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# A colorimetric and fluorescent chemosensor for the detection of an explosive—2,4,6-trinitrophenol (TNP)†

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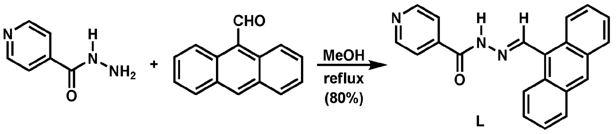
**A fluorescent and colorimetric receptor (L) for specific recognition of TNP was described. The origins of this remarkable affinity was disclosed by the crystal structure of corresponding host–guest complex L·TNP.**

Supramolecular chemistry based on host–guest interaction and self-organization first harnessed preorganization for the design of tailor-made molecular receptors effecting molecular recognition from metal ions to anions and chiral molecular substrates.[1] Especially, recognition of neutral guests has attracted much attention owing to their great biological and environmental relevance.[2] However, relatively few examples that rely on color change[3] have been reported so far, although they represent a convenient visual detection method in classical chemical analysis.

In particular, rapid detection of explosives such as trinitrotoluene (TNT) is important owing to their broad applications including tactical and humanitarian demining, and forensic and criminal investigations *etc.*[4] Homeland security applications are attracting increased research, because terrorists frequently employ bombs.[5] Most of available sensors are composed of polymers, nanomaterials *etc.*[6] and fewer are organic small molecules.[7] Surprisingly, less attention has been paid to picric acid (2,4,6-trinitrophenol, TNP),[8] although its explosive power is somewhat superior to that of TNT and it is also widely used in the manufacture of rocket fuels, fireworks, matches and so on.[9] Also TNP has been recognized as an environmental contaminant and is harmful to wildlife and humans.[10] So the development of fast, convenient and specific analytical methods for TNP is highly desirable.[11] In connection with our continuing research of sensors for biologically and environmentally important guest species,[12] herein, we present the first colorimetric and fluorescent receptor (**L**) with multiple hydrogen-bonds and π–π interactions for specific recognition of TNP.



**Scheme 1** Synthesis of receptor **L**.

Stimulated by some known pyridyl anthracene sensors,[13] we designed and synthesized *N*-acylhydrazone **L**[14] starting from isonicotinohydrazide and anthracene-9-carbaldehyde (Scheme 1, see ESI† for details).

Anthracene is a polycyclic aromatic hydrocarbon (PAH), which can emit strong fluorescence at about 420 nm for monomer formation and at above 470 nm for excimer formation.[15] When interacting with a compound containing strong electron-withdrawing groups, fluorescence quenching of anthracene might occur due to the formation of a possible non-fluorescent complex. Guided by this rational analysis, we surmised that the differences of fluorescent properties between compound **L** and its complex **L·TNP** might enable it to be used as a sensor to detect the presence of TNP in solution. As shown in Fig. 1, **L** only displays an excimer emission band at 483 nm when excited at 419 nm in DMF solution (low solubility in other solutions). Upon the addition of TNP, a prominent quenching and color change of fluorescence were observed. The total fluorescence intensity of **L** decreased to 3% when 3.0 equiv. of TNP was present. These results indicated that the formation of complex **L·TNP** destroyed the π–π interactions between anthracene rings of **L** in solution.[16] The corresponding quantitative analytical data

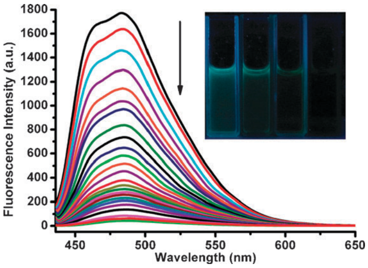


**Fig. 1** Fluorescence quenching of **L** (50.0 μM) upon the addition of TNP (0 to 3.0 equiv.) in DMF ($\lambda_{ex}$ = 419 nm). Inset: Fluorescence change of **L**. Left to right: **L** only, **L** + TNP (1.0 equiv.), **L** + TNP (2.0 equiv.), **L** + TNP (3.0 equiv.).

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† Electronic supplementary information (ESI) available: Details of synthesis, powder XRD pattern, UV-vis titrations. CCDC 809217. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc10400d

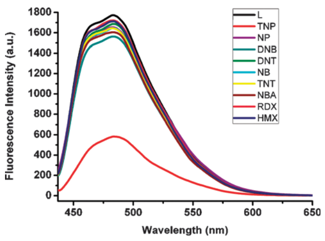

**Fig. 2** Fluorescence spectra of **L** (50.0 μM) with various nitro-compounds (1.0 equiv.) in DMF ($\lambda_{ex}$ = 419 nm).

(linear concentration range, RSD, LOD, LOQ)[17] were carried out and calculated (Fig. S1, ESI†).

Other nitroaromatics such as TNT (2,4,6-trinitrotoluene), DNT (2,6-dinitrotoluene), NB (nitrobenzene), NP (4-nitrophenol), DNB (1,3-dinitrobenzene) and NBA (4-nitrobenzoic acid) and nitroamines (RDX, HMX) were used to investigate the selectivity of **L** by fluorescence spectra (Fig. 2). Upon the addition of these compounds to a DMF solution containing compound **L**, only TNP caused the remarkable quenching of the fluorescence emission band, while other nitro-compounds quenched the emission intensity only to a small extent. These results implied that there are strong interactions between **L** and TNP. Moreover, a color change from pale yellow to deep yellow was observed by naked-eye upon the addition of TNP (Fig. 3). In the profile of the UV-vis spectra generated from the addition of TNP to **L**, the increase of the absorption peak at about 390 nm is in good agreement with the color change (Fig. S2, ESI†).

To explore the interactions between **L** and TNP in solution further, $^1$H NMR titration experiments were also carried out. As shown in Fig. 4, the signals of H2A, H1 and H5, H2 and H4 of **L** were downfield shifted obviously upon the addition of TNP (1.0 equiv.) ($\Delta\delta$ = 0.33, 0.31, 0.54 ppm, respectively), which indicated that the hydrazone group and the pyridine group of **L** with TNP formed strong hydrogen bonds.[7c] No further changes occurred upon addition of further TNP, indicating the 1 : 1 (host–guest) binding mode was formed in solution.

**Fig. 3** Color change of **L** ([**L**] = 0.45 mM, [various nitroaromatics] = 1.0 mM). Left to right: **L** only, TNP, TNT, DNT, NB, NP, DNB and NBA.

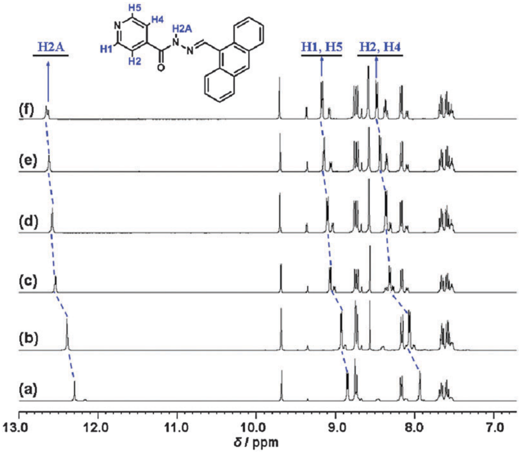

**Fig. 4** Partial $^1$H NMR spectra (400 MHz) of **L** (5.0 mM) with TNP in $d_6$-DMSO: (a) **L** only; (b) **L** + TNP (0.2 equiv.); (c) **L** + TNP (0.4 equiv.); (d) **L** + TNP (0.6 equiv.); (e) **L** + TNP (0.8 equiv.); (f) **L** + TNP (1.0 equiv.).

Next, the interactions of **L** with the nitroaromatics were also investigated in the solid state. When 1.5 mL of TNP (3.0 × $10^{-3}$ M) solution was added to 1.5 mL of **L** (9.0 × $10^{-4}$ M) solution in ethanol (0.5% DMF, v/v), a vermilion precipitate was observed. Upon increase of the concentration of TNP, futher precipitate were generated (Fig. S3, ESI†). However, when 1.5 mL of other nitro-compounds (10.0 × $10^{-3}$ M) solution was added to 1.5 mL of **L** (9.0 × $10^{-4}$ M) solution in ethanol (0.5% DMF, v/v), neither precipitation nor color change occurred.

Then we studied the precipitate generated from the **L**–TNP system in order to understand the interactions in the solid state. The precipitate can be isolated by filtration and is soluble in DMF. After a few days, vermilion block crystals were obtained by slow evaporation of the solvent at room temperature (Fig. 5a). A single-crystal X-ray diffraction analysis reveals that a 1 : 1 host–guest complex **L·TNP**[18] was formed (Fig. 5a) by **L** and TNP as in solution. The crystal structure shows that the nitrogen of the pyridine group of **L** is protonated to form a cation while picric acid is deprotonated to form the anion,[19] where the pyridine group is changed from a hydrogen-bond acceptor to the hydrogen-bond donor (Fig. 5a). Molecules of **L** adopt the *E* form exclusively in the complex. The **L** cations and picrate anions are self-assembled

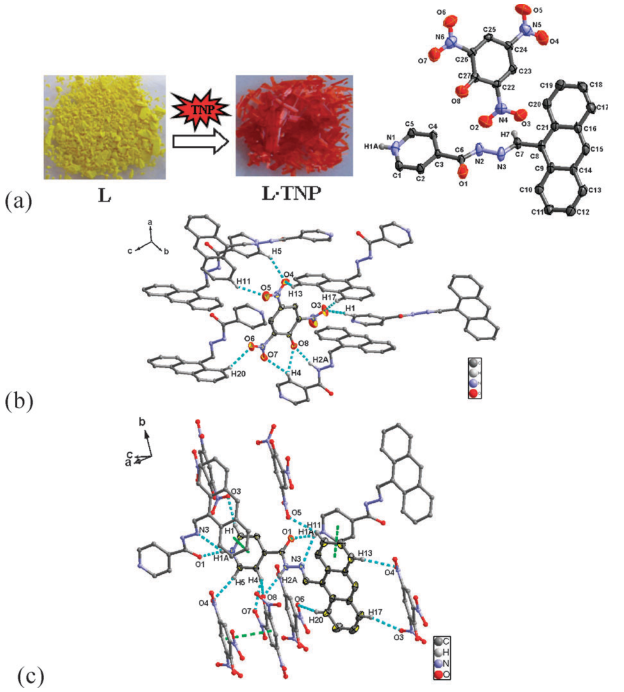

**Fig. 5** (a) Photos of **L** and **L·TNP** and the X-ray structure of the host–guest complex **L·TNP**; (b) The hydrogen-bond interactions around TNP in the complex; (c) The hydrogen-bond interactions and π–π interactions around **L** in the complex (the hydrogen-bond interactions and π–π interactions are indicated with dashed turquoise and bright green lines, respectively. Some hydrogen atoms are omitted for clarity).

to form a supramolecular structure *via* multiple hydrogen-bond and π–π interactions. As shown in Fig. 5b and c, each picrate acts as a hydrogen-bond acceptor to connect six ligands *via* 9 hydrogen-bonds, and each **L** acts as hydrogen-bond donor and acceptor to connect six picrates and two other ligands *via* 13 hydrogen-bonds in which the D–A distances vary from 2.713 to 3.470 Å and the corresponding D–H···A angles are in the range 114.8–169.9° (Table S2, ESI†), while relatively weak C–H···O interactions can not be ignored.[20] It is noteworthy that the two hydrogen-bonds between N1 of the pyridine group and O1 of the hydrazone group and N2 of the hydrazone group and O8 of the picrate group are very strong[21] owing to their short distance. These results implied that the pyridine group and the hydrazone group of **L** were the key sites for specific interaction with TNP, which was in good agreement with the results of $^1$H NMR titration experiments in solution. Three intermolecular face-to-face π–π stacking interactions are also evident (Fig. 5c). The first one, between two picrate rings, presents a $\pi_{\text{centroid}}$–$\pi_{\text{centroid}}$ distance of 3.569 Å and a dihedral angle of 0.00°. The second and the third interactions, between the anthracene ring and pyridine ring from different **L**, are the same and both have a $\pi_{\text{centroid}}$–$\pi_{\text{centroid}}$ distance of 3.640 Å and a dihedral angle of 5.44°. No π–π stacking interactions between anthracene rings were observed which indicated the origin of the prominent fluorescence quenching. In addition, a powder X-ray diffraction study of the precipitate was also conducted (Fig. S4, ESI†) and the resulting experimental powder XRD pattern is in good agreement with the corresponding simulated one of the crystal **L·TNP**. The above results showed that there is an organized self-assembly between **L** and TNP during the sensing process.

In summary, we report a specific, colorimetric and fluorescent receptor (**L**) for TNP. As a general design strategy, structural modifications of **L** may allow us to create further fluorescent sensor candidates for TNP in the future.

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