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Designing liquid-crystalline gold nanoparticles *via* the olefin cross-metathesis reaction

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Dedicated to Professor Tomás Torres on the occasion of his 65th birthday

ABSTRACT: Liquid-crystalline gold nanoparticles were prepared by grafting mesomorphic α,β-unsaturated carbonyl olefins onto the organic shell of gold nanoparticles containing terminal olefin ligands by applying the olefin cross-metathesis. The latter reaction was performed under standard conditions using second-generation Grubbs catalyst. The title materials were found to be stable up to 200 °C and gave rise to the formation of smectic A phases in agreement with the structure and nature of the liquid-crystalline promoters. The olefin cross-metathesis proved to be a reaction of choice for the design of liquid-crystalline nanoparticles.

KEYWORDS: olefin cross-metathesis, liquid crystals, gold nanoparticles.

INTRODUCTION

Ordering gold nanoparticles (AuNPs) within liquid-crystalline phases gives the possibility to build up materials with unique photoelectronic properties, such as the metamaterials [1]. Precise functionalization of AuNPs with specific mesogens is a critical step to obtain the target materials with tailored-made properties [2]. Thus, both the design of the mesogens (shape, length, chirality) and the synthesis of the AuNPs (mild reaction conditions and versatility of the reactions) have to be carefully considered.

Intensive efforts have been devoted to the synthesis of liquid-crystalline AuNPs by applying the ligand-exchange reaction. In this approach, the thioalkanes used to stabilize the AuNPs are partially replaced by various thiol- or amino-based mesogens, such as rod-like [3], discotic [4], bent-core [3b], dendritic [5], and laterally-branched mesogens [6], as well as chiral mesogens [7]. A variety of mesophases have been observed, including nematic, smectic, cubic, columnar, and helical twisted columnar phases.

An alternative concept to the ligand-exchange reaction is the chemical grafting of mesogens onto the organic shell surrounding the AuNPs. Literature examples include: (i) amide-bond formation between amino-based liquid-crystalline dendrons with AuNPs functionalized with carboxylic acid functions (highly ordered simple cubic phases were obtained) [8] and (ii) hydrosilylation of laterally-branched silylated mesogens onto AuNPs coated with terminal olefins (nematic phases were observed) [9]. In parallel, our group has reported the click chemistry as an elegant synthetic tool for the synthesis of liquid-crystalline AuNPs [10]: grafting first- and second-generation liquid-crystalline dendrons containing alkyne functions onto azide-based AuNPs *via* the Huisgen 1,3-dipolar cycloaddition reaction in the presence of copper catalyst [11] gave liquid-crystalline AuNPs which displayed smectic A phases [10]. This strategy allowed also the synthesis of liquid-crystalline [60]fullerene-AuNPs hybrids [10b].

Recently, we have successfully applied the olefin cross-metathesis reaction [12] to prepare *Janus*-type liquid crystals for which smectic C, smectic A, nematic and chiral nematic phases were observed [13]. Its tolerance

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towards a wide range of functional groups and the mild reaction conditions that it requires, have made the olefin cross-metathesis a popular reaction in organic chemistry and materials science [14, 15], *e.g.* for the synthesis of liquid-crystalline polymers [14] and functionalization of AuNPs with ferrocene derivatives [15b].

With the view to exploit new chemical reactions for the design of liquid-crystalline AuNPs, we decided to functionalize AuNPs with mesogenic units *via* the olefin cross-metathesis reaction. Indeed, based on our results with organic-type liquid crystals [13], this reaction should allow to decorate AuNPs with a great variety of liquid-crystalline promoters, including rod-like, disc-like, dendritic and chiral mesogens. Furthermore, careful selection of the catalyst and reaction conditions allows control of the stereochemistry of the newly formed carbon–carbon double bonds in the cross-metathesis molecules [16].

We report, herein, the synthesis, characterization and mesomorphic properties of two novel liquid-crystalline AuNPs **1** and **2** (Scheme 1), the design of which is based on the grafting of mesomorphic type II olefins **5** and **6** (α, β-unsaturated carbonyl olefins, Fig. 1) onto AuNPs **3** carrying type I olefins (terminal olefins, Scheme 1) *via* the olefin cross-metathesis reaction in the presence of second-generation Grubbs catalyst. We clearly demonstrate the wide scope of the olefin cross-metathesis reaction for the functionalization of AuNPs with mesogenic units.

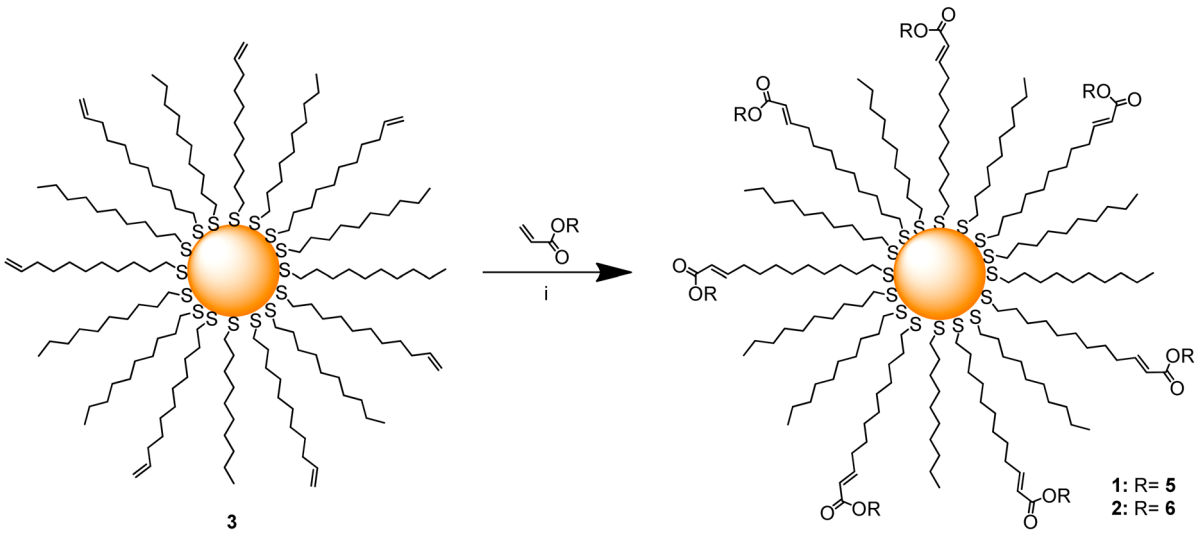
RESULTS AND DISCUSSION

Synthesis and characterization

AuNPs **1** and **2** were synthesized following the general procedure shown in Scheme 1. In a typical reaction, a mixture of AuNPs **3** (1 eq. of 10-undecene-1-thiol), mesogen **5** or **6** (2 eq.) and second-generation Grubbs catalyst (0.05 eq.) in CH_2Cl_2 was heated under reflux for 16 h. Purification by ultrafiltration (30 kDa membrane, CH_2Cl_2) gave pure AuNPs **1** or **2**, respectively. The structure and purity of AuNPs **1** and **2** were confirmed by ^{1}H NMR spectroscopy. By TEM analysis, the size of the AuNPs was found to be 1.5 ± 0.5 nm which indicates that the olefin cross-metathesis did not modify the size of the nanoparticles (*vide infra*). The weak plasmon band observed for AuNPs **1** and **2** in the UV-vis spectrum at 520 nm (see Fig. S7 in the ESI) supported the size of the nanoparticles obtained by TEM.

AuNPs **3** were prepared by ligand-exchange reaction from decanethiol-stabilized gold nanoparticles (1.5 ± 0.5 nm) and 10-undecene-1-thiol in *n*-heptane. In order to obtain *ca.* a 1:1 ratio between the two ligands grafted on the AuNPs **3**, an excess of 10-undecene-1-thiol (2.5 eq. with respect to decanethiol) was used with a reaction time of 72 h. Under such reaction conditions, AuNPs **3** (1.5 ± 0.5 nm) were found to be covered by a mixture of 60% of decanethiol and 40% of 10-undecene-1-thiol (^{1}H NMR). Experimental details are given in the ESI. Olefins **5** and **6** were synthetized by esterification of 2-carboxyethyl acrylate with the corresponding first-generation phenol-based poly(arylester) dendrons [17]. Their structure and purity were confirmed by ^{1}H NMR spectroscopy, MS and elemental analysis (see ESI).

^{1}H NMR spectroscopy confirmed the formation and purity of the cross-metathesis products AuNPs **1** and **2**. The data obtained for the synthesis of AuNPs **2** are presented in Fig. 2 as an example. Firstly, the disappearance of the olefinic signals of **3** (H_b) and **6** (H_c and H_d) in the spectrum of AuNPs **2**, and the chemical



Scheme 1. Synthesis of AuNPs **1** and **2** by olefin-cross metathesis. (i) second-generation Grubbs catalyst, CH_2Cl_2, 40 °C, 16 h

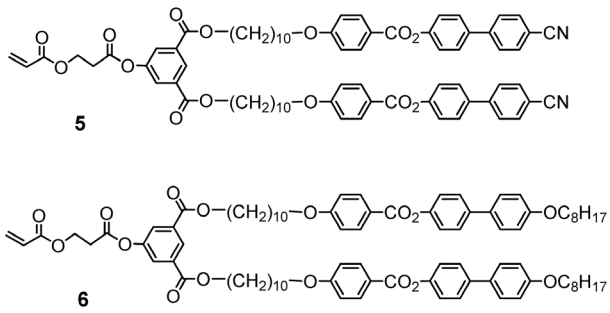


Fig. 1. Structures of type II olefins **5** and **6**

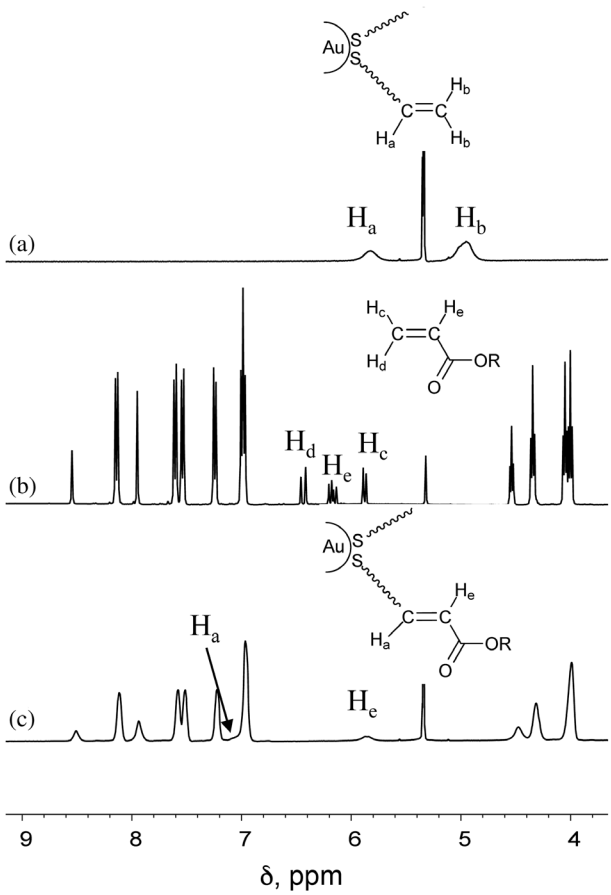


Fig. 2. Part of ^{1}H NMR spectra (3.7 to 9.1 ppm) in CD_2Cl_2 of (a) AuNPs **3**, (b) mesogen **6**, (c) AuNPs **2**.

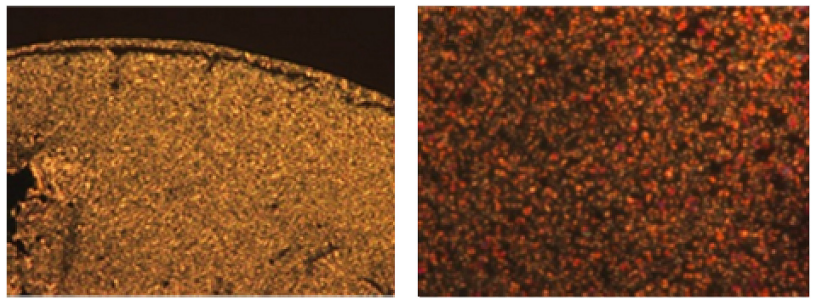
shifts of H_a (5.83 → 6.94 ppm) and H_e (6.16 → 5.84 ppm) proved the formation of the internal carbon–carbon double bond. Secondly, all peaks found in the spectrum of AuNPs **2** are broad (this is expected for AuNPs) which indicate that AuNPs **2** are free of non-reacted mesogen **6**. Thirdly, from the integration of the olefinic and CH_3 signals, loading of mesogen **6** was estimated to be around 40% in agreement with the ligand ratio in AuNPs **3**. This result is important as it shows that the cross-metathesis was complete and the reaction conditions as well as the work-up procedure did not alter the chemical composition of the AuNPs. Finally, no coupling constants could be determined in the spectrum of AuNPs **2** because of the broadness of the signals. However, based on our recent study with similar reaction conditions and analogous liquid-crystalline promoters [13], we can assume the *E*-configuration of the carbon–carbon double bond in the cross-metathesis AuNPs **2**. Similar results were obtained for AuNPs **1**.

Liquid-crystalline properties

The mesomorphic and thermal properties of compounds **1**, **2**, **5** and **6** were investigated by Polarized Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC). All compounds gave rise to liquid-crystalline properties. Olefins **5** and **6** showed limited thermal stability as they polymerized when heated. This behavior was not unexpected taking into account the acrylate nature of the olefinic function, and was already observed for related materials [13]. However, by POM, both **5** (Cr → SmA: 103 °C; SmA → N: 186 °C; N → I: > 200 °C) and **6** (Cr → SmA: 124 °C; SmA → N: 168 °C; N → I: > 170 °C) displayed characteristic textures of liquid-crystalline phases (smectic A phase: focal-conic fan texture and hometropic areas; nematic phase: *schlieren* texture; see Figs S8 and S9 in the ESI). The formation of smectic A and nematic phases for **5** and **6** is in agreement with the structure and nature of the mesogens [17].

AuNPs **1** (SmA → I: 155 °C) and **2** (SmA → I: 132 °C) gave rise to the formation of smectic A phases (small focal-conic fan textures, Fig. 3). In both cases, liquid-crystalline ranges of about 60 °C were observed. The textures developed after annealing the samples for several hours near the clearing points. The clearing temperature was observed by DSC only for AuNPs **2**. The fact that no clearing point could be determined for AuNPs **1** is not surprising for such polydispersed materials [18]. By thermogravimetry analysis, AuNPs **1** and **2** were found to be stable up to 200 °C (Fig. S11 in the ESI). This result indicated that the mesomorphic properties arose from the AuNPs themselves and not from ligands released because of decomposition.

The supramolecular organization of AuNPs **1** and **2** within the smectic A phases (Fig. 4) can be explained based on our former studies on liquid-crystalline AuNPs obtained with similar mesogens [10]: AuNPs **1** and **2** form cylinder-like structures with the mesogens oriented upward and downward. The cylinders self-organize into layers which lead to the formation of the smectic A phases.



(a) (b)

Fig. 3. Thermal polarized optical micrographs of small focal-conic fan texture in the smectic A phase displayed by (a) **1** at 145 °C, and (b) **2** at 130 °C after annealing the samples for several hours

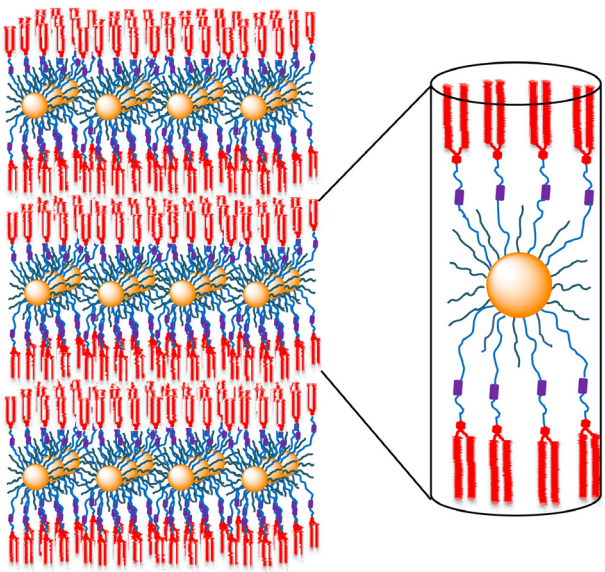


Fig. 4. Postulated model of the organization of AuNPs **1** and **2** within the smectic A phase (gold core: orange, mesogens: red, internal olefin groups: violet)

CONCLUSION

We have demonstrated that the olefin cross-metathesis is an effective and elegant reaction for the design of liquid-crystalline AuNPs. The desired mesogens were grafted onto the organic corona of AuNPs without altering the size of the nanoparticles. Our results open the doors for the design of a great variety of liquid-crystalline AuNPs as numerous mesogens can be used in the olefin cross-metathesis reaction. By careful selection of the mesogens used as liquid-crystalline promoters, the mesomorphism of the AuNPs can thus be controlled by design at the molecular level. Finally, our approach based on the olefin cross-metathesis is not limited to AuNPs but can be applied to other nanoparticles and polyfunctional platforms.

EXPERIMENTAL

Synthesis

General procedure for AuNPs 1 and 2. To a solution of AuNPs **3** (1 eq. 10-undecene-1-thiol) and olefin **5** or **6** (2 eq.) in CH_2Cl_2, was added second-generation Grubbs catalyst (0.05 eq.). The reaction mixture was heated under reflux for 16 h under Ar. Unreacted olefins and catalyst were removed by ultrafiltration (30 kDa membrane, CH_2Cl_2; checked by TLC, silica gel, CH_2Cl_2/AcOEt 100:1). A few milliliters of CH_2Cl_2 containing the nanoparticles were left on the filter. The latter solution was concentrated to dryness, and pure AuNPs **1** or **2** were obtained.

Synthesis of AuNPs 1. From AuNPs **3** (27.0 mg, 0.015 mmol 10-undecene-1-thiol), **5** (36.5 mg, 0.030 mmol) and second-generation Grubbs catalyst (0.7 mg, 0.05 eq.) in CH_2Cl_2 (2 mL): AuNPs **1** (6.5 mg, 24% mass yield). ^{1}H NMR (CD_2Cl_2): δ, ppm 8.52 (br. s, arom. H), 8.11 (br. s, arom. H), 7.93 (br. s, arom. H), 7.71 (br. s, arom. H), 7.65 (br. s, arom. H), 7.31 (br. s, arom. H), 6.97 (br. s, C*H*=CHCO$_2$ and arom. H), 5.85 (br. s, CH=C*H*CO$_2$), 4.45 (br. s, CO$_2$C*H*$_2$CH$_2$CO$_2$), 4.31 (br. s, ArCO$_2$CH$_2$), 4.02 (br. s, CH$_2$OAr), 2.95 (br. s, CH$_2$CO$_2$), 2.19 (br. s, C*H*$_2$CH=CH), 1.77 (br. s, C*H*$_2$CH$_2$OAr and ArCO$_2$CH$_2$C*H*$_2$), 1.43–1.34 (br. m, aliph. H), 0.88 (br. s, CH$_3$). UV-vis (CH_2Cl_2): weak plasmon band at 520 nm.

Synthesis of AuNPs 2. From AuNPs **3** (27.0 mg, 0.015 mmol 10-undecene-1-thiol), **6** (42.7 mg, 0.030 mmol) and second-generation Grubbs catalyst (0.7 mg, 0.05 eq.) in CH_2Cl_2 (2 mL): AuNPs **2** (21.0 mg, 78% mass yield). ^{1}H NMR (CD_2Cl_2): δ, ppm 8.49 (br. s, arom. H), 8.09 (br. s, arom. H), 7.92 (br. s, arom. H), 7.53 (br. d, arom. H), 7.20 (br. s, arom. H), 6.94 (br. s, C*H*=CHCO$_2$ and arom. H), 5.84 (br. d, CH=C*H*CO$_2$), 4.46 (br. s, CO$_2$C*H*$_2$CH$_2$CO$_2$), 4.29 (br. s, ArCO$_2$CH$_2$), 3.97 (br. s, CH$_2$OAr), 2.95 (br. s, CH$_2$CO$_2$), 2.20 (br. s, C*H*$_2$CH=CH), 1.77 (br. s, C*H*$_2$CH$_2$OAr and ArCO$_2$CH$_2$C*H*$_2$), 1.46–1.32 (br. m, aliph. H), 0.88 (br. s, CH$_3$). UV-vis (CH_2Cl_2)): weak plasmon band at 520 nm. TEM: 1.5 ± 0.5 nm.

Acknowledgements

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Supporting information

Figures S1–S12 and Schemes S1–S2 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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