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Acetylene-bridged dyes with high open circuit potential for dye-sensitized solar cells⁺

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A series of simple metal-free organic dyes MS1-MS3 have been designed and synthesized, and their optical, electrochemical, and photovoltaic properties were investigated. The molecular structures are based on a push-pull framework with a triphenylamine, naphthyldiphenylamine, or anthracenyl diphenylamine as the donor connected to a carboxyphenyl acceptor via a C=C bond. The speciality of this new dye design is to obtain higher device open-circuit potentials. The dye-sensitized solar cells using this new sensitizer in combination with I^{-}/I_{3}^{-} exhibited exceptionally high V_{OC} values of 810, 844, and 866 mV for MS1, MS2, and MS3, respectively. The absorption bands of the anthracene-bridged dye MS3 showed remarkable peak broadening and red shifts due to the strong electronic coupling between the donor and bridge facilitated by the C-C triple bond, significantly promoting the light-harvesting capability. The resulting devices of MS3 showed large IPCE values of 75-80% in the region 370-590 nm, giving J_{SC} /mA cm⁻² = 8.16, V_{OC} /mV = 866, FF = 0.76, and η = 5.44% under standard AM 1.5G one sun irradiation.

Introduction

The increasing global energy demand and environmental challenges have prompted scientists to explore new sources of energy to support the lifestyle in modern society. Among all energy sources, solar energy is the most attractive and viable option because sunlight hits 120 000 TW of solar energy on the earth, which provides us more than enough energy in a clean and sustainable fashion.¹ Dye-sensitized solar cells (DSSCs) have appeared a promising alternative to conventional silicon-based devices because of lower production costs since Grätzel

and co-workers first reported an efficient DSSC in 1991.² The best DSSCs based on ruthenium polypyridine dyes exhibit power conversion efficiencies over 11%.³ In view of the rareness and environmental concerns about ruthenium dyes, considerable efforts have been devoted to the development of new and efficient non-ruthenium sensitizers suitable for practical use. Inspired by the efficient energy and electron transfer performed by chlorophylls at the active site of photosynthetic center, numerous porphyrins and related analogues have been prepared for use in photovoltaic devices.⁴ The present best performing DSSCs employ porphyrins as sensitizers in combination with cobalt complexes as redox electrolyte, which, have shown a power conversion efficiency of 12–13%.⁵

Apart from porphyrins, organic sensitizers have emerged as attractive candidates for use in DSSCs due to their low cost, ease of synthesis and structural modification, high molar absorption coefficient, environmental benignity, and good stability. In the past two decades, a large number of metal-free organic dyes have been developed and their photovoltaic properties investigated. These includes triarylamine,6 cyclopenta[1,2-b:5,4-b']dithiophene (CPDT),⁷ dithieno[3,2-b:2',3'-d]pyrrole (DPT),⁸ carbazole,9 thiophene,10 and benzothiadiazole.11 It is well known that organic dyes featuring a donor- π -conjugated unitacceptor (D- π -A) structure exhibit high performance. In such a structure, the electron density of HOMO is mainly distributed on the donor and that of LUMO is mainly located on the acceptor. The judicious electron distribution for the frontier orbitals facilitates electron injection and retards charge recombination. The best organic sensitizers based on the D- π -A structure have achieved presently power conversion efficiency (PCE) over 10%.12

Anthracene derivatives have received great attention due to their unique photophysical properties, thermal stability, and potential application in molecular electronics such as organic light-emitting devices,¹³ small molecule solar cells,¹⁴ and organic thin-film transistors.¹⁵ However, organic dyes incorporating an anthracene moiety for use in DSSCs are rare. Thomas *et al.* synthesized a series of organic dyes containing

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anthracene-based triarylamine donor and cyanoacrylic acid acceptor for the study of the role of the anthracene unit played on the absorption and photovoltaic properties.16 A power conversion efficiency of 3.32% was achieved with the most efficient dye in this series. Sun and co-workers systematically designed and synthesized a series of metal-free organic dyes bridged by anthracene-containing π -conjugations as new chromophores for the application of DSSCs. The best performing dye shows a cell efficiency of 7.03% due to improvement of J_{SC} attributed to the much broader absorption spectra of the dyes with the anthracene moiety. Choi et al. employed an anthracene unit to bridge the donor and acceptor that extend the spectral response and increase the molar extinction coefficient of the sensitizers, leading to a cell efficiency of 3.34%.¹⁷ Recently, Lin and co-workers reported a series of 2,6-conjugated anthracene sensitizers.18 The best performing anthracene dye achieved a PCE of 9.11%.

Previous work showed that the use of a vinyl unit in the conjugated-linker of indoline-based D- π -A organic dyes is detrimental to the molecular dipole moment, giving a lower photovoltage.19 We anticipated that incorporation of a C-C triple bond at the appropriate position of dye molecules would increase the molecular dipole moment and enhance the $V_{\rm OC}$ of the devices. Herein, we describe the molecular design and synthesis of three new and simple D- π -A sensitizers MS1-MS3, where the arene unit is directly connected to the diphenylamine and varies from benzene to naphthalene and anthracene. An acetylene group is employed to bridge the donor and acceptor (Fig. 1). We investigate their optical, electrochemical, and photovoltaic properties along with DFT calculations to understand how the structural feature influences the cell performance of the DSSCs. The best performing dye MS3 achieves an efficiency of 5.44% with $J_{\rm SC}/{\rm mA~cm^{-2}}=8.16, V_{\rm OC}/{\rm mV}=866,$ FF = 0.76. To the best of our knowledge, the **MS3** dye shows the highest V_{OC} for DSSC devices using I^{-}/I_{3}^{-} as the electrolyte.

Results and discussion

In anthracene-containing molecules, most unsaturated bridges such as C–C double bond and arene twist out of plane with anthracene ring to avoid steric strain. Insertion of a C–C triple bond in between the anthracene and unsaturated units is the only way of making effective conjugated connections. Previous studies on mixed-valence systems, of which two redox centres were coupled by a variety of arene bridges, showed that the strength of electronic communication decreased in the order of bridging units: benzene > naphthalene > anthracene.²⁰ However, in the presence of C–C triple bonds the



Fig. 1 Molecular structures of triarylamine-based organic dyes MS1, MS2 and MS3.

ethynylanthracene-type of bridges effectively mediates the electronic coupling between the redox centers, thus playing the role of a "molecular wire" allowing efficient charge transfer.²¹ As mentioned, the most widely used donor for efficient organic dyes is triphenylamine unit, which is generally connected to the acceptor via a C-C double bond, aromatic ring, or oligoaromatic units for effective conjugation. In contrast, 9-(diphenylamino) anthracene-type moieties have not been used as a donor for DSSC application. Therefore, we designed MS3 by employing for the first time such a aminoanthracene donor in combination with a highly conjugated C-C triple bond connected to the acceptor for use in DSSCs. Compared to traditional triphenylamine based organic dye, the molecular design of MS3 combines several merits, *i.e.* simple molecular structure, strong coupling between the donor and acceptor by the acetylene unit, facile modification of the molecular structure with the presence of a π -extended donor being able to cause the absorption broadening and red-shifted spectral response. Sensitizers MS1 and MS2 were also designed and prepared for comparison to demonstrate the significance of anthracene moiety.

The synthesis of **MS1–MS3** is simple and straightforward. As an example, Scheme 1 shows the synthetic route for **MS3**. Amination of 9-bromoanthracene with diphenylamine 1 gave triarylamine donor 2, which was than brominated with NBS to afford 3. Sonogashira coupling of 3 with silylated acetylene produced intermediate 4. Desilylation of 4 followed by Sonogashira coupling with 4-iodobenzoic acid afforded the desired product **MS3**. A procedure similar to that of **MS3** was employed for the synthesis of **MS1** and **MS2** except that the starting materials for the amination step were different. All these new sensitizers were characterized by a variety of spectroscopic techniques. Detailed synthetic procedures and characterization data are given in the ESI.[†]

The absorption spectra of the three dyes in THF are shown in Fig. 2 and the data are listed in Table 1. The absorption increases on going from **MS1** to **MS3** along with significant red shifts of the maximum as the π -system of the donor is expanded. Dyes **MS1** and **MS2** exhibits absorption bands at 375 ($\varepsilon = 3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 408 ($\varepsilon = 1.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$),



Scheme 1 Synthesis of organic dye MS3. (a) $Pd(OAc)_2$, $P(t-Bu)_3$, NaO-t-Bu, toluene (83%). (b) NBS, CH_2Cl_2 (96%). (c) Ethynyltrimethylsilane, $Pd(PPh_3)_2Cl_2$, Cul, THF, Et_3N (47%). (d) (i) TBAF/THF; (ii) $Pd(PPh_3)_2Cl_2$, Cul, Et_3N, THF (62%).



respectively, due to $\pi - \pi^*$ transition. Sensitizer **MS3** shows two absorption bands at 400 nm ($\varepsilon = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 485 nm ($\varepsilon = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The band at 400 nm can be attributed to $\pi - \pi^*$ transition of the conjugated system whereas the one at 485 nm corresponds to intramolecular charge transfer from the donor to the acceptor. Replacement of benzene or naphthalene by an anthracene unit leads to a significant red shift of the absorption, showing that introduction of an anthracene unit successfully decreases the band gap and gives improved light-harvesting efficiency for **MS3** as compared to **MS1** and **MS2**. A trend similar to the absorption properties was also observed for the emission behaviour, dye **MS3** showing an emission maximum at 535 nm, which is 69 and 102 nm red-shifted as compared to **MS2** and **MS1**, respectively.

Electrochemical properties

Electrochemical analysis employed cyclic voltammetry to determine the redox potentials of **MS1**, **MS2** and **MS3**, cyclic voltammetry using dry CH_3CN as a solvent and 0.1 M TBAPF₆ as supporting electrolyte and ferrocene as internal reference. The temperature was 25 °C and the potentials *vs.* Fc⁺/Fc were converted to normal hydrogen electrode (NHE) by addition of +0.63 V. The electrochemical data are summarized in Table 1. All the organic sensitizers exhibit reversible waves for the first oxidation with potentials at +1.17, +1.18, and +1.09 V for **MS1**, **MS2**, and **MS3**, respectively, corresponding to the HOMO energy levels (Fig. 3). Replacing anthracene by benzene elevated the HOMO energy level. The HOMO levels of these organic dyes are

all more positive than the oxidation potential for I^-/I_3^- redox mediator (+0.4 V vs. NHE),²² providing ample driving force for effective dye regeneration (Fig. 4).²³ The excited-state oxidation potentials (E_{0-0}^*) are obtained from the equation, $E_{0-0}^* = E_{0x1} - E_{0-0}$, in which E_{0x1} is the first oxidation potential of the organic dye and the E_{0-0} is the zero-zero excitation energy corresponding to the LUMO levels determined from the intersection of the corresponding absorption and emission spectra.²⁴ The derived E_{0-0}^* values are all more negative than the conduction edge (-0.50 V vs. NHE) of TiO₂, indicating that the driving force is sufficient for electron injection from the photo-excited sensitizers to the conduction band (CB) of TiO₂.

To gain insight into the electron distribution of the frontier and close-lying orbitals, we performed quantum-chemical calculations on these sensitizers using density-functional theory (DFT) at the B3LYP/6-31G(d) level (Spartan 08 package). To simplify the computations, methyl groups replaced the alkyl groups attached to the phenyl rings. As shown in Fig. S1 (ESI),† the HOMOs of these organic sensitizers are mainly distributed on the diarylamine, phenyl, naphthalene or anthracene segments whereas the electron distribution of the LUMOs is primarily located on the benzene, naphthalene or anthracene, and the pull unit. The HOMO–LUMO band gap decreases upon extension of π -conjugation, which is consistent with the trend shown in Fig. 4. The electron distribution of the frontier orbitals for these dyes is suitable for efficient DSSC devices, *i.e.*, the C–C



Fig. 3 Cyclic voltammograms of MS1, MS2 and MS3 in CH_3CN containing 0.1 M TBAPF_6 at 25 $^\circ\text{C}.$

Table 1 Spectral, electrochemical and photovoltaic properties of MS1, MS2 and MS3. ^{a,b}									
Species	Absorption $\lambda_{\max} [nm] (\epsilon/10^3 M^{-1} cm^{-1})$	Emission λ_{\max} [nm]	Oxidation $E_{1/2}$ [V]	Reduction $E_{\rm pc}$ [V]					
MS1	375(30)	433	+1.11	-1.74, -2.25					
MS2	408(16)	466	+1.12	-1.61, 1.92, -2.24					
MS3	400(13), 485(12)	535	+1.15	-1.48, -1.87					

^{*a*} Absorption and emission data were measured in THF at 25 °C. ^{*b*} Electrochemical measurements were performed at 25 °C for **MS1–MS3** in THF containing TBAPF₆ (0.1 M) as supporting electrolyte. Potentials were reported *versus* NHE with the ferrocene/ferrocenium (Fc/Fc⁺) couple in CH₃CN: (+0.63 V *vs* NHE). The excitation wavelengths were 433, 466, and 535 nm for **MS1**, **MS2**, and **MS3**, respectively.



Fig. 4 Schematic energy levels of MS1, MS2 and MS3 based on electrochemical, absorption and emission data.

triple bond efficiently relay electron density from the donor to the acceptor facilitating charge separation upon photo-excitation of the dyes.

Photovoltaic characteristics

Double layer TiO₂ films are sensitized by dipping in a dye a solution in CHCl₃-EtOH = (1 : 4, v/v) as a solvent mixture for 12 h. The devices used a solution of 1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.03 M I₂, 0.1 M guanidinium thiocyanate in a mixture of acetonitrile-valeronitrile (85:15, v/v) as the redox electrolyte (Z959). The photovoltaic performance of all the devices is summarized in Table 2. The photocurrent densityvoltage (J-V) curves of liquid DSSCs based on MS1, MS2, and MS3 under simulated AM1.5G irradiation are shown in Fig. 5. The most striking feature is that the DSSCs of this dye series exhibited very high V_{OC} values exceeding 800 mV. The broadened absorption band of MS3 results in much higher photocurrent than those of MS2 and MS1. As a consequence, MS3 produced an enhancement of power conversion efficiency (PCE) by around 2- and 2.8-fold relative to MS2 and MS1, respectively. The resulting MS3-based devices showed PCE of 5.44% with a $J_{\rm SC}$ of 8.16 mA cm⁻², a $V_{\rm OC}$ of 866 mV, and an FF of 0.76. Given the relatively low $J_{\rm SC}$ values the obtained $V_{\rm OC}$ values are extraordinary high, which is the characteristic property of the newly designed dyes.

The maximum IPCE values for all three dyes reach around 80%, indicating efficient charge separation and carrier



Fig. 5 I-V characteristics of the devices made with MS1, MS2, MS3 and (MS3 with 2 mM CDCA) dyes used Z959 redox electrolyte.

collection, although the overall cell efficiencies are not very high due to the narrow absorption band in the visible region (Fig. 6). **MS3** showed much broader incident photon-to-current conversion efficiencies (IPCE) compared to references **MS1** and **MS2** is in good agreement with the absorption spectra, integration of the IPCE spectra is consistent with J_{SC} values observed in the J-V curves shown in Fig. 5.

EIS analysis of MS1, MS2 and MS3

We performed electrochemical impedance spectroscopy to ascertain the cause of the high V_{OC} values exhibited by the 3



Fig. 6 Photocurrent action spectrum (IPCE) of the same devices made with MS1, MS2, MS3 and (MS3 with 2 mM CDCA).

Table 2 Photovoltaic characteristics for DSSCs based on MS1, MS2 and MS3 using $CHCl_3$ -EtOH (1 : 4) as sensitizing bath solvent and Z959 (volatile) as electrolyte, with or without CDCA as co-adsorbent^a

Species	$\mathrm{DL}^{b}\left[\mathrm{nmol}\ \mathrm{cm}^{-2} ight]$	Power $[mW \ cm^{-2}]$	CDCA	$J_{ m SC}[{ m mA~cm^{-2}}]$	$V_{\rm OC} [{\rm mV}]$	FF	η [%]
MS1	181	99.47	0 mM	3.10	810	0.76	1.92
MS2	178	99.60	0 mM	4.35	844	0.75	2.75
MS3	141	98.90	0 mM	8.16	866	0.76	5.44
MS3	128	99.35	2 mM	8.30	856	0.76	5.45

^{*a*} The active area of DSSCs is 0.283 cm² however they are measured using a black metal mask with an aperture area of 0.159 cm². ^{*b*} The amounts of dye loading indicated as **MS1**, **MS2**, **MS3** and (**MS3** with 2 mM CDCA) were determined from the desorption of dye molecules on immersion of sensitized TiO₂ electrodes in a basic solution 0.05 M tetrabutylammonium hydroxide in EtOH and the calibrated absorption spectra of each dye.



Fig. 7 (a) Dark current during the EIS measurement for devices employing sensitizers MS1 (red), MS2 (blue) and MS3 (green). (b) Main parameters extracted from the EIS measurement (R_{CT} = circles; R_{trans} = squares; C_{chem} = triangle). Inset shows the potential plotted against the DOS.

sensitizers. The dark currents of the 3 devices sensitized by **MS1** to **MS3** show similar behaviour, though the **MS1** device exhibits a lower dark current in the potential region where the mesoporous TiO_2 is insulating (<450 mV) and a slightly higher dark current at higher forward bias.

The dark current of the devices nicely mirrors the behaviour of the charge transfer resistance ($R_{\rm CT}$, representing at low forward bias the electron transfer from the FTO of the photoanode to triiodide anions and at higher forward bias the reduction of from the mesoporous TiO₂ to the oxidized form of the redox couple) extracted from the EIS measurements by the transmission line model (see Fig. 7). Furthermore Fig. 7 shows the R_{trans} the resistance for electron transport within the nanocrystalline TiO₂ film and the chemical capacitance $(C_{\text{chem}}; \text{ representing the filling of the density of states (DOS)}$ inside the TiO₂). From these data (see Fig. 7B and also the inset) there does not appear to be a difference in the TiO₂ conduction band edge position between the 3 dyes. This indicates that the dipole moment of the dyes plays a minor role in influencing the device $V_{\rm OC}$. Therefore the differences in $V_{\rm OC}$ of devices with MS1-MS3 can only originate from the amount of charges injected into the TiO₂ by the dye under illumination and the difference in their recombination behaviour.

In Fig. 8 we plot the electron lifetime (τ_e) and electron transport time (τ_{trans}), calculated from the product of the respective resistance with the chemical capacitance, (*i.e.* $\tau_e = R_{CT} \times C_{chem}$ and $\tau_{trans} = R_{trans} \times C_{chem}$), against the density of states. Values are similar for **MS2** and **MS3** under forward bias close to the V_{OC} while **MS1** shows a two times shorter electron lifetime. Expressing the change in the V_{OC} by the diodide equation in terms of electron lifetimes and short circuit current density change yields the following formula:

$$\Delta V_{\rm OC} = (k_{\rm B}T/q)\ln((J_{\rm SC,dye1}/J_{\rm SC,dye2})(\tau_{\rm n,dye1}/\tau_{\rm n,dye2}))$$
(1)

where $k_{\rm B}$ is the Boltzmann constant, q the elementary charge and T the absolute temperature (the diode ideality factor is assumed to be one). The difference in the electron lifetimes can be calculated on the basis of formula (1) yielding a gain of $V_{\rm OC}$ for the dyes **MS2** to **MS1** of 28 mV and **MS3** in relation to **MS1** of about 45 mV in close agreement with the observed values (36 and 56 mV). The increase in the electron lifetime of **MS2** and **MS3** compared to **MS1** might be due to the bulkier size of the donor retarding the approach of triiodide closer to the TiO₂ surface and reducing the recombination rate. The combination of higher charges injected into the TiO₂ and the bulkier



Fig. 8 Electron lifetime (solid) and electron transport time (dotted) plotted against the DOS. Inset shows the electron lifetime and electron transport time plotted against the applied potential.



Fig. 9 Main EIS parameters of devices made with MS3 with (black) and without (green) CDCA plotted against applied potential. Inset shows the electron transport and electron lifetime plotted against the chemical capacitance.

anthracene group of **MS2** and **MS3** is responsible for the observed higher $V_{\rm OC}$.

We also investigated the effect of chenodeoxycholic (CDCA) on the performance of devices sensitized by **MS3**. CDCA is often added to the solution of sensitizers to prevent aggregation. Normally, CDCA addition increases $J_{\rm SC}$ but decreases the $V_{\rm OC}$ values due to a downward shift of the TiO₂ conduction band.

The EIS measurements in the dark confirmed the downward shift in the conduction band of the TiO_2 by 15 to 20 mV due to the protons of CDCA (Fig. 9), while there is practically no change in the electron lifetime (see inset in Fig. 9).

Conclusions

In summary, a series of novel D- π -A organic dyes were synthesized and used in DSSCs in combination with a liquid I^{-}/I_{3}^{-} electrolyte. This series of sensitizers help to elucidate the structure-property relationships influencing the cell performance. Incorporation of an anthracene unit into the donor as well as acetylene as an effective bridge significantly increases the spectral coverage of the dye, giving an improved light-harvesting efficiency. Considering the simplicity of the molecular structure of MS3, this benchmark anthracene-containing dye showed a good cell performance of 5.44% and an exceptionally high $V_{\rm OC}$ of 866 mV. Whereas the reference dyes $\rm MS1$ and $\rm MS2$ also exhibited high VOC values of 810 and 844 mV and lower overall efficiencies of 1.92% and 2.75%, respectively. This trend shows a systematic increase in the $V_{\rm OC}$ by increasing the π -conjugation from phenyl to anthracene. Substitution of anthracene with amino donor and acetylene bridge at the axial 9,10-positions has been demonstrated to be a promising approach for efficient dyes. We are modifying the molecular structures by extending the π -conjugation of the bridge to improve the light-harvesting capability and its influence on the device power conversion efficiency.

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