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Anchoring Groups for Dye-Sensitized Solar Cells

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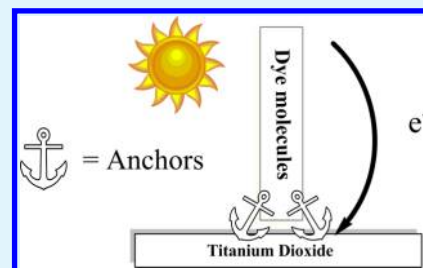
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ABSTRACT: The dyes in dye-sensitized solar cells (DSSCs) require one or more chemical substituents that can act as an anchor, enabling their adsorption onto a metal oxide substrate. This adsorption provides a means for electron injection, which is the process that initiates the electrical circuit in a DSSC. Understanding the structure of various DSSC anchors and the search for new anchors are critical factors for the development of improved DSSCs. Traditionally, carboxylic acid and cyanoacrylic acid groups are employed as dye anchors in DSSCs. In recent years, novel anchor groups have emerged, which make a larger pool of materials available for DSSC dyes, and their associated physical and chemical characteristics offer interesting effects at the interface between dye and metal oxide. This review focuses especially on the structural aspects of these novel dye anchors for TiO₂-based DSSCs, including pyridine, phosphonic acid, tetracyanate, perylene dicarboxylic acid anhydride, 2-hydroxylbenzonitrile, 8-hydroxylquinoline, pyridine-N-oxide, hydroxylpyridium, catechol, hydroxamate, sulfonic acid, acetylacetanate, boronic acid, nitro, tetrazole, rhodanine, and salicylic acid substituents. We anticipate that further exploration and understanding of these new types of anchoring groups for TiO₂ substrates will not only contribute to the development of advanced DSSCs, but also of quantum dot-sensitized solar cells, water splitting systems, and other self-assembled monolayer-based technologies.

KEYWORDS: dye-sensitized solar cells, anchor group, dye...TiO₂ adsorption, materials characterization



INTRODUCTION

Compared to traditional power cells, dye-sensitized solar cells (DSSCs) represent an effective alternative to provide clean energy from the sun.^{1,2} They mimic natural photosynthesis by using a molecular absorber, which converts light into electrical power.³ Immobilization of the adsorbing dye molecules onto the surface of semiconducting metal oxide nanoparticles, which collectively act as the working electrode of a DSSC, is crucial for initiating an electrical current via the injection of electrons from the dye into the conduction band of the metal oxide. This immobilization is usually achieved by addition of an “anchoring group”, i.e., a chemical substituent able to adsorb the dye molecule onto the surface of the metal oxide.

Historically, the most frequently used anchors in DSSCs are carboxylic acid and cyanoacrylic acid groups.^{4–10} Because of the recent exponential growth of DSSC research, many new anchors have emerged and been tested; this trend has significantly increased the choice of materials available, and facilitates the understanding of DSSCs. The region surrounding the anchoring group, i.e., the interfacial area of the DSSC’s working electrode, presents a highly complex structural environment, and several models have been proposed to describe the associated interfacial phenomena. A comprehensive review serving to collate recent studies on these new anchors is therefore both necessary and timely.

This review article starts by considering materials characterization techniques employed to explore the structural nature of DSSC anchors. This is followed by a detailed discussion of structure–function relationships of dye molecules bearing these anchors, as well as their optoelectronic properties, once they have

been adsorbed onto semiconductor surfaces. For those dyes that have been structurally analyzed, the adsorption modes of the anchors are quantified. While this review focuses on the structural aspects of the anchors, interfacial electron transfer (IET) will be discussed wherever relevant. For more detailed information regarding adiabatic and nonadiabatic IET, associated with the anchors and other parts of the molecules, the interested reader is kindly referred to the relevant reviews published previously.^{6,11–13}

GENERAL BACKGROUND FOR DSSC ANCHORS

Dye molecules can be assembled onto a metal oxide substrate surface through a multitude of mechanisms, including covalent attachment, electrostatic interaction, hydrogen bonding, hydrophobic interaction, van der Waals forces, or physical entrapment.¹⁴ DSSCs almost exclusively employ covalent bonding between the dyes and the TiO₂ surface atoms in order to ensure strong coupling, a homogeneous dye distribution, and device stability. In contrast to that, other interactions usually involve weaker bonds, and accordingly render adsorption quasi-reversible and unstable.¹⁴ Nevertheless, due to surface defects and the presence of superficial hydroxyl groups, hydrogen bonding cannot be neglected at the dye/TiO₂ interface. For the prototypical benchmark anchor carboxylic acid, six major types of possible anchoring modes have been identified: a mono-

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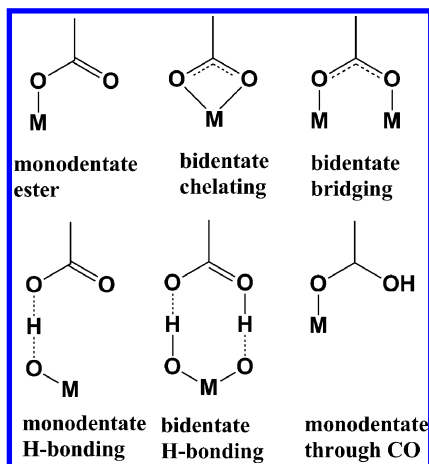
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dentate ester, bidentate chelating, bidentate bridging, monodentate and bidentate H-bonding, as well as monodentate coordinating mode through a C=O group (Scheme 1).^{4,14}

Scheme 1. Possible Binding Modes for Carboxylic Acid Anchors onto a Metal Oxide (M = Si, Sn, Ti)^a



^aAdapted with permission from ref 4. Copyright (2004) Elsevier.

Because of the intimate contact between carboxylate anchor-based dyes and the metal oxide surface, the structures with bidentate modes (chelating or bridging), usually exhibit superior stability compared to other types of anchoring modes.⁹

MATERIALS CHARACTERIZATION TECHNIQUES FOR STUDYING ANCHORING MODES

Specific material characterization tools are dedicated to the structural examination of adsorption modes at the anchor/substrate interface, the most popular being conventional Fourier transform infrared spectroscopy (FTIR) in transmission geometry, attenuated total reflectance FTIR (ATR-FTIR), and photoelectron spectroscopy (PES).

Deacon and Phillips have correlated the difference ($\Delta\nu$) between symmetric ($\Delta\nu_s$) and asymmetric ($\Delta\nu_{as}$) bond stretching frequencies of a carboxylic acid group and its corresponding coordination type:¹⁵ if $\Delta\nu$ of the adsorbed structure is much smaller than that of the free molecule, a bidentate adsorption mode (either bridging or chelating) dominates; otherwise, a monodentate anchoring mode exists. More specifically, $\Delta\nu$ values follow the order monodentate > bidentate bridging > bidentate chelating.⁹

$$\Delta\nu = \nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-) \quad (1)$$

This empirical method involving identification of vibrational frequencies surrounding anchoring groups is widely accepted in the scientific literature.^{9,10,16,17} FTIR is a natural choice for the identification of anchor frequencies and measures $\Delta\nu$ of both the free dye and dye/TiO₂ samples. FTIR spectra, generally measured between 4000 and 400 cm⁻¹, include fingerprint vibrational frequencies for the carboxylate's symmetric and antisymmetric stretching modes (usually 1300–1650 cm⁻¹) and for the C=O stretching mode (around 1720 cm⁻¹).¹⁰

Unfortunately, conventional transmission-based FTIR only yields poor signal-to-noise ratios, and as a result, ATR-FTIR is frequently used instead. The total reflection capabilities of ATR-FTIR allow the wave to propagate along the region near the dye/TiO₂ interface, which enhances the anchor-specific signal. In

addition, ATR-FTIR can probe the structure of a dye-sensitized TiO₂ film without destroying it.

Raman spectroscopy is frequently used as a complementary tool for FTIR, as it can detect vibrational bands, which are inactive in the IR measurements. It can be used to study the anchor by exploring the symmetry changes of the dye molecule and its chemical bonding upon adsorption. Because of the low concentration of adsorbate, conventional Raman scattering lacks accuracy, but this obstacle can be overcome through the use of resonance Raman spectroscopy, or time-resolved resonance Raman spectroscopy.^{18–20}

Photoelectron spectroscopy (PES) measures the energy of electrons emitted from a surface as a result of the photoelectric effect. It can be used to detect the changes of binding energies and surface composition upon dye adsorption, and thus allows the type of anchoring modes to be determined.²¹ PES has been employed to indicate the extent of dye coverage by comparing the peak intensities of elements such as C, O, Ti, Ru, N, and S between coated and uncoated substrates.²² The crude alignment of dye molecules on the substrate surface (perpendicular or flat) can also be deduced by PES, namely by a comparison of peak intensities between different chemical elements at varying distances from the surface.^{23,24} Other modified spectroscopy techniques employing X-rays have also been applied to study the anchoring effects in DSSCs, e.g., X-ray absorption fine structure (XAFS) spectroscopy, which similarly exploit the sensitivity of X-rays to changes in chemical bonding near a surface.²²

Single-crystal X-ray diffraction is a widely used technique for the structural determination of various organic and inorganic materials. Because the self-assembled monolayer of dyes on TiO₂ is usually not crystalline, this technique cannot be used to directly visualize its structure. Still, much information can be obtained indirectly from the bond geometry of the dyes.^{25–27} Moreover, recent developments on polyoxotitanate-based complexes have facilitated a clear visualization of the anchor region at dye/titania interfaces.²⁸ Bonding modes and bond lengths can be quantified for carboxylates, acetylacetonates, and phosphonates. Both bidentate chelating and bidentate bridging modes have been found for carboxylate groups in polyoxotitanate clusters, depending on the number of titanium atoms in the core complex and the surrounding chemical environment.²⁸

X-ray reflectometry has been used to determine the orientation and molecular density of dyes on TiO₂ substrates,²⁹ as well as to demonstrate that an increased molecular size of the dyes will result in an increased thickness of the dye layer. Moreover, this technique can be used to estimate the intermolecular spacing of the dyes. Crystal structures of the TiO₂ films have also been examined frequently by grazing incidence X-ray diffraction^{30–33} and small-angle X-ray scattering.^{34–36}

The adsorption geometry and electronic characteristics of the dye/TiO₂ interface can be imaged in situ by scanning tunneling microscopy at the atomic scale.³⁷ The dye-substrate coupling, the strain in the molecular chromophore, the supramolecular interaction, and the atomic-scale structure of the dye–semiconductor interface have all been shown to affect optimal photoelectron injection. Surface morphologies and particle sizes of DSSC electrodes have been investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).^{30,33} In addition, atomic force microscopy (AFM) has been employed to probe the surface morphologies of substrates as well as examine their film roughness.^{30,38}

Given that the dominant operational assignments of the dye/TiO₂ interface in a DSSC working electrode are light harvesting and electron injection, the variation of anchors affects virtually every aspect of a DSSC device. The changes in the interfacial phenomena induced by anchor changes can thus be observed with almost all the optical and electrochemical characterization techniques that are employed to characterize the components of the solar cell device, including UV–vis spectroscopy (effects of anchors on molecular optical properties and dye adsorption), cyclic voltammetry (CV; determination of frontier orbital energy levels), electrochemical impedance spectroscopy (EIS; electron recombination), transient absorption spectroscopy (TAS; time evolution of electrons and electron injection/recombination), incident photon-to-current efficiency (IPCE) measurements and current density–voltage (*J*–*V*) test (overall device efficiency).^{22,39,40}

Experimental Parameters to Quantify DSSC Performance. To quantify the performance of solar cells, short circuit current (*J*_{sc}), open circuit voltage (*V*_{oc}), fill factor (FF), and overall photoconversion efficiency (PCE, or *η*) diagnostic parameters have been used, and their relationship is represented by the following equation:

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$$

where *P*_{in} is a constant associated with the incident light power.

*J*_{sc} is strongly influenced by the HOMO–LUMO band gap of the dyes, electron traps, and the energy alignment of dye/TiO₂/electrolyte interface. This optical band gap can be reduced either by lowering the LUMO, or elevating the HOMO energy level. Ideally, the LUMO energy level should not be lowered too much, so as to facilitate thermodynamically favorable electron injection into the conduction band (CB) of TiO₂. Conversely, the HOMO energy level should not be elevated excessively, since the HOMO should remain sufficiently below the redox energy level of the electrolyte in order to be regenerated.

*V*_{oc} describes the difference between the redox level and the quasi-Fermi level of the semiconductor

$$V_{oc} = \frac{E_{CB}}{q} + \frac{kT}{q} \ln \left(\frac{n}{N_{CB}} \right) - \frac{E_{redox}}{q}$$

where *n* is the number of the electrons in TiO₂, *N*_{CB} is the effective density of states in TiO₂, *E*_{CB} is the energy level of the lower end of the CB in TiO₂, *E*_{redox} is the energy level of the redox couple, and *q* is the unit charge. The following methods to increase *V*_{oc} have been suggested:⁴¹ (1) electron recombination from the CB of TiO₂ to the electrolyte should be reduced; (2) electron recombination from the CB of TiO₂ to the oxidized sensitizer should be reduced; (3) electron injection efficiency should be increased; (4) the energy of the CB edge of TiO₂ vs vacuum should be elevated; (5) the *E*_{redox} level should be lowered; and (6) a greater proportion of the solar spectrum should be made use of, for example, via tandem solar cells.

The FF is related to the series resistance and *V*_{oc}: a larger *V*_{oc} and smaller series resistance generally lead to a larger FF. The diode rectifying effect of a solar cell is a complex parameter. Among other things, FF is strongly related to the charge recombination reactions. The FF is much less understood compared to *J*_{sc} and *V*_{oc}. The external quantum efficiency (EQE), or the related quantity, the incident photon-to-current efficiency (IPCE), is another fundamental indicator of the performance of a

DSSC. It is defined as the ratio of photocurrent density produced in the external circuit under monochromatic illumination of the cell and the incident photon flux

$$IPCE = \frac{J_{sc}(\lambda)}{q\Phi(\lambda)}$$

Density Functional Theory Approaches to Investigate Anchoring in DSSCs. In addition to experimental efforts, computational tools have been widely applied to study the interface phenomena in DSSCs. Density functional theory (DFT) is a technique that treats energies as functions of electron densities. DFT is well suited to study anchoring processes, because the dye/TiO₂ interfacial structure and interfacial charge transfer is a central concept in the adsorption process, and DFT is sensitive to the associated energy perturbations.

For TiO₂, different phases (e.g., rutile, brookite, and anatase) exist, and the choice of TiO₂ surface structure can significantly affect the final result of a DFT calculation. The preferred adsorption surfaces of the crystalline structures existing at room temperature have been summarized by Diebold.⁴² Nevertheless, DFT modeling of dye/TiO₂ interfaces generally employs the (101) crystal face of the anatase phase of TiO₂ as the preferred adsorption site, because it is the most stable surface at the nanoscale. Defects such as surface termination and Brønsted structures, which manifest in real-case scenarios, are typically neglected in simulations, whereas 5-fold unsaturated titanium atoms and 2-fold oxygen atoms are used as the primary anchoring sites in most DFT calculations.

For theoretical calculations, the TiO₂ substrate clusters can be of a periodic or isolated cluster in nature, depending on the computational method employed.⁴³ Representative sizes of TiO₂ clusters have been studied and compared with experimental methods.⁴⁴ The anchoring mode is determined by a comparison of various proposed adsorption mode energies, whereby the one with the lowest total energy is considered as the most favored, which in turn acts as a platform for further analysis. Because of their structural simplicity, the adsorption modes of water, formic acid, catechol, and bi-isonicotinic acid on TiO₂ have so far been the primary area of dye/TiO₂ interfacial studies.⁶ Detailed modeling techniques for various hybrid/organic photovoltaics are discussed in a recent review by De Angelis et al.⁴⁵

■ TYPES OF ANCHORS

Carboxylic and Cyanoacrylic Acids. A comprehensive review on the structures and optoelectronic performance of DSSC dyes featuring carboxylic and cyanoacrylic acid anchors has been presented by Hagfeldt et al.⁹ Because of its excellent electron withdrawing ability, cyanoacrylic acid is used in most organic D–π–A dyes, whereas carboxylic acid anchors are typically used for transition metal complexes, in which metal-to-ligand-charge-transfer (MLCT) dominates. In addition to their role in surface adsorption, these anchoring groups typically act as electron acceptors, given their excellent electron-withdrawing capabilities. Accordingly, intramolecular charge transfer is promoted from the donor region of the dye to the region in the vicinity of the TiO₂ substrate. Interestingly, Ooyama et al.⁴⁶ have suggested that the bifunctionality of the anchor group (adsorption and electron withdrawal) is not essential as far as cyanoacrylate anchors are concerned. There, the intimate contact that CN can forge with the TiO₂ surface affords the necessary electron-withdrawing group, while the carboxylate group functions as the anchor. In another study involving cyanoacry-

Table 1. Molecular Structures and Optoelectronic Properties of Dyes with Pyridyl Anchors

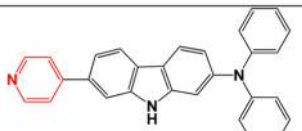
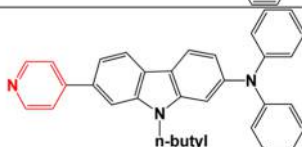
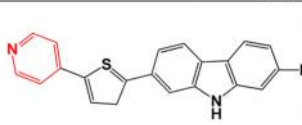
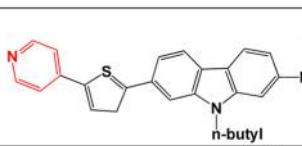
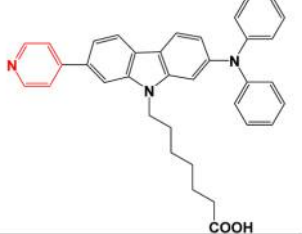
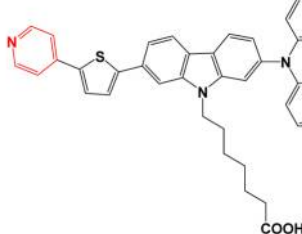
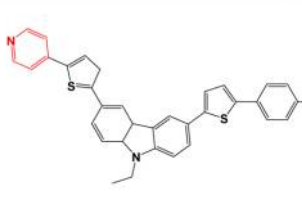
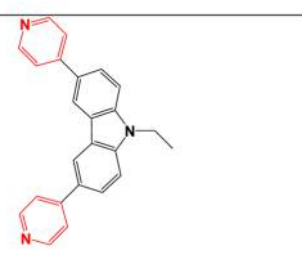
No.	Name	Compound	λ_{max} /nm	V_{oc} V	J_{sc} /mA cm ⁻²	FF	$\eta/\%$	Ref.
1	NI3		372	0.52	3.16	0.63	1.04	¹⁶
2	NI4		375	0.52	3.35	0.62	1.15	¹⁶
3	NI5		394	0.54	5.80	0.60	1.89	¹⁶
4	NI6		396	0.54	5.63	0.60	1.84	¹⁶
5	NI7		375	0.56	5.16	0.62	1.81	⁵⁸
6	NI8		396	0.56	7.04	0.59	2.35	⁵⁸
7	TTC-105		372	0.67	4.20	0.67	1.88	⁵⁹
8	YNI-1		327	0.49	1.84	0.63	0.57	⁶⁰

Table 1. continued

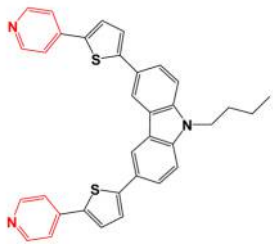
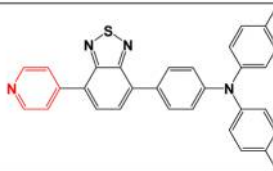
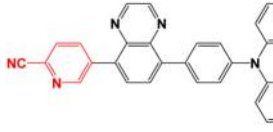
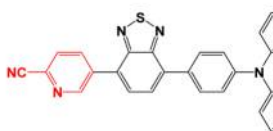
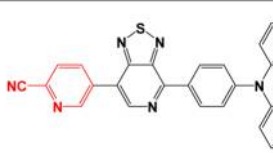
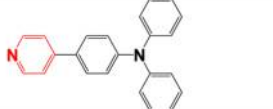
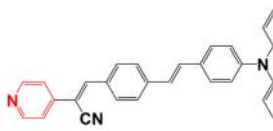
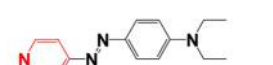
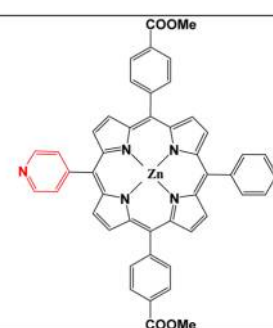
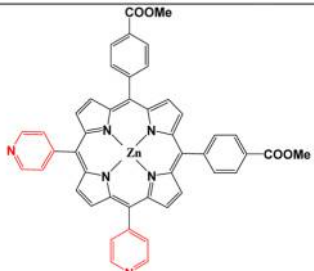
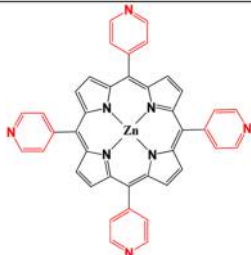
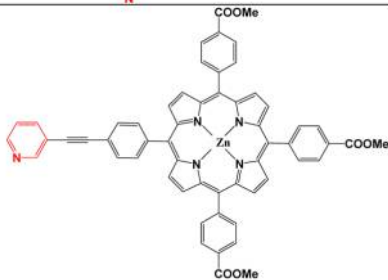
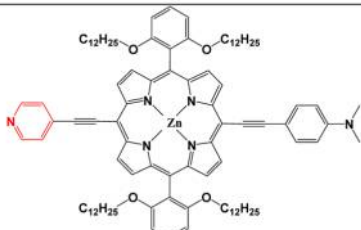
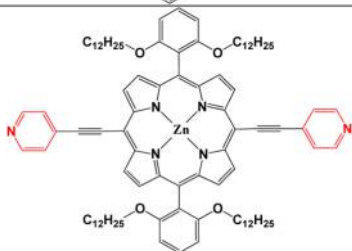
No.	Name	Compound	λ_{max} /nm	V_{oc} V	J_{sc} /mA cm ⁻²	FF	$\eta/\%$	Ref.
9	YNI-2		378	0.56	4.72	0.61	1.61	⁶⁰
10	P-II		461	0.57	5.24	0.70	2.10	⁶¹
11	CP-1		419	0.52	1.00	0.69	0.36	⁶¹
12	CP-II		473	0.60	9.45	0.70	4.02	⁶¹
13	CP-III		519	0.45	0.62	0.60	0.17	⁶¹
14	WL-101-R		347	0.63	1.98	0.81	1.01	⁶²
15	D3		457	0.51	4.1	0.67	1.40	⁶³
16	4		462	0.39	0.26	0.53	0.05	⁴³
17	P1		558	0.60	9.2	0.56	3.10	⁶⁴

Table 1. continued

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
18	P2		558	0.64	10.56	0.60	3.90	⁶⁴
19	P3		558	0.60	7.6	0.54	2.46	⁶⁴
20	-		400- 500	0.64	9.38	0.56	3.36	⁶⁵
21	LW11		457	0.63	8.2	0.77	3.96	⁶⁶
22	LW12		453	0.54	2.84	0.74	1.24	⁶⁶

late-containing dyes, the separation of the adsorbing substituent and the electron acceptor by a phenyl moiety, to form a D- π -A- π_{phenyl} -Ads chemical motif (A = acceptor; Ads = adsorber), demonstrated substantial gains in DSSC performance, i.e., the DSSC efficiency was improved more than 6-fold relative to an analogous conventional D- π -A molecular architecture.⁴⁷ This increase was attributed to the diode-like effect of the A- π_{phenyl} -Ads moiety resulting in a decrease of electron back transfer from TiO₂ to the dye. This decoupling of A and Ads has exciting implications regarding the development of systematic molecular design approaches for DSSC dyes.⁴⁸ Although cyanoacrylate and carboxylate anchors are usually substituents on conjugated

phenyl rings in the DSSC dyes, they have also demonstrated the same functionality when substituted onto other molecular fragments, such as vinyl^{39,49,50} and alkyl chains.^{51,52} In the case of the latter, detrimental effects on the electron transfer are usually observed, although higher solar-to-electron conversion efficiencies have been achieved for dyes featuring ionic hemicyanine molecules.^{7,53-55}

Pyridine Groups. In 2011, Ooyama et al.¹⁶ employed a pyridyl anchor in a class of carbazole-based organic dyes (**1-4**). The overall efficiencies of DSSC devices containing such dyes with a prototypical triarylamine donor⁵⁶ (1–2% c.f. Table 1) are comparable to those generated using a traditional phenyl-

carboxylate anchor.¹⁶ The TiO₂ anchoring site for the pyridyl group appears to be different from that of the carboxylate anchor. It was suggested that the formation of coordination bonds between the nitrogen atom in the pyridyl ring of **1** and the Lewis acidic sites of the TiO₂ surface leads to efficient electron injection (Figure 1). This pyridyl anchoring mode has also been studied by

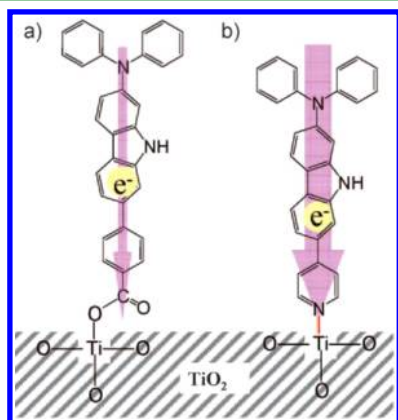


Figure 1. Anchoring modes for (a) a carboxylic-acid-based dye and (b) the analogous pyridyl-based dye **1** on a TiO₂ surface. Reproduced with permission from ref 16. Copyright 2011 Wiley–VCH.

FTIR spectroscopy. The adsorption of **1** onto the TiO₂ surface resulted in the emergence of a new IR band at ca. 1615 cm⁻¹, which was assigned to the aforementioned coordination complex between the pyridyl ring and the TiO₂. Moreover, a characteristic bathochromic shift in the optical absorption could be observed for the organic dyes, when adsorbed onto the TiO₂ substrate. The level of adsorption of **1**–**4** onto the TiO₂ surface was about half that of the analogous dyes containing a carboxylate anchor, which can be rationalized by the fewer Lewis acid sites necessary for the pyridyl-based adsorption, relative to the Brønsted acid sites employed for the adsorption of carboxylates.¹⁶

A detailed comparison between pyridyl and carboxylate anchors was presented in a case study on pyridyl-based dye **N14** (**2**) and its carboxylate-based counterpart (**N12**), which enabled further insights into their respective physical chemistry at the interface.⁵⁷ The preference of the pyridyl groups for adsorption at Lewis acidic sites, and the preference of the carboxylic acid group for adsorption at Brønsted acidic sites indicated the possibility of synergetic adsorption effects in DSSCs. Accordingly, a carboxylate anchoring group was incorporated into pyridyl-based **2**, yielding two exemplars, **N17** (**5**) (see Figure 2) and **N18** (**6**),⁵⁸ which indeed demonstrated higher overall conversion efficiencies.

The effect of incorporating a more bulky trithiophenyl-triarylamine-based group onto this family of pyridyl-based dyes, for example, in **7**, resulted in a DSSC power conversion efficiency of 1.88%,⁵⁹ which is smaller than that of a corresponding dye featuring a cyanoacrylate anchor. This difference was attributed to a decreased dye loading, an increased dark current, and a higher charge recombination rate for **7**.⁵⁹ The adsorption of the pyridyl group onto the Lewis acidic surface of TiO₂ was evident in **7** from the emerging vibrational band at 1612 cm⁻¹.¹⁶

Recently, the synthesis of fluorescent dyes **8** and **9**, hosting two pyridyl anchors, was reported.⁶⁰ The introduction of two pyridyl groups induces a bathochromic shift in the UV–vis spectrum and allows a higher dye loading onto the TiO₂ substrate. Compared with **8**, **9** contains additional thiophene units between the

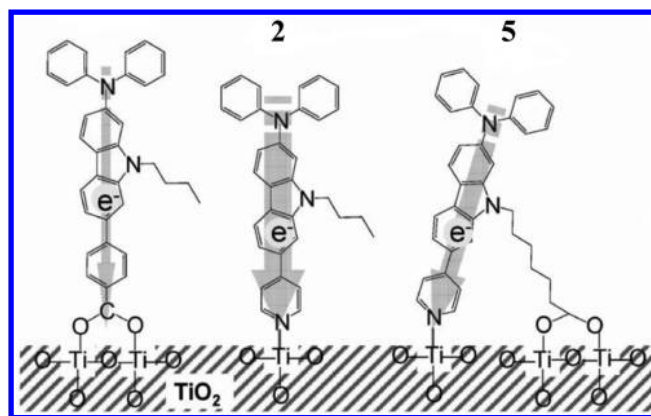


Figure 2. Proposed adsorption modes of **2** and **5**, and their carboxylate counterpart on a TiO₂ surface. Reproduced with permission from ref 58. Copyright 2011 Wiley–VCH.

carbazole moiety and pyridyl groups, and exhibits a higher DSSC efficiency, because of the higher degree of conjugation in this dye. The corresponding FTIR spectra indicate that **8** resides mainly on Brønsted acidic sites, whereas **9** primarily coordinates onto Lewis acidic sites. However, a few dye molecules adsorb at both anchoring sites. As pyridyl groups are moderately electron-withdrawing, a cyano substituent was introduced onto the pyridyl ring. The CN substituents in **11**–**13** are attached in the ortho-position with respect to the pyridyl nitrogen atom and in the para-position with respect to the main molecular fragment. The resulting dyes **11**–**13** exhibited superior DSSC device efficiencies relative to that of the corresponding dye **10**, which lacks a cyanopyridyl anchor.⁶¹ The 2-cyanopyridine unit induces a smaller HOMO–LUMO band gap, and the reduced electron recombination effects, typically associated with higher photovoltage, were confirmed for these dyes by EIS measurements. To date, the highest PCE among the organic dyes based on pyridyl anchors was reported for dye **12** (4.02%), which contains a benzo-[1,2,5]thiadiazole moiety.

Organic dyes with pyridyl anchors generally exhibit PCEs around 1%. For example, dye **WL101-R** (**14**), with a simple D– π –A triphenylamine-based molecular structure and a pyridyl anchor, exhibits a relatively low dye loading limit (0.56×10^{-8} mol/cm²) and a PCE of 1.01%.⁶² Dye **D3** (**15**) achieves a PCE of 1.40%, which is comparable to similar dyes with carboxylate and tetrazole anchors. DFT calculations indicate that **15** forms relatively long Ti...N distances (3.48 Å), leading to weaker dye/substrate interactions.⁶³ Pyridyl anchors have also been included in azo-based dyes such as **16**, and the optoelectronic properties were compared with other anchors.⁴³ Interestingly, dye sensitization onto the TiO₂ substrate surface was found to be strongly affected by the choice of solvent used in the sensitization process. Especially, the use of DMSO resulted in only a negligible amount of surface coverage.

Apart from organic D– π –A dyes, the pyridyl anchor has also been incorporated into zinc porphyrin dyes such as **P1**–**P3** (**17**–**19**), achieving PCEs of 2.5–3.9%.⁶⁴ Dye **18**, with two pyridyl groups, was thereby able to achieve a better photoelectrochemical performance compared to **17** and **19**, which contain one and four pyridyl groups, respectively. On the basis of EIS measurements, the better performance of **18** relative to **17** and **19** was attributed to a higher degree of dye loading, a more efficient electron injection, better dye regeneration processes, and a longer electron lifetime. Replacing the para-substituted pyridyl group in **17** with a 3-phenylethynylpyridyl group resulted in the

formation of **20**, which exhibited a higher overall PCE (4.48%), albeit with the assistance of an antiaggregating chenodeoxycholic acid (CDCA) coadsorbent.⁶⁵ In similar zinc porphyrin dyes, e.g., **21** and **22**, long alkyl chains have been introduced on the pyridyl anchoring groups in order to modify the intermolecular interaction of the self-assembled monolayer (SAM), which furnished PCEs of ca. 4%.⁶⁶

Phosphonic Acid Groups. After carboxylic and cyanoacrylic acid anchors, phosphonic acid is probably the most widely studied anchor for DSSC purposes. The phosphonate group provides excellent anchoring stability, whereby its adsorption strength onto metal oxide surfaces was estimated to be approximately 80 times higher than that of the carboxylic acid, and desorption in the presence of water was negligible.^{9,67} The surface functionality of phosphonic acid has been summarized in a review by Guerrero et al.⁶⁸ The versatile coordination chemistry of the phosphonate group allows binding to different metal ions via P–O–M bonds, and various tests confirmed that carboxylic acid desorbs from the substrate surface 5–1000 times faster than phosphonic acid.⁶⁸ Unfortunately, the charge transfer rate of phosphonic acid can hardly be compared with carboxylic acid, because of the tetrahedral geometry of the phosphorus center and the loss of conjugation.⁶⁸ The phosphoryl oxygen atom can bind to metal oxide surfaces via Lewis acidic sites, but in the absence of Lewis acidity, also via heterocondensation reactions (Scheme 2).⁶⁹ The presence of three oxygen atoms allows various anchoring modes, such as mono-, bi-, and tridentate, as well as hydrogen-bonding modes.

The optoelectronic performance of the phosphonate anchor, when incorporated in DSSC devices, is moderate but nevertheless acceptable.⁷⁰ The peak IPCE value for **23** (Table 2) exceeds 70% at 510 nm.⁶⁷ A series of porphyrin dyes (**24–28**) with phosphonate anchors has been synthesized and their impact on the IPCE performance was demonstrated to be similar to that

of carboxylate anchors.⁷¹ More dyes with varying numbers of phosphonate anchors (**29–31**) have been studied,⁷² and it was observed that because of the strength of the phosphonate anchor, the presence of only one such group is necessary in order to maintain contact with the surface. No evidence supporting the assumption that additional anchoring groups provide significantly stronger adsorption was observed, and the overall device performance is likely to be more closely related to the light absorption performance of the dyes.⁷² Nonetheless, complexes containing phosphonate anchors support a wider pH range for dye adsorption on the TiO₂ substrate and their binding constants are usually by an order of magnitude higher than those of carboxylate anchors.

To reduce undesirable aggregation and interfacial recombination of phosphonate dyes, long alkyl chains and aryl rings have been incorporated to form phosphinic acid anchor, e.g., in **32–33**.⁷³ For these dyes, the presence of a phosphinic acid anchor results in stronger binding properties, while the presence of a carboxylate anchor leads to a higher level of surface adsorption. The phosphinic acid anchor can be chemically modified, e.g. through the introduction of a phenyl ring or an *n*-octyl chain, while still preserving its desirable coordination characteristics on metal oxide surfaces.⁷³

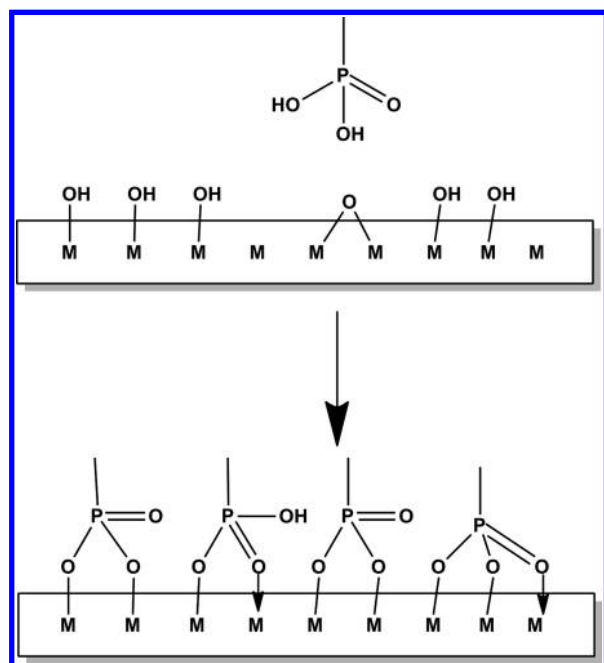
A series of chalcogenorhodamine dyes bearing phosphonate anchors (**34–37**) have been investigated.⁷⁴ There, the phosphonate anchor provides stability and ensures inertness of the chalcogenorhodamine–TiO₂ interface, without detrimentally affecting aggregation and interfacial electron transfer. In contrast to that, the PCE of devices based on chalcogenorhodamine dyes with carboxylic acid anchors decays significantly within the first hour of exposure to solar radiation, mostly because of dye desorption from the substrate. Introducing carboxylate and phosphonate anchors in the same molecule can provide both stability and efficient charge transfer. This concept has been validated by Brown et al. on zinc-phthalocyanine dyes, such as **38**.⁷⁵

The injection time through phosphonic acid anchors as a function of different binding modes on TiO₂ substrates has been studied computationally.⁷⁶ The injection time was observed to depend strongly on the anchoring mode (phosphonate monodentate < carboxylic acid < phosphonate bidentate), and the fastest injection times were found for fully dissociative bidentate geometries, where both hydroxyl protons of the phosphonic acid adsorbed on the TiO₂ surface.

Tetracyanate Groups. The tetracyanate anchor is derived from tetracyanoquinodimethane (TCNQ), and enables the formation of a surface complex through the nucleophilic reaction of TCNQ with superficial hydroxyl groups on TiO₂ nanoparticles. Thus, a negatively charged TCNQ adsorbate is generated,⁷⁷ and the interfacial charge transfer transition enhanced. Tetracyanate anchors have been included in several organic dyes, e.g., **39–42** in Table 3, and demonstrated the capacity to sensitize TiO₂ surfaces.⁷⁸ However, the PCE of the devices is usually low (<0.25%). Apart from its coordination capacity, the tetracyanate group is a strong electron acceptor, and has shown good performance in the presence of additional anchors such as rhodanines and carboxylic acids.⁷⁹

Perylene Dicarboxylic Acid Anhydride Groups. Perylene dicarboxylic acid anhydride dyes have shown good performance as DSSC dyes, both on SnO₂ and TiO₂ substrates.^{80–82} In the early stages of DSSC developments, the majority of papers discussed perylene dicarboxylic acid anhydride dyes with phosphonic acid and/or carboxylic acid anchors attaching onto

Scheme 2. Reaction of Phosphonic Acids with Metal Oxide Surfaces via Lewis and Brønsted Acidic Sites^a



^aAdapted with permission from ref 68. Copyright 2013 Royal Society of Chemistry.

Table 2. Molecular Structures and Optoelectronic Properties of Dyes with Phosphonate Anchors

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
23	1		498	-	-	-	-	69
24	1		408	-	-	-	-	71
25	2		418	-	-	-	-	71
26	3		418	-	-	-	-	71
27	5		409	-	-	-	-	71
28	6		420	-	-	-	-	71
29	P2		455	0.67	1.36	0.68	0.8	72
30	P4		488	0.53	0.22	0.58	0.09	72

Table 2. continued

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
31	P6		464	0.80	2.87	0.62	1.9	⁷²
32	TT30		-	0.54	4.94	0.72	1.90	⁷³
33	TT32		-	0.54	6.03	0.73	2.39	⁷³
34	3-O		567	0.24	3.25	0.28	0.36	⁷⁴
s35	3-Se		600	0.21	3.39	0.27	0.33	⁷⁴
36	4-O		550	0.25	3.69	0.28	0.48	⁷⁴
37	4-Se		580	0.22	3.07	0.27	0.34	⁷⁴

TiO₂, which exhibited a femtosecond interfacial electron transfer rate.⁸² Perylene dicarboxylic acid anhydride itself can be used as an anchoring group for TiO₂ sensitization purposes, without the need for additional anchoring groups on the perylene dicarboxylic acid anhydride photosensitizers, as shown e.g. in *N*-(2,5-ditert-butylphenyl)peryene-3,4-dicarboximides **43-45**

(Table 4).⁸¹ These dyes exhibit better electron injection and light absorption properties than the corresponding dyes containing carboxylate anchors.

Other perylene dicarboxylic acid anhydride dyes without additional anchoring groups were examined, especially with respect to their optoelectronic properties. Zafer et al. have

Table 3. Molecular Structures and Optoelectronic Properties of Dyes with Tetracyanate Anchors

No.	Name	Compound	λ_{max} /nm	V_{oc} V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
39	1		-	0.12	0.12	0.42	0.0058	⁷⁸
40	2		-	0.24	1.41	0.61	0.20	⁷⁸
41	3		-	0.19	0.65	0.52	0.06	⁷⁸
42	4		-	0.24	1.71	0.61	0.25	⁷⁸

studied the effect of varying the chain length of the alkyl substituents attached to the nitrogen atom, on the photoelectrochemical performance of perylenemonoimide (PMI) dyes **46–50**; these achieved overall PCEs of up to 1.61%, whereby dyes with longer and branched alkyl chains exhibited higher device efficiencies.⁸³ Edvinsson et al. have demonstrated that dyes **51–55** exhibit improved optoelectronic properties and stability (external quantum efficiency >70%; overall conversion efficiencies ~3%).⁸⁴ Even better optoelectronic properties were observed for **56** containing thiophenol groups (IPCE = 87%; PCE = 6.8%).⁸⁵ In the presence of high adsorbate concentrations on the surface of TiO₂ nanoparticles, moderate electron injection and cell voltages have been observed for **57** (PCE = 3.15%).⁸⁶ Unfortunately, most reports on perylene dicarboxylic acid anhydride anchors in the scientific literature suffer from a lack of detailed structural analyses of the dye/TiO₂ interface.

2-Hydroxybenzonitrile Groups. Similar to the tetracyanate anchor, the 2-hydroxybenzonitrile anchor allows a one-step electron injection from the dyes directly into the TiO₂ substrate by photoexcitation of the dye/TiO₂ surface complex. This has been demonstrated for dyes **58–61** (Table 5).⁸⁷ These dyes are accordingly categorized as type II dyes, whereas other dyes with a two-step process (i.e., photoexcitation of the adsorbed dyes followed by electron injection from the excited dye into the TiO₂ substrate) are referred to as type I dyes.^{87,88} The color change of type II dyes **58–61** in solution and after sensitization onto a TiO₂ substrate is shown in Figure 3. Dyes bearing a 2-hydroxybenzonitrile anchor exhibit much larger solar-to-electron conversion

rates compared to those with tetracyanate anchors; for example, dye **60** achieved a PCE of 3.4%.

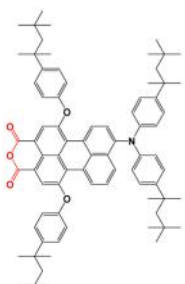
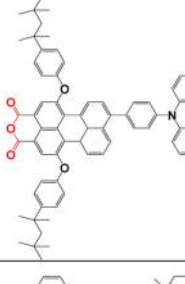
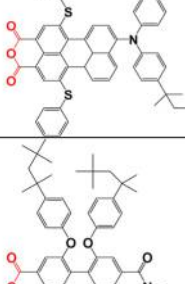
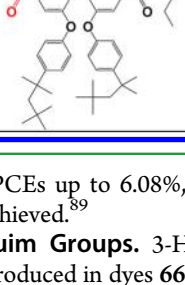
8-Hydroxyquinoline Groups. The 8-hydroxyquinoline (OQ) anchor was implemented in the TPPZn-OQ dye **62** (Table 6) and resulted in a PCE of 1.56%.⁴⁰ The electron recombination behavior of **62** was examined by EIS, and the series resistance, charge transfer resistance for electron recombination, and the capacitance at the TiO₂-electrolyte interface were observed to be similar to carboxylate analogues. In the presence of acetic acid, only negligible dissociation of **62** from the TiO₂ substrate was observed, while a similar dye based on a carboxylate anchor dissociated from the TiO₂ nanoparticles after 3 h of exposure to solar irradiation. The superior surface coordination of the former was explained by the chelating anchoring mode of the oxygen and nitrogen atoms onto the titanium atoms, as evident from DFT calculations on the structurally simpler dinuclear model compound [Ti₂O₂(OH)₂(H₂O)₄]²⁺.⁴⁰

Pyridine-N-oxide Groups. Wang and co-workers have studied dyes with pyridine-N-oxide acting as electron acceptor and anchoring groups, e.g. in **63–65** (Table 7).⁶² An overall conversion efficiency of 3.72% was achieved for **64**. After sensitization, the peak associated with the N=O vibration in the FTIR measurement was bathochromically shifted, indicative of the formation of a coordinative bond between the oxygen atom in the pyridine-N-oxide moiety and a superficial hydroxyl group of the TiO₂ substrate.⁶² The introduction of a long alkyl chain onto the thiophenyl spacer in **65** did not improve the optoelectronic properties of the device. More pyridine-N-oxide

Table 4. Molecular Structures and Optoelectronic Properties of Dyes with Perylene Anchors

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm^{-2}	FF	$\eta/\%$	Ref.
43	P1		556	0.41	4	-	0.59	⁸¹
44	P2		560	0.54	8.9	-	1.92	⁸¹
45	P4		509	0.32	4.5	-	0.45	⁸¹
46	PMI-DA1		Ca. 522	0.3	9.79	0.55	1.61	⁸³
47	PMI-DA2		Ca. 522	0.3	8.40	0.46	1.16	⁸³
48	PMI-MA		Ca. 522	0.26	6.73	0.37	0.65	⁸³
49	PMI-AR		522	0.25	4.1	0.58	0.60	⁸³
50	PMI-CH		Ca. 522	0.27	0.24	0.6	0.37	⁸³
51	ID17		527	0.44	7.32	0.43	1.4	⁸⁴
52	ID22		458	0.60	7.50	0.54	2.4	⁸⁴
53	ID28		478	0.65	10.4	0.58	3.9	⁸⁴

Table 4. continued

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
54	ID34		470	0.70	7.96	0.59	3.2	⁸⁴
55	ID35		430	0.65	6.13	0.55	2.2	⁸⁴
56	5		620	0.73	12.60	0.74	6.8	⁸⁵
57			580	0.52	9.20	0.66	3.15	⁸⁶

dyes have been synthesized and PCEs up to 6.08%, as well as good stability values, have been achieved.⁸⁹

3-hydroxy-*N*-methylpyridinium Groups. 3-Hydroxy-*N*-methylpyridinium groups were introduced in dyes **66–69** (Table 8) to serve both as electron acceptor and anchor groups.⁹⁰ The hydroxyl group in the hydroxylpyridinium moiety provides suitable coordination properties, but also appreciable electron donating characteristics. Accordingly, a 2.6% overall device conversion efficiency of as well as an IPCE value of 80% at 440 nm have been achieved for **66**.

Catechol Groups. Most DSSC dyes, where the charge transfer emanates from the excited dye to the TiO₂ layer, are classified as “type I” dyes. Other dyes, such as those with catechol and 2-hydroxybenzonitrile anchors, involve additional charge-transfer contributions that manifest through the ground state dye to the TiO₂ band pathway; such chromophores are called “type II” dyes. Dyes containing catechol anchors are classified as type II dyes (vide supra). Even though extensive research has been carried out on dyes with catechol anchors in the early stages of the development of DSSCs, especially with respect to sensitization and interfacial charge transfer on TiO₂ sub-

strates,^{91–95} their optoelectronic properties are not extraordinary. For example, the flavonoid anthocyanin dye **70** (Table 9) was used to sensitize TiO₂ nanoparticles, which subsequently exhibited a PCE of 0.56%, and a maximum IPCE efficiency of 20% in a photoelectrochemical cell. However, transient absorption spectroscopy assigned an electron injection rate of less than 100 fs.⁹¹ A series of catechol dyes with electron donating groups (**71–75**) were studied by Tae et al., who observed increased PCE for **74** and **75**.⁸⁸

Thiophene-modified catechol dyes (**76–78**) and their application in DSSCs were reported by An et al.,⁹⁶ who found that the binding strength of these dyes onto TiO₂ proportionally increases with increasing molecular weight and acidity of the catechol. The authors suggested that the observed low V_{oc} and J_{sc} values of these catechol dyes is driven by strong parasitic recombination, and that the type II process might actually consist of a two-step process involving a ligand-to-metal transition followed by exciton separation.⁹⁶ Even though further strong surface complexes have been obtained upon dye sensitization from several other catechol dyes, e.g., **79–81**,⁹⁷ the PCE of catechol-anchored dyes unfortunately still remained below 1%.

Table 5. Molecular Structures and Optoelectronic Properties of Dyes with 2-Hydroxybenzonitrile Anchors

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
58	LS201		376	0.62	6.3	0.71	2.8	⁸⁷
59	LS202		356	0.65	6.9	0.70	3.1	⁸⁷
60	LS203		351	0.67	7.4	0.69	3.4	⁸⁷
61	LS204		364	0.55	6.9	0.69	2.6	⁸⁷

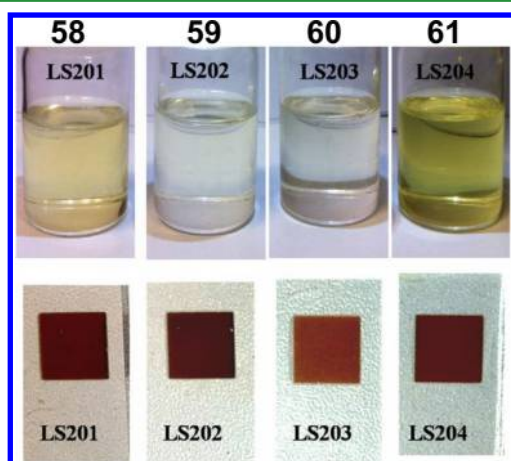


Figure 3. Color changes of 2-hydroxybenzonitrile-based dyes 58–61 on TiO₂ substrates, where they form surface complexes (bottom row), compared with in solution (top row). Reproduced with permission from ref 87. Copyright 2012 Elsevier.

These low efficiencies might be partly explained by the poor electron withdrawing ability of the hydroxyl groups in the catechol moiety, which can be quantified by the Hammett value

and ultimately result in poor intramolecular charge transfer properties.^{98,99}

The preferred anchoring mode for the catechol group was proposed to be bidentate chelating or bridging (Scheme 3).⁹⁷ The interfacial charge transfer of catechol dyes has been examined computationally by Abuabara et al. (Figure 4).¹⁰⁰ The LUMO+2 molecular orbital of the catechol dye [Mn-(H₂O)₃(catechol-terpy)]₂ (82) undergoes a time-dependent charge distribution, following instantaneous light excitation. Their results indicated that the charge transfer occurs efficiently from the sensitizer onto the TiO₂ substrate via the catechol anchor on the fs time scale.

Hydroxamate Groups. Hydroxamate groups are known to act as a bidentate ligands in coordination complexes of iron and TiO₂.^{101,102} McNamara et al. introduced hydroxamates in DSSC dyes such as 83 (Table 10), in order to generate highly water-stable anchors.¹⁰³ The observed disappearance of the C=O stretching band at 1635 cm⁻¹ in the IR spectra concurs with the coordination of the -O-CR=N-O- group in 83 onto TiO₂, whereby the terpyridine moiety points away from the substrate surface. Theoretical calculations suggested that the hydroxamate anchor is by ca. 33% more stable on TiO₂ (anatase) than the corresponding carboxylates.¹⁰³ Various organic and organo-metallic dyes with hydroxamate anchors have been developed,

Table 6. Molecular Structure and Optoelectronic Properties of Dye 62 with a Hydroxyquinone Anchor

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
62	TPPZn-OQ		423	0.56	3.86	0.72	1.56	⁴⁰

Table 7. Molecular Structures and Optoelectronic Properties of 63–65 with Pyridine-N-oxide Anchors

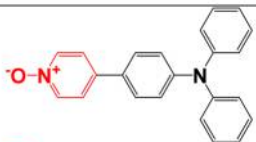
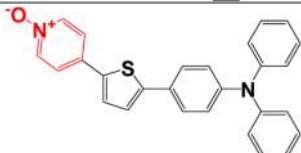
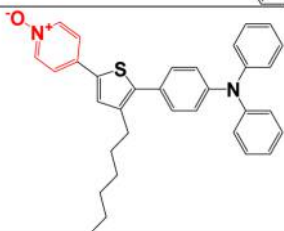
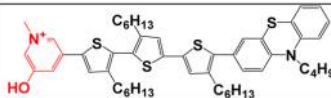
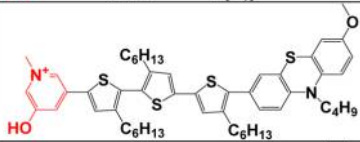
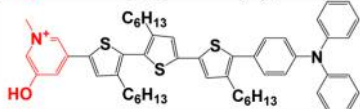
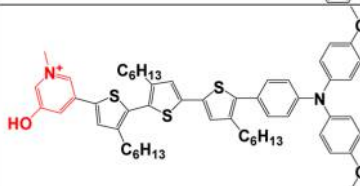
No.	Name	Compound	λ_{\max} /nm	V_{oc} / V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
63	WL-101		370	0.63	3.67	0.79	1.82	⁶²
64	WL102		405	0.61	8.65	0.70	3.72	⁶²
65	WL103		ca. 390	0.62	7.09	0.71	3.11	⁶²

Table 8. Molecular Structures and Optoelectronic Properties of Dyes 66–69 with Hydroxypyridium anchors

No.	Name	Compound	λ_{\max} /nm	V_{oc} / V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
66	JH401		381	0.61	6.35	0.68	2.6	⁹⁰
67	JH402		397	0.52	5.40	0.66	1.9	⁹⁰
68	JH403		377	0.58	5.87	0.60	2.1	⁹⁰
69	JH404		383	0.57	5.23	0.64	1.9	⁹⁰

and especially **84–85** have been examined with respect to their stability and longevity on TiO₂ nanoparticles under aqueous conditions.¹⁰⁴ Their stability on TiO₂ surfaces was observed to be consistently higher (ca. 20%) than the respective carboxylates. An investigation of the ultrafast interfacial electron transfer by terahertz spectroscopy revealed that dyes **84–85** complete IET within 500 fs.¹⁰⁴

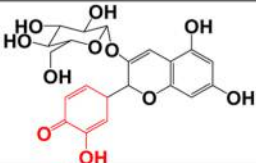
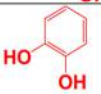
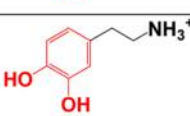

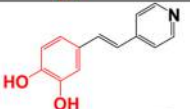
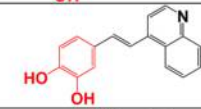
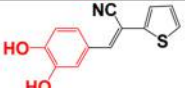
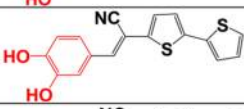
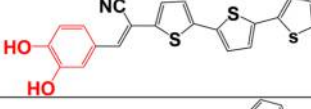
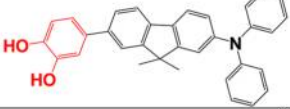
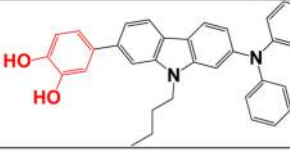
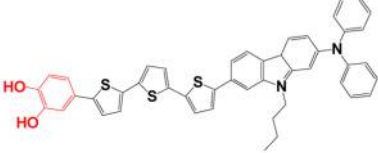
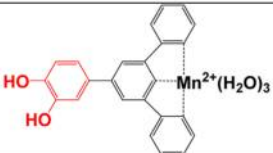
However, despite their excellent stability, the results from the experimental solar-to-electron conversion efficiency tests of dyes containing hydroxamate anchors are not convincing, and reports on acceptable device conversion efficiencies remain scarce. For example, Brewster et al. reported a PCE of merely 0.09% for dye **86**.¹⁰⁵ An exception is the recent hydroxamate modified dye MK-2HA, which exceeds 6% PCE.¹⁰⁶

Sulfonic Acid Groups. Although sulfonic acid groups can sensitize TiO₂ substrates, the resulting device efficiencies are low.

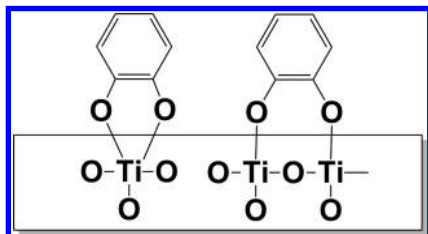
Porphyrins, squaraine, and azo dyes such as **87–89** (Table 11) have been investigated and PCE below 0.4% were observed.^{43,107,108} On the basis of DFT calculations, both bidentate and tridentate bridging anchoring modes have been proposed for this type of anchor.^{43,109} Their ionic nature, resulting from the incorporation of sulfonate anchors into pyridium hemicyanine and merocyanine dyes such as **90–95**, can induce improved device performances.

Acetylacetonate (acac) Groups. Acetylacetonate (acac) derivatives are known for their outstanding coordination properties toward transition metals and their stability over a wide pH range.^{113,114} On a TiO₂ substrate, **96** (Table 12) exhibited an IPCE value of more than 30% at peak wavelength, but a slightly lower coverage (ca. 20% less) compared to the carboxylate group. Such IPCE values result from a lack of conjugation in these molecules, which is markedly different from

Table 9. Molecular Structures and Optoelectronic Properties of Dyes 70–81 with Catechol Anchors

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm^{-2}	FF	η /%	Ref.
70	-		-	0.4	2	-	0.56	⁹¹
71	Cat		-	0.56	1.51	0.67	0.6	⁸⁸
72	Dop		-	0.45	0.40	0.68	0.1	⁸⁸
73	Bpg		-	0.45	0.79	0.63	0.2	⁸⁸
74	Cat-V-P		-	0.56	2.74	0.68	1.1	⁸⁸
75	Cat-v-Q		-	0.56	3.53	0.67	1.3	⁸⁸
76	C1		372	-	-	-	0.61	⁹⁶
77	C2		411	-	-	-	0.70	⁹⁶
78	C3		429	-	-	-	0.76	⁹⁶
79	YM-1		362	0.42	1.36	0.51	0.29	⁹⁷
80	YM-2		364	0.42	1.51	0.50	0.31	⁹⁷
81	YM-3		478	0.32	0.75	0.47	0.11	⁹⁷
82	-		-	-	-	-	-	¹⁰⁰

Scheme 3. Proposed Anchoring Modes for Catechol Groups on TiO₂ Surfaces, Forming Either a Bidentate Mononuclear Chelate (left) or a Bidentate Dinuclear Bridging Link (right)^a



^aAdapted with permission from ref 97. Copyright 2014 Royal Society of Chemistry.

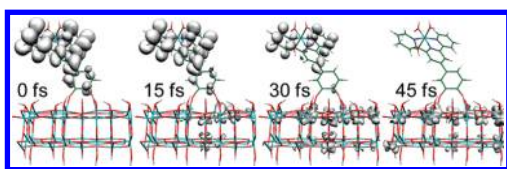


Figure 4. Time-dependent (0–45 fs) electron distribution in the LUMO+2 of **82** on a TiO₂ substrate. Reproduced with permission from ref 100. Copyright 2007 American Chemical Society.

the conventional D- π -A molecular architecture. The ruthenium sensitizer **97** was studied in ZnO-based DSSCs. TD-DFT calculations revealed both lower levels of conjugation and electronic coupling in the dye relative to corresponding carboxylates. Nevertheless, a moderate overall conversion efficiency of 1.05% was achieved for a device containing **97**.¹¹⁵

Transition metal complexes of **98** were studied under aqueous and oxidative conditions.¹¹⁶ For such dyes, interfacial electron

injection rates of less than picoseconds were confirmed by optical pump-terahertz probe transient measurements, which are sensitive to the free electrons in the TiO₂ conduction band. The UV-vis spectra of these dyes on TiO₂ surfaces indicated appreciable stability under aqueous conditions, while carboxylate-anchored analogues detached from the TiO₂ surfaces and only 30% remained after 24 h.¹¹⁶

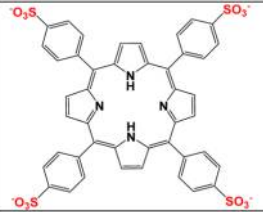
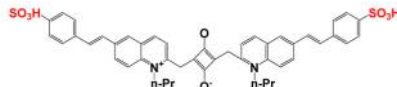
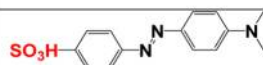
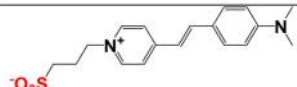
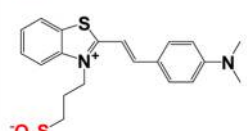
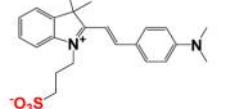
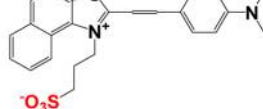
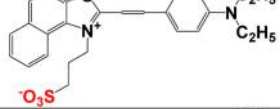
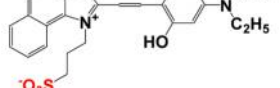
Boronic Acid Groups. Boronic acid anchors and their applications in DSSCs have been reported for ruthenium complexes **99–101** (Table 13).¹¹⁷ The wavelength of the characteristic absorption peaks in the UV-vis spectra of terpyridine-based **100–101** is bathochromically shifted (ca. 30 nm) compared to bipyridine-based **99**. The photoelectrochemical properties of these dyes are strongly dependent on the number of boronic acid anchors in the dye.¹¹⁷ Because of the higher surface coverage resulting from two boronic acid anchors, complex **99** exhibits a larger maximum IPCE value (>60%), compared to those of **100** (22%) and **101** (7%). The observed inferior device performance of **101** was tentatively ascribed to the free rotation of the phenyl group bound to the terpyridine ring.

Nitro Groups. Papers reporting the exclusive replacement of a carboxylic acid with a nitro group anchor still remain elusive, but FTIR spectroscopy measurements suggest that, in the presence of a carboxylic acid anchor, the nitro group exhibits sensitization behavior as well as interesting interfacial phenomena on TiO₂ substrates.¹⁷ Nitro-anchored dye **102** (Table 14) showed an unusual color change upon reversal of applied voltages. The coordination between the nitro group and the TiO₂ surface causes optical bleaching of the light absorption, increases the dye/TiO₂ coupling, and facilitates electron transfer (Figure 5). For **102**, an approximately 5-fold increased device efficiency

Table 10. Molecular Structure and Optoelectronic Properties of Dye 83–86 with a Hydroxamate Anchor

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
83	-		-	-	-	-	-	103
84	-		-	-	-	-	-	104
85	-		-	-	-	-	-	104
86	-		-	0.38	0.51	0.48	0.09	105

Table 11. Molecular Structures and Optoelectronic Properties of Dyes 87–95 with Sulfonate Anchors

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm^{-2}	FF	$\eta/\%$	Ref.
87	-		418	0.29	-	0.44	0.04	¹⁰⁷
88	4c		770	0.51	1.54	0.51	0.40	¹⁰⁸
89	2		430	0.39	0.21	0.53	0.04	⁴³
90	PS		514	0.75	0.56	0.63	0.26	⁵⁴
91	BTS		557	0.41	15.1	0.32	2.1	¹¹⁰
92	IDS		565	0.48	3.5	0.73	1.34	¹¹¹
93	Dye 1		532	0.50	10.7	0.62	4.1	¹¹²
94	Dye 2		542	0.47	11.1	0.62	4.0	¹¹²
95	Dye3		552	512	15.6	0.63	6.3	¹¹²

was observed from repetitive solar cell testing relative to the observation before voltage reversal.

Tetrazole group. Recently, the tetrazole group has been reported as a suitable anchor for DSSC applications.⁶³ The photovoltaic properties of tetrazole-anchored **103** (PCE = 5.27% in Table 15; IPCE > 80% at peak wavelength) rival those of the benchmark anchor carboxylic acid.⁶³ DFT calculations indicate a bidentate bridging mode for the nitrogen atoms with uncoordinated Ti sites on the substrate surface. Moreover, the device stability for **103** can be maintained for several weeks under ambient conditions.

Rhodanine and Rhodanine-3-acetic Acid Groups. The introduction of a rhodanine anchor in the dyes **104–105** (Table 16) provided strong electron accepting abilities, strong electron coupling between the O/N atoms of rhodanine and the TiO₂ substrate, as well as shorter electron transfer distances.^{79,118}

DSSC devices based on **105** were able to achieve a PCE of 7.11%, which is higher than that for the corresponding cyanoacrylic acid analogues. The N–H stretching and bending frequencies, as well as the C=O stretching mode, disappeared from the FTIR spectrum upon dye sensitization onto the TiO₂ substrates, suggesting the formation of coordination bonds between the O and N atoms of the rhodanine tautomers and the Lewis acidic sites of the TiO₂ surface.⁷⁹ Ganesan et al. have studied D- π -A organic sensitizers **106–107** containing rhodanine anchors.¹¹⁹ Dye **106**, with a strong cyano acceptor and a chelating anchoring mode through the N and O atoms of the amide moiety, exhibited a large PCE of 3.23%, whereas dye **107** displayed higher recombination rates relative to **106** as evident from the transient photovoltage decay.¹¹⁹ DFT calculations showed that unfavorable electron recombination might occur for dyes with rhodanine anchors, because of the strong propensity of the

Table 12. Molecular Structures and Optoelectronic Properties of Dyes 96–98 with Acetylacetonate Anchors

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm^{-2}	FF	η /%	Ref.
96	bpy-acac		462	0.49	2.02	-	-	113
97	Ru-acac		538	0.39	4.25	0.64	1.05	115
98	-		-	-	-	-	-	116

Table 13. Molecular Structures and Optoelectronic Properties of Dyes 99–101 with Boronic Acid Anchors

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm^{-2}	FF	η /%	Ref.
99	-		-	-	-	-	-	117
100	-		-	-	-	-	-	117
101	-		-	-	-	-	-	117

Table 14. Molecular Structure and Optoelectronic Properties of Dye 101 Containing a Nitro Anchor

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm^{-2}	FF	η /%	Ref.
102	JY1		448	0.59	2.12	0.66	0.81	17

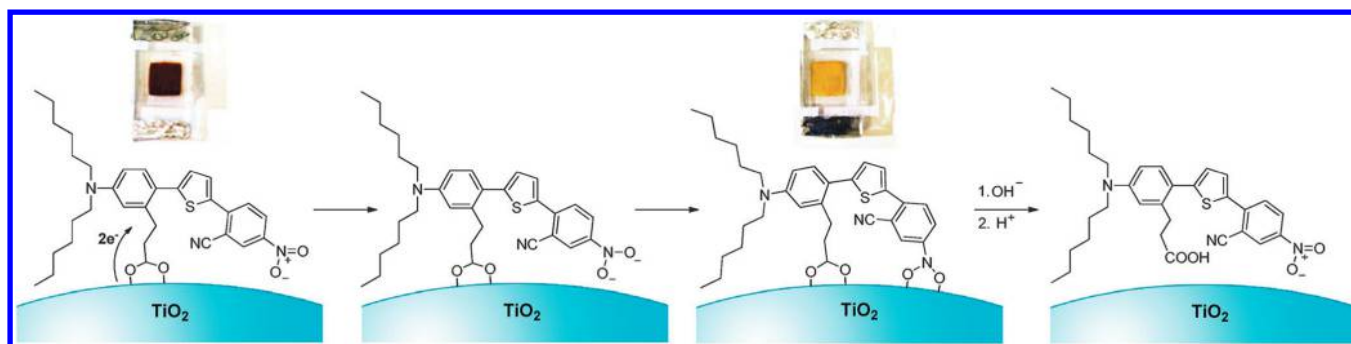
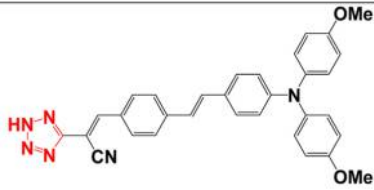


Figure 5. Postulated $\text{NO}_2 \cdots \text{TiO}_2$ coordination mechanism for dye **102** after reversal of the applied voltage, resulting in a macroscopic color change. Reproduced with permission from ref 17. Copyright 2012 Royal Society of Chemistry.

Table 15. Molecular Structure and Optoelectronic Properties of Dye **102** with a Tetrazole Anchor

No.	Name	Compound	λ_{max} /nm	V_{oc} V	J_{sc} /mA cm^{-2}	FF	$\eta/\%$	Ref.
103	D1		465	0.72	10.1	0.72	5.27	63

rhodamine group to form complexes with the DSSC electrolyte redox-couple intermediate, I_2 .¹²⁰ A large variety of organic dyes containing both rhodamine and carboxylic acid anchors, such as **108–123**, have been reported,^{23,121–125} and for these, usually high PCEs were achieved, e.g., for dyes **108–109** (> 8%).

Salicyclic Acid Group. Dye **124** (Table 17) with a salicyclic anchor and an azo group was incorporated in DSSCs and compared with a similar molecule (**125**), where the hydroxyl group is meta-, instead of ortho-positioned with respect to the carboxylic acid group.¹²⁷ For the salicyclic acid anchor, a tridentate binding mode onto TiO_2 substrates has been proposed, as this coordination should facilitate the electron transport in, for example, **124**, which consequently achieved an overall conversion efficiency ca. four times higher than that of **125**. On the basis of the sterically more demanding position of the hydroxyl group in **125**, a bidentate coordination mode was proposed. Especially for zinc-based porphyrin dyes **126–127**, the salicyclic anchor has demonstrated higher device performance parameters compared to analogues with carboxylate anchors.¹²⁸

Aldehyde Group. An aldehyde group was introduced as an electron acceptor and anchor in triphenylamine-based dyes that feature a diketopyrrolopyrrole core.¹²⁹ The UV/vis absorption peak wavelength of one of these dyes, **128** (Table 18), is comparable to that of the analogous cyanoacrylic-acid anchor-containing dye. Ooyama et al.¹³⁰ have prepared fluorescent dye **129**, with an aldehyde group as the electron-accepting group and a carboxyl group as an anchoring group. The presence of a carboxylic acid group renders strong dye $\cdots\text{TiO}_2$ adsorption and efficient electron injection. However, for the aldehyde-based dye **130**, which lacks a carboxyl group, a much more modest conversion efficiency in a solar cell is reported, because of its lower dye-loading efficiency onto TiO_2 ; this, in turn, diminishes the dye $\cdots\text{TiO}_2$ electron injection efficiency through the aldehyde group.¹³⁰

■ GENERAL PHYSIOCHEMICAL PROPERTIES OF DSSC ANCHORS

Anchor Orientation. Anchors attached to dye molecules via a phenyl moiety can be attached in ortho-, meta-, or para-positions with respect to the dye fragment. In most dyes, the anchor is positioned in the para-position, so that the molecule is attached perpendicularly to the TiO_2 surface. The carboxylic acid anchors in zinc porphyrin dyes attached in para- and meta-positions¹³¹ were found to exhibit better optoelectronic properties compared with their ortho-substituted analogues. This was supported by femtosecond TAS, indicating substantial charge recombination for the ortho-dyes. The effect of the anchoring position in D- π -A organic azo dyes has also been evaluated, but the anchoring position has there significantly less impact on the intramolecular charge transfer of the molecules. However, the PCE efficiencies vary for ortho-, meta-, and para-anchored dyes.⁹⁹

Protonation from Anchor Groups. Many anchors have acidic properties and hence strongly affect the band structure at the interface due to the protonation of the TiO_2 surface, as the accumulation of positive charge at the interface results in a lowering of the TiO_2 conduction bands.⁶ Associated with this is a larger J_{sc} value due to the driving force for the electron transfer from the LUMO of the dye to the conduction band of TiO_2 , as well as a lower V_{oc} value, which is defined by the difference between the quasi Fermi level of TiO_2 and the redox level of the electrolyte upon increasing the number of acid anchoring groups.⁷²

■ COMPARING THE RELATIVE MERITS OF ANCHORING GROUPS

In the majority of cases in this study, where anchors attach to the dye via phenyl moieties, the electron-withdrawing ability of the anchoring group can be ordered in strength according to the Hammett parameter (σ);⁹⁸ the anchor may lie at either the -meta

Table 16. Molecular Structures and Optoelectronic Properties of Dyes 104–123 with Rhodanine or Rhodanine-3-Acetic Acid Anchors

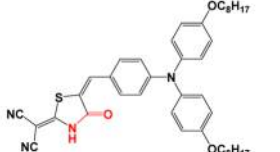
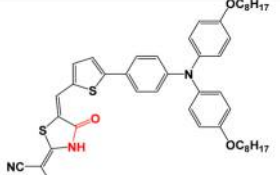
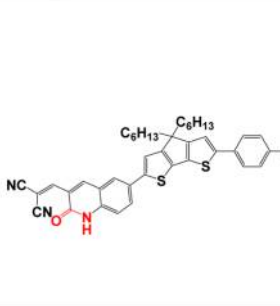
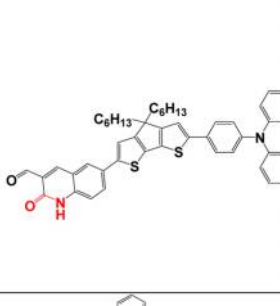
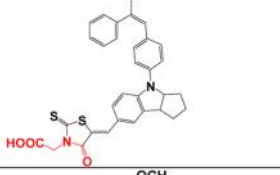
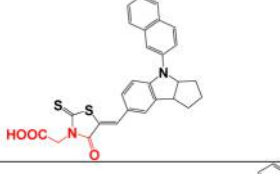
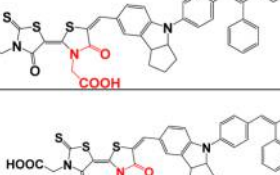

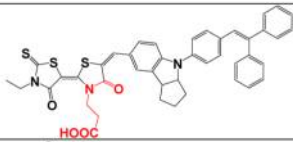
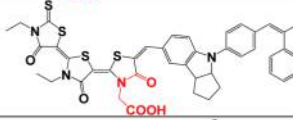
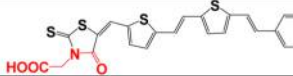
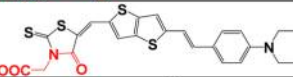
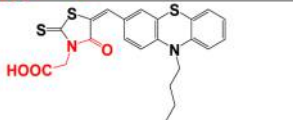
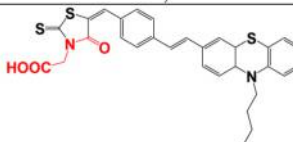
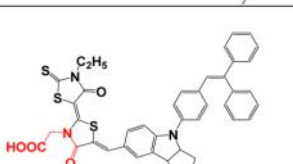
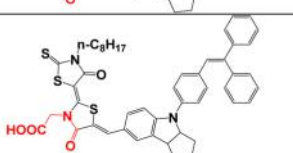
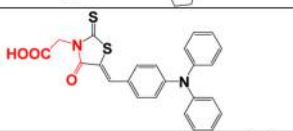
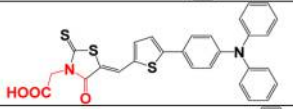
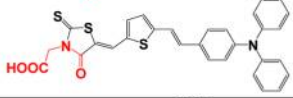
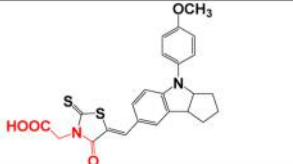
No.	Name	Compound	λ_{max} /nm	V_{oc} V	J_{sc} /mA cm ⁻²	FF	η /%	Ref.
104	RD-I		473	742	9.31	0.72	5.00	⁷⁹
105	RD-II		477	746	13.94	0.68	7.11	⁷⁹
106	PQ3		470	6.81	0.637	0.73	3.23	¹¹⁹
107	PQ2 ALD		518	0.58	0.98	0.77	0.45	¹¹⁹
108	1		604	0.60	17.76	0.57	6.1	¹²³
109	2		559	0.56	18.07	0.55	5.5	¹²³
110	1		526	0.65	17.75	0.54	6.51	¹²⁴
111	2		532	0.58	17.50	0.54	5.50	¹²⁴

Table 16. continued

No.	Name	Compound	λ_{\max} /nm	V_{oc} /V	J_{sc}/mA cm^{-2}	FF	$\eta/\%$	Ref.
112	3		531	0.63	17.38	0.51	5.60	¹²⁴
113	4		-	0.57	19.56	0.53	5.93	¹²⁴
114	D-SS		513	0.52	10.64	0.70	3.9	¹²¹
115	D-ST		488	0.56	15.23	0.73	6.2	¹²¹
116	T2-3		481	0.53	4.8	0.74	1.9	¹²²
117	T2-4		465	0.57	5.9	0.71	2.4	¹²²
118	D149		Ca. 530	0.64	19.08	0.68 2	8.26	¹²⁵
119	D205		Ca. 530	0.66	18.99	0.67 8	8.43	¹²⁵
120	L0		459	0.5	10.0	0.54	2.7	²³
121	L1		476	0.44	10.5	0.50	2.3	²³
122	L2		501	0.41	7.7	0.54	1.7	²³
123	Indoline Dye 1		483	0.59	14.8	0.59	5.11	¹²⁶

substituent position (σ_m) or -para position (σ_p) relative to the main dye fragment. Anchoring groups that donate electrons have negative σ values while groups that withdraw electrons have positive σ parameters. Considering anchoring groups that substitute at the para position, and the availability of an associated Hammett reference value, the electron-withdrawing ability of certain anchors in this review can be ordered: $-\text{CHO}$ (σ

$= 0.22$) $< -\text{COOH}$ ($\sigma = 0.43$) $< -\text{B}(\text{OH})_2$ ($\sigma = 0.45$) $< -\text{SO}_3\text{H}$ ($\sigma = 0.50$) $< -\text{CN}$ ($\sigma = 0.66$) $< -\text{NO}_2$ ($\sigma = 0.78$). In terms of relative electron-withdrawing ability, the carboxylic acid group is not so strong. However, other factors commonly manifest to complicate this simple comparison. For example, the electron accepting ability of phosphonic acid is weaker than that of carboxylic acid and the absorption band is shifted to shorter

Table 17. Molecular Structures and Optoelectronic Properties of Dyes 124–127 with Salicyclic Anchors

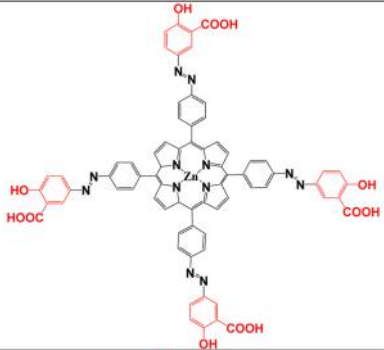
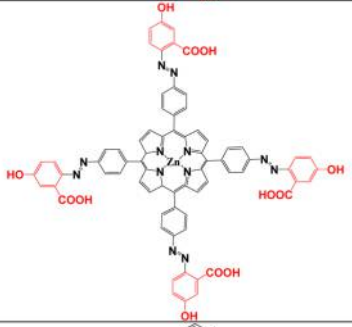
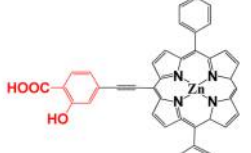
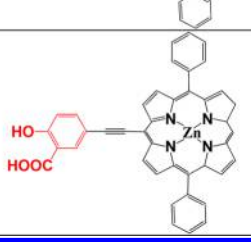
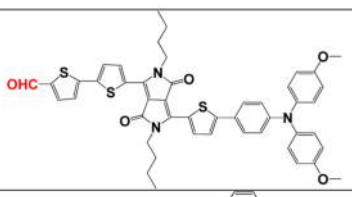
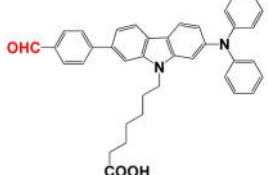
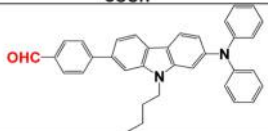
No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm^{-2}	FF	$\eta/\%$	Ref.
124	G201Zn		432	0.56	5.14	0.71	2.04	¹²⁷
125	G202Zn		433	0.55	1.73	0.60	0.56	¹²⁷
126	PESp		439	0.63	11.14	0.65	4.55	¹²⁸
127	PESm		437	0.56	3.55	0.62	1.22	¹²⁸

Table 18. Molecular Structures and Optoelectronic Properties of Dyes 128–130 with Aldehyde Anchors

No.	Name	Compound	λ_{max} /nm	V_{oc} /V	J_{sc} /mA cm^{-2}	FF	$\eta/\%$	Ref.
128	I		643	0.43	7.47	0.58	1.87	¹²⁹
129	YJY-1		384	0.60	7.56	0.71	2.04	¹³⁰
130	YJY-2		384	0.39	0.40	0.60	0.56	¹³⁰

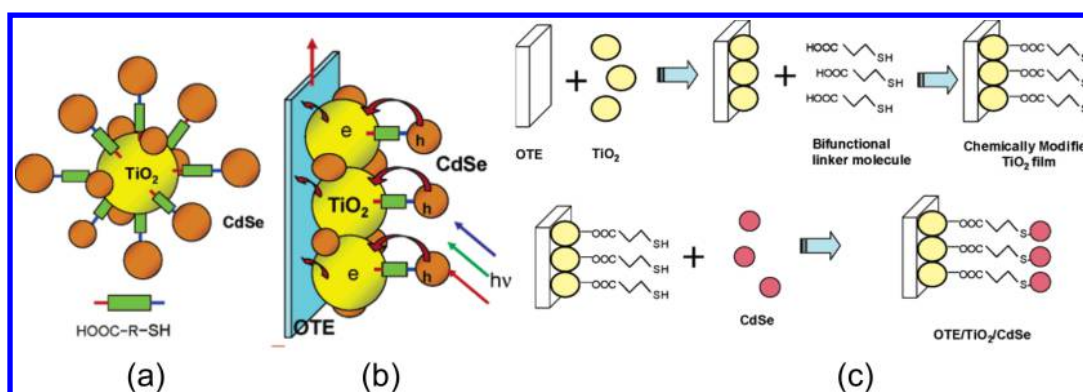


Figure 6. (a) Anchoring CdSe quantum dots to TiO₂ substrate surfaces via carboxylic acid/thiol bifunctional surface modifier. (b) The light harvesting assembly is deposited on optically transparent electrode. (c) The steps to link CdSe quantum dots to TiO₂ substrate with the carboxylic acid/thiol linker. Reproduced with permission from ref 137. Copyright 2006 American Chemical Society.

wavelength.^{70,132–134} Pyridine and sulfonic acid achieve similar UV/vis absorption peak wavelengths and dye coverage compared with carboxylic acid. The hydroxyl group cannot be used alone as an anchor, because of negligible adsorption on TiO₂ surfaces.⁴³

As a general rule though, the peak UV/vis absorption wavelength of contrasting dyes, bearing different anchors but otherwise the same structures, follow the trend that the larger Hammett value, the more electron withdrawing ability and corresponding red shift in UV/vis absorption spectra. However, in real-case scenarios, this is often complicated by other factors such as dye aggregation, solvent effects, proton transfer and temperature effects, both in solution and on the TiO₂ surface. The molecular orbital distribution of a dye, especially the nature of its Frontier orbitals (HOMO and LUMO), can help assess the electron withdrawing strength of a given anchor. For all cases where such orbital features are displayed for subject dyes in this review article, their LUMO distributions essentially juxtapose the anchor and electron acceptor, while their HOMO spatial renderings connect to the electron donor group.

Although the carboxylic acid anchor offers optimal physical properties in terms of UV/vis absorption wavelength, dye coverage and optimal photon-electron conversion efficiency, more newly tested anchors excel in various aspects. For example, a phosphonic acid anchor provides strong electronic coupling with the TiO₂ semiconductor, whereas the hydroxamate anchor affords a dye with good water stability.

Although these general trends have been established, full and quantitative comparison studies of anchoring groups are currently difficult with the state-of-the-art results available from the literature; this is because key dye property information is only partly tractable, not tractable at all, or is only available in a form that does not permit ready comparison. For example, much of the materials characterization experimentation discussed earlier, for enabling the direct visualization of anchoring processes, is still in the early stages of development; so qualifiers such as the exact coordination mode of most of these anchors onto the substrate surface is either missing or controversial.

Nevertheless, anchors have shown pronounced effects on all DSSC operating parameters, such as light absorption, molecular orbital distribution, frontier orbital energy levels, band structures of working electrode semiconductors, interfacial electron transfer, charge recombination, and overall solar-to-electron conversion efficiencies of the solar-cell device. Although, it should be noted that detailed comparisons of dyes, which are

qualified by DSSC property attributes from devices fabricated and tested by different research groups, should be approached with some caution; this is because there is wide variability between DSSC results emanating from research groups from different laboratories around the world. To this end, better normalized DSSC device results should be advocated in order to enhance the consistency of reports from fabricated cells in one research group and between different groups. A very simple, but effective, adjustment in DSSC measurement protocol has been demonstrated by Cole et al.,⁴⁸ who express a preference for presenting device efficiency of a new dye, not as the absolute parameter, η , but as a relative parameter with respect to that of N719 made using the same DSSC fabrication and testing procedures, i.e., a $\eta_{\text{dye}}/\eta_{\text{N719}}$ ratio; in that case study, this ratio was found to be highly reproducible between DSSC devices fabricated and tested using two different laboratories which housed disparate fabrication equipment, instrument calibration levels for device testing, fabrication methods and fabrication and testing personnel. Wide adoption of this very simple adjustment in DSSC device reporting would substantially help gain consistency within the literature in the short term. This said, the ultimate goal should of course be to raise the worldwide level of DSSC fabrication and testing standards; to help establish best practice protocols, Snaith¹³⁵ has addressed the inconsistency issue of DSSCs during cell measurement. With this all told, comparing the currently available DSSC device properties from dyes measured between different research groups still offer exclusive insights on the development of the DSSCs and anchoring effects.

■ RELATED APPLICATIONS FOR ANCHORING GROUPS

Anchors for Quantum Dot-Sensitized Solar Cells. The anchoring group not only has a significant impact on DSSCs but is also important for quantum dot-sensitized solar cells, which feature a desirable tunability of the band gap and are simultaneously very cost efficient.^{68,136} In quantum dot-sensitized solar cells, the coupling between the quantum dot particles and the TiO₂ substrate can be weak, potentially inducing parasitic charge recombination and inferior electron injection. However, anchoring groups can be attached in order to increase the magnitude of coupling between the quantum dots and the metal oxide substrate. For example, carboxylate anchors assisted by a thiol group can be used to anchor CdSe quantum dots onto TiO₂ for DSSC applications (Figure 6),¹³⁷ as the

carboxylic acid group has a high affinity toward TiO_2 , whereas the thiol group has high affinity toward the CdSe quantum dots. Typically, IPCE values around 12% are observed for this type of solar cell.

Similarly, phosphonate anchors have been employed to link CdS quantum dot-sensitized solar cells.¹³⁸ There, the anchor acts both as an agent to compensate defects and as a charge recombination barrier. As a result, the overall device conversion efficiencies with phosphonate anchors are approximately three times higher than those without anchors.

Anchors for Water Splitting Systems. For the photocatalytic generation of hydrogen from water, anchors are indispensable to attach dyes onto the substrate surface.¹³⁹ Bae et al. have compared the anchoring effects between carboxylate and phosphonate anchors on the photocatalytic properties and stability of two ruthenium compounds.¹⁴⁰ For the phosphonate anchor, higher photocatalytic activity and higher hydrogen production was observed, but both dyes were found to be unstable in water, be it under exposure to sunlight or in the dark. It is feasible to assume that several other anchors described in this review could offer suitable alternatives for such water splitting systems.

CONCLUSIONS

The molecular structures and optoelectronic properties of a broad variety of DSSC anchors have been surveyed, including pyridine, phosphonic acid, tetracyanate, perylene dicarboxylic acid anhydride, 2-hydroxybenzonitrile, 8-hydroxyquinoline, pyridine-N-oxide, 3-hydroxy-N-methylpyridinium, catechol, hydroxamate, sulfonic acid, acetylacetanate, boronic acid, nitro, tetrazole, rhodanine, and salicylic acid substituents. The judicious choice of anchor can provide custom-tailored performance parameters for the solar cell, such as stability and overall conversion efficiency. The physicochemical behavior of these anchors has been examined with the help of various analytical tools, but many of the new anchors still remain to be exhaustively and systematically investigated. Furthering the herein described developments in materials characterization that are specifically associated with probing dye anchoring onto the semiconductor surface of the DSSC working electrode will significantly aid these investigations. Most informative stands to be the in situ or in operando developments in such analytical tools whereby physicochemical measurements on the dye–semiconductor interface or DSSC performance tests on the operational device are, respectively, being simultaneously performed on the sample under characterization. This way, one will be able to relate directly the nanoscopic structure of the dye–semiconductor interface and its structural dynamics to the macroscopic device performance of a DSSC.

Although this review focuses on singular dye anchors, it is reasonable to expect that multiple different anchors can be attached onto the same dye in order to induce synergetic effects. Moreover, several dyes may be adsorbed onto the same semiconductor nanoparticulate surface to the same effect via cosensitization which is becoming an increasingly popular practice in DSSC device fabrication.⁹ This review of the full scope of current anchoring types will aid the choice of complementary anchors in their cohosting on the same dye or mixing between dyes in order to realize these synergic goals.

Beyond DSSCs, this review also highlights the need for further studies on the application of these anchors to cognate fields such as quantum dot DSSCs, water splitting systems, self-assembled monolayers, and organic/inorganic interfaces (molecular

switches, surface uphill movement, molecular junctions, etc.) in order to fully exploit the strengths of the described anchoring moieties.

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Author Contributions

This manuscript contains contributions of all authors, and all authors have approved of the final version of the manuscript.

Notes

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