

STM Imaging of a Heptanuclear Ruthenium(II) Dendrimer, Mono-Add Layer on Graphite

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Abstract: Scanning tunneling microscopy (STM) and molecular mechanics calculations were used to investigate the long-range packing and the structure of an heptanuclear ruthenium (II) dendritic species, as a PF₆⁻ salt. STM imaging was carried out on a mono-add layer of the ruthenium dendrimer formed by physisorption from a 1,2,4-trichlorobenzene solution at the liquid–graphite interface. The packing of the molecules on the surface was visualised by the

formation of ordered patterns and a distance of 27 ± 2 Å was measured between two adjacent lamellae. The comparison of this dimension with the molecular-modelling data indicates that the lamellae were formed by rows of dendrimer molecules in which the counter-

ions (PF₆⁻) were strongly associated with the Ru atoms. The images acquired with higher spatial resolution revealed the presence of repeating units within the lamellae. The comparison of the STM images with the modelling results allowed the attribution of the repeating units observed in the imaged pattern to the STM signature of single dendrimer molecules.

Keywords: dendrimers • modelling • ruthenium • scanning probe microscopy

Introduction

Various monometallic Ru^{II} complexes that contain the 1,4,5,8,9,12-hexaazatriphenylene (HAT) ligand have been prepared in the last decade. Figure 1a shows, as an example, the homoleptic [Ru(hat)₃]²⁺ and heteroleptic [Ru(phen)₂(hat)]²⁺ complexes (phen = 1,10-phenanthroline). These rigid octahedral species are ideal candidates to be used as DNA photoprobes and photoreagents.^[1, 2]

Furthermore, the HAT ligand has three chelating sites (Figure 1a) so that it can behave as a symmetric bridging ligand. Two strategies have been followed to assemble building blocks with the HAT ligand. In the first, two or three [Ru(L)₂]²⁺ units (L = 2,2'-bipyridine or 1,10-phenanthroline) (Figure 1b)^[3, 4] are attached to the central HAT. The so-formed di- and trinuclear complexes (Figure 1b, Scheme 1)

are luminescent and their interactions with DNA have been investigated.^[1, 2] Another possibility is to start from [Ru(hat)₃]²⁺ as a central core and chelate two further [Ru(L)₂]²⁺ moieties per HAT, in order to obtain the heptanuclear complex shown in Figure 1c;^[5] this complex contains the two types of mononuclear building blocks depicted in Figure 1a. The heptanuclear dendritic complex (Ru7; Figure 1c) has been characterised by electrospray mass spectrometry^[5] and its excited state has been studied by femto-second transient absorption spectroscopy.^[6]

In this contribution, the structure of the heptanuclear dendritic species as a PF₆⁻ salt, is examined by a dual experimental and theoretical approach based on scanning tunneling microscopy (STM) and molecular mechanics calculations. The two- and three-dimensional representations of Ru7 are presented in Scheme 1 and Figure 1c, respectively.

STM is particularly suitable for the structure determination of stable molecular films adsorbed at the graphite basal plane.^[7] In particular, this technique allows atomic resolution by local probing. STM has been used to study the molecular packing structure of several organic molecules^[8, 9] and to correlate the contrast in the STM images with the molecular structure.^[9–13]

In this contribution, STM imaging of the Ru-heptanuclear dendrimer Ru7 adsorbed on graphite is presented. To the best of our knowledge, dendrimers in general and, more particularly, a purely supramolecular Ru^{II} complex (i.e., composed only of polyazaaromatic ligands and Ru^{II} ions) have not been

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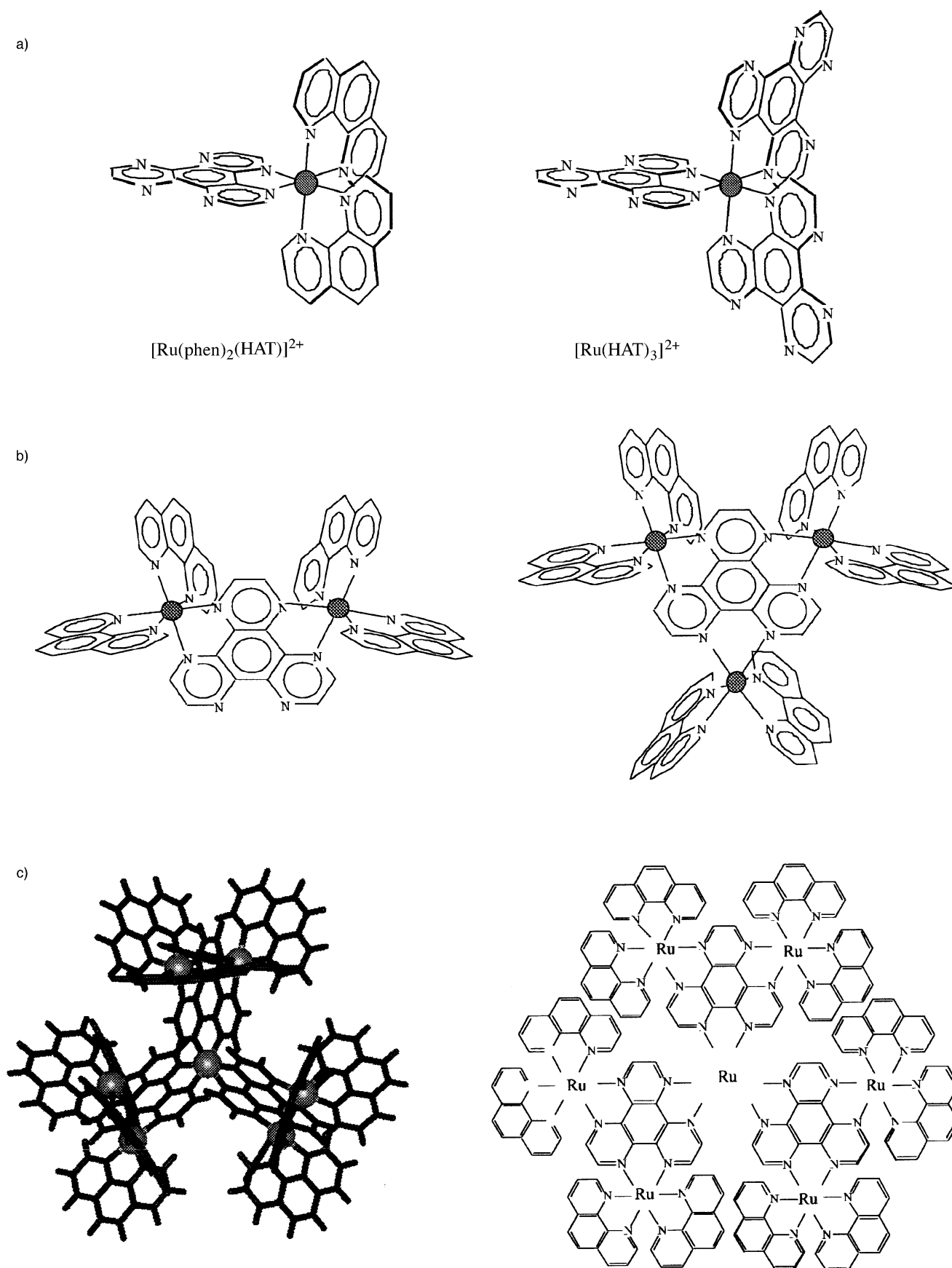
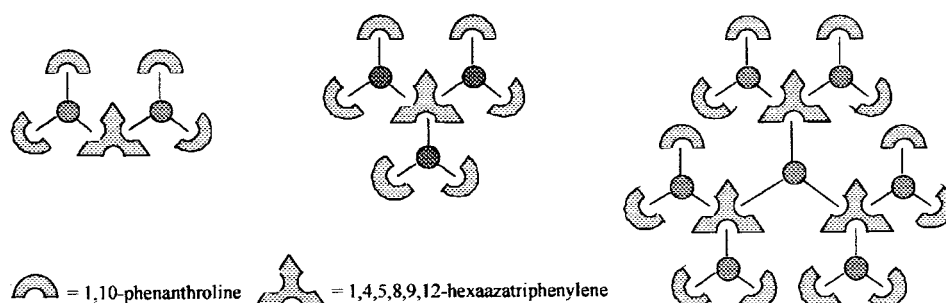


Figure 1. a) The octahedral mononuclear complexes $[\text{Ru}(\text{phen})_2(\text{hat})]^{2+}$ and $[\text{Ru}(\text{hat})_3]^{2+}$ in three dimensions. b) Three-dimensional representation of the dinuclear $[[\text{Ru}(\text{phen})_2]_2(\text{hat})]^{4+}$ and trinuclear $[[\text{Ru}(\text{phen})_2]_3(\text{hat})]^{6+}$ complexes. c) Three-dimensional view of the heptanuclear complex Ru_7 .



Scheme 1. Schematic representation of the compounds shown in Figure 1b, dinuclear $[[\text{Ru}(\text{phen})_2]_2(\text{hat})]^{4+}$ (left) and trinuclear $[[\text{Ru}(\text{phen})_2]_3(\text{hat})]$ (middle), and Figure 1c, the heptanuclear complex Ru7 (right).

imaged with submolecular resolution using STM. STM imaging has been carried out on Ru7 adsorbed on graphite to obtain information on the long-range packing of such a dendrimer. Only if the counterions remain tightly associated^[5] with the highly positively-charged oligomer would self-assembly of a Ru7 monolayer on graphite occur. Furthermore, the high resolution achievable with STM provides structural information on the dendrimer under investigation with submolecular resolution. The dimensions of the packed structures are compared with a computational model.

Results

STM images of a mono-add layer of the Ru-dendrimer:

Figure 2 shows an STM image obtained over a $230 \times 230 \text{ \AA}^2$ area of a mono-add layer of Ru7 adsorbed onto the basal plane of highly oriented pyrolytic graphite (HOPG) from a solution of Ru7 in 1,2,4-trichlorobenzene. Imaging was carried out through a thin film of the starting solution, by approaching the graphite surface with the STM tip. In the image, ordered patterns are observed that indicate the packing of the

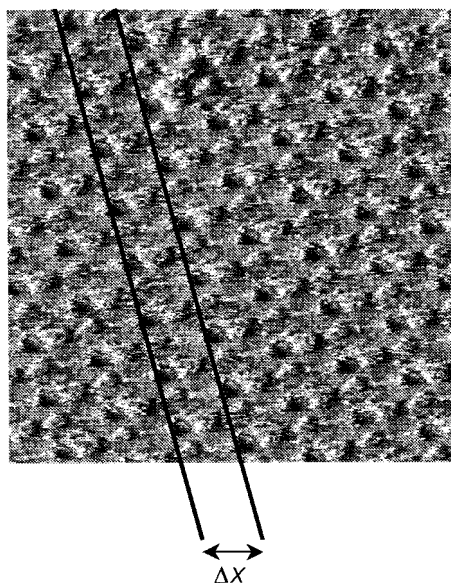


Figure 2. STM image of an ordered monolayer of Ru7 formed by adsorption from 1,2,4-trichlorobenzene at the liquid–graphite interface. Image size $230 \times 230 \text{ \AA}^2$; tunneling current and voltage are 0.5 nA and -0.55 V , respectively.

molecules on the surface. In particular alternating lines of brighter and darker spots are observed over the whole area. The formation of these patterns was observed when 1.0 mg mL^{-1} solutions of Ru7 in 1,2,4-trichlorobenzene were deposited and spread on the basal plane of HOPG. For concentrations higher than 1.5 mg mL^{-1} precipitation of Ru7 clusters occurred. Using the lattice structure

of the underlying graphite as an internal calibration, we determined the dimension and the orientation of the repeating units. A distance, ΔX , of $25\text{--}29 \text{ \AA}$ was measured between two consecutive lamellae oriented along the graphite axis, as indicated by the lines in Figure 2. This dimension agrees, within the experimental error, with the value obtained by molecular modelling (see below) indicating that the lamellar width results from one row of molecules.

Figure 3a is a zoom-in image obtained by scanning a $90 \times 90 \text{ \AA}^2$ area. The image does not achieve atomic resolution, owing to the impossibility for the molecule to flatten down on the graphite; this is caused by the molecular rigidity (see below). The pattern observed in Figure 3a is characterised by a repeating unit, defined by a solid line in Figure 3b. The most striking aspect of this image is that the repeating unit of the pattern seems to contain three distinct features as indicated by the dashed white lines of areas 1, 2 and 3. The larger feature 1 has a maximum size of $13 \pm 1 \text{ \AA}$ and is larger than features 2 and 3. All the three features are smaller in size than what is expected for the dendrimer molecule. This observation suggests that the whole repeat unit, made up of features 1, 2 and 3, is the STM signature of one dendrimer molecule. The distance between equivalent locations within adjacent repeat units, denoted as d on Figure 3b, is $27 \pm 2 \text{ \AA}$ and corresponds to the lamellar width.

Modelling: In order to elucidate the findings of the STM imaging, computer modelling of the dendrimer on graphite has been carried out on the basis of molecular mechanics calculations based on the universal force field.^[15, 16] It should be pointed out that these computations were carried out without a priori input based on STM data, but with the intent to understand and interpret the structural information present in the experimental data.

Since each ruthenium atom is a chiral center (Δ or Λ)^[17], a molecule such as Ru7 possesses, in principle, 128 stereoisomers. If we consider, in a first step, the stereoisomer in which the metallic core is in the Λ configuration and the outer six Ru atoms are in any combinations of Δ and Λ forms, no change of position of the six peripheral Ru atoms appears in these different stereoisomers of the dendrimer. Indeed, as the Λ configuration of the metallic core determines each position of the three HAT ligands in space, evidently the positions of the six surrounding metallic ions are also determined independently of the Δ or Λ configuration adopted by each of these six peripheral Ru atoms. This is true as long as the same

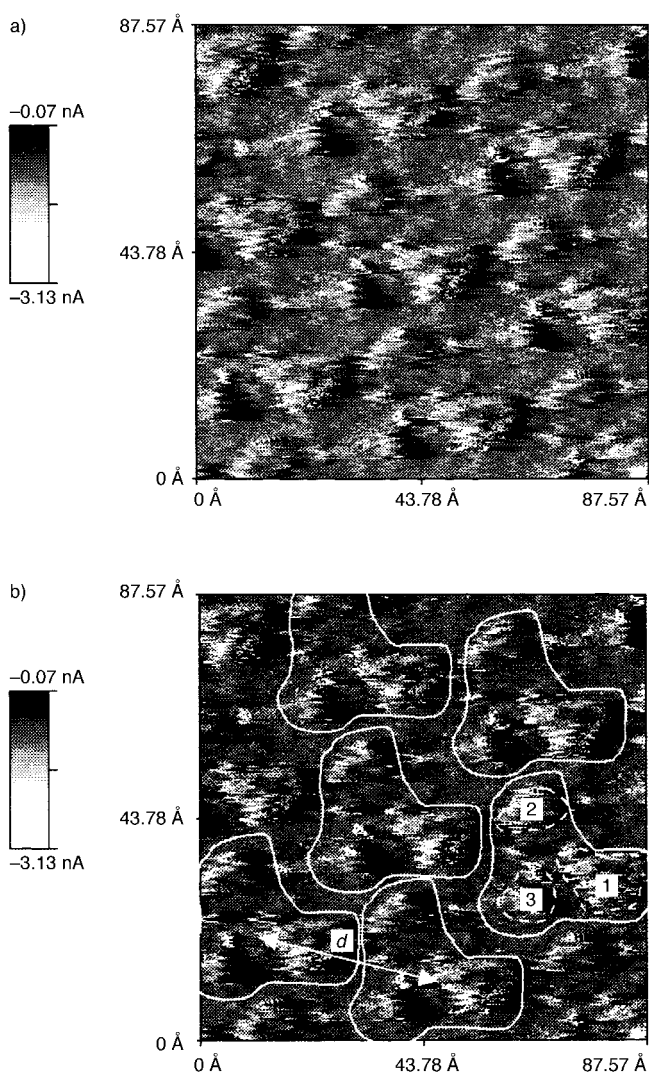


Figure 3. a) STM image of an ordered monolayer of Ru7 formed by adsorption from 1,2,4-trichlorobenzene at the liquid–graphite interface. Image size $90 \times 90 \text{ \AA}^2$; tunneling current and voltage are 0.5 nA and -0.55 V , respectively. b) STM image described in a) with the arrangement of the dendrimers on the graphite surface: solid lines mark the repeating units; 1, 2 and 3 mark the three domains appearing within a repeating unit; and d represents the distance separating two adjacent units.

Λ configuration for the central Ru atom is kept. Of course, if in a second step, the core Ru atom changes from a Λ to a Δ configuration, the positions of the six peripheral Ru atoms do change. As the Ru core can only adopt two configurations Δ or Λ , two families of stereoisomers can be defined: one with the Ru core in the Δ and the other in the Λ configuration. Within each of these families all the Ru atoms occupy the same position. We have, therefore, compared one stereoisomer of one family with that of the other, that is, extreme cases where the six Ru and consequently the twelve phen ligands occupy different positions in space. The computational model of the two stereoisomers shows that the overall shape of the dendrimer and its interaction with the surface are similar. Moreover, changing the configuration of only one peripheral Ru atom does not introduce significant variation in the shape or interaction. Thus, the results of the calculations do not depend on the stereoisomer chosen. The model

arbitrarily given in this paper for the simulation corresponds to the completely Δ stereoisomer.

Among all the possible orientations of the Ru7 dendrimer on graphite, one is found to be at least 30 kcal mol^{-1} more stable than the others. This orientation is shown in Figure 4 and corresponds to the configuration in which the highest number of phen ligands (in this case five) interacts with graphite. The modelling shows that there are no significant structural changes in the dendrimer when its geometry is optimized in interaction with the graphite or in vacuum. This is due to the Ru–N bonds that impart strong rigidity to the dendrimer.

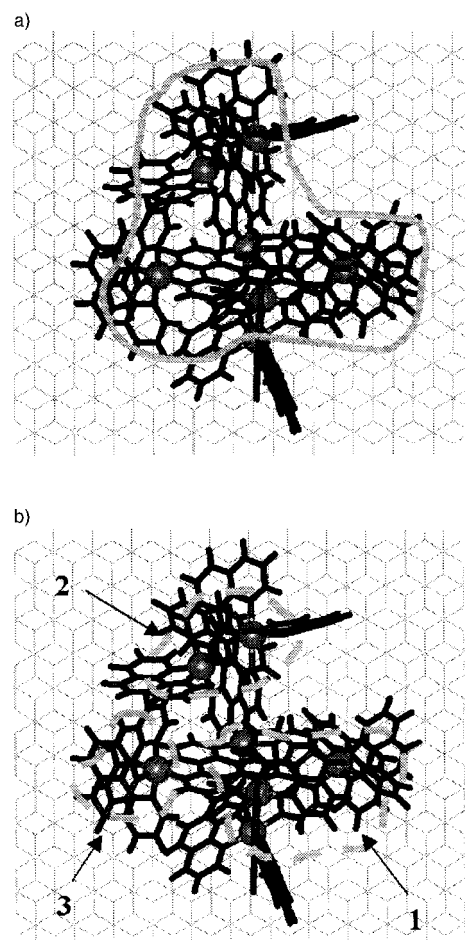


Figure 4. Representation of the most stable orientation of the heptanuclear dendrimer interacting with the graphite surface. The ruthenium atoms are depicted as grey balls. a) The correspondence of the shapes between the calculated molecular conformation and the repeating units observed in the STM image. b) Domains 1, 2 and 3 mark that appear within a dendrimer molecule in the STM images.

Comparison between STM imaging and modelling: It is important to notice that the overall shape of the molecule on the surface, when a “top view” in the simulation is considered (Figure 4a), is very similar to the shape of the repeating unit in the STM image (solid white line in Figure 3b). Furthermore, the calculated structure of the adsorbed molecule can be divided into three regions (denoted 1, 2 and 3 on Figure 4b),

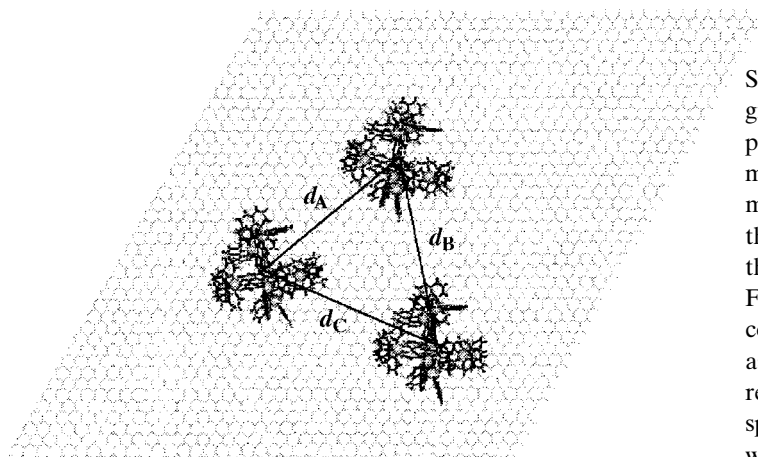


Figure 5. Conformation of three dendrimer molecules on graphite. The ruthenium atoms are depicted by balls. d_A , d_B and d_C are the distances between the core atoms. Their values are 33.14, 35.40 and 34.50 Å, respectively.

whose size and relative position are reminiscent of the three subunits observed in the experimental images (Figure 3b).

The STM images also display brighter spots corresponding to higher tunneling current within the domains 1, 2 and 3, which together make up one dendrimer molecule. Some of these bright spots might be attributed to the ruthenium atoms present in these domains (Figure 4b), since their larger electronic density should increase the current intensity measured by the STM tip. The presence of these bright spots is consistently found in all the structures observed experimentally.

Starting from the most stable configuration (Figure 4), we computed the packing of three dendrimer molecules on the surface.^[18] When the effect of the counterions is not taken into account, the distances between the core ruthenium atoms (Figure 5) of each dendrimer are all around 34 Å; this value is larger than that measured for the separation between equivalent sites of different molecules on the STM images (about 27 ± 2 Å). This discrepancy can be attributed to two effects: i) the packing can be expected to be denser when the surface is covered with a more extended dendrimer monolayer, rather than just the three molecules used in the simulation, and ii) the calculations have been performed with a net charge of +14 on each dendrimer; this implies large repulsive Coulomb interactions and overestimation of the distances between the dendrimers. However, within the actual layer, the positive charges present on each ruthenium atom are screened by two counterions. The observed precipitation of Ru₇ clusters on graphite at high concentration of the starting solutions favours this screening effect by the counterions (PF₆⁻). This indicates also that the counterions remain in close proximity of the Ru^{II} ions. When implicitly considering the presence of the counterions by imposing a zero global charge on the dendrimers in the calculations, a significant reduction of the inter-dendrimer distances occurs. The core-to-core distances between the three dendrimers decrease down to about 29 Å, which is in very good agreement with the 27 ± 2 Å experimental distance.

Conclusion

STM imaging has been carried out on Ru₇ adsorbed on graphite from a 1,2,4-trichlorobenzene solution. Ordered patterns have been observed which indicate packing of the molecules on the surface. A distance of 27 ± 2 Å has been measured between two adjacent lamellae. The comparison of this dimension with the molecular modelling data indicates that the lamellae were formed by rows of Ru₇ molecules. Furthermore, the close-packing structure suggests that the counterions (PF₆⁻) are strongly associated with the Ru atoms, as the screening effects of PF₆⁻ reduce the intramolecular repulsive interactions. The images acquired with higher spatial resolution reveal the presence of repeating units within the lamellae. A comparison has been carried out between the dimensions of features observed on the STM images with the intramolecular distances determined by computer modelling of the dendrimer on a graphite surface. On this basis, one repeating unit observed in the imaged pattern has been attributed to the STM signature of a single dendrimer molecule.

Experimental Section

The synthesis of the stereoisomerically unresolved heptanuclear ruthenium complex [Ru{Ru(phen)₂}]₃⁺¹⁴[14PF₆]⁻ (Ru₇, Figure 1c) was described previously.^[5] 1,2,4-trichlorobenzene (Aldrich, spectro-grade) was used as solvent without further purification.

STM experiments were performed with a Discoverer scanning tunnelling microscope (Topometrix) along with an external pulse-function generator (model HP 8111 A).^[14] Tips were electrochemically etched from a Pt/Ir wire (80%–20%, diameter 20 μm) in an aqueous solution of 2 N KOH/6 N NaCN. The compound under investigation was dissolved in 1,2,4-trichlorobenzene (b.p. 214 °C); typically a concentration of 10⁻⁴ M was used. The samples were prepared by spreading a drop of the solution on the freshly-cleaved plane of highly ordered pyrolytic graphite (HOPG, ZYB-grade, Advanced Ceramics). All the STM images were acquired in the variable current mode under ambient conditions. Typically, a tunnelling current of 0.5–1.0 nA and a bias voltage of 0.5–0.8 V referenced to the graphite surface were employed. STM images obtained at low bias voltages (<0.1 V) revealed the atomic structure of HOPG, which provided an internal calibration standard for the study of the mono-add layer.

The deposition of one or three dendrimers on graphite was modelled with the Cerius-2 molecular mechanics package^[15] by using the universal force field^[16]. When depositing a single dendrimer, the graphite surface was modelled by a double layer of sp²-hybridized carbon atoms with lateral size of 49 × 49 Å². In the case of calculations with the three dendrimers, the surface was a single layer of sp²-carbon atoms with lateral dimensions of 98 × 98 Å². The surface was kept rigid during all geometry optimizations; no constraints were imposed to the adsorbates in order to allow for their full relaxation. The conjugated gradient algorithm was used in all energy minimizations, with a convergence criterion set to 0.005 kcal mol⁻¹.

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