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Journal of Colloid and Interface Science 304 (2006) 431–436

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Metal-cation-mediated nanocrystal arrays of sandwich-type (phthalocyaninato) [tetrakis(4-pyridyl)porphyrinato] cerium complex formed at the water–chloroform interface

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Received 21 July 2006; accepted 5 September 2006

Abstract

Regular square, wirelike, quadrate, and rodlike nanocrystal arrays of Cd^{2+}, Hg^{2+}, or Ag^{+} metal-cation-mediated sandwich-type mixed (phthalocyaninato) [5,10,15,20-tetrakis(4-pyridyl)poprhyrinato] cerium(III) double-decker complex Ce(Pc)(TPyP) have been successfully prepared at the water–chloroform interface. The nanocrystal growth processes were monitored by transmission electron microscopy (TEM), which reveals that different morphologies of nanocrystals have been fabricated from double-decker molecules connected by different kinds of metal cations, forming coordination polymers. These nanoscaled coordination polymers were characterized by FT-IR spectra and energy-dispersive X-ray spectra (EDS). EDS results clearly revealed the elements of the nanocrystals and the FT-IR spectra give evidence for the coordination interaction between the double-decker molecules and metal cations. The UV–vis absorption spectrum indicates the formation of J-aggregates of the double-decker molecules in the nanocrystals formed.

Keywords: Phthalocyanine; Porphyrin; Cerium; Sandwich complex; Transmission electron microscopy; Nanocrystal

1. Introduction

The self-assembly of molecular building blocks into targeted nanoscaled architectures at interfaces represents one of the major goals of supramolecular chemistry and material science, given the perspective of the potential applications of these systems in nanotechnology [1–4]. On the other hand, the liquid–liquid interface offers great potential for assembly and for the chemical manipulation of nanoparticles [5,6]. The assembly of particles at liquid–liquid interfaces provides a favorable means of preparing various kinds of materials because the particles at the fluid interface are highly mobile and can rapidly achieve an equilibrium assembly [7,8]. For instance, nanoparticles including metal, metal oxide, and metal sulfide [9–12], protein film [13,14], and composite film [15] have been prepared recently at liquid–liquid interfaces.

Supramolecular structures formed from porphyrin derivatives, including phthalocyanines, have received increasing attention recently due to their potential applications, ranging from molecular electronics [16–20], photovoltaic cells [21–23], and field effect transistor (FET) [24–28], to gas sensors [29–33]. The highly ordered supramolecular structures of porphyrin and phthalocyanine derivatives are usually formed in solution driven by noncovalent intermolecular forces such as π–π stacking [34–36], hydrogen bonding [37,38], or metal–ligand bonding [39–41]. Other than the self-assembly of porphyrin and phthalocyanine derivatives in solution, assembly at the immiscible phase interfaces of air–water, air–solid, or liquid–liquid has also attracted much research interest. Most previous research focuses on the self-assembly of porphyrin and/or phthalocyanine derivatives at the air–water interface, which formed various aggregates and assembled into unique functional films [27,28,42–

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doi:10.1016/j.jcis.2006.09.003

44]. Moreover, the self-assembly at the air–solid interface has been successfully used to control the molecular arrangement in two dimensions [45,46]. Recently, metal-mediated multiporphyrin nanocrystals and coordination polymer nanotubes of tetrapyridylporphin compounds have been successfully grown at the water–chloroform interface [47,48].

However, to the best of our knowledge, all the research about metal-mediated multiporphyrin arrays reported thus far seems to be limited to the nanoscale networks of monomeric porphyrin and/or phthalocyanine derivatives. There seems to be no report on the metal-mediated assembly of sandwich-type tetrapyrrole metal complexes at the liquid–liquid interface. Owing to the rich optical and electrochemical properties, as well as the special electronic structure of sandwich-type porphyrinato and/or phthalocyaninato rare earth complexes, it is worth trying to assemble sandwich tetrapyrrole rare earth complexes into supramolecular structures with special functionalities.

Here we describe the self-assembly of a sandwich-type (phthalocyaninato) [tetrakis(4-pyridyl)porphyrinato] cerium double-decker compound, Ce(Pc)(TPyP), driven by metal coordination bonds together with the supramolecular interactions at the water–chloroform interface. The progress of nanocrystal growth of sandwich-type double-decker complexes was monitored by transmission electron microscopy (TEM). In particular, the aggregation of Ce(Pc)(TPyP) mediated by Ag^+ has been found to be concentration-dependent and at least two coordination modes of silver cations with pyridyl nitrogen atoms are formed. This is different from that reported previously [46].

2. Experimental section

2.1. Materials

Sandwich-type (phthalocyaninato)[tetrakis(4-pyridyl)porphyrinato] cerium double-decker compound, Ce(Pc)(TPyP), was prepared following the previously published procedures [19]. $CdCl_2$, $HgCl_2$, and $AgNO_3$ were all analytical grade reagents purchased from the Shanghai Chemical Reagent Co. All chemicals were used as received without further purification. Double distilled water was used to prepare aqueous solutions.

2.2. Nanocrystal growth of Ce(Pc)(TPyP) networks at the water–chloroform interface

A typical procedure for the preparation of Cd^{2+} mediated nanocrystal growth is described below. A 0.036 M $CdCl_2$ water solution and a 0.097 mM Ce(Pc)(TPyP) chloroform solution were used as the water phase and organic phase, respectively. During the experiments, the aqueous solution of metal ions was slowly added to the chloroform phase surface at which the interfacial reaction occurs.

2.3. Characterization of nanocrystals

The TEM images were taken on a JEM-100CX II electron microscope operated at 100 kV (JEOL, Japan). Energy-depressive X-ray spectra (EDS) (OXFORD, UK) were performed on a high-resolution transmission electron microscope (HRTEM) JEM-2100 (JEOL, Japan) operating at 200 KV. FT-IR spectra were recorded on KBr-matrix pellets on a BIORAD FTS-165 spectrometer (PerkinElmer Ltd., UK) with a resolution of 2 cm^{-1}. UV–vis spectra for Ce(Pc)(TPyP) in chloroform solution and the nanocrystal Langmuir–Blodgett (LB) films were measured on a Hitachi U4100 (Japan) UV–vis spectrophotometer.

3. Results and discussion

3.1. Formation of metal-mediated Ce(Pc)(TPyP) network nanocrystals

As noticed by Qian and co-workers [47], the key point for the successful growth of nanocrystals at the water–chloroform interface is that the products do not dissolve into either water or chloroform. Fortunately, we found that the metal cations, namely Cd^{2+}-, Hg^{2+}-, and Ag^+-mediated Ce(Pc)(TPyP) nanocrystals, do not dissolve in either water or chloroform solution. It has also been found that the formation rate of nanocrystals was strongly dependent on the metal cation species: Some fine nanowires of Hg^{2+}-mediated double-decker compound Ce(Pc)(TPyP) could be found in the chloroform phase after 15 min of interfacial reaction when 0.01 M $HgCl_2$ solution was used. In contrast, for the Cd^{2+}-mediated system, 36 h was needed to get regular nanocrystals when $CdCl_2$ (0.039 M) was used.

3.2. TEM images of metal-mediated double-decker nanocrystals

By employing a similar procedure of studying the metal-mediated monomeric porphyrin compounds [47,48], the formation process of nanocrystals of the double-decker compound Ce(Pc)(TPyP) mediated with different metal cations at the water–chloroform interface has been systematically investigated through studying the size and framework of nanocrystals formed as a function of reaction time and concentrations of either metal cations or Ce(Pc)(TPyP) by TEM technology.

3.2.1. Cd-[Ce(Pc)(TPyP)] nanocrystals

Fig. 1 shows a series of TEM images of Cd-[Ce(Pc)(TPyP)] nanocrystals and microcrystals taken at different reaction time. As can be seen from these figures, many nanocrystals with size ca. 200 nm were formed within 1 h, indicating that the reaction at the water–chloroform interface was relatively rapid. Along with increasing the reaction time, the TEM images revealed that the nanocrystals increase gradually in size; for example, crystals with sizes ca. 200–300 nm and 2 μm formed after 2 and 36 h, respectively. It was also found that the nanocrystals formed were not very regular at first, then became regular crystals after 2 h (Fig. 1b), and finally grew into well-defined regular crystals after 36 h (Fig. 1c). Examination of the TEM images seems to reveal that in line with the previous report on metal-mediated monomeric porphyrin compounds [47], the crystals grow not only by the coordination reaction of Cd^{2+} with TPyP