Self-assembled nanostructures of linear arylacetylenes and their aza-substituted analogues

Xu, Jia-Ju; Yang, Xiong-Bo; Feng, Hua; Wang, Yu-Long; Shan, Hai-Quan; Xu, Zong-Xiang; Ng, Chi-On; Huang, Long-Biao; Ko, Chi-Chiu; Roy, V. A L

Published in:
AIP Advances

Published: 01/06/2016

Document Version:
Final Published version, also known as Publisher's PDF, Publisher's Final version or Version of Record

License:
CC BY

Publication record in CityU Scholars:
Go to record

Published version (DOI):
10.1063/1.4954036

Publication details:

Citing this paper
Please note that where the full-text provided on CityU Scholars is the Post-print version (also known as Accepted Author Manuscript, Peer-reviewed or Author Final version), it may differ from the Final Published version. When citing, ensure that you check and use the publisher's definitive version for pagination and other details.

General rights
Copyright for the publications made accessible via the CityU Scholars portal is retained by the author(s) and/or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights. Users may not further distribute the material or use it for any profit-making activity or commercial gain.

Publisher permission
Permission for previously published items are in accordance with publisher's copyright policies sourced from the SHERPA RoMEO database. Links to full text versions (either Published or Post-print) are only available if corresponding publishers allow open access.

Take down policy
Contact lbscholars@cityu.edu.hk if you believe that this document breaches copyright and provide us with details. We will remove access to the work immediately and investigate your claim.

Download date: 14/11/2019
Self-assembled nanostructures of linear arylacetylenes and their aza-substituted analogues

Jia-Ju Xu, Xiong-Bo Yang, Hua Feng, Yu-Long Wang, Hai-Quan Shan, Zong-Xiang Xu, Chi-On Ng, Long-Biao Huang, Chi-Chiu Ko, and V. A. L. Roy

Citation: AIP Advances 6, 065210 (2016); doi: 10.1063/1.4954036
View online: https://doi.org/10.1063/1.4954036
View Table of Contents: http://aip.scitation.org/toc/adv/6/6
Published by the American Institute of Physics

Articles you may be interested in

Tetra-methyl substituted copper (II) phthalocyanine as a hole injection enhancer in organic light-emitting diodes
AIP Advances 5, 107205 (2015); 10.1063/1.4932633

Organic electroluminescent devices with improved stability

Organic phototransistor based on intramolecular charge transfer in a bifunctional spiro compound

Small molecular weight organic thin-film photodetectors and solar cells
Journal of Applied Physics 93, 3693 (2003); 10.1063/1.1534621

Organic electroluminescent diodes

Optical and electrical properties study of sol-gel derived Cu2ZnSnS4 thin films for solar cells
AIP Advances 4, 097115 (2014); 10.1063/1.4895520
Self-assembled nanostructures of linear arylacetylenes and their aza-substituted analogues

Jia-Ju Xu,1,2 Xiong-Bo Yang,2 Hua Feng,3 Yu-Long Wang,1 Hai-Quan Shan,1 Zong-Xiang Xu,1,a Chi-On Ng,3 Long-Bliao Huang,2 Chi-Chiu Ko,3,a and V. A. L. Roy2,a
1Department of Chemistry, South University of Science and Technology of China, Shenzhen, P. R. China, 518055
2Department of Physics and Materials Science and Centre of Super Diamond and Advanced Films (COSDAF), City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
3Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

(Received 12 May 2016; accepted 2 June 2016; published online 10 June 2016)

A series of linear phenylene ethynylene molecules have been synthesized, and aza-substitution has been used as a strategy to fine-tune the properties of the molecules. All the compounds exhibited pure blue emission both in solution and solid state, and fluorescence quantum yields as high as 0.66, 0.63 and 0.82 were found in chloroform solutions. The well-defined nanostructures such as quasi-cubes, cubes and rods were fabricated by self-assembly method from these compounds. The photophysical properties and aggregation behavior of self-assembled structures were analyzed in detail. The morphology as well as photophysical properties of these nanostructures have been tuned with selective requirements. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4954036]

Arylacetylene materials have received considerable attention as optoelectronic or electronic materials due to their abundant π-conjugation.1–3 Over the last decade, significant progress has been made for the development of this class of functional materials, and some of them (linear phenylene ethynylene molecules) have been found to exhibit desirable properties in charge transport, energy transfer and luminescence.4–11 One of the most appealing characteristic of phenyl acetylene molecules is their linear structure that potentially offers efficient π-stack between neighbouring molecules.10 It has been reported that in the solid state phenyl acetylene molecules can self-organize via cofacial interactions, resulting in close packed molecular aggregates.10 On the other hand, structural modification of such materials can be easily achieved by controlling the length of π-conjugation of the molecules or introducing substituents or hetero-atoms to the linear primary frameworks, leading to the systematical change in the physical, electronic, and optoelectronic properties. With this in mind, a series of linear phenylene ethynylene molecules as well as their aza-substituted analogues (Scheme 1) have been synthesized and studied in this report.

As a matter of fact, the properties of materials not only depend on intrinsic properties of molecules but also depend on molecular aggregation state, particularly, when molecules were fabricated into nanostructures, the morphologies of nanoscale semiconductors usually bring significant changes to electronic properties, and play an important role in electronic devices.12–14 Recent self-assembly studies reveal that weak noncovalent intermolecular interactions can be employed to fine-tune molecular alignments, and create well-defined supramolecular structures.15–18 However, studies of linear molecules with extended π-conjugated system that assemble into well-defined nanostructures are relatively uncommon. Such linear molecules are particularly attractive.

---

1Author to whom correspondence should be addressed. Electronic mail: xuzx@sustc.edu.cn, vinccko@cityu.edu.hk, val.roy@cityu.edu.hk
SCHEME 1. Linear molecules studied herein.

building blocks for supramolecular chemistry because: 1) their phenyl, pyrimidine, and C≡C triple bond moieties offer π-π interaction to enhance the stacking of molecules in aggregated state;\textsuperscript{19,20} 2) the introduction of hetero-atoms to linear primary frameworks provides C–H···X (X: O, N, and etc.) or dipole-dipole interaction between molecules, and thus could lead to molecules that form well-defined arrays in solution; and 3) such self-organized nanostructures are expected to show interesting performance in optoelectronics, sensors, and electronic circuits\textsuperscript{21} because of their well-defined channels for charge carriers. Herein, we describe self-assembled nanostructures fabricated from the above materials (2, 3, 4, and 5, Scheme 1).

In order to better understand the electronic structures of the synthesized compounds, we explored their properties using density functional theory (DFT). Molecular-orbital calculations of 2, 3, 4 and 5 were carried out at the B3LYP/6-31G (d) level, and all the compounds were predicted to adopt planar geometries (optimized geometries) (Fig. S1 in the supplementary material\textsuperscript{22}). The calculated results showed that with the replacement of CH groups by nitrogen atoms, both HOMO and LUMO energy levels of pyrimidine-containing molecules (HOMO level -5.80 eV and LUMO level -2.12 eV for 2, and HOMO level -5.71 eV and LUMO level -2.53 eV for 3) decreased significantly compared with their corresponding phenylene ethynylene molecules (HOMO level -5.42 eV and LUMO level -1.71 eV for 4, and HOMO level -5.25 eV and LUMO level -2.07 eV for 5). Also, the reduction of HOMO-LUMO energy band gaps was observed by the introduction of pyrimidine moieties to the linear molecules, and the calculated band gap ($E_{\text{gap}}$) was found to decrease in the following order of 4 > 2 > 5 ∼ 3 (Table S1 in the supplementary material\textsuperscript{22}).

The calculated results were consistent with UV-Vis and fluorescence spectra in dilute solutions. As shown in Fig. 1(a), the lowest energy bands in the absorption spectra of 2-5 in dilute chloroform solutions occurred between 250 and 402 nm, the absorption spectra of 2 showed structured absorption with maximum ($\lambda_{\text{max}}$) at 326 nm and a shoulder at ca. 341 nm, undergoing a slight red-shift (6 nm) in the absorption maximum relative to that of 4 ($\lambda_{\text{max}}$ at 320 nm). Similarly, the introduction of nitrogen atoms to the linear phenylene ethynylene structure resulted in the reduction of HOMO-LUMO energy gap, and led to a slight red-shift (4 nm) in the absorption maximum from 3 to 5. According to the UV-Vis spectra, the optical band gaps determined from the initial absorption were 3.42, 3.09, 3.52,
FIG. 1. (a) Normalized UV-Vis absorption spectra of 2, 3, 4 and 5 in chloroform solutions. (b) Normalized emission spectra of 2, 3, 4 and 5 in chloroform solutions. The emission spectra were measured upon excitation at 310 nm.

and 3.17 eV for 2-5, respectively, which are in good agreement with the calculated data (Table S1 in the supplementary material). In addition, red-shifts of emission bands in fluorescence spectra have been observed due to aza-substitution (Fig. 1(b)). Upon excitation at 310 nm, compounds 3, 4 and 5 exhibited deep blue photoluminescence with highly structured emission band peaking at 393, 347 and 387 nm for 3, 4 and 5, respectively. Fluorescence quantum yields were determined by excitation at 310 nm in dilute chloroform solutions (1×10^-6 M) at 298 K, and quantum yields as high as 0.66, 0.63 and 0.82 were found for 3-5, respectively (Table S2 in the supplementary material). Compound 2 in contrast exhibited a broad and slightly structured emission band with maximum at 387 nm and a shoulder at ca. 364 nm. The broadening of the emission band is due to the formation of molecular aggregation in solution, which can be further supported by the non-linear concentration-dependent effect of the emission in solutions (Fig. S4 in the supplementary material). Moreover, a relatively low quantum yield of 0.04 observed for 2 (Table S2 in the supplementary material) is suggestive of an efficient non-radiative decay occurring in solution.

Recent research on the conformation-dependent photophysical properties indicates that the twisting angle for the aryl versus the linear ethynyl units plays an important role on the spectral variations, therefore, investigating the factors that affect the changes of conformation as well as the formation and characteristics of molecular aggregation becomes basically crucial. For phenylene ethynylene molecules, for instance, 4 and 5, the cylindrical symmetry of the C≡C triple bond can maintain conjugation between adjacent phenyl units regardless of the relative orientations of their aromatic planes, and one interesting representation of this structural feature was the relatively free rotation along the aryl-alkyne single bonds, typically resulting in coexistence and rapid equilibration of coplanar and twisted structures. For nitrogen-free compounds (4 and 5), intermolecular interaction in solution can be attributed, at least partly, to π-π interaction between adjacent molecules, and such close association of π system often causes a substantial decrease in the photoluminescence quantum yield compared with isolated chromophores. The existence of twisted structures suppressed the self-quenching effects through hindering or minimizing the cofacial aggregations, and thus higher quantum yields than that of 2 were observed for 4 and 5. Particularly, a relatively high quantum yield of 0.82 was observed for 5 due to the increase of twisted conformal population because of the increase of number of triple bonds within the molecule, which caused a substantial increase in the fluorescence quantum yield relative to 4 (0.62). As revealed in the theoretical studies C–H⋯N intermolecular interactions are common in various purine and pyrimidine based molecules. Thus, unlike 4 and 5, the intermolecular C–H⋯N interaction in 2 would minimize the intermolecular distance, which lead to the increase of π-π interaction between molecules and molecular aggregation, resulting in efficient self-quenching effect of the photoluminescence. In contrast to 2, a relatively high emission quantum yield (0.66) was observed in solution of another nitrogen-containing compound (3). This can be explained as follows. Although intermolecular distance could also be decreased due to C–H⋯N interaction between adjacent molecules of 3, the effective cofacial π-π interaction between molecules is hindered in some degree due to the
FIG. 2. Caption SEM images of self-assembled nanostructures fabricated from linear molecules: (a) compound 2, acetone/H$_2$O = 1/125; (b) compound 3, DMSO/H$_2$O = 1/5; (c) compound 4, acetone/H$_2$O = 1/125; and (d) compound 5, DMSO/H$_2$O = 1/5.

increase of twisted conformational population with the increase in the number of the triple bonds (similar to 5), which suppressed aggregation and the resulting self-quenching effect.

In order to study the aggregation behavior of such linear molecules, a phase transfer (PT) method with an acetone/H$_2$O binary solvent system was adopted to prepare the nanostructures from compound 2 and 4. Due to the lower solubility of compound 3 and 5, a DMSO/H$_2$O binary solvent system was employed for the fabrication of their nanostructures. The resulting nano-products were investigated by SEM. Samples were prepared by casting a drop of solution onto a silicon wafer, and then dried in a vacuum box prior to analysis. As illustrated in Fig. 2(a), quasi-cubic nanostuctures with the size ranging from 180 to 300 nm were found for 2. For investigation on the morphology of self-assembled nanostructures due to the influence on the extension of $\pi$-conjugation of the pyrimidine-containing linear molecules, compound 3 was also fabricated into aggregates using the similar method. As shown in Fig. 2(b), well-defined nano-cubes with the size ranging from 400 to 600 nm is observed from compound 3. Unlike 2 and 3, rod-shaped aggregates with the length of ca. 850 nm and diameter of ca. 330 nm is observed for 4 (Fig. 2(c)). The SEM images (Fig. 2(d)) revealed that the aggregates of 5 consisted of a large quantity of rice-like rods with the length of several micrometers, while their maximum diameters were in the range of 700 nm to 1.2 $\mu$m.

Self-assembly is a complicated process that is affected by various factors such as molecule size and structure, intermolecular interaction, solvent effect, temperature, solubility of the sample, etc. Therefore, comprehensive understanding of the above factors to construct different morphologies has been the focus of current research interests on this area. In this report, nanostructures of phenylene ethynylene molecule and its corresponding aza-substituted analogue were fabricated under the same condition (i.e. acetone/H$_2$O = 1/125 for 2 and 4, and DMSO/H$_2$O = 1/5 for 3 and 5). Thus molecular interplay depending on molecular structures should play an important role on the behavior of self-organization and so the morphologies of the resulting nanostructures. Phenylene ethynylene molecules, for instance, 4 and 5, are of typical extended $\pi$-conjugated structures with intrinsic intermolecular interaction via $\pi$-$\pi$ stacking. Tuning intermolecular interaction of such kind of linear molecules can be easily achieved by introducing pyrimidine moieties onto the primary backbones of the molecules, which provides a way to enhance C–H···N interaction between molecules during the self-assembly process. The morphology of nanostructures fabricated from 4 was
confirmed by TEM (Fig. 3(a)), and the measurement of the selected area electronic diffraction (SAED) pattern suggested the crystalline characteristics of the sample (Fig. 3(b)). Compound 4 was reported to possess a linear, coplanar structure and adopt a S-shaped crystal packing in the solid state, as shown in Fig. 3(c). Hence, we describe the possible formation mechanism of nano-rods of 4 in Fig. 3(c). The S-shaped π-π stacking facilitated the extension of the molecule aggregates along the a direction, while molecules were weakly held together by van der Waals force in the b direction, which hindered the extension of the aggregates in this direction, and thus rod-shaped nanostructure was formed. Similar crystalline feature was observed for the nanostructures fabricated from 2 (Fig. 4(b)), and according to the literature the molecules should adopt a linear and coplanar structure in crystalline state. Due to the existence of nitrogen atoms within the molecule, the main driving force operating in self-organization was assigned to the C–H⋯N interaction as well as π-π stacking of molecules. The possible mechanism of the formation of the quasi-cubic nanostructures fabricated from 2 was depicted in Fig. 4(c). Molecular blocks adopted a face-to-face π stack along the b direction, while in a direction, unlike 4, molecules were bound together via C–H⋯N interaction rather than the relatively weak interaction of van der Waals force, which facilitated the efficient growth of the aggregates along this direction, and as a result, quasi-cubic nanostructures is formed. For compounds 3 and 5, due to the lack of crystal data, DFT calculation was employed to predict the molecule packing in solid state. The result obtained on the basis of geometry optimization and energy minimized molecular structures of 3 and 5 utilizing Gaussian 03 program at B3LYP/6-31G (d) level (Fig. S1 in the supplementary materials) suggested that 3 and 5 should also adopt a linear and coplanar structure in solid state. Based on this, we proposed that molecules could thermodynamically find an energy minimized molecular packing conformation...
FIG. 4. (a) TEM image of self-assembled nanostructures of 2 fabricated by acetone/H$_2$O = 1/125. (b) SAED pattern of the nanostructures of 2. (c) Schematic illustration of possible mechanism of the formation of nanostructures fabricated from 2.

(i.e. linear coplanar structure) to enhance effective $\pi$-$\pi$ stacking and maximized orbital overlapping during self-organization. Similar to 4, the main driving force operating in the self-assembly process is $\pi$-$\pi$ stacking interaction for 5, where the aggregates tended to grow in one main direction, and thus rice-shaped nano-rods is formed. Unlike 5, C–H···N interaction would also play an important role on the self-organization of molecules for 3, and the formation mechanism should be similar to 2, and therefore the nano-cubes were formed.

The samples for fluorescence measurement of self-assembled nanostructures fabricated from 2-5 were prepared by casting drops of solution onto a silicon wafer and dried in vacuum box prior to use. For the purpose of comparison, emission spectra of bulk solid as well as solution samples have also been examined, and the results were illustrated in Fig. 5. As expected, all the emission spectra of nanostructures were significantly different from those of the corresponding solution and bulk solid samples. The emission spectra of nanostructures of 2 displayed a broad emission band with maximum at 405 nm (Fig. 5(a)), undergoing a red shift of 28 nm relative to that of the solution
FIG. 5. Normalized emission spectra of 2, 3, 4 and 5 in solution, nanostructures and bulk solid state. The emission spectra were measured upon excitation at 310 nm. The self-assembled nanostructures were fabricated as follows: (a) compound 2, acetone/H$_2$O = 1/125; (b) compound 3, DMSO/H$_2$O = 1/5; (c) compound 4, acetone/H$_2$O = 1/125; and (d) compound 5, DMSO/H$_2$O = 1/5.

sample and a blue shift of 45 nm relative to that of the bulk solid. Similarly, the emission maximum of the nanostructures fabricated from 3 was found to appear at 403 nm with a red-shift of 11 nm relative to that of the solution and a blue-shift of 52 nm relative to that of the bulk solid (Fig. 5(b)). Typically, red shift and broadening of emission bands are attributed to the formation or increase of molecular aggregation in solid state. The red shift at the emission band of bulk solids relative to that of nanostructures suggested the increase of π–π stacking in bulk solid state with the increase of particle sizes from nanoscale to microscale. Similar results are observed for 4 and 5. The emission maximum of nanostructures of 4 exhibited a red-shift of 48 nm relative to that of the solution as well as a blue-shift of 33 nm relative to that of bulk solid (Fig. 5(c)). Molecular aggregation also brought significant spectral change when molecules of 5 were fabricated into nanostructures, the broadening and blue-shift of emission band relative to that of the solution is observed. It should be noted that smaller spectral changes of the nanostructures relative to the solution-phase samples were observed than those to the bulk solid samples. Since the properties of the nanostructure are affected by various factors including molecular aggregation, molecular packing, sizes and shapes of the nanostructures and so on, the spectral change becomes complicated and the reason is still under discussion. Generally, such self-assembled nanostructures acting as intermediates between molecules and bulk solids were found to exhibit different photophysical properties from their solutions and bulk solids, which made them the promising materials that are expected to exhibit interesting electronic and optical properties for device application in future.

A series of nanostructures with different sizes and shapes were fabricated from 2 by changing the preparation conditions, as illustrated in Fig. 6. The experimental results showed that by adjusting the ratio of the acetone/H$_2$O, different nanostructures such as particles, quasi-cubes and rods are obtained. Particles with the size of ca. 60 nm were observed in the condition of acetone/water = 1/500 and 1/250 (Fig. 6(a), 6(b)), quasi-cubes with the size in the range of 180–300 nm were formed at acetone/water = 1/125 (Fig. 6(c)), rod-shaped nanostructures with the width of ca. 200 nm and the length in the range of 270–400 nm were found at acetone/water = 2/125 (Fig. 6(d)), and it has also been observed that with the increase of the ratio of acetone/water (from 2/125 to
FIG. 6. TEM images and fluorescence emission spectra of nanostructures of 2. Nanostructures were prepared under the following conditions: (a) acetone/H_2O = 1/500; (b) acetone/H_2O = 1/250; (c) acetone/H_2O = 1/125; (d) acetone/H_2O = 2/125; and (e) acetone/H_2O = 1/25.

1/25), the rod-shaped nanostructures with the increased size (i.e. the width of ca. 400 nm and the length of ca. 750 nm) is obtained (Fig. 6(e)). The emission spectra have also been measured to find out the influence of the morphologies of such nanomaterials on the photophysical properties. The fluorescence behavior was found to exhibit a morphology-dependent characteristics. As illustrated in Fig. 6(a)–6(e), the emission bands of such self-assembled nanostructures were shifted to longer wavelength with the change of their shapes as well as the increase of their sizes, namely, maximums at 394, 395, 405, 410 and 420 nm were found corresponding to different aggregation modes. Note that photoluminescence properties of the self-assembled nanostructures can be tuned by adjusting the preparation conditions, therefore the application of such materials for optoelectronic devices with selective requirements in the photophysical properties of semiconductors is promising.

In conclusion, a series of linear phenylene ethynylene molecules have been synthesized, and aza-substitution has been used as a strategy to fine-tune the properties of the molecules. All the compounds exhibited pure blue emission both in solution and solid state, fluorescence quantum yields of 0.66, 0.63 and 0.82 were found for compound 3–5 in chloroform solutions, respectively. The well-defined nanostructures such as quasi-cubes, cubes and rods were fabricated by self-assembly method, and all the nanostructures demonstrated distinct luminescence properties in comparison with their solution and bulk solid samples. Moreover, it has been found that the morphologies as well as the photophysical properties of nanostructures fabricated from 2,5-bis(2-phenylethynyl)pyrimidine (2) can be tuned by adjusting the preparation conditions, suggesting the potential application of such materials for optoelectronic devices with selective requirements on the photophysical properties of semiconductors.

We acknowledge the Special Funds for the Development of Strategic Emerging Industries in Shenzhen City, China (Grant No. JCYJ20120830154526537), grants from City University of Hong Kong’s Applied Research Grant Project no. 7004198 and the Research Grants Council of the Hong Kong Special Administrative Region (Project No.T23-713/11).

22. See supplementary material at http://dx.doi.org/10.1063/1.4954036 for materials synthesis, structural characterization data, DFT calculation results and photophysical parameters.