Electronic Supplementary Information (ESI)

Ultralong room-temperature phosphorescence material based on the combination of small singlet-triplet splitting energy and H-aggregation

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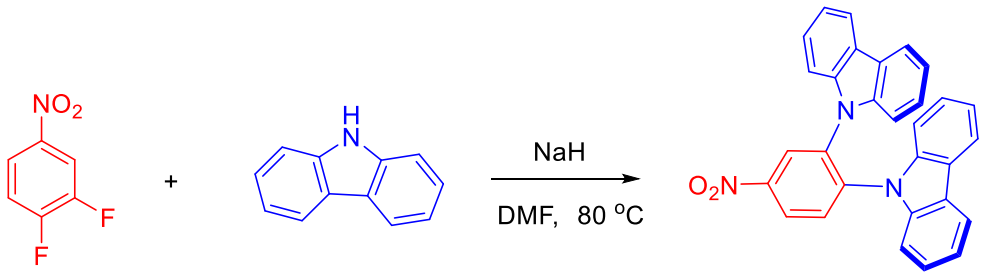
1. General information

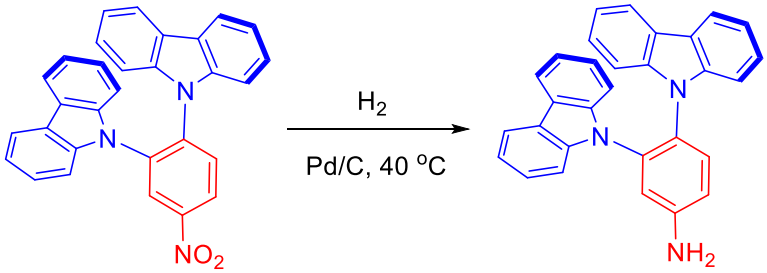
All reagents were obtained from commercial sources without further purification, and solvents were used as received except specifically mentioned. NMR spectra were recorded on AVIII 300-500 MHz NMR spectrometers. Mass spectra and high resolution mass spectra were recorded with Thermo Fisher® Exactive highresolution LC-MS spectrometer. Ultraviolet spectra were measured on a PerkinElmer® UV/Vis/NIR spectrometer (Lambda 950). The steady fluorescence spectra and lifetimes were recorded on Edinburgh Instruments FLS 980 spectrometer. The single crystals of **AI-Cz** and **AI-N-Cz** were used to perform the transient PL measurements and phosphorescence spectrum (size of **AI-Cz** is about 0.7mm × 0.7mm × 1.5mm; size of **AI-N-Cz** is about 0.8mm × 1.1mm × 1.3mm). Phosphorescence spectra were measured with a delay time of 1 ms in the crystalline states at room temperature. The values of lifetime were calculated by exponential function fitting with luminescence spectrometer software F900. Theoretical calculations were carried out using the Gaussian 09 program.

2. Synthesis and characterization

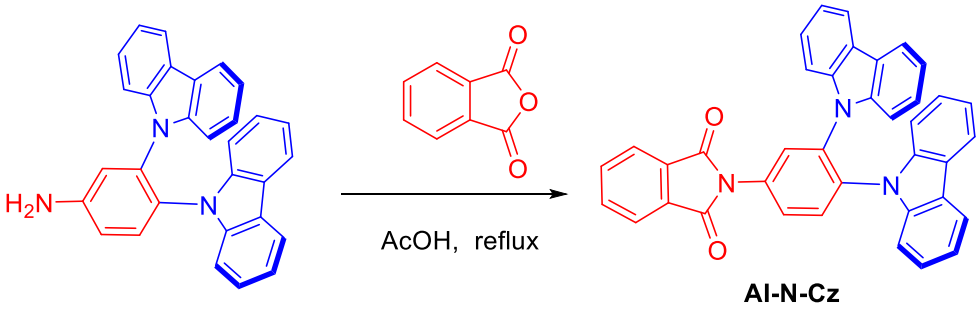


9,9'-(4-Nitro-1,2-phenylene)bis(9H-carbazole): To a solution of carbazole (3.51 g, 21 mmol.) in dry DMF (30 mL) under argon atmosphere was added Cs_2CO_3 (8.12 g, 25 mmol) at room temperature, and the mixture was stirred for 30 minutes. 1,2-difluoro-4-nitrobenzene (1.59 g, 20 mmol) was added, and the mixture was then stirred for 12 hours

at 80 °C. The mixture was poured into water (100 mL) and filtered to obtain the solid, which was washed by dichloromethane and petroleum ether (1:5, v/v) to give 9,9'-(4-nitro-1,2-phenylene)bis(9H-carbazole) (3.62g, 80 %) as a yellow solid. M.p. 250-251 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (d, *J* = 2.6 Hz, 1H), 8.53 (dd, *J* = 8.8, 2.6 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.84-7.75 (m, 4H), 7.08-7.10 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 139.0, 138.9, 141.0, 126.0, 125.8, 124.0, 123.8, 123.2, 120.9, 120.8, 120.1, 109.4, 109.1, 77.2, 77.0, 76.7. HR-MS (APCI): *m/z* calcd for $C_{30}H_{19}N_3O_2$ $[M + H]^+$ 453.1477, found 454.1545.



3,4-Di(9H-carbazol-9-yl)aniline: To a three-necked flask with palladium carbon (100 mg) and 9,9'-(4-nitro-1,2-phenylene)bis(9H-carbazole) (3 g, 6.6 mmol) in nitrogen was added THF (25 mL). Hydrogen was then introduced into the three-necked flask by hydrogenated balloon. The mixture was reacted at 40 ° C for 12 h, cooled to room temperature, and then filtered to give the product (2.75 g, 98 %) as a white solid. M.p. 247-248 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 7.2, 1.6 Hz, 4H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.26-7.19 (m, 2H), 7.18-7.10 (m, 2H), 7.10-6.89 (m, 10H), 3.97 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.1, 140.4, 140.1, 131.3, 125.2, 125.2, 123.2, 123.1, 119.8, 119.6, 119.4, 115.6, 115.3, 110.0, 109.8. HR-MS (APCI): *m/z* calcd for $C_{30}H_{21}N_3$ $[M + H]^+$ 423.1735, found 424.1802.



AI-N-Cz

AI-N-Cz: A mixture of isobenzofuran-1,3-dione (700 mg, 4.73 mmol) and 3,4-di(9H-carbazol-9-yl)aniline (2 g, 4.73 mmol) in glacial acetic acid (20 mL) was refluxed for 12 hours. The mixture was cooled to room temperature, and then filtered to give the product **AI-N-Cz** (2.41 g, 82 %) as a white solid. M.p. 244-245 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05-7.94 (m, 4H), 7.88-7.74 (m, 7H), 7.32-7.18 (m, 5H), 7.10-7.03 (m, 7H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.9, 139.6, 139.5, 134.8, 131.6, 130.8, 128.1, 126.0, 125.6, 125.5, 124.0, 123.6, 123.5, 120.1, 120.1, 119.9, 119.8, 109.8, 109.7. HR-MS (APCI): *m/z* calcd for $C_{38}H_{23}N_3O_2$ $[M + H]^+$ 553.1790, found 554.1852.

3. X-Ray crystallographic data

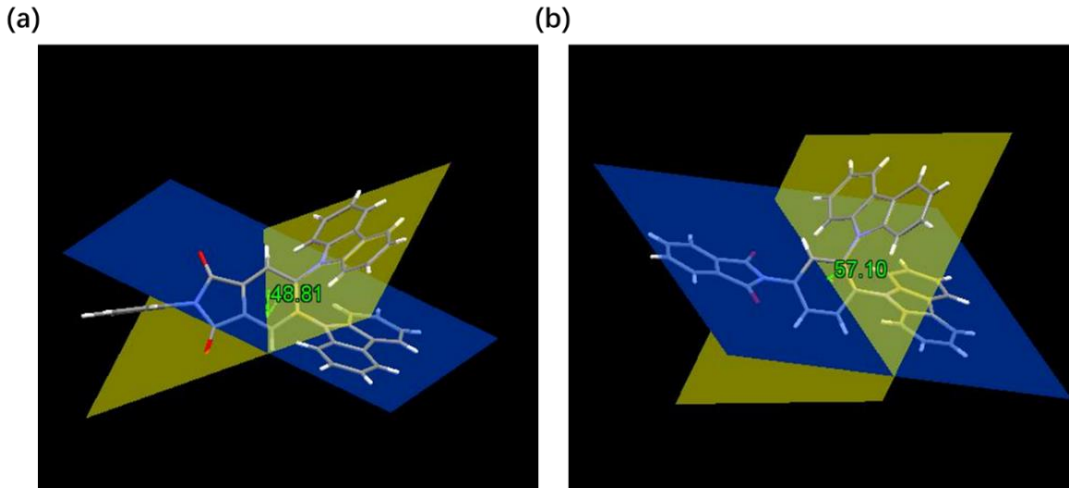


Fig. S1 Dihedral angles of (a) **AI-Cz** and (b) **AI-N-Cz** between the carbazole and carbazole group, respectively.

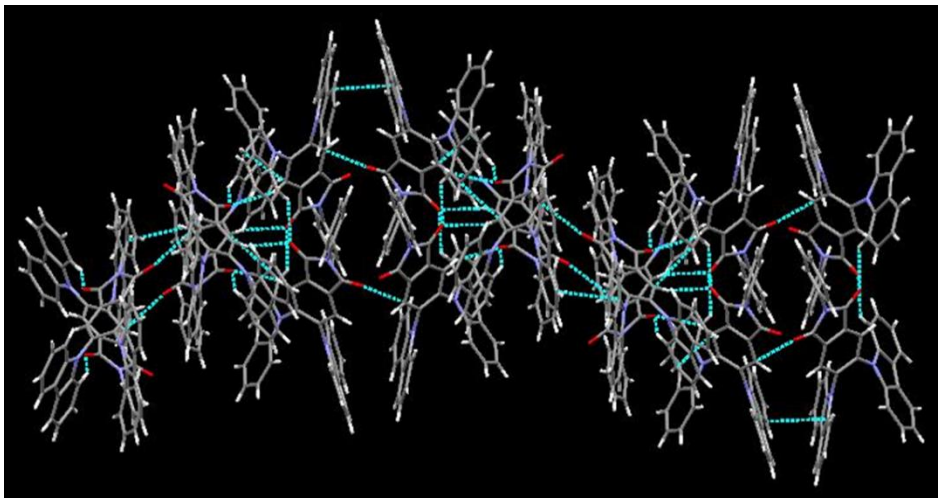


Fig. S2 Intermolecular interactions of **AI-Cz** (C-H···O;2.406-2.512 Å, C-H···π;3.372-3.386 Å).

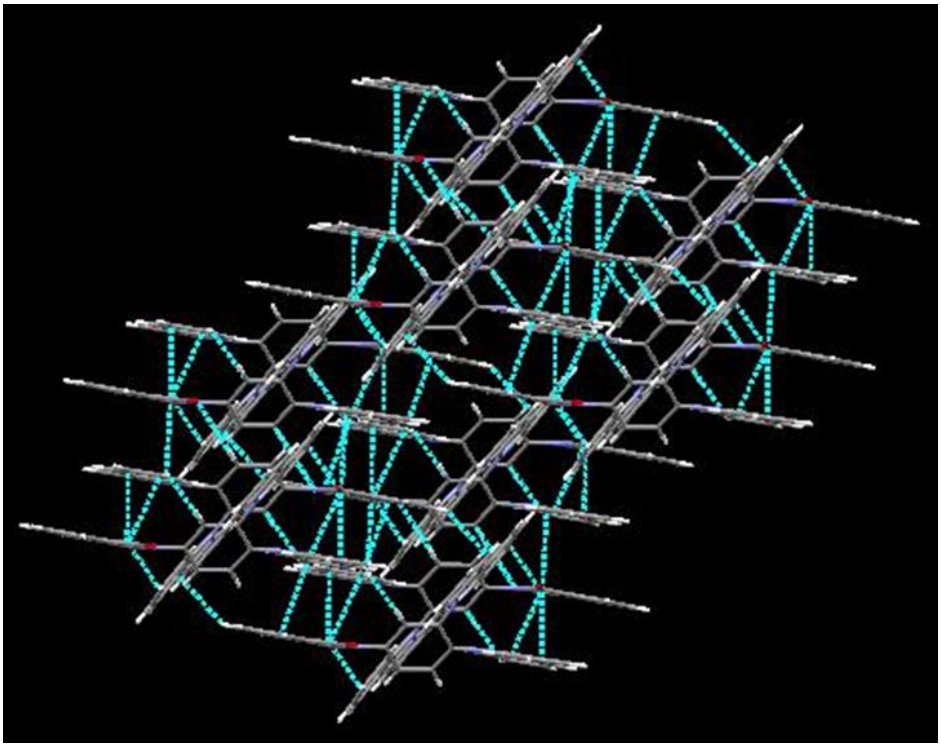


Fig. S3 Intermolecular interactions of **AI-N-Cz** (C-H···O; 2.616 Å, C-H···π; 3.312-3.346 Å).

Table S1. Crystal data and structure refinement for **AI-N-Cz**

Identification code	**AI-N-Cz**
Empirical formula	$C_{39}H_{25}Cl_2N_3O_2$
Formula weight	638.52
Temperature/K	170.00(11)
Crystal system	triclinic
Space group	P-1
a/Å	9.44150(10)
b/Å	11.5767(2)
c/Å	15.2148(2)
α/°	91.7300(10)
β/°	103.5750(10)
γ/°	110.2320(10)
Volume/Å3	1505.45(4)
Z	2
ρcalcg/cm3	1.409
μ/mm-1	2.276
F(000)	660.0
Crystal size/mm3	0.423 × 0.321 × 0.311
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.202 to 150.748
Index ranges	-10 ≤ h ≤ 11, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19
Reflections collected	25723
Independent reflections	6008 [Rint = 0.0317, Rsigma = 0.0148]
Data/restraints/parameters	6008/0/415
Goodness-of-fit on F2	1.054
Final R indexes [I>=2σ (I)]	R1 = 0.0425, wR2 = 0.1090
Final R indexes [all data]	R1 = 0.0444, wR2 = 0.1120
Largest diff. peak/hole / e Å-3	0.49/-0.53

Table S2. Crystal data and structure refinement for **AI-Cz**

Identification code	**AI-Cz**
Empirical formula	$C_{38}H_{23}N_3O_2$
Formula weight	553.59
Temperature/K	169.99(11)
Crystal system	tetragonal
Space group	$P4_1$
a/Å	15.82204(12)
b/Å	15.82204(12)
c/Å	44.7484(4)
α/°	90
β/°	90
γ/°	90
Volume/Å3	11202.2(2)
Z	16
ρcalcg/cm3	1.313
μ/mm-1	0.651
F(000)	4608.0
Crystal size/mm3	0.2 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.586 to 151.176
Index ranges	-19≤ h ≤19, -16≤ k ≤17, -56≤ l ≤ 48
Reflections collected	37665
Independent reflections	19098 [Rint = 0.0361, Rsigma = 0.0462]
Data/restraints/parameters	19098/1/1549
Goodness-of-fit on F2	1.038
Final R indexes [I>=2σ (I)]	R1 = 0.0463, wR2 = 0.1147
Final R indexes [all data]	R1 = 0.0599, wR2 = 0.1278
Largest diff. peak/hole / e Å-3	0.36/-0.26
Flack parameter	-0.14(18)

4. Photophysical properties

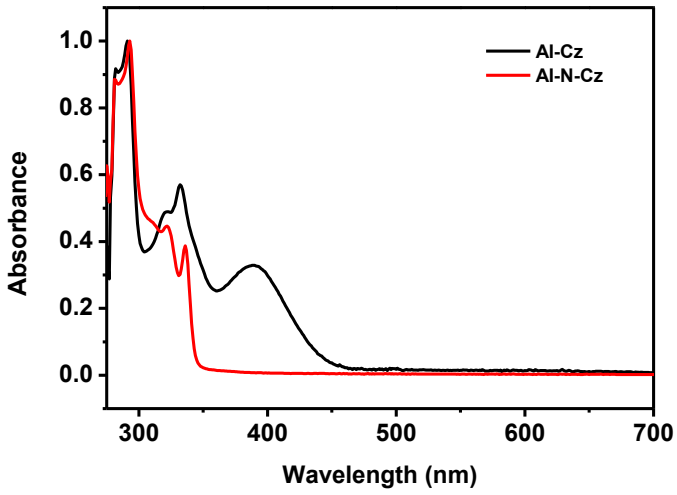


Fig. S4 Absorption spectra of **Al-Cz** and **Al-N-Cz** in toluene (c = 1.0 × 10^{-5} M).

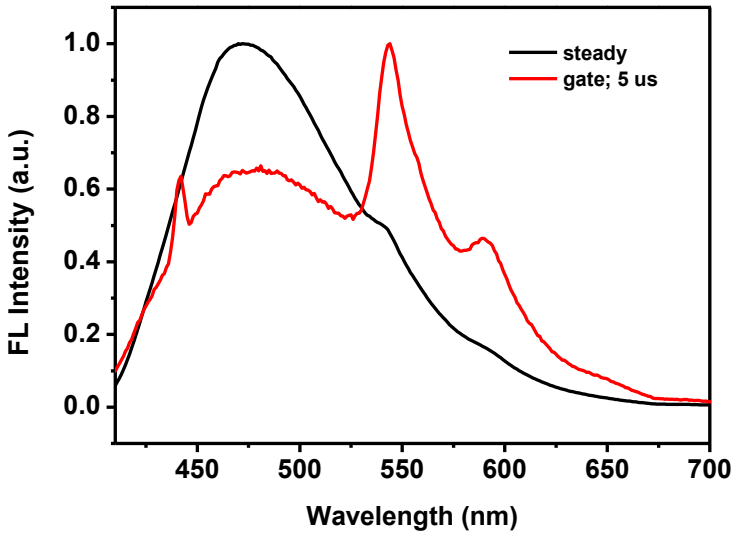


Fig. S5 Normalized steady-state and time-gated emission spectra (λ_{ex}=340 nm) of **Al-N-Cz** in the crystal state.

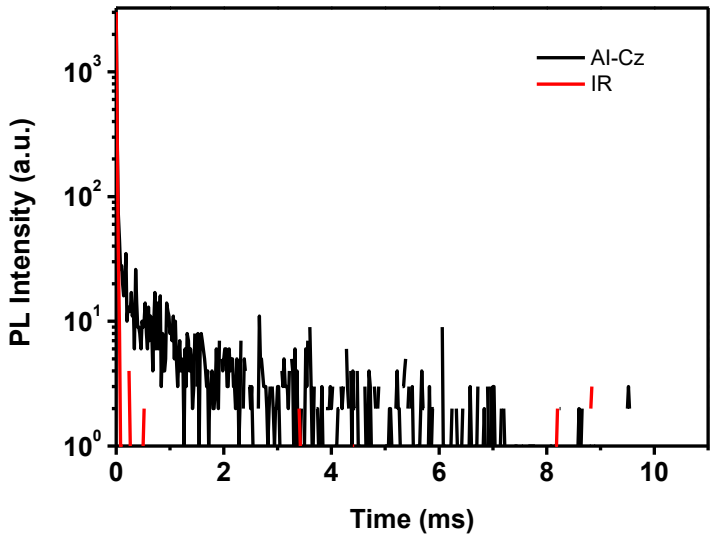


Fig. S6 Transient PL curves of **AI-Cz** (λ_{em}=520 nm) at room temperature in crystalline state (crystal of **AI-Cz** was obtained in a mixture of hexane and dichloromethane).

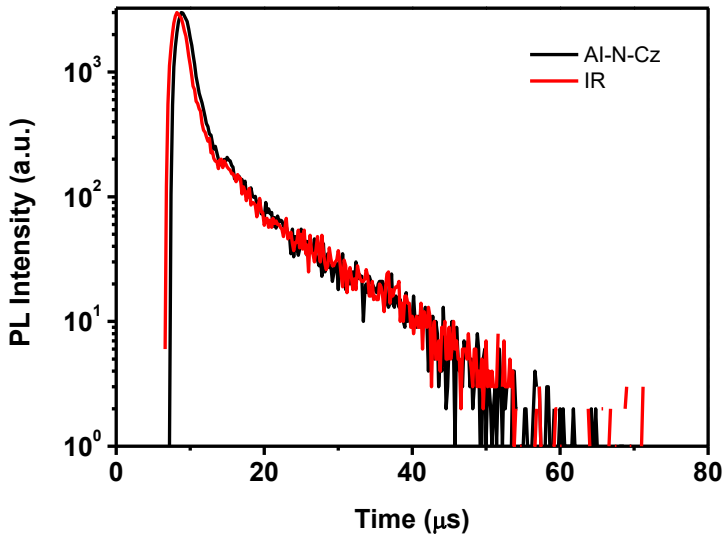


Fig. S7 Transient PL curves of **AI-N-Cz** (λ_{em}=445 nm) at room temperature in crystalline state. In order to avoid influence of instrument noise when using the microflash lamp for the phosphorescence lifetime spectral test, the IR (instrument reference) of the microflash lamp was measured. And related parameter settings of repetition rate of the flashlamp were as follows: The frequency and pulse peried of flashlamp settings for phosphorescence spectra were 100 Hz and 10 ms, respectively. For lifetime of **AI-Cz**, they were 40 Hz and 20 ms respectively, while for lifetime of **AI-N-Cz**, they were 0.1 Hz and 10s, respectively.

5. Theoretic calculations

DFT calculations were performed with the Gaussian 09 revision D.01. The excited state geometries of **AI-Cz**/**AI-N-Cz** were optimized by DFT with B3LYP method. In order to investigate the energy difference between the lowest singlet (S_1) and triplet (T_1) excited states, time-dependent density functional theory (TD-DFT) with B3LYP method, was used to optimize the geometries of S_1 and T_1, respectively. Finally, we could get the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the ground state of **AI-Cz**/**AI-N-Cz**. All the above calculations were carried out by using Gaussian 09 software with the 6-31G(d,p) basis set and the molecular orbitals were visualized by using Gauss View 5.0 software.[S1]

Table S3. Optimized atomic coordinates of **AI-Cz** obtained from DFT calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.182779	-0.672106	-0.235336
2	6	0	-0.182781	0.672122	0.235278
3	6	0	1.037425	1.342283	0.446315
4	6	0	2.217875	0.662943	0.212552
5	6	0	2.217877	-0.662899	-0.212682
6	6	0	1.037428	-1.342256	-0.446398
7	6	0	3.628749	1.115591	0.360102
8	7	0	4.429027	0.000026	-0.000073
9	6	0	3.628752	-1.115528	-0.360282
10	8	0	4.032857	-2.204896	-0.706666
11	8	0	4.032851	2.204924	0.706600
12	6	0	5.857567	0.000007	-0.000012

13	6	0	6.554404	-1.122083	0.462842
14	6	0	7.948048	-1.117679	0.453184
15	6	0	8.649838	-0.000026	0.000083
16	6	0	7.948105	1.117643	-0.453067
17	6	0	6.554461	1.122081	-0.462819
18	7	0	-1.381615	-1.371515	-0.500832
19	7	0	-1.381615	1.371519	0.500813
20	6	0	-1.707081	-2.632573	0.028764
21	6	0	-2.920854	-3.073959	-0.551490
22	6	0	-3.334648	-2.054305	-1.493803
23	6	0	-2.363098	-1.025139	-1.447761
24	6	0	-1.707101	2.632582	-0.028758
25	6	0	-2.920863	3.073952	0.551530
26	6	0	-3.334627	2.054283	1.493840
27	6	0	-2.363071	1.025125	1.447763
28	6	0	-4.413327	-1.947346	-2.378291
29	6	0	-4.501212	-0.832098	-3.205821
30	6	0	-3.516049	0.167471	-3.162965
31	6	0	-2.433188	0.084741	-2.289899
32	6	0	-1.040615	-3.388140	0.996563
33	6	0	-1.604511	-4.607712	1.369425
34	6	0	-2.804077	-5.062691	0.799635
35	6	0	-3.467243	-4.299863	-0.157895
36	6	0	-1.040665	3.388167	-0.996564
37	6	0	-1.604580	4.607738	-1.369399
38	6	0	-2.804136	5.062701	-0.799575
39	6	0	-3.467273	4.299856	0.157962
40	6	0	-4.413283	1.947306	2.378354
41	6	0	-4.501140	0.832047	3.205872
42	6	0	-3.515971	-0.167514	3.162981
43	6	0	-2.433131	-0.084766	2.289890
44	1	0	1.038418	2.363135	0.811583
45	1	0	1.038421	-2.363110	-0.811661
46	1	0	6.010399	-1.990601	0.810942
47	1	0	8.484640	-1.992626	0.807360
48	1	0	9.735585	-0.000040	0.000119
49	1	0	8.484741	1.992579	-0.807205
50	1	0	6.010500	1.990611	-0.810959
51	1	0	-5.165922	-2.729184	-2.422429

52	1	0	-5.333402	-0.735586	-3.896092
53	1	0	-3.594995	1.026022	-3.822834
54	1	0	-1.678510	0.861322	-2.274512
55	1	0	-0.114188	-3.046990	1.445883
56	1	0	-1.101803	-5.214873	2.116135
57	1	0	-3.217056	-6.017176	1.110518
58	1	0	-4.398290	-4.650063	-0.593856
59	1	0	-0.114244	3.047031	-1.445909
60	1	0	-1.101894	5.214911	-2.116115
61	1	0	-3.217131	6.017186	-1.110437
62	1	0	-4.398311	4.650043	0.593949
63	1	0	-5.165883	2.729138	2.422519
64	1	0	-5.333313	0.735521	3.896162
65	1	0	-3.594894	-1.026073	3.822843
66	1	0	-1.678447	-0.861340	2.274475

Table S4. Optimized atomic coordinates of **AI-N-Cz** obtained from DFT calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	8.243349	-0.882741	0.340931
2	6	0	8.120633	0.432162	-0.127016
3	6	0	6.866954	0.979337	-0.427446
4	6	0	5.757260	0.167308	-0.242062
5	6	0	5.879488	-1.142016	0.221582
6	6	0	7.116310	-1.694100	0.522454
7	6	0	4.315411	0.457426	-0.471902
8	7	0	3.622626	-0.729244	-0.113985
9	6	0	4.520959	-1.746049	0.305507
10	8	0	4.212007	-2.866446	0.650029
11	8	0	3.807276	1.479555	-0.882006
12	6	0	2.211200	-0.883350	-0.201531
13	6	0	1.655533	-2.060373	-0.714065
14	6	0	0.275161	-2.167035	-0.819542
15	6	0	-0.579320	-1.124229	-0.434397
16	6	0	-0.013501	0.048775	0.116168
17	6	0	1.378385	0.148903	0.228333

18	7	0	-0.798547	1.144598	0.551868
19	7	0	-1.975676	-1.285716	-0.617738
20	6	0	-0.638372	2.469484	0.112415
21	6	0	-1.561580	3.294667	0.801279
22	6	0	-2.287183	2.441738	1.719413
23	6	0	-1.786673	1.127318	1.548677
24	6	0	-2.731915	-2.356228	-0.118994
25	6	0	-4.056016	-2.254712	-0.613778
26	6	0	-4.096607	-1.087912	-1.470641
27	6	0	-2.798307	-0.520422	-1.459679
28	6	0	-3.279847	2.684491	2.675349
29	6	0	-3.747198	1.627168	3.449771
30	6	0	-3.223810	0.334634	3.282195
31	6	0	-2.236666	0.066674	2.336378
32	6	0	0.233706	2.987947	-0.849272
33	6	0	0.163553	4.355026	-1.114168
34	6	0	-0.748922	5.186460	-0.444876
35	6	0	-1.612181	4.662787	0.513400
36	6	0	-5.099366	-0.502852	-2.252011
37	6	0	-4.794655	0.621629	-3.012694
38	6	0	-3.497036	1.159592	-3.003471
39	6	0	-2.481619	0.597479	-2.232898
40	6	0	-2.351684	-3.383091	0.749543
41	6	0	-3.320199	-4.317419	1.113506
42	6	0	-4.635828	-4.233420	0.629567
43	6	0	-5.009067	-3.204637	-0.231124
44	1	0	9.229548	-1.277481	0.564932
45	1	0	9.013666	1.035489	-0.257770
46	1	0	6.759033	1.996134	-0.790010
47	1	0	7.198164	-2.714248	0.882476
48	1	0	2.294126	-2.873154	-1.034252
49	1	0	-0.165108	-3.062532	-1.244181
50	1	0	1.801941	1.047517	0.656378
51	1	0	-3.673248	3.687345	2.814952
52	1	0	-4.517886	1.801609	4.194260
53	1	0	-3.593431	-0.477382	3.901128
54	1	0	-1.839056	-0.934324	2.222662
55	1	0	0.959479	2.362977	-1.357619
56	1	0	0.835610	4.782355	-1.852350

57	1	0	-0.776952	6.247090	-0.675152
58	1	0	-2.317104	5.306455	1.031775
59	1	0	-6.099497	-0.926439	-2.268313
60	1	0	-5.563431	1.086224	-3.622417
61	1	0	-3.275863	2.034088	-3.607948
62	1	0	-1.484963	1.021910	-2.237034
63	1	0	-1.337825	-3.457048	1.128097
64	1	0	-3.047391	-5.125789	1.785448
65	1	0	-5.366714	-4.977304	0.931200
66	1	0	-6.028286	-3.138332	-0.600866

6. ^{1}H NMR and ^{13}C NMR spectra

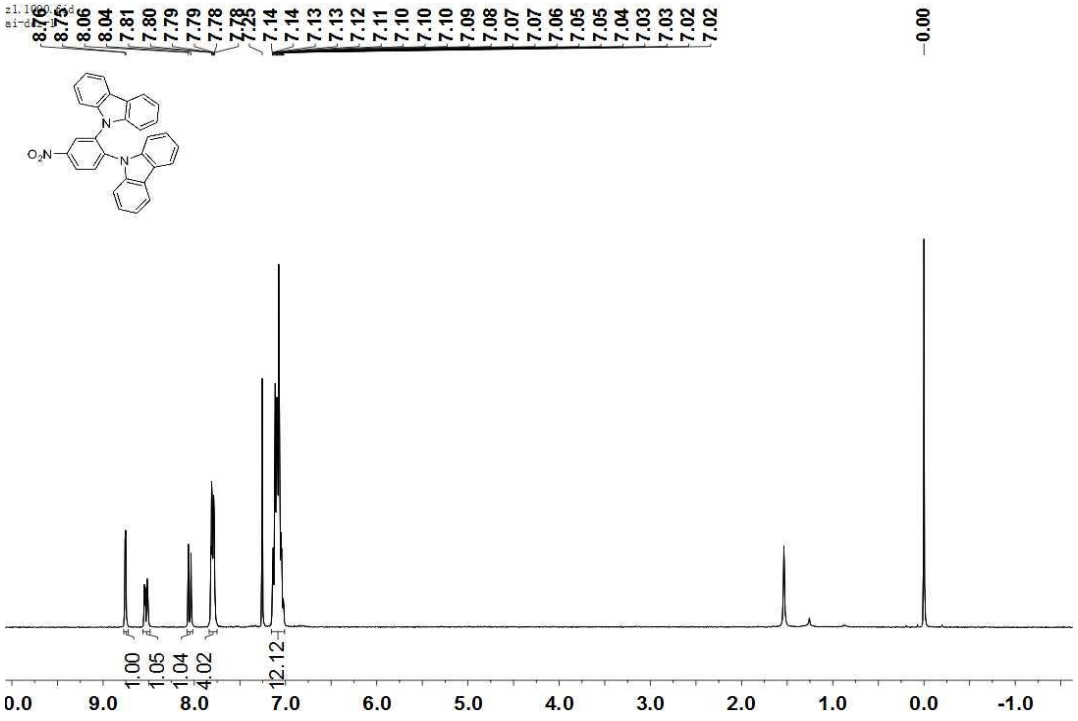


Fig. S8 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 9,9'-((1s,2s)-4-nitro-1,2-phenylene)- bis(9H-carbazole).

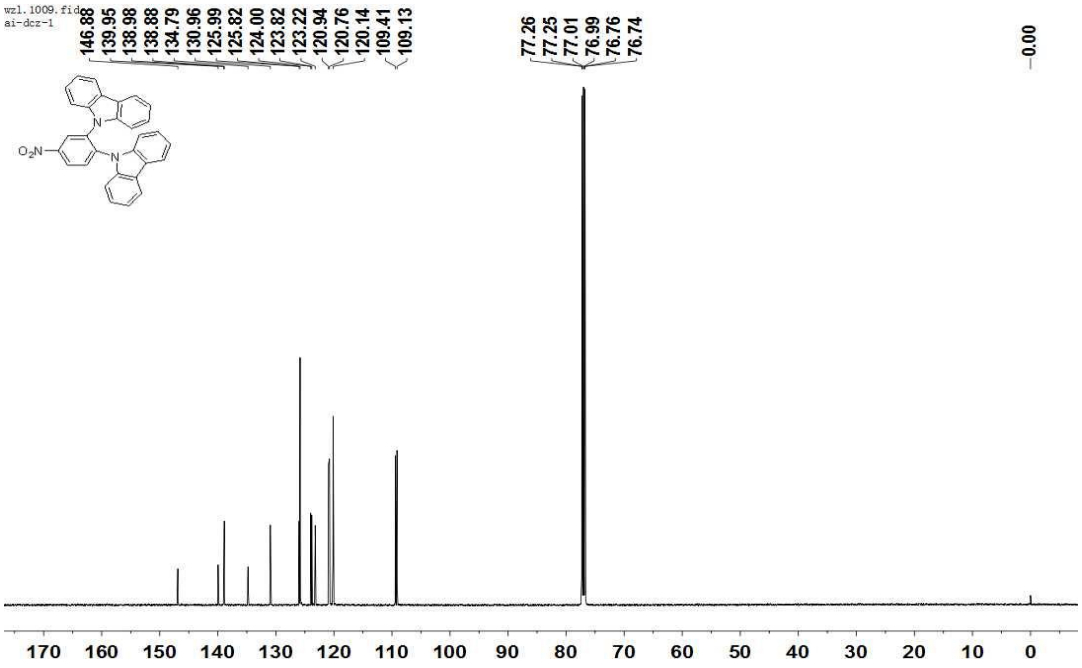


Fig. S9 ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 9,9'-((1s,2s)-4-nitro-1,2-phenylene)-bis(9H-carbazole).

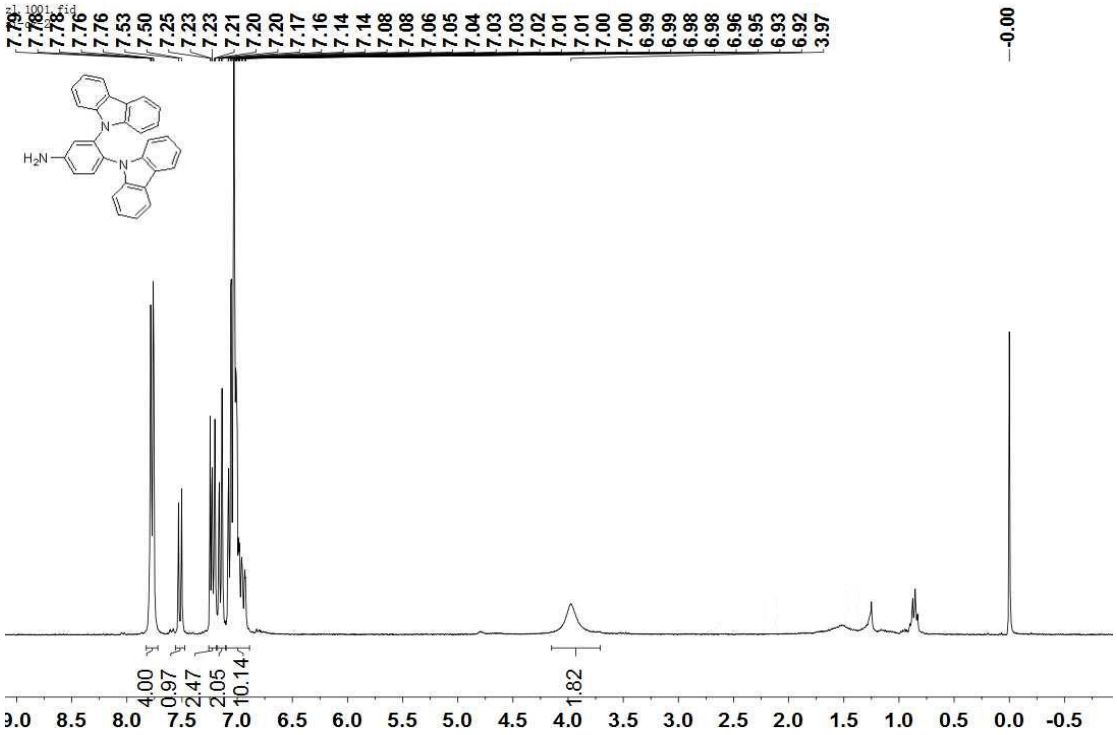


Fig. S10 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (3s,4s)-3,4-di(9H-carbazol-9-yl)aniline.

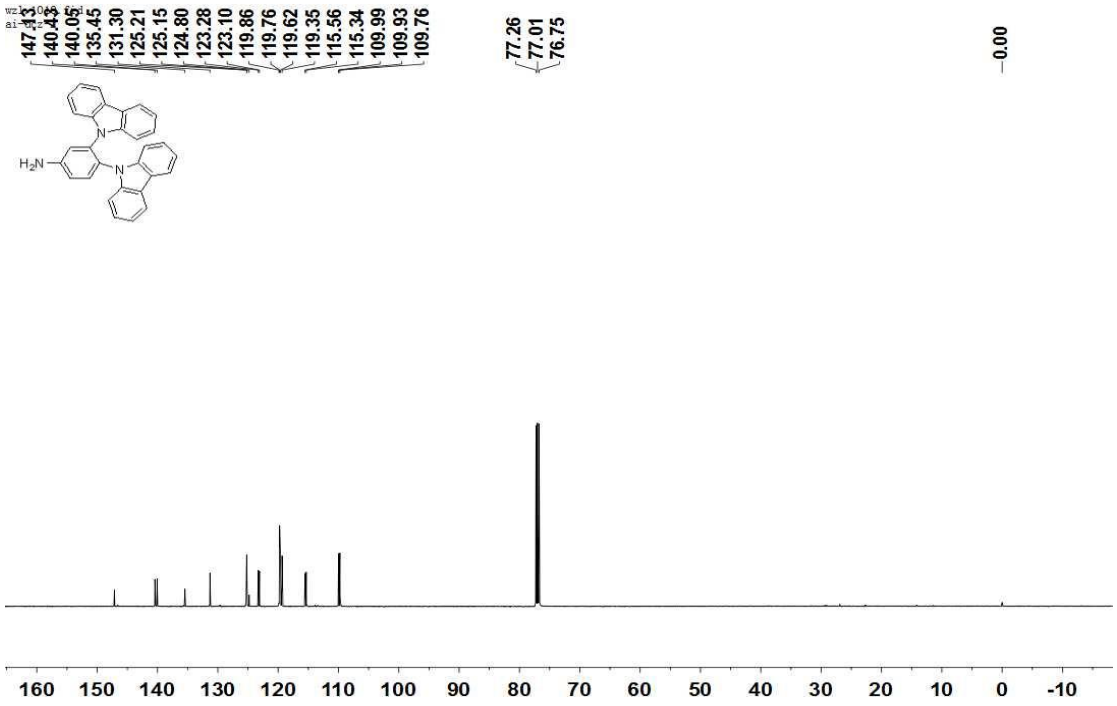


Fig. S11 ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of (3s,4s)-3,4-di(9H-carbazol-9-yl)aniline.

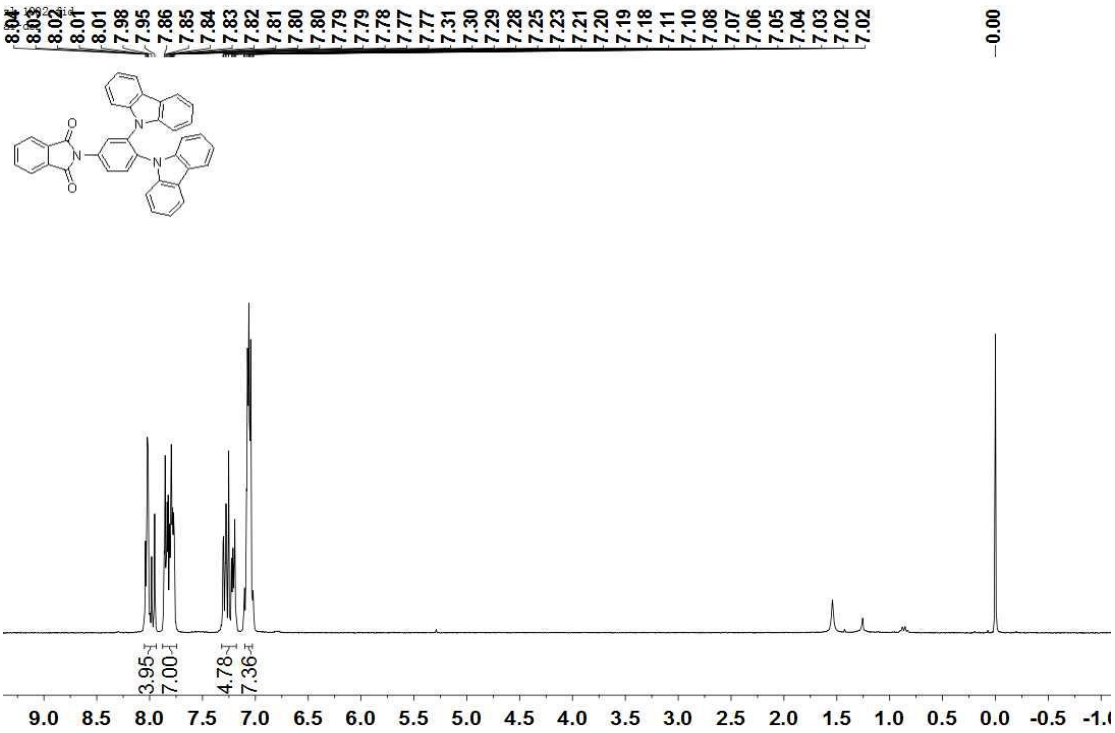


Fig. S12 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **AI-N-Cz**.

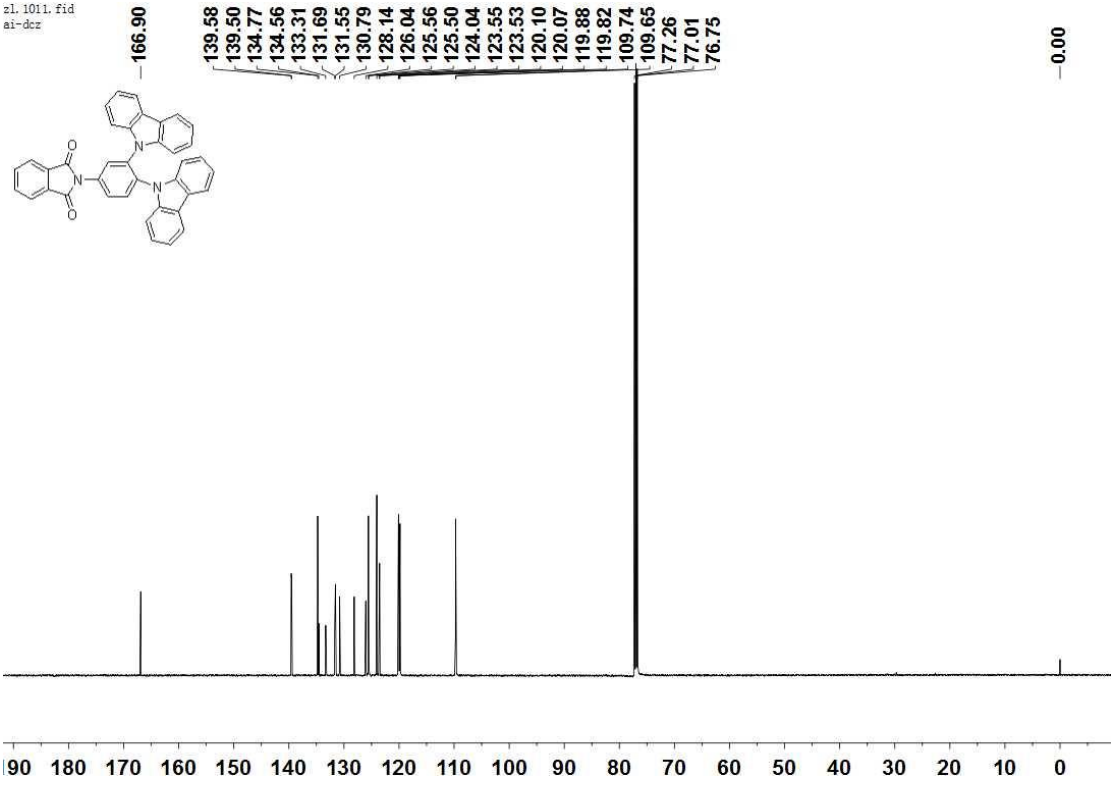


Fig. S13 ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **AI-N-Cz**.

7. Reference

S1. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.