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2-Ethynyl-6-methylthieno[3,2-*b*]thiophene as an efficient π spacer for porphyrin-based dyes

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ABSTRACT: In this study, three donor- π -acceptor (D- π -A) type unsymmetrical porphyrin-based dyes have been designed and synthesized for dye-sensitized solar cells (DSSCs). The photophysical, electrochemical and photovoltaic properties of the dyes were successfully adjusted by using functionalized arylamines (triphenylamine or N, N-dimethyl-4-(acetylene)-aniline) as donor, porphyrin derivatives as conjugated π bridge, ethynyl-thiophene or ethynyl-thiophthene as π spacer and carboxylic acid as anchor group. Compared with the dye containing ethynyl-thiophene as π spacer, the dyes containing 2-ethynyl-6-methylthieno[3,2-b]thiophene as π spacer between the porphyrin macrocycle and the carboxylic acid anchoring group show broadened absorption spectra on TiO₂ films and red-shifted absorption spectra in solution. The dye based on triphenylamine and 2-ethynyl-6-methylthieno[3,2-b]thiophene exhibited a power conversion efficiency (PCE) of 4.53% under simulated air mass 1.5 global sunlight. indicate introduction These results of that the

2-ethynyl-6-methylthieno[3,2-*b*]thiophene in the meso-positions of porphyrin dyes is an effective approach to improve the photovoltaic performance. **Keywords:** Conjugated π bridge; Porphyrin-based dyes; Power conversion efficiency; Dye-sensitized solar cells; Synthesis

1. Introduction

As the fossil energy gradually reduces and the demand of energy increases in the world, the exploration of new energy has became a hot scientific research. Solar energy, as a kind of widely distributed, ample and eco-friendly energy, has caused the world's research. Dye-sensitized solar cells (DSSCs) were one of the most effective renewable photovoltaic devices because they were found to display low cost, ease of fabrication, short energy pay back time, low sensitivity to temperature changes and environmental friendliness compared with the conventional inorganic solar cells [1]. The sensitizer was one of the key components for achieving the device with high efficiency and durability. Up to now, a recorded power conversion efficiency (PCE) above 13.0% has been reported for DSSCs [2, 3]. The ruthenium polypyridyl complex as sensitizers in the DSSCs was the first one reached PCE of 10% [4]. However, ruthenium was a noble and expensive metal, which may limit the large-scale application as sensitizers. For this reason, porphyrin and its derivatives with large π -conjugated systems have been received considerable attention as sensitizers for DSSC applications [5, 6].

The structure of porphyrin exhibits four meso-positions and eight β -positions, which can serve to functionalization. β -Linked porphyrin derivatives were reported to

show promising device performances with a benchmark efficiency of 7.1% in 2007 [7]. Meso-linked porphyrin derivative sensitizers with a push-pull framework appeared in 2009 [8]. With a structural design involving long alkoxyl chains to envelop the porphyrin core to suppress the dye aggregation for a push-pull zinc porphyrin, the DSSC device achieved a record PCE of 13.0% in 2014 [2]. Recently, unsymmetrical porphyrin sensitizers [9-11] with unique directionality have been proven to be high-performance sensitizers. In the past decades, various functional groups and their derivatives [12-14] have been employed at meso-positions of porphyrin macrocycles to develop an effective part of the donor- π -acceptor (D- π -A) structure.

According to previous reports, the PCE of porphyrin sensitizers could be significantly improved by grafting the molecule with properly chosen donor, π spacer and acceptor/anchoring groups. Combination of a wide range of donor moieties, such as functionalized arylamines, polyaromatic or heterocyclic donors, with ethynyl benzoic acid anchoring group at the meso-position of the porphyrin has revealed a significantly improved cell performance [9-12]. Thiophene derivatives have been widely utilized in metal-free organic sensitizers [15-17] and porphyrin-based sensitizers [18, 19] as an effective π bridge in DSSCs. Compared with thiophene, thiophthene [20] exhibits larger π delocalization, so it was widely used as π bridge for metal-free organic sensitizers. However, it rarely used as π bridge in porphyrin sensitizers. It was revealed that, in porphyrin dyes, the elongation of π conjugation or loss of molecular structure symmetry could cause a split in π and π^* energy levels and

a decrease in the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), thus resulted in broadening and red-shifting of the absorption band together with an increasing intensity of the Q band relative to that of the Soret band [21]. In this article, in contrast to many available porphyrin sensitizers which have been reported with ethynyl benzoic acid anchoring group [22, 23], we attempted to introduce either ethynyl-thiophene or 2-ethynyl-6-methylthieno[3,2-*b*]thiophene as π spacer between the porphyrin macrocycle and the carboxylic acid anchoring group and studied its influence on solar cell performance.

Herein, we reported three new unsymmetrical zinc-porphyrin dyes, as shown in Fig. 1, appended with ethynyl-thiophene or ethynyl-thiophthene π spacer between porphyrin and anchoring group to facilitate the shift of the absorption towards the red region in solution. We predicted that increasing the conjugated degrees of π -bridge moieties could improve the light-harvesting capability and reduce the intermolecular aggregation [24]. Thus, a higher short circuit current density (J_{sc}) and a higher PCE could be achieved. The photophysical, electrochemical and photovoltaic properties of the porphyrin dyes with different donors and π spacers were fully investigated.

2. Experimental section

2.1 Materials and reagents

All starting materials were purchased from commercial suppliers at analytical grade. Tetrahydrofuran (THF) was distilled from sodium-benzophenone prior to use. N,N-Dimethylformamide (DMF) was dried and distilled under reduced pressure.

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Phosphorus oxychloride (POCl₃) and 1,2-dichloroethane were achieved by atmospheric distillation. All other solvents and chemicals used in this work were analytical grade without further purification. All chromatographic separations were carried out on silica gel (200-300 mesh). Compound **8**, **9**, **13** [3, 25, 26] and compound **14** were synthesized according to the methods reported in the literatures [27].

2.2 Instruments and characterizations

¹H NMR spectra was measured on a Bruker Avance 400 instrument, using CDCl₃ and deuterated dimethyl sulfoxidi (DMSO-d6) as solvents and tetramethylsilane (TMS; δ =0 ppm) as internal standard. MALDI-TOF mass spectrometric measurements were performed on Bruker Autoflex III instrument. GC-MS were measured on an Agilengt-7890A-5975C instrument. UV-Visible spectra of the dyes were measured on a Perkin-Elmer Lamada 25 spectrometer. The total amounts of the three dyes adsorbed on the TiO₂ films were determined by measuring the absorbance of the sensitizers, which were dissolved from the dye-coated TiO_2 films into DMF/H₂O = 4:1 with 0.1 mol L^{-1} NaOH. The PL spectra were obtained using Perkin-Elmer LS-50 luminescence spectrometer. Electrochemical impedances were measured on an electrochemistry workstation in the dark. Electrochemical redox potentials were obtained by cyclic voltammetry, which measured by a three-electrode configuration and an electrochemistry workstation at a scanning rate of 50 mV s⁻¹. The silver electrode (SCE), platinum disk electrode and Pt electrode were used as reference electrode, working electrode electrode, respectively. and the counter

Tetrabutylammonium perchlorate (TBAP) 0.1 M was used as supporting electrolyte in nitrogen-purged anhydrous CHCl₃. Ferrocene/ferrocenium redox couple was used for potential calibration.

2.3 General procedure for preparation of porphyrin-modified TiO₂ electrode and photovoltaic measurements

Fluorine-doped SnO₂ conducting glass (FTO) were cleaned by ultrasonication in water, acetone, ethanol, isopropanol, respectively, and subjected to an O₃ treatment for 10min. The substrates were treated in a 40 mM TiCl₄ solution at 70 °C for 30 min, then rinsed with deionized water and ethanol, sintered at 450 °C for 30 min. The TiO₂ suspension was composed of P25 (Degussa AG, Germany) [28], acetylacetone, 1 wt% magnesium acetate, and magnetic stirring for 24 h. Then the paste was deposited onto the substrates by the method of blade coating to obtain a TiO₂ film of 10-15 μ m thickness. The TiO₂ film was gradually heated to 450 °C, baked at this temperature for 30 min. The 200 nm particles sized TiO₂ colloid was coated on the electrode by the same method, resulting in a TiO₂ light-scattering layer of 4-6 μ m thickness. The double-layer TiO₂ were sintered at 450 °C for 30 min. After the substrate was cooled to the room temperature, then treated with TiCl₄ solution at 70 °C for 30 min and sintered at 450 °C for 30 min.

After the film was cooled to room temperature, it was immersed in optimized solvent system of THF and ethanol (volume ratio 1:4) with 0.25 mM porphyrin dyes and 10 mM Chenodeoxycholic acid (CDCA) for 3 h in the dark. The sensitized electrode was then rinsed with ethanol and dried. A drop of electrolyte was deposited

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onto the surface of the electrode and a Pt foil counter electrode was clipped onto the top of the TiO₂ electrode to assemble the dye sensitized solar cells for photovoltaic performance measurements. The electrolyte consisted of 0.5 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butylpyridine (TBP) in 3-methoxypropionitrile and the efficient irradiated area of the cell was 0.196 cm². The photocurrent-voltage (*J*–*V*) characteristics were recorded on Keithley 2602 Source meter. Dye sensitized TiO₂ electrodes were measured under simulated air mass 1.5 global sunlight. The power conversion efficiency (η) of the DSSC was calculated from short-circuit photocurrent (*J*_{sc}), the open-circuit photovoltage (*V*_{oc}), the fill factor (*FF*) and the intensity of the incident light (*P*_{in}) according to the following equation:

$$\eta = \frac{J_{sc}(mA \ cm^{-1}) \times V_{oc}(V) \times FF}{P_{in}(mW \ cm^{-1})}$$

The measurement of monochromatic incident photo-to-current conversion efficiency (IPCE) for the solar cell was also detected with a Zolix DCS300PA data acquisition system.

2.4 Synthesis

N-(4-(di(1H-pyrrol-2-yl)methyl)phenyl)-4-methyl-N-p-tolylbenzenamine (2)

Compound **1** (3.01 g, 10 mmol) and pyrrol (17.40 mL, 0.25 mmol) were added to a dry round-bottomed flask and degassed with a stream of argon for 30 min. Indium trichloride (0.22 g, 1 mmol) was added, and the solution was stirred under argon at room temperature for 30 min and then quenched with 0.1 M aqueous NaOH. The organic phase was washed with water and dried over anhydrous MgSO₄. Then the solvent was removed under vacuum to afford an orange crude product, and then it was

purified by column chromatography using a hexane/ethyl acetate mixture (5/1) as eluent. A brownish yellow solid was obtained. Yield 2.51 g (59.9%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.95 (s, 2H), 7.05–7.04 (d, *J*=2 Hz, 6H), 6.98–6.94 (d, *J*=8 Hz, 6H), 6.70 (s, 2H), 6.16 (s, 2H), 5.94 (s, 2H), 5.40 (s, 1H), 2.30 (s, 6H).

1-(3-Bromothiophen-2-yl)ethanone (3)

To a stirred solution of 3-bromothiophene (10 g, 62.00 mmol) in refined DMF (200 mL), acetyl chloride (5.80 g, 74.40 mmol) was added, and then slowly added AlCl₃ (16.35 g, 124 mmol). The solution was stirred at 0 °C for 3 h and then quenched with water. The organic phase was washed with 0.1 M aqueous NaOH and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give the product without any purification.

3-Methylthieno[3,2-b]thiophene-2-carboxylate (4)

To a degassed solution of compound **3** (5 g, 24.38 mmol) and K₂CO₃ (6.77 g, 48.76 mmol) in refined DMF (100 mL), ethyl-2-mercaptoacetate (3.52 g, 29.26 mmol)was added. After the solution was stirred at room temperature under argon for 24 h, NaOH (178 mg, 4.46 mmol) in ethanol (5 mL) was added and the mixture was stirred for an additional 24 h, and then quenched with water. The organic phase was washed with water and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate=5/1 to as eluent. A white solid was obtained. Yield 2.12 g (41.0%). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.56–7.55 (d, *J*=2 Hz, 1H), 7.31–7.30 (d, *J*=2 Hz, 1H), 4.39–4.36 (m, 3H), 2.69 (s, 3H).

5-Bromo-3-methylthieno[3,2-b]thiophene-2-carboxylate (5)

To a stirred solution of compound **4** (2.12 g, 10 mmol) in DMF (50 mL), a solution of N-bromosuccinimide (NBS) (2.15 g, 12 mmol) in DMF (20 mL) was slowly added at 0 °C, and then the mixture was warmed up to 60 °C for 24 h. After the reaction was quenched with acetone (5 mL), the mixture was poured into water and extracted with dichloromethane (DCM). The solvent was removed under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate = 5/1 to as eluent. A white crystal was obtained. Yield 2.05 g (70.9%). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.30 (s, 1H), 4.39–4.34 (m, 3H), 2.69 (s, 3H).

3-Methyl-5-(2-(trimethylsilyl)ethynyl)thieno[3,2-b]thiophene-2-carboxylate (6)

A mixture of compound **5** (2.05 g, 7.09 mmol), trimethylsilylacetylene (3 mL, 21 mmol), Pd(PPh₃)₄ (32 mg, 46.60 µmol), CuI (13 mg, 69.90 µmol), THF (30 mL) and Et₃N (5 mL) was gently refluxed for 12 h under argon. The reaction liquid was poured into water and extracted with DCM. The solvent was removed under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate = 5/1 to as eluent to give the product. Yield 1.42 g (65.1%) as a light yellow solid. ¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.38 (s, 1H), 4.42–4.37 (m, 3H), 2.68 (s, 3H), 0.30 (s, 9H).

5-Ethynyl-3-methylthieno[3,2-b]thiophene-2-carboxylic acid (7)

2 M aqueous NaOH (3.75 mL, 7.50 mmol) was added into a solution of compound **6** (1.16 g, 3.75 mmol) in MeOH (10 mL) at 0 $^{\circ}$ C. The reaction mixture was stirred for 5 h at room temperature. The mixture was neutralized and concentrated in

vacuo. The mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with brine, and dried over anhydrous MgSO₄. Filtration and concentration under vacuum gave **7** as a brown solid. Yield 0.81 g (97.6 %). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.38 (s, 1H), 3.87 (s, 1H), 2.68 (s, 3H).

5-(4-(Di-p-tolylamino)phenyl)-10,20-bis(2,6-dioctoxyphenyl)porphyrin (10)

To a degassed solution of dipyrromethane (0.40 g, 2.74 mmol), compound **2** (1.15 g, 2.74 mmol) and compound **8** (2.00 g, 5.50 mmol) in DCM (700 mL), trifluoroacetic acid (0.27 mL, 3.73 mmol) was added. After the solution was stirred at 25 °C under argon for 4 h, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2 g, 8.27 mmol) was added and the mixture was then stirred for additional 1 h. Then, the mixture was basified with Et₃N (5 mL). The solvent was removed under reduced pressure and the residue was purified by column chromatography using DCM/hexane =1/2 as eluent to give a red solid. Yield 0.68 (18.5%). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 10.13 (s, 1H), 9.77–9.69 (m, 4H), 9.12–9.04 (m, 4H), 8.97 (s, 2H), 8.90 (s, 2H), 8.83 (s, 2H), 7.98–7.96 (m, 4H), 7.88 (s, 2H), 7.21 (s, 2H), 6.88 (s, 4H), 3.92–3.87 (m, 8H), 2.32–2.26 (s, 6H), 0.95–0.88 (m, 8H), 0.87–0.82 (m, 8H), 0.68–0.61 (m, 8H), 0.59–0.54 (m, 28H), 0.49–0.42 (m, 8H), -3.02 (s, 2H). MALDI-TOF MS (C₈₄H₁₀₃N₅O₄) m/z: calcd for 1246.808; found 1246.905.

5-Bromo-15-(4-(di-p-tolylamino)phenyl)-10,20-bis(2,6-dioctoxyphenyl)porphyrin (11)

To a stirred solution of porphyrin **10** (0.68 g, 0.55 mmol) in DCM (350 mL), was slowly added a solution of NBS (97 mg, 0.55 mmol) in DCM (40 mL) in a period of 6 h at 0 $^{\circ}$ C under argon. After the reaction was quenched with acetone (10 mL), the

solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using DCM/hexane=1/2 as eluent. Recrystallization from MeOH/DCM gave the product as a purple powder. Yield 0.53 g (72.6%). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 9.77–9.69 (m, 4H), 9.12–9.04 (m, 4H), 8.97 (s, 2H), 8.90 (s, 2H), 8.83 (s, 2H), 7.98–7.96 (m, 4H), 7.88 (s, 2H), 7.21 (s, 2H), 6.88 (s, 4H), 3.92–3.87 (m, 8H), 2.32–2.26 (s, 6H), 0.95–0.88 (m, 8H), 0.87–0.82 (m, 8H), 0.68–0.61 (m, 8H), 0.59–0.54 (m, 28H), 0.49–0.42 (m, 8H), -2.98 (s, 2H). MALDI-TOF MS (C₈₄H₁₀₂N₅O₄Br) m/z: calcd for 1326.717; found 1326.530.

[5-Bromo-15-(4-(di-p-tolylamino)phenyl)-10,20-bis(2,6-dioctoxyphenyl)porphyrinato] zinc(II) (12)

A suspension of compound **11** (0.53 g, 0.40 mmol) and Zn(OAc)₂•2H₂O (1.04 g, 4.40 mmol) in a mixture of DCM (60 mL) and methanol (40 mL) were stirred at 23 ^oC for 3 h. The reaction was quenched with water (100 mL), and the mixture was extracted with DCM (2 × 100 mL). The combined extracts were washed with water and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give the product. Yield 0.52 g (98.1%). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 9.77–9.69 (m, 4H), 9.12–9.04 (m, 4H), 8.97 (s, 2H), 8.90 (s, 2H), 8.83 (s, 2H), 7.98–7.96 (m, 4H), 7.88 (s, 2H), 7.21 (s, 2H), 6.88 (s, 4H), 3.92–3.87 (m, 8H), 2.32–2.26 (s, 6H), 0.95–0.88 (m, 8H), 0.87–0.82 (m, 8H), 0.68–0.61 (m, 8H), 0.59–0.54 (m, 28H), 0.49–0.42 (m, 8H). MALDI-TOF MS (C₈₄H₁₀₀N₅O₄BrZn) m/z: calcd for 1387.600; found 1387.706.

[5,15-bis(2,6-dioctoxyphenyl)-10-(4-(di-p-tolylamino)phenyl)-20-(5-carboxythiophen

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e-2-yl-ethynyl)porphyrinato] zinc(II) (SF)

Compound SF was prepared under modified conditions of literature procedure. Pd(PPh₃)₄ (12 mg, 0.01 mmol) and CuI (2 mg, 0.01 mmol) was added into a solution of compound 12 (139 mg, 0.10 mmol) and compound 13 (40 mg, 0.30 mmol) in fresh distilled THF (35.0 mL) and anhydrous Et₃N (6 mL) under argon. The reaction was stirred at 45 °C for 14 h. Then, the reaction was quenched with water (100 mL), and the mixture was extracted with DCM (2×50 mL). The combined extracts were washed with water and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give the product. The crude product was purified using silica gel column chromatography (eluent: $DCM/CH_3OH = 25.1$) to give a green solid. Yield 95 mg (65.2%). ¹H NMR (400 MHz, DMSO, δ /ppm): 9.56–9.49 (m, 4H), 9.13–9.04 (m, 4H), 8.83 (s, 2H), 8.78-8.77 (m, 3H), 8.67-8.60 (m, 2H), 7.96-7.92 (m, 5H), 7.69 (s, 2H), 7.21 (s, 2H), 6.89 (s, 4H), 3.92–3.87 (m, 8H), 2.48 (s, 6H), 0.95–0.88 (m, 8H), 0.87-0.82 (m, 8H), 0.68-0.61 (m, 8H), 0.59-0.54 (m, 28H), 0.49-0.42 (m, 8H). FT-IR (v_{max}/cm^{-1}) : 2177 $(v_{C=C})$. MALDI-TOF MS $(C_{91}H_{103}N_5O_6SZ_n)$ m/z: calcd for 1458.699; found 1458.706.

[5,15-bis(2,6-dioctoxyphenyl)-10-(4-(di-p-tolylamino)phenyl)-20-(5-carboxy-6-methyl thieno[3,2-b]thiophene-2-yl-ethynyl)porphyrinato] zinc(II) (**BSF**)

The synthetic procedure for **BSF** was similar to that for **SF**, except that compound **7** (66 mg, 0.3 mmol) was used instead of compound **13**. The crude product was purified using silica gel column chromatography (eluent: DCM/CH₃OH = 25:1) to give a green solid. Yield 89 mg (58.2%). ¹H NMR (400 MHz, DMSO, δ /ppm): 9.57–9.49 (m, 4H), 9.13–9.04 (m, 4H), 8.83 (s, 2H), 8.78–8.77 (m, 2H), 8.67–8.60 (m, 2H), 8.05 (s, 1H), 7.96–7.92 (m, 4H), 7.69 (s, 2H), 7.21 (s, 2H), 6.89 (s, 4H), 3.92–3.87 (m, 8H), 2.48 (s, 6H), 2.33 (s, 3H), 0.95–0.88 (m, 8H), 0.87–0.82 (m, 8H), 0.68–0.61 (m, 8H), 0.59–0.54 (m, 28H), 0.49–0.42 (m, 8H). FT-IR (v_{max} /cm⁻¹): 2177 ($v_{C=C}$). MALDI-TOF MS ($C_{94}H_{105}N_5O_6S_2Z_n$) m/z: calcd for 1528.687; found 1528.984.

[5,15-bis(2,6-dioctoxyphenyl)-10-((4-N,N-dimethylamino-phenyl)ethynyl)-20-(5-carb oxy-6-methylthieno[3,2-b]thiophene-2-yl-ethynyl)porphyrinato] zinc(II) (NSF)

The synthetic procedure for **NSF** was similar to that for **SF**, except that compound **14** (138 mg, 0.11 mmol) and compound **7** (132 mg, 0.60 mmol) were used instead of compound **12** and compound **13**, respectively. The crude product was purified using silica gel column chromatography (eluent: DCM/CH₃OH = 25:1) to give a green solid. Yield 94 mg (61.0%). ¹H NMR (400 MHz, DMSO, δ /ppm): 9.57 (s, 2H), 9.29 (s, 2H), 8.85–8.74 (m, 4H), 8.05 (s, 1H), 7.90–7.89 (d, *J*=2 Hz, 2H), 7.69 (s, 2H), 7.47–7.46 (d, *J*=2 Hz, 2H), 6.99 (s, 4H), 3.92–3.87 (m, 8H), 2.60–2.55 (s, 6H), 2.16 (s, 3H), 0.95–0.88 (m, 8H), 0.87–0.82 (m, 8H), 0.68–0.61 (m, 8H), 0.59–0.54 (m, 28H), 0.49–0.42 (m, 8H). FT-IR (ν_{max} /cm⁻¹): 2177 ($\nu_{C=C}$). MALDI-TOF MS (C₈₄H₉₇N₅O₆S₂Z_n) m/z: calcd for 1399.620; found 1399.721.

3. Results and discussion

3.1 Synthesis

The detailed synthetic routes of three porphyrin dyes as well as the intermediates were shown in Scheme 1. Firstly, the compound **2** was synthesized from

4-(dip-tolylamino) benzaldehyde in pyrrol using InCl₃ as catalyst. Then compound **2** was reacted with compound **8** and **9** to obtain the key intermediate **10**. Subsequently, compound **10** was reacted with NBS in DCM to convert to **11**. Finally, compound **11** was treated with Zn(OAc)₂•H₂O to obtain the key intermediate **12**. Compound **3** was synthesized from 3-bromine thiophene by Vilsmeier formylation reaction. Compound **4** was prepared from **3** with ethyl-2-mercaptoacetate by free radical reaction. Then, by means of Sonogashira reaction, **5** was reacted with trimethylsilylacetylene to afford **6**. Finally, **7** was obtained from ordinary hydrolysis reaction. Compound **8**, **9**, **13** and **14** were synthesized according to the methods reported in the literatures. The target molecules were produced with the Sonogashira cross-coupling method [25].

3.2 Photophysical properties

The photophysical properties of **SF**, **BSF** and **NSF** were investigated by UV-Vis absorption spectroscopy in diluted (10⁻⁵ M) chloroform solution. The spectra and data are shown in Fig. 2 and Table 1, respectively. The three dyes showed typical absorption bands associated with porphyrins, namely, an intense Soret band at around 450 nm and a series of lower-intensity Q bands at longer wavelength (550–650 nm). Among all the three dyes, **NSF** displayed a relatively weaker Soret band absorption, indicating the inferior ability of light harvesting. The values of the molar extinction coefficient (ε) at the maximum absorption wavelength (λ_{max}) were 2.12, 1.42, 0.86 × 10⁵ M⁻¹cm⁻¹ for **SF**, **BSF**, **NSF** dyes, respectively. As expected, all of the Soret-bands and Q bands of **BSF** and **NSF** were obvious red-shifted significantly relative to **SF**. In CHCl₃ solution, the maximum absorption wavelength (λ_{max}) for these dyes were 450,

457, 458 nm, respectively. The Soret-bands of **BSF** and **NSF** which used 2-ethynyl-6-methylthieno[3,2-*b*]thiophene as π spacer were 7–8 nm red-shifted than **SF**. The Q bands of **BSF** and **NSF** were 4 nm and 28 nm red-shifted relative to **SF**, respectively. The red-shift of **BSF** and **NSF**, which might be due to the electronic effect of the π spacer and the Q band red-shift of **NSF** in solution is more obvious than **BSF**, which may be largely affected by the dimethyl aniline electron donor group. This result conformed that the ethynyl-thiophthene groups linking at the meso-position of porphyrin had positive effect on improving the UV-Vis absorption of the porphyrin dyes.

We also measured the adsorption of those three porphyrin dyes on TiO_2 films (Fig. 3). The corresponding data were also summarized in Table 1. The corresponding absorption peaks in Soret-bands were 452, 440 and 477 nm for **SF, BSF** and **NSF**, respectively. The absorption peak of the dye **BSF** was blue-shifted on the TiO_2 surface in comparison with those in solutions, due to the formation of *H*-aggregation. However, the absorption peaks of the dyes **SF** and **NSF** were red-shifted compared to those in solution, which should result from the formation of the *J*-aggregation of porphyrins on the TiO_2 surface [29, 30]. In addition, the absorption spectra of these three dyes on the TiO_2 film were broadened relative to the solution spectra.

The emission spectra of the three porphyrin dyes are presented in Fig. 4 and fluorescence data are also listed in Table 1. The maximum fluorescence emission wavelength (λ_{em}) of **BSF** was 640 nm, which was a little red-shifted to **SF** (636 nm). The observed red-shift of λ_{em} should be attributed to the increase of the effective

conjugation in **BSF** molecules compared to **SF**. But the λ_{em} of **NSF** (623 nm) displays an antipodally blue-shifted relative to **SF** due to different donor units.

3.3 Electrochemical properties

To evaluate the thermodynamic possibility of electron transfer from the excited dye molecule to the conductive band of TiO₂, cyclic voltammetry (CV) was performed in CHCl₃ with 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte (Fig.5). The first oxidation potential (E_{ox}) versus normal hydrogen electrode (NHE) E_{ox} , which corresponds to the highest occupied molecular orbital (HOMO versus NHE), was calibrated by addition of 0.63 V to the potential (versus silver electrode) versus Fc/Fc⁺ by CV. The reduction potential versus NHE (E_{red}), which corresponds to the lowest unoccupied molecular orbital (LUMO versus NHE), could be calculated by E_{ox} - E_{0-0} . And the zerothezeroth energies (E_{0-0}) were determined by the intersection of the normalized UV-Vis absorption spectrum and steady-state fluorescence emission spectrum. All the data are summarized in Table 2.

The Eox energies of SF, BSF and NSF were found to locate at 0.83, 0.79 and 0.64 V, respectively. Compared with SF, the E_{ox} s of BSF and NSF were shifted to negative, which could be attributed to the expansion of their π -conjugated units [31]. The reduction potentials of the three dyes (SF, BSF and NSF) were -1.23, -1.25 and -1.43, respectively. It was evident that the HOMO levels of dyes BSF and NSF were more negative than SF, which resulted in the decrease of their energy gaps between the HOMO and LUMO. At the same time, the decrease of their energy gaps showed a positive effect on the DSSCs performance due to the narrower gap between the

HOMO level and the redox potential of iodine/iodide leading to less waste of energy. It was evident that the LUMO values were more negative than the conduction band of TiO₂ (about –0.5 V versus NHE), which the electrons could be efficiently injected into the conduction band of TiO₂ from the excited dyes. The E_{gap} between the conduction band and the E_{red} (versus NHE) of **SF**, **BSF** and **NSF** were 0.73, 0.75 and 0.93 eV. Theoretically, an energy gap of 0.2 eV was necessary for efficient electron injection [32]. The above experimental results indicated that the three dyes could be used as the qualified sensitizers for efficient DSSCs.

3.4 Photovoltaic properties of porphyrin-sensitized TiO₂ cells

The incident photo-to-current conversion efficiencies (IPCE) plots for the DSSCs based on the three porphyrin dyes are shown in Fig. 6. All the three dyes responded in the broad range of 300–750 nm and showed the maximum IPCE values around 460 nm, which was in accord with the spectra of the dyes on TiO₂. It was noticed that the solar cell sensitized by dye **SF** presented an IPCE value of 55% at 466 nm. Dyes **BSF** and **NSF** got higher IPCE values of 71% at 467 nm and 82% at 470 nm, respectively. Among the three dyes, **SF** showed inferior IPCE relative to other two dyes which mainly resulted from its worse light harvesting ability in long wavelength region in solution.

The photocurrent density-voltage curves (J-V) of DSSCs based on **SF**, **BSF** and **NSF** are shown in Fig. 7 and the detailed photovoltaic parameters are summarized in Table 3. The **SF**-based cell gave a short circuit current density (J_{sc}) of 6.09 mA cm⁻², an open circuit voltage (V_{oc}) of 0.52 V, and a fill factor (FF) of 0.67, which yielded an

overall power conversion efficiency (PCE) of 2.10%. And the cell based on NSF showed a J_{sc} of 9.41 mA cm⁻², a V_{oc} of 0.62 V, and a FF of 0.68, leading to a PCE of 3.98%. Under the same conditions, the **BSF**-based cell showed the highest PCE among the three dyes of 4.53%, with a highest J_{sc} of 10.66 mA cm⁻². The V_{oc} values were in the order of NSF \approx BSF > SF, the lowest V_{oc} of SF which might due to the higher charge recombination rate in $TiO_2/dye/electrolyte$ interface. The measured J_{sc} increased in the order of SF (6.09 mA cm⁻²) < NSF (9.41 mA cm⁻²) < BSF (10.66 mA cm⁻²), consistent with the increased tendency of IPCE. To investigate the absorptive abilities and explain the J_{sc} of the three dyes, the thin films were evaluated for the total amount of the porphyrin adsorbed. The adsorbed amounts (Γ) of the three dyes on TiO₂ film are exhibited in Table 1. The amount of the three dyes (SF, BSF and NSF) absorbed on TiO₂ film were 7.72×10^{-9} , 8.19×10^{-9} , 1.58×10^{-8} mol cm⁻², respectively. These data suggested that SF had the worst light-harvesting ability on TiO₂ film thus caused the low J_{sc} [33]. Although NSF exhibited the highest Γ , its lowest ε brought about the lower J_{sc} than **BSF**. Finally, the maximum conversion efficiency has been achieved for the cell sensitized with BSF.

3.5 Electrochemical impedance spectroscopy studies

To particularly elucidate correlation of V_{oc} with the three dyes the electrochemical impedance spectroscopy (EIS) was measured in the dark [34]. The Nyquist plots of **SF**, **BSF** and **NSF** based DSSCs are shown in Fig. 8. Two semicircles were observed in the Nyquist plots. The small and large semicircles, respectively located in the high and middle frequency regions, were assigned to the

charge transfer at Pt/electrolyte and TiO₂/dye/electrolyte interface [35, 36], respectively. The charge recombination resistance (R_{rec}) on the TiO₂ surface, which was related to the charge recombination rate between injected electron and electron acceptor (I_3^-) in the electrolyte, was estimated by the large semicircle [37]. A large R_{rec} means a small charge recombination rate and vice versa. The R_{rec} values for **SF**, **BSF** and **NSF** were estimated to be 23 Ω , 37 Ω and 46 Ω , respectively. The result was consistent with the changing tendencies of V_{oc} values in the cells of the three dyes mentioned above.

DSSCs based on **BSF** and **NSF** produced higher V_{oc} values than **SF** (0.52 V < 0.61 V \approx 0.62 V), which could also be explained by the electron lifetime. Fig. 9 showed the Bode plot for DSSCs based on **SF**, **BSF** and **NSF**. The peaks located at the high-frequency (right) and middle-frequency (left) respectively correspond to the small semicircle (left) and large semicircle (right) in the Nyquist plots (Fig. 9). The reciprocal of the peak frequency for the middle-frequency peak was regarded as the electron lifetime since it represented the charge transfer process at the TiO₂/dye/electrolyte interface. Therefore we could speculate that the electronic lifetime of the DSSC based on **BSF** and **NSF** was longer than that of DSSC based on **SF**, thereby explaining the tendencies of V_{oc} for the three dyes.

4. Conclusions

In summary, three new donor- π -acceptor type unsymmetrical porphyrins (SF, BSF and NSF) were designed and synthesized. The photophysical, electrochemical and photovoltaic properties of the porphyrin dyes were greatly influenced by the 19

donor units and π spacers. It showed that the absorption spectra of both **BSF** and **NSF** dyes which used 2-ethynyl-6-methylthieno[3,2-*b*]thiophene as π spacer were red-shifted in solution and broadened on TiO₂ films, respectively, and the amount of the two dyes absorbed on TiO₂ film significantly increased. Under simulated air mass 1.5 global sunlight, **BSF**-based DSSC exhibited the highest η of 4.53% among the three dyes.

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dyes	$\label{eq:labs} \begin{split} \lambda_{abs} / nm \\ (\epsilon, \ 10^5 \ M^{-1} \ cm^{-1})^a \end{split}$	λ_{max}/nm (on TiO ₂) ^b	$\Gamma/$ (mol cm ⁻¹) ^c	λ_{em} $(nm)^d$	λ_{int} $(nm)^e$
SF	450(2.12), 621(0.23)	<mark>452</mark>	$7.72 imes 10^{-9}$	636	602
BSF	457(1.42), 625(0.19)	<mark>440</mark>	8.19×10^{-9}	640	607
NSF	458(0.86), 649(0.20)	<mark>477</mark>	$1.58 imes 10^{-8}$	623	599

 Table 1
 Maximum absorption and emission data of SF, BSF and NSF dyes.

^{*a*} Absorption spectra was measured in CHCl₃ solution. ^{*b*} Absorption spectra was obtained on TiO₂ films. ^{*c*} Amount of the dyes adsorbed on TiO₂ films. ^{*d*} Wavelengths for emission spectra in CHCl₃ solution by exciting at Soret wavelength. ^{*e*} Measured by the intercept of the normalized absorption and emission spectra.

Dye	$\lambda^a_{int}\!/nm$	E^{b}_{0-0}/eV	$E^{\rm c}_{\rm ox}/{\rm V}$ vs NHE	E ^d _{red} /V/ vs NHE	$E^{ m e}_{ m gap}\!/ m V$	
SF	602	2.06	0.83	-1.23	0.73	
BSF	607	2.04	0.79	-1.25	0.75	
NSF	599	2.07	0.64	-1.43	0.93	

 Table 2
 Electrochemical data of SF, BSF and NSF dyes

^{*a,b*} Measured by the intercept of the normalized absorption and emission spectra. ^{*c*} First oxidation potentials (vs. NHE). ^{*d*} Excited-state oxidation potentials approximated from E_{ox} and E_{0-0} (vs. NHE). ^{*e*} Driving forces for electron injection from the porphyrin excited singlet state(E_{ox}) to the conduction band of TiO₂ (-0.5 V vs. NHE).

Dye	$J_{\rm sc}$ (mA cm ⁻²)	$V_{ m oc}\left({ m V} ight)$	FF	η (%)
SF	6.09	0.52	0.67	2.10
BSF	10.66	0.61	0.69	4.53
NSF	9.41	0.62	0.68	3.98

Table 3 Photovoltaic performances of DSSCs based on SF, BSF and NSF dyes.

Captions for Figures and Scheme

- Fig. 1 Molecular structures of SF, BSF and NSF dyes.
- Scheme. 1 Synthetic routes of SF, BSF and NSF dyes.
- **Fig. 2** Absorption spectra of **SF**, **BSF** and **NSF** dyes in $CHCl_3$ solutions (10⁻⁵ M).

Fig. 3 Normalized absorption spectra of SF, BSF and NSF dyes on TiO₂ thin-films.

Fig. 4 Normalized emission spectra for SF, BSF and NSF dyes in solution.

Fig. 5 Cyclic Voltammogram of SF, BSF and BSF dyes.

Fig. 6 IPCE action spectrum for the DSSC based on the SF, BSF and NSF dye-sensitized TiO_2 films.

Fig. 7 J–V curves for DSSCs with SF, BSF and NSF dyes.

Fig. 8 EIS Nyquist plots for DSSCs based on the three dyes measured in the dark under -0.70 V bias.

Fig. 9 EIS Bode plots for DSSCs based on the three dyes measured in the dark under -0.70 V bias.



Fig. 1 Molecular structures of SF, BSF and NSF dyes.



Scheme. 1 Synthetic routes of SF, BSF and NSF dyes.

□, pyrrol, InCl₃, room temperature, NaOH; □, acetyl chloride, AlCl₃, 0 °C; □, K₂CO₃, DMF, ethyl-2-mercaptoacetate, NaOH; □, NBS, DMF, 60 °C, 24 h; □, trimethylsilylacetylene, Pd(PPh₃)₄, CuI, Et₃N /THF, 12 h, 45 °C; □, NaOH, MeOH, 5h; □, trifluoroacetic acid, DDQ; □, NBS, DCM, 0 °C; □, Zn(OAc)₂•2H₂O, room temperature; □, Pd(PPh₃)₄, CuI, Et₃N /THF, 14 h, 45

°C.



Fig. 2 Absorption spectra of **SF**, **BSF** and **NSF** dyes in $CHCl_3$ solutions (10⁻⁵ M).



Fig. 3 Normalized absorption spectra of SF, BSF and NSF dyes on TiO₂ thin-films.



Fig. 4 Normalized emission spectra for SF, BSF and NSF dyes in solution.





Fig. 6 IPCE action spectrum for the DSSC based on the SF, BSF and NSF dye-sensitized TiO_2 films.



Fig. 7 *J*–*V* curves for DSSCs with **SF**, **BSF** and **NSF** dyes.



Fig. 8 EIS Nyquist plots for DSSCs based on the three dyes measured in the dark under -0.70 V bias.



Fig. 9 EIS Bode plots for DSSCs based on the three dyes measured in the dark under -0.70 V bias.

Highlights

- 1. Three new D- π -A type unsymmetrical porphyrin dyes were synthesized.
- 2. 2-Ethynyl-6-methylthieno[3,2-b]thiophene as π spacer broadened the absorption.
- 3. Dye **BSF** exhibited higher conversion efficiency than that of **SF** and **NSF**.