Synthesis and Electrochemical Properties of Organic Hole Transport Materials

Sung Jie Yeh, Chih-Yen Huang, Che Yu Tsai,
Shu-Hua Cheng, Guey-Sheng Liou,
Yulong Oliver Su
Department of Applied Chemistry,
National Chi Nan University
Puli, Nantou Hsien, Taiwan 545

We have synthesized several triarylamine and *p*-phenylenediamine compounds. Their electrochemical properties are examined by cyclic voltammetry and spectroelectrochemistry.

Cyclic voltammograms of the triarylamine series are very complicated both in the oxidation and reduction scan. Only one reversible redox in the reduction scan was observed for compound (III). The triarylamine series show electrochemically irreversible, which indicates the electrogenerated cation radicals and anion radicals are very reactive.

On the other hand, the cyclic voltammograms of the *p*-phenylenediamine series are well defined. Compound (1) exhibited two reversible oxidation redox couples at +0.95 and +1.21 V. Besides, one reversible reduction redox couple appeared at –1.06 V and one irreversible wave appeared with Ep,c at –1.68 V. The first electron removal from compound (1) yielded a stable delocalized radical cation $(1)^{+\cdot}$, and the second, a quinonoid-type dication $(1)^{2+}$. The both triarylamine center are strongly coupled by the fact that the redox couple separation is very large (△E = 260 mV).

There are two reversible redox couples at +0.34 and +0.57 and two additional oxidation waves at +1.07 and +1.50 V for compound (2). However, no reduction waves were observed within the solvent window. The electron-donating properties of amine may contribute to the oxidation potential shift to the negative direction. Changing the substituents to cyano groups formed compound (3), which exhibited two reversible oxidation redox couples at +0.92 and 1.25 V. Carboxylic acid - substituted phenylenediamine, compound (4), exhibited a very different kind of voltammetric graph. The featureless graph may be resulted from the oxidation of carboxylic substituent. The cyclic voltammogram of the tetra-cyano-substituted phenyldiamine, compound (5), was different from compound (3). Only one reversible redox couple was observed at –1.47 V.

Optically transparent thin-layer electrode (OTTLE) coupled with UV/VIS/NIR spectroscopy was used to examine the oxidation product of above reactions. Compound (1) exhibited absorption spectrum at 305 and 416 nm. After one-electron oxidation, the absorbance at 305 and 416 nm decreased gradually, while a new peak at 866 nm appeared. The spectral pattern was very similar to the chemical oxidation of methoxy-substituted phenylenediamine, where a broad and intense absorption band rises near 1000 nm. When the oxidation potential was adjusted to +1.360 V, responsible for the second-electron oxidation, the absorbance at 866 nm decreased and a new peak at 556 nm appeared. The one-electron and two-electron oxidation of compound (3) exhibited absorption spectra quite similar to those of compound (1).

The oxidation products of compound (2) were also examined by OTTLE methods. The first electron oxidation product exhibited a spectrum with three new peaks at 422, 653 and 1117 nm. The second-electron oxidation product exhibited a spectral pattern with peak at 978 nm and two shoulders at 562 and 782 nm. Oxidation of compound (2) exhibited a distinguished absorption spectral pattern, which is different from those of compound (1) and compound (3). The differences may be resulted from the transferring acidic proton in the amine groups after oxidation.

References

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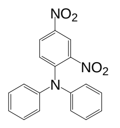
Triarylamine series



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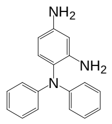

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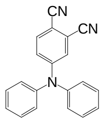

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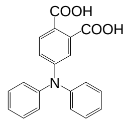
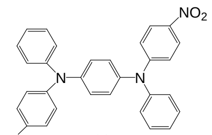


(IV)

p-phenylenediamine series



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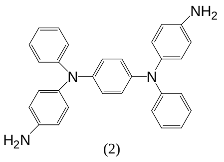

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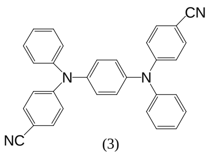

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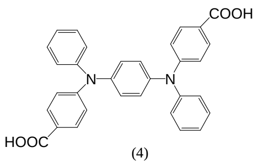

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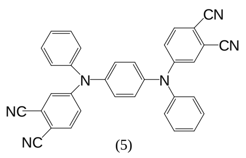

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