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Synthesis of a deep cavity calix[4]arene by fourfold Sonogashira cross-coupling reaction and selective fluorescent recognition toward *p*-nitrophenol

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ABSTRACT

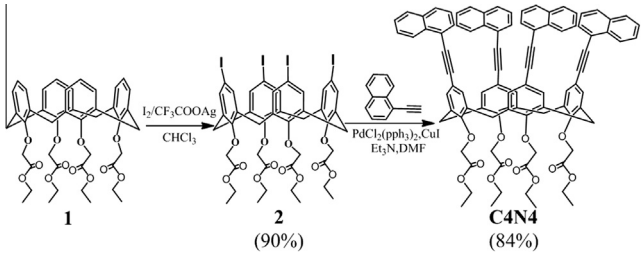
A new tetranaphthyl-calix[4]arene (**C4N4**) was synthesized by a fourfold Sonogashira cross-coupling reaction, and exhibited high affinity and selectivity for *p*-nitrophenol (**3c**) by fluorescence spectroscopy. The NMR, AFM, IR, MALDI-TOF mass spectroscopy, and computational calculations revealed the formation of a host–guest complex driven by π–π stacking interactions.

Geometric isomers with small differences in structure can have distinctly different properties. This includes geometric isomers such as trans and *cis* isomers or 1,2-, 1,3-, and 1,4-disubstituted benzene derivatives.[1] Fundamental investigations into the selective probe of isomerization of organic molecules are of great importance.[2–5] For instance, nitrophenol isomers are known to play a prominent role as indicators, synthetic dyes, and as intermediates for other substances. The selective probe of such geometric isomers is, however, difficult,[6] and little research has been done into fluorescence probe to date.[7]

Macrocyclic compounds, specifically calixarenes are one of the best known host molecules,[8,9] with adjustable cavity by modifying the substituents of the upper and lower rims. They are therefore widely used as receptors for ionic and molecular recognition,[10] especially for neutral molecules.[11] Calixarenes form supramolecular complexes by electrostatic, donor–acceptor, hydrophobic, and π–π stacking interactions to small molecules and ions through the aromatic system of the macrocyclic cavity. Research is ongoing, and some neutral organic compounds can be recognized based on functionalized calixarenes.[12] For example, the Kim group has used functionalized calixarenes to recognize ions and molecules. In addition, our group have synthesized fluorescent calix[4]arenes which showed highly selectivity toward *p*-nitroaniline.[13] However, the size of the cavity in calix[4]arene comes with certain restrictions, and some neutral organic compounds cannot fit into the cavity. To achieve neutral organic molecules recognition, a design including deep cavity calixarenes is of interest. To date, deep cavity calixarenes have not been largely explored.[14]

The fourfold Sonogashira cross-coupling reaction is described as efficient synthetic tool for the preparation of calixarenes with relatively deep electron-rich cavities. In this study, we report the design and synthesis of a deep cavity tetranaphthyl-calix[4]arene (**C4N4**) as a fluorescence probe system for an isomer of nitrophenol, which is highly selective toward *p*-nitrophenol (**3c**).

The novel deep cavity fluorescent calix[4]arene, **C4N4**, was synthesized by a fourfold Sonogashira cross-coupling reaction as shown in Scheme 1.[15] Initially, the tetraester-calix[4]arene,[16] iodine, and silver trifluoroacetate were stirred in chloroform to



Scheme 1. Synthetic route to **C4N4**.

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afford tetraiodo-calix[4]arene **2** in 90% yield.[17] Compound **2**, $PdCl_2(PPh_3)_2$ and CuI were stirred in Et_3N and DMF under a N_2 atmosphere, and 1-ethynylnaphthalene was then added. The mixture was stirred at 100 °C for 14 h. The evaporated crude product was then purified by column chromatography to give a white powder **C4N4** in 84% yield. The structure of **C4N4** was characterized by MALDI-TOF-MS (Fig. S3), NMR spectra, and microanalysis (Figs. S1 and S2). The compound was confirmed by the presence of two doublets (3.36–3.40 and 4.96–5.00 ppm) for the bridging methylene groups in the ^{1}H NMR spectra.[18]

The fluorescence spectrum of **C4N4** (λ_{ex} = 300 nm) in CH_3CN exhibited a characteristic emission band at 378 nm. The molecular recognition behavior of the **C4N4** was studied with respect to nitrobenzenes derivatives **3a**–**h** by fluorescence spectroscopy. Figure 1 shows the fluorescence response of **C4N4** with eight equivalents of the nitrobenzenes derivatives (**3a**–**h**), including *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, 2,4,6-trinitrophenol, nitrobenzene, 1,3-dinitrobenzene, 2,6-dinitrotoluene, and 2,4,6-trinitrotoluene. Interestingly, *p*-nitrophenol caused the most significant quench of **C4N4**, but the other nitrobenzene derivatives had very little effect on fluorescence. This shows that fluorescence quenching by *p*-nitrophenol was not only due to the quenching of the nitro group, but also due to the host–guest interaction by matching size.

In order to investigate the binding constant and stoichiometry between host and guest, the fluorescence spectra of **C4N4** (1×10^{-5} M) at increasing concentrations of **3c** are depicted in Figure 2. It was found that while no shift in the fluorescence maximum was observed, the fluorescence intensity of **C4N4** decreased with increasing concentrations of **3c**. The association constant of **C4N4** for **3c** was evaluated using the Benesi–Hildebrand equation and was found to be 10.06×10^3 M^{-1} (Fig. 2).[19] Meanwhile, in the Job plot, the maximum fluorescence change was observed when the molar fraction of **C4N4** to **3c** was 0.5, implying that a 1:1 inclusion complex has been formed (Fig. S6).[20] An important

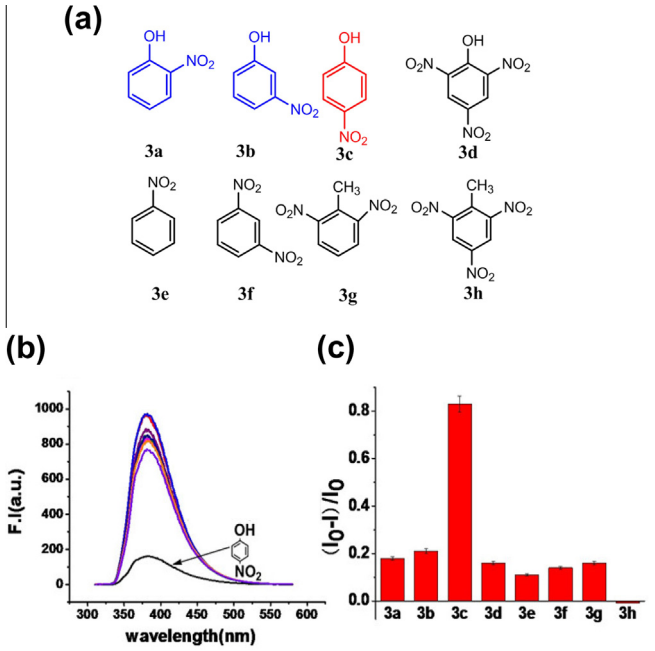

Figure 1. (a) The structures of the guests. (b) Fluorescence intensity changes for **C4N4** (1×10^{-5} M) in CH_3CN upon addition of **3a**–**h** (8×10^{-5} M). (c) $[((I_0 - I)/I_0)]$. (λ_{ex} = 300 nm). I_0 is the fluorescent emission intensity of the host, and I is the fluorescent intensity after adding **3a**–**h**. The **C4N4** as a fluorescence probe system for isomeric nitrophenol, as selective binding of *p*-nitrophenol, results in a significant change in the fluorescence intensity.

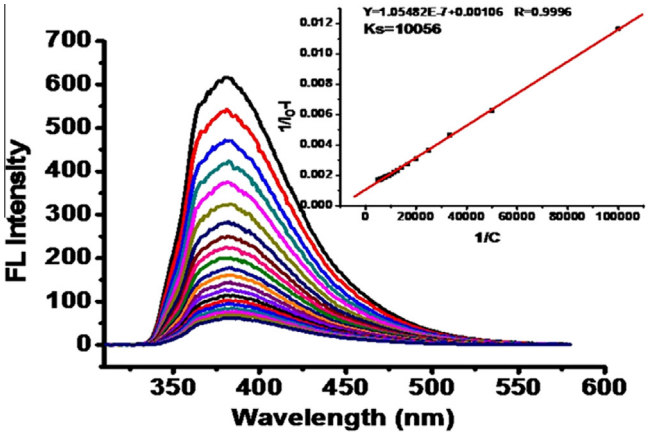

Figure 2. Fluorescence spectra titration of **C4N4** (1×10^{-5} M) with various equivalents of **3c** in CH_3CN (0, 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 33, 36, 39, 42, 45, 48, 51, 54, 57, 60 equiv, λ_{ex} = 300 nm). Inset: Benesi-Hildebrand analysis of the fluorescence changes for the complexation between **C4N4** and **3c** (λ_{ex} = 300 nm). With increasing concentrations of **3c**, the fluorescence intensities of **C4N4** gradually decreased.

feature of **C4N4** is the high binding affinity toward **3c** over other nitrobenzenes. Based on fluorescence titration experiments between **C4N4** and other nitrobenzenes derivatives, including *o*-nitrophenol and *m*-nitrophenol, their association constants (K_a) were determined as shown in Table 1 (Figs. S4 and S5). The K_a of the **3c** inclusion complex was far higher indicating **C4N4** binds selectively to **3c**.

The ^{1}H NMR spectra of mixtures of **C4N4** and **3c** were investigated as depicted in Figure 3. The signals from the aromatic ring protons of **3c** slight shifted downfield (H_a, 0.013 ppm; H_b, 0.024 ppm; Scheme S2). This phenomenon may be due to π–π stacking interactions between **3c** and **C4N4**.[21] Because of the reciprocity, the inclusion complex of **C4N4** with **3c** through the host and guest inclusion induces a strong fluorescence quenching due to a well-defined electron transfer. Moreover, **3c** is an electron-poor molecule, with low electron density and caused shielding to reduce. As a result, the aromatic ring of **3c** is in a relatively high magnetic field position and caused the downfield shifting of H_a and H_b. Characteristic changes in the infrared absorption (IR) can also be seen (Fig. S7). The vibration localized in the benzene ring of the calixarene cavity moves from 1530 cm^{-1} to 1550 cm^{-1}, while the other peaks do not change significantly, indicating that a π–π interaction occurs between **C4N4** and **3c**.

To understand the match between **C4N4** and **3c**, computational calculations were carried out at the B3LYP/6-31G level using Gaussian 03.[22] The results from the molecular mechanics calculation were generally consistent with the ^{1}H NMR and fluorometric experimental results. Figure S8 shows the optimized structure of the host–guest complex (Tables S1 and S2). Compound **3c** was partially located inside the deep, electron-rich cavity of **C4N4**. The π–π stacking interactions between the benzene ring of **3c** and alkynyl group of **C4N4** (d_1 = 4.0 Å, d_2 = 4.1 Å) are also shown in Figure S8.

Meanwhile, molecular orbitals (MOs) were calculated for **C4N4** and **C4N4** ⊃ **3c**, also using the B3LYP/6-31G level (Fig. 4). In **C4N4** and **C4N4** ⊃ **3c**, HOMOs are both majorly localized on the naphthalene ring and alkynyl group. The LUMOs of **C4N4** are

Table 1
The complex constants between **C4N4** and other nitrophenol isomers

	3a	3b	3c
K_a (10^3)	0.34	3.21	10.06

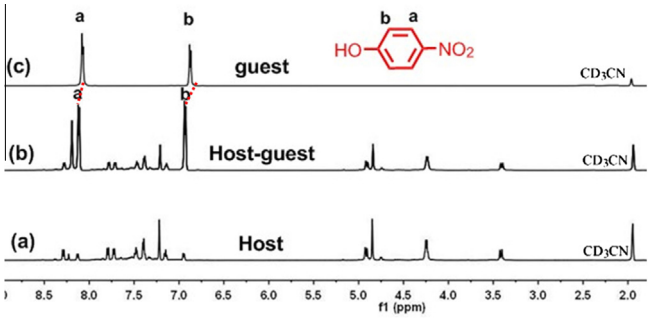

Figure 3. ^{1}H NMR spectra (CD_3CN, 400 MHz, 298 K) of (a) **C4N4** (8 mM); (b) **C4N4** and **3c** (8 mM each); (c) **3c** (8 mM).

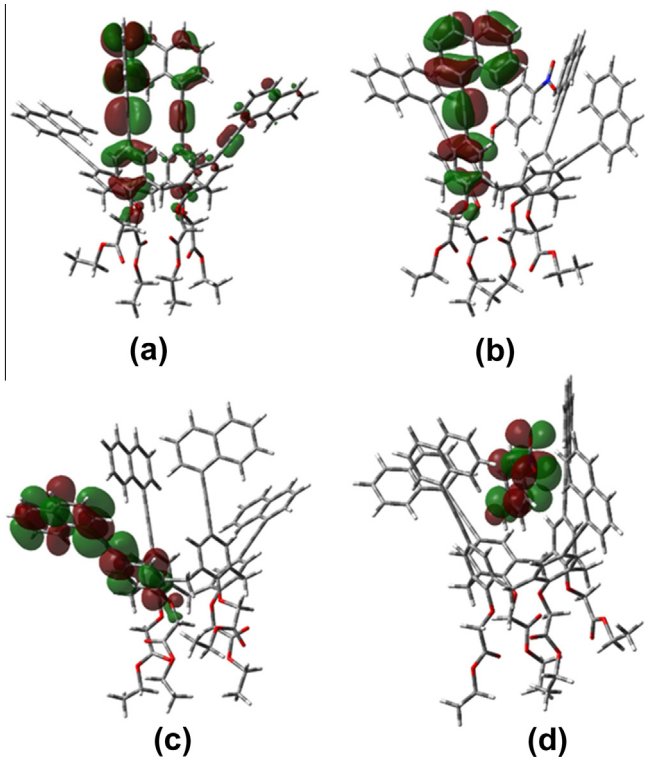

Figure 4. Pictorial representation of the molecular orbital (MOs) present on different fragments: (a) HOMO of **C4N4**; (b) HOMO of **C4N4** ⊃ **3c**; (c) LUMO of **C4N4**; (d) LUMO of **C4N4** ⊃ **3c**.

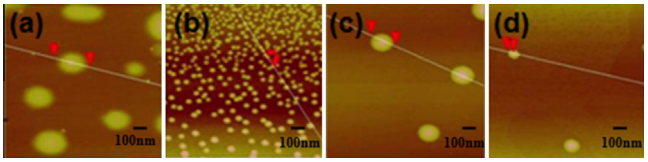

Figure 5. AFM images of **C4N4** added to *p*-nitrophenol, *o*-nitrophenol, and *m*-nitrophenol. (a) **C4N4**; (b) **C4N4** ⊃ *p*-nitrophenol; (c) **C4N4** ⊃ *o*-nitrophenol; (d) **C4N4** ⊃ *m*-nitrophenol. The lines refer to the sweep path of the instrument probe, and red arrows refer to the size of the particles.

present on the naphthalene ring and alkynyl group. In the case of **C4N4** ⊃ **3c**, the LUMOs are majorly localized on the benzene ring of **3c**.[23] Therefore, the computational studies further support the π–π stacking interactions between **3c** and **C4N4**.

To determine whether forming the inclusion complex of **C4N4** with *p*-nitrophenol is reflected in the nanostructural features, AFM studies were performed on **C4N4**, **C4N4** ⊃ *p*-nitrophenol, **C4N4** ⊃ *o*-nitrophenol and **C4N4** ⊃ *m*-nitrophenol. The corresponding micrographs and particle size distributions are shown in Figure 5 and Figure S9. **C4N4** forms spherical particles in the range of 270–300 nm (Fig. 5a). When *p*-nitrophenol is added to **C4N4**, the size of the particles decreases to 30–60 nm (Fig. 5b). For **C4N4** ⊃ *o*-nitrophenol and **C4N4** ⊃ *m*-nitrophenol, the particle size decreases to 190–220 nm and 120–150 nm (Fig. 5c and d), respectively. Rational explanation may be that the larger size of the particles observed in case of **C4N4** may be attributable to the aggregation due to the presence of hydrophobic groups, and these become small in the presence of **3c** owing to the π–π stacking interactions between **3c** and **C4N4**.[24] In addition, **C4N4** ⊃ *p*-nitrophenol forms almost uniform particles and good separation. This large difference in nanostructural features also confirms that **C4N4** shows selective recognition of *p*-nitrophenol.

Based on the above analysis, a possible mechanism of selective recognition is proposed. The fluorescence quenching by adding **3c**, and computational calculations indicated the complexation model is driven by π–π interactions. The observed selective size in the AFM images was the result of preferential complexation between **C4N4** and **3c**. The characteristic changes are represented schematically in Figure S10.

In summary, we have synthesized a fluorescent tetranaphthylcalix[4]arene by a Sonogashira cross-coupling reaction, which exhibits high binding affinity and selectivity toward *p*-nitrophenol (**3c**). By a combination of π–π stacking interactions, as revealed by NMR, IR, and computational calculations, a **C4N4** ⊃ **3c** complex has been formed. The electron-poor aromatic guests were included in the electron-rich cavity of the host calix[4]arene in a 1:1 complex, which induces the fluorescence quenching. The reasoned probe design is an effective strategy to enhance the binding affinity and fluorescence modulation, which is of use in practical probe applications.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.02.029.

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