

# Effects of potential shift and efficiency of charge collection on nanotube-based porphyrin-sensitized solar cells with conjugated links of varied length†

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**For dye-sensitized solar-cell devices fabricated from porphyrin sensitizers with links of varied length (PE1–PE4) adsorbed on anodic titanium-oxide nanotube arrays, we measured induced photocurrent and photovoltage decays under constant bias illumination; the evaluated efficiencies of charge collection of the devices show a systematic trend PE4 > PE3 > PE2 > PE1 at a large short-circuit current, implying that a long link would improve the charge separation if the electrons were effectively injected into the semiconductor.**

Dye-sensitized solar cells (DSSC) are prospective photovoltaic devices because they are transparent, flexible, readily processed, economical and environmentally safe.<sup>1</sup> Among efficient sensitizers, porphyrin dyes are particularly attractive because their molecular structures are readily modified to harvest sunlight efficiently from the visible region to the near infrared.<sup>2</sup> A device made of a ‘push–pull’ zinc porphyrin sensitizer has attained an efficiency of power conversion as great as 11% under one-sun irradiation, stimulating hope that porphyrin dyes might yield highly efficient DSSC applications.<sup>3</sup>

From a mechanistic point of view, electron injection, charge recombination, dye regeneration and electron collection at the electrode are fundamental processes that control the total efficiency ( $\eta$ ) of power conversion of a DSSC.<sup>4</sup> Charge separation occurs initially in the dye upon irradiation; electrons subsequently migrate to the interface between the dye and TiO<sub>2</sub> through a bridge or link. To improve the cell performance, careful design of the structure of the dye with an appropriate link can thus minimize the rate of charge recombination.<sup>5</sup> To enhance our understanding of the role of a link with respect to the performance of a porphyrin-based DSSC device, we have designed zinc porphyrins with the length of the link controlled by the number of phenylethynyl (PE) units for a porphyrin, from one PE unit (denoted PE1) up to four PE units (PE4).<sup>6</sup> With PE1–PE4 sensitized on anodic titanium-oxide (ATO) films of one-dimensional nanostructure to make nanotube (NT)-based DSSC devices, the values of  $\eta$  decreased

systematically with increasing length of the link.<sup>7</sup> We thus concluded that the aggregate-induced energy transfer is more significant with a long link than a short link to decrease the injected electrons for the observed dependence of the cell performance on length.<sup>7</sup> Because the distance attenuation for the rate coefficient of electron injection of the PE system was small,<sup>7,8</sup> a porphyrin with a long PE link might improve the charge separation, thus increasing the efficiency of charge collection, if the problem of dye aggregation became resolved. In this communication we provide experimental evidence to consolidate the above concept based on an analysis of the kinetics of charge transport obtained from measured photocurrent and photovoltage transients.

We fabricated ordered nanochannel arrays of ATO films at 25 °C on anodizing titanium foil (Aldrich, 99.7%) at a constant voltage 60 V, as reported previously.<sup>9</sup> The ATO films (active size 0.4 × 0.4 cm<sup>2</sup>) were then immersed in a THF solution containing PE1–PE4 (1 × 10<sup>−4</sup> M) at 40 °C for 3 h to serve as working electrodes; the corresponding absorption spectra of the dye-sensitized films are shown in Fig. S1, ESI†. The fluorine-doped tin oxide (FTO; 30 Ω/sq, Sinonar, Taiwan) glasses (typical size 1.0 × 2.0 cm<sup>2</sup>) coated with Pt particles served as counter electrodes, and the corresponding NT-DSSC devices of sandwich type were fabricated according to a procedure reported elsewhere.<sup>7</sup> Current–voltage characteristics were measured with a digital source meter (Keithley 2400) with the devices under AM1.5 one-sun irradiation from a solar simulator (SAN-EI, XES-502S) calibrated with a standard silicon reference cell (VLSI standards, Oriel PN 91150V). Fig. 1 shows the photovoltaic characteristics of the four porphyrin-based DSSC devices fabricated with identical ATO films. Consistent with reported results,<sup>6a,7</sup> the efficiencies of power conversion of these NT-DSSC devices decreased systematically from 3.1% (PE1), 2.5% (PE2), 0.89% (PE3) to 0.22% (PE4). This systematic variation of the cell performance is consistent with the variation of the short-circuit photocurrent density ( $J_{SC}/\text{mA cm}^{-2}$ ), which decreased from 8.3 (PE1), 6.7 (PE2), 2.5 (PE3) to 0.66 (PE4) as the length of the PE link increased accordingly. To acquire an understanding of the observed dependence of performance on the length of the porphyrin-based DSSC, we applied pulsed transients of photocurrent and photovoltage to measure the kinetics of electron transport of the NT-DSSC devices after electron injection from porphyrins.

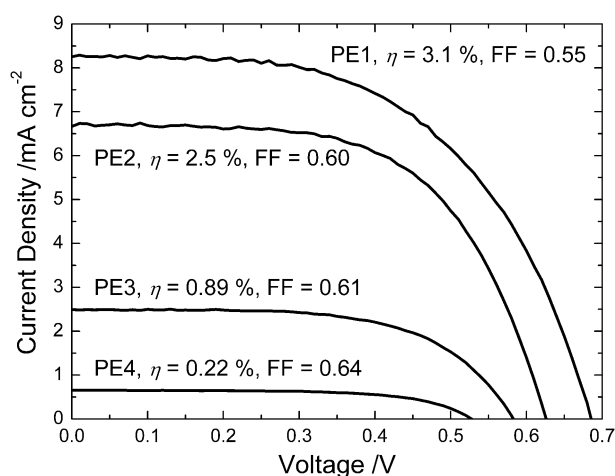
The experiment to measure the photocurrent decay has been described;<sup>7</sup> the system has been modified (Fig. S2, ESI†) to

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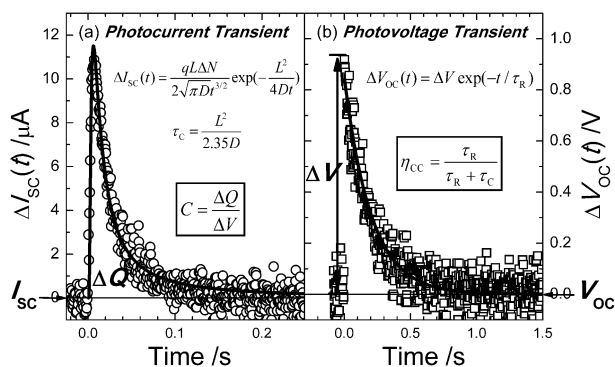
† Electronic supplementary information (ESI) available: Absorption spectra of PE1–PE4 on ATO films; experimental setup for transient photocurrent and photovoltage measurements; photocurrent and photovoltage transients of the NT-DSSC devices formed from PE1–PE4. See DOI: 10.1039/c0cp00458h



**Fig. 1** Current–voltage characteristics of NT-DSSC devices with sensitizers PE1–PE4 collected under one-sun illumination (AM 1.5,  $100 \text{ mW cm}^{-2}$ ).

measure both transient photocurrent and photovoltage decays. The NT-DSSC devices were irradiated from the counter-electrode side with a weak pulse ( $\sim 1 \mu\text{J pulse}^{-1}$ ) of light at 430 nm (NT342, EKSPLA, pulse duration  $\sim 8 \text{ ns}$ ) under background (bias) illumination at 632.8 nm. The intensity of the bias light was varied in five steps (photon flux/ $10^{15} \text{ cm}^{-2} \text{ s}^{-1} = 2.2\text{--}11$ ) with neutral-density filters. The resulting photocurrent and photovoltage transients were recorded on a digital oscilloscope (LeCroy 9350), with the signals passing a current preamplifier (SR570, SRC) at a short-circuit condition and a voltage preamplifier (SR560, SRC) at an open-circuit condition, respectively. Fig. 2a and b show the typical photocurrent and photovoltage transients, respectively; the raw data and the corresponding analysis of the kinetics of photocurrent transients (Fig. S3–S6<sup>†</sup>) and photovoltage transients (Fig. S7–S10) of PE1–PE4 devices are reported in the ESI.<sup>†</sup>

In principle, the large bias illumination provides a constant short-circuit current ( $I_{\text{SC}}$ ) or open-circuit voltage ( $V_{\text{OC}}$ ) at the background level shown in Fig. 2, and the small probe pulse generates a perturbation of the photostationary state for which the relaxation of the transient, either  $\Delta I_{\text{SC}}(t)$  or  $\Delta V_{\text{OC}}(t)$ , is describable with a suitable kinetic model.<sup>10</sup> For



**Fig. 2** (a) Photocurrent and (b) photovoltage transients of a typical NT-based porphyrin-sensitized solar cell device characterized with equations and key parameters indicated.

photocurrent decays (Fig. 2a), the transients were fitted with a diffusion equation dependent on time,<sup>7,11</sup>

$$\Delta I_{\text{SC}}(t) = \frac{qL\Delta N}{2\sqrt{\pi Dt^{3/2}}} \exp\left(-\frac{L^2}{4Dt}\right) \quad (1)$$

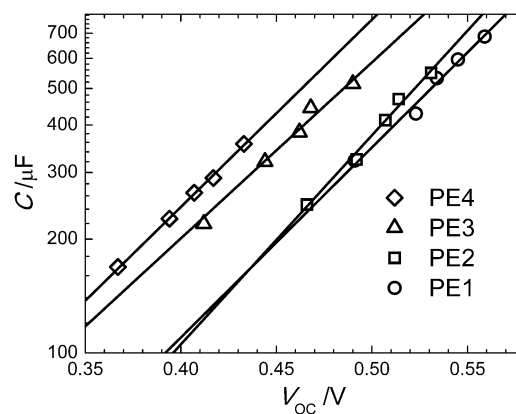
in which  $L$  ( $= 15 \mu\text{m}$ ) represents the length of NT arrays; the fitted parameters are the number  $\Delta N$  and the diffusion coefficient  $D$  of the electrons at the short-circuit condition. The collection time coefficient ( $\tau_{\text{C}}$ ) is related to the diffusion coefficient *via*  $\tau_{\text{C}} = L^2/(2.35D)$ .<sup>10</sup> For photovoltage decays (Fig. 2b), the transients were fitted with a single exponential decay,  $\Delta V_{\text{OC}}(t) = \Delta V \exp(-t/\tau_{\text{R}})$ , in which fitted parameters are the photovoltage amplitude  $\Delta V$  and the recombination time coefficient  $\tau_{\text{R}}$  of the electrons at an open-circuit condition. The chemical capacitance ( $C$ ) of the  $\text{TiO}_2$ /porphyrin interface is evaluated as  $C = \Delta Q/\Delta V$ ,<sup>12</sup> in which the injected electron charge  $\Delta Q$  is determined from integrating the photocurrent transient with time as shown in Fig. 2a.

The chemical capacitance measures the amount of charge that can be stored in trap states of  $\text{TiO}_2$ ; it thereby provides direct information on the density of states (DOS) of the ATO films.<sup>12,13</sup> According to the thermodynamic model of chemical capacitance in nanostructured  $\text{TiO}_2$ ,  $C$  is characterized with an exponential dependence on the bias potential.<sup>13</sup> We therefore display  $C$  as a function of  $V_{\text{OC}}$  at five bias intensities for NT-DSSC of PE1–PE4; the corresponding semilogarithmic plots are shown in Fig. 3. The solid lines are simulated results obtained according to the following expression:<sup>13,14</sup>

$$C(V_{\text{OC}}) = C_0 \exp\left(\frac{qV_{\text{OC}}}{k_{\text{B}}T_0}\right) = C_0 \exp\left(\frac{V_{\text{OC}}}{m_{\text{C}}}\right) \quad (2)$$

in which  $C_0$  is the pre-exponential factor,  $T_0$  is a characteristic temperature, and  $m_{\text{C}}$  is the characteristic energy describing the curvature of the DOS distribution.<sup>12–14</sup> These plots of  $C$  vs.  $V_{\text{OC}}$  of the devices exhibit a systematic trend from PE1 to PE4; *i.e.*, at the same  $V_{\text{OC}}$  value the order of chemical capacitances is  $\text{PE4} > \text{PE3} > \text{PE2} \geq \text{PE1}$ .

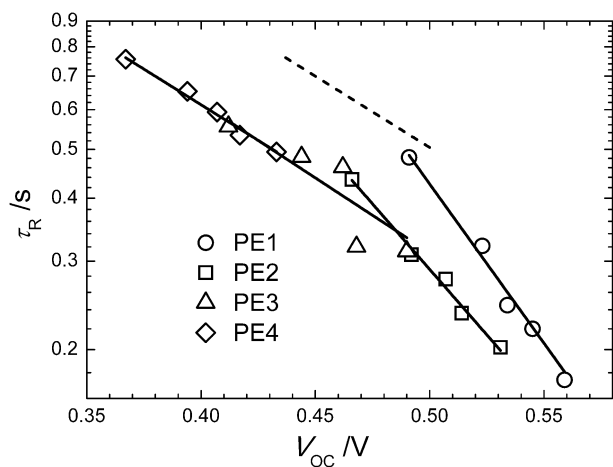
Because  $V_{\text{OC}}$  represents the potential difference between the Fermi level of the ATO film and the  $\text{I}^-/\text{I}_3^-$  redox couple of electrolyte,<sup>1,4</sup> and  $C$  is proportional to the DOS at that  $V_{\text{OC}}$ ,<sup>12</sup> this observation indicates that the DOS of  $\text{TiO}_2$  decreases



**Fig. 3** Semilogarithmic plots of chemical capacitance ( $C$ ) of NT-DSSC devices of PE1–PE4 as a function of  $V_{\text{OC}}$ . The solid lines represent exponential fits according to eqn (2).

systematically from PE4 to PE1 at the same Fermi level. The trend of the trap electrons in the conduction band of TiO<sub>2</sub> to reach the same Fermi level for PE1–PE4 must hence result from a systematic band-edge shift of the TiO<sub>2</sub> potential for PE1–PE4;<sup>15</sup> the shift from PE1 to PE4 was observed to be as great as 70 mV. This varied feature of potential shift with dye adsorbed on the TiO<sub>2</sub> surface was also observed on solid-state DSSC, for which a high  $V_{OC}$  was related to an upward shift of the TiO<sub>2</sub> conduction band edge toward more negative potentials.<sup>16</sup> The fits of the experimental data according to eqn (2) give  $m_C/mV = 87 \pm 16, 79 \pm 13, 93 \pm 20$  and  $88 \pm 6$  for PE1–PE4, respectively. These results reflect a systematic trend of the steepness of the trap-state distribution of the TiO<sub>2</sub> potentials for PE1–PE4. We conclude that the porphyrin with a long link attached to the surface of ATO results in a slightly broadened TiO<sub>2</sub> potential with a significantly smaller band edge. This conclusion is consistent with the photovoltaic performance of the system (Fig. 1) showing a systematic trend of  $V_{OC}/mV$  decreasing from 685 (PE1), 626 (PE2), 583 (PE3) to 528 (PE4).

Mori and co-workers<sup>17</sup> found only a small influence on TiO<sub>2</sub> potential for coumarin dyes with oligothiophene links, and concluded that the smaller  $V_{OC}$  for organic DSSC with a long link was due to a smaller electron lifetime resulting from rapid charge recombination. The same conclusion was made for thienylenevinylene oligomers with varied lengths.<sup>18</sup> Moreover, for triphenylpolyene dyes<sup>19</sup> electron recombination is enhanced on increasing the length of the vinylene–thiophene link. The larger dyes were suggested to have a larger polarizability to interact more efficiently with the surrounding species in the electrolyte.<sup>19</sup> In our case, the smaller  $V_{OC}$  for the device with a long link was attributed mainly to the factors that fewer electrons were injected into TiO<sub>2</sub> because of dye aggregation,<sup>7</sup> and a downward shift and broadening of the TiO<sub>2</sub> conduction band upon dye uptake (Fig. 3). Fig. 4 shows plots of  $\tau_R$  vs.  $V_{OC}$  for PE1–PE4 devices. With a potential shift upwards by 70 mV for PE4 (dashed line in Fig. 4) to match the chemical capacitance of PE1, the durations of charge



**Fig. 4** Semilogarithmic plots of electron lifetime ( $\tau_R$ ) of NT-DSSC devices of PE1–PE4 as a function of  $V_{OC}$ . The solid lines represent exponential fits for PE1–PE3. The dashed line shows the fit of PE4 on shifting the potential 70 mV upwards to match the capacitance of PE1 as indicated in Fig. 3.

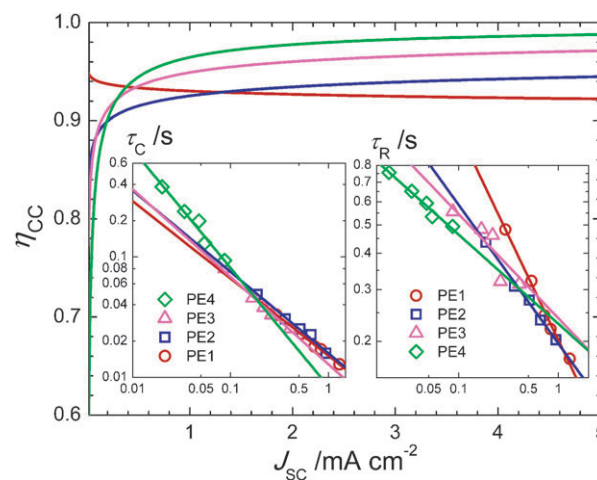
recombination of PE4 are significantly larger than those of PE1, but the slopes of the plots shown in Fig. 4 vary appreciably: they decreased systematically from PE1 to PE4. Our results might indicate that the dominant recombination was caused by the bulk trapped states for PE3 and PE4, but by the surface-trapped states for PE1 and PE2 in the open-circuit conditions. The PE links in the dye/ATO interface hence affect the depth of distribution of DOS and alter the recombination lifetimes, as we have observed.

The charge collection efficiency ( $\eta_{CC}$ ) of a NT-DSSC device is evaluated as  $\eta_{CC} = \tau_R/(\tau_C + \tau_R)$ ,<sup>20</sup> in which  $\tau_C$  and  $\tau_R$  were determined from fitting the photocurrent and photovoltage decays demonstrated in Fig. 2a and b, respectively. To relate short-circuit and open-circuit measurements for a given light intensity, one must consider the discrepancy of the charge densities on TiO<sub>2</sub> (or the shift of the Fermi levels) between the two conditions.<sup>21</sup> We predict  $\eta_{CC}$  based on  $\tau_C$  and  $\tau_R$  values obtained at the same  $J_{SC}$  level so as to correlate the two time coefficients at the same photocharge density. Fig. 5 shows plots of  $\eta_{CC}$  as a function of  $J_{SC}$  for PE1–PE4 based on simulated values of  $\tau_C$  and  $\tau_R$ ; the details are described below.

Both the diffusion correlation time  $\tau_C$  and the duration of charge recombination  $\tau_R$  depend strongly on the bias light intensity and are satisfactorily described with a power-law relation with  $J_{SC}$ ,<sup>10,15</sup>

$$\tau_C \text{ or } \tau_R = A(J_{SC})^n \quad (3)$$

in which  $A$  is a pre-exponential factor and  $n$  is the exponent of the power dependence. The insets of Fig. 5 show logarithmic plots of the two time coefficients as a function of  $J_{SC}$ , fitted according to eqn (3) at five bias light intensities for each porphyrin. For the diffusion time  $\tau_C$ ,  $n$  is determined to be  $-0.64 \pm 0.04, -0.67 \pm 0.10, -0.73 \pm 0.08$  and  $-0.98 \pm 0.23$  for PE1–PE4, respectively;  $(n + 1)$  is related to the steepness of the exponential distribution of trap states, which is inversely proportional to the characteristic energy parameter  $m_C$ .<sup>15</sup> The dependence of  $\tau_C$  vs.  $J_{SC}$  on power is mild for all porphyrins



**Fig. 5** Efficiency of charge collection ( $\eta_{CC}$ ) of NT-DSSC devices of PE1–PE4 as a function of  $J_{SC}$  predicted according to  $\eta_{CC} = \tau_R/(\tau_C + \tau_R)$ . The left and right insets show logarithmic plots of  $\tau_C$  and  $\tau_R$  vs.  $J_{SC}$ , respectively, with the solid lines representing fits of the power-law dependence according to eqn (3).

except PE4 that involves a large experimental uncertainty. The order of curvatures of the  $\text{TiO}_2$  potential predicted from  $\tau_C$  vs.  $J_{SC}$  is hence  $\text{PE1} \geq \text{PE2} \geq \text{PE3} > \text{PE4}$ , which is consistent with the results obtained from  $C$  vs.  $V_{OC}$  discussed above.

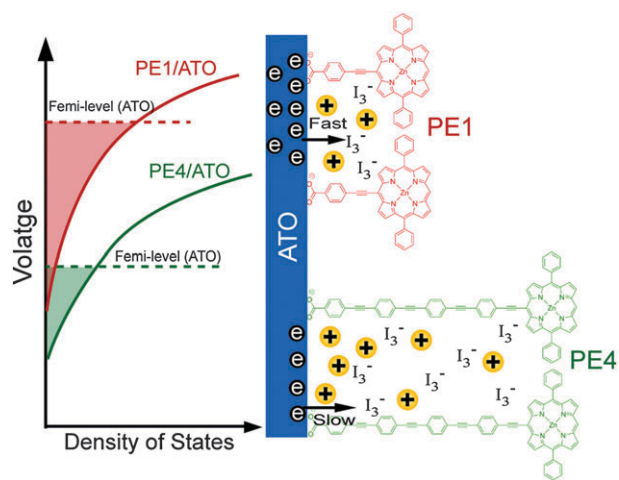
For the duration  $\tau_R$  of charge recombination,  $n$  was determined to be  $-0.71 \pm 0.06$ ,  $-0.47 \pm 0.04$ ,  $-0.36 \pm 0.18$  and  $-0.31 \pm 0.08$  for PE1–PE4, respectively, indicating that the variation of  $\tau_R$  vs.  $J_{SC}$  is much larger than that of  $\tau_C$  vs.  $J_{SC}$ . Furthermore, the order of variation of the former is  $\text{PE1} > \text{PE2} > \text{PE3} > \text{PE4}$ , which is the reverse of the latter. This observation is contrary to the Ru-dye/ $\text{TiO}_2$  nanoparticle (NP) system<sup>10</sup> based on a model of recombination limited by transport, for which the observed change in the diffusion period was equal to the change in the recombination period, *i.e.*,  $\tau_R \propto \tau_C$ .<sup>10,14</sup> Both  $\tau_R$  and  $\tau_C$  increased upon increasing lithium intercalation on  $\text{TiO}_2$  NP electrodes; their values have comparable magnitudes. In our case, we used PE1–PE4/ $\text{TiO}_2$  NT instead of N719/ $\text{TiO}_2$  NP electrodes to fabricate the devices. Our values of  $\tau_R$  are  $\sim 10$  times those of  $\tau_C$ , consistent with the results of a N719/ $\text{TiO}_2$  NT system obtained from IMPS/IMVS measurements.<sup>22</sup> The observed larger values of  $\tau_R$  indicate the superior charge collection characteristic of the NT system relative to the NP system,<sup>22</sup> and the variation of  $\tau_R$  vs.  $J_{SC}$  for PE1–PE4 reflects the effect of the length of the link affecting the charge recombination of the system for which a transport-limited model cannot account. The values of  $\tau_R$  exhibit a systematic trend  $\text{PE4} > \text{PE3} > \text{PE2} > \text{PE1}$  at greater  $J_{SC}$ , implying that charge recombination can be diminished with a long link under the condition of many injected electrons on  $\text{TiO}_2$  films.

Fig. 6 shows a schematic model to rationalize the observed correlations  $C$  vs.  $V_{OC}$ ,  $\tau_R$  vs.  $V_{OC}$ ,  $\tau_C$  vs.  $J_{SC}$  and  $\tau_R$  vs.  $J_{SC}$  for NT-DSSC devices formed from PE1–PE4. At the left of Fig. 6, we illustrate the conduction band potentials of ATO films adsorbed with a short link (PE1) and a long link (PE4); the potential of the former exceeds that of the latter because of the positive shift of the potential band edge for the system with a long link (Fig. 3). The shift of potential band edge due to dye uptake has not been reported for a conventional

DSSC,<sup>5c,d,17–19</sup> but a positive potential shift was due to  $\text{Li}^+$  addition<sup>14,15</sup> and the dipole effect in a solid-state DSSC.<sup>16</sup> Porphyrins of this kind might form small aggregated clusters on the surface of semiconductor films.<sup>7</sup> At the right side of Fig. 6 we show a schematic picture to represent the spaces of PE1 and PE4 aggregates (only two of each are presented for clarity) attached on the ATO surface, for which the latter has more room for cations (for instance,  $\text{Li}^+$  in the electrolyte)<sup>10,14</sup> to stay near the surface of ATO than the former. As a result, more electrons are expected to be attracted near the ATO surface for PE4 than for PE1, which reasonably accounts for the system with a small potential involving a long link.

We interpret the variations of diffusion and recombination times vs. injected electrons under two conditions. With few injected electrons (small  $J_{SC}$ ), the trap electrons dominate. The PE4 device is expected to have more electrons than the PE1 device trapped on the surface of ATO to interact with cations, so that electrons diffused more slowly for the former than for the latter. We thus expect the duration of diffusion  $\tau_C$  to decrease from PE4 to PE1 (left inset of Fig. 5) at small  $J_{SC}$ . If the trap electrons interact with nearby  $\text{I}_3^-$  in the electrolyte, we expect the recombination time  $\tau_R$  measured at an open-circuit condition to increase from PE4 to PE1 (right inset of Fig. 5) at small  $J_{SC}$ . In contrast, when many electrons were injected into the conduction band of ATO (large  $J_{SC}$ ), the electron diffusion would be strongly affected by the shape of the potential. Our results indicate that the short link with a steep potential might have a small rate of diffusion, which leads to the observed  $\tau_C$  featuring an order  $\text{PE1} > \text{PE2} > \text{PE3} > \text{PE4}$  at large  $J_{SC}$ . The variation of  $\tau_R$  exhibits an order the reverse of that of  $\tau_C$  at large  $J_{SC}$  because the charge recombination between detrapped electrons and  $\text{I}_3^-$  near the porphyrin core is controlled by the length of the link as indicated in the right part of Fig. 6. Therefore, increasing the distance between the redox active center of the sensitizer and the  $\text{TiO}_2$  surface effectively decreases the rate of recombination, consistent with the conclusion made elsewhere.<sup>5b–d</sup> The simulated efficiencies of charge collection of PE1–PE4 (Fig. 5) consequently exhibit a systematic trend  $\text{PE4} > \text{PE3} > \text{PE2} > \text{PE1}$  at large  $J_{SC}$ , demonstrating the advantage of a long link with an improved separation of charge. As porphyrins in this series suffer dye aggregation on  $\text{TiO}_2$  films, the efficiencies of electron injection have an order  $\text{PE1} > \text{PE2} > \text{PE3} > \text{PE4}$ , which predominately determine their cell performances (Fig. 1).

In conclusion, we report the effects of potential shift, electron diffusion and charge recombination on the cell performance for NT-based porphyrin-sensitized solar cells according to our analysis of photocurrent and photovoltage transients. The system with a long link exhibits a positive shift of the  $\text{TiO}_2$  potential, consistent with the variation of  $V_{OC}$  for PE1–PE4. Both diffusion and recombination times vs.  $J_{SC}$  are satisfactorily described with a power-law expression and a reverse trend of variation for PE1–PE4, which is rationalized with a model based on the potential shape of  $\text{TiO}_2$  and the trap electrons on ATO surface affected by the adsorbed porphyrins with links of varied length. The efficiencies of charge collection of the devices predicted from the simulated  $\tau_C$  and  $\tau_R$  values show a systematic trend  $\text{PE4} > \text{PE3} > \text{PE2} > \text{PE1}$  at large  $J_{SC}$ , implying that a long link improves the charge separation



**Fig. 6** A model proposed to rationalize the observed correlations of  $C$  vs.  $V_{OC}$ ,  $\tau_C$  vs.  $J_{SC}$  and  $\tau_R$  vs.  $J_{SC}$  for NT-DSSC devices made of porphyrins with varied length of PE link.

if the electrons are effectively injected into the semiconductor. This conclusion might assist the design of a new dye/TiO<sub>2</sub> system for DSSC applications.

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