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 π-π 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 π-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 π-π 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 π-π 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 decomposition 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 ‘H NMR, MS and FT-IR. ‘H NMR (400 MHz, DMSO-d6, 20°C, TMS, ppm): 8: 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 -1. MS (MALDI-TOF): 494.1 (calcd. 494.5, M)

Characterization
NMR spectra were measured on a Bruker Ultrashield 400 (1H 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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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 π-π 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 structures. As shown in Figure 1c, displayed walnut-like self-assembly behavior fibers cross-linked with each other to form a three-dimensional network. Figure 1d revealed the formation of aggregates in the mixed solution, 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. 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 π-π interaction between IN units.

To explore π-π 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 π-π stacking among IN and bases molecules. Meanwhile, self-assembled π 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 π-π 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 π-π 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^-3 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 π-π 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 π-π interaction (Figure S3).

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

Figure 1: SEM images, (a) for IN: A=1: 1.5 ([IN]=5 × 10^{-5} M); (b) for IN: T=1: 1.5 ([IN]=5 × 10^{-5} M); (c) for IN: G=1.5: 1 ([IN]=5 × 10^{-4} M); (d) for IN: U=1.5: 1 ([IN]=5 × 10^{-2} 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 (black line for IN, red line for IN/A). [IN]=10^{-4} M and [A]=1.5 × 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 × 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 × 10^{-4} M and [G]=3.0 × 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 × 10^{-4} M and [U]=2.25 × 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 × 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 × 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 × 10^{-4} M and [G]=3.0 × 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 × 10^{-4} M and [U]=2.25 × 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.

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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 π-π 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.

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References

1. Zhang S (2003) Fabrication of novel biomaterials through molecular self-assembly. Nat Biotechnol 21: 1171-1178.
2. Lai YT, Tsai KL, Sawaya MR, Asturias FJ, Yeates TO (2013) Structure and flexibility of nanoscale protein cages designed by symmetric self-assembly. J Am Chem Soc 135: 7738-7743.
3. Quan Z, Xu H, Wang G, Wen X, Wang Y, et al. (2014) Solvent-mediated self-assembly of nanocube superlatives. J Am Chem Soc 136: 1352-1359.
4. Kumar DK, Steed JW (2014) Supramolecular gel phase crystallization: orthogonal self-assembly under non-equilibrium conditions. Chem Soc Rev 43: 2080-2088.
5. Ghandri MR, Granja JR, Milligan RA, McBee DE, Khazanovich N (1993) Self-assembly of organic nanotubes based on a cyclic peptide architecture. Nature 366: 324-327.
6. Yang R, Chen L, Zhang T, Yang S, Leng X, et al. (2014) Self-assembly of ferritin nanocages into linear chains induced by poly (α-L-lysine). Chem Commun 50: 481-483.
7. Vauthey S, Santoso S, Gong H, Watson N, Zhang S (2002) Molecular self-assembly of surfactant-like peptides to form nanotubes and nanovesicles. Proc Natl Acad Sci USA 99: 5355-5360.
8. Zastavker YV, Asherie N, Lomakin A, Pande J, Donovan JM, et al. (1999) Self-assembly of helical ribbons. Proc Natl Acad Sci USA 96: 7883-7887.
9. Kuzuyk A, Schreiber R, Fan Z, Pardatscher G, Roller EM, et al. (2012) DNA-based self-assembly of chiral plasmic nanostructures with tailored optical response. Nature 453: 311-314.
10. Aggeli A, Bell M, Boden N, Keen JN, Knowles PF, et al. (1997). Responsive gels formed by the spontaneous self-assembly of peptides into polymeric β-sheet tapes. Nature 386: 259-262.
11. Reches M, Gazit E (2003) Casting metal nanowires within discrete self-assembled peptide nanotubes. Science 300: 625-627.
12. Cao H, Zhu X, Liu M (2013) Self-assembly of Racemic Alanine Derivatives: Unexpected Chiral Twist and Enhanced Capacity for the Discrimination of Chiral Species. Angew Chem Int Ed Engl 52: 4122-4126.
13. Raeburn J, Carcino AZ, Adams DJ (2013) The importance of the self-assembly process to control mechanical properties of low molecular weight hydrogels. Chem Soc Rev 42: 5143-5156.
14. Hartgerink JD, Beniaeh E, Stupp SI (2001) Self-assembly and mineralization of peptide-aminephilic nanofibers. Science 294: 1684-1688.
15. Allen TM, Cullis PR (2004) Drug delivery systems: entering the mainstream. Science 303: 1818-1822.
16. Schnur JM (1993) Lipid tubules: a paradigm for molecularly engineered structures. Science 262: 1669-1676.
17. Yang C, Wang Z, Ou C, Chen M, Wang L, et al. (2014) A supramolecular hydrogelator of curcumin, Chem Commun 50: 8413-8415.
18. Ibrahim S, Narinesingh D, Guiseppi-Elie A (2002) Bio-smart hydrogels: co-joined molecular recognition and signal transduction in biosensor fabrication and drug delivery. Biosens Bioelectron 17: 973-981.
19. Sun C, Chen X, Han Q, Zhou M, Mao C, et al. (2013) Fabrication of glucose biosensor for whole blood based on Au hyperbranched polyester nanoparticles multilayers by antibiofouling and self-assembly technique. Anal Chim Acta 778: 17-23.
20. Sun X, Xu Q, Kim G, Flower SE, Lowe JP, et al. (2014) A water-soluble boronate-based fluorescent probe for the selective detection of peroxynitrite and imaging in living cells. Chem Sci 5: 3368-3373.
21. Zhang Q, Ariga K, Okabe A, Aida T (2004) A condensable amphiphile with a cleavable tail as a “lizard” template for the sol-gel synthesis of functionalized mesoporou silica. J Am Chem Soc 126: 988-989.
22. Zhang X, Rehm S, Safont-Sempere MM, Würtzner F (2009) Vesicular perylene dye nanocapsules as supramolecular fluorescent pH sensor systems. Nat Chem 1: 623-629.
23. Naluri SKM, Berdugo C, Javid N, Frederix PW, Ulijn RV (2014) Biocatalytic Self-Assembly of Supramolecular Charge-Transfer Nanostructures Based on n-Type Semiconductor-Attached Peptides. Angew Chem Int Ed Engl 53: 5882-5887.
24. Zhao YS, Fu H, Peng A, Ma Y, Xiao D, et al. (2008). Low-Dimensional Nanomaterials Based on Small Organic Molecules: Preparation and Optoelectronic Properties. Adv Mater 20: 2859-2876.
25. Sukul PK, Ashdana D, Mukhopadhyay P, Summa D, Muccioli L, et al. (2011) Assemblies of perylene diimide derivatives with melamine into luminescent hydrogels. Chem Commun 47: 11858-11860.
26. Holman GG, Zewail-Boothe M, Smith AR, Johnson KA, Iverson BL (2011) A sequence-specific threading tetra-intercalator with an extremely slow dissociation rate constant. Nat Chem 3: 875-881.
27. Sakai N, Bhosale R, Emery D, Mareda J, Matile S (2010) Supramolecular n/p-heterojunction photosystems with antiparallel redox gradients in electron-and hole-transporting pathways. J Am Chem Soc 132: 6923-6925.
28. Bhosale SV, Jani CH, Langford SJ (2008) Chemistry of naphthalene diimides. Chem Soc Rev 37: 331-342.
29. Tu S, Kim SH, Joseph J, Modarelli DA, Parquette JR (2011) Self-Assembly of a Donor–Acceptor Nanotube. A Strategy To Create Bicontinuous Arrays. J Am Chem Soc 133: 19125-19130.
30. Narayanaswamy N, Avinash MB, Govindaraju T (2013) Exploring hydrogen bonding and weak aromatic interactions induced assembly of adenine and thymine functionalised naphthalenediimides. New J Chem 37: 1302-1308.