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#### Article

## Synthesis of peripherally tetra substituted neutral azophenoxy zinc phthalocyanine and its application in bulk hetero junction solar cells

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#### Abstract

Neutral zinc phthalocyanine bearing 4-phenylazopohenoxy group at the periphery (ZnPc-4) has dihydrateZn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O 4been synthesized from zinc acetate and (phenylazophenoxy)phthalonitrile. The synthesized zinc phthalocyanine ZnPc-4 was characterized using UV-visible, FTIR, <sup>1</sup>H NMR and MALDI-TOF mass spectral measurements. Solution processed bulk hetero junction solar cells were fabricated using ZnPc-4 as the donor material and [6,6]-Phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) as the acceptor material. A power conversion efficiency of 0.69% was achieved by optimizing the donor:acceptor weight ratio. Variation in device performance with the donor:acceptor weight ratio was investigated using atomic force microscopy.

Keywords: soluble zinc phthalocyanine, 4-(phenylazophenoxy)phthalonitrile, bulk hetero junction solar cell, [6,6]-phenyl  $C_{61}$  butyric acid methyl ester, solution processing

#### 1. Introduction

The world is rapidly approaching a precarious environmental state owing to the extensive use of fossil fuels, which may be depleted in the near future. Solar energy is a promising sustainable developmental resource to overcome this energy crisis. The emerging trend in the development of photovoltaics addresses the key issue, i.e., the production of electricity from the renewable solar power. An organic solar cell is a device that uses small organic molecules or conductive organic polymers for light absorption and charge transport to produce electricity from sunlight by the photovoltaic effect[1,2]. Polymeric blend based organic photovoltaics have many advantages over silicon based inorganic-semiconductor technology in terms of low cost production, easy fabrication of device, light weight, thin film deposition over large surface and the fine tuning optical properties of the acceptor-donor materials by slight structural modification[3-6]. Small molecular organic semiconductors with appropriate properties can also be used as electron donor materials in OPV devices. Phthalocyanines have drawn significant research interest from the very beginning of organic solar cell research. Copper phthalocyanine was used as the donor material in the first bilayer solar cell demonstrated by Tang[7]. The double-layer structure of a p-and n-type organic semiconductor OSC device was made using copper phthalocyanine CuPc as the electron donor, a perylenetetracarboxylic derivative as the electron acceptor and the device attained a power conversion efficiency (PCE) of about 1%. In 1995, the discovery of ultrafast charge transfer from polymer to fullerene or its functionalized derivatives [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)facilitated the development of bulk hetero-junction (BHJ) solar cells and fullerene derivatives are considered as the interesting class of acceptor materials in the active layer of OSCs[8]. In 2004, Gebeyehu et al. fabricated the solar cell device by high vaccum co-evaporation technique using ZnPc as donor and fullerene C<sub>60</sub> as acceptor, the device showed PCE of 3.9% [9]. Pfuetzner et al. fabricated a BHJOSC in which  $ZnPc:C_{60}$  blend as photoactive layer and studied the effect of substrate temperatures during the deposition of active layer on the substrate[10]. Despite all these attractive features, the insolubility of phthalocyanines in common organic solvents and their narrow absorption band at ultraviolet and red wavelengths have limited their widespread application in the low-cost organic solar cell technology. The insolubility makes them inappropriate for solution processing and compels the researchers to stick to vacuum thermal evaporation for solar cell fabrication[11–15], which is not suitable for depositing thin-films over large area. On the other hand, solutionprocessing techniques like ink-jet printing, spray coating and spin coating are inexpensive and highly suitable for large area photovoltaics. The solubility of phthalocyanines can be improved by substituting the peripheral, non-peripheral or axial positions of Pc core with appropriate

substituents[16,17]. Recently, several research groups have reported the synthesis of soluble phthalocyanines for BHJ solar cell applications. Fischer et al. achieved a power conversion efficiency (PCE) of 1.6% using soluble ruthenium(II) phthalocyanine complex as the donor material[18]. Varotto et al. fabricated parallel tandem BHJ solar cells using self-organised blends of phthalocyanine derivatives and obtained a 4-fold increase in efficiency compared to single phthalocyanine based devices[19]. Abdullah et al. demonstrated BHJ solar cell with efficiency around 1.1% using vanadyltetraphenoxy phthalocyanine complexes as the acceptor material[20]. In this paper, we report the synthesis, characterization and BHJ solar cell fabrication of zinc phthalocyanine (ZnPc-4) peripherally substituted with 4-phenylazophenol moiety by oxygen linkage. Herein we have utilized the solubility of ZnPc-4 in 1,2-dichlorobenzene (1,2-DCB) for the solution processed fabrication of bulk heterojunction organic solar cells, using ZnPc-4 as the donor material and PCBM as the acceptor material.

#### 2. Experimental

#### 2.1. Materials & Methods

All chemicals were commercially purchased and used without further purification. The purity of the products and the progress of the reaction were monitored in each step by TLC (TLC Silica gel 60 F<sub>254</sub>).UV-visible absorption spectra were recorded on a Schimadzu UV-Visible 2600 Spectrophotometer with quartz cuvette and fluorescence spectra were obtained from Perkin Elmer LS 45 fluorescence spectrophotometer. FT-IR spectra (KBr pellets) were recorded on a JASCO FT-IR 4700 spectrometer. <sup>1</sup>H NMR spectra were obtained in deuterated chloroform CDCl<sub>3</sub>, using a BrukerAvance III, 400MHz FT-NMR spectrometer with TMS as internal reference. MALDI-TOF measurements were done on a Voyager-DE PRO from Applied Biosystems using dihydroxybenzoic acid as the MALDI matrix. Chloroform was used as solvent in mass analysis and mass analysis was conducted in positive ion mode. The absorption spectra and photoluminescence (PL) measurements of thin films of ZnPc-4, PCBM and ZnPc-4:PCBM blend were recorded using Perkin-Elmer lambda-35 spectrophotometer. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of ZnPc-4 were evaluated from cyclic voltammetry measurements using a CH-instruments Inc, USA (Model: CHI660E) equipped with potentiostat/galvanostat with Fourier Transform AC Voltammeter. The electrochemical cell consists of a three electrode cell assembly; platinum as

working electrode, standard calomel electrode (SCE) as reference electrode and a platinum wire as the counter electrode. The concentration of ZnPc-4 was fixed as 0.5 mM. All the measurements were performed at  $25^{\circ}$ C in DCM under N<sub>2</sub> atmosphere using 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte at a scan rate of 100mV/sec. The current density-voltage (J-V) measurements of the photovoltaic devices were carried out with Agilent B2902A Source/Measure unit by keeping the devices under AM 1.5 illumination (Photo Emission Tech SS50AAA solar simulator) with a power density of 100 mW/cm<sup>2</sup>.The surface morphology of the ZnPc-4:PCBM films of different weight ratio were investigated using atomic force microscopy (AFM; WITec, Alpha300RA).

#### 2.2. Synthesis

#### 2.2.1. Preparation of 4-phenylazophenol(1)

4-phenylazophenol was synthesized according to the reported literature method[21]. Aniline (5.0 g, 53.7 mmol) was dissolved in HCl (16 ml) and water (16 ml) and digested in a water bath for an hour. The resulting hydrochloride was cooled to  $5^{\circ}$ C and diazotized with ice-cold aqueous NaNO<sub>2</sub> solution (3.7 g, 53.6 mmol, 25 ml). A cold solution of phenol (7.78 g,53.6 mmol), previously dissolved in 10% NaOH solution (5 g, 50 ml), was then added to the cold diazonium salt solution with vigorous stirring. A yellow colour developed almost immediately and the stirring is continued for 1 h. The reaction mixture was kept overnight in a refrigerator followed by 2h at room temperature. The resulting yellow precipitate was filtered, washed several times with water to remove soluble starting materials, and then dried in air. The crude product was re-precipitated from ethanol-water system several times to yield pure yellow precipitate.

UV-vis (MeOH):  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 239 (4.12), 348 (4.47), 451 (2.97); FTIR (KBr) ( $\nu_{max}$ , cm<sup>-1</sup>): 3165 (broad O-H str.), 1602, 1588, 1506 (Ar C=C str.), 1416 (N=N str.), 1143 (C-N str.), 1240 (C-O str.), 836, 767, 680 (Ar =C-H *oop* bending);<sup>1</sup>HNMR (CDCl<sub>3</sub>, 400MHz) 7.88 (2H, d, J<sup>3</sup>=9.2Hz), 7.86 (2H, d, J<sup>3</sup>=7.2Hz), 7.5 (2H, t, J<sup>3</sup>=7.2Hz), 7.44 (1H, t, J<sup>3</sup>=7.2Hz), 6.94 (2H, d, J=9.2Hz), 5.3 (1H, O-H, broad)

#### 2.2.2. Preparation of 4-(4-(phenylazophenoxy)phthalonitrile(3):

4-(4-(phenylazophenoxy)phthalonitrile was prepared by adopting the reported literature procedures for base catalyzed aromatic nucleophilic ipso-nitro substitution reactions[22,23].4-

phenylazophenol (1.500 g, 11.00 mmol) (1) and 4-nitrophthalonitrile (1.900 g, 11.00 mmol) (2) were added successively with stirring to dry DMF (50 mL). After dissolution, anhydrous  $K_2CO_3(4.550 \text{ g}, 33.00 \text{ mmol})$  was added and the reaction mixture was stirred at 60°C for 24 h under nitrogen. The progress of the reaction was monitored by TLC. The reaction mixture was poured into 250 mL of cold water and stirred for 15 min. The precipitate was filtered, washed several times with cold water until the filtrate became neutral. It was dried in vacuo.

UV-vis (CHCl<sub>3</sub>):  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 325 (4.365), 436 (2.865); FTIR (KBr) ( $v_{max}$ , cm<sup>-1</sup>): 2232 (C=N str.), 1606, 1589, 1562 (Ar C=C str.), 1485 (N=N str.), 1203 (C-N str.), 1257 (Ar-O-Ar str.), 861, 775, 690 (Ar =C-H *oop* bending); <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.03 (2H, d, J<sup>3</sup>=9 Hz), 7.93 (2H, dd, J<sup>3</sup>=8.2 Hz, J<sup>4</sup>=1.8 Hz), 7.76 (1H, d, J<sup>3</sup>=8.8 Hz), 7.56-7.50 (3H, m, J<sup>3</sup>=8.8 Hz, J<sup>4</sup>=1.8 Hz), 7.38 (1H, d, J<sup>4</sup>=2.4 Hz), 7.31 (1H, dd, J<sup>3</sup>=8.6 Hz, J<sup>4</sup>=2.4 Hz), 7.22 (2H, d, J<sup>3</sup>=9 Hz)

## 2.2.3. Preparation of 2,9,16, 23-Tetra-(4-phenylazophenoxy) zinc(II) phthalocyanine, ZnPc-4 (4):

A mixture of 4-(4-(phenylazophenoxy) phthalonitrile (**3**) (0.288 g, 0.889 mmol), Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O (0.0488 g, 0.222 mmol) and a catalytic amount of DBU in dry n-pentanol (dried over molecular sieves) was then refluxed at 170°C with stirring under nitrogen for 16 hours. After cooling to room temperature, the reaction mixture was precipitated by adding 1:1 ethanol- methanol mixture. The crude product was centrifuged and washed several times with methanol-ethanol mixture until the washings was neutral. The green precipitate was filtered and dried in vaccum desiccator. The pure green product was isolated by column chromatography over silica gel using EtOAc/hexane in 3:2 ratio as eluent. Yield: 34% (0.123g). UV-Vis (CHCl<sub>3</sub>):  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 681 (5.45), 614 (4.74), 350 (5.33).

Two step synthesis of the compound ZnPc-4 was given in Scheme 1 below.



Scheme 1.Syntheticroute for the preparation of 2,9,16,23-Tetra-(4-phenylazophenoxy) zinc(II)phthalocyanine, ZnPc-4 (Compound 4); (i) K<sub>2</sub>CO<sub>3</sub>/DMF, 60 °C, N<sub>2</sub>, 48 hours and (ii)Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O/n-pentanol-DBU, 170 °C, N<sub>2</sub>, 16 hours

#### 3. Results and discussion

#### **3.1.** Characterization

The synthesis of the phthalocyanine precursor bearing 4-phenylazophenoxy substituted phthalonitrile was achieved by a base-catalyzed nucleophilic aromatic displacement of 4-phenylazophenol (1) with4-nitrophthalonitrile (2). The peripherally tetra substituted zinc phthalocyanine ZnPc-4 was prepared by the template cyclotetramerization of 4-(4-(phenylazophenoxy) phthalonitrile in n-pentanol/DBU with Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O at 170°C under N<sub>2</sub> atmosphere overnight. The crude product was precipitated by adding 1:1 ethanol-methanol mixture washed and centrifuged several times with ethanol and then performed the silica column using ethyl acetate-hexane in 3:2 ratio. The synthesized compound was characterized with spectroscopic techniques such as UV-visible, FTIR, <sup>1</sup>HNMR and MALDI-TOF Mass Spectroscopy and analyses were consistent with the predicted structures. The characterization details are given in ESI.

Phthalocyanines are always a mixture of four constitutional isomers of symmetry  $D_{2h}$ ,  $C_s$ ,  $C_{2v}$ ,  $C_{4v}$ , and no successful separation method have yet been reported to isolate the isomers by common column chromatography, precipitation or recrystallization techniques[24]. The <sup>1</sup>HNMR data of precursor nitrile derivative revealed a well resolved spectrum, while ZnPc-4 showed broader signals probably due to the presence of four constitutional positional isomers and a possibility for chemical exchange resulting in aggregation-disaggregation equilibrium[25](Figs S3 – S5 in ESI). The disappearance of broad O-H peak of 4-phenylazophenol at 3165 cm<sup>-1</sup> as well as the asymmetric and symmetric NO<sub>2</sub> stretching bands of 4-nitrophthalonitrile at 1539, 1356 cm<sup>-1</sup> in the FT-IR spectra confirmed the formation of desired product, 4-(4-phenylazophenoxy)phthalonitrile, **3**(Fig.S6 in ESI). The ZnPc-4 formation resulted by the cyclotetramerization of the modified dinitrile derivative **3** was also clearly confirmed by the disappearance of the C=N stretching band at 2232 cm<sup>-1</sup>(Fig.S7).

The mass spectrum of ZnPc-4 in Fig. 1 showed the fragments of the analyte mixed with the fragments of the matrix. Four major peaks were observed. Molecular ion peak  $[M]^+$  was observed at m/z = 1361.3 (peak 4), assigned to zinc phthalocyanine ZnPc-4. The intense base peak (peak 2) obtained was that corresponding to the matrix, dihydroxy benzoic acid (DHB-H+). The peaks obtained at m/z = 106 and 272 indicated the fragmentation of phenyl diazonium (peak 1) ion and the dimer of isoindoline-1,3-diimine ion (peak 3) respectively.



Fig. 1. MALDI-TOF mass spectrum of ZnPc-4

UV-visible spectroscopy is the most worthwhile characterization techniques for the structural elucidation of phthalocyanines. The UV-visible spectrum of ZnPc-4 represented the typical electronic spectra of a metal phthalocyanine exhibiting two strong absorption peaks, namely Q band at about 600-700 nm in the visible region and Soret B band at about 300-400 nm in UV region[25]. The sharp strong Q band at 684 nm observed for the synthesized metal phthalocyanine (in Fig. 2) was attributed to the  $\pi$ - $\pi$ \* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of ZnPc-4 of D<sub>4h</sub> symmetry in the monomeric state. The broad Soret B band situated at a  $\lambda_{max}$  of 353 nm was of significantly higher intensity, comparable to the intensity of Q band of Pc core, which can be attributed to the combinatorial absorption of diazo group at the periphery and a deep  $\pi$  to LUMO transition[26]. The shoulder peak situated at 615 nm near the Q band was aroused by aggregation of phthalocyanine rings[27].



Fig. 2.The absorption spectrum of ZnPc-4 in 1,2-dichlorobenzene

# **3.2.** Application of ZnPC-4 in Bulk Hetero Junction (BHJ) organic solar cell fabrication:

Solution processed BHJ organic solar cells are attractive candidates for inexpensive and large area photovoltaics [28,29]. On account of the facile and fast fabrication procedure, the deposition of the active layer from solution has significant advantages over other methods. Fullerenes based derivatives and zinc or copper phthalocyanine derivatives have emerged as the exemplary acceptor and donor materials respectively, in efficient solution processed BHJ devices[30].

In the present study, organic bulk heterojunction (BHJ) solar cells with structure  $ITO/V_2O_5/ZnPc-4:PCBM/LiF/Al$  were fabricated. The active layer blend of ZnPc-4 and phenyl-C61-butyric acid methyl ester (PCBM) was prepared by stirring the compounds in 1,2-dichlorobenzene at a temperature of 65 °C overnight. Three different ZnPc-4:PCBM weight

ratios of 1:0.5, 1:1 and 1:1.5, with 20 mg of ZnPc-4 in 1ml of 1,2-dichlorobenzene were taken. Indium Tin Oxide (ITO) with a sheet resistance 8–12  $\Omega$ /sq was used as the anode. ITO was patterned into 3 mm wide parallel strips with a 3 mm separation in between them. Prior to organic layer deposition, patterned ITO substrates were cleaned in an ultrasonic bath in detergent, de-ionized water, methanol, isopropanol, and acetone successively. Cleaned ITO anodes were treated with oxygen plasma for 10 minutes. A V<sub>2</sub>O<sub>5</sub> anode buffer layer was spin coated from 0.05 molar isopropanol solution of vanadium(V)oxitriisopropoxide at a speed of 4000 rpm for 35 s. Then the substrates were annealed at a temperature of 100 °C for 10 minutes. The active layer blend was spin coated on the V<sub>2</sub>O<sub>5</sub> layer at 1000 rpm for 60 s. The active layer film was allowed to self-anneal for 30 minutes and then annealed at 130 °C for 10 minutes. A lithium fluoride cathode buffer layer of 1.2 nm and an aluminum electrode of 100 nm were thermally evaporated in sequence at a base pressure of 1×10<sup>6</sup> mbar. All the devices were having an active area of 9 mm<sup>2</sup>. The representative architecture of the bulk heterojunction organic solar cell is shown in Fig. 3.



Fig. 3. Architecture of bulk heterojunction organic solar cell.

The absorption spectra of thin films of ZnPc-4, PCBM and ZnPc-4:PCBM blend are shown in Fig. 4 with the chemical structure of PCBM represented in the inset. The ZnPc-4 thin film exhibited two significant absorption bands: one in the wavelength range of 300 to 450 nm with a peak at 350 nm and the other in the wavelength range of 575 to 775 nm with peaks at 637 nm and 692 nm. However, PCBM showed absorption in the wavelength range of 400 to 600 nm, where ZnPc-4 exhibits only a weak absorption. So a

combination of the two materials would help in realizing absorption over a wide range of solar spectrum. Fig. 5 revealed the photoluminescence (PL) spectra of pristine ZnPc-4 and ZnPc-4:PCBM blend films excited at 630 nm. ZnPc-4 film showed an emission maximum at 732 nm with a shoulder at 822 nm. Significant PL-quenching was observed for the ZnPc-4:PCBM composite film. This indicated that the PCBM could help in efficient dissociation of photogenerated excitons[31].



**Fig. 4**.UV–visible absorption spectra of thin films of ZnPc-4,PCBM and ZnPc-4/PCBM blend. The inset shows the chemical structure of PCBM.



Fig. 5. Photoluminescence spectra of pristine ZnPc-4 and ZnPc-4/PCBM blend films excited at 630 nm.

Fig.6 (a) shows the cyclic voltammogram of ZnPc-4. The HOMO and LUMO levels of ZnPc-4 were calculated as 4.79 and 3.63 eV, respectively, from the oxidation onset potential ( $E_{Ox-onset}$ ) and reduction onset potential ( $E_{Red-onset}$ ) using the equation put forward by de Leeuw et al.[32,33]:

$$\mathbf{E}_{\mathrm{HOMO}} = -(\mathbf{E}_{\mathrm{Ox-onset}} + 4.4)\mathbf{eV} \tag{6}$$





**Fig.6.** a)Cyclic voltammogram of ZnPc-4 in DCM containing 0.1M TBAP as supporting electrolyte with scan rate 100 mV/s. b) Schematic energy band diagram of the photovoltaic device.

Fig.6(b) shows the energy band diagram of the solar cell. The energy levels of all the materials other than ZnPc-4 were taken from the literature. The HOMO and LUMO energy levels of ZnPc-4 and PCBM were appropriate to ensure efficient exciton dissociation at the ZnPc-4/PCBM interface. Thus from the UV-Vis absorption study, photoluminescence measurement and cyclic voltammetry, it was clear that ZnPc-4 and PCBM can act as an effective donor/acceptor pair.

Current density-voltage (J-V) characteristics of the photovoltaic devices under dark and illumination for different ZnPc-4:PCBM weight ratios are shown in Fig. 7 (a)-(c). Comparison of J-V characteristics under illumination are shown in Fig. 7 (d) and the detailed solar cell

parameters are summarized in Table 1. The device with ZnPc-4:PCBM blend ratio 1:0.5 exhibited a short-circuit current density ( $J_{sc}$ ) of 2.19 mA/cm<sup>2</sup>, an open-circuit voltage ( $V_{oc}$ ) of 0.63 V, and a fill factor (FF) of 32.24%, leading to a power conversion efficiency (PCE) of 0.45%. The device with a weight ratio of 1:1 showed the best PCE of 0.69% with a  $J_{sc}$  of 3.23 mA/cm<sup>2</sup>,  $V_{oc}$  of 0.62, and FF of 34.34%. When the weight ratio was changed to 1:1.5, the device efficiency decreased to 0.63%. These results indicated that the optimum ZnPc-4:PCBM weight ratio is 1:1. The power conversion efficiency achieved in this study is slightly smaller than the values reported in the literature for unsubstituted zinc phthalocyanines. However, the main advantage of ZnPc-4 over unsubstituted ZnPc is its good solubility in organic solvents, so that ZnPc-4 based BHJ solar cells can be fabricated by the relatively less expensive solution processing techniques. Table 2 provides the comparison of some previous literature reported PCE values for the BHJ devices fabricated by solution processing techniques and by employing similar kind of photoactive layers consisting of substituted zinc phthalocyanine derivatives as acceptors.



**Fig.7.J-V** characteristics of photovoltaic devices under dark and illumination for different ZnPc-4:PCBM weight ratios (a) 1:0.5, (b) 1:1, (c) 1:1.5 and (d) comparison of J-V characteristics under illumination.

ZnPc-4:PCBM weight ratio	$J_{sc} (mA/cm^2)$	$V_{oc}(V)$	FF (%)	PCE (%)
1:0.5	2.19	0.63	32.24	0.45
1:1	3.23	0.62	34.34	0.69
1:1.5	3.02	0.62	33.61	0.63

Table 1.Detailed photovoltaic parameters of devices with different ZnPc-4:PCBM weight ratios.

SI.	Donor	Acceptor	PCE	Year	References
No.			(η%)		C
1	Blend of tertiary butyl and thioalkyl substituted ZnPcs	Pyridine functionalized Fullerene $C_{60}$ derivative	0.12	2010	[19]
2	Tertiary butyl substituted ZnPc ( <sup>t</sup> Bu <sub>4</sub> ZnPc)	PC <sub>61</sub> BM	0.77	2011	[34]
3	Octylthiol substituted ZnPc	РСВМ	0.42	2018	[35]

**Table 2**.Comparison of the literature reported PCE values of the devices fabricated by solution processing technique

 by using similar kind of photoactive layers

The morphology of photoactive layer plays a key role in determining the performance of BHJ solar cells[36–39], which could be influenced by the donor:acceptor weight ratio. Fig. 8 shows the tapping mode 2D and 3D AFM images of the photoactive layer for different ZnPc-4: PCBM weight ratios. The active layer films with weight ratios 1:0.5, 1:1 and 1:1.5 exhibited RMS roughness around 0.99 nm, 0.53 nm and 0.63 nm, respectively. Thus, the film with 1:1weight ratio showed smoother surface compared to other films. This smoother surface is a clear indication of homogeneous miscibility between the donor and acceptor materials, which results in a larger donor-acceptor (D-A) interfacial area with nanoscale phase separation. The smooth and uniform surface morphology with low molecular aggregation observed for the 1:1 weight ratio helped in efficient exciton dissociation and better charge carrier transport leading to higher  $J_{sc}$  and PCE values. The AFM results are thus in good agreement with the device performance shown in Table 1.



**Fig. 8.**2D and 3DAFMimages of photoactive layer for differentZnPc-4: PCBM weight ratios: (a) 1:0.5, (b) 1:1 and (c)1:1.5.

#### 4. Conclusion

In summary, peripherally tetra-(4-phenylazophenoxy) substituted zinc phthalocyanine; ZnPc-4 was synthesized by conventional methods and characterized by UV-visible, FT-IR, <sup>1</sup>HNMR and MALDI-TOF Mass Spectrometric techniques. BHJ solar cells were fabricated by solution processing technique using ZnPc-4 as the donor material and PCBM as the acceptor material in different donor: acceptor weight ratios. The device with a weight ratio of 1:1exhibited the highest PCE, around 0.69%. This better performance is attributed to efficient exciton dissociation and better charge carrier transport due to the smooth and uniform morphology of the active layer. Present study revealed that the compound,ZnPc-4 has a great potential as a donor material for solution processed BHJ solar cells.

#### **Conflict of interest:**

The authors declare no conflict of interest.

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- Synthesised peripherally 4-phenylazophenoxy substituted zinc phthalocyanine (ZnPc-4)
- Fabricated solution processed BHJ solar cells with ZnPc-4 (donor) and PCBM (acceptor)
- Investigated variation in device efficiency with donor:acceptor weight ratios
- Highest efficiency of 0.69% was observed for 1:1 weight ratio
- Investigated the morphology of photoactive layer using atomic force microscopy