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Orange−Blue−Orange Triblock One-Dimensional Heterostructures of Organic Microrods for White-Light Emission

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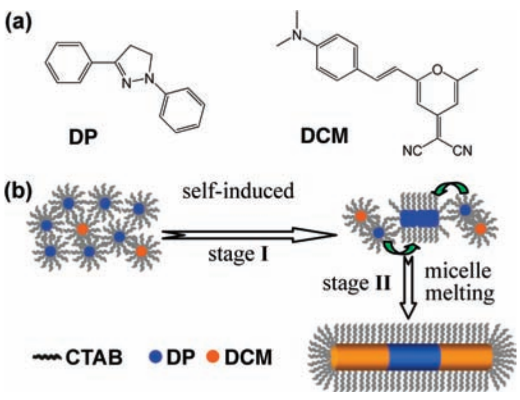
Patterning on the nanoscale is crucial for rational design and synthesis of low-dimensional nanomaterials with enhanced and/or novel electronic and photonic functions.[1] In this regard, multisegmented one-dimensional (1D) nanostructures of metals, semiconducotrs, and conducting polymers, prepared by hard template methods combined with electrochemical deposition techniques,[2] have attracted considerable interest, due to its combination of multifunctionality for integration of miniaturized devices, such as nanobarcodes,[3a] magnetism,[3b] and P/N junctions.[3c] Recently, controlled assembly of block copolymers[4a] and peptides[4b] has been explored as a powerful tool to fabricate striped cylindrical assemblies, which can also serve as patterned templates for the growth of other materials.[4c] However, although single-component 1D organic nanostructures can be readily prepared based on self-assembly of the planar π-conjugated molecules,[5] multicomponent ones encoded with submicrometer stripes of functional organic molecules remain a challenge.

White-light emission (WLE) is pivotal to full color displays and the backlight of portable display devices.[6] Several supramolecular approaches have been reported for WLE generation by self-assembly[7a] or gelation[7b] of molecular building blocks that emit the three primary red, green, and blue colors, respectively. Based on the CIE chromaticity diagram, generation of WLE can also be achieved by mixing a blue fluorescent dye with a yellow or an orange one.[7c] Herein, we report a supramolecular synthesis of triblock microrods of 1,3-diphenyl-2-pyroline (DP, a blue-emissive molecule, Scheme 1a) doped with an orange dye of 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethyl-aminostyryl)-4*H*-pyran (DCM, Scheme 1a) selectively at both ends, induced by cetyltrimethylammonium bromide (CTAB) micelles.[8] Although these triblock microrods show microarea heterogeneity, they exhibit macroscopic high-quality WLE in both the colloidal suspension and the solid state.

Scheme 1. (a) Molecular Structures of DP and DCM and (b) Cartoon for the Formation Mechanism of Triblock Microrods



In a typical preparation, 200 μL of a stock solution of DP (C_{DP} = 5 mM) and DCM (C_{DCM} = 0.01 mM) in the good solvent of ethanol (DCM/DP = 2:1000) was rapidly injected into the poor solvent of water in the presence of CTAB (5 mL, C_{CTAB} = 0.9 mM) under vigorous stirring.[9] An off-white colloidal suspension was obtained within several minutes. Scheme 1b illustrates the formation mechanism of triblock microrods. As we established previously,[8] under the present conditions, some of the DP molecules would first dissolve into the hydrophobic core of spherical CTAB micelles due to a process called solubilization (the left image) just after injection, as do DCM molecules as a result of its low concentration.[9] Most importantly, those DP molecules which dissolve into spherical micelles can induce the formation of rod-like micelles (stage I),[8] which then act as templates directing the primary growth of DP particles along a 1D direction (the middle image). Finally, the micelle melting process (stage II) caused by the micellar sphere-to-rod transition (shown by green arrows) leads to codeposition of DP and DCM molecules at both ends of the as-formed primary 1D particles, generating the triblock microrods (the bottom image).[9]

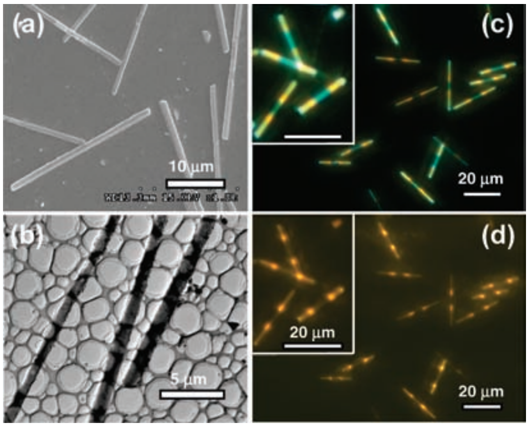


Figure 1. (a) SEM and (b) TEM images of triblock microrods. (c and d) Fluorescence microscopy images of same microrods excited with unfocused UV (330−380 nm) and blue light (460−490 nm), respectively.

Figure 1a and b depict typical scanning and transmission electron microscopy (SEM and TEM) images of as-prepared colloids. It can be seen that 1D rod-like structures with a smooth outer surface were formed and each individual rod has a quite uniform diameter (~1 μm) throughout the entire length (20−25 μm). Figure 1c shows a fluorescence microscopy image of microrods placed on a quartz slide by excitation with unfocused UV light (330−380 nm). In sharp contrast to the uniform morphologies observed by SEM and TEM, triblock heterostructures with striping patterns are clearly apparent: the middle stripe exhibits blue photoluminescence (PL), while the two ends present orange PL. The length of the microrods is 21.2

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± 2.4 μm, which is consistent with electron microscopy observations, while the lengths of the middle and end stripes are 7.6 ± 1.2 and 6.9 ± 1.5 μm, respectively. The absorption spectrum of the colloidal suspension of triblock microrods (Figure S1a) is similar to that of DP nanowires,[8] including $n-\pi^*$ (at 320 nm), $\pi-\pi^*$ (at 375 nm), and *J*-aggregate (at 420 nm) bands, respectively, while the absorption of DCM in the region 450−550 nm (Figure S1b) is hardly observed as a result of DCM/DP = 2:1000. Factually, the UV light cannot excite DCM molecules because of its weak absorption between 330 and 380 nm (Figure S1b). Note that there is a good spectral overlap between DP emission and DCM absorption (Figure S1). Therefore, the orange emission from the end stripes of the triblock microrods might be a result of Förster energy transfer (FET) from excited DP to DCM molecules.[7c,10] To selectively excite DCM components (and not to excite DP), we switch the excitation source to blue light (440−480 nm). Interestingly, the blue-emissive middle stripes of the triblock microrods that are clearly observed in Figure 1c disappear in Figure 1d, while the yellow-emissive end stripes remain detectable. This suggests that the middle stripe of the triblock microrod is mainly composed of DP components, while DCM molecules distribute at both ends.

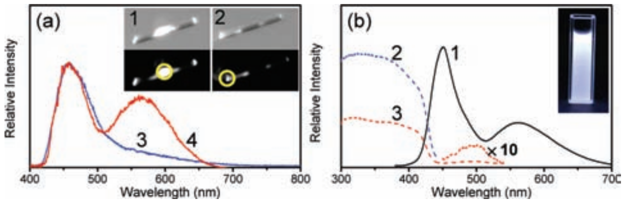

Figure 2. (a) Spatially resolved spectra recorded by local excitation at the middle (curve 3) and end (curve 4) stripes of a single triblock microrod. Images 1 and 2 show corresponding bright (top) and dark field (bottom) images. (b) Steady-state emission (curve 1) and excitation (curves 2, 3) spectra of a colloidal suspension (inset) of triblock microrods. The excitation spectra of 2 and 3 were recorded by monitoring the DP emission at 450 nm and DCM emission at 560 nm, respectively.

Further structure characterization of triblock microrods was performed by scanning near-field optical microscopy (SNOM). The insets of Figure 2a present the bright and dark field images of a single rod under excitation with a continuous-wave laser (325 nm) focused down to the diffraction limit at different positions. It can be seen that local excitation (circled region) at the middle (image 1) or end positions (image 2) of the single rod leads to bright PL spots at both junction points and ends. This is not only evidence for triblock heterostructures but also a sign of waveguide properties.[11] That is, the rod is able to absorb the excitation light and propagate the PL along the 1D direction, which either leaks at junction points or outcouples at the ends. Furthermore, the spatially resolved PL spectrum recorded in the reflection mode at the middle strip (curve 3) verifies a single peak at 457 nm, which is consistent with that of a DP nanowire.[8] However, the spectrum recorded at the end strip (curve 4), presents an additional band at 560 nm, which is in agreement with the emission of DCM molecules well-dispersed in a solid medium.[10]

Remarkably, although triblock microrods show microarea heterogeneity of the striping pattern, its colloidal suspension exhibits macroscopic high-quality WLE (the inset of Figure 2b) under a UV lamp (365 nm). The CIE coordinates calculated from the ensemble emission spectrum of the colloidal suspension (curve 1 in Figure 2b) are (0.338, 0.281), which are shifted to (0.305, 0.332) for triblock microrod solids filtered on the surface of an AAO membrane (Figure S2), while the absolute PL efficiencies for colloidal and solid samples are determined to be similar ∼36 ± 5% (Figure S2). The steady-state excitation spectrum (curve 3) recorded by monitoring the DCM emission at 560 nm reveals energy levels including not only DCM but also DP molecules. This is clear evidence for the efficient FET from excited DP to DCM molecules. The X-ray diffraction (XRD) pattern of triblock microrods filtered on the surface of an AAO membrane reveals that they are crystalline in nature, however, are mainly related to the DP component (Figure S3). Note that besides the spectral overlap, the efficiency of FET also depends upon the distance between the donor and acceptor molecules, which is typically ∼2−6 nm.[12] Therefore, the efficient FET process suggests that DCM molecules are uniformly embedded in a DP crystalline matrix at both end stripes of the triblock microrods.[7c]

In summary, 1D triblock hetrostructures with striping patterns have been synthesized by doping DP microrods with DCM molecules selectively at both ends. The middle stripe emits blue light, while both ends emit orange light. Although triblock microrods show microarea heterogeneity of the striping pattern, we found that they generate macroscopic high-quality WLE in both the colloidal suspension and the solid state with a PL efficiency as high as 36 ± 5%.

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Supporting Information Available: Experimental conditions and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

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