

Fluorescence Properties of Bis-pyrene Modified Photochromic Molecules

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Photochromic molecules such as diarylethenes and azobenzenes change their chemical and physical properties reversibly with their structural change by photoirradiation. The development of fluorescent photochromic compounds is important for applications to optical memories, biological markers, and super-high resolution imaging.^[1,2]

In this study, dithienylethenes or azobenzenes with two pyrene units were prepared as targets at a dual-mode fluorescence switch, and their photophysical, and fluorescence properties were investigated in acetonitrile. A bis-pyrene modified dithienylethen, 1,2-bis(2-methyl-5-(1-pyrenyl-methylcarbamoyl)-3-thienyl) cyclopentene (dae-py) was prepared by reaction of 1,2-bis(5-carboxy-2-methylthien-3-yl) cyclopentene^[3] with 1-aminopyrene using DMT-MM as a coupling reagent, and bis-pyrene modified azobenzenes, 4,4'-bis((pyrene-1-yl) butyl)carbamoyl azobenzene (azo-py1) and 3,3'-bis((pyrene-1-yl) butyl)carbamoyl azobenzene (azo-py2) were obtained by amidation of diaminoazobenzene with 1-pyrene butyric acid using COMU as a coupling reagent. These compounds showed reversible fluorescence switching according to photoisomerization of photochromic moieties. In the case of compound dae-py, the open form exhibited the strong broad fluorescence assigned to the intramolecular pyrene excimer in addition to pyrene monomer fluorescence. Upon irradiation with UV (313 nm), the open form underwent photoisomerization to closed form, and the both monomer and excimer emissions of pyrene units quenched, due to efficient quenching by resonance energy transfer to the diarylethene unit. In the case of azo-py1, and 2, the trans form exhibited pyrene monomer, and excimer emissions. In contrast, the cis form of azo-pys converted by irradiation with UV(365 nm), the intensity of excimer emission remained constant, and only pyrene monomer fluorescence quenched due to the energy transfer. The time-dependent density function theory (TD-DFT) calculations were carried out at the B3LYP/6-31+G (d,p) level using the standard Gaussian 09 software package. The conformational analysis simulation and the fluorescence time resolved spectroscopy studies suggested that there are relatively strong π - π interactions between pyrene units of dae-py in the ground state, although peaks assigned as dimer were not observed in their ¹H-NMR and uv-vis absorption spectra. We also report the results of the simulation and the fluorescence time resolved spectroscopy of azo-pys.

References:

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