

1 **Click-modified hexahomotrioxacalix[3]arenes as fluorometric**  
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3 **and colorimetric dual-modal chemosensor for**  
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5 **2,4,6-trinitrophenol**  
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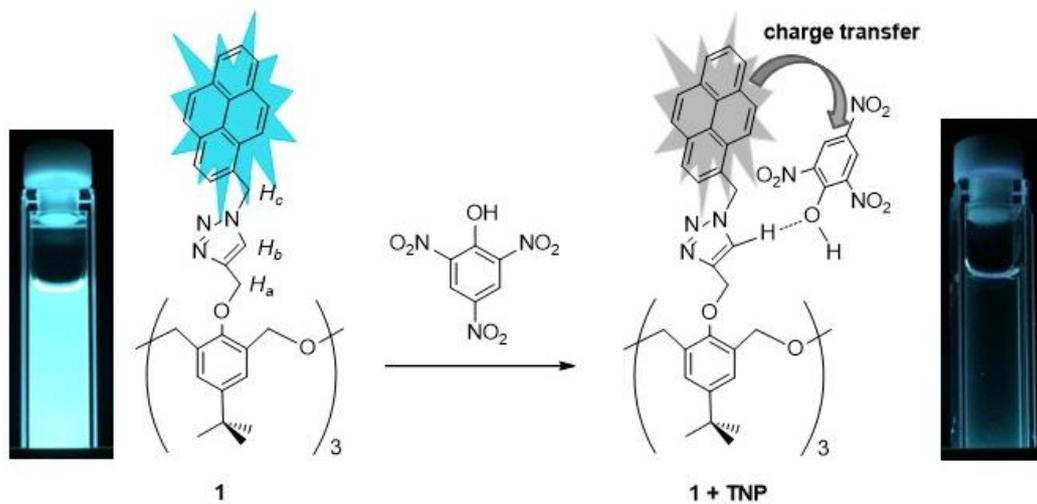
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31 **ABSTRACT:** A new type of chemosensor-based approach to the detection of  
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33 2,4,6-trinitrophenol (TNP) is described in this paper. Two  
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35 hexahomotrioxacalix[3]arene-based chemosensors **1** and **2** were synthesized through  
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37 click chemistry, which exhibited high binding affinity and selectivity toward TNP as  
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39 evidenced by UV-vis and fluorescence spectroscopy studies. <sup>1</sup>H NMR titration  
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41 analysis verified that CH...O hydrogen bonding is demonstrated as the mode of  
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43 interaction, which possibly facilitates effective charge-transfer.  
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53 **Keywords:** Hexahomotrioxacalix[3]arene, Click chemistry, Colorimetric  
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55 chemosensor, Fluorometric chemosensor, 2,4,6-Trinitrophenol.  
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# Graphical Abstract



**Highlight:**

➤ Click-modified hexahomotrioxacalix[3]arene is developed for the first time to detection TNP.

➤ Fluorometric and colorimetric dual-modal chemosensor for TNP.

➤ Highly selective and sensitive are obtained and the detection limit is 70 ppb.

➤ A novel design strategy for developing chemosensors for TNP has been demonstrated.

## 1. Introduction

The design of chemosensors that are able to selectively recognize and sense specific analytes is an attractive research area in supramolecular chemistry [1-4]. In particular, the rapid and accurate detection of nitro-containing explosives is a high priority for security and health/environmental issues [5-6]. Various analytical techniques such as gas chromatography coupled with different detectors [7,8], high performance liquid chromatography [9,10], ion-mobility spectroscopy [11,12], Raman or surface enhanced Raman spectroscopy [13,14], electrochemical methods [15,16] and fluorescence spectroscopy [17,18] have been used for the detection of nitro-containing explosives. Among these techniques, fluorescence-based detection offers several advantages over other analytical methods with respect to high sensitivity, specificity, and real-time monitoring with fast response times [19]. To date, considerable effort has been devoted to the development of fluorescence sensing materials to detect nitro-containing explosives [20,21]. Even though several  $\pi$ -conjugated polymers [22] and metal-organic frameworks [23] have been employed to detect nitro-containing explosives, the development of reliable and efficient organic chemosensors possessing high selectivity for nitro-containing explosives remains a very challenging task [24,25].

Calixarenes are ideal frameworks for the development of chemosensors in the molecular recognition of chemical and biological targets of interest since the incorporation of a suitable sensory group into the calixarene results in a tailored

1 chromogenic receptor [26,27]. In particular, since Sharpless et al. developed click  
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3 chemistry as a new coupling strategy in 2001 [28], numerous calixarene derivatives  
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5 incorporating click-derived triazoles have been reported, which can be used as metal  
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7 ions chemosensors via coordination at nitrogen atom [29-31]. However, these  
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9 fluorescence systems have scarcely been exploited for the sensing of nitro-containing  
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11 explosives. As a matter of fact, given the strong dipolar character of the triazole ring,  
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13 the C–H bond of the heterocycle makes a surprisingly good hydrogen bond donor  
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15 [32,33]. On the other hand, nitro-containing explosives often act as good electron  
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17 acceptors due to the presence of electron withdrawing nitro (-NO<sub>2</sub>) group/s [34].  
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19 Considering these two opposite properties of triazole and nitro-containing explosives,  
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21 one might consider if noncovalent interactions exist between them?  
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31 In molecular recognition processes, noncovalent interactions such as hydrogen  
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33 bonding, aromatic  $\pi$ -stacking and weak intermolecular interactions play a crucial role.  
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35 With this in mind, can we utilize the click-derived triazole to design chemosensors for  
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37 nitro-containing explosive sensing? Herein, we report two triazole-modified  
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39 hexahomotrioxacalix[3]arenes **1** and **2** as a new type of chemosensor for the selective  
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41 detection of 2,4,6-trinitrophenol (TNP) explosive. To the best of our knowledge, this  
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43 is the first report where a triazole-modified hexahomotrioxacalix[3]arene serves as a  
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45 selective chemosensor for TNP.  
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## 52 **2. Experimental section**

### 53 *2.1. General*

1 Unless otherwise stated, all reagents were purchased from commercial  
2 sources and used without further purification. All solvents were dried and  
3 distilled by the usual procedures before use. Melting points were determined  
4 using a Yanagimoto MP-S1. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a  
5 Nippon Denshi JEOL FT-300 NMR spectrometer and a  
6 Varian-400MRvnmrs400 with SiMe<sub>4</sub> as an internal reference: *J*-values are  
7 given in Hz. IR spectra were measured as KBr pellets or as liquid films on  
8 NaCl plates in a Nippon Denshi JIR-AQ2OM spectrophotometer. UV spectra  
9 were measured by a Shimadzu UV-3150UV-vis-NIR spectrophotometer.  
10 Fluorescence spectroscopic studies of compounds in solution were performed in  
11 a semi-micro fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with  
12 a Varian Cary Eclipse spectrophotometer. Mass spectra were obtained on a  
13 Nippon Denshi JMS-01SG-2 mass spectrometer at an ionization energy of 70  
14 eV using a direct inlet system through GLC. Elemental analyses were  
15 performed by a Yanaco MT-5.

## 2.2. General procedure for synthesis of compound 1 and 2.

### Insert Scheme 1 in here

46 A solution of 1-azidomethylpyrene (230 mg, 0.89 mmol) and copper iodide (10 mg)  
47 was added to 3 (185 mg, 0.27 mmol) or 4 (200 mg, 0.27 mmol) in THF/H<sub>2</sub>O (v/v, 5:1,  
48 30 mL), respectively, and the heterogeneous mixture was stirred at 70 °C for 24 h.  
49 The resulting solution was cooled and extracted twice with CH<sub>2</sub>Cl<sub>2</sub>. The organic  
50 extracts were combined, dried over MgSO<sub>4</sub>, and then evaporated to give the solid  
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1 crude products. Column chromatography on silica gel eluting with 1:1  
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3 hexane/chloroform gave white solid compounds **1** and **2** in 63 % and 72 % yield,  
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6 respectively.  
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9 *Compound 1*. Mp. 139–141°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.97$  (s, 27H, *t*Bu),  
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11 4.21 (s, 6H, ArO- $\text{CH}_2$ -triazole), 4.23–4.34 (AB q, 12H, ether bridge,  $J = 10.8$  Hz),  
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13 5.75 (s, 6H, triazole- $\text{CH}_2$ -pyrene), 6.78 (s, 6H, ArH), 7.21 (s, 3H, triazole-H),  
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15 7.62–7.64 (d, 3H, pyrene-H,  $J = 7.6$  Hz), 7.80–7.93 (m, 18H, pyrene-H), 7.99–8.00  
16  
17 (d, 3H, pyrene-H,  $J = 7.6$  Hz), 8.07–8.10 (d, 3H, pyrene-H,  $J = 9.2$  Hz).  $^{13}\text{C NMR}$   
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19 (100 MHz,  $\text{CDCl}_3$ )  $\delta = 31.4, 34.1, 51.7, 66.8, 69.5, 121.9, 123.4, 124.1, 124.5, 124.7,$   
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21 125.4, 125.5, 125.9, 126.0, 127.0, 127.2, 127.3, 127.9, 128.6, 128.7, 130.2, 130.8,  
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23 130.9, 131.6, 144.2, 146.2, 152.1. MS:  $m/z$  1462.68 ( $\text{M}^+$ ). Anal. Calcd for  
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25  $\text{C}_{96}\text{H}_{87}\text{N}_9\text{O}_{12}$  (1462.77): C 78.82, H 5.99, N 8.62. Found: C 78.99, H 6.14, N 8.47.  
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33 *Compound 2*. Mp. 214–216 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.27$ –1.31 (t, 9H,  
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35  $\text{COOCH}_2\text{CH}_3$ ,  $J = 6.8$  Hz), 4.17–4.20 (d, 6H, Ar $\text{CH}_2$ (*eq*)O,  $J = 13.2$  Hz), 4.19–4.24  
36  
37 (q, 6H,  $\text{COOCH}_2\text{CH}_3$ ,  $J = 6.8$  Hz), 4.31 (s, 6H, ArO- $\text{CH}_2$ -triazole), 4.31–4.34 (d, 6H,  
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39 Ar $\text{CH}_2$ (*ax*)O,  $J = 13.2$  Hz), 5.78 (s, 6H, triazole- $\text{CH}_2$ -pyrene), 7.29 (s, 3H,  
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41 triazole-H), 7.39 (s, 6H, ArH), 7.64–7.66 (d, 3H, pyrene-H,  $J = 8.0$  Hz), 7.80–7.88  
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43 (m, 12H, pyrene-H), 7.90–7.94 (t, 6H, pyrene-H,  $J = 8.0$  Hz), 7.98–8.00 (d, 3H,  
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45 pyrene-H,  $J = 8.0$  Hz), 8.02–8.04 (d, 3H, pyrene-H,  $J = 8.0$  Hz).  $^{13}\text{C NMR}$  (100  
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47 MHz,  $\text{CDCl}_3$ )  $\delta = 14.3, 51.8, 60.6, 66.9, 68.9, 121.7, 123.4, 124.1, 124.6, 124.7,$   
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49 125.5, 125.6, 126.1, 126.1, 126.9, 127.0, 127.3, 127.9, 128.6, 128.7, 130.2, 130.8,  
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51 131.1, 131.7, 131.8, 143.6, 158.2, 165.4. FABMS:  $m/z$  1510.56 ( $\text{M}^+$ ),  
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1 1511.57(M+H<sup>+</sup>). Anal. calcd for C<sub>9</sub>H<sub>7</sub>N<sub>9</sub>O<sub>12</sub> (1510.64): C 73.94, H 5.00, N 8.34.

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3 found: C 73.89, H 5.04, N 8.36.

### 4 5 6 2.3 General procedure for the UV-vis and fluorescence titrations

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9 For absorption or fluorescence measurements, compounds were dissolved in  
10 acetonitrile to obtain stock solutions (1 mM). The stock solutions were diluted with  
11 acetonitrile to the desired concentration. In titration experiments, typically, aliquots of  
12 freshly prepared standard solutions (10<sup>-3</sup> M to 10<sup>-6</sup> M) of various analytes in  
13 acetonitrile were added to record the UV-vis and fluorescence spectra.  
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## 23 3. Results and discussion

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25 Sensors **1** and **2** were synthesized through **click** chemistry following our  
26 previous reports [35,36]. During this synthesis process, the Cu(I) was **shown**  
27 **not only to catalyze** the cycloaddition of alkynes and azides, but also produced  
28 a metal template effect. Thus, **1** and **2** were immobilized to the *cone* conformation.  
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Insert Fig. 1 in here

To explore the potential application of compounds **1** and **2** as chemosensors for the  
detection of **nitro-containing** explosives, several analytes were used for fluorescence  
titration experiments. The fluorescence titration of **1** and **2** with TNP revealed that the

1 fluorescence emission intensity rapidly died down upon addition of increasing  
2 amounts of TNP (Fig. 1 and Fig. S1); the decrease in fluorescence emission could be  
3 readily observed under illumination at 365 nm (Fig. 1, insert). These results implied  
4 that there are strong interactions between the sensors and TNP, and that the quenching  
5 of fluorescence emission might occur due to the formation of a possible  
6 non-fluorescent complex. Based on the fluorescence titration results, the  
7 Stern–Volmer plot was found to be linear at lower concentrations (up to 100  $\mu\text{M}$ , Fig.  
8 2), which indicates that fluorescence quenching involves a static quenching  
9 mechanism at lower concentrations of TNP. The Stern–Volmer constants were  
10 calculated to be  $K_{sv} = 2.23 \times 10^4 \text{ M}^{-1}$  (1) and  $K_{sv} = 1.04 \times 10^4 \text{ M}^{-1}$  (2), respectively. In  
11 particular, at higher concentrations, the plot was found to be a hyperbolic curve (Fig.  
12 S2), which may be attributed to a combination of both static and dynamic (collision)  
13 quenching [37-39].

### Insert Fig. 2 in here

14 The relative fluorescence quenching efficiencies of various analytes towards  
15 sensors 1 and 2 are summarized in the bar diagram (Fig. 3). The quenching efficiency  
16 was high for the electron deficient nitroaromatic compounds having an acidic -OH  
17 group. The order of the quenching efficiency was found to be  $\text{TNP} > \text{NP}$ , which is in  
18 complete agreement with the order of acidity of these analytes ( $\text{TNP} > \text{NP}$ ). This may  
19 explain the unprecedented selectivity for TNP, as other nitro-compounds do not have a  
20 hydroxyl group and so they cannot interact strongly with the chemosensor and so  
21 result in a very low quenching effect. TNP, with its highly acidic hydroxyl group,

1 interacts strongly with the chemosensor and results in very high fluorescence  
2  
3 quenching. These results demonstrate that both chemosensors **1** and **2** have high  
4  
5 selectivity for TNP compared to other nitro-compounds. Importantly, the detection  
6  
7 limit for TNP lies in the ppb range (70 ppb for sensor **1**) (Fig. S3 and S4) and  
8  
9 the response time is very fast (seconds). Moreover, the extent of emission  
10  
11 quenching of **1** in the presence of 100 equiv. of TNP after 10 seconds was practically  
12  
13 identical to that after 2 hours (Fig. S5). These experimental results demonstrate that  
14  
15 compounds **1** and **2** can be used as fluorescent sensor for TNP detection. Furthermore,  
16  
17 **1** and **2** behave as better TNP sensor compared with many previous sensors  
18  
19 reported in terms of selectivity, sensitivity and detection limit (Table S1). This  
20  
21 analyte-induced reduction in emission intensity is ascribed to the formation of  
22  
23 charge-transfer complexes between the electron donor (chemosensor) and the electron  
24  
25 acceptor (analyte) [40]. Such a mechanistic rationale is consistent with previous  
26  
27 reports in which it was suggested that thermodynamically favourable exciplex  
28  
29 formation between a fluorophore and a quencher involves strong coupling of the  
30  
31 respective  $\pi$  electrons, which in turn leads to deactivation of the fluorophore excited  
32  
33 singlet state [41].  
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48 **Insert Fig. 3 in here**

49  
50 The high sensitivity of sensor **1** towards TNP and the non-linear nature of the  
51  
52 Stern–Volmer plot for TNP suggested that an energy transfer process might also be  
53  
54 involved in the quenching process. As a matter of fact, when the absorption band of  
55  
56 the non-emissive analyte display overlaps with the emission spectra of the fluorophore,  
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1 resonance energy transfer can effectively occur [42,43]. As shown in Fig. 4, a distinct  
2  
3 spectral overlap of the absorption spectrum of TNP and the emission spectrum of  
4  
5 sensor **1** over the range 375–475 nm was observed. In particular, there is a larger  
6  
7 spectral overlap when TNP exists as picrate in the presence of the amine.  
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9 Resonance energy transfer from sensor to picrate could make an additional  
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11 contribution to the fluorescence quenching process [44,45]. Therefore, in solution  
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13 both charge-transfer and resonance energy transfer contributed to the amplified  
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15 quenching of fluorescence of the present systems.  
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22 **Insert Fig. 4 in here**

23 **Insert Fig. 5 in here**

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28 Efforts were also made to determine whether sensor **1** could be used as a naked-eye  
29  
30 detectable colorimetric chemosensor for TNP. As shown in Fig.5 (insert), on addition  
31  
32 of TNP to solutions of **1**, a remarkable and easily visible color change was observed  
33  
34 from pale yellow to reddish orange, which indicated the formation of the **1**•TNP  
35  
36 complex. This color change is characterized by corresponding changes in the UV-Vis  
37  
38 absorption spectrum. UV-Vis absorption titrations of **1** and **2** with TNP showed a  
39  
40 steady increase in the peak intensity on increasing the concentration of TNP (Fig. 5  
41  
42 and Fig. S6). It thus provides further support for the proposed charge-transfer  
43  
44 interaction between the electron-rich receptor and the electron deficient analyte and is  
45  
46 consistent with the proposed charge-transfer based fluorescence quenching. According  
47  
48 to the titration results, a linear relationship between the absorption intensity (at 343  
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1 nm) and concentration of TNP was observed (Fig. S7 and Fig. S8), which indicates  
2  
3 that chemosensor **1** and **2** can be used for colorimetric detection of TNP.  
4

5  
6 **Insert Fig. 6 in here**  
7

8  
9 In order to employ the detection in a feasible method, a test strip was conveniently  
10 prepared by dip coating a solution of **1** onto a filter paper and then subsequently  
11  
12 drying in air. As shown in Fig. 6, with the increase of TNP, there was an obvious  
13  
14 difference of quenching. When the concentration of TNP reached the 0.5 mM level,  
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18 the fluorescence was completely quenched.  
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22 **Insert Fig. 7 in here**  
23

24 **Insert Fig. 8 in here**  
25

26  
27 To explore the mechanism and to identify the actual binding position of TNP, <sup>1</sup>H  
28 NMR titrations involving TNP and sensors **1** and **2** were performed. As shown in Fig.  
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30  
31 **7**, the signals of *H<sub>a</sub>*, *H<sub>b</sub>* and *H<sub>c</sub>* were clearly shifted downfield upon the addition of 15  
32  
33 equiv. of TNP into the solution of sensor **1** ( $\Delta\delta = 0.17, 0.47$  and  $0.14$  ppm,  
34  
35 respectively). In the case of sensor **2**, upon addition of 30 equiv. of TNP to the  
36  
37 solution of **2**, the peaks for *H<sub>a</sub>*, *H<sub>b</sub>* and *H<sub>c</sub>* exhibited a similar but smaller  
38  
39 downfield shift by  $\Delta\delta = 0.17, 0.33$  and  $0.13$  ppm, respectively (Fig. S9). From the  
40  
41 spectral shifts, it was observed that proton *H<sub>b</sub>* underwent the maximum chemical shift,  
42  
43 whereas protons *H<sub>a</sub>* and *H<sub>c</sub>* proximal to the triazole rings underwent a smaller  
44  
45 chemical shift. These downfield shifts were ascribed to TNP withdrawing electron  
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47 density from the sensor. The significant change in the chemical shift of proton *H<sub>b</sub>*  
48  
49 suggested that the C–H bond of the triazole group acts as the receptor site. It is  
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1 possible that CH $\cdots$ O hydrogen bonding between  $H_b$  and TNP was formed, thus a  
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3 plausible binding mode between **1** and TNP is presented (Fig. 8). Hence, these  
4  
5 results clearly indicate that intermolecular charge transfer takes place between  
6  
7 the sensor and TNP. Based on the differences in the induced fluorescence  
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9 quenching response, greater changes in the chemical shift for sensor **1** were  
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#### 4. Conclusions

In summary, we have designed and synthesized two click-modified hexahomotrioxacalix[3]arenes **1** and **2**, each of which can be utilized as fluorometric and colorimetric chemosensor for 2,4,6-trinitrophenol. Chemosensor **1** and **2** exhibited high binding affinity and selectivity toward 2,4,6-trinitrophenol as evidenced by UV-vis and fluorescence studies.  $^1\text{H}$  NMR spectroscopic titrations revealed **1**•TNP complex formed via CH $\cdots$ O hydrogen bonding interaction. As a general design strategy, structural modifications by click chemistry may allow us to develop further chemosensor candidates for the future detection of nitro-containing explosives.

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5 travel grant to CR.  
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## 8 **Appendix A. Supplementary data**

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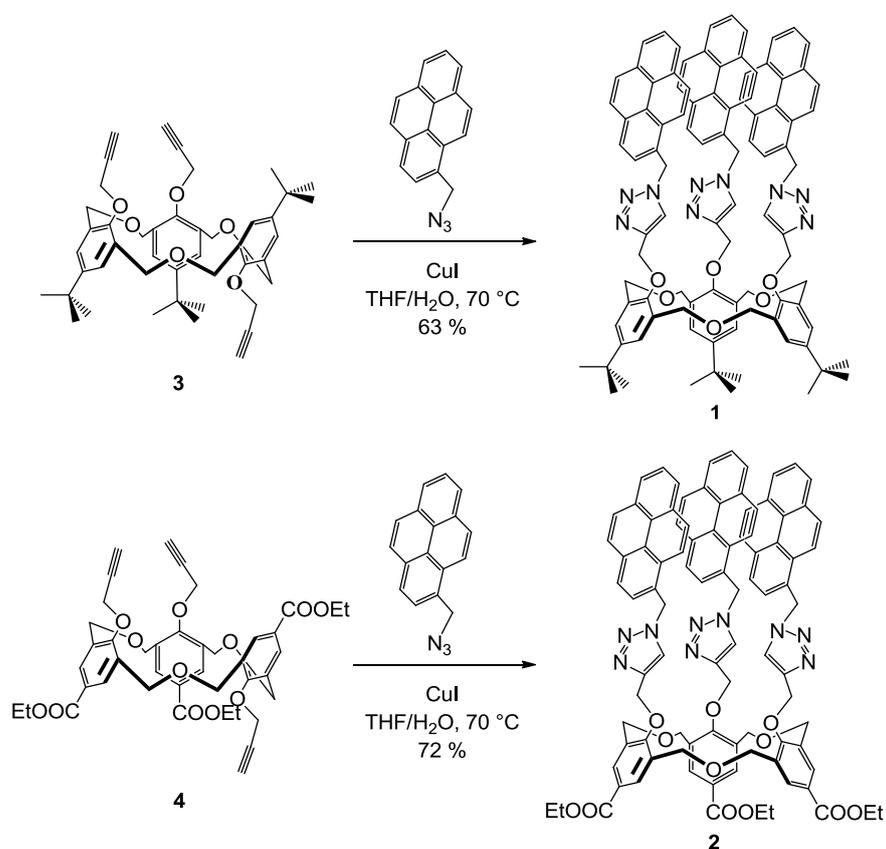
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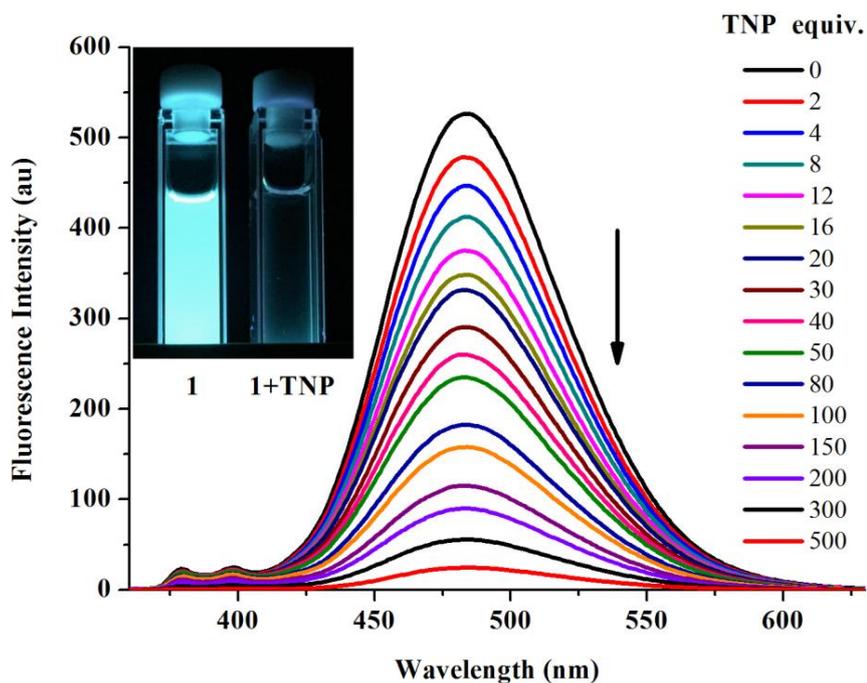
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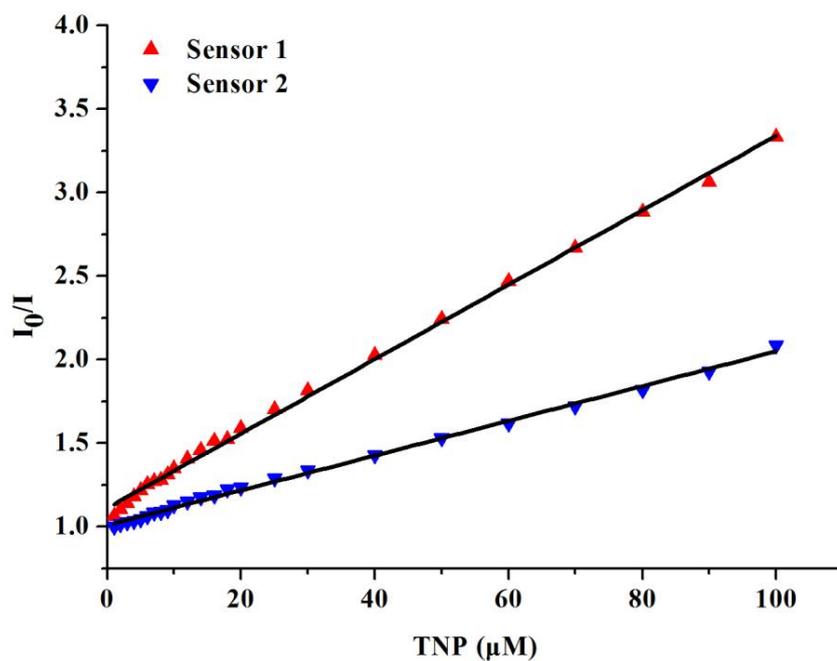
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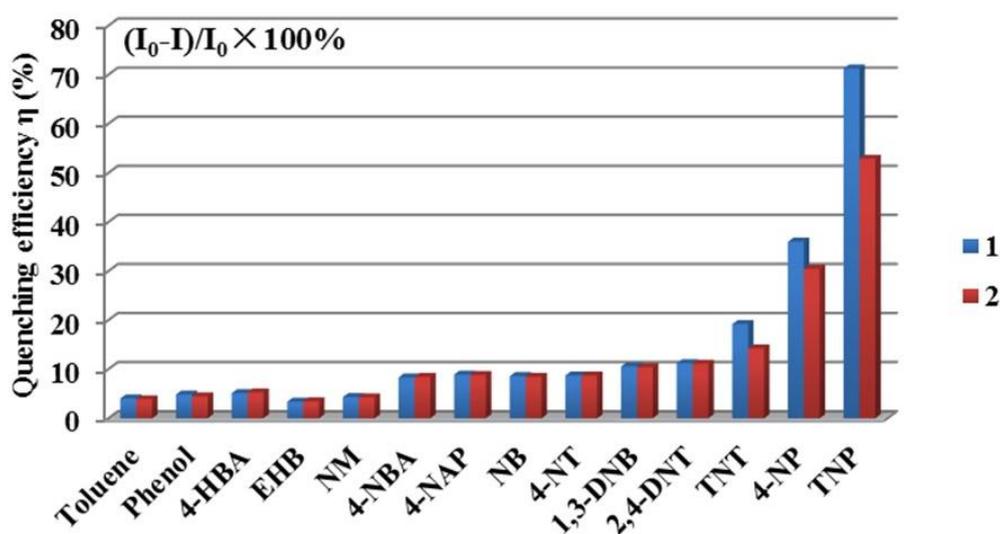
**Scheme 1** The synthetic route of chemosensors **1** and **2**.



**Fig. 1** Fluorescence emission spectra of **1** (1.0  $\mu\text{M}$ ) upon the addition of increasing concentrations of TNP in  $\text{CH}_3\text{CN}$ .  $\lambda_{\text{ex}} = 343 \text{ nm}$ . The inset shows the fluorescence color of **1** before and after the addition of TNP.

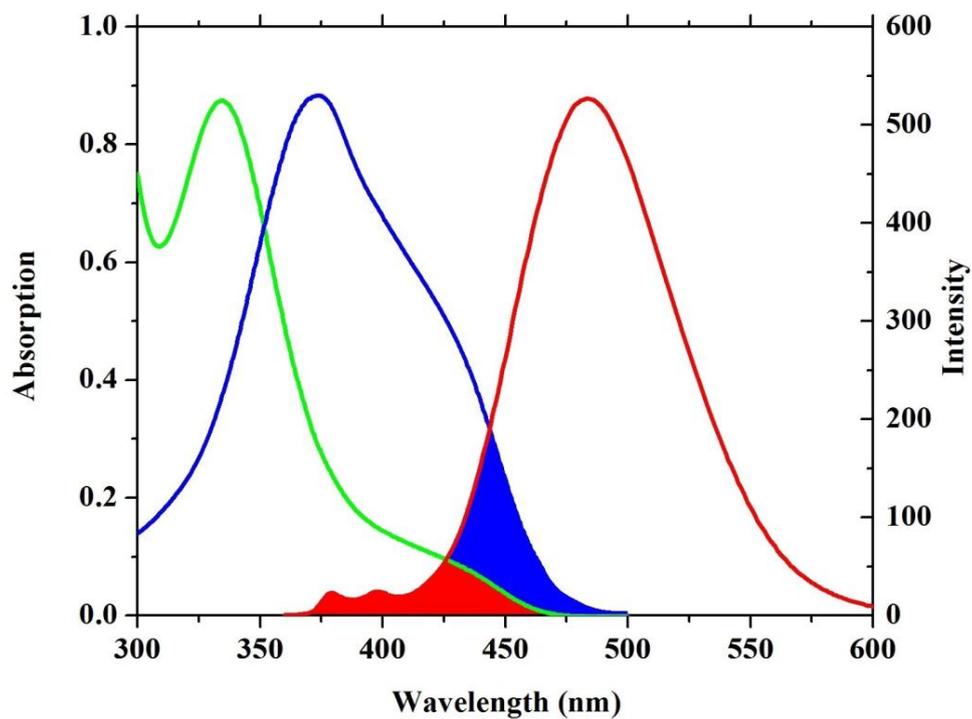


**Fig. 2** Stern–Volmer plots for the titration of sensors **1** and **2** with TNP at lower concentrations (up to 100  $\mu\text{M}$ ).

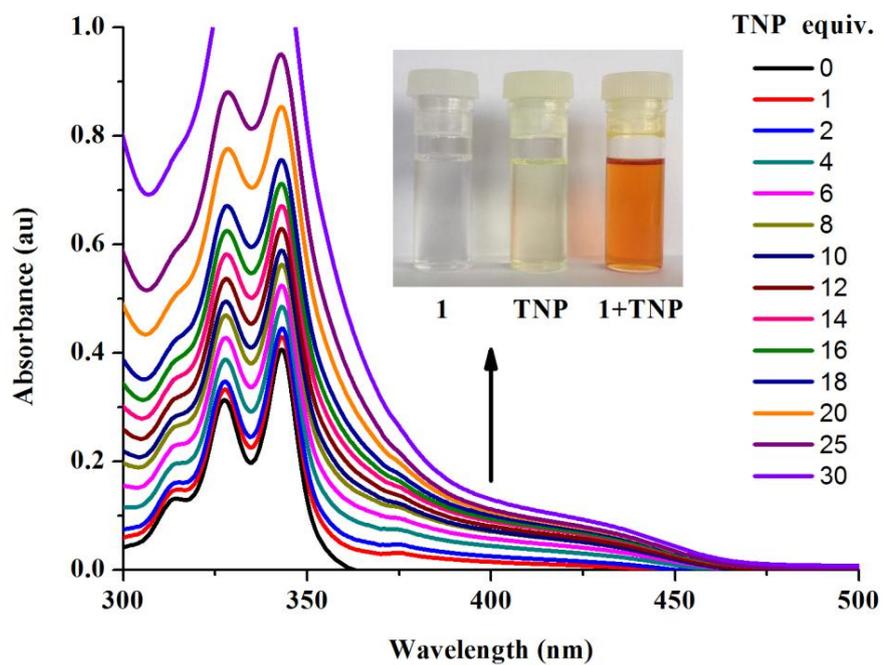


**Fig. 3** Reduction in fluorescence intensity (plotted as quenching efficiency) seen upon the addition of 100 equiv. of analytes. 4-HBA = 4-hydroxybenzoic acid, EHB = ethyl 4-hydroxybenzoate, NM = nitromethane, 4-NBA = 4-nitrobenzoic acid, 4-NAP = 4-nitroacetophenone, NB = nitrobenzene, 4-NT = 4-nitrotoluene, 1,3-DNB = 1,3-dinitrobenzene, 2,4-DNT = 2,4-dinitrotoluene, TNT = 2,4,6-trinitrotoluene, 4-NP = 4-nitrophenol and TNP = 2,4,6-trinitrophenol.

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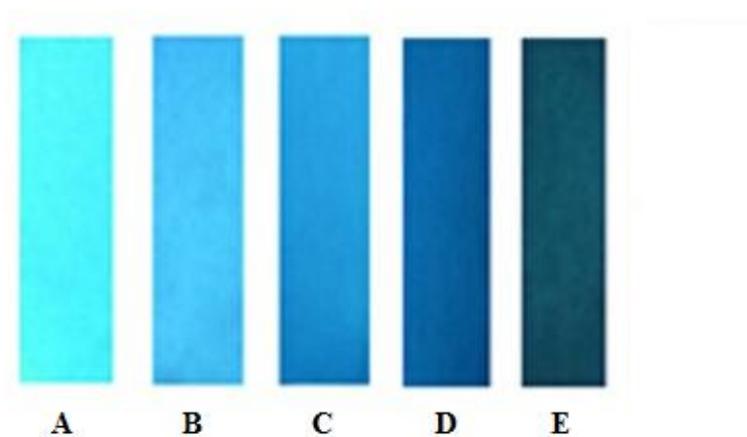


**Fig. 4** Spectral overlaps between absorption spectra of TNP (green line), TNP in the presence of amine (blue line) and the emission spectrum of **1** (red line).

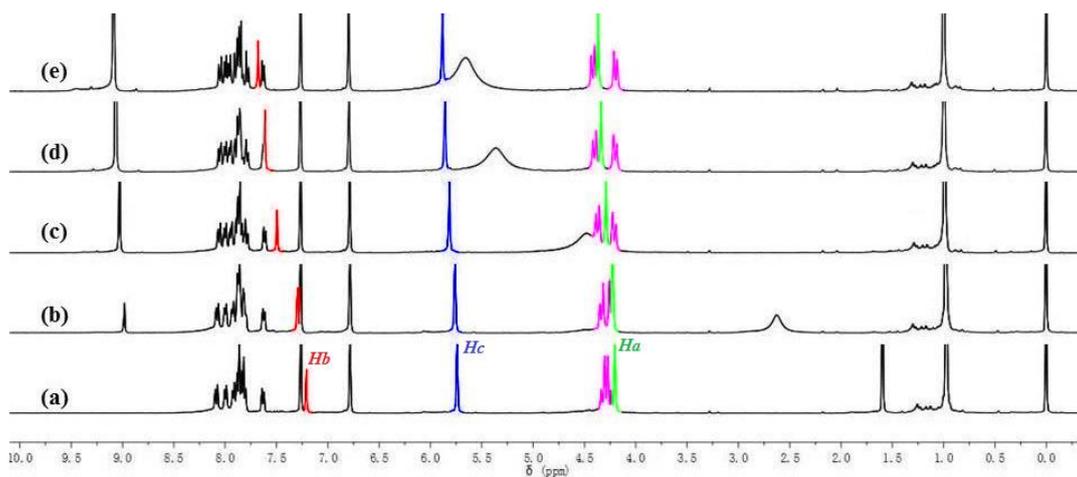


**Fig. 5** Change in absorption spectra of sensor **1** (5.0  $\mu\text{M}$ ) with the addition of TNP in  $\text{CH}_3\text{CN}$ . Inset: visual colour change due to the formation **1**•TNP complex.

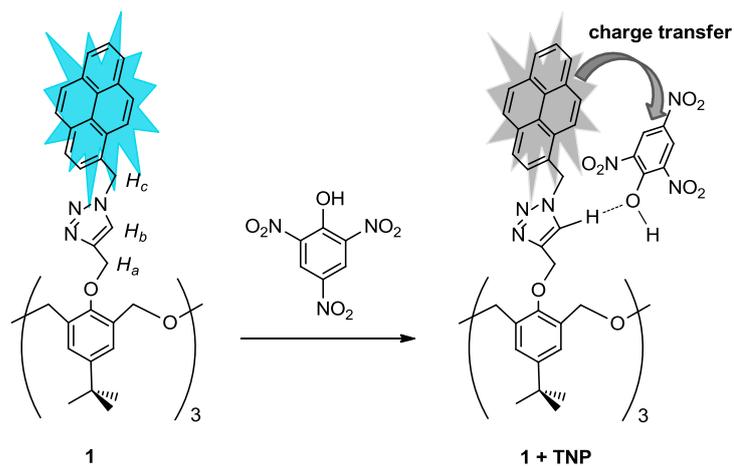
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**Fig. 6** Photographs (under 365 nm UV light) of the fluorescence response of **1** on test strips after contact with various concentrations of TNP: (A) 0.0  $\mu\text{M}$ , (B) 5.0  $\mu\text{M}$ , (C) 10.0  $\mu\text{M}$ , (D) 100.0  $\mu\text{M}$  and (E) 0.5 mM.



**Fig. 7** The  $^1\text{H}$  NMR spectra of **1** (5.0 mM) upon titration with TNP in  $\text{CDCl}_3$ . (a) **1** only, (b c d and e) in the presence of 1.0, 5.0, 10.0 and 15.0 equiv. of TNP, respectively.



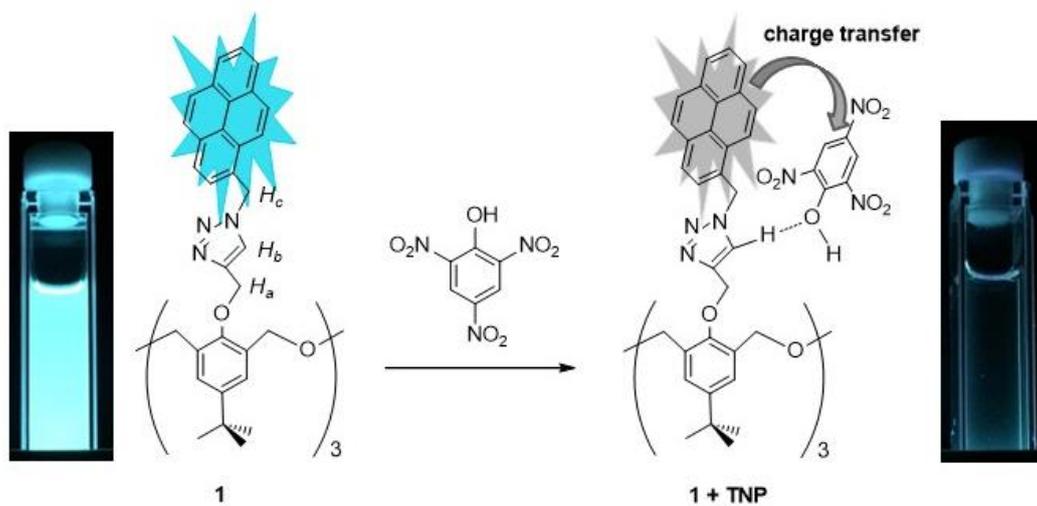
**Fig. 8** Plausible binding mode between **1** and TNP.

**Electronic Supplementary Material (online publication only)**

[Click here to download Electronic Supplementary Material \(online publication only\): 6. 0620 SI R1.pdf](#)



# Graphical Abstract



**Highlight:**

➤Click-modified hexahomotrioxacalix[3]arene is developed for the first time to detection TNP.

➤Fluorometric and colorimetric dual-modal chemosensor for TNP.

➤Highly selective and sensitive are obtained and the detection limit is 70 ppb.

➤A novel design strategy for developing chemosensors for TNP has been demonstrated.

## 1. Introduction

The design of chemosensors that are able to selectively recognize and sense specific analytes is an attractive research area in supramolecular chemistry [1-4]. In particular, the rapid and accurate detection of nitro-containing explosives is a high priority for security and health/environmental issues [5-6]. Various analytical techniques such as gas chromatography coupled with different detectors [7,8], high performance liquid chromatography [9,10], ion-mobility spectroscopy [11,12], Raman or surface enhanced Raman spectroscopy [13,14], electrochemical methods [15,16] and fluorescence spectroscopy [17,18] have been used for the detection of nitro-containing explosives. Among these techniques, fluorescence-based detection offers several advantages over other analytical methods with respect to high sensitivity, specificity, and real-time monitoring with fast response times [19]. To date, considerable effort has been devoted to the development of fluorescence sensing materials to detect nitro-containing explosives [20,21]. Even though several  $\pi$ -conjugated polymers [22] and metal-organic frameworks [23] have been employed to detect nitro-containing explosives, the development of reliable and efficient organic chemosensors possessing high selectivity for nitro-containing explosives remains a very challenging task [24,25].

Calixarenes are ideal frameworks for the development of chemosensors in the molecular recognition of chemical and biological targets of interest since the incorporation of a suitable sensory group into the calixarene results in a tailored

1 chromogenic receptor [26,27]. In particular, since Sharpless et al. developed click  
2 chemistry as a new coupling strategy in 2001 [28], numerous calixarene derivatives  
3 incorporating click-derived triazoles have been reported, which can be used as metal  
4 ions chemosensors via coordination at nitrogen atom [29-31]. However, these  
5 fluorescence systems have scarcely been exploited for the sensing of nitro-containing  
6 explosives. As a matter of fact, given the strong dipolar character of the triazole ring,  
7 the C–H bond of the heterocycle makes a surprisingly good hydrogen bond donor  
8 [32,33]. On the other hand, nitro-containing explosives often act as good electron  
9 acceptors due to the presence of electron withdrawing nitro (-NO<sub>2</sub>) group/s [34].  
10 Considering these two opposite properties of triazole and nitro-containing explosives,  
11 one might consider if noncovalent interactions exist between them?  
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31 In molecular recognition processes, noncovalent interactions such as hydrogen  
32 bonding, aromatic  $\pi$ -stacking and weak intermolecular interactions play a crucial role.  
33 With this in mind, can we utilize the click-derived triazole to design chemosensors for  
34 nitro-containing explosive sensing? Herein, we report two triazole-modified  
35 hexahomotrioxacalix[3]arenes **1** and **2** as a new type of chemosensor for the selective  
36 detection of 2,4,6-trinitrophenol (TNP) explosive. To the best of our knowledge, this  
37 is the first report where a triazole-modified hexahomotrioxacalix[3]arene serves as a  
38 selective chemosensor for TNP.  
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## 53 **2. Experimental section**

### 54 *2.1. General*

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1 Unless otherwise stated, all reagents were purchased from commercial  
2 sources and used without further purification. All solvents were dried and  
3 distilled by the usual procedures before use. Melting points were determined  
4 using a Yanagimoto MP-S1. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a  
5 Nippon Denshi JEOL FT-300 NMR spectrometer and a  
6 Varian-400MRvnmrs400 with SiMe<sub>4</sub> as an internal reference: *J*-values are  
7 given in Hz. IR spectra were measured as KBr pellets or as liquid films on  
8 NaCl plates in a Nippon Denshi JIR-AQ2OM spectrophotometer. UV spectra  
9 were measured by a Shimadzu UV-3150UV-vis-NIR spectrophotometer.  
10 Fluorescence spectroscopic studies of compounds in solution were performed in  
11 a semi-micro fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with  
12 a Varian Cary Eclipse spectrophotometer. Mass spectra were obtained on a  
13 Nippon Denshi JMS-01SG-2 mass spectrometer at an ionization energy of 70  
14 eV using a direct inlet system through GLC. Elemental analyses were  
15 performed by a Yanaco MT-5.

## 2.2. General procedure for synthesis of compound 1 and 2.

### Insert Scheme 1 in here

47 A solution of 1-azidomethylpyrene (230 mg, 0.89 mmol) and copper iodide (10 mg)  
48 was added to **3** (185 mg, 0.27 mmol) or **4** (200 mg, 0.27 mmol) in THF/H<sub>2</sub>O (v/v, 5:1,  
49 30 mL), respectively, and the heterogeneous mixture was stirred at 70 °C for 24 h.  
50 The resulting solution was cooled and extracted twice with CH<sub>2</sub>Cl<sub>2</sub>. The organic  
51 extracts were combined, dried over MgSO<sub>4</sub>, and then evaporated to give the solid  
52

1 crude products. Column chromatography on silica gel eluting with 1:1  
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3 hexane/chloroform gave white solid compounds **1** and **2** in 63 % and 72 % yield,  
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6 respectively.  
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9 *Compound 1.* Mp. 139–141°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 0.97 (s, 27H, *t*Bu),  
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11 4.21 (s, 6H, ArO–CH<sub>2</sub>–triazole), 4.23–4.34 (AB q, 12H, ether bridge, *J* = 10.8 Hz),  
12  
13 5.75 (s, 6H, triazole–CH<sub>2</sub>–pyrene), 6.78 (s, 6H, ArH), 7.21 (s, 3H, triazole–H),  
14  
15 7.62–7.64 (d, 3H, pyrene–H, *J* = 7.6 Hz), 7.80–7.93 (m, 18H, pyrene–H), 7.99–8.00  
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17 (d, 3H, pyrene–H, *J* = 7.6 Hz), 8.07–8.10 (d, 3H, pyrene–H, *J* = 9.2 Hz). <sup>13</sup>C NMR  
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19 (100 MHz, CDCl<sub>3</sub>) δ = 31.4, 34.1, 51.7, 66.8, 69.5, 121.9, 123.4, 124.1, 124.5, 124.7,  
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21 125.4, 125.5, 125.9, 126.0, 127.0, 127.2, 127.3, 127.9, 128.6, 128.7, 130.2, 130.8,  
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23 130.9, 131.6, 144.2, 146.2, 152.1. MS: *m/z* 1462.68 (M<sup>+</sup>). Anal. Calcd for  
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25 C<sub>96</sub>H<sub>87</sub>N<sub>9</sub>O<sub>12</sub> (1462.77): C 78.82, H 5.99, N 8.62. Found: C 78.99, H 6.14, N 8.47.  
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34 *Compound 2.* Mp. 214–216 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.27–1.31 (t, 9H,  
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36 COOCH<sub>2</sub>CH<sub>3</sub>, *J* = 6.8 Hz), 4.17–4.20 (d, 6H, ArCH<sub>2</sub>(*eq*)O, *J* = 13.2 Hz), 4.19–4.24  
37  
38 (q, 6H, COOCH<sub>2</sub>CH<sub>3</sub>, *J* = 6.8 Hz), 4.31 (s, 6H, ArO–CH<sub>2</sub>–triazole), 4.31–4.34 (d, 6H,  
39  
40 ArCH<sub>2</sub>(*ax*)O, *J* = 13.2 Hz), 5.78 (s, 6H, triazole–CH<sub>2</sub>–pyrene), 7.29 (s, 3H,  
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42 triazole–H), 7.39 (s, 6H, ArH), 7.64–7.66 (d, 3H, pyrene–H, *J* = 8.0 Hz), 7.80–7.88  
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44 (m, 12H, pyrene–H), 7.90–7.94 (t, 6H, pyrene–H, *J* = 8.0 Hz), 7.98–8.00 (d, 3H,  
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46 pyrene–H, *J* = 8.0 Hz), 8.02–8.04 (d, 3H, pyrene–H, *J* = 8.0 Hz). <sup>13</sup>C NMR (100  
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48 MHz, CDCl<sub>3</sub>) δ = 14.3, 51.8, 60.6, 66.9, 68.9, 121.7, 123.4, 124.1, 124.6, 124.7,  
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50 125.5, 125.6, 126.1, 126.1, 126.9, 127.0, 127.3, 127.9, 128.6, 128.7, 130.2, 130.8,  
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52 131.1, 131.7, 131.8, 143.6, 158.2, 165.4. FABMS: *m/z* 1510.56 (M<sup>+</sup>),  
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1 1511.57(M+H<sup>+</sup>). Anal. calcd for C<sub>9</sub>H<sub>7</sub>N<sub>9</sub>O<sub>12</sub> (1510.64): C 73.94, H 5.00, N 8.34.

2  
3 found: C 73.89, H 5.04, N 8.36.

### 4 5 6 2.3 General procedure for the UV-vis and fluorescence titrations

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9 For absorption or fluorescence measurements, compounds were dissolved in  
10 acetonitrile to obtain stock solutions (1 mM). The stock solutions were diluted with  
11 acetonitrile to the desired concentration. In titration experiments, typically, aliquots of  
12 freshly prepared standard solutions (10<sup>-3</sup> M to 10<sup>-6</sup> M) of various analytes in  
13 acetonitrile were added to record the UV-vis and fluorescence spectra.  
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## 22 3. Results and discussion

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25 Sensors **1** and **2** were synthesized through click chemistry following our  
26 previous reports [35,36]. During this synthesis process, the Cu(I) was shown  
27 not only to catalyze the cycloaddition of alkynes and azides, but also produced  
28 a metal template effect. Thus, **1** and **2** were immobilized to the *cone* conformation.  
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Insert Fig. 1 in here

To explore the potential application of compounds **1** and **2** as chemosensors for the detection of nitro-containing explosives, several analytes were used for fluorescence titration experiments. The fluorescence titration of **1** and **2** with TNP revealed that the

1 fluorescence emission intensity rapidly died down upon addition of increasing  
2 amounts of TNP (Fig. 1 and Fig. S1); the decrease in fluorescence emission could be  
3 readily observed under illumination at 365 nm (Fig. 1, insert). These results implied  
4 that there are strong interactions between the sensors and TNP, and that the quenching  
5 of fluorescence emission might occur due to the formation of a possible  
6 non-fluorescent complex. Based on the fluorescence titration results, the  
7 Stern–Volmer plot was found to be linear at lower concentrations (up to 100  $\mu\text{M}$ , Fig.  
8 2), which indicates that fluorescence quenching involves a static quenching  
9 mechanism at lower concentrations of TNP. The Stern–Volmer constants were  
10 calculated to be  $K_{sv} = 2.23 \times 10^4 \text{ M}^{-1}$  (1) and  $K_{sv} = 1.04 \times 10^4 \text{ M}^{-1}$  (2), respectively. In  
11 particular, at higher concentrations, the plot was found to be a hyperbolic curve (Fig.  
12 S2), which may be attributed to a combination of both static and dynamic (collision)  
13 quenching [37-39].

### Insert Fig. 2 in here

14 The relative fluorescence quenching efficiencies of various analytes towards  
15 sensors 1 and 2 are summarized in the bar diagram (Fig. 3). The quenching efficiency  
16 was high for the electron deficient nitroaromatic compounds having an acidic -OH  
17 group. The order of the quenching efficiency was found to be  $\text{TNP} > \text{NP}$ , which is in  
18 complete agreement with the order of acidity of these analytes ( $\text{TNP} > \text{NP}$ ). This may  
19 explain the unprecedented selectivity for TNP, as other nitro-compounds do not have a  
20 hydroxyl group and so they cannot interact strongly with the chemosensor and so  
21 result in a very low quenching effect. TNP, with its highly acidic hydroxyl group,

1 interacts strongly with the chemosensor and results in very high fluorescence  
2  
3 quenching. These results demonstrate that both chemosensors **1** and **2** have high  
4  
5 selectivity for TNP compared to other nitro-compounds. Importantly, the detection  
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7 limit for TNP lies in the ppb range (70 ppb for sensor **1**) (Fig. S3 and S4) and  
8  
9 the response time is very fast (seconds). Moreover, the extent of emission  
10  
11 quenching of **1** in the presence of 100 equiv. of TNP after 10 seconds was practically  
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13 identical to that after 2 hours (Fig. S5). These experimental results demonstrate that  
14  
15 compounds **1** and **2** can be used as fluorescent sensor for TNP detection. Furthermore,  
16  
17 **1** and **2** behave as better TNP sensor compared with many previous sensors  
18  
19 reported in terms of selectivity, sensitivity and detection limit (Table S1). This  
20  
21 analyte-induced reduction in emission intensity is ascribed to the formation of  
22  
23 charge-transfer complexes between the electron donor (chemosensor) and the electron  
24  
25 acceptor (analyte) [40]. Such a mechanistic rationale is consistent with previous  
26  
27 reports in which it was suggested that thermodynamically favourable exciplex  
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29 formation between a fluorophore and a quencher involves strong coupling of the  
30  
31 respective  $\pi$  electrons, which in turn leads to deactivation of the fluorophore excited  
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33 singlet state [41].  
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47 **Insert Fig. 3 in here**

48  
49 The high sensitivity of sensor **1** towards TNP and the non-linear nature of the  
50  
51 Stern–Volmer plot for TNP suggested that an energy transfer process might also be  
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53 involved in the quenching process. As a matter of fact, when the absorption band of  
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55 the non-emissive analyte display overlaps with the emission spectra of the fluorophore,  
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1 resonance energy transfer can effectively occur [42,43]. As shown in Fig. 4, a distinct  
2  
3 spectral overlap of the absorption spectrum of TNP and the emission spectrum of  
4  
5 sensor **1** over the range 375–475 nm was observed. In particular, there is a larger  
6  
7 spectral overlap when TNP exists as picrate in the presence of the amine.  
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9 Resonance energy transfer from sensor to picrate could make an additional  
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11 contribution to the fluorescence quenching process [44,45]. Therefore, in solution  
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13 both charge-transfer and resonance energy transfer contributed to the amplified  
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15 quenching of fluorescence of the present systems.  
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22 **Insert Fig. 4 in here**

23 **Insert Fig. 5 in here**

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28 Efforts were also made to determine whether sensor **1** could be used as a naked-eye  
29  
30 detectable colorimetric chemosensor for TNP. As shown in Fig.5 (insert), on addition  
31  
32 of TNP to solutions of **1**, a remarkable and easily visible color change was observed  
33  
34 from pale yellow to reddish orange, which indicated the formation of the **1**•TNP  
35  
36 complex. This color change is characterized by corresponding changes in the UV-Vis  
37  
38 absorption spectrum. UV-Vis absorption titrations of **1** and **2** with TNP showed a  
39  
40 steady increase in the peak intensity on increasing the concentration of TNP (Fig. 5  
41  
42 and Fig. S6). It thus provides further support for the proposed charge-transfer  
43  
44 interaction between the electron-rich receptor and the electron deficient analyte and is  
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46 consistent with the proposed charge-transfer based fluorescence quenching. According  
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48 to the titration results, a linear relationship between the absorption intensity (at 343  
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1 nm) and concentration of TNP was observed (Fig. S7 and Fig. S8), which indicates  
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3 that chemosensor **1** and **2** can be used for colorimetric detection of TNP.  
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6 **Insert Fig. 6 in here**  
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9 In order to employ the detection in a feasible method, a test strip was conveniently  
10 prepared by dip coating a solution of **1** onto a filter paper and then subsequently  
11 drying in air. As shown in Fig. 6, with the increase of TNP, there was an obvious  
12 difference of quenching. When the concentration of TNP reached the 0.5 mM level,  
13 the fluorescence was completely quenched.  
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22 **Insert Fig. 7 in here**  
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24 **Insert Fig. 8 in here**  
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27 To explore the mechanism and to identify the actual binding position of TNP, <sup>1</sup>H  
28 NMR titrations involving TNP and sensors **1** and **2** were performed. As shown in Fig.  
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30  
31 **7**, the signals of *H<sub>a</sub>*, *H<sub>b</sub>* and *H<sub>c</sub>* were clearly shifted downfield upon the addition of 15  
32 equiv. of TNP into the solution of sensor **1** ( $\Delta\delta = 0.17, 0.47$  and  $0.14$  ppm,  
33 respectively). In the case of sensor **2**, upon addition of 30 equiv. of TNP to the  
34 solution of **2**, the peaks for *H<sub>a</sub>*, *H<sub>b</sub>* and *H<sub>c</sub>* exhibited a similar but smaller  
35 downfield shift by  $\Delta\delta = 0.17, 0.33$  and  $0.13$  ppm, respectively (Fig. S9). From the  
36 spectral shifts, it was observed that proton *H<sub>b</sub>* underwent the maximum chemical shift,  
37 whereas protons *H<sub>a</sub>* and *H<sub>c</sub>* proximal to the triazole rings underwent a smaller  
38 chemical shift. These downfield shifts were ascribed to TNP withdrawing electron  
39 density from the sensor. The significant change in the chemical shift of proton *H<sub>b</sub>*  
40 suggested that the C–H bond of the triazole group acts as the receptor site. It is  
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1 possible that CH $\cdots$ O hydrogen bonding between  $H_b$  and TNP was formed, thus a  
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3 plausible binding mode between **1** and TNP is presented (Fig. 8). Hence, these  
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5 results clearly indicate that intermolecular charge transfer takes place between  
6  
7 the sensor and TNP. Based on the differences in the induced fluorescence  
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9 quenching response, greater changes in the chemical shift for sensor **1** were  
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#### 4. Conclusions

In summary, we have designed and synthesized two click-modified hexahomotrioxacalix[3]arenes **1** and **2**, each of which can be utilized as fluorometric and colorimetric chemosensor for 2,4,6-trinitrophenol. Chemosensor **1** and **2** exhibited high binding affinity and selectivity toward 2,4,6-trinitrophenol as evidenced by UV-vis and fluorescence studies.  $^1\text{H}$  NMR spectroscopic titrations revealed **1**•TNP complex formed via CH $\cdots$ O hydrogen bonding interaction. As a general design strategy, structural modifications by click chemistry may allow us to develop further chemosensor candidates for the future detection of nitro-containing explosives.

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## 8 **Appendix A. Supplementary data**

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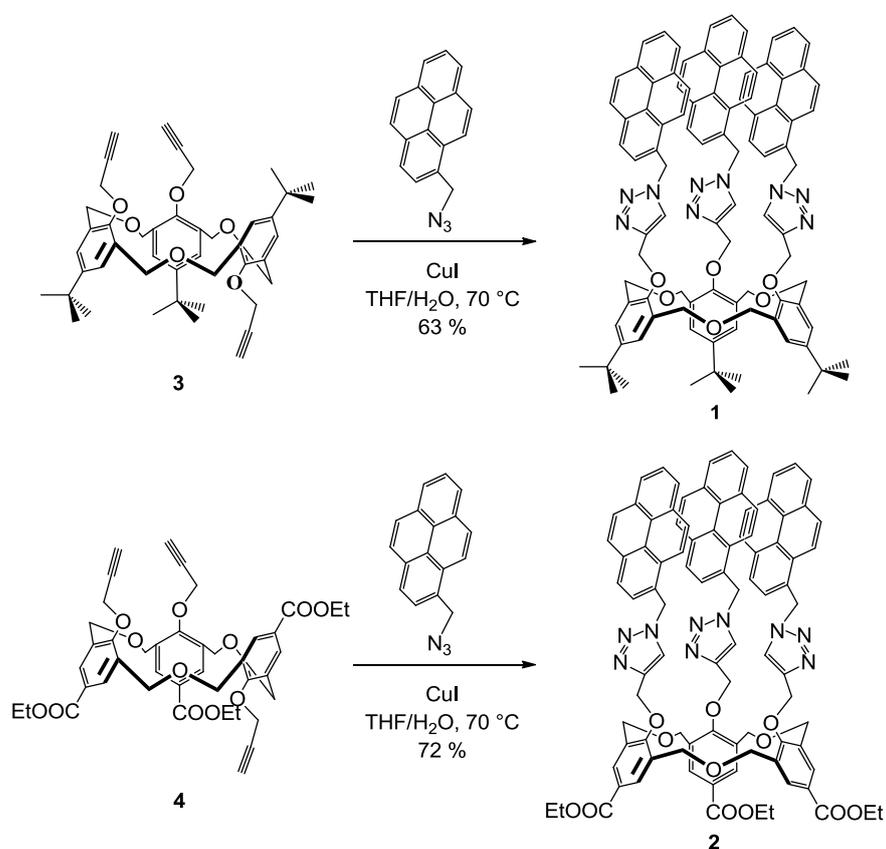
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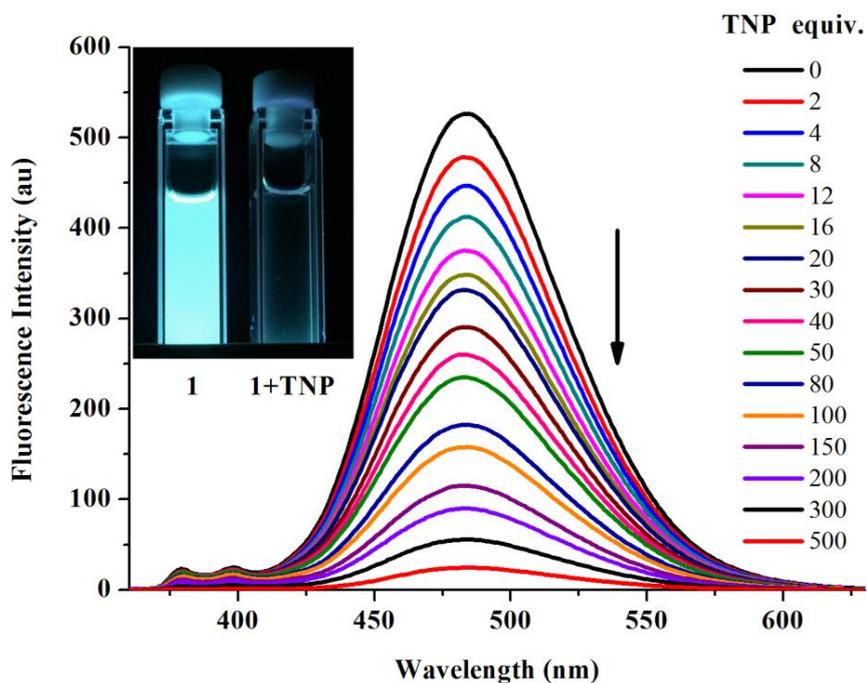
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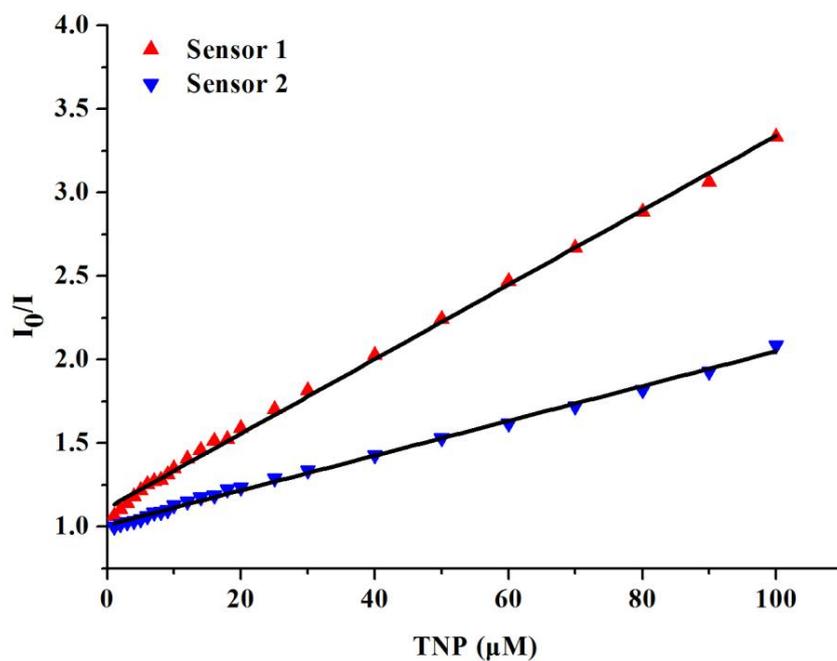
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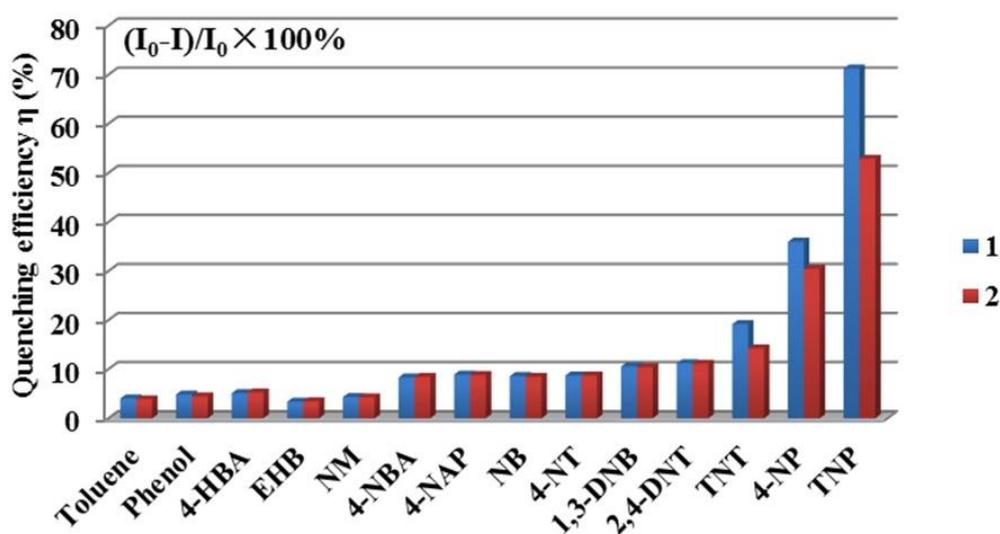
**Scheme 1** The synthetic route of chemosensors **1** and **2**.



**Fig. 1** Fluorescence emission spectra of **1** (1.0  $\mu\text{M}$ ) upon the addition of increasing concentrations of TNP in  $\text{CH}_3\text{CN}$ .  $\lambda_{\text{ex}} = 343 \text{ nm}$ . The inset shows the fluorescence color of **1** before and after the addition of TNP.

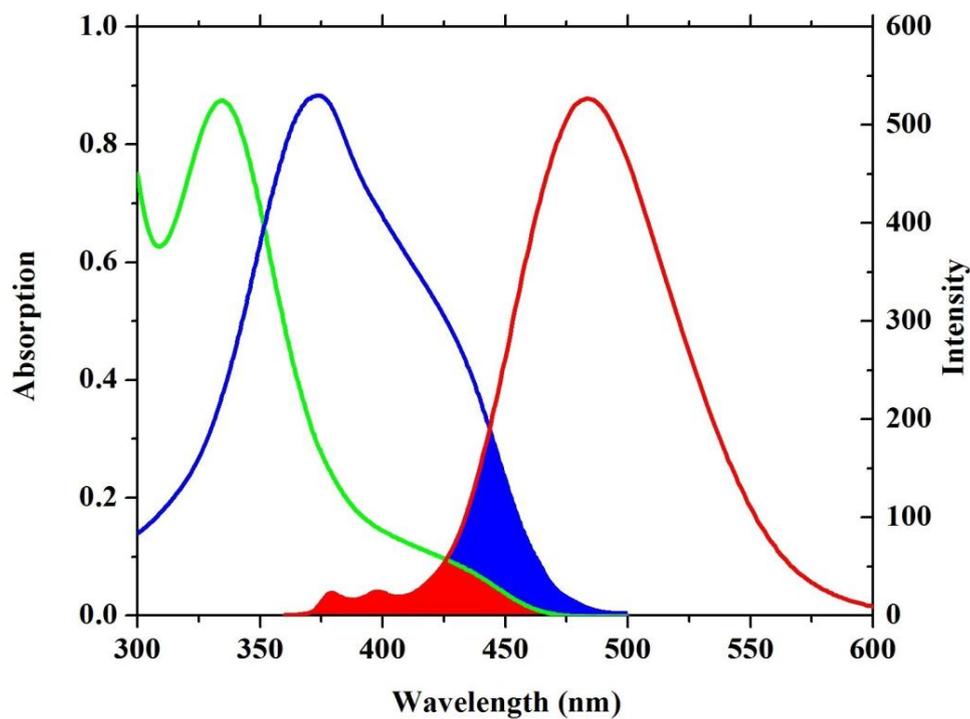


**Fig. 2** Stern–Volmer plots for the titration of sensors **1** and **2** with TNP at lower concentrations (up to 100  $\mu\text{M}$ ).

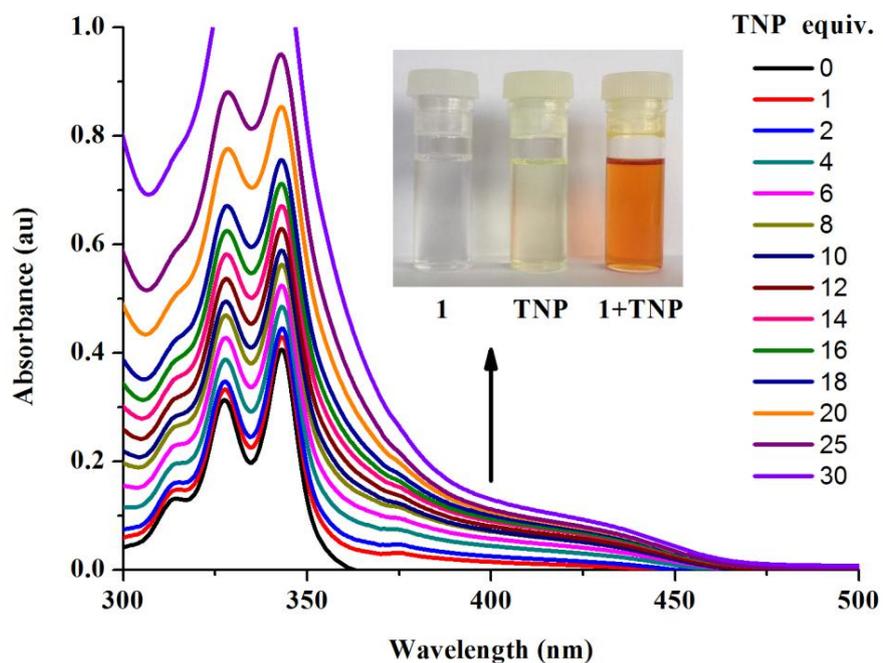


**Fig. 3** Reduction in fluorescence intensity (plotted as quenching efficiency) seen upon the addition of 100 equiv. of analytes. 4-HBA = 4-hydroxybenzoic acid, EHB = ethyl 4-hydroxybenzoate, NM = nitromethane, 4-NBA = 4-nitrobenzoic acid, 4-NAP = 4-nitroacetophenone, NB = nitrobenzene, 4-NT = 4-nitrotoluene, 1,3-DNB = 1,3-dinitrobenzene, 2,4-DNT = 2,4-dinitrotoluene, TNT = 2,4,6-trinitrotoluene, 4-NP = 4-nitrophenol and TNP = 2,4,6-trinitrophenol.

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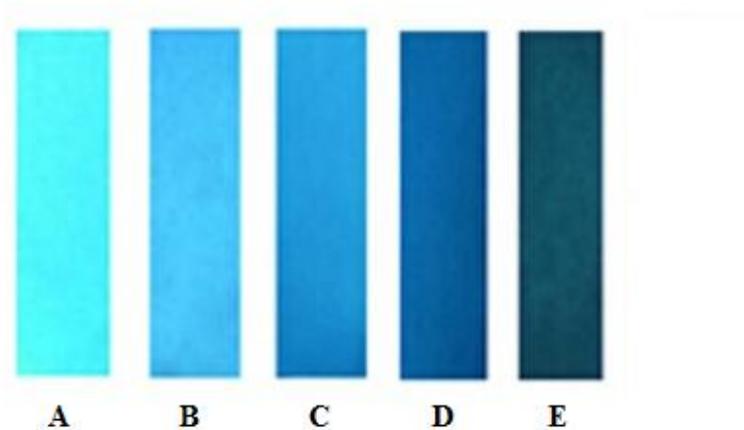


**Fig. 4** Spectral overlaps between absorption spectra of TNP (green line), TNP in the presence of amine (blue line) and the emission spectrum of **1** (red line).

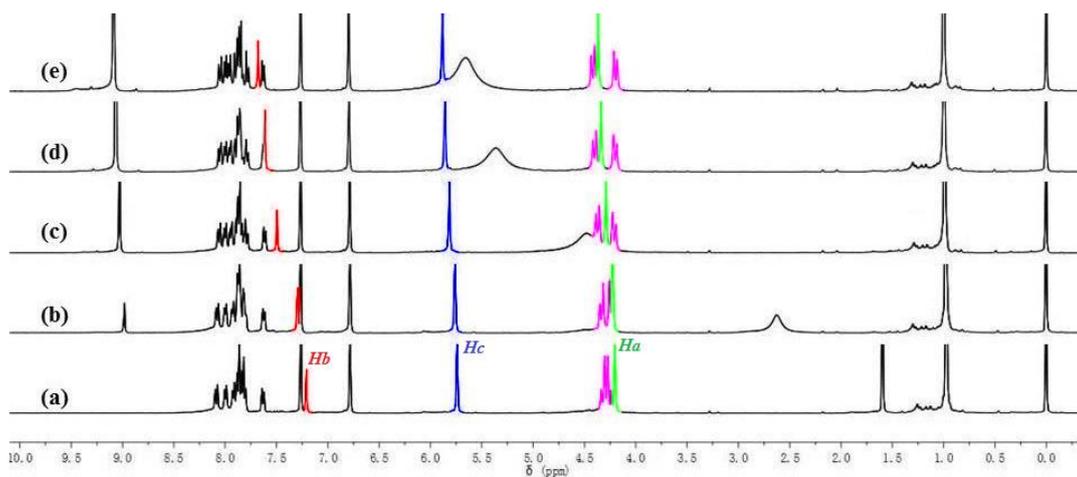


**Fig. 5** Change in absorption spectra of sensor **1** (5.0  $\mu\text{M}$ ) with the addition of TNP in  $\text{CH}_3\text{CN}$ . Inset: visual colour change due to the formation **1**•TNP complex.

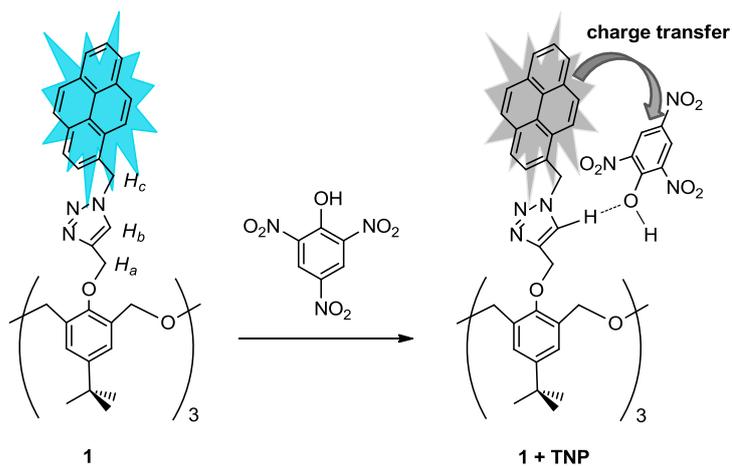
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**Fig. 6** Photographs (under 365 nm UV light) of the fluorescence response of **1** on test strips after contact with various concentrations of TNP: (A) 0.0  $\mu\text{M}$ , (B) 5.0  $\mu\text{M}$ , (C) 10.0  $\mu\text{M}$ , (D) 100.0  $\mu\text{M}$  and (E) 0.5 mM.



**Fig. 7** The  $^1\text{H}$  NMR spectra of **1** (5.0 mM) upon titration with TNP in  $\text{CDCl}_3$ . (a) **1** only, (b c d and e) in the presence of 1.0, 5.0, 10.0 and 15.0 equiv. of TNP, respectively.



**Fig. 8** Plausible binding mode between **1** and TNP.