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Fluorescent phenylethynylene Calix[4]arenes for sensing TNT in aqueous media and vapor phase

Kanokthorn Boonkitpatarakul,[a] Yamonporn Yodta,[b] Nakorn Niamnont,[c] Mongkol Sukwattanasinitt[*,b]

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The upper-rim of calix[4]arene is modified with phenylacetylene derivatives via Sonogashira coupling reaction to produce a wider cavity for entrapping TNT. The modified calix[4]arene with amino groups on the wider rim exhibits highly selective fluorescence quenching toward TNT compared to the other nitro aromatic compounds in an aqueous medium due to the shape and hydrophobicity of the modified cavity. The limit of detection of TNT is 0.3 μM (68ppb) in water and the Stern-Volmer fluorescence quenching constant is 1.09 x 10^5 M^{-1}.

Introduction

Trinitrotoluene (TNT) is one of the most commonly used landmines and military explosives, partly owing to its insensitivity to shock and friction.[1] Beside being highly explosive; TNT has also been recognized as a toxic substance causing skin irritation, anemia, liver cancer and adversely affects male fertility.[1] TNT can contaminate the environment through armament processing. TNT concentrations in ground water and soil in the vicinity of munitions plants can be found at least 500 ppb.[1a] According to the US Environmental Protection Agency (EPA), the limit of TNT in drinking water is 2 ppb.[2] For these reasons, the development of sensors for quick and facile detection of TNT is of great importance in environmental monitoring and remedying, detecting buried unexploded ordnance, and locating underwater mines.[3]

Various techniques for TNT detections are available such as chromatography, surface-enhanced Raman spectroscopy, amperometry, X-ray dispersion, cyclic voltammetry and ion mobility spectrometry.[3a,4] Among various sensing techniques available, fluorescence chemosensors have attracted much attention due to their high sensitivity and selectivity, short response time, cost-effectiveness in instrumentation and also operational simplicity suitable for on-site analysis.[5] In particular, fluorescent conjugated polymers including poly(phenylene ethynylene),[6] polymetalloles,[7] poly(p-phynylene vinylenes)[8] and diaryl poly(acetylenes)[8b,9] have been widely studied.[10] These conjugated fluorescent polymers can give high fluorescence quenching sensitivity owing to excitonic migration amplifying mechanisms.[11] Their solid state dense films however generally have low permeability for analyte molecules.[12] Their random and unpredictable conformation of the polymer chains may also lead to molecular orientation at the film surface unsuitable for binding analysts. Recently, development of small or single molecule fluorophores as efficient sensor has gain more attention due to its well-defined structures, monodispersity, simpler synthesis and purification allowing a clear understanding of structure-property relationships.[11a,12] However, single-molecule-based fluorescent sensors for explosive detection have been investigated at a much lesser extent and they are mostly applied in organic solvents.[12,13] The fluorescent sensory materials for TNT detection based mainly on photoinduced electron transfer (PET) fluorescent quenching process. However, most of fluorescent compounds have low selectivity between nitrotoluene and nitrophenol derivatives because both classes are strong electron acceptors[14] and trinitrophenol (TNP) usually appeared to give higher quenching efficiencies than TNT in most cases because of its high absorptivity at the excitation wavelength.[15] To increase the selectivity toward TNT, it is interesting to include a binding site for nitrotoluene moiety. We selected calix[4]arene scaffolds because of its pre-organized three-dimensional structures with suitable hydrophobic cavity. Recently, calix[4]arene derivatives have been used for fluorescence detection of TNT and other nitroaromatic compounds. Lee et al. have prepared dipyrenylcalix[4]arene as fluorescence-based chemosensor for trinitroaromatics in acetonitrile and chloroform.[16] Costa et al. have reported phenylene-ethynylene π-conjugated system containing calix[4]arene receptor for detecting nitroaromatic compounds.[17] In 2013, Kandpal et al. have reported the upper-rim modification of calix[4]arene with benzimidazole moiety that efficiently served as a TNT receptor both in solution and solid state.[18] The cavity of calix[4]arene has been reported to accommodate various aromatic and electron deficient compounds including toluene[19] and nitromethane.[20] Most recently, Cao et al. have prepared a deep cavity tetranaphthyl-calix[4]arene which exhibited selectivity toward p-nitrophenol in acetonitrile.[21] In our molecular design, the upper-rim of calix[4]arene is extended with a π-conjugated system of phenylacetylene to produce a wider cavity for entrapping TNT. The sensing study in high water content media is particularly emphasized here as it is more relevant to real environmental samples. We hypothesized that the more hydrophilic TNP would be less likely to be included into the hydrophobic cavity of calix[4]arene in aqueous medium. However hydrophilic groups such as carboxyl, hydroxyl and amino groups were placed on the modified wider rim to ensure sufficient solubility in aqueous media (Fig. 1). The placement of these groups should also provide different electronically push-pull effects in connection with the electron donating alkoxy groups on the other rim, the narrow rim.

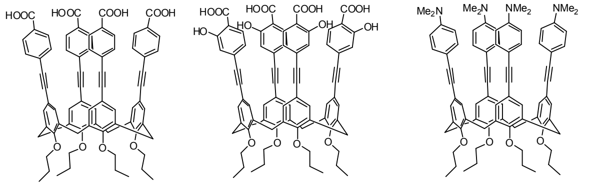

Fig. 1 Structures of fluorophores BAC, SAC and ANC

Experimental

General information

All reagents were purchased from Sigma-Aldrich, Fluka® (Switzerland) and Merck® (Germany). Organic solvents for reaction work up and chromatography were commercial grades, which were distilled prior to use. Thin layer chromatography (TLC) was performed on silica gel coated aluminum sheets (Merck Kieselgel 60 F_{254}) (Merck KgaA, Darmstadt, Germany). Column chromatography was performed on silica gel (Merck Kieselgel 60G) (Merck KgaA, Darmstadt, Germany).

Analytical Instruments: All ^{1}H NMR and ^{13}C NMR spectra were obtained from $CDCl_3$ solutions, unless stated otherwise, on a Varian Mercury NMR spectrometer, which operated at 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei (Bruker 400 MHz NMR spectrometer). Absorption spectra were measured from THF and 1%THF aqueous solutions in a 3.5 mL quartz cuvette with 1 cm light path, using Shimadzu UV-2550 UV-Vis spectrophotometer. Fluorescence spectra were obtained from THF and 1%THF aqueous solutions in a 1.5 mL quartz cuvette with 1 cm light path, a Varian Cary Eclipse spectrofluorometer.

Synthesis of compound 2

A typical synthesis of compound **2**[22] was performed by mixing $PdCl_2(PPh_3)_2$(40 mol %) and CuI (40 mol %) with 5,11,17,23-tetraiodo-25,26,27,28-tetra-(n-propoxy)calix[4]arene **1**[23] (0.1 mmol) in dry and degassed triethylamine (20 mL) at room temperature for 30 min followed by an addition of a 4-ethynylbenzene derivative (0.8 mmol). The stirring was continued under nitrogen for 48 h before the solvent was removed by a rotating evaporator. The residue was dissolved in ethylacetate (100 mL) and extracted with water (100 mL × 3). The organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated to provide a crude product which was purified by column chromatography on silica gel.

2a: The crude product was purified by column chromatography (SiO_2, gradient 0-10% CH_2Cl_2 in hexanes) to give the desired product **(2a)** as a white solid (36 % yield) ^{1}H NMR (400 MHz): δ (ppm) 7.79 (d, *J* = 8.2 Hz, 8H), 7.41 (d, J = 8.1 Hz, 8H), 6.95 (s, 8H), 4.44 (d, J = 13.4 Hz, 4H), 3.94-3.74 (m, 20H), 3.19 (d, J = 13.4 Hz, 4H), 1.98-1.88 (m, 8H), 1.00 (t, J = 7.4 Hz, 12H). ^{13}C NMR (100 MHz): δ (ppm) 166.68, 157.54, 135.06, 132.22, 131.34, 129.39, 128.96, 128.37, 116.67, 93.06, 87.80, 77.22, 52.22, 31.00, 23.36, 10.42. HRMS m/z Calcd for $C_{80}H_{72}NaO_{12}$ $[M + Na]^+$: 1247.4921 Found: 1247.4970.

2b: The crude product was purified by column chromatography (SiO_2, gradient 0-10% CH_2Cl_2 in hexanes) to give the desired product **(2b)** as a white solid (46% yield) ^{1}H NMR (400 MHz): δ (ppm) 10.60 (s, 4H), 7.61 (d, J = 8.1 Hz, 4H), 7.05-6.84 (m, 16), 4.44 (d, J = 13.4 Hz, 8H), 3.92 (s, 12 H), 3.89 (t, J = 7.5 Hz, 8H), 3.18 (d, J = 13.5 Hz, 4H), 1.99-1.84 (m, 8H), 1.00 (t, J = 7.2 Hz, 12H). ^{13}C NMR (100 MHz): δ (ppm) 170.34, 161.16, 157.61, 135.07, 132.30, 131.07, 129.56, 122.51, 119.96, 116.58, 111.47, 93.25, 87.70, 77.16, 52.33, 30.97, 23.35, 10.41. HRMS m/z Calcd for $C_{80}H_{72}NaO_{16}$ $[M + Na]^+$: 1311.4718 Found: 1311.4684.

ANC: The crude product was purified by column chromatography (Al_2O_3, gradient 0-25% EtOAc in hexanes) to give the desired product (**ANC**) as pale yellow powder (46% yield) ^{1}H NMR (400 MHz): δ (ppm) 7.31 (d, J = 8.3 Hz, 8H), 6.49 (d, J = 8.6 Hz, 8H), 4.40 (d, J = 13.2 Hz, 4H), 3.86 (t, J = 7.5 Hz, 8H), 3.14 (d, J = 13.0 Hz, 4H), 2.92 (s, 24H), 1.93 (m, 8 Hz, 8H), 0.99 (t, J = 7.3 Hz, 12H). ^{13}C NMR (100 MHz): δ (ppm) 156.42, 149.73, 134.66, 132.82, 131.73, 118.03, 111.94, 111.28, 89.09, 87.85, 77.06, 40.36, 31.00, 23.32, 10.45. HRMS m/z Calcd for $C_{80}H_{84}N_4NaO_4$ $[M + Na]^+$: 1187.6390 Found: 1187.6392.

1.1.

1.2. Hydrolysis of ester 2

BAC: A mixture of **2a** (80 mg, 0.065 mmol) in THF (10 mL) and methanol (10 mL) was added with saturated KOH aqueous solution (0.5 mL) and the mixture was stirred at room temperature. After 24 h the solution was evaporated and the residue was dissolved in water (10 mL) and was added 1M HCl cool in ice-bath. The solution in suspension was centrifuge to afford **BAC** as a white solid (42 mg, 55% yield). ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 7.74 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 7.5 Hz, 2H), 6.93 (s, 2H), 4.47 (d, J = 13.2 Hz, 4H), 3.93 (m, 2H), 3.24 (d, J = 13.2 Hz, 4H), 2.00-1.91 (m, 8H), 1.03 (t, J = 7.4 Hz, 12H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ (ppm) 167.13, 158.35, 136.12, 132.83, 131.86, 130.80, 130.33, 128.68, 117.43, 93.42, 88.16, 77.94, 31.23, 23.98, 10.57. HRMS m/z Calcd for $C_{76}H_{64}O_{12}$ $[M - H]^-$: 1167.4325 Found: 1167.4302.

SAC: A mixture of **2b** (98 mg, 0.08 mmol) in THF (10 mL) and methanol (10 mL) was added with saturated KOH aqueous solution (0.5 mL) and the mixture was stirred at room temperature After 24 h the solution was evaporated and the residue was dissolved in water (10 mL) and was added 1M HCl cool in ice-bath. The solution in suspension was centrifuge to afford **SAC** as a white solid (67 mg, 72% yield). ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 7.58 (d, *J* = 8.4 Hz, 4H), 6.91(bs, 2H), 6.80 (bs, 2H), 4.45 (d, *J* = 13.6 Hz, 4H), 3.91 (m, 8H), 3.22 (d, *J* = 13.5 Hz, 4H), 1.93 (dd, *J* = 14.7, 7.5 Hz, 8H), 1.01 (t, *J* = 7.4 Hz, 13H). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 170.34, 161.16, 157.61, 135.07, 132.30, 131.07, 129.56, 122.51, 119.96, 116.58, 111.47, 93.25, 87.70, 52.33, 30.97, 23.35, 10.41. HRMS m/z Calcd for $C_{76}H_{64}O_{16}$ $[M - 2H]^{2-}$: 615.2019 Found: 615.2038

Electrochemical measurements

Cyclic voltammetry (CV) measurements were carried out in a three-electrode system consisting of Ag/Ag^+ (0.01 M $AgNO_3$) as the reference electrode, glassy carbon as the working electrode and the platinum-wire as the counter electrode using a scan rate of 50 mV/s under nitrogen atmosphere to find HOMO levels of the fluorophores (Fig. S2). Ferrocene was used as the external standard for calibration CV curves. All samples and the external standard were dissolved in the supporting electrolyte (0.1 M of tetra-n-butylammonium hexafluorophosphate in anhydrous dimethylformamide) to give final concentrations of 1 mM.

The HOMO energy levels of the fluorophores were calculated from the onset oxidation potential (E_{ox}^{onset}) based on the following equations: $E_{HOMO} = -[\ E_{ox}^{onset} - E_{1/2} + 4.8]$ eV, which E_{ox}^{onset} is the onset oxidation potential relative to the Ag/AgCl reference electrode. The half-wave potential of the ferrocene/ferrocenium ($E_{1/2}$) was measured as the average of the anodic and cathodic peak potentials. The LUMO energy levels were calculated from $E_{LUMO} = E_{HOMO} + E_{gap}$ determined from $1240/\lambda_{cut\ off}$ in which the cut off wavelength ($\lambda_{cut\ off}$) is the longest wavelength giving the minimum absorption.

Preparation of ANC fluorescent paper sensor:

A filter paper strip (Whatman No.1, 4 cm × 1.1 cm^2) was immerged in a CH_2Cl_2 solution of ANC 1 mM for 1 min. After removal from the solution, the coated filter paper was allowed to dry in the air at room temperature for 2 hours.

For the TNT vapor sensing, 0.50 g of TNT solid was placed in a 1 mL eppendorf, covered with cotton gauze and cap-closed overnight to maintain a constant saturation vapor pressure before a ANC fluorescent paper sensor was placed on top of the cotton in the eppendorf and then cap-closed again for 5 and 10 minutes. The quenching results were recorded by a commercial digital camera.

Results and discussion

The key step in the synthesis of the fluorophores (BAC, SAC, and ANC) was the Sonogashira cross coupling reaction between tetraiodo-calix[4]arene **1** and the ethynylbenzene derivative (i.e. methyl 4-ethynylbenzoate or methyl 4-ethynylsalixylate or *N,N*-dimethyl-4-ethynylaniline) according to Fig. 2 to afford **2a**, **2b**, and **ANC** in moderate yield. The base-catalyzed hydrolysis of ester **2a** and **2b** readily gave **BAC** and **SAC**, respectively. The ^{1}H NMR revealed that all fluorophores were obtained in cone conformation by having the characteristic doublet signals of H_{exo} and H_{endo} of the bridged methylene protons ($ArCH_2Ar$) around 4.4 and 3.2 ppm.

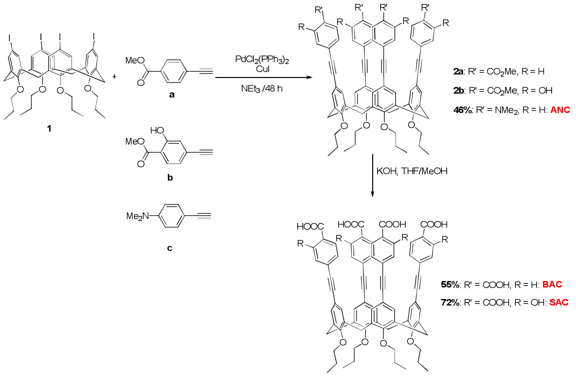

Fig. 2 Synthetic routes of fluorophores

The normalized electronic absorption and emission spectra of the fluorophore solutions in THF are depicted in Fig. 3 and their photophysical data are presented in Table S1. The UV-vis absorption spectrum of each fluorophore showed a broad absorption band with λ_{max} around 310-315 nm associated with the π–π* electronic transition of the substituted diphenylacetylene conjugated system. The similar λ_{max} values of these fluorophores indicate their comparable electronic energy band gap. The emission spectra of SAC and BAC appeared at lower energy indicating a larger Stokes shifts comparing with that of ANC. These results may be attributed to the fact that SAC and BAC contain both electron donor and electron acceptor substituents allowing for an intramolecular charge transfer (ICT).

The HOMO and LUMO electronic energy levels of the fluorophores were summarized in Table S1. Their LUMO energy levels in the range of -2.18 to -1.54 eV are clearly higher than those of TNT, DNT and PA (Fig. S1) that allow for an electron transfer from the excited fluorophores to TNT, DNT and PA in the PET process.

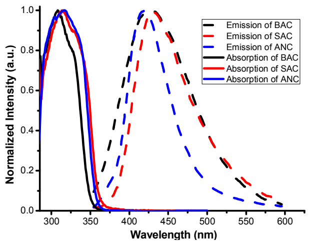

Fig. 3 Normalized absorption (solid line) and emission (dash line) spectra of the fluorophores in THF. The λ_{max} of each fluorophore was used as the excitation wavelength in the corresponding emission spectrum.

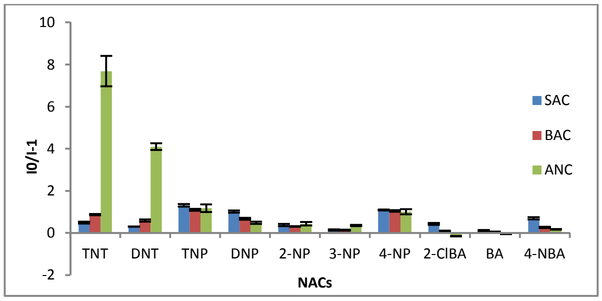

Fig. 4 Fluorescence quenching effects of various electron deficient aromatic compounds (50μM) on the fluorophores (0.5 μM) in 1%THF/H_2O.

The response of ANC, BAC and SAC to various electron deficient aromatic compounds such as (2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), picric acid (PA), 2,4-dinitrophenol (DNP), 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP), 4-nitrobenzoic acid (4-NBA), benzoic acid (BA), and 2-chlorobenzoic acid (2-ClBA)) in aqueous solutions were studied (Figure 4). The fluorescence signals of SAC and BAC was quenched by about 2 times or less by the electron deficient aromatic compounds depending upon tested. On the other hand, the fluorescence signal of ANC was selectively quenched by TNT (~8 times) and DNT (~4 times). As designed, the quenching effect of PA on ANC was also much lesser than TNT and DNT owing to the more hydrophilicity of PA. It is also important to note that the electron donating amino groups on the phenyl ring on ANC enhances the sensitivity toward TNT comparing with BAC and SAC. The results suggest that TNT molecule interact with the phenyl rings on the wider rim of the fluorophore.

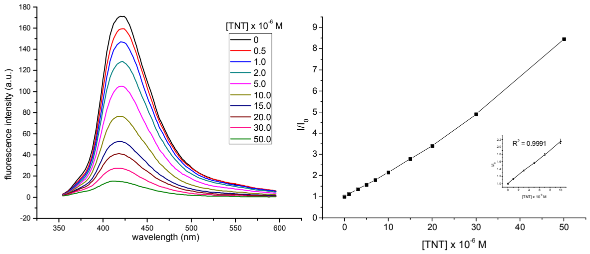

Fig. 5 The fluorescence quenching ratio of ANC upon the addition of TNT (left). Stern-Volmer plots for fluorescence quenching of the fluorophores with TNT (right).

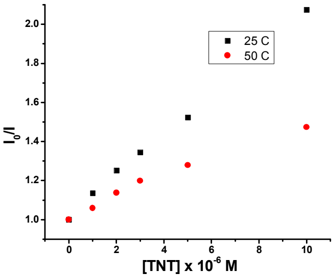

Fig. 6 Stern-Volmer plots at 25 and 50 °C

The Stern-Volmer plots of the fluorescence intensity ratio (I_0/I) of ANC against the TNT concentration as shown in Fig. 5 gave the Stern-Volmer constant (K_{sv}) of 1.09 x 10^5 M^{-1}. The plot also showed a very good linearity in the range of 0-10 μM TNT with the limit of detection (LOD) of 0.3 μM (68ppb) which is lower than TNT level found in ground water and soil sites near a munitions plant (LOD at the three times noise = 3σ/K where σ is the standard deviation of the blank measurements, and K is the slope of the calibration curve). Meanwhile, the K_{sv} constant for DNT and PA was found to be 5.97 x 10^4 M^{-1} and 2.09 x 10^4 M^{-1} respectively. Fig. 6 shows Stern-Volmer plots at 25 and 50°C with the K_{sv} values of 1.09 x 10^5 M^{-1} and 5.08 x 10^4 M^{-1}, respectively (fig. S3). The decrease in K_{sv} values with the increase in temperature supports a static quenching mechanism.[24]

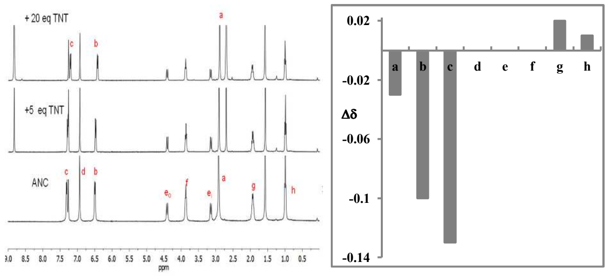

Fig. 7 ^{1}H NMR of ANC in $CDCl_3$ in the absence and presence of TNT (left). Chemical shift change (Δλ) plot (right).

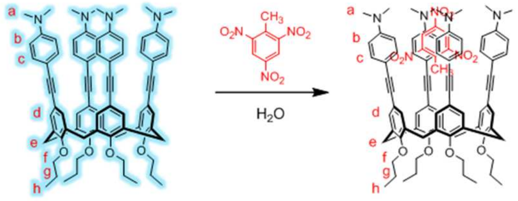

Fig. 8 Proposed structure of ANC-TNT interaction.

The interaction between ANC and TNT were further examined by ^{1}H NMR titration (Fig. 7). Upon increasing amount of TNT added to ANC solution, the aromatic proton signals (b and c) of the phenyl ring at the wider rim gradually upfield shifted, whereas proton signals of the phenyl ring at the narrower rim showed no significant shifts confirming the interaction of TNT with the aniline rings at the extended wider rim of calix[4]arene, probably via an insertion into the ANC cavity (Fig. 8).

On the basis of Job plot, the complex ratio between ANC and TNT obtained from emission data showed 1:1 stoichiometric complexation (Fig. S6). This interaction is consistent with the nonradiative PET from the LUMO energy level of the electron rich ANC in its excited state to the LUMO of the electron poor TNT.

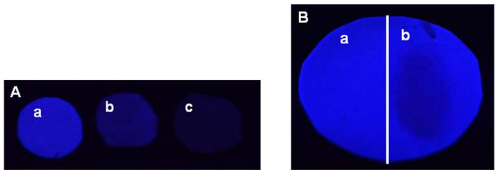

Fig. 9 Photographic images of ANC on filter paper strips under 365 nm UV light under different experimental conditions. (A) Vapor-mode detection of TNT (a) before (b) 5 min after (c) 10 min after exposure to TNT vapor. (B) Impression of a glove-wearing thumb (a) before (b) after rubbing with TNT.

The pH-dependent titration of ANC was investigated in the pH range of 3-10. There was no significant change of the intensity as shown in fig. s5 indicating that the protonation at dimethyl amine system on ANC did not affect the fluorescence of ANC. Furthermore, we also compared the quenching of fluorescence of ANC to TNT in DMF with aqueous solution (1%THF) (Fig. S7). The quenching in aqueous solution (~90%) was much higher than in DMF (~20%). The result showed that water can forced TNT to insert into ANC cavity.

We further carried out TNT detection both in vapor mode and contact mode by using paper strips. Upon exposure to TNT vapor (8.02×10^{-6} mm Hg at 25 °C), the fluorescence spot on a filter paper strip was quenched (Fig. 9, left). In contact mode test, the glove-wearing thumb, rubbed with TNT was pressed on a paper strip. Under UV light, the dark finger print of the thumb appeared (Fig. 9, right). These results demonstrate that the paper strips coated with ANC may be applied for a visual on-site detection of trace residues of TNT and its vapor.

Conclusions

The fluorescent arylethynyl calix[4]arenes were successfully synthesized. With aniline rings on the wider rim, ANC exhibited high sensitivity and selectivity of fluorescence quenching by TNT in aqueous medium. The electron rich aniline rings provide high sensitivity while the size and hydrophobicity of the cavity of the modified calix[4]arene provide high selectivity as evidenced by the shift of ^{1}H NMR signals. The Stern-Volmer constant for TNT fluorescence quenching was 1.09 x 10^5 M^{-1} with the detection limit of 0.3 μM (68ppb). In addition, the filter paper strips coated with ANC are potentially useful for visual detection of trace residues of TNT and its vapor.

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Notes and references

[a] *Program of Petrochemistry, Faculty of Science, Chulalongkorn University, Bangkok 10300, Thailand. Tel: +6681 815 4973; E-mail: keng_knb@hotmail.com*
[b] *Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10300, Thailand. Tel: +6681 901 0730; E-mail: msukwatt@gmail.com*
[c] *Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand.*

† Electronic Supplementary Information (ESI) available: Experimental and spectroscopic data. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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