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Article

(Fluoren-9-ylidene)methanedithiolato Complexes of Gold: Synthesis, Luminescence, and Charge-Transfer Adducts[1]

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Piperidinium 9*H*-fluorene-9-carbodithioate and its 2,7-di-*tert*-butyl-substituted analogue [(pipH){$S_2CCH(C_{12}H_6R_2$-2,7)}, R = H (**1a**), *t*-Bu (**1b**)] and 2,7-bis(octyloxy)-9*H*-fluorene-9-carbodithioic acid [$HS_2CCH(C_{12}H_6(OC_8H_{17})_2$-2,7), **2**] and its tautomer [2,7-bis(octyloxy)fluoren-9-ylidene]methanedithiol [$(HS)_2C{=}C(C_{12}H_6(OC_8H_{17})_2$-2,7), **3**] were employed for the preparation of gold complexes with the (fluoren-9-ylidene)methanedithiolato ligand and its substituted analogues. The gold(I) compounds $Q_2[Au_2\{\mu\text{-}\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}_2]$, where $Q^+ = PPN^+$ or Pr_4N^+ for R = H (Q_2**4a**) or $Q^+ = Pr_4N^+$ for R = OC_8H_{17} [$(Pr_4N)_2$**4c**], were synthesized by reacting $Q[AuCl_2]$ with **1a** or **2** (1:1) and excess piperidine or diethylamine. Complexes of the type $[\{Au(PR'_3)\}_2\{\mu\text{-}\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}_2]$ with R = H and R′ = Me (**5a**), Et (**5b**), Ph (**5c**), and Cy (**5d**) or R = *t*-Bu and R′ = Me (**5e**), Et (**5f**), Ph (**5g**), and Cy (**5h**) were obtained by reacting $[AuCl(PR'_3)]$ with **1a**,**b** (1:2) and piperidine. The reactions of **1a**,**b** or **2** with $Q[AuCl_4]$ (2:1) and piperidine or diethylamine gave $Q[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}_2]$ with $Q^+ = PPN^+$ for R = H [(PPN)**6a**], $Q^+ = PPN^+$ or Bu_4N^+ for R = *t*-Bu (Q**6b**), and $Q^+ = Bu_4N^+$ for R = OC_8H_{17} [(Bu_4N)**6c**]. Complexes Q**6a**–**c** reacted with excess triflic acid to give $[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}\{\kappa^2\text{-}S,S\text{-}S_2CCH(C_{12}H_6R_2\text{-}2,7)\}]$ [R = H (**7a**), *t*-Bu (**7b**), OC_8H_{17} (**7c**)]. By reaction of (Bu_4N)**6b** with $PhICl_2$ (1:1) the complex $Bu_4N[AuCl_2\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6(t\text{-}Bu)_2\text{-}2,7)\}]$ [(Bu_4N)**8b**] was obtained. The dithioato complexes $[Au\{SC(S)CH(C_{12}H_8)\}(PCy_3)]$ (**9**) and $[Au_n\{S_2CCH(C_{12}H_8)\}_n]$ (**10**) were obtained from the reactions of **1a** with $[AuCl(PCy_3)]$ or $[AuCl(SMe_2)]$, respectively (1:1), in the absence of a base. Charge-transfer adducts of general composition $Q[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}_2]\cdot 1.5TCNQ\cdot xCH_2Cl_2$ [$Q^+ = PPN^+$, R = H, *x* = 0 (**11a**); $Q^+ = PPN^+$, R = *t*-Bu, *x* = 2 (**11b**); $Q^+ = Bu_4N^+$, R = OC_8H_{17}, *x* = 0 (**11c**)] were obtained from Q**6a**–**c** and TCNQ (1:2). The crystal structures of **5c**·THF, **5e**·$^{2}/_{3}CH_2Cl_2$, **5g**·CH_2Cl_2, (PPN)**6a**·$2Me_2CO$, and **11b** were solved by X-ray diffraction studies. All the gold(I) complexes here described are photoluminescent at 77 K, and their emissions can be generally ascribed to LMMCT (Q_2**4a**,**c**, **5a**–**h**, **10**) or LMCT (**9**) excited states.

Introduction

The chemistry of transition metal complexes containing dithiolates and related ligands continues to attract considerable interest in such active research fields as molecular conducting and magnetic materials,[2] metalloenzyme modeling and function,[3] nonlinear optics,[4] sensor[5] and photoresponsive[6] materials, and selective olefin coordination/separation.[7] The recent interest in metal complexes of 1,1-ethylenedithiolates ($XYC{=}CS_2^{2-}$) is mainly due to their photophysical properties. Platinum complexes with certain

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[1] (Fluoren-9-ylidene)methanedithiolato Complexes. 1.

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ligands of this kind display solvatochromic behavior and room-temperature luminescence in solution[8,9] and have been the subject of intensive research to explore their suitability for applications as photocatalysts in light-to-chemical energy conversion processes.[10] Additionally, 1,1-ethylenedithiolates are versatile ligands which may facilitate the formation of clusters[11,12] and heteropolynuclear complexes,[13] stabilize high oxidation states,[14,15] or make use of multiple donor atoms to form coordination polymers.[16] Certain polynuclear complexes containing 1,1-ethylenedithiolates display semiconducting behavior.[17]

1,1-Ethylenedithiolates are usually obtained by reacting methylene-active compounds XYCH$_2$ (X and/or Y = CN, COOR, COR, CONH$_2$, NO$_2$, etc.) with CS$_2$ and a base,[18−20] the presence of strongly electron-withdrawing functional groups being therefore a common feature of many of them. The majority of 1,1-ethylenedithiolato metal complexes described to date contain *i*-mnt (X = Y = CN),[19,21,22] which is also the case for the gold complexes,[23−28] while other frequently used ligands are those with X = CO$_2$R and Y = CN[8,29] or CO$_2$R[12,14,15,30] (R = Et, *t*-Bu). Part of our recent research work has been devoted to the synthesis and study of the reactivity and properties of gold, palladium, and platinum complexes containing the 2,2-diacetyl-1,1-ethylenedithiolato ligand [X = Y = C(O)Me], including heteropolynuclear complexes.[31−33] In this paper, we describe the synthesis, structural characterization, emission properties,

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Chart 1

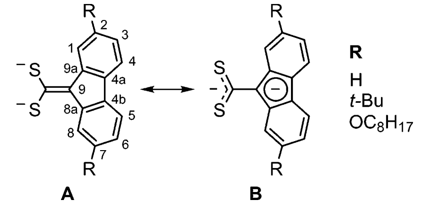
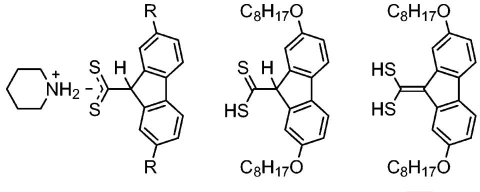


Chart 2



1a,b 2 3

R = H (**1a**), *t*-Bu (**1b**)

and reactivity of the first complexes of gold with (fluoren-9-ylidene)methanedithiolate and its 2,7-di-*tert*-butyl- and 2,7-bis(octyloxy)-substituted derivatives (Chart 1). These new ligands can be classified as 1,1-ethylenedithiolates but show remarkable differences with respect to the previously described ligands of this kind, which are expected to markedly affect the photophysical properties and redox behavior of their metal complexes. Thus, although some degree of negative charge is delocalized over the fluoren-9-ylidene moiety (Chart 1, resonance form **B**), the absence of strong electron-withdrawing substituents makes them stronger *S*-donors. In addition, they feature a planar core which provides extensive conjugation, can be functionalized to modify their electronic and steric properties, and constitutes a π-stackable fragment suitable for the formation of charge-transfer complexes. The only previously described 1,1-ethylenedithiolato ligand with similar properties is (cyclopentadienylidene)-methanedithiolate, but relatively few metal complexes with this ligand have been reported and only one of them was structurally characterized.[34]

Experimental Section

General Considerations, Materials, and Instrumentation. All preparations were carried out under an atmosphere of nitrogen using Schlenk techniques except in the cases of the gold(III) complexes. Solvents were dried by standard methods and distilled under nitrogen before use. $[AuCl(SMe_2)]$ was prepared as described for $[AuCl(tht)]$[35] (tht = tetrahydrothiophene). The compounds $[AuCl(PR_3)]$ (R = Me, Et, Ph, Cy) were prepared by reacting $[AuCl(SMe_2)]$ with the corresponding phosphine in 1:1 molar ratio in dichloromethane. $Q[AuCl_4]$ [$Q^+ = PPN^+ = (Ph_3P)_2N^+$, Bu_4N^+] were prepared by reacting $Na[AuCl_4]\cdot xH_2O$ with QCl in acetone. $Q[AuCl_2]$ ($Q^+ = PPN^+$, Pr_4N^+),[36] $PhICl_2$,[37] and the ligand precursors piperidinium 9*H*-fluorene-9-carbodithioate (**1a**) and its 2,7-di-*tert*-butyl-substituted analogue (**1b**) and 2,7-bis(octyloxy)-9*H*-fluorene-9-carbodithioic acid (**2**) and its tautomer [2,7-bis(octyloxy)fluoren-9-yliden]methanedithiol (**3**) were prepared following literature methods (Chart 2).[38] All other reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded on Bruker Avance 200, 300, or 400 spectrometers usually at 298 K, unless otherwise indicated. Chemical shifts are referred to internal TMS (^1H and $^{13}C\{H\}$) or external 85% H_3PO_4 ($^{31}P\{H\}$). The assignments of the ^1H and $^{13}C\{H\}$ NMR spectra were made with the help of HMBC and HSQC experiments. Chart 1 shows the atom numbering of the dithiolato ligands. Solution conductivities were measured in acetone with a Crison microCM 2200 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets or KBr pellets. UV−visible absorption spectra were recorded on Unicam UV500 (range 190−900 nm) or Hitachi U-2000 (range 190−1100 nm) spectrophotometers. Excitation and emission spectra were recorded on a Perkin-Elmer LS-55 spectrofluorometer by using finely pulverized dispersions of the samples in KBr or degassed dichloromethane solutions.

X-ray Structure Determinations. Crystals of **5c**·THF, **5e**·$^2/_3$-CH_2Cl_2, **5g**·CH_2Cl_2, (PPN)**6a**·$2Me_2CO$, and **11b** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into solutions of the compounds in THF (**5c**), CH_2Cl_2 (**5e**,**g**, **11b**), or acetone [(PPN)**6a**]. Numerical details are presented in Table 1. Data were recorded at low temperature on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). Absorption corrections were based on indexed faces (**5c**,**g**, **11b**) or multiple scans (program SADABS). Structures were refined anisotropically on F^2 using the program SHELXL-97 (Prof. G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model or rigid methyl groups.

Special Features of Refinement. 5e, **11b:** One dichloromethane molecule is disordered over two positions. **5g**: Apart from the well-resolved dichloromethane molecule, there is an extensive region of badly resolved electron density, associated with a 2-fold axis, that could not be interpreted. The program SQUEEZE (part of the PLATON system: Prof. A. L. Spek, University of Utrecht) was therefore used to "remove" this electron density mathematically. Values for the formula mass and other derived parameters do not take account of this solvent region.

$(PPN)_2[Au_2\{\mu\text{-}\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_8)\}_2]$ [$(PPN)_2$4a]. To a solution of **1a** (90 mg, 0.27 mmol) in THF (20 mL) were added piperidine (0.1 mL, 1.01 mmol) and $PPN[AuCl_2]$ (202 mg, 0.25 mmol). An orange precipitate formed immediately. The suspension was stirred for 25 min, and the solid was filtered off, washed with ethanol (2 × 3 mL) and diethyl ether (3 mL), and vacuum-dried to give $(PPN)_2$**4a**. Yield: 220 mg, 90%. Anal. Calcd for $C_{100}H_{76}Au_2N_2P_4S_4$: C, 61.54; H, 3.92; N, 1.43; S, 6.57. Found: C, 61.16; H, 3.97; N, 1.48; S, 6.40. Mp: 211 °C (dec). Λ_M (acetone, 2.5×10^{-4} M): 199 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1480, 1470. ^1H NMR (400.9 MHz, CD_2Cl_2): δ 9.32 (d, $^3J_{HH}$ = 8.1 Hz, 4 H, H1, H8), 7.75 (d, $^3J_{HH}$ = 7.4 Hz, 4 H, H4, H5), 7.62−7.59 (m, 12 H, PPN^+), 7.47−7.42 (m, 48 H, PPN^+), 7.15 (t, $^3J_{HH}$ = 7.6 Hz, 4 H, H2, H7), 7.04 (t, $^3J_{HH}$ = 7.2 Hz, 4 H, H3, H6). $^{13}C\{^1H\}$

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Table 1. Crystallographic Data for **5c**·THF, **5e**·$^2/_3$$CH_2Cl_2$, **5g**·$CH_2Cl_2$, (PPN)**6a**·$2Me_2CO$, and **11b**

	5c·THF	**5e**·$^2/_3$$CH_2Cl_2$	**5g**·CH_2Cl_2	(PPN)**6a**·$2Me_2CO$	**11b**
formula	$C_{54}H_{46}Au_2OP_2S_2$	$C_{28.67}H_{43.33}Au_2Cl_{1.33}P_2S_2$	$C_{59}H_{56}Au_2Cl_2P_2S_2$	$C_{70}H_{58}AuNO_2P_2S_4$	$C_{200}H_{176}Au_2Cl_8N_{14}P_4S_8$
fw	1230.90	955.23	1355.53	1332.32	3833.44
T (K)	133(2)	133(2)	133(2)	133(2)	133(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$	$P2_1/n$	$P\bar{1}$
(Å)	17.0606(12)	29.0247(16)	23.380(2)	9.4807(4)	16.0361(6)
b (Å)	14.5181(11)	17.3765(11)	19.4509(14)	22.3323(12)	17.1629(6)
c (Å)	19.1280(12)	21.5570(12)	25.424(2)	13.7936(8)	18.7000(6)
α (deg)	90	90	90	90	72.593(4)
β (deg)	106.300(5)	109.674(4)	100.004(4)	93.834(5)	85.251(4)
γ (deg)	90	90	90	90	66.974(4)
V (Å)	4547.3(5)	10237.5(10)	11386.0(16)	2913.9(3)	4516.3(3)
Z	4	12	8	2	1
ρ_{calcd} (Mg m^{-3})	1.798	1.476	1.582	1.518	1.409
μ (mm^{-1})	6.647	4.647	5.407	2.771	1.926
R1[a]	0.0182	0.0267	0.0273	0.0173	0.0271
wR2[b]	0.0439	0.0550	0.0558	0.0457	0.0754

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

NMR (100.8 MHz, CD_2Cl_2): δ 177.3 (CS_2), 140.8 (C8a, C9a), 136.4 (C4a, C4b), 129.6 (C9), 127.2 (C1, C8), 125.4 (C2, C7), 121.9 (C3, C6), 117.9 (C4, C5).

$(Pr_4N)_2[Au_2\{\mu$-κ^2-*S*,*S*-$S_2C{=}C(C_{12}H_8)\}_2]$ [$(Pr_4N)_2$4a]. This orange compound was prepared as described for $(PPN)_2$**4a**, starting from **1a** (116 mg, 0.35 mmol) and $Pr_4N[AuCl_2]$ (151 mg, 0.33 mmol). Yield: 199 mg, 96%. Anal. Calcd for $C_{52}H_{72}Au_2N_2S_4$: C, 50.07; H, 5.81; N, 2.24; S, 10.28. Found: C, 49.70; H, 5.86; N, 2.28; S, 9.91. Mp: 209 °C (dec). Λ_M (acetone, 2.3×10^{-4} M): 137 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν(C=CS_2), 1474. ^{1}H NMR [400.9 MHz, $(CD_3)_2SO$]: δ 9.18 (d, $^3J_{HH}$ = 8.3 Hz, 4 H, H1, H8), 7.80 (d, $^3J_{HH}$ = 7.6 Hz, 4 H, H4, H5), 7.18 (t, $^3J_{HH}$ = 7.6 Hz, 4 H, H2, H7), 7.08 (t, $^3J_{HH}$ = 7.3 Hz, 4 H, H3, H6), 3.07−3.03 (m, 16 H, NCH_2), 1.55−1.53 (m, 16 H, CH_2), 0.84 (t, $^3J_{HH}$ = 7.3 Hz, 24 H, Me). ^{13}C{^{1}H} NMR [100.8 MHz, $(CD_3)_2SO$]: δ 175.5 (CS_2), 139.7 (C8a, C9a), 135.6 (C4a, C4b), 128.7 (C9), 126.3 (C1, C8), 125.2 (C2, C7), 122.1 (C3, C6), 118.0 (C4, C5), 59.3 (NCH_2), 14.8 (CH_2), 10.6 (Me).

$(Pr_4N)_2[Au_2\{\mu$-κ^2-*S*,*S*-$S_2C{=}C(C_{12}H_6(OC_8H_{17})_2$-2,7$)\}_2]$[$(Pr_4N)_2$4c]. To a solution of **2** (279 mg, 0.56 mmol) in THF (15 mL) were added successively diethylamine (0.1 mL) and $Pr_4N[AuCl_2]$ (242 mg, 0.53 mmol). Reaction took place immediately to give an orange solution and a white precipitate of Et_2NH_2Cl. The mixture was stirred for 15 min, and the precipitate was removed by filtration. The clear orange filtrate was evaporated to dryness and the residue dissolved in dichloromethane (5 mL). Addition of diethyl ether (25 mL) led to the slow formation of a bulky precipitate which was purified by recrystallization from dichloromethane/diethyl ether and vacuum-dried to give $(Pr_4N)_2$**4c** as an orange solid. Yield: 440 mg, 94%. Anal. Calcd for $C_{84}H_{136}Au_2N_2O_4S_4$: C, 57.32; H, 7.79; N, 1.59; S, 7.29. Found: C, 57.23; H, 8.08; N, 1.70; S, 7.16. Mp: 103 °C. Λ_M (acetone, 4.8×10^{-4} M): 98 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν(C=CS_2), 1480, 1466. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.79 (d, $^4J_{HH}$ = 2.0 Hz, 4 H, H8, H1), 7.32 (d, $^3J_{HH}$ = 8.2 Hz, 4 H, H4, H5), 6.55 (dd, 4 H, H3, H6), 3.86 (br t, OCH_2, 8 H), 2.48 (br, 16 H, NCH_2), 1.70 (br m, 8 H, OCH_2CH_2), 1.29 (br, 40 H, CH_2, C_8H_{17}), 1.11 (br, 8 H, CH_2, Pr_4N^+), 0.89 (app t, 12 H, Me, C_8H_{17}), 0.65 (app t, 24 H, Me, Pr_4N^+). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ 175.7 (CS_2), 157.2 (C2, C7), 141.1 (C8a, C9a), 129.8 (C9), 129.6 (C4a, C4b), 117.2 (C4, C5), 112.7 (C1, C8), 110.4 (C3, C6), 68.1 (OCH_2), 58.7 (NCH_2), 31.9, 29.6, 29.5, 29.3, 26.2, 22.7 (all CH_2, C_8H_{17}), 15.2 (CH_2, Pr_4N^+), 14.1 (Me, C_8H_{17}), 10.9 (Me, Pr_4N^+).

$[\{Au(PMe_3)\}_2\{\mu$-κ^2-*S*,*S*-$S_2C{=}C(C_{12}H_8)\}]$ (5a). To a suspension of $[AuCl(PMe_3)]$ (213 mg, 0.69 mmol) in THF (20 mL) were added successively piperidine (0.1 mL) and compound **1a** (115 mg, 0.35 mmol). The resulting yellow suspension was stirred for 30 min, and the solvent was evaporated to dryness. The residue was treated with diethyl ether, and the solid was collected by filtration, washed with ethanol (2 × 5 mL) and diethyl ether (2 × 3 mL), and recrystallized from dichloromethane/diethyl ether to give **5a** as a yellow powder. Yield: 253 mg, 93%. Anal. Calcd for $C_{20}H_{26}Au_2P_2S_2$: C, 30.55; H, 3.33; S, 8.15. Found: C, 30.33; H, 3.32; S, 7.90. Mp: 270 °C (dec). IR (Nujol, cm^{-1}): ν(C=CS_2), 1484. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 9.02 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, H1, H8), 7.81−7.73 (m, 2 H, H4, H5), 7.31−7.12 (m, 4 H, H2, H3, H6, H7), 1.63 (d, $^2J_{HP}$ = 9.7 Hz, 18 H, PMe_3). ^{31}P{^{1}H} NMR (81 MHz, CD_2Cl_2): δ −3.64 (br). The ^{13}C{^{1}H} NMR spectrum of **5a** could not be measured; see Results and Discussion.

$[\{Au(PEt_3)\}_2\{\mu$-κ^2-*S*,*S*-$S_2C{=}C(C_{12}H_8)\}]$ (5b). A solution of $[AuCl(PEt_3)]$ (138.9 mg, 0.40 mmol) in THF (15 mL) at 0 °C was treated successively with piperidine (0.1 mL, 1.01 mmol) and **1a** (69 mg, 0.21 mmol). The resulting yellow suspension was stirred for 20 min, and the solvent was removed under vacuum. Treatment of the oily residue with diethyl ether (40 mL) gave a yellow solid which was filtered off, washed with methanol (3 × 3 mL) and diethyl ether (2 × 3 mL), and vacuum-dried to give **5b**. Yield: 113 mg, 65%. Anal. Calcd for $C_{26}H_{38}Au_2P_2S_2$: C, 35.87; H, 4.40; S, 7.37. Found: C, 36.23; H, 4.46; S, 7.31. Mp: 163 °C (dec). IR (Nujol, cm^{-1}): ν(C=CS_2), 1486. ^{1}H NMR (400.9 MHz, CD_2Cl_2): δ 9.05 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, H1, H8), 7.75 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, H4, H5), 7.24 (m, 2 H, H2, H7), 7.15 (m, 2 H, H3, H6), 1.85 (m, 12 H, CH_2), 1.24 (dt, $^3J_{HP}$ = 18.3 Hz, $^3J_{HH}$ = 7.6 Hz, 18 H, Me). ^{13}C{^{1}H} NMR (100.8 MHz, CD_2Cl_2, −10 °C): δ 162.7 (CS_2), 139.6 (C8a, C9a), 137.4 (C4a, C4b), 132.4 (C9), 126.7 (C1, C8), 125.7 (C2, C7), 124.2 (C3, C6), 118.2 (C4, C5), 18.0 (d, J_{CP} = 32.9 Hz, CH_2), 8.8 (Me). ^{31}P{^{1}H} NMR (162.3 MHz, $CDCl_3$): δ 34.1 (s).

$[\{Au(PPh_3)\}_2\{\mu$-κ^2-*S*,*S*-$S_2C{=}C(C_{12}H_8)\}]$·THF (5c). A solution of $[AuCl(PPh_3)]$ (314 mg, 0.64 mmol) in THF (20 mL) was treated successively with piperidine (0.1 mL, 1.01 mmol) and **1a** (104.0 mg, 0.317 mmol). The resulting yellow suspension was stirred for 1 h and filtered to remove the precipitate of piperidinium chloride. Partial evaporation of the clear yellow filtrate (to ca. 5 mL) led to the precipitation of a yellow solid. Diethyl ether (20 mL) was added, and the solid was filtered off, washed with ethanol (2 × 3 mL) and diethyl ether (2 × 3 mL), and recrystallized from THF/diethyl ether to give **5c**·THF as a yellow microcrystalline solid. Yield: 333 mg, 85%. Anal. Calcd for $C_{54}H_{46}Au_2OP_2S_2$: C, 52.70; H, 3.77; S, 5.21. Found: C, 52.27; H, 3.75; S, 5.08. Mp: 122 °C (dec). IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1488, 1480. ^1H NMR (400.9 MHz, CD_2Cl_2): δ 9.13 (d, $^3J_{HH} = 8.0$ Hz, 2 H, H1, H8), 7.78 (d, $^3J_{HH} = 7.4$ Hz, 2 H, H4, H5), 7.51−7.41 (m, 18 H, PPh_3), 7.32−7.26 (m, 14 H, PPh_3 + H2, H7), 7.18 (t, $^3J_{HH} = 7.2$ Hz, 2 H, H3, H6), 3.70 (m, 4 H, CH_2, THF), 1.83 (m, 4 H, CH_2, THF). $^{13}C\{^1H\}$ (100.8 MHz, CD_2Cl_2, −10 °C): δ 160.5 (CS_2), 139.6 (C8a, C9a), 137.7 (C4a, C4b), 134.1 (d, $^2J_{CP} = 13.7$ Hz, *o*-C, PPh_3), 132.7 (C9), 131.5 (*p*-C, PPh_3), 129.5 (d, $^1J_{CP} = 57.1$ Hz, *i*-C, PPh_3), 129.1 (d, $^3J_{CP} = 11.4$ Hz, *m*-C, PPh_3), 126.8 (C1, C8), 125.9 (C2, C7), 124.5 (C3, C6), 118.3 (C4, C5), 67.9, 25.6 (both CH_2, THF). $^{31}P\{^1H\}$ NMR (162.3 MHz, CD_2Cl_2): δ 35.4 (br).

[{Au(PCy$_3$)}$_2${μ-κ^2-*S,S*-S$_2$C=C(C$_{12}$H$_8$)}] (5d). This yellow complex was prepared as described for **5b**, starting from [AuCl(PCy$_3$)] (230 mg, 0.45 mmol) and compound **1a** (79 mg, 0.24 mmol). Yield: 174.3 mg, 65%. Anal. Calcd for $C_{50}H_{74}Au_2P_2S_2$: C, 50.25; H, 6.24; S, 5.37. Found: C, 50.15; H, 6.33; S, 5.29. Mp: 200 °C (dec). IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1489. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.26 (d, $^3J_{HH} = 8.0$ Hz, 2 H, H1, H8), 7.71 (d, $^3J_{HH} = 7.2$ Hz, 2 H, H4, H5), 7.23 (m, 2 H, H2, H7), 7.11 (m, 2 H, H3, H6), 1.94−1.15 (m, 66 H, PCy_3). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, −15 °C): δ 162.1 (CS_2), 140.0 (C8a, C9a), 137.2 (C4a, C4b), 132.5 (C9), 126.6 (C1, C8), 125.2 (C2, C7), 123.5 (C3, C6), 117.9 (C4, C5), 32.8 (d, $^2J_{CP} = 27.5$ Hz, C1, PCy_3), 30.1 (C2, PCy_3), 27.0 (d, $^3J_{CP} = 11.8$ Hz, C3, PCy_3), 25.7 (C4, PCy_3). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 54.9 (s).

[{Au(PMe$_3$)}$_2${μ-κ^2-*S,S*-S$_2$C=C(C$_{12}$H$_6$(*t*-Bu)$_2$-2,7)}] (5e). This yellow microcrystalline compound was prepared as described for **5b**, starting from [AuCl(PMe$_3$)] (288 mg, 0.93 mmol) and **1b** (222 mg, 0.50 mmol). Yield: 346 mg, 82%. Anal. Calcd for $C_{28}H_{42}Au_2P_2S_2$: C, 37.42; H, 4.71; S, 7.14. Found: C, 37.32; H, 4.92; S, 6.69. Mp: 181 °C (dec). IR (Nujol, cm^{-1}): $\nu(C{=}CS_2)$, 1486. ^1H NMR (200 MHz, $CDCl_3$): δ 9.22 (br, 2 H, H1, H8), 7.61 (br d, $^3J_{HH} = 7.9$ Hz, 2 H, H4, H5), 7.18 (dd, $^3J_{HH} = 7.9$, $^4J_{HH} = 1.7$ Hz, 2 H, H3, H6), 1.53 (br, 18 H, PMe_3), 1.38 (s, 18 H, *t*-Bu). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ −3.67 (br). The $^{13}C\{^1H\}$ NMR spectrum of **5e** could not be measured; see Results and Discussion.

[{Au(PEt$_3$)}$_2${μ-κ^2-*S,S*-S$_2$C=C(C$_{12}$H$_6$(*t*-Bu)$_2$-2,7)}] (5f). This yellow complex was prepared as described for **5b**, starting from [AuCl(PEt$_3$)] (182 mg, 0.52 mmol) and **1b** (126 mg, 0.26 mmol). Yield: 234 mg, 92%. Anal. Calcd for $C_{34}H_{54}Au_2P_2S_2$: C, 41.55; H, 5.54; S, 6.52. Found: C, 41.85; H, 5.48; S, 6.53. Mp: 176 °C (dec). IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1487. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.25 (d, $^4J_{HH} = 1.5$ Hz, 2 H, H1, H8), 7.58 (d, $^3J_{HH} = 7.9$ Hz, 2 H, H4, H5), 7.16 (dd, 2 H, H3, H6), 1.78 (m, 12 H, CH_2, PEt_3), 1.38 (s, 18 H, *t*-Bu), 1.18 (dt, $^3J_{HP} = 18.3$ Hz, $^3J_{HH} = 7.8$ Hz, 18 H, Me, PEt_3). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, −10 °C): δ 157.9 (CS_2), 147.8 (C2, C7), 140.1 (C8a, C9b), 135.4 (C4a, C4b), 133.6 (C9), 124.1 (C1, C8), 121.3 (C3, C6), 117.0 (C4, C5), 35.0 [$C(CH_3)_3$], 31.8 [$C(CH_3)_3$], 17.8 (d, $J_{CP} = 32.7$ Hz, CH_2, PEt_3), 8.7 (Me, PEt_3). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 33.8 (s).

[{Au(PPh$_3$)}$_2${μ-κ^2-*S,S*-S$_2$C=C(C$_{12}$H$_6$(*t*-Bu)$_2$-2,7)}]·THF (5g). This yellow complex was prepared as described for **5b**, starting from [AuCl(PPh$_3$)] (249 mg, 0.50 mmol) and **1b** (125 mg, 0.26 mmol). Yield: 324 mg, 96%. Anal. Calcd for $C_{62}H_{62}Au_2OP_2S_2$: C, 55.44; H, 4.65; S, 4.77. Found: C, 55.65; H, 4.85; S, 4.54. Mp: 140 °C. IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1499. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.30 (d, $^4J_{HH} = 1.5$ Hz, 2 H, H1, H8), 7.63 (d, $^3J_{HH} = 7.9$ Hz, 2 H, H4, H5), 7.46−7.24 (m, 30 H, PPh_3), 7.19 (dd, 2 H, H3, H6), 3.75 (m, 6 H, CH_2, THF), 1.85 (m, 6 H, CH_2, THF), 1.36 (s, 18 H, *t*-Bu). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, −10 °C): δ 156.0 (CS_2), 148.0 (C2, C7), 140.0 (C8a, C9a), 135.7 (C4a, C4b), 134.0 (d, $^2J_{CP} = 13.7$ Hz, *o*-C, PPh_3), 131.4 (C9), 131.2 (*p*-C, PPh_3), 129.6 (d, $^1J_{CP} = 55.9$ Hz, *i*-C PPh_3), 128.9 (d, $^3J_{CP} = 11.4$ Hz, *m*-C, PPh_3), 124.0 (C1, C8), 120.7 (C3, C6), 116.9 (C4, C5), 68.0 (CH_2, THF), 35.0 [$C(CH_3)_3$], 31.8 [$C(CH_3)_3$], 25.5 (CH_2, THF). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 35.7 (br).

[{Au(PCy$_3$)}$_2${μ-κ^2-*S,S*-S$_2$C=C(C$_{12}$H$_6$(*t*-Bu)$_2$-2,7)}] (5h). This yellow complex was prepared as described for **5b**, starting from [AuCl(PCy$_3$)] (235 mg, 0.46 mmol) and **1b** (117 mg, 0.25 mmol). Yield: 244 mg, 82%. Anal. Calcd for $C_{58}H_{90}Au_2P_2S_2$: C, 53.29; H, 6.94; S, 4.91. Found: C, 53.16; H, 7.13; S, 4.97. Mp: 202 °C (dec). IR (KBr, cm^{-1}): $\nu(C{=}CS_2)$, 1491. ^1H NMR (400.9 MHz, $CDCl_3$): δ 9.33 (d, $^4J_{HH} = 1.6$ Hz, 2 H, H1, H8), 7.56 (d, $^3J_{HH} = 7.9$ Hz, 2 H, H4, H5), 7.13 (dd, 2 H, H3, H6), 7.95−7.66 (m, 36 H, PCy_3), 1.39 (m, 30 H, *t*-Bu + PCy_3), 1.26−1.15 (m, 18 H, PCy_3). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, −15 °C): δ 158.9 (CS_2), 147.3 (C2, C7), 140.5 (C8a, C9a), 135.1 (C4a, C4b), 133.6 (C9), 123.9 (C1, C8), 120.7 (C3, C6), 116.9 (C4, C5), 34.9 [$C(CH_3)_3$], 32.8 (d, $^2J_{CP} = 27.4$ Hz, C1, PCy_3), 31.9 [$C(CH_3)_3$], 30.1 (C2, PCy_3), 27.0 (d, $^3J_{CP} = 11.8$ Hz, C3, PCy_3), 25.7 (C4, PCy_3). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ 54.7 (s).

PPN[Au{κ^2-*S,S*-S$_2$C=C(C$_{12}$H$_8$)}$_2$] [(PPN)6a]. A suspension of PPN[AuCl$_4$] (878 mg, 1.00 mmol) in THF (50 mL) was treated successively with piperidine (0.1 mL, 1.01 mmol) and compound **1a** (678 mg, 2.07 mmol). The resulting dark green suspension was stirred for 6 h. The solvent was removed, and the remaining residue was treated with diethyl ether to give a green solid which was filtered off and washed with ethanol (2 × 5 mL) and diethyl ether (2 × 5 mL). The product was recrystallized from dichloromethane/diethyl ether to give (PPN)**6a**. Yield: 1.049 g, 86%. Anal. Calcd for $C_{64}H_{46}AuNP_2S_4$: C, 63.20; H, 3.81; N, 1.15; S, 10.54. Found: C, 63.53; H, 4.03; N, 1.23; S, 10.40. Mp: 259 °C. Λ_M (acetone, 2.5×10^{-4} M): 101 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): $\nu(C{=}CS_2)$, 1538; $\nu(Au{-}S)$, 364. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.44−8.42 (m, 4 H, H1, H8), 7.78−7.76 (m, 4 H, H4, H5), 7.52−7.47 (m, 6 H, PPN^+), 7.39−7.32 (m, 24 H, PPN^+), 7.24−7.17 (m, 8 H, H2, H3, H6, H7). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 157.6 (CS_2), 138.4 (C8a, C9a), 137.2 (C4a, C4b), 129.5 (C9), 126.2 (C2, C7), 124.1 (C3, C6), 123.9 (C1, C8), 118.7 (C4, C5).

PPN[Au{κ^2-*S,S*-S$_2$C=C(C$_{12}$H$_6$(*t*-Bu)$_2$-2,7)}$_2$] [(PPN)6b]. This green complex was prepared as described for (PPN)**6a**, starting from PPN[AuCl$_4$] (1.004 g, 1.14 mmol) and **1b** (1.078 g, 2.45 mmol). Yield: 1.230 g, 74%. Anal. Calcd for $C_{64}H_{46}AuNP_2S_4$: C, 66.70; H, 5.46; N, 0.97; S, 8.90. Found: C, 66.42; H, 5.51; N, 0.92; S, 8.77. Mp: 272 °C. Λ_M (acetone, 4.9×10^{-4} M): 70 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C{=}CS_2)$, 1536; $\nu(Au{-}S)$, 372. ^1H NMR (400.9 MHz, $CDCl_3$): δ 8.53 (d, $^4J_{HH} = 1.3$ Hz, 4 H, H1, H8), 7.64 (d, $^3J_{HH} = 8.0$ Hz, 4 H, H4, H5), 7.45−7.29 (m, 30 H, PPN^+), 7.23 (dd, 4 H, H3, H6), 1.36 (s, 36 H, *t*-Bu). $^{13}C\{^1H\}$ (50.3 MHz, $CDCl_3$): δ 155.5 (CS_2), 148.8 (C2, C7), 138.9 (C8a, C9a), 134.9 (C4a, C4b), 129.9 (C9), 121.3 (C3, C6), 121.0 (C1, C8), 117.9 (C4, C5), 34.9 [$C(CH_3)_3$], 31.8 [$C(CH_3)_3$].

Bu$_4$N[Au{κ^2-*S,S*-S$_2$C=C(C$_{12}$H$_6$(*t*-Bu)$_2$-2,7)}$_2$] [(Bu$_4$N)6b]. This green complex was prepared as described for (PPN)**6a**, starting from Bu$_4$N[AuCl$_4$] (405 mg, 0.70 mmol) and **1b** (630 mg, 1.43 mmol). Yield: 531 g, 67%. Anal. Calcd for $C_{60}H_{84}AuNS_4$: C, 62.96; H, 7.40; N, 1.22; S, 11.21. Found: C, 62.66; H, 7.53; N, 1.29; S, 11.09. Mp: 311 °C (dec). Λ_M (acetone, 2.6×10^{-4} M): 88 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C{=}CS_2)$, 1532; $\nu(Au{-}S)$, 374. ^1H NMR (200 MHz, CD_2Cl_2): δ 8.47 (d, $^4J_{HH} = 1.7$ Hz, 4 H, H1, H8), 7.65 (d, $^3J_{HH} = 7.9$ Hz, 4 H, H4, H5), 7.29 (dd, 4 H, H3, H6), 2.89 (m, 8 H, NCH_2), 1.40 (s, 36 H, *t*-Bu), 1.30 (m, 8 H, CH_2), 1.20 (m, 8 H,

$\mathrm{CH_2}$), 0.78 (t, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, Me). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (50.3 MHz, $\mathrm{CD_2Cl_2}$): δ 153.9 ($\mathrm{CS_2}$), 149.8 (C2, C7), 138.7 (C8a, C9a), 135.2 (C4a, C4b), 130.5 (C9), 122.5 (C3, C6), 121.2 (C1, C8), 118.6 (C4, C5), 58.9 ($\mathrm{NCH_2}$), 35.2 [*C*($\mathrm{CH_3}$)$_3$], 31.9 [C(*C*$\mathrm{H_3}$)$_3$], 24.1, 20.0 (both $\mathrm{CH_2}$), 13.7 (Me, $\mathrm{Bu_4N^+}$).

$\mathrm{Bu_4N[Au\{\kappa^2\text{-}\mathit{S,S}\text{-}S_2C{=}C(C_{12}H_6(OC_8H_{17})_2\text{-}2,7)\}_2]}$ [($\mathrm{Bu_4N}$)6c]. To a solution of **2** (432 mg, 0.87 mmol) in THF (15 mL) were added successively diethylamine (0.1 mL) and $\mathrm{Bu_4N[AuCl_4]}$ (228 mg, 0.39 mmol). Reaction took place immediately to give a dark green suspension, which was stirred for 45 min and filtered to remove the white precipitate of $\mathrm{Et_2NH_2Cl}$. The clear dark green filtrate was evaporated to dryness, and the residue was dissolved in dichloromethane (5 mL). Addition of ethanol led to the formation of a green precipitate, which was collected by filtration, recrystallized from dichloromethane/ethanol, and vacuum-dried to give ($\mathrm{Bu_4N}$)**6c**. Yield: 290 mg, 52%. Anal. Calcd for $\mathrm{C_{76}H_{116}AuNO_4S_4}$: C, 63.70; H, 8.16; N, 0.98; S, 8.95. Found: C, 63.67; H, 8.32; N, 1.06; S, 8.86. Mp: 164 °C. Λ_{M} (acetone, 4.9×10^{-4} M): 76 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$. IR ($\mathrm{cm^{-1}}$): ν($\mathrm{C{=}CS_2}$), 1538; ν(Au−S), 368. ^{1}H NMR (200 MHz, $\mathrm{CD_2Cl_2}$): δ 7.91 (d, $^{4}J_{\mathrm{HH}} = 2.2$ Hz, 4 H, H8, H1), 7.46 (d, $^{3}J_{\mathrm{HH}} = 8.4$ Hz, 4 H, H4, H5), 6.72 (dd, 4 H, H6, H3), 3.96 (t, $^{3}J_{\mathrm{HH}} = 6.6$ Hz, 8 H, $\mathrm{OCH_2}$), 2.57 (br m, 8 H, $\mathrm{NCH_2}$), 1.78 (m, 8H, $\mathrm{OCH_2}$C*H*$_2$), 1.50−1.30 (br m, 40 H, $\mathrm{CH_2}$, $\mathrm{C_8H_{17}}$), 1.10 (br m, 16 H, $\mathrm{CH_2}$, $\mathrm{Bu_4N^+}$), 0.90 (m, 12 H, Me, $\mathrm{C_8H_{17}}$), 0.76 (m, 12 H, Me, $\mathrm{Bu_4N^+}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (50.3 MHz, $\mathrm{CDCl_3}$): δ 157.9 (C2, C7), 155.5 ($\mathrm{CS_2}$), 139.0 (C8a, C9a), 130.7 (C4a, C4b), 129.6 (C9), 118.7 (C4, C5), 111.8 (C1, C8), 109.9 (C3, C6), 68.3 ($\mathrm{OCH_2}$), 57.7 ($\mathrm{NCH_2}$), 31.8, 29.5, 29.4, 29.3, 26.2 (all $\mathrm{CH_2}$, $\mathrm{C_8H_{17}}$), 23.5 ($\mathrm{CH_2}$, $\mathrm{Bu_4N^+}$), 22.7 ($\mathrm{CH_2}$, $\mathrm{C_8H_{17}}$), 19.45 ($\mathrm{CH_2}$, $\mathrm{Bu_4N^+}$), 14.1 (Me, $\mathrm{C_8H_{17}}$), 13.7 (Me, $\mathrm{Bu_4N^+}$).

$\mathrm{[Au\{\kappa^2\text{-}\mathit{S,S}\text{-}S_2C{=}C(C_{12}H_8)\}\{\kappa^2\text{-}\mathit{S,S}\text{-}S_2CCH(C_{12}H_8)\}]}$ (7a). A solution of (PPN)**6a** (142 mg, 0.117 mmol) in dichloromethane (20 mL) was treated with trifluoromethanesulfonic acid (21 μL, 0.23 mmol). A red precipitate formed immediately, which was filtered off, washed with dichloromethane (2 × 5 mL), and vacuum-dried to give **7a**. Yield: 74 mg, 94%. Anal. Calcd for $\mathrm{C_{28}H_{17}AuS_4}$: C, 49.55; H, 2.52; S, 18.90. Found: C, 49.13; H, 2.53; S, 18.91. Mp: 202 °C (dec). IR ($\mathrm{cm^{-1}}$): ν($\mathrm{C{=}CS_2}$), 1548, ν(Au−S), 366. NMR data for **7a** could not be obtained because of its very low solubility.

$\mathrm{[Au\{\kappa^2\text{-}\mathit{S,S}\text{-}S_2C{=}C(C_{12}H_6(\mathit{t}\text{-}Bu)_2\text{-}2,7)\}\{\kappa^2\text{-}\mathit{S,S}\text{-}S_2CCH(C_{12}H_6\text{-}(\mathit{t}\text{-}Bu)_2\text{-}2,7)\}]}$ (7b). This complex was obtained as a dark red solid by following the procedure described for **7a**, starting from (PPN)**6b** (220 mg, 0.15 mmol) and trifluoromethanesulfonic acid (27 μL, 0.30 mmol). Yield: 132 mg, 96%. Anal. Calcd for $\mathrm{C_{44}H_{49}AuS_4}$: C, 58.52; H, 5.47; S, 14.20. Found: C, 58.35; H, 5.47; S, 14.22. Mp: 276 °C (dec). IR ($\mathrm{cm^{-1}}$): ν($\mathrm{C{=}CS_2}$), 1570, 1558; ν(Au−S), 380. ^{1}H NMR (200 MHz, $\mathrm{CD_2Cl_2}$): δ 8.18 (d, $^{4}J_{\mathrm{HH}} = 1.3$ Hz, 2 H, H1, H8, dithiolato), 7.75−7.71 (br m, 4 H, H1, H4, H5, H8, dithioato), 7.63 (d, $^{3}J_{\mathrm{HH}} = 8.0$ Hz, 2 H, H4, H5, dithiolato), 7.59−7.54 (m, 2 H, H6, H3, dithioato), 7.33 (dd, $^{3}J_{\mathrm{HH}} = 8.0$, $^{4}J_{\mathrm{HH}} = 1.7$ Hz, 2 H, H3, H6, dithiolato), 1.39 (s, 18 H, *t*-Bu), 1.37 (s, 18 H, *t*-Bu) (H9 not observed). The $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum of **7b** could not be measured because of its very low solubility.

$\mathrm{[Au\{\kappa^2\text{-}\mathit{S,S}\text{-}S_2C{=}C(C_{12}H_6(OC_8H_{17})_2\text{-}2,7)\}\{\kappa^2\text{-}\mathit{S,S}\text{-}S_2CCH(C_{12}H_6\text{-}(OC_8H_{17})_2\text{-}2,7)\}]}$ (7c). This complex was obtained as a dark red solid by following the procedure described for **7a**, starting from ($\mathrm{Bu_4N}$)**6c** (302 mg, 0.21 mmol) and trifluoromethanesulfonic acid (40 μL, 0.46 mmol). Yield: 218 mg, 87%. Anal. Calcd for $\mathrm{C_{60}H_{81}AuO_4S_4}$: C, 60.48; H, 6.85; S, 10.76. Found: C, 60.20; H, 7.14; S, 10.74. Mp: 218 °C (dec). IR ($\mathrm{cm^{-1}}$): ν($\mathrm{C{=}CS_2}$), 1550, ν(Au−S), 370. ^{1}H NMR (400.9 MHz, $\mathrm{CDCl_3}$): δ 7.66 (d, $^{4}J_{\mathrm{HH}} = 1.7$ Hz, 2 H, H1, H8 of dithiolato), 7.58 (d, $^{3}J_{\mathrm{HH}} = 8.4$ Hz, 2 H, H4, H5, dithioato), 7.49 (d, $^{3}J_{\mathrm{HH}} = 8.4$ Hz, 2 H, H4, H5, dithiolato), 7.14 (s, 2 H, H1, H8, dithioato), 7.02 (dd, $^{4}J_{\mathrm{HH}} = 1.7$, $^{3}J_{\mathrm{HH}} = 8.4$ Hz, 2 H, H3, H6, dithioato), 6.80 (dd, $^{4}J_{\mathrm{HH}} = 1.7$, $^{3}J_{\mathrm{HH}} = 8.4$ Hz, 2 H, H3, H6, dithiolato), 5.17 (s, 1 H, H9, dithioato), 4.00 (m, 8 H, $\mathrm{OCH_2}$), 1.80 (m, 8 H, $\mathrm{CH_2}$), 1.46 (m, 8 H, $\mathrm{CH_2}$), 1.29 (m, 40 H, $\mathrm{CH_2}$), 0.88 (m, 12 H, Me). The $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum of **7c** could not be measured because of its very low solubility.

$\mathrm{Bu_4N[AuCl_2\{\kappa^2\text{-}\mathit{S,S}\text{-}S_2C{=}C(C_{12}H_6(\mathit{t}\text{-}Bu)_2\text{-}2,7)\}]}$ [($\mathrm{Bu_4N}$)8b]. A solution of $\mathrm{PhICl_2}$ (174 mg, 0.63 mmol) in dichloromethane (15 mL) was added dropwise to a stirred solution of ($\mathrm{Bu_4N}$)**6b** (622 mg, 0.54 mmol) in the same solvent (50 mL) over a period of 10 min. The resulting brown solution was stirred for 2 h and concentrated to ca. 15 mL. Addition of diethyl ether (25 mL) led to the precipitation of a pale green solid, which was filtered off, washed with a 1:2 mixture of dichloromethane and diethyl ether (2 × 5 mL), and vacuum-dried to give ($\mathrm{Bu_4N}$)**8b**. Yield: 348 mg, 74%. Anal. Calcd for $\mathrm{C_{38}H_{60}AuCl_2NS_2}$: C, 52.89; H, 7.01; N, 1.62; S, 7.43. Found: C, 52.81; H, 7.26; N, 1.65; S, 7.25. Mp: 200 °C. Λ_{M} (acetone, 3.8×10^{-4} M): 96 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$. IR ($\mathrm{cm^{-1}}$): ν($\mathrm{C{=}CS_2}$), 1572, 1564; ν(Au−S), 384; ν(Au−Cl), 318, 302. ^{1}H NMR (400.9 MHz, $\mathrm{CD_2Cl_2}$): δ 8.13 (dd, $^{5}J_{\mathrm{HH}} = 0.4$, $^{4}J_{\mathrm{HH}} = 1.7$ Hz, 2 H, H1, H8), 7.64 (dd, $^{5}J_{\mathrm{HH}} = 0.4$, $^{3}J_{\mathrm{HH}} = 7.9$ Hz, 2 H, H4, H5), 7.33 (dd, $^{4}J_{\mathrm{HH}} = 1.7$, $^{3}J_{\mathrm{HH}} = 7.9$ Hz, 2 H, H3, H6), 3.07 (m, 8 H, $\mathrm{NCH_2}$), 1.53 (m, 8 H, $\mathrm{CH_2}$), 1.38 (m, 26 H, *t*-Bu + $\mathrm{CH_2}$), 0.96 (t, $^{3}J_{\mathrm{HH}} = 7.3$ Hz, Me, $\mathrm{Bu_4N^+}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75 MHz, $\mathrm{CD_2Cl_2}$): δ 150.3 (C2, C7), 139.3 ($\mathrm{CS_2}$), 138.4 (C8a, C9a), 135.7 (C4a, C4b), 130.5 (C9), 123.5 (C3, C6), 120.0 (C1, C8), 119.0 (C4, C5), 59.4 ($\mathrm{NCH_2}$), 35.2 [*C*($\mathrm{CH_3}$)$_3$], 31.8 [C(*C*$\mathrm{H_3}$)$_3$], 24.4 ($\mathrm{CH_2}$), 20.1 ($\mathrm{CH_2}$), 13.8 (Me, $\mathrm{Bu_4N^+}$).

$\mathrm{[Au\{SC(S)CH(C_{12}H_8)\}(PCy_3)]}$ (9). To a solution of **1a** (100 mg, 0.31 mmol) in dichloromethane (15 mL) was added $\mathrm{[AuCl(PCy_3)]}$ (143 mg, 0.28 mmol), and the resulting orange solution was stirred for 20 min. Partial evaporation of the solvent (3 mL) and addition of diethyl ether (15 mL) led to the precipitation of an orange-pink solid, which was filtered off, washed with ethanol (2 × 2 mL) and diethyl ether (2 mL), and vacuum-dried to give **9**. Yield: 174 mg, 87%. Anal. Calcd for $\mathrm{C_{32}H_{42}AuPS_2}$: C, 53.47; H, 5.89; S, 8.92. Found: C, 53.60; H, 5.95; S, 9.14. Mp: 157 °C (dec). IR (Nujol, $\mathrm{cm^{-1}}$): ν($\mathrm{CS_2}$), 970. ^{1}H NMR (400.9 MHz, $\mathrm{CD_2Cl_2}$): δ 7.76−7.73 (m, 4 H, H1, H4, H5, H8), 7.42−7.38 (m, 2 H, H2, H7), 7.35−7.31 (m, 2 H, H3, H6), 5.64 (s, 1 H, H9), 2.07−2.02 (m, 3 H, CH, $\mathrm{PCy_3}$), 2.00−1.15 (m, 30 H, $\mathrm{CH_2}$, $\mathrm{PCy_3}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100.8 MHz, $\mathrm{CD_2Cl_2}$): δ 255.2 ($\mathrm{CS_2}$), 146.3 (C8a,C9a), 141.5 (C4a, C4b), 128.1 (C3,C6), 127.6 (C2, C7), 125.3 (C1, C8), 120.1 (C4, C5), 74.9 (C9), 33.8 (d, $^{2}J_{\mathrm{CP}} = 27.8$ Hz, C1, $\mathrm{PCy_3}$), 31.0 (C2, $\mathrm{PCy_3}$), 27.5 (d, $^{3}J_{\mathrm{CP}} = 11.9$ Hz, C3, $\mathrm{PCy_3}$), 26.3 (C4, $\mathrm{PCy_3}$). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (162.3 MHz, $\mathrm{CD_2Cl_2}$): δ 56.8 (s).

$\mathrm{[Au_{\mathit{n}}\{S_2CCH(C_{12}H_8)\}_{\mathit{n}}]}$ (10). To a suspension of $\mathrm{[AuCl(SMe_2)]}$ (106 mg, 0.36 mmol) in THF (12 mL) was added **1a** (123 mg, 0.38 mmol). A red precipitate formed immediately. The suspension was stirred for 30 min, and the solid was filtered off, washed with THF (3 × 3 mL) and dichloromethane (3 × 3 mL), and vacuum-dried to give **10**. Yield: 124 mg, 79%. Anal. Calcd for $\mathrm{C_{14}H_9AuS_2}$: C, 38.36; H, 2.07; S, 14.63. Found: C, 38.75; H, 2.05; S, 14.35. Mp: 196 °C (dec). IR (Nujol, $\mathrm{cm^{-1}}$): ν($\mathrm{CS_2}$), 1074, 1032, 1004. The ^{1}H NMR spectrum of this compound in $\mathrm{(CD_3)_2SO}$ shows very complex signals in the aromatic region; see Results and Discussion.

$\mathrm{PPN[Au\{\kappa^2\text{-}\mathit{S,S}\text{-}S_2C{=}C(C_{12}H_8)\}_2]\cdot 1.5TCNQ}$ (11a). To a solution of (PPN)**6a** (122 mg, 0.10 mmol) in dichloromethane (30 mL) was added tetracyano-7,7,8,8-quinodimethane (TCNQ) (35 mg, 0.17 mmol). The resulting dark brown solution was stirred for 2 h and concentrated to ca. 8 mL. Addition of diethyl ether (2 mL) led to the precipitation of a dark blue microcrystalline solid, which was filtered off, washed with a 4:1 mixture of dichloromethane/diethyl ether (2 × 5 mL), and vacuum-dried to give **11a**. Yield: 140 mg, 92%. Anal. Calcd for $C_{82}H_{52}AuN_7P_2S_4$: C, 64.69; H, 3.44; N, 6.44; S, 8.42. Found: C, 64.29; H, 3.39; N, 6.62; S, 8.32. Mp: 200 °C (dec). IR (Nujol, cm^{-1}): $\nu(C{\equiv}N)_{TCNQ}$, 2216; $\nu(C{=}CS_2)$, 1530; $\delta(C{-}H)_{TCNQ}$, 832; $\nu(Au{-}S)$, 368. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.36 (m, 4 H, H1, H8), 7.76 (m, 4 H, H4, H5), 7.63−7.40 (m, 30 H, PPN^+), 7.26 (m, 8 H, H2, H3, H6, H7).

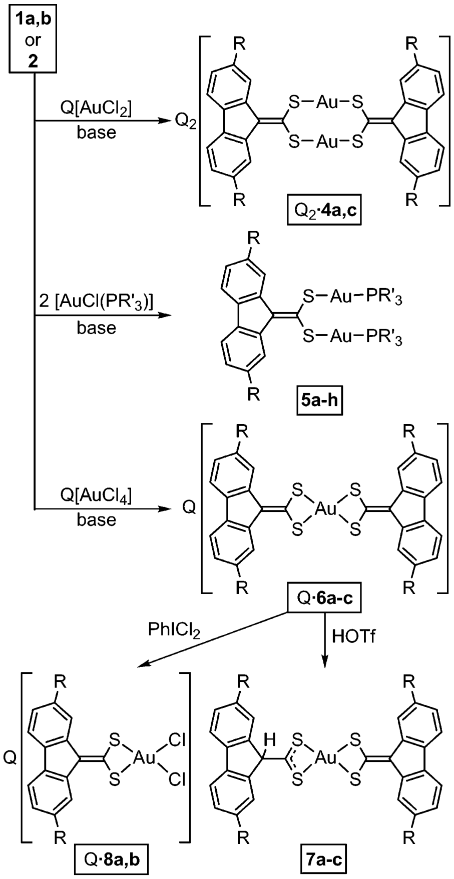
$PPN[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6(t\text{-}Bu)_2\text{-}2,7)\}_2]\cdot 1.5TCNQ\cdot 2CH_2Cl_2$ (11b). A solid mixture of (PPN)**6b** (138 mg, 0.1 mmol) and TCNQ (24 mg, 0.12 mmol) was treated with dichloromethane (25 mL), and the resulting dark brown solution was stirred for 7 h. Partial evaporation of the solvent (10 mL) and addition of diethyl ether (20 mL) led to the precipitation of a black microcrystalline solid, which was filtered off, washed with a 1:2 mixture of dichloromethane/diethyl ether (2 × 5 mL), and vacuum-dried to give **11b**. Yield: 132 mg, 72%. Anal. Calcd for $C_{100}H_{88}AuCl_4N_7P_2S_4$: C, 62.66; H, 4.63; N, 5.12; S, 6.69. Found: C, 62.74; H, 4.94; N, 5.19; S, 6.33. Mp: 270 °C. IR (Nujol, cm^{-1}): $\nu(C{\equiv}N)_{TCNQ}$, 2216; $\nu(C{=}C)_{TCNQ}$, 1544; $\nu(C{=}CS_2)$, 1526; $\delta(C{-}H)_{TCNQ}$, 834; $\nu(Au{-}S)$, 370. ^1H NMR (300.1 MHz, CD_2Cl_2): δ 8.45 (d, $^4J_{HH}$ = 1.5 Hz, 4 H, H1, H8), 7.64−7.39 (m, 34 H, H4, H5 + PPN^+), 7.29 (dd, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 8.1 Hz, 4 H, H3, H6), 1.41 (s, 36 H, *t*-Bu).

$Bu_4N[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6(OC_8H_{17})_2\text{-}2,7)\}_2]\cdot 1.5TCNQ$ (11c). A solid mixture of (Bu_4N)**6c** (145 mg, 0.10 mmol) and TCNQ (42 mg, 0.21 mmol) was treated with dichloromethane (15 mL), and the resulting solution was stirred at room temperature for 16 h. A dark green precipitate gradually formed, which was filtered off, washed with a 4:1 mixture of dichloromethane/diethyl ether (5 mL), and vacuum-dried to give **11c**. Yield: 145 mg, 82%. Anal. Calcd for $C_{94}H_{122}AuN_7O_4S_4$: C, 64.91; H, 7.07; N, 5.64; S, 7.37. Found: C, 64.74; H, 7.12; N, 5.71; S, 7.16. Mp: 215°C. IR (Nujol, cm^{-1}): $\nu(C{\equiv}N)_{TCNQ}$, 2216; $\nu(C{=}CS_2)$, 1542; $\delta(C{-}H)_{TCNQ}$, 834; $\nu(Au{-}S)$, 370. ^1H NMR (400.9 MHz, CD_2Cl_2): δ 7.90 (d, $^4J_{HH}$ = 1.5 Hz, 4 H, H1, H8), 7.47 (d, $^3J_{HH}$ = 8.3 Hz, 4 H, H4, H5), 7.78 (dd, 4 H, H3, H6), 4.05 (t, $^3J_{HH}$ = 6.5 Hz, 8 H, OCH_2), 2.88 (m, 8 H, NCH_2 of Bu_4N^+), 1.81 (m, 8 H, OCH_2CH_2), 1.53−1.26 (m, 56 H, CH_2 of C_8H_{17} and Bu_4N^+), 0.93−0.87 (m, 24 H, Me of C_8H_{17} and Bu_4N^+).

Results and Discussion

Synthesis and Properties of Gold Complexes with (Fluoren-9-ylidene)methanedithiolato and Substituted Derivatives. Gold(I) and gold(III) complexes with the (fluoren-9-ylidene)methanedithiolato ligand and its 2,7-di-*tert*-butyl- and bis(octyloxy)-substituted derivatives were prepared by reacting the dithioates $(pipH)\{S_2CCH(C_{12}H_6R_2\text{-}2,7)\}$, where R = H (**1a**) or *t*-Bu (**1b**), or the dithioic acid $HS_2CCH(C_{12}H_6(OC_8H_{17})_2\text{-}2,7)$ (**2**) or its stable dithiol tautomer $(HS)_2C{=}C(C_{12}H_6(OC_8H_{17})_2\text{-}2,7)$ (**3**) (Chart 2) with chlorogold(I) or -gold(III) precursors in the presence of piperidine or diethylamine (Scheme 1). The formation of the complexes takes place through the displacement of the chloro ligands by the dithioates (when the dithioic acid **2** or the dithiol **3** are used, the dithioate is generated in situ upon reaction with the base) and the subsequent deprotonation of the C9 carbon atom of the 9-fluorenyl moiety by the base. Given that the piperidinium dithioates **1a**,**b** do not react with excess piperidine, it is clear that their deprotonation takes place only after their coordination to the metal center, which must increase the acidity of the H9 hydrogen atom. These reactions give piperidinium or diethylammonium chloride as the only byproduct, which can usually be separated by washing the crude products with methanol or ethanol.

Scheme 1



	Q	R		R	R'
$Q_2\cdot$**4a**	PPN^+ or Pr_4N^+	H	**5a**	H	Me
$Q_2\cdot$**4c**	Pr_4N^+	OC_8H_{17}	**5b**	H	Et
$Q\cdot$**6a**	PPN^+	H	**5c**	H	Ph
$Q\cdot$**6b**	PPN^+ or Bu_4N^+	*t*-Bu	**5d**	H	Cy
$Q\cdot$**6c**	Bu_4N^+	OC_8H_{17}	**5e**	*t*-Bu	Me
$Q\cdot$**8a**	PPN^+	H	**5f**	*t*-Bu	Et
$Q\cdot$**8b**	PPN^+ or Bu_4N^+	*t*-Bu	**5g**	*t*-Bu	Ph
			5h	*t*-Bu	Cy

The gold(I) compounds $Q_2[Au_2\{\mu\text{-}\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}_2]$, where $Q^+ = PPN^+$ or Pr_4N^+ for R = H (Q_2**4a**) or $Q^+ = Pr_4N^+$ for R = OC_8H_{17} [$(Pr_4N)_2$**4c**], were prepared in high yields by reacting the corresponding $Q[AuCl_2]$ salts with the dithioate **1a** and piperidine or the dithioic acid **2** and diethylamine in THF (Scheme 1). The dithiol **3** can also be used as ligand precursor for the preparation of $(Pr_4N)_2$**4c**. Complexes Q_2**4a**,**c** are slowly oxidized under atmospheric conditions in solution, giving the corresponding gold(III) complexes $Q[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}_2]$ (Q**6a**,**c**; see below) and unidentified species. The reaction of $PPN[AuCl_2]$ with **1b** and piperidine or diethylamine in THF gave an orange precipitate which, according to its ^1H NMR data, contained the desired dianionic complex $[Au_2\{\mu\text{-}\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6(t\text{-}Bu)_2\text{-}2,7)\}_2]^{2-}$ (**4b**) as a mixture of PPN^+ and piperidinium or diethylammonium salts that could not be separated by washing with methanol or ethanol. The oxidation of this product by atmospheric oxygen in chloroform or dichloromethane solutions is much faster than in the cases of Q_2**4a**,**c**, taking place within 1 h with formation of an unidentified orange-yellow precipitate and salts of the gold(III) complex $[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6(t\text{-}Bu)_2\text{-}2,7)\}_2]^-$ (**6b**; see below), which were identified by their ^1H NMR data. Although it was not possible to grow crystals of Q_2**4a**,**c**, we assume that they possess a dinuclear structure analogous to those of other gold(I) complexes containing *i*-mnt,[27] trithiocarbonato,[39] or dithiocarbimato[40] ligands. This structure is compatible with their ^1H and ^{13}C NMR spectra, which show only one set of signals for the dithiolato ligand.

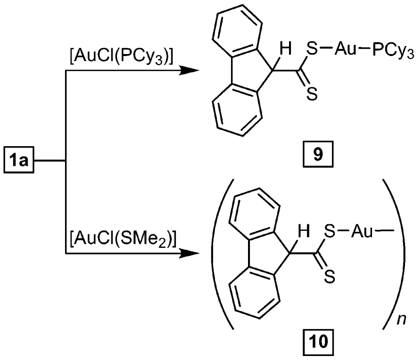
The neutral dinuclear phosphino complexes $[\{Au(PR'_3)\}_2\text{-}\{\mu\text{-}\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}_2]$ with R = H and R′ = Me (**5a**), Et (**5b**), Ph (**5c**), and Cy (**5d**) or R = *t*-Bu and R′ = Me (**5e**), Et (**5f**), Ph (**5g**), and Cy (**5h**) were obtained in moderate to high yields by reacting the corresponding $[AuCl(PR'_3)]$ precursors with the dithioates **1a** or **1b** and excess piperidine in THF. This series was prepared to obtain an insight into the influence of the nature of the dithiolato and phosphine ligands on their emission properties (see below). Complexes **5a**−**h** are stable, yellow solids. However, they slowly decompose in solution at room temperature to give complex mixtures. Like Q_2**4a**,**c**, in the presence of atmospheric oxygen they are slowly oxidized in solution, giving mixtures containing the gold(III) anionic complexes **6a** or **6b**, $[Au(PR'_3)_2]^+$, and other unidentified species.

The gold(III) complexes $Q[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}_2]$ with $Q^+ = PPN^+$ for R = H [(PPN)**6a**], $Q^+ = PPN^+$ or Bu_4N^+ for R = *t*-Bu (Q**6b**), and $Q^+ = Bu_4N^+$ for $R = OC_8H_{17}$ [(Bu_4N)**6c**] were obtained from the reactions of the corresponding $Q[AuCl_4]$ salts with the dithioates **1a**,**b** or the dithioic acid **2** in the presence of piperidine or diethylamine in THF. These compounds are remarkably stable, green solids.

The reactions of Q**6a**−**c** with excess triflic acid (HO_3SCF_3, HOTf) in dichloromethane resulted in the protonation of one of the dithiolato ligands at the C9 carbon atom of the 9-fluorenylidene moiety and the formation of the neutral compounds $[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}\{\kappa^2\text{-}S,S\text{-}S_2CCH(C_{12}H_6R_2\text{-}2,7)\}]$ [R = H (**7a**), *t*-Bu (**7b**), OC_8H_{17} (**7c**)], which precipitated as dark red solids and were isolated in almost quantitative yields. Complexes **7a**−**c** are easily deprotonated when exposed to weak bases. Thus, they slowly dissolve in deuterated dimethyl sulfoxide or acetone to give green solutions which, according to their ^1H NMR data, contain the corresponding parent anionic complexes **6a**−**c**. The deprotonation may be caused by small amounts of water that are usually present in the solvent or by the solvent itself.

The reaction of (Bu_4N)**6b** with 1 equiv of $PhICl_2$ resulted in the oxidation of one of the dithiolato ligands and the formation of the dichloro complex $Bu_4N[AuCl_2\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6(t\text{-}Bu)_2\text{-}2,7)\}]$ [(Bu_4N)**8b**], which was isolated in high yield as a pale green solid.[41] Attempts to prepare the salts $PPN[AuCl_2\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_8)\}]$ [(PPN)**8a**] and (PPN)-**8b** by following the same procedure gave oily materials which, according to their ^1H NMR data, contained the desired products but could not be purified. We have previously reported the halogen oxidations of $[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(COMe)_2\}_2]^-$ [32] and $[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}S\}_2]^-$,[37] which afforded analogous results.

Scheme 2



Gold Complexes with 9*H*-Fluorene-9-carbodithioato. Gold(I) complexes containing the 9*H*-fluorene-9-carbodithioato ligand have been prepared by reacting **1a** with chlorogold(I) precursors in absence of base. The reaction of $[AuCl(PCy_3)]$ with 1 equiv of **1a** in dichloromethane resulted in the displacement of the chloro ligand by the dithioate and the formation of $[Au\{SC(S)CH(C_{12}H_8)\}(PCy_3)]$ (**9**) (Scheme 2), which was isolated in high yield. Attempts to prepare analogous complexes with PMe_3 or PPh_3 gave mixtures containing the desired compounds, along with the deprotonated complexes **5a** or **5c** and unidentified species. Crystals of **9** suitable for X-ray diffraction studies could not be obtained, but we assume that the dithioato coordinates to gold through only one of its sulfur atoms. Previously described mononuclear gold(I) complexes with dithioato ligands display a linear coordination around the gold atom.[42,43] The NMR and IR data of **9** (see below) are consistent with this structure.

Compound **1a** also reacted with 1 equiv of $[AuCl(SMe_2)]$ in dichloromethane to give a red precipitate, whose elemental analysis is consistent with the formulation $[Au_n\{S_2CCH(C_{12}H_8)\}_n]$ (**10**). Due to its very low solubility in all common solvents, crystals of **10** suitable for X-ray diffraction studies could not be obtained. Its ^1H NMR spectrum in $(CD_3)_2SO$ shows very complex signals in the aromatic region, suggesting a polymeric structure. Previously described gold(I) dithioates have been found to possess oligomeric structures, like $[Au_6(S_2CC_6H_4Me\text{-}2)_6]$[44] and $[Au_4(S_2CMe)_4]$,[45] or assumed to be polymeric, like $[Au_n(S_2CC_6H_4Me\text{-}4)_n]$.[43]

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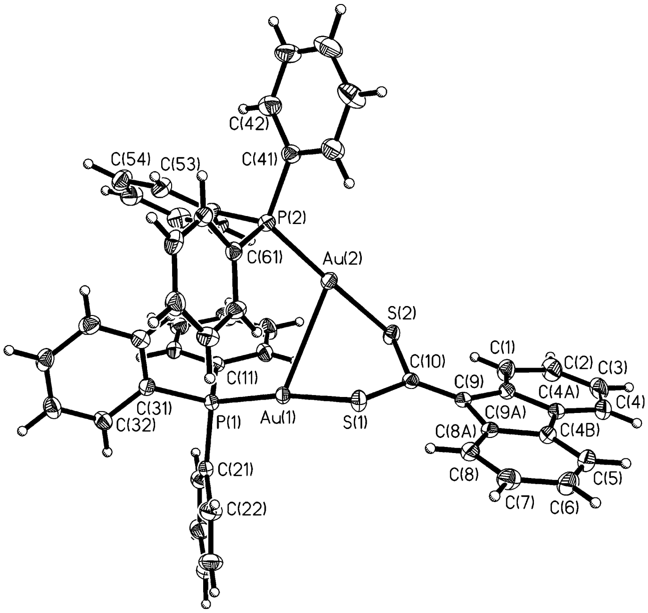

Figure 1. Structure of complex **5c**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **5c**·THF, **5e**·$^2/_3$CH$_2$Cl$_2$, and **5g**·CH$_2$Cl$_2$

	5c	**5e**	**5g**
Au(1)−P(1)	2.2600(5)	2.2544(10), 2.2533(10), 2.2611(10)	2.2517(8)
Au(1)−S(1)	2.3330(5)	2.3258(9), 2.3143(9), 2.3244(9)	2.3118(8)
Au(1)−Au(2)	3.05910(18)	2.9994(2), 2.9714(2), 2.9828(3)	3.0738(3)
Au(2)−P(2)	2.2713(6)	2.2650(9), 2.2533(12), 2.2463(10)	2.2561(8)
Au(2)−S(2)	2.3390(5)	2.3250(9), 2.3277(10), 2.3101(9)	2.3180(8)
S(1)−C(10)	1.762(2)	1.775(4), 1.780(4), 1.756(4)	1.775(3)
S(2)−C(10)	1.772(2)	1.763(4), 1.760(4), 1.760(4)	1.775(3)
C(9)−C(10)	1.371(3)	1.367(5), 1.366(5), 1.380(5)	1.362(4)
P(1)−Au(1)−S(1)	171.95(2)	175.57(4), 175.26(4), 175.22(4)	171.34(3)
P(2)−Au(2)−S(2)	177.23(2)	167.46(4), 175.23(4), 167.95(4)	172.44(3)
C(10)−S(1)−Au(1)	101.42(7)	100.57(12), 102.71(12), 102.72(12)	101.69(10)
C(10)−S(2)−Au(2)	100.85(7)	107.15(12), 104.07(13), 106.81(12)	100.27(10)
S(1)−C(10)−S(2)	116.37(11)	116.78(19), 117.7(2), 118.0(2)	116.31(16)

Crystal Structures of Complexes. The crystal structures of **5c**·THF, **5e**·$^2/_3$CH$_2$Cl$_2$, and **5g**·CH$_2$Cl$_2$ were solved by X-ray diffraction studies and show very similar structural arrangements for the dinuclear complexes. Compound **5e** crystallizes with three independent molecules of the complex and two dichloromethane molecules in the asymmetric unit, while in the other cases the asymmetric unit contains one molecule of the complex and one of the solvent. The molecular structure of **5c** is shown in Figure 1. Selected bond distances and angles for the three compounds are listed in Table 2. The fluoren-9-ylidene fragment is practically planar (mean deviations of C1−C9A: 0.032; 0.071, 0.078, 0.021; 0.015 Å, with C10 lying 0.19; 0.40, 0.55, 0.26; 0.14 Å out of the plane) and slightly rotated (by 15; 14, 19, 16; 7°) with respect to the CS$_2$ plane. The coordination around the gold atoms is essentially linear, but in some cases the deviation of the P−Au−S angles (range 167.46−177.23°) from the ideal value of 180° is significant. The P−Au−S axes lie out of the CS$_2$ plane and are considerably twisted with respect to each other [the torsion angles S(1)−Au(1)−Au(2)−S(2) and P(1)−Au(1)−Au(2)−P(2) fall in the ranges 57.8−67.6 and 58.0−77.0°, respectively]. This arrangement seems to help the formation of the Au···Au short contact in all cases, because it allows the approach of the gold atoms while keeping the phosphine ligands as far as possible from each other. The trimethylphosphine complex **5e** displays a slightly shorter Au···Au contact [2.9994(2), 2.9714(2), 2.9828(3) Å] than the triphenylphosphine analogues [3.05910(18) Å for **5c**, 3.0738(3) Å for **5g**]. The complex [{Au(PPh$_3$)}$_2$(μ-κ^2-*i*-mnt)] has a similar structure,[46] but the Au···Au contact is appreciably longer [3.156(1) Å]. The C(9)−C(10) bond distances in **5c**,**e**,**g** [range 1.362(4)−1.380(5) Å] are close to the higher limit of the range found for C(sp^2)=C(sp^2) double bonds (1.294−1.392 Å)[47] and very similar to or slightly shorter than the C=C bond distances found for the *i*-mnt ligand in its gold(I) complexes [range 1.37(1)−1.401(19) Å].[23,24,27,28,46]

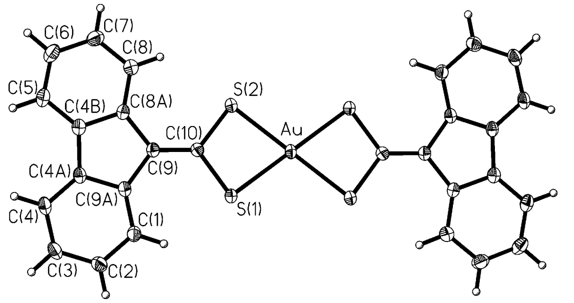

Figure 2. Structure of the anion of complex (PPN)**6a**.

Table 3. Selected Bond Distances (Å) and Angles (deg) for (PPN)**6a**·2Me$_2$CO

Au−S(1)	2.3224(4)	S(1)−Au−S(2)	74.728(12)
Au−S(2)	2.3407(4)	S(1)−Au−S(2)$^{\#1}$	105.272(12)
S(1)−C(10)	1.7576(14)	C(10)−S(1)−Au	89.35(5)
S(2)−C(10)	1.7596(14)	C(10)−S(2)−Au	88.72(5)
C(9)−C(10)	1.3575(18)	S(1)−C(10)−S(2)	107.15(7)

The crystal structure of **5d** was solved as a dichloromethane monosolvate and refined, but the high *R* values and large residual electron density indicated twinning problems (optical examination of the crystals with polarized light generally indicated twinning, although the crystal that was measured seemed to be untwinned). For this reason we do not present the full structure. The intramolecular Au···Au distance was 3.167(1) Å.

The structure of complex (PPN)**6a** was solved as an acetone disolvate. Figure 2 shows the molecular structure of the anion. Selected bond distances and angles are listed in Table 3. The asymmetric unit contains half an [Au{κ^2-*S*,*S*-S$_2$C=C(C$_{12}$H$_8$)}$_2$]$^-$ anion, half a PPN$^+$ cation (both with inversion symmetry; this is quite rare for PPN$^+$, with only 30 of 999 PPN$^+$ cations in the Cambridge Crystallographic Database displaying P−N−P angles above 170°), and one acetone molecule. The anion is almost planar (mean deviation 0.066 Å). The gold atom is in a square-planar environment distorted by the small bite of the (fluoren-9-ylidene)-methanedithiolato ligand [S(1)−Au−S(2), 74.728(12)°; S(1)−

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Au−S(2)[#1], 105.272(12)°]. The C(9)−C(10) bond distance of 1.3575(18) Å is slightly shorter than those found in **5c**,**e**,**g** and similar to the C═C distances found in PPN[Au{κ^2-*S*,*S*-S_2C═C(COMe)$_2$}$_2$] [1.353(6) and 1.365(4) Å],[31] K[Cu{κ^2-*S*,*S*-S_2C═C(CO_2Et)$_2$}$_2$] [1.32(2) Å], and ($BzPh_3P$)$_2$[Ni{κ^2-*S*,*S*-S_2C═C(CO_2Et)$_2$}$_2$] [1.367(6) Å].[15]

NMR Spectra. The ^1H NMR spectra of the gold complexes with the (fluoren-9-ylidene)methanedithiolato ligand and its substituted derivatives show the signals corresponding to the aromatic protons of the ligands between δ 9.33 and 7.04, the most remarkable feature being that the resonances of the H1 and H8 protons are shifted downfield by 1.72−1.31 ppm for the gold(I) complexes Q_2**4a**,**c** and **5a**−**h** or 0.86−0.46 ppm for the gold(III) complexes Q**6a**−**c**, **7b**,**c**, and (Bu_4N)**8b**, with respect to the resonances observed for the corresponding dithioates **1a**,**b** or the dithioic acid **2**. This fact might be attributable to the magnetic anisotropy of the C(9)═CS_2 double bond, which produces a considerable deshielding of the H1 and H8 atoms situated at its nodal plane. The ^1H NMR spectrum of **7a** could not be measured due to its very low solubility in most common organic solvents; the analogous complexes **7b**,**c** are slightly more soluble, and their ^1H NMR spectra show two different sets of signals corresponding to one dithiolato and one dithioato ligand.

The $^{13}C\{^1H\}$ NMR spectra of Q_2**4a**,**c**, Q**6a**−**c**, and **8b** were measured at room temperature, while those of **5b**−**d**,**f**−**h** had to be measured at −10 or −15 °C because of their very low stability in solution. All of them show the resonance of the C9 atom within a very narrow range around δ 130, whereas the chemical shift of the *C*S_2 carbon atom undergoes significant variations, decreasing in the sequence Q_2**4a**,**c** (δ 177.3−175.5) > **5b**−**d**,**f**−**h** (δ 162.7−156.0) > Q**6a**−**c** (δ 157.6−153.9) > (Bu_4N)**8b** (δ 139.3). The *C*S_2 resonance is therefore markedly affected by the metal center(s), and its chemical shift decreases as the negative charge on the complex decreases or as the oxidation state of the metal center or its electron-accepting character increase.

The $^{13}C\{^1H\}$ NMR spectrum of the trimethylphosphine complex **5a** could not be measured because of its very limited solubility at low temperatures. In the case of **5e**, variable-temperature NMR experiments (^1H and $^{31}P\{^1H\}$) showed that this complex undergoes a fluxional process in solution, giving rise to multiple signals for the *t*-Bu groups (^1H NMR) or the phosphine ($^{31}P\{^1H\}$ NMR) between −30 and −10 °C. The existence of this process, whose nature could not be established, prevented an effective measurement of the $^{13}C\{^1H\}$ NMR spectrum of **5e**. The $^{13}C\{^1H\}$ NMR spectra of **7a**−**c** could not be measured due to their very low solubility.

The ^1H NMR spectrum of complex **9** shows that the resonances arising from the protons of the dithioato ligand are slightly shifted with respect to those found for the piperidinium salt **1a**, the main variation corresponding to the H9 resonance (δ 5.64 for **9** vs δ 5.85 for **1a**). The variations observed in the $^{13}C\{^1H\}$ NMR data for **9** relative to **1a** are also small, the most noticeable corresponding to the *C*S_2 resonance (δ 255.2 for **9** vs δ 263.3 for **1a**).

IR Spectra. The solid-state infrared spectra of the gold(I) complexes with the (fluoren-9-ylidene)methanedithiolato ligand and its substituted derivatives (Q_2**4a**,**c**, **5a**−**h**) show one or two bands between 1466 and 1486 cm^{-1} assignable to the ν(C═CS_2) mode.[20] For the gold(III) complexes, the wavenumbers of the corresponding bands fall in the range 1532−1572 cm^{-1} and increase in the sequence Q**6a**−**c** (1532−1538) < **7a**−**c** (1548−1570) < (Bu_4N)**8b** (1572 cm^{-1}). The observed variations in the energies of the ν(C═CS_2) bands can be connected to the strength of the π component of the C═CS_2 bond. Thus, the higher electron-accepting character of the gold(III) center must favor the contribution of the resonance form **A** of the dithiolato ligand (Chart 1) to a greater extent than do two gold(I) centers, resulting in higher energies for the ν(C═CS_2) band. In the series of gold(III) complexes, the variations are attributable to the different electron-donating character of the ligands coordinated to the metal center, which decreases in the sequence dithiolato > dithioato > chloro. Bands assignable to the ν(Au−S) mode can be observed only for the gold(III) complexes and lie in the range 364−384 cm^{-1}, which is typical for gold(III) compounds with a AuS_4 core.[32,37,48] The spectrum of the dichloro complex (Bu_4N)**8b** shows the expected ν(Au−Cl) bands at 318 and 302 cm^{-1}.

The infrared spectra of the dithioato complexes **9** and **10** show bands arising from ν(CS_2) modes;[43,45] in the case of the mononuclear complex **9** only one intense band is observed at 970 cm^{-1}, whereas the polymeric compound **10** gives bands at 1074, 1032, and 1004 cm^{-1}.

Electronic Absorption Spectra. The UV−visible absorption spectra of compounds **1**−**10** were measured in the range 200−700 nm in dichloromethane at 298 K (see Supporting Information for details). The spectra of the dithioates **1a**,**b** show the characteristic bands of the parent fluorenes slightly shifted and broadened, together with an intense band at 347 nm which most probably arises from n−π* transitions involving the CS_2 group; absorptions of related origin are observed as shoulders in the spectra of dithioic acid **2** (345 nm) and dithiol **3** (350 nm). Coordination of **1a** to gold(I) centers to give complexes **9** and **10** causes only slight variations in the absorption spectra, the most noticeable being the shift of the 347 nm band to 355 nm for **9** or 360 nm for **10**. The common features of the spectra of complexes **4**−**8** can be ascribed to the fluoren-9-ylidene moiety: an intense absorption at 230 nm is typical of aromatic rings (extinction coefficients are higher for compounds containing PPh_3 or PPN^+),[49] while the intense absorption around 250 nm and the less intense peak at ca. 300 nm (complexes **7a**−**c** show an absorption at 268 nm instead of the 300 nm peak) are related to the bands observed at 260−280 and 290−300 nm, respectively, for the underivatized fluorenes. In addition to these bands, the spectra of Q_2**4a**,**c** and **5a**−**h** show one band at ca. 450 or 415 nm, respectively. The lowest energy band in all gold(I) complexes can be assigned to dithiolate-to-gold charge-transfer transitions.[50,51] The energy of this band decreases in the sequence **9** ∼ **10** > **5a**−**h** > Q_2**4a**,**c**, as the

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Table 4. Excitation and Emission Data (nm) at 77 K for Compounds **1**, **4a**,**c**, **5a**−**h**, **9**, and **10**

compd	solid		CH_2Cl_2 glass	
	λ_{exc}[a]	λ_{emis}	λ_{exc}[a]	λ_{emis}
1	343, *399*, 438, 457	485 sh, 520	343, *358*, 395, 445 sh	526
(PPN)$_2$**4a**	340, 400, 412, 456, 469, *479*	664	357, 391, 402, 417, *469*	643
(Pr$_4$N)$_2$**4a**	342, 413, 457, 470, *479*	668	343, 404, 418, 443, *476*	648
(Pr$_4$N)$_2$**4c**	472, *479*, 503	666	323, 358, 400, 419, *459*, *467*	643
5a	342, *396*, 441	651	353, 417, *455*	546, 650 sh
5b	340, 395, 412, *442*	531	343, 389, 406, 411, *440*	514
5c	344, *391*, 411, 434	508	338, 411, *438*	502
5d	337, 413, *443*	512	337, 404, *438*	504
5e	383, 403, *435*	509	340, 418, *452*	530
5f	341, 397, 414, *440*	530	343, 400, 414, *435*	505
5g	343, *355*, 390, 412	564, 613	411, *441*	531
5h	344, 412, *442*	539	344, 411, *441*	513
9	284, 293, *306*, 336, 342, 358, 363	425 sh, 447	282, 291, *343*	436
10	343, 356, 393, 456, 469, *479*, 501, 564	684	342, 388, *470*, 569	640, 675 sh

[a] Excitation spectra are complex and broad: range 300−460 nm for **3**; 300−500 nm for **4a,c**; 300−450 nm for **5a**−**h**; 280−370 nm for **9**; 300−590 nm for **10**. The most intense peak is italicized.

negative charge of the ligand or the complex increases. In the spectra of the gold(III) compounds, bands above 300 nm are observed at ca. 340, 395, and 410 nm for Q**6a-c**, 360, 410, and 512−534 nm for **7a**−**c**, and 360 and 410 nm for (Bu$_4$N)**8b** and most probably arise from charge-transfer transitions between the dithiolato ligand and the metal center, although the very broad and low intensity band at 512−534 nm observed for complexes **7a**−**c** could correspond to a d−d transition.[22,52]

Luminescence Studies. Gold(I) complexes with a variety of S-donor ligands, including thiolates,[50,53−56] dithiocarbamates,[5,28,56,57] xanthates,[58,59] *O*-alkyldithiophosphonates[60,61] and *O*,*O*′-dialkyldithiophosphates,[62] have been found to be luminescent. However, the only (1,1-dithiolato)gold complexes for which luminescence studies have been carried out are those containing the *i*-mnt ligand.[24,25,28,49] In mononuclear and dinuclear gold(I) complexes containing both thiolate and phosphine ligands, the origin of the emission has been ascribed to a ligand-to-metal charge-transfer triplet state (LMCT, $RS^- \rightarrow Au$).[50,53,63] Lower emission energies are observed when the thiolate contains electron-donating substituents and also when short Au···Au contacts are present. In the latter case, the excited state is better described as a ligand-to-metal−metal charge transfer (LMMCT).[55] Similarly, the luminescence of $[(AuPPh_3)_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})]$[25] and $[Au(PEt_3)_2][Au(AuPEt_3)_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})_2]$[24] has been assigned to a charge transfer from the dithiolate ligand to the metal centers, which has been confirmed by ab initio calculations on the model complex $[(AuPH_3)_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})]$.[64] For annular dinuclear compounds of the type $[Au_2(\text{diphosphine})(\mu\text{-}\kappa^2\text{-}i\text{-mnt})]$ both MC (metal centered) and LMCT transitions have been proposed as responsible for the emission.[28] In the case of the dianionic complex $[Au_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})_2]^{2-}$, the emission has been assigned to intraligand and ligand-to-metal charge-transfer transitions;[60,61] a similar assignment has been made on the basis of ab initio calculations.[65]

All the gold(I) complexes described in this paper are luminescent at 77 K, and their excitation and emission spectra have been measured both in the solid state and in CH_2Cl_2 glass. Additionally, room-temperature luminescence in the solid state can be clearly observed for the CH_2Cl_2 and THF solvates of **5g**, while (PPN)$_2$**4a**, (Pr$_4$N)$_2$**4a**, and **10** emit very weakly and the rest of gold(I) complexes do not emit. None of the compounds emits in solution at 298 K. The results of the measurements at 77 and 298 K are summarized in Tables 4 and 5, respectively, and representative excitation and emission spectra are shown in Figures 3 and 4.

Table 5. Solid-State Excitation and Emission Data (nm) for **1**, **5g**, **4a**, and **10** at 298 K

compd	λ_{exc}[a]	λ_{emis}
1	*339*, 402, 416, 445, 456	529
5g	*334*, 389, 433	575, 619
(PPN)$_2$**4a**		612
(Pr$_4$N)$_2$**4a**		610
10		642

[a] The most intense peak is italicized. The excitation spectra of **4a** and **10** could not be effectively measured because of the very low intensity of their emissions; the wavelengths of the excitation maxima at 77 K were used to measure their emission spectra.

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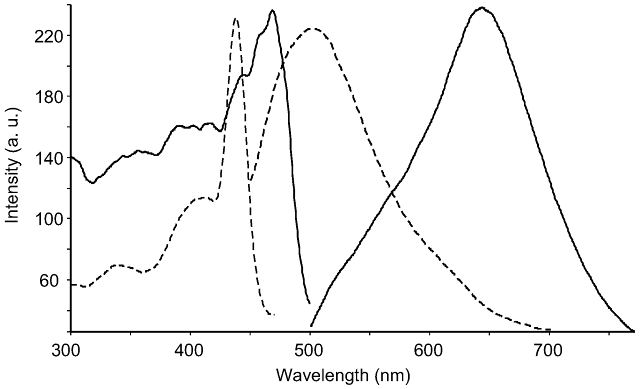

Figure 3. Excitation and emission spectra of complexes (PPN)**4a** (—) and **5c** (---) in CH_2Cl_2 glass at 77 K. Intensity in arbitrary units.

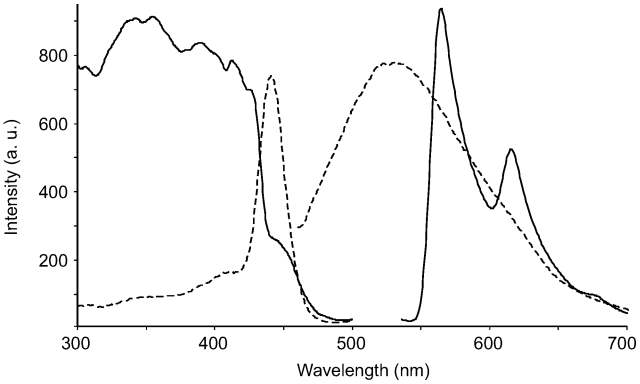

Figure 4. Excitation and emission spectra of complex **5g** in the solid state (—) and in CH_2Cl_2 glass (---) at 77 K. Intensity in arbitrary units.

The dianionic complexes Q_2**4a**,**c** emit around 665 nm in the solid state and 645 nm in CH_2Cl_2 glass at 77 K. At room temperature, the emission of Q_2**4a** in the solid state is blue-shifted to 610 nm. The neutral complexes **5a**−**h** generally emit at considerably higher energies, and their emission maxima fall in the range 502−546 nm, with the remarkable exceptions of the solid-state emissions of **5a** (651 nm) and **5g** (564, 613 nm) at 77 K, which are discussed below. The corresponding excitation spectra are broad and complex, but in most cases they show one absolute maximum which relates to the charge-transfer bands observed in the UV−visible absorption spectra (475 nm for Q_2**4a**,**c** and 440−455 nm for **5a**−**h** in CH_2Cl_2 glass).

A typical LMMCT transition could explain the luminescence of the dinuclear complexes Q_2**4a**,**c** and **5a**−**h**, as is the case of the related *i*-mnt complexes and some dinuclear gold(I) compounds with other dithio ligands.[59,61] The dramatic red-shift of the emission maximum of the dianionic compounds Q_2**4a**,**c** with respect to those of the neutral complexes **5a**−**h** (up to 4488 cm^{-1} in CH_2Cl_2 glass) is attributable to both the anionic character and the considerably stronger Au···Au interaction of the first. In fact, the Au···Au distances found in dianionic dinuclear complexes with an annular structure fall in the narrow range 2.800−2.811 Å,[27,39,40] while the distances found for **5c**−**e**,**g** (see above) are appreciably longer. The considerable blue-shift observed in the emission maximum of Q_2**4a** at 298 K with respect to the 77 K emission in the solid state (1280 cm^{-1}) is probably due to an increase in the Au···Au separation as a result of thermal expansion, suggesting a significant influence of the Au···Au contact on the energy of the emission. A similar effect has been reported by Fackler and co-workers to occur in dinuclear gold(I) dithiophosphonate complexes[61] and by Fackler, Schmidbaur, and co-workers in [AuCl(TPA)] and [AuCl(TPA-HCl)] (TPA = 1,3,5-triaza-7-phosphaadamantane), which form dimers through Au···Au contacts.[66] The considerably lower emission energies of Q_2**4a**,**c** and **5a**−**h**, when compared with their *i*-mnt counterparts $(Bu_4N)_2[Au_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})_2]$ (495, 527 nm)[60,61] and $[(AuPPh_3)_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})]$ (462 nm),[24,25] can be ascribed to the expected stronger electron-donating character of the (fluoren-9-ylidene)methanedithiolato ligands relative to *i*-mnt. Contribution of intraligand transitions to the emission of complexes Q_2**4a**,**c** and **5a**−**h**, as is the situation with $[Au_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})_2]^{2-}$, cannot be completely ruled out. Salts of the (fluoren-9-ylidene)methanedithiolate ligand or its substituted derivatives could not be isolated, and therefore, their emission spectra are not available. The dithioates **1a**,**b** and the dithioic acid **2** do not emit at 77 K, but the dithiol **3** is luminescent at 77 K both in the solid state and in CH_2Cl_2 glass, with an emission maximum at 525 nm, most probably associated with the $C{=}CS_2$ moiety. However, the above-discussed observations and the fact that the gold(III) complexes here described are not luminescent indicate that the gold(I) centers have a crucial participation in the luminescence of Q_2**4a**,**c** and **5a**−**h**.

The variation of the substituents of the fluoren-9-ylidene moiety does not produce any changes in the emission of complexes **4a**,**c**, and in the series **5a**−**h** the changes are not regular, suggesting that these substituents have little or no influence over the luminescence. The variations due to the phosphine ligands along the series **5a**−**h** do not follow a regular trend either. Initially, we expected significant changes in the Au···Au intramolecular distances and, therefore, in the observed emission, depending on the size of the phosphine. However, the variations in the Au···Au distances are small and do not have any effect on the emission. The most striking differences found in the series **5a**−**h** are the emissions of **5a** (R = H, R′ = Me) and **5g** (R = *t*-Bu, R′ = Ph) in the solid state. Because these differences disappear in CH_2Cl_2 glass, it is clear that they are attributable to effects of the supramolecular structures. Unfortunately, we have not been able to grow crystals of **5a** suitable for X-ray diffraction studies, but the low energy of its solid-state emission (651 nm) might be due to the presence of *inter*molecular Au···Au contacts. Although the structures of **5c**,**e**,**g** do not display intermolecular Au···Au contacts, in the case of **5a** they might be favored due to the absence of substituents on the (fluoren-9-ylidene)methanedithiolato ligand. The solid-state excitation and emission spectra of **5g** (Figure 4) are unique in the series **5a**−**h**. In addition, **5g** is the only compound of this series which emits intensely at room temperature. The two maxima observed in its emission spectrum (564, 613 nm) are considerably red-shifted relative to the only maximum observed for **5b**−**f**,**h** in the solid state (range 508−539 nm),

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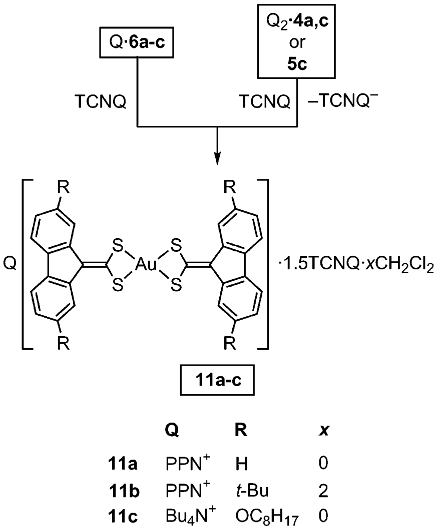
while the emission spectrum in CH_2Cl_2 glass is completely different and does not contain the peaks observed in the solid state. This means that the supramolecular order of **5g** strongly affects the LMMCT emitting state, leading to a substantially different emission spectrum. The crystal structure of **5g** (CH_2Cl_2 solvate) is similar to those of **5c**,**e**, but the crystal packings of the three structures are different: **5g** has a layer structure, with layers at $x = 0.25$ and 0.75; in the structure of **5e** the three independent molecules occupy the regions at $x = 0.5$, 0, and 0.25, respectively, while in **5c** the packing has no well-defined layers. The structure of the THF solvate of **5g** could not be refined satisfactorily because of solvent disorder, but this compound is isostructural with the CH_2Cl_2 solvate, consistent with their identical solid state emission spectra. Recently, several luminescent gold(I) complexes have been reported, which crystallize as different polymorphs with clearly distinct emission properties, thus revealing that the supramolecular order in the solid state can have a critical effect on the luminescence.[67]

The emission spectrum of the mononuclear dithioato complex **9** shows one maximum at 447 or 436 nm, respectively, in the solid state and in CH_2Cl_2 glass. Certain complexes of the type $[Au(SR)(PR'_3)]$ with no intermolecular Au···Au interactions display similar emission energies.[53] We assign the luminescence of **9** to a LMCT excited state, since an intraligand transition can be ruled out (the uncoordinated dithioate **1a** does not emit) and intermolecular Au···Au contacts are unlikely because of the presence of the bulky PCy_3 ligand. Also, the higher emission energy of **9** relative to the dinuclear PCy_3 complexes **5d**,**h** (504 and 513 nm, respectively, in CH_2Cl_2 glass) can be attributed to the absence of Au···Au contacts in **9** and the lower electron-donating character of the monoanionic dithioate as compared with the dianionic dithiolato ligand. In contrast, the polymeric derivative **10** displays the lowest emission energy of all compounds described in this work (684 nm in the solid state, 640 nm in CH_2Cl_2 glass at 77 K). As is the case with Q_2**4a**, the emission maximum of **10** is significantly blue-shifted at 298 K (956 cm^{-1}) with respect to the 77 K emission in the solid state. These observations are consistent with an emitting state strongly influenced by multiple Au···Au contacts, which are likely to exist in the structure of **10**. In fact, the structures of previously reported gold(I) dithioates show multiple Au···Au contacts.[44,45] Therefore, the emission of **10** most probably arises from LMMCT transitions, although MC transitions are also possible, since they are common in compounds with extended Au···Au interactions.[5,28,62]

Reactions with TCNQ. Crystal Structure of PPN[Au{κ^2-*S*,*S*-$S_2C{=}C(C_{12}H_6(t\text{-Bu})_2\text{-}2,7)$}]·1.5TCNQ·2CH$_2Cl_2$ (11b). Fluorene derivatives containing electron-withdrawing functional groups behave as acceptors[68] and have been used for the formation of charge-transfer complexes[69] and the synthesis of donor−π-acceptor molecules.[70] The (fluoren-9-ylidene)methanedithiolato ligand and the derivatives described in this work are not expected to function as electron acceptors, because they do not bear any electron-withdrawing substituents. On the contrary, the facile oxidations of the gold(I) complexes Q_2**4a**,**c** and **5a**−**h** under atmospheric conditions reveal the strongly donating character of our ligands, which could therefore behave as donors in the formation of charge-transfer π-adducts. To explore this possibility and to confirm the electron donating character of the coordinated ligands, we have carried out the reactions of the gold(III) complexes Q**6a**−**c** and (Bu_4N)**8b** and also the gold(I) complexes Q_2**4a**,**c** and **5c** with the widely used organic acceptor TCNQ (tetracyano-7,7,8,8-quinodimethane).

Scheme 3



	Q	R	x
11a	PPN^+	H	0
11b	PPN^+	*t*-Bu	2
11c	Bu_4N^+	OC_8H_{17}	0

The addition of TCNQ to dichloromethane solutions of the gold(III) complexes Q**6a**−**c** resulted in the formation of compounds with the general composition $Q[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6R_2\text{-}2,7)\}_2]\cdot 1.5TCNQ\cdot xCH_2Cl_2$ [$Q^+ = PPN^+$, R = H, $x = 0$ (**11a**); $Q^+ = PPN^+$, R = *t*-Bu, $x = 2$ (**11b**); $Q^+ = Bu_4N^+$, R = OC_8H_{17}, $x = 0$ (**11c**)] (Scheme 3). These formulations have been determined by means of elemental analyses and the crystal structure of **11b** (see below). The new compounds are sparingly soluble solids which precipitate from dichloromethane either spontaneously (**11c**) or by adding small amounts of diethyl ether (**11a**,**b**) and can be isolated in high yields. Their colors are dark blue (**11a**), black (**11b**), and dark green (**11c**), which are typical of charge-transfer complexes of TCNQ.

The crystal structure of **11b** was solved by X-ray diffraction studies. The asymmetric unit contains one $[Au\{\kappa^2\text{-}S,S\text{-}S_2C{=}C(C_{12}H_6(t\text{-Bu})_2\text{-}2,7)\}_2]^-$ (**6b**) anion, one PPN^+ cation,

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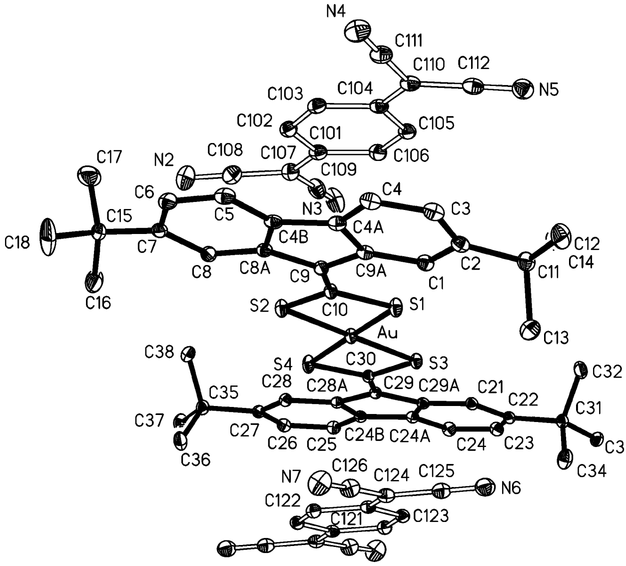

Figure 5. Structure of **11b** (H atoms, PPN cation, and solvent omitted for clarity). The half-TCNQ has been completed by inversion symmetry.

Table 6. Selected Bond Distances (Å) and Angles (deg) for **11b**

Anion **6b**			
Au−S(4)	2.3291(5)	S(2)−C(10)	1.7461(19)
Au−S(2)	2.3307(5)	S(3)−C(30)	1.7540(19)
Au−S(1)	2.3308(5)	S(4)−C(30)	1.7519(18)
Au−S(3)	2.3358(4)	C(9)−C(10)	1.361(2)
S(1)−C(10)	1.7652(18)	C(29)−C(30)	1.360(2)
S(4)−Au−S(2)	105.331(17)	C(10)−S(1)−Au	89.25(6)
S(4)−Au−S(1)	178.828(17)	C(10)−S(2)−Au	89.72(6)
S(2)−Au−S(1)	74.347(17)	C(30)−S(3)−Au	89.44(6)
S(4)−Au−S(3)	74.155(16)	C(30)−S(4)−Au	89.71(6)
S(2)−Au−S(3)	178.969(18)	S(2)−C(10)−S(1)	106.67(10)
S(1)−Au−S(3)	106.185(17)	S(4)−C(30)−S(3)	106.69(9)
TCNQ (General)			
C(101)−C(107)	1.369(3)	C(107)−C(108)	1.438(3)
C(101)−C(102)	1.442(3)	C(107)−C(109)	1.439(3)
C(101)−C(106)	1.444(3)	C(108)−N(2)	1.143(3)
C(102)−C(103)	1.342(3)	C(109)−N(3)	1.143(3)
C(103)−C(104)	1.442(3)	C(110)−C(112)	1.441(3)
C(104)−C(110)	1.368(3)	C(110)−C(111)	1.443(3)
C(104)−C(105)	1.448(3)	C(111)−N(4)	1.140(3)
C(105)−C(106)	1.342(3)	C(112)−N(5)	1.138(3)
C(102)−C(101)−C(106)	117.94(19)	N(3)−C(109)−C(107)	176.8(3)
C(103)−C(104)−C(105)	117.60(19)	C(112)−C(110)−C(111)	115.40(19)
C(108)−C(107)−C(109)	113.4(2)	N(4)−C(111)−C(110)	179.9(3)
N(2)−C(108)−C(107)	177.1(3)	N(5)−C(112)−C(110)	177.5(2)
TCNQ (Centrosymmetric)			
C(121)−C(124)	1.377(3)	C(124)−C(126)	1.430(3)
C(121)−C(122)	1.446(3)	C(124)−C(125)	1.437(3)
C(121)−C(123)	1.448(3)	C(125)−N(6)	1.145(3)
C(122)−C(123)$^{\#1}$	1.347(3)	C(126)−N(7)	1.146(3)
C(122)−C(121)−C(123)	117.83(17)	N(6)−C(125)−C(124)	177.2(2)
C(126)−C(124)−C(125)	115.49(18)	N(7)−C(126)−C(124)	178.9(3)

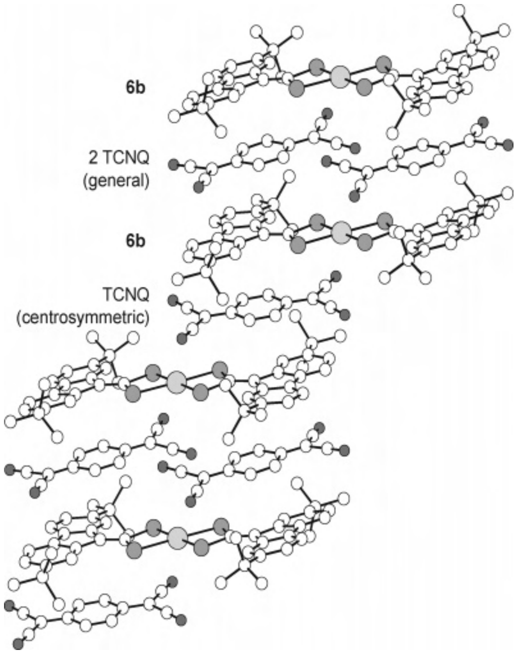

Figure 6. Anionic stack in the crystal structure of **11b**.

two CH_2Cl_2 molecules, one TCNQ molecule on a general position, and a further half TCNQ molecule, the second half of which is generated by inversion symmetry (Figure 5). Selected bond distances and angles are listed in Table 6. The anions and the TCNQ molecules form an infinite stack with the sequence ···TCNQ(centrosymmetric)·**6b**·2TCNQ(general)·**6b**···, with the stack direction perpendicular to (110) (Figure 6). The centers of the TCNQ molecules are located approximately above the chemically equivalent C9 and C29 atoms of the 2,7-di-*tert*-butylfluoren-9-ylidene groups; distances to the TCNQ planes are 3.38 and 3.34 Å and to the TCNQ ring centroids 3.46 and 3.45 Å. This arrangement indicates that a relatively high degree of negative charge is delocalized over the fluoren-9-ylidene groups. There are no significant interactions between the metal center and the CN groups, the shortest Au−N distances being 3.842 and 3.775 Å. The bond distances in the **6b** anion are very similar to those found for the analogous **6a** in its PPN salt, and in the TCNQ molecules they are only slightly different from those found for pure TCNQ,[71] indicating that these molecules are essentially neutral. Crystals of **11a**,**c** suitable for X-ray diffraction studies could not be obtained, but it is likely that they also comprise infinite anionic stacks. This arrangement could be responsible for the low solubilities observed: **11a**,**b** dissolve moderately in dichloromethane but **11c** only poorly, and none of them is soluble in chloroform or other common organic solvents.

Infrared spectra are frequently used for assigning the oxidation state and coordinative status of TCNQ in its compounds.[72,73] The most important bands of this organic acceptor correspond to the ν(C≡N), ν(C═C) (ν_{20}, b_{1u}), and δ(C−H) (ν_{50}, b_{3u}) modes, which appear at 2222, 1542, and 862 cm^{-1}, respectively, for neutral TCNQ (in our infrared spectrophotometer) and shift to lower frequencies as the degree of charge (ρ) increases. Linear dependences between the frequencies of the ν(C≡N), ν_{20}, and ν_{50} modes and ρ have been proposed.[74,75] However, in some cases deviations

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from linearity have been found for the dependence of the ν(C≡N) frequencies from ρ,[76] and some authors prefer to use the ν_{20} or ν_{50} modes to estimate the value of ρ.[75,77,78] The infrared spectra of **11a**−**c** show only one ν(C≡N) band at 2216 cm^{-1} in all cases. The ν(C═C) region is dominated by the intense and relatively broad ν(C═CS_2) band, which is shifted by ca. 10 cm^{-1} to lower frequencies for **11a**,**b** or 4 cm^{-1} to a higher frequency for **11c**, relative to the corresponding Q**6a**−**c** salts. The ν(C═C) band arising from TCNQ can be observed only for **11b** at 1544 cm^{-1} as a shoulder of the ν(C═CS_2) band, while for **11a**,**c** it must be obscured. The δ(C−H) band appears at 832 cm^{-1} for **11a** and 834 cm^{-1} for **11b**,**c**. These data reveal that the formation of the charge-transfer complexes produces only minor changes in the frequencies of the vibrational modes of both TCNQ and the gold(III) anion, with the exception of δ(C−H). The frequency of this band in **11a**−**c** is close to those found for salts of $TCNQ^-$ (820−825 cm^{-1}) and would correspond to a high ρ value. However, the frequencies of ν(C≡N) in **11a**−**c** and ν(C═C) in **11b** indicate a small degree of charge transfer, which is also consistent with the bond distances found for the TCNQ molecules of **11b**.

The ^{1}H NMR spectra of **11a**−**c** in CD_2Cl_2 show the resonances of the ligand protons slightly shifted with respect to those of the corresponding parent compounds Q**6a**−**c**, while the resonances of the TCNQ protons are not observed, which is indicative of a significant interaction between the **6a**−**c** anions and the TCNQ molecules in solution.[78,79] The electronic absorption spectra of diluted solutions of **11a**,**b** in dichloromethane (~10^{-5} M) show one band at 25 500 cm^{-1} which corresponds to neutral TCNQ[73] and partially overlaps other bands arising from the anions. One broad band at 9900 cm^{-1} is observable in the electronic spectrum of saturated solutions of **11a** in dichloromethane, which can be assigned to the intermolecular charge-transfer transition between the anion **6a** and the TCNQ molecules;[80] for **11b**, the maximum of this band falls below 9090 cm^{-1}, which is the lower limit of our spectrophotometer, while in the case of **11c** a highly concentrated solution could not be obtained because of its very low solubility in dichloromethane. The observation of these bands proves that the adducts **11a**,**b** are present in solution, probably as fragments of the stack observed in the structure of **11b**.

Unlike Q**6a**−**c**, the dichloro complex (Bu_4N)**8b** does not form an adduct with TCNQ under the conditions described above. It is reasonable that the fluoren-9-ylidene moiety in the anion **8b** has a lesser electron-donating character than in **6a**−**c** because of the chloro ligands, which make the unit $AuCl_2^+$ a stronger electron acceptor than Au{κ^2-*S*,*S*-S_2C═C($C_{12}H_6$(*t*-Bu)$_2$-2,7)}$^+$. This is consistent with the high energy of the ν(C═CS_2) band observed in the infrared spectrum of (Bu_4N)**8b** (see above), which indicates that the π component of the C═CS_2 bond is relatively strong and therefore the degree of negative charge delocalized over the fluoren-9-ylidene group must be low.

Attempts to obtain charge-transfer adducts of the gold(I) complexes **4a**,**c** and **5c** with TCNQ resulted in their oxidation to the corresponding gold(III) species **6a** or **6c** and the formation of salts of **6a**,**c**·1.5TCNQ. Thus, the reaction of (PPN)$_2$**4a** with TCNQ (1:4 molar ratio) gave **11a** and PPN-(TCNQ)$_2$, which were identified by their IR spectra and elemental analyses; an insoluble precipitate, probably containing a gold(I) species, was also obtained, but its nature could not be established. (Pr_4N)$_2$**4c** reacted with TCNQ (1:2) to give a scarcely soluble precipitate, which, in agreement with its IR spectrum, contains both (Pr_4N)**6c**·1.5TCNQ, neutral TCNQ, and a salt of $TCNQ^-$; its elemental analysis is consistent with the formulation (Pr_4N)$_2$**6c**·3.5TCNQ·0.33CH_2Cl_2. The neutral phosphino complex **5c** also reacted with excess TCNQ (1:4) to give a mixture, which, according to its IR spectrum, contained a salt of the charge-transfer adduct **6a**·1.5TCNQ and both neutral and anionic TCNQ; the rest of the products of this reaction could not be identified. Only a few examples of reactions of gold(I) complexes with organic acceptors have been reported to produce oxidation of the metal centers. The dinuclear ylide complex [Au_2{μ-κ^2-(CH_2)$_2PPh_2$}$_2$] reacted with TCNQ or DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) to give compounds in which the gold atoms are in fractional oxidation states higher than +1.[81] Trimers of the type [Au_3{μ-κ^2-*C*,*N*-RN═COR′}$_3$] and related complexes form charge-transfer adducts with TCNQ and other organic acceptors in which relatively short Au···Au distances indicate a partial oxidation of the metal centers.[69,82]

Molar Conductivities. The molar conductivities of the ionic compounds Q_2**4a**,**c**, Q**6a**−**c**, and (Bu_4N)**8b** have been measured in acetone at concentrations of ca. 5 × 10^{-4} M. The conductivity of (PPN)$_2$**4a** (199 Ω^{-1} cm^2 mol^{-1}) corresponds to a 2:1 electrolyte according to the range given by Geary[83] (160−200 Ω^{-1} cm^2 mol^{-1}). However, the Pr_4N^+ salts of **4a**,**c** give very low conductivity values (137 and 98 Ω^{-1} cm^2 mol^{-1}, respectively), probably because of the formation of ion pairs. The values obtained for the Q**6a**−**c** and (Bu_4N)-**8b** salts (between 70 and 101 Ω^{-1} cm^2 mol^{-1}) fall in most cases below the lower limit of the range given for 1:1 electrolytes (100−140 Ω^{-1} cm^2 mol^{-1}).

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Conclusions

The dithioates **1a**,**b** and the dithioic acid **2** (or its dithiol tautomer **3**) have been used as ligand precursors for the high-yield preparations of the first complexes with (fluoren-9-ylidene)methanedithiolate and its 2,7-di-*tert*-butyl- and 2,7-bis(octyloxy)-substituted analogues. The reactivity and properties of the gold complexes here described reveal the stronger electron-donating character of the new ligands as compared with previously described 1,1-ethylenedithiolates. A variable degree of negative charge is delocalized over the fluoren-9-ylidene groups, which depends on the electron-accepting character of the metal center(s). The gold(I) complexes **4a**−**c** and **5a**−**h** are readily oxidized under atmospheric conditions or through their reactions with the organic acceptor TCNQ to the corresponding gold(III) complexes **6a**−**c**, which in turn form anionic charge-transfer adducts with the stoichiometry **6a**−**c**·1.5TCNQ. The structure of (PPN)**6b**·1.5TCNQ·2CH_2Cl_2 (**11b**) shows infinite anionic stacks in which the TCNQ molecules are located above and below the fluoren-9-ylidene groups of the **6b** anions, thus revealing the ability of the coordinated ligands to act as donors in the formation of charge-transfer adducts.

The gold(I) complexes here described are photoluminescent at 77 K, and their emissions can be assigned to LMMCT (Q_2**4a**,**c**, **5a**−**h**, **10**) or LMCT (**9**) excited states. The low energies of the emission maxima relative to those of analogous *i*-mnt complexes can be attributed to the strongly electron-donating character of the new ligands.

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Supporting Information Available: UV−visible absorption data for complexes **1**−**10** and crystallographic data in CIF format for complexes **5c**·THF, **5e**·$^2/_3$$CH_2Cl_2$, **5g**·$CH_2Cl_2$, (PPN)**6a**·2$Me_2CO$, and **11b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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