

A facile strategy for preparation of nanoparticles from a novel hyperbranched coordination polymer

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Abstract: *N, N'*-bis(8-hydroxyquinolyl-5-methylene)-piperazine (BHQP) was synthesized and used as ligands to form a novel hyperbranched coordination polymer with aluminum ions, which further self-assembled into spherical nanoparticles. The morphology of the particles was observed by transmission electron microscopy (TEM) and the structure of the hyperbranched polymer was characterized by electrospray ionization mass spectrometry (ESI-MS). Particle sizes were measured from TEM images and narrow size distribution was evaluated according to the images of hundreds of particles. It was found that the formation of the nanoparticles depends on the molar ratio of the ligands and the metal ions. Photoluminescence of the particles was examined and the result was discussed.

Key words: coordination polymer; nanoparticles; 8-hydroxyquinoline; photoluminescence

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新颖的超支化配位聚合物制备纳米粒子的便捷方法

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摘要: 合成了 *N, N'*-双(8-羟基喹啉基-5-亚甲基)哌嗪, 并与铝离子配位形成了新颖的超支化配位聚合物, 进而自组装成了球形纳米粒子. 超支化聚合物的结构和纳米粒子的形态分别通过 ESI-MS 和 TEM 证实. 粒子的大小及其分布通过测量 TEM 照片上的数百个粒子得到, 结果表明粒子的大小分布较窄. 同时发现纳米粒子形成依赖于配体和铝离子的比例. 我们测定了这种配位聚合物纳米粒子的光致发光性质, 并对结果进行了讨论.

关键词: 配位聚合物; 纳米粒子; 8-羟基喹啉; 光致发光

0 Introduction

In recent years, micro-and nanomaterials have attracted much attention due to their potential

applications in many fields, including catalysis^[1-5], magnetics^[6,7], optics^[8,9], etc. In terms of chemical composition, nanoparticles can usually be classified into three types: organic,

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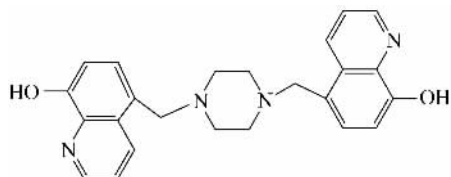
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inorganic and metal-organic particles. Metal-organic particles, which are prepared through metal ions and polydentate organic ligands, have recently become one of the most interesting subjects because of their promising applications. Therefore, a number of useful strategies for preparing metal-organic particles have been reported^[3,10~12]. Coordination polymers are more suitable candidates for preparation of particles with an additional level of tailorability through the choice of metal ion and organic ligands used^[3]. Most of metal-organic particles are fabricated from linear coordination polymers, and some of them are from coordination dendrimers and hyperbranched coordination polymers^[13~19].

8-Hydroxyquinoline (8HQ) is a very useful ligand in coordination chemistry^[20] and tris-(8-hydroxyquinoline) aluminum (AlQ₃) have been extensively studied as one of the most stable and fluorescent solid-state materials^[21,22]. There are a number of papers involving functionalization of AlQ₃ in order to get high quantum yield^[23], and enhance processability^[24~26] or solubility^[27,28], etc. It is well known that nanoparticles have very large specific surface which can increase optical absorption and enhance the intensity of luminescence. AlQ₃ nanoparticles were first reported by Wang and Perng^[29], which was fabricated via vapor condensation and possessed high emission intensity of luminescence in comparison with the thin film.

Here we report a facile strategy for preparation of nanoparticles via hyperbranched coordination polymers formed in situ from BHQP (shown in Scheme 1) and aluminum ions. The nanoparticles were successfully prepared by the



Scheme 1 Structure of *N,N'*-bis(8-hydroxyquinolyl)-5-methylene-piperazine (BHQP)

diffusion of diethyl ether into a solution of BHQP and AlCl₃ in *N,N*-dimethylformamide (DMF) and the morphology and structure of the nanoparticles were characterized.

1 Experimental

1.1 Materials

Piperazine and diisopropylethylamine were purchased from Acros and Aldrich respectively. DMF was purified by stirring over powdered calcium hydride overnight, and distilling under reduced pressure. 5-Chloromethyl-8-hydroxyquinoline hydrochloride (5-ClCH₂HQ · HCl) was prepared according to Ref. [30]. Other reagents were of analytical grade and used as received.

1.2 Synthesis of BHQP

A mixture of 5-ClCH₂HQ · HCl (5.424 0 g, 23.65 mmol) and DMF (100 mL) were added diisopropylethylamine (4.2 mL, 40.8 mmol) and piperazine (0.882 6 g, 10.2 mmol). The mixture was stirred for 24 h at room temperature. A white solid precipitated from the mixture was collected on a filter paper, treated with dilute ammonia, washed with water, and dried under vacuum in an exsiccator with silica gel to afford BHQP (2.780 7 g, 70% yield). ¹H NMR (300 MHz, CDCl₃): δ=2.44(s, 8H), 3.77(s, 4H), 7.06(d, J=7.8 Hz, 2H), 7.31(d, J=7.5 Hz, 2H), 7.48(dd, J=8.4, 8.7 Hz, 2H), 8.68(d, J=8.4 Hz, 2H), 8.78(d, J=2.7 Hz, 2H).

1.3 General procedure of preparation of nanoparticles

AlCl₃ well dispersed in DMF was slowly added to a solution of BHQP in DMF (1 mg/mL) at room temperature until AlCl₃ disappeared, and the light yellow precursor solution was obtained. Then diethyl ether was allowed to slowly diffuse into the precursor solution under stirring. The addition of diethyl ether to the polar precursor solution resulted in precipitation due to the low solubility of the particles in non-polar media. The resulting nanoparticle solution was dialyzed five times against diethyl ether to remove the residual DMF.

Three different precursor solutions were prepared by mixing BHQP/ AlCl_3 at the molar ratio of 3 : 1, 2.25 : 1, 2 : 1.

1.4 Characterization

^1H NMR spectra were recorded on a Bruker DMX-300 nuclear magnetic resonance instrument. Absorption spectra were recorded on a UV vis2401 spectrophotometer. Emission spectra were obtained on a RF-5301PC fluorometer. ESI-MS spectra were obtained on a LTQ mass spectrometer. TEM was performed on a JEOL-2010 microscope.

2 Results and discussion

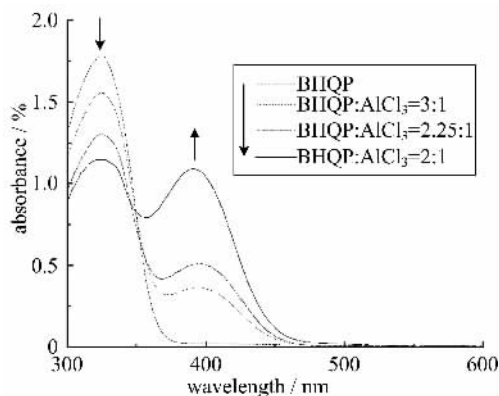
BHQP was prepared from the reaction of 5-chloromethyl-8-hydroxyquinoline hydrochloride and piperazine, and characterized by ^1H NMR spectrum. It is necessary to point out that the type of solvent is important for this reaction. It was found that the reaction proceeded effectively in DMF, but failed in the other solvents, such as chloroform, ethyl acetate.

When AlCl_3 solution was added slowly into BHQP solution in DMF, the coordination reaction of BHQP occurred with Al^{3+} ions. The absorption spectra (Fig. 1) demonstrate the formation of the metal-complexes in precursor solution. The absorption band at 395nm is ascribed to $\pi \rightarrow \pi^*$ transition of metal complex, and a peak at 326 nm is attributed to $n \rightarrow \pi^*$ transition of non-coordinated

8HQ groups. A new peak appeared at 395nm compared to BHQP illustrates the formation of metal-complexes.

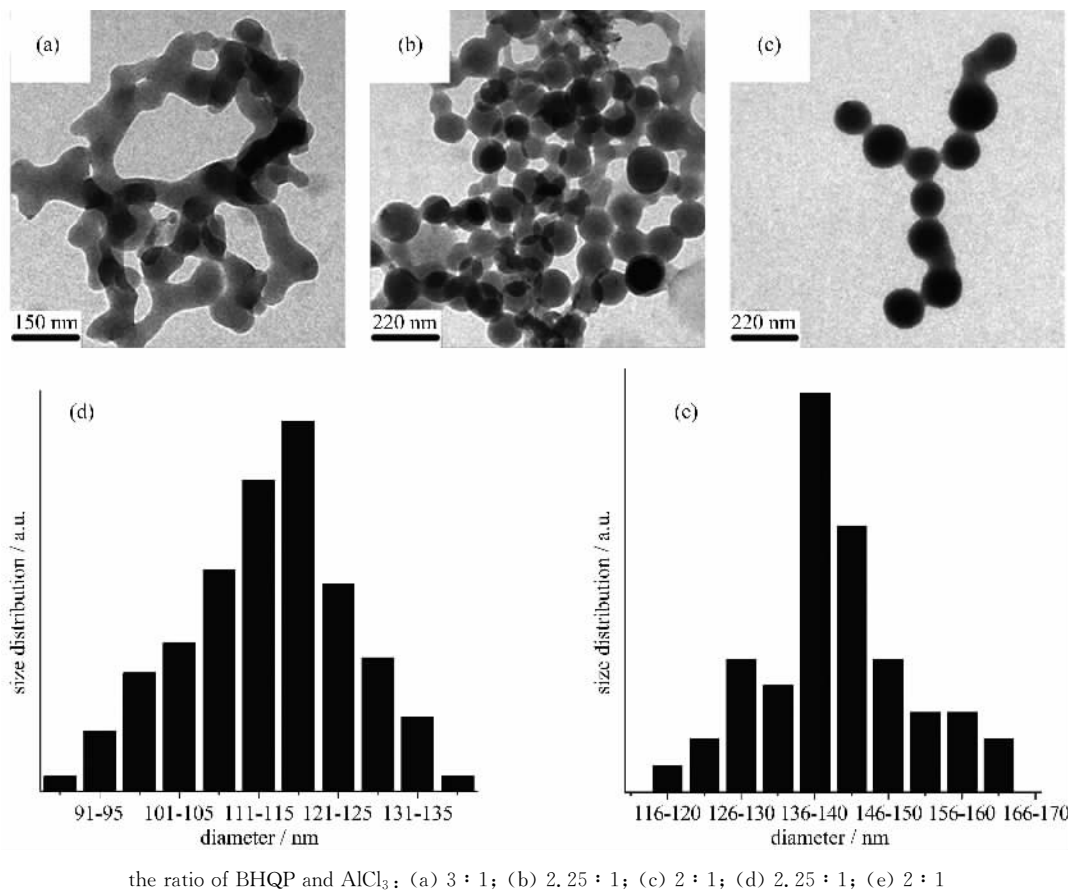
It is possible to form dendrimer or hyperbranched architecture theoretically if one Al^{3+} ion coordinates with three 8HQ groups by control of the molar ratios of ligands/metal ions, but the formation of dendrimer is actually very difficult because of the inevitable coordination defect in the reaction. In order to prove the hyperbranched structure, ESI-MS was performed for a precursor solution with the molar ratio of BHQP to Al^{3+} being 3 : 1. ESI-MS (m/z , DMF): calculated for $[(\text{BHQP})_2\text{Al}^+-2\text{H}]^+$, 825.90; found, 825.97; calculated for $[(\text{BHQP})_3\text{Al}-3\text{H}+\text{H}^+]^+$, 1 226.36; found, 1 226.98; calculated for $[\text{BHQP}-\text{Al}^+-\text{BHQP}-\text{AlCl}_2-3\text{H}]^+$, 922.88; found, 922.71. The molecular weight of the product from BHQP and Al^{3+} , given by ESI-MS analysis, indicates that the hyperbranched architecture of the coordination compounds was formed. Unfortunately the ESI-MS analysis of the products in low ratio of BHQP and Al^{3+} failed because of the high molecular weight. However, the according to the principles of step polymerization, the reaction of monomer A_2 (BHQP) with B_3 (Al^{3+}) should theoretically form hyperbranched oligomers with various molecular weights when the molar ratio of monomers is lower than that at gel point. Therefore we suggested that it was certainly possible to form the hyperbranched architecture under the present experimental condition.

Fig. 2 depicts a TEM micrograph of metal-organic nanoparticles. It was noticed that the formation of the nanoparticles relates to the ratio of BHQP to Al^{3+} ions. When the molar ratio is 2.25 : 1 and 2 : 1 respectively, nanoparticles were obtained (Fig. 2, (b) and (c)), but fiber-like morphology was observed in the case of 3 : 1 molar ratio (Fig. 2 (a)). The results show that the isolated nanoparticles are formed preferably at the lower molar ratio, which leads to a high faction of hyperbranched coordination polymers in the



Concentration of BHQP is 2.5×10^{-4} mmol/mL.

Fig. 1 Absorption spectra of hyperbranched coordination polymer in DMF



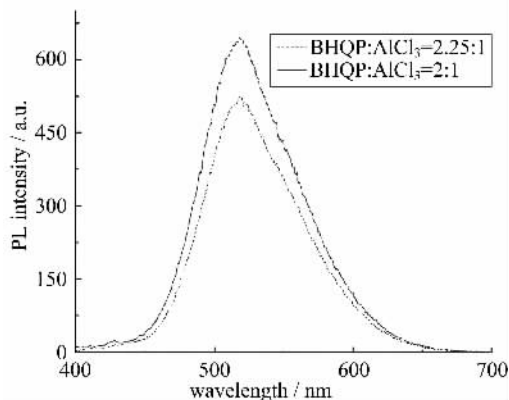
the ratio of BHQP and AlCl_3 : (a) 3 : 1; (b) 2.25 : 1; (c) 2 : 1; (d) 2.25 : 1; (e) 2 : 1

Fig. 2 TEM micrograph and the size distribution histogram of nanoparticles

reaction. However, the precipitation occurred while the molar ratio reached 1.6 : 1 (theoretical gel point at 1.5 : 1 ratio) in DMF. The mechanism of the morphology transition from the fiber-like aggregating to the nanospheres is not clear yet. Perhaps it involves the formation of intermolecular hydrogen bonds between BHQPs^[31,32]. In the high ratio of BHQP to Al^{3+} ions, the excess BHQPs tend to form one-dimensional hydrogen-bonded polymers, which result in fiber-like aggregates; but with the increase of Al^{3+} ion concentration, the molecules of BHQPs tend to form three-dimensional coordination polymers with Al^{3+} ions, which grow into the nanospheres. The mean diameter of the metal-organic nanoparticles was calculated from the TEM micrograph by averaging more than a few hundred nanoparticles. The nanoparticles with an average diameter of 114 nm (Fig. 2 (b)) and 141 nm (Fig. 2 (c)) were obtained respectively at the 2.25 : 1 and 2 : 1

molar ratios of BHQP to AlCl_3 , and the size (diameter) distribution of particles is quite narrow.

The emission spectra (Fig. 3) of the particles were measured by exciting at 380 nm. The peak of



All particles are dispersed in diethyl ether. Concentration of particles was calculated in terms of BHQP is 2.5×10^{-4} mmol/mL.

Emission spectra recorded on excitation at 380 nm

Fig. 3 Emission spectra of nanoparticles

the emission spectra of the particles is 518 nm. According to Ref. [29], the maximum emission intensity increases as the particle size decreases. However, in our case, the emission intensity of particles with average diameter of 114 nm is lower than that of particles with an average diameter of 141 nm. This phenomenon can be attributed to the difference of AlQ_3 group concentration in the particles with average diameters of 141 nm and 114 nm because the emission intensity depends mainly on the concentration of AlQ_3 groups besides the particle size. Actually the concentration of AlQ_3 groups in the particles with diameter of 141 nm is higher than that in the particles with diameter of 114 nm.

3 Conclusion

A facile strategy for the preparation of spherical nanoparticles from hyperbranched coordination polymers has been developed by the diffusion of diethyl ether into a homogeneous mixture solution of BHQP and $AlCl_3$ in DMF. The results demonstrate that the formation of nanoparticles depends on the molar ratio of the BHQP to the Al^{3+} ions and the nanoparticles with narrow size distribution were obtained in the range of 2.25 : 1 to 2 : 1 molar ratio. In addition, the nanoparticles show good optical absorption and high intensity of luminescence. Further research is underway to control the size of particles. This research provides a facile and promising strategy that may become a useful tool for the preparation of nanoparticles of coordination polymer materials with well-defined pores through design of the ligand structure.

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