

Three New -CF₃, -CN Containing π -Conjugated Heteroaromatic Compounds: Synthesis, Crystal Structure and Photoelectronic Properties

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Abstract

Three new π -conjugated hetero aromatic materials consisting of pyridine **3a**, furan **3b**, and thiophene **3c** have been synthesized by Knoevenagel condensation reaction. These molecules have been characterized by ¹H NMR, EI-MS and single crystal X-ray diffraction analysis. Molecule **3a** crystallized under monoclinic system with space group *C2/c*, molecule **3b** crystallized under triclinic system with space group *P-1* and the molecule **3c** crystallized under triclinic system with space group *P-1*. The optoelectronic properties of these compounds have been studied. Molecules **3a**, **3b** and **3c** showed strong absorption maxima wavelengths at 300, 419 and 418 nm, respectively. The molar extinction coefficients (ϵ) of the compounds **3a**, **3b** and **3c** suggested that molecule **3b** has better ability to absorb UV light; molecule **3a** has better fluorescence intensity than molecule **3b** and **3c**. Low energy gaps of HOMO and LUMO energy levels of these compounds suggests that these compounds may be a promising new class of lead compounds for developing high performance semiconductor materials. Compounds **3a**, **3b** and **3c** has emissions near to blue light, a slight modification of the structures by extending conjugation may find important applications in optoelectronic devices as blue light emitters in organic light-emitting devices for the development of new generation organic semiconducting materials.

Keywords

Organic Semiconducting Material, Knoevenagel Condensation, X-Ray Analysis, π -Conjugated Materials

1. Introduction

π -Conjugated systems are building blocks of organic semiconductors and have been of great interest due to their important applications in organic electronic circuits as semiconducting materials [1]-[7]. They have been used as semiconducting materials in organic photovoltaic cells, sensors, organic light-emitting diodes and organic field-effect transistors (OFETs) due to the offering of low-cost, large-area, and flexible electronic devices [8] [9] [10] [11]. N-type semiconductor materials are precise components in ambipolar transistors and complementary circuits [12] [13]. However, due to their limitations such as low air stability and difficult in design, synthesis these materials are being less explored. It has been documented that air stability and performance of n-type semiconducting material can be improved by substituting electron withdrawing groups such as fluorine, cyano, carbonyl etc. into the n-type semiconducting material [14]. It was reported that incorporation of electron withdrawing groups increases the air stability of their anions due to increase in electron affinity of materials, LUMO energy gap will be reduced [15] [16] [17]. Jones and co-workers have explored the n-type air stable perylene diimide derivatives by incorporating cyano (CN) and fluorine (F) substituent [18] [19]. Recently, we reported n-type transport characteristics of *p*-phenylenevinylene derivative of 3',3'-(1,4-phenylene)bis{2'-(4''-trifluoromethyl)phenyl}acrylonitrile having two cyano (CN) and two trifluoromethyl (CF₃) substituents [20]. We also reported the synthesis of 2,5-Difluoro-1,4-phenylene-bis{2-[4-(trifluoromethyl)phenyl]acrylonitrile} and fabricated OFET using this compound exhibited good n-channel OTFT properties with high electron mobility [21]. Herein, we report the synthesis, crystal structure and photoelectronic properties of three π -conjugated heteroaromatic materials having pyridine, furan, and thiophene and cyano, fluorine as electron withdrawing substituents. We hope this structural-property study will provide better insight for material chemists in designing more efficient and air resistant organic semiconducting materials, which are strongly desired for next generation optoelectronic application.

2. Experimental

2.1. Materials and Methods

All reagents were purchased from TCI and Sigma Aldrich and used without further purification. All the products were characterized by ¹H NMR, EI-MS and X-ray diffraction analysis. The NMR spectrum was recorded on a Bruker AMX-500 MHz instrument (Bruker, Yokohama, Japan) at room temperature. Absorption spectrum was measured by using JASCO V-550 UV/VIS Spectrophotometer (JASCO Corporation, Tokyo, Japan) and Fluorescence spectrum was measured by using Hitachi F-2500 Fluorescence Spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). X-ray data for the compound were collected at room temperature using a Bruker Apex II KY CCD diffractometer with graphite

monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) with ω -scan method.

2.2. Synthesis of Compounds **3a**, **3b** and **3c**

In a first Schlenk vessel 2,6-pyridine dicorboxaldehyde (**1a**) or 2,5-furan dicorboxaldehyde (**1b**) or 2,5-thiophene dicorboxaldehyde (**1c**) (680 mg, 0.40 mmol) and (4-trifluoromethyl)phenylacetonitrile **2** (740 mg, 0.40 mmol) were taken in absolute ethanol (50 mL). In a second Schlenk vessel, sodiummethoxide (0.400 g, 5.76 mmol) and freshly distilled dry pyridine (4.96 mmol, 0.40 mL) were taken in absolute ethanol (50 mL). The mixture was mixed and heated to reflux for 3 hours. Then, pyridine and volatiles were removed under reduced pressure. The residue was repeatedly extracted with small portions (15 mL) of dichloromethane. The organic layer was washed with water, dried over anhydrous MgSO₄, and then, filtered through a syringe filter. The extract was evaporated under reduced pressure to leave the residue affording the compounds **3a**, **3b** and **3c** in quantitative yield.

3a ¹H NMR (CDCl₃, 400 MHz) $\delta = 7.75$ (4H, d, Ar-H), 7.78 (2H, s, CH=CN), 7.89 (4H, d, Ar-H), 7.98 (1H, q, Ar-H), 8.04 (2H, s, Ar-H), 8.05 (2H, s-m, Ar-H); EI-MS: M⁺, 468.

3b ¹H NMR (CDCl₃, 400 MHz) $\delta = 7.40$ (2H, s, Ar-H), 7.52 (2H, s, CH=CN), 7.72 (2H, d, Ar-H), 7.80 (2H, d, Ar-H); EI-MS: M⁺, 457.

3c ¹H NMR (CDCl₃, 400 MHz) $\delta = 7.72$ (6H, m, Ar-H), 7.79 (4H, d, Ar-H), 7.88 (2H, s, CH=CN); EI-MS: M⁺, 473.

2.3. Single-Crystal X-Ray Analysis and Structure Determination

Crystallographic and structural refinement data for **3a**, **3b** and **3c** summarized in **Table 1**. Single crystals of **3a**, **3b** and **3c** were easily obtained at room temperature from a solution of dichloromethane using slow diffusion technique. Crystals of **3a**, **3b** and **3c** measuring good dimensions were mounted on a glass fiber. The data were collected on a Bruker APEX II KY CCD diffractometer by using a graphite-monochromatized Mo/K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a nominal crystal-to-area detector distance of ca. 83 mm.

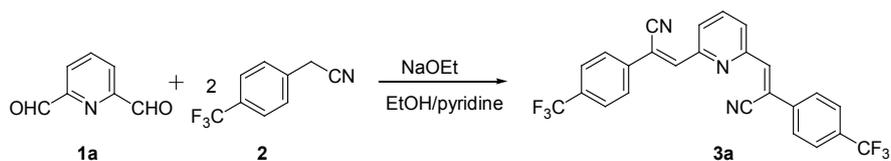
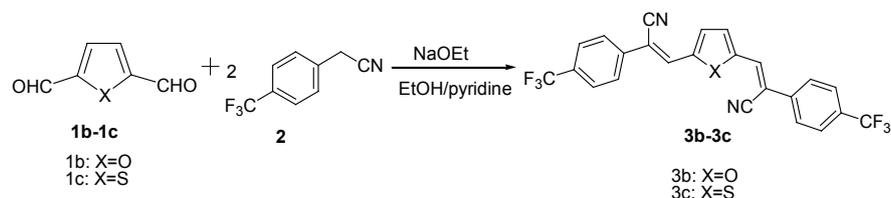
APEX2 software was used for preliminary determination of the unit cell. Determination of integral intensities [22] and unit cell refinement were performed using SAINT program [23]. And, data were corrected for absorption effects with SADABS using the empirical technique [24]. The structures were solved by the SHELXS-2014/7 direct method, and subsequent structure refinements were performed using SHELXL-2014/7.

3. Results and Discussion

The three n-type semiconducting materials **3a**, **3b** and **3c** have been synthesized by Knoevenagel condensation of pyridine dicorboxaldehyde **1a**, furan dicorboxaldehyde **1b**, thiophene dicorboxaldehyde **1c** with 4-(trifluoromethyl) phenyl acrylonitrile **2** in the presence of sodium ethoxide (**Scheme 1**, **Scheme 2**). Compounds **3a**, **3b** and **3c** have been characterized with ¹H NMR and EI-MS.

Table 1. Crystal data and structure refinements for **3a**, **3b** and **3c**.

parameters measured	3a	3b	3c
Empirical Formula	C ₂₅ H ₁₃ F ₆ N ₃	C ₂₄ H ₁₂ F ₆ N ₂ O	2(C ₂₄ H ₁₂ F ₆ N ₂ S)·C ₆ H ₆
Formula Weight (g·mol ⁻¹)	469.38	458.38	1026.94
Crystal shape, color	Prism, yellow	Needle, colorless	Prism, colorless
Temperature	120 K	90 K	120 K
Radiation type	Mo K α	Mo K α	Mo K α
Wavelength (Å)	0.7107	0.7107	0.7107
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>C2/c</i>	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions	a = 11.2641 (15) Å b = 18.568 (2) Å c = 10.0628 (15) Å $\alpha = 90^\circ$ $\beta = 103.960 (1)^\circ$ $\gamma = 90^\circ$	a = 4.470 (5) Å b = 13.016 (15) Å c = 16.904 (19) Å $\alpha = 79.018 (11)^\circ$ $\beta = 88.236 (12)^\circ$ $\gamma = 83.602 (11)^\circ$	a = 7.5572 (14) Å b = 15.746 (3) Å c = 19.641 (4) Å $\alpha = 84.754 (2)^\circ$ $\beta = 80.546 (2)^\circ$ $\gamma = 80.620 (2)^\circ$
Volume	2042.5 (5) Å ³	959.4 (19) Å ³	2269.6 (7) Å ³
Z	4	2	2
Calculated density (Mg·m ⁻³)	1.526	1.587	1.503
Absorption coefficient mm ⁻¹	0.130	0.138	0.212
<i>F</i> (000)	952	464	1044
Crystal Size (mm)	0.30 × 0.20 × 0.20	0.20 × 0.15 × 0.10	0.40 × 0.20 × 0.20
Theta range for data collection	2.2° to 25°	1.23° to 23.91°	1.1° to 25.0°
Limiting indices	-13 < <i>h</i> < 13 -22 < <i>k</i> < 22 -11 < <i>l</i> < 11	-5 < <i>h</i> < 5 -14 < <i>k</i> < 14 -19 < <i>l</i> < 19	-8 < <i>h</i> < 8 -18 < <i>k</i> < 18 -23 < <i>l</i> < 23
Reflections collected/unique	9738/1807 [<i>R</i> _{int} = 0.023]	7410/2919 [<i>R</i> _{int} = 0.046]	21937/7990 [<i>R</i> _{int} = 0.033]
Completeness to theta (%)	99.9	99.7	99.2

**Scheme 1.** Schematic representation of synthesis of compound **3a**.**Scheme 2.** Schematic representation of synthesis of compound **3b** and **3c**.

Further to confirm the molecular structures of molecules **3a**, **3b** and **3c**, suitable crystals for X-ray diffraction analysis were obtained by the slow evaporation of dichloromethane solution using slow diffusion method. The crystallographic details are summarized in **Table 1**. The compound **3a** crystallizes with monoclinic crystal system, space group $C2/c$. The molecular structure of **3a** was depicted in **Figure 1**.

The asymmetric unit of the title compound $C_{25}H_{13}F_6N_3$, contains one-half of the formula unit. The molecular structure appears to be planar from the top view. But, from the side view we can clearly see that three aromatic rings are slightly distorted from the planar geometry. Two aromatic ring planes, A (defined by C7, C8, C9, C10, C11, C12) and B (defined by N1, C1, C2, C3, C2, C1) were slightly leaned and the plane angles between two aromatic rings is 2.58° as shown in **Figure 1**. The two cyano groups, which are located in the same direction causes a deviation from planarity of the molecule **3a**. Triple bond lengths of the cyano group was $1.145(2) \text{ \AA}$ for C6N2. On the other hand, the bond angle consisting cyanoethenyl C-CN triple bond was slightly twisted, the angles is $173.95(2)^\circ$ for C5-C6-N2.

Crystal packing of the molecule **3a** was also illustrated in **Figure 2**. Intermolecular short contacts of the molecule **3a** were listed in **Table 2**. The molecular packing of the molecule **3a** has layer like geometry. In the crystal packing diagram, C-H...N and C...C short contacts between the molecules generated three dimensional molecular networks.

The compound **3b** crystallizes with triclinic crystal system, space group $P-1$. The molecular structure and packing diagram of **3b** was depicted in **Figure 3**.

The molecule **3b** appears to be planar from the top. But, from the side view clearly appears that molecule **3b** is a strained one. Three aromatic ring planes, A (defined by C18, C19, C20, C21, C22, C23), B (defined by C1, C2, C3, C4, O1) and C (defined by C8, C9, C10, C11, C12, C13) were slightly leaned and the plane angles between three aromatic ring moieties are 5.67° for A-B, 25.27° for

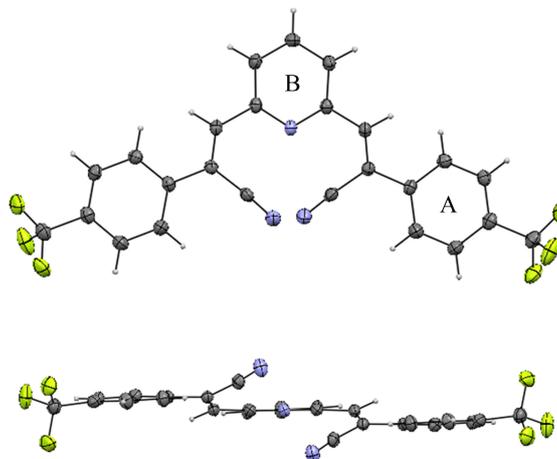


Figure 1. Top (above) and side (below) views of the molecule **3a** and thermal ellipsoids are drawn on 50% probability level. A and B represents phenyl and pyridine rings.

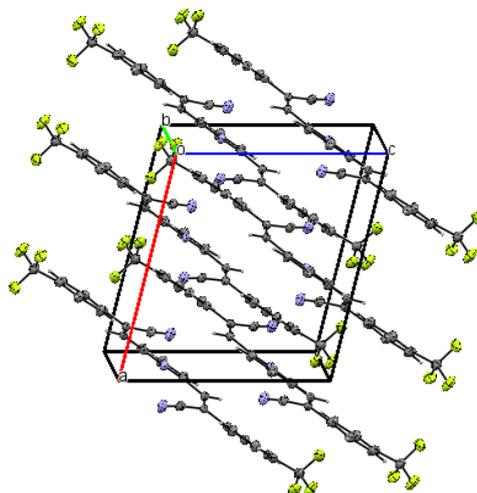


Figure 2. Molecular packing of the compound **3a** and thermal ellipsoids are drawn on 50% probability level. Blue and pale green ellipsoids represents N and F atoms, respectively.

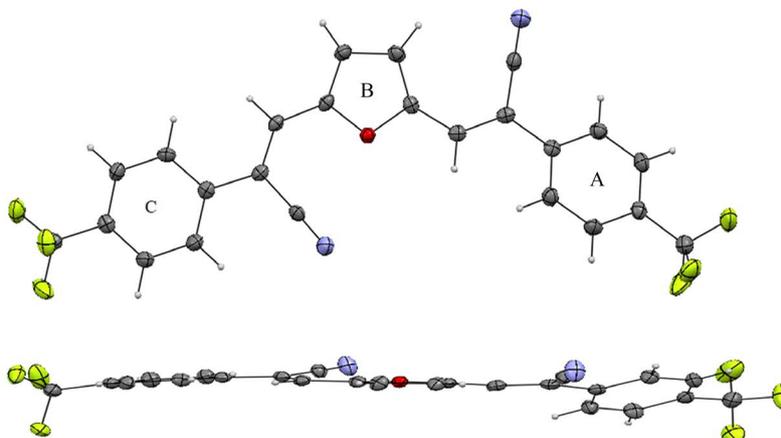


Figure 3. Top (above) and side (below) views of the molecule **3b** and thermal ellipsoids are drawn on 50% probability level. A, B and C represents phenyl and furan rings.

Table 2. Selected intermolecular short contacts (Å) of the molecule **3a**.

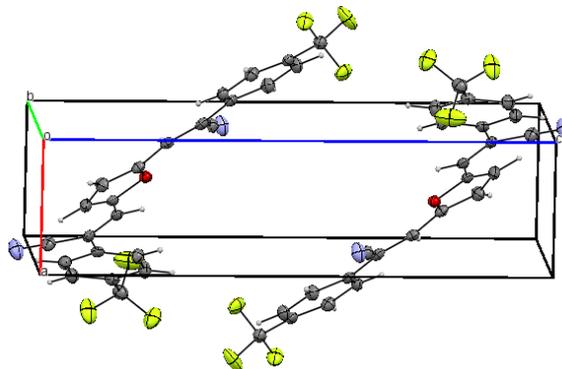
Short contacts (between the sidecolumns)		Short contacts (between molecules in the column)	
N2-H4	2.695	C4-C4	3.341
N2-H9	2.596	C4-C1	3.372

A-C and 5.67° for B-C respectively as shown in **Figure 1**. The plane angle between the end phenyl rings is 25.27° , this suggests that molecule **3b** is a strained one. Triple bond lengths of the cyano groups were $1.137(4)$ Å for C7N1 and $1.139(4)$ Å for C17N2, respectively. The bond angle consisting cyanoethenyl C-CN triple bonds are slightly twisted, the angles are $177.78(4)^\circ$ for C6-C7-N1 and $179.2(4)^\circ$ for C16-C17-N2, respectively.

Crystal packing of the molecule **3b** was also illustrated in **Figure 4**. Intermolecular short contacts of the molecule **3b** were listed in **Table 3**. The molecular

Table 3. Selected intermolecular short contacts (Å) of the molecule **3b**.

Short contacts (between the sidecolumns)		Short contacts (between molecules in the column)	
F6-H3	2.510		
H12-N1	2.702	C4-C5	3.367
F2-H11	2.491	C5-C13	3.370
F2-H6	2.595	C12-F3	3.145
F3-F3	2.754		

**Figure 4.** Molecular packing of the compound **3b** and thermal ellipsoids are drawn on 50% probability level. Blue, red and pale green ellipsoids represents N, O and F atoms, respectively.

packing of the molecule **3b** has layer like geometry. In the crystal packing diagram C-H...N, C-H...F and C...C short contacts between the molecules generated three dimensional molecular networks.

The compound **3c** crystallizes with triclinic crystal system, space group *P*-1 with two molecules and one benzene solvent molecule in the unit cell. The molecular structure and packing diagram of **3c** was depicted in **Figure 5**.

The molecule **3c** appears to be perfect planar from the top and side views. Three aromatic ring planes, A (defined by C8, C9, C10, C11, C12, C13), B (defined by C1, C2, C3, C4, S1) and C (defined by C18, C19, C20, C21, C22, C23) were slightly leaned (**Figure 1**) and the planeangles between three phenyl moieties are 2.11° for A-B, 6.42° for A-C and 7.92° for B-C respectively. The plane angle between the end phenyl rings is 7.92°, this suggests that molecule **3b** is less strained one than molecules **3a** and **3b**. Due to this reason electron carrier mobility of molecule **3c** seems to be relatively good compared with the compounds **3a** and **3b**. Triple bond lengths of the cyano groups were 1.145 (3) Å for C17N1 and 1.147 (4) Å for C7N2, respectively. The bond angle consisting cyanoethenyl C-CN triple bonds are slightly twisted, the angles are 178.88 (2)° for C16-C17-N1 and 177.98 (2)° for C6-C7-N2, respectively.

Crystal packing of the molecule **3c** was also illustrated in **Figure 6**. Intermolecular short contacts of the molecule **3c** were listed in **Table 4**. In the crystal packing diagram C-H...N, C-H...F and C...C short contacts between the molecules generated three dimensional molecular networks.

Further, the photophysical properties of molecules **3a**, **3b** and **3c**, the UV-Vis

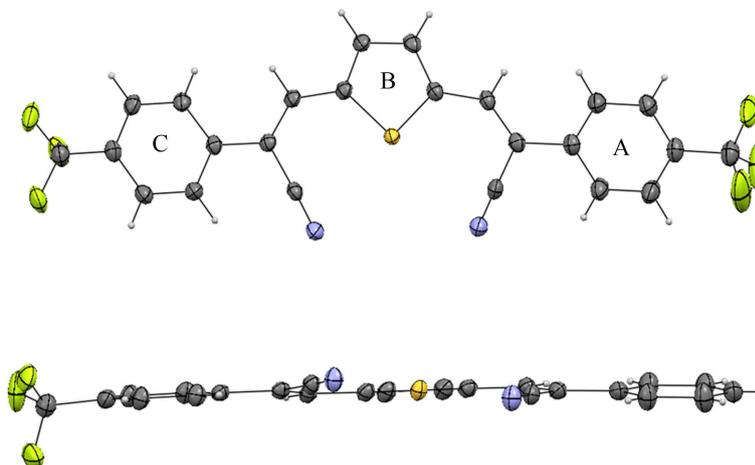


Figure 5. Top (above) and side (below) views of the molecule **3c** and thermal ellipsoids are drawn on 50% probability level. A, B and C represents phenyl and thiophene rings.

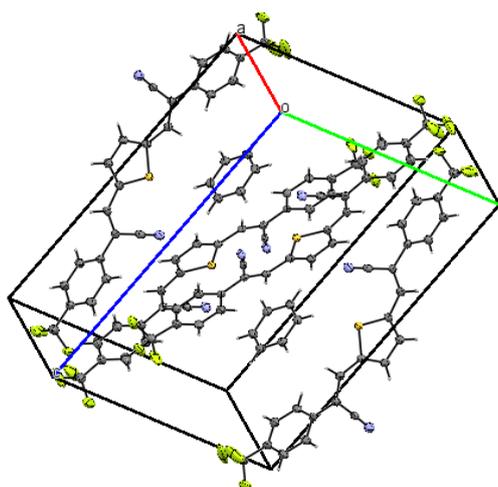


Figure 6. Molecular packing of the compound **3c** and thermal ellipsoids are drawn on 50% probability level. Blue, yellow and pale green ellipsoids represents N, S and F atoms, respectively.

Table 4. Selected intermolecular short contacts (Å) of the molecule **3c**.

Short contacts (between the sidecolumns)		Short contacts (between molecules in the column)	
H2-N3	2.621		
N2-H27	2.433		
H3-N4	2.720	F3-C19	3.157
N1-H36	2.626	C20-F8	3.157
H23-F7	2.597	C12-F3	3.145
N2-H53	2.705	F12-C33	3.109
H9-C51	2.878	C29-C43	3.383
F11-H34	2.508	F11-C34	3.021
H43-C53	2.792		
H37-C50	2.855		

absorption and Fluorescence emission of the molecules **3a**, **3b** and **3c** were measured in dichloromethane solution (1×10^{-5} mol/L), and their correspond-

ing spectra were shown in **Figure 7** and **Figure 8**, respectively. The molecules **3a**, **3b** and **3c** displayed absorption maxima wavelength at 300, 419 and 418 nm, respectively.

The molar extinction coefficients (ϵ) of the compounds **3a**, **3b** and **3c** were calculated as 2.4×10^4 (300 nm), 4.9×10^4 (419 nm) and 4.1×10^4 (418 nm), $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, respectively. As a basic rule, the molecule, which has higher extended π -conjugation shows better UV light absorbance. Conversely, molecule **3a**, which has higher conjugated π -system has less absorbance than molecules **3b** and **3c**. This may be due to the relatively highly strained geometry of molecule **3a** resulted in less π -orbital overlap. Among three molecules, **3b** has better

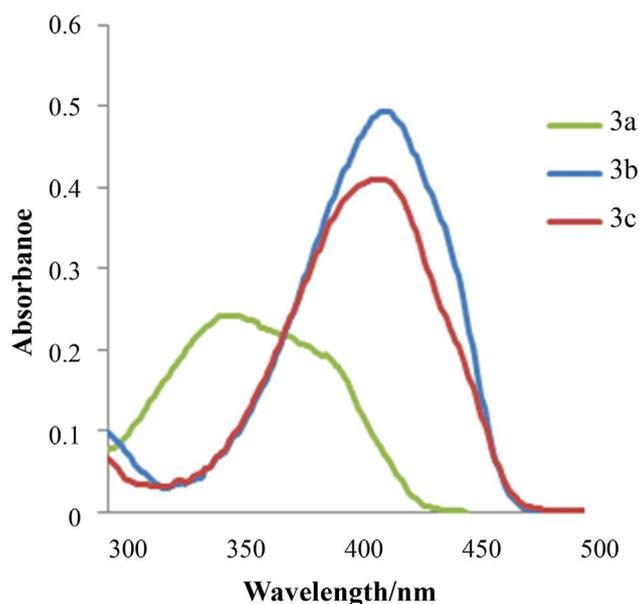


Figure 7. UV-Visible absorption spectra of molecules **3a**, **3b** and **3c**.

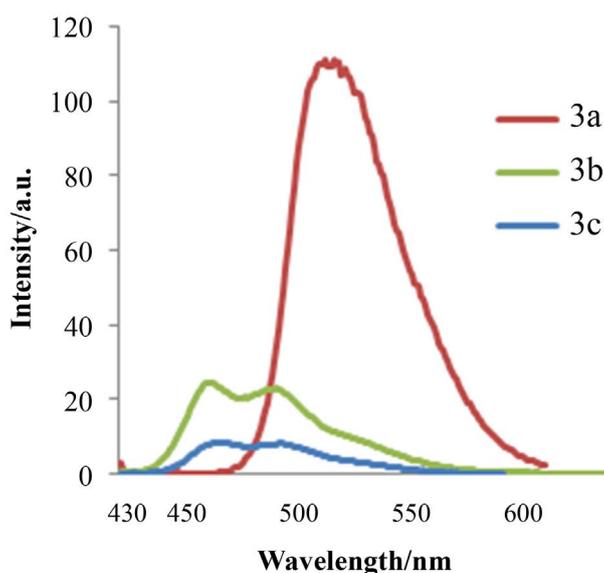


Figure 8. Emission spectra of molecules **3a**, **3b** and **3c**.

ability to absorb UV light because two cyano groups in molecule **3b** are far away to each other may be facilitated the effective π -orbital overlap.

The emission spectra of the molecules **3a**, **3b** and **3c** were recorded in dichloromethane solution (1×10^{-5} mol/L), and their emission spectra is shown in **Figure 8**. Emission spectra of the complexes were measured by exciting the complexes at their absorption maxima wavelengths 300, 419 and 418 nm, respectively. Among three molecules, **3a** has better fluorescence ability than molecule **3b** and **3c**. This may be due to the extended conjugation of molecule **3a** due to pyridine moiety than molecule **3b** and **3c**, which has furan and thiophene moiety in their structures. Noteworthy points from the structural and photo-physical properties are these compounds have emissions near to blue light. Further with slight modification of these structures by extending conjugation may find important applications in optoelectronic devices, such as blue emitters in organic light-emitting devices (OLEDs) for the development of new generation organic semiconducting materials.

Further, HOMO and LUMO energy level calculations of the π -systems of the compounds were carried out using density functional theory (DFT) B3LYP 6 - 31 G(d) level on SPARTAN16 Suite program [25]. Atomic coordinate data (x , y , z) of the X-ray analysis were used in calculations. The calculation results were HOMO -6.52 eV, LUMO -2.52 eV for **3a**, HOMO -6.05 eV, LUMO -3.07 eV for **3b** and HOMO -5.93 eV, LUMO -3.93 eV for **3c** (**Figure 9**). The energy gaps were 3.79 eV for **3a**, 3.88 eV for **3b** and 3.73 eV for **3c**. The low energy gaps suggest that that these compounds may be a promising new class of lead compounds for developing high performance semiconductor materials.

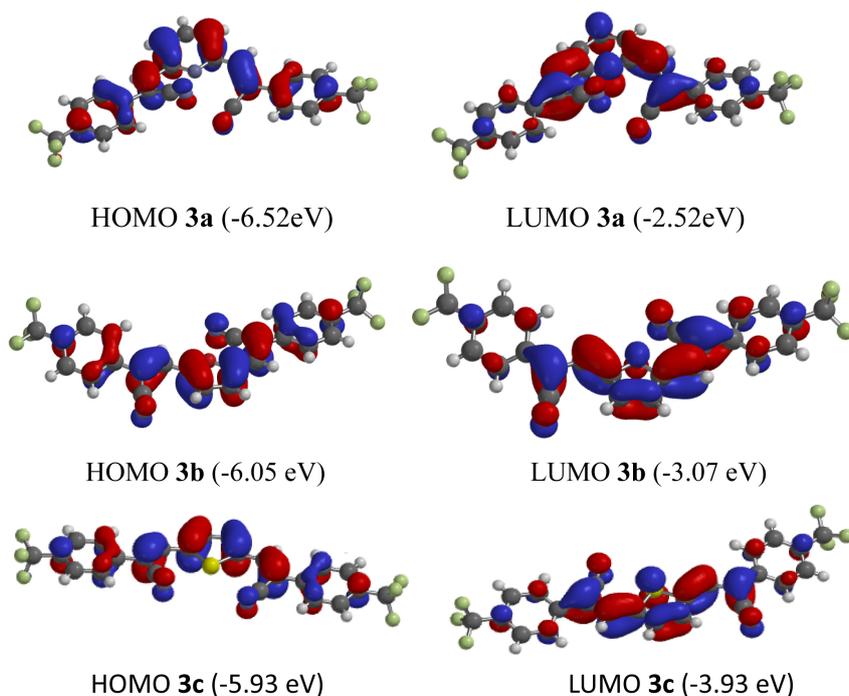


Figure 9. HOMO and LUMO orbitals in the crystals of the compounds **3a**, **3b** and **3c**.

4. Conclusion

Three new -CF₃, -CN containing π -conjugated heteroaromatic compounds consisting of pyridine **3a**, furan **3b**, and thiophene **3c** have been synthesized and these compounds have been characterized by ¹H NMR, EI-MS and X-ray diffraction analysis. Molecules **3a**, **3b** and **3c** showed strong absorption maxima wavelengths at 300, 419 and 418 nm, respectively. The molar extinction coefficients (ϵ) of the compounds **3a**, **3b** and **3c** indicated molecule **3b** has better ability to absorb UV light, molecule **3a** has better fluorescence intensity than molecule **3b** and **3c**. Low energy gaps of HOMO and LUMO energy levels of these compounds suggest that these compounds may be a promising new class of lead compounds for developing high performance semiconductor materials. Compounds **3a**, **3b** and **3c** has emissions near to blue light, a slight modification of the structures by extending conjugation may find important applications in optoelectronic devices as blue light emitters in organic light-emitting devices.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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