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ARTICLE TYPE

Promising ZnO-based DSSCs Performance Using HMP Molecular Dyes of High Extinction Coefficients†

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Employing newly synthesized *di*-substituted *tri*-phenyl amine (HMP-9) and carbazole (HMP-11) dyes (with limited acidic carboxyl anchor groups), a power conversion efficiency as high as 7.03% in ZnO nanocrystallite (NCs)-based dye-sensitized solar cells (DSSCs) is achieved. The specific molecular designs of HMP-09 and HMP-11 consisting of with and without hexyloxy spacer groups, and added *tri*-phenyl amine or 9-phenyl-9H-carbazole donor groups, respectively attached on the ancillary ligands are advantageous, evidenced from electrochemical impedance spectroscopy measurement, for ZnO NCs-based DSSCs.

As promising, low-cost, efficient conversion of visible light into electricity becomes inevitably important, dye-sensitized solar cells (DSSCs), a new class of photoelectrochemical cells based on porous metal oxide semiconductors, Ru-complexes as sensitizers and liquid electrolyte containing I/I₃⁻, have attracted significant attraction as potential alternatives to conventional Si based solar cells. New molecular sensitizing dyes, in addition to polypyridyl ruthenium compounds, of higher extinction coefficients that extend the absorption in the near-IR region of the solar spectrum and providing better charge generation and transport properties have attracted significant attention.^{1, 2} Few dyes with amphiphilic heteroleptic characteristics, e.g. Z907, C101 and C106 yielded 9-11% solar-to-electrical conversion efficiencies (η %) under 1 Sun illumination.³ After 20 years of research, the power conversion efficiency of DSSCs has just been increased from 11% to 12.3% in presence of YD2-o-C8 sensitizer and Co^(II/III) tris(bipyridyl)-based redox electrolyte.⁴ It seems that DSSCs based on TiO₂ reflect the limits imposed by its low

electron mobility due to which there is more chance of electron-hole recombination.⁵⁻⁷ The ZnO nanostructure-based photoanode with the similar band gap and conduction band positions of TiO₂ photoanode exhibited problems of chemical and thermal stabilities.⁸ ZnO form i.e. morphology, structure and phase are considered for good electron mobility and electrical conductivity. By Ga doping, 5-6% conversion efficiency of ZnO photoanode has been reported in the literature,⁹ which can be further improved either by surface treatment or by designing the dyes of higher molar extinction coefficients (ϵ).¹⁰ In one of the studies, ZnO photoanode composed of hierarchically assembled nanocrystallites has been envisaged for record 7.5% power conversion efficiency.¹¹

It is quiet accepted that the N719 (*cis*-dithiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium (II) and N3 sensitizers with 2 and 4 carboxylic acid groups incorporated on bipyridine ligands, respectively, facilitate anchoring to the photoanode surface and for the transfer of electrons from the dye to the metal oxides (MOs) conduction band. In ZnO nanostructures based DSSCs, preventing the formation of Zn²⁺/dye complex, an insulating layer that eventually blocks the overall electron injection efficiency by producing inferior power conversion efficiency, is presently a great challenge.¹⁰ Dye architecture, addition of donor, conjugated linker groups and electronic coupling between the lowest unoccupied molecular orbital (LUMO) level of dye and MOs conduction band can enhance the device performance to a greater extent by improving light harvesting efficiency and charge transport in photoanode.¹²

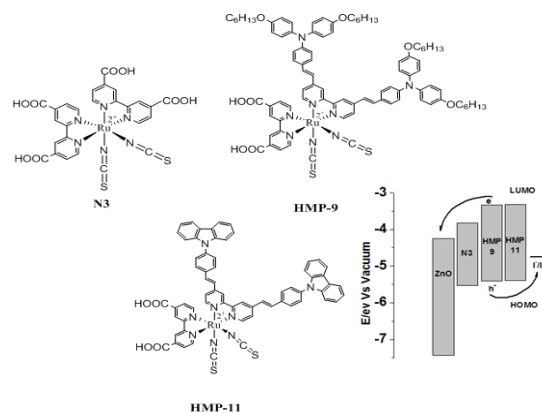


Figure 1. Molecular structures and respective energy levels of N3, HMP-2, HMP-9 and HMP-11 sensitizers (For experimental scheme, synthesis procedure and structural characterizations see SI).

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With this perspective, herein, we would like to stress on importance of newly designed dye molecules, *cis*-[Ru(H₂dc bpy)(L)(NCS)₂], where H₂dc bpy = 4,4'-dicarboxylic acid-2,2'-bipyridine and L = 4,4'-bis-(4-di-*p*-hexyloxyphenyl-amino)-styryl-2,2'-bipyridine (HMP-9) and 4,4'-bis-(4-(*N*-carbazolyl)-phenyl-2-vinyl)-2,2'-bipyridine (HMP-11) for efficient ZnO nanoparticles (NPs)-based DSSCs. The obtained conversion efficiencies are superior compared to Ru(H₂dc bpy) (4-(4-(*N,N*-di-(*p*-hexyloxyphenyl)-amino)styryl)-4'-methyl-2,2'-bipyridine) (NCS)₂, (HMP-2), recently reported by previously¹⁰ and N3 dyes.

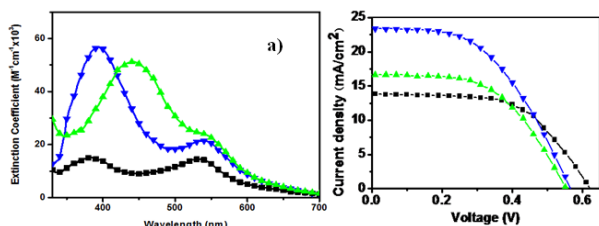


Figure 2. a) Electronic absorption spectra, and b) *J-V* characteristics of the devices employing different dyes. N3 (black, ■), HMP-9 (green, ▲) and HMP-11 (blue, ▼) under the illumination of AM 1.5G sunlight (100 mW/cm²).

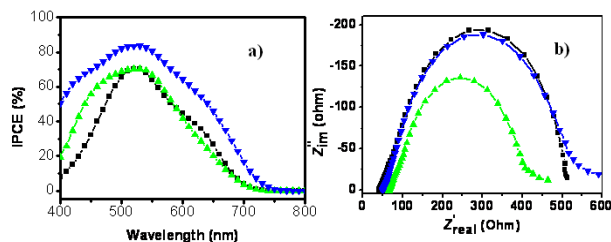


Figure 3. a) Photocurrent action spectra and b) EIS Nyquist plots measured under open circuit conditions in 1 Sun illumination for the devices employing different dyes. N3 (black, ■), HMP-9 (green, ▲) and HMP-11 (blue, ▼).

Synthetic procedures, structural characteristics, cyclic voltammograms, UV-Vis absorption spectra of HMP-9 and HMP-11 sensitizers can be obtained from the Supporting Information (SI). Synthesis of ZnO photoanodes and DSSCs device fabrication details, as well as efficiency measurements are also provided in SI. Final molecular structures of these newly *in-lab* designed dyes are shown in Figure 1. Our previous results on HMP-2 dye yielded a photo-conversion efficiency of 4.01% where soaking time for ZnO NPs electrode was as long as 24 h.¹³ While designing these new dyes with electron-rich moieties consisting of a planar heterocyclic fused-ring, carbazole molecule is explored.¹⁴

The carbazole unit acts as an electron donor to pump the electron to Ru metal in the excited state and improve the power conversion efficiency of DSSCs. Recently, carbazole has been used as an electron donating functional group in organic dyes¹⁵ where, DSSCs performance has been jumped from 6 to 8.3% for TiO₂-based DSSCs. Here, HMP-9 and HMP-11 dyes with and without hexyloxy spacer groups, and added *tri*-phenyl amine or 9-phenyl-9H-carbazole donor groups, respectively, attached on the ancillary ligands were engineered for optimizing acidity as well as visible light absorption to achieve high efficiency of ZnO-based DSSCs. The extinction coefficients (ϵ) and

electrochemical characteristics of HMP dyes are shown in Table 1. There is no noticeable difference in quantity of dyes adsorbed (due to the four hexyloxy chains incorporated on ancillary ligands, HMP-9 dye has relatively low adsorption than HMP-11 dye) onto ZnO NPs. The replacement of the carboxylic group of N3 bipyridine ligand site with strong donor functional groups has positively shifted the highest occupied molecular orbital (HOMO) level by 0.22 eV (*vs.* vacuum level, in HMP-11) which matches well with the redox potential of I⁻/I₃⁻. Whereas, the *tri*-phenyl amine donor functional group with hexyloxy groups, is shifting the HOMO position negatively to 0.11 eV from N3 dye position. Figure 2a shows UV-Vis absorption spectra of the HMP-9, and HMP-11 sensitizers along with N3 sensitizer (10⁻⁵ M). The absorption spectra of the HMP-9, and HMP-11 sensitizers are dominated by metal-to-ligand charge transfer transitions (MLCT), which are located at two positions, i.e. 441 and 526 nm, and 393 and 539 nm, respectively, and the high-energy bands below 320 nm are due to ligand π - π^* transitions. The peak position of the MLCT band at 441 nm in HMP-9 sensitizer is red-shifted compared to HMP-11 and N3. The presence of carbazole moiety has increased extinction coefficient significantly. The increased π -conjugation length of ancillary ligands with electron donation functional group in HMP-9 and HMP-11 might be responsible for the increased molar extinction coefficients in the visible region as compared to that of N3. The ϵ values of the low-energy MLCT absorption band for HMP-9 and HMP-11 are 23.5 × 10³ M⁻¹ cm⁻¹ and 21.4 × 10³ M⁻¹ cm⁻¹ which are significantly higher than the corresponding values for the N3 (14.5 × 10³ M⁻¹ cm⁻¹). Whereas, the other bands observed at 441 and 393 nm wavelength region show significant improvement in absorption characteristics peculiar to the nature of the dye donor molecular characteristics. A blue shift of 9 nm along with 3.76 times higher ϵ values of HMP-11 sensitizer compared to N3 would certainly fascinate its uniqueness in the DSSCs performance. Figure 2b presents typical current-voltage (*J-V*) spectra of the designed HMPs and N3 dyes immobilized on ZnO NPs photoanodes.

Table 1: Photophysical and electrochemical properties of N3 and HMP dyes (*vs.* vacuum level).

Dye	HOMO (eV)	HOMO -LUMO (eV)	LUMO (eV)	λ_{\max} (nm)	ϵ (M ⁻¹ cm ⁻¹)
N3	-5.52	1.68	-3.84	530	14,500
HMP 9	-5.41	2.06	-3.35	526	23,576
HMP 11	-5.38	2.05	-3.33	539	21,435

Devices sensitized with HMP-11 exhibited highest short circuit current density (J_{sc}) of 23.4 mA cm⁻² and overall power conversion efficiency (η %) of 7.09% whereas those sensitized with HMP-9 and N3 exhibited efficiencies of 5.34 and 4.94% (Table 2). All measurements were performed without mask. Open circuit voltage (V_{oc}) remained nearly same in all the cases. The high photocurrent in HMP-11 sensitized devices is attributed to its high extinction coefficient which increases light harvesting efficiency and to the superior electron transport through the device. We believe that, further improvement in V_{oc} and fill factor (ff) values can be achieved using surface treatment such as 4-*tert*-

butylpyridine, $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ and forming the core-shell structures, etc.^{16, 17}

Table 2: The standard device electronic parameters extracted from the J - V data for N3 and HMP dye sensitized photoanodes.

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	ff	$\eta\%$
N3	13.8	0.61	0.58	4.94
HMP-9	16.7	0.58	0.55	5.34
HMP-11	23.4	0.61	0.49	7.09

As seen in Figure 3a, the photocurrent action spectra shows the highest spectral response for the red shifted HMP-11 dye with a peak incident photon-to-current conversion efficiency (IPCE) of about 77% at 464 nm. HMP-9 dye with four hydrophobic hexyloxy substituent attached to impede the *tri*-iodide ions reaching the ZnO NPs surface and to prevent molecular aggregation due to π - π stacking, disadvantageously, has reduced the IPCE value to 51%. This is due to an intermolecular quenching or clouding of long alkyl, non-conjugated, hexyloxy substituents that generally diminishes the light absorption by the filtering effect. Despite of higher ϵ in HMP-9, it exhibits lower IPCE and $\eta\%$ (discussed later) suggesting that there is a need of *in*-depth investigation on the charge generation, collection and recombination kinetics across electrolyte/dye/ ZnO NPs/indium-tin-oxide (ITO) interfaces. The maximum IPCE value of HMP-11 dye is supposed to be obtained from better MLCT and hole conducting carbazole moieties. Electrochemical impedance spectroscopic (EIS) analysis is often performed to understand the interfacial charge transfer resistance, electron transport rate and recombination effect in DSSCs.¹⁸ Impedance spectra of DSSCs generally exhibit three semicircles. Small semicircle at high frequency region corresponds to interface between platinum and electrolyte, big semicircle in intermediate frequency range corresponds to photoanode-electrolyte interface whereas one in low frequency range is related to Warburg impedance of electrolyte. Figure 3b shows the Nyquist plots of ZnO NPs-based DSSCs with dyes, considered in present study, under 1Sun illumination and open circuit conditions. It is clear from the figure that photoanodes utilizing N3 and HMP-11 dyes demonstrate higher recombination resistance values confirming high electron lifetimes and obviously more photoconversion efficiencies. On the other hand, the photoanode utilizing HMP-9 dye has lower recombination resistance and thus electron recombination will be higher and lifetime will be lower.^{19, 20} The HMP-11 dye with electron rich carbazole moiety aids in superior electron transport within the device, and thus is expected to produce higher power conversion efficiency.

In summary, dye-sensitized solar cells utilizing ZnO NPs with newly synthesized *di*-substituted *tri*-phenyl amine (HMP-9) and carbazole (HMP-11) as donor moieties on bipyridine ligands with limited acidic carboxyl anchoring groups in addition to routinely used N3 dye are investigated, where electron-rich donor moieties increased the extinction coefficient and improved charge generation and transportation. The ZnO NPs electrode sensitized with HMP-11 dye demonstrated as high as 7.05% power conversion efficiency with an better short current density of ~23.4 mA cm^{-2} , under simulated AM 1.5, 100 mW cm^{-2} illumination. Electrochemical impedance measurement revealed that the devices constructed utilizing newly synthesized dyes, with and without hexyloxy spacer groups, and added *tri*-phenyl

amine or 9-phenyl-9H-carbazole donor groups attached on the ancillary ligands have improved charge generation and transport properties than N3 dye. It would be interesting to use gel electrolyte²¹ and compact metal oxide layers of relatively high band gaps²² for improving both the stability and performance.

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ASSOCIATED CONTENT

Supporting Information

Detailed electrode synthesis, dye synthesis, optical absorption, NMR details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

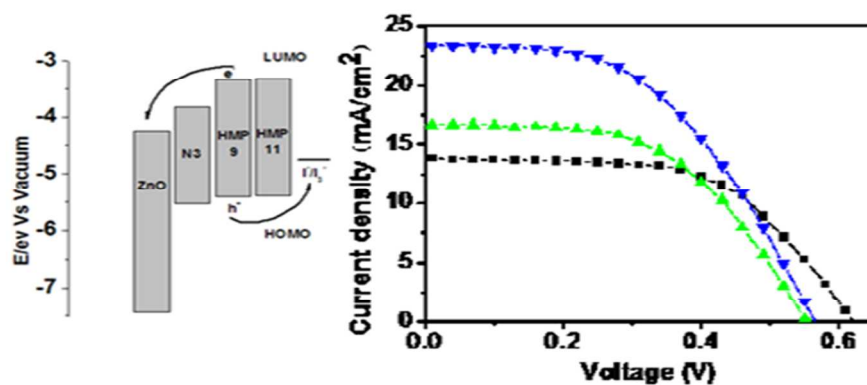
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Graphical abstract

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