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A supramolecular assembling of Zinc porphyrin with a π -conjugated oligo(phenylenevinylene) (oPPV) molecular wire for dye sensitized solar cell

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Abstract

A novel π -conjugated oligo(phenylenevinylene) (oPPV) (or **LC**) was prepared, as a new organic dye for dye-sensitized solar cells (DSSC), which contains a cyanoacrylic acid group on one end and a pyridyl group on the other. Solar cells sensitized by **LC** were fabricated, and were found to exhibit a power conversion efficiency (PCE) value of 2.45%. Furthermore, we describe the formation of a supramolecular dyad (**ZnTPP-LC**) via a metal-ligand bond between **LC**, since its pyridyl group allows it to interact with several metal centers, and Zinc-tetraphenyl-porphyrin (**ZnTPP**) onto the photoelectrode's TiO_2 surface of the solar cell. More specifically, **LC** was bound at first onto TiO_2 with its cyanoacrylic acid anchoring group, and then a metal-ligand supramolecular bond was formed, with the addition of a porphyrinic solution, between the nitrogen atom of **LC**'s pyridyl group and the Zinc. **ZnTPP-LC** solar cell was then fabricated resulting in a record PCE value of 5.27% concerning the supramolecular DSSCs. As shown by photovoltaic measurements (J–V curves) and incident photon to current conversion efficiency (IPCE) spectra of the two solar cells, the higher PCE value of the supramolecular one can be attributed to its enhanced photovoltaic parameters, and particularly its enhanced short circuit current (J_{sc}). This J_{sc} improvement is due to **ZnTPP-LC**'s higher light-harvesting efficiency and the larger electron injection of both **ZnTPP** and **LC** into TiO_2 's conduction band (CB) of the corresponding solar cell. These results are in accordance with electrochemical impedance spectra (EIS) of the DSSCs, which revealed longer electron lifetime, higher charge recombination resistance and shorter electron transport time for the solar cell based on **ZnTPP-LC** as compared to the one sensitized by **LC**.

Introduction

In the last decades, solar energy has been demonstrated to be a promising alternative to fossil fuels, and dye-sensitized solar cells (DSSCs) have attracted considerable interest owing to their relatively high power-conversion efficiencies, low production costs, ease of fabrication and modifiable aesthetic features such as vivid colours and high transparency.¹⁻⁸ Nowadays, DSSCs fabricated from environmentally friendly and inexpensive materials appear to be a very promising technology for low-cost and highly efficient solar energy conversion.^{9, 10} A typical device of this type consists of a wide-band-gap semiconductor photoanode (usually TiO_2) sensitized by a molecular dye, a redox electrolyte, and a platinum counter electrode. The sensitizer plays a key role in the operation of these devices because it

is responsible for the absorption of solar radiation, the generation of excited electrons, and their injection into the TiO₂ conduction band (CB). Ru complex photosensitizers such as N3, N719 and black dye exhibit efficiencies higher than 10%, and this is the reason why they have been so widely used.^{11, 12} The performance of DSSCs based on organic dyes have also recently been remarkably improved, as for example the highly efficient performance from a π -conjugated oligo-phenylenevinylene organic dye, which contains a diphenylamine donor group and a cyanoacrylic acid anchoring group.¹³ Furthermore, considerable efforts have been devoted to the construction of efficient sensitizers with typical donor- π -acceptor (D- π -A) “push-pull” structures.^{14, 15} In this respect, porphyrins have demonstrated their potential owing to the strong absorption in a large wavelength range and facile structural modification,¹⁶⁻²⁴ as for example it was reported a PCE value of 13% from a benzothiadiazole functionalized porphyrin.^{25, 26} To the best of our knowledge, this is the first example in the literature where a complex is formed between a chromophore and a molecular wire bearing an anchoring group. The nature of the coordination bond that is formed between the Zinc and the pyridyl group of the molecular wire provides a new supramolecular type architecture, with very promising properties.

Despite all the previous aspects, an intrinsic drawback for typical porphyrin-based dyes still remains their lack of absorption in the IR region, as well as in the region between the Soret and the Q bands, which hampers further improvement of the DSSC efficiencies,^{25, 27-29} and thus examples of porphyrin dyes exhibiting DSSC efficiencies higher than 10% are still very rare.^{25, 27-30} In an effort to further improve the performance of porphyrin based solar cells, multi-porphyrin arrays consisting of covalently linked porphyrin macrocycles or other units, such as Bodipy, linked either through suitable π -conjugated groups or directly, have been investigated as sensitizers.³¹⁻³⁴ There are several reports of covalently linked electron donor-bridge-acceptor (D-B-A) conjugates for numerous applications.³⁵⁻³⁸ However, the synthesis of extended chromophores and covalently linked electron D-B-A systems is challenging and therefore these materials are far from ideal for practical applications.

As it is known, in nature, self-assembly through non-covalent binding motifs,³⁹ such as hydrogen bonding and metal-ligand coordination, plays a dominant role. For example, photosynthetic antenna reaction center pigments use such intermolecular forces to precisely arrange the donor-acceptor entities in a protein matrix, exhibiting a cascade of vectorial energy and electron transfer processes.⁴⁰ Inspired by this revelation, several groups have constructed supramolecular photosynthetic architectures to mimic the photoinduced energy and electron transfer processes, with an ultimate goal of building efficient light-energy-

harvesting devices based on these biomimetic principles.⁴¹⁻⁴⁹ Supramolecular solar cells based on biomimetic principles could serve as an alternative to semiconductor-based ones for renewable energy production, though their efficiencies remain relatively low. The binding motif that has been widely used for the fabrication of supramolecular DSSCs is the versatile metal-ligand bond.⁵⁰⁻⁵⁵ On this aspect, D'Souza and coworkers used four ligands with different pK_a values, which bear from one side a carboxylic group, that enables the functionalization of the TiO_2 surface, and from the other a pyridyl or imidazolyl group that enables it to interact with a metal center via a supramolecular metal-ligand bond.⁵⁶ Thus, it becomes possible to connect an electron donor with an acceptor resulting in a D- π -A type supramolecular system.

Herein we demonstrate the synthesis of a novel π -conjugated oligo(phenylenevinylene) (oPPV) moiety (**LC**), which could be used as a promising organic dye in dye-sensitized solar cells (DSSCs). The DSSC based on **LC** organic dye showed a PCE value of 2.45%. **LC** contains a cyanoacrylic acid as anchoring group, a pyridyl group that allows the axial interaction with a bunch of metallated electron donor dyes and six dodecyloxy groups on its periphery preventing aggregations. In this work, we describe the fabrication of a supramolecular DSSC with **LC**, which acts as a π -Bridge, and Zinc-tetraphenylporphyrin (**ZnTPP**) (Scheme 1), that plays the role of an electron donor, as they form a novel supramolecular dyad onto the TiO_2 surface. More specifically, **LC** was firstly bound on TiO_2 and then the electrode was immersed in a ZnTPP solution in order for Zinc to form a metal-ligand bond with the oPPV's pyridyl group (Scheme 2), leading to the supramolecular dyad **ZnTPP-LC**, structurally similar to the record holder one of the organic dyes,¹³ and then its performance was monitored. The choice of the tetraphenylporphyrin is due to its high chemical activity and capacity to form stable coordination bonded derivatives with pyridyl moieties. Tetraphenylporphyrin metallated with zinc is an excellent donor unit with relatively straightforward synthesis. The main advantage of this approach is the highly effective prevention of aggregations, due to the presence of six dodecyloxy groups and the directionality of the metal-ligand bond. We observed an important improvement on the efficiency of the cell, since a PCE value equal to 5.27% was achieved.

Experimental detail:

Materials and Techniques: Solvents and reagents were purchased from the usual commercial sources and used as received, unless otherwise stated. Also, 4-{(E)-4-[(E)-2,5-bis(dodecyloxy)-4-((E)-2-(pyridin-4-yl)vinyl)styryl]-2,5-bis(dodecyloxy)styryl}-2,5-bis(dodecyloxy)benzaldehyde (**1**) was synthesized from our group.⁵⁰

NMR spectra: NMR spectra were recorded on a Bruker AVANCE III-500 MHz spectrometer using solutions in deuterated solvents by using the solvent peak as the internal standard.

Mass spectra: High-resolution mass spectra (HRMS) were recorded on a Bruker UltrafleXtreme MALDI-TOF/TOF spectrometer.

Photophysical measurements: All UV-vis absorption spectra were measured on a Shimadzu UV-1700 spectrophotometer using 10 mm path-length cuvettes.

Electrochemistry: Both cyclic voltammetry (CV) and square-wave voltammetry (SW) measurements were performed at room temperature by using an AutoLab PGSTAT20 potentiostat. Freshly distilled and deoxygenated THF was used while carrying out CV and SW measurements, with scan rate 100 mV/s, with a solute concentration of 1.0 mM in the presence of tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte. A three-electrode cell setup was used with a saturated calomel (SCE) reference electrode, a platinum working electrode and a platinum wire counter electrode.

Computational Details: Density functional theory (DFT) calculations⁵⁷ were performed using the GAUSSIAN 03 program suite.⁵⁸ Gas phase geometry optimizations were carried with B3LYP^{59, 60} functionals using the LANL2DZ basis set for Zn atoms and the 6-31G(d) basis sets for lighter atoms. The optimized minimum-energy structures were verified by vibrational frequency analysis calculation. Tomasi's Polarizable Continuum Model (PCM)⁶¹ was applied for describing the solvent effect (dichloromethane) with standard dielectric constant $\epsilon = 8.93$. The input geometries and molecular orbitals were modeled using *ChemCraft* software (version 1.6).

DSSC fabrication and characterization: The working and counter electrodes consisting of TiO₂ and thermally platinum films, respectively, were deposited onto F-doped tin oxide (FTO) conducting glass substrates by the same technique as reported earlier.⁶² For the fabrication of the supramolecular DSSC, the prepared TiO₂ substrate (particle size of TiO₂ is 25 nm, thickness of TiO₂ film is 12 μ m) was first immersed in a THF solution of the LC dye (0.20 mM) for 4h, which allowed the dye to anchor onto the TiO₂ surface and then it was washed with ethanol for the removal of the unbound dye. The dye-functionalized surface was then immersed in a CH₂Cl₂ solution of **ZnTPP** (2 mM) in order for the **ZnTPP-LC** dyads to be formed on the TiO₂ surface. Thus, a coordination bond between the pyridyl and Zinc forms the 1:1 complex between the molecular wire and the Zinc porphyrin during the second step, as observed from the dye loading amounts. The sensitized working electrode was assembled with the Pt coated FTO electrode into a sandwich type cell and sealed with the

hot-melt polymer surlyn. To complete the DSSC fabrication, the electrolyte solution containing LiI (0.05 M), I₂ (0.03 M), 1 methyl-3-n-propylimidazolium iodide (0.6 M) and *tert*-butylpyridine (0.5 M in a mixture of acetonitrile and valeronitrile, 85:15 volume ratio) was introduced into the space between the two electrodes through a drilled hole in the platinum coated FTO by vacuum backfilling. The DSSC sensitized by the LC organic dye was also fabricated, under the same conditions. We also measured the dye loading on both DSSCs sensitized by LC and LC-DSSC, and it was found to be 5.31×10^{-8} mol/cm² for the LC sensitized cell and 5.40×10^{-8} mol/cm² for the supramolecular DSSC. It is very clear that the two dye loading values are slightly different, since ZnTPP does not contain any anchoring unit and it only coordinated on the pyridyl end of the wire (LC) and accelerates the electron injection. The active area of both fabricated DSSCs was found to be around 0.25 cm².

The current–voltage (J–V) characteristics of the DSSCs under illumination were measured using a Keithley source meter and a solar simulator coupled with a 150 W xenon lamp and an AM optical filter to give an illumination intensity of 100 mW cm⁻² on the surface of the cells. The electrochemical impedance spectra (EIS) in the dark were recorded by using an electrochemical workstation (Auto lab PGSTAT) with a frequency response analyzer. The frequency range was from 10 mHz to 100 KHz, and an ac potential of 10 mV was used. A dc bias equivalent to the open-circuit voltage of the DSSC was applied. The impedance data were analyzed by the Z-View software with an appropriate equivalent circuit. The incident photon to current conversion efficiency (IPCE) was measured as a function of wavelength with a xenon lamp, a monochromator, and a Keithley source meter at 100 mWcm⁻². The photocurrent was measured under short circuit conditions. A standard silicon photodiode performed the intensity calibration for the IPCE measurement.

Synthesis of (Z)-3-(4-((E)-2,5-bis(dodecyloxy)-4-((E)-2-(dodecyloxy)-4-((E)-2-(pyridin-4-yl)vinyl)-5-((undecyloxy)methyl)styryl)styryl)-2,5-bis(dodecyloxy)phenyl)-2-cyanoacrylic acid (LC): An acetic acid (CH₃COOH) (5 mL) and tetrahydrofuran (THF) (2 mL) mixed solution of (1) (25 mg, 0,0165 mmol) and 2-cyanoacetic acid (11,21 mg, 0,1317 mmol) was stirred at 115°C for 24h under nitrogen and in the presence of piperidine (4μL). The resulting solution was evaporated to dryness under vacuum. The crude residue was purified by column chromatography over silica gel using CH₂Cl₂/MeOH (94:6 v/v) as an eluent to obtain the (LC) as a red solid (Yield 20 mg, 76,47%).

¹H NMR (500 MHz, CDCl₃): δ 0.84-0.86 (m, 18H), 1.24-1.38 (m, 96H), 1.52-1.54 (m, 12H), 1.85-1.88 (m, 12H), 4.03-4.08 (m, 12H), 7.04-7.07 (d, J=16,5Hz, 1H), 7.09

(s, 1H), 7.13-7.16 (m, 3H), 7.23 (s, 1H), 7.43-7.46 (m, 2H), 7.48-7.49 (m, 2H), 7.55-7.59 (d, $J=16.5\text{ Hz}$, 1H), 7.68-7.71 (d, $J=16.5\text{ Hz}$, 1H), 7.94 (s, 1H), 8.57 (s.b., 2H), 8.68 (s, 1H). ^{13}C NMR (500 MHz, CDCl_3): δ 14.06, 21.13, 22.66, 29.35, 29.37, 29.64, 29.67, 29.69, 29.73, 30.08, 30.26, 31.90, 34.19, 49.23, 49.40, 49.57, 125.47, 128.23, 135.79, 143.73, 145.06, 150.44, 150.95, 151.12, 151.36, 151.39, 151.69, 153.30. UV-vis: λ_{abs} (CH_2Cl_2) (ϵ , $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 340,0 (15.230,69), 471,0 (38.361,53). HRMS (ES^+) (MALDI-TOF). Calcd for $\text{C}_{105}\text{H}_{168}\text{N}_2\text{O}_8$: m/z 1585,28 ($[\text{M}]^+$). Found: m/z 1585,65. Anal. Calcd for $\text{C}_{105}\text{H}_{168}\text{N}_2\text{O}_8$: C, 79.49; H, 10.67; N, 1.77; O, 8.07. Found: C, 76.36; H, 9.38; N, 4.34; O, 9.92.

Results and discussion

Synthesis and Characterization: The synthetic route, which was followed for the preparation of oPPV LC, is shown in Scheme 3. More specifically, LC was synthesized according to the Knoevenagel condensation methodology,⁶³ via the reaction of 4-((E)-4-((E)-2,5-bis(dodecyloxy)-4-((E)-2-(pyridin-4-yl)vinyl)styryl)-2,5-bis(dodecyloxy) styryl)-2,5-bis(dodecyloxy)benzaldehyde (1) [57] and 2-cyanoacetic acid in a mixture of acetic acid (CH_3COOH)/tetrahydrofuran (THF) under refluxing conditions and in the presence of a catalytic amount of piperidine, followed by chromatographic purification. Compound LC was designed as an axially symmetrical ligand, capable of providing direct electronic communication between the cyanoacrylic ($-\text{CNCOOH}$) anchoring group and the pyridyl N-atom. Furthermore, upon complexation with **ZnTPP**, the electronic communication could expand between $-\text{CNCOOH}$ group and the metal center of **ZnTPP**. **ZnTPP** was prepared by following a previously reported procedure.⁶⁴ The dyad **ZnTPP-LC** was formed with non-covalent interactions throughout the fabrication of the DSSC devices.

The purity of dye LC was confirmed by ^1H and ^{13}C NMR (Fig. S1a-S1b and S2a-S2b), UV-vis absorption, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum (Fig. S3) and elemental analysis. Its ^1H NMR spectrum confirms the *E* configuration of the double bonds by a coupling constant of exactly 16.5 Hz for the AB system that corresponds to the vinylic protons of the oPPV moiety. Moreover, MALDI-TOF mass spectrum showed the expected molecular ion peak: m/z 1585,65 (LC). Due to the presence of the dodecyloxy groups, both the LC oPPV and **ZnTPP-LC** dyad are very soluble in a variety of organic solvents with different polarities such as CH_2Cl_2 , CHCl_3 , THF and toluene.

The terminal cyanoacrylic group enables oPPV's coordination to a variety of Lewis acids sites; hence, the **LC** compound has the prospective to anchor onto the TiO₂ surface of the DSSC photoelectrode. In addition, the presence of six long alkoxy (-OCH₂(CH₂)₁₀CH₃) chains at the periphery of both the **LC** oPPV and the **ZnTPP-LC** dyad prevents the formation of porphyrin aggregates on the TiO₂ surface, which is a major reason for the low performance of porphyrin-based DSSCs.

Photophysical properties: The optical absorption spectrum of the **ZnTPP-LC** dyad in CH₂Cl₂ solution is shown in Fig. 1a. The optical absorption spectra of the constituent chromophores (**ZnTPP** and **LC**) are also shown in Fig. 1a, for comparison reasons. The absorption spectrum of **ZnTPP-LC**, which shows the characteristic peaks of both **ZnTPP** and **LC** moieties, indicates negligible electronic interactions between those two units in the ground state of the supramolecular dyad. Upon coordination of **LC** on **ZnTPP**, we observed a slight increase in all the molar extinction coefficients concerning the four peaks shown in **ZnTPP-LC** dyad's spectrum. All the optical data that resulted from the three UV-vis spectra, which were described above, are listed in Table 1.

The absorption spectra of **LC** and **ZnTPP-LC** dyad adsorbed onto the TiO₂ film (Fig. 1b). Those two spectra are similar to the absorption spectra of **LC** and **ZnTPP-LC** in solution, but exhibit a small red shift and broadening, reflecting slight aggregation.

Electrochemical studies: In order for a complex to be considered an effective sensitizer in a DSSC, two processes should be considered: efficient dye regeneration and electron injection. Those two processes require suitably aligned lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels. Firstly, concerning the first process, the HOMO energy level of the dye should be lower than the corresponding redox potential of the electrolyte redox couple, while, concerning the second process, its LUMO energy level should be higher than the TiO₂ CB edge.^{7, 65}

The HOMO and LUMO energy levels of **LC** were determined by both square-wave voltammetry measurements (Fig. S4) and cyclic voltammetry measurements (Fig. S4). Also, the HOMO and LUMO energy levels of the **ZnTPP** are known from the bibliography.⁶⁶ So, the peak potentials for both those compounds are summarized in Table 2. The HOMO energy levels were found to be 1.09 and 0.82 V vs NHE, respectively, and they are lower than the oxidation potential for the I₃⁻/I⁻ redox couple. Additionally, their LUMO energy levels were found to be -1.49 and -1.31 V vs NHE, respectively, which are located higher than the TiO₂ CB (-0.5 V vs NHE). Therefore, electron injection from the excited states of both dyes into the TiO₂ CB edge and regeneration of the photooxidized dyes by transferring electrons from

I_3^- of the electrolyte, are favored. Finally, it was not able for us to determine the HOMO and LUMO energy levels of the **ZnTPP-LC** dyad, via neither cyclic nor square-wave voltammetry, due to the weakness of this metal-ligand bond. Nevertheless, since the HOMO and LUMO energy levels of the constituent chromophores were found to fulfill the DSSC requirements, we can assume that their dyad should also be a good DSSC dye-candidate.

DFT Calculations: Theoretical calculations within the framework of Density Functional theory were employed in order to further investigate the electronic properties of the final compound **ZnTPP-LC**. The total number of atoms of **ZnTPP-LC** is too large for DFT calculations in our computer cluster, therefore we simplified the structure by replacing the long dodecyloxy groups of the phenyl substituents of the **LC** with methoxy groups, which should not influence their HOMO and LUMO energy levels.³⁶ The gas-phase optimized coordinates are given in the Supporting Information in Table S1 and the gas-phase optimized structure is depicted in Fig. 2. In addition, a different view perspective of the gas-phase geometry structure of **ZnTPP-LC** is presented in Supporting Information (Fig. S5). We observe that the phenyl groups of the porphyrin ring are almost perpendicular to the phenyl substituents of the **LC**. Moreover the phenyl groups of the **LC** adopt a co-planar orientation to each other. For the optimized structure of **ZnTPP-LC** the corresponding HOMO and LUMO energies, the HOMO–LUMO gap and the dipole moment are listed in Table 3. The HOMO-LUMO gap was calculated in dichloromethane solution and was found to be 2.12 eV. The electronic density distribution and the corresponding energies of the frontier molecular orbitals (FMOs) are depicted in Fig. 3. In two of the highest molecular orbitals (HOMO and HOMO-2) the electron density is spread only on the central of the porphyrin unit. In case of the HOMO-1 though, the electron density is mainly located on the second and third phenyl substituents of the **LC**, with some additional distribution on the first and fourth phenyl group. Regarding the lowest molecular orbitals we observe that LUMO and LUMO+1 are entirely localized on the bridging phenyl groups and on the cyanoacrylic acid group, unlike the LUMO+2 that is spread over the porphyrin unit. The majority of the above mentioned distributions, namely HOMO, HOMO-2, LUMO and LUMO+1 indicate that intramolecular electron transfer is favorable. Hence, **ZnTPP-LC** could be described as a “push-pull” D- π -A (D: donor, A: acceptor,) compound that is a promising candidate for DSSCs applications. The phenyl substituents of the **LC** constitute the π -conjugated system that assist the electron transfer from the zinc porphyrin (donor) to the terminating cyanoacrylic group (acceptor). The cyanoacrylic is the anchoring group of the **ZnTPP-LC** that promotes the electron injection into the conduction band of the TiO₂. Finally, a collection of the corresponding

HOMO and LUMO energies as well as the HOMO-LUMO gap and the dipole moment are listed in Table 3.

Photovoltaic properties: The current-voltage characteristics of the DSSC based on **ZnTPP-LC** are shown in Fig. 4a. The J-V characteristics of The DSSC based on **LC** are also shown in Fig. 4a. The photovoltaic parameters of these DSSCs are summarized in Table 4. The DSSC sensitized by the **ZnTPP-LC** dyad showed a much higher J_{sc} value (11.54 mA/cm^2) and a higher V_{oc} value (0.66V) than those displayed by the **LC** based DSSC. Consequently, the DSSC based on the **ZnTPP-LC** dyad showed a power conversion efficiency (PCE) of 5.27%, which is higher than the PCE value of the **LC**, based DSSC (2.45 % with $J_{sc} = 7.55 \text{ mA/cm}^2$, $V_{oc} = 0.56 \text{ V}$ and $FF = 0.58$). The higher PCE of the cell based on our dyad can be attributed to its better light harvesting efficiency (LHE) over the wider wavelength region. The higher J_{sc} may also be related to the fact that upon photosensitization the dyad can undergo two step vectorial electron transfer to produce long-lived charge separated states in which electrons (in TiO_2) and holes (in **ZnTPP**) are further separated [75-76], whereas the charge recombination could be much faster in the cell sensitized by our novel organic dye due to the closer proximity of electrons and holes in the charge separated states.

The higher J_{sc} of the DSSC sensitized by **ZnTPP-LC** dye is one of the major reasons for its higher PCE value. Since the J_{sc} of the DSSC depends strongly on the incident photon to current efficiency (IPCE) response, the difference in the values of J_{sc} of these DSSCs can be reflected in the IPCE spectra (Fig. 4b). The IPCE spectra of the DSSC sensitized by the **ZnTPP-LC** dyad are broader as compared to DSSC based on the **LC** dye. The photocurrent generated in the 400-430 nm region is caused by the excitation of **ZnTPP** (Soret band), whereas, excitation of **LC** triggers the current generation in the 430-530 nm region, where **LC** exhibits strong absorption (Fig. 1a). In addition, excitation of both **ZnTPP** and **LC** contributes to the photocurrent in 530-650 nm region (*Q* bands of **ZnTPP**). The IPCE value of the DSSC sensitized by **ZnTPP-LC** dye reaches a peak at 35 and 40 % at 422 nm and 486 nm, respectively, i.e. Soret band of **ZnTPP** and absorption peak of **LC**. In contrast, the DSSC sensitized by dye produces photocurrent only at wavelengths where **LC** absorbs light and its IPCE is lower compared to that of the **ZnTPP-LC** based cell. The IPCE spectra of the DSSCs closely resemble the absorption spectra of the **LC** or **ZnTPP-LC** sensitized, in each case, TiO_2 photoelectrode. It can be seen in Fig. 4b, that the excitation of the cell at the wavelengths where the lower energy *Q*-bands absorb, also produces the current, indicating that it is also possible for the photoinduced charge transfer to be initiated that way as well.

Furthermore, the DSSC based on the **ZnTPP-LC** complex showed broader IPCE spectrum, which also indicates the formation of **ZnTPP** aggregations was successfully prevented due to the presence of the **LC** moieties, where each one bears six dodecyloxy chains on their periphery. The values of J_{sc} estimated from the integration of the IPCE spectra were found to be 7.43 mA/cm² and 11.44 mA/cm², for the **LC** and **ZnTPP-LC** based solar cells respectively, which are consistent with the values estimated from J-V characteristics (Table 4). The increase in the J_{sc} value in the case of the **ZnTPP-LC** complex can also be attributed to its higher dye loading onto the TiO₂ surface.

Another parameter that plays an important role for the higher PCE value of the supramolecular DSSC compared to the organic solar cell is the open circuit voltage (V_{oc}), which shows an improved value for the first cell. In general, the V_{oc} of a DSSC depends on the difference between the quasi Fermi level of TiO₂ and the redox potential of the electrolyte (E_{redox}) and is expressed by the followed equation:

$$V_{oc} = \frac{E_{CB}}{q} + \frac{kT}{q} \ln\left(\frac{n}{N_{CB}}\right) - \frac{E_{redox}}{q}$$

Where E_{CB} is the TiO₂ conduction band edge, q is the electronic charge, k is the Boltzmann constant, T is the absolute temperature, n is the concentration of electrons in TiO₂ and N_{CB} is the effective density of states. Since, in both DSSCs, we have used the same electrolytic pair, therefore, the difference in V_{oc} depends only on the E_{CB} and electron concentration in TiO₂. Since Both **ZnTPP** and **LC** in the DSSC based on the **ZnTPP-LC** complex, are able to inject electrons from their excited state into TiO₂, the electron concentration obviously becomes larger in this DSSC. Moreover, due to the anchoring group of **LC**, we can notice that in the **ZnTPP-LC** complex, the charge recombination may be suppressed in the TiO₂/dye/electrolyte interface, and also that this group enhances the electron lifetime, which leads to higher V_{oc} values.

Additionally, the dark current gives information about the recombination of the injected electrons with the I_3^- form of the electrolyte in a DSSC. The J-V characteristics under darkness of both DSSCs are shown in Fig. 5 and reveal that dark current is lower for the DSSC sensitized by **ZnTPP-LC** as compared to the other one, indicating the suppression of the charge recombination rate.

The electrochemical impedance spectroscopy (EIS) has been a very powerful tool in understanding of all interfacial processes in DSSCs.^{67, 68} To understand the relationship between the photovoltaic response and the charge transfer processes in the DSSCs, we have

recorded the EI spectra of the DSSCs in dark conditions, applying an external dc biasing equivalent to open circuit voltage of the DSSC. The typical Nyquist plots of EIS of the two DSSCs are shown in Fig. 6a. In general, the Nyquist plots of the EI spectra comprise three arcs that are associated with the charge transfer at the counter electrode /electrolyte interface (high frequency region), the electron transfer kinetics at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface (middle frequency region), and the Nernstian diffusion process of I^-/I_3^- in the electrolyte (low frequency region).^{69, 70} Since an identical counter electrode was used for both DSSCs, the arc observed in the high frequency region is identical and therefore ignored. So main emphasis is given to the arc located in the middle frequency region. The larger semicircle for the **ZnTPP-LC** complex as compared to the **LC** device suggests that the charge recombination resistance (R_{rec}) is higher for the supramolecular dyad as compared the organic dye. This is consistent with the lower dark current value for the DSSC sensitized by **ZnTPP-LC** as well. This also indicates that the back electron recombination with the I_3^- form of the electrolyte is suppressed in the DSSC based on the **ZnTPP-LC** complex.

The Bode phase plots of the DSSCs are shown in Fig. 6b. The peak frequency values (f_{max}) in the middle frequency region represent the electron transfer processes at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface, and were found to be 7.12 Hz and 4.54 Hz, for DSSCs based on **LC** and **ZnTPP-LC** dyes respectively. As it is known by the literature, f_{max} is associated with the electron lifetime (τ_e) according to the relation,⁷¹ i.e. $\tau_e = 1/2\pi f_{\text{max}}$. The values of τ_e for the DSSCs based on **LC** and **ZnTPP-LC** are 22 ms and 36 ms, respectively. The lower value of τ_e for the **ZnTPP-LC** based DSSC as compared to the **LC** based one, indicates a reduced rate of electron recombination. The higher value of R_{rec} and the lower value of τ_e for the solar cell based on **ZnTPP-LC**, result in an improved overall PCE value for the cell. Moreover, the adsorption of the **LC** moiety anchored onto the TiO_2 surface, in the supramolecular DSSC, forms an insulating layer that effectively prevents back electron transfer from the semiconductor to the I_3^- form of the electrolyte leading to higher V_{oc} and J_{sc} values, resulting to an overall enhancement in the cell's efficiency.

The Nyquist plots of EIS under illumination also give important information about the charge transport at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface. We have measured the EIS under illumination of the DSSCs at a forward bias equivalent to the open circuit voltage of each corresponding DSSC. From their Nyquist plots, the corresponding electron charge transfer resistance values (R_{tr}) were estimated and are compiled in Table 5. The R_{tr} value of the cell

sensitized by **ZnTPP-LC** is lower than that for the other DSSC. Both R_{tr} and R_{rec} values of a DSSC are related to the τ_e and electron transport time τ_d (which is a measure of average time taken by the injected electron to FTO electrode) according to the following relation⁷² $\tau_d/\tau_e = R_{tr}/R_{rec}$.

The values of R_{rec} , R_{tr} , τ_e and τ_d are displayed in Table 5. The τ_d value is lower for DSSC based on our **ZnTPP-LC** supramolecular dyad than the other one. This fact indicates that a faster transport of the injected electrons towards FTO electrode takes place. The faster τ_d value is associated with its higher J_{sc} value and indicates that the electrons are collected onto FTO at a faster rate.

In addition, the J_{sc} value of the supramolecular DSSC also depends on its charge collection efficiency η_{cc} , which is given by the following equation: $\eta_{cc} = (1 + \tau_d/\tau_e)^{-1}$.⁷³ The higher value of η_{cc} for the DSSC sensitized by the **ZnTPP-LC** complex can ultimately be the reason for such an improved PCE value.

Conclusions

In this work, we have synthesized a novel organic dye (**LC**), which is a π -conjugated oPPV moiety that contains a cyanoacrylic acid and a pyridyl group, as a promising sensitizer for DSSCs. The photophysical and electrochemical measurements of **LC** reveal that it has suitable energy levels for efficient electron injection and regeneration processes, when used as a sensitizer for DSSCs. We also demonstrated the formation of a supramolecular dyad (**ZnTPP-LC**) via a metal-ligand bond, between the nitrogen atom of **LC**'s pyridyl group and **ZnTPP**'s metal center. Theoretical calculations revealed that there is negligible electronic interaction between the two constituent units (**LC** and **ZnTPP**) in the ground state of our supramolecular dyad and also the dyad possesses frontier orbital energy levels which are suitable for use as sensitizers in DSSCs. The organic solar cell based on **LC**, as well as the supramolecular DSSC based on **ZnTPP-LC**, were both fabricated and reached PCE values of 2.45 and 5.27% respectively. As demonstrated by the J–V curves, the IPCE and EI spectra of the two DSSCs, the higher PCE value of the supramolecular one can be attributed to its enhanced short circuit current (J_{sc}) under illumination, its longer electron lifetime (τ_e) and more effective charge recombination resistance between the injected electrons and the electrolyte.

Table 1 Summary of spectroscopic data for **LC**, **ZnTPP** and **ZnTPP-LC**.

Compound	Absorption $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$) in solution ^a
LC	471 (38.4)
ZnTPP	421 (478.2), 556 (3.32), 596 (2.84)
ZnTPP-LC	421 (478.4), 471 (67.9), 556 (4.32), 596 (2.94)

^a Measured in CH_2Cl_2 at 298 K.

Table 2 Oxidation and Reduction Potentials of dyes **LC** and **ZnTPP**.

Compound	EOx 2 (V vs NHE)	EOx 1 (V vs NHE)	ERed 1 (V vs NHE)	ERed 2 (V vs NHE)
ZnTPP	1.13	0.82	-1.31	-1.82 ^a
LC	1.52 ^a	1.09 ^a	-1.49 ^a	-1.55 ^a

^a Peak potential of an irreversible wave.

Table 3 DFT calculated properties of **ZnTPP-LC**: HOMO and LUMO energies, HOMO-LUMO gap and dipole moment (μ).

Compound	HOMO (eV)	LUMO (eV)	HL (eV)	$\mu(\text{D})$
ZnTPP-LC	-4.807	-2.689	2.12	5.48

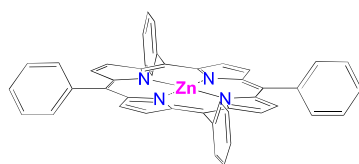
Table 4 Photovoltaic parameters of DSSCs sensitized with **ZnTPP**, **LC**, **ZnTPP-LC** dyes.

Compound	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE
LC	7.55	0.56	0.58	2.45
ZnTPP-LC	11.58	0.66	0.69	5.27

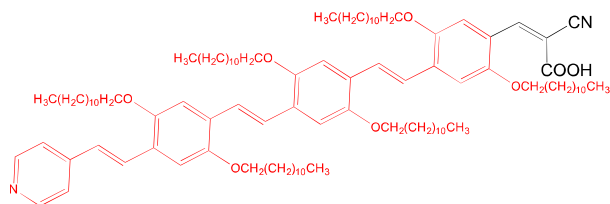
Table 5 EIS parameter and charge collection efficiencies of DSSCs based on **LC** and **ZnTPP-LC** dyes.

Compound	$R_{\text{rec}} (\Omega)$	$R_{\text{tr}} \Omega$	τ_e (ms)	τ_d (ms)	η_{cc}
LC	45	34	22	16.22	0.57

ZnTPP-LC	61	21	35	12.05	0.74
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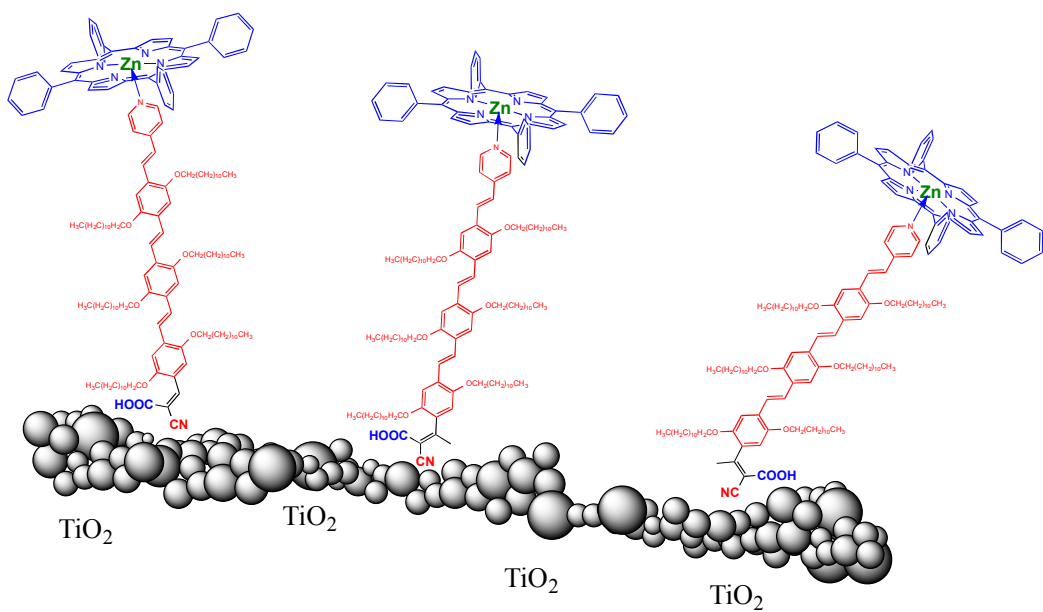


ZnTPP

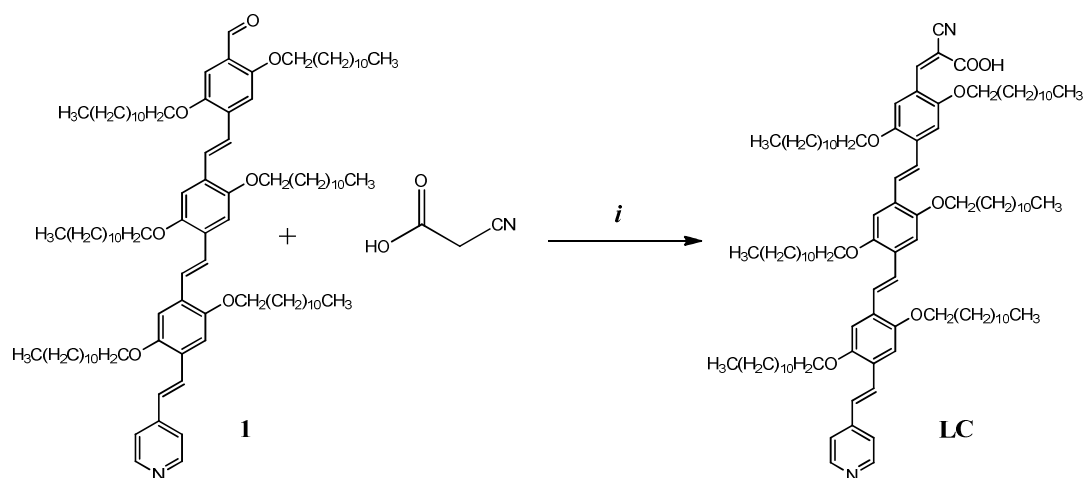


LC

Scheme 1



Scheme 2



Scheme 3 *i*: acetic acid, THF, piperidine, 110°C, N₂, 24 h.

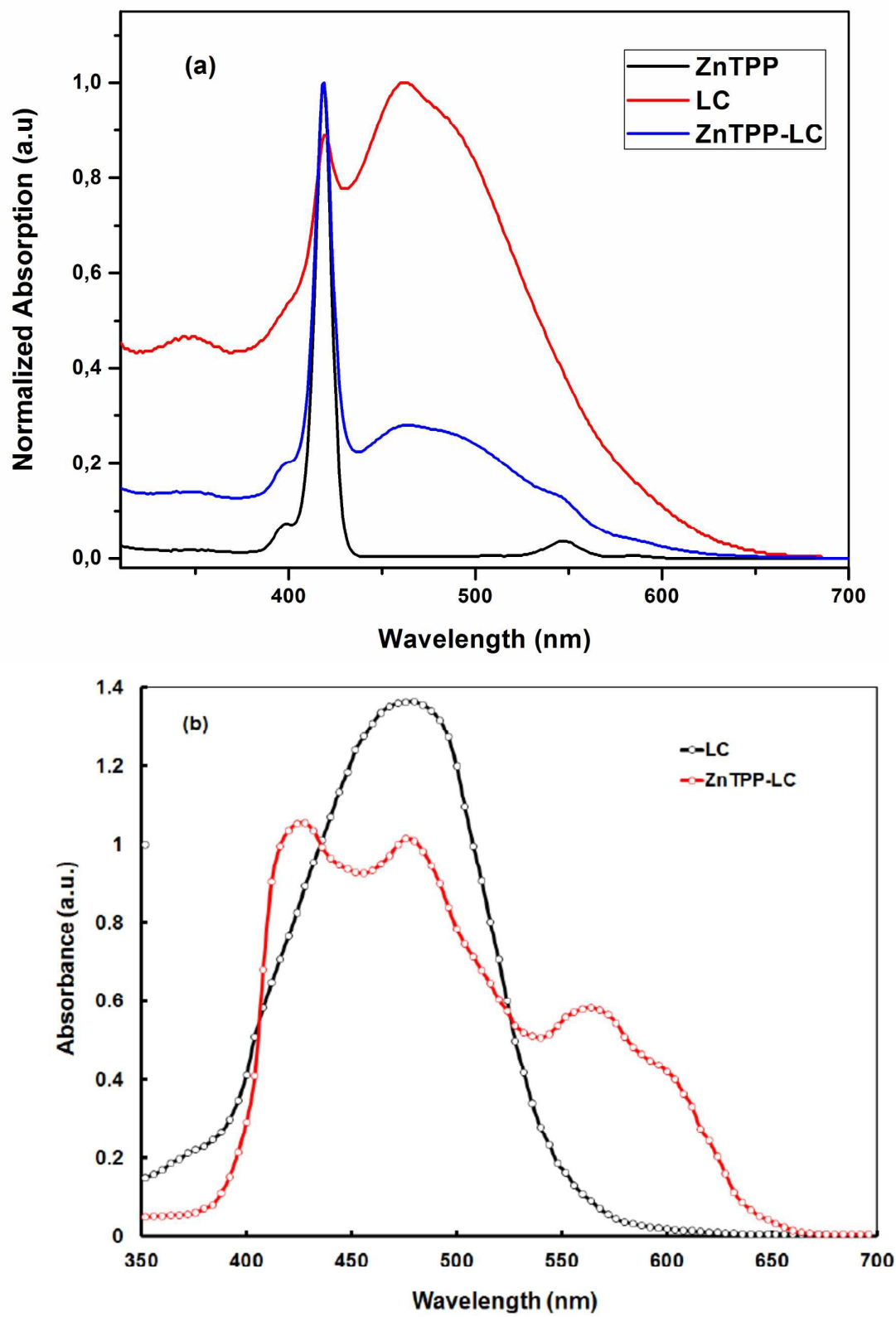


Fig. 1 Optical absorption spectra of (a) **ZnTPP**, **LC** and **ZnTPP-LC** in solution and (b) **LC** and **ZnTPP-LC** adsorbed onto **TiO₂** surface

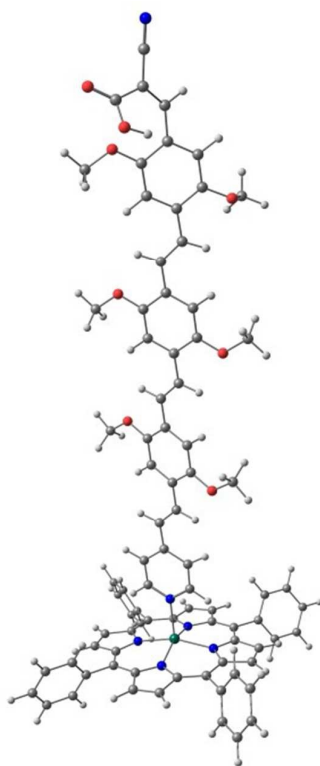


Fig. 2 Gas phase geometry optimized structure of **ZnTPP-LC**. Carbon, nitrogen, hydrogen, oxygen and zinc atoms correspond to grey, blue, white, red and green spheres, respectively.

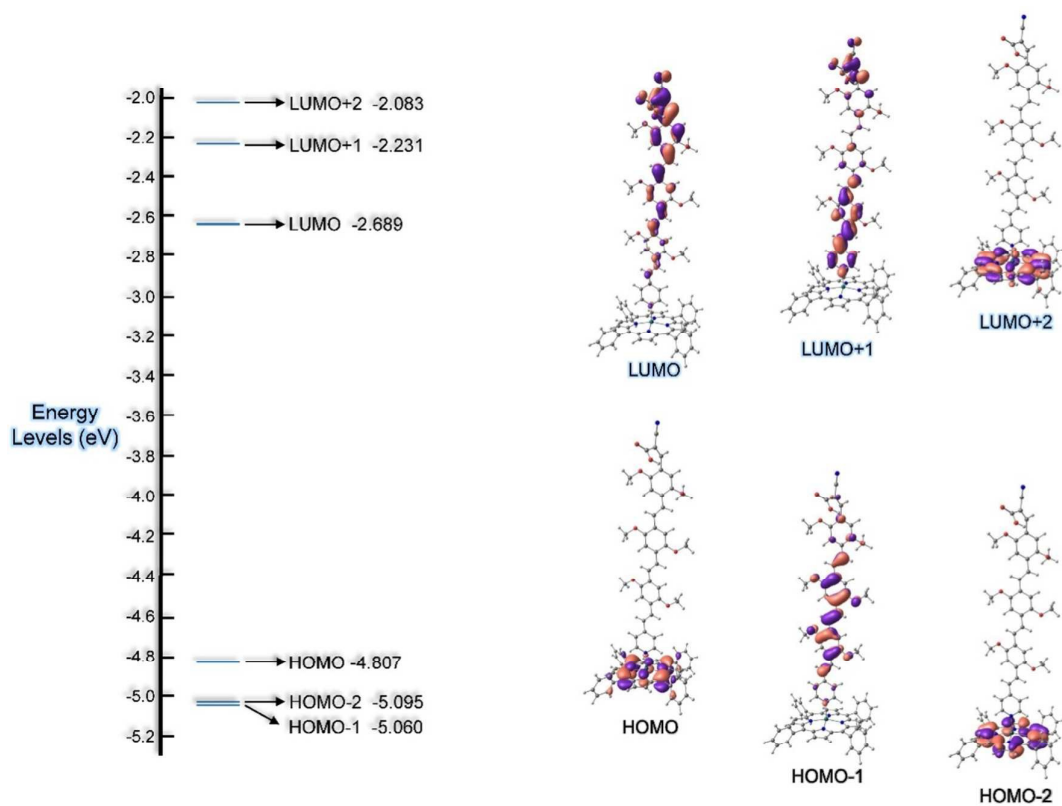


Fig. 3 Frontier molecular orbitals of **ZnTPP-LC** and corresponding energy levels from DFT calculation in CH_2Cl_2 .

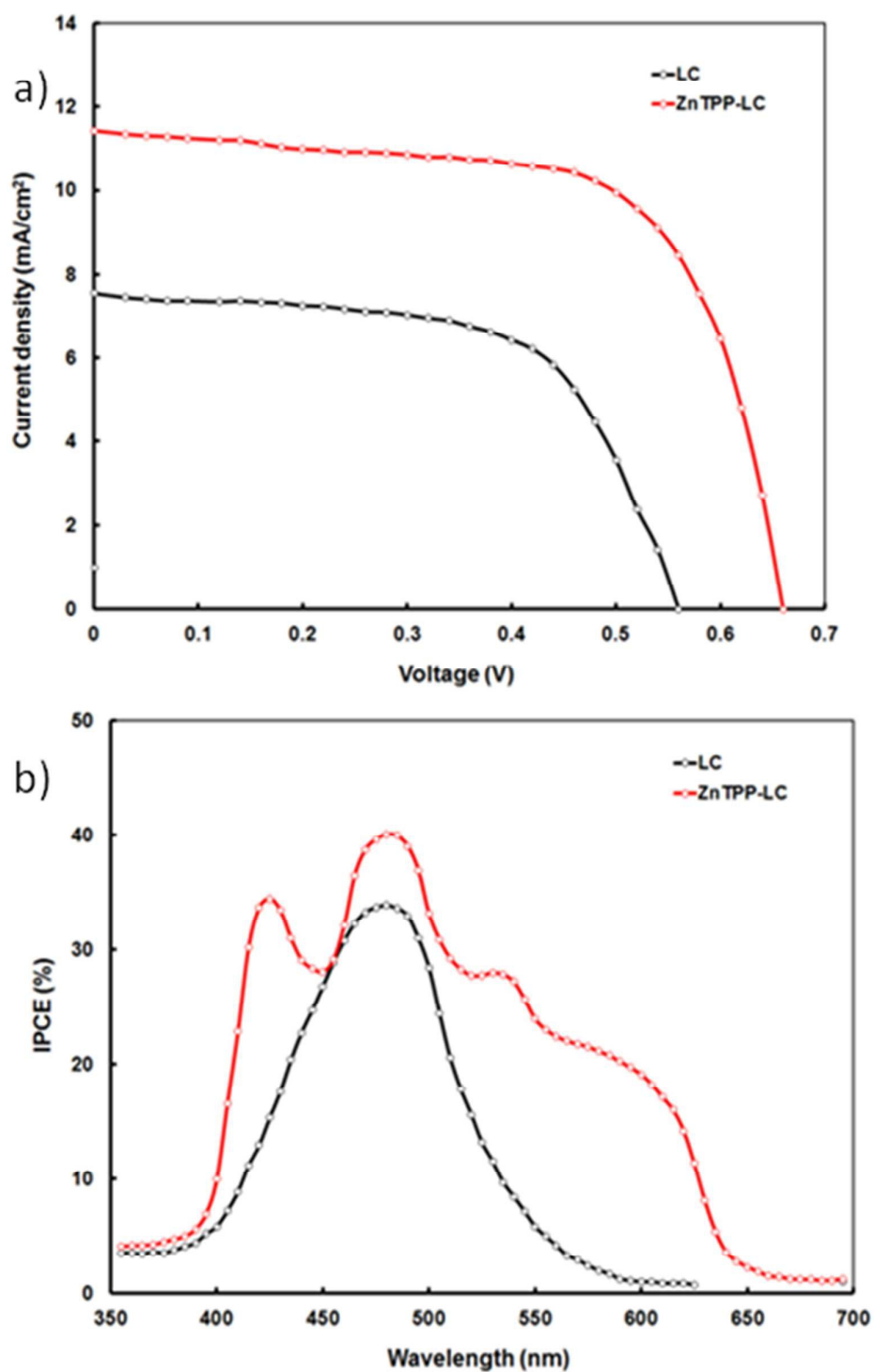


Fig. 4 (a) Current-voltage characteristics under illumination, and (b) IPCE spectra of the DSSCs based on LC, and ZnTPP-LC

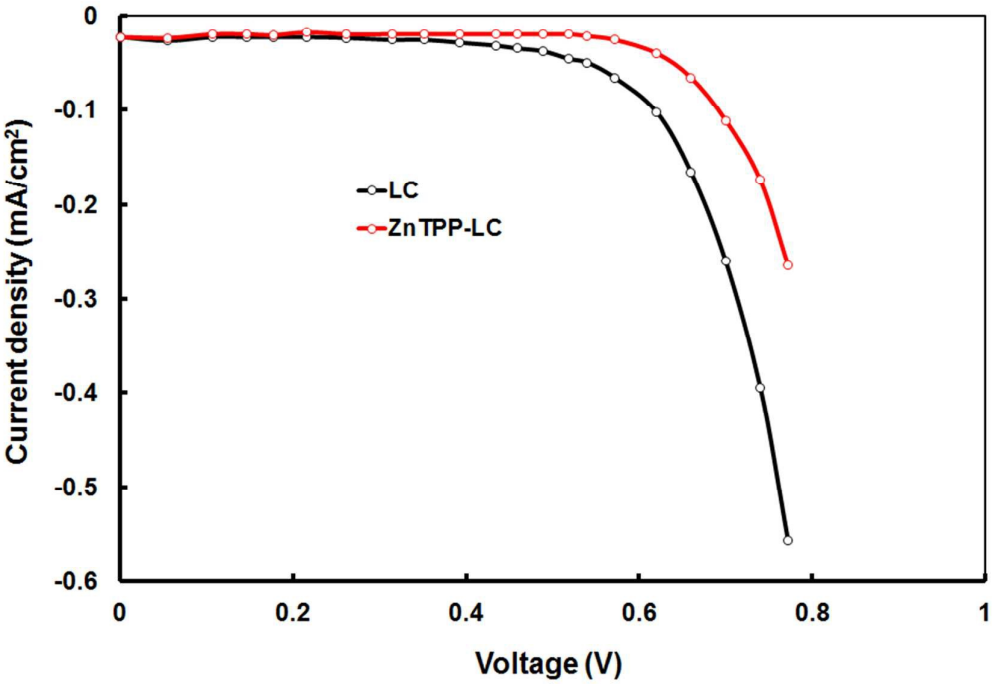


Fig. 5 Current–voltage (J–V) characteristics under dark conditions for DSSCs sensitized with **LC** and **ZnTPP-LC**

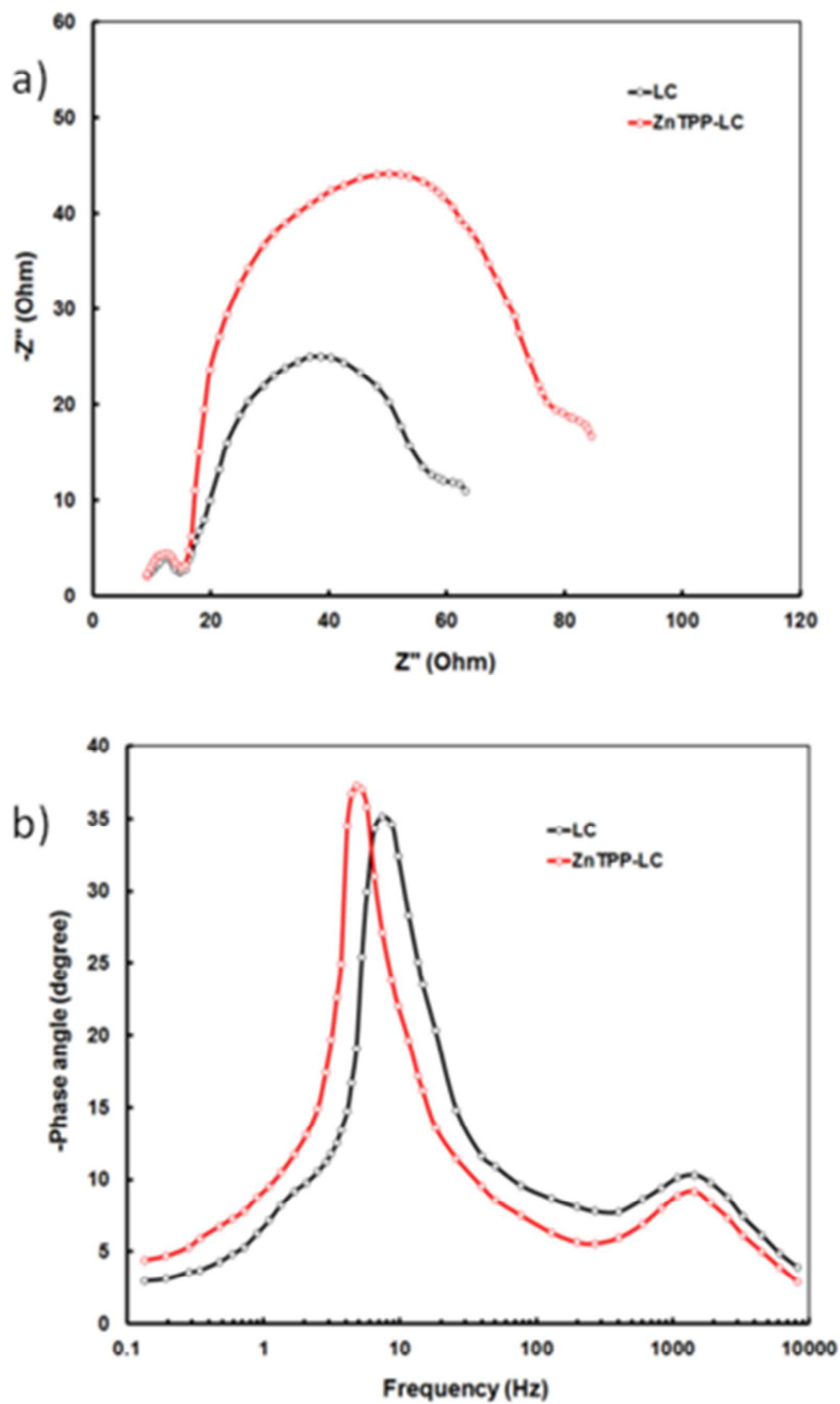


Fig. 6 (a) Nyquist and (b) Bode phase plots from EIS under dark conditions measured at a bias voltage of 0.65 V for DSSCs

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