Supporting Information

Narrow Emission band Ultraviolet/Deep-blue Thermally Activated Delayed Fluorescence Emitters Modified with Carbazole/Carboline as Donors

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1. General methods

$^{1}H/^{13}C$ NMR spectra (400 MHz) were recorded by a JEOL 400 MHz FT-400 NMR spectrometer referenced to 7.26 and 77.0 ppm for chloroform-D solvent with $SiMe_4$ as an internal reference: *J*-values are given in Hz. Mass spectra were obtained with a Bruker Microflex mass spectrometer in MALDI-TOF mode. Thermogravimetric analysis (TGA) was performed using a USA Waters Q600 under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. UV-vis absorption spectra were measured on a Shimadzu UV3600. Photoluminescence spectra were recorded on a PerkinElmer FL 8500 spectrofluorometer. Fluorescence quantum yields were measured using absolute methods with a Japan Hamamatsu C9920-06G. The frontier orbitals of the molecules based on the ground state geometries were calculated at B3LYP/6-31G* by Gaussian 16 program.[S1] Cyclic voltammograms were measured on a CHI 610E A14297 in a solution of *tetra-n*-butylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/Silver chloride (Ag/Ag^+) reference electrode in dichloromethane at a scan rate of 100 mV s^{-1} at room temperature under N_2 atmosphere. X-ray diffraction patterns were collected using an X-ray diffractometer from Rigaku Japan. The data collection from a single crystal was conducted using a Bruker D8 venture diffractometer, equipped with graphite-monochromated Cu K α radiation (λ = 1.54178 Å). Photoluminescence spectra were recorded on a PerkinElmer FL 8500 spectrofluorometer. Phosphorescence spectrum and transient PL curves were recorded on a horiba Fluorolog-QM and excited with a 365nm laser light source

Estimation of the rate constant for RISC. Rate constants (k_F, k_{IC}, k_{ISC}, and k_{RISC}) were determined from the measurements of quantum yields (Φ_F and Φ_{TADF}) and lifetimes (τ_p, τ_d) and of the prompt (fluorescence) and delayed (TADF) components according to Adachi's method.[S2]

$K_p = 1 / \tau_p$

$K_d = 1 / \tau_d$

$K_F = \Phi_F / \tau_p$

$\Phi = K_F / (K_F + K_{IC})$

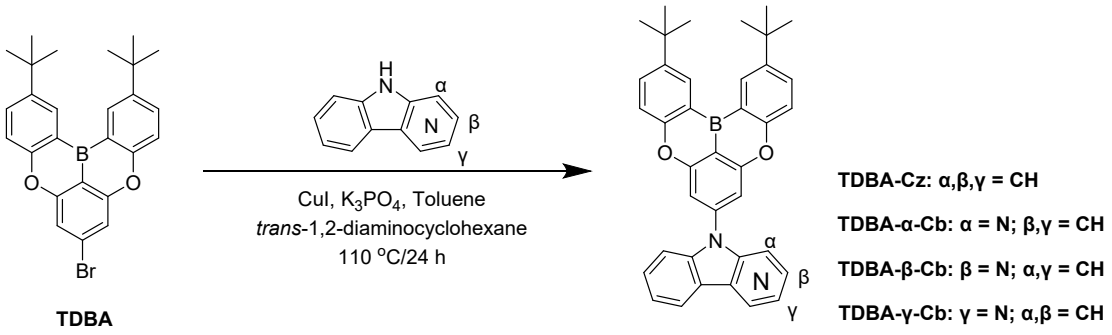
$\Phi_F = K_F / (K_F + K_{IC} + K_{ISC})$

$K_{RISC} = K_p K_d / (K_p - K_{ISC})$

2. Device fabrication

The multilayer OLEDs were fabricated by the vacuum-deposition method.[S3-4] Electronic grade HAT-CN, TCTA, TAPC, TPBi, CBP, LiF, and Al were obtained from commercial sources. **TDBA-Cz**, **TDBA-α-Cb**, **TDBA-β-Cb** and, **TDBA-γ-Cb** were purified by vacuum sublimation. Soak the glass coated with ITO in an ultrasonic cleaning agent for 30 minutes, sonicate with deionized water, acetone, and isopropanol solvents for 10 minutes each, and then dry. The cleaned ITO glass is treated with perfluoromethane (CF_4) plasma and then transferred to the evaporation chamber. In a high vacuum environment (1×10^{-5} Pa), the functional layer materials, luminescent materials, and cathode materials (Al) are sequentially deposited at high temperatures. When evaporating and depositing organic material thin films, the evaporation rate is controlled at 1-2 Å s^{-1}; When evaporating LiF, the evaporation rate is controlled at 0.1 Å s^{-1}; When evaporating Al, the evaporation rate is controlled at 2 Å s^{-1} and 9 mm^2 of the luminescent area. All the OLEDs were measured without encapsulation at room temperature in the dark. The Current density-Voltage-Luminance (*J-V-L*) characteristics were measured with a Keithley 2400 source meter and a LS110 luminance meter. The electroluminescence (EL) spectra were collected using a spectrascan PR650 spectrophotometer. The EQEs were calculated from the Luminance-Current density characteristics and EL spectra with the hypothesis of Lambertian distribution.

3. **Synthesis and characterizations**



Scheme S1. Synthetic route for compounds **TDBA-Cz**, **TDBA-α-Cb**, **TDBA-β-Cb** ,and **TDBA-γ-Cb**.

TDBA and **TDBA-Cz** were synthesized and characterized according to literature reported procedure.[S5-6]

Synthesis of 9-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)-9H-pyrido[2,3-b]indole (TDBA-α-Cb):

7-bromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (**TDBA**) (0.92 g, 2.0 mmol), 9H-Pyrido[2,3-b]indole (**α-Cb**) (0.67 g, 4.0 mmol), CuI (0.19 g, 1.0 mmol), K_3PO_4 (2.12 g, 10.0 mmol), and trans-1,2-diaminocyclohexane (1.20 mL, 10.0 mmol) were mixed in toluene (40 mL)with a flask containing nitrogen. The reaction mixture was stirred at 110 °C for 24 h under nitrogen. After it was cooled to room temperature, the reaction mixture was quenched with brine and extracted with CH_2Cl_2. The combined organic extracts were dried with anhydrous Na_2SO_4 and evaporated. The crude product was successfully purified by column chromatography using hexane: dichloromethane (2:1) as the eluent to give **TDBA-α-Cb** as white solid. Yield: 35% (0.38 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 2.40 Hz, 2H), 8.56-8.55 (dd, *J* = 1.60 Hz, 1H), 8.44-8.42 (dd, *J* = 1.60 Hz, 1H), 8.18-8.16 (d, *J* = 8.00 Hz, 1H), 7.81-7.78 (m, 3H), 7.60 (s, 3H), 7.53-7.51 (d, *J* = 8.80 Hz, 3H), 7.41-7.37 (t, ^1J = 8.00 Hz, ^2J = 7.20 Hz, 1H), 1.51 (s, 18H) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 158.92, 158.40, 151.84, 146.64, 145.30, 141.87, 139.73, 131.72, 130.42, 128.55, 127.35, 121.89, 121.38, 121.15, 118.16, 116.94, 116.75, 111.05, 107.17, 107.12, 34.72, 31.73. EI-MS (m/z): calcd for $C_{37}H_{33}BN_2O_2$, 548.2635; found, 548.2781 [M+].

Synthesis of 9-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)-9H-pyrido[3,4-b]indole (TDBA-β-Cb):

Compound **TDBA-β-Cb** was synthesized according to the same procedure described above for the synthesis of **TDBA-α-Cb**. **TDBA** (0.92 g, 2.0 mmol), 9H-Pyrido[3,4-b]indole (**β-Cb**) (0.67 g, 4.0 mmol), CuI (0.19 g, 1.0 mmol), K_3PO_4 (2.12 g, 10.0 mmol), trans-1,2-diaminocyclohexane (1.20 mL, 10.0 mmol), and to give **TDBA-β-Cb** as white solid. Yield: 36% (0.40 g). EI-MS (m/z): calcd for $C_{37}H_{33}BN_2O_2$, 548.2635; found, 548.8635 [M+].

Synthesis of 5-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)-5H-pyrido[4,3-b]indole (TDBA-γ-Cb):

Compound **TDBA-γ-Cb** was synthesized according to the same procedure described above for the synthesis of **TDBA-α-Cb**. **TDBA** (92 mg, 0.20 mmol), 5H-pyrido[4,3-b]indole (**γ-Cb**) (67.2 mg, 0.40 mmol), CuI (19 mg, 0.10 mmol), K_3PO_4 (212 mg, 1.0 mmol), trans-1,2-diaminocyclohexane (0.12 mL, 1.0 mmol), and to give **TDBA-γ-Cb** as white solid. Yield: 18% (20.0 mg). EI-MS (m/z): calcd for $C_{37}H_{33}BN_2O_2$, 548.2635; found, 548.8709 [M+].

4. Thermal properties

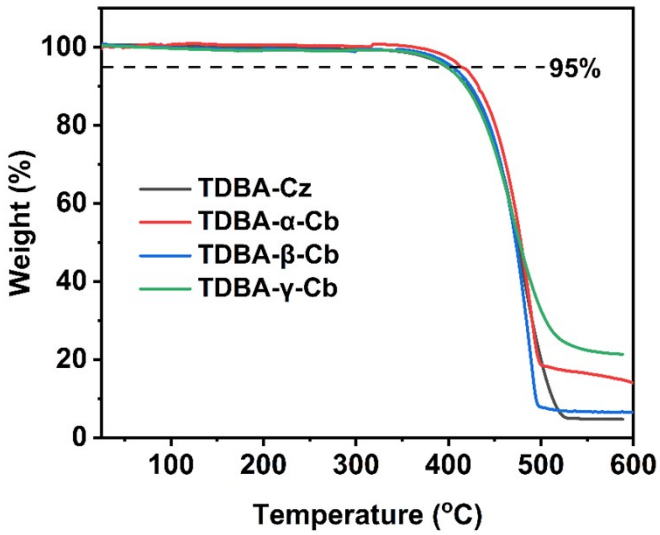


Figure S1. Thermal gravimetric analysis (TGA) of **TDBA-Cz**, **TDBA-α-Cb**, **TDBA-β-Cb** and **TDBA-γ-Cb**.

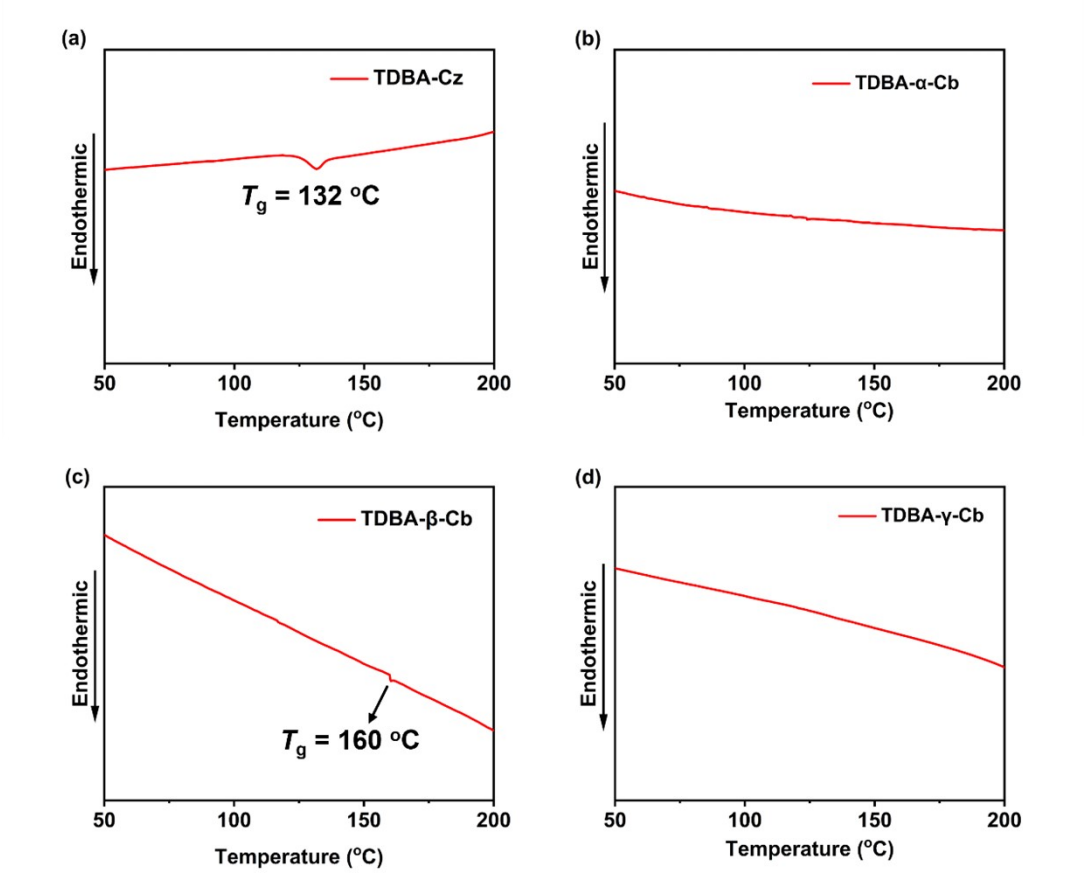


Figure S2. Differential scanning calorimetry (DSC) of **TDBA-Cz**, **TDBA-α-Cb**, **TDBA-β-Cb** and **TDBA-γ-Cb**.

5. X-Ray Crystallography

Table S1. Crystal data and structure refinement for **TDBA-α-Cb**.

Parameters	TDBA-α-Cb
CCDC number	2361056
Empirical formula	$C_{37}H_{33}BN_2O_2$
Formula weight	548.46
Temperature/K	200.00
Crystal system	triclinic
Space group	P-1
a/Å	8.6753(7)
b/Å	13.0352(11)
c/Å	13.1745(11)
α/°	81.753(4)
β/°	85.685(4)
γ/°	82.633(4)

Volume/Å^3	1459.8(2)
Z	2
ρ_{calc}g/cm^3	1.248
μ/mm^{-1}	0.595
F(000)	580.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.79 to 138.264
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	28126
Independent reflections	5288 [R_{int} = 0.0551, R_{sigma} = 0.0380]
Data/restraints/parameters	5288/0/385
Goodness-of-fit on F^2	1.771
Final R indexes [I>=2σ (I)]	R_1 = 0.1217, wR_2 = 0.3794
Final R indexes [all data]	R_1 = 0.1293, wR_2 = 0.3885
Largest diff. peak/hole / e Å^{-3}	0.57/-0.47

6. Theoretical calculations

Symbolic Z-matrix: **TDBA-Cz**

Charge = 0 Multiplicity = 1

C	2.24277	-1.25282	0.07514
C	0.85114	-1.21568	0.06679
C	0.11904	-0.01526	0.011
C	0.86787	1.17341	-0.05051
C	2.26012	1.18493	-0.05572
C	2.93848	-0.04001	0.01468
C	-1.117	2.50556	-0.20487
C	-2.01355	1.41253	-0.16711
C	-3.38038	1.7377	-0.31334
H	-4.09127	0.92024	-0.32726
C	-3.8696	3.03744	-0.46056
C	-2.9223	4.07838	-0.46321
C	-1.56374	3.82174	-0.34153
H	2.7665	-2.19802	0.11528
H	2.79625	2.12189	-0.14296

H	-3.24095	5.10929	-0.57048
H	-0.83465	4.62577	-0.3588
C	-2.03561	-1.40994	0.17684
C	-1.15525	-2.51646	0.20958
H	-4.1062	-0.8872	0.33705
C	-3.40755	-1.71514	0.31949
C	-1.62241	-3.82666	0.33724
C	-2.98472	-4.06328	0.45565
C	-3.91639	-3.00808	0.45845
H	-0.90544	-4.64155	0.34929
H	-3.31912	-5.08993	0.55563
B	-1.40212	-0.00356	0.00777
O	0.21341	-2.41869	0.12526
O	0.25067	2.38709	-0.11688
C	-5.4334	-3.2332	0.60842
C	-5.94367	-2.49935	1.87128
C	-6.16504	-2.67845	-0.63692
C	-5.79143	-4.72559	0.7461
H	-5.44802	-2.87849	2.77221
H	-5.75964	-1.42094	1.81932
H	-7.02422	-2.64735	1.98918
H	-5.82915	-3.18655	-1.54802
H	-7.24775	-2.8277	-0.54296
H	-5.98773	-1.60581	-0.76967
H	-6.87673	-4.83661	0.84888
H	-5.48347	-5.30273	-0.13338
H	-5.32914	-5.17689	1.63152
C	-5.38285	3.2842	-0.61431
C	-5.90175	2.55071	-1.87386
C	-6.12464	2.74748	0.6329
C	-5.71843	4.78093	-0.76112
H	-5.39877	2.91703	-2.77602
H	-5.73407	1.46999	-1.81528
H	-6.97972	2.71429	-1.99468
H	-5.78318	3.25612	1.54166
H	-7.20489	2.91185	0.53597
H	-5.9632	1.67319	0.77232
H	-6.80183	4.90747	-0.86588
H	-5.40293	5.3586	0.11537
H	-5.24854	5.2201	-1.64863
C	5.18927	0.78521	0.79037
C	5.17573	-0.84733	-0.7821
C	4.85051	1.71453	1.7781
C	6.5456	0.51995	0.4655

C	6.5358	-0.51747	-0.53972
C	5.88644	2.39366	2.41614
H	3.81688	1.8977	2.04859
C	7.56743	1.21675	1.12044
C	5.68582	-2.40107	-2.32958
C	7.50039	-1.21067	-1.27003
C	7.23235	2.15597	2.09048
H	5.64306	3.12082	3.18593
H	8.60848	1.02041	0.87771
C	7.0606	-2.17111	-2.18114
H	5.33236	-3.14996	-3.03569
H	8.5602	-1.00963	-1.1367
H	8.01522	2.70498	2.60564
H	7.76864	-2.74053	-2.77489
N	4.35812	-0.04608	0.02249
C	4.73236	-1.75438	-1.64497
H	3.83016	-1.83561	-2.29875

Symbolic Z-matrix: **TDBA-α-Cb**

Charge = 0 Multiplicity = 1

C	2.24277	-1.25282	0.07514
C	0.85114	-1.21568	0.06679
C	0.11904	-0.01526	0.011
C	0.86787	1.17341	-0.05051
C	2.26012	1.18493	-0.05572
C	2.93848	-0.04001	0.01468
C	-1.117	2.50556	-0.20487
C	-2.01355	1.41253	-0.16711
C	-3.38038	1.7377	-0.31334
H	-4.09127	0.92024	-0.32726
C	-3.8696	3.03744	-0.46056
C	-2.9223	4.07838	-0.46321
C	-1.56374	3.82174	-0.34153
H	2.7665	-2.19802	0.11528
H	2.79625	2.12189	-0.14296
H	-3.24095	5.10929	-0.57048
H	-0.83465	4.62577	-0.3588
C	-2.03561	-1.40994	0.17684
C	-1.15525	-2.51646	0.20958
H	-4.1062	-0.8872	0.33705
C	-3.40755	-1.71514	0.31949
C	-1.62241	-3.82666	0.33724
C	-2.98472	-4.06328	0.45565
C	-3.91639	-3.00808	0.45845

H	-0.90544	-4.64155	0.34929
H	-3.31912	-5.08993	0.55563
B	-1.40212	-0.00356	0.00777
O	0.21341	-2.41869	0.12526
O	0.25067	2.38709	-0.11688
C	-5.4334	-3.2332	0.60842
C	-5.94367	-2.49935	1.87128
C	-6.16504	-2.67845	-0.63692
C	-5.79143	-4.72559	0.7461
H	-5.44802	-2.87849	2.77221
H	-5.75964	-1.42094	1.81932
H	-7.02422	-2.64735	1.98918
H	-5.82915	-3.18655	-1.54802
H	-7.24775	-2.8277	-0.54296
H	-5.98773	-1.60581	-0.76967
H	-6.87673	-4.83661	0.84888
H	-5.48347	-5.30273	-0.13338
H	-5.32914	-5.17689	1.63152
C	-5.38285	3.2842	-0.61431
C	-5.90175	2.55071	-1.87386
C	-6.12464	2.74748	0.6329
C	-5.71843	4.78093	-0.76112
H	-5.39877	2.91703	-2.77602
H	-5.73407	1.46999	-1.81528
H	-6.97972	2.71429	-1.99468
H	-5.78318	3.25612	1.54166
H	-7.20489	2.91185	0.53597
H	-5.9632	1.67319	0.77232
H	-6.80183	4.90747	-0.86588
H	-5.40293	5.3586	0.11537
H	-5.24854	5.2201	-1.64863
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C	5.17573	-0.84733	-0.7821
C	4.85051	1.71453	1.7781
C	6.5456	0.51995	0.4655
C	6.5358	-0.51747	-0.53972
C	5.88644	2.39366	2.41614
H	3.81688	1.8977	2.04859
C	7.56743	1.21675	1.12044
C	5.68582	-2.40107	-2.32958
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H	5.64306	3.12082	3.18593
H	8.60848	1.02041	0.87771

C	7.0606	-2.17111	-2.18114
H	5.33221	-3.14718	-3.03854
H	8.5602	-1.00963	-1.1367
H	8.01522	2.70498	2.60564
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H	8.60848	1.02041	0.87771
C	7.0606	-2.17111	-2.18114
H	8.5602	-1.00963	-1.1367
H	8.01522	2.70498	2.60564
H	7.76864	-2.74053	-2.77489
N	4.35812	-0.04608	0.02249
C	4.73236	-1.75438	-1.64497
H	3.83016	-1.83561	-2.29875
N	5.68582	-2.40107	-2.32958

Symbolic Z-matrix: **TDBA-γ-Cb**

Charge = 0 Multiplicity = 1

C	2.24277	-1.25282	0.07514
C	0.85114	-1.21568	0.06679
C	0.11904	-0.01526	0.011
C	0.86787	1.17341	-0.05051
C	2.26012	1.18493	-0.05572
C	2.93848	-0.04001	0.01468
C	-1.117	2.50556	-0.20487
C	-2.01355	1.41253	-0.16711
C	-3.38038	1.7377	-0.31334
H	-4.09127	0.92024	-0.32726
C	-3.8696	3.03744	-0.46056
C	-2.9223	4.07838	-0.46321
C	-1.56374	3.82174	-0.34153
H	2.7665	-2.19802	0.11528
H	2.79625	2.12189	-0.14296
H	-3.24095	5.10929	-0.57048
H	-0.83465	4.62577	-0.3588
C	-2.03561	-1.40994	0.17684
C	-1.15525	-2.51646	0.20958
H	-4.1062	-0.8872	0.33705
C	-3.40755	-1.71514	0.31949
C	-1.62241	-3.82666	0.33724
C	-2.98472	-4.06328	0.45565
C	-3.91639	-3.00808	0.45845
H	-0.90544	-4.64155	0.34929
H	-3.31912	-5.08993	0.55563
B	-1.40212	-0.00356	0.00777
O	0.21341	-2.41869	0.12526
O	0.25067	2.38709	-0.11688
C	-5.4334	-3.2332	0.60842
C	-5.94367	-2.49935	1.87128
C	-6.16504	-2.67845	-0.63692
C	-5.79143	-4.72559	0.7461
H	-5.44802	-2.87849	2.77221
H	-5.75964	-1.42094	1.81932
H	-7.02422	-2.64735	1.98918
H	-5.82915	-3.18655	-1.54802
H	-7.24775	-2.8277	-0.54296
H	-5.98773	-1.60581	-0.76967
H	-6.87673	-4.83661	0.84888
H	-5.48347	-5.30273	-0.13338
H	-5.32914	-5.17689	1.63152
C	-5.38285	3.2842	-0.61431
C	-5.90175	2.55071	-1.87386

C	-6.12464	2.74748	0.6329
C	-5.71843	4.78093	-0.76112
H	-5.39877	2.91703	-2.77602
H	-5.73407	1.46999	-1.81528
H	-6.97972	2.71429	-1.99468
H	-5.78318	3.25612	1.54166
H	-7.20489	2.91185	0.53597
H	-5.9632	1.67319	0.77232
H	-6.80183	4.90747	-0.86588
H	-5.40293	5.3586	0.11537
H	-5.24854	5.2201	-1.64863
C	5.18927	0.78521	0.79037
C	5.17573	-0.84733	-0.7821
C	4.85051	1.71453	1.7781
C	6.5456	0.51995	0.4655
C	6.5358	-0.51747	-0.53972
C	5.88644	2.39366	2.41614
H	3.81688	1.8977	2.04859
C	7.56743	1.21675	1.12044
C	5.68582	-2.40107	-2.32958
C	7.50039	-1.21067	-1.27003
C	7.23235	2.15597	2.09048
H	5.64306	3.12082	3.18593
H	8.60848	1.02041	0.87771
H	5.33221	-3.14718	-3.03854
H	8.5602	-1.00963	-1.1367
H	8.01522	2.70498	2.60564
N	4.35812	-0.04608	0.02249
C	4.73236	-1.75438	-1.64497
H	3.67683	-1.90507	-1.73468
N	7.0606	-2.17111	-2.18114

Table S2. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for **TDBA-Cz**.

Excited state	E_g **[eV]**	E_g **[nm]**	*f*	**Transition (D: donor unit, A: acceptor unit)**			**Coefficient**
S1	3.1896	388.71	0.2243	HOMO	→	LUMO	0.70285
S2	3.3955	365.14	0.1275	HOMO-1	→	LUMO	0.69646
T1	2.8836	429.97	0.0000	HOMO-1	→	LUMO	0.69505
T2	2.9729	417.05	0.0000	HOMO-6	→	LUMO	0.14534
				HOMO-3	→	LUMO	0.11366

				HOMO	→	LUMO	0.64773
				HOMO	→	LUMO+2	0.11648
T3	3.1694	391.19	0.0000	HOMO-8	→	LUMO+9	-0.13371
				HOMO-4	→	LUMO+1	-0.14568
				HOMO-4	→	LUMO+8	-0.10815
				HOMO-2	→	LUMO	-0.13769
				HOMO-2	→	LUMO+1	0.58985
				HOMO	→	LUMO+6	-0.25141
T4	3.3113	374.43	0.0000	HOMO-5	→	LUMO+4	0.15060
				HOMO-3	→	LUMO	0.59346
				HOMO-3	→	LUMO+5	-0.14774
				HOMO-1	→	LUMO+4	0.17725
				HOMO	→	LUMO	-0.15646
T5	3.3941	365.29	0.0000	HOMO-4	→	LUMO+6	0.13228
				HOMO	→	LUMO+6	0.66707

Table S3. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for **TDBA-α-Cb**.

Excited state	E_g **[eV]**	E_g **[nm]**	*f*	**Transition (D: donor unit, A: acceptor unit)**			**Coefficient**
S1	3.3627	368.71	0.1242	HOMO	→	LUMO	0.69751
S2	3.5419	350.05	0.2967	HOMO	→	LUMO	0.70078
T1	2.8514	434.82	0.0000	HOMO	→	LUMO	0.69595
T2	3.1239	396.90	0.0000	HOMO-2	→	LUMO+1	0.56655
				HOMO-1	→	LUMO	0.11734
				HOMO-1	→	LUMO+1	0.23155
				HOMO-1	→	LUMO+4	0.19837
T3	3.1611	392.21	0.0000	HOMO-5	→	LUMO	-0.20254
				HOMO-3	→	LUMO	-0.29185

				HOMO-2	→	LUMO+1	-0.13871
				HOMO-1	→	LUMO	0.49998
				HOMO-1	→	LUMO+2	0.10711
				HOMO	→	LUMO+3	0.13567
				HOMO	→	LUMO+5	0.12794
T4	3.3626	368.72	0.0000	HOMO-3	→	LUMO	0.49702
				HOMO-3	→	LUMO+6	-0.10610
				HOMO-2	→	LUMO+1	-0.11379
				HOMO-1	→	LUMO	0.27294
				HOMO-1	→	LUMO+1	0.27924
				HOMO	→	LUMO+5	-0.10981
T5	3.3866	366.10	0.0000	HOMO-3	→	LUMO	-0.24265
				HOMO-2	→	LUMO+1	-0.18405
				HOMO-1	→	LUMO	-0.16228
				HOMO-1	→	LUMO+1	0.57208

Table S4. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for **TDBA-β-Cb**.

Excited state	E_g **[eV]**	E_g **[nm]**	f	**Transition (D: donor unit, A: acceptor unit)**			**Coefficient**
S1	3.3407	371.13	0.2448	HOMO	→	LUMO	0.70225
S2	3.4009	364.57	0.1311	HOMO-1	→	LUMO	0.69705
T1	2.8829	430.07	0.0000	HOMO-1	→	LUMO	0.69606
T2	3.0822	402.26	0.0000	HOMO-6	→	LUMO	0.17713
				HOMO-3	→	LUMO	0.18723
				HOMO-1	→	LUMO+3	-0.12119
				HOMO	→	LUMO	0.60345
				HOMO	→	LUMO+2	0.10250
T3	3.1941	388.16	0.0000	HOMO-2	→	LUMO+1	-0.25827

				HOMO	→	LUMO+1	0.61464
				HOMO	→	LUMO+5	0.11391
T4	3.2713	379.01	0.0000	HOMO-9	→	LUMO+9	-0.10241
				HOMO-7	→	LUMO+1	-0.15317
				HOMO-2	→	LUMO+1	0.51283
				HOMO	→	LUMO+1	0.29821
				HOMO	→	LUMO+5	-0.25666
T5	3.3201	373.44	0.0000	HOMO-5	→	LUMO+4	0.14003
				HOMO-3	→	LUMO	0.58851
				HOMO-3	→	LUMO+6	-0.13821
				HOMO-1	→	LUMO+4	0.16117
				HOMO	→	LUMO	-0.23890

Table S5. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for **TDBA-γ-Cb**.

Excited state	E_g **[eV]**	E_g **[nm]**	f	**Transition (D: donor unit, A: acceptor unit)**			**Coefficient**
S1	3.3997	364.70	0.1968	HOMO-1	→	LUMO	0.42325
				HOMO	→	LUMO	0.55676
S2	3.4166	362.89	0.2037	HOMO-1	→	LUMO	0.55367
				HOMO	→	LUMO	-0.42704
T1	2.8905	428.94	0.0000	HOMO-1	→	LUMO	0.68486
				HOMO	→	LUMO	0.12377
T2	3.1009	399.84	0.0000	HOMO-6	→	LUMO	-0.18157
				HOMO-3	→	LUMO	-0.20626
				HOMO-1	→	LUMO	-0.11079
				HOMO-1	→	LUMO+3	-0.12962
				HOMO	→	LUMO	0.57176
				HOMO	→	LUMO+2	0.12393
T3	3.2273	384.18	0.0000	HOMO-10	→	LUMO+9	0.10999
				HOMO-8	→	LUMO+1	-0.11250

				HOMO-2	→	LUMO	-0.13406
				HOMO-2	→	LUMO+1	0.58232
				HOMO	→	LUMO+4	0.22921
T4	3.3248	372.91	0.0000	HOMO-5	→	LUMO+5	-0.13527
				HOMO-3	→	LUMO	0.58397
				HOMO-3	→	LUMO+6	-0.12949
				HOMO-1	→	LUMO+5	-0.15246
				HOMO	→	LUMO	0.24785
T5	3.4027	364.37	0.0000	HOMO-7	→	LUMO+6	-0.10309
				HOMO-6	→	LUMO+3	-0.11216
				HOMO-5	→	LUMO	0.50374
				HOMO-5	→	LUMO+2	-0.11449
				HOMO-5	→	LUMO+6	-0.11610
				HOMO-3	→	LUMO+5	-0.25537
				HOMO-1	→	LUMO+2	0.19735
				HOMO	→	LUMO+6	-0.17484

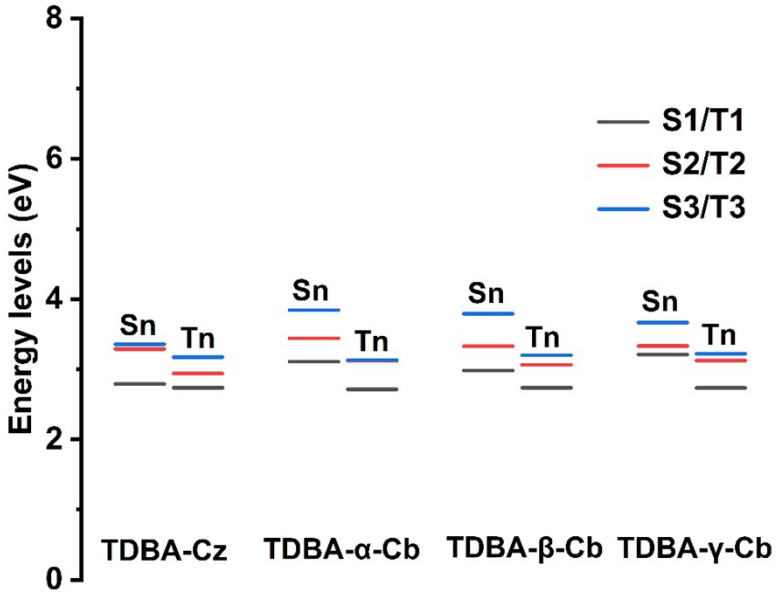

Figure S3. Energy levels of single and triple excited states of molecules are

calculated by TD-DFT.

Table S6. Energy levels of single and triple excited states of molecules.

Energy levels	S1	S2	S3	T1	T2	T3
TDBA-Cz	2.7912	3.2906	3.3586	2.7368	2.9422	3.1747
TDBA-α-Cb	3.1098	3.4411	3.8449	2.7156	3.1196	3.1336
TDBA-β-Cb	2.9823	3.3311	3.7925	2.7387	3.0667	3.2021
TDBA-γ-Cb	3.2113	3.3327	3.6649	2.7361	3.1245	3.2231

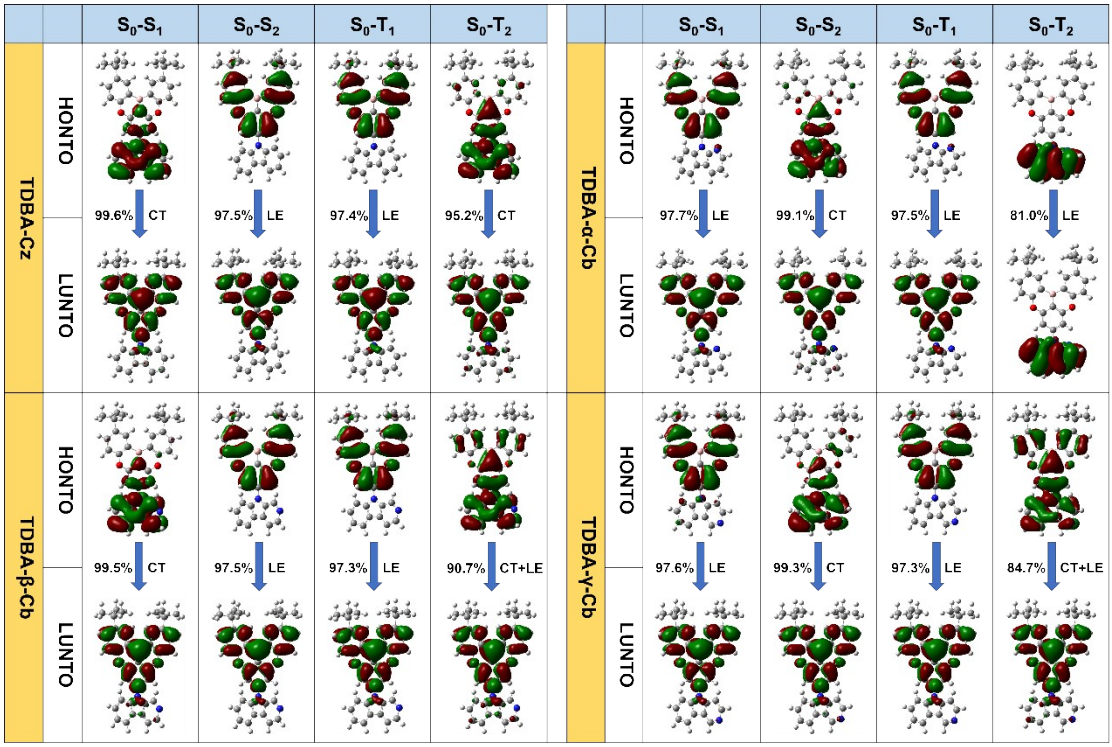

Figure S4. Highest occupied and lowest unoccupied NTOs (HONTOs and LUNTOs) of **TDBA-Cz**, **TDBA-α-Cb**, **TDBA-β-Cb** and **TDBA-γ-Cb**.

7. Photophysical Properties

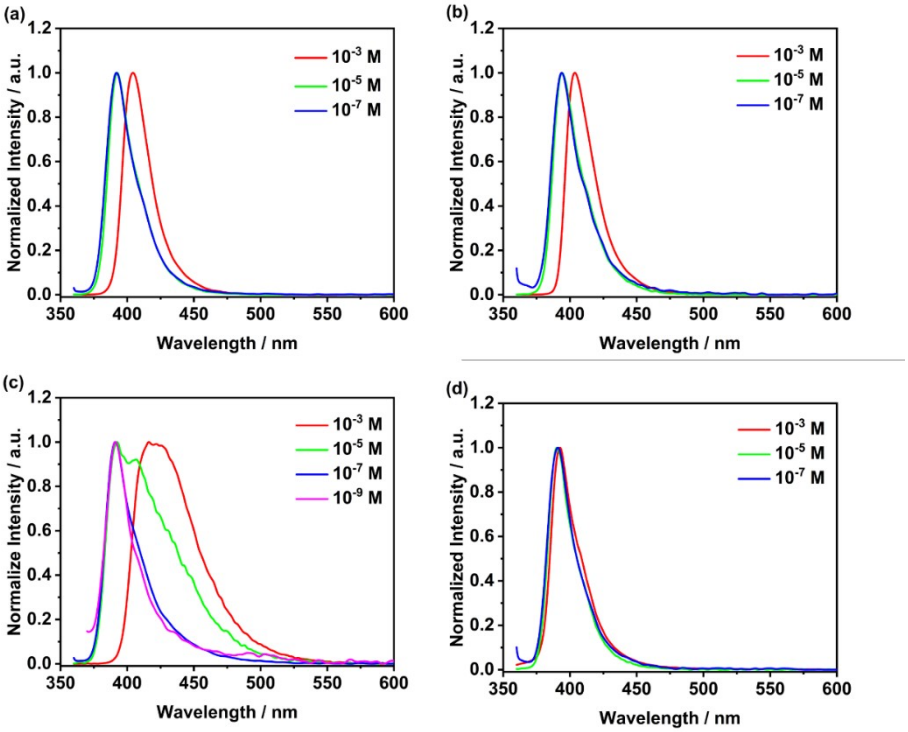

Figure S5. Fluorescence spectra of **TDBA-Cz** (a), **TDBA-α-Cb** (b), **TDBA-β-Cb** (c), and **TDBA-γ-Cb** (d) different concentrations in toluene.

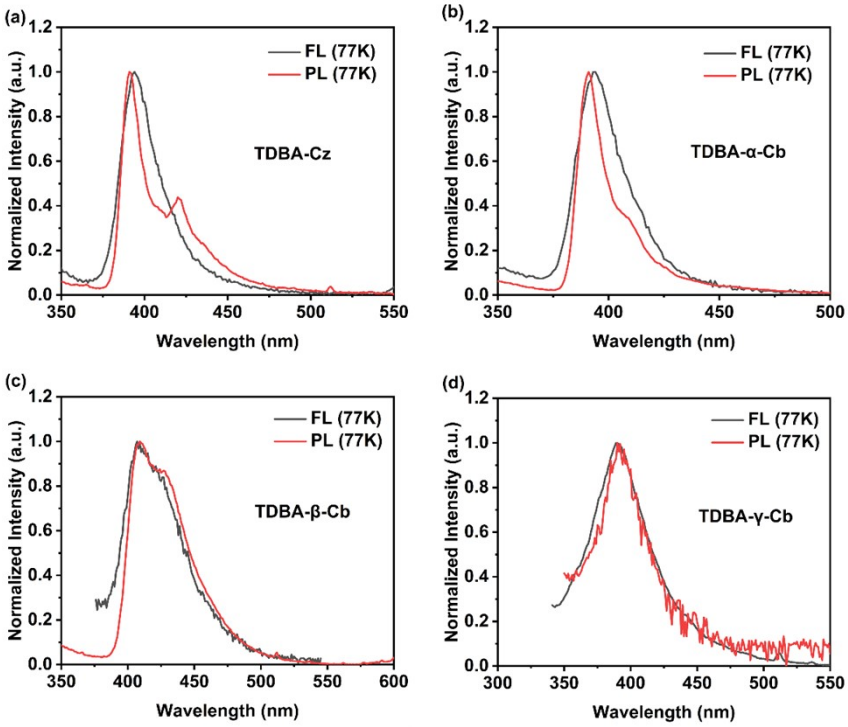

Figure S6. Fluorescence (77 K) and phosphorescence (77K) spectra of **TDBA-Cz** (a), **TDBA-α-Cb** (b), **TDBA-β-Cb** (c) and **TDBA-γ-Cb** (d).

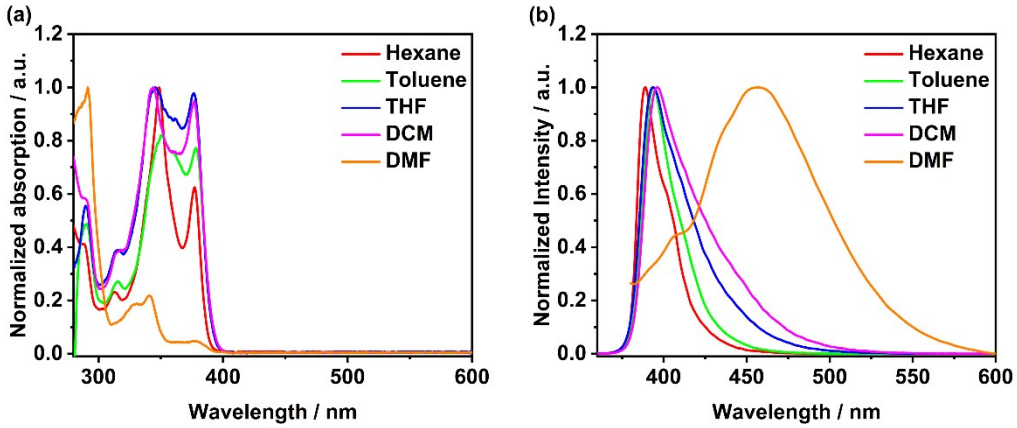

Figure S7. UV-vis absorption (a) and fluorescence spectra (b) of the compound **TDBA-Cz** were recorded in different solvents at ~10^{-5} M.

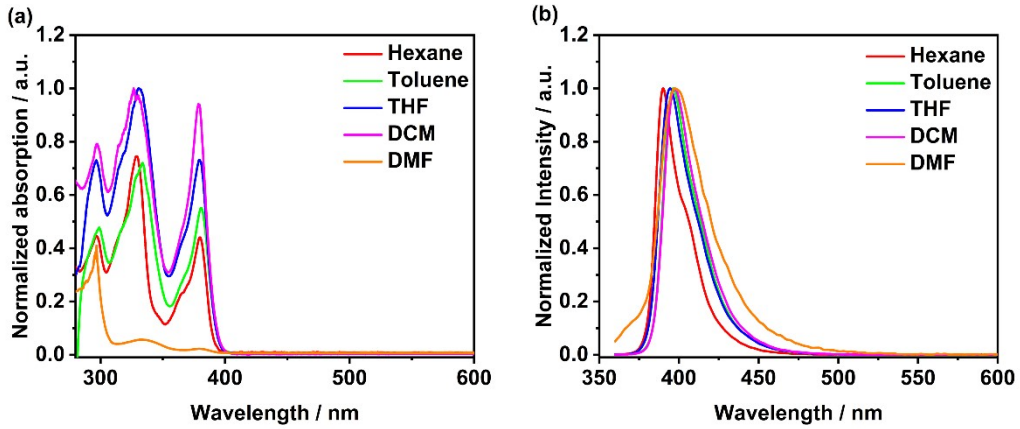

Figure S8. UV-vis absorption (a) and fluorescence spectra (b) of the compound **TDBA-α-Cb** were recorded in different solvents at ~10^{-5} M.

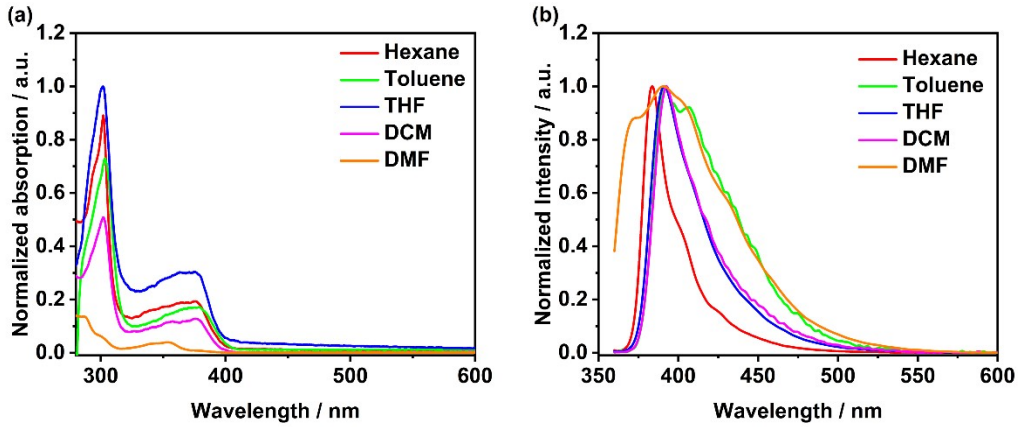

Figure S9. UV-vis absorption (a) and fluorescence spectra (b) of the compound **TDBA-β-Cb** were recorded in different solvents at ~10^{-5} M.

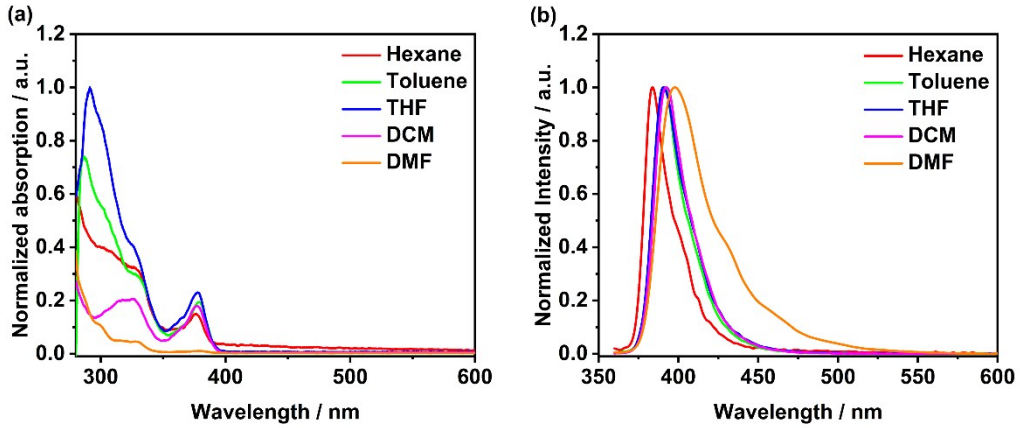

Figure S10. UV-vis absorption (a) and fluorescence spectra (b) of the compound **TDBA-γ-Cb** were recorded in different solvents at ~10^{-5} M.

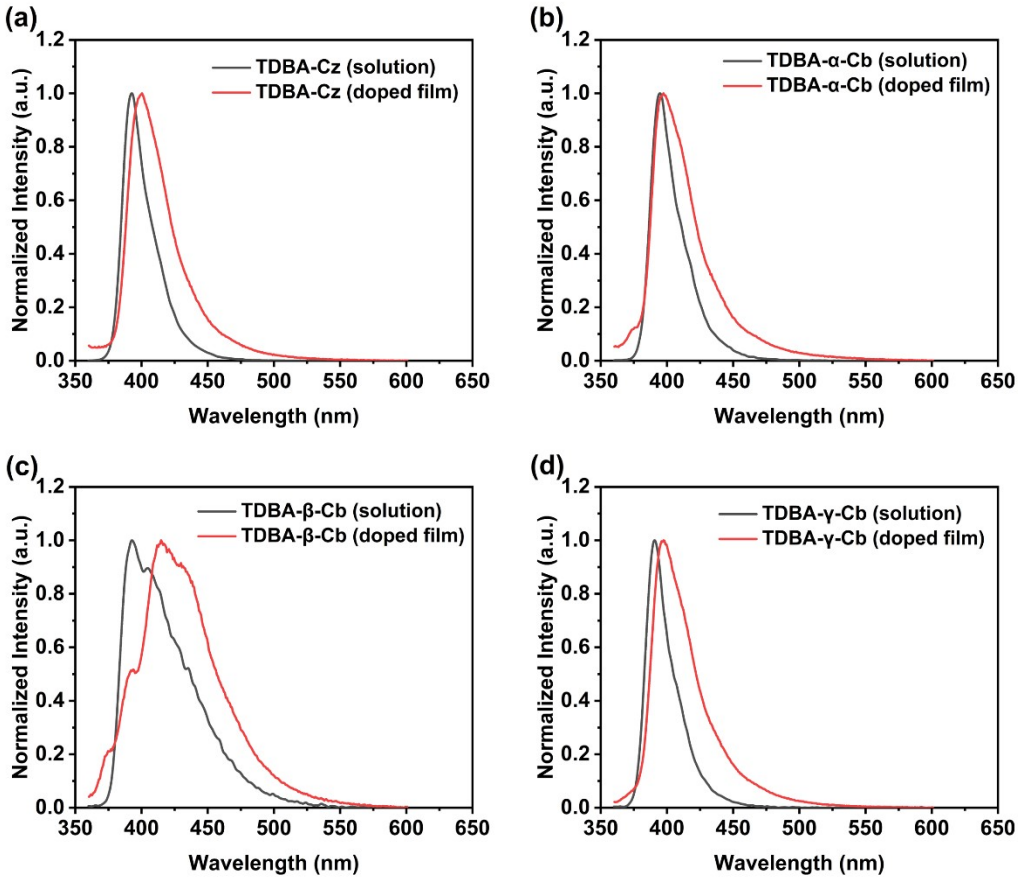

Figure S11. Normalized fluorescence spectra in dilute toluene solution (black) and CBP films with 3wt% doping concentration (red) of TDBA-Cz (a), TDBA-α-Cb (b), TDBA-β-Cb (c), and TDBA-γ-Cb (d).

Table S7. Emission peak and FWHM of **TDBA-Cz**, **TDBA-α-Cb**, **TDBA-β-Cb** and **TDBA-γ-Cb** in different solvents.

Compounds		TDBA-Cz	TDBA-α-Cb	TDBA-β-Cb	TDBA-γ-Cb
Hexane	λ_{em}(nm)	389	390	383	384
	FWHM(nm)	21	21	22	20
Toluene	λ_{em}(nm)	394	396	392/407	392
	FWHM(nm)	24	26	55	23
THF	λ_{em}(nm)	394	395	391	391
	FWHM(nm)	33	25	34	25
DCM	λ_{em}(nm)	396	397	392	392

	FWHM(nm)	38	26	35	25
DMF	λ_{em}(nm)	456	397	372/391	398
	FWHM(nm)	84	34	75	36

8. Transient PL decay

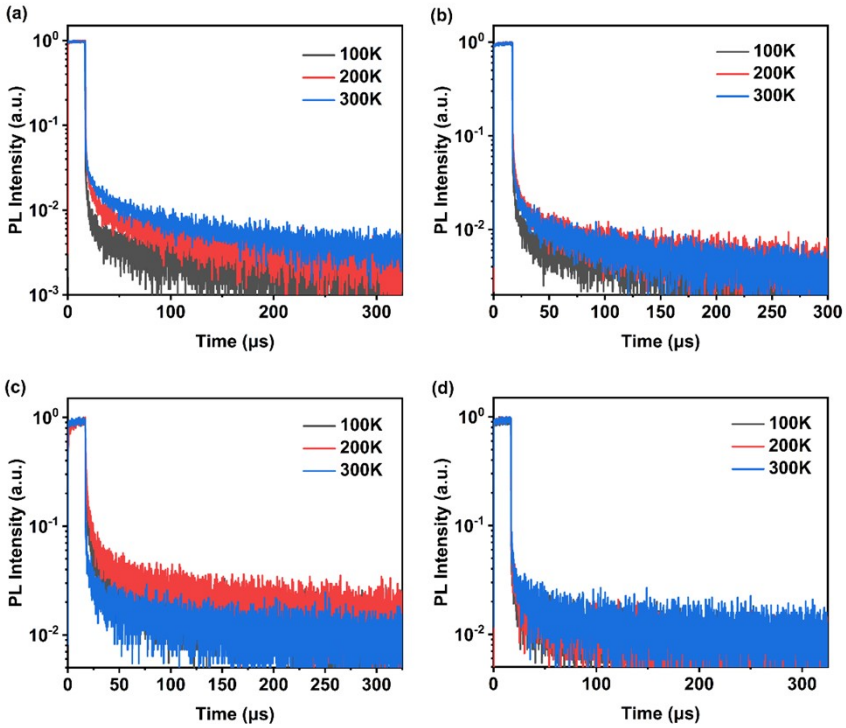

Figure S12. The transient PL decay spectra of **TDBA-Cz** (a), **TDBA-α-Cb** (b), **TDBA-β-Cb** (c), and **TDBA-γ-Cb** (d) in toluene at various temperatures.

9. Electrochemical properties

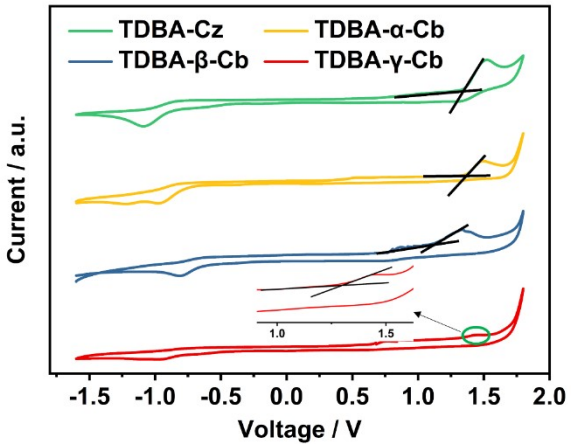

Figure S13. Cyclic voltammetry (CV) measurements of **TDBA-Cz**, **TDBA-α-Cb**, **TDBA-β-Cb**, and **TDBA-γ-Cb**.

10. Device performance

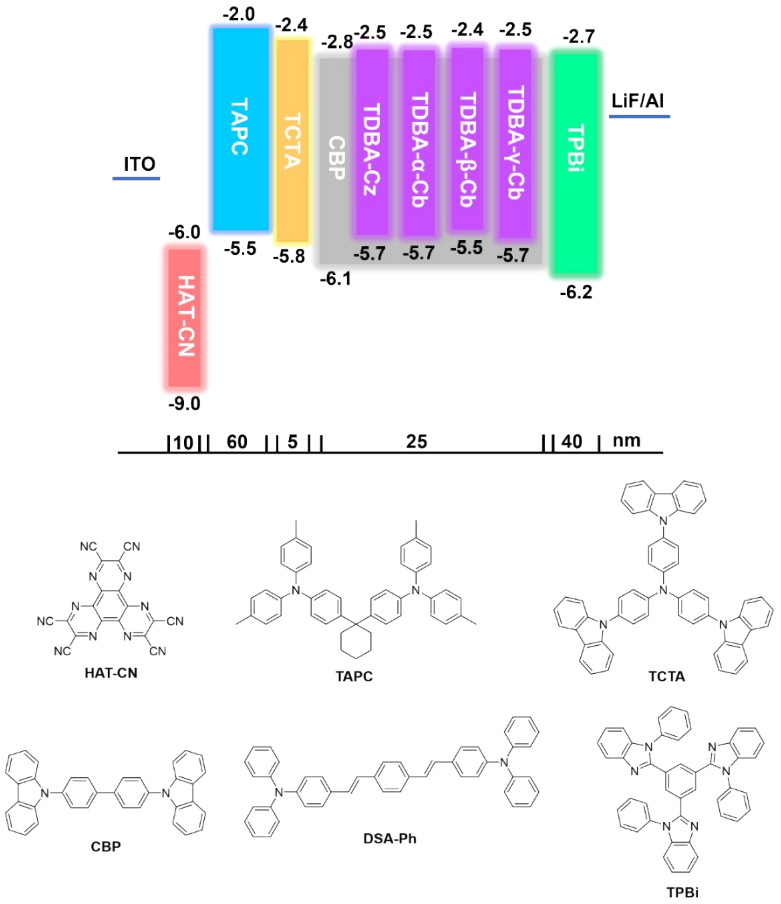

Figure S14. Device structure, energy levels, and molecular structures used in these devices.

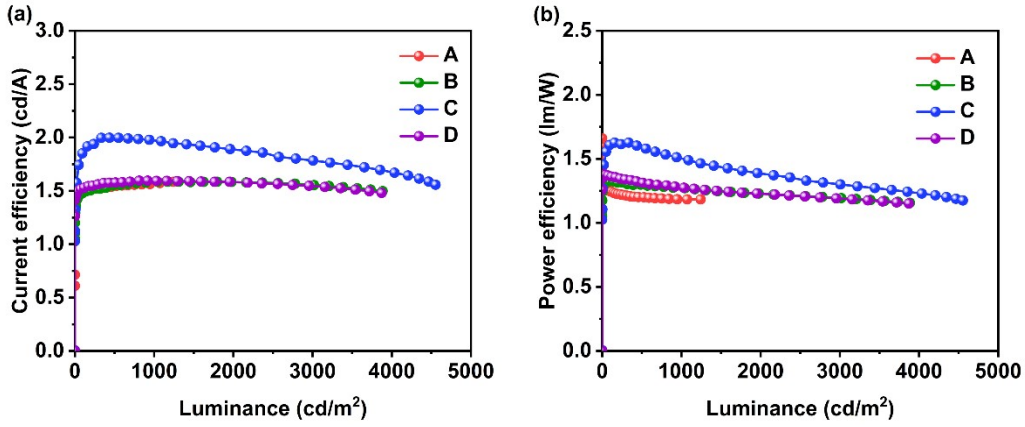

Figure S15. (a) Current Efficiency versus luminance curves, (b) Power Efficiencies versus luminance curves of Device **A-D** based CBP doped devices.

11. NMR spectra and Mass Spectra

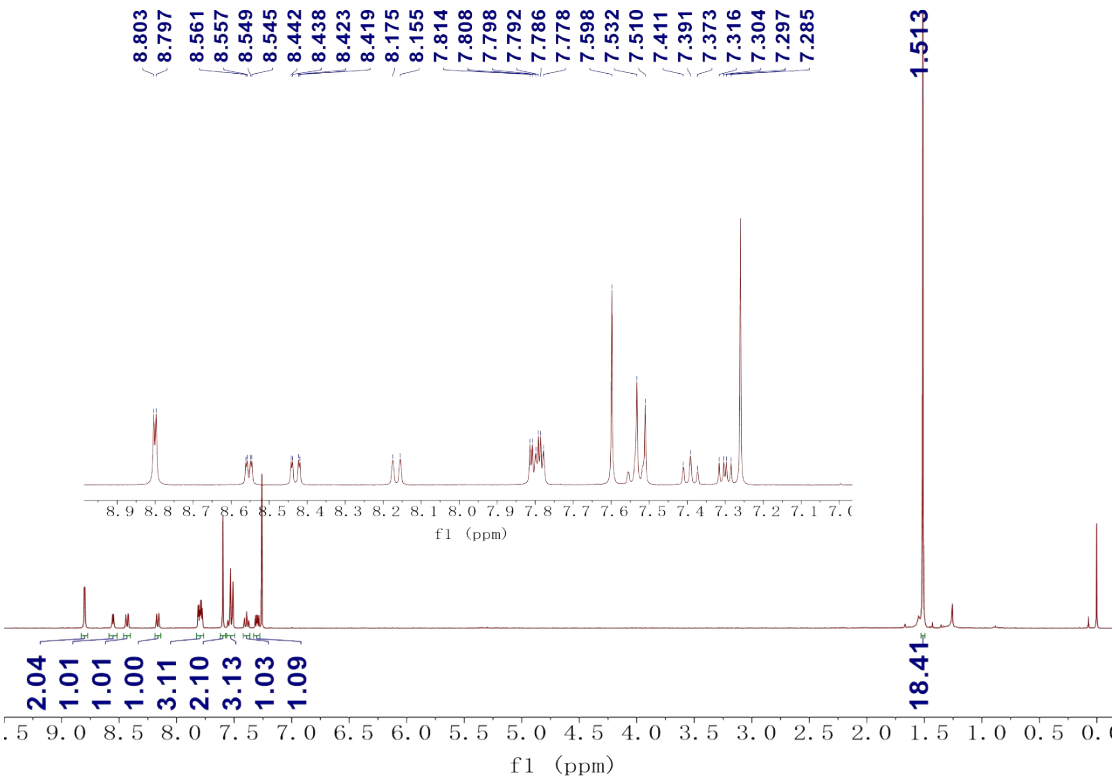

Figure S16. ^{1}H NMR spectrum of **TDBA-α-Cb** (400 MHz, $CDCl_3$, *r.t.*).

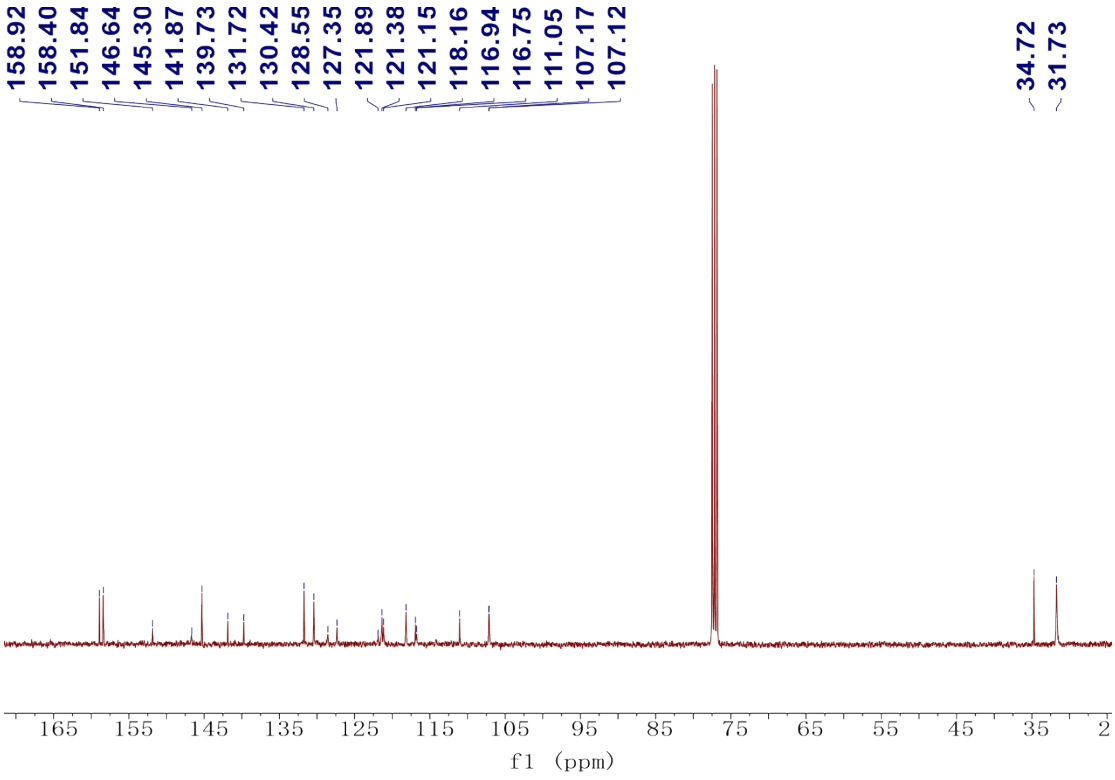

Figure S17. ^{13}C NMR spectrum of **TDBA-α-Cb** (400 MHz, $CDCl_3$, *r.t.*).

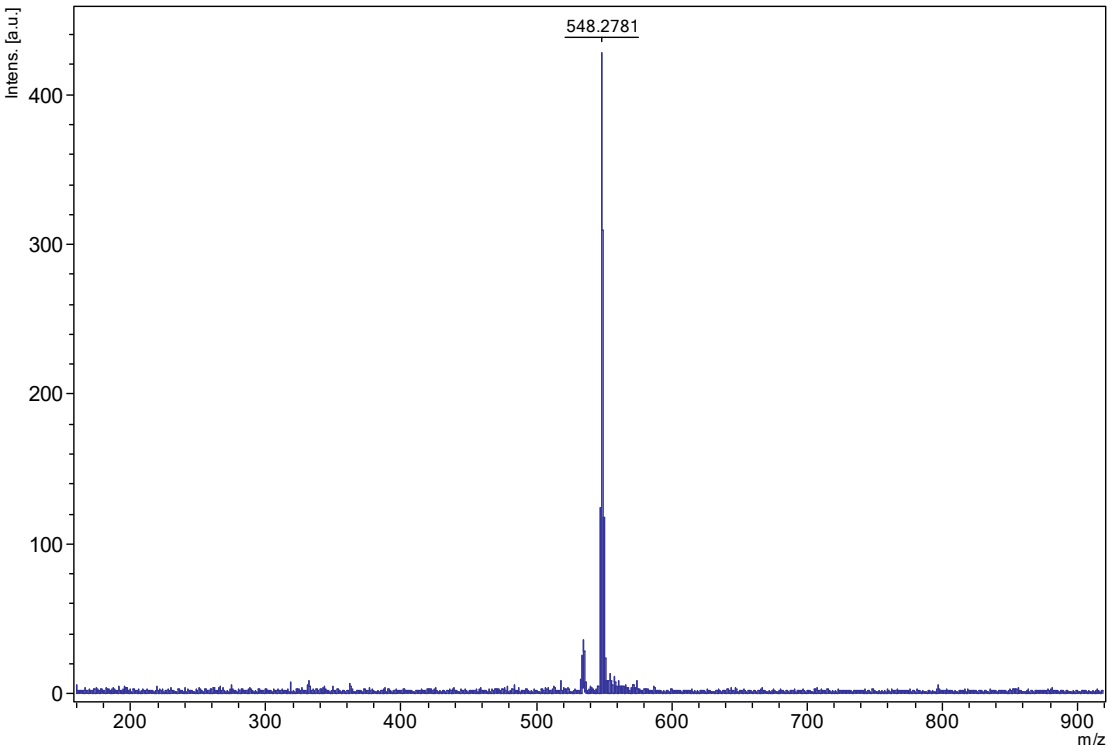

Figure S18. Mass spectra of **TDBA-α-Cb**.

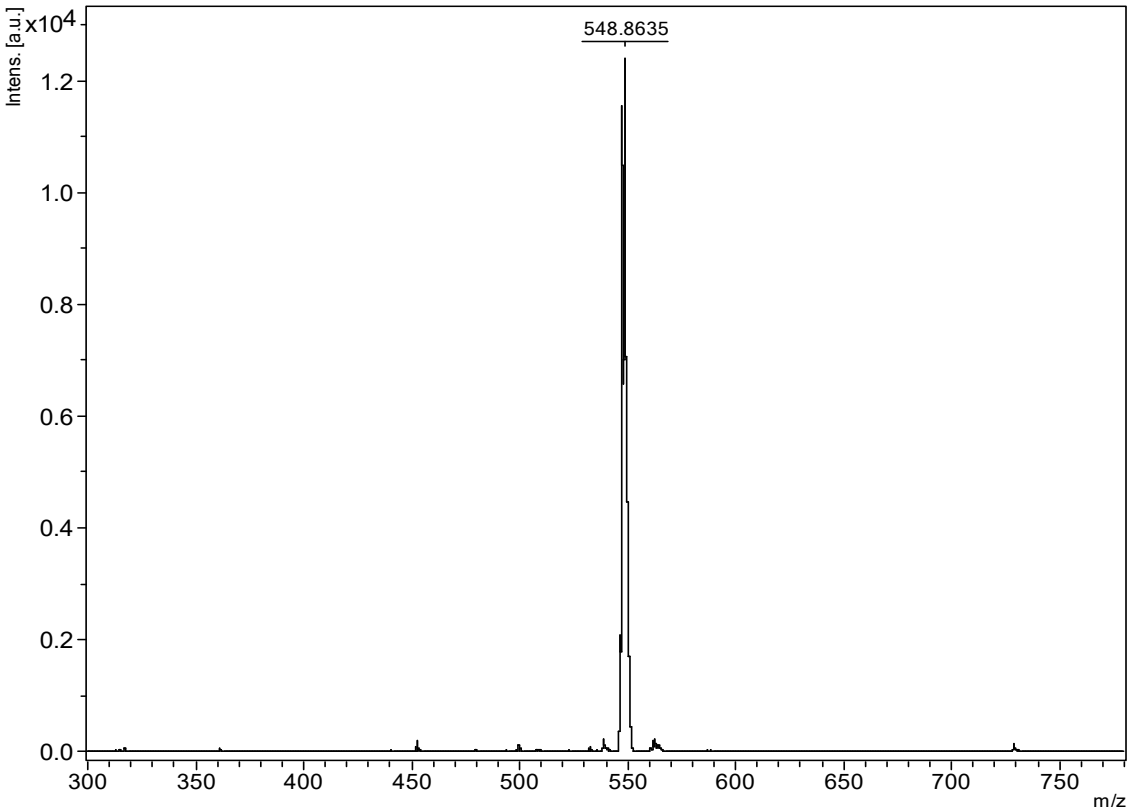

Figure S19. Mass spectra of **TDBA-β-Cb**.

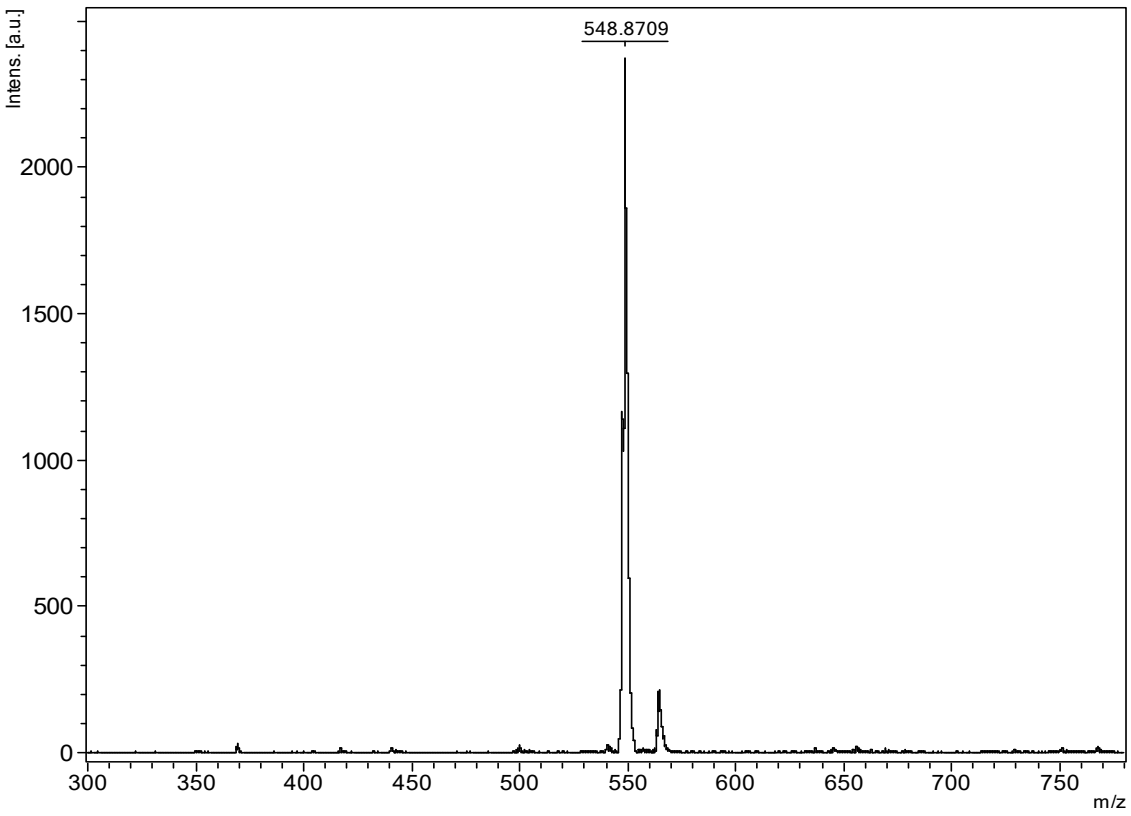

Figure S20. Mass spectra of **TDBA-γ-Cb**.

12. References

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