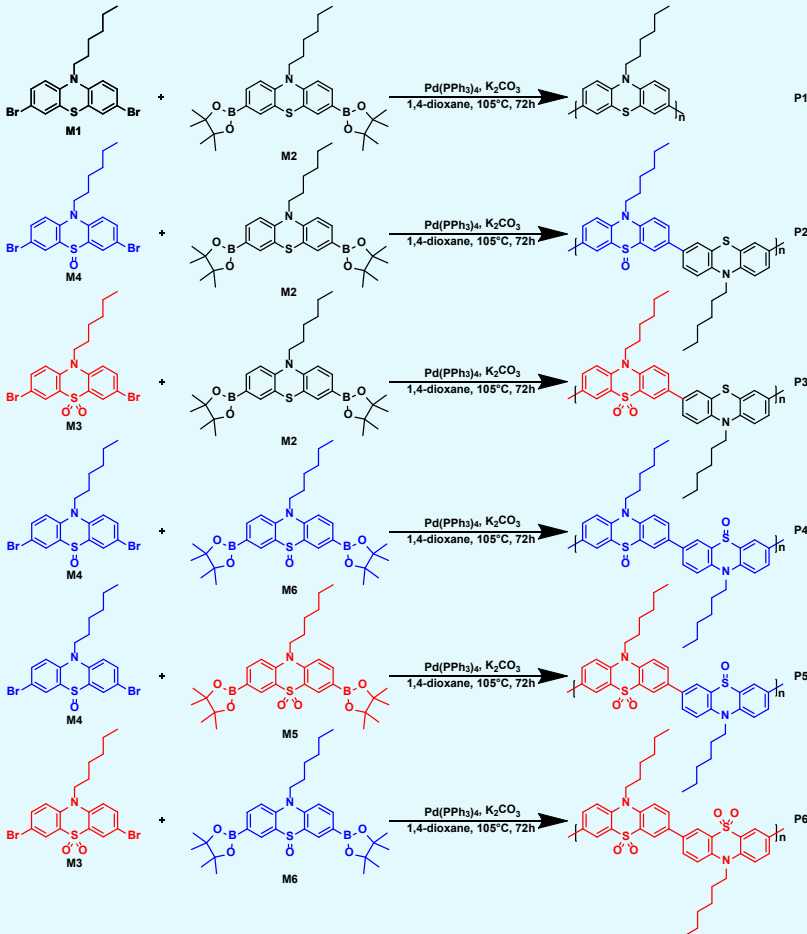


Introduction

We investigated the synthesis of conjugated polymers incorporating three phenothiazine derivatives including **10-hexylphenothiazine**, **10-hexyl-5-oxide-phenothiazine** and **10-hexyl-5,5-dioxide-phenothiazine**. These polymers were synthesized using **Suzuki-Miyaura coupling polymerization**. Our goal was to understand how the **oxidation state of sulfur** in the phenothiazine core influences their **optical, electrochemical, and electronic properties in organic field-effect transistors (OFETs)**.

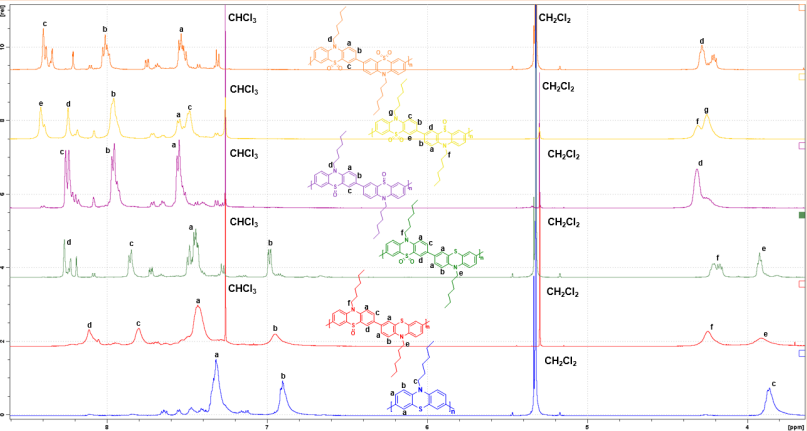
Synthesis

In general, six polymers (P1–P6) were synthesized via a **Pd-catalyzed Suzuki-Miyaura cross-coupling reaction**. The polymerization involved the reaction of corresponding monomers (M1–M6) using **10 mol% Pd(PPh₃)₄** as the catalyst and **K₂CO₃** as the base, in **1,4-dioxane at 105 °C for 3 days** under an argon atmosphere. The crude compounds were purified by **Soxhlet extraction** sequentially with **hexane, methanol and dichloromethane** to remove oligomers and impurities.



NMR Spectrum

The **¹H NMR spectra** of the polymers are shown in the following figures. Peaks between **6.90 and 8.45 ppm** are attributed to the **aromatic hydrogens** of the thiazine rings. Signals at **3.87–4.32 ppm** correspond to the **methylene hydrogens** bonded to the nitrogen atom. The observed **chemical shifts** are consistent with the expected structures and confirm the successful incorporation of the intended **monomer units** into each polymer.



Optical Properties

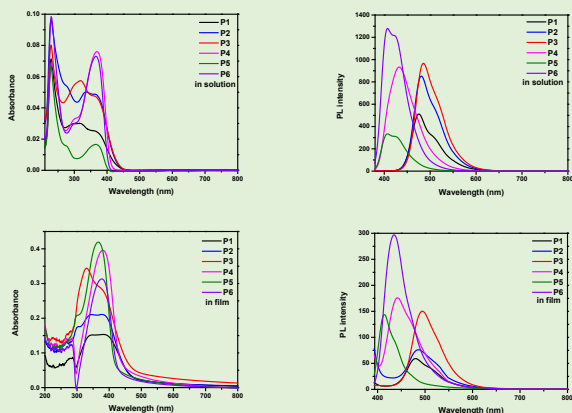
The **UV-Vis absorption** and **photoluminescence (PL)** spectra of the polymers were recorded in THF solution (**10⁻⁶ M**) and as **thin films**. Polymer films were prepared by **spin-coating a 3 mg/mL solution** onto glass substrates.

In solution, all polymers exhibited **three absorption peaks**:

- The peak at **229 nm** corresponds to **π–π*** transitions of the **phenothiazine units**.
- The weak, broad peaks between **275–337 nm** are attributed to **n–π*** transitions.
- The absorption band around **365 nm** arises from **polymer backbone π–π*** transitions and **intramolecular charge transfer (ICT)**.

P4–P6 showed a **red shift** in absorption compared to **P1–P3**, while their emission spectra displayed a **blue shift**, suggesting **enhanced electronic transitions** and altered excited-state properties due to the **increased oxygen content** in the phenothiazine units.

Among all samples, **P4** exhibited the **highest photoluminescence quantum yield in solid state (17.1%)**.



Electrochemical Properties

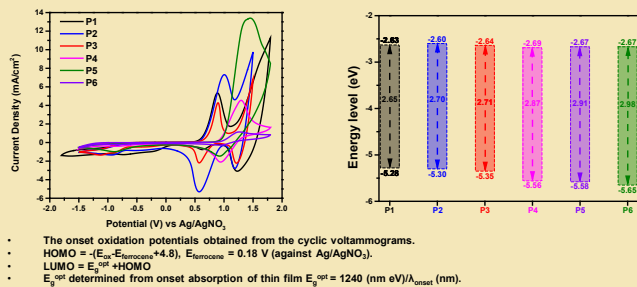
Cyclic voltammetry (CV) was used to investigate the redox behavior and energy levels of the resulting polymers. The **second scan** is presented to avoid the influence of interfacial charge accumulation.

- All samples exhibited **reversible oxidative and reductive peaks**.
- HOMO energy levels** of the oxygen-functionalized copolymers shifted toward **lower potentials** as the **oxidation state of sulfur** in the thiazine ring increased.

This is attributed to the **strong electronegativity of oxygen**, which makes the polymer backbone more resistant to oxidation.

- LUMO and E_g^{opt} energy levels** remained relatively unchanged.

This may result from the **reduced solubility** of highly oxidized polymers, leading to **lower molecular weights** and **shorter effective conjugation lengths**.

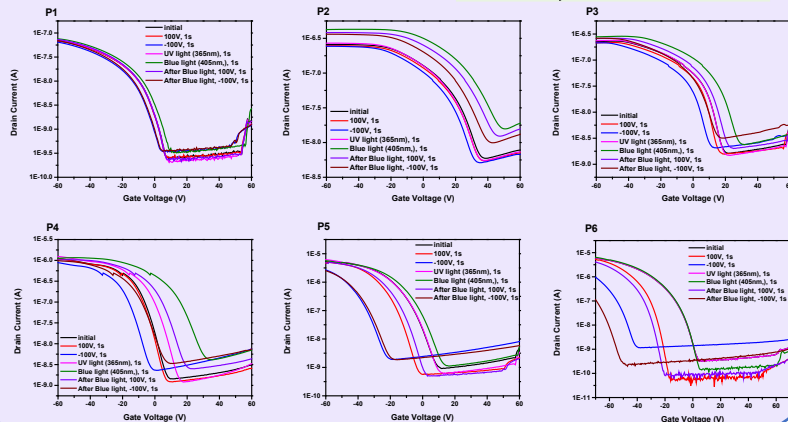
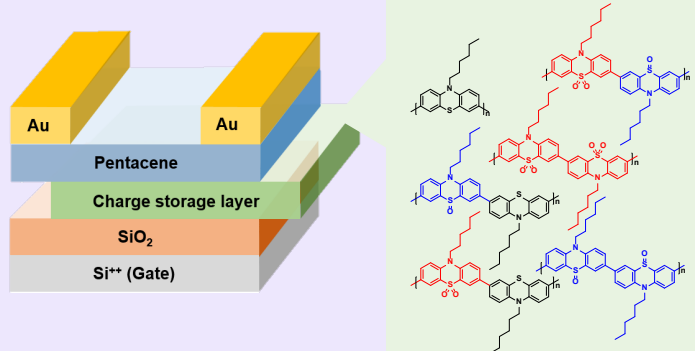


Organic Field Effect Transistor Memory

The devices employed in this study were constructed using a **bottom-gate, top-contact configuration**, with **charge-storage layers (P1–P6)** spin-coated onto **pre-cleaned 300 nm SiO₂/Si wafers**.

- All devices exhibited **photo-writing behavior** under **UV (365 nm)** and **blue light (405 nm)** irradiation.
- Transfer curves** showed that both **I_{on}/I_{off} ratios** and **memory windows** increased with **higher oxygen content**.

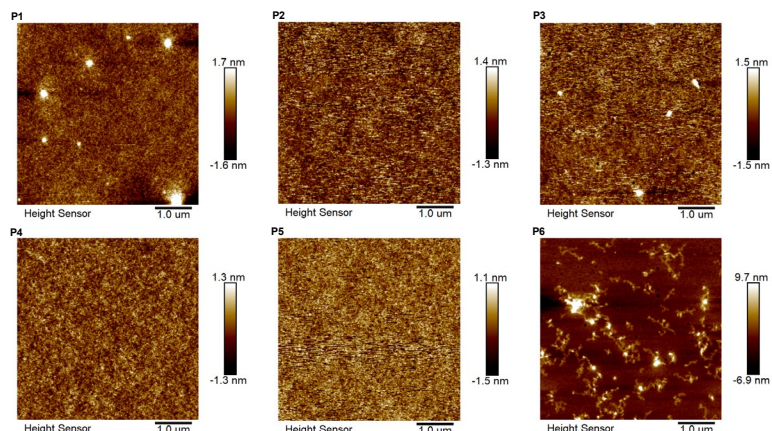
The improved performance is attributed to **enhanced charge-trapping** from the **stronger electron-withdrawing effect of oxygen** in the polymer backbone.



AFM Images

Atomic Force Microscopy (AFM) images revealed distinct surface morphologies among the samples.

- P1 and P3** displayed **spherical aggregates** with average diameters of approximately **200 nm** and **100 nm**, respectively.
- In contrast, **P6** exhibited **rod-like aggregates** with an average length of around **800 nm**.
- P2 and P4** showed **little aggregation** indicating a more uniform surface morphology.



Conclusions

- Conjugated polymers** incorporating three phenothiazine derivatives such as **10-hexylphenothiazine**, **10-hexyl-5-oxide-phenothiazine** and **10-hexyl-5,5-dioxide-phenothiazine** were successfully synthesized and fully characterized.
- Optical and electrochemical properties** as well as **devices performance** revealed that **oxygen substitution** in the phenothiazine core is an effective strategy to **tune the electronic and optical properties of phenothiazine-based polymers**.
- The results demonstrate that **modulating the oxidation state** of the phenothiazine unit enables **precise control over electronic behavior**.

References

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- S. Revoju, A. Matuhina, L. Canil, H. Salonen, A. Hiltunen, A. Abate and P. Vivo, *J. Mater. Chem. C*, **2020**, 8, 15486-15506.