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1	Artificial Zinc Chlorin Dyes for Dye Sensitized Solar Cell
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10 Abstract

11 Novel artificial zinc chlorin dyes comprising amine anchoring groups zinc aminochlorin 12 (ZnChl- NH_2), zinc monomethylaminochlorin (ZnChl-NHMe) and zinc dimethylaminochlorin 13 (ZnChl- NMe_2) are synthesized and their photovoltaic performances are evaluated in dye-14 sensitized solar cells. To the best of our knowledge, $-NH_2$ functionalized Zn chlorin dyes are 15 tested in dye-sensitized solar cells for the first time. Best efficiency is obtained with ZnChl-16 *NHMe* sensitizer with a 2.67 mA/cm² short circuit photocurrent density, 414 mV of open 17 circuit voltage, 0.64 of filling factor, and 0.68 of overall light to power conversion efficiency.

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20	Keywords: Zinc chlorin dyes, Dye sensitized solar cell, TiO ₂ nanoparticles
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30 **1. Introduction**

31 Capturing light energy and transforming it efficiently into electricity in a solar cell device 32 offers an attractive solution to the future energy quests [1-3]. Semiconductor based 33 photovoltaics (PV) provide an attractive solution for solar energy conversion systems [4-5]. 34 However there is a growing room for new technologies due to the increasing demand and 35 competitive market for solar cells [6, 7]. In this pursuit, dye sensitized solar cells are 36 successful alternatives providing a cheaper mean than traditional semiconductor based PV 37 system [8,9]. During the developmental journey and technical modification of the DSSC's, 38 various dye modules have been implemented, but the satisfactory results obtained only 39 ruthenium polypyridyl complexes [10-15]. However, ruthenium dyes are expensive and their 40 preparations include lengthy purification steps. In order to bypass the limitations imposed, 41 scientific attention has turned to go for cheaper and easy accessible light-harvesting (LH) 42 molecules [16-19]. In nature, plants have developed outstanding light-harvesting systems that 43 use supramolecular chlorophyll (Chl) aggregates for efficient energy conversion [20]. Natural 44 chlorophylls are derived from bacteriochlorin (BChl) units modified with long hydrophobic 45 side-chains [21]. The synthetic modules of the natural chlorins may offer a good building 46 platform to develop efficient solar cell materials sensitized with biomimetic chlorin dyes [22, 47 23].

48 Inspired by natural light-harvesting system, many people are looking for using Chl units and 49 their bio-inspired modifications for deployment in DSSC. Recently, many synthetic porphyrin 50 based dyes have been tested on TiO_2 layer to make dye sensitized solar cell [24, 26]. Using 51 the natural concept, we started getting interest in using BChl based biomimetic dyes to make 52 DSSC. Here we report DSSC studies of synthetically modified zinc chlorin (ZnChl) dyes to 53 make a cheaper assembly for light conversion into electricity. As natural Chl or BChl are not 54 stable structures owing to Mg center, thus we have prepared the semi-synthetic analogues 55 with zinc coordinating to tetrapyrrole type rings. Moreover, the synthetically prepared ZnChls 56 are also modified with amino group for the attachment onto TiO₂ matrices. For the light-57 harvesting chromophores, we prepared three model compounds of ZnChls, zinc aminochlorin 58 (ZnChl-NH₂), zinc monomethylaminochlorin (ZnChl-NHMe) and zinc dimethylaminochlorin 59 $(ZnChl-NMe_2)$, in which the group in 3¹-position has been substituted by an amino functional 60 group to make appropriate and efficient dyes for DSSCs (Fig. 1)

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- 62

- 64 **2.** Experimental Section
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66 2.1. Materials and Methods

Absorption spectra were recorded in a 1 cm path length quartz cell on a Shimadzu UV-2102
UV-Vis spectrophotometer. ¹H NMR spectra performed on Bruker 400 MHz spectrometer
using residual solvent peaks as internal standards. Mass analysis was performed in Waters
LCT Premier (ESI or APCI mode) or Waters GCT (EI and CI ionization modes). All
preparations and measurements were performed in reduced light conditions.

72 Anhydrous solvents were either distilled from appropriate drying agents or purchased from 73 Merck and degassed prior to use by purging with dry argon and kept over molecular sieves. 74 All chemicals were purchased from commercial sources, and used as received. 2, 4, 6-75 trimethylpyridine (collidine) were purchased from Fluka. Molecular sieves 4 Å activated 76 powder, triethylamine (99%) and OsO_4 were purchased from Aldrich. NaIO₄ (99%), 77 methylamine hydrochloride (99%), NaBH₃CN (95%) and zinc acetate dehydrate (98%) were 78 purchased from Acros. Dye sensitized solar cells were characterized by current-voltage (J-V)79 measurement. All current-voltage (J-V) measurements were done under AM 1.5 conditions. 80 450 W Xenon light source (Oriel) was used to give an irradiance of various intensities. J-V81 data collection was made by using Keithley 2400 Source-Meter and LabView data acquisition 82 software.

83 2.2 Synthesis of Zinc Aminochlorin Derivatives

Zinc aminochlorins were prepared from natural Chl *a*, which was isolated from Spirulina
Maxima algae, according to known literature procedures [31]. Further details of the
procedures and related experimental conditions for the preparation of ZnChl-*NH*₂, ZnChl-*NHMe* and ZnChl-*NMe*₂ are described in Supporting Information (Scheme S1).

88

89 2.2.1 Synthesis Procedures

90 The synthesis of zinc aminochlorin (ZnChl-*NH*₂), zinc methylaminochlorin (ZnChl-*NHMe*) 91 and zinc dimethylaminochlorin (ZnChl-*NMe*₂) are described below.

92

93 2.2.2 Methyl 13²-demethoxycarbonylpheophorbide *a* (Pheo *a*) (3)

94 Pheo *a* was prepared from Chl *a*, which was isolated from *Spirulina Maxima* algae, according

95 to known literature procedures 39, 40]. The obtained product was characterized by NMR,

96 UV/Vis and mass spectroscopy [26]. UV (CH₂Cl₂) λ_{max} : (Wavelengths and relative 97 intensities), 666 nm (0.36), 610 nm (0.06), 538 nm (0.063), 508 nm (0.07), 412 nm (0.79),

- 98 ¹H NMR (400 MHz, CDCI₃) δ ppm: 9.57 (s, 1H, CH-5), 9.45 (s, 1H, CH-10), 8.64 (s, 1H,
- 99 CH-20), 7.99 (q, 1H, J = 6.4 Hz, 3^{1}), 6.25, 6.19 (q, 1H + 1H, J = 16.8 Hz, 3^{2}), 5.25, 5.14 (d, 1H
- 100 + 1H, J = 20 Hz, 13^2 -CH₂), 4.51 (dq, 1H, J = 2 Hz, CH-18), 4.32 (dt, 1H, J = 8.4 Hz, CH-17),
- 101 3.67 (s, 3H, COOCH₃), 3.61 (s, 3H, CH₃-12¹), 3.55 (q, 2H, J= 8 Hz, CH₂-8¹), 3.41 (s, 3H, 2¹-
- 102 CH₃), 3.23 (s, 3H, CH₃- 7^{1}), 2.58-2.55, 2.34-2.27 (m, 2H + 2H, 17-CH₂CH₂), 1.83 (d, J= 7.2
- 103 Hz, CH₃-18¹), 1.67 (t, J= 7.6 Hz, CH₃-8²), -0.37, -2.07 (br,1H + 1H, NH). MS (ESI): m/z
- 104 calcd for $C_{34}H_{36}N_4O_3 [M+H]^+$: 548.
- 105

106 **2.2.3 Methyl 3-devinyl-3-formyl-13²-demethoxycarbonylpheophorbide** *a* (Methyl

107 **pyropheophorbide** *d*) (4)

108 Methyl pyropheophorbide d was prepared according to the reported procedures [41, 42]. The 109 final product was obtained by colum chromatography on silica gel (15% acetone-CCl₄) [26]. 110 m.p. 174-176 °C. UV (CH₂Cl₂) λ_{max}: 695 (0.52), 634 (0.052), 551 (0.092), 519 (0.077), 425 111 (0.638), 386 (0.567). ¹H NMR (400 MHz, CDCI₃) δ ppm: 11.51 (s, 1H, CHO), 10.30 (s, 1H, CH-5), 9.63 (s, 1H, CH-10), 8.89 (s, 1H, CH-20), 5.36, 5.16 (d, 1H + 1H, J= 20 Hz, 13²-CH₂), 112 113 4.59 (dq, 1H, J= 2 Hz, CH-18), 4.40 (dt, 1H, J= 8.4 Hz, CH-17), 3.72 (q, 2H, J= 8 Hz, CH₂-114 8¹), 3.75 (s, 3H, CH₃-2¹), 3.69 (s, 3H, CH₃-12¹), 3.62 (s, 3H, COOCH₃), 3.29 (s, 3H, CH₃-7¹), 115 2.78-2.70, 2.62-2.56, 2.36-2.26 (m, 1H + 1H + 2H, 17-CH₂CH₂), 1.86 (d, J= 7.2 Hz, CH₃-116 18^{1}), 1.69 (t, J= 7.6 Hz, CH₃-8²), -0.37, -2.07 (br,1H + 1H, NH). MS (EI): m/z calcd for 117 $C_{33}H_{34}N_4O_4[M+H]^+:551.$

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119 2.2.4 Methyl 3-devinyl-3-(methylamino)methyl-13²-demethoxycarbonylpheophorbide *a*

120 (5) (Chl-*NHMe*)

121 Metal-free aminochlorin was prepared according to the reported procedures [37]. Final 122 product was obtained with recrystallization from dichloromethane-hexane. m.p. 231-233 °C. 123 UV (CH₂C1₂) λ_{max} : 659 (0.63), 603 (0.087), 535 (0.092), 504 (0.1), 408 (1.39); ¹H NMR (400 124 MHz, CDCI₃) δ ppm: 9.36 (s, 1H, 10-H), 9.17 (s, 1H, 5-H), 8.56 (s, 1H, 20-H), 5.17, 4.99 (d, 125 1H + 1H, *J*= 20 Hz, 13²-CH₂), 4.72 (s, 2H, 3-CH2), 4.44 (dq, 1H, *J*= 1.6 Hz, 18-H), 4.24 (dt, 126 1H, *J*= 9.2 Hz, 17-H), 3.61 (q, 2H, *J*= 8 Hz, 8-CH₂), 3.59 (s, 3H, 12-CH₃), 3.48 (s, 3H, 127 COOCH₃), 3.3 (s, 3H, 2-CH₃), 3.2 (s, 3H, 7-CH₃), 2.72 (s, 3H, NHCH₃), 2.60-2.47, 2.24-2.10

128 $(m, 2H + 2H, 17-CH_2CH_2)$, 1.78 (d, 3H, J=7.2 Hz, 18-CH₃), 1.63 (t, 3H, J=7.6 Hz, 8-129 CH_2CH_3 , -0.09, -2.04 (br,1H + 1H, NH). MS (ESI): m/z calcd for $C_{34}H_{39}N_5O_3$ [M+H]⁺: 565. 130 131 2.2.5 Methyl 3-devinyl-3-(methylamino)methyl-13²-demethoxycarbonylpheophorbide-a 132 zinc complex (6) (ZnChl-NHMe) 133 Standard zinc-metallation of chlorins was carried out according to the reported procedures [134 28, 40]. Final zinc complex was obtained with the separation on iChroprep RP-18 (25-40 µm) 135 column (methanol/water/pyridine, 80:15:5, as an eluent) (75% yield). ¹H NMR (400 MHz, 136 CDCI₃ + 1%C₅D₅N) δ ppm: 9.48 (s, 1H, 10-H), 8.43 (s, 1H, 5-H), 8.22 (s, 1H, 20-H), 5.12, 137 4.99 (d, 1H + 1H, J= 20 Hz, 13²-CH₂), 4.58 (br, 2H, 3¹-CH₂), 4.32 (dq, 1H, J= 2,7 Hz, 18-H), 138 4.11 (dt, 1H, J= 8 Hz, 17-H), 3.67 (q, 2H, J= 8 Hz, 8-CH₂), 3.60 (s, 3H, 12-CH₃), 3.48 (s, 3H, 139 COOCH₃), 3.16 (s, 3H, 7-CH₃), 3.15 (s, 3H, 2-CH₃), 2.46 (br, 3H, NHCH₃), 2.52-2.48, 2.35-140 2.26, 2.22-2.13, 1.93-1.89 (m, 1H + 1H + 1H + 1H, $17-CH_2CH_2$), 1.64 (d, 3H, J= 7 Hz, 18-141 CH₃), 1.61 (t, 3H, J= 7.6 Hz, 8-CH₂CH₃). MS (ESI): m/z calcd for C₃₄H₃₇N₅O₃Zn [M+H]⁺: 142 629. 143 2.2.6 Methyl 3-devinyl-3-aminomethyl- 13^2 -demethoxycarbonylpheophorbide-a zinc 144 complex (6) (ZnChl-NH₂) 145 ¹H NMR (400 MHz, CDCI₃ + $1\%C_5D_5N$) δ ppm: 9.45 (s, 1H, 10-H), 8.48 (s, 1H, 5-H), 8.32 146 (s, 1H, 20-H), 5.14, 5.01 (d, 1H + 1H, J= 20 Hz, 13²-CH₂), 4.81 (br, 2H, 3¹-CH₂), 4.34 (dq, 147 1H, J= 2,7 Hz, 18-H), 4.15 (dt, 1H, J= 8 Hz, 17-H), 3.71 (q, 2H, J= 8 Hz, 8-CH₂), 3.61 (s, 3H, 148 12-CH₃), 3.51 (s, 3H, COOCH₃), 3.20 (s, 3H, 7-CH₃), 3.16 (s, 3H, 2-CH₃), 2.54-2.49, 2.37-149 2.28, 2.23-2.14, 1.94-1.89 (m, 1H + 1H + 1H + 1H, 17-CH₂CH₂), 1.66 (d, 3H, J= 7 Hz, 18-150 CH₃), 1.62 (t, 3H, J=7.6 Hz, 8-CH₂CH₃). MS (ESI): m/z calcd for C₃₃H₃₅N₅O₃Zn [M+H]⁺: 151 616. 2.2.7 Methyl 3-devinyl-3-(dimethylamino)methyl-13²-demethoxycarbonylpheophorbide-152 153 *a* zinc complex (6) (ZnChl-*NMe*₂) 154 ¹H NMR (400 MHz, CDCI₃ + $1\%C_5D_5N$) δ ppm: 9.37 (s, 1H, 10-H), 8.42 (s, 1H, 5-H), 8.20 (s, 1H, 20-H), 5.10, 4.96 (d, 1H + 1H, J= 20 Hz, 13^2 -CH₂), 4.48 (br, 2H, 3^1 -CH₂), 4.29 (dq, 155 156 1H, J= 2,7 Hz, 18-H), 4.06 (dt, 1H, J= 8 Hz, 17-H), 3.63 (q, 2H, J= 8 Hz, 8-CH₂), 3.57 (s, 3H, 157 12-CH₃), 3.45 (s, 3H, COOCH₃), 3.15 (s, 3H, 7-CH₃), 3.13 (s, 3H, 2-CH₃), 2.35 (br, 3H, 158 $NH(CH_3)_2$, 2.50-2.46, 2.32-2.24, 2.20-2.11, 1.91-1.86 (m, 1H + 1H + 1H + 1H, 17-CH₂CH₂), 159 1.63 (d, 3H, J=7 Hz, 18-CH₃), 1.58 (t, 3H, J=7.6 Hz, 8-CH₂CH₃). MS (ESI): m/z calcd for

160 $C_{35}H_{39}N_5O_3Zn [M+H]^+: 644.$

161 2.3 Fabrication of Dye Sensitized Solar Cell

162 FTO glass (TEC-15, 2.2 mm thickness, Solaronix) is used for the transparent conducting 163 electrodes. The glass substrates are first cleaned in the ultrasonic bath using helmanex 164 detergent solution, then water, acetone and ethanol (each step is 20 min. long). We have used 165 10 (transparent) + 4 (scattering) μm TiO₂ layers in this study. This term is added to 166 experimental part. The TiO₂ coated FTO glasses are immersed into the 0.5 mM dye solutions 167 of chlorins. Active area is 0.16 cm^2 . Counter electrodes are prepared by coating with a drop of 168 H₂PtCl₆ solution. The TiO₂ sensitized photoanode and Pt counter electrodes are assembled 169 into a sealed sandwich-type cell by a hot-melt ionomer film (Surlyn). Then electrolyte 170 solution is injected and the hole sealed by using surlyn patch and a cover glass. Electrolyte 171 consists of 0.6 M N-methyl-N-butyl imidazolium iodide (BMII), 0.1 M LiI, 0.05 M I₂, 0.5 M 172 4-tert-butyl pyridine (TBP) in acetonitrile.

173

174 **3. Results and Discussion**

175 Cyclic tetrapyrroles, such as porphyrins, bacteriochlorins, and phthalocyanines are an 176 important group of organic molecules possessing distinguished photophysical and 177 photochemical properties [20-25, 29]. Among them, porphyrins and bacteriochlorins possess 178 some intrinsic properties in photosynthesis including light-harvesting and energy- and electron-transferring processes [29, 32, 33]. Semi-synthetic zinc chlorins (ZnChls) that are 179 180 preprogrammed for self-assembly can easily mimic the intriguing architectural principle of 181 the supramolecular organization of dyes in chlorosomes [27, 29, 33, 34]. According to this 182 model, ZnChl molecules are able to self-organize into rod-shaped supramolecular structures 183 driven by three non-covalent interactions without requiring proteins for structural control; coordination of the 3^1 -oxygen unit to the central atom, hydrogen bonding between the 3^1 -184 185 alcohol to the 13-keto group and π - π stacking between the extended chlorin chromophores 186 yielding a strongly red-shifted J-type absorption band and extremely large exciton diffusion 187 lengths covering up to 200 monomers at room temperature [29, 35]. These supramolecular 188 arrays can function either as energy conductors (exciton transport) or as charge conductors 189 [32-34]. These highly unusual exciton and optical properties, unprecedented by any other 190 organic material known so far, let us expect novel, interesting electronic materials properties. 191 The most significant structural difference of ZnChls used in this work from other well-known 192 zinc chlorins is the presence of amino functional groups in 3¹-position instead of hydroxyl 193 group (Figure 1). Furthermore, these compounds would form as highly robust, single stack

194 rod structures under appropriate conditions (such as in non-polar solvents) probably due to the 195 fact that amino ligands coordinate to the central metal more strongly than oxygen ligands [26, 196 27]. Using such compounds we aim to make DSSC because of the fact that ZnChls can easily 197 bind to TiO₂ surface via its amino groups. Attachment of ZnChl-NMe₂ to the TiO₂ surface 198 will be a significant problem due to the steric hindrance in the presence of the methyl groups 199 attached to nitrogen, and this could be the biggest reason for low cell efficiency compared 200 with those of ZnChl-NH₂ and ZnChl-NHMe. Furthermore, ZnChl-NH₂ exhibit a higher self-201 aggregation features, which limits the injection from dyes to the TiO₂, compared to other two 202 semi-synthetic zinc chlorins used in this study. This could be responsible for lower efficiency 203 of ZnChl-NH₂ compared with those of methyl amino derivative (ZnChl-NHMe). The high 204 efficiency of ZnChl-NHMe could be explained by the fact that the lower self-aggregation 205 features when compared to the $ZnChl-NH_2$, as well as the high attachment capacity on the 206 TiO₂ surface.

207 Three Zinc chlorine dyes are designed for use in dye sensitized solar cells, coded ZnChl- NH_2 , 208 ZnChl-NHMe, ZnChl-NMe₂, with chemical structures depicted in Fig 1. All three dyes show 209 panchromatic absorption bands in Fig. 2. The incident photon to current conversion efficiency 210 of zinc chlorins is shown in Fig. 4. The IPCE for Zinc Chlorin dye, ZnChl-NHMe reached a 211 maxima of 7.5% at 425 nm. These results show that the ZnChl-NHMe sensitized cell revealed 212 a maximum IPCE value, extending the response of photocurrent generation to 700 nm. 213 Photovoltaic performances of dye sensitized solar cells based on Zinc Chlorins are shown and 214 summarized in Fig. 4 and Table 3. Table 3 also shows the adsorbed dye amounts on TiO_2 215 layer. Under the AM 1.5 conditions, ZnChl-NHMe sensitizer gave the best results with the 216 overall conversion efficiency of 0.68% (η), short-circuit photocurrent of 2.67 mA/cm² (J_{sc}), 217 open circuit photovoltage of 414 mV (V_{oc}), fill factor of 0.64 (FF). Photovoltaic performances 218 are determined in the order of $ZnChl-NHMe > ZnChl-NH_2 > ZnChl-NMe_2$ from I-V curves. 219 Lower photovoltaic performance was obtained with ZnChl-NMe2 dye. This results could be 220 explained by the steric hindrance of $-CH_3$ group in the molecular structure of ZnChl-*NMe*₂. It 221 is found that ZnChl-NHMe gives high efficiency in these classes of dye sensitizers. The UV-222 Vis spectra of the three of NH₂ functionalized ZnChl dyes, ZnChl-NH₂, ZnChl-NHMe and 223 ZnChl- NMe_2 , are shown in Fig. 2. All three ZnChl derivatives are soluble in CH₂Cl₂ and THF 224 but the UV-Vis spectra are preferred in the later. The most common Soret band in chlorin and 225 porphyrin type compounds that originate from the electron dipole movement that allows π - π * 226 transition was observed at 428 nm for all three ZnChl derivatives. The Q_{y} bands for the three 227 compounds are observed in the spectral region from 650 to 659 nm (Table 1). A slight blue

shift is observed in all three cases that might be due to the presence of the $-NH_2$, -NHMe and $-NMe_2$ groups which cause to the different self-aggregation features [26]. These UV-Vis images are characteristics for the presence of chlorins and derivative in the solution in monomeric form which is essential to develop the dye-solar cell [36, 38].

The electrochemical study of the three synthetic amino-functionalized ZnChl dyes $(1x10^{-3})$ 232 233 M) is conducted on a platinum working electrode (WE) electrode in dichloromethane system 234 in the presence of 0.1 M tetrabutyl ammonium hexafluorophosphate $TBA(PF_6)$. Figure 3 235 shows the cyclic voltammetry (CV) curves for the ZnChl-NH₂, ZnChl-NHMe and ZnChl-236 NMe_2 in the presence of ferrocene as internal standard. All CV's show the oxidative currents 237 from 0.65 V to 0.85 V (with reference to the ferrocene as internal standard). The 238 corresponding reduction waves are also observed at 0.75 V to 0.58 V. These redox waves 239 with at $E_{1/2} \sim 0.70$ V (vs. Ag/AgCl) are due to the ferrocenium/ferrocene redox couple. For 240 ZnChl- NH_2 , an oxidation wave appears in the potential region from 1.05 V to 1.30 V in the 241 present potential scale. This is attributed to the oxidation of the corresponding dye molecules 242 in the solution (Fig. 3). During the reverse sweep, this current wave is followed by a reduction 243 wave from 1.30 V to 0.09 V. The $E_{1/2}$ for the ZnChl-*NH*₂ sample is observed about 1.07 V. 244 Similarly, the electrochemical data for the zinc amino chlorins with mono- and di- substituted 245 methyl groups; ZnChl-NHMe and ZnChl-NMe₂, under similar condition show the redox 246 behavior in the potential window from 0.09 V to 1.30 V. In case on mono-methyl the zinc 247 amino chlorins derivative, the oxidative peak currents appear prior to that of the dimethyl 248 complex (Fig. 3). The oxidation currents for the simple $ZnChl-NH_2$ and $ZnChl-NMe_2$, under 249 same set-up are very much similar indicating no net effect on the dye. It is also observed that 250 these oxidative currents for the three compounds are followed by the corresponding reduction 251 responses with current peaks at about 1.00 V for ZnChl-NMe2, whereas it is around 110 mV 252 for ZnChl-*NH*₂ and ZnChl-*NHMe*.

253 The CV's for three zinc amino chlorins compounds are extended until 1.75 V in order to get 254 reduction insights of these samples. Reduction peaks appear to be very similar of these three 255 complexes. Electrochemical data were collected in CH₂Cl₂. Potentials are quoted with 256 reference to the internal ferrocene standard. The electrochemical data for zinc amino chlorine 257 complexes are compiled in Table 2. Cyclic voltammogram (Fig. 3) of chlorin dyes shows both 258 reversible oxidation and reduction peaks (Table 2). The lowest unoccupied molecular 259 (LUMO) energy of ZnChl-NHMe, ZnChl-NH₂, ZnChl-NMe₂ are 3.07 eV, 3.05 eV and 3.08 260 eV, respectively. LUMO energies of dyes are clearly higher than the conduction band of TiO₂ 261 (~ 4.2 eV), which suggests an efficient electron transfer from chlorin to TiO_2 electrode.

HOMO energy levels of ZnChl-*NHMe*, ZnChl-*NH*₂, ZnChl-*NMe*₂ are 5.01 eV, 4.99 eV, 4.99 eV, 4.99 eV.

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266

265 4. Conclusion

The dye sensitized solar cells based on ZnChl-*NHMe* exhibits the power conversion efficiency of 0.68%. This result is promising and shows that the addition of vinyl units at 3^{1} position which provide a more effective electronic conjugation could give rise to the higher power conversion efficiency. Considering the fact that chlorin dyes show an impressive performance, these class of sensitizers are very promising candidates in dye sensitized solar cells.

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398 399	Figure Captions
400	Figure 1. Chemical structures of zinc aminochlorin derivatives; zinc aminochlorin (ZnChl-
401	NH2), zinc methylaminochlorin (ZnChl-NHMe) and zinc dimethylaminochlorin (ZnChl-
402	NMe_2).
403	Figure 2. UV-Vis Absorption spectra for zinc chlorin amino- derivatives ZnChl- <i>NH</i> ₂ , ZnChl-
404	<i>NHMe</i> and ZnChl- <i>NMe</i> ₂ , obtained in THF (c: 1.5×10^{-5} M).
405	Figure 3. Cyclic voltammogram of zinc amino-chlorin derivatives.
406	Figure 4. J-V and IPCE spectrum of Dye Sensitized Solar Cells
407 408 409 410 411	Table Captions
412	Table 1. UV-Vis Absorption spectral data for zinc chlorin amino-derivatives ZnChl-NH ₂ ,
413	ZnChl- <i>NHMe</i> and ZnChl- <i>NMe</i> ₂ , measured in THF (c: 1.5×10^{-5} M).
414	Table 2. Electrochemical Properties of the Zinc Chlorin Sensitizers.
415	Table 3. DSSC Performances of Chlorin Dyes.
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463 Figure 2. UV-Vis Absorption spectra for zinc chlorin amino- derivatives ZnChl-*NH*₂, ZnChl-

NHMe and ZnChl-*NMe*₂, obtained in THF (c: 1.5×10^{-5} M).

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Figure 3. Cyclic voltammogram of zinc amino-chlorin derivatives.



Table 1. UV-Vis Absorption spectral data for zinc chlorin amino-derivatives ZnChl-NH₂,

ZnChl-*NHMe* and ZnChl-*NMe*₂, measured in THF (c: 1.5×10^{-5} M).

Dye	$\lambda_{\max} (nm) (\epsilon/10^{+4} \text{ M}^{1} \text{.cm}^{-1})$
ZnChl- <i>NMe</i> ₂	655 (8.53), 609 (1.72), 576 (0.92), 529 (0.32), 426 (10.8), 409 (8.7)
ZnChl-NHMe	656 (7.35), 610 (1.49), 576 (0.80), 529 (0.36), 427 (10.1), 409 (7.83)
ZnChl-NH ₂	657 (5.75), 612 (1.13), 569 (0.46), 523 (0.30), 428 (9.45), 412 (8.35)

Table 2. Electrochemical Properties of the Zinc Chlorin Sensitizers,

Dye	$E_{\rm ox}({\rm V})$	E_{fer}	$E_{ m red}$ (V)	HOMO (eV)	LUMO (eV)
ZnChl-NHMe	0.75	0.50	-1.190	5.01	3.07
ZnChl-NH ₂	0.70	0.50	-1.240	4.99	3.05
ZnChl- <i>NMe</i> ₂	0.72	0.50	-1.190	4.99	3.08

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Table 3. DSSC Performances of Chlorin Dyes.

Dye	$V_{\rm oc}~({\rm mV})$	$J_{\rm sc}$ (mA cm	ff	η(%)	Adsorbed dye $(x10^{-7} mol/cm^2)$	
ZnChl-NHMe	414	2.67	0.64	0.68	3.2	
ZnChl-NH ₂	417	2.42	0.62	0.59	2.9	
ZnChl- <i>NMe</i> ₂	350	0.82	0.52	0.15	1.6	

 $\frac{1}{4}V_{ac}$ is the open-circuit potential, J_{sc} , short curcuit current, ff is the fill factor, and η is the overall efficiency of the cell under standard

conditions.

545 **Highlights**

- 546 • Novel artificial zinc chlorin dyes have been synthesized
- Acceleration 547 • Bio-inspired dyes have been characterized