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ORIGINAL ARTICLE

Novel 4,4′-Fluoresceinoxy Bisphthalonitrile Showing Aggregation-Induced Enhanced Emission and Fluorescence Turn off Behavior to Fe^{3+} Ions

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Abstract

A novel 4,4′-fluoresceinoxy bisphthalonitrile FPN is synthesized from fluorescein and 4-nitrophthalonitrile by aromatic nucleophilic ipso nitro substitution reaction. The structure of FPN constitutes phthalonitrile-fluorescein-phthalonitrile, acceptor-donor-acceptor, A-D-A form and the solvatochromic study of newly synthesized compound FPN was done in hexane, cyclohexane, $CHCl_3$, DCM, DMF, acetonitrile, ethanol and in methanol. The aggregation behavior of FPN was investigated in good-poor solvent mixture DMF-water in various proportions and the molecule was found to be exhibiting Aggregation Induced Emission Enhancement AIEE for volume percentage of water beyond 50% with a significant hypsochromic shift of 70 nm in the emission maxima from 458 to 388 nm. This phenomenon is termed as Aggregation Induced Blue Shifted Emission Enhancement AIBSEE and was reported in substituted phthalonitrile for the first time. The chemo sensing activity of FPN with various transition metal ions also has been checked by fluorescence spectroscopy where the new molecule FPN exhibited fluorescence turn OFF behaviour towards Fe^{3+} ion in acetonitrile-methanol ACN-MeOH solution. The binding stoichiometry of FPN with Fe^{3+} was verified by Job's plot analysis and Density Functional Theory DFT-B3LYP computational methodology by using Gaussian 09 software.

Keywords 4,4′-fluoresceinoxy bisphthalonitrile FPN · Aggregation induced blue shifted emission enhancement AIBSEE · Substituted phthalonitrile · Chemo sensing · Fe^{3+} ion

Introduction

Fluorophores absorb a wide range of wavelengths of light and they generally emit or fluoresce at a higher wavelength. This property allows to create or develop a large number of luminescent systems to meet the versatile demand of modern technology [1, 2]. A major class of these fluorophores is organic molecules with fused aromatic systems with extended π delocalization. The luminescent properties of the fluorophores in solution could be affected by aggregates formation, which mainly depends on several external factors such as concentration, polarity, nature of the solvent, temperature etc. [3]. In most of the cases, water is referred to as the aggregation causing solvent, on account of the hydrophobic interaction of fluorophores [4]. The natural tendency of luminophores to quench its own fluorescence at high concentration and at solid state by virtue of aggregate formation is termed as Aggregation Caused Quenching (ACQ), as first reported by Foster and Kasper in 1954 [5, 6]. This phenomenon imposes so many restrictions and questions the efficiency and practical utility of fluorescent materials [7] for their vast variety of applications as emitting material (in light emitting diode LED) [8], energy harvesting material (in Organic Solar Cells OSCs) [9], biological probe [10] for cellular imaging in aqueous media etc. But later, in contrast to the ACQ effect, Tang et al. found out a milestone observation of an abnormal phenomenon termed as "aggregation-induced emission" (AIE) as the inherently non-luminescent silole molecules were induced to emit light by aggregate formation [11, 12]. This ultimately

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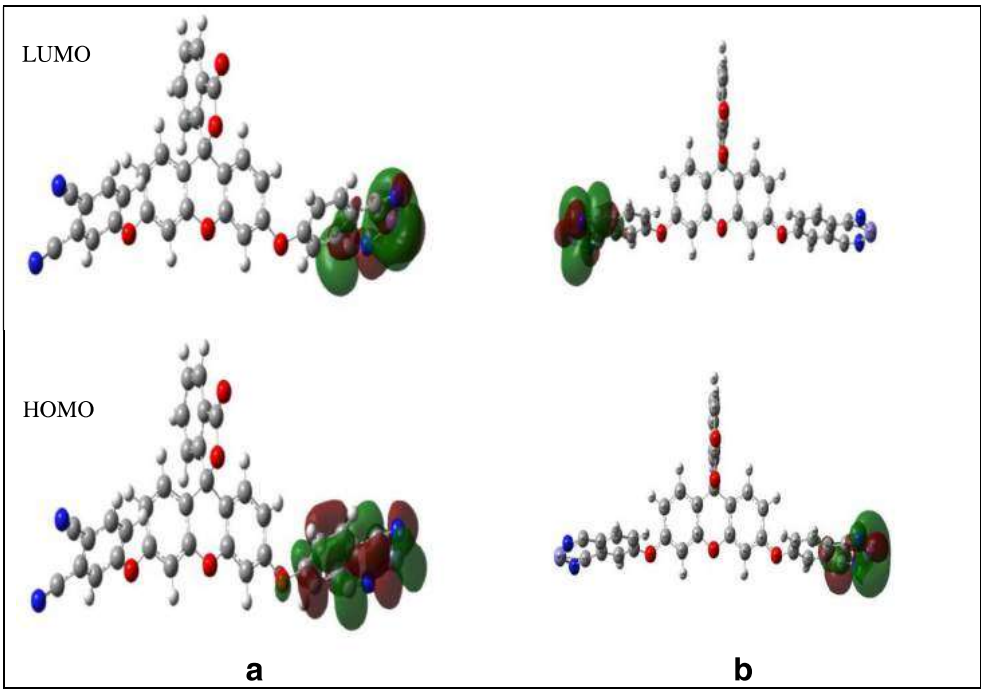

Fig. 13 HOMO-LUMO diagram of (**a**) 1:1 FPN-Fe complex, (**b**) 1:2 FPN-Fe complex

where it was found to be exhibiting AIEE property. As the volume of water exceeded beyond 50%, a hypsochromic shift of 70 nm was observed for λ_{em} from 458 to 388 nm, which is known as Aggregation Induced Blue Shifted Emission Enhancement, AIBSEE. This property can be explained on the basis of the Acceptor-Donor-Acceptor structural constitution of FPN, restricted intramolecular rotation (RIR) and twisted intramolecular charge transfer (TICT) processes and the formation of locally excited (LE) state of the molecule in the aggregated state. In addition to the aggregation study, chemo sensing behaviour of FPN was also checked towards various transition metal ions in ACN:MeOH (9:1 *v*/v) mixture, where the molecule FPN has selectively exhibited a fluorescence turn off behaviour towards Fe^{3+} ion with a LOD value of 14.49 μM. Job's plot analysis suggested that FPN binds with Fe^{3+} in 1:2 stoichiometric ratio where the two phthalonitrile units of one FPN unit bind with two Fe^{3+} ions. The computational studies pointed out that FPN could interact with Fe^{3+} both in 1:1 and 1:2 ratio as the HOMO of FPN-Fe complexes lies in range of the HOMO-LUMO gap of FPN. But the stabilization energy values of FPN-Fe complex invariably support the experimental observation, as E_{sta}(HF) of FPN-Fe complex in the 1:2 ratio is more negative than that in the case of 1:1 complex, so that the former one is more energetically favoured.

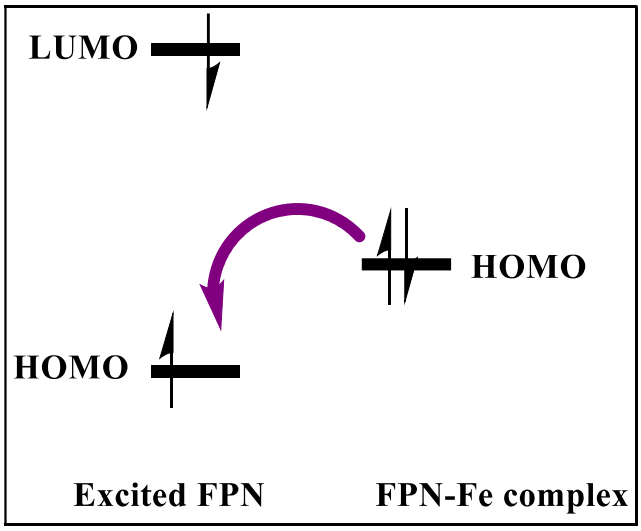

Fig. 14 Quenching of fluorescence

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Compliance with Ethical Standards

Conflict of Interest The authors declare no conflict of interest.

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