

## Synthesis, Characterization and Determination of HOMO-LUMO of the Substituted 1,3,5-Triazine Molecule for the Applications of Organic Electronics

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(Received June 9, 2019; Accepted July 18, 2019)

**ABSTRACT.** The most important parameter of organic molecules for energy harvesting application focuses mainly on their band gap (HOMO-LUMO). In this report, we synthesized differently substituted 1,3,5-triazine based organic molecule which on future processing can be used in organic electronics like solar cells and OLED's. The energy gap of the synthesized novel analogue was calculated using cyclic voltammetry, UV-Visible spectroscopy and compared with density functional theory (DFT) studies.

**Key words:** Electroactive material, Bandgap, Organic solar cell, Cyclic voltammetry, Density functional theory

### INTRODUCTION

The use of organic materials for electronic applications has got tremendous attention over the last two decades. Over the period, there have been considerable improvements in this field, leading to the wide use of organic materials in many existing applications such as xerographic and display technologies.<sup>1</sup> Electronic organic materials have even inspired the development of devices with potential applications such as field effect transistors and solar cells. This wide range of applications of small molecules as organic solar cells prompted us to synthesize novel analogues based on triazines and explore their potential in solar cell applications. Thus we anticipate to accomplish better control over the macroscopic properties of these materials and thus be able to tune them sensibly for the desired optoelectronic applications.<sup>2</sup> Materials based on arylamines have been extensively studied due to their fascinating physical, photochemical, and electrochemical properties.<sup>3,4</sup> These materials tend to form uniform amorphous layers and are highly luminescent chromospheres. This class of materials has been widely used as hole-transport layers in organic light emitting diodes (OLED).<sup>5,6</sup> Arylamine and the triazine-based system are commonly employed for hole transporting materials for OLED applications.<sup>7</sup>

Current research has had shown that organic materials display wide variety of properties like optical, electrical, pho-

toelectric, and magnetic properties in the solid state. Organic electroactive materials have been the subject of recent thought, including organic semiconductors, organic metals including superconductors, organic photoconductors, organic solar cells, organic non-linear optical materials, photo- and electrochromic organic materials, resist materials, liquid crystals,<sup>8</sup> and others.<sup>9,10</sup> Furthermore, organic materials have found some possible applications for use in electronic and optoelectronic devices such as sensors, plastic batteries, solar cells, field-effect transistors and several others. In contrast to inorganic materials, organic material is an independent molecule and categorized by weak intermolecular interactions.<sup>12</sup> Hence, molecular level designs of organic materials can be readily possible. Organic conjugated  $\pi$ -electron systems have the possible photo and electroactive materials. These organic materials are further processed into thin films and applied in electronic, optoelectronic devices.<sup>13</sup> Methods like spin coating, vacuum vapor deposition, and electrochemical deposition are some of the techniques used in the preparation of organic thin films.<sup>14,15</sup>

Organic molecules can be used in optoelectronic devices based on their HOMO and LUMO energy band structure. For engendering photocurrent in the organic solar cells, the material should have a definite band gap.<sup>16</sup> Mainly under illumination of light, an electron may be excited to the lowest unoccupied molecular orbital (LUMO) leaving a hole in highest occupied molecular orbital (HOMO). To generate

the photo-current, these band electron-holes (excitons) should be separated to free the electrons and holes.<sup>17</sup> After photo-excitation of an electron from HOMO to LUMO, the electron can be excited to LUMO of the acceptor and be collected by own electrode, provided that potential difference between the donor's ionization potential and acceptor's electron affinity is larger than the excitons binding energy. The estimation of energy band diagram is possible through cyclic voltammetry technique. Cyclic voltammetry can measure the oxidation potentials, and then the HOMO and LUMO value can be calculated.<sup>18</sup> The present study is focused on the synthesis of triazines derivatives and their electrical property determination.

## EXPERIMENTAL

The compound **C1**, **C4**, **C5** & **C6** were synthesized by mixing the compound **A1** with respective anilines in methanol/ethanol and heated to 170–200 °C for 12–24 h in seal tube (*Scheme 1*). The compound **C3** was prepared by taking compound **A1** in methanolic ammonia and heated to 50 °C for 4 h. Then followed by the addition of trifluoro methyl aniline in methanol and heated to 150 °C for 12 h. The compound **C2** was synthesized from **A1** with 4-amino phenol followed by the addition of water (*Scheme 1*).

The detailed procedure for individual compound synthesis is bellowed.

### Synthesis of N2,N4,N6-Triphenyl-1,3,5-triazine-2,4,6-triamine (C1)

Aniline (5 mL) was added to a solution of 2,4,6-trichloro-1,3,5-triazine (0.5 g, 0.0027 mol) in methanol (20 mL) at room temperature and heated to 150 °C in seal tube

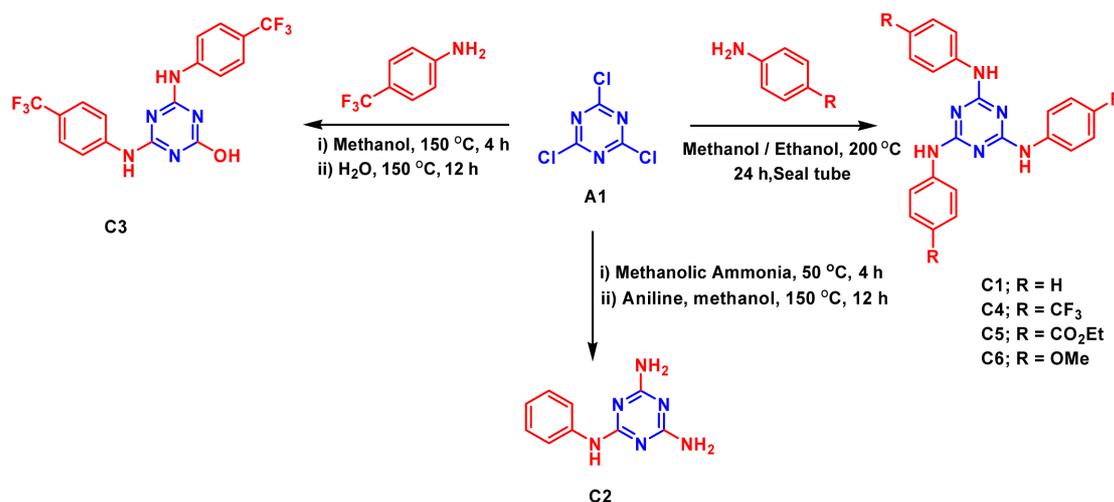
for 24 h. A white precipitate obtained was filtered and dried in vacuum for 4 h to obtain N2,N4,N6-triphenyl-1,3,5-triazine-2,4,6-triamine (**C1**) (0.6 g, 63% yield). White solid; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.24 (s, 3H), 7.81 (d, J = 8.0 Hz, 6H), 7.29 (t, J = 7.6 Hz, 6H), 7.00 (d, J = 7.2 Hz, 3H); LCMS: m/z calculated for C<sub>21</sub>H<sub>18</sub>N<sub>6</sub>: 354.4; Observed mass: 355.2 (M+H); Anal. Calculated for C<sub>21</sub>H<sub>18</sub>N<sub>6</sub>: C, 71.17; H, 5.12; N, 23.71; Found: C, 71.18; H, 5.13; N, 23.69.

### Synthesis of N2-Phenyl-1,3,5-triazine-2,4,6-triamine (C2)

Methanolic ammonia (5 mL) was added to a solution of 2,4,6-trichloro-1,3,5-triazine (1.0 g, 0.0054 mol) in methanol (20 mL) and heated to 150 °C in seal tube. A white precipitate formed was filtered and dried in vacuum for 4 h to get 6-chloro-1,3,5-triazine-2,4-diamine (0.75 g). The above compound was added to methanol (10 mL) followed by the addition of aniline (2 mL) in a seal tube and heated to 160 °C for 24 h to get N2-phenyl-1,3,5-triazine-2,4,6-triamine (**C2**) (0.5 g, 50% yield). White solid; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.702 (s, 4H), 9.22 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.02 (d, J = 7.2 Hz, 1H); LCMS: m/z calculated for C<sub>9</sub>H<sub>10</sub>N<sub>6</sub>: 202.2; Observed mass: 203.2 (M+H); Anal. Calculated for C<sub>21</sub>H<sub>18</sub>N<sub>6</sub>: C, 53.46; H, 4.98; N, 41.56; Found: C, 53.49; H, 4.96; N, 41.57.

### Synthesis of 4,6-Bis((4-(trifluoromethyl)phenyl)amino)-1,3,5-triazin-2-ol (C3)

To a solution of 2,4,6-trichloro-1,3,5-triazine (0.5 g, 0.0027 mol) in ethanol (20 mL), 4-trifluoromethyl aniline (1 mL) was added at room temperature and heated to 100 °C in a seal tube for 12 h. A white precipitate formed was filtered and dried in vacuum for 4 h to get compound (6-chloro-N,N'-bis-(4-trifluoromethyl-phenyl)-[1,3,5]triazine-



*Scheme 1.* Synthesis of compounds C1-C6.

2,4-diamine) (0.6 g). This is dissolved in ethanol (10 mL) and water was added water (2 mL) in seal tube. The reaction was further heated to 200 °C for 4h to get 4,6-bis((4-(trifluoro-methyl)phenyl)amino)-1,3,5-triazine-2-ol (**C3**) (0.5 g, 44% yield). White solid; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 11.5 (br. s, 1H), 9.5 (s, 2H), 8 (d, 4H), 7.5 (d, 4H); LCMS: m/z calculated for C<sub>17</sub>H<sub>11</sub>F<sub>6</sub>N<sub>5</sub>O: 415.29 observed mass: 415.15(M+H); Anal. Calculated for C<sub>17</sub>H<sub>11</sub>F<sub>6</sub>N<sub>5</sub>O: C, 49.15; H, 2.65; F, 27.44; N, 16.86; O, 3.80.

#### Synthesis of N<sub>2</sub>,N<sub>4</sub>,N<sub>6</sub>-Tris(4-(trifluoromethyl)phenyl)-1,3,5-triazine-2,4,6-triamine (**C4**)

4-Trifluoromethyl aniline (2 mL) was added to a solution of 2,4,6-trichloro-1,3,5-triazine (0.5 g, 0.0027 mol) in ethanol (20 mL) at room temperature and the reaction mixture was heated to 100 °C in seal tube for 24 h. A white precipitate formed was filtered and dried in vacuum for 4 h to get N<sub>2</sub>,N<sub>4</sub>,N<sub>6</sub>-tris(4-(trifluoromethyl)phenyl)-1,3,5-triazine-2,4,6-triamine (**C4**) (0.5 g, 33% yield). White solid; <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ 9.69 (s, 3H), 8.20 (bs, 3H), 7.98 (s, 3H), 7.53 (t J = 7.5 Hz, 3H), 7.36 (d, J = 7.2 Hz, 3H); LCMS: m/z calculated for C<sub>24</sub>H<sub>15</sub>F<sub>9</sub>N<sub>6</sub>: 558.4; Observed mass: 559.0 (M+H); Anal. Calculated for C<sub>24</sub>H<sub>15</sub>F<sub>9</sub>N<sub>6</sub>: C, 51.62; H, 2.71; F, 30.62; N, 15.05; Found: C, 51.64; H, 2.70; F, 30.61; N, 15.05.

#### Synthesis of Triethyl 4,4',4''-((1,3,5-Triazine-2,4,6-triyl)tris(azanediyl))tribenzoate (**C5**)

4-Methoxy aniline (2 mL) was added to a solution of 2,4,6-trichloro-1,3,5-triazine (0.5 g, 0.0027 mol) in ethanol (10 mL) at room temperature and the reaction mixture was heated to 200°C in seal tube for 24 h. A white precipitate formed was filtered and dried in vacuum for 4 h to get triethyl 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl)) tribenzoate (**C5**) (0.5 g, 26% yield). White solid; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.70 (s, 3H), 8.19 (s, 6H), 7.59 (d, J = 8.0 Hz, 3H), 7.41 (t, J = 8.0 Hz, 3H), 4.25 (q, J = 14.0, 7.2 Hz, 6H), 1.24 (t, J = 7.2 Hz, 9H); LCMS: m/z calculated for C<sub>30</sub>H<sub>30</sub>N<sub>6</sub>O<sub>6</sub>: 570.6; Observed mass: 571.0 (M+H); Anal. Calculated for C<sub>30</sub>H<sub>30</sub>N<sub>6</sub>O<sub>6</sub>: C, 63.15; H, 5.30; N, 14.73; Found: C, 63.14; H, 5.32; N, 14.73.

#### Synthesis of N<sub>2</sub>,N<sub>4</sub>,N<sub>6</sub>-Tris(4-methoxyphenyl)-1,3,5-triazine-2,4,6-triamine (**C6**)

To a solution of 2,4,6-trichloro-1,3,5-triazine (0.5 g, 0.0027 mol) in methanol (10 mL), 4-methoxy aniline (2 mL) was added at room temperature and the reaction mixture was heated to 170 °C in seal tube for 24 h. The white precipitate formed was filtered and dried in vacuum for 4 h to

get N<sub>2</sub>,N<sub>4</sub>,N<sub>6</sub>-tris(4-methoxyphenyl)-1,3,5-triazine-2,4,6-triamine (**C6**) (0.4 g, 33% yield). White solid; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 8.95 (s, 3H), 7.64 (bs, 6H), 6.86 (d, J = 8.8 Hz, 6H), 3.73 (s, 9H); LCMS: m/z calculated for C<sub>24</sub>H<sub>24</sub>N<sub>6</sub>O<sub>3</sub>: 444.4; Observed mass: 445.2 (M+H); Anal. Calculated for C<sub>24</sub>H<sub>24</sub>N<sub>6</sub>O<sub>3</sub>: C, 64.85; H, 5.44; N, 18.91; Found: C, 64.86; H, 5.45; N, 18.90.

#### UV-Visible Absorption Studies

The energy carried by the UV-Visible radiation corresponds to the energy levels of the electronic states of the organic molecules. The lower energy molecular orbital electron is promoted to higher energy molecular orbital at resonance of the molecules by absorbing the quantified energy provided by the electromagnetic radiation. UV-Visible spectrometer can be used to understand and study these transitions of electrons. E<sub>optical</sub> corresponds to the energy of the long wavelength edge of the exciton absorption band. The longest absorption wavelength λ is used to calculate the optical gap energy (E<sub>g</sub>). According to the equation, the optical band gap can be calculated by a formula.

$$E_g = 1242/\lambda \text{ nm}$$

#### Cyclic Voltammetry Studies

The cyclic voltammetry studies divulge the redox behavior of the as-synthesized compounds. The measurements were carried out on a glassy carbon electrode in acetonitrile solutions containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte using a three-electrode cell and potentiostat Biologic workstation. The potentials were measured using Pt wire as a reference electrode, and a Pt spiral wire was used as a counter electrode. Each measurement was done with an internal redox standard ferrocene/ferrocenium (FOC) as described in the literature.<sup>19,20</sup> The estimations were done with the empirical relation E<sub>LUMO</sub> = [(E<sub>red</sub> - E<sub>1/2(ferrocene)</sub>) + 4.8] eV (Where E<sub>red</sub> = Reduction potential and E<sub>1/2</sub> = half-wave potential of ferrocene).

#### HOMO/LUMO Estimation

The corresponding HOMO and LUMO levels were calculated using E<sub>ox</sub> (onset) for the measurements in solution. The estimations were done with the empirical relation E<sub>HOMO</sub> = [(E<sub>ox</sub> - E<sub>1/2(ferrocene)</sub>) + 4.8] eV. Ferrocene was used as external standard. E<sub>1/2(ferrocene)</sub> is equal to 0.304 V which can be used in the equation to calculate the E<sub>HOMO</sub>. From the absorption spectra, we can calculate the band gap (E<sub>g</sub>). The difference will give the LUMO.

### Computational Details

Geometrical optimization and excited state calculations were carried out using DFT and TDDFT with the UB3LYP functional<sup>21</sup> by the Gaussian 09 program.<sup>22</sup> The solvation effect was considered by the polarizable continuum model (PCM)<sup>23</sup> with acetonitrile as the solvent. 6-31G (d)<sup>24</sup> basis set was used for all the atoms in the calculation.

### Thermal Studies

The thermal stability of compounds was analyzed using a PerkinElmer STA-6000 thermogravimetric analyser (TGA) under a nitrogen atmosphere from 40 to 800 °C at 10 °C min<sup>-1</sup> using aluminium pans.

## RESULT AND DISCUSSION

The UV/Vis absorption spectra of compounds in acetonitrile (ACN) are given in Fig. 1. The optical energy band

gap of compounds was determined from the onset of UV/Vis spectra and are listed in Table 1. The band gap is ranging from 3.8 to 4.8 with the corresponding order **C3** > **C1** > **C2** > **C4** > **C6** > **C5**. The compound exhibited a band gap of 4.14 eV when one hydrogen of an amine of triazine is replaced by phenyl (**C2**). There is an increase in the band gap (4.17 eV) when one hydrogen of each amine of azine is replaced by phenyl (**C1**).

The band gap is shifted to 4.01 eV, 3.91 eV, and 3.84 eV respectively when the substitution of the phenyl group attached to triazine is changed to trifluoromethane (**C4**), methoxy (**C6**) and ester (**C5**). -CF<sub>3</sub> increased the bandgap than -OCH<sub>3</sub> and -CO<sub>2</sub>Et. Similarly, the replacement of hydrogen of two amine groups of triazine molecule by (trifluoromethyl) phenyl (**C3**) effected an increase in the band gap (4.83 eV). Thus, the change of functional group in the substituted triazine markedly affected the band gap. The band gap of a material can be tailored by choosing

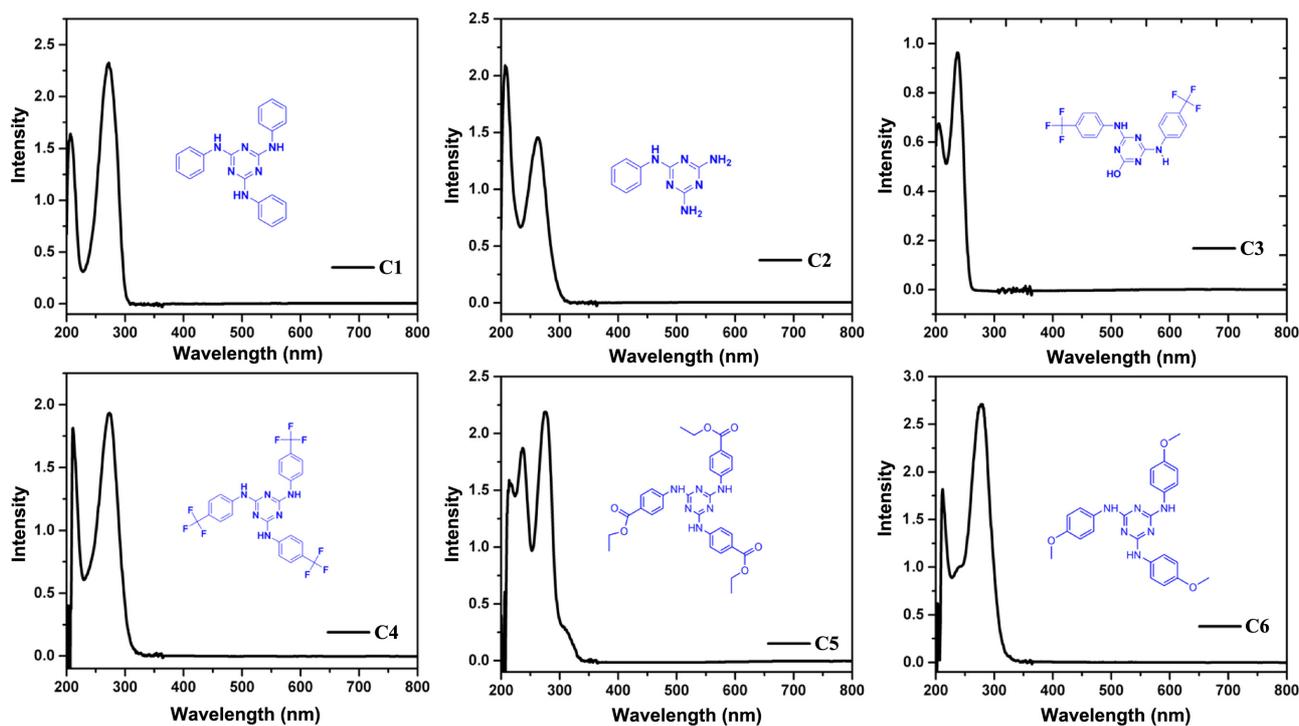
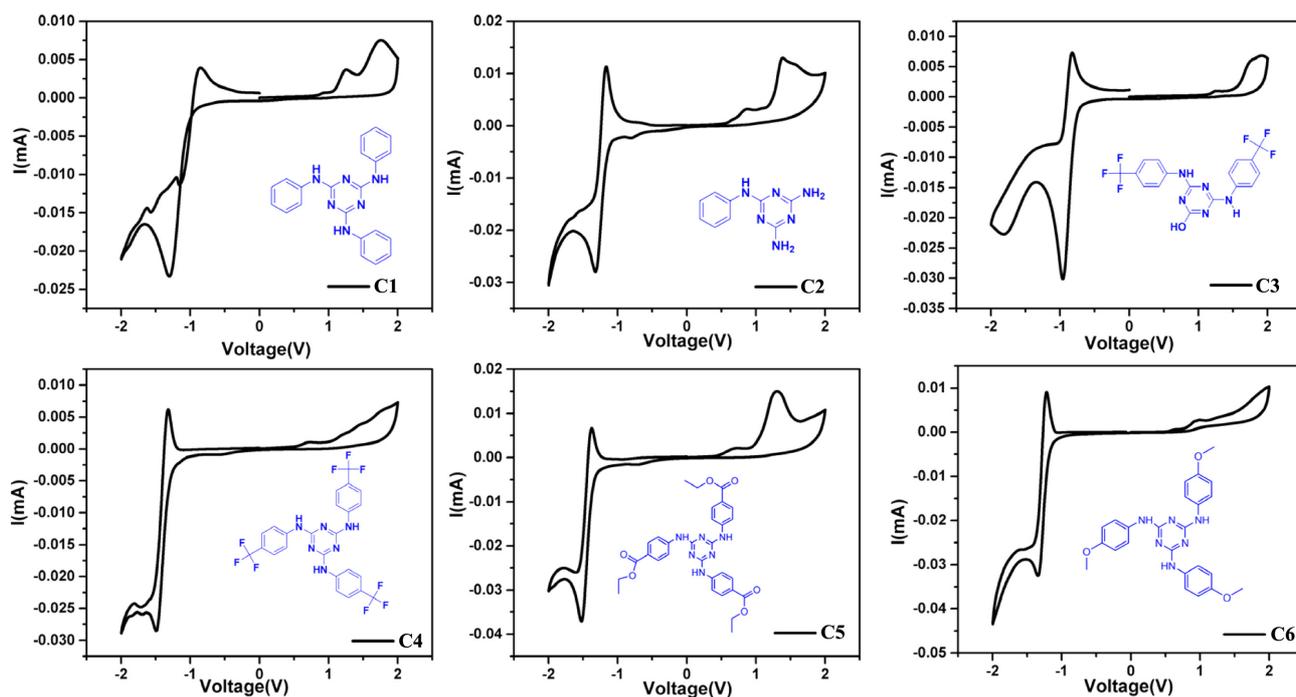


Figure 1. UV-Visible spectra of synthesized compounds.

Table 1. Optical band gap calculation from UV-Visible spectroscopy

No	Samples	Molecular Formula	Wavelength Max (nm)	Band gap (eV) 1242/λ (nm)
1	<b>C1</b>	C <sub>21</sub> H <sub>18</sub> N <sub>6</sub>	298	4.17
2	<b>C2</b>	C <sub>9</sub> H <sub>10</sub> N <sub>6</sub>	300	4.14
3	<b>C3</b>	C <sub>17</sub> H <sub>11</sub> F <sub>6</sub> N <sub>5</sub> O	257	4.83
4	<b>C4</b>	C <sub>24</sub> H <sub>15</sub> F <sub>9</sub> N <sub>6</sub>	310	4.01
5	<b>C5</b>	C <sub>30</sub> H <sub>30</sub> N <sub>6</sub> O <sub>6</sub>	323	3.84
6	<b>C6</b>	C <sub>24</sub> H <sub>24</sub> N <sub>6</sub> O <sub>3</sub>	318	3.91



**Figure 2.** Cyclic voltammogram of synthesized compounds.

**Table 2.** The HOMO-LUMO values from cyclic voltammetry using UV-Visible spectroscopy

Compound	$E_{ox}$ volt (From CV)	$E_{HOMO}$ eV [ $E_{ox} - E_{1/2} + 4.8$ ]	Optical Band gap (from absorption studies)	$E_{LUMO}$ ( $E_{HOMO}$ - Optical bandgap)
C1	0.9734	5.4694	4.17	1.2994
C2	0.6828	5.1788	4.14	1.0388
C3	1.1568	5.6528	4.83	0.8228
C4	0.5797	5.0757	4.01	1.0657
C5	0.4965	4.9925	3.84	1.1525
C6	0.5817	5.0777	3.91	1.1677

suitable functional groups.

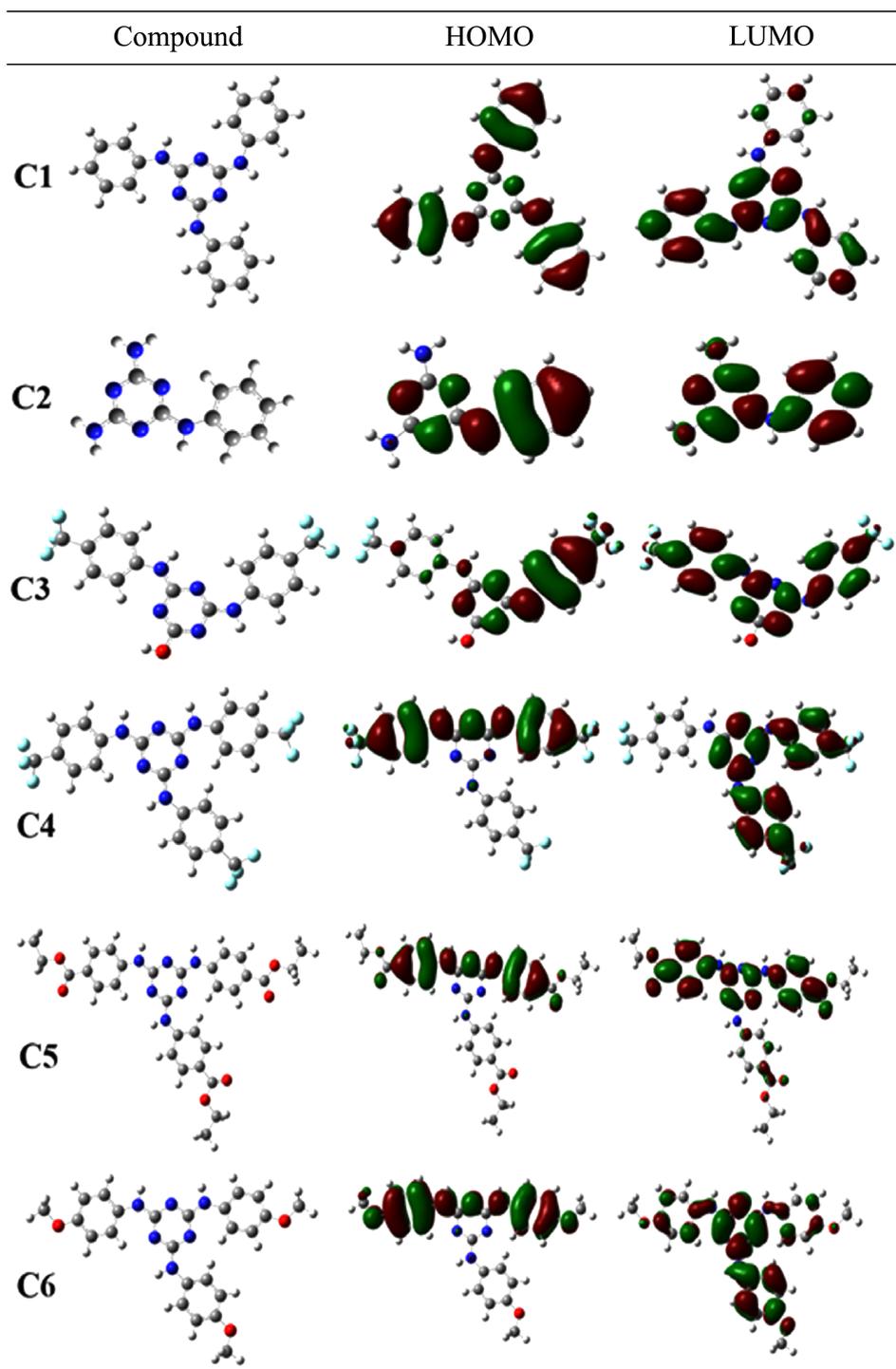
Electrochemical properties of compounds were investigated by cyclic voltammetry (CV). Cyclic voltammogram of synthesized compounds are given in *Fig. 2*. All the compounds underwent quasi-reversible redox behavior. LUMO, HOMO, and the energy gap ( $E_g$ ) are calculated from the onset potential of electrochemical reduction and oxidation (*Table 2*). Since substituents dominate the HOMOs

of compounds, their HOMO energy levels are similar with little variation.

Whereas, a significant difference was observed for LUMOs. This independent modification of HOMO and LUMO of compounds with different substituents can greatly facilitate the molecular design of the desired materials. In a comparison of the substitutions, compounds with electron releasing group (C1, C2, C6) shows an increase in

**Table 3.** DFT and TD-DFT computed HOMO-LUMO energy levels (in eV) for C1-C6

Compound	HOMO (eV)	LUMO (eV)	HOMO-LUMO energy gap (eV)	TD-DFT (eV)
C1	5.699	0.631	5.068	4.491
C2	5.506	0.208	5.299	4.810
C3	6.372	1.376	4.996	4.643
C4	6.293	1.364	4.929	4.322
C5	6.010	1.429	4.581	3.996
C6	5.093	0.288	4.804	4.234

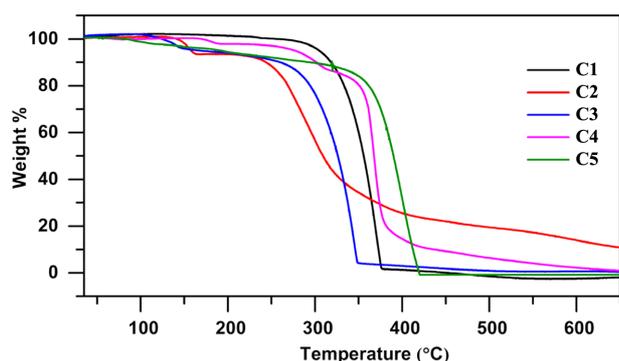


**Figure 3.** Spatial distributions of HOMOs and LUMOs of substituted triazine.

the LUMO, whereas electron withdrawing group results in the decrease of LUMO in the following order  $C2 > C6 > C1 > C4 > C3 > C5$ .

The HOMO-LUMO energy levels are calculated com-

putationally and given in *Table 3*. The spatial distribution of the HOMO and LUMO is shown in *Fig. 3*. From the molecular orbitals (MO's) of C1-C6, the LUMO is mainly distributed on the triazine core, and the HOMO is dis-



**Figure 4.** Thermogram of synthesized compounds.

**Table 4.** Thermo gravimetric analysis of synthesized compounds

Compounds	Molecular mass	Decomposition temperature
C1	354.15	273
C2	202.09	134
C3	415.08	104
C4	558.12	164
C5	314.14	324
C6	570.22	261

tributed over the substituents. The triazine core acts as an acceptor whereas the substituents as a strong donor. This donor-acceptor design of compounds can lead to separated electron density distribution between the HOMO and LUMO, which is shown in **C1**, **C2**, **C3**, **C4**, **C5**, **C6**. This separation is responsible for the efficient hole and electrontransporting properties for the materials.

The HOMO-LUMO calculation using the cyclic voltammetry (CV) and by the DFT studies are comparable. The lower LUMOs of compounds endorse to optoelectronic devices due to good electron ejection and transportation.

The thermal stability of the compounds are analyzed by thermo gravimetry. The TGA thermogram is given in *Fig. 4*, and decomposition temperature is listed in *Table 4*. All compounds show good thermal stability. The thermal stability order of the synthesized compound is **C5**>**C1**>**C6**>**C4**>**C2**>**C3**. Compound **C1**, **C4**, **C5** and **C6** have more phenyl group substitution than compound **C2** and **C3**. Thus, the decomposition temperature can also be tuned by changing the substitutions of different groups in the basic structure **A1**. The thermal properties of compounds are good for optoelectronic devices. The synthesized compounds have good solubility in acetonitrile and chloroform, which prominently increases the processing nature and applications of the triazine-based materials.

## CONCLUSION

In summary, a new series of conjugated differently substituted 1,3,5-triazines have been synthesized using a simple synthetic strategy that will greatly inspire the research of the triazine-based electroactive molecule. The results indicate the HOMO-LUMO values of 1,3,5 Triazine is influenced mainly by the substituent on the triazine ring as well as their symmetry. Here, we found that donor and acceptor can tune the energy level of the molecules. So, a superior material can be designed, and their thermal, electrochemical and optical property can be tuned by changing the substituent of 1,3,5-triazine. The synthesized compounds also showed good thermal stability, solubility and can be further processed for use in optoelectronic device applications.

**Acknowledgments.** The authors are extremely grateful and sincerely acknowledge Dr. Archana Velloth, Postdoctoral Researcher, Computational Chemistry Lab and Institute for Molecular Science, Okazaki, Aichi, Japan for providing the DFT studies. Publication cost of this paper was supported by the Korean Chemical Society.

**Supporting Information.** Additional supporting information is available in the online version of this article.

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