Nature Inspired Polymers: Promising Materials for OTFT-Based Sensing

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Introduction

Quinazolinones

Triphenodioxazine

Conclusion

Future Work
Organic Electronics

**Light Emitting Diode**
- Emitted light
- Transparent Cathode
- Emissive Layer
- Conductive Layer
- Anode
- Substrate

**Photovoltaic Cell**
- Incoming light
- Transparent Substrate
- Transparent Anode
- p-type Semiconductor
- n-type Semiconductor
- Cathode

**Thin-Film Transistor**
- Drain
- Source
- Source Voltage
- Gate Voltage
- Semiconductor
- Insulator
- Substrate
Background

TREND OF ORGANIC SEMICONDUCTOR AND ELECTRONICS RESEARCH
A race for high mobility, on-off current ratios, PCEs, FF, etc..

Shorting coming has been air stability...

Fabrication/processing/characterization typically in inert atmosphere to demonstrate key merits!

CAVEATS OF ORGANIC SEMICONDUCTORS
OSCs by their very nature are sensitive..

Photo-induced excitation
Doping/trapping occurs with the presence of oxygen, moisture, carbon dioxide, etc.

Can this intrinsic sensitivity be harnessed?
Device Architectures
Goals and Limitations

- Selectivity
- Calibration range
- Sensitivity
- Precision
- Accuracy
- Limits of detection and quantification

- Electronic output signal (transduction)
- High sensing performance level
- Low-cost fabrication
Natural/Nature Inspired

Core structure of several commercial dyes and pigments. Not naturally occurring, but reflects upon the long-term research aim to produce good brightness and fastness properties compared to naturally derived dyes and pigments.

**Quinazolinones**
Naturally occurring and can be found in over 150 alkaloids. They are actively studied as they represent an important class of compounds due to their wide range of intrinsic biological activities.
Quinazolinones

quinazolin-4(3H)-one moiety

pyrimido[4,5-g]quinazoline-4,9-dione
Reagents and conditions: (i) toluene, ammonium acetate, catalytic amount of acetic acid, 16 h (95%); (ii) n-butanol, sulfur, gentle reflux, 18 h (90%); (iii) DCM, 2-thiophenecarbonyl chloride, pyridine, 0 °C, 30 min, rt, 18 h (79%); (iv) ethanol, lithium hydroxide, 60 °C, 3 h (86%); (v) acetic anhydride, reflux, 3 h (78%); (vi) ammonium acetate, 170 °C, 1 h, 30% sodium hydroxide, ethanol, reflux, 1 h (95%); (vii) DMF, K₂CO₃, 130 °C, 16 h (73%); (viii) NBS, chloroform, 0 °C, rt, overnight (75%).

The synthetic route to PPQ2T-BT-24, PPQ2T-TT-24, and PPQ2T-TVT-24 polymers. Reagents and conditions: (i) Pd$_2$(dba)$_3$/P(o-tolyl)$_3$/chlorobenzene/130 °C.

**Electrochemical and Optical Properties**

<table>
<thead>
<tr>
<th>Name</th>
<th>LUMO (eV)</th>
<th>HOMO (eV)</th>
<th>$E_{g\text{opt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPQ2T-BT-24/40</td>
<td>-3.27</td>
<td>-5.30</td>
<td>2.03</td>
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<tr>
<td>PPQ2T-TT-24</td>
<td>-3.41</td>
<td>-5.42</td>
<td>2.00</td>
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<tr>
<td>PPQ2T-TV-T24</td>
<td>-3.27</td>
<td>-5.18</td>
<td>1.90</td>
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</tbody>
</table>
Acid Study

![Graph showing normalized absorbance vs. wavelength for PPQ2T-BT-24 with different TFA concentrations.]

- No TFA
- 10 μM
- 100 μM
- 1 mM
- 5 mM
- 10 mM
- 100 mM

![Chemical structure of PPQ2T-BT-24 with highlighted parts.]

- **Trifluoroacetic acid (TFA)**

![Images of PPQ2T-BT-24 solutions with different TFA concentrations.]

- No TFA
- 100 μM
- 10 mM

**Increasing TFA concentration**
I-V Characteristics

**BGBC**

- Semiconductor
- Insulator
- Substrate

**TGBC**

- Gate
- Source
- Drain

### Graphs

**BGBC**
- $V_{GS} = -100\text{V}$
- $V_{DS} = -100\text{V}$
- $I_{DS}$ (μA)

**TGBC**
- $V_{GS} = -80\text{V}$
- $V_{DS} = -80\text{V}$
- $I_{DS}$ (μA)
Air Stability

![Graphs showing the effect of different environments on material stability.]

- **Graph 1:**
  - Environment: Dry N₂ 1st, Air 1st, Dry N₂ 2nd, Air 2nd
  - Lines represent:
    - PPQ2T-BT-24
    - PPQ2T-TT-24
    - PPQ2T-TVT-24

- **Graph 2:**
  - Environment: Dry N₂ 1st, Dry Air, Dry N₂ 2nd, Moist N₂, Dry N₂ 3rd
  - Lines represent:
    - PPQ2T-BT-24
    - PPQ2T-TT-24
    - PPQ2T-TVT-24

**μ X 10⁻³ (cm² V⁻¹ s⁻¹)**
Aqueous Operation
Phototransistor
Optical Profile

LED

Power Density = 14 mW cm\(^{-2}\)
3000-3500K

Intensity

449
450
500
550
600
650
700

400
500
600
700

Wavelength (nm)

579

PPQ2T-BT-24
PPQ2T-TVT-24
PPQ2T-TT-24

Intensity

400
450
500
550
600
650
700

18
Pristine Characteristics

- PPQ2T-TVT-24
- PPQ2T-TT-24
- PPQ2T-BT-24

- $T_R \approx 3 \text{ ms}$
- $T_F \approx 59 \text{ ms}$

Drain Current vs. Time (s):

- ON
- OFF
Blend Characteristics

![Graph showing drain current over time for different blends with ON and OFF states.](image)

- PPQ2T-TVT-24:PC$_{61}$BM
- PPQ2T-TT-24:PC$_{61}$BM
- PPQ2T-BT-24:PC$_{61}$BM

**Time (s)\[0\text{\,\,}\quad 210\quad 220\quad 230\quad 240\quad 250\quad 260\quad 270\quad 280\quad 290\]**

**Drain Current**

- **TR ≈ 1 ms**
- **TF ≈ 8 ms**

![Molecular structure of PPQ2T-BT-24:PC$_{61}$BM (1:1 wt%)](image)
Triphenodiooxazines
Synthetic route to **FTPDO** and its polymer **PFTPDOBT**. i) $t$-BuOK, THF, r. t., 80%; ii) 90% HNO$_3$, 1,2-dichloroethane, reflux, 94%; iii) NH$_2$NH$_2$·H$_2$O (3.0 mL), Fe(acac)$_3$, ethylene glycol, 155 °C, 52%; iv) 4-toluenesulfonylchloride, nitrobenzene, 40 °C, 6%; v) Pd$_2$(dba)$_3$/P(o-tolyl)$_3$, chlorobenzene, 130 °C, 82%.

Electrochemical and Optical Properties

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Air Stability

![Graph showing hole mobility vs. temperature in different atmospheres.]

- (a) in nitrogen (annealed glovebox)
- (b) in air (annealed glovebox)
- (c) in air (annealed in air)
Air Stability

![Graph showing normalized absorbance across different wavelengths for various temperatures.]

- 50 °C
- 80 °C
- 100 °C
- 150 °C
- 200 °C
- 250 °C

Wavelength (nm)
Aqueous Operation
Novel Semiconductors
Series of PQ polymers and full characterization

Acid Affinity
Strong interaction with organic and Lewis acids

Modest Transistor Performance
Demonstrates modest hole mobility in TGB

Air stable operation in BGB

Stable aqueous operation

Thermal Stability
PFTPDOBT should exhibit excellent thermal stability in air

Phototransistor
Marked response times in OPTs
Thanks

Supervisor: Dr Yuning Li

Group: Yinghui He, Jenner Ngai, Dr. Mylène LeBorgne, Dr. Chang Guo, Dr. Bin Sun, Dr. Yun-Feng Deng, and Dr. Wei Hong