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Introduction

Phosphine-gold(i)-thiolate derivatives have been intensely studied due to their potential applications in the development of new materials,¹ chemosensors² as well as in the medical field as novel therapeutic agents.³ These wide range of possibilities have awakened an increasing interest in studying their structure and photophysical properties. In particular, thiolate derivatives are versatile ligands that allow the synthesis of coordination compounds with different features. They can accommodate one, two and even three gold centers,⁴ which might promote a completely different spatial distribution. Such great diversity of possible structures could induce diverse photophysical properties, either because gold(i)–gold(i) interactions can occur, or simply because the different packaging modes would alter the luminescence. Typically, emission of

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Different emissive properties in dithiolate gold(ı) complexes as a function of the presence of phenylene spacers†

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A family of dinuclear neutral thiolate gold complexes of the type $RPh_2PAuS(C_6H_4)_nSAuPPh_2R$ (n = 2, 3), $RPh_2PAuS(C_6H_4)S(C_6H_4)SAuPPh_2R$, $RPh_2PAuSCH_2(C_6H_4)_2CH_2SAuPPh_2R$ where R represents a pyridine or a phenylene ring, has been prepared and fully characterized. X-ray crystallographic studies showed the presence of aurophilic interactions for those species bearing two phenylene spacers between the gold metal centers, leading to infinite chains. The complexes are emissive in the solid state. Theoretical calculations together with the photophysical analysis seem to indicate that the main excitations involved in the emissive processes are due to a mixture of ILCT transition involving the thiolate and the conjugated phenylene rings, and LL'CT transitions comprising the thiolate and the pyridine or phenyl from the phosphine fragment which contrast with the typical gold thiolate emission, LMCT from the thiolate fragment to the metal center.

> thiolate-Au phosphine derivatives takes place between 400 nm and 700 nm and it mainly originates from ligand to metal charge transfer (LMCT) transitions, from the thiolate fragment to the gold metal center. However, thiolate to phosphine charge transfer (LL'CT), gold to thiolate charge transfer (MLCT) and thiolate centered (LC) transitions have been also described in the literature for these types of species.⁵ In addition, the incorporation of phenyl spacers between the metal centers seems to confer a different approach to the conventional photophysical properties of gold-thiolate derivatives. Previous work performed by Kosehovoy and coworkers described that, in those cases, thiolates and phosphine intraligand charge transfer processes are the primary responsible transitions for the emission.⁶ Furthermore, aurophilic interactions are relegated to a secondary role as their presence or absence is irrelevant. More examples supporting this theory were also reported for dinuclear gold complexes with diphosphines containing alkyne and/or phenylene spacers. Once again, the presence of phenylene spacers in the backbone seems to control the photophysical properties of the complexes. Therefore, in this work, a family of dithiolate phenyl derivatives was chosen as spacers to synthesize a new series of bimetallic thiolate-gold(I) phosphine derivatives. Then, a thorough analysis of their crystalline structure, together with photophysical studies and theoretical calculations, will attempt to shed some light on the influence of phenylene spacers in the emission properties of thiolate-gold(1) phosphine derivatives.



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[†] Electronic supplementary information (ESI) available: Structural features in the packing of complexes **2**, **4**, **6** (Fig. S1–S4); DRUV spectra of L1–L4 (Fig. S5); DRUV spectra of complexes **2**–**4**, **6–8** (Fig. S6); emission spectra of complexes **2**, **4**, **5**, 7 (Fig. S7); simulated absorption spectrum of **4** in the gas phase (Fig. S8); isosurface drawings of selected Kohn–Sham MOs calculated for **4** (Fig. S9). CCDC 976386–976389. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53530d

Synthesis and characterisation

Dithiolate Au^I complexes

Gold(I) complexes (1-8) were synthesized by reaction of the corresponding dithiolate ligand with either ClAuPPh3 or ClAuPPh₂Py in the presence of cesium carbonate to assist the thiol deprotonation and subsequent metal coordination (see Scheme 1). Spectroscopic characterization of each gold complex was performed using IR, ¹H, ³¹P and ¹³C NMR spectroscopy, and UV-vis spectroscopic measurements. Infrared spectroscopy showed in all cases the disappearance of a ν (S-H) stretching band at *ca.* 2550 cm^{-1} indicating the deprotonation of the thiol groups. ³¹P-NMR spectra presented a significant low-field shift of the phosphine peak, from ca. 33 ppm to ca. 38 ppm after coordination of the dithiolate species to the gold phosphine derivatives, which is in agreement with analogous NMR spectroscopy data reported for different thiolate-gold(I) phosphine complexes.⁷ Moreover, the chemical shifts observed in ¹³C-NMR and ¹H-NMR spectroscopy corroborate the success of the coordination reaction. Thus, the synthesized complexes 1-8 showed, in all cases, that the SC_{ipso} carbons were shifted to low field as well as the disappearance of the signal belonging to S-H protons in ¹H-NMR spectroscopy. Further analytical data provided by mass spectrometry are in concordance with the expected gold(1) species 1-8 (Table 1). Additionally, suitable crystals of 2, 4, 5 and 6 were obtained that allowed structural characterization by X-ray diffraction.



Scheme 1 Synthesis and numbering of gold(i) species synthesized. (i) Cs_2CO_3 , $CH_2Cl_2/MeOH$, 2 h, Ar.

Table 1 Relevant spectroscopic data for complexes 1–8

Complex	$^{31}\mathrm{P}\{^{1}\mathrm{H}\}\left(\mathrm{ppm}\right)$	$^{13}\mathrm{C}\{^{1}\mathrm{H}\}^{a}(\mathrm{ppm})$	m/z
1	38.75	141.7	1135.0^{b}
2	38.77	142.8	1210.1^{c}
3	38.88	142.3	1166.0^{c}
4	37.85	147.6	1162.1^{c}
5	37.98	141.2	1137.1 ^c
6	37.13	142.2	1213.2^{b}
7	38.01	142.6	1168.9^{c}
8	35.97	146.7	1164.9 ^c

NMR spectra measured in CD₂Cl₂. ^a -SC_{ipso}. ^b MS(ES). ^c MS(MALDI+).

X-ray analysis

Single crystals suitable for X-ray diffraction analysis of complexes 2, 4, 5 and 6 were obtained by slow diffusion of hexane into a dichloromethane solution. The unit cells of complexes 2, 4, and 5 are formed by 4 complex molecules each, whereas only 2 complex molecules are displayed in the unit cell of complex 6. Moreover, all of them presented half molecule as an asymmetric unit and species 2, 4 and 6 displayed an inversion center. As expected, in all cases the gold atom presented a distorted linear geometry with a S-Au-P angles between $175.06(4)^{\circ}$ and $179.16(7)^{\circ}$, and the Au-S and Au-P distances ranging from 2.286(2) Å to 2.3048(11) Å and from 2.244(2) Å to 2.2597(11) Å, respectively, which are within the expected values for S-Au-P derivatives.^{7c,8} A summary of distances and angles is presented in Fig. 1.

Only complex 5 showed intermolecular Au^I...Au^I interaction of 3.0336(11) Å, which lead to the formation of infinite chains in the crystal lattice together with point to face, C–H··· π , interactions⁹ between the phenylene spacer and one adjacent PPh₂Py unit and between two adjacent PPh₂Py molecules, see Fig. 2. Point to face interactions between the phenylene spacers and the phosphine derivative units were also observed for complexes **2** and **6**. Furthermore, these species presented S–S and S–(H-PyPh₂P) short contacts at *ca.* 3.235 Å and 2.743 Å, respectively. These short contacts and the C–H··· π interactions are responsible for their molecular packing (see ESI, Fig. S1–S3†). The closest Au^I···Au^I distances for complexes **2** and **6** are 4.565 Å and 5.484 Å respectively, values relatively long to be considered as aurophilic interactions (3.0–3.3 Å).¹⁰

In contrast, complex 4 did not show any phenylene–PPh₃ interaction and presented a torsion angle between the phenylene spacers of $1.1(4)^{\circ}$. Such torsion angle is much smaller than those found for complexes 2, 5 and 6, values between $30.63(8)^{\circ}$ and $35.31(1)^{\circ}$ (see Fig. 1). The short contacts present in complex 4 are those that were formed between the gold atom and a proton from a neighboring triphenylphosphine unit; the distance Au^I···H is 2.850 Å (ESI, Fig. S4†).

Optical properties

As commented previously L1 and L2 are similar ligands where the donating groups, the thiolates, are connected by 2 and 3 phenyl rings, respectively, acting as spacers, thus allowing the electronic communication between the two ends of the ligand. However, L3 and L4 do not have such properties due to the presence of a thioether between the two phenyl rings in the case of L3, and a methylene group between the phenyls and the donating thiolates in L4. As a result of this, a remarkable difference in the optical properties can be observed for the 4 families of complexes. UV-visible spectra of ligands L1-L4 and complexes 1-8 were measured in the solid state. Ligands L1, L2, and L3 showed the same absorption profile, a single structureless band around 300 nm that could be assigned to $\pi \rightarrow \pi^*$ transitions within the phenylene rings. By contrast L4 displayed two absorption bands centered at 215 nm and at 277 nm. In this case, the high energetic band transition could



Fig. 1 Diamond diagrams of species 2, 4, 5, 6 (hydrogen atoms omitted for clarity). Selected bond length, angles and torsion angles for: (2) Au(1)–S(1) 2.3048(11) Å, Au(1)–P(1) 2.2597(11) Å; S(1)–Au(1)–P(1) 175.06(4)°, Au(1)–S(1)–C(1) 109.34(16)°; C(9)–C(8)–C(4)–C(3) 30.63(8)°; (4) Au(1)–P(1) 2.2582(6) Å, Au(1)–S(1) 2.3035(6) Å; P(1)–Au(1)–S(1) 176.13(2)°, C(30)–S(1)–Au(1) 101.99(8)°; C(33)–C(34)–C(34)–C(35) 1.1(4)° (5) Au(1)–S(1) 2.286(2) Å, Au(1)–P(1) 2.244(2) Å, Au(1)–Au(1) 3.0336(11) Å, S(1)–Au(1)–P(1) 179.16(7)°, S(1)–Au(1)–Au(1) 76.83(5)°, P(1)–Au(1)–Au(1) 10.99(7)°, C(1)–S(1)–Au(1) 104.4(2)°; C(3)–C(4)–C(4)–C(5) 30.97(1)°; (6) Au(1)–P(1) 2.257(2) Å, Au(1)–S(1) 2.296(2) Å, P(1)–Au(1)–S(1) 178.16(9)°, Au(1)–S(1)–C(27) 104.1(3)°, C(29) C(30)–C(33) C(34) 33.77(1)°.

be assigned to $n\rightarrow\sigma^*$ transitions within the S–C bonds (–CH₂S– fragment), whereas the peak at 277 nm might be due to $\pi\rightarrow\pi^*$ transitions in the phenylene rings.¹¹ Analysis of the complexes absorption profile showed also a similar pattern to that of the single ligands. The maximum absorption is generally red-shifted by about 30 nm upon complexation, which could be tentatively assigned to transitions involving the thiolate and the conjugated phenylene rings as well as the thiolate and the pyridyl or phenyl groups from the phosphine



Fig. 2 (a) Diamond diagrams of aurophilic interactions and (b) ORTEP diagram of $C-H\cdots\pi$ interactions in complex **5**. Au(1)···Au(1): 3.0336(11) Å, C(15)-H(2)··· π : 2.894 Å, C(3)-H(22)··· π : 2.734 Å, C(21)-H(13)··· π : 2.792 Å, C(22)-H(13)··· π : 2.734 Å, C(23)-H(13)··· π : 2.866 Å.



Fig. 3 DRUV spectra of L1 and complexes 1 and 5.

fragments, *i.e.* LL'CT and ILCT respectively, see Fig. 3 for complexes 1 and 5 (see ESI, Fig. S5[†] for other ligands and Fig. S6 for the complexes). These results contrast with the typical behaviour observed for gold(1) thiolate complexes, *i.e.* electronic transitions from the thiolate to the gold metal center, LMCT,^{5b,12} highlighting the important role of the phenylene spacers in the spectroscopic properties of this family of complexes.

Emission and excitation spectra of ligands L1–L4 and complexes 1–8 were collected in the solid state at 298 K and 77 K. These experiments were performed only in the solid state due to the low solubility of the complexes. Table 2 includes the excitation and emission data and Fig. 4 shows some examples of the emission spectra of these complexes (see ESI, Fig. S7,† for the emission spectra of complexes 2, 4, 5, 7 and ligand L2).

In all cases, **L1**, **L3** and **L4** showed weak luminescence; only **L2** displayed a structured emission band centered at

Table 2 Luminescence data for complexes 1-8

	$\lambda_{\rm em}/{\rm nm} \left(\tau/\mu { m s} ight)$ 298 K	$\lambda_{ m em}/ m nm$ 77 K
1 2 3 4 5 6 7 8	442 (12), 516, 547 _{sh} , 593 _{sh} (54) ^a 448 (10), 544, 585 _{sh} , 632 _{sh} (662) ^b 467 (12), 546 (12) ^a 467 (12) ^e 418, 467, 513, 552 _{sh} ^c 464, 548, 582 _{sh} , 639 _{sh} ^d 467, 546 ^h 466	$516, 554_{\rm sh}, 598_{\rm sh}^{\ a}$ $540, 580_{\rm sh}, 630_{\rm sh}^{\ c}$ 532^d $473, 502, 541_{\rm sh}^{\ f}$ $510, 550_{\rm sh}, 590_{\rm sh}^{\ g}$ $539, 582_{\rm sh}, 632_{\rm sh}^{\ c}$ 532^g $473, 503, 542_{\rm sh}^{\ f}$

^{*a*} $\lambda_{\text{exc}} = 380 \text{ nm.}$ ^{*b*} $\lambda_{\text{exc}} = 385 \text{ nm.}$ ^{*c*} $\lambda_{\text{exc}} = 370 \text{ nm.}$ ^{*d*} $\lambda_{\text{exc}} = 400 \text{ nm.}$ ^{*e*} $\lambda_{\text{exc}} = 325 \text{ nm.}$ ^{*f*} $\lambda_{\text{exc}} = 350 \text{ nm.}$ ^{*g*} $\lambda_{\text{exc}} = 390 \text{ nm.}$ ^{*h*} $\lambda_{\text{exc}} = 360 \text{ nm.}$



Fig. 4 Emission spectra at 298 K (red line) and 77 K (blue line) of species (a) 1, (b) 6, (c) 3, (d) 8 (metallic species derived from L1, L2, L3 and L4 respectively).

ca. 400 nm that could be assigned to intra-ligand charge transfer (ILCT) transitions within the phenylene rings. Luminescence of ClAuPPh₃ and ClAuPPh₂Py, gold complexes used as the starting material in the reactions comes from transitions within the phosphine unit.13 Analysis of the photophysical properties of complexes 1-8 suggests that the different emission and excitation spectra patterns seem to be more influenced by the different ligands structure than by the metallic fragment, i.e. -(AuPPh3) and -(AuPPh2Py). Specifically, complexes 1, 2, 5 and 6, metallic species formed with L1 and L2, have a similar behavior. At room temperature they present two emission bands at ca. 450 nm and 550 nm, the latter being a well resolved structured band as well as the main component of emission. However, at 77 K the emission centered at ca. 450 nm disappears and only the well-structured band at ca. 550 nm remains, which did not show any apparent change. The energy gap between vibronic peaks, between 1200 and 1300 cm⁻¹, is typical for the excited states of aromatic systems, emphasizing the importance of the conjugated phenylene rings of the ligands L1 and L2 in the excited state. Therefore, it seems reasonable to associate the highly structured band to intra-ligand charge transfer (ILCT) transitions, involving the

thiolate and the conjugated phenylene rings. Moreover, ligand to ligand charge transfer (LL'CT) transitions can also happen from the thiolate to the pyridyl or phenyl groups from the phosphine fragments. In fact, complex 5 is thought to have both types of transitions as the emission profile is not as well structurally defined as the one seen for 1, 2 and 6, which might indicate an energy transfer process from the thiolate to the pyridyl of the phosphine fragment, in concordance with previous reports on similar complexes.6,14 Moreover, lifetimes in the microsecond domain together with the considerably large Stoke shift suggest a phosphorescent nature of this emission. It is also worth noting that the lifetime value of complex 2 (662 µs) is larger in comparison with that of complex 1 (54 µs). Such a difference was also previously seen in similar species and it could be related to the increase in the number of phenylene spacers, *i.e.* from 2 in complex 1 to 3 in complex 2.⁶ In contrast, the band at *ca.* 460 nm which is only observed at 298 K can be assigned LC (-PPh₃/-PPh₂Py) emission.^{15,16} At the same time, the short lifetime observed for this transition might indicate a fluorescent transition character. As commented previously, photophysical behavior of complexes 3, 7, 4 and 8, metallic species derived from L3 and L4 respectively, is likely to differ from those observed for complexes 1, 5, 2 and 6 due to the different electronic communication within the ligand system. Therefore, complexes 3 and 7 showed a broad band at 467 nm and a shoulder at ca. 525 nm of similar intensity, whereas complexes 4 and 8 presented a peak at 467 nm and a much smaller band around 550 nm at room temperature. These emissions are relatively weak in comparison with those seen for complexes 1, 2, 5 and 6 under the same conditions, and they are not observable with the naked eve under irradiation with a hand-held UVlamp. In both cases, the band at ca. 460 nm could be thought to be an LC (-PPh₃/PPh₂Py) transition.^{15,16} In contrast, at 77 K these complexes showed an increase in the luminescence intensity as well as changes in the band profile. A featureless broad emission band at ca. 540 nm and two differentiated bands at ca. 503 nm and 543 nm remained for complexes 3 and 7 and complexes 4 and 8, respectively. Assignment of these bands seems to have a much more complicated explanation, where not only the phenyl rings and the thiolate are implicated, but also the ancilliary ligands, *i.e.* PPh₃ and PPh₂Py, and the thioether in the case of complexes 3 and 7. Typically the emission displayed by luminescent phosphinegold(1)-thiolate fragments is attributed to ligand-to-metal charge transfer transitions (LMCT), which could be modified by changes in both the phosphine and the thiolate ligand and also by the presence of Au^I...Au^I interactions.^{5b} However, in this case, ancillary ligands, the thiolates and the phenylene spacers appear to be the primary contributors to the luminescence of these complexes, and aurophilic interactions do not seem to influence the photophysical behavior. Such results suggest that the phenylene spacers play a key role in the photophysical properties. Recently, a similar behavior was observed for gold (I)-thiolate complexes with phosphines bearing phenylene spacers.6

DFT calculations

In order to investigate the origin of the electronic transitions responsible for the absorption and emission properties of complexes 1-8, DFT calculations were carried out on representative members of the complex families. In particular, the investigation concerned complex 4 and a discrete model of complex 5, 5', featuring two L'₁AuPPh₂Py units joined by Au···Au interactions $(L'_1 = \text{monothiolate form of } L_1)$ (see the Experimental section for the computational set-up chosen). Ground state geometry optimization was performed in both cases and a good agreement was found between calculated and experimental geometrical parameters. In particular, for complex 4 the calculated Au-P (2.313 Å) and Au-S (2.327 Å) bond distances are slightly longer than the structural values, with a calculated S-Au-P angle of 178.64°, and the aromatic rings of the phenylene spacer are coplanar as observed in the crystal structure. Also the optimized geometry of complex 5' very well reproduces the structural features of the repetitive unit in the 1D chains held by Au-Au interactions in complex 5. The calculated Au-P, Au-S and Au-Au distances (2.347, 2.316, and 3.303 Å, respectively) are slightly overestimated. The gold-gold distance, although overestimated, accounts for a direct metal-metal interaction, also testified by a nonnegligible Wiberg bond index (0.150). The calculated bond angles are very close to those observed experimentally (P-Au-S 177.52, P-Au-Au 104.15, S-Au-Au 77.97°), including the torsion angle between the aromatic rings of the dithiolate spacer (34.74°).

The pattern of singlet excited states (ESs) was computed at the TD-DFT level for 4 and 5' at their optimized geometries. In both cases a good agreement was found between the experimental DRUV spectra recorded for 4 and 5 and the spectra simulated on the basis of computed vertical absorption transitions (see Fig. 3 for 5' and Fig. S8 in the ESI[†] for 4). In particular, the experimental broad absorption band observed at 320 nm for 5 is computed for 5' to be the sum of different electronic transitions, the most intense falling at 396, 321 and 249 nm and arising from the vertical transitions $S_0 \rightarrow S_{1,}$ $S_0 \rightarrow S_{16}$ and $S_0 \rightarrow S_{55}$, respectively (1, 2, and 3 in Fig. 5 and 6).



Fig. 5 Simulated absorption spectrum for **5**' in the gas phase with calculated TD-DFT singlet vertical transitions.



Fig. 6 Isosurface drawings of the Kohn–Sham MOs calculated for **5'** involved in the principal singlet vertical electronic transitions (1 and 2 in Fig. 5). Contour value = 0.05 e.

The transition $S_0 \rightarrow S_1$ (calculated at E = 3.130 eV, oscillator strength f = 0.131) presents a contribution from the 254/ HOMO $\rightarrow 255/LUMO$ and 253/HOMO-1 $\rightarrow 256/LUMO+1$ monoelectronic excitations from molecular orbitals (MOs) mainly localized on the S atom to orbitals mainly localized on the pyridine ring and therefore of the type LL'CT (Fig. 6). The transition $S_0 \rightarrow S_{16}$ (the most intense, f = 0.356; E = 3.867 eV) arises mainly from four excitations from 254/HOMO or 253/ HOMO-1 MOs to MOs mainly localized on the pyridine ring (264/LUMO+9 and 262/LUMO+7) or on the aromatic rings of the phenylene spacer (263/LUMO+8); hence, these transitions can be considered LL'CT and ILCT in nature. Transitions involving the Au^I centers fall in the UV region such as the $S_0 \rightarrow S_{55}$ calculated at 250 nm (E = 4.960 eV; f = 0.079). These MLCT transitions involve the excitations from MOs localized on the Au and S atoms to those on the ligand and the pyridine rings in particular. No transitions are found which involve a charge transfer between the two interacting Au^I centers.

Analogous conclusions can be drawn by analysing the simulated spectrum of **4**. The most intense computed vertical transitions correspond to mono-electronic excitations of the type LL'CT and ILCT. Excitations involving the metal centers are calculated at higher energies and are of the type MLCT (see ESI, Fig. S9†).

Conclusions

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In summary, we have synthesised and characterized new dithiolate gold phosphine complexes with different spacers between both thiolate units. Structural characterization by X-ray diffraction studies showed that only in one case, complex 5, aurophilic interactions are present and led to the formation of a chain polymer. Theoretical calculations combined with photophysical analysis indicate that the main emission originates from excited states due to a mixture of ILCT transition involving the thiolate and the conjugated phenylene rings and LL'CT transitions comprising the thiolate and the pyridine or phenyl from the phosphine fragment. Radiative relaxation could also occur through intersystem crossing (ISC) from these singlet excited states to triplet states. These results emphasize the importance of the phenylene spacers between the metal centers in the luminescent properties, as the typical gold thiolate emission was normally assigned to LMCT from the thiolate fragment to the metal center.

Experimental section

Instrumentation

Mass spectra were recorded on a BRUKER ESQUIRE 3000 PLUS, with the electrospray (ESI) technique and on a BRUKER MICROFLEX (MALDI-TOF), with a Dithranol or a T-2-(3-(4-*t*butyl-phenyl)-2-methyl-2-propenylidene)malononitrile matrix.

¹H, ¹³C{H} and ³¹P NMR spectroscopy, including 2D experiments, were recorded at room temperature on a BRUKER AVANCE 400 spectrometer (¹H, 400 MHz, ¹³C, 100.6 MHz, ³¹P, 162 MHz) with chemical shifts (δ , ppm) reported relative to the solvent peaks of the deuterated solvent. Infrared spectra were recorded in the range 4000–250 cm⁻¹ on a Perkin-Elmer Spectrum 100 FTIR spectrometer. UV/vis spectra were recorded with a Jasco V-670 spectrophotometer fitted with a Praying Mantis diffuse reflectance accessory. Room temperature steady-state emission and excitation spectra were recorded with a Jobin-Yvon-Horiba fluorolog FL3-11 spectrometer fitted with a JY TBX picosecond detection module. Phosphorescence lifetimes were recorded with a Fluoromax phosphorimeter

accessory containing a UV xenon flash tube. The lifetime data were fit using Origin 5.0.

Starting materials

ClAuPPh₃, ClAuPPh₂Py were prepared according to literature procedures.¹⁷ Other starting materials and solvents were purchased from commercial suppliers and used as received unless otherwise stated.

General procedure for the synthesis of the complexes 1-8

Synthesis of 1. Cs₂CO₃ (53.8 mg, 0.246 mmol) was added to a solution of L1 (22.5 mg, 0.103 mmol) in 15 ml of methanol. After stirring for few minutes a solution of ClAuPPh₃ (102.3 mg, 0.206 mmol) in 2 ml of CH₂Cl₂ was added dropwise into the mixture and it was further stirred for one hour at room temperature until a solid appeared. The precipitate was separated by filtration and washed several times with methanol and diethyl ether to give 1 as a pale green solid (85.3 mg, 73%). NMR (CD₂Cl₂ 20 °C): ³¹P NMR (162 MHz) 38.75, s; ¹H NMR (400 MHz) 7.27-7.33, m, 4H (3-thiol), 7.46-7.64, m, 34H (Ph and 2-thiol); ¹³C NMR (101 MHz) 126.7, s, (2-thiol), 130.0, d (J = 11.4 Hz), (m-Ph), 130.6, s, (ipso-Ph), 132.5, d, (J = 2.5 Hz), (p-Ph), 132.3, s, (1-thiol), 135.0, d, (J = 13.8 Hz), (o-Ph), 136.6, s, (4-thiol), 141.7, s, (3-thiol).). Anal. Calcd for C48H38Au2P2S2: C, 50.80; H, 3.38; found: C, 50.47; H, 3.15; MS (ES): m/z calcd for $C_{48}H_{38}P_2S_2Au_2$ (M⁺) 1134.1, found 1135.0.

Synthesis of 2. This compound was prepared similarly to 1 using L2 instead of L1. The product obtained was a yellow solid (90.0 mg, 81% yield).

NMR (CD₂Cl₂ 20 °C): ³¹P NMR (162 MHz) 38.77, s; ¹H NMR (400 MHz) 7.37–7.41, m, 4H (6-thiol), 7.47–7.64, m, 38H (Ph, 3-thiol and 2-thiol); ¹³C NMR (101 MHz) 127.1, s, (3-thiol), 127.5, s, (2-thiol), 130.1, d (J = 11.5 Hz), (m-Ph), 130.7, s, (ipso-Ph), 132.5, d (J = 2.5 Hz), (p-Ph), 133.5, s, (6-thiol), 135.0, d (J = 13.8 Hz), (o-Ph), 136.3, s, (5-thiol), 140.0, s, (4-thiol), 142.8, s, (1-thiol). Anal. Calcd for C₅₄H₄₂Au₂P₂S₂: C, 52.78; H, 3.61; found: C, 52.93; H, 3.23; MS(MALDI+/DIT): m/z = 1210.1 [M]⁺.

Synthesis of 3. This compound was prepared similarly to **1** using **L3** instead of **L1**. The product obtained was a yellow solid (97.5 mg, 83% yield).

NMR (CD₂Cl₂ 20 °C): ³¹P NMR (162 MHz) 38.88, s; ¹H NMR (400 MHz) 7.01–7.06, m, 4H (3-thiol), 7.42–7.60, m, 34H (Ph and 2-thiol); ¹³C NMR (101 MHz) 129.6, d (J = 11.5 Hz), (m-Ph), 130.1, s, (ipso-Ph), 130.8, s, (4-thiol), 131.2, s, (3-thiol), 132.1, d (J = 2.5 Hz), (p-Ph), 133.2, s, (2-thiol), 134.6, d (J = 13.8 Hz), (o-Ph), 142.3, 2, (1-thiol). Anal. Calcd for C₄₈H₄₈Au₂P₃S₃·0.5CH₂Cl₂: C, 48.17; H, 3.25; found: C, 47.97; H, 2.95; MS(MALDI+/DCTB): m/z = 1166.0 [M]⁺.

Synthesis of 4. This compound was prepared similarly to **1** using **L4** instead of **L1**. The product obtained was a white solid (74.4 mg, 74% yield).

NMR (CD₂Cl₂ 20 °C): ³¹P NMR (162 MHz) 37.85, s; ¹H NMR (400 MHz) 4.16, s, 4H (1-thiol), 7.28–7.33, m, 4H (4-thiol), 7.37–7.51, m, (Ph and 3-thiol); ¹³C NMR (101 MHz) 32.9, s, (1-thiol), 127.4, s, (4-thiol), 129.6, s, (3-thiol), 129.8, d (J =

11.2 Hz), (*m*-Ph), 130.9, d (J = 53.7), (*ipso*-Ph), 132.2, d (J = 2.4 Hz), (*p*-Ph), 134.9, d (J = 14.0 Hz), (*o*-Ph), 139.1, s, (5-thiol), 147.6, s, (2-thiol). Anal. Calcd for C₅₀H₄₂Au₂P₂S₂: C, 51.62; H, 3.64; found: C, 51.37; H, 3.46; MS(MALDI+/DCTB): m/z = 1162.1 [M]⁺.

Synthesis of 5. This compound was prepared similarly to **1** using ClAuPPh₂Py instead of ClAuPPh₃. The product obtained was a pale green solid (82.5 mg, 79%).

NMR (CD₂Cl₂, 20 °C): ³¹P NMR (162 MHz) δ 37.98, s; ¹H NMR (400 MHz) 7.27–7.34, m, 4H (3-thiol), 7.38–7.45, m, 2H (5-Py), 7.45–7.60, m, 16H (Ph and 2-thiol), 7.68–7.77, m, 8H (Ph), 7.82, ddd (J = 7.7, 3.8, 1.8 Hz), 2H (4-Py), 7.89, t (J = 7.4 Hz), 2H (3-Py), 8.77–8.83, m, 2H (6-Py); ¹³C NMR (101 MHz) 125.6, d (J = 2.4 Hz), (5-Py), 126.4, s (3-thiol), 129.5, d (J = 11.5 Hz), (m-Ph), 129.8, d (J = 56.9 Hz), (ipso-Ph), 131.4, d (J = 31.2 Hz), (3-Py), 132.2, d (J = 2.5 Hz), (p-Ph), 133.0, s, (2-thiol), 135.0, d (J = 13.7 Hz), (o-Ph), 136.3, s, (4-thiol), 137.0, d (J = 10.4 Hz), (4-Py), 141.2, s, (1-thiol), 151.7, d (J = 15.6 Hz), (6-Py), 155.2, d (J = 79.1 Hz), (ipso-Py). Anal. Calcd for C₄₆H₃₆Au₂N₂P₂S₂: C, 48.60; H, 3.19; N, 2.46; found: C, 48.24; H, 3.06; N, 2.28; MS(MALDI+/DIT): m/z = 1137.1 (15.5 m%) [M]⁺.

Synthesis of 6. This compound was prepared similarly to 1 using $ClAuPPh_2Py$ instead of $ClAuPPh_3$ and L2 instead of L1. The product obtained was a pale yellow solid (82.5 mg, 79% yield).

NMR (CD₂Cl₂ 20 °C): ³¹P NMR (162 MHz) 37.13, s; ¹H NMR (400 MHz) 7.34–7.46, m, 6H (5-Py and 6-thiol), 7.46–7.65, m, 20H (Ph, 3-thiol and 2-thiol), 7.68–7.78, m, 8H (Ph), 7.82, tdd (J = 7.7, 3.9, 1.8 Hz), 2H (4-Py), 7.85–7.92, m, 2H (3-Py), 8.77–8.84, m, 2H (6-Py); ¹³C NMR (101 MHz) 125.6, d (J = 2.3 Hz), (5-Py), 126.7, s, (3-thiol), 127.1, s, (2-thiol), 129.5, d (J = 11.5 Hz), (m-Ph), 131.4, d (J = 30.9 Hz), (3-Py), 132.2, d (J = 2.5 Hz), (p-Ph), 133.0, s, (6-thiol), 135.0, d (J = 13.8 Hz), (o-Ph), 135.9, s, (5-thiol), 137.0, d (J = 10.4 Hz), (4-Py), 139.6, s, (4-thiol), 142.2, s, (1-thiol), 151.7, d (J = 15.5 Hz), (6-Py). Anal. Calcd for C₅₂H₄₀Au₂N₂P₂S₂·0.5CH₂Cl₂: C, 50.23; H, 3.29; N, 2.23; found: C, 50.10; H, 3.33; N, 2.05; MS (ES): m/z calcd for C₅₂H₄₀P₂S₂N₂Au₂ (M+) 1212.1, found 1213.2.

Synthesis of 7. This compound was prepared similarly to 1 using $ClAuPPh_2Py$ instead of $ClAuPPh_3$ and L3 instead of L1. The product obtained was a pale yellow solid (64.9 mg, 71% yield).

NMR (CD₂Cl₂ 20 °C): ³¹P NMR (162 MHz) 38.01, s; ¹H NMR (400 MHz) 7.02–7.07, m, 2H (3-thiol), 7.37–7.43, m, 2H (5-Py), 7.43–7.5, m, 16H, (Ph and 2-thiol), 7.64–7.75, m, 8H (Ph), 7.75–7.87, m, 4H (4-Py and 3-Py), 8.78, ddd (J = 3.9, 1.7, 0.8 Hz), 2H (6-Py); ¹³C NMR (101 MHz) 126.1, d (J = 2.4 Hz), (5-Py), 129.9, d (J = 11.5 Hz), (m-Ph), 129.9, d (J = 57.1 Hz), (ipso-Ph), 131.3, s, (4-thiol), 131.7, s, (3-thiol), 131.8, d (J = 30.8 Hz), (3-Py), 132.6, d (J = 2.5 Hz), (p-Ph), 133.7, s, (2-thiol), 135.4, d (J = 13.7 Hz), (o-Ph), 137.5, d (J = 10.3 Hz), (4-Py), 142.6, s, (1-thiol), 152.1, d (J = 15.7 Hz), (6-Py), 155.5, d (J = 79.5 Hz), (ipso-Py). Anal. Calcd for C₄₆H₃₆Au₂N₂P₂S₃: C, 47.27; H, 3.10; N, 2.40; found: C, 46.94; H, 3.29; N, 2.15; MS(MALDI+/DIT): m/z = 1168.9 (18.73%) [M]⁺.

Synthesis of 8. This compound was prepared similarly to **1** using ClAuPPh₂Py instead of ClAuPPh₃ and **L4** instead of **L1**. The product obtained was a white solid (75.6 mg, 80% yield).

NMR (CD₂Cl₂ 20 °C): ³¹P NMR (162 MHz) 35.97, s wide; NMR (CDCl₃ 20 °C): ¹H NMR (400 MHz) 4.24, s, 4H (1-thiol), 7.25–7.29, m, 2H (4-Py), 7.29–7.33, m, 4H (4-thiol), 7.33–7.47, m, 12H (Ph), 7.49–7.64, m, 14H (Ph, C-Py and 3-thiol), 7.70, t (J = 7.5 Hz), 2H (4-Py), 8.71, ddd (J = 3.9, 1.7, 0.8 Hz), 2H (6-Py); ¹³C NMR (101 MHz) 32.6, s, (1-thiol), 125.0, d (J =2.2 Hz), (5-Py), 127.0, s, (4-thiol), 128.9, s, (3-thiol), 129.0, d (J = 2.4 Hz), (m-Ph), 131.4, d (J = 32.3), (3-Py), 131.5, d (J =2.3 Hz), (p-Ph), 134.6, d (J = 14.1 Hz), (o-Ph), 136.43, d (J =10.6 Hz), (4-Py), 138.6, s, (5-thiol), 146.7, s, (2-thiol), 151.2, d (J = 14.4 Hz), (6-Py). Anal. Calcd for C₄₈H₄₀Au₂N₂P₂S₂: C, 49.49; H, 3.46; N, 2.40; found: C, 49.28; H, 3.39; N, 2.24; MS(MALDI+/DIT): m/z = 1164.9 (18.80%) [M]⁺.

Crystallography

The crystals were mounted in an inert oil on glass fibers and transferred to the cold gas stream of an Xcalibur Oxford Diffraction (2, 4, 6) or a Bruker Smart 1000 CCD (5) diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Scan type: ω . Absorption correction based on multiple scans was applied using spherical harmonics implemented in SCALE3 ABSPACK¹⁸ scaling algorithm (2, 4, 6) or with a program SADABS (5). The structures were solved by direct methods and refined on F^2 using the program SHELXL-97.¹⁹ All non-hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms were included in calculated positions and refined using a riding model. Refinements were carried out by full-matrix least-squares on F^2 for all data. Additional details of the data collection and refinement are given in Table 3. CCDC 976386 (2), 976387 (4), 976388 (5) and 976389 (6).

DFT calculations

Quantum-chemical calculations based on the Density Functional Theory (DFT) were carried out on compounds 4 and 5' by adopting the mPW1PW²⁰ functional and using the commercial suite of program Gaussian09.21 Schäfer, Horn, and Ahlrichs double- ζ plus polarization all-electron basis sets (BSs)²² were used for all atomic species but gold, for which SBKJC BSs²³ with relativistic effective core potentials (RECP) were adopted. The geometry optimizations (with tight cut-off values on forces and step size) were performed without introducing any structural simplification or symmetry restrain. In all cases, a pruned (99 590) grid was adopted in order to avoid imaginary frequencies. NBO populations²⁴ and Wiberg bond indices²⁵ were calculated at the optimized geometries. Time-dependent (TD) DFT calculations were carried out in order to understand their absorption/emission spectroscopic features. The programs GaussView²⁶ and Molden 5.0²⁷ were used to investigate the natural charge distributions and MOs' shapes and to generate the simulated absorption spectra based on TD-DFT calculations.

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Table 3	X-ray crystallographic data of complexes 2, 4, 5 and 6	5
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Compound	2	4	5	6
Formula	$C_5H_{42}Au_2P_2S_2\cdot 2(CH_2Cl_2)$	$C_{50}H_{42}Au_{2}P_{2}S_{2}$	$C_{46}H_{36}Au_2N_2P_2S_2$	$C_{52}H_{40}Au_2N_2P_2S_2$
$M_{ m r}$	1380.72	1162.83	1136.76	1212.85
Crystal size (mm)	0.070 imes 0.06 imes 0.05	0.24 imes 0.18 imes 0.12	0.24 imes 0.20 imes 0.18	0.07 imes 0.06 imes 0.05
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	P2(1)/n	C2/c	$P\bar{1}$
Cell constants:				
a (Å)	23.2023(4)	14.4157(2)	14.480(3)	8.0066(16)
b (Å)	13.8267(2)	9.02110(10)	15.850(3)	10.946(2)
c (Å)	18.1353(3)	16.5956(2)	16.890(3)	13.085(3)
α(°)	90	90	90	83.58(3)
β(°)	104.409(2)	105.8050(10)	97.86(3)	73.91(3)
γ (°)	90	90	90	80.08(03)
$V(Å^3)$	5635.0(16)	2076.59(4)	3840.0(13)	1082.9(4)
Z	4	2	4	1
$D_{\rm x} ({\rm Mg}{\rm m}^{-3})$	1.628	1.860	1.966	1.860
$\mu (\mathrm{mm}^{-1})$	5.456	7.270	7.862	6.976
F(000)	2680	1124	2184	586
$T(\mathbf{K})$	100(2)	100(2)	100(2)	100(2)
$2\theta_{\rm max}$	55	55	55	55
No. of refl.: measured	27 864	20 406	24 212	6385
Independent	5209	3838	3558	4002
Transmissions	0.7686-0.6971	0.4758-0.2743	0.3319-0.2541	0.7218-0.6409
R _{int}	0.0323	0.0209	0.0567	0.0628
Parameters	334	253	245	271
Restraints	56	0	0	0
Goodness of fit on F^2	1.068	1.059	1.023	1.026
wR (F^2 , all refl.)	0.0746	0.0333	0.0998	0.0790
$R(I > 2\sigma(I))$	0.0287	0.0133	0.0383	0.0489
Max. $\Delta \rho$ (e Å ⁻³)	2.255	0.430	2.600	1.209

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