Supporting Information

Broadband near-IR absorbing Au-dithiolene complexes bearing redox-active oligothiophene ligands

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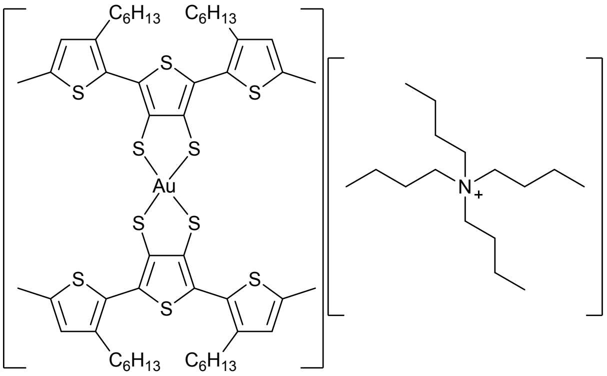
Synthetic Methods

General Experimental:

Absorption spectra were recorded in dichloromethane solution using a Shimadu UV-1800. CV measurements were taken using a BAS CV-50W potentiostat with iR compensation and performed using glassy carbon, platinum wire and silver wire as the working, counter, and reference electrodes respectively. Substrates were dissolved in anhydrous dichloromethane solution (ca. 10^{-4} M) containing n-Bu_4NPF_6 as the supporting electrolyte and all solutions were degassed with argon. All electrochemical measurements were referenced to the $E_{1/2}$ of the Fc/Fc^+ redox couple. For the cyclic voltammetry the measurements have been converted to Ag/Ag^+ by addition of +0.51 V[S1,S2] to allow for straightforward comparison with previous results. Spectroelectrochemical experiments were conducted using a UNICAM UV300 instrument and a CH Instruments 660A potentiostat. Measurements were taken of films drop-cast onto ITO coated glass and suspended in a solution of n-Bu_4NPF_6 in acetonitrile. Fourier transform infra-red spectroscopy were taken on a Perkin Elmer Spectrum 100 FT-IR spectrometer.

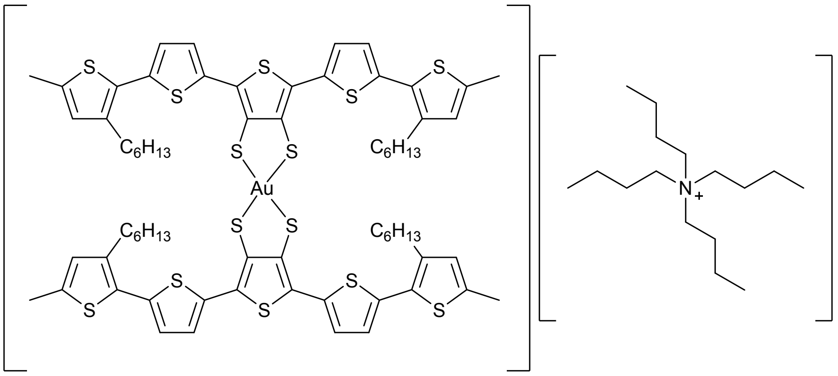


[Au(**3T**)$_2$][n-Bu_4N]:

To a solution of ligand precursor **12** (250 mg, 0.47 mmol) in dry THF (50 mL) under N_2, was added a freshly prepared solution of NaOMe (0.61 M solution in MeOH, 3.06 mL, 1.87 mmol) and the reaction mixture heated to reflux for 15 min. Upon cooling to room temperature, (n-Bu_4N)Br (152 mg, 0.47 mmol) was added, followed by $KAuCl_4$ (88 mg, 0.23 mmol) and the reaction was stirred overnight. The reaction mixture was filtered and the solvent removed under reduced pressure. The crude material was dissolved in ethyl acetate and filtered through celite to give a purple solution. The solvent was removed and the product crystallised from a THF/MeCN mixture (ca. 1:80) in the freezer over 14 days to give a grey/black crystalline powder (144 mg, 43%); m.p. = 148–149 °C.

MS (MALDI): m/z = 1209 [Au(**3T**)$_2$]$^-$

Anal. calc. for $C_{68}H_{104}AuNS_{10}$: C, 56.21; H, 7.21; N, 0.96; S, 22.06. Found: C, 56.26; H, 7.15; N, 0.67; S, 22.18.

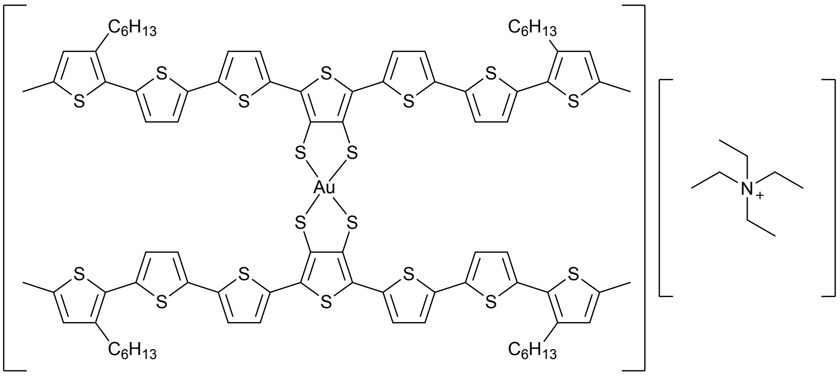


$[Au(\mathbf{5T})_2][n\text{-}Bu_4N]$:

Under N_2, ligand precursor **13** (250 mg, 0.36 mmol) was dissolved in dry THF (50 mL) before addition of a freshly prepared solution of NaOMe (0.61 M solution in MeOH, 2.34 mL, 1.43 mmol) and the reaction mixture heated to reflux for 15 min. The reaction was then allowed to cool to room temperature and $(n\text{-}Bu_4N)Br$ (116 mg, 0.36 mmol) was added, followed by $KAuCl_4$ (68 mg, 0.18 mmol) before the reaction was stirred overnight. The solvent was removed under reduced pressure and the crude material was dissolved in ethyl acetate then filtered through celite to give an emerald green solution. After removal of solvent the material was crystallised by diffusion of MeCN into a THF solution to give a dark green crystalline solid (153 mg, 48%); m.p. = 104–105 °C.

MS (MALDI): m/z = 1537 $[Au(\mathbf{5T})_2]^-$

Anal. calc. for $C_{84}H_{112}AuNS_{14}$: C, 56.63; H, 6.34; N, 0.79; S, 25.19. Found: C, 56.45; H, 6.23; N, 0.85; S, 25.09.



[Au(**7T**)$_2$][Et$_4$N]:

Ligand precursor **14** (250 mg, 0.29 mmol) was dissolved in dry THF (50 mL) under N_2 atmosphere before addition of a freshly prepared solution of NaOMe (0.34 M solution in MeOH, 3.41 mL, 1.16 mmol) and the reaction mixture heated to reflux for 15 min. The reaction was then allowed to cool to room temperature and $(Et_4N)Br$ (30 mg, 0.15 mmol) was added, followed by $KAuCl_4$ (57 mg, 0.15 mmol) before the reaction was stirred overnight. The reaction mixture was filtered and the solvent removed under reduced pressure prior to precipitation from hot THF with ethanol to give a brown powder (222 mg, 74%); m.p. = 188–190 °C.

MS (MALDI): m/z = 1865 [Au(**7T**)$_2$]$^-$

Anal. calc. for $C_{92}H_{104}AuNS_{18}$: C, 55.31; H, 5.25; N, 0.70; S, 28.88. Found: C, 51.60; H, 4.27; N, 0.52; S, 28.70.

Infra-red spectroscopy table of peaks

Table S1 Infrared band positions from of ligand precursors **3T**–**7T** and complexes $[\mathrm{Au}(\mathbf{3T})_2]^-$ – $[\mathrm{Au}(\mathbf{7T})_2]^-$

	n / cm^{-1}
3T	2926(vs), 2856(vs), 1714(m), 1653(vs), 1507(m), 1463 (m), 1436(m), 1377(w), 1138(w), 857(m), 846(m), 826(m), 729(w), 688(w), 676(w) 547(m)
5T	2955(vs), 2926(vs), 2854(s), 1707(s), 1651(s), 1498(s), 1458(m), 1436(m), 1377(w), 1231(w), 1136(w), 1060(w), 918(w), 892(w) 846(m), 829(s), 788(s), 692(w), 584(w), 556(w), 541(w), 513(w)
7T	2953(vs), 2922(vs), 2853(vs), 1707(s), 1654(s), 1492(s), 1463(m), 1439(m), 1376(w), 1220(w), 1132(w), 1069(w), 921(w), 898(w), 831(s), 785(s), 698(w), 542(w)
$[\mathrm{Au}(\mathbf{3T})_2]^-$	2956(vs), 2925(vs), 2869(s), 2853(vs), 1632(s), 1556(w), 1504(w), 1466(s), 1379(m), 1286(s), 1238(w), 1137(w), 931(w), 885(w), 861(w), 827(m), 795(w), 786(w), 737(w), 725(w), 563(w), 511(w)
$[\mathrm{Au}(\mathbf{5T})_2]^-$	2954(vs), 2923(vs), 2867(s), 2853(vs), 1632(s), 1561(m), 1527(s), 1478(s), 1455(s), 1440(s), 1377(m), 1324(w), 1279(s), 1221(w), 1205(w), 1133(w), 1060(w), 944(w), 877(w), 854(w), 827(w), 788(s), 734(w), 592(w), 515(w)
$[\mathrm{Au}(\mathbf{7T})_2]^-$	2954(vs), 2923(vs), 2866(s), 2853(vs), 1632(m), 1515(m), 1478(m), 1439(s), 1377(m), 1278(m), 1217(w), 1203(w), 1134(w), 1063(w), 944(w), 847(m), 828(w), 788(s), 735(w), 592(w)

X-Ray Crystallography

Single crystal diffraction data were collected from an orange needle-like crystal of dimensions 0.09 x 0.01 x 0.01 mm using Mo-Kα X-radiation (λ=0.71703Å). Data were collected using a Bruker-Nonius KappaCCD mounted at the window of a FR591 rotating anode. The crystal was cooled to 100K using an Oxford Cryosystems Cobra low temperature device. Data collection was carried out using COLLECT [S3] and data processed using *Denzo*.[S4] The absorption correction was made using SADABS [S5] and the structure solved by direct methods using *SHELXS97* [S6] and then refined using *SHELXL97* [S6] within *OLEX2*.[S7] CCDC 1861791 contains supplementary X-ray crystallographic data for [Ni(**3T**)$_2$][Et$_4$N]$_2$ This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax(+44) 1223-336-033 or email: deposit@ccdc.cam.ac.uk.

For the Ni(1) molecule one terminal methyl group of the alkyl chain was modelled as being disordered over 2 sites with occupancies 0.67(4)/0.33(4). For the Ni(1a) molecule the whole alkyl chain was modelled over two sites with occupancies 0.69(2)/0.31(2); a common U(iso) was used for minor component. Distance restraints were applied and partially occupied atoms were refined with isotropic adps, as were the carbon atoms of the N2N tetraethylammonium.

Table S2 The data collection and refinement parameters for complex (Et$_4$N)$_2$[Ni(**3T**)$_2$]

	[Ni(**3T**)$_2$][Et$_4$N]$_2$
Empirical Formula	$C_{68}H_{108}N_2NiO_{2.70}S_{10}$
Formula weight	1376.07
Crystal system	Triclinic
Space group	*P*-1 (no.2)
a / Å	12.2157(13)
b / Å	14.6041(13)
c / Å	21.186(2)
α / °	76.076(6)
β / °	76.307(4)
γ / °	89.934(7)
V / Å^3	3558.0(6)
T / K	120
Z	2
Reflections collected	38810
Independent reflections	11833
R_{int}	0.174
$R_w(F^2$, all data)	0.271

Computational Details

DFT methods were used to gain a further insight into the electronic properties of [Au(**3T**)$_2$]$^-$ and [Au(**5T**)$_2$]$^-$. The geometry was optimised and density contours of the frontier orbitals were calculated using ORCA v3.03.[S8] The BP86 functional was employed with the all-electron polarised triple-ζ (TZVP) basis set and TZVP/J auxiliary basis set alongside the zeroth-order regular approximation (ZORA) scalar relativistic.[S9] Stuttgart/Dresden (SDD) effective core potential was used for Au [S10,S11] and the calculation was resolved to a tight self-consistent field. Visualisation was performed using Avogadro v1.1.1 and an isovalue of 0.30.

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