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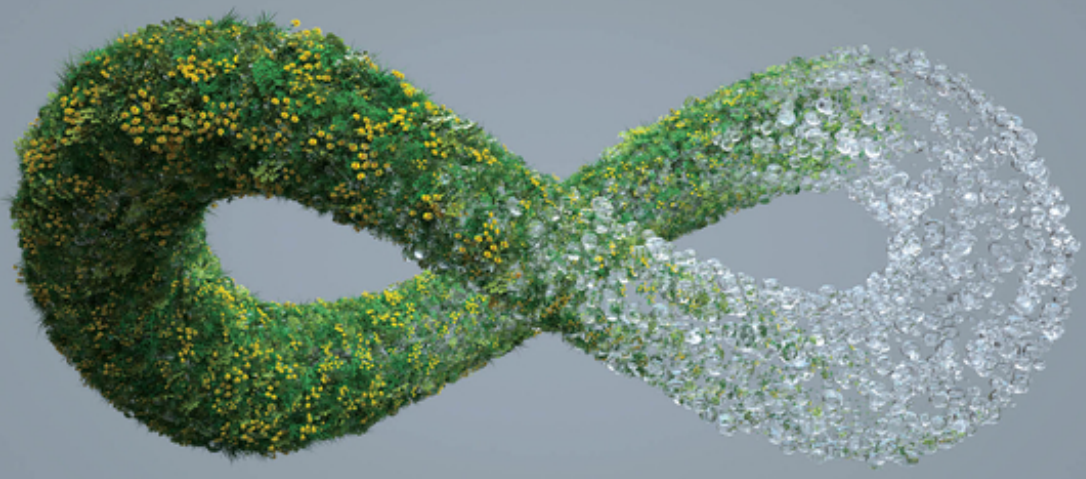
Water Photo- and Electro-Catalysis

Mechanisms, Materials, Devices, and Systems



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Cover Image: © Andriy Onufriyenko/
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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-34835-0
ePDF ISBN: 978-3-527-83099-2
ePub ISBN: 978-3-527-83101-2
oBook ISBN: 978-3-527-83100-5

Typesetting: Straive, Chennai, India

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Preface

> I believe that water will one day be employed as a fuel, that hydrogen and oxygen that constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable.
>
> —Jules Verne

Water, consisting of hydrogen and oxygen, could act as a sustainable reactant or product to participate in various chemical reactions along with clean energy conversion. As driven by solar energy or thus-generated electricity, water photo- and electro-catalysis for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) has been considered as an effective approach to green hydrogen production. In reverse electrocatalysis processes, hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) inevitably happen in a fuel cell, which has been considered as a promising technology for green electricity generation. It should be further noted that, by acting as the reactant for electrocatalysis, water could drive the reactions of CO_2 (CO_2RR) and N_2 (NRR) reduction to produce value-added chemicals and fuels (e.g. hydrocarbons and NH_3), and even realize organic transformations coupled with H_2 production. Thus, water photo- and electro-catalysis is becoming an increasingly important field while being considered as an important way to solve the global problems of energy shortage and environmental pollution, and is indeed the technology of the twenty-first century by significantly impacting on human activity,

This book aims to bring together the latest developments in water photo- and electro-catalysis with a focus on its impact on the energy agenda, which splits broadly into different technologies including photocatalysis, photoelectrocatalysis, electrocatalysis, and photovoltaic–electrocatalysis for HER, OER, HOR, ORR, CO_2RR, NRR, and organic transformations. This book shows how the underlying principles are being used across these fields to develop technology with improved functionality and high operating efficiency in terms of water-involved energy conversion reactions. It consists of 11 chapters and introduces different technologies of water photo- and electro-catalysis for energy conversion. The basic mechanisms, emerging materials, devices, and systems of water photo- and electro-catalysis for energy conversion are intrinsically linked, by covering: (i) the fundamentals, materials, and systems of semiconductor-based photocatalytic water

splitting; (ii) the mechanisms, photoelectrode/catalyst materials, and devices of photoelectrocatalytic and photovoltaic-electrocatalytic water splitting; (iii) the fundamentals, materials, and devices for water electrocatalysis, including HER, OER, HOR, and ORR; (iv) the materials and devices for electrocatalytic CO_2RR, NRR, and organic transformations; (v) the advanced characterizations on water photo- and electro-catalysis.

In the past years, exciting breakthroughs in materials and nanotechnology have stimulated a huge amount of renewed interest in this field, although some critical issues of materials, like poor sunlight absorption, poor electric conductivity, and retarded water electrocatalysis kinetics, have thwarted many earlier efforts to reach the "Holy Grail" of photo- and electro-catalysis for energy conversion with economic and ecological sustainability. While we cannot even hope to approach completeness of such technologies in a single book, we nevertheless hope that both scientists and engineers, experts and newcomers in this field find some useful information and details here those can help their academic research and industrial development.

We would like to appreciate the efforts from all the contributors and also the financial support from the National Natural Science Foundation of China (52225606, 51888103).

3 August 2023
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1

Solar Energy Conversion by Dye-sensitized Photocatalysis

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1.1 Introduction

Dye sensitization enables the generation of charge carriers in a wide-bandgap semiconductor under irradiation by visible light that cannot be absorbed by the semiconductor. Dye-sensitized photocatalysis (DSP) was first proposed by Gerischer in 1972 [1] and was later demonstrated by Grätzel et al. [2]. Because of its potential applications in solar energy conversion, DSP has been studied for decades, especially for H_2 evolution via water splitting [3–5]. The DSP H_2-evolution system consists of two building blocks—a light absorber and a semiconductor material (Figure 1.1)—and the H_2 evolution reaction proceeds as follows: First, the photosensitizer absorbs light and is excited (1). The excited dye injects an electron into a semiconductor (2). The injected electron is consumed via a proton-reduction reaction on the semiconductor's surface, and H_2 is evolved (3). The oxidized light absorber generated by the electron injection returns to the ground state by accepting an electron from a reductant (4). Unfortunately, some undesirable reactions can occur during this reaction scheme (5–7). To improve the overall efficiency of this system, researchers have devoted extensive effort to promoting the forward reactions and impeding the backward reactions.

In this chapter, we present the strategies for improving DSP systems by separating each building block, pointing out the important factors that influence the DSP performance. We survey recent achievements in the DSP field, especially those related to water-splitting systems, including electrochemical systems, and discuss how various factors can be controlled to improve the performance of dye-sensitized systems.

1.2 Light Absorbers

The development of photosensitizers has been rapidly promoted with the growth of the dye-sensitized solar cell (DSSC) field, which has been pioneered by

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First Edition. Edited by Shaohua Shen and Shuangyin Wang.

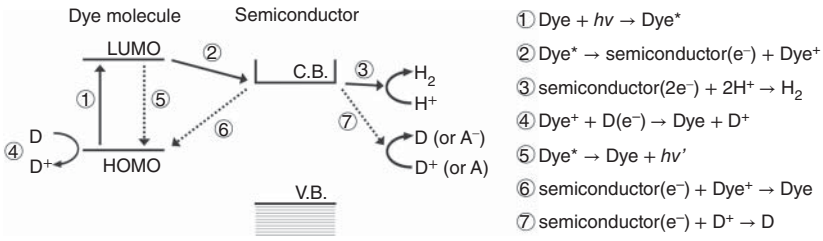


Figure 1.1 Electron transfer processes in a dye-sensitized photocatalysis system. C.B., conduction band; V.B., valence band; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; D, electron donor; D^+: oxidized electron donor; A, electron acceptor; A^-, reduced electron acceptor. Solid and broken arrows represent forward and backward electron transfers, respectively.

Tsubomura and coworkers [6] and by O'Regan and Grätzel [7]. The practical application of dye-sensitized photovoltaic cells became realistic with the development of a trinuclear Ru complex that possesses two cyano-bridges and four carboxyl-anchoring groups (Figure 1.2a) [8]. A substantial achievement in the DSSC field is the exploitation of the **N3** dye (Figure 1.2b); the electron-injection quantum yield (QY) from **N3** into TiO_2 has reached almost unity, with a solar-to-electric conversion efficiency of 10% under AM1.5G illumination [9]. The structure of **N3** is very similar to the anchoring unit of the trinuclear dye in that **N3** has four carboxyl-anchoring moieties and two isothiocyanato ligands. The next excellent dye developed was **N719** (Figure 1.2c), which gave a power conversion efficiency greater than 9.18% under AM1.5G. This value is still high even now, although the original work was published 20 years ago [10, 11]. These highly efficient dyes for DSSCs, however, have not been well utilized in DSP systems because of the difference in the DSSC and DSP catalytic cycles. In the case of DSSCs, the injected electrons in a semiconductor (e.g. TiO_2) should migrate quickly to reach the counter electrode through an external circuit. Because of the rapid collection of the injected electrons, acceleration of the electron-injection process by strong coupling between the dye and the semiconductor is effective for DSSC systems. In the case of DSP, however, a surface catalytic reaction involving multi-electron transfer (e.g. proton reduction) would become the rate-determining step, whose time scale is at least four orders of magnitude slower than that of the excited-charge-carrier transfer processes [5]. This is distinct from DSSCs, which are operated by single electron transfer processes. Accelerating the electron injection leads to an increase in the standby electrons in the conduction band for the catalytic reaction, which is not effective for DSP systems. On the contrary, the strong coupling may promote undesirable back electron transfer from the conductive substrate to the oxidized dye [12]. Therefore, the dyes developed for DSSCs need to be modified for use in DSP systems. In this section, new dyes developed for efficient DSSCs are introduced and then dye sensitizers optimized for DSP are discussed.

Before moving to the details, we here explain the basic molecular design of photosensitizers. One of the most studied classes of dyes is metal complexes, which have been used in pioneering research in DSP systems [2, 3, 5] and DSSCs

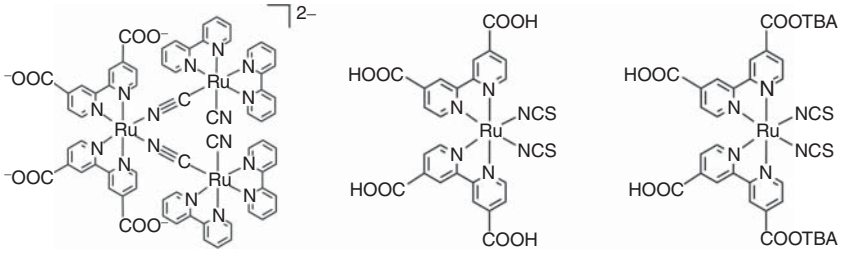


Figure 1.2 Molecular structures of (a) $[Ru(bpy)_2(CN)_2]_2Ru(bpy(COO)_2)_2^{2-}$ (bpy = 2,2′-bipyridine), (b) **N3**, and (c) **N719**. TBA: tetrabutylammonium.

[4, 7–11]. Recent advances in the DSP for H_2 evolution have included the development of Ru [13], Zn [14], and Ir [15] complexes, and these complexes are still mainstream materials used in the DSP field because their photo- and physicochemical properties are chemically controllable. Visible-light absorption by metal complexes used in dye-sensitized systems originates mainly from metal-to-ligand charge transfer (MLCT). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are distributed around the metal center and the ligands, respectively. There are three important properties for an effective sensitizer: (i) wide and strong absorption in the visible region, (ii) an efficient excited-charge-carrier transfer cycle, and (iii) high stability. Shifting the HOMO and LUMO levels varies the light-absorption properties of dyes. Efficient excited-charge-carrier transfer is achieved through vectorial electron transfer. Increased stability is attained via strong adsorption onto a semiconductor.

All three of the aforementioned important properties for designed dye molecules can be achieved through adaptation of the ligands of the metal complex. A tris(bipyridine)ruthenium(II) derivative is a good example for explaining the molecular design of metal complexes (Figure 1.3a). For a dye to adsorb onto a semiconductor, at least one of the bipyridine ligands should be functionalized with an anchoring moiety, which should be located at the position closest to the semiconductor substrate. In such a case, the LUMO of the complex is distributed at the functionalized bipyridine ligand, which enhances electron injection from the excited-state complex into the semiconductor. Therefore, if the other peripheral ligand(s) possess a higher energy than the anchoring ligand, the excited electrons would gather on the anchoring ligand, thereby accelerating the electron injection. In addition, because the electron density of the metal center should be increased to ensure wide visible-light absorption, the peripheral ligand(s) should demonstrate electron-donating behavior. Triphenylamine, which exhibits strong electron-donating ability, was introduced onto a Ru complex as a secondary electron donor unit [16]. Although a triphenylamine-based dye had been studied previously [17], excellent dyes that possess a triphenylamine moiety as an electron donor were developed in the same period [18–20]. The triphenylamine-based dyes have a donor–π–acceptor (D–π–A) conjugated structure, which consists of carbon–carbon double-bonded π-bridges and a cyano electron-acceptor group

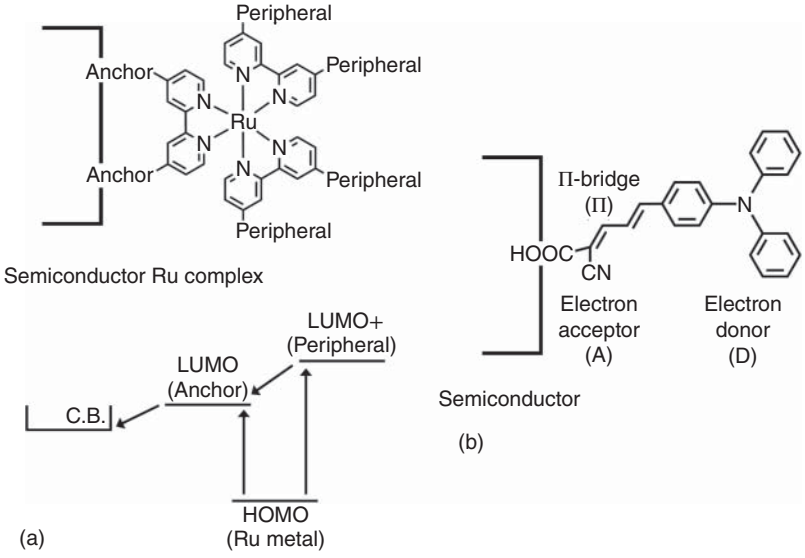


Figure 1.3 Structures of (a) a Ru trisdiimine complex and (b) a triphenylamine-based organic sensitizer. The bottom of figure (a) shows a schematic of the electron-transfer processes of a Ru complex–semiconductor hybrid material. LUMO+: an unoccupied molecular orbital with an energy level higher than that of the LUMO.

(Figure 1.3b). The D–π–A structure enables vectorial charge transfer, which is one of the aforementioned important characteristics of dye-sensitized systems. One of the triphenylamine-based dyes gave an overall **DSSC** efficiency of 5.3%, which is similar to the efficiency of N719 (7.7%). This advancement triggered the rapid development of organic dyes, which are now also used for DSP H_2 evolution. DSP for H_2 evolution has been studied using triphenylamine [21, 22], an organoboron complex [23], coumarin [24], perylene [25], calixarene [26], and tetrathiafulvalene [27], as building blocks for photosensitizers. During the development of these photosensitizers, numerous factors for improving dye-sensitized systems have been revealed. We here discuss these factors, along with some examples of dyes demonstrating the effect of each factor.

1.2.1 Extending the Light Absorption Spectra of Dyes

Extending the absorption spectrum of a dye is a common approach to efficiently utilizing sunlight for solar energy conversion. The strategy for extending the absorption of a dye appears simple: shift the LUMO downward and/or the HOMO upward. The reality, however, is not straightforward because two requirements must be met [28]. First, an excited-state dye must inject an electron into the semiconductor. Second, a sensitizer needs to oxidize a reductant or electron mediator to regenerate the ground state. Extensive efforts have been devoted to developing new photosensitizers that enable the more efficient utilization of solar energy while still achieving these two requirements.

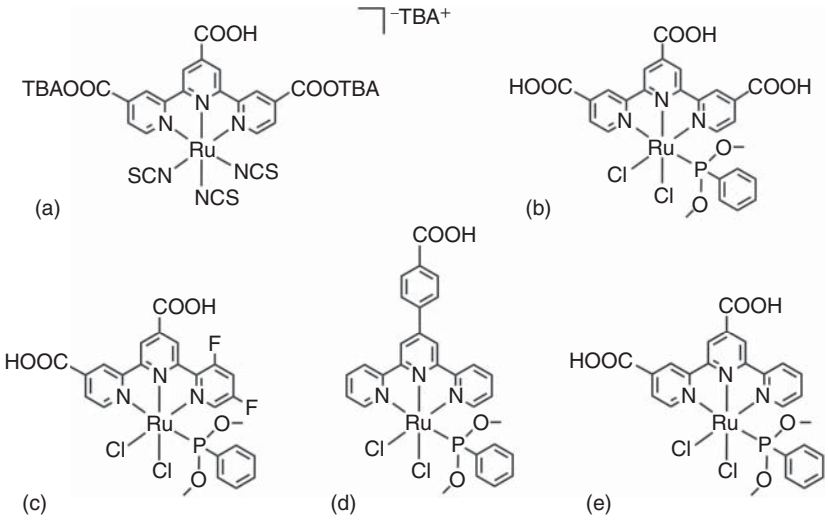


Figure 1.4 Molecular structures of the (a) **N749**, (b) **DX1**, (c) **GS11**, (d) **GS12**, and (e) **GS13** dyes.

Grätzel's group synthesized a panchromatic dye (black dye), **N749** (Figure 1.4a), using a tridentate terpyridine derivative ligand and three thiocyanato ligands [28]. The development of such a panchromatic dye is the ideal approach under the conventional strategy. The absorption spectrum of the sensitizer was extended by the introduction of three thiocyanato ligands that shift the ruthenium(II) t_{2g} orbitals upward. The LUMO level was kept at a more negative potential than the conduction band of TiO_2, and the HOMO was located at a sufficiently positive potential relative to the redox potential of the reductant (i.e. iodide). Recently, Segawa and coworkers developed a phosphine-coordinated Ru-complex sensitizer, **DX1** (Figure 1.4b) [29]. Their approach to extending the absorption of the dye is unconventional in that it involves a spin-forbidden transition. Figure 1.5a shows the absorption and emission spectra as functions of the energy diagrams of **DX1**, along with the spectrum of a black dye. In the case of **DX1**, the singlet–triplet transition is emphasized clearly, and this extension of the light-absorption spectrum improved the power conversion efficiency in a DSSC system.

DX1 and its derivatives have been investigated in a DSP for H_2 evolution [13]. Four phosphine-coordinated Ru complexes (Figure 1.4b–e) were synthesized; their energy diagrams are shown in Figure 1.5b. In all cases, the LUMO level was sufficiently negative for excited-electron injection into the conduction band of TiO_2. These four panchromatic photosensitizers were applied to the photocatalytic H_2-evolution reaction on Pt-modified TiO_2, where triethanolamine (TEOA) was used as a sacrificial electron donor. **GS12** showed the highest H_2-evolution activity, and the apparent quantum yield (AQY) for H_2 evolution under irradiation by a 400 W Hg lamp reached 5.16%. This value is 5.5 times greater than that of **N719** under the same conditions. The activity increased in the order **GS12** > **GS11** > **DX1** > **GS13**, and this trend obviously reflects the LUMO energy level. These results indicate that

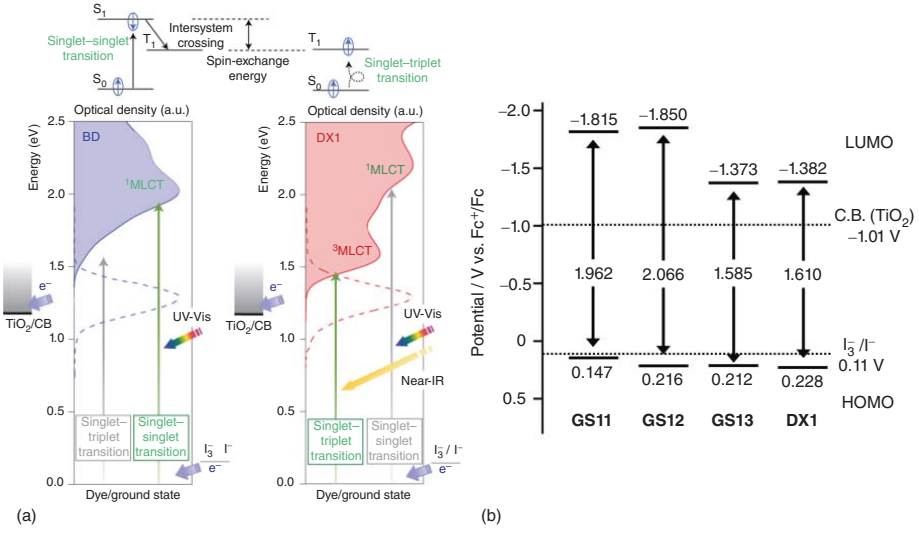


Figure 1.5 (a) Energy diagram of the components and the device performance of the sensitizers. Absorption (solid line) and emission (dashed line) spectra vs. the energy diagrams of BD (black dye, **N749**, left) and **DX1** (right). In the singlet-to-singlet transition, the electron transition from the S_0 to the T_1 excited states causes energy loss via spin-exchange energy (top). Source: Reproduced with permission from Kinoshita et al. [29]; © 2013, Springer Nature. (b) Schematic energy levels of **GS11**, **GS12**, **GS13**, and **DX1**. Source: Adapted with permission from Swetha et al. [13]; © 2015, American Chemical Society.

the DSP performance for the H_2-evolution reaction can be enhanced by negatively shifting the oxidation potential of the dye in the excited state. The use of a panchromatic dye in a dye-sensitized H_2-evolution system improved the photocatalytic activity, and an investigation of the **DX1** derivatives revealed that regulation of the LUMO energy level is an important consideration in the molecular design of sensitizers.

1.2.2 Enhancement of the Absorption Coefficient of Dyes

Increasing the molar extinction coefficient of dyes is a straightforward method of increasing the solar energy conversion efficiency in a dye-sensitization system. Making the π-chromophore more rigid is a common tactic to increase the molar extinction coefficient. Rigid molecules can suppress the rotational disorder and enhance the delocalization capacity of π-electrons [30]. At the same time, however, increasing the rigidity of molecules promotes aggregation, and undesirable aggregation often adversely affects the energy conversion performance via, e.g. competitive nonradiative quenching and a hypsochromic shift of the dye [31]. As an alternative approach to enhancing the molar extinction coefficient, Ning et al. proposed incorporating an additional electron donor unit into the dye to form a starburst 2D–π–A conjugate [32]. This approach is promising for increasing light-harvesting performance; however, the number of reported starburst 2D–π–A structures is limited because of their complicated synthetic pathways. To address this problem, organoboron complexes have been investigated as relatively small and simple π-chromophore units.

The approach of incorporating organoboron complexes has been applied to a phenothiazine-based dye [30]. Phenothiazine (Figure 1.6a) is one of the most extensively studied electron-donor components and exhibits strong electron-donating character because of its heterocyclic structure containing S and N [33]. Because of its strong electron-donating ability, an early phenothiazine-based dye achieved a solar-energy-to-electricity conversion efficiency comparable to that of **N3** dye [34]. Further improving the efficiency of the phenothiazine-based dye system is difficult because of its low molar extinction coefficient. Given this background, the incorporation of organoboron complexes into phenothiazine-based dyes is attractive. In particular, 4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (BODIPY, Figure 1.6b) dyes exhibit high molar absorptivity and sharp fluorescence peaks, along with a high QY [35]. A series of BODIPY derivatives, pyridomethene–BF_2 complexes (Figure 1.6c), exhibit a very large extinction coefficient ($5 \times 10^4 \leq \varepsilon \leq 1.4 \times 10^5\ M^{-1}\ cm^{-1}$). Among the emission quantum efficiencies of the derivatives, the highest was similar to that of **N719** [30]. To further improve BODIPY-sensitized systems, Erten-Ela et al. developed a dibenzo-BODIPY dye (Figure 1.6d) using a conventional strategy, with the objective of extending the π-conjugation and enabling longer-wavelength absorption [36]. The dibenzo-BODIPY was combined with phenothiazine (Figure 1.6e), and the absorption reached the near-infrared (NIR) region. The efficiency of BODIPY-sensitized solar cell systems eventually overtook that of **N719** systems [36]. The dibenzo-BODIPY and phenothiazine combined dye has

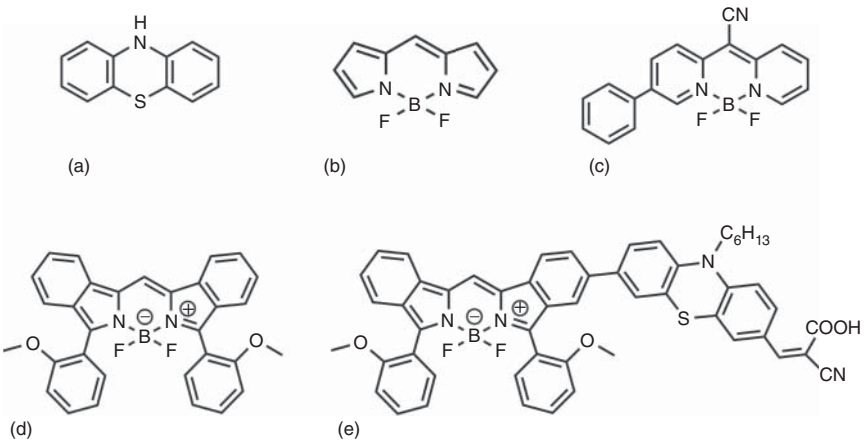


Figure 1.6 Molecular structures of (a) phenothiazine, (b) BODIPY, (c) the parent pyridomethene–BF_2 complex, (d) dibenzo-BODIPY dye, and (e) a phenothiazine dye with dibenzo-BODIPY incorporated.

been applied to the H_2-evolution reaction on Pt-modified hierarchical porous TiO_2, where ascorbic acid (AA) was used as a sacrificial electron donor [37]. The turnover number of the dye for H_2 evolution reached 11,100 under visible-light irradiation ($\lambda > 400$ nm) at an intensity of 100 mW cm^{-2}. The organoboron-phenothiazine dye improved the visible-light absorption performance and demonstrated high H_2 evolution activity in metal-free organic dyes. That is, a binary electron donor system comprising a small and simple π-chromophore unit incorporated into an electron-donor building block functioned well as a dye-sensitized photocatalyst system.

1.2.3 Molecular Design for Efficient Excited-Charge-Carrier Separation and Injection

Efficient charge-carrier separation and injection into a semiconductor strongly affects the efficiency of a dye-sensitized system. As previously described, the visible-light absorption of dyes relies predominantly on a charge-transfer (CT) transition between donor/acceptor units. The donor unit should be physically separated from the semiconductor to suppress back electron transfer from the semiconductor and to facilitate the reaction with a reductant in the reaction solution. The acceptor unit should be physically close to the semiconductor to enable the immediate transfer of an excited electron into the semiconductor. To improve the energy conversion efficiency through the molecular design of dyes, tracing the history of the development of sensitizer molecules and understanding the roles of the building blocks of dye molecules would be beneficial. Here, a triphenylamine-based dye, which is one of the most studied organic photosensitizers, is used as an example and the history of the development of dyes is described.

Triphenylamine has been studied extensively as an electron-donor unit since the early 2000s [20]. In the earliest study of triphenylamine as a donor unit,

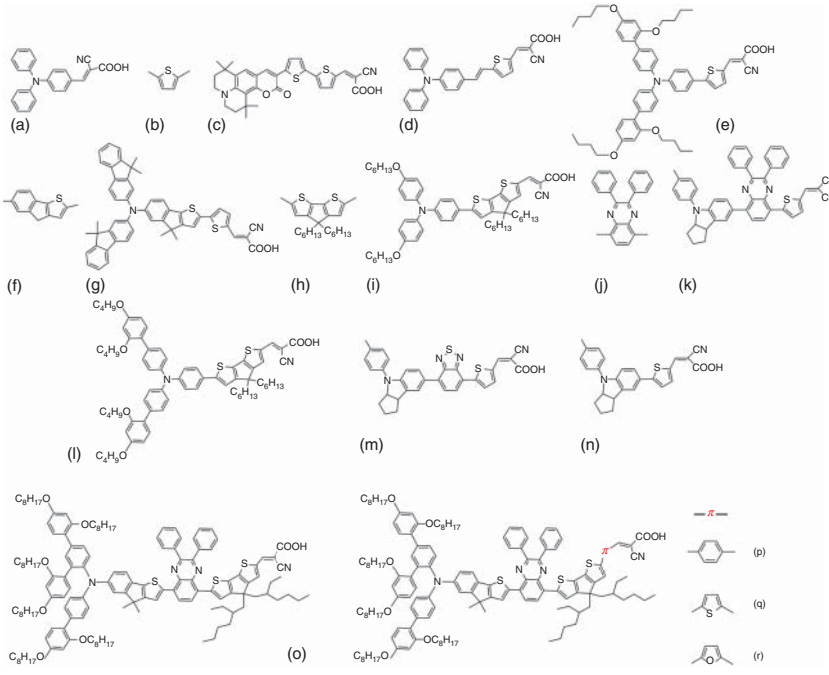


Figure 1.7 Molecular structures of (a) one of the earliest developed triphenylamine-based dyes, (b) the thiophene moiety, (c) a thiophene-bridged coumarin dye (**NKX-2677**), (d) dye **D5**, (e) dye **D35**, (f) the indeno[1,2-*b*]thiophene moiety, (g) an indeno[1,2-*b*] thiophene-bridged dye (**JK-225**), (h) the cyclopentadithiophene moiety, (i) a cyclopentadithiophene-bridged dye (**C218**), (j) a 2,3-diphenylquinoxaline unit, (k) a 2,3-diphenylquinoxaline-incorporated dye (**IQ4**), (l) **LEG4**, (m) **WS-2**, (n) **LS-1**, (o) **S5**, (p) **SD1**, (q) **SD2**, and (r) **SD3**.

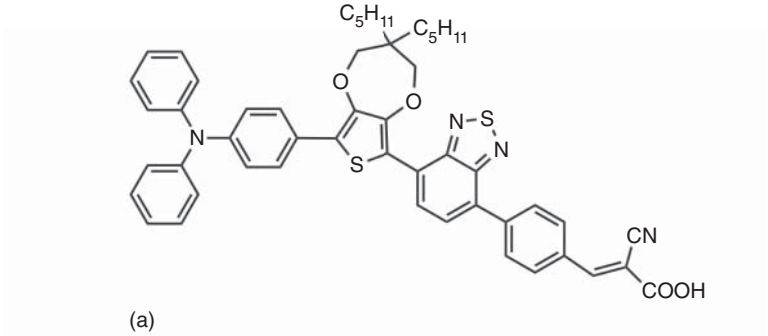
dyes consisting of carboxylic and cyano moieties as electron-donor and -acceptor groups, respectively, were developed (Figure 1.7a) [18]. Because the carbon–carbon double-bonded π-bridge in these dyes is problematic in terms of the synthesis and stability of the molecule, a thiophene moiety (Figure 1.7b) was incorporated as a new π-conjugation unit to address these problems in a coumarin dye (Figure 1.7c) [38]. Combining these moieties, Hadberg et al. developed one of the simplest-structured triphenylamine-based dyes, named **D5** dye (Figure 1.7d), which gave an energy conversion efficiency comparable to that of **N719** [39]. The para-position of the triphenylamine unit was subsequently substituted to increase the electron-donating character (Figure 1.7e) [40]. Indeno[1,2-*b*]thiophene (Figure 1.7f,g) [41] and cyclopentadithiophene (Figure 1.7h,i) [42] units were used to expand the π-conjugation system. A 2,3-diphenylquinoxaline unit (Figure 1.7j,k) [43] was introduced not only as an acceptor unit but also as a building block to limit intermolecular aggregation. The use of these good building blocks (electron donor, electron acceptor, and π-conjugation units) led to the development of a triphenylamine-based D–π–A-structured dye, **LEG4** (Figure 1.7l), and its derivatives [44].

Further improvement of D–π–A-structured dyes was realized through a new molecular design: the donor–acceptor–π–acceptor (D–A–π–A) structure [45]. To explain the effects of electron–acceptor insertion between the electron-donor and π-bridge, we here discuss two dyes (**WS-2** and **LS-1**, Figure 1.7m,n, respectively) as examples. They possess an indoline-based electron donor, a thienyl π-linker, and a cyanoacrylic acid electron acceptor. The D–A–π–A dye **WS-2** has benzothiadiazole (BTD) as an additional electron acceptor. The incorporation of an electron-acceptor unit between the electron-donor and π-conjugation units influences the electronic state of the molecule, as confirmed by a density functional theory simulation of the BTD-inserted D–A–π–A dye **WS-2**. The HOMO and LUMO distributions both clearly overlap the orbitals of the BTD unit, which is beneficial for the electron transition. Comparing these two sensitizers reveals four advantages of the **WS-2** dye: (i) strong light-harvesting ability because of the bathochromic shift of the absorption associated with CT, (ii) the appearance of an additional absorption band attributed to a secondary frontier orbital transition, (iii) suppression of the hypsochromic shift that accompanies adsorption onto a TiO_2 film, and (iv) improvement of the stability for light absorption because of the decrease in the LUMO level. The substantial improvement of the light-absorption capability as a result of the formation of the D–A–π–A structure contributed to a high power conversion efficiency of 9.04% [46].

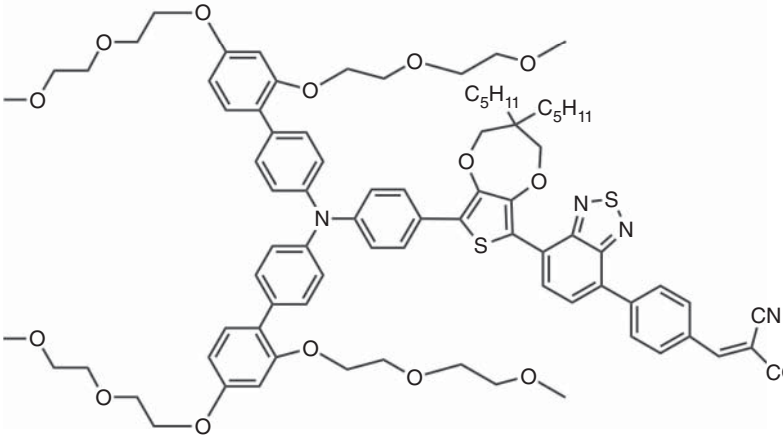
This new strategy led to the development of a derivative of the **LEG4** dye (**S5**, Figure 1.7o) [47], along with dyes with a different π-bridge, **SD1**–**3** (Figure 1.7p–r) [21]. The SD dye series was used in both DSSC and H_2-evolution DSP systems. Interestingly, the performance of the dyes was varied dramatically in the different systems. In the DSSC system, in which $[Co(bpy)_3]^{3+/2+}$ was used as an electron mediator, **SD1** exhibited the highest power conversion efficiency and the order of efficiency was **SD1** > **SD3** > **SD2**. These results are attributed to **SD1** reducing charge recombination as a result of its large torsional angle and large driving force for regenerating the dye ground state. In the DSP system, by contrast, **SD2** demonstrated the highest H_2-evolution activity on Pt/TiO_2, where AA was used as an electron donor. Spectroscopic and photoelectrochemical studies revealed that the fastest electron injection into Pt/TiO_2 and the lowest charge-carrier transfer resistance were achieved in the **SD2** system. The highest performance of **SD2** toward H_2 evolution is likely a consequence of its good electron transfer and electron–hole separation process. **SD1**, which exhibited the highest efficiency in the DSSC system, exhibited the lowest activity toward the H_2-evolution photocatalytic reaction. This different tendency is attributed to differences in the reaction conditions. The electrons injected into TiO_2 migrate to the electrode under an electrical bias in a DSSC system and are consumed by the surface H_2-evolution reaction in a DSP system. The different reaction solutions (organic solvent vs. aqueous solution) can render the dye hydrophilic or hydrophobic. The electron donor, which is the electron mediator and sacrificial reductant in each system, should influence the efficiency of the oxidation reaction. The importance of the hydrophilicity and the reaction with a reductant will be discussed in the next section.

1.2.4 Molecular Design for Facilitating the Regeneration of the Ground State

Accelerating the reduction reaction of a sensitizer in the oxidized state to regenerate the ground state is important for improving the stability of a dye because the oxidized state of a dye is decomposed via light absorption of the oxidized state itself. To investigate the influence of the electron-donor unit structure, in which the LUMO is distributed, for the regeneration reaction of the sensitizer, Bartolini et al. carried out H_2-evolution reactions using triphenylamine-based D–A–π–A dyes with and without functionalization by bulky hydrophilic substituents (Figure 1.8) [22]. **Dye1** has no special substituents on the terminal of triphenylamine, whereas **Dye2** has four bis(ethylene glycol) monomethyl ether (BEG) chains. The BEG chains improve the hydrophilicity of the sensitizer and also behave as a steric, bulky moiety. The H_2-evolution reactions were conducted in aqueous solutions containing TEOA or AA as a sacrificial electron donor (SED), and the activities were exactly opposite depending on the SED used. When TEOA was used as the SED, the H_2-evolution activity of the **Dye1** system was twofold greater than that of the **Dye2** system.



(a)



(b)

Figure 1.8 Molecular structures of (a) **Dye1** and (b) **Dye2**.

By contrast, when AA was used as the SED, the **Dye2** system exhibited twofold greater activity than the **Dye1** system. The amount of H_2 evolved when AA was used was eighteen-fold greater than that when aqueous TEOA solution was used. The large influence of the SEDs and the hydrophilic substituent on the activities can be explained in terms of the interaction between them. In the TEOA system, because no noticeable interaction occurs between the BEG chains and TEOA, such a steric bulky substituent would inhibit the access of TEOA to the electron-donor unit (triphenylamine). The suppression effect dramatically decreases the efficiency for regenerating the dye ground state, leading to very low activity for H_2 evolution. In the AA system, however, BEG chains would strongly interact with the highly polar SED, thereby accelerating the regeneration of the sensitizer ground state. That is, the hydrophilic substituent suppresses the oxidation reaction of TEOA but promotes that of AA. Therefore, a large difference in activity between the two SEDs was observed in the **Dye2** system.

The effects of hydrophobicity and hydrophilicity have also been studied in other sensitizer systems. In a carbazole-based dye system whose electron-donor unit is similar to triphenylamine, long alkoxy chains were found to improve the hydrophobicity of the dye and to increase the H_2-evolution activity in an aqueous TEOA solution [48]. Enhancing the hydrophobicity suppressed undesirable charge recombination and contributed to an improvement of the photocatalytic activity. Modification of phenothiazine with glucose through a triazole ring unit improved the hydrophilicity, thereby improving the photocatalytic H_2-evolution performance when TEOA was used as an electron donor [49]. The improvement of the activity was due to acceleration of the reaction with a reductant in aqueous solution and to suppression of intermolecular quenching, the latter of which was induced by insertion of a sterically bulky moiety. The effect of wetness around dye molecules on the excited electron-transfer process was investigated using Ru complexes [50]. Protons in water adsorbed onto the substrate oxide (TiO_2) tended to assemble around the dye molecules under dry conditions but not under wet conditions, causing instability in the oxidized form of the photosensitizer generated by electron injection. Destabilization of the oxidized dye decreased the efficiency of the electron injection.

1.2.5 Improving Stability by Forming a Strong Connection Between a Dye and a Semiconductor

A dye excited by light absorption can be desorbed from the substrate surface and/or decomposed because of its instability. The desorption and decomposition result in deactivation of the dye-sensitized system. As described in the Introduction, a dye sensitizer follows a cycle involving photoexcitation, electron injection, and regeneration. Fast regeneration of the ground state should improve the efficiency because deactivation is suppressed, as discussed in Section 1.2.4. Similarly, the excited state, which is more unstable than the oxidized form, needs to be transformed immediately to the oxidized state to improve the stability of the system; that is, fast electron injection into a semiconductor will improve the durability of a

dye-sensitized system. Robust adsorption of a dye onto a semiconductor suppresses desorption of the dye and simultaneously accelerates the electron injection via strong interaction between the sensitizer and the semiconductor. The electron-injection rate strongly depends on the electronic coupling between the density of states in the semiconductor and the electron-donating orbital of the sensitizer. In the **N3**–TiO_2 system, ultrafast electron injection was observed (~50 fs) because of the relatively high density of states of TiO_2 and favorable coupling with the electron-donating orbital (the π* orbital of the carboxyl-anchoring group of the substituted bipyridine of **N3**) [51]. Therefore, strong bonding between a dye and a semiconductor is a promising way to improve the longevity of a dye-sensitized system from the viewpoint of not only desorption but also decomposition.

A representative anchoring group used in DSSCs is the carboxyl moiety; however, the carboxyl moiety is prone to desorption in aqueous solution. A phosphonic acid moiety improves the stability in weakly acidic conditions, whereas most carboxylate-anchoring groups are desorbed at pH ≈ 6 [52]. Because metal complex dyes, especially those based on Ru(II) trisdiimine complexes, enable chemical functionalization with various ligands, the effect of the number of anchoring groups on the dyes' desorption stability and DSSC performance has been studied [52]. However, introducing multiple anchoring groups into an organic molecular dye is synthetically difficult, although the literature contains numerous reports related to multiple branching and anchoring metal-free molecular dyes [53].

A calix[4]arene-based organic dye, which is easy to synthesize and has multiple anchoring groups, was developed (Figure 1.9a) [54]. Calix[n]arene ([n]: number of units) is a ring oligomer constructed by several units that consist of methylene-substituted phenols. The four phenol units are combined with a π-conjugation unit and constitute an electron-acceptor unit. Therefore, the calix[4]arene-based dye has four D–π–A structures in one molecule. All the calix[4]arene-based dyes show a cone conformation (Figure 1.9c) with an electron-acceptor unit at the top and anchoring groups at the bottom of the cone. When this sensitizer was used as a DSSC device, the system operated for 500 hours with no degradation in performance and showed high stability under light irradiation. A calix[4]arene derivative, **HO-TPA**, was effective for DSP for the H_2-evolution and CO_2-reduction reactions (Figure 1.9b) [55]. Stable H_2-evolution activity was observed for 75 hours. The **HO-TPA** dye has calix[4]arene and triphenylamine moieties as electron-accepting and -donating units, respectively. The donor–acceptor units are conjugated by an oligothiophene moiety. This sensitizer has four –OH anchoring groups at the calix[4]arene ring, which is the conical top, and the unique structure is beneficial for suppressing dye aggregation and forming strong bonds with the substrate surface.

1.2.6 New Insights Based on the Light Harvesting of a Dye-sensitized Photocatalyst System

Dyes have been developed not only through the traditional strategy (as described in Section 1.2.1) but also through unconventional approaches based on a novel concept. To suppress dye aggregation, Manfredi et al. introduced a coadsorbent

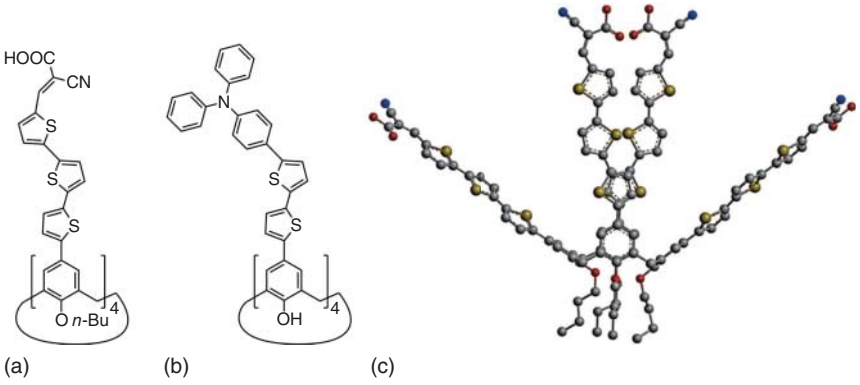


Figure 1.9 Molecular structures of (a) **Calix-3** and (b) **HO-TPA**. (c) The optimized geometry of the **Calix-3** dye was mimicked through molecular modeling with the GAUSSIAN 03 package. Source: Reproduced with permission from Tan et al. [54]; © 2015, John Wiley & Sons, Inc.

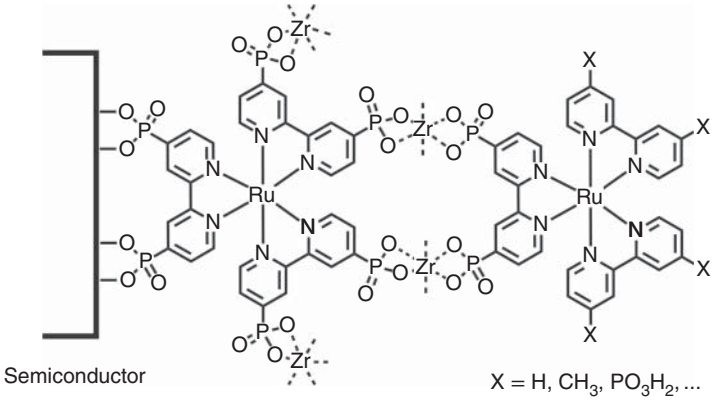


Figure 1.10 Schematic of the "layer-by-layer" assembly.

that does not function as a light absorber [56]. The H_2-evolution photocatalytic activity was doubled when the coadsorbent was adopted because it suppressed undesirable interaction among dye molecules. A direct electronic transition induced by visible light from a simple, small dye (an azoquinoline carboxylic acid) into a semiconductor (ZnO) was proposed [57]. This transition was enabled by the formation of a novel electronic state because of strong coupling between the dye and ZnO, and the transition could be used for a visible-light H_2-evolution reaction.

To effectively utilize the limited semiconductor surface, Mallouk and coworkers used a "layer-by-layer" (LBL) assembly approach [58]. This approach introduces multiple redox-active and/or chromophores onto a metal-oxide surface by forming phosphonate/Zr^{4+} coordination linkages (Figure 1.10) [59]. A bilayer assembly composed of two layers of Ru(II) complexes exhibited an approximately twofold increase in absorbance compared with a monolayer complex film. The assembly