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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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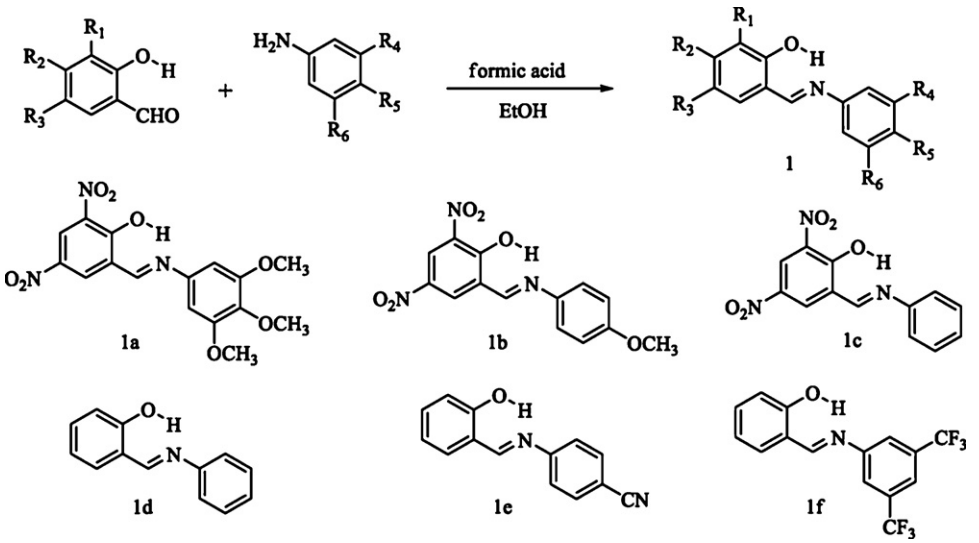

Scheme 1. The synthetic route of **1** and the structures of **1a**–**1f**.

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**

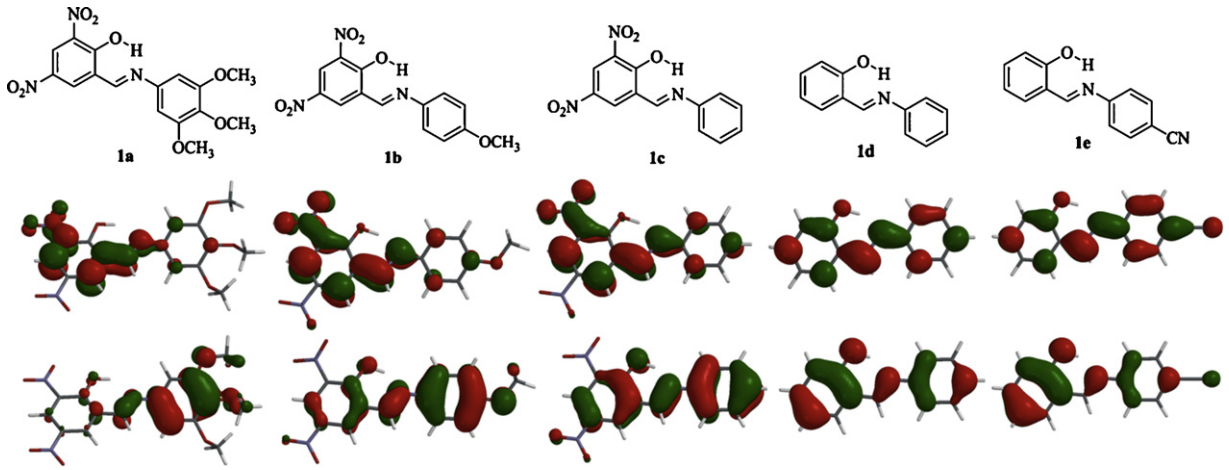

Fig. 1. DFT (B3LYP/6-31G**) geometry-optimized structures and computed frontier orbitals of **1a**–**1e**. The upper graphs are the LUMOs and the lower ones are the HOMOs.

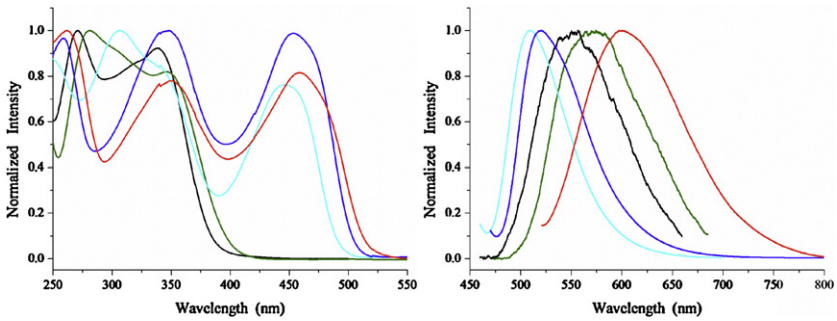

Fig. 2. Normalized absorption (left) and emission (right) spectra of **1a** (red line), **1b** (blue line), **1c** (cyan line), **1d** (black line) and **1e** (green line) in chloroform solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 1
Calculated (DFT/B3LYP) parameters for salicylideneaniline derivatives **1a**–**1f**.

Compounds	HOMO (eV)	LUMO (eV)	E_g (eV)	Compounds	HOMO (eV)	LUMO (eV)	E_g (eV)
1a	−5.88	−2.25	3.63	**1d**	−6.06	−2.11	3.95
1b	−6.49	−2.51	3.98	**1e**	−6.15	−2.44	3.71
1c	−6.87	−2.80	4.07	**1f**	−6.19	−2.37	3.82

are dominated by characteristic π–π* transitions at ∼350 nm (normal form). In addition to the higher energy absorption at 350 nm, compounds **1a**–**1c** exhibit a lower energy electronic transition at ∼460 nm (tautomer form). The enol-imine (normal form) ↔ keto-amine (tautomer form) tautomeric equilibrium in the ground electronic state of salicylideneaniline derivatives has also been reported recently [42]. As for the steady-state emission, the emission peak greatly shifts from 510 nm in **1c** to 615 nm in **1a** in chloroform. The occurrence of ESIPT in **1d**–**1f** is supported by the anomalously large Stokes shifted emission with respect to the absorption peak wavelength. The tendency of the spectral shift can be explained by the fact that the addition of electron-withdrawing groups (–NO_2) at the phenol ring (**1b** and **1c**) decreases the HOMO energy level and hence increases the keto-tautomer energy gap, while the addition of an electron-withdrawing group (–CN or –CF_3) at the benzene ring (**1e** or **1f**) decreases the LUMO energy level and hence decreases the energy gap. Note that the substitution of three of the hydrogen atoms in **1c** by three methoxy groups at the benzene ring, forming **1a**, increases the electron density on the benzene ring, so the HOMO (LUMO) energy level of **1a** is delocalized mainly on the benzene (salicylidene) moiety (Fig. 1). As a result, **1a** has a higher HOMO and a lower LUMO and hence a smaller energy gap relative to **1d** (Table 1).

2. Conclusion

A series of salicylideneaniline derivatives **1a**–**1f** have been synthesized and characterized by ^{1}H NMR, HRMS, UV–vis and emission spectra. *Via* a systematic derivatization of the excited-state intramolecular proton-transfer system, salicylideneaniline, the proton-transfer emission can be extensively tuned from green (**1c**) to red (**1a**), generating a new family of proton transfer fluorescent dyes.

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References

[1] S.T. Ha, T.L. Lee, G.Y. Yeap, et al. Chin. Chem. Lett. 22 (2011) 260.
[2] F. Deng, W. He, A.S. Luyt, et al. Chin. Chem. Lett. 22 (2011) 109.
[3] L.C. Wu, L.Q. Liu, H.S. Jin, et al. Chin. Chem. Lett. 21 (2010) 1263.
[4] S.H. Kim, I.J. Hwang, S.Y. Gwon, et al. Dyes Pigments 88 (2011) 84.

[5] V.Z. Shirinian, A.A. Shimkin, A.K. Mailian, et al. Dyes Pigments 84 (2010) 19.
[6] T. Aysha, S. Luňák, A. Lyčka, et al. Dyes Pigments 91 (2011) 170.
[7] G.K. Karaoğlan, G. Gümrükçü, A. Koca, et al. Dyes Pigments 88 (2011) 247.
[8] İ. Değirmencioğlu, E. Atalay, M. Er, et al. Dyes Pigments 84 (2010) 69.
[9] V. Arun, S. Mathew, P.P. Robinson, et al. Dyes Pigments 87 (2010) 149.
[10] Y.F. Sun, S.H. Xu, R.T. Wu, et al. Dyes Pigments 87 (2010) 109.
[11] G.K. Karaoğlan, G. Gümrükçü, A. Koca, et al. Dyes Pigments 90 (2011) 11.
[12] L. Yin, X. Jia, X.S. Li, et al. Chin. Chem. Lett. 21 (2010) 774.
[13] S.M. Seyedi, R. Sandaroos, G.H. Zohuri, Chin. Chem. Lett. 21 (2010) 1303.
[14] Y.L. Yang, N.N. Wan, W.P. Wang, et al. Chin. Chem. Lett. 22 (2011) 1071.
[15] S.T. Ha, L.K. Ong, S.L. Lee, et al. Chin. Chem. Lett. 21 (2010) 637.
[16] X.D. Li, M.S. Zhan, K. Wang, Chin. Chem. Lett. 22 (2011) 1111.
[17] S.T. Ha, K.L. Foo, R.T. Subramaniam, et al. Chin. Chem. Lett. 22 (2011) 1191.
[18] H. Naeimi, K. Rabiei, Chin. Chem. Lett. 22 (2011) 1273.
[19] S. Malek-Ahmadi, A. Abdolmaleki, Chin. Chem. Lett. 22 (2011) 439.
[20] A. Benvidi, M.T. Ghanbarzadeh, M. Mazloum-Ardakani, Chin. Chem. Lett. 22 (2011) 1087.
[21] S.L. Yu, Y.Y. Li, Z.R. Dong, et al. Chin. Chem. Lett. 22 (2011) 1269.
[22] P.J. Chai, Y.S. Li, C.X. Tan, Chin. Chem. Lett. 22 (2011) 1403.
[23] Y.L.N. Murthy, N. Karthikeyan, G. Boddeti, et al. Chin. Chem. Lett. 22 (2011) 567.
[24] T.N. Akhaja, J.P. Raval, Chin. Chem. Lett. 23 (2012) 446.
[25] A.O. de Souza, F.C.S. Galetti, C.L. Silva, et al. Quim. Nova 30 (2007) 1563.
[26] X.L. Zhong, F. Gao, Q. Wang, et al. Chin. Chem. Lett. 21 (2010) 1195.
[27] L. Xie, Y. Chen, W. Wu, et al. Dyes Pigments 92 (2012) 1361.
[28] W.H. Chen, Y. Pang, Tetrahedron Lett. 51 (2010) 1914.
[29] G.O.W. Lins, L.F. Campo, F.S. Rodembusch, et al. Dyes Pigments 84 (2010) 114.
[30] C.K. Lim, J. Seo, S. Kim, et al. Dyes Pigments 90 (2011) 284.
[31] C.M. Maupin, N. Castillo, S. Taraphder, et al. J. Am. Chem. Soc. 133 (2011) 6223.
[32] R.C. Santos, N.V. Silva Faleiro, L.F. Campo, et al. Tetrahedron Lett. 52 (2011) 3048.
[33] S. Ikeda, M. Toganoh, S. Easwaramoorthi, et al. J. Org. Chem. 75 (2010) 8637.
[34] Y. Ito, K. Amimoto, T. Kawato, Dyes Pigments 89 (2011) 319.
[35] Y.J. Zhang, X.P. He, M. Hu, et al. Dyes Pigments 88 (2011) 391.
[36] T. Li, Z. Yang, Y. Li, et al. Dyes Pigments 88 (2011) 103.
[37] W.H. Hong, C.C. Lin, T.S. Hsieh, et al. Dyes Pigments 94 (2012) 371.
[38] K.C. Tang, M.J. Chang, T.Y. Lin, et al. J. Am. Chem. Soc. 133 (2011) 17738.
[39] The general procedure for the synthesis of Schiff bases (**1a**–**1f**): To a stirred mixture of substituted 2-hydroxybenzaldehyde (4.7 mmol) and molecular sieves 4 Å (0.5 g) in ethanol (25 mL) was added substituted aniline (5.4 mmol) and formic acid (0.1 mL) at room temperature. The mixture was refluxed for 12 h. After cooling, the mixture was poured into the cold water and extracted with CH_2Cl_2 and dried with anhydrous $MgSO_4$. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent CH_2Cl_2 to afford the title compounds (**1a**–**1f**) in 90% yield. Characterization data: **1a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 17.19 (br, 1H), 9.04 (d, 1H, J = 3.0 Hz), 8.72 (s, 1H), 8.60 (d, 1H, J = 3.0 Hz), 6.70 (s, 2H), 3.94 (s, 9H); MS (FAB) m/z (relative intensity) 378 ($M+H^+$, 100); HRMS calcd. for $C_{16}H_{16}N_3O_8$ 378.0937, found 378.0932. Selected data for **1b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 17.10 (br, 1H), 9.02 (d, 1H, J = 2.0 Hz), 8.67 (d, 1H, J = 2.0 Hz), 8.55 (s, 1H), 7.46 (d, 2H, J = 9.0 Hz), 7.07 (d, 2H, J = 9.0 Hz), 3.90 (s, 3H); MS (FAB) m/z (relative intensity) 318 ($M+H^+$, 100); HRMS calcd. for $C_{14}H_{12}N_3O_6$ 318.0726, found 318.0728. Selected data for **1c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.93 (br, 1H), 9.04 (d, 1H, J = 2.0 Hz), 8.78 (d, 1H, J = 2.0 Hz), 8.59 (s, 1H), 7.58–7.46 (m, 5H); MS (FAB): m/z (relative intensity) 288 ($M+H^+$, 100); HRMS calcd. for $C_{13}H_{10}N_3O_5$ 288.0620, found 288.0624. Selected data for **1d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.26 (br, 1H), 8.62 (s, 1H), 7.36–7.44 (m, 4H), 7.30–7.25 (m, 3H), 7.04 (d, 1H, J = 8.5 Hz), 6.96 (t, 1H, J = 7.5 Hz); MS (FAB) m/z (relative intensity) 198 ($M+H^+$, 100); HRMS calcd. for $C_{13}H_{12}NO$ 198.0919, found 198.0916. Selected data for **1e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.60 (br, 1H), 8.59 (s, 1H), 7.71 (d, 2H, J = 8.0 Hz), 7.44 (m, 2H), 7.33 (d, 2H, J = 8.0 Hz), 7.03 (d, 1H, J = 8.5 Hz), 6.98 (t, 1H, J = 8.0 Hz); MS (FAB) m/z (relative intensity) 223 ($M+H^+$, 100); HRMS calcd. for $C_{14}H_{11}N_2O$ 223.0871, found 223.0875. Selected data for **1f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.44 (br, 1H), 8.67 (s, 1H), 7.80 (s, 1H), 7.70 (s, 2H), 7.45–7.48 (m, 2H), 7.08 (d, 1H, J = 8.5 Hz), 7.02 (t, 1H, J = 7.5 Hz); MS (FAB) m/z (relative intensity) 334 ($M+H^+$, 100); HRMS calcd. for $C_{15}H_{10}F_6NO$ 334.0667, found 334.0664.
[40] M.J. Chang, T.C. Fang, H.Y. Tsai, et al. Acta Crystallogr. E68 (2012) o904.
[41] L. Zhao, S.W. Ng, Acta Crystallogr. E66 (2010) o2474.
[42] V. Vargas, L. Amigo, J. Chem. Soc. Perkin Trans. 2 (2001) 1124.