



# Synthesis, photophysical and electrochemical properties of symmetric silicon-linked coumarin-oxadiazole derivatives



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## ABSTRACT

A novel, silicon-linked, symmetric, V-shaped, coumarin derivative (**1**) with an electron-deficient 1,3,4-oxadiazoles unit and a phenyl moiety was synthesized and characterized. An efficient multifunctional organic light-emitting diode material was obtained through the use of optical, electrochemical, thermal, and theoretical investigations. We show that the Si atom induces a V-shaped structure that weakens  $\pi$ - $\pi$  stacking and thus limits aggregation-induced quenching. As expected, a gradual transition from a locally excited state to an intramolecular charge-transfer state is observed with increasing solvent polarity. This new type of compound exhibits tunable light emission in solution making it a versatile emitter.

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## 1. Introduction

Luminescent organic materials have been widely used as active elements in optoelectronic devices, chemosensors, bioprobes, and organic light-emitting diodes.<sup>1–6</sup> Most of these fluorescent organic molecules, however, exhibit planar and well-conjugated structures with reasonable emission in dilute solutions and weak or nonexistent emission in the solid state owing to aggregation-caused quenching.<sup>7–10</sup> Recently, research has focused on reducing aggregation-induced quenching in the solid state to produce organic molecules capable of forming highly luminescent films. Multiple groups have independently reported an interesting phenomenon where in aggregated molecules are able to fluoresce more intensely than their dilute solutions. This observation has been explained in terms of the unique phenomenon of aggregation-induced emission (AIE).<sup>11,12</sup> Propeller-shaped molecules such as tetraphenylethene, hexaphenylsilole, and quinoline-malononitrile as well as their derivatives, are known for their unique ability to promote AIE.<sup>13–25</sup> Recently, a new V-shaped compound has displayed tunable light emission in solution and the solid state.<sup>26,27</sup> Additionally, the integration of intramolecular charge transfer (ICT) and AIE into one compound has led to a new phenomenon:

strong fluorescence not only in dilute solutions but also in the solid state or aggregated forms. For instance, Zhu and co-workers reported a new donor–acceptor system, tetraphenylethene–naphthalimide, which displayed dual photoluminescence activity from both ICT and AIE.<sup>5</sup> However, the integration of ICT and AIE into one molecule is still rare and not well understood and thus warrants further study to understand the relationship between molecular structure and optical properties. In particular, investigations about how molecular geometry and intermolecular distances affect fluorescence are rare. This gap in the literature along with the above-discussed recent advances inspired us to develop a new V-shaped fluorescent molecule with tunable light emission both in solution and in the solid state.

In recent years, organosilicon compounds have become the focus of several research efforts after recent reports indicate that organosilicon compounds, especially siloles, have excellent emission properties.<sup>28</sup> Si-based tetrahedral organic molecules and polymers have been intensively investigated as electroluminescent materials. For example, Liu and co-workers recently reported a series of tetrahedral luminescent materials comprising SiAr<sub>4</sub> cores.<sup>29,30</sup> They found that their fluorene derivatives were efficient blue light-emitting materials and that Si-centered materials were with good film-forming ability and quantum efficiency. One noteworthy feature of Si-centered tetrahedral materials is their high PL efficiency (nearly 100%).<sup>30</sup> We have recently reported a series of tetrahedral luminescent materials

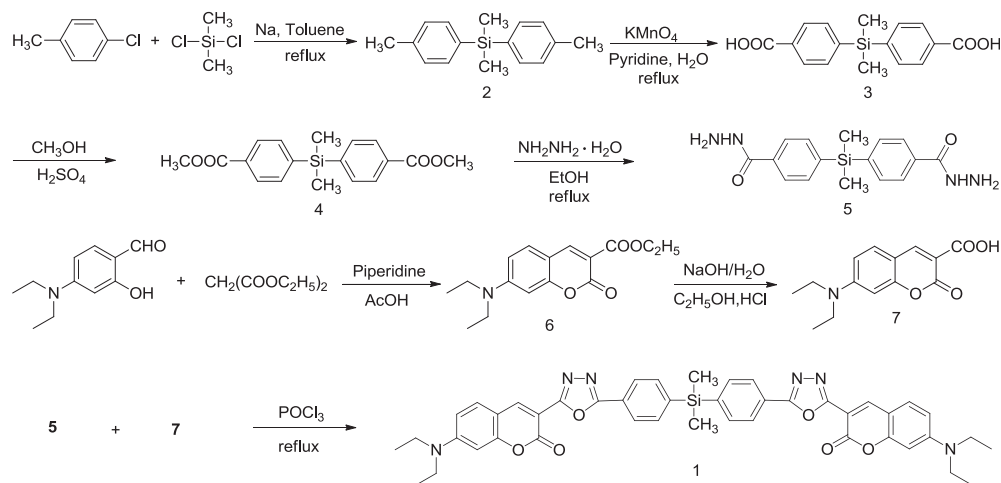
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comprising  $\text{SiAr}_2\text{Me}_2$  cores where the Si atom possesses a special V-shaped structure that exhibits tunable light emission in solution and in a solid-state thin film.<sup>27</sup> In a continuation on our research on V-shaped luminescent materials, herein we report the development of a novel V-shaped fluorescent molecule containing coumarin-1,3,4-oxadiazole and a Si core atom. We chose coumarin as a building unit because of its well-established good luminescent properties as well as its wide application in chemosensors, light-harvesting molecular arrays, photovoltaics, and particularly in organic light-emitting diodes.<sup>31–34</sup> Coumarin moieties' strong tendency to  $\pi$ – $\pi$  stack, however, generally leads coumarin-containing emitters to exhibit strong intermolecular interactions in the solid state, which causes aggregation-induced quenching. We found that our new V-shaped coumarin-1,3,4-oxadiazole derivative, however, does not suffer from this quenching mechanism as it exhibits strong and tunable light emission in solution and in the solid state.

## 2. Results and discussion

### 2.1. Synthesis and characterization

The synthetic procedure for target compound **1** is summarized in Scheme 1, and the detailed procedures are given in the experimental section. An important intermediate, silylbenzohydrazide moiety (**5**), was prepared quantitatively by the reaction of **4** with excess amounts of hydrazine monohydrate under reflux conditions. Finally the reaction of **5** and coumarin acid (**7**) in phosphoryl chloride as the refluxing solvent eventually produced compound **1**. The structure of **1** was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, mass spectra, and elemental analysis (see the Supplementary data).



Scheme 1. Synthetic routes to the target compound **1**.

Colorless crystals suitable for an X-ray diffraction study of the key precursor **5** was obtained by slowly evaporating  $\text{CH}_2\text{Cl}_2$ /hexane solutions of **5** at room temperature. Its crystal structures were determined by X-ray crystallography at room temperature revealing that compound **5** crystallizes in the monoclinic system with a space group of  $P2_1/n$  (Table S1). As shown in Fig. 1. In the crystal structure of compound **5**, the two phenyl moieties are both nearly planar and form a dihedral angle of  $89.97 (\pm 1)$ . Additionally, the molecule is composed of a V-shaped building unit separated by a silicon atom.

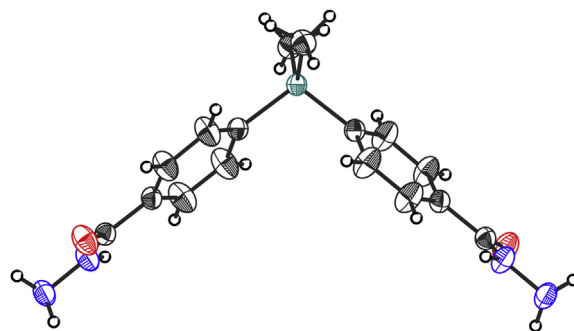


Fig. 1. Crystal structures of the key precursors **5**. Thermal ellipsoids are drawn at the 30% level.

Crystallographic data for the structure of **5** has been deposited with the Cambridge Crystallographic Data Centre as supplemental publications CCDC 1489385.

### 2.2. Photophysical and electrochemical properties

The ultraviolet–visible absorption and photoluminescence spectra of **1** in  $\text{CHCl}_3$  are displayed in Fig. 2. The three major absorption peaks located at 247, 284 and 432 nm originate from the  $\pi$ – $\pi^*$  absorption of the conjugated coumarin-phenyl 1,3,4-oxadiazole moiety. The shoulder peak at 448 nm can be attributed to the ICT transition character from the diethylamino to the 1,3,4-oxadiazole. The ICT transition was further confirmed by fluorescence spectra in solvents of varying polarity with the same concentration. These results are shown in Fig. 3. The emission peaks ( $\lambda_{\text{em}}$ ) are generally red shifted from  $\lambda=469$  nm in toluene to  $\lambda=496$  nm in DMSO. The bathochromic shift,

combined with the decreased quantum yield (QY), can be ascribed to stabilization of the excited state. This behavior originates from the ICT effect.<sup>26</sup> From the absorption edge of the ultraviolet–visible spectrum, the optical band gap (e.g.,) of **1** is estimated to be 3.47 eV. **1** exhibits broad and structureless emission bands with peaks at 474 nm in  $\text{CHCl}_3$ . The emission spectra, however, were different between the solution and film samples with regard to the broad emission peaks and red-shift shown in Fig. 2. The fluorescence QY of **1** measured at room temperature in dilute  $\text{CHCl}_3$  was moderate compared with the

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