STM Images of Individual Porphyrin Molecules on Cu(100) and Cu(111) Surfaces**

Nick Bampos, Charles N. Woodburn,
Mark E. Welland,* and Jeremy K. M. Sanders*

The pioneering work by Binnig and Rohrer on the development of scanning tunneling microscopy (STM)[1] has led to a new way with which to "see" molecules at the atomic level. Much of the work reported in recent years has centered on the long-range ordering/reconstruction of metal surfaces and investigations of the properties of the conducting surface itself.[2] Some of these images suffer from poor resolution due to thermally induced motion, poor adhesion of the substrate to the surface, poor instrumentation, or inferior tip preparation. Though many of these problems have been remedied by better surface preparation and molecular deposition or by improved instrumentation, sample preparation remains nontrivial. For organic molecules additional problems arise, mainly because interactions with the surface are often too weak to inhibit molecular motion. While STM images of organic systems, in particular, are notoriously difficult to interpret,[3, 4] studies of individual molecules have been reported.[5] In a seminal report of a highly symmetrical copper phthalocyanine molecule on Cu(100) image interpretation was achieved by using Elastic Scattering Quantum Chemistry (ESQC) calculations to successfully simulate the STM image.[6] Such simulation techniques, while often very useful, are computationally demanding, which rather limits their appeal. However, we show here that more complicated molecules designed for genuine chemical applications can provide valuable additional information which may be used to understand the mechanism behind image contrast.

While recent advances have produced excellent images of molecules physisorbed onto surfaces, chemisorption generally results in superior images (particularly at room temperature), as the molecules are immobilized and not subject to thermal drift. For example, alkanethiols have proved useful on gold surfaces due to the covalent S–Au bond which pins the molecule to the surface, resulting in dense, highly ordered adlayers, in which the molecules stand perpendicular to the surface.[7] In general, good images have been reported in air and in solution, but the images with the highest resolution have been obtained under ultrahigh vacuum (UHV) conditions. STM under UHV conditions has been used to image organic molecules such as coadsorbed benzene and CO on Rh(111),[8] benzene[9] and naphthalene[10] on Pt(111), and copper phthalocyanine on Cu(100).[11] However, recent work on the imaging and manipulation of symmetrical porphyrin monomers, which will adsorb predominantly flat on the surface, is of greater relevance to our work.[12, 13]

Although image contrast at the atomic level on idealized surfaces is feasible by STM, image contrast for molecules is the result of tip–molecule–surface interactions. Such contrast depends upon the symmetry and wavefunction mixing of the molecular orbitals with the substrate.[14] This mixing can perturb the electronic structure of the molecule from that of its isolated state. Additionally, the contrast will also depend upon the direction of tunneling and magnitude of the tunneling voltage. In the case of a well-documented copper phthalocyanine molecule,[11a] the fine structure of the image is in agreement with the calculated HOMO of the free molecule. High-resolution images have been obtained by Jung et al.[13] by employing a tetrasubstituted copper porphyrin on Cu(100), Au(110), and Ag(110) surfaces under UHV conditions. In their study a) Cu is used to enhance chemisorption with the metal surface, b) the porphyrin used is highly symmetrical and image interpretation simplified as a result, and c) the porphyrin is relatively rigid, with large *tert*-butyl feet resting on the surface. The (four) lobes observed in these images were attributed, within instrumentation accuracy, to the (four) *meso* di-*tert*-butylphenyl substituents. Images of a tetrasubstituted porphyrin monomer on iodine-modified Au(111) in solution have also been used for conformational analysis and to determine the orientation of individual molecules.[13a]

For a comprehensive understanding of the contrast observed whilst molecules are being imaged in the STM, significant modeling of the tip–molecule–surface interaction is required. Despite this, it is often possible to assign contrast in a qualitative way by directly comparing the known molecular structure with the STM images. In this case it is important to minimize the electronic contribution of the surface by choosing flat metallic surfaces with small corrugation amplitude. In this paper we describe the imaging of a porphyrin monomer, a linear porphyrin dimer, and cyclic oligomers which have not been chosen or engineered to maximize their interaction with the surface.

The Cu(111) and Cu(100) surfaces used in our studies were cleaned by cycles of sputtering by argon-ion bombardment and subsequent annealing at high temperature[15] to give atomically flat regions free of impurities.[16] This procedure must be repeated a number of times to give a workable surface, which can then be imaged by STM prior to sample deposition.

The lowest molecular weight molecule deposited (on Cu(111)) was the *meta*-substituted zinc porphyrin **1** ($M_w = 1119$), used previously as a building block in the preparation of cyclic oligomeric hosts.[17] In the solution state (^{1}H NMR spectrum) **1** exhibits two-fold symmetry, as rapid rotation occurs about the porphyrin–phenyl bond. In the solid state the trimethylsilylalkynyl arms may be directed to the same or the opposite sides of a plane of symmetry.

Monomer **1** was deposited at close to the decomposition temperature (300–330 °C) under vacuum (5×10^{-8} mbar) over six hours. The ideal deposition conditions were a compromise between a low temperature, which minimizes

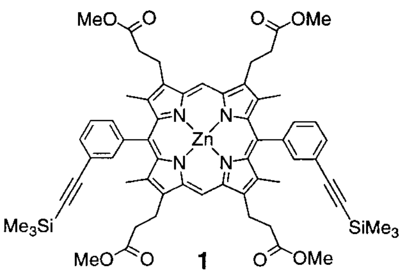
---

[*] Dr. M. E. Welland, Dr. C. N. Woodburn
Nanoscale Group, Department of Engineering
Trumpington Street, Cambridge CB21PZ (UK)
Fax: (+44) 1223-339263
E-mail: mew10@eng.cam.ac.uk

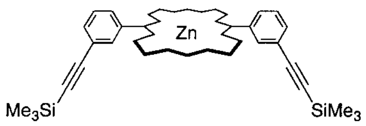
Prof. J. K. M. Sanders, Dr. N. Bampos
Cambridge Centre for Molecular Recognition
University Chemical Laboratory
Lensfield Road, Cambridge CB21EW (UK)
Fax: (+44) 1223-336017
E-mail: jkms@cam.ac.uk

[**] We thank the EPSRC (J.K.M.S. and N.B.) and ESPRIT project NANOWIRES (M.E.W. and C.N.W.) for financial support.

1433-7851/99/3818-2780 $ 17.50+.50/0



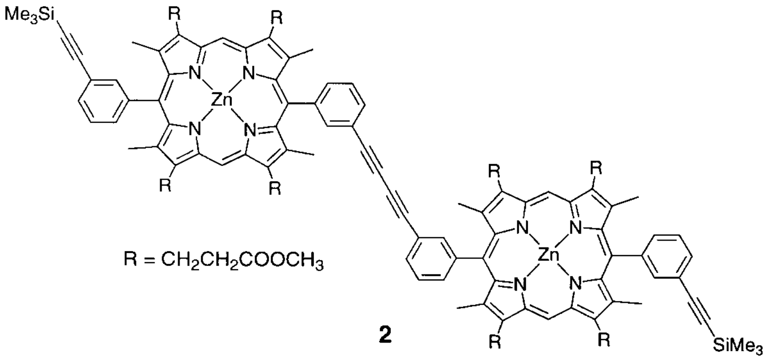
1



fragmentation of the molecule, and higher temperatures, which give greater deposition rates but increased likelihood of fragmentation. In all images presented here no significant fragmentation was observed. The best tunneling conditions for imaging were achieved at high gap impedances. To improve the contrast, tunneling currents below 0.2 nA were needed with approximately −3 V sample bias. The resulting images show the monomers preferentially populating the step edges. This may be due to the three-dimensional nature of the monomers, which would give the maximum interaction with the surface at the edges. In one region away from the step edge, two Zn monomers can be clearly identified (Figure 1). The spacing between the two bright peaks in the image was measured as approximately 12 Å, which corresponds to the distance between the phenyl groups in the individual monomers (for comparison, the smallest separation between trimethylsilyl (TMS) groups is approximately 19 Å) from molecular modeling (Cerius^2)[18] and single-crystal X-ray diffraction studies.[19] Such a visualization of the molecule is not unlikely if we assume that the dominant contribution to the image is due to the *meso*-bound phenyl groups. The orientation of the two units suggests common registration with the surface, though on the whole, mobility at room temperature eventually results in significant aggregation at the step edges.

Figure 1. STM image of two molecules of zinc monomer **1** with common registration orientation to the surface; image size: 65 × 65 Å; $V_s = -2711$ mV, $I = 0.1$ nA. The distance between the two bright regions per porphyrin molecule approximately corresponds to the distance between the two *meso*-substituted phenyl groups. In this image the porphyrin plane is assumed to be perpendicular to the surface. Note that all the STM images have been filtered with a low-pass filter to remove high-frequency noise; the gray scale has been coded so that a high topographic feature appears white.

Linear dimer **2** ($M_w = 2090$) is one in a series of porphyrin oligomers investigated as a building block for large hosts.[20] In the solution state (^{1}H NMR spectrum) the molecule exhibits symmetry by virtue of the rotation about the butadiyne linker. In contrast to the other molecules imaged in this study linear dimer **2** is a long molecule with a defined shape and the possibility of two structurally distinct conformations, which should simplify the image interpretation. In order to overcome molecular diffusion (on Cu(100)) the STM was cooled to 98 K (liquid nitrogen) over a period of three days. While deposition rates were very low (0.3 Å h^{-1} after 24 h), scanning the surface revealed isolated features on the surface terraces. The stability of the system permitted repeated scans at a variety of tip–substrate biases. Scanning at low temperature greatly improved resolution and allowed imaging at lower tip–substrate biases. The highest contrast was achieved with a sample bias of −1440 mV and a tunnel current of 0.08 nA. Lowering the impedance further (i.e. decreasing the distance between the tip and the conducting surface) resulted in the molecules being dragged by the tip.



R = $CH_2CH_2COOCH_3$

2

Under the UHV conditions employed scanning of the plateaus at low coverage provided many high-quality images of single molecules adopting one of two orientations. The best interaction with the surface is achieved when the molecule rests on its side, allowing the ester chains and the TMS groups to come into contact with the surface. In this configuration the porphyrin plane sits perpendicular to the copper surface, and as they rest on the surface, the molecules may adopt a cisoid or transoid orientation; examples of each can be clearly distinguished in the images (Figure 2).

Molecular modeling indicates that the phenyl–phenyl distance across the butadiyne linker is 9 Å, while across the porphyrin it is 12 Å. From the STM image the spacing between the bright lobes was measured at 11(±1) Å. In the images in Figure 2 the termini of the linear molecules exhibit features that can be attributed to the large TMS groups. It is, however, important to note that although the measured

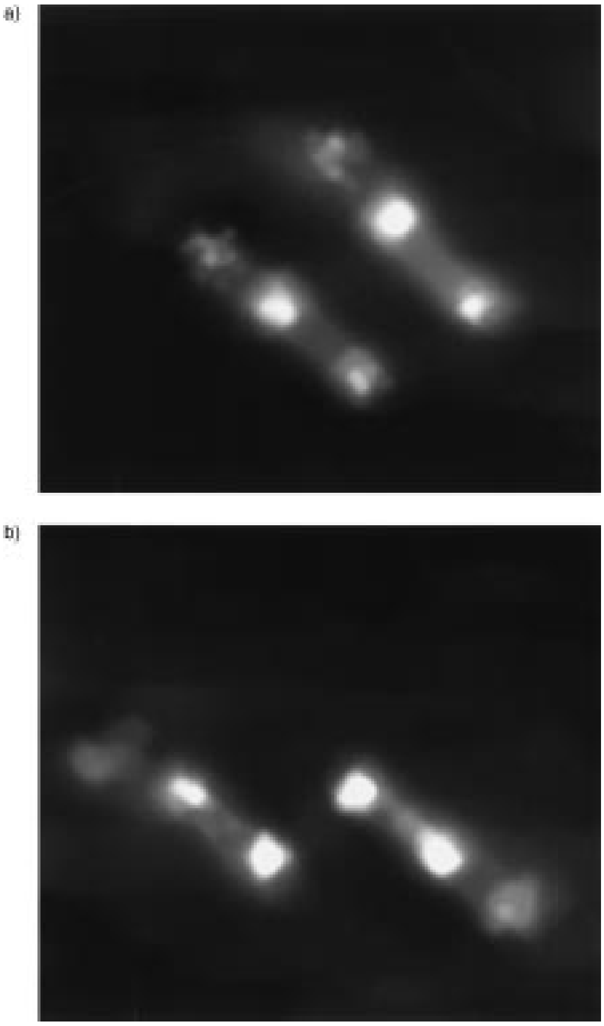
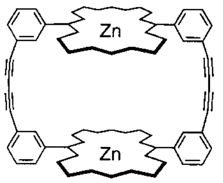


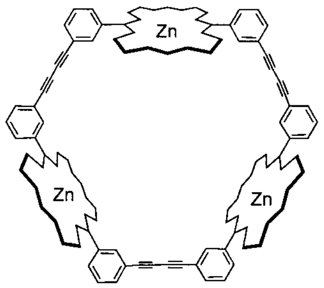
Figure 2. STM image of the linear dimer **2** in the cisoid (a) and transoid (b) conformations at 98 K; image size: 60 × 40 Å; $V_s = -1440$ mV, $I = 0.08$ nA. Conversion of one isomer to the other is achieved by rotation about the butadiyne linker prior to low-temperature imaging.

spacing of the groups within the molecules is consistent with molecular modeling, their positions are sometimes skewed relative to the rest of the molecule. This is probably due to a reorientation of the molecule as a result of the interaction with the surface. The bright features recorded may be attributed to the ester side chains pointing up and away from the surface, although their flexibility and distance from the conducting surface makes this very unlikely. We suggest that the image is the result of the interaction of the tip with the aromatic π system, and the distance between the bright lobes supports this. All the molecules we have investigated to date are *meta*-substituted on the phenyl groups and as a result are not flat.

The larger cyclic dimer **3** ($M_w = 1944$, on Cu(100)) and cyclic trimer **4** ($M_w = 2917$, on Cu(111)) give relatively simple ^{1}H NMR spectra by virtue of their C_n symmetry.[20] In the solid state the high degree of symmetry was expected to aid the identification of these large hosts. Unfortunately, significant decomposition of these compounds occurred during deposition, resulting in extremely low deposition rates. Even when images were identified molecular diffusion made imaging difficult. Images derived from these experiments were not very encouraging because long-range order or fine structure could not be detected. These results show the limits of sample deposition from the gas phase.



3



4

While these results have not in themselves led to a straightforward description of the mechanism of image contrast, they demonstrate the potential of STM to image molecular structure and conformation on a surface. This technique could act as an alternative to single-crystal X-ray diffraction for structure determination: crystals of this type of molecule are often difficult to obtain. For truly quantitative interpretation of the images, however, detailed modeling of the molecule–surface interaction is required. In addition, by using other molecules that differ in some controlled and predictable manner, the nature of image contrast can be studied in greater depth.

Received: June 4, 1998
Revised version: April 8, 1999 [Z11948IE]
German version: *Angew. Chem.* **1999**, *111*, 2949–2953

Keywords: porphyrinoids · scanning tunneling microscopy · ultrahigh vacuum

---

[1] a) R. M. Feenstra, *Surf. Sci.* **1994**, *300*, 965; b) G. Binnig, H. Rohrer, C. Gerber, E. Weibel, *Phys. Rev. Lett.* **1982**, *49*, 57.

[2] For example, see: a) J. Kuntze, J. Bomermann, T. Rauch, S. Speller, W. Heiland, *Surf. Sci.* **1997**, *394*, 150; b) S. Mizuno, H. Tochihara, Y. Matsumoto, K. Tanaka, *Surf. Sci.* **1997**, *393*, L69; c) T. Kawamura, S. Kojima, T. Kanzawa, *J. Appl. Phys.* **1997**, *82*, 6031; d) A. A. Baski, S. C. Erwin, L. J. Whitman, *Surf. Sci.* **1997**, *392*, 69; e) A. A. Saranin, T. Numata, O. Kubo, M. Katayama, K. Oura, *Appl. Surf. Sci.* **1997**, *121*, 183; f) H. E. Hoster, M. A. Kulakov, B. Bullemer, *Surf. Sci.* **1997**, *382*, L658; g) F. Besenbacher, *Rep. Prog. Phys.* **1996**, *59*, 1732; h) M. A. Kulakov, G. Henn, B. Bullemier, *Surf. Sci.* **1996**, *396*, 49; i) M. Bode, R. Pascal, R. Wiesendanger, *Surf. Sci.* **1995**, *344*, 185; j) M. Hohage, T. Michely, G. Comsa, *Surf. Sci.* **1995**, *337*, 249; k) W. Arabczyk, S. Hinrich, H. J. Mussig, *Vacuum* **1995**, *46*, 473; l) X. S. Wang, W. H. Weinberg, *Surf. Sci.* **1994**, *314*, 71; m) H. Onishi, Y. Iwasawa, *Surf. Sci.* **1994**, *313*, L783; n) Y. Hasegawa, P. Avouris, *Science* **1992**, *258*, 1763; o) V. S. Iyer, K. Yoshimura, V. Enkelmann, R. Epsch, J. P. Rabe, K. Müllen, *Angew. Chem.* **1998**, *110*, 2843; *Angew. Chem. Int. Ed.* **1998**, *37*, 2696.

[3] R. Weisendanger, *Scanning Probe Microscopy, Methods and Applications*, Cambridge University Press, Cambridge, UK, **1994**.

[4] S. Chiang, *Chem. Rev.* **1997**, *97*, 1083.

[5] a) J. K. Gimzewski, E. Stoll, R. R. Schlittler, *Surf. Sci.* **1987**, *181*, 267; b) J. A. Venables, D. J. Smith, J. M. Cowley, *Surf. Sci.* **1987**, *181*, 235.

[6] a) P. Sautet, C. Joachim, *Surf. Sci.* **1992**, *271*, 387; b) P. Sautet, *Chem. Rev.* **1997**, *97*, 1097.

[7] a) C. A. Alves, E. L. Smith, M. D. Porter, *J. Am. Chem. Soc.* **1992**, *114*, 1222; b) S. J. Stranick, A. N. Parikh, Y. T. Tao, D. L. Allara, P. S. Weiss,

J. Phys. Chem. **1994**, *98*, 7636; c) G. E. Poirier, M. J. Tarlov, *Langmuir* **1994**, *10*, 2853; d) M. Sprik, E. Dalamarche, B. Michel, U. Rothlisbrger, M. L. Klein, H. Wolf, H. Ringsdorf, *Langmuir* **1994**, *10*, 4116; e) W. B. Caldwell, D. J. Cambell, K. Chen, B. R. Herr, C. A. Mirkin, A. Malik, M. K. Durbin, P. Dutta, K. G. Huang, *J. Am. Chem. Soc.* **1995**, *117*, 6071; f) G. E. Poirier, E. D. Pylant, *Science* **1996**, *272*, 1145.

[8] H. Ohtani, R. J. Wilson, S. Chiang, C. M. Mate, *Phys. Rev. Lett.* **1988**, *60*, 2398.

[9] P. S. Weiss, D. M. Eigler, *Phys. Rev. Lett.* **1993**, *71*, 3139.

[10] V. M. Hallmark, S. Chiang, J. K. Brown, C. Woll, *Phys. Rev. Lett.* **1991**, *66*, 48.

[11] a) P. H. Lippel, R. J. Wolson, M. D. Miller, C. Woll, S. Chiang, *Phys. Rev. Lett.* **1989**, *62*, 171; b) T. Fritz, M. Hara, W. Knoll, H. Sasabe, *Mol. Cryst. Liq. Cryst.* **1994**, *253*, 269.

[12] a) M. Kunitake, U. Akiba, N. Batina, K. Itaya, *Langmuir* **1997**, *13*, 1607; b) N. J. Tao, G. Cardenas, F. Cunha, Z. Shi, *Langmuir* **1995**, *11*, 4445; c) M. Kunitake, U. Akiba, N. Batina, K. Itaya, *Langmuir* **1997**, *13*, 1607.

[13] a) T. A. Jung, R. R. Schlitter, J. K. Gimzewski, H. Tang, C. Joachim, *Science* **1996**, *271*, 181; b) T. A. Jung, R. R. Schlitter, J. K. Gimzewski, *Nature* **1997**, *386*, 696; c) J. K. Gimzewski, C. Joachim, R. R. Schlitter, V. Langlais, H. Tang, I. Johannsen, *Science* **1998**, *281*, 531.

[14] a) G. Binning, C. F. Quate, C. Gerber, *Phys. Rev. Lett.* **1986**, *56*, 930; b) M. M. D. Ramos, *J. Phys. Condens. Matter* **1993**, *5*, 2843.

[15] D. P. Woodruff, T. A. Delchar, *Modern Techniques of Surface Science*, Cambridge University Press, Cambridge, UK, **1986**.

[16] C. N. Woodburn, PhD Thesis, University of Cambridge, UK, **1996**.

[17] H. L. Anderson, J. K. M. Sanders, *J. Chem. Soc. Perkin Trans. 1* **1995**, 22.

[18] Cerius^2 Version 3, MSI Cambridge, Cambridge (England) running on an SGI R4000 computer.

[19] N. Bampos, M. R. Prinsep, H. He, A. Vidal-Ferran, A. Bashall, M. McPartlin, H. Powell, J. K. M. Sanders, *J. Chem. Soc. Perkin Trans. 2* **1998**, 715.

[20] S. Anderson, H. L. Anderson, J. K. M. Sanders, *J. Chem. Soc. Perkin Trans. 1* **1995**, 2247.

The Intrinsic ^{3}[dσ*pσ] Emission of Binuclear Gold(I) Complexes with Two Bridging Diphosphane Ligands Lies in the Near UV; Emissions in the Visible Region Are Due to Exciplexes[**]

Wen-Fu Fu, Kwok-Chu Chan, Vincent M. Miskowski, and Chi-Ming Che*

Since the first report on the photoluminescence of $[Au_2(dppm)_2]^{2+}$ (dppm = bis(diphenylphosphanyl)methane),[1, 2] luminescent gold(I) compounds, particularly those involving Au–Au interactions, have received considerable attention.[3] Polynuclear gold(I) phosphane complexes generally display long-lived emissions in the visible region, and this was usually attributed to excited states involving Au–Au bonding.[1–11] The Au–Au interaction is expected to lower the energy of the 5dσ* → 6pσ transition, where 5dσ* and 6pσ refer to the antibonding combination of the $5d_{z^2}$ and to the bonding combination of the $6s/6p_z$ orbitals, respectively, and the Au–Au axis is defined as the *z* axis. $[Au_2(dppm)_2](ClO_4)_2$ displays luminescence with λ_{max} at 575 nm in solution in acetonitrile.[1, 2] Importantly, this emission, which was assigned to the ^{3}[dσ*pσ] excited state, is substantially red-shifted relative to the spin- and dipole-allowed ^{1}(dσ* → pσ) electronic absorption transition at 290 nm, an apparent Stokes shift of 17100 cm^{-1} (2.1 eV). This is an extraordinarily large Stokes shift, particularly when compared to the Stokes shifts of 6000–8000 cm^{-1} reported for the phosphorescence of d^8–d^8 binuclear compounds from their ^{1}(dσ* → pσ) absorptions.[12] The emissive state for these latter compounds is well established as ^{3}[dσ*pσ] and hence should be nominally analogous to the emissive state of the d^{10}–d^{10} Au^I complexes. Our recent ab initio calculations on $[Au_2(H_2PCH_2PH_2)_2]^{2+}$ predicted that its ^{3}[dσ*pσ] excited state emits at 331 nm, that is, much higher in energy than reported in the literature, but readily forms an exciplex with acetonitrile molecules that is predicted to emit at 557 nm at room temperature.[13] Herein we describe experimental evidence for an intrinsic high-energy ^{3}[dσ*pσ] state and visible-region emissions of solvent or anion exciplexes for binuclear gold(I) phosphane complexes.

We synthesized complexes of the type $[Au_2(dcpm)_2]Y_2$ [dcpm = bis(dicyclohexylphosphanyl)methane, Y = ClO_4^- (**1**), PF_6^- (**2**), $CF_3SO_3^-$ (**3**), $[Au(CN)_2]^-$ (**4**), Cl^- (**5**), and I^- (**6**); see Figure 1], and **1**, **4**, and **6** were characterized by single-crystal X-ray structure determination.[14] The ligand conformations and Au–Au distances (2.9263(9), 2.9876(5), and 3.0132(6) Å for **1**, **4**, and **6**, respectively) are typical for bis(diphosphane)-bridged binuclear Au^I complexes.[15, 16] The structure of **6** features short Au···I contacts (3.069(1) Å) that result in a T-shaped AuP_2I geometry at the Au atoms. This is also typical; Mason et al.[15] reported a number of structures of halide (Cl^-, Br^-, I^-) salts of $[Au_2(diphosphane)_2]^{2+}$ cations [diphosphane = bis(dimethylphosphanyl)methane (dmpm) or bis(dimethylphosphanyl)ethane (dmpe)] that feature similar cation···anion interactions. Importantly for our present considerations, the closest Au···anion contacts in **1** (Au···$OClO_3$ 3.36[2] Å) and **4** (Au···NCAuCN 3.33(1) Å) are significantly longer than those of **6**.

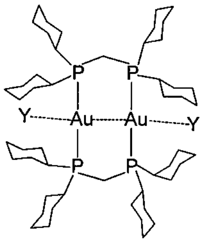


Figure 1. The structure of $[Au_2(dcpm)_2]Y_2$. Y = ClO_4^-, PF_6^-, $CF_3SO_3^-$, $[Au(CN)_2]^-$, Cl^-, I^-.

The UV/Vis spectroscopic data of the compounds are summarized in Table 1. For the compounds with weakly interacting counterions (ClO_4^-, PF_6^-, and $CF_3SO_3^-$) the absorption spectra feature an intense absorption band at 277 nm ($\varepsilon = 2.6$–2.9×10^4 mol^{-1} dm^3 cm^{-1}) and a weak shoulder at about 315 nm ($\varepsilon = 400$ mol^{-1} dm^3 cm^{-1}) (Figure 2), which are respectively assigned to the ^{1}(dσ* → pσ) and ^{3}(dσ* → pσ) transitions. These assignments are based on previous studies of binuclear gold(I) complexes[15] and are strongly supported by recent resonance Raman measurements that revealed

---

[*] Prof. Dr. C.-M. Che, Dr. W.-F. Fu, K.-C. Chan, Dr. V. M. Miskowski
Department of Chemistry, The University of Hong Kong
Pokfulam Road, Hong Kong (China)
Fax: (+852) 2857-1586
E-mail: cmche@hkucc.hku.hk

[**] We are grateful for financial support from The University of Hong Kong and for a postdoctoral fellowship to W. F. F., as well as from the Research Council of the Hong Kong Special Administrative Region, China [HKU 7298/99P].