聲明

本檔案之內容僅供下載者自我學習或推廣化學教育之非營利目的使用。並請於使用時註明出處。 例如「本頁取材自○○○教授演講內容」

Development of Novel Materials for Sustainable Environment

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Acknowledgement

Collaborators:

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Jiun-Haw Lee
Tien-Lung Chiu

All my hard-working students

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Recycling of organic waste solvent as fuel

- Cement kiln fuel can produced from the residues that remain after solvent recycling or organic solvent waste that cannot be recovered or economically recycled.
- Contamination of the waste, in particular, by halocarbons creates environmental problems.
- Fast pre-screening method for halo-carbon contamination is highly desired.

Photochromic Detection of C-X bond

Halocarbons: industrial solvent, refrigerant, and pesticide

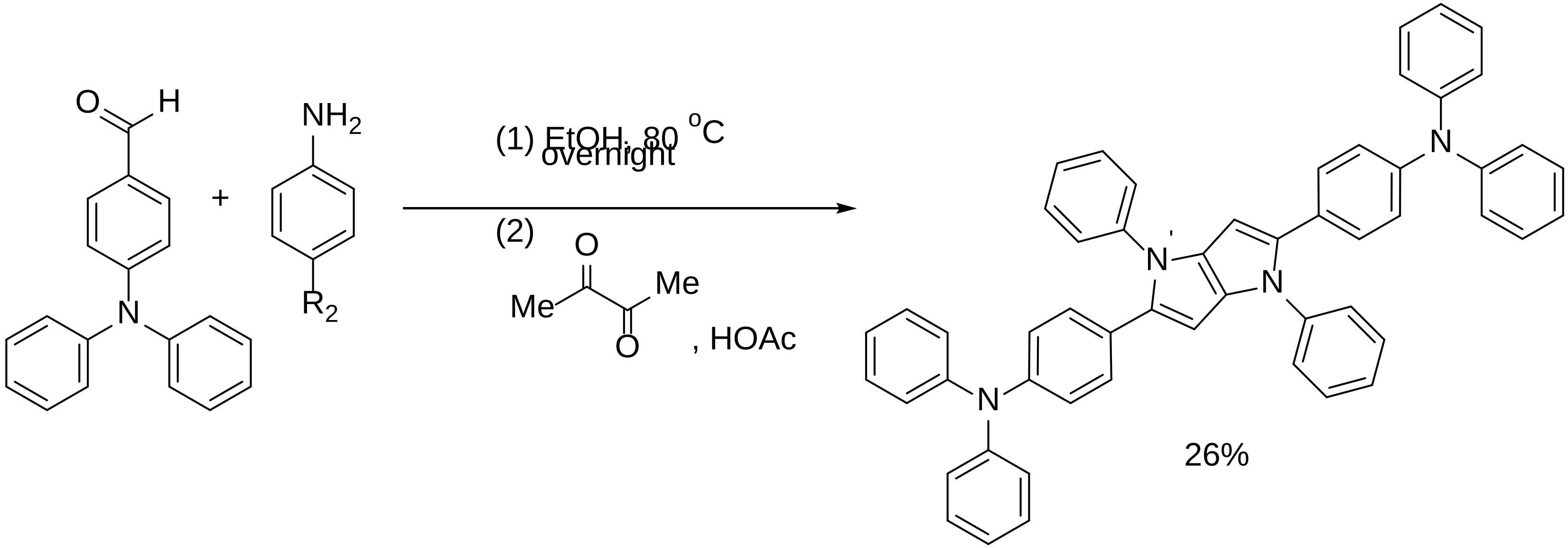
Toxic effects: threat to the environment, ecosystems, human health.

Any fast method to detect halocarbons??

C-X* antibonding orbital: Good electron accepting group.

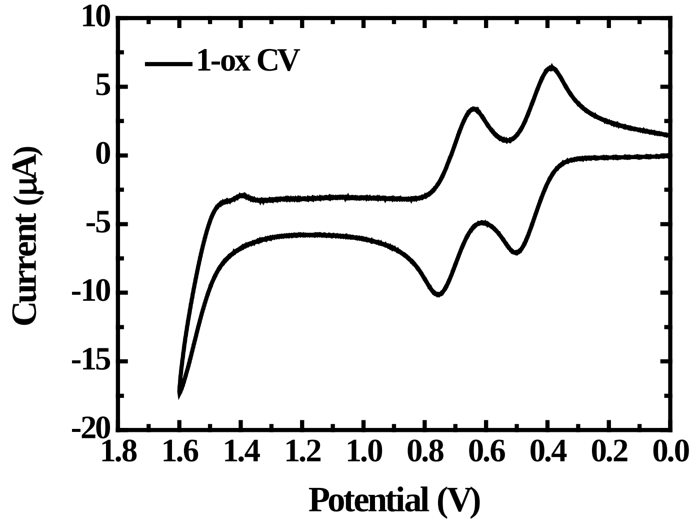
Ferrocene: Photo-induced electron transfer to C-X* antibonding orbital, leading to decomposition of the C-X bond.

2,5-Bis(triphenylamine)-*N,N'*-Diphenylpyrrolo-[3,2-b]pyrrole



(1) Oxidation potential is slightly low than that of ferrocene

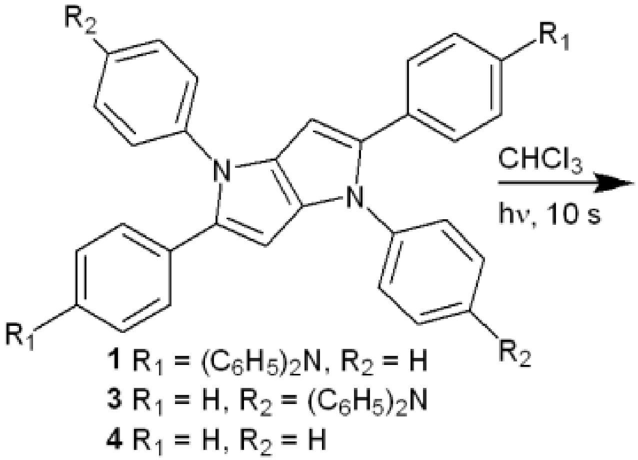
(2) Potentially useful photo-induced electron donor for halocarbons

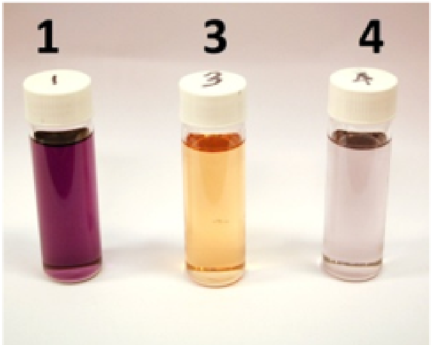


Anal Chem. 2016, 88, 1195-1201

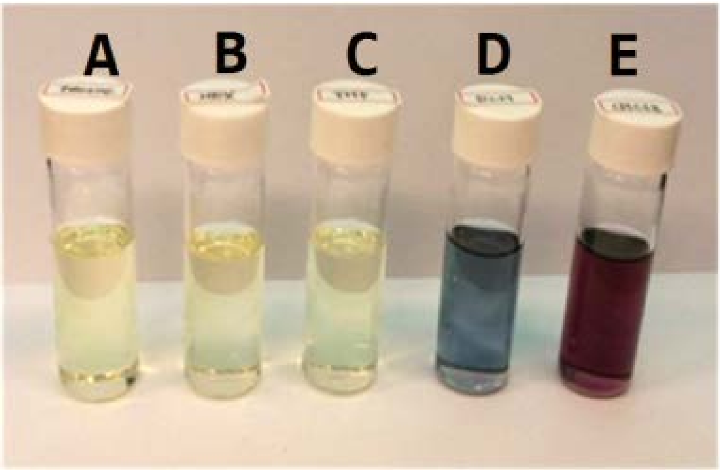
Photochromism of various pyrrolo-[3,2-b]pyrrole

Photochromic change of **1**, **3**, and **4** in $CHCl_3$/PhMe (1 M)





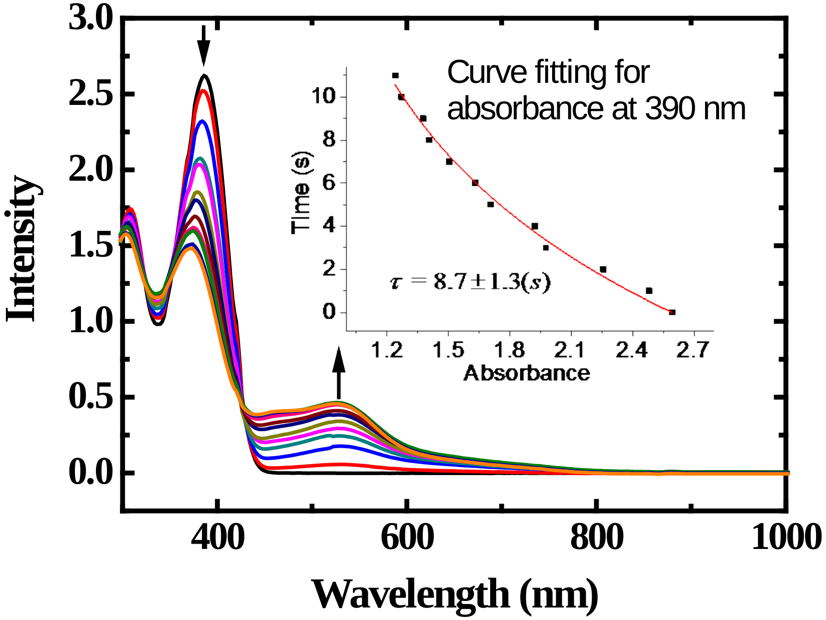
Photochromic change of **1** in (A-E) PhMe; *n*-hexane; THF;CH_2Cl_2;$CHCl_3$

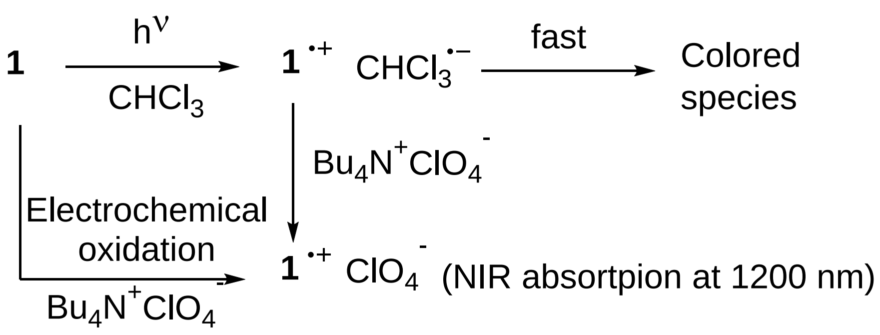


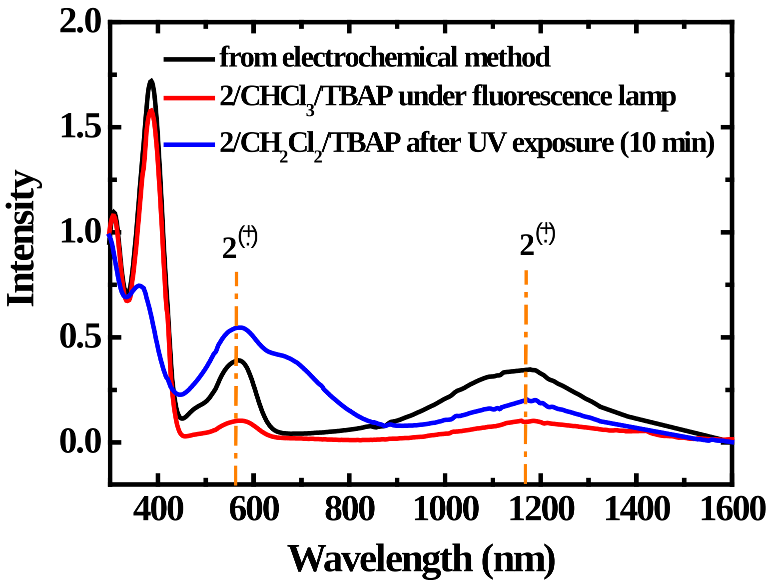
Time resolved photochromic change of **1** in $CHCl_3$ (1 M in MePh)

An isosbestic point at 427nm; the pseudo first order kinetics

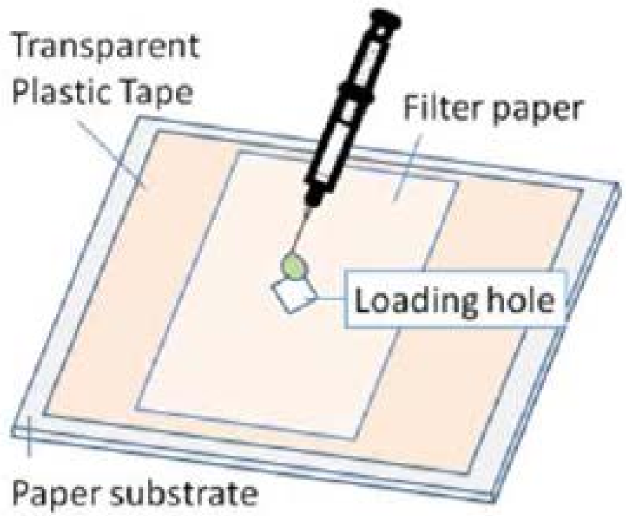
$$t = -\tau \cdot \ln((A - A_\infty)/(A_o - A_\infty))$$

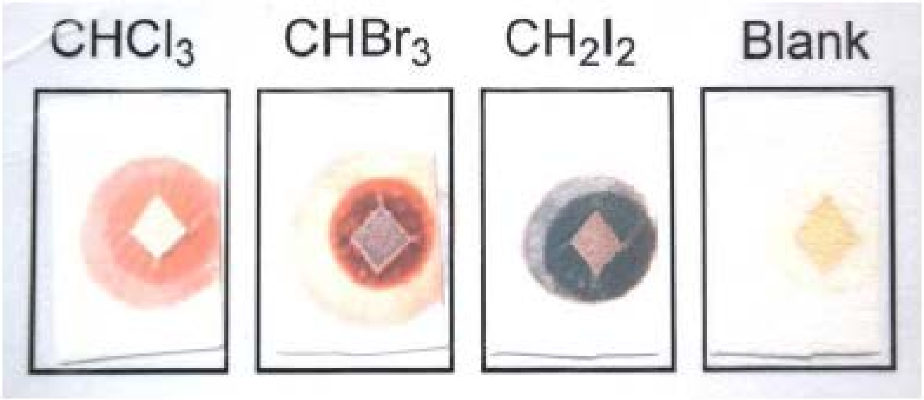






Test cartridge for halocarbons

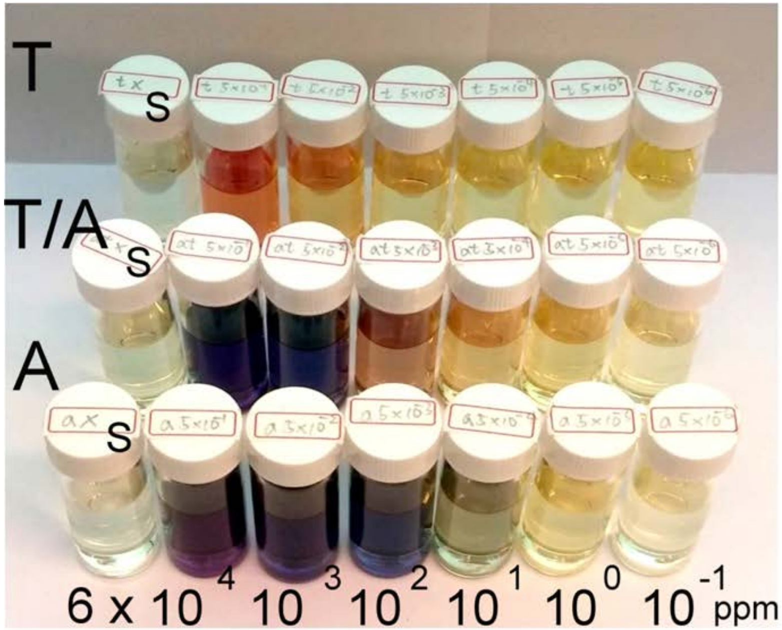


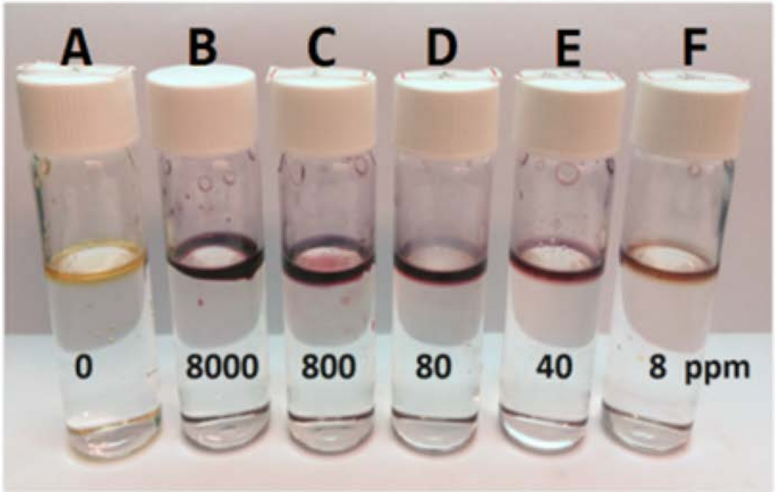


For the molecular sensor to be practically useful, it should meet some criteria, including

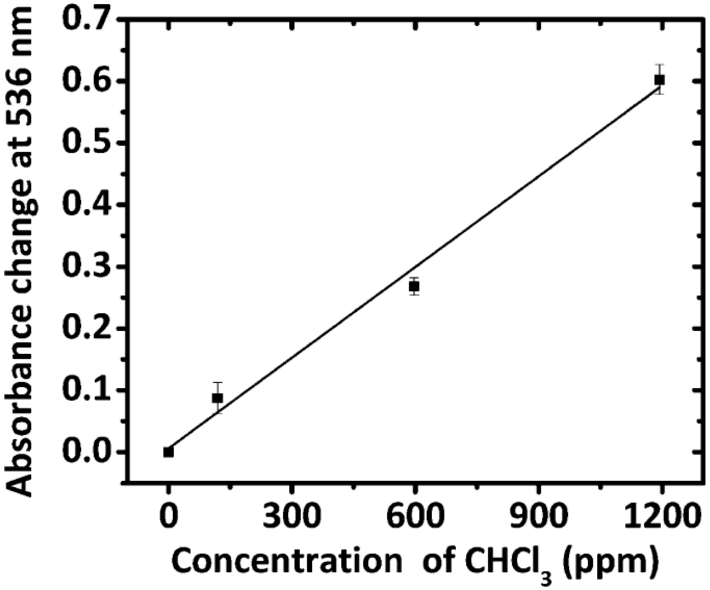
- •high stability without stimulus with light,
- •distinct spectral change upon UV irradiation in the presence of the targeting species,
- •high stability of the newly produced species so that the absorbance change can be used to quantify the targeting species.

Test cartridge for halocarbons



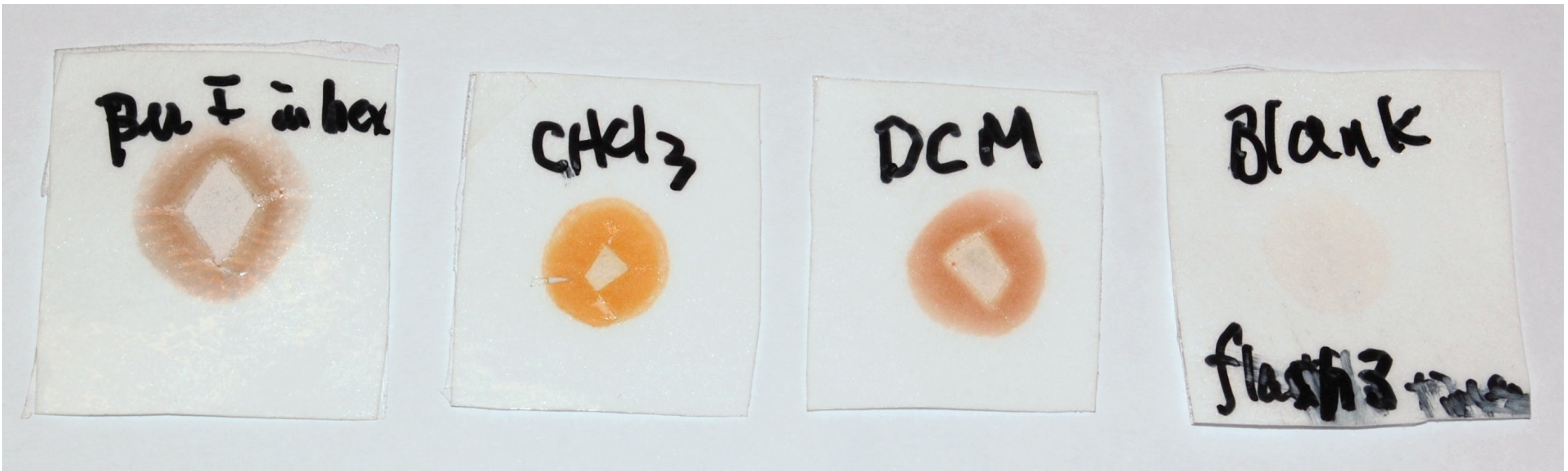


- (top) Solvatophotochromic response of 1 (1 M) and $CHCl_3$ ((0.5−5) × 10^{-6} M) in toluene (T), toluene/CH_3CN (T/A) (1:1), or CH_3CN (A)
- (bottom) Visual detection of $CHCl_3$ in water (B−F: 8000 to 8 ppm)



A calibration curve based on a correlation between the absorbance change at 536 nm versus the concentration of $CHCl_3$ at a fixed irradiation time of 135 s. The UV intensity is 1 mW/cm^2.

New class of test materials from ITRI for halocarbon detection



Short summary before going to next

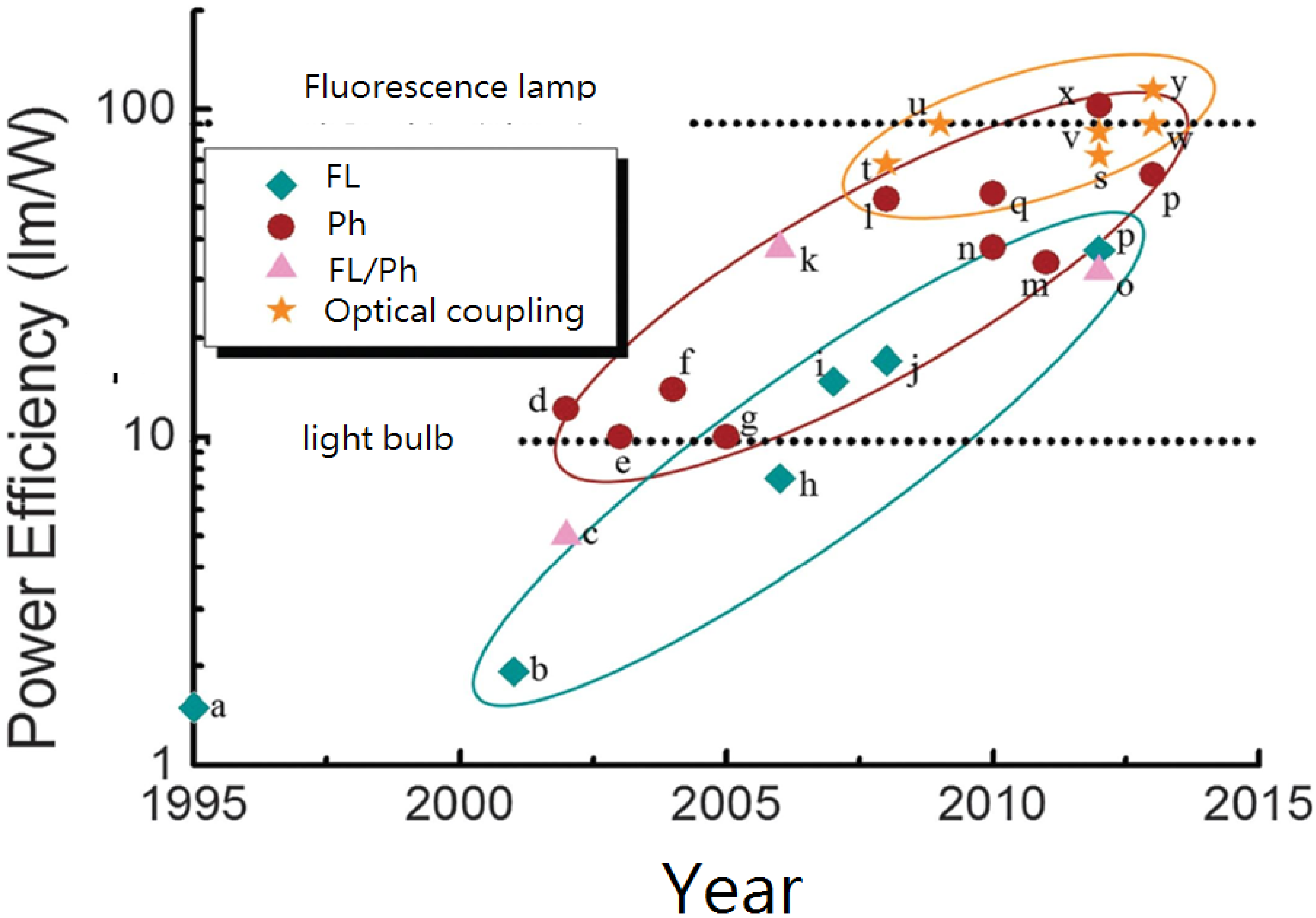
- **DPPH's are the family of compounds that are suitable for halo-containing compound detection.**

How much electricity is used for lighting in the United States?

- The U.S. Energy Information Administration (EIA) estimates that "In 2016, about 279 billion kilowatthours (kWh) of electricity were used for lighting by the residential sector and the commercial sector in the United States. This was about 10% of the total electricity consumed by both of these sectors and about 7% of total U.S. electricity consumption."

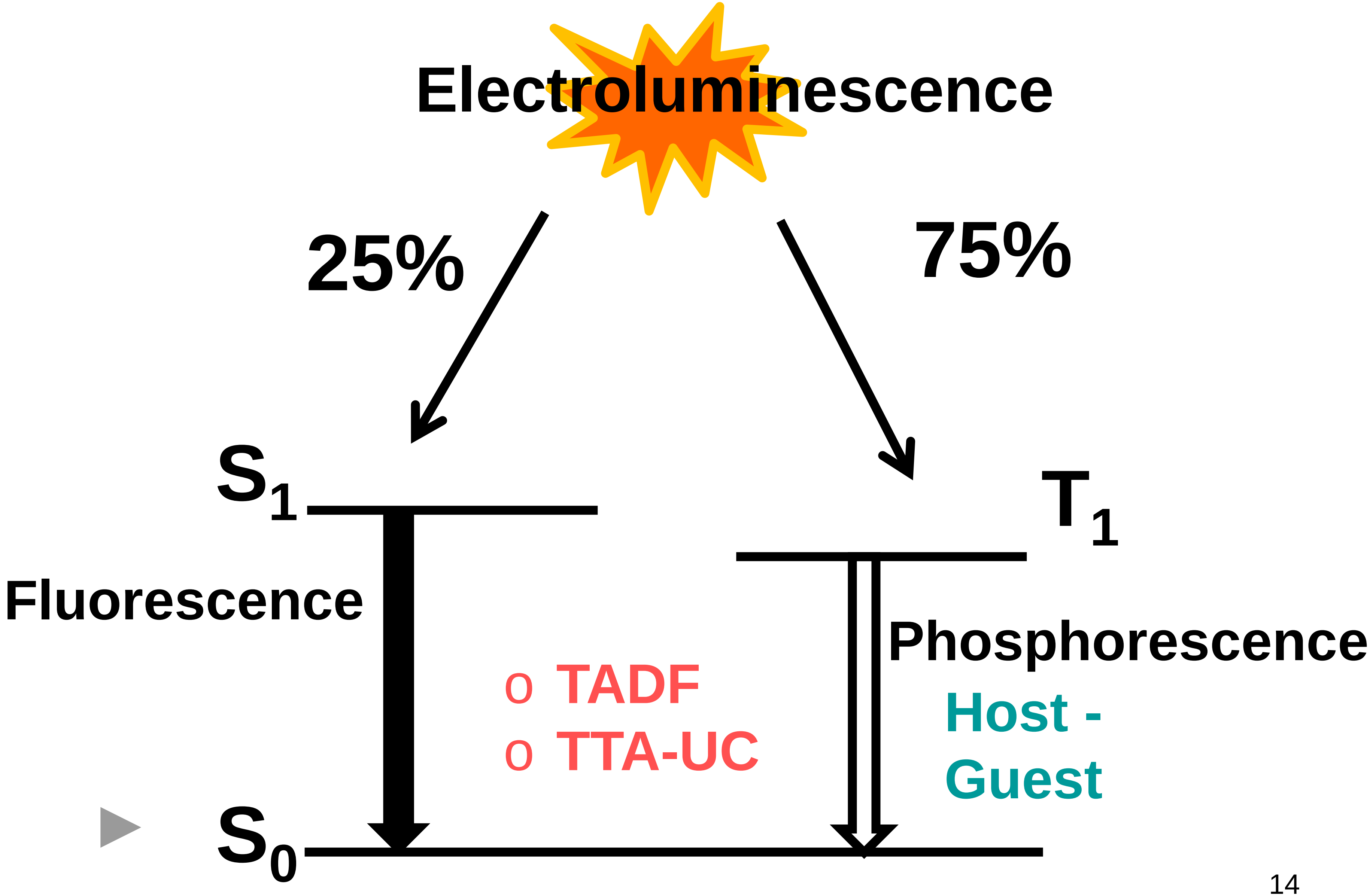
- *https://www.eia.gov/tools/faqs/faq.php?id=99&t=3*

Lighting efficiency :
Current efficiency and Power efficiency



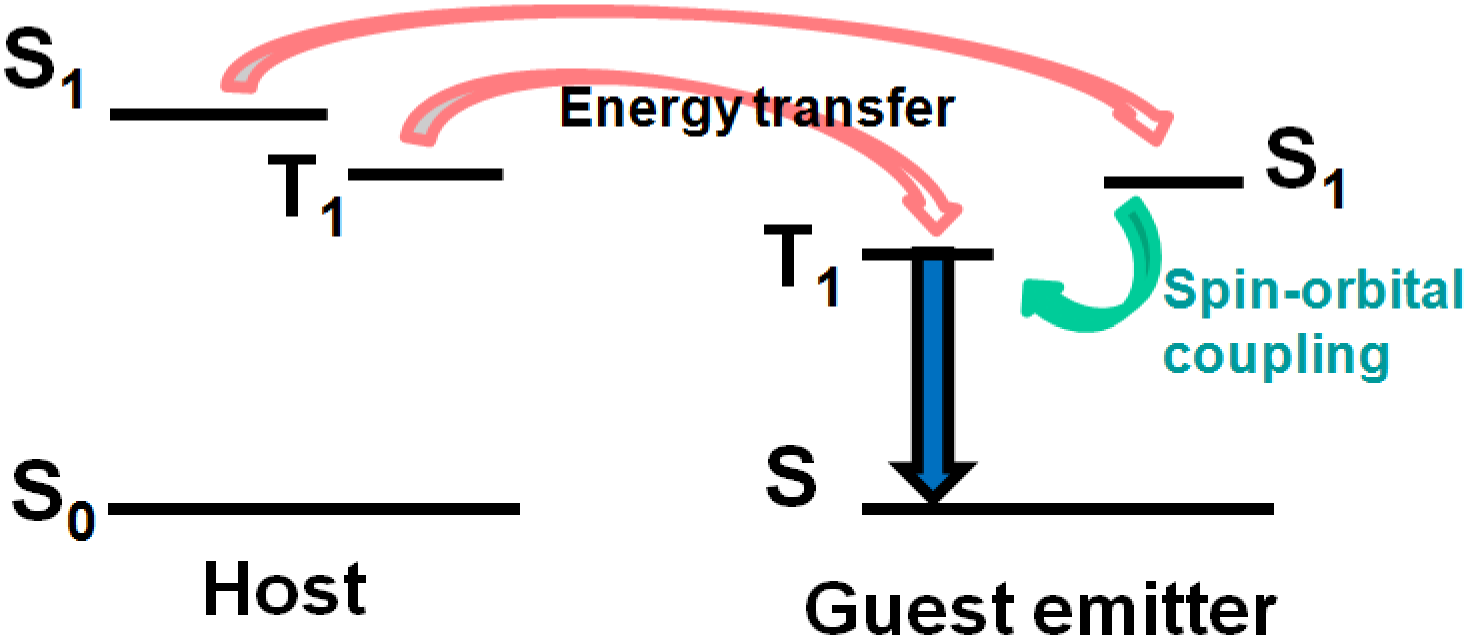
J.-H. Jou etal J. Mater. Chem. C, 2015, 3, 2974

OLED



Electroluminescence
25%
75%
S_1
T_1
Fluorescence
Phosphorescence
o TADF
o TTA-UC
Host - Guest
S_0

Host – Guest OLED System



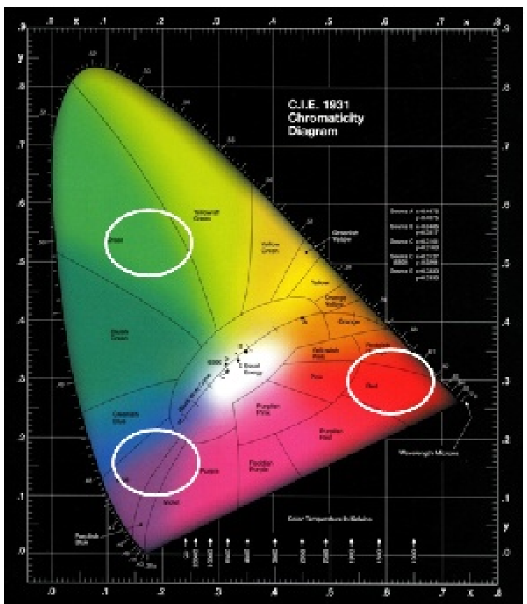
4 criteria for suitable host

- Higher singlet energy and triplet energy than guest for effective energy transfer.
- HOMO and LUMO should be matched for charge-transport
- Great carrier transporting ability is better for performance
- Great thermal and morphological stability

Recent Standard for PHOLED

PHOLED Performance (at 1000 cd/m²)	1931 CIE Color Coordinates	Luminous Efficiency (cd/A)	Operating Lifetime (hrs)	
			LT 95%	LT 50%
DEEP RED	(0.69, 0.31)	17	14,000	250,000
RED	(0.66, 0.34)	29	23,000	600,000
RED	(0.64, 0.36)	30	50,000	900,000
YELLOW	(0.44, 0.54)	81	85,000	1,450,000
GREEN	(0.31, 0.63)	85	18,000	400,000
LIGHT BLUE	(0.18, 0.42)	50	700	20,000

The results are for bottom-emitting structures (with no cavities) fabricated by vacuum thermal evaporation. Lifetime data are based on accelerated current drive conditions at room temperature without any initial burn-in.



UNIVERSAL DISPLAY CORPORATION

Y. Zhang; J. Lee; S. R. Forrest *Nat. Commun.* 2014, 5:5008

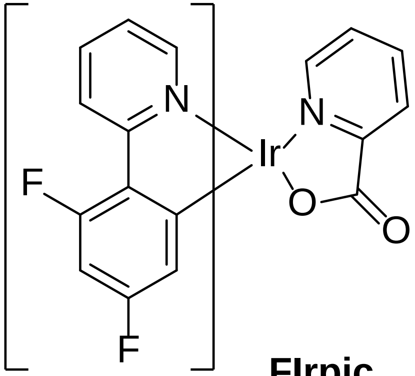
….a lifetime of 616±10 h (time to 80% of the 1,000 cdm^2 initial luminance) with chromaticity coordinates of (0.15, 0.29)

J. Lee; S. R. Forrest and coworker *Nat. Commun.* 2017, 8:15566

T80 = 334±5 h (time to 80% of the 1,000 cdm^2 initial luminance) with a chromaticity coordinate of (0.16, 0.31)

Novel Host to Achieve Highly Efficient Blue PHOLED Device

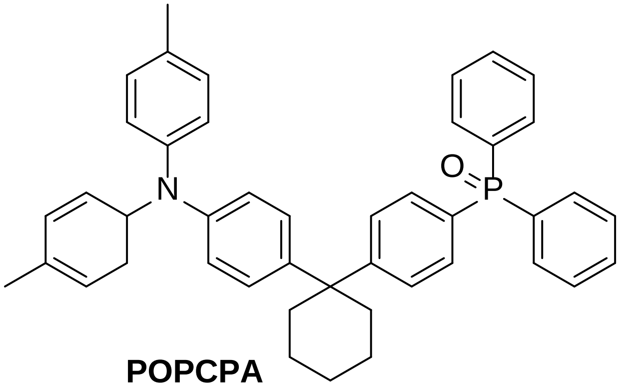
- Host properties and stability
- Emitter properties and stability
- Interactions between host/host, host/emitter and emitter/emitter
- Interactions between their excited states with their ground states



FIrpic

Selected hosts recently published in journals

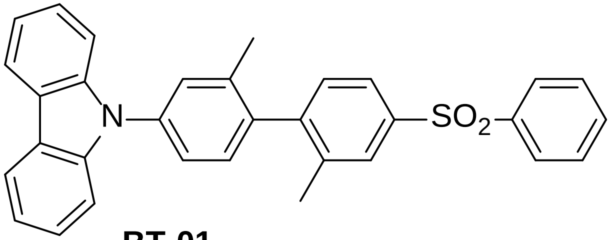
Usually the hosts are hole transport type or bipolar type



POPCPA

(sky blue) CIE (0.15, 0.26)
37.5 cdA^{-1}

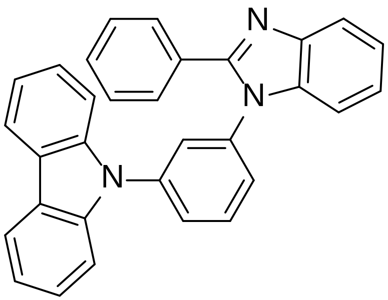
ZH Lu, C Yang, Chem. Mater. 2014, 26, 1463-1470.



BT-01

(sky blue) CIE (0.16, 0.36)
73.5 cdA^{-1}

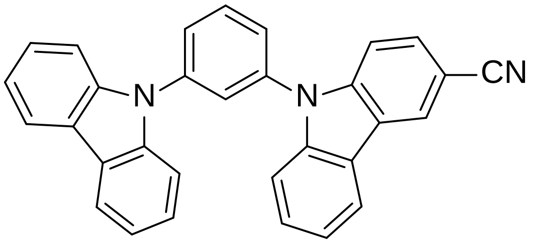
CC Cheng Chem. Mater. 2017,29,1527



mNBIC

(Bluish green) CIE (0.14, 0.32)
54.5 cdA^{-1}

D. Ma J. Mater. Chem. C 2014, 2, 2466-2469.



mCPCN

58.7cdA^{-1}

KT Wong J. Mater. Chem., 2012, 22, 16114

Our Motif

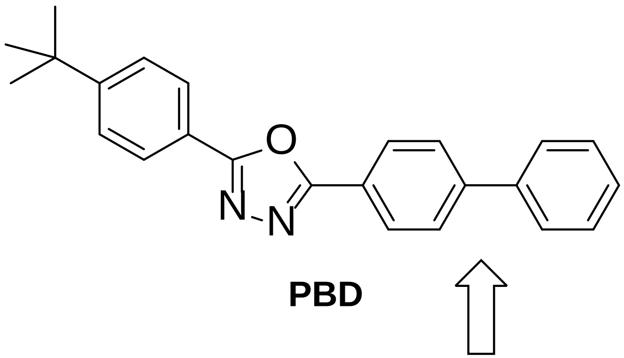
It has been shown that the host material stability is crucial for the lifetime of the PHOLED device.

S. C. Xia, R. C. Kwong, V. I. Adamovich, M. S. Weaver, J. J. Brown IEEE 07CH37867 45 th Annual International Reliability Physics Symposium, Phoenix 2007, 253-257.

"Novel materials for blue PHOLED are still highly desired."

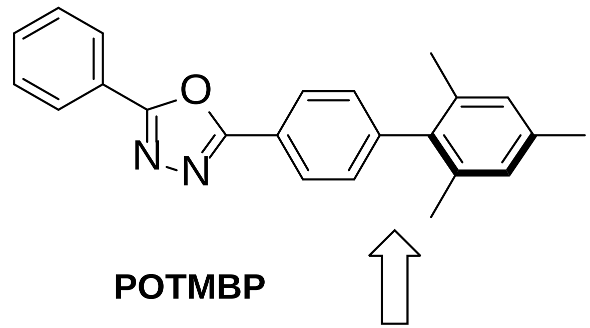
"Materials having similar HOMO/LUMO and photo-physical properties show different OLED device performance."

Attempts on reducing the triplet state energy



PBD

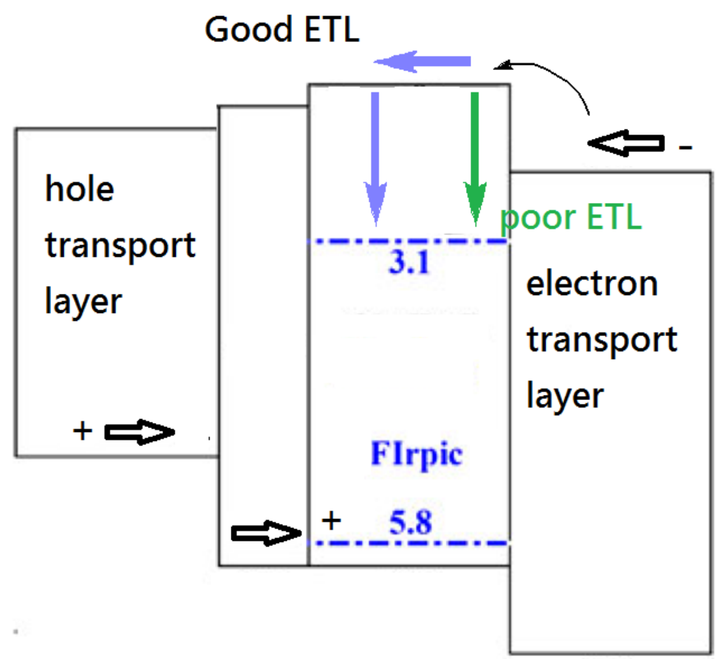
Pi-Conjugation may lead to lower triple energy



POTMBP

Steric effect may twist the conformation and reduce the pi conjugation

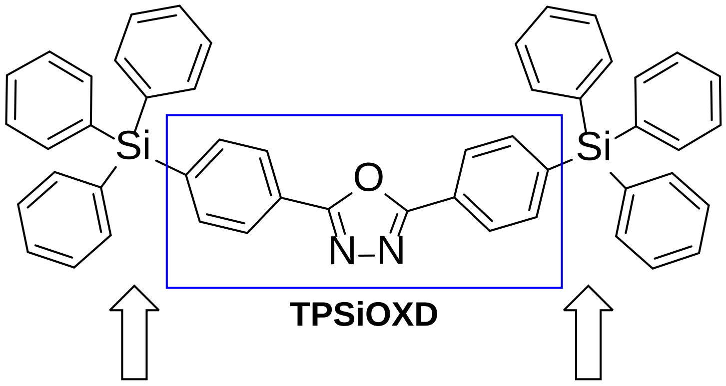
Host	emitter	color	current efficiency
POTMBP	FIrpic	blue	13.0 cd/A
PBD	FIrpic	blue	2.05 cd/A



J . Appl. Phys. 109, 084520 (2011)

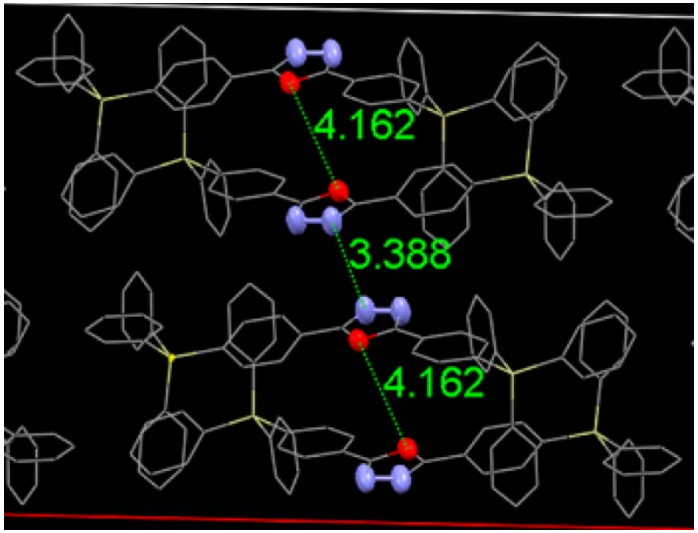
Attempts on reducing the triplet state energy

Unexpectedly good performance



TPSiOXD

interrupt the pi conjugation



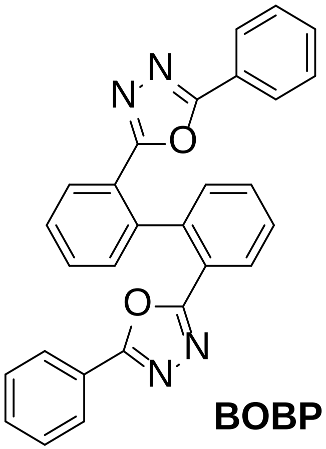
Host	emitter	color	current efficiency
POTMBP	FIrpic	blue	13.0 cd/A
PBD	FIrpic	blue	2.05 cd/A
TPSiOXD	FIrpic	blue	39.9 cd/A

ITO (1100 A˚)/NPB (500 A˚)/mCP (100 A˚) /host, 2, 3, 5-Firpic (15 wt %) (300 A˚) /TAZ (400 A˚)/LiF (12 A˚)/Al (1000 A˚)

- **Easily prepared in large scale**
- **maximum luminance of 5124 cd/m^2**

Org. Lett. **2012, 14, 4986–4989**

Design on electron transport host

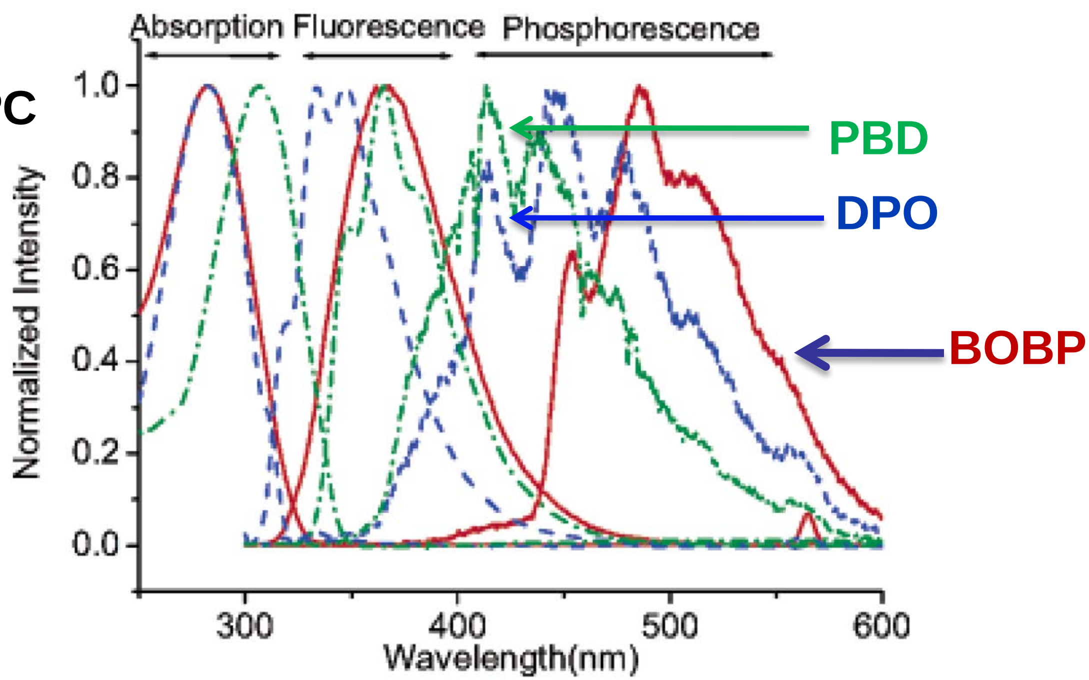


BOBP

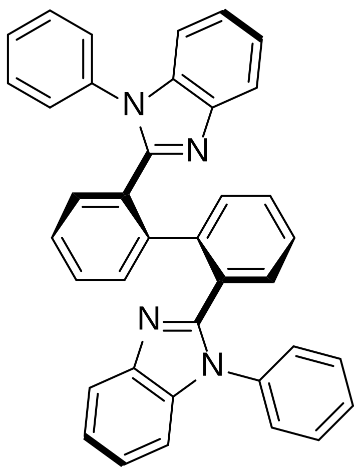
Host	emitter	color	max. brightness	current efficiency
BOBP	Ir(ppy)3	green	43,000	26 cd/A
BOBP	FIrpic	blue	—	6.7 cd/A
				12 cd/A (DEML)

Org. Lett. **2007**, 9, 235-238;
Appl. Phys. Lett. **2007**, *90*, 243501; *94*, 223301;
Appl. Phys. Lett. **2009**,
J. of Appl. Phys., **2011**, *109*, 0845

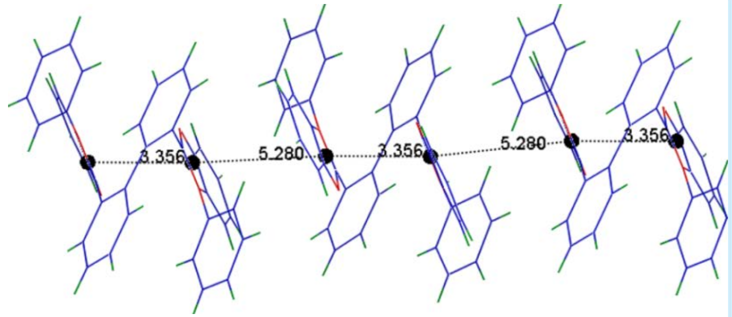
T_g: 44 ^{o}C



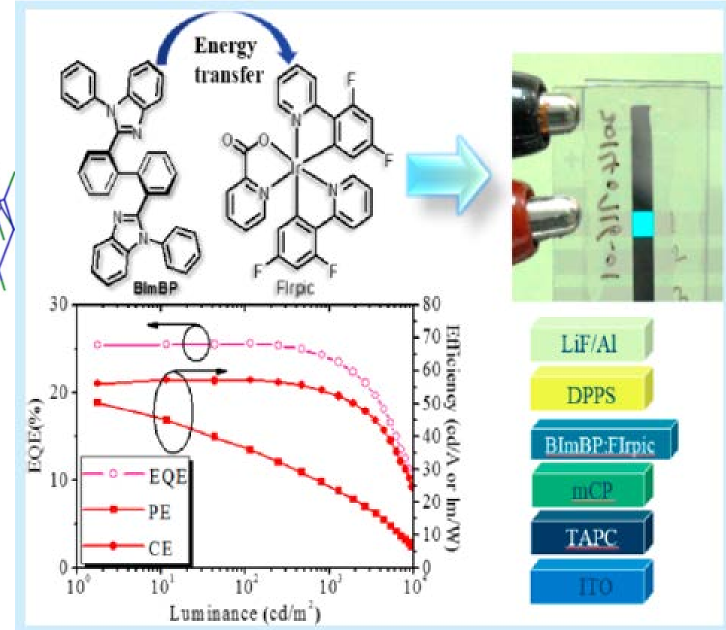
Importance of the thru-space pi-interactions of the molecules



BImBP



Current efficiency: 57.2 cd/A,
Power efficiency of 50.4 lm/W
External quantum efficiency 25.7%.



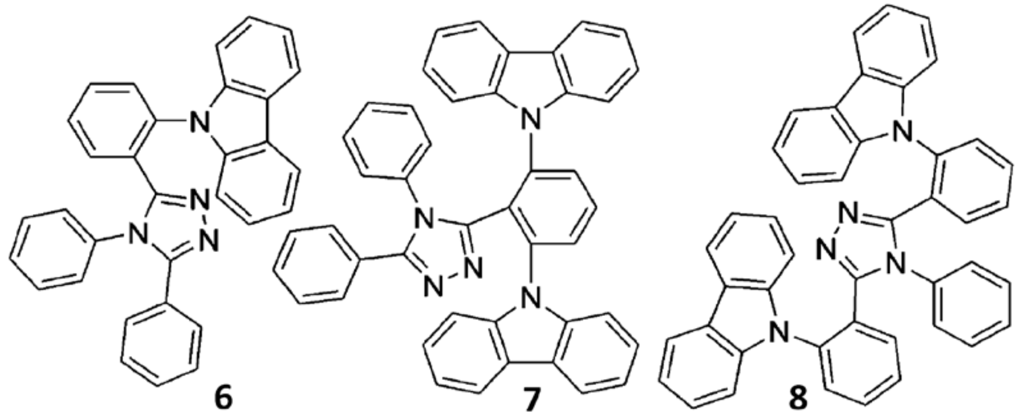
- **No T_g being observed below 270 ˚C**
- **BImBP favors a native crystalline form. T**
- **The high tendency of crystallization does not hamper thePHOLED performances**

Org. Lett., 2014, *16* (20), pp 5398–5401

Table 1. Electrochemical Data and Photophysical Data for BImBPs and the References

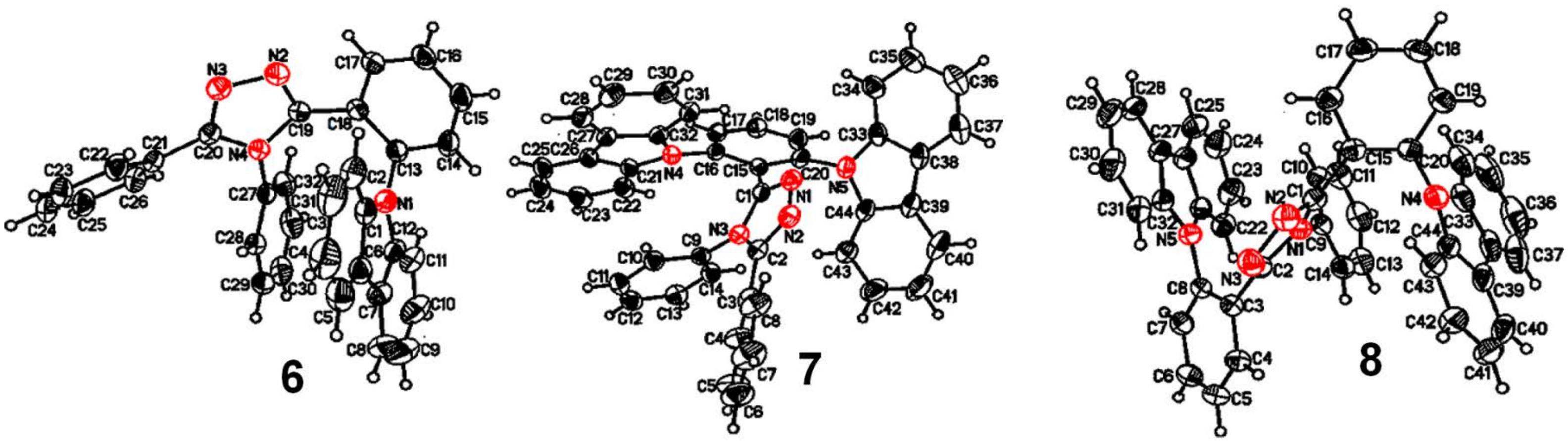
host	λ_{abs}^{onset} (nm)[a]	$\lambda_{PH}^{Max/onset}$ (nm)[b]	E_T/E_g (eV)	E_{HOMO}[c]/E_{LUMO}[d] (eV)
BImP	326	479/391	3.17/3.81	−6.22/−2.41 (−2.46)[e]
o-PhBz	328	480/403	3.08/3.78	−6.17/−2.39 (−2.44)[e]
BImBP	330	550/430	2.89/3.76	−6.12/−2.36 (−2.42)[e]
				−6.18/−2.36[f]

Ambipolar Orthogonal Donor Acceptor Host for Blue OLED



Org. Lett., 15 (2013) 4694

orthogonal alignments of the aromatic units were observed in this system



PHOLED performance

Table 2. Performances of PHOLED Devices **6 - 8**

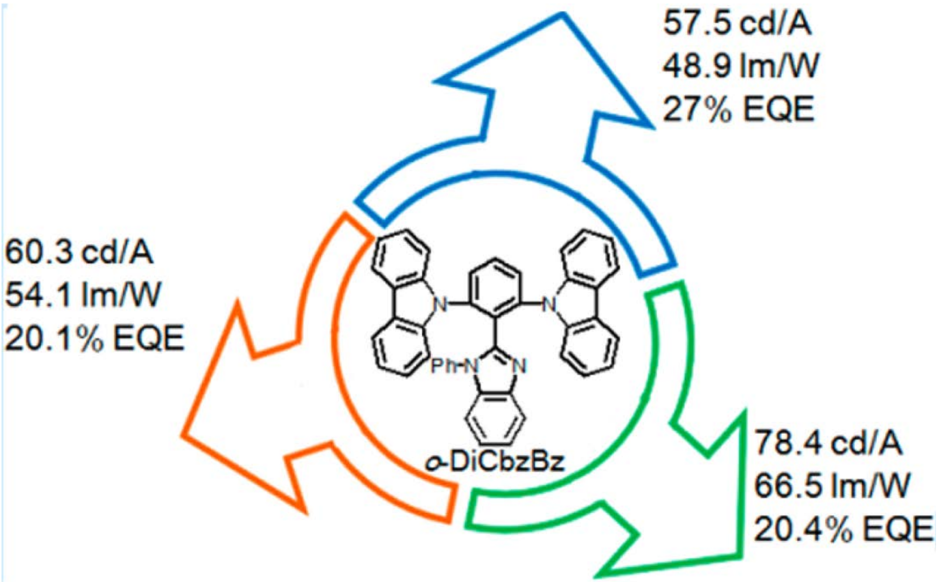
device[a]	L_{max}[b] (cd/m^2)	$\eta_{c.max}$[c] (cd/A)	$\eta_{p.max}$[d] (lm/W)	EQE_{max}	CIE shift Δx, Δy
6, 15%	17 770	47.1	41.2	20.2%	0.016, 0.043
7, 12%	17 510	43.3	38.6	17.9%	0.016, 0.039
8, 9%	15 730	40.2	36.1	17.1%	0.013, 0.031

[a] Host-FIrpic doping level. [b] At 12 V. [c] $E_{applied}$ for **6**, **7**, and **8** are 4, 4, and 3.5 V. [d] At 3.5 V.

After find tuning of the device,
maximum η_C of 52.1 cd/A,
maximum η_p of 46.1 lm/W
maximum η_{EQE} of 24.4%
Favorable efficiency roll-off at a high brightness of 1000 cd/m2 (η_C of 44.6 cd/A and η_{EQE} of 21%)

J. Phys. Chem. C 2015, 119, 16846−16852

Universal hosts for Red/Green/Blue emitters



Org. Lett. 2016, 18, 672−675

Molecular Structures and the Synthetic Routes of *o*-CbzBz and *o*-DiCbzBz

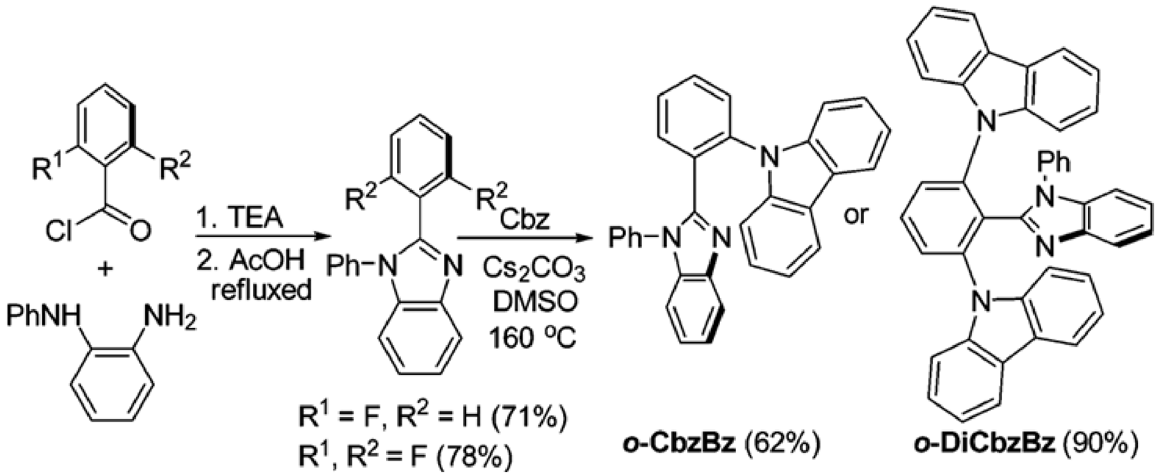
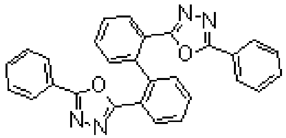
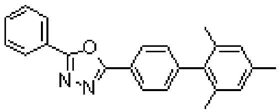
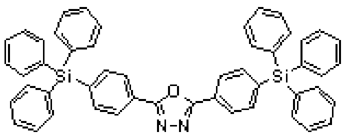
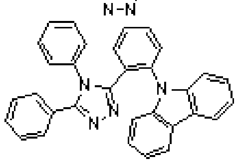
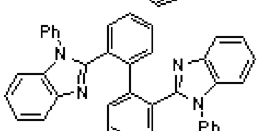
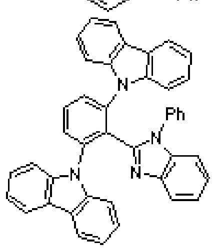
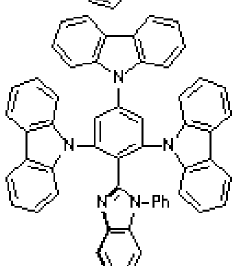
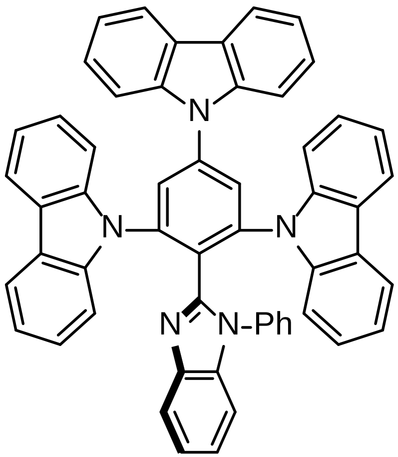


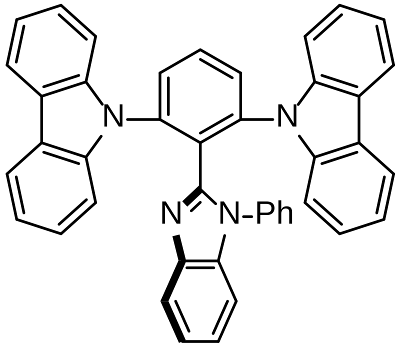
Table 1. Performance of ambipolar hosts and electron-transport hosts for PHOLED

	emitter	color	max. brightness	current efficiency	References
	$Ir(ppy)_3$	Green	43,000 cd/m^2	26 cd/A	*OL* **2007**, *9*, 235-238 *APL* **2007**, *90*, 243501 *APL* **2009**, *94*, 223301 *OE* **2011**, *12*, 756-765
	FIrpic	Blue	-	6.7 cd/A	
	FIrpic	Blue		13.0 cd/A	*JAP* ***2011**, 109, 08452*
	FIrpic	Blue	5124 cd/m^2	39.9 cd/A	*OL* **2012**,*14*, 4986
	FIrpic	Blue	17770 cd/m^2	47.1cd/A	*OL.* **2013**,*15*, 4694
	FIrpic	Blue	9513 cd/m^2	57.2cd/A	*OL* **2014**,*16*, 5398
	FIrpic	Blue and universal	11160 cd/m^2	57.5 cd/A	*OL* **2016**, *18*, 672–675
	FIrpic	Blue	16710 cd/m^2	58.2 cd A^{-1} and 59.4 lm W^{-1}	*JMC C* ***2017**, 5, 3600-3608.*

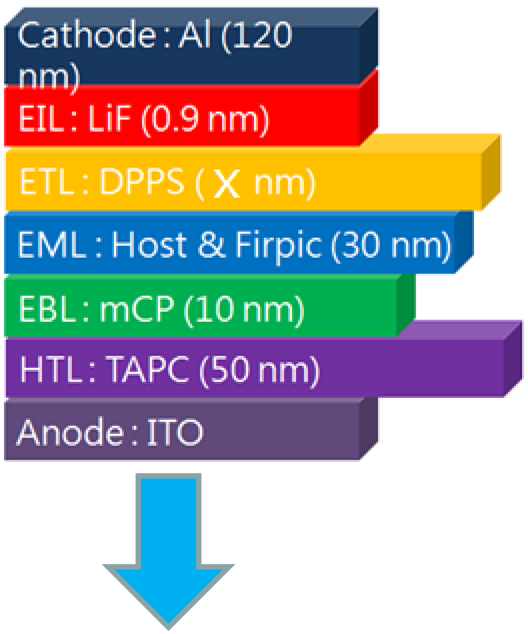
The use of *ortho*-benzimidazole-carbazole substituted benzenes as hosts for blue light PHOLED



TCbzBz

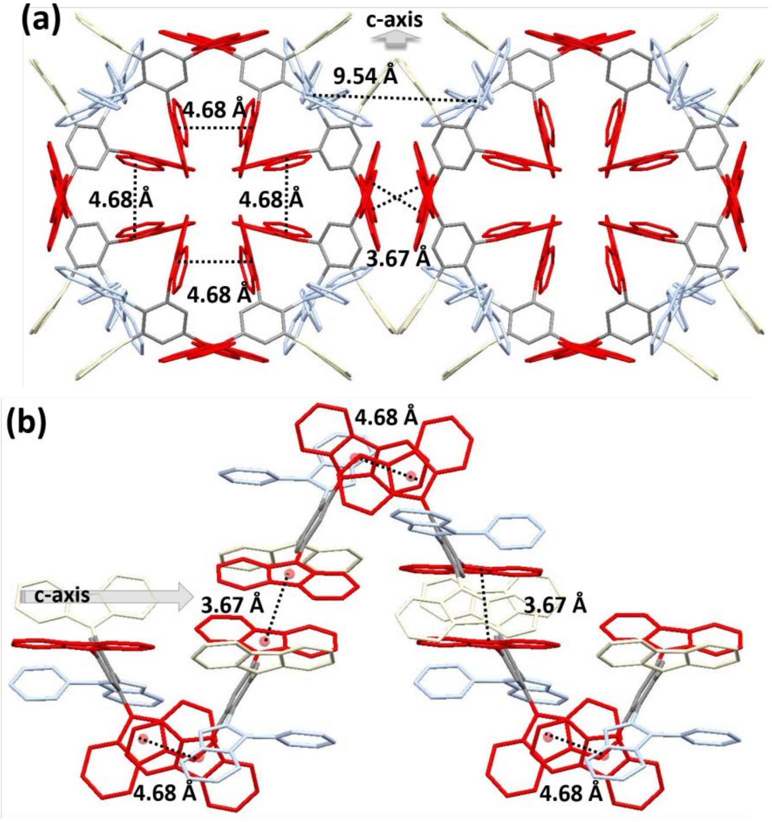


DCbzBz



	Lmax (cd m^{-2})	CE (cd A^{-1})	PE (lm W^{-1})	EQE (%)	CIE (ΔX,ΔY)
TCbzBz-6%	14480	58.2	59.4	28.0	(0.003, 0.008)
DCbzBz-6%	11160	57.5	48.9	27.0	(0.001, 0.004)

The use of *ortho*-benzimidazole-carbazole substituted benzenes as hosts for blue light PHOLED



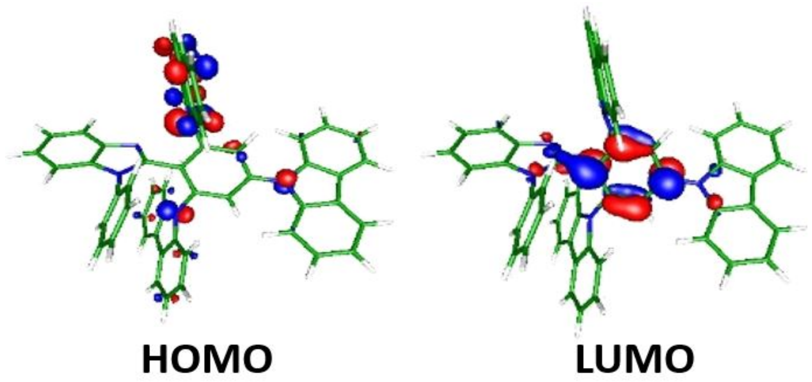


Fig. A The stacking structure of **TCbzBz**. with the measured distances between individual Cbz and Bz pairs, where highlighted Cbz and Bz units are labelled with red and light blue color, respectively. (a) The unit cell of **TCbzBz** viewed along the c-axis. (b) The illustration depicts the possible hole-transporting channel between the columns.

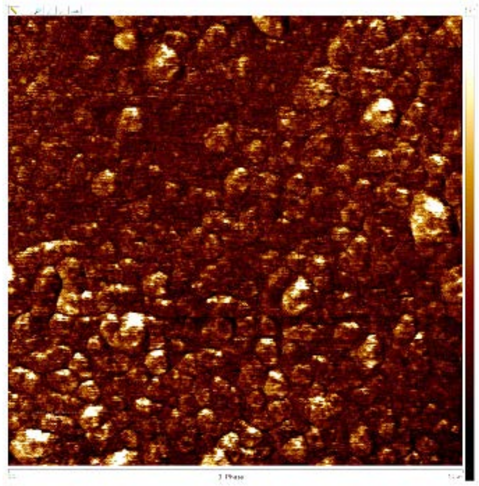


Fig. B. Nano-granules can clearly be observed in image of a vacuum deposited thin film of TCbzbz

Summary

We have successfully devised a series of electron transport and bipolar materials as hosts for PHOLED, with good efficiency performance. We believed that intermolecular stacking interactions play important roles in their performances.

Thanks you for your attention