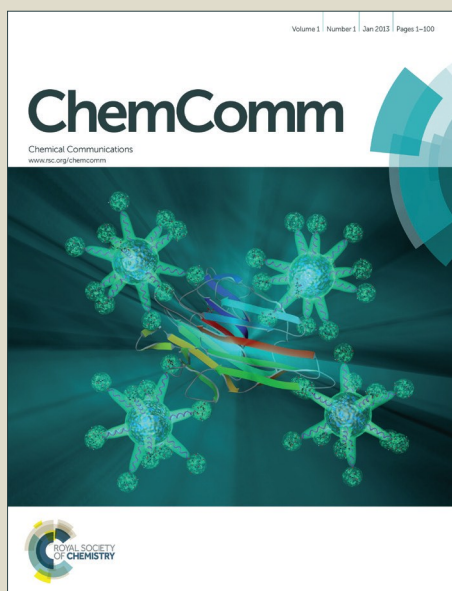


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## COMMUNICATION

# Click synthesis of a novel triazole bridged AIE active cyclodextrin probe for specific detection of Cd<sup>2+</sup>

Cite this: DOI: 10.1039/x0xx00000x

Lifang Zhang<sup>a</sup>, Wenping Hu<sup>a,b,c</sup>, Liping Yu<sup>a</sup> and Yong Wang<sup>\*a,b</sup>Received 00th January 2015,  
Accepted 00th January 2015

DOI: 10.1039/x0xx00000x

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**A novel aggregation induced emission (AIE) active cyclodextrin (CD) was synthesized by combining tetraphenylethene (TPE) and CD via click chemistry. The new material exhibits excellent selective turn-on fluorescence response to Cd<sup>2+</sup> in neutral environment with a low detection limit of 0.01 μM, which is the first report of clicked AIE probe for specific detection of Cd<sup>2+</sup>.**

Environmental contamination by heavy metals are attracting more and more concern with rapid development of the world economy.<sup>1</sup> The accumulated heavy metal pollutants in water and foods have led to great danger to public health.<sup>2</sup> As an extremely toxic metal, cadmium (Cd<sup>2+</sup>) is commonly found in industry and agriculture and can cause various lesions and diseases such as pneumonitis, pulmonary edema, emphysema and even cancer.<sup>3</sup> Therefore, it is highly desirable to develop economic and effective manners for qualitative and quantitative determination of 'real world' Cd<sup>2+</sup>.

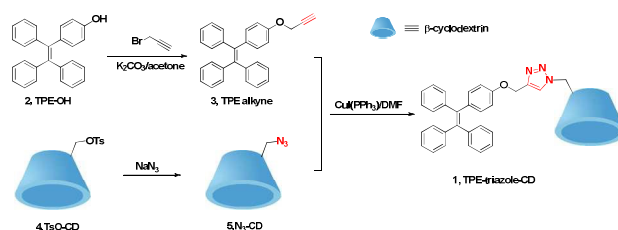
In recent years, as a simple, high sensitive and economic on-line detecting alternative, fluorescent sensors are attracting increasing interests of researchers and have shown great potential in detection of heavy toxic metal ions.<sup>4</sup> Large amounts of fluorescent sensors have been reported for the metal ion detection including Cd<sup>2+</sup> sensors.<sup>5</sup> However, most of the metal ion sensors are designed based on the fluorescent enhancement or quenching due to the complex formation or degradation between analytes and organic molecules, where the possible aggregation of organic molecules (aggregation-caused quenching, ACQ effect) may induce strong interference in the detection process, especially in water media.<sup>6</sup> For Cd<sup>2+</sup> sensors, another thorny problem is to avoid the serious interference from Zn<sup>2+</sup> which is one of the most abundant transition metal ion on earth and its property is similar to that of Cd<sup>2+</sup>.<sup>7</sup> Development of novel sensors based on new mechanism for specific detection of Cd<sup>2+</sup> in neutral environments remains as a great challenge to the modern researchers.<sup>8</sup>

In 2001, Tang et al first reported the luminogenic molecules with aggregation induced emission (AIE) characteristics, which provides

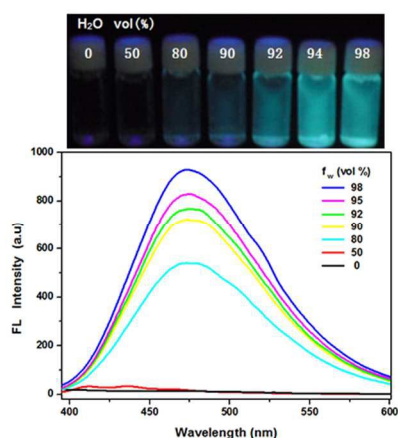
a new direction in the design of fluorescence sensors and many different sensors based on AIE features have been fabricated,<sup>9</sup> such as pH sensors,<sup>10</sup> explosive sensors,<sup>11</sup> sugar sensors,<sup>12</sup> DNA sensors,<sup>13</sup> protein sensors and anion sensors.<sup>14</sup> For heavy metal sensors, there have appeared Ag<sup>+</sup>, Hg<sup>2+</sup>, Zn<sup>2+</sup> and Al<sup>3+</sup> sensors.<sup>15</sup> As far as we know, very limited cases based on AIE probe for specific sensing of Cd<sup>2+</sup> have been reported.<sup>16</sup>

On a separate note, Cu(I) catalyzed 1,3-dipolar cycloaddition (click chemistry), as an efficient modular synthetic approach, is particularly suitable for the fabrication of novel biological and chemical sensors as the resultant triazole can serve either as a conjugating linker or as an effective metal ion binding site.<sup>17</sup> Mono-6-azido-β-cyclodextrin (N<sub>3</sub>-CD), as a commonly used clickable precursor, has been clicked into a large group of ligands or materials for diverse applications due to the unique features of native CDs.<sup>18</sup>

Herein, we report the modular synthesis of a novel AIE active CD (TPE-Triazole-CD), which exhibits excellent selective turn-on fluorescence response to Cd<sup>2+</sup> in neutral environments. Tetraphenylethylene (TPE) (the hydrophobic part) acts as the fluorescent unit and the triazole as well as the CD (the hydrophilic part) acts as the coordination sites. The synthetic pathway of the current sensor is depicted in Scheme 1. 1-(4-hydroxyphenyl)-1,2,2-triphenylethylene (TPE-OH, synthesized via McMurry coupling reaction<sup>19</sup>) was reacted with propargyl bromide in acetone in the



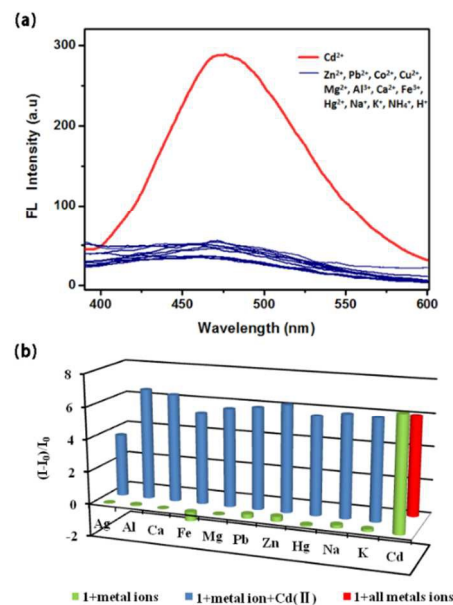
**Scheme 1** Synthetic pathway of TPE-triazole-CD. (Detailed procedures see ESI†)



**Fig. 1** Fluorescence emission spectra for solution of TPE-triazole-CD (50  $\mu\text{M}$ ) in different ratios of DMSO/H<sub>2</sub>O ( $\lambda_{\text{ex}} = 330\text{nm}$ , ex/em slits = 5/5) and the digital photos of **1** in DMSO/H<sub>2</sub>O mixtures under irradiation at 365 nm.

presence of K<sub>2</sub>CO<sub>3</sub> to afford TPE-alkyne<sup>20</sup> in a yield of 95%. N<sub>3</sub>-CD was obtained by reacting TsO-CD<sup>21</sup> with sodium azide in a yield of 97%. The novel probe TPE-Triazole-CD was finally synthesized via click chemistry<sup>22</sup> between TPE-alkyne and N<sub>3</sub>-CD in a yield of 90% (Detailed synthetic procedures and characterization data such as NMR and HR-MS are included in Fig.S1-S6 in ESI†).

The AIE characteristic of TPE-triazole-CD was evaluated by incremental addition of water into its solution in dimethyl sulfoxide (DMSO). As shown in Fig.1, upon photo excitation at 330 nm, TPE-triazole-CD is nonemissive in its dilute DMSO solution. However, when water fraction increases to 80%, the solution becomes strongly emissive at 476 nm and even clearly naked visible at water fraction of above 92%. To understand the AIE characteristic of TPE-triazole-CD, we conducted a group of NMR studies. Different from the TPE-CD reported by Tang et al.,<sup>23</sup> <sup>1</sup>H NMR studies reveal that the current TPE-triazole-CD does not form self-inclusion complex in DMSO even the CD concentration rises to 40 mM (Fig.S7). In DMSO/water mixture, the chemical shift of triazolyl and TPE protons shift slightly to the upfield with increase of water. This is due to the change of solvent polarity and possible hydrogen bond, which is classified by testing the <sup>1</sup>H NMR of a synthesized model compound without CD skeleton (TPE-triazole-Ph, synthetic procedures are included in ESI†) in the same solvent (Fig.S8). The results indicate that the new probe does not form self-inclusion complex in DMSO/water mixture. In 2D ROESY NMR spectra of TPE-triazole-CD in its DMSO and DMSO/water mixture, no cross-peaks are found between TPE/triazole protons and CD interior protons, which affirmed the above conclusion. A cross-peak is found between triazole proton and -OH proton at CD 6-position suggests a semi-rigid structure (Fig.S9(a)). After addition of water, there appears a new cross-peak between triazole proton and TPE H1 proton indicating a more rigid structure formed (Fig.S9(b)). Since TPE-triazole-CD is hardly dissolvable in water, the AIE characteristic is suggested to be caused by its aggregation from solvent system, which is affirmed by the gradual diminishment of TPE proton signals at higher water fraction (Fig.S10). The AIE-active property allows for the usage of TPE-triazole-CD as a potential probe for direct detection of heavy metal ions in water.



**Fig. 2** (a) The fluorescence intensity of TPE-triazole-CD (25  $\mu\text{M}$ ) in DMSO/H<sub>2</sub>O (1/1, v/v) in the presence of 5 equiv of different metal ions; (b) fluorescence response of **1** (25  $\mu\text{M}$ ) to 0.5 equiv of metal ions (the green bar) and to the mixture of 0.5 equiv of other metal ions with 0.5 equiv of Cd<sup>2+</sup> (the blue bar) and the fluorescence response of **1** toward Cd<sup>2+</sup> + all metal ions (the red bar) ( $\lambda_{\text{ex}}=330\text{nm}$ ,  $\lambda_{\text{em}}=476\text{nm}$ ).

Accordingly, we initially used water fraction of 10-20% to perform the metal ions assay, where the water solution of Cd<sup>2+</sup> (5 equiv) were added into the dilute DMSO solution of TPE-triazole-CD (25  $\mu\text{M}$ ). Unfortunately, no light-up fluorescence was observed. Considering its AIE feature in DMSO/H<sub>2</sub>O, we assume that the increase of water fraction could facilitate triggering the emission. With this idea, the following assays were performed with DMSO/H<sub>2</sub>O=50/50 (v/v). Fig.2(a) illustrates the fluorescence spectra of TPE-triazole-CD in DMSO/water mixture by addition of metal ions. It is interesting to find that Cd<sup>2+</sup> can significantly trigger the turn-on fluorescence of the TPE-triazole-CD. The emission maxima is also around 476 nm, which indicates similar aggregation process on addition of water and Cd<sup>2+</sup>. To evaluate its specific fluorescence response toward Cd<sup>2+</sup>, a group of metal ions such as Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup> and an ion mixture were chosen as the interfering ions to perform the fluorescence tests (Fig.2(b)). Except Ag<sup>+</sup>, it was found that all the rest metal ions exerted negligible or very small influence in the fluorescence spectra of TPE-triazole-CD. Our results indicate that TPE-triazole-CD can act as an excellently selective turn-on fluorescence sensor for Cd<sup>2+</sup> in neutral environment.

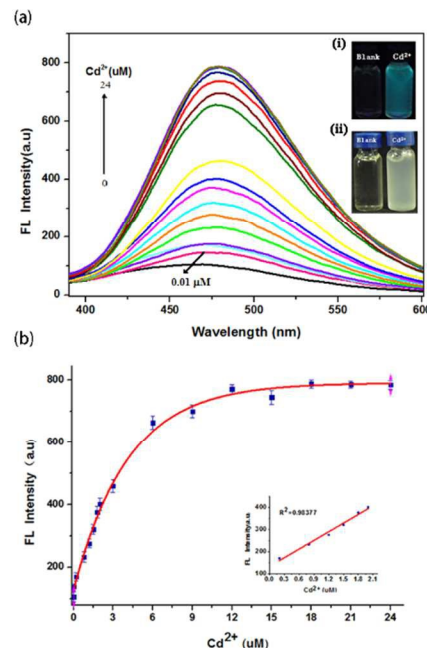
In order to evaluate the sensitivity of TPE-triazole-CD toward Cd<sup>2+</sup>, fluorescence titration experiments were conducted in the current study. The fluorescence intensities of TPE-triazole-CD (25  $\mu\text{M}$ ) in 50% DMSO/water on addition of Cd<sup>2+</sup> (0-1 equiv) are shown in Fig.3(a) and the titration curve is plotted in Fig.3(b). In the low concentration range (< 9  $\mu\text{M}$ ), the fluorescence emission intensity is enhanced rapidly upon the addition of Cd<sup>2+</sup> and a good linear response is found in the range of 0.2-2.0  $\mu\text{M}$  ( $R^2=0.98377$ ) (Fig.3(b), insert). After the Cd<sup>2+</sup> concentration reaches 12  $\mu\text{M}$ , the fluorescence

intensity levels off and remains unchanged due to the consumption-up of the TPE-triazole-CD in the complexing process. The Job's plot (Fig.S11) suggests that the complex of TPE-triazole-CD with  $\text{Cd}^{2+}$  has a possible binding ratio of 2:1. The association constant of the complex was calculated to be  $5.7 \times 10^5$  according to the non-linear fitting of the spectrometric titration curve (Fig.S12),<sup>24</sup> which suggests a relatively stable complex. It is worth to note that even a low  $\text{Cd}^{2+}$  concentration of  $0.01 \mu\text{M}$  can cause a distinct fluorescence intensity enhancement. By increasing the TPE-triazole-CD concentration, the detection of  $\text{Cd}^{2+}$  can be achieved without UV light excitation. Rapid precipitation can be observed by addition of  $\text{Cd}^{2+}$  (0.5 equiv) into the TPE-triazole-CD solution ( $100 \mu\text{M}$ ) in DMSO/ $\text{H}_2\text{O}$  mixture due to the strong aggregation effect (Fig.3(a) insert). Tris-HCl buffer system was chosen to investigate the pH effect on the  $\text{Cd}^{2+}$  assay, it was found that the fluorescence intensity only exhibits very slight enhancement with the buffer pH increasing from 4 to 10 (Fig.S13). In addition, the ionic strength produces no influence on the fluorescence intensity (Fig.S14). These results suggest that the TPE-triazole-CD affords satisfied and reproducible sensitivity toward  $\text{Cd}^{2+}$  and the sensitivity can be tuned by altering the sensor concentration or water fraction.

As stated previously, the AIE-active property of TPE-triazole-CD in DMSO/water mixture is ascribed to its aggregation caused by the poor solvent water. It has been proven that water can form a bridge between the hydroxyl groups of adjacent molecules of CD to induce aggregation.<sup>25</sup> By controlling the water fraction and sensor concentration, the rigid structure and pre-aggregation effects can provide appropriate conditions for the formation of complex between TPE-triazole-CD and  $\text{Cd}^{2+}$ , where the TPE moieties on different sensor skeletons are brought closer to realize the turn-on fluorescence sensing character based on the restricted intramolecular rotation (RIR) mechanism. Such coordination prevents the nonradiative deactivation of TPE moieties hence resulting in a remarkable fluorescence enhancement.

To further investigate the aggregation phenomena of TPE-triazole-CD upon addition of  $\text{Cd}^{2+}$ , particle size distribution analysis (Fig.S15) and transmission electron microscopy (TEM) (Fig.S16) measurements were performed in this study. As shown in Fig.S15, the relative average particle size of TPE-triazole-CD ( $100 \mu\text{M}$  in the mixture of DMSO and  $\text{H}_2\text{O}$ ) increases from  $240 \text{ nm}$  to  $1100 \text{ nm}$  after addition of  $\text{Cd}^{2+}$ . TEM images at micron-scale reveals that the introduction of  $\text{Cd}^{2+}$  leads to the more accentuated aggregation (Fig. S16(b)) than that without  $\text{Cd}^{2+}$  (Fig. S16(a)). Enlarging to nano-scale, we found that the presence of  $\text{Cd}^{2+}$  promotes the formation of the molecular clusters. Furthermore, Energy dispersive X-ray (EDX) spectrum of **1** in the presence of 0.5 equiv  $\text{Cd}^{2+}$  provides more direct evidence of the complex formation, where the number of Cd in low energy is far more than that in high energy indicating most of Cd were involved in coordination with probe **1** (Fig.S17). In addition, the downfield shift of triazole proton signal after addition of  $\text{Cd}^{2+}$  also affirmed the complex formation between probe **1** and  $\text{Cd}^{2+}$  (Fig.S18), which is consistent to the EDX result. To classify the role of triazole and CD in the complexation process, we made further studies on the response of TPE-triazole-Ph and  $\text{N}_3\text{-CD}$  toward  $\text{Cd}^{2+}$ . It is interesting to find that both of them does not show aggregation property on addition of  $\text{Cd}^{2+}$  under the same conditions with TPE-

triazole-CD (Fig.S19, no AIE phenomena was found with TPE-triazole-Ph and no



**Fig. 3** (a) Fluorescence emission spectra change of **1** exposed to  $\text{Cd}^{2+}$  of various concentrations: 0, 0.01, 0.2, 0.8, 1.2, 1.5, 1.8, 2, 3, 6, 9, 12, 15, 18, 21, 24  $\mu\text{M}$  from bottom to top (DMSO/ $\text{H}_2\text{O}$  = 1/1, v/v). Insert: images of **1** ( $100 \mu\text{M}$ ) under UV at 365 nm (i) and under daylight (ii) in DMSO- $\text{H}_2\text{O}$  (1/1, v/v) upon addition of 0.5 equiv of  $\text{Cd}^{2+}$ ; (b) Fluorescence titration curve of TPE-triazole-CD with  $\text{Cd}^{2+}$  in DMSO- $\text{H}_2\text{O}$  (1/1, v/v) solution. Inset shows the fluorescence responses at low  $\text{Cd}^{2+}$  concentration. ( $\lambda_{\text{ex}}=330 \text{ nm}$ ,  $\lambda_{\text{em}}=476 \text{ nm}$ ).

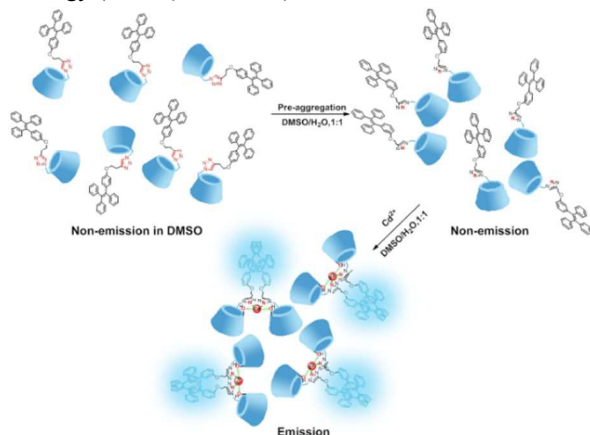
precipitation of  $\text{N}_3\text{-CD}$  appeared at a concentration of  $100 \text{ mM}$ . This indicates there exist synergistic effect in binding with  $\text{Cd}^{2+}$  between triazole and CD hydroxyl moieties, similar to the triazole-based Calix[4]arene reported by Kim et al.<sup>8a</sup> The synergistic effect from triazole and hydroxyl groups on CD rims may form a semi-rigid pocket for specific binding of  $\text{Cd}^{2+}$ .<sup>5c,8a</sup>

According to the achieved results, the possible sensing mechanism and binding mode of TPE-triazole-CD are proposed as shown in Scheme 2. The sensor undergoes rigidization and pre-aggregation with the addition of poor solvent, followed by a complexation process to trigger the turn-on fluorescence.

In conclusion, the first click derived AIE active CD sensor (TPE-triazole-CD) was synthesized. It exhibits highly selective turn-on fluorescence response toward  $\text{Cd}^{2+}$  with a detection limit of  $0.01 \mu\text{M}$ . The triazole bridges and CD hydroxyl groups provide interaction sites for specific coordination with  $\text{Cd}^{2+}$  and a novel sensing mechanism was proposed. This work provides a simple, efficient and cost-effective way for the detection of  $\text{Cd}^{2+}$  in neutral environment based on AIE effect. Except for detection of metal ions, TPE-triazole-CD is also expected to act as biological sensors due to its potential biocompatibility and ability in accommodating a large number of guest molecules.

We acknowledge the financial support from National Natural Science Foundation of China (No. 21205086) and Tianjin

Research Program of Application Foundation and Advanced Technology (13JCQNJC05400).



**Scheme 2** The proposed sensing mechanism of TPE-triazole-CD toward Cd<sup>2+</sup> in DMSO/H<sub>2</sub>O (1/1, v/v).

## Notes and references

<sup>a</sup> Department of Chemistry, School of Science, Tianjin University, Tianjin 300072. Email: wangyongtju@tju.edu.cn

<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China.

<sup>c</sup> Institute of Chemistry, Chinese Academy of Sciences (Beijing), Beijing 100190, China.

† Electronic Supplementary Information (ESI) available: [Experimental; Synthesis of characterization of TPE-triazole-CD; NMR spectra; Particle size distribution analysis results; TEM images; Energy X-ray dispersive results]. See DOI: 10.1039/c000000x/

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