

Surface Modification of Self-Assembled One-Dimensional Organic Structures: White-Light Emission and Beyond

Xiao Wang, Jing Yan, Yan Zhou, and Jian Pei*

Beijing National Laboratory for Molecular Sciences, the Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received July 18, 2010; E-mail: jianpei@pku.edu.cn

Abstract: Surface modification is an important method to functionalize micro-/nanostructures, but substrates are mainly confined to robust inorganic compounds. We develop here a facile method to modify the surface of a fragile organic 1D microstructure. The bulk molecules and surface modifier were designed with orthogonal solubility to protect the molecular crystals from destruction under the reaction conditions. As a proof of concept, white-light-emitting 1D microstructures were obtained by grafting red chromophores onto the surface of self-assembled blue-emissive microwires via a heterophase S_N2 reaction. Spatial distribution of the two species is visualized by fluorescent lifetime mapping, which reveals a core-shell structure. The ability to postfunctionalize organic 1D structures enables many applications, where the surface property plays key roles, such as an organic P–N junction and a biosensor.

Recently, one-dimensional (1D) organic micro-/nanostructures have attracted considerable attention for their application in optoelectronic devices, such as field-effect transistors (FET), photodetectors, and optical waveguides.¹ The device performance can be dramatically improved through screening new materials, fine-tuning the morphologies, and developing new fabrication techniques. However, as the properties of a material depend not only on the bulk but also on its surface state, surface engineering is a key step to improve the device performance.² Although surface modification is widely employed in inorganic nanowires and carbon nanotubes,³ it is still a challenge for an organic 1D structure due to its fragility. Moreover, lack of a suitable detection method might be another reason.

In this contribution, we address these two issues. By surface modification of 1D microstructures via facile chemistry, we deposit a sparse layer of a second material onto the existing structure and dramatically change its property. This strategy has several advantages: (1) potential to generate different 1D structures for different applications from *one* existing structure; (2) a very small amount of the second material is needed; (3) easy preparation. Therefore, as a proof of concept, we obtain white-light-emitting (WLE) wires, which can be potentially used in full color display and illumination via this method.⁴ However, potential applications go far beyond this.

Figure 1 illustrates the molecular structures used for this study. The synthesis and characterization of these new compounds, **Blue-Br**, **Blue-H**, and **Red-OH**, are detailed in the Supporting Information. Photophysical measurement (Figure S1) shows that the absorption band of **Red-OH** overlaps nicely with the emission band of **Blue-Br**. This is important for excitation energy transfer,⁵ which was initially designed as an amplification mechanism to detect the surface reaction.

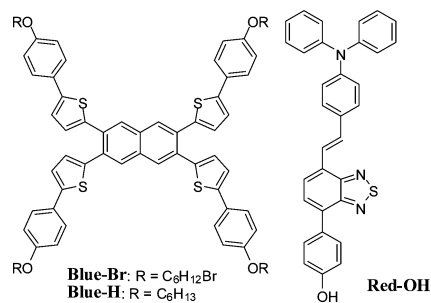


Figure 1. Chemical structures of molecules used for the study.

Uniform microwires, with widths of about 1–4 μm and lengths up to several hundred μm , were readily formed by heating a suspension of **Blue-Br** in a mixture of CHCl₃ and EtOH (1:1) and subsequent slow cooling (Figure S2). Owing to the aromatic core, **Blue-Br** exhibited the ability to grow preferentially in one direction.⁶ Similar self-assembled behaviors were also observed for model compound **Blue-H**, indicating that the terminal Br groups did not interfere with formation of 1D structures. All one-component microstructures emitted blue light with CIE coordinates of (0.14, 0.17) (see Table 1).

Table 1. Experimental Results under the Reaction Conditions of I–IV^a

No.	I	II	III	IV
Reaction Conditions	Blue-Br Red-OH K ₂ CO ₃	Blue-Br Red-OH	Blue-H Red-OH K ₂ CO ₃	Blue-Br
Fluorescent Microscope Images				

^a 1 mg of **Blue-Br** (or **Blue-H**) and 1 mg of K₂CO₃ (or without) were suspended in 2 mL of pure EtOH or a solution of 1.0 mM **Red-OH** in EtOH (2 mL) under reflux for 1 h. The fluorescent microscope images were obtained under irradiation of a mercury lamp. Only **Blue-Br** nanowires (I) emit the white color after surface modification.

Table 1 illustrates the optimized conditions for the modification of the wires. By suspending wires of **Blue-Br** in a mixture of **Red-OH** and K₂CO₃ (1.0 mM) in EtOH under reflux for 1 h and washing with copious EtOH (Table 1, condition I), these blue-emitting wires are transformed into WLE wires under UV irradiation. Such a dramatic change of emission light is the first evidence of surface reaction. The success of modification relies crucially on the *orthogonal* solubility of **Blue-Br** and **Red-OH**:

Blue-Br is insoluble in EtOH so the microstructure is preserved in the process (Table 1, condition IV, and Figure S3), while **Red-OH** is soluble (1.0 mM) in EtOH in the presence of K_2CO_3 . Powder X-ray Diffraction (XRD) patterns also indicate that the crystal structures do not change significantly after modification (Figure S9). Three additional evidential observations confirm that **Red-OH** had been covalently bonded onto the surface of **Blue-Br**: (1) product **Red-O-Blue** on modified microwires was detected by MALDI-TOF MS measurements (Figure S5); (2) under the same reaction conditions, **Blue-H** cannot be modified (condition III); (3) Although **Red-OH** can also physically adsorb onto the surface of **Blue-Br** without K_2CO_3 (condition II),⁷ they are readily washed away after resuspending the microwires in hot EtOH (Figure S6). In contrast, the covalent linkage between **Red-OH** and **Blue-Br** can withstand such conditions and the WLE wires are stable.

The state of the modifiers on the surface was revealed by the steady state and transient fluorescence emission features of the modified wires (as shown in Figure 2a–b). The emission maximum (580 nm) and lifetime (5.2 ns) of **Red** on the surface show excellent agreement with those in the molecular state (10^{-6} M in hexane, 550 nm, 5.5 ns), which are drastically different from those in the aggregated state of **Red-OH** (625 nm, 2.4 ns). This indicates that **Red** chromophores do not form aggregates on the surface. In other words, the surface density of **Red** is low, which is consistent with the fact that the amount of nitrogen element is below the detection limit of the surface sensitive X-ray photoelectron spectrum (XPS) measurement.

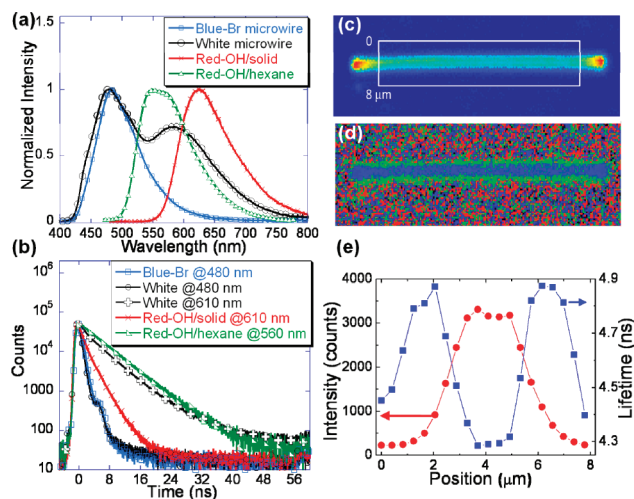


Figure 2. (a) Fluorescence spectra of **Blue-Br** microwires before and after modification; (b) transient fluorescence spectra of **Blue-Br** microwires before and after modification; (c) intensity mapping of the WLE microwires. Red color indicates the region with high intensity. (d) Lifetime mapping of WLE microwires excited at 485 nm; blue color indicates the region with a short lifetime. The white rectangle specifies the region used for analysis; (e) distribution of lifetime and intensity across the wire. Average lifetime is defined as the time it takes for the intensity at a certain pixel to decay to $1/e$ of its initial value after excitation. Each point is averaged over $57 \mu\text{m}$ along the wire in a specified region.

To further prove the success of the surface modification, we mapped the spatial distribution of **Red-OH** and **Blue-Br** wires by measuring the lifetime of different locations (Figure 2d). The lifetime of **Red-OH** (5.5 ns) is longer than that of **Blue-Br** (0.8 ns), so the average lifetime on one pixel depends on the ratio of **Red-OH** and **Blue-Br** in that region. It is expected that the average lifetime on the outer circle of the 1D structure be longer

than that of the body (Figure S8). This is indeed what we observed. Figure 2d shows that relatively long lifetime spots (green) regularly circle around the wire, which indicates a core–shell structure. To quantify such a distribution, both the intensity and averaged lifetime are plotted versus position across the wire, as shown in Figure 2e. Clearly, the position of the intensity peak coincides with the minimum of the average lifetime, where the ratio of **Blue-Br** is highest. In contrast, the average lifetime reaches maxima where the intensity starts to decay, because the ratio of **Red-OH** is much higher at the wall.⁸ Apart from heterogeneity across the wire, we also observed a higher intensity at the end of the wire, indicating a wave-guiding phenomenon.

Neglecting the light distribution on the wire, the whole wire appears to be a bright white color under illumination. It has CIE coordinates of (0.32, 0.36), very close to those of the standard white light (0.33, 0.33). Compared with other methods,⁹ our strategy only needs a very small amount of the acceptor (estimated to be 10^{-5} compared to that of the bulk from geometric calculation), because the acceptors are exposed at the surface and contribute better to the spectrum when viewing from the outside of the wire. In addition, after redissolving WLE microwires in chloroform and recrystallizing in ethanol, the new assembled microwires were blue-emissive, which demonstrated the advantage of postmodification over coassembly in this WLE system.

In conclusion, we have developed and demonstrated a new concept in the design of organic 1D heterostructures, i.e. via postmodification of their surface. A proof of concept example demonstrates its feasibility and usefulness: WLE structures are readily obtained from normal blue-emitting wires after modification with second red-emitting materials on their surface. We envisage many situations where such a modification will be desirable. For example, biosensors can be grafted onto the surface, with only a very small amount needed. Moreover, core–shell P–N structures can also be readily obtained in this way. Finally, the ability to control the surface property is important to devices such as FET, which is extremely sensitive to the surface layers.¹⁰ We hope our strategy would open a new avenue to explore in this area.

Acknowledgment. This work was financially supported by the Major State Basic Research Development Program (No. 2009CB623601) and by the National Natural Science Foundation of China (NSFC). We thank Professor Lindong Sun for discussions and Jiakai Zhou from Peking University for lifetime mapping experiments. We also thank Dr. Xiaoyun Li from Akron University for mass spectra experiments.

Supporting Information Available: Detailed experimental procedures and characterization data of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Tang, Q. X.; Jiang, L.; Tong, Y. H.; Li, H. X.; Liu, Y. L.; Wang, Z. H.; Hu, W. P.; Liu, Y. Q.; Zhu, D. B. *Adv. Mater.* **2008**, *20*, 2947. (b) Brisenio, A. L.; Mannsfeld, S. C. B.; Jenekhe, S. A.; Bao, Z.; Xia, Y. *Mater. Today* **2008**, *11*, 38. (c) Zang, L.; Che, Y.; Moore, J. S. *Acc. Chem. Res.* **2008**, *41*, 1596. (d) Zhou, Y.; Wang, L.; Pei, J.; Wang, J.; Cao, Y. *Adv. Mater.* **2008**, *20*, 3745. (e) Mynar, J. L.; Yamamoto, T.; Kosaka, A.; Fukushima, T.; Ishii, N.; Aida, T. *J. Am. Chem. Soc.* **2008**, *130*, 1530.
- (2) (a) Ryu, D. Y.; Shin, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P. *Science* **2005**, *308*, 236. (b) Dodabalapur, A.; Torsi, A.; Katz, H. E. *Science* **1995**, *268*, 270.
- (3) (a) Zheng, G.; Patolsky, F.; Cui, Y.; Wang, W. U.; Lieber, C. M. *Nat. Biotechnol.* **2005**, *23*, 1294. (b) Pastine, S. J.; Okawa, D.; Kessler, B.; Rolandi, M.; Llorente, M.; Zettl, A.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 4238.

- (4) For example, see: (a) Chen, Y.; Au, J.; Kazlas, P.; Ritenour, A.; Gates, H.; McCreary, M. *Nature* **2003**, *423*, 136. (b) Sun, Y.; Giebink, N. C.; Kanno, H.; Ma, B.; Thompson, M. E.; Forrest, S. R. *Nature* **2006**, *440*, 908.
- (5) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum Publishers: New York, 1999; Chapter 13.
- (6) Wang, X.; Zhou, Y.; Lei, T.; Hu, N.; Chen, E.-Q.; Pei, J. *Chem. Mater.* **2010**, *22*, 3735.
- (7) This might be caused by interaction between electronegative Br and the electron-deficient aromatic rings; see: (a) Gamez, P.; Mooibroek, T. J.; Teat, S. J.; Reedijk, J. *Acc. Chem. Res.* **2007**, *40*, 435. (b) Yoshizawa, M.; Kusakawa, T.; Kawano, M.; Ohhara, T.; Tanaka, I.; Kurihara, K.; Niimura, N.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 2798.
- (8) See Supporting Information for a detailed explanation and more evident pictures from tubular structure, also self-assembled from **Blue-Br**.
- (9) For example, see: (a) Abbel, R.; Grenier, C.; Pouderoijen, M. J.; Stouwdam, J. W.; Leclère, P. E. L. G.; Sijbesma, R. P.; Meijer, E. W.; Schenning, A. P. H. J. *J. Am. Chem. Soc.* **2009**, *131*, 833. (b) Zhao, Y. S.; Fu, H. B.; Hu, F. Q.; Peng, A. D.; Yang, W. S.; Yao, J. N. *Adv. Mater.* **2008**, *20*, 79. (c) Vijayakumar, C.; Praveen, V. K.; Ajayaghosh, A. *Adv. Mater.* **2009**, *21*, 2059.
- (10) Tulevski, G. S.; Miao, Q.; Afzali, A.; Graham, T. O.; Kagan, C. R.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1788.

JA106354M