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# Tetranuclear (Phosphane)(thiolato)gold(I) Complexes: Synthesis, Characterization and Photoluminescent Properties

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*Dedicated to Professor Vicente Gotor on the occasion of his 60th birthday*

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The reactions of the tetraphosphane donor ligand $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$ with the gold precursors [AuCl(tht)] or $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) leads to complexes $[Au_4R_4\{(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2\}]$ [R = Cl (**1**) or $C_6F_5$ (**2**)]. Further substitution of the chlorine atoms in **1** by the corresponding 4-substituted benzenethiolates gives rise to the tetranuclear (phosphane)(thiolato)gold(I) complexes $[Au_4(S\text{-}C_6H_4\text{-}X)_4\{(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2\}]$ [X = F (**3**), MeO (**4**), Me (**5**) and $NO_2$ (**6**)]. Complexes **2** and **4** were characterized by X-ray diffraction studies showing Au···Au interactions in the case of complex **4**. Complexes **3**–**6** display intense emissions in the solid state at 77 K with lifetimes in the microsecond range. The observed phosphorescent emissions are attributed to metal-to-ligand charge-transfer transitions. Nevertheless, the influence in the emission energies of gold–gold interactions or the contribution of the substituent in the 4-position of the benzenethiolate ring to the excited state cannot be neglected.

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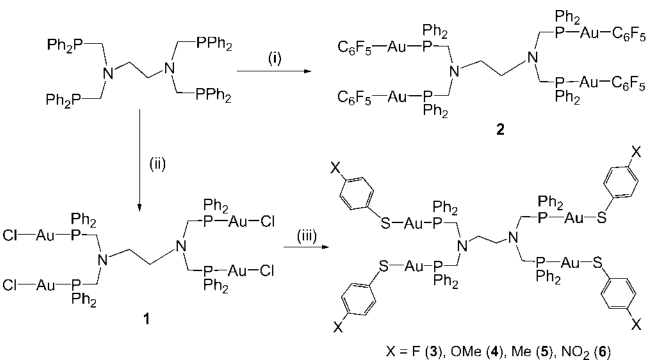
## Introduction

Polynuclear gold(I) complexes have attracted much interest in the last years mainly due to their intriguing structural dispositions, their rich photoluminescent properties[1] or even their potential applications in different fields as pharmaceutics, optical sensors, chemosensing, etc. In this sense, much of the interest has been generated by the clinical use of the mononuclear (phosphane)(thiolato)gold complex Auranofin,[2] employed in the treatment of reumathoid arthritis. Also, these types of complexes can be used as optical sensors for volatile organic compounds (VOCs) as shown by Eisenberg and coworkers[3] or as specific sensors for several cations as reported by Yam et al.[4]

(Thiolato)gold(I) complexes containing multidentate phosphane ligands can be considered an important class of polynuclear compounds, as the presence of several P–Au–S structural units in their structures permits the formation of aurophilic interactions. These interactions, which are comparable in strength with hydrogen bonding, are recognized as a structural motif that governs the amazing molecular and supramolecular arrangements found in the solid state for many types of gold(I) compounds.[5] Moreover, several (phosphane)(thiolato)gold(I) compounds also display very interesting photoluminescent properties over a wide range of the visible spectrum (400–700 nm), and the observed emissions are usually attributed to ligand-to-metal charge-transfer (LMCT) excited states that can be perturbed by the presence of the above-mentioned $Au^I\cdots Au^I$ interactions.[6]

In spite of several literature reports[7] on the synthesis of (phosphane)(thiolato)gold(I) complexes, the quest for high nuclearity compounds is often pursued through the use of



Scheme 1. Synthesis of complexes **1**–**6**. (i) $[Au(C_6F_5)(tht)]$; (ii) [AuCl(tht)]; (iii) NaOMe, $SH–C_6H_4–X$ (X = F, OMe, Me or $NO_2$).

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bi- or tridentate phosphorus donor ligands. We focused a part of our outgoing research on the synthesis of high nuclearity gold(I) complexes through the reaction of the appropriate gold(I) precursors with the tetradentate P donor ligand $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$[8] that permits the synthesis of tetranuclear (phosphane)(thiolato)gold(I) compounds (Scheme 1).

In this paper we report the synthesis of tetranuclear (phosphane)(thiolato)gold(I) compounds that are brightly luminescent in the solid state at 77 K. We analyzed the mechanism responsible for the luminescence in this type of complex by taking into account the presence of intramolecular aurophilic interactions or the electronic influence of the substituent in the 4-position of the benzenethiolato ligands bonded to gold.

## Results and Discussion

### Synthesis and Characterization

The tetranuclear gold(I) compounds $[Au_4R_4\{(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2\}]$ [R = Cl (**1**) or $C_6F_5$ (**2**)] were prepared by the reaction of 4 equiv. of the corresponding [AuCl(tht)] or $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) precursors and 1 equiv. of the tetradentate phosphane ligand $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$ (Scheme 1) in quantitative yields by displacement of the labile tht ligand as crystalline white solids. All analytical and spectroscopic data are in agreement with the proposed stoichiometries. Their $^{31}P\{^1H\}$ NMR spectra display a singlet at 17.7 (**1**) or 24.7 ppm (**2**), which shows a large shift downfield upon coordination of the four Cl–Au or $C_6F_5$–Au units to the tetraphosphane ligand (–28.5 ppm). The $^{19}F$ NMR spectrum of complex **2** shows the expected pattern of the $C_6F_5$ groups bonded to $Au^I$ with three signals at –115.4, –157.7 and –161.8 ppm, which correspond to the fluorine atoms in the *ortho*, *para* and *meta* positions, respectively. Both complexes show the corresponding signals of the different methylene groups that are present in the phosphane ligand in their $^1H$ NMR spectra, and they are also shifted downfield relative to those of the free ligand. Their IR spectra show absorptions arising from the Au–Cl or Au–$C_6F_5$ groups that appear at 326 or at 1504, 954 and 792 $cm^{-1}$.

The reaction of complex **1** with different 4-substituted benzenethiols affords the corresponding compounds $[Au_4(S{-}C_6H_4{-}X)_4\{(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2\}]$ [X = F (**3**), MeO (**4**), Me (**5**) and $NO_2$ (**6**)] as stable crystalline solids. The thiolato ligands are prepared in situ by the reaction of the benzenethiols with an excess amount of sodium methoxide. The analytical and spectroscopic properties are in accordance with the proposed formulations. Their $^{31}P\{^1H\}$ NMR spectra show very similar shifts for the corresponding singlets as a result of the similar chemical and magnetic environments around the P atoms at 23.5, 23.4, 23.5 and 23.5 ppm for complexes **3**–**6**, respectively. In all cases, their IR spectra display the characteristic absorptions due to $\nu$(C–S) at 1103, 857 (for **3**), 1101, 867 (for **4**), 1101, 867 (for **5**) and 1103, 857 $cm^{-1}$(for **6**).

### X-ray Structural Determination of Derivatives 2 and 4

Single crystals suitable for X-ray diffraction studies were obtained by layering diethyl ether or hexane into a solution of the complex in dichloromethane (for **2**) or toluene (for **4**). Both **2** and **4** crystallize in the $P\bar{1}$ space group of the triclinic system with one molecule of the complex and one half of a molecule of diethyl ether (for **2**) or one molecule of toluene (for **4**) in the unit cell. Both structures consists of tetranuclear molecules in which each phosphorus atom of the tetradentate phosphane binds a (pentafluorophenyl)gold(I) unit or a (thiolato)gold(I) unit for **2** and **4**, respectively (Figures 1 and 2), with Au–P distances of 2.2725(14) and 2.2799(14) Å for **2** and 2.260(2) and 2.267(2) Å for **4**, which compare well to those found in other related (pentafluorophenyl)-[9] or (benzenethiolato)(phosphane)gold(I)[6a,10,12] complexes. The gold(I) centres complete their usual lineal environment with the coordination of a carbon atom of the anionic ligand $C_6F_5$ or a sulfur atom of $S{-}C_6H_4{-}OMe$ for **2** or **4**, respectively. The Au–C bonds

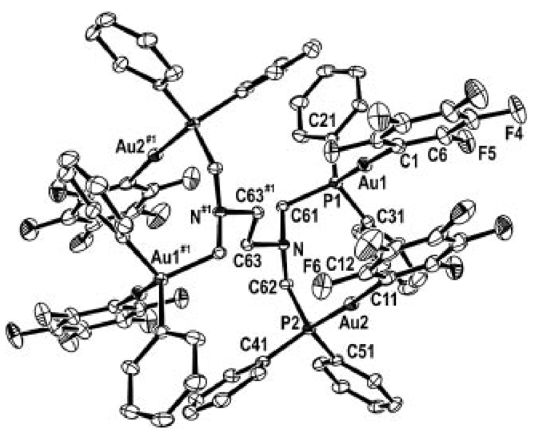

Figure 1. Molecular structure of complex **2**. Selected bond lengths [Å] and angles [°]: Au1–C1 2.049(6), Au2–C11 2.051(6), Au1–P1 2.2725(14), Au2–P2 2.2799(14), C1–Au1–P1 174.74(15), C11–Au2–P2 175.81(16).

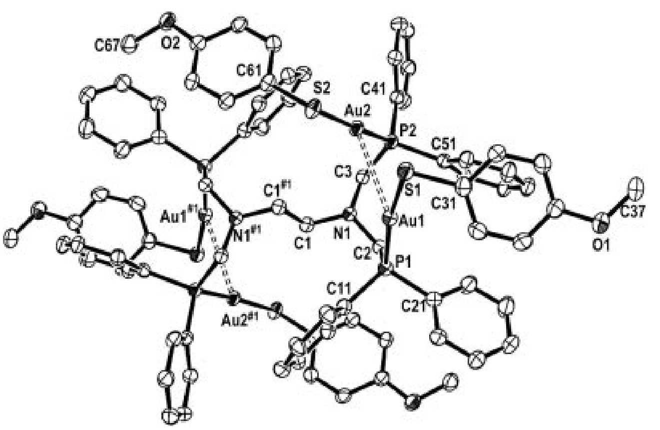

Figure 2. Molecular structure of complex **4**. Selected bond lengths [Å] and angles [°]: Au1–S1 2.318(2), Au2–S2 2.313(2), Au1–P1 2.260(2), Au2–P2 2.267(2), Au1–Au2 3.1485(4), S1–Au1–P1 169.13(8), S2–Au2–P2 173.13(7).

in **2**, of 2.049(6) and 2.051(6) Å, show typical values for pentafluorophenylphosphane gold(I) complexes,[9] whereas the Au–S bond lengths in **4** [2.318(2) and 2.313(2) Å] are slightly longer than the values found in a great number of (benzenethiolato)(phosphane)gold(I) complexes, but they are nearly identical to those observed in some derivatives containing the fragment Ph–S–Au–P.[6a,10a,10b,11] The main difference between these two structures is that whereas in **4** the metals associate into pairs through weak intramolecular Au···Au interactions of 3.1485(4) Å, the same disposition is not found in the case of complex **2**, in which the shortest Au–Au distance is 4.264 Å. The Au–Au distance in **4** is shorter than that in the related (diphosphane)(thiolato)gold(I) complexes $[Au_2(S\text{–}B15C5)_2(dcmp)]$ [dcmp = bis(dicyclohexylphosphanyl)methane, S–B15C5 = 4′-mercaptobenzo-15-crown-5] [3.2556(8) Å] or $[Au_2(dcmp)(S\text{–}B18C6)_2]$ (S–B18C6 = 4′-mercaptobenzo-18-crown-6) [3.284(1) Å],[12] but it is longer than that in $[Au_2(m\text{-tc})_2\{Ph_2P(o\text{-}C_6H_4)O(o\text{-}C_6H_4)\,PPh_2\}]$ (tc = thiocresol) [3.0065(15) Å],[13] $[Au_2(S\text{–}C_6H_4NH_2\text{-}2)_2(dppm)]$ [3.1346(4) Å][6b] or $[Au_2(S\text{–}C_6H_4\text{-}CONH_2\text{-}2)_2(dppp)]$ [dppp = bis(diphenylphosphanyl)propane] [2.9997(7) Å].[10a]

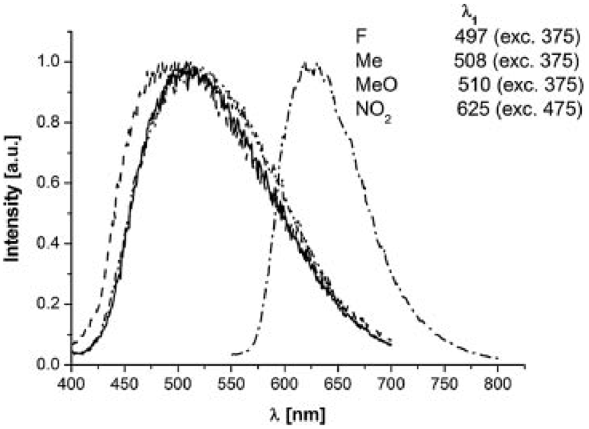

Figure 3. Emission spectra of complexes **3**–**6**.

### Photophysical Studies

The four phosphane–sulfide complexes display luminescence under UV light at 77 K, but they are not luminescent at room temperature or in solution. Thus, by excitation at 375 nm (complexes **3**–**5**) or 475 nm (complex **6**), emissions at 497, 508, 510 or 625 nm, respectively, are observed. The large Stokes shifts observed (>6500 for **3**, 6900 for **4**, 7000 for **5** and 5000 for **6**) implies that there is a large distortion in the excited state relative to the ground state, which is consistent with a charge transfer transition. In fact, in luminescent complexes containing S(thiolato)–Au–P(phosphane) units, the emissions are assigned to metal-to-ligand charge transfer (MLCT) transitions and, therefore, we propose a similar origin.[6] Nevertheless, the presence of phenyl groups in the ligands raises an alternative assignment, because emission bands near 500 nm in phenylphosphane metal complexes have previously been reported. These have their origin in $\pi$–$\pi^*$ transitions,[14] although this possibility appears remote as the chloro- and pentafluorophenylgold(I) derivatives **1** and **2**, which contain the same diphenylphosphane ligand, do not show luminescence neither in the solid state at different temperatures nor in solution.

The four complexes have long lifetimes in the microsecond range with values of 28.7 and 107.5 ($R^2$ = 0.997) for **3**, 32.4 ($R^2$ = 0.991) for **4**, 30.1 ($R^2$ = 0.991) for **5** and 399.7 µs ($R^2$ = 0.994) for **6**, suggesting that the excited states are of triplet parentage and, therefore, consistent with phosphorescent emissions (Figure 3).

As regards the position of the emission bands, previous studies in thiolate–phosphane–gold complexes carried out originally by Bruce et al.[15] and Fackler et al.[6a] point out two main factors that are responsible for the luminescent behaviour: electron-withdrawing groups on the thiolato ligands and the presence or absence of gold–gold interactions in the complexes. Electron-withdrawing groups on the thiolato ligand stabilize the sulfur orbital, which makes the ligand more difficult to oxidize and shifts the emissions to higher energies. By contrast, from these studies it was also concluded that the "gold–gold interaction is not a necessary condition for luminescence",[15] but "in some circumstances shift the emission maxima to lower energies".[6a] In our case, only the methoxy derivative was structurally characterized, and the metal–metal distance is 3.15 Å. As the emission band of the methyl derivative appears at similar energy and the electron withdrawing capability is similar for both groups, it is likely that this complex will display a similar gold–gold interaction. Nevertheless, when a fluorine atom is the substituent on the thiolato ligand its much higher electron-withdrawing ability only slightly shifts the emission band to higher energy; this can be attributed to a decreased effectiveness of this ability in the *para* position. Finally, the nitro derivative displays the longest wavelength emission in spite of its large electron-withdrawing ability. By taking into account that it is also placed in the *para* position where this effect is diminished, it is likely that the nitro group importantly contributes to the excited state or that this derivative presents a very short gold–gold interaction in the solid state.

## Conclusions

We report here the synthesis and characterization of new tetranuclear (phosphane)(thiolato)gold(I), in which a tetradentate phosphane with an ethylenediamine core and 4-substituted benzenethiols are employed as ligands. The X-ray structure of the precursor gold(I) complex with pentafluorophenyl groups bonded to gold does not show aurophilic interactions; meanwhile the corresponding (benzenethiolato)(phosphane)gold(I) complex **4** displays two $Au^I\cdots Au^I$ interactions leading to two pairs of P–Au–S units.

From the photophysical measurements it was shown that these (benzenethiolato)(phosphane)gold(I) tetranuclear derivatives display intense luminescence in the solid state at 77 K with lifetimes in the microsecond range. Both the presence of aurophilic interactions as well as the electron-withdrawing ability of the substituents in the 4-position of the benzenethiolato ligands were studied. It seems plausible that the electron-withdrawing abilities of the substituents in 4-position of the benzenethiolato ligand do not play a key role as it is not possible to correlate it with the emission energies. The results obtained could be more likely related to the presence of aurophilic interactions in the complexes, although the possibility of a contribution of the substituents to the excited state cannot be neglected.

## Experimental Section

**General:** The compounds [AuCl(tht)],[16] [Au($C_6F_5$)(tht)][17] and $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$[8] were synthesized by standard literature procedures. The starting materials $Ph_2PH$, *p*-formaldehyde and $NH_2CH_2CH_2NH_2$ were purchased from Sigma–Aldrich and used as received without further purification.

**Instrumentation:** Infrared spectra were recorded in the 4000–200 $cm^{-1}$ range with a Perkin–Elmer FTIR Spectrum 1000 spectrophotometer by using Nujol mulls between polyethylene sheets. C, H and N analyses were carried out with a C.E. Instrument EA-1110 CHNS-O microanalyzer. Mass spectra were recorded with a MICROFLEX MALDI-TOF spectrometer by using dithranol (DIT) as matrix. $^1H$, $^{19}F$ and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker ARX 300 in $CDCl_3$. Chemical shifts are quoted relative to $SiMe_4$ ($^1H$ external), $CFCl_3$ ($^{19}F$ external) and $H_3PO_4$ (85%) ($^{31}P$ external), respectively. Excitation and emission spectra as well as lifetime measurements were recorded with a Jobin–Yvon Horiba Fluorolog 3–22 Tau-3 spectrofluorimeter.

**[$Au_4Cl_4\{(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2\}$] (1):** To a dichloromethane solution (20 mL) of [AuCl(tht)] (0.20 g, 0.624 mmol) in dichloromethane (20 mL) was added $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$ (0.13 g, 0.145 mmol). After 30 min of stirring at room temp., the solvent was evaporated to ca. 5 mL. The addition of *n*-hexane (20 mL) led to the precipitation of compound **1** as a white solid. Yield: 83%. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.80–7.20 (m, 40 H, aromatic protons), 3.87 (s, 8 H, P-$CH_2$-N), 2.60 (s, 4 H, N-$CH_2CH_2$-N) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ = 17.7 (s, $PPh_2$) ppm. IR: $\tilde{\nu}$ = 1573 $\nu$(C–N), 327 $\nu$(Au–Cl) $cm^{-1}$. MS (MALDI+): *m/z* (%) = 1747.1 (100) [M – Cl]$^+$. $C_{54}H_{52}Au_4Cl_4N_2P_4$ (1782.57): calcd. C 36.38, H 2.94, N 1.57; found C 36.52, H 2.97, N 1.59.

**[$Au_4(C_6F_5)_4\{(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2\}$] (2):** To a dichloromethane solution (20 mL) of [$AuC_6F_5$(tht)] (0.15 g, 0.332 mmol) in dichloromethane (20 mL) was added $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$ (0.071 g, 0.083 mmol). After 30 min of stirring at room temp., the solvent was evaporated to ca. 5 mL. The addition of *n*-hexane (20 mL) led to the precipitation of compound **2** as a white solid. Yield: 75%. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.70–7.20 [m, 40 H, aromatic protons], 3.70 (s, 8 H, P-$CH_2$-N), 3.02 (s, 4 H, N-$CH_2CH_2$-N) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ = 24.7 (s, $PPh_2$) ppm. $^{19}F$ NMR (283 MHz, $CDCl_3$): $\delta$ = –115.36 (m, 8 F, $F_{ortho}$), –157.71 (t, $^3J_{Fp\text{-}Fm}$ = 19 Hz, 4 F, $F_{para}$), –161.82 (m, 8 F, $F_{meta}$) ppm. IR: $\tilde{\nu}$ = 1586 $\nu$(C–N), 1504, 954, 792 $\nu$(Au–$C_6F_5$) $cm^{-1}$. MS (MALDI+): *m/z* (%) = 1777.9 (100) [M – Au$(C_6F_5)_2$]$^+$. $C_{78}H_{52}Au_4F_{20}N_2P_4$ (2308.99): calcd. C 40.57, H 2.27, N 1.21; found C 40.96, H 2.38, N 1.25.

**General Procedure for the Preparation of [$Au_4(S\text{-}C_6H_4\text{-}X)_4\{(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2\}$] [X = F (3), MeO (4), Me (5) and $NO_2$ (6)]:** To a dichloromethane solution (20 mL) of the benzenethiol (0.337 mmol) was added an excess amount of NaOMe (0.073 g, 1.34 mmol). After 15 min of stirring, complex [$Au_4Cl_4\{(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2\}$] **1** was added (0.15 g, 0.084 mmol). The reaction mixture was stirred for 2 h, generating a white solid (NaCl) that was separated by filtration. The filtrate was evaporated to ca. 5 mL, and the addition of diethyl ether (20 mL) led to the precipitation of the compounds.

**3:** From 4-fluorobenzenethiol (0.043 g). Yield: 45%, white solid. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.70–7.20 (m, 40 H, Ph rings), 6.77 (m, 8 H, 3-H and 5-H in S-$C_6H_4$-F), 3.83 (s, 8 H, $PCH_2N$), 2.61 (s, 4 H, $NCH_2CH_2N$) ppm.$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ = 23.5 (s) ppm. $^{19}F$ NMR (283 MHz, $CDCl_3$): $\delta$ = –120.70 (s, 4 F) ppm. IR: $\tilde{\nu}$ = 1584 $\nu$(C–N), 1103, 857 $\nu$(C–S) $cm^{-1}$. MS (MALDI+): *m/z* (%) = 2022 (1.5) [M – (S-$C_6F_4$-F)]$^+$, 1698 (17) [M – Au(S-$C_6H_4$-F)$_2$]$^+$. $C_{78}H_{68}Au_4F_4N_2P_4S_4$ (2149.41): calcd. C 43.58, H 3.19, N 1.30, S 5.97; found C 43.33, H 3.16, N 1.35, S 5.90.

**4:** From 4-methoxybenzenethiol (0.047 g). Yield: 63%, yellow solid. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.70–7.20 (m,40 H, Ph rings), 7.41 (m, 8 H, 2-H and 6-H in S-$C_6H_4$-$OCH_3$), 6.64 (m, 8 H, 3-H and 5-H in S-$C_6H_4$-$OCH_3$), 3.83 (s, 8 H, $PCH_2N$), 3.69 (s, 12 H, MeO), 2.57 (s, 4 H, $NCH_2CH_2N$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ = 23.4 (s) ppm. IR: $\tilde{\nu}$ = 1589 $\nu$(C–N), 1101, 867 $\nu$(C–S) $cm^{-1}$. MS (MALDI+): *m/z* (%) = 2058 (4) [M – (S-$C_6H_4$-$OCH_3$)]$^+$, 1722 (28) [M – Au(S-$C_6H_4$-$OCH_3$)$_2$]$^+$. $C_{82}H_{80}Au_4N_2O_4P_4S_4$ (2197.55): calcd. C 44.82, H 3.67, N 1.27, S 5.84; found C 44.58, H 3.45, N 1.26, S 5.54.

**5:** From 4-methylbenzenethiol (0.042 g). Yield: 51%, yellow solid. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.70–7.20 (m,40 H, Ph rings), 7.42 (m, 8 H, 2-H and 6-H in S-$C_6H_4$-$CH_3$), 6.87 (m, 8 H, 3-H and 5-H in S-$C_6H_4$-$CH_3$), 3.82 (s, 8 H, $PCH_2N$), 2.59 (s, 4 H, $NCH_2CH_2N$), 2.21 (s, 12 H, Me) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ = 23.5 (s) ppm. IR: $\tilde{\nu}$ = 1587 $\nu$(C–N), 1101, 867 $\nu$(C–S) $cm^{-1}$. MS (MALDI+): *m/z* (%) = 2010 (1) [M – (S-$C_6H_4$-$CH_3$)]$^+$, 1690 (2) [M – Au(S-$C_6H_4$-$CH_3$)$_2$]$^+$. $C_{82}H_{80}Au_4N_2P_4S_4$ (2133.55): calcd. C 46.16, H 3.78, N 1.31, S 6.01; found C 46.12, H 3.62, N 1.36, S 5.98.

**6:** From 4-nitrobenzenethiol (0.052 g). Yield: 80%, orange solid. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.60–7.40 (m,40 H, Ph rings), 7.82 (m, 8 H, 3-H and 5-H in S-$C_6H_4$-$NO_2$), 7.37 (m, 8 H, 2-H and 6-H in S-$C_6H_4$-$NO_2$), 3.81 (s, 8 H, $PCH_2N$), 2.89 (s, 4 H, $NCH_2CH_2N$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ = 23.5 (s) ppm. IR: $\tilde{\nu}$ = 1569 $\nu$(C–N), 1499, 1328 $\nu$(C–$NO_2$), 1103, 857 $\nu$(C–S) $cm^{-1}$. MS (MALDI+): *m/z* (%) = 2103 (1) [M – (S-$C_6H_4$-$NO_2$)]$^+$, 1752 (11) [M – Au(S-$C_6H_4$-$NO_2$)$_2$]$^+$. $C_{78}H_{68}Au_4N_6O_8P_4S_4$ (2257.43): calcd. C 41.49, H 3.03, N 3.72, S 5.68; found C 41.46, H 2.93, N 3.91, S 5.89.

**Crystallography:** The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of a Nonius Kappa CCD diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected by monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Scan type $\omega$ and $\phi$. Absorption corrections: numerical (based on multiple scans). The structures were solved by direct methods and refined on $F^2$ by using the program SHELXL-97.[18] All non-hydrogen atoms were anisotropically refined with the exception of the solvent (diethyl ether) molecule in **2**. Hydrogen atoms were included using a mixed model. CCDC-647628 to -647629 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Crystal Data for 2:** $C_{78}H_{52}Au_4F_{20}N_2P_4\cdot 0.5Et_2O$, *Mr* = 2346.02, triclinic, $P\bar{1}$, $a$ = 12.183(2) Å, $b$ = 14.667(2) Å, $c$ = 14.991(2) Å, $\alpha$ = 116.97(10)°, $\beta$ = 110.67(10)°, $\gamma$ = 92.13(10)°, $V$ = 2170.4(5) Å$^3$, $Z$ = 1, $\rho_{\text{calcd.}}$ = 1.795 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 6.897 mm$^{-1}$, $R_1$ = 0.0388, $wR_2$ = 0.1144 for 10286 observed reflections [$I > 2\sigma(I)$].

**Crystal Data for 4:** $C_{82}H_{80}Au_4N_2O_4P_4S_4\cdot C_7H_8$, *Mr* = 2289.60, triclinic, $P\bar{1}$, $a$ = 9.173(2) Å, $b$ = 13.844(3) Å, $c$ = 18.582(5) Å, $\alpha$ = 105.40(1)°, $\beta$ = 89.69(1)°, $\gamma$ = 95.99(1)°, $V$ = 2261.89(9) Å$^3$, $Z$ = 1, $\rho_{\text{calcd.}}$ = 1.681 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 6.677 mm$^{-1}$, $R_1$ = 0.0510, $wR_2$ = 0.1400 for 9289 observed reflections [$I > 2\sigma(I)$].

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