Journal of
Materials Chemistry C

RSCPublishing

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**Cite this:** *J. Mater. Chem. C*, 2013, **1**, 2286

Received 5th December 2012
Accepted 8th February 2013

DOI: 10.1039/c3tc30112e

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# Preparation and ambipolar transistor characteristics of co-crystal microrods of dibenzotetrathiafulvalene and tetracyanoquinodimethane†

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**Co-crystal microrods of dibenzotetrathiafulvalene (DBTTF) and tetracyanoquinodimethane (TCNQ) molecules with the mixed-stack structure were prepared *via* a facile solution process and fully characterized. The as-prepared microrods were directly used for fabricating prototype devices, which exhibited typical ambipolar charge transport characteristics. The result indicated that the co-crystal microrods of DBTTF-TCNQ were potentially useful for miniaturized devices.**

Functional organic nano/microstructures have attracted increasing interest due to their great potential as building blocks of bottom-up assembled highly integrated miniaturized devices.[1–4] Up to now, most organic structures are single component, *i.e.*, consisting of one type of molecule. Meanwhile, charge-transfer (CT) complexes, representing a typical two-component system, are widely studied owing to their unique conduction and magnetism.[5–7] Moreover, recent studies indicate that they are ideal building blocks as active layers and source/drain electrodes in electronic devices.[8–14] It should be noted that most CT complexes have been prepared in bulk single-crystalline form,[15–18] which are fragile and difficult to process in nano/microdevices.

In spite of their excellent opto/electronic properties, studies on nano/microstructures of CT complexes are very limited. This is possibly because fabrication of nano- and microscale structures of CT complexes with well-defined shapes is still a great challenge. Recently, nanosheets of fullerene–ferrocene[19] and fullerene–cobalt porphyrin were prepared by Miyazawa *et al.*[14] Microribbons of sulfur-bridged annulene–TCNQ were prepared by Zhang *et al.* *via* a drop-casting method.[13] On the other hand, one-dimensional (1D) structures might play more important roles as interconnects and functional units in miniaturized devices in comparison with two-dimensional (2D) ones. Nevertheless, the drop-casting method fails to control the dimension and shape of structures.

Dibenzotetrathiafulvalene (DBTTF)–tetracyanoquinodimethane (TCNQ) represents a typical CT complex. The crystal structure of DBTTF–TCNQ, firstly reported by Hayao in 1981, belongs to the triclinic lattice with the mixed-stack in the [011] direction.[20] The devices based on bulk single crystals of DBTTF–TCNQ exhibit good-performance transistor and photovoltaic characteristics.[10,21] Moreover, theoretical study has indicated that the DBTTF–TCNQ co-crystals may have high mobility for holes (80 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$) and electrons (60 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$) along the stacking direction at room temperature.[22]

Herein, we report a facile solution method which has combined precipitation and self-assembly processes for the preparation of co-crystal microrods of DBTTF–TCNQ. The chemical structures of DBTTF and TCNQ are shown in Fig. S1.† The as-prepared co-crystal microrods were fully characterized and directly used for fabricating prototype field-effect transistors with the bottom-gate bottom-contact geometry. The results indicate that the co-crystal microrods have well-defined shapes and smooth surfaces and the devices based on them exhibit typical ambipolar charge transport characteristics.

In a typical synthesis, 0.5 mL chloroform solution of DBTTF ($\sim$4 mM) was fast injected into 0.5 mL chloroform solution of TCNQ ($\sim$4 mM). The mixed solution was shaken vigorously for 30 s and maintained for 5 minutes. Then, 3 mL *n*-hexane was added slowly to the surface of the mixed chloroform solution. The resulting two-layer mixture was stored at room temperature for 12 h without disturbance. The final solution was transparent and the brown precipitates were collected at the bottom. For the fabrication of devices, the precipitates could be dispersed by shaking the mixed solution for several seconds. Fig. 1 shows the typical scanning electron microscope (SEM) images of the microrods deposited on Si substrates. The microrods have

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† Electronic supplementary information (ESI) available: Experimental details, chemical structures of DBTTF and TCNQ, schematic structures of triclinic co-crystal of DBTTF–TCNQ. See DOI: 10.1039/c3tc30112e

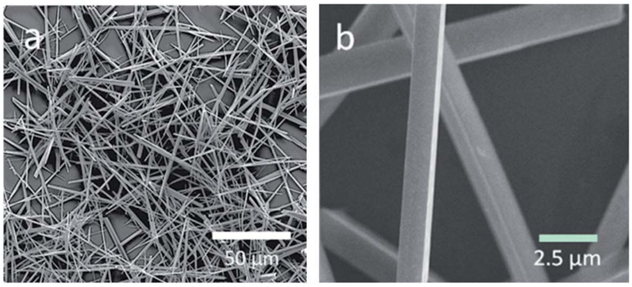

**Fig. 1** (a) and (b) SEM images of the DBTTF–TCNQ microrods recorded at different magnifications.

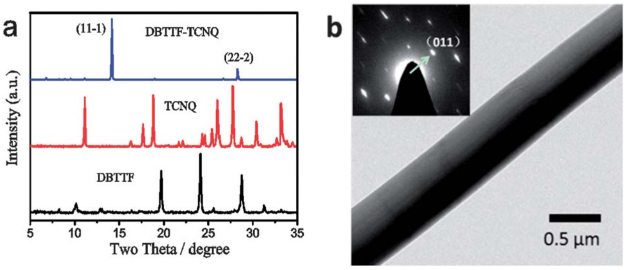

**Fig. 3** (a) XRD pattern of the DBTTF–TCNQ microrods along with those of the starting powders of DBTTF and TCNQ. (b) TEM image of a single DBTTF–TCNQ microrod. The inset is the corresponding SAED image. The arrow indicates the direction of the microrod.

well-defined shapes (*i.e.*, rectangular cross-section) and smooth surfaces (Fig. 1b). The width of the microrods is 1–2 μm, the thickness is 0.5–1 μm, and the length is tens of microns. In addition, the microrods could be produced on a large scale when larger quantities of DBTTF and TCNQ solutions are mixed.

To confirm the existence and locate the distribution of DBTTF and TCNQ molecules in the microrods, a scanning transmission electron microscope (STEM) mapping analysis was performed (Fig. 2). Both nitrogen and sulfur atoms are detected in the same microrod, as shown in Fig. 2b and c, respectively. It is clear that the distributions and concentrations of nitrogen and sulfur are uniform across the whole microrod. This finding indicates that nitrogen and sulfur atoms are uniformly dispersed in the microrod. This is powerful evidence that the co-crystal microrods consist of DBTTF and TCNQ molecules.

Fig. 3a represents the X-ray diffraction (XRD) pattern of microrods along with those of the starting powders of DBTTF and TCNQ. It can be seen that the XRD pattern of microrods is different from those of the DBTTF and TCNQ. The two peaks from microrods could be well indexed to the crystal planes of (11−1) and (22−2) of DBTTF–TCNQ co-crystal with the triclinic lattice.[20] Moreover, the intensity of the (11−1) plane is much stronger compared to the other peaks, indicating a preferred growth along (11−1). Fig. 3b shows a typical transmission electron microscope (TEM) image of a single microrod and the corresponding selected area electron diffraction (SAED) image. The TEM image reveals the formation of solid structures with smooth surfaces. The well-defined pattern of SAED could be recorded through the whole microrods (*i.e.*, a single crystal) and indexed as the [011] direction. This result is in good agreement with the XRD pattern because the [011] direction is parallel with the (11−1) plane and the (11−1) and (22−2) peaks are greatly enhanced. Based on the above analysis, it is concluded that the microrods are composed of DBTTF and TCNQ and have the triclinic lattice reported by Kobayashi and Nakayama.[20] In addition, the DBTTF and TCNQ molecules stack alternately along the [011] direction in the microrods (Fig. S2†).

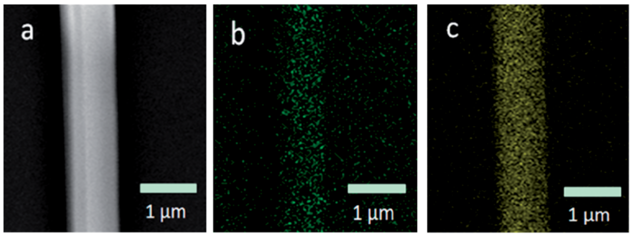

**Fig. 2** (a) SEM image and (b and c) corresponding STEM mapping images (b: nitrogen; c: sulfur) of a single DBTTF–TCNQ microrod.

Fig. 4a displays the Raman spectrum of microrods along with those of the starting powders of DBTTF and TCNQ. The Raman spectrum of microrods is almost the summed spectra of the starting powders of DBTTF and TCNQ. The strong peaks from DBTTF (marked by rectangles) and TCNQ (marked by circles) can be identified in the spectrum of microrods. This observation indicates that the microrods are composed of DBTTF and TCNQ molecules. Fig. 4b are the ultra-violet visible near-infrared (UV-Vis-NIR) spectra of microrods and the starting powders of DBTTF and TCNQ. Compared with the spectra of DBTTF and TCNQ, there is a new band between 700 and 2100 nm in the spectrum of microrods. The absorption centre is at around 1400 nm. It has been reported that DBTTF–TCNQ complex has an optical gap estimated as 0.9 eV,[10] corresponding to the wavelength of 1380 nm. Therefore, the new broad band can be assigned as the CT band, *i.e.*, the CT excitation from DBTTF to TCNQ along the mixed stack.

In order to investigate the charge transporting properties of the DBTTF–TCNQ microrods and explore their potential applications in miniaturized devices, prototype devices with the bottom-gate bottom-contact geometry were fabricated on the basis of individual microrods. The insets in Fig. 5a show the schematic diagram (top-left) and the optical microscopy

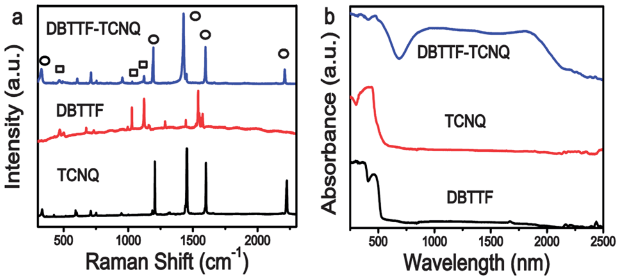

**Fig. 4** (a) Raman spectra and (b) UV-Vis-NIR spectra of the DBTTF–TCNQ microrods and the starting powders of DBTTF and TCNQ.

image of the as-fabricated one-co-crystal device (bottom-right). Source–drain gold electrodes were fabricated by photo-lithography and electron beam deposition of gold on Si substrate covered with 300 nm thick $SiO_2$. A drop of the mixed solution with dispersed microrods of DBTTF-TCNQ was directly deposited onto the prepatterned substrate. Randomly, some microrods could be attached to the gold electrodes, which bridge the source and drain electrodes. Fig. 5a and b show the typical output and transfer characteristics of the device based on an individual microrod of DBTTF–TCNQ co-crystal. It can be seen that both the output and transfer characteristics demonstrate typical ambipolar charge transporting behavior. The electron and hole mobilities calculated from the transfer characteristics are 0.13 and 0.04 $cm^2 V^{-1} s^{-1}$, respectively. These values are higher than those calculated from the devices based on the fullerene–cobalt porphyrin hybrid nanosheets and sulfur-bridged annulene–TCNQ microribbons with ambipolar characteristics.[13,14]

Previous studies on bulk single co-crystals of DBTTF–TCNQ indicated that electron transport could be achieved when using gold source and drain electrodes.[10] Ambipolar charge transport was achieved only when carrier injections were properly tuned by using metallic CT complexes as source and drain electrodes.[11] This is different from the present study in which ambipolar characteristics were obtained by using gold electrodes. The result indicates that a better contact has been formed between DBTTF–TCNQ microrod and gold electrodes than that with bulk crystals. As a consequence, hole injection becomes feasible, and balanced ambipolar transport is observed. Moreover, theoretical study has predicted that the DBTTF–TCNQ co-crystals have high mobility for both holes and electrons.[22] The predicted values have not been reached in the present study, and higher performance can be expected by further device optimization.

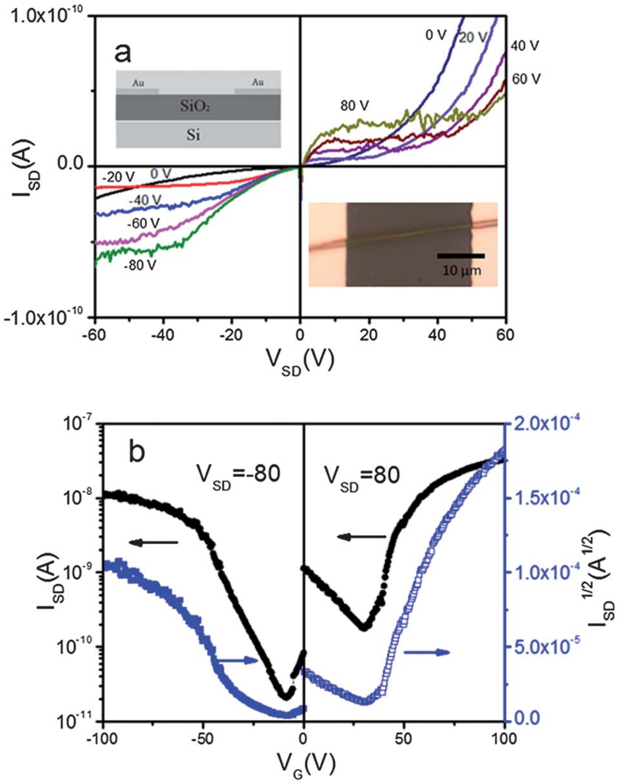

**Fig. 5** (a) Output and (b) transfer characteristics of the device based on a single microrod of DBTTF–TCNQ co-crystal. The schematic diagram (top left) and optical image (bottom right) of the device are shown as insets in (a). The channel length was $L = 27$ μm, and the channel width was $W = 1$ μm. All the measurements were carried out in the dark under ambient conditions and at room temperature.

In summary, co-crystal microrods with rectangle cross-section and smooth surfaces are prepared *via* a facile solution method, fully characterized, and used for fabricating prototype devices. The result indicates that the microrods are composed of DBTTF and TCNQ molecules, which are uniformly distributed and stack alternately along the [011] direction. Moreover, a characteristic broad CT band is observed at around 1400 nm. The devices based on an individual microrod of DBTTF–TCNQ exhibit ambipolar charge transport characteristics with the electron mobility of 0.13 $cm^2 V^{-1} s^{-1}$ and the hole mobility of 0.04 $cm^2 V^{-1} s^{-1}$. The simple and low-cost solution method is expected to be useful for both fundamental study and practical application of donor/acceptor co-crystal nano-materials in future miniaturized devices.

This work was financially supported by the National Basic Research Program of China (no. 2010CB934100), the National Natural Science Foundation of China (no. 21273272), and the Chinese Academy of Sciences.

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