SUPPRESSION OF KASHA'S RULE IN HIGHER EXCITED STATES OF 4-PYRYLOCYANINES

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Abstract

Spectral properties of the series of cationic polymethine dyes containing conjugated chain of different length and 4-pyrylium terminal groups were studied in details. Besides, the steady-state long-wavelength fluorescence from the lowest excited state and the fluorescence from higher excited states were experimentally revealed. The steady-state fluorescence band from the lowest excited state is shifted bathochromically with lengthening of the polymethine chain, which is also reflected in the absorption shift. According to quantum-chemical modeling, the appearance of unconventional fluorescence, which suppresses Kasha's rule, is associated with the different nature of the lowest excited states: the first and forth transitions are typical polymethine electron transitions involved only totally delocalized molecular orbitals (MOs), whereas the second and third transitions correspond to the electron jumping from the degenerated MOs localized only within the terminal groups (so called quasi-local MOs and hence quasi-local transitions). The forbidden transitions between the excited states of different types stimulate the fluorescence from the higher excited states.

Introduction

It is well known that the luminescence of the conjugated molecules originates normally from the lowest excited state; the generalization of this observation is formulated as Kasha's rule [1,2]. However, some spectral investigations have shown that there are exceptions to this rule, so some organic molecules give the emission from higher excited states (see, for example, the review [3] and refs therein). Such anomalous emission continues to attract the theoretical and experimental interest. Certainly, it is important to investigate a relation between the emission from higher electronic excited states and mechanisms of intramolecular electronic relaxation processes.

The azulenes, thiones, and pyrenes are the most known to be typical molecules that may exhibit the anomalous luminescence from higher excited states; nevertheless, there are another less-known molecules that show similar emission: systematic analysis has been extensively considered in the review [3]. Among the molecules with such unconventional luminescence, the 4-pyrylocyanines have become attractive for spectral studies, including symmetrical polymethine dyes containing the 4-pyrylium core as terminals groups [4-8]. Previous spectral and quantum-chemical studies have established that the specific local orbitals exist in the polymethine dyes with such terminal groups. Furthermore, there are two different types of electron transitions: 1) polymethine transition type, which involves only totally delocalized MOs; 2) quasi-local transition type involving one delocalized orbital and one local MO [6]. Since the transition between polymethine and quasi-local is hindered, the appearance of unconventional quasi-local transition in the spectra could lead to the suppression of Kasha's rule. Then, as a result, the luminescence from higher excited state occurs.

This paper presents the results of study for nature of the higher excited states in the 4-pyrylocyanines, including spectral measurements and quantum-chemical calculations.

Materials and methods

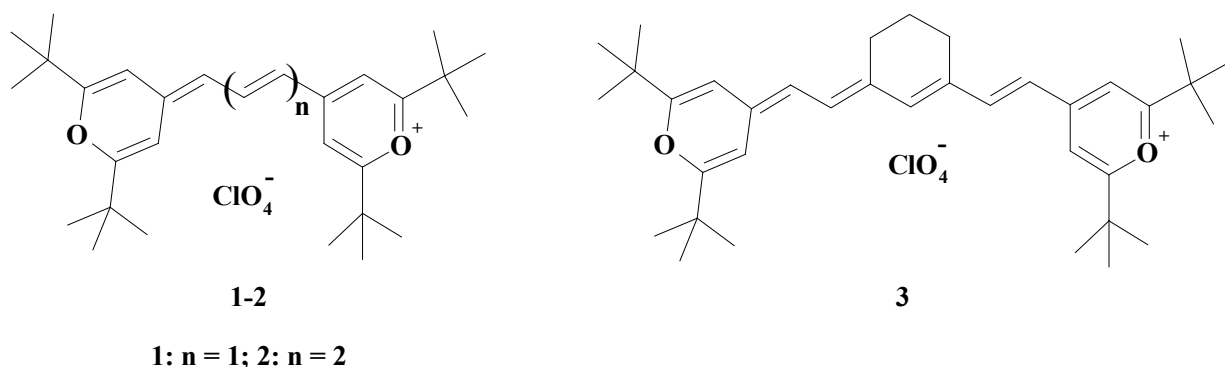The chemical structures of the investigated molecules **1-3** are presented in Fig. 1.

1-2

1: n = 1; 2: n = 2

3

Fig.1. Chemical structures of the studied dyes **1**-**3**

The synthesis of compounds **1-3** was described earlier [4].

All absorption and luminescence spectra were measured for spectral grade acetonitrile solutions of the dyes at the temperature 300 K. UV-Vis absorption spectra of the dyes were recorded on a UV-3100 spectrophotometer (Shimadzu). Luminescence spectra were measured with a USB2000+UV-VIS-ES spectrometer via 600μm optical fiber and with excitation of LLS-270 light-emitting diode (excitation wavelength maximum: $\lambda_{ex.}$ = 270 nm), picosecond pulse diode lasers EPL-385 ($\lambda_{ex.}$ = 385 nm) and LLS-530 ($\lambda_{ex.}$ = 518 nm) (all Ocean Optics B.V.). The maps of fluorescence excitation-emission, PLE maps, where the X axis is the wavelength of the fluorescence emission, $\lambda_{em.}$, and the Y axis is the wavelength of fluorescence excitation, $\lambda_{ex.}$, helped to analyze better the spectral data. PLE maps were recorded by a NanoLog excitation–emission spectrofluorometer (Horiba) using a silicon detector, a xenon lamp as an excitation light source, and 2 nm entrance/exit slits for the monochromators.

Quantum-chemical calculation of optimized molecular geometry were performed by DFT/CAM-B3LYP/6-31(d,p) methods; the electron transition characteristics were calculated by both semi-empirical ZINDO/S and non-empirical TD DFT/CAM-B3LYP/6-31(d,p) methods, using the package GAUSSIAN03 [9]. Essentially, there is no perfect match of the calculated and experimental data, that is typical, particularly for polymethine dyes [10-12]; however, it is enough to analyze correctly the nature of the first and higher excited states.

Results and Discussion

UV-Vis absorption spectra

The UV-Vis absorption spectra of dyes **1-3** in acetonitrile are shown on Fig. 2.
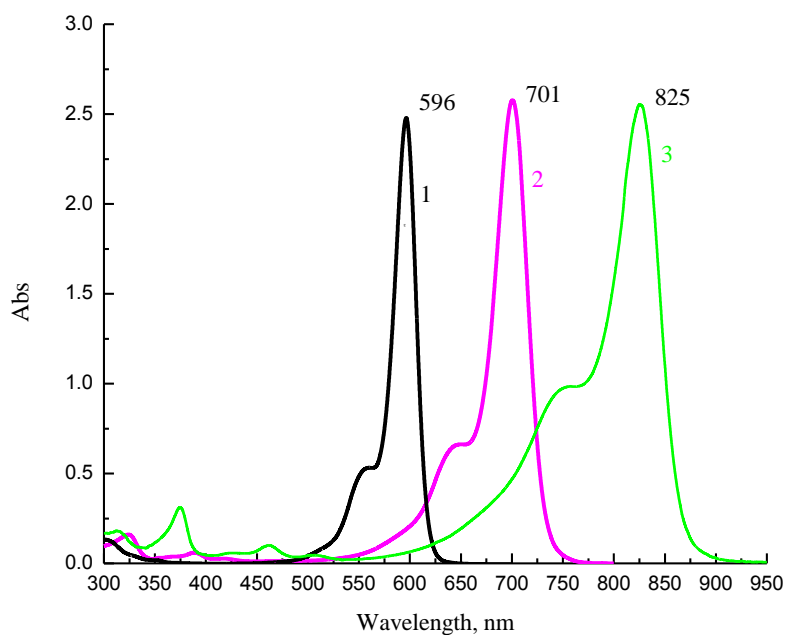

Fig. 2. UV-Vis absorption spectra and values of absorption maxima of the dyes **1-3** in acetonitrile ($C_M = 1 \cdot 10^{-5}$).

In Fig. 2, we observe the intensive long wavelength band in the visible and NIR spectral region. The extension of the conjugated system by introducing of new vinylene groups lengthening of the conjugated chain (**1** → **2, 3**) is accompanied by regular shift of the band maximum to longer wavelengths region. The additional appreciable peak at the short-wavelength side of the spectral band corresponds to the vibration $0 \rightarrow 1`$ transition that is typical for the polymethine (cyanine) dyes [6,10]. At the same time, broad unstructured spectral bands in the short-wavelength region are associated with the transitions from the higher electronic excited states.

The luminescence spectra

The maps of luminescence, PLE maps, for all three compounds are presented in Fig. 3 having excitation wavelengths $\lambda_{ex.} \geq 350$ nm; while steady-state luminescence spectra of compound **1** obtained by excitation at 270, 365, 518 nm are shown in Fig. 4.
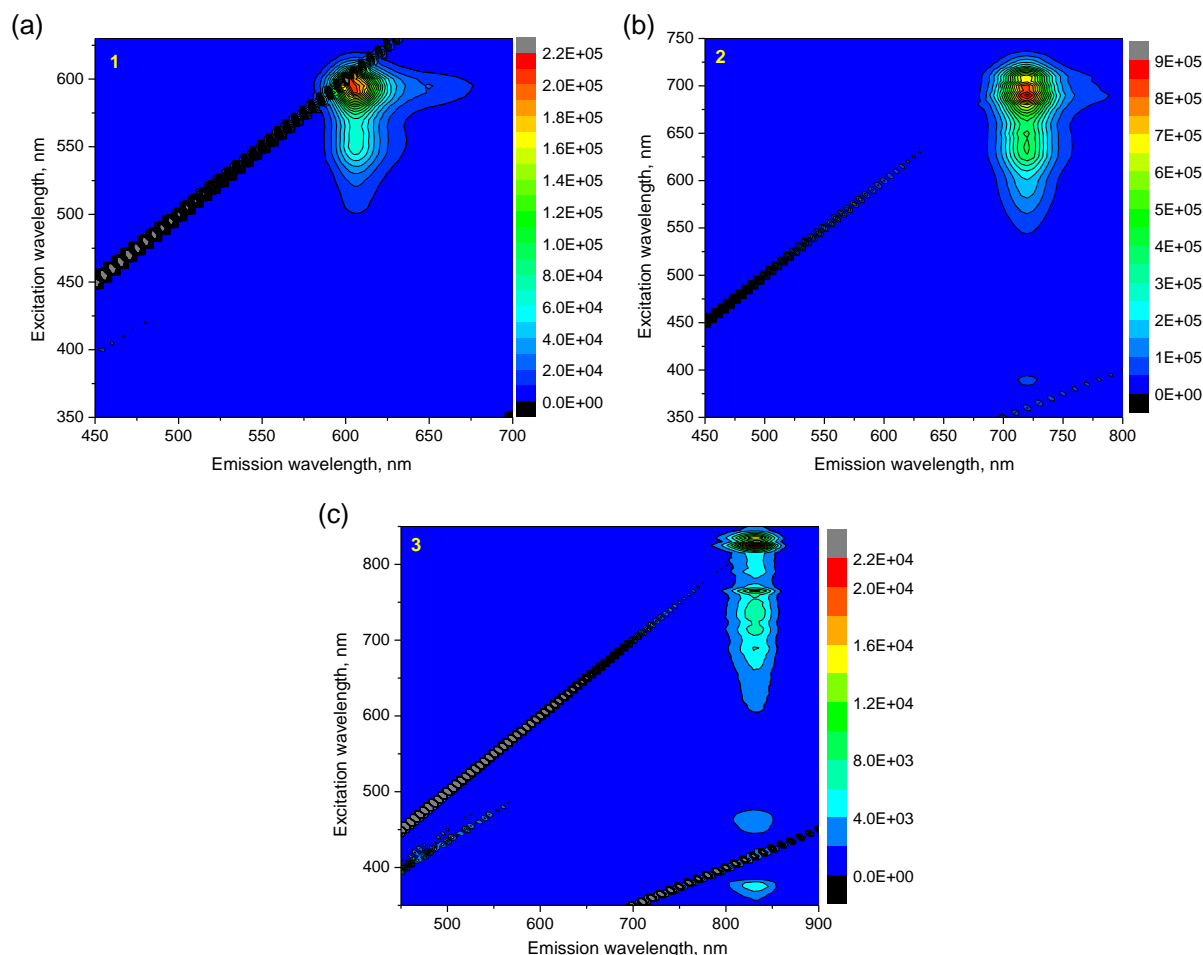

Fig. 3. PLE maps of dyes **1** (a), **2** (b) and **3** (c) measured in acetonitrile at the concentrations (C_M): $3.8 \cdot 10^{-6}$ (**1**), $3.7 \cdot 10^{-6}$ (**2**), $3.3 \cdot 10^{-6}$ (**3**).

It is clearly seen from both figures that the measured luminescence spectra explicitly and unambiguously depend on the excitation wavelength. As it follows from Fig. 3, the excitation nearby absorption region is accompanied by the trivial fluorescence from the lowest excited state; the fluorescence band maximum is regularly shifted to the long-wavelength region upon going to the higher homologues: dye **1** → dye **2** → dye **3**. The fluorescence maxima are in accord with absorption maxima in Fig. 2.

It is well-known that the long-wavelength fluorescence in cationic polymethine dyes corresponds to the Kasha's rule [11]. But in our case, as an interesting example, the different fluorescence bands are observed for the dye **1** upon populating the higher excited states: excitation at $\lambda_{ex.} = 270$, 385 or 518 nm.
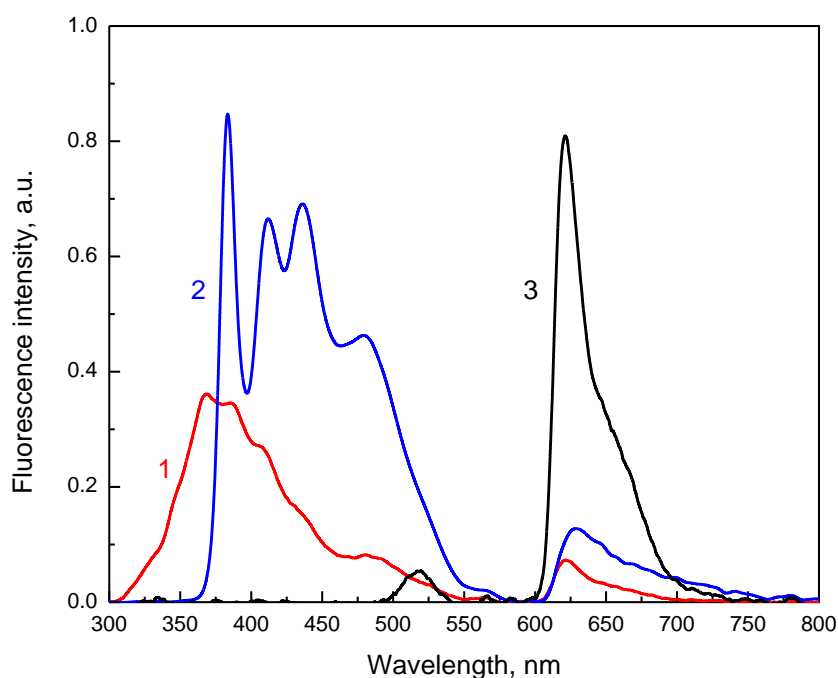

Fig. 4. Fluorescence spectra of the compound **1** in acetonitrile ($C_M = 1 \cdot 10^{-5}$) with $\lambda_{ex.} = 270$ nm (1), 385 nm (2) and 518 nm (3). The peaks of 385 nm in curve 2 and 518 nm in curve 3 are attributed to the scattered light of excitation.

Thus, Fig. 3 and Fig. 4 show that the luminescence of the all three compounds **1-3** in short-wavelength region from higher excited state should be associated with the higher excited electronic states. We suppose that these phenomena are related to the specific features of the excited states in the polymethine dyes containing the symmetrical pyrylium terminal groups.

Quantum-chemical modeling

To interpret correctly the nature of the lowest transitions, particularly appearance of unconventional luminescence, we performed the quantum-chemical calculations of the

molecular levels and electron transitions in the studied dye molecules. In Fig. 5, we demonstrate the generation of the frontier and nearest orbital involved in the lowest electron transitions.
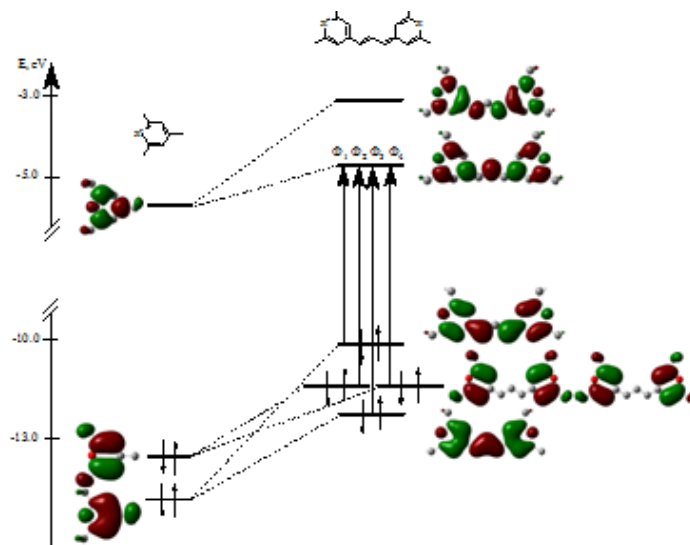

Fig. 5. Generation of MOs and excited configurations Φ_i from orbitals of initial heterocycle.

One can see that there are two following types of π-MOs in the dye molecules.

a) The *totally delocalized* orbitals; they are generated from the MOs of the initial heterocyclic moiety, which have not the MO mode at the carbon atom bonded with the conjugated chain, for example, LUMO, LUMO+1, HOMO, HOMO-3 (HOMO is the highest occupied MO and LUMO is the lowest unoccupied MO).

b) The *local* MOs; they are generated from the MOs of the both terminal residues, which have the MO mode at the bonding carbon, and hence these MO cannot take part in the total conjugation in the dye molecule (for example, HOMO-1, HOMO-2). As far as the dye molecules contain two terminal heterocycles, the initial levels are symmetrically double-split.

Correspondingly, two different types of the one-excited configurations should appear, as pictured in Fig. 5:

1) the configuration involved only the delocalized MOs;

2) the configurations involved also the local MO (so-called quasi-local

transitions) [3].

These configurations can be considered as components in the expansion of the functions Ψ^*_p (formula 1), which describe the electron excited state in the excited configurationally approximation:

$$\Psi^*_p = \sum T_{i \to j,p} | \Phi_{i \to j} >, \qquad (1)$$

where $| \Phi_{i \to j} >$ are the one-electron excited configurations involving *i-th* and *j-th* MOs, while $T_{i \to j,p}$ are expansion coefficients.

The calculated characteristics of some lowest electron transitions for the dyes **1-3** are collected in the Table 1. The analysis has shown that the both frontier MOs are totally delocalized along whole conjugated system; contrariwise, the HOMO-1 and HOMO-2 are located only within the terminal 6-membered pyrilium rings in all dyes. Then, the first electron transition $(| S_0 \to S_1 > = | HOMO \to LUMO >)$ is delocalized or polymethine transition. Also, the forth $(| S_0 \to S_4 > = | HOMO \to LUMO+1 >)$ transitions in the dyes **1** and **2** should be treated as a typical polymethine transition, by definition: the next lowest vacant is local MO, too. At the same time, in the dye **3** with the longest chain, the second and third transitions are delocalized (Table 1).

Table 1. Calculated characteristics of the lowest transitions in dyes **1-3** (ZINDO/S)

Dye	n	Transition	λ, nm	f	Main configuration
1	1	$S_0 \to S_1$	614 (435)	1.2945	0.98 $| HOMO \to LUMO >$
		$S_0 \to S_2$	382	0.0680	0.80 $| HOMO-2 \to LUMO >$
		$S_0 \to S_3$	381	0.1549	0.80 $| HOMO-1 \to LUMO >$
		$S_0 \to S_4$	342	0.1555	0.98 $| HOMO \to LUMO+1 >$
2	2	$S_0 \to S_1$	715 (492)	1.5788	0.94 $| HOMO \to LUMO >$
		$S_0 \to S_2$	380	0.1200	0.54 $| HOMO-2 \to LUMO >$ +0.63 $| HOMO-3 \to LUMO >$
		$S_0 \to S_3$	379	0.0616	0.63 $| HOMO-2 \to LUMO >$ -0.55 $| HOMO-3 \to LUMO >$
		$S_0 \to S_4$	369	0.2139	0.90 $| HOMO \to LUMO+1 >$
3	3	$S_0 \to S_1$	837 (562)	1.8113	0.97 $| HOMO \to LUMO >$
		$S_0 \to S_2$	412	0.0391	0.95 $| HOMO-1 \to LUMO >$
		$S_0 \to S_3$	400	0.2468	0.98 $| HOMO \to LUMO+1 >$
		$S_0 \to S_4$	378	0.0701	0.51 $| HOMO-2 \to LUMO >$ +0.56 $| HOMO-3 \to LUMO >$
		$S_0 \to S_5$	375	0.1203	0.56 $| HOMO-2 \to LUMO >$ -0.52 $| HOMO-3 \to LUMO >$

*ZINDO/S: OWF = 0.40; 25 lowest single excited configurations; bold numerals and letters point to the quasi-local transitions; wavelengths in bracket are obtained by TD DFT method

The transitions starting from any *quasi-local* orbital (HOMO-1 or HOMO-2) should be considered as *quasi-local transitions*. The results of calculations determine such nature for

the second and third transitions in the two dyes with the short chain (**1,2**), as well as the fourth and fifth transitions in the dye **3** with the longest conjugated chain. These transitions should be treated as *quasi-local* transitions with substantial charge transfer. As far as *polymethine* and *quasi-local* transitions differ substantially, the mutual transitions could be slower. It is the mutual disposition of polymethine and quasi-local excited states that leads to the suppression of Kasha's rule.

General scheme of luminescence in dyes **1-3**

Now, let us to consider a general scheme of electron transitions observed in absorption and luminescence (transitions upon the different equilibrium molecular geometries: ground S_0 and relaxed excited $S_i^{(R)}$ states), which is presented in Fig. 6.
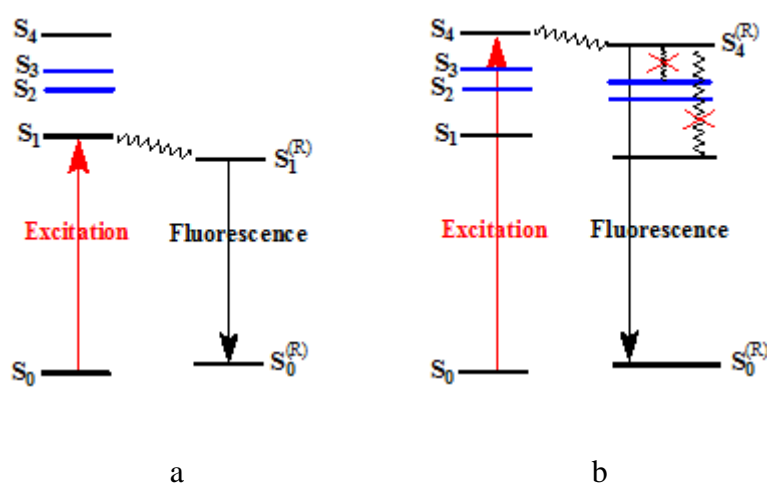

a   b

Fig. 6. Scheme of electron states and fluorescence-related transitions in dyes **1,2** (blue lines show quasi-local states).

One can see that two quasi-local states are squeezed between two delocalized excited states, S_1 and S_4, in dyes **1,2**. Similar picture is obtained from the calculations for the dye 3: the excited states are arranged one after another: S_1(deloc) — S_2(deloc) — S_3 (deloc) — S_4(loc) — S_5(loc) (see Table 1). Therefore, excitation by the photon of the enough low energy ($\lambda_{excitation} \approx \lambda^{absorption}$) leads to the ordinary relaxation in the state $S_1^{(R)}$ and further to

the conventional fluorescence (Fig.6a). Quite different process is observed upon excitation with the energy which is higher than the energies of the quasi-local transitions: $\lambda_{excitation} \ll \lambda^{local}$, i.e. $\lambda_{ex} < 400$ nm in our measurements (see Fig. 6b). This way, only the fluorescence from the higher excited state should appear that is observed experimentally.

Conclusions

Thus, the fluorescence from the higher excited states is experimentally detected in the vinylogous series of 4-pyrylocyanines. The conventional fluorescence band from the lowest excited state is shifted bathochromically with the lengthening of the polymethine chromophore, concurrently with shift in the absorption. According to the quantum-chemical modeling, the appearance of unusual fluorescence, which suppresses Kasha's rule, is associated with the different nature of the lowest excited states: the first and firth transitions are typical polymethine-type electron transitions involved only the totally delocalized MOs, whereas the second and third transitions correspond to the electron jumping from the degenerated MOs located only within the terminal groups (so called quasi-local MOs and hence quasi-local transitions). The forbiddance of the transitions between the excited states of different types stimulates the observed fluorescence from the higher excited states.

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