Supporting Information for:

Synthesis of two novel indolo[3,2-b]carbazole derivatives with aggregation-enhanced emission property

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Contents

Preparation of 5,11-dihexyl-6,12-di-p-tolyl-5,11-dihydroindolo[3,2-b]carbazole-2,8-dicarbaldehyde (compound 2)

DMF (7.4 mL, 100 mmol) was added in a 250 mL RBF, then gradually added drop-wise $POCl_3$ (9.2 mL, 100 mmol) until forming frozen salt in ice-bath. **1** (0.604 g, 1 mmol) was dissolved in 100 mL dichloromethane, added drop-wise in the above mixture at room temperature. The reaction mixture was refluxed for 24 h. Poured the mixture into ice water, adjusted pH to 7, extracted with 500 mL of CH_2Cl_2 and the organic layer was washed three times with distilled water, and then dried over anhydrous magnesium sulfate overnight. The solvent was removed under reduced pressure. The residue was purified by column chromatography (dichloromethane: petroleum ether = 3:5). Yield: 0.4 g (60%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.850-0.897 (t, 6H), 0.916-0.973 (m, 4H), 1.081-1.155 (m, 4H), 1.191-1.278 (m, 4H), 1.526-1.606 (m, 4H), 2.623 (s, 6H), 3.905-3.946 (t, 4H), 6.911-6.914 (d, J = 1.2 Hz, 2H), 7.327-7.349 (d, J = 8.8 Hz, 2H), 7.499-7.519 (d, J = 8.0 Hz, 4H), 7.542-7.562 (d, J = 8.0 Hz, 4H), 7.917-7.942 (m, 2H), 9.597 (s, 2H); FT-IR (KBr) ν (cm^{-1}): 2926, 2851, 1685, 1603, 1566, 1503, 1347, 1240, 1198, 1081, 814, 732; MALDI-TOF MS: m/z = 660.06 ([M-H]$^+$), calcd for $C_{46}H_{48}N_2O_2$: 660.89.

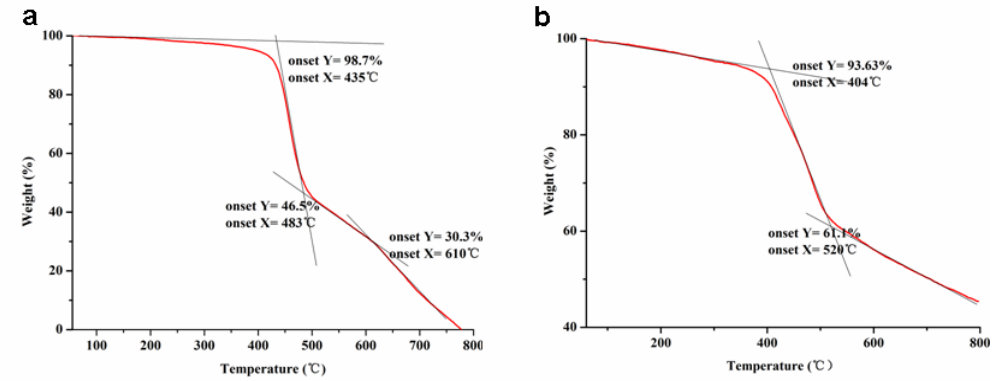

Fig. S1 TGA curves of compounds **3** (a) and **4** (b)

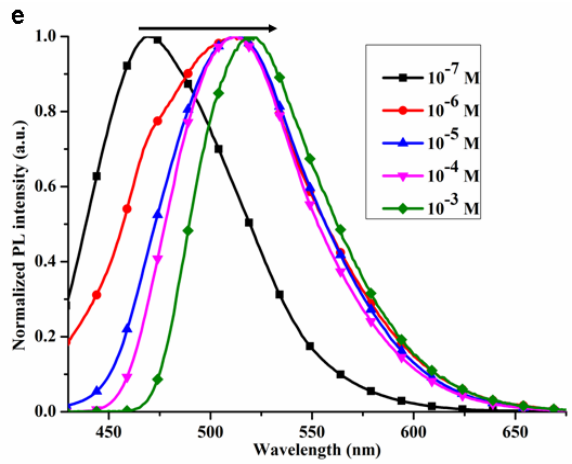

Fig. S2 Normalized PL spectra of **3** in THF solutions with different concentrations.

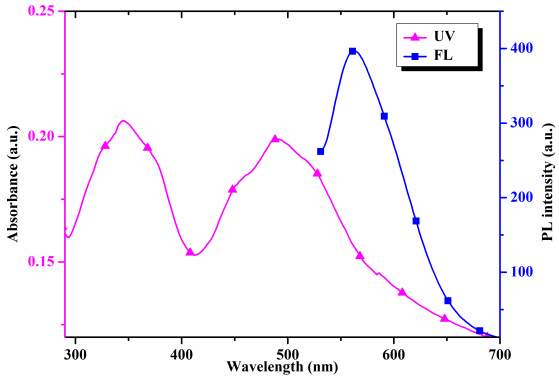

Fig. S3 UV-Vis absorption and PL of **4** in thin film

Table S1 The volume fractions of water effect on the absorption and fluorescence spectra of **3** in THF/water mixtures

Compound	*Water vol. fraction /%*	λ_{ex} / nm [a]	λ_{em} / nm [b]
3	0	345, 412	499
	10	345, 412	513
	20	345, 413	516
	30	345, 413	518
	40	345, 415	520
	50	345, 415	517
	60	345, 435	482, 569
	70	350, 440	489, 573
	80	345, 425	502, 573
	90	345, 430	495, 575
	100	350, 430	495, 557
	Thin film	344, 432	440, 544

[a] Absorption maximum. [b] Emission maximum.

Table S2 The volume fractions of water effect on the absorption and fluorescence spectra of **4** in THF/water mixtures

Compound	*Water vol. fraction /%*	λ_{ex} / nm [a]	λ_{em} / nm [b]
4	0	337, 462	559
	10	337, 463	563
	20	338, 464	565
	30	339, 465	569
	40	342, 462	567
	50	342, 468	560
	60	343, 490	564
	70	342, 488	574
	80	342, 484	574
	90	343, 481	573
	100	338, 468	579
	Thin film	345, 490	562

[a] Absorption maximum. [b] Emission maximum.

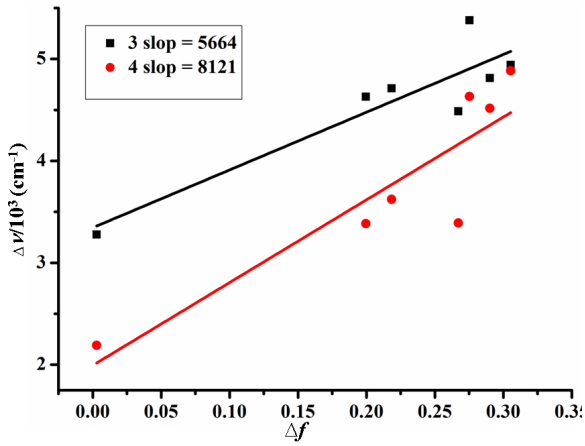

Fig. S4 Plot of Stokes shift ($\Delta\upsilon$) of **3** and **4** versus Δf of their solutions.

Table S3. UV-Vis and FL. data of **3** in different polarity solvents

Comp.	*Solvent*	λ_{ex} / nm [a]	$\varepsilon / 10^3[\varepsilon]$ [b]	λ_{em} / nm [c]	Φ_F [d]	Δν/cm^{-1} [e]
3	benzene	347, 414	37.7	479	0.0990	3277.76
	DCM	345, 417	61.5	519	0.0656	4712.99
	THF	345, 417	52.1	513	0.0757	4487.64
	acetic ether	344, 408	52.9	503	0.0590	4629.09
	ethanol	344, 414	47.0	517	0.0468	4812.23
	acetonitrile	344, 410	49.3	537	0.0389	5768.27
	DMSO	347, 420	42.5	530	0.1082	4941.60
	DMF	345, 413	52.2	531	0.0560	5380.68

[a] Absorption maximum. [b] Maximum molar extinction coefficient. [c] Emission maximum. [d] Fluorescence quantum yield. [e] Stokes shift (cm^{-1}).

Table S4. UV-Vis and FL. data of **4** in different polarity solvents

Comp.	*Solvent*	λ_{ex} / nm [a]	$\varepsilon / 10^3[\varepsilon]$ [b]	λ_{em}/nm [c]	Φ_F [d]	Δν / cm^{-1} [e]
4	benzene	337, 462	211	514	0.2498	2189.76
	DCM	338, 469	241	565	0.3381	3622.84
	THF	336, 460	172	545	0.4799	3390.50
	ethyl acetate	334, 458	234	542	0.4746	3383.87
	ethanol	335, 459	39.0	579	0.0869	4515.33
	acetonitrile	335, 455	62.0	585	0.0766	4884.00
	DMSO	336, 468	58.0	598	0.0286	4475.62
	DMF	336, 464	194	591	0.0290	4631.25

[a] Absorption maximum. [b] Maximum molar extinction coefficient. [c] Emission maximum. [d] Fluorescence quantum yield. [e] Stokes shift (cm^{-1}).

Table S5 Crystal data and details of collection and refinement for **4**

compound	**4**	a [Å]	9.2346(14)
empirical formula	$C_{52}H_{48}N_6$	b [Å]	10.1144(15)
formula weight	756.39	c [Å]	24.687(4)
temperature (K)	296(2)	α [deg]	79.828(2)
crystal system	triclinic	β [deg]	89.103(2)
space group	*P-1*	γ [deg]	72.210(2)
Z	64	V [Å^3]	2159.2(6)
D_{calcd} [g·cm^{-3}]	1.164	μ [mm^{-1}]	0.069
F (000)	804	GOF	1.030
Crystal size (mm)	0.30 × 0.20 × 0.20	Completeness to theta = 24.71	99.0 %
θ range [°]	0.84-24.71	Reflections collected / unique	15177/7278 [R(int) = 0.0214]
Final R indices [I>2sigma(I)]	R_1 = 0.0581, wR_2 = 0.1315	R indices (all data)	R_1 = 0.1183, wR_2 = 0.1522

Table S6 Weak interaction parameters for **4**

D–H···*A*[a]	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C19–H19···N3^{i}	0.930	2.649	3.534	159.36
C33–H33···N3^{ii}	0.931	2.652	3.488	149.96
C12–H12···N4^{iii}	0.930	2.705	3.421	134.46
C52–H52B···N4^{iv}	0.970	2.748	3.657	158.54
C15–H15···N5^{v}	0.930	2.708	3.423	134.31
C46–H46B···N5^{vi}	0.959	2.734	3.658	161.85
C23–H23···N6^{vii}	0.930	2.652	3.489	150.03
C8–H8···N6^{viii}	0.930	2.653	3.537	159.09

Table S7. Bond lengths [Å] and angles [°] for **4**

C(1)-C(6)	1.394(4)	C(2)-C(31)	1.455(4)
C(4)-N(1)	1.406(4)	C(29)-N(3)	1.145(5)
C(30)-N(4)	1.142(5)	C(32)-N(2)	1.375(4)
C(39)-N(6)	1.145(5)	C(40)-N(5)	1.145(5)
C(41)-N(1)	1.474(4)	C(44)-H(44A)	0.9700
C(45)-C(46)	1.511(7)	C(46)-H(46C)	0.9600
C(47)-N(2)	1.476(4)	C(47)-C(48)	1.513(5)
C(48)-C(49)	1.524(5)	C(49)-C(50)	1.463(6)
C(50)-C(51)	1.510(6)	C(51)-C(52)	1.491(7)

C(6)-C(1)-N(2)	129.8(3)	N(2)-C(1)-C(2)	108.6(3)
C(3)-C(4)-N(1)	129.4(3)	C(4)-C(3)-C(14)	127.5(3)
C(10)-C(11)-H(11)	119.2	N(3)-C(29)-C(28)	177.8(4)
N(4)-C(30)-C(28)	178.5(5)	N(2)-C(32)-C(33)	128.2(3)
N(2)-C(32)-C(31)	110.0(3)	N(1)-C(41)-H(41B)	108.8
C(22)-N(1)-C(4)	108.7(3)	C(1)-N(2)-C(47)	128.4(3)
C(24)-C(25)-C(27)	125.7(3)	C(27)-C(28)-C(29)	126.2(4)
C(36)-C(31)-C(32)	118.7(3)	C(36)-C(31)-C(2)	134.6(3)
C(32)-C(33)-H(33)	121.0	C(36)-C(35)-C(34)	118.9(3)
C(31)-C(36)-C(35)	120.8(3)	C(38)-C(37)-C(35)	133.0(4)
N(6)-C(39)-C(38)	177.3(4)	N(5)-C(40)-C(38)	179.4(5)
N(1)-C(41)-H(41A)	108.8	H(41A)-C(41)-H(41B)	107.7
C(41)-C(42)-C(43)	115.3(4)	C(43)-C(42)-H(42A)	108.4
N(2)-C(47)-H(47B)	108.9	C(22)-N(1)-C(4)	108.7(3)
C(22)-N(1)-C(41)	123.0(3)	C(4)-N(1)-C(41)	128.2(3)
C(32)-N(2)-C(47)	123.2(3)	C(1)-N(2)-C(47)	128.4(3)

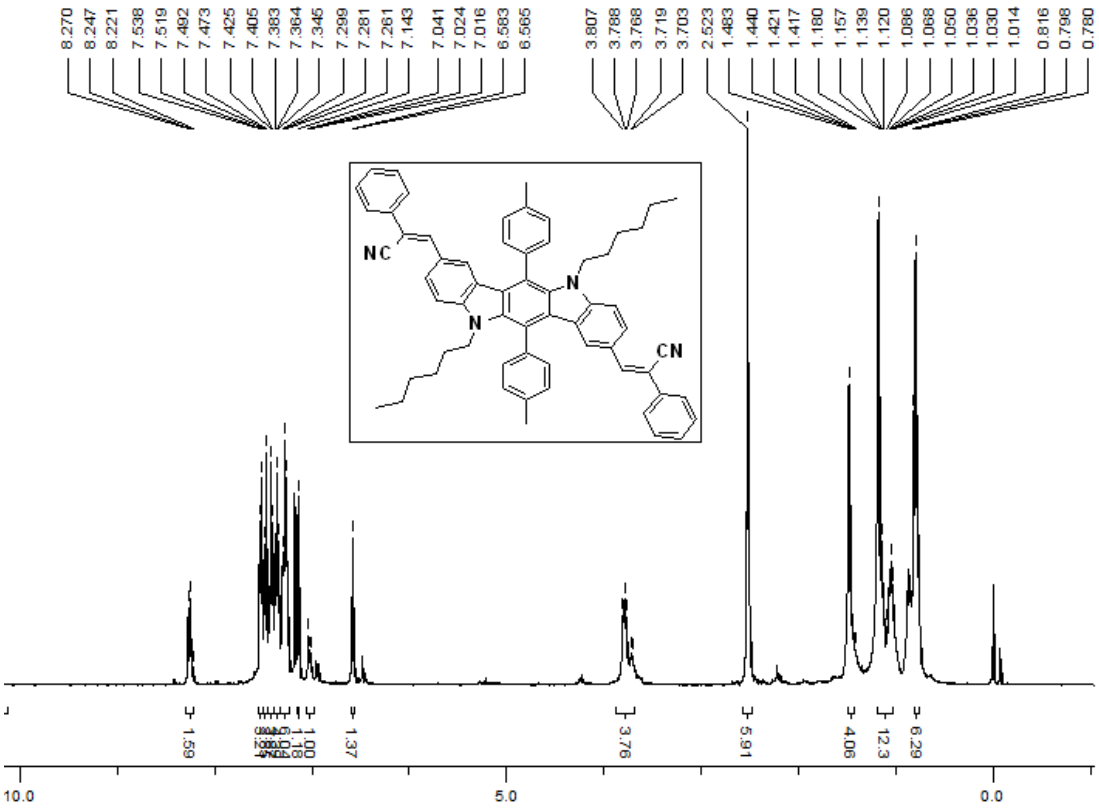

Fig. S5 ^{1}H NMR spectrum of compound **3**

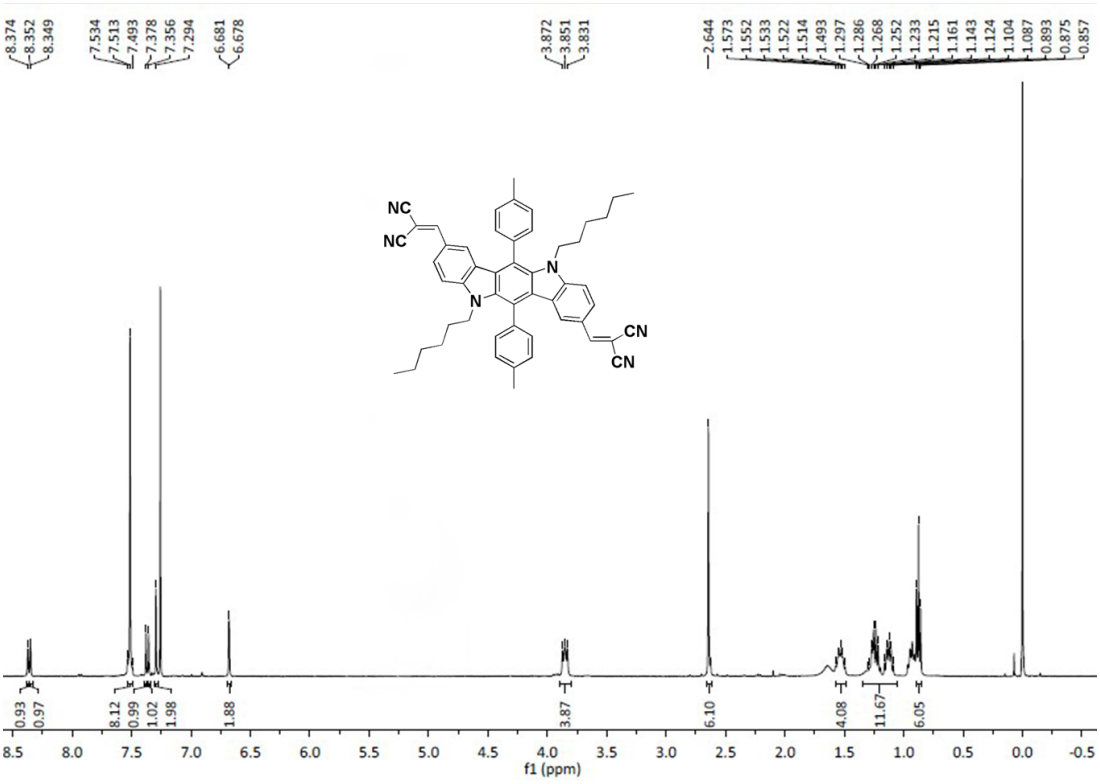

Fig. S6 ^{1}H NMR spectrum of compound **4**

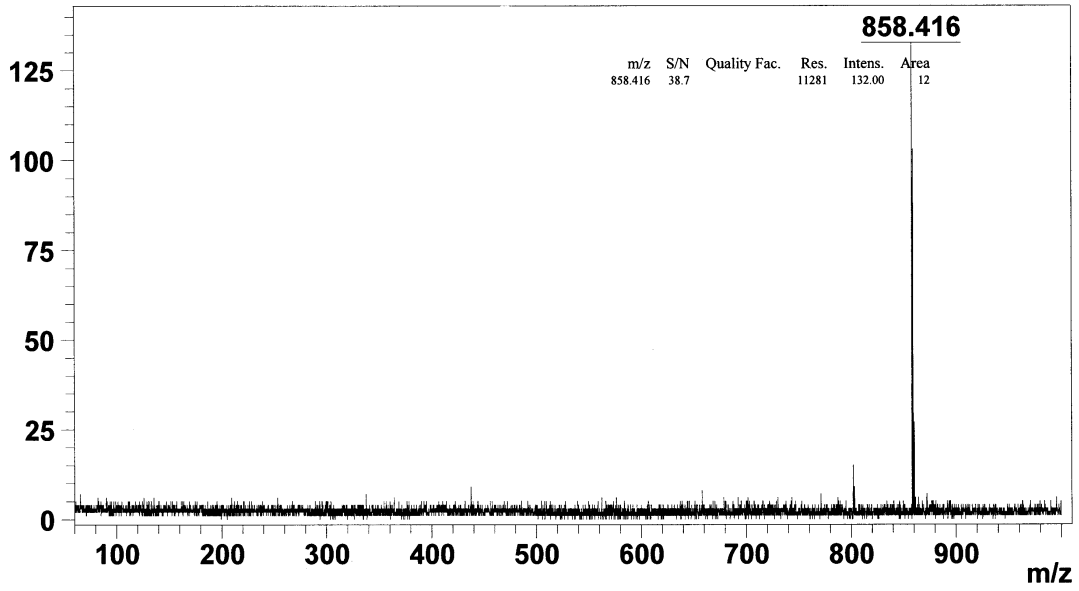

Fig. S7 Mass spectrum of compound **3**

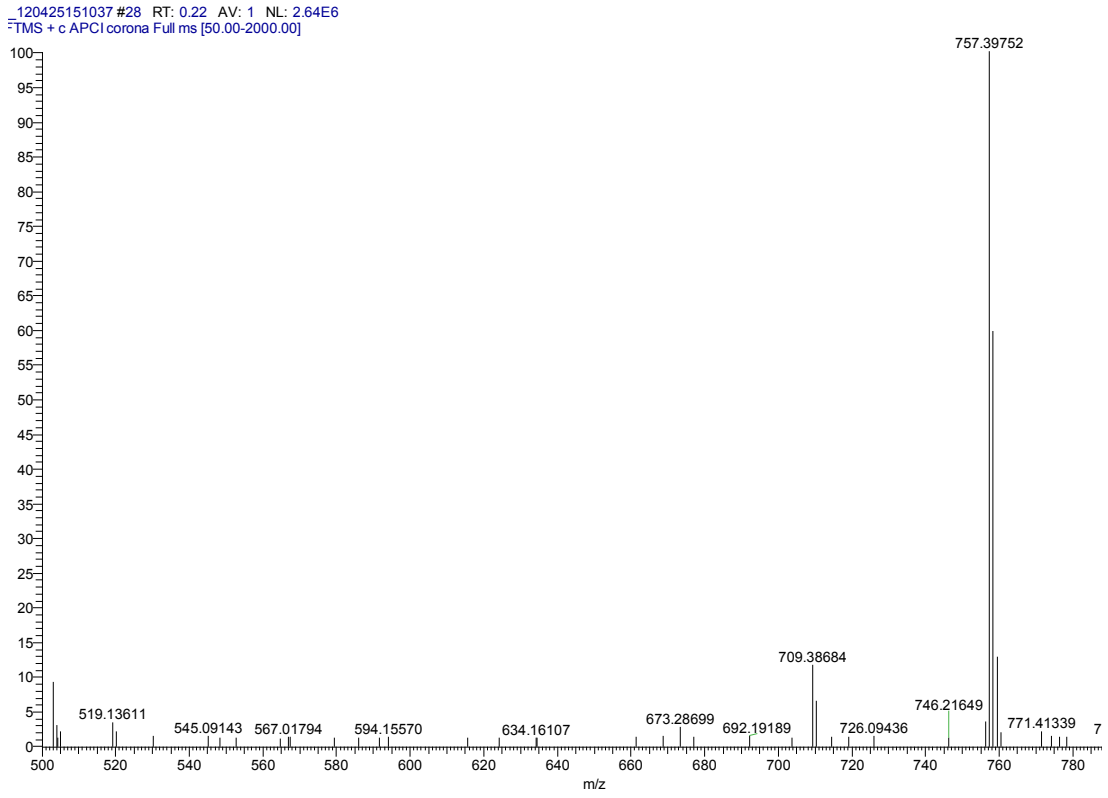

Fig. S8 Mass spectrum of compound **4**