

Photophysics and stability of cyano-substituted boradiazaindacene dyes.

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The solvatochromic photophysical properties of two fluorescent, cyano-substituted BODIPY dyes—8-(4-bromophenyl)-3,4,4,5-tetracyano-4-bora-3a,4a-diaza-s-indacene (4CN) and 8-(4-bromophenyl)-3,5-dicyano-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (2CN)—have been studied in various solvents by UV-vis spectrophotometry and steady-state and time-resolved fluorometry. These two BODIPY analogues have comparable photophysical properties, implying that displacement of F by CN at boron has a negligible effect. Both compounds have high fluorescence quantum yields (Φ_f) (0.65–0.90 for 4CN and 0.63–0.88 for 2CN) in the solvents studied and display mono-exponential fluorescence decay profiles in nonprotic solvents. A new, generalized treatment of the solvent effect based on four mutually independent, empirical solvent scales (dipolarity, polarizability, acidity, and basicity of the medium) indicates that solvent polarizability and, to a lesser degree, solvent (di)polarity are crucial factors causing the solvent-dependent shifts of the UV-vis absorption and fluorescence emission. The rate constants of radiative deactivation (k_f) are nearly independent of the nonprotic solvent [$k_f = (1.4 \pm 0.1) \times 10^8 \text{ s}^{-1}$ for 4CN and $(1.5 \pm 0.2) \times 10^8 \text{ s}^{-1}$ for 2CN]. Both compounds undergo a color change in polar aprotic solvents (acetone, acetonitrile, and N,N-dimethylformamide), which can be stopped by addition of HClO₄. The kinetics of this color change indicates that the decomposition of these cyano-substituted BODIPY compounds is complex.

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