An Unprecedented Application of Thermally Activated Delayed Fluorescence (TADF) in Light-Emitting Electrochemical Cells (LEECs)

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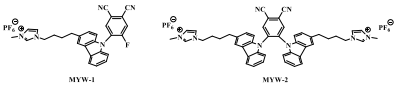
INTRODUCTION

While phosphorescent OLEDs have realized 100% internal quantum efficiency due to recruitment of both singlet and triplet excitons, most of these organometallic emitters are made of expensive metal complexes based on iridium(III) and platinum(II).

Recently, Adachi and co-workers have developed ground-breaking organic fluorescent emitters that operate via a thermally activated delayed fluorescence (TADF) mechanism (*Nature*, **2012**, *492*, 234-238). These emitters harvest both singlet and triplet excitons, which traditional fluorescent emitters are unable to achieve. OLEDs fabricated from these materials have achieved impressive and competitive performance compared to traditional phosphorescent emitters.

Light-emitting electrochemical cells (LEECs) represent another solid-state lighting device architecture that typically employ charged emitters as a key feature. Compared to OLEDs, they enjoy the advantages of using an air-stable cathode, are operated at lower potentials and possess a simpler single-layered device structure.

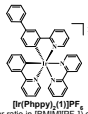
In this work we illustrated how small molecular charged organic emitters, **MYW1** and **MYW2**, operating through TADF are compatible in LEECs and we also present solution-processed OLED data.



PRIOR ART

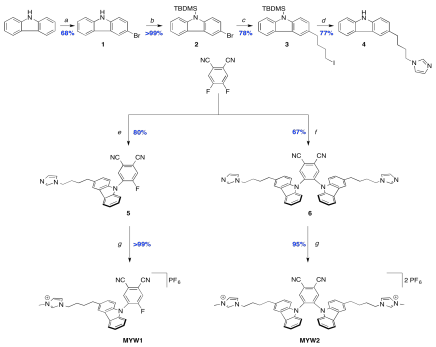
In 2012, Adachi and co-workers reported a TADF emitter, **2CzPN**, which achieved an external quantum efficiency (EQE) of 8.0%, breaking the fluorescent emitter EQE limit of 5% (outcoupling efficiency assumed to be 20%), hence suggesting the utilization of triplet excitons. Also shown below is the charged emitter employed in the most recent advance of LEEC devices, featured by its extraordinary long device half-life of 2800 h, reported by Bolink group.

2CzPN
Doped film (10 wt% in PMMA) emission max.: 492 nm
PLQY: 76.0%
OLED EQE: 8.0%
Nature, **2012**, *492*, 234-238



[Ir(Phppy)$_2$(1)]PF$_6$
Doped film (4:1 molar ratio in [BMIM][PF$_6$]) emission max.: 599 nm
PLQY: 20.0%
max. Luminance: 1024 cdm^{-2}, max. Efficacy: 3.5 cdA^{-1}
Chem. Sci., **2015**, *6*, 2843-2852

SYNTHESIS

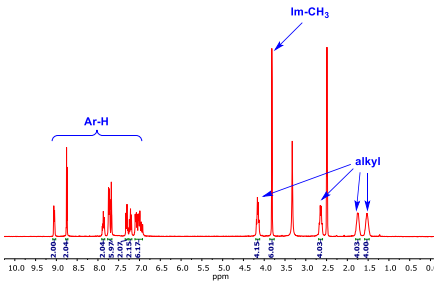


a. NBS, ACN, rt, 1 h. b. i) NaH, THF, rt, 30 min, ii) TBDMSCl c. i) *n*-BuLi, THF, -78 °C, 30 min, ii) excess 1,4-diiodobutane. d. NaH, imidazole, THF, reflux, 4 h. e. i) NaH, **4**, THF, rt, 30 min, ii) 2 equiv. 4,5-difluorophthalonitrile, rt, 4 h. f. i) NaH, **4**, THF, rt, 30 min, ii) 0.6 equiv. 4,5-difluorophthalonitrile, rt, 4 h. g. i) MeI, ACN, 40 °C, 2h ii) sat. NH_4PF_6 (aq). (NBS = *N*-bromosuccinimide; TBDMSCl = *tert*-butyldimethylsilyl chloride)

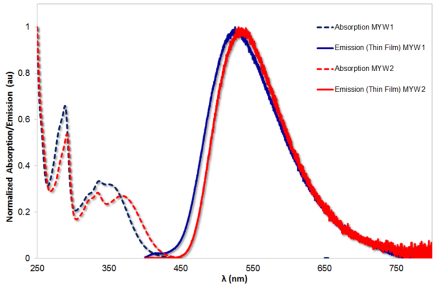
STRUCTURAL ELUCIDATION

The structures of **MYW1** and **MYW2** are confirmed by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy and High-Resolution Mass Spectrometry (HRMS).

^{1}H NMR spectrum of MYW2

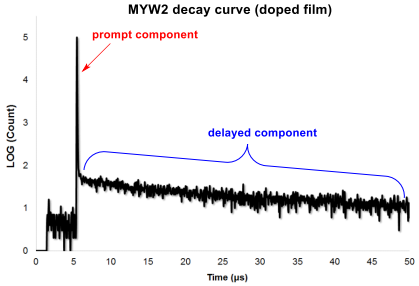


PHOTOPHYSICAL PROPERTIES



		Acetonitrile			Film (neat)			Film (10% doped in PMMA)		
		λ_{em} (nm)	Φ_{PL}	τ (ns)	λ_{em} (nm)	Φ_{PL}	τ_{avg} (µs)	λ_{em} (nm)	Φ_{PL}	τ_{avg} (µs)
MYW1	Aerated	556	0.01	2.90	530	0.09	0.26	490	0.45	2.54
	Degassed	558	0.03	3.26		010	0.96		0.56	6.14
MYW2	Aerated	574	0.02	4.44	536	0.21	0.97	500	0.73	1.08
	Degassed	572	0.03	4.97		0.21	2.73		**0.90**	6.34

MYW2 decay curve (doped film)

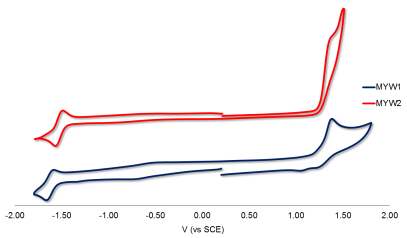


Both **MYW1** and **MYW2** show TADF characteristics:

- PLQY in N_2 atmosphere always higher than those in air. This is particularly prominent in doped films where ~20% enhancement is observed under a N_2 atmosphere.
- Emission decay curves always show both prompt and delayed components.

MYW2 shows a remarkable PLQY of 90% in doped thin film, suggesting its potency in OLED/LEEC applications.

ELECTROCHEMICAL PROPERTIES

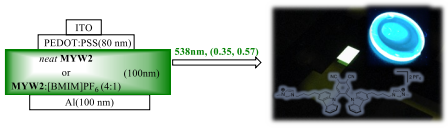


	E^{ox}_{pa} (V)[a]	$E^{red}_{1/2}$ (V)	ΔE^{red}_{p} (V)	HOMO (eV)	LUMO (eV)	ΔE (V)
MYW1	1.51	-1.50	0.064	-5.93	-2.92	3.01
MYW2	1.45	-1.43	0.079	-5.87	-2.99	2.88

Experiments were performed with sample concentration of ca. 10^{-4} M in 0.1M *n*-Bu_4NPF_6 under N_2-saturated MeCN at room temperature with ferrocene as the internal standard. The HOMO and LUMO energies were calculated using the relation $E_{HOMO/LUMO} = -(E^{ox}_{pa}/E^{red}_{1/2} + 4.8)$ eV, where $E^{ox}_{pa}/E^{red}_{1/2}$ are the oxidation or reduction peaks with respect to $E_{1/2}$ of ferrocene/ferrocenium redox couple.

Both **MYW1** and **MYW2** demonstrate bipolar characteristics, which are ideal for balanced charge injection and transport.

LEEC DEVICES



[BMIM]PF$_6$ = 1-butyl-3-methylimidazolium hexafluorophosphate

LEEC Devices[a]	Electroluminescence			
	Avg. Current Density (A·m^{-2})	Lum_{max} (cd·m^{-2})[a]	PCE_{max} (lm·W^{-1})[b]	EQE_{max} (%)
1	10	13	0.7	0.39
	25	24	0.4	0.29
	50	26	0.2	0.16
2	25	10	0.2	0.12
	50	17	0.1	0.10

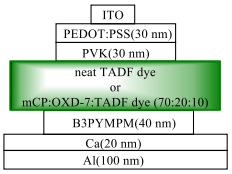
[a] Device 1: ITO/PEDOT:PSS/**MYW2**/Al; Device 2: ITO/PEDOT:PSS/**MYW2**:[Bmim][PF$_6$] 4:1/Al biased with a block wave-pulsed current at a frequency of 1000 Hz and a duty cycle 50% at different current densities.

Neat **MYW2** performed better than with the addition of ionic liquid (IL):

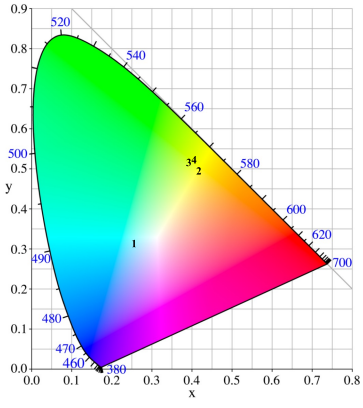
- Concentration quenching for **MYW2** in LEEC setting is not severe, on the contrary to most OLED emitters which show significant drop in efficiency when applied neat.
- Probably, the addition of the polar IL widens ΔE_{ST} which decreases TADF efficiency.

A very low operating voltage of 2.7 V

OLED DEVICES



OLED Devices	V_{on} (V)	λ_{peak} (nm)	FWHM (nm)	EQE_{max} (%)	CE_{max} (cd/A)	$PE_{max.}$ (lm/W)	CIE
1 (doped – MYW1)	9.5	467	148	0.3	0.5	0.2	(0.25, 0.31)
2 (doped – MYW2)	5.8	566	137	2.7	7.4	4.0	(0.42, 0.49)
3 (neat – MYW1)	7.5	532	132	0.3	0.7	0.3	(0.38, 0.52)
4 (neat – MYW2)	**3.6**	546	128	**5.1**	14.9	10.3	(0.41, 0.53)



Similar to LEEC results, **MYW2** outperform **MYW1**

OLED using neat **MYW2** gave consistent, yet surprisingly, better performance than the doped analogue.

A remarkable OLED device was fabricated using *neat* **MYW2** as solution-processed emitting layer with high EQE of 5.1% operating at voltage as low as 3.6 V.

CONCLUSIONS

- Two novel TADF-based emitters with charged groups, **MYW1** and **MYW2**, have been synthesized with good overall yields.
- **MYW2** was successfully applied in LEEC devices. Preliminary results gave EQE of 0.39% under a very low operating voltage of 2.7 V.
- Solution-processed OLEDs from MeCN using neat **MYW2** as the emitting layer gave high EQE of 5.1% with low operating voltage of 3.6 V.
- Surprisingly, in both LEEC and OLED devices, a neat emitting layer invariably outperformed doped analogues, which is a rare observation.
- It is expected that further optimization of LEEC device will give much higher EQE, enjoying both ease of fabrication and high efficiency.

ACKNOWLEDGEMENTS AND FUNDING