Synthesis and electrochemical oxidation of amino-substituted triphenylamines derivatives

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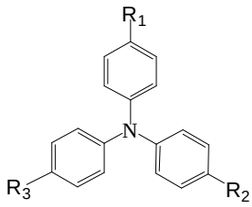
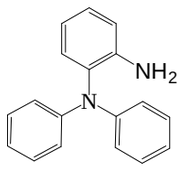
A series of amino-substituted triphenylamines (TPAs) derivatives (Figure 1) has been synthesized and their spectral and electrochemical characteristics have been investigated. When more amino groups were substituted at the phenyl position, electrochemical oxidation became easier. The TPA derivatives are more stable in CH_3CN than in CH_2Cl_2. The stability of the oxidation products were monitored with UV/VIS/NIR spectroelectrochemical investigations.

Triphenylamine (TPA) was test as a reference and showed irreversible oxidation at $E_{p,a}$ = 1.25 V in CH_2Cl_2 solution. *p*-Phenylenediamine (I) showed two reversible redox couples at $E_{1/2}$ = 0.59 and 1.09 V in CH_2Cl_2. Stable cation radical $I^{+\cdot}$ was generate electrochemically and exhibited strong bands in the visible region. The second oxidation product I^{2+} could be generated electrochemically, but was not very stable after long time electrolysis at applied potential higher than 1.15 V. The *ortho*-aminotriphenylamine (II), isomer of I, was irreversibly oxidized both in CH_2Cl_2 and CH_3CN solution. *p,p'*-Diaminotriphenylamine (III), *p*-methyl-*p',p''*-diaminotriphenylamine (IV) and *p,p',p''*-triaminotriphenylamine (V) are more stable in CH_3CN than in CH_2Cl_2 during cyclic scan at oxidation potentials. The oxidation potential of the various amino-substituted TPA derivatives and stability of the oxidized products are solvent-dependent and relate to the molecular structure.

Figure 1. Chemical structure of the amino-substituted triphenylamine compounds in this study.



TPA	R_1=H , R_2=H , R_3=H
I	R_1=NH_2 , R_2=H , R_3=H
III	R_1=NH_2 , R_2=NH_2 , R_3=H
IV	R_1=NH_2 , R_2=NH_2 , R_3=CH_3
V	R_1=NH_2 , R_2=NH_2 , R_3=NH_2



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