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Dual Purpose Schiff Base Complexes for DSSC Dye and Polymer Flame Retardant

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Background

- In recent years, social demand for solar cells is increasing gradually.
- Although there are several types of solar cells, such as silicon, semiconductor, organic, and dye-sensitized solar cell (DSSC), modular components are generally composed of polymer materials.
- Indeed, to formulate safety measures during fire fighting (electric shock) as well as building fire, flame retardants for polymer materials (typically oxides or halogen compounds) should be contained in the solar cells as effective components.
- However, some halogen-containing organic compounds have been prohibited to use as flame retardants from the viewpoint of environmental issues.

Solar cells & building fire

- Increasing demands (megasolar & buildings)

China solar valley （China）

http://www.celsias.co.nz/article/chinasolarvalley/

Solar Tower（Manchester, UK）

http://gigazine.net/news/20070423_solar_sky_scraper/

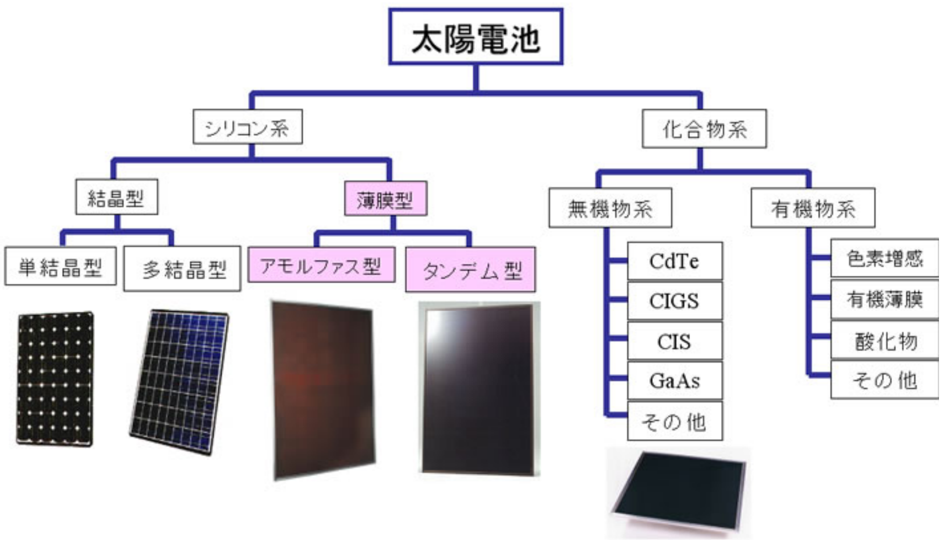
- Safety fire fighting (electric shock)

  Fire research technology 83 (2014) [Japan]

Types of solar cells and modules

Hybrid materials were used as modules.

太陽電池の種類と特徴



資料提供:三菱重工

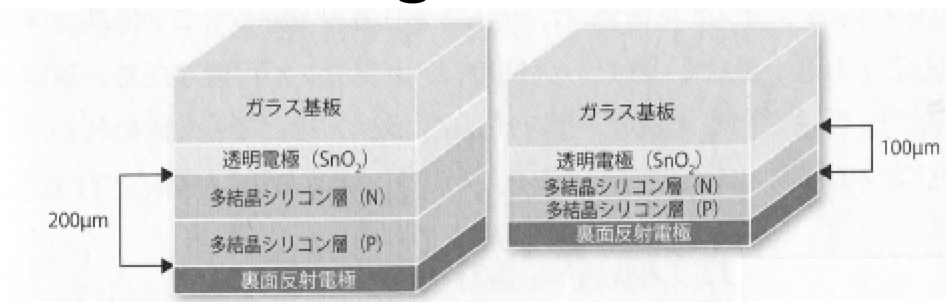
http://太陽光発電メリットデメリット検証.net/img/taiyoudennrisyurui.png

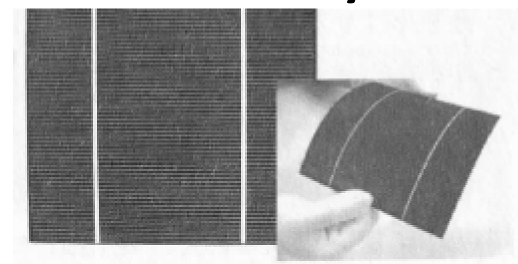
メーカー	種類	
	住宅用	公共・産業用
シャープ	多結晶シリコン	単結晶シリコン
		多結晶シリコン
		薄膜太陽電池（アモルファス+微結晶）
		薄膜太陽電池（アモルファス+微結晶）シースルータイプ
三洋電機	HIT型（単結晶+アモルファス）	
京セラ	多結晶シリコン	
三菱電機	多結晶シリコン	
カネカ	薄膜シリコンハイブリッド（アモルファス+多結晶）	
サンテックパワージャパン	単結晶シリコン	単結晶シリコン・多結晶シリコン
東芝（サンパワー）	単結晶シリコン	（他社製太陽電池を使用したエンジニアリング事業）
長州産業	単結晶シリコン	HPに掲載なし
	多結晶シリコン	
三菱重工	HPに掲載なし	微結晶タンデム（アモルファス+微結晶）
		アモルファス
富士電機		FWAVE（アモルファスシリコン+アモルファスシリコンゲルマニウム）

京極一樹「ラクラクわかる太陽電池のしくみ」アスキー・メディアワークス(2011)

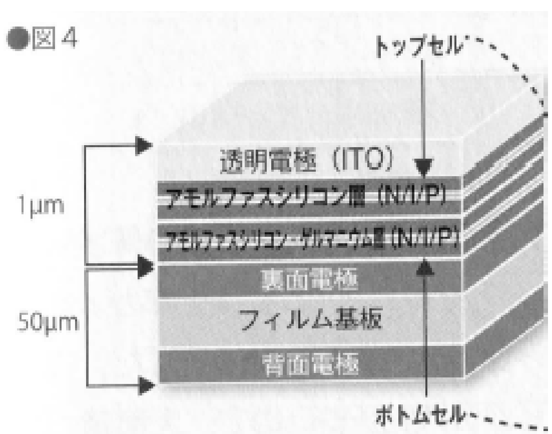
Polycrystalline silicon

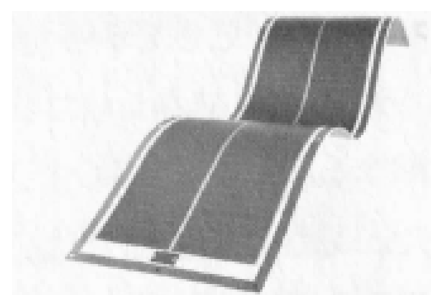
- module　（glass substrate & silicon layer）




（写真提供：三菱電機）

- FWAVE module（polymer film substrate）




（写真提供：富士電機）

京極一樹「ラクラクわかる太陽電池のしくみ」
アスキー・メディアワークス(2011)

Compound semiconductors

	III-V 族	II-VI 族	I-III-VI 族
元素	III族：Al, Ga, In V族：P, As, Sb	II族：Zn, Cd VI族：S, Se, Te	I族：Cu III族：Ga, In VI族：S, Se, Te
2 元化合物	AlAs, GaAs, InP InAs, AlSb, GaSb GaP, AlP	ZnS, ZSe, CdTe, CdS, ZnTe	
3 元化合物	AlGaAs, GaAsP GaInP, AlGaSb	ZnSSe, CdZnTe	CIS：$CuInS_2$
4 元化合物	InGaAsP, InGaAlP InAlGaAs, InGaAsSb		CIGS：$Cu(In,Ga)Se_2$

- semiconductor

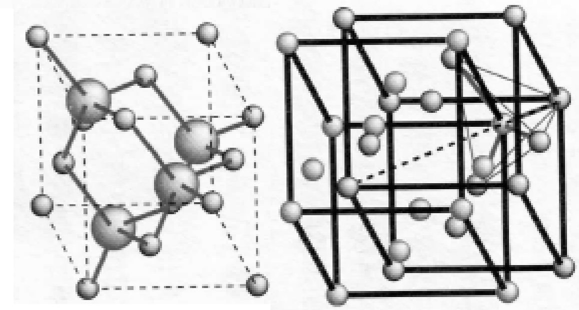
High-performance CdTe（Cd toxic?）

CdTe mp1041℃, bp1050℃

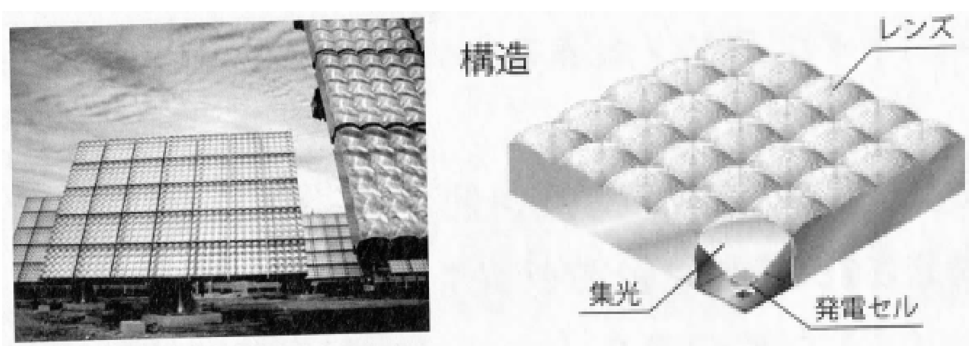
Sublimation(800℃, 0.003 atm)

CdS mp1750℃

Sublimation(800℃, 0.001 atm)



- Concentrating solar power plant



Concentrating solar power by Plastic lens

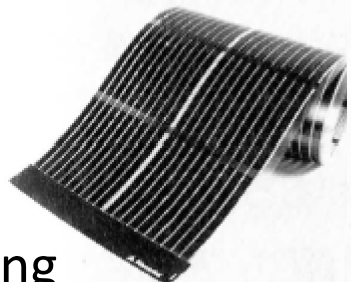
京極一樹「ラクラクわかる太陽電池のしくみ」アスキー・メディアワークス(2011)

Organic solar cells

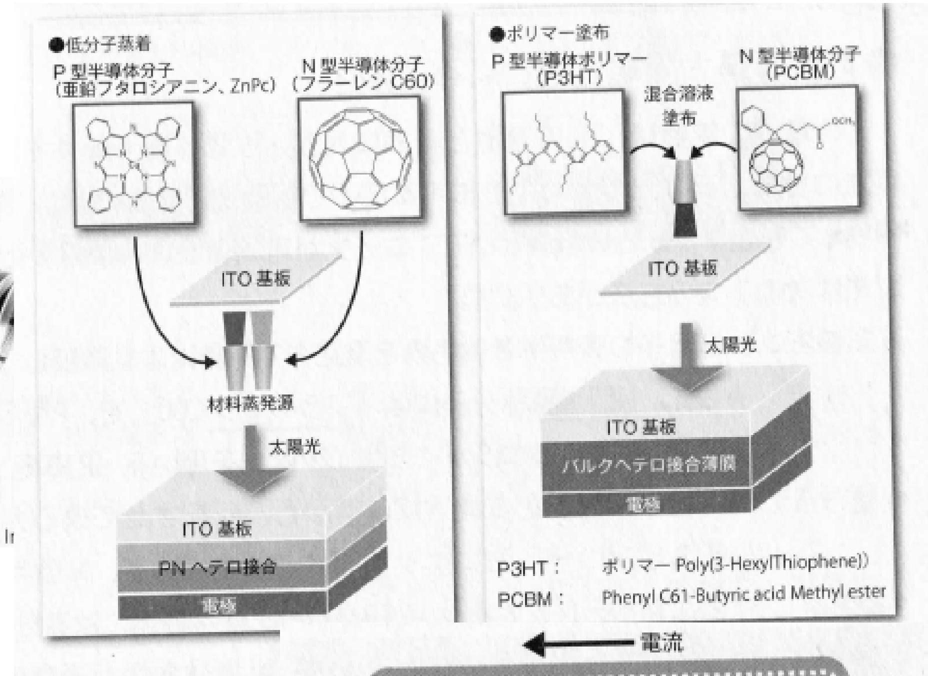
- Organic thin films

Organic semiconductor
（complex, C60）
Conducting polymer
ITO（metal oxides）
 vapor deposition coating

●図4　Power Plastic

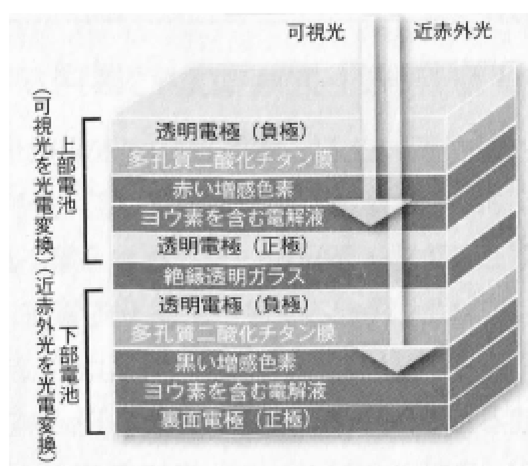


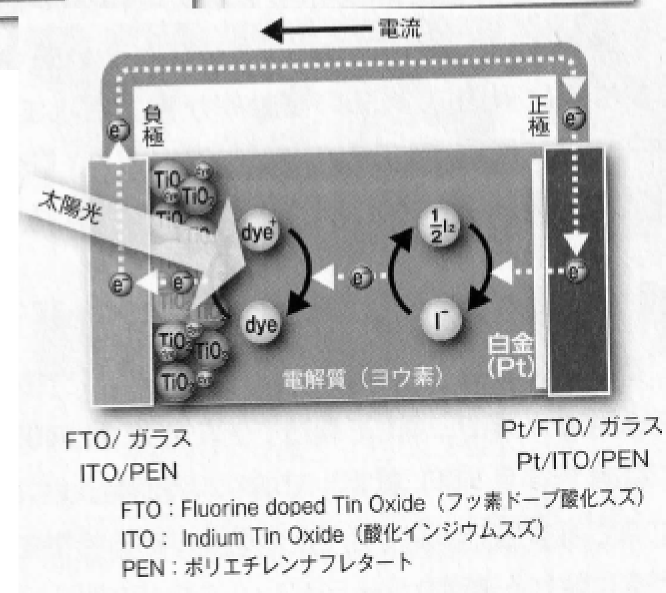
（出典：Konarka Technologies, I



- DSSC

Organic dye（complex）
polymer(PEN)
ITO（metal oxides）
Electrolyte（I^-）





京極一樹「ラクラクわかる太陽電池のしくみ」
アスキー・メディアワークス(2011)

Problems (solutions as plans)

- Flame Retardants for combustible module

  polymer flame retardants for films or lens

  → Br-complex retardants (TG-DTA)

・Mechanism & analysis of burning products

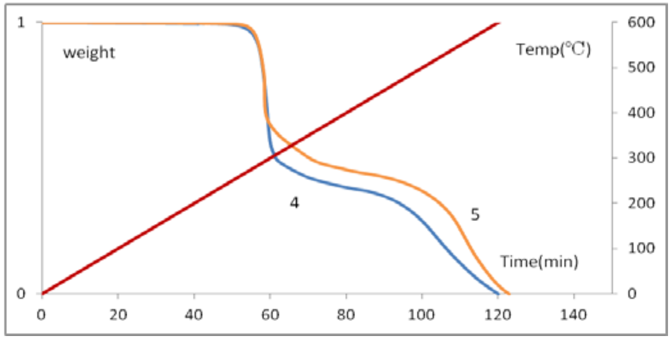
reaction mechanism（MD calculations）

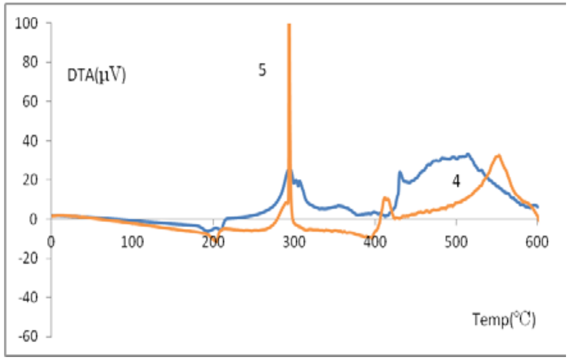
bond breaking（FT-IR, DFT calculations ）

analysis of products（FT-IR & DFT）

Complex flame retardants for polymer

- Br-complex endothermic phase transition (PMMA)





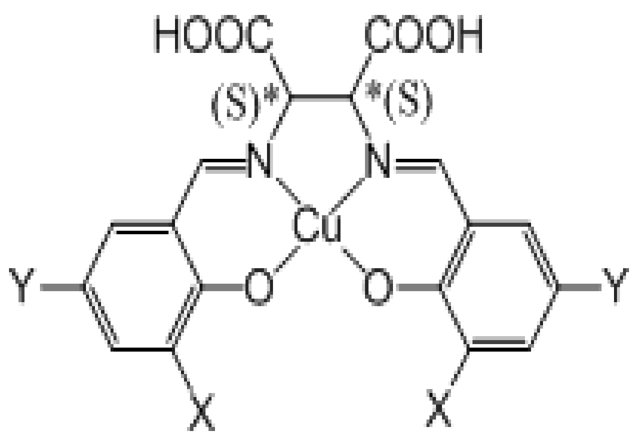
- Many patents (salen-type complexes)

[Japan]
特開平09-255879,特開2002-155038,
特開2011-178682,特開2001-089640,
特開2000-273157,特開2000-204227,
特開2012-067301,特開2010-126694

Dual Purpose Complexes for DSSC Dye & Polymer Flame Retardant

DSSC using salen-type complexes

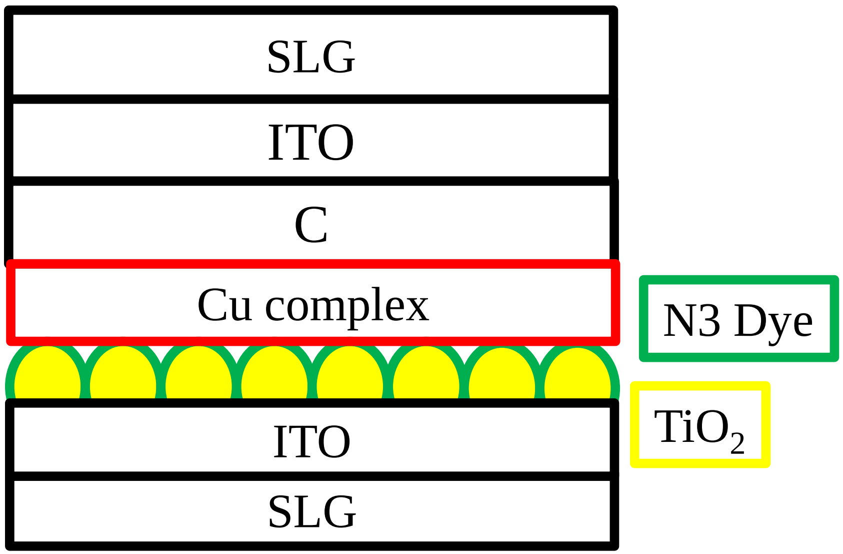
- We have designed new dyes of low-cost Cu complexes to tune…
- UV-VIS-NIR (long wave length) light absorption
- redox potentials (electrodes and mediators)
- adsorption onto surface of semiconductors



	X	Y
1	H-	H-
2	Cl-	Cl-
3	t-Bu-	t-Bu-
4	HO-	H-
5	H-	Cl-
6	H-	MeO-

R. Shoji, S. Ikenomoto, N. Sunaga, M. Sugiyama, T. Akitsu, J. Appl. Sol. Chem. Model., 5, 48 (2016).

DSSC performance test



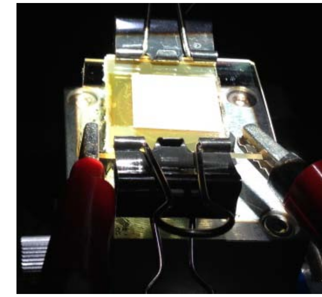
Dye：Complex1-7

DMF ： MeOH = 1: 9 (1mM)

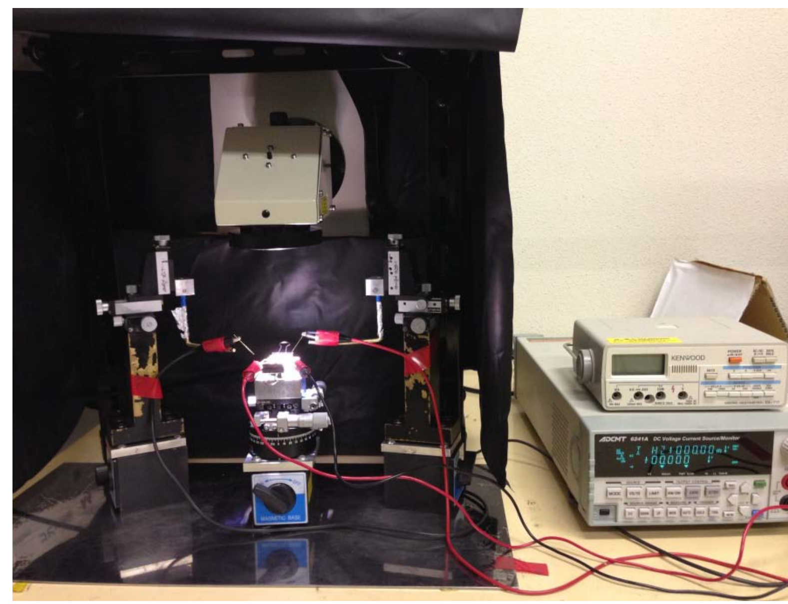
Electrolytes：I_2 (0.05 M)

LiI (2.0 M) in MeCN

After adsorption

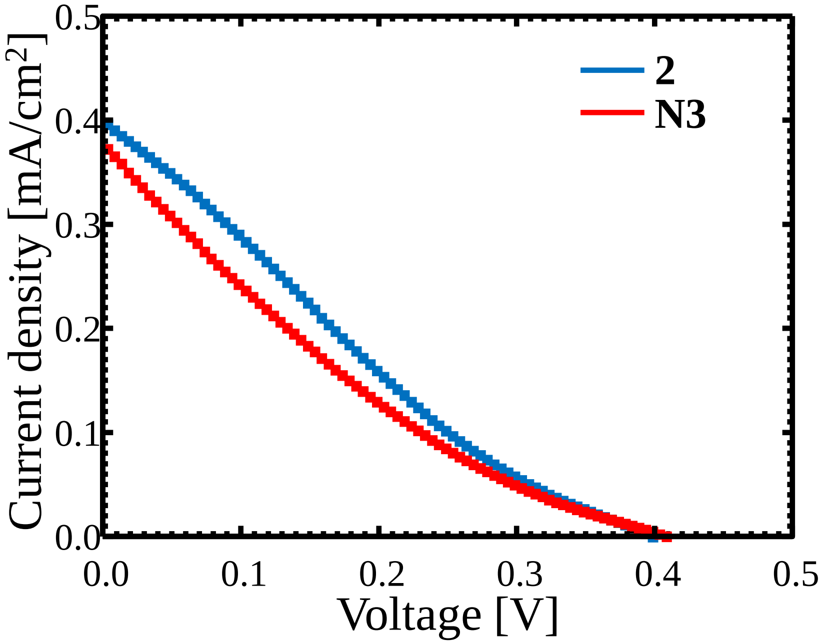


Test cell



Solar simulator

I-V Measurements



	Voc [V]	Jsc [mA·cm^{-2}]	FF [%]	η [×10^{-2}%]
1	0.301	0.071	29.0	0.6126
2	**0.397**	**0.400**	**21.0**	**3.3486**
3	0.271	0.052	30.0	0.4244
4	0.205	0.127	21.0	0.5493
5	0.189	0.032	28.0	0.1690
6	0.208	0.142	24.0	0.7071
7	0.132	0.021	26.0	0.0722
N3	**0.405**	**0.378**	**20.0**	**3.0609**

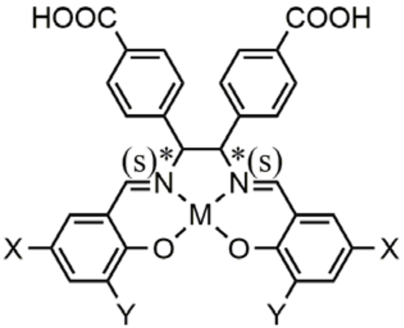
Complex **2** 3.3486×10^{-2} % > N3 (conventional Ru dyes) 3.0609×10^{-2} %

Electron-withdrawing Cl-, Br- groups resulted in increasing Jsc (as well as being good polymer flame retardant)

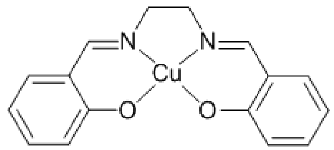
Preparations & characterization

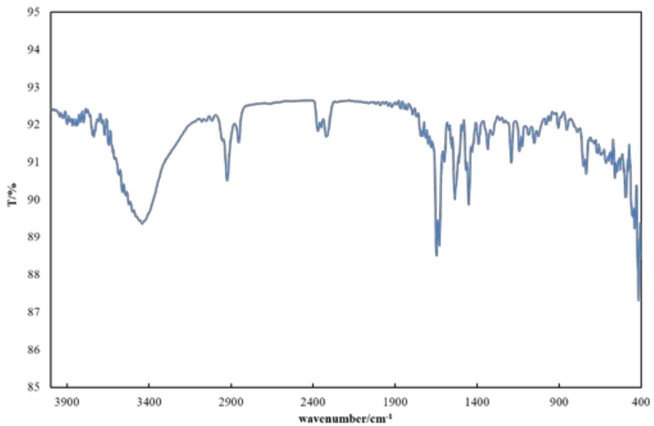
- Preparations of (X=) Br- complexes (FT-IR)

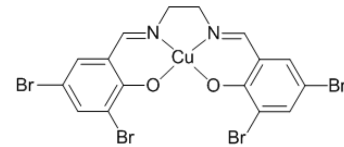
  -> Tuning for obtaining good DSSC dyes

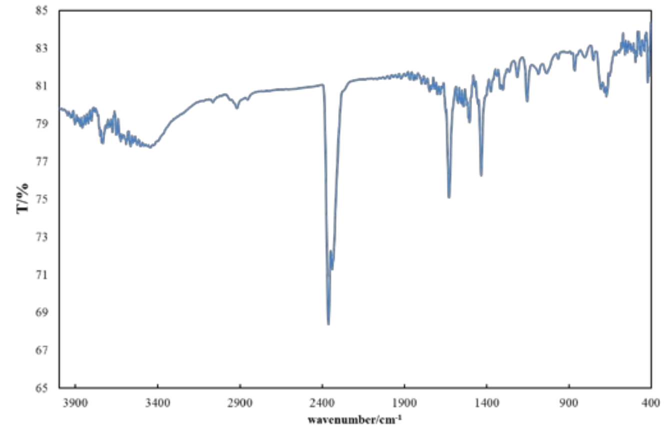


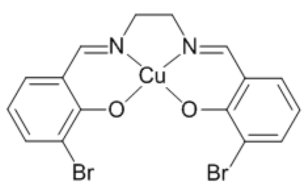
IR spectra

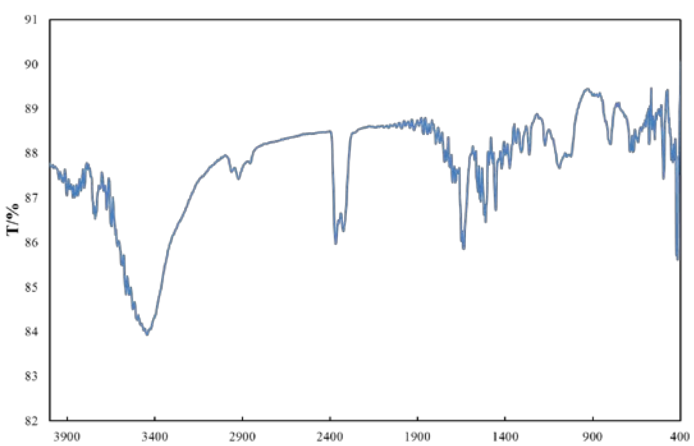










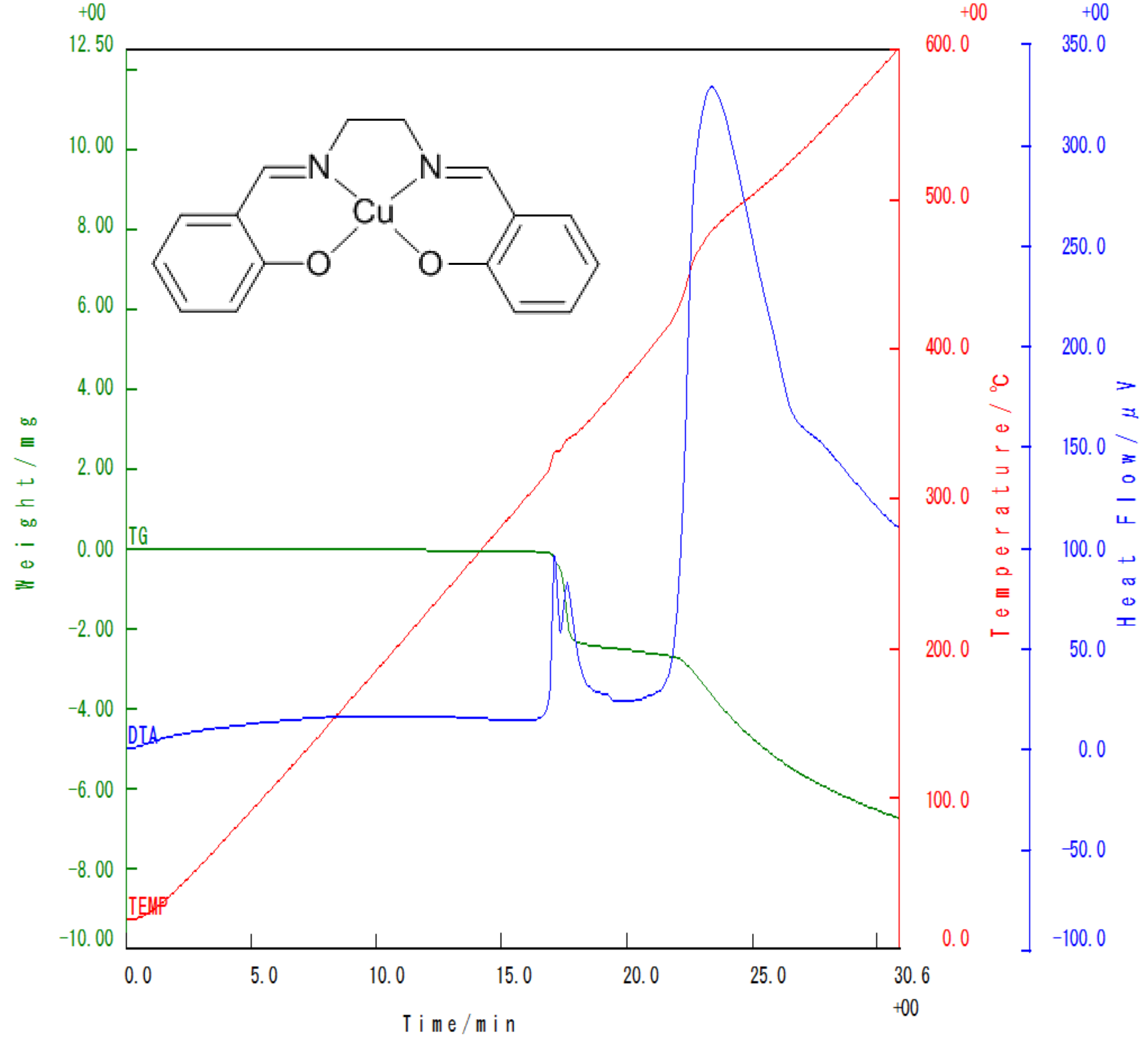


C

=

N

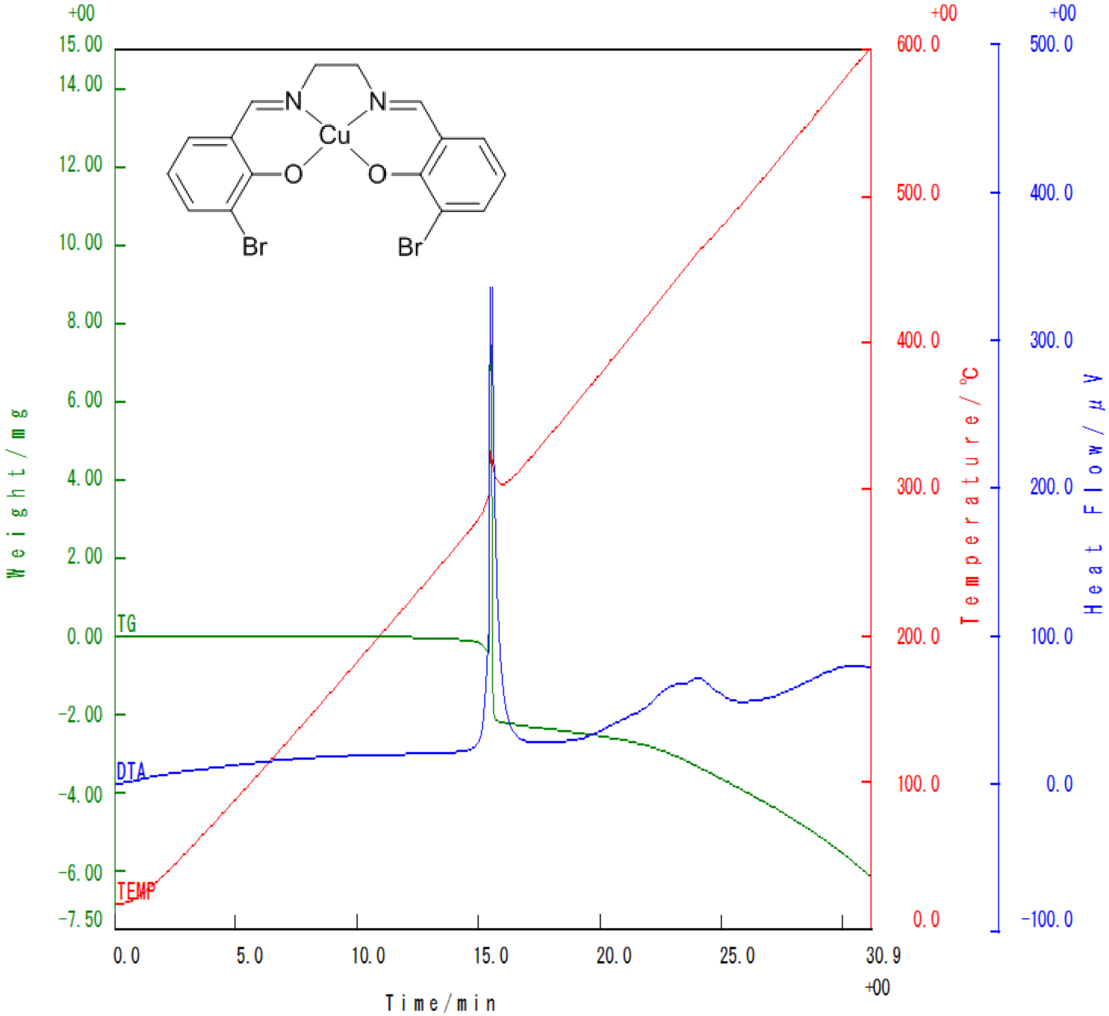
TG-DTA



Model (en) Br- complexes (TG-DTA)

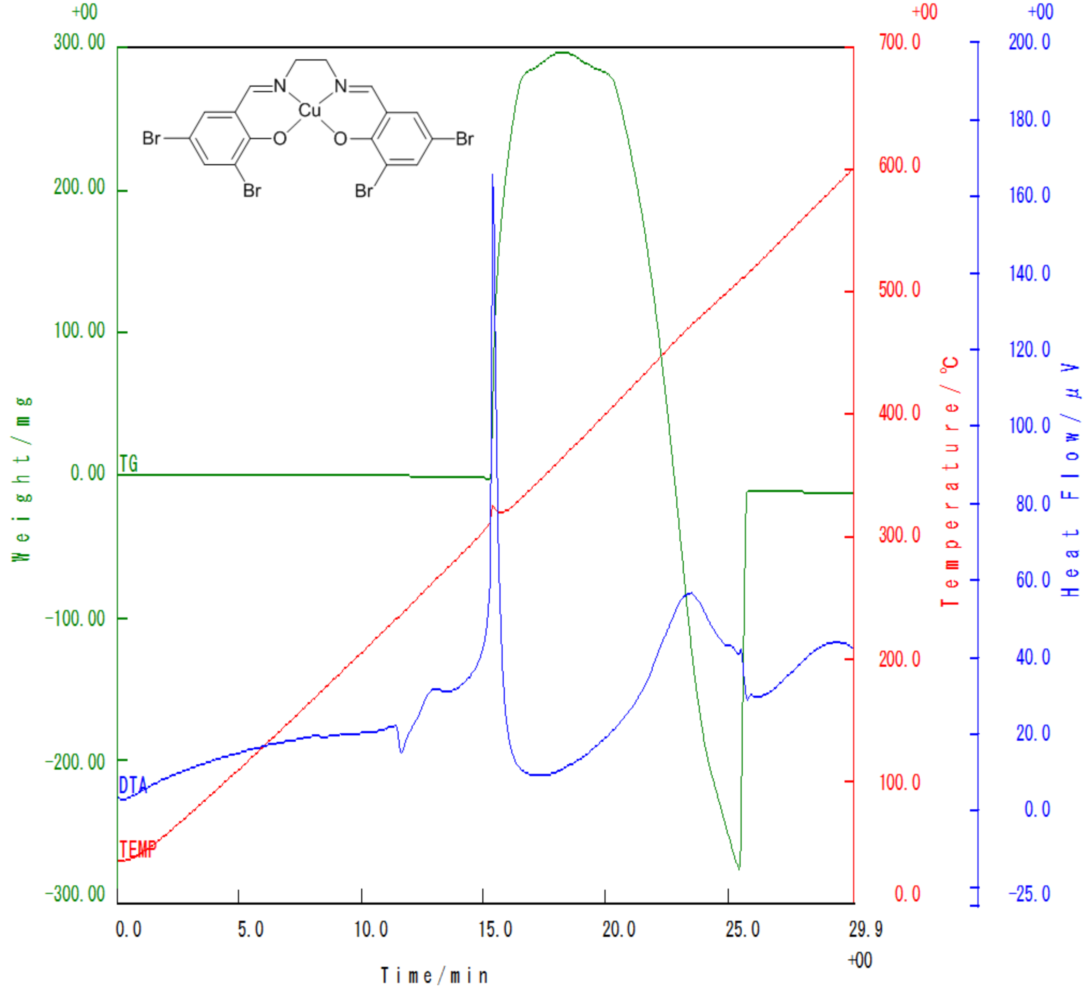
Decomposition temperature was measured.

TG-DTA



+00
15.00
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
-2.00
-4.00
-6.00
-7.50
Weight/mg
TG
DTA
TEMP
600.0
500.0
400.0
300.0
200.0
100.0
0.0
Temperature/℃
500.0
400.0
300.0
200.0
100.0
0.0
-100.0
Heat Flow/μV
0.0
5.0
10.0
15.0
20.0
25.0
30.9
Time/min
N
N
Cu
O
O
Br
Br

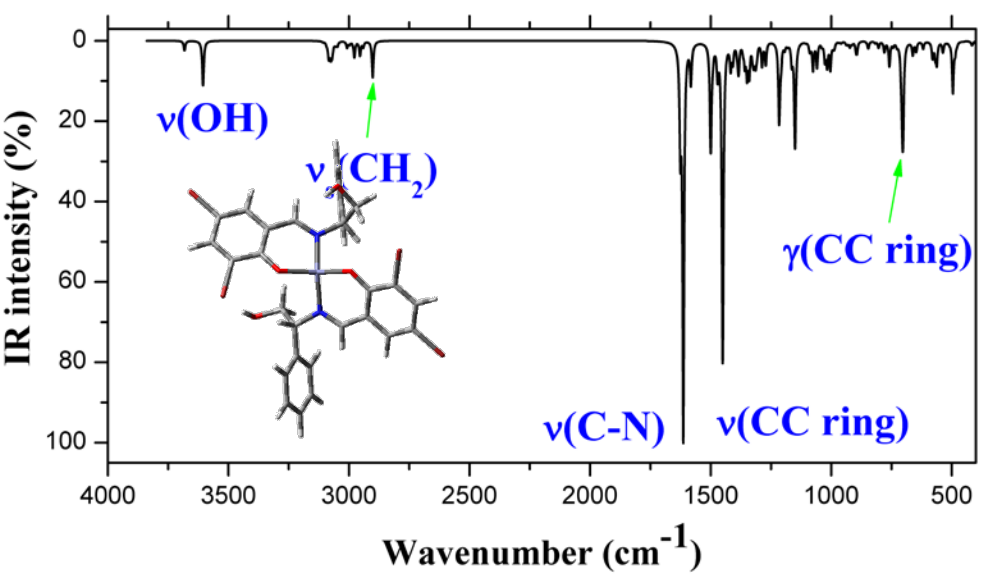
TG-DTA

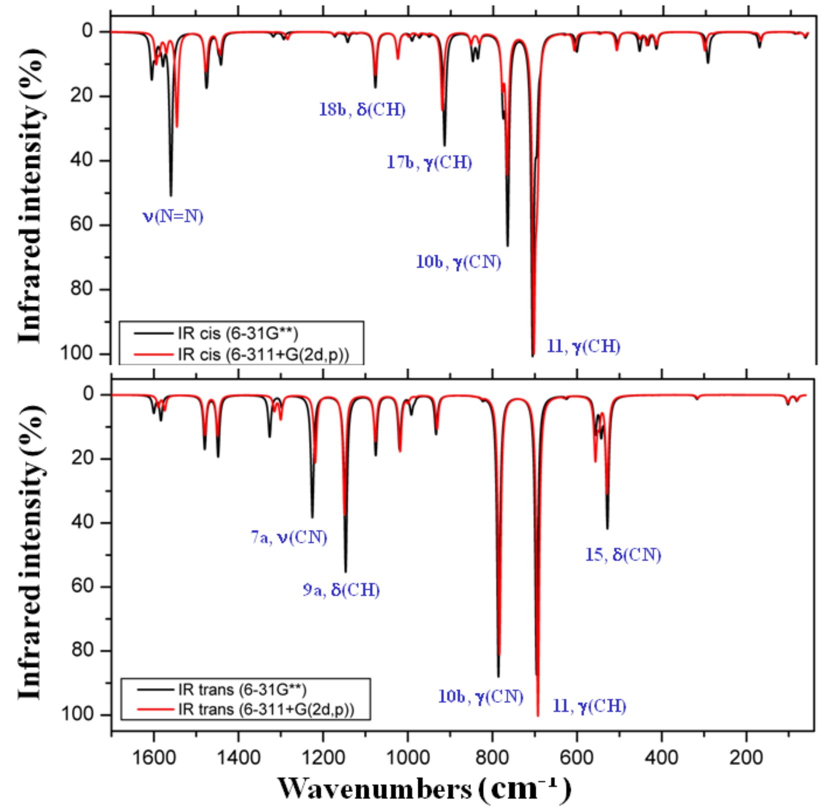


Br
Br
Br
Br
O
O
N
N
Cu
+00
300.00
200.00
100.00
0.00
-100.00
-200.00
-300.00
Weight/mg
TG
DTA
TEMP
+00
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
Temperature/℃
+00
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
-25.0
Heat Flow/μV
0.0
5.0
10.0
15.0
20.0
25.0
29.9
+00
Time/min

Theoretical supports (in future).

- Reaction mechanism & products (MD)
- Analysis of breaking bonds & products by calculated IR spectra





M. Ito, T. Akitsu, M.A. Palafox, *J. Appl. Sol. Chem. & Model.*, **5**, 30-47 (2016).

Summary

- To design high performance DSSC dyes of low cost, certain metal complexes may be superior to purely organic dyes. In our previous study, electron-withdrawing subsituent groups are appropriate to absorb long-wave lengths sunlight as well as proper tuning of redox potentials between of TiO_2 semiconductor and I^-/I_3^- mediators.
- For this purpose, introducing halogen groups into Schiff base metal complexes was found to be a good strategy.
- Herein, we proposed a concept of developing dual purpose Schiff base metal complexes