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Extensive spectral tuning of the proton transfer emission from green to red *via* a rational derivatization of salicylideneaniline

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Abstract

A series of salicylideneaniline derivatives **1a–1f** were synthesized under mild condition in high yields, and characterized by ^{1}H NMR, HRMS, UV–vis and emission spectra. In solid and aprotic solvents **1a–1f** exist mainly as *E* conformers that possess a six-membered-ring hydrogen bond and undergo excited-state intramolecular proton transfer (ESIPT) reactions, resulting in a proton-transfer tautomer emission. Depending on the electronic donor or acceptor strength of the substituent in either the HOMO or LUMO site, a broad tuning range of the emission from green (**1c**) to red (**1a**) has been achieved.

Keywords: ESIPT; Schiff bases; Salicylideneaniline derivatives; DFT calculations

Schiff bases are aldehyde- or ketone-like compounds in which the carbonyl group is replaced by an imine or azomethine group [1–6]. They are widely used as pigments and dyes [7–11], catalysts [12–14], liquid crystals [15–17], intermediates in organic synthesis [18–22] and also exhibit a broad range of biological activities [23,24]. For example, salicylideneaniline (**1d**, Scheme 1) derivatives are effective against *Mycobacterium tuberculosis* H37Rv, exhibiting an MIC value of 8 μg/mL [25]. On the other hand, the excited-state intramolecular proton transfer (ESIPT) reaction of salicylideneaniline derivatives has been investigated for past years [26,27], which incorporates transfer of a hydroxy proton to the imine nitrogen through an intramolecular six-membered-ring hydrogen-bonding system. The resulting proton-transfer tautomer possesses significant differences in structure and electronic configuration from its corresponding normal species. Accordingly, a large Stokes shifted $S_1' \rightarrow S_0'$ fluorescence (the prime sign denotes the proton-transfer tautomer) was observed. This unusual photophysical property has found many important applications. Prototypical examples are probes for solvation dynamics [28,29] and biological environments [30,31], fluorescence microscopy imaging [32], near-infrared fluorescent dyes [33], photochromic materials [34], chemosensors [35–37] and recent application in the field of organic light emitting diodes [38]. We now report the synthesis, characterization, spectroscopic properties and complementary density functional theory (DFT) calculations of X-salicylidene-Y-aniline compounds (**1a–1c**) with X = NO_2 as an electron acceptor substituent and Y = OMe as an electron donor substituent.

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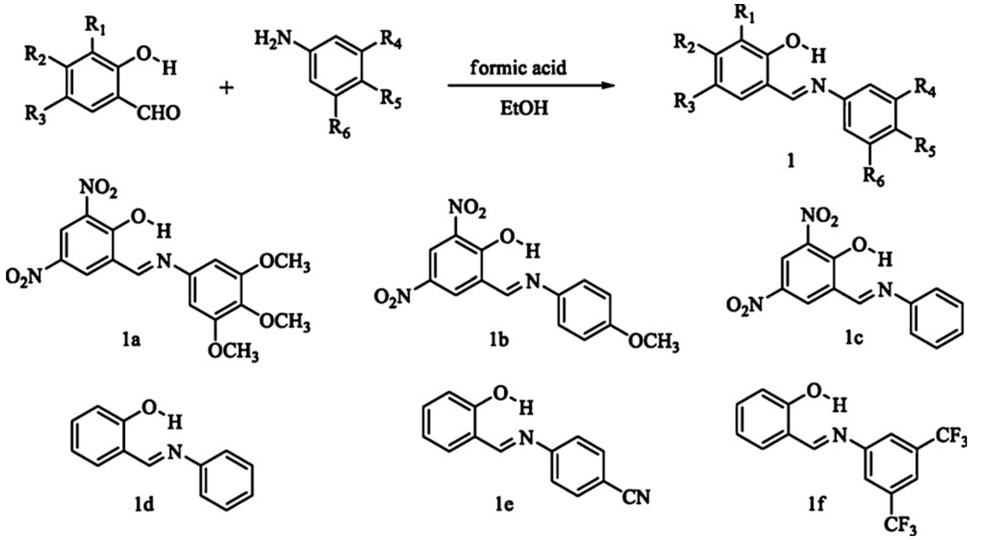

Scheme 1. The synthetic route of **1** and the structures of **1a–1f**.

1. Results and discussion

Scheme 1 shows the synthetic route of **1** and the structures of the salicylideneaniline derivatives **1a–1f**. These Schiff bases were prepared through condensation reactions between substituted salicylic aldehydes and substituted anilines. The structures of the products were characterized by ^{1}H NMR spectroscopy and high resolution mass spectrometry (HRMS) [39]. In the ^{1}H NMR studies, the existence of a strong intramolecular hydrogen bond between O–H and N is evidenced by the observation of a large downfield shift of the proton peak at $\delta > 12$ ppm for all compounds **1a–1f**, the values of which are in the order **1a** (17.19 ppm) > **1b** (17.10 ppm) > **1c** (16.93 ppm) > **1d** (13.26 ppm) > **1e** (12.60 ppm) > **1f** (12.44 ppm) in dry $CDCl_3$. The dominance of a *E* isomer for **1a–1f** is strongly supported by DFT geometry optimization (Fig. 1). These results are consistent with those of previous studies on other salicylideneaniline derivatives [40,41].

Fig. 2 shows the absorption and emission spectra of **1a–1e** in chloroform. For clarity, the absorption and emission spectra of **1f** are omitted in Fig. 2 because the difference between **1e** and **1f** is small. The absorption spectra of **1a–1f**

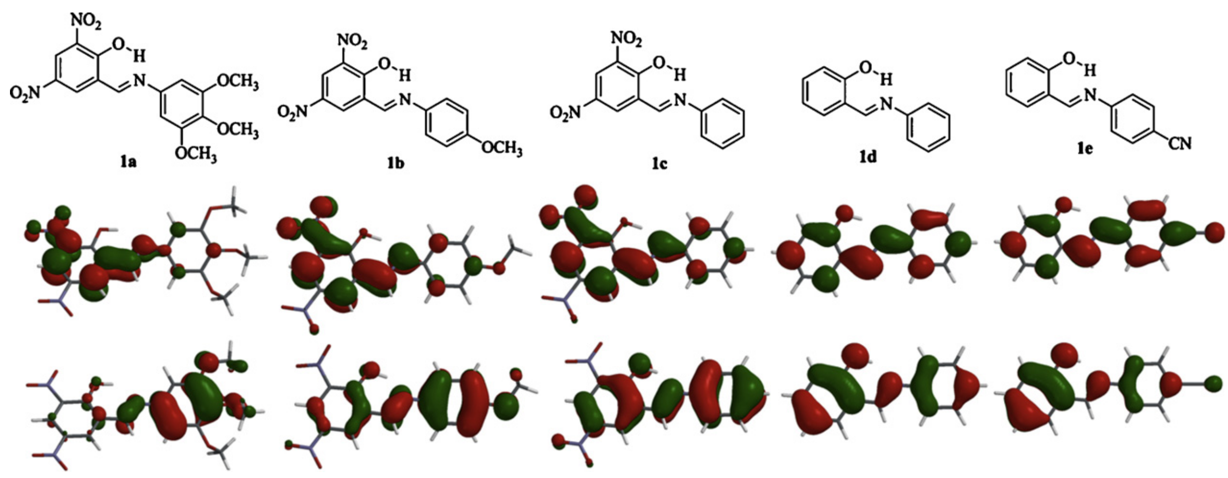

Fig. 1. DFT (B3LYP/6-31G**) geometry-optimized structures and computed frontier orbitals of **1a–1e**. The upper graphs are the LUMOs and the lower ones are the HOMOs.