Supplementary Information

Design and Synthesis of Extended Quinoxaline Derivativesis and Their Charge Transport Properties

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Experimental Section

Chemicals and reagents were purchased from Aldrich or Sinopham Chemical Reagent Company unless specifically stated. 1,4-Diphenylethyne was purchased from Tokyo Chemical Industry. Dimethylsulfoxide (DMSO) used without purification was of high pressure liquid chromatography grade. All other commercial reagents were used without further purification.

^{1}H and ^{13}C NMR spectra were measured on the Varian Mercury Plus 400 spectrometer in deuterated chloroform ($CDCl_3$) and chemical shifts were reported in ppm units with tetramethylsilane (TMS; δ=0 ppm) as an internal standard. Matrix assisted laser desorption time of flight mass spectrometry (MALDI-TOF) measurement was carried out on the AB SCIEX TOF/TOF™ 5800 Analyzer (AB Sciex, Framingham, MA, USA). UV/Vis absorption spectra (UV) spectra were obtained on a Perkin-Elmer Lamba 750 UV-visible spectrophotometer was employed for UV spectra in $CHCl_3$. Fluorescence spectra (PL) were measured on an Edinburgh FLS920 spectrometer at room temperature. The PL quantum yields(Φ_F) were estimated using quinine sulfate in 0.1 M H_2SO_4 (Φ_F =54%) as standard. Cyclic voltammetry (CV) was carried out on a CHI 600E electrochemical workstation. Using ferrocene (FOC) (4.8 eV under vacuum) as the internal standard, the measurements were performed in an electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in acetonitrile at a scan rate of 100 mV s^{-1} at room temperature. Thermogravimetric analysis (TGA) of the oligomers was evaluated on a PerkinElmer Pyris 1 TGA instrument under nitrogen at a heating rate of 10°C/min. The counter electrode was a platinum wire and an $Ag/AgNO_3$ electrode was used as the reference electrode. The two dimensional gazing-incidence X-ray diffraction (2D-GIXRD) pattern was obtained at BL14B1 at Shanghai Synchrotron Radiation Facility (SSRF) (λ= 1.24 Å). The incidence angle is 0.25° and the exposure time is 120 seconds. Sample were prepared on SiO_2/Si wafers after the volatilization of $CHCl_3$ solutions at room temperature. X-ray crystallographic data were collected on a P4 Bruker diffractometer equipped with a Bruker SMART 1K CCD area detector (employing the program SMART) and a rotating anode utilizing graphite-monochromated Mo K radiation (λ =0.71073 Å). Data processing was carried out by use of the program SAINT, while the program SADABS was utilized for the scaling of diffraction data, the application of a decay correction and an empirical absorption correction based on redundant reflections. The structures were solved by using the direct-methods procedure in the Bruker SHELXL program library and refined by full-matrix least-squares methods on F2. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded.

FET device fabrication

Some commercially available (300-nm-thick SiO_2/p++Si) substrates were washed by H_2O_2/H_2SO_4, deionized water, acetone and methanol in turn. The compounds in $CHCl_3$ solutions (1 mg/mL) were spin-coated on these clean SiO_2/Si wafers at the rotating speed of 6000 r/min. The obtained thin films were in a vacuum environment for 6h. Then, 50-nm-thick gold (Au) source and drain electrodes were vapor-deposited on the compound thin films (W = L = 1000 μm). For ion gel gate dielectric, composed of a triblock copolymer, poly(styreneblock-methyl methacrylate-block styrene) (PS-PMMA-PS; MPS = 4.3 kg/mol, MPMMA = 12.5 kg/mol, MW = 21.1 kg/mol) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ionic liquid were dissolved in ethyl propionate solution at a 0.7: 9.3: 20 ratio (w/w) and then drop-cast to cover the surfaces of the compound films with an Au drain and source contact. The transistor channels were covered with a thin Aluminum foil (thickness of 0.03 mm) to form the top-gate electrode. The transistor characteristics were measured using a semiconductor parameter analyzer (Keithley 4200, Keithley Co.) at room temperature.

Synthesis and Characterization

The phenylene-ethynylene arrays **1-4** were synthesized according to our previous published procedures.[1]

Synthesis of the oligomers: benzil *(**5a**).*

A 250 mL flask equipped with a magnetic stirrer and a reflux condenser was added 2.47 g (13.89 mmol) of **1a** and 2.49 mg (0.014 mmol) of $PdCl_2$, followed by the addition of dimethyl sulfoxide (DMSO) (120 mL). After being stirred for 48 h at 140 ^{o}C, the mixture was placed to room temperature. The resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (2.65g, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 (d, *J* = 7.2 Hz, 4H), 7.66 (t, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.57, 134.89, 132.99, 129.91, 129.03.

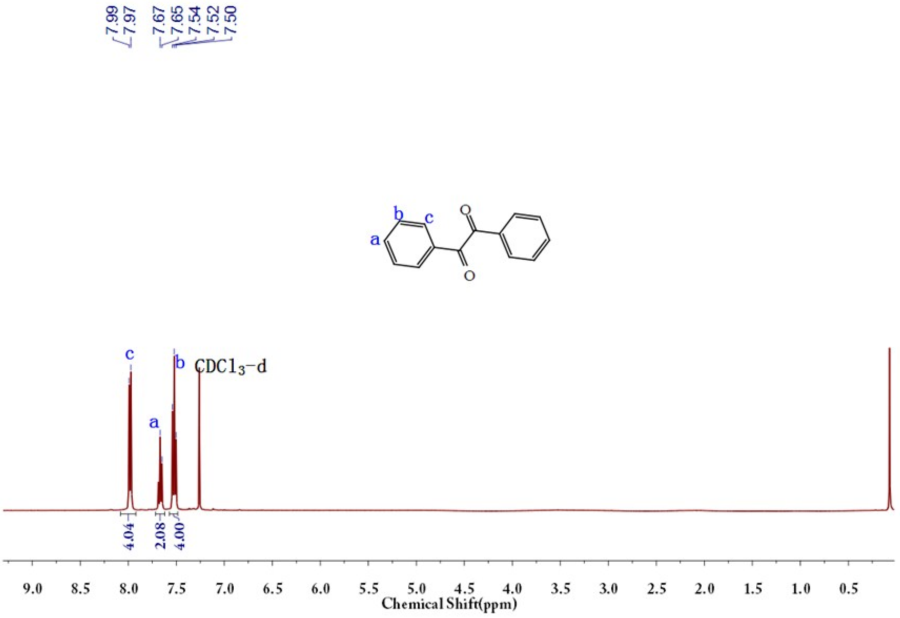


Fig. S1 The ^{1}H NMR spectrum of **5a**.

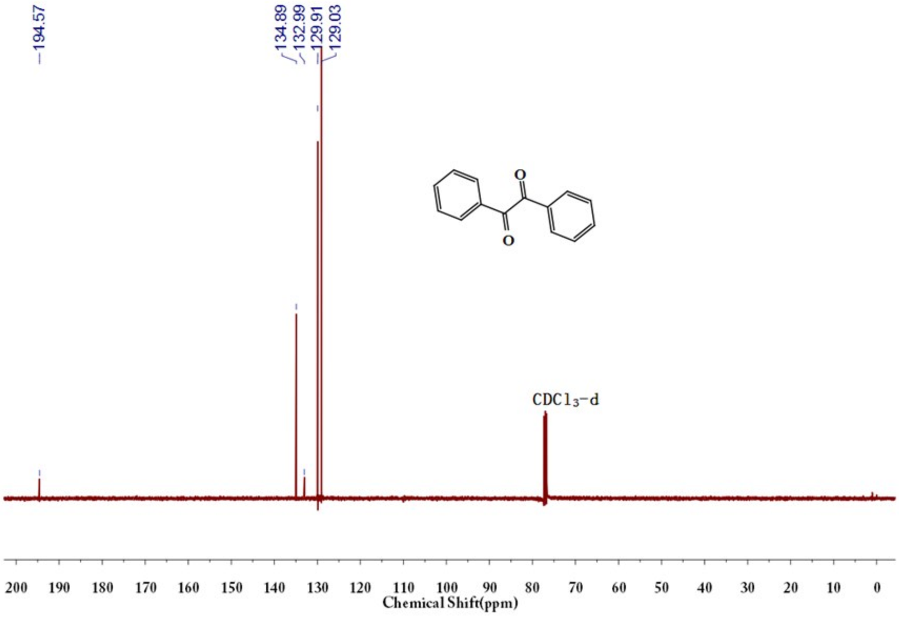


Fig. S2 The ^{13}C NMR spectrum of **5**a.

*1,2-bis(4-butylphenyl)ethane-1,2-dione (**5b**).*

A 250 mL flask equipped with a magnetic stirrer and a reflux condenser was added 2.90 g (10.00 mmol) of **1b** and 1.77 mg (0.01 mmol) of $PdCl_2$, followed by the addition of dimethyl sulfoxide (DMSO) (120 mL). After being stirred for 48 h at 140 ^{o}C, the mixture was placed to room temperature. The resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (2.92g, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88 (d, *J* = 7.6 Hz, 4H), 7.31 (d, *J* = 8.4 Hz, 4H), 2.68 (t, *J* = 7.6 Hz, 4H), 1.63-1.60 (m, 4H), 1.33 (m, 4H), 0.93 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.55, 150.96, 130.89, 130.07, 129.09, 35.92, 33.13, 22.30, 13.88.

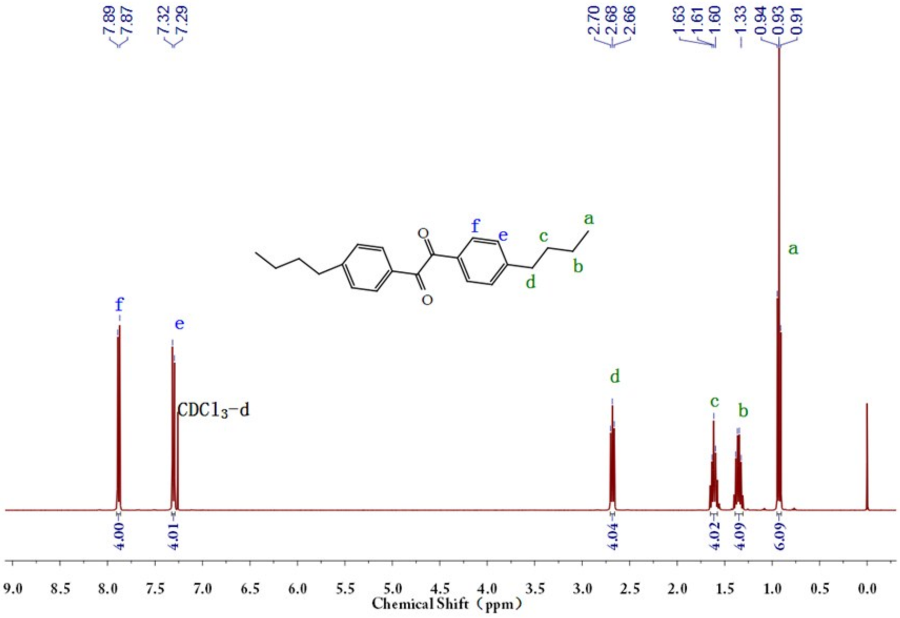


Fig. S3 The ^{1}H NMR spectrum of **5b**.

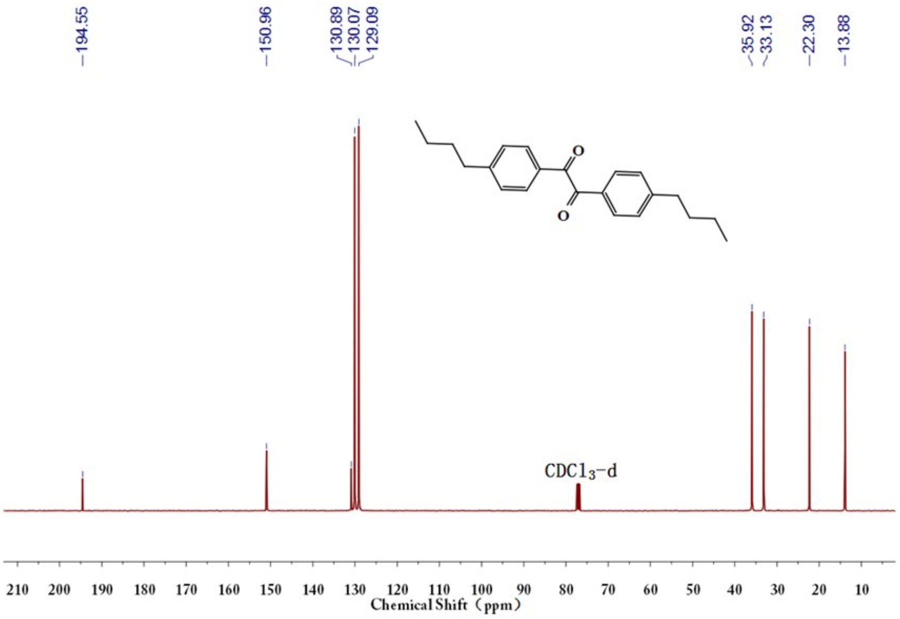


Fig. **S4**The ^{13}C NMR spectrum of **5b**.

*2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-dione) (**6a**).*

A 250 mL flask equipped with a magnetic stirrer and a reflux condenser was added 2.78 g (10.00 mmol) of **2a** and 1.77 mg (0.01 mmol) of $PdCl_2$, followed by the addition of dimethyl sulfoxide (DMSO) (120 mL). After being stirred for 48 h at 140 ^{o}C, the mixture was placed to room temperature. The resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (3.15g, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (s, 4H), 7.98 (d, J = 8.4 Hz, 4H), 7.69 (t, J = 7.2 Hz, 2H), 7.56 (t, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.52, 137.13, 135.27, 132.57, 130.26, 129.99, 129.17.

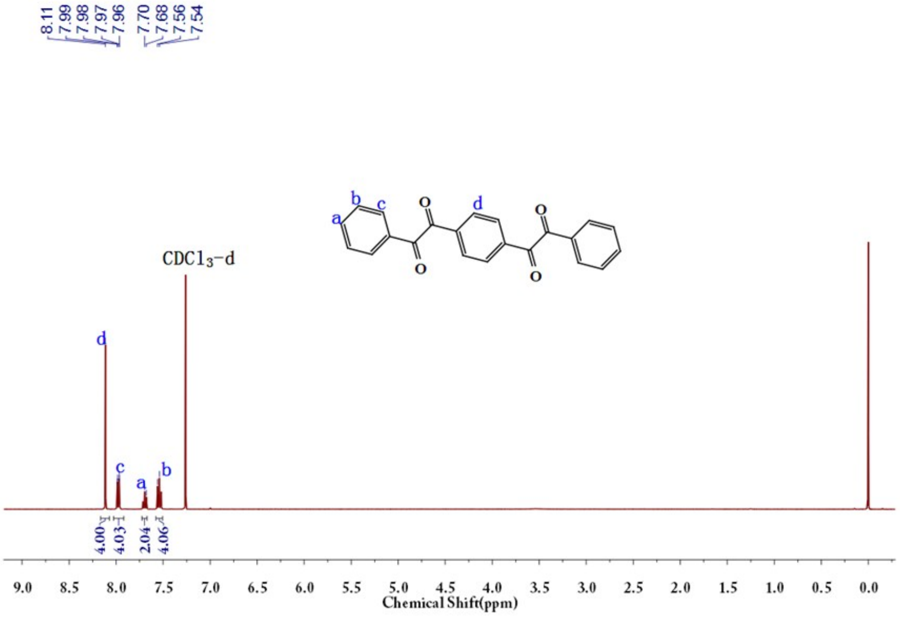


Fig. **S5** The ^{1}H NMR spectrum of **6a**.

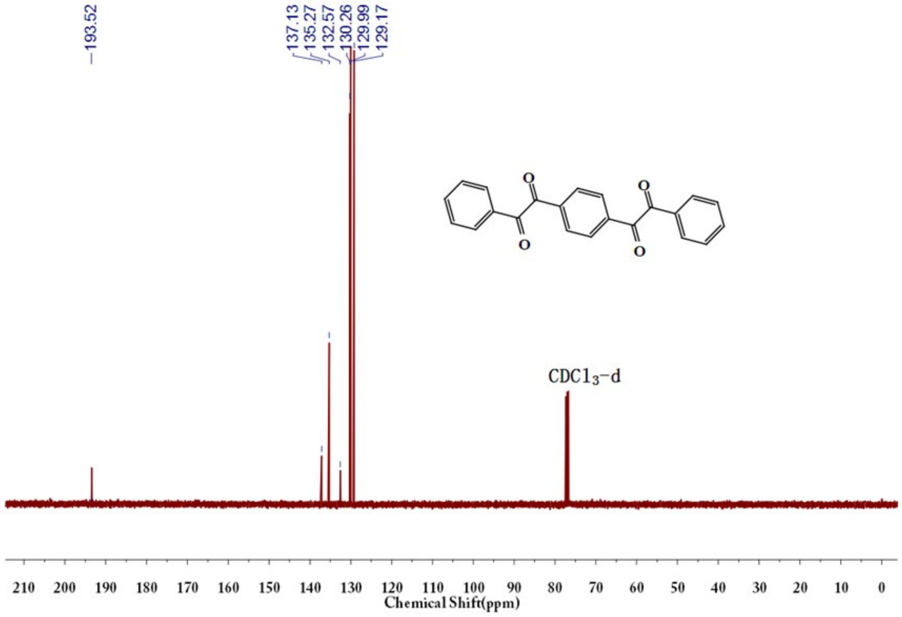


Fig. **S6** The ^{13}C NMR spectrum of **6a**.

*2,2'-(1,4-phenylene)bis(1-(4-butylphenyl)ethane-1,2-dione) (**6b**).*

A 250 mL flask equipped with a magnetic stirrer and a reflux condenser was added 1.95 g (5.00 mmol) of **2a** and 0.86 mg (0.005 mmol) of $PdCl_2$, followed by the addition of dimethyl sulfoxide (DMSO) (120 mL). After being stirred for 48 h at 140 ^{o}C, the mixture was placed to room temperature. The resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (2.07g, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (s, 4H), 7.88 (d, *J* = 8.4 Hz, 4H), 7.33 (d, *J* = 8.0 Hz, 4H), 2.70 (t, *J* = 7.6 Hz, 4H), 1.64-1.60 (m, 4H), 1.33 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm): 193.56, 193.20, 151.59, 137.19, 130.33, 130.21, 130.14, 129.26, 35.95, 33.07, 22.29, 13.85.

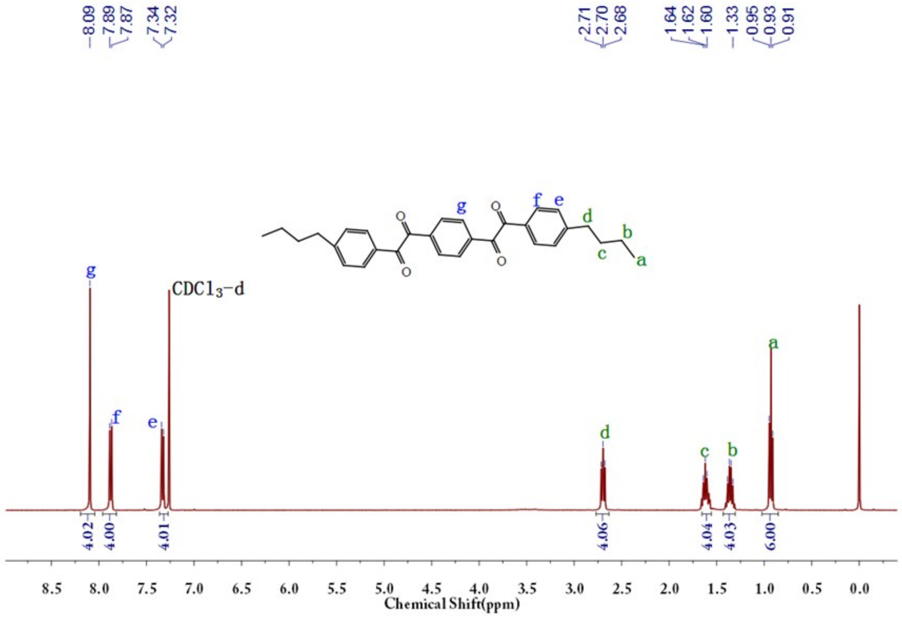


Fig. **S7** The ^{1}H NMR spectrum of **6b**.

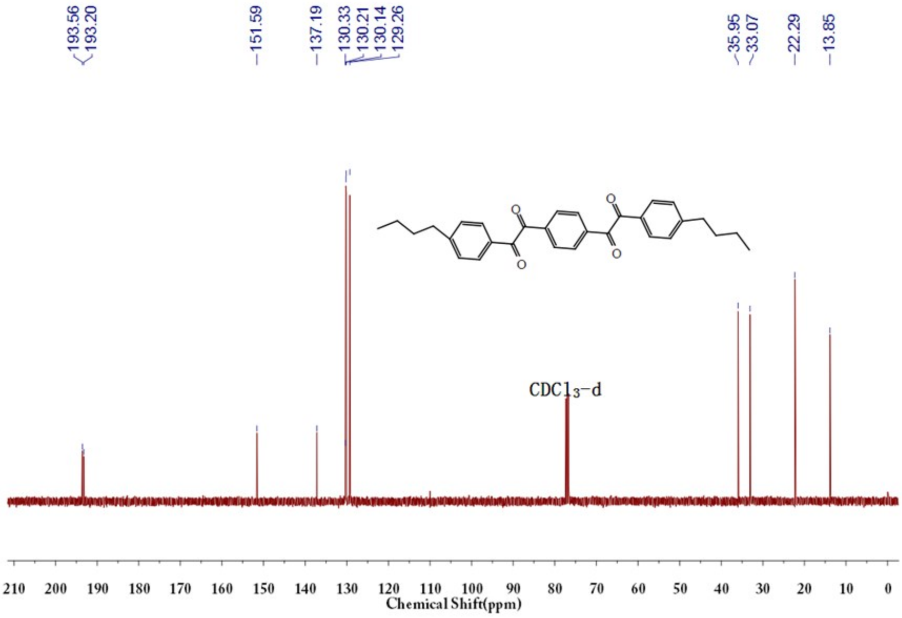


Fig. **S8** The ^{13}C NMR spectrum of **6b**.

*2,2'-(oxalylbis(4,1-phenylene))bis(1-phenylethane-1,2-dione)(7**a**)*

A 250 mL flask equipped with a magnetic stirrer and a reflux condenser was added 1.89 g (5.00 mmol) of **3a** and 0.86 mg (0.005 mmol) of $PdCl_2$, followed by the addition of dimethyl sulfoxide (DMSO) (130 mL). After being stirred for 48 h at 140 ^{o}C, the mixture was placed to room temperature. The resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (2.15g, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12 (s, 8H), 7.98 (d, *J* = 8.4 Hz, 4H), 7.70 (t, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.30, 192.12, 137.39, 136.65, 135.32, 132.52, 130.37, 130.00, 129.18.

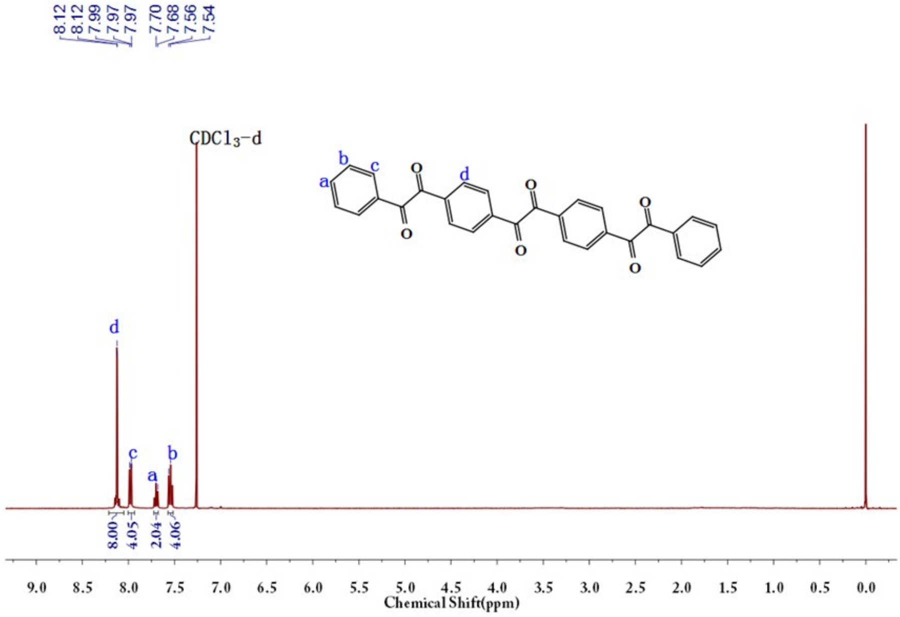


Fig. **S9** The ^{1}H NMR spectrum of **7a**.

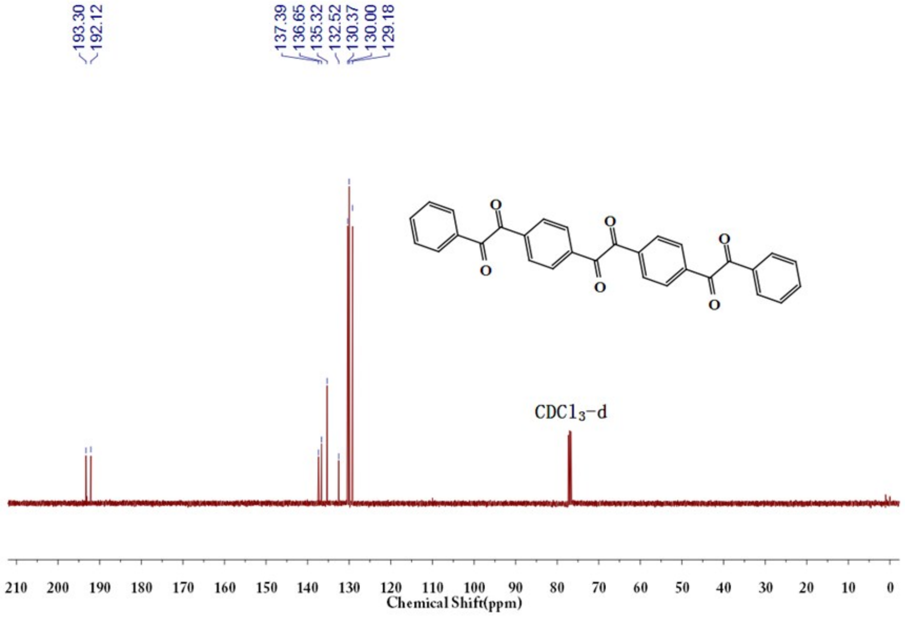


Fig. S10 The ^{13}C NMR spectrum of **7a**.

*2,2'-(oxalylbis(4,1-phenylene))bis(1-(4-butylphenyl)ethane-1,2-dione) (7**b**).*

A 250 mL flask equipped with a magnetic stirrer and a reflux condenser was added 2.45 g (5.00 mmol) of **3b** and 0.86 mg (0.005 mmol) of $PdCl_2$, followed by the addition of dimethyl sulfoxide (DMSO) (130 mL). After being stirred for 48 h at 140 °C, the mixture was placed to room temperature. The resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (2.69g, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (s, 8H), 7.88 (d, J = 8.4 Hz, 4H), 7.33 (d, J = 8.4 Hz, 4H), 2.69 (t, J = 7.6 Hz, 4H), 1.62-1.60 (m, 4H), 1.35 (m, 4H), 0.93 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.04, 192.21, 151.68, 137.53, 136.58, 130.33, 130.16, 129.28, 35.96, 33.08, 22.29, 13.86.

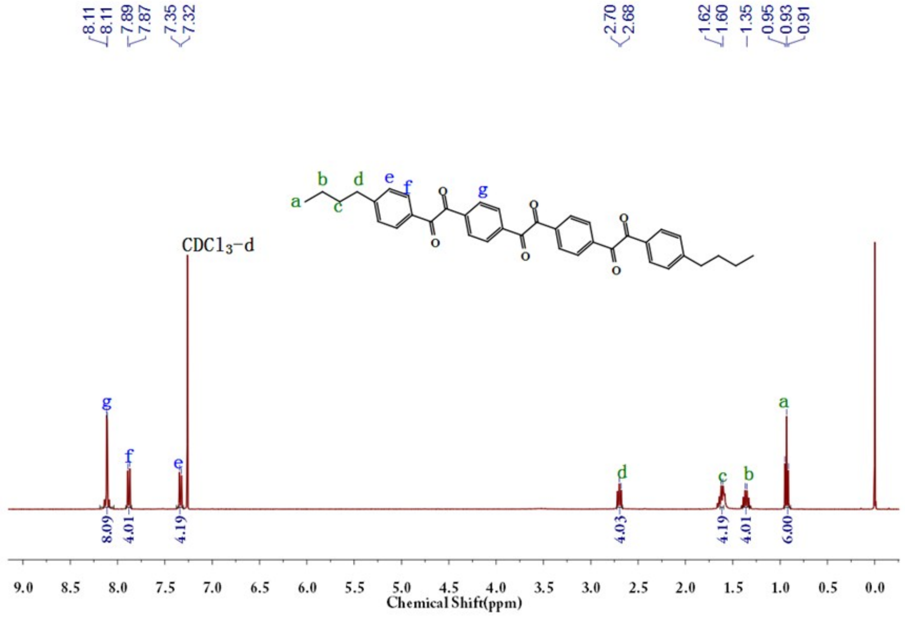


Fig. S11 The ^{1}H NMR spectrum of **7b**.

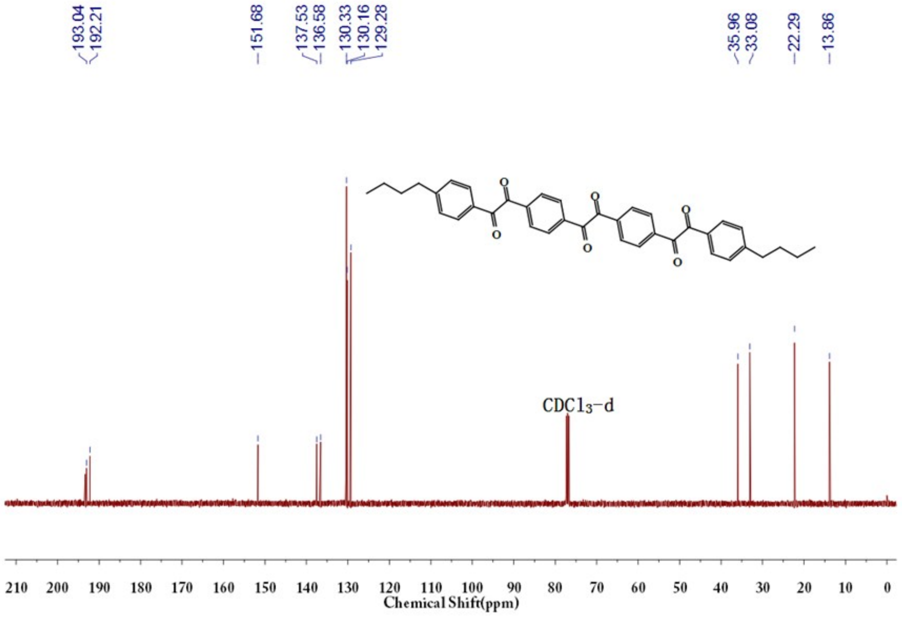


Fig. **S12** The ^{13}C NMR spectrum of **7b**.

*2,2'-(1,4-phenylene)bis(1-(4-(2-oxo-2-phenylacetyl)phenyl)ethane-1,2-dione) (**8a**).*

A 250 mL flask equipped with a magnetic stirrer and a reflux condenser was added 2.39 g (5.00 mmol) of **4a** and 0.86 mg (0.005 mmol) of $PdCl_2$, followed by the addition of dimethyl sulfoxide (DMSO) (140 mL). After being stirred for 48 h at 140 °C, the mixture was placed to room temperature. The resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (2.72g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.13 (s, 12H), 7.98 (d, *J* = 7.2 Hz, 4H), 7.70 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.02, 192.66, 136.60, 135.33, 132.52, 130.38, 130.35, 130.01, 129.19.

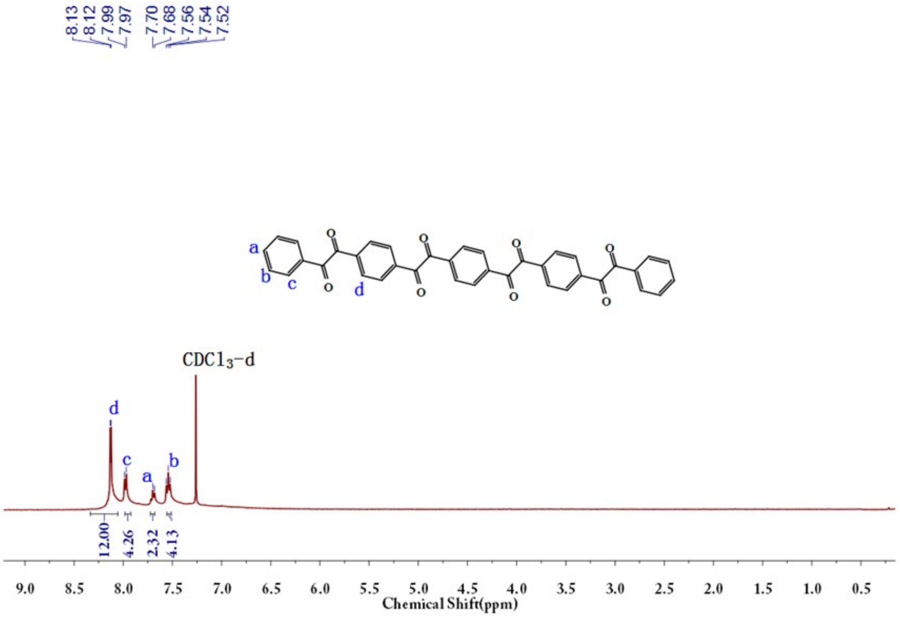


Fig. **S13** The ^{1}H NMR spectrum of **8a**.

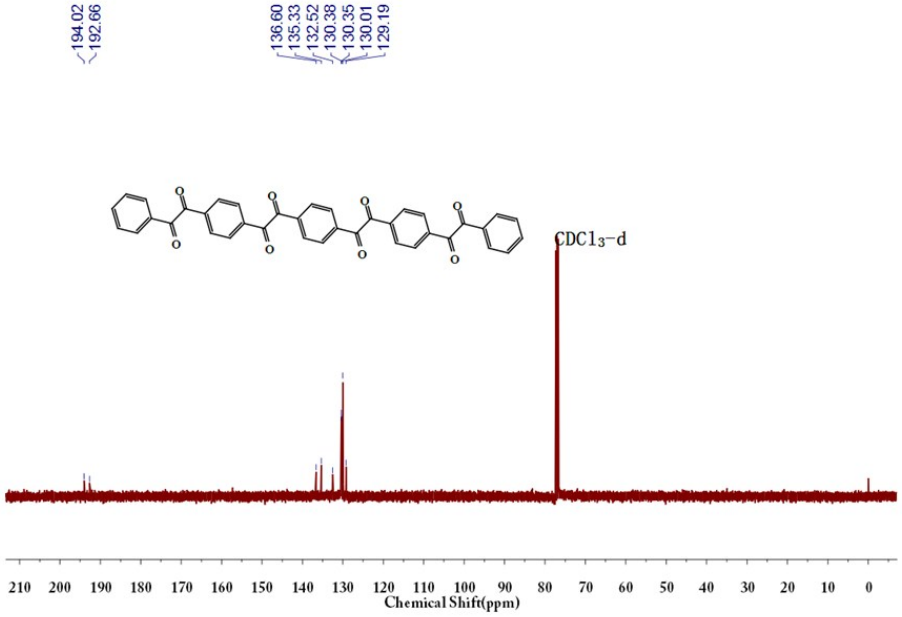


Fig. **S14** The ^{13}C NMR spectrum of **8a**.

*2,2'-(1,4-phenylene)bis(1-(4-(2-(4-butylphenyl)-2-oxoacetyl)phenyl)ethane-1,2-dione) (**8b**).*

A 250 mL flask equipped with a magnetic stirrer and a reflux condenser was added 2.95 g (5.00 mmol) of **4b** and 0.86 mg (0.005 mmol) of $PdCl_2$, followed by the addition of dimethyl sulfoxide (DMSO) (160 mL). After being stirred for 48 h at 140 ^{o}C, the mixture was placed to room temperature. The resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (3.26g, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12 (d, J = 6.5 Hz, 12H), 7.88 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 8.4 Hz, 4H), 2.70 (t, J = 7.6 Hz, 4H), 1.62 (m, 4H), 1.35 (m, 4H), 0.93 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.02, 192.58, 151.71, 136.93, 136.52, 130.44, 130.35, 130.16, 129.29, 35.96, 33.08, 22.29, 13.86.

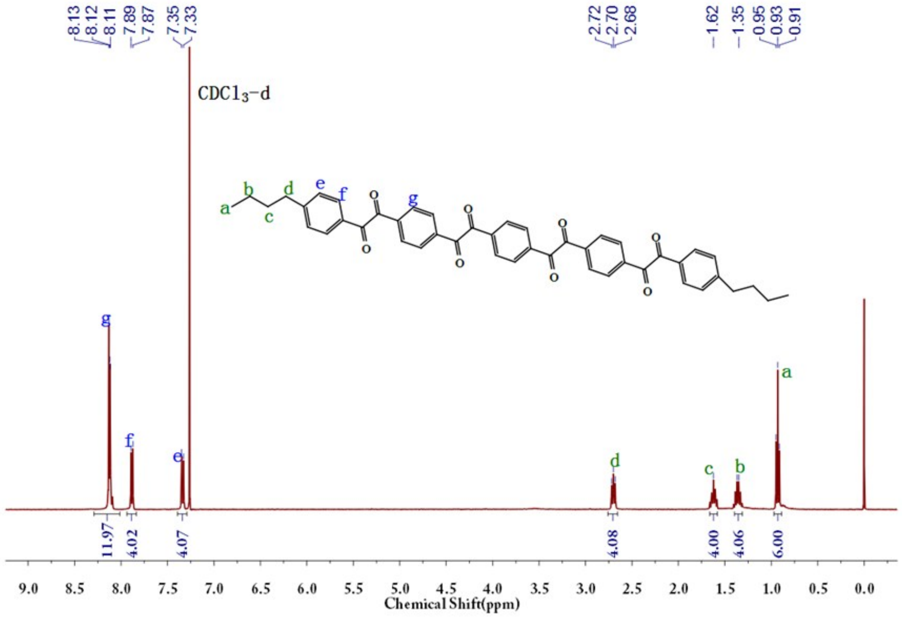


Fig. **S15** The ^{1}H NMR spectrum of **8b**.

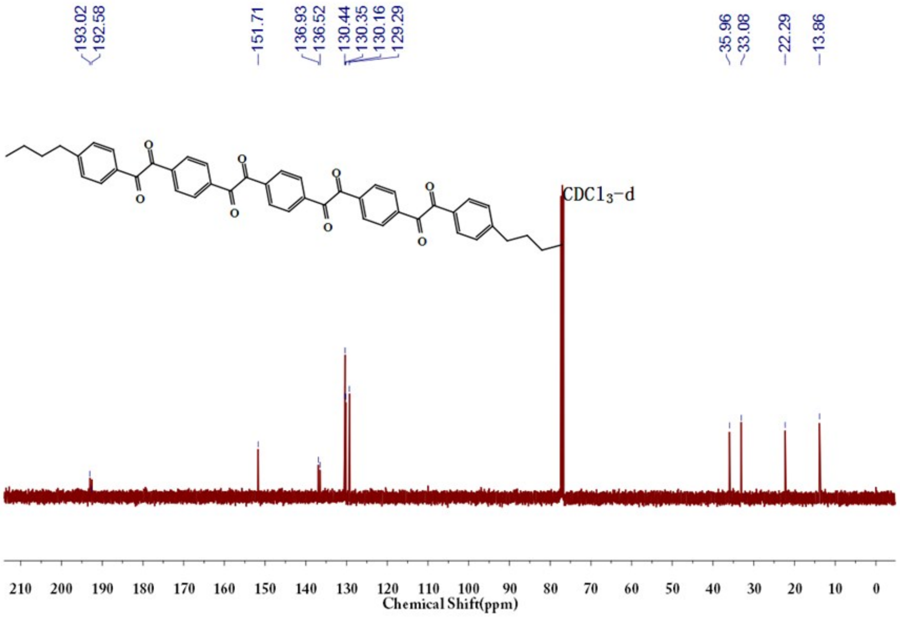


Fig. **S16** The ^{13}C NMR spectrum of **8b**.

*2,3-diphenylquinoxaline (**9a**).*

1,2-phenylenediamine (1.08 g, 10 mmol) and **5a** (2.10 g, 10 mmol) were added in a flask (250 mL) equipped with a reflux condenser, followed by the addition of acetic acid (120 mL). The mixture was stirred at 100℃ for 12h until the complete consumption of starting materials as judged by TLC. After the mixture was evaporated, the residue was then purified by column chromatography on silica gel to give **9a** (2.62 g, 92%).

MS (MALDI-TOF): m/z (%): 284.26 (100).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.19 (dd, *J* = 6.4Hz, 3.2 Hz, 2H), 7.77 (dd, *J* = 6.4Hz, 3.2Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 4H), 7.36-7.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.50, 141.22, 139.03, 129.84, 129.17, 128.28.

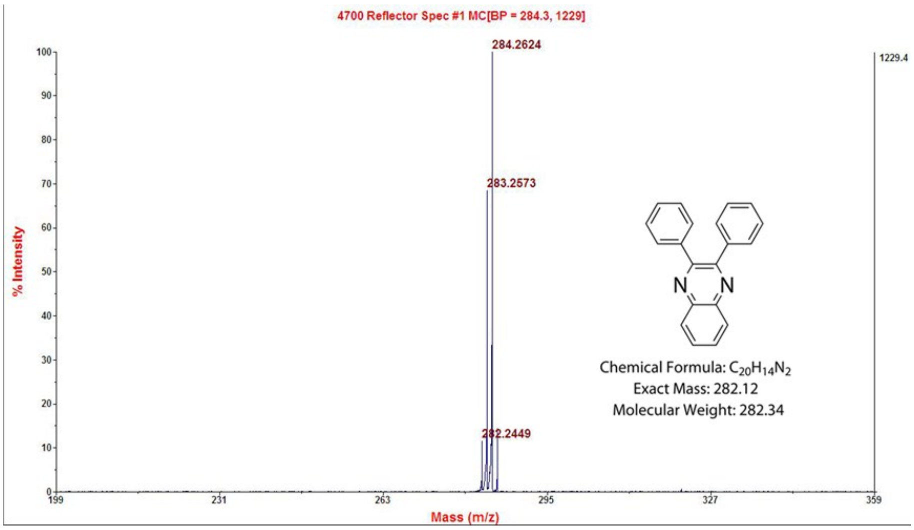


Fig. S17 The MALDI-TOF sprcturm of **9a**.

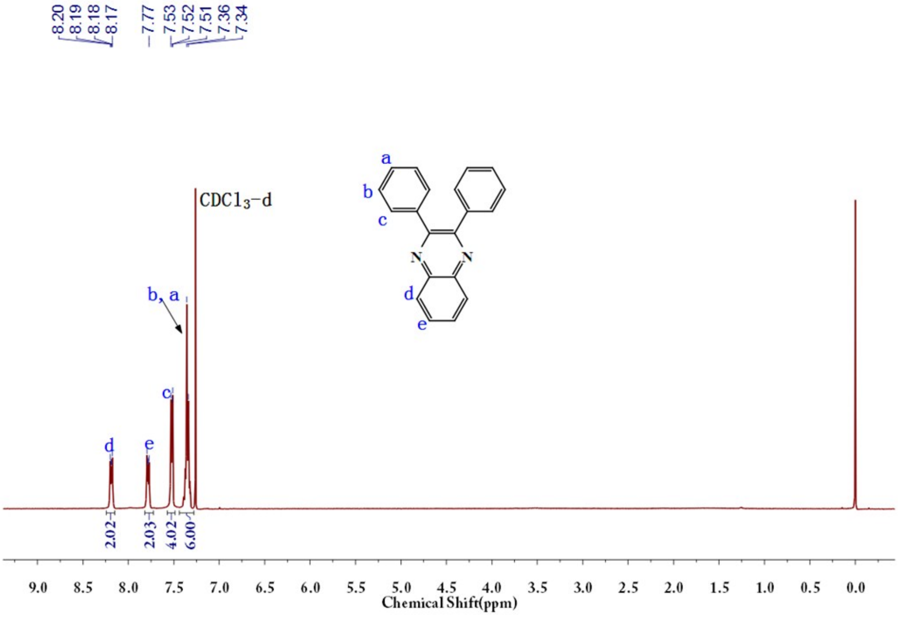


Fig. S18 The ^{1}H NMR spectrum of **9a**.

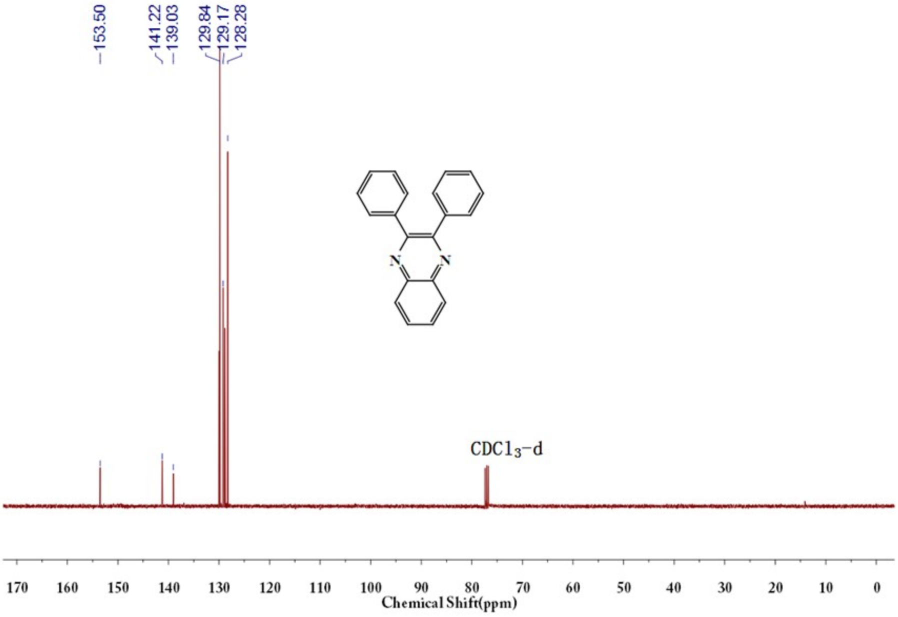


Fig. S19 The ^{13}C NMR spectrum of **9a**.

*2,3-bis(4-butylphenyl)quinoxaline (**9b**)*

1,2-phenylenediamine (0.95 g, 8.8 mmol) and **5b** (2.90 g, 8.8 mmol) were added in a flask (250 mL) equipped with a reflux condenser, followed by the addition of acetic acid (120 mL). The mixture was stirred at 100℃ for 12h until the complete consumption of starting materials as judged by TLC. After the mixture was evaporated, the residue was then purified by column chromatography on silica gel to give **9b** (3.24 g, 93%)

MS (MALDI-TOF): m/z (%): 396.42 (100).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (dd, J = 6.4Hz, 3.2 Hz, 2H), 7.73 (dd, J = 6.4 Hz, 3.2 Hz, 2H), 7.42 (d, J = 8.4 Hz, 4H), 7.14 (d, J = 8.0 Hz, 4H), 2.62 (t, J = 7.6 Hz, 4H), 1.61-1.59 (m, 4H), 1.33 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 153.62, 143.73, 141.16, 136.52, 129.70, 129.12, 128.35, 35.44, 33.40, 22.25, 13.95.

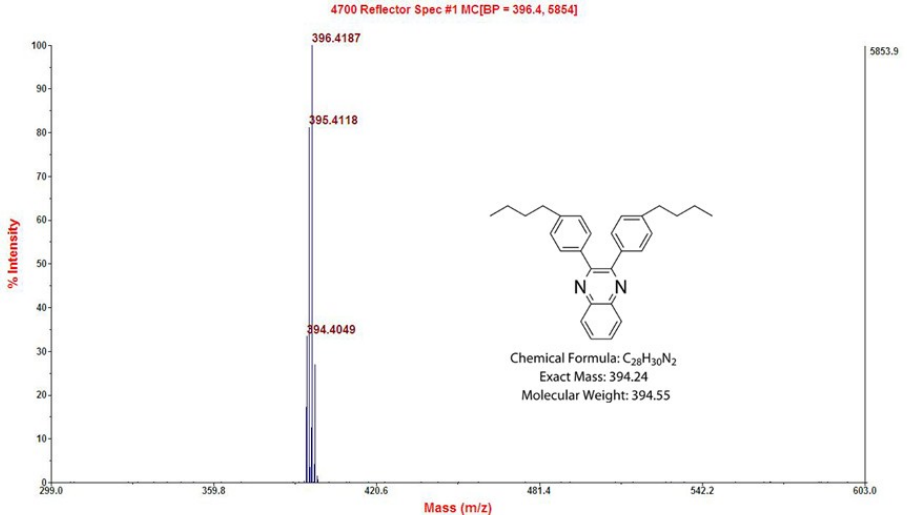


Fig. S20 The MALDI-TOF spectrum of **9b**.

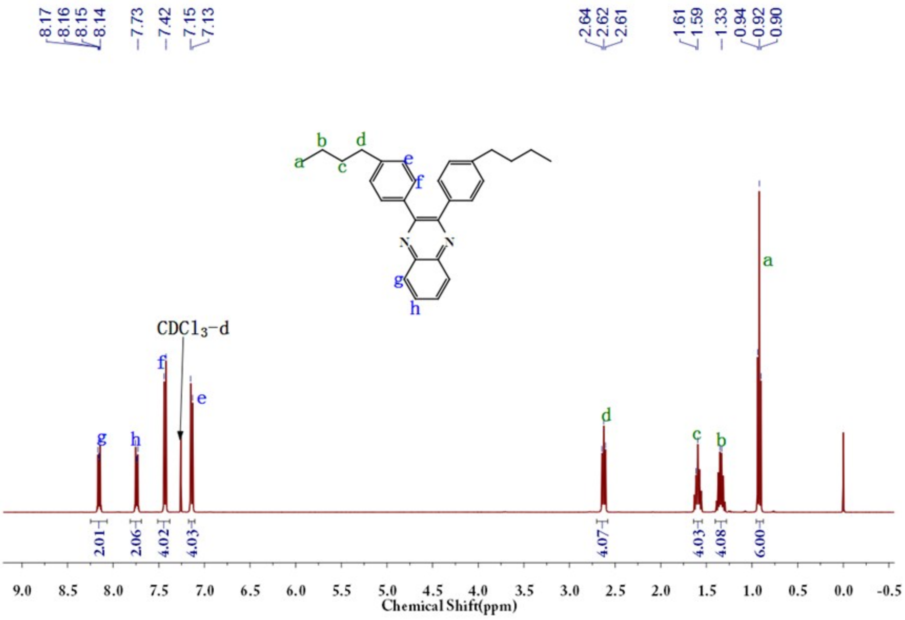


Fig. S21 The ^{1}H NMR spectrum of **9b.**

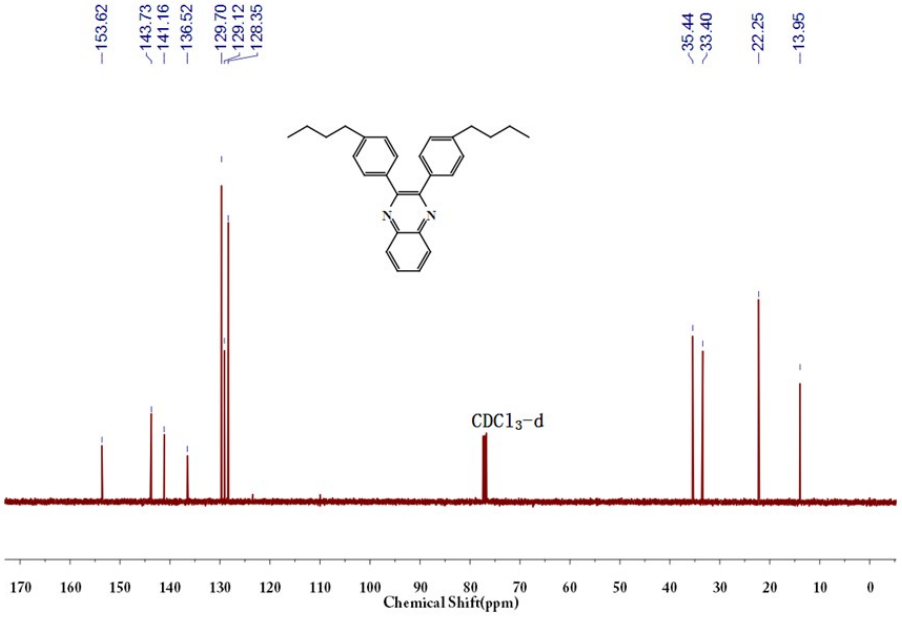


Fig. S22 The ^{13}C NMR spectrum of **9b**.

*1,4-bis(3-phenylquinoxalin-2-yl)benzene (**10a**)*

1,2-phenylenediamine (1.90 g, 17.6 mmol) and **6a** (3.00 g, 8.8 mmol) were added in a flask (250 mL) equipped with a reflux condenser, followed by the addition of acetic acid (120 mL). The mixture was stirred at 100℃ for 12h until the complete consumption of starting materials as judged by TLC. After the mixture was evaporated, the residue was then purified by column chromatography on silica gel to give **10a** (3.98 g, 93%)

MS (MALDI-TOF): m/z (%): 487.34 (100).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.22-8.20 (m, 4H), 7.82-7.79 (m, 4H), 7.55-7.51 (m, 8H), 7.34-7.32 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 153.43, 152.69, 141.19, 139.38, 138.86, 129.91, 129.84, 128.92, 128.36.

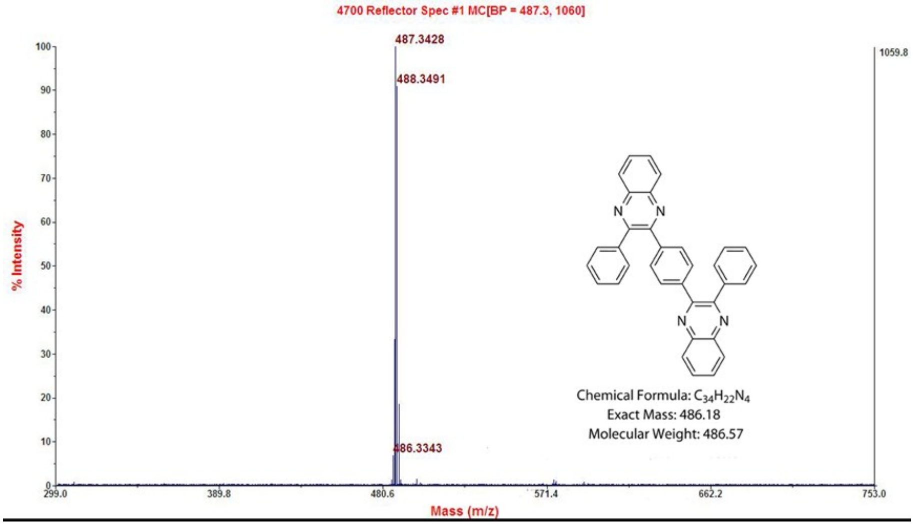


Fig. S23 The MALDI-TOF spectrum of **10a**.

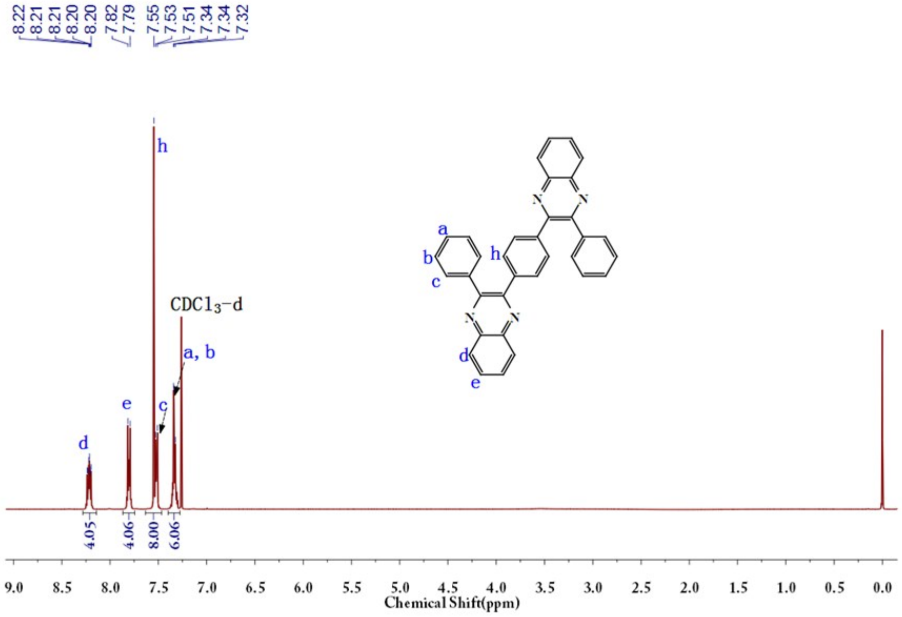


Fig. S24 The ^{1}H NMR spectrum of **10a**.

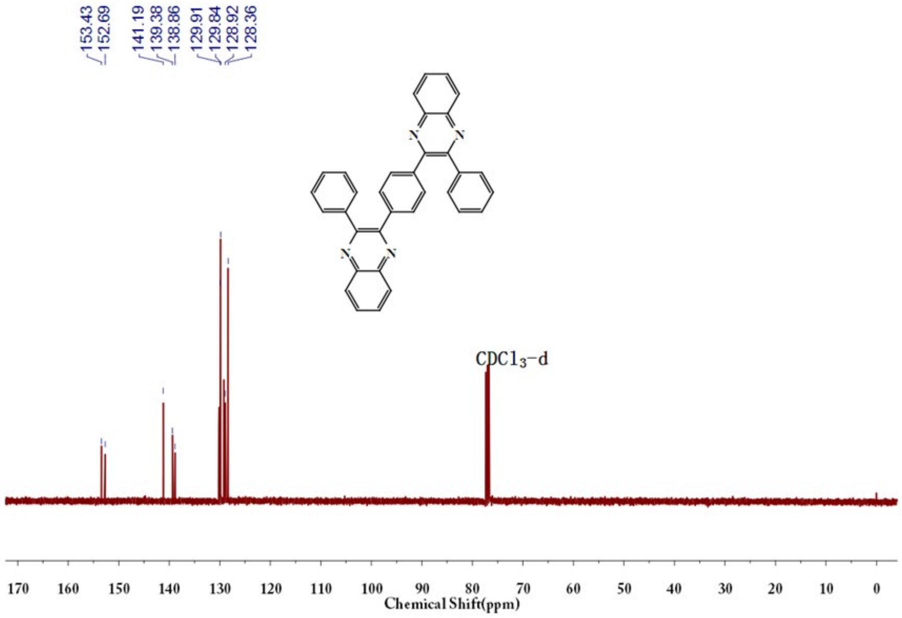


Fig. S25 The ^{13}C NMR spectrum of **10a**.

*1,4-bis(3-(4-butylphenyl)quinoxalin-2-yl)benzene (**10b**)*

1,2-phenylenediamine (0.95 g, 8.8 mmol) and **6b** (2.00 g, 4.4 mmol) were added in a flask (250 mL) equipped with a reflux condenser, followed by the addition of acetic acid (120 mL). The mixture was stirred at 100℃ for 12h until the complete consumption of starting materials as judged by TLC. After cooling, the resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (2.40 g, 91%).

MS (MALDI-TOF): m/z (%): 600.43 (100).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21-8.19 (m, 4H), 7.79 (dd, J = 6.4 Hz, 3.2 Hz, 4H), 7.56 (s, 4H), 7.42 (d, J = 8.0 Hz, 4H), 7.13 (d, J = 8.0 Hz, 4H), 2.59 (t, J = 7.6 Hz, 4H), 1.58-1.54 (m, 4H), 1.29 (m, 4H), 0.89 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.49, 152.76, 144.03, 141.08, 139.50, 136.09, 129.87, 129.78, 129.13, 129.12, 128.44, 35.43, 33.38, 22.29, 13.91.

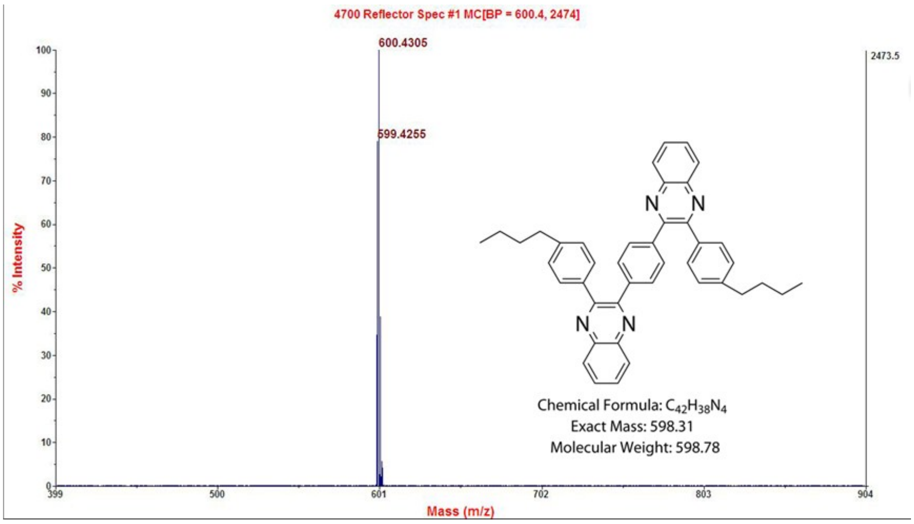


Fig. S26 The MALDI-TOF spectrum of **10b**.

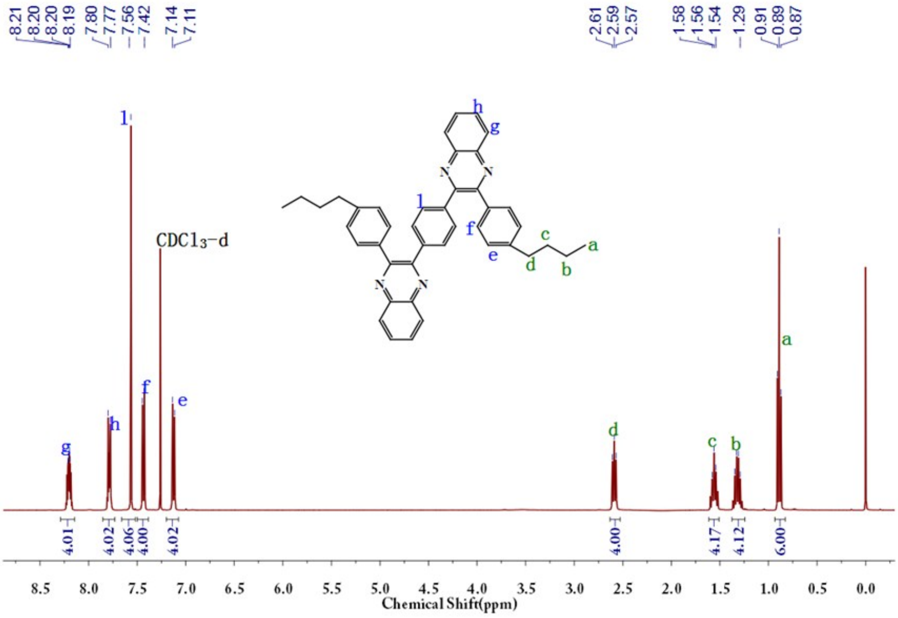


Fig. S27 The ^{1}H NMR spectrum of **10b**.

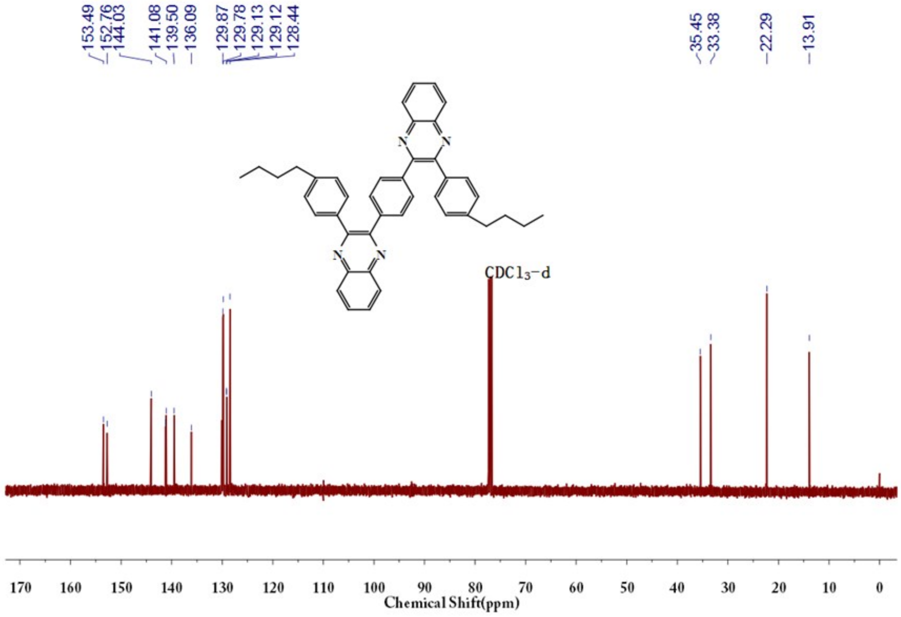


Fig. S28 The ^{13}C NMR spectrum of **10b**.

*2,3-bis(4-(3-phenylquinoxalin-2-yl)phenyl)quinoxaline (**11a**)*

1,2-phenylenediamine (1.36 g, 12.6 mmol) and **7a** (2.00 g, 4.2 mmol) were added in a flask (250 mL) equipped with a reflux condenser, followed by the addition of acetic acid (140 mL). The mixture was stirred at 100℃ for 12h until the complete consumption of starting materials as judged by TLC. After the mixture was evaporated, the residue was then purified by column chromatography on silica gel to give **11a**. (2.70 g, 93%).

MS (MALDI-TOF): m/z (%): 692.36 (100).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.20-8.19 (m, 6H), 7.80-7.77 (m, 6H), 7.46 (br, 12H), 7.25-7.23 (m, 4H), 7.18-7.17 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 152.75, 141.26, 139.46, 130.18, 130.10, 129.93, 129.87, 129.77, 129.21, 128.82, 128.36.

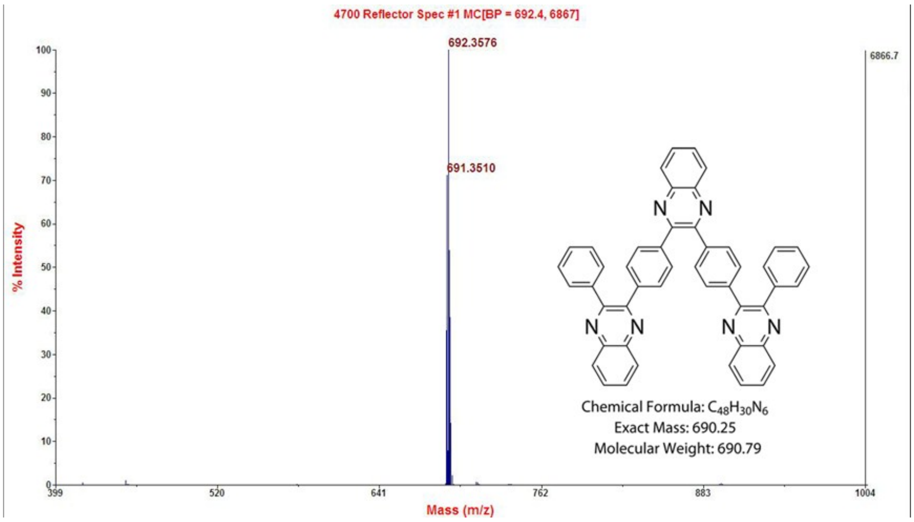


Fig. S29 The MALDI-TOF spectrum of **11a**.

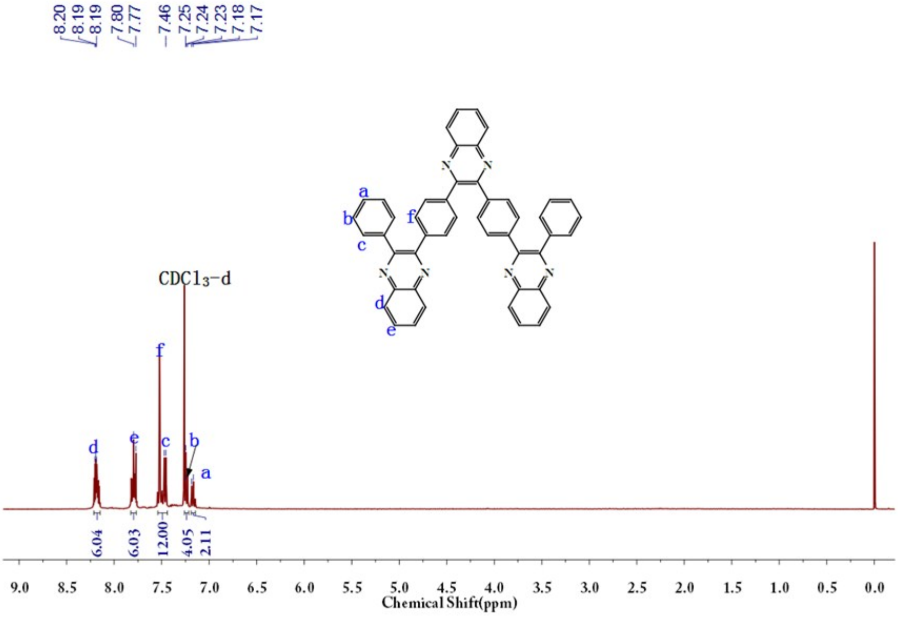


Fig. S30 The ^{1}H NMR spectrum of **11a**.

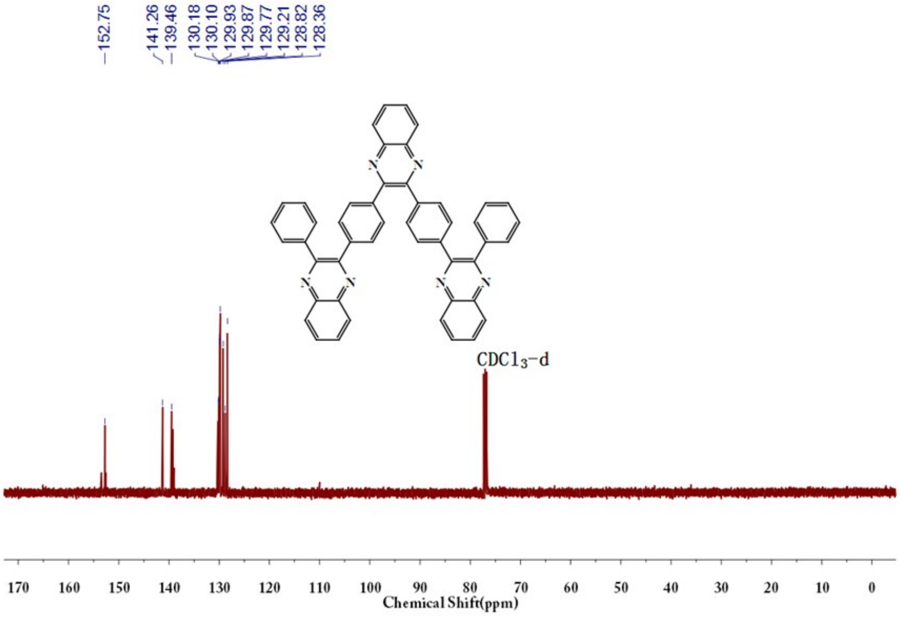


Fig. S31 The ^{13}C NMR spectrum of **11a**.

*2,3-bis(4-(3-(4-butylphenyl)quinoxalin-2-yl)phenyl)quinoxaline (**11b**)*

1,2-phenylenediamine (1.39 g, 12.9 mmol) and **7b** (2.50 g, 4.3 mmol) were added in a flask (250 mL) equipped with a reflux condenser, followed by the addition of acetic acid (140 mL). The mixture was stirred at 100℃ for 12h until the complete consumption of starting materials as judged by TLC. After cooling, the resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (3.15g, 91%).

MS (MALDI-TOF): m/z (%): 804.33 (100).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20-8.17 (m, 6H), 7.76 (m, 6H), 7.54 (s, 8H), 7.36 (d, J = 8.0 Hz, 4H), 7.05 (d, J = 8.4 Hz, 4H), 2.34 (t, J = 7.6 Hz, 4H), 1.43-1.41 (m, 4H), 1.15 (m, 4H), 0.82 (t, $J = 7.6$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.46, 152.71, 144.00, 139.67, 139.16, 136.00, 129.90, 129.72, 129.21, 128.45, 35.28, 33.34, 22.13, 13.87.

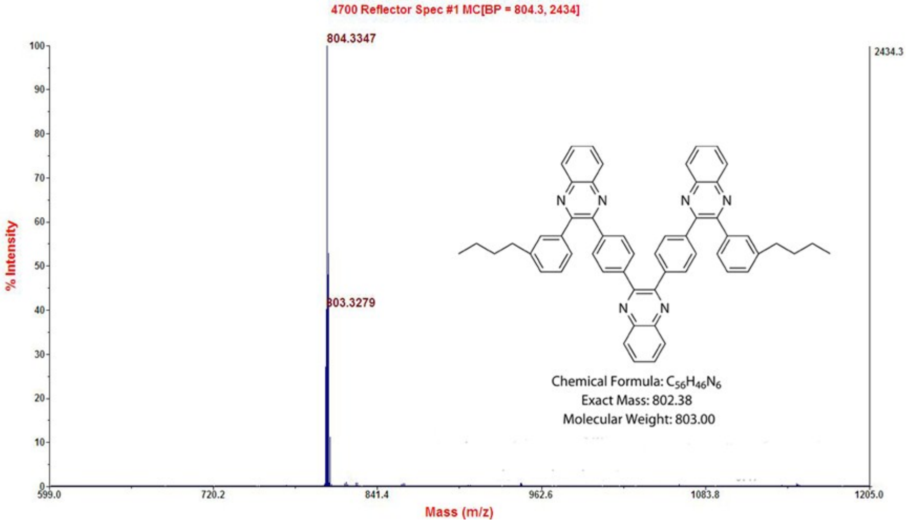


Fig. S32 The MALDI-TOF spectrum of **11b**.

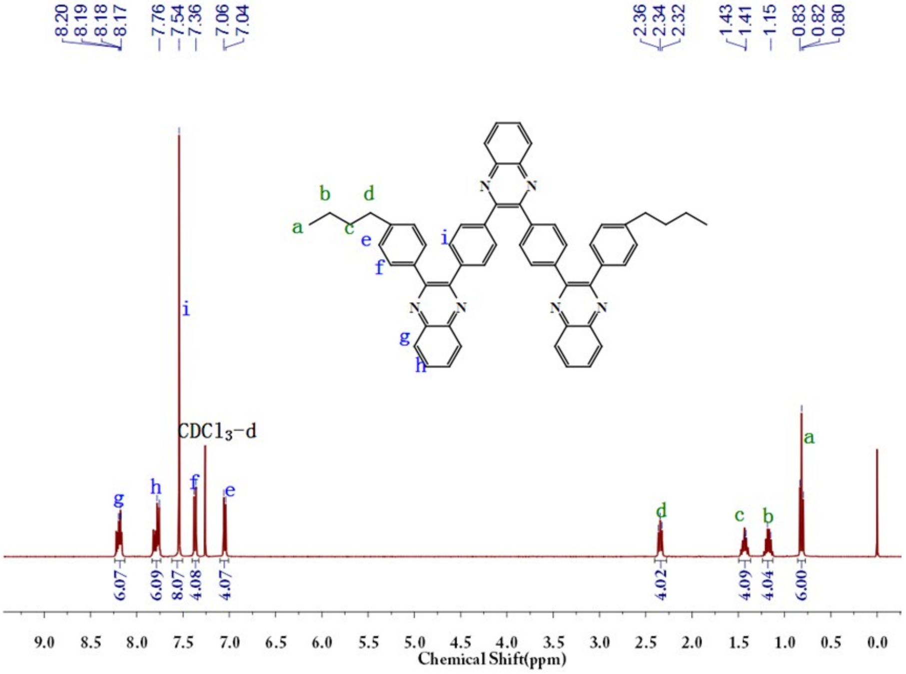


Fig. S33 The ^{1}H NMR spectrum of **11b**.

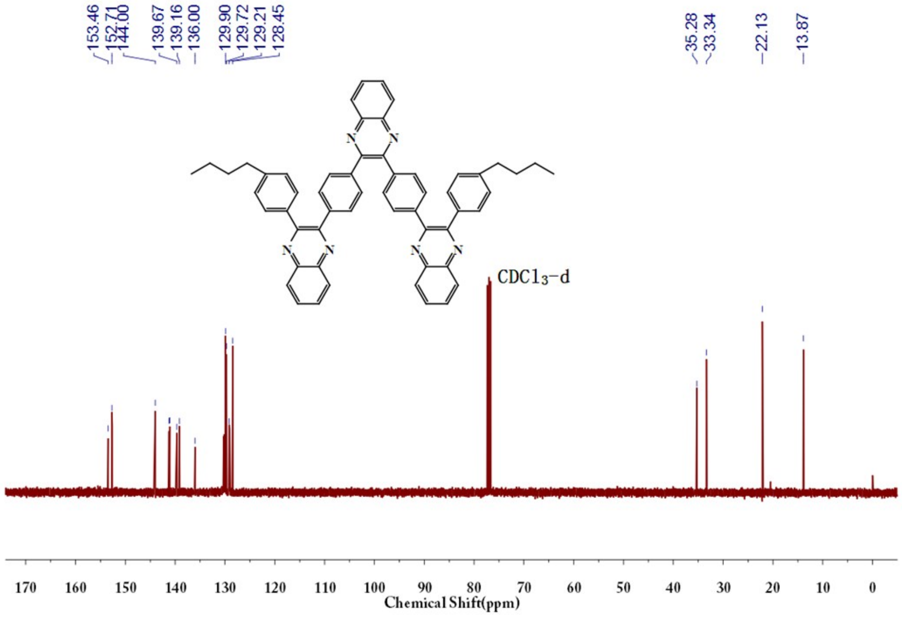


Fig. S34 The ^{13}C NMR spectrum of **11b**.

*1,4-bis(3-(4-(3-phenylquinoxalin-2-yl)phenyl)quinoxalin-2-yl)benzene (**12a**)*

1,2-phenylenediamine (1.77 g, 16.4 mmol) and **8a** (2.50 g, 4.1 mmol) were added in a flask (250 mL) equipped with a reflux condenser, followed by the addition of acetic acid (140 mL). The mixture was stirred at 100℃ for 12h until the complete consumption of starting materials as judged by TLC. After cooling, the resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (3.34 g, 91%).

MS (MALDI-TOF): m/z (%): 896.48 (100).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22-8.20 (m, 8H), 7.79-7.77 (m, 8H), 7.41 (br, 16H), 7.16 (t, *J* = 7.6 Hz, 4H), 6.99 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 152.66, 141.19, 139.27, 130.31, 129.93, 129.68, 129.39, 129.27, 128.33.

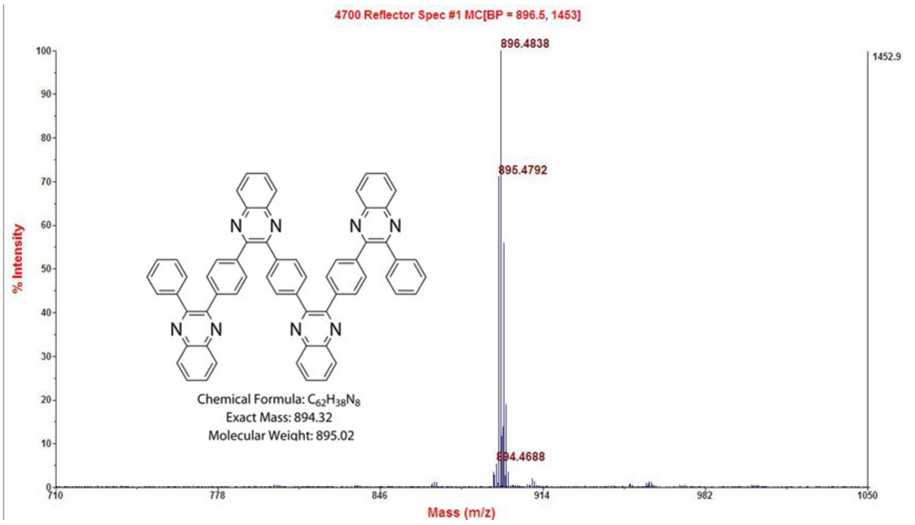


Fig. S35 The MALDI-TOF spectrum of **12a**.

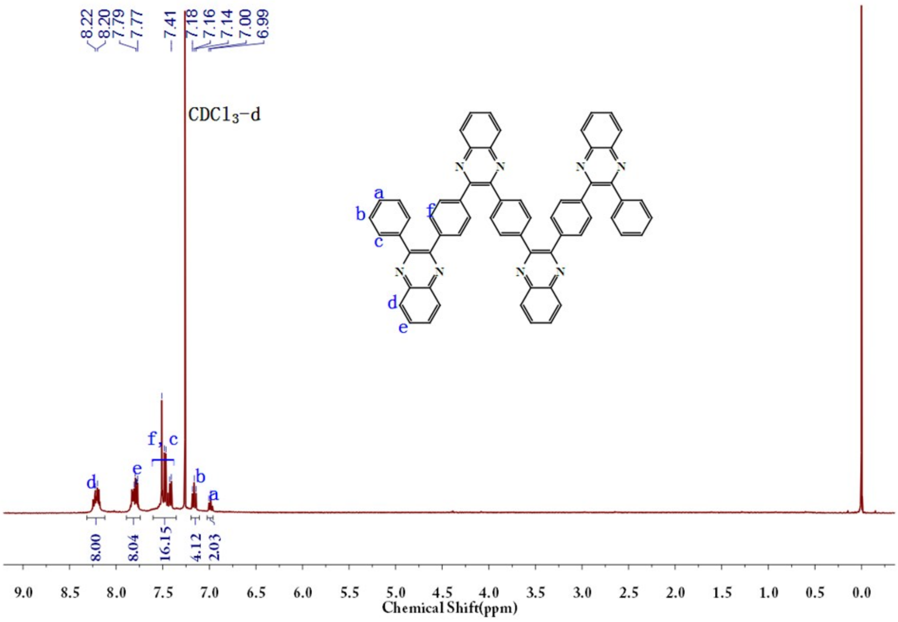


Fig. S36 The ^{1}H NMR spectrum of **12a**.

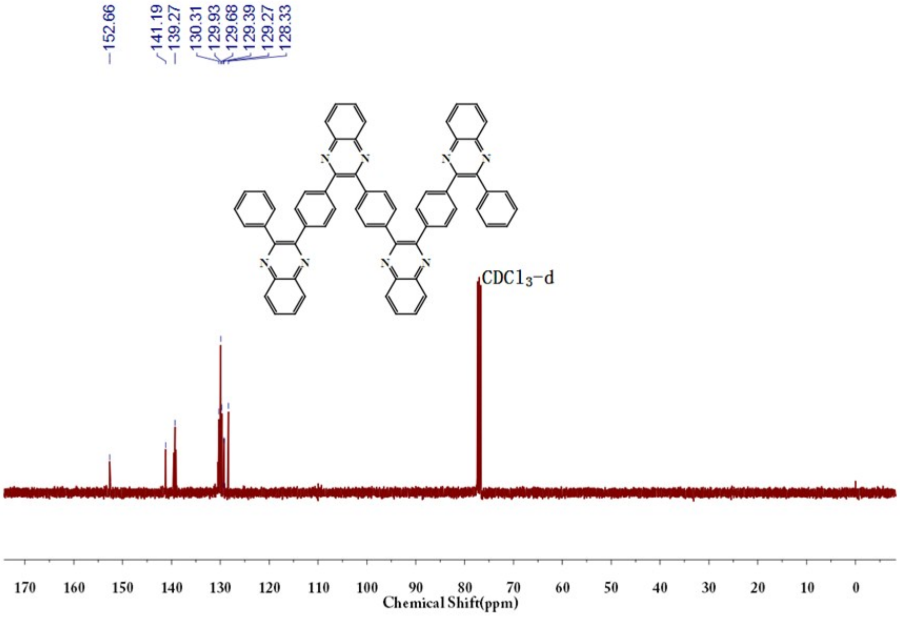


Fig. S37 The ^{13}C NMR spectrum of **12a**.

*1,4-bis(3-(4-(3-(4-butylphenyl)quinoxalin-2-yl)phenyl)quinoxalin-2-yl)benzene (**12b**)*

1,2-phenylenediamine (1.50 g, 13.9 mmol) and 8b (2.50 g, 3.5 mmol) were added in a flask (250 mL) equipped with a reflux condenser, followed by the addition of acetic acid (140 mL). The mixture was stirred at 100℃ for 12h until the complete consumption of starting materials as judged by TLC. After cooling, the resultant precipitate was collected by filtration. The crude product was washed with C_2H_5OH. After being dried, the product was obtained (3.59 g, 92%).

MS (MALDI-TOF): m/z (%): 1115.19 (100) $[M+Ag]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20-8.13 (m, 8H), 7.80 (m, 8H), 7.53-7.48 (m, 12H), 7.32 (d, J = 8.0 Hz, 4H), 6.96 (d, J = 8.0 Hz, 4H), 2.16 (t, J = 7.2 Hz, 4H), 1.34-1.31 (m, 4H), 1.04 (m, 4H), 0.75 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.41, 152.71, 143.83, 139.82, 139.49, 136.16, 129.91, 129.62, 122.33, 35.21, 33.35, 22.07, 13.82.

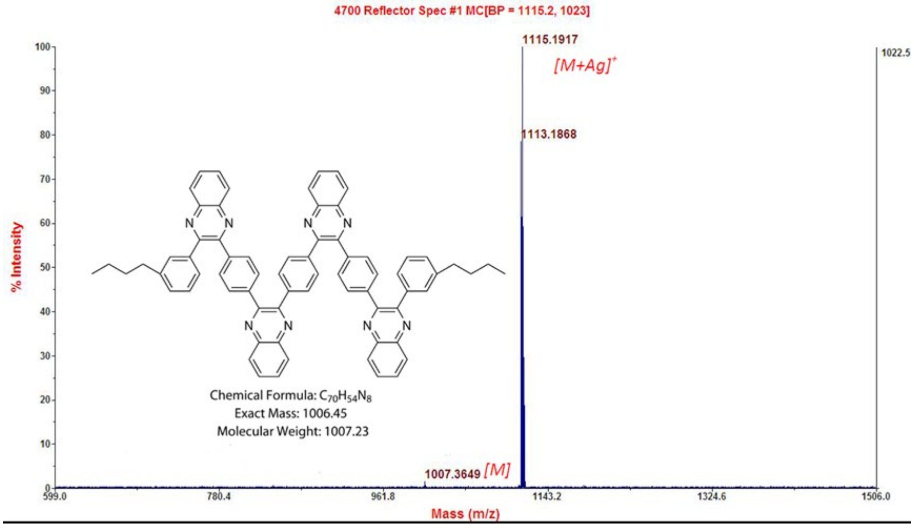


Fig. S38 The MALDI-TOF spectrum of **12b**.

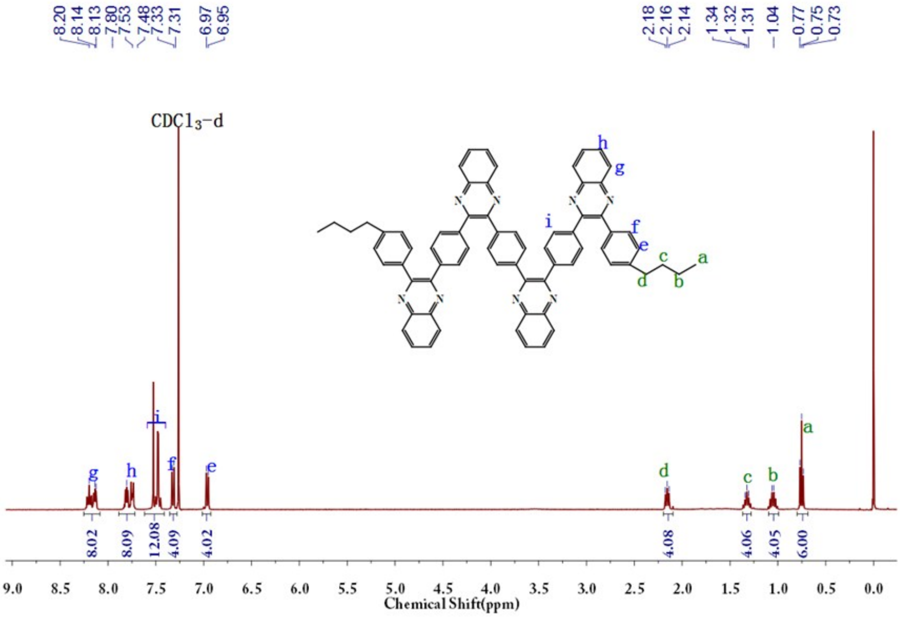


Fig. S39 The ^{1}H NMR spectrum of **12b**.

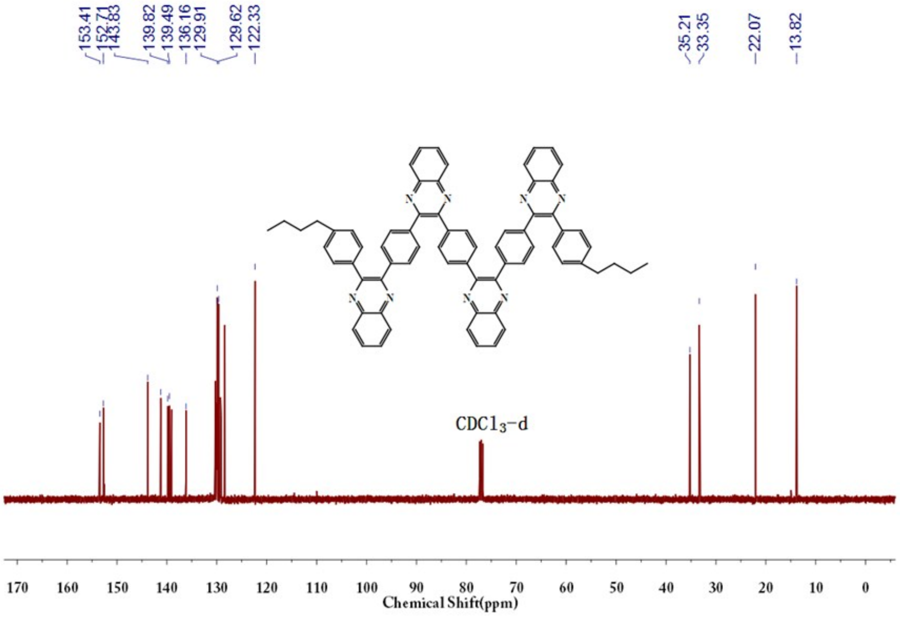
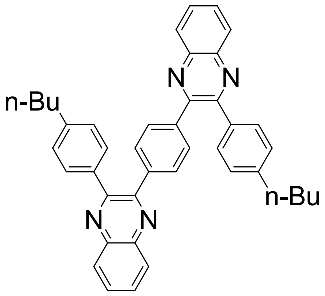


Fig. S40 The ^{13}C NMR spectrum of **12b**.

Table S1. Crystal data and reflection collection parameters for the molecules **10b**



Empirical formula	$C_{42}H_{38}$ N_4
Formula weight	598.78
Crystal size, mm	0.26 x 0.21 x 0.19
Crystal system	Monoclinic, P2(1)/n
space group	P2(1)/n
a, Å	5.981(4)
b, Å	14.384(4)
c, Å	19.951(3)
a, deg	90
β, deg	92.31(3)
γ, deg	90
V, Å^3	1714.9(12)
Z	2
Calculated density, Mg/m^3	1.160
F(000)	636.0
Temperature, K	296(2)
Wavelength, Å	0.71073
μ(Mo Ka), mm^{-1}	0.068
$2\theta_{max}$,deg (Completeness)	50.00(99.7 %)
no. of collected reflections	8379
no. of unique ref.(R_{int})	3006(0.0515)
Data/restraints/parameters	3006 / 20 / 209
R_1, wR_2 [obs I>2σ (I)]	0.0621, 0.1459
R_1, wR_2 (all data)	0.1107, 0.1596
residual peak/hole, e. Å^{-3}	0.404/-0.272
transmission ratio	0.9872/0.9825
Goodness-of-fit on F^2	1.085

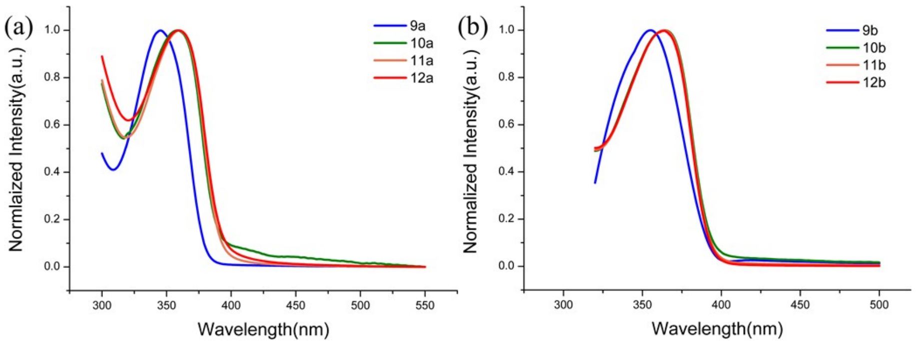


Fig. S41 The normalized UV spectra of compounds (a) **9a-12a** and (b) **9b-12b** in $CHCl_3$ solutions.

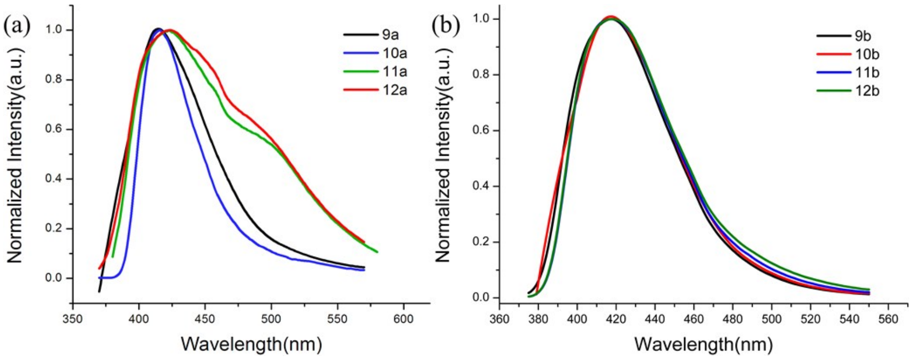


Fig. S42 The normalized PL spectra of compounds (a) **9a-12a** and (b) **9b-12b** in $CHCl_3$ solutions.

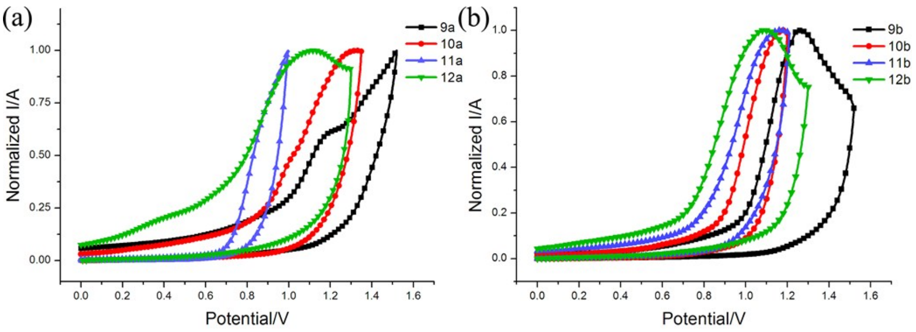


Fig. S43 The CV curves of compounds (a) **9a-12a** and (b) **9b-12b**.

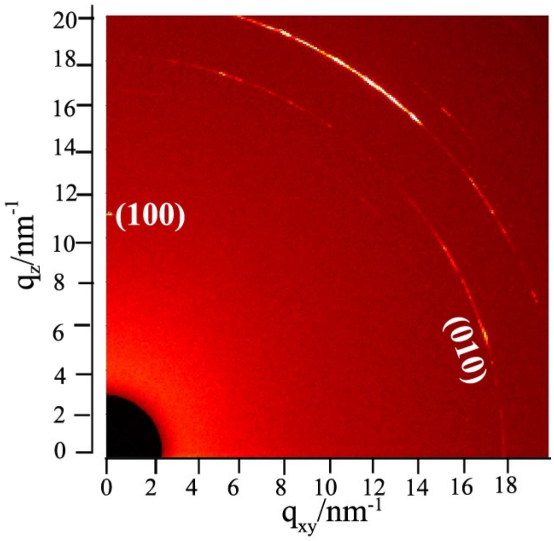


Fig. S44 The 2D-GIXRD pattern of **11a**.

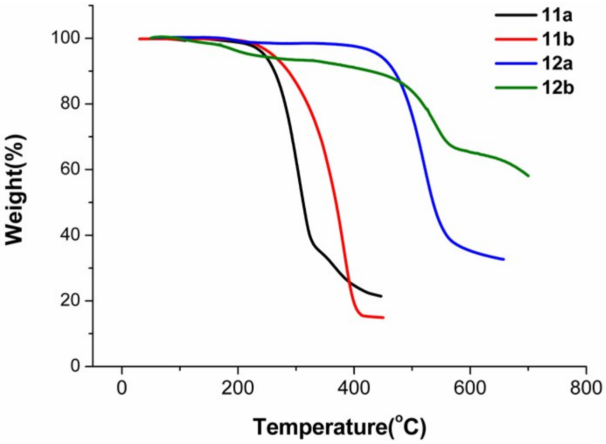


Fig. S45 The TGA spectra of **11a-12a** and **11b-12b**.

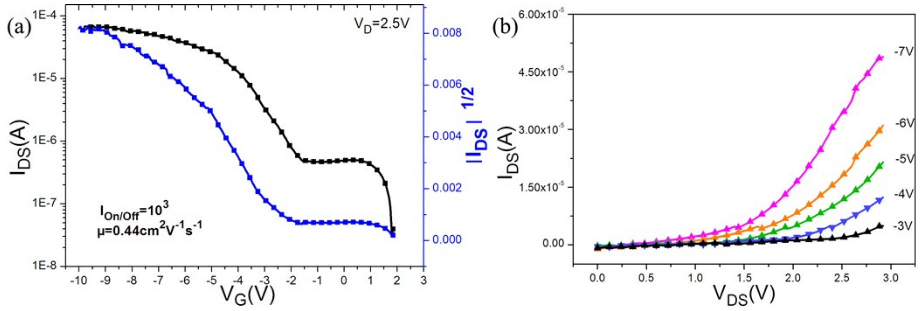


Fig. S46 (a) Transfer and (b) output characteristics of ion gel gated **11b** devices at a drain source voltage (V_{DS}) =2.5V.

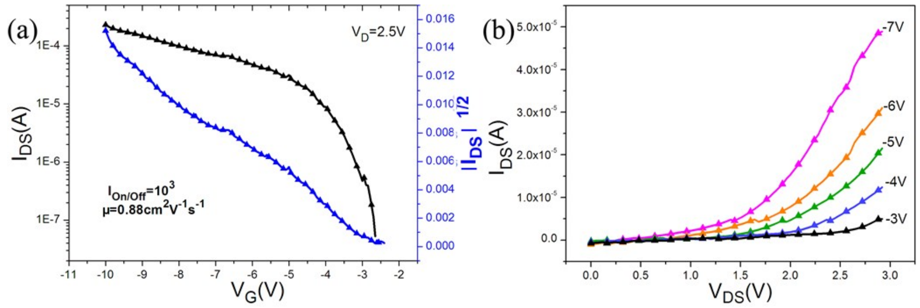


Fig. S47 (a) Transfer and (b) output characteristics of ion gel gated **12b** devices at a drain source voltage (V_{DS}) =2.5V.

Reference:

1. Yang, J.; Chen, M.; Ma, J.; Huang, W.; Zhu, H.; Huang, Y.; Wang, W. *J. Mater. Chem. C* **2015**, *3*, 10074.