

**CHARGE TRANSFER AND PROTON  
DOPING OF POLYANILINE  
IN SOLID STATE  
WITH TRIFLATE SALTS:  
EFFECT ON SPECTROSCOPIC AND  
ELECTRONIC PROPERTIES**

Karin Potje-Kamloth<sup>1</sup>, Brian Polk<sup>2</sup>,  
Mira Josowicz<sup>2</sup>, Jiri Janata<sup>2</sup>

<sup>1</sup>Dresden University of Technology, Institute for  
Macromolecular Chemistry and Textile Chemistry,  
D-01062 Dresden, Germany

<sup>2</sup>Georgia Institute of Technology, School of  
Chemistry and Biochemistry, Atlanta, GA 30332-  
0400

The role of protonic and charge transfer doping of solid-state mixtures of polyaniline and triflate salts were studied spectroscopically and by measurements of work function and conductivity.

Polyaniline emeraldine base can be protonated by photo-induced formation of triflic acid leading to the formation of emeraldine salt. Triflic acid is generated by photolysis of photoacid generator triphenylsulfonium triflate salt upon irradiation of UV light<sup>1</sup>. The structural changes induced by photochemical protonation are reflected in UV-Vis and FTIR spectra. A change in the protonation degree of PANI after irradiation is observed, which can be interpreted within the framework of the polaron structure model<sup>2</sup> used for conjugated conducting polymers.

Strong protonic acids such as triflic acid lower both the work function and increase the conductivity of polyaniline according to the known protonic form of doping mechanism. It can be shown that the doping level is linearly dependent on the irradiation dose. Measurements using a field effect transistor reveals that the photoacid doping process allows, in a definitive manner, the control of the both the work function and the threshold voltage of a polyaniline-gate field-effect transistor. Residual amounts of non-decomposed photo acid generator can be removed by dipping the irradiated film into methanol in order to prevent UV light sensitivity and inadvertent post-exposure acid doping. Consequently, fine control of the UV-dose can be used to adjust the affinity of polyaniline for electron in a controlled and stable manner<sup>3</sup>.

On the other hand addition of triflate salts to emeraldine base form of polyaniline in solid state causes lowering of its work function but not an increase of its conductivity. Results obtained indicate that polyaniline polaronic character is

increased with increasing concentration of triflate anion. The hypothesized model that explains the formation of polarons is a charge-transfer from the lone pair on the PANI imine nitrogen to the cation of the salt made possible by the highly polarizing nature of the triflate anion. The doping effects occur only in the solid-state. There is no charge transfer doping of PANI dissolved in DMF. This result is also corroborated by the spectral evidence in the near IR region.

The shift in polyaniline work function is not accompanied by a similar change of conductivity, as shown by impedance measurements.

According to the proposed segmented model of PANI-EB<sup>4</sup> and localized electronic states<sup>5</sup>. It is possible to speculate that the absence of mobile charge carriers is due to the strong electronic interaction in solid state between the strongly electron donating triflate anion and the electron poor emeraldine base form of PANI leading to the formation of a charge transfer complex and localized energy states in the bandgap that does not contribute to the conductivity.

This form of charge transfer doping is in stark contrast to the oxidative and protonic doping. This distinction has important implications for use of polyaniline in various types of electronic structures. When PANI is used as the replacement for the metal in the gate of insulated gate field-effect transistor the value of work function is critically important because it controls the threshold voltage. Since there is no current passing through the polyaniline layer in such a device, its conductivity is irrelevant. However, when PANI itself is used as a conductor of electronic current the type of doping that leads to conductivity changes is important. Moreover, in some devices, such as thin-film transistors both the charge transfer and protonic doping play role in the operational characteristics of the device.

**Literature:**

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