

## Synthesis and Langmuir-film formation of new dendritic DTPA-derived gadolinium(III) complexes

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**Abstract**—A series of dendritic DTPA-derived ligands and their corresponding gadolinium(III) complexes have been prepared and their spreading behaviour at the air–water interface has been investigated. The results show that these amphiphiles have the prerequisite qualities to form stable and reversible Langmuir monolayers opening the road to novel magnetic organic films.

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While building ‘nano’ objects is nowadays routinely performed in any chemistry laboratory, getting them properly ordered into 2D or 3D still remains a rare feat. It is clear, though, that the answer will be found within what is called ‘self-assembling processes’. Amongst all the elaborate strategies that have been devised for properly organizing molecules, the most efficient, and probably the oldest is simply based on hydrophilic–hydrophobic interactions. As a first step of a final goal of preparing stable 2D arrays of magnetic objects, we have synthesized amphiphilic dendritic complexes containing gadolinium ions. We shall describe their synthesis and interfacial properties. Previous attempts reported in the literature were mostly based on stearic acid complexes formed at the air–water interface.<sup>1</sup> From a physicist’s viewpoint such films are interesting as they give access to real low-dimensionality systems.<sup>2</sup> There are also reports of films made from  $Gd^{3+}$  complexes based on phthalocyanines<sup>3</sup> or  $\beta$ -diketonates.<sup>4</sup> We believe the main advantages of the present system are its enhanced stability as compared to stearate-based films, and its potential to form micellar structures in 3D.<sup>5</sup>

In this Letter we report the preparation and film-forming behaviour at the air–water interface of a series of dendritic DTPA-derived ligands **4**, **5** and **6** and their

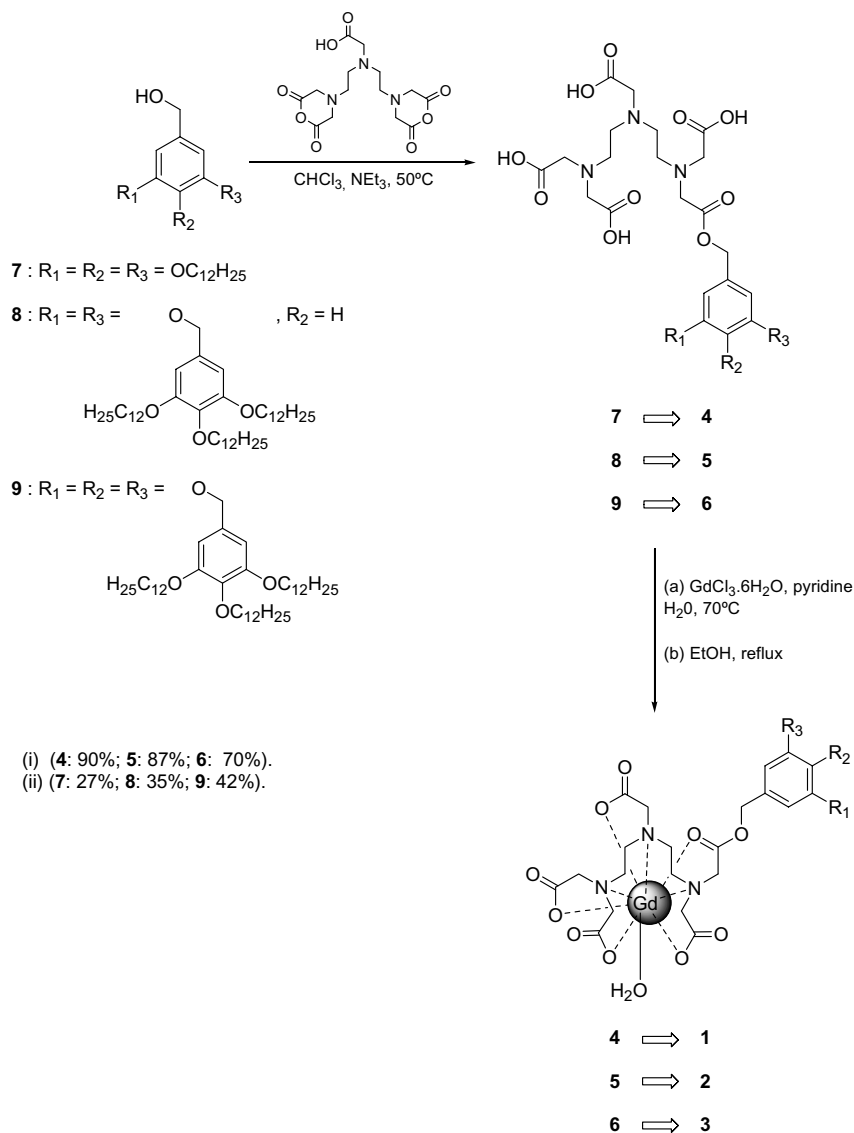
corresponding gadolinium(III) complexes **1**, **2** and **3** bearing, respectively, three, six or nine alkyl chains. This study is part of the research pursued in our group with the aim of developing new magnetic organic materials.

The synthesis of the compounds is depicted in [Scheme 1](#). Dendrons **7**, **8** and **9** were prepared as previously described in the literature.<sup>6</sup> Reaction of benzylic alcohols **7**, **8** and **9** with triethylenediamine pentaacetic dianhydride in chloroform at 50 °C in the presence of triethylamine resulted in the corresponding ligands **4**, **5** and **6**, respectively.<sup>7</sup> Complexes formed between these DTPA-derived ligands with gadolinium chloride in a mixture of pyridine and  $H_2O$  heated at 70 °C for 3 h, then under reflux in EtOH for 1 h gave the desired dendritic gadolinium(III) complexes **1**, **2** and **3**, respectively. All amphiphilic derivatives were obtained as white solids. Their structure and purity were confirmed by  $^1H$  and  $^{13}C$  NMR, elemental analysis and mass spectrometry.<sup>8,9</sup>

It has been possible to record isotherms for ligands **5**, **6** and complexes **1**, **2** and **3**. Unfortunately, ligand **4** was too hydrophilic to allow its solubilization in solvents suitable for Langmuir studies. In addition to those specifically discussed in the text, all the isotherms and hysteresis curves are given as [supplementary data](#). The pressure–area isotherms for ligands **5** and **6** are presented in [Figure 1a](#). Those compounds can withstand pressures up to  $\Pi_c \approx 40\text{--}45 \text{ mN m}^{-1}$ , while the corresponding gadolinium complexes begin to collapse

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**Scheme 1.** Synthesis of DTPA-derived ligands **4**, **5**, **6** and corresponding Gd(III) complexes **1**, **2** and **3**.

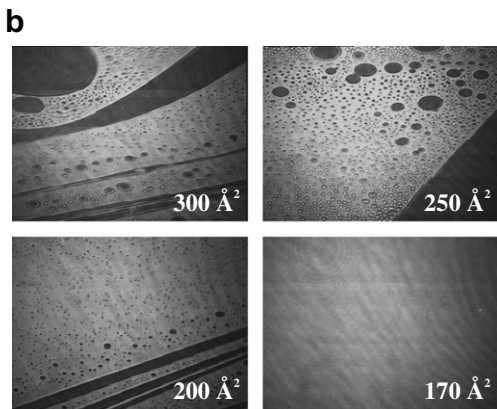
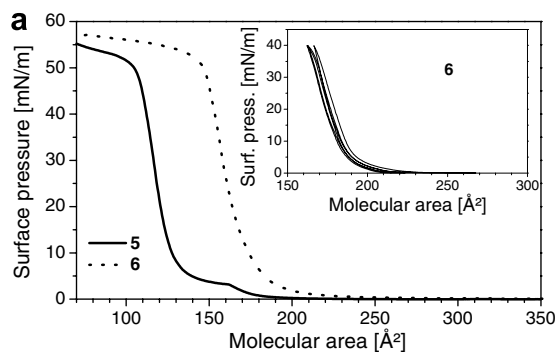
around  $20 \text{ mN m}^{-1}$  for **3** and **2** or  $30 \text{ mN m}^{-1}$  for complex **1**. These isotherms are perfectly reversible upon multiple compression–expansion cycles and no hysteresis is observed as long as the collapse pressure is not exceeded.

The final molecular areas extrapolated to zero surface pressure are  $125 \pm 6 \text{ \AA}^2$  and  $185 \pm 9 \text{ \AA}^2$  for **5** and **6**, respectively. Dividing these figures by the number of alkyl chains per molecule (three for **5** and six for **6**) gives a value of  $\sim 20 \text{ \AA}^2$  per chain. The final packing of the ligands must therefore be rather dense as a value of  $22 \text{ \AA}^2$  per alkyl chain is usually found in crystallized paraffins,  $18 \text{ \AA}^2$  per chain being a minimum. Moreover, the final part of the isotherms is very steep, indicating a low compressibility of the film.

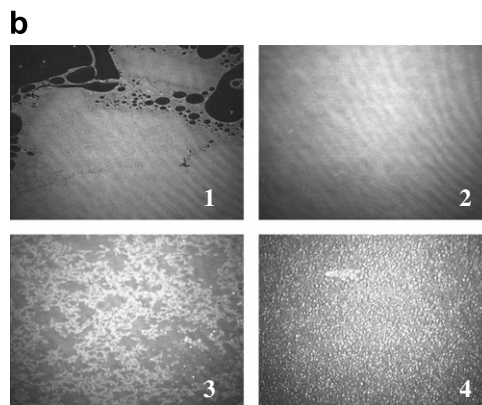
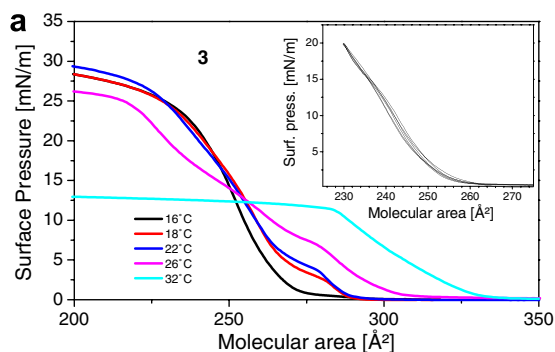
Finally, it should be noted that the collapse pressure varies linearly with the temperature of the aqueous sub-phase, as shown in the inset to Figure 2.

The isotherms of corresponding gadolinium(III) complexes **1**, **2** and **3** also showed some thermal dependency (Fig. 3a). The first isotherm has been recorded at  $22 \text{ }^\circ\text{C}$ , and showed some kind of plateau below  $190 \text{ \AA}^2$ . The height and extent of this plateau showed a strong temperature dependence. This very probably indicates the coexistence region of a first order phase transition. BAM observations have been made at different temperatures (Fig. 3b). At all temperatures, the film is liquid for larger values of the molecular area; a representative example is given in image 1. Upon compression the film eventually becomes homogeneous and defectless (image 2) as long as the collapse pressure or the critical point is not reached. BAM images taken on the plateau show white filamentous structures (image 3), whereas film collapse takes the form of numerous white dots (image 4) at all temperatures.

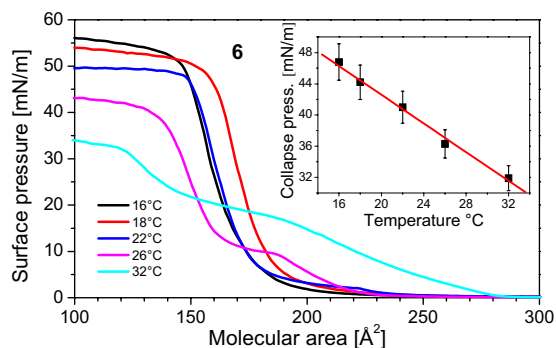
To conclude, we have prepared and studied a series of ligands and their corresponding gadolinium(III) com-



**Figure 1.** (a) Pressure–area isotherm for ligands **5** and **6** recorded at pH 8 and 16 °C. Inset: Three successive compression/expansion cycles with a monolayer of **6** showing the reversibility of the process (the small shift is due to the loss of product on the edges of the trough). (b) BAM pictures of a monolayer of ligand **6**, at 16 °C, pH 8. The film appears in white, the water in black.



**Figure 3.** (a) Pressure–area isotherm for complex **3** recorded at pH 8 as a function of temperature of the aqueous subphase. Inset: Three successive compression/expansion cycles with a monolayer of **3** showing the reversibility of the process. (b) Brewster angle microscopy images of complex **3** (9 chains) recorded at pH 8, (1) 18 °C, 440 Å<sup>2</sup>, (2) 32 °C, 290 Å<sup>2</sup>, (3) 24 °C, 280 Å<sup>2</sup>, (4) 24 °C, 260 Å<sup>2</sup>.



**Figure 2.** Isotherms of ligand **6** (9 chains) as a function of temperature of the aqueous subphase.

plexes, which are able to form good quality Langmuir films. Stable and reversible monolayers were easily obtained. The next step will be to transfer these films onto substrates in order to prepare thin molecular films and study their magnetic properties. It should be particularly interesting to look for possible crossover behaviour when the number of layers will gradually be increased from one to several hundreds.

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### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.05.013.

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8. General procedure for the formation of ligands **4**, **5** and **6**: TEA (10 equiv) was added to a stirred solution of diethylenetriaminepentaacetic dianhydride (1 equiv) and benzylic acid derivative (1 equiv) in  $\text{CHCl}_3$  (50 mL) heated to 50 °C. After 12 h of stirring, the reaction mixture was concentrated to 5 mL and acetone (50 mL) was added. The resulting suspension was cooled to 6 °C for 48 h. The white precipitate obtained was filtered off, washed with acetone ( $3 \times 50$  mL) and dried. No further purification was necessary to yield pure ligand (yield: **4**: 90%, **5**: 87%, **6**: 80%). Selected spectroscopic data: ligand **5**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.85 (t,  $J = 6.7$  Hz, 18H), 1.26–1.45 (m, 108H), 1.71–1.77 (m, 12H), 3.11–3.60 (m, 18H), 3.93 (t,  $J = 6.2$  Hz, 4H), 3.95 (t,  $J = 5.9$  Hz, 8H), 4.86 (s, 4H), 5.02 (s, 2H), 6.56 (t,  $J = 2.1$  Hz, 1H), 6.59 (s, 4H), 6.61 (d,  $J = 2.1$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 14.09, 22.67, 26.16, 29.36, 29.39, 29.46, 29.66, 29.69, 29.71, 29.76, 30.37, 31.91, 52.74, 55.50, 56.98, 63.10, 66.51, 69.13, 70.58, 73.42, 101.99, 106.28, 107.11, 131.48, 137.51, 138.00, 153.30, 160.14, 170.57, 174.49. Maldi-MS (negative mode):  $[\text{M}]^-$  1799.08 obtained for  $\text{C}_{107}\text{H}_{185}\text{N}_3\text{O}_{18}$  (1800.06). Microanalysis for  $\text{C}_{107}\text{H}_{185}\text{N}_3\text{O}_{18}$  (1800.36): calcd C, 71.33; H, 10.35; N, 2.33; found C, 71.47; H, 10.43; N, 2.27.
9. General procedure for the formation of gadolinium complexes **1**, **2** and **3**: a solution of  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  (0.11 mmol) in water (0.5 mL) was added to a stirred solution of the ligand (0.1 mmol) in pyridine (30 mL) and the resulting mixture was heated at 70 °C for 3 h. The solvents were evaporated under reduced pressure and the crude mixture was heated to reflux in EtOH (30 mL) for 1 h. Upon cooling to room temperature the gadolinium complex precipitated as a white powder. It was collected by filtration, washed with EtOH ( $3 \times 30$  mL) and dried. Absence of free gadolinium was checked with the Xylenol orange test.<sup>7</sup> (yield: **1**: 27%, **2**: 35%, **3**: 42%). Selected spectroscopic data: complex **3**: Maldi-MS (negative mode):  $[\text{M}]^-$  2291.74 obtained for  $\text{C}_{126}\text{H}_{211}\text{N}_3\text{O}_{23}\text{Gd}$  (2292.76).