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PAPER

Facile synthesis and optical properties of magic-number Au<sub>13</sub> clusters

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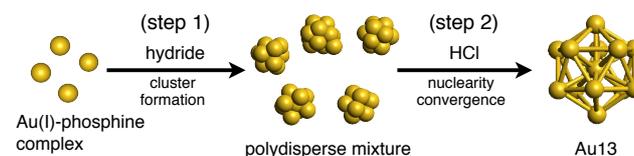
5 Synthesis of molecular gold clusters through the post-synthetic scheme involving HCl-promoted  
nuclearity convergence was examined with various phosphine ligands. Systematic studies with a series of  
bis(diphenylphosphino) ligands (Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>m</sub>-PPh<sub>2</sub>) using electrospray ionization mass spectrometry  
(ESI-MS) and electronic absorption spectroscopy demonstrated that the use of dppp (*m* = 3), dppb (*m* = 4)  
and dpppe (*m* = 5) as the ligand resulted in the formation of [Au<sub>13</sub>P<sub>8</sub>Cl<sub>4</sub>]<sup>+</sup> type clusters, whereas  
10 [Au<sub>13</sub>P<sub>10</sub>Cl<sub>2</sub>]<sup>3+</sup> type cluster was formed with dppe (*m* = 2). The cluster species did not survive the HCl  
treatment step when monophosphines PPh<sub>3</sub>, PMe<sub>2</sub>Ph, and POct<sub>3</sub> were employed, but [Au<sub>13</sub>(POct<sub>3</sub>)<sub>8</sub>Cl<sub>4</sub>]<sup>+</sup>  
was isolated as a minor product in the NaBH<sub>4</sub> reduction of Au(POct<sub>3</sub>)Cl in aqueous THF. Electronic  
absorption and photoluminescence studies of a series of Au<sub>13</sub> clusters revealed that their optical properties  
are highly dependent on the phosphine/chloride composition ratio, but are far less so on the phosphine  
15 structure.

## Introduction

Recent reports on unique properties of small metal clusters have revealed their enormous potentials for application towards nanotechnology.<sup>1</sup> Among them, “M<sub>13</sub>”-type cluster has enjoyed a  
20 special position, as it can take the smallest geometrically stable shell-closed structure (“magic number”).<sup>2</sup> For noble metal clusters, the successful single-crystal structure determination of Au<sub>13</sub> by Mingos et al.<sup>3</sup> and van der Velden et al.<sup>4</sup> are key milestones, and the icosahedral core motif has been widely  
utilised as structural models in catalyses<sup>5</sup> and theoretical studies.<sup>6</sup> Such icosahedral components are also interesting as they were observed as subunits in the structures of larger gold clusters<sup>7</sup> such as Au<sub>25</sub><sup>8</sup> and Au<sub>38</sub>.<sup>9</sup> Furthermore, the structures of some smaller clusters such as Au<sub>9</sub> and Au<sub>11</sub> may be described as fragments of  
25 icosahedral Au<sub>13</sub>.<sup>10</sup>

In spite of the important position and potential utility of Au<sub>13</sub> in cluster chemistry, further experimental studies have not been developed. This is probably because of the difficulty of the reported synthetic recipe that utilises non-conventional reducing  
35 agent (e.g., zerovalent titanium).<sup>3,11</sup> Although Au<sub>13</sub> clusters are expected to be thermodynamically stable due to the closed shell geometry, experimental reports showed that Au<sub>13</sub> species were not obtained as the primary products in the conventional hydride reduction reaction of gold ion.<sup>12</sup> Recently, we have reported a  
40 facile synthetic route to icosahedral Au<sub>13</sub> cluster protected by C<sub>2</sub>-bridged diphosphine ligand (Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>2</sub>-PPh<sub>2</sub>, dppe) by using unique capability of hydrochloric acid to promote the

convergence of nuclearity in polydisperse gold clusters (Scheme 1).<sup>13</sup> This synthetic method is quite simple and gives exclusively  
45 [Au<sub>13</sub>(dppe)<sub>5</sub>Cl<sub>2</sub>]<sup>3+</sup> (**1**) as the sole cluster species, allowing the large-scale preparation of Au<sub>13</sub> cluster.



**Scheme 1.** Schematic illustration of the two-step Au<sub>13</sub> cluster synthesis. Ligands are not shown for clarity.

50 In this paper, we investigated the versatility of the HCl-promoted post-synthetic scheme by using various monophosphines and alky-bridged diphosphines (Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>m</sub>-PPh<sub>2</sub>) (Scheme 1). Under similar experimental conditions to that employed for the synthesis of **1**, the use of dppp (*m* = 3), dppb (*m* = 4), and dpppe (*m* = 5) resulted in the preferential formation of specific cluster species, but they showed obviously different absorption spectral profiles from **1**. Studies coupled with ESI-MS measurements indicated that generated clusters have formula [Au<sub>13</sub>P<sub>8</sub>Cl<sub>4</sub>]<sup>+</sup>, which is of the same nuclearity as **1**  
60 ([Au<sub>13</sub>P<sub>10</sub>Cl<sub>2</sub>]<sup>3+</sup>) but is different in the numbers of coordinating phosphine and chloride ligands. When monophosphines PPh<sub>3</sub>, PPh<sub>2</sub>Me, and POct<sub>3</sub> were used, the cluster species did not survive the HCl treatment step, but we succeeded in the isolation of [Au<sub>13</sub>P<sub>8</sub>Cl<sub>4</sub>]<sup>+</sup>-type cluster as a minor product in the NaBH<sub>4</sub>  
65 reduction of Au(POct<sub>3</sub>)Cl. The two Au<sub>13</sub> species [Au<sub>13</sub>P<sub>8</sub>Cl<sub>4</sub>]<sup>+</sup> and [Au<sub>13</sub>P<sub>10</sub>Cl<sub>2</sub>]<sup>3+</sup> exhibited, though having the same nuclearity, different stability and optical properties.

## Experimental

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## Materials

Sodium tetrachloroaurate(III) dihydrate (>48% for gold) and tetrachloroauric(III) acid tetrahydrate (>47.5% for gold) were obtained Kojima Chemicals. Bis(diphenylphosphino)methane (dppm, 97%), bis(diphenylphosphino)ethane (dppe, 97%), 1,3-bis(diphenylphosphino)propane (dppp, 97%), 1,4-bis(diphenylphosphino)butane (dppb, 97%), 1,5-bis(diphenylphosphino)pentane (dpppe, 97%), 1,6-bis(diphenylphosphino)hexane (dpph, 97%), dimethylphenylphosphine (PMe<sub>2</sub>Ph, 97%), and sodium borohydride (99%) were obtained from Aldrich. Triphenylphosphine (PPh<sub>3</sub>, >97%), trioctylphosphine (POct<sub>3</sub>, 96%) and concentrated hydrochloric acid (35-37%) were purchased from Wako Pure Chemical Industries. Ethanol (99%) was obtained from Kawajiri Kogyo. Dichloromethane (>99%) and tetrahydrofuran (>98%) were obtained from Kanto Chemicals. All the above reagents were used as received. Chlorogold(I) phosphine complexes of diphosphine (Au<sub>2</sub>(L)Cl<sub>2</sub>) were prepared from sodium tetrachloroaurate(III) dehydrate according to literatures with some modifications.<sup>14</sup> [Au<sub>13</sub>(dppe)<sub>5</sub>Cl<sub>2</sub>]Cl<sub>3</sub> (1-Cl<sub>3</sub>) was prepared by a procedure reported previously.<sup>13</sup>

## Cluster synthesis

**Au<sub>n</sub>:dppp:** To a dichloromethane solution (120 mL) of Au<sub>2</sub>(dppp)Cl<sub>2</sub> (140 mg, 0.16 mmol) was added an ethanol solution (5 mL) of NaBH<sub>4</sub> (30.3 mg, 0.80 mmol) and the mixture was stirred at room temperature for 2 h. After removal of the solvent, the residue dissolved in dichloromethane was filtered to remove insoluble materials. The filtrate was evaporated to dryness to give Au<sub>n</sub>:dppp as a dark-brown solid (129.9 mg), which was used in the next step without further purification.

**[Au<sub>13</sub>(dppp)<sub>4</sub>Cl<sub>4</sub>]Cl (2-Cl):** Au<sub>n</sub>:dppp (120 mg) in ethanol (24.5 mL) was mixed with concentrated hydrochloric acid (0.5 mL, 6 mmol) and the mixture was stirred at room temperature for 68 h. After removal of precipitates by filtration, the filtrate was evaporated and redissolved in a minimum amount of dichloromethane, and passed through a Bio-Beads S-X3 column. The brownish orange fraction was collected as final product. Elemental analysis: calcd (%) for 2-Cl (C<sub>108</sub>H<sub>104</sub>Au<sub>13</sub>Cl<sub>5</sub>P<sub>8</sub>): C 29.57, H 2.39, Cl 4.04; found: C 29.16, H 2.45, Cl 4.43; no nitrogen was found.

**One-pot cluster synthesis from gold phosphine complex:** To an ethanol solution (9.5 mL) of chlorogold(I) phosphine complex (10 μmol) was added an ethanol solution (0.5 mL) of NaBH<sub>4</sub> (1.9 mg, 50 μmol) and the mixture was stirred at room temperature. After 1 h, the resulting brownish solution was mixed with 12 M HCl (60 μL, 720 μmol) and stirred for 24 h. An aliquot taken from the mixture was subjected to absorption spectroscopic measurement after dilution with a designated amount of ethanol.

**Synthesis of [Au<sub>13</sub>(POct<sub>3</sub>)<sub>8</sub>Cl<sub>4</sub>]Cl (5-Cl) via direct method:** To an aqueous solution of tetrachloroauric(III) acid tetrahydrate (15 mM, 100 mL) was added tetrahydrofuran solution (100 mL) of trioctylphosphine (560 mg, 1.5 mmol) and the mixture was stirred for 5 min. An aqueous solution (50 mL) of NaBH<sub>4</sub> (280 mg, 7.5 mmol) was added to this solution and the mixture was stirred for 1 h. The reaction mixture extracted with chloroform (150 mL) was washed twice with water, dried, and evaporated. The black powder thus obtained was redissolved into a minimum amount of

dichloromethane and passed through a Bio-Beads S-X1 column. An orange fraction eluted after a black fraction was collected and was subjected to spectrophotometric and ESI-MS measurements.

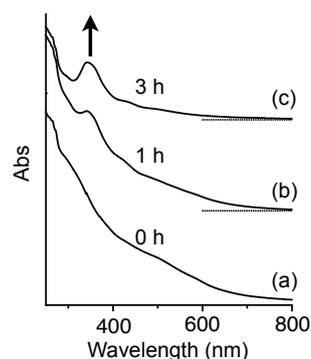
## Measurements

Electrospray ionization mass (ESI-MS) spectra were recorded on a Bruker micrOTOF-HS and optical absorption spectra were recorded using a JASCO V-670 spectrometer. Photoluminescence spectra were recorded with a JASCO FP-6500 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier tube detector.

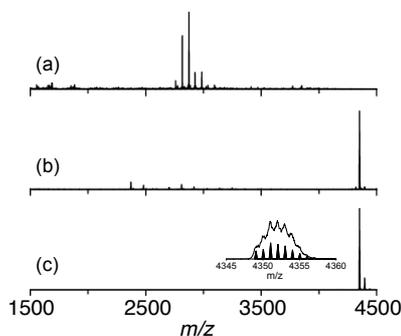
## Results and discussion

### HCl-promoted formation of [Au<sub>13</sub>(dppp)<sub>4</sub>Cl<sub>4</sub>]<sup>+</sup> (2).

Previously, we have reported two-step synthesis of icosahedral Au<sub>13</sub> cluster ligated by C2-bridged bis(diphenylphosphino) ligand (Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>m</sub>-PPh<sub>2</sub>, *m* = 2) (dppe) (Scheme 1). The first step involves the cluster formation by NaBH<sub>4</sub> reduction of Au<sub>2</sub>(dppe)Cl<sub>2</sub>, which gives a polydisperse gold cluster mixture. The second step is HCl-mediated nuclearity convergence of the polydisperse sample that exclusively affords [Au<sub>13</sub>P<sub>10</sub>Cl<sub>2</sub>]<sup>3+</sup>-type cluster cation (1). The absorption spectrum of the polydisperse sample was featureless, but distinct absorption bands at 360 and 490 nm emerged after the addition of hydrochloric acid. When dppp with a C3 bridge (*m* = 3) was used as the ligand, a similar change was observed in the absorption spectra. Thus, the as-reduced form (Au<sub>n</sub>:dppp) showed a monotonous pattern (Fig. 1a), but notable growth of new bands was observed after the addition of hydrochloric acid (Fig. 1b, c). The final spectrum of the reaction mixture after the spectral change reached saturation exhibited a distinct band at 340 nm together with a hump at 430 nm. This spectra was obviously different from that of the [Au<sub>13</sub>P<sub>10</sub>Cl<sub>2</sub>]<sup>3+</sup> type cluster 1,<sup>13</sup> and, rather, quite similar to that of [Au<sub>13</sub>(PMePh<sub>2</sub>)<sub>8</sub>Cl<sub>4</sub>]<sup>+</sup> reported by Mingos et al.<sup>11</sup> in shape and band position. Therefore, it is likely that [Au<sub>13</sub>P<sub>8</sub>Cl<sub>4</sub>]<sup>+</sup> rather than [Au<sub>13</sub>P<sub>10</sub>Cl<sub>2</sub>]<sup>3+</sup> was preferentially formed. Actually, the ESI-MS spectrum of the isolated cluster species showed a major set of signals at *m/z* ~4351, which could be assigned to the monovalent cluster cation [Au<sub>13</sub>(dppp)<sub>4</sub>Cl<sub>4</sub>]<sup>+</sup> (2) (Fig. 2c). It should be also noted that the formation of Au<sub>13</sub> cluster species was not detected before the HCl treatment. The precursor cluster (Au<sub>n</sub>:dppp), which was generated by the simple NaBH<sub>4</sub> reduction



**Fig. 1** Absorption spectra of Au<sub>n</sub>:dppp (a) and spectral changes after the HCl treatment (1 h (b), 3 h (c)) in ethanol at room temperature.

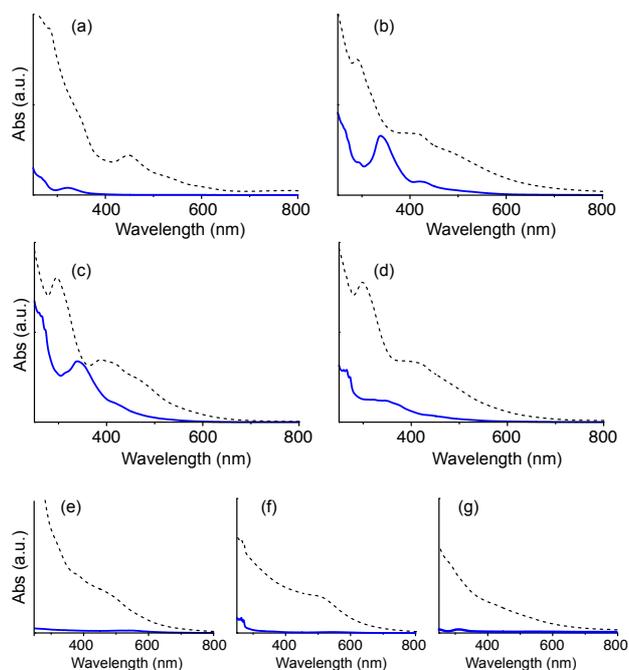


**Fig. 2** Positive-ion ESI mass spectra of  $Au_n:dppp$  (a), the reaction mixture after the HCl treatment for 3 h (b), and the cluster products after purification (c). The inset shows a comparison between the experimental data with the calculated isotope pattern of  $[Au_{13}(dppp)_4Cl_4]^+$ . For (a), two intense signals were assigned to  $[Au_{38}(dppp)_9Cl_2]^{4+}$  and  $[Au_{39}(dppp)_9Cl_3]^{4+}$ .

of  $Au_2(dppp)Cl_2$ , showed several ESI-MS signals at around  $m/z \sim 2800$  assignable to tetravalent cluster species (Fig. 2a), but after the HCl treatment these signals were disappeared and instead a single set of signals at  $m/z \sim 4351$  was observed dominantly (Fig. 2b). Thus, the HCl treatment caused effective nuclearity convergence through the selective etching of the cluster core.

#### Scope and limitation of the HCl-promoted cluster syntheses.

As we have seen, both dppe and dppp, which have a C2 and C3 methylene bridge respectively, are usable for the HCl-mediated two-step  $Au_{13}$  cluster syntheses, but the numbers of the coordinating phosphine and chloride ligands in the generated  $Au_{13}$  clusters are different from each other. This observation motivated us to examine the cluster synthesis with various phosphine ligands to investigate versatility of the HCl-treatment method and also the effect of the phosphine ligand structures on the composition of the generated cluster species. For screening, the *in-situ* generated hydride reduction product was directly treated with HCl without isolation of the intermediate cluster species (one-pot method). Thus, chlorogold(I) phosphine complex was reacted with  $NaBH_4$  in ethanol at room temperature for 1 h, and then the resulting solution was treated with concentrated hydrochloric acid for 24 h. Fig. 3a-d show the absorption spectra of the reaction mixtures before and after the addition of HCl when dppm ( $m = 1$ ), dppb ( $m = 4$ ), dpppe ( $m = 5$ ), and dpph ( $m = 6$ ) were used as ligands. When the ligand with a C4 (dppb) or C5 (dpppe) bridge was employed, the spectrum after the HCl treatment showed a major band at around 340 nm (Fig. 3b, c) and was almost similar to that observed with dppp ( $m = 3$ , Fig. 1c). This result implies the dominant formation of  $[Au_{13}P_8Cl_4]^+$  type clusters ( $[Au_{13}(dppb)_4Cl_4]^+$  (3),  $[Au_{13}(dpppe)_4Cl_4]^+$  (4)). On the other hand, when dppm with a shorter C1 bridge or dpph with a longer C6 bridge was used, the absorbance of the reaction mixture was much smaller (Fig. 3a, d), suggesting that the significant decomposition of the cluster species by the HCl treatment. More remarkably, negligible absorptions were observed above 300 nm when coupled with monophosphines,  $PPh_3$ ,  $PMe_2Ph$ , and  $POct_3$ , indicating the complete etching of the initially formed clusters (Fig. 3e, f, g). From these observations, chelating effects of the diphosphine ligands with an appropriate bridging moiety ( $m = 2 - 5$ ) may effectively suppress the acid-

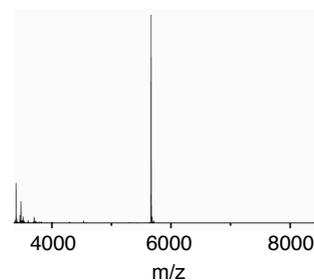


**Fig. 3** One-pot cluster syntheses with dppm (a), dppb (b), dpppe (c), dpph (d),  $PPh_3$  (e),  $PMe_2Ph$  (f), and  $POct_3$  (g) in ethanol. Absorption spectra of chlorogold phosphine complexes after the  $NaBH_4$  treatment for 1 h (black dotted), and the reaction mixtures after the successive treatment with hydrochloric acid for 24 h (blue solid).

induced disassembling of the metal atoms, allowing the exclusive formation of thermodynamically stable  $Au_{13}$  cluster species even in the presence of strong acid.

#### Synthesis of $[Au_{13}(POct_3)_8Cl_4]^+$ via direct method.

The above-mentioned results indicate that the HCl-treatment method was not usable for the synthesis of monophosphine/chloride-coordinated gold clusters, probably because of the lability of the intermediates towards strong acid. However, during the course of the optimisation of the reaction conditions of the hydride reduction process (step 1 in Scheme 1), we found that  $Au_{13}$  species was formed as a minor product when  $Au(POct_3)Cl$  was reduced with  $NaBH_4$  in aqueous tetrahydrofuran. The main product of this reaction was phosphine-coordinated large gold nanocluster ( $d = 1.2 - 1.5$  nm), which shows a monotonous tailing from UV to near-infrared in the absorption spectrum, but the reaction mixture showed a small shoulder at  $\sim 340$  nm overlapped with the tailing. The two cluster species were successfully separated by size exclusion

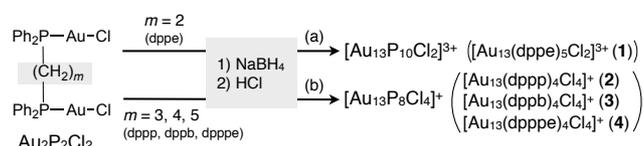


**Fig. 4** Positive-ion ESI mass spectrum of the orange fraction in the SEC separation of the reduction product of  $Au(POct_3)Cl$ .

chromatography with BioBeads S-X1, where a brownish orange fraction was isolated from the leading black fraction. The absorption spectrum of the orange fraction was almost identical to those of **2** and  $[\text{Au}_{13}(\text{PMePh}_2)_8\text{Cl}_4]^+$ , thus it was identified as  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]^+$  type cluster ( $[\text{Au}_{13}(\text{P}(\text{Oct})_3)_8\text{Cl}_4]^+$  (**5**)). Accordingly, the ESI-MS spectrum of the orange fraction showed a single set of signals at  $\sim 5670$  due to the monovalent ion ( $[\text{Au}_{13}(\text{P}(\text{Oct})_3)_8\text{Cl}_4]^+$  calcd  $m/z = 5667$ ) (Fig. 4).

### Optical properties of $\text{Au}_{13}$ clusters.

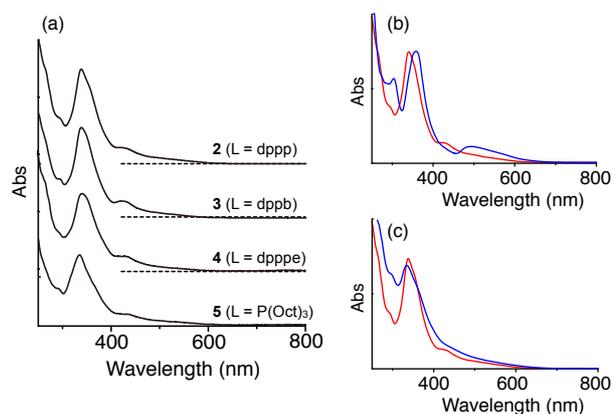
As we have shown in the above sections,  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]^+$  clusters were preferentially formed with dppp, dppb, dpppe (Scheme 2b) and  $\text{POct}_3$  ligands. On the other hand, the formation of  $[\text{Au}_{13}\text{P}_{10}\text{Cl}_2]^{3+}$  cluster was solely observed with dppe (Scheme 2a). In this regard,  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]^+$  seems more ubiquitous than  $[\text{Au}_{13}\text{P}_{10}\text{Cl}_2]^{3+}$ . We previously showed the icosahedral core structure of **1**- $(\text{SbF}_6)_3$  through crystallographic studies,<sup>13</sup> but the preparation of single crystals of  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]^+$  clusters (**2** – **5**) suitable for structural analysis has been unsuccessful. However, considering the crystallographically defined icosahedral cores of analogous bimetallic  $[\text{M}_{13}\text{P}_8\text{Cl}_4]^{n+}$  clusters (Au-Pd,<sup>15</sup> Au-Ag,<sup>11</sup> Au-Cu<sup>11</sup>), it should be reasonable to assume **2** – **5** also adopt icosahedral cores.



**Scheme 2.** Selective formation of two types of  $\text{Au}_{13}$  clusters through HCl-promoted post-synthetic scheme.

Fig. 5a summarises the absorption spectra of purified  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]^+$  clusters (**2**-Cl, **3**-Cl, **4**-Cl, **5**-Cl) in acetonitrile. All spectra are almost identical to show a strong band at  $\sim 340$  nm together with a hump at  $\sim 430$  nm, indicating that the influence of the phosphine structure on the electronic transition is negligible. On the other hand,  $[\text{Au}_{13}\text{P}_{10}\text{Cl}_2]^{3+}$  cluster (**1**) showed an evidently different spectral profile, as exemplified in the spectra of **1**-Cl<sub>3</sub> and **2**-Cl in acetonitrile (Fig. 5b). It is generally accepted that the absorption spectra of gold clusters are highly affected by the core nuclearity but are far less so by the coordinating ligands. However, the results clearly show that the absorption profiles are critically dependent on the numbers of phosphine/chloride ligands. This observation suggests that the ligand-to-metal charge transfer is involved in the electronic transitions in the  $\text{Au}_{13}$  clusters. Theoretical studies are in progress to obtain further insights into the structure-optical feature relationships.

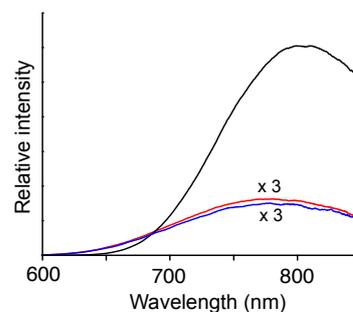
Fig. 5c shows the absorption spectra of **1**-Cl<sub>3</sub> (blue) and **2**-Cl (red) in dichloromethane. The spectrum of the  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]^+$  cluster (**2**-Cl) in dichloromethane almost coincided with that measured in acetonitrile (Fig. 5b and 5c, red). In contrast, the spectra of **1**-Cl<sub>3</sub> in dichloromethane (Fig. 5c, blue) and in acetonitrile (Fig. 5b, blue) were obviously different from each other. ESI-MS spectrum of **1**-Cl<sub>3</sub> in dichloromethane showed dominant signals due to  $[\text{Au}_{13}(\text{dppe})_5\text{Cl}_3]^{2+}$  ( $m/z \sim 2329$ ),  $[\text{Au}_{14}(\text{dppe})_5\text{Cl}_4]^{2+}$  ( $m/z \sim 2446$ ) and  $[\text{Au}_{13}(\text{dppe})_4\text{Cl}_4]^+$  ( $m/z \sim 4295$ ), and the signals due to  $[\text{Au}_{13}(\text{dppe})_5\text{Cl}_2]^{3+}$ , which were observed in acetonitrile as the sole set of signals,<sup>13</sup> were not



**Fig. 5** Absorption spectra of (a)  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]\text{Cl}$  clusters (**2**-Cl, **3**-Cl, **4**-Cl, **5**-Cl) in acetonitrile, (b) **1**-Cl<sub>3</sub> (blue) and **2**-Cl (red) in acetonitrile (red), and (c) **1**-Cl<sub>3</sub> (blue) and **2**-Cl (red) in dichloromethane.

detected at all. Therefore, it is likely that **1** in dichloromethane gives a cluster mixture as the result of intermolecular scrambling. This process appeared virtually reversible. When **1**-Cl<sub>3</sub> in dichloromethane was once evaporated and redissolved in acetonitrile, the resulting cluster solution showed an almost identical absorption spectrum to the fresh sample in acetonitrile.

Finally, we investigated the photoluminescence properties of the  $\text{Au}_{13}$  clusters, which should be interesting in relation to the recent reports of fluorescent small gold clusters.<sup>16</sup> In the previous paper,<sup>13</sup> we demonstrated that **1**-Cl<sub>3</sub> in acetonitrile shows a near-infrared emission when excited at 360 nm. Likewise,  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]^+$  clusters, such as **2**-Cl and **5**-Cl, showed photoluminescence at the near-infrared region (Fig. 6), but their quantum efficiencies ( $\sim 0.008$ ) were much lower than that of **1**-Cl<sub>3</sub> (0.062). Nevertheless the above observations indicate that near infrared photoluminescence activity is an intrinsic feature of  $\text{Au}_{13}$  clusters.



**Fig. 6** Corrected photoluminescence spectra of phosphine-protected gold clusters **1**-Cl<sub>3</sub> ( $\lambda_{\text{ex}} = 360$  nm, black), **2**-Cl ( $\lambda_{\text{ex}} = 340$  nm, blue) and **5**-Cl ( $\lambda_{\text{ex}} = 338$  nm, red) in acetonitrile at room temperature. The intensity was normalized based on the absorbance at the excitation wavelength.

## Conclusion

In summary, we have shown that the use of C2 – C5 –bridged bis(diphenylphosphino) ligands in the post-synthetic scheme involving the HCl-mediated nuclearity convergence process resulted in the preferential formation of  $\text{Au}_{13}$  clusters, but the composition ratios of the coordinating phosphine/chloride ligands were dependent on the length of the methylene bridge of the

diphosphine ligands. The formation of  $[\text{Au}_{13}\text{P}_{10}\text{Cl}_2]^{3+}$  cluster was favoured only for the C2-bridged dppe, while  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]^+$  clusters were formed for the ligands having a C3 - C5 methylene bridge (dppp, dppb, dpppe). These findings together with the isolation of  $[\text{Au}_{13}(\text{POct}_3)_8\text{Cl}_4]^+$  imply that  $[\text{Au}_{13}\text{P}_8\text{Cl}_4]^+$  type clusters are more ubiquitous than  $[\text{Au}_{13}\text{P}_{10}\text{Cl}_2]^{3+}$ . We have also shown that the optical properties of gold clusters are dependent not only on the core nuclearity/geometry but also on the numbers of anionic ( $\text{Cl}^-$ ) / neutral (phosphine) ligands. Crystal structure determination and theoretical studies to understand the optical properties are worthy of further investigations.

## Acknowledgements

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## Notes and references

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