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# Synthesis, characterization, photophysics, and anion binding properties of gold(1) acetylide complexes with amide groups†

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A series of mononuclear gold(i) acetylide complexes with amide groups,  $Ph_3PAuC \equiv CC_6H_4NHC(O)C_6H_4-R-4$  (R =  $NO_2$  (**3a**),  $CF_3$  (**3b**), H (**3c**), and OMe (**3d**)), has been synthesized and characterized. The crystal structure of  $Ph_3PAuC \equiv CC_6H_4NHC(O)C_6H_4-NO_2-4$  (**3a**) was determined by X-ray diffraction. The photophysical properties of gold(i) acetylide complexes **3b-3d** were studied and the complexes show luminescence both in the solid state and in degassed THF solutions at 298 K. The anion-binding abilities of complexes **3a-3d** in CDCl<sub>3</sub> were also studied through <sup>1</sup>H NMR titration experiments. They show similar anion selectivity trends and **3a** exhibits the highest binding affinity towards anions due to the strongest electron-withdrawing ability of the  $NO_2$  group. In DMSO, **3a** shows a dramatic color change upon addition of F<sup>-</sup>, which provides access to naked eye detection of F<sup>-</sup>.

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### 1. Introduction

Anions are one of the most important constituents of living systems because they play pivotal roles in ion transport, chemosensing, and especially in the environment and in biology.<sup>1-4</sup> Since the first anion sensor reported by Park and Simmons in 1968,<sup>5</sup> anion sensors have attracted much attention and become an important field in supramolecular chemistry. Various methods have been applied to design effective anion sensors over the past few decades. They usually consist of two main moieties: a recognition unit and a sensing unit, which are connected either directly or by a spacer. When the recognition unit interacts with an anion by non-covalent interaction, the photophysical or redox properties of the sensing unit can be changed.<sup>6-8</sup> Thus, anion sensing can be realized by detecting optical and electrical signals from receptors. Observations in natural anion binding systems have motivated researchers to develop several artificial receptors which employ hydrogen bonds offered by specific binding sites that are able to recognize and bind size- and shape-selective anionic guests on appropriate frameworks in various media.9,10 To date, a number of synthetic receptors incorporating a neutral

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N–H or cationic (N–H)<sup>+</sup> hydrogen bond donor, such as pyrrole,<sup>11</sup> ammonium,<sup>12,13</sup> guanidinium,<sup>14</sup> urea,<sup>15,16</sup> thiourea,<sup>15</sup> and amide,<sup>17–19</sup> have proven to be particularly effective anion receptors in organic solvents. It is interesting to note that anion binding by proteins is mostly achieved by way of neutral amide functional groups employing their N–H moiety as a hydrogen bond donor.<sup>20</sup> Thus, amide-based organic anion sensors with aromatic or heterocyclic groups have been reported in the literature.<sup>10,21</sup> Their structures are simple and their modification can be easily carried out through organic synthesis.

Although most past studies on the design of anion sensors have focused on organic receptors involving photo-induced electron transfer (PET) processes,<sup>22</sup> the utilization of transition metal complexes with amide groups as anion sensors has been relatively less explored.<sup>23-25</sup> Compared to common organic anion sensors, metal complexes with various properties like redox and luminescence have proven to be able to provide access to anion sensing. Some examples include ruthenium(II),<sup>26-29</sup> rhenium(I),<sup>30-33</sup> iridium( $\pi$ ),<sup>34</sup> platinum( $\pi$ )<sup>35,36</sup> and gold(1)-copper(1)<sup>37</sup> complexes which utilize MLCT or metal cluster-centered excited states for luminescent signal transduction. Among them, gold(I) complexes are one of the most important classes owing to their intriguing photoluminescence behavior and their propensity to form aurophilic Au...Au interactions.<sup>38</sup> Many studies showed that an increase in the strength of the Au···Au interaction would lead to a shift of the emission to lower energy.<sup>39</sup> The preference of gold(1) for a linear coordination geometry, together with the linearity of the acetylide unit and its p-unsaturated nature, have made gold(1) acetylide complexes attractive building blocks for

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Scheme 1 Synthetic route for gold()) acetylide complexes 3a-3d. (i) Pd(PPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>, Cul, (CH<sub>3</sub>)<sub>3</sub>Si-C=CH, NEt<sub>3</sub>, reflux, N<sub>2</sub>, overnight; (ii) ClC(O)C<sub>6</sub>H<sub>4</sub>-R, NEt<sub>3</sub>, CHCl<sub>3</sub>, reflux, N<sub>2</sub>, overnight; (iii) Ph<sub>3</sub>PAuCl, KF·2H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH, dark.

organometallic oligomeric and polymeric materials, which may possess unique properties such as optical non-linearity, electrical conductivity and liquid crystallinity.<sup>40</sup> The gold(1) acetylide complexes supported by an auxiliary phosphane ligand represent the major class of luminescent gold(1) complexes.40 Che,41-44 Yam,45-50 and other groups<sup>51-54</sup> have studied the photophysical, photochemical and ion-sensing properties of gold(1) acetylide complexes. However, to the best of our knowledge, no gold(1) acetylide complex with an amide group has ever been reported as an anion sensor until now.

Our group has a long-term interest in studying the relationship between the structures and properties of gold(1) acetylide complexes.<sup>44,53,54</sup> We have synthesized a series of gold(1) acetylide complexes with urea or amide groups, and studied their photophysical and ion-sensing properties.<sup>53,54</sup> To extend our studies on gold(1) acetylide complexes with different anion binding abilities, a series of mononuclear gold(1) acetylide complexes,  $Ph_3PAuC \equiv CC_6H_4NHC(O)C_6H_4-R-4$  (R = NO<sub>2</sub> (3a),  $CF_3$  (3b), H (3c) and OMe (3d); Scheme 1), has been synthesized and characterized in this work. The crystal structure of  $Ph_3PAuC \equiv CC_6H_4NHC(O)C_6H_4-NO_2-4$  (3a) was determined by X-ray diffraction. We envisaged that if the photophysical properties of these gold(1) acetylide complexes could be changed when they interact with anions, through hydrogen bonds between the anions and the amide N-H of the complexes, then they could be used as anion sensors. The sole binding site may be better matched to spherical anions than non-spherical ones. The effect of the structure, especially the nature of the R substituent on the acetylide ligand of the complex, on the binding abilities of the gold(1) acetylide complexes towards anions was also studied.

### 2. Results and discussion

### 2.1. Syntheses and characterization

Scheme 1 shows the synthetic route for acetylide ligands with amide groups (2a-2d) and mononuclear gold(1) acetylide complexes (3a–3d). The reaction of 4-[(trimethylsilyl)ethynyl]aniline with the corresponding acyl chloride in refluxing chloroform in the presence of triethylamine gave acetylide ligands 2a-2d. Mononuclear gold(1) acetylide complexes 3a-3d were obtained by reaction of Ph<sub>3</sub>PAuCl with the corresponding acetylide ligands 2a-2d in a molar ratio of 1:1 in the presence of an excess of KF in a dichloromethane-methanol mixture at 298 K. All gold(1) acetylide complexes 3a-3d are air-stable in the solid state at 298 K and can be well dissolved in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF and DMSO. They were all characterized by IR, <sup>1</sup>H NMR and <sup>31</sup>P NMR (Fig. S1-S12, ESI<sup>†</sup>) and gave satisfactory elemental analysis results.

The IR spectra of the gold(I) acetylide complexes 3a-3d reveal bands at 3389–3434 and 1656–1674  $\mathrm{cm}^{-1}$ , characteristic of the  $\nu$ (N–H) and  $\nu$ (C=O) vibrations of the acetylide ligands, respectively. The <sup>1</sup>H NMR spectra of complexes 3a-3d in CDCl<sub>3</sub> display singlets at  $\delta$  7.68–7.84 ppm, which are attributed to the resonances of the amide N-H of the acetylide ligands. The chemical shifts of these peaks are in the order  $3a > 3b \sim 3c >$ 3d, which is in line with the decreasing electron-withdrawing abilities of the R substituents on the acetylide ligand. In addition, the peaks in the region  $\delta$  7.40–8.31 ppm are attributed to the resonances of the protons on the aromatic rings of the acetylide and triphenylphosphine ligands. The <sup>31</sup>P NMR spectra of complexes 3a-3d in CDCl<sub>3</sub> show a singlet at *ca*.  $\delta$  43.3 ppm. The NMR spectra of complexes 3a-3d are similar owing to their similar structures and the fact that the R substituents on the acetylide ligands have little effect on the chemical shifts.

#### 2.2. Crystal structure of 3a

The crystal structure of the mononuclear gold(I) acetylide complex 3a was determined by X-ray diffraction crystallography. The crystallographic data are listed in Table S1 (ESI<sup>†</sup>) and selected bond distances and angles are listed in Table 1. Fig. 1 shows the crystal structure of 3a. The triphenylphosphine ligand coordinates to the gold(I) metal center and the remaining gold(1) site is occupied by an acetylide ligand to give a nearly linear geometry. The C(1)-Au(1)-P(1), Au(1)-C(1)-C(2) and C(1)-C(2)-C(41) angles of  $174.52(14)^{\circ}$ ,  $174.3(5)^{\circ}$  and  $177.0(6)^{\circ}$ , respectively, are deviated from the idealized angle of 180°, probably as a result of the steric demand of the ligands and the crystal packing forces. The Au(1)-C(1) and Au(1)-P(1) bond distances for 3a (2.012(5) and 2.2802(18) Å, respectively) are similar to those reported for other gold(1) arylacetylide complexes with triphenylphosphine ligands.<sup>55,56</sup> The C $\equiv$ C bond distance (1.187(8) Å) is in the range of those typical for gold(1)

Table 1 Selected bond lengths (Å) and angles (°) for ${\bf 3a}$				
Au(1)-C(1)	2.012(5)			
Au(1) - P(1)	2.2802(18)			
C(1)-C(2)	1.187(8)			
C(3) - O(1)	1.217(7)			
N(2) - O(2)	1.224(8)			
N(2) - O(3)	1.215(7)			
C(1) - Au(1) - P(1)	174.52(14)			
Au(1)-C(1)-C(2)	174.3(5)			
C(1)-C(2)-C(41)	177.0(6)			
N(1) - C(3) - C(51)	115.7(5)			
O(1) - C(3) - N(1)	123.7(6)			
O(1) - C(3) - C(51)	120.6(5)			
O(2) - N(2) - O(3)	124.0(6)			

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Fig. 1 A view of the crystal structure of **3a** with the atomic numbering scheme. Thermal ellipsoids are shown at the 30% probability level.

acetylide systems.<sup>44,55–67</sup> Because the angles of N(1)–C(3)–C(51), O(1)–C(3)–N(1) and O(1)–C(3)–C(51) are 115.7(5)°, 123.7(6)° and 120.6(5)°, respectively, the geometry of the carbonyl group is nearly trigonal planar. The C=O distance for **3a** (1.217(7) Å) also resembles those in analogous gold(1) acetylide complexes with carbonyl groups.<sup>50</sup> There are intermolecular hydrogen bonding interactions between the hydrogen atom of the amide group and the oxygen atom (O2) of the nitro group of the acetylide ligand of **3a** (Fig. 2). The hydrogen bond parameters of **3a** are listed in Table 2.

# 2.3. Electronic absorption and emission spectra of complexes 3a-3d

The photophysical data for complexes **3a–3d** are summarized in Table 3. Fig. 3 shows the electronic absorption spectrum of **3a** 



Fig. 2 A view of two molecules of **3a** showing the intermolecular hydrogen bonding. Thermal ellipsoids are shown at the 30% probability level.

Jable 2       Hydrogen bond parameters of <b>3a</b> (Å and °)						
D−H· · ·A	d(D-H)	$d(\mathbf{H}\cdot\cdot\cdot\mathbf{A})$	$d(\mathbf{D}\cdot\cdot\cdot\mathbf{A})$	∠(DHA		
$N(1)-H(1A)\cdots O(2)^{a}$	0.86	2.50	3.267(7)	149.7		

<sup>*a*</sup> Symmetry transformations used to generate equivalent atoms: -x + 4, y + 4, z + 2.

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Fig. 3 The electronic absorption spectrum of  $3a~(1.98\times 10^{-5}~mol~dm^{-3})$  in THF at 298 K.

in THF at 298 K. The absorption peak maxima of 3a appear at 267, 277, 292, 305 and 330 nm. The spacings of the adjacent absorption maxima of 3a at 267–305 nm are *ca.* 1300–1800  $\text{cm}^{-1}$ . Thus, the absorption bands of complex 3a at 267-305 nm are attributed to the  $\pi \to \pi^*$  transitions of the acetylide ligand.<sup>54</sup> The low-energy absorption band of 3a at 330 nm could be due to the charge-transfer transition from the amide to the NO<sub>2</sub> group of the acetylide ligand.<sup>54</sup> The electronic absorption spectra of non-nitro derivatives 3b-3d in THF at 298 K exhibit one shoulder (ca. 296 nm) and three additional bands (ca. 268, 277 and 312 nm) (Fig. S13-S15, ESI<sup>†</sup>). Overall there are three different values for the vibrational spacings, *ca.* 1200, 1700 and 2200  $\text{cm}^{-1}$ , which are ascribed to phenyl ring deformation, C=O stretching, and C=C stretching frequencies of the ground state, respectively.44,54,58 These absorption bands are assigned to the  $(\pi\pi^*)$  transitions involving the phenylic, carbonyl and acetylenic units of the acetylide ligand.

Upon excitation at  $\lambda > 300$  nm, gold(1) acetylide complexes **3b-3d** in the solid state and in THF exhibit luminescence in the visible light region at 298 K, with emission quantum yields of  $5.0 \times 10^{-3}$ – $1.02 \times 10^{-2}$  in THF solutions, and complex **3a** in THF exhibits luminescence under the same conditions with an emission quantum yield of  $4.2 \times 10^{-3}$ . Fig. S16–S18 (ESI†) show the emission spectra of **3b–3d** in the solid state at room temperature. A broad band at *ca*. 471 nm is observed for each complex and its lifetime is in the microsecond range (Table 3). Thus, the emission is attributed to come from the  ${}^{3}(\pi\pi^{*})$  excited state of the acetylide ligand in the gold(1) acetylide complexes. In THF, the emission spectra of complexes **3a–3d** exhibit three

Table 3 Photophysical data of complexes 3a-3u at 296 K					
Complex	Medium	$\lambda_{\rm abs}/\rm nm~(\epsilon/\rm dm^3~mol^{-1}~\rm cm^{-1})$	$\lambda_{\rm em}/{\rm nm} \left( \tau_{\rm em}/\mu s \right)$	$\Phi^a$	
3a	THF Solid	267 (32 170), 277 (35 350), 292 (sh, 44 040), 305 (39 950), 330 (14 240)	408 (max), 434, 465 Non-emissive	0.0042	
3b	THF Solid	268 (17 420), 276 (20 000), 296 (sh, 25 810), 315 (34 950)	408 (max), 432, 465 471 (2.6)	0.0059	
3 <b>c</b>	THF Solid	267 (16 310), 276 (18 640), 296 (sh, 33 230), 314 (43 640)	407 (max), 434, 465 471 (2.5)	0.0050	
3d	THF Solid	268 (19 900), 277 (22 420), 296 (sh, 37 630), 312 (47 320)	410 (max), 432, 471 484 (3.5)	0.0102	

<sup>a</sup> Quinine sulfate as reference.<sup>59</sup>

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bands at *ca.* 408, 434 and 465 nm with vibrational spacings of approximately 1300–1900 cm<sup>-1</sup>, which are assigned to the stretching of the phenyl and acetylene units of the acetylide ligand (Fig. S19–S22, ESI†). Thus, the lowest-lying emissive state of complexes **3a–3d** in THF is assigned as the <sup>3</sup>( $\pi\pi^*$ ) excited state of the acetylide ligand, which is promoted through spin–orbit coupling due to the introduction of a gold atom.<sup>54,58</sup> For the mononuclear gold(1) acetylide complexes studied in this paper, except the nitro-derivative **3a**, the R substituent on the acetylide ligand has little effect on the electronic absorption and emission spectra.

#### 2.4. Anion binding properties of complexes 3a-3d

Addition of the anions studied in this paper to the solutions of **3a–3d** caused UV-Vis spectral changes. However, these results



Fig. 4 (a) <sup>1</sup>H NMR spectral changes of **3a** upon addition of Cl<sup>-</sup>. (b) The corresponding binding plot (the shifts in the signal of the amide proton  $H_a$  as a function of [Cl<sup>-</sup>] and the theoretical fit for the 1:1 binding of **3a** with Cl<sup>-</sup>).

could not be used to obtain accurate binding constants of complexes 3a-3d towards anions. Thus, the interactions of 3a-3d with anions in CDCl<sub>3</sub> were investigated by <sup>1</sup>H NMR titration experiments. All of the anions used were in the form of tetra-n-butylammonium salts. Fig. 4(a) shows the <sup>1</sup>H NMR spectral changes of **3a** upon addition of Cl<sup>-</sup> in CDCl<sub>3</sub>. A significant downfield shift in the amide N-H (Ha) signal is observed upon gradual addition of Cl<sup>-</sup> from 0 to 5 equiv., while only small changes in the peak position are observed upon addition of more than 5 equiv. of Cl<sup>-</sup>. The other proton signals are found to undergo small or relatively negligible changes, suggesting the formation of hydrogen bonds between the amide N-H of 3a and Cl<sup>-</sup>. The slight downfield shifts of H<sub>b</sub> and H<sub>c</sub> on the phenyl ring are ascribed to the polarization effect of the C-H bond, which is introduced by the through-space effect.<sup>60–62</sup> The <sup>1</sup>H NMR spectral changes of **3b–3d** upon gradual addition of Cl<sup>-</sup> in CDCl<sub>3</sub> (Fig. S31, S32, S35, S36, S43 and S44, ESI<sup>†</sup>) are similar to that of 3a. Analogous investigations of 3a-3d with Y-shaped anion OAc<sup>-</sup> or other halides such as F<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> in CDCl<sub>3</sub> were also carried out, and they showed similar spectral changes in the <sup>1</sup>H NMR spectra (some are shown in Fig. S23–S42, ESI<sup>+</sup>). The amide N–H (H<sub>a</sub>) signals exhibit significant downfield shifts of 0.6 to 2.8 ppm, while the signals of the aromatic protons shift relatively less. The extent of the shift of H<sub>a</sub> upon the addition of Br<sup>-</sup>, I<sup>-</sup>, and OAc<sup>-</sup> is found to be obviously smaller than that for Cl<sup>-</sup>, while the addition of F<sup>-</sup> induced disappearance of the amide N-H signals for 3a and 3b, but larger shifts for 3c and 3d. Fig. S45 (ESI<sup>†</sup>) shows the shifts of the amide N-H (H<sub>a</sub>) signal of 3c upon addition of different anions in CDCl<sub>3</sub> at 298 K. Unfortunately, only the binding constant of 3c with F<sup>-</sup> can be determined because the amide N-H (H<sub>a</sub>) signal of 3d is too broad to be detected after the addition of 5 equiv. of  $F^-$ .

To determine the binding ratios between gold(1) acetylide complexes **3a–3d** and anions, Job's plot analyses were carried out. Fig. 5 shows the Job's plots of **3b** with Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and OAc<sup>-</sup> in CDCl<sub>3</sub>. A plot of the changes in N–H chemical shift *versus*  $X_{3b}$  ( $X_{3b} = [3b]/([anion] + [3b])$ ) shows a break point at a molar ratio of *ca.* 0.5, indicative of a 1:1 complexation stoichiometry.

Using the 1:1 binding model, the anion-binding constants of complexes **3a-3d** were obtained by nonlinear least-square fits of



Fig. 5 Job's plots of complex **3b** with  $Cl^-(\bullet)$ ,  $Br^-(\blacktriangle)$ ,  $l^-(\bullet)$  and  $OAc^-(\blacksquare)$  in  $CDCl_3$  (**[3b]** + [anion] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>).

Table 4 Binding constants of **3a-3d** for anions in CDCl<sub>3</sub><sup>a</sup>

Complex	$\mathbf{F}^{-}$	$\mathrm{Cl}^-$	OAc <sup>-</sup>	Br <sup>-</sup>	Ι-
3a	b	$126.40\pm 6.13$	$\textbf{77.35} \pm \textbf{7.80}$	$86.71 \pm 3.76$	$40.96\pm2.56$
3b	b	$61.00\pm5.54$	$47.28 \pm 2.38$	$41.46 \pm 1.84$	$30.53\pm3.73$
3c	$24.87\pm3.57$	$15.02 \pm 1.42$	$7.18 \pm 1.11$	$6.87\pm0.83$	$4.85\pm0.84$
3d	b	$15.56\pm1.65$	$8.02 \pm 1.28$	$8.95 \pm 1.29$	b

<sup>*a*</sup> Binding constants were determined by a 1:1 model using the nonlinear fitting method. <sup>*b*</sup> Chemical shifts were not suitable for the accurate measurement of binding constants.

the shifts of the amide N-H (H<sub>a</sub>) signals versus the concentration of the added anions. The binding constants (K) for different anions are summarized in Table 4. In general, the binding constants of the different complexes for the same anion are in the order  $R = NO_2$  $(3a) > CF_3 (3b) > H (3c) \approx OCH_3 (3d)$ , which is in line with the decreasing electron-withdrawing abilities of the R substituents on the acetylide ligand. This could be rationalized by the fact that the interactions between complexes (3a-3d) and anions are hydrogen bonds, as stronger electron-withdrawing groups could give rise to stronger hydrogen bond acceptors, which in turn could form stronger hydrogen bonds. The K values for the same complex with the various anions are in the order  $\rm Cl^- > OAc^- \approx Br^- > I^- \, (F^- >$  $Cl^- > OAc^- \approx Br^- > I^-$  for 3c), which is almost in line with the decreasing of the basicity of the anions  $(F^- > OAc^- > Cl^- >$  $Br^- > I^-$ ). The  $Cl^- > OAc^-$  order could be due to the mismatching between the mono hydrogen bond donor N-H and the Y-shape OAc<sup>-</sup> (two hydrogen bond donor) anion.

To confirm the reliability of our results regarding the order of the affinities of the gold(1) acetylide complexes **3a–3d** for anions, the anion-binding constants of the acetylide ligands,  $HC \equiv CC_6H_4NHC(O)C_6H_4$ –R-4 (R = NO<sub>2</sub> (**4a**), CF<sub>3</sub> (**4b**), H (**4c**), and OMe (**4d**)), were also determined (Fig. S46–S63 and Table S2, ESI†). For the same anion, the binding constants of the acetylide ligands are in the order R = NO<sub>2</sub> (**4a**) > CF<sub>3</sub> (**4b**) > H (**4c**)  $\approx$  OCH<sub>3</sub> (**4d**). For the same ligand, the *K* values for the various anions are in the order Cl<sup>-</sup> > OAc<sup>-</sup>  $\approx$  Br<sup>-</sup> > I<sup>-</sup>. These orders are in line with those observed for complexes **3a–3d**. In general, the acetylide ligands **4a–4d** have larger anion-binding constants than their corresponding gold(1) acetylide complexes **3a–3d** in CDCl<sub>3</sub>.

The interaction of 3a with F<sup>-</sup> was investigated in different solvents. Fig. S23 (ESI<sup>+</sup>) shows the <sup>1</sup>H NMR spectral changes of 3a in CDCl<sub>3</sub> upon addition of F<sup>-</sup>, which are quite different from those of 3a with  $Cl^-$  in  $CDCl_3$  (Fig. 4(a)). When 0.2 equiv. of  $F^$ was added to the CDCl<sub>3</sub> solution of **3a**, the signal of the N-H proton disappeared rapidly and the aromatic proton signals H<sub>b</sub> and H<sub>c</sub> showed slight downfield shifts. During the addition of F<sup>-</sup>, the color of the solution of **3a** in CDCl<sub>3</sub> changed from light yellow to bright yellow (Fig. 6). On the other hand, when 10 equiv. of F<sup>-</sup> was added into the solution of 3a in DMSO-d<sub>6</sub>, the solution showed a dramatic color change from light yellow to dark red (Fig. 6). Fig. S64(a) (ESI<sup> $\dagger$ </sup>) shows the <sup>1</sup>H NMR spectrum of 3a in DMSO-d<sub>6</sub> upon addition of 10 equiv. of F<sup>-</sup>. The signal of the N-H proton again disappeared and a distinct triplet centered at 16.08 ppm (J = 120 Hz) appeared, which was attributed to the formation of HF2<sup>-.63,64</sup> In addition, its <sup>19</sup>F NMR spectrum also displayed a distinct doublet centered at -143.13 ppm (J = 117 Hz)



(a) 3a (in CDCl<sub>3</sub>) (b) 3a+10 eq F<sup>•</sup> (in CDCl<sub>3</sub>) (c) 3a (in DMSO-d<sub>6</sub>) (d) 3a+10 eq F<sup>•</sup> (in DMSO-d<sub>6</sub>)

Fig. 6 Colors of the solutions of: (a) **3a** in CDCl<sub>3</sub>, (b) **3a** + 10 eq. F<sup>-</sup> in CDCl<sub>3</sub>, (c) **3a** in DMSO-d<sub>6</sub>, (d) **3a** + 10 eq. F<sup>-</sup> in DMSO-d<sub>6</sub>. The concentration of **3a** is  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>.

(Fig. S65, ESI<sup>†</sup>), suggesting the formation of  $HF_2^{-}$ .<sup>63,64</sup> These results indicate the deprotonation of the amide N–H of **3a** upon addition of  $F^-$  in DMSO-d<sub>6</sub>.

We also examined the color change of complex **3a** with different anions in DMSO. Except for with  $F^-$ , no significant color change could be observed (Fig. S66 and S67, ESI†). Thus, **3a** shows a selective color change towards  $F^-$  in DMSO. Considering this selective colour change, the anion-sensing properties of complexes **3b–3d** with different anions were also examined in various solvents. However, no significant color changes were observed.

### 3. Conclusions

In this work, amide based gold(i) acetylide complexes **3a–3d** have been synthesized and characterized. Complexes **3b–3d** show luminescence both in the solid state and in degassed THF solutions at 298 K. In CDCl<sub>3</sub>, the binding constants of **3a–3d** for the same anion are in the order  $R = NO_2$  (**3a**) > CF<sub>3</sub> (**3b**) > H (**3c**)  $\approx$  OCH<sub>3</sub> (**3d**). For the same complex, the binding constants follow the order Cl<sup>-</sup> > OAc<sup>-</sup>  $\approx$  Br<sup>-</sup> > I<sup>-</sup>. In DMSO, **3a** shows a selective color change towards F<sup>-</sup>. This makes the naked eye detection of F<sup>-</sup> possible. We envisage that this class of gold(i) complexes could have potential applications in life science and environmental science by using water-soluble auxiliary ligands.

### 4. Experimental

### 4.1. Materials and reagents

Ph<sub>3</sub>PAuCl<sup>65</sup> and 4-[(trimethylsilyl)ethynyl]aniline<sup>66</sup> were synthesized according to literature procedures. 4-Nitrobenzoyl chloride was purchased from TCI. 4-Iodoaniline, benzoyl chloride and tetra-*n*-butylammonium chloride hydrate were obtained from Alfa-Aesar.

4-Methoxybenzoyl and 4-trifluoromethylbenzoyl chloride were purchased from J&K. Tetra-*n*-butylammonium fluoride hydrate and tetra-*n*-butylammonium acetate were obtained from Sigma-Aldrich. All reactions were carried out under anhydrous and anaerobic conditions using standard Schlenk techniques under nitrogen. All solvents were purified and distilled using standard procedures before use. All other reagents were of analytical grade and were used as received.

#### 4.2. Physical measurements and instrumentation

Chemical shifts ( $\delta$ , ppm) were reported relative to tetramethylsilane for <sup>1</sup>H NMR, 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P NMR, and NaF ( $\delta$  = -122.4) for <sup>19</sup>F NMR on a Varian Mercury-Plus 300 spectrometer. Electronic absorption spectra were measured on a PGENERAL TU1901 UV-vis spectrophotometer. Emission spectra were obtained on a FLSP920 fluorescence spectrophotometer. Solution samples for emission spectra were degassed by four freeze-pump-thaw cycles.

#### 4.3. Crystal structure determination

Crystals of **3a** were grown by diffusion of diethyl ether into a THF solution of **3a**. Selected single crystals of **3a** were used for data collection on a Bruker SMART 1000 CCD diffractometer with graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.710 \times 73$  Å) at 110 K. An empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares based on  $F^2$  using the SHELXTL program package.<sup>67</sup> CCDC 1013703 contains the supplementary crystallographic data for **3a**.

### 4.4. Titrations and Job's plots

For a typical <sup>1</sup>H NMR titration experiment, 1 µL aliquots of a tetra-*n*-butylammonium salt  $(1.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ in CDCl}_3)$  were added into a 0.5 mL solution of the gold(1) acetylide complex in CDCl<sub>3</sub> ( $5.00 \times 10^{-3} \text{ mol dm}^{-3}$ ) *via* syringe, and the <sup>1</sup>H NMR spectral changes were recorded by a Varian Mercury-Plus 300 spectrometer at 298 K. The binding constant *K* values were determined by nonlinear fitting using a 1:1 model. Job's plots were obtained from a series of solutions in which the fraction of the corresponding anions varied, keeping the total concentration (complexes and anions) constant. The maxima of the plots indicated the binding stoichiometry of the complexes with anions.

#### 4.5. Synthesis

#### 4.5.1 Synthesis of acetylide ligands 2a-2d

 $(CH_3)_3SiC \equiv CC_6H_4NHC(O)C_6H_4-NO_2-4$  (2*a*). To a solution of 4-[(trimethylsilyl)ethynyl]aniline (100.8 mg, 0.53 mmol) and 4-nitromethylbenzoyl chloride (99.8 mg, 0.54 mmol) in CHCl<sub>3</sub> was added triethylamine (0.8 mL). The mixture was heated at reflux for 18 h. The solvent was removed under reduced pressure and the residue was washed with water and *n*-hexane to yield a pale yellow solid. Yield: 116.3 mg, 65%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 8.31$  (d, 2H, J = 9 Hz, aromatic ring), 7.97 (s, 1H, NH), 7.59 (d, 2H, J = 9 Hz, aromatic ring), 7.47 (d, 2H, J = 9 Hz, aromatic ring),

0.26 (s, 9H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3318 (N–H), 2154 (C=C), 1660 (C=O). Anal. calcd for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Si (%): C, 63.88; H, 5.36; N, 8.28. Found: C, 64.03; H, 5.37; N, 8.31.

 $(CH_3)_3SiC \equiv CC_6H_4NHC(O)C_6H_4$ -*CF*<sub>3</sub>-*4* (**2b**). To a solution of 4-[(trimethylsilyl)ethynyl]aniline (134.7 mg, 0.65 mmol) and 4-trifluorobenzoyl chloride (121.6 mg, 0.64 mmol) in CHCl<sub>3</sub> was added triethylamine (0.8 mL). The mixture was heated at reflux for 18 h. The solvent was removed under reduced pressure and the residue was washed with water and *n*-hexane to yield a pale incarnadine solid. Yield: 132.3 mg, 57%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.94 (d, 2H, *J* = 8 Hz, aromatic ring), 7.85 (s, 1H, NH), 7.73 (d, 2H, *J* = 8 Hz, aromatic ring), 7.59 (d, 2H, *J* = 8 Hz, aromatic ring), 7.46 (d, 2H, *J* = 9 Hz, aromatic ring), 0.26 (s, 9H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3432 (N–H), 2162 (C≡C), 1657 (C=O). Anal. calcd for C<sub>19</sub>H<sub>18</sub>F<sub>3</sub>NOSi (%): C, 63.14; H, 5.02; N, 3.88. Found: C, 63.40; H, 5.03; N, 3.90.

 $(CH_3)_3SiC \equiv CC_6H_4NHC(O)C_6H_5$  (2c). To a solution of 4-[(trimethylsilyl)ethynyl]aniline (101.4 mg, 0.54 mmol) and benzoyl chloride (76.6 mg, 0.54 mmol) in CHCl<sub>3</sub> was added triethylamine (0.8 mL). The mixture was heated at reflux for 18 h. The solvent was removed under reduced pressure and the residue was washed with water and *n*-hexane to yield a yellow solid. Yield: 95.5 mg, 61%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta =$  7.85–7.82 (m, 3H, NH + aromatic ring), 7.59 (d, 2H, J = 9 Hz, aromatic ring), 7.54–7.44 (m, 5H, aromatic ring), 0.25 (s, 9H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>):  $\nu =$  3270 (N–H), 2156 (C $\equiv$ C), 1647 (C $\equiv$ O). Anal. calcd for C<sub>18</sub>H<sub>19</sub>NOSi (%): C, 73.68; H, 6.53; N, 4.77. Found: C, 73.38; H, 6.54; N, 4.78.

 $(CH_3)_3SiC \equiv CC_6H_4NHC(O)C_6H_4$ –OMe-4 (2d). To a solution of 4-[(trimethylsilyl)ethynyl]aniline (104.9 mg, 0.55 mmol) and 4-methoxybenzoyl (94.4 mg, 0.55 mmol) in CHCl<sub>3</sub> was added triethylamine (0.8 mL). The mixture was heated at reflux for 18 h. The solvent was removed under reduced pressure and the residue was washed with water and *n*-hexane to yield a pale yellow solid. Yield: 119.4 mg, 67%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.81–7.77 (m, 3H, NH + aromatic ring), 7.57 (d, 2H, J = 8 Hz, aromatic ring), 7.43 (d, 2H, J = 8 Hz, aromatic ring), 6.93 (d, 2H, J = 9 Hz, aromatic ring), 3.85 (s, 3H, OCH<sub>3</sub>), 0.25 (s, 9H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3436 (N–H), 2152 (C $\equiv$ C), 1649 (C $\equiv$ O). Anal. calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>Si (%): C, 70.55; H, 6.54; N, 4.33. Found: C, 70.61; H, 6.55; N, 4.34.

*Ph*<sub>3</sub>*PAuC* ≡ *CC*<sub>6</sub>*H*<sub>4</sub>*NHC*(*O*)*C*<sub>6</sub>*H*<sub>4</sub>*−NO*<sub>2</sub>*-4* (*3a*). To a mixture of Ph<sub>3</sub>PAuCl (51.0 mg, 0.1031 mmol) and 2a (34.9 mg, 0.1031 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added KF·2H<sub>2</sub>O (19.2 mg, 0.2040 mmol) in methanol dropwise. The mixture was stirred overnight in the dark. After evaporation to dryness, the solid residue was extracted with THF. Subsequent diffusion of diethyl ether into the concentrated THF solution gave light yellow crystals. Yield: 53.8 mg, 72%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 8.31 (d, 2H, *J* = 9 Hz, aromatic ring), 8.00 (d, 2H, *J* = 9 Hz, aromatic ring), 7.84 (s, 1H, NH), 7.56–7.40 (m, 19H, aromatic ring). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  = 43.27. IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3389 (N–H), 1674 (C=O). Anal. calcd for C<sub>33</sub>H<sub>24</sub>AuN<sub>2</sub>O<sub>3</sub>P (%): C, 54.71; H, 3.34; N, 3.87. Found: C, 54.55; H, 3.88; N, 3.87.

*Ph*<sub>3</sub>*PAuC* ≡ *CC*<sub>6</sub>*H*<sub>4</sub>*NHC*(*O*)*C*<sub>6</sub>*H*<sub>4</sub>−*CF*<sub>3</sub>−4 (**3b**). To a mixture of Ph<sub>3</sub>PAuCl (51.3 mg, 0.1037 mmol) and **2b** (37.6 mg, 0.1040 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added KF·2H<sub>2</sub>O (19.5 mg, 0.2072 mmol) in methanol dropwise. The mixture was stirred overnight in the dark. After evaporation to dryness, the solid residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Subsequent diffusion of diethyl ether into the concentrated CH<sub>2</sub>Cl<sub>2</sub> solution gave pale yellow crystals. Yield: 40.1 mg, 52%. <sup>1</sup>H NMR (300 MHz, CDCl3, 298 K):  $\delta$  = 7.95 (d, 2H, *J* = 8 Hz, aromatic ring), 7.77 (s, 1H, NH), 7.73 (d, 2H, *J* = 8 Hz, aromatic ring), 7.57–7.40 (m, 19H, aromatic ring). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  = 43.31. IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3432 (N–H), 1666 (C=O). Anal. calcd for C<sub>34</sub>H<sub>24</sub>AuF<sub>3</sub>NOP (%): C, 54.63; H, 3.24; N, 1.87. Found: C, 54.50; H, 3.24; N, 1.86.

*Ph*<sub>3</sub>*PAuC* ≡ *CC*<sub>6</sub>*H*<sub>4</sub>*NHC*(*O*)*C*<sub>6</sub>*H*<sub>5</sub> (*3c*). To a mixture of Ph<sub>3</sub>PAuCl (55.6 mg, 0.1124 mmol) and **2c** (34.5 mg, 0.1175 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added KF·2H<sub>2</sub>O (24.8 mg, 0.2645 mmol) in methanol dropwise. The mixture was stirred overnight in the dark. After evaporation to dryness, the solid residue was extracted with THF. Subsequent diffusion of diethyl ether into the concentrated THF solution gave yellow crystals. Yield: 51.4 mg, 67%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.83 (d, 2H, *J* = 7 Hz, aromatic ring), 7.77 (s, 1H, NH), 7.57–7.40 (m, 22H, aromatic ring). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  = 43.32. IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3434 (N-H), 1657 (C=O). Anal. calcd for C<sub>33</sub>H<sub>25</sub>AuNOP (%): C, 58.33; H, 3.71; N, 2.06. Found: C, 58.35; H, 3.72; N, 2.07.

*Ph*<sub>3</sub>*PAuC* ≡ *CC*<sub>6</sub>*H*<sub>4</sub>*NHC*(*O*)*C*<sub>6</sub>*H*<sub>4</sub>*−OMe*-4 (*3d*). To a mixture of Ph<sub>3</sub>PAuCl (51.8 mg, 0.1047 mmol) and 2d (34.5 mg, 0.1067 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added KF·2H<sub>2</sub>O (24.9 mg, 0.2645 mmol) in methanol dropwise. The mixture was stirred overnight in the dark. After evaporation to dryness, the solid residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Subsequent diffusion of diethyl ether into the concentrated CH<sub>2</sub>Cl<sub>2</sub> solution gave pale yellow crystals. Yield: 44.3 mg, 60%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K): δ = 7.80 (d, 2H, *J* = 9 Hz, aromatic ring), 7.68 (s, 1H, NH), 7.57-7.40 (m, 19H, aromatic ring), 6.95 (d, 2H, *J* = 9 Hz, aromatic ring), 3.85 (s, 3H, CH<sub>3</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298 K): δ = 43.34. IR (KBr, cm<sup>−1</sup>):  $\nu$  = 3430 (N–H), 1662 (C=O). Anal. calcd for C<sub>34</sub>H<sub>27</sub>AuNO<sub>2</sub>P (%): C, 57.55; H, 3.84; N, 1.97. Found: C, 57.61; H, 3.85; N, 1.96.

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