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Short communication

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

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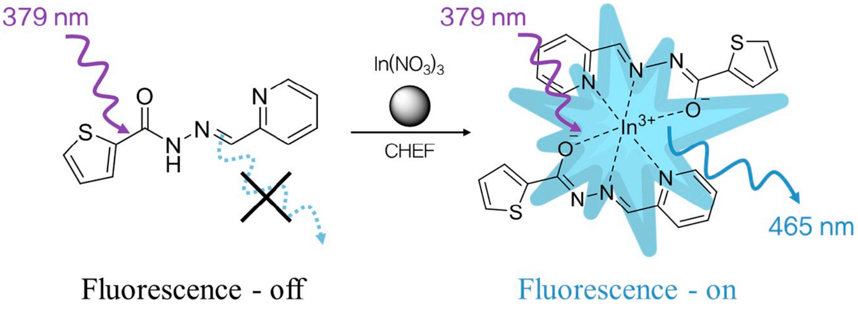
GRAPHICAL ABSTRACT



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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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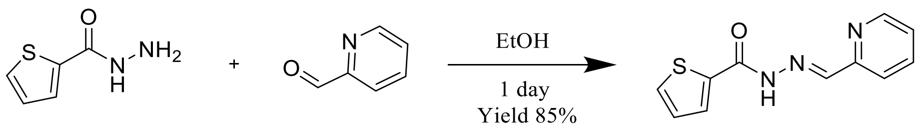


Scheme 1. Synthesis of **TP**.

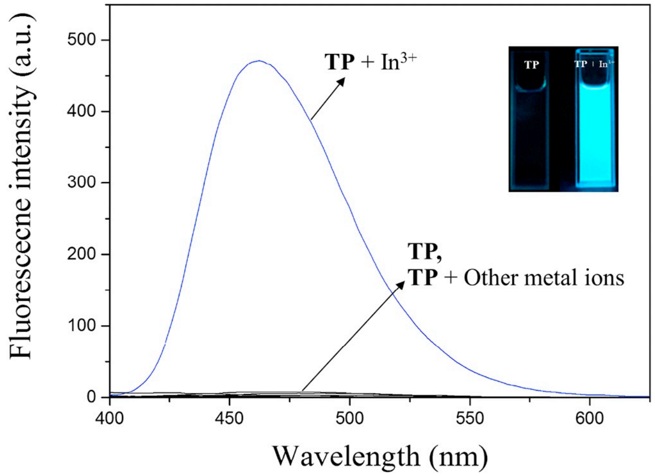


Fig. 1. Fluorescent variations of **TP** (5 μM) with various cations (5.0 equiv) with an excitation at 379 nm.

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 picolinalehyde.

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

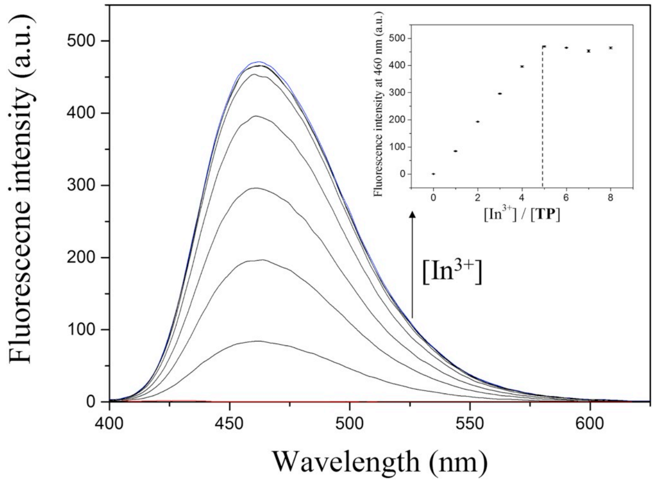


Fig. 2. Fluorescent changes of **TP** (5 μM) with the addition of In^{3+}. Inset: Fluorescent emission at 460 nm versus the number of In^{3+} added. Error bars represent standard deviations from three repeated experiments.

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 ^{1}H 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 (λ_{max} = 460 nm) was low (Φ = 0.00018), while the fluorescent intensity clearly increased in the presence of In^{3+} (Φ = 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

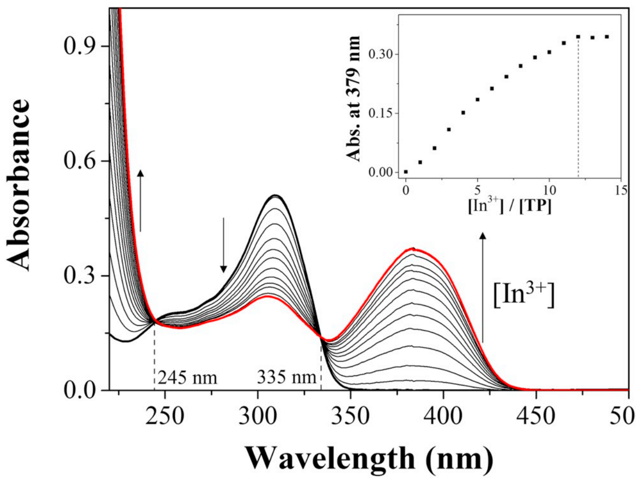


Fig. 3. UV–vis spectral variations of **TP** (10 μM) with the addition of In^{3+} ions by 1.0 equiv. Inset: Absorbance at 379 nm versus the number of In^{3+} added.

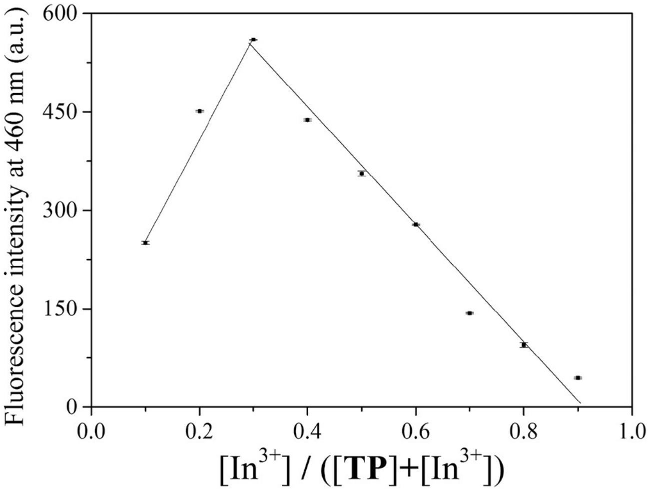


Fig. 4. Job plot for the reaction of **TP** with In^{3+}. Fluorescent emission at 460 nm was plotted as a function of the molar ratio $[In^{3+}]/([\mathbf{TP}] + [In^{3+}])$. The total concentration of indium ions with **TP** was 50 μM. Error bars represent standard deviations from three repeated experiments.

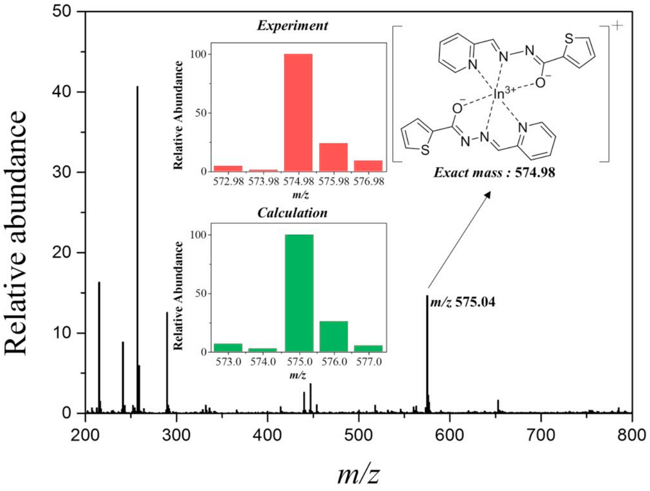


Fig. 5. Positive-ion mass spectrum of **TP** (0.1 M) upon addition of $In(NO_3)_3$ (5.0 equiv).

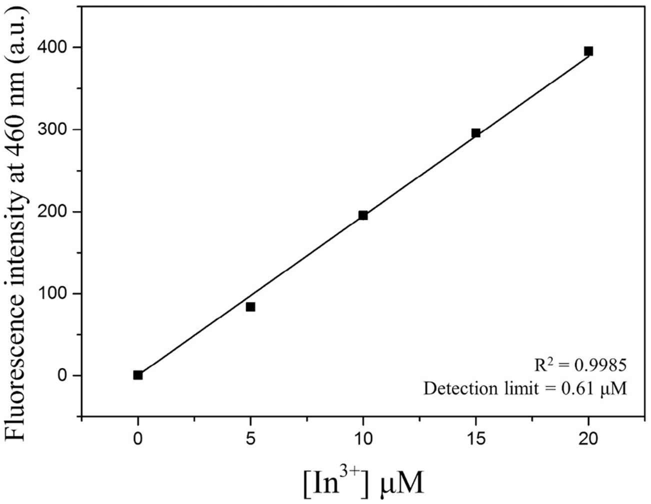
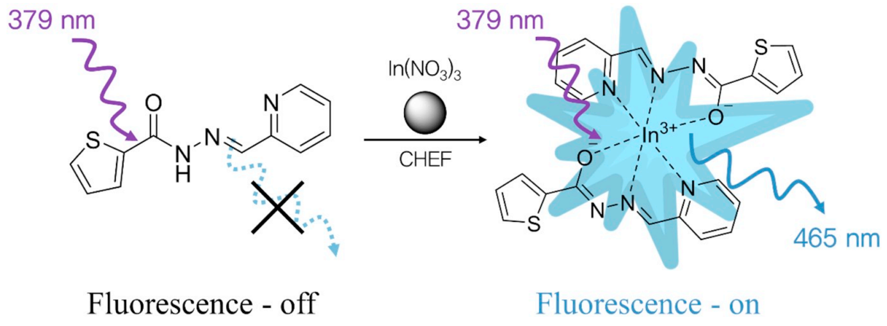


Fig. 6. Detection limit of **TP** (5 μM) towards In^{3+} based on 3σ/slope. Error bars represent standard deviations from three repeated experiments.

ratio. In addition, it was verified by ESI-mass spectrometry (Fig. 5). The mass spectrum displayed a peak at $m/z = 575.04$, which is assignable to $2\cdot\mathbf{TP} - 2H^+ + In^{3+}$ [calcd, $m/z = 574.98$], supporting the 2:1 binding mode. To further study the binding interaction of **TP** and In^{3+}, ^1H NMR titration was examined (Fig. S3). Upon addition of In^{3+} to the **TP** solution, the proton of amide group (H_4) completely disappeared. In addition, the imine proton H_5 and the protons H_7, H_8 and H_9 in the pyridine moiety shifted to downfield. These results led us to assume that the carbonyl oxygen, the imine nitrogen and the pyridyl nitrogen might coordinate to In^{3+}. On the basis of Job plot, ESI-mass spectrometry analysis, and ^1H NMR titration, we proposed the plausible structure of In^{3+}-2·**TP** (Scheme 2). The association constant of $8.1 \times 10^4\ M^{-2}$ was determined for In^{3+}-2·**TP** complex, based on Li's equation (Fig. S4) [33]. Detection limit (3σ/slope) of **TP** towards In^{3+} turned out to be 0.61 μM (Fig. 6) [34], which is the lowest among those of turn-on chemosensors previously reported for In^{3+} (Table S1).

To investigate the possible inhibition from other cations in the detection of In^{3+}, we conducted competition test with other competitive metal ions (Fig. S5). Most metal ions interfered fluorescent emission of **TP** (Fig. S5(a)). Nevertheless, as shown in Fig. S5(b), fluorescent emission was still observable with most cations, except Cu^{2+}, Ni^{2+} and Pb^{2+}.

On the basis of Job plot and ESI-mass analyses, the structures of **TP** and In^{3+}-2·**TP** were optimized using DFT calculation as shown in Fig. 7. **TP** with a dihedral angle of −0.031° (1O, 2N, 3C, 4N) has a nearly flattened structure (Fig. 7(a)). In^{3+}-2·**TP** shows a slightly distorted octahedral structure (Fig. 7(b)). Its dihedral angle for 1O, 2 N, 3C, and 4 N is 0.777°. Using energy-optimized structures of **TP** and In^{3+}-2·**TP**, TD-DFT calculations were conducted for studying transition energies and molecular orbitals. For **TP**, the main absorption band was originated from the HOMO → LUMO transition (321.90 nm, Fig. S6). Its transition character indicated $\pi \rightarrow \pi^*$ transition. On the other hand, red-shifted absorption band of In^{3+}-2·**TP** was originated from HOMO − 1 → LUMO + 1, and HOMO → LUMO transitions (408.59 nm, Fig. S7). These transition characters represented intramolecular charge transfer (ICT) from the thiophene ring to the pyridine one (Fig. S8). The red shift observed in the experimental UV–vis spectra is consistent with ICT and



Scheme 2. Proposed binding structure of In^{3+}-2·**TP**.

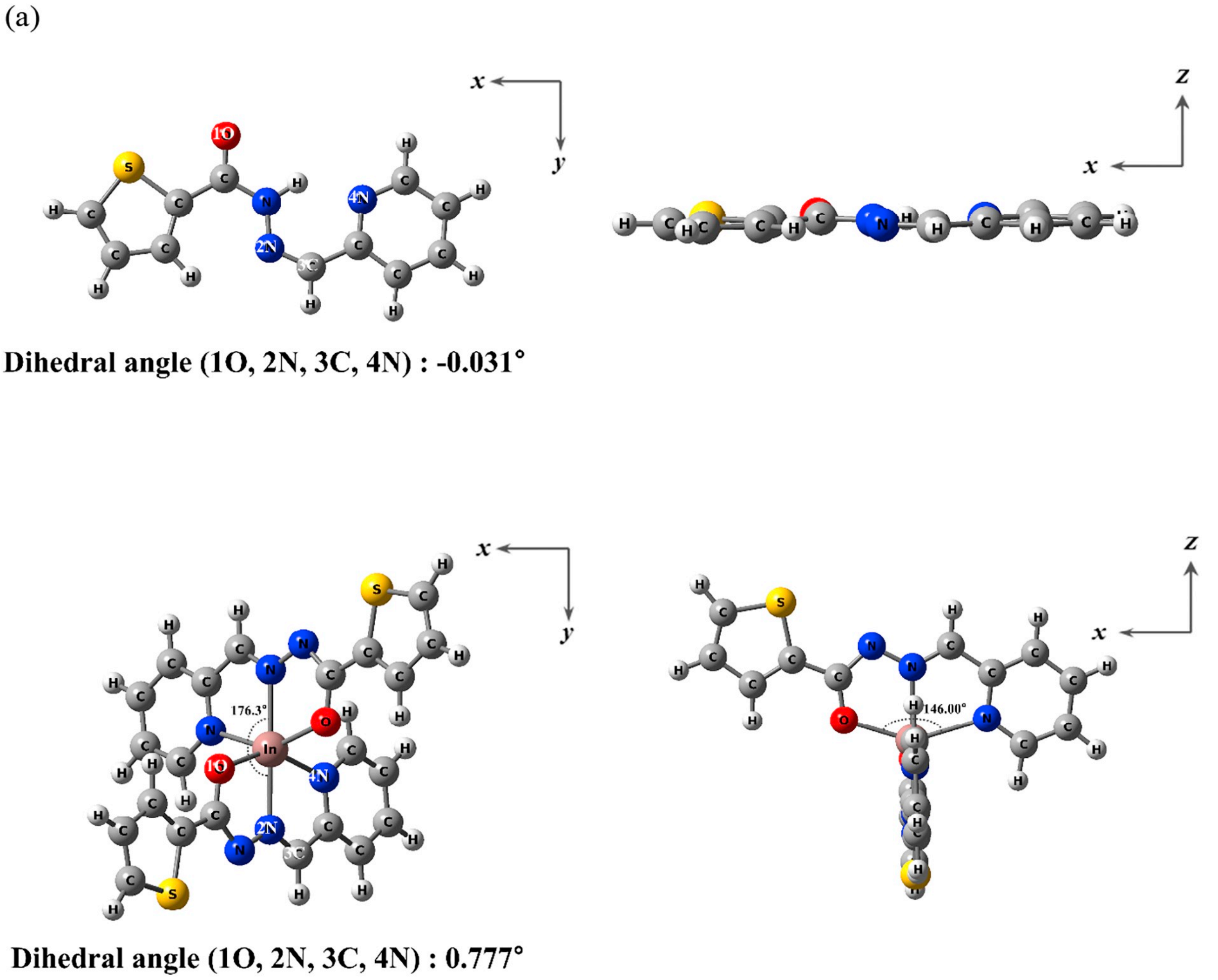


Fig. 7. Energy-optimized structures of (a) **TP** and (b) In^{3+}-2·**TP** complex.

also corresponded to decreased HOMO-LUMO energy gap.

In conclusion, we presented a novel fluorogenic chemosensor **TP** for In^{3+}. **TP** showed the high selectivity to In^{3+} by fluorescence turn-on method. In addition, **TP** could successfully distinguish In^{3+} from the same group metals, Al^{3+} and Ga^{3+}. Importantly, detection limit of **TP** for In^{3+} ion was calculated to be 0.61 μM, which is the lowest among those previously reported for fluorescent turn-on In^{3+} chemosensors. Fluorescence turn-on mechanism of **TP** towards In^{3+} was proposed as CHEF effect. We think that these results could contribute to developing a new kind of sensors for detection of In^{3+}.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2018.09.037.

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