Improving Carbon Nitride Photocatalysis by Supramolecular Preorganization of Monomers

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S *Supporting Information*

ABSTRACT: Here we report a new and simple synthetic pathway to form ordered, hollow carbon nitride structures, using a cyanuric acid−melamine (CM) complex in ethanol as a starting product. A detailed analysis of the optical and photocatalytic properties shows that optimum hollow carbon nitride structures are formed after 8 h of condensation. For this condensation time, we find a significantly reduced fluorescence intensity and lifetime, indicating the formation of new, nonradiative deactivation pathways, probably involving charge-transfer processes. Enhanced charge transfer is seen as well from a drastic increase of the photocatalytic activity in the degradation of rhodamine B dye, which is shown to proceed via photoinduced hole transfer. Moreover, we show that various CM morphologies can be obtained using different solvents, which leads to diverse ordered carbon nitride architectures. In all cases, the CM-C_3N_4 structures exhibited superior photocatalytic activity compared to the bulk material. The utilization of CM hydrogen-bonded complexes opens new opportunities for the significant improvement of carbon nitride synthesis, structure, and optical properties toward an efficient photoactive material for catalysis.

Molecular self-assembly is the spontaneous association of molecules under equilibrium conditions into stable aggregates, joined by non-covalent bonds, with well-defined composition and structure.[1] Hydrogen bonds are useful for controlling molecular self-assembly due to the reversibility, specificity, and directionality of this class of interactions.[2] One of the best known supramolecular aggregates which consists of hydrogen bonds is the cyanuric acid−melamine (CM) complex.[3,4] The CM complex is formed with up to three hydrogen bonds between cyanuric acid and melamine and can adopt various forms, depending on the solvent from which it is aligned and precipitated. Melamine, together with other triazine derivatives, is commonly used as a precursor for the synthesis of graphitic carbon nitride (C_3N_4),[5] which over the past few years has attracted widespread attention due to its outstanding catalytic and photocatalytic activity.[6,7] C_3N_4 materials have been found useful for many applications: as metal-free photocatalyst,[8] in water splitting,[9] and more. Its unique optical, chemical, and catalytic properties, along with its low price and remarkably high stability to oxidation, make it a very attractive material for photocatalytic applications.

In past years many modifications of C_3N_4 syntheses have been developed, including the use of organic molecules like barbituric acid[10] or molecules which lead to integration of heteroatoms[11,12] within the C_3N_4 structure, resulting in significant changes in the electronic and catalytic properties.[13] Nevertheless, it is still a standard problem of carbon nitride chemistry that only rather disorganized textures with small grain sizes are obtained. This is due to the fact that even though bulk C_3N_4 can be synthesized via simple condensation of monomers such as cyanamide or dicyandiamide (DCDA), as-formed intermediates only react under solid-state chemistry-like conditions to give the final two-dimensionally condensed structure.[14] This problem includes the incomplete condensation of remaining isolated functionalities, which makes current "C_3N_4 structures" rather look like partial crystalline polymers, not the ideal structure found in the publications.[15] Therefore, it is essential to find new and simple synthetic pathways to form more ordered structures of carbon nitride, for instance for photovoltaic applications. The CM complex as a starting product for the synthesis of C_3N_4 offers several advantages. The CM forms many different ordered textures, depending on the solvent from which it was mixed,[16] and can inhibit the sublimation of melamine. If this formation could be aligned along surfaces or device structures, such as with zone melting,[17] polycondensation could start from a preorganized state which is structurally very similar to the local rearrangement of the building blocks in the final material. This can lead to either templated growth or topotactic transformation. Both processes may lead to C_3N_4 structures with improved local order, charge separation, and electronic conductivities. In addition, templating of CM is simpler, safer, and cheaper as compared to previous approaches which involve silica nanostructures.[18,19] The use of the CM complex for preparation of C_3N_4 was very recently also approached by Thomas et al. but with DMSO as a solvent, which resulted in different and, in our opinion, less controlled and diverse structures.[20]

Here, we present the utilization of CM which was aligned from diverse solvents as the precursor for the preparation of organized C_3N_4. The CM complex particles from ethanol exhibit a highly ordered pancake-like morphology which leads to the formation of hollow carbon nitride boxes upon pyrolysis. Moreover, the effect of the solvent on the CM complex structure and the resulting C_3N_4 morphology was studied by using water and chloroform as alternative solvents for the formation of CM complexes. The chemical structure, morphology, and optical
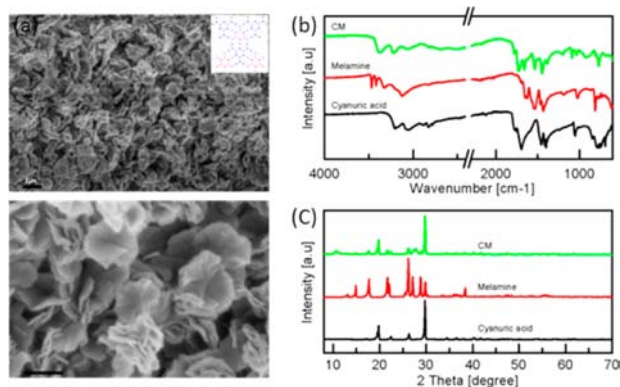
Figure 1. (a) SEM images of the CM complex as prepared in ethanol, (b) FT-IR spectra, and (c) XRD patterns of the CM complex, melamine, and cyanuric acid. A graphic representation of hydrogen-bonded CM is shown in the inset.

Figure 2. SEM images of CM prepared in ethanol after different condensation times.

properties of the resulting carbon nitrides were characterized by XRD, FT-IR, SEM, UV−vis absorption, and steady-state and time-resolved fluorescence spectroscopy. The photocatalytic activity was tested by measuring the degradation of rhodamine B (RhB) dye under visible light illumination in the presence of CM-C_3N_4.

Supramolecular structures of hydrogen-bonded CM were formed by mixing equal amounts of cyanuric acid and melamine in ethanol (Scheme S1). Even though both melamine and cyanuric acid are just slightly soluble in most solvents, the formation of ordered CM can be easily achieved in different solvents. Scanning electron microscopy (SEM) images of the uniform and organized pancake-like structure of CM prepared in ethanol are shown in Figure 1a. The CM morphology strongly depends on the solvent due to different surface energies of the hydrogen-bonded structures formed. For example, the CM complex that was precipitated from water forms a rod-like structure, while the one from chloroform shows a needle-like morphology (Figure S1). The high crystallinity of the CM complex is reflected in the X-ray diffraction (XRD) pattern (Figures 1b and S2). The appearance of new peaks for CM compared to melamine and cyanuric acid is strong evidence for the creation of a new arrangement. Evidence for an in-plane pattern in CM is shown in the well-resolved peaks at 10.67, 18.48, and 21.41°, which can be indexed as (100), (110), and (200) of the in-planar packing, respectively. In addition, a very well developed lamellar stacking peak, (002), is observed at 29.75°, supporting the observed sheet-like structure. We note, however, that due to the changes between the complex morphologies in different solvents, the intensity of these peaks is altered by serious morphology changes and the corresponding altered growth directions. Further evidence for the formation of the CM structure was achieved by measuring the Fourier transform infrared (FT-IR) spectrum as shown in Figure 1c. It is known that hydrogen-bonding between melamine and cyanuric acid results in several differences in their FT-IR spectra.[21] Our results show that the C=O stretching vibration of cyanuric acid is shifted to a higher wavenumber from 1691 to 1734 cm^{-1}, and the triazine ring vibration of melamine is shifted to a lower wavenumber from 812 to 769 cm^{-1}.

In order to create photoactive carbon nitride, the CM complex was heated to 550 °C for 2, 4, 8, and 12 h under nitrogen atmosphere (Scheme S1) with a heating ramp of 2.3 K/min. SEM images of the resulting carbon nitride (Figures 2 and S3)
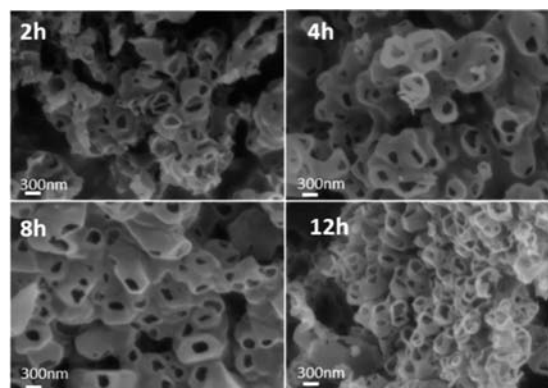
show slight variations in the morphologies, depending on the reaction time. The pancake-like morphology of the CM complex before heating resulted in hollow replicas made up of carbon nitride. This is typical for growth of a material on the surface of the precursor structure, which then dissolves through completion of the reaction. The hole size is then strictly related to the primary structure size; i.e., the process is self-templating. The calcination time seemed to indicate some structural ripening and coarsening of the structures. All the carbon nitride materials that were synthesized via this procedure, however, exhibit uniform and ordered hollow carbon nitride box morphologies with BET surface area of ca. 45 m^2/g.

Moreover, SEM images of C_3N_4 formed from CM in either water or chloroform each show a different morphology. The water-derived sample shows a sheet-like structure, while the chloroform-based material shows a tube-like structure, again reflecting the shape of the starting crystals (Figure S4). This demonstrates the ability to prepare multiple morphologies only by changing the solvent used to form the supramolecular complex. Moreover, due to the hydrogen-bonded complex, the initial shape of the aggregate was retained after calcination. Figure S5 shows that a very big entity of a CM complex (∼1 cm length) which was prepared in water turned into CM-C_3N_4 (after calcination at 550 °C) with complete preservation of the original aggregate shape. Controlling the CM complex texture therefore allows control over the final solid-state material.

Further evidence for the formation of carbon nitride was obtained by FT-IR and XRD analysis (Figure 3).[22] The vibrational spectra of the C_3N_4's that were condensed from DCDA were compared with the spectrum of the C_3N_4 that was condensed from CM (Figure 3a). Several strong bands in the 1200−1600 cm^{-1} region were found, which correspond to the typical stretching modes of CN heterocycles. Additionally, the characteristic breathing mode of the triazine units at 800 cm^{-1} is observed. The XRD pattern of the carbon nitride which was
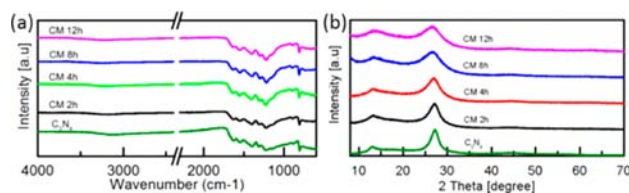

Figure 3. (a) FT-IR spectra and (b) XRD pattern of CM complex prepared in ethanol after calcination at 550 °C.

condensed from CM is similar to that of the one which was prepared by DCDA condensation (Figure 3b). The strong interplanar stacking peak of aromatic systems around 27.2° (indexed as (002)) is shifted and becomes less pronounced and broader for longer heating times. This indicates that tempering not only results in grain growth but involves other, polymer-like processes. Interestingly, we found that the local order of C_3N_4 depends on the solvent from which CM was precipitated (Figure S6). In all cases, the XRD pattern and FTIR analysis show the formation of C_3N_4. The interplanar stacking peak for the CM that was prepared in chloroform is, however, narrower than those for the ones that were prepared in ethanol and water. For water and ethanol, the peaks are slightly shifted to smaller angles, also indicating a higher defect rate. The formation of a near-to-C_3N_4 material is also confirmed by elemental analysis data. All the samples had a C/N molar ratio of 0.7 and less than 2% hydrogen, meaning specifically that during the condensation most of the NH_2 groups reacted. Moreover, the total weight of all the elements clearly indicates the absence of oxygen, meaning all the C=O groups in the cyanuric acid reacted with the melamine under the formation of water and C_3N_4.

The changes in the electronic properties of organic semiconductors are reflected in their photophysical properties, which can be detected as changes in the intensity or the shape of the recorded optical spectra. The different morphologies of C_3N_4 can directly influence its electronic structure by the creation of surface states or defects within its crystal structure. The UV−vis diffuse reflectance absorbance spectra of CM-C_3N_4 obtained after various heating times were compared to the spectrum of the one that was prepared from DCDA as a reference sample (Figure 4a). The absorption band edge of all the CM-C_3N_4 from ethanol is slightly blue-shifted compared to that of DCDA-C_3N_4. This shift becomes less pronounced as the heating time is longer, presumably due to the increasing layer thickness and extent of condensation.

The photoluminescence (PL) spectra of the CM-C_3N_4's prepared with different heating times as compared with the sample that was prepared from DCDA are shown in Figure 4b. The emission peak of all of the CM-C_3N_4's is shifted to higher energy with respect to that of DCDA-C_3N_4, with the trend following the heating time; however, the strongest shift occurs for the CM which was heated for 2 h. Moreover, the CM that was heated for 2 h showed the highest fluorescence intensity, which

decreased upon additional heating. Since time-resolved fluorescence measurements provide more information than is available from the steady-state data and fluorescence lifetimes are typically independent of the probe concentration,[23] we measured the intensity decays of the CM-C_3N_4 samples by use of a single photon counting setup (Figure S7). Fluorescence lifetimes extracted from the decay curves of CM-C_3N_4's prepared with different heating times and of that prepared from DCDA are given in Figure 4c. In accordance with the steady-state PL spectra, the fluorescence lifetime decreased from 5.6 ns for the CM-C_3N_4 which was condensed only for 2 h, down to 3.6 ns for the one which was condensed for 8 h. This is due to an increased nonradiative rate (k_{nr}) which follows an inverse trend with the fluorescence quantum yield, i.e., $k_{nr} = 0.29$ and 0.48 ns^{-1} for 2 and 8 h of heating, respectively. This new deactivation channel competing with the emission in depopulating the excited state is generated as a result of the tempering process. The quenching of the emission intensity and its lifetime indicate that the relaxation of a fraction of C_3N_4 excitons occurs via nonradiative paths, presumably by charge transfer of electrons and holes to new localized states which were formed during the growth of the CM-C_3N_4.

The new charge-transfer paths can be an indication for the photoactivity of materials. Similarly, we found that the solvent from which the CM complex was formed has a profound effect on the photophysical properties as well as on the morphology of the resulting C_3N_4's (Figure S8).

The absorption band edge of CM-C_3N_4 depends on the solvent from which CM was prepared (Figure S8a). The CM-C_3N_4's which were prepared from ethanol or water show a blue shift in their absorbance spectra compared to the spectra of those condensed in chloroform and DCDA. The samples prepared from chloroform exhibited a higher fluorescence intensity compared to those from other solvents (Figure S8b). Accordingly, the fluorescence lifetime of the CM-C_3N_4 prepared in water or in ethanol is shorter than that of the one prepared in chloroform, which again has implications on the photoactivity of these materials (Figure S8c).

A clear demonstration of the CM-C_3N_4 photocatalytic superiority is shown in the evolution of RhB degradation as a function of time under illumination at a wavelength of 420 nm (Figure 4d). All the carbon nitrides which were condensed from CM complex fully degraded the RhB dye already after 105 min (with different rate constants), while DCDA-C_3N_4 showed less activity in the degradation of RhB (less than 20% after 105 min). It is important to note that no degradation of RhB occurs under illumination without photocatalyst. For all C_3N_4 catalysts the amount of RhB dye adsorbed to the C_3N_4's is less than 15%, and the photodegradation yield was calculated after subtraction of this fraction. The photodegradation of RhB can occur in two ways: (1) cleavage of the all-conjugated structure or (2) N-de-ethylation.[24,25] In the first process the position of the main absorption peak at 554 nm remains constant while only the peak intensity decreases. For the second path the main absorption peak is blue-shifted up to 498 nm (RhB only). An example of the photodegradation of RhB under illumination in the presence of the CM-C_3N_4 which was condensed for 8 h is shown in Figure S9. The absorbance spectra of the RhB dye at different times show a decrease of the main peak at 554 nm, which is related solely to the cleavage of RhB structure. Almost 50% RhB degradation was observed after 15 min for all the CM-C_3N_4 polymers, except for the one which was condensed for only 2 h.
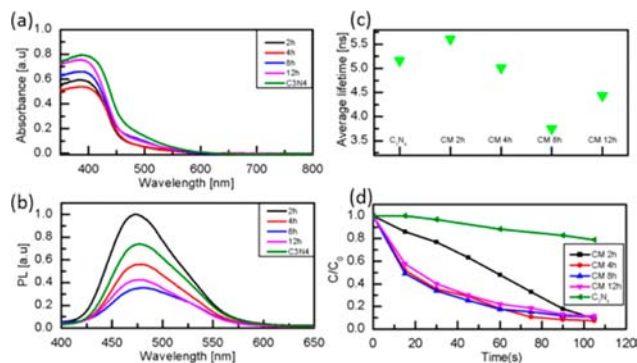

Figure 4. (a) Diffuse reflectance absorption spectra and (b) emission spectra of CM-C_3N_4 obtained after different condensation times in ethanol and DCDA-C_3N_4. (c) Average fluorescence lifetime of CM-C_3N_4's and DCDA-C_3N_4. (d) Relative concentration of RhB as a function of illumination time for CM-C_3N_4's and DCDA-C_3N_4.

The photodegradation results are mostly in line with the lifetime measurements; i.e., the vanishing of the longer radiative charge recombinations comes with a significantly increased photoreactivity. We note that although the florescence lifetimes of CM-2h and DCDA-C$_3$N$_4$ are similar, the photoactivity of CM-2h is higher, probably due to the different morphology and larger surface area. In addition, the solvent in which the CM complexes were prepared also strongly influenced their photoactivity (Figure S10). The photodegradation of RhB in the presence of both the CM-C$_3$N$_4$'s from ethanol and water was faster than when using CM-C$_3$N$_4$ prepared in chloroform. Nevertheless, in all CM-C$_3$N$_4$ cases, the photodegradation was completed within 2 h. The photodegradation mechanism of RhB can occur via both electron and hole transfer from the photoactive material to the solution, resulting in the creation of hydroxyl radicals which destroy the organic dye. In the case of electron transfer, the presence of oxygen is mandatory and the hydroxyl radicals form through reduction of oxygen to hydrogen peroxide. The creation of hydroxyl radicals by hole transfer, on the other hand, occurs directly by water oxidation. In order to distinguish between the activity of holes and electrons in the reaction, we added 10% of triethanolamine (TEOA) to the RhB solution in the presence of the most photoactive material (CM-8h). TEOA is commonly used as a hole scavenger, meaning that under illumination, holes should be easily removed by it and will not create hydroxyl radicals.[26] Consequently, in this case the photodegradation rate should dramatically decrease. The concentration changes of RhB as a function of illumination time for the CM-C$_3$N$_4$-8h with and without TEOA are shown in Figure S11. It is clear that the degradation of RhB is strongly inhibited (for example, after 30 min of illumination the degradation is inhibited by a factor of 3), meaning that the degradation mechanism mostly involves hole transfer from the photoactive material.

In conclusion, we used supramolecular chemistry in order to template hollow carbon nitride structures by using the hydrogen-bonded melamine and cyanuric acid complex as a starting product. The hollow carbon nitride box structure was fully characterized by FT-IR, XRD, and SEM, while elemental analysis confirmed carbon nitride formation. In addition, it was found that an optimal photofunctionality of the hollow carbon nitride boxes occurred after 8 h of condensation. The changes in the sample structure were evidenced by the blue-shifted peaks of the absorbance and the emission spectra of the CM-C$_3$N$_4$ compared to those of the bulk carbon nitride. Furthermore, the creation of new sites for charge transfer was indirectly manifested by the quenching of the fluorescence intensity and its lifetime. The formation of new energy states improves the charge separation process, resulting in high photocatalytic activity of CM-C$_3$N$_4$ in the photodegradation of RhB. Moreover, we showed that various CM morphologies can be obtained using different solvents, which leads to diverse carbon nitride architectures. In all cases, the CM-C$_3$N$_4$'s exhibited superior photocatalytic activity compared to the bulk material. The utilization of cyanuric acid and melamine hydrogen-bonded complexes therefore opens new opportunities for significant improvement of carbon nitride synthesis, structure, and photoactivity.

ASSOCIATED CONTENT

Ⓢ Supporting Information

XRD, FT-IR, SEM, elemental analysis, and optical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37.

(2) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382.

(3) Mathias, J. P.; Simanek, E. E.; Zerkowski, J. A.; Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4316.

(4) Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 905.

(5) Li, X. F.; Zhang, J.; Shen, L. H.; Ma, Y. M.; Lei, W. W.; Cui, Q. L.; Zou, G. T. *Appl. Phys. A-Mater. Sci. Proc.* **2009**, *94*, 387.

(6) Goettmann, F.; Fischer, A.; Antonietti, M.; Thomas, A. *New J. Chem.* **2007**, *31*, 1455.

(7) Zheng, Y.; Jiao, Y.; Chen, J.; Liu, J.; Liang, J.; Du, A.; Zhang, W.; Zhu, Z.; Smith, C. S.; Jaroniec, M.; Lu, Q. G.; Qiao, Z. S. *J. Am. Chem. Soc.* **2011**, *133*, 20116.

(8) Wang, X. C.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. *Nat. Mater.* **2009**, *8*, 76.

(9) Schwinghammer, K.; Tuffy, B.; Mesch, E.; W.; Martineau, C.; Taulelle, F.; Schnick, W.; Senker, J.; Lotsch, V. B. *Angew. Chem., Int. Ed.* **2013**, *52*, 2435.

(10) Zhang, J. S.; Chen, X. F.; Takanabe, K.; Maeda, K.; Domen, K.; Epping, J. D.; Fu, X. Z.; Antonietti, M.; Wang, X. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 441.

(11) Liu, G.; Niu, P.; Sun, C. H.; Smith, S. C.; Chen, Z. G.; Lu, G. Q.; Cheng, H. M. *J. Am. Chem. Soc.* **2010**, *132*, 11642.

(12) Li, J.; Shen, B.; Hong, Z.; Lin, B.; Gao, B.; Chen, Y. *Chem. Commun.* **2012**, *48*, 12017.

(13) Du, A.; Sanvito, S.; Li, Z.; Wang, D.; Jiao, Y.; Liao, T.; Sun, Q.; Ng, H. Y.; Zhu, Z.; Amal, R.; Smith, C. S. *J. Am. Chem. Soc.* **2012**, *134*, 4393.

(14) Lin, Z.; Wang, X. *Angew. Chem., Int. Ed.* **2009**, *113*, 4940.

(15) Zheng, Y.; Liu, J.; Liang, J.; Jaroniec, M.; Qiao, S. Z. *Energy Environ. Sci.* **2012**, *5*, 6717.

(16) Simanek, E. E.; Mammen, M.; Gordon, D. M.; Chin, D.; Mathias, J. P.; Seto, C. T.; Whitesides, G. M. *Tetrahedron* **1995**, *51*, 607.

(17) Tracz, A.; Jeszka, J. K.; Watson, M. D.; Pisula, W.; Mullen, K.; Pakula, T. *J. Am. Chem. Soc.* **2003**, *125*, 1682.

(18) Kailasam, K.; Epping, J. D.; Thomas, A.; Losse, S.; Junge, H. *Energy Environ. Sci.* **2011**, *4*, 4668.

(19) Liang, J.; Zheng, Y.; Liu, J.; Jurcakova, H. D.; Jaroniec, M.; Qiao, Z. S. *Angew. Chem., Int. Ed.* **2012**, *51*, 3892.

(20) Jun, Y. S.; Lee, E. Z.; Wang, X. C.; Hong, W. H.; Stucky, G. D.; Thomas, A. *Adv. Funct. Mater.* **2013**, DOI: 10.1002/adfm.201203732.

(21) Arrachart, G.; Carcel, C.; Trens, P.; Moreau, J. J. E.; Man, M. W. C. *Chem.—Eur. J.* **2009**, *15*, 6279.

(22) Jurgens, B.; Irran, E.; Senker, J.; Kroll, P.; Muller, H.; Schnick, W. *J. Am. Chem. Soc.* **2003**, *125*, 10288.

(23) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer: Berlin, 2009.

(24) Takizawa, T.; Watanabe, T.; Honda, K. *J. Phys. Chem.* **1978**, *82*, 1391.

(25) Fan, Y. Z.; Chen, G. P.; Li, D. M.; Luo, Y. H.; Lock, N.; Jensen, A. P.; Mamakhel, A.; Mi, J. L.; Iversen, S. B.; Meng, Q. B.; Iversen, B. B. *Int. J. Photoenergy* **2012**, 173865.

(26) Liu, S. W.; Yin, K.; Ren, W. S.; Cheng, B.; Yu, J. G. *J. Mater. Chem.* **2012**, *22*, 17759.