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Design of liquid-crystalline gold nanoparticles by click chemistry†

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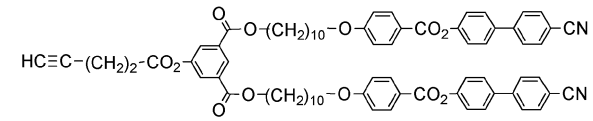
Mesomorphic alkyne-based first- and second-generation dendrons were grafted onto gold nanoparticles carrying azide groups under click reaction conditions. The nanoparticles decorated with the dendrons displayed liquid-crystalline properties and good thermal stability.

Gold nanoparticles (AuNPs) are used for the elaboration of electronic, optical and photonic devices.[1] On the other hand, liquid crystals display unique anisotropic properties due to their self-organizing behavior.[2] Therefore, liquid-crystalline AuNPs represent interesting materials for the development of nanotechnology by the "bottom-up" approach.[3] Recently, liquid-crystalline AuNPs which exhibit clear mesomorphic behavior have been reported: Mehl *et al*. described AuNPs showing nematic or complex phases,[4–6] Donnio *et al*. reported AuNPs displaying a cubic phase,[7] and Wojcik *et al*. described AuNPs exhibiting smectic and columnar phases.[8,9] The above-mentioned AuNPs were functionalized by ligand-exchange reactions.

The synthesis of AuNPs with tailor-made liquid-crystalline properties requires the preparation of compounds with specific molecular architectures. This goal can be reached only if effective synthetic tools are available.

The Huisgen 1,3-dipolar cycloaddition is an attractive reaction for the functionalization of AuNPs.[10–13] Indeed, click chemistry requires mild reaction conditions and no by-products are formed.[14] Recently, Nierengarten *et al*. demonstrated that click chemistry can be used for the design of highly functionalized [60]fullerene (C_{60}) materials: twelve click reactions were carried out around the C_{60} sphere.[15–17] Based on this beautiful study, we decided to functionalize AuNPs (containing azide groups) with liquid-crystalline dendrons (containing alkyne functions) by click chemistry. For the design of liquid-crystalline AuNPs, chemical reactions around AuNPs represent an alternative approach to the ligand-exchange reaction.

Alkyne derivatives **1** and **2** (Fig. 1) were synthesized by esterification of the corresponding first- and second-generation phenol-based poly(arylester) dendrons[18] with 4-pentynoic acid (see ESI† for experimental details). The azide-based AuNPs **3** were prepared by adapting literature procedures.[10,13,19] The latter



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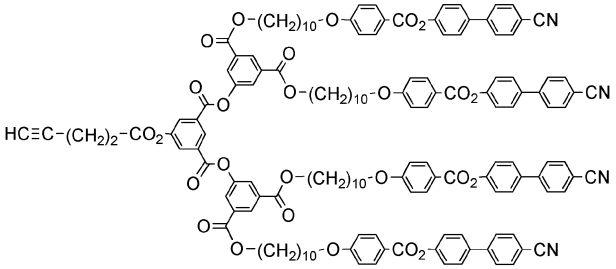

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Fig. 1 Structures of liquid-crystalline dendrons **1** and **2**.

particles were characterized by a diameter of 1.5 ± 0.5 nm (by Transmission Electron Microscopy, TEM) and by a mixed coverage of 30% of N_3-, 20% of Br- and 50% of CH_3-terminated alkanethiol (by NMR). Finally, click reaction between azido-AuNPs **3** with **1** or **2** using sodium ascorbate and $CuSO_4$ gave targets **4-G1** and **4-G2**, respectively (Scheme 1). The structure and purity of AuNPs **4-G*n*** (***n*** = **1** or **2**) were determined by ^{1}H-NMR, IR and TEM. The ^{1}H-NMR spectra of **4-G*n*** indicated that the dendrons are attached to the AuNPs. Indeed, all the signals arising from the dendrons are broad compared to the same signals of the free alkynes. This is a clear signature of the grafting of ligands on AuNP surfaces.[20] In other words, no free alkynes were detected in **4-G*n***.

The click reaction between **1** and **3** was found to be quantitative as shown by the disappearance of both the CH_2N_3 signal at δ = 3.26 ppm (^{1}H-NMR) and the azide absorption band at 2095 cm^{-1} (IR) (Fig. 2a–c). Therefore, AuNPs **4-G1** were covered with 30% of G1-cyanobiphenyl dendron, 20% of Br- and 50% of CH_3-terminated ligands.

The click reaction between **2** and **3** was not quantitative. The presence of unreacted azide groups in AuNPs **4-G2** was detected by ^{1}H-NMR and IR spectroscopies, as shown by the peak at 3.26 ppm and the band at 2095 cm^{-1} (Fig. 2d), respectively. This result can be explained by the fact that second-generation dendron **2** is much more sterically demanding than first-generation one **1**. ^{1}H-NMR spectroscopy indicated that AuNPs **4-G2** were covered with 10% of G2-cyanobiphenyl units, 20% of N_3-, 20% of Br- and 50% of CH_3-terminated ligands. The triazole proton signal was not detected by ^{1}H-NMR

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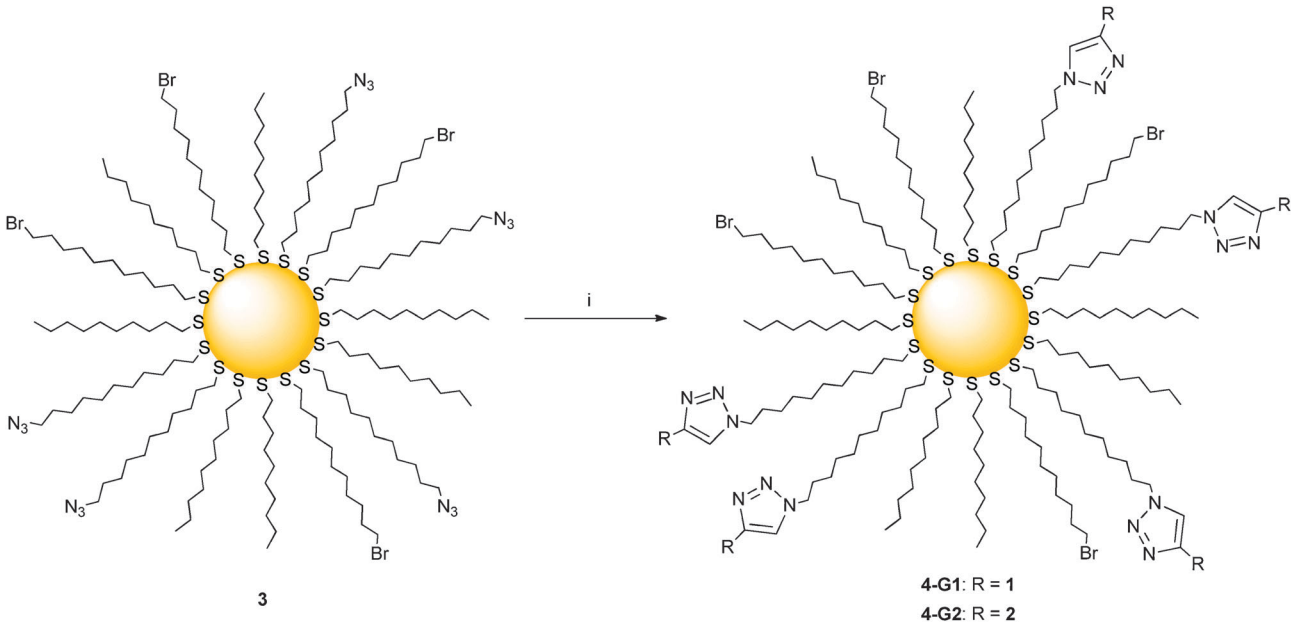

Scheme 1 *Reagents and conditions*: (i) **1** or **2**, $CuSO_4{\cdot}5H_2O$, sodium ascorbate, THF/H_2O (1 : 1), 30 °C, 3 d.

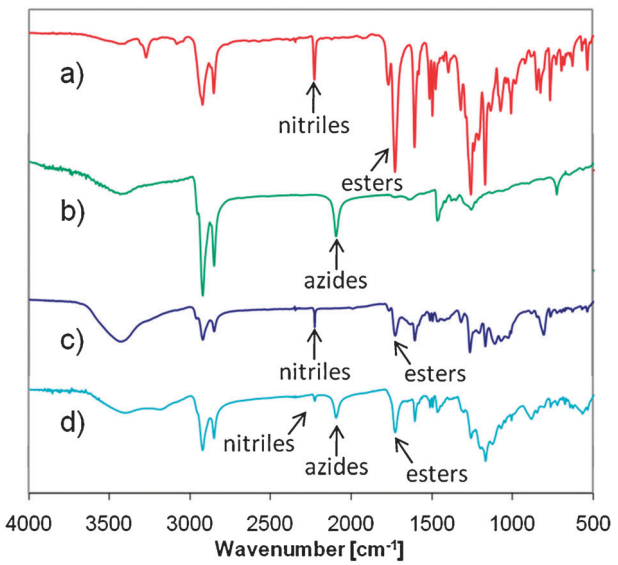

Fig. 2 IR spectra of: (a) alkyne derivative **1** with the absorption bands of the ester (1725 cm^{-1}) and nitrile (2225 cm^{-1}) groups, (b) AuNPs **3** with the azide vibration band at 2095 cm^{-1}, (c) AuNPs **4-G1** showing the absorbances of the ester and nitrile functions, (d) AuNPs **4-G2** showing the vibrations of the ester and nitrile functions and of the unreacted azide groups (2095 cm^{-1}).

spectroscopy because of overlapping of the signal of this proton with the aromatic protons signals of the dendron. TEM analyses of AuNPs **4-G*n*** gave diameters of 1.6 ± 0.6 nm which indicated that the size of the particles was not affected by the chemical reactions. This result was further confirmed by UV-vis spectroscopy: the weak plasmon band at *ca.* 520 nm remained unchanged after the click reaction.

The liquid-crystalline and thermal properties were investigated by Polarized Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC). The mesomorphic promoters **1** and **2** displayed smectic A phases (focal-conic fan texture and homeotropic areas); nematic (schlieren texture) and unidentified monotropic phases were also observed for **1** (Table 1). The formation of smectic A and nematic phases is in agreement with the structure and nature of cyanobiphenyl-based dendrons **1** and **2**.[21]

Table 1 Phase-transition temperatures and enthalpies of **1** and **2**[a]

Compd	T_g/°C	Transition	Temperature/°C	ΔH/kJ mol^{-1}
1	23	(M → SmA)[b]	(113)	1.6
		SmA → N	169	0.3
		N → I	185	3.0
2	37	SmA → I	213	8.6

[a] T_g = glass transition temperature, M = unidentified mesophase, SmA = smectic A phase, N = nematic phase, I = isotropic liquid. Transition temperatures (onset point) were obtained during the second heating run. [b] Monotropic transition.

Gold nanoparticles **4-G*n*** showed a monotropic liquid-crystalline behavior as observed by POM: a birefringent fluid was obtained between 145 and 90 °C for **4-G1** and between 165 and 90 °C for **4-G2**. For both materials, small focal-conic fan textures were observed after annealing the samples for several hours (Fig. 3). The textures indicated the formation of smectic A phases in agreement with the behavior of **1** and **2** and other related cyanobiphenyl materials.[18] Black areas were also observed and were attributed to the formation of aggregates obtained from AuNPs covered with a lower percentage of dendrons. The total number of ligands per AuNP was estimated by TEM and thermogravimetry (TG) (see ESI† for details). The following results were obtained: (a) for AuNPs **4-G1**: about 43 ligands, *i.e.*, 13 G1-dendritic ligands, 9 Br- and 21 CH_3-terminated ligands; (b) for AuNPs **4-G2**: about 43 ligands, *i.e.*, 4 G2-dendritic ligands, 9 N_3-, 9 Br- and 21 CH_3-terminated ligands. Despite the low coverage of AuNPs with G2 moieties, AuNPs **4-G2** still display liquid-crystalline properties because second-generation dendron **2** contains twice more mesogens than first-generation dendron **1**.

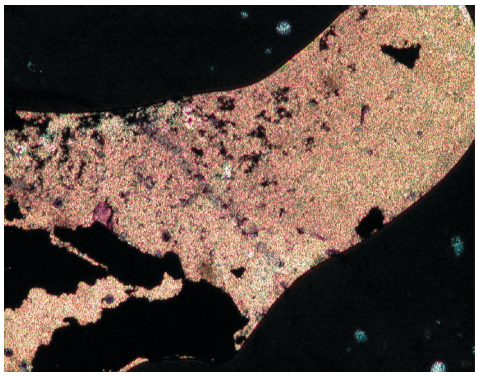

Fig. 3 Thermal polarized optical micrograph of the small focal-conic fan texture displayed by **4-G1** at 116 °C after annealing the sample for several hours (see the text for details).

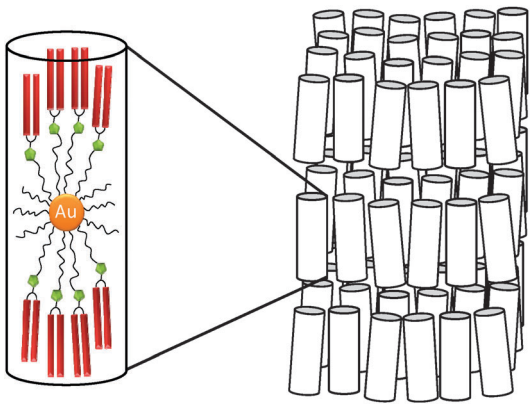

Fig. 4 Postulated model of the organization of AuNPs **4-G1** in the smectic A phase (gold core: orange, triazole: green, mesogens: red). AuNPs **4-G2** show similar behavior.

By DSC, no phase transition was detected for **4-G*n***. For nanoparticles, this result is not unexpected and is attributed to the fact that the transitions are broad because of the polydispersity of the nanoparticles. This behavior is similar to the one observed for polydispersed polymers.[22] However, the reversibility of the transitions observed by POM, associated with the TG measurements, attested that the AuNPs **4-G*n*** were stable up to 255 °C. For this reason, we can confirm that the observed liquid-crystalline behavior arises from the AuNPs themselves and not from ligands released because of decomposition.

The supramolecular organization of **4-G*n*** within the smectic A phase (Fig. 4) can be explained by analogy with liquid-crystalline hexa-adducts of C_{60}[23,24] and liquid-crystalline transition-metal clusters[25] for which a three-dimensional, non-mesomorphic core (C_{60}, organometallic framework or AuNPs) is surrounded by cyanobiphenyl mesogens: the AuNPs **4-G*n*** form cylinder-like structures with the mesogens oriented upward and downward. The cylinders self-organize into layers and give rise to the smectic A phases; furthermore, the layers are stabilized at the triazole level through π–π interactions.[26]

In summary, we have shown that click chemistry is an effective synthetic tool for the design of liquid-crystalline AuNPs. In this study, liquid-crystalline cyanobiphenyl-based dendrons were grafted around AuNPs. Interestingly, the mild reaction conditions which are applied in the click reaction allow the use of many other liquid-crystalline promoters. This opens the doors for the design of liquid-crystalline AuNPs with tailor-made mesomorphic behavior.

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