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Synthesis of Conjugated Polymer-Bonded Carbon Nanotubes with Large Third-Order Optical Nonlinearities

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Nonlinear optical materials are required for the construction of photonic devices that will be able to control the amplitude gain or extinction, phase, polarization, and reflection or refraction of optical beams for a wide range of important applications. The lack of appropriate nonlinear materials has been a significant barrier in the development of such photonic devices. Carbon nanotubes have been investigated for many potential applications. Their unique one-dimensional π -electron conjugation, mechanical strength, and high thermal and chemical stability, makes them very attractive for use in many applications. Theoretically, the extended Su-Schrieffer-Heeger (SSH) model with the Coulomb interaction taken into account has been used by Xie and Jiang estimated^[1-3] to study the optical nonlinearity of single-walled carbon nanotubes (SWNTs). They found the magnitudes of the second-order hyperpolarizabilities γ to be 10^{-29} esu. Marguulis and Sizikova^[4] and Wan et al.^[5] have also theoretically predicated γ to be larger than 10^{-29} esu for SWNTs. Multiwalled carbon nanotubes (MWNTs) were dispersed ultrasonically in a solution of polypyrrole/m-cresol and the third-order susceptibilities $\chi^{(3)}$ of the resulting dispersion of MWNTs/polypyrrole-m-cresol were measured by Liu et al.^[6] using degenerate four-wave mixing (DFWM) techniques. It should be noted that the above investigations were performed using carbon nanotubes dispersed in organic solvents, due to their poor solubility, and such dispersions were unstable at high concentrations. Hence it is highly desirable to obtain stable carbon-nanotube-containing solutions.

Polyheteroarylene methines exhibited an extremely narrow band gap ($E_g=0.7\text{eV}$) and large third-order NLO responses ($\chi^{(3)}=10^{-9}\text{-}10^{-7}\text{esu}$). In our previous study, a series of more than 10 poly(heteroarylene methine) derivatives were synthesized^[7] and the third-order NLO properties

were studied by using z-scan, DFWM, and time-resolved optical Kerr effect techniques. In this study, we report the functionalization and solubilization of MWNTs realized by attaching a polyheteroarylene methines with amino moieties, poly{[3-octylthiophene-2,5-diyl]-[p-aminobenzylidenequinomethane] } (POTABQ), to the tubes. Third-order NLO nonlinearities of POTABQ-bonded MWNTs (POTABQ-MWNTs) are studied by using DFWM techniques. POTABQ-MWNTs exhibited large NLO responses mainly due to the formation of an intramolecular photoinduced charge transfer system.

POTABQ was synthesized according to the procedure reported in the literature^[8]. To solubilize and functionalize MWNTs, we added POTABQ to MWNTs via the formation of an amide functionality. Purified MWNTs (100 mg) in 20 mL of SOCl_2 with 1 mL of dimethylformamide (DMF), were stirred at 70 °C for 24 h. The mixture was cooled and centrifuged at 2000 rpm for 30 min. The excess SOCl_2 was decanted and a black solid was recovered and dried under vacuum. POTABQ (0.90 g) was dissolved in 50 mL DMSO. SWNT- COCl (0.10 g) was then added to the solution. The mixture was heated at 100°C and stirred for 4 days. After cooling, the solid was poured into excess MeOH and stirred, and the washings were filtered through a membrane (pore size 0.2 μm). After drying, the black solid was treated with CHCl_3 . The black mixture was then filtered through coarse filter paper and the filtrate was dried on a rotary evaporator.

Figure 1 shows a micrograph of POTABQ-MWNTs at a magnification of 50 000, which exhibits a beads-shaped structure. Extensive microscopy studies have shown the diameter of polymer cluster is about 100nm, while the diameter of tubes is about 10nm. In

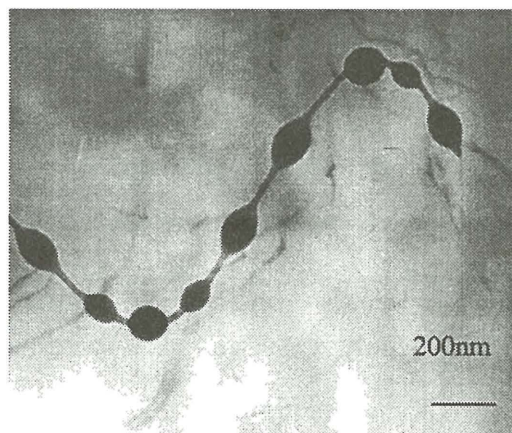


Fig. 1. TEM image of POTABQ-MWNTs.

our previous study, well-aligned polyaniline/ carbon-nanotube composite (PANI-MWNT) films with strong molecular interactions were prepared by in-situ aniline polymerization. Aligned MWNT films were encapsulated in the cores of the growing polymer chains, resulting in the formation of a PANI-MWNT hybrid material. In the case of POTABQ -MWNTs, the mechanism of wrapping is different. Carboxyl is introduced to

both the tips and the side-wall of the tubes, when MWNTs is refluxed in HNO_3 . The Carboxyl is then converted to acyl chlorine group. POTABQ is grafted to the tubes via amide reaction of $-\text{NH}_2$ group and acyl chlorine group. The morphology depends on the function group density on the tubes. Low acyl chlorine group density may lead to the formation of “beads-shaped structure”, while high acyl chlorine group density may lead to whole wrapping.

The IR spectra (KBr pressed pellet), of both POTABQ-MWNTs and POTABQ (Fig. 2) exhibit broad absorption bands at 3400 cm^{-1} arising from N-H stretching modes of the amide group. The amide carbonyl group appears as a broad peak at 1688 cm^{-1} . These peaks indicate the formation of an amide structure. Peaks at 2922 cm^{-1} and 2843 cm^{-1} are due to the C-H stretching modes in the alkyl chain (appearing at 2927 cm^{-1} and 2849 cm^{-1} in the parent polymer). An important feature for POTABQ is the weak absorption shoulder at 1640 cm^{-1} , which is attributed to C=C stretching vibration of the quinoid thiophene ring (it is concealed in the absorption band of amide at 1688 cm^{-1} for POTABQ-MWNTs). The sharp peaks at 1587 cm^{-1} and 1490 cm^{-1} are from the aromatic C=C bond stretching mode (1590 cm^{-1} and 1497 cm^{-1} in the parent polymer). Many of the same vibrational modes are seen in other forms of SWNTs.

Figure 3 shows the UV-vis absorption spectra of POTABQ and POTABQ-MWNTs in room-temperature chloroform. POTAB solution exhibits an absorption band around 400nm and a

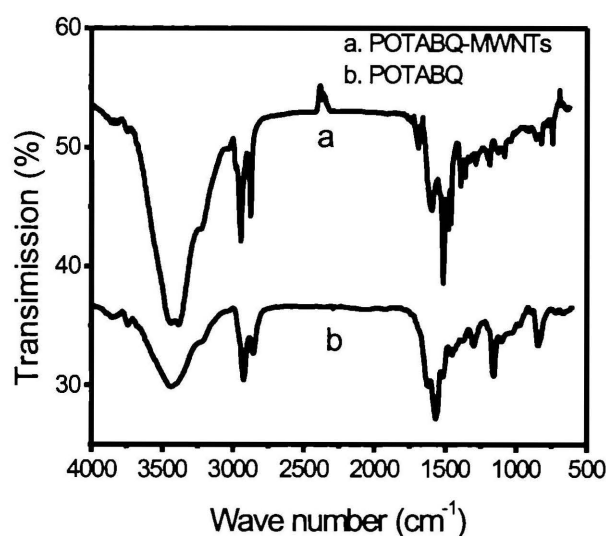


Fig. 2. FTIR spectra of POTABQ-MWNTs and POTABQ.

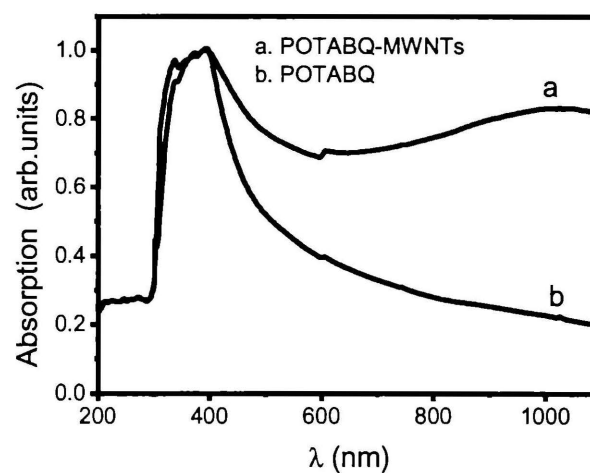


Fig. 3. Absorption spectra of POTABQ and POTABQ-MWNTs.

broad weak decaying tail in visible region. The absorption band in ultraviolet region ranging from 300-450nm is assigned to the π - π^* transition of aromatic thiophene ring in the main chain and benzene ring in the side chain. The broad weak decaying tail covering entire visible region arises from the π - π^* transition of methine bridge. POTABQ-MWNTs solution exhibits a strong absorption band around 400nm and a broad absorption band ranging from 800nm to 1100nm. The latter indicates that there is a significant ground-state interaction between POTABQ and MWNTs. Since POTABQ and MWNTs are jointed through π - π and p- π conjugated bond, the resulting POTABQ-MWNTs composites exhibit larger conjugation extend and charge delocation.

A considerable NLO enhancement effect was observed, which was attributed mainly to the formation of an intramolecular charger transfer system. The measured values of the nonlinear susceptibility, the figure of merit and the second-order hyperpolarizabilities of the sample are given in Table 1.

Table 1 Third order NLO properties for POTABQ-MWNTs and POTABQ

| Sample | $\chi^{(3)}(\times 10^{-9}\text{esu})$ | $\chi^{(3)}/\alpha(\times 10^{-13}\text{esu})$ | $\chi^{(3)}_{\text{MWNT-p}}(\times 10^{-9}\text{esu})$ | $\gamma(\times 10^{-31}\text{esu})$ |
|--------------|--|--|--|-------------------------------------|
| POTABQ | 6.22 \pm 0.74 | 6.28 \pm 0.75 | | $\gamma=98.60\pm 11.73$ |
| POTABQ-MWNTs | 144.12 \pm 26.94 | 93.58 \pm 17.49 | 137.90 \pm 26.94 | $\gamma_c=51.95\pm 9.71$ |

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