

Preparation and Electrochemical Properties of 3-Pyridinyl-6-aryl-1, 2, 4-triazolo [3, 4-b][1, 3, 4]thiadiazoles

Tai XIAO¹, Hui Xue LI¹, Chun Xia TAN¹, Miao CHEN*

¹College of Chemical & Engineering, Northwest Normal University, Lanzhou 730070

²Lanzhou Institute of Chemistry & Physics, Chinese Academy of Sciences, Lanzhou 730000

Abstract: A series of 3-pyridinyl-6-aryl-1, 2, 4-triazolo[3, 4-b][1, 3, 4]thiadiazoles (PATT) were prepared, the structures were confirmed by IR and ¹H NMR spectra. The results of cyclic voltammetry measurements imply that all these compounds have a higher electron affinity (E_A) than 2-(4-biphenyl)-5-(4-*tert*-butyl phenyl)-1, 3, 4-oxadiazole (PBD) which implies that PATT could be acting as better electron acceptors than widely used electron transporting material PBD.

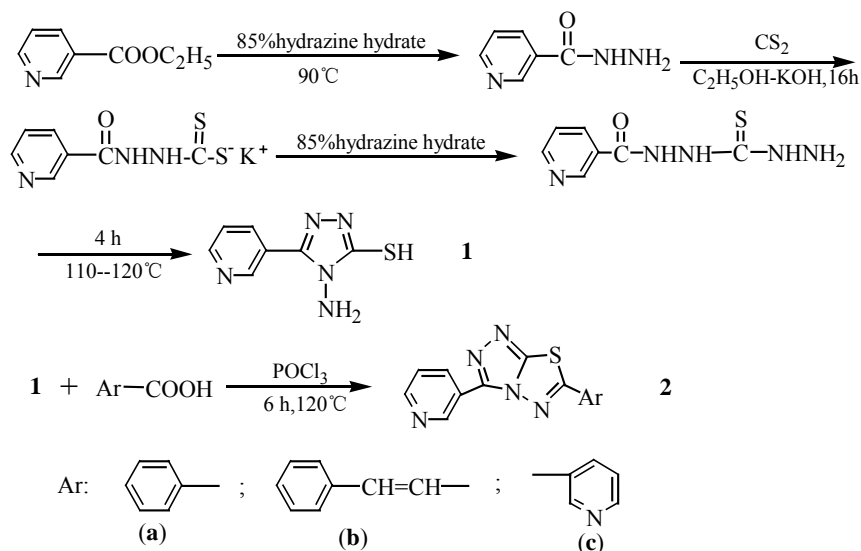
Keywords: Preparation, 3-pyridinyl-6-aryl-1, 2, 4-triazolo[3, 4-b][1, 3, 4]thiadiazoles, electrochemical properties.

In organic thin-film light-emitting diodes (LEDs), an electron transporting layer (ETL) plays an important role, it can increase electron drift mobility and block hole, and as a result, it balances injection of hole and electron, leading to more efficient exciton formation and improve quantum efficiency¹. 2-(4-Biphenyl)-5-(4-*tert*-butylphenyl)-1, 3, 4-oxadiazole (PBD) is widely used electron transporting material¹, it also appears to block holes efficiently. In this letter we reported a series of 3-pyridinyl-6-aryl-1, 2, 4-triazolo[3, 4-b][1, 3, 4]thiadiazoles (PATT), the structures of all the title compounds were confirmed by IR, ¹H NMR spectra, their electrochemical properties were carried on by cyclic voltammetry. The electron affinities (E_A) and ionization potentials (P_i) of the title compounds were calculated by the data of UV-Vis spectra. PATTs were synthesized according to the literature^{2,3}. The synthetic route is depicted in **Scheme 1**⁷.

The UV-visible spectra were taken on a Spect50 UV/Vis spectrometer, the test solution was 1×10^{-5} mol/L ethanol solution in room temperature. A CHI660 electrochemical analyzer was used for electrochemical acquisition with a three-electrode, the working electrode and counter electrode were both platinum plates, the saturated Hg/Hg₂Cl₂ was taken as the reference electrode. The basic electrolyte for the cyclic voltammetric measurement was 0.1 mol/L (Bu)₄NClO₄ in CH₃CN. The sweep rate was 50mV/s.

* E-mail: miaochen@lsl.ac.cn

Scheme 1



During the experiment of cyclic voltammetry, when electrode potential changes from positive to negative, the electron energy will be increased step by step and reach critical potential, in the result, the electrons flowed from the electrode to the lowest unoccupied molecular orbital (LUMO) of the electrolyte in solution. The critical potential is referred to onset potential during reduction ($E_{\text{onset}}^{\text{Red}}$). Also there is onset potential during oxidation ($E_{\text{onset}}^{\text{Ox}}$)⁴. The compounds electron affinity (E_A or LUMO) and ionization potential (P_I or HOMO) can be calculated by the formula as follows⁵:

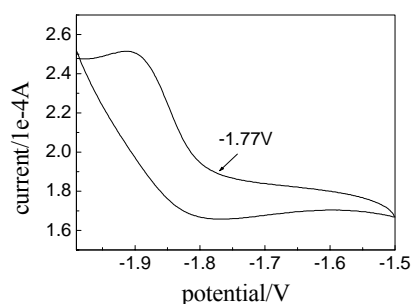
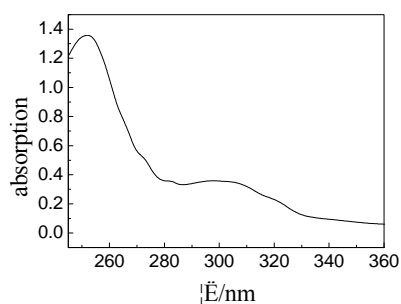
$$E_{\text{LUMO}} = E_{\text{onset}}^{\text{Red}} + 4.74$$

However, there were not oxidation peak in our experiment. In order to obtain HOMO energy level, we operated the compounds UV-Vis spectra and the band-gap were computed by onset wavelength.

Figure 1 is the cyclic voltammetry curve of compound **a**, there is a reduction peak as potential increases from -1.5 V to -2.0 V and the onset potential is -1.77 V. **Figure 2** shows the UV-Vis spectrum curve of compound **a**, onset absorption wavelength (λ_{onset}) is 330 nm, corresponding to 3.75 eV, namely the band gap is 3.75 eV.

Table 1 sets out all sorts of data from **a** to **c** and PBD. The synthesized compounds possess higher electron affinity compared with PBD, so these compounds may be good electron transport materials owing to higher E_A ⁶.

In addition, the DSC and TGA of PATT had been detected (in N_2 , $10^\circ\text{C}/\text{min}$). The onset decomposition temperatures of compound **a**, **b**, **c** are 284°C , 312°C and 293°C , respectively. However, the glass transition temperatures had not been observed in the condition.

Figure 1 The cyclic voltammetry of compound **a****Figure 2** The UV-Vis spectrum of **a****Table 1** The experimental data of a series of thiadiazole derivatives

Compound	reduction(onset/V)	UV-Vis(λ_{onset})	E _g /eV	E _A /eV	P _I /eV
a	-1.77	330	3.75	2.97	6.72
b	-1.45	355	3.49	3.29	6.78
c	-1.65	340	3.64	3.09	6.73
PBD	-1.92	---	---	2.82	6.52

References and Notes

- C. Adachi, T. Tsutsui, S. Saito. *Appl. Phys. Lett.*, **1990**, *57*(6),531.
- J. R. Reid, N. D. Heindel, *J. Heterocyco. Chem.*, **1976**, *13*, 925.
- Z. Y. Zhang, M. Li, L. Zhao, *et al.*, *Chin. J. Org. Chem.*, **1993**, *13*(4), 397.
- Z. M. Zhang, G. W. Li, Y. G. Ma, *et al.*, *Chem. J. Chin. Univ.*, **2000**, *21*(11), 1719
- K. A. Ashwini, A. J. Samson, *Chem. Mater.*, **1996**, *8*, 579.
- N. C. Greenham, S. C. Mouatti, D. D. Bradley, *Nature*, **1993**,*365*,628.
- a**: Yield 51%. m.p. 230-232°C. White crystal. IR (KBr pellet, cm⁻¹): 3062, 2930, 2910 (Ar-H), 1598(C=N), 1571, 1514, 1470, 1441 (aromatic ring skeleton vibration), 1274(N-N=C), 692 (C-S-C). ¹H NMR(DMSO-d₆, 200MHz), δ :7.52-7.59 (m, 4H, Ar-H), 7.93-8.40 (m, 4H, Ar-H), 9.21(s, 1H, Ar-H).
b: Yield 42%. m.p. 199-201°C. Pinkish white crystal. IR (KBr pellet, cm⁻¹): 3049(HC=CH), 3028, 2950, 2910 (Ar-H), 1627(C=N), 1610(C=C), 1568, 1522, 1499, 1461(aromatic ring skeleton vibration), 1262(N-N=C), 695(C-S-C). ¹H NMR(DMSO-d₆, 200MHz), δ : 7.43-7.71 (m, 6H, Ar-H), 7.80-7.83 (m, 2H, Ar-H), 8.53-8.73 (m, 2H, Ar-H), 9.39 (s, 1H, Ar-H).
c: Yield 40%. m.p. 220-222°C. White crystal. IR (KBr pellet, cm⁻¹): 3052, 2920, 2901 (Ar-H), 1590(C=N), 1574, 1525, 1457, 1427 (aromatic ring skeleton vibration), 1280(N-N=C), 697(C-S-C). ¹H NMR(DMSO-d₆, 200MHz), δ :7.65-7.70 (m, 2H, Ar-H), 8.46-8.85 (m, 5H, Ar-H), 9.26 (s, 1H, Ar-H).

Received 9 March, 2004