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Nanoscale Hollow Spheres of an Amphiphilic Mixed (Phthalocyaninato)(porphyrinato)europium Double-Decker Complex

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A novel amphiphilic sandwich-type mixed (phthalocyaninato)(porphyrinato)europium double-decker complex Eu(Pc)-[T(OH)$_3$PP] [Pc = phthalocyaninate, T(OH)$_3$PP = 5,10,15-tris(4-hydroxyphenyl)-20-(4-*tert*-butylphenyl)porphyrinate] (**1**) was designed, prepared, and characterized by a range of spectroscopic methods in addition to elemental analysis. By employing a solution injection method, this compound self-assembles into nanoscale hollow spheres with an average diameter of ca. 70 nm. The hollow spherical structure was determined by transmission electronic microscopy and scanning electronic microscopy. Comparison in the electronic absorption spectrum between the aggregate and the compound itself in solution reveals the *J*-aggregation packing mode of the amphiphilic double-decker molecules in nanoscale hollow spheres. The present work represents the first example of nanoscale hollow sphere morphology self-assembled from sandwich tetrapyrrole rare-earth complexes.

Introduction

One of the main goals of supramolecular chemistry is the development of new nanometer morphologies for inorganic and/or organic materials that open new opportunities in catalysis, advanced functional molecular materials, biomedicine, and nanoscale electronic and optoelectronic devices.[1] A wide variety of nanostructures such as hollow spheres, fibers, ribbons, and tubes have been fabricated from various functional molecular materials.[2–5] In particular, nanoscale hollow spheres are an important class of materials because of their wide range of applications such as drug delivery, chemical storage, light filters, chemical catalysis, and cosmetic foundations associated with their unique advantage of low effective density and high specific surface.[6] The common strategy for preparing hollow spheres from materials such as inorganic ceramics, organic polymers, and their hybrids is the template method,[7] which, however, usually leads to wastage of large quantities of surfactants in removing the core template by dissolution, evaporation, or thermolysis to create a hollow interior. As a result, modification in the molecular structure towards amphiphilic functional molecular compounds through molecular design and synthesis is highly desired for the self-assembly fabrication of organic nanostructures with a hollow sphere morphology.

Porphyrin and phthalocyanine compounds, in particular their sandwich-type rare-earth complexes, possess remarkable photo-, electro-, magnetic, and biochemical properties. The self-assembly of tetrapyrrole derivatives into nanostructures with a wide range of morphologies has therefore attracted considerable attention in recent years.[8–10] In particular, nanoscale hollow spheres of tetrapyrrole compounds have been intensively studied due to their rich potential applications in different fields. With the assistance of a surfactant, nanoscale hollow spheres were fabricated from an optically active metal-free phthalocyanine compound.[11] Self-assembled nanostructures with a hollow sphere morphology from amphiphilic porphyrin compounds were also produced.[12] However, to the best of our knowledge, nanoscale hollow spheres fabricated from sandwich-type porphyrinato and/or phthalocyaninato rare-earth complexes have not yet been reported thus far. It is therefore worthwhile to prepare nanoscale hollow spheres of sandwich tetrapyrrole rare-earth complexes with intriguing structures and functionalities.

In this paper, we describe the structural modification of a mixed (phthalocyaninato)(porphyrinato)europium double-decker complex. Introduction of three hydroxy groups onto the *meso*-attached phenyl substituents of the tetra(phenyl)porphyrin ligand in a mixed (phthalocyaninato)(porphyrinato)europium double-decker compound leads to the formation of a novel sandwich tetrapyrrole rare-earth complex with typical amphiphilic nature, Eu(Pc)[T(OH)$_3$PP] (**1**; Figure 1), which easily self-assembles into nanoscale hollow spheres. This work provides an effective pathway towards the design and fabrication of sandwich tetrapyrrole rare-earth complexes into nanostructures with a hollow sphere morphology.

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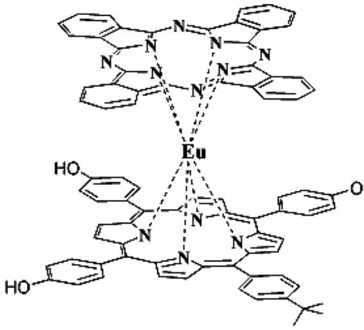

Figure 1. Schematic molecular structure of the mixed (phthalocyaninato)(porphyrinato)europium double-decker complex **1**.

Results and Discussion

Molecular Synthesis and Characterization

The target mixed (phthalocyaninato)(porphyrinato)europium double-decker compound Eu(Pc)[T(OH)$_3$PP] (**1**) was prepared according to a previously described procedure.[13] The synthesis involves prior generation of the half-sandwich complex Eu(Pc)(acac), generated in situ from Eu(acac)$_3$·*n*H$_2$O and phthalonitrile in *n*-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), followed by replacing *n*-pentanol with 1,2,4-trichlorobenzene (TCB) and treatment with metal-free porphyrin H$_2$T(OH)$_3$PP in refluxing TCB for 5 h. It is worth noting that actually the mixed-ring double-decker containing 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin, Eu(Pc)[T(OH)$_4$PP], is the original target compound. Unfortunately, efforts to use H$_2$[T(OH)$_4$-PP] failed to give Eu(Pc)[T(OH)$_4$PP] probably due to the very limited solubility of H$_2$T(OH)$_4$PP in TCB. As a consequence, **1** was synthesized as the target complex in the present case. In addition, for the purpose of comparative studies, Eu(Pc)(TBPP) [TBPP = 5,10,15,20-tetra(4-*tert*-butylphenyl)porphyrinate] (**2**), Eu(Pc)[T(OH)PP] [T(OH)PP = 5-(4-hydroxyphenyl)-10,15,20-tris(4-*tert*-butylphenyl)porphyrinate] (**3**), Eu(Pc)[*trans*-T(OH)$_2$PP] [*trans*-T(OH)$_2$PP = 5,15-bis(4-hydroxyphenyl)-10,20-bis(4-*tert*-butylphenyl)porphyrinate] (**4**), and Eu(Pc)[*cis*-T(OH)$_2$PP] [*cis*-T(OH)$_2$PP = 5,10-bis(4-hydroxyphenyl)-15,20-bis(4-*tert*-butylphenyl)porphyrinate] (**5**) were also prepared and characterized (Figure S1, Supporting Information). Satisfactory elemental analysis results were obtained for all the newly prepared mixed-ring, double-decker complexes after repeated column chromatographic purification and recrystallization (Table S1, Supporting Information). The MALDI-TOF mass spectra of **1**–**5** showed intense clusters corresponding to the molecular ion [M$^+$], and the data are also given in Table S1 (Supporting Information). These new sandwich double-decker compounds were also characterized with the ^{1}H NMR spectroscopic method. The ^{1}H NMR spectrum of **1** is shown in Figure S2 for exemplification. Table S2 (Supporting Information) collects the ^{1}H NMR spectroscopic data of double-deckers **1**–**5**. The spectral assignments could easily be reached on the basis of the integration and multiplicity of the signals.

Electronic Absorption Spectra

The electronic absorption spectra of the mixed-ring, double-decker compound Eu(Pc)[T(OH)$_3$PP] (**1**) together with those of **2**–**5** were recorded in THF, and the data are compiled in Table S3 (Supporting Information). Figure 2 and Figure S3 (Supporting Information) display the electronic absorption spectra of **1**–**5** in THF. As revealed, these five double-decker complexes, regardless of the number and location of hydroxy groups at the *meso*-attached phenyl substituents of the porphyrin ring, dissolved in THF, show just the same features in their electronic absorption spectra, revealing the nonaggregated molecular spectroscopic nature of all five compounds including **1** in THF. In line with the neutral analogues with trivalent central metal ions, M^{III}-(Pc)(TClPP) [M = Y, La–Lu except Ce and Pm; TClPP = 5,10,15,20-tetrakis(4-chlorophenyl)porphyrinate][14] and M^{III}-(Pc)(TPP) (M = La, Pr, Nd, Eu, Gd, Er, Lu, and Y; TPP = 5,10,15,20-tetraphenylporphyrinate),[15a,15b] the absorptions of double-decker **1** at about 320 and 406 nm can be attributed to the phthalocyanine and porphyrin Soret bands, respectively, whereas the absorption bands at 473 and 1008 nm are due to the electronic transitions involving the semioccupied orbital, which has higher phthalocyanine character. An additional characteristic near-IR band for the π-radical anion of trivalent europium double-deckers around 1350 nm can also be observed for the whole series, which confirms the neutral nature of **1**–**5**.[14,15] In a similar manner, the absorptions for **2**–**5** are also assigned.

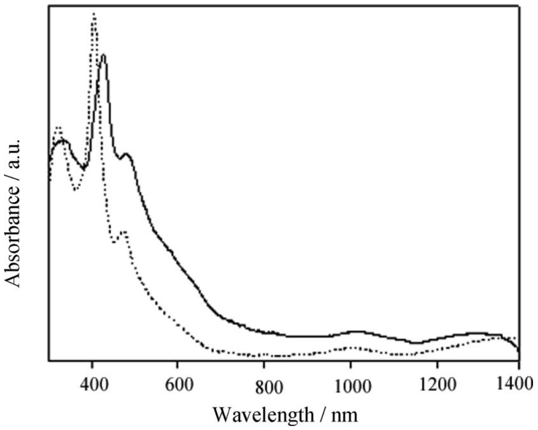

Figure 2. Electronic absorption spectra of Eu(Pc)[T(OH)$_3$PP] (**1**) in THF (dash line) and water (solid line).

The electronic absorption spectra of **1** together with those of **2**–**5** in water were also recorded and are given in Figure 2 and Figure S3 (Supporting Information), respectively. These spectra are significantly different from the spectrum of **1** dissolved in THF. The broadening and significant redshift for all the absorption bands except the near-IR band of **1** in water, in comparison with the corresponding absorptions in THF, reveal the formation of *J*-type aggregates and intensive intermolecular interaction in the nanoaggregates.[16]

IR Spectra

The IR spectra of mixed-ring double-decker compounds **1**–**5** together with their self-assembled nanostructures formed in water are shown in Figure S4 (Supporting Information). The similar feature in the IR spectra of the nanostructures to that of compounds **1**–**5** indicates the composition of nanostructures from the corresponding sandwich double-decker compounds. In particular, in the IR spectrum of the aggregates formed from double-decker **1**, the absorption at 3428 cm^{-1} due to the hydroxy group in the IR spectrum of **1** is broadened and shifts to lower frequency at 3384 cm^{-1}, indicating the formation of a hydrogen bond between the hydroxy oxygen atom in the *meso*-attached phenyl groups in the porphyrin ligand of the double-decker molecule with the neighboring one in the nanostructures of **1**.[17]

TEM and SEM Images

The nanostructures of the double-decker complex were fabricated by injecting a small volume of a solution of **1** in THF (1 mM) into a large volume of water. This is also true for **2**–**5**. Samples were prepared by casting a drop of sample solution onto a carbon-coated grid. The morphology of the aggregates was examined by transmission electronic microscopy (TEM) and scanning electron microscopy (SEM). As shown in Figure 3A, a large scale of nanostructures with a hollow sphere morphology and an average diameter of ca. 70 nm were formed from the self-assembly of **1** in water. High-magnification TEM image in the inset of Figure 3A shows the thickness of these hollow spheres to be in the range of ca. 20 nm. Further evidence to confirm the hollow sphere nanostructures comes from the SEM image (Figure 3B). As can be seen, the products remain intact and have a well-defined 3D spherical structure with a smooth, uniform surface texture and a relatively large size distribution. Few of them are deformed or cracked with a hole in the surface of each nanoscale hollow sphere, suggesting their potential application for drug delivery.[18]

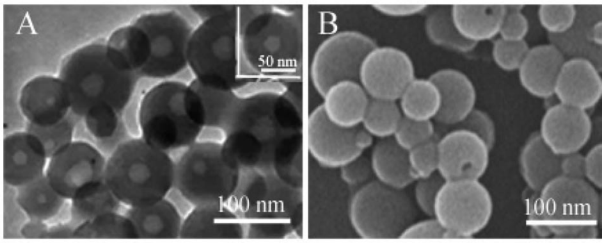

Figure 3. Nanoscale hollow spheres formed from **1** in water observed by TEM (A) and SEM (B).

According to the experimental results, the formation mechanism of the nanoscale hollow spheres of **1** was speculated and displayed in Figure 4A,B. Three hydroxy groups, which were incorporated onto the *meso*-attached phenyl groups of the porphyrin ligand, induce the change in the nature of the double-decker compound from hydrophobic to amphiphilic. It is well known that in selective solvents amphiphilic molecules like liposomes form micellar or vesicular supramolecular structures that would normally be due to the superstrong segregation limit (SSSL), mainly owing to the different solubility of the hydrophilic and hydrophobic units.[19] As suggested by the IR spectroscopic and electronic absorption results of the self-assembled nanoscale hollow spheres of **1**, during the self-assembly process of this compound, a dimeric supramolecular structure is formed first through an intermolecular hydrogen bond between two hydroxy groups of the porphyrinato ligands of two neighboring molecules. This formed dimer shows amphiphilic properties in nature because of the hydrophilic hydroxy groups and hydrophobic residual section, which then as the building block further self-assembles into the target hollow spheres depending mainly on the π–π interaction between the tetrapyrrole rings.

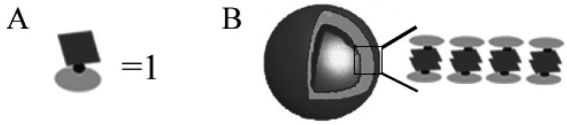

Figure 4. (A) Schematic representation of **1**; (B) schematic illustration of a hollow sphere formed in water with a close-up of the membrane showing the proposed structure.

At the end of this section, it is worth noting that despite the similarity in the electronic absorption spectra between **1** and **2**–**5**, the morphology of the nanostructures of double-decker **1** is different from that of **2**–**5** (Figure 3 and Figure S5, Supporting Information). As revealed, all four double-decker complexes Eu(Pc)(TBPP) (**2**) and Eu(Pc)[T(OH)$_n$PP] (n = 1, 2; **3**–**5**) self-assemble into nanostructures with just the same solid spherical morphology. The similarity in the morphologies of the nanostructures formed from typical hydrophobic compound **2** and hydroxy-attached compounds **3**–**5** reveals the similar molecular nature of these four double-decker compounds, suggesting that introduction of up to two hydroxy groups onto the *meso*-attached phenyl substituents of the porphyrin ligand in the mixed (phthalocyaninato)(porphyrinato)europium molecules is not enough to change the nature of the double-decker molecules from hydrophobic to amphiphilic. While in the case of compound **1** three hydroxy groups are incorporated onto the *meso*-attached phenyl groups of the porphyrin ligand, mixed-ring double-decker molecules become typical amphiphiles and, therefore, self-assemble into nanoscale hollow spheres.

Conclusions

In summary, a novel amphiphilic sandwich-type mixed (phthalocyaninato)(porphyrinato)europium double-decker compound Eu(Pc)[T(OH)$_3$PP] was designed, synthesized, and used as a building block to fabricate nanoscale hollow spheres via self-assembly. To the best of our knowledge, the present work is the first example of organic nanoscale hollow spheres self-assembled from sandwich tetrapyrrole rare-earth complexes. Owing to rich optical and electrochemical properties as well as the special electronic structure of the sandwich phthalocyaninato and/or porphyrinato rare-earth complexes, the nanoscale hollow spheres obtained are expected to be useful in the fields of drug delivery, chemical storage, and paper coating.

Experimental Section

Chemicals: TCB and *n*-pentanol were distilled from CaH_2 and sodium, respectively, under reduced pressure prior to use. Ultrapure water was used in all experiments. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 200–300 mesh) with the indicated eluent. All other reagents and solvents were of reagent grade and used as received.

Preparation of Materials and Measurements: The double-decker complex Eu(Pc)[T(OH)$_3$PP] (**1**) together with Eu(Pc)(TBPP) (**2**), Eu(Pc)[T(OH)PP] (**3**), Eu(Pc)[*trans*-T(OH)$_2$PP] (**4**), and Eu(Pc)[*cis*-T(OH)$_2$PP] (**5**) were prepared according to a reported procedure as detailed below.[13] MALDI-TOF mass spectra were carried out with a Bruker APEX47e ultra-high-resolution Fourier transform ion cyclotron resonance mass spectrometer with α-cyano-4-hydroxycinnamic acid as the matrix. IR spectra were recorded by using a BIORAD FTS-165 spectrometer with 2 cm^{-1} resolution (KBr pellets). Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences. ^{1}H NMR spectra were measured with a Bruker DPX 300 spectrometer (300 MHz).

Preparation of the Nanostructures and Measurements: The nanostructures of the five double-decker compounds **1**–**5** were fabricated by the phase-transfer method according to the following procedure.[4,8,12] A minimum volume (30–50 μL) of concentrated THF solution of compounds **1**–**5** (1 mM) was injected rapidly into 1 mL of water. The solution, which was allowed to equilibrate over 1 d, was used to record the electronic absorption spectra for the aggregates. One drop of the solution was transferred to the carbon-coated grid by pipetting for the TEM and SEM observation. The above equilibrated solution (20 mL) was evaporated under reduced pressure at room temperature, the residue was collected, dried under vacuum and subjected to IR spectroscopic measurements (KBr pellets). It is worth noting that the results were reproducible under the experimental conditions described above. Electronic absorption spectra were recorded with a Hitachi U-4100 spectrophotometer. TEM images were taken with a JEOL JEM-100CX II electron microscope operated at 100 kv. SEM images were obtained by using a JEOL JSM-6700F field-emission scanning electron microscope. For SEM imaging, Au (1–2 nm) was sputtered onto the grids to prevent charging effects and to improve image clarity.

General Procedure for the Preparation of Eu(Pc)(Por) (1–5): A mixture of Eu(acac)$_3$·*n*H$_2$O (0.05 mmol), phthalonitrile (0.20 mmol), and DBU (0.26 mmol) in *n*-pentanol (5 mL) was stirred at 120 °C for 2 h under a slow stream of nitrogen. The resulting blue solution was cooled to room temperature, followed by replacing *n*-pentanol with TCB and then treatment with the metal-free porphyrin H$_2$Por (0.05 mmol) in refluxing TCB for another 5 h under an atmosphere of nitrogen. The volatiles were removed under reduced pressure, and the residue was purified by chromatography with $CHCl_3$ as the eluent. A small amount of Eu(Pc)$_2$ and metal-free porphyrin were collected as the first and second fractions, respectively, and then the target mixed ring double-decker product Eu(Pc)(Por) (**1**–**5**) as the third fraction. Repeated chromatography followed by recrystallization from $CHCl_3$ and *n*-hexane gave pure Eu(Pc)(Por) (**1**–**5**) as brown solids.

Supporting Information (see footnote on the first page of this article): Schematic molecular structures of complexes **2**–**5**; ^{1}H NMR spectrum of **1**; electronic absorption spectra of **2**–**5**; IR spectra of **1**–**5** and aggregates of compounds **1**–**5** formed in water; self-assembled nanospheres formed from **2**–**5** in water observed by TEM and SEM; analytical and mass spectroscopic data for **1**–**5**; ^{1}H NMR spectroscopic data for the reduced form of **1**–**5**; and electronic absorption data for **1**–**5** in THF and their self-assemblies in water.

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[1] a) P. G. Schouten, J. M. Warman, M. P. de Haas, M. A. Fox, H. L. Pan, *Nature* **1991**, *353*, 736–737; b) J.-M. Lehn, *Science* **2002**, *295*, 2400–2403; c) G. Cao, *Nanostructures and Nanomaterials: Synthesis Properties and Applications*; Imperial College Press, London, **2004**; d) J. A. A. W. Elemans, R. van Hameren, R. J. M. Nolte, A. E. Rowan, *Adv. Mater.* **2006**, *18*, 1251–1566.

[2] a) S. A. Jenekhe, X. L. Chen, *Science* **1999**, *283*, 372–375; b) J. Hu, Y. Guo, H. Liang, L. Wan, C. Bai, Y. Wang, *J. Phys. Chem. B* **2004**, *108*, 9734–9738.

[3] a) M. Yun, N. V. Myung, R. P. Vasquez, C. Lee, E. Menke, R. M. Penner, *Nano Lett.* **2004**, *4*, 419–422; b) H. Gan, H. Liu, Y. Li, Q. Zhao, Y. Li, S. Wang, T. Jiu, N. Wang, X. He, D. Yu, D. Zhu, *J. Am. Chem. Soc. Chem.* **2005**, *127*, 12452–12453.

[4] K. Balakrishnan, A. Datar, T. Naddo, J. Huang, R. Oiker, M. Yen, J. Zhao, L. Zang, *J. Am. Chem. Soc. Chem.* **2006**, *128*, 7390–7398.

[5] a) J. M. Schnur, *Science* **1993**, *262*, 1669–1676; b) T. Shimizu, M. Masuda, H. Minamikawa, *Chem. Rev.* **2005**, *105*, 1401–1444; c) Q. Liu, Y. Li, H. Liu, Y. Chen, X. Wang, Y. Zhang, X. Li, J. Jiang, *J. Phys. Chem. C* **2007**, *111*, 7298–7301.

[6] J. Han, G. Song, R. Guo, *Adv. Mater.* **2006**, *18*, 3140–3144.

[7] a) F. Caruso, *Chem. Eur. J.* **2000**, *6*, 413–419; b) E. Donath, S. Moya, B. Neu, G. B. Sukhorukov, R. Georgieva, A. Voigt, H. Bäumler, H. Kiesewetter, H. Möhwald, *Chem. Eur. J.* **2002**, *8*, 5481–5485.

[8] a) G. Lu, Y. Chen, Y. Zhang, M. Bao, Y. Bian, X. Li, J. Jiang, *J. Am. Chem. Soc.* **2008**, *130*, 11623–11630; b) Y. Gao, X. Zhang, C. Ma, X. Li, J. Jiang, *J. Am. Chem. Soc.* **2008**, *130*, 17044–17052.

[9] a) Z. Wang, C. J. Medforth, J. A. Shelnutt, *J. Am. Chem. Soc.* **2004**, *126*, 15954–15955; b) T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Yoshishige Okuno, T. Mashiko, *Nature* **2001**, *413*, 619–621; c) M. Kimura, T. Muto, H. Takimoto, K. Wada, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayash, *Langmuir* **2000**, *16*, 2078–2082.

[10] G. Torre, C. G. Claessens, T. Torres, *Chem. Commun.* **2007**, 2000–2015.

[11] W. Lv, X. Zhang, J. Lu, Y. Zhang, X. Li, J. Jiang, *Eur. J. Inorg. Chem.* **2008**, 4255–4261.

[12] a) G. Lu, X. Zhang, X. Cai, J. Jiang, *J. Mater. Chem.* **2009**, *19*, 2417–2424; b) Y. Li, X. Li, Y. Li, H. Liu, S. Wang, H. Gan, J. Li, N. Wang, X. He, D. Zhu, *Angew. Chem. Int. Ed.* **2006**, *45*, 3639–3643; c) R. Charvet, D. L. Jiang, T. Aida, *Chem. Commun.* **2004**, 2664–2665.

[13] a) J. Jiang, W. Liu, W.-F. Law, J. Lin, D. K. P. Ng, *Inorg. Chim. Acta* **1998**, *268*, 141–144; b) J. Jiang, M. T. M. Choi, W.-F. Law, J. Chen, D. K. P. Ng, *Polyhedron* **1998**, *17*, 3903–3908; c) J. Jiang, J. Xie, M. T. M. Choi, Y. Yan, S. Sun, D. K. P. Ng, *J. Porphyrins Phthalocyanines* **1999**, *3*, 322–328; d) J. Jiang, D. Du, M. T. M. Choi, J. Xie, D. K. P. Ng, *Chem. Lett.* **1999**, 261–262.

[14] F. Lu, X. Sun, R. Li, D. Liang, P. Zhu, Ch.-F. Choi, D. K. P. Ng, T. Fukuda, N. Kobayashi, M. Bai, Ch. Ma, J. Jiang, *New J. Chem.* **2004**, *28*, 1116–1122.

[15] a) Y. Zhang, X. Cai, P. Yao, H. Xu, Y. Bian, J. Jiang, *Chem. Eur. J.* **2007**, *13*, 9503–9514; b) D. Chabach, M. Tahiri, A. De Cian, J. Fischer, R. Weiss, M. El Malouli Bibouts, *J. Am. Chem. Soc.* **1995**, *117*, 8548–8556; c) R. Wang, R. Li, Y. Li, X. Zhang, P. Zhu, P.-C. Lo, D. K. P. Ng, N. Pan, C. Ma, N. Kobayashi, J. Jiang, *Chem. Eur. J.* **2006**, *12*, 1475–1485.

[16] a) X. Gong, T. Milic, C. Xu, J. D. Batteas, C. M. Drain, *J. Am. Chem. Soc.* **2002**, *124*, 14290–14291; b) N. C. Maiti, S. Mazumdar, N. Periasamy, *J. Phys. Chem. B* **1998**, *102*, 1528–1538; c) C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534; d) K. Kano, H. Minamizono, T. Kitae, S. Negi, *J. Phys. Chem. A* **1997**, *101*, 6118–6124; e) R. Purrello, L. Monsu'Scolaro, E. Bellacchio, S. Gurrieri, A. Romeo, *Inorg. Chem.* **1998**, *37*, 3647–3648.

[17] M. Kimura, T. Kuroda, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, *Langmuir* **2003**, *19*, 4825–4830.

[18] a) F. Caruso, A. R. Caruso, H. Möhwald, *Science* **1998**, *282*, 1111–1114; b) Y. R. Ma, L. M. Qi, J. M. Ma, H. M. Cheng, *Langmuir* **2003**, *19*, 4040–4042; c) T. Nakashima, N. Kimizuka, *J. Am. Chem. Soc.* **2003**, *125*, 6386–6387; d) W. Meier, *Chem. Soc. Rev.* **2000**, *29*, 295–503.

[19] M. Antonietti, S. Förster, *Adv. Mater.* **2003**, *15*, 1323–1333.

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