Supporting Information:

Efficient non-doped yellow OLEDs based on thermally activated delayed fluorescence conjugated polymers with acridine/carbazole donor backbone and triphenyltriazine acceptor pendant

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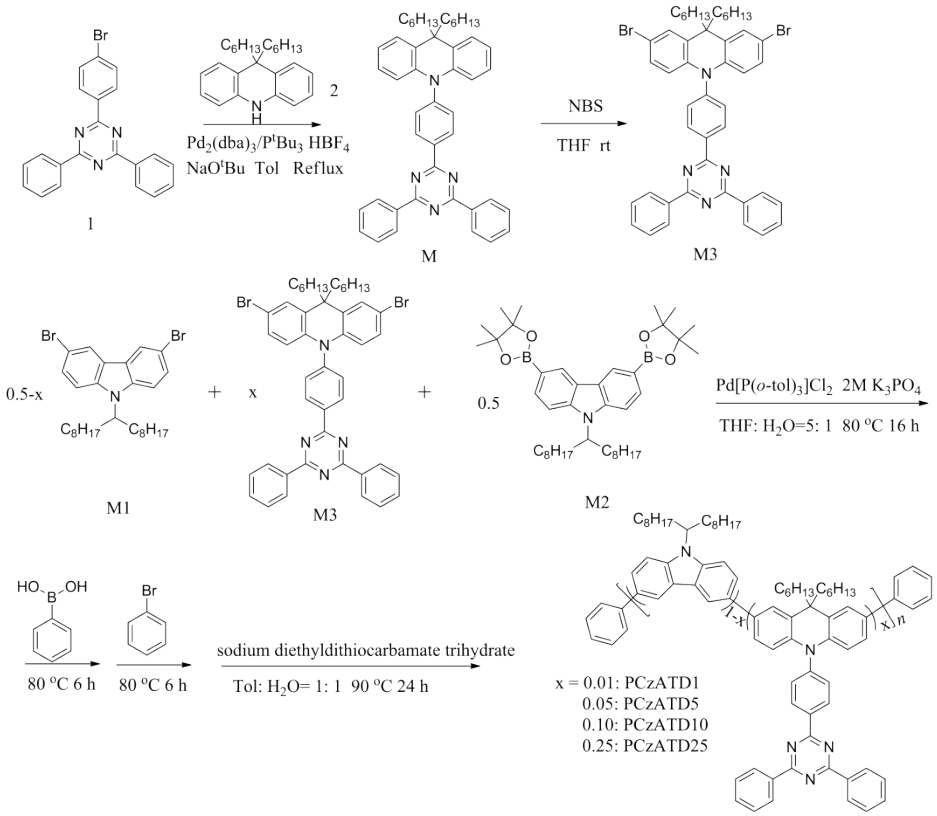
Experimental Section

General information: All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures. 2-Bromo-4,6-di-tert-butyl-1,3,5-triazine (**1**),[1] 9,9-dihexyl-9,10-dihydroacridine (**2**),[2] and 3,6-dibromo-9-(heptadecan-9-yl)-9H-carbazole (M1) and 9-(heptadecan-9-yl)-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (M2)[3] were prepared according to the reference.

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker Avance 400 NMR spectrometers. MALDI-TOF mass spectra were performed on an AXIMA CFR MS apparatus (COMPACT). Molecular weight of the polymers were determined by gel permeation chromatography (GPC) on a Waters 410 instrument with

polystyrene as a standard and THF as eluent. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C min^{-1} from 25 to 800 °C. Diferential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 at a heating rate of 10 °C min^{-1} from 25 to 300 °C under a nitrogen atmosphere. The glass transition temperature (T_g) was determined from the second heating scan. Elemental analysis was performed with Bio-Rad Co's elemental analyzer with element C, H, N. Cyclic Voltammetry experiments were performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. The films of PCzATDx were tested in acetonitrile using ferrocene as an internal reference and n-Bu_4NPF_6 as the supporting electrolyte. The HOMO energy levels were calculated according to the equation: EHOMO = − [E(onset,ox vs Fc/Fc+) + 4.8] (eV). UV-visible (UV-vis) absorption and Steady State photoluminescence spectra were measured with a Perkin-Elmer Lambda 35 UV-vis spectrometer and a Perkin-Elmer LS 50B spectrofluorometer, respectively. Absolute quantum efficiencies were measured by HAMAMATSU C9920 with an integration sphere. Fluorescence lifetimes were carried out with Edinburgh fluorescence spectrometer (FLS920) and measured using picosecond pulsed diode laser under the excitation at 375 nm.

Synthesis



Scheme S1. Synthetic routes for M3 and PCzATDx.

M: 9,9-dihexyl-10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,10-dihydroacridine

2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (**1**) (0.65 g, 3.60 mmol), 9,9-Dihexyl-9,10-dihydroacridine (**2**) (1.05 g, 3.00 mmol) , $Pd_2(dba)_3$ (0.055 g, 0.06 mmol), P^tBu_3•HBF_4(0.070 g, 0.24 mmol), ^{t}BuONa (0.72 g, 7.50 mmol) and dried toluene (30 mL) were added into 100 mL flask and purged with argon. The mixture was stirred and refluxed for 16 h. The cooled mixture was extracted with CH_2Cl_2 (DCM), washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by column chromatography (eluent: PE:DCM = 5:1, v/v) to get light green solid. Yield: 1.83 g, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 8.5 Hz, 2H), 8.82 (dd, *J* = 8.1, 1.6 Hz, 4H), 7.68-

7.57 (m, 6H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.33 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.96-6.85 (m, 4H), 6.23 (dd, *J* = 7.9, 1.4 Hz, 2H), 2.02-1.92 (m, 4H), 1.23-1.07 (m, 16H), 0.82 (t, *J* = 6.8 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 171.93, 170.89, 144.74, 140.63, 136.67, 135.99, 132.80, 131.99, 131.27, 129.44, 129.13, 129.05, 128.76, 128.07, 115.80, 113.22, 46.32, 44.62, 31.63, 29.62, 24.87, 22.67, 14.12. MALDI-TOF $[M+H]^+$ calcd. for $C_{46}H_{49}N_4$: 657.40; found, 657.4. HRMS $[M+H]^+$ calcd. for $C_{46}H_{49}N_4$: 657.3957; found, 657.3965.

M3: 9,9-dihexyl-2,7-dibromo-10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,10-dihydroacridine

9,9-dihexyl-10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,10-dihydroacridine (1.31 g, 2.00 mmol), NBS (0.73 g, 4.10 mmol) and THF (40 mL) were added into a 100 mL flask. The mixture was stirred at room temperature in the dark. After 14 h, the solvent was removed using a rotary evaporator. The crude product was purified by flash chromatography using PE/DCM (5:1) as eluent and re-crystallized from hot ethanol to give light yellow crystals. Yield: 1.55 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 8.5 Hz, 2H), 8.81 (dd, *J* = 8.2, 1.5 Hz, 4H), 7.69-7.56 (m, 6H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 2.3 Hz, 2H), 7.01 (dd, *J* = 8.9, 2.2 Hz, 2H), 6.10 (d, *J* = 8.9 Hz, 2H), 1.98-1.83 (m, 4H), 1.28-1.04 (m, 16H), 0.85 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.87, 171.14, 145.84, 141.92, 136.11, 136.09, 132.71, 131.82, 131.73, 129.05, 128.74, 126.46, 126.28, 126.19, 120.44, 113.92, 46.12, 44.16, 31.73, 29.89, 24.99, 22.74, 14.12. MALDI-TOF $[M+H]^+$ calcd. for $C_{46}H_{47}Br_2N_4$: 813.22; found, 813.2. HRMS $[M+H]^+$ calcd. for $C_{46}H_{47}Br_2N_4$: 813.2167; found,

813.2145.

Table S1. Weight-average and number-average molecular weights (M_w and M_n) and polydispersity index (PDI) values of PCzATDx evaluated by GPC.

Polymers	M_n (Da)	M_w (Da)	PDI
PCzATD1	5700	13000	2.3
PCzATD5	6600	13000	2.0
PCzATD10	7700	16700	2.2
PCzATD25	10600	22300	2.1

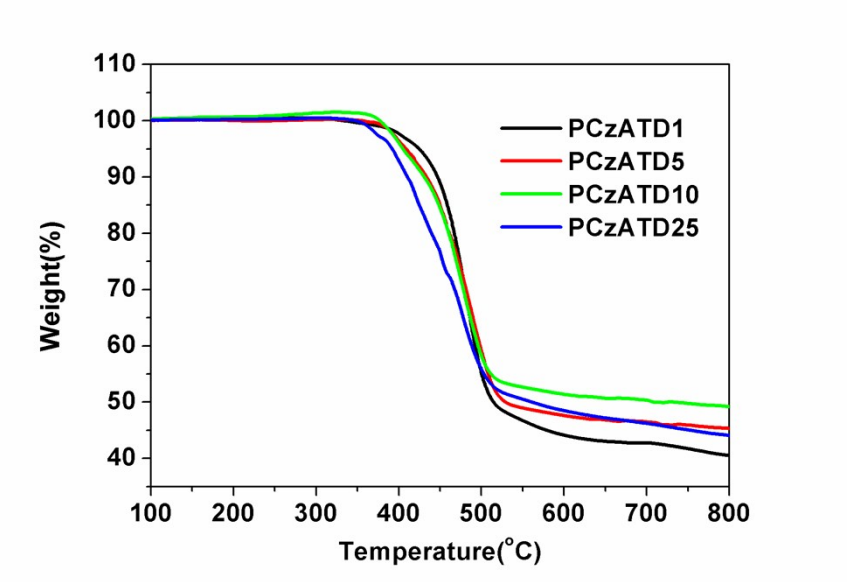


Figure S1. TGA curves of PCzATDx at a heating rate of 10 °C min^{-1} under N_2.

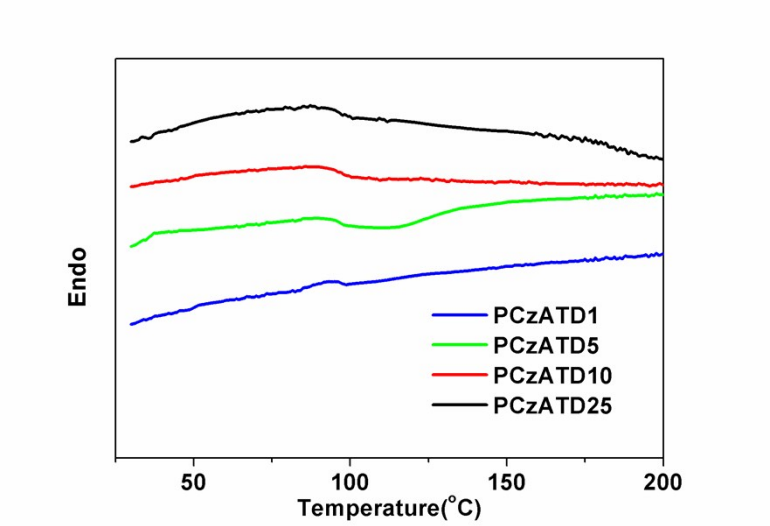


Figure S2. DSC thermograms of PCzATDx on second-heating processes at a scanning rate of 10 °C min^{-1} under N2.

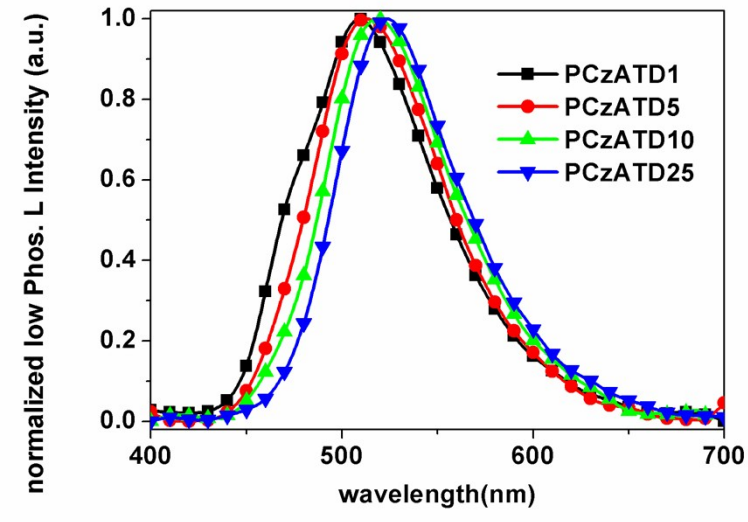


Figure S3. Phosphorescence spectra of PCzATDx in toluene at 77 K.

Table S2. HOMO, LUMO and the ΔE_{ST} of ATD, 2Cz-ATD and 4Cz-ATD obtained by time-depended density functional theory calculations B3LYP/6-31G(d).

	HOMO [eV]	**LUMO** [eV]	**ΔE_{ST}** [eV]
ATD	4.87	1.96	0.073
2Cz-ATD	4.54	1.96	0.044
4Cz-ATD	4.49	1.93	0.033

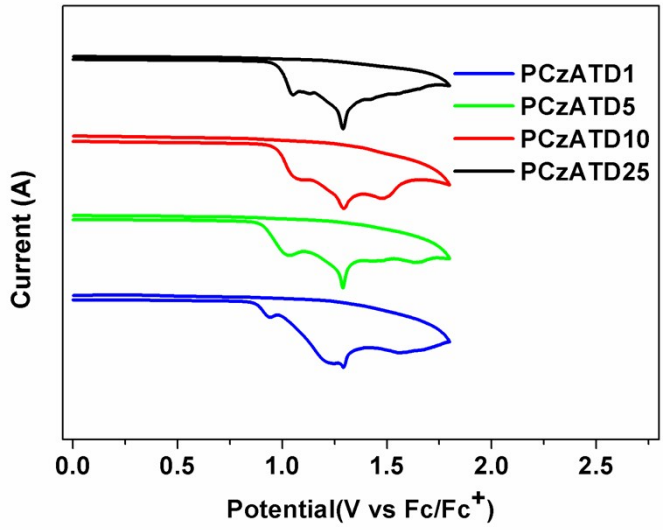


Figure S4. Cyclic Voltammogram of PCzATDx for oxidation.

Table S3. The optical properties of the TADF polymers.[4]

polymers	τ_p [ns][a)]	τ_d [μs][b)]	Φ_{PL} [%]	Φ_{PF} [%]	Φ_{DF} [%]	k_{PF} ($10^7 s^{-1}$)	k_{DF} ($10^5 s^{-1}$)	k_{ISC} ($10^7 s^{-1}$)	k_{RISC} ($10^6 s^{-1}$)	k_{CQ} ($10^5 s^{-1}$)
PCzATD1	25.2	1.4	0.90	0.39	0.51	-	-	-	-	-
PCzATD5	27.9	1.1	0.89	0.44	0.45	3.6	9.1	2.0	2.0	0
PCzATD10	28.2	1.1	0.87	0.46	0.41	3.5	9.1	1.9	-	1.0
PCzATD25	29.0	1.0	0.65	0.39	0.26	3.4	10.0	2.1	-	1.5

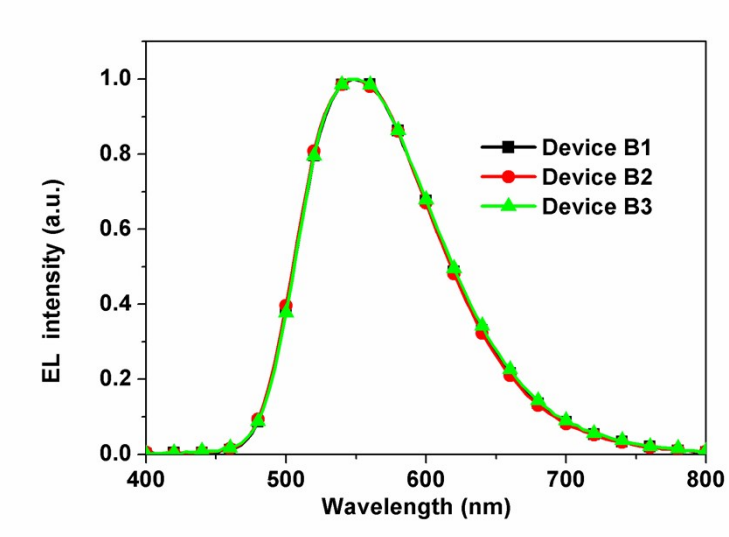


Figure S5. EL spectra measured for devices B1-B4 at 6 V.

Table S4. The EL data of the reported excellent non-doped TADF OLEDs.

Emitters	Type of Emitter	Fabrication process	EL_{max} [nm]	V_{on} (V)	EQE_{max} (%)	EQE_{1000} (%)	Ref
DMAC-TRZ	Small molecule	Solution processing	~504	4.0	16.8	13.7	5
DMAC–BP	Small molecule	Vacuum evaporation	510	2.6	18.9	18.0	6
DMAC–DPS	Small molecule	Vacuum evaporation	479	4.3	19.5	-	6
DMAC-TRZ	Small molecule	Vacuum evaporation	514	~3	20	12.4	7
PTSOPO	Small molecule	Vacuum evaporation	~530	2.5	17.0	~15.0	8
DBT-BZ-DMAC	Small molecule	Vacuum evaporation	~515	2.7	14.2	14.2	9
TA-3Cz	Dendrimer	Solution processing	546	2.4	11.8	-	10
3CzSO	Dendrimer	Solution processing	516	-	10.7	~2.0	11
*t*BuG2TAZ	Dendrimer	Solution processing	502	3.5	9.5	~7.8	12
Cz-CzCN	Dendrimer	Solution processing	510	3.1	17.1	~16.3	13
LEP	Polymer	Solution processing	535	3.0	10	~3.0	14
PAPTC	Polymer	Solution processing	521	2.6	12.6	~8.2	2
PCzATD5	Polymer	Solution processing	548	2.6	15.5	14.5	This work

NMR spectra for isolated compounds and polymers.

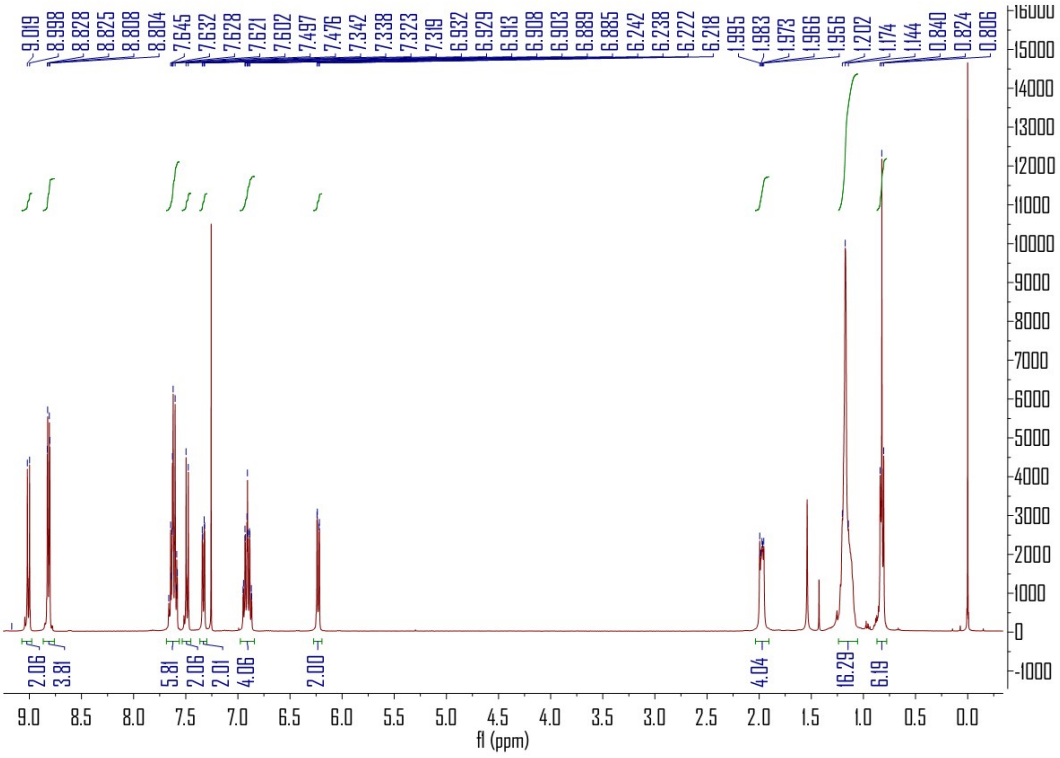


Figure S6. ^{1}H NMR spectrum of **M** in $CDCl_3$.

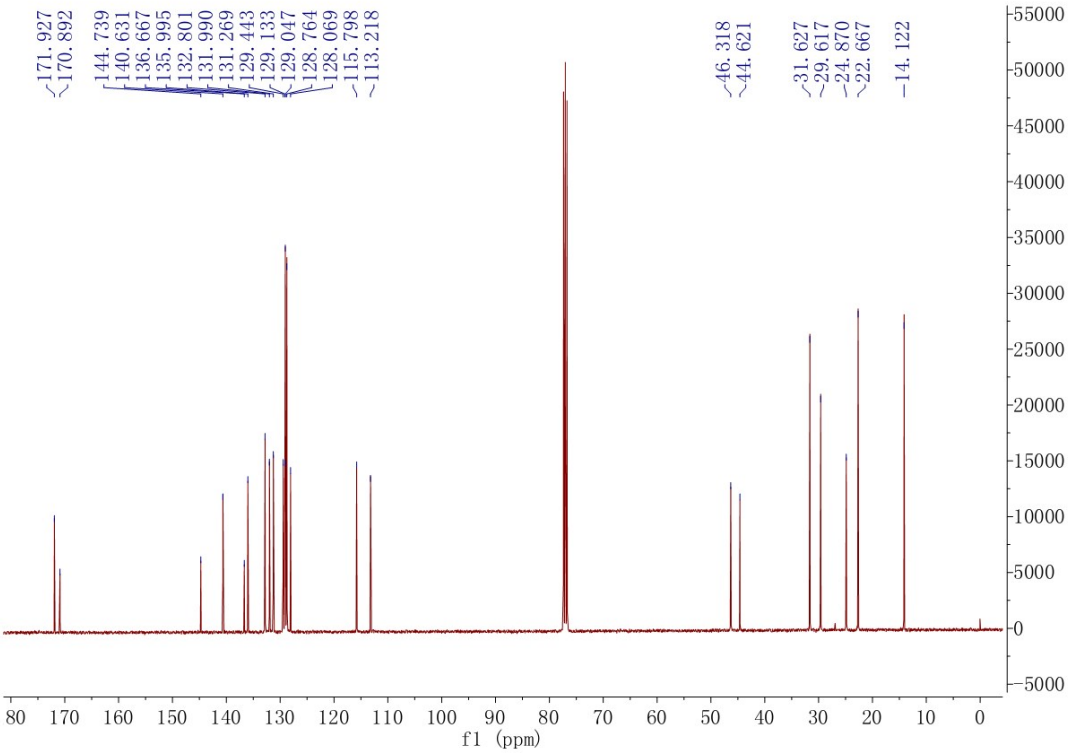


Figure S7. ^{13}C NMR spectrum of **M** in $CDCl_3$.

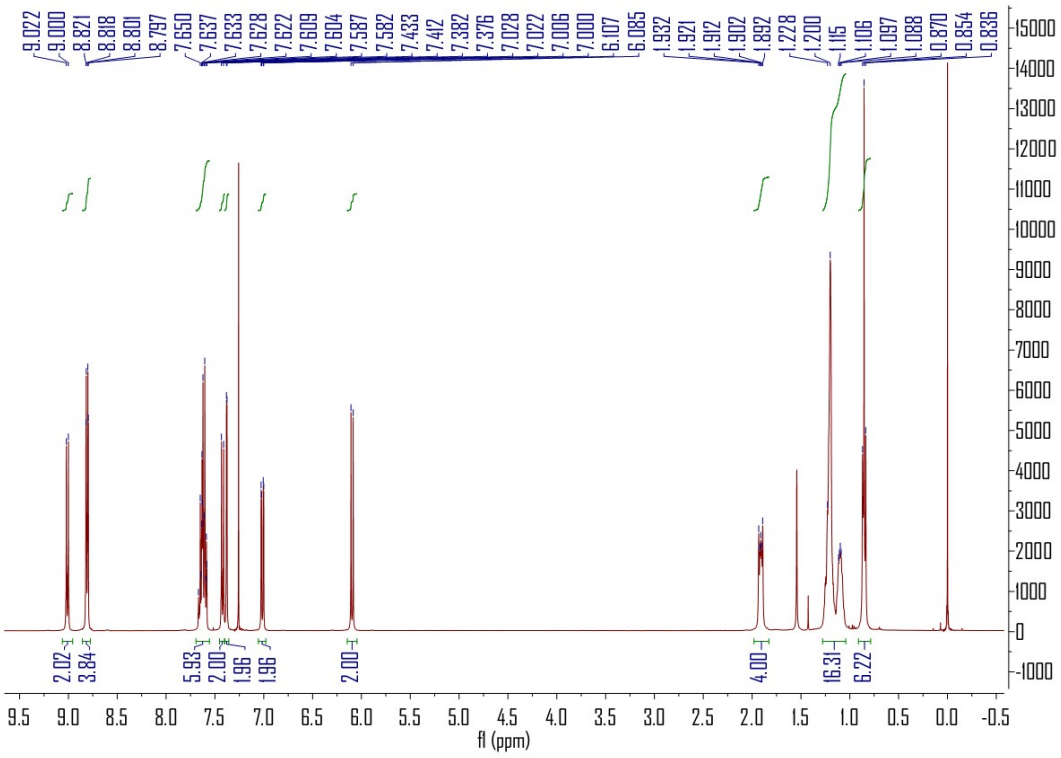


Figure S8. ^{1}H NMR spectrum of M**3** in $CDCl_3$.

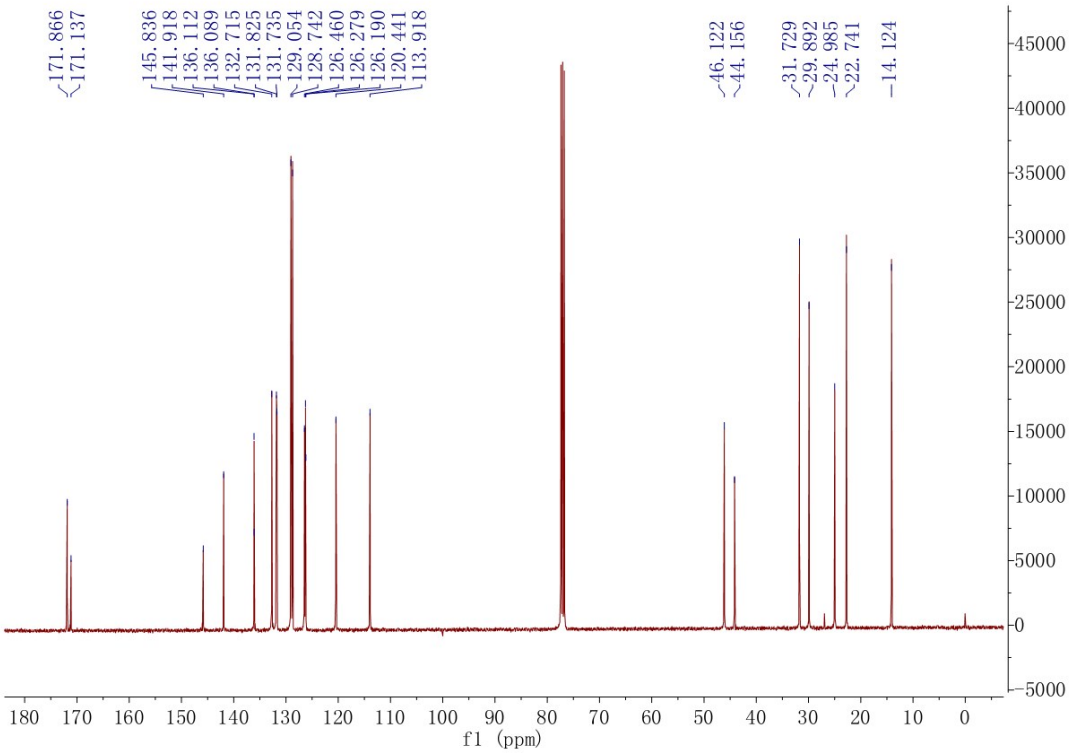


Figure S9. ^{13}C NMR spectrum of M**3** in $CDCl_3$.

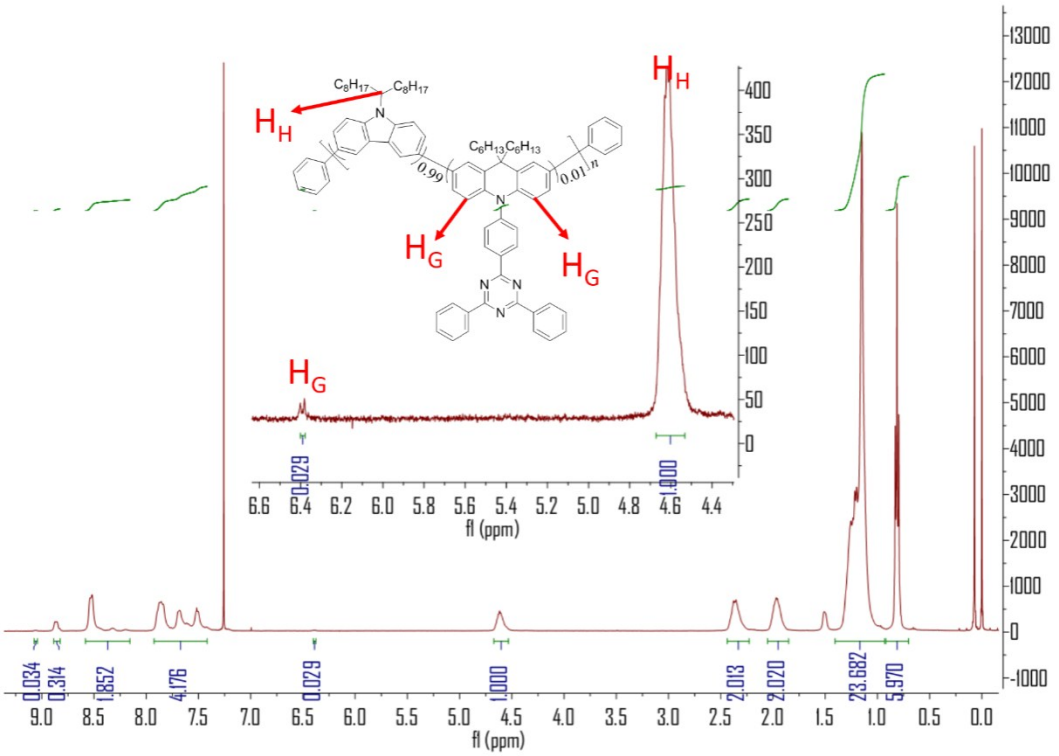


Figure S10. ^{1}H NMR spectrum of PCzATD1 in $CDCl_3$. The molar ratio (x) of the ATD unit in PCzATD1 can be calculated by the calculation formula: x% = $0.5H_G$ / ($0.5H_G$ + H_H) ×100% = 1.4%. And the calculation method below is the same as this one.

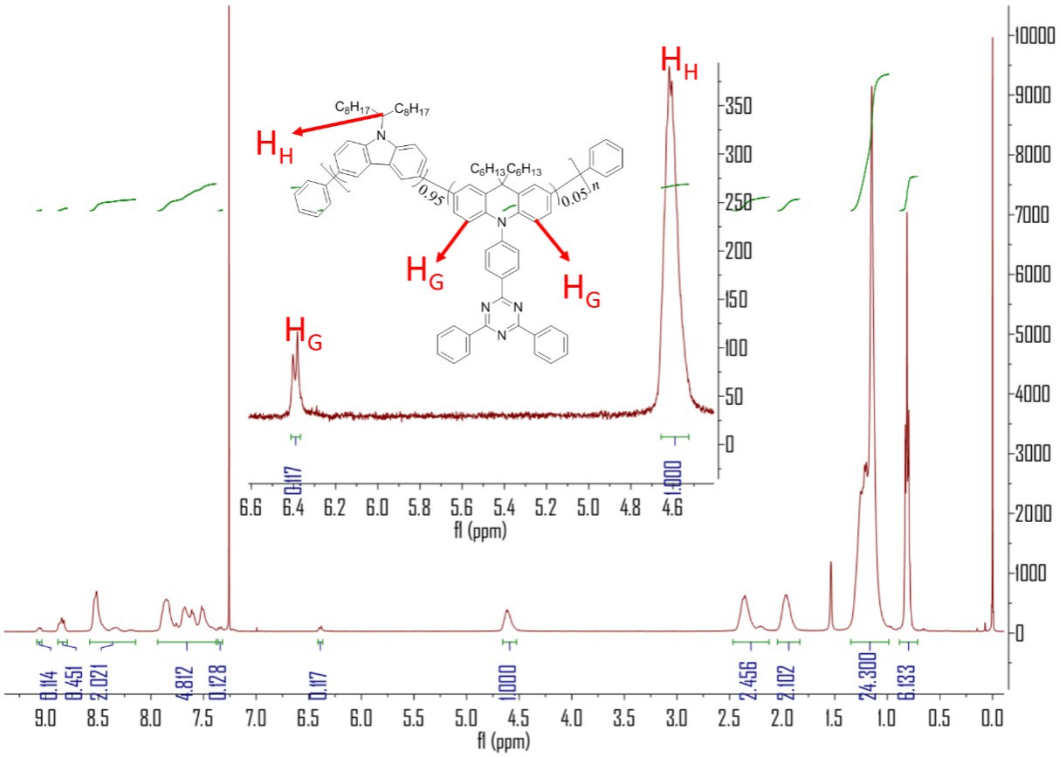


Figure S11. ^{1}H NMR spectrum of PCzATD5 in $CDCl_3$. x% = 5.5%.

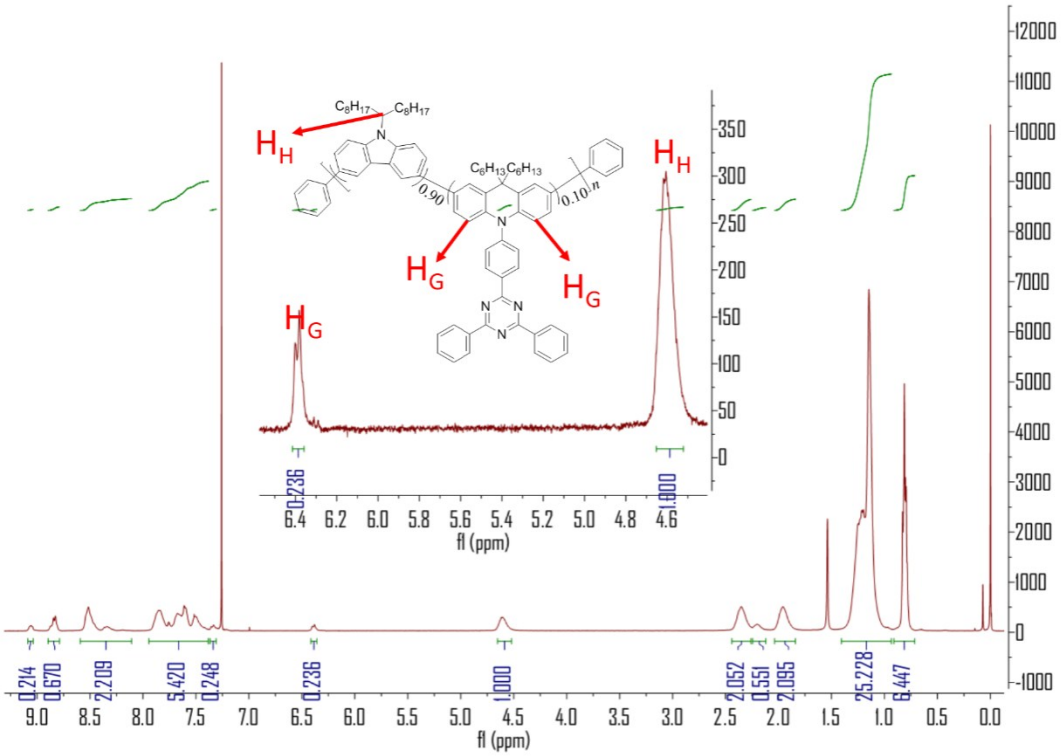


Figure S12. ^{1}H NMR spectrum of PCzATD10 in $CDCl_3$. x% = 10.5%.

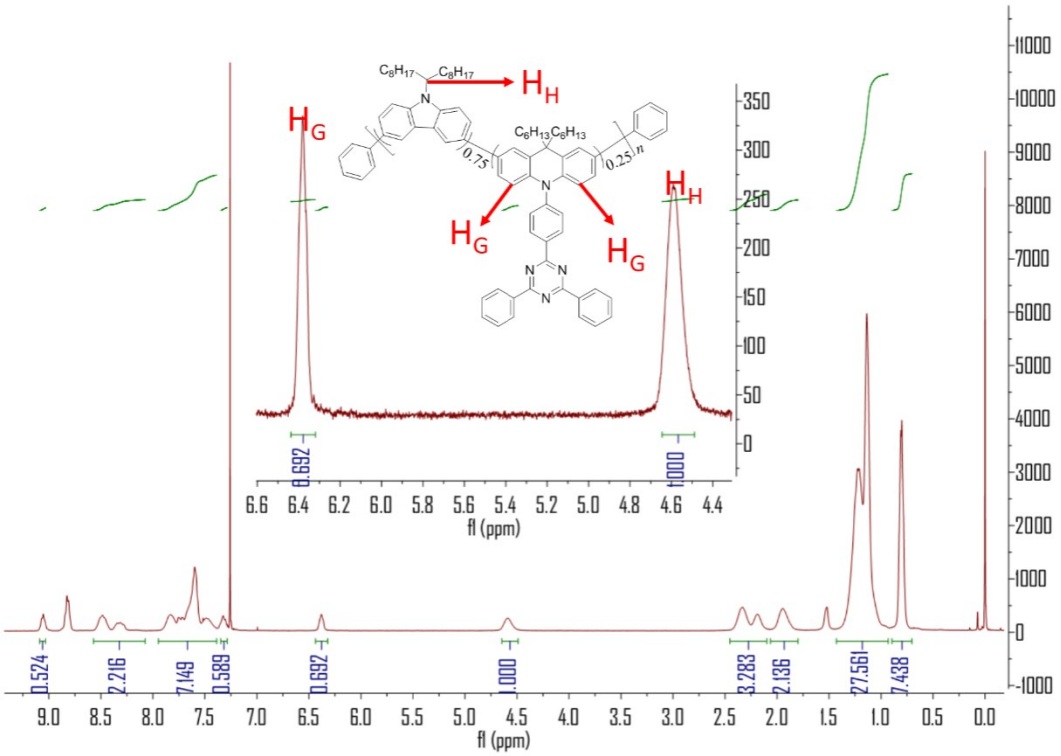


Figure S13. ^{1}H NMR spectrum of PCzATD25 in $CDCl_3$. x% = 26%

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