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Amphipathic metal-containing macromolecules with photothermal properties†

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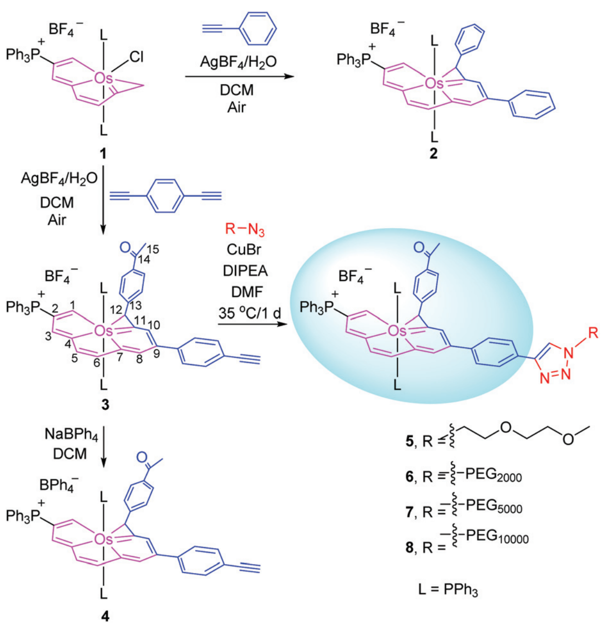
Metal-containing macromolecules with extraordinary properties have attracted a great deal of interest owing to their potential application in the development of functional materials. Here, we report the synthesis of novel amphipathic metal-containing macromolecules by the click reaction of methoxypolyethylene glycol azides with a unique metalla-aromatic complex containing a terminal alkynyl group. The resultant amphipathic macromolecules self-assembled into micellar nanoparticles with diameters of *ca.* 145 nm in water, which exhibited high stability, water-dispersibility, biocompatibility, and excellent photothermal behavior under 808 nm laser irradiation. Our study opens promising avenues for providing metal-containing macromolecules as photothermal materials.

Macromolecules that incorporate a metal as building blocks are interesting and valuable materials, because many of them can carry out the functions of both macromolecular and metal-containing units.[1] Metal-containing macromolecules have been developed as functional materials[2] on the basis of their electroactive,[3] photoactive,[3a] bioactive,[4] magnetic and other interesting properties.[5] For example, polyferrocenylsilane and its copolymers exhibit excellent properties,[6] including redox activity and an ability to grow into metallosupramolecular polymers.[7] Ferrocene-functionalized polyacetylenes and polyphenylenes have been used as precursors to prepare magnetic ceramics and nanoparticles.[8] Macromolecules with other metal-containing units have also been reported as functional materials with unexpected or exceptional properties.[9] However, to the best of our knowledge, metal-containing macromolecules that exhibit photothermal properties have not been reported.

Photothermal therapies for killing tumors using near-infrared (NIR) light with its superior tissue penetration ability[10] have recently become a promising theranostic method.[11] The reported photothermal materials mainly include NIR-absorbing organic molecules or polymers,[12] gold nanomaterials,[13] and inorganic and other materials.[14]

As a continuation of our efforts to synthesize new metalla-aromatic complexes,[15] we recently prepared an interesting metalla-aromatic complex **2** from the reaction of complex **1** with phenylacetylene in air (Scheme 1).[16] Complex **2** exhibits broad absorption in the UV–Vis–NIR regions and excellent photothermal behavior when exposed to an NIR laser with a wavelength of 808 nm. However, the metalla-aromatic complex **2** is water-in-



Scheme 1 Preparation of complexes **2–5** and macromolecules **6–8**.

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soluble and poorly biocompatible, thus hindering its application *in vivo*. When tentatively packed in an amphiphilic macromolecular micelle, complex **2** can be used as a biomaterial for the thermal ablation of cancer cells *in vivo*.[16] However, the stability of the micelle is a potential obstacle to its biomedical applications. Therefore, in this work, we for the first time covalently linked metalla-aromatic complex **2** with water-soluble mPEG polymers to form a new class of amphipathic macromolecules, with the aim of achieving micellization of the resultant macromolecules in water to afford novel photothermal materials with enhanced stability and biocompatibility (Fig. 1).

In order to synthesize the target amphipathic macromolecule, it is necessary to introduce organic functional groups into the metalla-aromatic complex **2**. To this end, we prepared complex **3**, which contained a terminal alkynyl group, from the reaction of complex **1** with 1,4-diethynylbenzene in the presence of $AgBF_4$ (Scheme 1). The structure of complex **3** was characterized by nuclear magnetic resonance (NMR), high-resolution mass spectrometry (HRMS) and elemental analysis (EA). The $^{31}P\{^1H\}$ NMR spectrum shows three signals at 9.71 (t, J_{PP} = 6.5 Hz, C*P*Ph$_3$), −9.50 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph$_3$) and −18.55 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph$_3$) ppm, which are similar to those of complex **2**.[16] The ^1H NMR spectrum shows a characteristic Os-C*H* signal as a doublet at 13.24 ppm with a J_{PH} coupling constant of 21.6 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the signals of C1, C4 and C7 are located at 207.9 (br, C1), 201.0 (dt, J_{PC} = 25.8 Hz, J_{PC} = 6.2 Hz, C4) and 231.0 (t, J_{PC} = 7.5 Hz, C7) ppm, respectively. These results show that the structure of complex **3** is similar to that of complex **2**. The molecular formula of complex **3** was also confirmed by HRMS (*m*/*z* = 1349.3782). Unfortunately, we failed to acquire high-quality single crystals of complex **3**. To further confirm the structure of complex **3**, we successfully grew single crystals of complex **4**, prepared by an anion exchange reaction of complex **3** with $NaBPh_4$ in methanol (Scheme 1); the obtained crystals were of sufficient quality for single-crystal X-ray diffraction analysis.

The structure of complex **4** is shown in Fig. 2 (the anion is omitted), and contains a terminal alkynyl and an acetyl groups. The crystal unit cell (a = 13.8 Å, b = 18.0 Å, c = 18.3 Å) contained only one molecule of complex **4**. The shape of complex **4** was like an ellipsoid with distances of *ca.* 11.7, 12.4, and 16.6 Å in three dimensions and was close to its unit cell. The osmium in complex **4** was surrounded by a conjugated 12-carbon chain (C1–C12). The metallacycle comprising Os1 and C1–C12 was approximately coplanar, as reflected by the small mean deviations from the least-squares plane (0.074 Å). The substructure of the metallacycle was similar to that of complex **2**. Structurally, the ethynylbenzene group in complex **4** was attached at C9, which was the same position as that of the ethynylbenzene group in complex **3**.

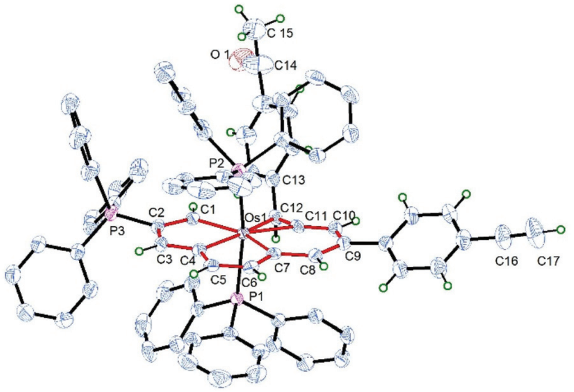

Fig. 2 ORTEP drawing of complex **4** with thermal ellipsoids at the 50% probability level. The anion (BPh_4^-) and hydrogen atoms on the phenyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°] are as follows: Os–C1 2.063(3), Os1–C4 2.113(3), Os1–C7 2.073(4), Os1–C11 2.013(3), Os1–C12 2.253(3), C1–C2 1.381(5), C2–C3 1.437(5), C3–C4 1.382(5), C4–C5 1.399(5), C5–C6 1.368(5), C6–C7 1.431(5), C7–C8 1.440(5), C8–C9 1.379(5), C9–C10 1.422(5), C10–C11 1.355(5), C11–C12 1.424(5); C1–Os1–C4 76.05(13), C7–Os1–C4 76.73(13), C11–Os1–C7 81.15(14), C11–Os1–C12 38.49(14).

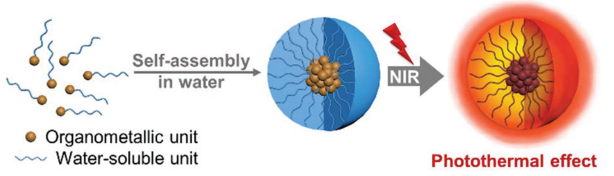

Fig. 1 Metal-containing macromolecules that assemble into micelles in water and exhibit photothermal properties.

Click reactions have been demonstrated to be a powerful method for preparing functional ferrocene-containing metallopolymers.[17] As complex **3** contains a functional terminal alkynyl group, we therefore tried the reaction of complex **3** with the water soluble methoxypolyethylene glycol azide (mPEG-N$_3$) to prepare the amphipathic macromolecules. To determine whether the expected click reaction could occur effectively in our system, we first used a small organic azide, 1-azido-2-(2-methoxyethoxy)ethane, to test our idea. On the basis of the NMR data, we deduced the structure of complex **5**. For example, the $^{31}P\{^1H\}$ NMR spectrum shows three signals at 9.61 (t, J_{PP} = 6.5 Hz, C*P*Ph$_3$), −9.24 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph$_3$), and −18.54 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph$_3$) ppm, which are similar to the signals of complex **3**, and confirm the presence of the organometallic unit. The ^1H NMR spectrum of complex **5** shows six signals of protons on the metallacycle: 13.20 (d, J_{PH} = 20.6 Hz, H1), 8.69 (s, H3), 7.91 (s, H10), 7.64 (s, H5), 7.57 (s, H6), and 6.58 (s, H12) ppm. The presence of the 1,2,3-triazole substructure was confirmed by the signal at 8.42 ppm as a singlet in the ^1H NMR spectrum. In addition, the $(CH_2)_2O(CH_2)_2OMe$ group was also confirmed by the signals at 4.70 (t), 4.02 (t), 4.48 (t), 3.70 (t), and 3.41 (s) ppm. These results show that the preparation of the title metal-containing macromolecule using a click reaction of complex **3** with mPEG-N$_3$ is reliable.

Osmium-containing macromolecules **6–8** were then readily prepared using mPEG-N$_3$ with higher molecular weights

(2000, 5000, and 10 000). The terminal organometallic substructure in macromolecules **6–8** was determined from $^{31}P\{^1H\}$ NMR experiments. For instance, the $^{31}P\{^1H\}$ NMR spectrum of **6** shows three signals at 9.61 (t, J_{PP} = 6.5 Hz, C*P*Ph$_3$), −9.50 (dd, apparent d, J_{PP} = 254.5 Hz, Os*P*Ph$_3$), and −18.54 (dd, apparent d, J_{PP} = 254.5 Hz, Os*P*Ph$_3$) ppm, similar to those of complexes **3** and **5**. The macromolecules attached by mPEG tails were also identified using MALDI-TOF experiments. For example, the molecular weight distribution of macromolecule **6** ranged from *ca.* 2700 to 3708 Da. These results showed that our strategy for the preparation of metal-containing macromolecules was successful.

We then turned to investigating the solubility and micellization of these novel metal-containing macromolecules in water. Experimentally, macromolecules **6–8** exhibited different dissolution/dispersion behaviors. When dissolved in water, precipitates were seen until concentrations of 1 mg mL^{-1}, 6 mg mL^{-1} and 15 mg mL^{-1} were reached for complex **6**, **7** and **8**, respectively. This can be explained by the fact that macromolecules with longer hydrophilic mPEG tails can exhibit better water solubility/dispersibility. Due to the amphipathic nature of the novel metal-containing macromolecules, they were expected to spontaneously assemble into micelles as a consequence of the aggregation of hydrophobic organometallic moieties in water.[18] As shown in Fig. 3, the average nanoparticle diameters of macromolecules **7** and **8** in aqueous solutions (1 mg mL^{-1}), as measured by dynamic light scattering (DLS), were *ca.* 142.5 nm (Fig. 3b) and 148.3 nm (Fig. 3d), respectively, while those observed by transmission electron microscopy (TEM) were *ca.* 80 nm (Fig. 3a) for **7** and 90 nm (Fig. 3c) for **8**. The sizes of these self-assembled micellar nanoparticles fall within the best range, from 50 to 200 nm, for enhanced permeability and retention (EPR) effects.[19]

As shown in Fig. 4a, macromolecules **6–8** exhibited a broad NIR absorption band at 700–900 nm in water. Obviously, this absorption was due to the organometallic moiety, which indicates that our strategy for constructing the functional metal-containing macromolecules is reliable. To verify their suitability as photothermal agents, **7** and **8** in solutions with concentrations ranging from 0.25 to 1.00 mg mL^{-1} were exposed to 808 nm NIR laser irradiation at a power density of 1.0 W cm^{-2}. A concentration-dependent temperature increase in solutions **7** and **8** was observed. In particular, solutions containing 0.75 mg mL^{-1} **7** and 1.00 mg mL^{-1} **8** exhibited rapid temperature increases from 26 to 52 °C and 26 to 47 °C, respectively, within 5 min at a laser power density of 1.0 W cm^{-2} (Fig. 4b and S34†), indicating excellent photothermal properties of **7** and **8**.

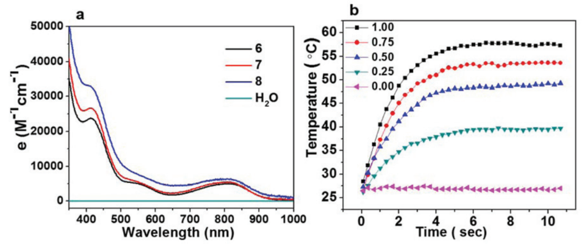

Fig. 4 (a) UV–Vis–NIR absorption spectra of water and macromolecules **6–8** (5.0 × 10^{-5} M) measured in water. (b) Temperature curves of water and different concentrations of macromolecule **7** (0.25, 0.5, 0.75 and 1.00 mg mL^{-1}) irradiated with an 808 nm laser at a power density of 1.0 W cm^{-2}.

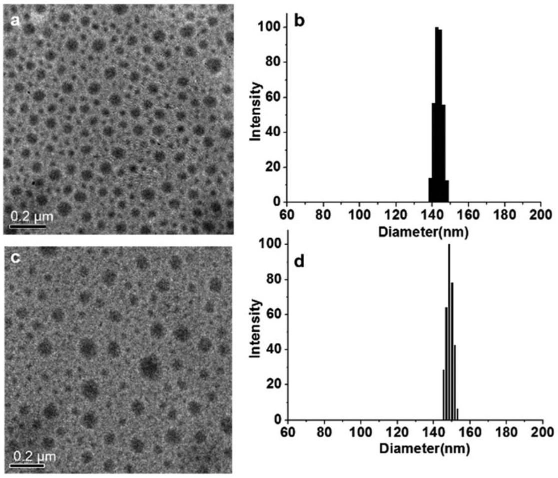

Fig. 3 TEM images of nanoparticles of macromolecules **7** (a) and **8** (c); DLS data for nanoparticles of macromolecules **7** (b) and **8** (d) in aqueous solutions (1 mg mL^{-1}).

To study the biocompatibility of **7** and **8**, standard methyl thiazolyl tetrazolium (MTT) assay experiments were carried out to determine the cytotoxicity of macromolecules **7** and **8** through the measurement of the relative viabilities of HeLa cells. The cells were incubated with **7** and **8** at concentrations ranging from 0.25 to 0.75 mg mL^{-1}. It was observed the macromolecules with longer mPEG exhibited lower cytotoxicity. The viability of the HeLa cells was greater than 80% after they had been incubated with macromolecule **8** at a substantially high concentration (0.75 mg mL^{-1}), indicating that **8** has low cytotoxicity similar to some other reported photothermal therapy agents (Fig. 5).[20]

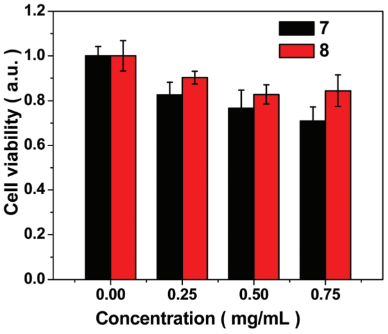

Fig. 5 Relative viabilities of HeLa cells after being incubated with various concentrations of **7** and **8** for 24 h.

In summary, we successfully prepared a new class of amphipathic metal-containing macromolecules with excellent photothermal properties. Self-assembly of the amphipathic macromolecules led to nanoparticles with very low cytotoxicity. These macromolecules have great potential for use as theranostic agents in photothermal therapy.

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