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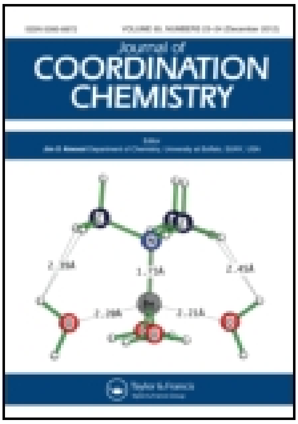

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Synthesis, structure, photochromic, and fluorescent imaging properties of sodium-3,3′-azobis(1,2,4-triazole)

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Synthesis, structure, photochromic, and fluorescent imaging properties of sodium-3,3′-azobis(1,2,4-triazole)

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A crystal of [Na_2(ABT)$\cdot 5H_2O$] (ABT = 3,3′-azobis(1,2,4-triazole)) (**1**) was characterized by single-crystal X-ray diffraction. Complex **1** features a 1-D chain and each ABT^{2-} is a $\mu_{1,2,6}$ bridge with three triazole nitrogen atoms coordinating to three different sodium(I). Aqueous solution of **1** (6.0×10^{-5} mol L^{-1}) shows photochromism. Fluorescence of solid **1** displays green photoluminescence under UV-light or laser irradiation and can be employed to label onion cell.

Keywords: 3,3′-Azobis(1,2,4-triazole); Crystal structure; Photoluminescence; Photochromism

1. Introduction

Molecules that change color or absorption spectra reversibly due to the transformation of two forms under radiation of various wavelengths are photochromic compounds [1, 2]. Although more than 100 years have past since the discovery of photochromism, research of photochromic compounds is still an active research area due to applications such as molecular photo-memory, photo-switches, and chemical sensing [2–5]. Among photochromic compounds, azo-based compounds with *trans* to *cis* isomerization upon UV-Vis or laser irradiation have been widely investigated [6, 7]. Organic small molecules containing azo as stimuli-responsive photochromic units, especially N-heterocyclic azo molecules, such as azotetrazole, azotriazole, and derivatives, have been widely applied to the construction of organic–inorganic photochromic materials [3, 8–11]. Very recently, photochromism of 5,5′-azotetrazole, 1,1′-azobis-1,2,3-triazole, and 1,1′-azobis-tetrazole were reported [12–15]. Fluorescent imaging analysis, widely used in biology and medicine, is an effective visual analysis technique. The fluorescent imaging agent plays a critical role in this process. Although numerous organic fluorescent imaging agents for labeling biomolecules have been designed, there still exists a major need for developing fluorescent chemosensors for the analysis of cell structures [16–18]. ABT is a good azo-based photochromic compound, which can be prepared by the oxidation-reduction of 3,5-diamino-1,2,4-triazole and sodium nitrite in

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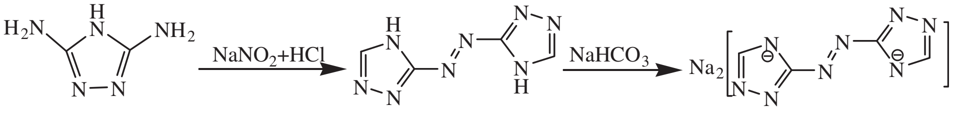

Scheme 1. The synthetic route to 3,3′-azobis(1,2,4-triazole) and sodium compound.

concentrated hydrochloric acid (scheme 1). The sodium salt of ABT can exhibit green photoluminescence under UV-light or laser irradiation and may be employed as a new label of biomolecules by forming noncovalent linkages due to deprotonated ABT containing multi-noncoordinated electron-donating nitrogen atoms. Here, the crystal structure, photochromism, and application as fluorescent imaging agent for onion cell of [Na$_2$(ABT) · 5H$_2$O] are reported.

2. Experimental

2.1. *Materials and physical measurements*

Commercial reagents and solvents were used without purification unless otherwise stated. Elemental analyses were carried out using a Perkin Elmer analyzer model 240. UV-Vis absorption spectra of **1** in an aqueous solution (6×10^{-5} mol L^{-1}) were recorded with a U-1800 UV-Vis Spectrophotometer. IR spectra were recorded as pressed KBr pellets on a Bruker Tensor 27 spectrophotometer. The excitation and emission spectra of the solid was recorded on an F-4500 Fluorescence Spectrophotometer.

2.2. *Synthesis of 1*

HCl (4.9 mL, 30 mmol) was added to 0.99 g (10 mmol) of 3,5-diamino-1,2,4-triazole in 20 mL of distilled water and the solution was cooled to 0°C in salt ice water. Then 1.38 g (20 mmol) of sodium nitrite in 15 mL of distilled water was added slowly and the new mixture was stirred for 24 h between 0°C and 5°C. After that, 1.68 g of NaHCO$_3$ was added to the mixture and then filtered. Yellow crystals were obtained by slow evaporation of the filtrate for several days, yield of 78%. IR (KBr, cm^{-1}): 3500s, 2085w, 1604m, 1400s, 1051m, 740 s. Elemental analysis Calcd for $C_4H_{12}Na_2N_8O_5$ (%): C, 16.10; H, 4.02; N, 37.56. Found (%): C, 16.07; H, 4.04; N, 37.54.

2.3. *Fluorescence imaging experiments*

The lamellae suitable for microscopy experiments were prepared by coating the powder sample on cover glasses and drying in air. Imaging experiments were conducted with a laser scanning confocal microscope (510 META DUO SCAN) with oil-immersion objective lens 63× (NA = 1.4, Plan-Apochromat). The incident beam (408 nm) was split by a beam splitter and focused into a small volume. The amplifier gain was set at 1.00 and the pixel time was 3.20 μs. For the plane imaging scan, green emission was collected with a 505–580 nm window.

Table 1. Crystallographic data and refinement parameters for **1**.

Empirical formula	$C_4H_{12}Na_2N_8O_5$
Formula weight	298.20
Color	Yellow
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.1162(13)
b	7.5855(13)
c	12.064(2)
α	79.743(3)
β	81.075(3)
γ	68.231(3)
Volume (Å^3), Z	592.25(18), 2
Calculated density (g cm^{-3})	1.672
F(000)	308
Absorption coefficient (mm^{-1})	0.204
Reflections collected	4957 [R(int) = 0.0148]
R indices (all data)	$^aR_1 = 0.0469$; $^bwR_2 = 0.1489$

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
$^bwR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2]^{1/2}$.

2.4. *Onion cell fluorescence imaging experiments*

The onion samples were first immersed in 8% HCl for 5 min and washed with H_2O, then immersed in 10^{-3} mol L^{-1} aqueous solutions of **1** for 20 min and washed with H_2O. Imaging experiments were conducted with a laser scanning confocal microscope (510 META DUO SCAN).

2.5. *X-ray single-crystal structure determination*

The crystal was filtered from the solution and immediately coated with hydrocarbon oil, and then put on the microscope slide. Suitable crystal was mounted on a glass fiber with silicone grease and placed in a Bruker Smart APEX(II) area detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 173(2) K. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). Hydrogen atoms were added theoretically, riding on their parent atoms. The crystal data and details on data collection and refinement are summarized in table 1 and selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *The crystal structure of 1*

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. Each unit of **1** consists of two sodium(I) ions, a *trans*-ABT^{2-}, and five water molecules. Both Na(1) and Na(2) exhibit distorted octahedral geometries, with Na(1) coordinating to two nitrogen atoms from two ABT^{2-} and four water molecules; Na(2) coordinates with one nitrogen atom

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Na(1)–N(1)	2.5281(19)	Na(2)–N(2)	2.4604(19)
Na(1)–N(6)i	2.570(2)	Na(2)–O(1)	2.4621(18)
Na(1)–O(1)	2.4888(18)	Na(2)–O(2)	2.3983(18)
Na(1)–O(2)	2.4217(18)	Na(2)–O(4)	2.3872(18)
Na(1)–O(3)	2.4324(18)	Na(2)–O(5)	2.3845(18)
Na(1)–O(3)i	2.4679(19)	Na(2)–O(5)ii	2.3693(17)
N(1)–Na(1)–O(1)	76.50(6)	N(2)–Na(2)–O(1)	77.82(6)
N(1)–Na(1)–O(2)	77.14(6)	N(2)–Na(2)–O(2)	83.37(6)
N(1)–Na(1)–O(3)	113.64(6)	N(2)–Na(2)–O(4)	90.17(6)
N(1)–Na(1)–O(3)i	106.36(6)	N(2)–Na(2)–O(5)ii	98.03(6)
N(6)i–Na(1)–O(1)	82.44(6)	O(5)–Na(2)–O(1)	85.60(6)
N(6)i–Na(1)–O(2)	81.76(6)	O(5)–Na(2)–O(2)	88.93(6)
N(6)i–Na(1)–O(3)	88.55(6)	O(5)–Na(2)–O(4)	105.02(6)
N(6)i–Na(1)–O(3)i	93.12(6)	O(5)–Na(2)–O(5)ii	89.34(6)
O(1)–Na(1)–O(2)	84.79(6)	O(1)–Na(2)–O(2)	85.88(6)
O(1)–Na(1)–O(3)	98.92(6)	O(1)–Na(2)–O(4)	164.98(7)
O(1)–Na(1)–O(3)i	174.20(6)	O(1)–Na(2)–O(5)ii	93.06(6)
O(2)–Na(1)–O(3)	169.11(6)	O(2)–Na(2)–O(4)	83.77(6)
O(2)–Na(1)–O(3)i	90.89(6)	O(2)–Na(2)–O(5)ii	178.03(7)
O(3)–Na(1)–O(3)i	84.65(6)	O(4)–Na(2)–O(5)ii	97.58(6)
N(1)–Na(1)–N(6)i	151.29(6)	O(5)–Na(2)–N(2)	162.14(7)

Symmetry codes: (i) $1-x$, $1-y$, $-z$; (ii) $-x$, $1-y$, $1-z$.

from ABT^{2-} and five water molecules (figure 1a). The bond lengths of Na(1)–N(1), Na(1)–N(6), and Na(2)–N(2) are 2.527, 2.572, and 2.461 Å, respectively, and Na–O bond lengths are 2.366–2.490 Å. Each ABT^{2-} is a $\mu_{1,2,6}$ bridge with three triazole nitrogen atoms coordinating to three different sodium(I) ions. Two coordinating water molecules and ABT^{2-} behave as bridges, resulting in a 1-D chain. ABT^{2-} rings exhibit face-to-face alignment along the crystallographic *b*-axis with separated interplanar distances of 3.453–3.728 Å, showing a face-to-face anion–anion π^{-}–π^{-} stacking interaction (figure 1b). Three kinds of hydrogen bonds are observed in **1**: (a) hydrogen bonds between coordinated water molecules with O···O distances 2.821 Å; (b) hydrogen bonds between coordinated water molecules and uncoordinated N(triazole) from ABT^{2-} with the shortest O···N = 2.915 Å; (c) hydrogen bonds between coordinated water molecules and carbon atoms from ABT^{2-} with the shortest C···O = 2.783 Å (figure 1c). The O–H···O, O–H···N, and C–H···O hydrogen bonds together with π–π stacking interactions link the 1-D complex chains into a 3-D supramolecular network (figure 1d). The π^{-}–π^{-} stacking interaction between two heteroaromatic rings and C···O hydrogen bonds for **1** were comparable to other coordination polymers constructed from alkali and alkaline earth metals [19–21].

3.2. *Photochromism of aqueous solutions of 1*

Azo derivatives are expected to exhibit *cis–trans* isomerism upon photoirradiation and usually exist in different tautomeric forms [1]. To understand the potential for the *cis–trans* isomerism of **1**, the UV-Vis spectral changes of **1** in aqueous solution at $6.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ under 312 nm UV light irradiation at regular time intervals were measured. As shown in figure 2, upon photoirradiation the absorption spectrum of **1** was steadily modulated, with the extinction coefficient corresponding to the π–π*

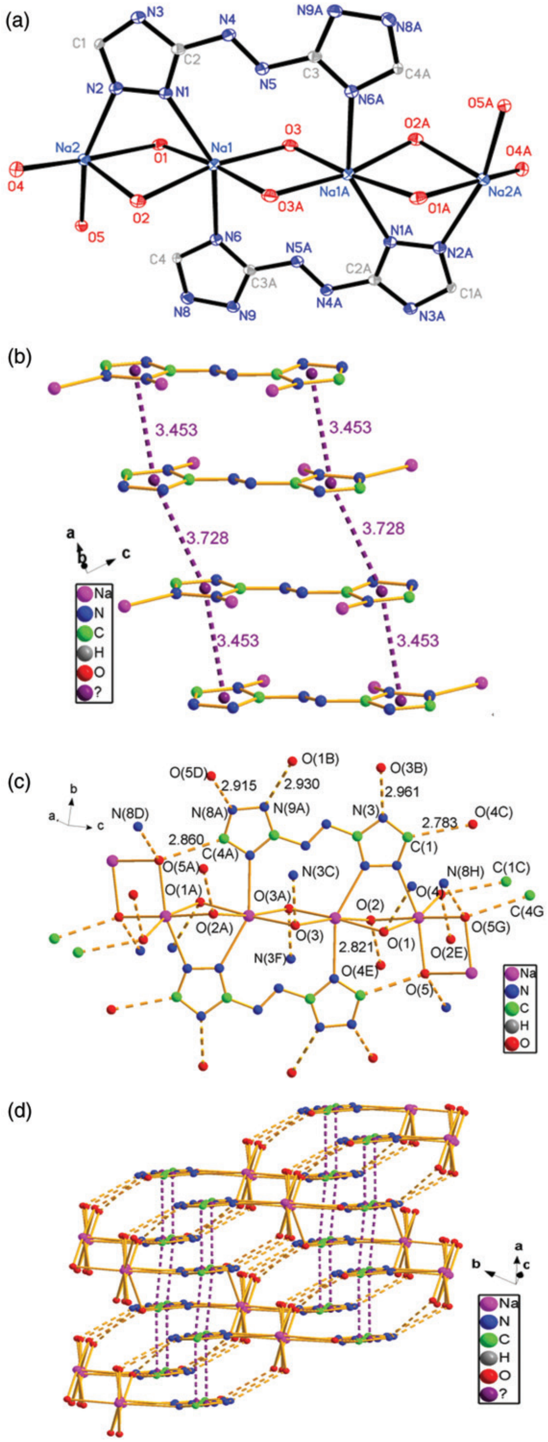

Figure 1. (a) View (30% thermal ellipsoids) of **1**; (b) face-to-face ABT^{2-} alignment showing the π–π stacking interaction in **1**; (c) the O–H···O, O–H···N and C–H···O hydrogen bonding interactions in **1**; (d) the 3-D supramolecular structure. Symmetry codes: $A = 1 - x, 1 - y, -z$; $B = -x, 2 - y, -z$; $C = -x, 2 - y, 1 - z$; $D = x, 1 + y, -1 + z$; $E = 1 - x, 1 - y, 1 - z$; $F = 1 + x, -1 + y, z$; $G = -x, 1 - y, 1 - z$; $H = -1 + x, 1 + y, z$.

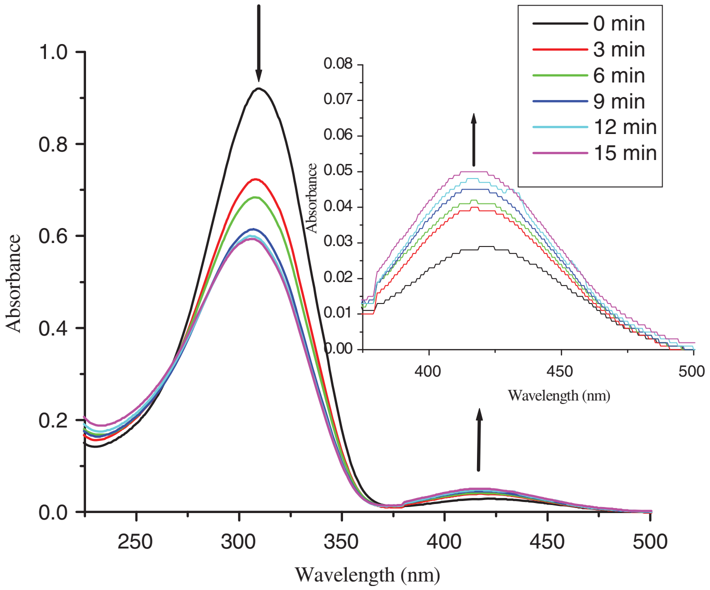

Figure 2. UV-Vis spectral change of **1** in aqueous solution ($6.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) upon irradiation at 312 nm at 3 min interval at room temperature.

electronic transition at 310 nm decreased, while that corresponding to the *n*–*π** electronic transition at 420 nm increased. The molar extinction coefficient corresponding to absorption at 310 nm decreases from $\epsilon = 1.5 \times 10^4\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ to $\epsilon = 9.9 \times 10^3\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ and that corresponding to absorption at 420 nm increases from $\epsilon = 4.8 \times 10^2\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ to $\epsilon = 8.3 \times 10^2\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$, suggesting that part of the *trans* isomer converted to the *cis* form in the solution [2, 3]. The observation of two isosbestic points at 270 and 375 nm in the spectra confirms the participation of the *cis* and *trans* isomers of $\mathrm{ABT^{2-}}$, as expected [22].

3.3. *Fluorescence of 1*

Figure 3 shows the emission spectrum of the crystal powder sample of **1** under 340 nm UV light excitation and the inset shows the excitation spectrum with the incident beam at 534 nm. Complex **1** exhibits a green fluorescence band at 534 nm, attributed to the *π**–*π* radiative relaxation from the excited state of $\mathrm{ABT^{2-}}$ [23]. Figure 4 shows green photoluminescent imaging of the solid sample of **1** taken by laser scanning confocal microscope under 408 nm laser excitation. Complex **1** displays a green confocal image that corresponds to the green emission at 505–580 nm. The green photoluminescence imaging by laser scanning confocal microscope is coincident with the solid photoluminescent behavior (F-4500 Fluorescence Spectrophotometer).

3.4. *Onion cell imaging*

The green photoluminescence of ABT fluorophore can be employed as imaging agent for onion cell. As shown in the "Supplementary material," under 408 nm laser excitation, the

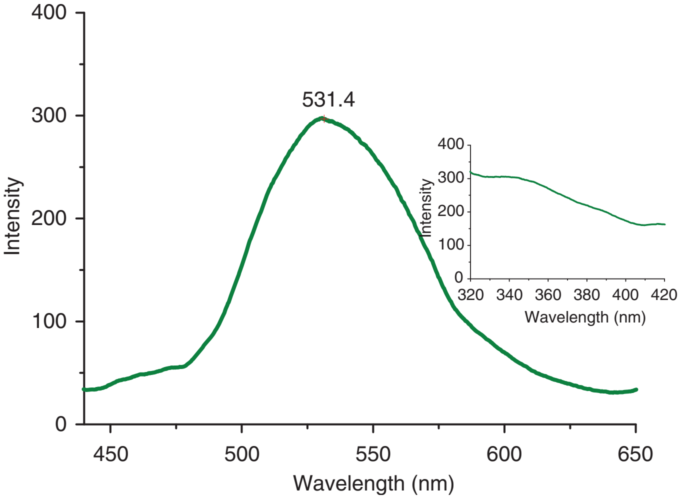

Figure 3. The emission spectrum of the crystal powder sample of **1** under 340 nm UV-light excitation. The inset shows the excitation spectrum with the monitored incident beam at 534 nm.

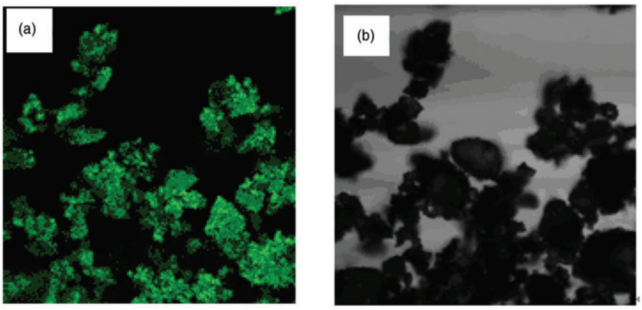

Figure 4. Confocal photoluminescence images of the solid sample of **1** under 408 nm laser excitation: (a) green image and (b) transparent image.

onion cell, which was dyed by the aqueous solution of **1** at 1×10^{-3} mol L^{-1}, shows green photoluminescent image. Clearly, the onion cell nucleus was dyed by fluorophore **1**. The green photoluminescence should be attributed to the π^*–π radiative relaxation from the excited state of ABT^{2-} in bioconjugates of the cell nucleus and **1**. The interactions of the onion cell nucleus with **1** may come from intermolecular noncovalent interactions, such as multiple hydrogen bonding interactions, because ABT^{2-} in **1** contains multiple electrostatic nitrogen atoms, which form hydrogen bonds with biological molecules.

4. Conclusions

In summary, crystal of **1**, which features a 1-D chain structure, was obtained. This work demonstrates that ABT^{2-} can be employed to assemble varied alkali or alkaline earth metals or even transition metal complexes. Aqueous solution of **1** shows photochromism and solid **1** emits green photoluminescence under UV light or laser excitation. The fluorophore **1** can be employed as labels for onion cell imaging.

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