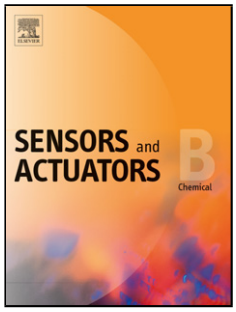

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Adenosine triphosphate-selective fluorescent turn-on response of a novel thiazole orange derivative via their cooperative co-assembly

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ABSTRACT

A novel Thiazole Orange (**TO**) derivative **3** has been synthesized and it could give the fluorescence turn-on responsive signal upon binding to nucleotides and besides, it exhibits high selectivity toward adenosine triphosphate (**ATP)** over other tested nucleotides. The nonlinear sigmoidal-responded pattern of the fluorescent spectra of **3** upon binding to **ATP** indicated that the positive cooperative interactions amplified the selective information. A possible co-assembled process of **3/ATP** was postulated based on the UV-Vis, fluorescent, ^{1}H NMR and DLS titrations.

1. Introduction

The molecular recognition and fluorescent sensing of nucleotides have attracted lots of attention and the adenosine triphosphate (**ATP**) is given particular concerns because of its role in energy source and extracellular signal-mediating functions in many biological processes [1,2]. In the last decade, a number of fluorescent responsive system toward **ATP** has been reported either by quenching or by increasing the fluorescent signal [3]. Among them, fluorescence "turn-on" responsive pattern would be of much more interests because the attained high signal-to-background ratio in this way is useful for their potential bioimaging studies [4], therefore, considerable efforts have been made to achieve this goal [5,6]. Although synthetic molecular receptors and fluorescent sensing systems for **ATP** have been extensively reported, however, the signaling mechanisms by their integration into molecular assemblies are still less investigated and the aggregation-induced emission (AIE) mechanism may represent one of this limited sensing methodologies.

Some conformationally restricted chromophores induced by target-triggered aggregation could switch its intrinsic non-fluorescent nature to a ''turn-on'' responsive character, which is called AIE. The applications of this mechanism for sensing DNA, proteins and biologically important small molecules like **ATP** have attracted increasingly attentions in recent years [7]. For examples [8], Zhang and his coworkers described that the silole's AIE could be used to monitor **ATP** hydrolysis as this molecule's fluorescence responded selectively toward **ATP** over **ADP** and **AMP**; Seiji Shinkai et al. reported that the **ATP**-induced self-assembly of guanidinium-tetraphenylethene produced the nonlinear fluorescence signal stronger than those induced by **ADP** and **AMP**. So far, however, the achieved selectivity of those limitedly reported AIE-based **ATP** sensing cases is usually remarkable over **ADP** and **AMP**, but less significant over other nucleobases, e.g., **GTP**. Considering the remarkable advantages of AIE mechanism, therefore, investigations of more specifically aggregated AIE molecules, could not only help to further understand this mechanism, but to elicit its more potentials acting as the more selective **ATP** sensing system, in terms not only of the phosphate anions of nucleotides, but also of their nucleobases moieties.

As AIE molecules usually own the intramolecular rotational and inherent nonradiative nature, thiazole orange (**TO**) would be categorized to this family. **TO** is actually nonfluorescent in aqueous solution because of its nonradiative deactivation caused by highly twisted exited-state conformation between the benzothiazole and quinoline groups around the monomethine bond, but it displays significant fluorescence enhancement once its torsional motion is restricted [9]. Although this unique responsive nature of **TO** makes it extensively explored and very popular in **DNA** intercalation and staining studies, its AIE properties receive attentions only recently in the investigation of its self-assembly properties in host-guest chemistry [10]. We herein synthesized a novel amphiphilic **TO** derivative, **compound 3** (**Scheme 1**) and found that it could cooperatively co-assembled with **ATP**, thus producing the non-linear responsive AIE signal. As such, taking the advantage of the AIE of **3** attained by its cooperative assembly with **ATP**, this molecule could give selectively response toward **ATP** over the other tested nucleotides.

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