Micrometer-level naked-eye detection of caesium particulates in the solid state

Taizo Mori¹,², Masaaki Akamatsu³, Ken Okamoto¹, Masato Sumita¹, Yoshitaka Tateyama¹, Hideki Sakai³, Jonathan P Hill¹,², Masahiko Abe³ and Katsuhiro Ariga¹,²

¹ WPI-International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1–1 Namiki, Tsukuba, Ibaraki 305–0044, Japan
² JST, CREST, Sanbancho, Chiyoda-ku, Tokyo 102–0075, Japan
³ Department of Pure and Applied Chemistry, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278–8510, Japan

E-mail: Jonathan.Hill@nims.go.jp and ARIGA.Katsuhiko@nims.go.jp

Received 5 November 2012
Accepted for publication 21 November 2012
Published 7 February 2013
Online at stacks.iop.org/STAM/14/015002

Abstract
Large amounts of radioactive material were released from the Fukushima Daiichi nuclear plant in Japan, contaminating the local environment. During the early stages of such nuclear accidents, iodine I-131 (half-life 8.02 d) is usually detectable in the surrounding atmosphere and bodies of water. On the other hand, in the long-term, soil and water contamination by Cs-137, which has a half-life of 30.17 years, is a serious problem. In Japan, the government is planning and carrying out radioactive decontamination operations not only with public agencies but also non-governmental organizations, making radiation measurements within Japan. If caesium (also radiocaesium) could be detected by the naked eye then its environmental remediation would be facilitated. Supramolecular material approaches, such as host–guest chemistry, are useful in the design of high-resolution molecular sensors and can be used to convert molecular-recognition processes into optical signals. In this work, we have developed molecular materials (here, phenols) as an optical probe for caesium cation-containing particles with implementation based on simple spray-on reagents and a commonly available fluorescent lamp for naked-eye detection in the solid state. This chemical optical probe provides a higher spatial resolution than existing radioscopes and gamma-ray cameras.

Keywords: radiocaesium, caesium cation recognition, optical probe, supramolecular, charge transfer

Online supplementary data available from stacks.iop.org/STAM/14/015002/mmedia

1. Introduction
Caesium-133 is the heaviest stable alkali metal and it has had only a few significant applications, such as in atomic clocks [1] or as gradient centrifugation reagents [2]. More recently, however, caesium compounds as their brines have emerged as important materials for deep drilling operations due to the high densities of their solutions [3] and their relatively low toxicity [4]. Radiocaesium, on the other hand, including the two longer-lived isotopes of caesium Cs-134 (half-life 2.07 years) and Cs-137 (half-life 30.17 years), is a major source of environmental contamination in the vicinity of radiation leaks such as those which occurred at Chernobyl,
Ukraine [5], and more recently at Fukushima, Japan [6, 7].

During nuclear reactor breaches, iodine I-131 (half-life 8.02 d) is released to the atmosphere. Concurrently Cs-137 is released as a microparticulate aerosol leading to long-term soil and water contamination [8].

In addition to the well-known nuclear reactor disasters, radiocaesium has been more gradually introduced into the biosphere through nuclear weapons testing over the last 60 years [9]. Dual environmental hazards are presented by radiocaesium in that background radiation exposure is increased and, more significantly, it is known to be bioaccumulated, leading to a much greater risk of carcinogenesis in organisms [10]. Although caesium is gradually eliminated from mammals when it is removed from dietary sources, levels of corporeal contamination may be maintained or increased in cases of chronic pollution surrounding nuclear disaster areas, where locally grown agricultural produce certainly contain significant amounts of radioactive contaminants. Uptake of radiocaesium by cultivated plants is therefore a significant source of risk to local populations [11] since radiocaesium is usually simply left to decay, meaning that radiation leaks (and nuclear weapons tests) result in major legacies of environmental contamination [12]. Materials that can be used to remove these toxic elements should be considered from the viewpoint of environmental protection.

Areas contaminated by accumulated Cs-134 and Cs-137 can be monitored from over-flying aircraft and, in Japan, both public agencies and non-governmental organizations undertake such measurements. Although the Japanese government is planning and implementing radioisotope decontamination operations, the serious problem of waste treatment remains. For instance, Toshiba [13] and JAXA [14] are developing a gamma ray camera to visualize radioactivity. Since caesium is released during reactor breaches in a particulate form it would be useful if these particulates could be detected within large volumes of contaminated ground soil in the solid state. For these reasons, it would be very useful to develop sensors for particles that contain caesium cations (Cs⁺) [5] that could be used to screen large areas of contaminated land, especially in the vicinities of radiation leaks. This would facilitate identification of contaminated soil and the actual volume of soil requiring treatment could be reduced by a factor of more than 100 000 by visualization of Cs⁺-containing particles (see the supplementary information available at stacks.iop.org/STAM/14/015002/mmedia). Apart from measurement using specially calibrated radiation meters, there are no materials that can be applied to the rapid detection of microscopically distributed caesium cations using a simple procedure. Host–guest supramolecular materials promise simple detection of a variety of chemical species, especially specific ions [15–18]. Host–guest interactions may be converted into detectable signals such as electrical and optical outputs while, for instance, fluorescent molecular sensing materials provide greater spatial resolution [19–21].

In this work, we have adopted the deprotonation of phenols as a probe reaction for detecting alkali metal cations. Phenols are a notable class of organic compound because of the acidity of their hydroxyl protons [22]. Thus, deprotonation can occur by treatment with an inorganic base (e.g. Na₂CO₃, K₂CO₃) yielding a phenolate anion with associated counterion such as Na⁺ or K⁺. For substituted phenols, such as 4-hydroxy-1-biphenyl and 1-hydroxy-4,4',4''-terphenyl [HTTP; 1-(4'-hydroxy phenyl)-4-phenyl benzene], substantial changes in fluorescence emission spectra are observed upon deprotonation [23, 24], which are strongly affected by the nature of the substituent, solvent and deprotonating reagent. Furthermore, intermolecular processes such as fluorescence resonance energy transfer (FRET) [25] or excimer emission [26] can be designed into molecules to optimize or tune any sensing output signal. Using these features, we initially designed a class of HTTP sensing elements and compounded one of them with an electron-accepting 4-nitrophenyl ether (4-NPE) group through a variable-length polyethylene glycol chain with the aim of selectively detecting alkali metal or alkali earth metal cations. Figure 1 shows the chemical structure of 4-NPE-substituted HTTP 1, which contains a tetraethylene glycol (TEG) linker separating the two aromatic moieties. Caesium cation-containing particles can be visualized after spraying with 1 in methanol. Significantly, because of our molecular design, the probe is selective for caesium cations making it useful for the detection of caesium in the environment. The probe is particularly suitable for detecting caesium salts in particulate form and allows them to be detected in the solid state with the naked eye.

2. Experimental section

2.1. Materials

Solvents and materials were purchased from Tokyo Chemical Industry Co Ltd (Tokyo, Japan) and Wako Pure Chemical Co (Osaka, Japan), and were used without further purification. H and 13C nuclear magnetic resonance (NMR) spectra were measured at 298 K from CDCl₃ or d₆-dimethyl sulfoxide (DMSO) solutions of the samples using a JEOL model AL300BX (300 MHz) spectrometer with tetramethylsilane (Me₄Si) as an internal standard. Chemical shifts (δ) and coupling constants (J) are given in parts per million (ppm) and hertz (Hz), respectively. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements were carried out using a Shimadzu-Kratos AXIMA+ mass spectrometer with dithranol as a matrix. High-resolution mass spectra (HRMS, ESI-positive) were acquired with JMS-M5700 (JEOL), and elemental analysis was performed with a PE 2400II (PerkinElmer) system.

2.2. Measurements

Electronic absorption spectra were measured from tetrahydrofuran solutions of the samples using a Shimadzu
Figure 1. Photographs of fluorescence changes of a mixture of 1 and various carbonate salts after addition of a drop of methanol.
(a) Fluorescence change of a powdered mixture of 1 and Cs$_2$CO$_3$ under UV irradiation (365 nm) after addition of a drop of methanol.
(b) Photographs of a mixture of 1 and various carbonate salts under UV irradiation (365 nm) after addition of a drop of methanol.
(c) Photographs of 1 + Cs$^+$ on dirt under room light (left) and under UV irradiation (365 nm, right) after spraying with methanol.
(d) Photographs of 1 + Cs$^+$ particles on filter paper (diameter 110 mm) under UV irradiation (365 nm) after spraying with methanol.

model UV-3600 UV/Vis/NIR spectrophotometer. Fourier transform infrared (FTIR) spectra were measured from KBr pellets using a Nicolet model 760X spectrometer. Fluorescence spectra were measured from solid samples using an Otsuka Electronics, model MCPD-7000 spectrometer. Fluorescence lifetimes were measured using a Horiba model FluoroCube UltraFast-3000U setup.

2.3. Synthesis

Synthetic routes of 1 and 2 are shown in scheme 1. Simple substituted derivatives are designated 3TEG (TEG = 2-[2-[2-(methoxyethoxy)ethoxy]ethoxy]) (scheme 2).

2.3.1. 4-Hydroxy-4′-(4,4′,5,5′-tetramethyl-1,3,2-dioxaborolan-2-yl) biphenyl (4).

2-[1-Hydroxy-[1,1′-biphenyl]-4-ol (0.498 g, 2 mmol), potassium acetate (KOAc, 0.588 g, 6 mmol), PdCl$_2$(dpdf) (dpdf = 1,1′-bis(diphenylphosphino)ferrocene; 0.043 g, 0.06 mmol), and bis(2,2,3,3-tetramethyl-2,3-butanedionato)diboron (0.761 g, 3.0 mmol) were dissolved in anhydrous DMSO (12 ml). The mixture was heated at 80°C for 4 h with stirring under N$_2$. The mixture was cooled to room temperature and the solid filtered off and washed with dichloromethane. After evaporation of the solvents under reduced pressure, the residue was purified by silica gel column chromatography (AcOEt/hexane = 1/2, where AcOEt stands for ethyl acetate), to give 0.351 g of 4 as a white powder in 59% yield. $^1$H-NMR (300 MHz, CDCl$_3$, 25°C): δ = 1.36 (s, 12H), 5.16 (s, 1H), 6.91 (d, $J$ = 9.0), 7.41–7.63 (m, 4H), 7.86 (d, $J$ = 9.0) ppm. MALDI-TOF (dithranol): $m/z$ = 296.1 [M]$^+$.

2.3.2. Tetraethylene glycol bis(4-toluene sulfonate) [38]

Sodium hydroxide (1.06 g, 26 mmol) dissolved in water (10 ml) and tetraethylene glycol (1.71 g, 8.8 mmol) in tetrahydrofuran (THF, 10 ml) were placed in a flask and the mixture was cooled on an ice bath with magnetic stirring. To the mixture was added dropwise p-toluenesulfonyl chloride (3.50 g, 17 mmol) in THF (10 ml) over 1 h with continuous stirring and cooling of the mixture below 5°C. The solution was stirred at 0–5°C for an additional 4 h, and then poured into ice water (50 ml). The mixture was extracted twice with dichloromethane. The combined organic extracts were washed with saturated aqueous sodium chloride solution, and then dried over anhydrous Na$_2$SO$_4$. After evaporation of the solvent, the resulting crude product was purified by chromatography on silica gel with ethyl acetate, giving the product as a colorless oil in an 83% yield. $^1$H-NMR
(300 MHz, CDCl₃, 25°C): \(\delta = 2.44\) (s, 6H), 3.55–3.58 (m, 8H), 3.67 (t, 4H, \(J = 4.6\)), 4.15 (t, 4H, \(J = 4.6\)), 7.33 (d, 4H, \(J = 8.1\)), 7.79 (d, 4H, \(J = 8.4\)) ppm. MALDI-TOF (dithranol): \(m/z = 525.15\) [M + Na]⁺, 541.16 [M + K]⁺.

2.3.3. 11-Iodo-3,6,9-trioxaundecyl-(4-nitrophenyl)ether (6). Potassium carbonate (0.691 g, 5.0 mmol) and potassium iodide (0.002 g, 0.1 mmol) were added to a CH₃CN (20 ml) solution of a mixture of 4-nitrophenol (0.347 g, 2.5 mmol) and

---

Scheme 1. Synthesis of the receptors 1 and 2.
5 (5.02 g, 10 mmol), and the resulting suspension was refluxed for 13 h under N₂. The reaction mixture was allowed to cool to room temperature and the solvents evaporated under reduced pressure. The residue was dissolved in CH₂Cl₂, washed with water and dried over anhydrous Na₂SO₄. After evaporation of the solvent under reduced pressure, the residue was dissolved in acetone (50 ml), NaI (15.0 g, 100 mmol) was added, and the mixture was heated at reflux for 24 h. The reaction mixture was allowed to cool to room temperature and then the solvent was removed under reduced pressure. The residue was taken into CH₂Cl₂ and the solution was washed with water, dried over anhydrous Na₂SO₄, and then the solvent was removed under reduced pressure. The crude product was subjected to column chromatography (SiO₂, AcOEt/hexane: 1/1 v/v) yielding the product as a white solid (0.213 g, 64%).

2.3.5. 11-(4-Bromophenoxy)-3,6,9-trioxaundecyl-(4-nitrophenoxy)ether (8). K₂CO₃ (0.349 g, 2.5 mmol) was added to a solution of a mixture of 4-bromophenol (0.128 g, 1.3 mmol) and 6 (0.305 g, 0.63 mmol) in CH₂CN (10 ml), and the resulting suspension was refluxed for 15 h under N₂. The reaction mixture was allowed to cool to room temperature and solvent removed under reduced pressure. The residue was dissolved in ethyl acetate and the solution was washed with water, dried over anhydrous Na₂SO₄, and then solvent was removed under reduced pressure. The crude product was subjected to column chromatography (SiO₂, AcOEt/hexane: 1/1 v/v) yielding the product as a white solid (0.213 g, 64%).

1H-NMR (300 MHz, CDC₁₅O, 25 °C): δ = 3.74–3.65 (m, 8H), 3.89–3.82 (m, 4H), 4.13–4.07 (m, 2H), 4.20 (t, 2H, J = 1.9), 6.78 (d, 2H, J = 9.0), 6.96 (d, 2H, J = 9.3), 7.33 (d, 2H, J = 8.7), 8.18 (t, 2H, J = 4.6) ppm. 13C-NMR (75 MHz, CDC₁₅O, 25 °C): δ = 29.2, 68.14, 69.34, 70.15, 70.57, 70.65, 70.87, 71.88, 114.52, 125.83, 141.50, 163.78 ppm. MALDI-TOF (dithranol): m/z = 448.0225 [M + Na]⁺, 464.11 [M + K]⁺. HRMS (ESI) m/z calculated for C₁₉H₂₀O₃N₃NaO₆ [M + Na]⁺: 448.0225, found 448.0233.

2.3.4. N-(11-Iodo-3,6,9-trioxaundecyl)naphthalene-1,8-dicarboxylic acid imide (7). 1H-NMR (300 MHz, CDC₁₅O, 25 °C): δ = 3.22–3.17 (m, 2H), 3.73–3.53 (m, 16H), 3.85–3.81 (m, 2H), 4.47–4.42 (m, 2H), 7.75 (t, 2H, J = 7.7), 8.22 (d, 2H, J = 8.3), 8.60 (d, 2H, J = 7.3) ppm. 13C-NMR (75 MHz, CDC₁₅O, 25 °C): δ = 29.2, 39.04, 67.88, 70.06, 70.11, 70.48, 70.58, 71.83, 122.50, 126.85, 128.08, 131.18, 131.46, 133.90, 164.11 ppm. MALDI-TOF (dithranol): m/z = 484.36 [M + H]⁺, 506.37 [M + Na]⁺, 522.26 [M + K]⁺.

Scheme 2. Synthesis of the receptors 3TEG.
2.3.7. 11-(4′′-Hydroxy-1′′-phenyl-1′,4′-phenyl-1,4-phenoxy)-3,6,9-trioxaundecyl-(4-nitrophenyl)ether (I). 4 (0.250 g, 0.53 mmol) and 8 (0.250 g, 0.50 mmol) were dissolved in THF (16 ml). 2.0 M aqueous Na$_2$CO$_3$ (16 ml) was added and the solution was purged with N$_2$ gas. Tetrakis(triphenylphosphine) palladium(0) (3 mg, 0.0031 mmol) was added and the mixture was heated at 80 ◦C for 24 h with vigorous stirring under N$_2$. After cooling to room temperature, solvents were removed under reduced pressure and the residue dissolved in ethyl acetate, followed by washing with water and drying of the organic phase over anhydrous Na$_2$SO$_4$. The solution was filtered and solvent removed under reduced pressure. The crude product was purified by column chromatography (silica gel) using THF/hexane = 9/1 as the eluent to yield 0.152 g (51%) as an orange solid. $^1$H-NMR (300 MHz, d$_6$-DMSO, 25 ◦C): $\delta$ = 3.58–3.56 (m, 8H), 3.78–3.76 (m, 4H), 4.12–4.10 (m, 2H), 4.24–4.21 (m, 2H), 6.85 (d, 2H, $J = 8.6$), 7.01 (d, 2H, $J = 8.8$), 7.14 (d, 2H, $J = 9.3$), 7.52 (d, 2H, $J = 8.6$), 7.62–7.59 (m, 6H), 8.17 (d, 2H, $J = 9.1$), 9.55 (s, 1H) ppm. $^{13}$C-NMR (75 MHz, d$_6$-DMSO, 25 ◦C): $\delta$ = 67.38, 68.43, 68.80, 69.14, 70.03, 70.13, 115.09, 115.23, 115.95, 126.07, 126.53, 126.67, 127.69, 127.75, 130.59, 132.30, 137.85, 138.67, 140.98, 157.33, 158.24, 164.04 ppm. MALDI-TOF (dithranol): $m/z$ = 559.02 [M + Na]$^+$. Calculated for C$_{32}$H$_{33}$NO$_8$ [M + Na]$^+$: %C, 68.68; %H, 5.94; %N, 2.50. Found: %C, 68.31; %H, 6.32; %N, 2.48.

2.3.8. N-[11-(4′′-Hydroxy-1′′-phenyl-1′,4′-phenyl-1,4-phenoxy)-3,6,9-trioxaundecyl]naphthalene-1,8-dicarboxylic acid imide (2). $^1$H-NMR (300 MHz, d$_6$-DMSO, 25 ◦C): $\delta$ = 3.56–3.47 (m, H), 3.68–3.64 (m, H), 4.09–4.06 (m, 4H), 4.25 (t, 2H, $J = 6.5$), 6.84 (d, 2H, $J = 8.6$), 6.99 (d, 2H, $J = 8.8$), 7.51 (d, 2H, $J = 8.6$), 7.61–7.57 (m, 6H), 7.86 (t, 2H, $J = 7.5$), 8.46 (d, 2H, $J = 7.5$), 8.50 (d, 2H, $J = 7.3$), 9.55 (s, 1H) ppm. $^{13}$C-NMR (75 MHz, d$_6$-DMSO, 25 ◦C): $\delta$ = 67.11, 67.32, 69.08, 69.85, 69.89, 70.00, 70.05, 115.08, 115.94, 122.21, 126.51, 126.66, 127.46, 127.60, 127.66, 127.74, 130.59, 131.01, 131.08, 131.52, 132.26, 134.60, 137.85, 138.65, 135.31, 158.21, 163.64 ppm. MALDI-TOF (dithranol): $m/z$ = 617.57 [M]$^+$, 640.58 [M + Na]$^+$, 656.54 [M + K]$^+$. HRMS (ESI) $m/z$ calculated for C$_{38}$H$_{35}$NNaO$_7$ [M + Na]$^+$: 640.2311, found 640.2292.

2.3.9. 2-Methoxyethyl-(4-nitrophenyl)ether (10). K$_2$CO$_3$ (0.552 g, 4.0 mmol) was added to a solution of 4-nitrophenol (0.278 g, 2.0 mmol) and 2-methoxyethoxy-4-toluenesulfonate (0.921 g, 4.0 mmol) in dimethylformamide (DMF, 10 ml), and the resulting suspension was refluxed for 12 h. The reaction mixture

Figure 2. Detection limit of Cs$_2$CO$_3$ by using I. (a) Photographs and plot of fluorescence emission maxima wavelengths for mixtures between I and Cs$_2$CO$_3$/K$_2$CO$_3$ under UV irradiation (365 nm) after addition of a drop of methanol. (b) Fluorescence spectra of mixtures used to construct the plot in (a). (c) Photographs and emission maxima for mixtures between I and Cs$_2$CO$_3$/K$_2$CO$_3$ under UV irradiation (365 nm) after addition of a drop of methanol.

Sci. Technol. Adv. Mater. 14 (2013) 015002 T Mori et al
was allowed to cool to room temperature and evaporated to dryness. CH$_2$Cl$_2$ solution of the residue was washed with water, dried over anhydrous Na$_2$SO$_4$, and evaporated to dryness. The residue and NaI (1.20 g, 8.0 mmol) were suspended in acetone (5 ml), and heated at reflux for 3 h. The reaction mixture was allowed to cool to room temperature and solvents removed under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$, washed with water, dried over anhydrous Na$_2$SO$_4$, and then solvent was removed under reduced pressure. The product was obtained as colorless yellow needles (0.065 g) in a 17% yield.

$^1$H-NMR (300 MHz, CDCl$_3$, 25$^{\circ}$C): $\delta$ = 3.46 (s, 3H), 3.79 (t, 2H, $J$ = 3.0), 4.22 (t, 2H, $J$ = 6.0), 7.00 (d, 2H, $J$ = 9.0), 8.20 (d, 2H, $J$ = 6.0) ppm. $^{13}$C-NMR (75 MHz, CDCl$_3$, 25$^{\circ}$C): $\delta$ = 59.28, 68.04, 70.58, 114.53, 125.85, 141.62, 163.78 ppm.

2.3.10. N-(2-Methoxyethyl)naphthalene-1,8-dicarboxyl acid imide (11). $^1$H-NMR (300 MHz, CDCl$_3$, 25$^{\circ}$C): $\delta$ = 3.39 (s, 3H), 3.74 (t, 2H, $J$ = 6.0), 4.46 (t, 2H, $J$ = 6.0), 7.76 (t, 2H, $J$ = 9.0), 8.22 (d, 2H, $J$ = 9.0), 8.62 (d, 2H, $J$ = 6.0) ppm. $^{13}$C-NMR (75 MHz, CDCl$_3$, $\delta$, ppm): 38.81, 58.38, 69.21, 122.15, 126.47, 127.89, 130.92, 131.14, 133.54, 163.88 ppm. MALDI-TOF (dithranol): $m/z$ = 255.09 [M]$^+$. HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{13}$NNaO$_3$ [M + Na]$^+$: 278.0793, found 278.0790.

2.3.11. 2-[2-(2-Methoxyethoxy)ethoxy]ethyl-4-methylbenzenesulfonate (12) [37]. Sodium hydroxide (0.9 g, 20 mmol) dissolved in water (20 ml) and triethylene glycol monomethyl ether (2.46 g, 15 mmol) in THF (20 ml) were placed in a flask and the mixture was cooled on an ice bath with magnetic stirring. To the mixture was added dropwise p-toluenesulfonfonyl chloride (2.88 g, 14 mmol) in THF (20 ml) over 1 h with continuous stirring and cooling of the mixture below 5$^{\circ}$C. The solution was stirred at 0–5$^{\circ}$C for an additional 4 h, and then poured into ice water (70 ml). The mixture was extracted twice with dichloromethane. The combined organic extracts were washed with saturated aqueous sodium chloride solution, and then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the resulting crude product was purified by chromatography on silica gel with ethyl acetate to give 12 as a colorless oil. $^1$H-NMR (300 MHz, CDCl$_3$, 25$^{\circ}$C): $\delta$ = 2.44 (s, 3H), 3.36 (s, 3H), 3.36–3.54 (m, 2H), 3.58–3.62 (m, 6H), 3.66–3.70 (m, 2H), 4.10–4.17 (m, 2H), 7.34 (d, 2H, $J$ = 8.6), 7.79 (d, 2H, $J$ = 8.3) ppm. $^{13}$C-NMR (75 MHz, CDCl$_3$, 25$^{\circ}$C): $\delta$ = 21.60, 58.99, 68.61, 69.19, 70.48, 70.51, 71.84, 127.92, 129.77,

Figure 3. Interaction of 1 (a) or its component chromophore moieties (3TEG) (b) with alkali metal cations. (c) Fluorescence spectra of the mixtures revealing the different spectrum in the presence of Cs$^+$. (d) In the simple mixture of component chromophores the shift in fluorescence maximum is rather small and is not sufficient for sensing activity. Numbers above the spectra in panels (c) and (d) indicate the wavelength of the fluorescence maximum.
Figure 4. Photographs (a)–(c) and spectra of fluorescence change (d)–(f) of a mixture of 1 and alkali metal salt under UV irradiation (365 nm) after addition of a drop of methanol. Fluorescence change of a powder mixture of 1 and Cs+ under basic conditions after spraying with methanol. Numbers in panels (a)–(c) indicate the wavelength of the fluorescence maximum.

132.91, 144.74 ppm. MALDI-TOF (dithranol): m/z = 341.0 [M + Na]+, 357.0 [M + K]+.

2.3.12. 1-(2-(2-(2-Methoxyethoxy)-ethoxy)ethoxy)-4-bromo-benzene (13). To a THF (15 ml) solution of mixture of 4-bromophenol (0.692 g, 4 mmol) and 12 (1.12 g, 3.5 mmol) was added KOH (1.0 g, 16 mmol), and the resulting suspension was refluxed for 15 h under N2. The reaction mixture was allowed to cool to room temperature and evaporated to dryness. The AcOEt solution of the residue was subjected to column chromatography (SiO2, AcOEt/hexane 1/1 v/v) to allow isolation of 13 as a colorless oil (0.7 g) in a 62% yield. 1H-NMR (300 MHz, CDCl3, 25 °C): δ = 3.37 (s, 3H), 3.54 (m, 2H), 3.72 (m, 6H), 3.84 (m, 2H), 4.09 (m, 2H), 6.80 (d, 2H, J = 9.0), 7.35 (d, 2H, J = 9.2) ppm. MALDI-TOF (dithranol): m/z = 356.94 [M + K]+.

2.3.13. 4-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy}-[1,1′; 4′,1″terphenyl-4″-ol (3TEG) [38]. A mixture of Na2CO3 (0.158 g, 1.5 mmol), Pd(OAc)2 (0.003 g, 0.5 mol%), 4 (0.236 g, 0.8 mmol), 13 (0.226 g, 0.7 mmol), distilled water
(7 ml) and acetone (6 ml) was stirred for 3 h at room temperature. Afterward, the reaction mixture was evaporated to dryness, and the solution was quenched with dilute aqueous hydrochloric acid. The precipitate was washed with water. The residue was subjected to column chromatography (SiO₂, AcOEt/hexane 1/1 v/v) to allow isolation of 3TEG as a white powder (0.414 g) in a 72% yield.¹H-NMR (300 MHz, d₆-DMSO, 25 °C): δ = 3.30 (s, 3H), 3.43 (m, 2H), 3.51 (m, 4H), 3.58 (m, 2H), 3.74 (m, 2H), 4.13 (m, 2H), 6.87 (d, 2H, J = 8.6), 7.03 (d, 2H, J = 8.8), 7.52 (d, 2H, J = 8.4), 7.62 (d, 6H, J = 8.1), 9.52 (s, 1H) ppm. ¹³C-NMR (75 MHz, d₆-DMSO, 25 °C): δ = 58.27, 67.41, 69.18, 69.83, 70.03, 70.17, 71.49, 115.14, 115.98, 126.56, 126.71, 127.73, 127.77, 130.61, 132.33, 137.90, 138.69, 141.25, 145.06, 148.69, 151.31, 154.34, 157.48 ppm.

Figure 5. Photographs of sunflowers and cross sections of their freeze-dried stems after immersion in water or an aqueous solution of potassium or caesium carbonate. The photographs were taken with the stems under UV irradiation (365 nm) after spraying only with methanol and with 1 in methanol.

Figure 6. Photographs and spectra illustrating the differences in fluorescence emission from (a) 1 and (b) 2 in the presence of carbonate salts of alkali metal cations after spraying with methanol.
Figure 7. Selected angles of the computed structures of the complexes of 1 with K⁺, Rb⁺ or Cs⁺ and 2 with K⁺, Rb⁺ or Cs⁺. Dihedral angles subtended at the indicated bonds are listed in the table on the right.

Table 1. Fluorescence lifetime of the mixtures of phenols and alkali metal carbonate after addition of methanol.

| Compound | Excitation (nm) | Emission (nm) | Fluorescence lifetime (ns) |
|----------|----------------|---------------|---------------------------|
| 3TEG     | 279            | 380           | 1.38 (56%), 3.72 (44%)    |
| 3TEG + K₂CO₃ | 375         | 460           | 1.27 (72%), 3.24 (28%)    |
| 3TEG + Cs₂CO₃ | 375       | 460           | 0.19 (10%), 1.58 (90%)    |
| 1        | 279            | 380           | 0.66 (43%), 1.18 (57%)    |
| 1 + K₂CO₃ | 375            | 460           | 0.33 (10%), 2.08 (90%)    |
| 1 + Cs₂CO₃ | 375            | 460           | 0.20 (14%), 2.97 (86%)    |
| 1 + Cs₂CO₃ | 375            | 505           | 0.14 (16%), 2.73 (84%)    |

157.35, 158.28 ppm. MALDI-TOF (dithranol): m/z = 408.0 [M]+, 431.0 [M+Na]+. HRMS (ESI) m/z calculated for C₂₅H₂₈NaO₅ [M+Na]+: 431.1834, found 431.1831.

3. Results and discussion

Figure 1 illustrates the selective sensing activity of 1 including its solid-state fluorescence response to the presence of Cs⁺ (figure 1(a)). Figure 1(b) shows the difference in fluorescence emission color from 1 in the presence of Li⁺, Na⁺, K⁺ or Cs⁺ (as their carbonate salts), following exposure to methanol by spraying a small amount of the solvent on the powdered solid⁶. The absence of fluorescence in the presence of Mg²⁺ and Ca²⁺ is also shown (figure 1(b)). Green fluorescence due to the presence of Cs⁺ on dry soil is shown after spraying of a solution of 1 in methanol so that the contaminated site can be easily identified and removed from the surrounding material (figure 1(c)). In addition, Cs⁺ particles can be visualized after spraying with 1 in methanol (see figure 1(d) and the supplementary information available at stacks.iop.org/STAM/14/015002/mmedia).

The limit of detection for Cs⁺ should depend on several parameters including counteranion, local pH and intercalation of Cs⁺ into clay contained in ground soils. We estimate a detection limit of 1 ppm under ideal conditions (see figure 2). This limit is significant since caesium is present in the Earth’s crust at 1 ppm: detection of caesium concentrations above this level would indicate possible local contamination. From figure 2 it is evident that the wavelength of the fluorescence emission maximum is dependent on the concentration of Cs⁺ present making construction of a calibration curve possible.

The form of the calibration curve suggests that concentrations of Cs⁺ far lower than 1 ppm could be detected, although this is not necessarily useful from a practical perspective. The importance of the connectivity of 4-NPE in 1 was investigated by comparing its response to that of a physical mixture of a triethylene glycol-substituted terphenol (3TEG), a simple ether of 4-nitrophenol (10) and the respective alkali metal carbonates in the presence of methanol (see figure 3). Notably, the green fluorescence characteristic of the presence of Cs⁺ in 1 was not observed, and all metal carbonates (Na⁺, K⁺ or Cs⁺) gave the standard blue fluorescence in the solid state moistened with methanol. This further demonstrates that Cs⁺ binding to 1 differs from that of the other alkali metal cations leading to the specificity in its fluorometric response.

⁶ Ethanol may also be used to circumvent use of toxic methanol.
Figure 8. Origin of the donor–acceptor (D–A) character of terphenol. As illustrated in the lower part, in the phenol both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are situated over the extent of the molecule. Upon deprotonation, HOMO is situated at the electron-rich phenoxide group while the LUMO is situated at the electron-deficient phenyl group remote from the phenol. Experimental and simulated electronic absorption spectra (top-right panel) reveal the accuracy of the model.

Recent research suggests that sulfate aerosols were the transport medium of radiocaesium from the Fukushima nuclear accident [8]. Accordingly, a mixture of 1 and caesium sulfate exhibited green fluorescence under basic conditions after spraying with methanol (figure 4). Diffusion behavior and the bioaccumulation processes of caesium can be easily and safely studied by using 1 and non-radioactive Cs-133. For instance, cut sunflowers were immersed in 1 wt% aqueous solution of caesium carbonate for several days. The sunflowers were subsequently freeze-dried at −40 °C. A sunflower stem cross section exhibited green fluorescence after spraying with 1 in methanol (figure 5; see also the supplementary information available at stacks.iop.org/STAM/14/015002/mmedia).

In ascertaining whether the fluorimetric response or selectivity of 1 could be varied, we prepared compound 2 where the 4-NPE group of 1 had been replaced by a fluorescent naphthalene-1,8-dicarboxylic imide unit. Compound 2 unexpectedly behaves as a selective sensor for Rb⁺ yielding a similar green fluorescence to that obtained for 1 and Cs⁺ under basic conditions (figure 6). Fluorescence lifetimes for 1 and 1 with K⁺ or Cs⁺ in methanol are summarized in table 1 and figure S2 (see the supplementary information at stacks.iop.org/STAM/14/015002/mmedia). Lifetimes of intermolecular fluorescence (i.e. that involving two chromophores linked in the same molecule), such as that occurring due to FRET or exciplex mechanisms, are an order of magnitude longer than those of intramolecular fluorescence (i.e. that involving an isolated chromophore). For instance, the fluorescence lifetime of the naphthalimide monomer is about 1 ns. If a naphthalimide dimer forms an excimer then the fluorescence lifetime is longer (about 20 ns). The difference in fluorescence lifetime between [1 + K₂CO₃] and [1 + Cs₂CO₃] is small. Fluorescence lifetimes for 1 in the presence of alkali metal cations are an order of magnitude shorter than those expected for FRET and exciplex fluorescence emission mechanisms and suggest an intra-moiety mechanism involving the deprotonated terphenol group.
To explain this disparity in the responses of the two sensor molecules, we considered the respective geometries of 1 and 2 during interaction with the analyte cations by applying density functional theory (DFT) [27] geometry optimization to the resulting complexes. The results (figure 7) show that the forms of the complexes of the cations with each ligand are very similar, with the electropositive metal cation being coordinated by oxygen atoms of the tetraethylene glycol chain, similar to the situation in the crown ether complexes. It is important to note that a weak hydrogen bond between the 4-nitro group of the NPE moiety and one methine of the terphenol is predicted and in fact could be detected in infrared spectra of 1 in the presence of alkali metal cations (see figure S3 in the supplementary information). This hydrogen bond apparently stabilizes a quasi-macrocyclic conformation of 1 while no similar interaction occurs in 2. This also explains why for the previously mentioned physical mixture involving disconnected components of 1 there is no differentiation between cations, as macrocyclization of the host’s component moieties is not possible. On the other hand, in 2 there are apparent CH...π interactions between the naphthalenedicarboxylic imide unit and the π-electronic system of its terphenyl. Now, considering the departure from ideal geometry in each case, measured by summing the angular departures from ideal tetrahedral geometry of the methylene groups of the tetraethylene glycol chain, we find that for 2, Rb⁺ is most easily accommodated, while for 1 Cs⁺ is favored. Perhaps serendipitously, the optimal binding geometry for 1.Cs⁺ and 2.Rb⁺ also leads to the respective cations being brought in closer proximity to

All density functional theory (DFT) calculations were carried out using the B3LYP exchange correlation functional implemented in Gaussian 09 [21] with LanL2DZ basis set.
the alkoxyphenyl end of the HTP group. To explain the selectivity of the response to Cs\(^+\) for 1, we consider that the deprotonated terphenol unit is formally a donor–acceptor (D–A) type moiety (figure 8). Deprotonation of the HTP unit leads to an electronic donor state for the phenol part of the molecule while the opposing alkoxyphenyl unit is relatively electron deficient. The fluorescence of the mixtures between 1 and alkali metal carbonates is bathochromically shifted by *intramolecular charge transfer* following addition of methanol by the mechanism proposed by Valeur [28, 29]. Fluorescence lifetime is slightly longer for 1 + Cs\(_2\)CO\(_3\) than 1 + K\(_2\)CO\(_3\) suggesting that excitation of 1 + Cs\(_2\)CO\(_3\) is more stable. When Cs\(^+\) interacts with the acceptor group of deprotonated 1 the excited state is stabilized more by Cs\(^+\) than the ground state, and this leads to a bathochromic shift of the fluorescence maximum (figure 9). For 2, Rb\(^+\) also approaches more closely than other alkali metal cations the electron-deficient part of the deprotonated phenol.

Although our initial molecular design was based on an expectation that FRET or exciplex phenomena might be observed in 1 due to intramolecular interaction, introduction of the 4-nitrophenyl ether group introduced a serendipitous point for intramolecular macrocyclization through hydrogen bonding (between the 4-nitro group and one HTP methane [30]) with no optical effects due to this group, except for changes in the fluorescence upon binding different cations due to *intramolecular* effects. Moreover, we believe that it would anyway be extremely difficult to detect any difference between complexes of 1 with the alkali metal cations if FRET or exciplex mechanisms operated in this case, due to the substantial similarities in structure between the complexes, especially with regard to the relative positioning of the donor and acceptor chromophores. In fact, FRET or exciplex emission would likely obstruct cation differentiation in this case due to the sublety of the effect of the proximity of the Cs\(^+\) to the HTP group.

4. Conclusions

This simple optical probe 1 has a higher spatial resolution for Cs-137 than existing radioscopes and gamma ray cameras (figure 10). Since only contaminated particles are detected by eye and can be easily removed, the volume of radioactively contaminated material for extraction is greatly reduced. The location of caesium in solid samples such as soil, foodstuffs and plants can be visualized by using this probe, allowing one to study its diffusion processes and accumulation behavior in those media. The availability of this and other similarly easily implemented tests for environmental contaminants is likely to increase the volume of data regarding rates of contamination around chemical and radiological hazards. This information will then be useful for constructing maps of contamination, which can be used to determine accommodation and agricultural policies involving local populations. Combination of the molecular optical probe described here with appropriate porous adsorptive materials [31–36] should also permit creation of materials for convenient detection–removal systems.

Acknowledgments

This research was supported by the World Premier International Research Center Initiative (WPI Initiative) on Materials Nanoarchitectonics, from MEXT Japan and the CREST program of the Japan Science and Technology Agency (JST), Japan.

References

[1] Essen L and Parry J V L 1995 *Nature* **176** 280
[2] Gnis V, Crkenjakov R and Byus C 1974 *Biochemistry* **13** 2633
[3] Butteman W C, Brooks W E and Reese R G Jr 2004 Mineral commodity profile: caesium *Open-File Report* 2004–1432 (Virginia: US Geological Survey) p 5
[4] Johnson G T, Lewis T R and Wagner W D 1975 *Toxicol. Appl. Pharmacol.* **32** 239
[5] International Atomic Energy Agency 2006 Environmental consequences of the Chernobyl accident and their remediation: twenty years of experience Report of the UN Chernobyl Forum Expert Group ‘Environment’ (Vienna: IAEA) STI/PUB/1239
[6] Brunstfel G 2011 *Nature* **478** 435
[7] Mangan J 2004 *Bull. Atom. Sci.* **60** 30
[8] Kanayasu N, Ohashi H, Suzuki F, Okada T and Ikemori F 2012 *Environ. Sci. Technol.** 46** 5720
[9] Langham W H and Andersen E C 1959 *Health Phys.* **2** 30
[10] Rowan D J and Rasmussen J B 1994 *Can. J. Fish. Aquat. Sci.* **51** 2388
[11] Rahman M M and Voigt G 2004 *Environ. Radioact.* **71** 127
[12] Turekian K K and Wedepohl K H 1961 *Science* **133** 899
[13] F¨orster T 1965 *Delocalized excitation and excitation transfer in solutions and in the solid state* (Wallingford, CT: VCH) ed O Sinanoglu p 93
[14] Frisch M J et al 2009 *Gaussian 09* revision A.01 (Wallingford, CT: Gaussian)
[29] Bourson J and Valeur B 1989 *J. Phys. Chem.* 93 3871
[30] Samshuddin S, Butcher R J, Akkurt M, Narayana B, Sarojini B K and Yathirajane H S 2012 *Acta Crystallogr.* E68 a74
[31] Abe H, Satoh A, Nishida K, Abe E, Naka T, Imai M and Kitazawa H 2006 *J. Solid State Chem.* 179 1521
[32] Ariga K, Vinu A, Yamauchi Y, Ji Q and Hill J P 2012 *Bull. Chem. Soc. Japan* 85 1
[33] Ariga K, Ishihara S, Abe H, Li M and Hill J P 2012 *J. Mater. Chem.* 22 2369
[34] Hu M, Sukegawa H, Nemoto Y., Reboul J, Kitagawa S and Yamauchi Y 2012 *Angew. Chem., Int. Ed. Engl.* 51 984
[35] Database of Promising Adsorbents for Decontamination of Radioactive Substances READS http://reads.nims.go.jp/index_en.html 13 December 2011
[36] Ishiyama T, Murata M and Miyaura N 1995 *J. Org. Chem.* 60 7508
[37] Ouchi M, Inoue Y, Liu Y, Nagamune S, Nakamura S, Wada K and Hakushi T 1990 *Bull. Chem. Soc. Japan* 63 1260
[38] Liu L, Zhang Y and Xin B 2006 *J. Org. Chem.* 71 3994