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Carbazole dye with phosphonic acid anchoring groups for long-term heat stability of dye-sensitized solar cells

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ABSTRACT

In dye-sensitized solar cells (DSSCs), the binding strength between the dye and TiO_2 surface may affect the heat stability of the DSSCs. Carboxylic acids have generally been used as the anchoring groups for the adsorption of dyes on TiO_2 surfaces. However, a phosphonic acid anchor is expected to effect more stable bonding to a TiO_2 surface because of its tridentate binding capability. In this study, we developed a new carbazole dye that employed a phosphonic acid anchor, MK-94. We studied the effect of the dye anchoring group on the heat stability of DSSCs by comparing MK-94, MK-2 (a carbazole dye with a carboxylic acid anchoring group), and Z-907 (a well-known, robust Ru complex dye with a carboxylic acid anchoring group).

In the initial performance assessment, the DSSC with MK-94 exhibited a lower short circuit current (j_{sc}) but a higher open circuit voltage (ΔV_{oc}) than MK-2. With respect to heat stability, decreases in j_{sc} and ΔV_{oc} were suppressed with MK-94, and the drop of the power conversion efficiency (PCE) was kept within 6% after 504 h of heating. In addition, MK-94 demonstrated the longest electron lifetime and largest charge transfer resistance than the other dyes during the stability test. In contrast, the PCE decreased 27% from the initial value in the DSSC with MK-2. Thus, the phosphonic acid anchor was effective in extending the long-term heat stability of the DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) are attractive photovoltaic devices because of the potential they offer in terms of color, transparency, and cost-effectiveness. Recently, commercial DSSC products appeared in the marketplace as light-harvesting devices. DSSCs have achieved over 11% performance (globally certified) and exhibited good heat stability at 60 °C [1,2]. However, for outdoor solar cell use, much higher heat stability at 85 °C is required [3–5]. Toward this end, ionic liquids and low volatility solvents such as 3-methoxypropionitrile have been used as candidate anti-volatile electrolytes [6,7], and improved sealing materials such as heat-stable polymer sealants and UV-cured resins have been applied [3,8]. The dyes are also important for enhancing the stability of the DSSCs; for example, dyes such as Z-907 bearing alkyl chains that increase the hydrophobicity at the TiO_2/electrolyte interface exhibited good stability [6,9]. In addition, the carbazole organic dye MK-2 showed good stability with an ionic liquid electrolyte [10–12]. The stability of the dye adsorption on TiO_2 is also important. Dissolution of the dye in trace amounts in the electrolyte may establish an adsorption equilibrium, which means that the dye adsorbed on TiO_2 may desorb at the TiO_2/electrolyte interface in the DSSCs. Therefore, a strong bond between the dye and TiO_2 is preferable to retain the dye in the photoelectrode, and the anchoring moiety is the significant part of the dye structure that mediates adsorption on TiO_2. Most ruthenium bipyridyl complexes used as dyes have more than two carboxylic acids as anchoring groups; they adsorb on TiO_2 through binding by these carboxylic acids [13,14]. In contrast, most organic dyes have a single carboxylic acid anchoring group and dye adsorption is primarily mono- or bidentate through the two oxygen atoms of the carboxylate [15]. Therefore, the single binding contact of the organic dye at the TiO_2 surface contributes less to the adsorption force than the doubly-bound adsorption on TiO_2 by the Ru bipyridyl complex dyes. By extension, a phosphonic acid anchoring group should result in even stronger bonding to the TiO_2 surface through bi- or tridentate contact [16,17]. In several reports, bipyridyl-based Ru complex dyes employed a phosphonic acid as the anchoring group [18–25]. Although a power conversion efficiency over 8% was achieved with an acetonitrile-based electrolyte, the difference in the long-term stabilities between dyes with carboxylic and phosphonic acids as anchors was not clear [26]. The effect of the anchoring group on the long-term heat stability should be clarified to develop dyes that are more robust.

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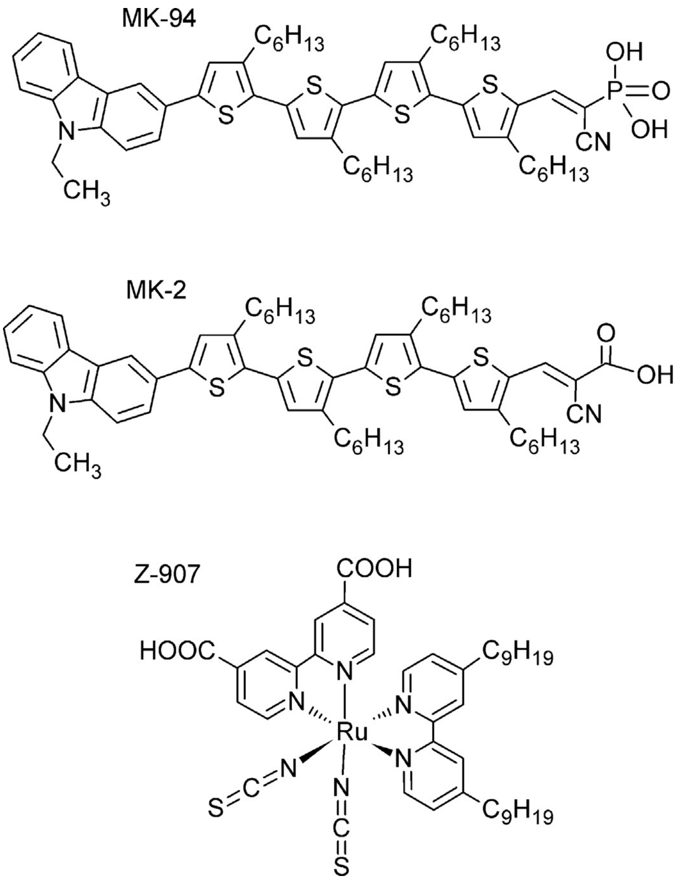

Fig. 1. Molecular structures of the dyes.

In this study, we prepared a new carbazole dye based on the MK-type structure [10] with a phosphonic acid anchor, MK-94, and compared its solar cell performance under heat stress at 85 °C to dyes with carboxylic acid anchors, MK-2 and Z-907 (Fig. 1). Thin (4 μm) transparent TiO$_2$ layers were employed as the photoelectrodes to observe the changes of the DSSC with greater sensitivity and to accurately measure the electron lifetimes and densities at open circuit by the stepped light-induced photocurrent and voltage transients (SLIM-PCV) [27,28] and the charge extraction [28,29] methods, respectively. Moreover, the changes in the impedance spectra with a long-term heat stability test were discussed.

2. Experimental

2.1. Synthesis of MK-94

High purity reagents and starting materials were used as obtained from Aldrich, Wako, Kanto Chemical, TCI, and Merck. All reactions were carried out under nitrogen atmosphere. Column chromatography was performed on silica gel (Kanto, Silica Gel 60 N, spherical, 40–50 μm). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance400 at 400 and 100 MHz, respectively. Chemical shifts are denoted in ppm relative to CDCl$_3$ or THF-d_8. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet), and br (broad). Mass spectra were obtained using a JEOL AccuTOF-CS (ESI-TOF-MS).

As depicted in Scheme 1, MK-94 having a phosphonic acid anchoring group was synthesized from aldehyde intermediate **1** with a quaterthiophene linker, which was synthesized in the same manner as previously described [10,11]. A Knoevenagel condensation with diethyl cyanomethylphosphonate was accomplished in the presence of piperidinium benzoate in benzene refluxing with water removal by a Dean-Stark apparatus. Finally, the diethyl phosphonate **2** was treated with bromotrimethylsilane and followed by methanol to obtain MK-94.

*2.1.1. Diethyl (1-cyano-2-(5″’-(9-ethyl-9H-carbazol-3-yl)-3′,3′’,3′”,4-tetrahexyl-[2,2′:5′,2′’:5′’,2′”-quaterthiophen]-5-yl)vinyl)phosphonate **2***

A solution of aldehyde **1** (100 mg, 0.11 mmol), diethyl cyanomethylphosphonate (199.0 mg, 1.10 mmol), and piperidinium benzoate (3.9 mg, 0.019 mmol) in benzene (18 mL) was refluxed with a Dean-Stark apparatus at 100 °C for 48 h. The resulting mixture was diluted with EtOAc. The organic layers were washed with H$_2$O and brine, dried over MgSO$_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (3:1 hexane/ethylacetate) to obtain diethyl phosphonate **2** (*cis* and *trans* mixture, 104 mg, 0.099 mmol, 88%) as a dark red solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.31 (1H, br d, J = 1.6 Hz), 8.18 + 8.13 (olefinic protons, *cis* and *trans*, total 1H, s), 8.14 (1H, d, J = 7.6 Hz), 7.71 (1H, dd, J = = 8.5, 1.6 Hz), 7.49 (1H, d, J = = 7.6 Hz), 7.40 (1H, t, J = 7.6 Hz), 7.37 (1H, d, J = 8.5 Hz), 7.26 (1H, t, J = 7.6 Hz), 7.20 (1H, s), 7.07 (1H, s), 7.03 (1H, s), 7.02 (1H, s), 4.35 (2H, br q, J = = 7.1 Hz), 4.29–4.19 (4H, m), 2.88–2.77 (8H, m), 1.81–1.62 (8H, m), 1.51–1.30 (33H, m), 1.44 (6H, t, J = 7.1 Hz), 0.96–0.90 (12H, m). ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.1, 147.6, 147.5, 144.1, 143.5, 142.9, 140.8, 140.6, 140.3, 139.5, 136.5, 135.2, 130.7, 130.5, 129.1, 129.0, 128.8, 128.5, 128.1, 126.9, 125.9, 125.1, 125.0, 123.7, 123.3, 122.8, 120.5, 119.0, 117.4, 116.4, 116.3, 108.7, 108.6, 92.2, 90.2, 63.3, 63.2, 37.6, 31.7, 31.63, 31.61, 31.5, 31.0, 30.5, 30.3, 30.2, 29.9, 29.7, 29.5, 29.3, 29.2, 29.1, 28.9, 28.8, 22.60, 22.57, 22.53, 22.49, 16.22, 16.16, 14.08, 14.05, 14.02, 13.97, 13.8.

2.1.2. (1-cyano-2-(5″’-(9-ethyl-9H-carbazol-3-yl)-3′,3′’,3′”,4-tetrahexyl-[2,2′:5′,2′’:5′’,2′”-quaterthiophen]-5-yl)vinyl)phosphonic acid, MK-94

To a solution of diethyl phosphonate **2** (100 mg, 0.096 mmol) in dry CH$_2$Cl$_2$ (2 mL) was added bromotrimethylsilane (0.10 mL, 0.76 mmol), and the reaction mixture was stirred at room temperature overnight. The reaction solvent was concentrated nearly to dryness under reduced pressure. MeOH (3 mL) was added to the residue and the mixture was stirred at room temperature for 48 h. The resulting mixture was diluted with chloroform. The organic layers were washed with 1 N HCl, H$_2$O, and brine, dried over Na$_2$SO$_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (chloroform → 10:1 chloroform/methanol) to obtain MK-94 (76 mg, 0.077 mmol, 80%) as a dark red solid, ^{1}H NMR (400 MHz, THF-d_8) δ 8.34 (1H, s), 8.10 (1H, d, J = 7.5 Hz), 7.73 (1H, br d, J = 8.9 Hz), 7.67 (1H, br d, JY= 8.5 Hz), 7.48–7.39 (3H, m), 7.27 (1H, s), 7.16 (1H, br t, J = 7.5 Hz), 7.05–6.95 (3H, m), 4.35 (2H, br q, JY= 6.7 Hz), 2.89–2.76 (8H, m), 1.79–1.60 (8H, m), 1.58–1.30 (27H, m), 0.95–0.86 (12H, m). ^{13}C NMR (100 MHz, THF-d_8) δ 152.0, 144.4, 143.1, 142.4, 141.5, 141.4, 141.2, 141.0, 140.6, 136.1, 135.8, 132.6, 132.4, 130.9, 130.4, 129.5, 129.4, 128.9, 127.5, 126.7, 126.2, 125.8, 124.43, 124.37, 123.9, 121.2, 119.8, 118.5, 117.9, 109.7, 109.6, 101.0, 38.1, 32.80, 32.75, 32.73, 32.0, 31.5, 31.4, 31.3, 31.0, 30.7, 30.5, 30.34, 30.29, 30.1, 29.5, 26.8, 23.61, 23.59, 14.5, 14.0, HRMS (ESI) Calcd for $[M–H]^-C_{57}H_{70}N_2O_3PS_4{}^-$: 989.4012; found: *m/z* 989.4039.

2.2. Materials

F-doped SnO$_2$-coated glass (FTO-glass), used as the transparent conductive glass for the photoelectrodes and counter electrodes, was purchased from Nippon Sheet Glass Co., Ltd. (TEC-10, ≤10 ohm/square) and from Dyesol Inc. (TEC-8, ≤10 ohm/square), respectively. TiO$_2$ paste (DSL18NRT) consisting of 20 nm