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The YZ-type USQs exhibit the power conversion efficiency of ~ 4%, which is approximately 300% higher than those of XZ-type USQs.



# Squaraine dyes containing diphenylamine group: Effects of different type structures on material properties and organic photovoltaic performances

Lin Yang, <sup>a, b, 1</sup> Youqin Zhu, <sup>c, 1</sup> Jianglin Wu,<sup>a</sup> Bin Hu,<sup>a</sup> Zhenguo Pang,<sup>a</sup> Zhiyun Lu,<sup>a</sup> Suling Zhao, <sup>c, \*\*</sup> Yan Huang <sup>a, \*</sup>

<sup>a</sup> Key Laboratory of Green Chemistry and Technology (Ministry of Education), College of Chemistry, Sichuan University, Chengdu 610064, P. R. China. E-mail: huangyan@scu.edu.cn

<sup>b</sup> School of Pharmaceutical Sciences, Southwest Medical University, Luzhou, Sichuan 646000, P. R. China

<sup>c</sup> Key Laboratory of Luminescence and Optical Information (Ministry of Education), Institute of Optoelectronics Technology, Beijing Jiaotong University, Beijing 100044, P. R. China. E-mail: slzhao@bjtu.edu.cn

<sup>1</sup> These authors contributed equally.

### Journal Pre-proo

Four donor-acceptor-donor (D-A-D') unsymmetrical squaraines (USQs) with different molecular skeletons (XZ-type and YZ-type), containing diphenylamine group with/without methoxy substituent were synthesized as donor materials in bulk-heterojunction (BHJ) organic photovoltaics (OPVs). The introduction of methoxy group in USQs has little different effects on the overall photovoltaic performance. Conversely, the different molecular skeleton types of the USQs have significant influence on their material properties and photovoltaic performance. Compared to BIDPSQ and BIDPOMeSQ with XZ-type molecular skeleton, IDPSQ and IDPOMeSQ with YZ-type molecular skeleton display closer solid-state packing, much lower highest occupied molecular orbital (HOMO) energy level, higher hole mobility and smaller phase separation domain size. Consequently, YZ-type USQs exhibit the most excellent performance with power conversion efficiencies (PCE) of ~ 4%, which is approximately 300% higher than those of XZ-type USQs. Surprisingly, even though IDPSQ and IDPOMeSQ show wide band gaps, the corresponding devices still achieve a highest PCE of ~ 4%, which is comparable to or even higher than the PCEs of some reported SQ-based devices with low band gaps. These results indicate the YZ-type molecular skeleton and the electron-donating diphenylamine group are very promising to construct highly efficient squaraine donor materials.

**Keywords**: squaraines; diphenylamine; organic photovoltaics; molecular skeletons; structure and performance

### Journal Pre-proof

Organic photovoltaics (OPVs) have attracted considerable interest as a kind of promising technology for renewable solar energy applications due to their cost-effectiveness and large-area flexible fabrication.[1-7] Recent advances have pushed the power conversion efficiencies (PCE) of OPVs to over 15%,[5, 8-10] which is inseparable from the material innovation, device optimization and fundamental understanding of device physics. Among them, the development and design of donor-acceptor (D-A) conjugated donor and acceptor materials plays a particularly important role in progress toward increased PCEs of OPVs.[4, 11-13] The core strategy of developing D-A conjugated photovoltaic materials is to select appropriate D or A units, and then combine D and A units in different ways, such as D-A, D-A-D, A-D-A, D-A-A, D-A-A, D-A-D, or A-D-A, etc. and then modify side chains to balance the absorption, energy level, carrier mobility and phase morphology of the photoactive layer. At present, most of the highest-performance donor and acceptor materials are generally constructed with conjugated backbones that have alternating D and A aromatic units, such as PBDB-TF, ITIC etc.[8, 14, 15]

Squaraines (SQs), a class of dyes with resonance stabilized zwitterionic structure, are synthesized from the condensation of squaric acid with two electron-rich moieties to form a donor-acceptor-donor (D-A-D) skeleton.[16] Recently, SQs have emerged as promising donor materials in OPVs due to their characteristics of strong absorption in the visible and near-infrared regions, simple synthetic routes, remarkable stability and wide molecular structure diversity.[17-22] According to the different kinds of electron-rich moieties, SQs can pertain to three general structures illustrated in Scheme 1.[18, 19, 23-26] X-type squaraines are the condensation products of squaric acid with appropriate anhydrobases,[24, 27] while Y-type squaraines are prepared starting from activated arenes or  $\pi$ -excessive heterocycles,[18, 28-31] Z-type squaraines are prepared starting from primary or secondary amines.[32, 33] The three types of SQs show very divergent photophysical, chemical, electric and molecular packing properties.[25, 34-36] Among the SQ photovoltaic materials, the Y-type SQs are the main ones, and show the obviously higher PCEs (4 ~ 6%) than those of X-type SQs (1 ~ 2%).[19] Relatively speaking, the Z-type SQs are rather rare, and only two cases of unsymmetrical YZ-type SQs (ASSQ and DPASQ, shown in Scheme 2), which contain diphenylamine group as electron-donating moiety, were reported to be employed as donor materials in planar heterojunction (PHJ) OPVs with the power conversion efficiency (PCE) of ~ 4%.[18, 35]



X-type structure Y-type structure Z-type structure

Scheme 1. Three types of photovoltaic squaraine dyes (D = electron-rich aromatic or heterocyclic rings; R = alkyl or aryl groups).[23]



Scheme 2. The molecular structures of ASSQ and DPASQ.

In fact, due to the good electron-donating and hole transporting capabilities of diphenylamine (DPA) group, many  $\pi$ -conjugated oligomers and small molecules containing diphenylamine in the bridging or terminal positions have been widely employed as the active ingredient in optical and electrical materials.[37, 38] Therefore, very recently, we also synthesized a novel unsymmetrical YZ-type SQ (IDPSQ, shown in Scheme 3) containing diphenylamine group, which was employed as donor materials in solution-processing bulk heterojunction (BHJ) OPVs with PCE of ~ 4%.[23] Furthermore, IDPSQ were also successfully applied to ternary solar cells and semitransparent solar cells, and the corresponding photovoltaic devices achieved excellent performance.[39, 40]

In this work, based on the molecular structure of IDPSQ (YZ-type), the other three unsymmetrical squaraines (USQs, namely BIDPSQ, BIDPOMeSQ and IDPOMeSQ, shown in Scheme 3) with XZ-type or YZ-type skeleton, containing diphenylamine or *p*-methoxy substituted diphenylamine as electron-donating

moiety, were synthesized to research the effects of the molecular structures of these different type SQs on their molecular properties and photovoltaic performances. The results show that the different type structures have effectively influence on their solid-state packing, energy level, carrier mobility and photovoltaic performance. Consequently, YZ-type SQs (IDPSQ and IDPOMeSQ) exhibit a highest PCE of ~ 4%, which is approximately 300% higher than those of XZ-type SQs (BIDPSQ and BIDPOMeSQ). In addition, the presence or absence of methoxy groups also has some slight effect on molecular properties and device performance.



Scheme 3. Molecular structures of the target USQs and IDPSQ.

### 2. Experimental section

### 2.1. Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance AV II 400 MHz instrument with tetramethylsilane as internal standard. High resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF. Absorption spectra of USQs in  $5 \times 10^{-6}$  mol L<sup>-1</sup> chloroform solution and thin film states were measured with a PerkinElmer Lambda 950 UV-Vis scanning spectrophotometer. The thin film samples were fabricated by spin-casting the USQ chloroform solution with a concentration of 5 mg mL<sup>-1</sup> on quartz substrates (1500 rpm, 30 s).

Cyclic voltammetry was performed in  $5 \times 10^{-4}$  mol L<sup>-1</sup> USQ anhydrous dichloromethane solution with a LK 2010 electrochemical work station, using a three-electrode cell with a Pt disk working electrode, a Pt wire counter electrode and a Ag/AgNO<sub>3</sub> (0.1 mol L<sup>-1</sup> in acetonitrile) reference electrode.

Tetrabutylammonium perchlorate (0.10 mol  $L^{-1}$ ) and ferrocenium/ferrocene redox couple were used as the supporting electrolyte and internal potential reference, respectively.

The crystallographic data for IDPSQ is obtained from the literature (CCDC 1487656)[23]. The crystallographic data for BIDPSQ and BIDPOMeSQ have been deposited in the Cambridge Database (CCDC 1487658 for BIDPSQ, and 1903751 for BIDPOMeSQ). Single crystal samples of BIDPSQ and BIDPOMeSQ were obtained from dichloromethane/methanol system. Single crystal X-ray diffraction data of BIDPSQ were obtained on a Xcalibur E X-ray single crystal diffractometer equipped with graphite monochromator Mo-K $\alpha$  ( $\lambda = 0.7107$  Å) radiation. The data collection was executed using CrysAlisPro program. The structures were determined using direct method and successive Fourier difference syntheses (SHELXS-97) and refined using full-matrix least-squares procedure on F2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). Single crystal X-ray diffraction data of BIDPOMeSQ were obtained on a Gemini X-ray single crystal diffractometer equipped with graphite monochromator Cu-K $\alpha$  ( $\lambda = 1.5418$  Å) radiation. The refinement details and the resulting factors for these USQs are given in Table S1.

Samples for atomic force microscopy (AFM) measurements were prepared by spin-casting from USQ:PC<sub>71</sub>BM = 1:3 in chloroform solution with a total concentration of 20 mg mL<sup>-1</sup> on glass substrates (1500 rpm, 50 s). The transmission electron microscopy (TEM) investigation was performed on a FEI Tecnai G2 F20 S-TWIN field emission transmission microscope. electron The poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) layer was prepared by spin-casting their water solution on the glass substrate (3000 rpm, 40 s) and then baked at 150 °C for 10 min. The specimen for TEM measurement was prepared by spin-casting the blend chloroform solution (USQ:PC<sub>71</sub>BM = 1:3, 20 mg mL<sup>-1</sup>) on the glass/PEDOT:PSS substrate, then floating the film on water surface, and transferring to copper grids.

### 2.2. Device preparation

LiF (0.8 nm)/ Al (100 nm). The ITO-coated glass substrates (sheet resistance = 15  $\Omega$  sg<sup>-1</sup>) were cleaned through sequential sonication in detergent, deionized water, acetone and ethanol for 10 min each, and finally blow-dried by high purity nitrogen. The substrates were treated by UV-ozone for 5 min, then immediately transferred into a high vacuum chamber for deposition of 8 nm MoO<sub>3</sub> at pressure of  $< 3 \times 10^{-4}$  Pa with a rate of 0.5 Å s<sup>-1</sup>. Subsequently, the photoactive layers were fabricated by spin-casting the USQ:PC<sub>71</sub>BM chloroform solution with a total concentration of 20 mg mL<sup>-1</sup> (1500 rpm, 50 s) in a N<sub>2</sub>-filling glove box at 25 °C. Then the substrates were loaded into a vacuum chamber to finish the deposition of LiF (0.8 nm) and Al (100 nm) under pressure of  $< 3 \times 10^{-4}$  Pa with a rate of 0.05 Å s<sup>-1</sup> and 1.5 Å s<sup>-1</sup>, respectively. Deposition rate and film thickness were in situ monitored using a quartz crystal oscillator mounted to the substrate holder. The active area of cells was 6 mm<sup>2</sup>. To obtain the average data related to device performance, several batches of devices (4 cells per batch) for each set of conditions were fabricated and tested. The current density-voltage curves under illumination were measured using an Abet solar simulator with a Keithley 4200 source measurement unit under AM 1.5G illumination (100 mW cm<sup>-2</sup>), after spectral mismatch correction under an ambient atmosphere at 25 °C. EQE measurements were performed in air using a QE/IPCE Measurements Solar Cell Scan 100 (ZOLIX) system.

Hole-only devices were fabricated with structure of ITO/  $MoO_3$  (8 nm)/ USQ (80 nm) or USQ:PC<sub>71</sub>BM (1:3, wt%, 80 nm)/Au (100 nm). The dark current density-voltage characteristics of these devices were measured and fitted the results using the space charge limited current (SCLC) model. The current density (*J*) is given by

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{L^3}$$

Where  $\varepsilon_0$  is the permittivity of free-space,  $\varepsilon_r$  is the relative dielectric constant of the active layer,  $\mu$  is the charge carrier mobility, and *L* is the thickness of the active layers.

### 2.3. Synthesis

The synthetic routes of intermediates and USQs are outlined in Scheme 4. Compounds IDPSQ and **1-8** were prepared according to the procedures described in the literatures.[18, 23, 41-43] The other chemicals, reagents, and solvents were used as received from the suppliers except as specifically mentioned.



Scheme 4. Synthetic routes of three USQs. Reagents/conditions: a) isopropanol, concentrated H<sub>2</sub>SO<sub>4</sub>, reflux, 3 h, 81%; b) diphenylamine, isopropanol, concentrated HCl, reflux, 8 h, 48%; c) acetone, 6 mol L<sup>-1</sup> HCl, reflux, 8 h, 55% (3), 73% (6); d) NaOBu-*t* (1.5 eq.), Pd(OAc)<sub>2</sub> (4% eq.), P(*t*-Bu)<sub>3</sub>HBF<sub>4</sub> (10% eq.), anhydrous toluene, reflux under Ar, 5 h, 72%; e) **1**, isopropanol, concentrated HCl, reflux, 8 h, 48%; f) quinoline, *n*-butanol/benzene = 4:1 (v/v), reflux, 13 h, 37% (**BIDPSQ**); g) quinoline, *n*-butanol/toluene = 1:3 (v/v), reflux, 13 h, 44% (**BIDPOMeSQ**); h) *n*-butanol/toluene = 1:3 (v/v), reflux, 13 h, 45% (**IDPOMeSQ**).

### 2.3.1. 3,4-Diisopropoxycyclobut-3-ene-1,2-dione (1)[18]

A mixture of squaric acid (2.00 g, 17.5 mmol), isopropanol (20 mL) and a drop of concentrated  $H_2SO_4$  was refluxed for 3 h, and the solvent was evaporated under reduced pressure. Then isopropanol was added, the mixture was refluxed for 30 min and the solvent was evaporated again. The crude product was purified

### 2.3.2. 3-(Diphenylamino)-4-isopropoxycyclobut-3-ene-1,2-dione (2)[18]

A mixture of diphenylamine (5.64 g, 33.3 mmol), **1** (6.00 g, 30.3 mmol), isopropanol (200 mL) and concentrated HCl (0.6 mL) was refluxed for 8 h, and the reaction was monitored by thin layer chromatography. Then reaction mixture was concentrated in vacuo. The resulting crude product was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 10:1) to afford **2** (4.54 g, 48%) as yellow solid. M.p. 156-158 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.38 (t, *J* = 7.2 Hz, 4H, ArH), 7.30 (t, *J* = 7.2 Hz, 2H, ArH), 7.11 (d, *J* = 7.6 Hz, 4H, ArH), 5.46-5.37 (m, 1H, CH), 1.28 (d, *J* = 6.0 Hz, 6H, CH<sub>3</sub>).

## 2.3.3. 3-(Diphenylamino)-4-hydroxycyclobut-3-ene-1,2-dione (3)[18]

**2** (4.54 g, 14.7 mmol) was added to acetone (100 mL), stirred and dissolved. After adding 6 mol L<sup>-1</sup> HCl (150 mL), the reaction mixture was refluxed for 8 h, and the reaction was monitored by thin layer chromatography. The reaction mixture was poured into water, and the yellow precipitate was obtained by filtration. The precipitate was recrystallized from acetone to afford **3** (2.15 g, 55%) as pale-yellow solid. M.p. 186-187 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm)  $\delta$  7.29 (t, *J* = 7.2 Hz, 4H, ArH), 7.10 (t, *J* = 7.2 Hz, 2H, ArH), 6.95 (d, *J* = 8.0 Hz, 4H, ArH).

### 2.3.4. Bis(4-methoxyphenyl)amine (4)[41]

4-Methoxybromobenzene (2.00 g, 10.7 mmol), 4-methoxyaniline (1.32 g, 10.7 mmol), Pd(OAc)<sub>2</sub> (96 mg, 4% eq.), P(*t*-Bu)<sub>3</sub>.HBF<sub>4</sub> (310 mg, 10% eq.), sodium *tert*-butoxide (3.08 g, 32.1 mmol) were added to anhydrous toluene (50 mL), and the mixture was heated at 110 °C for 5 h, then filtered. The filtrate was evaporated under reduced pressure, and the crude product was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 10:1) to afford **4** (2.04 g, 72%) as white solid. M.p. 102-103°C. <sup>1</sup>H NMR

### 2.3.5. 3-(Bis(4-methoxyphenyl)amino)-4-isopropoxycyclobut-3-ene-1,2-dione (5)[28]

**4** (0.80 g, 3.49 mmol), **1** (0.63 g, 3.17 mmol) were added to the mixture of isopropanol (30 mL) and concentrated HCl (0.1 mL). The mixture was refluxed for several hours, and the reaction was monitored by thin layer chromatography. When the reaction mixture was cooled, the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 10:1) to afford **5** (0.65 g, 59%) as grey solid. M.p. 162-163°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.03 (dt, *J* = 9.2 Hz, 3.2 Hz, 2.4 Hz, 4H, ArH), 6.87 (dt, *J* = 9.2 Hz, 3.2 Hz, 2.4 Hz, 4H, ArH), 5.46-5.37 (m, 1H, CH), 3.82 (s, 6H, CH<sub>3</sub>), 1.30 (d, *J* = 6.0 Hz, 6H, CH<sub>3</sub>).

### 2.3.6. 3-(Bis(4-methoxyphenyl)amino)-4-hydroxycyclobut-3-ene-1,2-dione (6)[37]

The preparation method is the same as **3**. After reaction, the mixture was poured into water to precipitate a viscous solid, and the supernatant was decanted. The viscous solid was dissolved in dichloromethane, and petroleum ether was added dropwise to precipitate a gray precipitate, filtered to afford **6** (0.44 g, 73%) as pale-yellow solid. M.p. 216-218°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.09 (dt, *J* = 9.2 Hz, 3.2 Hz, 2.4 Hz, 4H, ArH), 6.89 (dt, *J* = 9.2 Hz, 3.2 Hz, 2.4 Hz, 4H, ArH), 3.83 (s, 6H, CH<sub>3</sub>).

# 2.3.7. (E)-2-((3-butyl-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)methyl)-4-(diphenyliminio)-3oxocyclobut-1-en-1-olate (**BIDPSQ**)

**3** (1.00 g, 3.8 mmol), **7** (1.63 g, 3.8 mmol), mixed solvent (benzene: *n*-butanol = 1:4, v/v, 150 mL) and quinoline (0.6 mL) were refluxed for 13 h. Then the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (dichloromethane/methanol) and followed by recrystallization from dichloromethane/methanol to afford **BIDPSQ** as fuchsia crystal (0.85g, 37%). M.p. 251-252 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.12 (d, *J* = 8.4 Hz, 1H, ArH, H<sub>9</sub>), 7.89 (d, *J* = 8.8 Hz, 1H, ArH, H<sub>6</sub>), 7.87 (d, *J* = 9.2 Hz, 1H, ArH, H<sub>5</sub>), 7.55 (t, *J* = 7.6 Hz, 1H, ArH, H<sub>7</sub>), 7.45-7.40 (m, 5H, ArH, H<sub>2</sub>,

6.4 Hz, 2H, CH<sub>2</sub>, H<sub>12</sub>), 2.00 (s, 6H, CH<sub>3</sub>, H<sub>11</sub>), 1.87-1.79 (m, 2H, CH<sub>2</sub>, H<sub>13</sub>), 1.53-1.42 (m, 2H, CH<sub>2</sub>, H<sub>14</sub>), 0.99 (t, *J* = 7.6 Hz, 3H, CH<sub>3</sub>, H<sub>15</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 184.3, 174.1, 173.2, 140.8, 139.4, 134.5, 131.4, 129.8, 129.0, 128.7, 127.5, 127.4, 125.5, 124.6, 122.6, 110.3, 86.1, 51.5, 43.8, 29.5, 27.0, 20.4, 14.0. HRMS (ESI)<sup>+</sup> *m*/*z*: [M+H]<sup>+</sup> calcd. C<sub>35</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, 513.2537; found, 513.2532.

2.3.8. (E)-4-(bis(4-methoxyphenyl)iminio)-2-((3-butyl-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2ylidene)methyl)-3-oxocyclobut-1-en-1-olate (**BIDPOMeSQ**)

**6** (300 mg, 0.92 mmol), **7** (363 mg, 0.92 mmol), mixed solvent (toluene: *n*-butanol = 3:1, v/v, 20 mL) and quinoline (0.2 mL) were refluxed for 13 h. Then the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (dichloromethane/methanol) and followed by recrystallization from dichloromethane/methanol to afford **BIDPOMeSQ** as fuchsia crystal (0.25g, 44%). M.p. 276-278 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.11 (d, *J* = 8.4 Hz, 1H, ArH, H<sub>9</sub>), 7.88 (d, *J* = 8.4 Hz, 1H, ArH, H<sub>6</sub>), 7.85 (d, *J* = 8.8 Hz, 1H, ArH, H<sub>5</sub>), 7.53 (td, *J* = 7.6 Hz, 1.2 Hz, 1H, ArH, H<sub>7</sub>), 7.39 (td, *J* = 7.6 Hz, 1.2 Hz, 1H, ArH, H<sub>8</sub>), 7.27 (d, *J* = 8.0 Hz, 1H, ArH, H<sub>4</sub>), 7.18 (dt, *J* = 8.8 Hz, 3.6 Hz, 2.0 Hz, 4H, ArH, H<sub>1</sub>), 6.93 (dt, *J* = 8.8 Hz, 3.6 Hz, 2.0 Hz, 4H, ArH, H<sub>2</sub>), 5.96 (s, 1H, CH, H<sub>10</sub>), 4.06 (br, 2H, CH<sub>2</sub>, H<sub>12</sub>), 3.84 (s, 6H, CH<sub>3</sub>, H<sub>3</sub>), 1.99 (s, 6H, CH<sub>3</sub>, H<sub>11</sub>), 1.85-1.78 (m, 2H, CH<sub>2</sub>, H<sub>13</sub>), 1.51-1.42 (m, 2H, CH<sub>2</sub>, H<sub>14</sub>), 0.99 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>, H<sub>15</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  182.1, 174.2, 172.1, 158.8, 139.6, 134.2, 131.3, 129.8, 129.7, 128.7, 127.4, 126.5, 124.3, 122.5, 114.2, 110.2, 85.8, 55.6, 51.2, 43.6, 29.4, 27.0, 20.4, 14.0. HRMS (ESI)<sup>+</sup> *m*/*z*: [M+H]<sup>+</sup> calcd. C<sub>37</sub>H<sub>37</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>, 573.2748; found, 573.2741.

# 2.3.9. 4-(Bis(4-methoxyphenyl)iminio)-2-(2,6-dihydroxy-4-(indolin-1-yl)phenyl)-3-oxocyclobut-1-en-1-olate (IDPOMeSQ)

**6** (440 mg, 1.35 mmol), **8** (300 mg, 1.32 mmol) and the mixed solvent (toluene: *n*-butanol = 3:1, v/v, 20 mL) were refluxed for 13 h. Then the solvent was evaporated under reduced pressure and the crude product

was purified by column chromatography (dichloromethane/petroleum ether) and followed by recrystallization from dichloromethane/methanol to afford **IDPOMeSQ** as brown solid (0.27g, 45%). M.p. 249-250 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  11.89 (s, 2H, OH, H<sub>4</sub>), 7.41 (d, *J* = 8.0 Hz, 1H, ArH, H<sub>6</sub>), 7.21 (d, *J* = 7.2 Hz, 1H, ArH, H<sub>9</sub>), 7.19-7.14 (m, 5H, ArH, H<sub>1</sub>, H<sub>7</sub>), 6.96 (dt, *J* = 8.8 Hz, 3.6 Hz, 2.0 Hz, 4H, ArH, H<sub>2</sub>), 6.92 (td, *J* = 7.2 Hz, 0.8 Hz, 1H, ArH, H<sub>8</sub>), 6.26 (s, 2H, ArH, H<sub>5</sub>), 4.03 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>, H<sub>11</sub>), 3.86 (s, 6H, CH<sub>3</sub>, H<sub>3</sub>), 3.14 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>, H<sub>10</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  176.5, 175.9, 166.8, 163.4, 159.8, 153.7, 143.8, 133.4, 132.9, 127.5, 126.6, 125.5, 122.3, 114.5, 113.5, 105.0, 96.5, 55.7, 52.1, 28.1. HRMS (ESI)<sup>+</sup> m/z: [M+H]<sup>+</sup> calcd. C<sub>32</sub>H<sub>27</sub>N<sub>2</sub>O<sub>6</sub><sup>+</sup>, 535.1864; found, 535.1867.

### 3. Results and discussion

### 3.1. Synthesis and characterization

The synthetic routes of BIDPSQ, BIDPOMeSQ and IDPOMeSQ are outlined in Scheme 4. Compound IDPSQ and intermediates **1-8** were synthesized according to the literature. [18, 23, 41-43] The molecular structures of these USQs were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, HR-ESIMS and X-ray single crystallographic analysis. Moreover, all of the USQs show good solubility in chloroform at room temperature (> 15 mg mL<sup>-1</sup>), which is essential to preparing smooth, and uniform films through solution processing.

### 3.2. Single crystal X-ray crystallography

The crystallographic data for IDPSQ is obtained from the literature (CCDC 1487656).[23] The single crystals of BIDPSQ and BIDPOMeSQ were obtained by solvent evaporation from dichloromethane/methanol system. The corresponding crystal data have been deposited in the Cambridge Database (CCDC 1487658 for BIDPSO, and 1903751 for BIDPOMeSO). Unfortunately, the single crystal of IDPOMeSQ wasn't obtained from various solvent systems such as dichloromethane/methanol, dichloromethane/n-hexane, dichloromethane/cyclohexane, chloroform/n-hexane and chloroform/cyclohexane. Actually, when purifying the four USQs, the BIDPSQ, BIDPOMeSQ and IDPSQ were crystals with metallic luster by recrystallization from dichloromethane/methanol system, while IDPOMeSQ was brown powdery solid with no metallic luster. Therefore, the optimal conditions and method for cultivating the single crystal of IDPOMeSQ may be quite different from the other three USQs, which needs more time to explore. The relevant crystal data and crystal structure refinement parameters are shown in Table S1.

The single crystals of BIDPSQ, BIDPOMeSQ and IDPSQ are monoclinic, and the space groups are  $P2_1/c$ , P2<sub>1</sub>/c, and P2<sub>1</sub>/n, respectively. The molecular ellipsoid (ORTEP), corresponding dihedral angle and inter-molecular packing are shown in Fig. 1. As expected, the two phenyl rings of the diphenylamine group in the three USQs have a large dihedral angle which is greater than 70°. Comparing BIDPSQ and BIDPOMeSQ, it can be found that the bond lengths on the diphenylamine group of BIDPOMeSQ are slightly shortened, and the corresponding dihedral angle is slightly reduced. BIDPOMeSQ shows a more planar structure than that of BIDPSQ, which might be attributed to the electron-donating ability of methoxy substituent. Therefore, the shortest interplane  $\pi^{...}\pi$  distance of BIDPOMeSQ is 4.206 Å, smaller than that of BIDPSQ (4.528 Å), indicating that the introduction of methoxy substituent is beneficial to promote effective intermolecular packing. On the other hand, comparing BIDPSQ and IDPSQ, it can be found that the squarate ring and the benzindole unit in BIDPSQ are almost coplanar (the dihedral angle is only 3.30°). In IDPSQ, the torsional angle between squarate ring and dihydroxyphenyl group is 7.34°, additionally, the dihedral angle between the dihydroxyphenyl group and the indoline segment is as large as 27.16°. However, the shortest  $\pi^{...}\pi$  distance in IDPSQ single crystal is 3.864 Å, which is much shorter than that of BIDPSQ (4.528 Å). Moreover, the density of IDPSQ single crystal is calculated to be 1.407 mg mm<sup>-3</sup>, larger than that of BIDPSQ single crystal (1.214 mg mm<sup>-3</sup>). These results demonstrate that the intermolecular stacking of IDPSQ (YZ-type SQ) is confirmed to be more effective than that of BIDPSQ (XZ-type SQ), which should be propitious to the enhancement of charge carrier mobility. In addition, in IDPSQ, the bond lengths of O-H<sup> $\cdot$ </sup>O are calculated to be 1.765 and 1.822 Å (Fig. 1), indicative of the presence of relatively strong intramolecular hydrogen bonding interactions between the two hydroxyl groups of dihydroxyphenyl group and oxygen atoms on the central squarate ring.[44] According to our previous research result that the introduction of intramolecular hydrogen bond interactions in SQs is benefit to enhance the compatibility of SQ donor materials and [6,6]-phenyl-C<sub>71</sub>butyric acid methyl ester (PC<sub>71</sub>BM) then decrease the phase separation domain size of their blend film,[45] it could be deduced that IDPSQ-based blend film might obtain a smaller phase separation size than that of BIDPSQ-based one.



Fig. 1. The molecular ellipsoid (ORTEP), corresponding dihedral angle and inter-molecular packing models of BIDPSQ, BIDPOMeSQ and IDPSQ.

### 3.3. Optical properties

The UV-visible absorption spectra of BIDPSQ, BIDPOMeSQ, IDPSQ and IDPOMeSQ in dilute chloroform solution  $(5.0 \times 10^{-6} \text{ mol } \text{L}^{-1})$  and thin films are shown in Fig. 2. The corresponding data are summarized in Table 1. In the dilute chloroform solution, all USQs have similar strong absorption in the visible region, and

the maximum absorption wavelength  $(\lambda_{max})$  is located at 548 ~ 564 nm, with a relatively high molar extinction coefficient ( $\varepsilon$ , 7.36 ~ 9.90 × 10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>). Comparing the absorption spectra of two groups of USQs with or without methoxy substituent (BIDPSQ *vs.* BIDPOMeSQ, IDPSQ *vs.* IDPOMeSQ), it can be seen that the introduction of methoxy substituent causes a slight red shift in the absorption spectrum of the corresponding USQ, which may be attributed to the electron-donating ability of methoxy substituent, consistent with the above conclusion from the single crystal analysis. Meanwhile, the absorption spectra of IDPSQ and IDPOMeSQ have a red shift of 10 ~ 12 nm when compared with BIDPSQ and BIDPOMeSQ. In the film state, all USQs show the broadening and red shift absorption spectra with  $\lambda_{max}$  located at 572 ~ 582 nm. According to the onset of the absorption spectra in solid-state films, the optical band gap ( $E_g^{opt}$ ) of BIDPSQ, BIDPOMeSQ, IDPSQ and IDPOMeSQ are estimated to be 1.95 eV, 1.93 eV, 1.83 eV and 1.86 eV, respectively.[46] It means these USQs belong to the wide band gap donor materials, and has potential to prepare promising ternary organic photovoltaics with other low band gap materials.



Fig. 2. UV-visible absorption spectra of BIDPSQ, BIDPOMeSQ, IDPSQ and IDPOMeSQ in dilute chloroform solution (a) and solid films (b).

### 3.4. Electrochemical properties

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of USQs were determined via cyclic voltammetry (CV) measurements (shown in Fig. 3 and Table 1). In the anode scan, all these USQs show two-electron oxidation processes in the range of  $0.2 \sim 1$  V, and the

onset of the first oxidation wave vs. Fc/Fc<sup>+</sup> is located at 0.29 V for BIDPSQ, 0.21 V for BIDPOMeSQ, 0.56 V for IDPSQ, and 0.52 V for IDPOMeSQ. According to the energy level of Fc/Fc<sup>+</sup> redox couple (4.80 eV below vacuum),[46] the HOMO energy levels of BIDPSQ, BIDPOMeSQ, IDPSQ and IDPOMeSQ are calculated to be -5.09 eV, -5.01 eV, -5.36 eV and -5.32 eV, respectively. In the cathode scan, these USQs show an irreversible reduction oxidation process in the range of  $-1 \sim -1.6$  V, and the onset of the reduction wave vs. Fc/Fc<sup>+</sup> is located at -1.68 V for BIDPSQ, -1.67 V for BIDPOMeSQ, -1.39 V for IDPSQ, and -1.43 V for IDPOMeSQ. The LUMO energy levels of BIDPSQ, BIDPOMeSQ, IDPSQ and IDPOMeSQ are calculated to be -3.12 eV, -3.13 eV, -3.41 eV, and -3.37 eV, respectively. Obviously, the HOMO and LUMO levels of BIDPOMeSQ (IDPOMeSQ) with methoxy substituent are higher than those of the corresponding methoxy-free BIDPSQ (IDPSQ), which is attributed to the electron-donating ability of methoxy substituent. In addition, unexpectedly, the HOMO and LUMO levels of IDPSQ (IDPOMeSQ) are actually ~ 0.30 eV lower than the corresponding BIDPSQ (BIDPOMeSQ), which may be due to the formation of intramolecular hydrogen bonding between the hydroxyl groups and the oxygen atoms on the central squarate ring in IDPSQ (IDPOMeSQ) reducing the overall energy of the whole  $\pi$ -conjugated system.[45, 47]

	solution <sup>a</sup>	fil	film <sup>b</sup>		F	НОМО	
Compound	$\lambda_{\max} (nm, \varepsilon, 10^4 \text{ M}^{-1} \text{ cm}^{-1})$	λ <sub>max</sub> (nm)	$E_g^{opt}$ (eV) <sup>c</sup>	$(V)^d$	$(V)^d$	(eV) <sup>e</sup>	$(eV)^e$
BIDPSQ	548 (7.79)	572	1.95	0.29	-1.68	-5.09	-3.12
BIDPOMeSQ	552 (7.36)	576	1.93	0.21	-1.67	-5.01	-3.13
IDPSQ	558 (9.56)	578	1.83	0.56	-1.39	-5.36	-3.41
IDPOMeSQ	564 (9.90)	582	1.86	0.52	-1.43	-5.32	-3.37

Table 1 Optical data and energy levels of the four USQs.

<sup>*a*</sup> Measured in CHCl<sub>3</sub>,  $c = 5.0 \times 10^{-6} \text{ mol } \text{L}^{-1}$ .

<sup>b</sup> Thin films spin-casted from 5 mg mL<sup>-1</sup> CHCl<sub>3</sub> solution on quartz substrates.

<sup>c</sup> Obtained from the onset of UV-Vis absorption spectra in the thin film state.

<sup>d</sup> Redox potential values were measured by cyclic voltammetry vs. Fc/Fc<sup>+</sup>.

<sup>*e*</sup> HOMO =  $(-4.8 - qE_{ox})$  eV, LUMO =  $(-4.8 - qE_{red})$  eV.[46]



Fig. 3. Cyclic voltammograms of the four USQs in CH<sub>2</sub>Cl<sub>2</sub> solution.

### 3.5. Photovoltaic properties

To research the photovoltaic performance of these USQ compounds, BHJ-OPV cells using USQ as electron donor material and PC<sub>71</sub>BM as electron acceptor material were fabricated by solution processing with a device structure of ITO/ MoO<sub>3</sub> (8 nm)/ USQ:PC<sub>71</sub>BM (wt/wt, 80 nm)/ LiF (0.7 nm)/ Al (100 nm). Initially, the effect of different blend ratios of USQ:PC<sub>71</sub>BM on the photovoltaic performance of the devices were investigated, and the relative current density-voltage (*J*-*V*) curves and photovoltaic data are shown in Table 2 and Fig. 4. For these USQ-based systems, they display different trend in the dependence of photovoltaic performance on the USQ:PC<sub>71</sub>BM blend ratio. For BIDPSQ-based device, when the BIDPSQ:PC<sub>71</sub>BM blend ratio is varied from 1:1 to 1:3, the PCE is enhanced from 0.29% to 0.90% along with significantly increased  $J_{sc}$  and FF and slightly reduced  $V_{oc}$ . When the blend ratio is further varied from 1:3 to 1:8, the photovoltaic performances of the devices just show slight increment (0.90% ~ 1.10%) with increased  $J_{sc}$  and almost unchanged FF and  $V_{oc}$ . The optimal BIDPSQ:PC<sub>71</sub>BM blend ratio is found to be 1:8, and the resultant device shows the highest PCE of 1.10% with  $J_{sc} = 4.50$  mA cm<sup>-2</sup>,  $V_{oc} = 0.71$  V, and FF = 0.35. For BIDPOMeSQ-based device, when the blend ratio is varied from 1:1 to 1:3, the PCE is enhanced from 0.31% to 0.71% along with increased  $J_{sc}$  and FF and slightly reduced  $V_{oc}$ . When the blend ratio is further varied



Fig. 4. The *J-V* curves (a-d) of BIDPSQ-, BIDPOMeSQ-, IDPSQ-, IDPOMeSQ-based devices under different USQ:PC<sub>71</sub>BM blend ratio and the EQE curves (e) of the devices with USQ:PC<sub>71</sub>BM = 1:3.

from 1:3 to 1:8, the photovoltaic performances of the devices are almost unchanged (0.69% ~ 0.72%), since the  $J_{sc}$ , FF and  $V_{oc}$  change one after another. The optimal BIDPOMeSQ:PC<sub>71</sub>BM blend ratio is also 1:8, and the resultant device shows the highest PCE of 0.72% with  $J_{sc} = 3.27$  mA cm<sup>-2</sup>,  $V_{oc} = 0.67$  V, and FF = 0.31. For IDPSQ and IDPOMeSQ-based devices, when the blend ratio is varied from 1:1 to 1:8, they show a similar trend in photovoltaic performance. Taking IDPSQ-based device as an example, when the blend ratio is varied from 1:1 to 1:3, the  $V_{oc}$  of the device decreases, but the corresponding  $J_{sc}$  and FF significantly increase, resulting in an increase in PCE from 2.76% to 3.20%. When the blend ratio is varied from 1:3 to 1:8, the  $V_{oc}$  of the device is continued to decrease, and the corresponding  $J_{sc}$  and FF also decrease significantly, resulting in a decrease in efficiency from 3.20% to 1.70%. Finally, the optimal blend ratio of the IDPSQ-based device is 1:3, and the highest PCE is 3.20% with  $J_{sc} = 9.02$  mA cm<sup>-2</sup>,  $V_{oc} = 0.95$  V, and FF = 0.38. It is worth mentioning that the IDPSQ-based device achieves a  $V_{oc}$  of up to 1.00 V when the blend ratio is 1:1, which is related to the rather deep HOMO level (-5.34 eV) of IDPSQ. Similarly, the optimal blend ratio of the IDPOMeSQ device is also 1:3 with a highest PCE of 3.23% with  $J_{sc} = 9.15$  mA cm<sup>-2</sup>,  $V_{oc} =$ 0.88 V, and FF = 0.40.

In order to compare the device performance of the four systems, the photovoltaic performances of the blend ratio of 1:3 were discussed. Apparently, according to the photovoltaic data in Table 2, the

Table 2 The photovoltaic performance data of USQ-OPV devices with varied USQ:PC<sub>71</sub>BM blend ratio.

Dener		$V_{ m oc}$	$J_{\rm sc}$	FF	PCE
Donor		(V)	$(\mathrm{mA~cm}^{-2})$		(%)
BIDPSQ	1:1	0.75 (0.72±0.02)	1.39 (1.28±0.12)	0.31 (0.32±0.01)	0.32 (0.29±0.03)
	1:3	0.69 (0.70±0.02)	3.76 (3.61±0.15)	0.36 (0.36±0.01)	0.95 (0.90±0.05)
	1:5	0.70 (0.69±0.01)	4.10 (4.08±0.10)	0.35 (0.35±0.01)	1.01 (0.99±0.03)
	1:8	0.70 (0.71±0.01)	4.87 (4.50±0.37)	0.35 (0.35±0.01)	1.21 (1.10±0.11)
	1:3 <sup><i>a</i></sup>	0.76 (0.74±0.02)	3.89 (3.78±0.11)	0.36 (0.36±0.01)	1.06 (1.00±0.06)
BIDPOMeSQ	1:1	0.72 (0.73±0.01)	1.37 (1.24±0.13)	0.34 (0.34±0.01)	0.34 (0.31±0.03)
	1:3	0.71 (0.70±0.01)	2.96 (2.81±0.17)	0.37 (0.36±0.01)	0.78 (0.71±0.07)
	1:5	0.68 (0.66±0.02)	3.74 (3.30±0.44)	0.36 (0.32±0.03)	0.91 (0.69±0.22)
	1:8	0.68 (0.67±0.01)	2.90 (3.27±0.34)	0.41 (0.33±0.06)	0.81 (0.72±0.08)
	1:3 <sup><i>a</i></sup>	0.68 (0.69±0.01)	3.38 (3.31±0.13)	0.38 (0.37±0.01)	0.87 (0.84±0.03)
IDPSQ	1:1	1.01 (1.00±0.01)	7.88 (7.63±0.25)	0.36 (0.36±0.01)	2.90 (2.76±0.14)
	1:3	0.99 (0.95±0.03)	9.24 (9.02±0.22)	0.37 (0.38±0.01)	3.42 (3.20±0.22)
	1:5	0.88 (0.89±0.01)	8.22 (7.78±0.44)	0.35 (0.34±0.01)	2.56 (2.39±0.17)
	1:8	0.94 (0.90±0.03)	6.20 (6.06±0.14)	0.31 (0.31±0.01)	1.82 (1.70±0.12)
	1:3 <sup><i>a</i></sup>	0.96 (0.96±0.01)	9.20 (9.22±0.21)	0.39 (0.37±0.02)	3.42 (3.30±0.12)
IDPOMeSQ	1:1	0.98 (0.97±0.01)	7.33 (7.12±0.21)	0.39 (0.37±0.02)	2.81 (2.57±0.24)
	1:3	0.89 (0.88±0.01)	9.41 (9.15±0.26)	0.42 (0.40±0.02)	3.48 (3.23±0.25)
	1:5	0.87 (0.84±0.02)	8.78 (8.53±0.25)	0.39 (0.38±0.01)	2.95 (2.78±0.17)
	1:8	0.78 (0.78±0.01)	7.66 (7.47±0.19)	0.35 (0.35±0.01)	2.10 (2.02±0.08)
	1:3 <sup><i>a</i></sup>	0.93 (0.94±0.01)	9.77 (9.63±0.14)	0.45 (0.43±0.02)	4.06 (3.93±0.13)

<sup>*a*</sup> Thermally annealed at 90 °C for 10 min.

IDPSQ-based and IDPOMeSQ-based devices perform significantly better than the BIDPSQ-based and BIDPOMeSQ-based ones, mainly due to the much higher  $V_{oc}$  and  $J_{sc}$  of the first two devices. The  $V_{oc}$  of IDPSQ and IDPOMeSQ devices are 0.95 V and 0.88 V, respectively, which are much higher than those of BIDPSQ and BIDPOMeSQ devices (~ 0.70 V), which is mainly due to the fact that the HOMO levels of the former two USQs are deeper than the latter two. Meanwhile, the  $J_{sc}$  of the IDPSQ and IDPOMeSQ devices are 9.02 mA cm<sup>-2</sup> and 9.15 mA cm<sup>-2</sup>, respectively, which is also much higher than those of BIDPSQ and BIDPOMeSQ devices (3.61 mA cm<sup>-2</sup>, 2.81 mA cm<sup>-2</sup>). It is consistent with the corresponding EQE curves (Fig. 4e). Obviously, the EQE values of IDPSQ and IDPOMeSQ devices are much higher than BIDPSQ and BIDPOMeSQ devices in the entire region (300 ~ 750 nm), which is partly attributed to the better light capture ability of the first two USQs, such as their higher  $\varepsilon$  and wider absorption spectrum. Moreover, the difference of  $J_{sc}$  may also be related to the carrier mobility and film morphology of the active layer.

Therefore, the hole mobility of the pure films and the blend films were tested and calculated by the space charge limited current (SCLC) model with the device structure of ITO/MoO<sub>3</sub> (8 nm)/USQ or USQ:PC<sub>71</sub>BM (1:3)/MoO<sub>3</sub> (8 nm)/Au (100 nm). The corresponding *J*-*V* curves are shown in Fig. 5. For pure films, the hole mobility of BIDPSQ and BIDPOMeSQ are  $1.54 \times 10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, 2.50 × 10<sup>-6</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, which is much lower than those of IDPSQ ( $1.22 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and IDPOMeSQ ( $2.33 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), which may be mainly due to the much closer intermolecular pack of the latter two USQs, consistent with the conclusion of single crystal analysis. Moreover, the methoxy-containing systems display larger hole mobility than the corresponding methoxy-free systems, which is also consistent with the previous single crystal analysis. For the blend films, the hole mobility of BIDPSQ and BIDPOMeSQ is  $3.14 \times 10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, 7.20 × 10<sup>-6</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, which is also lower than those of IDPSQ and IDPOMeSQ ( $4.14 \times 10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, 1.12 × 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). Since the high hole mobility facilitates the charge transfer, the *J*<sub>sc</sub> can be effectively increased. Therefore, this is one of the reasons why the IDPSQ and IDPOMeSQ-based devices show much higher *J*<sub>sc</sub> than the BIDPSQ and BIDPOMeSQ-based devices.



Fig. 5. Current density-voltage characteristics of hole-only single-carrier devices using USQ and USQ:PC<sub>71</sub>BM (1:3) as active layer.

Then, atomic force microscopy (AFM) measurements were conducted on the blend films of USQ:PC71BM (1:3). AFM analysis (Fig. 6) demonstrates that all of the blend films exhibit a smooth surface morphology with small root-mean-square roughness ( $\delta_{RMS} = 0.20 \sim 1.59$  nm). However, IDPSQ vs. BIDPSQ, IDPOMeSQ vs. BIDPOMeSQ, the first two have relatively smaller  $\delta_{RMS}$ , which is beneficial to form good contact between the active layer and the electrode, and also facilitates charge transfer. Furthermore, transmission electron microscopy (TEM) measurements were carried on the blend films of USQ:PC71BM (1:3). As shown in Fig. 7, the phase separation size of the YZ-type USQ (IDPSQ and IDPOMeSQ) systems is significantly smaller than that of the XZ-type USQ (BIDPSQ and BIDPOMeSQ) ones, which is attributed to the intramolecular hydrogen bond interactions in IDPSQ (IDPOMeSQ) enhancing their compatibility with  $PC_{71}BM$ , according to our reported research results.[45] As the exciton diffusion length of SQs is generally quite short (1 ~ 10 nm),[35] the relatively smaller phase separation size of IDPSQ and IDPOMeSQ blend systems facilitates the diffusion of excitons to the D/A interface for dissociation, thereby improving  $J_{sc}$ . Therefore, this is also an important reason that the EQE values of the IDPSQ- and IDPOMeSQ-based devices in the absorption region of the PC<sub>71</sub>BM (300 ~ 500 nm) are still much higher than that of the BIDPSQ- and BIDPOMeSQ-based devices. Finally, the IDPSQ- and IDPOMeSQ-based devices showed much higher  $J_{sc}$  than that of the BIDPSQ- and BIDPOMeSQ-based ones.



Fig. 6. The AFM height map of BIDPSQ, BIDPOMeSQ, IDPSQ, and IDPOMeSQ blend films with  $USQ:PC_{71}BM = 1:3$ .



Fig. 7. The TEM images of BIDPSQ, BIDPOMeSQ, IDPSQ, and IDPOMeSQ blend films with  $USQ:PC_{71}BM = 1:3$ .

In addition, the PCE of BIDPOMeSQ-based device is slightly lower than that of BIDPSQ-based device, but the PCE of IDPOMeSQ-based device is slightly higher than that of IDPSQ-based device. It can be seen that the introduction of methoxy groups has different effects on the photovoltaic performance of different skeletal molecules, but the overall change is not large.

Upon thermal annealing at 90 °C for 10 min, the photovoltaic performances of the four devices were improved, with PCE values of 1.00% for the BIDPSQ-based device, 0.84% for the BIDPOMeSQ-based device, 3.30% for the IDPSQ-based device, and 3.93% for the IDPOMeSQ-based device. It is worth mentioning that even though IDPSQ and IDPOMeSQ show wide band gap, due to their deep HOMO level, tight intermolecular packing and small phase separation size, the corresponding devices still achieve PCEs of > 3.20%. Especially, the IDPOMeSQ-based device even obtains a highest PCE of 4.06%, which is comparable to or even higher than the PCEs of some reported SQ-based devices with low band gaps.[28, 31,

43, 45, 47, 48] The photoelectric parameters of some squaraine donor materials with low band gap and their corresponding photovoltaic performances are summarized in Table S2. By comparing these data, it can be found that the greatest advantage of IDPSQ and IDPOMeSQ is their much lower HOMO energy level (< -5.30 eV), which is significantly beneficial to obtain high  $V_{oc}$ , thereby promoting higher PCE. It shows that the YZ-typed molecular skeleton of IDPSQ and IDPOMeSQ is beneficial to construct highly efficient unsymmetrical squaraine donor materials with low HOMO energy levels. In addition, if another acceptor material with a low band gap matched to the IDPSQ and IDPOMeSQ is selected to prepare the active layer, the device may achieve more excellent photovoltaic performance.

### 4. Conclusions

Four D-A-D' USQs with XZ-type or YZ-type molecular skeletons, containing diphenylamine group with/without methoxy substituent were synthesized. By systematically comparing the differences between YZ-type USQ (IDPSQ and IDPOMeSQ) and XZ-type USQ (BIDPSQ and BIDPOMeSQ) systems from their single crystallographic data, absorption properties, HOMO/LUMO energy levels, carrier mobility, film morphology etc., it finds YZ-type USQs (IDPSQ and IDPOMeSQ) display closer solid-state packing, much lower HOMO energy level and higher hole mobility. Additionally, the intramolecular hydrogen bond interactions in IDPSQ and IDPOMeSQ are benefit to enhance their compatibility with PC<sub>71</sub>BM, leading to smaller phase separation domain size. Consequently, YZ-type USQs exhibit the most excellent performance with PCE of ~ 4%, which is approximately 300% higher than those of XZ-type USQs. Conversely, the introduction of methoxy group in USQs has little different effects on the overall photovoltaic performance. It is worth mentioning that even though IDPSQ and IDPOMeSQ show the wide band gap, the corresponding devices still achieve a highest PCE of  $\sim 4\%$ , which is comparable to or even higher than the PCEs of some reported SQ-based devices with low band gaps. Consequently, the YZ-type molecular skeleton and the electron-donating diphenylamine group are very promising to construct highly efficient squaraine donor materials.

### Journal Pre-proof

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/xxxxxxxx.

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- The different molecular skeleton types of the unsymmetrical squaraines (USQs) have significant influence on their material properties and photovoltaic performance.
- The YZ-type USQs exhibit the most excellent performance with power conversion efficiencies (PCE) of ~ 4%, which is approximately 300% higher than those of XZ-type USQs.
- The YZ-type molecular skeleton and the electron-donating diphenylamine group are very promising to construct highly efficient squaraine donor materials.

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