Dye Sensitized Solar Cells (DSSCs) and solar energy conversion

The Solar Spectrum



Anatomy of the leaf



A spectrum of incident solar radiation at the Earth's surface featuring superimposed absorption spectra of chlorophyll a (—), chlorophyll b (—), bacteriochlorophyll a (—) and bacteriochlorophyll b (—). [recorded in methanol/ethanol solution].





Light harvesting and electron transfer



(charge-separation via photoinduced e⁻ transfer)

Solar cell efficiencies (2013)

 Table I. Confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m²) at 25 °C (IEC 60904-3: 2008, ASTM G-173-03 global).

Classification ^a	Effic. ^b (%)	Area ^c (cm ²)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF ^d (%)	Test centre ^e (and date)	Description
Silicon							
Si (crystalline)	25.0 ± 0.5	4.00 (da)	0.706	42.7 ^f	82.8	Sandia (3/99) ^g	UNSW PERL [18]
Si (multicrystalline)	20.4 ± 0.5	1.002 (ap)	0.664	38.0	80.9	NREL (5/04) ^g	FhG-ISE [19]
Si (thin film transfer)	20.1 ± 0.4	242.6 (ap)	0.682	38.14 ^h	77.4	NREL (10/12)	Solexel (43 μ m thick) [4]
Si (thin film submodule)	10.5 ± 0.3	94.0 (ap)	0.492 ⁱ	29.7 ⁱ	72.1	FhG-ISE (8/07) ^g	CSG Solar (1–2 μm on glass: 20 cells) [20]
III–V Cells							9.000, 10 00.0, [10]
GaAs (thin film)	28.8 ± 0.9	0.9927 (ap)	1.122	29.68 ^j	86.5	NREL (5/12)	Alta Devices [21]
GaAs (multicrystalline)	18.4 ± 0.5	4.011 (t)	0.994	23.2	79.7	NREL (11/95) ^g	RTI, Ge substrate [22]
InP (crystalline)	22.1 ± 0.7	4.02 (t)	0.878	29.5	85.4	NREL (4/90) ^g	Spire, epitaxial [23]
Thin Film Chalcogenide							
CIGS (cell)	19.6 ± 0.6^k	0.996 (ap)	0.713	34.8 ^I	79.2	NREL (4/09)	NREL, on glass [24]
CIGS (submodule)	17.4 ± 0.5	15.993 (da)	0.6815 ⁱ	33.84 ⁱ	75.5	FhG-ISE (10/11)	Solibro, 4 serial cells [25]
CdTe (cell)	18.3 ± 0.5	1.005 (ap)	0.857	26.95 ^h	77.0	NREL (10/12)	GE Global Research [5]
Amorphous/							
Nanocrystalline Si							
Si (amorphous)	10.1 ± 0.3^m	1.036 (ap)	0.886	16.75 ^f	67.8	NREL (7/09)	Oerlikon Solar Lab, Neuchatel [26]
Si (nanocrystalline)	10.1 ± 0.2^n	1.199 (ap)	0.539	24.4	76.6	JQA (12/97)	Kaneka (2 µm on glass) [27]
Photochemical							
Dye sensitised	$11.9\pm0.4^{\circ}$	1.005 (da)	0.744	22.47 ^h	71.2	AIST (9/12)	Sharp [6]
Dye sensitised (submodule)	$9.9\pm0.4^{\circ}$	17.11 (ap)	0.719 ⁱ	19.4 ⁱ	71.4	AIST (8/10)	Sony, 8 parallel cells [28]
Organic							
Organic thin-film	$10.7\pm0.3^{\circ}$	1.013 (da)	0.872	17.75 ^h	68.9	AIST (10/12)	Mitsubishi Chemical $(4.4 \text{ mm} \times 23.0 \text{ mm})$ [10]
Organic (submodule)	$6.8\pm0.2^{\circ}$	395.9 (da)	0. 798 ⁱ	13.50 ⁱ	62.8	AIST (10/12)	Toshiba (15 series cells) [13]
Multijunction Devices							
InGaP/GaAs/InGaAs	$\textbf{37.7} \pm \textbf{1.2}$	1.047 (ap)	3.014	14.57 ^h	86.0	AIST (9/12)	Sharp [14]
a-Si/nc-Si/nc-Si (thin film)	$13.4\pm0.4^{\text{p}}$	1.006 (ap)	1.963	9.52 ^h	71.9	NREL (7/12)	LG Electronics [15]
a-Si/nc-Si (thin film cell)	$12.3\pm0.3\%^{q}$	0.962(ap)	1.365	12.93 ^r	69.4	AIST (7/11)	Kaneka [29]
a-Si/nc-Si (thin film submodule)	$11.7\pm0.4^{n,s}$	14.23 (ap)	5.462	2.99	71.3	AIST (9/04)	Kaneka [30]

A different type of "solar system"



Current state-of-the-art organic photovoltaics



Dye-sensitized solar cells (Grätzel cells)

- Dye-sensitized solar cells (DSSCs) are one of the most promising molecular photovoltaics and have been attracting considerable attention since the pioneering study of Grätzel et al. because of the potential of low-cost production.
- In order to improve the solar-to-electric power conversion efficiency (η) , both metal complexes and metal-free organic dyes, as sensitizers of nanocrystalline TiO₂ electrode, have been extensively investigated and developed in terms of optical absorption extension to the red or infrared region through molecular design.
- The highest η for DSSCs has so far reached ~15 % obtained from an all solidstate perovskite sensitized TiO₂ system.

$\eta = \text{maximum power output (P_{max})/ power input (P_{light})}$

- A DSSC is comprised of a **photoanode** and **cathode** electrode, with an interstitial **redox mediator** containing electrolyte, connected via an external circuit.
- The photoanode consists of an optically transparent electrode (OTE) surface [typically *fluorine-doped tin oxide* (FTO) glass], with a mesoporous layer (*ca*. 10 mm thickness) of anatase *TiO₂ nanoparticles* (*ca*. 10-20 nm diameter) boasting a remarkable surface area (> 1000 cm⁻²).
- The dye sensitizer is adsorbed on the high surface area TiO₂ by covalent attachment allowing a large absorption cross section (*light harvesting*).
- This adsorption process utilizes appropriate functional groups on the dye molecule for **dye immobilization**, carboxylic and phosphonic acid tethers being the most commonly used.
- The anode (counter electrode) typically consists of platinized FTO glass.

Just like chlorophyll in natural photosynthesis the dye typically plays the role of light harvester and electron transfer agent.



Light harvesting in DSSCs





CH

State of the art in DSSCs





Snaith *et al. Science 2012, 338, 643-647.* Graetzel *et al. Nature 2013 499, 316-319.*



Champion molecular based DSSC dyes



Yu Q. e. atl ACS Nano. 2010, 4, 6032. Zeng et. al Chemistry of Materials 2010, 22, 1915. Yella et al. Science 2011, 334 (6056), 629-634.

Operation of Dye Sensitized Solar Cells



• Charge separation and charge recombination are competitive!

Graetzel M. Nature 2001, 414, 338.

Semiconductor band energies

- Band positions of several semiconductors in contact with aqueous electrolyte at pH 1.
- The lower edge of the conduction band (red color) and upper edge of the valence band (green color) are presented along with the band gap in electron volts.
- The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference.
- On the right side the standard potentials of several redox couples are presented against the standard hydrogen electrode potential.



Schematic showing the electronic energy levels at the interface between an *n*-type semiconductor and an electrolyte containing a redox couple.



where no space-charge layer exists in the semiconductor.

electrons





Schematic showing the electronic energy levels at the interface between an *n*-type semiconductor and an electrolyte containing a redox couple.



b: accumulation layer

where excess electrons have been injected into the solid producing a downward bending of the conduction and valence band towards the interface.





+ Positive charge carriers

 Electrolyte anions

Schematic showing the electronic energy levels at the interface between an *n*-type semiconductor and an electrolyte containing a redox couple.



C: depletion layer

where electrons have moved from the semiconductor to the electrolyte, producing an upward bending of the bands





+ Positive charge carriers

Schematic showing the electronic energy levels at the interface between an *n*-type semiconductor and an electrolyte containing a redox couple.

d: inversion layer

where the electrons have been depleted below their intrinsic level, enhancing the upward band bending and rendering the semiconductor p-type at the surface.







Conduction band electrons

Positive charge + carriers

Electrolyte anions

Blank TiO₂ variable pH study

Scan rate 10mV/s.





Thickness:

x and x , 4.5µm ; x, 4.4 µm

Compare bare titanium dioxide currents for 5.5m LiTFSI/water solutions of different pH.





Voltammogram shifts to positive direction with increased acidity

Conduction band edge shift , in conformity with theory

Fermi Level

http://www.acsu.buffalo.edu/~wie/applet/fermi/functionAndStates/fu

Why TiO₂?

The cathode material requires several combined properties and...

- Transparent (80%) in the visible
- Ideal electronic band energetics (wide bandgap semiconductor)
- High internal surface area (x700) / porosity (40-60%)
- Chemical and electrochemical stability
- "Right" surface chemistry for modification with dye sensitizers
- Mechanically rugged

...undoped nanocrystalline (10 - 20nm) anatase TiO₂ provides these properties.

- Good optoelectronic properties
- Commercially available
- "Proven" nanomaterial



TiO₂ films can be printed to achieve reliable device properties.





- Screen-printed film
- 2-12 micron thick
- Uniform coating
- 80+% Transmission in the visible range
- Surface area ca. 85 m²/g
- Good adhesion to substrate

Preparation of TiO₂ nanoparticle films



Rochford J.; Chu D.; Hagfeldt A.; Galoppini E. J. Am. Chem. Soc. , 2007, 129, 4655.

TiO₂ & anchoring groups



Scanning electron micrograph of a sintered mesoscopic TiO_2 (anatase) film supported on an FTO glass. The average particle size is 20 nm.



Possible binding modes for a carboxylic acid anchoring group at TiO_2 (M = Ti)

The mesoporous nanocrystalline effect



The incident-photon-to-current conversion efficiency **(IPCE)** is plotted as a function of the excitation wavelength.

a) Single-crystal anatase TiO₂.

b) Nanocrystalline TiO₂ anatase film.



Incident photon-to-current conversion efficiency



The (IPCE), sometimes referred to also as "external quantum efficiency" (EQE), corresponds to the number of electrons measured as photocurrent in the external circuit divided by the *monochromatic photon flux* that strikes the cell.

 $IPCE_{\lambda} = [(hc/e) J_{SC}]/[I_{0\lambda}]$

 $IPCE_{\lambda} = LHE_{\lambda} \cdot \phi_{inj} \cdot \eta_{coll}$

 $\begin{array}{l} \textit{LHE}_{\lambda} \ = \ \text{light harvesting efficiency} \\ \varphi_{\textit{inj}} \ = \ \textit{quantum yield for charge injection} \\ \eta_{\text{coll}} \ = \ \text{charge collection efficiency at FTO electrode} \end{array}$

IPCE = monochromatic efficiency

Scattering Layer and TiCl₄ Pre/Post-treatment



Fig. 4. Bi-layer structure comprising G1 (~0.3 μ m)- and G2 (~0.5 μ m) light scattering layers and IPCE spectra of G1- and G2-contained nanocrystalline TiO₂ films along with pure nanocrystalline TiO₂ film.

Deposition of a second inert layer of TiO_2 is now standard practice to increase the light harvesting efficiency.

Treatment with $TiCl_4$ introduces a fresh layer of TiO_2 across the FTO back electrode and also increase conductivity throughout the mesoporous film enhancing charge-collection kinetics – ultimately decreasing charge recombination from FTO or TiO_2 to the oxidized dye or mediator.

DSSC efficiency



By increasing the resistive load on an irradiated cell continuously from zero (*short circuit*) to a very high value (*open circuit*) one can determine the maximum-power point, the point that maximizes V×I; i.e. the load for which the cell can deliver maximum electrical power at that level of irradiation.

(The output power is zero in both the short circuit and open circuit extremes)

 V_{OC} = open circuit voltage I_{SC} = short circuit current

A = area

 $J_{\rm SC}$ = short circuit current density = $I_{\rm SC}$ / A

 $ff = fill factor = A_1 / A_2$

 I_0 = incident light flux (e.g. AM 1.5)

Kinetic competition in DSCs

- Following absorption of incident light, the dye molecule undergoes rapid transition (< fs) to an excited state electronic configuration.
- This metastable excited state ($\tau_{N719} = 12 \text{ ns}$) affords rapid *charge injection* (fs ps) from the singly occupied, lowest unoccupied molecular orbital (LUMO) into the conduction band (CB) of the TiO₂ semiconductor ($E_{CB} = -0.50 \text{ V vs. NHE}$) thus creating a charge separated state, i.e. TiO₂^{•-}/dye^{•+} (*charge injection*).
- The ensuing fate of this exciton (electron/electron-hole pair) determines the quantum yield for photocurrent generation and thus η for the DSC device.
- The excited state electron can diffuse to the back electrode FTO/TiO_2 contact (ns ms) from where it is transported via an external circuit to the counter electrode. In this scenario the ground state dye is regenerated by a redox mediator in the electrolyte (typically I^-/I_3^- , $E^0 = 0.35$ V vs. NHE) and the circuit completed by regeneration of the redox mediator at the counter electrode.



(processes in kinetic competition have similar colors)

Nanorod & nanotube electrodes



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Prof. K. Rajeshwar and Dr. N. de Taccomi The University of Texas at Arlington

Galoppini E.; Rochford J. et. al *J. Phys. Chem. B*, 2006, 110, 16159. de Taccomi N. R. et. al *J. Phys. Chem. C*, 2009, 113, 2996.

Molecular engineering for DSSCs

- In general, the molecular structure of an organic dye for DSCs has been designed and synthesized based on several basic concepts:
 - ▶ energy matching of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dye with the energy levels of I^-/I_3^- redox potential and E_{CB} of the TiO₂ electrode, respectively.
 - > a **donor**- π -**conjugation**-linkage-acceptor (D- π -A) structure required for a wide range absorption extending to the near-infrared or infrared region.
 - one or two anchoring groups such as carboxylic acid or phosphonic acid groups are required for a strong adsorption onto the surface of TiO₂.
 - Steric/orientational design strategy for hindering charge recombination processes.

- According to the reports of organic dyes used in DSSCs so far, the combination of a triaryl amine (donor) with a cyanoacrylic acid (acceptor and anchor), brings about good matching of the above-mentioned energy levels.
- **Oligothiophenes** have been successfully employed as the conjugation unit of the dye molecule between the donor and acceptor groups, resulting in maximum absorption bands shifting to the longer wavelength.



Effect of Anchor Length on Charge Injection into TiO₂







^{*a*} MLCT band, in CH₃CN solutions. ^{*b*} Calculated using Spartan '02 (PM3 minimization). ^{*c*} Probe at 670 nm.
Effect of Anchor Length on Open Circuit Voltage at TiO₂





•The diode equation predicts a 59 mV increase in Voc for each order of magnitude decrease in the charge recombination rate constant for injected electrons with acceptors, $k_i[A]_i$, at room temperature provided that the electron injection flux into the semiconductor, l_{inj} , is constant.

•In efficient dye-sensitized solar cells with 1 sun irradiance (100 mW/cm²), the predominant acceptors are thought to be iodide oxidation products, I_2 and/or I_3^{-1}

• Charge recombination rates decreased by a factor of 20 for 2 and 280 for 3 relative to 1 when studied in regenerative dye sensitized solar cells.

Meyer G. J.; Galoppini E. et. al. J. Phys. Chem. B 2006, 110, 11044.





Tetrachelate Porphyrin Chromophores for Metal Oxide Semiconductor Sensitization: Effect of the Spacer Length and Anchoring Group Position

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Fluorescence Emission Studies on Insulating ZrO2

- ZrO₂ behaves as an insulator precluding electron injection from the lowest excited-state of all porphyrins studied here.
 (*E*_{bg} ~ 5 eV for ZrO₂; *E*_{bg} ~3 eV for TiO₂ and ZnO)
- H-type aggregation causes broadening and convergence of emission bands.
- Aggregation can give rise to exciton diffussion which may lower the charge injection efficiency.
- Emission bands of all meta-substituted porphyrins remain resolved in contrast to *p*-ZnTCPP.





Photoelectrochemical Properties





 $IPCE = LHE \times \phi_{ini} \times \eta_c$

Photoelectrochemical properties of tetra(triethylammonium)carboxyporphyrin salts

Porphyrin	I _{sc} (mA·cm ⁻²)	V _{oc} (V)	ſſ	430 n	IPCE (%) m 570 nm ^a	600nm ^b
<i>p</i> -ZnTCPP-[S]	0.39	0.44	0.54	18.50	1.44 (0.08)	0.86 (0.05)
<i>m</i> -ZnTCPP-[S]	3.33	0.51	0.41	58.60	29.40 (0.50)	16.30 (0.28)
<i>m</i> -ZnTCP ₂ P-[S]	3.72	0.50	0.42	56.90	34.50 (0.61)	21.10 (0.37)
<i>m</i> -ZnTC(PEP)P-[S]	1.36	0.43	0.45	25.30	9.00 (0.36)	4.81 (0.19)

In parentheses are the ^a Q(1,0) and ^b Q(0,0) vs. Soret peak intensity ratios

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REVIEW

Iodine/iodide-free redox shuttles for liquid electrolyte-based dye-sensitized solar cells

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- As the most widely used couple, I⁻/I₃⁻ has a favorable penetration ability into the porous semiconductor film, fast dye regeneration and relatively slow recombination with injected photoelectrons.
- Moreover, I⁻/I₃⁻ is the only redox couple which has been proven to have long term stability. However, several disadvantages limit its industrial application:
 - the corrosion of copper/silver lines, which are used to collect the electrons in large scale modules making the production of long-term stable modules much more difficult
 - the l₃⁻ and other possible polyiodides formed in the electrolyte absorb a considerable part of the visible light, downgrading the efficiencies of DSSCs.
 - > The complex redox chemistry in the electrolyte causes great energy loss.
 - > The redox potential of I^-/I_3^- limits the photovoltage.

To avoid these disadvantages, new kinds of redox couples have beendesigned and applied in DSSCs.

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

- The Voc can be significantly affected by the redox potential of the electrolyte.
 - \succ *n* is the number of photoelectrons in the TiO₂
 - \succ N_{CB} is the effective density of states of the TiO₂ conduction band
 - \succ E_{redox} is the redox potential of the electrolyte redox couple
 - \succ q is the unit charge.
- Thus, at open-circuit conditions, the number of electrons in the TiO₂, *n*, is determined by the balance between electron injection and charge recombination.
- From the above eqn it can concluded that the Voc is determined by a selection of processes
 - the irradiation level
 - > the properties of the semiconductor conduction band
 - the injection efficiency of the dye
 - the recombination loss rate of photoelectrons
 - the redox potential of the electrolyte redox couple.

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

- Generally, *n* is considerably lower than N_{CB} , and the maximum Voc is therefore determined by the difference between the E_{CB} of TiO₂ and the E_{redox} of the electrolyte.
- Therefore, the redox potential of the redox system plays a key role in the Voc obtained in a DSSC.
- For the I^-/I_3^- redox couple, the possibilities to increase the Voc are limited.
- Some modifications can be achieved by changing the concentrations and relative ratio of iodide and iodine, but nevertheless the redox potential of the redox system is more or less fixed.

 Otherwise, in the conventional I⁻/I₃⁻ based electrolyte, the redox mechanisms are complicated. The regeneration is a multi charge-transfer process whose exact mechanism is still debated, but a two-step process is generally accepted.

$$D^{+} + 2I^{-} \rightarrow D + I_{2}^{-}$$
$$2I_{2}^{-} \rightarrow I_{3}^{-} + I^{-}$$

- In the first step of the dye-regeneration process, the oxidized dye and iodide lead to the formation of a diiodide radical (I2^{•-}).
- The second step follows when the formed l₂^{•-} disproportionates into l⁻ and l₃⁻. This leads to a large loss in potential equal to the difference between l⁻ and l₂^{•-} redox potentials (approximately 0.4 eV in acetonitrile)



- Co^{II}-complexes are commonly in the high spin state, and Co^{III}-complexes are in the low spin state.
- Therefore, Co^{II}-complexes are more reactive than Co^{III}-complexes.
- Co^{II} in the electrolyte performs the function of regenerating the sensitizer in the photoanode because of its higher reactivity.
- At the counter electrode, Co^{III} is catalyzed to obtain an electron, and converted to Co^{II}.
- Co-based complex redox shuttles have the advantage of a tunable redox potential obtained through modification of the ligands.



Fig. 4 The structures of various Co-complexes used in DSCs. The charges of all complexes are either 2+ (reduced form) or 3+ (oxidized form).

- The efficiency obtained was initially much lower than for DSSCs based on the I^-/I_3^- electrolyte.
- Co^{III} is more likely to experience recombination with photoelectrons from the TiO₂ CB than I_3^- .
- Li⁺ as an electrolyte additive increases the electron lifetime for a Co^{III/II} based DSSCs due to a decrease in local conc. of Co^{III} at the TiO₂ surface.
- TBP (tert-butyl pyridine) facilitates charge transfer from Co^{II} to the dye cation by reducing the reorganization energy between Co^{II} and Co^{III}.
- A thin Al_2O_3 blocking layer over the mesoporous TiO_2 surface has also been used to minimize the charge recombination





- A major disadvantage of Co^{III/II} based DSSCs is how the photovoltaic performance is constrained by masstransport limitations of the mediator.
- Elliot et al. have found that the effective diffusion coefficient of $Co(dtb-bpy)_3^{3+}$ is about one order of magnitude slower than that of I_3^{-} .
- This may be attributed to the greater size and slower bulk diffusion of $Co(dtb-bpy)_3^{3+}$, greater viscosity of cobalt complex solutions, and a possible electrostatic surface interaction of $Co(dtb-bpy)_3^{3+/2+}$ within the TiO₂ film.



- In 2009, Sun reported a new strategy of organic dye design by adding multiple alkoxyl chains to the donor part of D- π -A dyes. The most efficient dye, D35, containing four insulating butoxy chains efficiently prevent photoelectrons in TiO₂ from recombining with redox species in the electrolyte.
- In 2010, Hagfeldt and co-workers introduced the dye D35 to the Co-complex redox system, an overall conversion efficiency of 6.7% with open-circuit potentials of more than 0.9 V under 100 mW cm⁻² AM1.5 G illumination using the combination of dye D35 and a Co(bpy)₃^{3+/2+} redox system.
- The key strategy was to reduce the recombination losses with blocking hydrophobic groups on the sensitizing dyes, rather than, as in previous studies, on the Co complexes.
- This approach allows the use of non-substituted Co complexes with higher diffusion constants.
- The strategy thus successfully reduces both the recombination losses and, at least partly, the mass-transport limitations.

Steric control of TiO₂ to Co(III) charge recombination

- For best performance the TiO_2 film porosity should be optimized.
- Organic dyes typically have higher extinction coefficients than the standard ruthenium sensitizers, which makes it possible to use thinner TiO₂ films in the DSSC devices.
- The use of a thinner TiO₂ film is advantageous, since it decreases both the effects of mass transport problems and the risk of recombination losses.



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Effects of Driving Forces for Recombination and Regeneration on the Photovoltaic Performance of Dye-Sensitized Solar Cells using Cobalt Polypyridine Redox Couples

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Table 1. Current–Voltage Characteristics under AM1.5G Illumination for DSCs Sensitized with D35 Employing Cobalt Phenanthroline-Based Electrolytes^{*a*}

redox couple	$E^{0\prime}$ (V vs NHE)	$V_{\rm OC}$ (V)	$E_{\rm F,n, OC}$ (V vs NHE)	$J_{\rm SC} ({\rm mA \ cm^{-2}})$	FF	η (%)
$[Co(phen)_3]^{n+}$	0.62	0.93	-0.37	7.33	0.59	4.01
$[\operatorname{Co}(\operatorname{Cl-phen})_3]^{n+}$	0.72	1.01	-0.35	6.35	0.56	3.57
$[Co(NO_2-phen)_3]^{n+}$	0.85	1.03	-0.24	4.38	0.51	2.29

^{*a*} The electrochemical potential in the TiO₂ under OC conditions is calculated as follows: $E_{\text{F,n,OC}} = E_{\text{redox}} - V_{\text{OC}}$. E_{redox} is calculated using the Nernst equation.



Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-Efficiency Dye-Sensitized Solar Cells

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Current density versus applied potential curves under 1000 W m⁻² AM1.5G for DSSCs sensitized with D35. The electrolytes were 0.5 M Co(bpy)₃(PF₆)₂, 0.1 M Co(bpy)₃(PF₆)₃, 0.5 M TBP, and 0.1 M LiClO4 in acetonitrile or 0.6 M 1-butyl-3-methylimidazoliumiodide, 0.03 M I₂, 0.5 M TBP, and 0.1 M guanidinium thiocyanate in acetonitrile, respectively.



Current transients measured at an illumination intensity of 1000 W m^{-2} for DSSCs sensitized with D35



Current transients measured at an illumination intensity of 1000 W m⁻² for $[Co(bpy)_3]^{2+/3+}$ based DSSCs sensitized with D35 using a different thickness of TiO2.

Record efficiency for a molecular DSSC sensitizer



Yella et al. Science 2011, 334 (6056), 629-634.

Device Fabrication by Graetzel Lab

- The photoanode used in this study consists of thin TiO₂ electrodes comprising a 5 μm mesoporous TiO2 layer (particle size, 20 nm, pore size 32 nm) and a 5 μm TiO₂ scattering layer (particle size, 400 nm).
- Thickness and the porosity of the photoanode was found to be very crucial in the cobalt based DSSCs. Porosity of the TiO2 paste was increased (from 23 nm pore size to 32 nm pore size) and the thickness was reduced compared to 1⁻/l₃⁻ based devices to avoid the mass transport limitations in cobalt based devices.
- The working electrode was prepared by immersing the 10 μ m (5 μ m thick transparent layer +5 μ m thick scattering layer) TiO2 film into dye solution for 18 h.
- A thermally platinized FTO glass counter electrode and the working electrode were then sealed with a 25 µm thick hot-melt film (Surlyn, by heating the system at 100°C. Devices were completed by filling the electrolyte by pre-drilled holes in the counter electrodes and finally the holes were sealed with a Surlyn sheet and a thin glass cover by heating. A black mask (6x6 mm²) was used in subsequent photovoltaic studies.

Yella et al. Science 2011, 334 (6056), 629-634 (Taken from supp info).

Absorption spectra & CV of porphyrins YD2 and YD2-o-C8



Fig. 1. The molecular structures of the (left) YD2 and (right) YD2-o-C8 porphyrin dyes.



Yella et al. Science 2011, 334 (6056), 629-634.



Yella et al. Science 2011, 334 (6056), 629-634 (Taken from supp info).

Performance at various light intensities (V_{oc} depdenence)



Table 1. Detailed photovoltaic parameters of the devices made with the dyes **YD2** and **YD2-***o***-C8** and cobalt-based AY1 electrolyte at different light intensities. *P*_{in}, incident intensity of AM1.5 solar light.

Dye	Electrolyte	P _{in} (mW/cm ²)	J _{sc} (mA/cm ²)	V _{oc} (mV)	FF	PCE (%)
YD2	AY1	9.4	1.5	745	0.82	9.5
		51.3	8.0	805	0.76	9.5
		99.8	14.9	825	0.69	8.4
YD2-o-C8	AY1	9.4	1.7	875	0.77	12.5
		51.2	9.3	940	0.74	12.7
		99.5	17.3	965	0.71	11.9

Yella et al. Science 2011, 334 (6056), 629-634 (Taken from supp info).

J-V and IPCE DSSC characterization



Fig. 1. The molecular structures of the (left) YD2 and (right) YD2-o-C8 porphyrin dyes.



Yella et al. Science 2011, 334 (6056), 629-634.



Fig. 1. The molecular structures of the (left) YD2 and (right) YD2-o-C8 porphyrin dyes.



Yella et al. Science 2011, 334 (6056), 629-634.

Comparison of mediators for a YD2-o-C8 DSSC device

Table S2 Comparison of photovoltaic parameters of devices made with dyeYD2-o-C8 porphyrin using different redox electrolytes.



 $AY1 = 0.165M [Co(bpy)_3](B(CN)_4)_2, 0.045M [Co(bpy)_3](B(CN)_4)_3, 0.8M \text{ tert-butyl pyridine (TBP) and } B(CN)_4)_3 = 0.165M [Co(bpy)_3](B(CN)_4)_2, 0.045M [Co(bpy)_3](B(CN)_4)_3, 0.8M \text{ tert-butyl pyridine (TBP) and } B(CN)_4)_3 = 0.165M [Co(bpy)_3](B(CN)_4)_3, 0.8M \text{ tert-butyl pyridine (TBP) and } B(CN)_4)_3 = 0.165M [Co(bpy)_3](B(CN)_4)_3, 0.8M \text{ tert-butyl pyridine (TBP) and } B(CN)_4)_3 = 0.165M [Co(bpy)_3](B(CN)_4)_3 = 0.165M [CO(bpy)_4)_3 = 0.165M [CO(bpy)_4)_4 = 0.165M [C$

0.1M LiClO₄ in acetonitrile.

AY2 = 0.165M 1,3-dimethylimidazolium iodide, 0.045M I₂, 0.8M *tert*-butyl pyridine (TBP) and 0.1M

LiClO₄ in acetonitrile.

Z959 = (1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.03M iodine, 0.1M guanidinium thiocyanate

and 0.5M tert-butylpyridine in a mixture of valeronitrile/ acetonitrile (15:85 v/v)).

Yella et al. Science 2011, 334 (6056), 629-634.

Ru sensitizers & Co(III/II) mediators

• Both Hagfeldt and Graetzel research groups have reported on the significant efficiency enhancement of Z907 vs N719 when used with Co(III/II) mediators.



Liu et al. *J. Phys. Chem. C* 2011, 115, 18847-18855. Feldt et al. *J. Am. Chem. Soc.* 2010, 132, 16714.



-1.0 ÇOOH ÇOOH TiO₂ COOH E_{CB} E_F SnO₂ -0.5 [Bu]₄NOOC [Bu]₄NOO [Bu]₄NOO 0.0 **V**_{OC} ↓**V**_{OC} |₃⁻/|⁻ 0.5 E(V) vs. NHE ^{,∧}≈_{C≈s} ^₄≈c≈s N≈c≈s 3.2 1.0 eV [Bu]₄NOOC [Bu]₄NOOC [Bu]₄NOOC 3.6 1.5 eV COOH COOH ĊOOH 2.0 2 3 1 2.5 E_{VB} 3.0 E_{VB} 3.5

Table 1. Absorption, Luminescence, and Electrochemical Properties of Ruthenium Complexes 1, 2, and 3

	absorption max/nm	emission	n (77 K) ^b	electrochemical properties (V) vs SCE^d		
complex	$(\epsilon/10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})^a \text{ MLCT band}$	$\lambda_{\rm max}/{\rm nm}$	E^{00c}/eV	$E_{\mathrm{Ru(III)/Ru(II)}}^{\epsilon}$	$E_{p,L/L} - f$	$E_{\mathrm{Ru}(\mathrm{III})/\mathrm{Ru}(\mathrm{II})^{*}^{g}}$
2	396 (13), 528 (14)	715	1.80	0.68	-1.12	-1.12
1	390 (sh, 8), 575 (13)	820	1.62	0.74	-0.99	-0.88
3	410 (sh, 9), 625 (12)	840	1.50	0.71	-0.91	-0.79

^a Measured in ethanol. ^b Measured in ethanol-methanol (4:1 v/v) glass at 77 K. ^c E⁰⁰ is estimated from a tangent to the high energy side of the corrected emission spectra at 77 K. d Measured in 0.1 M LiClO₄ acetonitrile solution. e Peak potential of the differential pulse voltammogram for ruthenium complexes bound to nanocrystalline TiO₂ film. ^f Reduction peak potential of ruthenium complexes adsorbed on F-SnO₂. ^g $E_{Ru(III)/Ru(II)} = E_{Ru(III)/Ru(II)} - E^{00}$.

SnO₂ – Ru– iodide – Pt based DSSCs ?

TiO₂ – Ru– iodide – Pt based DSSCs



Figure 2. Cyclic voltammograms of complexes 1 (–), 2 (---), and 3 (····) adsorbed on nanocrystalline TiO₂ electrodes in 0.1 M LiClO₄ acetonitrile solution. Inset shows cyclic voltammograms for the Ru(II)/Ru-(III) redox reaction of complexes 1, 2, and 3 adsorbed on TiO₂ film. Scan rate was 0.5 V s⁻¹.



Figure 1. UV-vis absorption spectra of 1 (-), 2 (---), and 3 (---) in ethanol at room temperature.

TiO₂ – Ru– iodide – Pt based DSSCs



Table 3. Amount of Ruthenium Complexes 1, 2, and 3 Adsorbed Per Square Centimeter of Geometrical Surface Area and Photovoltaic Performance in Electrolyte Solution with or without 4-*tert*-Butylpyridine (TBP) under AM 1.5 Illumination (100 mW cm^{-2})

			without TBP ^b				with 0.5 M	TBP	
complex	Γ^{a} (10 ⁻⁷ mol cm ⁻²)	$J_{\rm sc}$ (mA cm ⁻²)	V _{oc} (V)	ff ^c (%)	η^{c} (%)	$J_{\rm sc}$ (mA cm ⁻²)	V_{oc} (V)	ff (%)	η (%)
2	2.1	17.7	0.52	64	5.9	15.3	0.71	73	7.9
1	1.8	15.1	0.48	68	4.9	5.6	0.56	77	2.4
3	1.8	4.8	0.35	68	1.2	1.1	0.44	73	0.4

^{*a*} The amount of adsorbed ruthenium complex was determined by desorbing it from TiO₂ film into a 0.01 M NaOH 1:1 (v/v) ethanol—water solution and measuring its absorption spectrum. ^{*b*} The electrolyte solution was composed of 0.6 M (1,2-dimethyl-3-propyl)imidazolium iodide, 0.05 M I₂, and 0.1 M LiI in acetonitrile. ^{*c*} ff and η are the fill factor and the overall efficiency, respectively.

SnO₂ – Ru– iodide – Pt based DSSCs ?



Table 3 Photovoltaic performance of cis-Ru(H_2 dcbiq)₂(NCS)₂-sensitized oxide semiconductor solar cells ^a

Semiconductor	Particle size (nm)	IPCE at 517 nm ^b (%)	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}~({\rm mV})$	Fill factor	η (%)
TiO ₂	30-50	6.0	1.36	0.33	0.62	0.34
Nb ₂ O ₅	100	0.1	0.02	0.21	0.35	0.01
ZnO	100-400	3.8	0.74	0.21	0.29	0.05
SnO_2	15-20	6.6	2.12	0.26	0.52	0.29
In ₂ O ₃	100-500	3.2	1.17	0.11	0.28	0.04

^a Light source: a 500 W Xe lamp with a <420 nm cut-off filter and a ND 25 filter (83 mW cm⁻²); electrolyte: 0.3 M $Pr_4NI + 0.03$ M I_2 in ethylene carbonate–acetonitrile (60:40); surface area of electrodes: 1.0 cm².

^b Light source: a 500 W Xe lamp with a band-pass filter (517 nm).

p-Type DSSCs (a reverse Graetzel cell)

• Can we take a similar approach to *p*-type DSSCs ?



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COMMUNICATION

Enhanced open-circuit voltage of p-type DSC with highly crystalline NiO nanoparticles[†]

Xiao Li Zhang, \ddagger^a Fuzhi Huang, \ddagger^a Andrew Nattestad,^{*a*} Kun Wang,^{*a*} Dongchuan Fu,^{*a*} Amaresh Mishra,^{*b*} Peter Bäuerle,^{*b*} Udo Bach^{**a*} and Yi-Bing Cheng^{*a*}

Fig. 1 (a) XRD pattern and (b) SEM observation of NiO nanoparticles with SAED pattern (inset). (c) SEM image of a single NiO particle and (d) schematic illustration of an octahedral NiO crystal. (e) HRTEM image of NiO particle and corresponding SAED spot. (f) SEM images of cross sectional view of NiO film.



Fig. 2 (a) Chemical structure of dye 3 and (b) photocurrent density–voltage curve of dye-sensitized NiO photocathodes with and without underlayer.

Voc = 350 mV in a NiO, I/I3 p-DSC system. A solar to electric conversion efficiency (Z) of 0.14% was achieved.



Tandem np-DSSCs





PUBLISHED ONLINE: 29 NOVEMBER 2009 | DOI: 10.1038/NMAT2588

Highly efficient photocathodes for dye-sensitized tandem solar cells

A. Nattestad¹, A. J. Mozer², M. K. R. Fischer³, Y.-B. Cheng¹, A. Mishra³, P. Bäuerle^{3 *†} and U. Bach^{1,4 *†}





Current-density–voltage characteristics for dyes **1–3; green: 1; blue: 2; red: 3. in a p-type NiO device. c, Current–voltage characteristics of a** tandem solar cell (black) as well as p-DSCs (red) and n-DSCs (green) under illumination (AM1.5, 1,000Wm 2, solid lines) and in the dark (dashed lines). Identical NiO and TiO2 films were used for the construction of the tandem, p- and n-DSC.

Cobalt Polypyridyl-Based Electrolytes for p-Type Dye-Sensitized Solar Cells

Elizabeth A. Gibson,^{||,†} Amanda L. Smeigh,[‡] Loïc Le Pleux,[§] Leif Hammarström,[‡] Fabrice Odobel,[§] Gerrit Boschloo,^{*,†} and Anders Hagfeldt[†]

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THE JOURNAL OF PHYSICAL CHEMISTRY

redox electrolyte ^{<i>a</i>}	$E^{0'}(\text{Co}^{2+/3+})$ V vs Fc ^{0/+}	$D(\mathrm{Co}^{2+})^b imes 10^{-6} \mathrm{cm}^2 \mathrm{s}^{-1}$	$D({\rm Co}^{3+})^b imes 10^{-6} {\rm ~cm}^2 {\rm ~s}^{-1}$	$\Omega_{\mathrm{CT}}^{},^c}\Omega$
Co(dm-bpy) ₃ (PF ₆) _{2/3} MeCN	-0.21	6.7	6.6	<1
Co(dtb-bpy) ₃ (PF ₆) _{2/3} MeCN	-0.24	6.4	7.4	12
Co(dMeO-bpy) ₃ (PF ₆) _{2/3} MeCN	-0.24	6.7	5.6	3
$Co(dm-bpy)_3(ClO_4)_{2/3}$ PC	-0.23	1.1	0.75	10
Co(dtb-bpy) ₃ (ClO ₄) _{2/3} PC	-0.26	0.77	0.75	44
Co(dMeO-bpy) ₃ (ClO ₄) _{2/3} PC	-0.28	0.92	0.72	14
$Co(ttb-tpy)_2(ClO_4)_{2/3}$ PC	-0.32	1.4	1.2	29

^{*a*} 0.1 M [(*n*-butyl)₄N]PF₆ or 0.1 M [(*n*-butyl)₄N]ClO₄ supporting electrolyte; glassy carbon working electrode, platinum wire counter electrode; glassy carbon working electrode, platinum wire counter electrode. ^{*b*} 15 mM Co^{2+/3+}, 100 mM [(*n*-butyl)₄N]ClO₄ (PC) or [(*n*-butyl)₄N]PF₆ (MeCN); 20 μ m diameter platinum working electrode, glassy carbon counter electrode. ^{*c*} Pt FTO sandwich, 0.1 M Co²⁺, 0.1 M Co³⁺, 0.1 M LiClO₄ for ClO₄ salts (PC), no Li⁺ for PF₆ (MeCN). PC = propylene carbonate, area = 0.36 cm².

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Cobalt Polypyridyl-Based Electrolytes for p-Type Dye-Sensitized Solar Cells

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Table 2. Photoelectrochemical Characterisation of the p-DSCs Employing the Cobalt Redox Couples under AM1.5 G Simulated Sunlight (1000 W m^{-2})

redox couple ^{<i>a,b</i>}	η (%)	$V_{\rm OC}~({\rm mV})$	$J_{\rm SC}~({ m mA~cm^{-2}})$	FF	$IPCE^{c}$ (%)
$Co(dm-bpy)_3(ClO_4)_{2/3}$ PC	0.04	160	1.05	0.27	20
Co(dMeO-bpy) ₃ (ClO ₄) _{2/3} PC	0.09	200	1.45	0.31	25
Co(ttb-tpy) ₂ (ClO ₄) _{2/3} PC	0.13	240	1.61	0.33	31
Co(dtb-bpy) ₃ (ClO ₄) _{2/3} PC	0.24	340	2.00	0.35	33
$Co(dm-bpy)_3(PF_6)_{2/3}$ MeCN	0.08	125	2.32	0.29	28
Co(dMeO-bpy) ₃ (PF ₆) _{2/3} MeCN	0.17	200	2.42	0.34	30
Co(dtb-bpy) ₃ (PF ₆) _{2/3} MeCN	0.24	275	2.65	0.33	32
$3 \circ 1 \circ 1 \circ 2^{\pm} \circ 1 \circ 1 \circ 3^{\pm} \circ 1 \circ $		1 + b + 1 + c + c	3+ $3+$ $3+$ $3+$ $3+$ $3+$ $3+$ $3+$. 1	

^{*a*} 0.1 M Co²⁺, 0.1 M Co³⁺, 0.1 M LiClO₄ in propylene carbonate. ^{*b*} 0.1 M Co²⁺, 0.1 M Co³⁺ in acetonitrile. ^{*c*} At $\lambda_{max(IPCE)} = 520$ nm.

Solar Generation of Fuels

$$H_2O \xrightarrow{hv} H_2 + \frac{1}{2}O_2$$
$$CO_2 + 2H_2O \xrightarrow{hv} CH_3OH + \frac{1}{2}O_2$$

"By using suitable catalyzers, it should be possible to transform the mixture of water and carbon dioxide into oxygen and methane, or to cause other endo-energetic processes."

International Conference of Applied Chemistry, New York, September 11, <u>1912.</u>

At the University of Bologna from 1889 to 1922 G. Ciamician was inspired by the ability of plants to make use of solar energy, he was the first scientist to investigate photochemical reactions in a systematic way.



Prof. Giacomo Ciamician (1857–1922) "Godfather of photochemistry"



Prof. Ciamician surveys his collection of tubes and flasks exposed to the sun on the balcony of his institute

Heterogeneous Catalysts for Water Oxidation, Proton reduction and CO₂ reduction inspired by photosynthesis


Why study water oxidation ?



Gray H., Nocera D., Nature 2008, 452.

Fuel Cell = noitebixO rateW



Reaction coordinate

$\left(\right)$	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$E^{0}_{Ox} = -1.23 \text{ V}$	(1)
	$\underline{4H^+ + 4e^-} \rightarrow \underline{2H_2}$	$E^{0}_{Red} = 0.00 V$	(2)
	$2H_2O \rightarrow 2H_2 + O_2$	<i>E</i> _{cell} = -1.23 V	(3)
	$\Delta G^0 = +237$	7 kJ mol ⁻¹	

Photosynthesis

$\mathbf{6CO_2} + \mathbf{6H_2O} + \mathbf{hv} \rightarrow \mathbf{C_6H_{12}O_6} + \mathbf{6O_2}$



(charge-separation via photoinduced e⁻ transfer)

The oxygen evolving complex of PSII



H₂O oxidation by oxygen evolving complex (OEC) via *proton-coupled e⁻ transfer* (dark reaction)

C. W. Hoganson and G. T. Babcock, Science 1997, 277 (5334), 1953-1956.

Water Oxidation and the Blue-Dimer

- Homogenous catalyst
- Electrochemically Oxidizes water in absence of light

similar to Mn₄CaO OEC in photosystem II

- Inefficient catalyst (only 25 turnovers)
- Mechanism has been extensively investigated by Meyer, Hurst, Baik and others
- Proton-coupled oxidation of $\mathrm{Ru^{III}} \rightarrow \mathrm{Ru^{IV}} \rightarrow \mathrm{Ru^{V}}$
- Mechanism for O₂ evolution still unknown



T.J. Meyer et al. JACS 1982, 104, 4030



WOC's Inspired by Blue-Dimer

- Loss of 4 e⁻ and 4 H⁺ with formation of O-O bond
- Low over-potential
- High turnover number (stability)
- Steric requirements





Blue dimer T.J. Meyer '82



 $R = N(CH_3)_2$, CH_3 , CF_3

Thummel '06





Grätzel '87



Tanaka '03

"Forum on Making Oxygen" Inorg. Chem., 2008, 47, 1697-2232

The Tanaka Dimer

- Excellent electrocatalyst for water oxidation
- TN > 30,000 (1.7 V vs. Ag/AgCl @ pH 4)
- Unlike the Blue Dimer catalyst (Ru^{III}/Ru^V) two Ru atoms predominantly +2 during entire catalytic cycle
- Active redox couples are SQ/Q
- Catalytic activity controlled by a delicate balance of the charge distribution over the Q-Ru-OH framework to make the O-O bond
- Steric hindrance is required to suppress the deleterious Ru-O-Ru formation and allow the desired Ru-O-O-Ru formation
- Substitution of bpy for the quinone ligands results in negligible catalytic activity!!

K. Tanaka *et al.*, *Inorg. Chem.*, 2001, *40*, 329 & *J. Am. Chem. Soc.*, 2003, *125*, 6729. Muckerman J. *et al "Forum on making Oxygen", Inorg. Chem.* 2008, 47, 1787.



បុក្កស៊ុនុន្ត Tanaka monomer: <u>Proton management</u> !

- PCET occurs in PSII at OEC via adjacent Tyrosine residue (Ty_z)
- PCET precludes build up of excess positive charge within the complex, i.e. at metal or ligand.



Tsai M.-K.; Rochford J.; Polyansky D. E.; Wada T.; Tanaka K.; Fujita E.; Muckerman J. Inorg. Chem., 2009, 48 (10), 4372.

Mechanism of Tanaka Dimer for WOC (DFT)



Boyer J.; Rochford J.; Tsai M.-K.; Muckerman J.; Fujita E. *Coord. Chem. Rev.* 2010, 254, 309-330. Tsai M.-K.; Rochford J.; Polyansky D. E.; Wada T.; Tanaka K.; Fujita E.; Muckerman J. *Inorg. Chem.*, 2009, 48 (10), 4372.

Mononuclear water oxidation catalysts (WOC)

- Highly promising: less expensive, not as synthetically demanding
- Yet to be fully explored



J. J. Concepcion, J. W. Jurss, J. L. Templeton and T. J. Meyer. J. Amer. Chem. Soc. 2008, 130 (49), 16462-16463.



S. Romain, L. Vigara and A. Llobet. Acc. Chem. Res. 2009, 42 (12), 1944-1953.

Requirements for CO₂ reduction

- One electron reduction of CO_2 is unfavorable requiring an energy of -1.9 V.
- PCET and multi-electron transfer catalysts required to reduce large overpotentials
- Electricity as electron source (Electrochem)
- Photon as energy source (Photochem)

photoelectrochemistry

	Reaction	$E^{\mathrm{o}}(\mathrm{V})$
(i)	$CO_2 + e^- \longrightarrow CO_2^-$	-1.90
(ii)	$CO_2^- + e^- \longrightarrow CO_2^{2^-}$	-1.20
(iii)	$CO_2 + 2e^- \longrightarrow CO_2^{2^-}$	-1.55
(iv)	$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$	-0.53
(v)	$CO_2 + 2H^+ + 2e^- \longrightarrow HCO_2H$	-0.61
(vi)	$CO_2 + 4H^+ + 4e^- \longrightarrow C + 2H_2O$	-0.20
(vii)	$CO_2 + 4H^+ + 4e^- \longrightarrow H_2CO + H_2O$	-0.48
(viii)	$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$	-0.38
Comments Inorg(18))e Coord. Chem. Rev. 19	enfc:Q997,+198€7 ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O 299, 185, 373	-0.24

Photocatalytic CO₂ reduction by Re(I) carbonyls

• One of the most highly studied photocatalytic systems are the Re(I) polypyridyl tricarbonyl systems first inspired by the Lehn catalyst.



Hawecker, J.; Lehn, J. M.; Ziessel, R., J. Chem. Soc. Chem. Comm. 1984, 328-330

Photocatalytic CO₂ reduction by Re(I) carbonyls

• Ishitani has proposed a mechanism taking advantage of $\text{Re}(\text{bpy})(\text{CO})_3 X$ complexes as both photocatalyst and photosensitizer with one of the largest quantum yields reported to date at $\Phi = 0.59$.



Takeda et al. J. Am. Chem. Soc. 2008, 2023.



Morris A.; Meyer G.; Fujita E. Acc. Chem. Res. 2009, 42, 1983-1994.