#### Tetrahedron xxx (2018) 1–13



Contents lists available at ScienceDirect

## Tetrahedron



# Ferrocenyl Janus mixed-dendron stars and their stabilization of Au and Ag nanoparticles

Yue Liu <sup>a, b</sup>, Shengdong Mu <sup>a, b</sup>, Xiong Liu <sup>a, b</sup>, Qiangjun Ling <sup>a</sup>, Chaodong Hang <sup>a</sup>, Jaime Ruiz <sup>c</sup>, Didier Astruc <sup>c, \*</sup>, Haibin Gu <sup>a, b, \*\*</sup>

<sup>a</sup> Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu, 610065, China <sup>b</sup> National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu, 610065, China <sup>c</sup> ISM, UMR CNRS N<sup>o</sup> 5255, Univ. Bordeaux, 33405, Talence Cedex, France

#### ARTICLE INFO

Article history: Received 8 June 2018 Received in revised form 13 July 2018 Accepted 14 July 2018 Available online xxx

This article is dedicated to our distinguished colleague and friend Professor Léon Ghosez (IECB, University of Bordeaux).

Keywords: Ferrocene Dendrimer Janus Nanoparticule Redox

#### 1. Introduction

#### ABSTRACT

Janus molecular architectures have recently attracted attention due to their structures and properties that differ from those of traditional symmetric structures. Herein, two new small redox-reversible mixed-dendron star-shape molecules containing three ferrocenyl groups have been synthesized by linking two distinct dendrons using an esterification reaction. These organometallic nano structures were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, MS, IR and UV–vis. spectroscopies and cyclic voltammetry confirming the number of ferrocenyl groups and AFM and DLS showing micellar assemblies. Au and Ag nanoparticles were stabilized in the presence of a mixed-dendron structure having amidoferrocene termini upon reaction of the nanoparticle metal precursor with NaBH<sub>4</sub>. Compared reactions of the two star-molecules with HAuCl<sub>4</sub> showed a slow redox reaction leading to Au nanoparticles only with the star-molecule terminated with triazolyferrocene termini, which is taken into account by the difference of their redox potentials.

© 2018 Elsevier Ltd. All rights reserved.

**Tetrahedro** 

Metal-containing macromolecules have been known for a quarter of century for their multiple applications in various fields including biomedicine, sensing, nanomaterial science and catalysis [1–6]. A new class of macromolecules with Janus structures have more recently appeared [7–17]. They are usually synthesized by joining a hydrophilic and a hydrophobic dendron, which provides a single amphiphilic and heterofunctional macromolecule with distinctive features. These unique structures lead to the emergence of characteristic properties towards nanomaterials and biological applications, such as thermal actuators [7], ionic liquids [8], catalysis [9], light harvesting systems [10], bio-imaging [11], optoelectronics [12] and drug delivery [13].

In these Janus molecular structures, usually the hydrophilic

https://doi.org/10.1016/j.tet.2018.07.035 0040-4020/© 2018 Elsevier Ltd. All rights reserved. dendron is composed of polyethylene glycol (PEG) [14], amino [15], hydroxyl [16] and carboxyl groups [17], whereas the hydrophobic part of the structure is often constructed using aliphatic chains of various length [14], poly(benzyl ether) [9], etc. Ferrocene has been well known for more than sixty years with a variety of functions. Its chemistry is now providing applications in many areas such as redox devices, batteries and other materials, sensing, catalysis, including asymmetric and enantioselective catalysis, and nanomedicine [18].

Due to the functional applications of ferrocenyl-based macromolecules [19–23], the ferrocenyl group [Fe( $\eta$  [5]-C<sub>5</sub>H<sub>5</sub>)( $\eta$  [5] -C<sub>5</sub>H<sub>4</sub>–)], Fc, was integrated in Janus star-shaped mixed dendron structures containing a hydrophobic dendronic unit and a ferrocenyl-terminated dendron (Fig. 1).

Amphiphilic Janus dendrimers are already known for their biomedical applications [24]. The hydrophobic part of the new Janus structures presented here is composed of three ferrocenyl units, whereas the hydrophilic one contains three TEG termini. These two dendrons are connected using an esterification reaction upon chemoselective coupling [24]. The combination of the amphiphilicity of the Janus structures **17** and **19** and the redox

<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author. Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, China.

*E-mail addresses: didier.astruc@u-bordeaux.fr* (D. Astruc), guhaibinkong@126. com (H. Gu).

Y. Liu et al. / Tetrahedron xxx (2018) 1–13



Janus molecule

**Fig. 1.** Frame of the Janus structures introduced in this work. The 3 pink circles on the right represent hydrophobic ferrocene groups and the blue lines on the left hydrophilic triethyleneglycol (TEG) fragments.

activity of their Fc moieties [25–28] provides bifunctional macromolecules.

Ferrocene derivatives are typically stable under both oxidized Fe(III) and reduced Fe(II) forms and behave as electron reservoir compounds [29–31]. The reduction of Au(III) to AuNPs by ferrocene or simple ferrocene derivatives is known to form gold [32,33] and silver [34,35] nanoparticles [36–38], including with a Janus structure containing TEG dendron and a single ferrocenyl unit [38]. Ferrocenyl-containing macromolecule stabilization of gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) has been studied by Manners' group since 2005 [39,40] and more recently by our groups [41–43]. TEG-terminated dendrimers [44], as other polyols [45-49], are also known to reduce Au(III) to AuNPs and Ag(I) to AgNPs. Thus ferrocenyl-terminated dendrons [50] connected to TEG-terminated dendrons may eventually provide favorable conditions to reduce Au(III) and Ag(I) forming AuNPs and AgNPs respectively. It is necessary, however, to delineate the parameters controlling such redox processes.

#### 2. Experimental

#### 2.1. General data

Ferrocene, methyl gallate, TEG mono methyl ether were purchased from Energy Chemical, and used directly. 2-(2-(2-Methoxy)ethoxy)ethyl-4-methylbenzenesulfonate [51], carboxylferrocene **3** [52], **4–9** [53–55], **12–14** [56–58] and (3,4,5tris(2-(2-(2-methoxyethoxy)ethoxy)phenyl)formic acid **15** [59] were synthesized according to known procedures. All the other chemicals used were analytic grade, commercially purchased and used as received. All the solvents used were dried and freshly distilled.

<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were determined at 25 °C with a Bruker AV II-400 MHz spectrometer. All the chemical shifts are recorded in parts per million ( $\delta$ , ppm) with reference to tetramethylsilane (TMS). The mass spectra were recorded using a GCMS-QP2010 Plus spectrometer. The infrared spectra were measured with an America Thermo Scientific Nicolet iS10 FT-IR spectrophotometer using KBr disk in the range of 400–4000 cm<sup>-1</sup>. UV–visible absorption spectra were recorded on a Shanghai Jinghua UV1900 UV–vis. spectrometer. Cyclic voltammetry (CV) measurements were recorded on a PAR 273 potentiostat

under nitrogen (N<sub>2</sub>) atmosphere at 20 °C using dry dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) as solvent and [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] 0.1M as supporting electrolyte. The working and counter electrodes were Pt, and the reference electrode was Ag. The internal reference was [FeCp\*<sub>2</sub>] [60–62] (Cp\* =  $\eta$ <sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>), and the scan rate was 200 mV s<sup>-1</sup>. The Bard-Anson method [63] was used to determine the number of electrons involved in the oxidation of the Janus structures. The experiments were conducted by preparing a known amount of dendrimer in dry CH<sub>2</sub>Cl<sub>2</sub>, and a known amount of [FeCp\*<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> was added to the solution. After recording the CV, the intensities of the oxidation waves of the dendrimer and the internal reference [FeCp\*<sub>2</sub>] were measured. The values were introduced into equation (1) [64]:

$$n_{p} = \left(i_{dp} / C_{p}\right) / (i_{dm} / C_{m}) \left(M_{p} / M_{m}\right)^{0.275}$$
(1)

In equation (1),  $i_{dp}$  is the intensity of the CV wave of the metallopolymer,  $C_p$  the concentration of the metallopolymer,  $i_{dm}$  the intensity of the CV wave of the monomer,  $C_m$  concentration of the monomer,  $M_p$  the molecular weight of the metallopolymer, and  $M_m$ the molecular weight of the monomer. Equation (1) provides the final number of transferred electrons ( $n_p$ ). Dynamic light scattering (DLS) measurements are reported at 25 °C on a NanoZS leaser diffract instrument (Malvern, UK). Transmission electron microscopy (TEM) observations were measured with a JEM-2100 field emission Transmission electron microscope (JEOL). Samples for TEM were prepared by casting a drop of the solution on a silicon grid, followed by drying at 25 °C.

Synthesis of 10: Triethylamine (0.1 ml, 0.72 mmol) was injected dropwise into the CH<sub>2</sub>Cl<sub>2</sub> (40 ml) suspension of carboxyferrocene 3 (0.5 g, 2.17 mmol) at 0 °C under N<sub>2</sub> atmosphere. Oxalyl chloride (0.7 ml, 8.2 mmol) was then added dropwise into the solution. The reaction mixture was stirred at room temperature (r. t.) overnight. The solvent was then removed in vacuo, and the red solid residue, crude chlorocarbonylferrocene, was then dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml), added dropwise into the CH<sub>2</sub>Cl<sub>2</sub> solution (10 ml) of **9** (0.4 g)1.83 mmol) and Et<sub>3</sub>N (1.5 ml, 10.7 mmol). The obtained mixture was further stirred overnight at r. t. under N<sub>2</sub> atmosphere, and then washed successively with saturated NaHCO<sub>3</sub> solution  $(1 \times 100 \text{ ml})$ and distilled water  $(3 \times 100 \text{ ml})$ . The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and vacuumed to provide the crude product 10 that was then purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/ methanol  $(0\% \rightarrow 5\%)$  as the eluent and obtained as brown sticky oil. Yield: 0.7 g, 89%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS),  $\delta_{ppm}$ : 6.28  $(t, J = 9.3 \text{ Hz}, 1\text{H}, \text{NHCO}), 4.68 (t, J = 3.8 \text{ Hz}, 2\text{H}, \text{ sub. Cp}, \text{Cp} = \eta \text{ [5]}$ -C<sub>5</sub>H<sub>5</sub>), 4.32 (t, *J* = 3.4 Hz, 2H, sub. Cp), 4.19 (s, 5H, free Cp), 3.67–3.55 (m, 14H,  $7 \times CH_2$ ), 3.36 (t, J = 10.1 Hz, 2H,  $CH_2N_3$ ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS),  $\delta_{\rm ppm}$ : 170.4 (CONH), 70.8, 70.7, 70.4, 70.3, 69.8, 68.3 (Cp and CH<sub>2</sub>), 50.8 (CH<sub>2</sub>N<sub>3</sub>), 39.4 (NHCH<sub>2</sub>). MS (ESI, m/z), calcd. for C<sub>19</sub>H<sub>16</sub>O<sub>4</sub>N<sub>4</sub>Fe: 430.3; found: 453.1 (M+Na<sup>+</sup>). Selected IR (KBr,  $cm^{-1}$ ): 3335 ( $v_{NH}$ ), 2869 ( $v_{CH2}$ ), 2105 ( $v_{N3}$ ), 1634 (v<sub>C=0</sub>), 1539, 1453 (v<sub>C=C, Cp</sub>), 1299 (v<sub>C-N</sub>), 1106 (v<sub>C-O-C</sub>), 823 (v<sub>FeII</sub>).

**Synthesis of 17:** Oxalyl dichloride (1.04 g, 8.21 mmol, 5 equiv) was added dropwise at 0 °C under N<sub>2</sub> atmosphere to a solution of **15** (1.0 g, 1.64 mmol, 1 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 ml). The mixture was stirred overnight at r. t. under N<sub>2</sub> atmosphere. The mixture was concentrated to give crude **16**, which was used in the next step without further purification. Then, to a mixture of **14** (1.63 g, 1.64 mmol, 1 equiv) and Et<sub>3</sub>N (0.83 g, 8.21 mmol, 5 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added the crude **16** in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml) dropwise at 0 °C under N<sub>2</sub> atmosphere. The mixture was stirred at r. t. overnight. Distilled water (40 ml) was then added into the mixture, and the organic layer was separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (40 ml × 3). The organic layers were combined, washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and

concentrated to give a crude product that was purified by column chromatography ( $CH_2Cl_2/CH_3OH = 200/1$ ) to give **17** as brown solid. Yield: 2.03 g, 78%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS), δ<sub>ppm</sub>: 7.65 (s, 2H, 2 × C=CH of triazole), 7.62 (s, 1H, C=CH of triazole), 7.30 (s, 2H, ph), 6.72 (s, 2H, ph), 5.25 (s, 4H, 2 × ph–OCH<sub>2</sub>–triazole), 5.21 (s, 2H, ph-OCH<sub>2</sub>-triazole), 5.18 (s, 2H, COOCH<sub>2</sub>), 5.12 and 5.09 (ds, 4H+2H, 3 × N=N-N-CH<sub>2</sub>), 4.28, (t, I = 3.4 Hz, 4H, 2 × sub. Cp), 4.23–4.16 (m. 29H.  $3 \times ph$ -OCH<sub>2</sub>.  $4 \times sub$ . Cp and  $3 \times free$  Cp). 3.87-3.51 (m, 30H, 3 × CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>), 3.36 and 3.36 (ds, 9H, 3 × OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS),  $\delta_{ppm}$ : 1152.4 (COO), 152.2 (ph), 144.4 (ph), 143.8 and 143.7 (C of triazole), 142.7 (ph), 137.5 (ph), 132.2 (ph), 124.8 (ph), 123.2 and 122.8 (C of triazole), 109.1 (ph), 106.2 (ph), 61.3 (HOCH<sub>2</sub>), 81.4, 81.0, 72.5, 71.9, 70.8, 70.7, 70.6, 69.6, 69.0, 68.9, 66.6 and 66.3 (CH<sub>2</sub>O and Cp), 63.1 (COOCH<sub>2</sub>), 59.0  $(OCH_3)$ , 50.1 (OCH<sub>2</sub>-triazole), 49.9 (triazole–CH<sub>2</sub>–Fc). MS (ESI m/z), calcd. for C<sub>77</sub>H<sub>93</sub>Fe<sub>3</sub>N<sub>9</sub>O<sub>17</sub>: 1584.15; found: 1607.46 (M +Na<sup>+</sup>). Selected IR (KBr, cm<sup>-1</sup>): 3440 ( $v_{OH}$ ), 2876 ( $v_{CH2}$ ), 1713 ( $\delta_{C=O}$ ), 1590, 1500, 1431 ( $v_{C=C}$  of benzene), 1330(v<sub>C-N</sub>), 1206 (v<sub>ph-O-C</sub>), 1106, 1050, 1001, 823(v<sub>Fell</sub>).

Synthesis of 18: 10 (5.25 g, 12.2 mmol, 3.3 equiv) and 13 (1.0 g, 3.7 mmol, 1.0 equiv) were dissolved in 80 ml of tetrahydrofuran (THF). CuSO<sub>4</sub>·5H<sub>2</sub>O (3.05 g, 12.2 mmol, 3.3 equiv) aqueous solution (40 ml) was added into the obtained reaction mixture, followed by the dropwise addition of a freshly prepared sodium ascorbate (NaAsc, 4.84 g, 24.4 mmol, 6.6 equiv) aqueous solution (40 ml) to obtain a THF/water in a ratio of 1:1. The reaction mixture was stirred for 72 h at r. t. under N<sub>2</sub> atmosphere, and then vacuumed to remove THF. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, (80 ml) and aqueous ammonia (80 ml), and stirred for 30 min to remove the copper ions trapped inside the targeted compound as  $[Cu(NH_3)_2(H_2O)_2]^{2+}$ . The organic layer was collected, dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. Purification was conducted by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/ methanol  $(1\% \rightarrow 20\%)$  as eluent to provide **18** as orange-yellow oil. Yield: 4.62 g, 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS),  $\delta_{\text{ppm}}$ : 7.90  $(s, 2H, 2 \times C = CH \text{ of triazole}), 7.86 (s, 1H, C = CH \text{ of triazole}), 6.73 (s, 1H, C = CH \text{ of triaz$ 2H, ph), 6.59 (t, I = 10.8, 1H, NHCO), 6.51 (t,  $I = 10.8, 2H, 2 \times NHCO$ ), 5.17 (s, 6H,  $3 \times \text{ph-OCH}_2$ ), 4.72–4.69 (m, 6H,  $3 \times \text{sub. Cp}$ ), 4.60 (s, 2H, HOCH<sub>2</sub>), 4.53–4.46 (m, 6H, 3 × N=N–N–CH<sub>2</sub>), 4.30 (t, *J* = 3.8, 6H,  $3 \times$  sub. Cp), 4.17 (s, 15H,  $5 \times$  free Cp), 3.86–3.80 (m, 6H,  $3 \times N = N - N - CH_2 CH_2$ ), 3.59-3.48 36,  $3 \times OCH_2(-$ (m, CH<sub>2</sub>OCH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>N). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS), δ<sub>ppm</sub>: 170.6 (NHCO), 152.2 (ph), 144.4 and 143.7 (C of triazole), 136.3 (ph), 124.7 (ph), 124.6 (C of triazole), 106.2 (ph), 70.4, 70.3, 70.2, 70.1, 70.0 (HOCH<sub>2</sub>), 69.4, 69.3, 68.3, 66.3, 64.7, 62.9 (Cp), 50.2 (CH<sub>2</sub>), 50.0 (CH<sub>2</sub>), 39.3 (CH<sub>2</sub>NHCO). MS (ESI *m/z*), calcd. for C<sub>73</sub>H<sub>92</sub>Fe<sub>3</sub>N<sub>12</sub>O<sub>16</sub>: 1561.12; found: 781.24 (M<sup>+</sup>/2), 792.23 ((M + Na<sup>+</sup>)/2), 800.22  $((M + K^+)/2)$ , 803.73 $(M/2 + Na^+)$ , 1584.47  $(M + Na^+)$ . Selected IR (KBr, cm<sup>-1</sup>): 3346 ( $\nu_{OH}$ ), 2872 ( $\nu_{CH2}$ ), 1633 ( $\delta_{C=0}$ ), 1539, 1504, 1438 (v<sub>C=C</sub> of benzene), 1379, 1351, 1301(v<sub>C-N</sub>), 1227, 1106 ((v<sub>C-O-C</sub>), 824  $(v_{\text{FeII}})$ .

**Synthesis of 19:** Oxalyl dichloride (1.04 g, 8.21 mmol, 5 equiv) was added dropwise at 0 °C under N<sub>2</sub> atmosphere to a solution of **15** (1.0 g, 1.64 mmol, 1 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 ml). The mixture was stirred overnight at r. t. under N<sub>2</sub> atmosphere, and the mixture was concentrated to give a crude product **16**, which was used in the next step without further purification. Then, to a mixture of **18** (2.56 g, 1.64 mmol, 1 equiv) and Et<sub>3</sub>N (0.83 g, 8.21 mmol, 5 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was added the crude **16** in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml) dropwise at 0 °C under N<sub>2</sub> atmosphere. The mixture was stirred at r. t. overnight. Distilled water (50 ml) was then added into the mixture, and the organic layer was separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 ml × 3). The organic layers were combined, washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to give a crude product that was purified by column

chromatography ( $CH_2Cl_2$ /methanol = 200/1) to give **19** as brown oil. Yield: 2.93 g, 83%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS),  $\delta_{ppm}$ : 7.91 (s, 2H,  $2 \times C$ =CH of triazole), 7.89 (s, 1H, C=CH of triazole), 7.32 (s, 2H, ph), 6.83 (s, 2H, ph), 6.48 (t, J = 10.9 Hz, 1H, NHCO), 6.42 (t, J = 10.5 Hz, 2H, 2 × NHCO), 5.24 (s, 2H, ph-OCH<sub>2</sub>-triazole), 5.20 (s, 4H, 2 × ph-OCH<sub>2</sub>-triazole), 5.16 (s, 2H, COOCH<sub>2</sub>), 4.70–4.68 (m, 6H,  $3 \times$  sub. Cp), 4.52-4.47 (m, 6H,  $3 \times N=N-N-CH_2$ ), 4.29 (t, I = 3.7 Hz, 6H, 3 × sub. Cp), 4.23–4.16 (m, 21H, 3 × ph-OCH<sub>2</sub> and  $3 \times$  free Cp), 3.87-3.51 (m, 72H,  $3 \times (OCH_2CH_2)_2OCH_2$  and  $3 \times (CH_2OCH_2)_3CH_2$ ), 3.36 and 3.36 (ds, 9H,  $3 \times OCH_3$ ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS), δ<sub>ppm</sub>: 170.4 (NHCO), 152.6 (COO), 152.4 (ph), 143.9, 143.6 (C of triazole), 137.7 (ph), 132.5 (ph), 124.8 and 124.5 (C of triazole), 109.1 (ph), 108.2 (ph), 76.3 (Cp) 72.5, 72.0, 70.8, 70.7 (OCH<sub>2</sub>), 70.5, 70.4, 70.2, 70.1, 70.0 (OCH<sub>2</sub>), 69.8, 69.6, 69.3, 69.0, 66.2 (Cp), 63.1 (COOCH<sub>2</sub>) 50.2 (CH<sub>2</sub>), 50.0 (CH<sub>2</sub>), 39.3 (CH<sub>2</sub>NHCO). MS (ESI *m/z*), calcd. for C<sub>101</sub>H<sub>138</sub>Fe<sub>3</sub>N<sub>12</sub>O<sub>29</sub>: 2151.77; found: 718.26 ((M + H<sup>+</sup>)/3), 739.91 (M/3 + Na<sup>+</sup>), 1076.89 ((M + H<sup>+</sup>)/2), 1087.88 ((M + Na<sup>+</sup>)/2), 1098.97 (M/2 + Na<sup>+</sup>). Selected IR (KBr, cm<sup>-1</sup>): 3423 ( $\nu_{OH}$ ), 2874 ( $\nu_{CH2}$ ), 1713 ( $\delta_{C=0}$ ), 1592, 1540, 1431 (v<sub>C=C</sub> of benzene), 1379, 1331, 1299(v<sub>C-N</sub>), 1204, 1107(v<sub>C-O-C</sub>), 824 (v<sub>FeII</sub>).

3

**Synthesis of AuNPs-1: 19** (4.5 mg,  $2.1 \times 10^{-3}$  mmol, 2 equiv) and NaBH<sub>4</sub> (0.24 mg,  $6.3 \times 10^{-3}$  mmol, 6 equiv) were dissolved in methanol (6 ml) in a Schlenk flask, and HAuCl<sub>4</sub> (0.34 mg,  $1 \times 10^{-3}$  mmol, 1 equiv) dissolved in water (1.5 ml) was then injected dropwise into the above Schlenk flask and further stirred for 2 h at 30 °C under N<sub>2</sub> atmosphere to yield **AuNPs-1**, and the color changed immediately from light-yellow to pink. The obtained **AuNPs-1** were purified before TEM analysis by dialysis (molecular weight cut off (MWCO) = 3500 g mol<sup>-1</sup>) against a large volume of water.

**Synthesis of AuNPs-2:** HAuCl<sub>4</sub> (0.34 mg,  $1 \times 10^{-3}$  mmol, 1 equiv) dissolved in water (1.5 ml) was injected dropwise into a vigorously stirred methanol solution (5 ml) of **19** (9.0 mg,  $4.2 \times 10^{-3}$  mmol, 4 equiv) in a Schlenk flask, and further stirred for 30 h at 30 °C under N<sub>2</sub> atmosphere. Then NaBH<sub>4</sub> (0.24 mg,  $6.3 \times 10^{-3}$  mmol, 6 equiv) in methanol (1 ml) was injected dropwise into the above-mentioned solution in a Schlenk flask. The obtained mixture was stirred for 2 h at 30 °C under N<sub>2</sub> atmosphere to yield **AuNPs-2**, and the color changed immediately from light-yellow to purple. The obtained **AuNPs-2** were purified by dialysis (MWCO = 3500 g mol<sup>-1</sup>) against a large volume of water.

**Synthesis of AuNPs-3:** HAuCl<sub>4</sub> (0.16 mg,  $4.8 \times 10-4$  mmol, 1 equiv) dissolved in water (0.71 ml) was injected dropwise into a vigorously stirred methanol solution (5 ml) of **17** (1.5 mg,  $9.5 \times 10^{-4}$  mmol, 2 equiv) in a Schlenk flask, and further stirred overnight at 30 °C under N<sub>2</sub> atmosphere. The color changed slowly from light-yellow to deep purple. The obtained **AuNPs-3** were purified by dialysis (MWCO = 3500 g mol<sup>-1</sup>) against a large volume of water before analysis.

**Synthesis of AgNPs-1: 19** (4.5 mg,  $2.1 \times 10^{-3}$  mmol, 1 equiv) and NaBH<sub>4</sub> (0.238 mg,  $6.3 \times 10^{-3}$  mmol, 3 equiv) were dissolved in methanol (5 ml) in a Schlenk flask, and AgNO<sub>3</sub> (0.35 mg,  $2.1 \times 10^{-3}$  mmol, 1 equiv) aqueous solution (0.36 ml) was then injected dropwise into the flask under N<sub>2</sub> atmosphere with vigorous stirring. The obtained solution was further stirred for 2 h at 30 °C under N<sub>2</sub> atmosphere, and the color changed from light-yellow to brownish red. Dialysis (MWCO = 3500 g mol<sup>-1</sup>) was conducted against a large volume of distilled water before the TEM analysis of the produced **AgNPs-1**.

**Synthesis of AgNPs-2:** AgNO<sub>3</sub> (0.35 mg,  $2.1 \times 10^{-3}$  mmol, 1 equiv) was dissolved in distilled water (0.36 ml), and injected dropwise into a vigorously stirred methanol solution (5 ml) of **19** (4.5 mg,  $2.1 \times 10^{-3}$  mmol, 1 equiv) in a Schlenk flask. The obtained mixture was stirred overnight at 30 °C under N<sub>2</sub> atmosphere. Then

4

Y. Liu et al. / Tetrahedron xxx (2018) 1–13

NaBH<sub>4</sub> (0.238 mg,  $6.3 \times 10^{-3}$  mmol, 3 equiv) in methanol (1 ml) was injected dropwise into the above-mentioned solution. The obtained mixture was stirred for 2 h at 30 °C under N<sub>2</sub> atmosphere to yield **AgNPs-2**, and the color changed immediately from light-yellow to brown. The obtained **AgNPs-2** were purified by dialysis (MWCO = 3500 g mol<sup>-1</sup>) against a large volume of water.

**Preparation of micelles of 19:** A certain amount of **19** (14 mg) was dissolved in 10.5 ml of THF, followed by the addition of the deionized water of 3.5 ml under magnetic stirring for 2 h. Immediately, the Tyndall effect was observed very clearly when a beam of light passes through the solution, and the solution turned from absolutely transparent to slightly turbid, indicating the formation of micelles. The micellar solutions were finally obtained after the removal of the solvent THF by the dialysis (MWCO = 3500 g mol<sup>-1</sup>) against distilled water, and the obtained samples were investigated by AFM and DLS (Fig. 6).

#### 3. Results and discussion

#### 3.1. Synthesis and structure of the Janus mixed dendron 17

Both targeted Janus macromolecules 17 and 19 are synthesized

using a typical chemoselective coupling method in which two dendrons with complementary functionality are synthesized by a convergent route and coupled together in the last step [65]. The new Janus structure 17 is prepared by an esterification reaction between the hydrophilic dendron **15** containing three TEG termini and a new hydrophobic dendron **14** terminated by three ferrocenyl groups. To begin with, the starting methyl gallate **11** reacts with propargyl bromide, vielding the corresponding methyl 3.4.5tris(prop-2-yn-1-yloxy)benzoate 12 bearing methyl ester group that is then reduced to hydroxymethyl group by LiAlH<sub>4</sub> to provide the benzyl alcohol derivative 13. The key intermediate dendron 14 is then synthesized through copper(I)-catalyzed azide alkyne cycloaddition (CuAAC) "click" reaction between azidomethylferrocene 5 and the alkyne 13 using the classic Sharpless–Fokin catalyst [57]  $CuSO_4$  + NaAsc in THF/water (1:1). The reaction of 15 with oxalyl chloride results in 3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy) ethoxy)benzoyl chloride 16 that then reacts to 14 in the presence of triethylamine yielding the targeted Janus compound 17 (Scheme 1).

Fig. 2 shows the <sup>1</sup>H NMR spectra of the key intermediate dendron **14** and Janus mixed dendron **17**, and the comparison leads to the structure of **17**. As shown in Fig. 2A, the two peaks at 7.64 and 7.59 ppm correspond to the three triazole protons, confirming the



Scheme 1. Synthesis routes to the Janus mixed dendrons 17 and 19.

Y. Liu et al. / Tetrahedron xxx (2018) 1–13



success of the "click" reaction between **5** and **13**. The peaks at 4.30-4.17 ppm are assigned to the characteristic signals of the 27 protons of the substituted and free cyclopentadienyl (Cp) rings in the three ferrocenyl units, while the phenyl protons are observed at 6.65 ppm. The peak at 4.53 ppm is attributed to the hydroxymethyl protons, and the four peaks at 5.26, 5.20, 5.11 and 5.09 ppm originate from the CH<sub>2</sub> protons adjacent to the triazole rings. These results clearly indicate the successful synthesis of **14** and its structure.

As shown in Fig. 2B, the success of the esterification reaction between **14** and **16** yielding **17** is demonstrated by the disappearance of the signal for the hydroxymethyl protons of **14** at 4.53 ppm and its reappearance at 5.18 ppm corresponding to the methylene protons adjacent to the ester group. The two single peaks at 7.65 and 7.62 ppm correspond to the three triazolyl protons, and the characteristic signals of the 27 protons of the free and substituted Cp rings of the three ferrocenyl moieties are located at 4.29–4.16 ppm and mixed with those of the six methylene protons close to three phenoxy groups. The signals of the methylene protons of the three TEG termini are concentrated at 3.87–3.51 ppm, while the characteristic peak of nine terminal methoxyl protons (OCH<sub>3</sub>) is observed at 3.36 ppm.

The integrity of the ferrocenyl units and the structure of 17 are further confirmed by the <sup>13</sup>C NMR spectrum of **17** in CDCl<sub>3</sub> (Fig. S27). For instance, the peaks at 81.4 and 81.0 ppm are attributed to the substituted Cp carbon atoms of the ferrocenyl groups. The peak at 152.3 ppm is assigned to the carbon of the ester group, and the peak at 63.3 ppm to the methylene carbon adjacent to the ester group. The peaks at 143.8, 143.7, 123.3 and 122.8 ppm originates from the carbon of three triazolyl units, while the peak at 59.1 ppm corresponds to the methoxyl groups. All the other peaks in the <sup>1</sup>H and <sup>13</sup>C NMR spectra are clearly assigned and match well with the structure of 17. Furthermore, the mass spectrum of 17 (Fig. S28) shows the molecular peak at 1607.46 ( $M+Na^+$ ) Da, in good agreement with the theoretical value of 1607.15 Da. The UV-vis. spectrum of 17 (Fig. 3A) shows a maximum absorption  $(\lambda_{max})$  at 433 nm corresponding to the d-d<sup>\*</sup> transition of the ferrocenyl groups. The IR spectrum (Fig. S29) also provides complementary information for the structure of 17.

5

The Janus molecule **17** was obtained as yellow-brown solid. It is soluble in common organic solvents including  $CH_2Cl_2$ , chloroform, methanol, acetone, THF, and strong polar solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO), but it is insoluble in diethyl ether, petroleum ether, pentane and  $H_2O$ .

Y. Liu et al. / Tetrahedron xxx (2018) 1–13



Fig. 3. UV–vis. spectra of  ${\bf 17}$  (a) and  ${\bf 19}$  (b) in methanol.



A similar route was adopted for the synthesis of **19** (Scheme 1)



Fig. 5. CV curves of the ferrocenyl Janus mixed dendrons 17 (A) and 19 (B).



Please cite this article in press as: Y. Liu, et al., Ferrocenyl Janus mixed-dendron stars and their stabilization of Au and Ag nanoparticles, Tetrahedron (2018), https://doi.org/10.1016/j.tet.2018.07.035

6

#### Table 1

Redox potentials  $(E_{1/2})$ , chemical  $(i_c/i_a)$  and electrochemical  $(E_{pa} - E_{pc} = \Delta E)$  reversibilities for the Janus mixed dendrons **17** and **19** and their numbers of ferrocenyl groups calculated by the Bard–Anson electrochemical method.

17         0.610         0.08         1         3         3±0.3           19         0.680         0.05         1         3         3±0.3	Dendrimer	$E_{1/2}^{a}$	$\Delta E^{\rm b}$	$i_c/i_a$	$Fc_{theoretical}^{c}$	<i>Fc</i> <sub>experimental</sub> <sup>d</sup>
	17	0.610	0.08	1	3	$3 \pm 0.3$
	19	0.680	0.05	1	3	$3 \pm 0.3$

<sup>a</sup>  $E_{1/2} = (E_{pa} + E_{pc})/2$  vs. [FeCp<sub>2</sub>\*].

<sup>b</sup>  $\Delta E = E_{pa} - E_{pc}$ .

<sup>c</sup> Number of ferrocenyl groups of the targeted structure shown in Scheme 1.

<sup>d</sup> Number of ferrocenyl groups determined using the Bard-Anson electrochemical method.

by using the new hydrophobic dendron **18** containing three TEG branches terminated by ferrocenyl groups. Following the route in Scheme **1**, the two end-hydroxyl groups of the starting TeEG **6** are converted to azide and amino groups, respectively, and the latter further reacts with chlorocarbonyl ferrocene, yielding the key intermediate product 1-azido-11-ferroceneformamido-3,6,9-trioxaundecane **8** whose CuAAC "click" reaction with **13** leads to the formation of dendron **18**. Then, the esterification reaction between **13** and **16** in the presence of triethylamine yields the targeted Janus mixed dendron **19**.

The <sup>1</sup>H NMR spectrum of **19** is compared to that of dendron **18**. This comparison leads to the structure of **19**. In the <sup>1</sup>H NMR spectrum of **18** in CDCl<sub>3</sub> (Fig. 4A), the two peaks at 7.90 and 7.86 ppm correspond to the three triazole protons, indicating the success of the "click" reaction between **10** and **13**. The two triplet peaks at 6.59

and 6.51 ppm are assigned to the characteristic signals of NHC=0 protons, whereas the singlet peak at 6.73 is attributed to the phenyl protons. The characteristic signals of the substituted and free Cp are concentrated at 4.72–4.69, 4.30 and 4.17 ppm, respectively, whereas the CH<sub>2</sub> protons of the TEG fragments are located at 4.53–4.46, 3.86–3.80 and 3.59–3.48 ppm. The singlet peak at 5.17 ppm originates from the CH<sub>2</sub> protons between benzene and triazole rings, and the peak at 4.60 ppm is attributed to the hydroxymethyl protons. These results show the successful synthesis of **18** and its structure.

In the <sup>1</sup>H NMR spectrum of **19** in CDCl<sub>3</sub> (Fig. 4B), the success of the esterification reaction between 18 and 16 yielding 19 is demonstrated by the disappearance of the signal for the hydroxymethyl protons of **18** at 4.60 ppm and its reappearance at 5.16 ppm corresponding to the methylene protons adjacent to the ester group. The appearance of the signals for the triazolyl protons at 7.91 and 7.89 ppm, the characteristic signals of free Cp protons at 4.18 ppm, and that of the substituted Cp protons at 4.70-4.68 and 4.29 ppm confirm the integrity of triazolyl and ferrocenyl units. The two singlet peaks at 7.32 and 6.83 ppm originate from the protons of two substituted benzene rings. The signals of NHC=O protons are observed at 6.48 and 6.42 ppm, and the signals of methylene protons close to triazolyl units were found at 5.24, 5.20 and 4.52–4.47 ppm, respectively. The signals of the CH<sub>2</sub> protons in the three TEG termini and three TEG chains are concentrated at 3.51–3.87 ppm, while the two singlet peaks at 3.364 and 3.357 ppm correspond to the nine OCH<sub>3</sub> protons. The <sup>13</sup>C NMR spectrum of **19** (Fig. S37) also provides useful information for its structure. For



Fig. 6. Micellar morphology and size of 19 in water (1 mg ml<sup>-1</sup>). (A) Amplitude trace of the micelles by AFM; (B) Height profile of the micelles by AFM; (C) Statistical evaluation of the diameters by AFM; (D) DLS curve of the micelles.

8

Y. Liu et al. / Tetrahedron xxx (2018) 1–13

example, the carbon of the ester (COO) group is observed at 152.6 ppm, and its close CH<sub>2</sub> carbon is found at 63.1 ppm. The peak at 170.4 ppm corresponds to the carbon of NHC=O groups, while the carbons of triazolyl units are found at 143.9, 143.5124.8 and 124.5 ppm. The Cp carbons of ferrocenyl moieties are located at 76.3 and 68.2–69.8 ppm, and the peak at 59.0 ppm originates from the carbons of the OCH<sub>3</sub> groups in the three TEG termini. All the other peaks of <sup>1</sup>H and <sup>13</sup>C NMR spectra are assigned and match well with the structure of 19. Furthermore, the mass spectrum of 19 (Fig. S38) shows several fragment peaks at 718.26 ( $(M + H^+)/3$ ), 739.91 (M/  $3 + Na^+$ ), 1076.89 ((M + H<sup>+</sup>)/2), 1087.88 ((M + Na<sup>+</sup>)/2) and 1098.97 Da  $(M/2 + Na^+)$ , but no molecular peak for theoretical C<sub>101</sub>H<sub>138</sub>Fe<sub>3</sub>N<sub>12</sub>O<sub>29</sub> is observed at 2151.77 Da or so, probably owing to its large molecular weight and easy C-O bond cleavage. The UV-vis. spectrum of **19** (Fig. 3B) shows a  $\lambda_{max}$  value at 438 nm corresponding to the d-d\* transition of the ferrocenyl units. The IR spectrum (Fig. S39) is in accord with the formation of 19 with bands at 1713 cm<sup>-1</sup> ( $\delta_{C=0}$ ), 1592, 1540 and 1431 cm<sup>-1</sup> ( $\nu_{C=C}$  of benzene), 1379, 1331 and 1299 cm<sup>-1</sup> ( $\nu_{C-N}$ ), 1204 and 1107 cm<sup>-1</sup> ( $\nu_{C-O-C}$ ) and  $824 \, cm^{-1}$  (v<sub>FeII</sub>).

The Janus mixed dendron 19 is obtained as an orange-yellow oil

showing good solubility in common organic solvents such as  $CH_2Cl_2$ ,  $CHCl_3$ , THF, acetone, acetonitrile, methanol, DMF and DMSO; it is insoluble in diethyl ether, petroleum ether, pentane and  $H_2O$ , however.

#### 3.3. Electrochemical properties of the Janus molecules 17 and 19

The new Janus molecules **17** and **19** have been studied by cyclic voltammetry (CV) using decamethylferrocene [FeCp\*<sub>2</sub>] as the internal reference. [54–56] The CV curves (Fig. 5) were recorded in CH<sub>2</sub>Cl<sub>2</sub> at 20 °C under N<sub>2</sub> using [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] (0.1 M) as the supporting electrolyte with Pt as the working and counter electrodes and Ag as the quasi-reference electrode at a scan rate of 0.2 V s<sup>-1</sup>, and the  $E_{1/2}$  data (measured vs. [FeCp\*<sub>2</sub>]) are gathered in Table 1. For **17** and **19**, a single oxidation wave was observed for all the ferrocenyl groups. For **17**, the Fe<sup>III/II</sup> oxidation potential of the ferrocenyl redox center is at 0.610 V vs. [FeCp\*<sub>2</sub>], whereas for **19**, the potential are around 0.680 V vs. [FeCp\*<sub>2</sub>]. Unlike to the ferrocenyl-containing polymers [42] and the known symmetric ferrocenyl-terminated dendrimers [51], there is no adsorption phenomenon in the CVs for both **17** and **19**. The Fe<sup>III</sup>/Fe<sup>II</sup> waves of **17** and **19** are chemically



Scheme 2. Synthesis of gold and silver nanoparticles upon reactions of 19 with HAuCl<sub>4</sub> and AgNO<sub>3</sub>.

 $(i_a = i_c)$  and electrochemically reversible, although the  $E_{pa} - E_{pc}$  values are a little higher (0.08 V for **17**) or lower (0.05 V for **19**) than what is expected for a fast redox process in the case of a single Fc unit at 25 °C (0.059 V).

The number of ferrocenyl units in **17** and **19** were also determined using Bard–Anson's electrochemical method [57], which is a



Fig. 7. UV-vis. spectra of AuNPs-1 (a) and AuNPs-2 (b) in methanol/H<sub>2</sub>O.

good method for redox-active metallopolymers and metallodendrimers with relatively low molecular weight and has been used appropriately for ferrocenyl-containing polymers [42] and dendrimers [51]. In the CV measurements, the total number of electrons transferred in the oxidation wave for the metallomacromolecule  $(n_p)$  should be the same as the number of ferrocenyl units in this metallomacromolecule, because only one electron from Fe<sup>II</sup> (ferrocene) to Fe<sup>III</sup> (ferricinium) is transferred from each ferrocenyl unit to the anode. Thus this electron number  $n_{\rm p}$  can be estimated using the Bard–Anson empirical equation (1) that was previously derived for conventional polarography [57]. The intensities in the CVs of the polymers and monomer are compared, and consequently the electron numbers  $n_p$  are calculated, namely, the numbers of ferrocenyl units are obtained. Here, FeCp<sup>\*</sup><sub>2</sub> was used as the monomer reference, because (i) it has the same number of electron transferred between its reduced and oxidized forms as that of the monomer with one ferrocenyl unit and (ii) its redox potential is sufficiently far from that of FeCp<sup>\*</sup><sub>2</sub> and ferrocenyl redox center in the dendrimers, which allows a clear distinction of the CV wave of the reference and that of the dendrimers. As shown in Table 1, both the estimated values of ferrocenyl numbers ( $Fc_{experimental}$ ) for **17** and **19** are  $3 \pm 0.3$  (see Table S2 in Supporting Information for details of the calculations), which shows an excellent consistency with the theoretical number (Fctheoretical) of 3 from the targeted molecular structures in Scheme 1. In conclusion, the electrochemical measurements further



Fig. 8. TEM images and size distributions of AuNPs-1 (a) and AuNPs-2 (b).

#### 10

confirm the molecular structures of the new Janus ferrocenylcontaining mixed dendrons **17** and **19**.

#### 3.4. Self-assembly of the macromolecules 19 in water

The Janus macromolecule **19** containing the hydrophobic ferrocene units and the hydrophilic TEG and TGMME moieties is expected to form micelles in aqueous solution. Thus, its self-



Fig. 9. DLS curves of AuNPs-1 (a) and AuNPs-2 (b). The average sizes are 185 nm for AuNPs-1, and 235 nm for AuNPs-2, respectively.



Fig. 10. UV-vis. spectra of AgNPs-1 (a) and AgNPs-2 (b).

assembly capability was investigated by AFM and DLS (Fig. 6). AFM analysis was conducted on air-dried samples. The test sample was prepared by the dialyzed solution of **19** drop-casted onto clean mica substrate and left to air-dry for 24 h before tapping mode AFM analysis. Fig. 6A-C are the typical AFM images and statistical diameter analysis. The AFM images of amplitude profiles in different areas indicate that all the aggregates exhibit obvious particles with more or less spheroidal morphologies, and the statistical analysis [66] of these AFM image was conducted to yield the average particle diameter (DavAFM) of  $350 \pm 150$  nm. DLS (Fig. 6D) provides a hydrodynamic diameter of 400 nm with a polydispersity index (PDI) of 0.222 for these micelles. The size obtained by DLS is thus slightly larger than that determined using AFM, which is taken into account by their different states, dry state for AFM and solution for DLS. The size distribution by DLS reflects the dimensions of both the swollen core and the stretched TEG shell, whereas the size recorded by AFM provides only the assembly in the dry state [67–69]. These results demonstrate the self-assembly property of **19** in micelles on the nanoscale.

#### 3.5. AuNPs and AgNPs stabilized by the Janus molecule 19

The Janus mixed dendron **19** was selected for the preparation of AuNPs and AgNPs owing to its better hydrophilicity than **17**. Indeed in principle it could behave as reducing agents of Au(III) and Ag(I), and stabilizer of corresponding gold and silver nanoparticles.

As shown in Scheme 2, AuNPs-1 and AgNPs-1 were fabricated by a one-step process in which the triazole groups in the ferrocenyl-terminated Janus dendrimer 19 are expected to behave as stabilizing groups and NaBH<sub>4</sub> as the reductant of Au<sup>III</sup> and Ag<sup>I</sup> respectively. HAu<sup>III</sup>Cl<sub>4</sub> and Ag<sup>I</sup>NO<sub>3</sub> were reduced to Au<sup>0</sup> and Ag<sup>0</sup> upon dropwise addition of their aqueous solution into the methanol solution of 19 in the presence of NaBH<sub>4</sub> at 30 °C under N<sub>2</sub> atmosphere with vigorous stirring. The stoichiometry of Au<sup>III</sup>: **19**: NaBH<sub>4</sub> was 1: 2: 6, whereas that of Ag<sup>I</sup>: **19**: NaBH<sub>4</sub> was 1: 1: 3. Color changes were immediately observed from light yellow to pink for AuNPs-1 (Fig. 7a) and brownish red for AgNPs-1 (Fig. 10a), respectively. The mixed dendrons and salts were removed from the NPs solution by dialysis against a large amount of deionized water. The obtained NPs were characterized by UV-vis. spectroscopy, TEM and DLS. Since the UV-vis. spectrum after dialysis shows a strong plasmon band at 538 nm and the absence of ferrocenyl band





around 420 nm (Fig. 3b), it is concluded that the **AuNPs-1** are formed and stabilized. The interaction between **AuNP-1** and **19** is so weak that **19** can be removed upon dialysis. **AuNP-1** does not agglomerate, however, because the hydrogen-bonded polyborate network  $[(B(OH)_3]_n$  that is formed by hydrolysis of NaBH<sub>4</sub> around the **AuNP-1** is sufficient to stabilize these AuNPs as already reported [64]. The average core size determined by TEM is  $4 \pm 2$  nm, and the shape of the **AuNPs-1** core is quasi-spherical (Fig. 8a). The DLS curve (Fig. 9a) provides a hydrodynamic diameter of 185 nm with a PDI of 0.218 for **AuNPs-1**. The diameter of **AuNPs-1** provided by DLS is much larger than that determined by TEM, because the DLS reflects the overall dendron-nanoparticle ensemble (obviously with aggregation given the large size), whereas the TEM reflects only the nanoparticle core.

For **AgNPs-1**, the UV–vis. spectrum (Fig. 10a) shows a  $\lambda_{max}$  at 431 nm corresponding to the characteristic SPB of Ag<sup>0</sup> and d-d<sup>\*</sup> transition of ferrocenyl unit. The average core size determined by TEM is 10 ± 7 nm and the shape of the **AgNPs-1** core is also quasi-spherical (Fig. 11a), but with aggregation. The DLS (Fig. 12a) provides a hydrodynamic diameter of 61 nm with a PDI of 0.249.

#### 3.6. AuNPs-2 and AgNPs-2 prepared by late addition of NaBH<sub>4</sub>

In order to examine the influence of the interaction of 19 on HAuCl<sub>4</sub> and AgNO<sub>3</sub> on NP formation, addition of NaBH<sub>4</sub> was postponed by 30 h. In the meantime it was observed that mixing 19 and HAuCl<sub>4</sub> only provoked a color change from light yellow to gold color, indicating the typical gold ferrocene color. Thus interestingly there was no oxidation of 19 by HAuCl<sub>4</sub> or AgNO<sub>3</sub> contrary to what was observed previously with triazolylferrocene-terminated dendrimers. This is actually the first example of lack of oxidation of a ferrocene derivative by HAuCl<sub>3</sub> or AgNO<sub>3</sub> in a short time in an aqueous system. This is explained by the presence of a strongly electron-withdrawing amido group as the ferrocene substituent that shifts the redox potential of the ferricinium/ferrocene system towards more positive value than without substituent. Another inhibiting factor could be the coordination of the triazole ligand to the metal cation that makes the metal cation less strongly oxidizing. In earlier examples, the ferrocene group was linked to dendritic core through the triazolyl linker that is almost neutral in terms of ferrocenyl redox potential variation [43,70]. Thus what we learn here is that it is possible to tune the ferrocenyl macromolecule oxidation as a function of the nature of the linker between the ferrocenyl group and the core. It is also possible that after a very long time or upon heating such thermodynamically unfavorable ferrocenyl oxidation may be driven by the irreversibility of the AuNP or AgNP formation, but such attempts have not been further conducted here. Addition of NaBH<sub>4</sub> 30 h after mixing 19 and HAuCl<sub>4</sub>



Fig. 12. DLS curves of AgNPs-1 (a) and AgNPs-2 (b). The average sizes are 61 nm for AgNPs-1, and 158 nm for AgNPs-2, respectively.

or AgNO<sub>3</sub> gave **AuNPs-2** that have slightly distinct characteristics compared to **AuNPs-1**. In this case before dialysis the plasmon band is found at 568 nm, and the presence of **19** is noted by recording the usual ferrocenyl band at 420 nm (Fig. 3b). The DLS (Fig. 12b) provides the average size of 158 nm with a PDI of 0.278. Flocculent precipitates were observed during the dialysis process of **AgNPs-2** against water, and thus no TEM or UV—vis. analysis was conducted after dialysis.

## 3.7. AuNPs-3 prepared by reaction between dendron **17** and HAuCl<sub>4</sub> in the absence of NaBH<sub>4</sub>

Upon comparing the electrochemical properties of **17** and **19**, it appears that **17** is a better reductant than **19**. It was noticed that the reaction of **19** with HAuCl<sub>4</sub> does not produce AuNPs even after prolonged reaction times. This may be taken into account by both the weaker reducing power of **19** compared to **17** and coordination of the functional groups of **19** to the Au(III) centers that lower their oxidizing power. On the other hand, we find that **17** does slowly reduce HAuCl<sub>4</sub> in a methanol/water mixture over 24 h leading to a color change from light yellow to deep purple, the color of **AuNP-3**. The UV–vis. spectrum recorded one day after the reaction (Fig. 13). does show the plasmon band at 557 nm verifying the formation of AuNPs, and the recorded TEM of these AuNPs shows their size of  $9 \pm 5$  nm (Fig. 14).

#### 4. Conclusions

In this work, new amphiphilic triazolylferrocenyl Janus molecular star-shape architectures 17 and 19 with three TEG termini have been synthesized. Both Janus molecules have been easily synthesized by esterification reaction between azidomethylferrocene and the corresponding TEG-terminated acetylene. This reaction provides a convenient neutral ligand for the stabilization of AgNPs-1 and AuNPs-1 in water with NaBH<sub>4</sub> as the reductant of Au(III) and Ag(I). Whereas **19** is not electron-rich enough to reduced HAuCl<sub>4</sub> to AuNPs, 17 slowly forms 9-nm AuNPs upon reduction of HAuCl<sub>4</sub> by 17 in methanol/water mixture in 24 h. Reactions with Au(III) and Ag(I) have shown the decisive influence of the electronic properties of the ferrocenyl-core linker on the feasibility of the redox reaction, providing a way to control this process. Since a large body of research now concerns ferrocenyl-containing compounds including biomolecules towards nanomedicine, these findings should prove useful. Variation of the nature of redox active units of





Fig. 14. TEM image and size distribution histogram of AuNP-3.

the dendron may extend the spectrum of properties using such a strategy [71-74].

#### Acknowledgments

Valuable and helpful AFM observations by Wang Zhonghui (College of Light Industry, Textile and Food Engineering, Sichuan University) and financial support from the "Fundamental Research Fund for the Central Universities of China, the University of Bordeaux and the Centre National de la Recherche Scientifique (CNRS) are gratefully acknowledged.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.07.035.

#### References

- [1] G.R. Newkome, C.N. Moorefield, F. Vögtle, Dendrimers and Dendrons. Concepts, Syntheses, Applications, Wiley-VCH, Weinheim, 2001.
- [2] D.A. Tomalia, J.M.J. Fréchet (Eds.), Dendrimers and Other Dendritic Polymers, Wiley, Amsterdam, 2001.
- D. Astruc, E. Boisselier, C. Ornelas, Chem. Rev. 110 (2010) 1857.
   A.-M. Caminade, C.-O. Turrin, R. Laurent, A. Ouali, B. Delavaux-Nicot, Dendrimers towards Catalytic, Material and Biomedical Uses, Wiley, Chichester, UK. 2011.
- [5] S. Campagna, P. Ceroni, F. Puntoriero (Eds.), Designing Dendrimers, Wiley, Hoboken, NJ, 2012.
- [6] D.A. Tomalia, J.B. Christensen, U. Boas, Dendrimers, Dendrons and Dendritic Polymers, Cambridge University Press, Cambridge, U. K., 2012.
- V. Percec, M.R. Imam, M.R. Peterca, M. Peterca, P. Leowanawat, J. Am. Chem. [7] Soc. 134 (2012) 4408.
- [8]
- J.W. Choi, B.K. Cho, Soft Matter. 7 (2011) 4045. J.Y. Liu, Y.M. Feng, N.F. He, Q. Yang, H. Fan, New J. Chem. 36 (2012) 380. [9]
- [10] T. Tuuttila, J. Lipsonen, M. Lahtinen, J. Huuskonen, K. Rissanen, Tetrahedron 64 (2008) 10590.
- [11] M. Filippi, D. Patrucco, J. Martinelli, M. Botta, P. Castro-Hartmann, L. Tei, E. Terreno, Nanoscale 7 (2015) 12943.
- [12] C. Dengiz, B. Breiten, J.P. Gisselbrecht, C. Boudon, N. Trapp, W.B. Schweizer, F. Diederich, J. Org. Chem. 80 (2015) 882.
- [13] M. Peterca, V. Percec, P. Leowanawat, A. Bertin, J. Am. Chem. Soc. 133 (2011) 20507
- [14] V. Percec, D.A. Wilson, P. Leowanawat, C.J. Wilson, A.D. Hughes, M.S. Kaucher, D.A. Hammer, D.H. Levine, A.J. Kim, F.S. Bates, Science 328 (2010) 1009.
- [15] T. Wei, C. Chen, J. Liu, C. Liu, P. Posocco, X.X. Liu, Q. Cheng, S.D. Huo, Z.C. Liang, M. Fermeglia, Proc. Natl. Acad. Sci. U.S.A. 112 (2015) 2978.
- [16] E. Fedeli, A. Lancelot, J.L. Serrano, P. Calvo, T. Sierra, New J. Chem. 39 (2015) 1960
- [17] J.Z. Pan, M. Wen, D.Q. Yin, B. Jiang, D. He, S.,L. Guo, Tetrahedron 68 (2012) 2943.

- [18] D. Astruc, Why is Ferrocene so Exceptional? Eur. J. Inorg. Chem. 6 (2017).
- [19] G.R. Whittell, I. Manners, Metallopolymers: new multifunctional materials, Adv. Mater. 19 (2007) 3439.
- [20] C. Ornelas, J. Ruiz, C. Belin, D. Astruc, J. Am. Chem. Soc. 131 (2009) 590.
- [21] G.R. Whittell, M.D. Hager, U.S. Schubert, I. Manners, Nat. Mater. 10 (2011) 176. [22] A.S. Abd-El-Aziz, C. Agatemor, N. Etkin, Macromol. Rapid Commun. 35 (2014) 513.
- [23] M. Hadadpour, J. Gwyther, I. Manners, P.J. Ragogna, Chem. Mater. 27 (2015) 3430.
- [24] A.S. Abd-El-Aziz, E.A. Strohm, Polymer 53 (2012) 4879.
- [25] R.L.N. Hailes, A.M. Olivier, J. Gwyther, G.R. Whittel, I. Manners, Chem. Soc. Rev. 45 (2016) 5358.
- [26] C.M. Casado, I. Cuadrado, M. Moran, B. Alonso, B. Garcia, B. Gonzales, J. Losada, Coord. Chem. Rev. 185-6 (1999) 53.
- [27] C.M. Casado, B. Alonso, J. Losada, M.P. Garcia-Armada, S. Campagna, in: P. Ceroni, F. Puntoriero (Eds.), Designing Dendrimers, Wiley, Hoboken, NJ, 2012, pp. 219-262.
- [28] D.R. Sikwal, R.S. Kalhapure, T. Govender, Eur. J. Pharmaceut. Sci. 97 (2017) 113.
- [29] A.M. Madonik, D. Astruc, J. Am. Chem. Soc. 106 (1984) 2437.
- M. Lacoste, F. Varret, L. Toupet, D. Astruc, J. Am. Chem. Soc. 109 (1987) 6504. [30] [31] M.-H. Desbois, D. Astruc, J. Guillin, F. Varret, D. Astruc, J. Am. Chem. Soc. 111
- (1989) 5800.
- [32] M.-C. Daniel, D. Astruc, Chem. Rev. 104 (2004) 293.
- [33] N. Li, P. Zhao, D. Astruc, Angew. Chem. Int. Ed. 52 (2014) 1756.
- V.K. Sharma, R.A. Yngard, Y. Lin, Adv. Colloid Interface Sci. 106 (2009) 83.
- [35] M. Rycenga, C.M. Cobley, J. Zeng, W.Y. Li, C.H. Moran, Q. Zhang, D. Qin, Y.N. Xia, Chem. Rev. 111 (2011) 3669.
- [36] N. Li, P. Zhao, M.E. Igartua, A. Rapakousiou, L. Salmon, S. Moya, J. Ruiz, D. Astruc, Inorg. Chem. 53 (2014) 11802.
- [37] R. Ciganda, J. Irigoyen, D. Gregurec, R. Hernández, S. Moya, C. Wang, J. Ruiz, D. Astruc, Inorg. Chem. 55 (2016) 6361.
- [38] L. Zhao, Q. Ling, X. Liu, C. Hang, Q. Zhao, F. Liu, H. Gu, Appl. Organomet. Chem. 32 (2018) e4000.
- [39] X.S. Wang, H. Wang, N. Coombs, M.A. Winnik, I. Manners, J. Am. Chem. Soc. 127 (2005) 9824.
- [40] X.S. Wang, H. Wang, N. Coombs, M.A. Winnik, I. Manners, J. Am. Chem. Soc. 130 (2008) 12921.
- [41] A. Rapakousiou, C. Deraedt, H. Gu, L. Salmon, C. Belin, J. Ruiz, D. Astruc, J. Am. Chem. Soc. 136 (2014) 13995.
- [42] H. Gu, R. Ciganda, P. Castel, A. Vax, D. Gregurec, J. Irigoyen, S. Moya, L. Salmon, P.X. Zhao, J. Ruiz, D. Astruc, Chem. Eur. J. 21 (2015) 18177.
- [43] R. Ciganda, H. Gu, R. Hernandez, A. Escobar, A. Martinez, L. Yates, S. Moya, J. Ruiz, D. Astruc, Inorg. Chem. 56 (2017) 2784. [44] E. Boisselier, A.K. Diallo, L. Salmon, C. Ornelas, J. Ruiz, D. Astruc, J. Am. Chem.
- Soc. 132 (2010) 2729.
- [45] Y. Sun, B. Gates, B. Mayers, Y.N. Xia, Nano Lett. 2 (2002) 165.
- Y.G. Sun, B. Mayers, T. Herricks, Y.N. Xia, Nano Lett. 3 (2003) 955. [46]
- [47] M. Tsuji, M. Hashimoto, Y. Nishizawa, T. Tsuji, Mater. Lett. 58 (2004) 2326.
- [48] K. Patel, S. Kappor, D.P. Dave, T. Mukhergiee, Res. Chem. Intermed. 32 (2006) 103.
- Y. Wang, Y.Q. Zheng, C.Z. Huang, Y.N. Xia, J. Am. Chem. Soc. 135 (2013) 1941.
   S. Nlate, J. Ruiz, J.-C. Blais, D. Astruc, Chem. Commun. (2000) 417.
- [51] H. Gu, A. Rapakousiou, P. Castel, N. Guidolin, N. Pinaud, J. Ruiz, D. Astruc, Organometallics 33 (2014) 4323.
- [52] X. Wang, Q.J.B. Xia, X.Y. Dai, S.L. You, Sci. China Ser. B-Chem. 52 (2009) 1331.
- [53] S. Ciampi, P.K. Eggers, G. Le Saux, M. James, J.B. Harper, J.J. Gooding, Langmuir

Y. Liu et al. / Tetrahedron xxx (2018) 1–13

13

25 (2009) 2530.

- [54] C.G. Hardy, L. Ren, T.C. Tamboue, C. Tang, J. Polym. Sci. Pol. Chem. 49 (2011) 1409.
- [55] L. Wagner, A. Selig, A. Prokop, Beilstein J. Org. Chem. 10 (2014) 1630.
- A. Cho, Y. La, T.J. Shin, C. Park, K.T. Kim, Macromolecules 49 (2016) 4510. [56]
- [57] C.C. Cheng, H.W. Liao, J.K. Chen, D.J. Lee, Z. Xin, RSC Adv. 6 (2016) 23949.
- [58] V.V. Rostovsev, L.G. Green, V.V. Fokin, K.B. Sharpless, Angew. Chem. Int. Ed. 41 (2002) 2596.
- [59] A.K. Diallo, E. Boisselier, L. Liang, J. Ruiz, D. Astruc, Chem. Eur. J. 16 (2010) 11832.
- I. Ruiz, D. Astruc, C. R. Acad, Sci. Sér. IIc 1 (1998) 21. [60]
- [61] I. Novandri, K.N. Brown, D.S. Fleming, P.T. Gulyas, P.A. Lay, A.F. Masters, J. Phys. Chem. B 103 (1999) 6713.
- [62] J. Ruiz, M.-C. Daniel, D. Astruc, Can. J. Chem. 84 (2006) 288.
- [63] J.B. Flanagan, S. Margel, A.J. Bard, F.C. Anson, J. Am. Chem. Soc. 100 (1978) 4248.
- [64] C. Deraedt, L. Salmon, S. Gatard, R. Ciganda, R. Hernandez, J. Ruiz, D. Astruc, Chem. Commun. 50 (2014) 14194.

- [65] D.R. Sikwal, R.S. Kalhapure, T. Govender, Eur. J. Pharmaceut. Sci. 97 (2017) 113.
- [66] H.J. Butt, B. Cappella, M. Kappl, Surf. Sci. Rep. 59 (2005) 1.
- [67] K. Qi, Q.G. Ma, E.E. Remsen, C.G. Clark, K.L. Wooley, J. Am. Chem. Soc. 126 (2004) 6599.
- [68] D. Xiong, G.J. Liu, L.Z. Hong, E.J.S. Duncan, Chem. Mater. 23 (2011) 4357.
  [69] R.C. Murdock, L. Braydich-Stolle, A.M. Schrand, J.J. Schlager, S.M. Hussain, Toxicol. Sci. 101 (2008) 239.
- [70] Wang Q, Fu F, Martinez-Villacorta AM, Moya S, Salmon L, Vax A, Hunel J, Ruiz J, Astruc D. Chem. Eur. J. doi.org/10.1002/chem.201802289. [71] C. Jehoulet, Y.S. Obeng, Y.T. Kim, F.M. Zhou, A.J. Bard, J. Am. Chem. Soc. 114
- (1992) 4237.
- [72] C. Bossard, S. Rigaut, D. Astruc, M.-H. Delville, G. Félix, A. Février-Bouvier, J. Amiell, S. Flandrois, P. Delhaès, J. Chem. Soc. Chem. Commun. (1993) 333. [73] B.M. Quinn, P. Liljeroth, V. Ruiz, T. Laaksonen, K. Kontturi, J. Am. Chem. Soc.
- 125 (2003) 6644.
- [74] K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta, H. Chiba, Nature 415 (2002) 509