疏水作用对光化学和光物理过程的影响 IV: 不良溶剂中双-β-萘甲酸多亚甲基二醇酯分子的构象及分子内激基缔合物

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摘要 本文研究了双-β-萘甲酸多亚甲基二醇酯(Bn)在二甲基亚砜-水(DMSO-H2O)和乙二醇-水(EG-H2O)两种混合溶剂中的稳态和时间辨荧光光谱以及温度、溶剂组成对荧光光谱的影响. 发现疏水作用使B3、B4、B5和B10的两个发色团在基态时相互重叠, 因此被激发时, 很容易形成分子内激基缔合物. B2的激基缔合物中, 两个亚甲基为顺叠式构象, 在基态时两个发色团只能相互靠近. 以减小排斥能. 受激后, 两个发色团需稍作运动, 才能形成激基缔合物, 测定了B2激基缔合物形成的动力学和热力学参数, 并和β-

萘甲酸酯发色团形成分子间激基缔合物的参数进行了比较.

大键词水反应动力学光化学羧酸酯DMSO乙二醇 P发色团荧光分光光度法构象荧光衰減激基缔合物萘甲酸 P国家自然科学基金

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Hydrophobic effects on photophysical and photochemical processes IV: The conformation of polymethylene bis- $\beta$ -naphthoates in poor solvents and their intramolecular excimer

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Abstract The fluorescence properties of polymethylene bis-b-naphthoates I (n = 2, 3, 4, 5, 10) in poor solvents such as DMSO-water and ethylene glycol-water were measured under stationary and nonstationary conditions at various temps. Hydrophobic interactions bring the two chromophores of I (n = 3, 4, 5, 10) into a sandwich arrangement in ground state, thus promote intramol. excimer formation upon excitation. The perfect overlapping structure for I (n = 2) can not be formed in ground state because of the eclipsed conformation of two methylene groups in such a sandwich arrangement. The favorable conformation for I (n = 2) is the structure in which the two naphthyl rings are in proximity. The activation energy, ethalpy and entropy changes for excimer formation of I (n = 2) were calculated from the fluorescence decay parameters.

Key wordsWATERREACTION KINETICSPHOTOCHEMISTRYCARBOXYLIC ACID ESTERDMSOETHANEDIOL PCHROMOPHORFLUOROSPECTROPHOTOMETRYCONFORMATIONFLUORSCENCEDECAYEXCIMERNAPHTHALENECARBOXYLIC ACID PNSFC

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