Supplementary information for

Optical and Electrochemical Properties of Ethynylaniline Derivatives of Phenothiazine, Phenothiazine-5-oxide and Phenothiazine-5,5-dioxide

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1) Calculated geometries of ground and excited states
2) Cyclic voltammograms
3) Differential pulse voltammograms
4) FTIR spectra
5) $^1$H and $^{13}$C NMR spectra
6) Fluorescence Lifetime measurements
7) Solvatochromism
8) Multi-parameter solvent effect analysis
**Figure S1:** Calculated ground state and excited state geometries of 3a-3c

<table>
<thead>
<tr>
<th></th>
<th>Ground State ($S_0$)</th>
<th>Excited State ($S_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>3a</strong>&lt;br&gt;Top View</td>
<td><img src="image1" alt="Ground State" /></td>
<td><img src="image2" alt="Excited State" /></td>
</tr>
<tr>
<td><strong>3a</strong>&lt;br&gt;Side View</td>
<td><img src="image3" alt="Ground State" /></td>
<td><img src="image4" alt="Excited State" /></td>
</tr>
<tr>
<td><strong>3b_{ax}</strong>&lt;br&gt;Top View</td>
<td><img src="image5" alt="Ground State" /></td>
<td><img src="image6" alt="Excited State" /></td>
</tr>
<tr>
<td><strong>3b_{ax}</strong>&lt;br&gt;Side View</td>
<td><img src="image7" alt="Ground State" /></td>
<td><img src="image8" alt="Excited State" /></td>
</tr>
<tr>
<td><strong>3b_{eq}</strong>&lt;br&gt;Top View</td>
<td><img src="image9" alt="Ground State" /></td>
<td><img src="image10" alt="Excited State" /></td>
</tr>
<tr>
<td><strong>3b_{eq}</strong>&lt;br&gt;Side View</td>
<td><img src="image11" alt="Ground State" /></td>
<td><img src="image12" alt="Excited State" /></td>
</tr>
<tr>
<td><strong>3c</strong>&lt;br&gt;Top View</td>
<td><img src="image13" alt="Ground State" /></td>
<td><img src="image14" alt="Excited State" /></td>
</tr>
<tr>
<td><strong>3c</strong>&lt;br&gt;Side View</td>
<td><img src="image15" alt="Ground State" /></td>
<td><img src="image16" alt="Excited State" /></td>
</tr>
</tbody>
</table>
**Figure S2:** Cyclic Voltammograms in DMF of 3a (blue), 3b (green) and 3c (black) vs. Fc/Fc$^+$

**Figure S3:** Differential Pulse Voltammograms in DMF of 3a (blue), 3b (green), 3c (black) vs Fc/Fc$^+$. 
Figure S4: Normalized diffuse reflectance FTIR spectra in KBr of 3a, 3b and 3c
Figure S5: $^1$H and $^{13}$C NMR of all newly synthesized compounds.

1
2a

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{S} & \\
\text{N} & \\
\text{C}_{10}\text{H}_{21} & \\
\end{align*}
\]

\[
\begin{align*}
2.03 & \quad 1.83 & \quad 2.06 & \\
1.93 & \\
2.04 & \quad 2.11 & \quad 12.37 & \quad 3.01 & \\
\end{align*}
\]

\[
\begin{align*}
10 & \quad 9 & \quad 8 & \quad 7 & \quad 6 & \quad 5 & \quad 4 & \quad 3 & \quad 2 & \quad 1 & \quad 0 \\
143.79 & \quad 129.89 & \quad 128.49 & \quad 126.16 & \quad 116.38 & \quad 114.34 & \\
47.40 & \quad 31.78 & \quad 29.41 & \quad 29.36 & \quad 29.05 & \quad 26.66 & \quad 22.60 & \quad 14.10 \\
\end{align*}
\]

CDCl₃
3a

![Chemical structure and associated 1D and 2D NMR spectra](image-url)

**Chemical Structure:**
- N-C10H21
- C10H21
- C10H21
- N-C10H21

**1D NMR Spectra:**
- f1 (ppm) range: 0-10
- Peaks at 3.79, 1.68, 1.90, 3.94, 1.97, 7.95, 2.09, 7.21, 2.35, 8.32, 3.33, 15.00

**CDCl3**
- 147.82, 143.95, 132.71, 128.30, 124.95, 118.98, 111.21, 108.64, 70.97, 47.62, 31.89, 28.56, 29.51, 27.14, 22.67, 14.10
6 \( C_{10}H_{21}N\underbrace{C_{10}H_{21}}_{\text{SiMe}_3} \)

\[ \text{CDCl}_3 \]

f1 (ppm)
**Figure S6**: Transient lifetime (Black) and instrument response (Red) of 3a, 3b and 3c

3a

![Graph of 3a](image)

3b

![Graph of 3b](image)

3c

![Graph of 3c](image)
**Fig S7a.** a) Absorption and emission spectra of 3a in different solvents. b) Emission peak wavenumber as a function of solvent dipolarity (SdP) c) Emission peak wavenumber as a function of orientation polarizability.
Fig S7b. a) Absorption and emission spectra of 3b in different solvents. b) Emission peak wavenumber as a function of solvent dipolarity (SdP) c) Emission peak wavenumber as a function of orientation polarizability.
Fig S7c. a) Absorption and emission spectra of 3c in different solvents. b) Emission peak wavenumber as a function of solvent dipolarity (SdP) c) Emission peak wavenumber as a function of orientation polarizability.
S8. Multi-parameter solvent effect analysis of 3a, 3b and 3c

Using the approach described by Catalán\(^1\) to determine a multi-parameter general scale for describing the optical response in different solvents using solvent scales based on two specific scales (solvent acidity, SA and solvent basicity, SB) and two general scales (solvent polarizability, SP and solvent dipolarizability, SdP). The linear combination of solvent scales results in the following formula:

\[ \nu = bSA + cSB + dSP + eSdP + \nu_0 \]

where \( \nu \) is the optical property of interest (absorption or emission peak) in wavenumbers, \( \nu_0 \) is the frequency of the transition in absence of solvent (gas phase), SA, SB, SP and SdP are solvent parameters to describe solute-solvent interactions and coefficients \( b \) to \( e \) are regressions coefficients that correlate to the sensitivity of the optical property to the different solute-solvent parameters.

The multi-parameter regression analysis resulted in the following fits to the absorption and emission peaks.

3a (PTZ-thioether)

\[ \nu_{abs} = (-2712 \pm 522)SP - (783 \pm 100)SdP + (29221 \pm 349) \]
\[ n = 11; R^2 = 0.94 \]

\[ \nu_{em} = (142 \pm 72)SB - (1875 \pm 206)SP - (560 \pm 49)SdP + (22742 \pm 141) \]
\[ n = 11; R^2 = 0.98 \]

3b (PTZ-sulfoxide)

\[ \nu_{abs} = (-3350 \pm 559)SP + (642 \pm 82)SdP + (28818 \pm 349) \]
\[ n = 5; R^2 = 0.98 \]

\[ \nu_{em} = (669 \pm 403)SB + (4136 \pm 1380)SP - (1730 \pm 217)SdP + (21035 \pm 903) \]
\[ n = 5; R^2 = 0.98 \]

3c (PTZ-sulfone)

\[ \nu_{abs} = (-3593 \pm 297)SP - (445 \pm 60)SdP + (28823 \pm 194) \]
\[ n = 6; R^2 = 0.98 \]

\[ \nu_{em} = (2750 \pm 206)SB + (7936 \pm 547)SP - (4778 \pm 107)SdP + (19817 \pm 377) \]
\[ n = 6; R^2 = 0.99 \]