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Novel blue-light-emitting hybrid materials based on oligothiophene acids and ZnO

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Abstract

Novel blue-light-emitting materials based on ZnO and 2,2′-bithiophene-5,5′-dicarboxylic acid (DTDA), 4′,3″-dipentyl-5,2′: 5′,2″: 5″,2‴-quaterthiophene-2,5‴-dicarboxylic acid (QTDA) have been prepared. The hybrid materials show that the PL $\lambda_{\max}$ are at 450 and 425 nm for DTDA–ZnO and QTDA–ZnO, respectively.

1. Introduction

Blue luminescent materials in particular have been of intense interest in part because they are one of the key color components required for full-color displays and are still rare in applying to LEDs appropriately. Pursuing efficient and stable blue-light-emitting material remains a challenge. The materials based on inorganic materials are favorable in the full width at half maximum (FWHM), however, they are unstable over long periods and the color purity of light-emitting materials is not ideal for using in blue-light-emitting devices [1]. Polymeric light material is not satisfied in the color purity, too. ZnO is an important electronic and photonic material because of its wide band gap and high mechanical and thermal stabilities at room temperature. Thiophene-based monodisperse π-conjugated oligomers have much interest as active material in field effects transistors or light-emitting diodes. Mixing organic and inorganic compounds in an important hybrid material has appeared for a long time as a simple way to acquire specific properties not to be brought from each component and are presently largely used for advanced materials with desirable optical, electrical, and magnetic properties [2–4]. More recently, the possibility of combining inorganic and organic components in a more intimate way by means of covalent or non-covalent bonds has opened wide the application fields of inorganic–organic hybrid compounds [5]. These strong interactions not only allow self-assembly processes but also new interesting properties can arise from the close interactions between both components. In the present work we successfully designed to synthesize organic/inorganic hybrid nanomaterials based on ZnO and thiophene acid oligomers. And more interesting, the blue-light-emitting (at 450, 425 nm) was observed in the two hybrid materials.

2. Experimental

2.1. Materials and measurements

Most chemical reagents were purchased from Acros or Aldrich Corporation. All solvents were purified using standard procedures. Column chromatography was

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performed on silica gel (size 160–200 meshes). FT–IR spectra were measured on a Bruker EQUINOX55 spectrometer in KBr pellet at room temperature. The UV–Vis and fluorescence spectra were obtained on a Hitachi U-3010 and Hitachi F-4500 spectrometer, respectively. The XRD patterns were recorded with a Japan Rigaku D/max-2500 rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54178 Å, employing a scanning rate of 0.05° s^{-1} in the 2θ range from 10° to 70°. Transmission electron microscopy (TEM) images were collected on a Hitachi 800 instrument with a 100 keV accelerating voltage. Cyclic voltammograms (CV) and photocurrent were recorded on CHI660B voltammetric analyzer (CH Instruments, USA). Fluorescence lifetimes were calculated from time-resolved fluorescence intensity decays using a photo-counting streak camera (C2909, amamatstu). This machine uses a femto-second laser source running at 1 kHz.The laser's output wavelength can be set to the desired excitation with OPA (OPA-800CF, Spectra Physics).

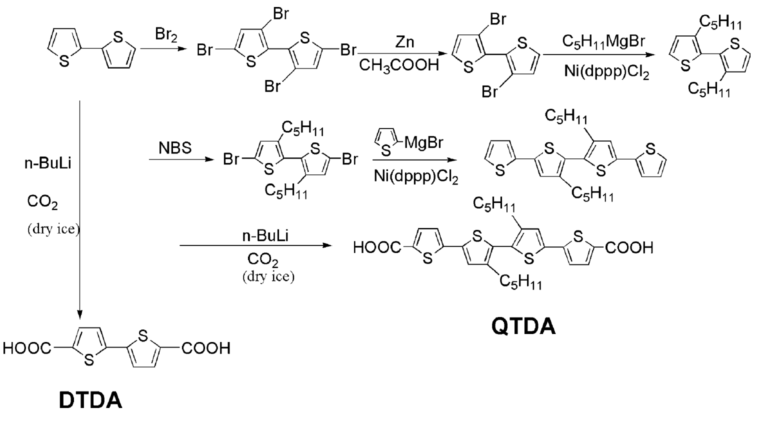
Bithiophene acid and quaterthiophene acid were prepared according to the previously reported procedure [6,7]. The synthesis route was shown in Scheme 1. 3,3′-Dipentyl-2,2′-bithiophene was synthesized using bithiophene as the starting material through bromination, debromination and the Grignard coupling reaction with corresponding reagent. Direct bromination of the bithiophene derivative with NBS afforded the 80% yield, after purification. Quaterthiophene was synthesized from 2-bromothiophene through the Grignard coupling reaction with its magnesium bromide. DTDA and QTDA were synthesized from the corresponding bithiophene and quaterthiophene derivative by lithiation with butyllithium and followed by carboxylation with dry ice. The chemical structures of the organic compounds were verified by ^{1}H NMR, FT–IR, Mass Spectra and Elemental Analyses. DTDA: ^{1}H NMR ($CDCl_3$, ppm) δ 10.34 (m, 2H), 7.76 (m, 2H), 7.00 (m, 2H); FT–IR (KBr) v (cm^{-1}) 1664 (C=O); Anal. Calc. for $C_{10}H_6O_4S_2$ C, 47.23; H, 2.38; Found: C, 47.20; H, 2.39. MS (EI): *m*/*z* 254. QTDA: ^{1}H NMR ($CDCl_3$, ppm) δ 7.74 (m, 2H), 7.46 (s, 2H), 7.36 (m, 2H), 2.09 (m, 4H), 1.59 (m, 4H), 1.28 (m, 8H), 0.86 (t, 6H, J = 6 Hz); FT–IR (KBr) v (cm^{-1}) 1666 (C=O); Anal. Calc. for $C_{28}H_{30}O_4S_4$ C, 60.18; H, 5.41; Found: C, 60.14; H, 5.42. MS (TOF): *m*/*z* 558.

The hybrid nanomaterials have been prepared by the reaction of ZnO and thiophene acid oligomers. In a typical synthesis, 15 mg (0.036 mmol) QTDA/DTDA was dissolved in 10 ml of aqueous solution of NaOH 7.2 mmol/L. The resulting brown solution were dropped to the solution of $Zn(Ac)_2 \cdot 2H_2O$ under stirring and keep for 2.5 h. After the mixture was centrifuged, the crude product was washed with water and dried at 70 °C in vacuum for 6 h. The QTDA–ZnO/DTDA–ZnO product was obtained, which was characterized by transmission electron microscopy (TEM), powders X-ray diffraction measurement (XRD) and infrared (IR).

3. Results and discussion

The TEM image (Fig. 1a) shows that the morphology of DTDA–ZnO is nanocuboids, which the average size is 100 nm × 250 nm. The size distribution histograms of nanocuboids are shown in Supplementary files. Fig. 1b displays the morphology of the QTDA–ZnO is nanorods. The diameter of these 1D rods is 80–200 nm, and the length is 250–600 nm. The powders XRD patterns of DTDA–ZnO and QTDA–ZnO (Fig. 2) show that the two prepared hybrid ZnO are wurtzite structure (JCPDS 36–1451). In Fig. 2, all diffraction peaks can be indexed perfectly to this crystal system. The sharp peaks of those patterns indicate the crystallites in the hybrid materials are high.

Shown in Fig. 3 are the UV–vis spectra recorded in room temperature colloid of the hybrid materials prepared from the oligothiophene acids and zinc oxide.



Scheme 1. The synthesis of DTDA and QTDA.

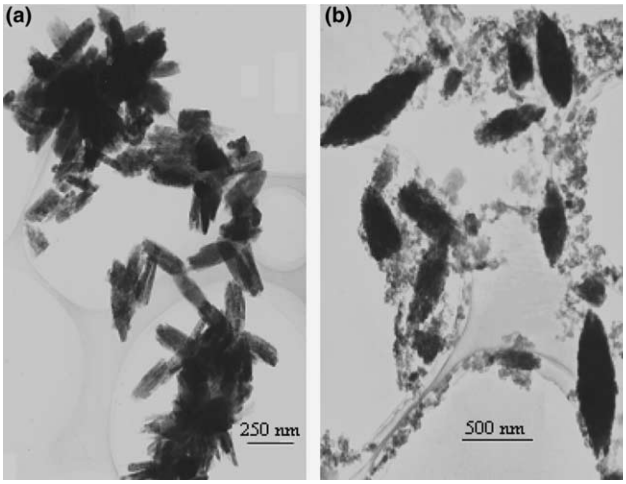


Fig. 1. TEM images of as prepared ZnO: (a) DTDA–ZnO nanocuboids; (b) QTDA–ZnO nanorods.

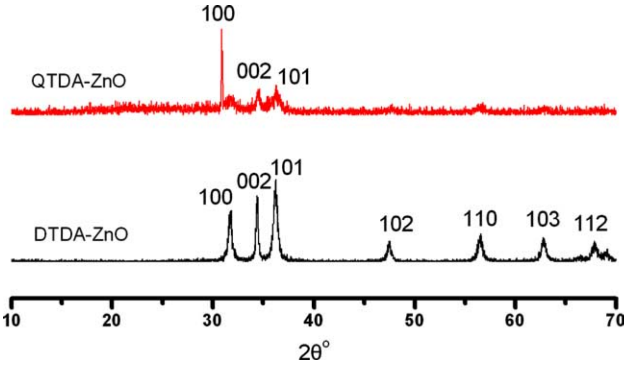


Fig. 2. XRD patterns of DTDA–ZnO, QTDA–ZnO.

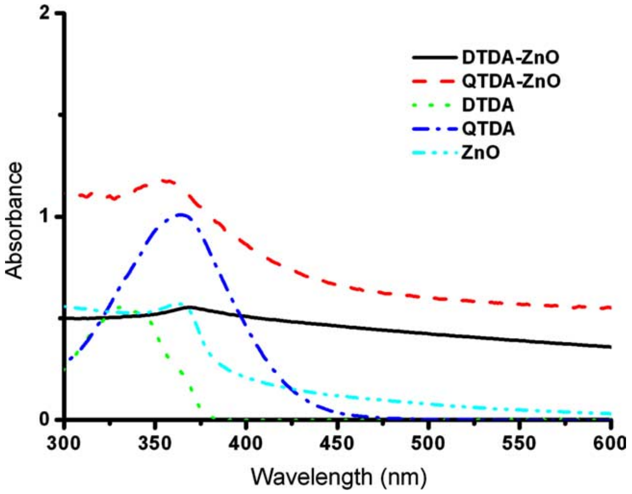


Fig. 3. Absorption spectra of DTDA–ZnO, QTDA–ZnO in suspension and DTDA, QTDA in ethanol solution.

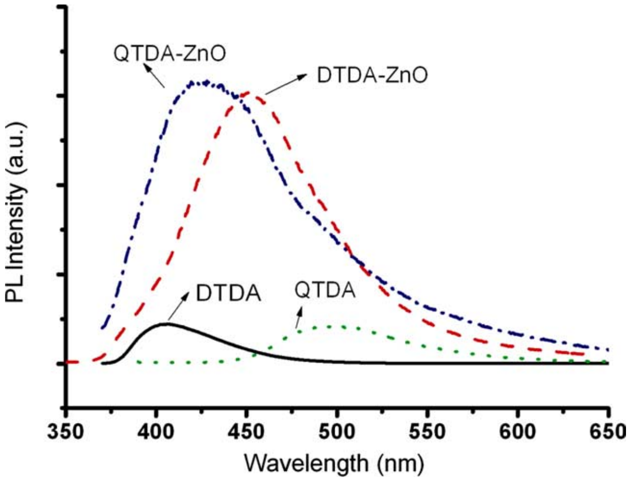
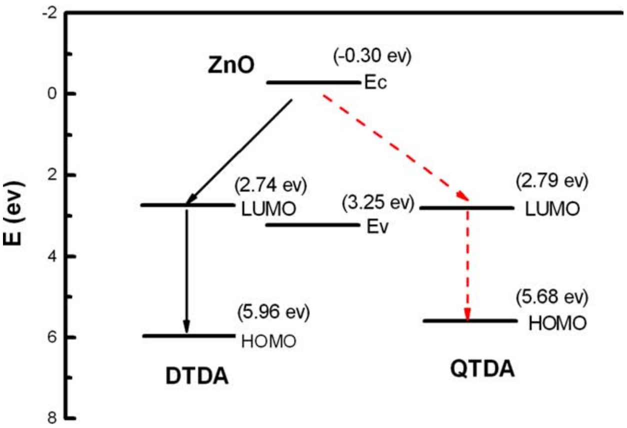


Fig. 4. The room temperature PL spectra: DTDA ($\lambda_{ex} = 330$ nm), QTDA ($\lambda_{ex} = 350$ nm) in ethanol, DTDA–ZnO ($\lambda_{ex} = 325$ nm) and QTDA–ZnO ($\lambda_{ex} = 345$ nm) colloid in ethanol.

The absorption spectra of DTDA–ZnO and QTDA–ZnO exhibit a promontory, centering at 369 and 353 nm. While the absorption peaks of the DTDA and QTDA are at 331 and 364 nm, respectively. There is obvious difference from the absorption of ZnO nanocrystals. It suggests that the hybrid materials containing ZnO and thiophene acid oligomer are formed.

Fig. 4 illustrates the room temperature photoluminescence (PL) spectra recorded DTDA, QTDA and the hybrid ZnO, respectively. It is clear that the PL peak of DTDA–ZnO at 450 nm and the peak of QTDA–ZnO at 425 nm are in the blue emission region. It is well known that the PL peaks of ZnO are about 385 and 500 nm, which the peak at 385 nm is resulted from the direct integration of induced exciton [8], and the green emission was caused by impurity and different intrinsic defects in ZnO, such as oxygen and zinc vacancies in the crystal [9,10], respectively. We observed at the first the blue emission at 450 and 425 nm of ZnO 1D nanomaterials, respectively, which were only observed in ZnO film [11]. In ZnO film, the blue emission included from the donor to the valence band and from the conduction band to the acceptor. In Fig. 4 the peaks of oligothiophene acids disappeared, which may attribute to the charge transfer from ZnO to DTDA and QTDA, as a result that the PL of DTDA and QTDA are quenched. This is consistent with the next result of electrochemical calculation. In our design, the oligothiophene acids play an ‘impurity’ role. DTDA and QTDA are connected with the surface of ZnO and Zn^{2+} have a tendency to the surface of ZnO crystal. The excess Zn^{2+} form the surface fluorescence centers and thereby the new blue emission band is excitated. The coordination of DTDA and QTDA make positive Zn^{2+} ions adsorbed at the carrier particle promote visible fluorescence by deforming interatomic bonds, thus it alters the surface energy level structure of ZnO by charge transfer. Therefore, the concept of surface fluorescence centers seems to be more realistic for blue emission band. As for the position difference of the two hybrid material PL peaks, this is maybe result from intrinsic defects depending on hybrid ZnO forms and preparation conditions.



Scheme 2. Electron transfer mechanism of oligothiophene acids and ZnO.

The direction of charge transfer may be concluded from energy levels calculated according to electrochemical data. The CV was performed in a solution of Bu_4NPF_6 (0.1 M) in DMF at a scan rate of 20 mV/s at room temperature under the protection of nitrogen. One platinum electrode was used as the working electrode and the other Pt wire was used as the counter electrode. An argentum electrode was used as the reference electrode. The HOMO energy level of DTDA is at 5.96 eV, which is obtained by cyclic voltammetry. Considering its onset of absorption peak at 386 nm, the LUMO energy level is at 2.74 eV, and the energy gap is 3.22 eV. In the same manner, the LUMO energy level of QTDA is at 2.79 eV, and the energy gap is 2.89 eV from the onset of UV absorption at 431 nm. The band gap of nanometer scale ZnO is 3.55 eV [12]. The conduction band (E_c) and valence band (E_v) of ZnO is at −0.30 and 3.25 eV, respectively, with respect to the vacuum energy level. The mechanism of the energy-transfer process between ZnO and oligothiophene acids can be proposed (shown in Scheme 2).

Table 1
Photophysical Parameters of the hybrid materials (298 K) investigated in ethanol

Hybrid material	τ_1 (ns)	τ_2 (ns)	τ_{av} (ns)	k_{ET}
DTDA–ZnO	0.64 (34%)	3.37 (66%)	2.44	4.1×10^8
QTDA–ZnO	0.05 (48%)	0.27 (52%)	0.16	6.0×10^9

When the ZnO nanoparticles are irradiated, electrons of ZnO can be excited from valence band (E_v) to conduct band (E_c). The charges at the E_c of ZnO can easily transfer to the ground state of oligothiophene acids. The energy levels of oligothiophene acid (HOMO and LUMO) and ZnO (E_v and E_c) are compatible for charge transfer. ZnO nanoparticles are as donors, and DTDA and QTDA are as acceptors in this system. Charge transfer processes from ZnO to oligothiophene acids result in the fluorescence of oligothiophene acid molecules are quenched.

The dynamics of energy-transfer behavior between the two chromophore units was examined by employing the time-resolved nanosecond fluorescence spectroscopy as shown in Fig. 5 and Table 1. The experiments on lifetime measurements are carried out by exciting hybrid materials at 355 nm and monitoring the visible band. ZnO emission should be a multiexponential process with a series of short and long (nanosecond–microsecond) component. But in the present investigation we did not observe any emission decay in microsecond time domain. The both hybrid materials show dual life from Table 1. For DTDA–ZnO the lifetime spectrum includes two components with 0.64 and 3.37 ns, respectively. Similarly the two component of QTDA–ZnO are 0.05 and 0.27 ns. We have determined the average time constant (τ_{av}) and energy-transfer rate constants (k_{ET}) out of these two decay components for the hybrids of different thiophene acids.

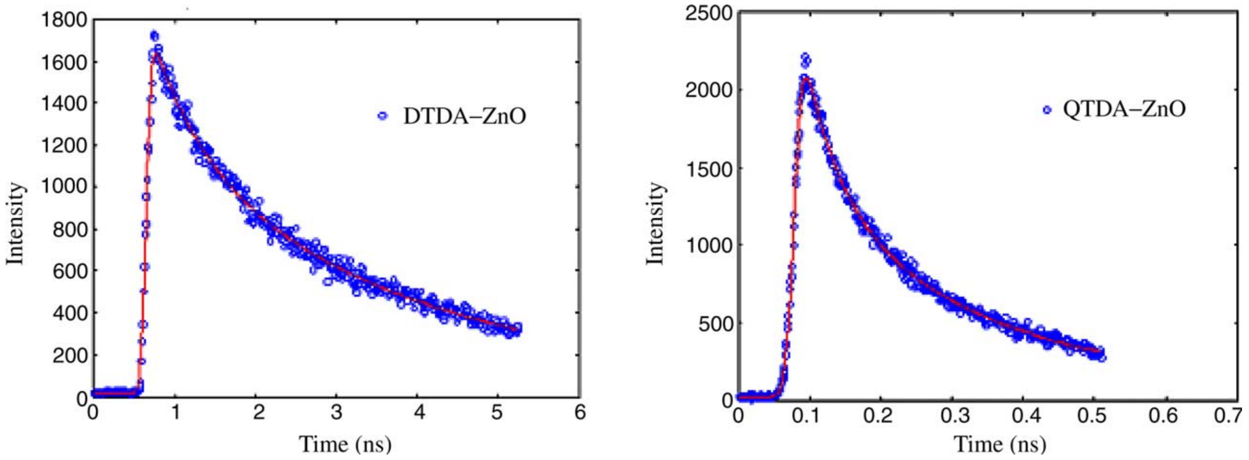


Fig. 5. Time-resolved photoluminescence decay profile of DTDA–ZnO and QTDA–ZnO in ethanol (circle).

4. Conclusion

In conclusion, both DTDA–ZnO and QTDA–ZnO show strong blue fluorescent emission with high brightness and good efficiencies, and they may be used as an advanced material for blue-light-emitting diode devices. The photophysical properties of hybrid materials have been monitored using steady-state and time-resolved emission and absorption spectroscopy. The hybrid materials may make it a candidate for thermally stable and solvent resistant blue fluorescent material for its low solubility in most common solvents.

Acknowledgements

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Appendix A. Supplementary files

Infrared spectrum and size distribution histograms of nanocuboids. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.cplett.2004.09.045.

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