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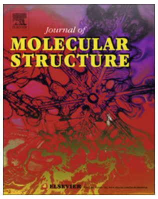

Electronic transitions in polymethine dyes involving local and delocalized levels

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HIGHLIGHTS

- Polymethine dyes producing *delocalized* and *local* molecular orbitals have been investigated.
- The *local* orbitals are characterized by the charge mainly localized within the terminal groups.
- Their existence leads to a generation of the specific *quasi-local* electronic transitions.
- They differ from the transitions between *delocalized* orbitals by sensitivity to the chain length.
- The *quasi-local* transitions can be experimentally detected by absorption or anisotropy spectra.

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ABSTRACT

Several series of polymethine dyes containing terminal groups, which can generate the *local levels* close to the HOMO/LUMO energy gap, have been investigated by spectroscopic and quantum-chemical methods. The analysis of the obtained data has shown that the participation of the *local levels* in the electronic transitions leads to the appearance of the specific *quasi-local transitions* which differ from the transitions between *delocalized* molecular orbitals by their sensitivity to the length of the π-conjugated chromophore and to the chemical constitution of the terminal groups. These *quasi-local transitions* can be experimentally detected by measuring of the ordinary absorption spectra or by the excitation anisotropy spectra, in case when their low-intensive bands are covered by the intensive absorption band. In the unsymmetrical dyes, containing different terminal groups, the *delocalized* and *quasi-local transitions* can be mixed producing complicated absorption spectra with two comparatively intensive bands, and their shapes can be gradually transformed upon the lengthening of the π-conjugated chromophore.

1. Introduction

The polymethine dyes (PDs) are well known for more than a century, however, their investigations are still continued due to permanent extension of their application areas (see, for example, reviews [1,2] and references therein). Besides traditional use of PDs as fluorescence probes and labels in chemistry and biology, initiators for polymerization reaction, active and passive components for tunable dye lasers [3–6], in the last decades they have shown a great potential for applications in nonlinear optics as optical materials exploring strong excited state absorption (ESA) and two-photon absorption (2PA) [2,7–10]. These variable applications stimulate further investigation of the electronic structures of PDs and the nature of their electronic transitions, especially, the nature of their high excited states, S_m ($m = 1, 2, \ldots, i$), serving as the final states in 2PA or ESA processes. Typically absorption spectra of PDs represent one highly intensive and relatively narrow ground-to-first excited state absorption band $S_0 \rightarrow S_1$, which can be easily shifted from the visible to near IR region by lengthening of the polymethine chain or/and by changing the donor–acceptor properties of the terminal groups [2,5,11]. Absorption into the higher lying states $S_0 \rightarrow S_m$ is typically much less intensive. One of the most powerful techniques for the investigation of these bands is known as excitation fluorescence anisotropy [2,4,6,12] allowing not only indicate the positions of $S_0 \rightarrow S_m$ bands but also estimate the angles between $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_m$ transition dipole moments. Excitation anisotropy spectra for many PDs with different length of conjugated chain and different terminal groups can be found in Refs. [2,13]. Modern laser systems and methodologies enable to probe S_2, S_3 and higher excited states by 2PA spectroscopy [2,9], or by ESA methods [12,13]. It was predicted by the quantum

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chemical calculations and observed experimentally that the $S_1 \rightarrow S_2$ electron transitions in the series of indopolymethinecyanine dyes are placed in the spectral region 1200–1400 nm [12]. However, their absorption cross sections are relatively small, in contrast to intensive ESA spectra in the visible region, 400–600 nm, corresponding to higher-lying $S_1 \rightarrow S_m$ transitions, with the cross sections comparable to ground state cross sections [14]. Despite of many linear and nonlinear properties of PDs are well studied, the properties of their higher electronic transitions still remain unclear and sometimes unpredictable. One of the important features in the electronic transitions of PDs is an appearance of the transitions connected with the molecular orbitals (MOs), which are mainly localized within the terminal groups, and thus could exhibit small transition dipole moments between the excited states. The existence of the different types of the electronic transitions in PDs, involving the *delocalized* and *local MOs*, recently shown in our previous paper [15], demands the detailed understanding of the nature of the higher electron transitions including their positions in the absorption spectra, symmetry, polarizations, intensities, etc. Thus, the goal of the current work is to investigate the influence of the different types of MOs on the nature of electronic transitions and some spectral properties of the symmetrical and unsymmetrical PDs with the different types of the terminal groups.

2. Materials and methods

The molecular structures of the investigated compounds are shown in Fig. 1. They are: model compounds, presented by the cationic unsubstituted polymethines (compound **1**) and PDs with the simplest branched phenyl terminal groups (compound **2**); PDs with the benzimidazol (compound **3**) and 2-azaazulene (compound **4**) terminal groups; a series of 2,6-diphenylthiopyrylium dyes with the different length of the chain (compounds **5**) and the corresponding salt (compound **6**), and a series of unsymmetrical dyes (compounds **7**) where one terminal group (xanthylium) remains the same, and another terminal group is changing to indolenine (compound **7b**), benzothiazole (compound **7c**) and quinoline (compound **7d**); compound **7a** corresponds to symmetrical PD with both xanthylium terminal groups. These dyes were chosen to illustrate the most typical cases of the formation of the *local* MOs and their influence to the electronic transitions displaying in the absorption spectra.

Synthetic procedures for compounds **3**, **4**, **5**, **6** and **7** are described earlier, correspondingly, in the Refs. [16–18]. All absorption spectra are recorded by a Shimadzu UV-3100 spectrophotometer in the small concentrations 10^{-5}–10^{-6} M to avoid aggregation effects.

2.1. Quantum-chemical calculations

The equilibrium geometries of the dye molecules in the ground state are optimized by the non-empirical HF/6-31G(d,p) and DFT/6-31G(d,p)/CAM-B3LYP methods (package Gaussian 03 [19]); the electronic transitions are calculated by TD DFT and semi-empirical ZINDO/S methods. Applied methods give a considerable divergence between the calculated and experimental data, which is known for PDs, especially absorbing in the near IR spectral region. However, important to note that these different methods are giving the same order of the MOs and same charge distributions within them, therefore, we suppose that we are able to analyze correctly the nature of the electronic transitions in a series of the investigated dyes.

3. Local and delocalized MOs

3.1. Model compounds *1* and *2*

It is obvious that in the unsubstituted linear π-electronic compounds, such as polymethine-cations, polymethine-anions and polyenes, all MOs are totally delocalized within the whole π-electronic system. As an illustration, the shapes of the frontier HOMO–

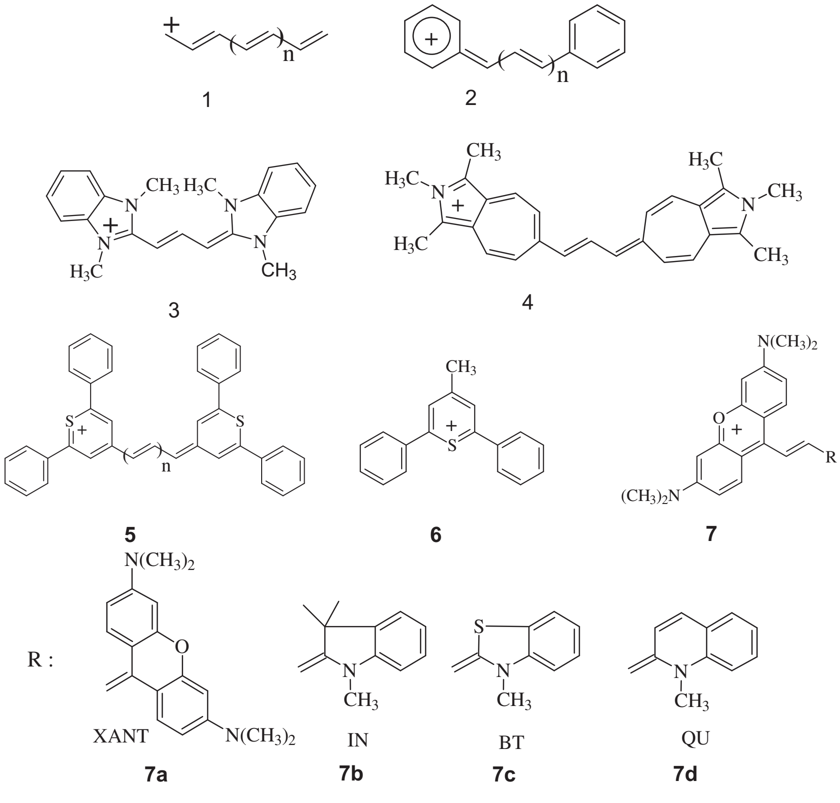

Fig. 1. Molecular structures of the investigated compounds.