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### **Graphical Abstract**

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Bifunctional fluorescent quenching detection of 2, 4, 6-trinitrophenol (TNP) and acetate ions via 4,4'-(9,9-dimethyl-9H-fluorene-2,7diyl)dibenzoic acid We reported a compound as an exclusive fluorescence sensor for TNP and acetate ions for the first time.

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# Bifunctional fluorescent quenching detection of 2, 4, 6-trinitrophenol (TNP) and acetate ions via 4,4'-(9,9-dimethyl-9H-fluorene-2,7-diyl)dibenzoic acid

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#### ABSTRACT

The 4,4'-(9,9-dimethylfluorene-2,7-diyl)dibenzoic acid (5) was synthesized using commercial fluorene as the starting material followed by processes of bromination, methylation, Suzuki coupling and hydrolysis. We reported it as an exclusive fluorescence sensor for 2, 4, 6-trinitrophenol (TNP) and acetate ions for the first time. The experimental results suggested a high efficiency for TNP detection with  $K_{SV}$  values of 21215 M<sup>-1</sup>, which has achieved to micromolar level (10  $\mu$ M) of this material. Moreover, the detection limit (1.39  $\times$  10<sup>-6</sup> M) was measured according to the fluorescence intensity changes of Ac<sup>-</sup> in CH<sub>3</sub>CN.

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Nitro aromatics, such as nitrobenzene (NB), 4-nitrotoluene (4-NT), 2, 4, 6-trinitrophenol (TNP), and 2, 4, 6-trinitrotoluene (TNT) are common ingredients of explosives.<sup>1</sup> Among various nitro aromatic compounds, 2, 4, 6-trinitrophenol (TNP) is an extremely hazardous chemical with strong explosive capacity and a low safety coefficient.<sup>2</sup> It violently explodes when it contacts with flames or friction shock.<sup>3</sup> In addition, as a toxicant, the ingestion of TNP can cause severe poisoning in humans, including headache, nausea, vomiting, abdominal pain and destruction of erythrocytes.<sup>4</sup> While all the nitro explosives show strong electron affinity, it is very difficult to separate TNP from mixture of other nitro-compounds.<sup>5</sup> Hence, development of efficient selective sensor for detection TNP is highly desirable.<sup>6</sup>

On the other hand, Ac ions plays a significant role in numerous metabolic processes and has been widely investigated in prostate cancer and its metastases.<sup>7</sup> It also plays an important role in industry such as dyes, paper, paints and plastics.<sup>8</sup> Due to its wide application in many medical and industry, researchers pay more attention on the detection method of Ac ions, especially in chromogen and fluorescence.<sup>9</sup>

Currently, fluorescent organic materials, for example, pyrene, styrene and biphenyl have attracted tremendous attention in the field of technology and science.<sup>10</sup> However, fluorene with the similar conjugated structure to other fluorescent organic materials doesn't get enough attention.<sup>11</sup> Fluorene, a major component of fossil fuels, has unique structural features: two benzene rings are fused into one plane by a five-member ring, providing high electron delocalization through increased overlap of  $\pi$  molecular orbitals between the rings.<sup>12</sup> Fluorene can be directly connected to aromatic hydrocarbon via aromatic

coupling at the 2 and 7 positions, yielding a series of fluorenederived compounds.<sup>13</sup> In the past two decades, a large amount of studies on structure modification of fluorene derivatives have been reported.<sup>14</sup> Recently, fluorene-derived compounds are also well documented in the literature that they have good coordination ability, which is due to the electron-rich property and conjugate structure.<sup>15</sup>

Until now, lots of researchers focused on the synthesis and coordination of fluorene derivatives, <sup>16</sup> but there is little information for detecting anions and nitro explosives. Here we explored the selectivity of 4, 4'-(9, 9-dimethylfluorene-2, 7-diyl)dibenzoic acid (5) for acetate ions and TNP respectively by the changes of fluorescence intensity. The reason for choosing fluorene derivatives is due to its strong fluorescence nature as well as the high electron richness.<sup>17</sup> Furthermore, the conjugate carboxylic fluorene compound has been selected as fluorescent sensors because of the potential to form an intermolecular supramolecular architecture<sup>18</sup> such as  $\pi$ - $\pi$  interaction<sup>19</sup> and hydrogen-bonded in solution.<sup>17</sup>

The synthetic routes and detailed procedures of **5** are shown in Scheme 1. Among them, 2,7-Dibromofluorene (**1**) and 2,7-Dibromo -9,9-dimethylfluorene (**2**) were synthesized by the reported procedures.<sup>20</sup> Compound **4** (yield 45%) took the modified literature method, <sup>16b</sup> which was the Suzuki coupling. Fortunately, we obtained the compound **3** by Suzuki coupling reaction, which was not on any literature before.

The X-ray single crystal structural of the compound 2 (Figure S1A) is the same with that reported on literature before.<sup>21</sup> For the

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Scheme 1. Synthetic Routes of compound 5

compound **2**, the dihedral angle between two benzene rings (C7, C8, C9, C10, C11, C12; C7A, C8A, C9A, C10A, C11A, C12A) and the five-member ring (C7, C12, C13, C12A, C7A) are both 0.0 (0.0) °. X-ray single crystal study shows that compound **3** (Figure S1B) is crystallized in a monoclinic system with P2<sub>1</sub>/c space group. The dihedral angle between benzene rings (C11, C12, C13, C14, C15, C16; C18, C19, C23, C20, C21, C22) and the five-member ring (C14, C15, C17; C19, C18) are 2.1 (0.2) ° and 1.8 (0.2) °, which are larger than compound **2**. And the dihedral angle between benzene ring (C3, C4, C5, C6, C7, C8) and the fluorene moiety is 43.6 (0.1)°, showing that C-C single bond distorting between benzene ring and the fluorene moiety is strong.

#### **Fluorescence measurements**

The emission spectra of the fluorene and the compounds 1-5 were shown in Figure 1 and the luminescent spectra of them were analyzed under excitation wavelength (280 nm) with 400V and slit width (5:5). For compounds 1 and 2, almost no fluorescence responds were observed. While, the maximum emission wavelength was 313 nm for fluorene, 436 nm for compound 3, 408 nm for compound 4, 380 nm for compound 5. Compared with fluorene, there are fluorescence quenching phenomenon occurring in compounds 1, 2, 3 and the red shift in the maximum emission wavelength for compounds 3, 4, 5.

All of compounds 1, 2 and 3 are containing bromine atoms. In this condition of containing halogen atoms,  $^{22}$  the excited state of the compounds and heavy atom form the composite in a ratio of 1:1. The degree of spin orbit coupling in this compound is much larger than normal compound. This excited state complex has a strong charge transfer property, normally is the fluorescence quenching process. In compounds 3, 4 and 5, fluorene moiety is conjugated with benzene ring after the Suzuki coupling reaction of bromination derivatives of fluorene, which make the fluorescence enhance and a red shift occurs in the maximum emission wavelength but compound 3 still has the heavy atom effect. At the same time, the dihedral angle between two benzene rings and the five-member ring increased, showing that the fluorene molecular skeleton is distorted by the effect of benzene rings. Compared with 3, compound 4 has two benzene rings leading to distorted structure which made the conjugated effect weak and blue shift. Finally, the compound 4 turned into compound 5 by hydrolysis reaction, which made the fluorescence intensity decrease because it contains the carboxyl group which is an electron-withdrawing group.



Figure 1. The fluorescence spectra of fluorene and Compounds 1-5 in  $CH_3CN$ 

#### Sensing of nitroaromatic compounds

Compound 5 (sensor) is highly soluble in some organic solvents such as acetonitrile, methanol. We take the acetonitrile as the solvent for sensing study. The sensor exhibits strong emission peak at 367 nm ( $\lambda_{ex} = 280$  nm).

The changes in luminescence intensity with the increasing addition of nitroaromatic compounds (up to 100 ppm) in the sensor are shown in Figure 2 and Figure S6, respectively. In the current study, the NACs used are nitrobenzene (NB), 4nitrotoluene (4-NT), 4-nitrobenzaldehyde (4-NBA), 1,3-dinitrobenzene (DNB), 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP), 2,4,6-trinitrophenol (TNP), and 2,4,6trinitro toluene (TNT) (Figure 3) to judge the selectivity of sensing towards nitroaromatic compounds. The most effective quencher is TNP with QP (quenching percentage =  $(I_0 - I)/I_0 \times$ 100%, I<sub>0</sub> and I are luminescence intensity of sensor before and after exposure to the nitro compound) of 97.91%. Other NACs can weaken the photo luminescent intensity of sensor to different level. The order of quenching efficiency is TNP > 2-NP > 4-NBA  $\approx$  NB  $\approx$  TNT  $\approx$  4-NP > 3-NP > 4-NT > DNB. In all the cases, the initial fluorescence intensity of the sensors decreased considerably upon gradual addition of the NACs. The rate of quenching, which is essentially related to the Stern - Volmer constant  $(K_{SV})$ , revealed that TNP has faster fluorescence quenching over the other nitroaromatic compounds. To better understand this fact, we need to calculate the Stern-Volmer constants of the quenching process.



Figure 2. Reduction of the fluorescence emission intensity of the sensor upon gradual addition of TNP



Figure 3. Luminescence quenching percentage when sensor was dispersed in nine different nitro compounds in  $CH_3CN$  (excited and monitored at 280 nm and 367 nm, respectively). nitrobenzene (NB), 4-nitrotoluene (4-NT), 4-nitrobenzaldehyde (4-NBA), 1,3-dinitro benzene (DNB), 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP), 2,4,6-trinitrophenol (TNP), and 2,4,6-trinitro toluene (TNT).

To understand the sensitivity, the Stern-Volmer plots were used to calculate the quenching constants of the analytes (Figure 4) using the SV equation  $(I_0/I) = K_{SV}[Q] + 1$ , where  $I_0$  and I are the luminescence intensities before and after the addition of the analyte, [Q] is the molar concentration of the analyte, and  $K_{SV}$  is the quenching constant. As shown in Figure 4A, at low concentrations (up to 50 ppm) of all nitro analytes, a linear proportional in  $(I_0/I-1)$  was observed. The SV plot diverged from linearity and began to bend upwards in case of nitroaromatic compounds with the concentration increasing. The linear variation at lower concentration is mainly due to static quenching, whereas the steep curves at higher concentrations are presumably due to dynamic quenching (Figure 4B). The static quenching can be attributed to the ground state interaction between the analytes and the sensor. The dynamic quenching is mainly due to the energy and electron transfer processes between the analytes and the sensor. Fitting of linear parts of the plots allows the determination of the quenching constants  $(K_{SV})$  to be 21215  $M^{-1}$  for TNP, 9877  $M^{-1}$  for 2-NP, 8082  $M^{-1}$  for 4-NP, 7737  $M^{-1}$  for 4-NBA, 6377  $M^{-1}$  for NB, 10584  $M^{-1}$  for TNT, 5662  $M^{-1}$ for 3-NP, 2345 M<sup>-1</sup> for 4-NT and 2353 M<sup>-1</sup> for DNB. The larger observed Ksv values revealed extremely high sensitivity, which made the sensor to be one of the best sensitive luminescence, based metal-organic detectors of TNP due to the electron richness and the fluorescent behaviour of the fluorene moiety. In addition, the determination of the individual Stern-Volmer constants indicated that the fluorescence quenching mainly occurs through charge transfer. To further establish the formation of charge transfer, NMR titration was carried out with TNP for the sensor. In a typical titration 10 µM of the sensor was taken in DMSO- $d_6$ .





**Figure 4.** (A) Plot of  $I_0/I$  of sensor (at 367 nm) vs. concentration of analytes in lower concentration ranges of analytes (up to 50 ppm).  $I_0$  and I are luminescence intensities in the absence and presence of analyte, respectively. (B) Stern–Volmer plots of analytes in higher concentration ranges of analytes (up to 100 ppm).



Figure 5. NMR with addition TNP to sensor in DMSO- $d_6$ 

To 50 ppm solution of TNP in DMSO- $d_6$  was added and the corresponding NMR spectrum was recorded. On addition of TNP, a significant chemical shift of the protons was observed in the <sup>1</sup>H NMR spectra for the sensor (Figure 5). More importantly, the fluorene protons are shifted more prominently (by 0.04 ppm) than the phenyl protons (by 0.01 ppm). This observation clearly suggests two facts: firstly, the TNP is mainly interacting with the fluorene moiety of the sensors though  $\pi$ - $\pi$  interaction. Secondly, the ability of hydrogen bonds formation between the senior and TNP is weak. If the sensor forms the hydrogen bonds with the TNP, the phenyl protons will be affected much more than the fluorene protons by adding TNP.

#### Sensing properties towards anions

Compound **5** emitted strong blue fluorescence with the maximum excited wavelength centered at around 390 nm. Various anions were tested in parallel under the same conditions for evaluating the specific sensing behavior of the compound **5**, (Figure 7A), upon the addition of other ions such as  $F^{-}$ ,  $CI^{-}$ , Br<sup>-</sup>, CIO<sup>-</sup>, SCN<sup>-</sup>, HPO<sup>4-</sup>, H<sub>2</sub>PO<sup>4-</sup>, SO<sup>3-</sup>, NO<sup>3-</sup> etc. Surprisingly, it is found that sensor displayed an extremely good selectivity for Ac<sup>-</sup> only, instead of the other ions examined.

In order to furthermore investigate influence of the luminescent responds of sensor, we tried to add Ac<sup>-</sup> into the diluted solution of the sensor, and investigated the sensing behavior of **5** towards Ac<sup>-</sup> carefully. As shown in Figure 6, excitingly, the emission spectra showed significant decrease with



Figure 6. The fluorescence spectra of sensor (10  $\mu$ M) in the presence of Ac<sup>-</sup> (0 $\sim$ 60 equiv.)



**Figure 7.** (A) The fluorescent response of probe sensor (10  $\mu$ M) to different species (50 equiv.) (B) Effect of Ac<sup>-</sup> on probe sensor (10  $\mu$ M) in the presence of different interferents (50 equiv)

the increase of Ac<sup>-</sup>. With the increase of the concentration of Ac<sup>-</sup> ions in this system, the emission peak intensity decreased correspondingly. The peak intensity reached the minimum with the 5.4-fold (I<sub>0</sub>/I) decreasing when 50 equiv. of Ac<sup>-</sup> ions were added in. However, here no significant difference were observed when the concentration of Ac<sup>-</sup> ions increased from 50 equiv. to 60 equiv.. Plotting the normalized fluorescence intensity changes intensity at 390 nm as a function of [Ac<sup>-</sup>] resulted in a nice linear relationship (Figure 6), the point at which this line crossed the ordinate axis is regarded as the detection limit and found to be  $1.39 \times 10^{-6} \, \text{M.}^{23}$ 

To examine the interfering effects of the analytes as mentioned above on Ac<sup>-</sup> recognition, competition assays were subsequently carried out (Figure 7B). The results show that the same concentration of co-existence ions will not affect the Ac<sup>-</sup> ions, which shows a highly anti-interference property.

In conclusion, a new compound (compound 3) is synthesized by Suzuki coupling and characterized by single crystal X-ray diffraction. At the same time, a new pathway has found by Suzuki coupling to synthesize fluorene derivatives containing carboxyl group. This compound shows a high fluorescence quenching efficiency and low detection limit for TNP and Ac<sup>-</sup> ions. Then we have a discussion about the fluorescence quenching mechanism based on the effects of  $\pi$ - $\pi$  staking interaction and hydrogen bonding. Therefore, the syntheses of these kinds of compounds were very successful and the finding of their unique physicochemical properties could also help explore some new types of semiconducting and sensing materials.

#### Acknowledgments

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#### **Supplementary Material**

Experimental Section, Figures of crystal structure, <sup>1</sup>H NMR, <sup>13</sup>C NMR, fluorescence spectra and the bond lengths (Å) and angles (°) are presented in the supplementary material. CCDC 1494725.

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## ACCEPTED MANUSCRIPT Tetrahedron

## Highligths

- We developed a novel pathway to synthesise fluorene derivatives (compound 4).
- The single crystal of new intermediate **3** was obtained by Suzuki coupling reaction.
- We examined the emission spectrum of the fluorene and compound 1-5.
- New experiment was firstly carried out about sensing of NACs and anions based on 5.
- ۲ We discussed the quenching mechanism based on the effects of  $\pi - \pi$  interaction. Accepter

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