Electronic Supplementary Information (ESI)

Deep-Red TADF Dendronized Polymer for Efficient Non-Doped Solution-Processed OLEDs

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1. Characterization.

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV400 (400 MHz) spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS; δ = 0) as the internal reference. ^{1}H NMR spectra data are reported as chemical shift, relative integral, multiplicity (s = singlet, d = doublet, m = multiplet), coupling constant (*J* in Hz), and assignment. UV−vis absorption spectra were recorded on a Hitachi U-2900 spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA Q2000 differential scanning calorimeter 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. Thermogravimetric analysis (TGA) was performed with a METTLER TOLEDO TGA/DSC 1/1100SF 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. Cyclic voltammetry (CV) was carried out in nitrogen-purged acetonitrile at room temperature with a CHI 660E voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF6) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consisted of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/ AgCl pseudoreference electrode with ferrocenium−ferrocene (Fc^{+}/Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 50 mV s^{-1}. The onset potential was determined from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammogram. Gel permeation chromatography (GPC) analysis was carried out on a Waters 515-2410 system using polystyrene standards as molecular weight references and tetrahydrofuran (THF) as the eluent. PL spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. The temperature dependence of transient PL decay curves in films and PL spectra in vacuum/air were determined using a spectrometer (FLS980) from Edinburgh Instruments Limited. The PLQYs of solid films were measured on an FLS980 instrument with an integrating sphere (Φ = 150 mm). Density functional theory (DFT) and time dependent -DFT (TD-DFT) calculations were performed using Gaussian 09

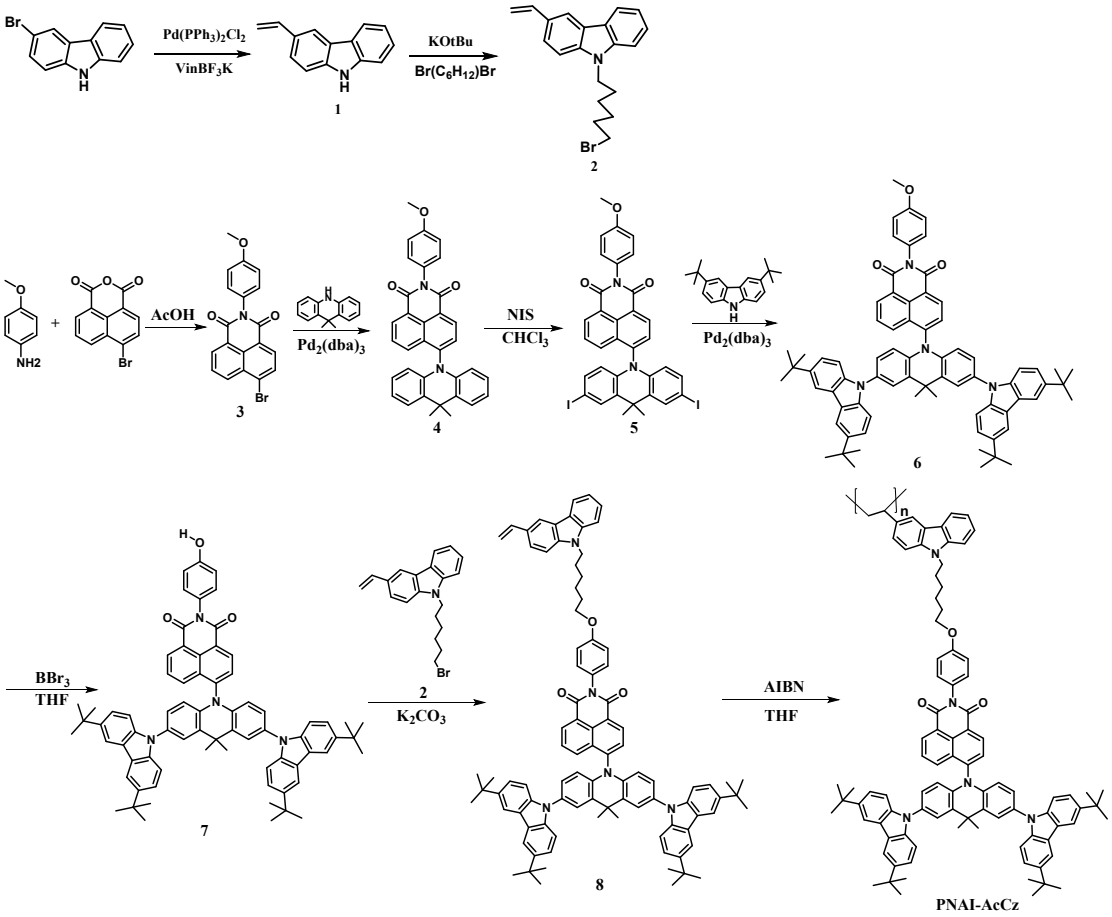
on the nodes of a supercomputer.

2. Device Fabrication and Characterization.

The hole-injection material PEDOT:PSS (8000) and electron-transporting material TmPyPB were obtained from commercial sources. ITO coated glass with a sheet resistance of 10 Ω per square was used as the substrate. Before device fabrication, the ITO-coated glass substrate was precleaned and exposed to UV-ozone for 2 min. PEDOT:PSS was then spin-coated onto the clean ITO substrate as a hole-injection layer. Next a solution of emitter in chlorobenzene was spin-coated (1 mg ml^{-1}; 2000 rpm) to form a 40 nm-thick emissive layer and annealed at 80 °C for 30 min to remove the residual solvent. Finally, a 45 nm-thick electron-transporting layer of 1,3,5-tris(3-pyridyl-3-phenyl)benzene (TmPyPB) was vacuum deposited, and a cathode composed of a 1 nm-thick layer of LiF and aluminum (100 nm) was sequentially deposited onto the substrate through shadow masking with a pressure of 10^{-6} Torr. Deposition rates are 1–2 Å. s^{-1} for organic materials, 0.1 Å. s^{-1} for LiF, and 6 Å. s^{-1} for Al, respectively. The current density-voltage-luminance (*J-V-L*) characteristics of the devices were measured using a Keithley 2400 Source meter and a Keithley 2000 Source multimeter. The EL spectra were recorded using a JYSPEX CCD3000 spectrometer. The EQE values were calculated from the luminance, current density, and electroluminescence spectrum. All measurements were performed at room temperature under ambient conditions.

3. Materials Synthesis

The synthesis of **PNAI-AcCz** is shown in Scheme S1.



Scheme S1. Synthesis of **PNAI-AcCz**.

3-vinyl-9H-carbazole (**1**): A solution of potassium vinyltrifluoroborate (1.34 g, 10 mmol), $Pd(PPh_3)_2Cl_2$ (140.4 mg, 0.2 mmol), Cs_2CO_3 (9.78 g, 30 mmol), and 3-bromo-9H-carbazole (2.46 g, 10 mmol) in THF/H_2O (9:1) (20 mL) was heated at 85 °C under an N_2 atmosphere in a three-port flask. The reaction mixture was stirred at 85 °C for 22 h, then cooled to room temperature and diluted with H_2O (30 mL) followed by extraction with CH_2Cl_2 (30 mL × 3). The solvent was removed in vacuo, and the crude product was purified by silica gel chromatography (eluting with 5:1 *n*-pentane/ CH_2Cl_2) to yield 3-vinyl-9H-carbazole as a white solid (1.64 g, 0.848 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.01 (m, 3H), 7.59 – 7.53 (dd, 1H), 7.43 (dd, J = 16.3, 6.3 Hz, 3H), 6.93 (dd, J = 17.6, 10.8 Hz, 1H), 5.80 (d, J = 17.6 Hz, 1H), 5.23 (d, J = 10.9 Hz, 1H).

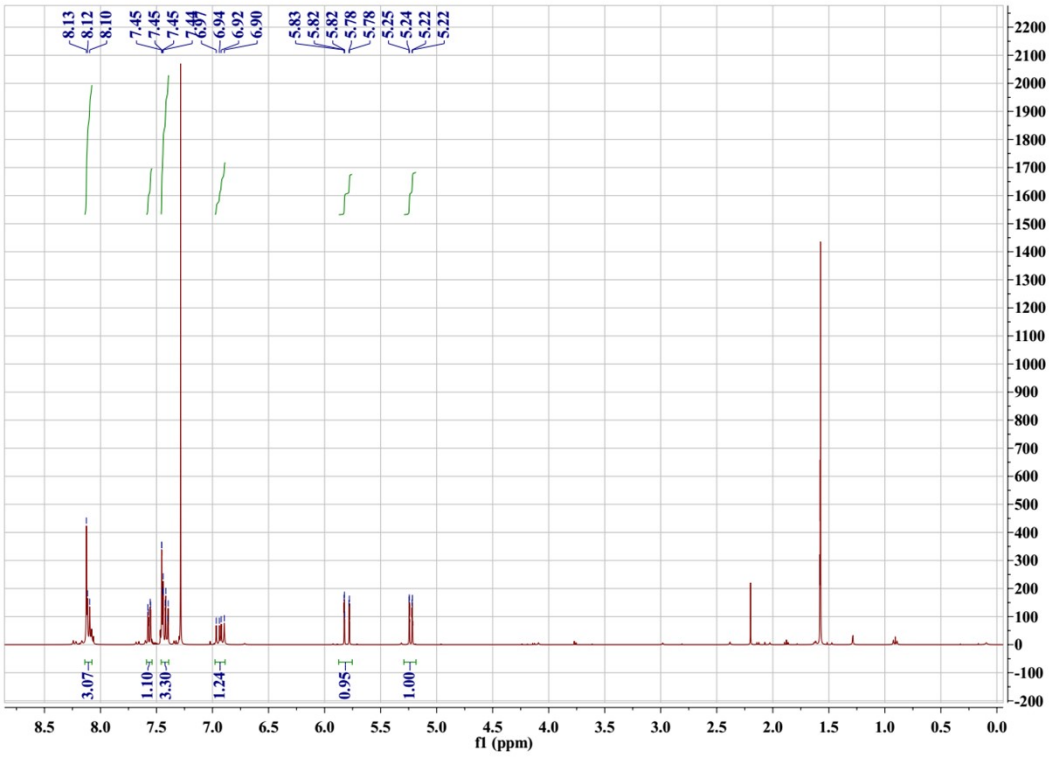


Fig. S1 ^{1}H NMR spectrum of 3-vinyl-9H-carbazole (**1**).

9-(6-bromohexyl)-3-vinyl-9H-carbazole (**2**): To a solution of **1** (1.93 g, 10 mmol) in dry THF (20 ml) was added KO^{t}Bu (1.41 g, 12.6 mmol) in several portions. The resulting solution was stirred for 10 min at room temperature, followed by dropwise addition to a refluxing solution of 1,6-dibromohexane (9.0 ml, 60 mmol) in THF (20 ml). After refluxing for 24 h, the reaction mixture was cooled to room temperature and quenched by adding several drops of water to destroy the excess KO^{t}Bu. The solvent THF and excess 1,6-dibromohexane were removed by rotatory evaporation and vacuum distillation, respectively. The residue was dissolved in CH_2Cl_2, washed with water three times, dried over anhydrous Na_2SO_4, filtered and concentrated for flash column chromatography (CH_2Cl_2/petroleum ether 1:5 v/v as eluent), affording **2** as a white solid (2.85 g 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.8, 4.7 Hz, 2H), 7.65 (dd, J = 8.5, 1.6 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.34 – 7.27 (m, 1H), 6.99 (dd, J = 17.6, 10.9 Hz, 1H), 5.90 – 5.76 (m, 1H), 5.28 (dd, J = 10.9, 0.8 Hz, 1H), 5.03 (ddd, J = 10.2, 9.6, 1.4 Hz, 2H), 4.34 (t, J = 7.2 Hz, 2H), 2.15 (td, J = 7.2, 1.2 Hz, 2H), 2.00 – 1.84 (m, 3H), 1.59 – 1.47 (m, 3H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 140.85, 140.34, 138.26, 137.60, 128.91, 125.81, 125.65, 124.04, 123.06, 122.98, 120.47, 120.42, 119.01, 118.51, 115.05, 115.02, 111.03, 108.86, 108.72, 43.03, 33.51, 28.46, 26.57. HRMS-ASAP-TOF$^+$ (m/z) calcd. for $C_{20}H_{22}BrN$ $[M+H]^+$: 356.1014; found: 356.1014. Anal. calcd for $C_{20}H_{22}BrN$ (%): C, 67.42; H, 6.22; N, 3.93. found: C, 67.44; H, 6.20; N, 3.92.

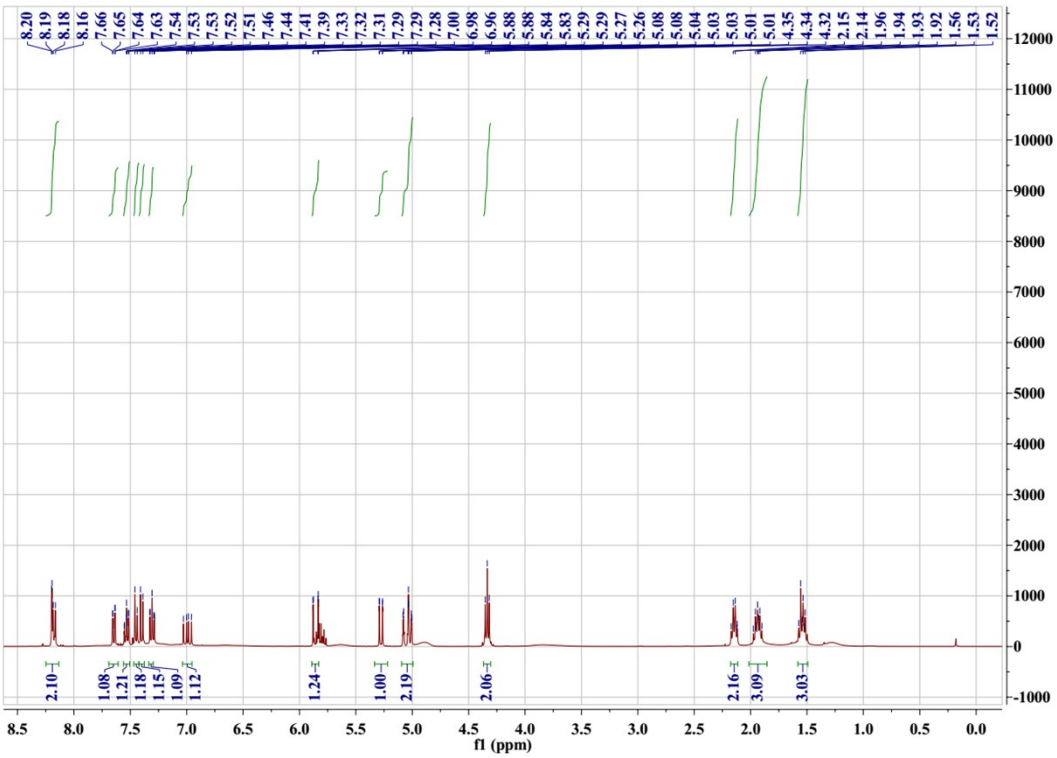


Fig. S2 ^{1}H NMR spectrum of 9-(6-bromohexyl)-3-vinyl-9H-carbazole (**2**).

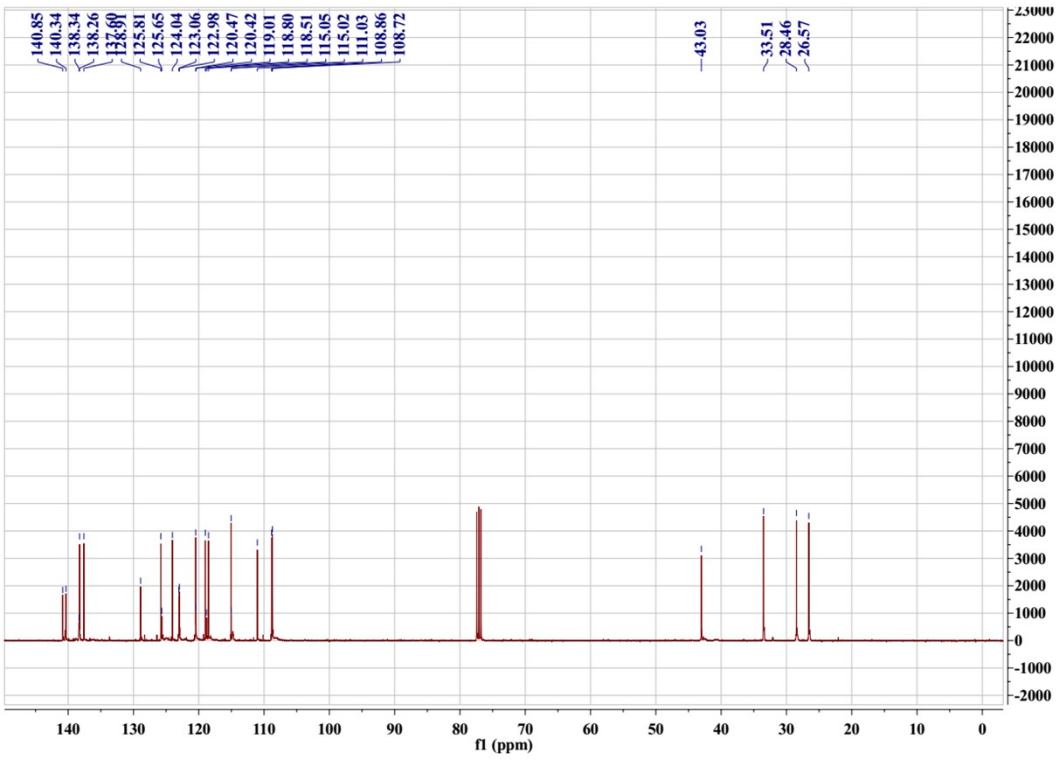


Fig. S3 ^{13}C NMR spectrum of 9-(6-bromohexyl)-3-vinyl-9H-carbazole (**2**).

6-bromo-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (3): A mixture of 6-bromo-1H,3H-benzo[de]isochromene-1,3-dione (2.77 g, 10 mmol) and 4-methoxyaniline (1.48 g, 12 mmol) was added into a flask, then dissolved in acetic acid (50 mL). The reaction mixture was stirred and heated at reflux under nitrogen for 24 h. After cooling, the mixture was poured slowly into water and extracted with dichloromethane (50 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, and the filtered solution was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with dichloromethane and *n*-hexane (v/v=1/2) as eluent. A white powder was obtained with a yield of 90% (3.44 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, J = 28.7, 7.8 Hz, 2H), 8.48 (d, J = 7.8 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.91 (t, J = 7.9 Hz, 1H), 7.34 – 7.20 (m, 2H), 7.09 (d, J = 8.7 Hz, 2H), 3.90 (s, 3H).

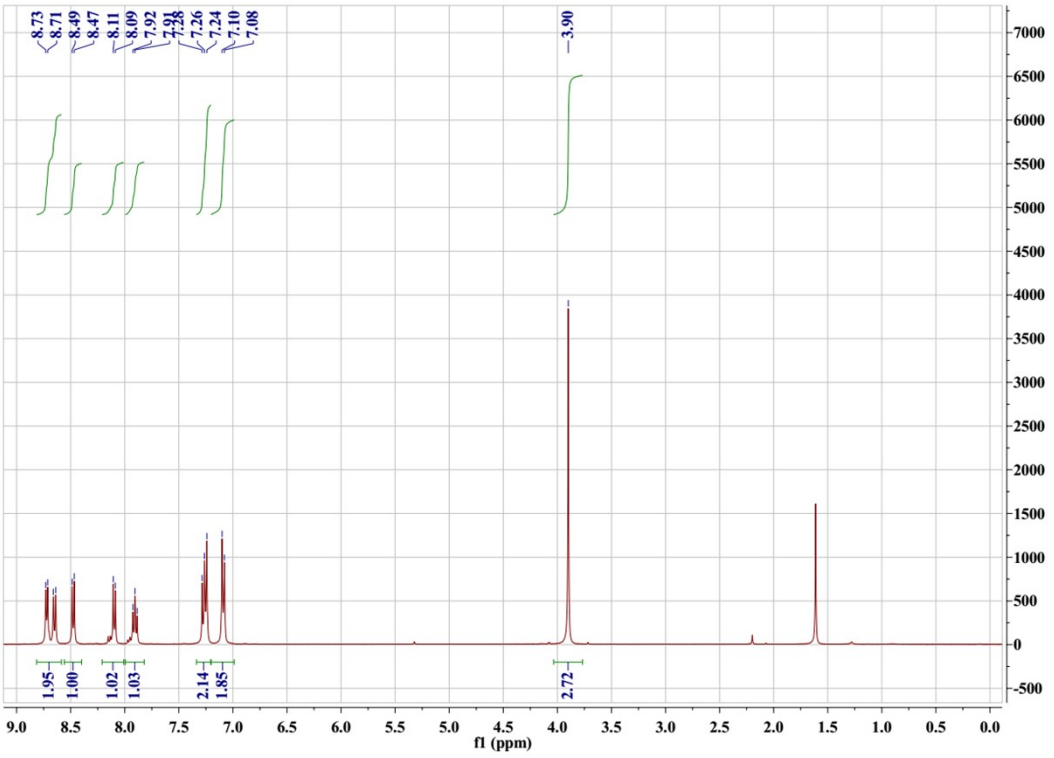


Fig. S4 ^{1}H NMR spectrum of 6-bromo-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**3**).

6-(9,9-dimethylacridin-10(9H)-yl)-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (4): Compound **3** (2.29 g, 6.0 mmol) , 9,9-dimethyl-9,10-dihydroacridine (1.26 mg, 6.0 mmol), tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3 \cdot CHCl_3$) (38 mg, 37 μmol), (t-Bu)$_3$PH-BF$_4$ (21 mg, 73 μmol) and sodium *tert*-butoxide (NaO^{t}Bu) (960 mg, 10 mmol) in toluene (30 ml) was stirred at 100 °C under argon for 24 h. After cooling to room temperature, the mixture was washed with brine and the organic phase was dried with anhydrous sodium sulfate. After removing of the solvent, the mixture was applied to a silica gel column, eluting with cyclohexane/dichloromethane 4/1 v/v to give the crude product as a white power. The powder was further crystallized from a mixture of hexane and CH_2Cl_2 to afford the pure product **4** (2.6 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.90 (dd, *J* = 10.6, 6.5 Hz, 1H), 8.78 – 8.67 (m, 1H), 8.18 – 8.07 (m, 1H), 7.91 – 7.83 (m, 1H), 7.69 (ddd, *J* = 10.0, 6.7, 3.2 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.32 – 7.29 (m, 2H), 7.17 – 7.08 (m, 2H), 7.03 – 6.96 (m, 2H), 6.94 – 6.85 (m, 2H), 6.04 – 5.97 (m, 2H), 3.98 – 3.88 (m, 3H), 2.10 – 2.05 (m, 2H), 1.92 – 1.74 (m, 6H), 1.62 – 1.55 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.98, 159.68, 144.48, 140.10, 132.98, 132.39, 130.82, 130.64, 130.45, 129.97, 129.56, 128.10, 127.73, 126.76, 126.02, 123.94, 123.20, 121.33, 114.85, 114.03, 60.42, 55.54, 36.09, 32.78, 32.12, 14.22. HRMS-ASAP-TOF$^+$ (m/z) calcd. for $C_{34}H_{26}N_2O_3$ $[M+H]^+$: 511.2022; found: 511.2008. Anal. calcd for $C_{34}H_{26}N_2O_3$ (%): C, 79.98; H, 5.13; N, 5.49. found: C, 79.96; H, 5.12; N, 5.50.

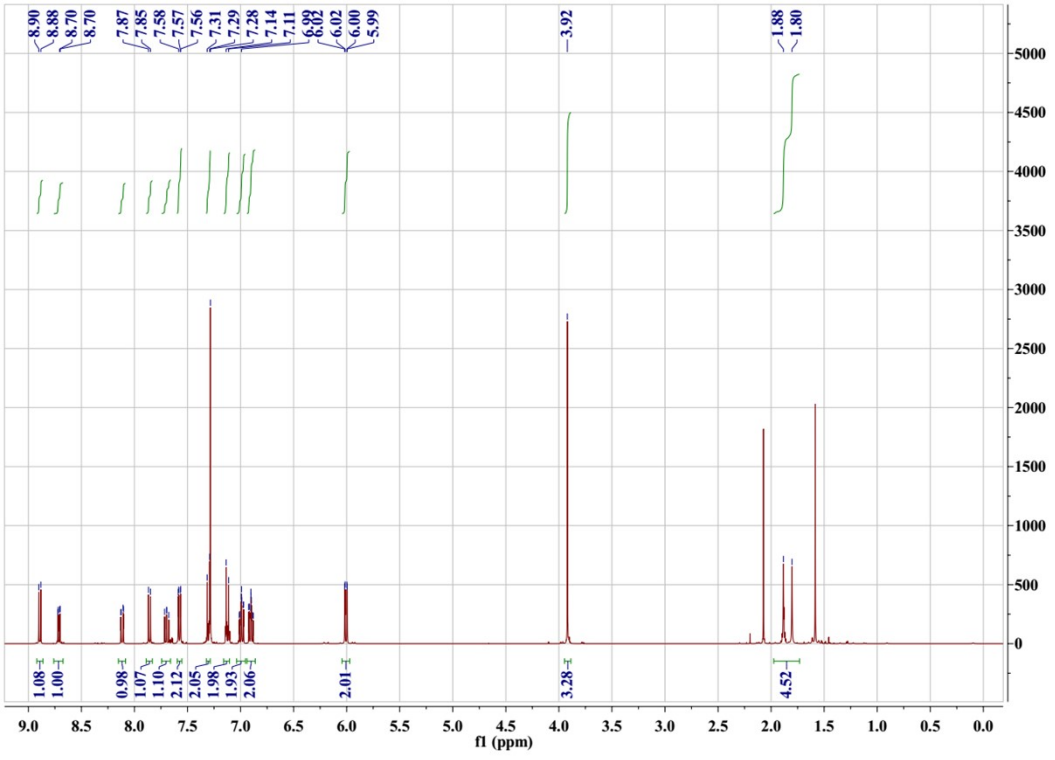


Fig. S5 ^{1}H NMR spectrum of 6-(9,9-dimethylacridin-10(9H)-yl)-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**4**).

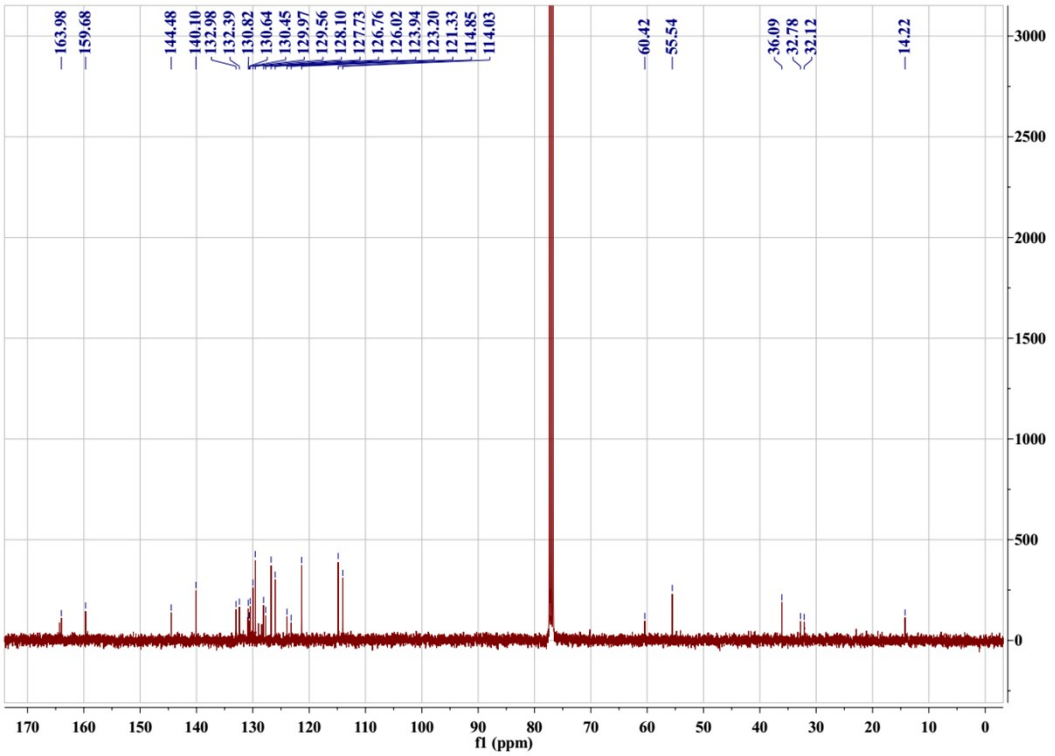


Fig. S6 ^{13}C NMR spectrum of 6-(9,9-dimethylacridin-10(9H)-yl)-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**4**).

6-(2,7-diiodo-9,9-dimethylacridin-10(9H)-yl)-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (5): A solution of *N*-iodosuccinimide (472 mg, 2.1 mmol) in dry chloroform (10 ml) was dropped into a solution of **4** (762 mg, 1.0 mmol) in dry chloroform (10 ml). The mixture was placed away from light and stirred at 50 ^{o}C for 48 hours. After that time, the reaction mixture was slowly cooled to room temperature, washed with aqueous sodium thiosulfate solution (3 x 50 ml). The mixture was extracted with CH_2Cl_2 and the organic phase was separated and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was purified by column chromatography (silica, hexane/CH_2Cl_2 v/v: 3:1) to give **7** as a red powder (511 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 – 8.87 (m, 1H), 8.72 (ddd, J = 7.2, 2.6, 1.2 Hz, 1H), 8.01 – 7.95 (m, 1H), 7.84 – 7.78 (m, 2H), 7.72 (ddd, J = 7.2, 6.6, 3.4

Hz, 1H), 7.30 – 7.28 (m, 3H), 7.19 – 7.11 (m, 4H), 5.77 – 5.75 (m, 2H), 3.92 (s, 4H), 1.84 – 1.74 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.11, 163.77, 159.73, 143.00, 139.50, 135.69, 134.77, 132.88, 132.58, 132.49, 132.19, 130.64, 130.38, 130.20, 129.79, 129.51, 128.46, 127.56, 124.12, 123.74, 116.30, 114.87, 84.19, 55.55, 36.06, 32.82, 31.68. HRMS-ASAP-TOF$^+$ (m/z) calcd. for $C_{34}H_{24}I_2N_2O_3$ $[M+H]^+$: 762.9944; found: 762.9939. Anal. calcd for $C_{34}H_{24}I_2N_2O_3$ (%): C, 53.57; H, 3.17; N, 3.67. found: C, 53.58; H, 3.16; N, 3.67.

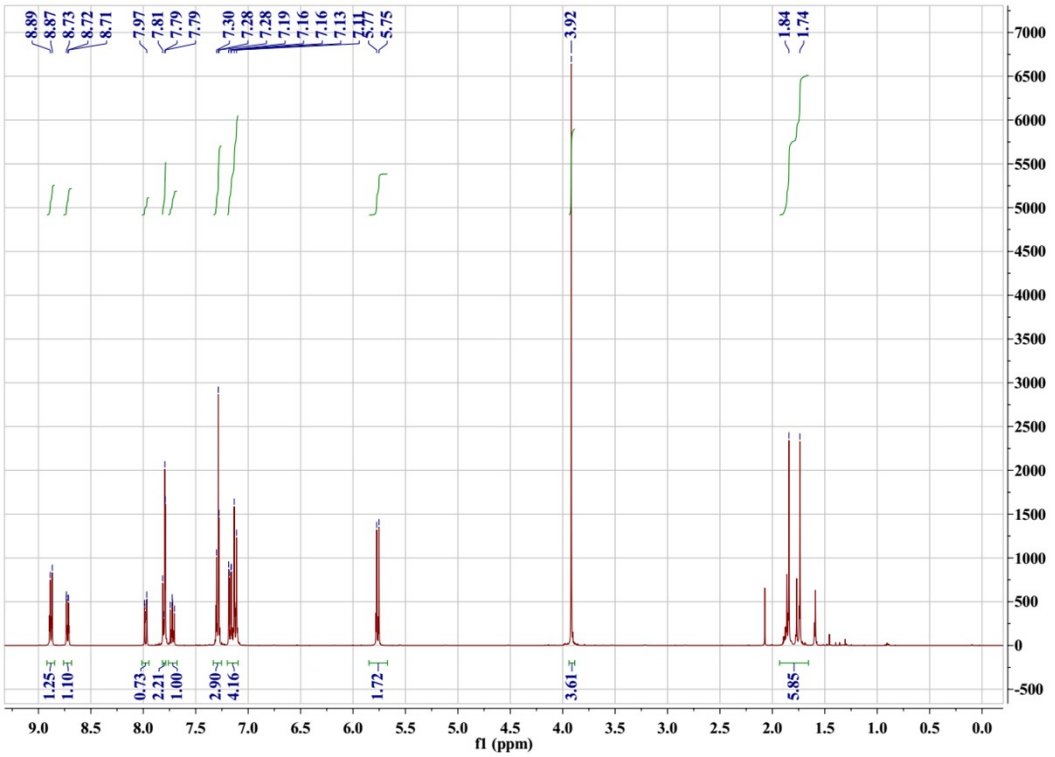


Fig. S7 ^1H NMR spectrum of 6-(2,7-diiodo-9,9-dimethylacridin-10(9H)-yl)-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**5**).

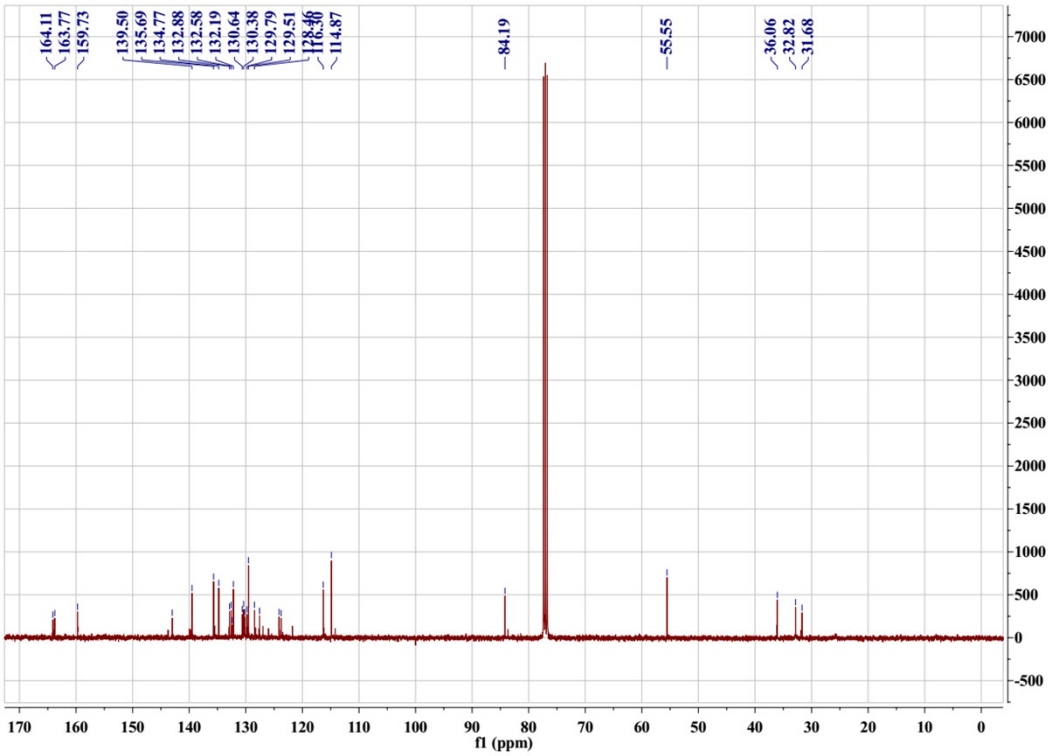


Fig. S8 ^{13}C NMR spectrum of 6-(2,7-diiodo-9,9-dimethylacridin-10(9H)-yl)-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**5**).

6-(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (6): A mixture of compound **5** (556 mg, 0.73 mmol), 3,6-di-*tert*-butyl-9H-carbazole (408 mg, 1.46 mmol), tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3 \cdot CHCl_3$) (38 mg, 37 μmol), (t-Bu)$_3$PH-BF_4 (21 mg, 73 μmol) and sodium *tert*-butoxide (NaO^tBu) (210 mg, 2.19 mmol) in toluene (20 ml) was stirred at 100 °C under argon for 24 h. After cooling to room temperature, the mixture was washed with brine and the organic phase was dried with anhydrous sodium sulfate. After removing the solvent, the mixture was applied to a silica gel column, eluting with cyclohexane/dichloromethane 8/1 v/v to give the crude product as a white power. The powder was further crystallized from a mixture of hexane and CH_2Cl_2 to afford the pure product **6** (684 mg, 88% yield). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 9.00 – 8.98 (m, 1H), 8.86 – 8.78 (m, 1H), 8.36 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.17 (d, *J* = 2.0 Hz, 4H), 8.10 – 8.03 (m, 1H), 7.94 – 7.85 (m, 1H), 7.74 (t, *J* = 6.2 Hz, 2H), 7.54 – 7.45 (m, 4H), 7.36 – 7.28 (m, 7H), 7.19 – 7.09 (m, 3H), 6.30 – 6.23 (m, 2H), 3.92 (s, 3H), 1.62 – 1.53 (m, 5H), 1.52 – 1.42 (m, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.72, 152.99, 142.67, 139.62, 139.46, 138.76, 135.83, 131.83, 130.89, 129.55, 129.16, 127.89, 125.83, 125.37, 124.90, 123.57, 123.16, 116.31, 115.18, 114.87, 109.93, 109.05, 55.54, 34.75, 32.05. MALDI-MS$^+$ (m/z) calcd. for $C_{74}H_{72}N_4O_3$ $[M]^+$:1064.5; found: 1064.3. Anal. calcd for $C_{74}H_{72}N_4O_3$ (%): C, 83.42; H, 6.81; N, 5.26. found: C, 83.40; H, 6.82; N, 5.23.

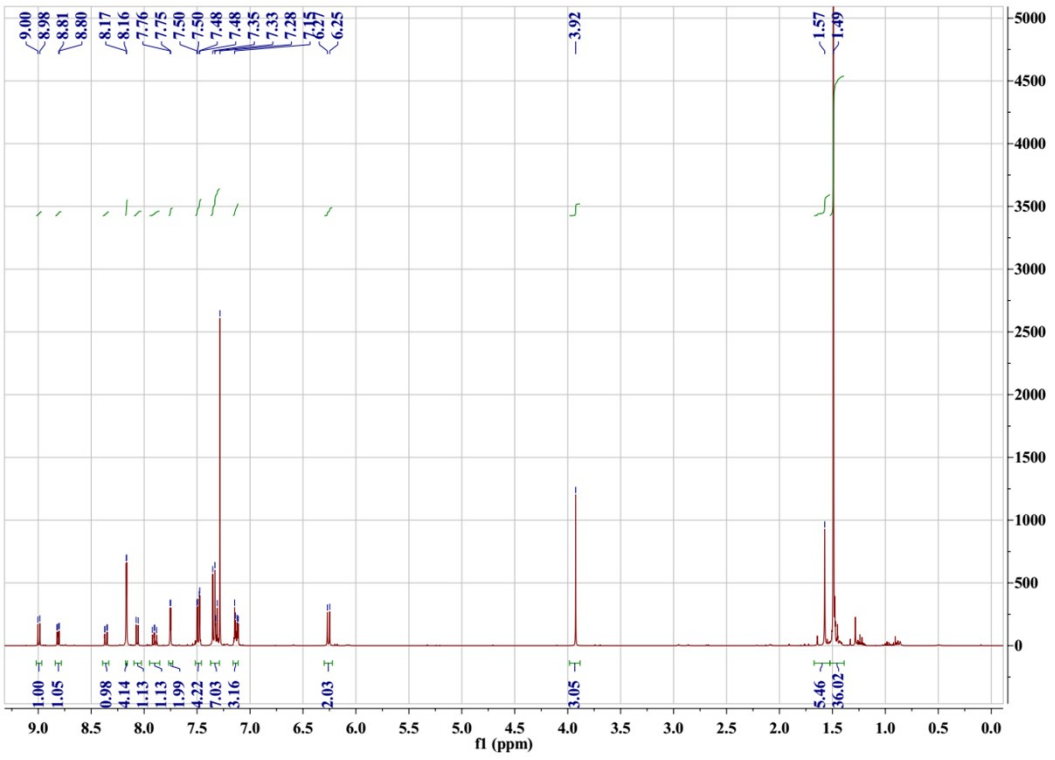


Fig. S9 ^{1}H NMR spectrum of 6-(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**6**).

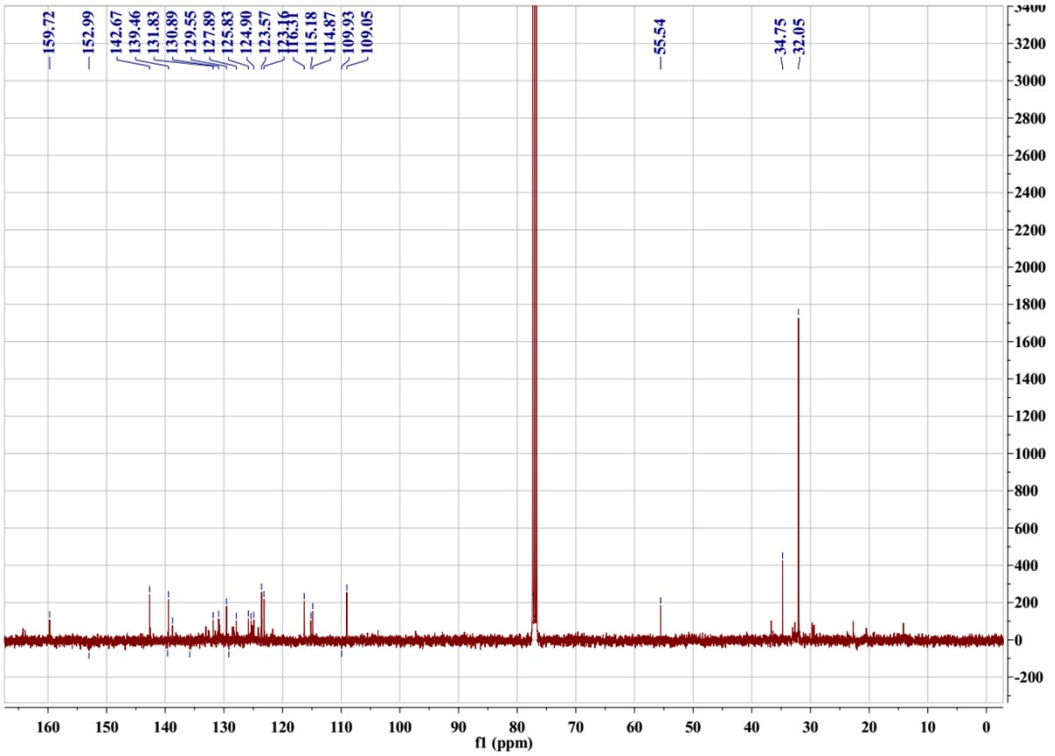


Fig. S10 ^{13}C NMR spectrum of 6-(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)-2-(4-methoxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**6**).

6-(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)-2-(4-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7**): To a stirred solution of **6** (1065 mg, 1 mmol) in dehydrated dichloromethane at -78 °C was added BBr_3 (0.3 g, 1.2 mmol). After the addition was completed, the mixture was stirred for 24 h. The reaction was quenched by methyl alcohol. The solution was evaporated in vacuo. The crude product was further purified using column chromatography to produce a pale red solid (967 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 – 8.97 (m, 1H), 8.87 – 8.78 (m, 1H), 8.44 – 8.33 (m, 1H), 8.17 – 8.16 (d, J = 8.17 Hz, 3H), 8.14 – 8.03 (m, 2H), 7.95 – 7.87 (m, 1H), 7.82 – 7.71 (m, 2H), 7.57 – 7.42 (m, 4H), 7.38 – 7.31 (m, 3H), 7.29 – 7.21 (m, 3H), 7.18 – 7.08 (m, 2H), 7.06 – 6.99 (m, 3H), 6.37 – 6.22 (m, 2H), 1.53 – 1.44 (m, 40H), 1.33 – 1.31 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$)

δ 171.22, 164.37, 164.01, 156.58, 142.68, 141.34, 139.46, 135.79, 133.14, 130.76, 129.55, 128.60, 125.53, 123.85, 123.58, 123.18, 119.56, 116.55, 116.31, 115.26, 109.05, 60.43, 36.72, 34.74, 34.24, 32.04, 32.00, 31.93, 31.80, 31.61, 30.32, 29.72, 29.38, 22.71, 22.67, 21.06, 14.21, 14.13. MALDI-MS$^+$ (m/z) calcd. for $C_{73}H_{70}N_4O_3$ $[M]^+$: 1050.5; found: 1050.4. Anal. calcd for $C_{73}H_{70}N_4O_3$ (%): C, 83.39; H, 6.71; N, 5.33. found: C, 83.40; H, 6.72; N, 5.35.

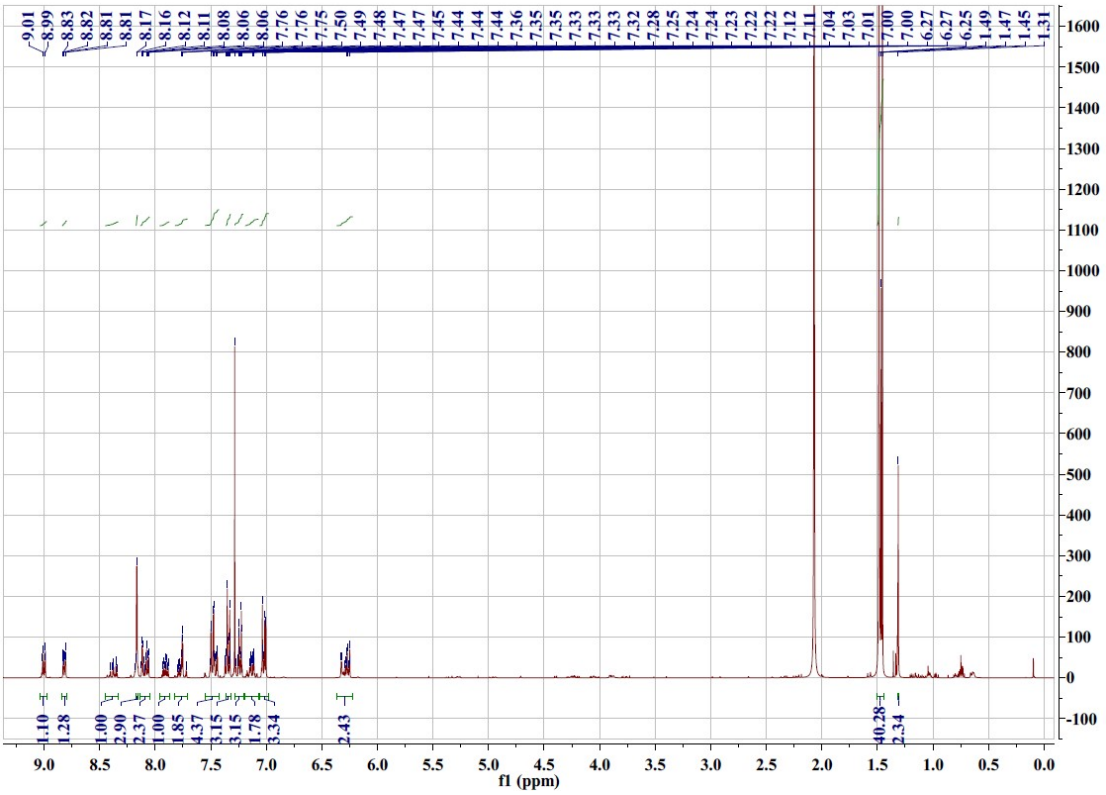


Fig. S11 ^{1}H NMR spectrum of 6-(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)-2-(4-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7**).

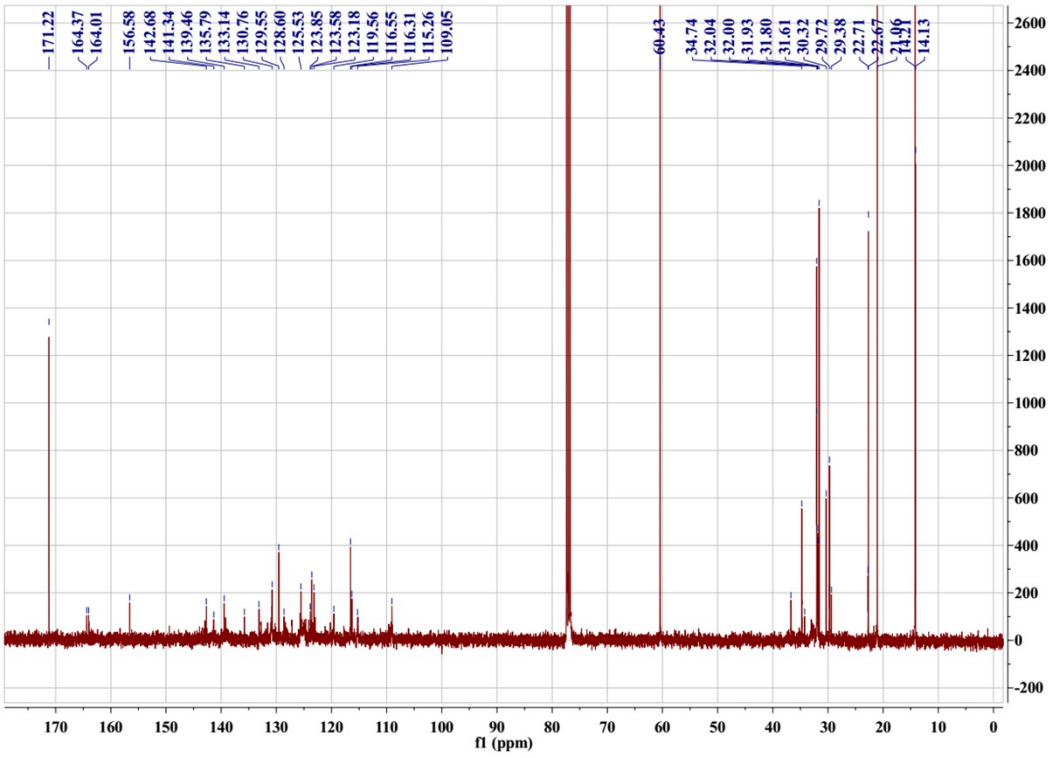


Fig. S12 ^{13}C NMR spectrum of 6-(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)-2-(4-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7**).

6-(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)-2-(4-((6-(3-vinyl-9H-carbazol-9-yl)hexyl)oxy)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8**): A mixture of **9** (1050 mg, 1.0 mmol), **2** (355 mg, 1.0 mmol) and K_2CO_3 (166 mg, 1.2 mmol) was added to 10 mL N,N-dimethylformamide solution. The reaction was heated at 100 °C under nitrogen for 24 h. After cooling, the mixture was poured into 200 mL water. The crude products were filtered and purified by silica gel column chromatography. The target product was recrystallized by ethyl acetate to give the green product (1193 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ9.01 (dd, *J* = 7.7, 2.6 Hz, 1H), 8.82 (d, *J* = 7.3 Hz, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.25 – 8.01 (m, 7H), 7.91 (dd, *J* = 9.8, 5.9 Hz, 1H), 7.83 – 7.71 (m, 2H), 7.63 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.57 – 7.31 (m, 11H), 7.30 – 7.21 (m, 3H), 7.21 – 7.04 (m, 4H), 6.96 (dd, *J* = 17.6, 10.9 Hz,

1H), 6.38 – 6.21 (m, 2H), 5.82 (dd, *J* = 17.5, 0.8 Hz, 1H), 5.29 – 5.17 (m, 1H), 4.37 (t, *J* = 7.1 Hz, 2H), 4.03 (t, *J* = 6.2 Hz, 2H), 1.97 (dd, *J* = 12.0, 6.3 Hz, 4H), 1.91 (d, *J* = 7.3 Hz, 3H), 1.85 (s, 2H), 1.49 (d, *J* = 8.2 Hz, 28H), 1.42 (s, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.26, 163.90, 159.22, 142.69, 140.84, 140.33, 139.48, 138.78, 137.57, 133.06, 131.85, 130.77, 129.51, 128.88, 128.58, 127.46, 125.81, 124.91, 124.06, 123.59, 123.19, 123.03, 122.95, 120.45, 118.98, 118.48, 116.33, 115.34, 110.99, 109.07, 108.85, 108.71, 67.92, 43.08, 36.72, 35.25, 34.77, 33.05, 32.67, 32.07, 32.04, 31.97, 31.83, 29.74, 29.70, 29.40, 29.11, 29.00, 27.04, 25.96, 22.74, 14.17. MALDI-MS$^+$ (m/z) calcd. for $C_{93}H_{91}N_5O_3$ $[M+H]^+$: 1326.7; found:1326.4. Anal. calcd for $C_{93}H_{91}N_5O_3$ (%): C, 84.19; H, 6.91; N, 5.28. found: C, 84.18; H, 6.90; N, 5.29.

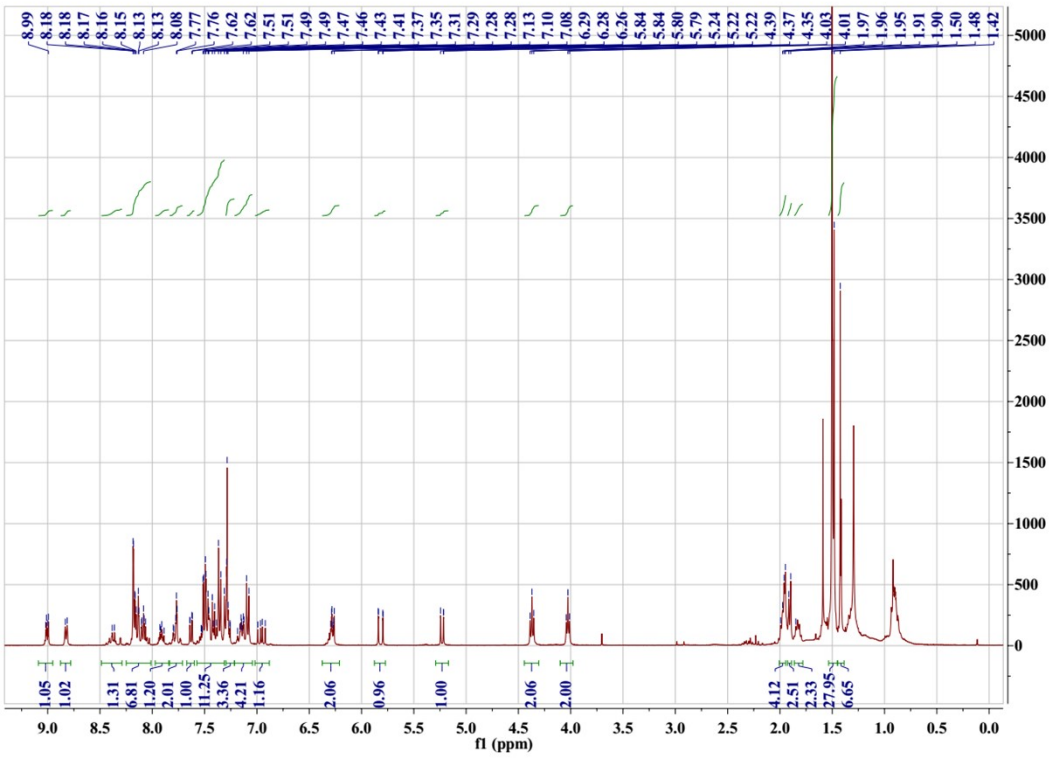


Fig. S13 ^{1}H NMR spectrum of 6-(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)-2-(4-((6-(3-vinyl-9H-carbazol-9-yl)hexyl)oxy)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8**).

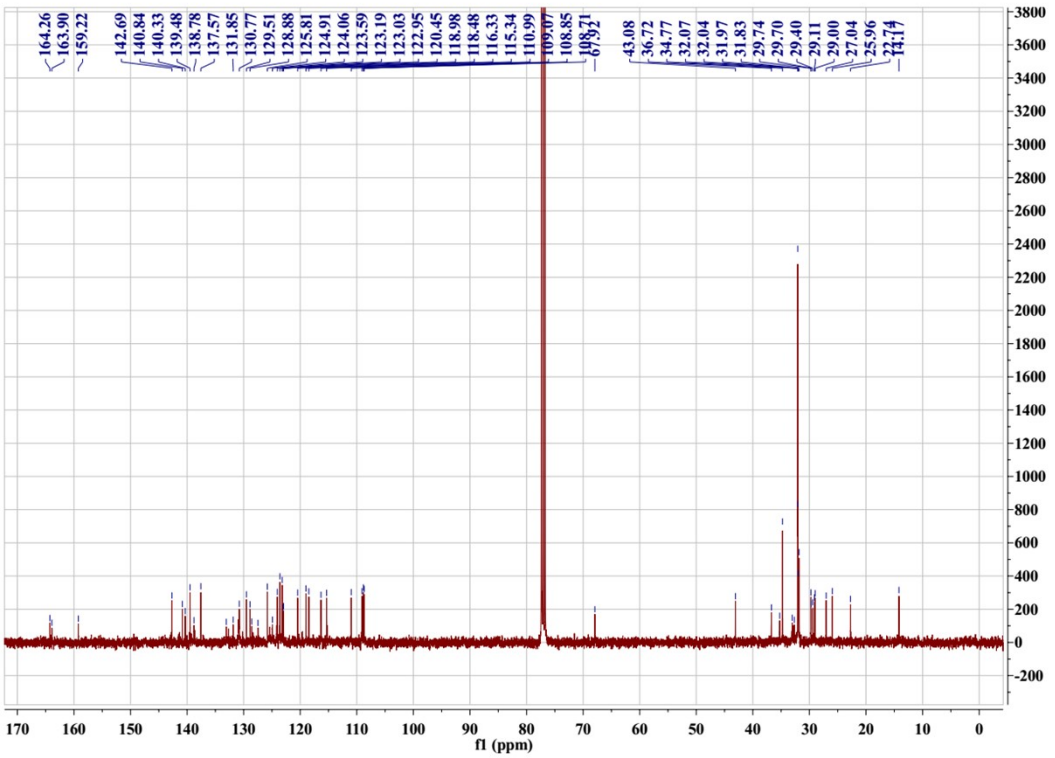


Fig. S14 ^{13}C NMR spectrum of 6-(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)-2-(4-((6-(3-vinyl-9H-carbazol-9-yl)hexyl)oxy)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8**).

PNAI-AcCz: A mixture of AIBN (1 mg, 0.006 mmol), THF (2 ml), and **8** (531.6 mg, 0.4 mmol) was placed in an ampule, which was cooled, degassed, and sealed in vacuo. After stirring at 60 °C for 40 h, the reaction mixture was poured into a large excess of methanol. The polymer (436 mg, 82% yield) was obtained by filtration and then was dried in vacuo. The polymer was fractionated by Soxhlet extraction using hexane. Elemental analysis. found: C, 84.6; H, 7.05; N, 5.27%.

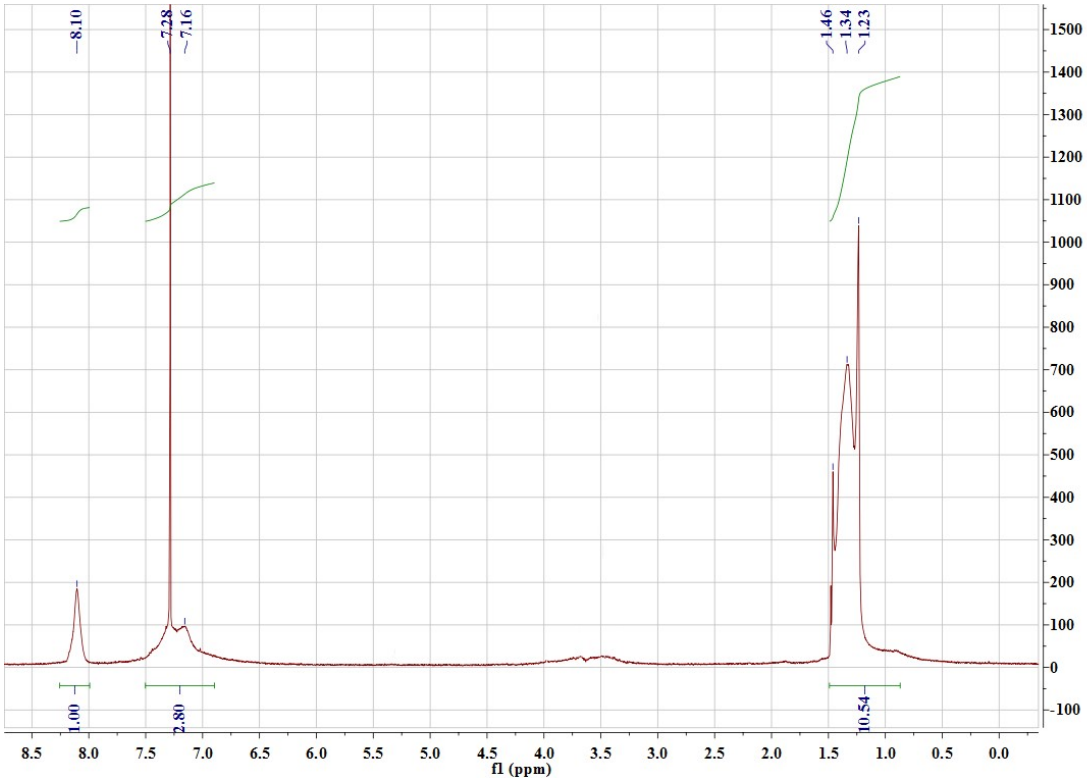


Fig.15 ^{1}H NMR spectrum of **PNAI-AcCz**.

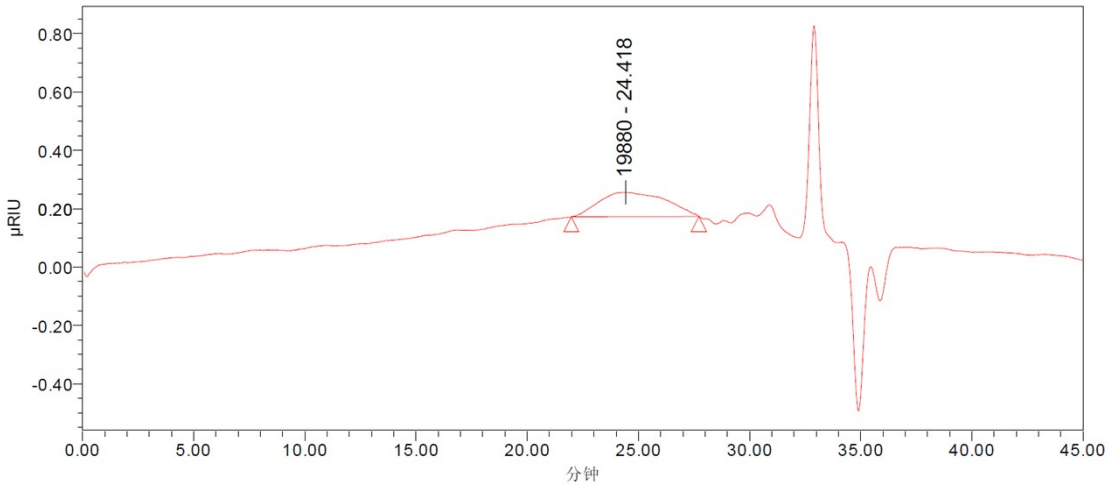


Fig. S16 GPC trace of **PNAI-AcCz**.

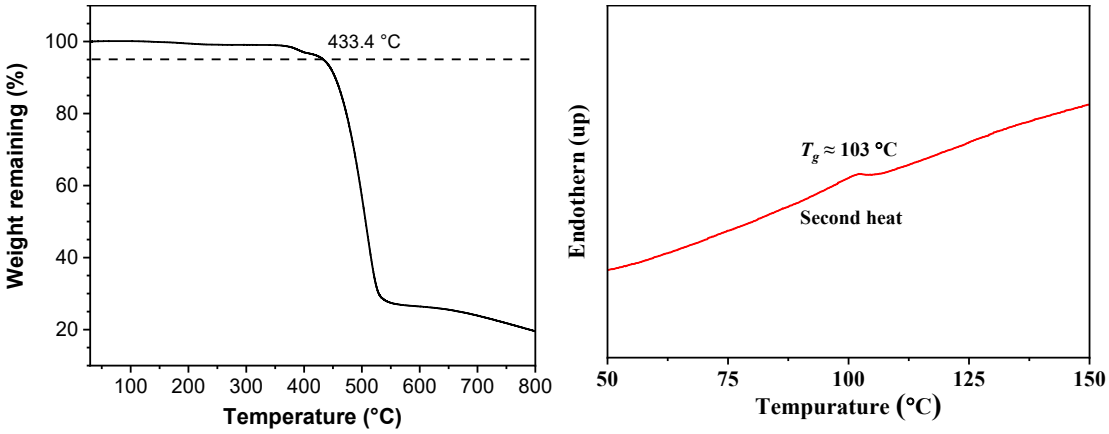


Fig. S17 TGA and DSC traces of **PNAI-AcCz** recorded at a heating rate of 10 °C min^{-1}.

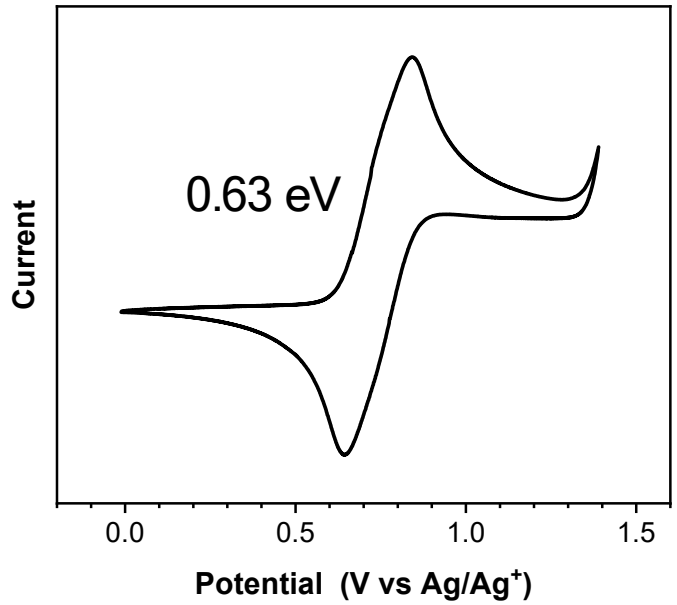


Fig. S18 Cyclic voltammogram of **PNAI-AcCz** in acetonitrile.

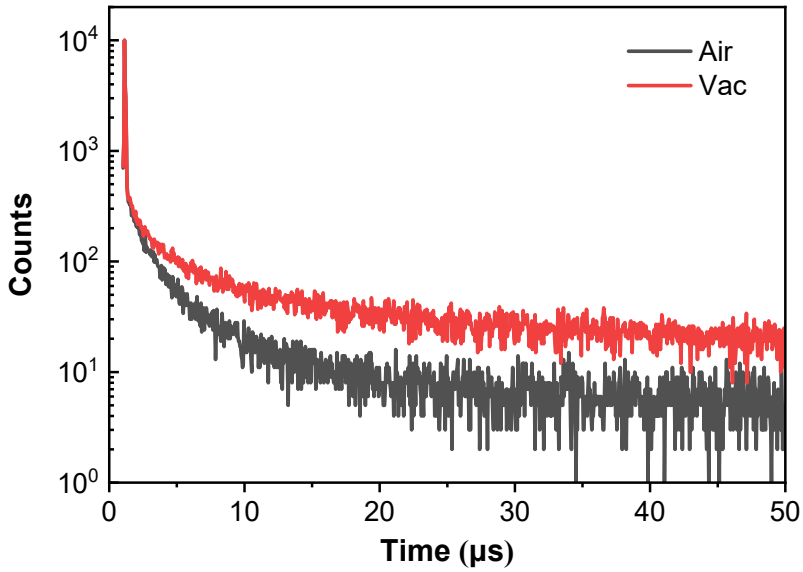


Fig. S19 PL lifetime decay curves of **PNAI-AcCz** film under oxygenated and oxygen-free

conditions.

Table S1. The summary of OLED characteristics from this work and reported solution-processed non-doped deep-red OLEDs.

No.	EL peak (nm)	EQE_{max} (%)	Reference
1	659	2.6	This work
2	668	0.6	Adv Funct Mater 2020; 30: 2002493
3	660	1.4	Adv Funct Mater 2020; 30: 2002493
4	728	0.064	Organic Electronics 2017, 48, 389-396.
5	715	0.254	Organic Electronics 2017, 48, 389-396.
6	660	2.4	Macromolecules 2020, 53, 23, 10375–10385
7	653	0.7	Macromolecules 2020, 53, 23, 10375–10385
8	804	2.17	Angew. Chemie Int. Ed. 2022, 61, e202204279.
9	715	0.3	Chem. – A Eur. J. 2019, 25, 1010.
10	685	0.3	J. Mater. Chem. C, 2025, 13, 6123-6135
11	780	0.04	J. Mater. Chem. C, 2025, 13, 6123-6135
12	676	0.73	ACS Appl. Mater. Interfaces 2024, 16, 50, 69670–69678