

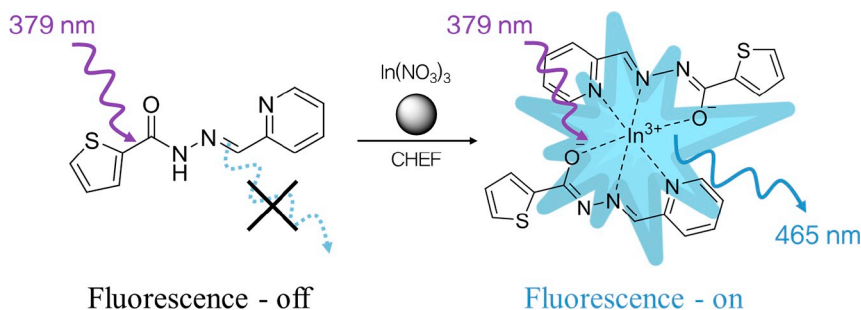
Short communication

A thiophene-based blue-fluorescent emitting chemosensor for detecting indium (III) ion

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GRAPHICAL ABSTRACT



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ABSTRACT

A thiophene-based chemosensor **TP**, ((*Z*)-*N'*-(pyridine-2-ylmethylene)thiophene-2-carbohydrazide), was synthesized and characterized. **TP** showed a significant fluorescence enhancement only in the presence of In^{3+} . Importantly, the detection limit was calculated to be 0.61 μM , which is the lowest one reported to date. Job plot and ESI-mass analyses indicated that two **TP** molecules bind to one In^{3+} ion. In addition, the sensing mechanism of **TP** towards In^{3+} was proposed as chelation-enhanced fluorescence (CHEF) effect from the theoretical calculations.

Indium, as one of the elements of group 13, is usually used in semiconductor devices like transparent electrical conducting films or screens, because compounds such as indium phosphide (InP) and indium tin oxide (ITO) are known to have high transmission in visible and near infrared regions [1,2]. In addition, indium could be used in biological fields such as radiopharmaceuticals or cancer therapy due to its relatively low toxicity and ability to damage DNA in cancer cells [3,4]. However, several reports have suggested that indium compounds such as ITO and InP have a potential risk for lung diseases [5].

With the increasing usage of indium, the possible dangers from indium are increasing. Therefore, methods for selectively detecting indium are highly demanded. Recently, various methods for detecting

indium ion have been reported such as molecularly imprinted polymer sensor [6], ion exchange chromatography [7], and adsorptive stripping voltammetry [8], but the methods need complicated procedures or skilled experts [9]. By contrast, chemosensors consisting of receptor-chromophore/fluorophore systems have attracted great attention due to their several benefits like economic efficiency or easy-handling [10–12]. Therefore, a number of chemosensors have been recently studied and developed for sensing metal ions [13–15]. In particular, fluorescent chemosensors are known to exhibit the low detection limit and high selectivity [16,17]. To date, several chemosensors for Al^{3+} and Ga^{3+} have been reported, but only a few chemosensors were developed for In^{3+} because of inhibition from the same group metal ions,

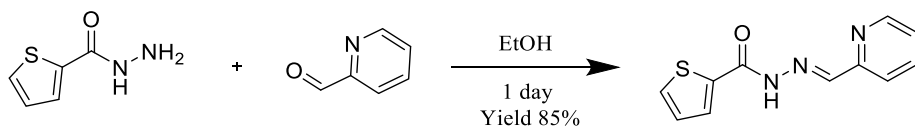
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Scheme 1. Synthesis of TP.

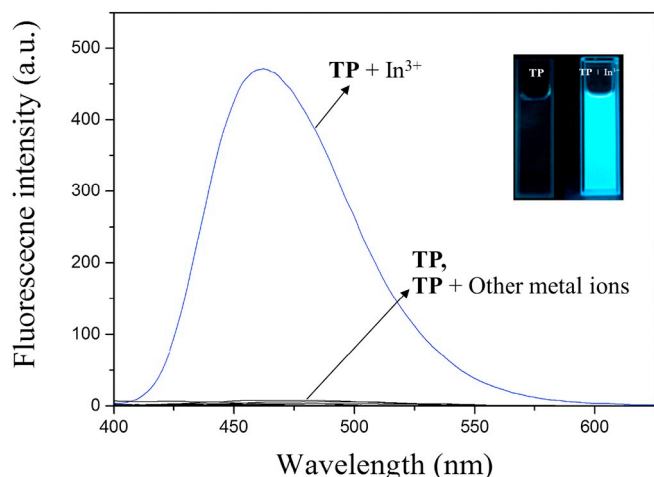


Fig. 1. Fluorescent variations of TP (5 μM) with various cations (5.0 equiv) with an excitation at 379 nm.

Al^{3+} and Ga^{3+} [18–21]. In addition, some chemosensors for In^{3+} simultaneously detect other trivalent cations together, and fluorescence quenching method is used instead of fluorescence enhancement [22–25]. Generally, fluorescence quenching is known as a less effective method than fluorescence enhancement because of their defects such as difficult detection against a dark background and false-positive signals [26]. Therefore, it is highly desirable to develop sensitive and selective chemosensors capable of distinguishing In^{3+} from Al^{3+} and Ga^{3+} ions by fluorescence turn-on method [22,23,27].

Thiophene is broadly used as light-emitting materials due to its excellent photophysical property [28]. Thus, the thiophene moiety with unique photo-property could be used in a part of chemosensor as a functional group [29,30]. Considering this feature, we designed to synthesize a new chemosensor TP, by combining thiophene-2-carbohydrazide with picolinaldehyde.

Herein, we present a novel chemosensor TP having high selectivity and sensitivity towards In^{3+} through fluorescence turn-on. TP can

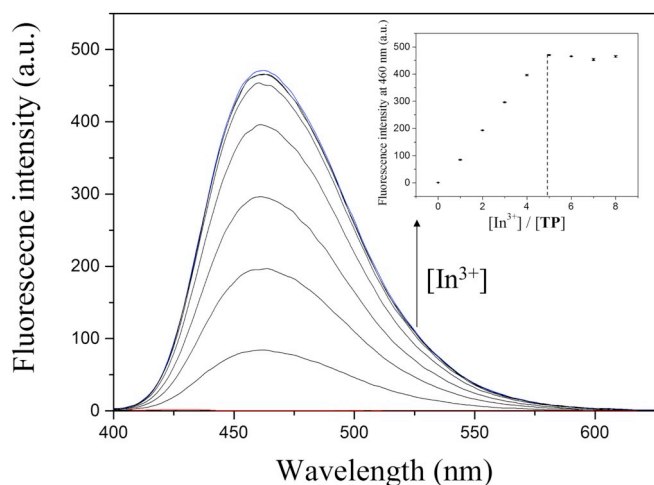


Fig. 2. Fluorescent changes of TP (5 μM) with the addition of In^{3+} . Inset: Fluorescent emission at 460 nm versus the number of In^{3+} added. Error bars represent standard deviations from three repeated experiments.

distinguish In^{3+} from Al^{3+} and Ga^{3+} with no interference. In addition, based on the spectroscopic experiments and theoretical calculations, probable binding mode and sensing mechanism for In^{3+} were described.

TP was produced by the combination of thiophene-2-carbohydrazide and picolinaldehyde with 85% yield in EtOH (Scheme 1; see Supporting information for details) and analysed through ^1H NMR, ^{13}C NMR and ESI-mass (Figs. S1 and S2). The fluorescent selectivity of TP towards various cations was achieved in EtOH (see Supporting information for details). When 5.0 equiv of the cations (Fe^{2+} , Co^{2+} , Mn^{2+} , In^{3+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Al^{3+} , Cu^{2+} , Na^+ , Fe^{3+} , Mg^{2+} , Ga^{3+} , Cr^{3+} , Hg^{2+} , Ca^{2+} , Ag^+ , Ni^{2+} and K^+) were added to the TP, only In^{3+} enhanced significantly a fluorescence emission at 460 nm (Fig. 1). By contrast, no obvious fluorescent response was observed from other metal cations under the identical conditions. The unique selectivity of TP to In^{3+} might be due to the combination of the size effect and the Hard-Soft principle. This result signified that TP could operate as a “turn-on” type fluorescent probe for In^{3+} . Importantly, TP could selectively detect In^{3+} from the same group metal ions Ga^{3+} and Al^{3+} , while several previously reported chemosensors for In^{3+} have difficulty in distinguishing In^{3+} from Al^{3+} and Ga^{3+} due to their similar properties [22,23].

To comprehend the spectroscopic characters of TP to In^{3+} , we performed the fluorescent titration. On the addition of In^{3+} to TP, the fluorescent intensity at 460 nm constantly increased until In^{3+} reached 5.0 equiv. (Fig. 2). Quantum yield (Φ) of TP at the fluorescence emission ($\lambda_{\text{max}} = 460 \text{ nm}$) was low ($\Phi = 0.00018$), while the fluorescent intensity clearly increased in the presence of In^{3+} ($\Phi = 0.01093$). The fluorescence enhancement might be due to CHEF effect. The non-radiative transitions such as C=N isomerization were inhibited, resulting in increase of fluorescence emission [31,32]. For studying binding properties between TP and In^{3+} , UV–vis titration was conducted (Fig. 3). The addition of In^{3+} to TP showed that the absorption band at 310 nm gradually decreased and a new band at 379 nm increased. Two defined isosbestic points were shown at 245 and 335 nm, signifying that only one species was produced from the reaction of TP with In^{3+} .

Job plot experiment was executed to analyze the binding mode between TP and In^{3+} (Fig. 4). The fluorescent emission at 460 nm reached a maximum at the molar ratio of 0.3, suggesting a 2:1 binding

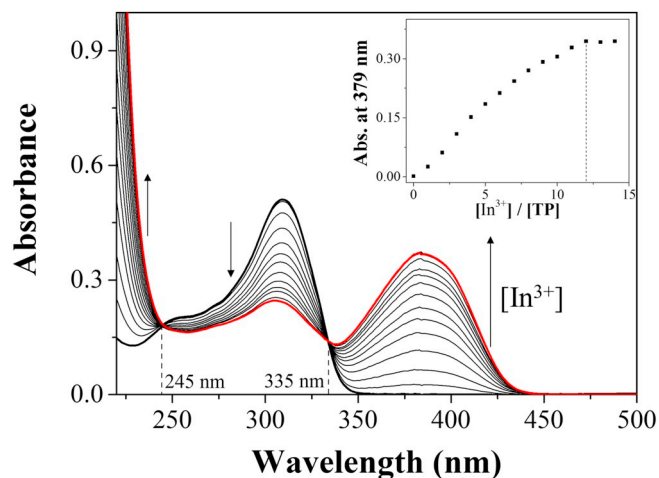


Fig. 3. UV–vis spectral variations of TP (10 μM) with the addition of In^{3+} ions by 1.0 equiv. Inset: Absorbance at 379 nm versus the number of In^{3+} added.

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