Switchable Nanoassembly from an Azobenzene-Containing Dye

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In this work, we investigated optical properties and the morphology of the amphiphilic azobenzene dye 1 containing hydroxyl azobenzene and C10 alkyl chains. Since the hydroxyl group on 1 has a pK_a of 9.38, the deprotonation of the hydroxyl group occurs at pH > pK_a (9.38) and thus the 1 nanoparticles are negatively charged. The deprotonated hydroxyl group is hydrophilic relative to the long alkyl chain that is hydrophobic, while the hydrophobic and hydrophilic parts are connected by covalent bonds. When such an azobenzene molecule 1 with both hydrophobic and hydrophilic groups exists in solution, “self-aggregation” may occur due to the hydrophobic interaction between the long alkyl chains. The scattered morphology at pH 7.0 (neutral state) and the aggregated morphology at pH 10.5 (anionic state) of 1 were demonstrated by transmission electron microscopy (TEM) and atomic force microscopy (AFM) images. Formation of supramolecular aggregation-induced vesicular-like structures are highly interesting due to the ability to respond to external triggers, pH. The pH value can be reversed by adding acid or base to the system, that is, switching the aggregation “on” and “off” can be repeated.

Keywords: Nanoassembly, Switchable, pH, Morphology, Dye, Azobenzene-Containing.

1. INTRODUCTION

Supramolecular assemblies obtained by self-organization of small building units are of high interest in nanotechnology, and in the associated development of functional materials such as soft materials, electronic materials, nanomaterials and molecular machines. The fabrication of nanometer-scaled, supramolecular architectures with unique structures and functions is a key aspect in supramolecular chemistry and nanoscience. Azo dyes are a versatile class of colored organic compounds that have been used as metal-chelates for dyeing protein fibers and chromogenic indicators in analytical chemistry, etc. Self-assembled aggregates of azobenzene derivatives have also been reported. The optical and electronic properties of organic-based materials are highly dependent on their size and shape. With regard to the growing field of nanotechnology, it is thus highly desirable to develop new concepts for self-assembly and responsive nanostructures.

Previously, the azo dye 1 was synthesized and demonstrated to be an effective colorimetric chemosensor toward zinc ions. The structure of 1 was shown in Figure 1. 1, with a pK_a of 9.38, was not affected by pH values ranging from pH 5 to pH 9. At neutral state, 1 has two tautomeric forms, the azo form and hydrazone form (see Fig. 1(a)). At anionic state, 1 exists as the azo form alone (see Fig. 1(b)). In the UV-vis spectra, the bands at approximately 325 nm and 477 nm were assigned to the π-π* transition of the azo form and the band at approximately 384 nm was assigned to the π-π* transition of the hydrazone form. In this work, we further investigated the optical properties and the pH controlled supramolecular structure of 1. It should be mentioned that 1 exhibited unique pH-dependent aggregation-induced vesicular-like structures in MeOH/H_2O solution.

2. EXPERIMENTAL DETAILS

2.1. Chemicals and Instruments

1 was derived from 2,2′-dihydroxyazobenzene (DHAB) and 10-undecenoyl chloride according to the procedure previously reported by the authors. A pH 64 Radiometer (Copenhagen, Denmark) combined with a GK 2401 B electrode was used for the pH measurements. 0.2 M NaOH was used to give the required pH 10.5. The UV-vis spectra and the fluorescence emission spectra were measured using Hitachi U-2010 and F-4500 spectrometers, respectively. The transmission electron microscopy (TEM) images were obtained using a JEOL-JEM2010 electron microscope operated at 200 kV. The atomic force

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3. RESULTS AND DISCUSSION

3.1. Effect of Water Content

At neutral state, 1 was not soluble in water and can be easily dissolved in organic solvents such as MeOH. The solvent polarity can greatly influence the absorption and fluorescence emission spectra of 1. Herein, we studied the response of the absorption and fluorescence spectra of 1 to the water ratios in MeOH/H₂O cosolvents as shown in MeOH/H₂O (v/v, 7/3) solution. This solution was monitored spectrophotometrically and found to be stable for months. More dilute solutions were prepared by further dilution of the stock. To prepare the TEM samples for the examination of the size and the morphology of the aggregation, a drop of the dilute MeOH/H₂O (v/v, 7/3) solution was deposited onto a copper grid, which had been precoated with a thin film of polyvinyl formal and then coated with carbon. Two minutes after the deposition, the excess solution was blotted away with a strip of filter paper. This process was repeated for several times to ensure that there was enough sample absorbed on the grid. For the AFM measurements, nanoparticles were transferred onto a quartz substrate from MeOH/H₂O (v/v, 7/3) solution.

2.2. Measurements

3 × 10⁻⁴ M stock solution of the azo dye 1 was prepared by dissolving the appropriate weight of the solid in microscropy (AFM) images were collected using a Digital Instruments Nanoscope III microscope, operated in tapping mode in ambient air using a silica glass as substrates.

Fig. 1. (a). Two tautomeric forms (azo form (left) and hydrazone form (right)) of 1 at neutral state; (b) structure of 1 at anionic state.

Fig. 2. (a) UV-vis absorption spectra of 1 (6 × 10⁻⁵ M) at different water ratios in MeOH/H₂O cosolvents, (b) effect of water ratios on the absorption spectra of 1, (c) fluorescence emission spectra of 1 (6 × 10⁻⁵ M) at different water ratios in MeOH/H₂O cosolvents λₑ = 320 nm, and (d) the maximum emission wavelength of 1 (6 × 10⁻⁵ M) at different water ratios in MeOH/H₂O cosolvents.
Fig. 3. Absorption spectra (left) of 1 under different concentrations ($10^{-6}$ M–$10^{-4}$ M) in MeOH/H$_2$O cosolvents (v/v, 7/3, pH 7.0); fluorescence spectra (right) of 1 under different concentrations ($10^{-6}$ M–$10^{-4}$ M) in MeOH/H$_2$O cosolvents (v/v, 7/3, pH 7.0); and plot of the $A_{384}/A_{325}$ in the absorption spectra and $F/F_{10^{-6}}$ in the fluorescence spectra versus concentration of 1 in MeOH/H$_2$O cosolvents (v/v, 7/3, pH 7.0), where A and F denote the absorption and the fluorescence intensity, respectively.

Figure 2. The changes of the fluorescence emission intensity and the maximum emission wavelength were observed when excited at 320 nm by changing the water ratios (Figs. 2(c, d)). With increasing water fraction, the maximum emission wavelength initially showed a significant red shift. However, a prominent blue shift was observed at a MeOH/H$_2$O ratio > 7:3. An increasing water fraction enhances the polarity of the system, which produces a red shift in emission because the alkyl chain of 1 can rotate internally more freely with respect to the benzene ring. Aggregation can occur when water dominates the system. In this case, the nanoparticles that are formed restrict the rotation of the alkyl chain with respect to the benzene ring, resulting in a blue shift in emission. Therefore, the polarity effect of water reaches a maximum at a MeOH/H$_2$O ratio of approximately 7:3. However, when the water ratio is increased further, the aggregation effect of the system due to dominating water rules out the polarity effect. Similar results were obtained in the absorption spectra (Figs. 2(a, b)). As indicated above, the amount of water in the final solution affects the absorption and fluorescence: a MeOH/H$_2$O ratio of approximately 7:3 has

Fig. 4. Absorption spectra of 1 ($3.0 \times 10^{-7}$ M) at pH 7.0 and pH 10.5 in MeOH/H$_2$O cosolvents (v/v, 7/3).
Fig. 5. (a) TEM image of $1$ ($3.0 \times 10^{-5}$ M) was transferred onto a quartz substrate from MeOH/H$_2$O (v/v, 7/3) solution at pH 7.0. (b) TEM image of $1$ ($3.0 \times 10^{-5}$ M) was transferred onto a quartz substrate from MeOH/H$_2$O (v/v, 7/3) solution at pH 10.5. (c) AFM height image of $1$ ($3.0 \times 10^{-5}$ M) was transferred onto a quartz substrate from MeOH/H$_2$O (v/v, 7/3) solution at pH 10.5, and (d) AFM 3D image of $1$ ($3.0 \times 10^{-5}$ M) was transferred onto a quartz substrate from MeOH/H$_2$O (v/v, 7/3) solution at pH 10.5.

To obtain an insight into the concentration dependence of absorption spectra and fluorescence spectra, the solutions of $1$ at concentrations ranging from $10^{-6}$ M to $10^{-4}$ M were prepared in MeOH/H$_2$O (v/v, 7/3, pH 7.0). As shown in Figure 3, the $A_{325}/A_{384}$ and F/F$_1$ ratios of $1$ remained almost unchanged by altering the solution concentration of $1$ which suggested the absence of any self-aggregation under the experimental concentrations from $10^{-6}$ M to $10^{-4}$ M at neutral state in MeOH/H$_2$O cosolvents (v/v, 7/3, pH 7.0).$^{46-47}$

3.2. Effect of pH on the Morphology of $1$

$1$ is a hydrophobic compound, containing the hydroxyl azobenzene and a 10 C alkyl chains which has the ability to form an amphiphile by deprotonating the hydroxyl groups on $1$. The absorption spectra of the dye $1$ ($6 \times 10^{-5}$ M) at different pH values ranging from 1 to 14 had been shown in our previous works.$^{43}$ This system is stable ranging from pH 5 to pH 9 with two absorption peaks, 325 nm (azo form) and 384 nm (hydrazone form), while the azo form is the predominant form. At higher pH value, a new absorption peak appeared at 477 nm which was attributed to the deprotonation of the hydroxyl group and the peak at 384 nm for the hydrazone form disappeared, that is, $1$ existed as the azo form at higher pH values (Figs. 1 and 4).$^{43}$ The pK$_{a}$ value of $1$ was established to be 9.38 which was calculated by using the absorbance centered at 325 nm and 477 nm. Because the hydroxyl group on $1$ has a pK$_{a}$ of 9.38, at acid and neutral pH values, the nanoparticles are stable and are mainly hydrophobic with hydrophobic alkyl long chain and one hydrophile of the hydroxyl group$^{32}$ which participates in intramolecular hydrogen bonding.$^{43-44}$ The deprotonation of the hydroxyl group occurs at pH > pK$_{a}$ (9.38), in this case, the nanoparticles are negatively charged. The deprotonated hydroxyl group is hydrophilic relative to the long alkyl chain which is hydrophobic, while the hydrophobic and hydrophilic parts are connected by covalent bonds. In other words, the two opposite parts cannot be separated without destroying the bonds. When such an azobenzene molecule $1$ with a dual hydrophobic–hydrophilic exists in solution, the self-aggregation may occur due to the hydrophobic interaction between the long alkyl chains.$^{29}$ In order to demonstrate the above expectations, a pH dependent test experiment was carried out. Two pH values, pH 7.0 (neutral state) and pH 10.5 (above pK$_{a}$ 9.38, anionic state) was selected to study the controlled morphology of $1$ by pH values. The
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morbidity of 1 was examined by using TEM and AFM microscopic techniques (Figs. 5, 6, 7). As illustrated by the results in Figures 5(a) and 7, TEM (Fig. 5(a)) and AFM images (Fig. 7) of 1 revealed scattered nanoparticles with some roughness at pH 7.0, that is, no aggregates were present. At pH 10.5, 1 exists as the anionic state (Fig. 1(b)) because of the fully deprotonation of the hydroxyl group. Contrary to the results observed at pH 7.0, both TEM (Fig. 5(b)) and AFM images (Figs. 5(c, d) and 6) of 1 provided a clearer indication of the self-assembly aggregation structures at pH 10.5. Interestingly, the TEM images was assumed to form vesicular aggregates (Fig. 5(b)), Figure 5(b) (inset) demonstrated that the spheres were actually hollow. The vesicles shown in the AFM image formed a large size distribution when the nanoparticles were transferred from a MeOH/H2O cosolvent to a quartz substrate, these vesicular nanoparticles had a bigger average size and a diameter in the range of 280–720 nm. According to AFM data (Figs. 5(c, d) and 6), the nanoparticles of 1 self-assembles into a typical vesicular structure, the interior of the vesicles was hollow, similar to that visualized from the TEM images. In our case, aggregates are present at pH 10.5, subsequent addition of acid then allows switching back to the scattered state (pH 7.0). The aggregated state and scattered state of 1 was switchable and this reversibility of the morphological transition can be attributed to the reversible protonation and deprotonation of the hydroxyl group on 1. These observations clearly showed that the nanoparticle aggregation of 1 was pH dependence and the morphology of 1 was controllable as a function of pH. As the pH value can be reversed by adding sodium hydroxide or acid to change pH from 7.0 to 10.5 or from 10.5 to 7.0. In addition to 1, the synthesis of new, organic-based materials is important for the formation of supramolecular aggregates with uniform volume and size distribution. We are currently working along these lines.

4. CONCLUSIONS

In conclusion, the aggregation of o,o’-dihydroxy azo dye 1 in solution is highly affected by pH. At neutral state (pH 7.0), there is no aggregation behavior of 1 under the experimental concentrations (10^{-6} – 10^{-4} M, MeOH/H2O, v/v, 7/3), while at the anionic state (pH 10.5), self-assembly occurs. In our case, the supramolecular vesicular-like structures are highly interesting due to the ability to respond to external triggers, pH. The aggregation can be repeatedly switched “on” and “off” by pH which is adjusted through adding sodium hydroxide or acid to change pH from 7.0 to 10.5 or from 10.5 to 7.0. In addition to 1, the synthesis of new, organic-based materials is important for the formation of supramolecular aggregates with uniform volume and size distribution. We are currently working along these lines.

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References and Notes

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