

Generalized solvent scales as a tool for investigating solvent dependence of spectroscopic and kinetic parameters. Application to fluorescent BODIPY dyes.

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Streszczenie

Two difluoroboron dipyrromethene (BODIPY) based fluorescent dyes - 4,4-difluoro-3-{2-[4-(dimethylamino)phenyl]ethenyl}-8-[4-(methoxycarbonyl)phenyl]-1,5,7-trimethyl-3a,4a-diaza-4-bora-s-indacene (1) and 4,4-difluoro-3-[2-(4-fluoro-3-hydroxyphenyl)ethenyl]-8-[4-(methoxycarbonyl)phenyl]-1,5,7-trimethyl-3a,4a-diaza-4-bora-s-indacene (3) - have been synthesized via condensation of p-N,N-dimethylaminobenzaldehyde and 4-fluoro-3-hydroxybenzaldehyde, respectively, with 4,4-difluoro-8-[4-(methoxycarbonyl)phenyl]-1,3,5,7-tetramethyl-3a,4a-diaza-4-bora-s-indacene (2). UV-vis spectrophotometry and steady-state and time-resolved fluorometry have been used to study the spectroscopic and photophysical characteristics of in various solvents. The multi-parameter Kamlet-Taft { π^* , α , β } solvent scales and a new, generalized treatment of the solvent effect, proposed by Catalán (J. Phys. Chem. B, 2009, 113, 5951-5960), have been used in the analysis of the solvatochromic shifts of the UV-vis absorption and fluorescence emission maxima of 1-3, and the rate constants of excited-state deactivation via fluorescence ($k(f)$) and radiationless decay ($k(nr)$). The four Catalán solvent scales (dipolarity, polarizability, acidity and basicity of the medium) are the most appropriate for describing the solvatochromic effects. Solvent dipolarity and polarizability are the important causes for the solvatochromism of 1. Conversely, the absorption and emission maxima of 2 and 3 are hardly dependent on the solvent: the small changes reflect primarily the polarizability of the solvent surrounding the dye. Fluorescence decay profiles of 1 can be described by a single-exponential function in aprotic solvents, whereas two decay times are found in alcohols. The fluorescence decays of 2 (lifetimes τ in 1.9-2.9 ns range) and 3 (τ between 3.5 and 4.0 ns) are mono-exponential in all solvents studied. The fluorescence properties of dye are very sensitive to the solvent:

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upon increasing solvent dipolarity, the fluorescence quantum yields and $k(f)$ values decrease and the emission maxima become more red-shifted. The $k(f)$ values of 2 $[(1.6 \pm 0.3) \times 10^8 \text{ s}^{-1}]$ and 3 $[(1.5 \pm 0.2) \times 10^8 \text{ s}^{-1}]$ are practically independent of the solvent properties. The crystal structure of reveals that the BODIPY core is nearly planar with the boron atom moved out of the plane. The angle between the phenyl group at the meso-position and the BODIPY plane equals 80 degrees.

Adres publiczny

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