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Synthesis of novel amphiphilic zinc phthalocyanines and fabrication of zinc phthalocyanine–titanium oxide multilayers

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Abstract

Two novel amphiphilic zinc phthalocyanines (TAZnPc and ASZnPc) have been synthesized. It has been shown that they form stable monolayers on a nanometer-sized colloidal TiO_2 subphase and are suitable for the fabrication of alternating zinc phthalocyanine-titanium oxide multilayers via the Langmuir–Blodgett method. Surface pressure-area isotherm and absorption spectroscopic studies show that uniform TAZnPc (ASZnPc)–TiO_2 alternating multilayers are formed. It has been found that the TAZnPc molecules lie almost flat on the substrate surface, while ASZnPc molecules are oriented nearly perpendicular to the substrate surface. Transparent SnO_2 electrodes coated with alternating ASZnPc–TiO_2 multilayers were found to exhibit a higher photovoltage response than TAZnPc–TiO_2 coated electrodes. This demonstrates that the molecular arrangement of the zinc phthalocyanine moiety in the multilayers has an important influence on the photovoltaic properties of the sensitized SnO_2 electrode. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Phthalocyanine; Titanium-oxide; Langmuir–Blodgett films; Monolayer; Multilayer; Photoelectric effect

1. Introduction

Although highly efficient solar cells using a nanoporous TiO_2 electrode sensitized with ruthenium complex have been reported [1], there remains the need for alternative photosensitizers for use with TiO_2-based photovoltaic devices, especially those that absorb at longer wavelengths than a ruthenium complex. With this in mind, phthalocyanines that are very stable and strongly absorbing in the visible region have received increasing attention as a functional material for solar energy conversion and appear to offer promising candidates [2]. Results of previous investigations involving phthalocyanine films demonstrated that surface morphology and molecular orientation, which are controlled by growth rate and substrate properties during vacuum deposition, have a significant influence on the photoelectrochemical efficiency of phthalocyanines [3]. In contrast to vapor deposition, the formation of thin films by using the Langmuir–Blodgett (LB) technique causes molecules to be arranged in an orientation-specific manner on a solid surface and the reproducibility of film deposition is enhanced.

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In this paper, we report the use of two novel amphiphilic zinc phthalocyanines (Fig. 1) in the fabrication of alternating zinc phthalocyanine–TiO_2 multilayers using the LB method. The relationships between photoelectric properties and the molecular arrangement of the phthalocyanines in films are reported.

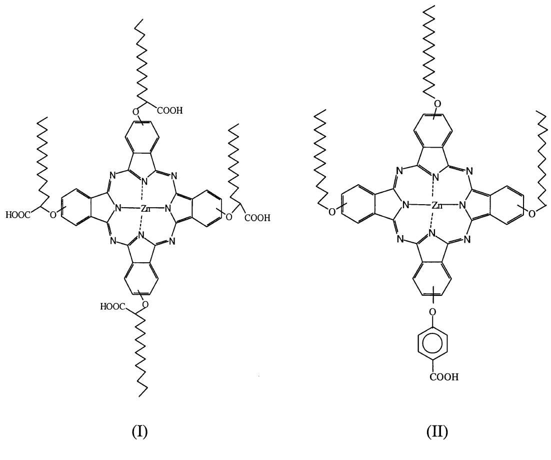
2. Experimental

2.1. Synthesis of zinc phthalocyanines

Since the synthesis of TAZnPc (**I**) has been reported [4], we describe here the synthesis of ASZnPc (**II**).

2.2. 4-(4′-Hydroxyphenoxy) phthalonitrile

4-Hydroxybenzoic acid (6.95 g, 50 mmol), 4-nitrophthalonitrile (4.35 g, 25 mmol), and anhydrous K_2CO_3 (13.8 g, 100 mmol) were suspended in freshly distilled DMSO (100 ml) and stirred at room temperature under N_2 for 2 days. The reaction mixture was poured into water (300 ml) and the pH of the deep yellow solution was adjusted to 1 by addition of hydrochloric acid (0.1 M, 25 ml). The mixture was filtered, and the cake was washed with water, dried, and recrystallized from methanol (30 ml) to give a white solid (6.1 g, 92%). ^{1}HNMR (DMSO-d_6): δ: 7.25 (m, 2H), 7.52 (d, 1H), 7.91 (d, 1H), 8.02 (m, 2H), 8.15 (d, 1H), 13.05 (S, 1H). IR ν_{max}: 3107 (m, ArH), 2230 (s, CN), 1675, 1580 (s, C=O), 1254 (s, C–O–C), cm^{-1}. EI-MS: *m*/*z* 264 (M^+, 100%), 247 (M^+-OH, 47%), 219 (M^+-COOH, 10%).



(I) (II)

Fig. 1. Structures of TAZnPc (**I**) and ASZnPc (**II**).

2.3. Tetradecyloxy phthalonitrile

Tetradecyl alcohol (10.72 g, 50 mmol), 4.35 g (25 mmol) of 4-nitrophthalonitrile and anhydrous K_2CO_3 (6.9 g (50 mmol) were suspended in freshly distilled DMSO (100 ml) and stirred at room temperature under N_2 for 2 days. The reaction mixture was poured into water (1000 ml) and the pH of the solution was adjusted to 5–6 using hydrochloric acid (0.1 M, 15 ml). The precipitate was collected by filtration and purified by recrystallization from methanol (30 ml) to give 6.12 g (71.6%). IR (cm^{-1}) ν: 2210 (s, C≡N), 1247 (s, C–O–C). EI-MS: *m*/*z* 340 (M^+, 100%).

*2.4. 2-(4′-Carboxyphenoxy)-9,16,23-tri(tetradecyloxy) phthalocyanine zinc (ASZnPc, **I**)*

4-(4′-Carboxyphenoxy) phthalonitrile (0.76 g, 2.88 mmol) and 4-tetradecyloxy phthalonitrile (2.94 g, 8.64 mmol) were suspended in freshly distilled dry *n*-pentanol (40 ml) at 140°C under N_2. Then lithium (400 mg) was added and stirring was continued for 1 h. After cooling the reaction mixture to room temperature, glacial acetic acid (120 ml) was added. The precipitate was collected, washed with water (500 ml), and dried, giving 0.60 g dry solid. A portion (0.14 g) of the solid was stirred under reflux for 6 h with zinc acetate (0.20 g) in DMF (30 ml). The reaction mixture was concentrated to ca. 5 ml with the aid of a rotary evaporator, and the addition of methanol (50 ml) afforded a green precipitate. This product was dissolved in a minimum amount of chloroform and chromatographed on a silica gel column (GF254) with chloroform as the initial eluent. When the first band was eluted from the column, the eluent was changed to chloroform:methanol (9:1), and the next band contained the desired product. Removal of the solvent left ASZnPc (0.72 g, 8.5%). IR (cm^{-1}) ν: 2921, 2852 (s,CH_2), 1714 (s, C=O), 1606 (s, ArH), 1250 (s, C–O–C). MS: m/z 1349 (M^+, 100%). UV–vis: λ_{max} (DMF): 680 (log ϵ 5.0) nm. Elemental analysis for $C_{81}H_{104}O_6N_8Zn$—calc. (found) %: C, 72.00 (71.53); H, 7.76 (8.12); N, 8.29 (7.89).

2.5. Preparation of nanometer-sized colloidal TiO_2

Boiling water (600 ml) was poured into a flask containing $TiCl_4$ (3.5 ml) with vigorous stirring, and the resultant solution was cooled to room temperature as quickly as possible. The pH of the solution was adjusted to 2–3 using HNO_3 and diluted to 0.1 $moll^{-1}$ for spectroscopic studies. The average particle size of the colloidal TiO_2 was determined to be 6 nm via TEM analysis.

2.6. Monolayer and LB film deposition [5]

Surface pressure-area isotherm determinations and LB film depositions were carried out using a JDLB 200 model LB balance (Jilin University, China), at ~20°C. The monolayer was spread on a subphase containing 5×10^{-4} mol^{-1} colloidal TiO_2, from solutions of TAZnPc and/or ASZnPc (10^{-4} mol^{-1}) in chloroform. The multilayers were constructed on a glass, CaF_2, and/or transparent SnO_2 electrode for spectroscopic and photoelectric measurements, using the vertical lifting method. The surface pressure was maintained at 33 mN m^{-1} for the pure TAZnPc (or ASZnPc) film and at 23 mN m^{-1} for the mixed films, with a deposition speed of 5 mm min^{-1}, resulting in acceptable deposition of Y-type films.

2.7. Instrument and methods

Absorption spectra were recorded on a Hitachi-557 UV-visible spectrophotometer, ^1H NMR spectra were recorded on a Varian Gemini 300 NMR instrument, and IR spectra were recorded on a Perkin-Elmer 983G model spectrophotometer. Mass spectra (EI) were recorded on Finnigen 4021 instrument. The photovoltage was measured on a JL-100 electrometer and a 150 W Xe lamp (150 mW cm^{-2}) was used as the light source. The TAZnPc (or ASZnPc) LB film coated SnO_2 served as the photocathode, Pt electrode as the counter electrode, and 0.1 M KCl as the electrolyte.

3. Results and discussion

3.1. Surface pressure–area isotherms

Fig. 2(a) and (b) shows the surface pressure–area isotherms at ~20°C for the monolayers of TAZnPc and ASZnPc (from chloroform and water) on colloidal TiO_2. There are distinct phase transitions, indicating that well-condensed monolayers were formed. The limiting area per molecule ($A_{\pi\to0}$) was calculated and the results are listed in Table 1. The increase in area covered by monolayer molecules on colloidal TiO_2 compared with that on pure water indicates that TiO_2 is inserted among the TAZnPc and/or ASZnPc molecules. Based on a CPK molecular model, the amphiphilic phthalocyanine moiety occupies a minimum area of ~300 Å^2 per molecule. It was also determined that TAZnPc molecules lie virtually flat within the monolayer plane, while ASZnPc molecules are tilted from the surface.

3.2. UV–visible spectra of TAZnPc (ASZnPc)–TiO_2 multilayers

Fig. 3(a) and (b) shows the UV–visible absorption spectra of alternating TAZnPc and (ASZnPc)–TiO_2 multilayers. Smooth layer-by-layer growth of the alternating films was confirmed by the linear dependence of absorbance intensities at 685 nm (for TAZnPc) and 675 nm (for ASZnPc) on the number of transferred monolayers.

The IR spectrum of TAZnPc–TiO_2 multilayers show that there is no carbonyl stretching vibration arising from carboxylic acid groups, in the range of 1750–1700 cm^{-1}. The two broad bands near 1620 and 1410 cm^{-1} are due to the asymmetric and symmetric stretching vibrations of carboxylate groups, indicating that TiO_2 particles are bound to TAZnPc to form carboxylic acid salts. The absorption spectra of TAZnPc–TiO_2 films show broad absorption peaks at 640 and 685 nm, while ASZnPc–TiO_2 films show an absorption peak at 675 nm and a shoulder at 630 nm. These results

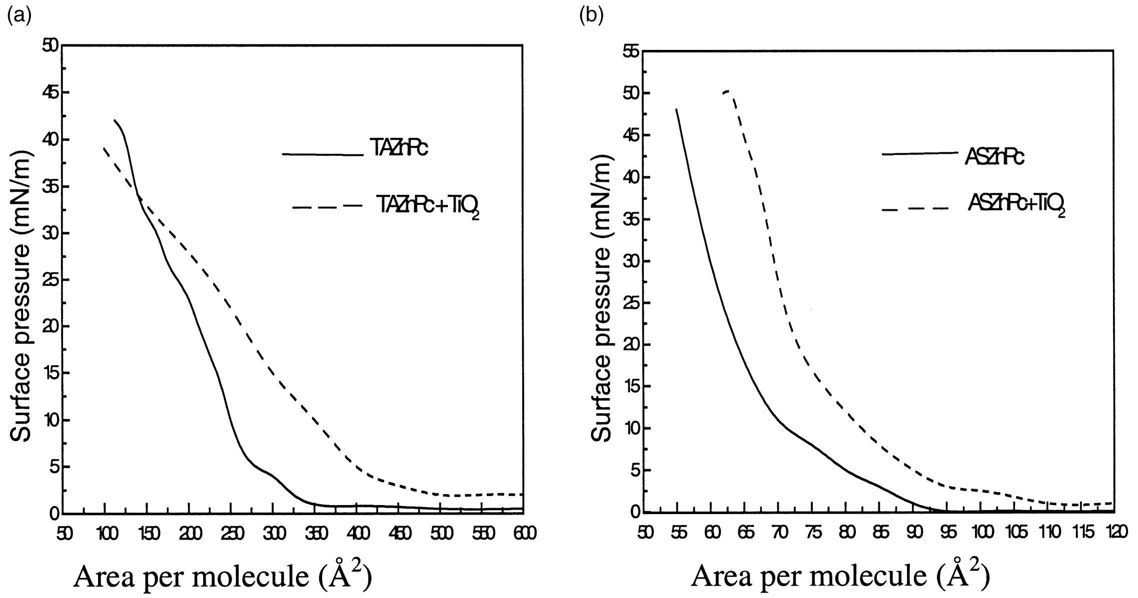


Fig. 2. π–A isotherm of TAZnPc (a) and ASZnPc (b) (in CHCl$_3$) on water (—) and colloidal TiO$_2$ (- - - -).

Table 1
Surface pressure–area isotherm data for TAZnPc and ASZnPc monolayers

PC used	Area occupied per molecule (Å^2)	
	On water subphase	On colloidal TiO$_2$ subphase
TAZnPc	275	350
ASZnPc	68	78

indicate that the mono- or multilayer films contain a large amount of non-aggregating macrolayers, which give rise to the 675 and 685 nm absorptions. This provides additional evidence that the embedded TiO$_2$ moieties prevent intralayer aggregation of phthalocyanine molecules. The 630–640 nm blue-shifted absorption can be attributed to interlayer interactions between phthalocyanine molecules.

Table 2
The results of photovoltage measurements

Electrode material	Number of layers	V oc (mV)	I sc (μA)
TAZnPc	1	51.4	0.27
	3	53.3	0.31
	5	58.3	0.31
	7	57.1	0.28
TAZnPc + TiO$_2$	1	75.4	0.31
	3	104.6	0.31
	5	113.4	0.31
	7	315.4	0.31
ASZnPc	1	72.0	0.34
	3	89.4	0.45
	5	124.1	0.56
	7	198.4	0.75
ASZnPc + TiO$_2$	1	305.1	0.48
	3	521.5	0.52
	5	742.7	0.53
	7	989.2	0.57

3.3. Photoelectric conversion

The results of photovoltage measurements are summarized in Table 2. It can be seen that the photovoltage response of the SnO$_2$ electrodes fabricated with TAZnPc and/or ASZnPc multilayers was improved by incorporating TiO$_2$ nanoparticles and that the photovoltage increased with increasing number of layers. This can be attributed to the transfer of electrons generated in the phthalocyanine layers to the TiO$_2$ conduction band and their subsequent distribution within the TiO$_2$ plane. The positive holes correspond to the phthalocyanine layers. Charge separation at the

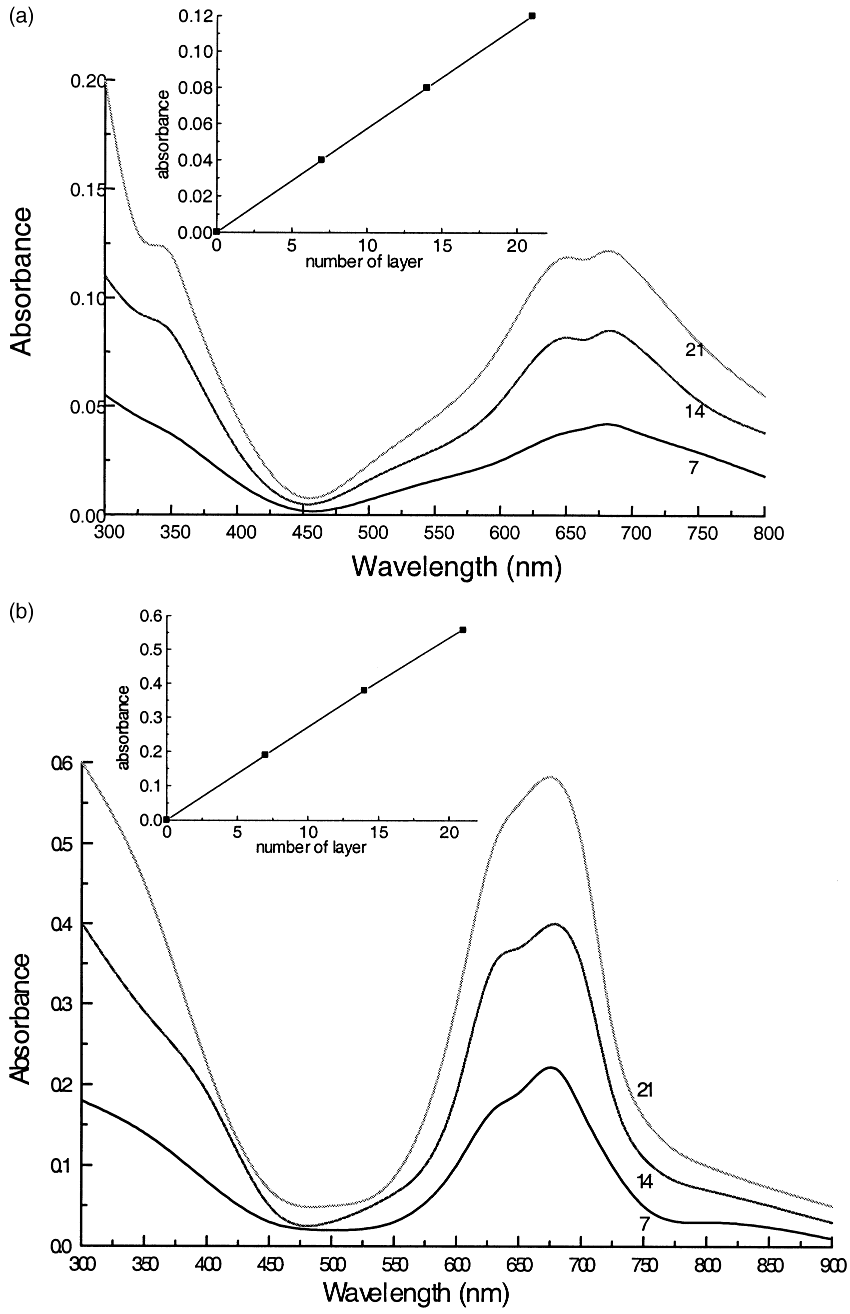


Fig. 3. UV–visible absorption spectra of alternating TAZnPc–TiO_2 multilayers (a) and alternating ASZnPc–TiO_2 multilayers (b).

interface results in a reduced probability of charge recombination. It is also clear that the photovoltage response of the SnO_2 electrode coated with ASZnPc–TiO_2 multilayers is higher than that of the electrode containing TAZnPc–TiO_2 multilayers. This may be attributed to differences in the orientation of phthalocyanine molecules on the SnO_2 electrode surface, causing more dye molecules to be deposited on the substrate surface. Although TAZnPc molecules lie almost flat on the SnO_2 electrode surface, ASZnPc molecules are oriented nearly perpendicular to the electrode surface. Consequently, the number of ASZnPc molecules adsorbed on the electrode surface is larger than in the case of TAZnPc. As a result, more light energy is harvested in the former case, which is consistent with the absorbance data shown in Fig. 3(a) and (b). Hence, it is not surprising that the photovoltage response is higher in the case of the ASZnPc coated SnO_2 electrode.

4. Conclusions

Alternating zinc phthalocyanine–TiO_2 multilayers fabricated by the Langmuir–Blodgett method and deposited on SnO_2 electrodes show potential utility in solar energy conversion. In this regard, it has been shown that differences in the molecular arrangement of zinc phthalocyanine molecules on the resultant film surfaces influences the light harvesting efficiency of the electrodes.

Acknowledgements

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