Supporting Information for publication

**Improved TTF functionalization of polymers for two-dimensional charge-transfer networks**

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I. UV-Vis spectra and TTF functionalization calculation based on UV-Vis spectra

As shown in Fig. S1, the maximum absorbance peak of TTF and phmTTFMA are identical (320 nm), whereas the much more concentrated pNHSMA shows little to none absorbance around that region. Thus, we can use Beer’s law to determine how much TTF was incorporated into the polymer during the PPM process.

![UV-Vis absorbance spectra of TTF (0.25 mM), phmTTFMA (0.25 mM), and pNHSMA (2.00 mM) in DMSO.](image)

**Figure S1.** UV-Vis absorbance spectra of TTF (0.25 mM), phmTTFMA (0.25 mM), and pNHSMA (2.00 mM) in DMSO.

As shown in Fig. S1, the maximum absorbance peak of TTF and phmTTFMA are identical (320 nm), whereas the much more concentrated pNHSMA shows little to none absorbance around that region. Thus, we can use Beer’s law to determine how much TTF was incorporated into the polymer during the PPM process.

![Calibration curve of TTF in DMSO and its comparisons with phmTTFMA, P1 to P7, where 100% TTF substitution was assumed.](image)

**Figure S2.** Calibration curve of TTF in DMSO and its comparisons with phmTTFMA, P1 to P7, where 100% TTF substitution was assumed.
As shown in Fig. S2, the concentrations of phmTTFMA in DMSO are calculated under the assumption that 100% conversion from NHS to TTF was achieved. However, based on the slope of the trendline for each series, we determined that the actual % conversion is lower than 100%. For example, for 100 mol. equiv. of P1, only 1.1094/2.6081 = 42.54 mol was phmTTFMA. Since the molecular weight of hmTTFMA monomer (302.44 g/mol) differs from that of NHSMA monomer (183.16 g/mol), the mol. equiv. of unreacted pNHSMA is (100-42.54)x302.44/183.16 = 94.93 mol. Thus, the actual % TTF functionalization is 42.54/(42.54+94.93) = 31%. Analogously, we can determine the % TTF functionalization for P2-P11.

![Figure S3](image-url). Calibration curve of TTF in DMSO and its comparison with phmTTFMA, P8 to P11, where 100% TTF substitution was assumed.
II. NMR spectra and TTF functionalization calculation based on $^1$H NMR integration

$^1$H NMR of compound 1

$^13$C NMR of compound 1
$^1$H NMR of P1:

$^1$H NMR of P2:
$^1$H NMR of P3:

$^1$H NMR of P4:
$^1$H NMR of P5:

$^1$H NMR of P6:
$^1$H NMR of P7:

$^1$H NMR of P8:
$^1$H NMR of P9:

$^1$H NMR of P10:
$^1$H NMR of P11:

Table S1. Relative proton integration values of P1 to P11 from $^1$H NMR spectra.

<table>
<thead>
<tr>
<th>Relative proton integration value from $^1$H NMR</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
<th>P8</th>
<th>P9</th>
<th>P10</th>
<th>P11</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Compound 1" /></td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td><img src="image2.png" alt="Compound 2" /></td>
<td>1.30</td>
<td>2.39</td>
<td>3.83</td>
<td>4.86</td>
<td>6.13</td>
<td>7.80</td>
<td>6.09</td>
<td>5.65</td>
<td>5.73</td>
<td>5.41</td>
<td>5.73</td>
</tr>
<tr>
<td><img src="image3.png" alt="Compound 3" /></td>
<td>0.88</td>
<td>1.52</td>
<td>2.68</td>
<td>3.41</td>
<td>4.12</td>
<td>4.52</td>
<td>4.10</td>
<td>3.75</td>
<td>3.84</td>
<td>3.62</td>
<td>3.80</td>
</tr>
</tbody>
</table>
**Table S2.** Percent TTF functionalization of the obtained polymer (P1 to P11) after PPM based on relative proton integration values.

<table>
<thead>
<tr>
<th>% TTF functionalization based on H integration</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
<th>P8</th>
<th>P9</th>
<th>P10</th>
<th>P11</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td>30</td>
<td>44</td>
<td>56</td>
<td>62</td>
<td>67</td>
<td>72</td>
<td>67</td>
<td>65</td>
<td>66</td>
<td>64</td>
<td>66</td>
</tr>
<tr>
<td><img src="image2.png" alt="Diagram" /></td>
<td>31</td>
<td>43</td>
<td>57</td>
<td>63</td>
<td>67</td>
<td>69</td>
<td>67</td>
<td>65</td>
<td>66</td>
<td>65</td>
<td>66</td>
</tr>
</tbody>
</table>

Sample calculation of %TTF functionalization of P1.

%TTF functionalization of P1 based on TTF proton = (1.3/3)/(1.3/3+4/4)x100% = 30%.

%TTF functionalization of P1 based on -OCH2- = (0.88/2)/(0.88/2+4/4)x100% = 31%

**1H NMR of p(NHSMAs60-co-MMA40)**

Based on the relative proton integration value, we can determine that the molar ratio between MMA and NHSMA in the copolymer is 2:3 (as calculated by (3/3) : (6/4)).
$^1$H NMR of p(hmTTFMA$_{60}$-co-MMA$_{40}$)(TTF functionalized polymer from p(NHMSM$_{60}$-co-MMA$_{40}$)

Analogous to the calculations for P1 to P11, % TTF functionalization for phmTTFMA-co-MMA was determined to be 85 mol% (based on relative proton integration value on TTF) and 83 % (based on proton integration value on –OCH$_2$–).

$^1$H NMR of p(hmTTFMA-co-MMA) (Obtained polymer from p10 reacted with methanol)

Based on the analysis of $^1$H NMR spectra, proton TTF/(NHS+TTF) ratio increased from 64% to 71% after subjecting phmTTFMA (P10) with methanol. Additional methyl peak from MMA appeared which is
consistent the $^1$H NMR spectrum of phmTTFMA-co-MMA (TTF functionalized polymer from p(NHSMA$_{60}$-co-MMA$_{40}$). This indicated that the remaining NHS group in phmTTFMA (P10) remains active and is replaced by methoxy, a less sterically congested group.

III. Elemental analysis data and TTF functionaization calculation based on weight percent of sulfur and nitrogen

Table S3. Elemental analysis results of sulfur and nitrogen for P1 to P11.

<table>
<thead>
<tr>
<th>Weight % from elemental analysis</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
<th>P8</th>
<th>P9</th>
<th>P10</th>
<th>P11</th>
</tr>
</thead>
<tbody>
<tr>
<td>S analysis</td>
<td>18.06</td>
<td>20.88</td>
<td>30.57</td>
<td>32.66</td>
<td>34.32</td>
<td>34.00</td>
<td>33.66</td>
<td>33.63</td>
<td>33.33</td>
<td>33.30</td>
<td></td>
</tr>
<tr>
<td>N analysis</td>
<td>4.22</td>
<td>3.41</td>
<td>2.13</td>
<td>1.76</td>
<td>1.46</td>
<td>1.57</td>
<td>1.64</td>
<td>1.70</td>
<td>1.82</td>
<td>1.76</td>
<td></td>
</tr>
</tbody>
</table>

Table S4. Percent TTF functionalization of the obtained polymer (P1 to P11) after PPM based on elemental analysis data.

<table>
<thead>
<tr>
<th>% TTF functionalization based on elemental analysis</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
<th>P8</th>
<th>P9</th>
<th>P10</th>
<th>P11</th>
</tr>
</thead>
<tbody>
<tr>
<td>S analysis</td>
<td>31</td>
<td>37</td>
<td>61</td>
<td>67</td>
<td>72</td>
<td>72</td>
<td>71</td>
<td>70</td>
<td>69</td>
<td>69</td>
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</tr>
<tr>
<td>N analysis</td>
<td>33</td>
<td>43</td>
<td>61</td>
<td>67</td>
<td>72</td>
<td>70</td>
<td>70</td>
<td>69</td>
<td>68</td>
<td>66</td>
<td>67</td>
</tr>
</tbody>
</table>

Sample calculation of %TTF functionalization of P1.

%TTF functionalization of P1 based on S:

$$\frac{4 \ast 32.06x}{302.44x + 183.16(1 - x)} \times 100% = 18.06$$

Solve for x, where x = 31.
%TTF functionalization of P1 based on N:

\[
\frac{14.01y}{302.44(1 - y) + 183.16y} \times 100\% = 4.22
\]

Solve for y, where y = 67. % TTF functionalization = 100 - 67 = 33.

Elemental analysis data of \(p(\text{NHSMA}_{60-\text{co-MMA}}_{40})\): C(54.46); H(5.59); N (5.61).

Elemental analysis data of \(\text{phmTTFMA-\text{co-MMA}}\): S (30.24); C(47.50); H(4.40); N (0.73).

Analogous to the calculations for P1 to P11, % TTF functionalization for \(\text{phmTTFMA-\text{co-MMA}}\) was determined to be 82 mol %

Elemental analysis data of \(p(\text{NAS})\): C(49.71); H(4.24); N (8.26).

Elemental analysis data of \(\text{phmTTFMA-r-NAS}\): S (37.98); C (43.01); H(3.03); N (1.12).

Analogous to the calculations for P1 to P11, % TTF functionalization for \(\text{phmTTFMA-\text{co-MMA}}\) was determined to be 78 mol %

IV. IR of \(\text{phmTTFMA and phmTTFMA-\text{co-MMA from PPM using pNHSMA-\text{co-MMA and phmTTFMA as polymer precursors}}}

![Figure S4](image-url)  
**Figure S4.** IR spectra of \(\text{phmTTFMA and phmTTFMA-\text{co-MMA from PPM using different polymer precursors.}}**
V. GPC data

\[ \text{p(hmTTFMA}_{60\text{-co-MMA}_{40}) \text{ (TTF functionalized polymer from p(NHSMMA}_{60\text{-r-MMA}_{40}) \text{ (black curve)}}] \]

\( Mn = 20.7 \text{ kDa, PDI = 1.24} \)

\[ \text{pTTFA-co-NAS (TTF functionalized polymer from pNAS) (red curve)}] \]

\( Mn = 44.5 \text{ kDa, PDI = 1.67} \)

VI. TGA data of 4-(hydroxymethyl)TTF

\[ \text{Figure S5. TGA curve of 4-(hydroxymethyl)TTF where } T_d = 179 \ ^\circ \text{C at 5 \% weight loss with a heating rate of 10} \ ^\circ \text{C min}^{-1}. \]
VII. XRD data

![XRD data graph](image)

**Figure S6.** X-ray patterns of the cast films of pTTF-CA (both low and high % TTF functionalization), TTF-CA, CA. When TTF incorporation to the polymer backbone is decreased, phase separation between pTTF and chloranil was observed.

VIII. Film-forming phmTTFMA

![Film images](image)

**Figure S7.** (a) Free-standing film of phmTTFMA; (b) phmTTFMA-chloranil film on glass substrate for electrical conductivity measurement.
IX. Attempted syntheses of TTF-derivatives with primary amine

Scheme S1. Attempted syntheses of TTF-derivatives with primary amine, where the starting materials were synthesized following literature reports.\textsuperscript{1,2}

Conditions attempted:
1) Pd/C, H\textsubscript{2}, ACN/EtOAc/THF/DCM, overnight
2) PPh\textsubscript{3}, H\textsubscript{2}O, THF, reflux, overnight
3) LAH, Et\textsubscript{2}O/THF, reflux, overnight
4) NaBH\textsubscript{4}, CuSO\textsubscript{4}, ACN/THF, reflux 24h
5) Zn, NH\textsubscript{4}Cl, THF, r.t./reflux, overnight

References: