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ORIGINAL RESEARCH

Study of excited state relaxation by time-resolved spectroscopy in conjugated substituted polyene bis-oxazoles

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Abstract

The simultaneous quantum-chemical and spectral investigations of the possible relaxation pathways in the excited state for the two α,ω-di-substituted polyenes were performed. Lengthening of the polymethine chain is accompanied by the considerable decreasing of the first electron transition and hence is manifested as the bathochromic shift of both absorption and fluorescence spectra; however, the nature of transition does not change. It is established that the considerable changes of the bond lengths in polymethine chain for both vinylogs in the excited state cause firstly the appearance of the fast component in short wavelengths spectral region; after relaxation, the intensity of the fast component decreases, and it disappears, but then the spectral band, shifted bathochromically, appears, so that its maximum coincide with the band maximum in the steady-state fluorescence maximum, what corresponds to the final symmetrical relaxation of bond lengths. The parallel quantum-chemical calculation shows that two highest levels are mainly formed by the donor levels of both terminal groups and hence twice occupied splitting levels. Upon excitation, one of the splitting MO (HOMO) becomes single occupied; this causes the molecule in the excited state to be unstable and could transform it to the unsymmetrical form. Such relaxation path is confirmed by the time-resolved spectra: the spectral band in both molecules, with the different polymethine chains, undergoes the subsequent bathochromical shifting.

Keywords Time-resolved fluorescence spectra · Substituted polyenes · Excited state · Symmetry breaking · Quantum-chemical calculations