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Supporting information

Novel Carbazole-based Multifunctional Materials with Hybridized Local and Charge-Transfer Excited State Acting as Deep Blue Emitters and Phosphorescent Hosts for Highly Efficient Organic Light-Emitting Diodes

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Content

Experimental section

General information

Chemicals and solvents used in the process were reagent grades and purchased from commercial companies without further purification. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured using a Bruker AM400 spectrometer. Mass spectra (MS) were obtained on a Waters LCT Premier XE spectrometer. The ultraviolet-visible (UV-Vis) absorption spectra of the samples were characterized using a Agilent spectrophotometer. Photoluminescence (PL) measurements were conducted by a Agilent fluorescence spectrophotometer at room temperature. The photoluminescence quantum yield (PLQY) was measured by a HAMAMATSU Quantaurus-QY C11347-11 fluorescence spectrophotometer. The cyclic voltammetry (CV) experiments were performed by a Versastat II electrochemical workstation(Princeton applied research). The $E_{1/2}$ values were determined by $(E_{pa}+E_{pc})/2$, where E_{pa} and E_{pc} were the anodic and cathodic peak potentials, respectively. The differential scanning calorimetry (DSC)analysis was performed under a nitrogen atmosphere using a SHIMADZU DSC-60Plus instrument with a heating scan rate of10 ^{o}C/min. Thermogravimetric analysis (TGA) was carried out using a SHIMADZU TGA-50/50H instrument under a nitrogen atmosphere with a heating scan rate of 10 ^{o}C/min.

All OLEDs were fabricated on the pre-patterned indium tin oxide (ITO) glass substrate with sheet resistance of 10Ω/□. OLEDs have an active area of 3.0×3.0 mm^2, defined by the overlap between the ITO anode and Al cathode. The ITO substrates were cleaned first with acetone, deionized water and acetone, and then dried in drying cabinet, and treated with ultraviolet-ozone for 15 min. After these processes, the cleaned ITO glass substrates were loaded in a vacuum chamber, a base pressure of $\leqslant 5\times10^{-4}$ Pa, for film deposition using thermal evaporation technology. The deposition rate and film thickness were monitored controlled by the calibrated crystal quartz sensors, e.g., the deposition rates of organic materials, MoO_3, LiF, and cathode Al were controlled at about 1 Å/s, 0.3 Å/s, 0.1 Å/s, and 3−6 Å/s, respectively.

The EL spectra and CIE coordinates of all OLEDs were measured by a computer controlled PR-655 spectra scan spectrometer. The current density-voltage-luminance characteristics, current efficiency, and power efficiency were recorded by a computer-controlled Keithley 2400 source integrated with a BM-70A luminance meter. The EQE was calculated from the current density-voltage-luminance curve and spectra data. All samples were immediately characterized after thin films deposition without encapsulation in ambient atmosphere at room temperature.

Synthesis

Synthesis of 2-(4-fluorophenyl)benzo[d]oxazole (IM1)

4-Fluorobenzoic acid (5.0 g, 35.7 mmol) and 2-aminophenol (3.9 g, 35.7 mmol) was added to a three-necked round bottle flask and followed by polyphosphoric acid (20 g). And the resulting mixture was stirred intensely at 160 ^{o}C for 5 h. After cooling down to 70-80 ^{o}C, water (50 mL) was dropwise added to the mixture. The precipitate was filtered, washed to neutral with water and washed with ethanol. The filter cake was then purified by silicon column to afford a white solid (4.3 g, 56.6%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.24-8.29 (m, 2H),7.74-7.79 (m, 1H), 7.56-7.60 (m, 1H), 7.34-7.39 (m, 2H), 7.19-7.25 (m, 2H).

Synthesis of 2-(4-(3-bromo-9H-carbazol-9-yl)phenyl)benzo[d]oxazole (IM2)

A mixture of **IM1** (4.0 g, 18.8 mmol),3-bromo-9H-carbazole (4.6 g, 18.7 mmol) and *t*-BuONa (5.4 g, 56.2 mmol) in DMF (40 mL) was added to a round bottle flask and the resulting mixture was stirred at 100 ^{o}C for 8 h under N_2 protection. The reaction mixture was cooled down to room temperature, poured into $H_2O$and filtered the precipitate, then washed with water and ethanol. The filter cake was then recrystallized with toluene and ethanol (1/1, v/v) to afford a white solid (3.8 g, 46.1%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.50 (d, J = 8.8 Hz, 2H), 8.26 (d, J=2.0, 1H), 8.10 (d, J= 7.6, 1H), 7.80-7.85 (m, 1H),7.74 (d, J= 2.0, 2H), 7.62-7.67 (m,1H),7.46-7.54 (m, 3H),7.31-7.43 (m, 4H).

Synthesis of 2-(4-(3-(4-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl)-9H-carbazol-9-yl)phenyl)benzo[d]oxazole (OCI)

A mixture of **IM2** (1.0 g, 2.28 mmol), (4-(1-phenyl-1H-benzo[d]imidazole -2-

yl)phenyl)boronic acid (0.75 g, 2.39 mmol), K_2CO_3 (0.94 g, 6.80 mmol) and $Pd(PPh_3)_2Cl_2$ (0.03 g, 0.043 mmol) was added to a round bottle flask, followed by toluene (6 mL), ethanol (3 mL) and deionized water (3 mL) and the resulting mixture was refluxed for 5 h under N_2 protection. After phase separation, the organic layer was concentrated under vacuum and purified by column chromatography with dichloromethane and petroleum ether (1/1, v/v) as eluent to afford a light yellow solid (0.60 g, 41.9%). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.51 (d, J = 8.8 Hz, 2H), 8.36 (d, J= 2.0, 1H), 8.18 (d, J=8.0 Hz, 1H), 7.93 (d, J= 8.0 Hz, 1H), 7.80-7.84 (m, 1H), 7.75-7.79 (m, 2H), 7.62-7.72 (m, 6H), 7.31-7.58 (m, 12H), 7.25-7.29 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$, δ): 162.19, 152.13, 150.84, 142.61, 142.11, 140.78, 140.45, 140.02, 137.29, 137.08, 132.75, 129.95, 129.86, 129.23, 128.63, 127.50, 126.95, 126.93, 126.47, 125.91, 125.47, 125.35, 124.76, 124.32, 123.76, 123.31, 123.03, 120.73, 120.13, 119.70, 118.87, 110.66, 110.41, 110.10, 109.96. HRMS (ESI, *m/z*): $[M+H]^+$calcd for: $C_{44}H_{29}N_4O$,629.2336, found, 629.2336.

Synthesis of 2-(4-(3-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9H-carbazol-9-yl)phenyl)benzo[d]oxazole (OCT)

A mixture of **IM2** (1.0 g, 2.28 mmol), 2,4-diphenyl-6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine (1.04 g, 2.39 mmol),K_2CO_3 (0.94 g, 6.80 mmol) and $Pd(PPh_3)_2Cl_2$ (0.03 g, 0.043 mmol) was added to a round bottle flask, followed by toluene (6 mL), ethanol (3 mL) and deionized water (3 mL)and the resulting mixture was refluxed for 5 h under N_2 protection. After phase separation, the organic layer was concentrated under vacuum and purified by column chromatography with dichloromethane and petroleum ether (1/2, v/v) as eluent to afford an off-white solid (0.56 g, 36.8%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 9.11 (t, J = 1.6 Hz, 1H),8.77-8.83 (m, 5H), 8.49-8.57 (m, 3H), 8.27 (d, J=7.6, 1H), 7.96-7.99 (m, 1H), 7.83-7.87 (m, 4H), 7.56-7.73 (m, 10H), 7.47-7.52 (m, 1H), 7.36-7.44 (m, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, δ):171.72, 171.66, 162.23, 150.82, 142.36, 141.96, 140.82, 140.64, 139.96, 136.79, 136.20, 133.72, 132.50, 131.50, 129.30, 129.11, 128.97, 128.63, 127.77, 127.32, 127.02, 126.47, 125.89, 125.79, 125.40, 124.81, 124.36, 123.84, 120.71, 120.61, 120.09, 119.19, 110.68, 110.17, 109.97. HRMS (ESI, *m/z*): [M+H]$^+$calcd for: $C_{46}H_{30}N_5O$,668.2445, found, 668.2462.

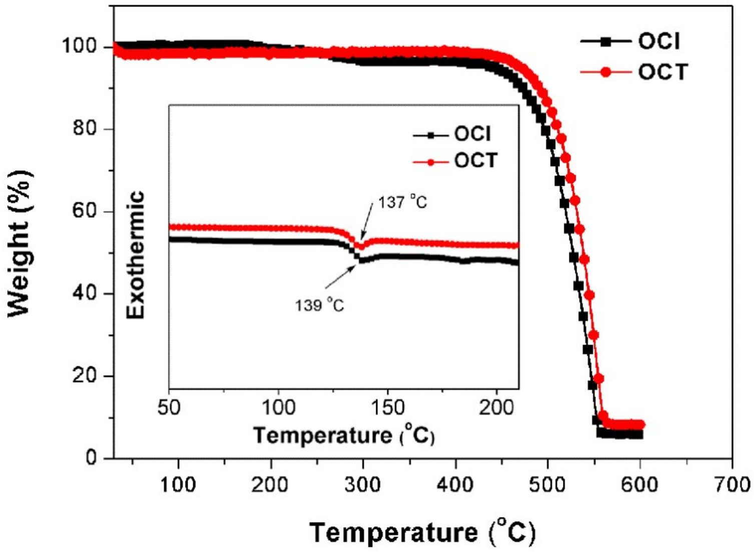


Fig. S1 The thermal properties of **OCI** and **OCT**.

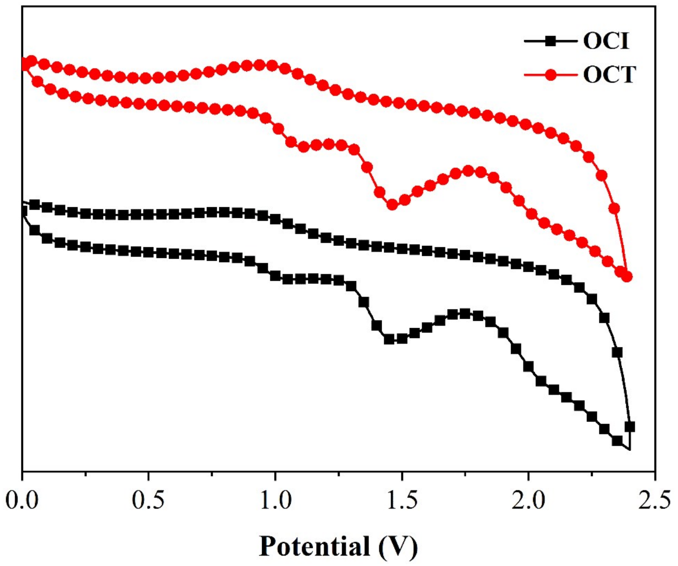


Fig. S2 Cyclic voltammograms of **OCI** and **OCT** in CH_2Cl_2 solution containing 0.1 M $TBAPF_6$ electrolytes, scanning rate: 100 mV/s.

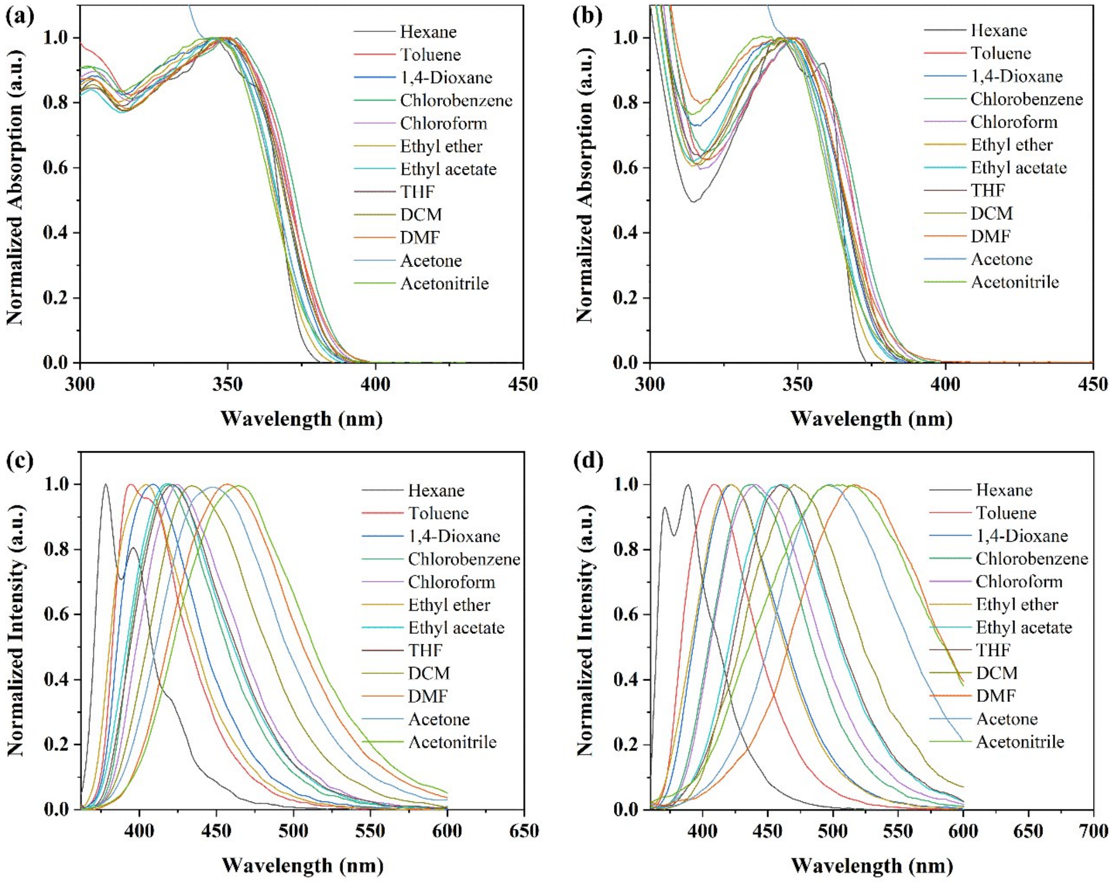


Fig. S3 Normalized absorption spectra of **OCI** (a) and **OCT** (b) in various polarity solvents. Normalized emission spectra of **OCI** (c) and **OCT** (d) in various polarity solvents (Concentration: 10^{-5} M).

Table S1 Detailed data of **OCI** and **OCT** for fitting photophysical results in different solvents based on Lippert-Mataga equation.

OCI

Solvent	ε	n	f(ε,n)	λ_{abs} (nm)	λ_{Pl} (nm)	υ_a (cm^{-1})	υ_f (cm^{-1})	$\upsilon_a - \upsilon_f$ (cm^{-1})
Hexane	1.9	1.3749	0.00126	345	396	28985.507	25252.525	3732.982
Toluene	2.38	1.497	0.01321	350	405	28571.429	24691.358	3880.071
1,4-Dioxane	2.25	1.422	0.02465	346	409	28901.734	24449.878	4451.856
Chlorobenzene	5.62	1.5248	0.14294	351	419	28490.028	23866.348	4623.68
Chloroform	4.81	1.4458	0.14829	350	425	28571.429	23529.412	5042.017
Ethyl ether	4.33	1.3524	0.16675	347	404	28818.444	24752.475	4065.969
Ethyl acetate	6.02	1.3724	0.19964	346	419	28901.734	23866.348	5035.386
THF	7.58	1.4072	0.20957	349	422	28653.295	23696.682	4956.613
DCM	8.93	1.424	0.21717	349	434	28653.295	23041.475	5611.82
DMF	36.7	1.4305	0.27438	349	457	28653.295	21881.838	6771.457
Acetone	20.7	1.3587	0.28431	345	447	28985.507	22371.365	6614.142
Acetonitrile	37.5	1.3441	0.30542	345	464	28985.507	21551.724	7433.783

OCT

Solvent	ε	n	f(ε,n)	λ_{abs} (nm)	λ_{Pl} (nm)	υ_a (cm^{-1})	υ_f (cm^{-1})	$\upsilon_a - \upsilon_f$ (cm^{-1})
Hexane	1.9	1.3749	0.00126	350	389	28571.429	25706.941	2864.488
Toluene	2.38	1.497	0.01321	348	409	28735.632	24449.878	4285.754
1,4-Dioxane	2.25	1.422	0.02465	346	422	28901.734	23696.682	5205.052
Chlorobenzene	5.62	1.5248	0.14294	350	437	28571.429	22883.295	5688.133
Chloroform	4.81	1.4458	0.14829	350	440	28571.429	22727.273	5844.156
Ethyl ether	4.33	1.3524	0.16675	345	422	28985.507	23696.682	5288.825
Ethyl acetate	6.02	1.3724	0.19964	345	459	28985.507	21786.492	7199.015
THF	7.58	1.4072	0.20957	347	460	28818.444	21739.13	7079.313
DCM	8.93	1.424	0.21717	348	472	28735.632	21186.441	7549.192
DMF	36.7	1.4305	0.27438	346	521	28901.734	19193.858	9707.876
Acetone	20.7	1.3587	0.28431	346	496	28901.734	20161.290	8740.444
Acetonitrile	37.5	1.3441	0.30542	341	506	29325.513	19762.846	9562.667

The dipole moment of ground state μ_g can be estimated by DFT calculation, and the dipole moment of excited state (μ_e) are determined from the slope of linear fitted Stokes' shift (ν_a-ν_f) against orientation polarizability f(ε,n) in different solvents according to Lippert-Mataga equation:

$$hc(\upsilon_a - \upsilon_f) = hc(\upsilon_a^0 - \upsilon_f^0) + \frac{2(\mu_e - \mu_g)^2}{a_0^3} f(\varepsilon, n),$$

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} + \frac{n^2 - 1}{2n^2 + 1},$$

Among which ε and n are dielectric constant and refractive index of solvent respectively, and a_0 is the solvent cavity radius

$$a_0 = \left(\frac{3M}{4N\pi d}\right)^{1/3},$$

where N is Avogadro number, M is molecular weight, and d is density. Two-region trends found in **OCI** and **OCT** are steady slopes of 6480 and 13563 for low-polar solvents and sharp slopes of 23038 and 29136 for high-polar solvents.

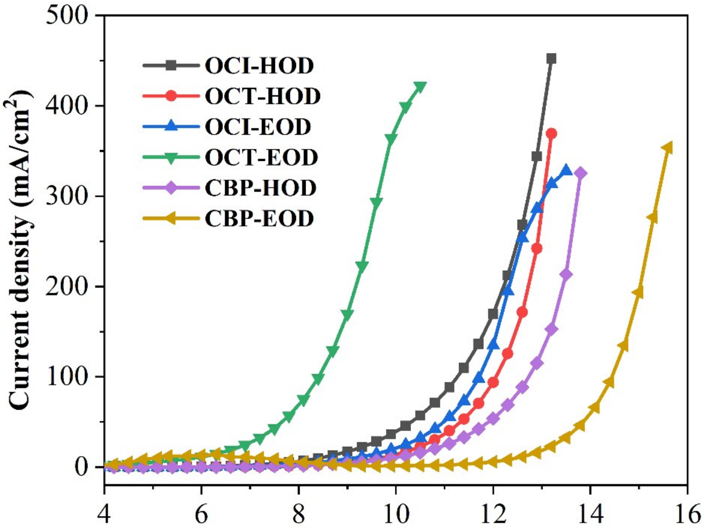


Fig. S4 Current density-voltage curves of the hole-only and electron-only devices of **OCI**, **OCT** and **CBP**.

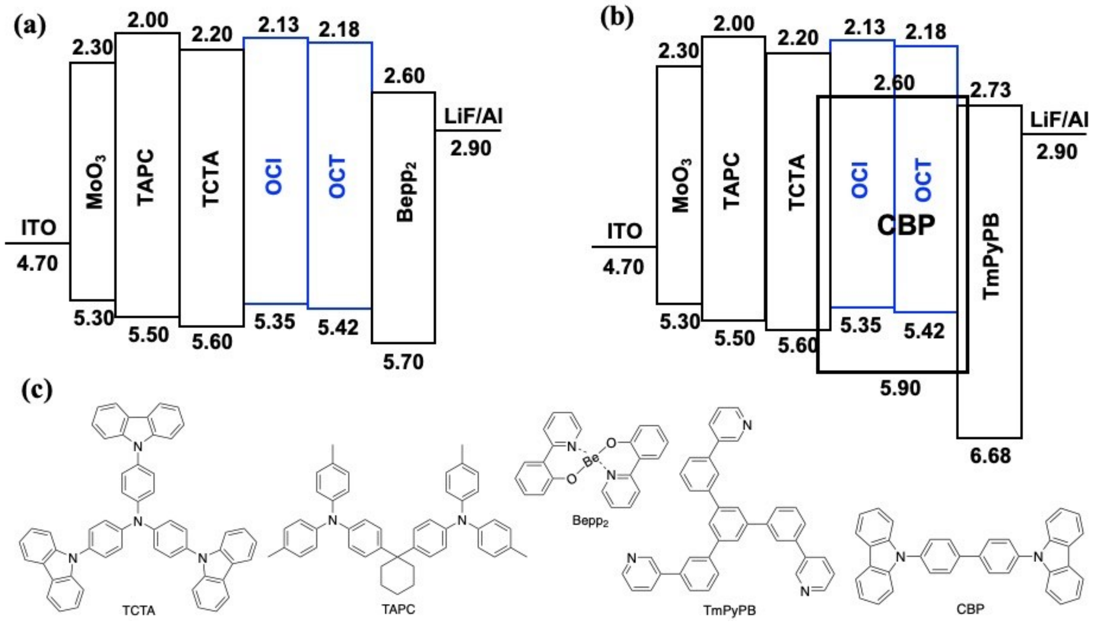


Fig. S5 (a) The energy diagram of devices A1-A4 and B1-B4. (b) The energy diagram of devices A5 and B5. (c) The structures of materials used in the devices.

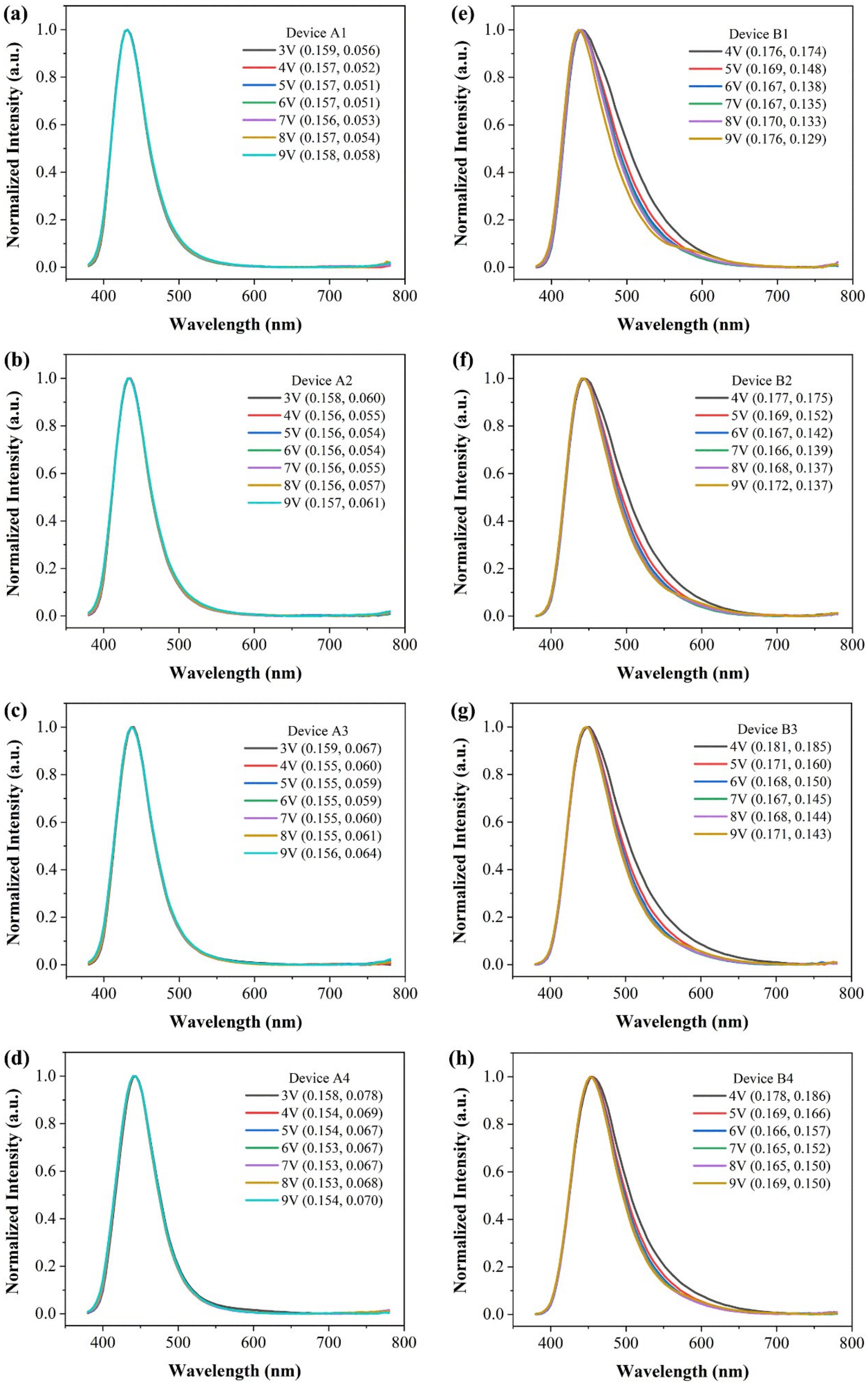


Fig. S6 (a)-(d) The EL spectra of devices A1-A4 at 3-9 V. (e)-(h)The EL spectra of devices B1-B4 at 4-9 V.

Table S2 EL performance of blue OLEDs based on **OCI** and **OCT**.

Devices	Thickness of EML (nm)	V_{on}(V)[a]	L_{max}(cd m^{-2})[b]	η_{c}(cd A^{-1})[c]	η_{p}(lm W^{-1})[d]	η_{ext}(%)[c]	CIE(x, y)[e]
A1	15	3.0	7219	1.41	1.43	3.16	0.157, 0.051
A2	20	3.0	8024	1.57	1.47	3.19	0.156, 0.054
A3	25	3.0	8056	1.64	1.44	2.92	0.155, 0.059
A4	30	3.0	8532	1.55	1.38	2.45	0.153, 0.067
B1	15	3.0	4276	1.75	1.75	1.30	0.167, 0.138
B2	20	3.0	4638	1.76	1.68	1.29	0.167, 0.142
B3	25	3.0	3299	1.69	1.61	1.19	0.168, 0.150
B4	30	3.0	3216	1.62	1.54	1.13	0.166, 0.157

[a] V_{on}, turn-on voltage, at 1 cd m^{-2};

[b] L_{max}, maximum luminance;

[c] Maximum value;

[d] Maximum value;

[e] Measured at 6 V.

Table S3 Comparison of performance between **OCI** and other reported HLCT-based deep-blue emitters.

Compounds	**λ_{EL} (nm)**	**CIE**		**EQE$_{\mathrm{max}}$ (%)**	**Reference**
		x	y		
OCI	424	0.158-0.159	**0.036-0.038**	5.06	This work
TPA-DFCP	436	0.153	0.077	8.30	J. Mater. Chem. C, 2020, 8, 14117-14124.
CzPAF-TFMP	436	0.155	0.066	5.40	ACS Appl. Energy Mater. 2018, 1, 3243−3254.
DFPBI	425	0.157	0.039	4.96	J. Mater. Chem. C, 2019, 7, 592-600.
TFPBI	440	0.153	0.051	6.01	
2EHO-CNPE	452	0.150	0.090	7.06	ACS Appl. Mater. Interfaces 2019, 11, 44474−44486.
3a	443	0.150	0.080	7.10	Adv. Funct. Mater., 2017, 27, 1605245.
TPEA	445	0.150	0.090	8.00	J. Mater. Chem. C,

					2018, 6, 745-753.
Ph-BPA-BPI	448	0.150	0.080	4.56	Chem. Eur. J., 2016, 22, 12130-12137.
TPA-2PI	458	0.150	0.080	2.60	Dyes Pigments, 2020, 180, 108511.
4	428	0.160	0.060	6.50	Chem. Commun., 2017, 53, 11802-11805.

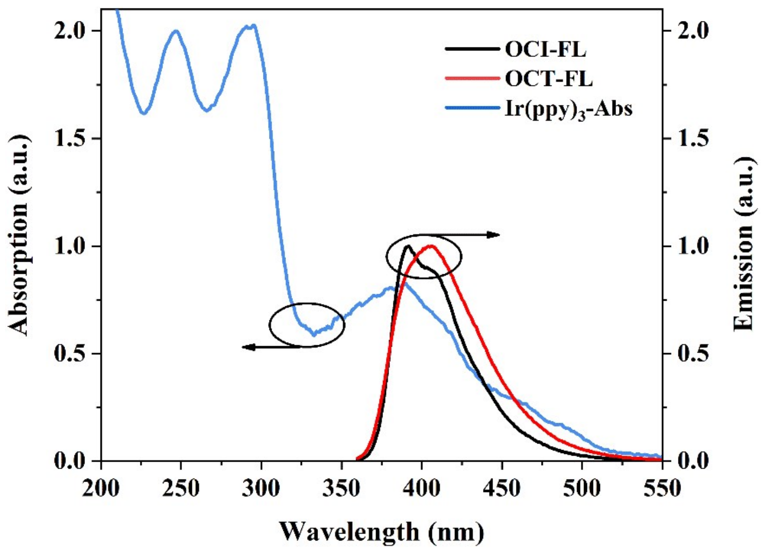


Fig. S7 The fluorescent spectra of **OCI** and **OCT**, and the absorption spectrum of Ir(ppy)$_3$.

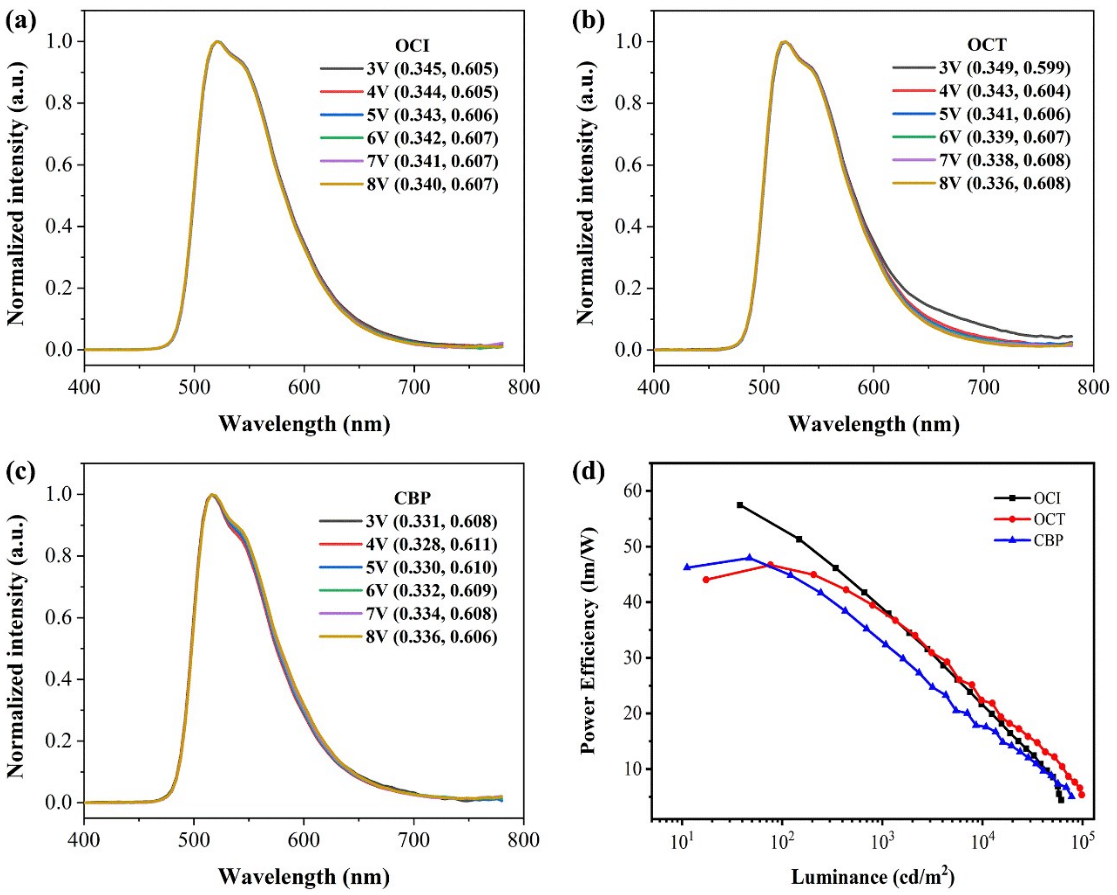


Fig. S8 (a)-(c) The EL spectra of devices A6, B6 and C at 3-8 V. (d) Power efficiency versus luminance of devices A6, B6 and C.

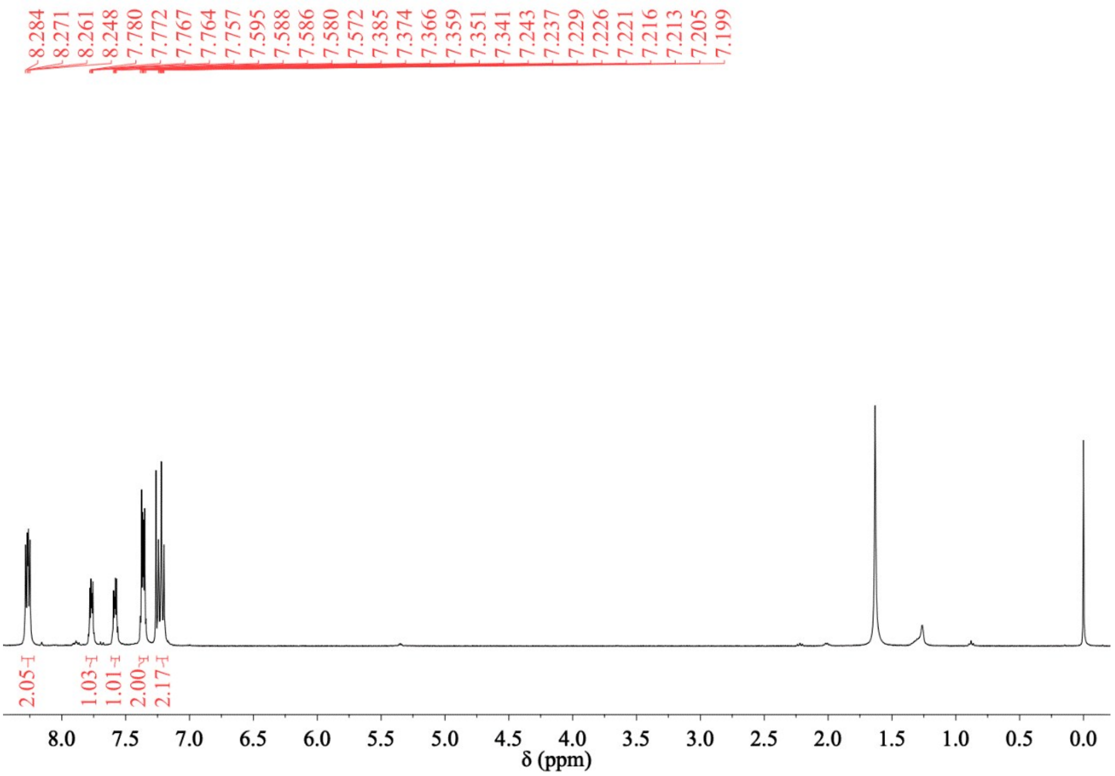


Fig. S9 The ^{1}H NMR spectra of **IM1**.

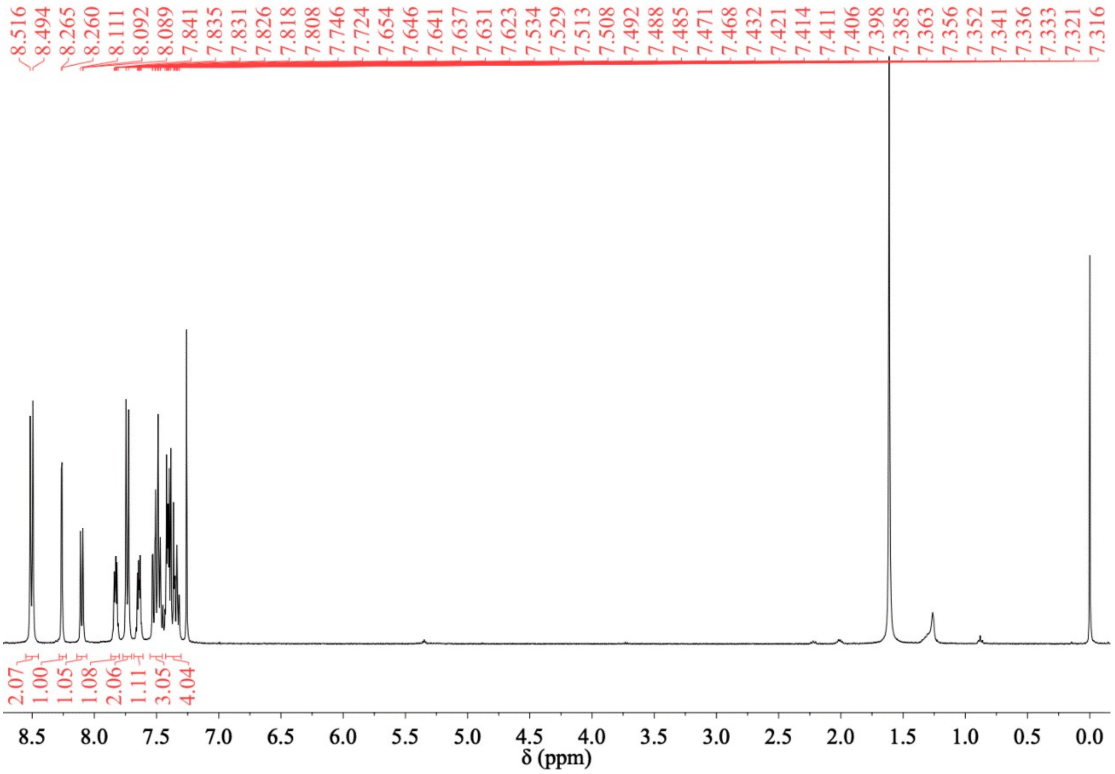


Fig. S10 The ^{1}H NMR spectra of **IM2**.

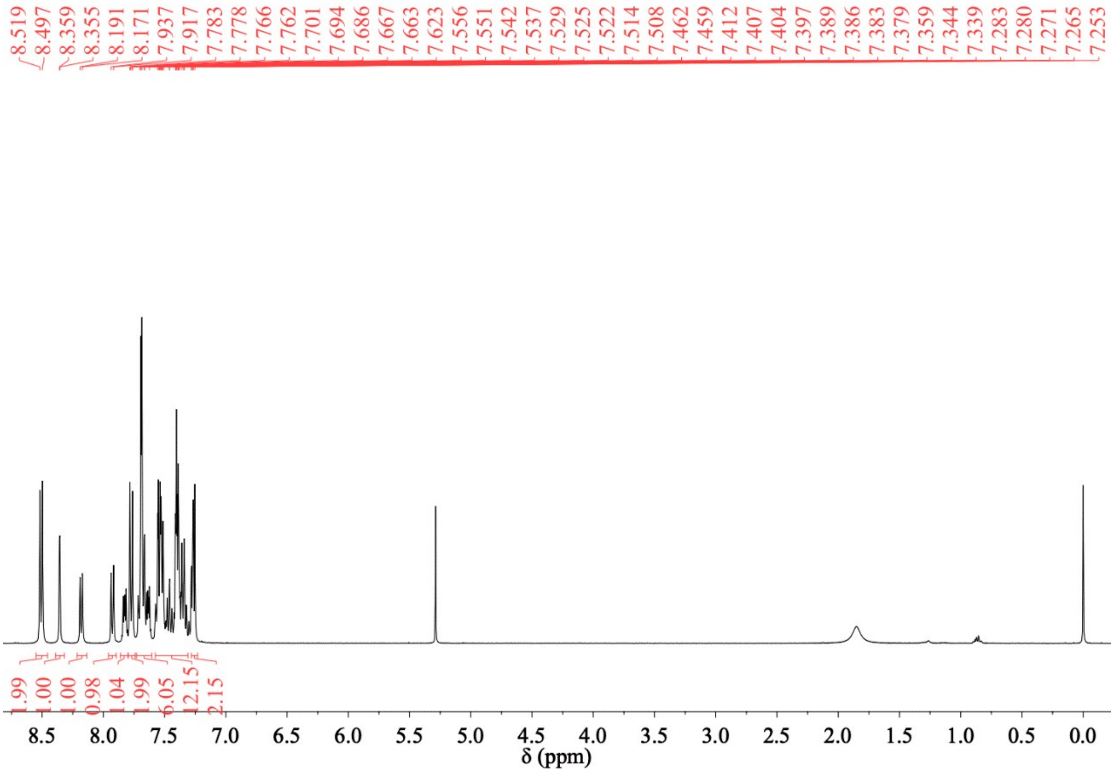


Fig. S11 The ^{1}H NMR spectra of **OCI**.

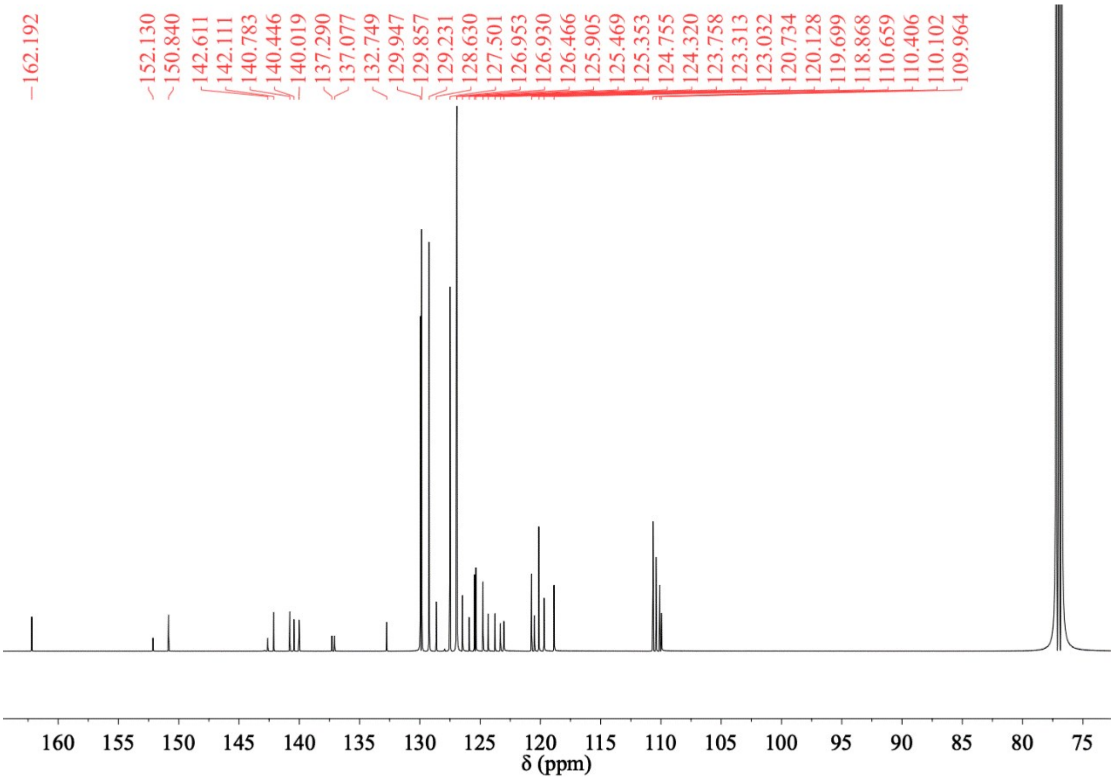
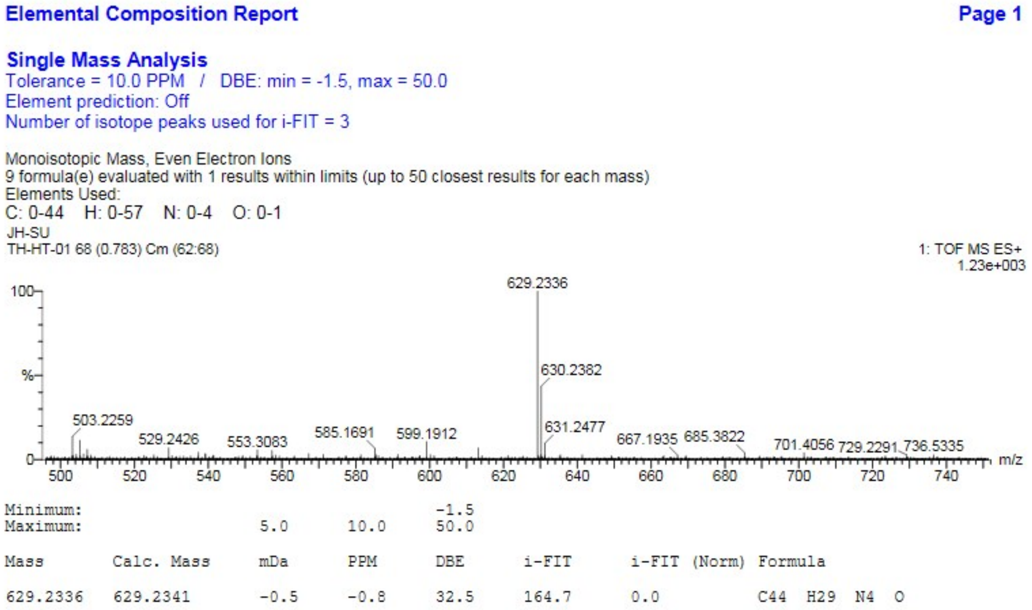


Fig. S12 The ^{13}C NMR spectra of **OCI**.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-44 H: 0-57 N: 0-4 O: 0-1
JH-SU
TH-HT-01 68 (0.783) Cm (62:68)

```
Minimum:                             -1.5
Maximum:               5.0    10.0   50.0

Mass     Calc. Mass    mDa    PPM    DBE    i-FIT    i-FIT (Norm) Formula

629.2336  629.2341     -0.5   -0.8   32.5   164.7    0.0          C44  H29  N4  O
```

Fig. S13 The MS spectra of **OCI**.

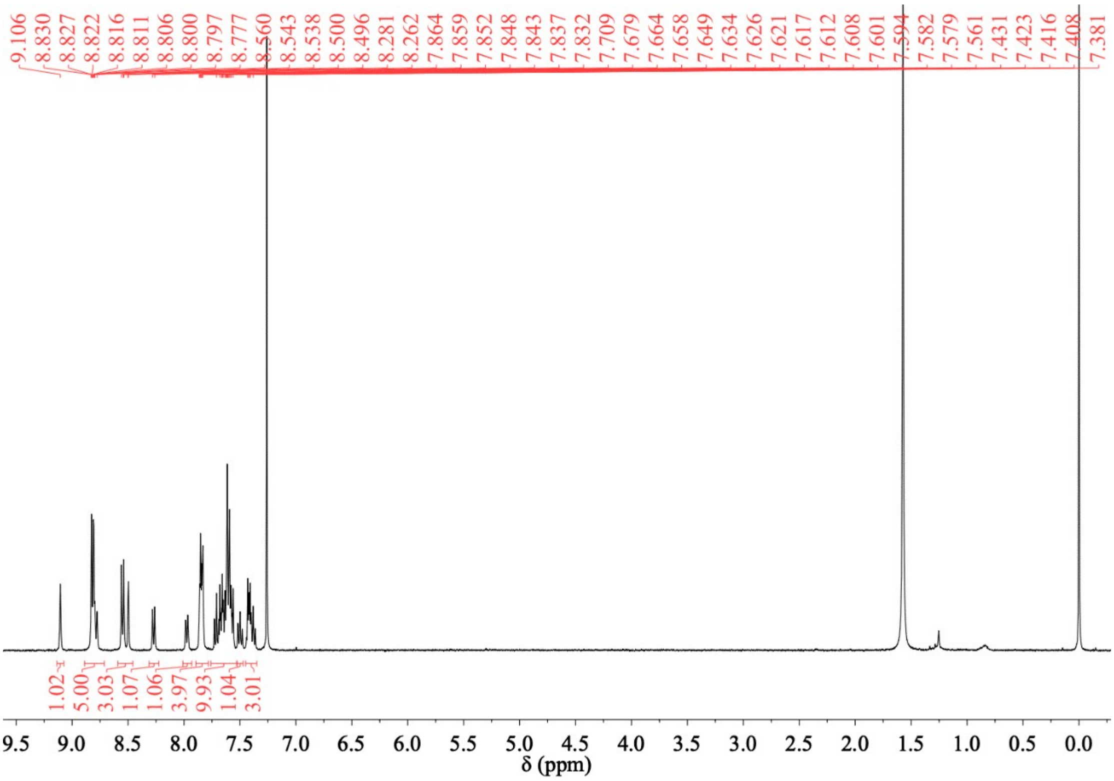


Fig. S14 The ^{1}H NMR spectra of **OCT**.

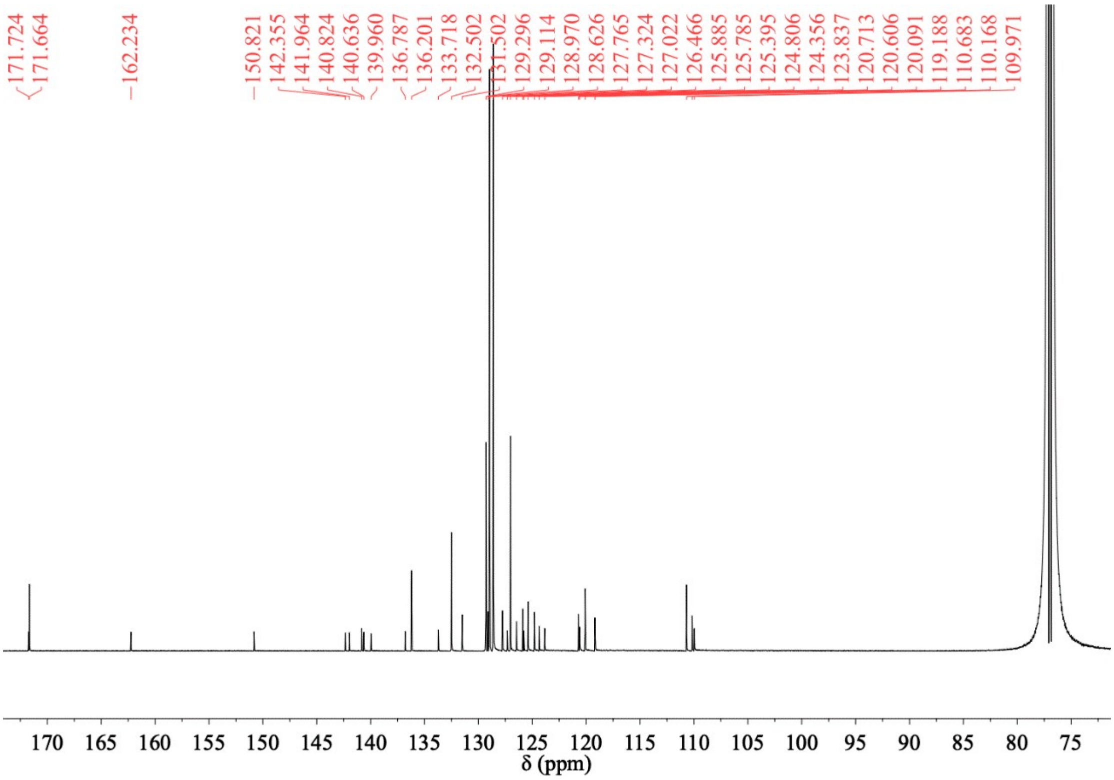
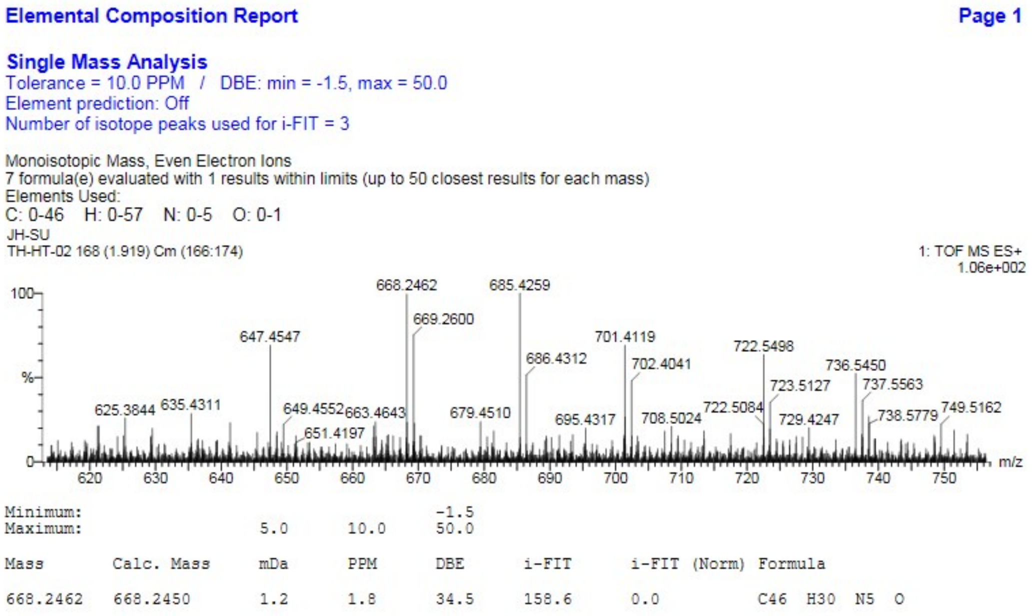


Fig. S15 The ^{13}C NMR spectra of **OCT**.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-46 H: 0-57 N: 0-5 O: 0-1
JH-SU
TH-HT-02 168 (1.919) Cm (166:174)
1: TOF MS ES+
1.06e+002

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Minimum:                                    -1.5
Maximum:                  5.0      10.0     50.0

Mass      Calc. Mass     mDa      PPM      DBE      i-FIT     i-FIT (Norm) Formula

668.2462  668.2450       1.2      1.8      34.5     158.6     0.0          C46  H30  N5  O
```

Fig. S16 The MS spectra of **OCT**.