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Bovine Serum Albumin Coated CuInS₂ Quantum Dots as a Near-infrared Fluorescence Probe for 2, 4, 6-Trinitrophenol Detection

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ABSTRACT:

In this paper, a novel near-infrared fluorescence probe for the determination of 2, 4, 6-trinitrophenol (TNP) was developed based on bovine serum albumin (BSA) coated CuInS₂ quantum dot (QD). Water-soluble CuInS₂ QDs were directly synthesized in aqueous solution with mercaptopropionic acid (MPA) as stabilizers, and it was coated by BSA via an amide link interacting with carboxyl of the MPA-capped CuInS₂ QDs. The obtained BSA coated CuInS₂ QDs (BSA-CuInS₂ QDs) can bind TNP in water via the acid-base pairing interaction between electron-rich amino groups of BSA and electron-deficient nitroaromatic rings, and leading the fluorescence quenching of BSA-CuInS₂ QDs. The quenched fluorescence intensity of BSA-CuInS₂ QDs was proportional to the concentration of TNP in the concentration ranges from 50 nmol/L to 3.0 μmol/L. The detection limit (LOD) for TNP was 28 nmol/L. The developed fluorescence probe showed a excellent resistant to interference of metal ions such as K⁺, Na⁺, Zn²⁺, Cu²⁺, Hg²⁺, and Pb²⁺. The developed biosensor was applied to the determination of TNP in spiked water samples with satisfactory results.

Keywords

CuInS₂ QDs; Bovine serum albumin; Fluorescence quenching; 2, 4, 6-Trinitrophenol; Near-infrared fluorescent probe

1. Introduction

Nitroaromatic compounds that are highly explosive and environmentally deleterious substances deserve societal concern. They are environmental contaminants associated with anthropogenic activities, such as production and use of dyes, explosives, pesticides, and pharmaceuticals [1, 2]. Because nitroaromatic compounds have strong electron-withdrawing groups, they are poorly biodegradable in the environment [3]. 2, 4, 6-trinitrophenol (TNP), as the first synthesized explosives in the world with strong explosion ability and low safety coefficient, may extensively exist in the soil and ground water near military and industrial facilities. That may lead to skin irritation, anemia, and abnormal liver functions, when people inhale, ingest or touch it [4, 5]. Besides, TNP has harmful effects on male fertility and is now regarded as a possible human carcinogen [6]. Therefore, it is very important to develop simple and rapid analytical methods to identify and quantify nitroaromatic compounds.

In the past decades, a number of analytical methods, such as liquid and gas chromatography, surface-enhanced Raman spectroscopy, resonance Rayleigh scattering, enzyme linked immunosorbent assays, and electrochemical analysis, etc [7-15] have been applied to detect nitroaromatic explosives. However, some drawbacks such as complicated extraction, high cost, long operation time and low anti-interference ability existed in these methods limited their applications.

Fluorescence measurements have attracted more attention owing to its low-cost, operational simplicity, high sensitivity, and real-time detection. A series of fluorescence sensors have been designed for the detection of biological molecules, and environmental contaminants, etc [16-24].

Some research groups introduced the fluorescence measurements into the determination of nitroaromatic compounds in real water samples. So far, most of the reports on the fluorescence determination of nitroaromatic compounds were based on some special fluorescence polymers [25-33]. Trogler et al. reported the fluorescence quenching phenomenon of copolymers containing tetraphenylsilole or tetraphenylgermole with Si-Si, Ge-Ge, and Si-Ge backbones induced by nitroaromatic compounds [26]. Patil and coworkers developed a novel fluoranthene based fluorescent chemosensor for the detection of TNP. In the detection process, static fluorescence quenching was the dominant by intercalative π - π interaction between fluoranthene and nitroaromatics [32].

In comparison with organic dyes and fluorescent proteins, QDs are promising fluorescence material for biosensors that show unique advantages such as high emission quantum yields, narrow and symmetric emission peaks with a broad range of excitation wavelengths, and good chemical and optical stabilities [34-38]. Simonet et al. reported the first observation of selective and specific recognition of chiral L-cysteine (L-Cys) - or D-cysteine (D-Cys)-capped CdSe/ZnS QDs with carnitine enantiomers in aqueous solution [34]. Kim et al. demonstrated inhibition assay of avidin concentration based on fluorescence resonance energy transfer (FRET) between QDs and gold nanoparticles [35]. Most of traditional QDs were nanomaterials with cadmium, and yet the leaks of cadmium from the QDs were toxic to biological systems and eventually caused serious environmental problems. Recently, a novel kind of I-III-VI CuInS₂ QDs that does not contain any toxic class A elements (Cd, Pb, and Hg) or class B elements (Se and As) just came into view [39-41]. Based on this consideration, we have previously presented a one-pot synthesis of water-soluble CuInS₂ QDs capped with mercaptopropionic acid (MPA) [42].

In this paper, bovine serum albumin (BSA) was covalently linked to the MPA-capped CuInS₂ QDs. The obtained BSA coated CuInS₂ QDs (BSA-CuInS₂ QDs) could effectively bind TNP via the acid-base pairing interaction between electron-rich amino groups of BSA and electron-deficient nitroaromatic rings, that might lead to the fluorescence changes of BSA-CuInS₂ QDs. Thus, we developed a novel fluorescence probe for rapid and highly sensitive detection of explosive TNP molecules.

2. Experiment

2.1 Apparatus

The fluorescence spectra were obtained by using a Shimadzu RF-5301 PC spectrofluorophotometer equipped with a xenon lamp using right-angle geometry. UV-vis absorption spectra were obtained by a Varian GBC Cintra 10e UV-vis spectrometer. In both experiments, a 1 cm path-length quartz cuvette was used. FT-IR spectra were recorded with a Bruker IFS66V FT-IR spectrometer equipped with a DGTS detector (32 scans). Dynamic Light Scattering spectra (DLS) were obtained by Zetasizer Nano S90.

2.2 Reagents

All reagents were of at least analytical grade. The water used in all experiments had a resistivity higher than 18 MΩ cm⁻¹. Copper (II) chloride dihydrate (CuCl₂·2H₂O), sodium hydroxide (NaOH), sulphourea (CS(NH₂)₂), sodium dehydrogenized phosphate (NaH₂PO₄) and disodium hydrogen phosphate (Na₂HPO₄) were purchased from Shanghai Qingxi Technology Co., Ltd.. BSA, indium (III) chloride tetrahydrate (InCl₃·4H₂O) 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), phenol, TNP,

dinitrotoluene(DNT), 4-nitrophenol(4-NP), and 2-nitrophenol(2-NP) were purchased from Sigma-Aldrich Corporation. The 0.1 mol/L PBS (pH 7.0, 0.1 mol/L NaH_2PO_4 - Na_2HPO_4) was used as the medium for detection process.

2.3 Preparation of MPA-capped CuInS_2 QDs

MPA-capped CuInS_2 QDs were synthesized in aqueous solution, according to our previous report [42]. 0.15 mmol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ were dissolved in 10.5 mL distilled water, and then 1.8 mmol MPA was injected into the solution. The pH value of the mixture solution was adjusted to 11.3 by adding 2 mol/L NaOH solution with stirring during this process. After stirring for 10 minutes, 0.30 mmol $\text{CS}(\text{NH}_2)_2$ was dissolved in above solution. The previous process was all finished at room temperature, and then the mixture solution was finally transferred into a 15 mL autoclave. Then it was heated and maintained at 150 °C for 21 h and then cooled down to room temperature by a natural process. Ethanol was added to the stock solution to obtain CuInS_2 QDs precipitate, and the process was repeated three times. The unreacted residues were removed by the cycled washing. The purified CuInS_2 QDs were dissolved in PBS (0.1 mol/L, pH 7.0), and stored in the darkroom.

2.4 Preparation of BSA coated CuInS_2 QDs

BSA has amino groups available for the conjugation with carboxylic acid group capping CuInS_2 QD via amide formation, using the EDC/NHS coupling reaction. The BSA coated CuInS_2 QDs (BSA- CuInS_2 QDs) were prepared according to previous report [43-45]. A reaction mixture containing 0.12 mmol/L CuInS_2 QDs, 2.0 g/L BSA, 5 mmol/L NHS, 0.05mol/L EDC in pH 7.4 PBS was prepared and kept at room temperature for 4 h, then stored at 4 °C overnight. This allows

the unreacted EDC to hydrolyze and lose its activity. The conjugate solution was centrifuged to separate unreacted BSA (The mass of the unreacted BSA was weighed after drying). And then one can dialyze the solution with Spectra/Por 4 Membrane, MWCO 12 000-14 000 to remove the remaining small molecules. The purified BSA-CuInS₂ QDs solution was stored in the darkroom. The mass concentration of BSA coated CuInS₂ QDs could be calculated (0.6 mg/mL) after the purified BSA-CuInS₂ QDs was precipitated by the addition of excess acetonitrile, dried and weighed. And the mass ratio of the BSA to CuInS₂ QDs was calculated to be 4.9:1.

2.5 The detection process

The BSA-CuInS₂ QDs solution (200 μ L, 0.6 mg/mL), 0.1 mol/L PBS buffer (pH 7.0, 1.0 mL), and different amount of TNP or other aromatic compounds (DNT, 4-NP, 2-NP and phenol) were successively added into a 10 mL calibrated test tube. Then, the solution was diluted to the mark with deionized water followed by the thoroughly shaking and equilibrated for 2 min until the solution was fully mixed. The fluorescence spectra were recorded from 600 nm to 850 nm, and the sampling interval was 1.0 nm. The slit widths of excitation and emission were both 10 nm. The fluorescence (FL) intensity of the maximum emission peak was used for the quantitative analysis of the target molecules.

3. Results and discussions

3.1 Spectral characteration of BSA- CuInS₂ QDs

As well-known that, the fluorescence properties of QDs had a close connection to the composition of surface capped layers. Recently, many fluorescence probes have been proposed to

recognize molecules and ions by employing some special receptors or ligands to functionalize the original QDs [34, 36, 43]. In this work we selected BSA to modify the MPA-capped CuInS₂ QDs. The fluorescence emission and UV-vis absorption spectra of MPA-capped CuInS₂ QDs and BSA-CuInS₂ QDs were shown in **Fig. 1A**. It could be seen that the fluorescence emission peak of MPA-capped CuInS₂ QDs around 660 nm was narrow and symmetrical, and the UV-Vis absorption peak was around 570 nm, which were consistent with our previous report [42]. After the BSA was connected to CuInS₂ QDs, the surface capped layer of the CuInS₂ QDs was changed from MPA with negatively charged to BSA that existed amounts of amino groups, and the formed new coated layer increased the size of CuInS₂ QDs. As a result, the fluorescence emission peak of the BSA-CuInS₂ QDs exhibited a significant red shift to 680 nm.

Fig.S1 showed the FT-IR spectra of the MPA-capped CuInS₂QDs (curve a) and BSA-CuInS₂ QDs (curve b). As curve **a** in **Fig. S1** shown, the majority of MPA functional groups could be clearly found through the C=O stretching peak (1730cm⁻¹), and C-H stretching mode (2850cm⁻¹, 2920cm⁻¹, 2960cm⁻¹). The characteristic peak of S-H did not appear within 2550-2680 cm⁻¹, which might be caused by the covalent bonds between thiols and metal. As **curve b** in **Fig.S1** shown, the amide I band (1660 cm⁻¹) and amide II (1540 cm⁻¹) band for -CONH group appeared, which was due to the conjugation of BSA to the MPA capped CuInS₂ QDs. In order to prove the presence of BSA after the conjugation, UV-vis absorption spectra (230-500 nm), the fluorescence emission spectra (300-500 nm) and the dynamic light scattering (DLS) of the BSA-CuInS₂ QDs were performed. As shown in **Fig. S2A**, the typical UV-Vis absorption peak around 260 nm and fluorescence emission peak around 345 nm (excitation at 280 nm) belonging to BSA were observed in the BSA-CuInS₂ QDs, and not observed in the original MPA-capped CuInS₂ QDs. As

shown in **Fig.S2B**, the increase of the particle sizes after the conjunction could be observed, which was due to the new capped BSA layers.

3.2 The interactions between TNP and BSA- CuInS₂ QDs

As shown in **Fig.1B**, the developed BSA- CuInS₂ QDs could bind TNP molecule. In this work, the interaction between TNP and BSA-CuInS₂ QDs was systematically discussed based on the fluorescence changes of BSA-CuInS₂ QDs. **Fig.2** shows the evolution of fluorescence spectra of BSA-CuInS₂ QDs with increasing TNP concentration. It could be seen that the fluorescence intensity (FL) of BSA-CuInS₂ QDs obviously decreased with TNP concentration increasing from 0 to 4.0 $\mu\text{mol/L}$. Furthermore, **Fig.2Inset** showed that there was a good linear relationship between the fluorescence quenching ratios $(F_0-F)/F_0$ (F_0 and F are the fluorescence intensity of BSA-CuInS₂ QDs without or with TNP) of BSA-CuInS₂ QDs and the TNP concentration in the range from 50 nmol/L to 3.0 $\mu\text{mol/L}$. The regression equation is:

$$(F_0-F)/F_0 = 0.0028 + 0.1777[\text{TNP}], \mu\text{mol/L} \quad (1)$$

The corresponding regression coefficient is 0.999, and the detection limit for TNP was 28 nmol/L, calculated following the 3σ IUPAC criteria. The standard deviation for nine replicate measurements of 0.2 $\mu\text{mol/L}$ TNP is 2.3%.

The organic amino ligands modified nanocrystals utilized as the receptors of nitroaromatic compounds have been mentioned in some previous reports [46-48]. The electron transfer from amino groups to aromatic rings leads to the formation of a Meisenheimer complex between nitroaromatic and the amine group [49-54]. In this study, TNP is a typically electron-deficient compound due to the strong electron-withdrawing effect of the three nitro groups. As shown in **Fig.1B**, the BSA-coated CuInS₂ QDs with high content of electron-rich amino groups could

effectively bond to TNP by the acid-base pairing interaction, and the charge transfer complexing interaction would lead to the fluorescence quenching of BSA-CuInS₂ QDs.

As shown in **Fig.S3A**, we systematically investigated the influence of pH value on the fluorescence intensity of BSA-CuInS₂ QDs and BSA-CuInS₂ QDs quenched by TNP. It can be seen that when the pH value changed from 6.6 to 9.0, the FL intensity of BSA-CuInS₂ QDs solution gradually decreased and the FL intensity of BSA-CuInS₂ QDs with TNP solution nearly remained the same. At pH 7.0, the fluorescence quenching ratio $(F_0 - F) / F_0$ (F_0 and F are the fluorescence intensity of BSA-CuInS₂ QDs without or with TNP) gave the best result for the determination of TNP. **Fig.S3B** showed the temporal evolution of the fluorescence intensity of BSA-CuInS₂ QDs after the addition of 2.5 $\mu\text{mol/L}$ TNP. It could be seen that the fluorescence intensity of BSA-CuInS₂ QDs rapidly decreased after the addition of TNP, and reached equilibrium, in 2 minutes. Therefore, pH 7.0 and reaction time of 2 minutes were the suitable conditions for the detection process.

3.3 The interactions between DNT, 4-NP or 2-NP and BSA-CuInS₂ QDs

As indicated earlier, the electron-withdrawing effect of nitro group played a key role in the interaction between the nitroaromatic TNP and BSA-CuInS₂ QDs. In this study, we further investigated the interactions of other nitroaromatic DNT, 4-NP or 2-NP and BSA-CuInS₂ QDs. **Fig.S3B** showed the temporal evolution of fluorescence intensity of BSA-CuInS₂ QDs in the presence of 2.5 $\mu\text{mol/L}$ DNT, 4-NP, 2-NP or phenol respectively. The results demonstrated that the fluorescence intensity of BSA-CuInS₂ QDs decreased to some extent after the addition of 2.5 $\mu\text{mol/L}$ DNT, 4-NP or 2-NP, and remained nearly constant in 2 minutes. The phenol that had no electrophilic nitro groups could not induce the fluorescence quenching of the BSA-CuInS₂ QDs.

As shown in **Fig.3** and **Fig.4A**, we compared the fluorescence quenching of BSA-CuInS₂ QDs response to TNP, DNT, 4-NP and 2-NP. The results demonstrated that the fluorescence quenching ability of the four nitroaromatic followed the order TNP>DNT>4-NP>2-NP, that was consistent with the numbers of nitro groups in the corresponding aromatic ring. **Fig.4B** showed the FL intensity of MPA-capped CuInS₂ QDs in the presence of different concentration of TNP, DNT, 4-NP or 2-NP. It could be seen that the nitroaromatic TNP, DNT, 4-NP or 2-NP cannot induce obviously fluorescence quenching of MPA capped CuInS₂ QDs under the same condition. Therefore, the BSA coating layer of CuInS₂ QDs was necessary for the detection process, and it was further confirmed that the fluorescence quenching of BSA-CuInS₂ QDs induced by nitroaromatic compounds was due to the acid-base pairing interaction between electron-rich amino groups of BSA and electron-deficient nitroaromatic rings.

3.4 Interference study

In this study, we discussed the effect of a series of foreign metal ions and organics on the fluorescence of BSA-CuInS₂ QDs. From **Fig.5**, it could be seen that the fluorescence intensity of BSA-CuInS₂ QDs system showed the high tolerance concentrations to most common metal ions and organics in water samples. The fluorescence of BSA-CuInS₂ QDs remained almost the same even in the presence of 10 $\mu\text{mol/L}$ heavy metal ions such as Cu²⁺, Hg²⁺, Ag⁺ or Pb²⁺. These results indicated that the conjugated BSA layers prevented these metal ions being adsorbed on the surface of CuInS₂ QDs. And other common organics such as phenol, benzoic acid, pyridine, etc. also could not induce the fluorescence quenching of BSA-CuInS₂ QDs under the same conditions. Therefore, this method has high selectivity and excellent resistance to interference.

Up to now, considerable efforts have been devoted to the development of fluorescence detection

for nitroaromatic. For examples, the functionalized fluorescence polymers that usually contain certain amount of aromatic structures have been extensively reported to probe nitroaromatic via π - π electronic attraction [25-33]. However, the complex and expensive polymer synthesis, and the poor water solubility of the fluorescence polymer restricted its application in the detection of nitroaromatics compounds in water samples. Recently, some functionalized nanoparticles such as L-cysteine capped Mn-doped ZnSe QDs and dendrimer PAMAM capped CdSe QDs, etc were successfully applied to detect nitroaromatic in water samples [49-56]. However, the fluorescence of these functionalized nanoparticles were easily interfered by some foreign metal ions such as Cu^{2+} , Hg^{2+} and Pb^{2+} , etc. We proposed a water-soluble fluorescence probe BSA-CuInS₂ QDs to effectively detect nitroaromatic TNP with high tolerance concentrations to the interference of heavy metal ions. Compared with the previous reports about fluorescence detection for TNP, such as the copolymers containing tetraphenylsilole or tetraphenylgermole as the fluorescence probe for TNP with the dynamic range of 10-100 $\mu\text{mol/L}$ [26], the fluoranthene based fluorescence sensor for the detection of the TNP with the dynamic range of 0.5-10 $\mu\text{mol/L}$ [32], and the paper sensor for TNP-selective detection with the dynamic range of 0.05–7.0 mg/L and the limit detection of 32.3 mg/L[56], our method had the similar detection limit and dynamic range.

3.5 Analytical applications

To test the applicability of the proposed methods, it was applied to determine TNP in tap water, spring water and chemical plant wastewater samples. The water samples were filtered several times through qualitative filter paper. The pH was adjusted to 7.0 using NaOH solution before analysis. The results showed that TNP was not detected in these real samples, so the samples were spiked with standard TNP solution. The averages of three replicate determination results were presented

in **Table 1**. The accuracy of the proposed method was evaluated by determining the average recovery of TNP in real samples. From **Table 1**, it can be seen that the RSD was lower than 3.8%, and the average recoveries of TNP in the real samples was in the range of 90-110%.

4. Conclusion

In summary, we have demonstrated that the BSA coated CuInS₂ QDs could be utilized as a near-infrared fluorescence probe for the detection of TNP. The fluorescence of BSA-CuInS₂ QDs was quenched by TNP via the acid-base pairing interaction between electron-rich amino groups of BSA and electron-deficient nitroaromatic rings. Moreover, obvious difference in quenching efficiency was observed for different types of nitroaromatic compounds (TNP, DNT, 4-NP and 2-NP), which is dependent on their electron-accepting ability. The proposed method was simple, convenient and had more resistant to the interference of heavy metal ions and other organics.

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Figure captions

Fig. 1(A) The UV-vis absorption and fluorescence emission spectra of MPA-capped CuInS₂ QDs (Dash line) and BSA-CuInS₂ QDs. (Solid line). (B) The schematic illustration of the synthetic process of BSA-CuInS₂ QDs and the TNP detection

Fig.2 The fluorescence spectra of BSA-CuInS₂ QDs upon the addition of different concentration of TNP in the range from 0 to 4.0 $\mu\text{mol/L}$ (0,0.05,0.10,0.2,0.5,1.0,1.5,2.0,2.5,3.0,4.0 $\mu\text{mol/L}$).

Inset: Plot of fluorescence quenching ratios $(F_0-F)/F_0$ of BSA-CuInS₂ QDs at 680 nm versus the concentration of TNP. PBS: 10 mmol/ L phosphate buffer solution (pH 7.0) at room temperature.

Fig.3 The fluorescence spectra of BSA-CuInS₂ QDs without or with 2.5 $\mu\text{mol/L}$ (A)TNP, (B)DNT, (C)4-NP or (D)2-NP PBS: 10 mmol/ L phosphate buffer solution (pH 7.0) at room temperature.

Fig.4 (A) Plot of fluorescence quenching ratios $(F_0-F)/F_0$ of BSA-CuInS₂ QDs at 680 nm versus the concentration of TNP, DNT, 4-NP and 2-NP. (B) Fluorescence intensity of MPA-capped CuInS₂ QDs with the increasing concentration of TNP, DNT, 4-NP or 2-NP. PBS: 10 mmol/ L phosphate buffer solution (pH 7.0) at room temperature.

Fig.5 **0:** The fluorescence intensity of BSA-CuInS₂ QDs. **1:** The fluorescence intensity of BSA-CuInS₂ QDs with 2.5 $\mu\text{mol/L}$ TNP. The fluorescence intensity of BSA-CuInS₂ QDs with 10 $\mu\text{mol/L}$ **2:** K⁺, **3:** Ca²⁺, **4:** Na⁺, **5:** Mg²⁺, **6:** Ba²⁺, **7:** Fe³⁺, **8:** Zn²⁺, **9:** Cu²⁺, **10:** Hg²⁺, **11:** Ag⁺, **12:** Pb²⁺, **13:** Cd²⁺, **14:** sodium citrate, **15:** tartaric acid, **16:** glucose, **17:** catechol, **18:** resorcinol, **19:** hydroquinone, **20:** benzoic acid, **21:** 8-hydroxylquinoline, **22:** phenol, **23:** ethylene diamine

tetraacetic acid, **24**: dimethyl formamide, **25**: acetonitrile, **26**: pyridine, **27**: furan. PBS: 10 mmol/ L phosphate buffer solution (pH 7.0).

Highlights :

- APBA functionalized CuInS₂ QDs was used as a near-infrared fluorescence probe.
- The fluorescence of APBA functionalized CuInS₂ QDs was quenched by dicyandiamide.
- The fluorescence quenching was via the acid-base pairing interaction between BSA and nitroaromatic.

Table.1 Determination of TNP in real water samples according to equation (1)

Samples	Added ($\mu\text{mol/L}$)	Found ($\mu\text{mol/L}$)	Recovery (%)	RSD (n=3, %)
Tap water	0.20	0.18	90	3.5
	1.0	1.02	102	2.7
Spring water	0.20	0.19	95	2.6
	1.0	1.05	105	2.3
Chemical plant wastewater	0.20	0.22	110	3.8
	1.0	1.02	102	3.6

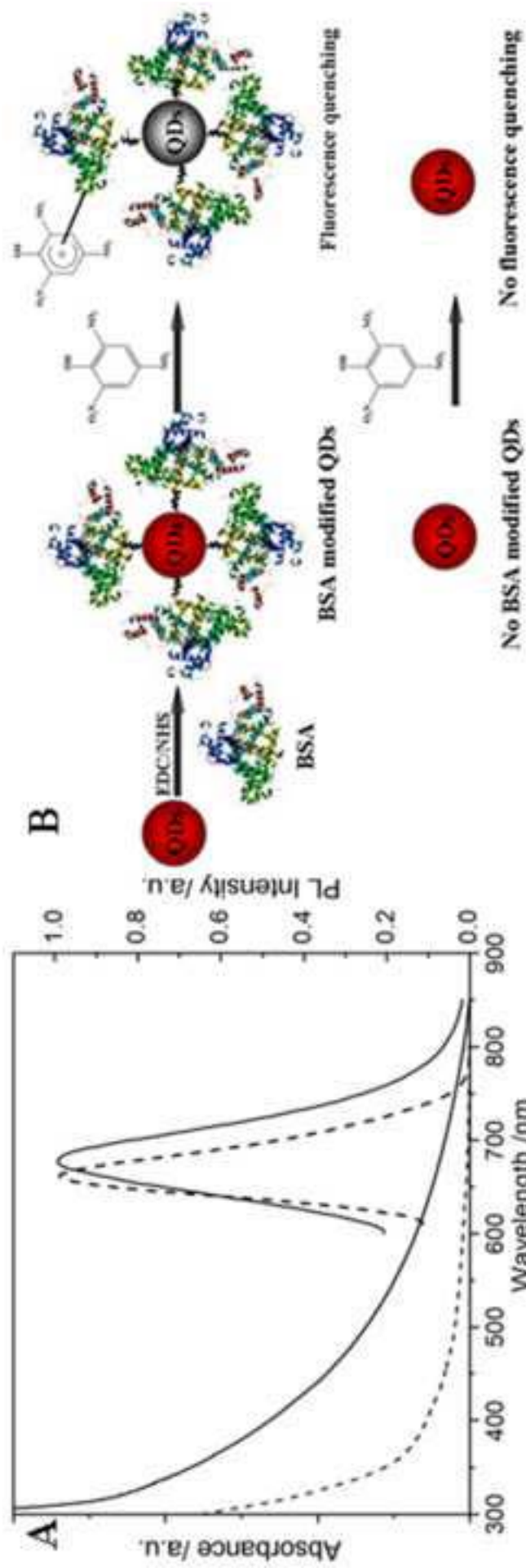


Figure 1

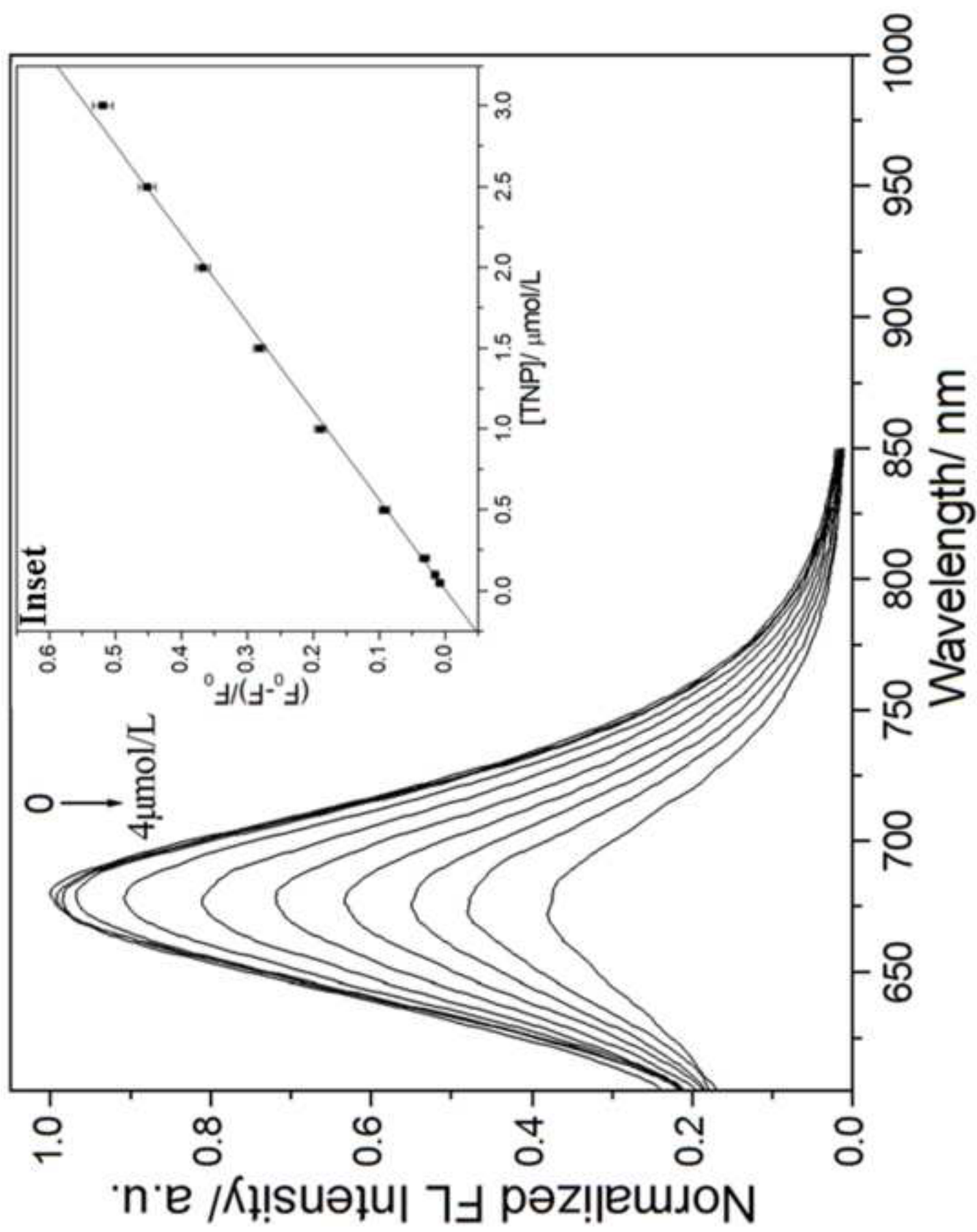


Figure 2

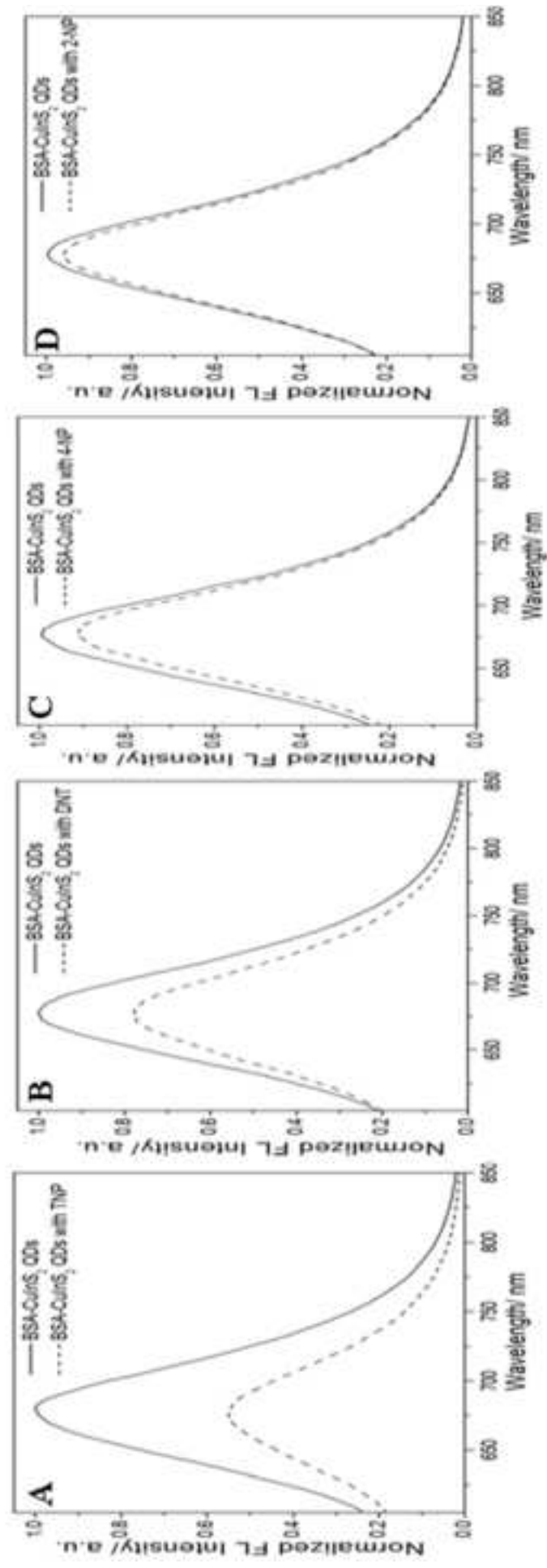


Figure 3

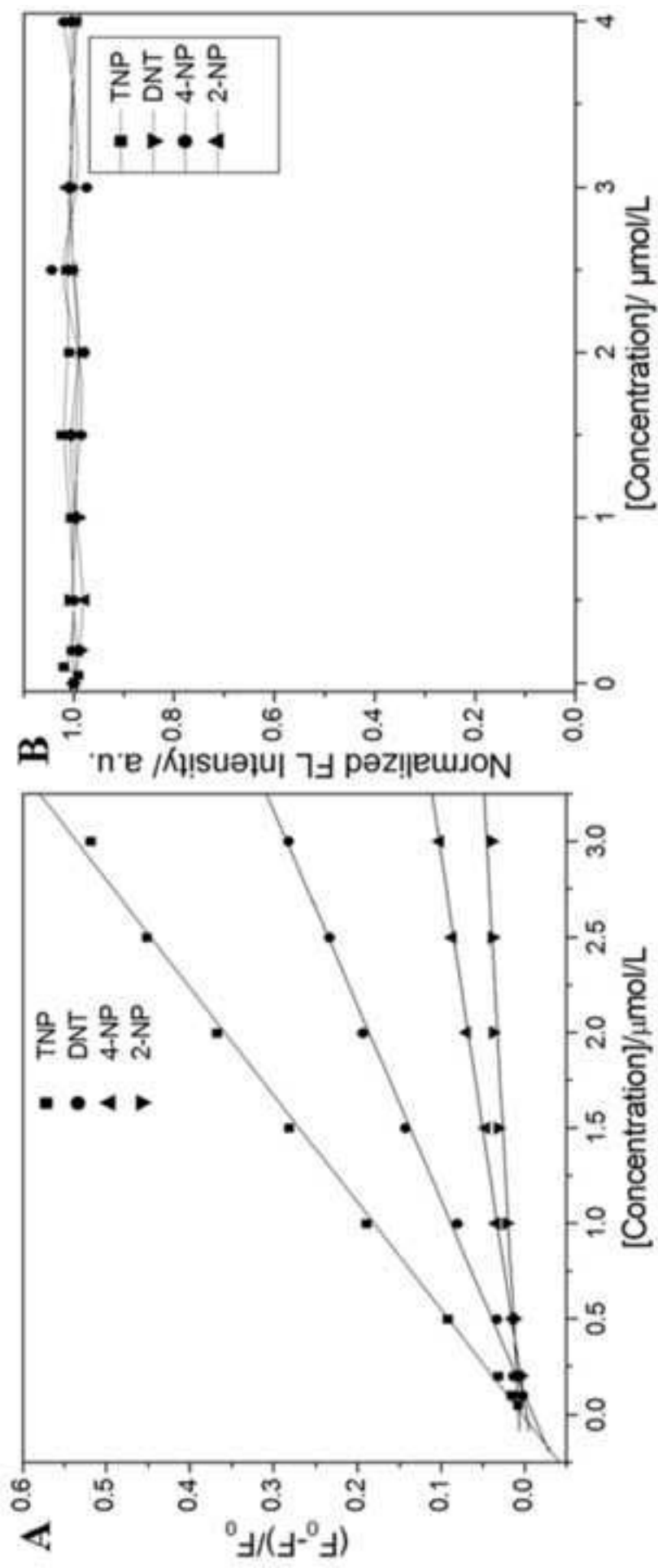


Figure 4

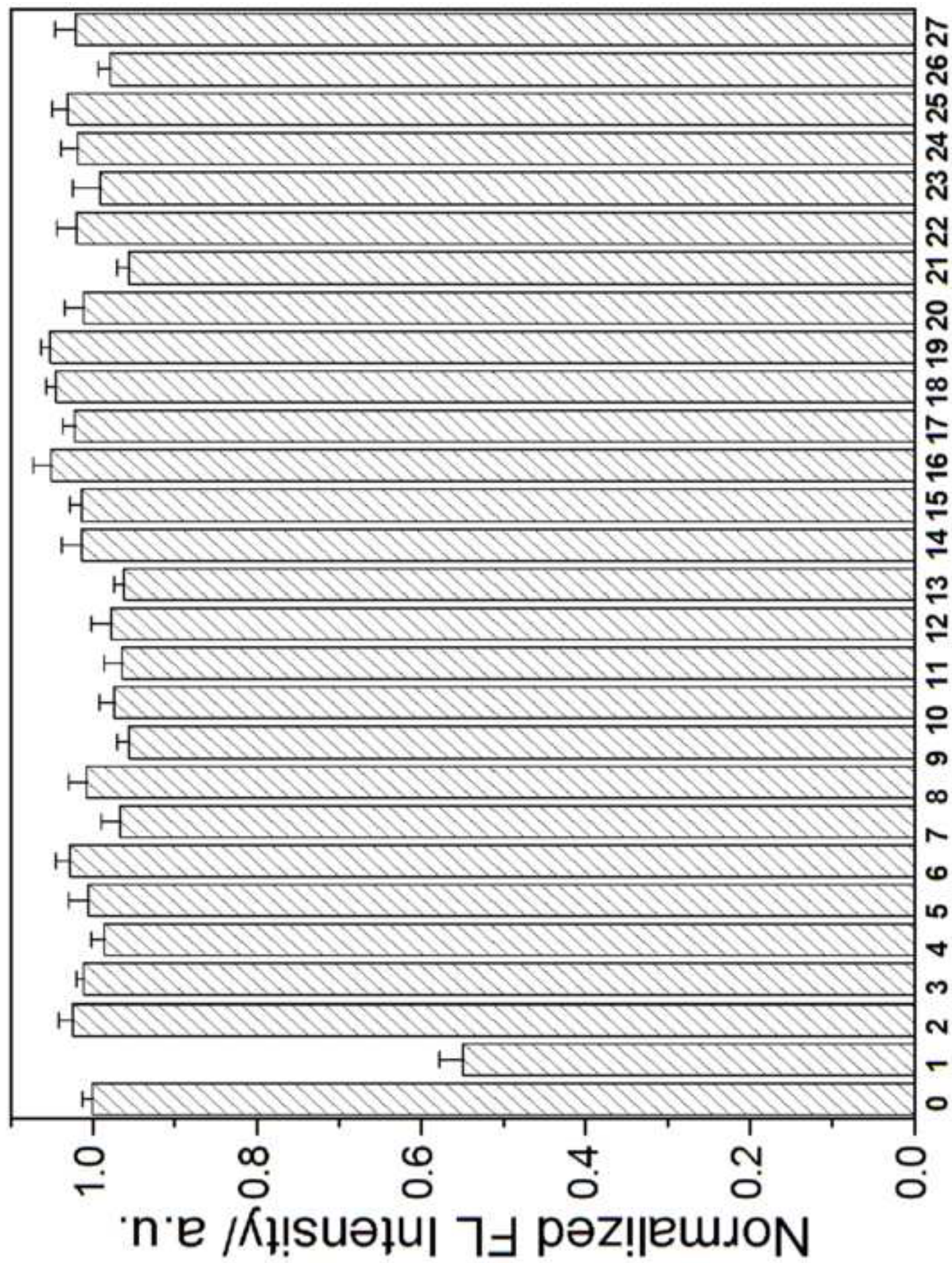


Figure 5

