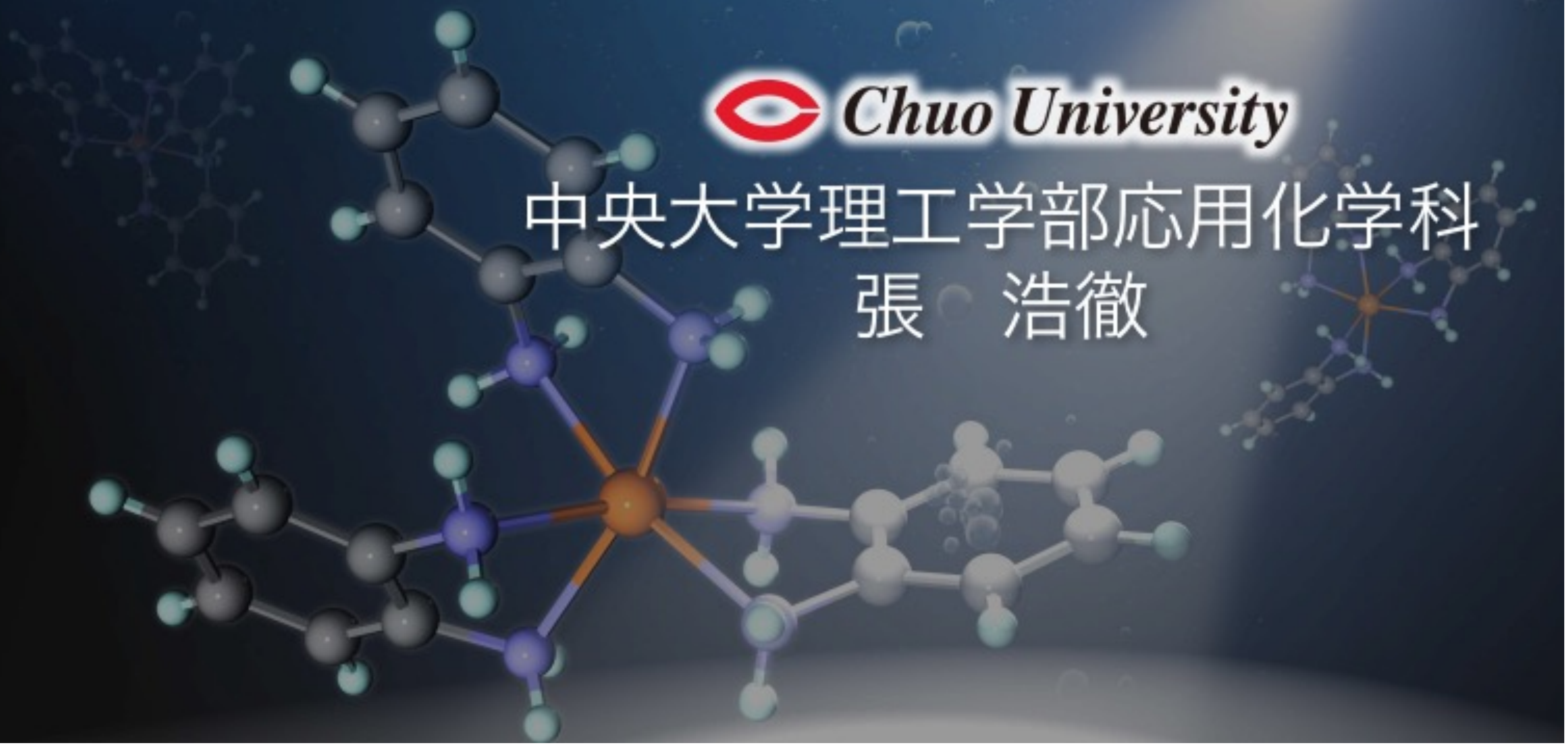
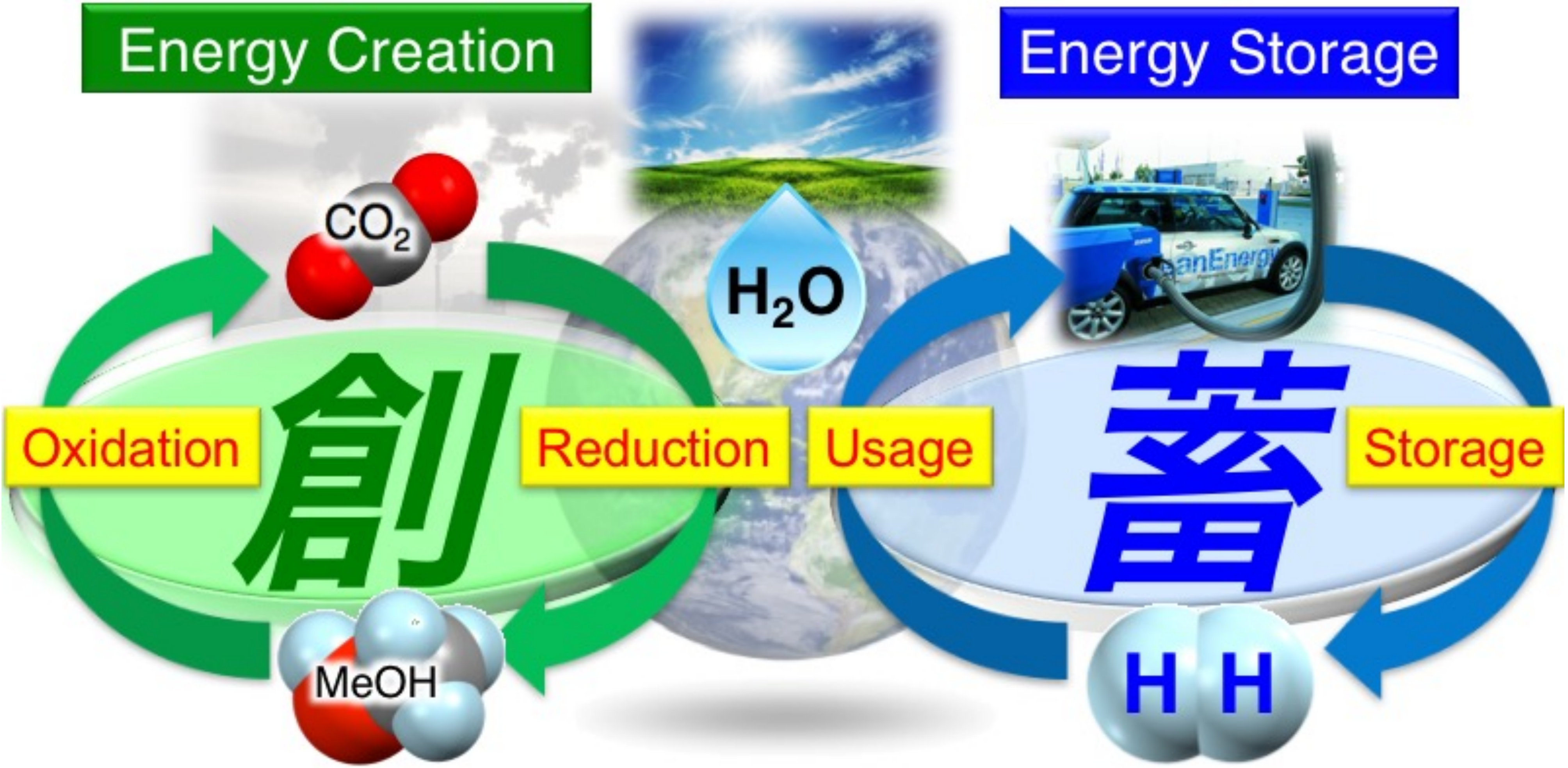
第３５回無機材料に関する最近の研究成果発表会　2018.1.30@住友会館
主催：公益財団法人　日本板硝子材料工学助成会

電子・プロトンプーリング型配位子に基づいた光駆動型水素キャリアの構築

Chuo University
中央大学理工学部応用化学科
張　浩徹



Big Aims



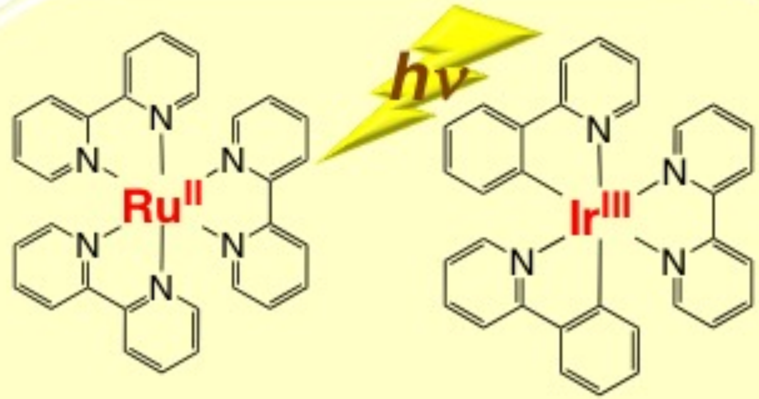
Carbon Neutral Cycle

High Efficiency Carrier

Most pressing issues facing 21st century

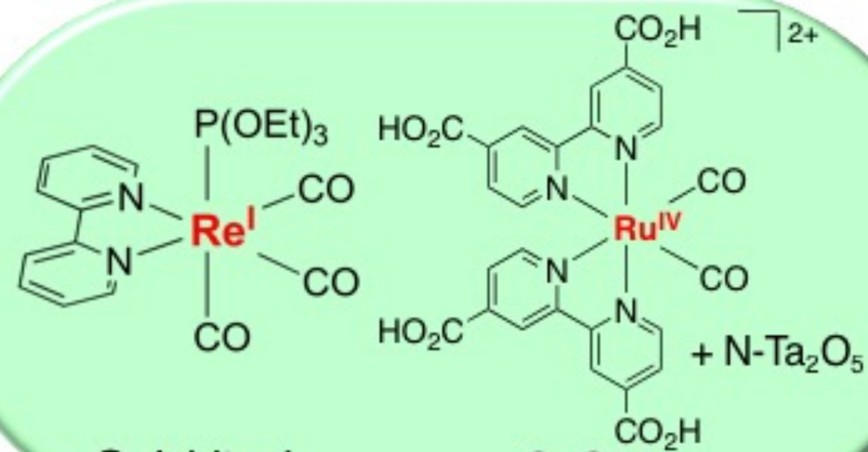
Molecular Catalysts

Photosensitizer



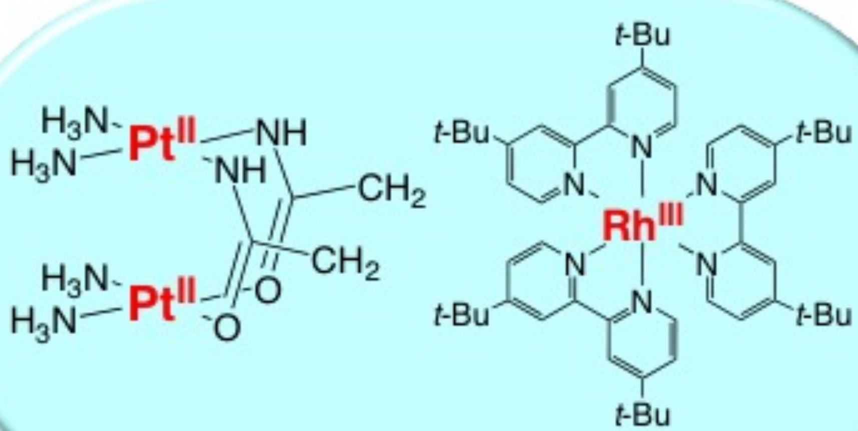
M. Grätzel S. Bernhard

CO_2 Reduction



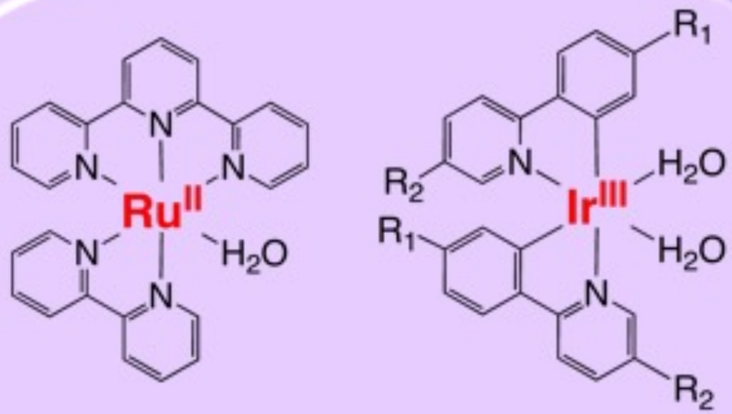
O. Ishitani S. Sato

H_2 Evolution



K. Sakai S. Bernhard

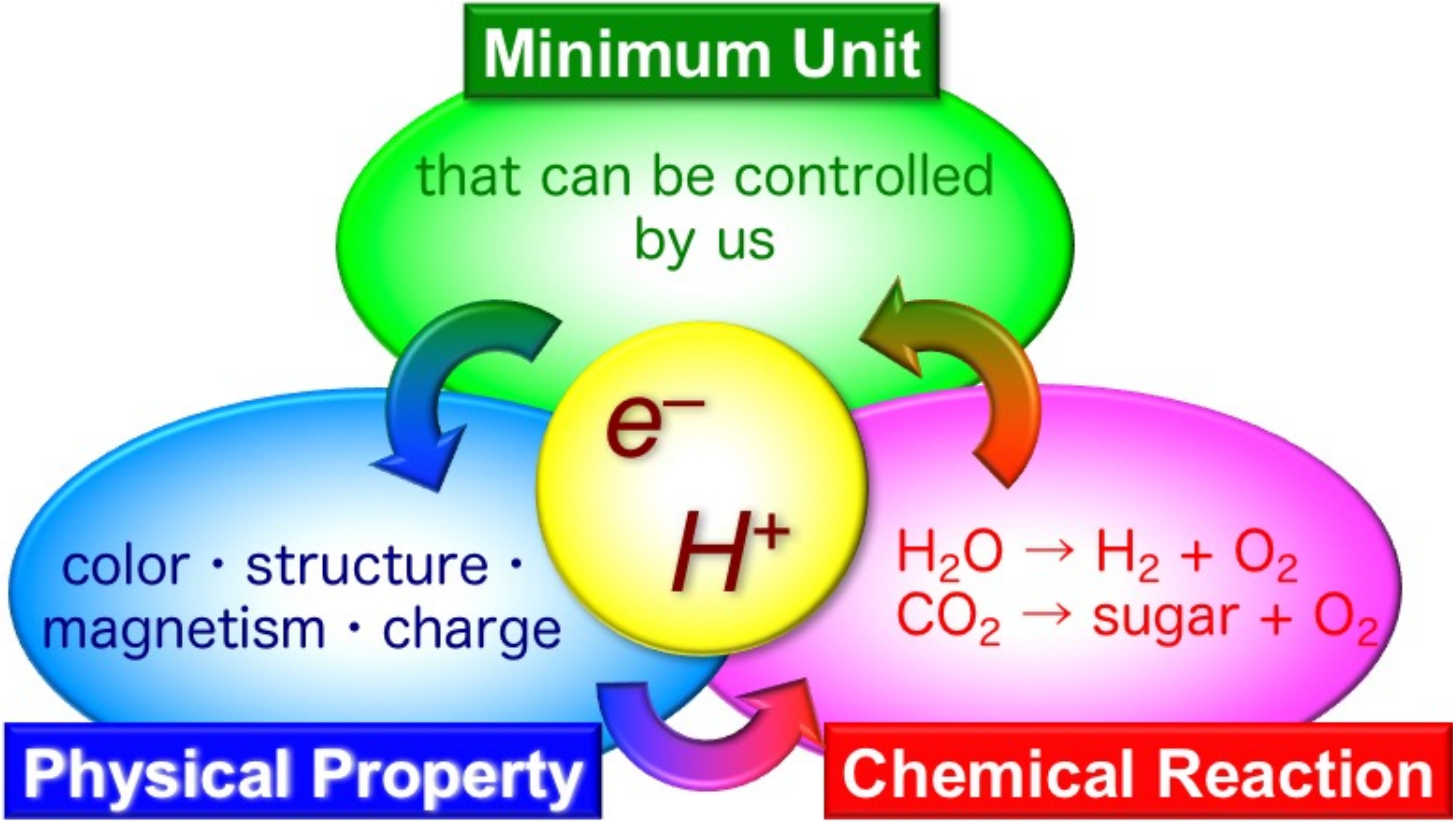
O_2 Evolution



K. Sakai S. Bernhard

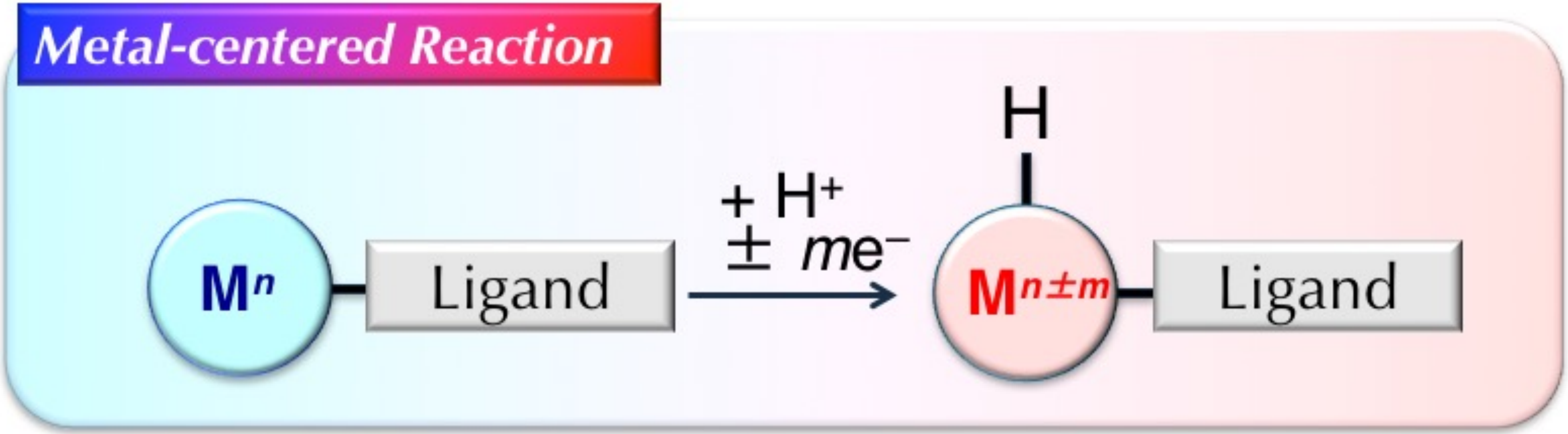
Well-defined molecules based on precious metal

Our Viewpoint

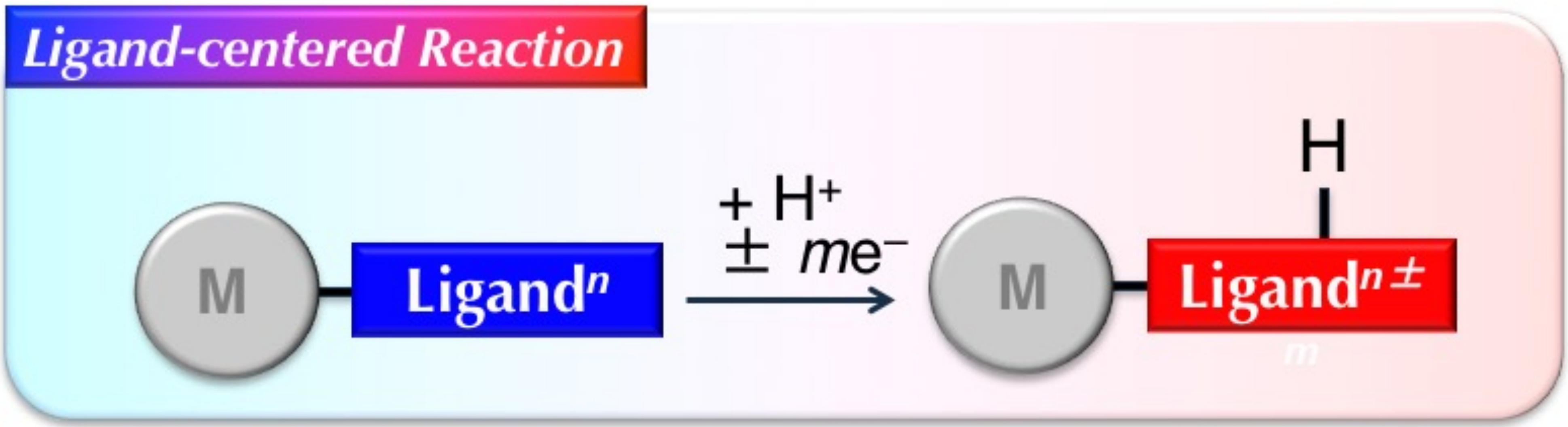


Electron/proton transfer is a key

Two Regimes



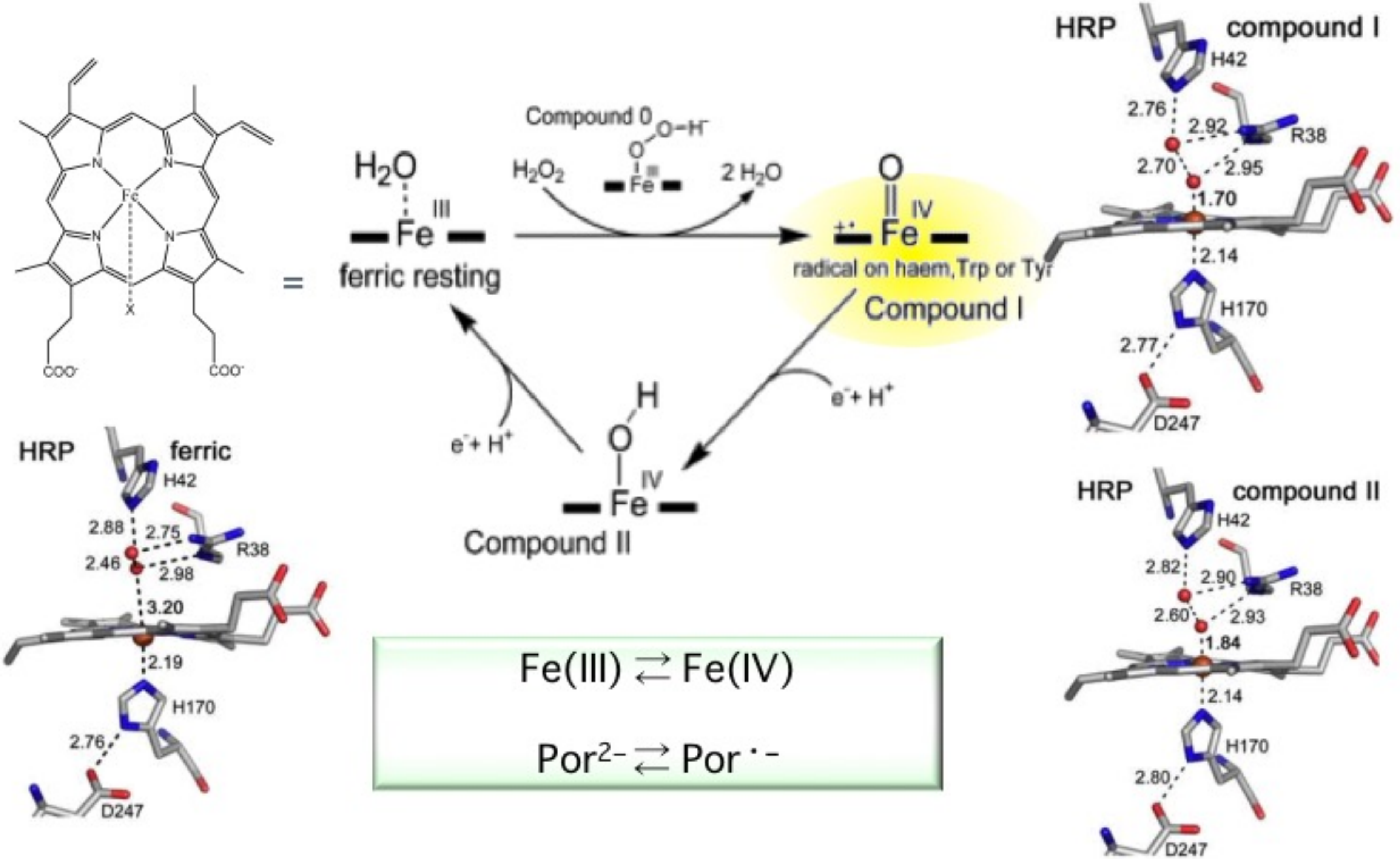
vs.



"Ligand" could be electron and proton pooler

Redox on Organic Unit

K. Kristoffer Andersson et al, *J. Inorg. Biochem*, **2006**, *100*, 460

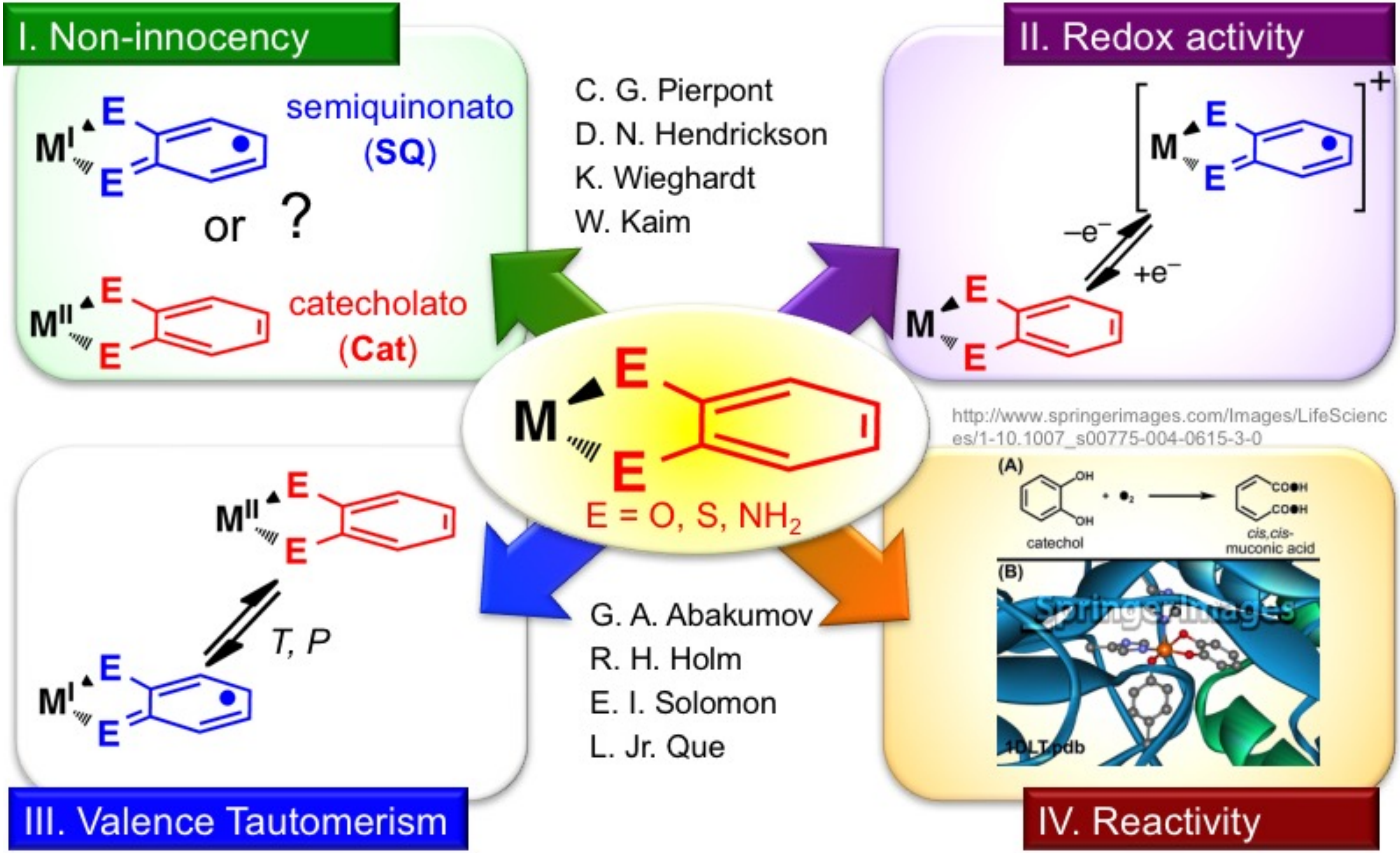


$Fe(III) \rightleftarrows Fe(IV)$

$Por^{2-} \rightleftarrows Por^{\cdot -}$

The organic parts act as an electron donor

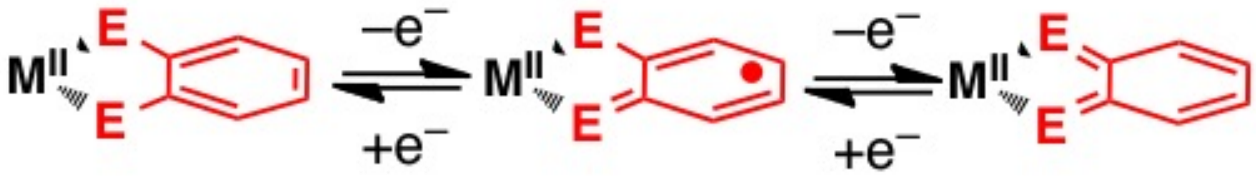
Redox-active, Non-innocent Ligands



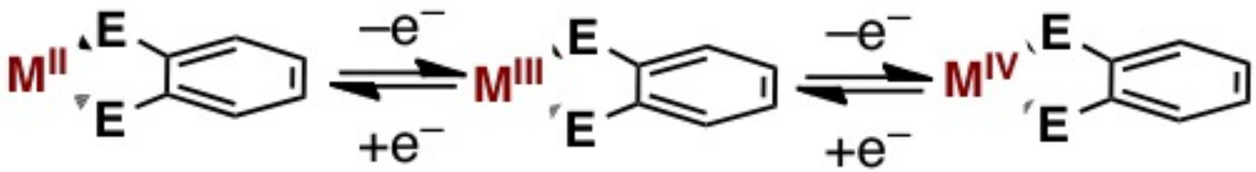
The molecular chemistry has been developed

Redox-active/Non-Innocent Ligand

Redox on ligand

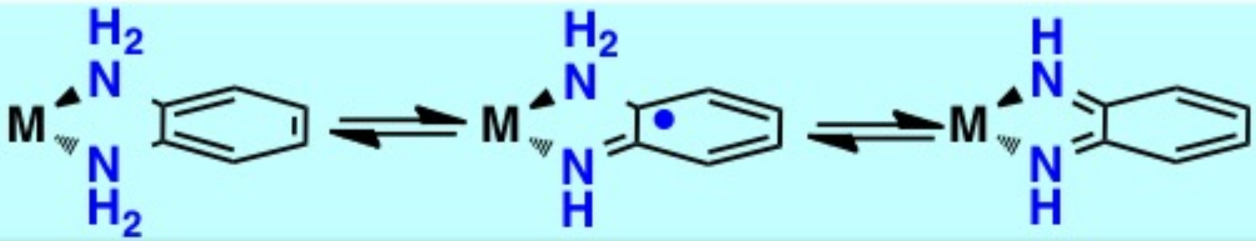


Redox on metal

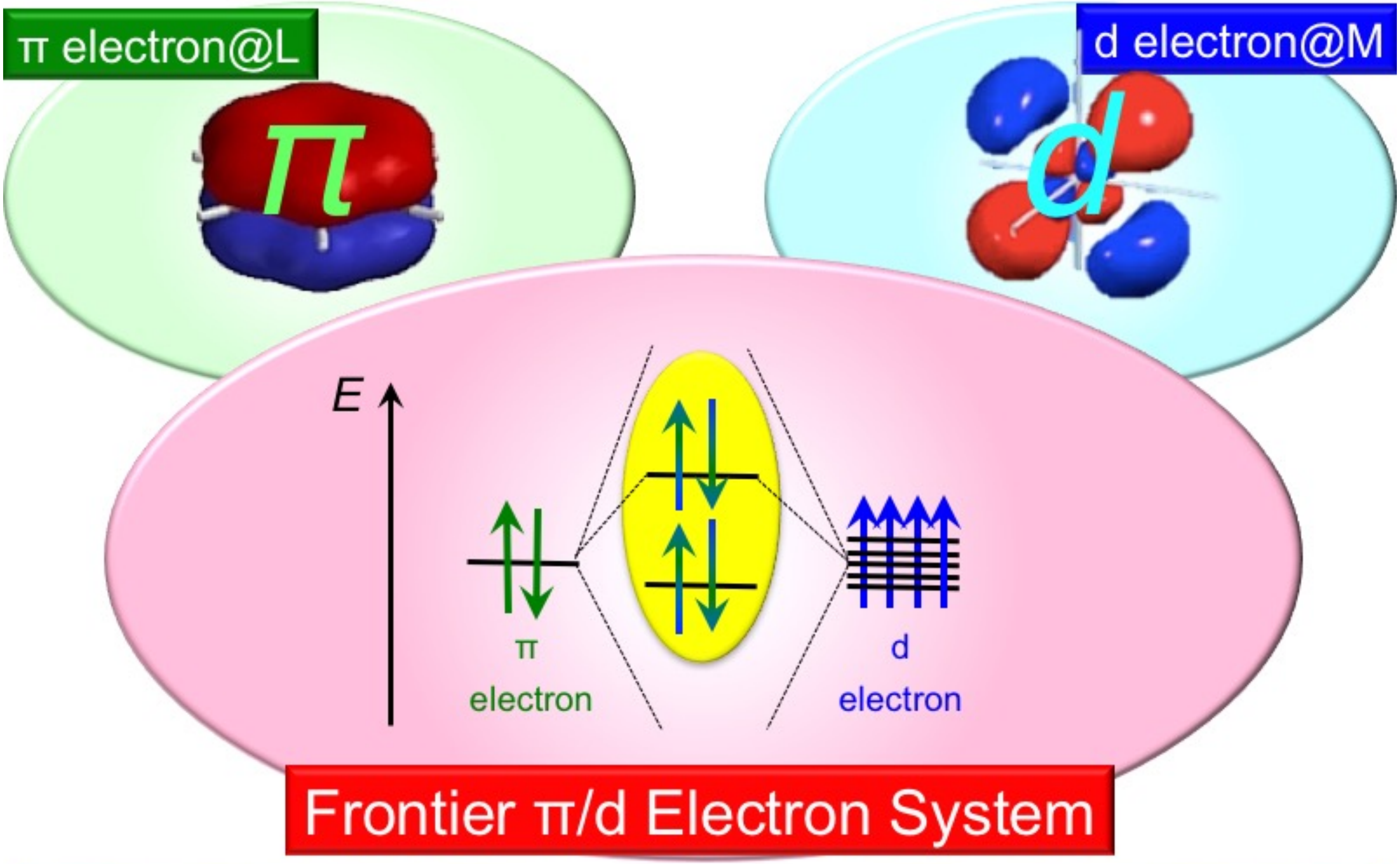


Valence tautomerism

PCET



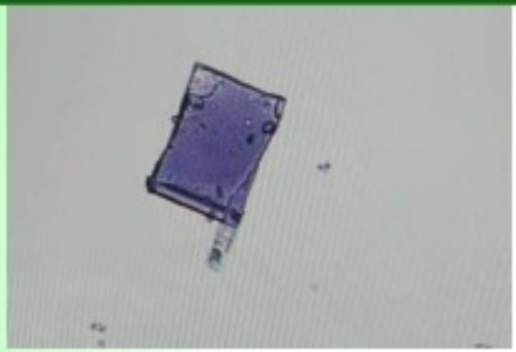
Why Redox-active Ligand ?



Hybrid d/π electron system

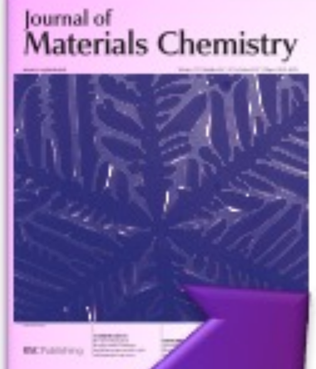
Recent Our Works

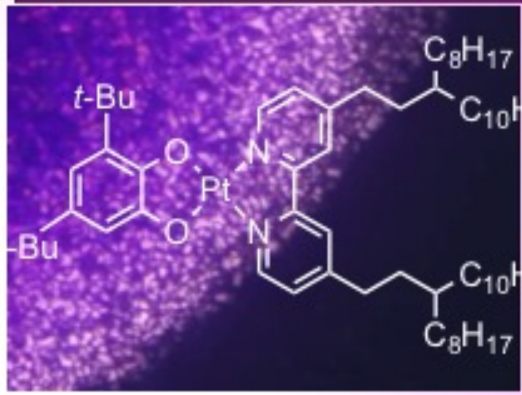
Molecular Switch



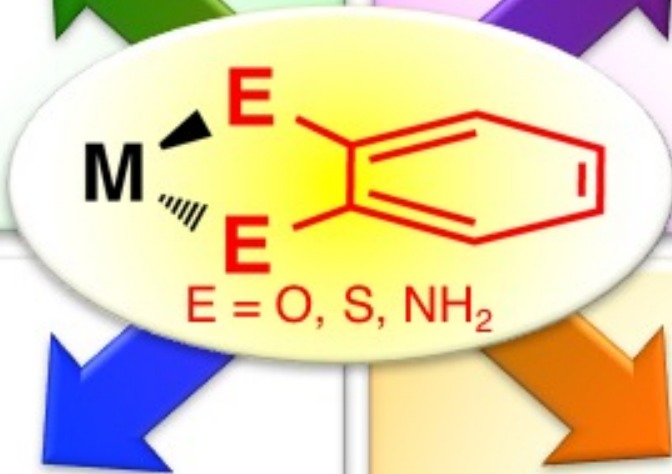
EJIC, **2013** (Review)
Chem. Commun., **2010**, *ibit*, **2009**
Chem. Mat., **2009**, *JACS*, **2008**
Dalton Trans., **2006**

Redox-active LC



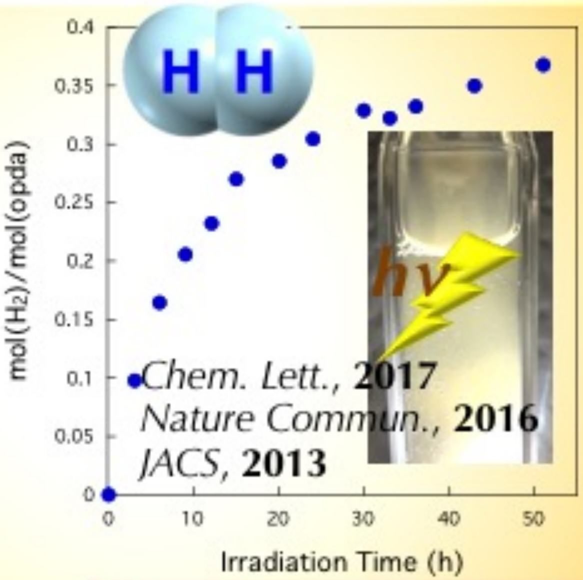


Chem. Lett., **2014** *Dalton Trans.*, **2013**
Inorg. Chem., **2013** *Inorg. Chem.*, **2011**
J. Mat. Chem., **2007**



Eur. J. Inorg. Chem., **2017**
Chem. Eur. J., **2017**
Dalton Trans., **2015**
Bull. Chem. Soc. Jpn., **2015**
Dalton Trans., **2012**
Inorg. Chem., **2011**

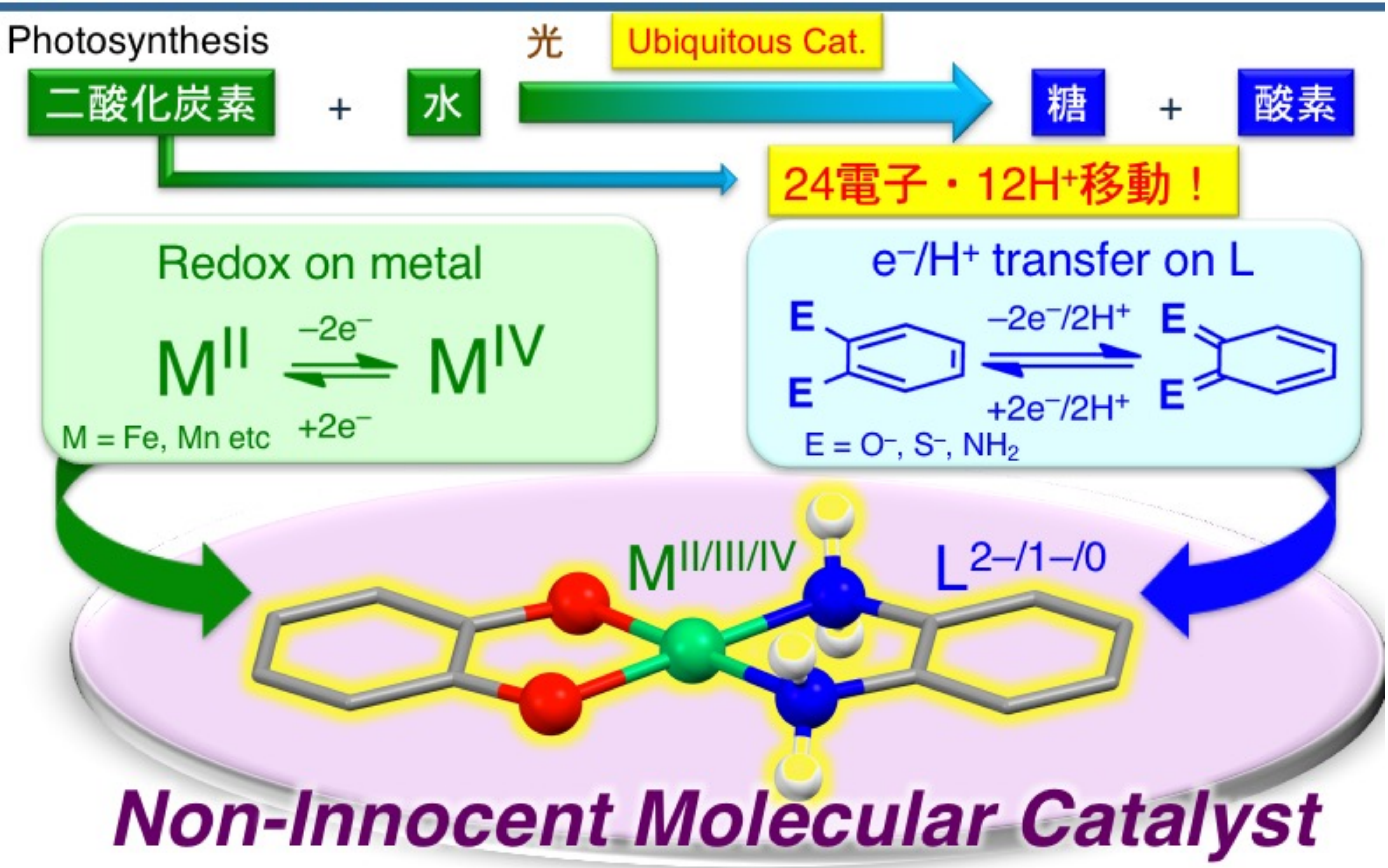
Multi-electron Transfer



Chem. Lett., **2017**
Nature Commun., **2016**
JACS, **2013**

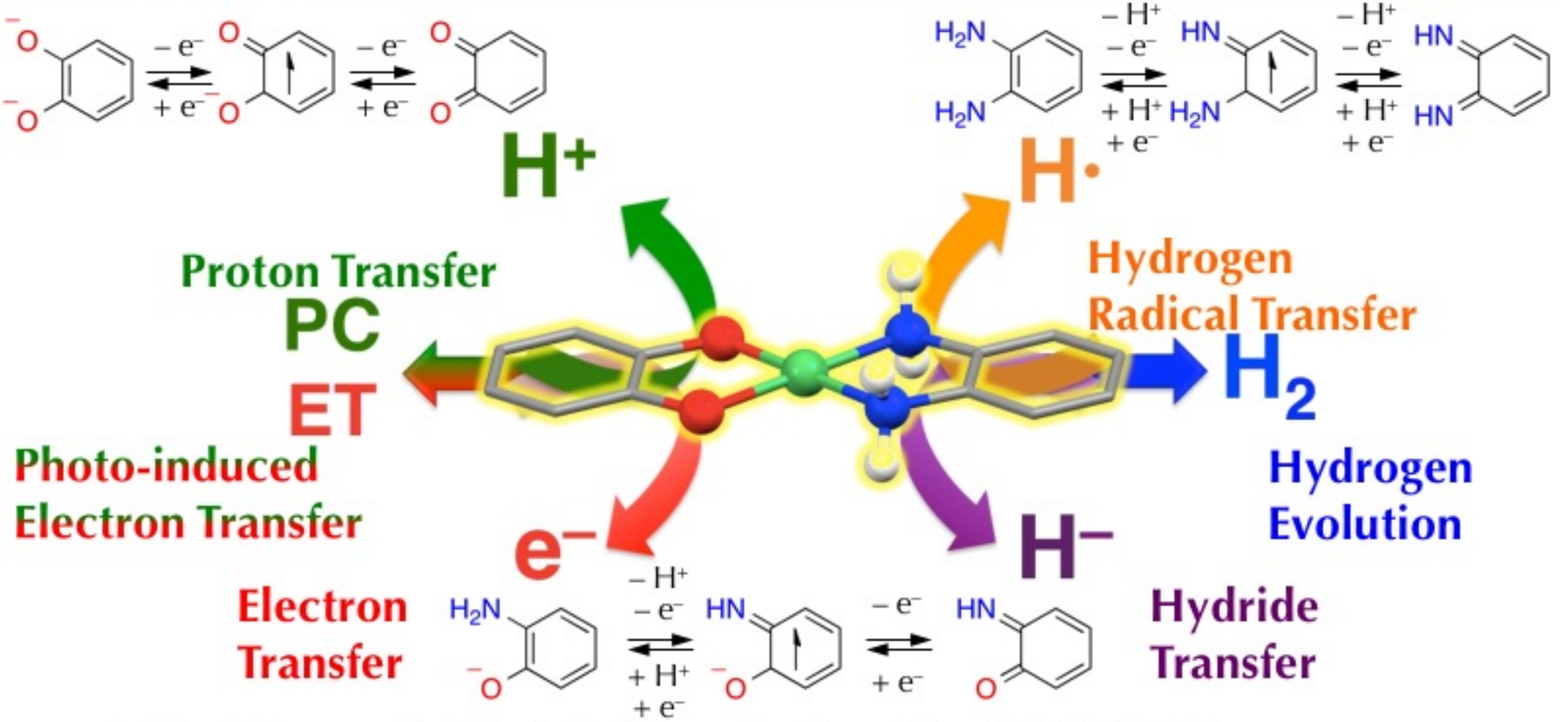
Hydrogen Evolution

Towards A New Molecular Material



Cooperative electron/proton transfer

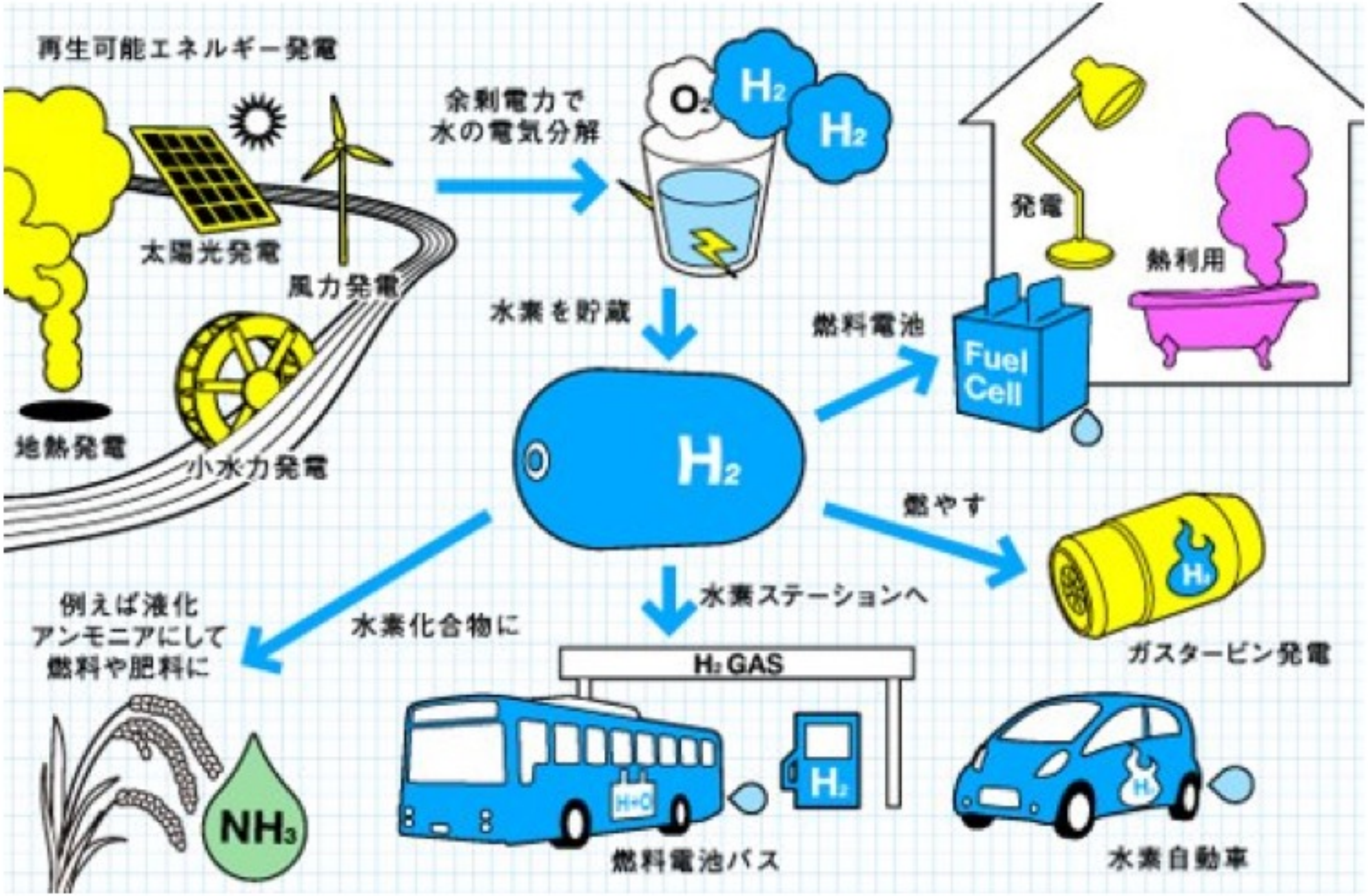
Concept



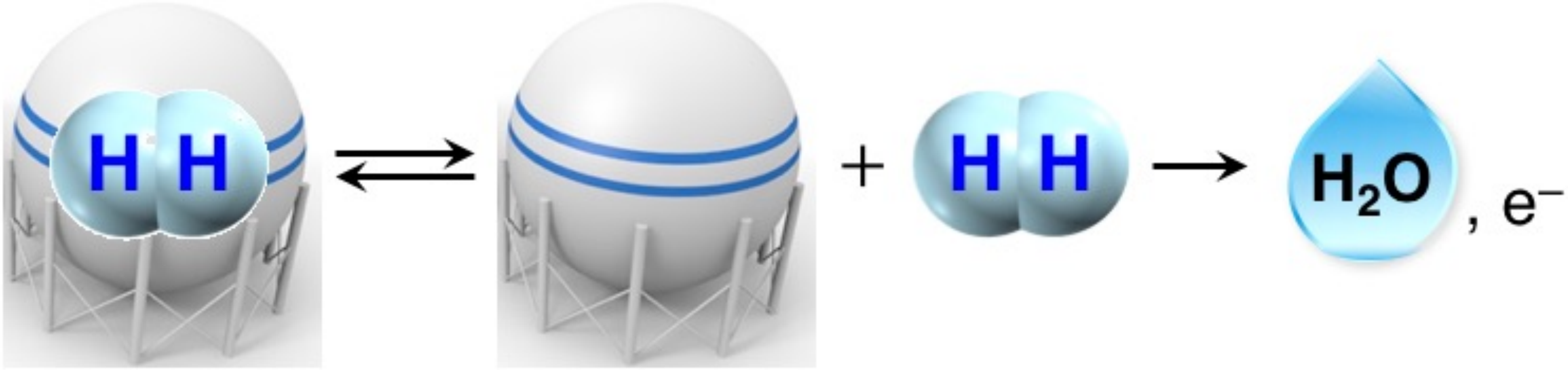
1. T. Ito, T. Matsumoto, M. Wakizaka, H.-C. Chang, *Eur. J. Inorg. Chem.*, **2017**, 3498-3507.
2. M. Wakizaka, T. Matsumoto, A. Kobayashi, M. Kato, H.-C. Chang, *Chem. Eur. J.*, **2017**, *23*, 9919-9925.
3. T. Matsumoto, J. Ishii, M. Wakizaka, H.-C. Chang, *Chem. Lett.*, **2017**, *46*, 232-235.
4. M. Wakizaka, T. Matsumoto, R. Tanaka, H.-C. Chang, *Nat. Commun.*, **2016**, *7*, 12333.
5. M. Wakizaka, T. Matsumoto, A. Kobayashi, M. Kato, H.-C. Chang, *Dalton. Trans.*, **2015**, *44*, 14304-14314.
6. T. Matsumoto, H. Yano, H.-C. Chang, and M. Kato, *et. al.*, *Bull. Chem. Soc. Jpn.*, **2015**, *88*, 74-83.
7. T. Matsumoto, M. Wakizaka, H.-C. Chang, and M. Kato, *et. al.*, *J. Am. Chem. Soc.*, **2013**, *135*, 8646-8654.
8. T. Matsumoto, M. Wakizaka, H.-C. Chang, and M. Kato, *et. al.*, *Dalton Trans.*, **2012**, *41*, 8303-8315.
9. T. Matsumoto, H.-C. Chang, and M. Kato, et. al., *Inorg. Chem.*, **2011**, *50*, 2859-2869.

Catalyst design based on H^+/e^- pooling ligand

Hydrogen Society

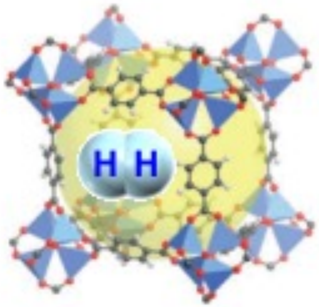


http://ok63.exblog.jp/15970997



Hydrogen Storage Materials

Metal-organic Framework



O. M. Yaghi

Metal Hydride

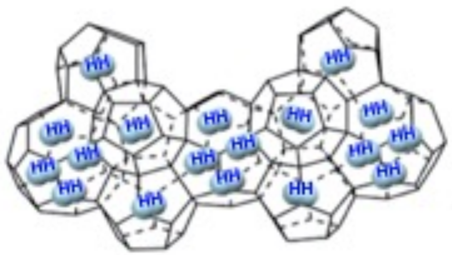
MgH_2

$LiAlH_4$

$LaNi_5H_6$

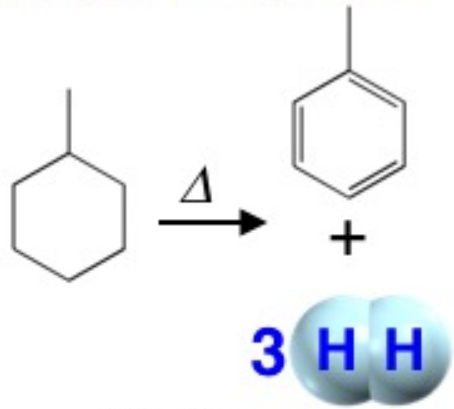
Sakintuna B.

Clathlate



Y.-T. Seo

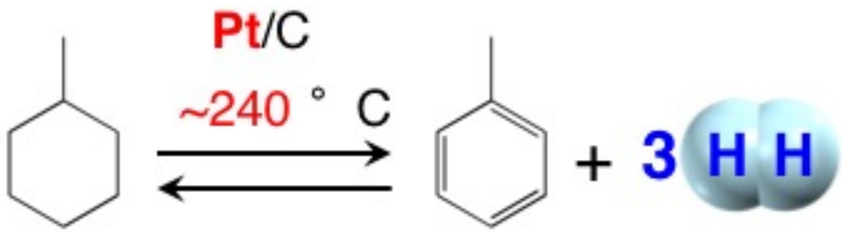
Organic Hydride



M. Ichikawa

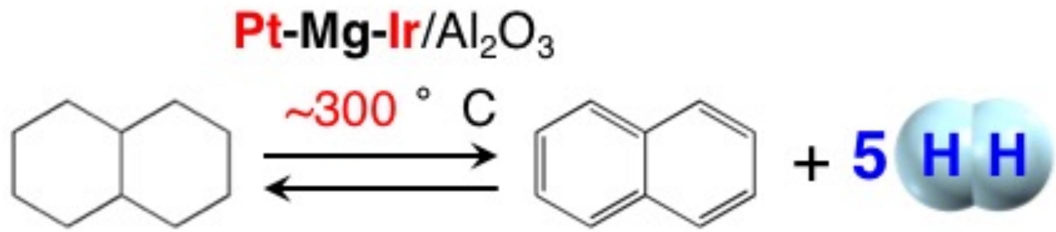
Development of new hydrogen storage materials is important

Hydrogen Evolution from Organic Hydrides



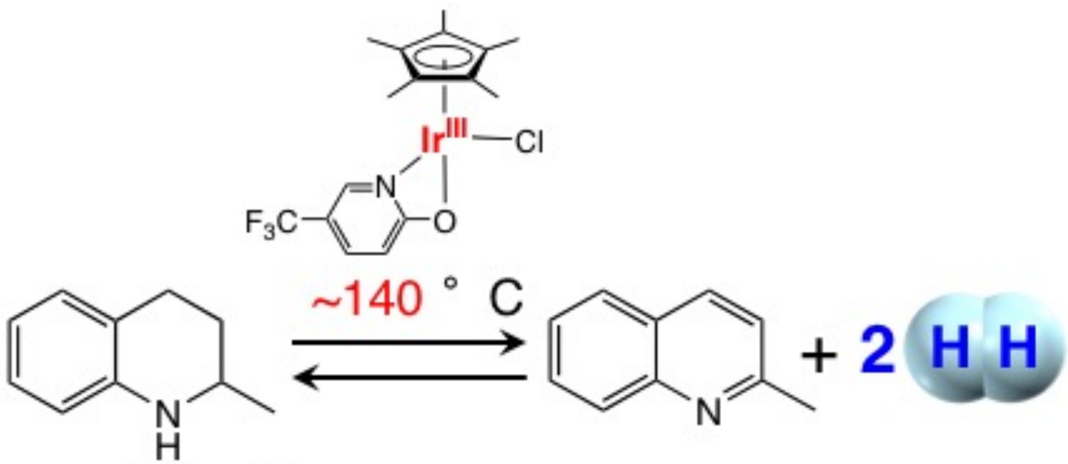
6.2 wt%

S. Hodoshima, *et. al.*, *Energy & Fuels* **2008**, *22*, 2559.



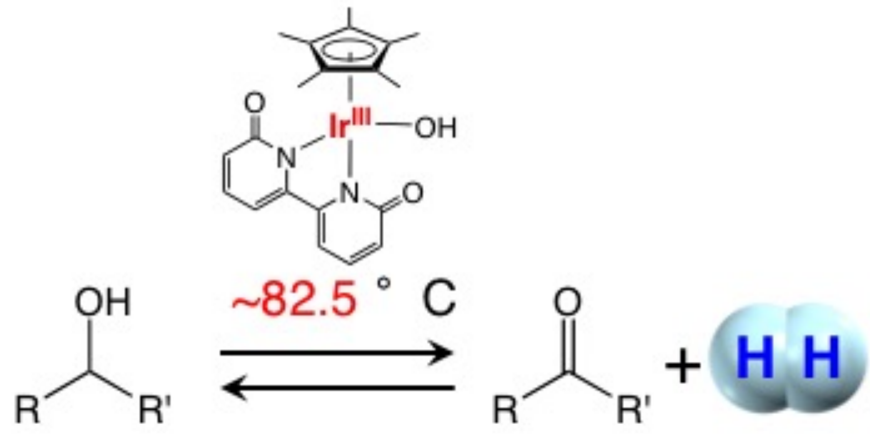
7.3 wt%

C. L. Pieck, *et. al.*, *Appl. Catal. A: General* **2013**, *452*, 48.



2.7 wt%

R. Yamaguchi *et. al.* *J. Am. Chem. Soc.* **2009**, *131*, 8410.



3.4 wt%

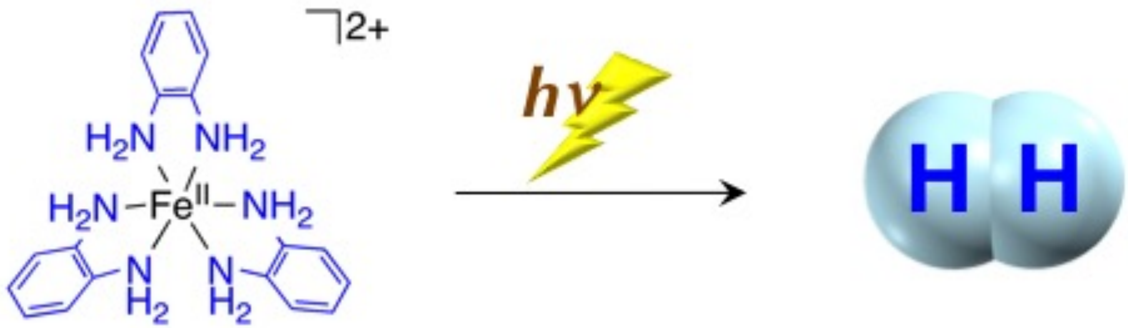
R. Yamaguchi *et. al.* *Angew. Chem. Int. Ed.* **2012**, *51*, 12790.

Precious metal-free system operable under RT is required

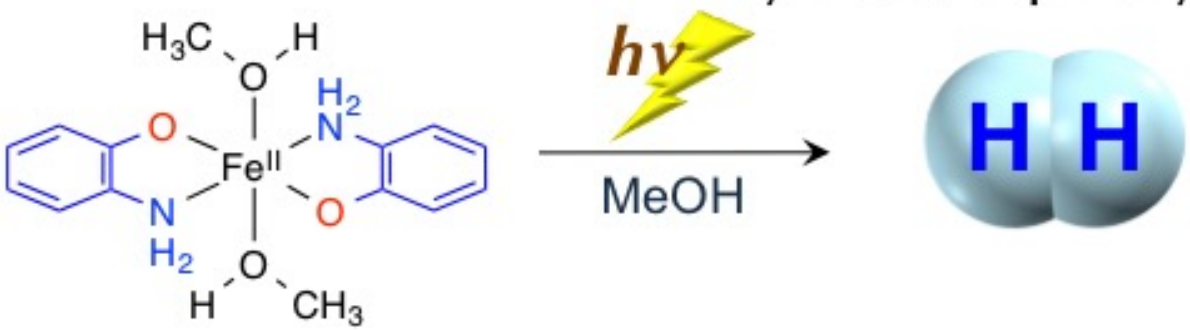
Contents

1. Motivation and targets of this study

2. Photochemical hydrogen evolution
from Fe(II)/*o*-phenylenediamine



3. Photochemical dehydrogenation from anhydrous MeOH
by Fe(II)/o-phenylenediamine

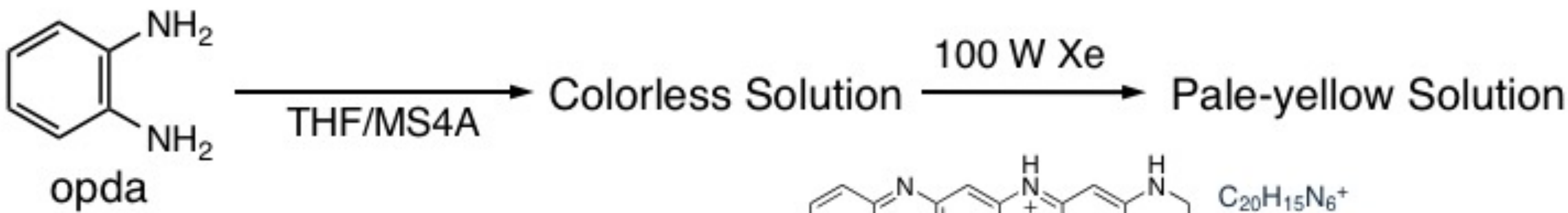


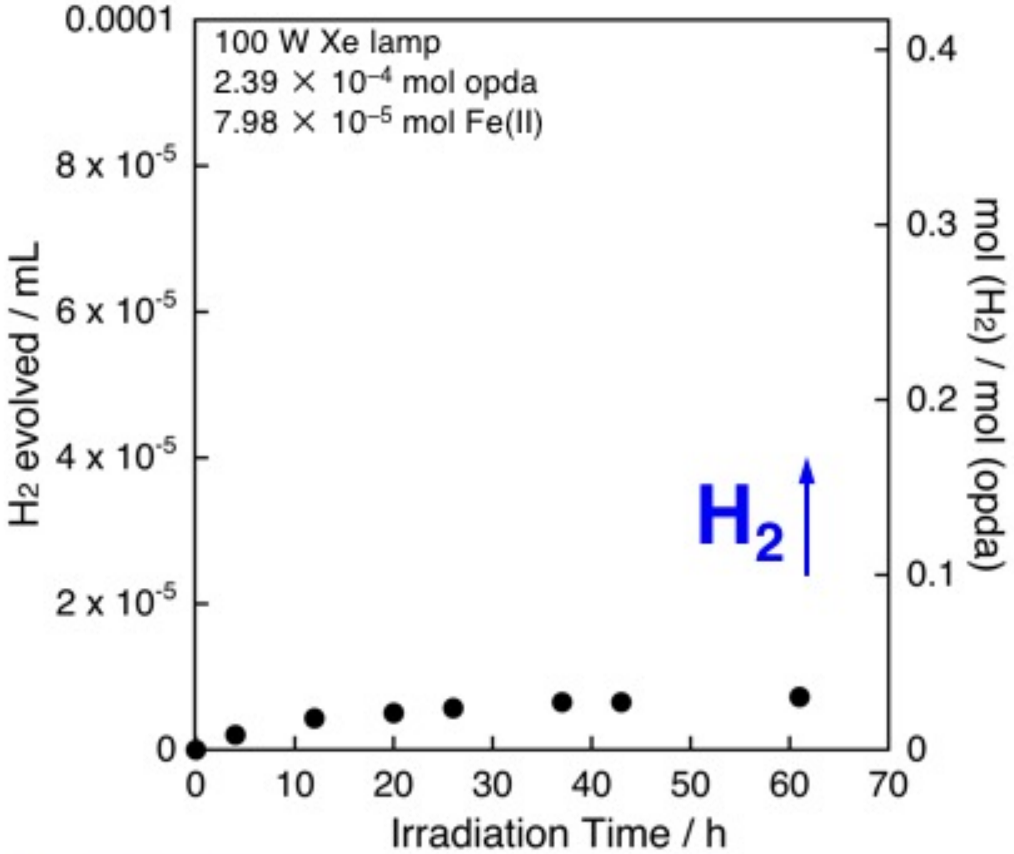
This Work

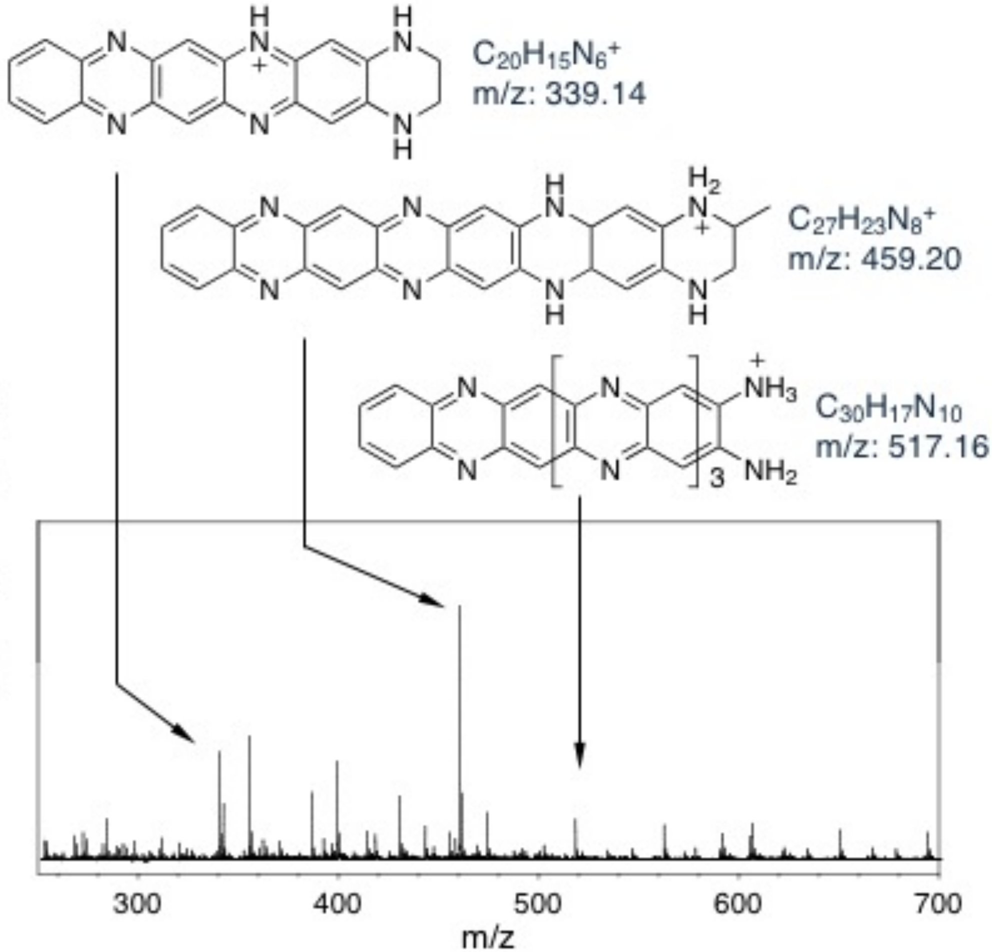
1. Photochemical Reactivity
2. Characterization of Key Species
3. Reaction Mechanism

Photochemical reaction of Fe(II)/opda system

Photochemical Reaction of o-Phenylenediamine (opda)

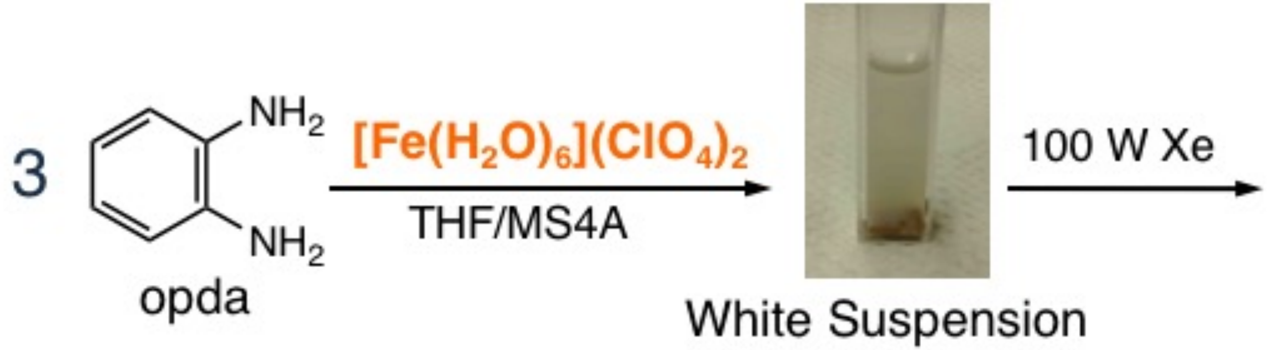


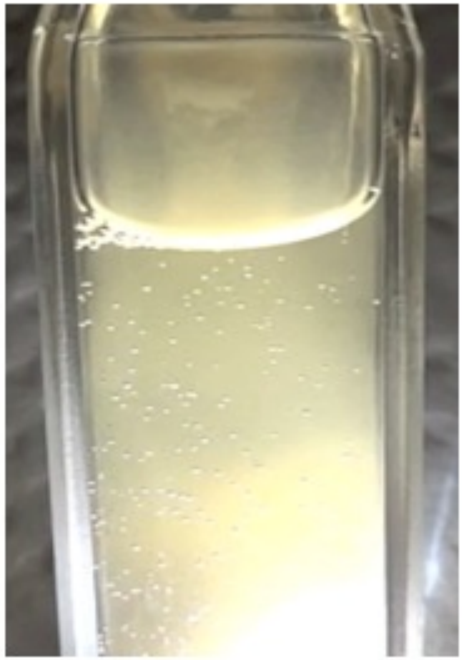


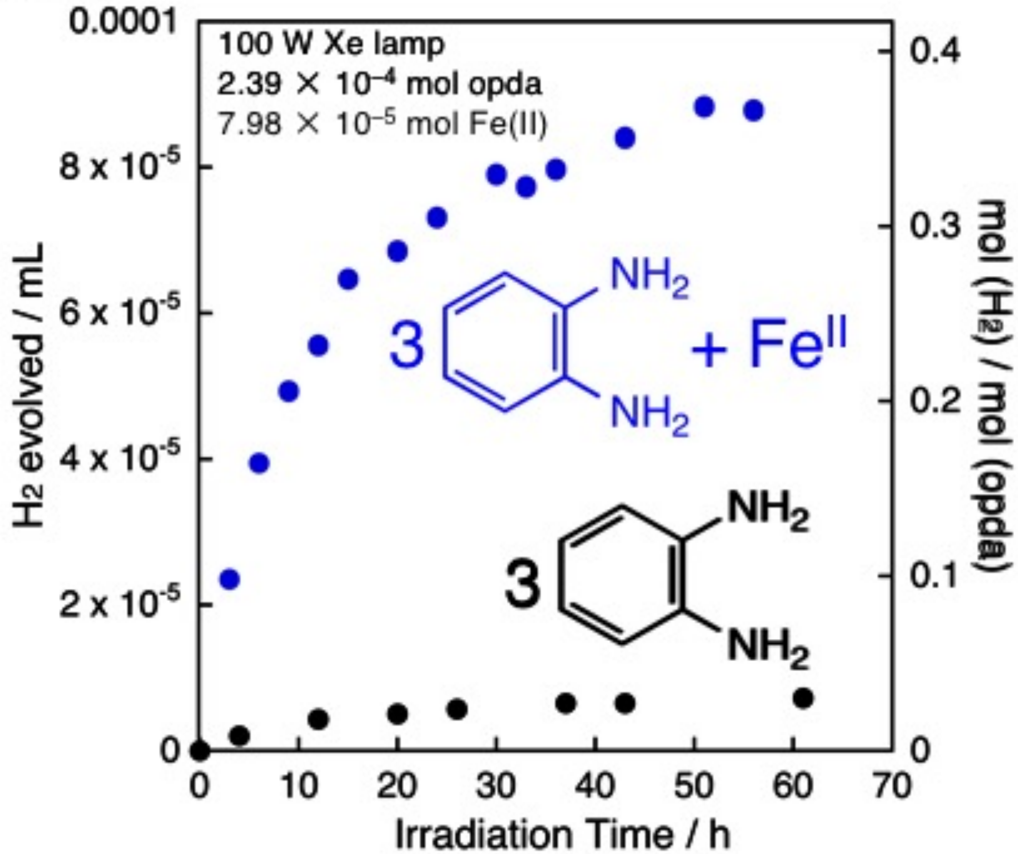


Oxidative oligomerization occurred during photoirradiation

J. Am. Chem. Soc., **2013**, *135*, 8646



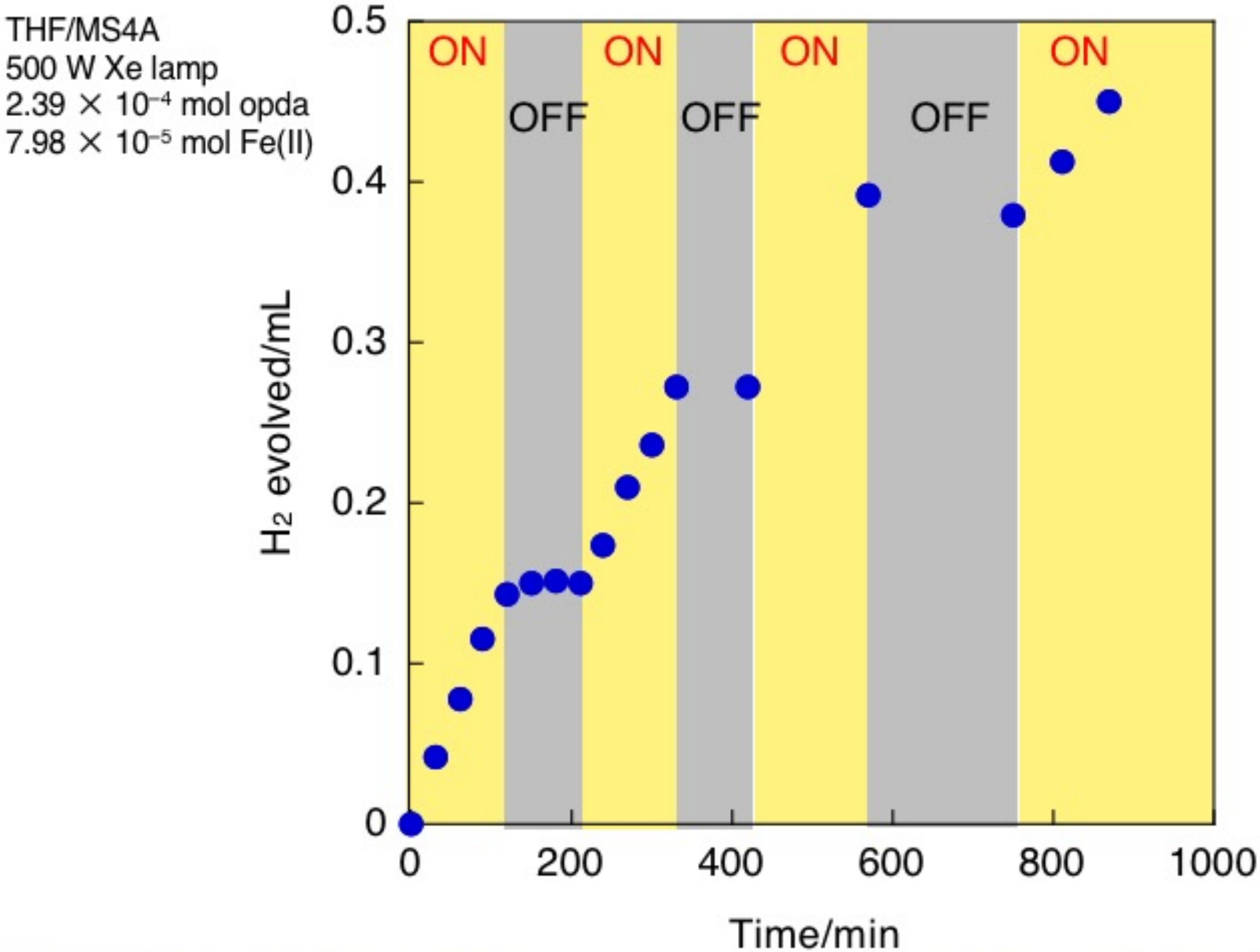




Remarkable enhancement of evolved hydrogen

The Effect of Light

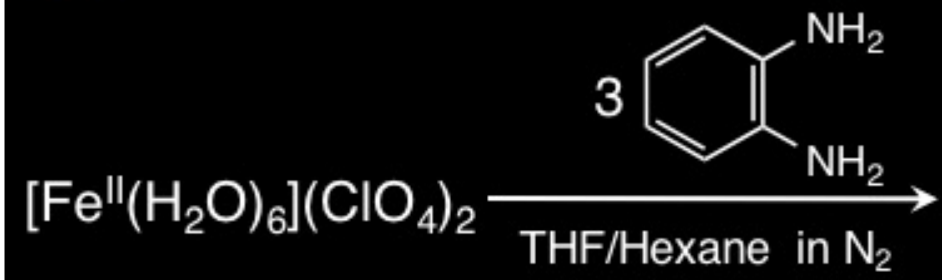
J. Am. Chem. Soc., **2013**, *135*, 8646



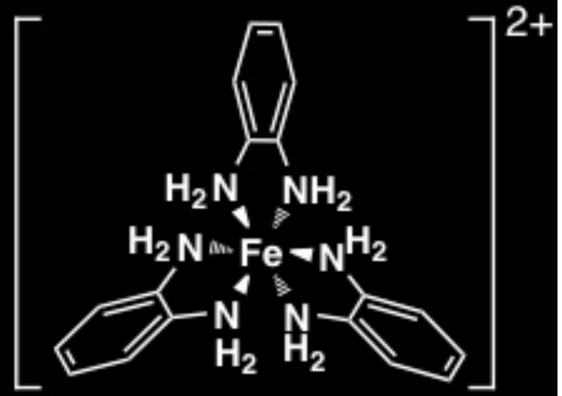
Light-driven hydrogen evolution

Crystal Structure of a Key Species

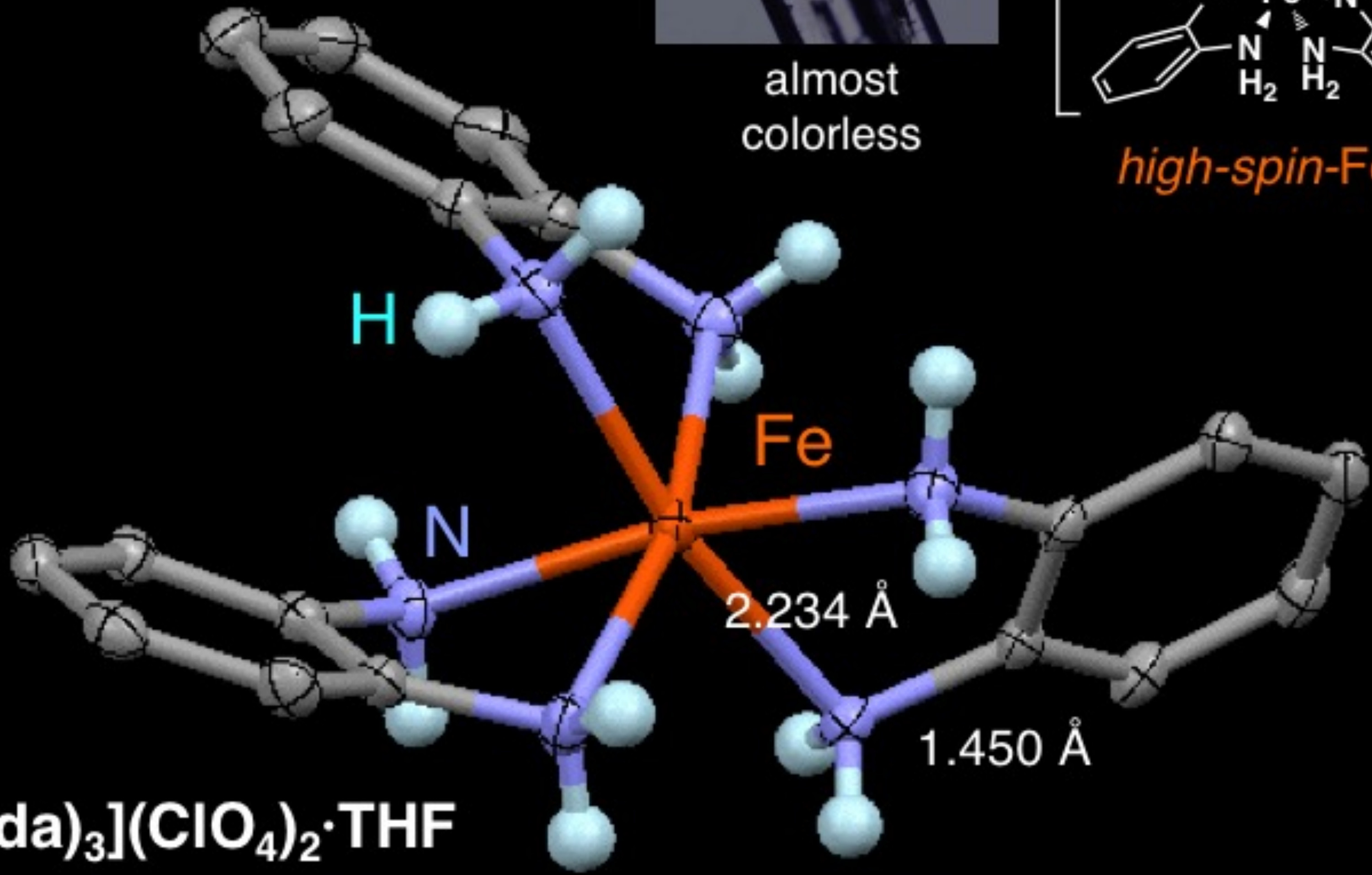
J. Am. Chem. Soc., **2013**, *135*, 8646



almost colorless



high-spin-Fe(II)

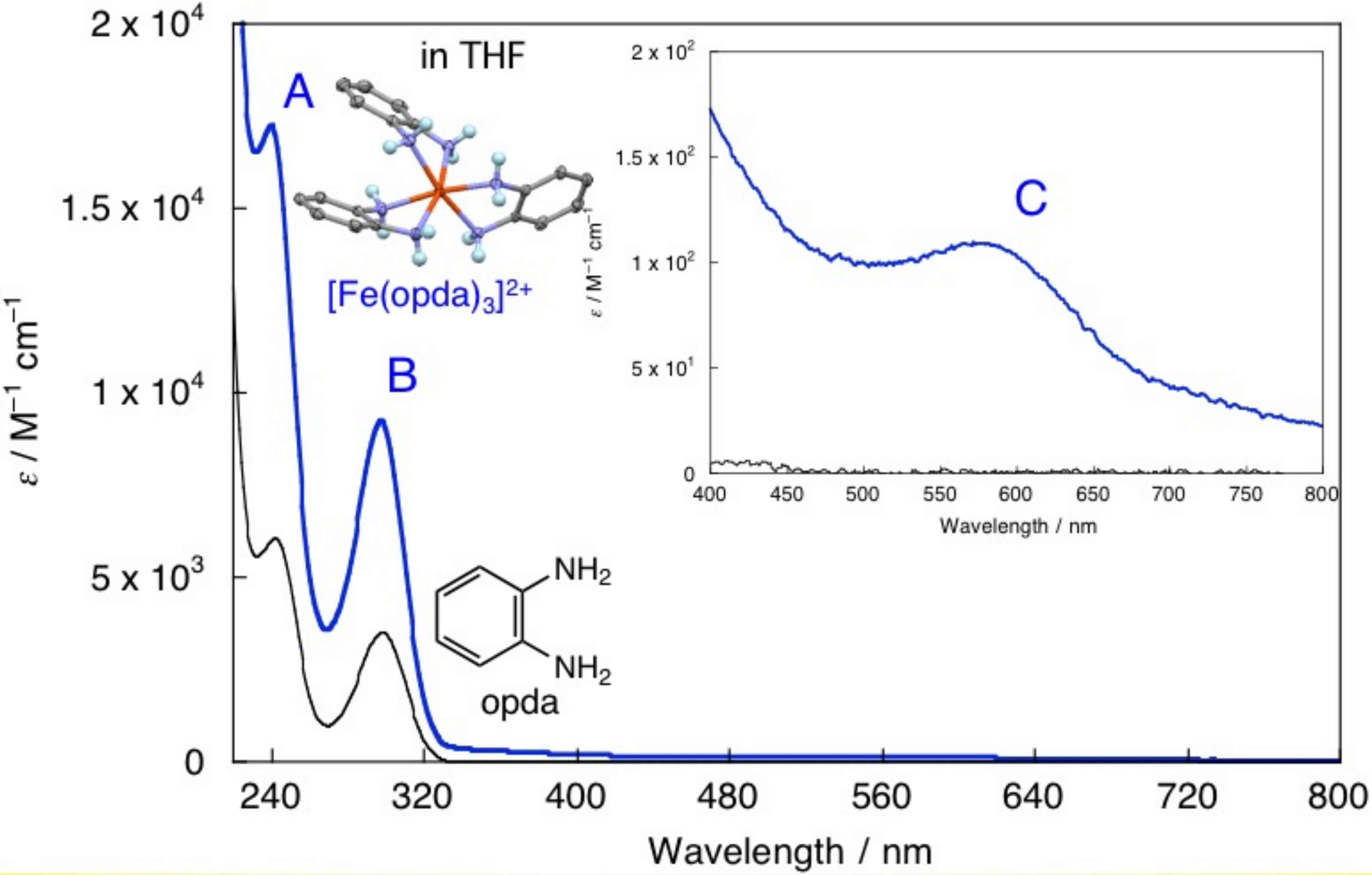


$[Fe^{II}(opda)_3](ClO_4)_2 \cdot THF$

Dicationic Iron(II) tris-ortho-phenylenediamine complex

Absorption of Light

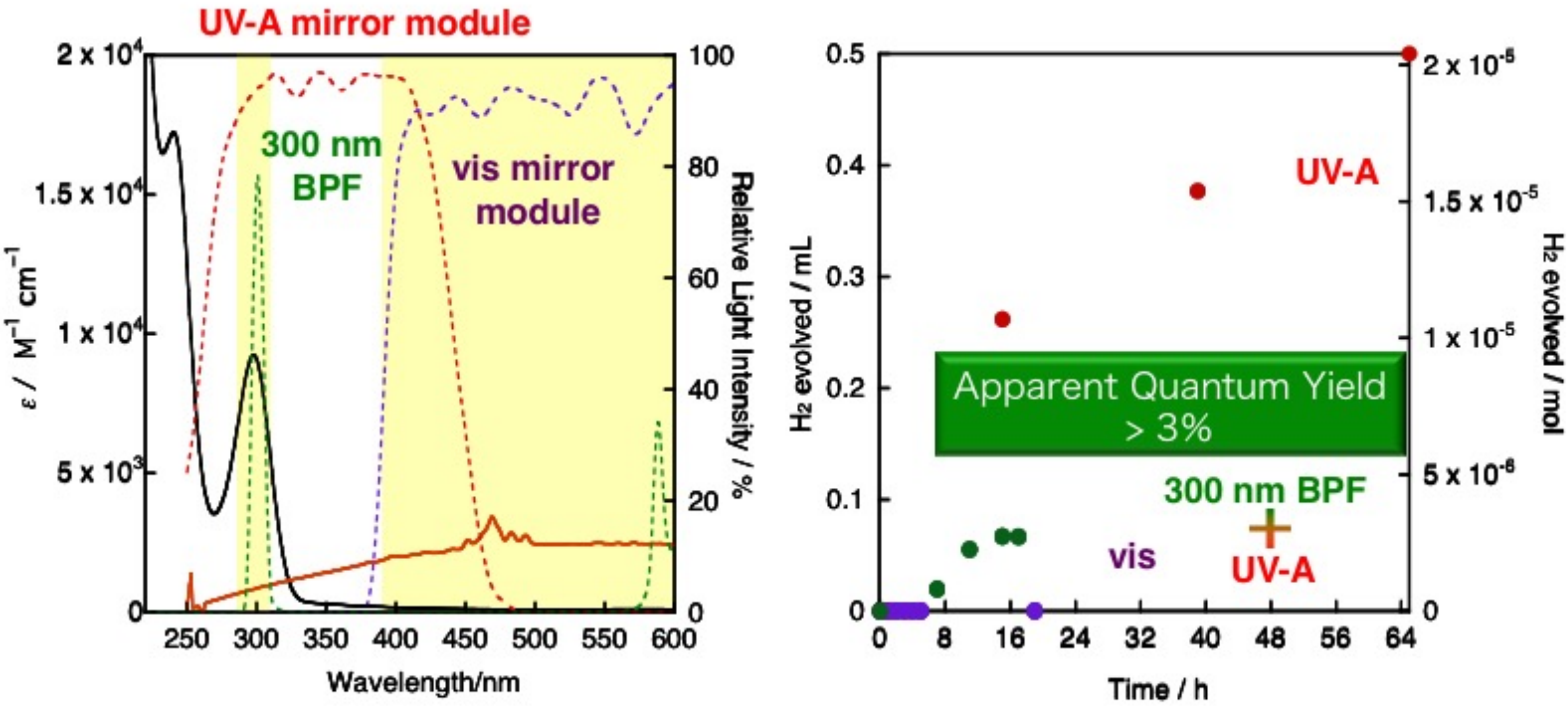
J. Am. Chem. Soc., **2013**, *135*, 8646



Three bands are found in UV and visible region

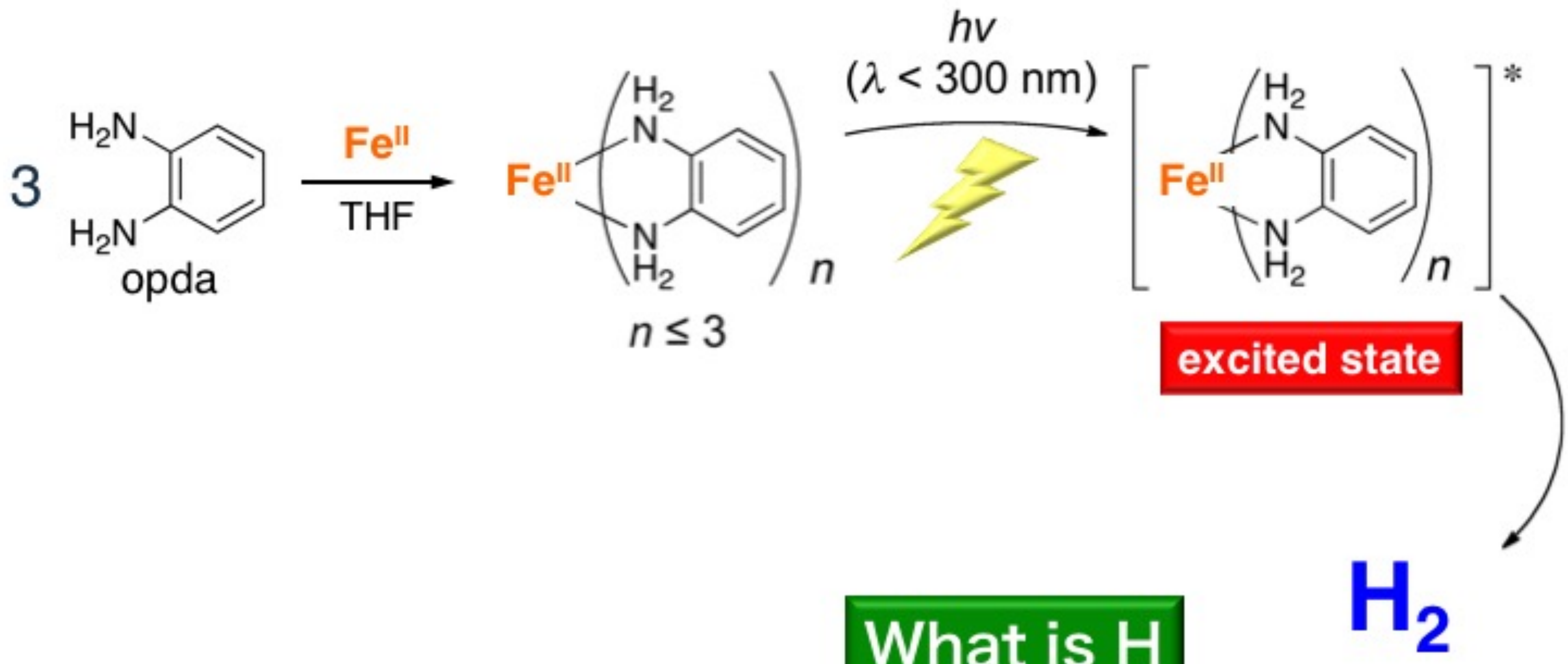
Irradiation Light Dependence in HER

J. Am. Chem. Soc., **2013**, *135*, 8646



The π-π* transition at B band triggers the photochemical HER

Mechanism



What is H source ?

Identification of H source in this photochemical HER

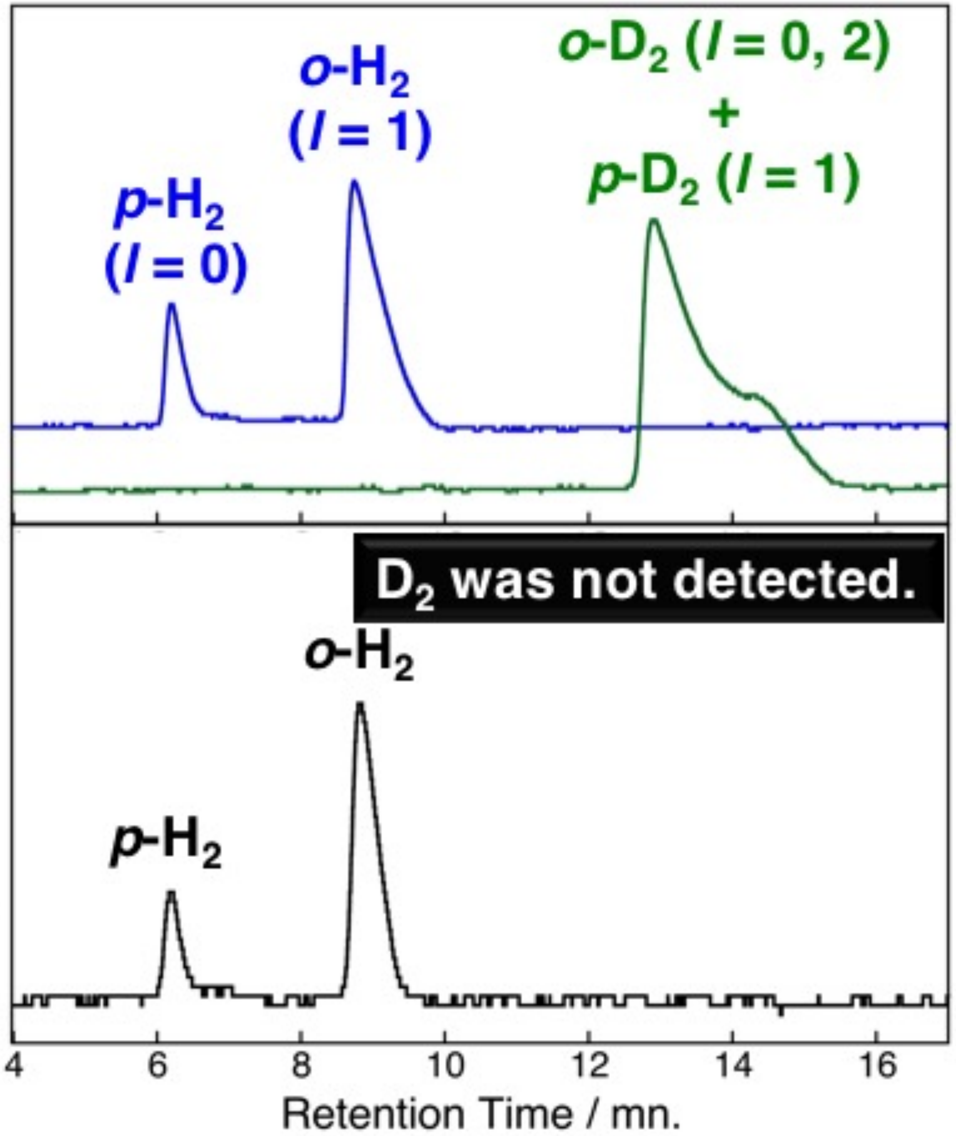
Identification of H Source

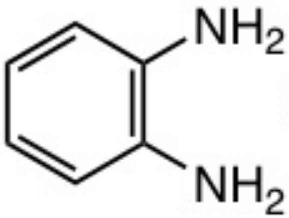
J. Am. Chem. Soc., **2013**, *135*, 8646

Shimadzu GC-2014ATF + GC-Solution
8%(w/w) KOH Activated Armina
77 K/He/TCD

standard 5% H_2

standard 5% D_2



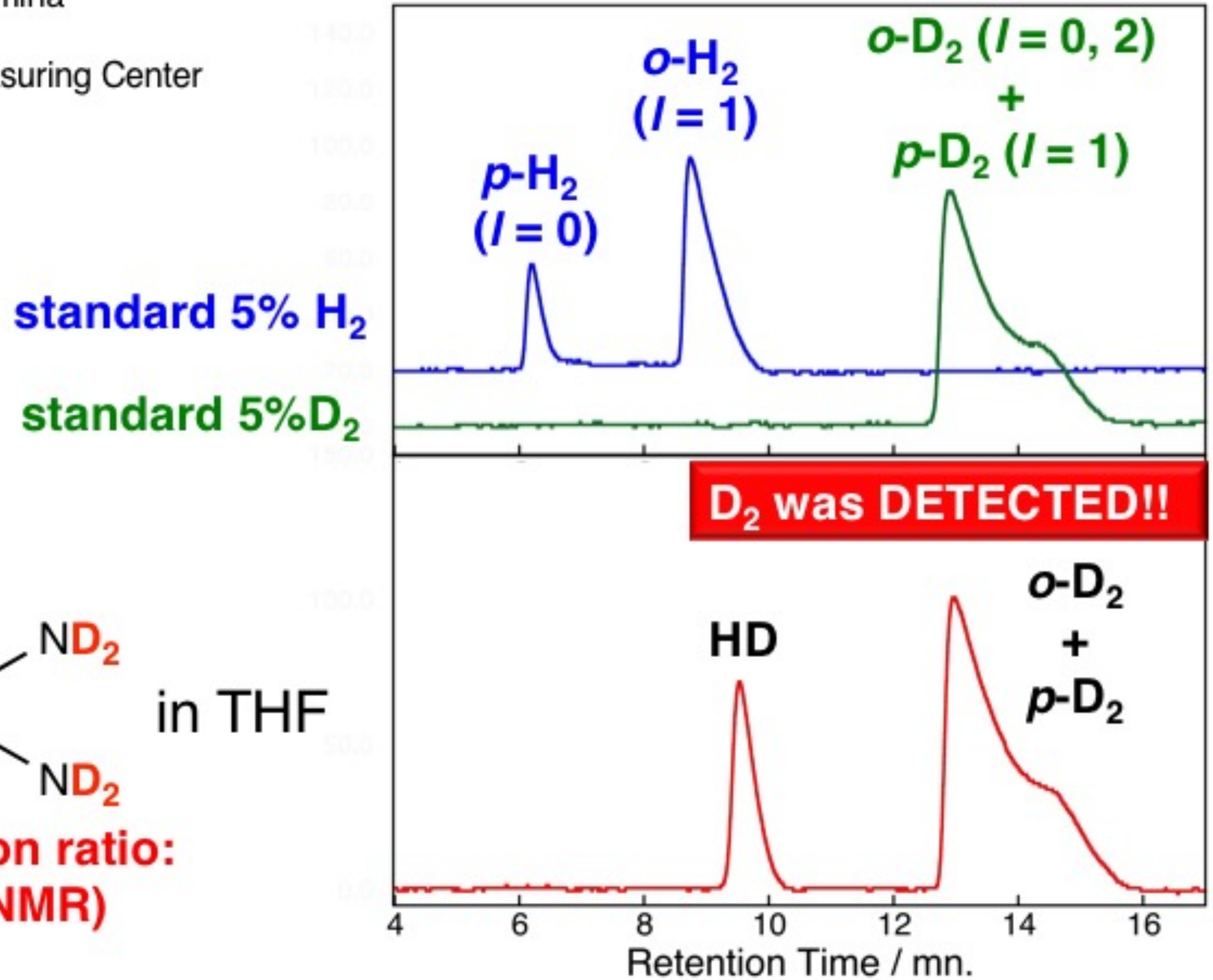
Fe^{II} + 3  in THF-d_8

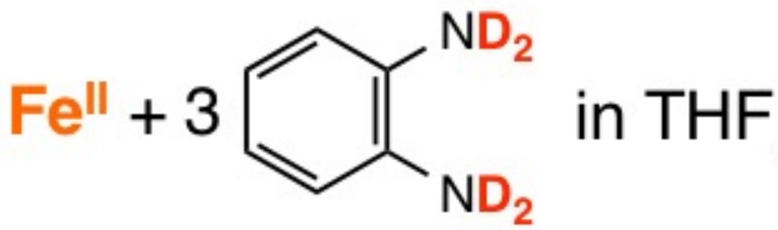
THF is NOT the H source

Identification of H Source

J. Am. Chem. Soc., **2013**, *135*, 8646

Shimadzu GC-2014ATF + GC-Solution
8%(w/w) KOH Activated Armina
77 K/He/TCD
Shimadzu Analytical & Measuring Center
Mr. Koichi Shiomi

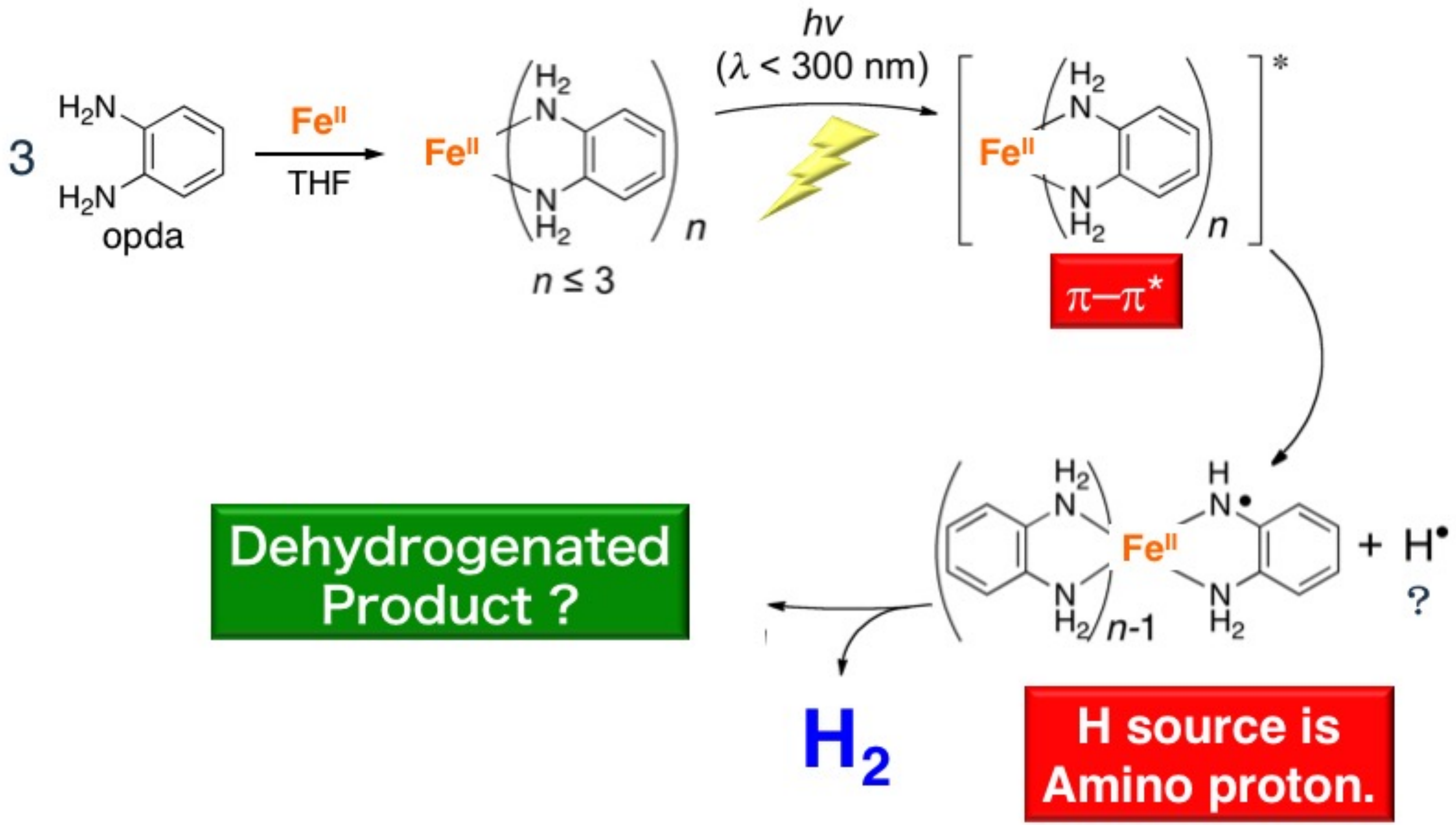




Deuteration ratio:
92 % (NMR)

Amino proton(s) in Opda could be a H source

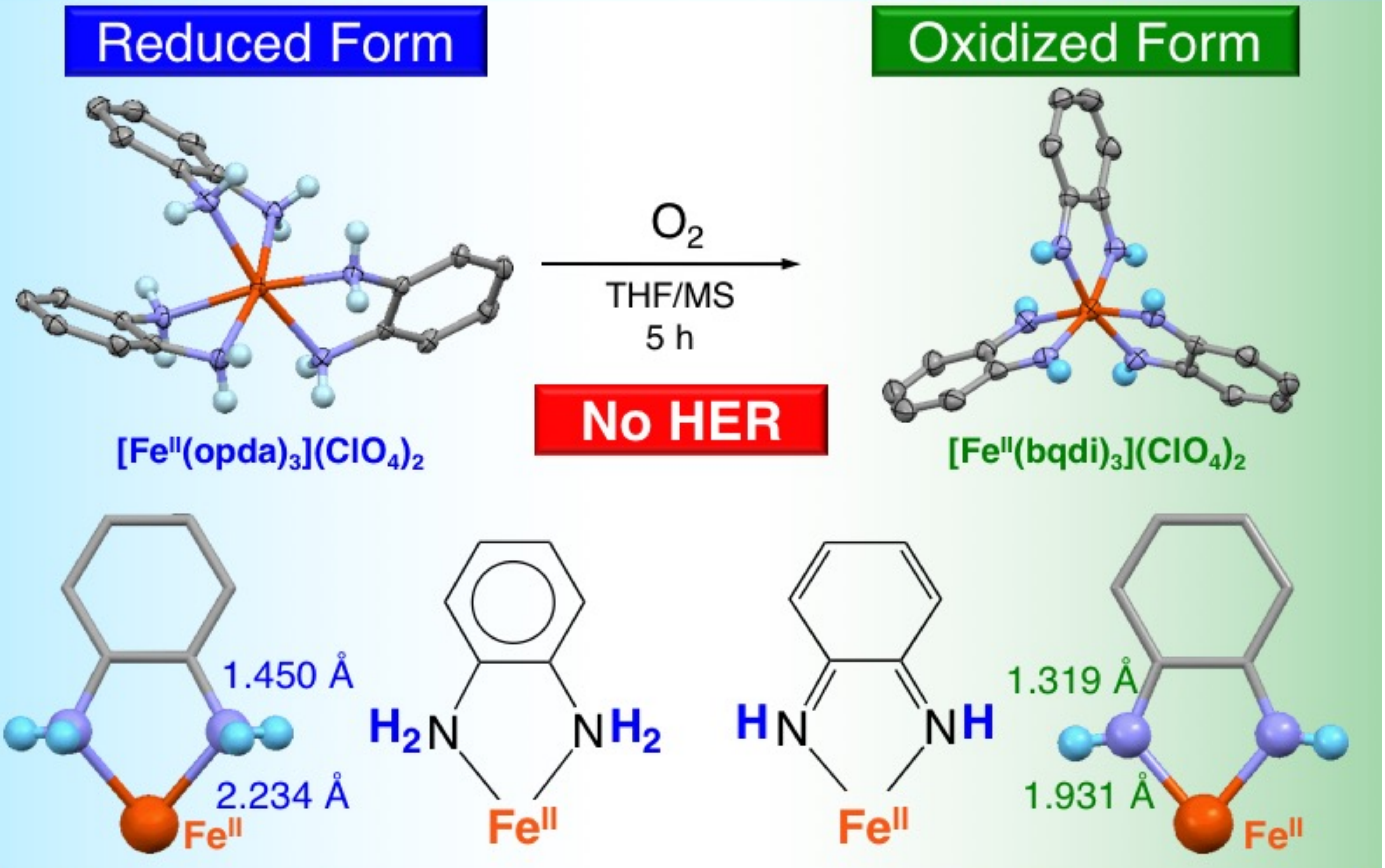
Plausible Reaction Mechanism



Identification of dehydrogenated product after HER

The Structure of Oxidized Form

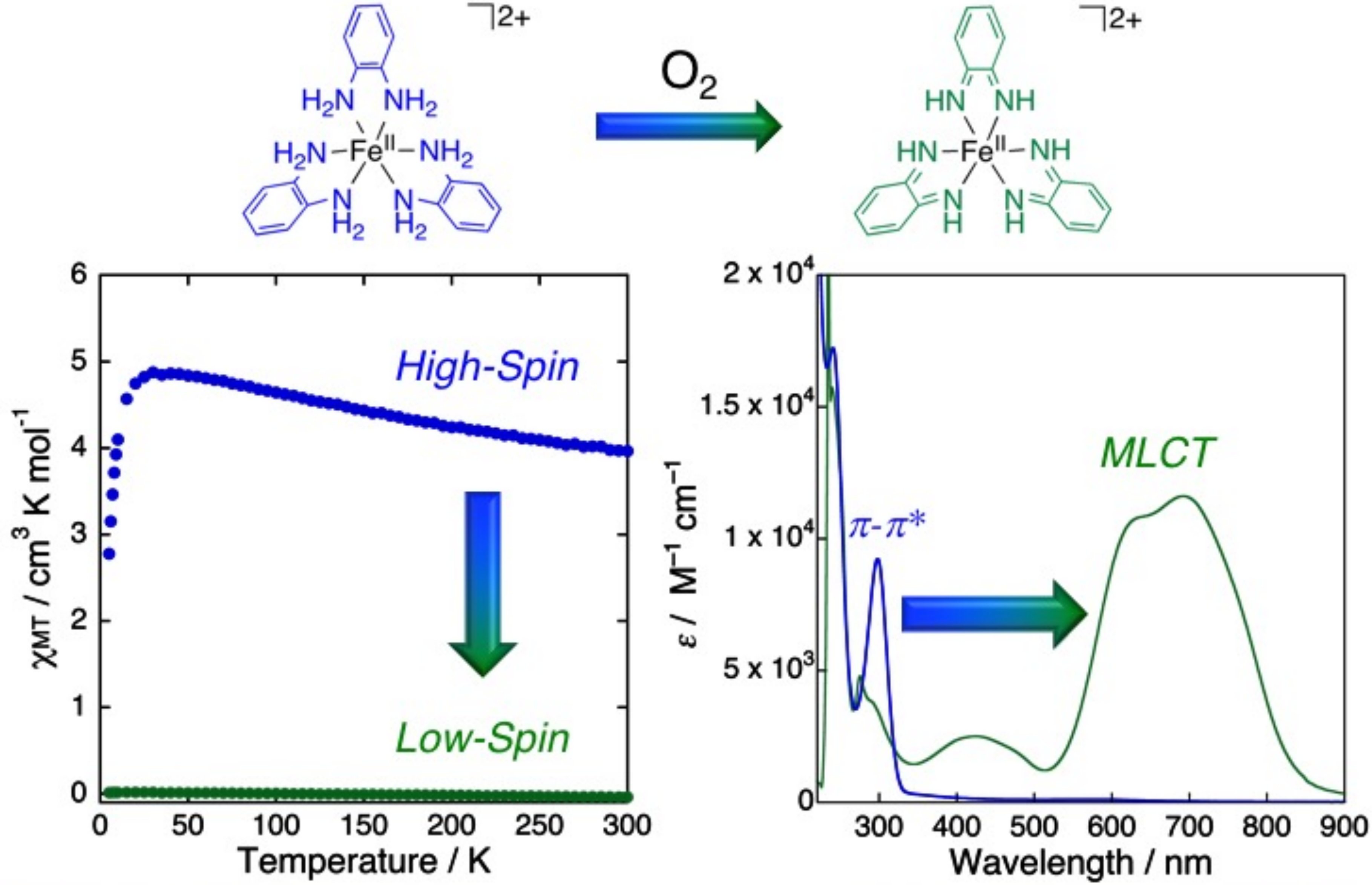
J. Am. Chem. Soc., **2013**, *135*, 8646



$2H^+/2e^-$ transfer from opda ($6H^+/6e^-$ in Total)

Changes in Electronic Properties

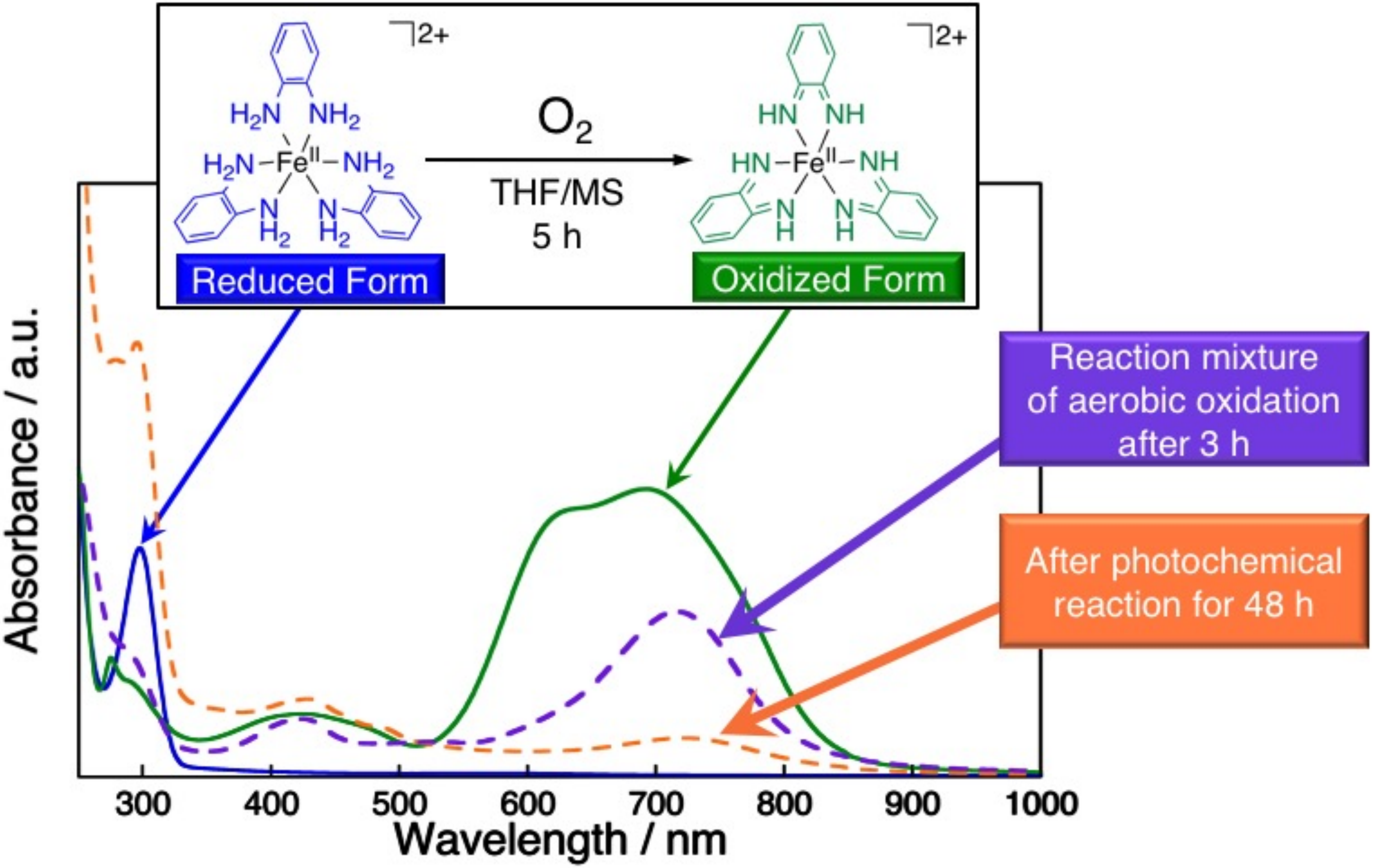
J. Am. Chem. Soc., **2013**, *135*, 8646



Changes in magnetic and optical Properties by $6H^+/6e^-$ transfer

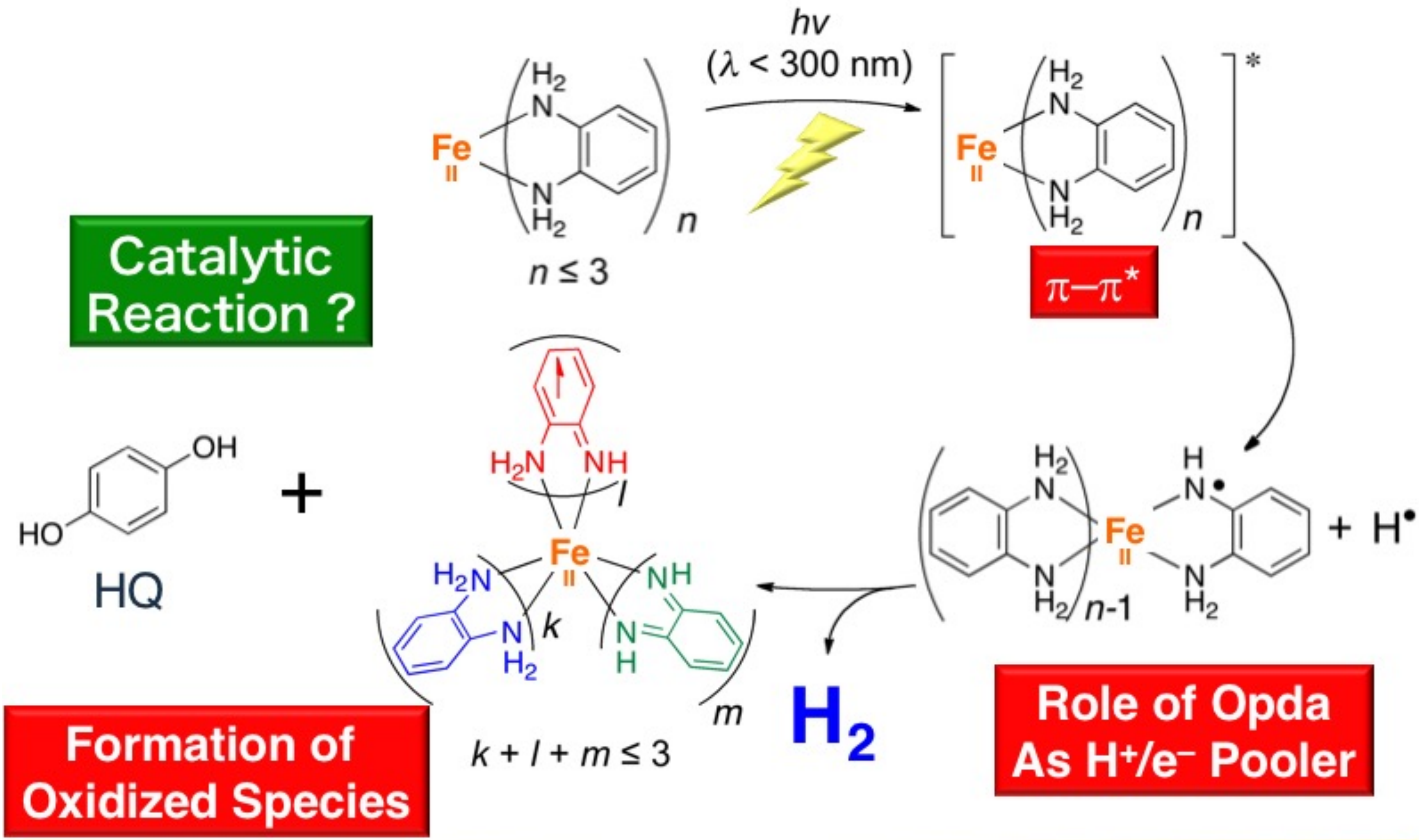
UV-vis Spectrum of HER Product

J. Am. Chem. Soc., **2013**, *135*, 8646



Formation of partially oxidized species

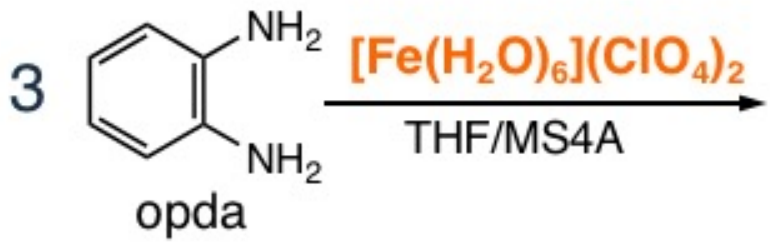
Towards Catalytic Cycle

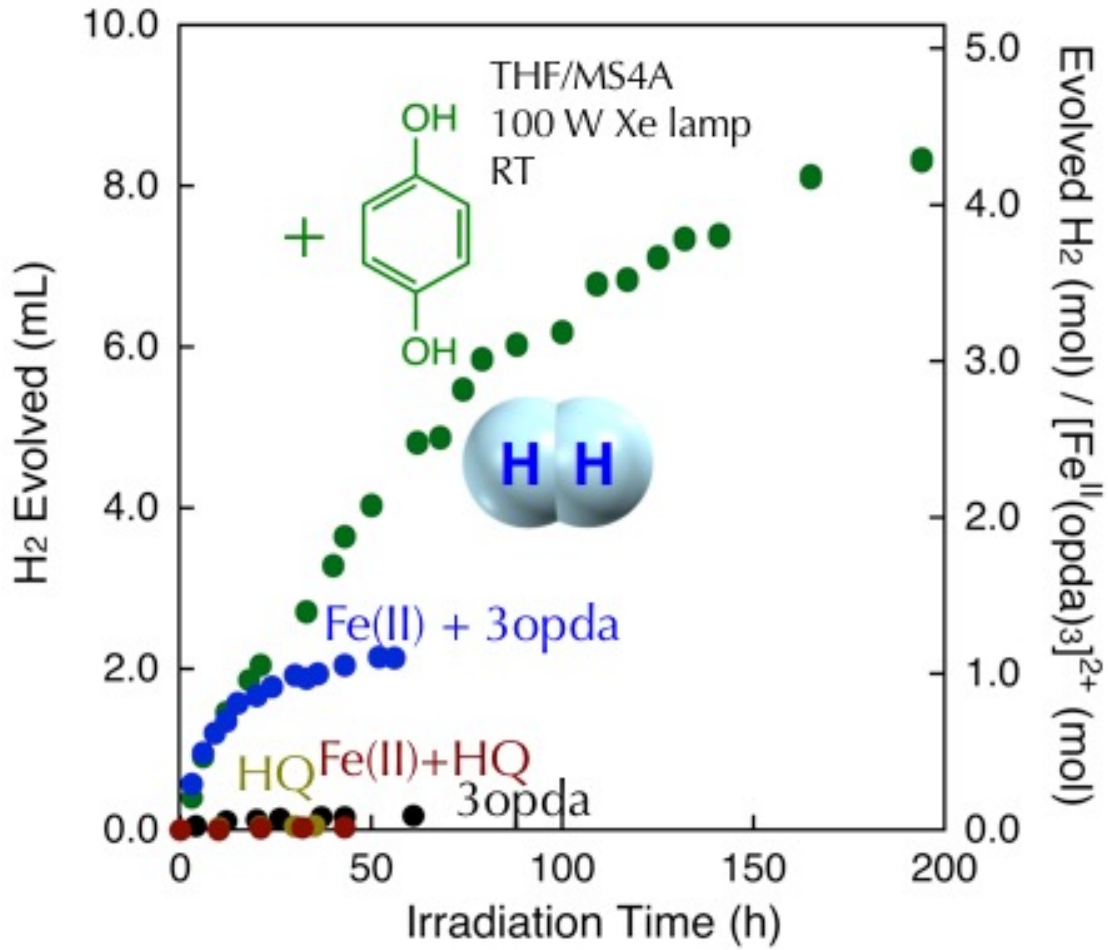


Introduction of HQ as H^+/e^- donor

The Effect of HQ

J. Am. Chem. Soc., **2013**, *135*, 8646





Photochemical hydrogen evolution from the Fe(II)/opda mixture

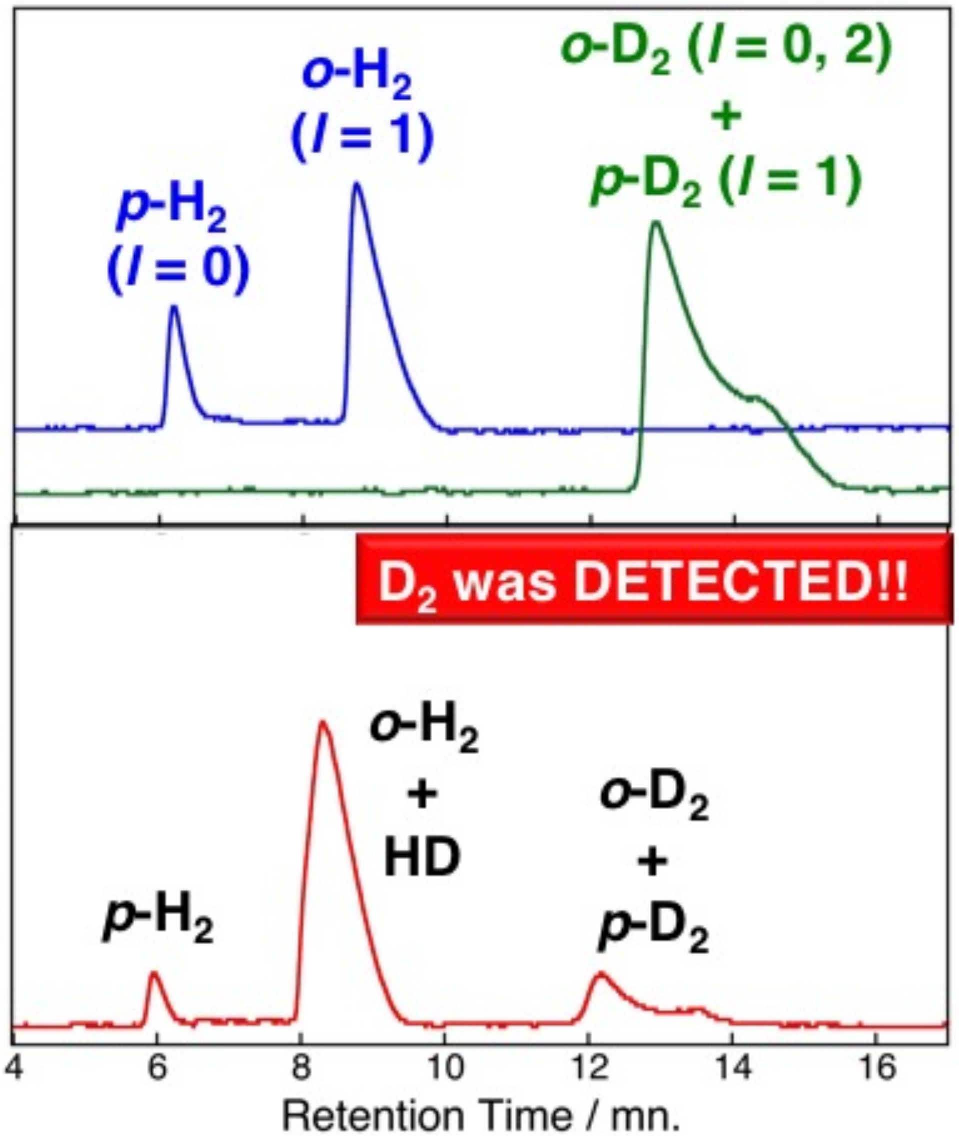
Identification of H Source

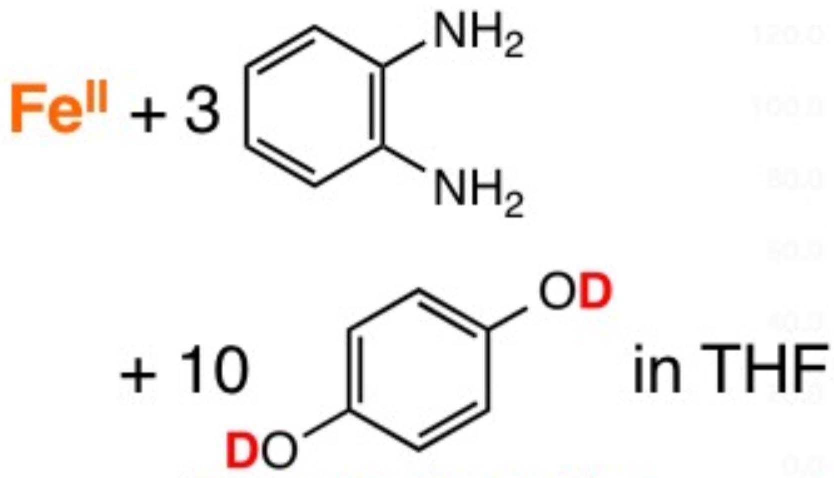
J. Am. Chem. Soc., **2013**, *135*, 8646

Shimadzu GC-2014ATF + GC-Solution
8%(w/w) KOH Activated Armina
77 K/He/TCD
Shimadzu Analytical & Measuring Center
Mr. Koichi Shiomi

standard 5% H_2

standard 5%D_2



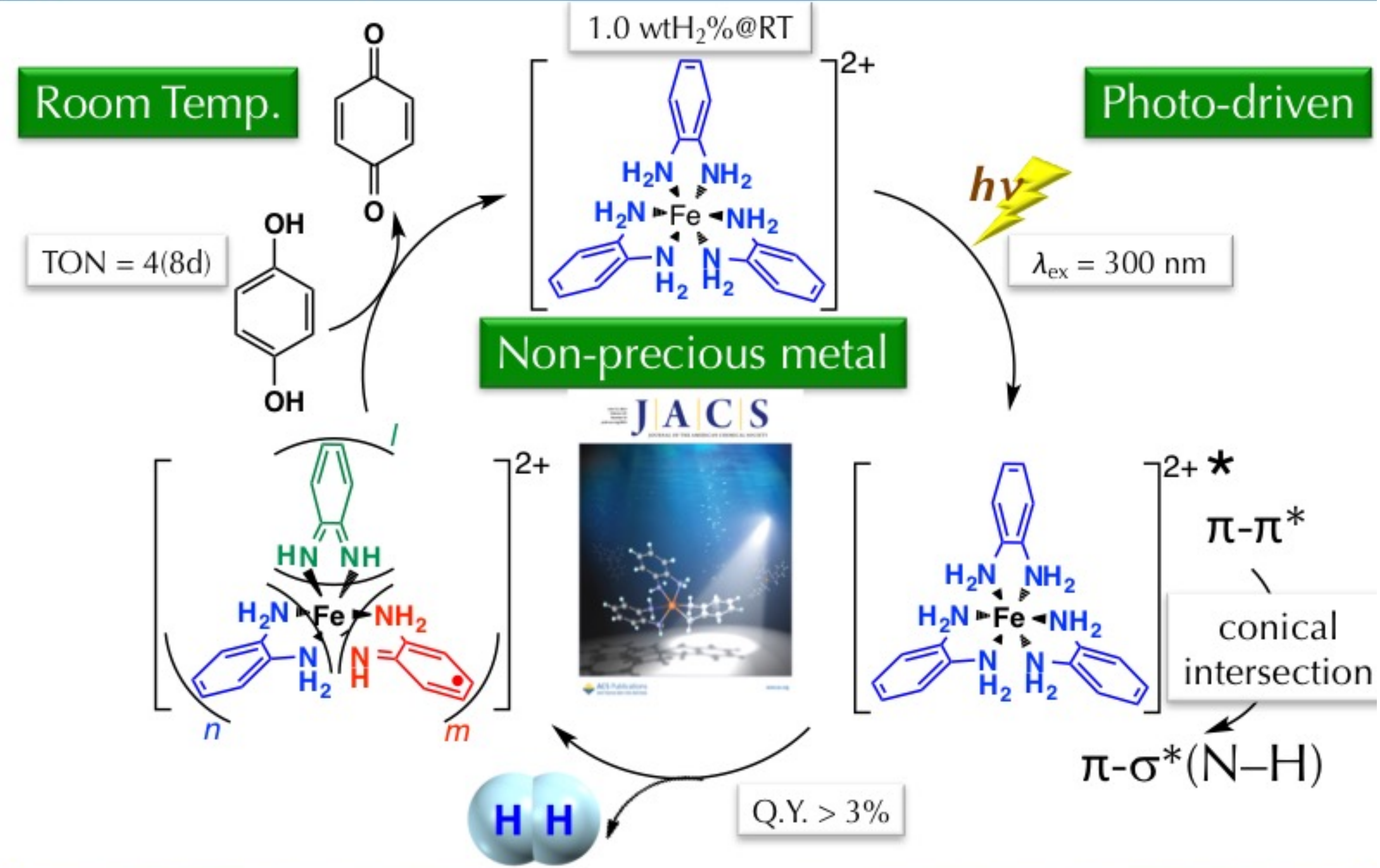


Deuteration ratio: 85 % (NMR)

Hydroxyl proton would be H source of evolved H_2

The First Report

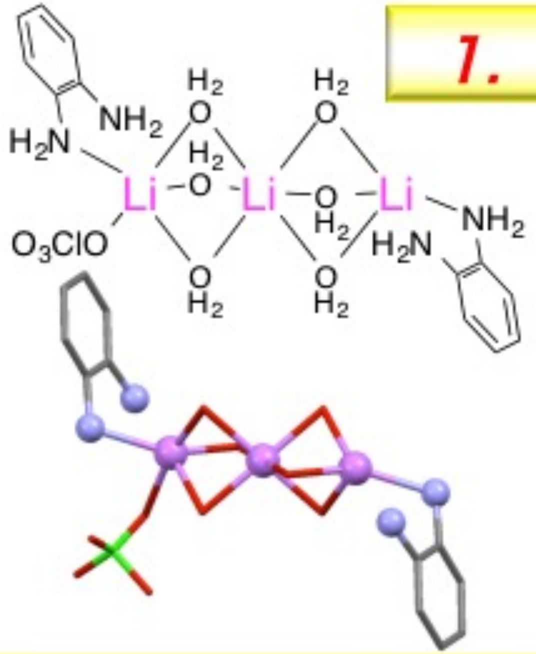
J. Am. Chem. Soc., **2013**, *135*, 8646

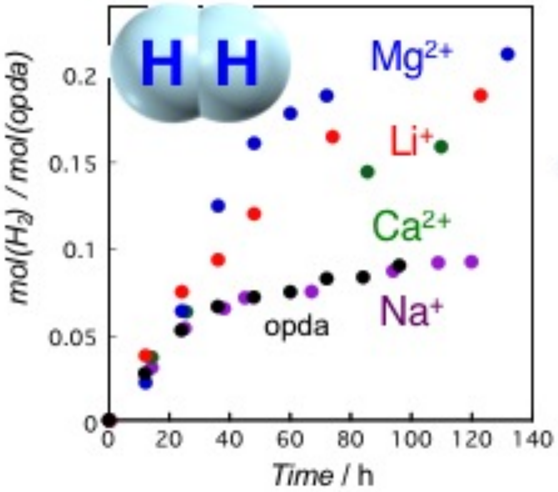


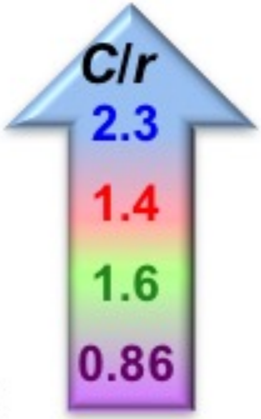
Photochemical HER utilizing Ligand as H^+/e^- pooler

軽金属/フェニレンジアミン錯体の光水素活性特性

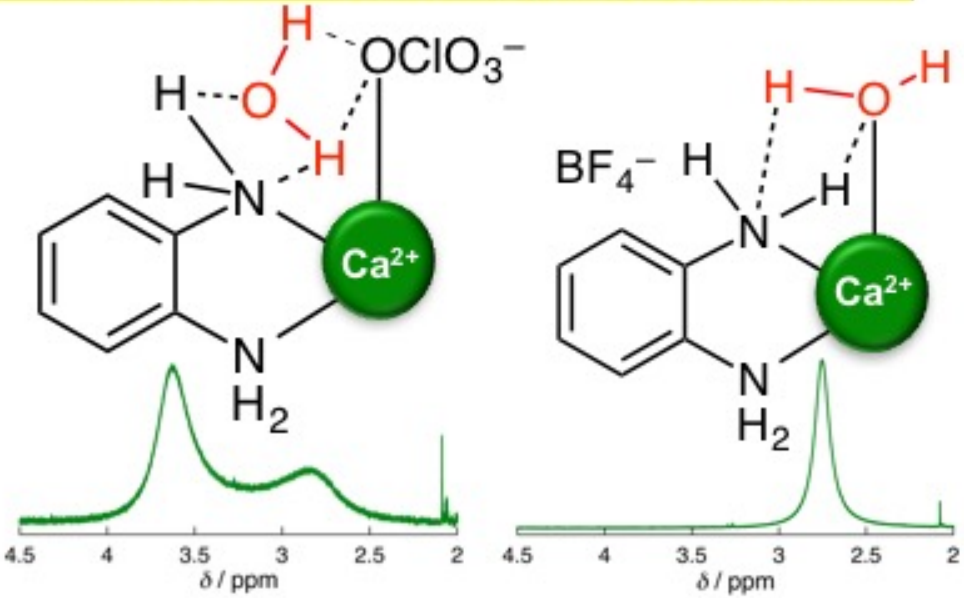
1.　金属種の分極能に相関し水素発生



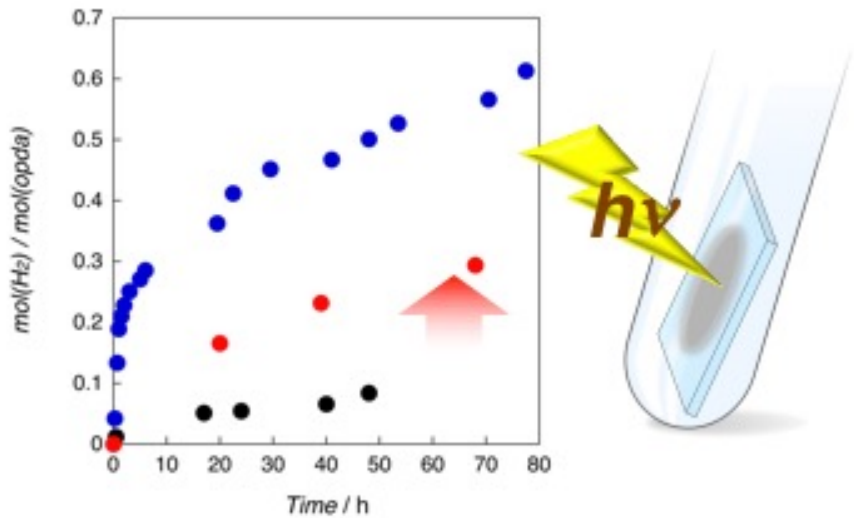




2.対アニオンに依存した環境



3.固相状態における光水素発生



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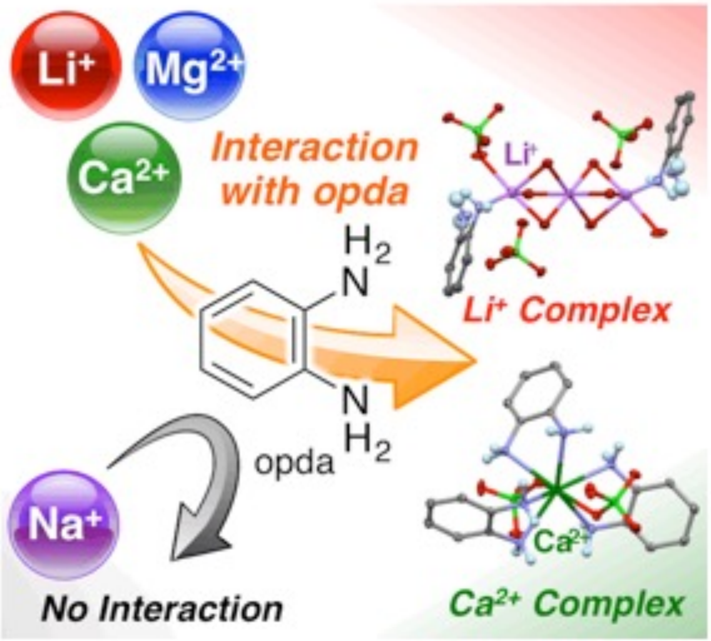
平成２６年度公益財団法人日本板硝子材料工学助成会研究助成

軽金属/芳香族ジアミンからなる
ハイブリッド型水素キャリアの創出

Structural and spectroscopic studies on the interactions of ortho-phenylenediamine and Li^{+}, Na^{+}, Mg^{2+}, or Ca^{2+} ions
Takeshi Matsumoto, Junki Ishii, Masanori Wakizaka, Ho-Chol Chang
Chem. Lett., **2017**, *46*, 232-235.



将来展望

光駆動型

空間・エネルギー選択性

室温駆動　制御性

非平衡性

ユビキタス元素

Fe^{2+}　Ca^{2+}　C　N　H

短所補完　**既存キャリアの光活性化**　用途拡大

光駆動型　**新規MπA水素キャリアの開発**　非貴金属

水素社会実現に資する新技術及び新規材料を提供

将来展望

熱源フリーキャリア

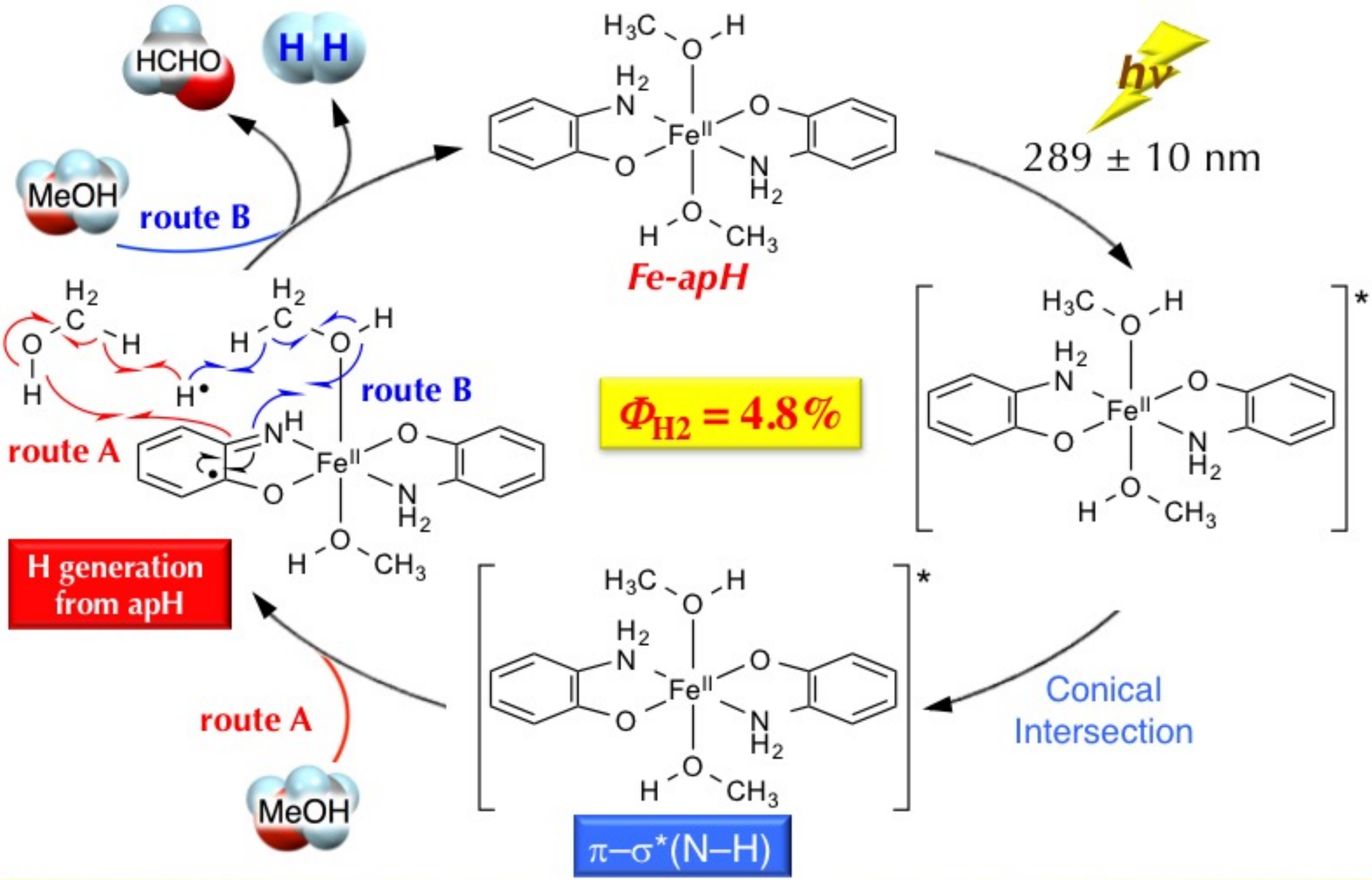
光電池・電極触媒

光酸化還元触媒

従来材料が持ち合わせないポテンシャル

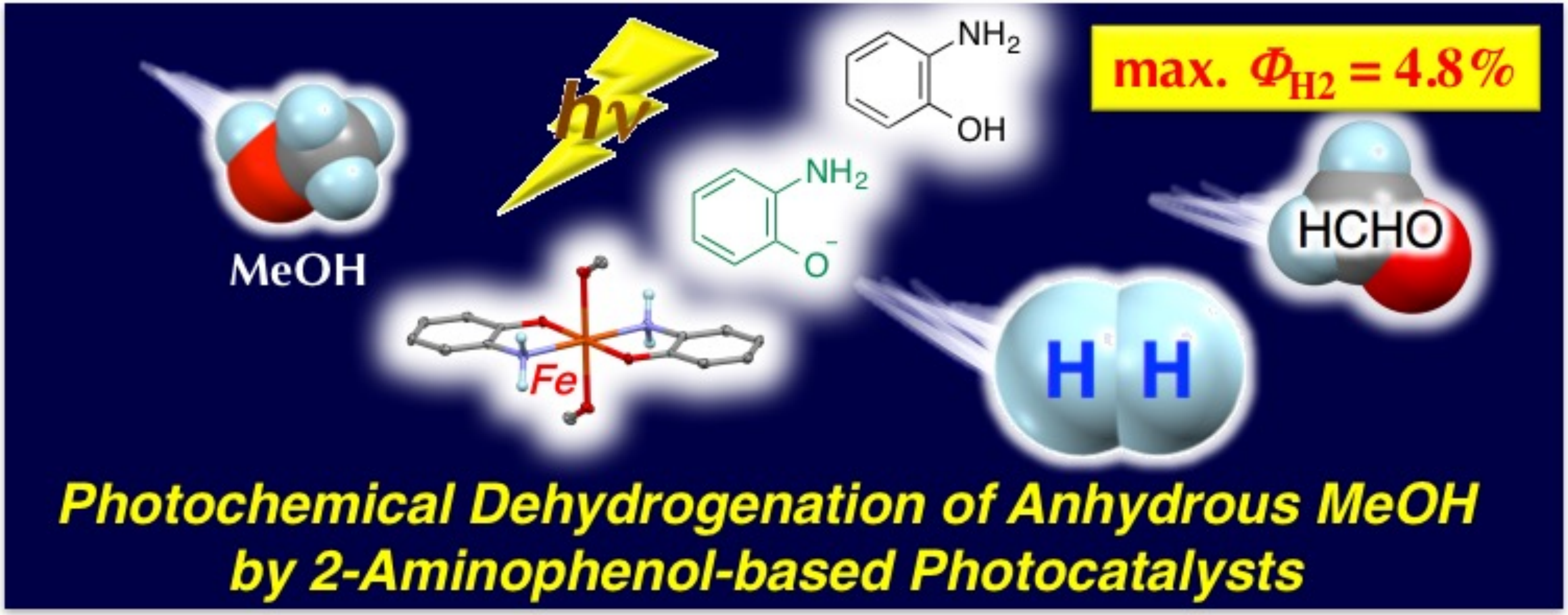
A Plausible Mechanism

Nat. Commun. **2016**, *7*, 12333.



H radical generation from apH ligand in the Fe Complex

Photochemical Dehydrogenation of Anhydrous MeOH



1. *Photochemical hydrogen evolution from MeOH Catalyzed by 2-Aminophenol-based Photocatalysts at Room Temperature*
2. *H radical generation 2-Aminophenol-based Photocatalysts*

M. Wakizaka, T. Matsumoto, R. Tanaka, H.-C. Chang, *Nat. Commun.* **2016**, *7*, 12333.

PHER from MeOH catalyzed by apH$_2$-based non-precious metal catalyst

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