Thenil and Furil-imidazole Based Efficient Ionic Green Emitters with High Color Purity for Non-doped Light Emitting Electrochemical Cells

Puthanveedu Archana,[a] Kanagaraj Shanmugasundaram,[a] Sunghyun Yoon,[a] Youngson Choe [a]*

[a]School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609-735, Republic of Korea.

SUPPORTING INFORMATION

Table of Contents

Materials and methods

All the chemicals, reagents and solvents used were purchased from Sigma-Aldrich and TokyoChemical Industries and are used without further purifications. All reactions were carried out under an inert Argon atmosphere. The ^{1}H NMR spectra for the synthesized compounds were acquired using Varian Unity Inova 500 MHz FT-NMR Spectrometer in DMSO- d_6 and $CDCl_3$ with tetramethyl silane (TMS) as the internal standard. The high-resolution mass spectra was recorded using fast atom bombardment (FAB) Tandem Atom Spectrometer MS/MS system. The UV-Vis absorption spectra of both compounds were obtained using 8453 UV-vis Agilent spectrophotometer. The photoluminescence (PL) spectra for both solution as well as thin films were recorded using an F-7000 FL spectrophotometer. To determine the thermal stability of the organic compounds, thermogravimetric analysis (TGA) was carried out using Netzsch TG 209 instrument under nitrogen atmosphere at 20 ℃ min^{-1} heating rate and differential scanning calorimetry (DSC) using TA Instruments Q200 at 10 ℃ min^{-1} heating rate. From the second heating scan T_g was determined. The cyclic voltammetric analysis was carried out with a concentration of 10^{-3} M of the two compounds in acetonitrile solvent using supporting electrolyte 0.1 M tetra n-butylammonium hexafluorophosphate ($TBAPF_6$) at a scan rate of 100 mV s^{-1}. CV model of potentiostat/galvanostat (Iviumstat) voltrammetric analyser was employed with Ag/AgCl as the reference electrode, Platinum wire as counter electrode and Platinum as the working electrode. The potential values were measured with respect to the ferrocenium/ferrocene (Fc+/Fc) as the internal standard.

Fabrication and LEC Device Characterization

Glass substrates coated with Indium tin oxide (ITO) were procured from AMG Korea Co. The validation of all the LEC devices fabricated were done and the resistance of the ITO substrate was found to be 15 Ω ohm/sq. The hole injection layer which consists of Poly(3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS), the buffer layer, was purchased from H.C. Starck Clevios (PVP AI 4083) Aluminum, which serves as the cathode material, was procured from CERAC, Inc. Initially, the Glass substrate coated with ITO substrate was washed with a solution containing a mixture of acetone, ethanol, and isopropanol in an ultrasonic bath. Later on, this was exposed to ozone treatment for a time gap of 30 min in order to improve the hole injection and also to remove the plausible organic residue if present. At first, PEDOT: PSS was spin-coated onto the ITO substrate at 2000 rpm for 20 s to form a layer of 50 nm thickness and then was dried at a temperature of 120 °C for 1 h in a vacuum oven. Prior to coating, PEDOT: PSS was filtered using a hydrophilic (0.2 μm) PTFE filter from its aqueous dispersion. PEDOT: PSS acts as a hole-injecting material which reduces short contacts by forming a smooth uniform layer over ITO. The emissive layer solution is composed of 10 mg of compounds in 1mL of acetonitrile. Before coating the active layer, the emissive layer solutions were filtered using a hydrophobic PTFE filter (0.1 μm). This coated active layer (80 nm) was exposed to thermal evaporation under high vacuum which contains a metal evaporating chamber for aluminum (cathode) deposition using a shadow mask. The final structural configuration obtained was ITO/ PEDOT: PSS/active layer/Al. Keithley characterization systems were used to measure the electroluminescent properties of the fabricated devices under ambient conditions.

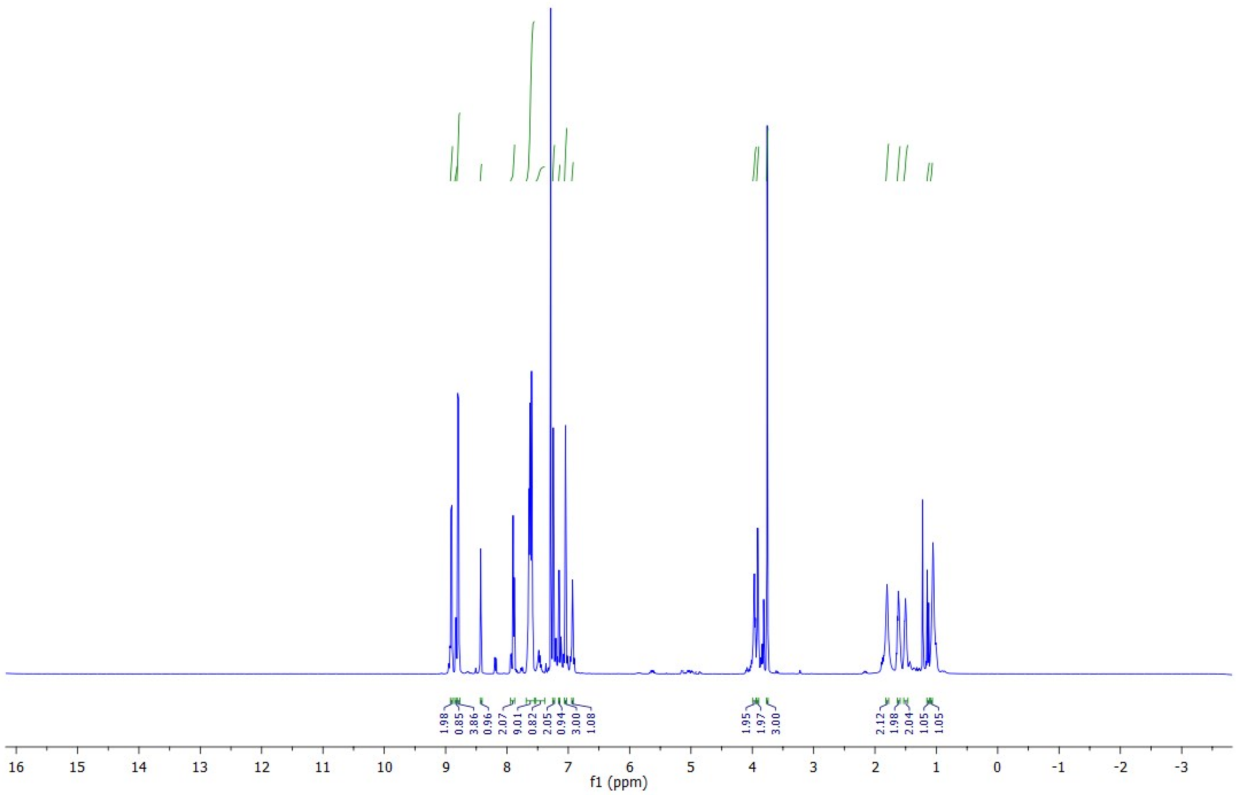

Fig. S1. [1] H NMR Spectra of **ThAz.**

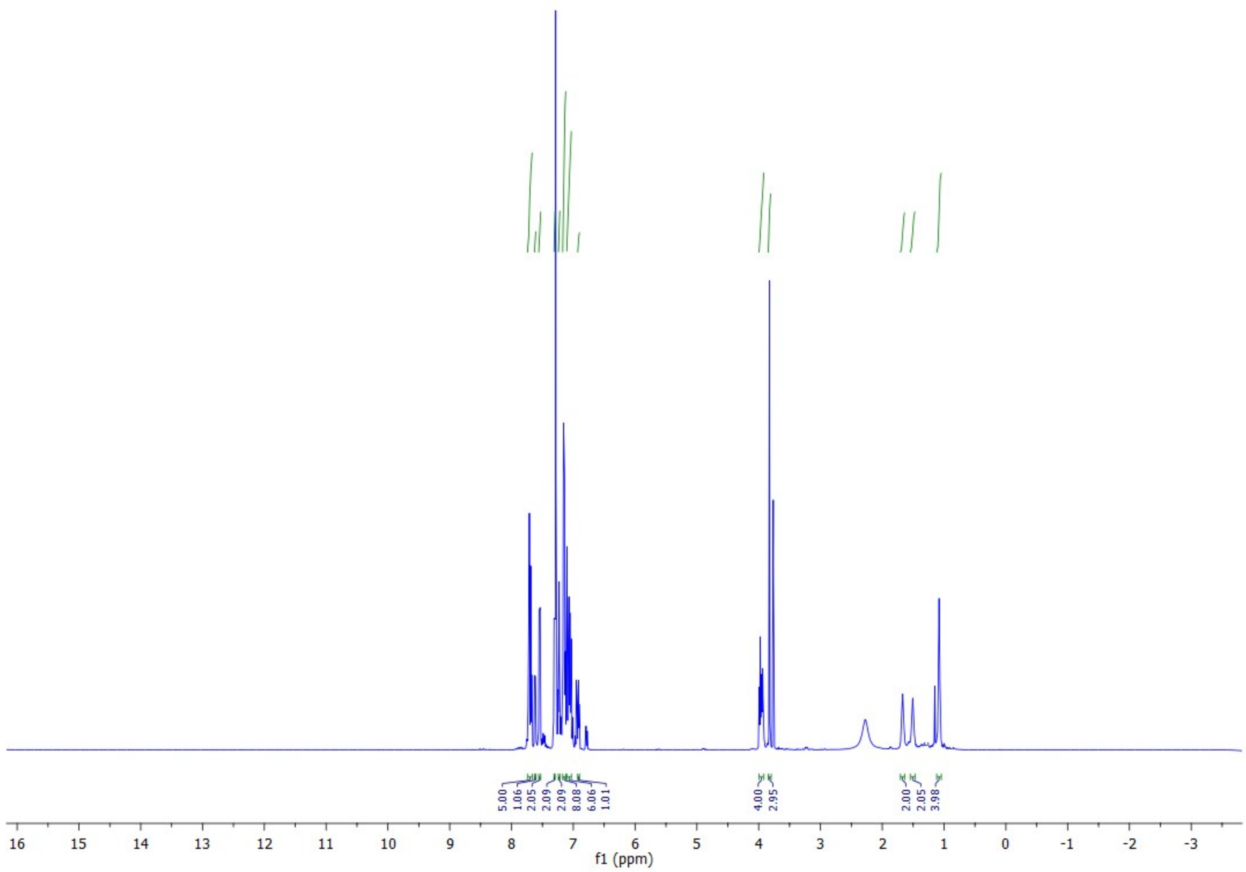

Fig. S2. [1] H NMR Spectra of **FuAz**

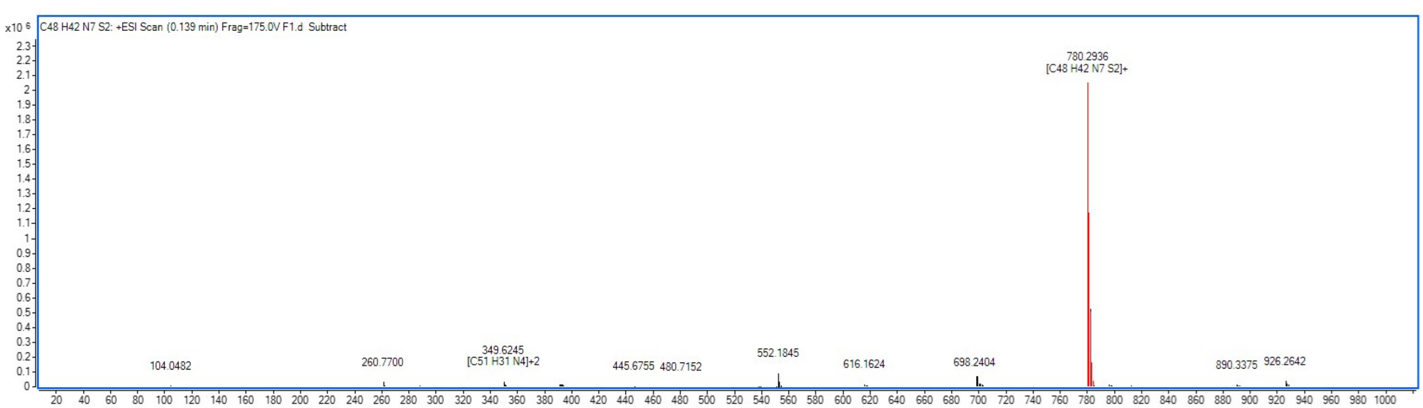

Fig. S3. Mass Spectra of **ThAz**.

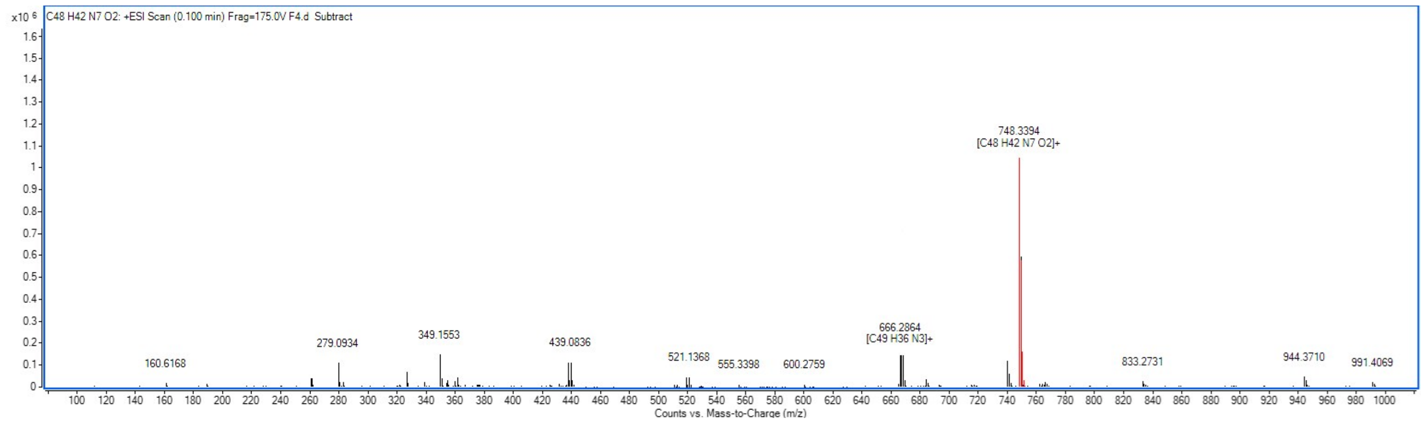

Fig. S4. Mass Spectra of **FuAz**.

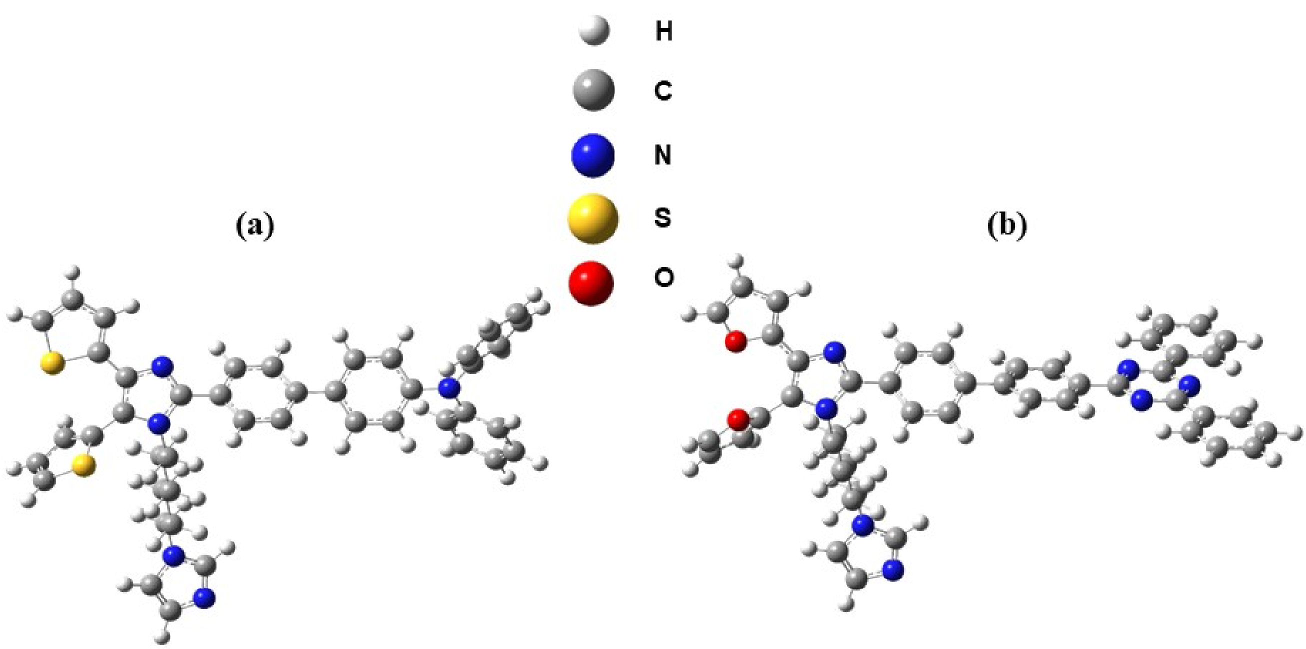

Fig. S5. Optimised electronic structures of the target compounds **ThAz** (a) and **FuAz** (b).

Computational ground state geometry of **ThAz** using B3LYP/6-31G (d,p) basis set of Gaussian 09 program set.

C	-1.55697	-0.62279	-0.52934
C	-0.99962	0.648435	-0.57666
N	0.379127	0.454668	-0.58316
N	-0.55596	-1.56958	-0.48048

C	0.588703	-0.90289	-0.50883
C	1.909588	-1.54903	-0.45208
C	2.961952	-1.19029	-1.31002
C	2.11528	-2.59671	0.460196
C	4.190863	-1.8392	-1.23449
H	2.813259	-0.41716	-2.05707
C	3.342796	-3.24627	0.530196
H	1.298086	-2.89722	1.107445
C	4.408642	-2.8757	-0.30995
H	4.995025	-1.52907	-1.89427
H	3.471395	-4.06524	1.231024
C	1.349194	1.521871	-0.31243
C	1.489262	1.795281	1.188408
H	1.011574	2.417789	-0.83859
H	2.310686	1.236503	-0.73741
C	2.488663	2.919521	1.475132
H	0.504331	2.055671	1.59374
H	1.807603	0.870797	1.686484
C	2.646264	3.202818	2.973266
H	3.467299	2.658065	1.049627
H	2.164049	3.835997	0.963432
H	1.667223	3.462964	3.39882
H	2.970098	2.285388	3.483863
C	3.645009	4.32797	3.262264
H	3.322737	5.251224	2.764588
H	4.629013	4.073694	2.848978
C	5.718745	-3.56316	-0.22795
C	6.479498	-3.81546	-1.38471
C	6.238401	-3.98374	1.010434
C	7.707885	-4.461	-1.30817
H	6.090869	-3.52606	-2.35607
C	7.465889	-4.63057	1.09064
H	5.684504	-3.77932	1.921377
C	8.219141	-4.87887	-0.0685
H	8.280032	-4.6574	-2.20751
H	7.858788	-4.94232	2.051463
C	3.794264	4.59541	4.763952
H	2.83003	4.872443	5.202362
H	4.138605	3.694328	5.280253

N	4.751071	5.660831	5.052668
C	4.537853	7.017364	4.91194
C	6.056323	5.507912	5.421786
C	5.737206	7.614846	5.216698
H	3.576275	7.413198	4.622296
H	6.484475	4.529686	5.597231
H	5.966559	8.672	5.230204
N	6.684686	6.664348	5.536285
C	9.526173	-5.56899	0.014607
N	9.958284	-5.95354	1.226241
C	11.14723	-6.57605	1.253645
C	11.38324	-6.40101	-1.00339
N	11.89368	-6.82108	0.165063
N	10.20422	-5.77115	-1.12642
C	11.66846	-7.02113	2.56826
C	10.92829	-6.79246	3.740279
C	12.908	-7.67656	2.655985
C	11.41985	-7.21138	4.974818
H	9.972137	-6.28701	3.668541
C	13.39618	-8.09404	3.892362
H	13.47606	-7.85131	1.749576
C	12.6543	-7.86299	5.054695
H	10.84072	-7.0303	5.875421
H	14.35535	-8.59987	3.950447
H	13.03625	-8.18898	6.017813
C	12.17095	-6.64814	-2.23486
C	11.68865	-6.22265	-3.48393
C	13.40802	-7.31052	-2.16603
C	12.43017	-6.45588	-4.64019
H	10.73404	-5.71165	-3.53311
C	14.14648	-7.54217	-3.32458
H	13.77707	-7.63726	-1.20071
C	13.66032	-7.11602	-4.56427
H	12.04933	-6.12327	-5.60123
H	15.10151	-8.05523	-3.26167
H	14.23718	-7.29735	-5.46654
C	-2.95182	-1.03535	-0.56529
C	-3.4112	-2.33404	-0.56954
S	-4.30064	0.088368	-0.63324

C	-4.83158	-2.43563	-0.62848
H	-2.73424	-3.17869	-0.53765
C	-5.44993	-1.21598	-0.67144
H	-5.36828	-3.37762	-0.6402
H	-6.50832	-0.99789	-0.71808
C	-1.61486	1.970653	-0.61377
C	-2.21741	2.652844	0.41665
S	-1.70818	2.904777	-2.09999
C	-2.75071	3.917395	0.027414
H	-2.27693	2.248122	1.420303
C	-2.54694	4.192209	-1.29837
H	-3.25933	4.593104	0.705093
H	-2.83888	5.075432	-1.85069

Computational ground state geometry of **FuAz** using B3LYP/6-31G (d,p) basis set of Gaussian 09 program set.

C	-1.74123	-0.65156	-0.75466
C	-1.20936	0.634058	-0.71781
N	0.172874	0.456384	-0.67235
N	-0.73156	-1.58419	-0.7251
C	0.401916	-0.89952	-0.67215
C	1.730437	-1.52907	-0.57614
C	2.81214	-1.14287	-1.38346
C	1.915411	-2.58425	0.332281
C	4.049222	-1.76865	-1.25919
H	2.68337	-0.36596	-2.12981
C	3.151378	-3.21037	0.451756
H	1.076729	-2.90731	0.93996
C	4.246668	-2.80855	-0.33428
H	4.875753	-1.43581	-1.87905
H	3.264789	-4.03366	1.150138
C	1.154674	1.513959	-0.41294
C	1.536209	1.594189	1.068613
H	0.716952	2.454089	-0.7539

H	2.040823	1.330361	-1.02001
C	2.542678	2.715757	1.340553
H	0.629382	1.7454	1.667512
H	1.957611	0.629583	1.376773
C	2.957093	2.794396	2.814121
H	3.436086	2.562055	0.719869
H	2.113038	3.678164	1.029984
H	2.064535	2.951032	3.435496
H	3.381697	1.829261	3.122926
C	3.972092	3.909234	3.085659
H	3.551652	4.878597	2.79001
H	4.871378	3.756471	2.476029
C	5.568176	-3.46422	-0.19395
C	6.389505	-3.68987	-1.31414
C	6.039581	-3.87658	1.066231
C	7.630978	-4.30044	-1.18134
H	6.039353	-3.4065	-2.30178
C	7.280184	-4.48797	1.202679
H	5.437265	-3.69253	1.950389
C	8.094963	-4.70818	0.080121
H	8.250637	-4.47615	-2.05307
H	7.635967	-4.79289	2.179972
C	4.380731	3.970705	4.561506
H	3.504675	4.140054	5.195955
H	4.8296	3.02293	4.873604
N	5.352457	5.027327	4.831635
C	5.091148	6.37914	4.930401
C	6.705396	4.882998	4.940825
C	6.313922	6.9813	5.105359
H	4.085698	6.767874	4.874214
H	7.176506	3.909974	4.893671
H	6.521464	8.035304	5.233286
N	7.321537	6.038993	5.11189
C	9.417741	-5.35723	0.224305
N	9.805583	-5.72729	1.455268
C	11.01158	-6.31086	1.538589
C	11.34543	-6.12954	-0.70562
N	11.815	-6.53178	0.486008
N	10.15361	-5.53804	-0.88393

C	11.48587	-6.73815	2.876652
C	10.68692	-6.53011	4.013383
C	12.73929	-7.35579	3.022136
C	11.13458	-6.93201	5.270077
H	9.720244	-6.05385	3.897017
C	13.18347	-7.75633	4.280506
H	13.35251	-7.51508	2.142721
C	12.38327	-7.54581	5.4075
H	10.51022	-6.76701	6.143127
H	14.1538	-8.23293	4.383279
H	12.73101	-7.85849	6.387835
C	12.19638	-6.35233	-1.89906
C	11.75722	-5.94676	-3.17047
C	13.45104	-6.97153	-1.77142
C	12.55834	-6.15689	-4.29083
H	10.78878	-5.46936	-3.26517
C	14.24922	-7.18007	-2.8942
H	13.78657	-7.28329	-0.78907
C	13.80581	-6.77377	-4.15638
H	12.21047	-5.83998	-5.26952
H	15.21749	-7.65962	-2.78586
H	14.4292	-6.93703	-5.03072
C	-3.1218	-1.08229	-0.78173
C	-3.68438	-2.32342	-0.93244
C	-5.10121	-2.14092	-0.84186
H	-3.142	-3.24353	-1.08907
C	-5.30245	-0.80799	-0.6414
H	-5.86562	-2.90104	-0.91791
H	-6.1822	-0.19597	-0.51564
C	-1.85008	1.934359	-0.76004
C	-1.75441	3.067336	0.006897
C	-2.66923	4.019327	-0.54632
H	-1.127	3.194464	0.876976
C	-3.26124	3.400954	-1.6066
H	-2.86367	5.02185	-0.19351
H	-4.01171	3.705072	-2.32014
O	-4.1071	-0.14765	-0.59975
O	-2.7716	2.139514	-1.75906

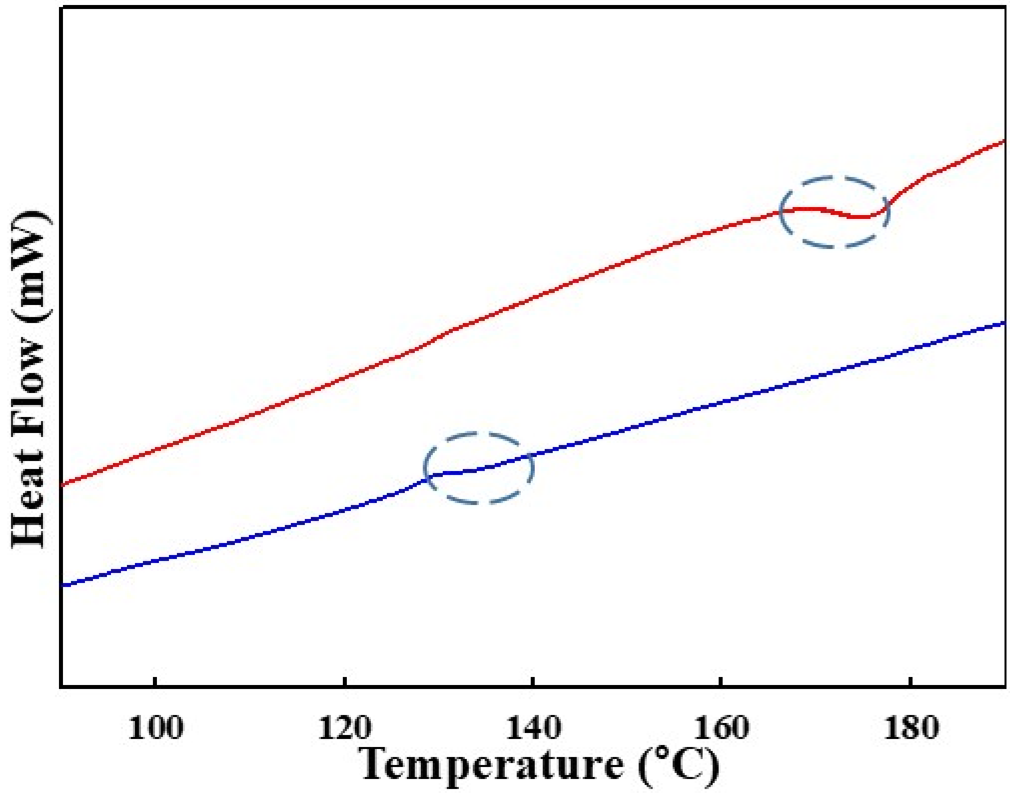

Fig. S6. DSC thermograms of target compounds **ThAz** (red) and **FuAz** (blue).

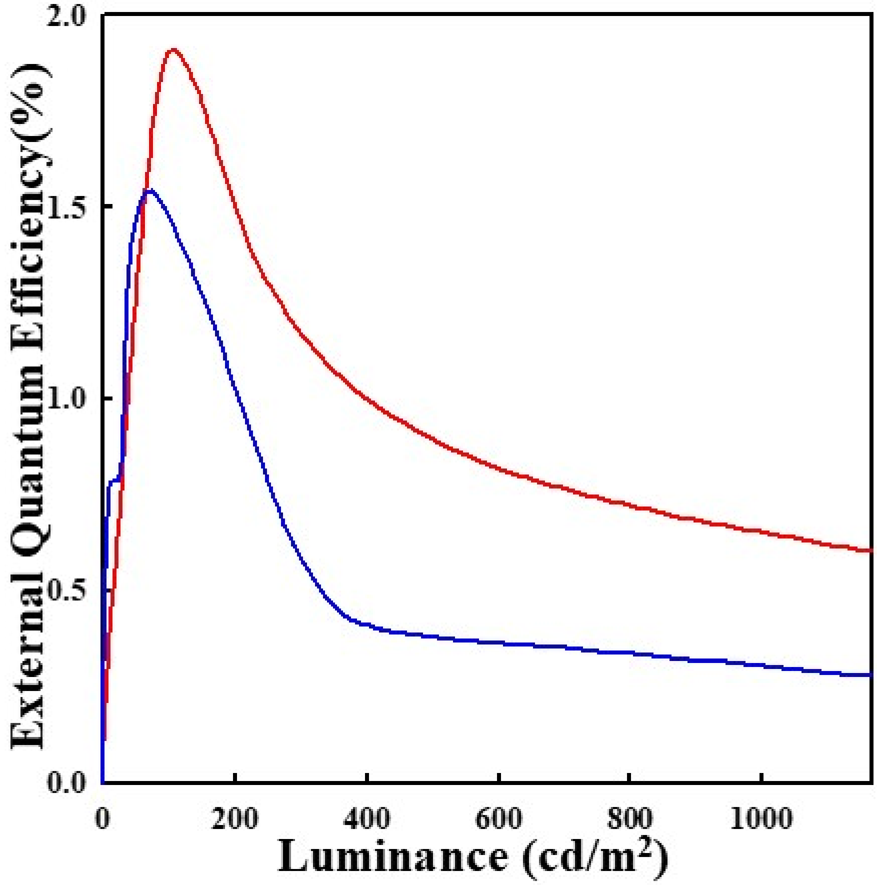

Fig S7. Luminescence vs EQE plot for **ThAz** (red) and **FuAz (**blue**)** LECs

Table S1. Comparison of EL properties for single component ionic small molecules based LECs.

Emitters	Λmax (nm)	EQE (%)	Current efficiency (cd/A)	Luminance (cd/m^2)	CIE (x/y)	Ref.
PPP	**530**	**-**	**-**	**499**	**-**	**[1]**
PYR1	**451**	**-**	**-**	**180**	**(0.17, 0.18)**	**[2]**
PYR2	**487**	**-**	**-**	**72**	**(0.18, 0.25)**	**[2]**
NPzN	**499**	**-**	**-**	**129**	**(0.28, 0.43)**	**[3]**

NPzN-IL	**505**	**-**	**-**	**59**	**(0.32, 0.41)**	**[3]**
CPC	**484**	**1.05**	**1.29**	**430**	**(0.16, 0.33)**	**[4]**
CPC-IL	**-**	**1.6**	**1.33**	**454**	**(0.17, 0.33)**	**[4]**
PPPSO2	**498**	**-**	**-**	**509**	**-**	**[5]**
PhTz	**505**	**1.65**	**2.83**	**1453**	**(0.28.,0.54)**	**[6]**
BzTz	**499**	**1.23**	**1.71**	**1048**	**(0.27, 0.52)**	**[6]**
ThAz	**525**	**1.90**	**3.77**	**1556**	**(0.23, 0.69)**	**This work**
FuAz	**540**	**1.54**	**2.86**	**1173**	**(0.26, 0.67)**	**This work**

References

(1) K. Shanmugasundaram, M. S. Subeesh, C. D. Sunesh, R. K. Chitumalla, J. Jang and Y. Choe, *J. Phys. Chem. C*, 2016, **120**, 20247-20253.

(2) H. Lee, C.D. Sunesh, M.S. Subeesh, Y. Choe, *Opt. Mater.*, 2018, **78**, 44-51.

(3) K. Jongseong, K. Shanmugasundaram, R. K Chitumalla, J. Jang and Y. Choe, *J. Lumin.*, 2018, **197**, 383-388.

(4) K. Shanmugasundaram, J.C. John, S. Chitumalla, J. Jang, and Choe, Y., *Org. Electron.,* 2019, **67**, 141-145.

(5) K. Shanmugasundaram, R. K. Chitumalla, J. Jang and Y. Choe, *New J Chem*, 2017, **41**, 9668-9673.

(6) A. Puthanveedu, K. Shanmugasundaram, J. C. John and Y. Choe, *The Journal of Physical Chemistry C*, 2020, **124**, 19273-19281.