Novel Photovoltaics based on Direct Interfacial Charge Transfer Transition from Surface-Bound Organic Compounds to Semiconductor

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Contents

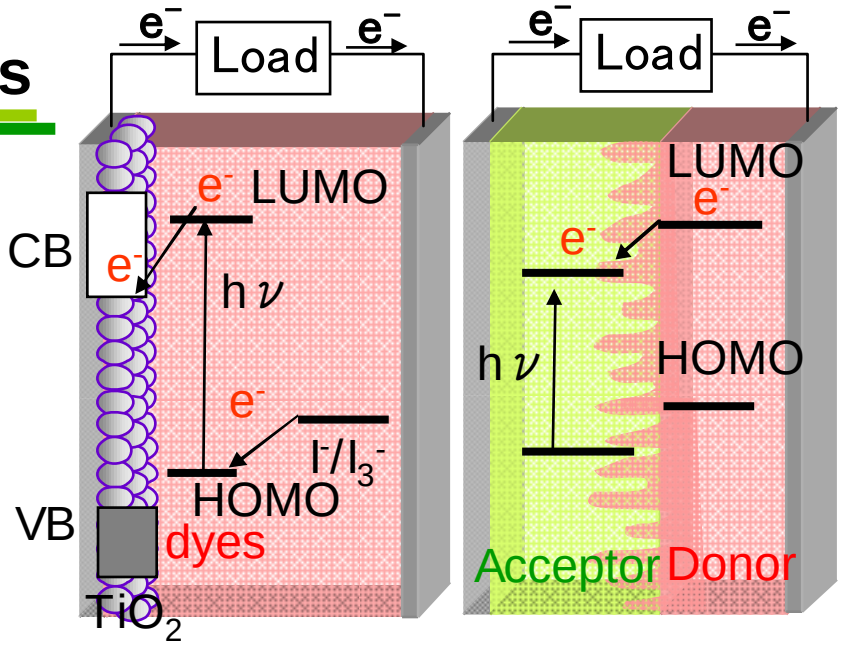
1. Introduction: organic solar cells

A potential candidate for efficient and low-cost photovoltaic devices

(i) Dye-sensitized solar cells (DSSC)
(ii) Organic thin film solar cells (OPV)

(General mechanism)

a. Light absorption by **dyes**
b. Charge separation from **dyes** to carrier-transporting materials
c. Carrier transport



Dye-sensitized solar cell | Organic thin film solar cell

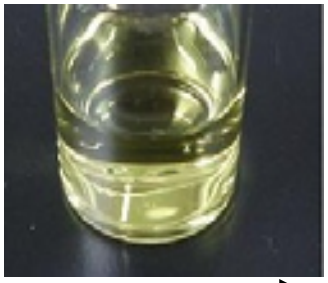
	DSSC	OPV
Conversion efficiency	~11% [1)]	~4.9% [2)]

Development of solar cells based on a novel principle for efficient interfacial charge separation

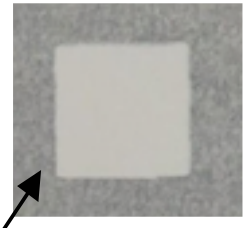
1) M. K. Nazeeruddin et al., *J. Am. Chem. Soc.* 2005, **127**, 16835.
2) M. R. Reyes et al., *Appl. Phys. Lett.*, 2005, **87**, 083506.

Recent our work
: Novel chemical coloration of TiO_2

Dicyanomethylene compounds
Electron acceptor for organic charge-transfer complexes

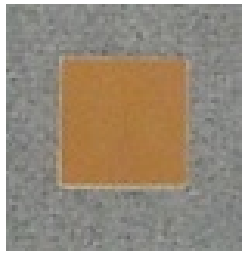


$TCNQ/CH_3CN$

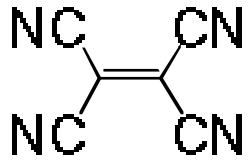


TiO_2

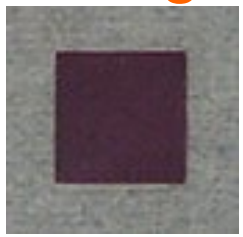
Wide band gap semiconductor (Eg～3.2 eV) used for photocatalyst



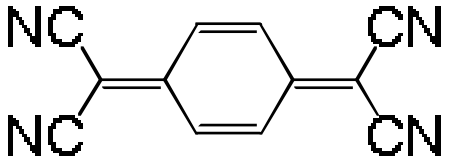
Orange



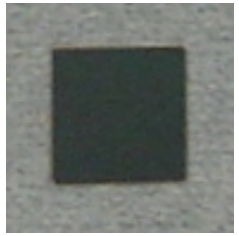
TCNE



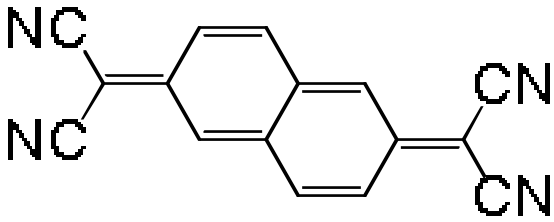
Violet



TCNQ



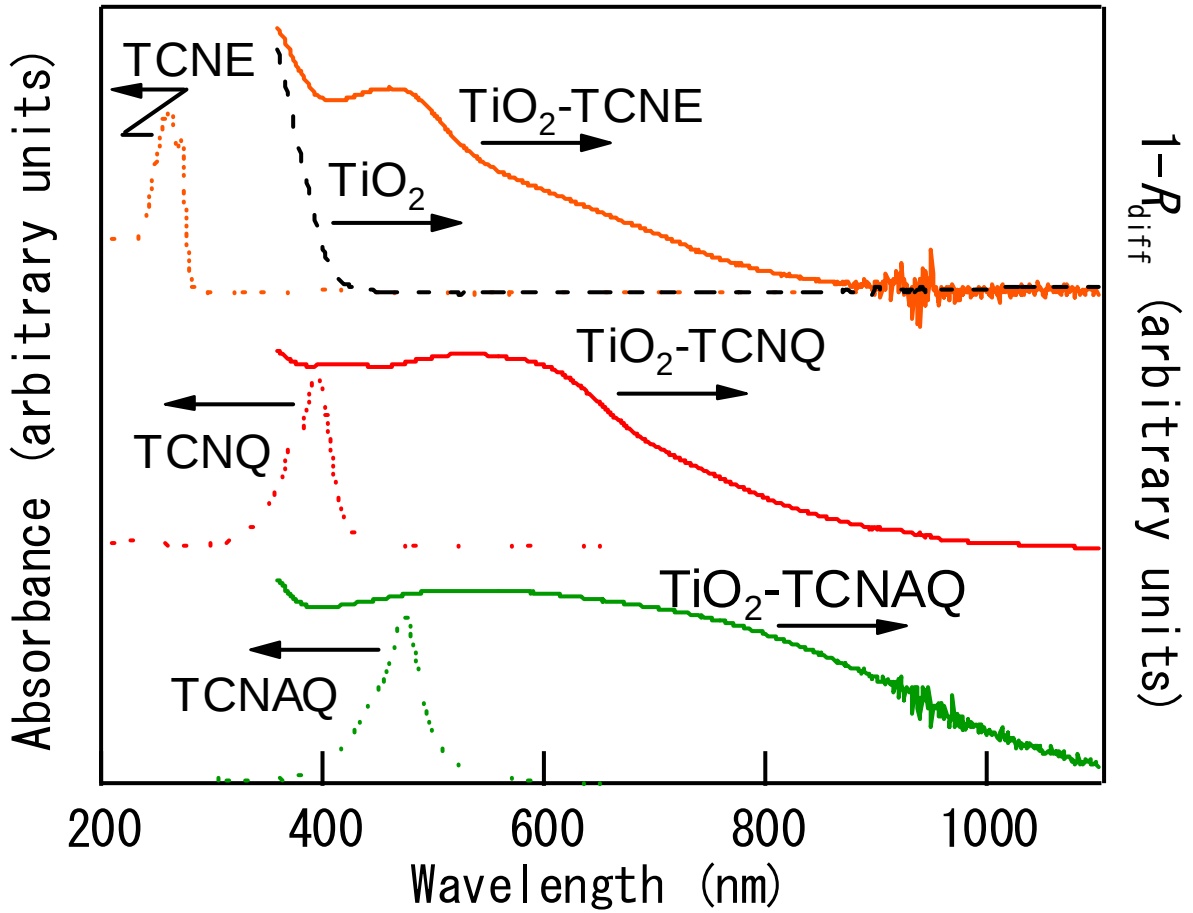
Green

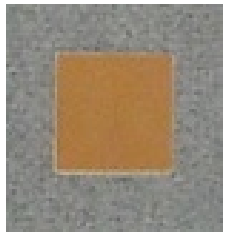


TCNAQ

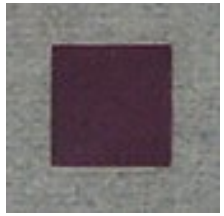
- **TiO_2 is colored by dicyano-methylene compounds (TCNX)**
- **The color is dependent on the kind of TCNX**

Appearance of novel absorption band

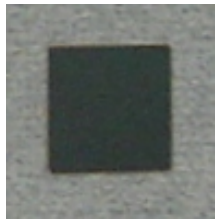




TiO_2-TCNE



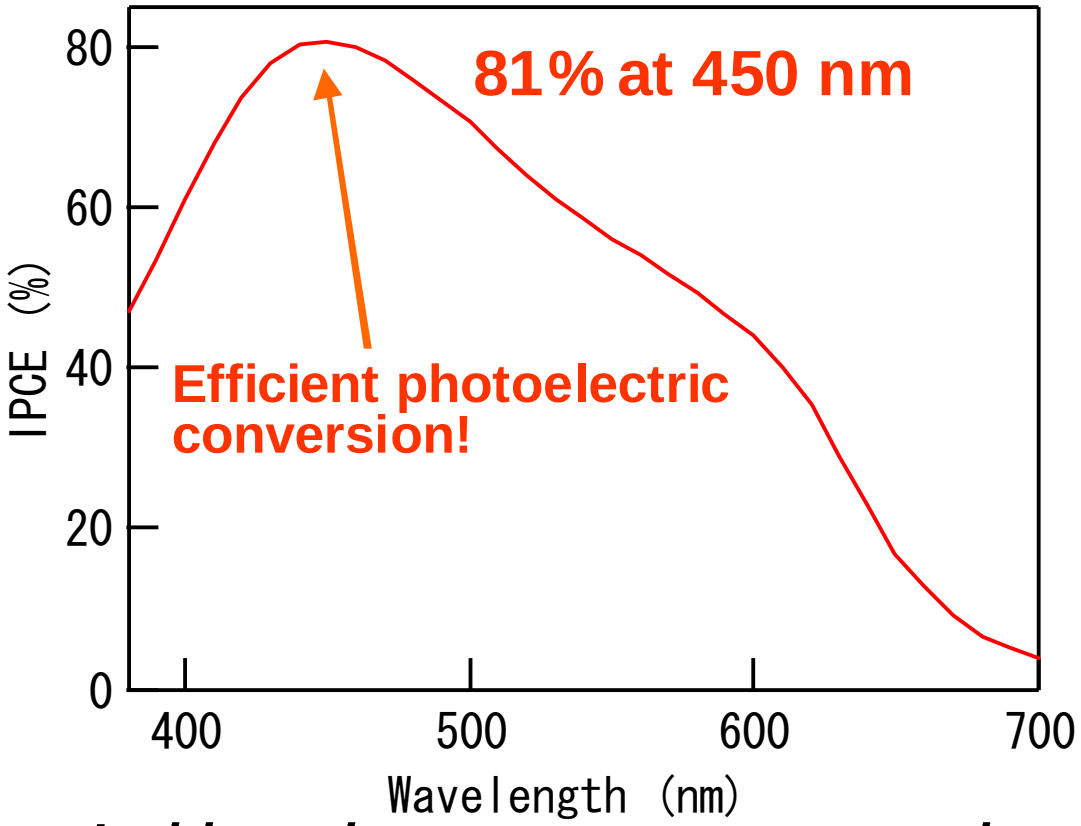
TiO_2-TCNQ



TiO_2-TCNAQ

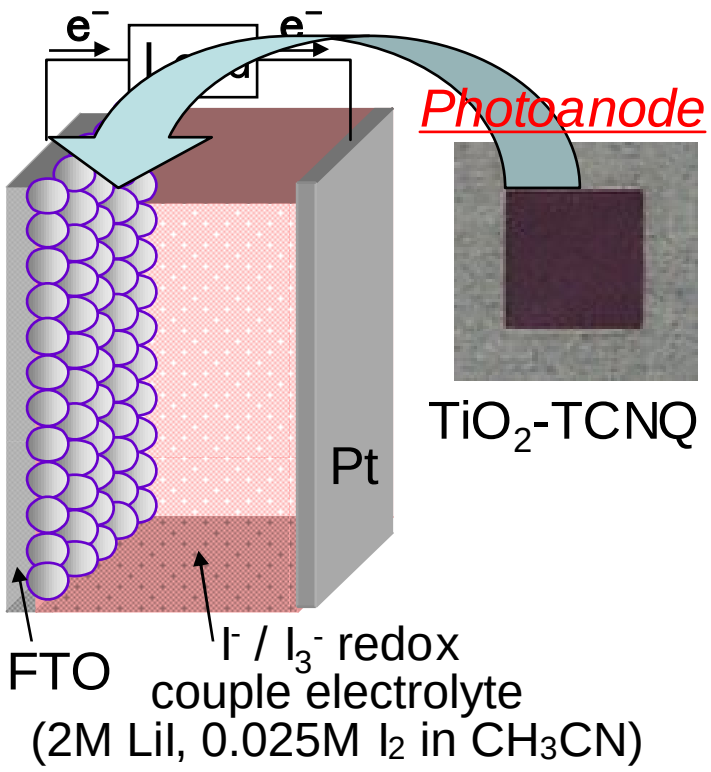
Novel absorption appears in the visible to near IR region

Efficient photon-to-current conversion



Incident photon-to-current conversion efficiency (IPCE) spectrum

Electrochemical solar cell



TiO_2-TCNX is very promising for efficient photoelectric conversion

2. Purpose

(i) Structure and formation mechanism of TiO_2-TCNX surface complexes

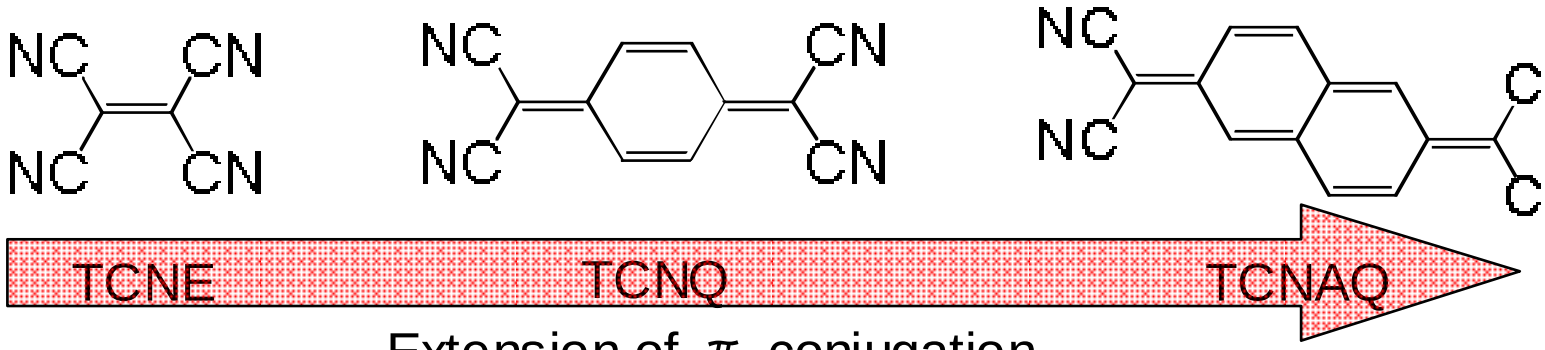
(ii) Assignment of the absorption band of TiO_2-TCNX surface complexes

(iii) Photoelectric conversion of TiO_2-TCNX based solar cells

Chemical control of photoelectric conversion

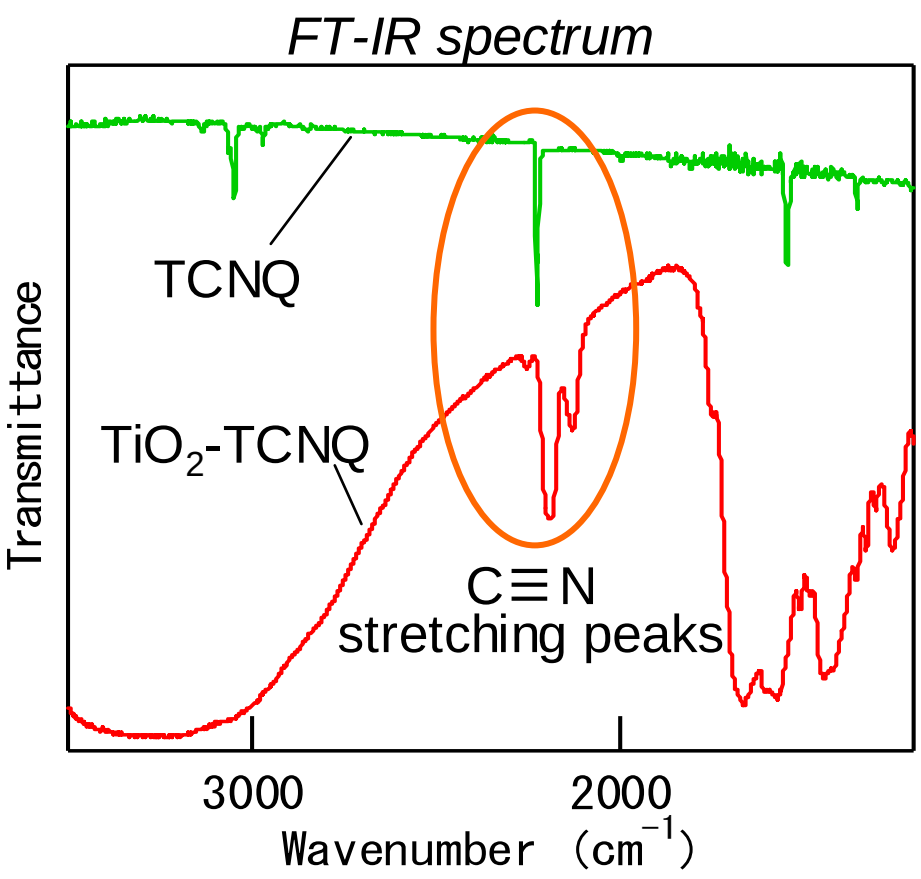
a. Extension of π-conjugation of TCNX

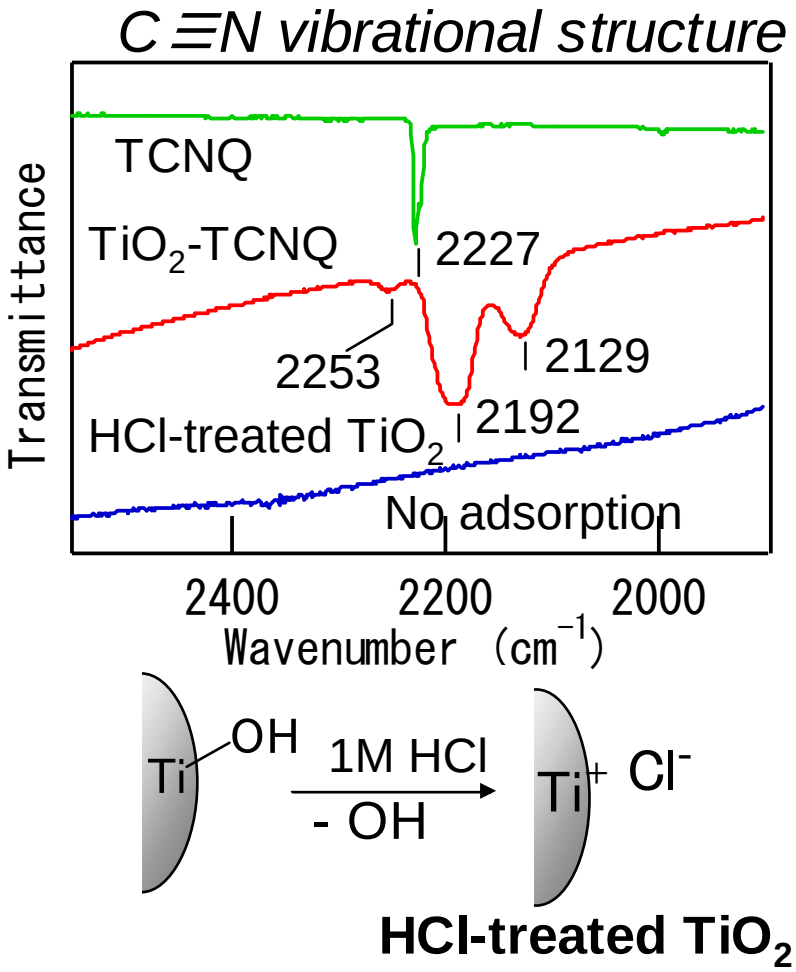
b. Chemical modification of conduction band of TiO_2



Extension of π-conjugation

3.Structure and formation mechanism of TiO_2-TCNQ : Vibrational structure of TiO_2-TCNQ

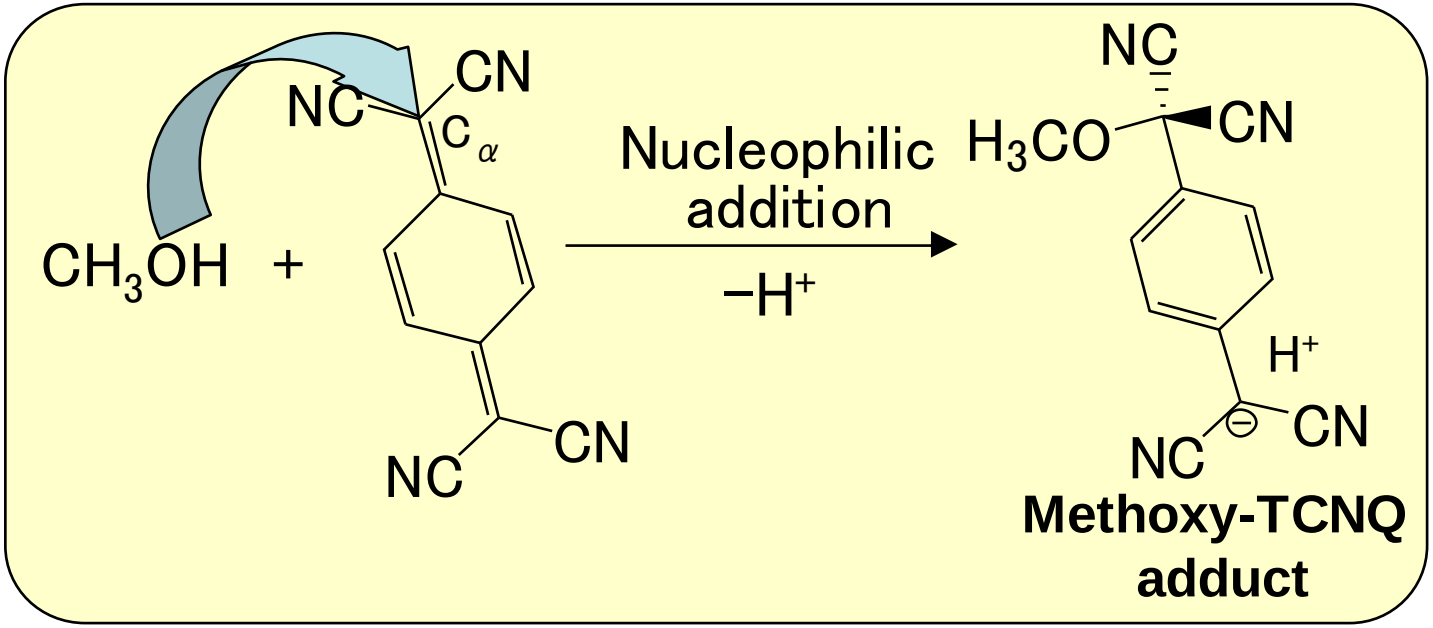


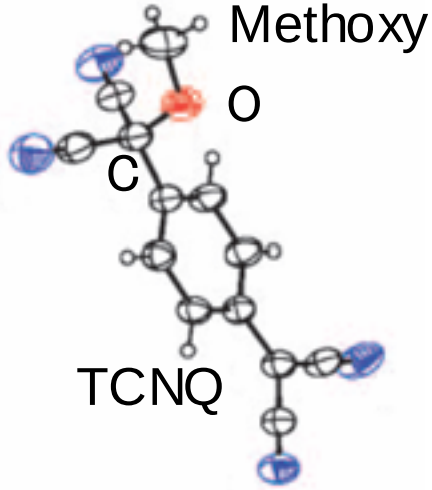


HCl-treated TiO_2

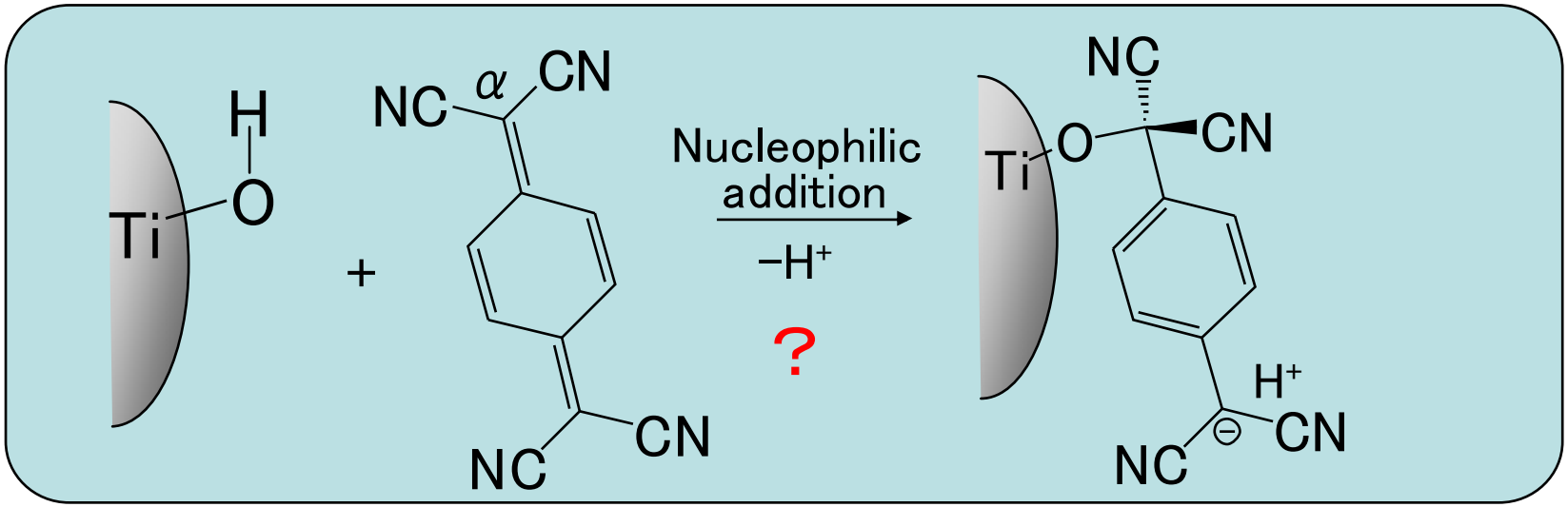
- **Large structural change of TCNQ adsorbed on TiO_2**
- **TCNQ adsorption due to reactions with hydroxyl groups**

Nucleophilic addition of TCNQ with alcohol



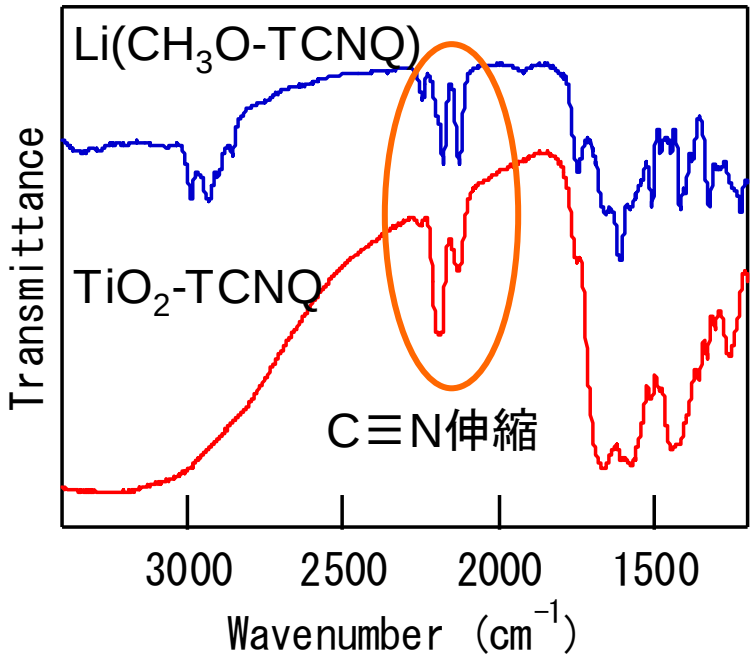


Murata et al. (*Bull. Chem. Soc. Jpn*, 2008, 81, 331)
σ bond between the O and C atoms ($d_{O\text{-}C}$ = 1.4 Å)

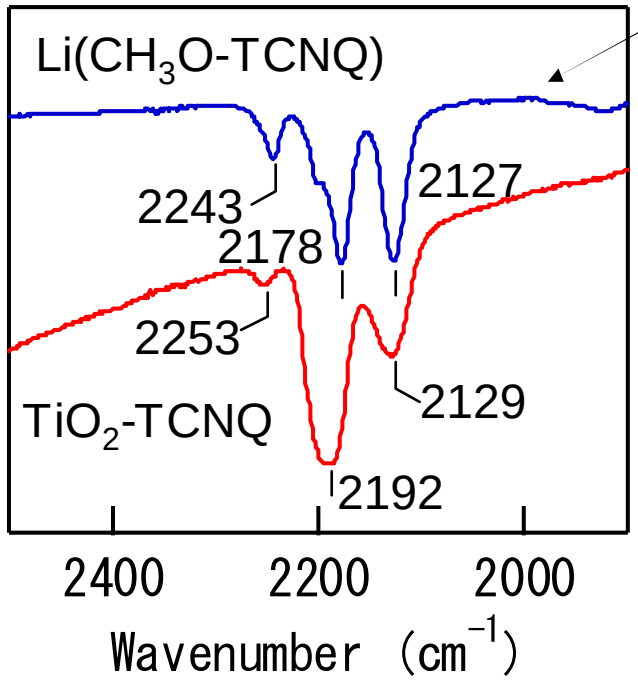


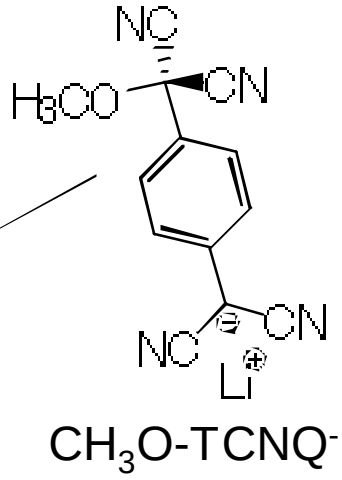
Nucleophilic addition of TCNQ with TiO_2

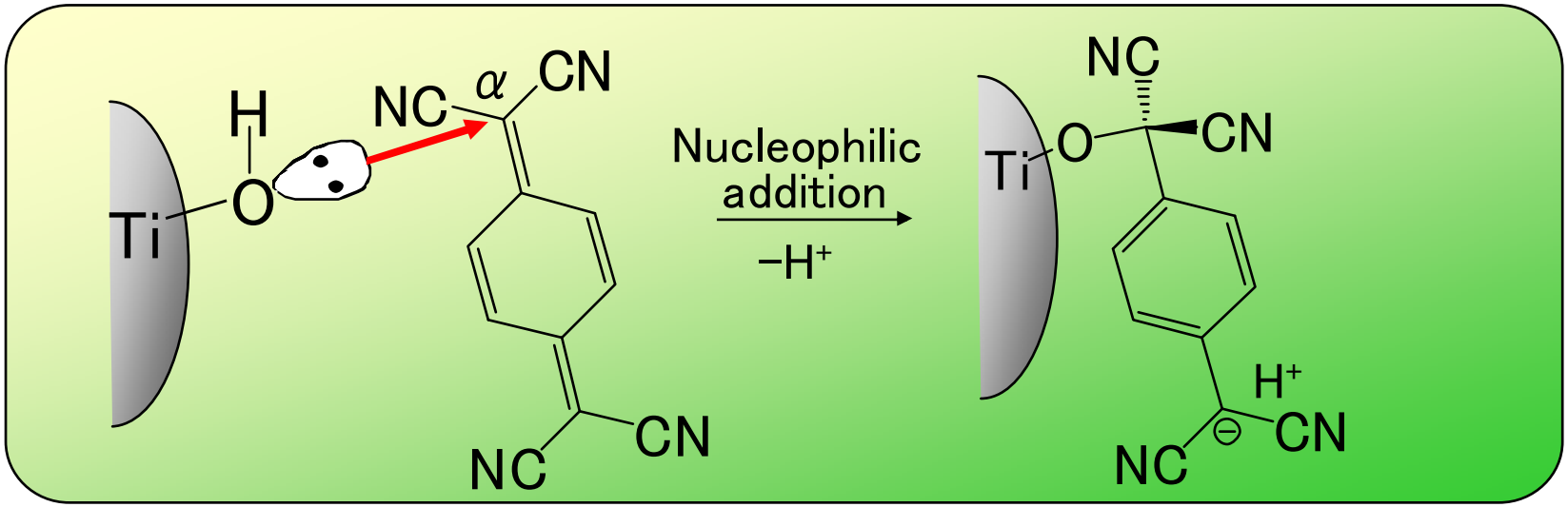
FT-IR spectra



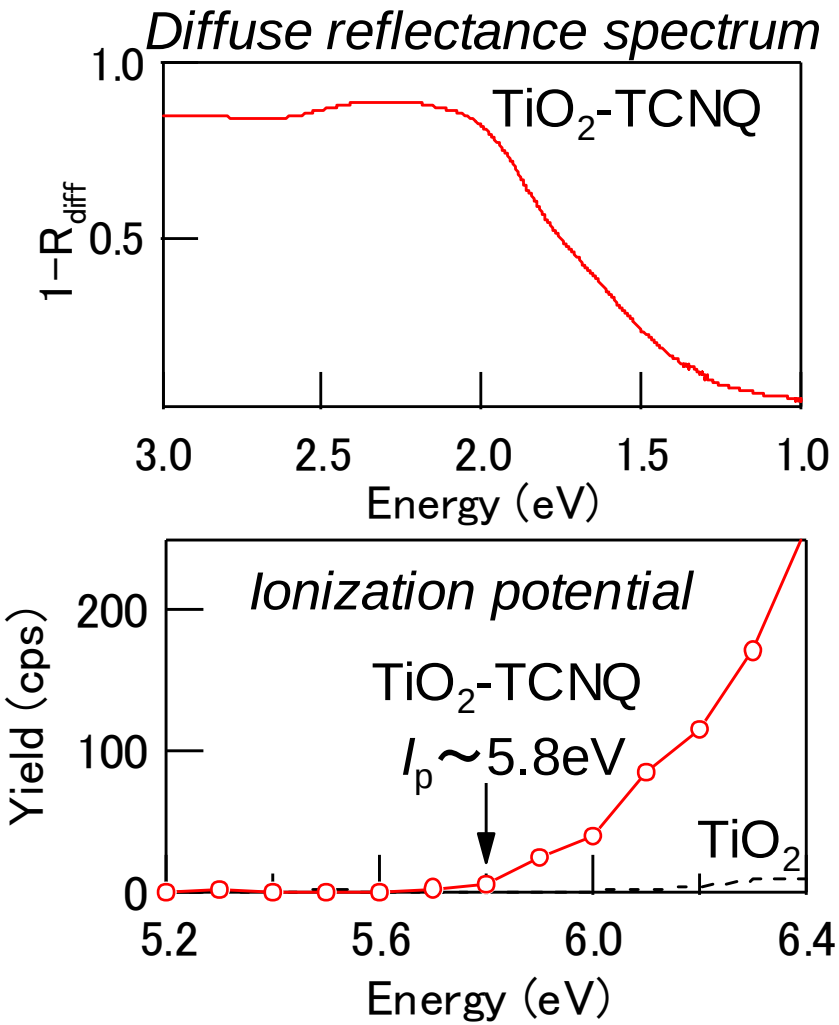
C≡N stretching modes

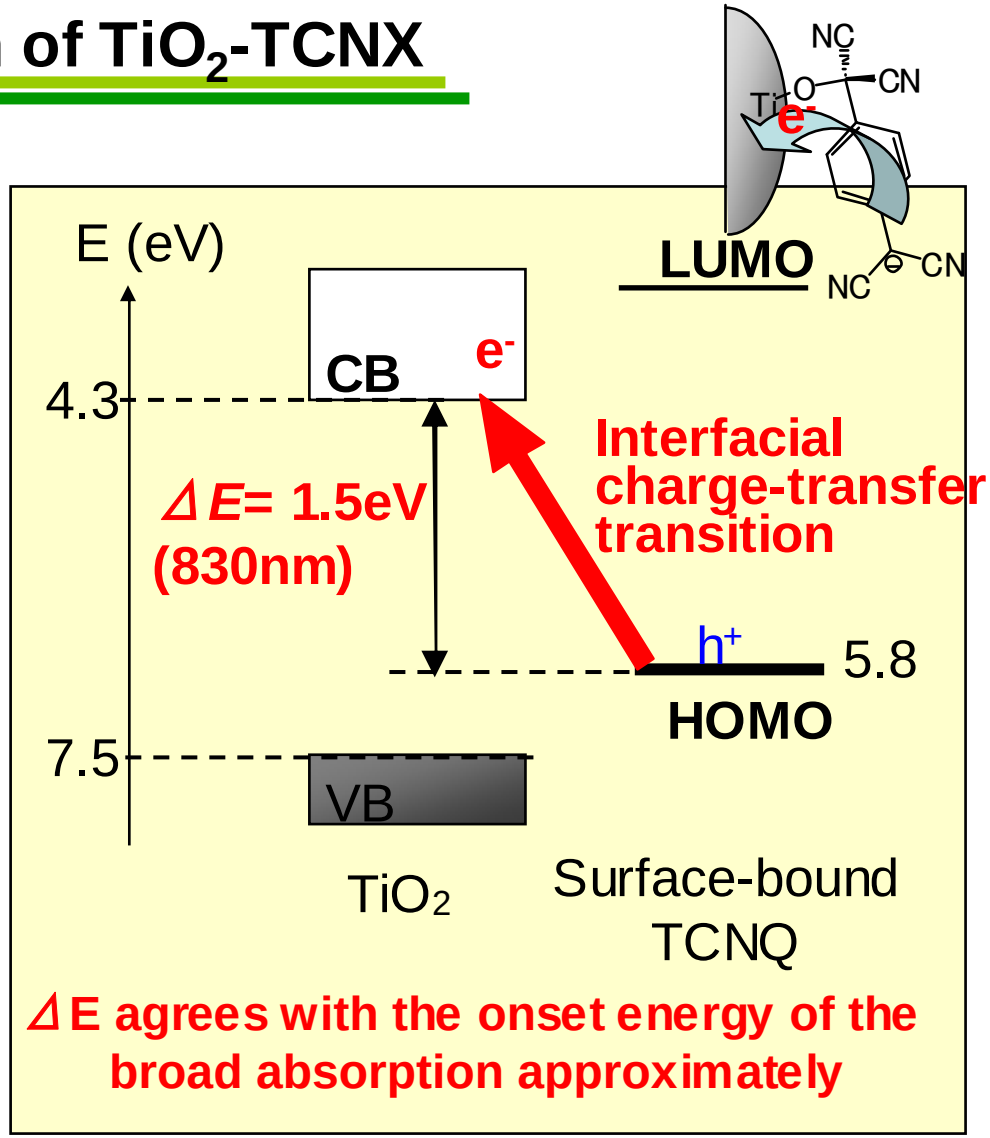






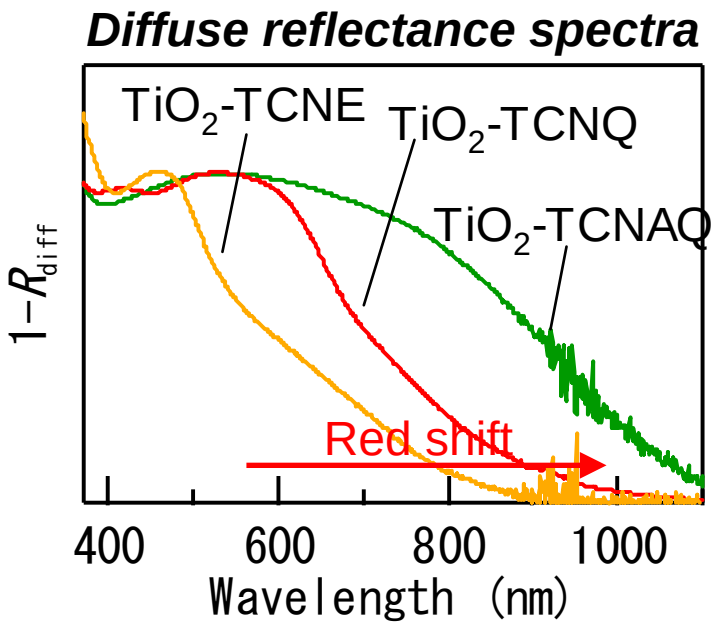
4. Assignment of absorption of TiO_2-TCNX

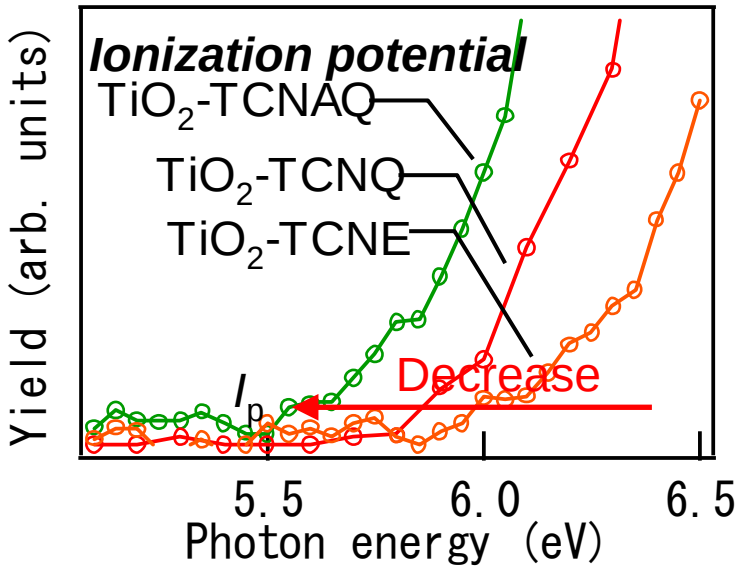


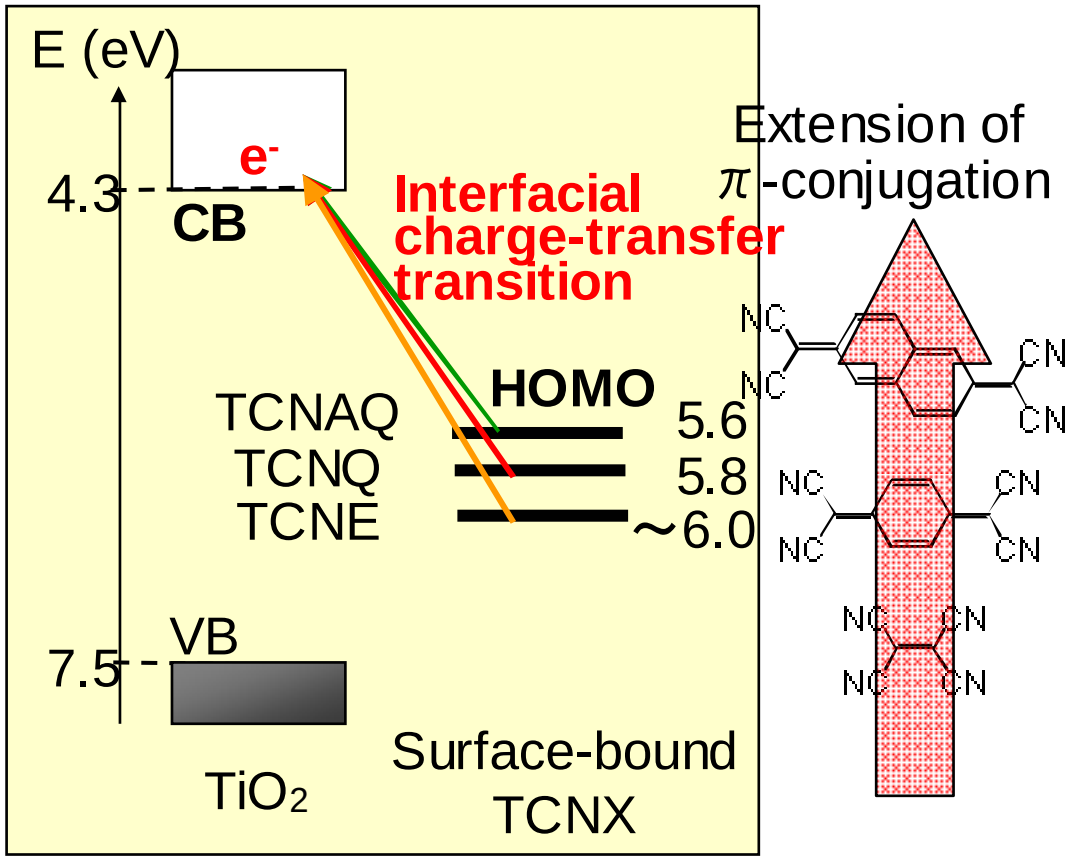


Interfacial charge-transfer transitions from surface-bound TCNQ to TiO_2

(ii) π-conjugation effect

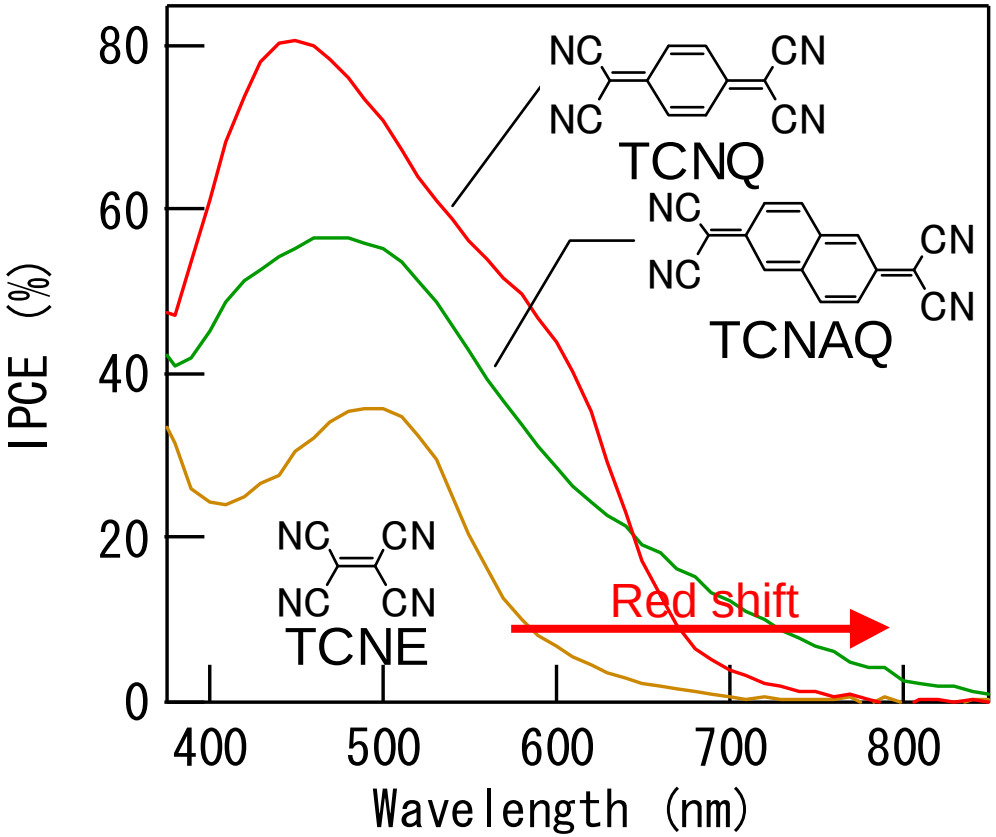


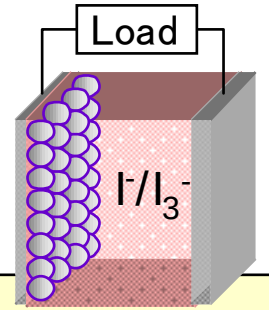


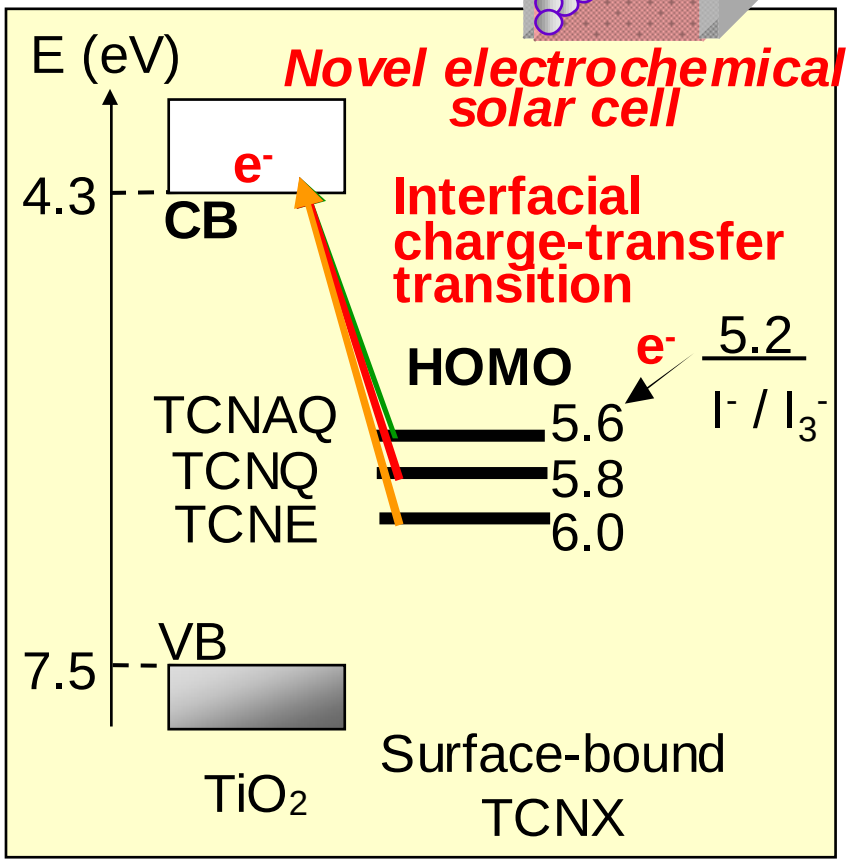


- Longer wavelenght shift due to increase of HOMO energy of the surface-bound TCNX with the extension of π-conjugation
- TCNX dependence suppports our assignment

5. TiO_2-TCNX based solar cells : π -conjugation effect on IPCE spectra

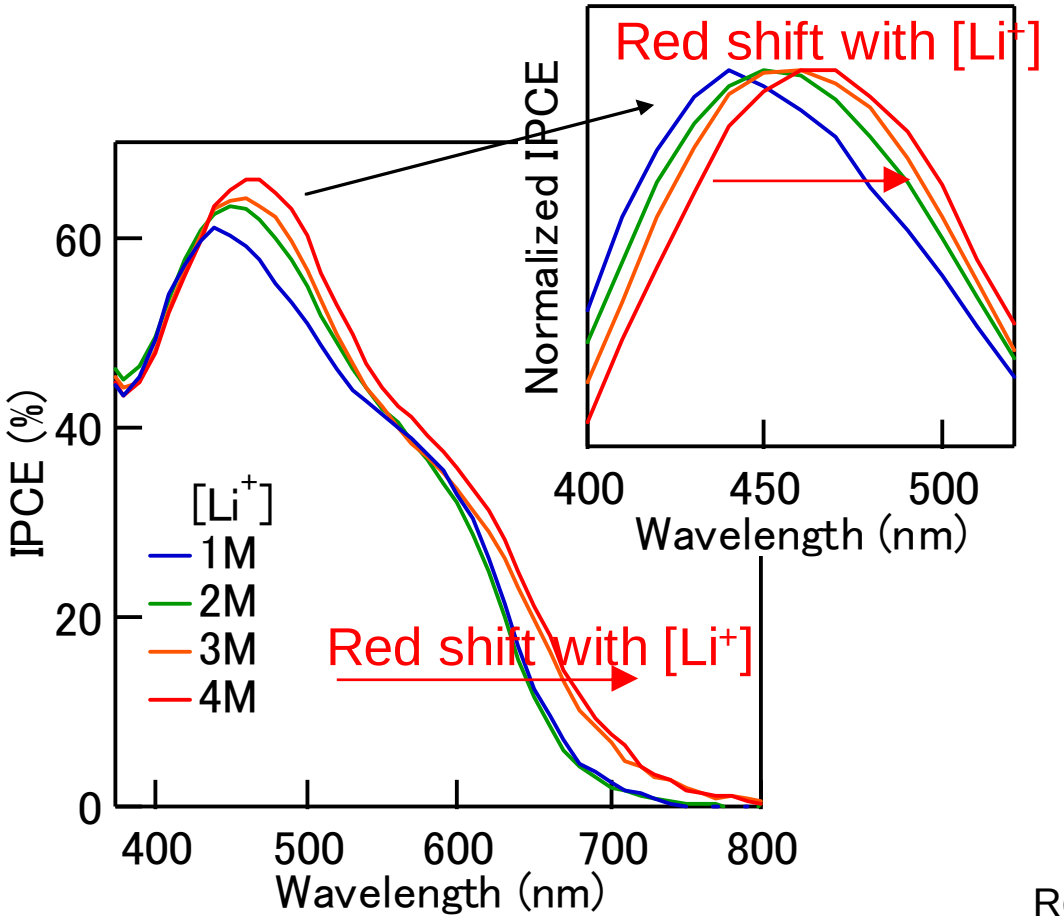


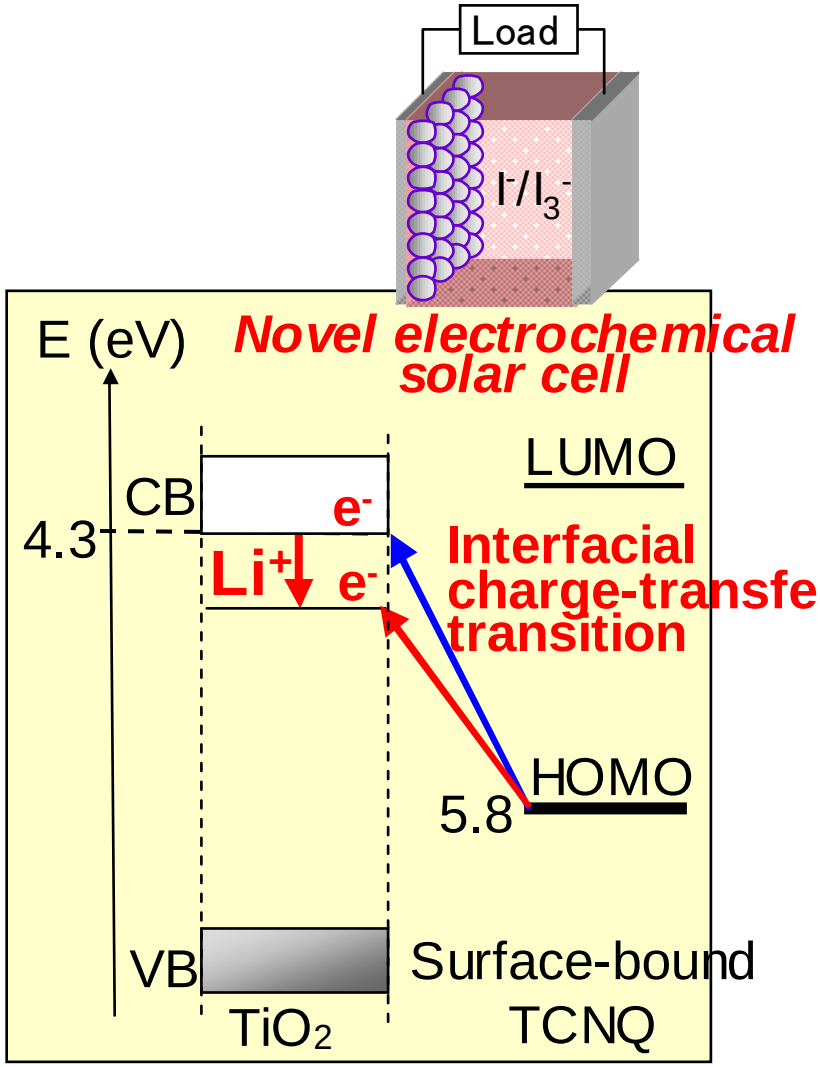




- Photoelectric conversion occurs in the visible to near IR region.
- Near IR photoelectric conversion can be enhanced by π -conjugation extension → Control of spectral region by chemical modification of TCNX

Effect of Li^+ on IPCE spectra



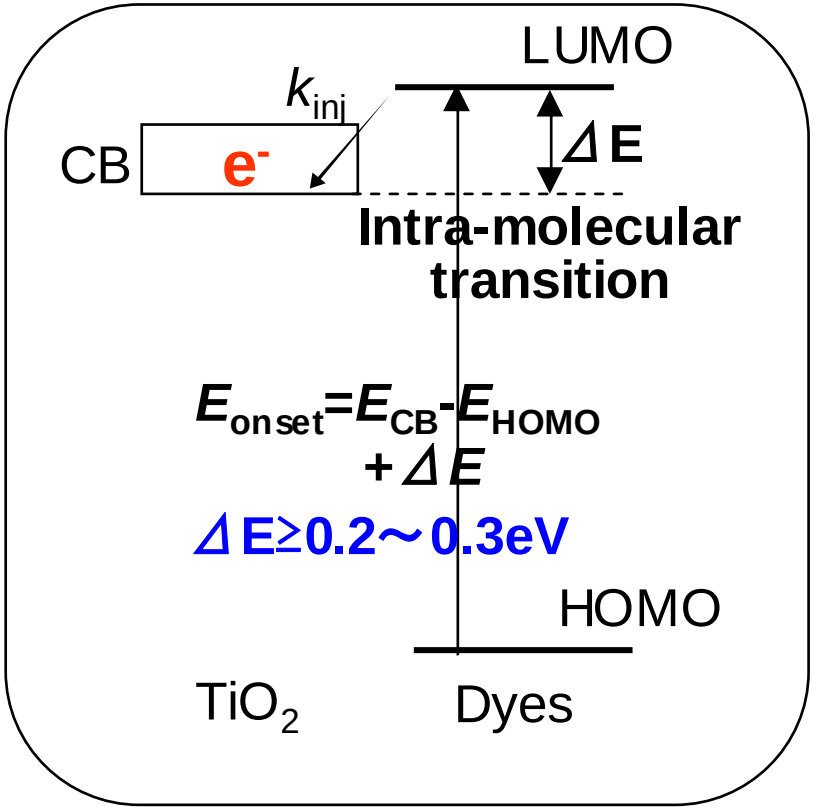


Redmond et al. *J. Phys. Chem.* 1993, **97**, 1426.
Kelly et al. *Langmuir*, 1999, **15**, 7047.

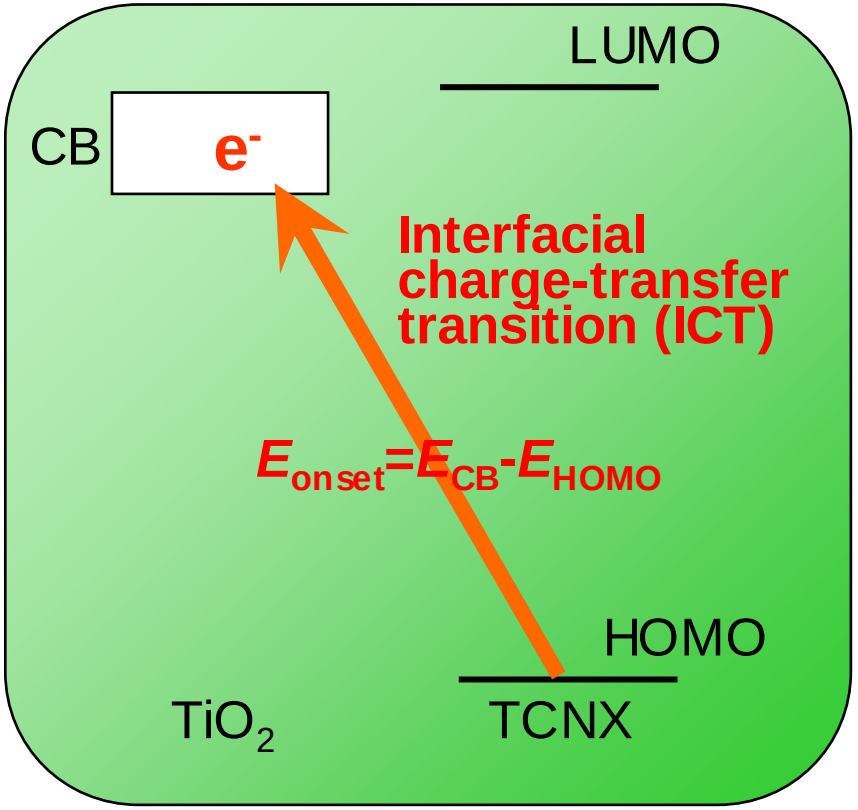
Spectral region is controllable by chemical band modification of TiO_2

Features of ICT-based solar cells

Conventional organic solar cells



ICT-based solar cells



ICT is effective for efficient charge separation, in particular, advantageous in near IR photoelectric conversion.

Summary

Novel organic solar cells based on interfacial charge-transfer transitions

(i) Interfacial charge-transfer transitions from surface-bound TCNX to TiO_2 enables wide light absorption

(ii) Efficient photocurrent conversion occurs with IPCE exceeding 80%.

(iii) Spectral region is controllable by chemical modifications of not only TCNX but also TiO_2.