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Liquid-crystalline fullerene-gold nanoparticles†

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We report the design, synthesis and properties of the title compounds which were prepared *via* click chemistry from azide-containing gold nanoparticles and mesomorphic alkyne-functionalized [60]fullerene ligands. The material displays the smectic A phase and shows a good thermal stability.

Liquid-crystalline gold nanoparticles (AuNPs) have attracted considerable attention for the development of metamaterials.¹ A common strategy which has been followed for the design of liquid-crystalline AuNPs is the ligand-exchange reaction: thio-alkanes, used to stabilize AuNPs,² are replaced by mesomorphic ligands bearing a –SH function.³ Various mesophases have been observed, including nematic, smectic, columnar and cubic phases, as well as more complex systems, such as 3D superlattices.⁴ The story of liquid-crystalline AuNPs is in its infancy. More sophisticated systems are to be studied in order to understand in depth their self-organizing and self-assembling behaviors and to establish clear and reliable “structure–supramolecular organization” and “structure–property” relationships. Structural parameters which influence the properties of liquid-crystalline AuNPs are the nature and loading of the ligands, and the size and size distribution of the AuNPs. The design of liquid-crystalline AuNPs which display tailor-made properties represents a scientific challenge.

We reported an alternative concept to the ligand exchange reaction: by applying the Huisgen 1,3-dipolar cycloaddition reaction,⁵ liquid-crystalline dendrons carrying alkyne functions were grafted onto azide-based AuNPs. The resulting AuNPs displayed the smectic A phase.⁶ Our approach was inspired by a series of reports published by Nierengarten *et al.* who demonstrated that click chemistry can be used for the synthesis of highly functionalized [60]fullerene (C₆₀) materials,⁷ and can be

applied for the multiple functionalization of azido-based materials.⁸

On the other hand, C₆₀–AuNPs hybrids have been considered as promising advanced organic–inorganic materials for optoelectronic applications (super capacitors, solar cell devices).⁹ For example, homogeneous films with high photoconductivity were obtained from *in situ* cross-linking of C₆₀–AuNPs hybrids.¹⁰ Also, a hexa-adduct of C₆₀ was used as a stabilizing agent to assemble homogeneous sub-3 nm AuNPs.¹¹ Such assemblies are potential candidates in catalysis.¹²

Liquid-crystalline C₆₀–AuNPs have not yet been described. Such assemblies are of interest as they would display the properties of C₆₀ (photoactivity, electron transfer) and AuNPs (magnetism, metamaterials) and the characteristics of liquid crystals (fluidity, organization). Furthermore, the supramolecular organization (mesophases) could be tuned by the choice of the mesogens used to functionalize the AuNPs. In other words, structural engineering at the molecular level will lead to C₆₀–AuNPs hybrids with controllable supramolecular organizations associated with exploitable photoelectronic properties in nanosciences and nanotechnology.

We report, herein, the design, synthesis and mesomorphic properties of the first liquid-crystalline C₆₀–AuNPs hybrid **1** which was prepared under click conditions by reacting AuNPs **2** carrying azide groups with the mesomorphic alkyne-based fullerene derivative **3**. In order to avoid strong C₆₀–C₆₀ interactions,¹³ which could prevent the formation of mesophases, compound **3** was “diluted” with fullerene-free analogue **4** (Fig. 1).⁶ Owing to their similar structures, we anticipated that ligand **3** would be homogeneously incorporated into the matrix

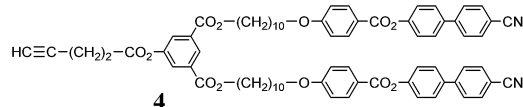


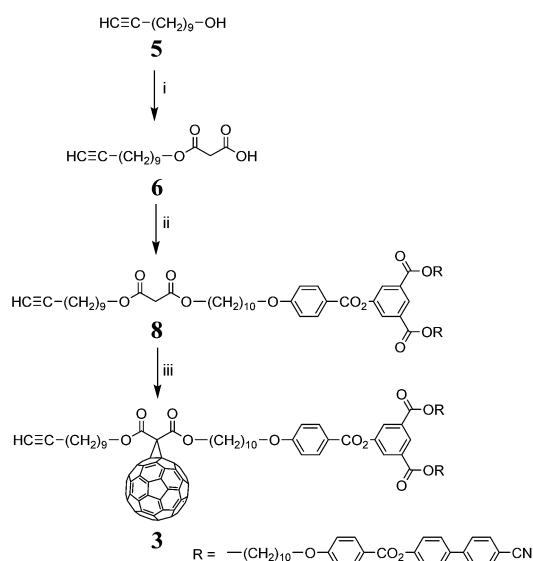
Fig. 1 Structure of the fullerene-free mesogen **4**.⁶

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made from ligand **4**. The loading of C_{60} can be modulated by changing the **3** : **4** ratio for the click reaction. As a first example, a low content of [60]fullerene derivative **3** was chosen (**3**: 10%; **4**: 90%).

The syntheses of fullerene derivative **3** and AuNPs **1** are described in Schemes 1 and 2, respectively. Meldrum acid was reacted with 10-undecyn-1-ol (**5**) at 95 °C to give acid intermediate **6** in 95% yield. Esterification of the latter with first-generation phenol-based dendron **7**¹⁴ (see structure in ref. 15) under EDC-mediated reaction conditions gave malonate derivative **8** in 76% yield. Addition of the latter to C_{60} *via* Bingel¹⁶ reaction (I_2 , DBU) in toluene gave ligand **3** in 40% yield.

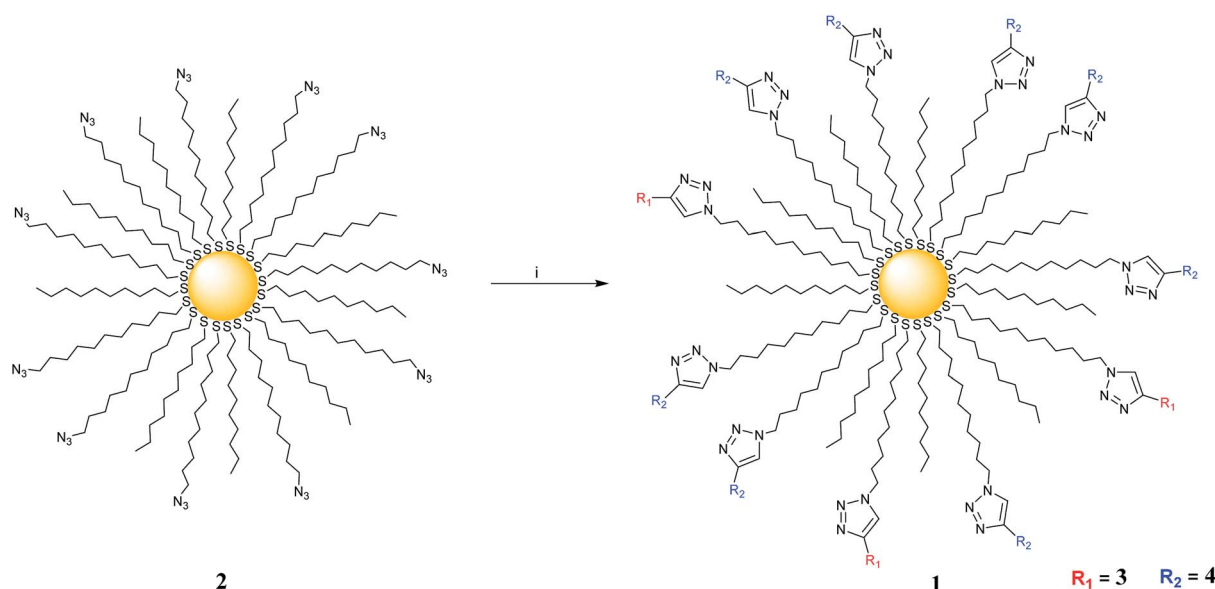


Scheme 1 Synthesis of **3**. Reagent and conditions: (i) meldrum acid, 95 °C, 5 h, 95%; (ii) **7**, DPTS, EDC, CH_2Cl_2 , 0 °C then r.t., 18 h, 76%; (iii) C_{60} , I_2 , DBU, toluene, r.t., 4 h, 40%. For the structure of **7**, see ref. 15.

Finally, click reaction between azido-AuNPs **2** with **3** and **4** under $CuSO_4$ /sodium ascorbate conditions in THF/ H_2O (4/1) gave target **1** in 60% yield. Purification required washing a solution of AuNPs **1** in CH_2Cl_2 with an aqueous NH_3 solution, followed by ultrafiltration (CH_2Cl_2 , see ESI for details[†]). The azide-based AuNPs **2** were prepared by adapting literature procedures.¹⁷ The latter particles were characterized by a diameter of 1.5 ± 0.4 nm (by Transmission Electron Microscopy, TEM) and a mixed coverage of *ca.* 45% of N_3 - and 55% of CH_3 -terminated alkanethiol (by NMR).

The analytical data of compounds **6**, **8** and **3** are in agreement with their structure (ESI[†]). The structure and purity of **1** were determined by 1H -NMR, IR, UV-vis spectroscopies and TEM. The 1H -NMR and IR results indicated that the click reaction was quantitative as shown by the disappearance of the CH_2N_3 signal at 3.26 ppm and the azide absorption band at 2095 cm^{-1} (Fig. 2). As expected, in the 1H -NMR spectrum of **1**, all the signals are broad (compared to the signals of **3** and **4**, see ESI[†]). This observation indicated that both dendrons are attached onto the AuNPs and the latter species are not contaminated with free alkynes. The presence of the fullerene derivative onto the AuNPs was confirmed by the small signal at 4.43 ppm which corresponds to the $C_{60}C(CO_2CH_2)_2$ protons of ligand **3** (Fig. 3). By taking into account the integration of the peaks at 4.43 and 8.51 ppm, the latter signal corresponding to the proton between the two $-CO_2R$ ester functions in mesogens **3** and **4**, the percentage of **3** and **4** was estimated to be approximately 15 and 85%, respectively. Those values correspond roughly to the initial ratio used in the reaction. Overall, AuNPs **1** are covered with *ca.* 7% of **3**, 38% of **4**, and 55% of CH_3 -terminated ligand.

The presence of the fullerene derivative **3** in AuNPs **1** was also confirmed by UV-vis spectroscopy. The UV-vis spectrum of **3** shows the characteristic peaks of [60]fullerene monoadducts¹⁸ at 427, 490 and 688 nm (Fig. 4a). Thus, the absorption peak at



Scheme 2 Synthesis of AuNPs **1**. Reagent and conditions: (i) **3** and **4**, $CuSO_4$, sodium ascorbate, THF/ H_2O (4/1), 30 °C, 3 days, 60%.

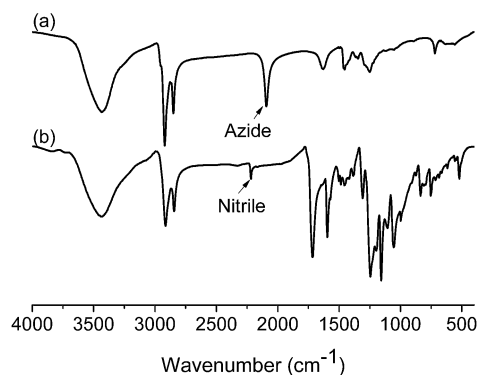


Fig. 2 FT-IR spectra (KBr) of (a) 2 and (b) 1.

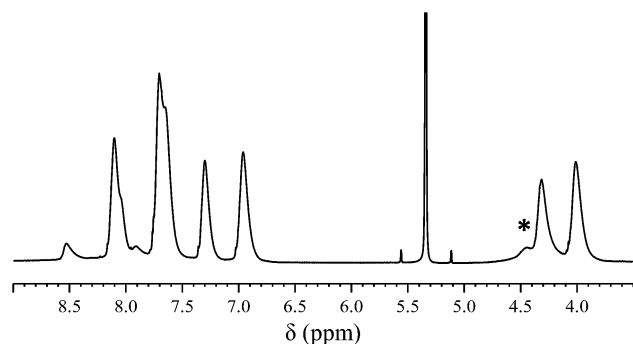


Fig. 3 Part of the ^1H -NMR spectrum of AuNPs 1 in CD_2Cl_2 . The asterisk shows the signal of the $\text{C}_{60}\text{C}(\text{CO}_2\text{CH}_2)_2$ protons.

427 nm (Fig. 4b) is a signature of the C_{60} -ligand anchored on the AuNPs 1. TEM analyses of AuNPs 1 gave a diameter of 1.5 ± 0.4 nm which indicated that their size and size distribution were not affected by the click reactions and the work-up procedures.

The liquid-crystalline and thermal properties of all compounds were examined by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The phase transitions and enthalpy changes of 3 and 8 are reported in Table 1. For comparative purposes, the properties of ligand 4 are also mentioned in Table 1. Malonate derivative 8 displayed a smectic A (SmA) phase and a short-range nematic (N) one (Fig. S10(a) and (b)†). During the first heating run, melting of the sample was observed at 87°C (crystal-to-smectic A phase transition, $\Delta H = 72 \text{ kJ mol}^{-1}$). Fullerene derivative 3 showed a SmA phase (Fig. S10(c)†). The mesophases were identified by POM from the formation of typical textures (SmA: focal-conic fan texture and homeotropic areas; N: schlieren texture). The mesophases observed for 3 and 8 are in agreement with the nature and structure of cyanobiphenyl-based mesogens.¹⁹ The disappearance of the nematic phase on going from malonate 8 to ligand 3 demonstrates the influence of the C_{60} sphere which destabilizes the liquid-crystalline state. This is further confirmed by the fact that fullerene derivative 3 shows a lower clearing temperature (140°C) than malonate 8 (148°C). This trend was already observed for other fullerene-containing liquid crystals.¹⁹

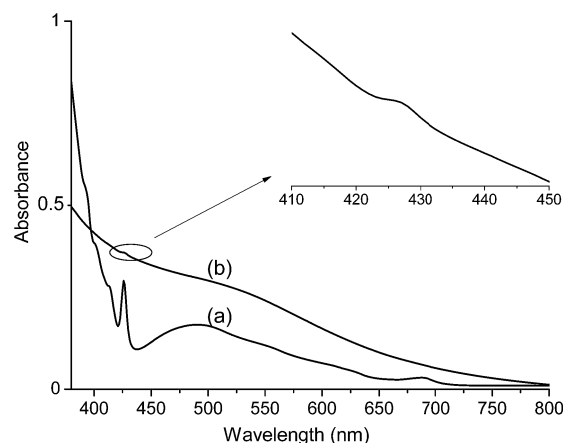


Fig. 4 UV-vis spectra of (a) 3 and (b) 1 in CH_2Cl_2 and characteristic absorbance of the methanofullerene unit at 427 nm.

Table 1 Phase transition and enthalpy changes of 3, 4 and 8^a

Compound	T_g ($^\circ\text{C}$)	Transitions	T ($^\circ\text{C}$)	ΔH (kJ mol^{-1})
4 ⁶	23	(M \rightarrow SmA) ^b	113	1.6
		SmA \rightarrow N	169	0.3
		N \rightarrow I	185	3.0
8	c	SmA \rightarrow N	147 ^d	—
		N \rightarrow I	148 ^d	2.1 ^e
3	c	SmA \rightarrow I	140	12.2

^a T_g : glass transition temperature, M: unidentified mesophase, SmA: smectic A phase, N: nematic phase, I: isotropic liquid. Transition temperatures were obtained during the second heating run (onset point, $10^\circ\text{C min}^{-1}$). ^b Monotropic transition. ^c Not detected. ^d Obtained from the first heating run (2°C min^{-1}). ^e Combined enthalpy.

For AuNPs 1, a reversible, broad transition observed by DSC at 172°C (Fig. 5) was identified as the clearing temperature by POM. On cooling slowly the sample from the isotropic melt into the liquid-crystalline phase, small focal-conic fan textures were observed (Fig. 6) after annealing the sample for several hours. The texture indicated the formation of a SmA phase, which is in agreement with the behavior of 3, 4, and other materials functionalized with cyanobiphenyl-based dendrimers.²⁰ Fluidity of the sample was observed from 172 to about 110°C . Note that AuNPs functionalized with ligand 4 gave a monotropic smectic A phase between 145 and 90°C .⁶ No decomposition was detected up to 200°C by thermogravimetry (Fig. S11†) which confirmed a good stability of AuNPs 1.

The supramolecular organization of AuNPs 1 within the SmA phase is shown in Fig. 7. This model is explained as follows: the AuNPs 1 form cylinder-like-structures with the cyanobiphenyl mesogens oriented upward and downward. The cylindrical units self-organize into layers and give rise to the SmA phase. As for the C_{60} units, they are embedded into the organic envelope. Such a supramolecular structure was already reported for related materials in which a hard core is decorated with analogous dendrons, *i.e.* liquid-crystalline hexa-adducts of C_{60} ,²¹

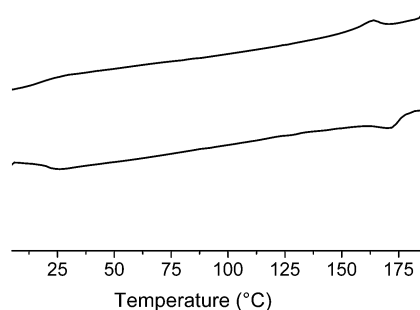


Fig. 5 DSC curves of **1** recorded during the second heating (bottom)-cooling (top) cycle at $10\text{ }^{\circ}\text{C min}^{-1}$.

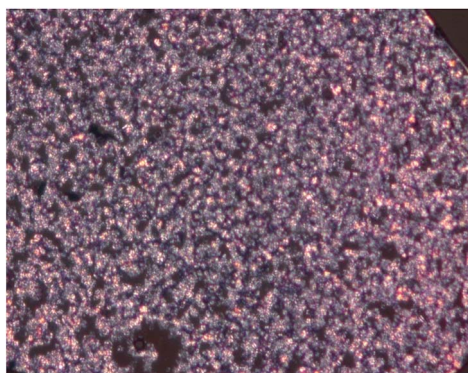


Fig. 6 Thermal polarized optical micrograph of the small focal-conic fan texture displayed by AuNPs **1** at $125\text{ }^{\circ}\text{C}$ in the SmA phase.

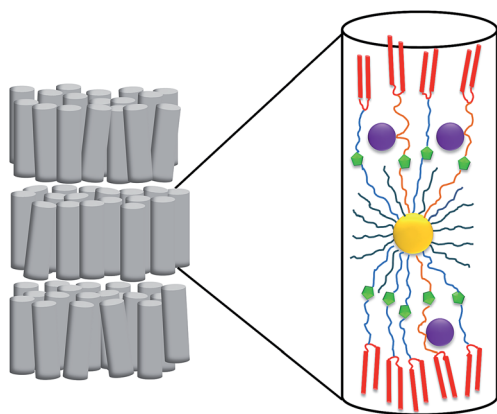


Fig. 7 Postulated model of the organization of AuNPs **1** in the smectic A phase (gold core: yellow, triazoles: green, mesogens: red, C₆₀: violet).

liquid-crystalline transition metal clusters,²² and our previously reported liquid-crystalline AuNPs.⁶

In summary, we have designed a novel liquid-crystalline organic-inorganic hybrid based on [60]fullerene and gold nanoparticles. Our concept, the functionalization of AuNPs with two mesomorphic ligands *via* click chemistry offers huge possibilities to obtain multifunctional AuNPs based on various ligands (chiral/achiral, polar/apolar, linear/bent-core). Those

variations will allow to exploit the unique structures and properties of [60]fullerene and gold nanoparticles for the design and study of novel supramolecular materials.

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