SUPPORTING INFORMATION

Photophysical, Crystallographic, and Electrochemical Characterization of Symmetric and Unsymmetric Self-Assembled Conjugated Thiopheno Azomethines

Department of Chemistry, Pavillon JA Bombardier, University of Montreal, CP 6128, succ.
Centreville, Montreal, Quebec, CANADA, H3C 3J7,

w.skene@umontreal.ca
**TABLE OF CONTENTS**

- Materials and general experimental .......................................................... 5
- Spectroscopic Measurements ....................................................................... 5
- Electrochemical Measurements .................................................................... 6
- Figure 1. $^1$H spectrum of 1 (400MHz, Acetone-d$_6$) .................................... 7
- Figure 2. $^{13}$C spectrum of 1 (100MHz, Acetone-d$_6$) ............................... 8
- Figure 4. $^{13}$C spectrum of 2 (100MHz, Acetone-d$_6$) ............................. 10
- Figure 7. $^1$H spectrum of 4 (400MHz, Acetone-d$_6$) ............................... 13
- Figure 10. $^{13}$C spectrum of 5 (100MHz, Acetone-d$_6$) ........................... 16
- Crystal Structure Determination ................................................................ 21
- Figure 15. Normalized absorption (closed squares), fluorescence (closed circles), recorded in deaerated acetonitrile of 1, $\lambda_{ex} = 350$ nm ................................................................. 23
- Figure 16. Normalized absorption (closed squares), fluorescence (closed circles), recorded in deaerated acetonitrile, and phosphorescence (closed triangles) recorded at 77 K in a matrix of 4:1 ethanol / methanol of 2, $\lambda_{ex} = 305$ nm......................................................... 24
- Figure 17. Normalized absorption (closed squares), fluorescence (closed circles), recorded in deaerated acetonitrile, and phosphorescence (closed triangles) recorded at 77 K in a matrix of 4:1 ethanol / methanol of 3, $\lambda_{ex} = 400$ nm ................................................................. 25
Figure 18. Normalized absorption (closed squares), fluorescence (closed circles), recorded in deaerated acetonitrile, and phosphorescence (closed triangles) recorded at 77 K in a matrix of 4:1 ethanol / methanol of 4, $\lambda_{\text{ex}} = 466$ nm. .................................................................................................................................26

Figure 19. Normalized absorption (closed squares), fluorescence (closed circles), recorded in deaerated acetonitrile, and phosphorescence (closed triangles) recorded at 77 K in a matrix of 4:1 ethanol / methanol of 5, $\lambda_{\text{ex}} = 440$ nm. .................................................................................................................................27

Figure 20. Normalized absorption (closed squares), fluorescence (closed circles), oxidatively polymerized 5 on ITO plates, $\lambda_{\text{ex}} = 431$ nm. .................................................................................................................................28

Figure 21. Normalized absorption (closed squares), fluorescence (closed circles), recorded in deaerated acetonitrile, and phosphorescence (closed triangles) recorded at 77 K in a matrix of 4:1 ethanol / methanol of 6, $\lambda_{\text{ex}} = 492$ nm. .................................................................................................................................29

Figure 22. Normalized absorption (closed squares), fluorescence (closed circles) of oxidatively polymerized 6 on ITO plates, $\lambda_{\text{ex}} = 431$ nm. .................................................................................................................................30

Figure 23. Normalized absorption (closed squares), fluorescence (closed circles), recorded in deaerated acetonitrile, and phosphorescence (closed triangles) recorded at 77 K in a matrix of 4:1 ethanol / methanol of 7, $\lambda_{\text{ex}} = 472$ nm. .................................................................................................................................31

Figure 24. Normalized absorption (closed squares) and fluorescence (closed circles) on oxidatively polymerized 7 on ITO plates, $\lambda_{\text{ex}} = 431$ nm. .................................................................................................................................32

Figure 25. Uncorrected cyclic voltammogram of 3 recorded in deaerated dichloromethane solution of 0.1 M of TBAPF$_6$ using Ag/AgCl as reference and Pt as working electrodes. ........................................33

Figure 26. Uncorrected cyclic voltammogram of 4 recorded in deaerated dichloromethane solution of 0.1 M of TBAPF$_6$ using Ag/AgCl as reference and Pt as working electrodes. ........................................34
Figure 27. Uncorrected cyclic voltammogram of 5 recorded in deaerated dichloromethane solution of 0.1 M of TBAPF₆ using Ag/AgCl as reference and Pt as working electrodes. ...............................35

Figure 30. Uncorrected cyclic voltammogram of 6 recorded in deaerated dichloromethane solution of 0.1 M of TBAPF₆ using Ag/AgCl as reference and Pt as working electrodes. ...............................38

Figure 32. Uncorrected cyclic voltammogram of 7 recorded in deaerated dichloromethane solution of 0.1 M of TBAPF₆ using Ag/AgCl as reference and Pt as working electrodes. ...............................40
Materials and general experimental

All reagents were commercially available and were used as received unless otherwise stated. Anhydrous and deaerated solvents were obtained with an aluminum column solvent purification system. Isopropanol was dried over activated molecular sieves and stored under nitrogen. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a 400 MHz spectrometer with the appropriate deuterated solvents. Product distributions were quantitatively determined by HPLC using a C18 60 Å 4 μm, 3.9 mm x 15.0 mm column and 70 % acetonitrile 30 % water as the mobile phase along with a monitoring wavelength of 430 nm. The reactions were heated to between 60° and 80° C and aliquots for analysis were removed after 22 hours.

Spectroscopic Measurements

Absorption measurements were done on a UV-Vis-IR spectrometer and fluorescence studies were carried out on a combined time-resolved/steady-state fluorimeter after deaerating the samples thoroughly with nitrogen for 20 minutes. Fluorescence quantum yields were measured at 10^{-5} M by exciting the corresponding compounds at 303 nm in spectroscopic grade acetonitrile and compared to bithiophene ($\phi_{303\text{ nm}} = 0.013$)$^{15,16,17,18,19}$ excited at the same wavelength. The actinometer absorbances, and those of the compounds, were matched at the excitation wavelength to within 5 %. The phosphorescence measurements were done on in a 1:4 methanol/ethanol glass matrix at 77 K, exciting at the compound’s absorption maximum. The triplet-triplet absorption spectra were measured in anhydrous acetonitrile with a laser flash photolysis system excited at 355 nm with the third harmonic from a YAG:Nd laser. The triplet quantum yields were measured by optically matching samples within 5 % at 355 nm and by quenching with xanthone. The xanthone triplet was monitored at 620 nm ($\Phi_T = 1$), which was used the actinometer reference.$^{20,21}$ Phosphorescence
quantum yields were determined by comparing optically matched samples relative to fluorenone ($\Phi_{\text{phosphorescence}} = 0.06$ in ethanol) at 77 K.\textsuperscript{22}

**Electrochemical Measurements**

Cyclic voltammetric measurements were performed on a standard potentiostat with a scan rate of 100 mV/s. The compounds were dissolved in anhydrous and deaerated dichloromethane at $10^{-4}$ M along with the addition of 0.1 M NBu\textsubscript{4}PF\textsubscript{6} and the oxidation potentials were measured after deaerating the solution with nitrogen for 20 minutes. A glassy carbon electrode and a platinum electrode were employed as working and auxiliary electrodes, respectively. A saturated Ag/AgCl electrode was used as the reference electrode and the values were corrected to SCE in dichloromethane by using ferrocene as an internal reference (0.46 V).\textsuperscript{23} The cross-coupled products were electrochemically deposited onto ITO plates from (18 Ω resistance) by 50 repeated oxidative scans from 0 to 1.4 V at 100 mV/sec. Alternatively, the electrochemical oxidative product cross-coupling was done by applying an anodic potential 100 mV greater than the corresponding radical cation and held at that potential for 10 minutes. A final potential of -100 mV was applied for 2 minutes to ensure the resulting products were in the neutral form. Large amounts of the cross-coupled products were obtained by electrochemical oxidation of 5 in anhydrous dichloromethane as outlined above using a mesh working electrode. A potential of +1.3 V was applied for 40 minutes after which the solvent was evaporated and the residual electrolyte was filtered. The soluble fraction of the product was isolated from the unreacted monomer via a preparative GPC column with THF as the mobile phase to give $M_p = 1\ 557$ g/mol.
Figure 1. $^1$H spectrum of $1$ (400MHz, Acetone-d$_6$)
Figure 2. $^{13}$C spectrum of 1 (100MHz, Acetone-d$_6$)
Figure 3. \(^1\)H spectrum of 2 (400MHz, Acetone-\(d_6\))
**Figure 4.** $^{13}$C spectrum of 2 (100MHz, Acetone-$d_6$)
Figure 5. $^1$H spectrum of 3 (400MHz, Acetone-d$_6$)
Figure 6. $^{13}$C spectrum of 3 (100MHz, Acetone-$d_6$)
Figure 7. $^1$H spectrum of 4 (400MHz, Acetone-d$_6$)
Figure 8. $^{13}$C spectrum of 4 (100MHz, DMSO-d$_6$)
Figure 9. $^1$H spectrum of 5 (400MHz, Acetone-d$_6$)
Figure 10. $^{13}$C spectrum of 5 (100MHz, Acetone-$d_6$)
Figure 11. $^1$H spectrum of 6 (400MHz, Acetone-d$_6$)
Figure 12. $^{13}$C spectrum of 6 (100MHz, DMSO-d$_6$)
Figure 13. \(^1\)H spectrum of 7 (400MHz, Acetone-d\(_6\))
Figure 14. $^{13}$C spectrum of 7 (100MHz, Acetone-d$_6$)
Crystal Structure Determination

Diffraction data for 7 was collected on a Enraf-Nonius-CAD4 diffractometer using graphite-monochromatized CuKα radiation with 1.54178 Å. The structures were solved by direct methods (SHELXS97). All non-hydrogen atoms were refined based on Fobs2 (SHELXS97), while hydrogen atoms were refined on calculated positions with fixed isotropic U, using riding model techniques.

**Table 1.** Details of Crystal Structure Determination of 7.

<table>
<thead>
<tr>
<th></th>
<th>C_{24} H_{20} N_{2} O_{4} S_{4}</th>
</tr>
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<tbody>
<tr>
<td><strong>Formula</strong></td>
<td></td>
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<tr>
<td><strong>Mw (g/mol); F(000)</strong></td>
<td>528.66</td>
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<tr>
<td><strong>Crystal color and form</strong></td>
<td>Red Plate</td>
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<tr>
<td><strong>Crystal size (mm)</strong></td>
<td>0.39 0.17 0.02</td>
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<tr>
<td><strong>T(K); d_{calcd.} (g/cm^3)</strong></td>
<td>293(2) 1.443</td>
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<tr>
<td><strong>Crystal System</strong></td>
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<td><strong>Space Group</strong></td>
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<tr>
<td><strong>Unit Cell: a (Å)</strong></td>
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<tr>
<td><strong>b (Å)</strong></td>
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<tr>
<td><strong>c (Å)</strong></td>
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<td><strong>α (°)</strong></td>
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<tr>
<td><strong>β (°)</strong></td>
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<tr>
<td><strong>γ (°)</strong></td>
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<td><strong>V (Å^3); Z</strong></td>
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<tr>
<td><strong>θ range (°); completeness</strong></td>
<td>1.69 - 56.14; 0.966</td>
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<tr>
<td><strong>Reflections: collected / independent; R_{int}</strong></td>
<td>10.37; 0.105</td>
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<td><strong>μ (mm^{-1}); Abs. Corr.</strong></td>
<td>3.883; multi-scan</td>
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<tr>
<td>R1(F); wR(F^2) [I &gt; 2σ(I)]</td>
<td>0.1733; 0.4073</td>
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<tr>
<td>R1(F); wR(F^2) (all data)</td>
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<tr>
<td>GoF(F^2)</td>
<td>1.527</td>
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<tr>
<td>Max. residual e− density</td>
<td>1.774 Å⁻³</td>
</tr>
</tbody>
</table>
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Figure 16. Normalized absorption (closed squares), fluorescence (closed circles), recorded in deaereated acetonitrile, and phosphorescence (closed triangles) recorded at 77 K in a matrix of 4:1 ethanol / methanol of 2, $\lambda_{ex} = 305$ nm.
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Figure 26. Uncorrected cyclic voltammogram of 4 recorded in deaereated dichloromethane solution of 0.1 M of TBAPF$_6$ using Ag/AgCl as reference and Pt as working electrodes.
Figure 27. Uncorrected cyclic voltammogram of 5 recorded in deaereated dichloromethane solution of 0.1 M of TBAPF$_6$ using Ag/AgCl as reference and Pt as working electrodes.
Figure 28. Uncorrected electrodeposition of 5 recorded in deaereated dichloromethane solution of 0.1 M of TBAPF₆ using Ag/AgCl as reference and Pt as working electrodes at a 100 mV/s scan rate.
Figure 29. Uncorrected cyclic voltammogram of oxidatively polymerized 5 deposited on the working electrode. Recorded in deaerated dichloromethane solution of 0.1 M of TBAPF$_6$ using Ag/AgCl as reference and Pt as working electrodes at a 100 mV/s scan rate.
Figure 30. Uncorrected cyclic voltammogram of 6 recorded in deaerated dichloromethane solution of 0.1 M of TBAPF₆ using Ag/AgCl as reference and Pt as working electrodes.
Figure 31. Uncorrected cyclic voltammogram of oxidatively polymerized 6 deposited on the working electrode. Recorded in deaerated dichloromethane solution of 0.1 M of TBAPF₆ using Ag/AgCl as reference and Pt as working electrodes at a 100 mV/s scan rate.
Figure 32. Uncorrected cyclic voltammogram of 7 recorded in deaerated dichloromethane solution of 0.1 M of TBAPF$_6$ using Ag/AgCl as reference and Pt as working electrodes.
**Figure 33.** Uncorrected cyclic voltammogram of oxidatively polymerized 7 deposited on the working electrode. Recorded in deaerated dichloromethane solution of 0.1 M of TBAPF₆ using Ag/AgCl as reference and Pt as working electrodes at a 100 mV/s scan rate.