SYNTHESIS OF PHENOTHIAZINE DERIVATIVES AS NOVEL MOIETIES TOWARD UTILIZATION IN ALTERNATIVE DONOR – ACCEPTOR CONJUGATED POLYMERS

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ABSTRACT

Two new phenothiazine – based structures, including 4-(10H-phenothiazin-10-yl)-N,N-diphenylaniline (PDA) and 10-(pyren-1-yl)-10H-phenothiazine (PyP) were synthesized via Buchwald-Hartwig C-N coupling amination using catalytic palladium modulated by electron-rich ligands. Chemical structures were analysed via proton nuclear magnetic resonance (¹H NMR) spectroscopy. Then, photo-properties were characterized by UV – Vis absorption spectroscopy in various concentrations of each product. The results showed that PDA and PyP are highly potential donor units for well-performed donor – acceptor conjugated polymers.

Keywords: C-N coupling, Buchwald-Hartwig amination, phenothiazine – based structures, donor units.

1. INTRODUCTION

Since Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa were awarded jointly the Nobel Prize in Chemistry 2000 for their discovery and development of conductive polymers, conjugated polymers have been attracting great concern from scientists as well as businesses thanks to their widespread applications in a broad range of fields. Among the various types of this materials that have been researched and developed for the many years the donor – acceptor conjugated polymers (D – A CPs) with its distinctive structure have offered a large variety of applications, especially in the field of flexible electronic applications.

The most noticeable point in the structure of D – A CPs is that they have two alternating moieties along their polymer backbone, involving an electron-rich donor and an electron-deficient acceptor. When compared with the classic classes, such as poly(3-hexylthiophene-2,5-diyl), polyacetylene, having only one moiety, this type of CPs have presented obvious advantages, especially the low energy bandgap, high mobility charge carriers and the ability to
tune energy level [1, 2]. As a result of well-performed properties, this kind of CPs have been researched and applied in several devices, such as organic field-effect transistors (OFETs) [3-5], electrochromic device (ECDs) [6, 7], and organic solar cells (OSCs) [2, 8]. The development of novel donor and acceptor units have also achieved dramatic progresses. While diketopyrrolopyrrole, isoindigo, and indacenodithiophene are currently considered the most common acceptor units, the evolution of donor moieties have branched in many routes, such as cyclopenta[2,1-b:3,4-b']dithiophene, dithieno[3,2-b:2',3'-d]silole, dithieno[3,2-b:2',3'-d]pyrrole, and 2,7-carbazole [8]. Although there are not many reports about phenothiazine derivatives for synthesis D–A CPs presenting high performance in OFETs [9-11], this aromatic class still has great potential due to its modification and combination ability. Therefore, in this study, we have described the synthesis and investigated the chemical structures as well as photo-characteristics of two novel modified phenothiazine compounds that can be used as electron-rich units in D-A CPs.

2. EXPERIMENTAL SECTION

2.1. Materials

All reagents or starting materials used in this research were commercial products. Triphenylamine (98 %), pyrene (98 %), phenothiazine (PT, 99 %), Pd(OAc)_2 (99 %), N-bromosuccinimide (NBS), sodium tert-butoxide (NaOt-Bu, 98 %), and tri-tert-butylphosphine (P(t-Bu)_3, 99 %) were supplied by Sigma Aldrich. Potassium carbonate (K_2CO_3, 99 %) was purchased from Merck. All solvents, including toluene, hexane, ethyl acetate (EtOAc), dimethyl formamide (DMF), and chloroform (CHCl_3), were used as received or purified or dried by known methods. Silica gel 60A (Fisher Scientific) was used in the separation and purification of compounds by column chromatography.

2.2. Instrumentation

_1^H NMR spectra were recorded at room temperature in deuterated chloroform (CDCl_3) with tetramethylsilane (TMS) as an internal reference, on a Bruker Avance spectrometer (500 MHz) while UV - Vis absorption spectra were obtained on a UV-Vis 2450 spectrophotometer.

2.3. Synthesis of 4-bromo-N,N-diphenylaniline (4BA)

The reaction condition for 4BA synthesis was similar to the literature [12]. Firstly, triphenylamine (294.4 mg, 1.20 mmol) and anhydrous DMF (4 mL) were added to a 50 mL two – necked flask at 0 °C. Aluminum foil was thoroughly wrapped around to cover the reaction vial, blocking out light. In the dark, N-bromosuccinimide (NBS) (213.6 mg, 1.20 mmol) in 2 mL anhydrous DMF was slowly added to this solution using dropping funnel, and stirred for 4 h at 0 °C and 20 h at room temperature. Then, the reaction was terminated with a 2 M HCl solution, extracted with CHCl_3 and dried with anhydrous K_2SO_4. The product was purified using column chromatography (hexane) to afford white solid (376.9 mg, 96.9 %). _1^H NMR (500 MHz, CDCl_3), δ (ppm): 7.30 (m, 6H), 7.07 (m, 6H), 6.93 (d, 2H). Percent purity (%), by _1^H NMR: 97 %.
2.4. Synthesis of 1-Bromopyrene (1BP)

The procedure resembles that for preparing 4BA. Pyrene (242.7 mg, 1.20 mmol) and anhydrous dimethyl formamide (DMF) (4 mL) were added to 50 mL 2-necked flask at 0 °C. Aluminum foil was thoroughly wrapped around to cover the reaction vial, blocking out light. In the dark, N-bromosuccinimide (NBS) (213.6 mg, 1.20 mmol) in 2 mL anhydrous DMF was slowly added to this solution using dropping funnel, and stirred for 4 h at 0 °C and 20 h at room temperature. Next, the reaction was terminated with a 2 M HCl solution, extracted with CHCl₃ and dried with anhydrous K₂SO₄. The product was purified using column chromatography (hexane) to afford white solid (329.6 mg, 97.7 %).

1H NMR (500 MHz, CDCl₃), δ (ppm): 8.41 (d, 1H), 8.24 - 8.19 (m, 3H), 8.16 (d, 1H), 8.09 (d, 1H), 8.04 - 7.98 (m, 3H). Percent purity (%), by 1H NMR: 96 %.

2.5. Synthesis of 4-(10H-phenothiazin-10-yl)-N,N-diphenylaniline (PDA)

The experiment conditions were referred and chosen based on the literature [13-15]. A 50 mL storage flask equipped with a magnetic stir bar was flamed under vacuum and back filled with nitrogen three times. The flask was then charged with NaOt-Bu (72.1 mmg, 0.750 mmol, 1.5 eq), Pd(OAc)₂ catalyst (4.5 mg, 0.020 mmol, 4 mol%), P(t-Bu)₃ ligand (8.1 mg, 0.040 mmol, 8 mol%), PT (129.5 mg, 0.650 mmol, 1.3 eq), 4BA (162.1 mg, 0.500 mmol, 1.0 eq) and dry toluene (5 mL). Next, the flask was placed in an oil bath at 110 °C with stirring for 6 h. After being cooled to room temperature, the mixture was diluted with CHCl₃, washed with brine, water, dried with K₂SO₄, and purified using column chromatography (EtOAc: hexane = 1:30). The product was dried under reduced pressure to gain 157.4 mg of a white solid (71.1 % yield).

1H NMR (500 MHz, CDCl₃), δ (ppm): 7.30 (t, 4H), 7.19 (m, 8H), 7.07 (t, 2H), 6.97 (d, 2H), 6.88 (t, 2H), 6.79 (t, 2H), 5.98 (d, 2H). Percent purity (%), by 1H NMR: 97 %.

2.6. Synthesis of 10-(pyren-1-yl)-10H-phenothiazine (PyP)

This reaction was also carried out in oven-dried flask under purified nitrogen. To simplify the issue, the procedure for synthesizing PyP was calculated in regard to the reaction PDA. The only difference was the adding substance step, instead of 4BA, 1BP (140.6 mg, 0.500 mmol, 1.0 eq) was added to the flask. After the similar treatment and purification processes, the product was dried under reduced pressure to gain 146.4 mg of a yellowish white solid (73.3 % yield).

1H NMR (500 MHz, CDCl₃), δ (ppm): 8.38 - 8.06 (m, 9H), 7.06 (d, 2H), 6.78 (t, 2H), 6.67 (t, 2H), 5.98 (d, 2H). Percent purity (%), by 1H NMR: 96 %.

3. RESULTS AND DISCUSSION

The structure and synthesis routes of two new monomers are illustrated in Scheme 1. In the first step, the brominations of triphenylamine and pyrene, which were carried out by using NBS in DMF, performed high conversions with 96.9 % and 97.7 %, respectively. The chemical structures of these intermediate products were characterized via 1H NMR spectra. When compared to corresponding results in reported articles [12, 16], the chemical shifts and protons’s integration of prepared 4BA and 1BP were revealed the similar outcomes. After that, two new monomers, involving PDA and PyP, were gained through the amination reactions. The results which were based on Buchwald-Hartwig C-N coupling method.
[17] performed upper 70% yields in both two reactions. At the final step, the chemical structures and optical properties of these substances were analysed and discussed.

Scheme 1. Synthetic routes of PDA and PyP.

Figure 1, 2 presented the $^1$H NMR spectra of two novel phenothiazine – based compounds, PDA and PyP. After analyzed, the data showed that chemical shifts and integration of protons in each spectrum are in accordance with the designed molecule structures. As can be seen from Figure 1, specific peaks of the phenothiazine ring and triphenylamine moiety were found between 7.30-6.32 ppm while the peak corresponding to nitrogen-bounded proton (in PT molecule) could not be found, which means that the C-N bond have been formed. In Figure 2, the $^1$H NMR spectra also exhibited specific peaks belonging to phenothiazine moiety along with the multiple-peaked range from 8.38 to 8.06 ppm corresponding to pyrene aromatic. These results indicated that targeted materials have been prosperous produced by virtue of the selected procedures.

Figure 1. $^1$H NMR spectrum of PDA.
Synthesis of phenothiazine derivatives as novel moieties toward utilization in …

Figure 2. $^1$H NMR spectrum of PyP.

Figure 3. UV-Vis absorption spectra of PDA (a) and PyP (b) in CHCl$_3$.

The absorption spectra of PDA and PyP were demonstrated in Figure 3a, 3b with five different concentrations from 10 to 50 µM. All samples were dissolved in chloroform and loaded in cuvettes having 1 cm path length. By applying the Beer-Lambert-Bouguer law, the molar absorption coefficient $\varepsilon$ of each $\lambda_{\text{max}}$ was defined as the slope of the linear interpolant (demonstrated in corresponding graphs on the left of spectra). From an overall perspective, these phenothiazine – cored compounds exhibited remarkably absorption in ultraviolet range from about 230 to 355 nm. In Figure 3a, there were two separate peaks at 258 and 304 nm that giving maximum coefficients $\varepsilon$ of 33450 and 27160 (M$^{-1}$cm$^{-1}$) respectively. In Figure 3b, beside a peak at 252 nm, two other peaks at 341 and 326 nm were performed noticeable $\varepsilon$ values of 41670 and 42160 (M$^{-1}$cm$^{-1}$) when being compared to those values of quite similar chemical structures in previous reports [18, 19].
Figure 4. Difference in molar absorption coefficient $\varepsilon$ between PDA and PyP. Both samples were taken at 50 $\mu$M in chloroform.

The distinctions in molar absorption coefficient $\varepsilon$ between PDA and PyP in the same concentration were illustrated in Figure 4. PyP presented totally better absorption ability with much higher coefficient values, and its absorption wavelength extended to the near-violet range. These mentioned consequence have implied that both products can be used as donor units for the utilization of D – A CPs, especially PyP.

4. CONCLUSIONS

Two new phenothiazine derivatives, PDA and PyP, have been successfully synthesized via Buchwald-Hartwig C-N coupling amination with the present of catalytic palladium. The chemical structures of these products were analyzed by $^1$H NMR spectra while light absorption properties were characterized via UV – Vis spectroscopy in a series of different concentrations of each compound. The analyzed data showed that these products are able to absorb ultraviolet between 230 and 355 nm with exceptional molar absorption coefficients. In next procedure, these potential monomers will be used as donor units in the polymerization of novel D-A conjugated polymers.

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REFERENCES


