DOI: 10.1002/adma.200700542

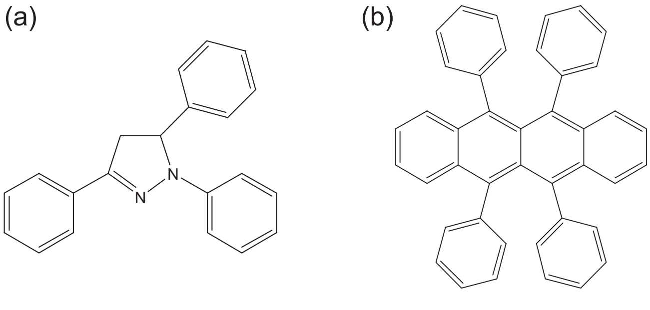
Tunable Emission from Binary Organic One-Dimensional Nanomaterials: An Alternative Approach to White-Light Emission**

By *Yong Sheng Zhao*, *Hongbing Fu*, *Fengqin Hu*, *Aidong Peng*, *Wensheng Yang*, and *Jiannian Yao**

Their unique optical and optoelectronic properties as well as prospective applications in nanometer-scale devices have sparked a wide range of investigations on organic nanomaterials.[1] Most work, however, has been focused on zero-dimensional (0D) organic nanoparticles with amorphous structures.[2] Compared with their 0D counterparts, one-dimensional (1D) nanomaterials are more suitable for the construction of active nanodevices and interconnects,[3] which is especially applicable to crystalline 1D nanomaterials because crystals reveal the intrinsic properties of materials more exactly. In our recent work,[4] we developed an adsorbent-assisted physical vapor deposition (PVD) method for the fabrication of crystalline organic nanowires of a single component, in which the introduction of adsorbents was proven to be indispensable for improving the uniformity of the products.

In the work reported here, we extend the adsorbent-assisted PVD method to doped binary organic systems. Doping is widely used in electroluminescent (EL) devices to improve the luminescence efficiency and to tune the emission colors.[5] For example, white-light emission, which is pivotal to full-color displays and backlight of portable display devices, can be obtained by doping blue fluorescent dyes with green and red ones. From the CIE (Commission Internationale de l'Eclairage) chromaticity diagram one can see that white luminescence can also be achieved by merely blending a blue dye with an orange or a yellow one. Up to now, most organic doping systems are amorphous,[2b,5] although the crystallinity of nanomaterials can improve their charge carrier transport and enhance the performance of optical and optoelectronic devices.[4,6] In this work, 1,3,5-triphenyl-2-pyrzoline (TPP, a blue-light emitter and hole-transporting material for EL use), and rubrene (Scheme 1), a good orange dye widely used as the dopant in host/guest organic light-emitting devices (OLEDs) with good transport properties,[7] were chosen as the model compounds, which were fabricated into uniformly doped crystalline nanorods and nanowires using adsorbent-assisted PVD. Figure 1A reveals that the absorption spectrum of rubrene shows good overlap with the fluorescence spectrum of TPP in the 400–550 nm wavelength range, which may result in efficient energy transfer in the doping systems. The emission wavelengths of both TPP and rubrene nanostructures do not show obvious differences from those of the monomers, so the emission color of the as-prepared binary 1D nanostructures is mainly dependent on the doping ratio.

For PVD, the monodispersity of the products is hard to control when small organic molecules are selected as deposition sources, and the degree of saturation is the predominant factor in controlling the morphology and monodispersity of the products.[4,8] We introduced neutral aluminum oxide used widely in column chromatography as an adsorbent into our PVD system to improve the uniformity of the nanomaterials. Aluminum oxide was mixed uniformly with either TPP or rubrene at a w/w ratio of 100:1, and each mixture was subsequently placed in a quartz boat. The uniformity of the nanorods/wires improves with increasing w/w ratio when the ratio is below 100:1; when the ratio is increased further it remains approximately the same. The quartz boats loaded with the mixtures were then put into a quartz tube, which was inserted into a horizontal tube furnace. The thermogravimetric analysis (TGA) plots of pure dyes and mixtures of the dyes with ad-



Scheme 1. Molecular structures of TPP (A) and rubrene (B).

---

[*] Prof. J. N. Yao, Dr. Y. S. Zhao, H. B. Fu, F. Q. Hu, A. D. Peng
Center for Molecular Science
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100080 (P.R. China)
E-mail: jnyao@iccas.ac.cn

Dr. Y. S. Zhao
Graduate School, Chinese Academy of Sciences
Beijing 100039 (P.R. China)
E-mail: yszhao@iccas.ac.cn

Prof. W. S. Yang
College of Chemistry, Jilin University
Changchun 130021 (P.R. China)

[**] This work was supported by the National Natural Science Foundation of China (Nos. 50221201, 90301010, 20373077, 20471062, 50573084), the National Research Fund for Fundamental Key Projects, No. 973(2006CB806200), and the Chinese Academy of Sciences. Prof. Lei Jiang and Dr. Jinjie Xu are gratefully acknowledged for their helpful measurements. Supporting Information is available online from Wiley InterScience or from the authors.

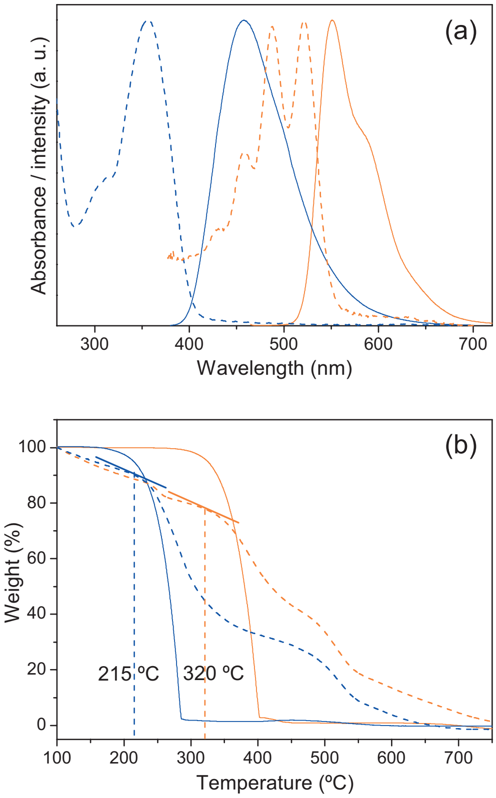


Figure 1. A) Absorption (dashed) and fluorescence emission (solid) spectra of TPP (blue) and rubrene (orange) monomers in ethanol. B) TGA plots of pure dyes (solid) and the mixtures of adsorbent and dye with w/w ratio of 100:1 (dashed). All plots were measured in nitrogen atmosphere at a heating rate of 10 °C min^{-1}, and the weights of dyes were normalized to 100 %.

sorbent (Fig. 1B) indicate that the introduction of adsorbent decreases the sublimation temperatures and slows the weight-loss processes of both TPP and rubrene markedly, through which the degree of saturation can be readily controlled during PVD experiments. The decrease of both the sublimation temperature and rate of weight loss should result from the strong adsorption of the organic vapors by the adsorbent. The slopes of the plots indicate that the rate of weight loss of TPP at 215 °C approximately equals that of rubrene at 320 °C. Therefore the deposition sources of TPP and rubrene were placed in regions at ca. 215 °C and 320 °C, respectively, to ensure doping uniformity (see Supporting Information, Fig. S1). The doping content can be tuned by changing the molar ratio of the two sources.

Figure 2 shows typical scanning and transmission electron microscopy (SEM and TEM) images of the binary nanostructures with a TPP/rubrene molar ratio of 100:1. The images indicate that the products obtained here are 1D nanorods and nanowires with high monodispersity, and each individual rod/wire has uniform diameter throughout the entire length. It has been proved that[4] single-crystalline 1D nanostructures are produced using adsorbent-assisted PVD when only one source is used for deposition. The selected area electron diffraction (SAED) pattern in Figure 2 indicates that the addition of a very small amount of dopant decreases the crystallinity of TPP to polycrystalline.

To investigate further the crystal structure of the binary nanomaterials, we characterized the X-ray diffraction (XRD) spectra of the doped nanowires with different dopant contents; the results are shown in Figure 3. When the rubrene doping ratio is very low, the XRD mainly shows the peaks of TPP, and the diffraction peaks of (001) and (002) lattice planes are strengthened significantly. This means that, at this doping ratio, the TPP single-crystal structures have not been destroyed notably, and the nanowires grow along the *c*-axis of the TPP crystal. When the doping ratio is increased to 5:1, the diffraction peaks of rubrene emerge. It is important to note that the addition of rubrene does not change the crystal structure of TPP, and the diffraction pattern of the binary nanowires is just the superposition of the patterns of the two compounds without any peak shifts or the appearance of new diffraction peaks. This indicates that the rubrene is also crystalline in the doped nanomaterials, but there is no formation of a co-crystal or superlattice-type composite crystal,[9] which may be determined by the fact that the crystal structures of the two compounds do not match each other[10] and there is no recognition factor such as hydrogen bonds[11] between the two kinds of molecules. To further prove this, we also deposited TPP and rubrene sequentially, whereby the two compounds grew into 1D nanostructures separately (see Supporting Information, Fig. S2).

The conservation of the TPP crystal structures indicates that there is phase separation rather than co-crystal formation in the doped nanowires. This can also be proved by the fact that increasing the rubrene content influences the preferential growth of TPP along the *c*-axis, which is reflected by the relative diffraction intensities in Figure 3. The phase separation

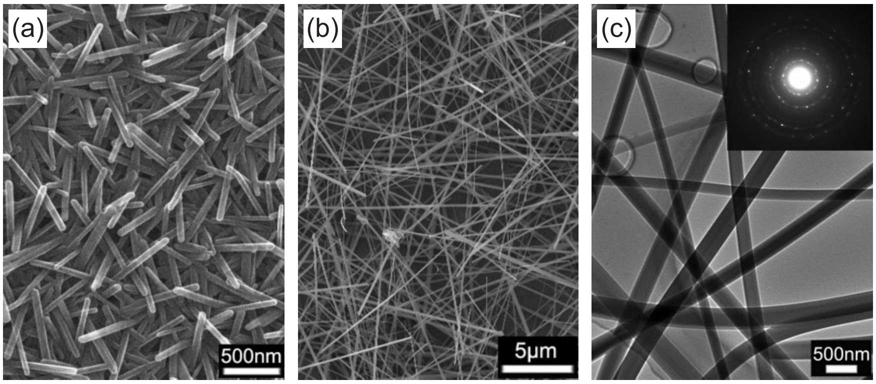


Figure 2. FE-SEM (A,B) and TEM (C) images of the binary nanostructures with a TPP/rubrene molar ratio of 100:1 prepared under different conditions. Inset: SAED pattern of the nanowires.

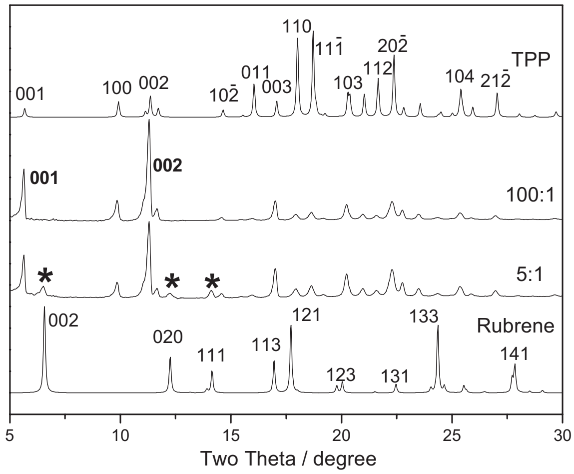


Figure 3. XRD patterns of the 1D nanomaterials with TPP/rubrene molar ratios of 100:1 and 5:1. The stars indicate the diffraction peaks of rubrene. For comparison, the patterns of TPP and rubrene powders are also displayed.

cannot be observed with TEM because the two compounds are both small molecules with light atoms and there is no contrast between them. Although the rubrene phase is also crystalline, its diffraction is still much weaker than that of the TPP even when the ratio is as high as 20 %. This indicates that rubrene is the dispersed phase in each wire and the size of the rubrene crystal grains is very small compared with that of the TPP matrix. The emission color of each single wire is very uniform, as illustrated below, so the rubrene crystal grains are dispersed very uniformly in the TPP matrix. The crystallinity[12] of rubrene in our work will significantly increase the color stability of the doped materials[12,13] since amorphous rubrene is apt to be oxidized when exposed to air directly, which will be discussed later.

The rubrene content shows no evident influence on the shape and size of the as-prepared nanostructures, but the length and diameter can be readily controlled to a large extent by altering the deposition time and substrate temperature, respectively (see Supporting Information, Table S1). In comparison, the length can be tuned to a much larger extent, which means that the deposition time is the predominant factor for determining the aspect ratio of the nanostructures. In the adsorbent-assisted PVD method used in the work reported here, no catalyst was employed and no droplets were found on the tops of the wires, so the growth of the nanowires should be controlled by a vapor–solid (VS) process.[14] The doped nanomaterials present good thermal stability and can withstand temperatures as high as 220 °C for several hours under the protection of nitrogen.

Figures 4A–C show the fluorescence microscopy images of the binary nanostructures with various doping contents (see Supporting Information, Fig. S3, for more colors). The homogeneous emission color from all of the nanorods/wires in each sample testified that rubrene crystal grains were dispersed uniformly in the TPP matrix, which is also evidenced by the spatially resolved fluorescence spectra (see Supporting Information, Fig. S4), which reveal that the emission colors from different areas of each single wire were still homogeneous even when the doping ratio was as high as about 20 % (the highest doping ratio in this work). It is interesting to note that there is a bright luminescent point (known as the outcoupling light)[15a] at the top of every rod. Characterization by micro-area fluorescence microscopy of a single nanorod (insets in Fig. 4C) suggests that the bright points are induced by the optical waveguiding property of the 1D nanostructures. Generally, light emission can only be observed within the immediate vicinity of the excitation position in micro-area fluorescence images. However, for the present binary nanorod sample, the excitation light can be propagated to the top along the length direction, irrespective of the excitation position. The nanoscale optical waveguides can act as building blocks for miniaturized optoelectronics in the future. To the best of our knowledge, nanostructured organic optical waveguides have attracted much less attention than those based on inorganic materials.[15] The optical waveguiding property should result from the high degree of molecular orientation in the crystalline 1D nanostructures.[4]

It is revealed by fluorescence microscopy images that the color of the emitted light evolves from blue to orange with increasing rubrene content and, more interestingly, white-light emission can be achieved when the proper TPP/rubrene molar ratio is used. For example, the CIE coordinates of the emission from the sample with TPP/rubrene molar ratio of 100:1 is (0.340, 0.345), which is very close to the coordinates for pure white light, (0.333, 0.333). The tunable emission can also be observed from the evolution of fluorescence spectra of the nanostructures as a function of rubrene content (Fig. 4D). For the measurements of the emission spectra, the excitation wavelength of pure rubrene was 485 nm, and that of the other samples was 365 nm. When the pure rubrene nanorods were excited with 365 nm the emission intensity was too weak. However, when the doped nanorods were excited with 365 nm, where the absorption of TPP is very strong and that of rubrene is very weak, both the blue-light emission from TPP and the orange-light emission from rubrene can be obtained, and with increasing rubrene content the emission from rubrene increased gradually at the expense of that of TPP. More importantly, with excitation at 365 nm the emission from rubrene in the range 520–700 nm is obviously enhanced compared with that obtained with an excitation wavelength of 485 nm (20 times for nanorods with TPP/rubrene molar ratio of 5:1, see Supporting Information, Fig. S5). These results indicate that efficient energy transfer from TPP to rubrene must occur in the present binary nanostructures, through which the emission of TPP was partially quenched and the emission from rubrene was significantly enhanced. The energy transfer can also be evidenced by the fact that the excitation spectrum of the doped nanorods monitored at 600 nm (the emission from rubrene) agrees well with the absorption spectrum of TPP, but not with that of rubrene (see Supporting Information, Fig. S6).

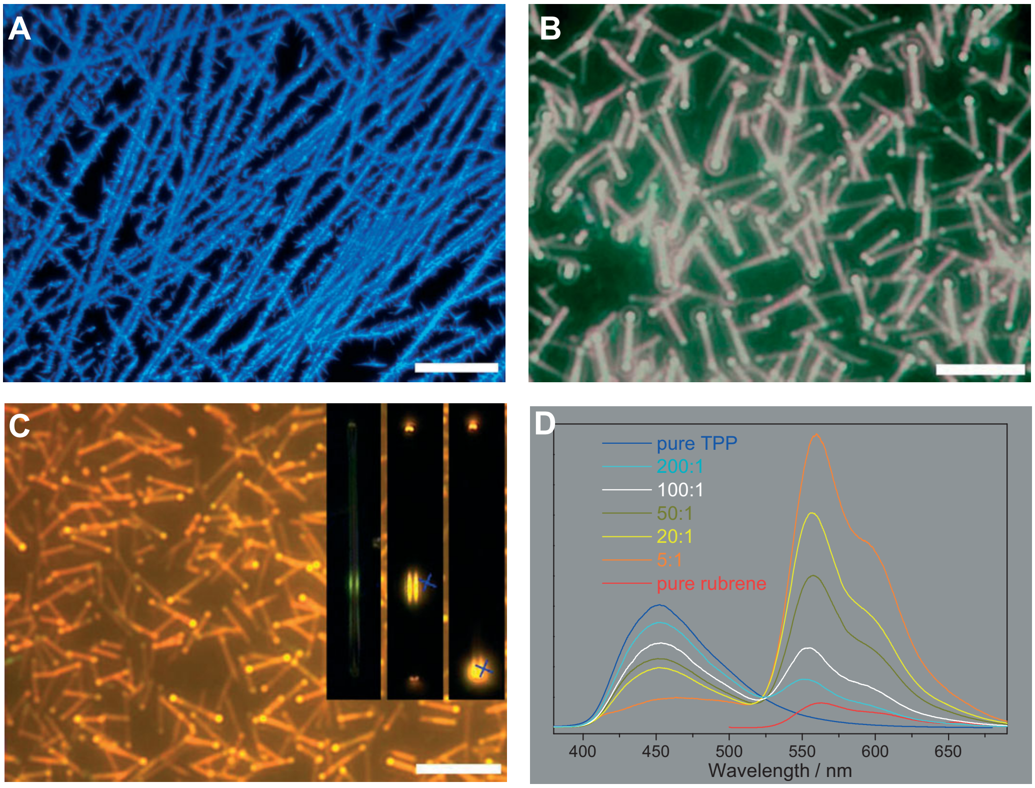


Figure 4. A–C) Fluorescence microscopy images of the nanostructures with different rubrene contents. A) Pure TPP, excited with UV (330–385 nm), B) 100:1 or molar TPP/rubrene, excited with UV, C) pure rubrene, excited with blue light (460–490 nm); all scale bars are 5 μm. D) Emission spectra of the nanowires deposited onto quartz wafers with different rubrene contents. Insets: Bright-field image (left), and micro-area fluorescence images of a single nanorod obtained by exciting the middle part (middle) and top area (right) using a focused laser. The blue crosses indicate the excitation position.

In contrast, neither quenching of the emission from TPP nor enhanced emission from rubrene can be observed from mixed solutions with the same molar ratios, which indicates that uniform dispersion and the compact contact of TPP and rubrene are indispensable for the occurrence of efficient energy transfer. Since molecular diffusion is restricted by the solid state of the doped systems, the mechanism of energy transfer must be of long-range character.[16] The decay of the emission from TPP becomes faster with increasing rubrene content (see Supporting Information, Fig. S7), so nonradiative intermolecular fluorescence resonance energy transfer (IFRET) should be the dominant energy transfer mechanism in the doped 1D nanomaterials. The rise stages of the fluorescence decay profiles of rubrene lag behind those of TPP by about 3 ns in all the doped materials (see Supporting Information, Fig. S7), which further proves the energy transfer between the two components.

For comparison, we also prepared doped amorphous thin films using a co-evaporation technique.[17] The colors of the doped films are not stable because of the oxidation of rubrene (see Supporting Information, Fig. S8). In contrast, the results of time-dependent changes of the white emission spectra (see Supporting Information, Fig. S9) indicate that the emission colors of the binary nanowires are very stable. It has been mentioned above that this can be ascribed to the crystallinity of rubrene.[12,13] In the amorphous films, the emission of TPP can be quenched almost completely at 4 % rubrene doping content, which is caused by the higher energy transfer efficiency. In contrast, the emission of TPP could not be quenched completely even when the dopant content was as high as 20 % in the doped nanowires (Fig. 4D). This is because of the separation of the two phases, in which some of the TPP exitons cannot diffuse to the rubrene phase and cannot be quenched through energy transfer. Both the color stability and the incomplete quenching are essential to the realization of white-light emission.

In our previous work,[4] the adsorbent-assisted PVD method adopted in this work has been proven to be a general method for the preparation of crystalline 1D nanostructures of a single component. In the work reported here, to demonstrate the extensive applicability of this strategy in the fabrication of binary organic nanomaterials, 1D nanostructures of TPP doped with another energy acceptor compound, namely 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran (DCM), were also successfully obtained with the same method (see Supporting Information, Fig. S10). Actually, when other preparation methods were used, these two compounds tended to form doped 0D nanoparticles with amorphous structures.[2b] It should also be noted that there is no coupling emission at the tops of the TPP-DCM nanorods, which indicates that the waveguiding property of the binary 1D nanomaterials is provided mainly by the rubrene, which can also be proved by Figure S2.

In summary, crystalline 1D nanostructures of TPP doped with rubrene were prepared using adsorbent-assisted PVD. The 1D binary nanomaterials show a unique optical waveguiding property. IFRET was observed in the doping system, based on which the emission color of the binary nanomaterials can be readily tuned by modulating the molar ratio of the two compounds. White-light emission was obtained when the proper TPP/rubrene molar ratio was adopted. The crystal structure can significantly improve the color stability of the doped nanomaterials. The adsorbent-assisted PVD method was proven to be a general method for the preparation of binary 1D nanomaterials with crystalline structures. The strategy described here should serve as guidance for the design and fabrication of novel optoelectronic nanodevices.

Experimental

The TPP used in this work was synthesized according to the literature [18]. Rubrene and other chemicals were purchased from Acros and were used without further treatment. The doped binary nanorods and nanowires were fabricated by adsorbent-assisted PVD. In a typical preparation, neutral aluminum oxide was mixed uniformly with TPP and rubrene, separately, at a w/w ratio of 100:1, and each mixture was subsequently put into a quartz boat. The quartz boats loaded with the mixtures were then placed in a quartz tube, which was inserted into a horizontal tube furnace. Cooling water flowed inside the cover caps to achieve a reasonable temperature gradient in the tube. A flowing nitrogen atmosphere was employed during the process of vapor deposition to prevent the dyes from being oxidized. The flow rate of nitrogen was kept at 100 sccm (standard cubic centimeters per minute). Various substrates were placed downstream to collect the products. The kind of substrate did not influence the growth of the nanomaterials. The instrument is illustrated schematically in the Supporting Information (Fig. S1). The deposition sources of TPP and rubrene were placed in regions at temperatures of ca. 215 °C and 320 °C, respectively, to ensure doping uniformity.

The as-prepared nanorods and nanowires were characterized by field emission SEM (FE-SEM, Hitachi S-4300), TEM (JEOL JEM-2010), XRD (Rigaku D/max-2500), fluorescence microscopy (Olympus IX71), micro-area fluorescence spectra and images (AlphaSNOM scanning near-field optical microscope), UV-visible absorbance spectra (PE Lambda 35), fluorescence emission spectra (Hitachi F-4500), time-resolved fluorescence spectra (Horiba NAES-1100 PC), and fluorescence anisotropy (Horiba NAES-1100 PC). The rate of weight loss of the dyes and the dye/Al_2O_3 mixtures were measured using TGA (PE TGA-7) in nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

Received: March 5, 2007
Revised: July 24, 2007

[1] a) H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Matsuda, H. Nakanishi, *Jpn. J. Appl. Phys.* **1996**, *35*, L221. b) B. K. An, S. K. Kwon, S. D. Jung, S. Y. Park, *J. Am. Chem. Soc.* **2002**, *124*, 14410. c) A. J. Gesquiere, T. Uwada, T. Asahi, H. Masuhara, P. F. Barbara, *Nano Lett.* **2005**, *5*, 1321. d) Y. S. Zhao, F. Hu, W. Yang, Y. Ma, H. Fu, J. Yao, *J. Nanosci. Nanotechnol.* **2007**, *7*, 1201. e) Y. S. Zhao, W. Yang, G. Zhang, Y. Ma, J. Yao, *Colloids Surf. A* **2006**, *277*, 111.

[2] a) S. J. Lee, B. K. An, S. D. Jung, M. A. Chung, S. Y. Park, *Angew. Chem. Int. Ed.* **2004**, *43*, 6346. b) A. Peng, D. Xiao, Y. Ma, W. Yang, J. Yao, *Adv. Mater.* **2005**, *17*, 2070. c) J. Jang, J. H. Oh, *Adv. Mater.* **2003**, *15*, 977.

[3] a) Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* **2003**, *15*, 353. b) Y. Liu, H. Li, D. Tu, Z. Ji, C. Wang, Q. Tang, M. Liu, W. Hu, Y. Liu, D. Zhu, *J. Am. Chem. Soc.* **2006**, *128*, 12917. c) Y. S. Zhao, W. Yang, D. Xiao, X. Sheng, X. Yang, Z. Shuai, Y. Luo, J. Yao, *Chem. Mater.* **2005**, *17*, 6430. d) Y. S. Zhao, W. Yang, J. Yao, *Phys. Chem. Chem. Phys.* **2006**, *8*, 3300. e) J. K. Lee, W. K. Koh, W. S. Chae, Y. R. Kim, *Chem. Commun.* **2002**, 138.

[4] a) Y. S. Zhao, C. Di, W. Yang, G. Yu, Y. Liu, J. Yao, *Adv. Funct. Mater.* **2006**, *16*, 1985. b) Y. S. Zhao, D. Xiao, W. Yang, A. Peng, J. Yao, *Chem. Mater.* **2006**, *18*, 2302. c) Y. S. Zhao, H. Fu, F. Hu, A. Peng, J. Yao, *Adv. Mater.* **2007**, *19*, 3554.

[5] a) C. W. Tang, S. A. VanSlyke, C. H. Chen, *J. Appl. Phys.* **1989**, *65*, 3610. b) J. Kido, K. Kimura, K. Nagai, *Science* **1995**, *267*, 1332.

[6] a) B. S. Ong, Y. L. Wu, P. Liu, S. Gardner, *J. Am. Chem. Soc.* **2004**, *126*, 3378. b) L. Qu, G. Shi, *Chem. Commun.* **2004**, 2800.

[7] a) F. Steuber, J. Staudigel, M. Stössel, J. Simmerer, A. Winnacker, H. Spreitzer, F. Weissörtel, J. Salbeck, *Adv. Mater.* **2000**, *12*, 130. b) V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* **2004**, *303*, 1644.

[8] a) Z. R. Dai, Z. W. Pan, Z. L. Wang, *Adv. Funct. Mater.* **2003**, *13*, 9. b) H. Liu, Y. Li, S. Xiao, H. Gan, T. Jiu, H. Li, L. Jiang, D. Zhu, D. Yu, B. Xiang, Y. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 10794.

[9] N. Shan, F. Toda, W. Jones, *Chem. Commun.* **2002**, 2372.

[10] TPP is a monoclinic crystal system with $a = 8.929$ Å, $b = 5.901$ Å, $c = 15.595$ Å, $a = \gamma = 90°$, $ß = 93.391°$. Rubrene belongs to the orthorhombic system with $a = 14.44$ Å, $b = 7.18$ Å, $c = 26.97$ Å, $a = ß = \gamma = 90°$.

[11] B. R. Bhogala, A. Nangia, *Cryst. Growth Design* **2003**, *3*, 547.

[12] D. Käfer, G. Witte, *Phys. Chem. Chem. Phys.* **2005**, *7*, 2850.

[13] M. Kytka, A. Gerlach, F. Schreiber, J. Kovác, *Appl. Phys. Lett.* **2007**, *90*, 131911.

[14] a) P. D. Yang, C. M. Lieber, *J. Mater. Res.* **1997**, *12*, 2981. b) Z. R. Dai, Z. W. Pan, Z. L. Wang, *Solid State Commun.* **2001**, *118*, 351. c) C. Liu, Z. Hu, Q. Wu, X. Wang, Y. Chen, H. Sang, J. Zhu, S. Deng, N. Xu, *J. Am. Chem. Soc.* **2005**, *127*, 1318.

[15] a) K. Takazawa, Y. Kitahama, Y. Kimura, G. Kido, *Nano Lett.* **2005**, *5*, 1293. b) F. Balzer, V. G. Bordo, A. C. Simonsen, H.-G. Rubahn, *Appl. Phys. Lett.* **2003**, *82*, 10.

[16] N. J. Turro, *Modern Molecular Photochemistry*, Benjamin Cummings, Menlo Park, CA **1978**.

[17] R. Aroca, T. Del Cano, J. A. de Saja, *Chem. Mater.* **2003**, *15*, 38.

[18] S. R. Sandler, K. C. Tsou, *J. Chem. Phys.* **1963**, *39*, 1062.