Charge-Transfer complexes and their applications

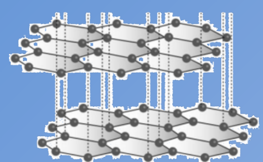
Chun-Sing LEE

Department of Chemistry &
Center of Super-Diamond and Advanced Film,
City University of Hong Kong

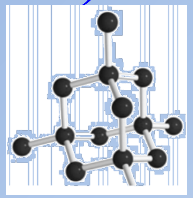
8 April 2021

How to obtain new material properties?

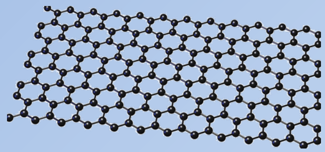
- Chemical reaction: $2H_2 + O_2 \rightarrow 2H_2O$
- Different allotropes (forms/crystal structure):



Graphite → (Hi T + Hi P) → Diamond



Graphite → (Electric arc) → Graphene



https://www.elevise.co.uk/g-o-gc-h-p1-s1-q17-a.html

https://analyticalscience.wiley.com/do/10.1002/gitlab.15487/full/

- Extreme small sizes: → Nanotechnology

*Gold particles of 2 → 150 nm

- "Mixing" of "some" molecules to form CTCs.

*http://www.malvern.com/LabEng/industry/nanotechnology/gold_silver_nanoparticles.htm

Outline

- What is charge transfer complex (CTC)?
- Characteristic signatures of CTCs.
- Why CTC is important in optoelectronic devices?
- Examples on CTCs' optoelectronic applications.
- Biomedical applications of CTCs.
- Energy & environmental applications.
- Conclusion.

What is Charge Transfer Complex (CTC)

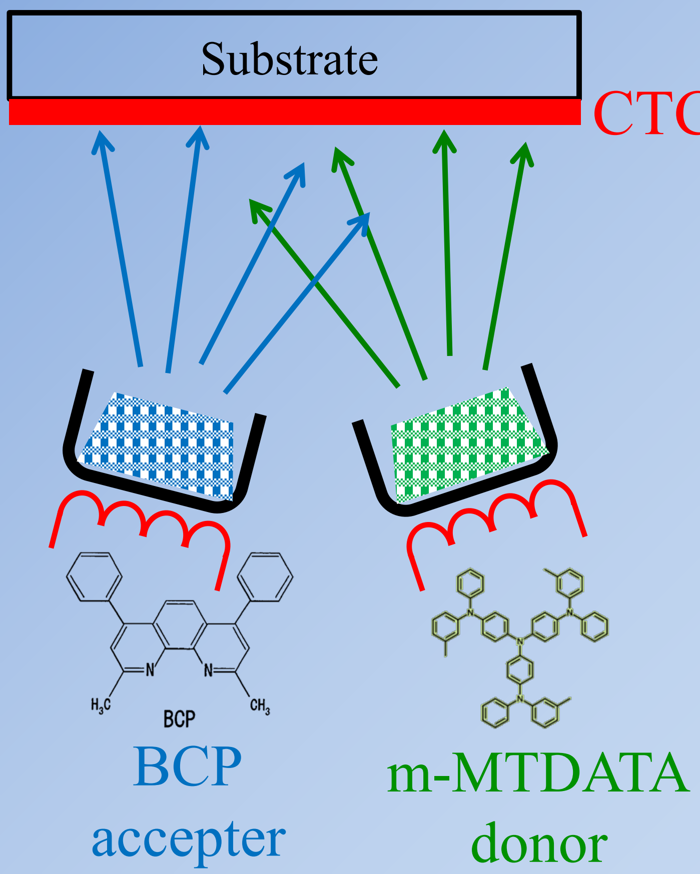
- Many related terminologies:
  - Charge transfer state (Thompson);
  - Germinated polaron pairs (Friend);
  - Charge-transfer excitons, Interfacial geminate charge pair etc.
- No precise definition agree by all.
- Adopt a simple definition:

Substantial charge transfer between ***donor*** & **acceptor** to give ***different properties*** from parents → CTC

How to make CTC & it 1st signature quenching of photoluminescence (PL)

Often accompanied by ***red-shifted & board emission peaks***

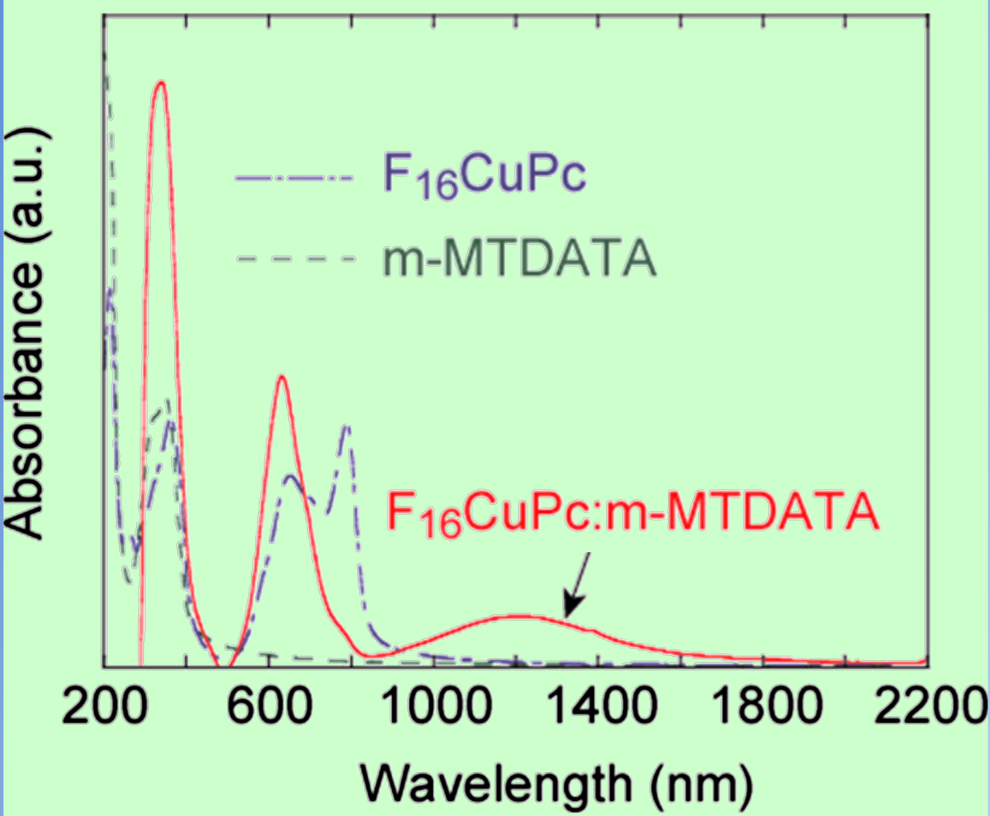
How do we know that they form CTC instead of simple physical mixing?



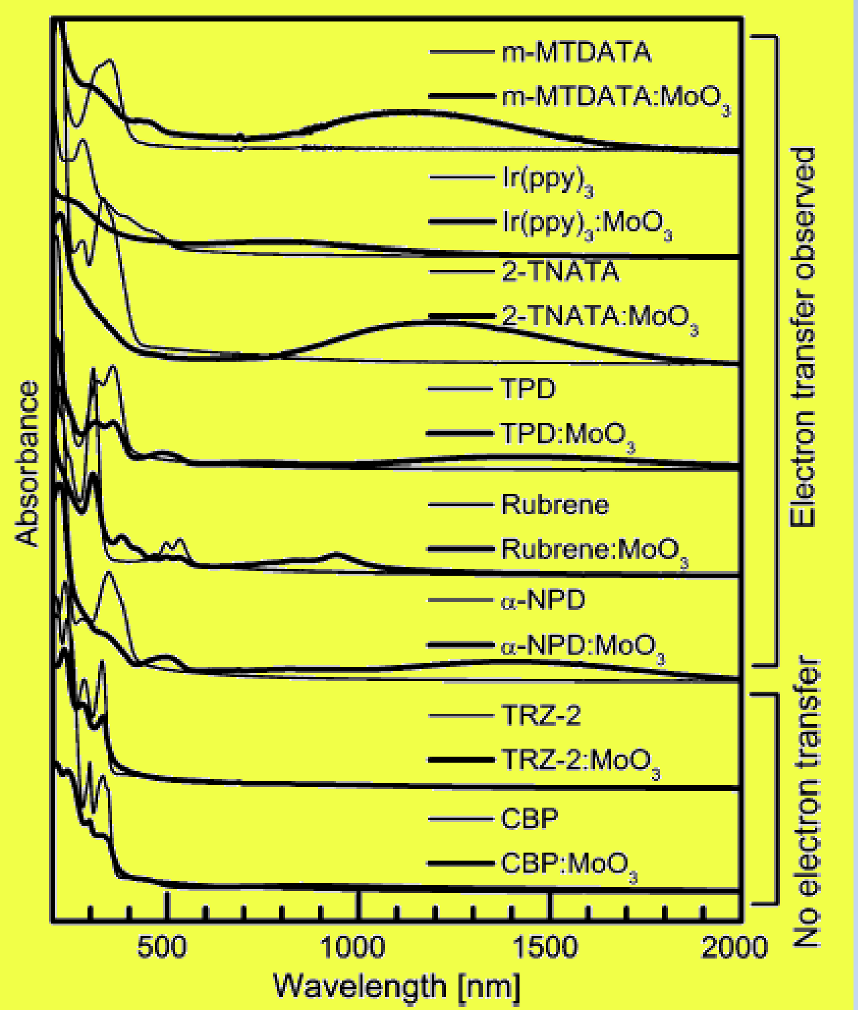
W. L. Li, et. al. J. Luminescence. 17, 451 (2007)
W. L. Li, et. al. Adv. Mater. 13, 1241 (2001)

Identification of CTC

- New long wavelength absorption band
- Also organic + inorganic



Adachi, et al. J. Appl. Phys. 105, 114502 (2009)



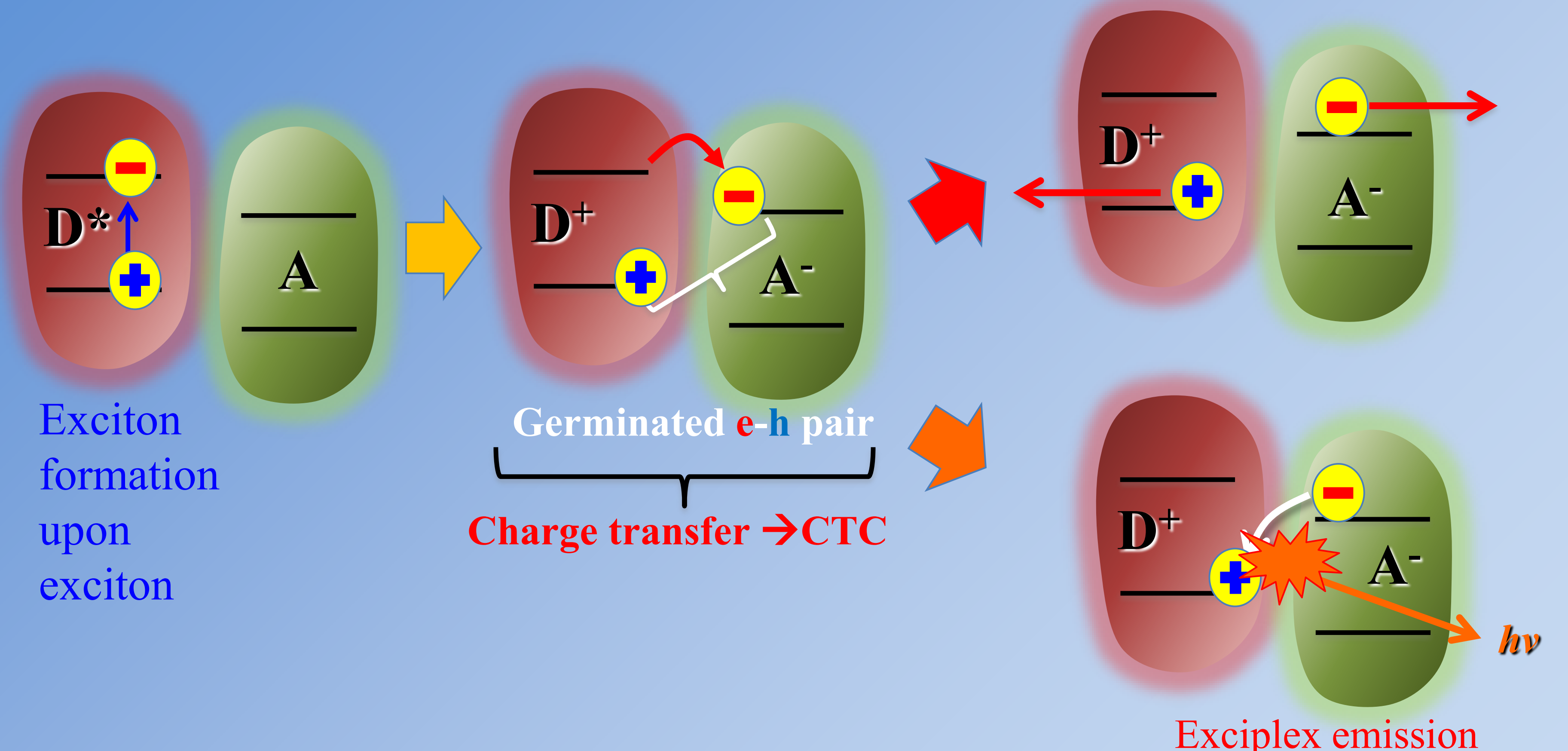
H. Murata, et al. Org. Electron. 12, 520 (2011)

Outline

- What is charge transfer complex (CTC)?
- Characteristic signatures of CTCs.
- Why CTC is important in optoelectronic devices?
- Examples on CTCs' optoelectronic applications.
- Biomedical applications of CTCs.
- Energy & environmental applications.
- Conclusion.

CTC – Photovoltaic vs Exciplex Emission

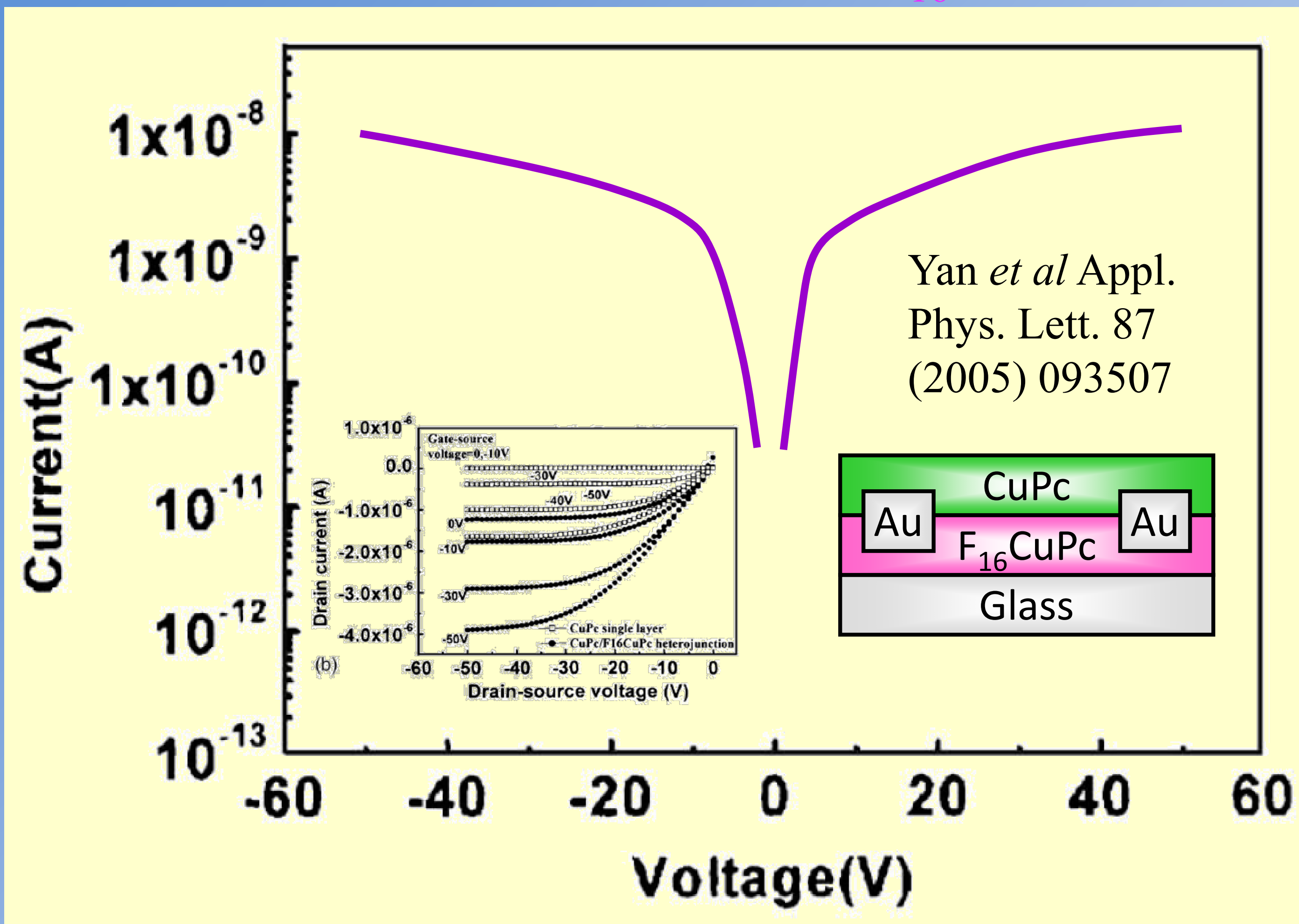
- Red-shifted & broadened emission & absorption.
- Small energy gaps then parents.
- Influences both photovoltaic & emission.



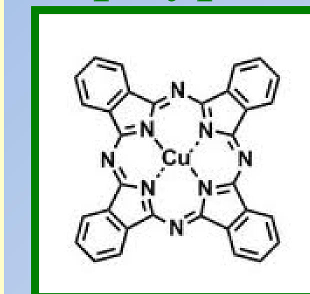
CityU Department of Chemistry
香港城市大學
City University of Hong Kong

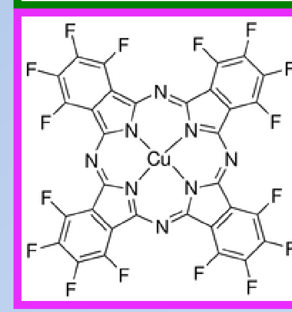
Electronic Applications – Ambipolar Transistor

- Yan et al reported the 1st organic ambipolar thin film transistor.
- With a new device structure with a $F_{16}CuPc$/CuPc junction.



Donor
p-type



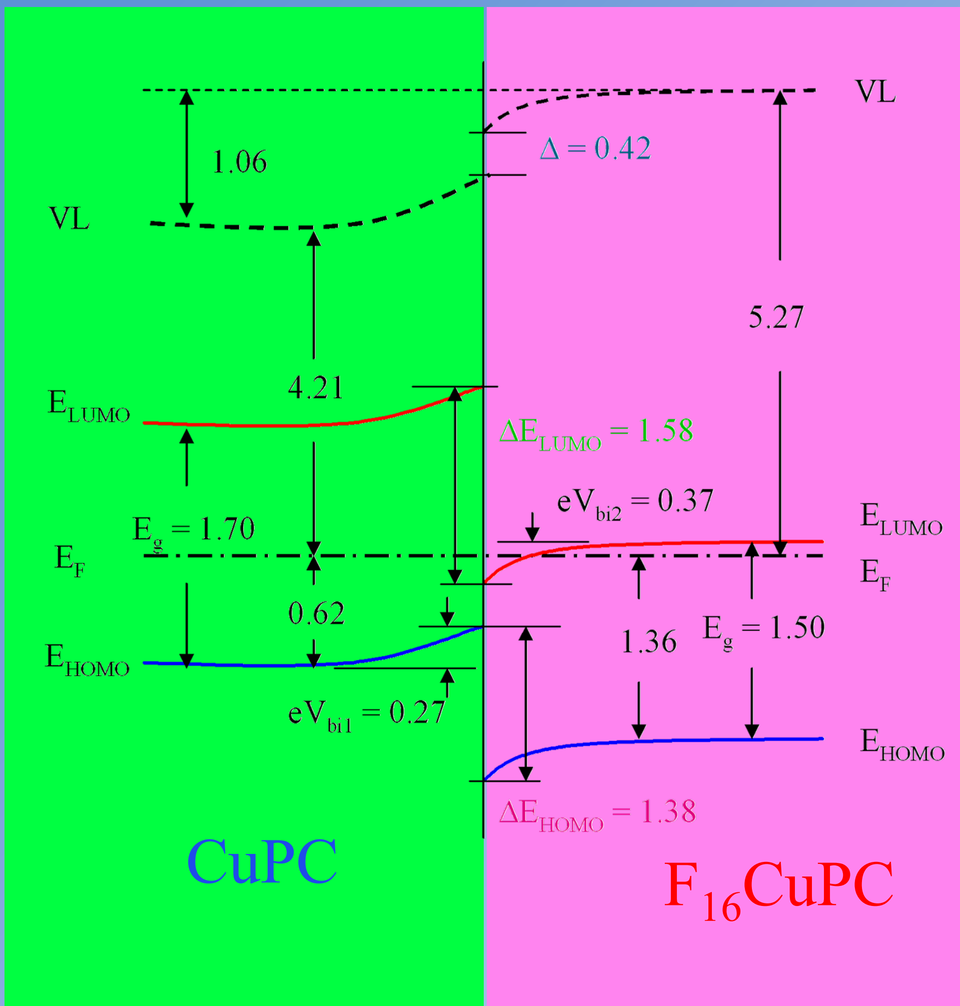


Acceptor
n-type

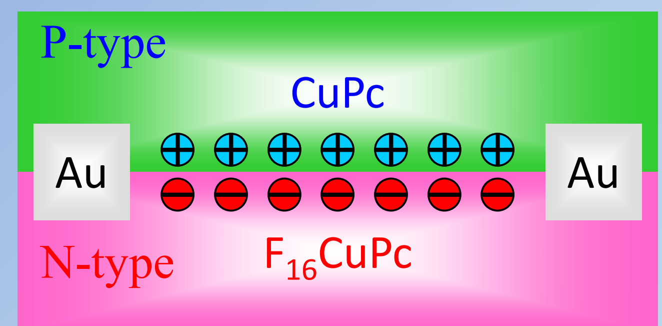
Yan *et al* Appl. Phys. Lett. 87 (2005) 093507

Ultrahigh carrier densities at CTC interface

Ultraviolet photoelectron spectroscopy (UPS):



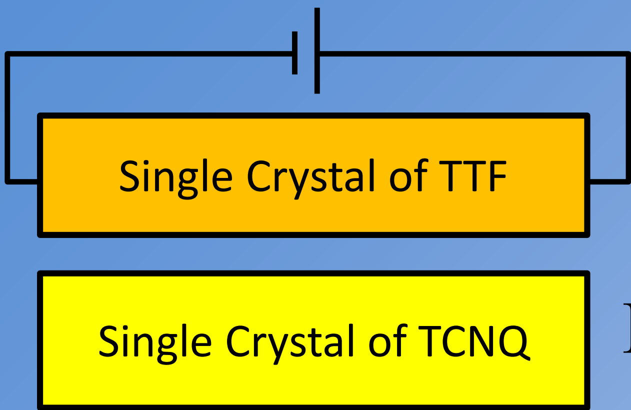
- Significant band bending.
- Carrier density estimated to be 10^{18} cm^{-3}.
- 6 order higher than typical organics.



- Free holes and electrons in CuPc and $F_{16}CuPc$ can be easily driven along the interface by an electric field applied across the drain and source electrodes

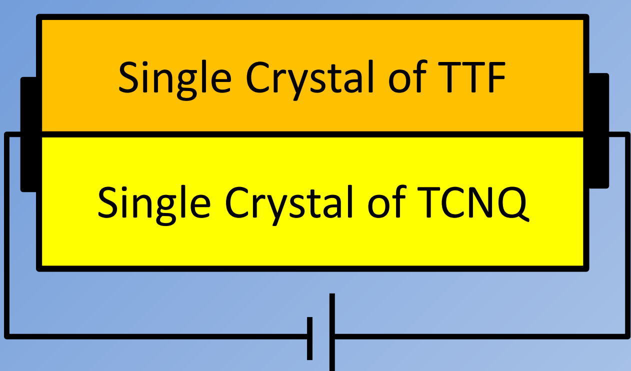
Lau & Lee *et al* Appl. Phys. Lett. 88 (2006) 173513

Identification of CTC –Abnormally high conductivity

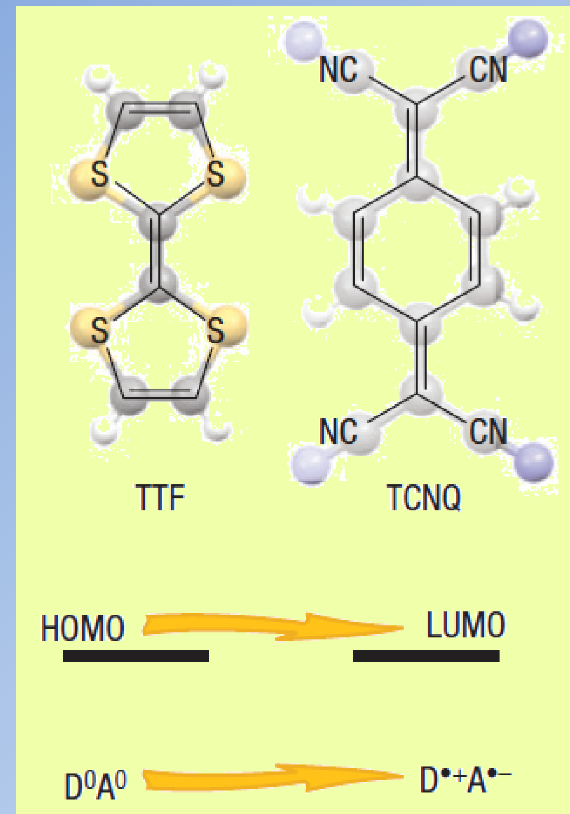


R > 1GΩ

Mechanically pressed together

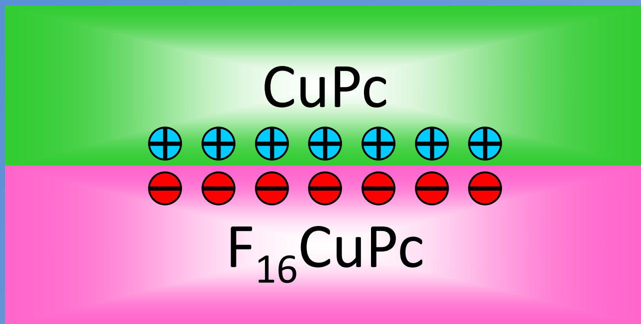


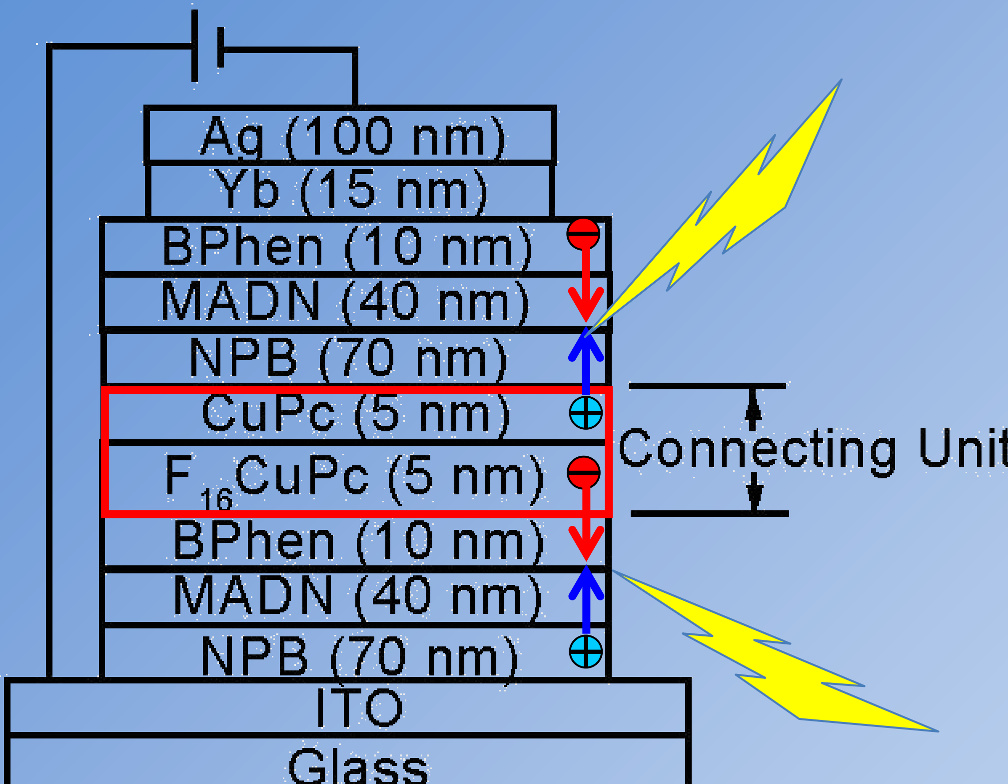
R < 100kΩ

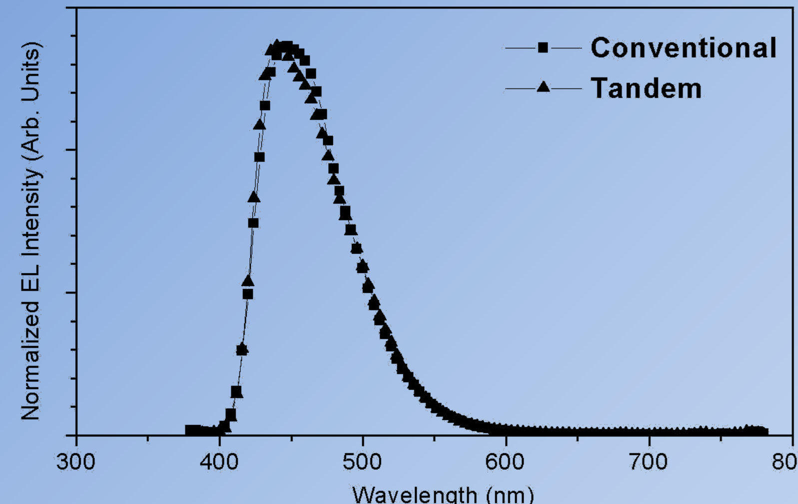


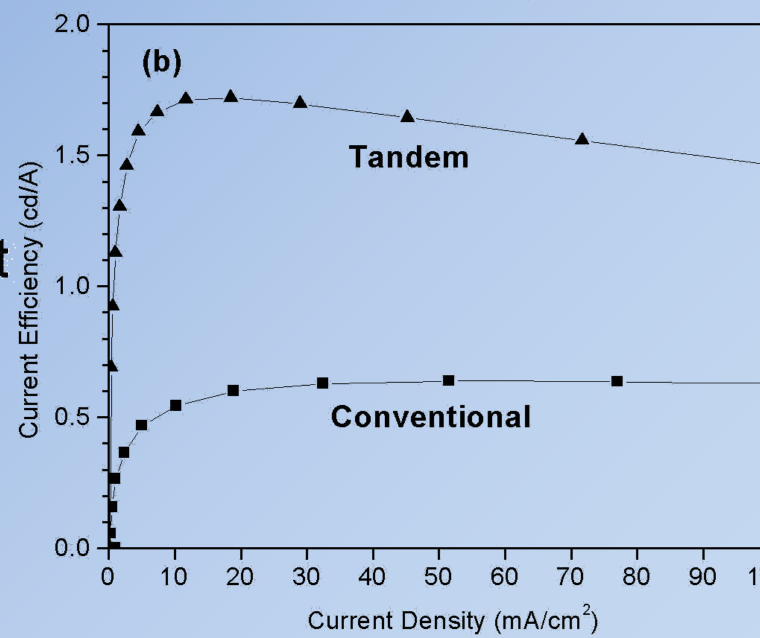
H. Alves et al , Nature Mater. 7, 574 (2008)

CTC used as connecting unit in tandem OLED









Lai & Lee at al, J. Appl. Phys. 101, 014509 (2007).

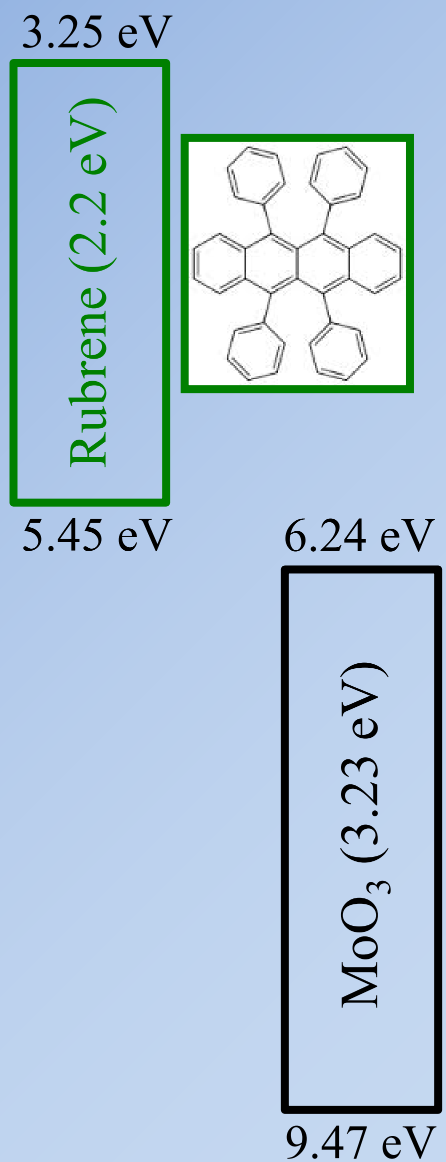
Department of Chemistry
香港城市大學
City University of Hong Kong

Application of CTC in photovoltaic devices

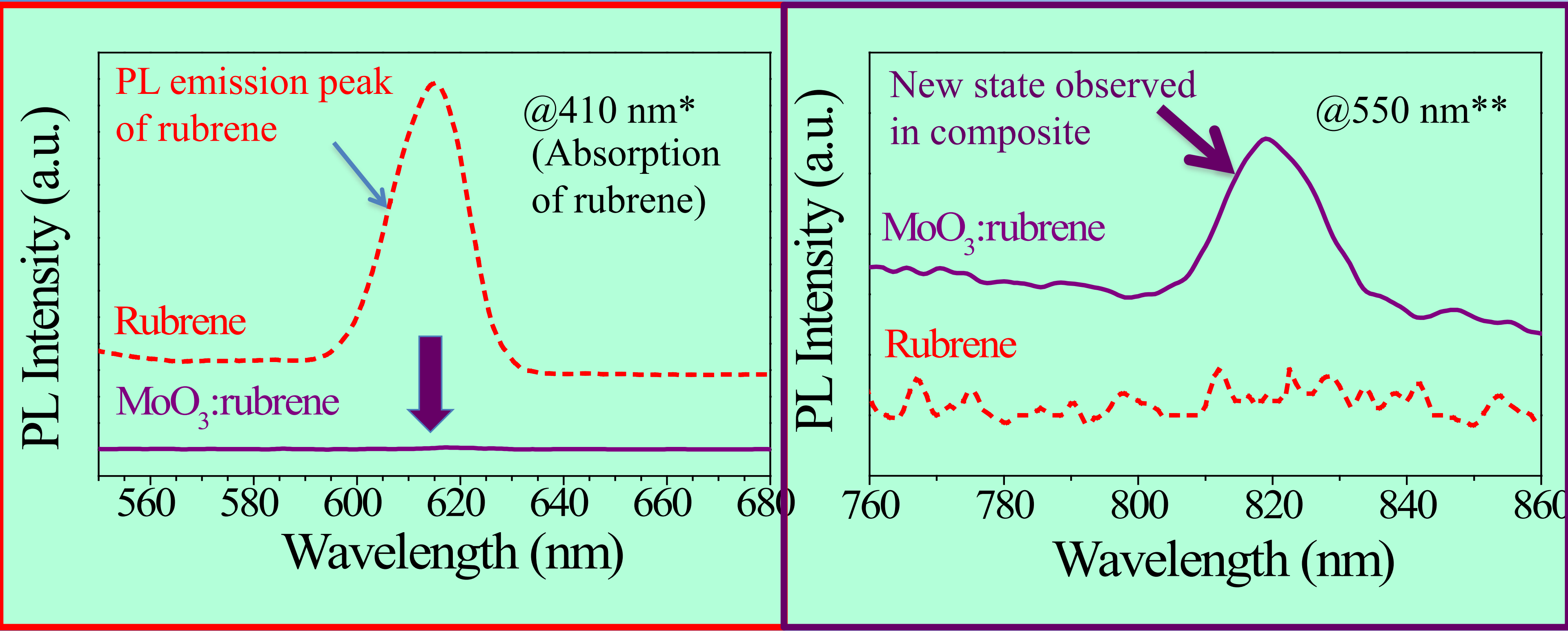
- CTC → new absorption peaks at long wavelength.
- Not applied in any device.
- We explore the possibility IR photovoltaic device using CTC.

- We choose a pairs of wide energy gap materials:
  - Rubrene $+MoO_3$.

Rubrene: Donor; MoO_3: Acceptor



Evidence of CTC in MoO_3:Rubrene

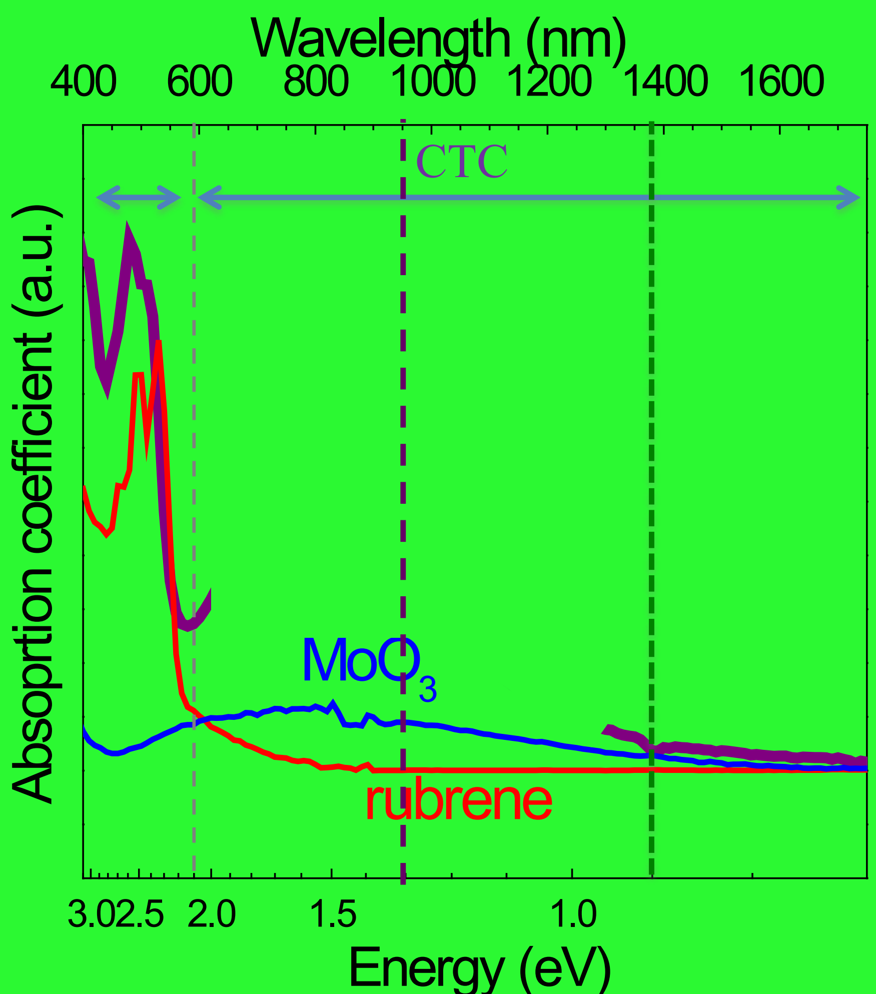


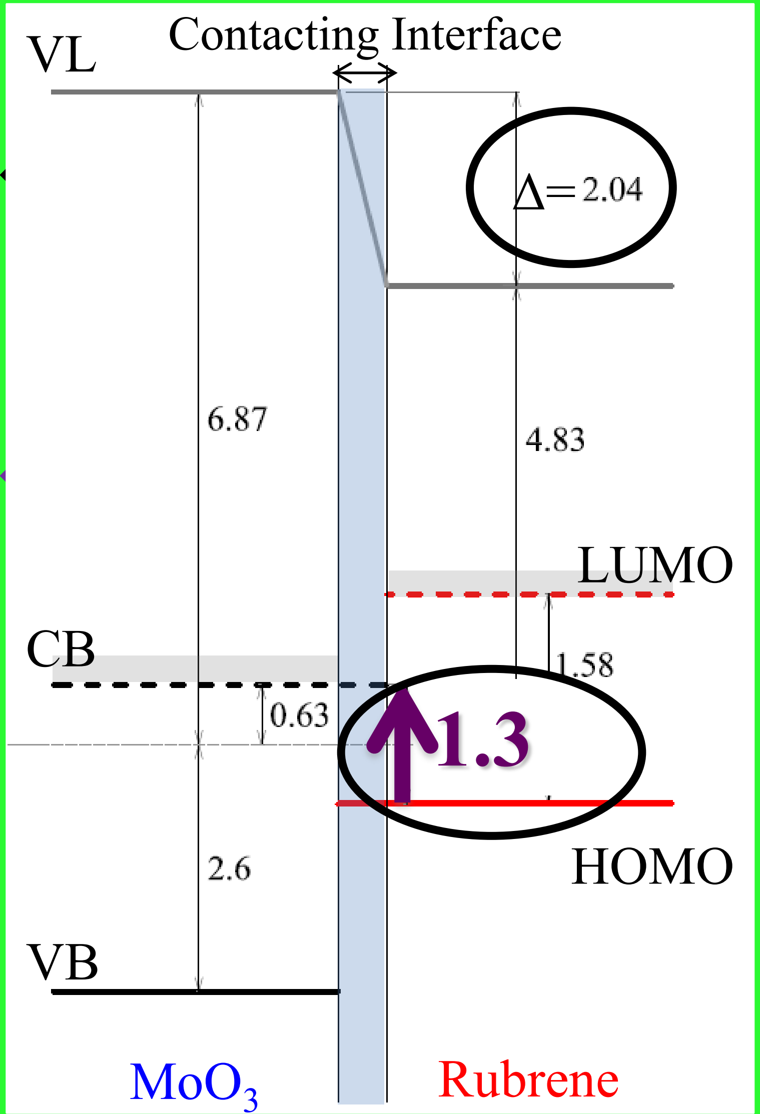
- Rubrene PL totally quenched upon mixing with MoO_3.
- A new red-shifted PL appears at ~ 820 nm.

Ng & Lee, et al. Adv. Func. Mater., 22, 3035 (2012).

Department of Chemistry
香港城市大學
City University of Hong Kong

CTC of MoO_3 & rubrene for IR solar cell

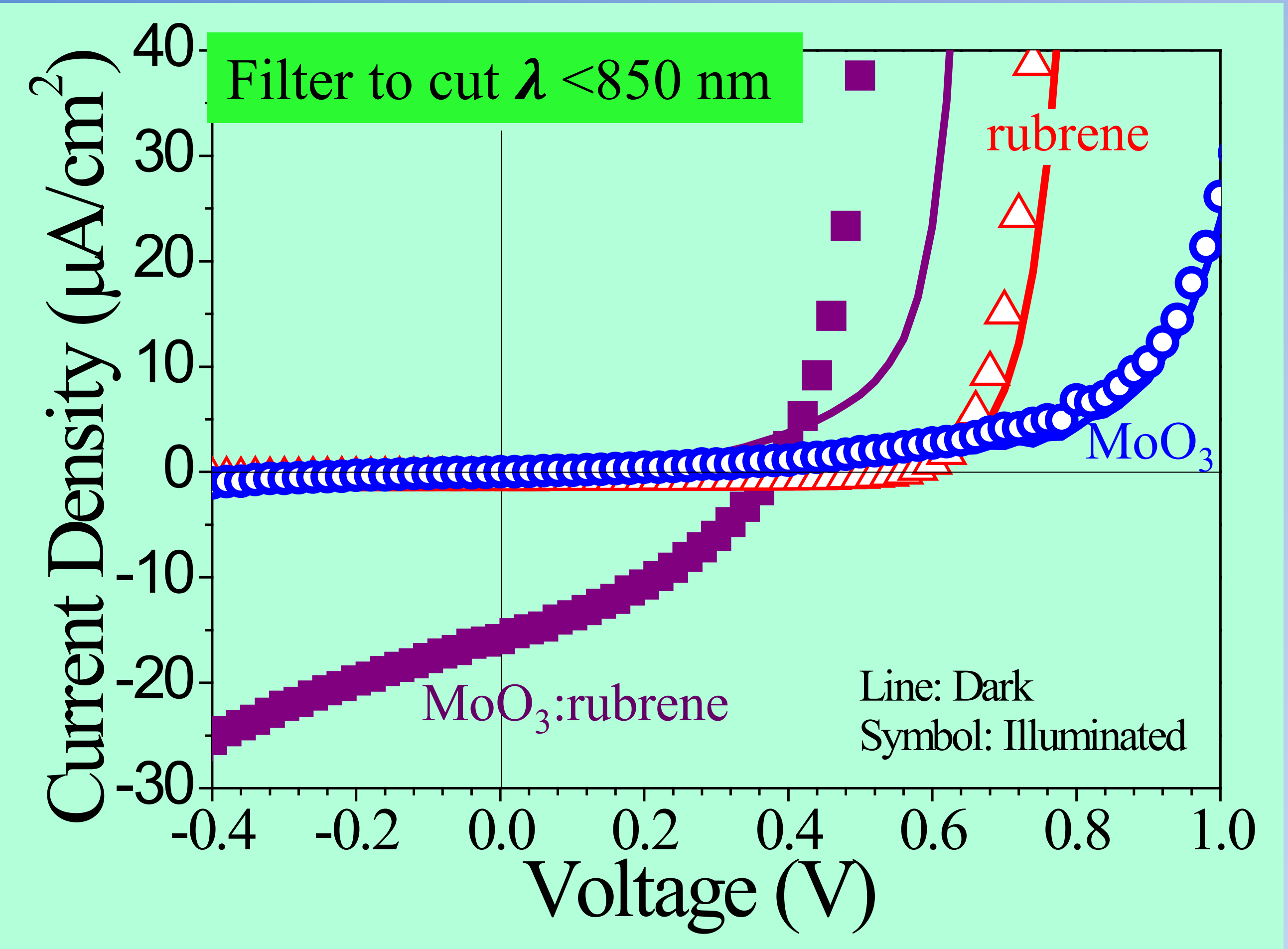




Ng & Lee, et al. Adv. Func. Mater., 22, 3035 (2012).

Infra-Red Solar Cell based on CTC's Absorption

- Solar cell: ITO/ ■ or △ or ○ / C_{60} /BCP/Al.
- Solar simulator @ 50mW/cm^2 with a 850 nm filter.



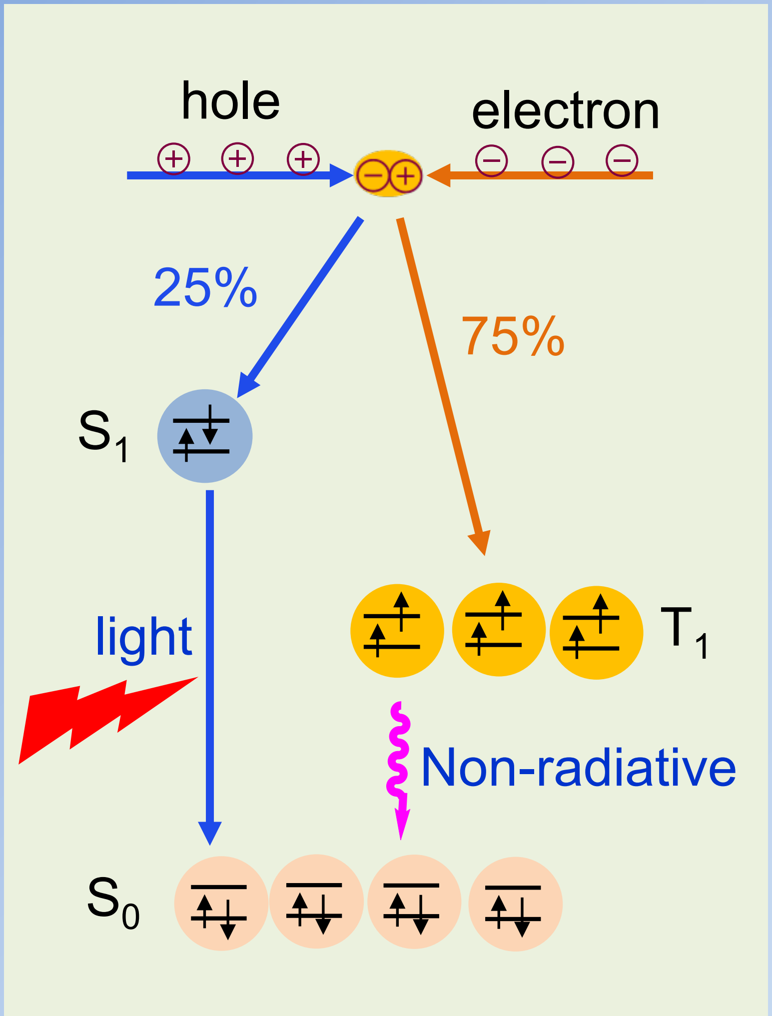
1st IR solar cell based on CTC absorption.

Ng & Lee, et al. Adv. Func. Mater., 22, 3035 (2012).

Department of Chemistry
香港城市大學
City University of Hong Kong

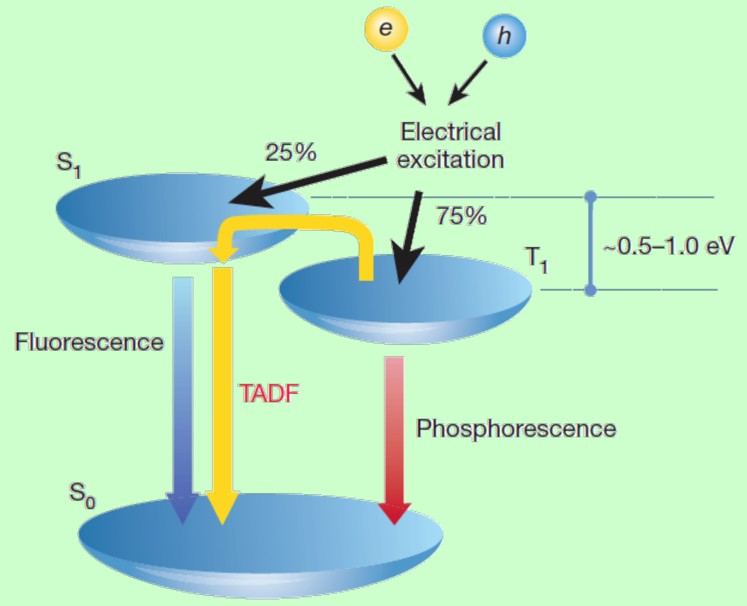
Efficiency of Organic light-emitting devices (OLEDs)

- In OLED electron & hole combine to form excitons: 25% S1 + 75% T1.
- Quantum efficiency of OLEDs with fluorescent materials < 25%.
- Energy of T1 exciton can only be used in phosphorescent emitters with heavy metals (e.g. Ir, Pt etc)
- Phosphorescent emitters are typically expensive & unstable.
- Can we get 100% quantum efficiency without using heavy meal complexes?
- A breakthrough in 2012 on Thermally Activated Delayed Fluorescence.



Thermally Activated Delayed Fluorescence

- Some special fluorescent emitters with very small singlet-triplet energy offset, (e.g. $\Delta E_{S\text{-}T} \sim 0.1eV$)
- Triplet → singlet transition can be achieved via thermal activation.
- Enable OLED of 100% quantum efficiency without using heavy metals.

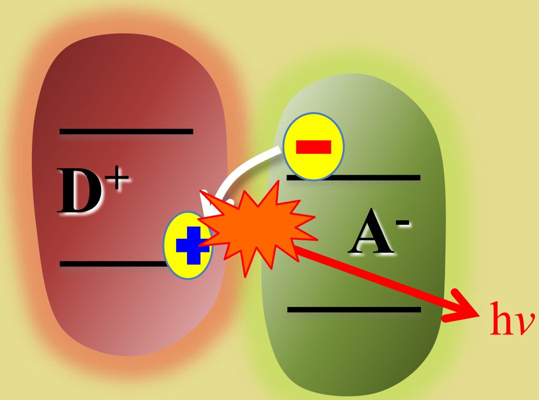


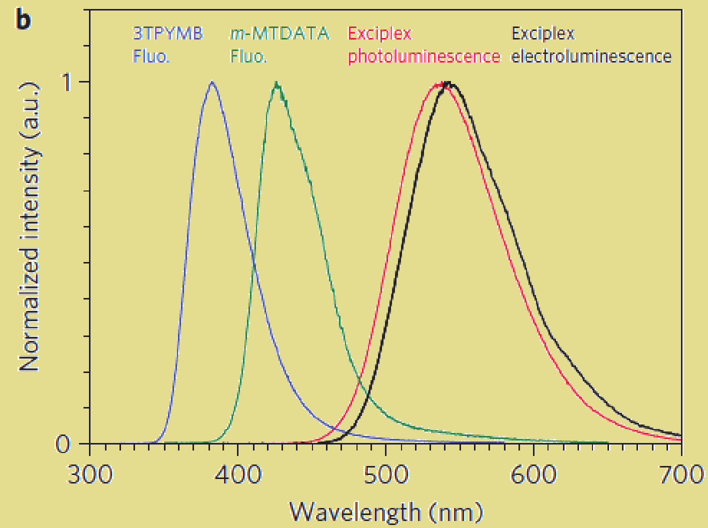
Adachi et al, *Nature*, **492** 234 (2012)

- Thermally activated delayed fluorescence (TADF).
- Break the efficiency limit without heavy metal complex emitter!

How to get materials with small singlet-triplet split?

- $\Delta E_{S\text{-}T}$ ↓ for more separated HOMO & LUMO.
- Adachi et al used highly twisted → $\Delta E_{S\text{-}T}$ ~ 0.1 eV with. (*Nature*, **492** 235(2012)).





- Ultimate HOMO-LUMO separation, if contributed by two molecules!
- Adachi et al showed TADF from a mixture of m-MTDATA & 3TPYMB (Nat. Phot. 6, 253 (2012)).
- 86.5% of triplet → singlet.

Which pairs work?

- Many D-A pairs give nothing but their original emissions.

- Some D-A pairs give new exciplex emission, but no TADF.
- Some give both both.

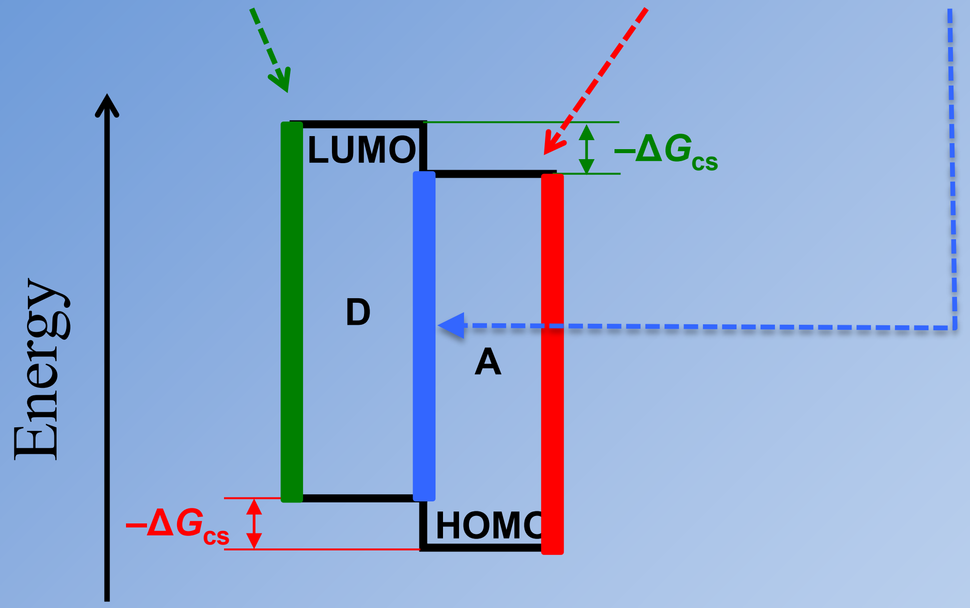
- Which pairs work?

Department of Chemistry
香港城市大學
City University of Hong Kong

Driving Force for Exciplex Formation

- Exciplex formed by:

  D + A + hν → D* + A or D+ A* → (D-A)*



- Driving force is -ΔG_{cs}= $E_{exciton}$ (E_{A*} or E_{D*}) – $E_{exciplex}$
- -ΔG_{cs}= HOMO offset or LUMO offset

Liu & Lee at al *Adv Mater*, **27**, 2378-2383 , (2015)

CityU Department of Chemistry
香港城市大學
City University of Hong Kong

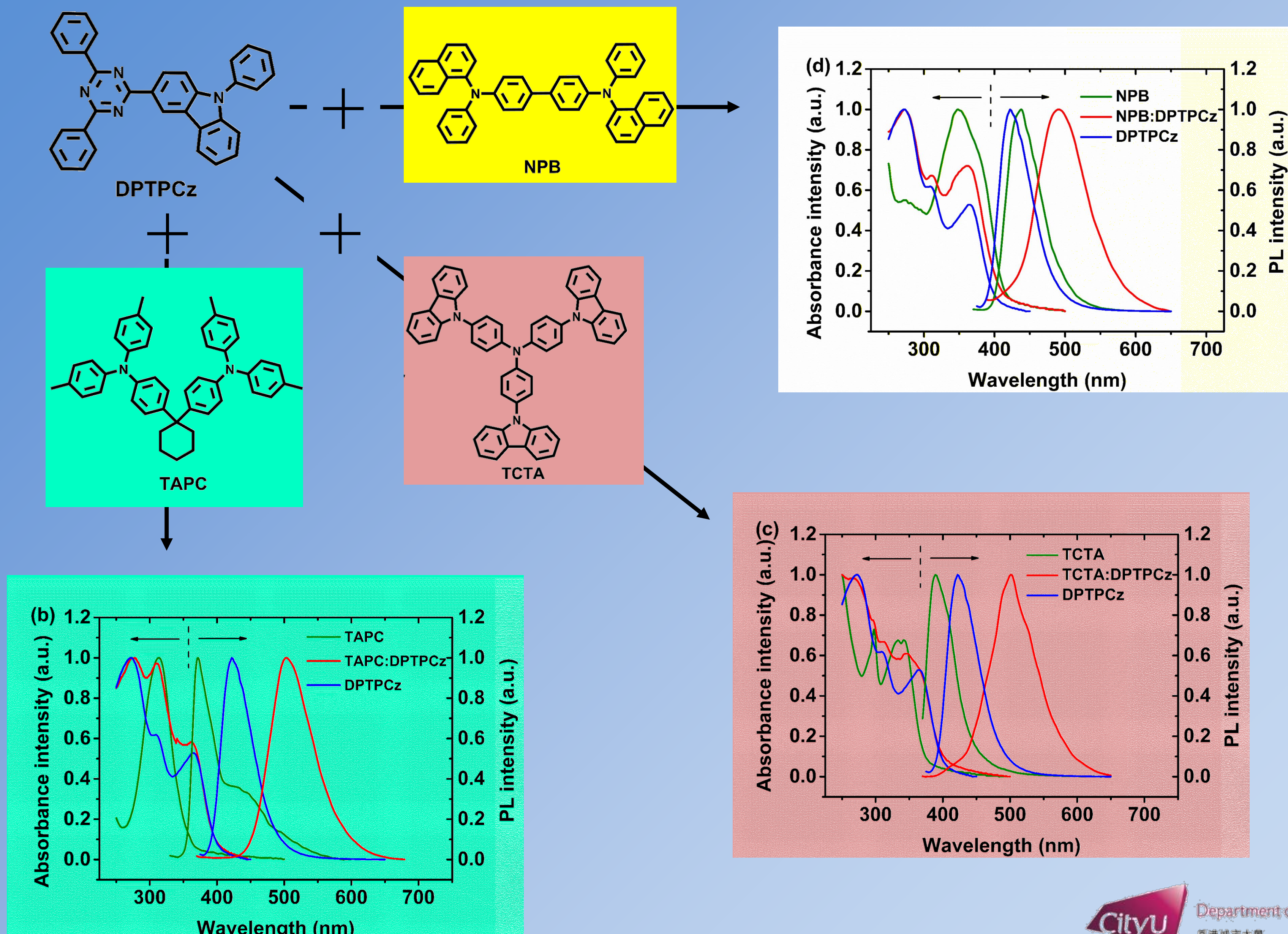
Driven force for exciplex formation

Donor	Acceptor	HOMO offset (eV)	LUMO offset (eV)	Exciplex emission
BCPO	POT2T	1.74	1.11	Yes
CDBP	PO-T2T	1.24	0.89	Yes
TAPC	SPPO13	1.21	0.92	Yes
TAPC	SPPO1	1.16	0.75	Yes
TAPC	Bphen	1.01	1.02	Yes
NPB	DPTPCz	0.64	0.52	Yes
TAPC	DPTPCz	0.61	0.92	Yes
TCTA	DPTPCz	0.53	0.75	Yes
TAPC	TPOA	0.51	1.01	Yes
POA	DPTPCz	0.40	0.38	Yes
TAPC	BPOA	0.37	0.90	Yes
TAPC	POTA	0.32	0.90	No
NPB	Alq3	0.26	0.47	No
TAPC	PTA	0.25	0.73	No
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Some exciplex emitters gives TADF and some do not.

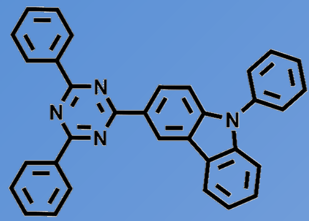
How about these?

All 3 pairs give exciplex, do they gives TADF?

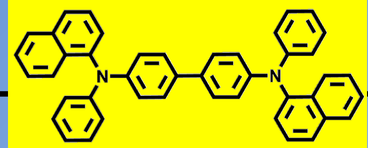


CityU Department of Chemistry
香港城市大學
City University of Hong Kong

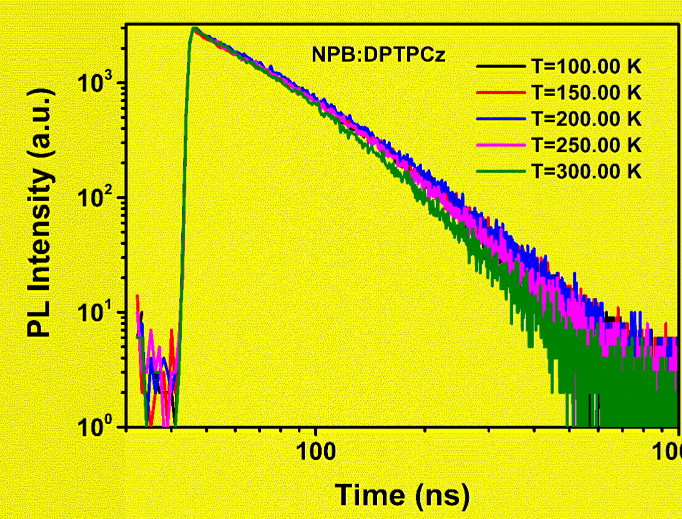
Time dependent photoluminescence



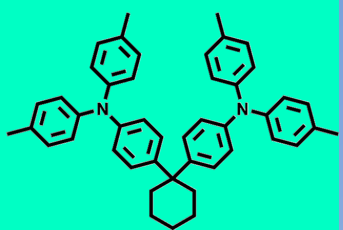
DPTPCz



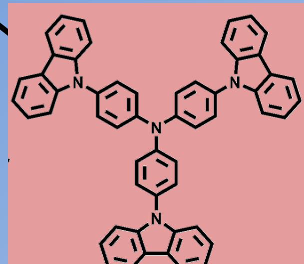
NPB



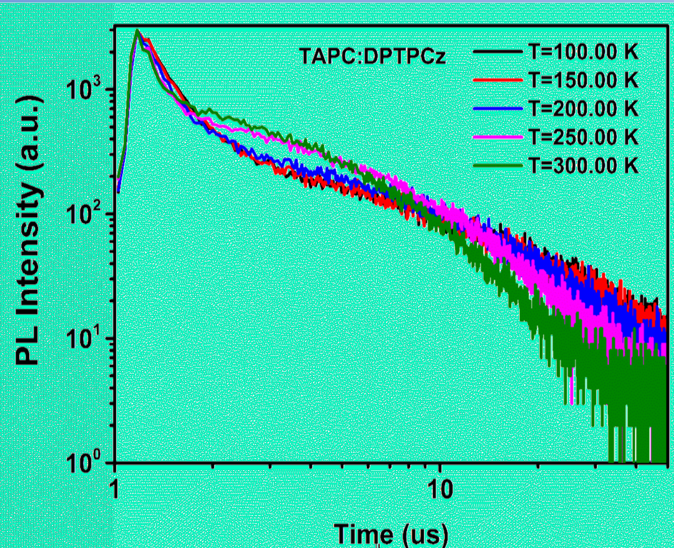
NPB:DPTPCz
T=100.00 K
T=150.00 K
T=200.00 K
T=250.00 K
T=300.00 K
PL Intensity (a.u.)
Time (ns)
10⁰
10¹
10²
10³
100
1000



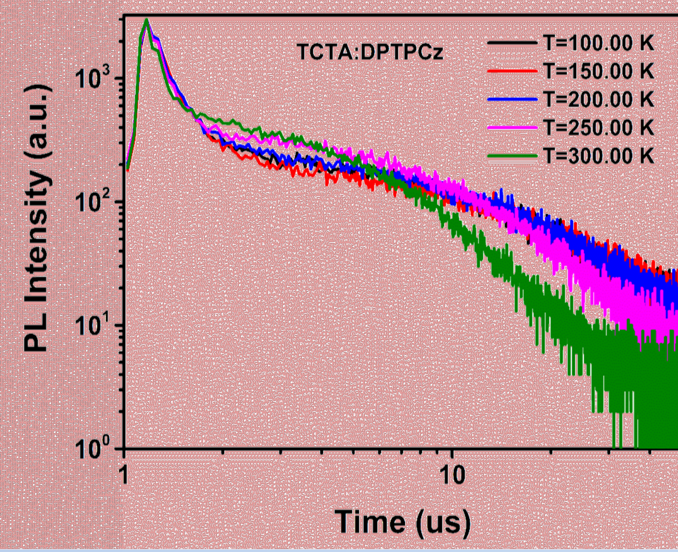
TAPC



TCTA



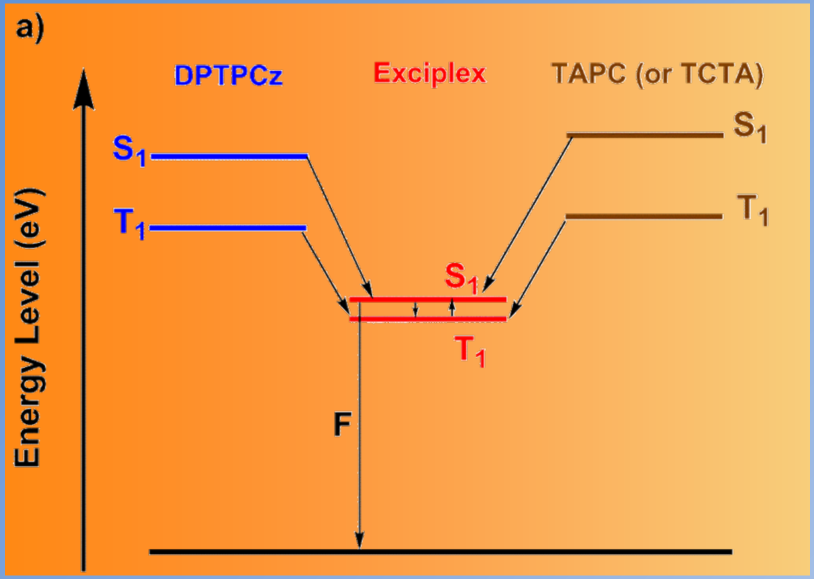
TAPC:DPTPCz
T=100.00 K
T=150.00 K
T=200.00 K
T=250.00 K
T=300.00 K
PL Intensity (a.u.)
Time (us)
10⁰
10¹
10²
10³
1
10



TCTA:DPTPCz
T=100.00 K
T=150.00 K
T=200.00 K
T=250.00 K
T=300.00 K
PL Intensity (a.u.)
Time (us)
10⁰
10¹
10²
10³
1
10

Photoluminescence efficiency

Two cases with TADF



- S_1 of D & A → S_1 of exciplex.
- T_1 of D & A → T_1 of exciplex.
- Exciplex T_1 → S_1 via reverses intersystem crossing
- Harvest both S_1 and T_1 energy.
- High PL efficiencies.

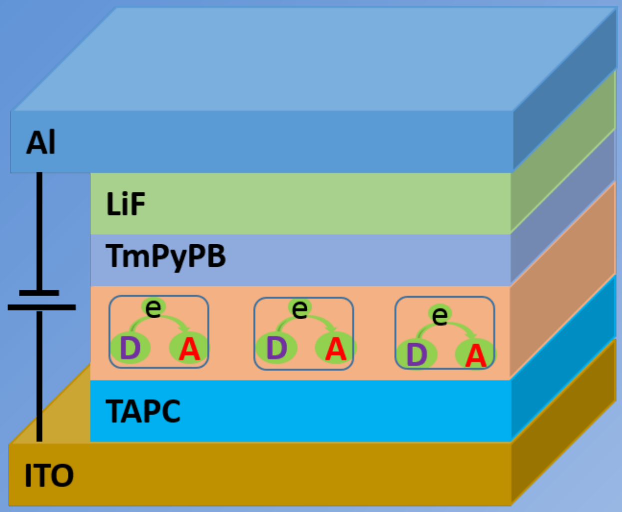
Φ_f = 0.68 for TAPC:DPTPCz
Φ_f = 0.55 for TCTA:DPTPCz

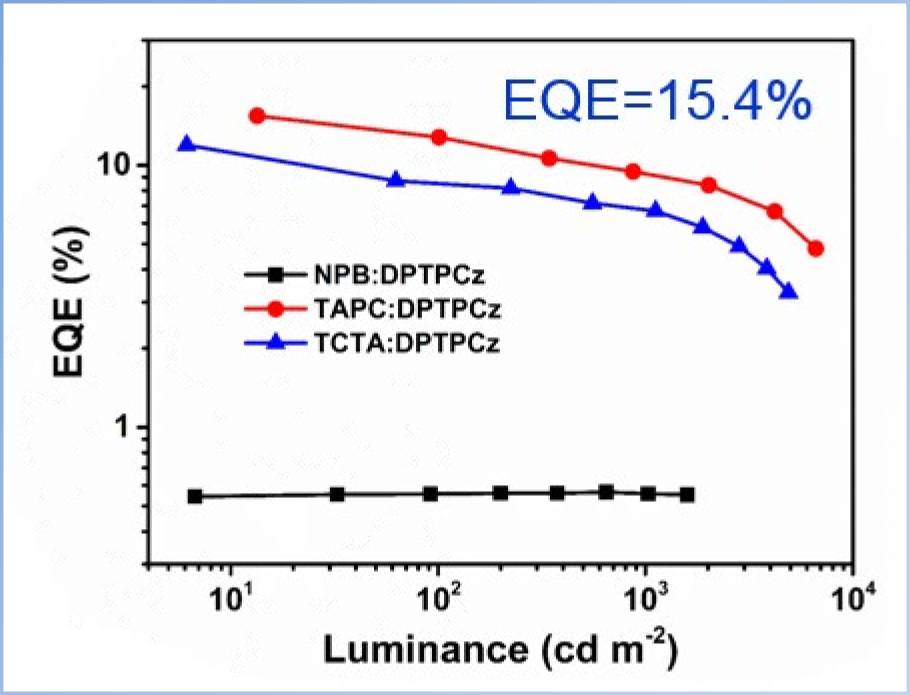
Constituting molecules with T_1 energy > that of the exciplex is necessary for TADF emission and thus high PL efficiency.

Liu & Lee at al *Adv Mater*, **27**, 2378-2383 , (2015)

Department of Chemistry
香港城市大學
City University of Hong Kong

Performance in OLEDs





EML	V_{on} (V)	L_{max} (cd m^{-2})	CE/ PE/ EQE (cd A^{-1}/ lm W^{-1}/ %)	CIE(x, y)
TAPC:50 wt% DPTPCz	2.7	8660	45.7/ 47.9/ 15.4	(0.27, 0.52)
TCTA:50 wt% DPTPCz	2.8	4890	34.2/ 35.8/ 11.9	(0.26, 0.50)
NPB:50 wt% DPTPCz	3.4	1590	1.4/ 1.2/ 0.6	(0.25, 0.41)

Liu & Lee at al *Adv Mater*, **27**, 2378-2383 , (2015)

Other works on CTC & TADF OLED/PV devices

- CTC-based NIR PV devices: *Adv Mater*, **26**, 5569-5574, (2014).
- As host for fluorescent dopants: *Adv Mater*, **27**, 2025-2030, (2015).
- Single emitting layer OLED: *Adv. Mater*., **27**, 7079 (2015).
- TADF molecule as a CTC component: *Adv. Funct. Mater*., **26**, 2002-2008 (2016).
- Dual conformation TADF emitters: *Adv Mater*., 29, 1701476 (2017).
- Single molecule CTC:: *Adv Funct Mater*, **29**, 1903112, 2019.
- Near Infrared OLED: *Angew. Chem*., 58 14660 (2019); 60 2478 (2021).

CityU Department of Chemistry
香港城市大學
City University of Hong Kong

Outline

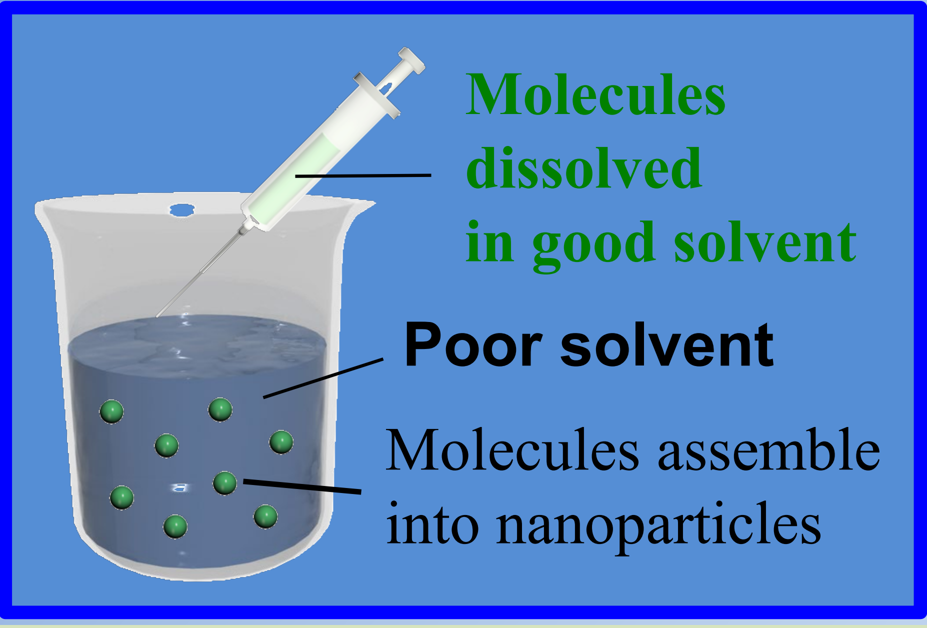
- What is charge transfer complex (CTC)?
- Characteristic signatures of CTCs.
- Why CTC is important in optoelectronic devices?
- Examples on CTCs' optoelectronic applications.
- Biomedical applications of CTCs.
- Energy & environmental applications.
- Conclusion.

Challenges for biomedical applications

- Has to be non-toxic until activated.
- Has to be water soluble/dispersible.
  - Most organic electronics molecules are not soluble!
  - In fact, > 40% molecules as anticancer drug candidates abandoned for poor water solubility.
- We address this by packing the molecules into nanoparticles: a bit of surface charge will suspend these mutually repelling very small particles in water.
- They will be suspending in water and blood without precipitation and aggregation for months.

Preparation of Self-Assembled organic NPs

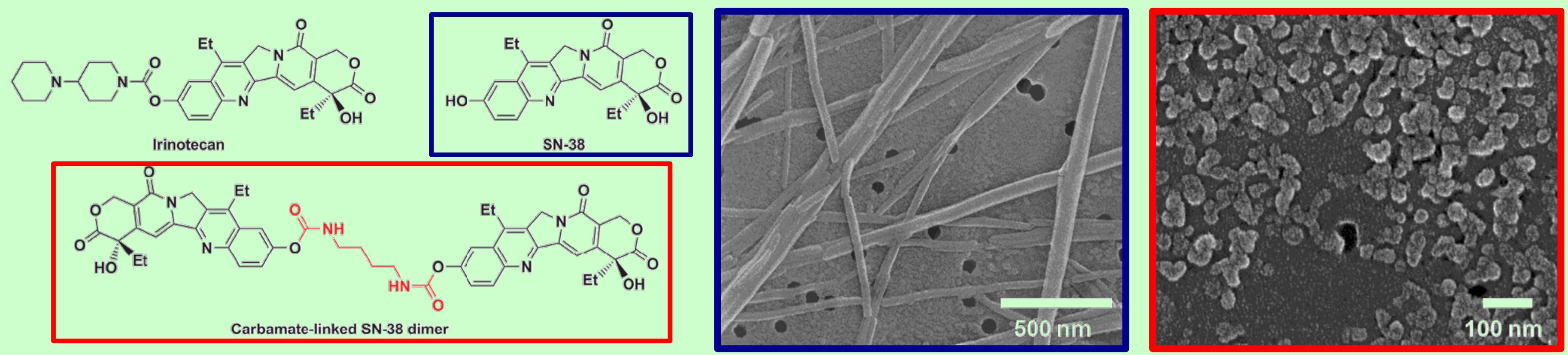
- Most commonly prepared by ***reprecipitation*** method.
- Extremely simple.



- Relatively large sizes (100 to 500 nm)
- Low production rate & poor reproducibility.
- Nanodrugs with 20-50 nm reported to show improved pharmacokinetics.
- Can NP with sub 100 nm sized prepared this way?

Sub-100 nm self-assembled drug particles

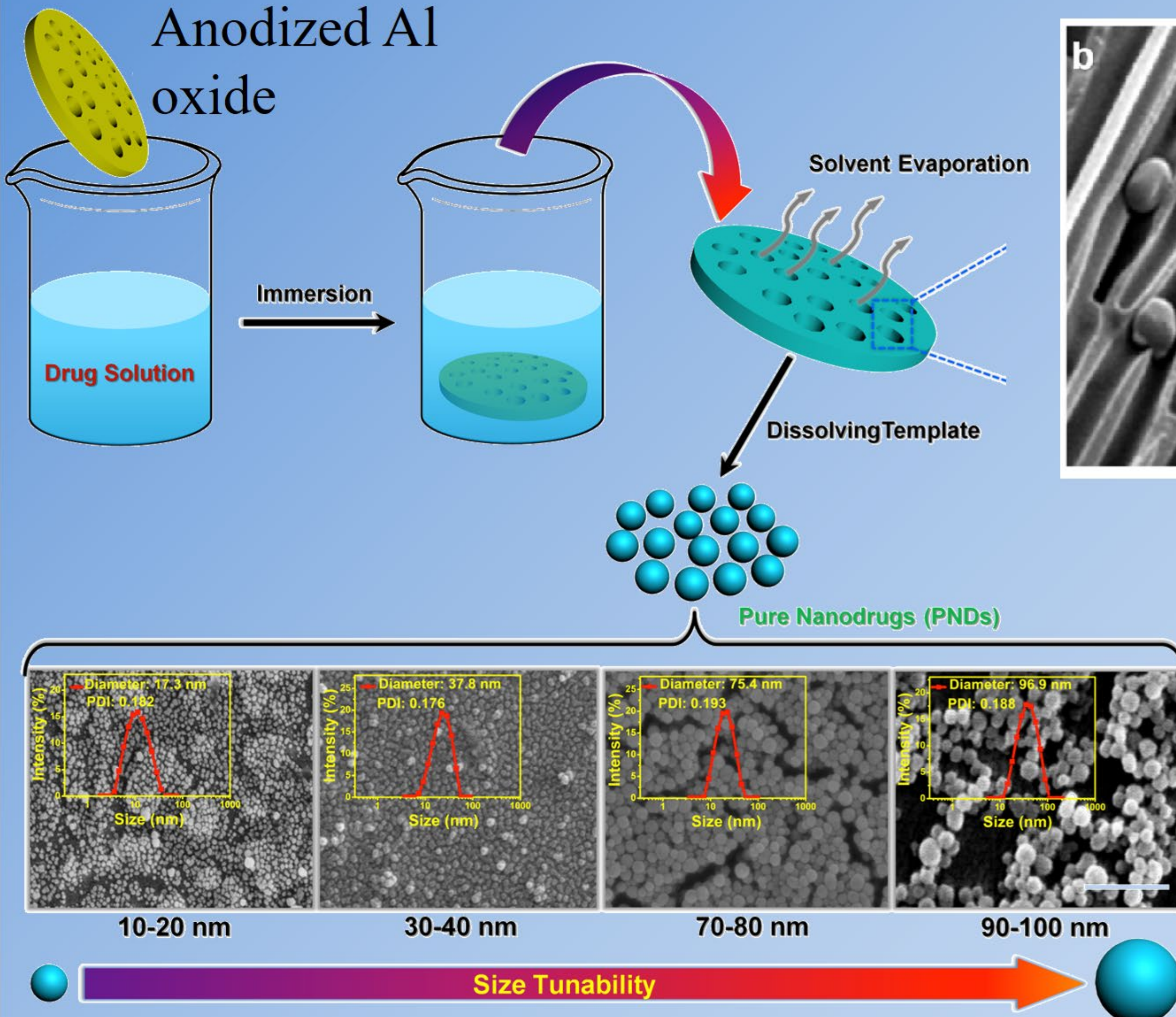
- Sizes of NP controlled by molecules-solvent interactions.
- Small sized polymeric NPs can be easily obtained.
- Sub-100 nm NP of small molecules are rare.
- Kasai et al achieved this via increasing the molecular size:

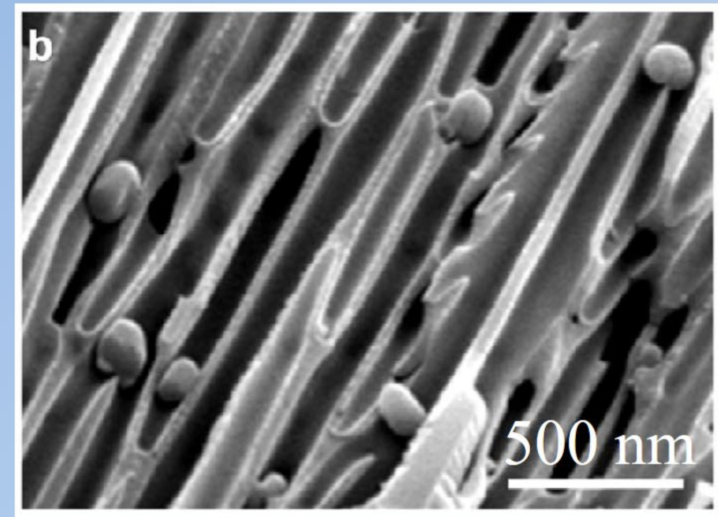


- Obtained drug NP with 30-50 nm size.
- Viable solution, but ***each drug need custom chemical modification*** without changing the therapeutic properties.

Kasai et al, *Ang. Chem.*, **51** 10315 (2012)

Sub-100 nm self-assembled drug particles



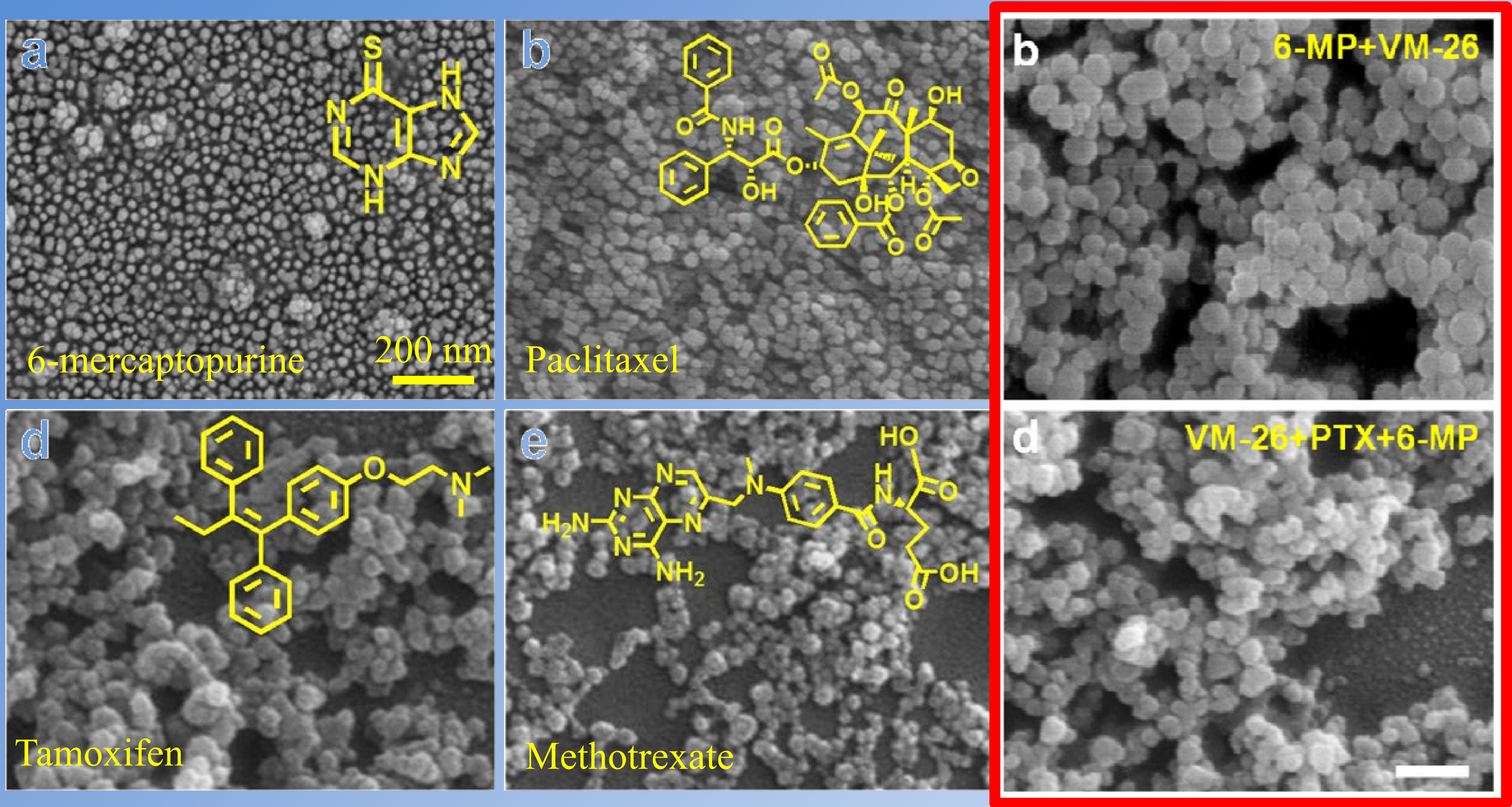


- We use AAO as template.
- Precise size control from 10 to 100nm.

Zhang & Lee et al, *Nano Lett.*, **15** 313 (2015)

Department of Chemistry
香港城市大學
City University of Hong Kong

Work with different drugs & cocktail



- Work well with various hydrophobic molecules.

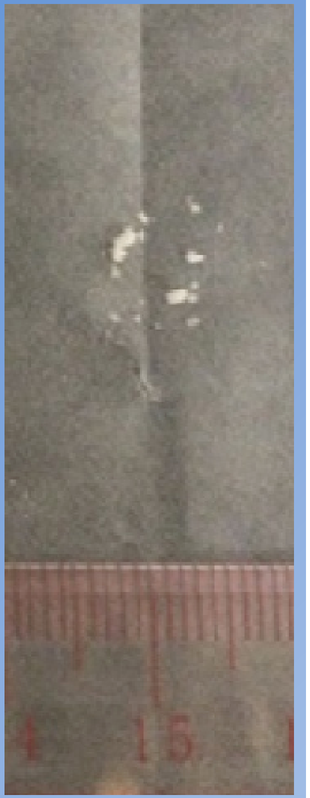
Zhang & Lee et al, *Nano Lett.*, **15** 313 (2015)

Department of Chemistry

High production rate

AAO

reprecipitation



Reference (Year)	Material	Method	Concentration	Mass	Theoretical maximum concentration #
Our result with AAO	Drug VM-26 NPs	Immersed an AAO template of 50 mm diameter in 10 mL of 12 mM drug solution	~1.26 mM	~35 mg	NA
Our result with reprecipitation	Drug VM-26 NPs	200 μL of 3 mM VM-26 solution in THF was injected into 10 mL of MilliQ water	~0.05 mM	~0.28 mg*	0.06 mM
Ref. 1 (2007)	Photosensitizer HPPH NPs	200 μL of 3 mM HPPH\DMSO solution was injected into 10 mL of water	Not given	Not given	0.06 mM
Ref. 2 (2010)	Semiconducting polymer PFBT dots	5 mL of 50 μg\mL PFBT\THF solution was quickly added to 10 mL of MilliQ water	Not given	Not given	~0.00016 mM
Ref. 3 (2011)	Semiconducting polymer PFPV dots	200 μL of 1 mg/mL PFPV dissolved in 5 mL THF, then injected into 10 mL of water	Not given	Not given	~0.0001 mM
Ref. 4 (2012)	Drug HCPT NPs	300 μL of 1 mM HCPT in ethanol solution was poured into 5 mL of aqueous solution	Not given	Not given	0.06 mM
Ref. 5 (2012)	Drug SN-38 dimer NPs	Not given	0.05 mM	Not given	NA
Ref. 6 (2012)	Dye TBADN NPs	250 μL of 1 mM TBADN/THF solution was injected into 5 mL of water solution	Not given	Not given	0.05 mM
Ref. 7 (2013)	Drug PTX NRs	200 μL of 3 mg/mL PTX\ethanol solution was poured into 5 mL of water	Not given	Not given	0.14 mM
Ref. 8 (2013)	Semiconducting polymer PVK dots	5 mL of 20 μg/mL PVK/THF solution was quickly injected into 10 mL of water	Not given	Not given	~0.0002 mM
Ref. 9 (2014)	Photosensitizer TPP NPs	50 μL of 1 mM TPP/THF solution was injected into 5 mL of ultrapure water	Not given	Not given	0.01 mM
Ref. 10 (2014)	Drug HCPT NRs	200 μL of 500 mg\L HCPT in THF was dropped into 10 mL aqueous solution	Not given	Not given	0.055 mM
Ref. 11 (2014)	Semiconducting polymer SP1 NPs	1 mL of 0.25 mg/mL SP1/THF solution was rapidly injected into 9 mL of deionized water	Not given	Not given	~0.0013mM
Ref. 12 (2014)	Organic NIR dye NPs	0.1 mL of 1 mM solution of dye in THF is added in 9.9 mL of pure water	Not given	Not given	0.01 mM

Zhang & Lee et al, *Nano Lett.*, **15** 313 (2015)

Department of Chemistry
香港城市大學
City University of Hong Kong

Merits & limits of AAO-templated self-assembly

Advantages:

- Highly precise & reproducible size & morphology.
- Applicable to all hydrophobic molecules.
- Feasibility of multi-component, multifunctional drugs.
- High production rate.

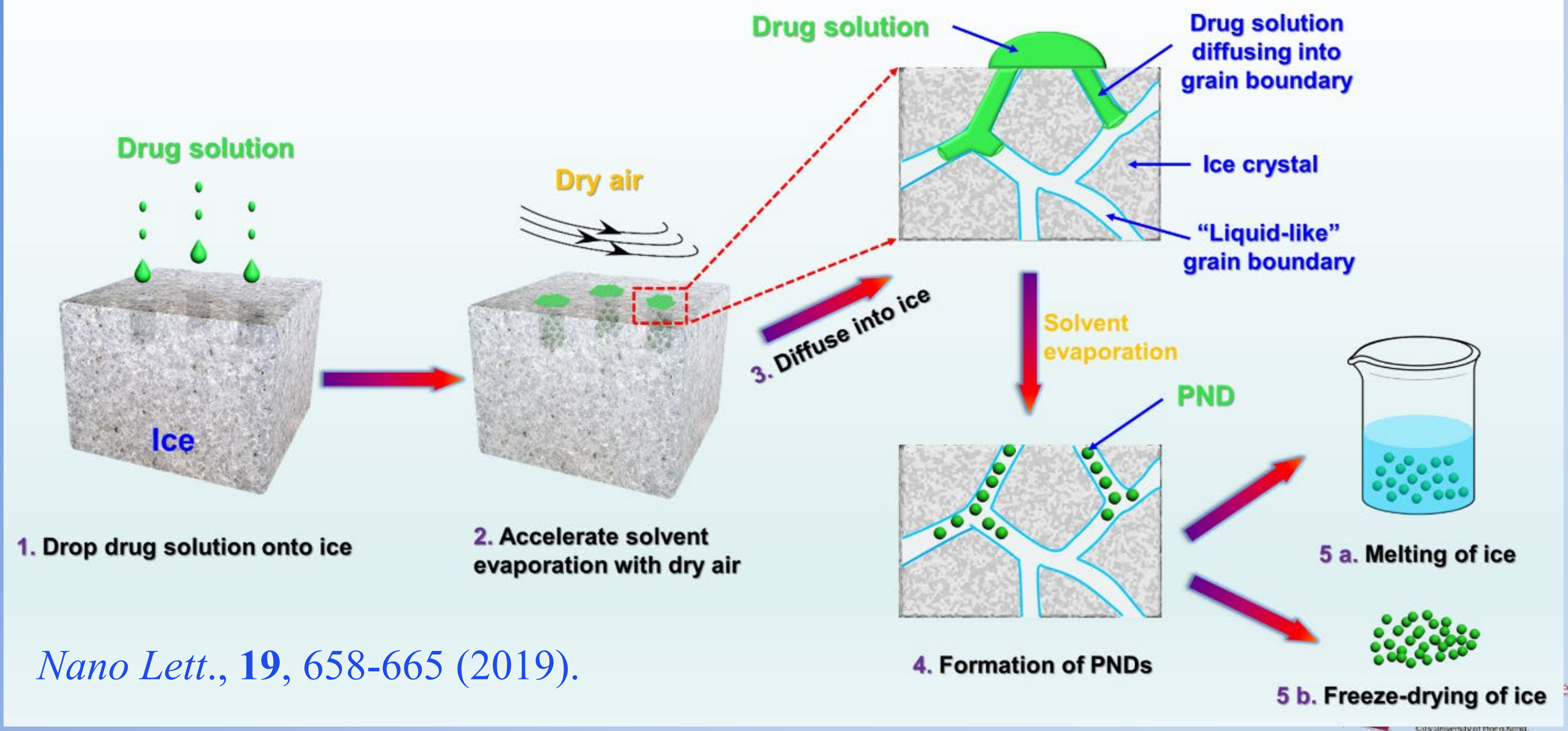
Limits:

- Slow dissolution of AAO template in mild acid/base.
- May affect drug molecules sensitive to acid/base.
- May c … O.
- Consu …

Can we use a more biocompatible & green template?

How about ice?

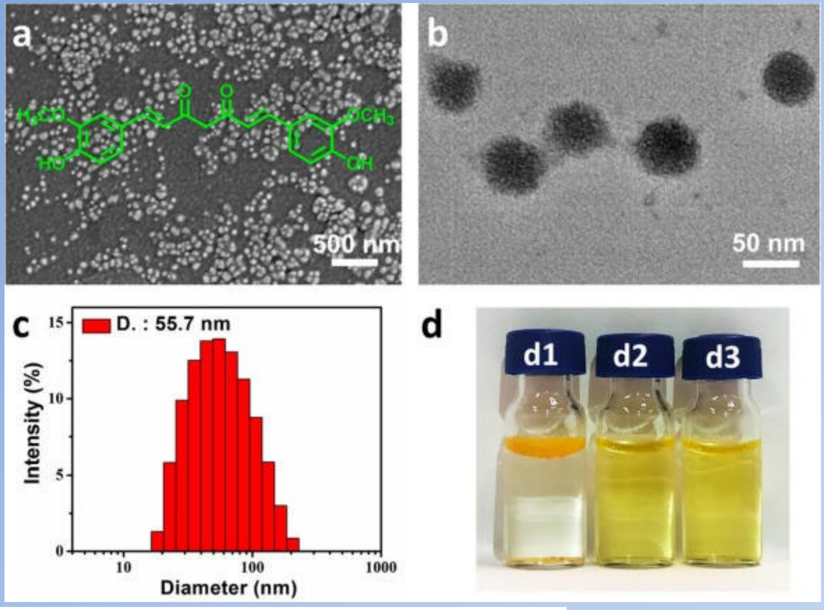
- Use the grain boundaries of ice crystals as template.
- Controlling NP size via grain boundary microstructures.
- Melting => NP dispersion; freeze-drying => NP powder.
- Fully biocompatible & green.

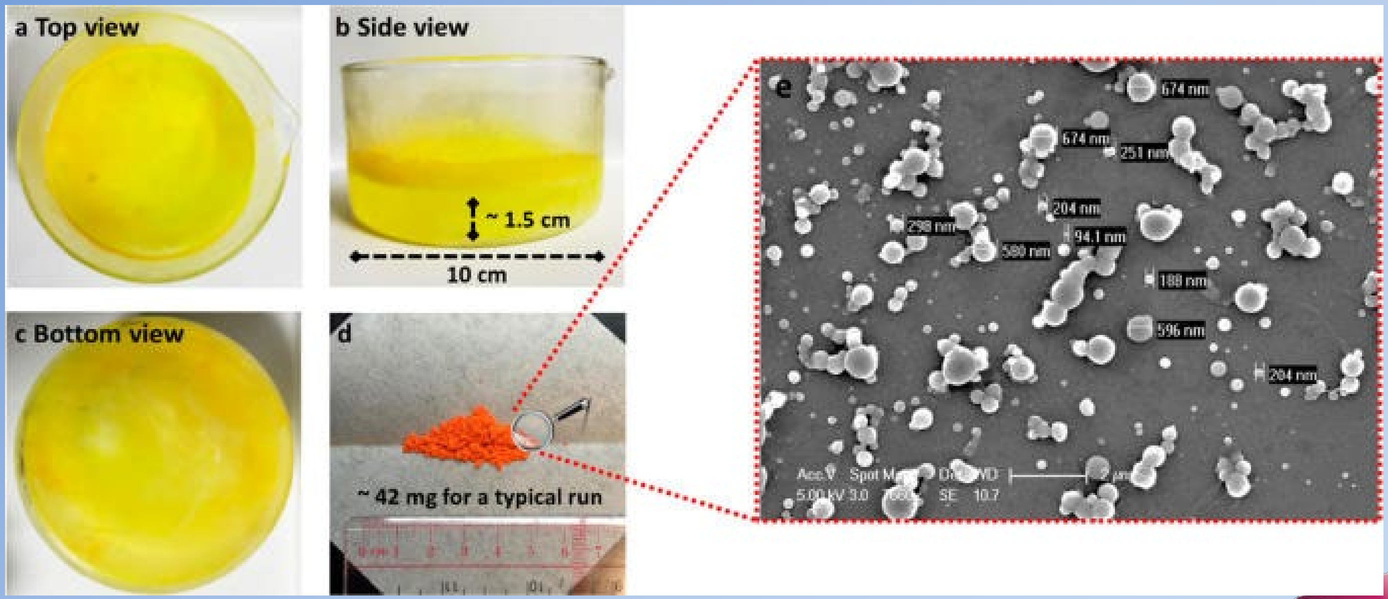


Nano Lett., **19**, 658-665 (2019).

Curcumin NPs prepared with ice template

- Can produce sub-100 nm NP with good size control.
- NPs have good dispersibility.
- High production rate: ~42 mg from a 10 cm breaker.
- Easy to scale up.

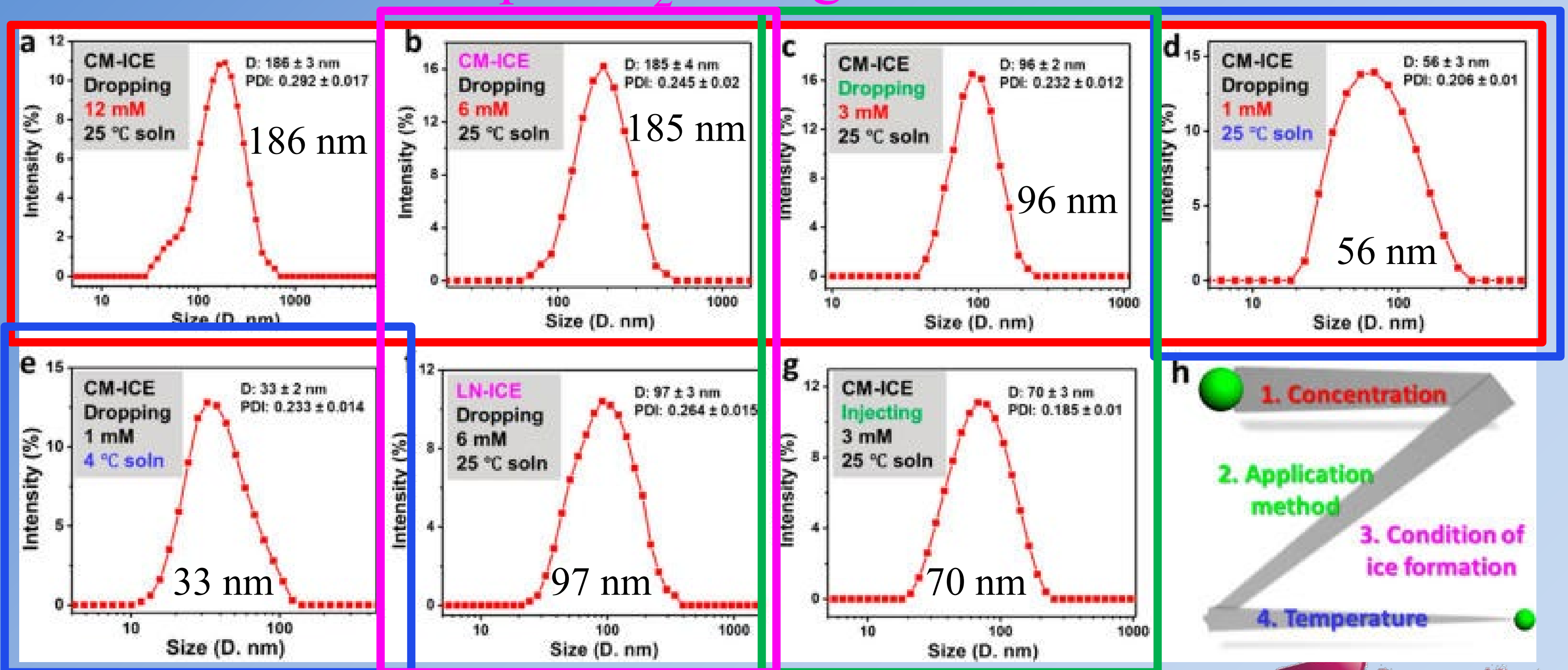




Zhang & Lee et al, *Nano Lett.*, **19**, 658-665 (2019).

Size control in the ice template approach

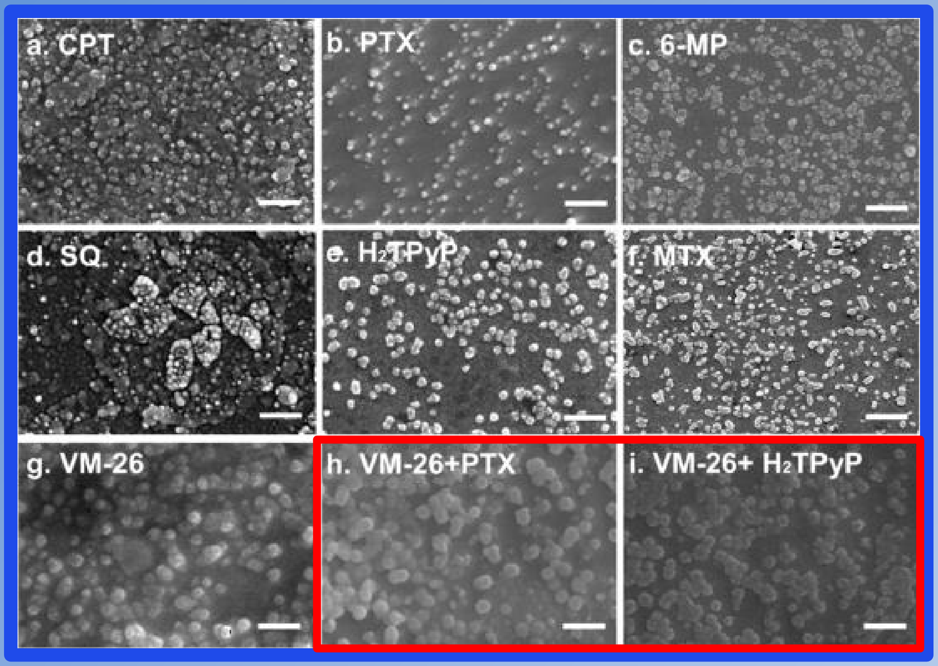
- NP size & PDI increase as drug solution concentration.
- Lower solution temperature => smaller sized NPs.
- Injection gives smaller size & injection Vs dropping.
- Ice formed at liquid N_2 bath give smaller sized NPs.

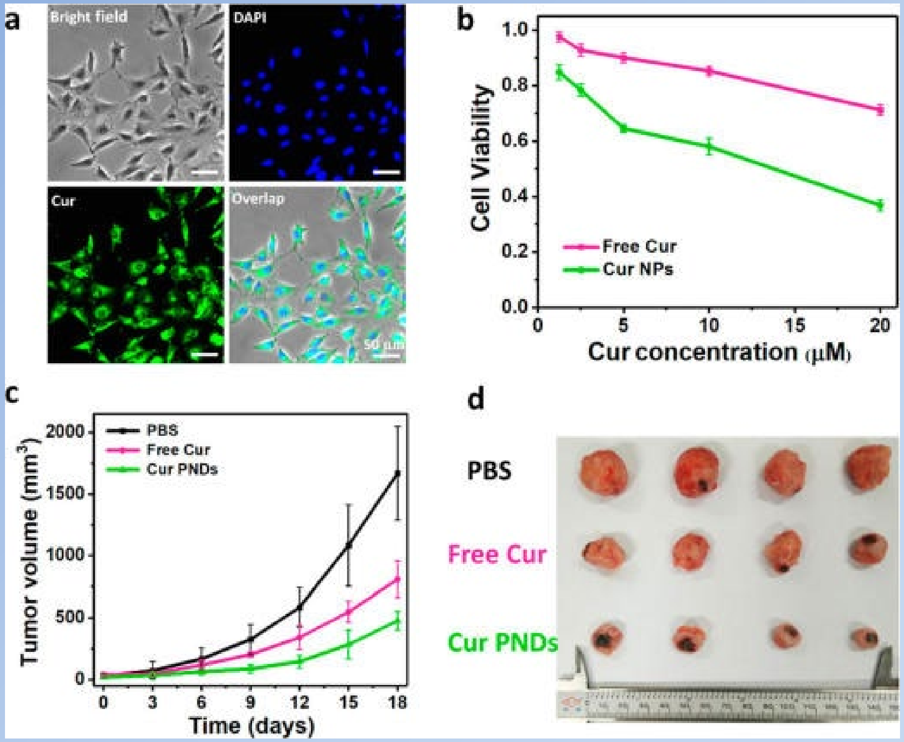


CityU Department of Chemistry
香港城市大學
City University of Hong Kong

Versatility & performance of NP from ice template

- Applicable to most hydrophobic drug molecules
- Can prepare composite NPs.
- Similar performance comparing to drug NP prepare with conventional approach.



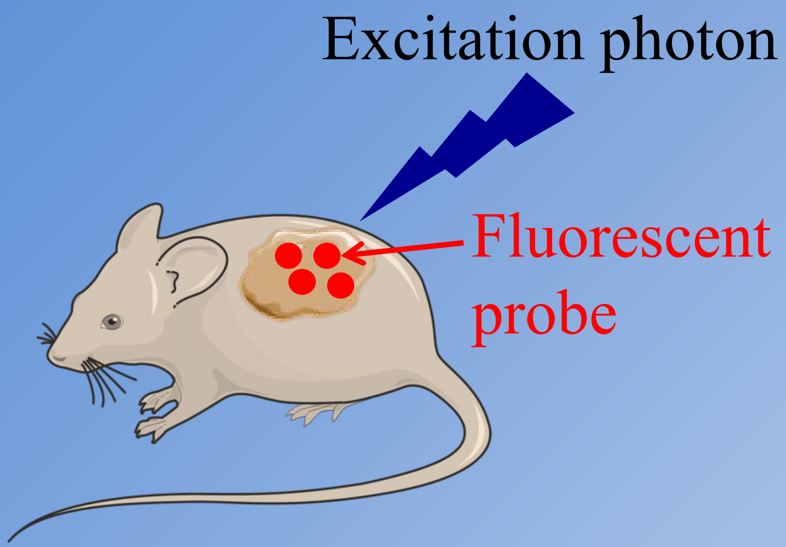


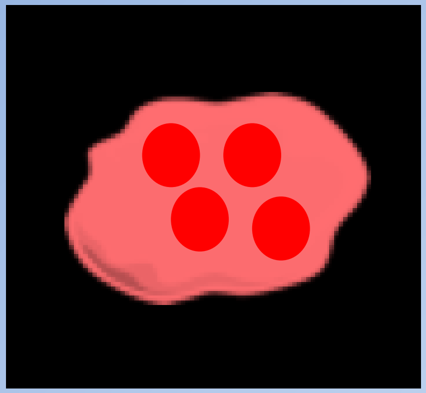
Zhang & Lee et al, *Nano Lett.*, **19**, 658-665 (2019).

CityU
Department of Chemistry
香港城市大學
City University of Hong Kong

CTC for biomedical applications

- The first biomedical application we think of is to use its delayed fluorescence for “time-gated” bioimaging.



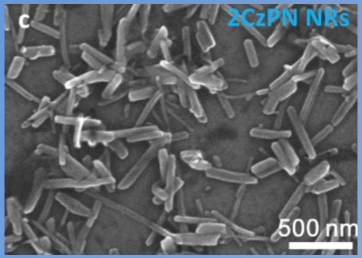


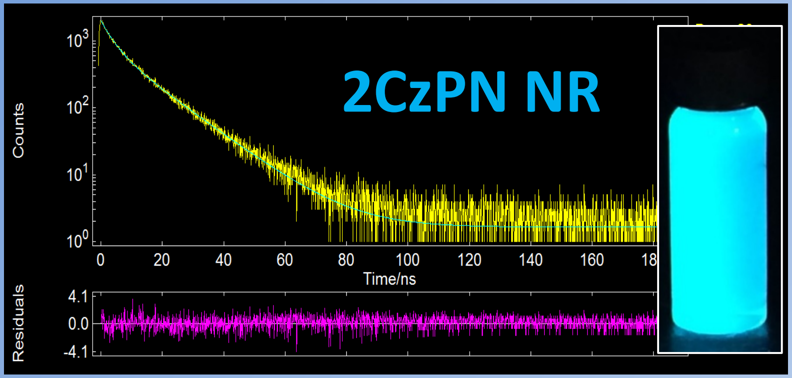
Some time after turn excitation off

- While these materials show delayed fluorescence in OLEDs.
- NOT in cell!???

CityU Department of Chemistry
香港城市大學
City University of Hong Kong

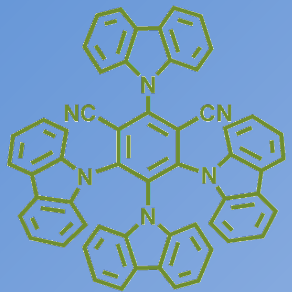
TADF nanoparticles with only nanosecond delays

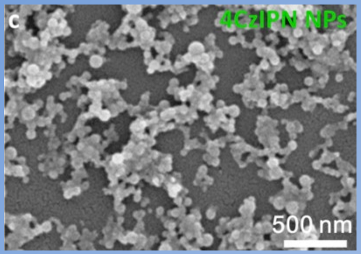


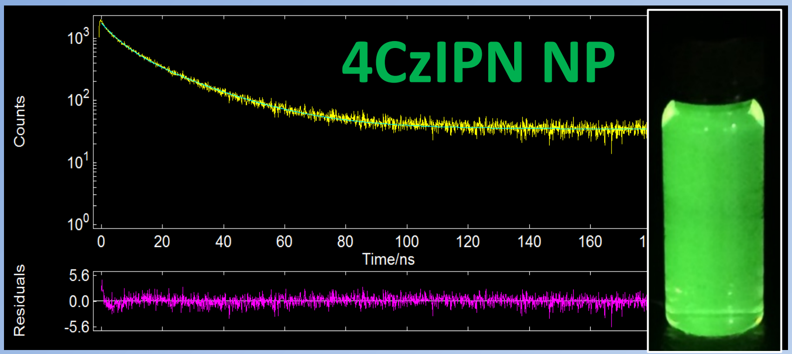


τ1=3.68 ns;

τ2=12.89 ns;

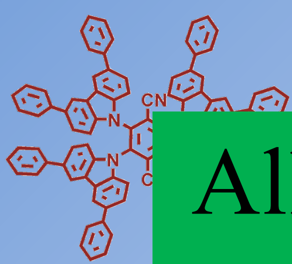


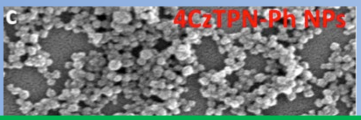




τ1=5.45 ns;

τ2=19.90 ns;





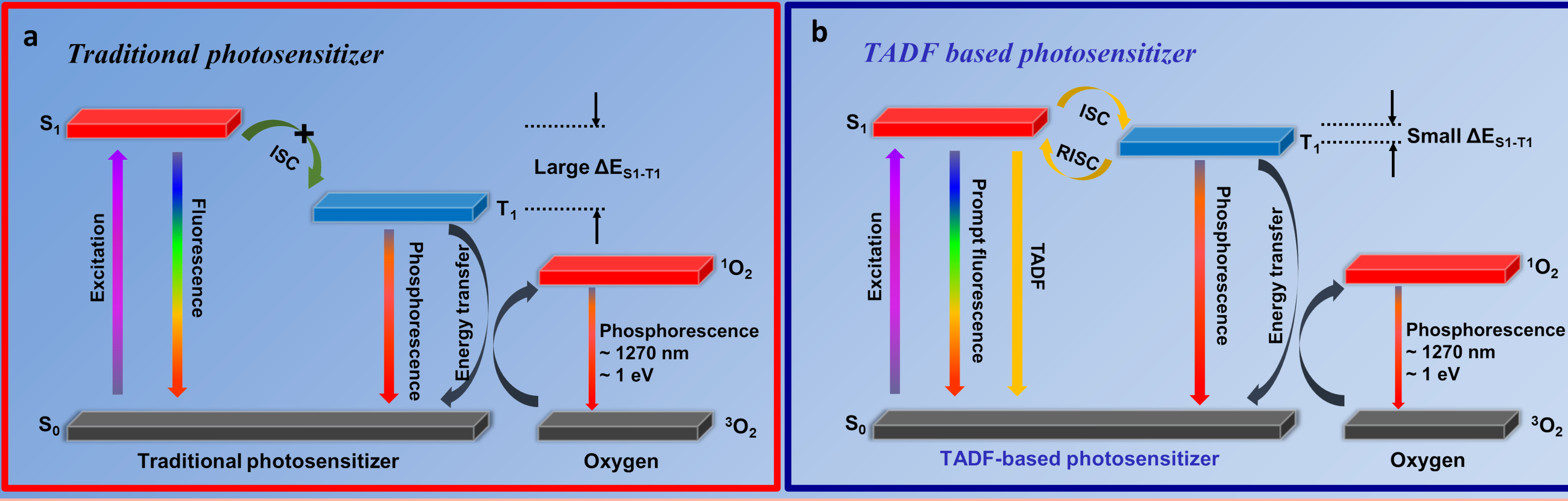
. ns;

All triplet excitons were quenched by the surround H_2O/O_2 !

Department of Chemistry
香港城市大學
City University of Hong Kong

Thermally Activated Delayed Fluorescence (TADF) for photodynamic therapy (PDT)

➢ Photoexcitation → singlet oxygen to kill cancer cells.



➢ Conventional photosensitizers – inefficient ISC.

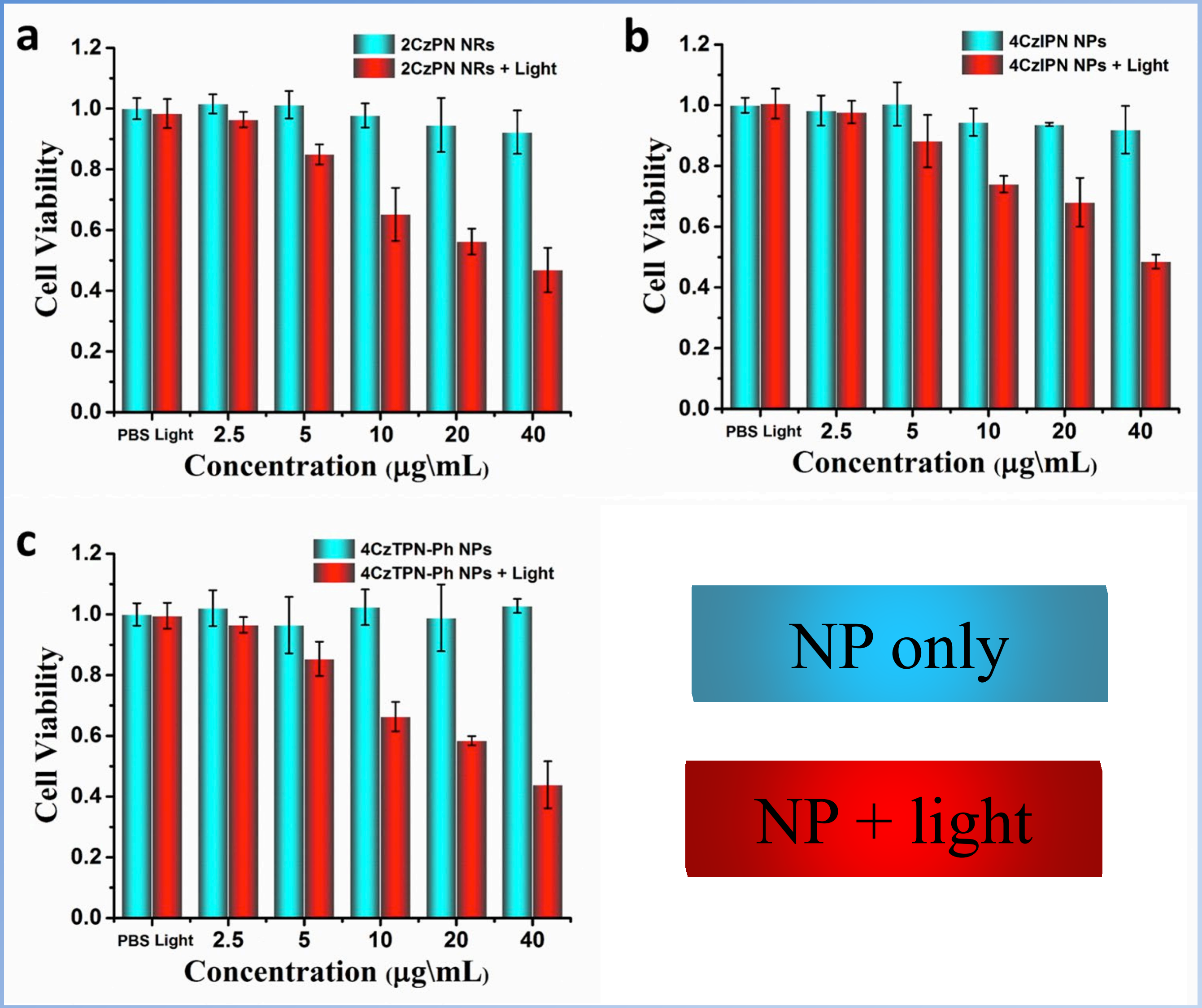
➢ Introducing heavy metal atoms can help – but undesirable.

➢ TADF photosensitizers – efficient ISC.

➢ Self-assembled into NPs for water dispersibility.

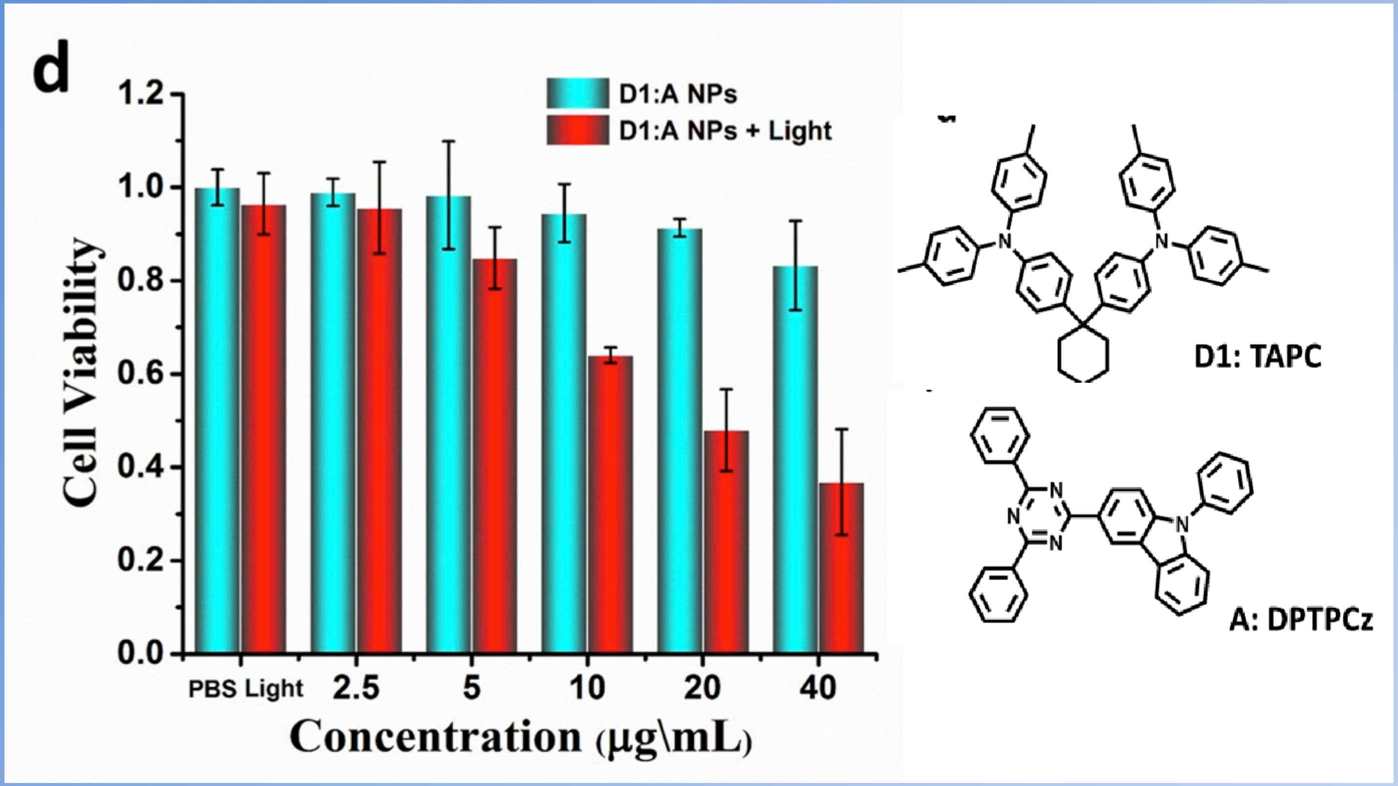
Zhang & Lee et al, *Chem. Comm.*, **52**, 11744 (2016).

TADF for photodynamic therapy (PDT)



Zhang & Lee et al, *Chem. Comm.*, **52**, 11744 (2016).

Photodynamic therapy with TADF CTC

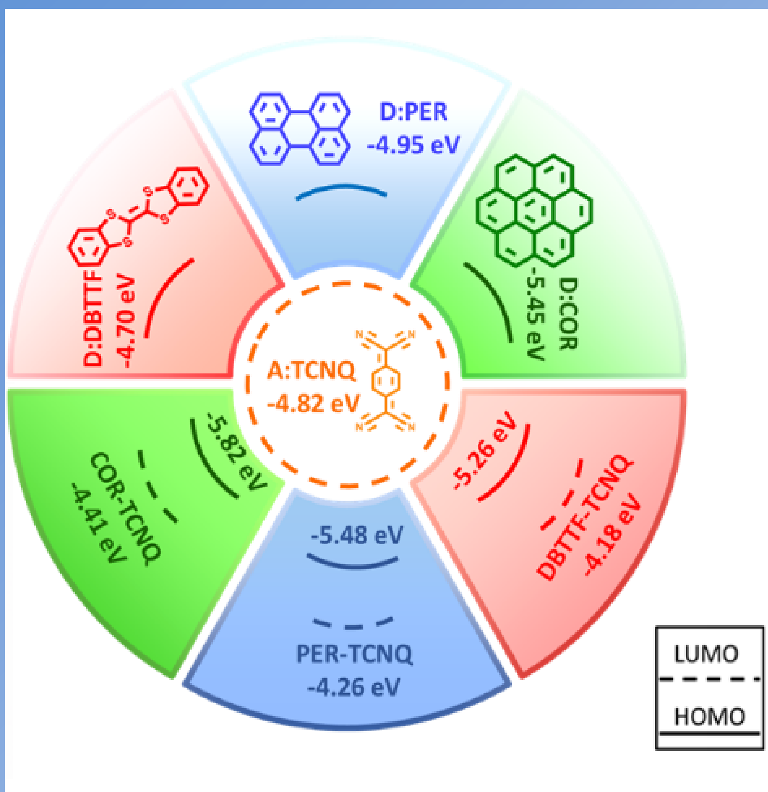


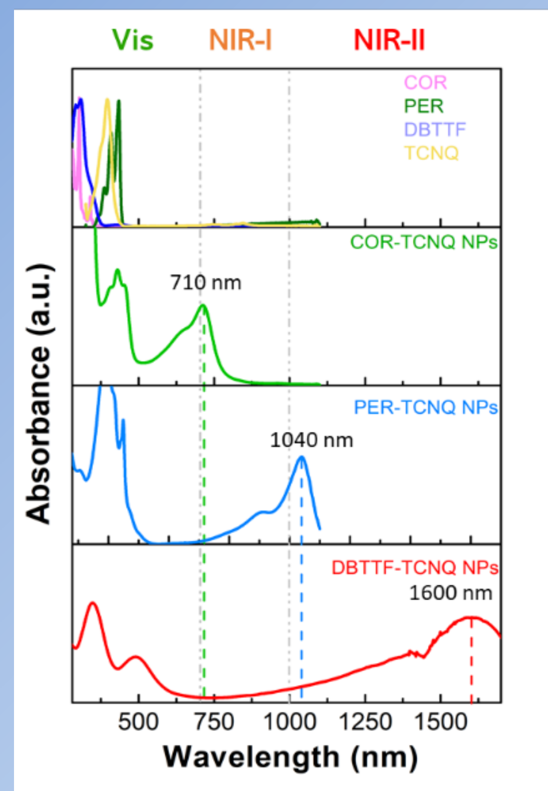
- Good PDT performance using TADF CTC form by TAPC:DPTPCz
- No effect if only TAPC or DPTPCz is used.

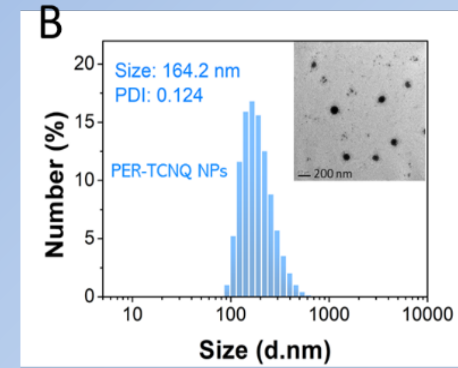
Zhang & Lee et al, *Chem. Comm.*, **52**, 11744 (2016).

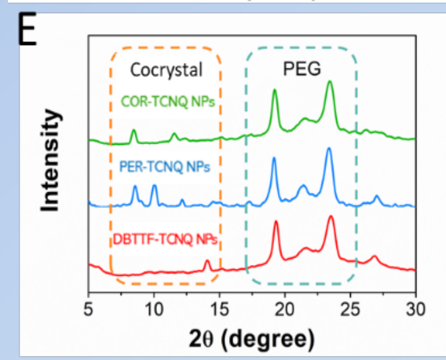
CTC for killing bacteria

- Prepared nanoparticles of :A of TCNQ + D of { DBTTF / PER / COR }
- All have no absorption > 500 nm.
- Their CTC nanoparticles show absorption peaks at 1600, 1040, 710 nm.





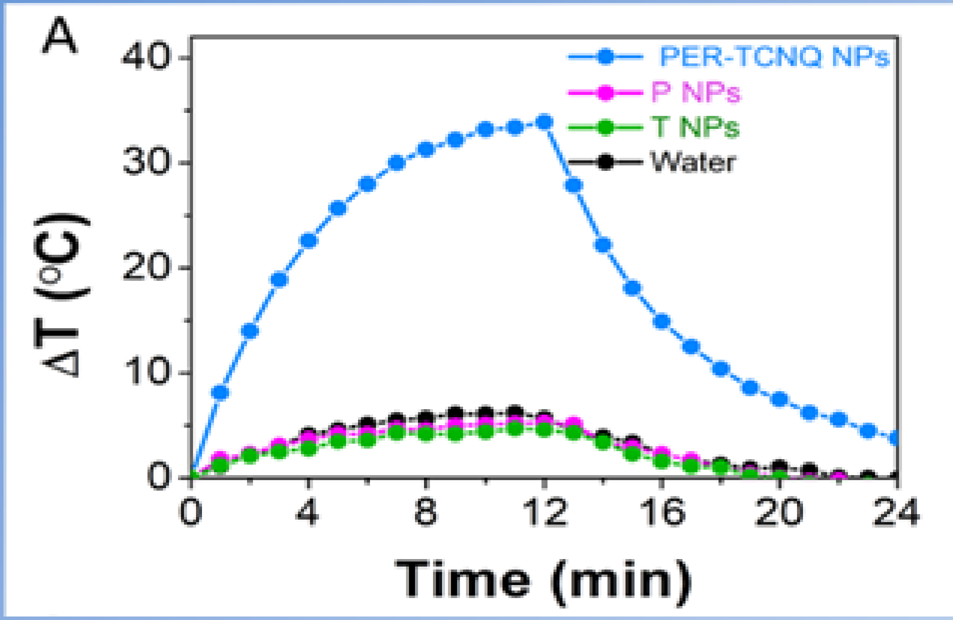


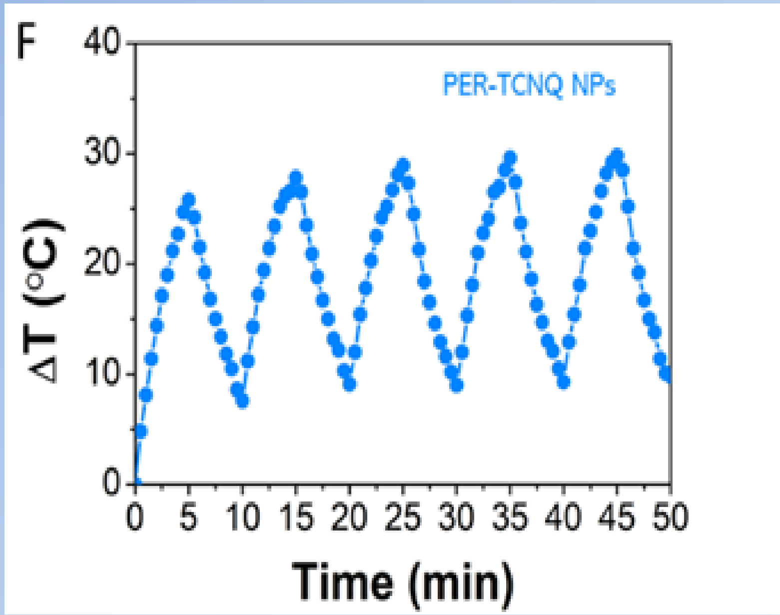


Tian & Lee et al, Angew. Chemie., https://doi.org/10.1002/anie.202101406

Perylene:TCNQ CTC Nanoparticles

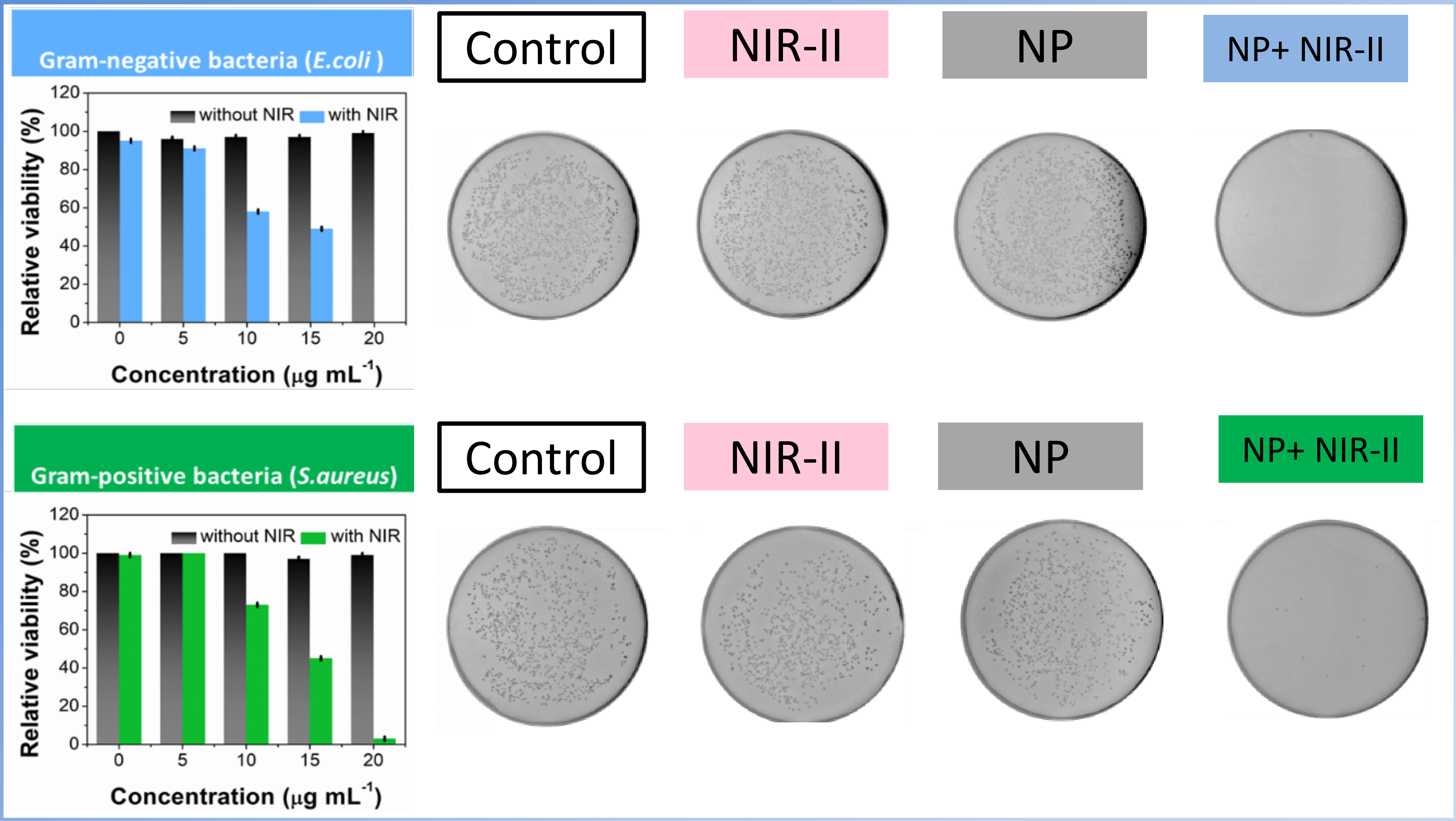
- Good photothermal conversion efficiency up to ~42% under 1064 nm excitation.
- Stable nanoparticles.





NIR-II triggered antibacterial effects

➢ Kill both Gram -Ve & Gram +Ve bacteria under 1064 nm



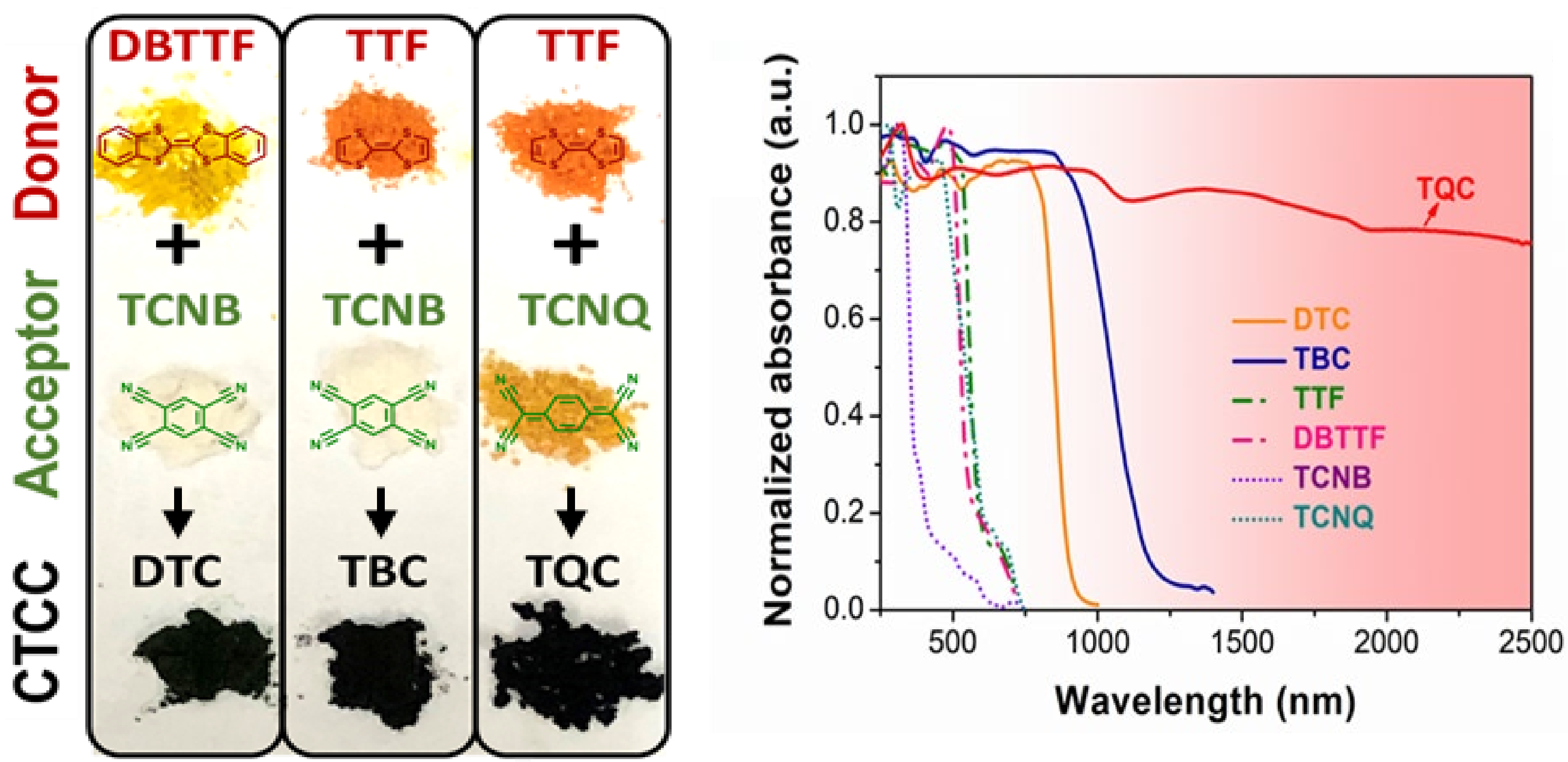
Tian & Lee et al, Angew. Chemie., https://doi.org/10.1002/anie.202101406

Outline

- What is charge transfer complex (CTC)?
- Characteristic signatures of CTCs.
- Why CTC is important in optoelectronic devices?
- Examples on CTCs' optoelectronic applications.
- Biomedical applications of CTCs.
- Energy & environmental applications.
- Conclusion.

CTC co-crystals

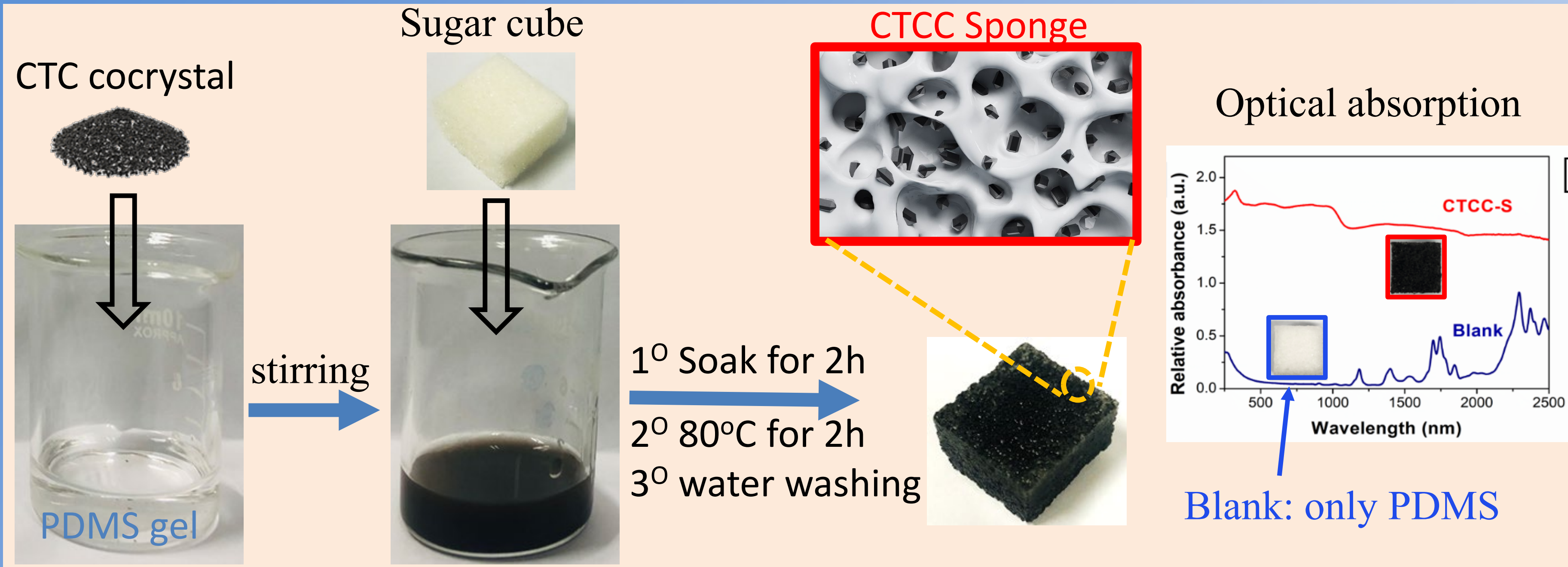
Mix donor & acceptor solutions to form co-crystals



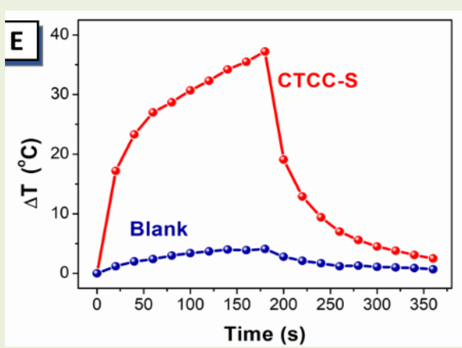
Tian & Lee et al, *ACS Energy Letts*, **5**, 2698 (2020)

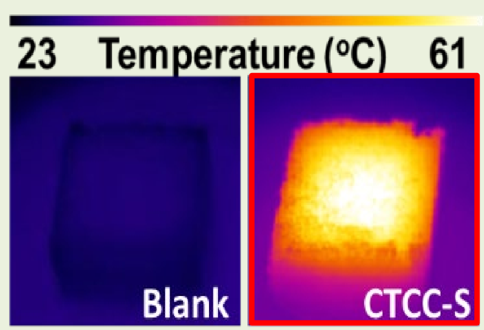
Preparation of CTC co-crystal sponge (CTCCS)

- PDMS+co-crystals to fill pores of a sugar cube template.

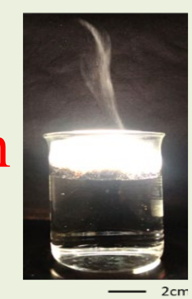


Upon 1 Sun irradiation:





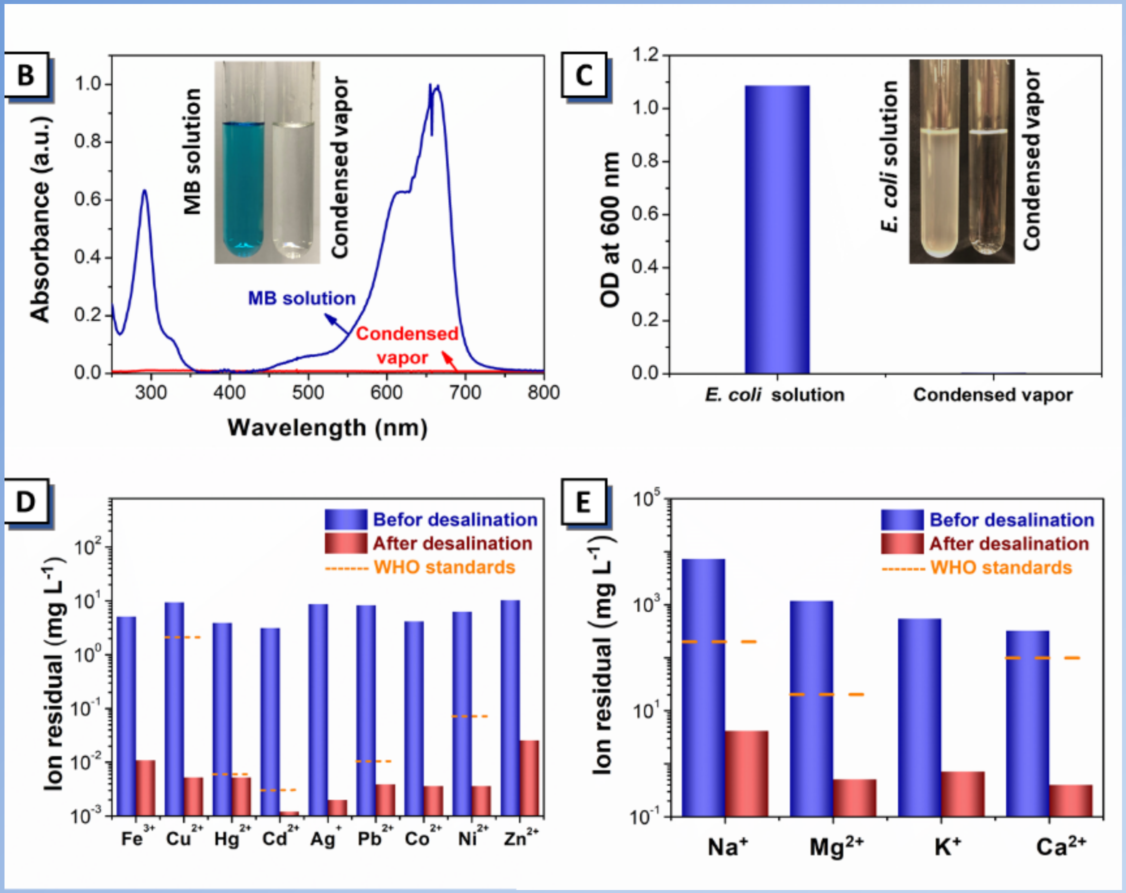
3 Sun



Evaporation & purification performance

- Water evaporation rate: 1.67 kg m^{-2} h^{-1} under 1 Sun.
- Fresh & clean water vapor from contaminated/sea water.
- Remove dye, E coli, metal ions

Tian & Lee et al, *ACS Energy Letts*, **5**, 2698 (2020)



Department of Chemistry
香港城市大學
City University of Hong Kong

Conclusion

- Formation of CTC is a simple way of getting new and unconventional properties from organic materials.
- High electrical conductivity, interfacial charge, red-shifted absorption and emission of CTC have been applied in various organic optoelectronic devices.
- CTCs can have various novel applications beyond optoelectronics --- biomedical, energy & environmental etc.

Acknowledgement

Funding:

CityU, RGC, ITC.

Co-Workers:

M.Y. Chan, W.C. Chen, S.L. Lai, K.M. Lau, M.F. Lo, S.L. Li, X.K. Liu, T.W. Ng, J.X. Tang, S. Tian, C.J. Zheng, J.F. Zhang,

Prof C. Adachi (Kyushu U)

Prof B.Z. Tang (HKUST)

Prof W.J. Zhang (CityU)

Prof X.H. Zhang (Soochow U)

Thank you