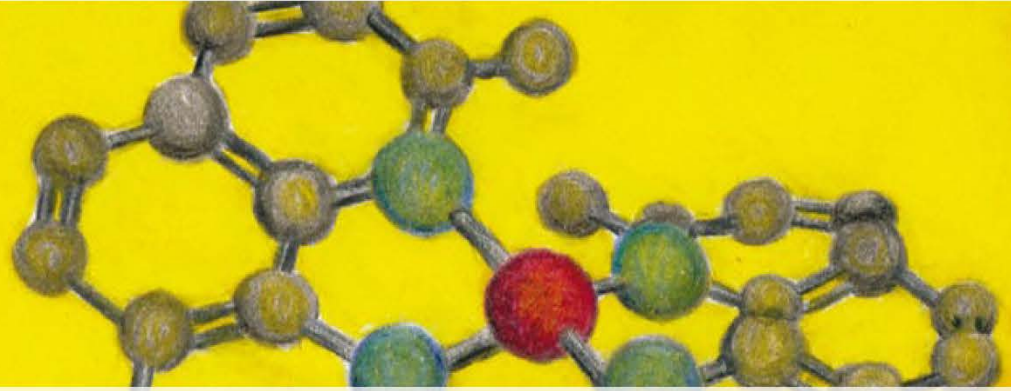
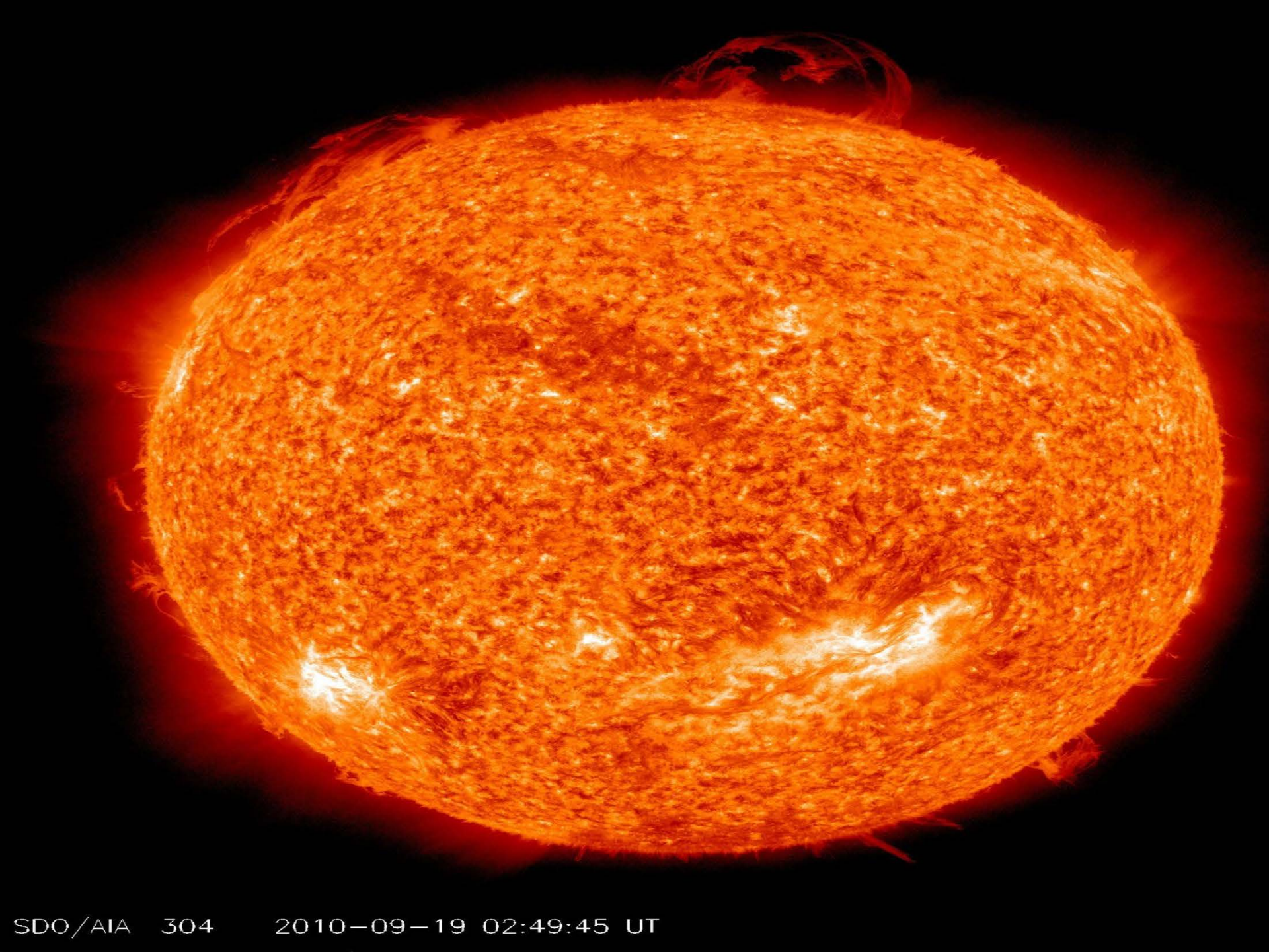


Diffuse Light Harvesting to Structured Information with Hybrid Photovoltaics

Marina Freitag
Newcastle University, School of Enviromental and Natural Sciences

E-mail: marina.freitag@newcastle.ac.uk


SDO/AIA 304 2010-09-19 02:49:45 UT

Dyson Spheres, The Ultimate Megastructures, building a shell around a star that harnesses all of it's energy…Forbes

1. **WHY ARE YOU DOING THIS?**
2. **HOW?**
3. **WHERE ARE YOU GOING?**

Dyson Spheres, The Ultimate Megastructures, building a shell around a star that harnesses all of it's energy…Forbes


IoT

PERSPECTIVES

ENERGY

Internet of Things: Energy boon or bane?

Hittinger & Jaramillo, *Science* **2019**, 364, 6438, 326.

- **growing deployment of technologies grouped under the term "Internet of Things" (IoT) - a worldwide network of interconnected objects that are uniquely addressable**
- **By 2025, there may be as many as 30 billion objects connected to the internet, all of which require energy.**
- **These devices may yield direct energy savings, but it is much less clear what their net effect on the broader energy system will be.**
- **Many of these systems will not be placed in direct sunlight, it is therefore crucial to find an energy source that yields high efficiencies in ambient and low light environments.**

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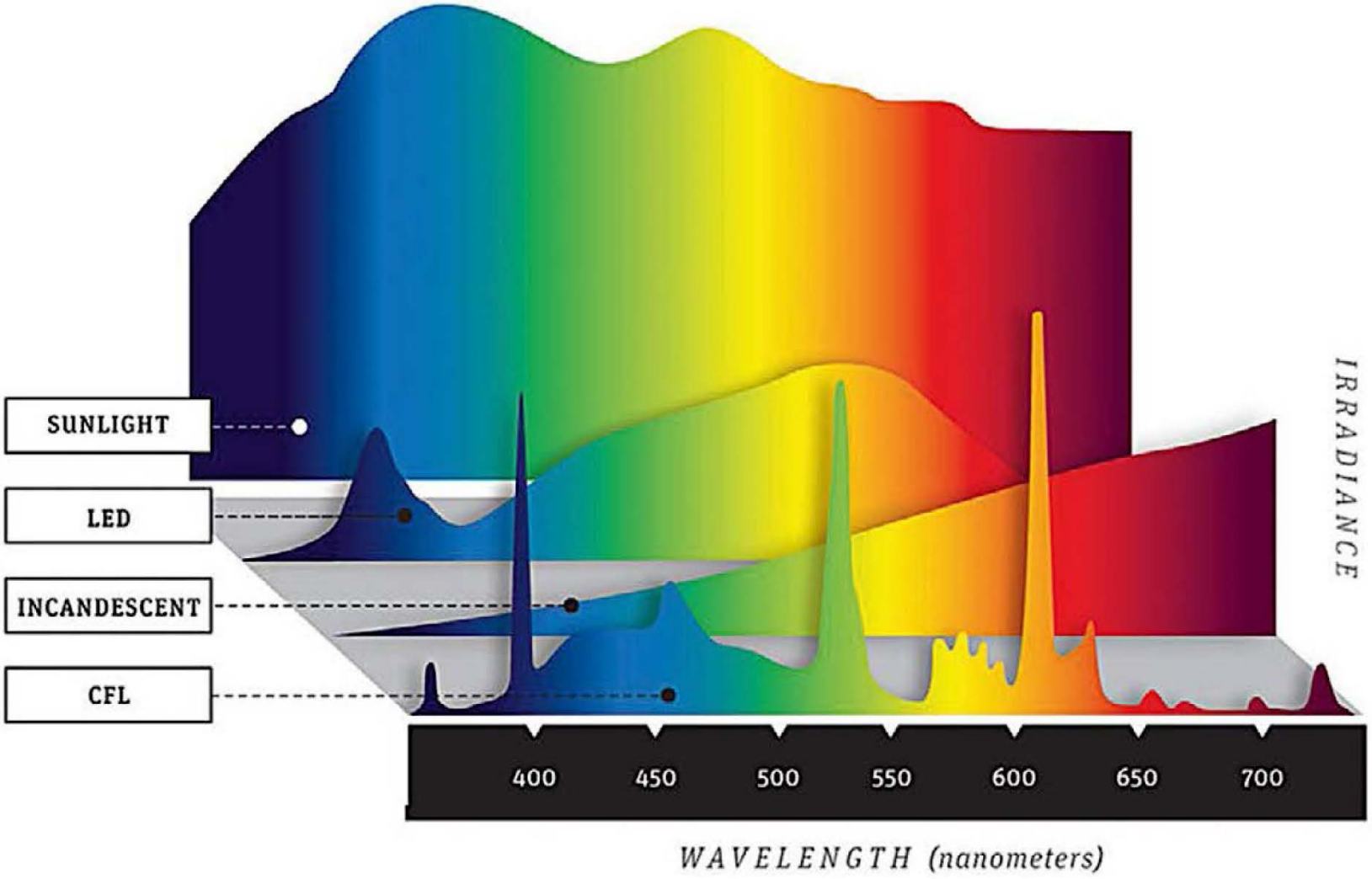
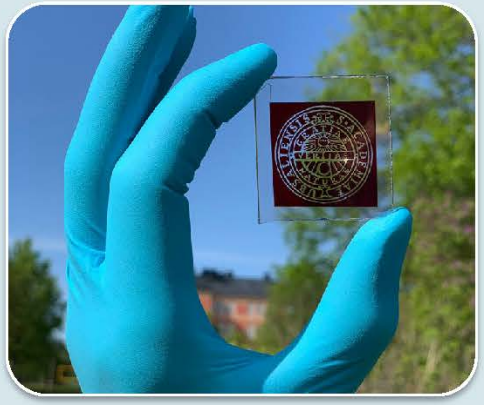
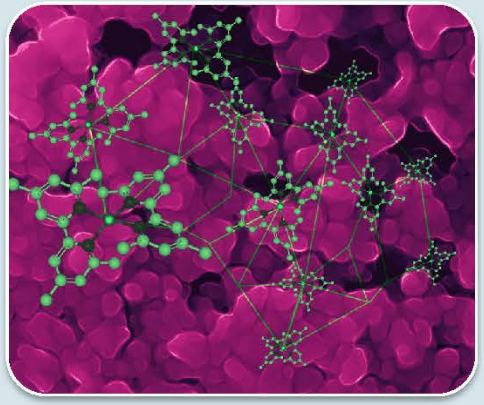
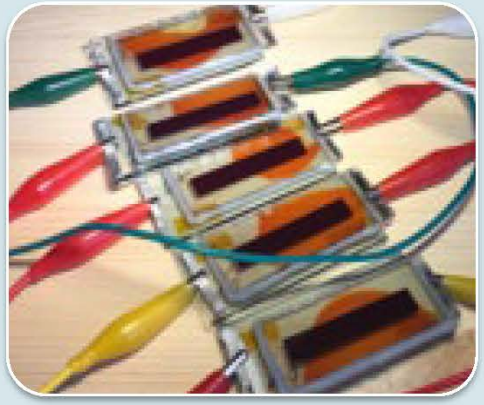


Ambient Photovoltaics- Progress

Newcastle University





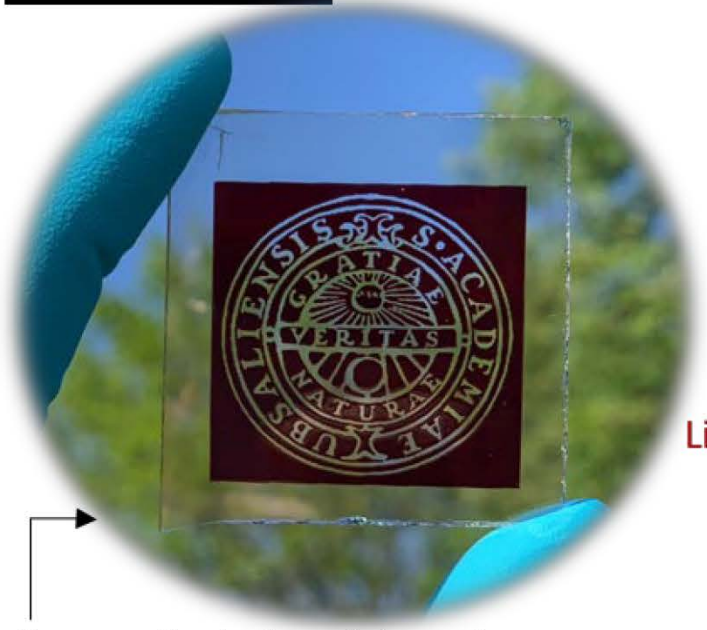


Spectral match	Surface passivation	Electrolyte adaption
to the light source	to reduce recombination	to low light
η =29%	η =34%	η =40%

Future Technology:
DSCs for Self-Powered Intelligent IoT

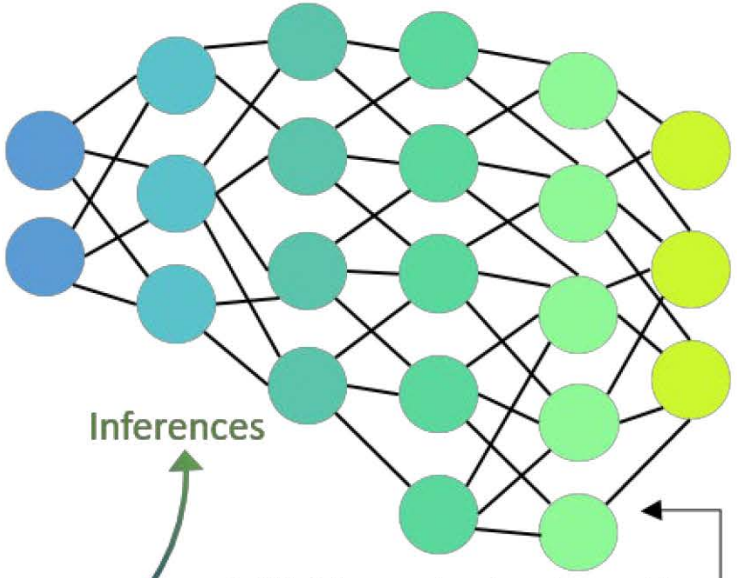
Newcastle University

LIGHT HARVEST



Dye-sensitized solar cells harvest energy from diffuse light with high efficiency.

ARTIFICIAL INTELLIGENCE

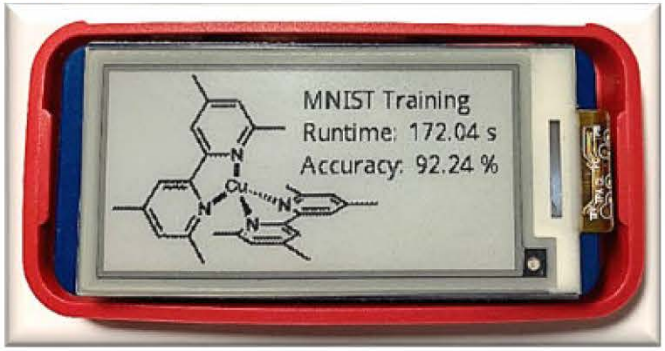


Artificial neural networks enable recognition of patterns in large data.

Light → Information → Inferences

A SMART AUTONOMOUS INTERNET OF THINGS

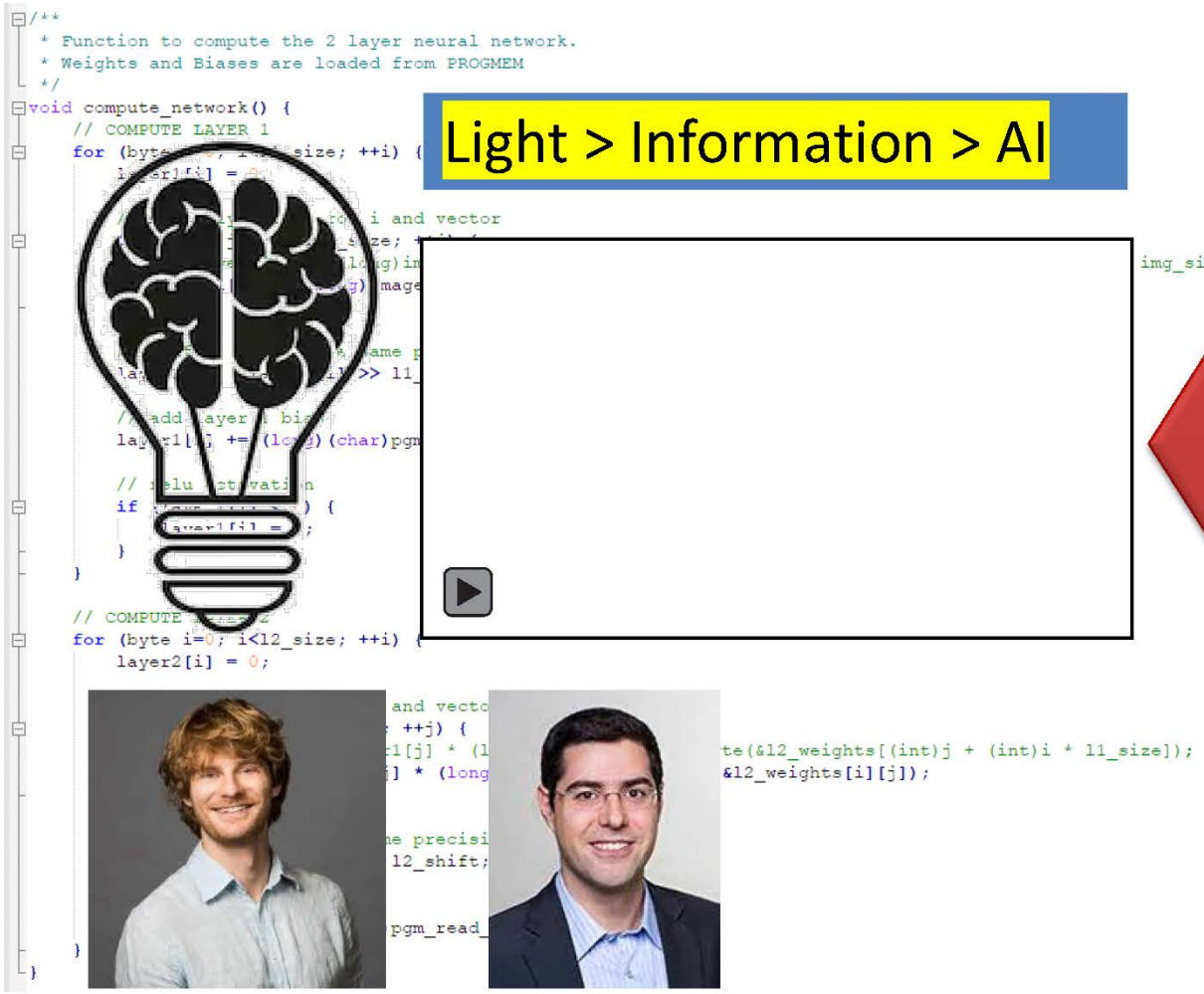
Collecting energy from diffuse light enables the broad installation of wireless sensor devices. Utilizing artificial neural networks, light-powered IoT devices gain the ability to infer information about their surrounding.



Chem. Sci., 2020,**11**, 2895-2906

Future Technology:
DSCs for Self-Powered Intelligent IoT

Newcastle University



Light > Information > AI

Richard Socher, you.com

Alessio Gagliardi, TUM

Predict

Millijoules per Inference

Sense

Multiple per minute

Communicate

Multiple times per second

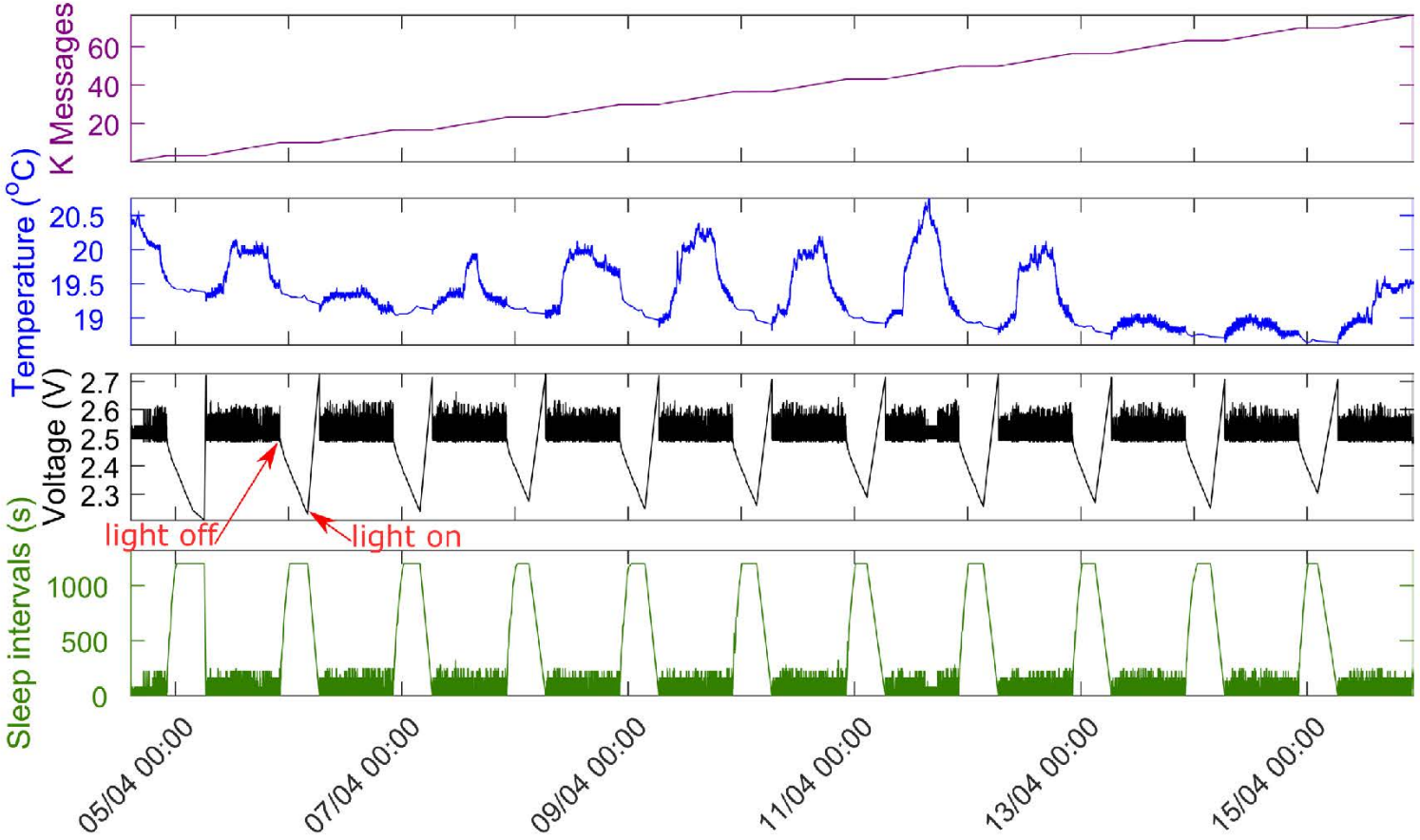
Train

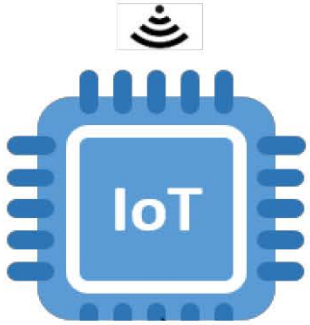
MNIST-training: 100-150 Joule

Chem. Sci., 2020,**11**, 2895-2906

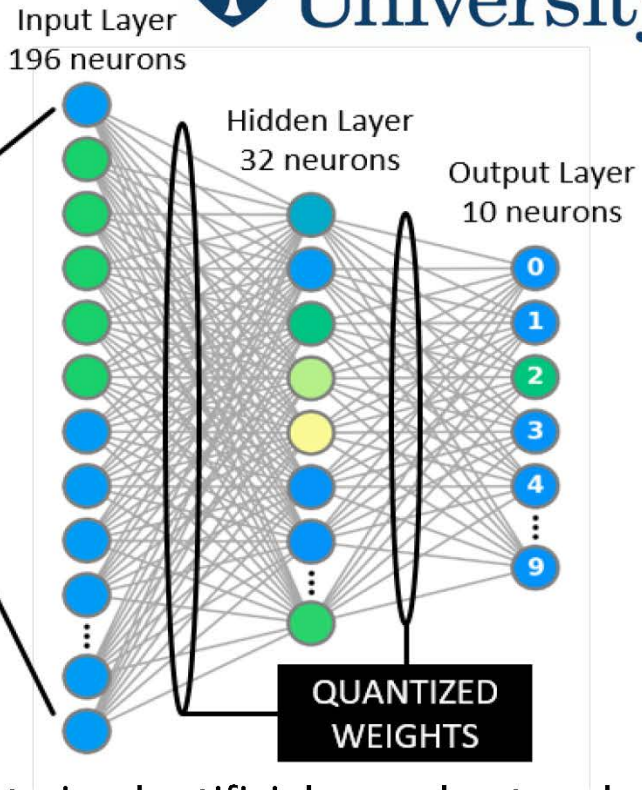
The DSCs for smart IoT

The sensor was tested in simulated light intervals of 16 hours “day” (1000 lux) and 8 hours darkness (10 pm – 6 am, red arrows).





prediction accuracy exceeding 90%

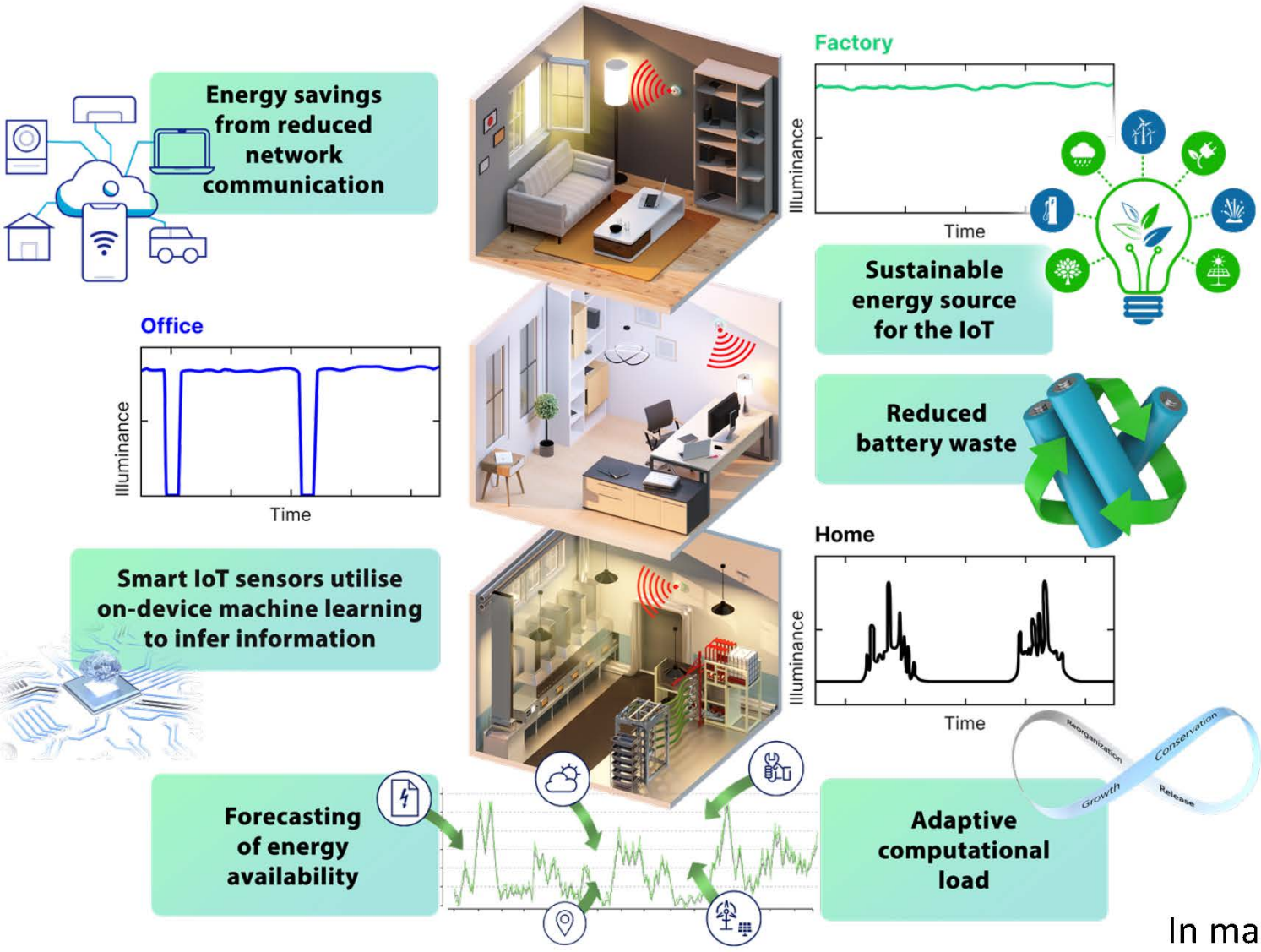


pre-trained artificial neural network

Battery	Power apacity (mAh)	Energy (J)	Days to harvest
AA	2400	12960	15.8
AAA	1000	5400	6.6
CR2032	200	2160	1.3

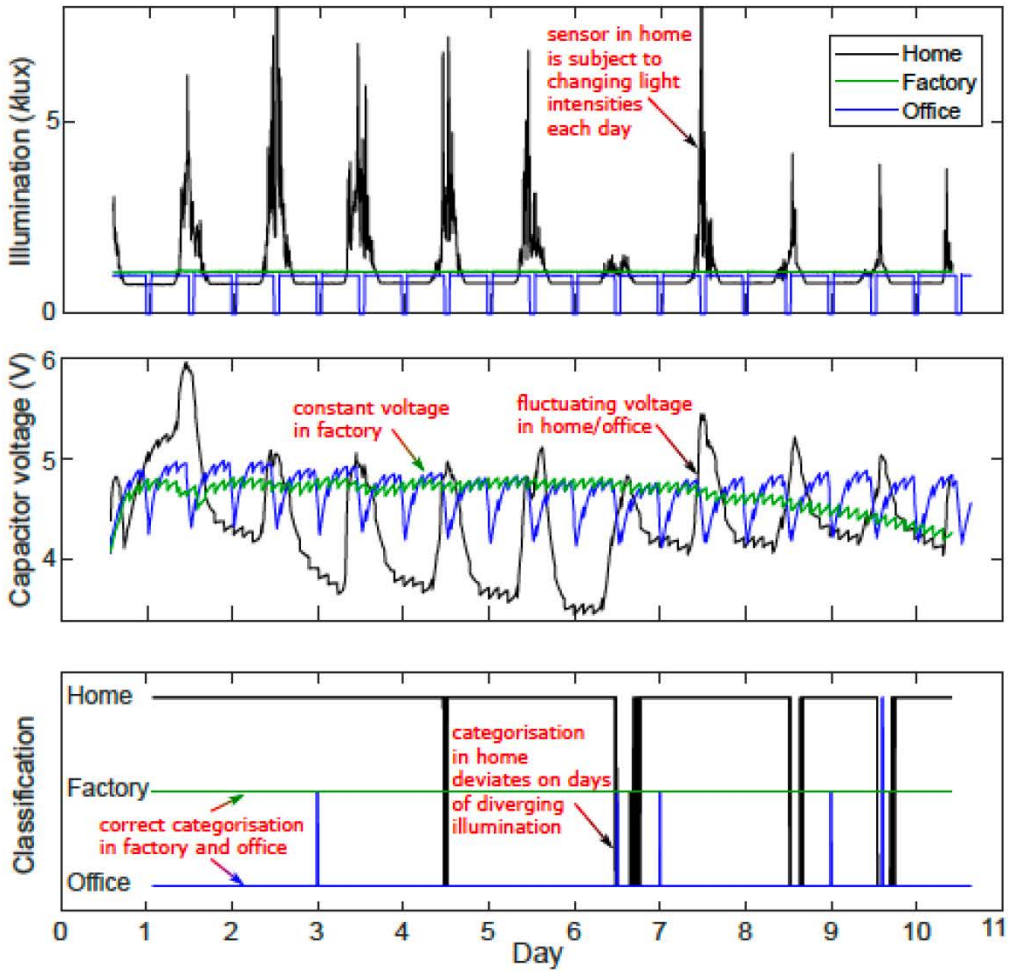
- 1.0 mJ or $2.72 \cdot 10^{15}$ photons is needed to compute one inference
- 152 J or $4.41 \cdot 10^{20}$ photons required for training and verification of an artificial neural network with a 64 cm^2 photovoltaic area in less than 24 hours of **1000 lux** illumination.

Newcastle University



In manuscript be kind ☺

Dynamic energy management through photovoltaic-powered IoT sensors

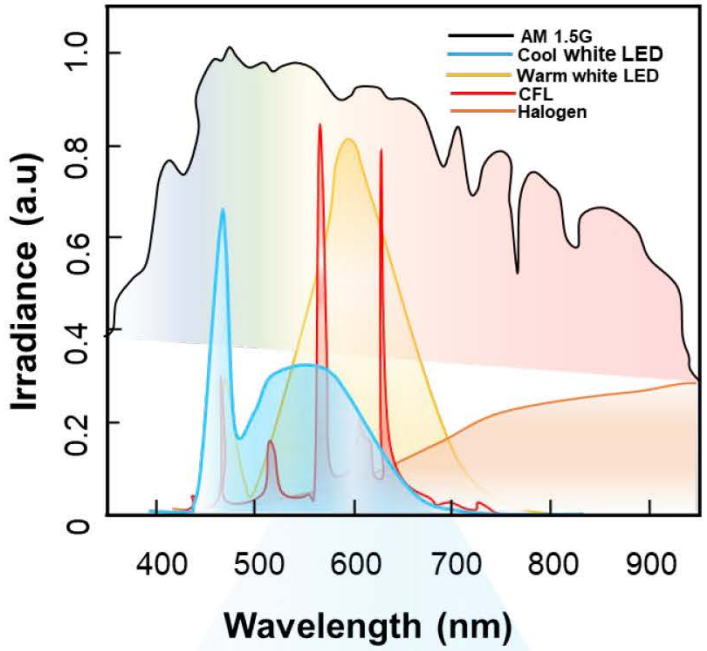


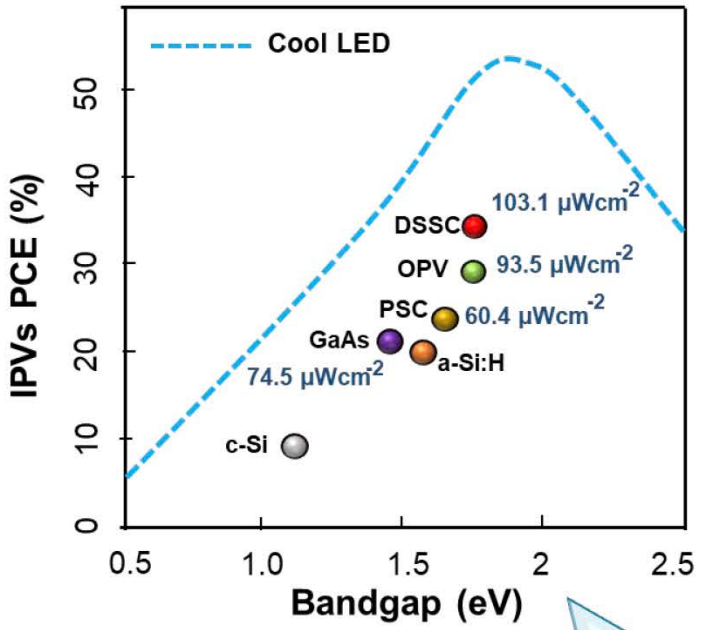
- Photovoltaic specifically adapted to ambient light intensity and spectrum
- autonomous device dynamically infers its deployment scenario based on real-time acquired illumination data

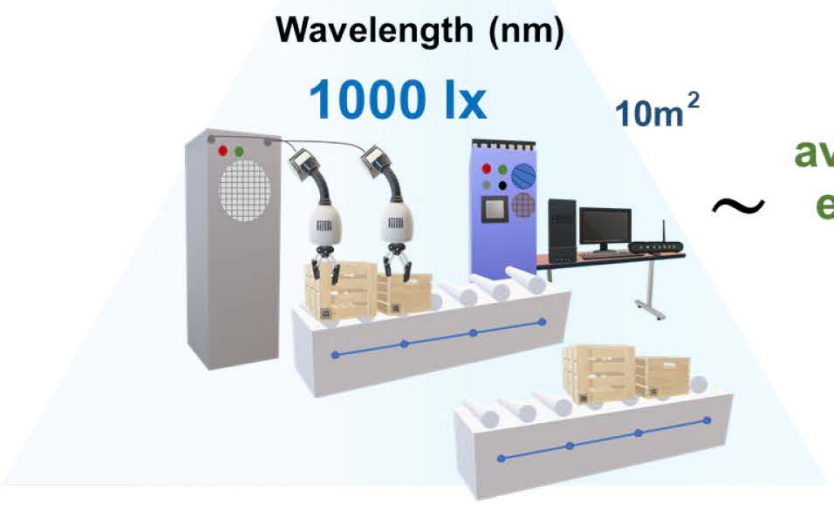
SNEAK PEAK

Freitag & Gagliardi in manuscript

Newcastle University

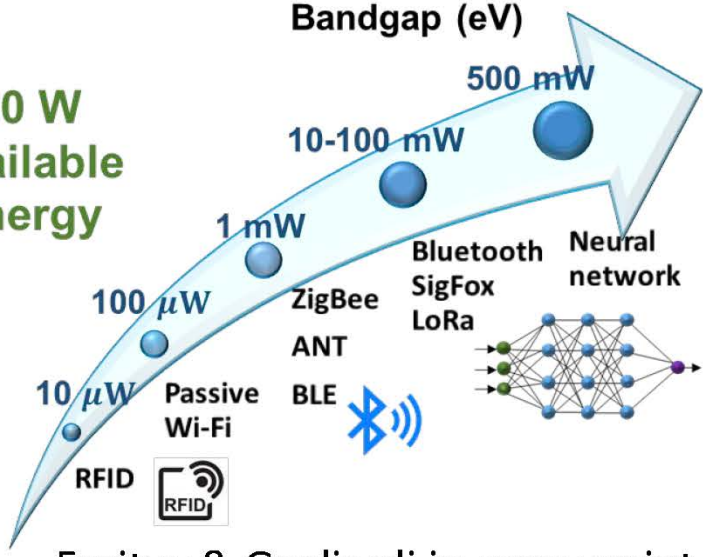






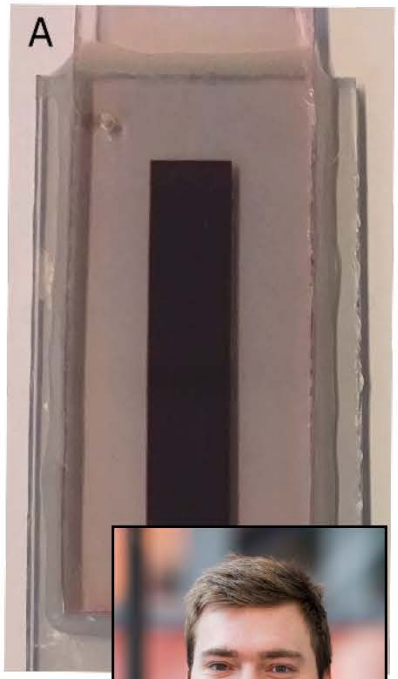
~

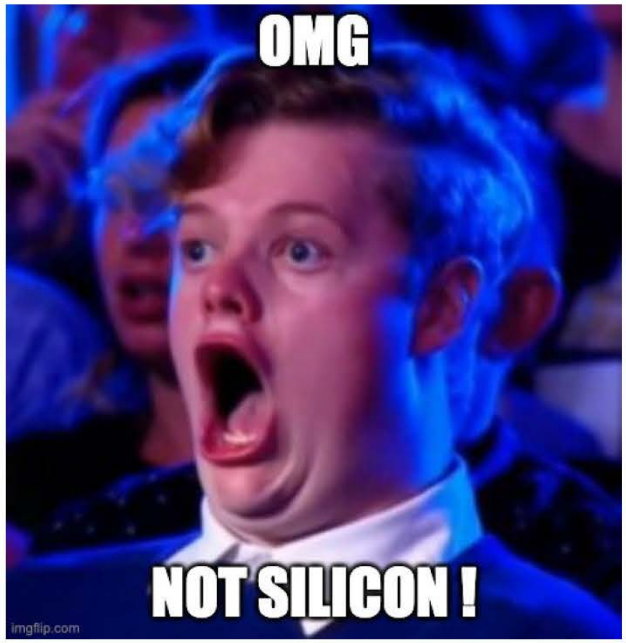
30 W available energy



Freitag & Gagliardi in manuscript

The ”Zombies” for smart IoT



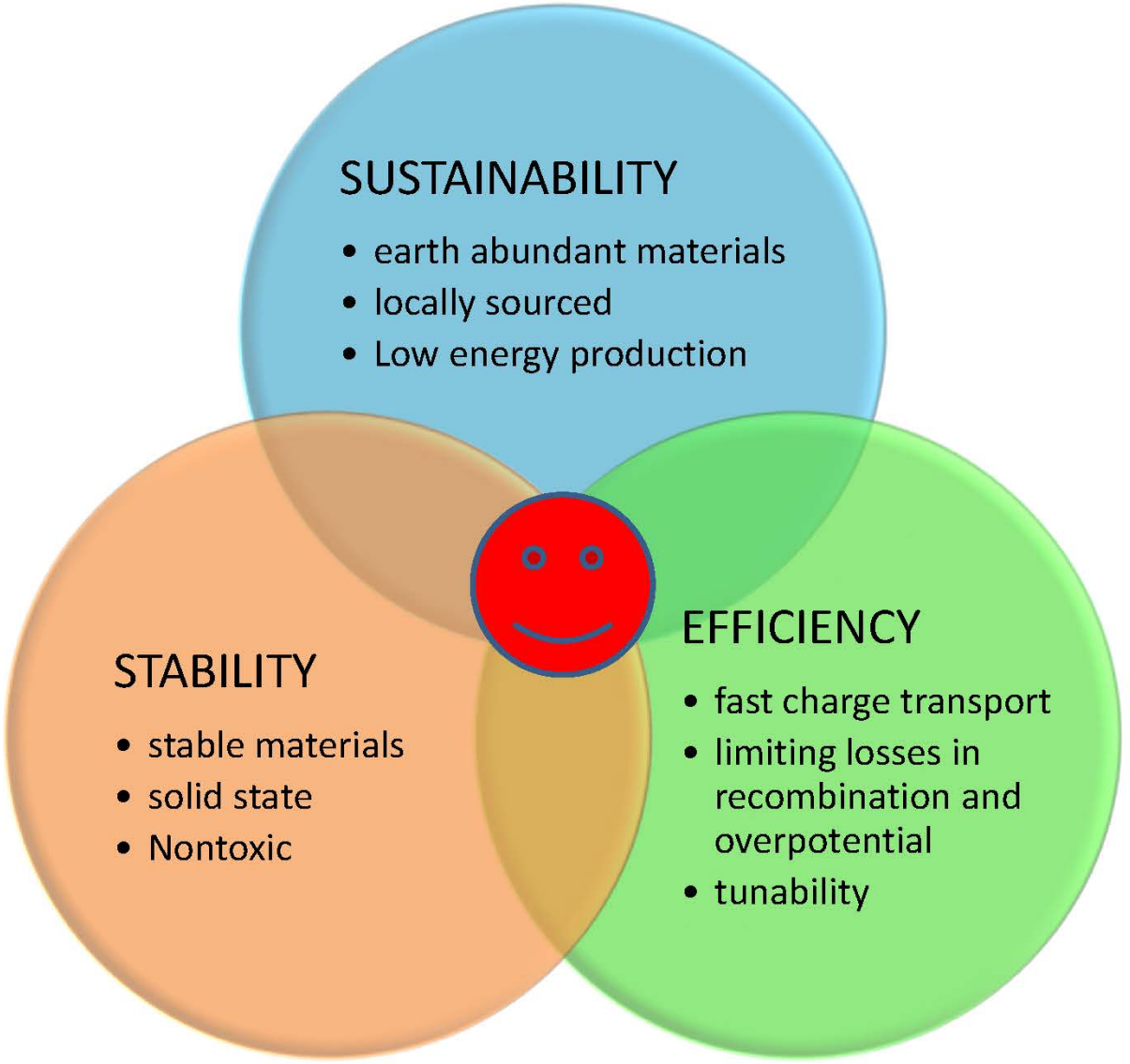


Hannes Michaels

SMART ZOMBIES

Chem. Sci., 2020,**11**, 2895-2906

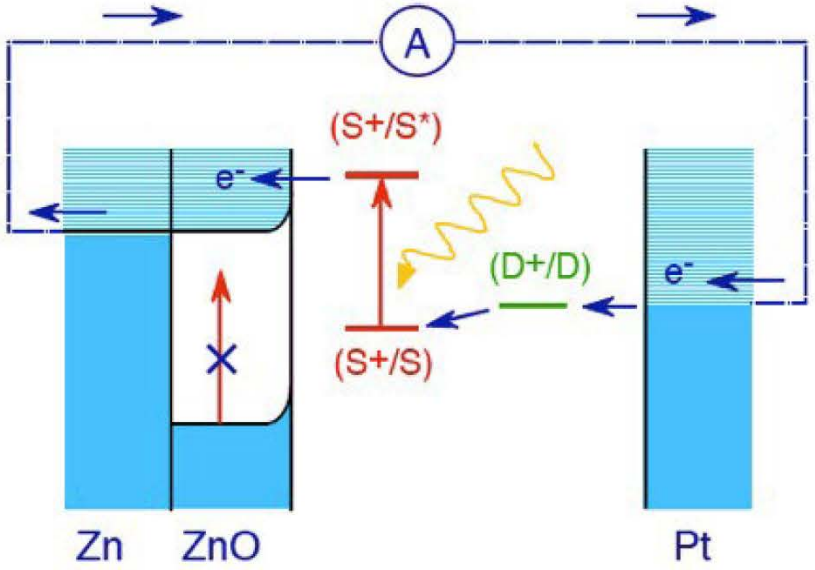
What can chemistry fix ?

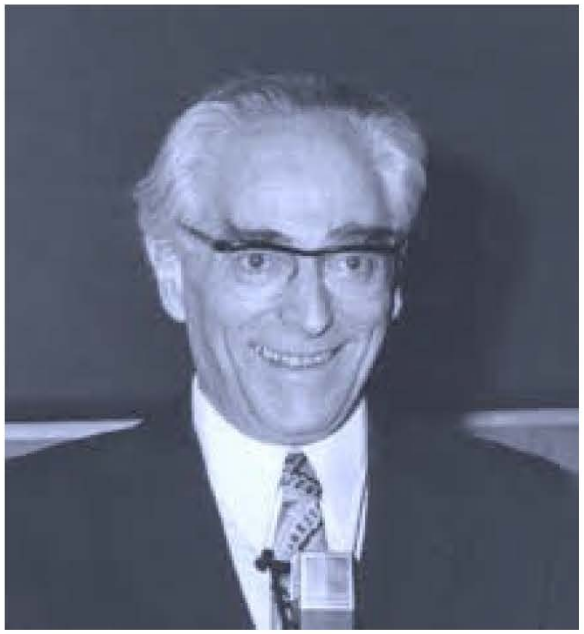


52% ambient
28% solar

The First Dye-sensitized Photogalvanic Cell

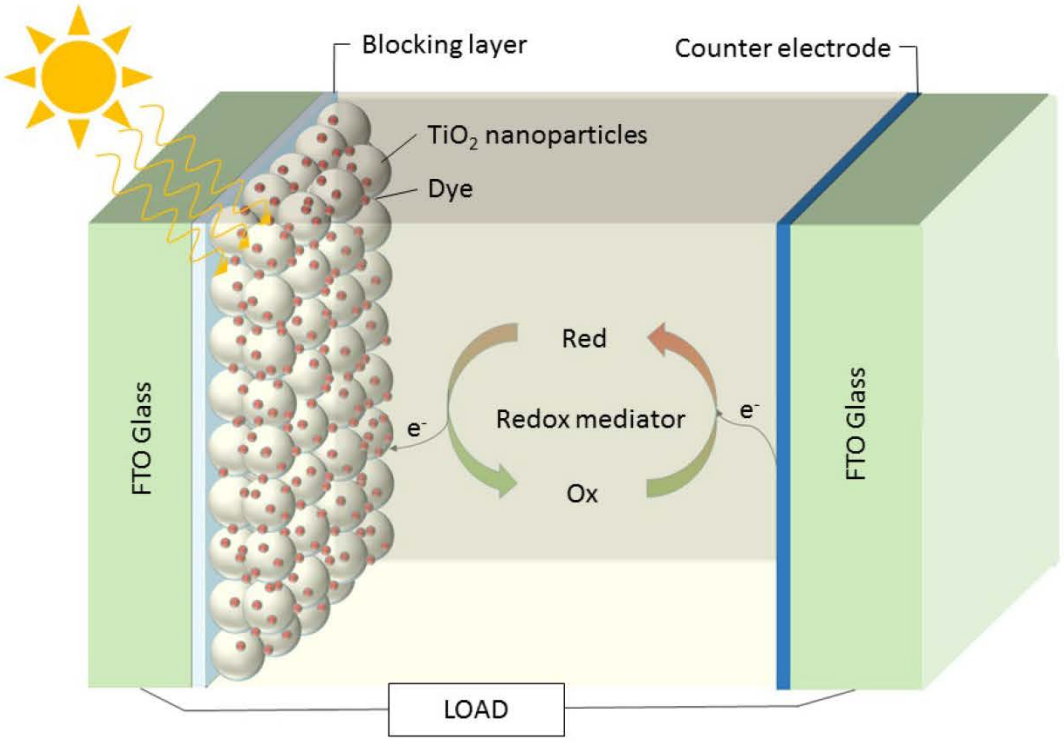
Heinz Gerischer (1968):
Dye-sensitized photogalvanic cell





While multilayer absorption of dye has very low quantum yield, a significant roblem of this device is incomplete light absorption, because of a monolayer of dye attached to a smooth surface absorbed less than 1% of the incident monochromatic light.

DSC and the Redox Mediator



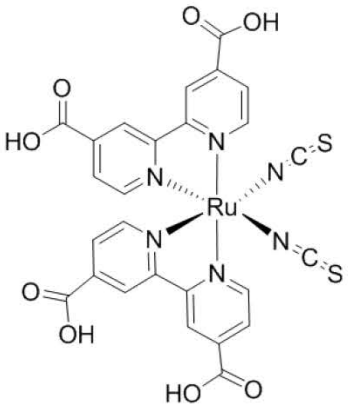
O'Regan, B. & Grätzel, M. A LOW-COST, HIGH-EFFICIENCY SOLAR-CELL BASED ON DYE SENSITIZED COLLOIDAL TIO_2FILMS. Nature, 353(6346), 737-740 (1991).

1991

Dye-Sensitized Solar Cell Components

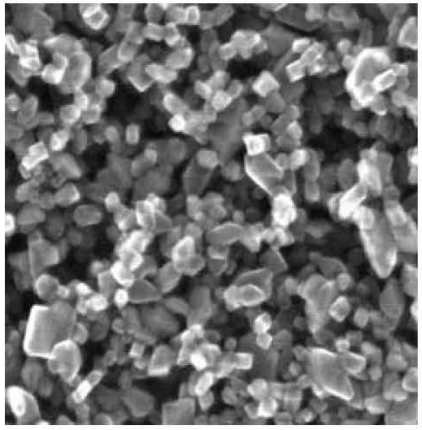
Newcastle University

Sensitizing Dye



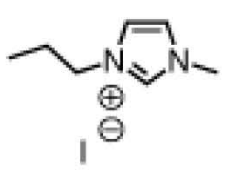
Chemical Structure of N3 Dye

Titania Nanoparticles



Titania nanoparticles

Electrolyte



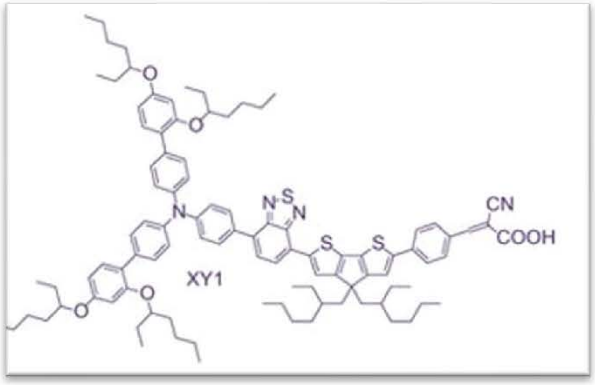
Iodide/Tri-iodide
Redox Couple

2021

Newcastle University

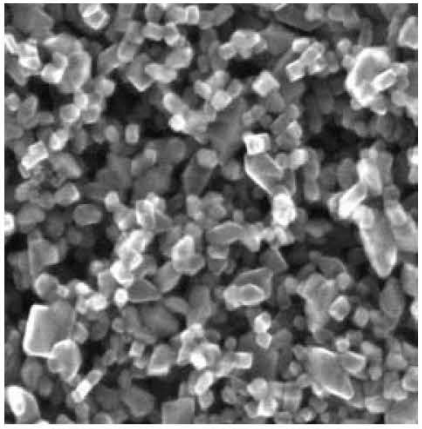
Dye-Sensitized Solar Cell Components

Sensitizing Dye



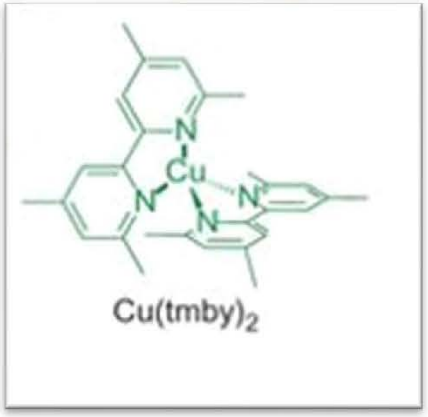
Dye

Titania Nanoparticles



Titania nanoparticles

Electrolyte

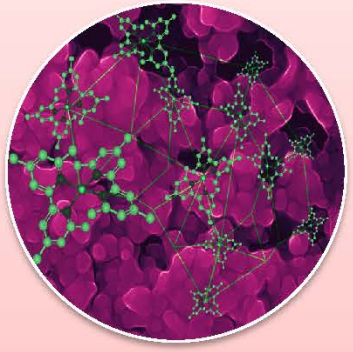


Redox Couple

Freitag M., et. al Nature Photonics 11, 372–378 (2017); Freitag M., et. al EES 8 (9), 2016, 2634.;
Freitag M., et. al Nature Comm. 8, 15390, 2017 , Chemical Science 2020

Newcastle University

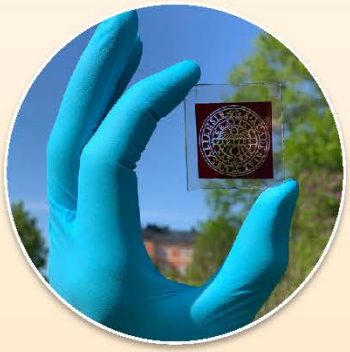
FREITAG LAB



Materials

Charge Transport Materials

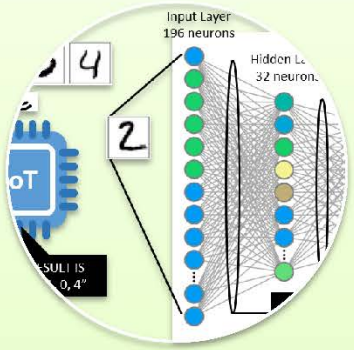
Coordination Complexes and Polymers



Devices

Dye sensitized solar cells

Ambient Photovoltaics



Application

Power wireless sensor systems

Smart autonomous IoT

Coordination Materials and Charge Transport

Newcastle University

Molecular building blocks

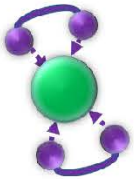
Metal center
Cu, Ni, …

Bidentate ligands (η^2)
Bipyridines, phenanthrolines, …

Tetradentate ligands (η^4)
Phthalocyanine, porphyrine,
Substituted bipyridines, polypyridines…

Bridging ligands
Halides, polyacids, polythiols, …

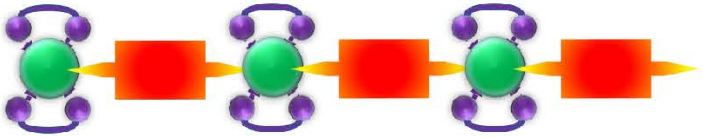
Coordination complexes



Coordination complex from *bi*dentate ligands

Coordination complex from *tetra*dentate ligands

Coordination polymers



Coordination polymers for emerging molecular devices

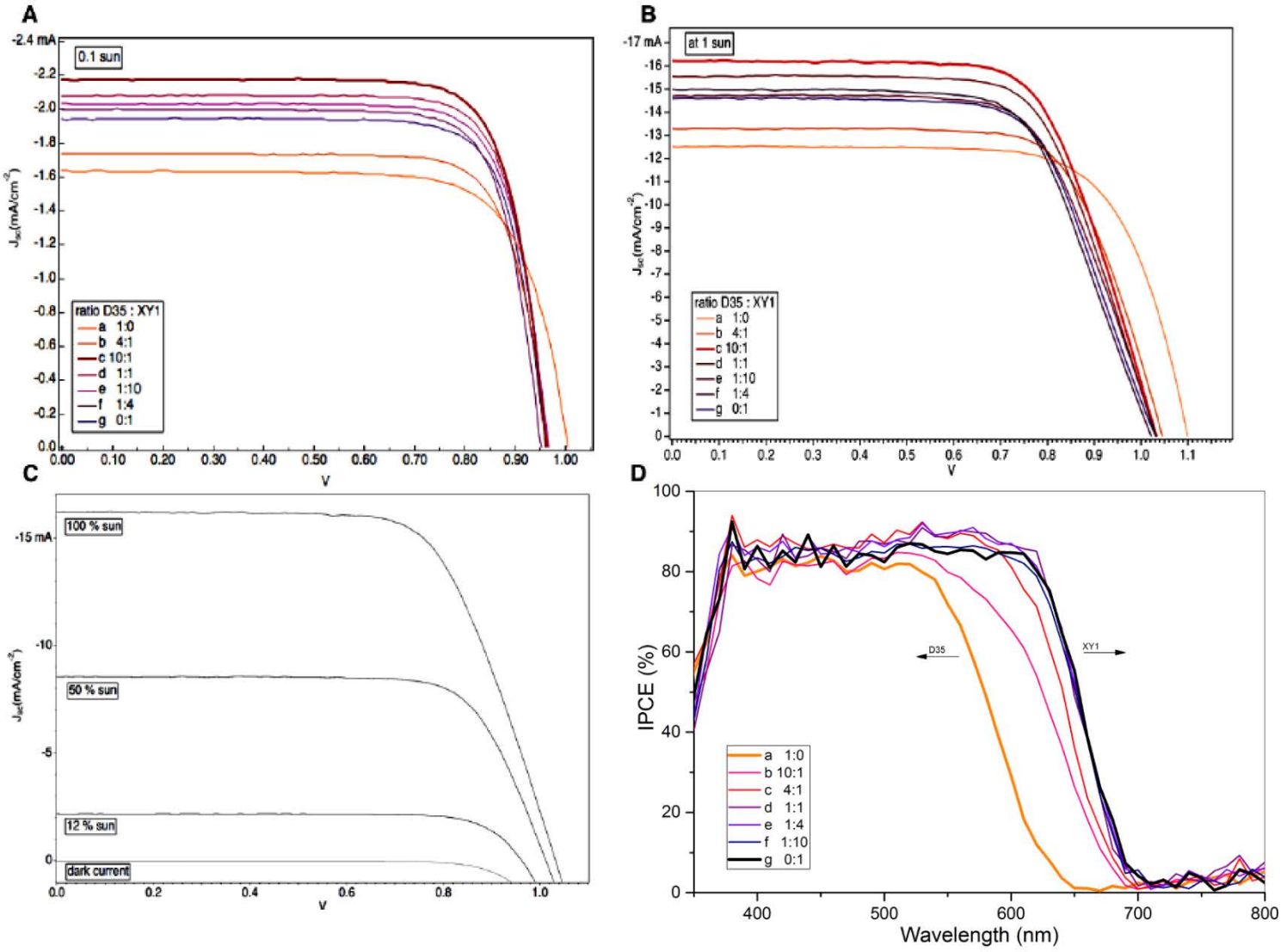
GH Morritt, H Michaels, M Freitag
Chemical Physics Reviews 3 (1), 011306

Ambient Photovoltaics

Freitag M., et. al : **Dye-Sensitized Solar Cells for Efficient Power Generation under Ambient Lighting**, Nature Photonics, 2017

Benesperi, *Chem*, **2022**, 8 (2), 439-449.

Copper Complexes as Redox Mediator



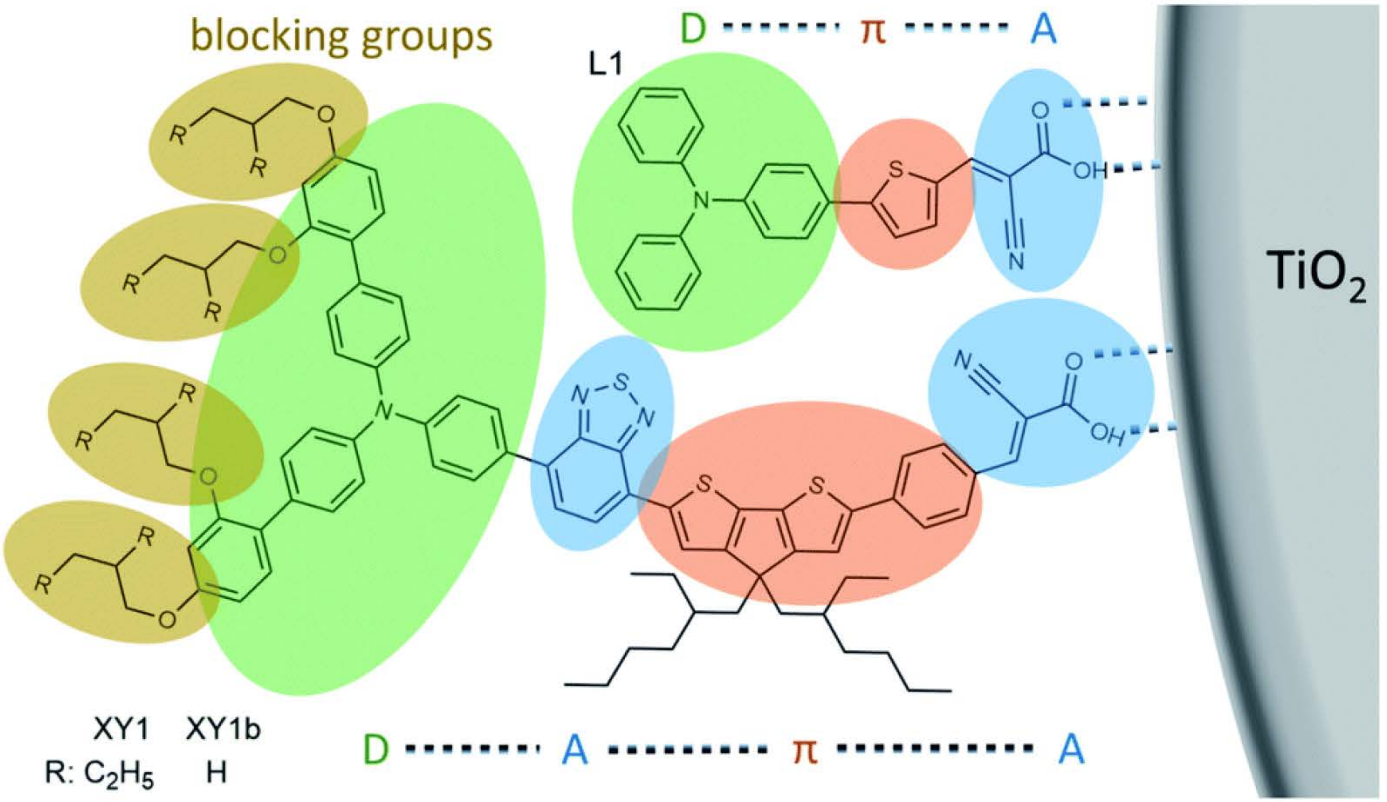
Newcastle University

Copper Complexes as Redox Mediator

Solar Cell	Light source	Light intensity	J_{sc} ($\mu A/cm^2$)	V_{oc} (mV)	FF (%)	P_{in} ($\mu W/cm^2$)	P_{out} ($\mu W/cm^2$)	PCE (%)
DSC[a]	OSRAM Warm White 930	200 lux	27.2	732.0	0.79	61.3	**15.6**	25.5
DSC[b]		200 lux	24.8	700.0	0.79	61.3	**13.7**	22.3
DSC[a]		1000 lux	138.0	797.0	0.80	306.6	**88.5**	28.9
DSC[b]		1000 lux	137.2	766.0	0.80	306.6	**84.1**	27.4
flexi GaAs Alta	OSRAM Warm White 827	200 lux	20.1	870.0	0.75	70.6	**13.1**	18.6
flexi GaAs Alta		1000 lux	99.0	940.0	0.80	354.0	**74.5**	21.0

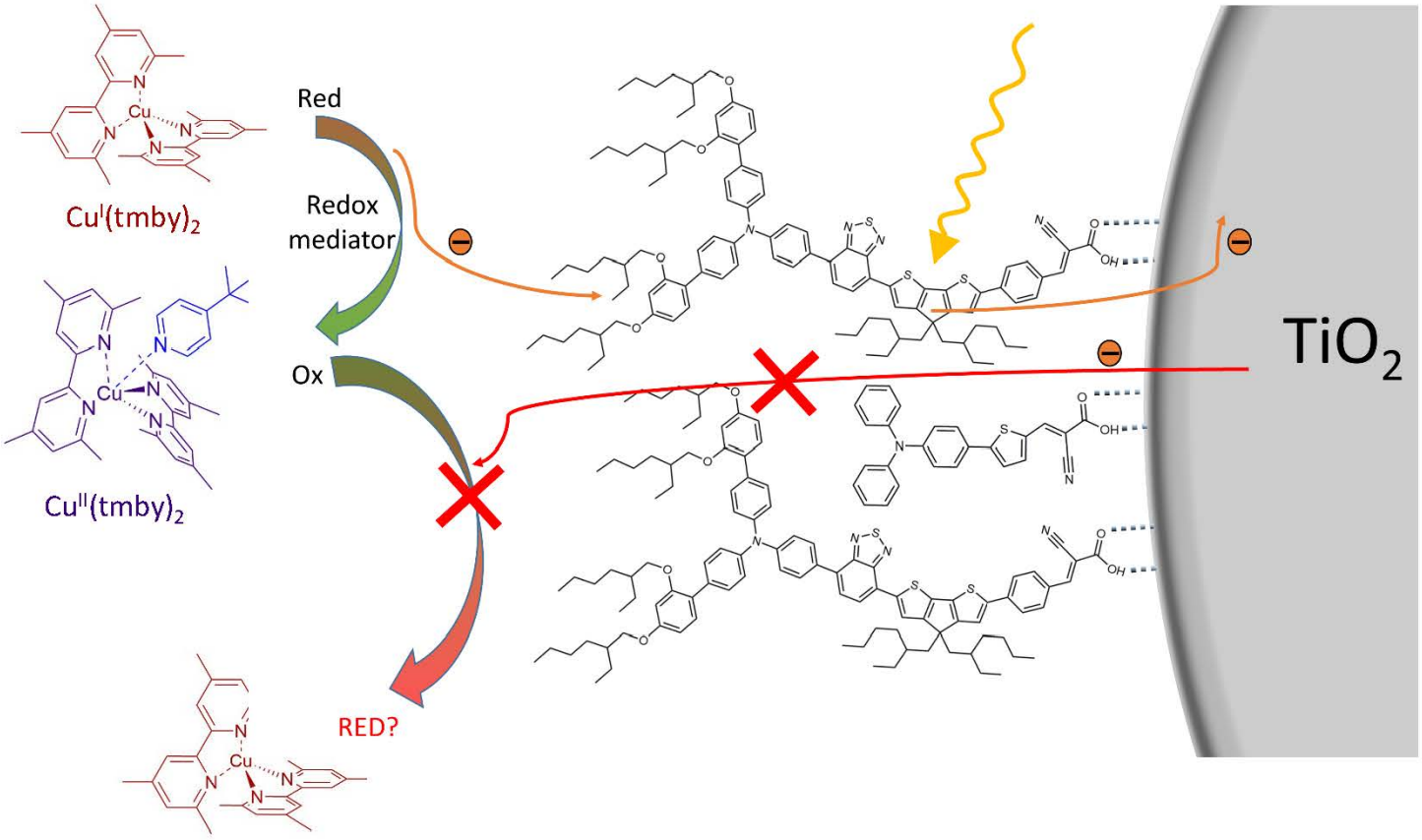
Freitag M., et. al : A New Dye-Sensitized Solar Cell Embodiment for Efficient Ambient Light Harvesting, Nature Photonics, 2017

Photoanode Engineering for
Lower Recombination

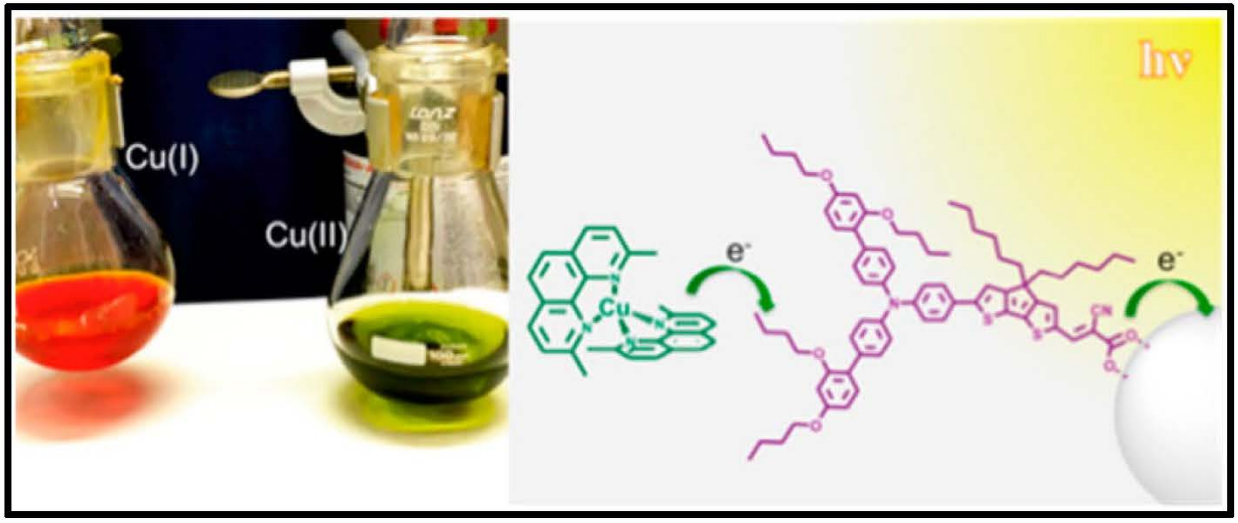


Chem. Sci., 2021, **12**, 5002-5015

Suppressing recombination



Coordination Complexes



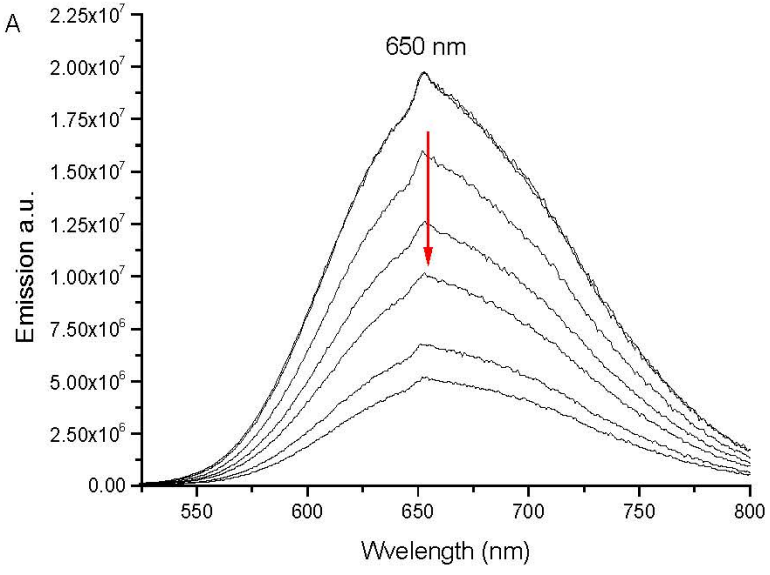
The Journal of Physical Chemistry C 120 (18), 9595-9603, Journal of the American Chemical Society 138 (45), 15087-15096

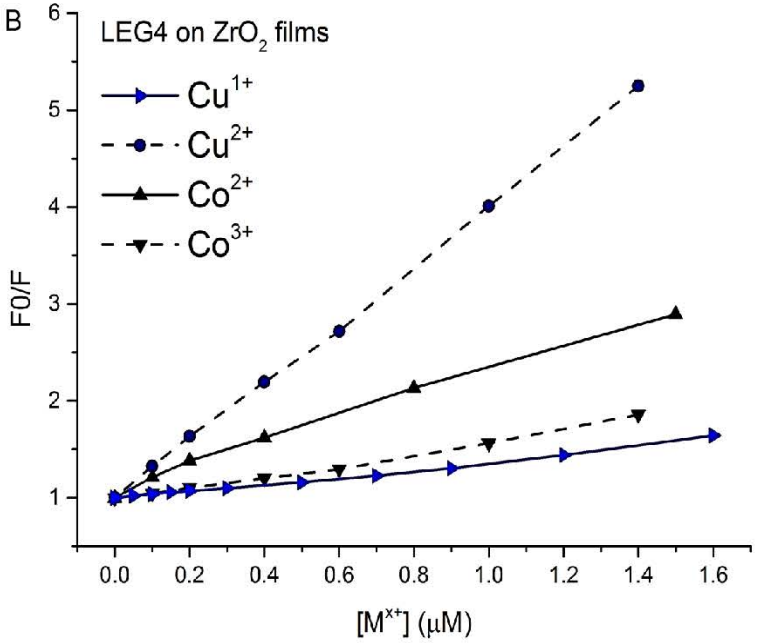
Copper Redox Mediators: Stern-Volmer

$$LEG4^* + [Cu(dmp)_2]^{1+} \rightarrow LEG4^- + [Cu(dmp)_2]^{2+} \quad (r1)$$

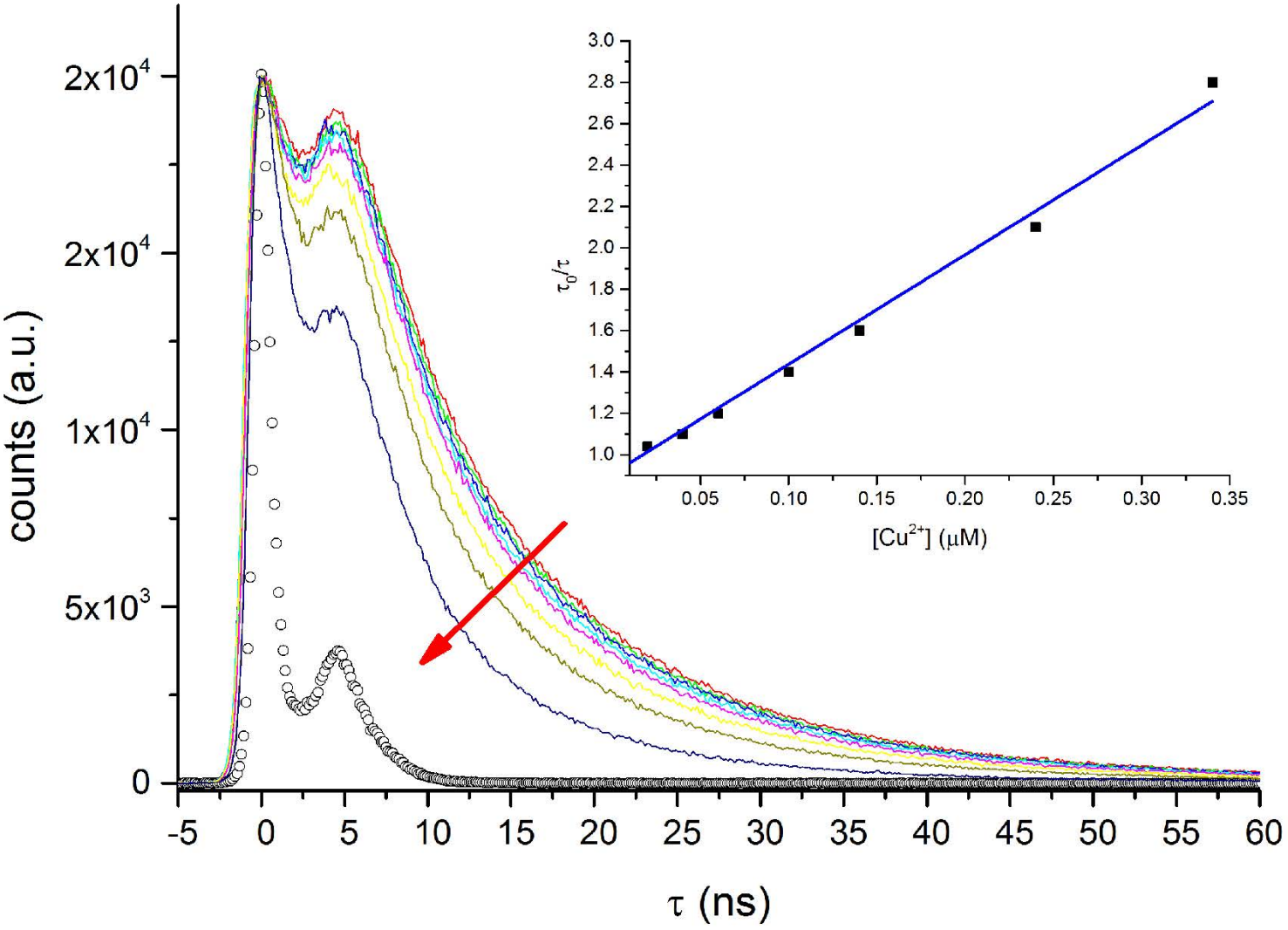
$$LEG4^* + [Cu(dmp)_2]^{2+} \rightarrow LEG4^+ + [Cu(dmp)_2]^{1+} \quad (r2)$$

$$LEG4^* + [Cu(dmp)_2]^{2+} \rightarrow LEG4 + [Cu(dmp)_2]^{2+} \quad (r3)$$





Copper Phenanthroline Redox Mediators: TC-SPC



Copper Coordination Complexes as redox mediators in DSCs

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Copper Bipyridyl Redox Mediators for Dye-Sensitized Solar Cells with High Photovoltage

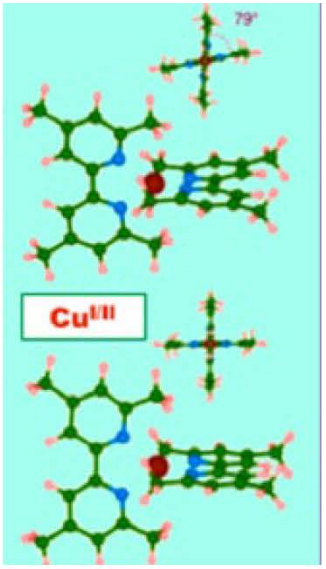
Yasemin Saygili,[†] Magnus Söderberg,[‡] Norman Pellet,[§] Fabrizio Giordano,[§] Yiming Cao,[§] Ana Belen Muñoz-García,[∥] Shaik M. Zakeeruddin,[†] Nick Vlachopoulos,[†] Michele Pavone,[∥] Gerrit Boschloo,[⊥] Ladislav Kavan,[§,#] Jacques-E. Moser,[‡] Michael Grätzel,[§] Anders Hagfeldt,[†] and Marina Freitag*[,†,⊥]

[†]Laboratory of Photomolecular Science, [‡]Photochemical Dynamics Group, and [§]Laboratory for Photonics and Interfaces, Institute of Chemical Sciences Engineering, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

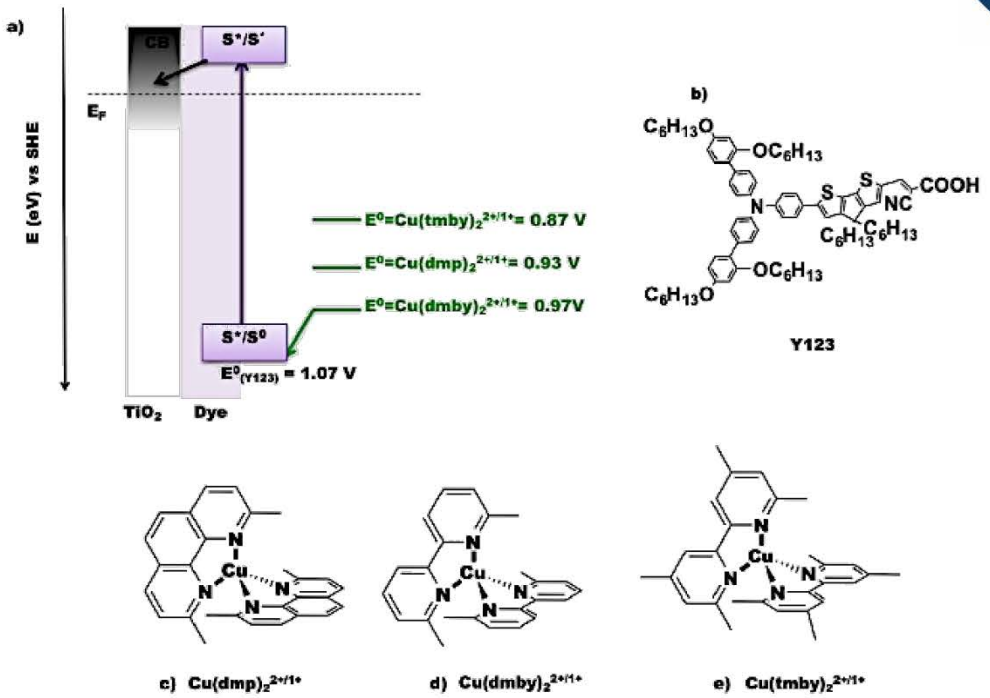
[∥]Department of Chemical Sciences, University of Naples Federico II, 80126 Naples, Italy

[⊥]Department of Chemistry, Ångström Laboratory, Uppsala University, 751 20 Uppsala, Sweden

[#]J. Heyrovsky Institute of Physical Chemistry, 1823 Prague, Czech Republic



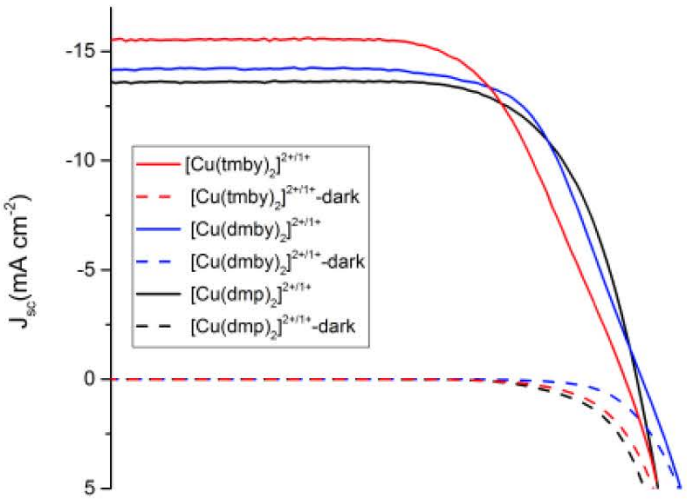
Copper Bipyridyl Redox Mediators

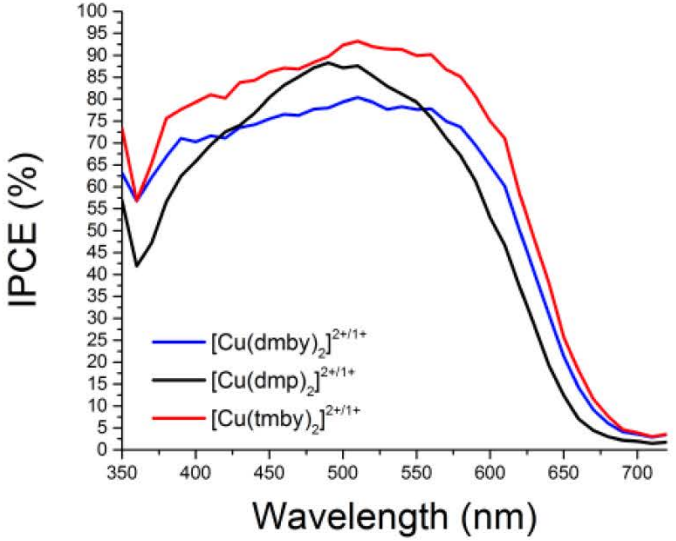


	ε ($M^{-1}cm^{-1}$)	λ_{max} (nm)	D (10^{-6} cm^2 s^{-1}])	$E^{0'}$ (V vs SHE)
Cu(I)(dmp)$_2$TFSI	7300	457	12.6	0.93
Cu(II)(dmp)$_2$(TFSI)$_2$	850	360	14.4	
Cu(I)(dmby)$_2$TFSI	6900	455	11.7	0.97[a]
Cu(II)(dmby)$_2$TFSI/Cl	1300	360	33.3	
Cu(I)(tmby)$_2$TFSI	5300	451	11.2	0.87[a]
Cu(II)(tmby)$_2$TFSI/Cl	1400	360	22.0	

Saygili et. al. J. Am. Chem. Soc., 2016, 138 (45), 15087–15096.

Copper Bipyridyl Redox Mediators

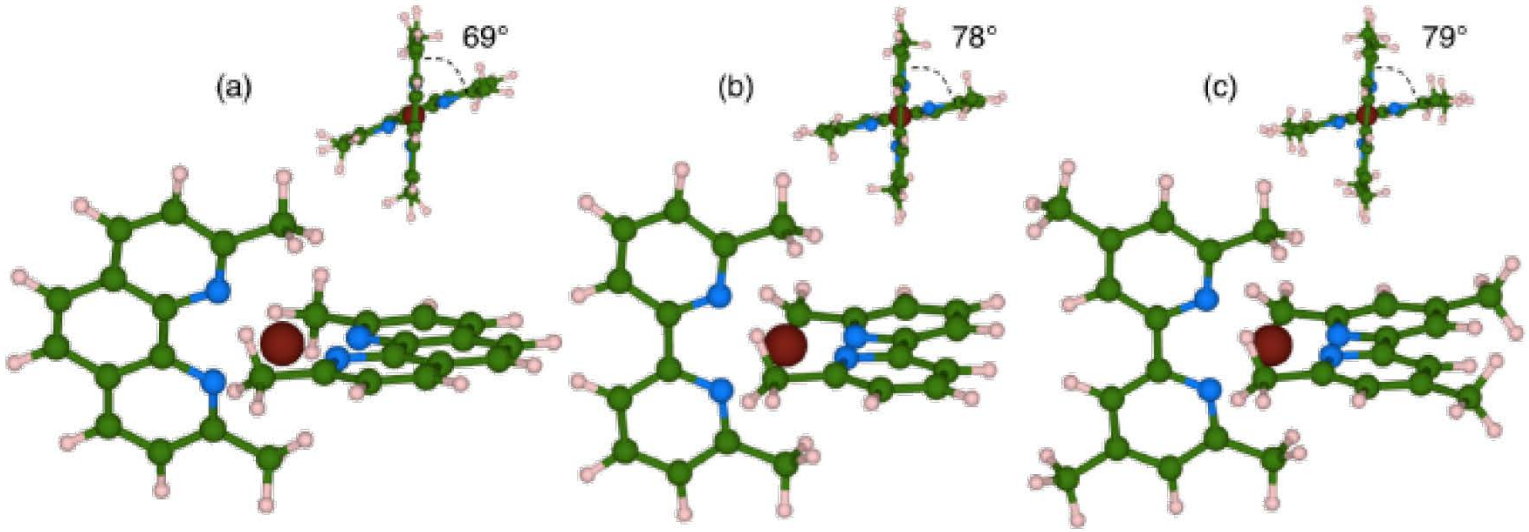




Redox couple	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
[Cu(tmby)$_2$]$^{2+/1+}$	1.04	15.53	0.640	10.3
[Cu(dmby)$_2$]$^{2+/1+}$	1.07	14.15	0.687	10.0
[Cu(dmp)$_2$]$^{2+/1+}$	1.06	13.61	0.692	10.3

Saygili et. al. J. Am. Chem. Soc., 2016, 138 (45), 15087–15096.

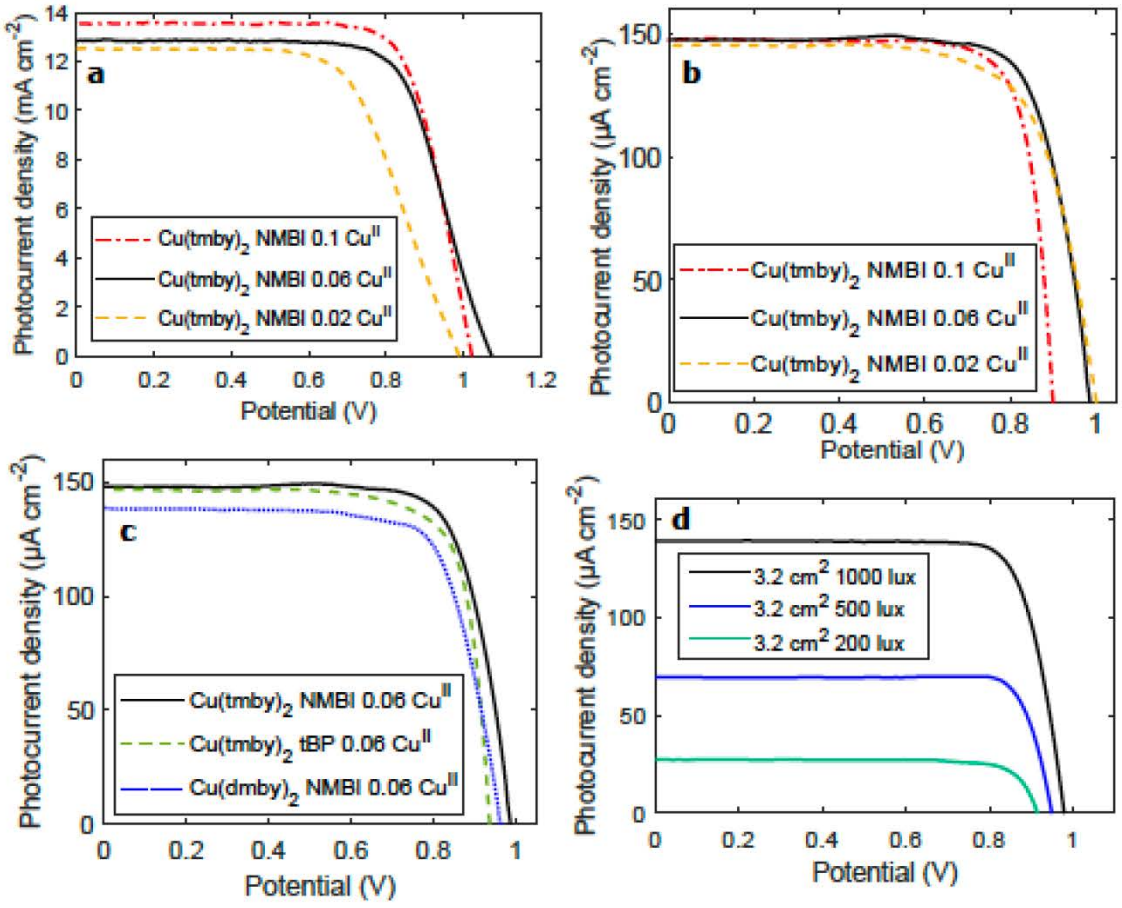
Copper Bipyridyl Redox Mediators



	ΔG_{ox} (eV)	λ_{in} (eV)
$[Cu(dmp)_2]^{1+/2+}$	4.68	**0.281**
$[Cu(dmby)_2]^{1+/2+}$	4.64	**0.301**
$[Cu(tmby)_2]^{1+/2+}$	4.47	**0.294**
$[Co(bpy)_2]^{2+/3+}$ (low-spin)[36]	5.00	**0.613**

Saygili et. al. J. Am. Chem. Soc., 2016, 138 (45), 15087–15096.

Dynamic energy management through photovoltaic-powered IoT sensors



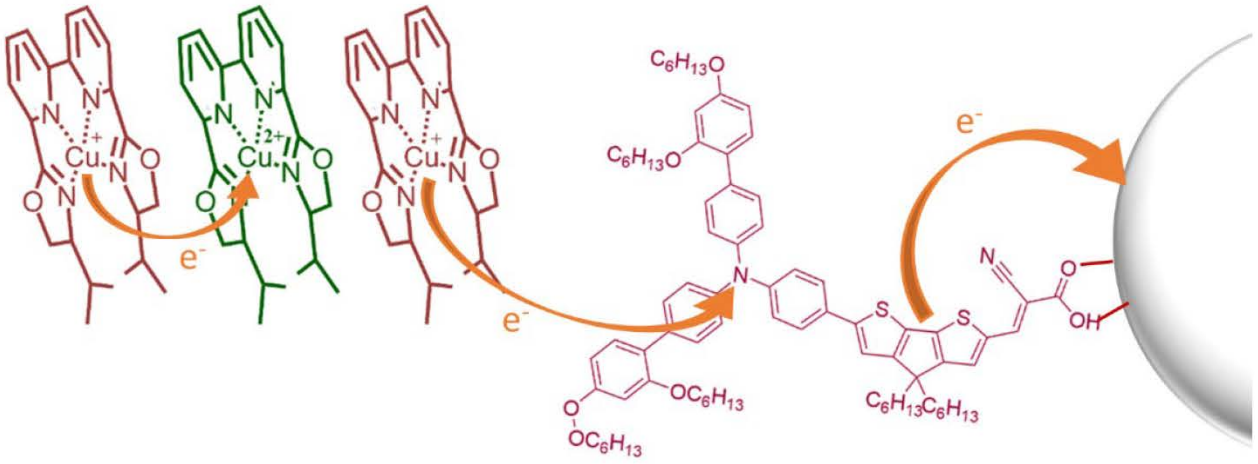
- Photovoltaic specifically adapted to ambient light intensity and spectrum
- autonomous device dynamically infers its deployment scenario based on real-time acquired illumination data

SNEAK PEAK

Freitag & Gagliardi in manuscript

Tetradentate copper complexes

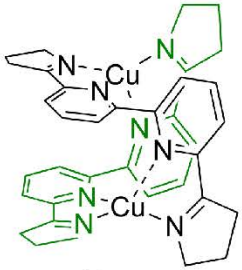
Enhanced charge transport in Dye-sensitized Solar Cells



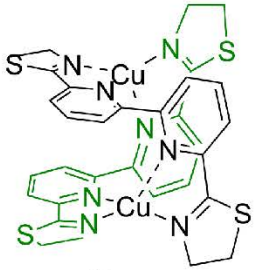
Michaels, H. *et al.*, *Inorganics* **2018**, *6*(2), 53.

NEW

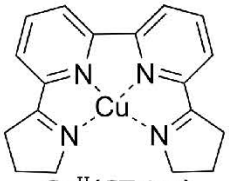
DYNAMIC Dimer copper redox mediators



Cu^{I}(CTetra)

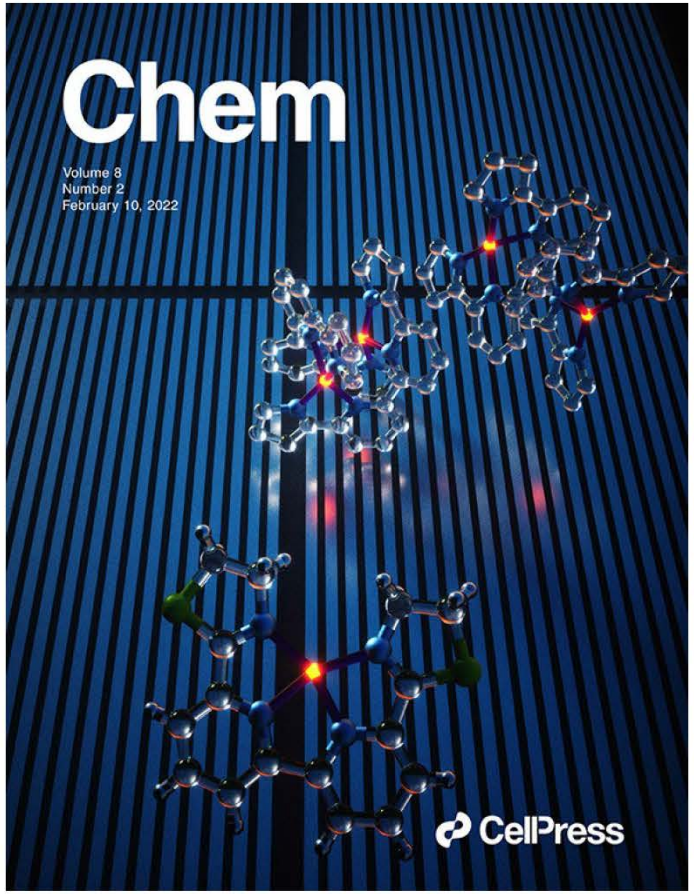


Cu^{I}(STetra)



Cu^{II}(CTetra)

Cu^{II}(STetra)



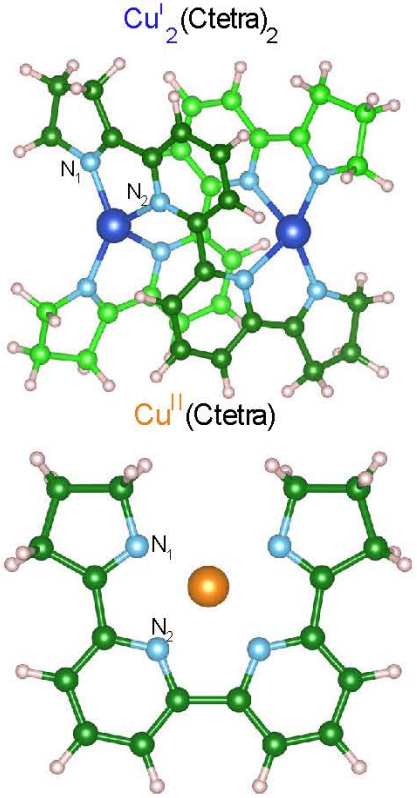
Iacopo Benesperi

Benesperi, *Chem*, **2022**, 8 (2), 439-449.

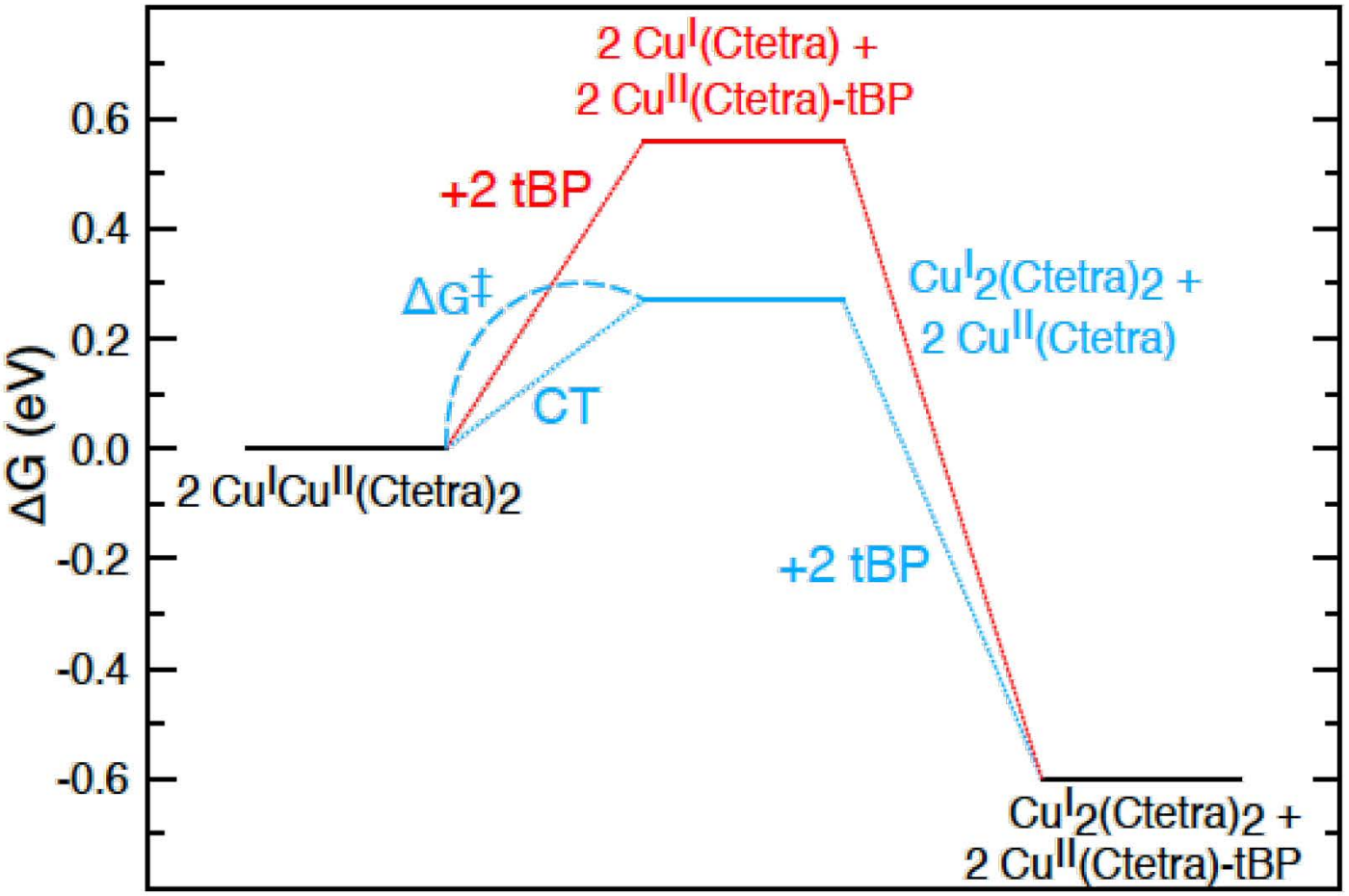
NEW

DYNAMIC Dimer copper redox mediators

- Copper complexes form dimers or monomers depending on metal oxidation states
- Upon single oxidation of two dimers, these undergo disproportionation
- Reduction of Cu(II) monomers to Cu(I) monomers is highly energetically unfavorable
- The stability of the Cu(II) monomer reduces charge recombination in solar cells

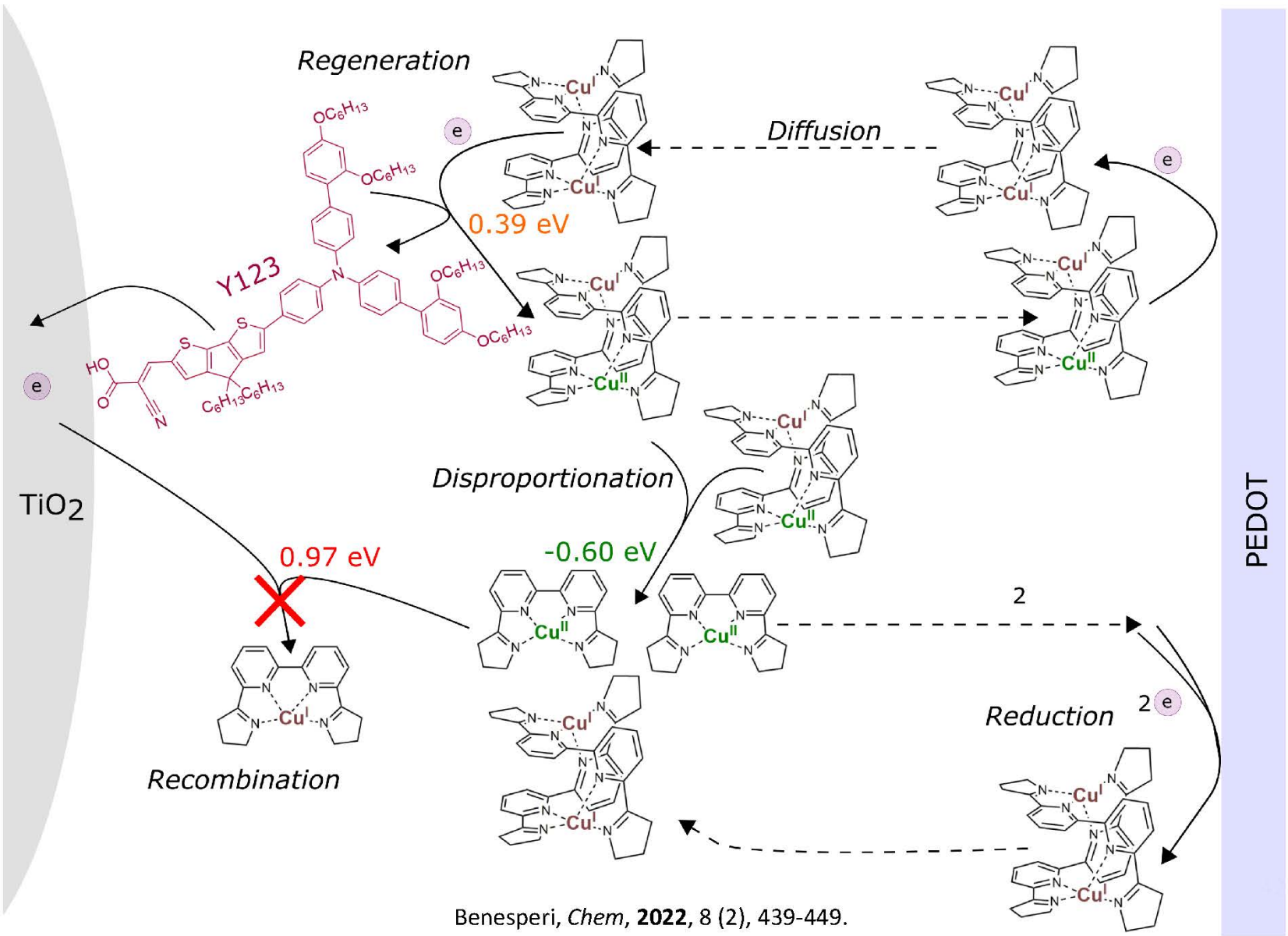


Benesperi, *Chem*, **2022**, 8 (2), 439-449.



Benesperi et al., Chem 8, 439–449.

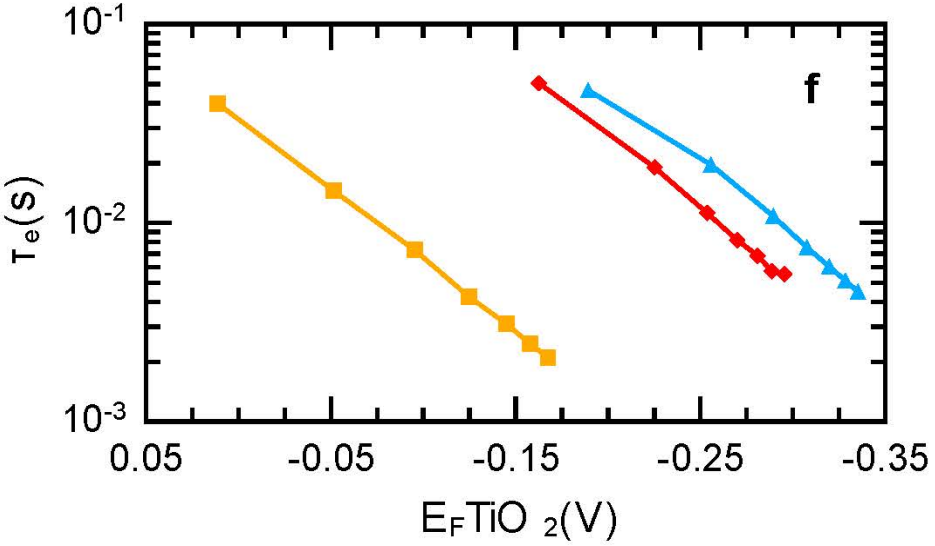
NEW

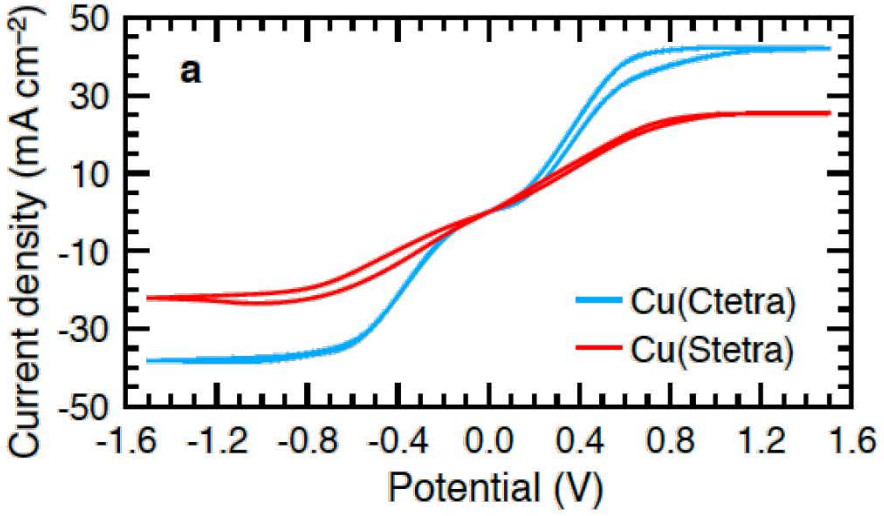


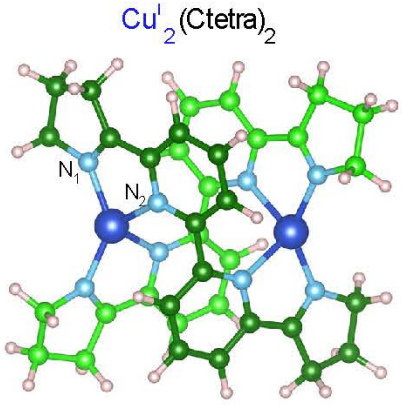
Benesperi, *Chem*, **2022**, 8 (2), 439-449.

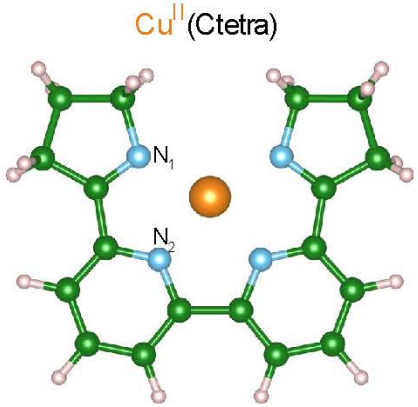
NEW

Dimer copper redox mediators



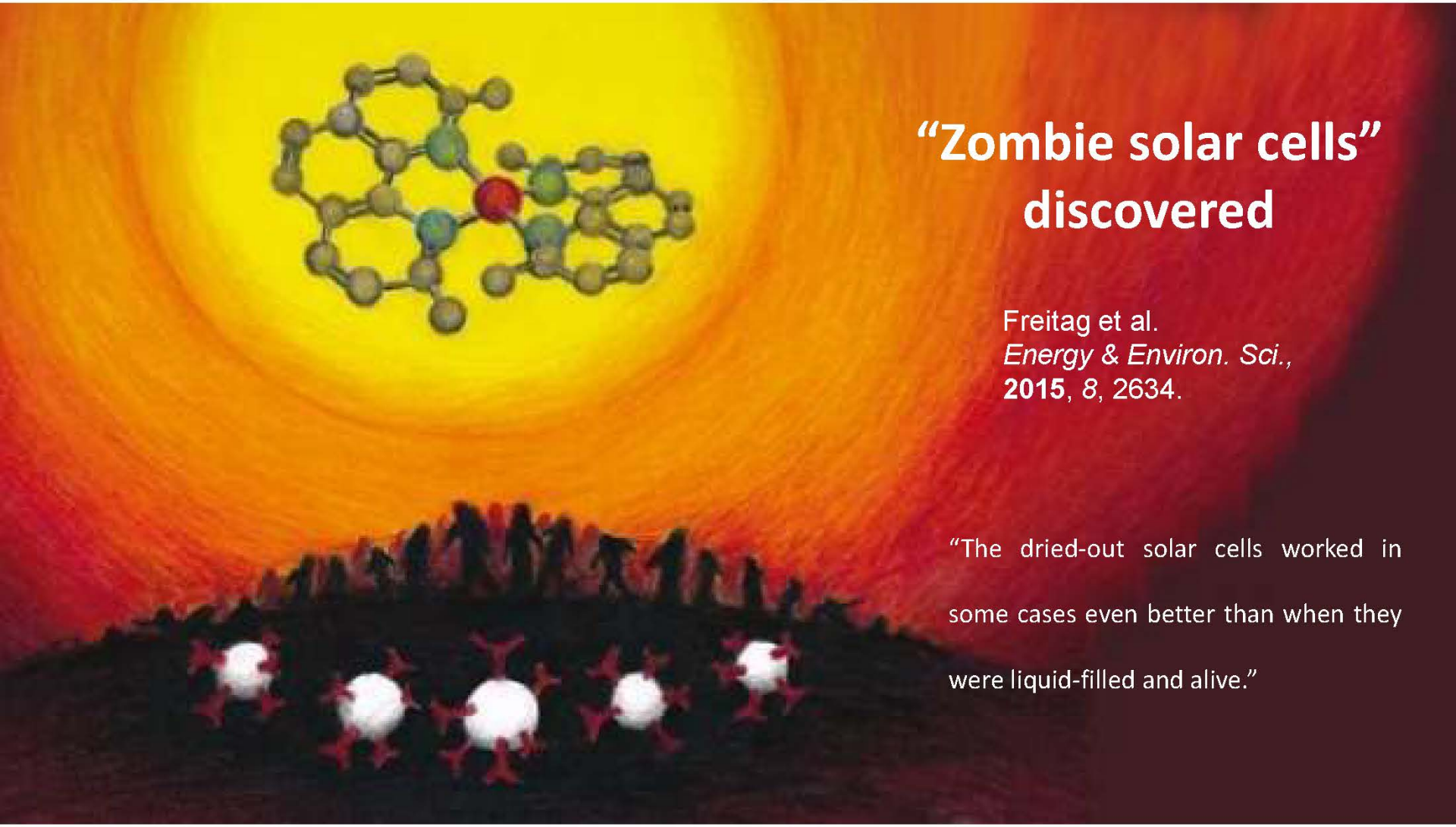






Benesperi, *Chem*, **2022**, 8 (2), 439-449.

Newcastle University

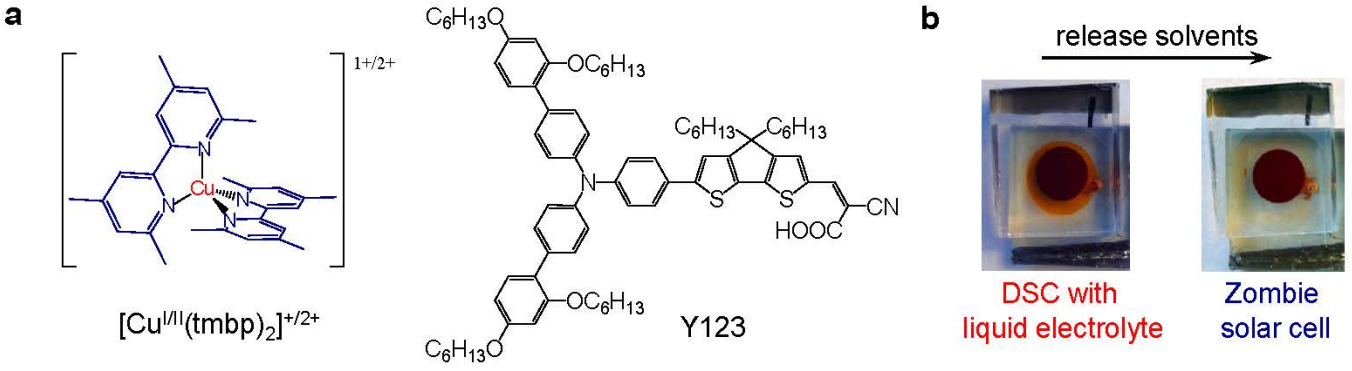


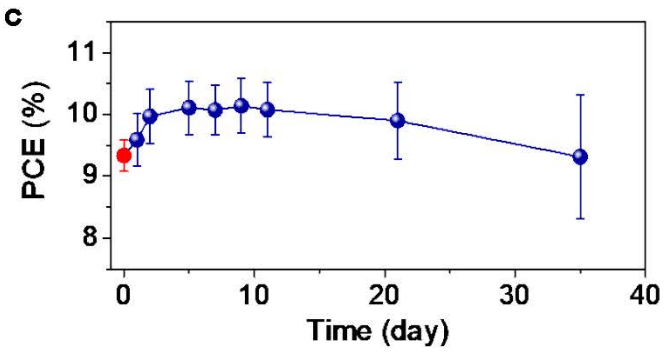
"Zombie solar cells" discovered

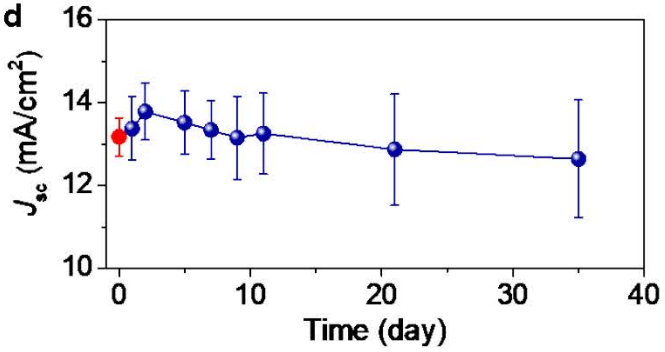
Freitag et al.
Energy & Environ. Sci.,
2015, *8*, 2634.

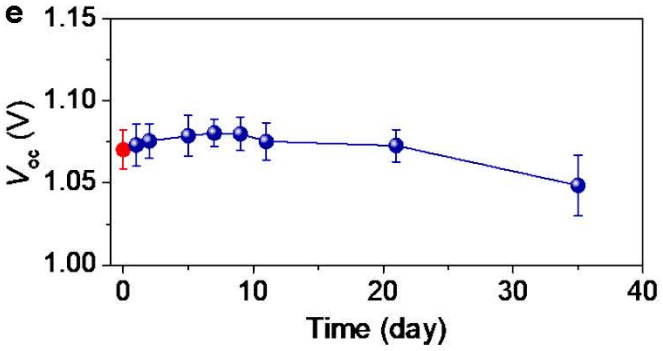
"The dried-out solar cells worked in some cases even better than when they were liquid-filled and alive."

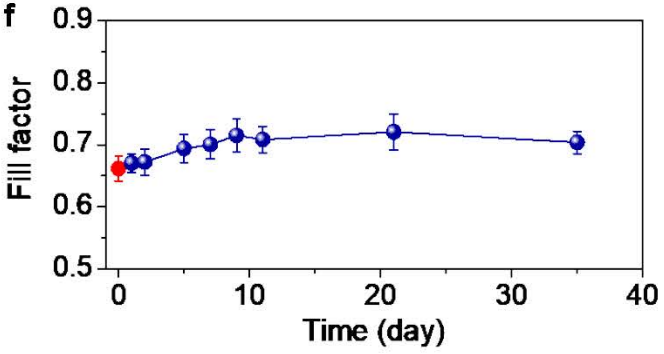
Solid State Charge Transport Materials





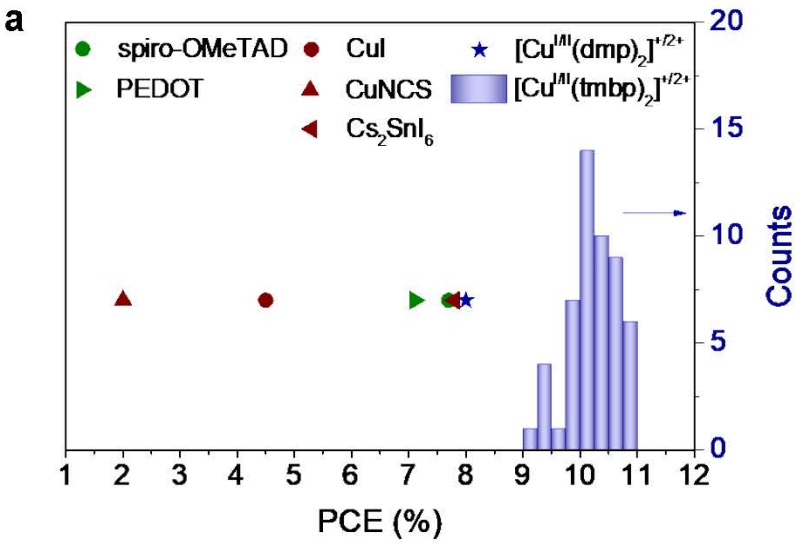


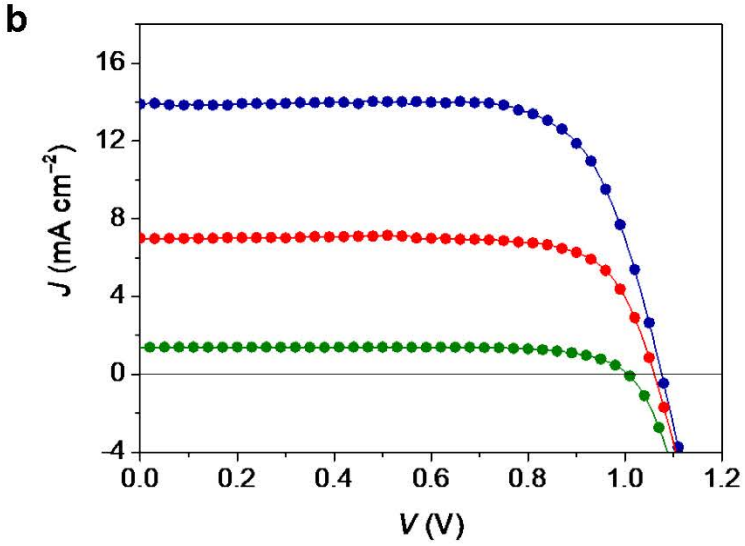


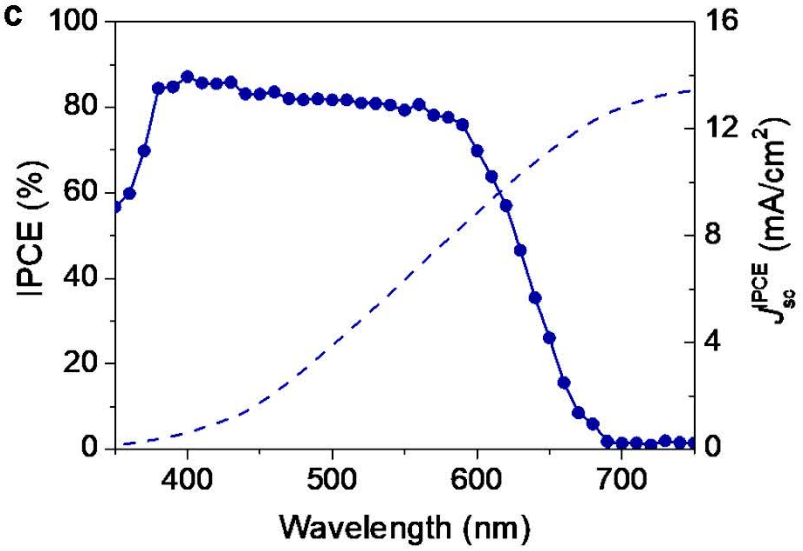


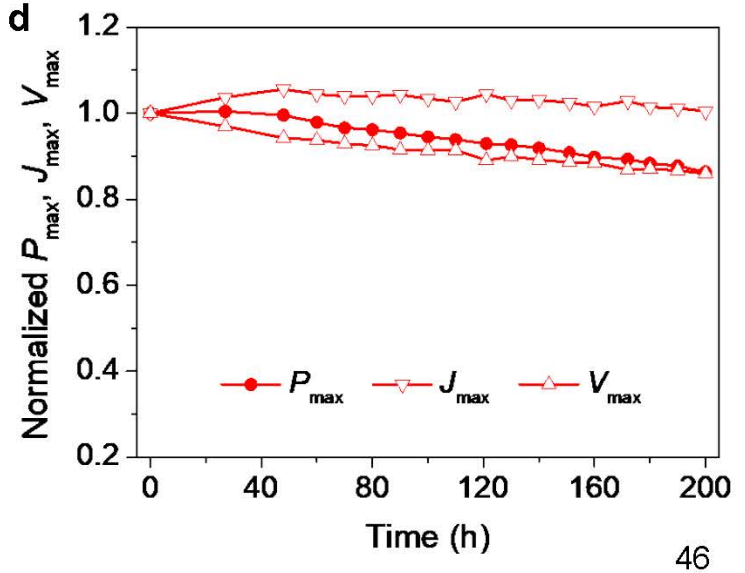
Copper Complexes as HTM

Newcastle University

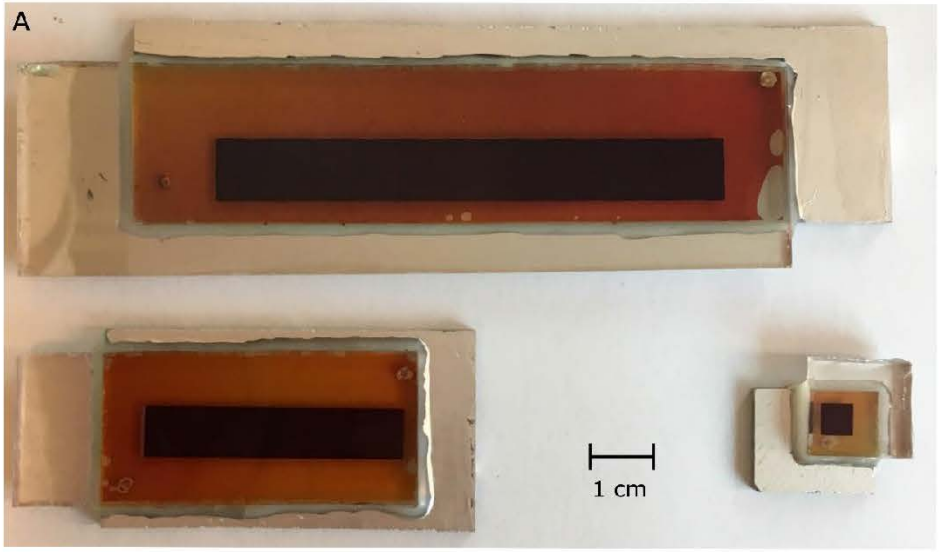


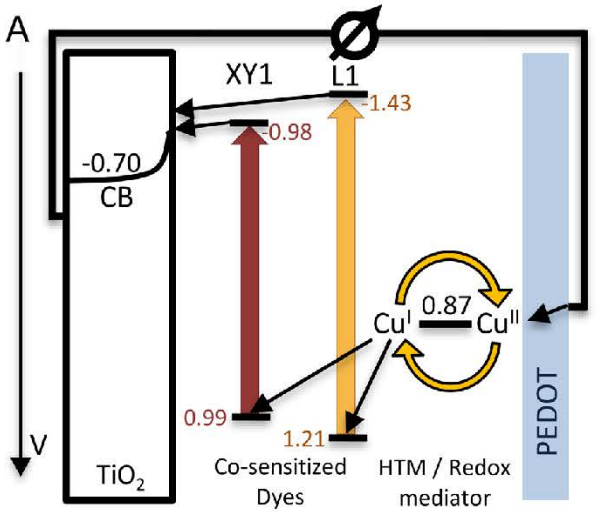


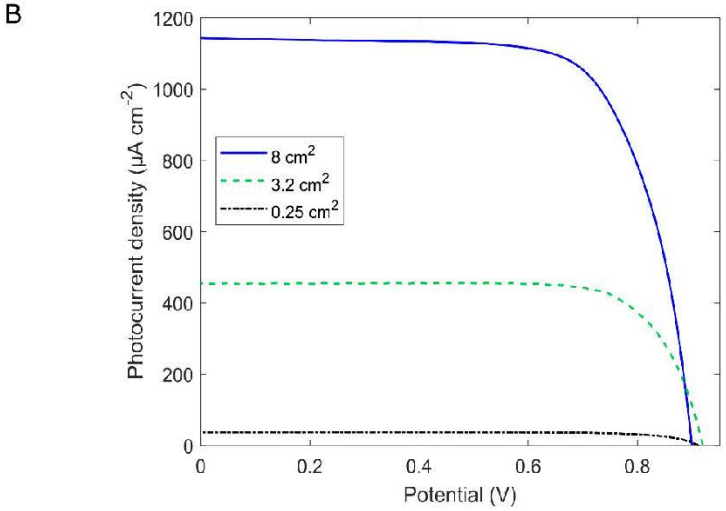




Photoanode Engineering for Lower Recombination



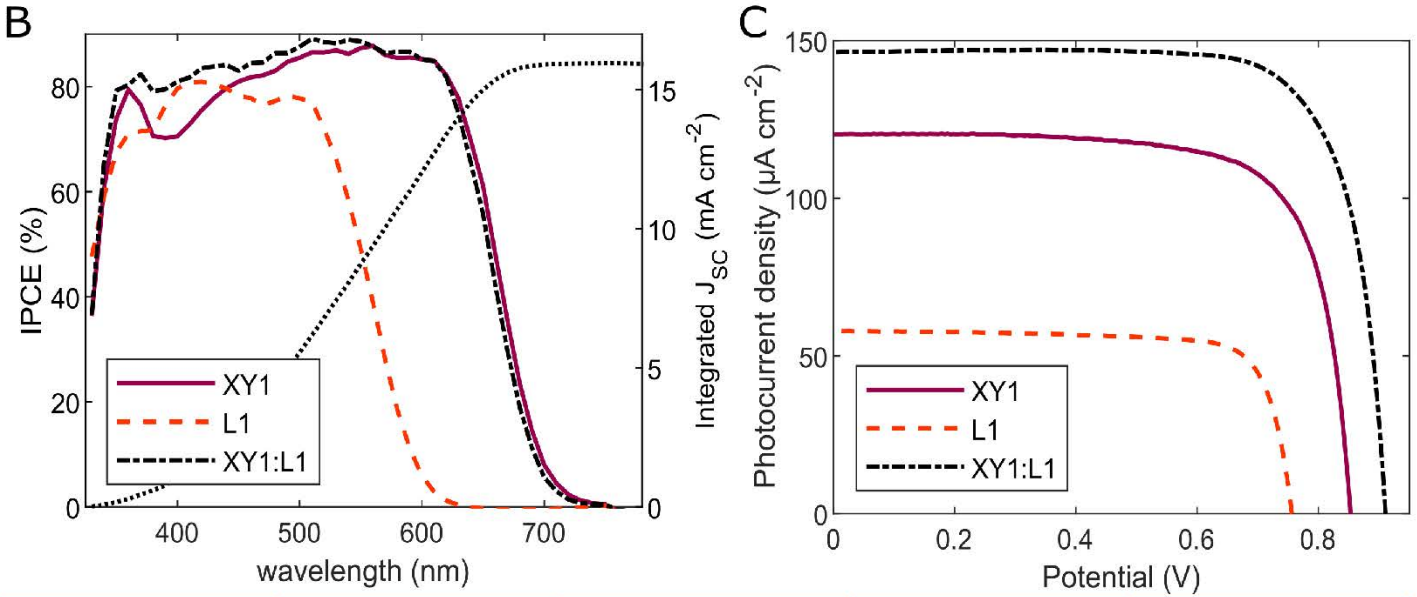




	XY1	L1	XY1:L1	XY1:D35
V_{OC} (mV)	1000 (930)	910 (830)	1080 (980)	1070 (980)
J_{SC} (mA cm^{-2})	13.3 (1.59)	9.4 (1.00)	15.9 (1.80)	15.3 (1.69)
Fill Factor	0.67 (0.80)	0.71 (0.80)	0.67 (0.77)	0.67 (0.77)
PCE (%)	8.9 (11.8)	6.1 (6.7)	11.5 (13.7)	11.0 (13.0)

Chem. Sci., 2020,**11**, 2895-2906

The DSCs for smart IoT



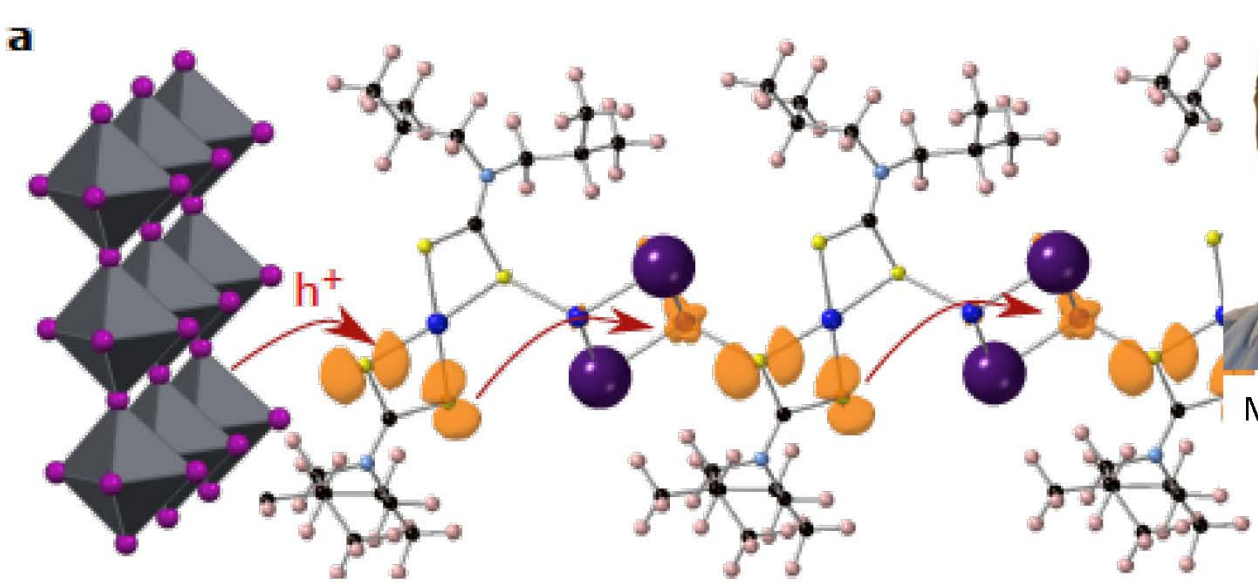
	XY1	L1	XY1:L1	XY1:D35
V_{OC} (mV)	850	750	910	880
J_{SC} (μA) (($\mu A\ cm^{-2}$))	30.0 (120)	14.5 (58)	36.7 (147)	33.0 (132)
Fill Factor	0.74	0.78	0.77	0.77
P_{max} (μW) (($\mu W\ cm^{-2}$))	18.9 (75.4)	8.6 (34.4)	25.7 (103.1)	22.4 (89.4)
PCE (%)	24.9	11.3	34.0	29.5

Chem. Sci., 2020,**11**, 2895-2906

Max theoretical energy available (office): ~150 μW cm^{-2}

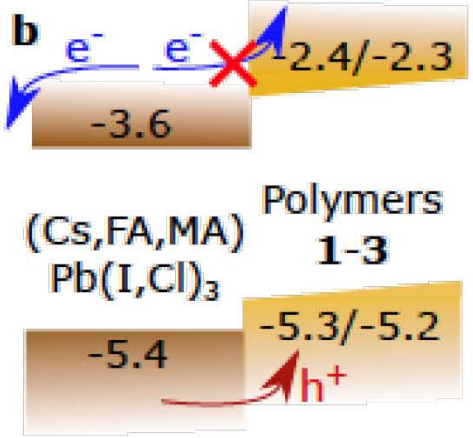
Copper coordination polymers with selective hole conductivity

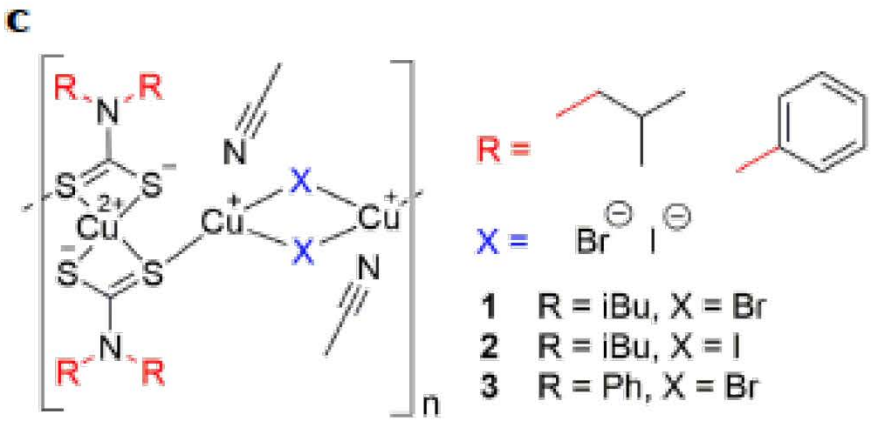
Newcastle University



Matthias J Golomb & Aron Walsh

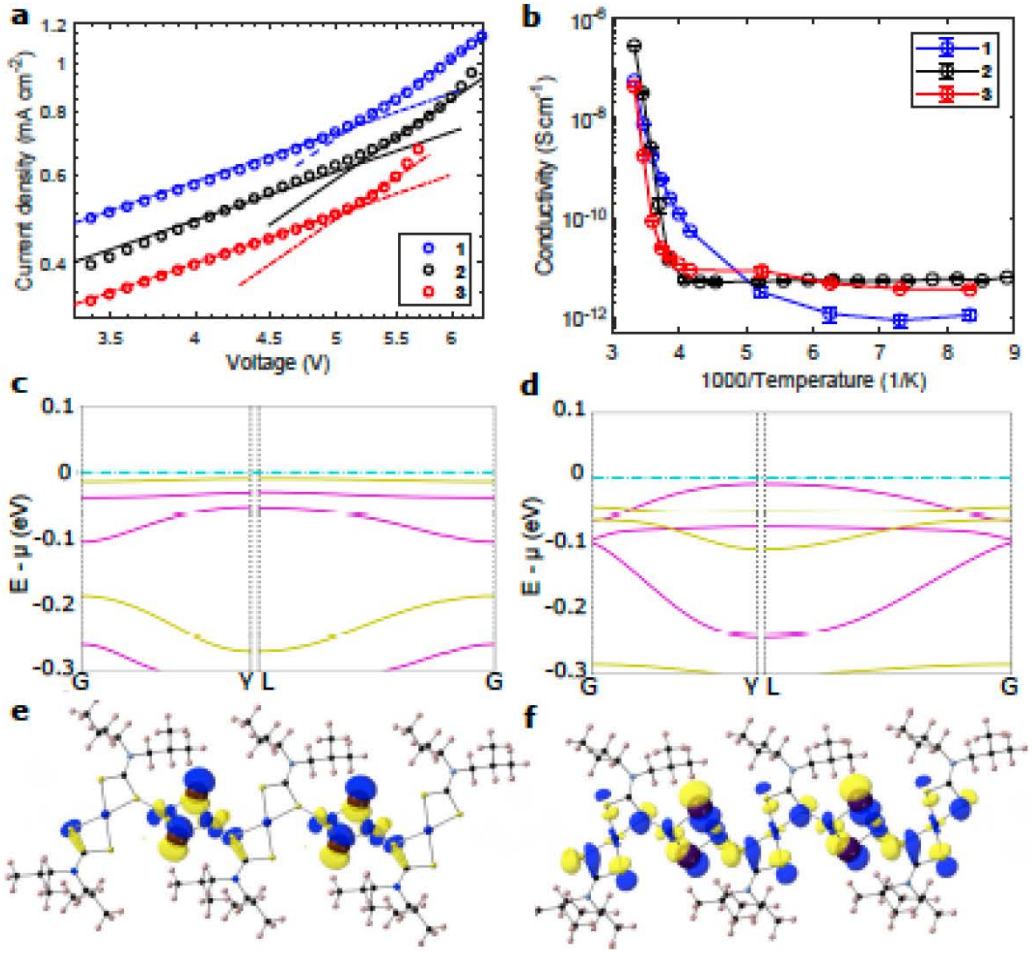
Imperial College London





Just accepted in JMCA

Solid State Charge Transport Materials



H. Michaels, M. J. Golomb, B. Kim, T. Edvinsson, F. Cucinotta, P. G. Waddell, M. Probert, S. J. Konezny, G. Boschloo, A. Walsh and M. Freitag, J. Mater. Chem. A, 2022,

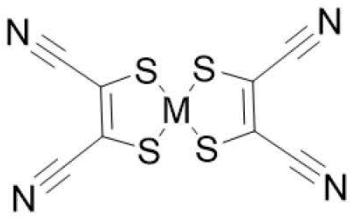
Solid State Charge Transport Materials

	RT conductivity ($S\ cm^{-1}$)	E_A (eV)	ln(*A*)	μ_h ($cm^2\ (Vs)^{-1}$)
Spiro-MeOTAD (Li/tBP/Co)	$3.7\ 10^{-4}$ ($5\ 10^{-4}$) [41]	0.371	0.144	$4.0\ 10^{-4}$ ($4\ 10^{-4}$) [42]
Spiro-MeOTAD (pristine)	$1\ 10^{-7}$ ($5\ 10^{-7}$) [42]	0.503	-0.148	$8\ 10^{-5}$ ($1.6\ 10^{-4}$) [42]
1 (tBP)	$3.9\ 10^{-6}$	1.29	2.68	$1.1\ 10^{-4}$
2 (tBP)	$1.0\ 10^{-3}$	1.68	4.33	$5.8\ 10^{-4}$
3 (tBP)	$4.9\ 10^{-6}$	2.01	4.34	$2.4\ 10^{-4}$

The copper coordination polymers present a unique class of sustainable, high-performing hole conducting materials.

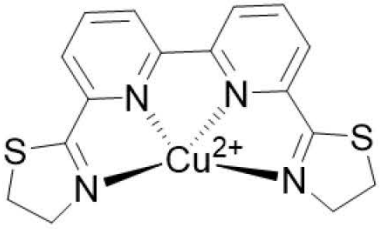
H. Michaels, M. J. Golomb, B. Kim, T. Edvinsson, F. Cucinotta, P. G. Waddell, M. Probert, S. J. Konezny, G. Boschloo, A. Walsh and M. Freitag, J. Mater. Chem. A, 2022,

Salty Stuff

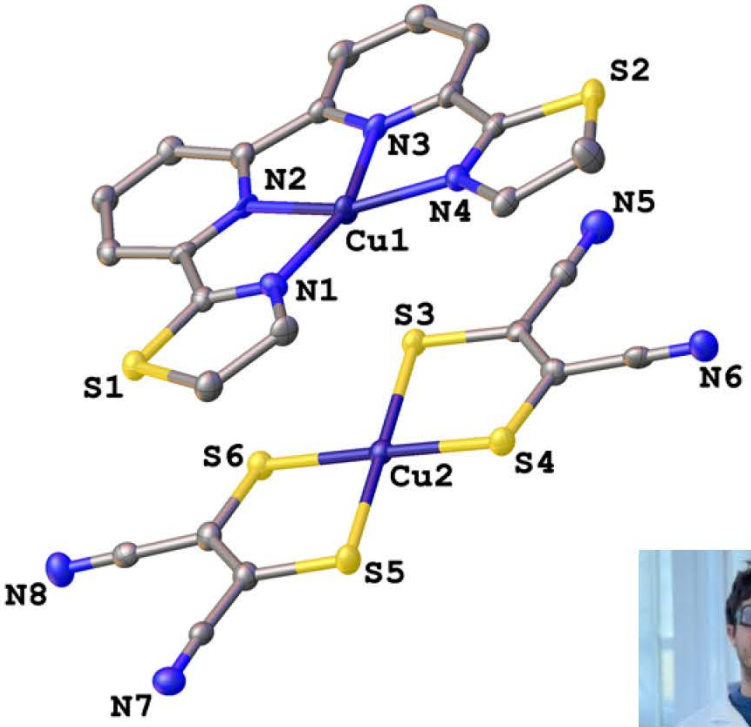


$M(mnt)_2$

$M = Cu^{2+}, Ni^{2+}$



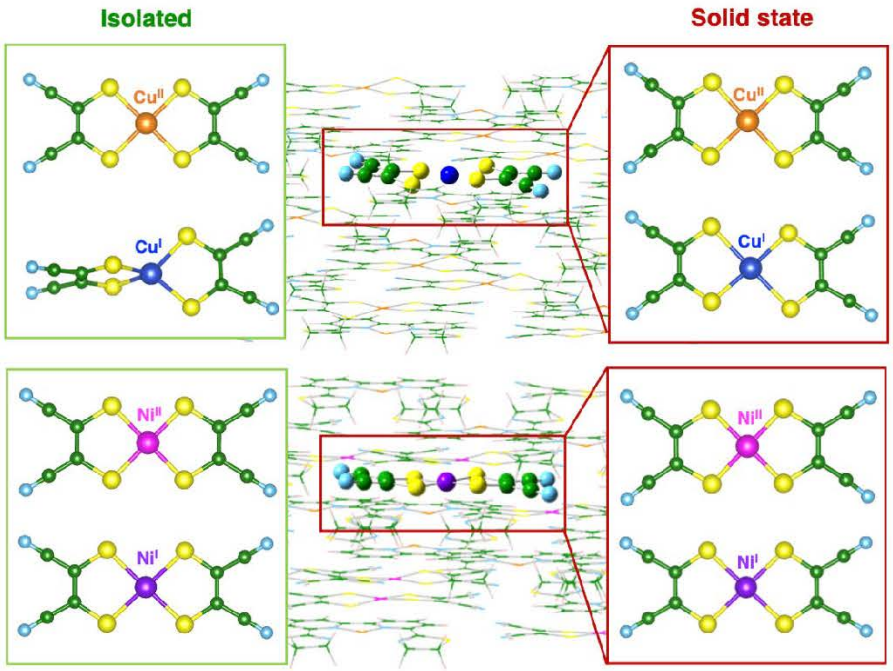
Cu(Stetra)



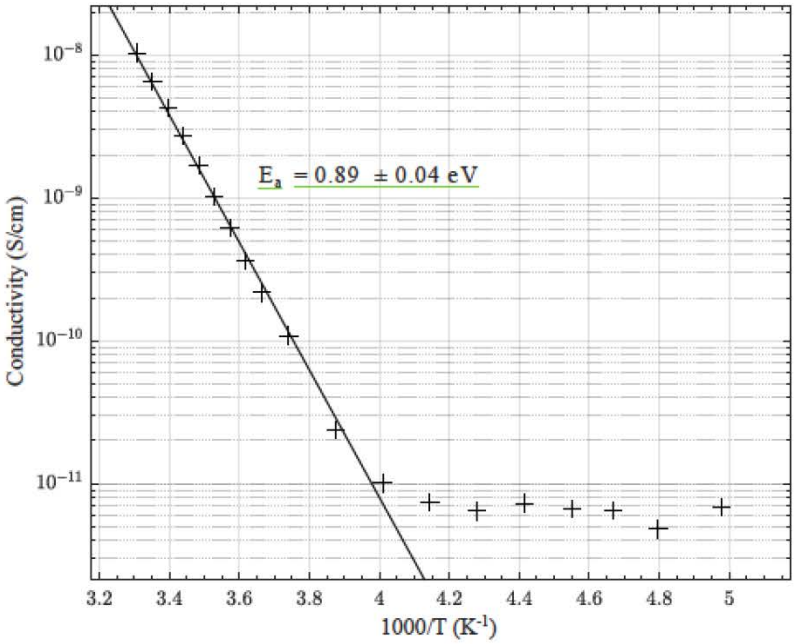
Giovanni Spinelli

In manuscript
be kind ☺

Salty Stuff

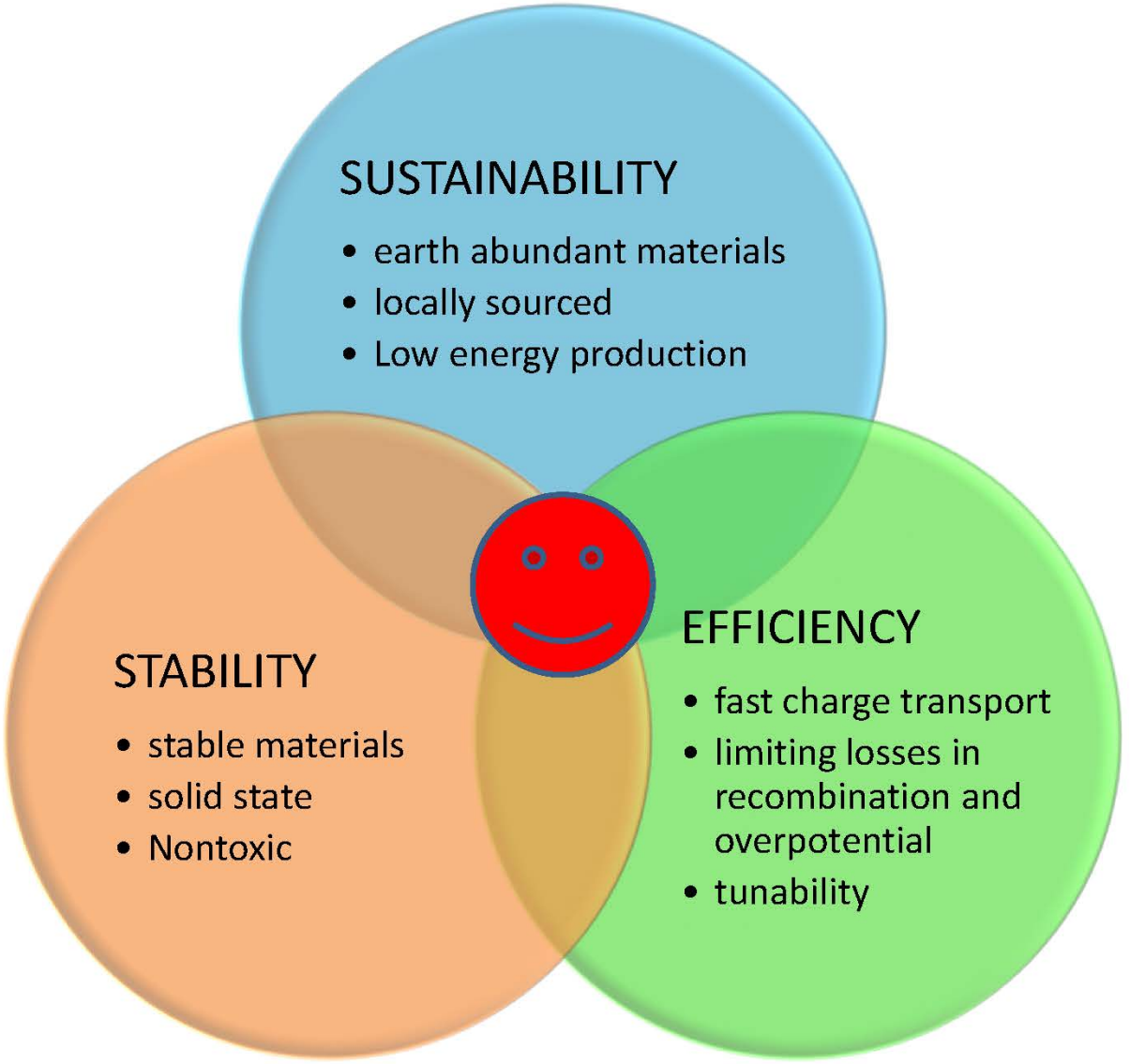


Minimum energy structures of CuII(mnt)2 and CuI(mnt)2 com plexes both as isolated moieties and within the Cu-Cu crystal



Arrhenius plot for Cu-Cu compound displaying clear semiconductor behavior.

What can chemistry fix ?



52% ambient
28% solar

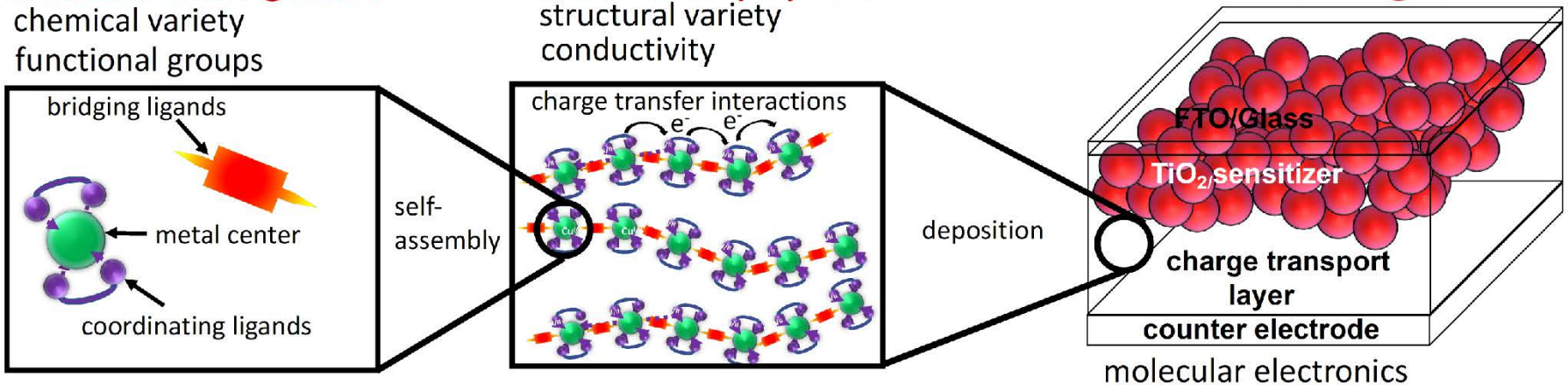
SNEAK PEAK

Newcastle University

molecular building blocks
chemical variety
functional groups

coordination polymers
structural variety
conductivity

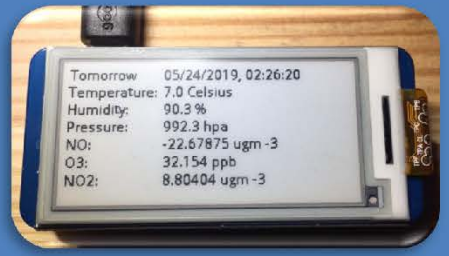
device integration



molecular electronics

Goals
- Efficient, sustainable and stable functional materials

Action needed now
- Developing new technologies and materials



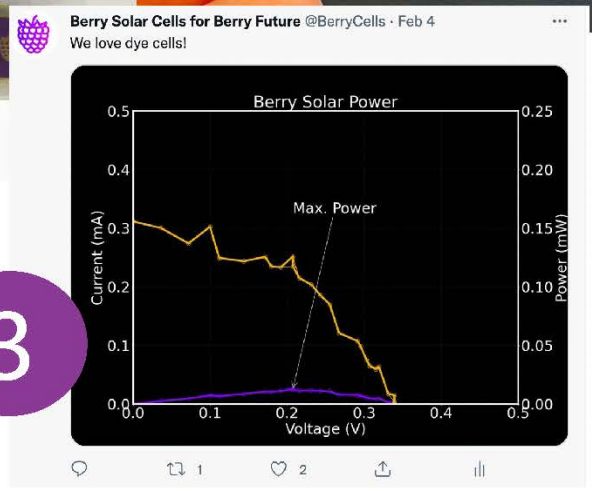
Create new breakthroughs
- Integrate high shares of light harvesting to power smart systems

BERRY SOLAR CELLS

FREITAG LAB

Newcastle University

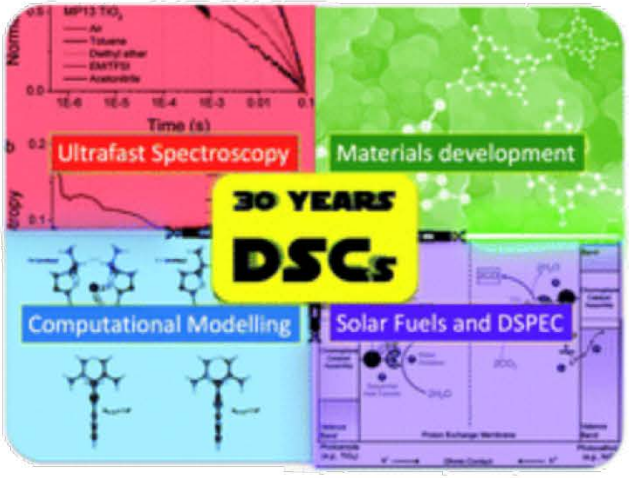
WWW.BERRYCELLS.COM



Dye-sensitized solar cells strike back

Ana Belén Muñoz-García, Iacopo Benesperi, Gerrit Boschloo, Javier J. Concepcion, Jared H. Delcamp, Elizabeth A. Gibson, Gerald J. Meyer, Michele Pavone, Henrik Pettersson, Anders Hagfeldt and Marina Freitag

Dye-sensitized solar cells (DSCs) are celebrating their 30th birthday and they are attracting a wealth of research efforts aimed at unleashing their full potential. Righteous font designed by Astigmatic and licensed under the Open Font License.



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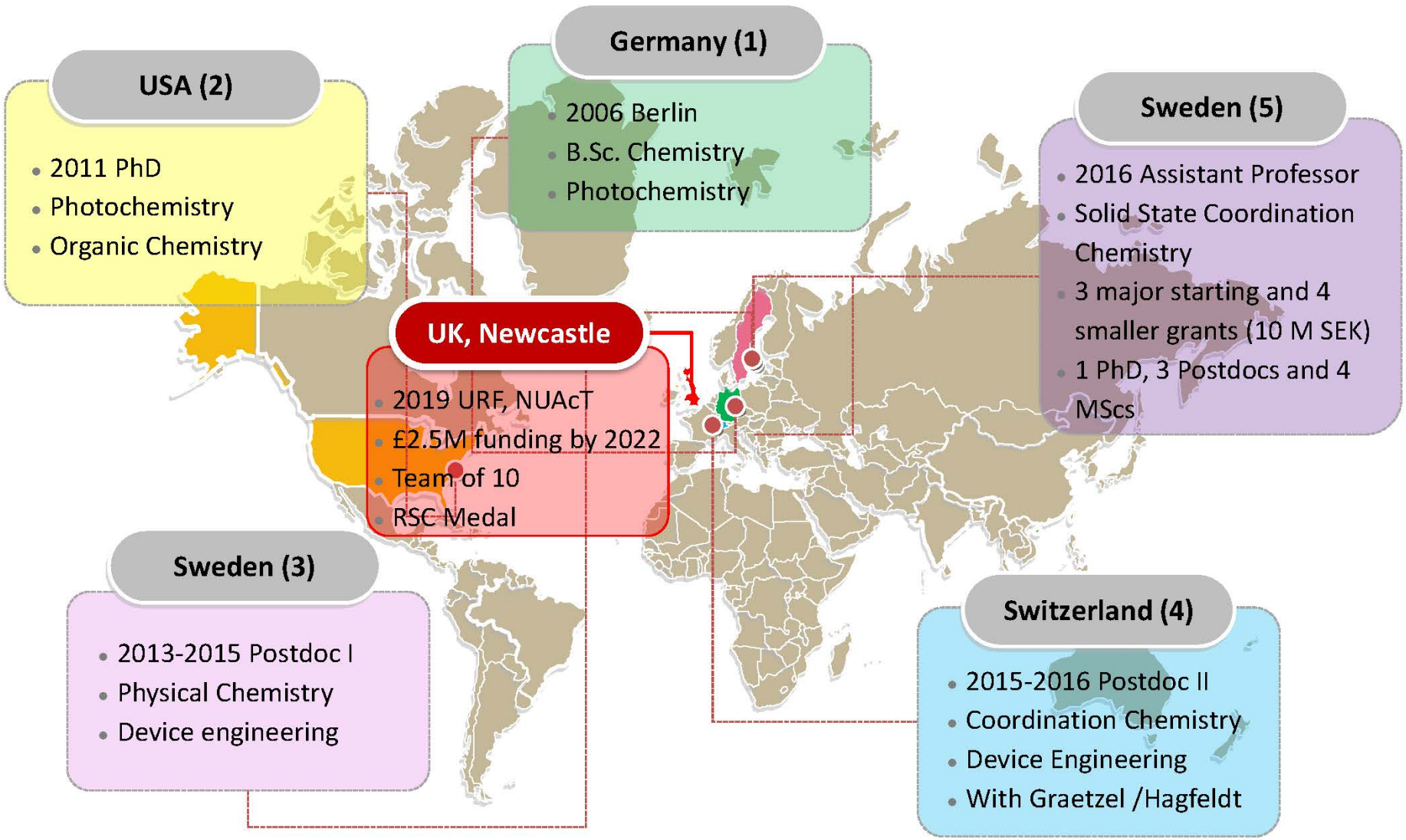
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2011 PhD
Photochemistry
Organic Chemistry
Germany (1)
2006 Berlin
B.Sc. Chemistry
Photochemistry
Sweden (5)
2016 Assistant Professor
Solid State Coordination Chemistry
3 major starting and 4 smaller grants (10 M SEK)
1 PhD, 3 Postdocs and 4 MScs
UK, Newcastle
2019 URF, NUAcT
£2.5M funding by 2022
Team of 10
RSC Medal
Sweden (3)
2013-2015 Postdoc I
Physical Chemistry
Device engineering
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