Supporting Information

Tuning the extended structure and electronic properties of gold(I) thienyl pyrazolates

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Procedures

1-[(4-Methylphenyl)sulfonyl]-4-(2-thienyl)-1H-pyrazole (TsPzT):

A degassed 2:1 THF/water (24 mL) solution of K_2CO_3 (0.304 g, 2.20 mmol), 2-thienyl boronic acid (0.128 g, 1.00 mmol), 4-iodo-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrazole (0.347 g, 1.00 mmol), and $Pd(PPh_3)_4$ (0.0648 g, 0.0560 mmol) was heated to reflux for 16 hours. The reaction mixture was cooled to room temperature and most of the THF was removed *in vacuo*. CH_2Cl_2 (20 mL) was added to the resulting mixture and was washed with H_2O (3 × 10 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo* to give an orange solid. The crude product was purified *via* column chromatography on silica gel with CH_2Cl_2 as the eluent to give a white solid in 70 % yield. *m/z*: 304. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.93 (d, J = 9 Hz, 2 H), 7.89 (s, 1H), 7.35 (d, J = 8 Hz, 2H), 7.25 (dd, J = 1 Hz, J = 8 Hz, 1 H), 7.14 (dd, J = 1 Hz, J = 3 Hz, 1H), 7.04 (dd, J = 3 Hz, J = 8 Hz), 2.43 (s, 3H).

3,5-Dimethyl-1-[(4-methylphenyl)sulfonyl]-4-(2-thienyl)-1H-pyrazole (TsPz*T):

A procedure similar to that used for the synthesis of TsPzT was used with reagents K_2CO_3 (0.304 g, 2.20 mmol), 2-thienyl boronic acid (0.128 g, 1.00 mmol), 3,5-dimethyl-4-iodo-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrazole (0.376 g, 1.00 mmol), and $Pd(PPh_3)_4$ (0.058 g, 0.050 mmol) to give an orange solid. The crude product was purified *via* column chromatography on silica with CH_2Cl_2 as the eluent to give a white solid in 69 % yield. *m/z*: 332. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 8 Hz, 2H), 7.35 (m, 3H), 7.09 (dd, J = 3 Hz, J = 5 Hz), 6.91 (dd, J = 1 Hz, J = 3 Hz), 2.57 (s, 3H), 2.44 (s, 3H), 2.27 (s, 3H).

4-[5-(2,2'-Bithiophene)]-1-[(4-methylphenyl)sulfonyl]-1H-pyrazole ($TsPzT_2$):

A procedure similar to that used for the synthesis of TsPzT was used with reagents K_2CO_3 (0.304 g, 2.20 mmol), 2,2'-bithiophene-5 boronic acid pinacol ester (0.292 g, 1.00 mmol), 4-iodo-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrazole (0.348 g, 1.00 mmol), and $Pd(PPh_3)_4$ (0.058 g, 0.050 mmol) to give an orange solid. The crude product was purified *via* column chromatography on silica with CH_2Cl_2 as the eluent to give a light yellow solid in 51 % yield. *m/z*: 386. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.93 (d, J = 8 Hz, 2H), 7.89 (s, 1H), 7.35 (d, J = 8 Hz, 2H), 7.23 (dd, J = 1 Hz, 5 Hz), 7.16 (dd, J = 1 Hz, J = 3 Hz, 1H), 7.09 (d, J = 1 Hz, J = 7 Hz, 1H), 7.05

(m, 2H), 2.44 (s, 3H).

4-[5-(2,2'-Bithiophene)]-3,5-dimethyl-1-[(4-methylphenyl)sulfonyl]-1H-pyrazole (TsPz*T_2):

A procedure similar to that used for the synthesis of TsPzT was used with reagents K_2CO_3 (0.304 g, 2.20 mmol), 2,2'-bithiophene-5 boronic acid pinacol ester (0.292 g, 1.00 mmol), 3,5-dimethyl-4-iodo-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrazole (0.376 g, 1.00 mmol), and $Pd(PPh_3)_4$ (0.058 g, 0.050 mmol) to give an orange solid. The crude product was purified *via* column chromatography on silica with CH_2Cl_2 as the eluent to give a light yellow solid in 49 % yield. *m/z*: 414. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 8 Hz, 2H), 7.35 (d, J = 8 Hz, 2H), 7.23 (dd, J = 1 Hz, 5 Hz), 7.16 (dd, J = 1 Hz, J = 3 Hz, 1H), 7,14 (d, 3 Hz, 1H), 7.02 (dd, J = 3 Hz, J = 5 Hz, 1H), 6.81 (d, J = 3 Hz, 1H), 7.09 (d, J = 1 Hz, J = 7 Hz, 1H), 2.60 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H).

1-Boc-4-[2-(3-hexylthienyl)]-1H-pyrazole (BocPz3HT):

A degassed 3:1 THF/water (20 mL) solution of K_2CO_3 (0.304 g, 2.20 mmol), 2-bromo-3-hexylthiophene (0.247 g, 1.00 mmol), 1-boc-pyrazole-4-boronic acid pinacol ester (0.294 g, 1.00 mmol), and PEPPSI-IPr (0.0340 g, 0.0500 mmol) was heated to 50 °C for one day. The reaction mixture was cooled to room temperature and most of the THF was removed *in vacuo*. CH_2Cl_2 (20 mL) was added to the resulting mixture and was washed with H_2O (3 × 10 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed evaporated *in vacuo* to give a brown oil. The crude product was purified *via* column chromatography on silica gel with CH_2Cl_2 (with 0.1 % triethylamine) as the eluent giving a light yellow oil in 52 % yield. *m/z*: 334. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.83 (s, 1H), 7.19 (d, J = 5 Hz, 1H), 6.95 (d, J = 5 Hz, 1H), 2.65 (t, J = 8 Hz, 2H), 1.69 (s, 9H), 1.58 (m, 2H), 1.31 (m, 6H), 0.88 (t, J = 7 Hz, 3 H).

1-Boc-3,5-dimethyl-4-[2-(3-hexylthienyl)]-1H-pyrazole (BocPz*3HT):

A procedure similar to that used for the synthesis of BocPz3HT was used with reagents K_2CO_3 (0.304 g, 2.20 mmol), 2-bromo-3-hexylthiophene (0.247 g, 1.00 mmol), 1-boc-3,5-dimethyl-pyrazole-4-boronic acid pinacol ester (0.322 g, 1.00 mmol), and PEPPSI-IPr (0.0340 g, 0.0500 mmol) to give a brown oil. The crude product was purified *via* column chromatography on silica gel with CH_2Cl_2 (with 0.1 % triethylamine) as the eluent giving a light yellow oil in 44 % yield. *m/z*: 362. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, J = 5 Hz, 1H), 6.99 (d, J = 5 Hz, 1H), 2.36 (s, 3H), 2.34

(t, J = 8 Hz, 2H), 2.17 (s, 3H), 1.63 (s, 9H), 1.47 (m, 2H), 1.20 (m, 6H), 0.85 (t, J = 7 Hz, 3H).

1-Boc-4-[5-(3,3'-dihexyl-2,2'-bithienyl)]-1H-pyrazole (BocPz3HT$_2$):

A procedure similar to that used for the synthesis of BocPz3HT was used with reagents K_2CO_3 (0.304 g, 2.20 mmol), 5-bromo-3,3'-dihexyl-2,2'-bithiophene (0.413 g, 1.00 mmol), 1-boc-pyrazole-4-boronic acid pinacol ester (0.294 g, 1.00 mmol), and PEPPSI-IPr (0.0340 g, 0.0500 mmol) to give a brown oil. The crude product was purified *via* column chromatography on silica gel with CH_2Cl_2 (with 0.1 % triethylamine) as the eluent giving a light yellow oil in 38 % yield. *m/z*: 500. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.90 (s, 1H), 7.31 (d, J = 5 Hz, 1H), 7.04 (s, 1H), 6.97 (d, J = 5 Hz, 1H), 2.54 (t, J = 8 Hz, 2H), 2.48 (t, J = 8 Hz, 2H), 1.68 (s, 9H), 1.56 (m, 4H), 1.23 (m, 12H), 0.86 (m, 6H).

1-Boc-4-[5-(3,3'-dihexyl-2,2'-bithienyl)]-3,5-dimethyl-1H-pyrazole (BocPz*3HT$_2$):

A procedure similar to that used for the synthesis of BocPz3HT was used with reagents K_2CO_3 (0.304 g, 2.20 mmol), 5-bromo-3,3'-dihexyl-2,2'-bithiophene (0.413 g, 1.00 mmol), 1-boc-3,5-dimethyl-pyrazole-4-boronic acid pinacol ester (0.322 g, 1.00 mmol), and PEPPSI-IPr (0.0340 g, 0.0500 mmol) to give a brown oil. The crude product was purified *via* column chromatography on silica gel with CH_2Cl_2 (with 0.1 % triethylamine) as the eluent giving a light yellow oil in 36 % yield. *m/z*: 528. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, J = 5 Hz, 1H), 6.98 (d, J = 5 Hz, 1H), 6.80 (s, 1H), 2.61 (s, 3H), 2.58 (t, J = 8 Hz, 2H), 2.53 (t, J = 8 Hz, 2H), 2.37 (s, 3H), 1.67 (s, 9H), 1.57 (m, 4H), 1.27 (m, 12H), 0.86 (m, 6H).

4-(2-Thienyl)-1H-pyrazole (HPzT):

TsPzT (0.152 g, 0.500 mmol) was added to 2:1 MeOH/5 M NaOH (6 mL). The mixture was refluxed for five hours. Upon cooling the reaction mixture to room temperature, the reaction volume was reduced by half, 15 mL of CH_2Cl_2 was added, and the organic layer was washed with (4 × 6 mL). The organic layer was dried over $MgSO_4$, filtered, and dried *in vacuo* to give a white solid in 88 % yield. Crystals suitable for SCXRD were grown from slow evaporation of CH_2Cl_2 to give colorless crystals of HPzT. *m/z*: 150. ^{1}H NMR (400 MHz, Acetone-d_6): δ 11.86 (s, 1H), 7.88 (s, 2H), 7.27 (dd, 1 Hz, 5 Hz, 1H), 7.18 (dd, 1 Hz, 3 Hz, 1H), 7.03 (dd, 3 Hz, 5 Hz, 1H). ^{13}C NMR (100 MHz, Acetone-d_6): δ 137.2, 137.0, 128.9, 124.1, 124.0, 123.6. FT-IR (cm^{-1}): 3101 (m, br),

2930 (m, br), 2840 (w, br), 1589 (w), 1516 (w), 1494 (w), 1434 (w), 1386 (w), 1346 (m), 1213 (m), 1148 (m), 1045 (w), 1018 (m), 950 (m), 908 (w), 855 (m), 840 (s), 808 (s), 688 (vs), 657 (s), 619 (s), 576 (m), 559 (w), 498 (m), 405 (m) Elem Calc for $C_7H_6N_2S$: C, 55.98; H, 4.03; N, 18.65. Found: C, 55.51; H, 4.16; N, 17.85.

3,5-Dimethyl-4-(2-thienyl)-1H-pyrazole (HPz*T):

A procedure similar to that used for the synthesis of HPzT was used with 3,5-dimethyl-4-iodo-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrazole (0.199 g, 0.600 mmol). A white solid was obtained in 93 % yield. Crystals suitable for SCXRD were grown from layering hexanes on a solution of HPz*T in CH_2Cl_2. *m/z*: 178. ^{1}H NMR (400 MHz, Acetone-d_6): δ 11.59 (s, 1H), 7.38 (dd, J = 1 Hz, J = 6 Hz, 1H), 7.10 (dd, J = 3 Hz, J = 5 Hz, 1H), 6.99 (dd, J = 1 Hz, J = 6 Hz, 1H), 2.31 (s, 6H). ^{13}C NMR (100 MHz, Acetone-d_6): δ 132.2, 128.7, 125.3, 124.5, 122.0, 113.7, 30.0. FT-IR (cm^{-1}: 3156 (w, br), 3101 (m), 3063 (m), 3020 (m), 2921 (m, br), 2829 (m, br), 1588 (w), 1550 (m), 1496 (w), 1433 (m), 1415 (m), 1304 (q), 1249 (m), 1209 (w), 1157 (w), 1053 (w), 1034 (m), 1002 (w), 942 (m), 819 (m, br), 698 (s), 686 (s), 631 (m), 587 (w), 517 (m), 476 (w). Calc for $C_9H_{10}N_2S$: C, 60.64; H, 5.65; N, 15.72. Found: C, 60.63; H, 5.53; N, 15.65.

4-[5-(2,2'-Bithienyl)]-1H-pyrazole ($HPzT_2$):

A procedure similar to that used for the synthesis of HPzT was used with $TsPzT_2$ (0.154 g, 0.400 mmol), and 30 mL CH_2Cl_2 was used to extract $HPzT_2$. The crude product was was *via* centrifugation thrice in 1:1 CH_2Cl_2/hexanes to gives a yellow solid in 92 % yield. *m/z*: 232. ^{1}H NMR (Acetone-d_6): δ 7.93 (s, 2H), 7.39 (d, J = 5 Hz, 1H), 7.24 (d, J = 3 Hz, 1H), 7.18 (d, J = 4 Hz, 1H), 7.14 (d, J = 4 Hz, 1H), 7.07 (dd, J = 3 Hz, J = 5 Hz, 1H). ^{13}C NMR (100 MHz, Acetone-d_6): 135.5, 133,7, 129.0, 126.6, 126.2, 125.3, 124.3, 124.1, 123.1. δ FT-IR (cm^{-1}): 3103 (m, br), 2927 (m, br), 1513 (m), 1427 (m), 1381 (m), 1348 (m), 1331 (w), 1197 (w), 1145 (m), 1045 (w), 1014 (m), 950 (m), 909 (w), 862 (w), 835 (s), 818 (w), 796 (vs), 700 (s), 658 (m), 623 (m), 541 (m), 479 (m). Elem Calcd for $C_{11}H_8N_2S_2$: C, 56.87; H, 3.47; N, 12.06. Found C, 56.52; H, 11.70; N, 3.52.

4-[5-(2,2'-Bithienyl)]-3,5-dimethyl-1H-pyrazole (HPz*T_2):

A procedure similar to that used for the synthesis of HPzT was used with $TsPz*T_2$ (0.166 g, 0.400 mmol), and 30 mL CH_2Cl_2 was used to extract HPz*T_2. The crude product was was *via*

centrifugation thrice in 1:1 CH_2Cl_2/hexanes to gives a yellow solid in 89 % yield. *m/z*: 260. ^{1}H NMR (400 MHz, Acetone-d_6) δ 11.64 (s, 1H), 7.39 (dd, J = 1 Hz, J = 6 Hz, 7.27 (dd, J = 1 Hz, J = 6 Hz, 1 H), 7.24 (d, J = 5 Hz, 1H), 7.07 (dd, J = 3 Hz, J = 5 Hz, 1H), 6.95 (d, J = 4 Hz, 1H), 2.36 (s, 6H). ^{13}C NMR (100 MHz, Acetone-d_6): δ 136.5, 135.9, 129.7, 129.0, 126.1, 125.3, 125.0, 124.2, 124.0, 111.6, 30.2. FT-IR (cm^{-1}): 3055 (m, br), 2917 (m, br), 1581 (m), 1553 (w), 1521 (m), 1452 (w), 1413 (m), 1378 (w), 1298 (m), 1256 (m), 1219 (w), 1149 (w), 1034 (m), 1007 (w), 979 (w), 944 (m), 881 (w), 831 (m), 796 (vs), 779 (s), 686 (vs), 637 (m), 575 (w), 542 (m), 502 (w), 474 (m), 427 (m). Elem Calc for $C_{13}H_{12}N_2S_2$: C, 59.97; H, 4.65; N, 10.76. Found: C, 59.85; H, 4.51; N, 10.46.

4-[2-(3-Hexylthienyl)]-1H-pyrazole (HPz3HT):

BocPz3HT (0.167 g, 0.500 mmol) was dissolved in 2:1 MeOH/4 M HCl (6 mL) and heated to 60 °C for two hours. Upon cooling the reaction mixture to room temperature, the volume was reduced by half, 8 mL of CH_2Cl_2 was added, and the organic layer was washed with H_2O (4 × 5 mL). The organic layer was dried over $MgSO_4$, filtered, and dried *in vacuo* to give a yellow oil in 89 % yield. *m/z*: 234. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 2H), 7.15 (d, 5 Hz, 1H), 6.95 (d, 5 Hz, 1H), 2.65 (t, 8 Hz, 2H), 1.62 (m, 2H), 1.29 (m, 6H), 0.88 (t, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 138.8, 133.0, 129.5, 122.7, 119.0, 31.7, 30.6, 29.2, 29.0, 22.6, 14.1. FT-IR (cm^{-1}): 3160 (m, br), 2953 (s), 2923 (vs), 2854 (s), 1592 (w), 1464 (m), 1367 (m), 1259 (w), 1144 (m), 1067 (w), 1023 (s), 947 (m), 912 (m), 855 (m), 836 (w), 799 (m), 721 (w), 662 (m), 625 (m), 505 (m). Elem Calc for $C_{13}H_{18}N_2S$: C, 66.62; H, 7.74; N, 11.95. Found: C, 65.45; H, 8.36; N, 11.28.

4-[2-(3-Hexylthienyl)]-3,5-dimethyl-1H-pyrazole (HPz*3HT):

A procedure similar to that used for the synthesis of HPz3HT was used with BocPz*3HT (0.152 g, 0.420 mmol). A yellow oil was obtained in 92 % yield. *m/z*: 262. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.67 (s, 1H), 7.28 (d, J = 5 Hz, 1H), 7.02 (d, J = 5 Hz, 1H), 2.40 (t, J = 7 Hz, 2H), 2.20 (s, 6H), 1.51 (m, 2H), 1.21 (m, 6H), 0.84 (t, J = 7 Hz, 3H). ^{13}C (100 MHz, CD_2Cl_2): δ 144.3, 141.9, 129.1, 128.6, 125.0 111.1, 32.2, 31.1, 29.6, 29.1, 23.2, 14.4, 11.6. FT-IR (cm^{-1}): 3172 (m), 3127 (w), 3063 (w), 2953 (s), 2922 (vs), 2854 (s), 1596 (w), 1553 (w), 1455 (m), 1376 (m), 1307 (m), 1259 (w), 1154 (m), 1042 (m), 1000 (w), 834 (m), 777 (m), 718 (s), 686 (m), 653 (m), 531 (m), 457 (w). Elem Calc for $C_{15}H_{22}N_2S$: C, 68.66; H, 8.45; N, 10.68. Found: C, 67.57; H, 8.59;

N, 11.14.

4-[5-(3,3'-Dihexyl-2,2'-bithienyl)]-1H-pyrazole ($HPz3HT_2$):

A procedure similar to that used for the synthesis of HPz3HT was used with $BocPz3HT_2$ (0.175 g, 0.350 mmol). A yellow oil was obtained in 82 % yield. *m/z*: 400. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.30 (d, J = 5 Hz, 1H), 6.98 (s, 1H), 6.97 (d, J = 5 Hz, 1H), 2.55 (t, J = 8 Hz, 2H), 2.49 (t, J = 8 Hz, 2H), 1.56 (m, 4H), 1.25 (m, 12H), 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 142.4, 135.4, 131.0, 128.6, 128.5, 126.7, 125.3, 124.5, 123.1, 31.6, 30.7, 30.6, 29.7, 29.1, 29.0, 28.9, 28.8, 22.6, 14.1. FT-IR (cm^{-1}): 2955 (m), 2921 (s), 2852 (s), 1588 (m), 1521 (w), 1456 (m), 1372 (m),1260 (s), 1196 (w), 1094 (s), 1040 (s), 1020 (s), 873 (w), 818 (s), 801 (s), 692 (m), 641 (m). Elem Calc for $C_{23}H_{32}N_2S_2$: C, 68.95; H, 8.05; N, 6.99. Found: C, 68.73; H, 8.21; N, 7.15.

4-[5-(3,3'-Dihexyl-2,2'-bithienyl)]-3,5-dimethyl-1H-pyrazole ($HPz*3HT_2$):

A procedure similar to that used for the synthesis of HPz3HT was used with $BocPz*3HT_2$ (0.158 g, 0.300 mmol). A yellow oil was obtained in 87 % yield. *m/z*: 428. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 5 Hz, 1H), 6.97 (d, J = 5 Hz, 1H), 6.83 (s, 1H), 2.56 (t, J = 8 Hz, 2H), 2.52 (t, J = 8 Hz, 2H), 2.43 (s, 6H), 1.57 (m, 4H), 1.28 (m, 12H), 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 142.4, 142.3, 136.3, 134.7, 127.4, 126.5, 125.3, 124.0, 31.6, 30.7, 30.2, 29.7, 29.1, 29.0, 28.9, 28.8, 22.6, 14.0, 12.2. FT-IR (cm^{-1}): 3188 (w), 3064 (w), 2954 (s), 2922 (vs), 2853 (s), 1586 (w), 1539 (w), 1509 (w), 1456 (m), 1415 (w), 1377 (m), 1303 (w), 1261 (m), 1157 (w), 1086 (m), 1014 (m), 833 (m), 798 (s), 738 (s), 660 (w). Elem Calc for $C_{25}H_{36}N_2S_2$: C, 70.04; H, 8.46; N, 6.53. Found: C, 70.36; H, 8.81; N, 6.22.

tris-(μ-N,N'-(4-(2-Thienyl)pyrazolato)trigold(I)) (AuPzT):

AuCl(tht) (0.320 g, 1.00 mmol) and HPzT (0.150 g, 1.00 mmol) were dissolved in 1:1 MeOH/-THF. Slow diffusion of triethylamine in 1:1 MeOH/THF over three days afforded colorless needles of AuPzT suitable for SCXRD in 41% yield. *m/z*: 1038. FT-IR (cm^{-1}), 3111 (w), 2961 (w), 1584 (m), 1391 (m), 1358 (m), 1316 (m), 1258 (m), 1217 (m), 1179 (w), 1106 (s), 1076 (m), 1052 (m), 1034 (m), 911 (m), 818 (s), 701 (s), 686 (s), 650 (m), 632 (m), 578 (w), 504 (m), 454 (m). Elem Calcd for $C_{21}H_{15}N_6S_3Au$: C, 24.29; H, 1.46; N, 8.09. Found C, 25.02; H, 2.03; N, 7.99.

tris-(μ-N,N'-(4-(2-Thienyl)3,5-dimethylpyrazolato)trigold(I)) (AuPz*T):

AuCl(tht) (0.320 g, 1.00 mmol) and HPz*T (0.150 g, 1.00 mmol) were dissolved in 1:1 MeOH/-THF. Slow diffusion of triethylamine in 1:1 MeOH/THF over two days afforded a white microcrystalline powder of AuPz*T in 43 % yield. *m/z*: 1122. FT-IR (cm^{-1}): 2956 (m) 2908 (m), 2971 (m), 1557 (m), 1505 (m), 1430 (s) 1373 (m), 1316 (w), 1258 (m), 1233 (m), 1215 (w), 1156 (m), 1120 (w), 1022 (m), 1003 (m), 952 (m), 846 (m), 806 (m), 770 (w), 686 (s), 675 (s), 621 (w), 601 (w), 581 (w), 559 (w), 497 (m), 462 (m). Elem Calcd for $C_{27}H_{27}N_6S_3Au_3$: C, 28.89; H, 2.42; N, 7.49. Found: C, 29.32; H, 2.21; N 7.68.

tris-(μ-N,N'-(4-[5-(2,2'-Bithienyl)]pyrazolato)trigold(I)) ($AuPzT_2$):

AuCl(tht) (0.320 g, 1.00 mmol) and $HPzT_2$ (0.232 g, 1.00 mmol) were dissolved in 1:1 MeOH/-THF. Slow diffusion of triethylamine in 1:1 MeOH/THF over five days afforded gold feathered crystals of $AuPzT_2$ in 39 % yield. *m/z*: 1284. FT-IR (cm^{-1}): 3108 (w), 2847 (w), 1584 (m), 1539 (w), 1463 (w), 1423 (w), 1387 (m), 1346 (m), 1293 (w), 1258 (w), 1173 (m), 1102 (m), 1053 (m), 1028 (m), 913 (m), 878 (w), 817 (m), 802 (m), 780 (s), 686 (s), 636 (m), 535 (m), 476 (m), 432 (m). Elem Calcd for $C_{33}H_{21}N_6S_6Au_3$: C, 30.85; H, 1.65; N, 6.54. Found: C, 30.63; H, 1.78; N, 6.30.

tris-(μ-N,N'-(4-[5-(2,2'-Bithienyl)]3,5-dimethylpyrazolato)trigold(I)) ($AuPz*T_2$):

AuCl(tht) (0.320 g, 1.00 mmol) and $HPz*T_2$ (0.260 g, 1.00 mmol) were dissolved in 1:1 MeOH/-THF. Slow diffusion of triethylamine in 1:1 MeOH/THF over one week afforded a yellow powder of $AuPz*T_2$ in 36 % yield. *m/z*: 1368. FT-IR (cm^{-1}): 3066 (w), 2910 (w), 1565 (m), 1532 (m), 1490 (w), 1424 (m), 1372 (m), 1308 (w), 1263 (m), 1223 (w), 1199 (w), 1104 (w), 1045 (w), 1001 (m), 951 (m), 837 (s), 817 (w), 784 (s), 740 (w), 683 (vs), 634 (w), 581 (m), 478 (s). Elem Calcd for $C_{39}H_{33}N_6S_6Au_3$: C, 34.22; H, 2.43; N, 6.14. Found: C, 34.36; H, 2.27; N, 5.81.

tris-(μ-N,N'-(4-[2-(3-Hexylthienyl)]pyrazolato)trigold(I)) (AuPz3HT):

AuCl(tht) (0.032 g, 0.10 mmol) and HPz3HT (0.023 g, 0.10 mmol), and triethylamine (14 μL, 0.10 mmol) were dissolved in THF (15 mL) and stirred at room temperature for 20 minutes.

The reaction was evaporated to dryness, and the resulting residue was suspended in hexanes and centrifuged. The supernatant was collected, evaporated to dryness, and purified *via* column chromatography on silica with 4:1 hexanes:CH_2Cl_2 as the eluent to give a white solid in 62 % yield. *m/z*: 1290 (100 %), 2578 (18 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 6H), 7.10 (d, J = 5 Hz, 3H), 6.91 (d, J = 5 Hz, 3H), 2.58 (t, J = 8 Hz, 6H), 1.58 (m, 6H), 1.30 (m, 18H), 0.90 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 138.0, 129.5, 128.3, 122.2, 115.7, 31.8, 30.5, 29.7, 29.1, 22.7, 14.2. FT-IR (cm^{-1}: 2955 (s), 2921 (vs), 2851 (vs), 1580 (w), 1522 (w), 1463 (m), 1390 (w), 1361 (w),1338 (w), 1260 (m), 1180 (w), 1084 (s), 1041 (m), 915 (w), 820 (m), 802 (s), 730 (w), 691 (w), 647 (m). Elem Calcd for $C_{39}H_{51}N_6S_3Au_3$: C, 36.29; H, 3.98; N, 6.51. Found: C, 35.99; H, 3.72; N, 6.84.

tris-(μ-N,N'-(4-[2-(3-Hexylthienyl)]3,5-dimethylpyrazolato)trigold(I)) (AuPz*3HT):

AuCl(tht) (0.032 g, 0.1 mmol), HPz*3HT (0.028 g, 0.11 mmol), and triethylamine (14 μL, 0.10 mmol) were dissolved in THF (5 mL) and stirred at room temperature for one hour. The reaction mixture was evaporated to dryness, and the resulting residue was dissolved in CH_2Cl_2 (5 mL) and washed with H_2O (2 × 3 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness. The crude white solid was purified *via* column chromatography on silica with 4:1 hexanes:CH_2Cl_2 as the eluent to give a white solid in 84 %. Colorless crystals of AuPz*3HT suitable for SCXRD were grown from layering methanol on a $CHCl_3$ solution. *m/z*: 1347. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, J = 5 Hz, 3H), 6.97 (d, J = 5 Hz, 3H), 2.33 (t, J = 8 Hz, 6H), 2.08 (s, 18H), 1.44 (m, 6H), 1.19 (m, 18H), 0.84 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 141.1, 128.7, 128.4, 124.3, 110.4, 31.7, 30.6, 29.7, 29.1, 22.6, 12.5. FT-IR (cm^{-1}): 2955 (m), 2922 (vs), 2852 (s), 1580 (w), 1500 (w), 1463 (m), 1375 (m), 1260 (m), 1172 (w), 1093 (m, br), 1016 (m), 958 (w), 873 (w), 799 (s), 722 (m), 704 (m), 684 (w), 659 (m), 571 (m), 468 (w). Elem Calcd for $C_{45}H_{63}N_6S_3Au_3$: C, 39.31; H, 4.62; N, 6.11. Found C, 39.50; H, 4.12; N, 6.42.

tris-(μ-N,N'-(4-[5-(3,3'-Dihexyl-2,2'-bithienyl)]pyrazolato)trigold(I)) (AuPz3HT_2):

AuCl(tht) (0.032 g, 0.10 mmol) and $HPz3HT_2$ (0.040 g, 1 mmol), and triethylamine (14 μL, 0.1 mmol) were dissolved in THF (15 mL) and stirred at room temperature for one hour. The reaction was evaporated to dryness, and the resulting residue was suspended in hexanes (10 mL) and centrifuged. The supernatant was collected, evaporated to dryness, and purified *via* column chromatography on silica with 4:1 hexanes:CH_2Cl_2 as the eluent to give a white solid in 86 %

yield. *m/z*: 1788. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (s, 6H), 7.28 (d, J = 5 Hz, 3H), 6.97 (d, J = 5 Hz, 3H), 6.88 (s, 3H), 2.56 (t, J = 8 Hz, 6H), 2.46 (t, J = 8 Hz, 6H), 1.54 (m, 12H), 1.25 (m, 36H), 0.86 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 135.8, 134.6, 128.6, 128.5, 128.4, 125.5,125.3, 123.9, 117.0. FT-IR (cm^{-1}: 2955 (s), 2922 (vs), 2854 (s), 1588 (m), 1520 (w), 1461 (m), 1399 (w), 1371 (m), 1318 (w), 1262 (s), 1173 (w), 1095 (s), 1041 (vs), 1024 (s), 929 (w), 874 (m), 820 (vs), 801 (vs), 719 (m), 694 (w), 642 (m), 567 (m). Elem Calcd for $C_{69}H_{93}N_6S_6Au_3$: C, 46.30; H, 5.24; N, 4.70. Found C, 46.39; H, 4.91; N, 4.85.

tris-(μ-N,N'-(4-[5-(3,3'-Dihexyl-2,2'-bithienyl)]3,5-dimethylpyrazolato)trigold(I)) (AuPz*3HT_2):

AuCl(tht) (0.032 g, 0.10 mmol) and HPz*3HT_2 (0.043 g, 0.11 mmol), and triethylamine (14 μL, 0.1 mmol) were dissolved in THF (15 mL) and stirred at room temperature for one hour. The reaction was evaporated to dryness, and the resulting residue was suspended in hexanes (15 mL) and centrifuged. The supernatant was collected, evaporated to dryness, and purified *via* column chromatography on silica with 4:1 hexanes:CH_2Cl_2 as the eluent to give a white solid in 87 % yield. *m/z*: 1872. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, J = 5.4 Hz, 3H), 6.97 (d, J = 5.4 Hz, 3H), 6.76 (s, 3H), 2.56 (t, J = 8.1 Hz, 6H), 2.51 (t, J = 8.1 Hz, 6H), 2.28 (s, 18H), 1.54 (m, 12H), 1.25 (m, 36H), 0.86 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 142.2, 142.1, 136.3, 128.5, 126.3, 125.6, 125.1, 111.7, 31.7, 31.6, 30.8, 30.7, 30.3, 29.2, 29.1, 29.0, 28.9, 22.6, 22.5, 14.1, 13.6. FT-IR (cm^{-1}: 2954 (s), 2922 (vs), 2853 (s), 1573 (w), 1546 (m), 1501 (m), 1450 (m), 1426 (s), 1374 (s), 1361 (m), 1361 (m), 1198 (w), 1086 (m), 1033 (m), 920 (w), 874 (w), 832 (m), 802 (s), 757 (w), 722 (m) 651 (m), 592 (w), 478 (m). Elem Calcd for $C_{75}H_{105}N_6S_6Au_3$: C, 48.07; H, 5.65; N, 4.48. Found: C, 48.23; H, 5.31; N: 4.40.

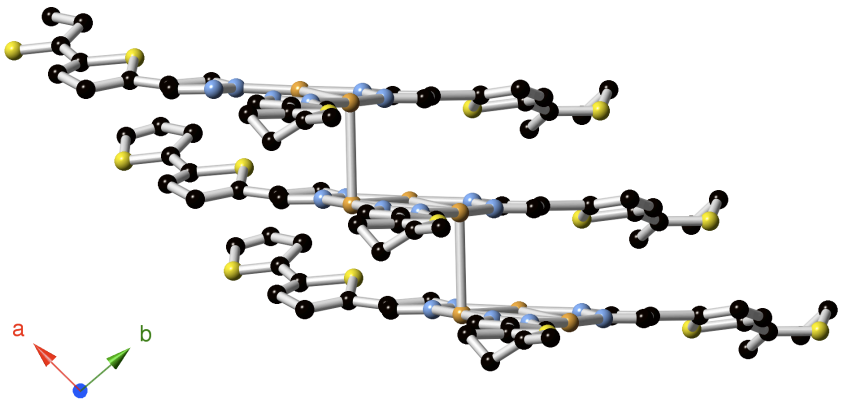

Figure S1: Preliminary solid state molecular structure of $AuPzT_2$ viewed along the *c*-axis.

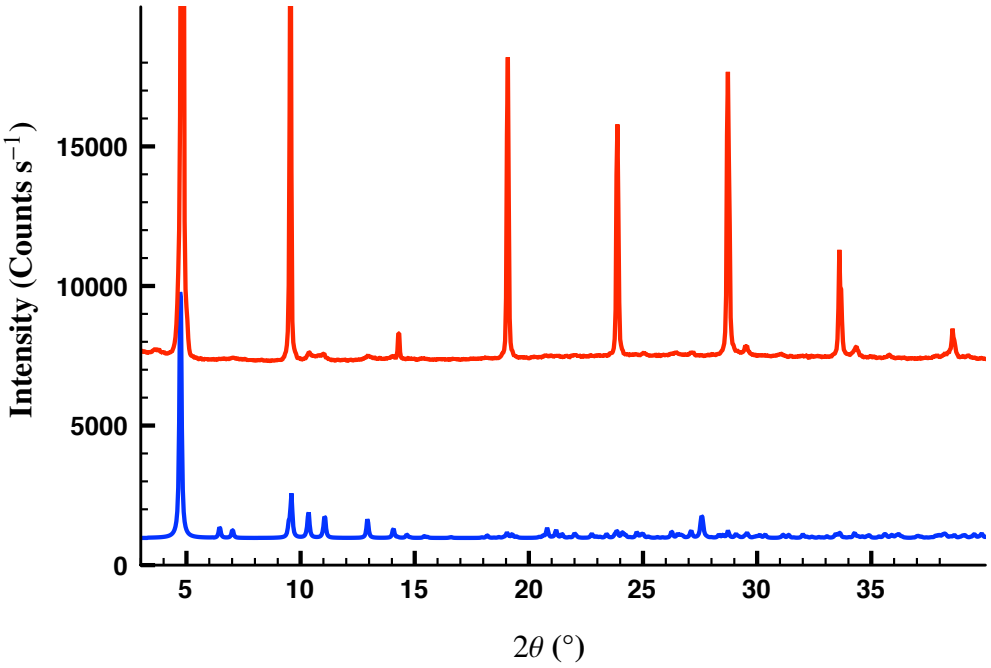

Figure S2: Experimental (red) and predicted (blue) PXRD patterns of $AuPzT_2$. Space group: P-1. a: 4.8896(15) Å; b: 18.522(6) Å; c: 18.700(6) Å; α: 94.701(4)°; β: 91.002(4)°; γ: 93.964(6)°.

Table S1: Selected crystallographic data for AuPzT and AuPz*3HT.

	AuPzT	AuPz*3HT
Formula	$C_{21}H_{15}N_6S_3Au_3$	$C_{45}H_{63}N_6S_3Au_3$
Crystal color, shape	colorless, needle	colorless, plate
Dimensions / mm	$0.36 \times 0.05 \times 0.02$	$0.21 \times 0.10 \times 0.02$
Temperature / K	90	90
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	C2/c
a / Å	25.9877(14)	34.404(5)
b / Å	3.4134(8)	22.375(3)
c / Å	6.8232(4)	13.0426(19)
α / deg	90	90
β / deg	90	103.142(2)
γ / deg	90	90
V / Å^3	2378.5(2)	9777(2)
Z	4	8
2θ (max) / deg	54.71	50.63
Total reflections	17988	36578
Unique reflections	5148	8908
ρ_{calc} / g cm^{-3}	2.900	1.868
μ (kα) / mm^{-1}	18.746	9.145
R1[a] (I>2.00σ(I))	0.0409	0.0612
ωR2[a] (I>2.00σ(I))	0.0750	0.1969
Goodness of fit	1.042	1.061

[a] Function minimized. $\Sigma\omega(|F_o|-F_c|)^2$, R1=$\Sigma$ $||F_o| - |F_c||/\Sigma|F_o|$, ωR2=$[\Sigma(\omega(|F_o| - |F_c|)^2)/\Sigma\omega(|F_o|)^2]^{1/2}$

Table S2: Total calculated bond energies of complex AuPzT

Compound	**Energy** (eV)
Ground state, monomer	-305.85388037
Excited state, monomer	-303.26534755
Ground state, dimer	-611.60236759

Table S3: Atomic coordinates for the optimized ground state geometry of AuPzT (monomer)

Atom	**X (Å)**	**Y (Å)**	**Z (Å)**
1.H	4.385291	-1.789667	-0.069535
2.C	3.165732	-3.689226	-0.092745
3.C	1.763214	-3.754956	-0.088400
4.H	1.108861	-4.617782	-0.094234
5.C	4.127783	-4.776762	-0.118644
6.C	5.470138	-4.752457	0.206821
7.H	5.973313	-3.856815	0.561782
8.C	6.113573	-6.008723	0.058113
9.H	7.165250	-6.180699	0.272651
10.C	5.262981	-6.993281	-0.378227
11.H	5.476751	-8.038341	-0.571172
12.C	-3.727284	-1.821977	-0.089077
13.H	-3.756803	-2.903344	-0.122265
14.C	-4.778606	-0.890274	-0.088098
15.C	-4.126433	0.352208	-0.057899
16.H	-4.540541	1.352554	-0.035822
17.C	-6.205280	-1.160579	-0.112212
18.C	-6.873650	-2.330369	0.193142
19.H	-6.363134	-3.229277	0.528816
20.C	-8.282775	-2.231444	0.055805
21.H	-8.970372	-3.048254	0.260104
22.C	-8.692137	-0.986911	-0.352357
23.H	-9.699399	-0.628296	-0.530550
24.S	-7.347431	0.067885	-0.586832
25.C	0.281871	4.128662	-0.079196
26.H	-0.643461	4.689173	-0.109793

Table S3 (Continued)

27.C	1.611653	4.581111	-0.091291
28.C	2.368252	3.398744	-0.055697
29.H	3.442382	3.261989	-0.041493
30.C	2.074931	5.956498	-0.134075
31.C	1.366135	7.115317	0.118051
32.H	0.322502	7.112865	0.421435
33.C	2.136790	8.297029	-0.034925
34.H	1.748528	9.299384	0.126759
35.C	3.434721	8.041997	-0.400262
36.H	4.240419	8.744912	-0.578359
37.S	3.715707	6.348447	-0.571667
38.N	2.282597	-1.618723	-0.039979
39.N	1.247103	-2.510876	-0.058869
40.N	-2.545484	-1.176213	-0.059451
41.N	-2.792442	0.168341	-0.042196
42.N	0.257606	2.783197	-0.038501
43.N	1.547254	2.331146	-0.026228
44.S	3.668122	-6.381589	-0.619910
45.Au	-0.653311	-1.854588	-0.056932
46.Au	-1.273192	1.481945	-0.033368
47.Au	1.925748	0.357838	-0.021619
48.C	3.437017	-2.311326	-0.062518

Table S4: Atomic coordinates for the optimized lowest energy triplet excited state, 1^3A geometry of AuPzT (monomer)

Atom	**X (Å)**	**Y (Å)**	**Z (Å)**
1.H	4.425163	-1.700725	0.012286
2.C	3.240600	-3.651393	0.059269
3.C	1.810323	-3.725733	0.052423
4.H	1.168194	-4.596541	0.071975
5.C	4.163277	-4.692703	0.093119
6.C	5.627581	-4.616415	0.101601
7.H	6.154970	-3.667186	0.082953

Table S4 (Continued)

8.C	6.227160	-5.840528	0.136201
9.H	7.303659	-5.994969	0.147648
10.C	5.307310	-6.935368	0.156726
11.H	5.546159	-7.992444	0.186330
12.C	-3.680325	-1.884063	0.042370
13.H	-3.682309	-2.965664	0.080698
14.C	-4.754226	-0.979104	0.038174
15.C	-4.133735	0.279623	0.003316
16.H	-4.572730	1.269248	-0.022420
17.C	-6.173309	-1.286076	0.062435
18.C	-6.811093	-2.471856	-0.246665
19.H	-6.277681	-3.356469	-0.584778
20.C	-8.222352	-2.409405	-0.109590
21.H	-8.888727	-3.243077	-0.315910
22.C	-8.663134	-1.176820	0.302291
23.H	-9.679039	-0.844428	0.482272
24.S	-7.346141	-0.088535	0.539943
25.C	0.222907	4.137828	-0.054784
26.H	-0.708340	4.688949	-0.033986
27.C	1.547787	4.605491	-0.055995
28.C	2.317345	3.431603	-0.065934
29.H	3.392962	3.307027	-0.079440
30.C	1.997339	5.986109	-0.042464
31.C	1.278629	7.132510	-0.321865
32.H	0.236395	7.113816	-0.629519
33.C	2.037725	8.324332	-0.191319
34.H	1.641101	9.319289	-0.376805
35.C	3.336606	8.089416	0.184197
36.H	4.135083	8.803653	0.349364
37.S	3.632580	6.402761	0.393505
38.N	2.323920	-1.576965	-0.000575
39.N	1.291653	-2.489150	0.019283
40.N	-2.514988	-1.208546	0.009703
41.N	-2.795620	0.129544	-0.012144
42.N	0.213070	2.791631	-0.063851
43.N	1.508361	2.353899	-0.068751
44.S	3.631322	-6.415905	0.133741

Table S4 (Continued)

45.Au	-0.611535	-1.850264	0.012519
46.Au	-1.302963	1.472008	-0.041800
47.Au	1.922349	0.388958	-0.042106
48.C	3.487296	-2.239951	0.022584

Table S5: Atomic coordinates for the optimized ground state geometry of AuPzT (dimer)

Atom	**X (Å)**	**Y (Å)**	**Z (Å)**
1.C	0.044981	1.929527	-3.936416
2.H	-0.701329	1.780357	-4.705935
3.C	1.421017	2.188637	-4.052699
4.C	1.866516	2.251663	-2.722734
5.H	2.855979	2.447404	-2.329321
6.C	2.186064	2.356200	-5.275781
7.C	1.742721	2.731708	-6.528718
8.H	0.705148	2.983838	-6.731819
9.C	2.772435	2.784727	-7.504198
10.H	2.610731	3.068886	-8.540992
11.C	4.004061	2.452269	-6.998633
12.H	4.960954	2.420840	-7.507013
13.C	1.514026	2.303750	3.068874
14.H	2.533970	2.524636	2.782866
15.C	0.924613	2.232384	4.342588
16.C	-0.416307	1.911623	4.073035
17.H	-1.243116	1.751535	4.753827
18.C	1.568084	2.437298	5.627677
19.C	2.885941	2.756231	5.898157
20.H	3.629270	2.903007	5.118910
21.C	3.169049	2.877683	7.283620
22.H	4.149633	3.124776	7.682586
23.C	2.069449	2.652112	8.072913
24.H	1.992407	2.679059	9.153794
25.S	0.678191	2.289084	7.119568
26.C	-5.092521	0.540800	0.880024

Table S5 (Continued)

27.H	-5.360893	0.437861	1.923571
28.C	-5.860993	0.321476	-0.275943
29.C	-4.973355	0.603411	-1.326768
30.H	-5.135755	0.583012	-2.397261
31.C	-7.250235	-0.094973	-0.351185
32.C	-8.225788	-0.040566	0.625378
33.H	-8.044222	0.370150	1.615233
34.C	-9.485426	-0.536026	0.198711
35.H	-10.370972	-0.563767	0.828568
36.C	-9.473396	-0.972031	-1.102432
37.H	-10.285780	-1.389524	-1.686152
38.S	-7.911099	-0.784021	-1.810470
39.N	-0.294061	1.850871	-2.636395
40.N	0.830845	2.048263	-1.887000
41.N	0.591127	2.044944	2.124104
42.N	-0.601825	1.802566	2.744021
43.N	-3.847738	0.921965	0.534656
44.N	-3.773396	0.959299	-0.829275
45.S	3.904730	2.061423	-5.319894
46.Au	0.725643	2.015703	0.119654
47.Au	-2.229875	1.358470	1.649761
48.Au	-2.039527	1.414941	-1.740599
49.Au	2.039528	-1.414901	-1.740429
50.C	-1.513953	-2.303805	3.069161
51.H	-2.533814	-2.525034	2.783150
52.C	-0.924510	-2.232533	4.342859
53.C	0.416332	-1.911415	4.073301
54.H	1.243166	-1.751393	4.754079
55.C	-1.567848	-2.438136	5.627911
56.C	-2.885587	-2.757623	5.898325
57.H	-3.628923	-2.904238	5.119054
58.C	-3.168538	-2.879991	7.283743
59.H	-4.149002	-3.127667	7.682652
60.C	-2.068927	-2.654585	8.073070
61.H	-1.991761	-2.682239	9.153924
62.C	5.092208	-0.539680	0.880215
63.H	5.360438	-0.436299	1.923756

Table S5 (Continued)

64.C	5.860884	-0.320982	-0.275743
65.C	4.973229	-0.602840	-1.326569
66.H	5.135641	-0.582441	-2.397061
67.C	7.250139	0.095430	-0.350964
68.C	8.225583	0.041315	0.625729
69.H	8.043910	-0.369133	1.615673
70.C	9.485276	0.536620	0.199050
71.H	10.370757	0.564497	0.828987
72.C	9.473366	0.972353	-1.102184
73.H	10.285812	1.389693	-1.685928
74.S	7.911183	0.784009	-1.810384
75.C	-0.045050	-1.929687	-3.936142
76.H	0.701255	-1.780680	-4.705698
77.C	-1.421084	-2.188843	-4.052354
78.C	-1.866552	-2.251722	-2.722381
79.H	-2.855999	-2.447446	-2.328917
80.C	-2.186120	-2.356710	-5.275392
81.C	-1.742711	-2.732567	-6.528184
82.H	-0.705151	-2.984847	-6.731103
83.C	-2.772339	-2.785740	-7.503741
84.H	-2.610564	-3.070138	-8.540458
85.C	-4.003991	-2.453122	-6.998341
86.H	-4.960844	-2.421778	-7.506801
87.S	-3.904790	-2.061982	-5.319661
88.N	-0.591139	-2.044706	2.124395
89.N	0.601789	-1.802157	2.744289
90.N	3.847597	-0.921424	0.534841
91.N	3.773357	-0.959054	-0.829089
92.N	0.294034	-1.850909	-2.636142
93.N	-0.830849	-2.048281	-1.886704
94.S	-0.677870	-2.290539	7.119816
95.Au	2.229796	-1.358014	1.649976
96.Au	-0.725652	-2.015545	0.119943

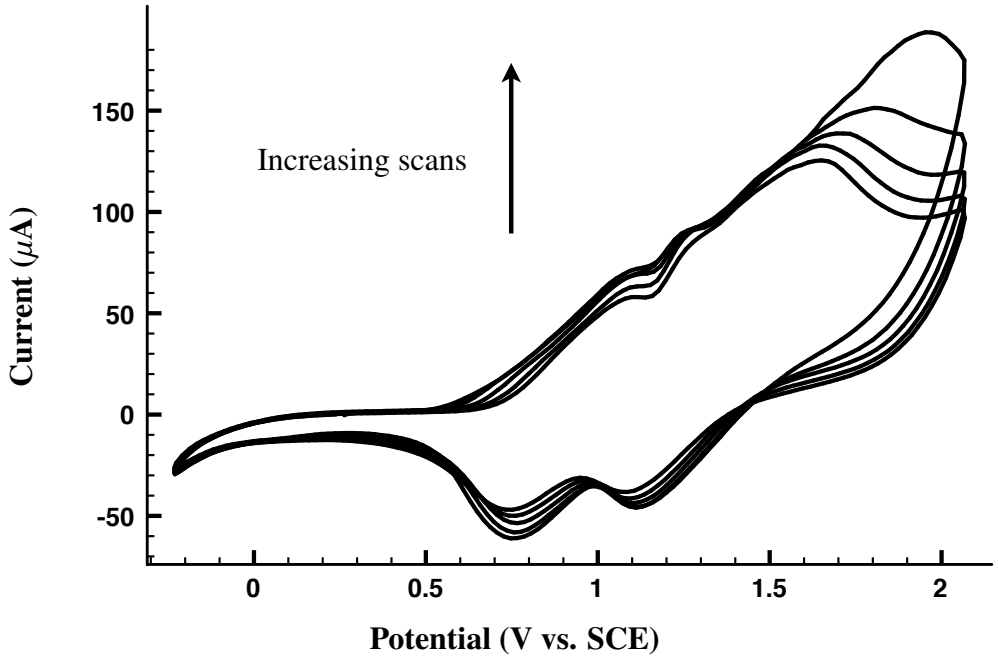

Figure S3: Successive cyclic voltammograms of AuPz3HT on ITO. Data were collected at a scan rate of 100 mV s^{-1} in CH_2Cl_2 with 0.1 M [*n*-Bu_4N][PF_6] as the supporting electrolyte.

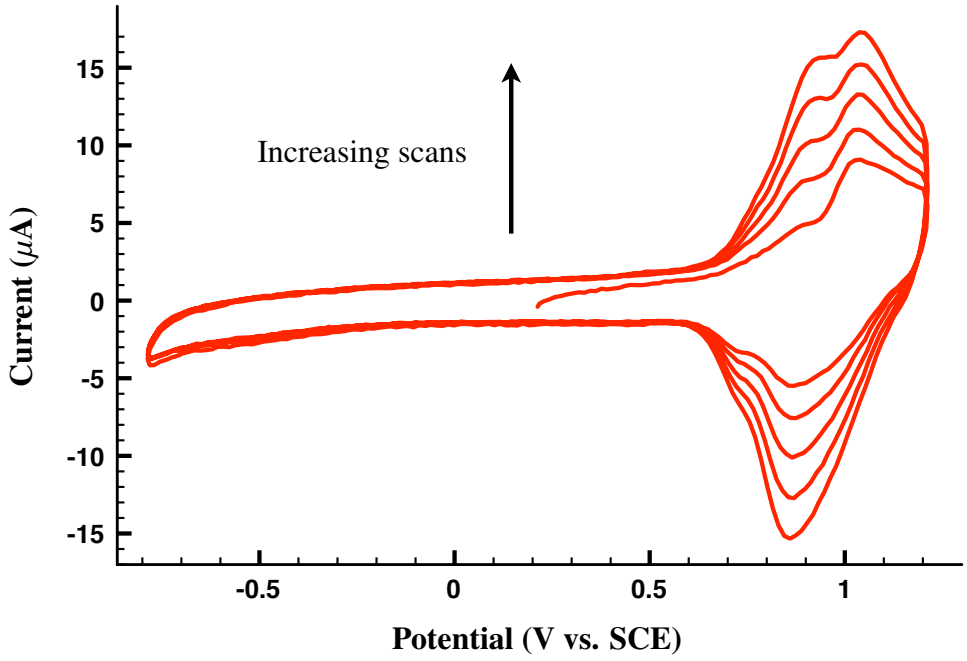

Figure S4: Cyclic voltammogram of AuPz*3HT$_2$ on ITO. Data were collected at a scan rate of 100 mV s^{-1} in CH_2Cl_2 with 0.1 M [*n*-Bu_4N][PF_6] as the supporting electrolyte.