

## Supporting Information

### Indazole-based deep blue-emitting hot exciton material: Conjugated polycyclic aromaticity molecular design

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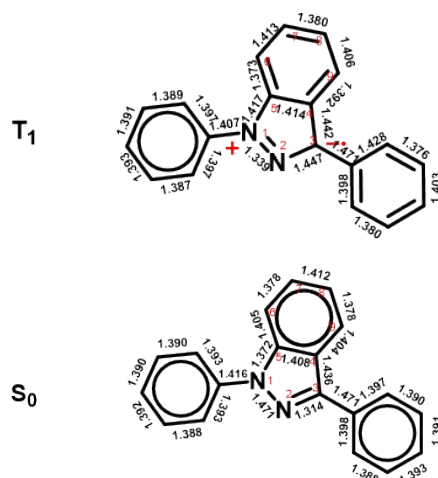
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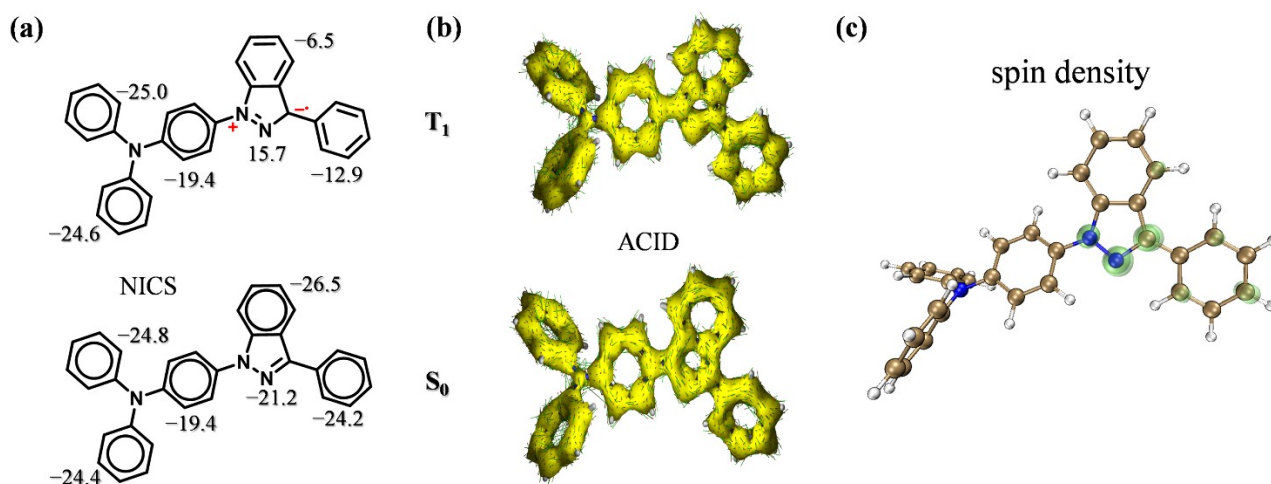
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## 1. Theoretical Calculations.



**Figure S1.** Bond length (Å) of IND in the  $S_0$  and  $T_1$  states.



**Figure S2.** Aromaticity analysis for IND-DPA. (a) NICS(1)<sub>zz</sub> values (ppm) and (b) ACID plots in the  $S_0$  and  $T_1$  states. (c) Spin density distributions (isovalue: 0.015 a.u.) in the  $T_1$  state.

In the ground state ( $S_0$ ), all heterocycles and benzene rings of IND-DPA exhibit negative NICS(1)<sub>zz</sub> values (-21.2, -26.5, -24.2, -19.4, -24.4 and -24.6 ppm). This observation clearly indicates the presence of unique aromaticity within this system (Figure S2a). In the  $T_1$  state, the N-position benzene ring and diphenylamine continue to display negative NICS(1)<sub>zz</sub> values, while the other two benzene rings show a slight weakening of their NICS(1)<sub>zz</sub> values to negatives (-6.5 ppm), suggesting antiaromaticity. Conversely, positive NICS(1)<sub>zz</sub> values are observed on the heterocycles (15.7 ppm), indicating antiaromaticity. Additionally, ACID analysis yielded similar conclusions (Figure S2b). In the  $S_0$  state, clockwise ring currents indicate that all rings are aromatic; however, in contrast, in the  $T_1$  state all benzene rings maintain their aromaticity while the heterocycles exhibit slight

counterclockwise currents indicating weak antiaromaticity. To further investigate the origin of aromaticity of benzene rings in T<sub>1</sub> state we conducted an extensive study of their spindensity (Figure S2c). It is found that the spin density is not only mainly delocalized on the heterocycle, but also presents on the adjacent and one of peripheral benzene rings, resulting in the aromaticity differences in the T<sub>1</sub> state.

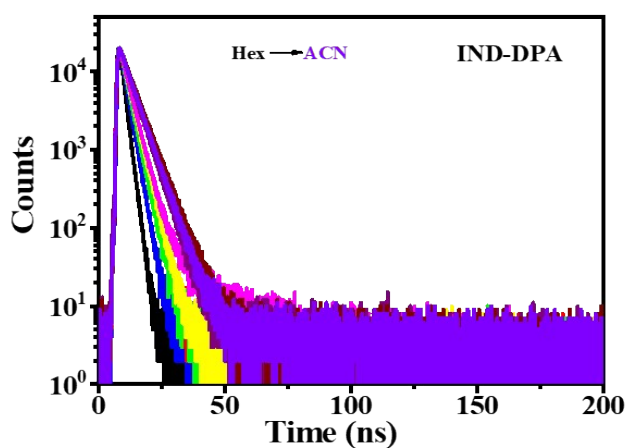
**Table S1.** Vertical excitation energies (Unit: eV) of IND at the level of TDA-M06-2X/6-311G(d).

IND	Excitation Energy (eV)		Excitation Energy (eV)
S <sub>1</sub>	3.77	T <sub>1</sub>	2.28
S <sub>2</sub>	4.80	T <sub>2</sub>	3.75
S <sub>3</sub>	4.95	T <sub>3</sub>	3.99
S <sub>4</sub>	5.02	T <sub>4</sub>	4.13
S <sub>5</sub>	5.06	T <sub>5</sub>	4.41
S <sub>6</sub>	5.41	T <sub>6</sub>	4.57
S <sub>7</sub>	5.50	T <sub>7</sub>	4.65
S <sub>8</sub>	5.68	T <sub>8</sub>	4.78
S <sub>9</sub>	5.76	T <sub>9</sub>	4.89
S <sub>10</sub>	5.92	T <sub>10</sub>	4.94

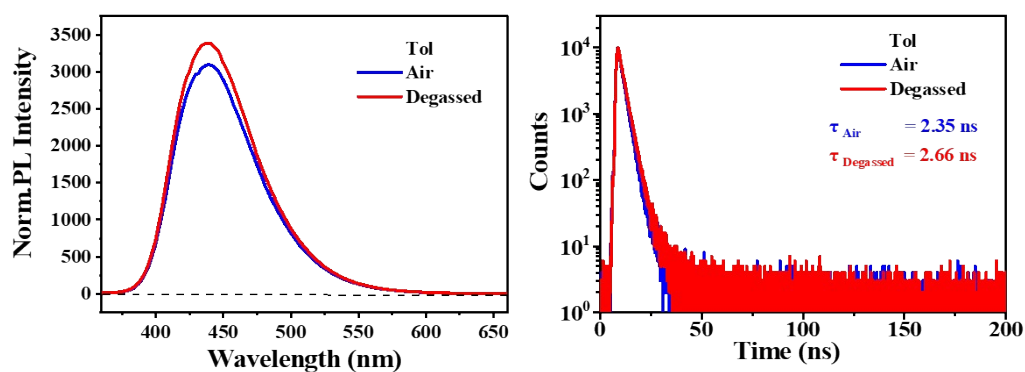
**Table S2.** Vertical excitation energies (Unit: eV) of IND-DPA at the level of M06-2X/6-311G(d).

	Excited States	Excitation Energy (eV)	Excited States	Excitation Energy (eV)
IND-DPA	S <sub>1</sub>	3.34	T <sub>1</sub>	2.02
	S <sub>2</sub>	4.02	T <sub>2</sub>	3.25
	S <sub>3</sub>	4.13	T <sub>3</sub>	3.34
	S <sub>4</sub>	4.24	T <sub>4</sub>	3.57
	S <sub>5</sub>	4.65	T <sub>5</sub>	3.57
	S <sub>6</sub>	4.71	T <sub>6</sub>	3.70
	S <sub>7</sub>	4.80	T <sub>7</sub>	3.93
	S <sub>8</sub>	4.83	T <sub>8</sub>	4.09
	S <sub>9</sub>	5.00	T <sub>9</sub>	4.14
	S <sub>10</sub>	5.06	T <sub>10</sub>	4.17
	S <sub>8</sub>	5.03	T <sub>8</sub>	4.03
	S <sub>9</sub>	5.05	T <sub>9</sub>	4.14
	S <sub>10</sub>	5.15	T <sub>10</sub>	4.21
	S <sub>6</sub>	4.23	T <sub>6</sub>	3.55
	S <sub>7</sub>	4.46	T <sub>7</sub>	3.62
	S <sub>8</sub>	4.55	T <sub>8</sub>	3.64
	S <sub>9</sub>	4.58	T <sub>9</sub>	3.79
	S <sub>10</sub>	4.64	T <sub>10</sub>	3.83

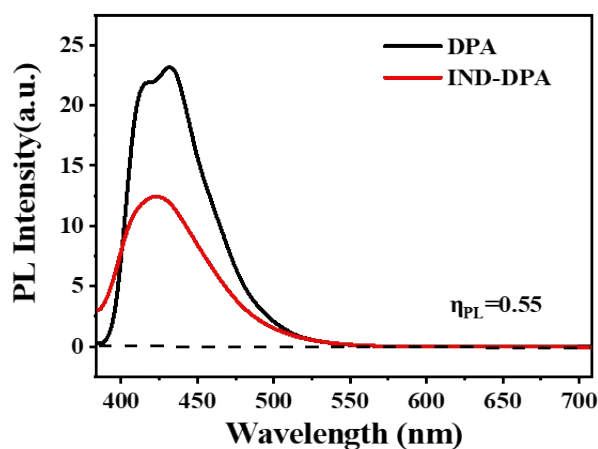
## 2. Photophysical Properties.



**Figure S3.** The time-resolved PL decay spectra of IND-DPA in different solvents.



**Figure S4.** The PL and time-resolved PL measurements of IND-DPA solution (Toluene  $10^{-5}$  M) in oxygen and deoxygenated conditions.



**Figure S5.** The relative fluorescence quantum yield determination of IND-DPA in cyclohexane solution.

### 3. Electrochemical and Thermal Properties.

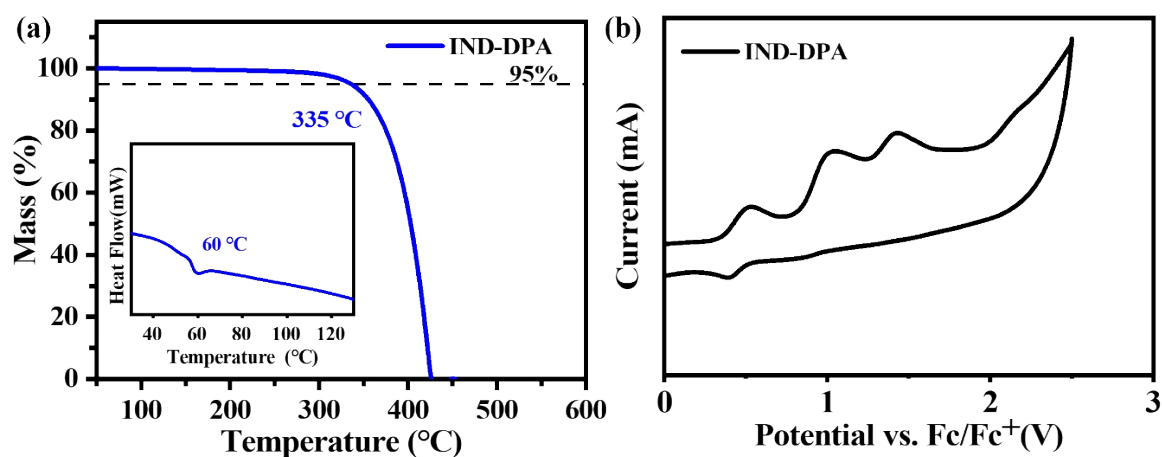


Figure S6. (a) TGA (insert: DSC curves) and CV curve of IND-DPA.

### 4. Electroluminescence Performance.

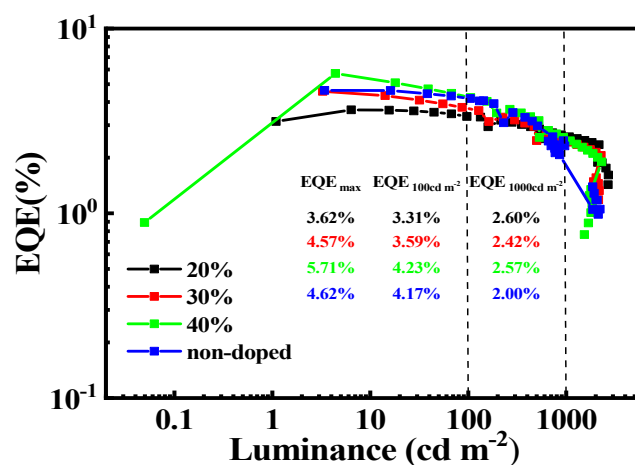


Figure S7. *L*-EQE curves of Device A, A1, A2, A3

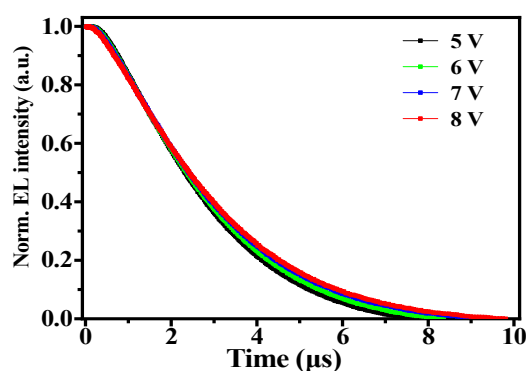
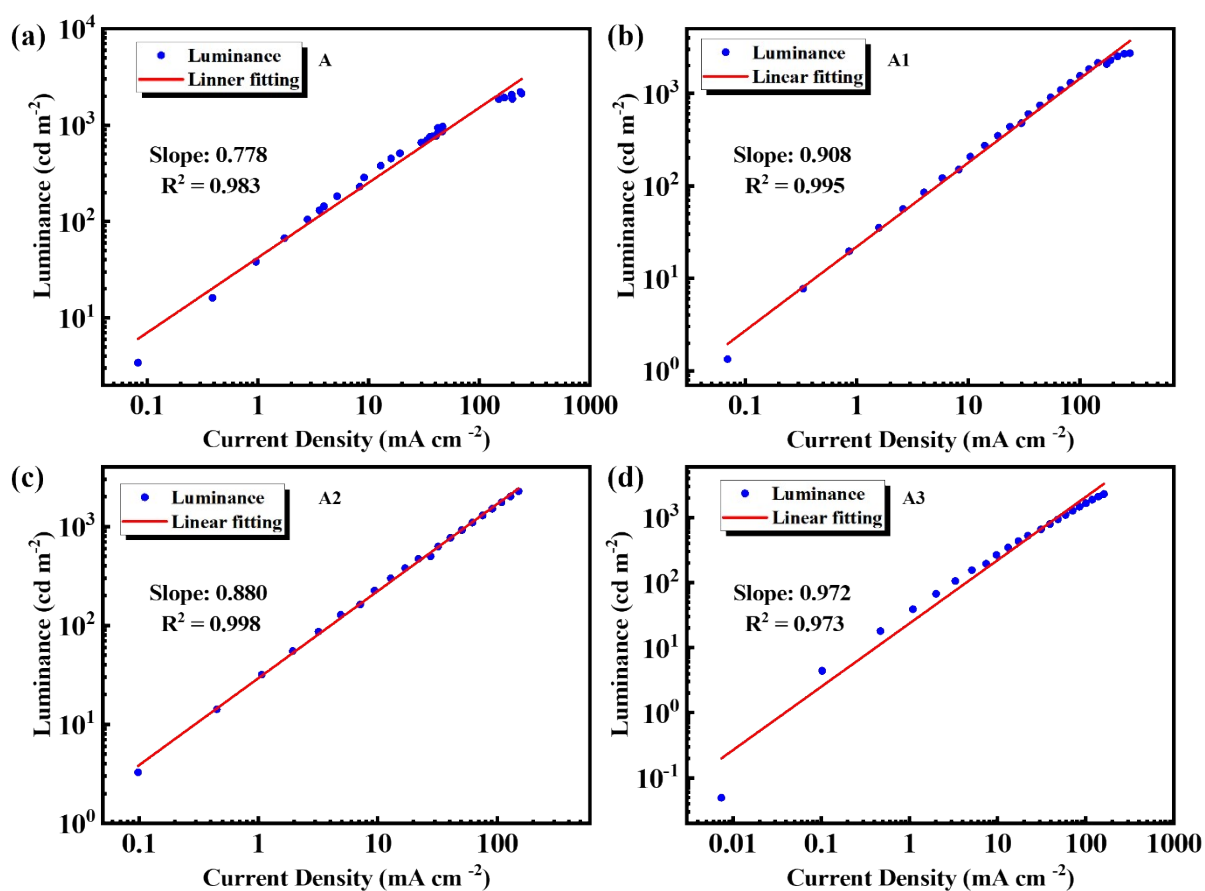


Figure S8. The transient EL decay curves of the IND-DPA doped device A3.



**Figure S9.** Current density luminance curve of the non-doped device (a) A, and the doped device (b) A1, (c) A2, and (d) A3.

## 5. Appendix.

### NMR Spectra.

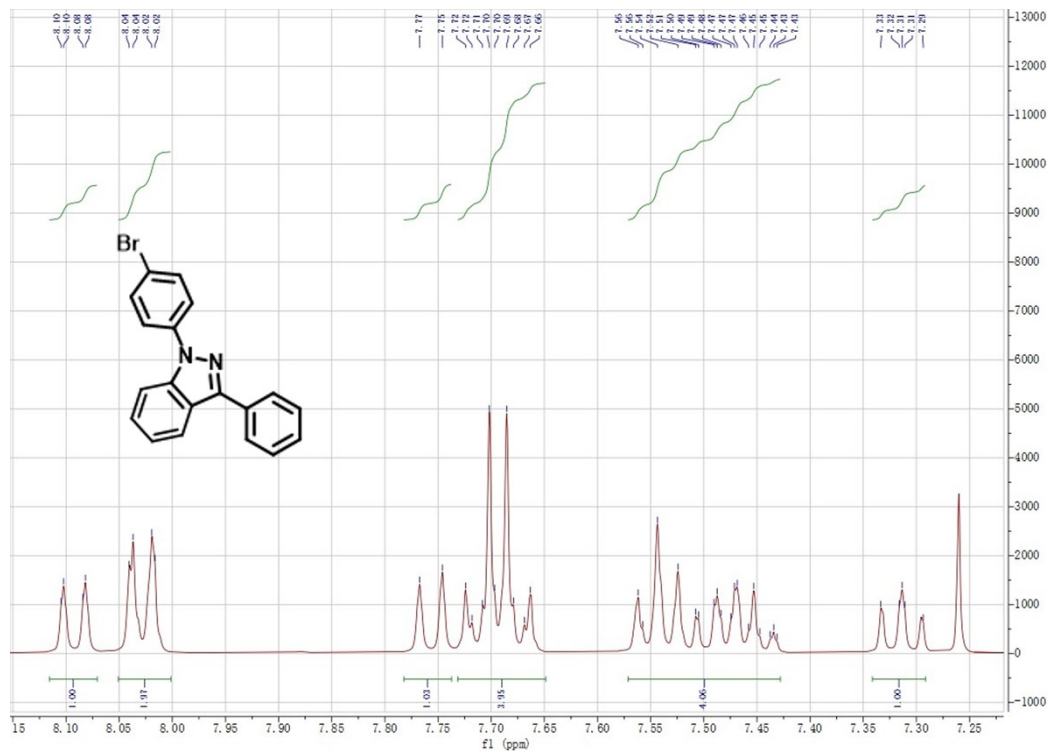


Figure S10. <sup>1</sup>H NMR of the intermediate M2 molecule (CDCl<sub>3</sub>, 298 K).

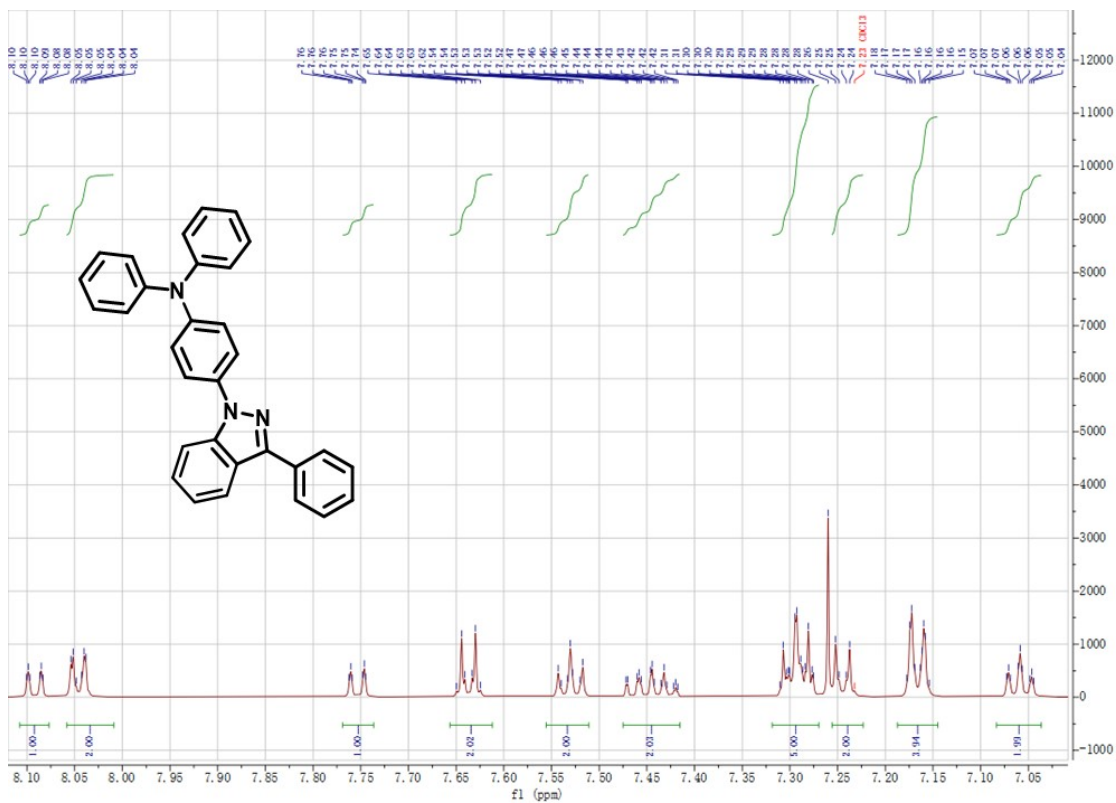
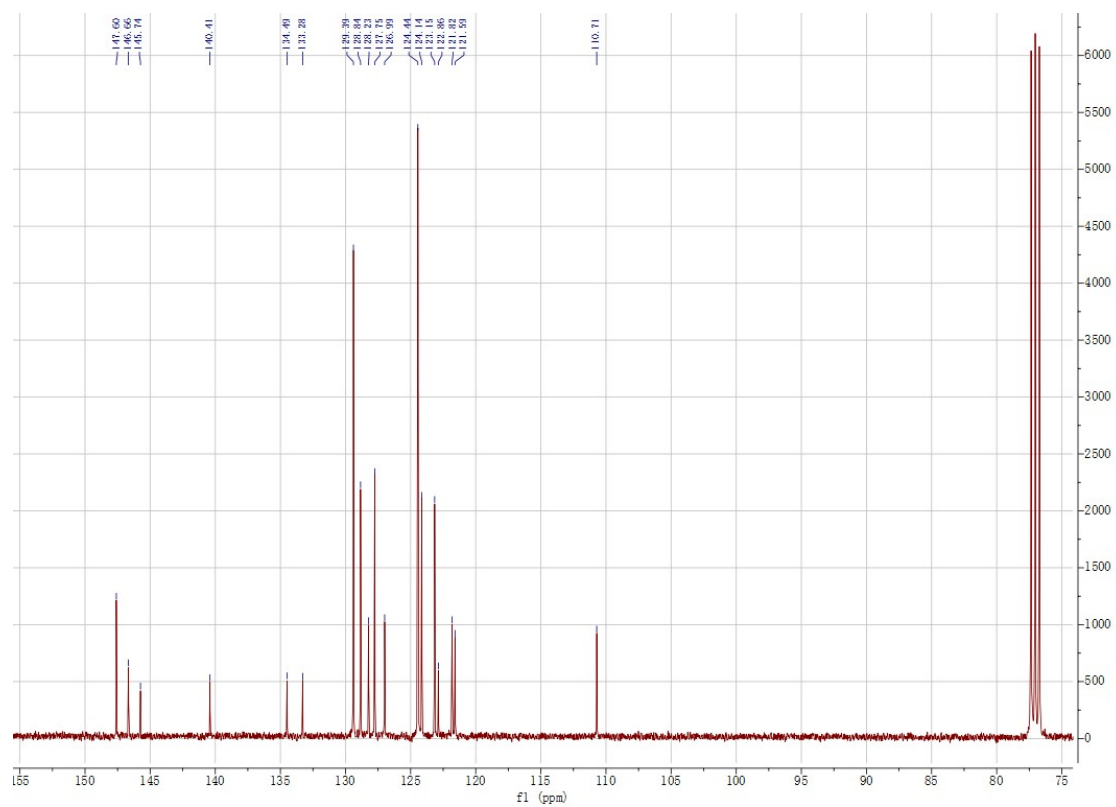


Figure S11. <sup>1</sup>H NMR of IND-TPA molecule (CDCl<sub>3</sub>, 298 K).





**Figure S12.**  $^{13}\text{C}$  NMR of IND-DPA molecule ( $\text{CDCl}_3$ , 298 K).

### Single Crystal Data of IND-DPA.

Compound	IND-DPA (CCDC: 2349041)
Empirical formula	C <sub>31</sub> H <sub>23</sub> N <sub>3</sub>
Formula weight	437.52
Temperature/K	303.68(10)
Crystal system	triclinic
Space group	P-1
a/b/c/Å	9.9644(3)/ 10.5293(4)/ 13.1479(4)
α/β/γ/°	66.575(3)/86.720(3)/68.737(3)
Volume/Å <sup>3</sup>	1173.48(7)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.238
μ/mm <sup>-1</sup>	0.566
F(000)	460.0
Crystal size/mm <sup>3</sup>	0.14 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.366 to 152.194
Index ranges	-11 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 16
Reflections collected	13931
Independent reflections	4680 [R <sub>int</sub> = 0.0257, R <sub>sigma</sub> = 0.0255]
Data/restraints/parameters	4680/0/308
Goodness-of-fit on F <sup>2</sup>	1.067
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0394, wR <sub>2</sub> = 0.1095
Final R indexes [all data]	R <sub>1</sub> = 0.0431, wR <sub>2</sub> = 0.1125
Largest diff. peak/hole/e Å <sup>-3</sup>	0.16/-0.16

### Cartesian Coordinates

**IND (S<sub>0</sub>)**

C	-0.73960400	1.28836600	0.00380300
C	0.66738000	1.34117500	-0.01430900
C	1.07789300	-0.03574800	-0.01340800
N	0.02825500	-0.82777100	-0.00937900
N	-1.07292600	-0.04333000	-0.00893900
C	-1.52603500	2.45055000	0.06424600
C	-0.85851300	3.65689600	0.05623100
C	0.55039100	3.72955300	-0.01742800
C	1.31920000	2.58612000	-0.04913800
C	-2.36044200	-0.63362200	0.02234500
C	2.44108200	-0.58991800	-0.03860900
C	3.48965600	0.06522500	0.61313900
C	4.77461400	-0.46677200	0.58923500
C	5.02495800	-1.66021300	-0.08038400
C	3.98208200	-2.32378500	-0.72288900
C	2.69911200	-1.79244300	-0.70426800
C	-3.39770000	-0.08578300	-0.72917400
C	-4.65880200	-0.67026000	-0.68066700
C	-4.87915400	-1.80476700	0.09325900
C	-3.82919600	-2.35825100	0.82202900
C	-2.56984300	-1.77359000	0.79606500
H	-2.60565500	2.40846500	0.12645900
H	-1.43146700	4.57575800	0.10368700
H	1.02837300	4.70146400	-0.04351000
H	2.39921700	2.64872500	-0.10774000
H	3.29559800	0.97663800	1.16739700
H	5.57859900	0.04822600	1.10249900
H	6.02679700	-2.07363000	-0.09937600
H	4.17086100	-3.25498800	-1.24486300

H	1.88549100	-2.29970500	-1.20971300
H	-3.21270900	0.76845800	-1.36916200
H	-5.46549100	-0.24440700	-1.26570000
H	-5.86173500	-2.26047500	0.12275000
H	-3.99245200	-3.24539100	1.42272300
H	-1.74520600	-2.18782100	1.36230300

**IND (T<sub>1</sub>)**

C	0.72637400	1.30598900	-0.02913500
C	-0.68503400	1.39281900	-0.04231500
C	-1.16012100	0.03080400	-0.00601300
N	-0.03031300	-0.87463600	-0.01635400
N	1.04289300	-0.07447300	0.03334400
C	1.54816100	2.40050800	-0.14506500
C	0.93023300	3.66778200	-0.23777200
C	-0.44498900	3.78615400	-0.23451700
C	-1.27137300	2.65170600	-0.14979100
C	2.33046100	-0.64335900	0.03766900
C	-2.44419800	-0.52403300	0.04643500
C	-3.63167900	0.25777200	0.18026400
C	-4.87016000	-0.34175800	0.21331100
C	-4.99599700	-1.73621700	0.12062800
C	-3.84735200	-2.52457400	0.00731200
C	-2.59546200	-1.94468200	-0.02469000
C	3.36999300	-0.04340300	0.75279400
C	4.62896500	-0.63078900	0.74942900
C	4.85524500	-1.81278800	0.05032100
C	3.80712200	-2.41654600	-0.64130600
C	2.54525100	-1.84029500	-0.65128200
H	2.62489800	2.31258200	-0.18908400

H	1.55239600	4.55059100	-0.32085400
H	-0.90206300	4.76526600	-0.31370000
H	-2.34264500	2.78209100	-0.19892100
H	-3.56536800	1.33076400	0.28784200
H	-5.75723600	0.27211300	0.32076400
H	-5.97608300	-2.19714900	0.14576400
H	-3.93818000	-3.60321400	-0.05489700
H	-1.70797200	-2.55651600	-0.11106400
H	3.18509400	0.84552400	1.34238900
H	5.43196000	-0.16775700	1.31077400
H	5.83925800	-2.26614900	0.05232500
H	3.97411100	-3.34085300	-1.18198800
H	1.72111800	-2.29407500	-1.18594000

**IND (S<sub>I</sub>)**

C	-0.74964100	1.33238700	0.05737600
C	0.66293800	1.40002200	-0.04383100
C	1.10807500	0.02331100	-0.03526300
N	0.03790700	-0.82819100	0.01339300
N	-1.06613000	-0.03368200	0.02734600
C	-1.54975700	2.44915100	0.23812900
C	-0.91699600	3.70723700	0.21753300
C	0.45306400	3.80242800	0.03423100
C	1.26251600	2.66141500	-0.09412100
C	-2.30906900	-0.62548500	0.00050500
C	2.42095400	-0.52859900	-0.04324400
C	3.60191000	0.25649700	0.02892800
C	4.84792100	-0.33804900	0.02275600
C	4.97618700	-1.73049200	-0.05599700
C	3.82652600	-2.52284200	-0.11825800

C	2.57191700	-1.94548300	-0.10857400
C	-3.45321200	0.06047700	-0.46849700
C	-4.67622800	-0.58146900	-0.47568700
C	-4.79662500	-1.89980900	-0.02510900
C	-3.65979600	-2.58872400	0.40507000
C	-2.42144300	-1.97734400	0.40898900
H	-2.61058800	2.37957800	0.42844700
H	-1.51358600	4.60143900	0.34664200
H	0.92104800	4.77955800	0.00076500
H	2.32476900	2.79017300	-0.23851500
H	3.53807200	1.33061900	0.12152300
H	5.73458200	0.28266000	0.08601800
H	5.95841000	-2.18848900	-0.06400700
H	3.91808400	-3.60190400	-0.17632600
H	1.68275100	-2.55950700	-0.16780400
H	-3.36315400	1.04902200	-0.89494300
H	-5.54508400	-0.05759300	-0.85622000
H	-5.76283200	-2.38960200	-0.02835100
H	-3.74501600	-3.61542500	0.74143900
H	-1.53534100	-2.49519600	0.74656200

**IND-DPA (S<sub>0</sub>)**

C	-5.175475	-0.899959	0.677995
C	-6.387675	-1.027132	-0.00554
C	-7.427109	-1.773927	0.539199
C	-7.265645	2.405056	1.768629
C	-6.056475	-2.289861	2.450515
C	-5.018905	-1.541675	1.910856
C	-4.064618	-0.12018	0.108321
N	-2.816328	-0.465162	0.33836

C	-4.115317	1.064647	-0.701995
N	-2.023448	0.434568	-0.285103
C	-0.615331	0.300766	-0.21285
C	-2.764589	1.381179	-0.946117
C	-2.390958	2.466385	-1.756118
C	-3.408464	3.243983	-2.266706
C	-4.76663	2.972741	-1.987937
C	-5.130001	1.890539	-1.215567
C	0.196629	1.423798	-0.077736
C	1.575091	1.280641	-0.015129
C	2.163351	0.01191	-0.040568
C	1.332602	-1.11085	-0.14498
C	-0.040948	-0.96814	-0.247755
N	3.562651	-0.135047	0.049402
C	4.219685	-1.184831	-0.64171
C	4.325496	0.745652	0.858423
C	5.55836	1.221248	0.402913
C	6.317848	2.069136	1.1992
C	5.853776	2.467671	2.449534
C	4.621985	2.00126	2.900155
C	3.864008	1.138538	2.117424
C	5.239017	-1.905857	-0.013962
C	5.896333	-2.923376	-0.694352
C	5.535848	-3.248234	-1.998954
C	4.514587	-2.536387	-2.621789
C	3.86411	-1.504944	-1.954795
H	-6.508625	-0.56785	-0.980465
H	-8.361372	-1.869347	-0.002388
H	-8.076555	-2.986013	2.192962
H	-5.924368	-2.779421	3.408846

H	-4.078025	-1.442286	2.439793
H	-1.354496	2.682286	-1.981661
H	-3.158276	4.091033	-2.895251
H	-5.529309	3.626691	-2.393584
H	-6.173448	1.689381	-1.003397
H	-0.244516	2.410435	-0.002279
H	2.200467	2.160845	0.076184
H	1.770615	-2.101953	-0.154959
H	-0.680628	-1.837912	-0.330832
H	5.917392	0.918662	-0.574488
H	7.273121	2.428658	0.833355
H	6.446119	3.132997	3.066632
H	4.25191	2.298399	3.874947
H	2.912201	0.765426	2.479161
H	5.513744	-1.661505	1.006133
H	6.686987	-3.472207	-0.195027
H	6.045865	-4.046836	-2.524893
H	4.228917	-2.774452	-3.640319
H	3.078621	-0.943635	-2.448707

**IND-DPA (S<sub>1</sub>)**

C	-5.150727	-0.951041	0.461147
C	-6.482566	-0.725114	0.054807
C	-7.49551	-1.597403	0.419568
C	-7.219493	-2.72468	1.195143
C	-5.90406	-2.973039	1.589609
C	-4.884073	-2.108988	1.228258
C	-4.064126	-0.073271	0.097625
N	-2.788831	-0.499828	0.256352
C	-4.095656	1.259483	-0.430519
N	-1.982857	0.52882	-0.150254



C	-0.633487	0.389972	-0.047693
C	-2.739422	1.617655	-0.634482
C	-2.3663	2.787986	-1.277964
C	-3.38078	3.684489	-1.639339
C	-4.715898	3.396353	-1.35521
C	-5.091292	2.196171	-0.76059
C	0.258709	1.498342	-0.085058
C	1.611662	1.30901	-0.01272
C	2.162446	0.001254	0.091276
C	1.267857	-1.096191	0.201725
C	-0.085672	-0.914687	0.154579
N	3.530584	-0.200187	0.0901
C	4.08478	-1.390067	-0.451615
C	4.411516	0.793395	0.593749
C	5.57635	1.11327	-0.110832
C	6.431561	2.089198	0.37988
C	6.133709	2.757083	1.566031
C	4.972094	2.436979	2.264448
C	4.112209	1.456689	1.787417
C	5.153818	-2.020477	0.19336
C	5.695265	-3.179552	-0.344576
C	5.175895	-3.724043	-1.517259
C	4.109927	-3.094635	-2.155905
C	3.565389	-1.93031	-1.632742
H	-6.720475	0.111015	-0.588609
H	-8.509424	-1.404433	0.086239
H	-8.015981	-3.402451	1.479592
H	-5.674125	-3.849616	2.18601
H	-3.866093	-2.301233	1.544143
H	-1.341976	3.012337	-1.535904

H	-3.117666	4.607955	-2.139781
H	-5.483067	4.117441	-1.614741
H	-6.135784	2.011758	-0.551815
H	-0.122997	2.507563	-0.109716
H	2.270445	2.167685	-0.043162
H	1.67069	-2.092512	0.339267
H	-0.761319	-1.751539	0.250946
H	5.797917	0.601182	-1.040223
H	7.330594	2.336361	-0.172603
H	6.803666	3.52009	1.944058
H	4.738487	2.94437	3.193167
H	3.216018	1.191459	2.337125
H	5.547627	-1.602456	1.112821
H	6.521059	-3.666144	0.161441
H	5.599467	-4.631541	-1.930748
H	3.706917	-3.504344	-3.074843
H	2.748997	-1.427563	-2.138776

**IND-DPA (T<sub>1</sub>)**

C	-5.187746	-0.887636	0.607335
C	-6.554916	-0.480245	0.589236
C	-7.541398	-1.295952	1.097555
C	-7.225352	-2.545074	1.650722
C	-5.890558	-2.956782	1.699848
C	-4.886193	-2.152997	1.199179
C	-4.144954	-0.108126	0.086432
N	-2.792318	-0.560693	0.290287
C	-4.135807	1.130709	-0.653965
N	-2.027538	0.411187	-0.230523
C	-0.631554	0.293359	-0.17828
C	-2.771784	1.438514	-0.865036

C	-2.350892	2.49901	-1.630475
C	-3.34636	3.338735	-2.179402
C	-4.685074	3.076725	-1.971236
C	-5.099302	1.962633	-1.219256
C	0.187035	1.421403	-0.06535
C	1.562282	1.278995	-0.001517
C	2.155262	0.009692	-0.021063
C	1.323018	-1.116449	-0.102595
C	-0.049746	-0.979279	-0.184832
N	3.55218	-0.131887	0.056108
C	4.205709	-1.198379	-0.613557
C	4.32161	0.771475	0.835259
C	5.540523	1.252214	0.34997
C	6.302415	2.123132	1.118889
C	5.853724	2.537816	2.369714
C	4.635854	2.064436	2.849978
C	3.876083	1.179302	2.095008
C	5.234692	-1.898774	0.021444
C	5.886042	-2.932829	-0.639596
C	5.510707	-3.293073	-1.930615
C	4.480848	-2.600055	-2.560698
C	3.836051	-1.552726	-1.913759
H	-6.826181	0.492376	0.204826
H	-8.572658	-0.961613	1.077201
H	-8.008948	-3.180569	2.045594
H	-5.638805	-3.916784	2.136847
H	-3.853777	-2.473364	1.2391
H	-1.306464	2.685317	-1.838136
H	-3.044756	4.190752	-2.776697
H	-5.435283	3.727468	-2.404721

H	-6.156559	1.7626	-1.123302
H	-0.247719	2.409499	0.01298
H	2.18567	2.161255	0.081591
H	1.762391	-2.106966	-0.103351
H	-0.68964	-1.849969	-0.243544
H	5.886433	0.936806	-0.628162
H	7.247129	2.487959	0.731539
H	6.447755	3.221221	2.964971
H	4.278777	2.374035	3.825656
H	2.935275	0.7998	2.478418
H	5.520992	-1.627016	1.031292
H	6.683969	-3.46662	-0.135606
H	6.016348	-4.104337	-2.441151
H	4.184143	-2.865393	-3.569169
H	3.044319	-1.005333	-2.413308