Design, Synthesis, Photophysics, and Anion-Binding Studies of Bis(dicyclohexylphosphino)methane-Containing Dinuclear Gold(I) Thiolate Complexes with Urea Receptors

Xiaoming He,[a] Fernando Herranz,[b, c] Eddie Chung-Chin Cheng,[a] Ramon Vilar,*[b] and Vivian Wing-Wah Yam*[a]

Abstract: A series of bis(dicyclohexylphosphino)methane (dcpm)-containing gold(I) thiolate complexes with urea receptors, **1–3**, has been successfully designed and synthesized, and their photophysical and anion-binding properties have been studied. The linker between the thiolate and the urea group, and the electronic environment of the urea moiety, have been found to exert a great influence on the photophysical and anion-binding properties of the complexes. Complex **3** displays an intense long-lived orange-red luminescence at around 620 nm in the solid state and in the glass state at 77 K, which is considerably red shifted from the band seen in a solution of dichloromethane at room temperature, suggesting the presence of Au···Au interactions. Upon introducing an electron-withdrawing NO_2 group, complex **1** was found to show high selectivity and sensitivity for F^- through a drastic color change from yellow to red. The anion-binding constants of the complexes have been determined from electronic absorption and ^1H NMR spectroscopy titration studies and the data were found to fit well to a 1:1 binding model for the interactions between the complexes and the anions. Complexes **1** and **2** show the same anion selectivity trend of $F^- > AcO^- > H_2PO_4^- > Cl^- \approx Br^- \approx I^-$, which is consistent with the trend in anion basicity. In addition, complex **1** has been shown to exhibit higher binding affinity for anions compared with those of complexes **2** and **3**, probably due to the higher acidity of the urea moiety as a result of the introduction of the NO_2 group.

Keywords: anions · gold · P ligands · S ligands · urea receptors

Introduction

The chemistry of gold has grown rapidly in recent years, particularly as a result of the growing interest in its rich photophysical properties and associated Au···Au interactions.[1,2] Many studies have shown that the presence of Au···Au interactions plays an important role in governing the unique electronic absorption and emission features of these complexes. Gold(I) thiolate complexes are among the most important classes of gold(I) complexes due to their wide range of applications in medicine[3] and surface technology,[4] as well as their capacity to exhibit strong photoluminescence.[1,5] Their photoluminescence has often been attributed to thiolate-to-gold ligand-to-metal charge-transfer (LMCT) excited states, in some cases modified by Au···Au interactions.[5] The rich photophysical properties of gold(I) complexes have rendered them excellent candidates in the design of optically addressable chemosensors. We have reported a number of gold(I) complexes with different receptors for cation binding.[6–11] Utilization of the switching on

[a] Dr. X. He, Dr. E. C.-C. Cheng, Prof. Dr. V. W.-W. Yam
Centre for Carbon-Rich Molecular and Nano-Scale
Metal-Based Materials Research, Department of Chemistry
and HKU-CAS Joint Laboratory on New Materials
The University of Hong Kong
Pokfulam Road, Hong Kong (P.R. China)
Fax: (+852) 2857-1586
E-mail: wwyam@hku.hk

[b] Dr. F. Herranz, Dr. R. Vilar
Department of Chemistry
Imperial College London, London SW7 2AZ (UK)
Fax: (+44) 2075941139
E-mail: r.vilar@imperial.ac.uk

[c] Dr. F. Herranz
Instituto de Estudios Biofuncionales, Universidad Complutense
Centro de Investigación Biomédica
en Red de Enfermedades Respiratorias (CIBERES)
Paseo Juan XXIII n° 1, 28040 Madrid (Spain)

and off of Au···Au interactions has also been successfully demonstrated as a novel strategy for optical signal transduction for chemosensing.[8–10]

Studies of anion binding and sensing have become increasingly widespread as the realization of the important roles that anions play in biology, medicine, and the environment has grown.[12–14] Anion receptors that are positively charged or neutral represent two important classes. Those of the former type mainly rely on electrostatic interactions, whereas the latter are mainly based on hydrogen-bonding interactions. In contrast to electrostatic interactions, hydrogen-bonding interactions, which are capable of discriminating between anions of different geometries and hydrogen-bonding requirements due to their directional nature, have been extensively studied. The urea unit, as an excellent hydrogen-bond donor forming two hydrogen bonds, has been widely used in the construction of various anion receptors. There is also a current interest in the synthesis of colorimetric neutral chemosensors for anions.[15] A number of previous reports have shown that the covalent linking of a chromogenic fragment to one or more urea moieties is capable of establishing effective and selective colorimetric chemosensing through visible color changes.[16]

Anion receptors based on transition-metal complexes constitute a fast-growing field of research in this area, due to the diversity of their geometries, redox activities, photophysical properties, and their abilities to act as Lewis acids. A wide range of metal complexes, such as those of iron(II),[17] cobalt(II),[17] ruthenium(II),[18] rhenium(I),[19] palladium(II),[20] platinum(II),[21] copper(II),[22] and zinc (II),[23] have been used in the design of anion sensors. However, examples of anion receptors based on gold(I) complexes are rare in the literature.[24]

In our previous work, we demonstrated the successful use of a series of dinuclear gold(I) complexes with bridging diphosphines and crown-ether-functionalized thiolate ligands for metal-ion sensing.[8] We have also previously shown that a range of urea-substituted thiolates are versatile ligands for the development of metal-based anion receptors.[20] As an extension of the earlier research on gold(I) chemistry and host–guest chemistry,[6–11,20] we report herein the design, synthesis, and photophysical properties of a series of dinuclear phosphine gold(I) thiolate complexes **1–3** (Scheme 1) with bridging bis(dicyclohexylphosphino)methane (dcpm) auxiliary ligand and various urea receptor pendants. The anion-binding abilities of these complexes have been investigated by UV/Vis spectrophotometry and NMR spectroscopy. The
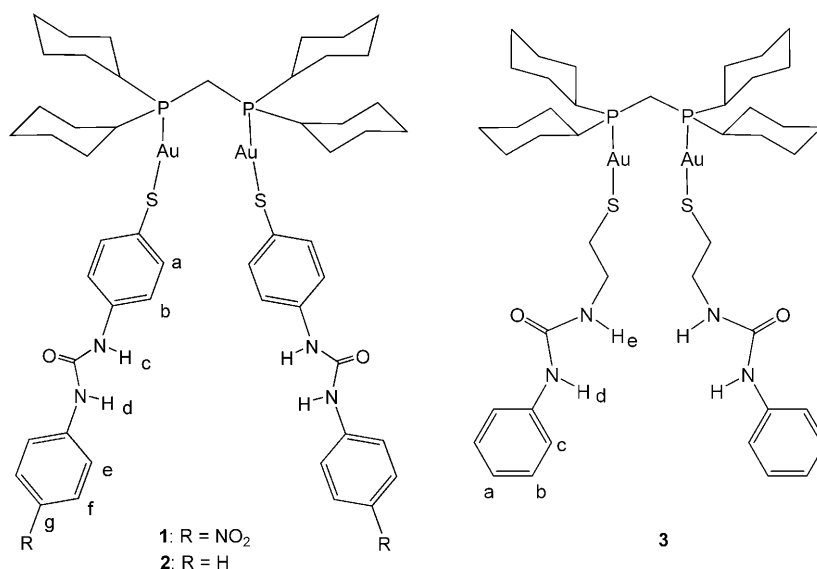
Scheme 1. Structures of complexes **1–3**.

presence of the electron-withdrawing nitro group in complex **1** was expected to enhance the acidity and hence the hydrogen-bond donating property of the receptor, which would help to increase its binding affinity to anions. In addition, the strong absorption in the visible region of the chromogenic nitrophenyl group would provide an opportunity for naked-eye detection of the anion-recognition process.

Experimental Section

Synthesis

phere. The precipitate formed was collected by filtration and washed twice with CH_2Cl_2 to yield the product as a yellow solid. Yield: 1.4 g, 97%. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, TMS): $\delta = 8.00$ (m, 8H; SC_6H_4), 8.21 (d, $J = 7.2$ Hz, 4H; $C_6H_4NO_2$), 8.72 (d, $J = 7.2$ Hz, 4H; $C_6H_4NO_2$), 9.62 (s, 2H; NH), 10.00 ppm (s, 2H; NH); MS (FAB$^+$): m/z: 576 [M]$^+$; elemental analysis calcd (%) for $C_{26}H_{20}N_6O_6S_2$: C 54.16, H 3.50, N 14.58; found: C 54.33, H 3.72, N 14.57.

HSC$_6$H$_4$NHCONHC$_6$H$_4$NO$_2$-4: This compound was prepared according to a procedure similar to that used for $C_6H_5NHCONHC_6H_4SH$.[24] Concentrated HCl (5 drops) was added to a suspension of [4-$NO_2C_6H_4NHCONHC_6H_4S$-]$_2$ (0.95 g, 1.65 mmol) and triphenylphosphine (0.45 g, 1.72 mmol) in dioxane/water (17:3, v/v; 40 mL) and the mixture was allowed to stir overnight at 60 °C under a nitrogen atmosphere. The solvent was then evaporated under reduced pressure, the residue was redissolved in 5% aqueous NaOH solution (20 mL), and the resulting solution was washed three times with diethyl ether. 10% HCl (20 mL) was added to the aqueous phase to precipitate out the desired product, which was collected by filtration and washed with water. Subsequent drying gave the product as a yellow solid. Yield: 0.74 g, 77%. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, TMS): $\delta = 5.23$ (s, 1H; SH), 7.24 (d, $J = 8.4$ Hz, 2H; SC_6H_4), 7.38 (d, $J = 8.4$ Hz, 2H; SC_6H_4), 7.68 (d, $J = 9.2$ Hz, 2H; $C_6H_4NO_2$), 8.19 (d, $J = 9.2$ Hz, 2H; $C_6H_4NO_2$), 8.90 (s, 1H; NH), 9.42 ppm (s, 1H; NH); MS (ESI$^+$): m/z: 289 [M]$^+$; elemental analysis calcd (%) for $C_{13}H_{11}N_3O_3S$: C 53.97, H 3.83, N 14.52; found: C 54.01, H 3.99, N 14.78.

[Au$_2$(dcpm)(SC$_6$H$_4$NHCONHC$_6$H$_4$NO$_2$-4)$_2$] (1): Triethylamine (50 μL, 0.36 mmol) was added to a solution of [Au$_2$(dcpm)Cl$_2$] (50 mg, 0.057 mmol) and HSC$_6$H$_4$NHCONHC$_6$H$_4$NO$_2$-4 (35 mg, 0.12 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 2 h at room temperature, after which the solvent was removed under reduced pressure. The residue was recrystallized by dissolving it in CH_2Cl_2 and then diffusing diethyl ether vapor into the solution to give **1** as a yellow solid. Yield: 72 mg, 92%. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, TMS): $\delta = 1.20$–2.30 (m, 46H; C_6H_{11} and PCH$_2$P), 7.17 (d, $J = 8.5$ Hz, 4H; SC_6H_4), 7.31 (d, $J = 8.5$ Hz, 4H; SC_6H_4), 7.66 (d, $J = 9.2$ Hz, 4H; $C_6H_4NO_2$), 8.16 (d, $J = 9.2$ Hz, 4H; $C_6H_4NO_2$), 8.69 (s, 2H; NH), 9.32 ppm (s, 2H; NH); ^{31}P NMR (202 MHz, [D$_6$]DMSO, 298 K, 85% H$_3$PO$_4$): $\delta = 49.40$ ppm; MS (FAB$^+$): m/z: 1378 [M]$^+$, 1575 [$M+$Au]$^+$; elemental analysis calcd (%) for $C_{51}H_{66}Au_2N_6O_6P_2S_2$: C 44.42, H 4.82, N 6.09; found: C 44.19, H 4.82, N 6.07.

[Au$_2$(dcpm)(SC$_6$H$_4$NHCONHC$_6$H$_5$)$_2$] (2): This compound was synthesized according to a procedure similar to that used for **1**, except that HSC$_6$H$_4$NHCONHC$_6$H$_5$ (29 mg, 0.12 mmol) was used in place of HSC$_6$H$_4$NHCONHC$_6$H$_4$NO$_2$-4. Subsequent recrystallization of the product by diffusion of diethyl ether vapor into a solution in CH_2Cl_2 gave **2** as a white solid. Yield: 66 mg, 90%. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, TMS): $\delta = 1.15$–2.28 (m, 46H; C_6H_{11} and PCH$_2$P), 6.93 (t, $J = 7.4$ Hz, 2H; C_6H_5), 7.13 (d, $J = 8.0$ Hz, 4H; SC_6H_4), 7.25 (m, 8H; C_6H_5 and SC_6H_4), 7.40 (d, $J = 8.0$ Hz, 4H; C_6H_5), 8.42 (s, 2H; NH), 8.53 ppm (s, 2H; NH); ^{31}P NMR (202 MHz, [D$_6$]DMSO, 298 K, 85% H$_3$PO$_4$): $\delta = 49.35$ ppm; MS (FAB$^+$): m/z: 1045 [$M-$L]$^+$, 1289 [M]$^+$, 1486 [$M+$Au]$^+$; elemental analysis calcd (%) for $C_{51}H_{68}Au_2N_4O_2P_2S_2 \cdot C_4H_{10}O$: C 48.46, H 5.77, N 4.11; found: C 48.88, H 5.43, N 4.66.

[Au$_2$(dcpm){S(CH$_2$)$_2$C$_6$H$_4$NHCONHC$_6$H$_5$}$_2$] (3): A mixture of [Au{S-(CH$_2$)$_2$NHCONHC$_6$H$_5$}]$_\infty$ polymer (75 mg, 0.19 mmol) and dcpm (36 mg, 0.087 mmol) in CH_2Cl_2 (15 mL) was stirred overnight under N$_2$. The mixture was then filtered and the solvent was removed under reduced pressure. The residue was redissolved in CH_2Cl_2 and recrystallized by the diffusion of diethyl ether vapor into this solution to give **3** as a white solid. Yield: 89 mg, 80%. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, TMS): $\delta = 1.20$–2.20 (m, 46H; C_6H_{11} and PCH$_2$P), 3.32 (t, $J = 5.0$ Hz, 4H; SCH$_2$C), 3.58 (q, $J = 5.0$ Hz, 4H; CCH$_2$N), 6.70 (s, 2H; NH), 6.90 (t, $J = 7.8$ Hz, 2H; C_6H_5), 7.19 (t, $J = 7.8$ Hz, 4H; C_6H_5), 7.49 (d, $J = 7.9$ Hz, 4H; C_6H_5), 8.13 ppm (s, 2H; NH); ^{31}P NMR (202 MHz, CDCl$_3$, 298 K, 85% H$_3$PO$_4$): $\delta = 48.13$ ppm; MS (FAB$^+$): m/z: 998 [$M-$L]$^+$, 1194 [$M+$1]$^+$, 1390 [$M+$197]$^+$; elemental analysis calcd (%) for $C_{43}H_{68}Au_2N_4O_2P_2S_2 \cdot H_2O$: C 42.63, H 5.82, N 4.63; found: C 42.70, H 5.77, N 4.79.

Physical measurements and instrumentation: UV/Vis spectra were recorded on a Hewlett–Packard 8452 A diode-array spectrophotometer. ^{1}H NMR spectra, with chemical shifts relative to tetramethylsilane (Me$_4$Si), were recorded on a Bruker Avance 400 FT-NMR spectrometer. Positive-ion fast-atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Positive electrospray-ionization (ESI) mass spectra were obtained on a Finnigan LCQ mass spectrometer. Elemental analyses of the new compounds were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry of the Chinese Academy of Sciences in Beijing.

Steady-state excitation and emission spectra were recorded on a Spex Fluorolog-3 model FL3–211 fluorescence spectrofluorimeter equipped with an R2658P PMT detector. All solutions for photophysical studies were prepared under high vacuum in a 10 cm^3 round-bottomed flask equipped with a sidearm 1 cm pathlength fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell through no less than four successive freeze-pump-thaw cycles. Solid-state photophysical measurements were carried out with the solid sample loaded in a quartz tube inside a quartz-walled Dewar flask. Measurements of ethanol/methanol/dichloromethane (4:1:1, v/v) glasses or solid samples at 77 K were conducted by filling the optical Dewar flask with liquid nitrogen. Excited-state lifetimes of samples in fluid solution or in the solid state were measured using a conventional laser system. The excitation source used was the 355 nm output (third harmonic, 8 ns) of a Spectra Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence decay signals were detected by means of a Hamamatsu R928 photomultiplier tube, recorded on a Tektronix model TDS-620 A (500 MHz, 2 GSs^{-1}) digital oscilloscope, and analyzed by using a program for exponential fits.

Binding constant determination: Electronic absorption spectral titrations for binding constant determination were performed on a Hewlett–Packard 8425 A diode-array spectrophotometer at 25 °C, which was controlled by a Lauda RM6 compact low-temperature thermostat. Supporting electrolyte (0.1 mol dm^{-3} nBu$_4$NPF$_6$) was added to maintain constant ionic strength of the sample solution during the titration. Binding constants for 1:1 complexation were obtained by a nonlinear least-squares fit[28] of the absorbance (A) versus the concentration of anion added (C_A) according to the following equation [Eq. (1)]:

$$A = A_0 + \frac{A_{\text{lim}}-A_0}{2C_0}\{C_0 + C_A + \frac{1}{K_s} - [(C_0 + C_A + \frac{1}{K_s})^2 - 4C_0C_A]^{1/2}\} \qquad (1)$$

in which A_0 and A are the absorbances of the complex at a selected wavelength in the absence and presence of the anion, respectively, [C_0] is the total concentration of the complex, [C_A] is the concentration of the anion, A_{lim} is the limiting value of absorbance in the presence of excess anion, and K_s is the stability constant.

^{1}H NMR spectroscopy titrations for binding constant determination were performed on a Bruker Avance 400 FT-NMR spectrometer. Each NMR spectroscopy titration was carried out three times at 300 K in [D$_6$]DMSO (complexes **1** and **2**) or CDCl$_3$ (complex **3**). ^{1}H NMR spectroscopy titrations were performed to quantify K_s values. These titrations were carried out by following the chemical induced shift (CIS) in one or several protons of the host as the concentration of the complex was changed by the addition of one of the components. There are many ways of fitting the data from a titration, but nonlinear curve-fitting is generally accepted as the method with the lowest degree of error in the determination of K_s values, in comparison to others that employ approximations to reach a linear relationship between δ and K_S To fit the experimental data and determine the binding constants, the EQNMR program[29a] and the Sigmaplot program[29b] were used. The relationship between chemical shifts (δ), concentrations of host H, guest G, and complex C, and the stability constant K_s for a 1:1 stoichiometry was considered according to the following equation [Eq. (2)]:

$$\delta_{\text{OBS}} = (\delta_C - \delta_H)\left[\frac{1 + \frac{[G]}{[H]} + \frac{1}{K_s[H]}}{2} - \left(\frac{(1 + \frac{[G]}{[H]} + \frac{1}{K_s[H]})^2}{4} - \frac{[G]}{[H]}\right)^{1/2}\right] + \delta_H \qquad (2)$$

To obtain K_s values with the lowest error, the titrations were carried out in the 20–80% saturation range for the compound of which the CIS was being followed. This condition determined the concentrations of both the host and guest to be used in the titrations and a calculation was necessary to find those concentrations that best covered the whole saturation range to obtain the maximum information from the titration curve. The error determined by this methodology is intrinsic to the measurement method and it is not reflected by the standard deviation (S_d), which is a measure of the goodness of fit of the data employed.

Job's plots: A series of solutions covering the whole range of molar fractions for host or guest, keeping the total concentration constant, was prepared. The chemical shifts for each solution were measured, and by plotting the molar fraction of the host versus the product of the increment in chemical shift and host concentration (Job's plot), a curve was generated, the maximum point of which indicated the stoichiometry of the complex.

Results and Discussion

Synthesis and characterization: Complexes **1** and **2** could be readily prepared in high yield by direct ligand substitution reaction of two equivalents of HS–R with [Au₂(dcpm)Cl₂]. For complex **3**, this method proved unsuccessful, and instead the complex was synthesized by depolymerization of the gold(I) polymer [Au(S–R)]∞ with the phosphine ligand. The failure of the direct substitution may have been due to the lower acidity of the aliphatic thiol group compared with the aryl thiol group, which renders the deprotonation step difficult. All of the newly synthesized complexes were characterized by ¹H NMR and ³¹P NMR spectroscopy, and by FAB- or ESI-MS, and gave satisfactory elemental analyses. Complexes **1** and **2** were found to be soluble only in DMSO, and almost insoluble in CH₂Cl₂, CHCl₃, and THF, whereas complex **3** could be dissolved in all of these common organic solvents. The poor solubilities of **1** and **2** in common organic solvents may be ascribed to their tendency to form intermolecular hydrogen bonds in these media, making them only soluble in DMSO, in which such intermolecular hydrogen bonds would most likely be destroyed. On the other hand, complex **3** is expected to mainly form intramolecular hydrogen bonds and therefore be soluble in a wider range of solvents. The formation of intramolecular hydrogen bonds in **3** was supported by the observation of low-energy emissions in the solid state and in a glass at low temperature (see below).

Electronic absorption and emission properties: All of the complexes showed intense high-energy absorption bands in the region 240–300 nm in fluid solution. A low-energy tail extending to about 400 nm and a low-energy band at 310 nm

were also observed for **2** and **3**, respectively. Introduction of the electron-withdrawing NO₂ group on the thiolate ligand in complex **1** gave rise to an additional intense low-energy absorption band at around 360 nm, which could be ascribed to an intramolecular charge-transfer transition from the amide to the NO₂ group. The photophysical data for complexes **1–3** are tabulated in Table 1. On the basis of previous studies on related phosphinogold(I) thiolate systems,[5] the high-energy absorption bands at around 240–300 nm were tentatively assigned as the intraligand transitions of the phosphine and urea-functionalized thiolate ligands, whereas the low-energy tail for **2** and the low-energy band at around 310 nm for **3**, which were absent in the spectra of the corresponding phosphinogold(I) chloride and the free ligands, were characteristic of the phosphinogold(I) thiolate systems and were tentatively assigned to the thiolate-to-gold ligand-to-metal charge-transfer (LMCT) transition.

Table 1. Photophysical data for complexes **1–3**.

Complex	Absorption[a] λ_{abs}/nm ($\varepsilon \times 10^{-4}$/dm³ mol⁻¹ cm⁻¹)	Medium T/K	Emission λ_{em}/nm (τ_0/μs)
1	280 (3.74), 300 (3.66), 360 (3.87)	DMSO (298)	–[b]
		solid (298)	–[b]
		solid (77)	–[b]
		glass (77)	–[b]
2	288 (5.52)	DMSO (298)	443 (0.14), 534 (55)
		solid (298)	570 (2.57, 0.22)
		solid (77)	515 (23.56, 5.05)
		glass (77)	–[c]
3	244 (5.36), 272 sh (1.18), 310 sh (0.33)	CH₂Cl₂ (298)	531 (0.80)
		solid (298)	576 (1.75)
		solid (77)	620 (18.4)
		glass (77)[d]	620 (8.9)

[a] In DMSO solution. [b] Non-emissive. [c] Not soluble. [d] In EtOH/MeOH/CH₂Cl₂ (4:1:1, v/v).

Excitation of complexes **2** and **3** in degassed solution at room temperature gave rise to intense long-lived low-energy emissions at around 530–560 nm. A high-energy emission band at around 443 nm was also obvious for **2**, but its intensity was lower. However, complex **1** was non-emissive, probably due to the quenching effect of the NO₂ group. With reference to previous spectroscopic work on gold(I) phosphine thiolate complexes,[1,5,8] the lower-energy emissions in **2** and **3** with lifetimes in the microsecond range were tentatively assigned as originating from a thiolate-to-gold ligand-to-metal charge-transfer (LMCT) excited state of phosphorescent nature. The high-energy emission of **2**, which has a lifetime in the nanosecond regime, was tentatively assigned to states arising from a metal-perturbed intraligand transition of fluorescent nature.

Interestingly, at low temperature (77 K), excitation of **3** in the solid state and in a glass led to an intense long-lived orange-red luminescence at about 620 nm, which exhibited a large red shift from that in dichloromethane solution at room temperature, suggesting the presence of Au···Au interactions in the solid state and in the glass state at 77 K. Such an interesting phenomenon could be thought of as the over-

all result of the complementary aurophilic interaction and intramolecular urea–urea hydrogen-bonding interaction. Self-assembly through inter- or intramolecular urea–urea hydrogen-bonding interactions has proved to be an important and predictable secondary noncovalent bond, similar to the hydrophobic interactions, π–π interactions, and van der Waals forces that have commonly been exploited in the design of self-assembled supramolecular architectures, such as sol-gels,[30] supramolecular capsules,[31] fibers,[32] and columnar structures with guest-accessible channels.[33] It is likely that, in the solid state, complex **3** could form intramolecular urea–urea hydrogen bonds that could force the two gold atoms into close proximity, whereas in solution the Au···Au interactions would no longer exist. Such a cooperative aurophilic interaction and hydrogen-bonding interaction to afford supramolecular entities has also been reported previously.[34]

Anion-binding properties

Electronic absorption spectroscopic studies: The anion-binding abilities of complexes **1–3** towards various anions were studied by the electronic absorption spectrophotometric method. All of the anions used were in the form of tetra-*n*-butylammonium salts. Distinct UV/Vis spectral changes were observed upon the addition of basic anions, such as F⁻, AcO⁻, or $H_2PO_4^-$, whereas the addition of Cl⁻, Br⁻, or I⁻ led to negligible changes. This may be rationalized in terms of the basic anions binding strongly with the hydrogen-bond donor with acid character. The most pronounced effect was seen in the UV/Vis spectrum of complex **1** upon addition of F⁻, namely a drastic color change from yellow to red, making **1** a highly selective colorimetric sensor for F⁻. The interaction of receptor **1** with F⁻ was investigated in detail by UV/Vis spectrophotometric titration studies, whereupon rather complex spectral behavior was observed.

Figure 1 shows the evolution of the electronic absorption spectrum of **1** in solution in DMSO (0.1 M *n*Bu₄NPF₆) upon

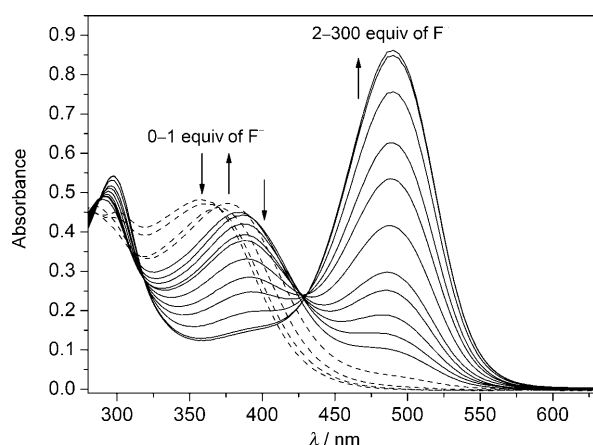Figure 1. UV/Vis spectral changes of [Au₂-(dcpm)(SC₆H₄NHCONHC₆H₄NO₂-4)₂] (**1**) (1.17×10^{-5} M) in DMSO (0.1 M *n*Bu₄NPF₆) upon addition of F⁻.

addition of F⁻, in which two different stages can be discerned. In the range of 0–1 equivalents of F⁻ added, the band at 358 nm was found to gradually decrease in intensity, while a lower-energy band developed at 373 nm, accompanied by the emergence of two isosbestic points at 288 and 370 nm, indicating a clean reaction with only two absorbing species in the solution. This stage could be interpreted in terms of the formation of hydrogen-bonding interactions between F⁻ and complex **1**. No noticeable change in color was seen to accompany this process. When more F⁻ was added, a new lower-energy absorption band at about 490 nm gradually appeared, with two isosbestic points at 314 and 428 nm. Accompanying this stage, a drastic color change from yellow to red was observed. The new band at 490 nm responsible for this drastic color change could be attributed to deprotonation of **1**. This was confirmed by Brønsted acid–base titration with the strong base *n*Bu₄NOH, which led to similar UV/Vis spectral changes. Such deprotonation could be ascribed to the acidity of the NH group and the strong basicity of F⁻, as well as the high stability of the $[HF_2]^-$ species.[16] The fluoride-induced deprotonation process was also found to be fully reversible. Addition of methanol as a protic solvent resulted in reversible color change from red to yellow, as befits the well-known fact that protic solvents can compete with the urea NH moiety for F⁻.[15]

The interactions between **1** and other basic anions ($H_2PO_4^-$, AcO⁻) were also investigated. Figure 2 shows the evolution of the electronic absorption spectrum of **1** in solu-
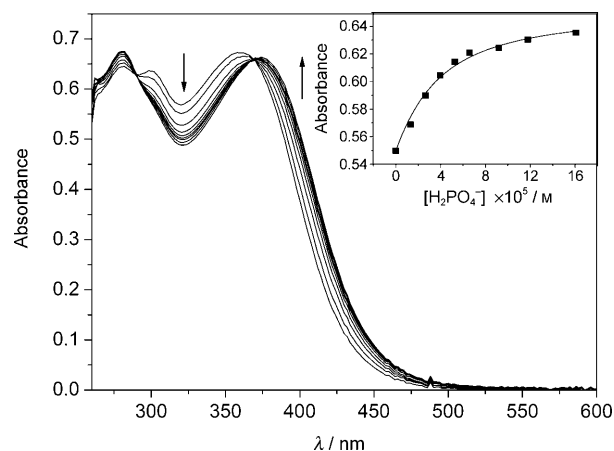

Figure 2. UV/Vis spectral changes of **1** (1.76×10^{-5} M) in DMSO (0.1 M *n*Bu₄NPF₆) upon addition of $H_2PO_4^-$. Inset: Plot of absorbance at 385 nm as a function of $H_2PO_4^-$ concentration and its theoretical fit for the 1:1 binding of complex **1** with $H_2PO_4^-$.

tion in DMSO (0.1 M *n*Bu₄NPF₆) upon addition of $H_2PO_4^-$. It can be seen that the absorbance at 358 nm gradually decreased, while a lower-energy band at 374 nm developed, with two isosbestic points at 290 and 370 nm. The UV/Vis spectral changes were similar to those observed upon the formation of hydrogen-bonding interactions between complex **1** and F⁻. The inset in Figure 2 shows close agreement between the experimental data and the theoretical fit for 1:1

binding. Similar UV/Vis spectral changes were observed for AcO⁻. However, no obvious color changes could be observed in the presence of an excess of $H_2PO_4^-$ or AcO⁻, further suggesting that **1** could serve as a selective colorimetric sensor for F⁻ (Figure 3). Unlike in the case of **1**, no drastic
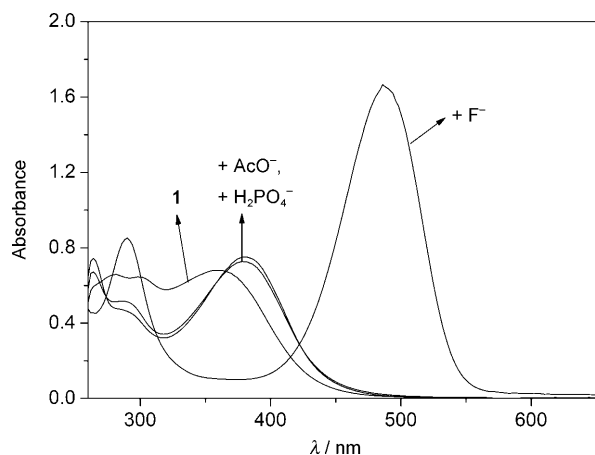

Figure 3. UV/Vis spectral changes of **1** (2.0×10^{-5} M) in DMSO upon addition of 300 equiv of F⁻, AcO⁻, and $H_2PO_4^-$.

color changes or significant NMR spectral changes of the aromatic proton signals were seen to accompany the interaction between F⁻ and complex **2**. This might be ascribed to the fact that the deprotonation induced by F⁻ became more difficult due to the rather weak acidity of the urea NH moiety in the absence of the electron-withdrawing NO_2 group.

The anion-binding constants of complexes **1**–**3** were obtained by nonlinear least-squares fits of the absorbance versus the concentration of the added anions. The titration data showed a nice fit to a 1:1 binding model. The binding constants for different anions are summarized in Table 2. Complexes **1** and **2** in DMSO showed the same anion selectivity trend of $F^- > AcO^- > H_2PO_4^- > Cl^- \approx Br^- \approx I^-$, which is consistent with the trend in anion basicity. In addition, complex **1** was shown to exhibit higher binding affinity for anions compared with that of complex **2**, probably due to the higher acidity of the urea moiety as a result of the introduction of the NO_2 group. Complex **3** binds very weakly to anions in DMSO (data not shown) and therefore its anion-binding properties were studied in less competitive solvents

(in CH_2Cl_2 for UV/Vis spectrophotometry and $CDCl_3$ for NMR spectroscopic studies; see below). As can be seen in Table 1, complex **3** binds more strongly to fluoride than the other anions under study. This is consistent with the results obtained for complexes **1** and **2**.

Unlike in previous work on dinuclear gold(I) complexes with crown ether pendants, which could be used as luminescent probes for metal ions based on the switching on and off of Au···Au interactions,[8] the emission response of the present systems to anion binding was found to be essentially negligible. One possible reason might arise from the fact that anions are usually larger than the corresponding isoelectronic cations and therefore have a lower charge density, and might not have the correct size and geometry to bring the two gold atoms sufficiently close (< 3.4 Å) for an interaction to occur.

NMR spectroscopy: The anion-binding properties of complexes **1**–**3** were also investigated by ¹H NMR spectroscopy. Binding constants were determined using the EQNMR and SigmaPlot 8.1 programs. Addition of Cl⁻ to **1** or **2** in [D₆]DMSO resulted in a large downfield shift of the urea NH proton signals as a result of the formation of a hydrogen-bonding interaction between Cl⁻ and the urea group, while the other proton signals remained unchanged. Figures 4 and 5 show the ¹H NMR spectral changes of complexes **1** and **2** in [D₆]DMSO upon addition of Cl⁻. Besides the large downfield shift of the urea NH proton signals, addition of basic anions, such as $H_2PO_4^-$ to complex **2** also led to a slight shift of the aromatic proton signals. This could be attributed to a slight perturbation of the electron density of the aromatic rings as a result of the strong binding affinity, which is consistent with the selectivity trend observed in the UV/Vis titration experiments. The $\log K_s$ values of **1** for Cl⁻ and of **2** for Cl⁻ and $H_2PO_4^-$ were determined to be 2.12 ± 0.03, 1.90 ± 0.03, and 2.72 ± 0.04 M^{-1}, respectively. The experimental data were found to be in good agreement with the theoretical fits obtained with the EQNMR program using a 1:1 binding model. The larger binding affinity of complex **1** for Cl⁻ than that of **2** could be ascribed to the higher acidity of the urea receptor as a result of the presence of the electron-withdrawing NO_2 group.

The process of F⁻-induced deprotonation of **1** was further investigated by ¹H NMR spectroscopy. Figure 6a shows the ¹H NMR spectral changes of **1** in [D₆]DMSO upon addition of F⁻. For comparison, the interaction of **2** upon addition of F⁻ was also studied, as shown in Figure 6b. In the presence of 0–1 equivalent of F⁻, the two urea N−H proton signals of complex **1** disappeared rapidly, and all of the aromatic proton signals showed a slight upfield shift, similar to that observed in complex **2** upon the addition of F⁻, which could be attributed to the hydrogen-
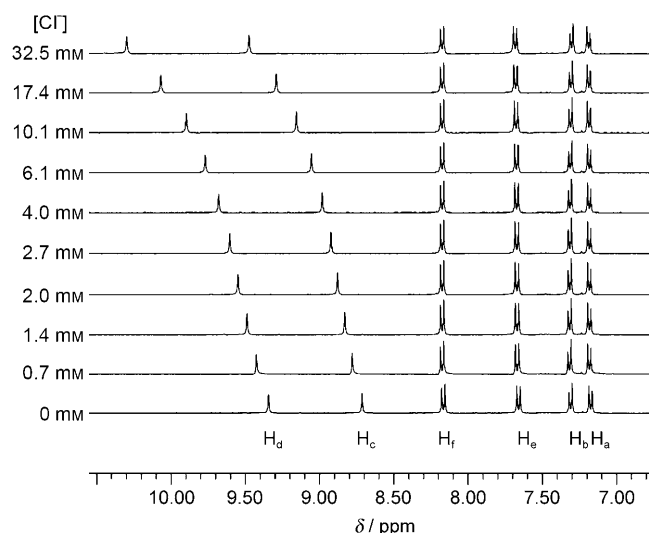
Table 2. Binding constants ($\log K_s$) of complexes **1**–**3** for various anions.[a]

Anion	**1**		**2**		**3**	
	UV/Vis[b]	¹H NMR[b]	UV/Vis[b]	¹H NMR[b]	UV/Vis[c]	¹H NMR[d]
F⁻	5.2 ± 0.08	—[f]	4.0 ± 0.05	—[c]	4.70 ± 0.04	4.00 ± 0.09
Cl⁻	—[e]	2.12 ± 0.03	—[e]	1.90 ± 0.03	—[e]	3.60 ± 0.06
AcO⁻	5.14 ± 0.06	—[f]	3.72 ± 0.03	—[c]	4.19 ± 0.02	3.02 ± 0.01
$H_2PO_4^-$	4.52 ± 0.06	—[f]	3.67 ± 0.02	2.72 ± 0.04	4.30 ± 0.07	3.50 ± 0.07

[a] Anions used were in the form of tetra-*n*-butylammonium salts. [b] Measured in DMSO. [c] Measured in CH_2Cl_2. [d] Measured in $CDCl_3$. [e] The spectral changes were too small for an accurate determination of the binding constant. [f] Not measured.

Figure 4. ^{1}H NMR spectral changes of **1** (2.7 mM) upon addition of Cl$^-$ in [D$_6$]DMSO. For proton labeling see Scheme 1.

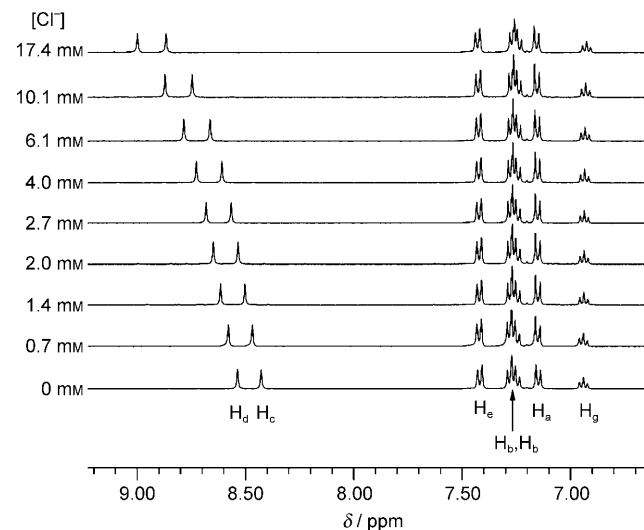Figure 6. ^{1}H NMR spectral changes of a) complex **1** (2.7 mM) and b) complex **2** (2.7 mM) upon addition of F$^-$ in [D$_6$]DMSO.

Figure 5. ^{1}H NMR spectral changes of [Au$_2$-(dcpm)(SC$_6$H$_4$NHCONHC$_6$H$_5$)$_2$] (**2**) (2.3 mM) upon addition of Cl$^-$ in [D$_6$]DMSO.

bonding process. At this stage, no significant color changes could be observed. On addition of more F$^-$, significant upfield shifts of the proton signals for H$_e$ and H$_f$ were observed, while on the contrary that of H$_a$ started to show a downfield shift. This was accompanied by a drastic color change from yellow to red, which could be attributed to the deprotonation process. The upfield shifts of the signals of H$_e$ and H$_f$ could be ascribed to the deshielding effect resulting from the increased electron density of the phenyl ring, induced by the deprotonation of the urea N−H$_d$ unit, which has a higher acidity as a result of the presence of the electron-withdrawing NO$_2$ group. In the deprotonation step, the

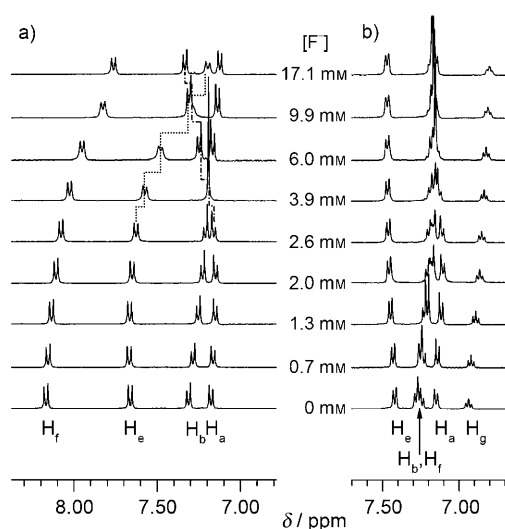anion would be expected to move away from the receptor, and therefore the downfield shift of the signal of H$_b$ could be rationalized in terms of the disappearance of the polarization effect of the C−H bond induced by the hydrogen-bonding interaction. On the contrary, no such large chemical shift and drastic color change in the presence of a large excess of F$^-$ were observed for **2**, suggesting that only a hydrogen-bonding interaction was responsible for the interaction between **2** and F$^-$ and that no further deprotonation took place upon addition of more F$^-$ (more than 1 equivalent).

As indicated in the previous section, due to the low anion-binding affinity of **3** in DMSO, a less competitive solvent (CDCl$_3$) was chosen to determine the binding constants. As for **1** and **2**, addition of the anions under study resulted in downfield shifts of the urea NH proton signals (see Figure 7 for an example) as a result of the formation of hydrogen-bonding interactions between the respective anion and the urea group. In addition, to confirm the binding stoichiometry (as suggested by the good theoretical fits obtained from Sigmaplot using a 1:1 binding model), Job's plots were constructed.

The lower binding affinity of receptor **3** towards anions (due to which binding affinities were measured in CH$_2$Cl$_2$ and CDCl$_3$ rather than DMSO) as compared with those of complexes **1** and **2** was not unexpected. In the latter two complexes, the spacer between the coordinating thiolate group and the anion-binding urea is a phenyl unit, whereas in the case of **3** it is an ethylene unit. It is well established that ureas substituted with aromatic groups bind anions more strongly than their aliphatic counterparts due to the higher acidity of the urea protons. In addition, it is likely that steric constraints imposed by the phenyl spacer yield more defined binding pockets for analyte binding with **1** and **2**.
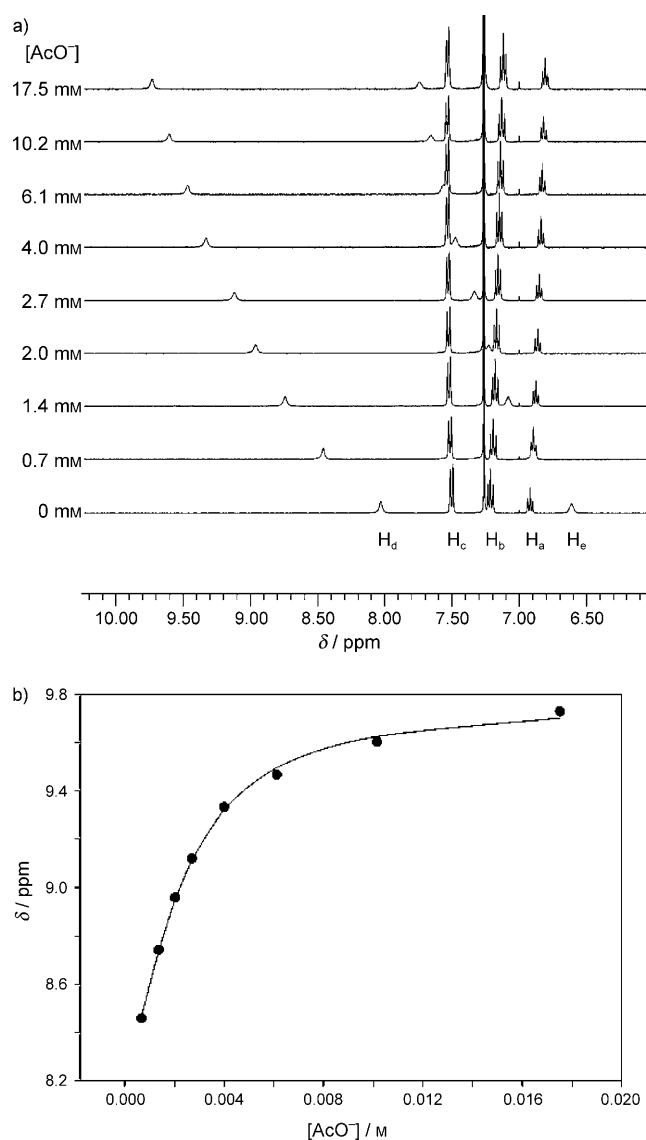
a)

b)

Figure 7. a) ^1H NMR spectroscopy titration of complex **3** with AcO^- and b) the corresponding binding plot (chemical shift of urea proton H_d as a function of AcO^- concentration and its theoretical fit for the 1:1 binding of complex **3** with AcO^-).

Conclusion

In summary, we have designed and synthesized a series of dcpm-containing gold(I) thiolate complexes with different urea receptors, **1–3**, and their photophysical properties and anion-binding abilities have been studied. Through variation of the linker between the thiolate and the urea group, as well as the electronic environment of the urea moiety, complexes **1–3** showed interesting photophysical and anion-binding properties. Excitation of complexes **2** and **3** in degassed solution at room temperature gave rise to intense LMCT emissions at around 530–560 nm. In the solid state and in the glass state at 77 K, complex **3** showed an intense low-energy orange-red luminescence at about 620 nm, which could be thought of as the overall result of the complemen-

tary aurophilic interaction and intramolecular urea–urea hydrogen-bonding interaction. Distinct UV/Vis spectral changes were observed upon addition of basic anions, such as F^-, AcO^-, or $H_2PO_4^-$, whereas the addition of Cl^-, Br^-, or I^- led to negligible changes. The large anion-binding constants of complexes **1** and **2** towards these basic anions were consistent with the distinct UV/Vis changes. The most pronounced UV/Vis spectral changes, accompanied by a drastic color change from yellow to red, were observed upon addition of F^- to complex **1**, suggesting the potential use of **1** as a highly selective colorimetric probe for F^- ion sensing.

Acknowledgements

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