

## Modulation of Luminescent Nanostructures Using Bases with Amino Acid Derivative through Co-Assembly

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### Abstract

In this study, charming luminescent nanostructures have been obtained from two components between amino acids functionalized naphthalene derivative (IN) and bases (Adenine (A), Thymine (T), Guanine (G) and Uracil (U)) units via co-assembly. These fluorescent nanotubes, walnut-like structures, nanofibers and sponge-like structures have been investigated by means of Ultraviolet Spectra (UV), Fluorescence Spectra and Scanning Electron Microscopy (SEM). The results illustrated that these nanostructures were of strong fluorescence and the drive forces were the intermolecular hydrogen bonding and  $\pi$ - $\pi$  stacking interactions.

**Keywords:** Ultraviolet spectra; Luminescent; Nanostructures; Spectrophotometer

### Introduction

Molecular self-assembly plays an important role in controlling spatiotemporal structures for the bottom-up construction design and fabrication of functional nanoscale architectures and materials from simple molecular building blocks [1-4]. Through self-assembly of nucleic acids, peptides, phospholipids and amphiphiles, varieties of charming morphologies include nanotubes, nanovesicles, nanofibers, and nanotapes emerge [5-14]. These nanostructure morphologies have been shown to be of great importance in many research fields. For instance, nanovesicles are useful for drug or gene delivery and nanotechnology [15], nanotubes and nanofibers for electrical and medical devices [16,17], biosensor fabrication [18-20] and templates for processing well-defined materials [21]. The widely application of these nanostructures in area of research is due to their unique properties superior to those of their bulk counterparts. In recent years, more and more researchers devote themselves to obtaining nanomaterials with perfect optical or electronic properties [22-25]. However, luminescent nanostructures fabricated from the amino acid analogues with bases through co-assembly have less been well studied.

Amino acids, because of their biocompatibility, structural and functional diversity, have significant advantages as building blocks for the construction of self-assembled nanostructures. As a promising  $\pi$ -conjugated chromophore, naphthalene diimide (NDI) [26-29] has been used to build a range of organized structures in solution due to its pronounced capabilities of self-assembly by means of  $\pi$ - $\pi$  stacking. Besides, bases [30] with low biotoxicity and good biocompatibility play an important role not only in the system of life but also in the field of creating self-assembled nanostructures.

Herein, we are aimed at acquiring luminescent nanostructures fabricated from the co-assembly of amino acid derivatives with bases. The amino acid derivatives contain an aromatic naphthalene core and two amino acid residues as terminal groups, which are able to form complementary hydrogen bonding interaction with bases. Thereafter, the synergist interaction between hydrogen bonding interaction and the  $\pi$ - $\pi$  stacking interaction drive the formation of well-ordered nanostructures in solution.

### Experimental Section

#### Materials

All starting materials were purchased from commercial suppliers and used without any further processing.

#### Synthesis and characterization of IN

0.2682 g (1 mmol) naphthalene-1, 4, 5, 8-tetracarboxylic dianhydride, 0.2623 g (2 mmol) isoleucine and 2.0 g imidazole were mixed and then heated to 120°C for 6 hrs. under nitrogen atmosphere. Then 100 mL ethanol was poured into the hot mixture, refluxed for 6 hrs. and kept for overnight to precipitate out. Afterward using dilute HCl to acidify solution, the resulting light yellow precipitate was concentrated by decompression filters, washed with deionized water to neutral, filtrated and dried at 80°C under vacuum. The 0.3501 g yellow powder was obtained (Yield: 70.8%). The structure and purity of the product were confirmed by <sup>1</sup>H NMR, MS and FT-IR. <sup>1</sup>H NMR (400 MHz, DMSO-d, 20°C, TMS, ppm):  $\delta$ : 8.65-8.76 (d, 4.02 H), 5.17-5.26 (d, 2.09 H), 1.91 (m, 2.04 H), 1.18-1.28 (m, 4.06 H), 0.93-0.97 (d, 6.05 H), 0.68-0.76 (t, 6.03 H). FT-IR (KBr): 3414.8, 2968.2, 2357.3, 2320.0, 1707.1, 1662.4, 1451.8, 1342.2, 1251.6, 1116.8, 770.7, 619.4, 485.2 cm<sup>-1</sup>. MS (MALDI-TOF): 494.1 (calcd. 494.5, M)

#### Characterization

NMR spectra were measured on a Bruker Ultrashield 400 (<sup>1</sup>H NMR 400 MHz) spectrometer. UV absorption spectra were obtained using a UV-2700 UV-Vis spectrophotometer. The luminescence spectra were measured on a LS55 fluorescence spectrophotometer. The path length of the quartz cell is 1 cm, while the emission band-width was 5 nm. The FT-IR spectra were recorded on an AVATAR 360 FTIR

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Received March 28, 2016; Accepted November 30, 2016; Published December 06, 2016

Citation: Liu W, Li Y, Chen L, Fan Y, Li X, et al. (2016) Modulation of Luminescent Nanostructures Using Bases with Amino Acid Derivative through Co-Assembly. Med Chem (Los Angeles) 6: 690-693. doi:10.4172/2161-0444.1000416

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spectrophotometer. The powdered samples were mixed with KBr to prepare the thin films in the solid-state FTIR studies. SEM images of these samples were recorded using FEI QUANTA 450 with accelerating voltage 5.0-15.0 kV. Samples were obtained through dropping the gels on a flat surface of a cylindrical aluminium substrate and allowed to dry at room temperature. Then the samples were coated with gold using a MSP-1S Magnetron Sputter (Japan) Coater.

### Preparation of nanostructures

Mixed the IN solution in DMF with the solution of bases which were dissolved in dilute ammonia in different ratios of the volume. Kept for a period of time and then characterized the properties of the aimed nanostructures.

## Results and Discussion

### Molecular design

The molecular structures of IN, A, T, G and U were exhibited in Scheme 1. As for the compound IN, it contains two isoleucine groups as terminal groups and a naphthalene core. The isoleucine groups have charming properties of harmless, biocompatible and biodegradable, which may contribute to biomedicine applications. Besides, as an interesting class of chromophores, 1, 4, 5, 8-naphthalenetetracarboxylic acid diimide (NDI) due to its enhanced stability and pronounced capabilities of self-assembly by means of  $\pi$ - $\pi$  stacking, which may play a vital role in functional devices.

### Morphology and driving force of nanostructures

According to the method described in the experimental section, we got the anticipated nanostructures. The morphological properties of these assembled nanostructures were initially examined by SEM.

Interestingly, a solution of IN in DMF-diluent ammonia mixed solution generated irregular flake structures (Figure S1a), which was ascribed to a slight weakening of hydrogen bonding interactions in the process of self-assembly. Figure 1a revealed the formation of nanotubes, which appeared as hollow tubular structures. As shown in Figure 1b, condensed entangled nanofibers generated a close-knit morphology, in which thinner and smaller fibers cross-linked with each other to form a three-dimensional network. Figure 1c displayed walnut-like self-assembly behavior in DMF-diluent ammonia mixed solution with IN: G=1.5: 1. The fascinating morphology was generated from thin hollow capsules

which were collapsed mostly after solvent evaporation under high vacuum. This phenomenon illustrated that the charming structures observed by SEM are hollow walnut-like structures. SEM image of IN/U=1.5: 1 system was exhibited in Figure 1d, in which a sponge-like nanostructure with charming appearance was found. The sponge-like nanostructure was composed of thin and curved nanosilk. All the silk are connected together through their cores and form sponge-like structures. However, no ordered structures could be observed by SEM with IN/base at certain molar ratio in diluent ammonia solution or in pure DMF, respectively. This phenomenon was presumably attributed to weakening of hydrogen bonding interactions in the process of aggregation and exaggerated solubility in pure DMF.

All these interesting nanostructures were attributed to complementary hydrogen bonds between adjacent IN and base molecules and the  $\pi$ - $\pi$  interaction between IN units.

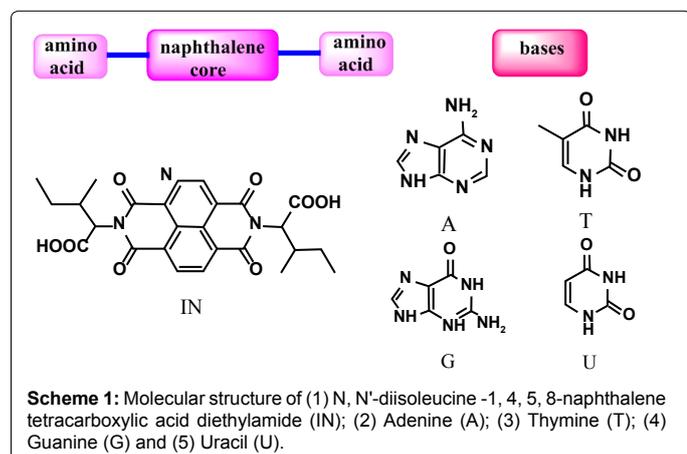
To explore  $\pi$ - $\pi$  stacking of NDI chromophores within the nanostructure of IN, UV absorption spectra were obtained using a UV-Vis spectrophotometer. IN/A in DMF-diluent ammonia mixed solution with concentration of  $10^{-4}$  M showed intense absorption at 263 nm, 362 nm and 381 nm. However, in diluent ammonia mixed solution, only absorption at about 353 nm appeared (Figure 2a). Red-shift of 9 nm and the appearance of a new absorption peak of 381 nm at a longer wavelength, which occurred going from diluent ammonia mixed solution to DMF-diluent ammonia mixed solution, are consistent with the improved aromatic  $\pi$ - $\pi$  stacking among IN and bases molecules. Meanwhile, self-assembled  $\pi$  stacks of IN/T, IN/G and IN/U exhibited nearly identical optical signature (Figures 2b-2d). Moreover, when compared IN/A to IN in DMF-diluent ammonia mixed solution, both IN and IN/A exhibited two absorption peaks (362 nm and 381 nm). This phenomenon illustrated the existence of  $\pi$ - $\pi$  stacking interaction in both IN molecules and IN/A molecules (Figure S2).

This inference could also be supported by the SEM images provided in Figure S1a. Interestingly, the UV spectra of IN/T, IN/G and IN/U were quite similar to IN, which demonstrated that  $\pi$ - $\pi$  stacking interaction was also exist between molecules in IN/T, IN/G and IN/U systems.

The difference was researched by the fluorescence spectra between IN and IN/A in DMF-diluent ammonia mixed solution. Compared to spectrum of IN ([IN]= $10^{-4}$  M) in the absence of A, the spectrum of IN/A=1: 1.5 ([IN]= $10^{-4}$  M) showed an emission peak at about 543 nm with highly enhanced fluorescence intensity and a tiny emission band at 570-600 nm (Figure 3a), which was similar to the spectrum of IN/T=1: 1.5([IN]= $10^{-4}$  M) (Figure 3b). As for the spectra of IN/G and IN/U in Figure 3c and 3d at favourable molar ratio, a broad emission band with the peak at about 543 nm with stronger fluorescence emerged, compared to pure IN in mixed solution. This phenomenon could be ascribed to the formation of aggregates in the mixed solution, which was due to the  $\pi$ - $\pi$  electronic coupling between NDI chromophores.

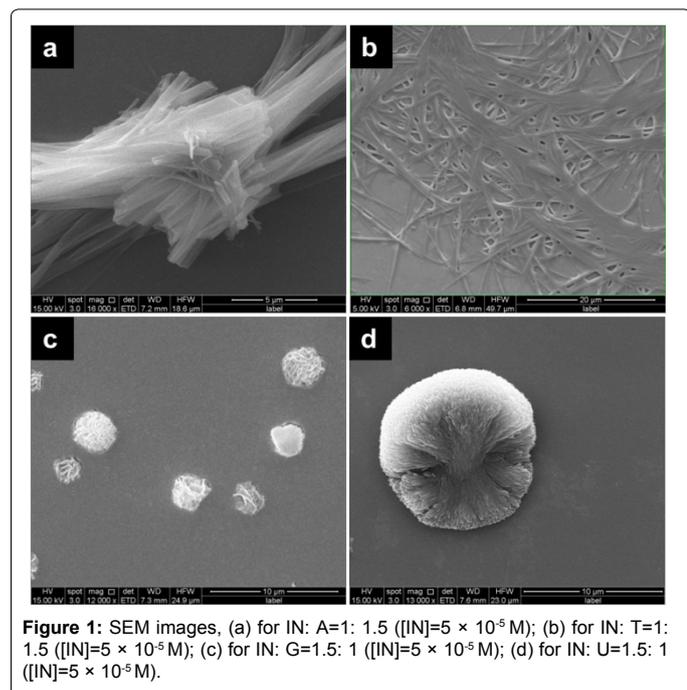
### Formation mechanism of nanostructures

By correlating the above information, the formation of all sorts of morphologies during the co-assembly can be understood using the schematic model presented in Figure 4. From the SEM images, we observed that IN, IN/A, IN/G, IN/T and IN/U systems generated various nanostructures. We also found that IN/A

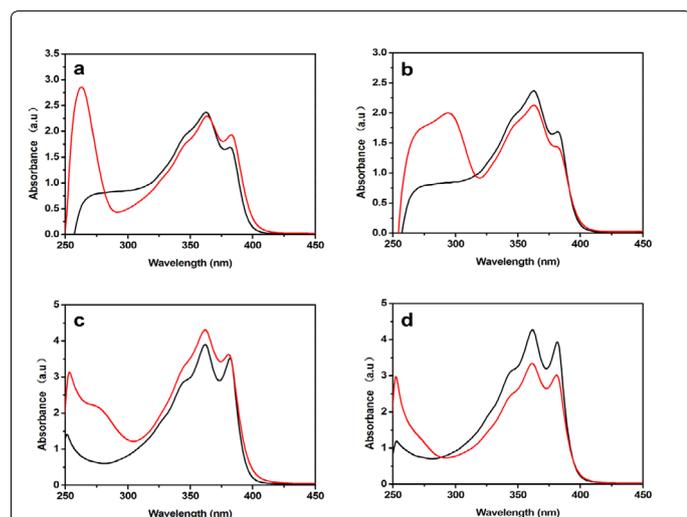


formed nanotubes, IN/G displayed walnut-like structures, IN/T exhibited nanofibers and IN/U shown sponge-like nanostructures. Interestingly, nanotubes and walnut-like structures were hollow while nanofibers and sponge-like nanostructures were solid. The generating of these hollow and solid nanostructures was attributed to the complementary hydrogen bonds and the  $\pi$ - $\pi$  interaction (Figure S3).

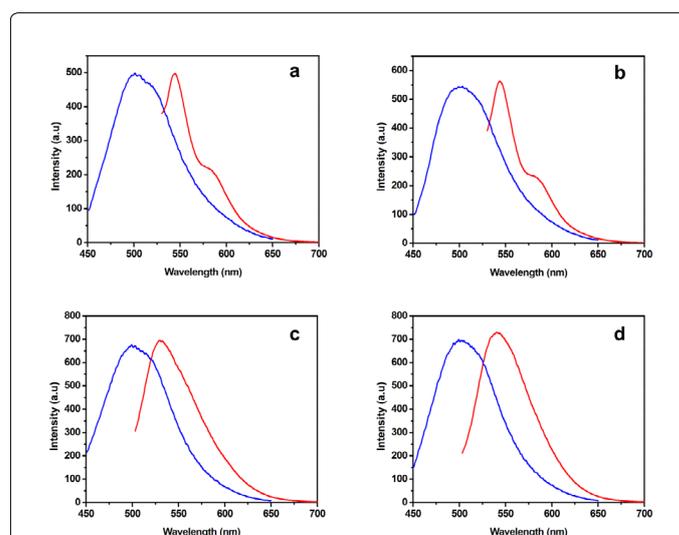
The conjectures to the formation of different nanostructures were below. Due to both A and G have five nitrogen atoms and



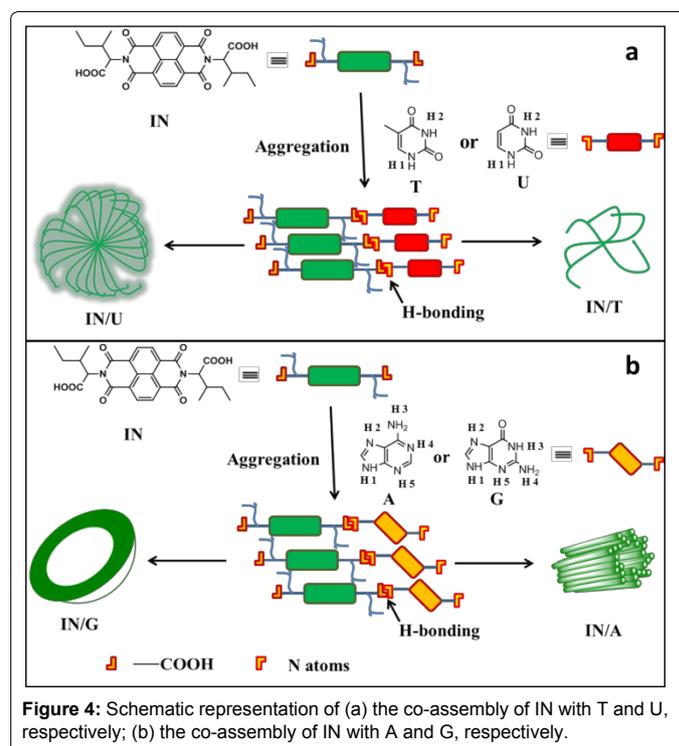
**Figure 1:** SEM images, (a) for IN: A=1: 1.5 ([IN]= $5 \times 10^{-5}$  M); (b) for IN: T=1: 1.5 ([IN]= $5 \times 10^{-5}$  M); (c) for IN: G=1.5: 1 ([IN]= $5 \times 10^{-5}$  M); (d) for IN: U=1.5: 1 ([IN]= $5 \times 10^{-5}$  M).



**Figure 2:** UV-Vis spectra of IN with base (A, T, G, U) in different solutions (blue line for IN/base in diluent ammonia solution, red line for IN/base in DMF-diluent ammonia mixed solution). (a) spectra of IN/A=1: 1.5 solutions at room temperature. [IN]= $10^{-4}$  M and [A]= $1.5 \times 10^{-4}$  M, at  $\lambda_{ex}$ =445 nm [path length=5 mm]; (b) UV-Vis spectra of IN and IN/T=1: 1.5 (black line for IN, red line for IN/T). [IN]= $10^{-4}$  M and [T]= $1.5 \times 10^{-4}$  M at  $\lambda_{ex}$ =445 nm [path length=5 mm]; (c) UV-Vis spectra of IN and IN/G=1.5: 1 (black line for IN, red line for IN/G). [IN]= $4.5 \times 10^{-4}$  M and [G]= $3.0 \times 10^{-4}$  M; (d) Spectra of IN and IN/U=2: 1 (black line for IN, red line for IN/U). [IN]= $4.5 \times 10^{-4}$  M and [U]= $2.25 \times 10^{-4}$  M.



**Figure 3:** (a) Fluorescence spectra of IN solution and IN/A=1: 1.5 solution at room temperature (black line for IN, red line for IN/A). [IN]= $10^{-4}$  M and [A]= $1.5 \times 10^{-4}$  M [path length=1.0 mm]; (b) UV-Vis spectra of IN and IN/T=1: 1.5 (black line for IN, red line for IN/T). [IN]= $10^{-4}$  M and [T]= $1.5 \times 10^{-4}$  M; (c) UV-Vis spectra of IN and IN/G=1.5: 1 (black line for IN, red line for IN/G). [IN]= $4.5 \times 10^{-4}$  M and [G]= $3.0 \times 10^{-4}$  M; (d) UV-Vis spectra of IN and IN/U=2: 1 (black line for IN, red line for IN/U). [IN]= $4.5 \times 10^{-4}$  M and [U]= $2.25 \times 10^{-4}$  M.



**Figure 4:** Schematic representation of (a) the co-assembly of IN with T and U, respectively; (b) the co-assembly of IN with A and G, respectively.

the nitrogen atoms participated in H-bond formation were diverse, the hydrogen bonds between carboxyl groups of IN and nitrogen atom of A and G were dissimilar. It speculated that the combination of carboxyl groups of IN with nitrogen atoms H1, H3 (separated by five bonds) of A through hydrogen bonds made it possible to generate tubular structures (Figure 4a). However, in consequence of steric effect, only the nitrogen atoms H1, H4 (separated by four bonds) of G participate in H-bonding, which

led to forming of walnut-like structures (Figure 4a). Similarly, the nitrogen atoms involved in H-bonding in T or U were close to each other, which enabled the generation of solid nanostructures (Figure 4b).

## Conclusions

In summary, we have obtained luminescent nanostructures with highly intense fluorescence fabricated from the co-assembly of amino acid derivatives IN with bases in DMF-diluent ammonia mixed solution. These components assembled into well-defined nanotubes, walnut-like structures, nanofibers and sponge-like structures based on the complementary hydrogen bonds between adjacent IN and bases molecules and the  $\pi$ - $\pi$  interaction between IN units. These interactions are responsible for the formation of luminescent nanostructures. The nanostructures may play potential application as biomaterials in the field of biomedical.

## Acknowledgements

This work was supported by National Natural Science Foundation of China (Nos. 51463002, 21303024, 21365003, 21473041, 21463003, 51478123). The Jiangxi outstanding youth fund (20153BCB23001) and Jiangxi Provincial project of scientific and technological innovation team (20152BCB24008) are also gratefully acknowledged.

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