Photophysical and Photoelectric Properties of 2-{[4-(*N*-Hexadecyl-*N*-methylamino)phenyl]methylene}-propanedinitrile

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2-{[4-(*N*-Hexadecyl-*N*-methylamino)phenyl]methylene}-propanedinitrile (HMAPN) with typical donor-π-acceptor (D-π-A) structure was synthesized. It could be easily assembled into stable films by LB technique. The photophysical properties of HMAPN were investigated in solution and on LB films. The photoelectric properties of HMAPN were examined and the anodic photocurrent of the ITO electrode modified by the monolayer LB film of HMAPN was measured as 835 nA/cm² under the white light of 218.2 mW/cm² without bias voltage. The effects of light intensity, bias voltage on the photocurrent were discussed. The possible mechanism of the photocurrent formation was given.

Keywords propanedinitrile, LB film, photoelectric conversion

Introduction

During the past decades photoelectric conversion of solar energy has drawn more and more attentions[1-3] for the sake of the latent mineral energy source crisis. Many groups have been focusing their attentions on preparing various chromophores that can serve as light-harvesting arrays or extending chromophoric systems for various applications. Visible light harvesting portions have been prepared by using a variety of chromophores including porphyrin,[4] phthalocyanine[5] and transition metal complexes[6] having metal-to-ligand charge-transfer (MLCT) excited states. Besides, the compounds involving the electron donor (D)-π-acceptor (A) structure were found as prospective materials in photoelectric conversion field in addition to their ideal non-linear photorefractive abilities.[7] The LB technique is widely used in photoelectric field to make the photosensitive compounds into the functional devices because it can assemble compounds in molecular level.[8-13]

In this contribution, the syntheses and photoelectric conversion property of 2-{[4-(*N*-Hexadecyl-*N*-methylamino)phenyl]methylene}-propanedinitrile (HMAPN) with a typical D-π-A structure are reported. It can be synthesized by multi-step routine reaction and purified easily. The structure of HMAPN is shown in Fig. 1.

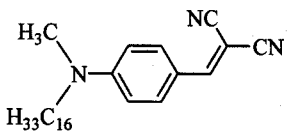

Fig. 1 Structure of HMAPN.

The dye was successfully assembled into LB films on indium-tin oxide (ITO) or quartz substrates. The photoelectric conversion properties of the ITO electrode modified by the monolayer LB film of HMAPN were examined.

Experimental

Materials and instruments

All reagents were purchased from Aldrich Chemical Company and used without further purification except *N*-methyl aniline, which was distilled under vacuum before use. Stearic acid (SA) and methanol were of spectra-grade and were used for preparation of LB films and for absorption and emission spectral measurements, respectively. Water used as subphase was deionized and distilled three times.

IR spectra were recorded on a PE Spectrum BX FT-IR System spectrometer. ^{1}H NMR spectra were measured on a Bruker DPX-400 spectrometer with TMS as an internal sandard. Mass spectra were obtained on a VG ZAB-HS (UK) Organic Mass Spectrometer. Element analyses were performed on an HERAUS CHN-RAPID element analysis spectrometer. UV absorption spectra were measured on a Lambda 20 PE UV/VIS Spectrometer. Fluorescence spectra were measured on a PE LS 50B luminescence spectrometer. The LB films were prepared by using a Joyce Loebl Langmuir Trough 4 machine. The photoelectrochemical studies were performed by using a model 600 voltametry analyzer (CH Instruments, USA).

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Preparation of LB *films*

A solution of HMAPN (5×10^{-4} mol/L) and SA (molar ratio = 1:3) in chloroform was spread onto a distilled water subphase at a subphase temperature of (20 ± 1) ℃. The solvents were allowed to evaporate for 15 min, and the floating film was then compressed at a rate of 0.8 cm^2/min. The substrate monolayer was transferred onto an ITO-coated glass by perpendicular raising technique with a constant surface pressure of 25 mN/m and a raising rate of 5 mm/min. The transfer ratio was 0.95 ± 0.05.

Photoelectrochemical measurements

The photoelectric properties were investigated by using the traditional three-electrode cell[8-13] with an ITO electrode modified by a monolayer LB film of HMAPN as working electrode, a saturated calomel electrode as reference electrode, a platinum foil as counter electrode and 0.5 mol/L KCl aqueous solution was used as electrolyte. Irradiation of the cell was carried out using a 500 W xenon lamp. The light intensity was measured with an energy and power meter (Scientech Co., Boulder, CO). The IR light was filtered throughout the experiment with a Toshiba IRA-25S filter. The current changes induced by switching on and off the light were recorded. The current direction was expressed based on the ITO electrode as the working electrode.

Preparation of HMAPN

HMAPN and all intermediates were synthesized as the reported metheod.[14-16]

N-Hexadecyl-N-methyl aniline (HMA)

A solution of *N*-methyl aniline (0.7 g, 10 mmol) and *n*-hexadecyl bromide (3.66 g, 12 mmol) in anhydrous ethanol (50 mL) was stirred under reflux for 16 h. The solvent was evaporated and the yellow residue was separated by column chromatography (silica gel, the mixed eluant of petroleum ether and ethyl acetate with ratio of 10:1 in volume). Colorless transparent liquid (2.95 g) was obtained in 89% yield.

4-(*N-Hexadecyl-N-methylamino*)*benzoaldehyde* (HMABA)

Dimethylformamide (DMF) (2 mL) was maintained in an ice-salt bath, phosphoryltrichloride ($POCl_3$) (0.46 mL) was added dropwise with the inner temperature under 0 ℃, HMA (1.16 g, 5 mmol) was added and the system was stirred for 10 min followed by another 2 h stirring at 90 ℃. After cooling down to room temperature, the residue was poured into a large amount of ice water and neutralized by sodium hydroxide. The mixture was extracted with dichloromethane and the organic layer was washed with water, dried with anhydrous $MgSO_4$. After evaporating the solvent, a light yellow solid was obtained. Twice recrystallization in anhydrous ethanol yielded the product (1.28 g, 71.3%). M.p. 35 ℃; ^{1}H NMR ($CDCl_3$) δ: 9.79 (s, 1H, CHO), 7.62 (d, J = 3.3 Hz, 2H, Ph-CHO), 6.62 (d, J = 3.3 Hz, 2H, N-Ph), 3.50 (t, J = 4.95 Hz, 2H, $NCH_2C_{15}H_{31}$), 2.98 (s, 3H, CH_3N), 1.28 [s, 28H, $(CH_2)_{14}$], 0.90 (t, J = 3.57 Hz, 3H, $CH_3C_{15}H_{30}N$).

2-{[4-(*N-Hexadecyl-N-methylamino*)*phenyl*]*methylene*}-*propanedinitrile* (HMAPN)

A solution of HMABA (1.08 g, 3 mmol) and malononitrile (0.36 g, 5.45 mmol) and a mixture of piperidine and acetic acid (0.1 mL, 1:3 in volume) as catalyst in anhydrous ethanol (12 mL) was stirred for 12 h under the temperature of 20—40 ℃. After filtration a yellow powder was obtained. Twice recrystallization in anhydrous ethanol gave pure product (0.92 g, 75.3%). M.p. 74 ℃; ^{1}H NMR ($CDCl_3$) δ: 7.78 (d, J = 8.79 Hz, 2H, N-Ph), 7.45 (s, 1H, =CHPh), 6.68 (d, J = 8.83 Hz, 2H, PhCH=), 3.43 (t, J = 5.59 Hz, 2H, $NCH_2C_{15}H_{31}$), 2.98 (s, 3H, CH_3N), 1.26 [s, 28H, $(CH_2)_{14}$], 0.88 (t, J = 6.81 Hz, 3H, $CH_3C_{15}H_{30}N$); MS (EI) (%): 407 (31.76, M^+), 196 (100, $M - C_{15}H_{31}$). Anal. calcd for $C_{27}H_{41}N_3$: C 79.61, H 10.07, N 10.32; found C 79.45, H 10.12, N 10.22.

Results and discussion

Photophysical properties of HMAPN *in solutions*

The absorption and fluorescence spectra of HMAPN in several representative solvents were recorded and shown in Figs. 2 and 3, respectively. It is observed that both the absorption and the fluorescence spectra are strongly dependent on the solvent polarity. The dielectric constant of the

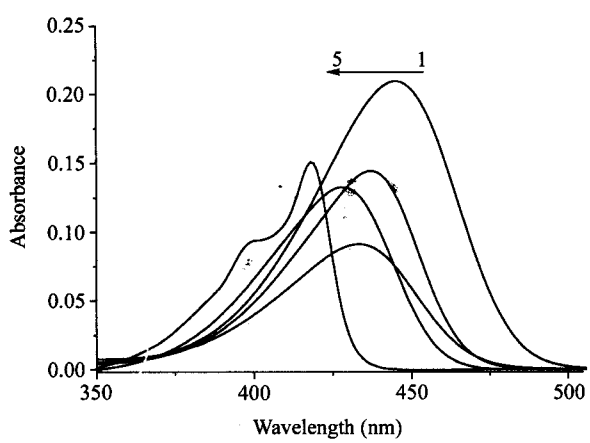

Fig. 2 Absorption spectra of HMAPN in several representative solvents (1 DMSO, 2 chloroform, 3 methanol, 4 ethyl acetate, 5 cyclohexane).

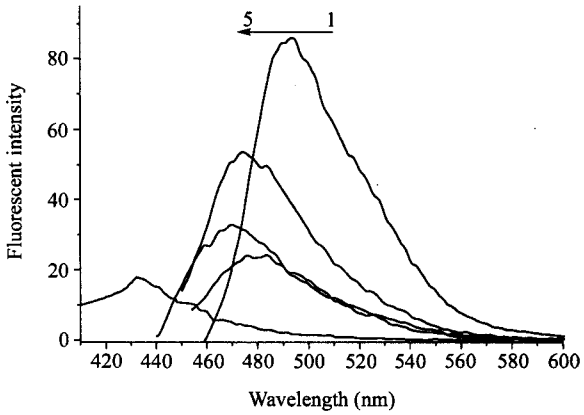

Fig. 3 Fluorescence spectra of HMAPN in several representative solvents (1 DMSO, 2 chloroform, 3 methanol, 4 ethyl acetate, 5 cyclohexane).

solvent increases with the increase of the polarity of the solvent. Both the absorption and the fluorescence peaks of HMAPN shift to longer wavelength with increasing the polarity of the solvent. It is obvious that the absorption peak of HMAPN in DMSO with stronger polarity has a 27 nm red-shift compared with that in cyclohexane with lower solvent polarity, while a large 61 nm red-shift is observed in the case of fluorescence emission at the same situation (Fig. 3).

The solvatochromism of HMAPN should be caused by the molecular structure and different solvent polarity. The ground state of HMAPN molecule exhibits a certain dipolarity in solution because of the asymmetric molecular structure. Therefore there is a 27 nm red-shift in absorption from cyclohexane to DMSO. When HMAPN is excited to the singlet excited state, intramolecular charge transfer occurs. The polarity of the molecule is much stronger than that of the ground state. Therefore the total red-shift of the fluorescence is much larger than that of the absorption in the same solvents.

Characterization of LB *films*

HMAPN can be easily assembled into monolayer in the presence of SA on the air-water interface. Fig. 4 shows the surface pressure-area (π-A) isotherm of a mixture of HMAPN and SA with the molar ratio of 1:3. There is a plateau-like region in the isotherm from 17 mN/m to 25 mN/m surface pressure which corresponds to a typical phase transition process possibly caused by a configuration rearrangement. The isotherm shows that when the surface pressure is above 25 mN/m a stable and condensed monolayer was formed. By extrapolating the curve under 25 mN/m, a total area of 0.94 nm^2 was obtained. The limiting area per HMAPN molecule is determined as *ca*. 0.31 nm^2 by excluding the area of three SA molecules (about 0.63 nm^2) from the total area. This area is slightly larger than that obtained from the PCMODEL calculation (*ca*. 0.28 nm^2) assuming the HMAPN molecule is in an extended conformation and vertical to the subphase surface with the hydrophobic alkyl chain stretching against the substrate, which indicates that there is a small angle (about 1.8°) between the molecule and the normal of the substrate. Fig. 5 shows a representative picture of monolay structure of HMAPN and SA on water-air surface or ITO substrate.

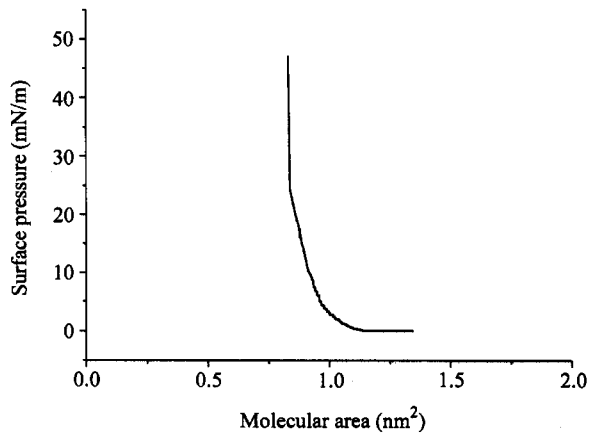

Fig. 4 Surface pressure-area (π-A) isotherm of the mixture of HMAPN and SA (1:3) at the air/water interface [(20 ± 1) ℃].

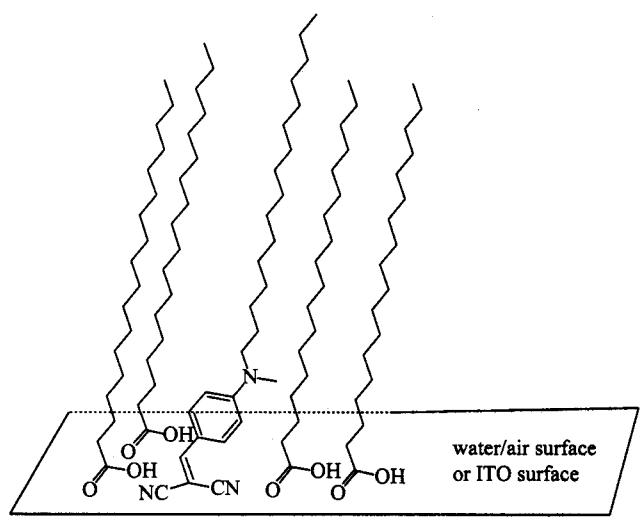

Fig. 5 Pictorial monolayer structure of HMAPN and SA formed on water-air surface or ITO substrate.

The electronic spectra of HMAPN in LB monolayer and that in chloroform solution are shown in Fig. 6. A red-shift of 16 nm can be obtained, indicating that aggregate of HMAPN is formed in the monolayer LB film.

Photoelectric conversion properties (PEC)

The photocurrent of the HMAPN monolayer LB film coated ITO electrode was measured with a Pt counter electrode in 0.5 mol/L KCl aqueous solution. An anodic photocurrent of 639 nA/cm^2 was detected when the electrode was illuminated by the white light with light intensity of 156.8 mW/cm^2. Only 10 nA/cm^2 anodic photocurrent was detected for the bare ITO electrode under the identical

conditions. This suggests that the HMAPN film on the ITO electrode substrate is responsible for the photoelectric response. A regular photocurrent changes when switching on and off the irradiation can be repeated for many times as shown in Fig. 7.

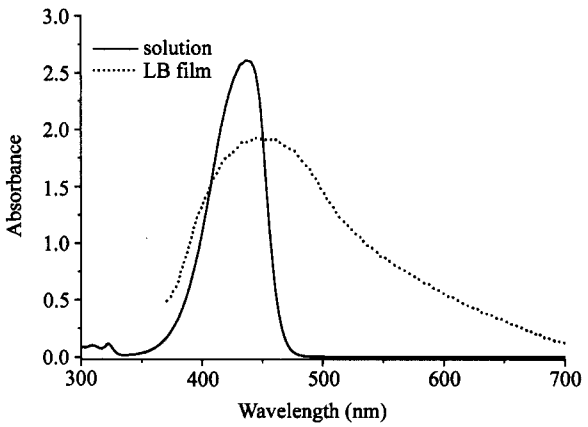

Fig. 6 Absorption spectra of HMAPN in solution of $CHCl_3$ and on monolayer LB film.

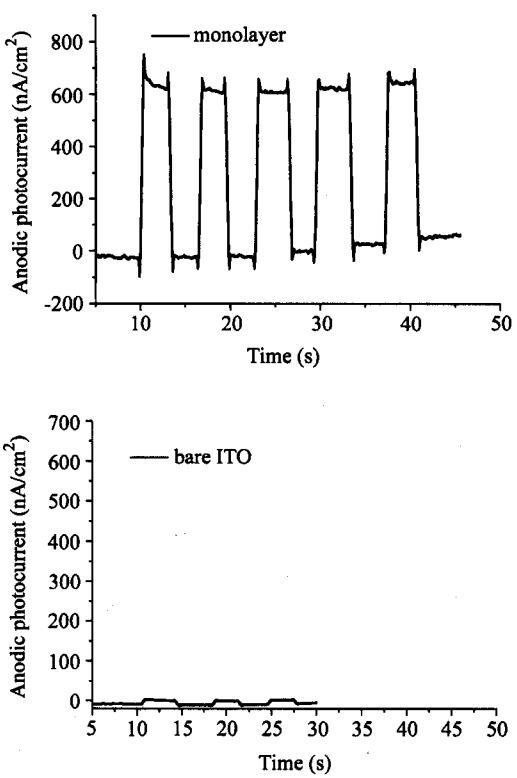

Fig. 7 Photocurrent response of HMAPN monolayer (a) and bare ITO electrode (b) upon white light irradiation of 156.3 mW/cm^2 in 0.5 mol/L KCl solution.

To understand the effect of bias voltage on photoinduced electron injection, the relationship between bias voltage and photocurrent was investigated as shown in Fig. 8. A linear relationship with a slope of 3.09 between the photocurrent and the bias voltage in the range of -0.2 V to 0.2 V vs. SCE was observed. The photocurrent increases with the increase of adscititious positive bias voltage of the electrode, indicating that the polarity of the electrical field caused by the adscititious voltage has the opposite polarity of the inner electrical field caused by intramolecular charge separation, and the electrons flow from the electrolyte through the LB film to the ITO electrode.

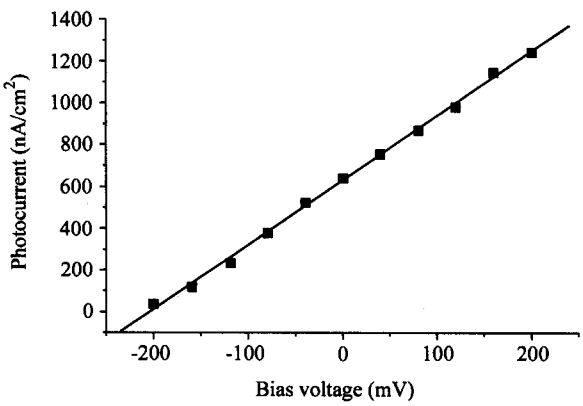

Fig. 8 Photocurrent vs bias voltage for HMAPN LB films ITO electrodes in 0.5 mol/L KCl aqueous solution under ambient conditions, upon irradiation with a 156.3 mW/cm^2 white light.

The influence of the light intensity on the photocurrent was also investigated to get more information about the generation and recombination of the charge. In general the photocurrent (i_{ph}) has a dependence on light intensity (I) according to Donovan equation, $i_{ph} = KI^m$, where $m = 1$ is the characteristics of unimolecular recombination process and $m = 1/2$ is the characteristics of bimolecular recombination process. The dependence of the photocurrent on the light intensity from 3.5 mW/cm^2 to 218 mW/cm^2 was investigated for HMAPN monolayer LB film modified ITO electrode without any bias voltage. The result is shown in Fig. 9, which displayed that the photocurrent increases with the incerase of light intensity. An anodic photocurrent of 835 nA/cm^2 was obtained when the light intensity increases to 218.2 mW/cm^2. From 218.2 mW/cm^2, an equation of $i_{ph} = 12.55 \times I^{0.78}$ is obtained by least square fitting, indicating that the separated charge relaxation pro-

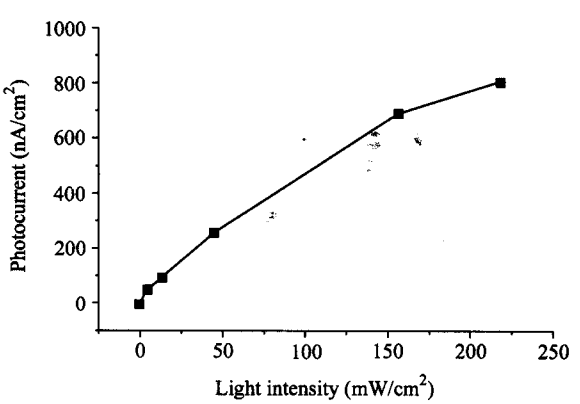

Fig. 9 Light intensity dependence of the photocurrent measured versus SCE for three electrodes in 0.5 mol/L KCl electrolyte solution under ambient condition without bias voltage.

cess occurred in the LB monolayer film contains both the unimolecular and the bimolecular recombination processes.

In addition, the photocurrent of the HMAPN monolayer LB film coated ITO electrode changes with the addition of the electron donor (hydroquinone, H_2Q) or electron acceptor (methyl viologen, MV^{2+} or oxygen, O_2) in the electrolyte solution. The photocurrent increased slightly with the addition of H_2Q into electrolyte solution at low H_2Q concentration. If MV^{2+} was added to the electrolyte solution, the photocurrent decreased slightly. When the electrolyte solution was bubbled by oxygen, the photocurrent decreased too. All these results indicate that H_2Q acts as an electron donor in the photocurrent formation process by giving an electron to the charge separated state of HMAPN in LB film, while the added MV^{2+} or O_2 in electrolyte acting as electron acceptors are unfavorable to the production of an anodic photocurrent in this system. Nevertheless the influence of H_2Q, MV^{2+} or O_2 is so weak to the photocurrent that the maximum change of photocurrent was only about 50—60 nA/cm^2.

Mechanism of photocurrent generation

Evidently the photocurrent generation is consistent with the following electron flowing process (Fig. 10). At first, the HMAPN molecule in LB film was irradiated and excited. Subsequently the intramolecular electron transfer occurred within the excited HMAPN and the electron acceptor, nitrile group, which is hydrophilic and near to the ITO substrate surface is partly negatively charged. Then the negative nitrile group injects an electron to the conduction band of the ITO electrode. The electrons were enriched in the ITO electrode and flowed to the counter electrode through the external circuit. The electron on the surface of the counter electrode flowed through the electrolyte to the working electrode and thus the photocurrent was formed. The electron donor H_2Q in the electrolyte will prompt the charge separation in the LB film of ITO electrode by giving an electron to the negatively charged nitrile group and consequently facilitate the anodic photocurrent. While the electron acceptor in the electrolyte is surely unfavorable to the anodic photocurrent because they hinder the charge separation process in the working electrode. It is reasonable that either the electron donors or acceptors in the electrolyte solution have relatively weak influence to the photocurrent because the long alkyl part of HMAPN molecule prevents to some extent the electron transfer process between HMAPN and electron donors or acceptors present in the electrolyte.

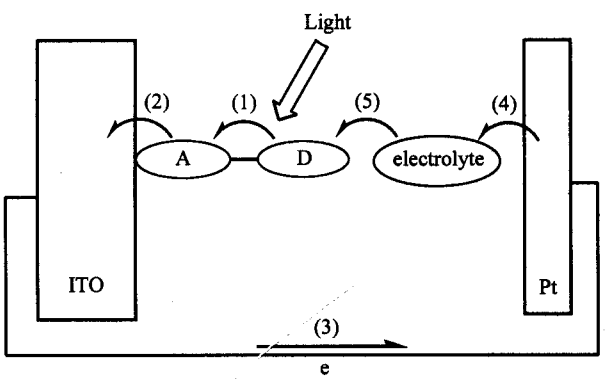

Fig. 10 A schematic representation of photocurrent generation mechanism.

Conclusion

HMAPN can be synthesized by several classical reactions and purified easily. Its absorption and fluorescent properties in solution are strongly dependent on the polarity of the solvents. It can be easily assembled into monolayer film by LB technique. The HMAPN monolayer LB film modified ITO electrode exhibits good photoelectric properties with the maximum photocurrent of 835 nA/cm^2 under the white light of 218.2 mW/cm^2 without bias voltage. The relationship between the photocurrent and bias voltage is linear and that between the photocurrent and light intensity corresponds to the equation of $i_{ph} = 12.55 \times I^{0.78}$. The intramolecular charge separation of HMAPN in LB film is suggested to be responsible for the photocurrent formation.

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