Aggregation-induced emission active tetraphenylethene-based sensor for uranyl ion detection

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Abstract: A novel tetraphenylethene-based fluorescent sensor, **TPE-T**, was developed for the detection of uranyl ions. The selective binding of **TPE-T** to uranyl ions resulted in a detectable signal owing to the quenching of its aggregation-induced emission. The developed sensor could be used to visually distinguish UO_2^{2+} from lanthanides, transition metals, and alkali metals under UV light; the presence of other metal ions did not interfere with the detection of uranyl ions. In addition, **TPE-T** was successfully used for the detection of uranyl ions in river water, illustrating its potential applications in environmental systems.

Key words: Uranium recognition; Fluorescent sensor; Aggregation-Induced Emission; DFT calculation

Uranium is an actinide metal with natural radioactivity; the most stable and common ionic form of uranium is UO_2^{2+} , and because uranyl is water soluble, it is readily migrated to the environment. Therefore, uranyl is widely distributed in the environment [1]. It is used as fuel for nuclear energy generation, and it has also been used in nuclear weapons [2]. With the growing demand for nuclear energy, uranium consumption is continuously increasing worldwide [3]. Unfortunately, uranium is radioactive and chemically toxic, and human exposure to uranium was reported to result in lung cancer, urinary system ailments, and genetic diseases [4].

Considering the widespread use of uranium and its toxicity, the development and improvement of analytical methods for the determination of uranium and uranyl ions are vital. As such, many techniques have been developed for the determination of uranium and uranyl ions, including nuclear techniques [5], spectrometric techniques [6], electrochemistry [7], and ion chromatography [8]. Although these methods have good sensitivities, they involve the use of expensive equipment with high operating costs and often require strict control of experimental conditions. Among the available analytical methods, fluorescence detection is a simple, rapid, highly selective, and inexpensive method for the determination of metal ions. However, only a few reports on the use of this technique for uranium ion analysis have been published. Viswanathan et al. reported the use of 2,6-pyridinedicarboxylic acid (PDA) as a fluorescence sensitizing agent for the determination of uranium [9]. However, PDA is known to chelate a variety of metal ions, and the selective recognition of uranyl ions was hampered in the presence of competing ions. Our group previously reported a phosphorylated cyclic peptide as a uranium sensor [10]. In recent studies by Attia et al., a thin film fluorescence sensor, trimetazidine, was successfully used for the sensitive determination of uranium [11]. Hua and co-workers reported the determination of uranium concentrations in aqueous media using a thermoresponsive, porphyrin-terminated polymeric fluorescent sensor [12]. However, the presence of some transition metals and thorium ions interfered with the detection of uranium using these sensors.

Recently, aggregation-induced emission (AIE) sensors [13] have garnered considerable attention as a new type of fluorescence sensor for the selective and sensitive identification of different metal ions, including Fe^{3+} , Cu^{2+} , Zn^{2+} , Ag^+ , Hg^{2+} , and As^{3+} [14]. Molecules that exhibit AIE do not exhibit any emission upon dissolution, but exhibit strong emission upon aggregation owing to the suppression of nonradiative deactivation associated with restricted intramolecular rotation. Therefore, these AIE active sensors facilitate the colorimetric determination of metal ions due to their strong emission, which can simplify the recognition process even without expensive instruments. Nonetheless, reports on the determination of radioactive metals using AIE-based sensors are very rare. Recently, our group reported an AIE-based sensor based on tetraphenylethene modified with 2,6-pyridinedicarboxylic acid for thorium detection [15]. Furthermore, Chen et al. reported an AIE-active sensor, 4-pethoxycarboxyl salicylaldehyde azine (PCSA), which exhibited excellent sensitivity towards uranyl ions [16]. However, this sensor is

sensitive to pH; it should work at pH 10.3, yet uranyl may precipitate as $\text{UO}_2(\text{OH})_2$ due to the low precipitation constant (1.22×10^{-22}), which may cause the test to generate inaccurate results. Moreover, the coordination of Schiff bases with many transition metals may interfere with the determination of uranyl ions in the presence of other naturally abundant ions [17]. Therefore, the development of highly selective fluorescent sensors for uranium recognition that are viable at a wide range of pH values remains a challenge. Moreover, the use of AIE-based sensors may provide a workable approach for the colorimetric recognition of uranium, owing to their unique photo-physical properties. Herein, we present a novel AIE-active sensor based on tetraphenylethene (TPE) modified with 2-(4,5-dihydrothiazol-2-yl) phenol for the highly selective and sensitive detection of uranyl ions in aqueous media. Using this sensor, uranyl ions can be visually distinguished from lanthanides, transition metals, and alkali metals under UV light.

Table 1. Comparison of the analytical parameters of the **TPE-T** with some of the previously fluorescence sensors.

Fluorescence sensor	pH range	Colorimetric determination	Concentration range (mol/L)	Interfering ions	References
2,6-pyridinedicarboxylic acid	6~8	No	$2.6 \times 10^{-7} \sim 8.8 \times 10^{-6}$	Tb^{3+}	[9]
cyclic peptide	6	No	$3.6 \times 10^{-7} \sim 4.2 \times 10^{-5}$	-	[10]
porphyrin-terminated polymeric	2~5	No	$10^{-7} \sim 10^{-3}$	Cu^{2+} , Fe^{3+} , Ni^{2+} , Zn^{2+}	[12]
trimetazidine	-	No	$4.9 \times 10^{-8} \sim 1.7 \times 10^{-6}$	Th^{4+} , Al^{3+} , Fe^{3+}	[11]
PCSA	10.3	No	$3.7 \times 10^{-9} \sim 9.2 \times 10^{-8}$	Cu^{2+}	[16]
TPE-T	2~10	Yes	$1.0 \times 10^{-6} \sim 2.0 \times 10^{-5}$	-	This work

2. Experimental

2.1 Instrumentation and measurements

^1H -NMR and ^{13}C -NMR spectra were measured on a Bruker AM400 NMR spectrometer (400 MHz or 100 MHz, respectively). ESI-MS spectral data were recorded on a Finnigan LCQDECA mass spectrometer. Absorption spectra were recorded on PELambda 650 (PerkinElmer). Fluorescence spectra were obtained using LS-55 (PerkinElmer). Unless otherwise mentioned, all measurements

were carried out at room temperature (about 293 K).

2.2 Reagents and solutions

Unless otherwise noted, all materials were obtained from commercial suppliers and were used as received without further purification. All solvents used in the optical spectroscopic studies were either of HPLC or spectroscopic grade. All the metal ions used are standard solution of metal ions from National Standards Centre (China).

2.3 Preparation of **TPE-T**

Scheme 1. Synthesis of **TPE-T**.

The synthetic route for **TPE-T** is shown in Scheme 1.

Experimental Procedure:

Synthesis of Compound 2: Under nitrogen, **1** (200 mg, 1.0 equiv.), 4-bromo-2-hydroxybenzonitrile (129.6 mg, 1.5equiv.), $Pd(PPh_3)_4$ (100 mg, 0.2 equiv.), and K_2CO_3 (600 mg, 10.0 equiv.) were dissolved in 1,4-dioxane (10 mL) in a flask equipped with a magnetic stirring bar. The reaction vessel was placed in an $85\text{ }^\circ\text{C}$ oil bath, and then stirred for 10 h. The reaction mixture was allowed to cool to room temperature, and was quenched with water. Next, the reaction mixture was extracted with CH_2Cl_2 , and the organic phase was dried with $MgSO_4$. After the organic phase was concentrated in vacuo, the crude product was purified by column chromatography (CH_2Cl_2) to obtain **2** as a yellow solid.

Synthesis of **TPE-T:** **2** (150 mg, 1.0 equiv.), 2-aminoethanethiol (645.6 mg, 25.0 equiv.), and 1,3-dibromo-5,5-dimethylimidazolidine-2,4-dione (DBDMH, 20 mg, 0.2 equiv.) were dissolved in ethanol (15 mL) in a flask equipped with a magnetic stirring bar. The reaction vessel was placed in a $110\text{ }^\circ\text{C}$ oil bath, and then stirred for 0.5 h. The reaction mixture was allowed to cool to room temperature, and was subsequently quenched with water. Next, the reaction mixture was extracted

with CH_2Cl_2 , and the organic phase was dried with MgSO_4 . After the organic phase was concentrated in vacuo, the crude product was purified by column chromatography (CH_2Cl_2) to give a yellow solid, which was recrystallized in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:1) to give **TPE-T** in 86% yield as a yellow solid.

2.4 Spectroscopic measurements

Most of the AIE sensor researches used methanol, DMSO, THF or acetonitrile as the solvent. However, **TPE-T** has poor solubility in methanol and DMSO, and the solubility of THF is better than acetonitrile, so we choose THF as the solvent to dissolve **TPE-T**. Water was used as the poor solvent to test the AIE characteristics of **TPE-T**, because **TPE-T** is poorly soluble in water, more importantly, most metal ions soluble in water, it could facilitate the detection of metal ions. For spectroscopic measurements, a 20 μL aliquot of **TPE-T** in THF (10^{-3}M) was added to a 5.0 mL glass tube, and 1980 μL THF/water (0–0.95, v/v) was added. After the solution was mixed and left at room temperature for 10 min, the solution was subjected to AIE measurements.

For the detection of metal ions, 20 μL of **TPE-T** in THF (10^{-3}M) and 100 μL of metal ions in water ($4\times 10^{-4}\text{M}$) were added to a 5.0 mL glass tube, and diluted to 2000 μL with THF/water (water volume fraction, $f_w = 95\%$). After mixing and equilibrating at room temperature for 10 min, each solution was subjected to fluorescence measurements (excitation and emission at 280 and 494 nm, respectively).

3. Results and discussion

3.1 AIE of **TPE-T**

Tetraphenylethene (TPE) is a typical AIE-active compound, and many AIE sensors have been prepared for the identification of metal ions by functionalizing the TPE core [14]. Thus, we first investigated the AIE of **TPE-T**. The fluorescence of 10^{-5} M TPE-T was investigated in mixtures of THF/water with various water volume fractions (f_w). Figure 1 shows the emission of **TPE-T** in various THF/ H_2O mixtures. The fluorescence of **TPE-T** gradually increased when f_w was increased from 0% to 70%. When f_w reached 80%, blue emission was observed at 465 nm. When f_w was increased to 95%, the maximum emission wavelength of the solution was red-shifted to 494 nm. Because **TPE-T** is poorly soluble in water, it aggregates in aqueous mixtures with high

water fractions. When f_w was increased to 99%, the mixture exhibited a decrease in its emission intensity, as **TPE-T** may quickly agglomerate to form an amorphous species with decreased emission [18]. To confirm the presence of aggregates, particle size analysis was carried out using dynamic light scattering (DLS) (Figure 2). While no particles (> 3 nm) could be detected when **TPE-T** was dissolved in THF, particles with an average size of ca. 149.2 nm ($f_w=95\%$) and 206.1 nm ($f_w=99\%$) were observed in solvent mixtures with high water ratios. SEM and TEM were used to observe the aggregation [19], a comparison of the micrographs of two samples ($f_w=0\%$, $f_w=95\%$) shows two distinct morphologies: micro powder ($f_w=0\%$) and micro sheet ($f_w=95\%$) respectively (see Figure S7 in the Supporting Information). It is observed that one dimensional growth of particles, from micro powder to micro sheet. These results confirming that the **TPE-T** indeed aggregated into nanoparticles, confirming the AIE of **TPE-T**.

Figure 1. (A) Fluorescence spectra of **TPE-T** (10 μ M) in H_2O /THF mixtures with f_w ranging from 0% to 99% ($\lambda_{ex} = 280$ nm, slit = 12 nm/8 nm). (B) Change in fluorescence (FL) intensity of **TPE-T** (10 μ M) at 494 nm in various THF/water mixtures.

Figure 2. Particle size distributions of (A) **TPE-T** in THF/water mixture (5:95 v/v), (B) **TPE-T** in THF/water mixture (1:99 v/v), and (C) **TPE-T** with UO_2^{2+} in THF/water mixture (5:95 v/v).

$$[\text{TPE-T}] = 10 \mu\text{M}, [\text{UO}_2^{2+}] = 20 \mu\text{M}.$$

3.2 Effect of pH on the fluorescence of **TPE-T**

Due to the dihydrothiazole and phenol moieties on **TPE-T**, we envisioned that the emission of **TPE-T** would be affected by the pH of the solution. In neutral, weakly acidic, and basic aqueous

solutions (pH 3–10), **TPE-T** aggregated and exhibited emission (Figure 3). However, the emission decreased in media with low pH values (pH < 3). At low pH values, the dihydrothiazole unit can be protonated, which may increase the solubility of **TPE-T** in water.

Figure 3. Change in fluorescence (FL) intensity of **TPE-T** (10 μ M) and **TPE-T** (10 μ M)+UO₂²⁺ (20 μ M) at 494 nm in aqueous media at different pH [THF/water mixture =5:95 (v/v)] (λ_{ex} = 280 nm, slit = 12 nm/7 nm).

3.3 Detection of metal ions using **TPE-T**

The emission characteristics of **TPE-T** were investigated in the presence of various metal ions. The conditions were optimized by titrating 10⁻⁵ M solutions of **TPE-T** with an f_w of 95% with fixed concentrations of metal ions (4 $\times$ 10⁻⁴M in water). Figure 4 shows the emission intensity of **TPE-T** at 494 nm in the presence of various metal ions. Metals that commonly coexist with uranium, such as most transition metals, lanthanide metals, and thorium, had no obvious effect on the emission of **TPE-T**. Cu²⁺ and Fe³⁺ quenched the emission of **TPE-T** by more than half (quenching efficiency ($I_0 - I$)/ I_0 : Cu: 72%, Fe: 67%). However, when 2 equiv. of uranyl was added to the solution of **TPE-T**, the fluorescence intensity of **TPE-T** was quenched almost completely (quenching efficiency: UO₂²⁺: 96%). Figure 5 shows **TPE-T** in a mixture of H₂O/THF in the presence of various metal ions, including alkali metals, transition metals, lanthanide metals, and thorium under UV light (365 nm). The green emission was completely quenched in the presence of uranyl ions, suggesting that **TPE-T** is highly selective toward uranyl ions, and that uranyl ions could be visually distinguished from other metal ions using **TPE-T**. We also studied the effect of

pH on the interaction between **TPE-T** and UO_2^{2+} . Figure 3 shows that when the pH was 2-10, the emission of **TPE-T** could be quenched completely by UO_2^{2+} , indicating that **TPE-T** has a wide effective pH range in the detection of uranyl. Notably, this quenching was weakened at low pH (pH=1), and thus the coordination of **TPE-T** with UO_2^{2+} may be blocked at very low pH values.

Figure 4. Fluorescence intensity of **TPE-T**+ M^{n+} at 494 nm in the presence of various metal ions.

Conditions: **TPE-T** (10 μM) at 95% f_w and 2.0 equiv. of metal ions ($4 \times 10^{-4} \text{M}$ in water); $\lambda_{\text{ex}} = 280$ nm, slit = 12 nm/7 nm.

Figure 5. Photograph of solutions of **TPE-T** (10 μM)/cation (20 μM) mixtures at f_w of 95% under UV illumination (365 nm).

3.4 Titration of **TPE-T** with UO_2^{2+} ions

To further evaluate the response of **TPE-T** toward uranyl ions, titrations with various concentrations of UO_2^{2+} were performed. As shown in Figure 6, increasing concentrations of UO_2^{2+} ions gradually diminished the emission intensity of **TPE-T**, and the fluorescence of **TPE-T** was essentially quenched by 2.0 equiv. of UO_2^{2+} ions. The binding constant (K) derived from the fluorescence titration data was found to be 370 ($R^2 = 0.997$, Figure S2) using a Benesi–Hildebrand plot [20].

Figure 6. Fluorescence (FL) of **TPE-T** (10 μM) in the presence of various concentrations of UO_2^{2+} in $\text{H}_2\text{O}/\text{THF} = 95:5$ ($\lambda_{\text{ex}} = 280 \text{ nm}$, slit = 12 nm/7 nm).

3.5 Effect of added metal ions

An important feature of metal ion sensors is their capacity to function in the presence of other relevant metals. Thus, competition experiments were performed, and changes in the fluorescence intensity of a solution of **TPE-T** and uranyl ions (2.0 equiv.) in $\text{H}_2\text{O}/\text{THF} = 95:5$ (v/v) at 494 nm upon addition of 2.0 equiv. of different metal ions were monitored (Table 2). The added metal ions did not lead to drastic changes in the fluorescence intensity of **TPE-T**, thus indicating that they did not displace uranyl ions from the complex.

Table 2. Fluorescence response of mixtures of **TPE-T** (20 μM) and UO_2^{2+} (40 μM) in the presence of other metal ions (40 μM). Conditions: $\text{H}_2\text{O}/\text{THF} = 95:5$; excitation and emission wavelengths: 280 and 494 nm, respectively. I_0 : Fluorescence response of **TPE-T** (20 μM) + UO_2^{2+} (40 μM); I_1 : Fluorescence response of **TPE-T** (20 μM) + UO_2^{2+} (40 μM) + other metal ions (40 μM).

Added species	I_1/I_0 (%)	Added species	I_1/I_0 (%)	Added species	I_1/I_0 (%)
Li^+	99.3	Co^{2+}	97.5	Sm^{3+}	97.3
Na^+	101.3	Ni^{2+}	98.3	Eu^{3+}	101.1
K^+	100.4	Cu^{2+}	95.6	Gd^{3+}	97.6
Mg^{2+}	98.3	Zn^{2+}	98.6	Tb^{4+}	97.4

Ca ²⁺	100.6	Ag ⁺	98.4	Dy ³⁺	98.8
Al ³⁺	96.9	Au ⁺	100.4	Ho ³⁺	97.7
Mn ²⁺	98.9	La ³⁺	99.3	Er ³⁺	98.4
Cr ³⁺	101.3	Ce ³⁺	101.4	Tm ³⁺	99.6
Cd ²⁺	102.4	Pr ³⁺	98.6	Yb ³⁺	98.9
Fe ³⁺	95.1	Nd ³⁺	99.2	Th ⁴⁺	100.9

3.6 Analytical application

To evaluate the practical applications of the developed sensor, we used fluorescence spectroscopy to measure the concentration of uranyl ions in aqueous, uranyl-containing solutions, which were prepared using river water. Table 3 shows that the **TPE-T** sensor could be used to reliably determine the concentration of uranyl ions with a mean error of $\pm 5\%$ (Table 3). Therefore, this sensor may have potential applications in water contamination studies near uranium mining facilities.

Table 3. Uranyl determination in aqueous samples.

Sample ^a	Added (M) ^b	Determined by VA Computrace ^c	Found (M) ^c	Recovery (%)
River water 1	0.50×10^{-5}	$0.48(\pm 0.01) \times 10^{-5}$	$0.47 (\pm 0.02) \times 10^{-5}$	94
River water 2	1.00×10^{-5}	$0.99(\pm 0.01) \times 10^{-5}$	$0.95 (\pm 0.04) \times 10^{-5}$	95
River water 3	1.50×10^{-5}	$1.50(\pm 0.01) \times 10^{-5}$	$1.56 (\pm 0.07) \times 10^{-5}$	104

^a Uranyl-free river water from same river. ^b Added uranyl from standard solution and determined by ICP-OES. ^c Average of three determinations.

3.7 Mechanistic studies

The UV spectra of **TPE-T** upon titration of UO_2^{2+} are shown in Figure S3 in the Supporting Information. The absorption peak at 343 nm shifted to 356 nm, which may be caused by conformational changes introduced by the coordination of **TPE-T** with uranyl ions. Next, we carried out NMR titrations to analyze the mechanism of coordination (Figure S8); when uranyl ions were added to the solution of **TPE-T**, the hydroxyl peaks of the ligand shifted downfield in the ¹H NMR spectrum due to the coordination between the hydroxyl moiety and uranyl ions. We

also used the continuous variation method, also known as Job's plot [21], to determine the stoichiometry of the complex formed between uranyl ions and **TPE-T**. The total concentration of **TPE-T** and UO_2^{2+} was maintained at 10 μM , and the fluorescence intensity at 494 nm was monitored as the concentration ratio of $[\text{UO}_2^{2+}]$ to $([\text{UO}_2^{2+}] + [\text{TPE-T}])$ was varied (Figure 7). The maximum change in fluorescence was observed when the molecular fraction was approximately 0.33. As such, the binding ratio was calculated to be 2:1 (**TPE-T** to UO_2^{2+}). This was also supported by Density Functional Theory (DFT) calculations. As shown in Figure 8, the complex $(\text{TPE-T})_2\text{UO}_2^{2+}$ formed by the coordination of the **TPE-T** with uranyl ions in 2:1 ratio was determined at the BB1K/6-31G(d), SDD-MWB60 level of theory. The calculation shows that this complex with C_i symmetry adopts an octahedral-coordination environment around the U (VI) center, in which the hydroxyl oxygen atoms and nitrogen atoms of the 2,5-dihydrothiazole ring are situated on the equatorial plane. The bond distances between the U(VI) center and the coordinating oxygen and nitrogen atoms were 2.462 and 2.404 Å, respectively, which is in the typical range of U–O and U–N single bond lengths (2.2–2.6 Å) reported for other U(VI) complexes. According to the optimized structure, the aggregation-induced emission is quenched due to two factors: (1) the aggregation of **TPE-T** may be disrupted upon coordination to UO_2^{2+} , and the complex may have better solubility in water, which would result in decreased emission; (2) the heavy atom effect of uranyl. To determine whether the aggregates dissociated or not after coordination with uranyl ions, particle size analysis using DLS was carried out (Figure 2C). Particles with an average size of ca. 206.7 nm were observed in the presence of 2 equiv. of UO_2^{2+} . SEM and TEM were used to observe the aggregation, It is observed that micro balls were formed when **TPE-T** with UO_2^{2+} in THF/water mixture with $f_w=95\%$ and the particles size were about 200nm (see Figure S7 in the Supporting Information), indicating that the aggregation was not disrupted upon coordination. Next, we calculated the HOMOs and LUMOs of **TPE-T** and $(\text{TPE-T})_2\text{UO}_2^{2+}$ (Figure 9). In the free **TPE-T** ligand, the LUMO contains partial TPE and 2-(4,5-dihydrothiazol-2-yl) phenol moieties. When UO_2^{2+} is coordinated to the **TPE-T** ligand, the receptor LUMO mainly locates on the UO_2^{2+} moiety. The calculated receptor LUMO (–7.62 eV) in the $(\text{TPE-T})_2\text{UO}_2^{2+}$ complex is much lower than the fluorophore LUMO (–0.92 eV) in the free **TPE-T** ligand. The HOMO–LUMO energy gap also decreased from 4.87 eV to 1.36 eV. As a result, electron relaxation is allowed from the fluorophore LUMO (in free **TPE-T**) to the receptor

LUMO (**TPE-T**)₂UO₂²⁺ after the initial HOMO→LUMO excitation of the fluorophore causes the quenched fluorescence. According to these results, we speculated that the fluorescence quenching is mainly due to the chelation-enhanced quenching caused by the heavy atom effect of uranyl.

Figure 7. Job's plot of **TPE-T** and UO₂²⁺. The emission intensity at 494 nm was plotted against the molar fraction of [UO₂²⁺] to ([UO₂²⁺]+[**TPE-T**]) at a fixed total concentration of 1.0×10⁻⁵ mol/L in H₂O/THF (v/v=95/5).

Figure 8. The DFT predicted (**TPE-T**)₂UO₂²⁺ complex. The U–O and U–N bond lengths are given in Å.

Figure 9. Molecular orbitals of the free **TPE-T** ligand and **(TPE-T)₂UO₂²⁺** complex.

4. Conclusion

In summary, a 2-(4, 5-dihydrothiazol-2-yl) phenol-containing TPE derivative was synthesized and its optical properties were investigated. This molecule can function as a “turn-off” fluorescent chemosensor for uranyl ions in aqueous solutions. Uranyl can be detected by the naked eye using the developed sensor, as its AIE is quenched upon binding. The sensor showed a wide effective pH range and higher selectivity toward uranyl ions compared to all other tested metals, and other metals did not interfere with the detection of uranyl ions. This sensor showed good accuracy in the determination of uranyl concentrations in river water and may have potential applications for the detection of uranyl ions in environmental systems.

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Aggregation-induced emission active tetraphenylethene-based sensor for uranyl ion detection

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A novel tetraphenylethene-based fluorescent sensor, **TPE-T**, was developed for the detection of uranyl ions with high selectivity and sensitivity owing to the AIE phenomenon.