Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Data for

1,3,5,9-Tetra(4-(1,2,2-triphenylvinyl)phenyl)pyrene (TTPE(1,3,5,9)Py): A Prominent Blue AIEgen for Highly Efficient Nondoped Pure-Blue OLEDs

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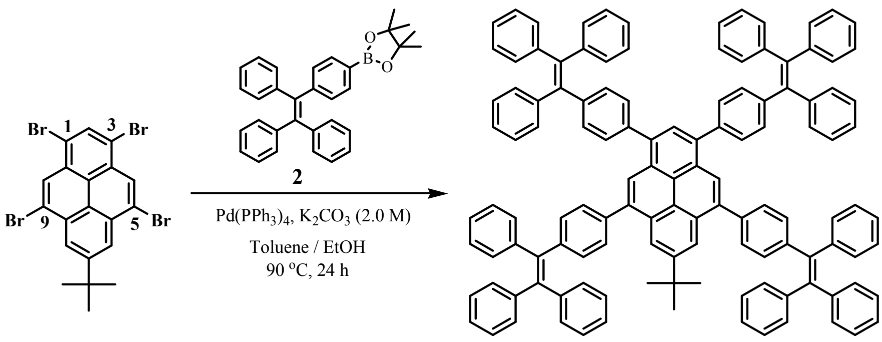
Content

1. Materials and Instruments

All commercially available reagents and chemicals were used as received without further purification. ^{1}H NMR spectra were measured on a JEOL 400 MHz FT-400 NMR spectrometer. Mass spectra were obtained with a Bruke microflex mass spectrometer in MALDI-TOF mode. Thermogravimetric analysis (TGA) analysis was performed on a USA Waters Q600 under nitrogen atmosphere at a heating rate of 10 ^{o}C min $^{-1}$ and Differential scanning calorimetry (DSC) analysis was carried out on METTLER TOLEDU DSC at a heating rate of 10 ^{o}C min^{-1}. X-ray diffraction patterns were collected using an X-ray diffractometer from Rigaku Japan. The data collection from single crystal was conducted using a Bruker D8 venture diffractometer, equipped with graphite-monochromated Cu K α radiation (λ = 1.54178 Å). Cyclic voltammetry (CV) were performed on a BAS 100W Bioanalytical Systems, using a platinum wire as the auxiliary electrode, a glass carbon disk as the working electrode and a silver/Silver chloride (Ag/Ag^{+}) as the reference electrode, standardized for the redox couple ferricinium/ferrocene (Fc/Fc^{+}). Absorption spectrum were measured on a PerkinElmer UV-Lambda 950 spectrophotometer. Photoluminescence spectra were recorded on a Shimadzu F-7000 spectrofluorometer. Absolute PL quantum yields were measured with a Japan Hamamatsu C9920-06G. Fluorescence lifetimes were determined with a Edinburgh FLS1000

Quantaurus-Tau time-resolved spectrometer. The frontier orbitals of the molecules based on the ground state geometries were calculated at B3LYP/6-31G* by Gaussian 16 program.

2. Synthesis and Characterization



1 **TTPE(1,3,5,9)Py**

Scheme S1. The synthetic route of the target compound **TTPE(1,3,5,9)Py**.

Synthesis of TTPE(1,3,5,9)Py: To a mixture of 1,3,5,9-tetrabromo- 7-*tert*-butylpyrene[S1] (1.40 g, 2.00 mmol), 4-(1,2,2-Triphenylvinyl)phenyl boronic acid (5.50 g, 12 mmol), $Pd(PPh_3)_4$ (0.32 g, 0.28 mmol), and potassium carbonate (3.80 g, 27.50 mmol) in degassed toluene/ethanol (120 mL/30 mL) and sodium carbonate solution (30 mL, 2 M) was heated to reflux for 24 h under nitrogen. The precipitate was purified by column chromatography, recrystallization and sublimation, obtained yellow solid in 42.8% yield (1.21g, 0.85 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.18 (s, 2H), 7.98 (s, 2H), 7.84 (s, 1H), 7.35 (dd, J = 8.1, 3.8 Hz, 10H), 7.22 (s, 4H), 7.19 (d, J = 4.1 Hz, 12H), 7.16 (s, 2H), 7.12 (t, J = 6.5 Hz, 32H), 7.08–7.04 (m, 10H), 6.98 (d, J = 7.5 Hz, 4H), 6.81 (t, J = 7.3 Hz, 2H), 1.37 (s, 9H). MS (MALDI-TOF): m/z calcd. for $[C_{124}H_{90}]^+$, 1580.04; found 1580.5881. Anal. calcd. for $C_{124}H_{90}$: C,94.17; H, 5.83%. Found: C, 94.15; H, 5.84%.

3. Device Fabrication

Commercial ITO glass substrate was pre-cleaned carefully with alkaline detergent, boiled deionized water, and deionized water thoroughly in ultrasonic bath and then treated with UV/O_3 for 2 min. **TTPE(1,3,5,9)Py** emitter was purified by and vacuum sublimation. All the organic layers were deposited onto the ITO-coated substrates by high-vacuum (1×10^{-5} Pa) thermal evaporation.[S2-S3] The active area of each device was 9 mm^2. The thicknesses of the organic materials and the cathode layers were controlled using a quartz-crystal thickness monitor. The electroluminescence spectra, the current density-voltage characteristics and the current density-voltage-luminance curves characterizations of the OLEDs were carried out with a Photo Research SpectraScan PR-650 Spectroradiometer and a Keithley 2400 Source Meter and they are recorded simultaneously. All measurements were carried out on the devices without encapsulations in ambient atmosphere in the dark.

4. Thermal Properties

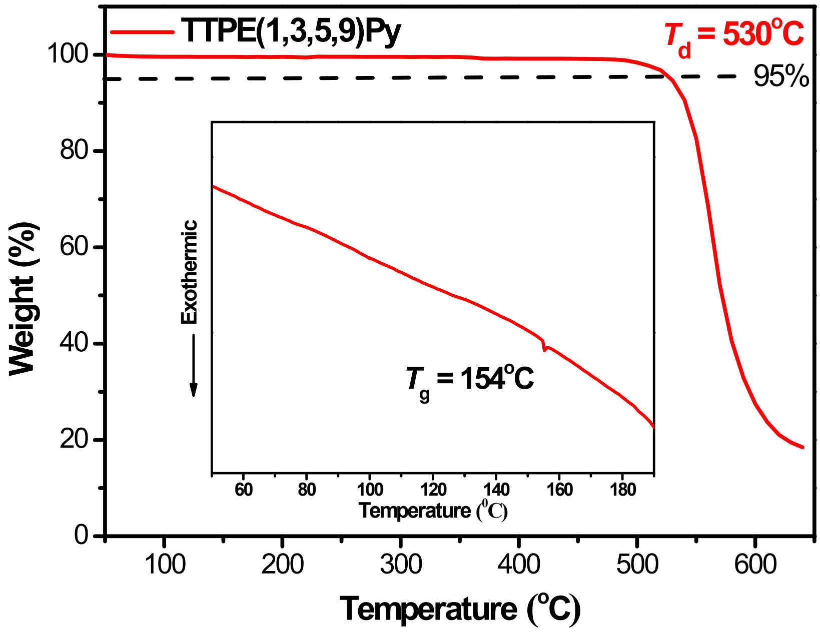


Fig. S1 TGA and DSC thermograms of **TTPE(1,3,5,9)Py**.

5. DFT Calculations

Table S1 Atom coordinates and absolute energies for **TTPE(1,3,5,9)Py** Standard orientation.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-0.164369	-4.132581	0.528643
2	6	0	1.063235	-3.468743	0.550770
3	6	0	1.164765	-2.069547	0.446686
4	6	0	-0.028726	-1.284739	0.380571
5	6	0	-1.294278	-1.955561	0.368382
6	6	0	-1.324377	-3.356171	0.417776
7	6	0	2.448691	-1.393376	0.417663
8	6	0	0.039429	0.143338	0.322846
9	6	0	1.312666	0.791859	0.361302
10	6	0	2.489231	-0.024784	0.391806
11	6	0	1.368808	2.208568	0.301814
12	6	0	0.174915	2.925934	0.183299
13	6	0	-1.085428	2.319708	0.157429
14	6	0	-1.165843	0.905528	0.221090
15	6	0	-2.412934	0.200582	0.167307
16	6	0	-2.505765	-1.161157	0.261797
17	1	0	-3.325432	0.777763	0.072753
18	1	0	1.979213	-4.035341	0.647363
19	1	0	-2.289055	-3.846519	0.367471
20	1	0	3.454897	0.464966	0.340244
21	1	0	0.224700	4.010906	0.166932
22	6	0	7.566127	-4.181564	0.270262
23	6	0	8.321174	-4.308545	-0.861819
24	6	0	6.255001	-3.465554	0.290559
25	6	0	5.255826	-3.730692	-0.661759
26	6	0	5.958878	-2.538999	1.304566
27	6	0	4.023590	-3.085804	-0.612702
28	1	0	5.453033	-4.447089	-1.453063
29	6	0	4.731537	-1.882619	1.344857
30	1	0	6.702249	-2.330501	2.068865
31	6	0	3.736328	-2.143091	0.389443
32	1	0	3.276926	-3.302813	-1.371350
33	1	0	4.530214	-1.166595	2.137043
34	6	0	7.989124	-4.745613	1.589149
35	6	0	7.087032	-5.489281	2.370346
36	6	0	9.271353	-4.501472	2.109490
37	6	0	7.464149	-5.998499	3.611959
38	1	0	6.084115	-5.671320	1.994242

39	6	0	9.645287	-5.000288	3.356435
40	1	0	9.975850	-3.914271	1.528719
41	6	0	8.745658	-5.755733	4.110965
42	1	0	6.754102	-6.581714	4.192740
43	1	0	10.641056	-4.794488	3.740578
44	1	0	9.037952	-6.145806	5.082318
45	6	0	8.043493	-3.531474	-2.108576
46	6	0	7.860961	-2.138501	-2.075278
47	6	0	8.015060	-4.174524	-3.358801
48	6	0	7.636263	-1.417360	-3.246954
49	1	0	7.897860	-1.621681	-1.121358
50	6	0	7.778630	-3.455678	-4.529467
51	1	0	8.175046	-5.248022	-3.407352
52	6	0	7.588188	-2.073165	-4.478632
53	1	0	7.501546	-0.339996	-3.196950
54	1	0	7.747649	-3.975862	-5.483430
55	1	0	7.410646	-1.510991	-5.391603
56	6	0	9.491418	-5.234686	-0.951729
57	6	0	9.391216	-6.579309	-0.555802
58	6	0	10.711313	-4.792221	-1.493510
59	6	0	10.477308	-7.444734	-0.677496
60	1	0	8.452007	-6.944357	-0.152115
61	6	0	11.801428	-5.653865	-1.604023
62	1	0	10.802113	-3.761579	-1.824919
63	6	0	11.689091	-6.984888	-1.196643
64	1	0	10.374573	-8.482018	-0.369314
65	1	0	12.738651	-5.286084	-2.013850
66	1	0	12.536134	-7.659407	-1.289802
67	6	0	-0.281646	-5.666546	0.609796
68	6	0	-1.151972	-6.055111	1.828679
69	6	0	-0.946209	-6.197364	-0.683088
70	6	0	1.088396	-6.354066	0.762725
71	1	0	-0.702097	-5.695831	2.761370
72	1	0	-2.161212	-5.635959	1.760722
73	1	0	-1.248105	-7.145797	1.896036
74	1	0	-0.343879	-5.947184	-1.563927
75	1	0	-1.047662	-7.288863	-0.639022
76	1	0	-1.945284	-5.774016	-0.831099
77	1	0	0.951006	-7.439859	0.819751
78	1	0	1.747318	-6.149117	-0.088476
79	1	0	1.603610	-6.037317	1.676663
80	6	0	2.644881	2.973568	0.378801
81	6	0	2.960825	3.921646	-0.608570
82	6	0	3.532814	2.817255	1.457051

83	6	0	4.128024	4.680846	-0.527356
84	1	0	2.288438	4.050208	-1.452598
85	6	0	4.699400	3.576937	1.539619
86	1	0	3.293018	2.108127	2.244386
87	6	0	5.002862	4.510670	0.546892
88	1	0	4.355484	5.403443	-1.306853
89	1	0	5.368218	3.444621	2.386175
90	6	0	-2.285799	3.200426	0.084785
91	6	0	-3.290001	3.161098	1.067318
92	6	0	-2.406875	4.141637	-0.950910
93	6	0	-4.381629	4.027218	1.009446
94	1	0	-3.201540	2.458184	1.890880
95	6	0	-3.498988	5.007351	-1.009929
96	1	0	-1.641443	4.181318	-1.721394
97	6	0	-4.491703	4.952556	-0.030296
98	1	0	-5.143426	3.983774	1.783528
99	1	0	-3.575468	5.722797	-1.824666
100	6	0	-8.394265	-4.131633	-0.826496
101	6	0	-7.860968	-3.462327	0.238928
102	6	0	-7.567445	-4.590652	-1.984666
103	6	0	-6.382302	-5.320479	-1.790773
104	6	0	-7.990015	-4.350591	-3.304041
105	6	0	-5.634714	-5.774563	-2.876265
106	1	0	-6.050691	-5.532549	-0.779022
107	6	0	-7.236639	-4.793816	-4.389937
108	1	0	-8.914867	-3.806591	-3.474530
109	6	0	-6.055000	-5.508072	-4.180793
110	1	0	-4.723605	-6.341337	-2.702032
111	1	0	-7.575668	-4.584643	-5.401303
112	1	0	-5.470793	-5.859940	-5.026918
113	6	0	-9.848378	-4.463808	-0.926761
114	6	0	-10.261340	-5.755439	-1.299003
115	6	0	-10.836853	-3.488312	-0.711733
116	6	0	-11.614221	-6.069021	-1.419088
117	1	0	-9.511487	-6.517999	-1.490125
118	6	0	-12.189598	-3.798158	-0.843559
119	1	0	-10.537073	-2.480558	-0.441724
120	6	0	-12.584940	-5.091080	-1.192138
121	1	0	-11.910324	-7.077767	-1.695417
122	1	0	-12.936093	-3.025771	-0.677305
123	1	0	-13.639708	-5.332666	-1.293282
124	6	0	-6.476885	-2.899885	0.225006
125	6	0	-6.020453	-2.097485	-0.833062
126	6	0	-5.604291	-3.111340	1.307325

127	6	0	-4.739146	-1.551792	-0.822105
128	1	0	-6.678035	-1.902816	-1.674515
129	6	0	-4.318252	-2.579358	1.311216
130	1	0	-5.941728	-3.700519	2.155492
131	6	0	-3.857581	-1.789039	0.243839
132	1	0	-4.409189	-0.937841	-1.655672
133	1	0	-3.667283	-2.758559	2.162601
134	6	0	-8.613765	-3.235938	1.510865
135	6	0	-9.266551	-4.291136	2.170496
136	6	0	-8.635651	-1.964296	2.110571
137	6	0	-9.934728	-4.078424	3.375336
138	1	0	-9.245413	-5.283960	1.732040
139	6	0	-9.313683	-1.748382	3.309236
140	1	0	-8.119359	-1.140108	1.626272
141	6	0	-9.966267	-2.805201	3.947502
142	1	0	-10.428388	-4.910977	3.869932
143	1	0	-9.328026	-0.753895	3.747871
144	1	0	-10.488522	-2.639399	4.886054
145	6	0	6.355346	4.698874	0.653873
146	6	0	6.882219	5.740632	-0.034394
147	6	0	8.402759	5.816633	-0.266304
148	6	0	8.965220	5.233693	-1.401808
149	6	0	9.217637	6.469118	0.659248
150	6	0	10.342747	5.302861	-1.611825
151	1	0	8.322981	4.719692	-2.131516
152	6	0	10.594899	6.537897	0.449587
153	1	0	8.773832	6.929004	1.554243
154	6	0	11.157634	5.954256	-0.686154
155	1	0	10.785964	4.842515	-2.506745
156	1	0	11.237601	7.051496	1.179276
157	1	0	12.243499	6.008271	-0.851307
158	6	0	7.271947	3.590798	1.204880
159	6	0	7.813792	3.706064	2.484984
160	6	0	7.559909	2.471308	0.423708
161	6	0	8.643979	2.701978	2.984056
162	1	0	7.586608	4.588228	3.100871
163	6	0	8.390270	1.467648	0.922412
164	1	0	7.132214	2.380501	-0.585403
165	6	0	8.932744	1.583234	2.202872
166	1	0	9.071621	2.793515	3.993009
167	1	0	8.618046	0.585440	0.306683
168	1	0	9.587603	0.792060	2.595937
169	6	0	5.965618	6.848709	-0.585401
170	6	0	5.424572	6.733915	-1.865885

171	6	0	5.675993	7.967217	0.196563
172	6	0	4.594022	7.737786	-2.364784
173	1	0	5.652533	5.852209	-2.482142
174	6	0	4.846032	8.971112	-0.302331
175	1	0	6.102396	8.057261	1.206289
176	6	0	4.305180	8.856484	-1.583563
177	1	0	4.168249	7.647352	-3.374626
178	1	0	4.618101	9.853230	0.313471
179	1	0	3.651045	9.648086	-1.976973
180	6	0	-6.929954	4.604374	0.767746
181	6	0	-5.954000	5.155686	0.006080
182	6	0	-8.327849	4.364076	0.167958
183	6	0	-9.303858	5.356745	0.254914
184	6	0	-8.618074	3.153763	-0.462378
185	6	0	-10.570415	5.139165	-0.288192
186	1	0	-9.075083	6.310835	0.751419
187	6	0	-9.884453	2.935982	-1.004959
188	1	0	-7.848207	2.371427	-0.531151
189	6	0	-10.861019	3.928900	-0.917499
190	1	0	-11.339902	5.921672	-0.218795
191	1	0	-10.113797	1.981834	-1.501243
192	1	0	-11.859506	3.757087	-1.345052
193	6	0	-6.645896	4.217355	2.231005
194	6	0	-6.175043	2.940319	2.536004
195	6	0	-6.859059	5.144415	3.251560
196	6	0	-5.917552	2.589986	3.861687
197	1	0	-6.006693	2.209688	1.731653
198	6	0	-6.602103	4.794082	4.576995
199	1	0	-7.229920	6.151363	3.010742
200	6	0	-6.131536	3.516324	4.882144
201	1	0	-5.547079	1.582864	4.101888
202	1	0	-6.770690	5.524317	5.381751
203	1	0	-5.929198	3.240055	5.927147
204	6	0	-6.238058	5.542705	-1.457179
205	6	0	-6.710058	6.819346	-1.762060
206	6	0	-6.022726	4.616392	-2.477957
207	6	0	-6.967119	7.169826	-3.087787
208	1	0	-6.879486	7.549605	-0.957598
209	6	0	-6.280154	4.966562	-3.803343
210	1	0	-5.650179	3.610026	-2.237313
211	6	0	-6.752842	6.243590	-4.108274
212	1	0	-7.339959	8.176133	-3.327744
213	1	0	-6.111225	4.236446	-4.608134
214	1	0	-6.956034	6.519564	-5.153189

6. X-ray crystallography

Table S2 Summary of crystal data for **TTPE(1,3,5,9)Py**.

Parameters	**TTPE(1,3,5,9)Py**
Empirical formula	$C_{124}H_{90}$
Formula weight	1579.95
Temperature/K	153(2)
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a=15.5495(8)Å,α=90.00^0
	b=38.2440(19)Å,β=105.124(2)^0
	c=15.8621(8)Å,γ=90.00^0
Z	4
Density (calculated)	1.152 g/cm^3
Volume	9106.1(8) Å^3
F(000)	3336.0
Theta range for data collection	7.396^0 to 136.906^0
Index ranges	$-18 \leq h \leq 18$
	$-46 \leq k \leq 46$
	$-18 \leq l \leq 19$
Reflections collected	94866
Independent reflections	16618
	[R_{int} = 0.0519, R_{sigma} = 0.0324]
Data/restraints/parameters	16618/6616/1259
Goodness-of-fit on F^2	1.170
Final R indexes [I>=2σ (I)]	R_1 = 0.1894, wR_2 = 0.3239
Final R indexes [all data]	R_1 = 0.2220, wR_2 = 0.3342
Largest diff. Peak/hole	1.53/-0.63 e Å^{-3}

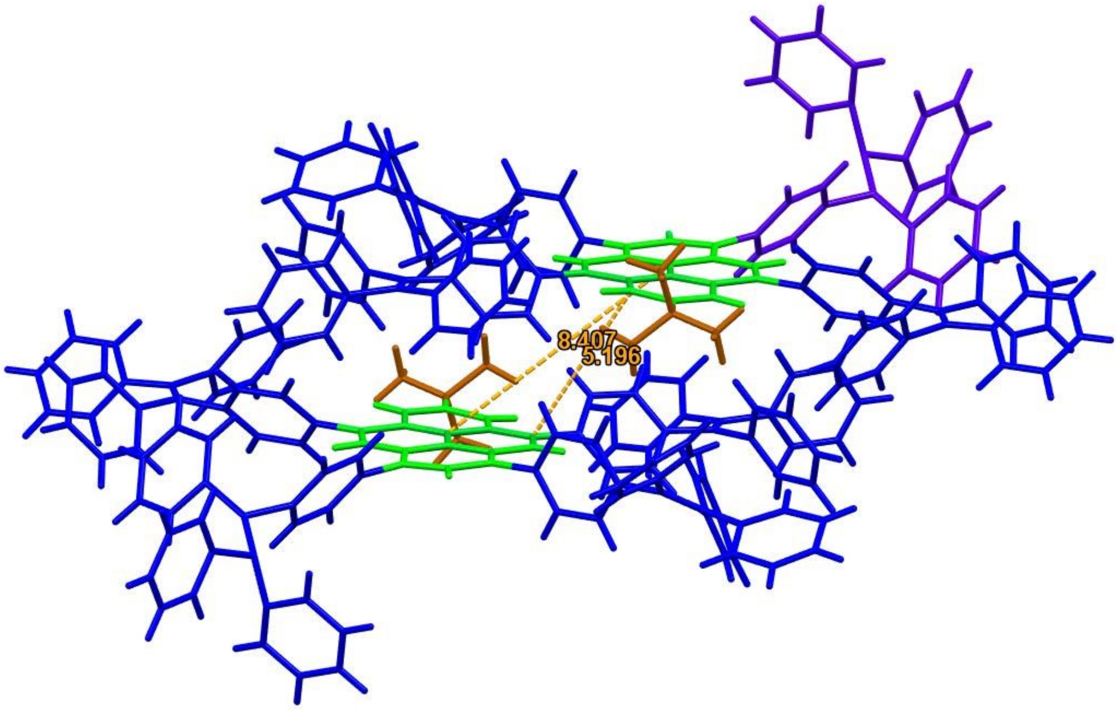


Fig. S2 Packing distances and conformations in **TTPE(1,3,5,9)Py**: The shortest contact between pyrene ring and a substituent on a neiboring molecule is 5.196 Å, and the centroid···centroid distance is 8.407 Å.

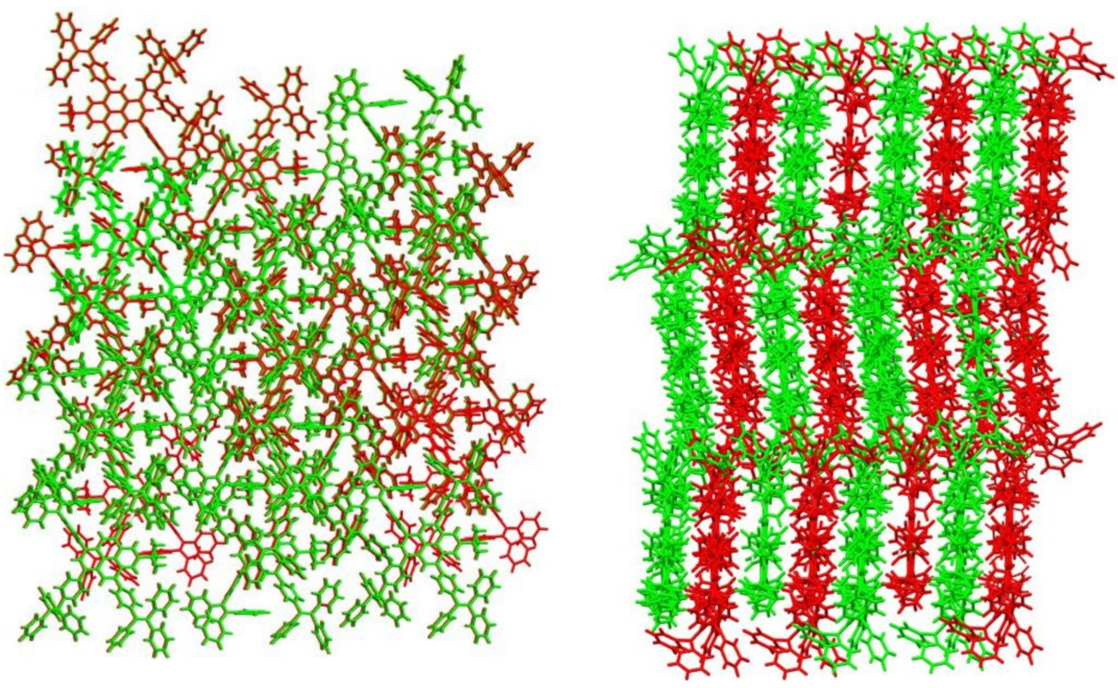


Fig. S3 Packing plots for **TTPE(1,3,5,9)Py**: Top view (left) and side view (right).

7. Photophysical Properties

Table S3 Photophysical properties of **TTPE(1,3,5,9)Py**.

	Φ_F[c] [%]			τ[d] [ns]			k_r/k_{nr} ($\times 10^8$ s^{-1})		
	soln[a]	film[b]	powder	soln[a]	film[b]	powder	soln[a]	film[b]	powder
TTPE(1,3,5,9)Py	2%	78%	61%	0.43	2.22	2.69	0.5/22.5	3.5/1.0	2.3/1.4

[a]In THF, 1.0 × 10^{-5} M. [b]Evaporated film on quartz plate. [c]Fluorescence quantum yield. [d]Fluorescence lifetime, measured at room temperature in air. The radiative decay rate, $k_r = \Phi_F/\tau$. The nonradiative decay rate, $k_{nr} = 1/\tau - k_r$.

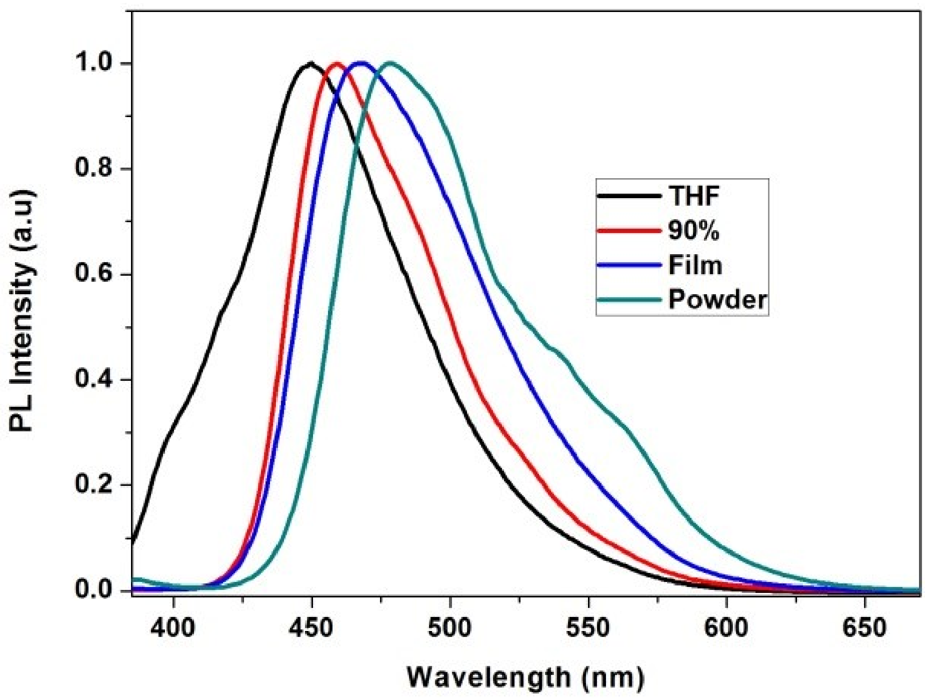


Fig. S4 The PL spectrum of **TTPE(1,3,5,9)Py** in different states: (a) THF: concentration in THF solution, 1.0 x 10^{-5} M, (b) 90%: in THF/water mixtures, the water fraction is 90%, (c) film: 50 nm, made by vacuum thermal evaporation.

8. Photoelectron Yield Spectroscopy (PESA) Spectra

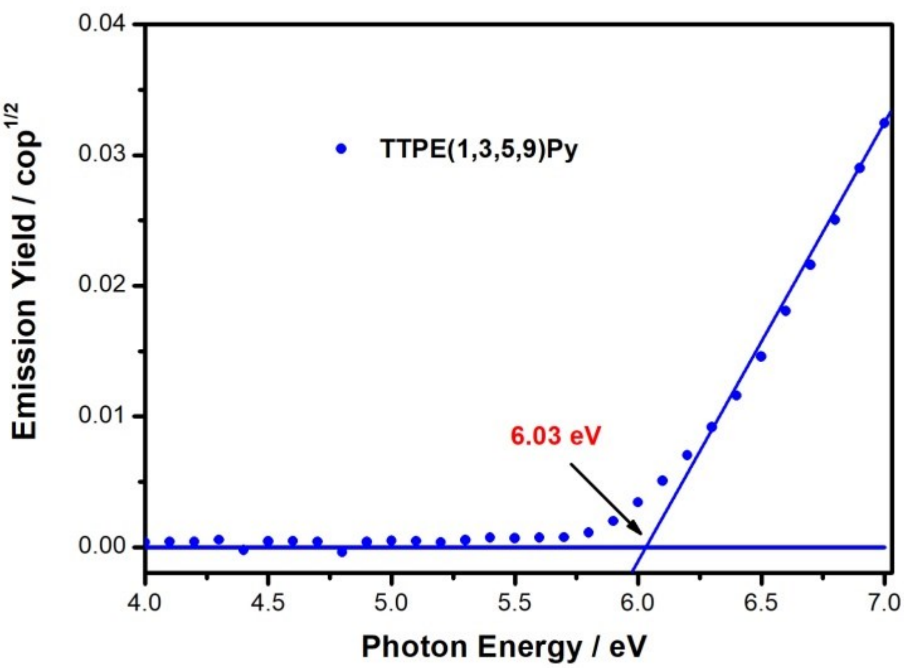
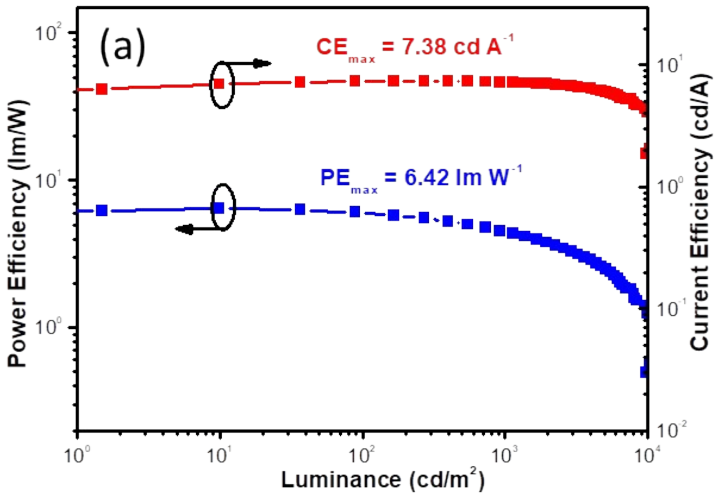
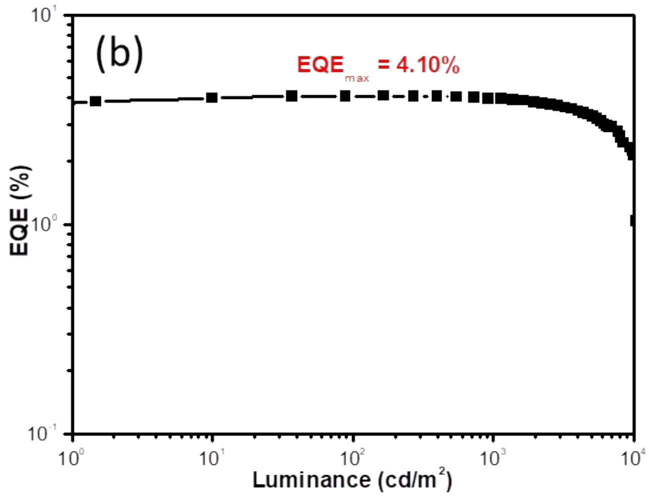


Fig. S5 PESA spectra of **TTPE(1,3,5,9)P**y film on evaporated film on precleaned ITO substrates.

9. Device performance





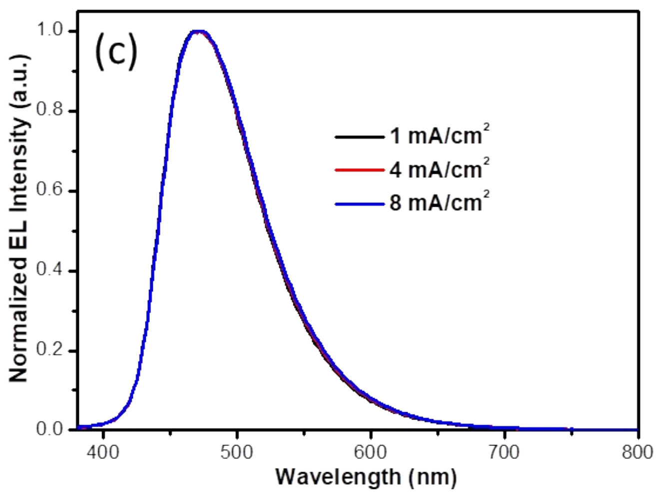


Fig. S6 (a) Current efficiency–luminance–power efficiency, and (b) external quantum efficiency with luminance characteristics, and (c) EL spectra stability of OLED under different current densities of **TTPE(1,3,5,9)Py**.

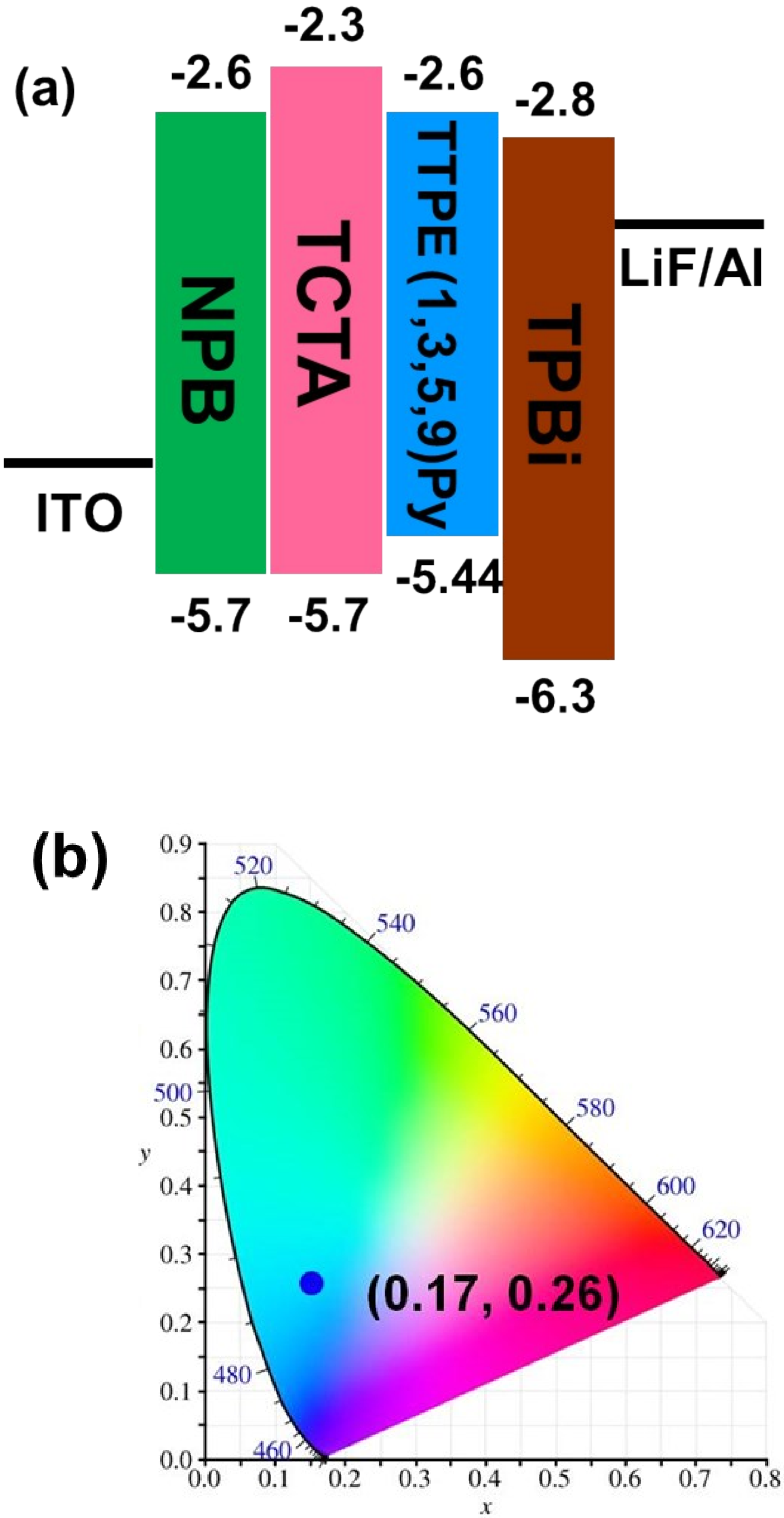
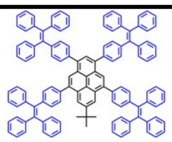
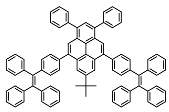
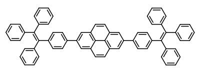
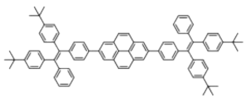
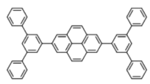
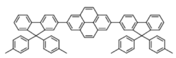
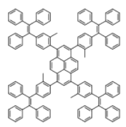
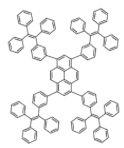
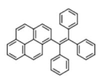
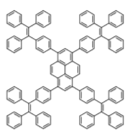


Fig. S7 (a) Energy level diagrams and device configurations of **TTPE(1,3,5,9)Py**; (b) Commission Internationale de l'Eclairage (CIE) chromaticity coordinate of the device.

Table S4 Summary of representative performances of OLEDs using pyrene-based AIEgens.

Emitter	V_{on} (v)	L_{max} (cd m^{-2})	$\eta_{C,max}$ (cd A^{-1})	$\eta_{P,max}$ (lm W^{-1})	λ_{EL} (nm)	CIE (x,y)	EQE (%)	Year/Ref.
	3.2	11849	7.38	6.42	468	(0.17,0.26)	4.10	This work
	3.2	11450	6.51	6.24	488	(0.19,0.28)	3.35	2020/[S4]
	3.2	5453	7.82	6.40	484	(0.22,0.34)	3.66	2019/[S5]
	4.2	18287	2.94	1.79	448	(0.15,0.09)	3.46	2016/[S6]
	4.3	1996	2.27	1.37	452	(0.16,0.11)	1.70	2016/[S6]
	4.3	1996	2.27	1.37	452	(0.16,0.11)	1.70	2016/[S7]
	3.5	9824	4.02	3.08	436	(0.18,0.16)	2.50	2015/[S8]
	3.5	9824	4.02	3.08	436	(0.18,0.16)	2.50	2015/[S9]
	4.6	25470	4.00	2.70	504	—	2.00	2011/[S7]
	4.9	15546	6.91	3.55	484	(0.20,0.29)	3.25	2010/[S10]

10. FT-IR Spectrum

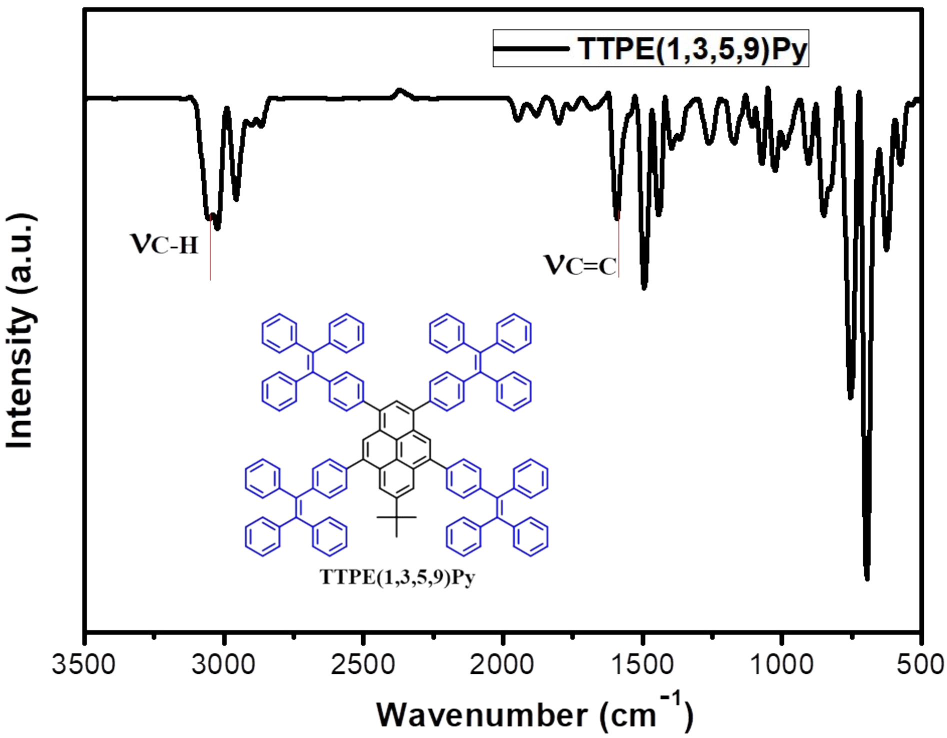


Fig. S8 FT-IR spectra of **TTPE(1,3,5,9)Py**.

11. NMR Spectra

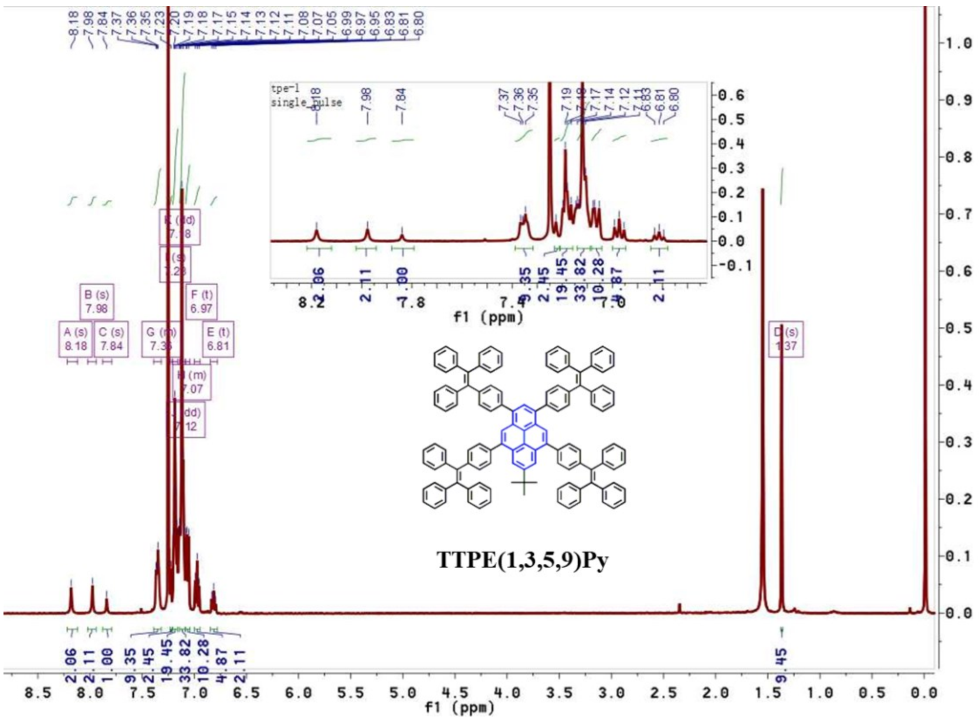


Fig. S9 ^{1}H NMR spectrum of **TTPE(1,3,5,9)Py** (400 MHz, $CDCl_3$).

12. Mass Spectra

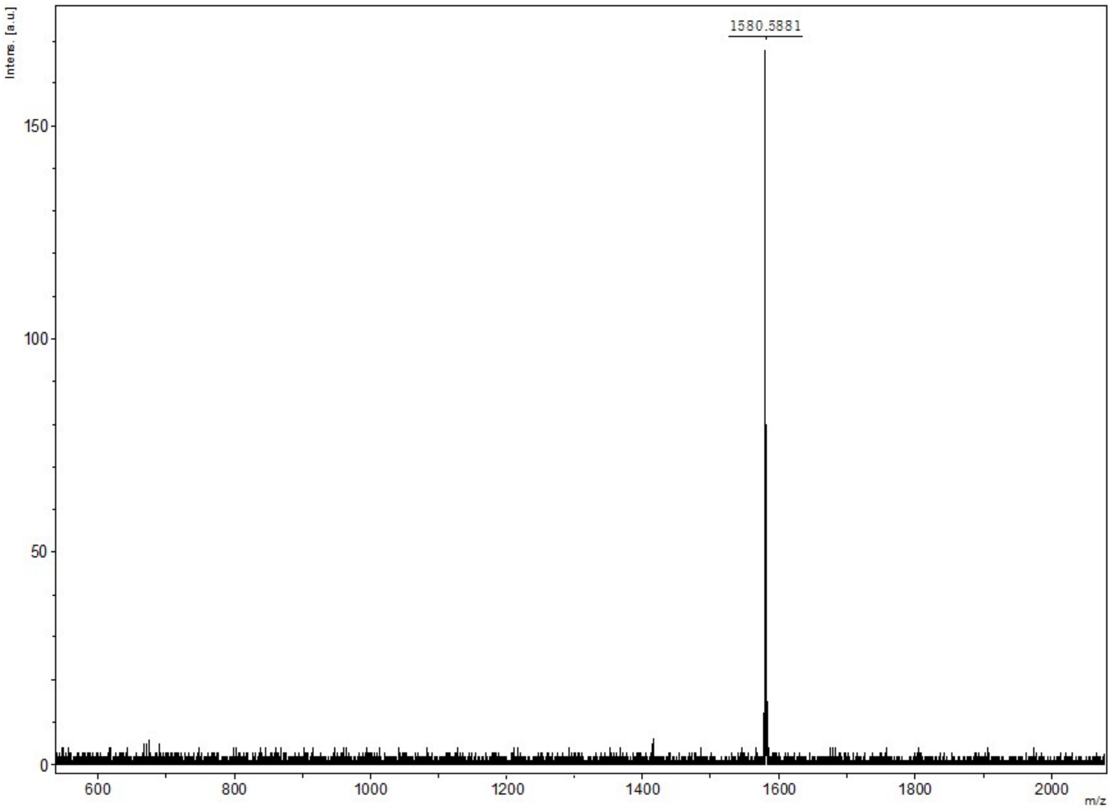


Fig. S10 MALDI-TOF Mass spectra of **TTPE(1,3,5,9)Py**.

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