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Novel synthesized near infrared cyanine dyes as sensitizer for dye sensitized solar cells based on nano-TiO₂

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ABSTRACT

The shortage of energy resources and increasing demand of alternative resources has become urgent priority for the world. Therefore research in this area is extremely important and promising as in renewable energy. Thus complete solar cells sensitized with cyanine dyes 3-5, having near infrared absorption band optimized for solar cell, are synthesized, characterized and studied in the sun light conversion efficiency. The obtained results should be valid for large studies to reveal the main problems in obtaining sufficient performance of near infrared absorbing dyes.

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Capsule Summary: Novel cyanine dyes have been prepared and investigated as sensitizer for solar cell application.

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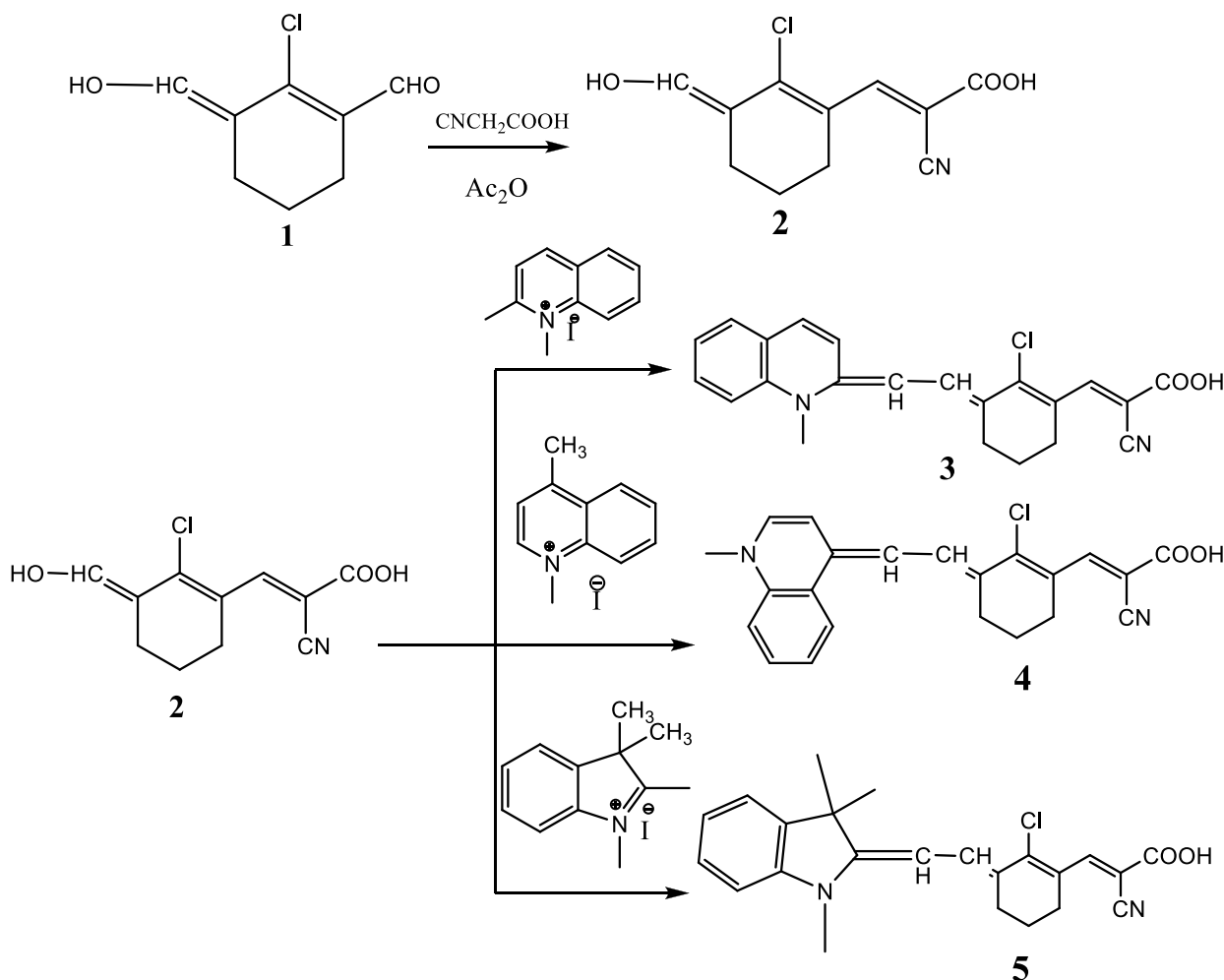
INTRODUCTION

Searching for clean and sustainable energy sources has become urgent necessity for the world. Solar energy is regarded as one of the most suitable energy resources. Cyanine dyes are a class of organic dyes which generically consist of a conjugated system based on polymethine chain linking two nitrogen-containing heterocycles, are known of their outstanding optical properties such as the high spectral absorption maximum by the methine chain, large molar extinction coefficients and moderate fluorescence quantum yield (Gorka et al., 2015 and Henary and Levitz, 2013) is one of the most important parameters in the performance and potential application of such photovoltaic devices. Various procedures for Cyanine dyes of diverse molecular structure have been synthesized (Abdel Aal et al., 2015, Gomaa, 2014,

Kurutos et al., 2015 and Kurutos et al., 2016) that have been extensively employed in various applications such as solar cells (Zhang et al., 2016), nonlinear optical materials (Li et al., 2015), electroluminescent materials (Seo et al., 2014), bio imaging (Liu et al., 2016), photosensitizer (James et al., 2016) and semiconductor (Duleepa et al., 2015).

The heptamethine cyanine dyes which have absorption/emission in the near infrared NIR region are widely used in various applications, such as solar cell (Funabiki et al., 2016).

Therefore, the synthesis of new heptamethine cyanine dyes that show no absorption in the visible region is still required before they can be more widely used in material and biomedical applications. Heptamethine dyes are a subclass of chemical compounds within the cyanine dye family and have many uses as fluorescent dyes (Shershov et al., 2013).



Scheme 1: Synthesis of novel cyanine dyes 2/4-(2-((E)-3(2-carboxy-2-cyanoethylidene)-2-chlorocyclohex-1-enyl) vinyl)-1-methyl quinolinium and/or 1,3,3-trimethyl-3H-indolium iodide.

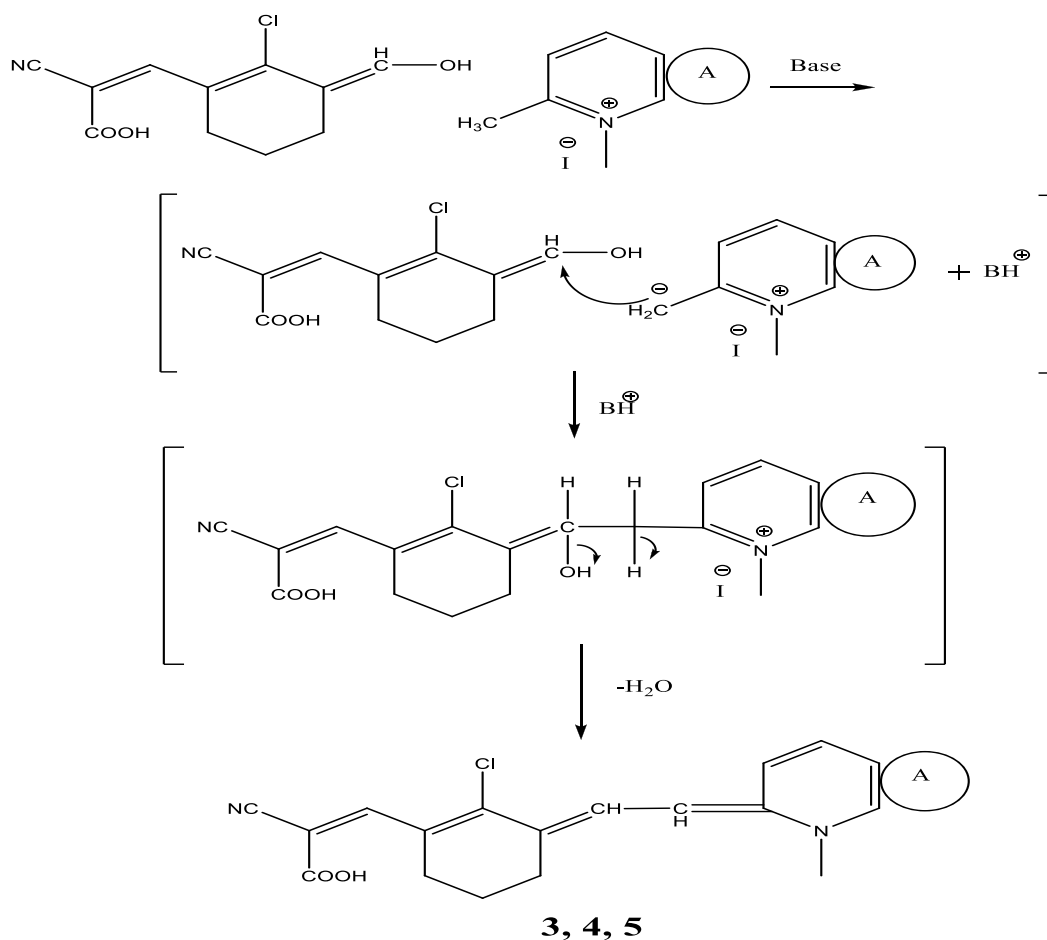
Herein, we describe a molecular design and synthesis of novel heptamethine cyanine dyes, characterization, photovoltaic properties, molecular orbital calculations and photovoltaic performance of the newly synthesized heptamethine cyanine dyes.

MATERIAL AND METHODS

Chemicals, reagents and instruments

All melting points are uncorrected. Elemental analyses were carried out at the micro analytical center (Cairo-University) the photovoltaic performance and design of solar cell were carried out at (Physics and electronics lab, Ovidius University Constanta, Romania). The IR spectra were determined with Perkin Elmer Infrared 127 β spectrophotometer (Cairo University). $^1\text{H-NMR}$ spectra were recorded with Burker AMX-300 spectrometer (Cairo-University). Mass spectra were recorded on HpMs 6988 spectrometer (Cairo University). The electronic absorption spectra were recorded within the wavelength range (350-800) on Shimadzu 1601-A

UV/visible automatic recording spectrophotometer, with 1cm quartz cell used for absorbance and spectra measurements, faculty of Science, Suez University. The TiO_2 films (4-5 μm in thickness) with a scattering layer (10 pcs) were prepared according to (Ito et al., 2008 and Krasovec et al. 2009) The TiO_2 photoanodes were dipped into a solution of containing 4×10^{-3} M dye for 2 h in the dark. After adsorption of the dye, the films were rinsed with distilled water and dried. The dye sensitized TiO_2/FTO electrode together with Pt counter electrode was assembled into sandwich type solar cells. The electrolyte is iodolyte TG-50 (Solarinx), drawn into the space between the electrodes by capillary action (Millington et al. 2007 and Smestad et al. 1998). The current density-voltage (J_eV) characteristics of the DSSCs were measured by recording J_ev using a Keithley 2400 source meter under simulated AM 1.5 G (100 mw/cm^2) illumination with a solar light simulator. The incident monochromator photo-to-current conversion efficiency (IPCE) was performed on a Spectral Products DK240 monochromator from 300 to 800 nm region.

**Equation 1**

Scheme 2: The reaction and its pathway, 3: A=1,2-dimethylquinolin-2-ium iodide, 4: A=1,4-dimethylquinolin-2-ium iodide, 5: A=1,3,3-trimethyl-3H-indolin-2-ium iodide

Synthesis of (E)-3-(2-chloro-3-formylcyclohex-2-enylidene)-2-cyanoacetic acid (2)

Compound 1 was synthesized via the Vilsmier reaction (Rajagopal, et al. 1990) (0.5, 0.0029 mole) and cyanoacetic acid (0.25g, 0.0029 mole) were wetted by acetic anhydride (2mL) and fused for nearly 10 minutes. The second step was refluxing in ethanol for 1 hour and half. The solution was cooled and then poured into 250 mL beaker to evaporate excess solvent. The solid product was collected and recrystallized from ethanol, Scheme 1.

Yield= 75%; mp =135-137; ¹H-NMR: δ (ppm): 1.6 (m, 2H, CH₂), 2.6 (t, J=7.2, 4H, 2CH₂), 4.95 (s, 1H, -OH), 16(S, 1H, COOH) and 7.5 (S, 1H, CHCN). IR (cm⁻¹):1467, 1770, 1324, 1400. LC-MS: m/z= 240.5 [M+1]. Anal Calcd for C₁₁H₁₁N₃OCl: C, 55.13; H, 2.21; N, 5.84. Found: C, 53.21; H, 3.56; N, 4.50.

General procedure for aynthesis of 2/4-(2-((E)-3(2-carboxy-2-cyanoethylidene)-2-chlorocyclohex-1-enyl) vinyl)-1-methyl quinolinium and/or 1,3,3-trimethyl-3H-indolium iodide

To a solution of compound 2 (0.15g, 0.00062 mole) and 1,2-dimethylquinolin-2-ium iodide/1,4-dimethyl quinolin-2-ium iodide and/or 1,3,3-trimethyl-3H-indolin-2-ium iodide (0.186g, 0.00062 mole) in equimolar ratio, respectively in the presence of piperidine (0.7mL) as basic catalyst. The reaction mixture was refluxed for 10 h, filtered hot, cooled and neutralized with acetic acid (0.3mL) to afford 3, 4 and 5, respectively. The precipitated solid was collected and recrystallized from ethanol to give the corresponding compounds 3, 4 and 5, Scheme 1.

Synthesis of 2/4-(2-((E)-3(2-carboxy-2-cyanoethylidene)-2-chlorocyclohex-1-enyl) vinyl)-1-methyl quinolinium iodide (3)

Yield= 85%; mp =210-216; ¹H-NMR: δ (ppm): 1.6 (m, 2H, CH₂), 2.6 (t, J=7.2, 4H, 2CH₂), 3.2 (s, 3H, CH₃), 6-8 (m, 8H, CH+Het. +CH), 11(S, 1H, COOH) and 7.3 (S, 1H, CHCN). IR (cm⁻¹):1450, 2910, 1420, 1600, 1560, 805, 785, 749, 720. LC-MS: m/z= 380.5 [M+2], (Table 1).

Table 1: Characterization data of 2/4-(2-(E)-3-(2-carboxy-2-cyanoethylidene)-2-chlorocyclohex-1-enyl)vinyl)-1methyl quinolinium and 2-(2-2-((E)-3-(2-carboxy-2-cyanoethylidene)-2-chlorocyclohex-1-enyl)vinyl)-1,3,3-trimethyl-3H-indolium iodide cyanine dyes.

No Comp.	M. P °C	Yield %	Colour	Mol. Formula	Calcd. % (found)			Abs Spectra, EtOH	
					C	H	N	λ_{max} (nm)	$\epsilon_{max} \times 10^3$ (L M ⁻¹ cm ⁻¹)
3	>300°C	66	Violet	C ₂₂ H ₁₉ ClN ₂ O ₂	79.75	5.05	7.39	712.7	712.7
					-69.89	-3.85	-6.5	600	600
								560	560
4	>300°C	86	Green-violet	C ₂₂ H ₁₉ ClN ₂ O ₂	79.75	5.05		729sh	
					-75.55	-3.9	7.39	707.5	729
							-6.5	669.5	707.5
								585.3	669.5
								463.5	585.3
5	>300°C	37	Red	C ₂₃ H ₂₃ ClN ₂ O ₂	69.95	5.87	7.09	778.5	1557
					-67.8	-4.7	-8.2	547	1094
								513	1026
								465	930

Synthesis of 4-(2-(E)-3-(2-carboxy-2-cyanoethylidene)-2-chlorocyclohex-1-enyl)vinyl)-1methyl quinolinium iodide (4)

¹H-NMR: δ (ppm): 1.6 (m, 2H, CH₂), 2.6 (t, $J=7.2$, 4H, 2CH₂), 3.3 (s, 3H, CH₃I), 6-8 (m, 8H, CH+Het. +=CH), 11(S, 1H, COOH) and 7.3 (S, 1H, CHCN). IR (cm⁻¹):1440, 3110, 2940, 2980 1600, 1560, 805, 785, 749, 720. LC-MS: $m/z=380.5$ [M⁺+2], (Table 1).

Synthesis of 2-(2-2-((E)-3-(2-carboxy-2-cyanoethylidene)-2-chlorocyclohex-1-enyl)vinyl)-1,3,3-trimethyl-3H-indolium iodide (5)

¹H-NMR: δ (ppm): 1.6 (m, 2H, CH₂), 1.7 (S, 6H, 2CH₃), 2.81 (t, $J=7.2$, 4H, 2CH₂), 3.44 (s, 3H, CH₃I), 6-8 (m, 8H, CH+Het. +=CH), 11(S, 1H, COOH) and 7.3 (S, 1H, CHCN). IR (cm⁻¹):1449, 2950, 2970, 1600, 1540, 805, 735, 758, 710. LC-MS: $m/z=396.5$ [M⁺+2], (Table 1).

RESULTS AND DISCUSSION

Characterization

All titled synthesized cyanine dyes 3, 4 and 5 were confirmed by elemental analysis, (Table 1). Firstly compound (E)-3-(2-chloro-3-formylcyclohex-2-enylidene)-2-cyanopropanoic acid 2 was synthesized through reaction of compound 1 and cyanoacetic acid, followed by formation of cyanine dyes through reaction of compound 2 and 2/4 quinolin-2-ium and/ or 1,3,3-trimethyl -3H indolin-2-ium methiodide to afford dye 3, 4 and 5, respectively.

The formation of 2[2(4)]-heptamethine cyanine dyes 3, 4 and 5 was suggested to proceed through nucleophilic addition reaction between active methyl of N-methyl quaternary salt moieties and carbonyl group of compound 2 to afford compounds 3, 4, 5. The reaction and its pathway were presented as follows in scheme 2.

The 2/4-(2-(E)-3-(2-carboxy-2-cyanoethylidene)-2-chlorocyclohex-1-enyl)vinyl)-1methyl quinolinium and 2-(2-2-((E)-3-(2-carboxy-2-cyanoethylidene)-2-chlorocyclohex-1-enyl)vinyl)-1,3,3-trimethyl-3H-indolium iodide compounds are highly coloured compounds their colour in ethanol ranges from greenish violet, easily soluble in polar and non-polar organic solvents exhibiting coloured solutions (red/violet) concomitant with slight or intense greenish red fluorescence depending upon the solvent used. They are soluble in concentrated H₂SO₄ acid liberating iodine vapour on warming.

Photophysical properties

Electronic absorption spectrum features (λ_{max} . and ϵ_{max} . Values) of newly synthesizes cyanine dyes 3, 4 and 5 in ethanol (alcoholic behavior) solution are shown in (Table 1). The visible absorption maxima of newly synthesized cyanine dyes in ethanol undergo a bathochromic shift or hypsochromic shift depending on the nature of heterocyclic quaternary residue A. Thus substitution of A=N-methyl quinolin-2-ium in compound 3 by A=1,3,3-trimethyl indolin-2-u=ium in compound 5 resulted in a bathochromic shift of 66 nm with increasing number of absorption bands at 778.5, 547, 513 and 465, this can be attributed to the changed donor increasing the electron-donating ability and extended

the π -conjugation system which enhances the electron delocalization over the whole molecule.

Also, the change of linkage position may result in bathochromic shift or hypsochromic shift, such as

Table 2: Photophysical and electrochemical parameters of dye 3-5

Dye	$\lambda_{\text{max}}/\text{nm}^a/(\epsilon/\text{M}^{-1}\text{cm}^{-1})$	λ_{max} on $\text{TiO}_2(\text{nm})$	$\lambda(\text{nm})^b$	HOMO ^c (vs.NHE) (V)	LUMO ^d (vs.NHE) (V)	E_{0-0} ^e (eV)
3	558	571	564	0.710	-1.49	2.20
4	739	573	620	0.714	-1.19	2.00
5	787	638	610	0.710	-1.32	2.03

a: Absorption maximum of dyes measured in EtOH with concentration 10^{-3} M. ϵ : Molar extinction coefficient at λ_{max} .

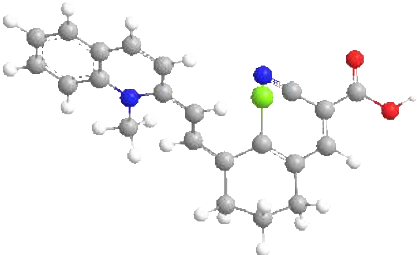
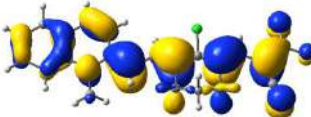
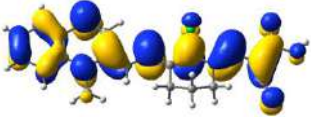
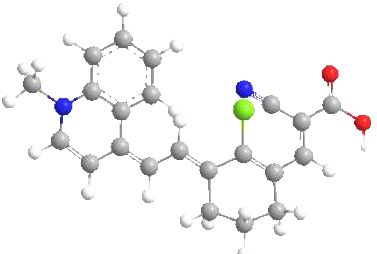
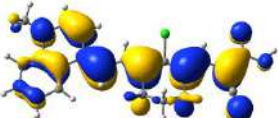
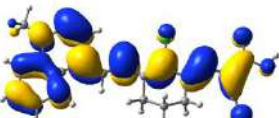
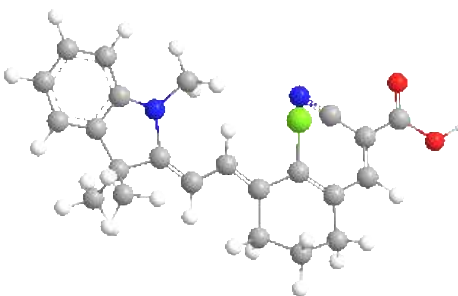
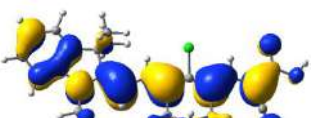
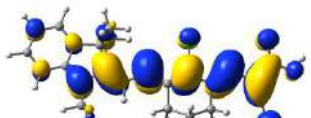
b: λ intersection obtained from the cross point of normalized absorption and emission spectra in EtOH solution.

c: HOMO of the dyes by cyclic voltammetry in 0.1 M TBAPF₆ in dry MeCN solutions as supporting electrolyte, Ag/AgCl as the reference electrode and Pt wire as counter electrode, scanning rate of 50 mV s⁻¹.

d: LUMO was calculated by HOMO - E_{0-0} .

e: $E_{0-0} = 1240/\lambda$ intersection.

Table 3: Optimized structures and electron distributions in HOMO and LUMO levels of dye 2.2.1-2.2.3

Dye	Optimized structure	HOMO	LUMO
3			
4			
5			

substitution of A=N-methylquinolin-2-ium in compound 3 by A=N-methylquinolin-4-ium in compound 4 resulted in a bathochromic shift of 17 nm with increasing number of absorption bands at 707.5, 669.5, 585.3 and 463.5, (Fig. 1). It is worth noting that the three dyes have high molar extinction coefficients (ϵ : 713×10^3 to $1557 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), which indicates that dyes 3-5 have excellent light harvesting ability. The electrochemical data are listed in (Table 2). The estimated ground state oxidation versus normal hydrogen

electrode (vs NHE) is corresponding to the highest occupied molecular orbital (HOMO) energy level of dye molecule. The HOMO levels of dye 3-5 are 0.710, 0.714 and 0.710 respectively. It is obviously appear that the HOMO levels are more positive than I⁻/I₃⁻ redox couples (0.4V vs NHE) (Lee, et al., 2015), referring that the driving force for dye molecule regeneration are sufficient. The energy gap E₀₋₀ of 3-5 determined from the intersection point of normalized absorption spectra are 2.20, 2.00 and 2.03 eV, respectively.

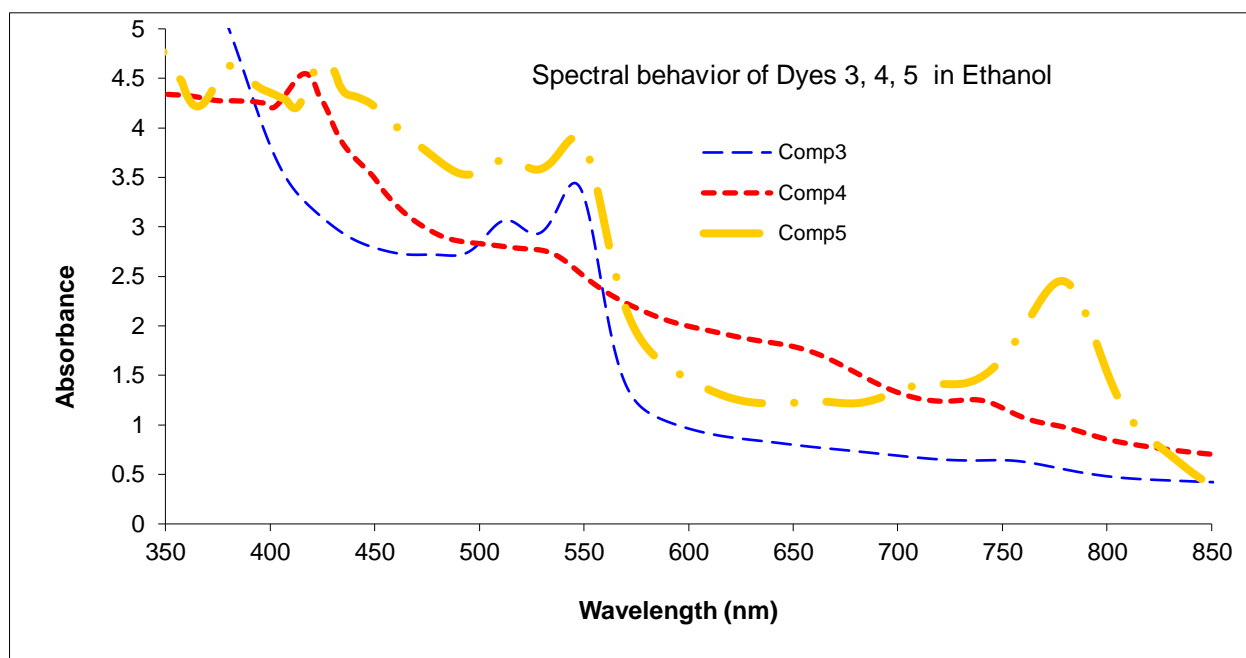


Fig. 1: Absorption spectra of dye 3-5 in ethanol solution

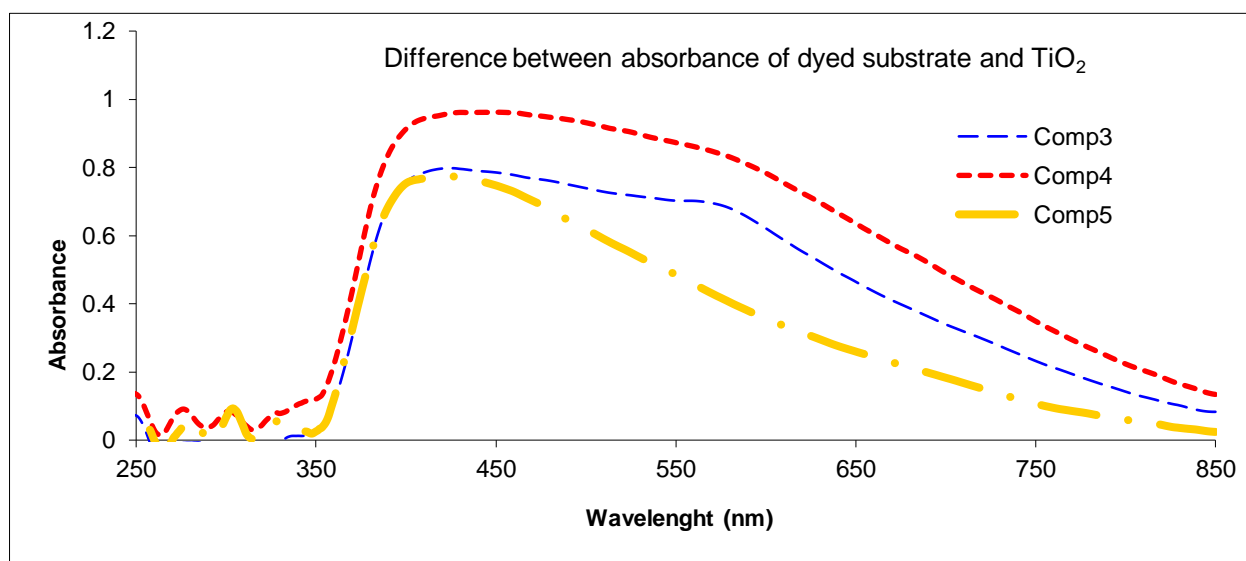


Fig. 2: Absorption spectra of dye 3-5 on TiO₂ films

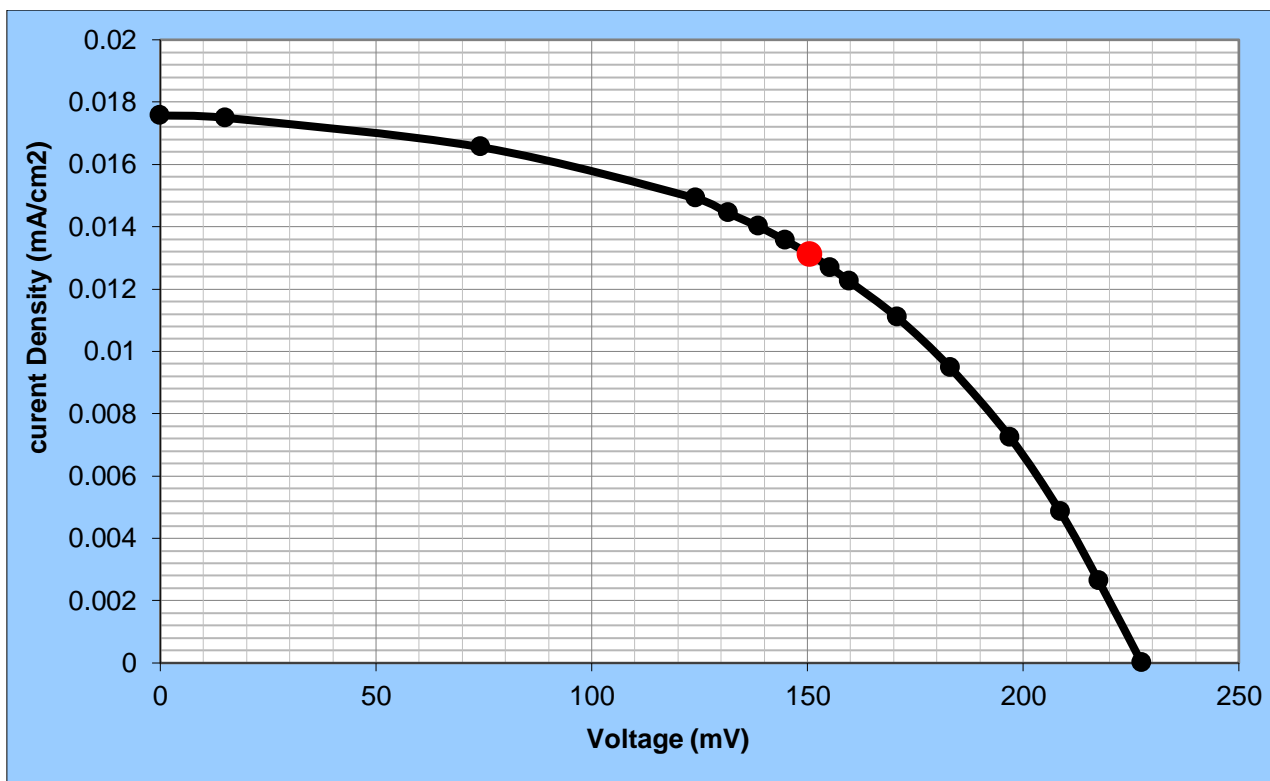


Fig. 3: J-V curves of the DSSCs based on dye 3

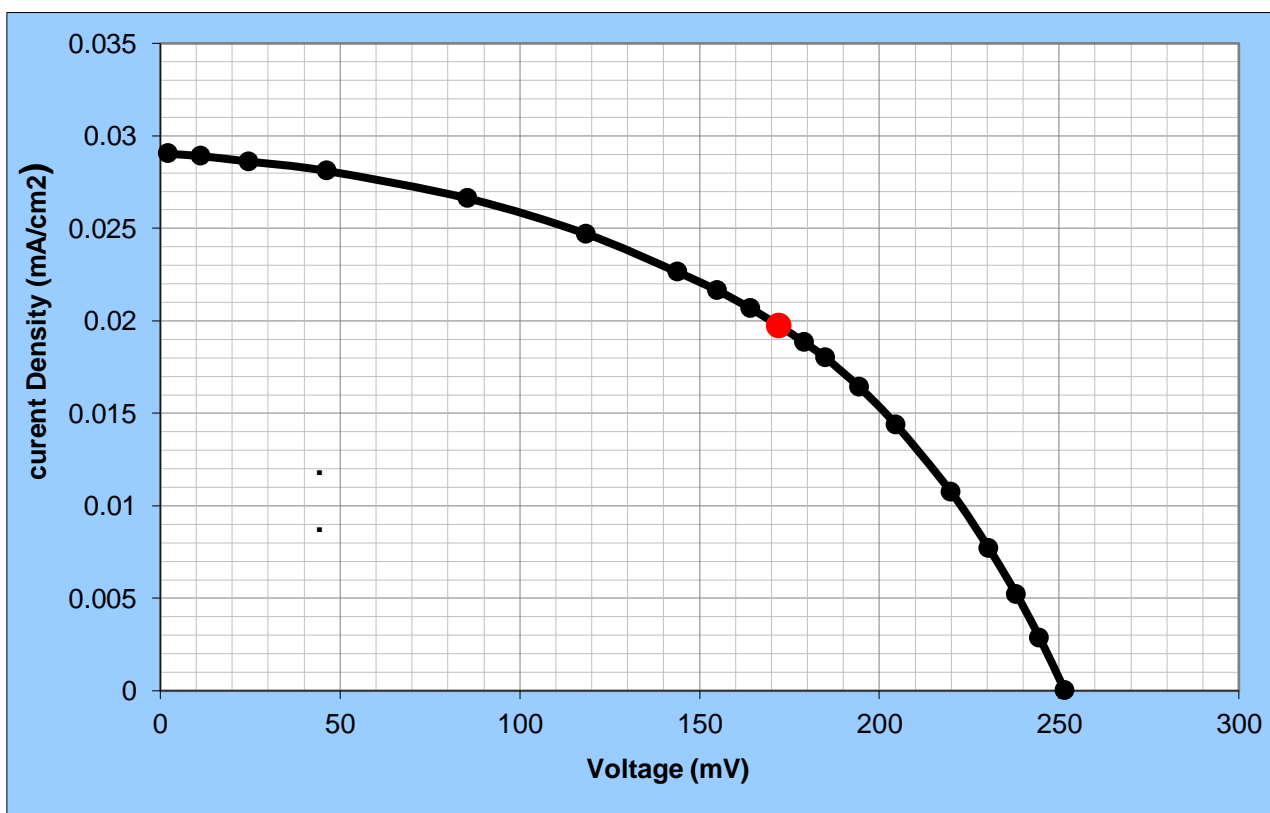


Fig. 4: J-V curves of the DSSCs based on dye 4

Table 4: Calculated TD-DFT Wavelengths, Excitation energies (eV), and composition in terms of Molecular Orbital Contributions of the dyes 3-5 with Oscillator Strengths (f) larger than 0.5

Dye	Wavelength	E(eV)	Composition ^a	F
3	581.74	2.1313	H→L:99%,H-1→L:1% H→L:99%	0.71033
	432.14	2.8691		0.68289
4	608.49	2.0376	H→L:99%,H-1→L:1% H→L:99%	0.71399
	401.82	3.0856		0.44311
5	549.53	2.2562	H→L:99%,H-1→L:1% H→L:99%	0.71008
	370.09	3.3501		0.6758

^a: H=HOMO, L=LUMO, H-1=HOMO⁻¹, L-1=LUMO⁻¹

Table 5: Photovoltaic performance parameters of dyes 3-5

Dye	Jsc (mA cm ⁻²)	V _{oc} (mv)	η	FF
3	0.018	227.5	0.0020	0.494
4	0.029	251.6	0.0034	0.465
5	0.131	361.7	0.0301	0.636

The LUMO levels were calculated from the equation, LUMO=HOMO-E₀₋₀ is -1.49, -1.19 and -1.32 V, respectively. The LUMO values of the three dyes are all more negative than the conduction edge (-0.5 V vs NHE) (Wan et al., 2015) of TiO₂ which shows that electron injection from the excited dye to the TiO₂ film is energetically permitted.

Molecular orbital calculation

According to density functional theory (DFT) calculations at the B3LYP16-31G level were performed to further understand the geometrical configurations and electron distributions of the three dyes. It is obviously clear from (Table 3) that all the three dyes, the HOMO are mainly distributed on the electron donor, while the LUMO is delocalized over the cyanoacetic acid segment on the π-bridge. These types of distributions allow charge transfer from the dyes to the TiO₂ films upon photoexcitation. We can see that the maximum absorptions of 3-5 mainly come from the transition from HOMO→LUMO and small part from HOMO-1→LUMO (Table 4).

Photovoltaic Performance of DSSCs

The power conversion efficiencies of the DSSCs sensitized by 3-5 were obtained by measuring J-v characteristics at 100 mwcm⁻² simulated Am 1.5 G solar light (Fig. 3-5). The detailed photovoltaic parameters of Jsc, open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency η are

summarized in (Table 5). The DSSCs sensitized by dye 5 exhibits the best η of 0.03% with Jsc of 0.131 mA cm⁻², V_{oc} of 362 mV and FF of 0.636. The other two dyes 3 and 4 obtained efficiencies of 0.002% and 0.0034%, respectively. The variation of Jsc values are agreed with the results obtained in IPCE measurement. The best DSSC performance of dye 5 can be attributed to the two methyl group in the indole ring which restricts the intramolecular interactions. The effective way to prevent π-aggregation and charge recombination is still the incorporating of the alkyl chain into the π-bridge (Liu et al., 2012).

The novel synthesized cyanine dyes 3-5 shows a low efficiency values, this may be attributed to the intermolecular aggregations of the dyes on TiO₂ films. For the sensitizer 3-5, the lowest unoccupied molecular orbital (LUMO) energy level is about -3.5 eV (Nazerrudin et al., 2005) which is much higher than TiO₂ conduction band energy level (-4.0 eV) (Wang et al., 2005), therefore it seems plausible to broaden the energy conversion region of the sensitizers by downshifting the sensitizer LUMO energy level (ELUMO). However one problem is that it will bring down the electron injection efficiency and increase the charge recombination, which lead to reduction of the efficiency (Tian, et al., 2009). Therefore, in order to overcome this problem and improve the efficiency of DSSCs, hard work is needed to reduce the charge recombination and electron injection efficiency are nearly related with the open-circuit voltage (V_{oc}), which means that V_{oc} becomes the principle factor among many

factors calculating for improvement of the performance of the DSSCs (Oregan et al. 2009 and Hamann et al., 2008).

The heptamethine cyanine dyes incorporating cyclohexene ring may facilitate dye aggregation. One of the most effective factors accounting for the low photovoltaic performance of DSSCs is the dye aggregation that formed on the semiconductor surface (Ning et al., 2009 and Li et al. 2009). Aggregation may lead to intermolecular quenching or molecules residing in the system which restricted from attaching to the TiO₂ surface, which will decrease the electron injection. Also, the sensitizer regeneration by redox couple will be affected by molecular aggregation (Wang et al. 2008 and Duleepa et al. 2015).

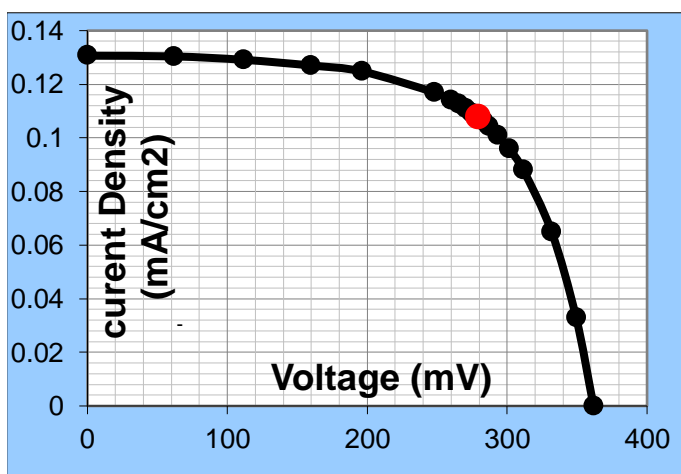


Fig. 5: J-V curves of the DSSCs based on dye

CONCLUSIONS

In this study we designed, synthesized and systematically investigated three novel cyanine dyes with excellent optical properties. We expect that the three novel cyanine dyes will exhibit good photon to current energy conversion but we found low efficiency of the cells. The main reason may be related to dye aggregation on TiO₂ surface usually decreases the electron injection efficiency due to various energy migration routes. Our group will hardly work in the coming days to modify the sensitizer structure to increase the sensitizer performance and eliminate the factors limiting the performance of DSSCs.

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