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Highly sensitive fluorescent sensor targeting CuCl_2 based on thiophene attached anthracene compound (TA)

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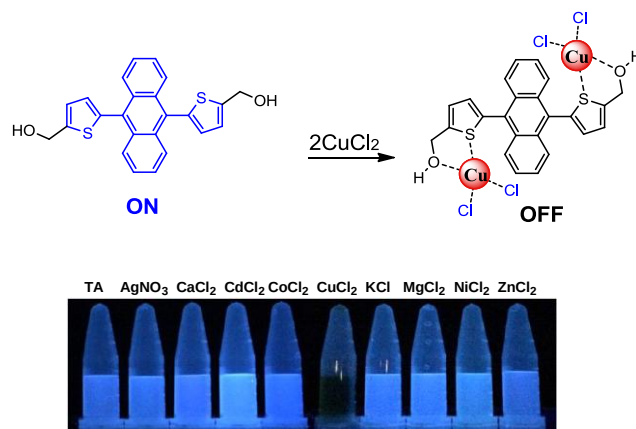
ABSTRACT

A novel thiophene attached anthracene (**TA**) based fluorescent compound was designed and synthesized. The **TA** showed a high quantum yield ($Q_y=0.34$) in regard to fluorescence. We applied this **TA** compound to detect specific metal compound and found that it could identify CuCl_2 from other metals through dramatic fluorescence change at $\lambda_{\text{max}} = 460$ nm. It showed strong quenching fluorescence property with CuCl_2 while with other metal compounds it exhibited strong blue fluorescence emission. UV/Vis absorption spectroscopy clearly demonstrated that the quenching property of **TA** at $\lambda_{\text{max}} = 460$ nm was due to overlapping of the fluorescence peak of **TA** at $\lambda_{\text{max}} = 460$ nm and the absorption band of CuCl_2 (from 190 nm to 525 nm). Binding constant (K'), which was 0.0895 mM^{-2} , indicated a complexation ratio between **TA** and CuCl_2 as 1:2 and this interaction induced quenching property.

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Development of novel types of photochromic compound is exceedingly important due to the possibility of their diverse applications especially for sensing of metal,¹ small molecule,² macromolecule³ and biomolecule.⁴ Fluorescent molecules are particularly sensitive to the changes in environment⁵ and thus they could be used for diverse diagnostics, molecular imaging, and biophysics areas.⁶ Thus, our goal is to develop novel fluorescent compound which is very sensitive to a specific material. Anthracene is a unique fluorescence material that has high fluorescence quantum yield, and can form dimerized structure under light illumination.⁷ Thiophene is also a unique heterocyclic aromatic compound that can be used in thiophene-based oligopolymers to utilize the high electrical transfer property.⁸ Our strategy to develop a photochromic compound involved combination of two units of anthracene and thiophene to generate a material with novel photophysical property. Based on this concept we designed and synthesized a thiophene attached anthracene compound (**TA**). Herein, we report a particular photophysical property of thiophene-based anthracene (**TA**) which has remarkable sensitivity to a specific metal, CuCl_2 .

First, to obtain thiophene attached anthracene compound at two symmetric positions, a two-step reaction was performed. In the first step, (5-bromothiophen-2-yl) methanol (**2**) compound was



Scheme 1. Structure of thiophene attached anthracene (**TA**) and its photo sensing ability to the specific metal.

synthesized from 5-bromo-2-thiophenecarboxaldehyde (**1**) via reduction using sodium borohydride (NaBH_4). Next, we coupled it with anthracene-9,10-diboronic acid bis(pinacol) ester (**3**) to produce thiophene attached anthracene compound (**TA**) using Suzuki coupling condition (Scheme 2).

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