Synthesis and Characterization of Pyrazine Derived Compounds as Potential Materials for Hole Transporting Layer (HTL)

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Abstract

Three simple compounds that have the potential as a hole transporting layer (HTL) based on pyrazine derivatives conjugated with electron donor groups in the form of triphenylamine have been successfully synthesized and characterized. The synthesis began with a substitution reaction at high temperatures between 4- bromoaniline and 4-iodoanisole to produce 4-bromo-N,N-bis(methoxyphenyl) aniline, followed by substitution of bromo atoms with tributylstannan at low temperatures and inert atmosphere (N2) producing 4-methoxy-N-(4- (tributylstannyl)phenyl)aniline. The conjugation reaction was carried out through a Stille coupling reaction between 1,2-bis (4-bromophenyl)ethane-1,2-dione with 4-methoxy-N-(4-(tributylstannyl)phenyl)aniline at high temperatures with the aid of a Pd(PPh3)4, catalyst in an inert atmosphere (N2). The reaction was continued with the imination reaction with 3 compounds, i.e., 1,2-diaminobenzene, 3,3- diaminobenzidine and 2,3-diaminopiridin to produce three HTL compounds that were namely 4',4''-(quinoxaline-2,3-diy)bis (N,N-bis(4(methoxyphenyl)-[1,1'-biphenyl]-4-amine) (DNB), 4',4'' -(quinoxaline-2,3-diy)bis (N,N-bis([6,6'-biquinoxaline]-2,2',3,3'- tetrayl) tetrikis(N,N-bis(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine) (bDNB), and 4',4''-(pyrido[2,3-b]pyrazine-2,3-diy)bis(N,N-bis-(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine) (DNP). The optical and electrochemical properties of DNB, bDNB, and DNP were analyzed by UV-Vis and Differential Pulse Voltammetry (DPV). The optical and electrochemical properties show the energy levels of the HOMO and LUMO of the three compounds. Hence their potential can be estimated as HTL compounds. The three compounds show λmax of 348 nm, 356 nm, and 350 nm for DNB, bDNB, and DNP. Based on DPV results, the HOMO values for DNB, bDNB, and DNP are -5.03 eV, -5.02 eV, and -4.98 eV and LUMO values of -2.46 eV, -2.76 eV and -2.87 eV, respectively. The three compounds' thermal properties were analyzed using TGA, with the results showing that the three compounds had good thermal resistance with a decomposition point above 400°C. Based on optical, electrochemical, and thermal analysis, DNB and bDNB have almost the same properties. Thus, it is expected that the three compounds have the potential as HTL material, with DNB and bDNB better than DNP.

1. Introduction

The development of electronic technology has been developing quickly; this is followed by the increasing need for electricity usage. Coal is still the primary energy source used in electricity generation. However, the use of coal causes many losses, such as environmental pollution, air pollution [1], or even respiratory disorders [2].

Based on these problems, we need a renewable electricity source that is more environmentally friendly such as hydroelectric energy [3], geothermal electric energy [4], or solar electric energy (solar panels). From several renewable energy sources, solar panels are promising renewable sources because of their unlimited sources. However, the use of solar panels as an energy source still has its challenges in its application, such as
expensive materials or low energy conversion. Based on data compiled by the National Renewable Energy Laboratory (NREL), solar panels made from Si–active crystals still hold the highest conversion efficiency, compared to solar panels with other active ingredients, such as organic solar panels, or perovskite. To that end, researchers in the field of materials to date have tried to find ways to optimize the value of power conversion energy (PCE) from solar panels, both research in the manufacture of devices (devices) or the synthesis of potential compounds for solar panels [5].

Several solar panels have evolved, such as organic photovoltaic (OPV) with active ingredients in the form of small organic compounds or polymers, Si–crystalline, and Perovskite Solar Cells (PSC). Perovskite is a calcium titanium oxide (CaTiO₃) mineral that was discovered by Gustave Rose in 1839. In perovskite solar panels, the term perovskite used does not refer to CaTiO₃ crystals, but crystalline compounds that have the same structure as CaTiO₃ [6]. During its development, one of the perovskites used in solar cells was methylammonium lead halide (CH₃NH₃PbI₃) developed by Miyasaka. CH₃NH₃PbI₃ as an active component in solar cells has advantages such as low exciton binding energy, sharp optical absorption, and good carrier diffusion–length [7].

PSC is composed of several essential parts, such as transparent conductive layers (IOP, indium tin oxide), the electron transporting layer (ETL), active layer (perovskite), the hole transporting layer (HTL), and metal electrodes. The composition of the PSC can be seen in Figure 1(i). HTL is a part that functions to transfer holes (positive charges) to the electrodes. Generally, this section uses Spiro-OMeTAD (Figure 1(ii)) as its forming material. However, Spiro-OMeTAD is a compound that is difficult to synthesize and purify, so we need a new compound that is easier to make and has a high PCE when used in PSC[8].

![Figure 1. (i) PSC composition; (ii) Spiro-OMeTAD structure](image)

Liu et al. [9] succeeded in making a simple HTL based on carbazole derivatives with three electron–rich groups in the form of triphenylamine, named LD22 with λ_max of 381 nm. LD22 has HOMO and LUMO of −5.27 eV and −2.30 eV, respectively, while Spiro-OMeTAD (λ_max = 386 nm) with the same measurement method, has HOMO and LUMO values of −5.14 eV and −2.15 eV. LD22 achieved PCE up to 13% when applied to the PSC, while Spiro-OMeTAD produced PCE 17.18% when applied to the same device. Cui et al. [10] could also synthesize simple HTL compounds from hexaphenylbenzene (HPB) derivatives with the donor group triphenylamine. HPB has HOMO and LUMO values of −5.20 eV and −2.10 eV with λ_max of 367 nm and can reach PCE up to 12.9%. Based on this, then, in this study, developed an organic material based on pyrazine derivatives with an electron donor group triphenylamine, which can be used as HTL.

![Figure 2. (i) LD22 structure; (ii) HPB structure](image)

2. Methodology

The synthesis of 4′,6′- ((quinoksalin–2,3-diol)bis(N,N-bis(4-methoxyphenyl)–[1,1′-biphenyl]–4-amine) (DNB), 4′,4′′,4′′′,4′′′′-(16,6′-biquinoxaline)–2,2′,3,3′-tetracyl) tetraakis(N,N-bis(4-methoxyphenyl)–[1,1′-biphenyl]–4-amine) (bDNB), and 4′,4′′′-(pyridine2,3-b)pyrazine–2,3-diylibis(N,N-bis(4-methoxyphenyl)–[1,1′-biphenyl]–4-amine) (DNP) started from synthesis 4′-bromo-N,N-bis(4-methoxyphenyl)aniline (a) using starting material 4′-bromoanilin (i) and 4′-iodoanisole (j) (step i). In stage ii, the transformation of Br group to tributyltin chloride was carried out through a substitution reaction between compound (a) and tributyltin chloride (d) to produce 4′-methoxy-N-(4′-tributylstanyl)phenyl)aniline (b). Furthermore, the Stille coupling reaction (step iii) was carried out between compound (b) and 1,2-bis(4-bromophenyl)ethane-1,2-dione (e) so that the compound 1,2-bis(4′-bis(4-methoxyphenyl)amino)–[1,1′-biphenyl]–4-iiethane-1,2-dion (c) was obtained. From these compounds, an imitation was carried out using 1,2-diaminobenzidine (f), 2,3-diaminopyridin (g), and 3,3′-diaminobenzidine (h) to obtain the desired HTL. The complete scheme can be seen in Figure 3.

![Figure 3](image)
Figure 3. Synthesis of DNB, bDNB, and DNP

2.1. Equipment and Materials

The materials used in the experiment included 4-bromoaniline, 1-iodo-4-methoxybenzene, dry toluene, 2.5 M n-butyl lithium, tributyltin chloride, dry tetrahydrofuran (THF), 4,4’-dibromobenzil, tetrakis (triphenylphosphine) palladium (Pd(PPh)4), 1,2-diaminobenzidine, 2,3-diaminopiridin, 3,3’-diaminobenzidene, ethanol, n-butanol, chloroform-d, ethyl acetate, dichloromethane (DCM), and n-hexane. For compound characterization, 1H-NMR and 13C-NMR Bruker Model 300Hz and 500 Hz, Hitachi UV-Vis spectrophotometer, Differential pulse voltammetry (DPV) with Pt and Ag/AgCl electrodes, and Perkin Elmer TGA-7 were used.

2.2. Synthesis of 4-bromo-N,N-bis(4-methoxyphenyl)aniline (a)

4-bromoaniline (10 g, 58.13 mmol), 1-iodo-4-methoxybenzene (35.52 g, 14.53 mmol), CuI (0.554 g, 2.91 mmol), KOH (25.44 g, 45.34 mmol), 1,10-phenanthroline (0.419 g, 2.33 mmol) were put into 250 mL of a round bottom flask which has been conditioned on N2 atmosphere. Then in the mixture, 60 mL of dried toluene was added. The mixture was stirred and refluxed for 24 hours at 120°C. After that, some methanol was added to the mixture, and all the solvents were evaporated. The result of the evaporation was extracted using dichloromethane (DCM) and water. The product was purified using column chromatography with hexane: ethyl acetate (49:1) eluent to obtain compound a (16.5 g, 81.84%) as a white solid. 1H NMR (500 MHz, CDCl3): δ 7.232 ppm (d, 2H, J = 8.50), δ 7.023 ppm (d, 4H, J = 9.00), δ 6.820 ppm (d, 4H, J = 9.00), δ 6.787 ppm (d, 2H, J = 8.50), δ 3.790 ppm (s, 6H).

2.3. Synthesis of 4-methoxy-N-(4-methoxyphenyl)-N-(4’-(tributylstaniol)phenyl)aniline (b)

Compound a (2.01 g, 5.78 mmol) was put into a 100 mL round bottom flask conditioned in N2 atmosphere, then dissolved using 40 mL dry THF. After that, 2.5 M n-butyl lithium (2.5 mL, 6.36 mmol) was added to the solution of the compound a slowly, at –78°C and stirred for 2 hours (maintaining temperature). After 2 hours, Bu3SnCl (1.74 mL, 6.35 mmol) was added at –78°C, and the temperature was allowed to rise slowly until it reached room temperature and left overnight. After overnight, the NaCl solution was added to the mixture and extracted using diethyl ether/water. The organic layer obtained was dried using anhydrous sodium sulfate and evaporated. The crude was purified by distillation to obtain compound b (2.5 g, yield 72.89%) as a yellow liquid. 1H NMR (500 MHz, CDCl3): δ 7.229 ppm (d, 2H, J = 8.00), δ 7.057 ppm (d, 4H, J = 8.50), δ 6.886 ppm (d, 2H, J = 8.00), δ 6.817 ppm (d, 4H, J = 9.00), δ 3.789 ppm (s, 6H).

2.4. Synthesis of 1,2-bis(4’-bis(4-methoxyphenyl)amino)-[1,1’-biphenyl]-4-ilene-1,2-dion (c)

Compounds b (1.29 g, 2.17 mmol), Pd(PPh)4 (63 mg, 0.055 mmol), and 1,2-bis(4-bromophenyl)ethane-1,2-dione (200 mg, 0.54 mmol) were put into a 100 mL round bottom flask which had been conditioned on N2 atmosphere. Then, it was dissolved using 30 mL dry toluene. The solution was refluxed for 48 hours. After that, the reaction mixture was filtered using celite and washed with ethyl acetate. Then, all the solvents were evaporated. The evaporation results were purified using column chromatography with eluents of hexane: ethyl acetate (4:1) to obtain compound c (260 mg, 59.09% yield) as an orange solid. 1H NMR (500 MHz, CDCl3): δ 8.099 ppm (d, 2H, J = 8.50), δ 7.072 ppm (d, 2H, J = 8.50), δ 7.452 ppm (d, 2H, J = 9.00), δ 7.101 ppm (d, 4H, J = 8.50), δ 6.968 (d, 2H, J = 8.50), δ 6.857 ppm (d, 4H, J = 8.50), δ 3.866 ppm (s, 6H).

2.5. Synthesis of DNB

Compounds c (75 mg, 0.09 mmol) and 1,2-diaminobenzene (11 mg, 0.101 mmol) were mixed into a 100 mL round bottom flask and dissolved in 30 mL ethanol. The mixture was refluxed for 24 hours. After that, the reaction mixture was filtered and the solids were washed using ethanol, so that a DNB (68 mg, 82.93% yield) was obtained as a yellow solids 1H NMR (500 MHz, CDCl3): δ 8.177 ppm (dd, 2H, J = 6.00), δ 7.766 ppm (dd, 2H, J = 6.00), δ 7.013 ppm (d, 4H, J = 8.50), δ 7.545 ppm (d, 4H, J = 8.00), δ 7.444 (d, 4H, J = 8.50), δ 7.083 (d, 8H, J = 8.50), δ 6.980 (d, 4H, J = 8.50), δ 6.842 ppm (d, 8H, J = 8.50), δ 3.804 ppm (s, 12H).

2.6. Synthesis of bDNB

Compounds c (55 mg, 0.07 mmol) and 3,3-diaminobenzidine (6.5 mg, 0.03 mmol) were mixed into 100 mL round bottom flask and dissolved in 30 mL butanol. The mixture was refluxed for 24 hours. After that, the reaction mixture was filtered and the solid was washed using ethanol, so bDNB (50 mg, 92.59% yield) was obtained in the form of orange solids. 1H NMR (500 MHz, CDCl3): δ 8.593 ppm (s, 2H), δ 8.310 ppm (d, 2H, J = 9.00), δ 8.232 ppm (d, 2H, J = 8.50), δ 7.661 ppm (d, 2H, J = 8.50), δ 7.572 (d, 8H, J = 7.00), δ 7.462 (d, 8H, J = 8.50), δ 7.091 (d, 16H, J = 8.50), δ 6.991 (d, 8H, J = 9.00), δ 6.848 ppm (d, 16H, J = 9.00), δ 3.808 ppm (s, 24H).

2.7. Synthesis of DNP

Compounds c (75 mg, 0.09 mmol) and 2,3-diaminopiridin (11 mg, 0.101 mmol) were mixed into 100 mL round bottom flask and dissolved in 30 mL ethanol. The mixture was refluxed for 24 hours. After that, the reaction mixture was filtered, and the solid was washed using methanol. Then the crude was purified by column chromatography with hexane: ethyl acetate (2:1) eluent.
to obtain DNP (58 mg, 70.73% yield) in the form of orange solids. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.156 ppm (s, 1H), $\delta$ 8.518 ppm (d, 1H, J = 7.00), $\delta$ 7.733 ppm (m, 3H), $\delta$ 7.643 ppm (m, 2H), $\delta$ 7.570 (d, 4H, J = 9.00), $\delta$ 7.457 ppm (b, 4H), $\delta$ 7.077 ppm (b, 8H), $\delta$ 6.842 ppm (d, 4H, J = 8.50), $\delta$ 6.845 ppm (d, 8H, J = 8.00), $\delta$ 3.804 ppm (s, 12H).

2.8. NMR analysis

NMR is a qualitative analysis method for determining the chemical structure of a compound. In this study, $^1$H-NMR was used, spectra were recorded with 300 MHz Bruker and 500 MHz using CDCl$_3$ solvent.

2.9. Ultraviolet-visible (UV-Vis) analysis

All final compounds were analyzed using a UV-Vis spectrophotometer. 0-dichlorobenzene was used as a solvent and a blank solution. The cuvette was made of orz with a thickness of 10 mm. The results of the UV analysis were used to calculate the energy gap ($E_g$) with the formula:

$$E_g = \frac{1243}{\lambda_{\text{onset}}} \text{eV}$$

2.10. Differential Pulse Voltammetry (DPV) Analysis

Differential Pulse Voltammetry (DPV) analysis is used to determine the HOMO-LUMO level of the final compound. 0-dichlorobenzene was used as a solvent. DPV was measured in an inert condition (N$_2$) and was used ferrocene as an internal standard in measurement.

3. Results and Discussion

3.1. Optical properties

The results of the UV-Vis analysis of DNB, bDNB, and DNP compounds are presented in Figure 4. Based on these spectra results, the values of $\lambda_{\text{max}}$ for DNB, bDNB, and DNP are 348.5 nm, 356 nm, and 350 nm. In the bDNB compound, the absorption peak produced was not significantly different even though it was more conjugated than the other two compounds. This can be explained because, in bDNB compounds, the bond between C atoms in one benzene ring and C in another benzene rotates (there is a dihedral angle), so the conjugation of bDNB becomes imperfect [11]. This gives an effect on the value of $\lambda_{\text{max}}$ obtained. Based on these data, the three compounds have $\lambda_{\text{max}}$ below 400 nm, as well as the Spiro-OMeTAD uptake ($\lambda_{\text{max}} = 386$ nm) [9], so that the absorption does not overlap with the absorption of perovskite. The existence of additional peaks that overlap with the perovskite absorption often leads to reduced photocurrent in the solar panel, thus disrupting the efficiency of the solar panel [12].

3.2. Electrochemical properties

DPV analysis is used to obtain the reduction potential and oxidation potential of DNB, bDNB, and DNP, so the HOMO-LUMO value of each compound can be calculated. The values of HOMO, LUMO, reduction potential, oxidation potential, and $E_g$ of the three compounds are summarized in Table 1. The LUMO values for the three compounds are $-2.46$ eV, $-2.76$ eV, and $-2.87$ eV for DNB, bDNB, and DNP. In DNB and bDNB compounds, different LUMO values are obtained, because bDNB has more electron-pushing groups than DNB, so the LUMO level of bDNB is more negative. The LUMO value on DNP is more negative when compared to the analogs, namely DNB. This more negative value is due to the presence of more electronegative N atoms in the pyridine ring. In contrast to LUMO, the HOMO values in the three compounds do not differ significantly. The overall energy level of HOMO-LUMO in the three compounds is illustrated using the diagram in Figure 5.

Spiro-OMeTAD is a commercial compound used as HTL material in general, having HOMO, LUMO, and $E_g$
values of −5.14 eV, −2.15 eV, and 2.99 eV, respectively[9]. For PSC applications, the HOMO value must be more positive than the HOMO value of perovskite (HOMO value \(CH_3NH_3PbI_3 = -5.4\) eV) [13], so that the hole more easily flow towards the electrode. In line with HOMO, the LUMO value from HTL must be more positive than the LUMO from perovskite (LUMO value \(CH_3NH_3PbI_3 = -3.9\) eV) [13], thus preventing electrons from flowing towards HTL. The three new HTL compounds that have been synthesized, both DNB, bDNB, and DNP, have HOMO-LUMO characteristics that are not much different from Spiro-OMeTAD. Thus, it is expected that these compounds can be applied as HTL in PSC.

| Compound | \(E_{oc}(V)\) | \(E_{on}(V)\) | LUMO (eV) | HOMO (eV) | \(E_{gap}\) (eV) |
|----------|---------------|---------------|-----------|-----------|----------------|
| DNB      | −1.74         | 0.83          | −2.46     | −5.03     | 2.57           |
| bDNB     | −1.44         | 0.82          | −2.76     | −5.02     | 2.26           |
| DNP      | −1.33         | 0.78          | −2.87     | −4.98     | 2.10           |

Figure 5. Energy level diagram of DNB, bDNB, and DNP

3.3. Thermal properties

Thermal properties were analyzed using Thermogravimetric analysis (TGA) to determine the heat resistance of the three final compounds synthesized. Besides TGA, the melting point apparatus is also used to determine the melting point of each compound. Based on the melting point apparatus results, the melting points for DNB, bDNB, and DNP were obtained respectively 254.3°C, 290.2°C, and 257.5°C. The melting point of the three compounds is higher than that of Spiro-OMeTAD (commercial HTL), which has a melting point of 240°C. Based on the TGA results, a decomposition point (5% weight loss) for DNB, bDNB, and DNP were obtained at temperatures of 437.3°C, 445.6°C and 400.9°C respectively, while Spiro-OMeTAD was at 424°C [14]. Based on these data, it is obtained that bDNB has the highest decomposition point. This is possible because bDNB has a higher molecular weight than the other two. From the TGA results, it can be concluded that the three compounds have good thermal stability to be used as HTL material.

Figure 6. TGA graph of DNB, bDNB, and DNP

4. Conclusions

Three new pyrazine-based compounds, DNB, bDNB, and DNP have been successfully synthesized and characterized. Based on UV-Vis observations, the three compounds had \(\lambda_{max}\) each of 348.5 nm, 356 nm, and 350 nm for DNB, bDNB, and DNP (while in commercial Spiro-OMeTAD, \(\lambda_{max} = 386\) nm). Based on DPV results, the HOMO values for DNB, bDNB, and DNP are −5.03 eV, −5.02 eV, and −4.98 eV, while the LUMO values are −2.46 eV, −2.76 eV, and −2.87 eV, respectively. The HOMO-LUMO value of the three compounds is not much different from the HOMO-LUMO from Spiro-OMeTAD (HOMO = −5.14 eV, LUMO = −2.14 eV). The melting points for DNB, bDNB, and DNP are 254.3°C, 290.2°C, and 257.5°C respectively, which is higher than that of Spiro-OMeTAD (240°C), with a decomposition point of 437.3°C, 445.6°C, and 400.9°C. The decomposition point of the three compounds is above 400°C, so it can be said that the three compounds have good thermal stability. With the appropriate optical, electrochemical, and thermal properties (almost the same as the commonly known HTL, Spiro-OMeTAD), it is expected that DNB, bDNB, and DNP have the potential to be applied as HTL on perovskite solar panels, with DNB and bDNB being better than with DNP.

Acknowledgments

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1.2. 1H NMR (500 MHz) 4-
metoksi-N-(4-
metoksifennil)-N-
(tributilstanil)anilin (b)

1.1. 1H NMR (500 MHz) 4-
bromo-N,N-bis(4-metoxiphenil)anilin (a)
1.3. $^1$H NMR (500 MHz) 1,2-bis(4′-bis(4-methoxyphenyl)amino)-[1.1′-biphenyl]-4-il)ethane-1,2-dion (c)

1.4. $^1$H NMR (500 MHz) DNB
1.5. $^1$H NMR (500 MHz) DNP

Di-N-Pyridine (STL)

1.6. $^1$H NMR (500 MHz) bDNB
1.7. $^{13}$C NMR (500 MHz) DNB

20190725 DNB-2TPA

1.8. $^{13}$C NMR (500 MHz) bDNB

20190625 bDNB-4TPA

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2. Mass Spectra (MS)

2.1. Mass Spectra of DNB (Exact Mass = 888.3676)
2.2. Mass Spectra of DNP (Exact Mass = 889.3628)
2.3. Mass Spectra of bDNB (Exact Mass = 1774.7195)

![Mass Spectra of bDNB](image)

3. Optical, Thermal and Electrochemical Properties of Final Compounds

| Compound | TGA (°C) | UV-Vis $\lambda_{\text{max}}$ (nm) | $E_{\text{gap}}$ (eV) | DPV (eV) |
|----------|---------|-----------------------------------|-----------------------|-----------|
|          |         |                                   | DPV                   | UV-Vis    | E_{re} (V) | E_{ox} (V) | HOMO | LUMO |
| DNB      | 437.3   | 348                               | 2.57                  | 2.65      | -1.74      | 0.83       | -5.03 | -2.46 |
| bDNB     | 445.6   | 356                               | 2.26                  | 2.50      | -1.44      | 0.82       | -5.02 | -2.76 |
| DNP      | 400.9   | 350                               | 2.10                  | 2.49      | -1.33      | 0.78       | -4.98 | -2.87 |

*a 5% weight loss, measured by TGA.

b Use o-dichlorobenzene as a solvent.

c $E_{\text{gap}} = \text{LUMO-HOMO}$.

d Calculated based on $\lambda_{\text{onset}}$, $E_{\text{gap}} = 1240/\lambda_{\text{onset}}$.

e All potential reported by DPV with ferrocene as internal standard in o-dichlorobenzene, LUMO = -(E_{ox} + 4.2), HOMO = -(E_{re} + 4.2)