SUPPORTING INFORMATION

A Simple and Efficient Route to *N*-Functionalized Dithieno[3,2-*b*:2',3'-*d*]pyrroles: Fused-Ring Building Blocks for New Conjugated Polymeric Systems.

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***N*-Hexyldithieno[3,2-*b*:2',3'-*d*]pyrrole (12a):** mp 41.7-42.5 °C; IR (KBr) 3100, 3077, 2925, 2854, 1523, 1465, 1405, 1376, 1279, 1095, 1078, 845, 801, 787, 715, 693, 652 cm⁻¹; R_f 0.086 (Hexanes).

***N*-Octyldithieno[3,2-*b*:2',3'-*d*]pyrrole (12b):** mp 34.6-35.2 °C; IR (KBr) 3102, 3081, 2926, 2853, 1523, 1463, 1406, 1376, 1280, 1097, 1079, 847, 798, 790, 720, 692, 652 cm⁻¹; R_f 0.086 (Hexanes).

***N*-Decyldithieno[3,2-*b*:2',3'-*d*]pyrrole (12c):** mp 31.2-32.0 °C; FT (KBr) 3102, 3081, 2924, 2852, 1523, 1464, 1406, 1376, 1280, 1097, 1079, 848, 798, 766, 719, 692, 652 cm⁻¹; R_f 0.086 (Hexanes).

***N*-*tert*-Butyldithieno[3,2-*b*:2',3'-*d*]pyrrole (12d):** mp 102.3-102.9 °C; IR (KBr) 3123, 3104, 2982, 2935, 1506, 1455, 1411, 1369, 1270, 1216, 1114, 819, 761, 697, 658 cm⁻¹; R_f 0.071 (Hexanes).

***N*-(*p*-Hexylphenyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (12e):** mp 57.4-58.0 °C; IR (KBr) 3104, 3032, 2925, 2854, 1519, 1403, 1303, 1106, 1085, 808, 691, 654 cm⁻¹; R_f 0.11 (Hexanes).

Crystallography. X-ray quality crystals of the DTPs were grown by the slow evaporation of isopropanol solutions. The X-ray intensity data were measured at 298K on a Bruker SMART 1000 CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$) operated at 2000 watts of power. The detector was placed at a distance of 5.047 cm from the crystal. A total of 1321 frames were collected with a scan width of 0.3° in ω and exposure time of 10 sec./frame. The total data collection time was 3.7 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. All data was integrated using a triclinic unit cell and the structures were refined using the Bruker SHELXTL (Version 5.1) Software Package.

A clear colorless plate-like crystal of **12b**, approximate dimensions 0.60 mm x 0.20 mm x 0.10 mm, was used for X-ray crystallographic analysis. The integration of the data using a triclinic unit cell yielded a total of 9629 reflections to a maximum 2θ angle of 56.54° ($0.75 \text{ \AA}$ resolution), of which 3679 were independent (redundancy 2.62, $R_{\text{int}} = 4.64\%$) and 3495 (36.3%) were greater than $2\sigma(F)$. The final cell constants of $a = 13.089(2) \text{ \AA}$, $b = 9.3002(14) \text{ \AA}$, $c = 13.861(2) \text{ \AA}$, $\beta = 108.97(3)^\circ$, volume = $1595.7(4) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 1758 reflections above $20 \sigma(I)$. Analysis of the data showed negligible decay during data collection. The data were corrected for absorption using the SADABS program, with maximum and minimum transmission coefficients of 0.928 and 0.653, respectively.

The structure was refined using the space group $P2_1/n$, with $Z = 4$ for the formula unit $C_{16}H_{21}NS_2$. The final anisotropic full-matrix least-squares refinement on F^2 converged at $R1 = 4.70\%$, $wR2 = 10.34\%$ and a goodness-of-fit of 0.851. The largest peak on the final difference map was $0.194 \text{ e}^-/\text{\AA}^3$. The calculated density for $C_{16}H_{21}NS_2$ is 1.213 g/cm^3 and $F(000)$ is 624 e.

A clear light yellow tabular crystal of **12d**, approximate dimensions 0.76 mm x 0.42 mm x 0.30 mm, was used for X-ray crystallographic analysis. The integration of the data using a triclinic unit cell yielded a total of 14,595 reflections to a maximum 2θ angle of 56.68° ($0.75 \text{ \AA}$ resolution), of which 5531 were independent (redundancy 2.64, $R_{\text{int}} = 1.93\%$) and 8874 (60.8%) were greater than $2\sigma(F)$. The final cell constants of $a = 12.8020(7) \text{ \AA}$, $b = 11.5375(7) \text{ \AA}$, $c = 17.6364(10) \text{ \AA}$, $\beta = 110.7740(10)^\circ$, volume = $2435.6(2) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 5229 reflections above $20 \sigma(I)$. Analysis of the data showed negligible decay

during data collection. The data were corrected for absorption using the SADABS program, with maximum and minimum transmission coefficients of 0.894 and 0.658, respectively.

The structure was refined using the space group $P2_1/c$, with $Z = 8$ for the formula unit $C_{12}H_{13}NS_2$. The final anisotropic full-matrix least-squares refinement on F^2 converged at $R1 = 5.88\%$, $wR2 = 17.65\%$ and a goodness-of-fit of 1.143. The largest peak on the final difference map was $0.413 \text{ e}^-/\text{\AA}^3$. The calculated density for $C_{12}H_{13}NS_2$ is 1.284 g/cm^3 and $F(000)$ is 992 e. A clear colorless prismatic crystal of **12e**, approximate dimensions $0.44 \text{ mm} \times 0.32 \text{ mm} \times 0.20 \text{ mm}$, was used for X-ray crystallographic analysis. The integration of the data using a triclinic unit cell yielded a total of 21,744 reflections to a maximum 2θ angle of 56.56° ($0.75 \text{ \AA}$ resolution), of which 8317 were independent (redundancy 2.61, $R_{\text{int}} = 4.31\%$) and 7784 (35.8%) were greater than $2\sigma(F)$. The final cell constants of $a = 12.9396(12) \text{ \AA}$, $b = 7.9145(7) \text{ \AA}$, $c = 35.458(3) \text{ \AA}$, $\beta = 96.465(2)^\circ$, volume = $3608.2(6) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 3761 reflections above $20 \sigma(I)$. Analysis of the data showed negligible decay during data collection. The data were corrected for absorption using the SADABS program, with maximum and minimum transmission coefficients of 0.928 and 0.627, respectively.

The structure was refined using the space group $P2_1/n$, with $Z = 8$ for the formula unit $C_{20}H_{21}NS_2$. The final anisotropic full-matrix least-squares refinement on F^2 converged at $R1 = 4.53\%$, $wR2 = 10.48\%$ and a goodness-of-fit of 0.805. The largest peak on the final difference map was $0.210 \text{ e}^-/\text{\AA}^3$. The calculated density for $C_{20}H_{21}NS_2$ is 1.250 g/cm^3 and $F(000)$ is 1440 e.

Full crystallography data are attached as a separate CIF file.

Figure S1. UV-vis spectrum of **12e**

Figure S2. Emission spectrum of **12e**

Table S1. Electrochemical Data for compounds **15a-e**.^a

<i>n</i>	R	<i>E</i> _{ox1} (V)	<i>E</i> _{ox2} (V)	<i>E</i> _{ox3} (V)
a	C ₆ H ₁₃	0.37	0.66	-
b	C ₈ H ₁₇	0.37	0.66	1.19
c	C ₁₀ H ₂₁	0.37	0.67	1.18
d	^t Bu	0.51	-	-
e	<i>p</i> -C ₆ H ₁₃ Ar	0.47	0.73	1.06

^aAll potentials vs. Ag/Ag⁺. Voltammetric data were measured in millimolar argon-sparged CH₃CN solutions with 0.1 M TBAPF₆ as supporting electrolyte.

Table S2. UV-vis Absorption Data for compounds **15a-e**.

<i>n</i>	R	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹)
a	C ₆ H ₁₃	296	6111
b	C ₈ H ₁₇	297	6333
c	C ₁₀ H ₂₁	286	5542
d	^t Bu	287	4870
e	<i>p</i> -C ₆ H ₁₃ Ar	294	13764