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Chemical compatibility between a hole conductor and organic dye enhances the photovoltaic performance of solid-state dye-sensitized solar cells[†]

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A series of organic dyes having an unsymmetrical geometry, $3-(5'-\{4-[(4-tert-butyl-phenyl)-(4-fluoro$ $phenyl)-amino]-phenyl}-[2,2']bithio-phenyl-5-yl)-2-cyano-acrylic acid ($ **D-F** $), <math>3-(5'-\{4-[(4-tert-butyl$ $phenyl)-p-tolyl-amino]-phenyl}-[2,2'] bithiophenyl-5-yl)-2-cyano-acrylic acid ($ **D-CH**₃), and <math>3-(5'- $\{4-[(4-tert-butyl-phenyl)-(4-methoxy-phenyl)-amino]-phenyl\}-[2,2']bithiophenyl-5-yl)-2-cyano-acrylic$ acid (**D-OCH**₃), were designed and synthesized for use in solid-state dye-sensitized solar cells (sDSCs).The dye regeneration energy levels and surface properties were characterized to determine the holetransfer yield from the oxidized dye to the hole conductor (spiro-OMeTAD) by measuring the degree ofpore-filling by the spiro-OMeTAD and the transient absorption spectra (TAS). An electrode sensitizedwith**D-OCH** $₃ exhibited the highest spiro-OMeTAD filling fraction and hole transfer quantum yield (<math>\Phi$) to spiro-OMeTAD, resulting in an enhanced photocurrent and a power conversion efficiency of 3.56% in the sDSC, despite a lower energy driving force for hole transfer compared to those of **D-F**, or **D-CH**₃. This result illustrates the importance of the chemical compatibility between the hole conductor and the dye on the surface of TiO₂.

Introduction

Despite the successful demonstration of dye-sensitized solar cells (DSCs) by O'Regan and Grätzel in 1991,¹ problems associated with liquid electrolyte leakage or the use of corrosive iodine as a redox couple have limited the commercial applications of DSCs.² Alternative iodine-free solid-state DSCs (sDSCs) that use organic hole conductors or hole transport materials (HTMs) that could replace the liquid electrolytes have been considered, and these materials may also be useful in flexible solar cells.³⁻¹¹ Among the HTMs, 2,2',7,7'-tetrakis-(*N*,*N*-di-*p*-methoxyphenyl-amine) 9,9'-spirobifluorene (spiro-OMeTAD)³ has been used most frequently. sDSCs with power conversion efficiencies (PCE) exceeding 6% were recently demonstrated, ^{12,13} although this PCE remains significantly lower than the PCE typical of liquid electrolyte-based DSCs, around 11%.^{14,15}

In sDSCs, electrons are injected from the excited state of the dyes into the conduction band of the TiO_2 upon light absorption by the dye. The electrons then undergo trap-limited diffusion through the interconnected TiO_2 layer. The resulting oxidized

dyes are then regenerated to their original state by hole transfer to the HTMs. An interfacial recombination reaction between the injected electrons in TiO₂ and the cationic HTMs (HTM⁺) or dye cations (dye⁺) constitutes a major loss mechanism that competes with these transport processes.¹⁶ Among the electrochemical reactions in sDSCs, hole transfer and recombination processes are crucial for determining the device performances because electron injection occurs on the femto- to picosecond time scale, whereas hole transfer and recombination reactions generally occur more slowly, on the microsecond and micro- to millisecond time scales, respectively.¹⁷ Two main factors affect the efficiency of hole transfer: the driving force for hole transfer and the pore filling characteristics. Haque et al. tested a variety of dye and HTM combinations with various energetic driving forces for hole transfer ($\Delta G_{dve-HTM}$). They showed that the $\Delta G_{dve-HTM}$ was strongly related to the hole transfer yield from the dye⁺ to the HTM via transient absorption spectroscopy (TAS) measurements. That is, large values of $\Delta G_{dye-HTM}$ resulted in high hole transfer yields.7 The pore filling characteristics of the HTM into the porous TiO₂ network determine the hole transfer efficiency by affecting the degree of interfacial contact.¹⁸⁻²⁰ Because organic HTMs are solid-state hole conductors, physical contact between the HTM and the TiO₂ surface is not perfect, and defect sites could not facilitate hole transfer. Schmidt-Mende et al. qualitatively investigated the pore filling characteristics of various HTMs using scanning electron microscopy (SEM) and reported that spiro-OMeTAD exhibited good filling of a 2 µm thick TiO₂

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film.¹⁸ Kroeze *et al.* compared several polymeric HTMs with spiro-OMeTAD and revealed that the hole transfer yield was affected by pore filling (or filling fraction) rather than the HTM conductivity. In addition, they reported that the hole transfer yield was linearly correlated with the photocurrent in the devices.¹⁹

Intensive efforts have been devoted to enhancing the pore filling characteristics of HTMs into TiO₂ by investigating the interfacial properties with various HTMs; however, other parameters, including the HTM molecular weight, hole mobility, energetic driving forces, and morphology of the HTMs, often limit the utility of a direct comparison of the HTMs. Here, we used unsymmetrical organic dyes which have similar structures except one substituent, thus this could be able to control the hole transfer yield caused by the parameters. To the best of our knowledge, no studies have addressed a comparison of the pore filling characteristics of spiro-OMe-TAD in the presence of different dyes. We found that good compatibility between the dyes and spiro-OMeTAD was important. Here the chemical compatibility means wetting properties of two different media as a general rule in chemistry, 'like dissolve like', to make better physical contact. This is consistent with the suggestion by Snaith et al. that spiro-OMe-TAD infiltration may be influenced by the chemical nature of the pendant groups on the dyes.²¹ In the present report, a series of unsymmetric organic dyes with various energy levels and chemical natures were designed to systematically investigate the dye regeneration properties and photocurrent in devices. Unsymmetric organic dyes may be prepared simply by changing the end functional groups in the dye architecture, which provides a method for controlling the energy levels of the dyes and surface properties without introducing significant differences in their chemical properties. For example, a fluorinated organic dye (D-F) would have a deep HOMO level, whereas a methoxy-substituted organic dye (D-OCH₃) would have a high HOMO level, and a methyl-substituted organic dye (D-CH₃) would have a moderate HOMO level. Given the $\Delta G_{dve-HTM}$ values of the organic dyes, the pore filling characteristics were examined according to the method reported by Ding et al. using absorption spectroscopy and cross-sectional scanning electron microscopy (SEM).²⁰ The hole transfer yields were studied by TAS and were correlated with the factors mentioned above as well as the short-circuit current density (J_{SC}) of the sDSCs. The structures of the organic dyes and the spiro-OMeTAD used in this study are shown in Fig. 1.

Fig. 1 Chemical structures used in this study: (a) organic dyes D-F, D-CH₃, and D-OCH₃ and (b) hole transport material, spiro-OMeTAD.

Spiro-OMeTAD

Results and discussion

Properties of the organic sensitizers

The absorption and emission spectra of the organic dyes in an ethanolic solution are shown in Fig. 2(a). The absorption maxima were slightly red-shifted from 440 to 456 and 449 nm on going from D-F to D-CH₃, and D-OCH₃ due to the electrondonating (-CH₃) and mesomeric (-OCH₃) effects, which induced strong intramolecular charge complexation of the donor (D)– π – acceptor (A) system of organic dyes. Other optical properties, including the width of the absorption windows and the extinction coefficients (36 400 M⁻¹ cm⁻¹ for D-F and D-CH₃, and 35 300 M^{-1} cm⁻¹ for **D-OCH₃** as summarized in Table 1) were comparable across the three dyes, indicating similar light harvesting behavior for the generation of a photocurrent based on the device architecture. The absorbance band edges of the dyecoated TiO₂ films in Fig. 2(b) were 10 nm red-shifted compared with the values in solution, properties which favor better light harvesting. These effects appeared to result from interactions between the anchoring groups and the surface titanium ions, as well as from the scattering effects of light in the mesoporous TiO₂.22

The electrochemical properties of the organic dyes were measured using cyclic voltammetry (Fig. 3), and the resulting



Fig. 2 (a) Normalized absorbance (solid line) and emission (dashed line) spectra of **D-F** (red square), **D-CH**₃ (blue circle), and **D-OCH**₃ (green triangle) in an ethanolic solution and (b) normalized absorbance of **D-F**, **D-CH**₃, and **D-OCH**₃-coated TiO₂ films.

Table 1 Absorption–emission spectral data and the electrochemical properties of D-F, D- CH_3 , and D- OCH_3

	Abs _{max} (nm)			_	_	_	_
	Solution	Film	ϵ (M ⁻¹ cm ⁻¹)	Em _{max} (nm)	$E_{(S+/S)}$ [V]	$E_{(0-0)}$ [V]	E _(S+/S*) [V]
D-F D-CH ₃	440 445	448 456	36 400 36 400	614 622	1.13 1.09	2.38 2.35	-1.25 -1.26

D-CH₃: R = CH₃



Fig. 3 Cyclic voltammograms for the D-F (red square), D-CH₃ (blue circle), and D-OCH₃ (green triangle)-coated TiO_2 electrodes.

 $E_{(S+/S)}$ (HOMO) and $E_{(S+/S^*)}$ (LUMO) levels are summarized in Table 1 together with the optical properties. The LUMO level of a dye is directly related to electron injection from the dye to TiO_2 . The value can be calculated from the ground-state oxidation potential and zeroth-zeroth excitation energy $E_{(0-0)}$ based on the equation: $E_{(S+/S^*)} = E_{(S+/S)} - E_{(0-0)}$. From the crossing point of the absorption and emission spectra, the $E_{(0-0)}$ energies of 2.38, 2.35, and 2.36 eV were extracted for D-F, D-CH₃, and D-OCH₃, respectively. The LUMO levels of these dyes exceeded -1.25 V vs. NHE and were more negative than the conduction band of TiO₂, thereby favoring rapid electron injection. The HOMO levels of the organic dyes fell in the range 1.02-1.13 V vs. NHE. Considering that the oxidation potential of spiro-OMeTAD was 0.81 V vs. NHE, it was thought that the driving force that enabled dye regeneration to compete with the back reaction of the injected electrons with the oxidized dyes was sufficient (see Fig. 6).

The dipole moment of an organic molecule at the organicinorganic interface affects the position of the band edge level. Surface modification by a sensitizer or organic co-adsorbent with a high dipole moment has been employed to obtain a high $V_{\rm OC}$ for the dye-sensitized solar cells²³⁻²⁵ because the $V_{\rm OC}$ is determined by the energy difference between the quasi-Fermi level of the TiO₂ and the HOMO level of HTM under illumination. For our system, the three organic dyes were expected to have different dipole potentials, which would result in variations in $V_{\rm OC}$ for the sDSCs. We performed DFT calculations to determine whether the $V_{\rm OC}$ could be tuned according to the surface dipole upon adsorption onto the TiO2 surface. As a simple comparison, we assumed a monodentate coordination mode through the carboxylic group of the sensitizer with transfer of the acidic proton to the surface. The location effects of the protons and counter ions on the dipole potentials of the TiO₂ surface were negligible in the comparison of the three dyes having identical main chain structures. As shown in Fig. 4, the optimized geometric structures of the three dyes were similar; however, the orientations of their dipole moments differed slightly. Along with x and y axes, **D-F** showed the highest dipole moment projections, -0.76 and 1.47 Debye, respectively, whereas the projection along the z axis was the lowest among the dyes (1.07 Debye). This prediction was reasonable based on a comparison of the HOMO levels of the three dyes because the main backbone of the dye, connecting the donor to the acceptor, lay along the z axis rather than the x or y axis, indicating less charge complexation between the donor and acceptor for D-F. This provided a deeper HOMO



Fig. 4 Optimized geometrical structures of the D-F (left), D-CH₃ (middle), and D-OCH₃ (right) dyes adsorbed onto a $Ti_{44}O_{78}$ cluster.

level, as seen in the cyclic voltammetry measurements. The dipole component normal to the TiO₂ surface also provided information about the degree of shifting in the energy level of the conduction band in TiO₂. The dipole moments normal to the TiO₂ surface (along the z axis) calculated for D-F, D-CH₃, and D-OCH₃ were 1.07, 1.45, and 1.61 Debye, respectively, as summarized in Table 2. A higher positive dipole moment along this direction indicated a negative sign in the dipole component, *i.e.*, a negative pole was localized close to the TiO_2 surface. Therefore, D-OCH₃ was expected to induce a higher electron density at the TiO₂ surface compared to that of D-F, and D-CH₃, resulting in a higher $V_{\rm OC}$ in the solar cell device. We note that the differences between the dipole components along the z axis for the three dyes were much too small to affect the $V_{\rm OC}$. Significant differences in the dipole moment, for example, -30.1 for the N621 dye and 7.7 for the JK2 dye, yielded a difference in the $V_{\rm OC}$ of less than 0.2 V.²³ The approximate difference in V_{OC} between D-F- and D-CH₃-sensitized devices, according to the literature, provided only a 2.7 mV difference, which fell within the experimental error.

Photovoltaic properties

Fig. 5 shows the current–voltage characteristics of sDSCs sensitized with the organic dyes, and the photovoltaic parameters are listed in Table 3. Although the open circuit voltages (V_{OC}) for the three devices were similar, 0.71–0.72 V, as expected based on the DFT calculations, the short-circuit current density (J_{SC}) gradually increased from 7.58 to 8.45 or 9.26 mA cm⁻² on going from sDSCs sensitized with **D-F** to that with **D-CH3** or **D-OCH3**. Overall efficiencies of 2.68%, 3.07%, and 3.56% were achieved in sDSCs sensitized with **D-F**, **D-CH3**, and **D-OCH3**, respectively. Considering that the light harvesting characteristics of the three dyes were similar, other factors, such as charge separation at the

Table 2 Calculated dipole components for the D-F, D-CH₃, and D-OCH₃ dyes^{α}

	Dipole components (Debye)			
Sensitizer	μ_x	μ_y	μ_z	
D-F D-CH ₃ D-OCH ₃	$-0.76 \\ -0.69 \\ -0.56$	1.47 1.19 1.01	1.07 1.45 1.61	

^{*a*} The *z* axis corresponds to the TiO_2 surface normal.



Fig. 5 Current–voltage characteristics of sDSC incorporating D-F (red square), D-CH₃ (blue circle), and D-OCH₃ (green triangle).

Table 3Photovoltaic performance of solid-state DSCs incorporating D-F, D-CH₃, and D-OCH₃ under 1 sun light intensity^a

Dye	$J_{\rm SC}~({\rm mA~cm^{-2}})$	$V_{\rm OC}({\rm mV})$	ff (%)	η (%)
D-F ^b D-CH ₃ ^b D-OCH ₃ ^b	$\begin{array}{c} 7.58 \pm 0.04 \\ 8.45 \pm 0.08 \\ 9.26 \pm 0.07 \end{array}$	$\begin{array}{c} 723 \pm 4.27 \\ 710 \pm 4.57 \\ 717 \pm 5.80 \end{array}$	$\begin{array}{c} 48.2 \pm 1.61 \\ 50.4 \pm 1.41 \\ 53.5 \pm 1.29 \end{array}$	$\begin{array}{c} 2.68 \pm 0.07 \\ 3.07 \pm 0.10 \\ 3.56 \pm 0.11 \end{array}$

 a Values were obtained using the average over 4 devices for each experiment. b Active area of 0.16 cm² and AM 1.5G photon flux.

 TiO_2 -dye-HTM surface or charge transport phenomena, may be more significant in determining J_{SC} .

From an energetic point of view, electron injection from the excited dye to the conduction band of TiO₂ and hole transfer from the cationic spiro-OMeTAD to the oxidized dye are governed by the energy differences, $\Delta G_{\text{TiO}_{7}-\text{dye}}$ and $\Delta G_{\text{dye}-\text{HTM}}$, respectively. As shown in Fig. 6, D-OCH₃ yielded the largest $\Delta G_{\text{TiO}_{7}-\text{dve}}$ and was expected to have the highest energetic driving force for electron injection. $\Delta G_{dye-HTM}$ was largest for D-F, which resulted in the highest driving force for hole transfer. Because the energy differences between the TiO₂ conduction band and the dye LUMO levels were sufficiently large ($\Delta G_{\text{TiO}_2-\text{dye}} > 0.75 \text{ V}$) and the electron injection process was ultrafast, occurring on the femtosecond to picosecond time scale, slight differences in the LUMO levels of the dyes did not appear to contribute to the photocurrent differences.¹⁷ Dye regeneration generally occurs more slowly than electron injection, on the micro- to millisecond time scale, indicating regeneration-limited charge separation at the heterogeneous interface. We showed previously that the energetic driving force $\Delta G_{dve-HTM}$ is directly



Fig. 6 Relative energy levels of the components in solid-state dyesensitized solar cells.

related to the hole transfer yield;⁷ therefore, we can deduce that the different HOMO levels of the dyes affected the hole transfer yield from the oxidized dye to the HTM cation. The trend in J_{SC} for the three devices, however, did not follow the trend in $\Delta G_{dye-HTM}$: the sDSC sensitized with **D-OCH3** showed the highest J_{SC} despite having the smallest $\Delta G_{dye-HTM}$, indicating that the energetic driving force was not a limiting factor for the photocurrent in these organic dye systems.

Characterization of the interfacial properties

The charge transfer characteristics at the TiO2-dye-HTM interface, which can affect device performance, were investigated using electrochemical impedance spectroscopy (EIS) measurements under dark conditions.^{26,27} Charge recombination between the electrons in TiO₂ and the holes in spiro-OMeTAD, as well as charge transfer resistance at the spiro-OMeTAD-Ag interface, could be conveniently obtained using the EIS technique. Fig. 7(a) shows three distinct regions that depended on the frequency of the alternating current. The first semicircle in the high frequency range (1 MHz to 6.6 kHz), the second semicircle in the midfrequency range (6.6 kHz to 353 Hz), and the third semicircle in the low frequency range (353-0.1 Hz) were related to the charge transfer resistance at the spiro-OMeTAD-Ag counter electrode interface, the electron transport resistance in the TiO₂ particles, and the recombination resistance at the TiO2-dye-spiro-OMe-TAD interface, respectively.16,25

Here, we focused on a comparison of the recombination resistances (R_{ct}) at the TiO₂-dye-spiro-OMeTAD interfaces because the same counter electrode (silver) was used in the three devices. Fig. 7(a) shows the values of R_{ct} for the sDSCs sensitized



Fig. 7 (a) Nyquist plot of the EIS measurement for the sDSCs sensitized with **D-F** (red square), **D-CH₃** (blue circle), and **D-OCH₃** (green triangle) at a -0.65 V forward bias, along with the fit (solid line) to a transmission line model. (b) Recombination resistance (R_{ct} , solid line) and electron lifetimes (τ_e , dashed line) of **D-F** (red square), **D-CH₃** (blue circle), and **D-OCH₃** (green triangle)-coated sDSCs as a function of the applied forward bias, over the range -0.55 to -0.70 V.

with D-F, D-CH₃, and D-OCH₃ at a -0.65 V forward bias. The $R_{\rm ct}$ of the sDSCs gradually decreased from 3530 to 2630 or 2130 W cm⁻² for the devices sensitized with D-F, D-CH₃, or D-OCH₃, respectively, indicating a lower degree of charge recombination in the sDSC sensitized with **D-F** as compared with the sDSCs sensitized with D-CH₃ or D-OCH₃. Such result seems to be due to different physical contacts between TiO2 and spiro-OMeTAD at the TiO₂-dve-HTM interface. This trend did not, however, follow the short-circuit current density trend for the solar cells, which increased in the order of D-OCH₃, D-CH₃, and D-Fsensitized devices. This may be because the differences in charge recombination were too small to affect the J_{SC} , or the physical contact between the TiO2 surface and spiro-OMeTAD is a minor factor to govern the photocurrent in these organic-sDSC systems. Similar interfacial charge transfer characteristics were mainly attributed to the physical contact between the TiO₂ and the organic dyes rather than that with the spiro-OMeTAD. Pore filling by the spiro-OMeTAD into the mesoporous TiO₂ network was expected to be less extensive than pore filling by the liquid electrolyte.²⁸ The values of R_{ct} did not vary significantly over applied biases of -0.55 to -0.70 V (Fig. 7(b)). The electron lifetimes (τ_e) for the three devices, which could be extracted from the EIS data according to the following equation: $\tau_e = 1/2\pi f_{max}$, where f_{max} is the frequency at the peak in the Nyquist plot, provided similar values at a -0.65 V forward bias (9.8, 8.4, and 7.2 ms for the devices from D-F, D-CH₃, and D-OCH₃, respectively) and at all other biases (Fig. 7(b)), which was consistent with the measured values of R_{ct} . The EIS measurements showed that the charge transfer characteristics for the three devices were similar. This result was not surprising considering that the organic dyes varied by only a few atoms.

The enhanced photocurrent in the sDSC with D-OCH₃ could be explained in terms of the enhanced hole transfer yield. The hole transfer yield is sensitive to the energetic driving force as well as the extent of pore filling by the spiro-OMeTAD into the porous TiO₂ network. Ding et al. recently reported a method for estimating the filling fraction of spiro-OMeTAD using absorption spectroscopy together with scanning electron microscopy (SEM).²⁰ By dissolving the spin-coated spiro-OMeTAD layer on the dye-coated TiO₂ electrode, the total amount of spiro-OMe-TAD in the porous TiO_2 and overlayer could be estimated. Fig. 8(a) shows the UV-Vis spectra of the spiro-OMeTAD after immersing the spin-coated electrode in chlorobenzene for 2 hours. The solution was further diluted until the absorbance approached 1.0, to improve the measurement accuracy. The quantity of spiro-OMeTAD was highest for the D-OCH₃-coated TiO₂ electrode, whereas that for **D-F** showed the lowest value. Higher amounts of spiro-OMeTAD were, therefore, spin-coated onto D-OCH₃, although it was not possible to determine whether the coating infiltrated the TiO₂ pores or remained on top of the electrode, forming a thick overlayer. To estimate the filling fraction, cross-sectional SEM measurements were performed, and the thickness of the overlayer is shown in Fig. 8(b)-(d). The overlayer thickness was 308, 268, and 244 nm for D-F, D-CH₃, and D-OCH₃-coated TiO₂ electrodes, respectively. Because the thicknesses of the TiO_2 electrodes were similar (2 µm), the overlayer thickness was a direct indication of the pore filling characteristics. The absorption of spiro-OMeTAD after dissolving the spin-coated electrode was higher for the D-OCH₃-



Fig. 8 (a) Absorbance spectra of the spiro-OMeTAD solutions obtained by dissolving the spin-coated spiro-OMeTAD on the TiO_2 electrodes in chlorobenzene solvent: **D-F** (red square), **D-CH₃** (blue circle), and **D-OCH₃** (green triangle) anchored films. (b), (c), and (d) show crosssectional SEM images of the spiro-OMeTAD spin-coated TiO_2 electrode stained by **D-F**, **D-CH₃**, and **D-OCH₃**, respectively.

coated electrode than for the D-F and D-CH₃ electrodes, which had thinner overlayers. The filling fraction was estimated using the following parameters: spiro-OMeTAD molar extinction coefficient in chlorobenzene = $7.47 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, porosity of the TiO_2 film without dye modification = 0.68, porosity shrinkage for 20 nm TiO₂ particles after ruthenium dye modification = 30%²⁹ and spiro-OMeTAD density = 1.82 g cm^{-3} ²⁰ The filling fraction was calculated by dividing the volume of spiro-OMeTAD by the volume of the pores. The estimated filling fractions were 48%, 51%, and 64% for D-F, D-CH₃, and D-OCH₃-coated electrodes, respectively (Table 4). These values were not precise due to the 30% porosity shrinkage after dye modification in the case of the ruthenium complexes; however, the values are sufficient for comparing the series of organic dyes having similar volumes and densities at the TiO₂ surface. The enhanced photocurrent of the sDSC sensitized with D-OCH₃ appeared to result from better pore filling, which may have been due to better physical compatibility between the -OCH₃ group in the dye and the -OCH₃ group in the spiro-OMeTAD. The -CH₃ group was moderately compatible, and the -F group was poorly compatible with the spiro-OMeTAD.

The pore filling characteristics were verified by further investigating the hole transfer yields using transient absorption spectroscopy (TAS). The hole transfer yield (Φ) could be obtained by comparing the amplitude of the dye cation band in the presence of the spiro-OMeTAD with that in the absence of the spiro-OMeTAD.²² In the TAS experiments, the dye-coated electrodes

Table 4 The peak absorbances in Fig. 8(a), the overlayer thickness of the spiro-OMeTAD in Fig. 8(b)–(d), and the estimated filling fraction of the spiro-OMeTAD into the **D-F**, **D-CH**₃, and **D-OCH**₃-coated TiO₂ films

Dye	D-F	D-CH ₃	D-OCH ₃
Abs _{max}	1.15	1.21	1.42
Overlayer thickness (nm)	308	268	244
Filling fraction (%)	48	51	64

were initially excited by the pulsed laser and induced changes in the optical density (ΔOD) of the materials, including the oxidized dye and the cationic form of the spiro-OMeTAD. In the absence of spiro-OMeTAD, the decay of the Δ OD for the oxidized dye was related to the recombination reaction between the electrons in TiO₂ and the holes in the dye, which generally occurred on the micro- to millisecond time scale. On the other hand, in the presence of spiro-OMeTAD, the decay in the Δ OD for the oxidized dye was related to both hole transfer from the oxidized dye to the spiro-OMeTAD and to the recombination reaction mentioned above. Within 10 μ s of excitation, the Δ OD decay is associated with the efficiency of hole transfer from the oxidized dye to the spiro-OMeTAD. The signal for the recombination reaction appears in the range 10 µs to 1 ms. Therefore, detection of $\Delta OD 5 \mu s$ after laser excitation in the absence or presence of spiro-OMeTAD provided a direct indication of the hole transfer. In other words, the hole transfer quantum yield was $(\Phi) = 1 - \Phi$ $[\Delta OD(+HTM)]/[\Delta OD(-HTM)]$, where ΔOD should be measured at the peak absorbance of the dye cation. Fig. 9(a) shows the photoinduced absorption spectra 5 µs after excitation by the pulsed laser of a 2 μ m thick TiO₂ film stained with the organic dyes. The peak ΔOD at 710-750 nm reflected the oxidized dye, consistent with the spectra measured from organic dyes having similar structures, reported previously.²² The signal at wavelengths longer than 1000 nm was not included here due to the limitations of the experimental setup and the laser system. The signal at 1300 nm did not clearly indicate ΔOD by the oxidized dye due to weak absorption of the photoinduced electrons in the TiO₂ film.³⁰ Estimation of Φ , therefore, was difficult. The ΔOD of the oxidized dye in the absence of spiro-OMeTAD was reduced relative to that in the presence of spiro-OMeTAD, indicating that hole transfer occurred. Hole transfer was easily determined from the spectra because the three dyes exhibited



Fig. 9 (a) Photoinduced absorption spectra of a 2.5 μ m TiO₂ film stained with organic dyes in the absence (filled) or presence (empty) of spiro-OMeTAD. (b) Transient absorption data of the dye–TiO₂ films in the absence (upper trace) or presence (lower trace) of spiro-OMeTAD at 710 nm, following 530 nm excitation.



Fig. 10 Short-circuit current density (J_{SC}) and hole transfer yield (Φ) as a function of the spiro-OMeTAD filling fraction, determined using TAS.

different degrees of reduction, as reflected in the ΔOD , before and after infiltration of the spiro-OMeTAD. The changes in ΔOD were smallest for the electrode stained with **D-F** and largest for that stained with D-OCH₃. The calculated hole transfer yield to the spiro-OMeTAD was 50%, 60%, and 78% for D-F, D-CH₃, and D-OCH₃-coated electrodes, respectively. This result was consistent with the pore filling characteristics, indicating that better physical contact would provide more chances for hole transfer. Fig. 9(b) shows the transient absorption spectra for the electrodes, which yielded similar decay kinetics for the dye cation. The recombination kinetics at the electrodes stained by the dyes were similar, regardless of the spiro-OMeTAD. These results were consistent with the EIS measurements in which we observed no big difference in recombination resistance. One might expect that better physical contact between D-OCH₃ and the spiro-OMeTAD results in not only enhanced Φ but also more chances for charge recombination. However, at the heterogeneous TiO₂-dye-HTM interface, the interfacial properties were somewhat different from those in a liquid electrolyte system, as mentioned previously. Contact between TiO₂ and the spiro-OMeTAD was poor in comparison to the contact between the dye and the spiro-OMeTAD due to the passivation effects of the dye at the solid-state interface.²⁸ As a result, the hole transfer yield was dominated by the infiltration of spiro-OMeTAD rather than the energetic driving forces for the systems of organic dye sDSCs. Finally, the filling fractions (ff) of the spiro-OMeTAD in the mesoporous TiO₂ network, which depended on the chemical compatibility and determined the Φ and J_{SC} values for the solar cell devices, are plotted in Fig. 10. Apart from the fact that Φ was linearly correlated with J_{SC} , as reported by Kroeze *et al.*,¹⁹ it is worth noting that Φ and $J_{\rm SC}$ were linearly related to the filling fraction of the spiro-OMeTAD, i.e., the degree of infiltration into the TiO2. These results underline the importance of designing dyes and hole conductors with consideration for the chemical properties.

Conclusions

We studied interfacial charge transfer in sDSCs using unsymmetrically functionalized organic dyes. End functionalization shifted both the energy levels and surface properties at the TiO_2 film interface. The energetic driving forces and the pore filling characteristics of the spiro-OMeTAD into the mesoporous TiO_2 film are required for efficient hole transfer from an oxidized dye to an HTM. Small changes in the functional groups on a dye structure provide significant differences in the photocurrent density and power conversion efficiencies as well. Through systematic interfacial characterization, we revealed that the enhancement in $J_{\rm SC}$ for the **D-OCH**₃-sensitized sDSC resulted from good compatibility with the spiro-OMeTAD layer, resulting in a high hole transfer yield. Other parameters, including the light harvesting yield and interfacial recombination, were similar for all dyes, suggesting that end-functionalization provides a useful approach to tuning dye structures for use in sDSCs.

Experimental

Characterization of sensitizers

Cyclic voltammetry measurements (CV) were carried out in an acetonitrile solution containing tetrabutylammonium tetrafluoro-borate, TBA(BF₄), using a dye-coated TiO₂ film (2 μ m) as a working, Ag–AgCl reference electrode and a Pt wire as a counter electrode with a scan rate of 50 mV s⁻¹. Ferrocenium– ferrocene (Fc–Fc⁺) redox couple was used as an internal reference and potentials measured were converted to normal hydrogen electrode (NHE) by addition of +0.69 V.²² The UV-Vis absorption spectra of the dye solution in ethanol and dye-coated TiO₂ films were recorded on a Cary 5 spectrophotometer and emission spectra were recorded on a JASCO FP-6500.

Fabrication of dye sensitized solar cell

Dye-sensitized solar cells were fabricated on a fluorine-doped SnO₂ glass substrate (15 Ω sq⁻¹, Pilkington) after cleaning the substrate with Helmanex solution, deionized water, ethanol, and acetone in sequence. A 100 nm compact layer of TiO₂ was coated by aerosol spray pyrolysis of precursor solution at 450 °C using oxygen as the carrier gas.³¹ The 20 nm of nanocrystalline TiO₂ (Solaronix, T20/SP series) was deposited by the doctor blade technique to give a thickness of 2 μ m. The resulting TiO₂ films were then sintered at 500 °C under an oxygen flow. After cooling, the TiO₂ films were immersed in 40 mM of TiCl₄ solution at 70 °C for 30 min and then rinsed with deionized water. The TiCl₄-treated TiO₂ films were sintered at 450 °C for 30 min and then cooled to 80 °C followed by immersing in dye solution (0.3 mM of dye dissolved in ethanol) for 12 hours at room temperature. Then the hole transporting material 2,2',7,7'-tetrakis(N,N-di-p-methoxy-phenyl-amine) 9,9'-spirobifluorene (spiro-OMeTAD) solution (0.17 M) with additives of tBP (30 mM) and Li[CF₃SO₂]₂N (21 mM) was spin-coated at 2000 rpm for 30 s on top of the TiO₂ film. Finally, a 100 nm silver layer was evaporated on the top of the spiro-OMeTAD under ultrahigh vacuum (UHV).

Photovoltaic characterizations

A 450 W xenon light source (model no. 94022A, Oriel, USA) was used to give an irradiance of 100 mW cm⁻² (the equivalent of one sun at airmass (AM 1.5)) at the surface of solar cells to simulate solar light irradiation. The incident light intensity was calibrated with reference to a Si solar cell equipped with an IR-cut-off filter (KG-5, Schott). Comparison of the simulated light to the true solar spectrum in the region 350-750 nm determined a spectral mismatch of less than 2%. The *I*–*V* characteristics were obtained by measuring the photocurrent generated by the cells (under an applied external bias) using a Keithley model 2400 digital source meter (Keithley, USA). The voltage step and delay time for the measurement were 10 mV and 40 ms, respectively.

Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectra of sDSCs were measured using a computer-controlled potentiostat (SP-200, BioLogic, France) producing a small amplitude harmonic voltage, and a Frequency Response Analyzer module. The EIS experiments were performed at a constant temperature of 20 °C under dark conditions. The impedance spectra of the sDSC devices were obtained at various potentials (from -0.7 V to -0.55 V) at frequencies ranging from 0.05 Hz to ~1 MHz, the oscillation potential amplitudes having values of approximately 10 mV. In the EIS experiments, the photoanode (the dye sensitized TiO₂ electrode) was used as the working electrode, the Ag counter electrode (CE) being used simultaneously as both the auxiliary electrode and the reference electrode. The measured spectra were fit to an appropriate simplified circuit¹⁶ using the Z-fit software provided by BioLogic (EC-Lab).

DFT calculations

The molecular structures of dyes on a $Ti_{44}O_{78}$ cluster are performed using the Dmol3 package based on density functional theory (DFT).³² In the Dmol3 electronic structure calculations, the double numerical with d-polarization (DND) basis set is chosen. The density function is treated with the generalized gradient approximation (GGA)³³ with the Perdew–Burke–Ernzerhof (PBE) exchange correlation potential.³⁴ Dipole moments are calculated by using the Hirshfeld population analysis method.

Transient absorption spectroscopy (TAS)

Transient absorption experiments were conducted as reported previously.^{7,19,35–37} Pulsed laser excitation was applied using Continuum Surelite-II Q-switched Nd³⁺:YAG laser ($\lambda = 355$ nm, 10 Hz repetition rate). The output of the OPO (pulse width at half-height 5 ns) was tuned at 490 nm and attenuated to 20 µJ per pulse. The analyzer light, produced by a 150 W Xe arc lamp, was passed through the sample, and was detected by the avalanche photodiode (APD). A 1 GHz band-pass digital signal analyzer was employed to record the time course of the optical absorbance changes induced by laser excitation of the films. Satisfactory signal-to-noise ratios were typically obtained by averaging over 64 laser shots.

Estimation of filling fraction of spiro-OMeTAD

Sample preparation for the estimation of filling fraction of spiro-OMeTAD into mesoporous TiO₂ film is reported elsewhere.²⁰ After spin coating the spiro-OMeTAD solution, excess spiro-OMeTAD that was not on top of the TiO₂ film was removed by chlorobenzene. The thickness of the spiro-OMeTAD overlayer was measured by imaging cross-sectional scanning electron microscopy (Hitach S-4800) operated at an accelerating voltage of 3.0 kV. After the overlayer thickness measurement, the sample was immersed in chlorobenzene for one hour at room temperature. The resulting solution was further diluted until the optical density is close to 1.0 for accuracy. The absorption measurement was carried out in a Cary 5 spectrophotometer.

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