

# Optoelectronic and nonlinear optical properties of *t*Bu<sub>4</sub>PcTiO/polymer composite materials

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Received 17 February 2006; received in revised form 2 May 2006; accepted 19 June 2006

Available online 14 August 2006

## Abstract

The optoelectronic and nonlinear optical (NLO) properties of a soluble 2,(3)-(tetra-*tert*-butylphthalocyaninato)titanium(IV) oxide (*t*Bu<sub>4</sub>PcTiO) in solutions and in the solid states have been described. The nonlinear response demonstrated that *t*Bu<sub>4</sub>PcTiO exhibited strong RSA at 532 nm for both solution and solid-state based experiments. The decrease in the effective intensity dependent nonlinear absorption coefficient with increasing input intensities possibly results from high order triple state transitions of the excited-state population. No evidence of film fatigue or degradation was observed in the PMMA/*t*Bu<sub>4</sub>PcTiO film, after numerous scans at varying laser intensity. The doping of *t*Bu<sub>4</sub>PcTiO into poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene-vinylene] (MEH-PPV) results in the apparent increases of the open circuit voltage (Voc) and the short circuit photocurrent density under illumination with 40 mW cm<sup>-2</sup> white-light. The light absorption of *t*Bu<sub>4</sub>PcTiO incorporated into polymer represents the dominant contribution to the enhancement of the photocurrent. The dependence of the short circuit photocurrent in an ITO/*t*Bu<sub>4</sub>PcTiO-doped MEH-PPV/Al cell on the incident light intensity (*I*<sub>in</sub>) between 30 and 200 mW cm<sup>-2</sup> was also investigated.

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**Keywords:** Optoelectronic properties; Phthalocyanine/polymer composite materials; Nonlinear optics; Optical properties; Synthesis of phthalocyanine

## 1. Introduction

Since the titaniumoxo-phthalocyanine (PcTiO) was first reported by Lever in 1960 [1], as one of the most efficient charge generation materials, a tremendous amount of attention has been paid to PcTiO and its peripherally and/or axially substituted soluble derivatives over the past 20 years [2,3]. For example, a SciFinder 2004 search gave more than 470 hits (153 in the last four years) for patents dealing with titanium phthalocyanines [3]. These materials have found their potential/practical application in many high-technology fields, e.g. in nonlinear optics, photoconductivity, photovoltaic cells, recordable compact discs (CDs) and digital versatile discs (DVDs), photodynamic cancer therapy and others because of their excellent

optoelectronic properties and the possibility of preparing flexible films.

From the optimized molecular structure of the peripherally unsubstituted PcTiO [4], one can clearly see that the Ti atom sits slightly above the plane of the ring (around 0.3 Å) and there is very little distortion of the plane of the conjugated macrocyclic ring. The calculated Ti=O bond distance is about 1.69 Å (compared well with the value of 1.64 Å determined from X-ray crystallography [2b]). The calculated ground-state ( $\mu_g$ ), excited-state ( $\mu_e$ ), and transition ( $\mu_{eg}$ ) dipole moments are 4.48, 4.44 and 12.76 Debye, respectively [4]. PcTiO shows weak electronic conductivity of  $5 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$  at room temperature [2b]. Doping of PcTiO with *I*<sub>2</sub>, however, is accompanied by an increase of conductivity up to  $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ . The presence of the axial O ligand on the central Ti atom induces a perpendicular dipole moment with respect to the macrocycle plane, which alters the electronic structure of the macrocycle and introduces new steric effects modifying the spatial relationships between neighboring molecules [2,5]. The electron transfers

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from macrocycle  $\pi$  orbitals to metal Ti 3d orbital make a substantial contribution to the third-order nonlinear optical (NLO) response for the PcTiO [6]. Crystalline forms of PcTiO are chemically stable. Coupling between Pc molecules in the solid state creates an exciton band structure with much broader and strong absorption bands in a visible region [7], often covering about half the useful solar spectrum. With the Al/C<sub>60</sub> (acceptor)/PcTiO (donor)/ITO configuration, the energy conversion efficiencies ( $\eta$ ) for this type of organic solar cells are found to be high at low incident light intensities ( $P_{in}$ ) as a result of the formation of a p–n junction between C<sub>60</sub> and PcTiO, but decrease with an increase in  $P_{in}$  [8]. On the contrary, the photovoltaic cells with ITO/C<sub>60</sub>/PcTiO/Cr.Au configuration are stable even under white-light illumination at high  $P_{in}$ .

It is known that the disadvantage of peripherally unsubstituted phthalocyanines is their poor solubility in organic solvents. To overcome this problem, a variety of substituents, for example, alkoxy, alkyl, aryl, F, CF<sub>3</sub> and others, have been attached to the macrocycle, in varying numbers and different substitution patterns. In comparison with octasubstituted phthalocyanine, tetra-substituted phthalocyanine exhibits the much higher solubility mainly due to a lower degree of order in the solid state, which facilitates solvation by the more pronounced interaction with solvent molecules. Also, the less symmetric isomers possess a higher dipole moment caused by the more asymmetric arrangement of the substituents in the periphery of the macrocycle. Tetra(*tert*-butyl)-substituted Pcs and their metal complexes are the most frequently used when solubility is required [9]. Hanack and his co-workers have systematically studied the effect of the various peripheral substituents, e.g. alkyl, fluoroalkyl, and fluoroalkoxy, and substitution patterns on the solubility and photoconductivity properties of titaniumoxo-phthalocyanines [10]. The results show that the alkyl- and fluoroalkoxy-substituted PcTiO compounds are highly soluble in nonpolar solvents, while the fluoroalkyl-substituted compounds are better soluble in polar aprotic solvents such as acetone. Tuning of electronic and optical properties is effectively achieved by functionalization of the edges of the conjugated Pc ring [4,10]. Semiempirical quantum chemical calculations also demonstrate that the nature of peripheral substituents has a strong bearing on the valence electronic properties, including the state dipole moments and absorption wavelength [4]. The structural and photochemical properties of peripherally substituted 1,(4)- or 2,(3)-R<sub>x</sub>PcTiO, 2,(3)-NcTiO and 1,2-NcTiO (Nc: naphthalocyanine) have been intensively investigated for a better understanding of the carrier generation process [10a]. The nonlinear optical properties of some phthalocyaninatotitanium(IV) oxides, e.g. PcTiO, Me<sub>4</sub>PcTiO, (MeO)<sub>4</sub>PcTiO, (MeO)<sub>8</sub>PcTiO, and others, have been reported in order to study how the different peripheral substituents and substitution patterns of the rings can influence the reverse saturable absorption (RSA) of the respective oxo-titanium Pc's solutions [4]. The results showed that the functionalization of the edges of the conjugated rings could result in a fine tuning of the NLO properties of Pcs when TiO constituted the central metal–ligand combination. Fewer studies have, however, considered the practical application of such Pc complexes which would almost inevitably involve the solid-state casting of these

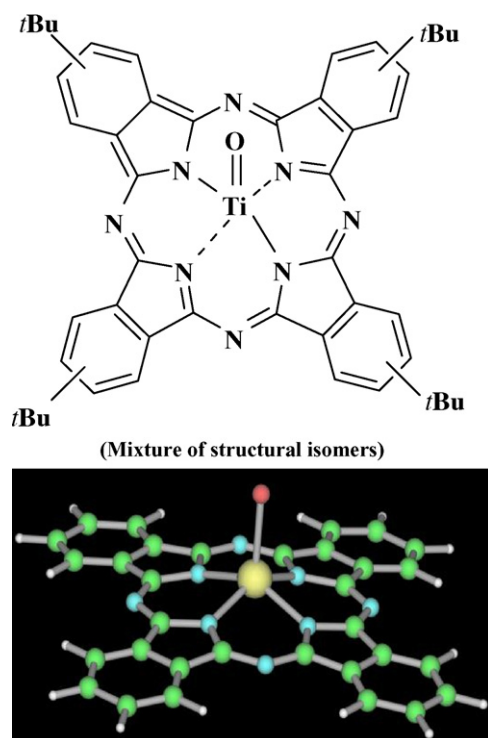


Fig. 1. Molecular structure of *t*Bu<sub>4</sub>PcTiO (upper panel) and optimized structure of peripherally unsubstituted PcTiO calculated by HF/3-21G level using Gaussian-98 package (lower panel).

compounds in some manner. In this contribution, we report the nonlinear optical and photovoltaic properties of a known soluble 2,(3)-(tetra-*tert*-butylphthalocyaninato)-titanium(IV) oxide compound (*t*Bu<sub>4</sub>PcTiO, Fig. 1) in the solid states. The focus of the nonlinear optical experiments was to characterize the response of *t*Bu<sub>4</sub>PcTiO both in solution and incorporated in a host polymer film. The photovoltaic behavior of *t*Bu<sub>4</sub>PcTiO-doped MEH-PPV films was also initially studied.

## 2. Results and discussion

Goedken et al. described the synthesis, reactivity and X-ray crystal structure of peripherally unsubstituted dichloro(phthalocyaninato)titanium (IV) (PcTiCl<sub>2</sub>) in 1985 [11]. The reaction of phthalodinitrile and titanium tetrachloride in  $\alpha$ -chloronaphthalene leads to a highly crystalline pure PcTiCl<sub>2</sub>, which is moderately stable to air, but is easily hydrolyzed by moist organic solvents. Solutions of this complex are extremely sensitive to trace amounts of water, producing the corresponding PcTiO [13]. In this contribution, we used the similar synthetic method to prepare soluble tetra-*tert*-butyl-substituted PcTiO (i.e., *t*Bu<sub>4</sub>PcTiO) in 35% yield. The absorption of the symmetric and antisymmetric Ti–Cl modes in the far-IR region at 395 and 350 cm<sup>-1</sup> were not observed in the IR spectrum of the resultant compound, suggesting non-existence of the residual *t*Bu<sub>4</sub>PcTiCl<sub>2</sub>. The characteristic stretching vibration of Ti=O at 974 cm<sup>-1</sup> was detected in the IR spectrum of *t*Bu<sub>4</sub>PcTiO. Its field desorption (FD) mass spectrum showed a cluster of peaks centered at  $m/z$  (%) = 801.0

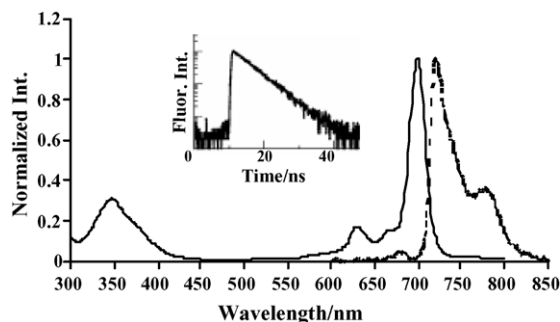


Fig. 2. UV-vis absorption spectrum (solid line) and photoluminescence spectrum ( $\lambda_{\text{ex}} = 630$  nm, dashed line) of *t*Bu<sub>4</sub>PcTiO in dilute toluene. Inset: Logarithm of fluorescence intensity at 730 nm vs. time.

(100), assigned to the molecular peak. The elementary analysis results are in agreement with the calculated values.

The synthetic precursor of *t*Bu<sub>4</sub>PcTiO, 4-*tert*-butylphthalonitrile, was prepared starting from *o*-xylene in a six-step synthesis. Refinements to original synthetic route published by Luk'yanets and co-workers [12] were developed in the group of Hanack [13]. It is known that asymmetric precursors, like 3-, 4-, 3,4- or 3,5-substituted phthalonitriles, form a mixture of structural isomers [i.e., (C<sub>4h</sub>) 1,8,15,22-, (D<sub>2h</sub>) 1,11,15,25-, (C<sub>2v</sub>) 1,8, 18,25- and (Cs) 1,8,15,25-tetra-substituted complexes] during the cyclotetramerization. Hanack and co-workers [14] firstly separated the four isomers of tetra-substituted Pcs to undertake detailed and extensive NMR-studies probing the influence of isomers on the NMR spectra of the Pcs. The NMR-spectrum of an isomeric mixture is somewhat different from those of the pure isomers, but it is still possible to draw definite conclusions about the structure.

As shown in Fig. 2, the UV-vis absorption spectrum of *t*Bu<sub>4</sub>PcTiO displays a typical pattern of tetra-substituted metal phthalocyanines, with an intense Q-band absorption at 699 nm and its vibrational satellites Q(1,0) and Q(2,0), as well as lower intensity  $\pi-\pi^*$  transitions within the heteroaromatic  $\pi$ -system near 347 nm [9]. As expected, its steady-state fluorescence spectrum shows the mirror image of the corresponding UV-vis absorption bands with small Stokes-shift [9,15]. The fluorescence decay time profile of *t*Bu<sub>4</sub>PcTiO (Fig. 2) displays a single exponential decay with the fluorescence lifetime of 5.1 ns which was measured by a single-photon counting method. The excitation-wavelength dependence of the steady-state fluorescence spectra of *t*Bu<sub>4</sub>PcTiO is observed in toluene solution, as shown in Fig. 3. In the solid state, the absorption spectrum of *t*Bu<sub>4</sub>PcTiO (Fig. 4) is very different from the solution spectrum in which the Q-band looks like very sharp. As we described in the introduction section, in the solid state, coupling between dye molecules creates an exciton band structure with much broader absorption bands [7]. Double layer device containing *t*Bu<sub>4</sub>PcTiO as an electron donor and *N,N'*-bis(methyl)-3,4,9,10-perylenebiscarboximide as an electron acceptor with their high absorption coefficient almost absorb most parts of the visible solar radiation [7,16].

Upon excitation with nanosecond laser pulse at 355 nm, i.e., roughly at the center of the B band, the transient absorption

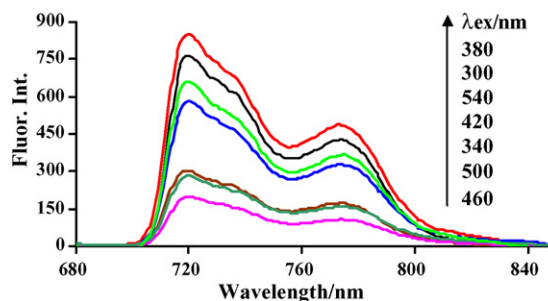


Fig. 3. Photoluminescence spectra of *t*Bu<sub>4</sub>PcTiO in toluene at different excitation-wavelengths.

spectrum of *t*Bu<sub>4</sub>PcTiO was observed in argon-saturated anhydrous toluene (Fig. 5). The transient absorption band appeared at 510 nm after the laser pulse irradiation is attributed to the triplet-triplet absorption of the phthalocyanine compounds [15]. The presence of oxygen gives rise to the acceleration of the decay for the absorption band centered at 510 nm. This would indicate the quenching of Pc's triplet state by oxygen. In the absence of oxygen, the decay rates depend on the laser powers. The time profile at 510 nm observed for [3] *t*Bu<sub>4</sub>PcTiO\* under the irradiation of low laser power also shows a single exponential decay, as displayed by the fluorescence decay time profile of *t*Bu<sub>4</sub>PcTiO. Strong triplet excited-state absorption in the high-transmittance region between the Q- and B-bands in the UV-vis absorption spectrum of *t*Bu<sub>4</sub>PcTiO ensures the absorption cross-section of the excited-state is always larger than that of the ground-state in this region, which is one of the prerequisites for the design of new positive nonlinear optical devices for high-speed information processing and optical communications [17].

A practical NLO device built from phthalocyanines would inevitably involve the solid-state casting of these compounds

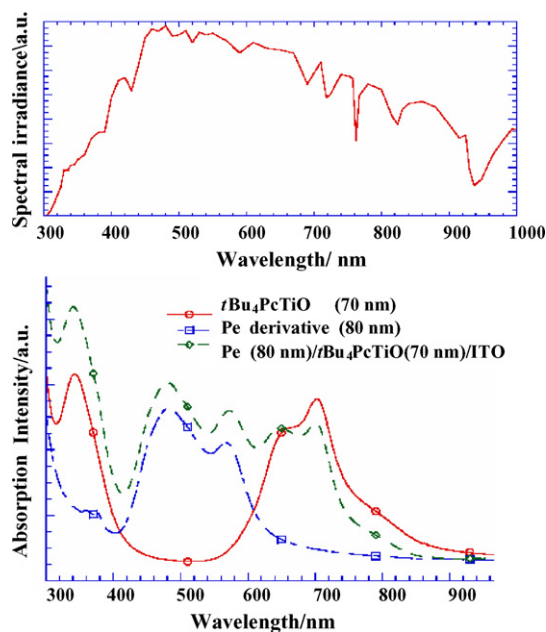


Fig. 4. Solar spectrum (upper panel) and UV-vis absorption spectra of the thin films of *t*Bu<sub>4</sub>PcTiO, perylene derivative and of the double layer films of Pe/*t*Bu<sub>4</sub>PcTiO onto ITO (lower panel).

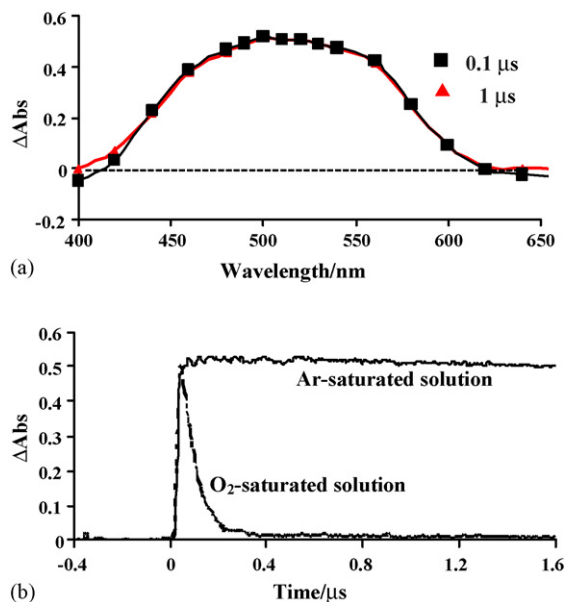


Fig. 5. (a) Nanosecond-transient absorption spectra of  $t\text{Bu}_4\text{PcTiO}$  (0.5 mM) in deaerated toluene at different times observed by excitation of 355 nm laser light; (b) Decay time profiles at 510 nm.

in some manner [18–21]. Polymerizing the phthalocyanines, or embedding in a polymer host to form a composite material, would allow traditional methods such as spin casting to be employed to produce suitable films for these solid-state applications. The use of guest–host systems is a feasible method toward applying the phthalocyanine moiety “en route” for real-world NLO (including optical limiting) applications. Blau and co-workers have produced and discussed high quality, relatively smooth, polymer–phthalocyanine composite films, e.g. PMMA/ $t\text{Bu}_4\text{PcZn}$  and PMMA/(PhS) $_4\text{PcZn}$  thin films with surface roughness of the order of only nanometers as passive solid-state optical limiters [22,23]. For each composite film its nonlinear absorption coefficient is two orders of magnitude higher than that value exhibited by the corresponding phthalocyanine in solution. In this study, the linear optical absorption coefficient,  $\alpha_0$ , (at 532 nm) calculated for  $t\text{Bu}_4\text{PcTiO}$  in solution, and embedded in PMMA, increased from  $(1.8 \pm 0.2) \text{ cm}^{-1}$  to  $(25.8 \pm 2.6) \text{ cm}^{-1}$  for these systems, respectively. This increase is due to the sharp rise in packing density of phthalocyanine in the solid state, compared to that of the solution based system. The thickness of the polymer–phthalocyanine film was calculated as  $61.2 \mu\text{m}$  using the white-light interferometry technique [23], with an average surface roughness value of 46 nm.

Presented in Fig. 6 are open aperture curves with normalized transmission plotted as a function of sample position,  $z$ , for solution samples of  $t\text{Bu}_4\text{PcTiO}$ . The three curves represent three increasing focal intensities, ( $I_0$ ), of 0.3, 0.6 and  $1.2 \text{ GW cm}^{-2}$ . The curves are characteristic of reverse saturable absorption (RSA), an effect which has been widely investigated for phthalocyanine molecules [23–32]. The absorption mechanism, in which the transmission decreases as a function of intensity, is due to population of excited-states through a multi-step nonlinear absorption. No evidence of film fatigue or degradation was noted in the PMMA/ $t\text{Bu}_4\text{PcTiO}$  film, after numerous scans

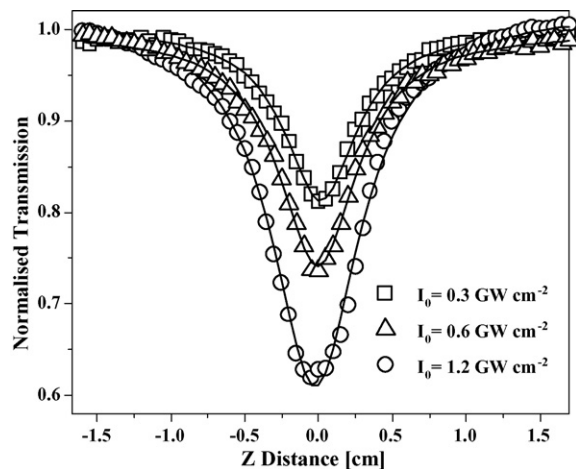


Fig. 6. Resulting open aperture curves with normalized transmission plotted as a function of sample position,  $Z$  for the solution sample of  $t\text{Bu}_4\text{PcTiO}$ . The three curves represent three increasing focal intensities, ( $I_0$ ), of 0.3, 0.6 and  $1.2 \text{ GW cm}^{-2}$ .

at varying laser intensity. This can be observed in Fig. 6, where the normalized transmission curves are completely symmetric. A decrease in the normalized transmission from  $Z=0 \text{ cm}$  (focal point) and  $Z=+1.5 \text{ cm}$  would be indicative of varying degrees of molecular damage due to the high focal intensity. In addition, no change was noted in the UV–vis spectra for  $t\text{Bu}_4\text{PcTiO}$ , both before and after this experimental procedure.

For focal intensities of 0.3, 0.6 and  $1.2 \text{ GW cm}^{-2}$ , the nonlinear absorption coefficients were  $(1.9 \pm 0.4) \times 10^{-8} \text{ cm W}^{-1}$ ,  $(1.7 \pm 0.3) \times 10^{-8} \text{ cm W}^{-1}$ ,  $(1.5 \pm 0.3) \times 10^{-8} \text{ cm W}^{-1}$ , for  $t\text{Bu}_4\text{PcTiO}$  in solution, respectively. The plots of normalized transmission as a function of  $z$  distance (cm) for the PMMA/ $t\text{Bu}_4\text{PcTiO}$  film are presented in Fig. 7. With the polymer–phthalocyanine composite film, values of  $(7.3 \pm 1.5) \times 10^{-7} \text{ cm W}^{-1}$ ,  $(1.5 \pm 0.3) \times 10^{-7} \text{ cm W}^{-1}$ ,  $(2.0 \pm 0.4) \times 10^{-7} \text{ cm W}^{-1}$  were calculated for focal intensities of 0.3, 0.35,  $0.4 \text{ GW cm}^{-2}$ . For both systems, it was noted that the nonlinear

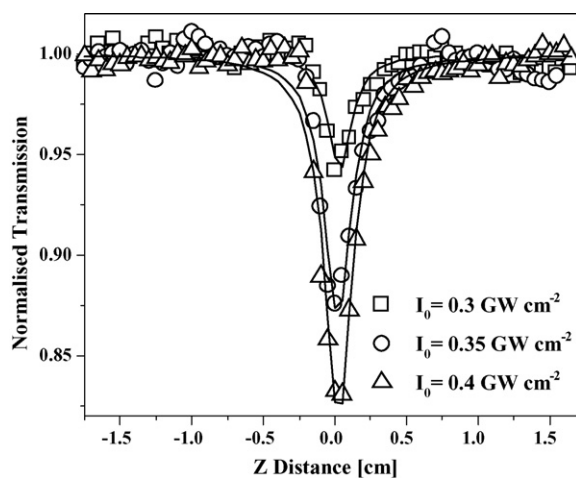


Fig. 7. Resulting open aperture curves with normalized transmission plotted as a function of sample position,  $Z$  for the solid-state sample of PMMA ( $t\text{Bu}_4\text{PcTiO}$ ). The three curves represent three increasing intensities at the lens' focus ( $I_0$ ) of 0.3, 0.35 and  $0.4 \text{ GW cm}^{-2}$ .

absorption coefficient,  $\beta_1$ , decreased with increasing incident intensity. The decrease in the effective intensity dependent nonlinear absorption coefficient with increasing input intensities possibly results from high order triple state transitions of the excited-state population. Within the model used here to estimate the nonlinear absorption coefficient higher order triplet effects are not considered and this in turn could manifest itself as a decrease in the effective ‘three-level’ absorption coefficient with increasing irradiance.

Solar cells based on the photovoltaic properties of inorganic semiconductors, e.g. single-crystalline silicon (energy conversion efficiency ( $\eta$ ) reaches up to 24%), GaAs/AlGaAs ( $\eta \sim 30\%$ ), amorphous silicon ( $\eta \sim 12\text{--}15\%$ ) and others, offer an efficient method of converting solar light into electrical energy [33]. In these solid-state solar cells, electron-hole pairs are created by light absorption in a semiconductor, with charge separation and collection accomplished under the influence of electric fields within the semiconductors [33]. Because of their high cost of production and technical difficulties in the fabrication of large-area cells, however, such devices are unlikely to be competitive with fossil fuel and nuclear fission as a significant source of power generation. The solar cells based upon organic photoconductors dispersed in large flexible plastic sheets have thus been suggested as a partial solution [34,35]. A large number of research results have demonstrated that an ideal photovoltaic materials and devices must meet the following several conditions [33–35]: (1) strong absorption across the solar spectrum: a high absorption coefficient is required for efficient light use in thin film devices; (2) high hole or electron mobility and high exciton diffusion length; (3) high stability and durability: without decomposing, reacting, and chemical or photochemical degradation; (4) easy and reproducible deposition technique, suitable for large-area production; and (5) widely separated Fermi levels: appropriate materials should have electrochemical potentials sufficiently different to produce appreciable junction barriers for high open-circuit voltages. Over the past 10 years there are more than 1000 articles already concerning the synthesis of organic or polymeric photovoltaic materials and the fabrication of the corresponding solar cell devices. The highest energy conversion efficiency reported for photoelectrochemical photovoltaic cell is around 10% under AM (air mass) 1.5 ( $1000 \text{ W cm}^{-2}$ ) irradiation [36]. The main problems for this device are evaporation of the electrolyte, stability or degradation of the electrolyte or dye. For the most organic solar cells already reported so far, the efficiencies are within 0.1–5% [8,35,37]. The main limitation of these organic or polymer solar cells is still their low efficiency and the limited lifetime of the devices. This has been a primary barrier to the development of commercial organic solar cells. For these reasons, there has been a continuing pronounced interest in the search for novel functional materials coupled with desirable physical properties and a low cost.

Conjugated organic and polymeric materials have continuously issued in the scientific community with their unexpected electron-optical properties over the last two decades. Poly(1,4-phenylene vinylene) [PPV] and its soluble derivatives, e.g. MEH-PPV, HO-PPV [poly(2,5-diheptyloxy-p-phenylene-vinylene)], MDMO-PPV [poly(2-methoxy-5-(3',7'-dimethyl

octyloxy)-1,4-phenylenevinylene] and others are well-known good hole transporting materials used for the fabrication of organic solar cells [38]. The overall energy conversion efficiency of a solar cell with ITO/PEDOT:PSS/MDMO-PPV:PCBM/Al configuration strongly increases with the temperature and is only weakly dependent on the light intensity, reaching the maximum value of 1.9% at 302 K and  $100 \text{ mW cm}^{-2}$  and 2.5% at  $0.7 \text{ mW cm}^{-2}$  (white-light) illumination [38a]. Although these  $\pi$ -conjugated polymers possess many advantages such as comparatively easy manufacture of thin film devices by spin coating or screen-printing technologies, larger optical absorption coefficients exceeding  $10^5 \text{ cm}^{-1}$ , and low cost preparation, the largest disadvantages are their low charge carriers mobility ( $10^{-3}\text{--}10^{-4} \text{ cm}^2/\text{Vs}$ ), the low exciton diffusion lengths ( $\sim 10 \text{ nm}$ ), and narrow absorption bands at around 450–470 nm (the UV–vis absorption spectra of the conjugated polymer-based device only covers about 10–15% of the solar light spectrum). Only the light absorbed at the depletion layer of the interface or the exciton diffusion range of the materials to the junction can create charge carriers. These factors limit the further improvement of conjugated polymers-based photovoltaic cells. On the other hand, phthalocyanines have in general relatively longer exciton diffusion lengths (a few hundreds nm  $\sim 1 \mu\text{m}$ ), broader absorption bands covering about 50% of solar spectrum in the solid state, and larger charge carriers mobility ( $0.1\text{--}1 \text{ cm}^2/\text{Vs}$ ) [7,16]. These outstanding properties make them the promising candidates required for the practical organic solar cells. A possible way for improvement of energy conversion efficiency is thus to combine the outstanding properties of conjugated polymers and metal phthalocyanines such as *t*Bu<sub>4</sub>PcTiO. From Table 1 it can be clearly seen that the doping of *t*Bu<sub>4</sub>PcTiO into MEH-PPV results in the apparent increases of the open circuit voltage ( $V_{oc}$ ) and the short circuit photocurrent density ( $J_{sc}$ ) under illumination with  $40 \text{ mW cm}^{-2}$  white-light. The  $J_{sc}$  value reaches four-times higher than that of ITO/MEH-PPV/Pe/Al cell when the concentration of *t*Bu<sub>4</sub>PcTiO in MEH-PPV is 50 wt.%. However, the fill-factor (FF) decreases apparently at this concentration. It is known that the  $J_{sc}$  value is mainly determined by the amount of absorbed light and the internal conversion efficiency, while the FF value is greatly influenced by the series and shunt resistance of cells. These findings show that the broad light absorption range of *t*Bu<sub>4</sub>PcTiO incorporated into polymer represents the dominant contribution to the enhancement of the photocurrent. Decrease of FF value is explained with the increase of series and shunt resistance caused by *t*Bu<sub>4</sub>PcTiO. The dependence of the short circuit photocurrent

Table 1

Effect of the doping of *t*Bu<sub>4</sub>PcTiO into MEH-PPV on the photovoltaic parameters under illumination of  $40 \text{ mW cm}^{-2}$  white-light

Device configuration	$V_{oc}$ (V)	$J_{sc}$ ( $\mu\text{A cm}^{-2}$ )	FF
ITO/MEH-PPV/Pe/Al	0.35	4.5	0.44
ITO/10 wt.% <i>t</i> Bu <sub>4</sub> PcTiO-doped MEH-PPV/Pe/Al	0.40	6.6	0.46
ITO/50 wt.% <i>t</i> Bu <sub>4</sub> PcTiO-doped MEH-PPV/Pe/Al	0.40	18.0	0.32

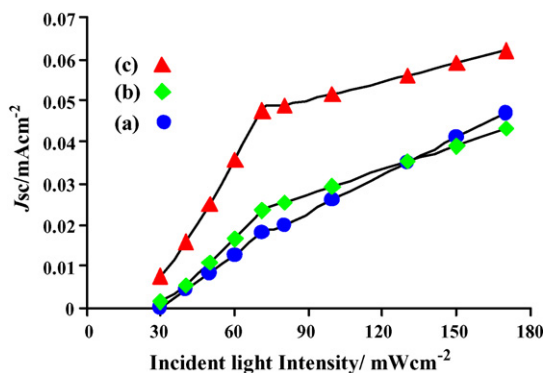


Fig. 8. Incident light intensity dependence of  $J_{sc}$  in cells: (a) ITO/MEH-PPV/Pe/Al; (b) ITO/10 wt.%  $t\text{Bu}_4\text{PcTiO}$ -doped MEH-PPV/Pe/Al; and (c) ITO/50 wt.%  $t\text{Bu}_4\text{PcTiO}$ -doped MEH-PPV/Pe/Al; illumination through the ITO side.

in an ITO/ $t\text{Bu}_4\text{PcTiO}$ -doped MEH-PPV/Al cell on the incident light intensity ( $I_{in}$ ) between 30 and 200  $\text{mW cm}^{-2}$  was investigated, as shown in Fig. 8.  $J_{sc}$  of ITO/MEH-PPV/Al is nearly proportional to the light intensity although a turning-point comes out at about 70  $\text{mW cm}^{-2}$ . For the  $t\text{Bu}_4\text{PcTiO}$ -doped MEH-PPV cells, the short circuit photocurrent density rapidly increases with the intensity of the incident light at lower illumination intensity. When the incident light intensity reaches 70  $\text{mW cm}^{-2}$ , the line remarkably diverges from the primary direct, implying that  $J_{sc}$  is limited probably due to the decrease of the internal conversion efficiency and partially to the degradation of the Al electrode at higher intensity of incident light.

### 3. Conclusion

The fluorescence decay time profile of  $t\text{Bu}_4\text{PcTiO}$  displays a single exponential decay giving the fluorescence lifetime of 5.1 ns. The excitation-wavelength dependence of the steady-state fluorescence spectra of  $t\text{Bu}_4\text{PcTiO}$  is observed in toluene solution. Strong triplet excited-state absorption in the high-transmittance region between the Q- and B- bands in the UV-vis absorption spectrum of  $t\text{Bu}_4\text{PcTiO}$  suggests the absorption cross-section of the excited-state is larger than that of the ground-state in this region. The nonlinear response demonstrated that  $t\text{Bu}_4\text{PcTiO}$  exhibited strong RSA at 532 nm for both solution and solid-state-based experiments. The absorption mechanism is due to population of excited-states through a multi-step nonlinear absorption. The decrease in the effective intensity dependent nonlinear absorption coefficient with increasing input intensities possibly results from high order triple state transitions of the excited-state population. Film fatigue or degradation was not observed in the PMMA/ $t\text{Bu}_4\text{PcTiO}$  film, after numerous scans at varying laser intensity. The doping of  $t\text{Bu}_4\text{PcTiO}$  into MEH-PPV results in the apparent increases of the open circuit voltage and the short circuit photocurrent density under illumination with 40  $\text{mW cm}^{-2}$  white-light. The  $J_{sc}$  value reaches four-times higher than that of ITO/MEH-PPV/Pe/Al cell when the concentration of  $t\text{Bu}_4\text{PcTiO}$  in MEH-PPV is 50 wt.%. The light absorption of  $t\text{Bu}_4\text{PcTiO}$  incorporated into polymer rep-

resents the dominant contribution to the enhancement of the photocurrent. The dependence of the short circuit photocurrent in an ITO/ $t\text{Bu}_4\text{PcTiO}$ -doped MEH-PPV/Al cell on the incident light intensity ( $I_{in}$ ) between 30 and 200  $\text{mW cm}^{-2}$  was investigated. Further studies on the dependence of the photovoltaic parameters in such a cell on the incident light intensity are in progress.

## 4. Experimental

### 4.1. Synthesis of $t\text{Bu}_4\text{PcTiO}$

To the hot solution of 4-*tert*-butylphthalonitrile [12,13] (1.8553 g) in  $\alpha$ -chloronaphthalene was added 1.5 ml of  $\text{TiCl}_4$  (Aldrich, d 0.964  $\text{g ml}^{-1}$ ) via a syringe under highly purified argon atmosphere. The reaction mixture was then heated at 220 °C for 14 h with stirring under static argon. One hundred milli litre of methanol was poured into the cooled reaction mixture, followed by the stirring for additional 5 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (toluene/ $\text{CHCl}_3$  as the eluent) to remove the metal-free  $t\text{Bu}_4\text{PcH}_2$  and any possible impurities. The pure  $t\text{Bu}_4\text{PcTiO}$  was obtained by recrystallization from a mixture of  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (v/v, 4:3) by slowly evaporating the more volatile dichloromethane in a rotary evaporator at 40–60 °C under slightly reduced pressure. Yield 35% (706 mg);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  ppm $^{-1}$  = 1.95–1.89(s, 36H,  $\text{CH}_3$ ); 8.39–8.29(m, 4H, H-1); 9.23–9.12(m, 8H, H-2,2'); IR(KBr): 2956s, 2905s, 2363m, 2338m, 1734w, 1718s, 1613m, 1484m, 1393m, 1364m, 1326s, 1280m, 1256ms, 1200w, 1152m, 1072s, 974m ( $\nu_{\text{Ti=O}}$ ), 925m, 894w, 864vw, 830m, 757vw, 762m, 751m, 694m, 670m, 601w, 566w, 525w  $\text{cm}^{-1}$ ; EA:  $\text{C}_{48}\text{H}_{48}\text{N}_8\text{OTi}$  (800.84): calcd. C 71.99, H 6.04, N 13.99; found C 71.61, 6.27, 13.62; FD-MS:  $m/z$  = 801.0 ( $\text{M}^+$ )

### 4.2. Steady-state and time-resolved photophysical measurements

UV-vis absorption spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence spectra and lifetimes were measured by a single-photon counting method using an argon ion laser, a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3960, fwhm 150 fs) with a pulse selector (Spectra-Physics, 3980), a second harmonic generator (Spectra-Physics, GWU-23PS), and a streakscope (Hamamatsu Photonics, C4334-01). Each sample was excited in deaerated anhydrous toluene with 410 nm laser light. Nanosecond-transient absorption measurements were carried out using third harmonic generation (THG, 355 nm) of an Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 6 ns FWHM) as an exciting source. For transient absorption spectra in the near-IR region (600–1400 nm), monitoring light from a pulsed Xe-lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834). For transient absorption spectra in the visible and near-IR region (400–1000 nm), monitoring light from a pulsed Xe-lamp was detected with a Si-PIN photodiode (Hamamatsu Photonics, S1722-02).

### 4.3. NLO measurements

The open aperture of the Z-scan experiment [25] was used probing total transmittance through the samples. The second harmonic, 532 nm, of a Q-switched Nd:YAG laser was with a pulse repetition rate of 10 Hz and the beam was spatially filtered to remove the higher order modes and tightly focused with a 9 cm focal length lens. All solution based NLO experiments were undertaken in quartz cuvettes with a path length of 1 mm. The solid-state nonlinear optical investigation of the phthalocyanine–polymer composite system was conducted by depositing the composite onto quartz glass slides via conventional multi-layer spin coating techniques.

For the solution based experiments, the phthalocyanine, *t*Bu<sub>4</sub>PcTiO, was freshly dissolved in toluene at a concentration of 0.5 g l<sup>-1</sup> and gently agitated for approximately one hour in a low power (60 W) sonic bath to ensure homogeneous and uniform dispersion. In order to fabricate the solid-state polymer–phthalocyanine composite a 100 g l<sup>-1</sup> solution of poly(methylmethacrylate) [PMMA] in cyclohexanone was prepared. This was placed in a low power sonic bath for 48 h until completely dissolved. The phthalocyanine was then added at a partial concentration of ~3.3 g l<sup>-1</sup>, and was sonically agitated at low power until a completely dissolved, homogeneous solution was formed. The solid-state composite film was cast on quartz substrates using conventional spin coating. A multi-layer film was built by sequentially spinning composite solution with approximately one hour of baking at 60 °C between each successive layer to facilitate the removal residual solvent [23,25].

### 4.4. Photovoltaic measurements

The *t*Bu<sub>4</sub>PcTiO-doped MEH-PPV (10, 50 wt.%) as p-type material was dissolved into anhydrous toluene and filtered through 13 mm Aerodisc CR syringe filters (Gelman Laboratories). The p-type material was then spin-coated onto the indium–tin oxide (ITO) glass from this toluene solution at 1400 rpm. Before fabrication of the device, commercial ITO-coated glass substrates (Colorado Concept Coating) were cleaned with soap and ultrasonicated sequentially in a detergent solution, deionized water, methanol, isopropanol and acetone [39]. The substrates were treated with oxygen plasma for 10 min in a SPi Plasma Prep II (Structure Probe Inc.). The perylenetetracarboxylic acid diimide derivative (Pe) with bismethyl substituents at the imide nitrogen atom [*N,N'*-bis(methyl)-3,4,9,10-perylenebiscarboximide] as n-type material was then evaporated onto the top of the p-type material from alumina crucibles resistance-heated by a tungsten wire in a high vacuum system (Cooke Vacuum Products) inside an argon atmosphere dry box (Vacuum Atmosphere Co) at pressures in the range ~1 × 10<sup>-6</sup> Torr. A 40 nm thick Al (99.999%, Alfa Aesar) was deposited onto the Pe layer. The thickness of each layer was measured on a Sloan Dektak 3030 surface profiler. The current-voltage characteristics of this type of solar cells (ITO/*t*Bu<sub>4</sub>PcTiO-doped MEH-PPV/Pe/Al) were measured on a Hewlett Packard 4155B semiconductor parameter analyzer.

White-light was obtained through an IR cut-off filter and a sharp cut-off filter from a 300 W xenon lamp.

### Acknowledgements

We are grateful for the financial support of National Natural Science Foundation of China, ECUST (YJ0142124), China/Ireland Science and Technology Collaboration Research Foundation (CI-2004-06), SRF for ROCS, NCET (050413), Shanghai Shuguang project (05SG35) and STCSM (05XD14004), respectively.

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