Asian Journal of Chemistry; Vol. 35, No. 9 (2023), 2143-2147

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2023.28092

Synthesis, Characterization, Photoluminescence Emission and Antibacterial Properties of Some Schiff Base Derivatives of Substituted Salicylaldehyde

V.B. Nagaveni[1], G.L. Aruna[2,*] and K.M. Mahadevan[3]

[1]Department of Chemistry, Government Science College, Chitradurga-577501, India
[2]Post-Graduate Department of Microbiology, Maharani's Science College for Women, Mysore-570005, India
[3]Department of Chemistry, Kuvempu University, P.G. Centre, Kadur-577548, India

*Corresponding author: E-mail: microarunagl@gmail.com

Received: 4 June 2023; *Accepted*: 11 July 2023; *Published online*: 31 August 2023; AJC-21355

Schiff bases such as 4-{[(2-hydroxyphenyl)methylidene]amino}benzoic acid (**SB1-SB3**) have been synthesized by the condensation of mole equivalent of 4-amino benzoic acid and various substituted salicylaldehyde. The synthesized compounds **SB1-SB3** were analyzed by FT-IR, ^{1}H NMR and mass spectroscopy techniques. Light emitting properties of the compounds have been studied by photoluminescence (PL) and diffuse reflectance (DR) spectra. Photoluminescence spectra of the compounds **SB1-SB3** revealed that these molecules emit light from bright yellow to orange red colour following exposure to UV light. From diffuse reflectance spectra, the measured optical band energy for Schiff base compounds **SB1-SB3** was found to be 2.14, 2.06 and 2.26 eV, respectively. This study revealed that the Schiff base derivatives of substituted salicylaldehyde become promising material for light emitting devices. The antibacterial activity of Schiff base compounds were screened by using Kirby-Bauer diffusion method. The results revealed that the all the synthesized compounds exhibit potent antimicrobial activity.

Keywords: 4-Aminobenzoic acid, Schiff base, Photoluminescence, Light emission, Kirby-Bauer diffusion method.

INTRODUCTION

The class of organic compounds known as Schiff bases are significant and found to have applications in the field of biology, medicine and industrial colours [1-3]. Its application in display devices is expanded by the fact that the π-system in a Schiff base frequently imposes a geometrical architecture and influences the electronic structure [4,5]. Due to the excellent stability of the corresponding coordination compounds and their superior solubility in common organic solvents as well as the thermal stability and breakdown process of Schiff bases and their metal complexes containing substituted salicylaldehyde derivatives have all received attention [6,7].

The Schiff base ligands are frequently employed in organic light emitting diodes (OLEDs) because of their superior photoluminescent qualities and great stability [8]. The structure of the salicylaldehyde Schiff base ligand is relatively similar to 8-hydroxyl quinoline ligand, where the latter has a delocalized-conjugated system, a coordination nitrogen atom and at least one hydroxyl group. According to numerous sources, salicylaldehyde Schiff base metal complexes were found to have good luminous properties [9,10].

The *bis*(salicylidene)propylene-1,3-diaminatozinc complex had good thermal stability and a high glass transition temperature appropriate for OLEDs. This compound generates a blue-green emission when exposed to UV light [11]. Because of their adaptability and structural variety, a great deal has been investigated about the behaviour of Schiff base compounds. Schiff bases are generally bi-, tri- or tetra-dentate chelate ligands and form relatively stable complexes with metal ions [12]. There are several papers, which concentrate mainly on the OLED application and photophysical characteristics of the Schiff base ligand containing metal complexes [13-16]. Due to the presence of two functional groups, 4-aminobenzoic acid have coordination chemistry similar to other well-known ligands as well as much easier synthesis and rich photophysical properties. In this work, few Schiff base derivatives of 4-aminobenzoic acid analogue were synthesized from substituted salicylaldehyde and 4-aminobenzoic acid and explore their photoluminescent properties. The synthesized compounds were also characterized by FT-IR, ^{1}H NMR and Mass spectral analysis.

EXPERIMENTAL

For the synthesis of Schiff bases **SB1-SB3**, chemicals and reagents were purchased from Sigma-Aldrich, USA. Analytical reagent grade solvents were used without any purification. By using electrothermal equipment in open capillaries melting points of the synthesized compounds were determined and are uncorrected. The FT-IR spectra were recorded by Agilent FT-IR and Bruker FT-IR spectrometers using a scan technique in the range 4000-500 cm^{-1}. The ^{1}H NMR (400 MHz) spectra of the synthesized Schiff base compounds were captured in DMSO-d_6 with TMS acting as an internal standard. A Jobin Yvon Spectro-flourimeter Fluorolog-3 was used to measure the photoluminescence (PL) using a 450W Xenon lamp as excitation source.

Synthesis of 4-{(5-bromo-2-hydroxyphenyl)methylidene]-amino}benzoic acid (SB1): A catalytic amount of acetic acid was added to a mixture of 5-bromosalicylaldehyde (**1a**) (0.537 g, 0.01 mol) and 4-aminobenzoic acid (**2**) (0.50 g, 0.01 mol) in 25 mL ethanol and the reaction mixture was agitated continuously for 20 min at room temperature. Using TLC (PE/ethyl acetate, 9:1 v/v), the reaction development was carefully observed. Once the reaction was completed, the obtained solid product was filtered, washed and recrystallized from hot ethanol. Yellow coloured solid; yield: 82%; m.p.: 240-242 ºC; m.f.: $C_{14}H_{10}BrNO_3$; IR (KBr, ν_{max}, cm^{-1}): 3648.32 (phenolic-OH), 2819.11 (Ar-C-H), 2550.68 (AcOH), 1678.16 (C=O), 1276.06 (C-N), 691.32 (C-Br). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 6.95 (d, *J* = 9.20 Hz, 1H), 7.45 (d, *J* = 8.00 Hz, 2H), 7.55-7.58 (m, 1H), 7.89 (d, *J* = 2.40 Hz, 1H), 8.00 (d, *J* = 8.00 Hz, 2H), 8.93 (s, 1H), 12.58 (s, 1H), 12.92 (s, 1H); MS: *m/z* = 320.90 (M+1).

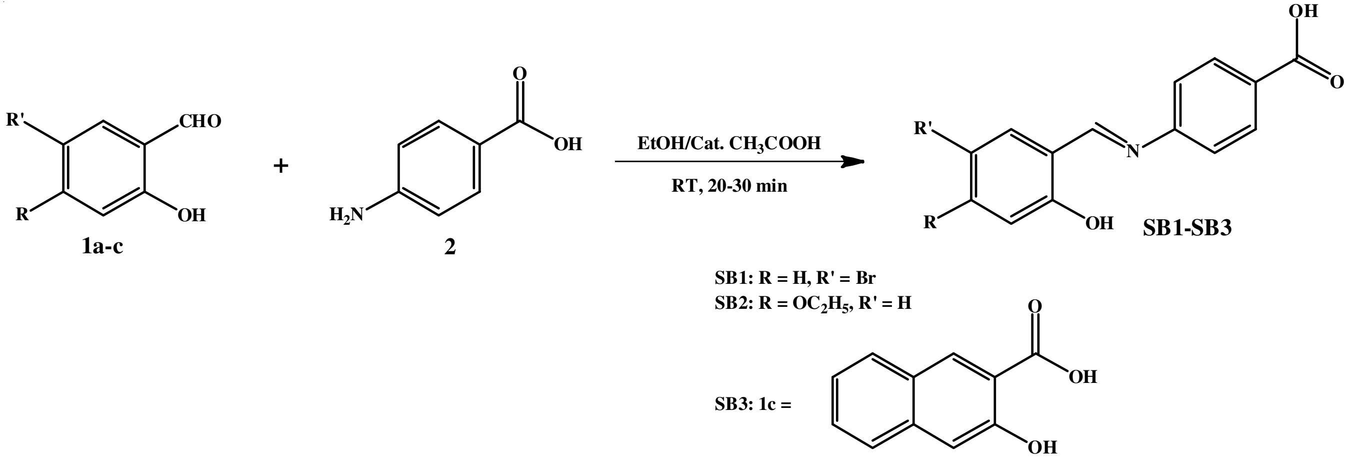
Synthesis of 4-(4-ethoxy-2-hydroxyphenyl)methylidene]-amino}benzoicacid (SB2): In 25 mL of ethanol, a mixture of 3-ethoxy salicylaldehyde (**1b**) (0.45 g, 0.01 mol) and 4-aminobenzoic acid (**2**) (0.50 g, 0.01 mol) was refluxed for 25 min at room temperature in the presence of a tiny quantity of acetic acid. Using TLC (PE/ethyl acetate, 9:1 v/v), the progress of the reaction was examined. The precipitated solid was filtered, washed with distilled water followed by cold ethanol. At the end, compound **SB2** was recrystallization using hot ethanol. Yellow coloured solid; yield: 80%; m.p.: 245-247 ºC; m.f.: $C_{16}H_{15}NO_4$; IR (KBr, ν_{max}, cm^{-1}): 3648.32 (phenolic-OH), 2976.96 (Ar-C-H), 2875.03 (Ac-OH), 2537.31 (alkane C-H), 1688.14 (Ac-C=O), 1281.83 (C-N). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 1.34 (t, *J* = 7.20 Hz, 3H), 4.07 (q, *J* = 6.80 Hz, 2H), 6.89 (t, *J* = 8.00 Hz, 1H), 7.13 (d, *J* = 8.00 Hz, 1H), 7.25 (d, *J* = 7.20 Hz, 1H), 7.47 (d, *J* = 8.40 Hz, 2H), 8.00 (d, *J* = 8.40 Hz, 2H), 8.97 (s, 1H), 12.83 (s, 1H), 12.92 (s, 1H); MS: *m/z*=285.01 (M+1).

Synthesis of 4-(2-hydroxynaphthalen-1-yl)methylidene]-amino}benzoic acid (SB3): In a 250 mL round-bottom flask, 25 mL of ethanol was added to a mixture of 2-hydroxy-1-naphthaldehyde (**1c**) (0.62 g, 0.01 mol) and 4-aminobenzoic acid (**2**) (0.50 g, 0.01 mol). It was allowed to reflux for around 30 min at room temperature in the presence of catalytic amount of acetic acid. The progress of was thoroughly monitored by TLC technique using PE/ethyl acetate, 9:1 v/v. The precipitated product was filtered and washed with water followed by cold ethanol. Recrystallization with hot ethanol had afforded the solid product in pure form. Yellow coloured solid; yield: 85%; m.p.: 275-277 ºC; m.f.: $C_{18}H_{13}NO_3$; IR (KBr, ν_{max}, cm^{-1}): 3648.31 (phenolic -OH), 2976.24 (Ar-C-H), 1704.31 (C=O), 1282.20 (C=O) 1249.39 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 6.97 (d, *J* = 9.20 Hz, 1H), 7.34 (t, *J* = 7.60 Hz, 1H), 7.47 (t, *J* = 87.60 Hz, 1H), 7.69 (s, 1H), 7.72-7.76 (m, 2H), 7.78 (s, 1H), 7.97 (q, *J* = 9.20 Hz, 2H), 8.48 (d, *J* = 8.40 Hz, 1H), 9.65 (d, *J* = 4.00 Hz, 1H), 12.92 (s, 1H), 15.48 (s, 1H); MS: *m/z* = 292.07 [M+1].

Antibacterial activity: The antibacterial activity of synthesized Schiff base compounds **SB1**, **SB2** and **SB3** was determined against pathogenic bacteria *Escherichia coli* and *staphylococcus* sp. by Kirby-Bauer disc diffusion method in comparison with standard antibiotics such as streptomycin and penicillin. The MIC (minimal inhibitory concentration) and MBC (minimal bactericidal concentration) were also evaluated.

RESULTS AND DISCUSSION

Three Schiff base derivatives of substituted salicylaldehyde were synthesized by reacting equimolar amounts of



Scheme-I: Synthesis of Schiff bases **SB1–SB3**

substituted salicylaldehyde (**1a-c**) with 4-aminobenzoic acid (**2**) in 25 mL of ethanol and acetic acid as a catalytic agent and is represented in **Scheme-I**. The product yields were in the range of 80-85%. The structures were identified using IR, NMR and mass spectral analysis.

Photoluminescence (PL) studies: Using 30-50 mg of synthesized Schiff base compounds at a constant UV excitation wavelength of 445 nm, the PL emission spectra were observed in the wavelength range of 400 to 800 nm. The PL emission peaks in Schiff base compounds **SB1**, **SB2** and **SB3** Schiff bases

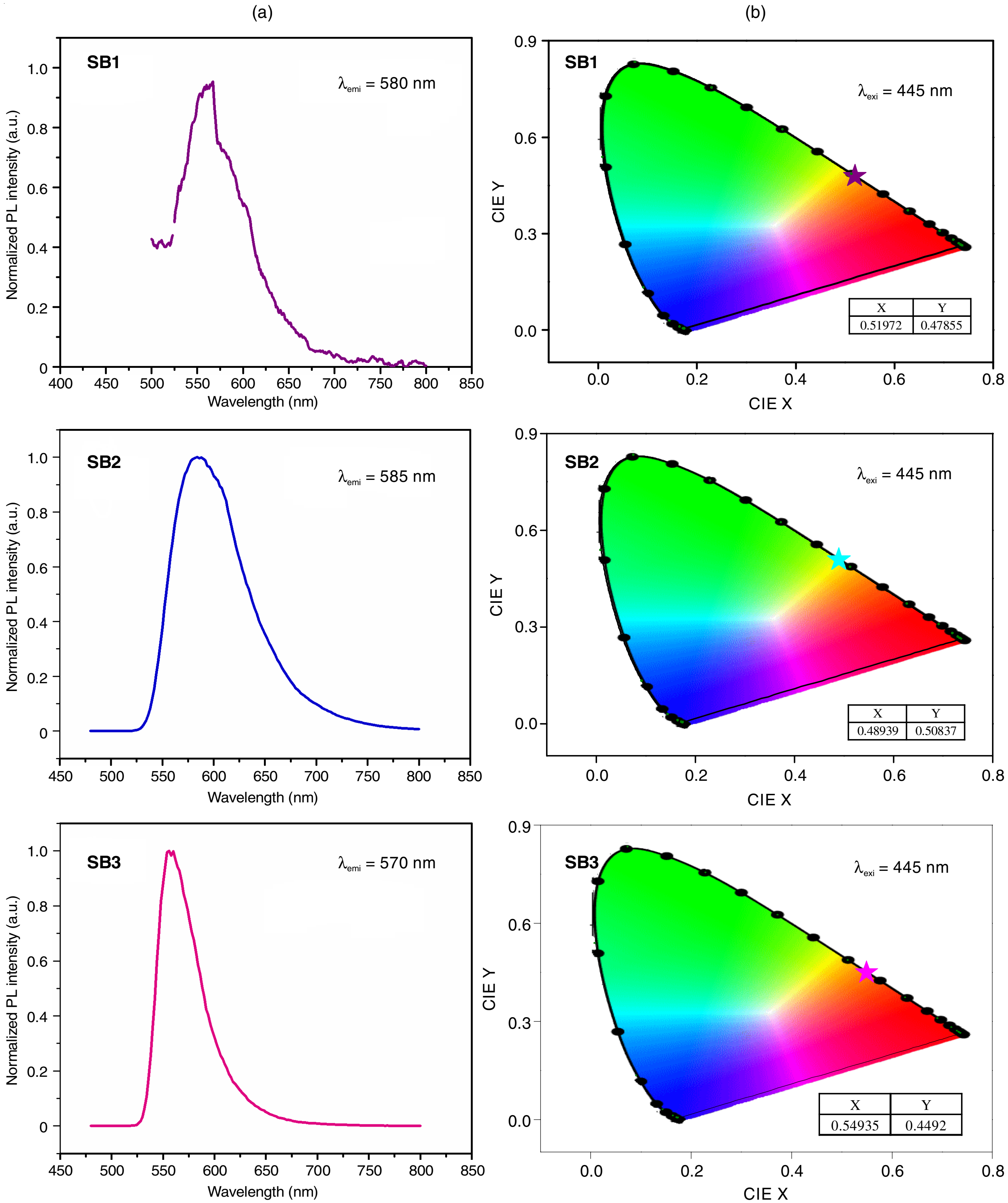


Fig. 1. (a) Photoluminescence spectra of the Schiff bases (**SB1-SB3**), (b) CIE graphs of the Schiff bases **SB1-SB3**

had been observed at 580, 585 and 570 nm, respectively (Fig. 1a). The location of the colour coordinates represented in the CIE chromaticity diagram by sign (star) indicated the colour of nanopowder. From Fig. 1, it was observed that **SB1** displays a yellow-orange colour, **SB2** demonstrates a yellow, while **SB3** display an orange colour (Fig. 1b).

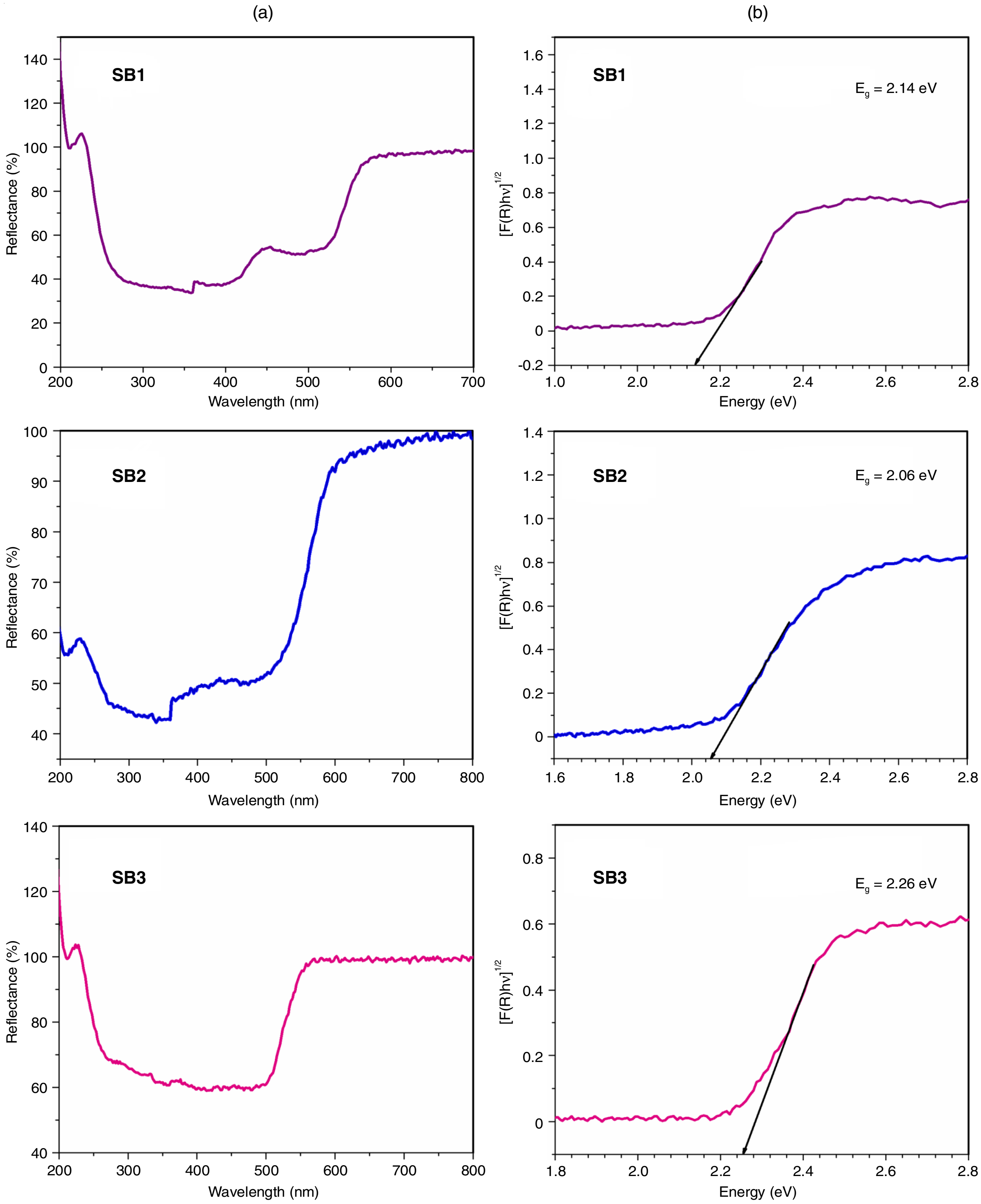


Fig. 2. (a) Diffuse reflectance spectra of Schiff bases (**SB1-SB3**), (b) plots of $[F(R_\infty)h\gamma]^{1/2}$ against photon energy (eV) for Schiff bases (**SB1-SB3**)

Schiff bases **SB1-SB3** have diffuse reflectance spectra that were measured between 200 and 900 nm. The spectra showed prominent peaks in the 400-800 nm wavelength region as a result of the electron transition from the conduction band to the valence band. Furthermore, using the Kubelka-Munk function theory [17] (Fig. 2a) and diffuse reflectance spectra (DRS), the optical band gaps for the Schiff bases **SB1-SB3** were also computed. The synthesized Schiff bases **SB1-SB3** optical band gaps were found to be 2.14, 2.06 and 2.26 eV, respectively (Fig. 2b). By taking into account their band gaps, the synthesized Schiff bases could be employed as promising light emitting diodes for creating robust electroluminescent materials as emissive layers.

Antibacterial activity: The antibacterial activity of synthesized Schiff base compounds **SB1**, **SB2** and **SB3** was evaluated in comparison with streptomycin and penicillin as standard antibiotics. All the compounds showed the antibacterial activity against tested pathogens. Compound **SB1** showed maximum zone of inhibition (20 mm) against *Staphylococcus* sp. and *Escherichia coli* (10 mm) among all the tested compounds. Interestingly, Schiff base compound **SB1** has shown higher inhibitory activity than antibiotic streptomycin (19 mm) against *Staphylococcus* sp. (Fig. 3).

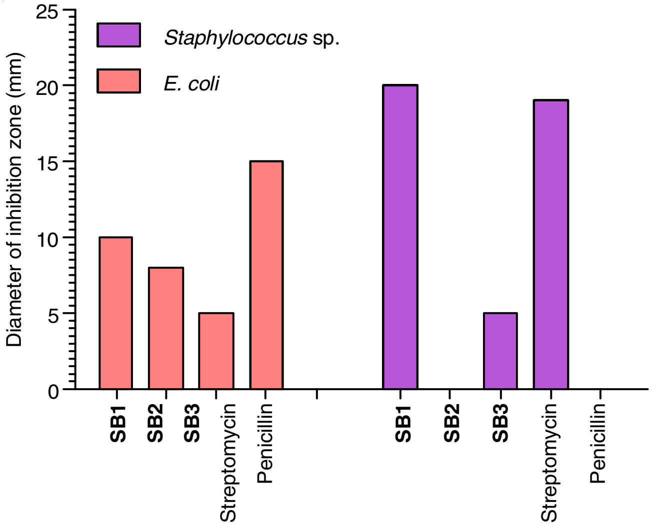


Fig. 3. Antibacterial activity of synthesized Schiff base compounds (**SB1-SB3**)

Compound **SB1** showed MIC value of 50 μg/mL against *Escherichia coli* and 25 μg/mL against *Staphylococcus* sp. Compounds **SB2** and **SB3** showed MIC value 100 μg/mL against both *E. coli* and *Staphylococcus* sp. Present studies suggested that synthesized Schiff base compounds **SB1-SB3** have significant antibacterial activity against tested bacteria.

Conclusion

The current study effectively examined the satisfactory light emission properties of synthesized Schiff base derivatives derived from substituted salicylaldehyde and 4-aminobenzoic acid **(SB1-SB3)**. These Schiff bases **SB1-SB3** exhibited a high degree of solubility in several organic solvents, indicating their potential as effective materials for the development of light emitting devices, as supported by their optical band gaps. The photoluminescence (PL) emission spectra and the Commission Internationale de I'Elcairage (CIE) graphs in respect of the aforementioned Schiff bases that confirmed different colours of emission could further substantiate the use of the above materials in the fabrication of light emitting devices. The synthesized Schiff bases **SB1-SB3** were also found to exhibit the antibacterial activity against selected pathogens.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. K. Shivakumar, S. Shashidhar, P. Vithal Reddy and M.B. Halli, *J. Coord. Chem.*, **61**, 2274 (2008); https://doi.org/10.1080/00958970801905239
2. C.H. Chen and C.W. Tang, *Appl. Phys. Lett.*, **79**, 3711 (2001); https://doi.org/10.1063/1.1420583
3. M.S. More, P.G. Joshi, Y.K. Mishra and P.K. Khanna, *Mater. Today Chem.*, **14**, 100195 (2019); https://doi.org/10.1016/j.mtchem.2019.100195
4. N. Novoa, C. Manzur, T. Roisnel, S. Kahlal, J.-Y. Saillard, D. Carrillo and J.-R. Hamon, *Molecules*, **26**, 5316 (2021); https://doi.org/10.3390/molecules26175316
5. S.M. Gomha, H.A. Ahmed, M. Shaban, T.Z. Abolibda, M.S. Khushaim and K.A. Alharbi, *Materials*, **14**, 3718 (2021); https://doi.org/10.3390/ma14133718
6. Z.H. Chohan, A. Munawar and C.T. Supuran, *Met. Based Drugs*, **8**, 137 (2001); https://doi.org/10.1155/MBD.2001.137
7. B. Hemmateenejad, M. Yazdani and H. Sharghi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **91**, 198 (2012); https://doi.org/10.1016/j.saa.2012.01.023
8. S. Kagatikar and D. Sunil, *J. Electron. Mater.*, **50**, 6708 (2021); https://doi.org/10.1007/s11664-021-09197-9
9. J. Zhang, L. Xu and W.-Ye. Wong, *Coord. Chem. Rev.*, **355**, 180 (2018); https://doi.org/10.1016/j.ccr.2017.08.007
10. M. Mustapha, B.R. Thorat, S. Sawant, R.G. Atram and R. Yamgar, *J. Chem. Pharm. Res.*, **3**, 1045 (2011).
11. N. Al-Najjar, *Iraqi J. Sci.*, **50**, 271 (2009).
12. A.R. Haque and M.A. Salam, *Cogent Chem.*, **1**, 1045212 (2015); https://doi.org/10.1080/23312009.2015.1045212
13. R.C. Maurya, P. Patel and S. Rajput, *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 817 (2003); https://doi.org/10.1081/SIM-120021648
14. V. Nishal, D. Singh, R.K. Saini, V. Tanwar, S. Kadyan, R. Srivastava and P.S. Kadyan, *Cogent Chem.*, **1**, 1079291 (2015); https://doi.org/10.1080/23312009.2015.1079291
15. M. Srinivas, G.R. Vijayakumar, K.M. Mahadevan, H. Nagabhushana and H.S. Bhojya Naik, *J. Sci. Adv. Mater. Dev.*, **2**, 156 (2017); https://doi.org/10.1016/j.jsamd.2017.02.008
16. B.X. Yang, C. Yao and G. Zhou, *Platin. Met. Rev.*, **57**, 2 (2013); https://doi.org/10.1595/147106713X659019
17. B. Becerir, *Fibers Polym.*, **6**, 224 (2005); https://doi.org/10.1007/BF02875646