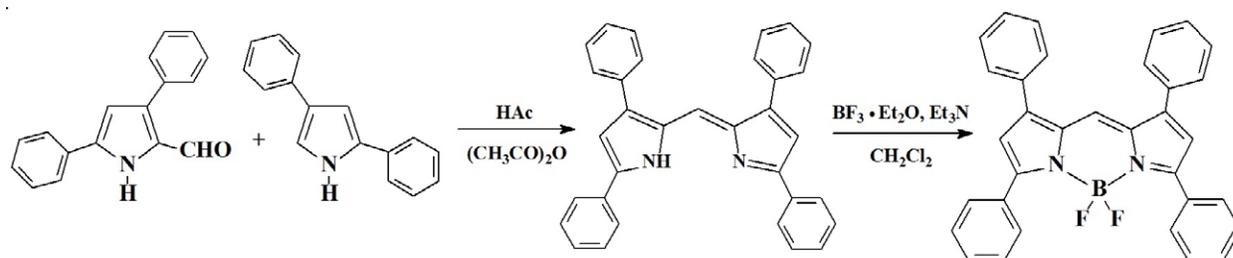
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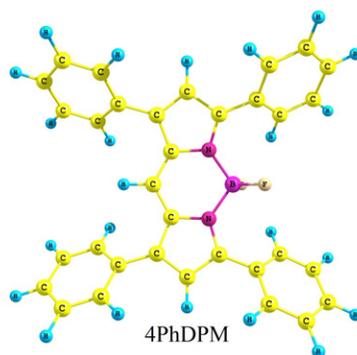
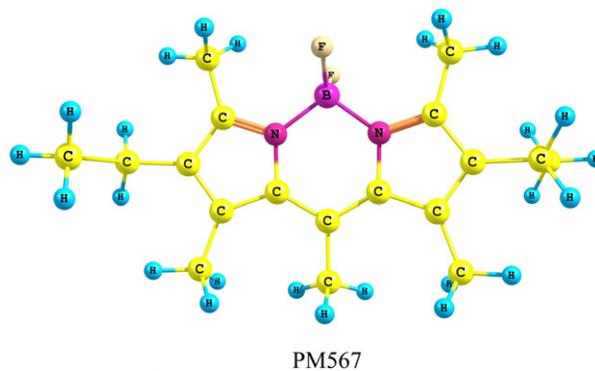
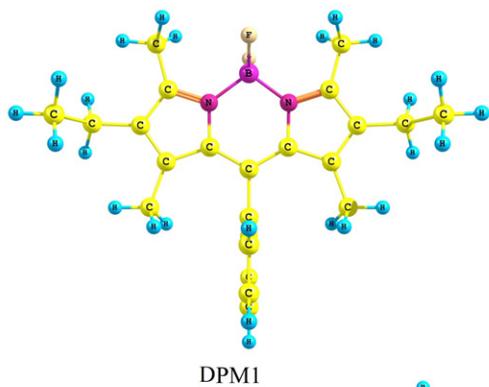
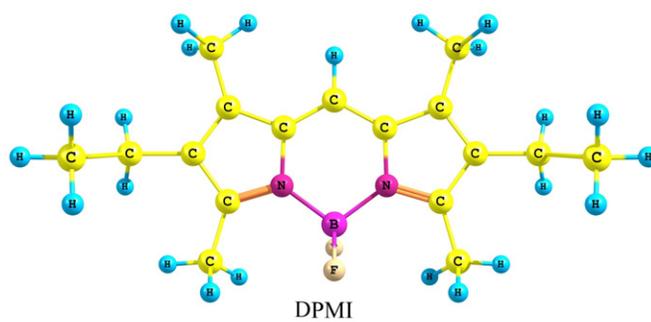
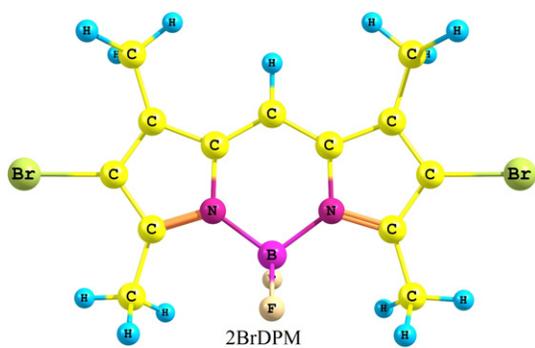
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Table 1. Contributions of the most relevant configuration state functions (the weights are given in parenthesis) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first four electronic excited states of 2BrDPM compound.

State	CASSCF		XMCQDPT2	Experiment
	single	double	E(f)	E(f)
S <sub>1</sub>	H→L (0.61)	H→L;H-2→L (-0.17)	2.14(0.19)	2.3(0.2)
	H-1→L (-0.21)			
S <sub>2</sub>	H→L (0.59)	H→L;H-1→L (0.23)	2.85(0.04)	3.24(0.03)
		H→L;H→L (-0.20)		
S <sub>3</sub>	H-1→L (0.60)		2.90(0.02)	
	H→L (-0.24)			
S <sub>4</sub>	H-3→L (-0.37)	H→L;H→L (-0.68)	4.11(0.01)	
	H-4→L (-0.30)			
T <sub>1</sub>			1.70	1.56 <sup>a</sup>
T <sub>2</sub>			2.27	

<sup>a</sup>Measured in ethanol [32].

Table 2 Contributions of the most relevant configuration state functions (the weights are given in parentless) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first two electronic excited states of DPML compound.

State	CASSCF		XMCQDPT2	Experiment
	single	double	E(f)	E(f)
S <sub>1</sub>	H→L (-0.63)	H-3→L;H-→L (-0.19)	2.23(0.22)	2.33(0.30)
S <sub>2</sub>	H-1→L (0.53)	H→L;H-1→L (0.19)	2.98(0.02)	
	H-2→L (0.33)			
T <sub>1</sub>			1.52	
T <sub>2</sub>			2.25	

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Table 3. Contributions Contributions of the most relevant configuration state functions (the weights are given in parentless) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first four electronic excited states of DPMII compound.

State	CASSCF		XMCQDPT2	B3LYP/6-31G(d,p) [45]	Experiment
	single	double	E(f)	E	E(f)
S <sub>1</sub>	H→L (-0.59)	H→L;H-2→L (-0.16)	2.03(0.17)	3.40	2.30(0.20)
	H-1→L (-0.27)				
S <sub>2</sub>	H-1→L (-0.55)	H→L;H-2→L (-0.24)	2.68(0.01)		3.26(0.02)
	H→L (0.29)				
S <sub>3</sub>	H-2→L (0.59)	H→L;H-2→L (0.31)	2.85(0.01)		
S <sub>4</sub>	H-5→L (0.39)	H→L;H→L (0.71)	4.05(0.03)		
		H-5→L;H-5→L (0.27)			
T <sub>1</sub>			1.71		1.70 <sup>a</sup>
T <sub>2</sub>			2.29		

<sup>a</sup>Measured in ethanol [32].

Table 4. Contributions of the most relevant configuration state functions (the weights are given in parentless) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first four electronic excited states of PM567 compound.

State	CASSCF		XMCQDPT2	B3LYP/6-31G(d,p) [45]	Experiment
	single	double	E(f)	E	E(f)
S <sub>1</sub>	H→L (0.6)	H→L;H-2→L (-0.19)	2.08(0.17)	3.40	2.30(0.20)
	H-1→L (-0.22)				
S <sub>2</sub>	H-2→L (-0.45)	H→L;H→L (-0.44)	3.45(0.01)		3.30(0.03)
		H→L;H-1→L (0.18)			
S <sub>3</sub>	H-1→L (0.53)	H→L;H-3→L (0.24)	3.55(0.01)		
S <sub>4</sub>	H-3→L (-0.29)	H→L;H→L (-0.48)	4.11(0.03)		
	H-2→L (-0.28)				
T <sub>1</sub>			1.71		
T <sub>2</sub>			2.29		

Table 5. Contributions of the most relevant configuration state functions (the weights are given in parentless) of CASSCF calculation, the XMCQDPT2 calculated and experimental electronic excitation energies (E) and oscillator strengths (f) for the first four electronic excited states of 4PhDPM compound.

State	CASSCF		XMCQDPT2	Experiment
	single	double	E(f)	E(f)
S <sub>1</sub>	H→L (-0.64)	H→L;H-4→L (0.20)	2.01(0.19)	2.18(0.20)
S <sub>2</sub>	H-2→L (-0.62)	H-2→L;H→L (-0.26)	2.55(0.01)	3.30
S <sub>3</sub>	H-2→L (0.62)	H-2→L;H→L (0.30)	2.72(0.01)	
S <sub>4</sub>	H-3→L (-0.37)	H→L;H→L (-0.75)	3.45(0.001)	
	H-5→L (0.20)			
T <sub>1</sub>			1.47	
T <sub>2</sub>			2.20	

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Table 6. The excitation energies ( $\text{cm}^{-1}$ ) and oscillator strengths ( $f$ ) for the  $S_1 \rightarrow S_i$  and  $T_1 \rightarrow T_i$  electronic transitions of 4PhDPM compound calculated by XMCQDPT2 level of theory.

Type	E(f)	Type	E(f)
$S_1 \rightarrow S_2$	4370(0.0)	$T_1 \rightarrow T_3$	6950(0.09)
$S_1 \rightarrow S_3$	5700(0.012)	$T_1 \rightarrow T_4$	15000(0.6)
$S_1 \rightarrow S_4$	11600(0.001)	$T_1 \rightarrow T_5$	18500(0.1)
$T_1 \rightarrow T_2$	5700(0.04)		

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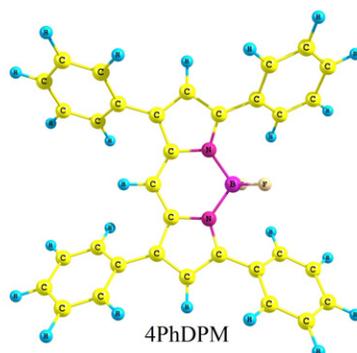
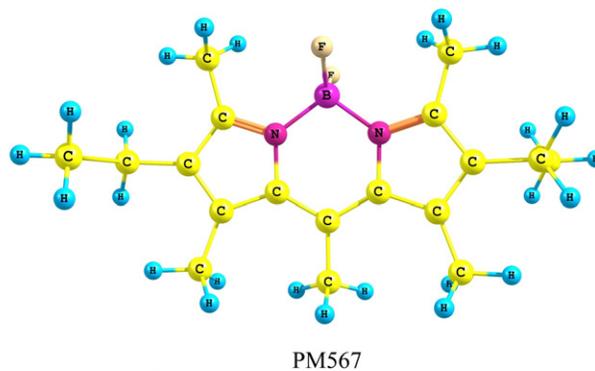
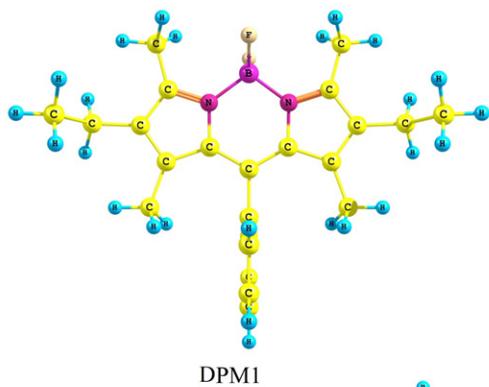
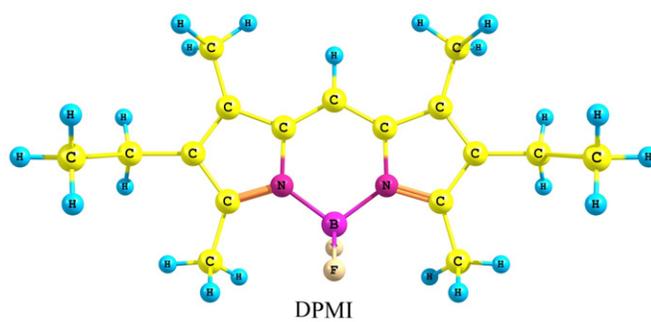
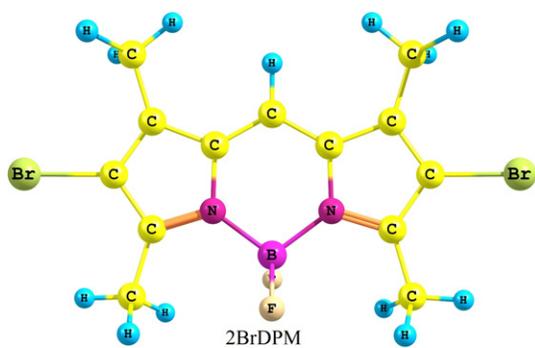
Table 7. The excitation energies (in eV) and oscillator strengths (f), the single and double contributions of the excitation levels to excited states are calculated with using CC2 level of theory.

2BrDPM				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.72(0.6)	2.3(0.2)	88	12
T <sub>1</sub>	1.95	1.7	90	10
T <sub>2</sub>	2.95		89	11
DPMI				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.73(0.6)	2.33(0.3)	88	12
T <sub>1</sub>	1.95		97	3.0
T <sub>2</sub>	2.95		97	3.0
DPMII				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.75(0.6)	2.30(0.3)	88	12
T <sub>1</sub>	1.96	1.61	91	8.0
T <sub>2</sub>	2.95		89	11
PM567				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.77(0.6)	2.18(0.3)	88	12
T <sub>1</sub>	2.02		91	8.0
T <sub>2</sub>	3.02		89	11
4PhDPM				
Type	E(f)	Exp	Single %	Double %
S <sub>1</sub>	2.54(0.6)	2.18(0.2)	86	14
T <sub>1</sub>	1.98		91	8.0
T <sub>2</sub>	2.95		87	13

Table 8. The calculated rate constants (in  $s^{-1}$ ) for the photophysical processes of the 2BrDPM, DPMI, DPML, PM567 and 4PhDPM compounds are given. The obtained fluorescence quantum yields are compared to experimental values.

	2BrDPM	DPML	DPML	PM567	4PhDPM
$k_r$	$4.0 \cdot 10^7$	$2.7 \cdot 10^7$	$3.2 \cdot 10^7$	$3.7 \cdot 10^7$	$3.5 \cdot 10^7$
$k_{IC}$	$1.1 \cdot 10^6$	$5.3 \cdot 10^6$	$4.2 \cdot 10^6$	$5.5 \cdot 10^6$	$2.7 \cdot 10^6$
$k_{S_1T_1}$	$4.3 \cdot 10^7$	$4.9 \cdot 10^4$	$2.4 \cdot 10^6$	$4.9 \cdot 10^5$	$2.0 \cdot 10^6$
$\phi_f$	0.47	0.87	0.83	0.87	0.92
$\phi_f$ (exp)	0.45	0.90	0.90	0.90-1.00	0.90

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Graphical abstract

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- The electronic excited states of BF<sub>2</sub> dipyrromethene complexes were investigated.
- The photonics of pyrromethenes are studied.
- The very low lasing efficiency (7.8%-8.4%) of 4PhDPM compound was explained.

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