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Spectroelectrochemistry

Robust Benzo[*g,h,i*]perylene-triimide Dye-Sensitized Electrodes in Air-Saturated Aqueous Buffer SolutionHung-Cheng Chen, René M. Williams, Joost N. H. Reek, and Albert M. Brouwer^{*[a]}

Abstract: Highly electron deficient benzo[*gh*]perylene-triimide (BPTI) chromophores were persistently anchored to a metal oxide electrode surface and reversible formation of their radical anions was shown in air-saturated aqueous buffer solution. Our results show a very low reaction-rate constant of BPTI^{•-} with O₂ ($k = 1.92 \pm 0.05 \times 10^{-2} \text{ s}^{-1}$). BPTI is a robust chromophore that can be used as the electron acceptor in molecule-based artificial photosynthetic devices for direct water splitting in aqueous phase.

Solar energy to fuel conversion by using artificial photosynthesis is a promising approach to produce sustainable energy, in particular water splitting for hydrogen generation.^[1,2] Among the molecule-based device designs, the dye-sensitized photoelectrochemical cells (DS-PECs) and organic photovoltaic photoelectrochemical cells (OPV-PECs) for direct solar-driven water-splitting have been intensively investigated in the past few years.^[3–8] In particular, molecular chromophore–catalyst assemblies in DS-PECs provide a promising way for the direct process of solar energy to fuel production.^[9] Molecular building blocks allow accurate tuning of electronic properties, but chemical stability is often insufficient.

Coupling light-absorbing sensitizers consisting of electron donor–acceptor (D–A) molecules to catalyst systems has been a useful approach to prepare artificial photosynthetic devices.^[10,11] To make D–A molecules capable of photoactivating the catalyst in a photoelectrode, it is necessary to efficiently photogenerate the long-lived charge-separated species D^{•+}–A^{•-} with a μs – ms lifetime.^[12,13] An example of the key D^{•+}–A^{•-} state in photosystem II (PSII) is P680^{•+}–Q_A^{•-}, with a lifetime that is longer than 1.0 ms when limited only by charge recombination to its ground state.^[14] Owing to the low potential of the O₂ redox couple ($E(\text{O}_2/\text{O}_2^{\bullet-}) = -160 \text{ mV}$) and the long lifetime of P680^{•+}–Q_A^{•-},^[15] Q_A^{•-} can react with O₂, producing the superoxide radical anion (O₂^{•-}), which is the precursor of most reactive oxygen species (ROS).^[15,16] It is well known that these ROS can cause the degradation of photosynthetic organisms.^[15,17]

Therefore, a highly efficient antioxidant defense system against oxidative damage has evolved in PSII.^[17]

Likewise, in molecule-based artificial photosynthetic devices, reaction with oxygen leads to loss of device efficiency, but also produces reactive oxygen species that can damage virtually all components of the system. As both oxygen (up to 0.25 mm) and water are inevitably present at a photoanode for oxidation of water, a robust device design implies that the radical anion of the acceptor (A^{•-}) is virtually inert to oxygen in air-saturated aqueous solution and that the molecular materials are chemically resistant to ROS.

Similarly, oxidation by dioxygen also causes dramatic decrease of electron mobility in many n-type organic field-effect transistors.^[18] In this context it has been shown that, to avoid O₂/H₂O electron traps, the energy level of the lowest unoccupied molecular orbital (LUMO) of the electron acceptor has to be more negative than -4.0 eV .^[19,20] This requirement is a crucial issue in OPV-PEC design.^[6,7] Another key issue in devices for light-driven water oxidation is proton management.^[21,22] Because water oxidation leads to progressive acidification of the reaction medium, this results in less favorable thermodynamics.^[23] In addition, proton-coupled electron-transfer plays a key kinetic role in water oxidation mechanisms.^[24] Because water is a poor proton acceptor at pH 7, buffer systems are required to facilitate efficient proton release during water oxidation.^[25] Phosphate buffers are most commonly used as a reaction medium, due to their high buffer capacity and ideal pH range, 6.0–8.0. Altogether, the light-absorbing sensitizers of electron donor and acceptor molecules have to be (photo)electrochemically stable in air-saturated buffer solution to arrive at artificial photosynthetic devices with long-term stability.

In this communication, we report novel benzo[*gh*]perylene-triimide (BPTI) derivatives (Figure 1) that give remarkably stable radical anions on an electrode surface in air-saturated buffer

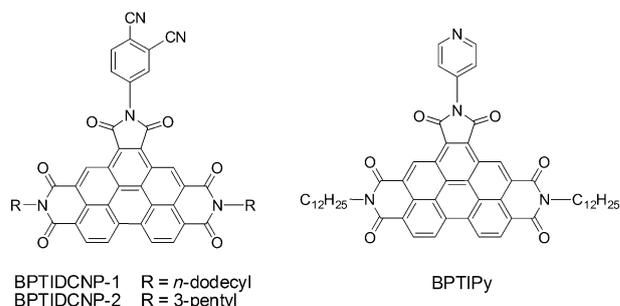


Figure 1. Chemical structures of BPTI derivatives

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solution. These compounds should therefore be suitable for use in several types of molecular electronic devices. The BPTI derivatives studied include two analogs with different side chains on the six-membered imide ring, a long linear (*n*-dodecyl) and a short α -branching (3-pentyl) chain. Moreover, a strongly electron-withdrawing group (3,4-dicyanophenyl or pyridine) is attached to the five-membered imide ring. In addition, the preparation of dye-sensitized FTO|TiO₂|BPTI electrodes is reported here for the investigation of long-term charge/discharge stability in air-saturated phosphate buffer solution (pH 8.0, 0.2 M). The BPTI chromophore has several advantages as electron acceptor for artificial photosynthetic molecular device design including high triplet-state energy ≈ 1.67 eV, intense optical absorption ($\epsilon_{466\text{ nm}} \approx 6.2 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) in the range of 300–500 nm and a tunable reduction potential by varying the substituent on the five-membered imide ring.^[26]

Firstly, electrochemical investigations using cyclic and differential pulse voltammetry were carried out (details in the Supporting Information), with the results summarized in Table 1.

	$E_{1/2}$ (V vs. NHE)				LUMO ^[b] [eV]
	X/X ⁻	X ⁻ /X ²⁻	X ²⁻ /X ³⁻	X ³⁻ /X ⁴⁻	
BPTIDCNP-1 ^[a]	-0.09	-0.42	-0.65	-1.02	-4.07
BPTIDCNP-2 ^[a]	-0.19	-0.44	-0.64	-1.02	-3.97
BPTIPy ^[a]	-0.27	-0.39	-0.64		-3.89

[a] Potential values from DPV measurements. [b] $E_{\text{LUMO}} = -(E_{\text{red vs. SCE}} + 4.4) \text{ eV} = -(E_{\text{red vs. NHE}} + 4.16) \text{ eV}$, refs. [18] and [27]. SCE = saturated calomel electrode; NHE = normal hydrogen electrode.

The first reduction potentials for BPTIDCNP-1, BPTIDCNP-2, and BPTIPy were observed at -0.09, -0.19, and -0.27 V versus NHE, respectively. Therefore, the corresponding LUMO energies of BPTIDCNP-1, BPTIDCNP-2, and BPTIPy were -4.07, -3.97, and -3.89 eV, respectively. This result indicates that the introduction of a 3,4-dicyanophenyl unit onto the five-membered imide ring on BPTIDCNP-1 shifts the LUMO energy to such an extent that O₂/H₂O electron traps can be avoided. All three BPTI derivatives show three reduction events due to reduction of the BPTI core. Because the 3,4-dicyanophenyl group is itself an effective electron acceptor unit, four reduction waves were observed in BPTIDCNP-1 and BPTIDCNP-2.

FTO|TiO₂|BPTI electrodes were prepared by adsorption of the dyes from chloroform solution onto the commercially available FTO/nanostructured TiO₂ electrodes. In Figure 2, UV/Vis absorption spectra of representative dye-sensitized FTO|TiO₂|BPTI electrodes in phosphate buffer solution and BPTIDCNP-1 in chloroform are displayed. Compared to BPTIDCNP-1 in chloroform, the loss of vibrational fine structure and a broader, redshifted spectrum of BPTI on these electrodes can be clearly observed. This suggests that molecular aggregation of BPTI occurs on the TiO₂ surface. The surface coverages Γ were estimated for BPTIDCNP-1, BPTIDCNP-2, and BPTIPy on FTO|TiO₂, giving values of 1.73×10^{-8} , 0.47×10^{-8} , and $1.45 \times$

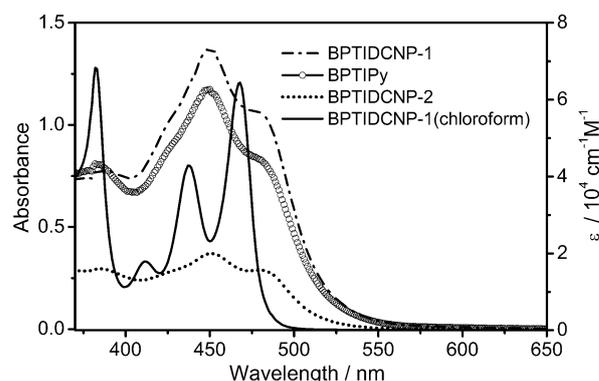


Figure 2. UV/Vis absorption spectra of FTO|TiO₂|BPTI electrodes in phosphate buffer solution (pH 8.0, 0.2 M) and BPTIDCNP-1 (solid line, right axis, representing the molar absorption coefficient ϵ) in chloroform.

$10^{-8} \text{ mol cm}^{-2}$, respectively (details in the Supporting Information). Although BPTIDCNP-1 and BPTIDCNP-2 have the same anchoring group, the steric effect of the branched 3-pentyl side chains probably causes the lower surface coverage. Importantly, for the FTO|TiO₂|BPTIDCNP-2 electrode with the 3,4-dicyanophenyl anchoring group, no noticeable dissociation of BPTIDCNP-2 from the TiO₂ surface was observed by UV/Vis absorption spectroscopy even after one day in phosphate buffer solution (see Figure S4 in the Supporting Information). In contrast, the widely used -PO₃H₂, -COOH anchoring groups of dye-sensitized photoelectrodes are easily desorbed in pH ≥ 7.0 phosphate buffer solution.^[28] To enhance the stabilization of metal-oxide-bound chromophores by these two anchoring groups at elevated pHs, the atomic layer deposition of ultrathin metal oxide passivation layers and hydrophobic poly(methyl methacrylate) overlayer approaches have been developed.^[28,29] However, noticeable desorption of dyes ($\approx 15\%$) was still observed in pH ≥ 7.0 phosphate buffer solution within one hour. The 3,4-dicyanophenyl anchoring group on the other hand shows stable binding onto the TiO₂ surface in highly concentrated phosphate buffer. Moreover, similar surface coverage or absorbance was obtained in FTO|TiO₂|BPTIDCNP-1 and FTO|TiO₂|BPTIPy electrodes. This indicates that 3,4-dicyanobenzene has comparable adsorption strength as pyridine on TiO₂. To the best of our knowledge, the binding of dicyanobenzene derivatives to TiO₂ has not been described in the literature, and the mode of binding is at present not known.^[30]

In cyclic voltammograms (CV) of FTO|TiO₂|BPTI electrodes in phosphate buffer solution, the initial reduction waves of all BPTI electrodes are more positive by 150–200 mV than that of trapped states of TiO₂ with a potential of -0.36 V versus NHE, (Figure S5 in the Supporting Information). This implies that electron transfer from the radical anion of BPTI to TiO₂ will be thermodynamically unfavorable. Thus, in order to use BPTI as a charge relay to transfer an electron to an electrode, a material with a lower-lying conduction band should be used, for example, SnO₂. Here, we make use of the lack of electron injection into TiO₂ as it allows an easy determination of the O₂/H₂O electron trapping kinetics of the BPTI radical anion (BPTI⁻) on the

FTO|TiO₂|BPTI electrode. The BPTI^{•-} on the electrode surface can be prepared by the addition of the sacrificial reductant sodium dithionite (Na₂S₂O₄) in aqueous solution.^[31] When the FTO|TiO₂|BPTIDCNP-1 electrode was immersed in a sodium dithionite solution, the initially yellow electrode gradually turned green (see inserted picture in Figure 3a). The spectral features

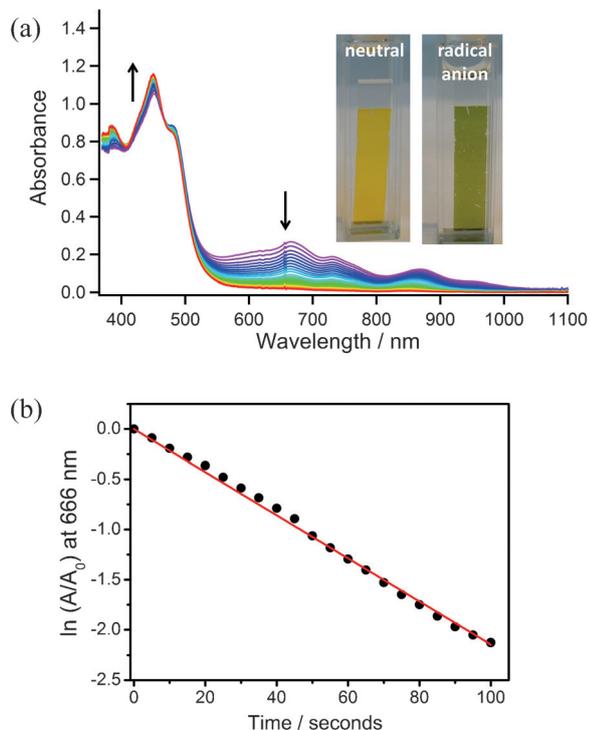


Figure 3. a) Time-resolved absorption spectra of BPTIDCNP-1 radical anion on FTO|TiO₂|BPTIDCNP-1 electrode in air-saturated buffer solution. The inserted color pictures show the neutral and reduced states of the FTO|TiO₂|BPTIDCNP-1 electrode; b) time-profile $\ln(A/A_0)$ of BPTIDCNP-1 radical anion at 666 nm.

of the greenish electrode are similar to the spectra of the electrochemically generated radical anion of BPTIDCNP-1 in phosphate buffer solution, evidencing the formation of the radical anion on the electrode (Figure S6 in the Supporting Information). The spectra are similar to those of previously reported BPTI radical anions.^[26] Figure 3a shows the time-resolved absorption spectra of BPTIDCNP-1 radical anions on an FTO|TiO₂|BPTIDCNP-1 electrode after transfer to an air-saturated phosphate buffer solution not containing Na₂S₂O₄.

The characteristic absorption features of the radical anion in the range of 500–1100 nm gradually decreased over time. Because the number of dioxygen molecules in solution is much greater than that of BPTIDCNP-1 radical anion on the electrode and the experiment is performed in an open air system, the O₂/H₂O electron trapping follows first-order kinetics. A rate constant $k = 1.92 \pm 0.05 \times 10^{-2} \text{ s}^{-1}$ was obtained, corresponding to a half-life of 36 seconds. The same experiment with the FTO|TiO₂|BPTIPy electrode is shown in Figure S7 in the Supporting Information. The rate constant $k = 2.66 \pm 0.04 \times 10^{-2} \text{ s}^{-1}$ and a half-life of 26 seconds were obtained in this case. Al-

though the LUMO energy of BPTIDCNP-1 is more negative than that of BPTIPy ($\Delta E = 190 \text{ meV}$), the radical anion lifetimes are similar. Clearly, the long lifetime of the BPTI radical anion on the electrode demonstrates that it can be used in long-lived D⁺-A⁻ systems that photoactivate water oxidation catalysts in air-saturated phosphate buffer solution.^[13] Furthermore, to investigate the chemical stability towards ROS, the BPTI-sensitized electrode was repeatedly reacted with Na₂S₂O₄ under air. Even after five days virtually no degradation was observed (Figure S9 in the Supporting Information). This result indicates that BPTI is a robust electroswitchable chromophore.

After chemical redox switching we studied the long-term electrochemical stability of BPTI dye-sensitized electrodes by applying hundreds of voltammetry cycles. The results are shown in Figure 4 and Figure S10 in the Supporting Information. Although the FTO|TiO₂|BPTIDCNP-1 and FTO|TiO₂|

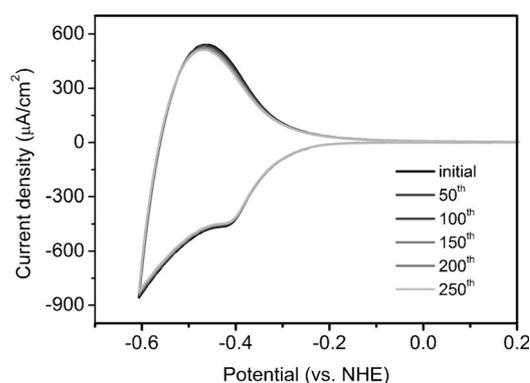


Figure 4. Repeated scanning cyclic voltammograms of FTO|TiO₂|BPTIDCNP-1 with 100 mVs⁻¹ scanning rate in air-saturated phosphate buffer solution (pH 8.0, 0.2 M).

BPTIPy electrodes show a very slight decrease in current after hundreds of CV scans, the absorption spectra (Figure S11 in the Supporting Information) of both BPTI dye-sensitized electrodes were still identical with the initial spectra. Thus, the major reason for decreasing current is not the electrochemical degradation of BPTI. It probably results from the water or phosphate electrolyte adsorbed on TiO₂ surface that influences the electronic properties of TiO₂.^[32–34] More importantly, both BPTI-sensitized electrodes still show BPTIs persistently anchored on the surface after hundreds of voltammetry cycles.

The observation of reversible color changes of the BPTI dye-sensitized electrodes induced by the reduction and re-oxidation (Figure 3a) prompted us to study their stability by rapidly switching the applied potential. Figure 5 shows the associated current of electrochromic conversion and the peak absorbance at 666 nm of the BPTI radical anion.

Fully reversible current changes were observed for the FTO|TiO₂|BPTIDCNP-1 electrode upon potential cycling between +0.40 and -0.60 V versus NHE in phosphate buffer solution. After 30 seconds for each oxidation and reduction period, this resulted in almost complete color switching (yellow \rightleftharpoons green), maintaining good stability in each state. The electrochromic changes are persistent for more than hundreds of cycles. To

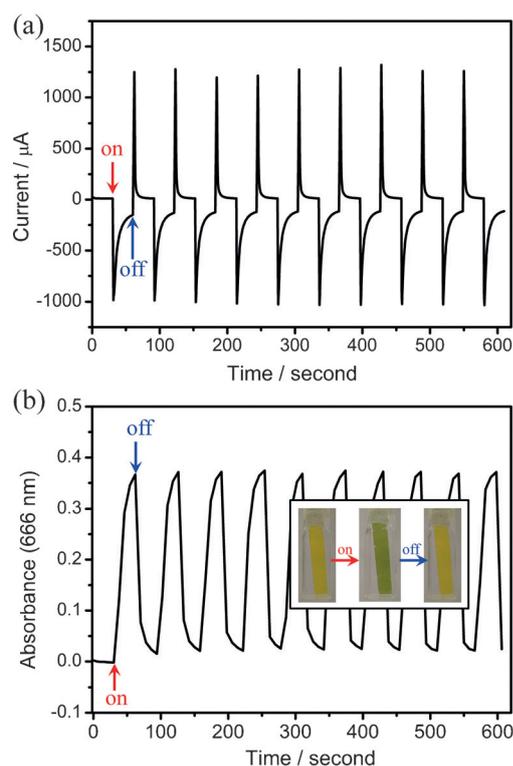


Figure 5. a) Chronoamperometric cycles (30 s–30 s) with stepping potentials between +0.40 V and –0.60 V vs. NHE. The arrows labeled “on” and “off” indicate where the potential is set to –0.60 V and reset to +0.40 V, respectively. b) Variation of the FTO|TiO₂|BPTIDCNP-1 electrode absorbance at 666 nm upon potential cycling between +0.40 V and –0.60 V vs. NHE. Insert: photograph of the FTO|TiO₂|BPTIDCNP-1 electrode following a potential step from +0.40 V to –0.60 V (on) and from –0.60 V to +0.40 V (off).

the best of our knowledge, such highly stable electrochromic electrodes of metal-oxide-bound organic chromophore systems in this simple aqueous electrolyte solution are demonstrated here for the first time. It is notable that both electrochemical studies (continuous and alternating applied potential) show highly stable reversible switching in air-saturated phosphate buffer solution.

In conclusion, we synthesized novel BPTI derivatives as electron-acceptor molecules that bind persistently to the surface of an FTO|TiO₂ electrode, and we studied charge-transfer properties by electrochemical and spectroelectrochemical methods. These FTO|TiO₂|BPTI dye-sensitized electrodes show remarkable stability, allowing hundreds of charge/discharge processes in air-saturated, concentrated phosphate buffer solution. Because of their resistance to oxygen and water, substituted BPTIs like the ones we studied here should be ideal for application in organic electron-conducting materials, for example, in OFETs and OPV-PECs.^[18] In our laboratory we are currently pursuing the use of the robust BPTI dye with a lower-lying conduction band metal-oxide semiconductor (e.g., SnO₂)^[3] as dye-sensitized photoanodes, by coupling them with novel high-potential light-absorbing sensitizers^[35] and water oxidation catalysts.^[36]

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Keywords: artificial photosynthesis · dyes · electron acceptor · reactive oxygen species

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