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Review Report on the

Doctoral Thesis: *"Thermal and Electrical Properties of Nanolayer Polymers"*
Candidate/Author: Ameneh Mikaeeli

Reviewer: Marius Orlowski

The submitted doctoral thesis by Ms. Ameneh Mikaeeli addresses a highly timely and technologically relevant challenge in the field of organic electronics: the coupled electrical and thermal transport properties of PEDOT:PSS thin films. Given the material's prominence in flexible electronics and thermoelectric energy conversion, a comprehensive understanding of its transport mechanisms—particularly the elusive link between charge and heat conduction—is of paramount importance.

The candidate has undertaken an exceptionally ambitious, multi-technique experimental program. The work combines macroscopic electrical characterization (Van der Pauw), nanoscale current mapping (Conductive AFM), and sophisticated optical thermal metrology (Photothermal Infrared Radiometry and Frequency-Domain Thermoreflectance) to investigate transport across different thicknesses, substrates, temperatures, and transport directions. Furthermore, a major highlight of the thesis is the development of a custom-built electric-field-assisted spin-coating system with *in-situ* current monitoring, which constitutes a genuine technical innovation. This is a technically creative approach that provides access to the dynamic evolution of a conducting polymer film during formation rather than only to its final properties. The thesis demonstrates outstanding experimental craftsmanship and a broad command of advanced characterization techniques. While the theoretical interpretation of the coupled transport data contains points of scientific tension—particularly regarding the applicability of the Wiedemann–Franz law to a tunneling-dominated system—these issues are presented as open questions for future investigation (e.g., via Seebeck measurements).

The thesis is logically structured into seven chapters:

Chapter 1 (Introduction): Provides an excellent historical and scientific motivation. The candidate clearly situates PEDOT:PSS within the broader landscape of conductive polymers, identifies the research gap regarding thermal-electrical coupling, and explicitly outlines 8 distinct scientific objectives and 7 original contributions.

Chapter 2 (Experimental Methods – Preparation): Details the sample fabrication, including layer-by-layer spin-coating and the use of multiple substrates (glass, ITO, GaAs). The candidate systematically varies film thickness and formulation.

Chapter 3 (Experimental Methods – Characterization): Describes the complex measurement setups with great precision. The description of the PTR and FDTR optical paths (laser wavelengths, modulation frequencies, lock-in parameters) is highly commendable. The sensitivity analysis and the implementation of a multi-start Trust-Region Reflective algorithm for thermal fitting demonstrate state-of-the-art data processing skills.

Chapter 4 (Theoretical Background): Presents a pedagogically sound exposition of transport mechanisms in disordered organic semiconductors, covering Anderson localization, polaronic transport, Mott-VRH, and fluctuation-induced tunneling. The schematics (e.g., Figure 4.6 distinguishing VRH from tunneling) are excellent.

Chapter 5 (Electrical Transport): Presents a systematic study of charge transport as a function of temperature, thickness, and substrate. The strong quantitative statistical arguments ($R^2 = 0.9998$ for tunneling versus 0.9606 for VRH) provide compelling evidence for the dominance of tunneling transport in the FHC Solar formulation.

Chapter 6 (Thermal Transport): Presents the thermal conductivity measurements (in-plane and cross-plane) and attempts to correlate them with the electrical data via the Wiedemann–Franz framework. This is the most complex and controversial chapter, yielding Lorenz numbers that deviate significantly from the metallic value.

Chapter 7 (Field-Induced Anisotropy): Details the design and application of a custom electric-field-assisted spin-coater. The observation of directional electrical anisotropy with resistance ratios up to ~27 is the most striking experimental result of the thesis. The correlation between macroscopic anisotropy and nanoscale C-AFM contrasts is well-executed.

Experimental Innovation and Technical Skill: The candidate's development of the electric-field-assisted spin-coating system is a genuine engineering achievement. The rolling-contact bearing mechanism to reduce noise during rotation is a thoughtful solution. More importantly, the ability to monitor the current *in situ* during the drying transition provides unique insight into the ionic-to-electronic conduction transition, a phenomenon rarely observed directly in the literature. The initial current maximum followed by a decay during spinning is plausibly associated with the transition from ionic conduction in the wet dispersion to predominantly electronic transport in the increasingly dry polymer network. This capability alone opens new research avenues.

The sheer volume of systematically collected data is impressive. The candidate has successfully measured and analyzed:

- Electrical conductivity across a thickness range of 160–480 nm.
- Temperature-dependent transport from 8 K to 300 K.
- In-plane and cross-plane thermal conductivity using orthogonal optical techniques.

- Local conductivity variations via C-AFM.
- Directional anisotropy induced by an external field.

The reproducibility (<3% deviation in conductivity measurements, Table 5.1) speaks to the candidate's careful experimental handling in assessing the reproducibility of the data. Anisotropy ratios of up to ~27 (Table 7.4) represent a significant step forward compared to the modest effects (typically <2) reported in previous electric-field post-deposition treatments. This result has clear potential implications for the design of organic electronic devices requiring directional charge transport.

The treatment of the FDTR/PTR data, particularly the sensitivity analysis (Figures 3.11–3.13), is rigorous. The candidate correctly identifies the mathematical coupling between thermal conductivity and volumetric heat capacity and applies advanced minimization algorithms to resolve the fitting, demonstrating a high level of methodological maturity.

The thesis has specific points in methodology and interpretation that merit critical scrutiny; nevertheless, these points, listed below, in no way detract from its overall excellence.

Van der Pauw Geometry: The description regarding the contact placement is inconsistent (edges vs. corners). The candidate should clarify this with a photograph of the actual samples.

Thermal Contact of Contacts (Soldering): The use of a 350 °C soldering iron to attach contacts is of some concern, as PEDOT:PSS degrades well below this temperature. The candidate could provide I-V curves proving the contacts are Ohmic and undamaged.

C-AFM Quantification: The C-AFM measurements add an important nanoscale perspective. The current maps reveal spatially heterogeneous conductive regions and support a percolative picture of transport through PEDOT-rich domains. The use of the equation $\sigma = I \cdot L/(V \cdot A)$ to extract quantitative cross-plane conductivity from C-AFM could be physically problematic, as it ignores spreading-resistance at the nano-scale tip. The data is excellent for qualitative mapping, but the absolute numbers in Tables 7.6 and 7.7 should be treated with caution.

The most intriguing scientific tension in the thesis arises in the comparison of Chapter 5 and Chapter 6. In Chapter 5, the candidate convincingly demonstrates ($R^2 = 0.9998$) that charge transport in PEDOT:PSS (F HC Solar) is tunneling-dominated. In Chapter 6, the extracted in-plane Lorenz number reaches ~60 times the Sommerfeld value (L_0), and the cross-plane is ~3.5 times L_0. The exceptionally large in-plane effective Lorenz number, approximately 60 times the Sommerfeld value, is evidence that the classical metallic Wiedemann-Franz interpretation is not directly applicable. It should therefore be treated as an effective correlation parameter rather than as a direct measurement of electronic thermal conductivity. The field-induced anisotropy is one of the strongest claims in the thesis. The proposed interpretation that the field reorients dipolar PEDOT:PSS complexes and reorganizes PEDOT-rich and PSS-rich pathways physically reasonable. However, the available evidence is mainly indirect. The C-AFM images demonstrate heterogeneous conduction and differences among processing conditions, but they do not directly establish the orientation of polymer chains or the direction of PSS-rich barriers. This discrepancy may imply that the Wiedemann–Franz law as applied to this disordered polymer is either invalid or requires a more nuanced framework. An elevated Lorenz number L (above L_0) is a classic signature of bipolar conduction (two-carrier transport), which cannot be ruled out without Seebeck coefficient measurements. This theoretical ambiguity demonstrates the candidate has touched upon a scientifically rich and unresolved frontier.

This thesis represents a substantial body of work by a highly skilled experimentalist. The candidate has successfully:

- Built custom equipment to perform experiments that are not standard in the field.
- Acquired a vast and robust dataset using complementary advanced techniques.
- Discovered remarkably high electrical anisotropy (~27x).
- Provided the foundation for resolving the fundamental debate on transport mechanisms in conductive polymers.

Overall, the thesis fully meets all the requirements for a doctoral degree, demonstrating independent scientific work, technical innovation, and a valuable contribution to the field. I therefore recommend that the thesis be accepted without reservation and awarded the grade of "very good".

In my opinion, the doctoral dissertation of M.Sc. Ameneh Mikaeeli meets the requirements of the Article 187 of the Act on Higher Education and Science of July 20, 2018 (as amended) necessary to obtain the academic degree of Doctor.

Sincerely,

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