Aurophilic towards H-Bonding Interactions in Phosphine-pyrazolato-gold(I) Complexes: Luminescence Studies and Crystal Structure of {3,5-Bis-[4-(octyloxy)phenyl]-1*H*-pyrazolato-κN^1}(triphenylphosphine)gold−{3,5-Bis-[4-(octyloxy)phenyl]-1*H*-pyrazole} ([Au(pz^{op_2})(PPh$_3$)]·(Hpz^{op_2}))

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Compounds [{Au(pz^{R_2})(PPh$_3$)}$_2$] (pz^{R_2} = 3,5-disubstituted pyrazolato; R = BuOC$_6$H$_4$ (bp), **1**; R = C$_8$H$_{17}$OC$_6$H$_4$ (op), **2**; R = C$_6$H$_{13}$OC$_6$H$_4$ (hp), **3**) were easily obtained by reaction of [Au(NO$_3$)(PPh$_3$)] and the corresponding pyrazolato ligand. They exhibit similar NMR patterns, their ESI-MS or FAB-MS data being in agreement with a monomeric molecular formulation [Au(pz^{R_2})(PPh$_3$)]. By contrast, **1** crystallizes as the dimer [{Au(pz^{R_2})(PPh$_3$)}$_2$] and exhibits aurophilic Au ··· Au contacts, while crystallization of **2** in CH$_2$Cl$_2$/hexane gives rise to compound **4**, [Au(pz^{op_2})(PPh$_3$)]·(Hpz^{op_2}). The X-ray structure of **4** was solved, showing a H-bond interaction between the monomer of **2** and Hpz^{op_2}. Reactions between [{Au(pz^{R_2})(PPh$_3$)}$_2$] and their corresponding 1*H*-pyrazole (Hpz^{R_2}) were also explored. Compounds **1**–**3** exhibit luminescence in the solid state. Their emission spectra are reported and analyzed.

A recent topic of interest in the study of gold(I) complexes deals with the contribution of new supramolecular structures associated with the presence of Au ··· Au interactions. These contacts have been considered to be comparable to H-bonding forces [1], being responsible for most of the structural features and architectures found in gold(I) complexes [1b][2]. An additional interest derives from the luminescence properties of such molecular materials, which, in several cases, have also been related to the existence of Au ··· Au contacts [1d][3].

In a previous work on gold(I) derivatives based on 3,5-disubstituted pyrazolato ligands (pz^{R_2}), we found that [{Au(pz^{pb_2})(PPh$_3$)}$_2$] (bp = BuOC$_6$H$_4$; **1**) exhibited a dimeric molecular structure in the solid state with an Au ··· Au distance of 3.029(1) Å, characteristic of aurophilic interactions [4]. A similar molecular array was also suggested for related compounds bearing longer alkyloxy chains, *i.e.*, of eight or six C-atoms ([{Au(pz^{op_2})(PPh$_3$)}$_2$] (op = C$_8$H$_{17}$OC$_6$H$_4$, **2**); [{Au(pz^{hp_2})(PPh$_3$)}$_2$] (hp = C$_6$H$_{13}$OC$_6$H$_4$; **3**)) [4]. Complex **1** was luminescent in the solid state at 77 K [4]. We now are interested in the knowledge of the luminescence properties of compound **1** in solution where the aurophilic interactions could be absent, as well as in extending the luminescence studies to the related compounds **2** and **3** containing longer substituent

chains at the pyrazol ring. The actual work is focused as an additional contribution to the study of the aurophilic interactions/luminescence properties relationship.

On the other hand, it is also interesting to note that a new compound **4** was obtained when we tried to grow crystals from the solid **2**. It was identified by X-ray diffraction as the association compound $[Au(pz^{op_2})(PPh_3)] \cdot (Hpz^{op_2})$ (**4**). Compound **4** was also prepared by direct synthesis from $[\{Au(pz^{op_2})(PPh_3)\}_2]$ (**2**) and Hpz^{op_2} and characterized by analytical and spectroscopic techniques.

Synthetic and Structural Studies. – Compounds **1** – **3** were synthesized and their IR, ¹H- and ³¹P-NMR, and mass spectra studied (see *Exper. Part*). The IR spectra in the solid state and the ¹H-NMR spectra in $CDCl_3$ solution confirm the presence of both coordinated PPh_3 and pyrazolato ligands, the NMR data indicating a 1:1 molar ratio between them. The presence of two equivalent substituents of the coordinated pyrazolato ligand is also deduced from the NMR spectra, which suggests a metallotropic equilibrium [5]. The ³¹P-NMR spectra exhibit only one resonance ($\delta(P)$ *ca.* 32.8), which appears in the region usually observed for PPh_3 coordinated to a Au^I atom in related compounds: ($[Au(imd)(PPh_3)]$ (imd = imidazolato), $\delta(P)$ 32.4 [6]; $[Au(1,2,4-triaz)(PPh_3)]$ (triaz = triazolato), $\delta(P)$ 31.5 [7]; $[Au(pz)(PPh_3)]$ (pz = pyrazolato), $\delta(P)$ 31.7 [6]). The ESI-MS data provide direct evidence for the monomeric form of **1** and **2**, showing peaks at 823.6 and 935.6, respectively, associated with the parent ion $[M+H]^+$. The molecular ion M^+ could be observed in the FAB-MS of **3**. The above data agree with a monomeric nature of the compounds **1** – **3** in solution, avoiding therefore the presence of $Au \cdots Au$ interactions. By contrast, the evidence for short $Au \cdots Au$ distances in the dimer **1**, determined by its X-ray crystal structure [4], suggests those associations to be characteristic of the solid state. In a recent paper, this proposal has also been confirmed in related compounds containing the 3,5-diphenyl-pyrazolato ligand [8]. Following those precedents, we tried to get adequate crystals of **2** to assess its structure. However, when a solid sample of **2** was left to crystallize from CH_2Cl_2/hexane solutions, crystals of a new compound **4**, characterized by its X-ray structure as $[Au(pz^{op_2})(PPh_3)] \cdot (Hpz^{op_2})$, were isolated.

On this basis we thought that the addition of pyrazole (Hpz^{R_2}) to the monomeric $[Au(pz^{R_2})(PPh_3)]$ derivatives could produce an association through H-bonds involving a N-atom of the pyrazolato ligand and the NH group of the free pyrazole, which should modify or avoid the aurophilic interactions. In fact, the reaction of **2** with equimolar quantities of Hpz^{op_2} gave rise to the expected product **4**. Its IR spectrum in KBr discs shows, in addition to other bands, a $\tilde{\nu}(NH)$ absorption at 3223 cm⁻¹, which is consistent with the presence of pyrazole. This band appears almost unmodified with respect to that of the free ligand [9]. Because related pyrazoles have shown H-bonds in the solid state [5b][10], the above result agrees with the presence of the H-bonding interaction in **4**. The pattern of its ¹H-NMR spectrum consists of one H–C(4) resonance and two aromatic signals from protons of equivalent aryl substituents at the heterocycles. The alkyl chains are also equivalent as deduced from their observed signals. The relationship found between the PPh_3 and H–C(4) protons is 15:2, in agreement with the proposed formulation. The ¹H-NMR results could be explained by considering a rapid exchange between uncoordinated and coordinated pyrazole moieties, making both to be equivalent on the NMR timescale. The ³¹P-NMR spectrum presents a unique

resonance at $\delta(P)$ 32.8 in the region of a coordinated PPh$_3$ ligand [6][7]. The ESI-MS of **4** shows a peak at 1409.1 for the $[M - H]^+$ ion, confirming the association pyrazole · pyrazolato in the compound.

Looking for getting a related complex $[Au(pz^{bp2})(PPh_3)] \cdot (Hpz^{bp2})$ containing shorter chains as substituents, we carried out the reaction of **1** with its corresponding pyrazole Hpz^{bp2}. However, in this case, only a mixture of the starting compounds could be isolated, indicating that the expected reaction did not take place.

The above results are summarized in the *Scheme*. In **1**, the Au ··· Au interactions in the solid state are favored towards the H-bonds found in **4**. Then it could be suggested that, for two-coordinate gold(I) complexes of the type $[Au(pz^{R2})(PPh_3)]$, the steric and electronic consequences of the pyrazole group are responsible for the potentially different intermolecular interactions in the solid.

Scheme

a) Crystallization process in CH$_2$Cl$_2$/hexane; R = BuOC$_6$H$_4$. *b*) Crystallization process in CH$_2$Cl$_2$/hexane; R = C$_8$H$_{17}$OC$_6$H$_4$.
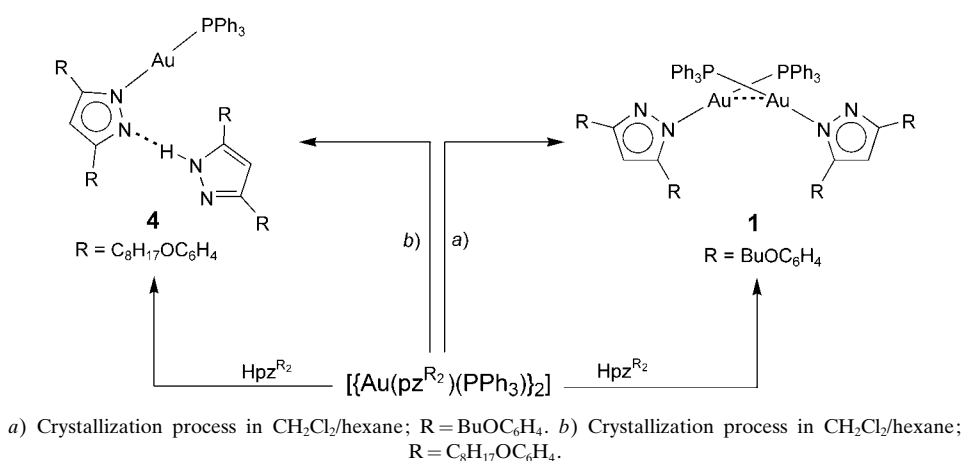
Crystal Structure of $[Au(pz^{op2})(PPh_3)] \cdot (Hpz^{op2})$ (4). The molecular structure of **4** with the atom numbering scheme is depicted in *Fig. 1*. The compound crystallizes in the triclinic system, space group $P\bar{1}$.

The molecule is composed of two entities, $[Au(pz^{op2})(PPh_3)]$ and 1*H*-pyrazole, linked by a strong H-bond with a N(3) ··· N(2) distance of 2.941(5) Å and a N(3)−H(3) ··· N(2) angle of 172.2(2)°. Both entities are crossed as it is evidenced by the dihedral angle between the heterocyclic planes of 65.5(2)°. It is remarkable to note that the aryl substituents of the uncoordinated pyrazole are approximately parallel to the own heterocyclic ring (5.3(1) and 10.1(1)°). However the coordinated pyrazolato ligand shows one aryl substituent to be almost parallel (6.8(1)°) and the other twisted (53.7(1)°) to its own heterocyclic plane.

The geometry around the Au-atom is, as expected, almost linear, the P(1)−Au(1)−N(1) angle being 176.2(1)°. The Au(1)−N(1) and Au(1)−P(1) bond lengths are 2.034(3) and 2.239(1) Å, respectively, similar to those found in related complexes [4][6−8][11]. No intermolecular Au ··· Au interactions were found, the
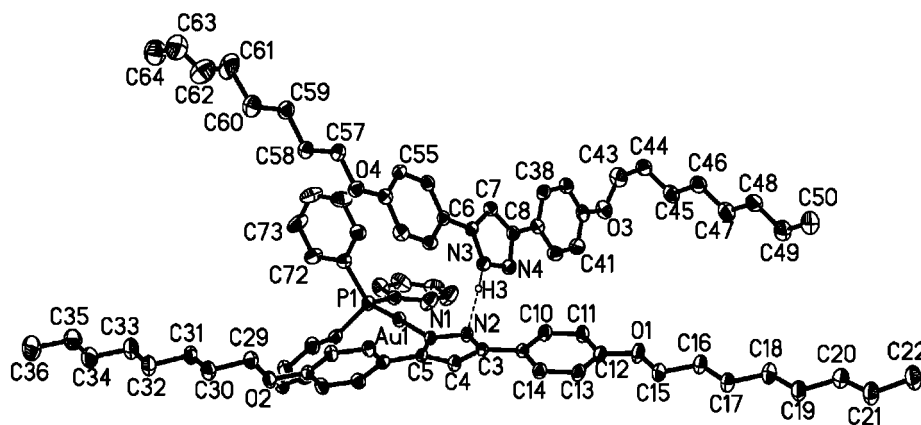
Fig. 1. *Perspective ORTEP plot of* **4**. H-Atoms, except H(3), and the labelling of some atoms are omitted for clarity. The thermal ellipsoids are at 35% probability level. Selected bond lengths [Å] and angles [°]: Au(1)−N(1) 2.034(3), Au(1)−P(1) 2.239(1), N(1)−N(2) 1.367(4), N(3)−N(4) 1.366(5), N(3)−H(3) 0.9988, N(2)···H(3) 1.95, N(2)···N(3) 2.941(5), P(1)−Au(1)−N(1) 176.2(1), Au(1)−N(1)−N(2) 119.0(2), N(3)−H(3)···N(2) 172.2(2).

shortest distance being 6.50 Å. Further structural details are listed in the legend of *Fig. 1*.

The molecular packing indicated a layer-like molecular distribution, by considering two types of layers (**A** and **B**). Layer **A** (*Fig. 2,a*) is defined for the uncoordinated pyrazole units, the lateral chains being bent *ca.* 105° from the hypothetical O(3)··· C(61) line, which passes through the three planar rings. This folded layer lies almost parallel to the (0 1 1) plane.

Layer **B** contains the $[Au(pz^{op_2})(PPh_3)]$ units, and it lies almost parallel to the *ac* plane. This layer is formed by two sheets containing the $Au(PPh_3)$ groups in a head-to-tail disposition. Weak C−H···O(N) contacts between the two sheets of a layer (C(75)···O(2) (*x*+1, *y*, *z*) 3.42 Å; C(81)···N(2) (−*x*+1, −*y*+2, −*z*+1) 3.34 Å) define a two-dimensional network (*Fig. 2,b*).

Both layers **A** and **B** are crossed with the chains of the uncoordinated pyrazole units (**A**) occupying the free space between the sheets of the layer of $[Au(pz^{R_2})(PPh_3)]$ (**B**) (*Fig. 2,c*). This structural feature could be related to the molecular crossing observed in the asymmetric unit.

Luminescence Properties. – The emission spectra of compounds **1**–**3** were studied both in the solid state and in acetone solution (*Table 1*). Only dimer **1** is slightly luminescent at room temperature, although the emissions are weak (*Fig. 3,a*), and none of them show emissions in acetone solution. At 77 K in the solid state, **1**–**3** are all luminescent and display similar spectra consisting of a broad band in which three maximum are found (*Fig. 3,b*). So, in all cases, the excitation at *ca.* 330 nm produces an emission maximum located at *ca.* 450 nm (see *Table 1* and *Fig. 3*). The pattern and energies of the observed band resemble closely those recently reported by *Fackler* and co-workers for a family of related pyrazolato-gold(I) complexes, the emissions being
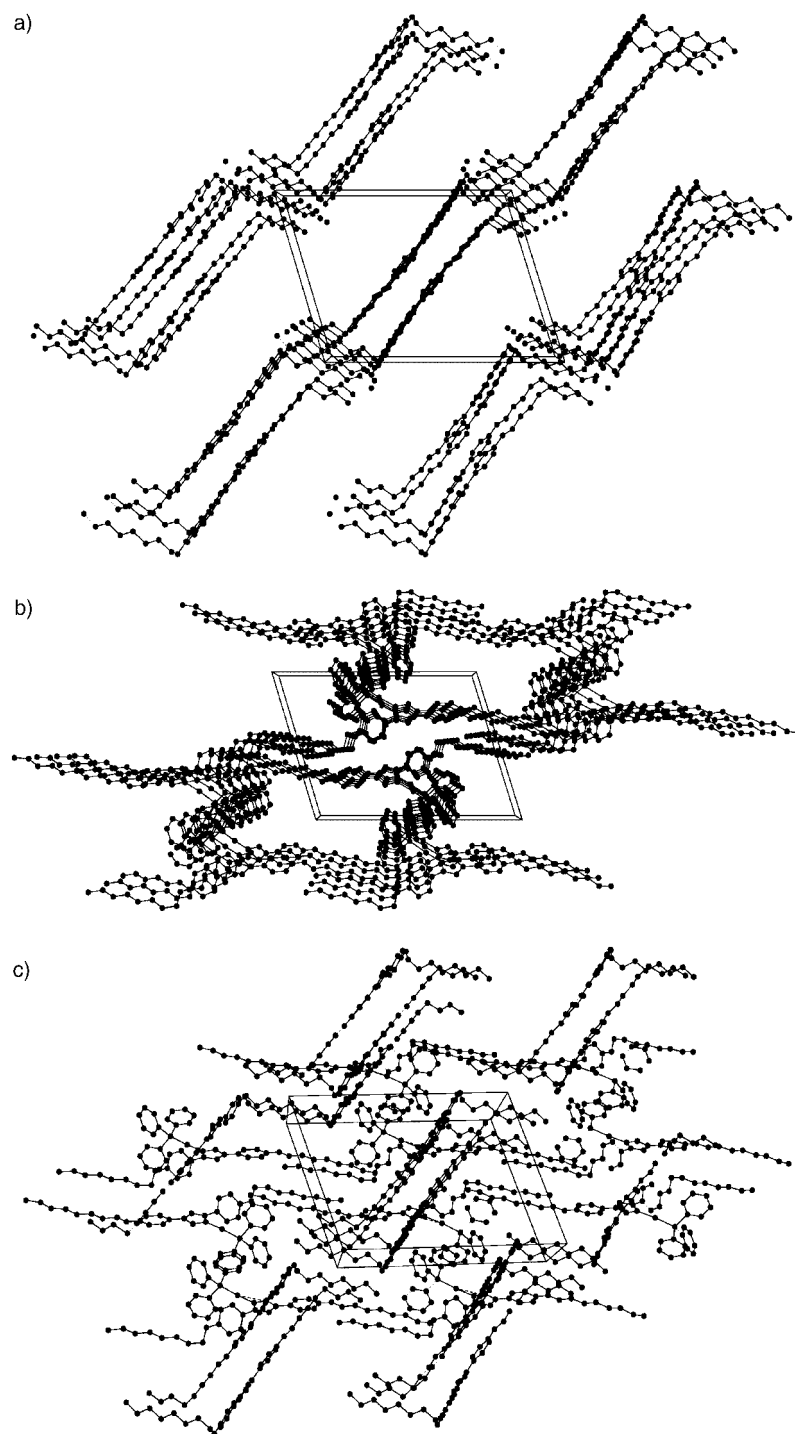
a)

b)

c)

Fig. 2. a) *View of layer* **A**. b) *View of layer* **B**. c) *Molecular packing of* **4** *showing the crossing of the two different types of layers.*

Table 1. *Emission and Excitation Maxima (λ in nm) Measured for Complexes* **1–3**

	Solid (298 K)		Solid (77 K)		Solution (298 K)[a]
	λ_{exc}	λ_{em}	λ_{exc}	λ_{em}	
1	321	421, 447	320	415, 445, 470	[b]
2		[b]	321	419, 446, 482	[b]
3		[b]	337	428, 446, 482	[b]

[a] 5×10^{-4} M in acetone. [b] No emission observed.

assigned to ligand-to-metal charge-transfer processes [8]. On the other hand, it has been observed for several gold(I) derivatives containing inter- or intramolecular Au ⋯ Au contacts that emissions attributed to Au ⋯ Au metal-centered transitions appear at lower energies (λ_{max} *ca.* 600 nm) than those above mentioned for our complexes [12]. On these bases, the emissions observed in **1–3** could be assigned to ligand-to-metal charge-transfer processes. Despite this assignation and taking into account the non-emissive nature in solution of our compounds, it could be suggested that the Au ⋯ Au interactions contribute to the observed emissions. However, the presence of such interactions alone is not sufficient to produce luminescence properties, in agreement with evidence previously established by *Fackler* and co-workers [8].

Experimental Part

General. The starting Au-complex [Au(NO₃)(PPh₃)] and the 3,5-bis[4-(alkyloxy)phenyl]-1*H*-pyrazoles (Hpz^{bp_2}, Hpz^{hp_2}, and Hpz^{op_2}) were prepared by known procedures [9][10][13]. All commercial reagents were used as supplied. Luminescence: *Perkin-Elmer LS-50B* luminescence spectrometer; emission and excitation spectra were not corrected for instrumental response; solid-state samples were packed into capillary tubes and introduced into the *Perkin-Elmer* variable-temp. accessory; solns. in acetone, 5×10^{-4} M. IR Spectra: *Nicolet FTIR-Magna-550* spectrophotometer; KBr discs; 4000–350 cm^{-1} region; in cm^{-1}. ¹H- and ³¹P{¹H}-NMR Spectra: *Bruker DPX-300* (300.13 and 121.49 MHz for ¹H and ³¹P, resp.) or *Bruker AC-200* (200.13 MHz for ¹H) spectrophotometers; CDCl₃ solns.; chemical shifts $\delta(H)$ in ppm rel. to SiMe₄, with the signal of the deuterated solvent as reference, and $\delta(P)$ in ppm rel. to 85% H₃PO₄; J in Hz; $\delta(H)$ and $\delta(P)$ accurate to ± 0.01 and ± 0.1 ppm, resp., $J(H,H)$ to ± 0.3 Hz. ESI-MS: *LC-Squire* spectrometer; dry MeCN, CHCl₃, or MeOH as solvents; in *m/z*. FAB-MS: *VG-AutoSpec* spectrometer; in *m/z*. Elemental analyses (C, H, N) were carried out by the Centre for Elemental Microanalysis of the Complutense University.

Bis[3,5-bis(4-butoxyphenyl)-1H-pyrazolato-κN¹]bis(triphenylphosphine)digold(Au−Au) ([{Au(pz^{bp_2})-(PPh₃)}₂]) (bp = BuOC₆H₄) **1**). To a soln. of 44 mg (0.084 mmol) of [Au(NO₃)(PPh₃)] in THF (20 ml) was added Na(pz^{bp_2}) (obtained *in situ* from Hpz^{bp_2} (30.7 mg, 0.084 mmol) and an excess of 60% NaH in THF (15 ml)). After 24 h stirring, the produced white powder of NaNO₃ was filtered and the colorless clear filtrate evaporated. The residue was dissolved in CH₂Cl₂ and precipitated with hexane. IR(KBr): 1611 (CN). ¹H-NMR (CDCl₃, r.t.): 7.81 (*d*, $J = 8.7$, H$_o$); 7.54–7.44 (*m*, PPh₃); 6.90 (*d*, $J = 8.7$, H$_m$); 6.75 (*s*, H−C(4)); 3.99 (*t*, $J = 6.5$, CH₂O); 1.77 (*m*, CH₂); 1.51 (*m*, CH₂); 1.00 (*t*, $J = 7.3$, Me). ³¹P{¹H}-NMR (CDCl₃, r.t.): 32.7. ESI-MS: 823.6 ([$M + H$]⁺). Anal. calc. for C₄₁H₄₂AuN₂O₂P: C 59.9, H 5.2, N 3.4; found: C 59.7, H 5.2, N 3.5.

Bis[3,5-bis[4-(octyloxy)phenyl]-1H-pyrazolato-κN¹]bis(triphenylphosphine)digold(Au−Au) ([{Au(pz^{op_2})-(PPh₃)}₂]) (op = C₈H₁₇OC₆H₄); **2**). As described for **1**, from 30 mg (0.057 mmol) of [Au(NO₃)(PPh₃)] and 27.4 mg (0.057 mmol) of Hpz^{op_2}. IR(KBr): 1611 (CN). ¹H-NMR (CDCl₃, r.t.): 7.78 (*d*, $J = 8.7$, H$_o$); 7.54–7.44 (*m*, PPh₃); 6.91 (*d*, $J = 8.7$, H$_m$); 6.74 (*s*, H−C(4)); 3.98 (*t*, $J = 6.6$, CH₂O); 1.73–1.29 (*m*, (CH₂)₆); 0.89 (*t*, $J = 7.0$, Me). ³¹P{¹H}-NMR (CDCl₃, r.t.): 32.9. ESI-MS: 935.6 ([$M + H$]⁺). Anal. calc. for C₄₉H₅₈AuN₂O₂P: C 63.0, H 6.3, N 3.0; found: C 63.2, H 6.3, N 3.1.
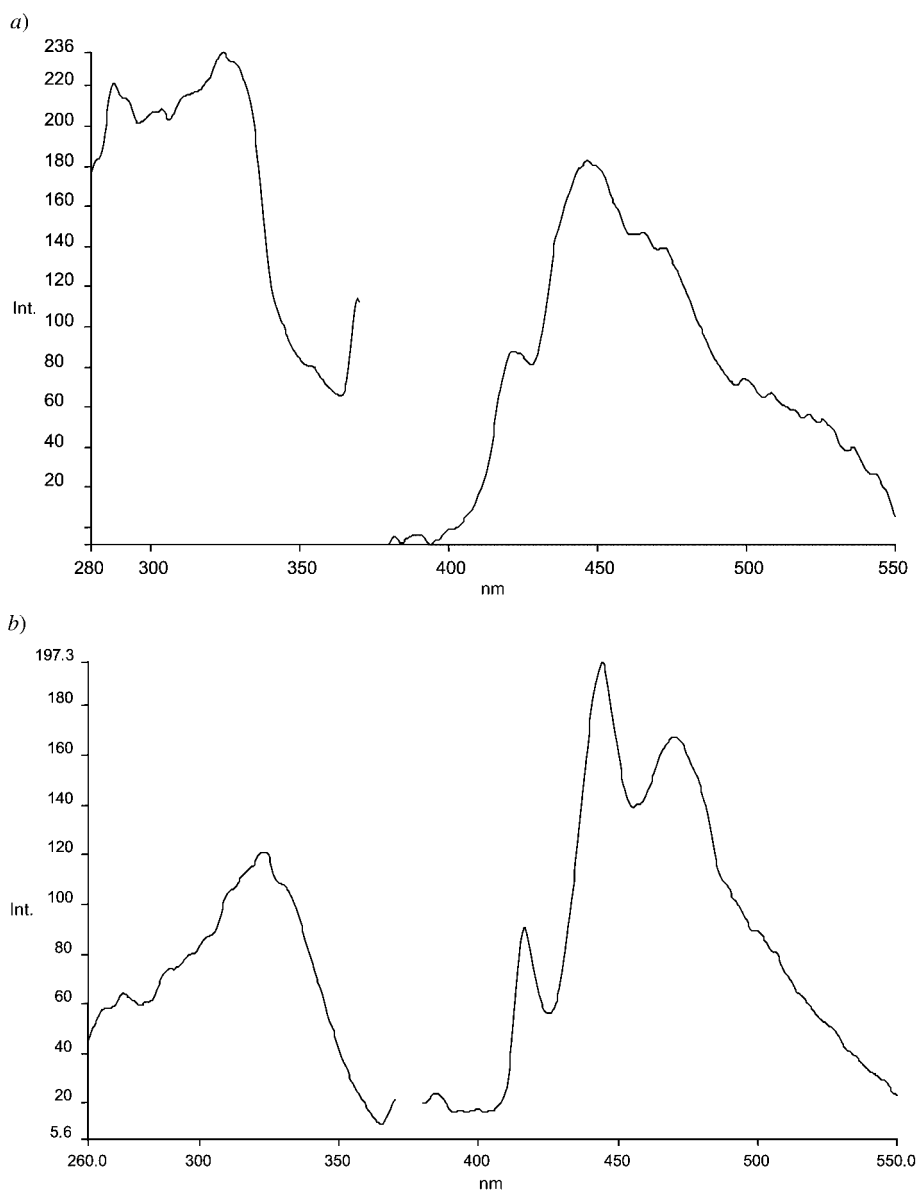
a)

b)

Fig. 3. *Excitation and emission spectra of* **1** *in the solid state* a*) at 298 K and* b*) at 77 K*

Bis{3,5-bis[4-(hexyloxy)phenyl]-1H-pyrazolato-κN^1}bis(triphenylphosphine)digold(Au−Au) ([{Au(pz^{hp_2})-(PPh$_3$)}$_2$] (hp = C$_6$H$_{13}$OC$_6$H$_4$); **3**). As described **1**, from 52 mg (0.101 mmol) of [Au(NO$_3$)(PPh$_3$)] and 42.5 mg (0.101 mmol) of Hpz^{hp_2}. IR(KBr): 1610 (CN). ^{1}H-NMR (CDCl$_3$, r.t.): 7.79 (*d*, *J* = 8.5, H$_o$); 7.50 – 7.45 (*m*, PPh$_3$); 6.91 (*d*, *J* = 8.5, H$_m$); 6.75 (*s*, H−C(4)); 3.99 (*t*, *J* = 6.6, CH$_2$O); 1.80 – 1.27 (*m*, (CH$_2$)$_4$); 0.92 (*t*, *J* = 7.0, Me). ^{31}P{^{1}H}-NMR (CDCl$_3$, r.t.): 32.8. FAB-MS: 878 (*M*$^+$). Anal. calc. for C$_{45}$H$_{50}$AuN$_2$O$_2$P: C 61.5, H 5.7, N 3.2; found: C 61.4, H 5.6, N 3.0.

*{3,5-Bis[4-(octyloxy)phenyl-1*H-*pyrazolato-κN¹](triphenylphosphine)gold−{3,5-Bis[4-(octyloxy)phenyl-1*H-*pyrazole}* ([Au(pz^{op_2})(PPh$_3$)]·(Hpz^{op_2}) (op = C$_8$H$_{17}$OC$_6$H$_4$); **4**). To a soln. of 24 mg (0.0125 mmol) of [{Au(pz^{op_2})(PPh$_3$)}$_2$] (**2**) in THF (20 ml) was slowly added a soln. of Hpz^{op_2} (14.6 mg, 0.025 mmol) in THF (15 ml). The mixture was stirred 24 h, and the resulting soln. evaporated. The residue was then dissolved in CH$_2$Cl$_2$ and precipitated with hexane. IR(KBr): 3223 (NH), 1611 (CN). ^{1}H-NMR (CDCl$_3$, r.t.): 7.71 (*d*, *J* = 8.7, H$_o$); 7.53 – 7.43 (*m*, PPh$_3$); 6.94 (*d*, *J* = 8.7, H$_m$); 6.71 (*s*, H−C(4)); 4.00 (*t*, *J* = 6.3, CH$_2$O); 1.73 – 1.29 (*m*, (CH$_2$)$_6$); 1.00 (*t*, *J* = 6.8, Me). ^{31}P{^{1}H}-NMR (CDCl$_3$, r.t.): 32.8. ESI-MS: 1409.1 ([*M* − H]$^+$). Anal. calc. for C$_{80}$H$_{102}$AuN$_4$O$_4$P: C 68.1, H 7.3, N 4.0; found: C 68.4, H 7.3, N 4.2.

X-Ray Structure Determination of **4**. Colorless prismatic single crystals were obtained by slow diffusion of hexane in a CH$_2$Cl$_2$ soln. of **4**. The data were collected on a *Bruker Smart-CCD* diffractometer with graphite-monochromated Mo-*Kα* radiation (*λ* 0.71073 Å), operating at 50 kV and 20 mA. The data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 10 s covered 0.3° in *ω*.The first 50 frames were recollected at the end of the data collection to monitor crystal decay. No appreciable decay in the intensities of standard reflections was observed. A summary of the fundamental crystal and refinement data is given in *Table 2*. Data were corrected for *Lorentz* and polarization effects, but not for absorption. The structure was solved by direct methods and refined by full-matrix least-squares on *F*^{2} [14]. Anisotropic thermal parameters were used in the last cycles of refinement for all non-H-atoms with some exceptions. All C-atoms of the octyloxy chains were refined with geometrical restraints and a variable common C−C distance. The C(62), C(63), and C(64) atoms showed non-resolvable positional disorder, and they were refined anisotropically in two cycles, and in the subsequent cycles, their thermal parameters were kept constant. The H-atoms were calculated and refined as riding on their C-bonded atom with a common isotropic displacement parameter, except for H(3) which was found in a difference *Fourier* map, included, and refined as riding on the N(3) atom.

Table 2. *Crystal and Refinement Data for Compound* **4**

Formula	C$_{80}$H$_{102}$AuN$_4$O$_4$P
M	1411.59
Crystal system	triclinic
Space group	*P*$\bar{1}$
a/Å	11.1229(7)
b/Å	15.910(1)
c/Å	21.782(1)
α/°	72.494(1)
β/°	89.760(1)
γ/°	84.520(1)
U/Å^3	3658.0(4)
Z	2
F(000)	1472
D$_c$/g cm^{-3}	1.282
Temp./K	298(2)
μ(Mo-*Kα*)/mm^{-1}	2.083
Crystal size/mm	0.37 × 0.23 × 0.07
Scan technique	*ϕ* and *ω*
Data collected	(− 11, − 18, − 23) to (13, 18, 25)
θ/°	1.41 – 25.00
Refls. collected	19263
Unique refls.	12682 (*R*$_{int}$ = 0.0275)
Data, restraints, parameters	12682, 28, 794
G.o.f. (*F*^{2})	1.109
R(*F*) ((*F*^{2}) > 2*σ*(*F*^{2}))^a)	0.041 (9775 refls.)
wR(*F*^{2}) (all data)^b)	0.089
Largest residual peak/e Å^{-3}	1.26

^{a}) $\Sigma[|F_o| − |F_c|]/\Sigma|F_o|$.　^{b}) $\{\Sigma[w(F_o^2 − F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Supplementary crystallographic data have been deposited with the *Cambridge Crystallographic Data Center* (CCDC deposition No. 231742). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 EZ, UK; fax: +441223336033; e-mail: deposit@ccdc.cam.ac.uk).

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