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

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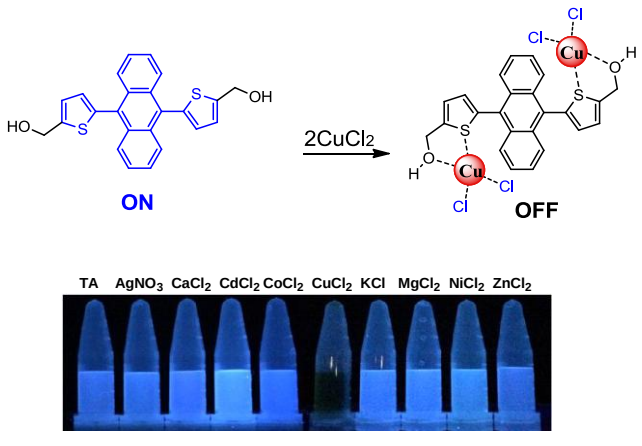
ABSTRACT

A novel thiophene attached anthracene (**TA**) based fluorescent compound was designed and synthesized. The **TA** showed a high quantum yield (Qy=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 λ_{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 λ_{max} = 460 nm was due to overlapping of the fluorescence peak of **TA** at λ_{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.

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] macromolecule[3] and biomolecule.[4] Fluorescent molecules are particularly sensitive to the changes in environment[5] 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-bromothien-2-yl) methanol (**2**) compound was 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).



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

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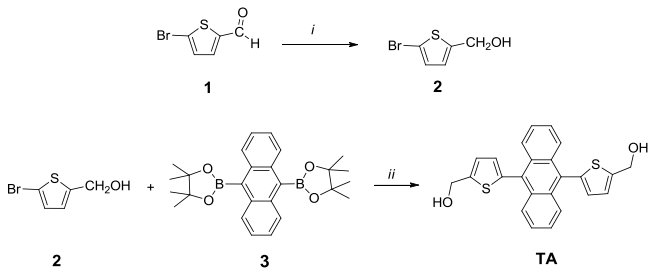

Scheme 2. Design and synthesis of thiophene attached anthracene fluorescence compounds. Reagents and conditions: i. $NaBH_4$, MeOH, rt, 2hr, 63% yield; ii. $Pd(PPh_3)_4$, K_2CO_3, 1,4-dioxane-H_2O, reflux, 90˚C, 2hr, 62% yield.

To check the basic photo physical property of our **TA** compound, we measured the UV/Vis spectra and chose the excitation wavelength at λ_{max}=374 nm. Emission wavelength was obtained at λ_{max}=460 nm using the excitation wavelength, λ_{max}=374 nm (Fig. 1). To note, the **TA** exhibited a high quantum yield Qy=0.34 in MeOH, which was strong enough for diverse applications (see supplementary information).

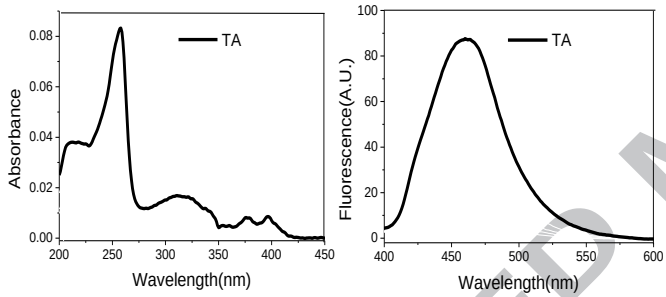

Figure 1. UV/Vis absorption spectra and fluorescence spectra of **TA** compound. All samples were prepared at a concentration of 1 µM of **TA** in MeOH. We used λmax=374 nm wavelength for the excitation.

We examined the potential of TA as a metal sensor by screening several different metal compounds, such as **$ZnCl_2$**, **$AgNO_3$**, **$CaCl_2$**, **$CdCl_2$**, **$CoCl_2$**, **$CuCl_2$**, **KCl**, **$MgCl_2$**, and **$NiCl_2$** in DMSO solvent. Noticeably, as shown in Fig.2a, fluorescence spectra exhibited selective discrimination property toward the above-mentioned metals. All the metals, viz. **$ZnCl_2$**, **$AgNO_3$**, **$CaCl_2$**, **$CdCl_2$**, **$CoCl_2$**, **KCl**, and **$MgCl_2$** exhibited high fluorescence signal at the λ_{max}= 440 nm except **$NiCl_2$,** which exhibited a small redshifted emission at λ_{max} = 465 nm. Furthermore, with addition of the **TA** compound to a solution contain 50mM of **$CuCl_2$**, a dramatic quenching property could be realized which can be used to identify **$CuCl_2$** from other metals. The photo in Fig. 2b clearly shows the quenching property for **$CuCl_2$**, while all other metals exhibited a moderate fluorescence (Fig. 2b).

To understand the origin of this fluorescence signal change, UV/Vis absorption spectra of each metal were measured (Fig. 2c). The UV absorption spectra indicated that the absorption wavelengths of the metals except **$CuCl_2$** did not overlap with the emission wavelength of **TA.** The absorption wavelength of **$CuCl_2$** completely overlapped with the fluorescence wavelength of **TA** broadly covering the absorption wavelength from 190 nm to 520 nm. From these results, we assume that the fluorescence quenching of **TA** by **$CuCl_2$** may be originated from the excited electron of **TA** transfer to the absorption of **$CuCl_2$**.

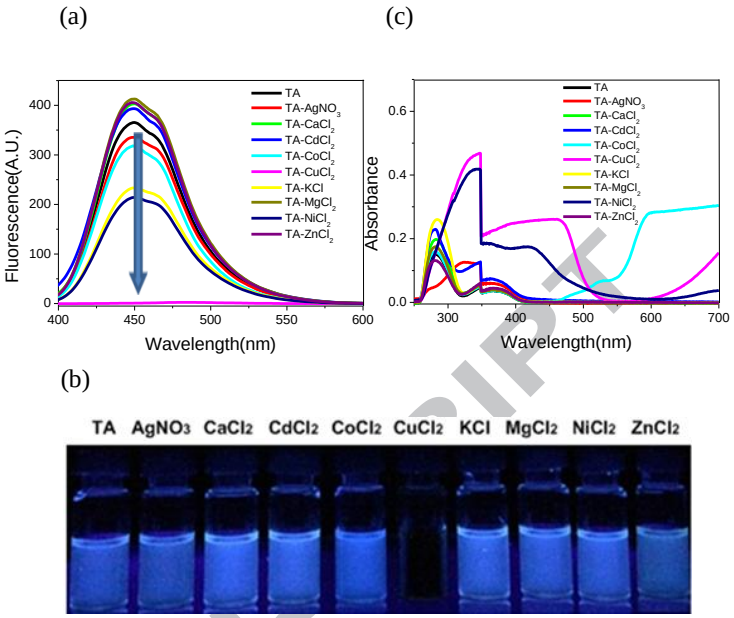

Figure 2. (a) Fluorescence spectra, (b) Photo image, and (c) UV/Vis spectra of **TA** compound with different metals in DMSO. All samples were prepared in DMSO at 25ºC in a concentration of 3 µM of **TA** and 30 mM of each metal. We used λmax=374 nm wavelength for the excitation.

To further clarify the quenching property of **TA** we changed the solvent from DMSO, the polar aprotic solvent to water, which is a polar protic solvent and measured the UV/Vis absorption spectra (Fig. S10A). Interestingly, the absorption wavelength of **$CuCl_2$** changed to the range from (190 nm – 520 nm) to (190 nm – 310 nm), which did not overlap with the wavelength of fluorescence of **TA** at λ_{max}=460 nm and no quenching property could be observed (Fig. S10B). This result strongly suggested that the quenching of **TA** by **$CuCl_2$** originated from overlapping of the fluorescence wavelength of **TA** and the absorption wavelength of **$CuCl_2$**.

Next, we focused on studying the interaction between **$CuCl_2$** and **TA** compound. For this purpose, fluorescence titrations of **TA** (3 µM) with various concentrations of **$CuCl_2$** in DMSO were performed (Fig. S11). As shown in Fig 3, the fluorescence emission intensity at 460 nm decreased gradually upon the addition of from 1mM **$CuCl_2$** and complete quenching could be observed at 30 mM of **$CuCl_2$**. To determine interaction ratio and binding constant (K) of this complex, the Benesi–Hildebrand double reciprocal method was employed using the following two equations (see supporting information for detail information): [9]

We calculated both the equations and obtained two corresponding graphs at high concentration of **$CuCl_2$** range from 3 mM to 30 mM. Equation (1) did not produce a linear fit line to calculate binding constant value (Fig. S12). Thus, any possibility of binding between **$CuCl_2$** and **TA** in the ratio 1:1 was excluded. However, following equation (2), we could obtain a linear fit line with 1:2 complexions. From this result, we confirm that **$CuCl_2$** molecule tend to bind with S and O atoms on each side. As shown in figure 4, the intercept and slope of the fitted straight line gave the binding constant, K' = 0.0895 mM^{-2}. This result also indicated that interaction ratio between **TA** and **$CuCl_2$** was 1:2. Therefore, it can be inferred that two **$CuCl_2$** molecules and one **TA** molecule formed complex through S and O atoms at both symmetric sides of the **TA** molecule and exhibited a complete quenching.

$$\frac{1}{F_0 - F} = \frac{1}{F_0 - F_m} + \frac{1}{K[CuCl_2](F_0 - F_m)} \quad (1)$$

$$\frac{1}{F_0 - F} = \frac{1}{F_0 - F_m} + \frac{1}{K'[CuCl_2]^2(F_0 - F_m)} \quad (2)$$

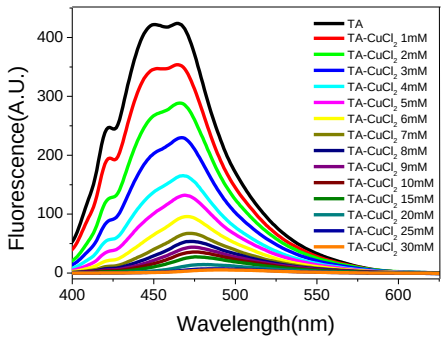

Figure 3. UV/Vis spectra and Fluorescence spectra of **TA** compound in DMSO with the present of **$CuCl_2$** at the different concentrations. All samples were prepared at 25ºC at a concentration of 3 µM of **TA**. We used λ_{max}=374 nm wavelength for excitation.

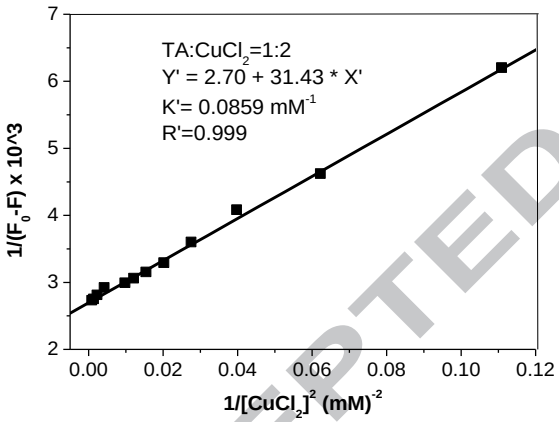

Figure 4. Plot of 1/(Fo−F) vs. 1/[**$CuCl_2$**]^2 to determine the binding constant and the stoichiometry for **$CuCl_2$** binding to **TA** in DMSO. The concentration of **$CuCl_2$** is ranging from 3 mM to 30 mM. The samples were measured at 374 nm.

From all the above-mentioned results, we suggest that the **TA** compound can be used as a novel fluorescence material to sense specific metal, such as **$CuCl_2$**.

In conclusion, a thiophene attached anthracene compound (**TA**) was developed as a novel fluorescence material to sense specific metal. **TA** exhibited fluorescence emission at λ_{max}=460 nm using 370 nm excitation and showed a high quantum yield Qy=0.34. We applied this **TA** compound to detect selective metal compounds. In this regard, the **TA** was able to identify **$CuCl_2$** from other metals through dramatic fluorescence quenching property. Furthermore, we demonstrated that this dramatic fluorescence quenching property originated from overlap between fluorescence wavelength of **TA** and absorption wavelength of **$CuCl_2$**. This hypothesis was further supported by using water, a polar protic solvent in which the absorption wavelength shifted without overlapping with the fluorescence wavelength of **TA.** Thus, no fluorescence quenching could be observed. Binding constant (K'), which is 0.0895 mM^{-2}, clearly indicated that the complexation ratio between **TA** and **$CuCl_2$** was 1:2 and further support the quenching property of **TA** with **$CuCl_2$**. We believe that this **TA** fluorescence compound maybe used in the application to sense **$CuCl_2$**.

Acknowledgments

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Supplementary Data

Electronic Supplementary Information (ESI) available: The sample preparation details, synthetic procedure, quantum yield, UV absorption, and fluorescence spectra, are available online.

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Novel thiophene-attached anthracene fluorescent compound (**TA**) was designed and developed. **TA** compound showed highly selective fluorescence quenching property to the **$CuCl_2$**. Binding constant (K'= 0.0895 mM^{-2}) clearly indicated that the complexation ratio between **TA** and **$CuCl_2$** was 1:2.

Graphical Abstract

We designed and synthesized a novel thiophene attached anthracene (**TA**) based fluorescent compound and applied for sensing **$CuCl_2$**.

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

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