Supporting Information

Materials

2,7-dibromofluorene, palladium, 10% on carbon (10% Pd/C), 4-fluorobenzeneboronic acid, 1-fluoro-4-nitrobenzene, hydrazine monohydrate ($NH_2NH_2 \bullet H_2O$), tetrakis(triphenylphosphine)palladium ($Pd[P(C_6H_5)_3]_4$), Aliquat 336 (tri-caprylylmethylammonium chloride), and potassium tert-butoxide(t-BuOK) were purchased from the Alfa-Aesar company and were used as received. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. All other solvents and reagents were purchased as analytical grade from the Guangzhou Dongzheng Company and were used without further purification.

Instrumentation

All NMR spectra were recorded at room temperature on a Varian Unity Inova 500 NB spectrometer, operating at 499.774 MHz for ^1H with indirect detection probe and at 125.682 MHz for ^{13}C with broadband probe. Samples were made composed of a solution of 5~15 mg of each compound in 0.7 mL of deuterated dimethyl sulfoxide (DMSO) using tetramethylsilane (TMS) as the internal reference. Inverse gated decoupling was exploited for quantitative carbon nuclei intensities, using a 248 pulse angle, 0.45 s acquisition times, and 2.0 s relaxation delays for about 5000 scans. Two-dimensional spectra were performed by using standard Varian software and the parameters used were as follows: COSY spectra were collected with four transients for each 256 increments and the spectral windows were 4096.5 Hz in both dimensions. Mass spectra were measured on a Thermo MAT95XP-HRMS spectrometer. Elemental analysis was performed on a CHNS elemental analyzer. Infrared spectra were recorded on a BRUKER TENSOR 27 Fourier-transform infrared (FT-IR) spectrometer. UV-Vis absorption spectra (UV) were recorded on a Hitachi UV-Vis spectrophotometer (U-3900). Fluorescence spectra (PL) of WuFDA in different solutions and solid were determined on a Shimadzu RF-5301PC spectrometer with a slit width of 3 nm for emission on 365 nm. Photoluminescence spectra of WuFDA in mixed solvents of THF/H_2O and time-resolved spectrum of WuFDA in solid state were recorded by a FLS920-Combined Time Resolved and Steady state fluorescence spectrometer (Edinburgh Instruments) using the Xe lamp as the excitation source and R1527 photomultiplier tube as the detector. Time-resolved fluorescence experiments of WuFDA in different solvents have been performed with 355 nm pulse laser from Ekama PG401SH/DFG2-10 pumped by a 25 ps pulse laser (Eksma PL 2143B) as an excitation source, and a Tektronix TDS 3052C digital phosphor osciloscope as a recorder; PL signals were collected at the maximal emission peak of WuFDA in different solvents; decay in the PL intensity (I) with time (τ) was fitted by a single-exponential function. The PL quantum yields of WuFDA in solid-state and solutions were measured according to an absolute method by using a fluoroSENS-fluorimeter that was excited with a Xe lamp. Thermogravimetric analyses (TGA) were performed with a TA thermal analyzer (Q50) under N_2/air with a heating rate of 20 °C/min from 30 to 1000 °C; the sample was heated under flowing nitrogen/air (40 mL/min). Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204) at a heating rate of 25 °C/min from 30 to 250 °C under flowing nitrogen. Molecular simulations of WuFDA were carried out with the Gaussian 03 (revision E.03) program package. Equilibrium ground state geometry and electronic properties of the molecule was optimized by means of the density functional theory (DFT) method at the B3LYP level of theory (Beckes-style three-parameter density functional theory using the Lee-Yang-Parr correlation functional) with the 6-31 G(d) basic set. Single-crystal data was collected at 173 K on a single crystal diffractometer (Bruker, Smart 1000 CCD) with Mo Kα radiation (λ=0.71073A °). All empirical absorption corrections were applied by using the SADABS program. The structures were solved using direct methods, which yielded the positions of all hydrogen atoms. All calculations were performed using the SHELXTL system of computer programs.

Synthesis of 2,7-dibromo-9,9-bis(4-nitrophenyl)-9H-fluorene (WuBrDN).

2,7-Dibromofluorene (32.401 g, 0.1 mol), 1-fluoro-4-nitrobenzene (42.33 g, 0.3 mol) and potassium tert-butoxide(11.2 g, 0.1 mol), were mixed in a 500-mL flask and DMF (300 mL) were added. The mixture was stirred for 24 h under argon at 120 °C. After reaction, the product was concentrated and purified by silica gel column chromatography using dichloromethane/n-hexane (v/v= 1/2). The yield of the product is about 92%. IR (KBr, v, cm^{-1}): 701(C-Br stretching), 1516(-NO_2 stretching), 1100~700(Ar–H stretching). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.40~7.45 (d, 4H), 7.66~7.70 (d, 2H), 7.70~7.73 (d, 2H), 7.99~8.03 (d, 2H), 8.13~8.18 (d, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 64.98, 121.85, 123.34, 123.99, 128.76, 128.97, 131.99, 137.89, 146.77, 150.35, 150.62. MS (EI, m/z): 566 ($[M]^+$, calcd for $C_{25}H_{14}Br_2N_2O_4$, 566.2). Anal. Calcd for $C_{20}H_{14}Br_2N_2O_4$ (566.2, wt %): C, 53.03; H, 2.49 and N, 4.95; found: C, 53.50; H, 2.88 and N, 4.84.

Synthesis of 2,7-bis(4-fluorophenyl)-9,9-bis(4-nitro-phenyl)-9H-fluorene (WuFDN).

4-Fluorobenzene-boronic acid (6.996 g, 0.05 mol) and 2,7-dibromo-9,9-bis(4-nitrophenyl)-9H-fluorene (11.124 g, 0.02 mol) were dissolved in THF (150 mL) and mixed in a 250-mL flask. Then 2 M aqueous K_2CO_3 solution (75 mL) and 15 drops of Aliquat336 were added. The mixture was stirred for 45 min under argon at room temperature. Then the tetrakis(triphenylphosphine) palladium ($Pd(Pph_3)_4$) catalyst (catalytic amount) was added and the reaction mixture was stirred at 75 °C for 24 h. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography using dichloro-methane/n-hexane (v/v=1/1). Yield of the product is about 85 %. IR (KBr, v, cm^{-1}): 1228(C-F stretching), 1602(-NO_2 stretching), 1100~700(Ar–H stretching). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.23~7.28 (t, 4H), 7.52~7.56 (d, 4H), 7.69~7.73 (m, 4H), 7.77~7.79 (d, 2H), 7.79~7.80 (d, 2H), 8.10~8.13 (d, 2H), 8.13~8.18 (d, 4H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$, δ, ppm): 65.06, 115.54(d, 2J=56.3), 121.90, 123.42, 124.02, 127.53, 128.75(d, 3J=6.4), 135.94, 138.42, 139.40, 146.40, 149.48, 151.84, 161.88(d, 1J=243.9). MS(EI, m/z): 597 ([M]$^+$, calcd for $C_{37}H_{22}F_2N_2O_4$, 596.58). Anal. Calcd for $C_{37}H_{22}F_2N_2O_4$ (596.58, wt %): C, 74.49; H, 3.72 and N, 4.70; found: C, 74.66; H, 3.96 and N, 5.00.

Synthesis of 4-(9-(4-aminophenyl)-2,7-bis(4-fluoro-phenyl)-9H-fluoren-9-yl)benzenamine (WuFDA).

A mixture of 2,7-bis(4-fluorophenyl)-9,9-bis(4-nitrophenyl)-9H-fluorene (11.9316 g, 0.02 mol), 10% Pd/C catalyst (0.5 g), hydrazine monohydrate(16 ml), and ethanol (200 ml) was placed in a three-necked flask and heated at 85 °C for 24 h. The mixture was then filtered to remove the Pd/C catalyst. After cooling to room temperature, the precipitated crystals were isolated by filtration, recrystallized from ethanol twice, ground into powder, and dried under vacuum. Yield: 92 %. IR (KBr, v, cm^{-1}): 1100~700 (Ar–H stretching), 1277 (C-N stretching), 1624 (δ N-H), 3340 (N-H stretching). ^{1}H NMR (500 MHz, DMSO-*d*$_6$, δ, ppm): 4.969 (s, 4H), 6.47~6.50 (d, 4H), 6.91~6.95 (d, 4H), 7.25~ 7.29 (t, 4H), 7.60 (s, 2H), 7.64~7.67 (m, 6H), 7.96~7.99 (d, 2H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$, δ, ppm): 63.89, 113.72, 115.70(d, 2J=21.3), 120.88, 123.79, 125.84, 128.31, 128.57(d, 3J=8), 132.60, 136.67, 138.23, 138.44, 147.13, 153.55, 160.82(d, 1J=239.9). MS (EI, m/z): 537 ([M]$^+$, calcd for $C_{37}H_{26}F_2N_2$, 536.61). Anal. Calcd for $C_{37}H_{26}F_2N2$ (536.61, wt %) C, 82.82; H, 4.88 and N, 5.22; found: C, 82.86; H, 4.96 and N, 5.30.

Table S1 Thermal properties of WuFDA

Compound	T_g [°C][a]	T_d [°C][b]	
		5%	10%
WuFDA	**161**	**399**	**414**

[a] Measured by DSC at a heating rate 25°C/min.
[b] Measured at a heating rate of 20 °C/min under N_2.

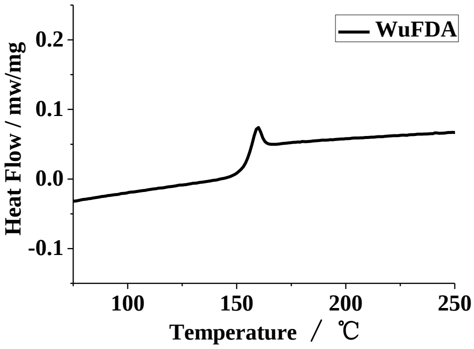

Fig. S1. DSC curve of WuFDA

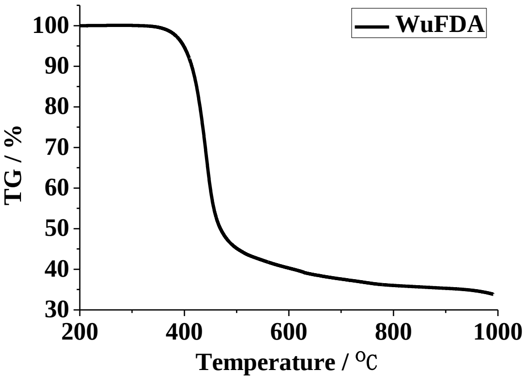

Fig. S2. TGA curve of WuFDA

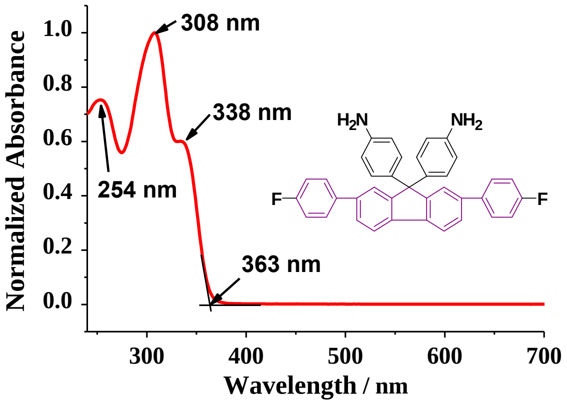

Fig. S3. UV-visble absorption spectrum of WuFDA in 1×10^{-5} mol/L THF solution.

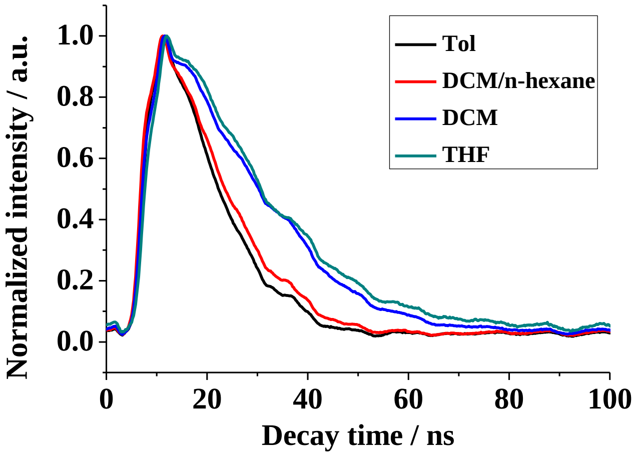

Fig. S4. Fluorecence decay curves of WuFDA in different solvents.

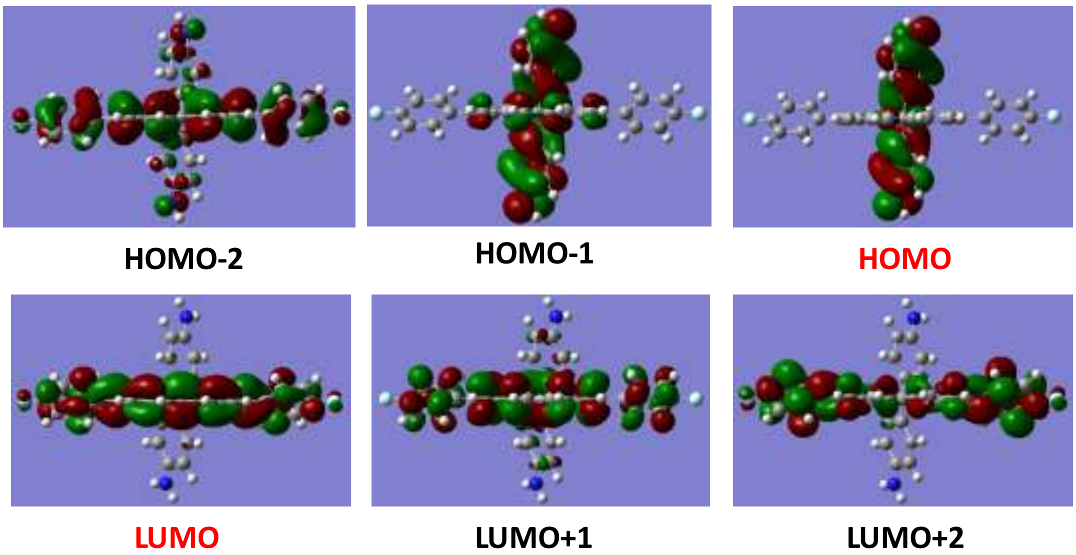

Fig. S5. The lower ground states and higher excited states (HOMO+2 to LUMO+2) molecular orbitals of WuFDA by DFT study.

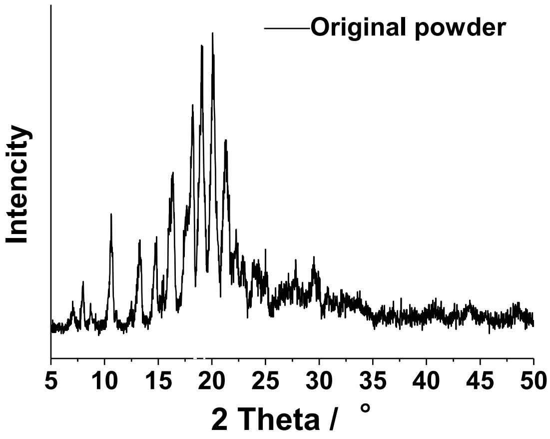

Fig. S6. WAXD pattern of the original powder of WuFDA.

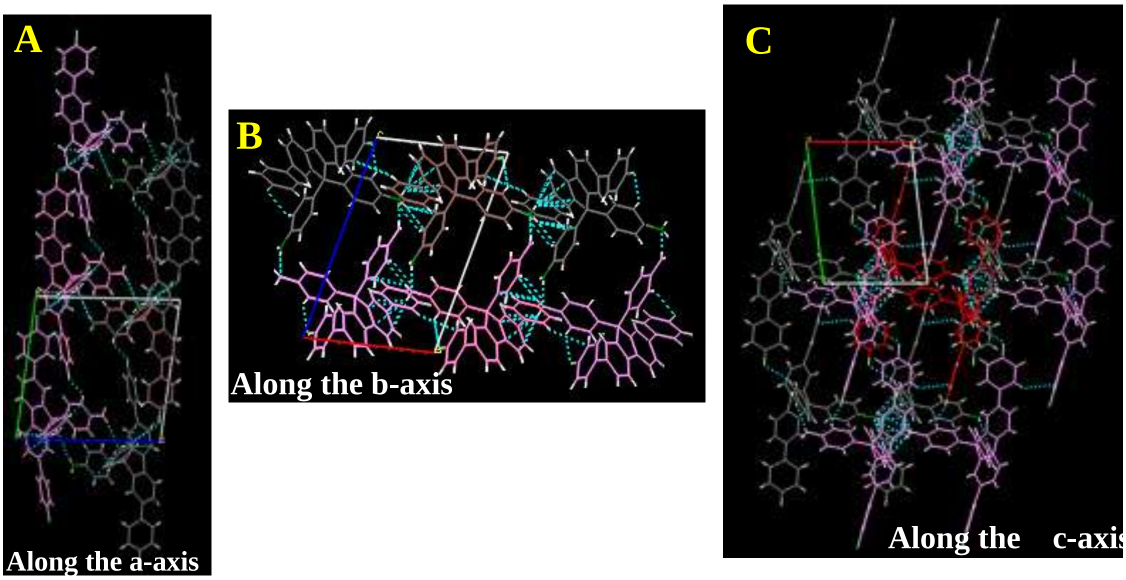

Fig. S7. The single-crystal X-ray structure of WuFDA along the a-axis (A), b-axis (B), and c-axis (C).

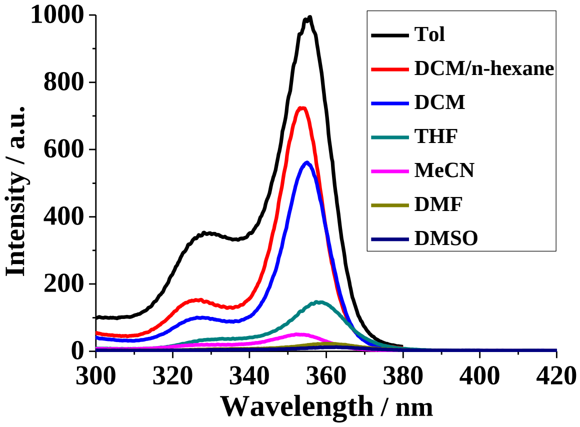

Fig. S8. Fluorescence excitation spectra of WuFDA in different solvents.

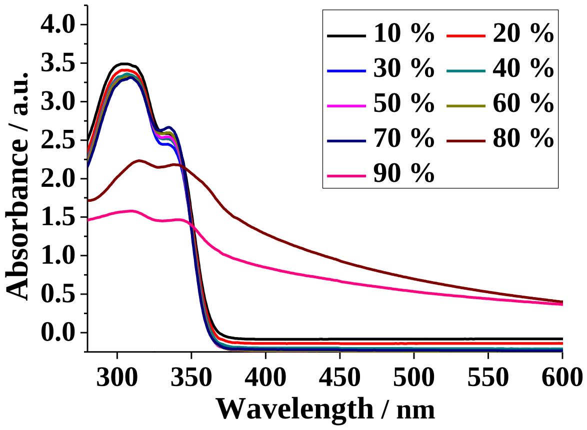

Fig. S9. UV-visible absorption spectra of WuFDA in mixed solvents of THF/H_2O.

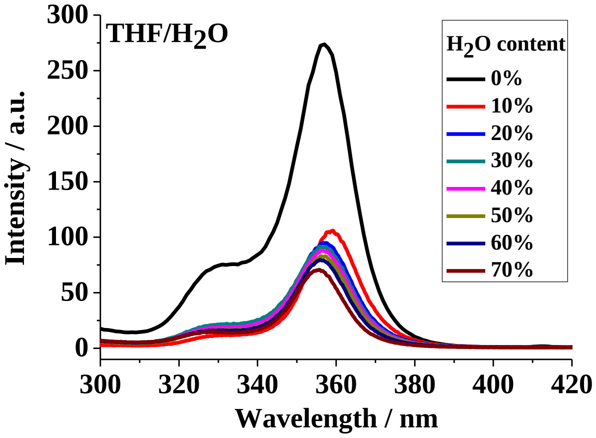

Fig. S10. Fluorescence excitation spectra of WuFDA in mixed solvents of THF/H_2O.