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基于对二烷基氨基苯甲酰苯胺分子内电荷转移的单糖比值法荧光受体

刘力宏, 张晗, 张焯, 江云宝\*

厦门大学化学化工学院化学系, 现代分析科学教育部重点实验室, 厦门 361005

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**摘要** 将苯甲酰苯胺(Benzanilide, BA)类CT反应基团与对二甲氨基苯甲酰胺(*p*-Dimethylaminobenzamide, DMABA)类CT反应基团耦合, 设计合成了对二烷基氨基苯甲酰苯胺硼酸衍生物1和2。荧光光谱研究表明, 1和2具有典型的双重荧光发射特征, 长波长荧光对溶剂极性表现出较强的依赖性, 为分子内电荷转移荧光。溶剂效应实验表明, 在极性较低的溶剂(如乙醚或环己烷/乙醚混合溶剂)中, CT荧光位于较长波长处, 荧光量子产率低, 为BA型CT荧光。随溶剂极性提高至乙醇, CT发射态转变为DMABA型, CT荧光位于较短波长处, 荧光量子产率较高。认为1和2的激发态同时存在着两类相互竞争的电荷转移通道。

1和2分子中均含有硼酸基团( $m\text{-B}(\text{OH})_2$ ), 其Hammett取代基常数为-0.01, 性质类似于-H。水溶液中, 随pH值提高, 硼原子的杂化态由 $sp^2$ 变更为 $sp^3$ , 成为硼负离子( $m\text{-B}(\text{OH})_3^-$ ), 后者的Hammett取代基常数为-0.48, 为强推电子取代基。它的产生促进了BA型分子内电荷转移, 导致荧光量子产率降低。

中性水溶液中, 硼酸基团与单糖发生反应, 亦可导致硼原子杂化态由 $sp^2$ 向 $sp^3$ 的转变。随单糖分子的加入, 1和2荧光光谱中的短波长荧光强度降低, 长波长荧光强度略有升高, 总荧光量子产率降低, 认为系由单糖与硼酸基团的结合改变了硼原子的杂化态, 使其推电子能力提高, BA型分子内电荷转移被促进所致。基于建立了单糖分子选择性传感的荧光强度比值法, 发现1和2对果糖的结合常数高于半乳糖、葡萄糖。将短波长荧光强度与单糖浓度关联, 拟合数值同样表明对果糖的结合能力强。比较1和2对果糖的结合常数, 表明将二甲氨基替换为二正丁氨基改善了该类分子对果糖的识别特性。

**关键词** [双重荧光, 比值法, 分子内电荷转移, 硼酸, 单糖](#)

分类号

## Ratiometric Fluorescent Receptors for Monosaccharides Based on the Intramolecular Charge Transfer in *p*-Dialkylaminobenzanilides

LIU Li-Hong, ZHANG Han, ZHANG Xuan, JIANG Yun-Bao\*

Department of Chemistry, the Key Laboratory of Analytical Sciences of the Ministry of Education, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, China

**Abstract** Two dual fluorescent receptors (1 and 2) for monosaccharides based on 4-dialkylaminobenzanilides (alkyl = methyl and *n*-butyl) containing boronic acid group at the amido aniline were synthesized and their spectral properties were investigated. These receptors exhibited dual fluorescence with the long-wavelength band displaying strong solvent-polarity dependence, indicating the occurrence of the excited-state intramolecular charge transfer (ICT). With increasing pH value in aqueous solutions, the hybridization of the boron atom changed from  $sp^2$  to  $sp^3$ , inducing a decrease in the total fluorescence quantum yield. The experimental results indicated that the anionic form of the boronate group acted as an electron donor and the benzanilide-like charge transfer was promoted upon hybridization change. In the presence of monosaccharides, the boronic acid in 1 and 2 changed from neutral to anionic form. The intensity of the locally excited (LE) state emission decreased in the presence of sugars while a slight increase in the intensity at the charge transfer (CT) emission occurred. Based on the change in the CT to LE intensity ratios of 1 and 2 due to sugar binding, ratiometric fluorescent assays for monosaccharide sensing were established.

**Key words** [dual fluorescence](#) [ratiometric receptor](#) [intramolecular charge transfer](#) [boronic acid](#) [monosaccharide](#)

DOI:

通讯作者 江云宝 [ybjiang@xmu.edu.cn](mailto:ybjiang@xmu.edu.cn)

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