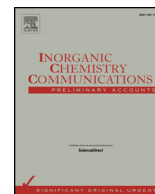




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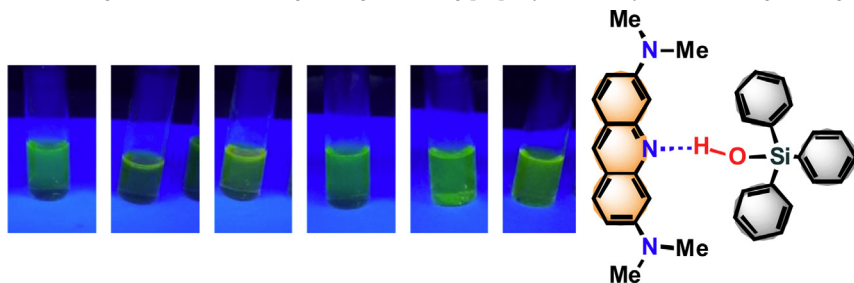
Short communication

First luminescent triphenyl silanol enabled by non-innocent acridine orange

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GRAPHICAL ABSTRACT

The first organosilanol with blue-green light emitting property enabled by acridine orange through weak interaction is reported.



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ABSTRACT

The isolation of photoluminescent triphenylsilanol induced by acridine orange is reported. The photophysical, and structural properties of triphenylsilanol-acridine orange salt are investigated. The reported silanol-amine salt is the first of its kind that portrays the blue-green emission. In solid-state, the triphenylsilanol molecule associates with acridine orange molecule through O–H...N hydrogen bond.

1. Introduction

Though the systematic studies on interaction between amine and organosilanol systems have been the subject of interest for more than 30 years [1–9] the structural interaction between organosilanol and biologically important dye such as acridine orange (3,6-bis(dimethylamino)acridine) (AO) is not known. Besides, the AO is known as cationic-basic fluorescent dye and used mainly as bio-marker in cell [10]. We assume that the interaction between organosilanol and acridine orange dye should reveal the challenges that are associated with understanding of degradation of organic dyes on Earth's crust as it is

composed of mainly silicates [5]. Thus silanol and organic dye can be considered as model system for investigating the interaction between organosilanol and organic dye such as AO. Besides, the organic-inorganic hybrid material derived from confinement of organosilanol and organic dye is limited [11–13]. Thus, in this paper we report the first structural evidence for organosilanol and AO.

2. Results and discussion

The 1:1 salt of triphenylsilanol and acridine orange (AO), Ph₃Si(OH):AO (1) was isolated in excellent yield from one-pot reaction

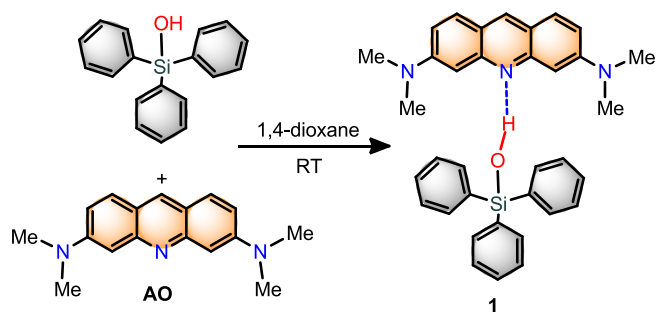
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Scheme 1. Synthesis of 1.

between triphenylsilanol and AO in 1,4-dioxane at RT (Scheme 1). 1 is soluble in polar and mid polar solvents such as DMSO, CHCl_3 , MeCN etc. The salt 1 was characterized by CHN analysis, FT-IR, ^1H NMR, ^{13}C NMR, UV-vis and fluorescence spectroscopy. The solid state structure of 1 was unambiguously determined by single crystal X-ray diffraction technique. Molecular structure of 1 is depicted in Fig. 1. The crystallographic data for 1 is provided in Table S1. The suitable single crystals of 1 for the X-ray analysis were obtained from the saturated solution of 1,4-dioxane. 1 crystallized in the monoclinic space group, $P2_1/n$. The asymmetric unit of 1 consists of AO and triphenylsilanol. The AO and triphenylsilanol molecules are orientated nearly in vertical position (119.26°). Though several hundred silanol-amine salts have been reported in the literature, silanol-acridine orange has never been isolated as of our knowledge. Molecule 1 is the first structurally characterized silanol-acridine orange salt.

1 depicts an unusual hydrogen bonding interactions that results in a strong interaction between triphenylsilanol and AO. The triphenylsilanol and AO are held together through $\text{N}\cdots\text{H}-\text{O}(\text{Si})$, $(\text{SiPh})\text{C}\cdots\text{H}-\text{C}(\text{PhSi})$ and $(\text{Si})\text{O}\cdots\text{H}-\text{C}(\text{PhSi})$ hydrogen bonds. The $\text{N}\cdots\text{H}-\text{O}(\text{Si})$ (bond distance of $\text{N}\cdots\text{H}$, 2.714 Å; bond angle of $\text{N}\cdots\text{H}-\text{O}(\text{Si})$, 166.06°) hydrogen bond is much stronger than $(\text{SiPh})\text{C}\cdots\text{H}-\text{C}(\text{PhSi})$ (bond distance of $\text{C}\cdots\text{H}$, 2.899 Å; bond angle of $\text{C}\cdots\text{H}-\text{C}$, 157.97°) and $(\text{Si})\text{O}\cdots\text{H}-\text{C}(\text{PhSi})$ (bond distance of $\text{O}\cdots\text{H}$, 3.355 Å; bond angle of $\text{O}\cdots\text{H}-\text{C}$, 131.65°) hydrogen bond. The $\text{N}\cdots\text{H}-\text{O}(\text{Si})$ (bond distance of $\text{N}\cdots\text{H}$, 2.714 Å; bond angle of $\text{N}\cdots\text{H}-\text{O}(\text{Si})$, 166.06°) hydrogen bond found in 1 is slightly shorter than that of triphenylsilanol-acridine salt ($\text{N}\cdots\text{H}$, 2.7631(14) Å and $\angle\text{N}\cdots\text{H}-\text{O}(\text{Si})$, $176(2)^\circ$) [11]. As shown in Fig. 1(II), AO are associated in double column fashion, which are separated by triphenylsilanol (See ESI, Fig. S4). Interestingly, the AO molecules are associated in a side-on fashion with same orientation (Fig. 2). The existence of $\text{N}\cdots\text{H}-\text{O}$ hydrogen bond in 1 is confirmed by corresponding FT-IR stretching frequency observed at 3397 cm^{-1} . In the ^1H NMR, the chemical shift value of $\text{Si}-\text{OH}$ proton in 1 appeared at δ 7.90.

The hydrogen bonding pattern of 1 is not comparable with that of triphenylsilanols and 1,4-diazabicyclo[2.2.2]octane or 1,2-bis(4-pyridyl)ethane [12]. The striking difference between acridine orange vs biphenyl and bypyridyl is that the absence of $\text{C}-\text{H}\cdots\pi$ interaction in 1. As a result the packing pattern of triphenylsilanols and AO is unique. Moreover, the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond strength in 1 is much stronger than that of triphenylsilanols and 1,4-diazabicyclo[2.2.2]octane or 1,2-bis(4-pyridyl)ethane. The $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond strength in 1 is slightly weaker than that of triphenylsilanols and 1,4-diazabicyclo[2.2.2]octane or 1,2-bis(4-pyridyl)ethane.

The UV-vis spectrum of 1 was measured in different solvents which is shown in Fig. 3. Acridine orange has an important property-molecular aggregation as a result of dipole-dipole interaction and hence its spectrum does not agree with Lambert-Beer's law [14–16]. In particular dimers show different photophysical and spectroscopic properties compared to the monomer. The photophysical and spectroscopic properties of a dye molecule in general depend upon the type of molecular aggregation [17,18]. The absorption spectrum of acridine

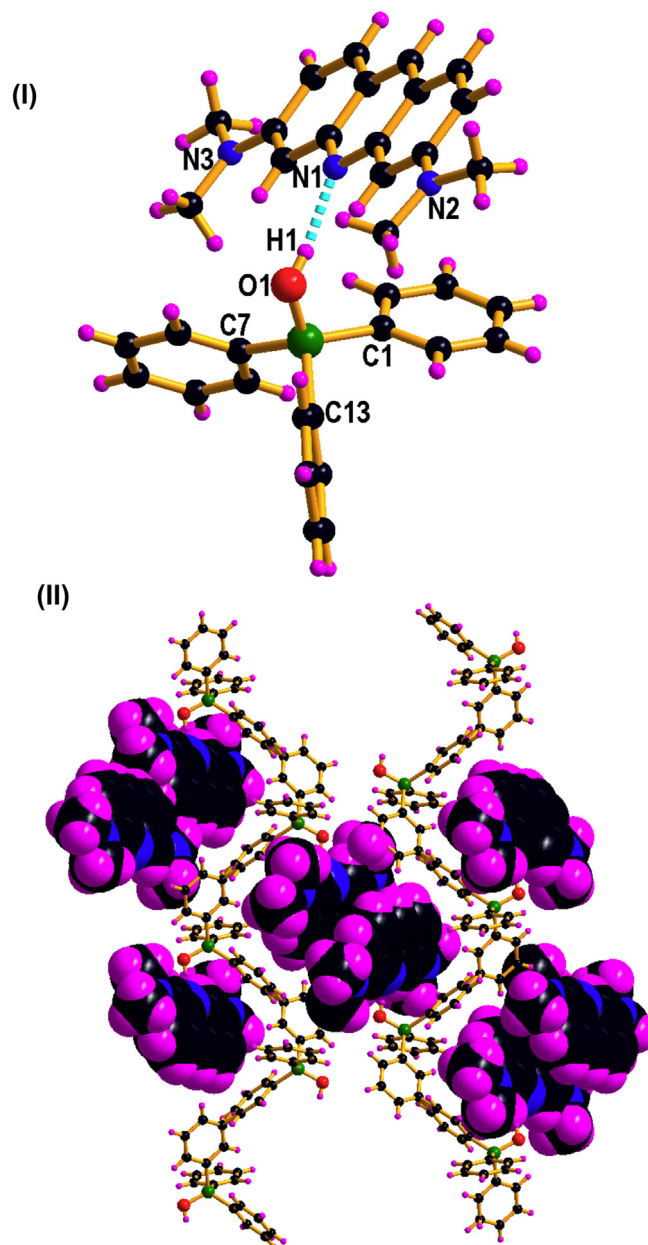


Fig. 1. (I) The solid state structure of 1. (II) The molecular packing in 1. The selected bond lengths [Å] and bond angles [$^\circ$]: C1–Si1 1.874(3), O1–Si1 1.618(19), Si1–C7 1.872(2), Si1–C13 1.875(3), O1–Si1–C1 112.91(10), C7–Si1–O1 110.05(12), C13–Si1–O1 107.45(11).

orange in water shows two bands at 468 and 490 nm, which can be attributed to the dimer $((\text{AOBH})_2^{2+})$ and monomer (AOBH^+) species respectively [19–21]. As shown in Fig. 3, 1 shows absorption maxima at 273, 310 and 429 nm in DMSO; 269, 291 and 490 nm in MeOH and 275, 294 and 495 nm in chloroform. The absorption maximum at ~ 490 nm in chloroform and methanol can be assigned to monomer (AOBH^+) species whereas a shoulder at ~ 460 nm can be assigned to the dimer $((\text{AOBH})_2^{2+})$, whereas no such peak is observed in DMSO. The peak observed at 429 nm in DMSO is due to the deprotonated form of acridine orange. These observations clearly indicate that in methanol and chloroform the formation of both the dimer $((\text{AOBH})_2^{2+})$ and monomer (AOBH^+) are favored. DMSO favors the deprotonated form.

The fluorescence emission of 1 was sensitive to solvent. Thus the emission spectra was measured in different solvents (Fig. 4). The solution of 1 fluoresce in methanol, chloroform and DMSO in UV light of

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