

Supporting information

1. Experimental materials

4-Fluorobenzoic acid, 3-bromo-4-fluorobenzoic acid, hydrazine sulfate, phosphorus pentoxide (P_2O_5), methanesulfonic acid (99%+), toluene, cesium carbonate, ethanol, 4-iodophenol, phenylacetylene, phenylboronic acid, *N,N*-dimethylformamide (DMF), dichloromethane, sodium hydroxide, cuprous iodide (CuI), triphenylphosphine (PPh_3), bromoethane, magnesium powder, dimethyldichlorosilane, 2-methyl-3-butyn-2-ol, hydrochloride, triethylamine (NEt_3), tetrahydrofuran (THF) and acetic acid were obtained from Shanghai Titan Scientific Co., Ltd, China. Palladium chloride was purchased from Shanghai Macklin Biochemical Co., Ltd. THF must be dried by sodium. All solvents were refluxed and dried before used. T300 carbon fibre cloth was purchased from Toray Industries, Inc, Japan.

2. Instruments and measurements

1H -NMR spectrum was obtained on AVANCE500 spectrometer (Bruker, Massachusetts, USA) operating at 400 MHz with tetramethylsilane as internal standard and $CDCl_3$ -d as a solvent. The FT-IR spectrum was obtained using a Nicolet iS10 infrared spectrometer (Thermo Scientific, Madison, USA) by the KBr method. The melting points (M.P.) were determined with a X4 melting apparatus (Shanghai Analytic Instrument Factory, China), sample is placed in a capillary glass tube. Rheological behaviours were determined on a Thermo Haake RS600 Rheometer system (Thermo Electron Corporation, Germany) in the range of rt-200°C, the shear rate and heating rate for the viscosity measurements were $0.01\ s^{-1}$ and $2^\circ C \cdot min^{-1}$, respectively. DSC analyses were performed on a TA Instruments Q2000 analyser (TA, New Castle, USA) at a heating rate of $10^\circ C \cdot min^{-1}$ under nitrogen flow of $50\ ml \cdot min^{-1}$. TGA tests were performed on a TGA/DSC 1LF analyser (METTLER TOLEDO, Greifensee, Switzerland) at a heating rate of $10^\circ C \cdot min^{-1}$ in nitrogen flow of $60\ ml \cdot min^{-1}$. DMA analysis was performed on a DMA 1 mechanical analyser (METTLER TOLEDO, Greifensee, Switzerland) at a heating rate of $5^\circ C \cdot min^{-1}$ and frequency of 1Hz in nitrogen. UV-Vis was performed on Ultraviolet-Visible Spectrometer (Lambda 950, 175-3300nm), X-ray diffraction (XRD) were carried out on Rotating Anode X-ray Powder Diffractometer (18KW/D/max2550VB/PC). Raman spectroscopy was performed on a laser micro-Raman spectrometer (Renishaw, England), the excitation wavelength is 785 nm, sample is solid powder. The small-angle X-ray scattering

(SAXS) measurements were collected on a Bruker NanoSTAR U by Xeuss 2.0 SAXS system (Xenocs France) using Metaljet Ga $K\alpha$ radiation at 220 W. The flexural properties were measured in a 3-point bend test at a crosshead speed of 2 mm·min⁻¹ at room temperature on a CMT 4204 universal testing machine (SANS, Shenzhen, China) according to GB/T 2570-1995 standard. The impact strengths were determined on a CEAST 9050 impact strength tester (CEAS, Italy) according to GB/T 1843-2008 standard.

3. Synthesis of monomers and resins

(1) 2,5-Bis-(4-fluoro-phenyl)- [1,3,4]-oxadiazole (BFOD)

300 g Methanesulfonic acid, 30 g phosphorus pentoxide were stirred, after the reaction had proceeded for 1-2 h at 55°C, the solution became clear. And then, 4-fluorobenzoic acid (42.0 g, 0.30 mol) and hydrazine sulfate(21.0 g, 0.16 mol) were carefully added to the flask. The mixture was stirred for 1-2 h at 80°C and then poured into crushed ice to precipitate the solids. The precipitated solids were filtered, washed with water and purified by recrystallization from ethanol to obtain BFOD (Yield: 97.1%, m.p.: 201-203°C). ¹H-NMR (400MHz, CDCl₃; ppm): 7.20-7.30 (t, 4H, Ar-H); 8.08-8.21 (t, 4H, Ar-H). FT-IR (KBr, cm⁻¹): 3103, 3064 (Ar-H), 1607 ([1,3,4]-oxadiazole ring), 1227 (Ar-F), 1067(C-O-C).

(2) 2,5-Bis(4-(4-iodophenoxy) phenyl)- [1,3,4]-oxadiazole (BIPOD)

BFOD (25.8 g, 0.10 mmol), 4-iodophenol (48.0 g, 0.22 mmol), cesium carbonate (78 g, 0.24 mmol) and 150 ml DMF were added into the 250 ml flask under the nitrogen atmosphere, the mixture was heated at 110°C for 12 h. After completion of the reaction, the mixture was cooled to room temperature, and carefully poured into the crush-ice to get the crude product. And then, the solid was filtered, washed by water and recrystallized by ethanol to obtain BIPOD (Yield: 95.2%, m.p.: 234-236°C). ¹H-NMR (400MHz, CDCl₃; ppm): 8.12 (q, 4H, Ar-H), 7.72 (q, 2H, Ar-H), 7.14 (m, 6H, Ar-H), 6.89 (m, 8H, Ar-H). FT-IR (KBr, cm⁻¹): 3083 (Ar-H), 1611 ([1,3,4]-oxadiazole ring), 1221 (Ar-OAr), 1007 (C-O-C), 500 (Ar-I).

(3) 2,5-Bis(4-(4-(3-methyl-3-hydroxybutynyl)-phenoxy) phenyl)- [1,3,4]-oxadiazole (BMHPOD)

BIPOD (66 g, 0.10 mol) was dissolved into 300 ml THF/NEt₃ (2:1, vol) solution under the nitrogen atmosphere, the mixture was heated at 50 °C for 1 h. Then, 2-methyl-3-butyn-2-ol (25.2 g,0.30 mol) was slowly added into the mixture under nitrogen atmosphere. The reaction mixture was heated to 80°C and maintained 5 h. After the completion of reaction, the resulting mixture was filtered through Buchner funnel and

the filtrate was concentrated under low pressure to remove all the solvent. The residue was recrystallized with ethyl acetate/petrol ether to obtain BMHPOD (Yield: 90.3%, m.p.: 237-238°C). ¹H-NMR (400MHz, CDCl₃; ppm): 8.10 (m, 4H, Ar-H), 7.45 (m, 4H, Ar-H), 7.12 (m, 4H, Ar-H), 7.02 (m, 4H, Ar-H), 1.56 (s, 12H, -CH₃). FT-IR (KBr, cm⁻¹): 3426 (-OH), 2982 (-CH₃), 2231 (C≡C), 1600 ([1,3,4]-oxadiazole ring), 1221 (Ar-O-Ar), 1014 (C-O-C).

(4) 2,5-Bis(4-(4-ethynylphenoxy) phenyl)- [1,3,4]-oxadiazole (BEPOD)

BMHPOD (40 g, 0.07 mol), sodium hydroxide (10 g, 0.25 mol) and 700 ml toluene were added into 1000 ml flask under the nitrogen atmosphere, the mixture was heated to reflux and maintained about 12 h. After the completion of reaction, the resulting mixture was filtered through Buchner funnel and the filtrate was concentrated under low pressure to remove all the solvent, the crude product was recrystallized by ethanol to get BEPOD (Yield: 88.5%, m.p.: 193-194°C, purity: 98.9%). ¹H-NMR (400MHz, CDCl₃; ppm): 8.11 (m, 4H, Ar-H), 7.53 (m, 4H, Ar-H), 7.14 (m, 4H, Ar-H), 7.02 (m, 4H, Ar-H), 3.08 (s, 2H, ≡C-H). FT-IR (KBr, cm⁻¹): 3282 (≡C-H), 2220 (C≡C), 1598 ([1,3,4]-oxadiazole ring), 1104 (Ar-O-Ar), 963 (C-O-C).

(5) 2,5-Bis-(3-bromo-4-fluoro-phenyl)- [1,3,4]-oxadiazole (BFBOD)

40 g Methanesulfonic acid, 4 g phosphorus pentoxide were stirred, after the reaction had proceeded for 1-2 h at 55°C, the solution became clear. And then, 3-bromo-4-fluorobenzoic acid (9.03 g, 0.04 mol) and hydrazine sulfate (2.86 g, 0.022 mol) were carefully added to the flask. The mixture was stirred for 1-2 h at 80°C and then poured into crushed ice to precipitate the solids. The precipitated solids were filtered, washed with water and purified by recrystallization from ethanol to obtain 8.83 g BFBOD. (Yield: 93.3%, m.p.: 165-167°C). ¹H-NMR (400MHz, CDCl₃; ppm): 8.30-8.40 (m, 2H, Ar-H), 8.08-8.12 (m, 2H, Ar-H), 7.28-7.33 (t, 2H, Ar-H). FT-IR(KBr): 3089, 3063 cm⁻¹(Ar-H), 1605 ([1,3,4]-oxadiazole ring), 1272 (Ar-F), 548 (Ar-Br).

(6) 2,5-Bis(4-fluoro-3-(phenylethynyl) phenyl)-1,3,4-oxadiazole (BFOD-2E)

BFBOD (37.5 g, 0.09 mol) was dissolved into 300 ml THF/NEt₃ (2:1, vol) solution under the nitrogen atmosphere, the mixture was heated at 50°C for 1 h. Then, phenylacetylene (27 g, 0.23 mol) was slowly added into the mixture under nitrogen atmosphere. The reaction mixture was heated to 80°C and maintained 15 h. After the completion of reaction, the resulting mixture was filtered through Buchner funnel and the filtrate was concentrated under low pressure to remove all the solvent. The residue was recrystallized with ethyl acetate/petrol ether to obtain BFOD-2E. (Yield: 90.2%,

m.p.: 156-158°C). ¹H-NMR (400MHz, CDCl₃; ppm): 7.27-7.31(t, Ar-H, 2H), 7.36-7.41(m, Ar-H, 6H), 7.57-7.61(m, Ar-H, 4H), 8.11-8.15(m, Ar-H, 2H), 8.31(s, Ar-H, 2H). FT-IR(KBr): 3057 (Ar-H), 2219 (C≡C), 1613, 1596 ([1,3,4]-oxadiazole ring), 1262 (Ar-H).

(7) 2,5-Bis(4-(4-iodophenoxy)-3-(phenylethynyl) phenyl)-1,3,4-oxadiazole (BIPOD-2E)

BFOD-2E (45.6 g, 0.1 mmol), 4-iodophenol (48.0 g, 0.22 mmol), cesium carbonate (78.0 g, 0.24 mmol) and 150 ml DMF were added into the 250 ml flask under the nitrogen atmosphere, the mixture was heated at 110°C for 12 h. After completion of the reaction, the mixture was cooled to room temperature, and carefully poured into the crush-ice to get the crude product. And then, the solid was filtered, washed by water and recrystallized by ethanol to obtain BIPOD-2E. (Yield: 89.8%, m.p.:195-196°C). ¹H-NMR (400MHz, CDCl₃; ppm): 6.87-6.89(d, Ar-H, 4H), 7.06-7.08(d, Ar-H, 2H), 7.32-7.35(m, Ar-H, 6H), 7.41-7.42(d, Ar-H, 2H), 7.42-7.43(d, Ar-H, 2H), 7.68-7.71(d, Ar-H, 4H), 8.06-8.09(m, Ar-H,2H), 8.34(s, Ar-H, 2H). FT-IR(KBr): 3081, 3059 (Ar-H), 2214 (C≡C), 1609, 1597 ([1,3,4]-oxadiazole ring), 1221 (Ar-O-Ar), 1006 (C-O-C), 492 (Ar-H).

(8) 2,5-Bis(4-(4-ethynylphenoxy)-3-(phenylethynyl) phenyl)-1,3,4-oxadiazole (BEPOD-2E)

BIPOD-2E (66 g, 0.10 mol) was dissolved into 300 ml THF/NEt₃ (2:1, vol) solution under the nitrogen atmosphere, the mixture was heated at 50°C for 1 h. Then, PdCl₂(PPh₃)₂(2.0 g), PPh₃(1.0 g), CuI(1.0 g) and 2-methyl-3-butyn-2-ol (25.2 g, 0.30 mol) were slowly added into the mixture under nitrogen atmosphere. The reaction mixture was heated to 80°C and maintained 5 h. After the completion of reaction, the resulting mixture was filtered through Buchner funnel and the filtrate was concentrated under low pressure to remove all the solvent. The residue was recrystallized with ethyl acetate/petrol ether to obtain BMHPOD-2E. (Yield: 85.5%, m.p.: 236-237°C). ¹H-NMR (400MHz, CDCl₃; ppm): 1.65(s, -CH₃, 12H), 7.05-7.07(d, Ar-H, 4H), 7.09-7.11(d, Ar-H, 2H), 7.33-7.37(m, Ar-H, 6H), 7.44-7.49(m, Ar-H, 8H), 8.09-8.11(d, Ar-H, 2H), 8.37(s, Ar-H, 2H). FT-IR(KBr): 3385 (-OH), 3080 (Ar-H), 2977 (-CH₃), 2223(C≡C), 1613, 1595 ([1,3,4]-oxadiazole ring), 1221 (Ar-O-Ar), 1006 (C-O-C).

BMHPOD-2E (40 g, 0.07 mol), sodium hydroxide (10 g, 0.25 mol) and 700 ml toluene

were added into 1000 ml flask under the nitrogen atmosphere, the mixture was heated to reflux and maintained about 12 h. After the completion of reaction, the resulting mixture was filtered through Buchner funnel and the filtrate was concentrated under low pressure to remove all the solvent, the crude product was recrystallized by ethanol to get BEPOD-2E. (Yield: 90.3%, m.p.: 206-207°C, purity: 98.5%). ¹H-NMR (400MHz, CDCl₃; ppm): 3.07(s, ≡C-H, 2H), 7.03-7.06(d, Ar-H, 4H), 7.10-7.12(d, Ar-H, 2H), 7.30-7.35(m, Ar-H, 6H), 7.40-7.42(m, Ar-H, 8H), 7.52-7.54(d, Ar-H, 4H), 8.08-8.11(d, Ar-H, 2H), 8.36(s, Ar-H, 2H). FT-IR(KBr): 3286 (≡C-H), 3051 (Ar-H), 2223 (Ar-C≡C-Ar), 2108 (C≡C), 1612, 1594 ([1,3,4]-oxadiazole ring), 1221 (Ar-O-Ar), 1013 (C-O-C).

(9) 2,5-Bis(6-fluoro-[1,1'-biphenyl]-3-yl)-1,3,4-oxadiazole (BFOD-2P)

BFOD-2P (60 g, 0.15 mol) was dissolved into 1000 ml toluene/H₂O (2:1, vol) solution under the nitrogen atmosphere, the mixture was heated at 50°C for 1 h. Then, Pd(PPh₃)₄(4.0 g), PPh₃(2.0 g) and phenylboronic acid (38.7 g, 0.32 mol) were slowly added into the mixture under nitrogen atmosphere. The reaction mixture was heated to 80°C and maintained 20 h. After the completion of reaction, the resulting mixture was filtered through Buchner funnel and the filtrate was concentrated under low pressure to remove all the solvent. The residue was recrystallized by toluene to obtain BFOD-2P (Yield: 89.2%, m.p: 195-196°C). ¹H-NMR (400MHz, CDCl₃; ppm): 7.31-7.35(t, Ar-H, 2H), 7.42-7.45(d, Ar-H, 2H), 7.46-7.52(t, Ar-H, 4H), 7.61-7.62(d, Ar-H, 4H), 8.10-8.13(m, Ar-H, 2H), 8.22-8.24(d, Ar-H, 2H). FT-IR(KBr): 3063 (Ar-H), 1613, 1599 ([1,3,4]-oxadiazole ring), 1256 (Ar-F).

(10) 2,5-Bis(6-(4-iodophenoxy)-[1,1'-biphenyl]-3-yl)-1,3,4-oxadiazole (BIPOD-2P)

BFOD-2P (53 g, 0.13 mmol), 4-iodophenol (64 g, 0.29 mmol), cesium carbonate (105 g, 0.32 mmol) and 300 ml DMF were added into the 250 ml flask under the nitrogen atmosphere, the mixture was heated at 120°C for 12 h. After completion of the reaction, the mixture was cooled to room temperature, and carefully poured into the crush-ice to get the crude product. And then, the solid was filtered, washed by water and recrystallized by ethanol to obtain BIPOD-2P (Yield: 94.3%, m.p: 210-212°C). ¹H-NMR (400MHz, CDCl₃; ppm): 6.75-6.77(d, Ar-H, 4H), 7.08-7.10(d, Ar-H, 2H), 7.35-7.38(t, Ar-H, 2H), 7.40-7.44(t, Ar-H, 4H), 7.56-7.58(d, Ar-H, 2H), 7.60-7.62(d, Ar-H, 4H), 8.05-8.08(d, Ar-H, 2H), 8.20-8.21(d, Ar-H, 2H). FT-IR(KBr): 3058 (Ar-H), 1612 ([1,3,4]-oxadiazole ring), 1221 (Ar-O-Ar), 1005 (C-O-C), 492 (Ar-I).

**(11) 2,5-Bis(6-(4-ethynylphenoxy)-[1,1'-biphenyl]-3-yl)-1,3,4-oxadiazole
(BEPOD-2P)**

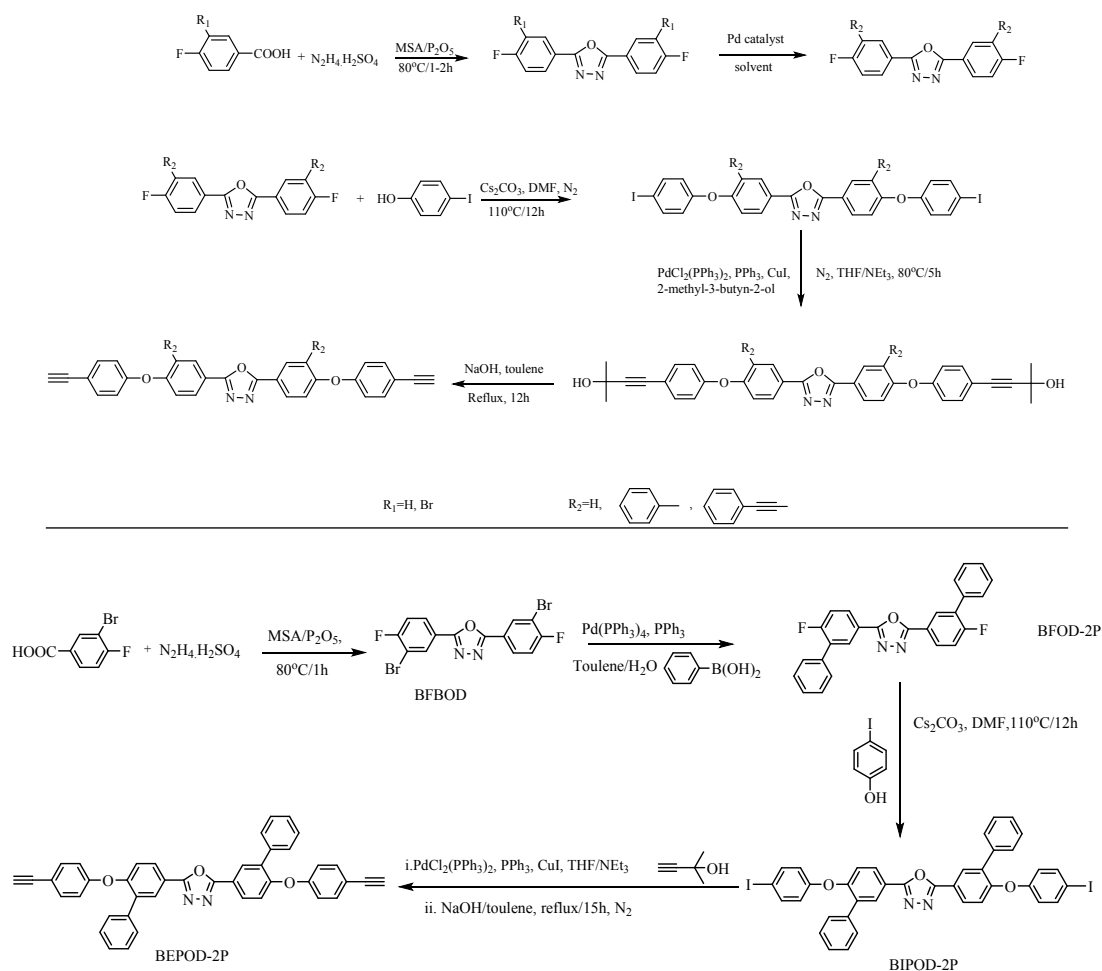
BIPOD-2P (66 g, 0.10 mol) was dissolved into 500 ml THF/NEt₃ (2:1, vol) solution under the nitrogen atmosphere, the mixture was heated at 50 °C for 1 h. Then, PdCl₂(PPh₃)₂(1.8 g), PPh₃(1.4 g), CuI(0.6 g) and 2-methyl-3-butyn-2-ol (25.2 g, 0.30 mol) were slowly added into the mixture under nitrogen atmosphere. The reaction mixture was heated to 80°C and maintained 12 h. After the completion of reaction, the resulting mixture was filtered through Buchner funnel and the filtrate was concentrated under low pressure to remove all the solvent. The residue was recrystallized with ethyl acetate/petrol ether to obtain BMHPOD-2P (Yield: 92.3%, m.p: 185-187°C). ¹H-NMR (400MHz, CDCl₃; ppm): 1.60-1.62 (s, 12H, CH₃), 6.90-6.93(m, 4H, Ar-H), 7.08-7.11(m, 2H, Ar-H), 7.33-7.43(m, 8H, Ar-H), 7.56-7.58(d, 4H, Ar-H), 8.06-8.08(d, 2H, Ar-H), 8.20-8.21(d, 2H, Ar-H). FT-IR(KBr): 3385 (-OH), 3057 (Ar-H), 2979 (-CH₃), 2226 (C≡C), 1598 ([1,3,4]-oxadiazole ring), 1221 (Ar-O-Ar), 1002(C-O-C).

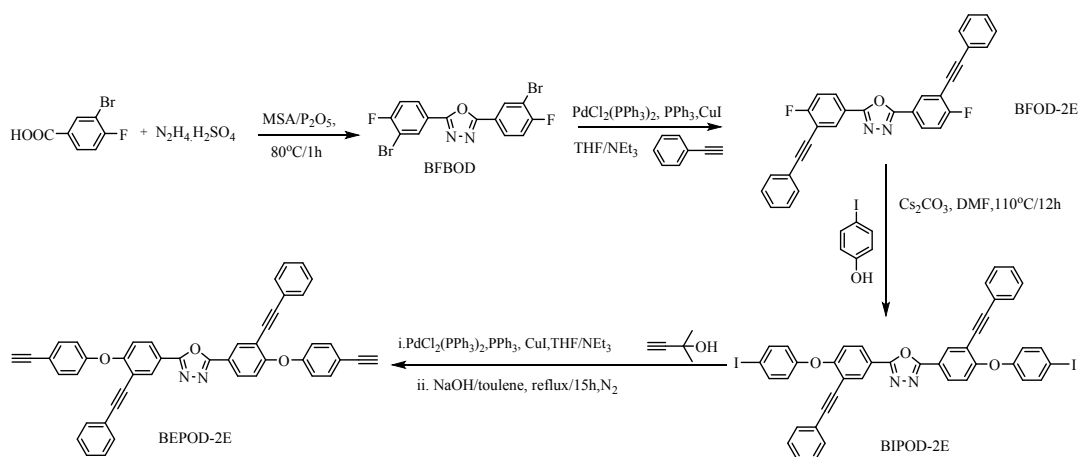
BMHPOD-2P (40 g, 0.07 mol), sodium hydroxide (10 g, 0.25 mol) and 700 ml toluene were added into 1000 ml flask under the nitrogen atmosphere, the mixture was heated to reflux and maintained about 12 h. After the completion of reaction, the resulting mixture was filtered through Buchner funnel and the filtrate was concentrated under low pressure to remove all the solvent, the crude product was recrystallized by ethanol to get BEPOD-2P. (Yield: 88.3%, m.p.: 171-173°C, purity: 98.8%). ¹H-NMR (400MHz, CDCl₃; ppm): 3.04(s, 2H, ≡C-H), 6.92-6.94(d, 4H, Ar-H), 7.11-7.13(d, 2H, Ar-H), 7.34-7.46(m, 8H, Ar-H), 7.56-7.58(d, 4H, Ar-H), 8.07-8.10(m, 2H, Ar-H), 8.22(d, 2H, Ar-H). FT-IR(KBr): 3292, 3266 (≡C-H), 3091, 3037(Ar-H), 2105 (C≡C), 1615, 1599 ([1,3,4]-oxadiazole ring), 1222 (Ar-O-Ar), 1004 (C-O-C).

(12) Synthesis of silicon-containing arylacetylene resins

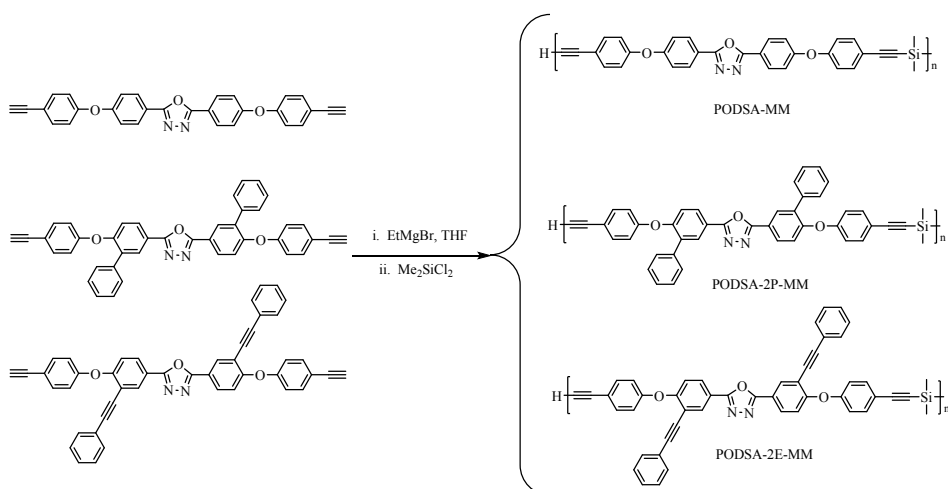
The synthetic procedures of novel resins are showed at Scheme 2. Take PODSA-2E-MM as an example, Magnesium powder (1.44 g, 0.60 mol) and THF (20 ml) were added to a 500 ml four-necked round-bottomed flask equipped with a condenser, a funnel and mechanical stirring bar. The mixture of bromoethane (5.6 g, 0.05 mol) and 20ml THF was added dropwise at nitrogen atmosphere, and the addition of the solution was finished in about 0.5 h. And then, the mixture was stirred for 1 h at 40°C. After that, the solution was cooled with an ice/water bath. A solution of 2,5-bis(4-(4-

ethynylphenoxy)-3-(phenylethynyl) phenyl)-1,3,4-oxadiazole (16.2 g, 0.025 mol) and 120 ml THF was added dropwise into the flask. The mixture was stirred constantly for 2 h at reflux temperature. And then, the white emulsion was cooled with the ice/water bath, a solution of dimethyldichlorosilane (2.13 g, 0.016 mol) and THF (20 ml) was added into the flask, the mixture was refluxed for 2 h. Most of THF was removed by distillation. The mixture was cooled with an ice/water bath, toluene (150 ml) was added into the flask. Afterwards, a solution of acetic acid (10.8 g, 0.180 mol) in toluene (20 ml) and 100 ml 10% aqueous hydrochloric acid were dropwise added to in turn the flask. The resulting organic phase was separated out, washed with deionized water to neutral solution and then dried by using anhydrous sodium sulphate. The solvent was evaporated under low pressure to give yellow solid.





Scheme 1 The synthetic routes of BEPOD, BEPOD-2P and BEPOD-2E



Scheme 2 The synthetic route of silicon-containing arylacetylene resins

The synthetic routes of PODSA-MM and PODSA-2P-MM are similar with that of PODSA-2E-MM by the replacement of BEPOD-2E with BEPOD, BEPOD-2P, respectively.

4. Preparation of cured resins and T300 carbon fibre composites

The resin was put in aluminum pan and the solvent was removed by vacuum at 160°C in oven. And then, according to heating procedure: 170°C/2 h+210°C/2 h+250°C/2 h+280°C/2 h, the black cured resins were obtained. The mechanical properties were tested according to ISO 178: 2010 standard.

PODSA-MM, PODSA-2P-MM and PODSA-2E-MM were dissolved in THF to prepare 30-33 wt% resin solution, separately. T300 (10 cm×15 cm) carbon fiber cloth of 12 layers were prepregated in solution and dried, and then pressed between two steel plates. Molding procedure: 170°C/2 h+210°C/2 h+250°C/2 h+280°C/2 h under the pressure of 3.0 MPa. The mechanical properties were tested according to ISO 14125: 1998 and ISO 527-4: 1997 standards. Interlaminar shear strength is abbreviated as

ILSS.

5. The DSC data of diynes

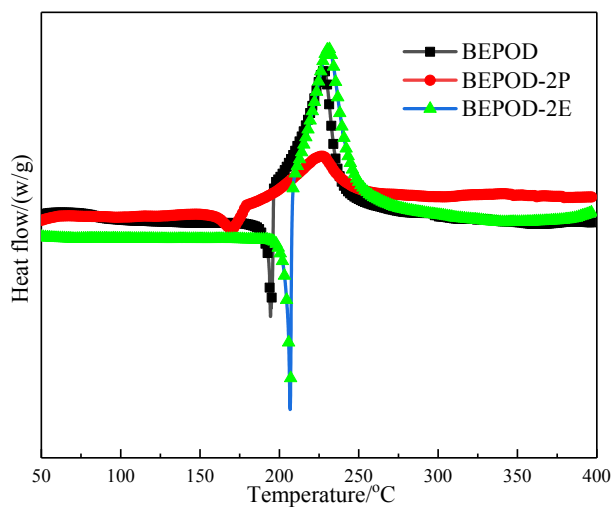


Figure S1 The DSC curves of three aromatic diynes

Table S1 The DSC data of three aromatic diynes

Sample	T_m (°C)	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
BEPOD	193	208	228	239	365.8
BEPOD-2P	173	225	242	255	360.3
BEPOD-2E	206	211	231	251	370.1

6. The 3D structures of diynes

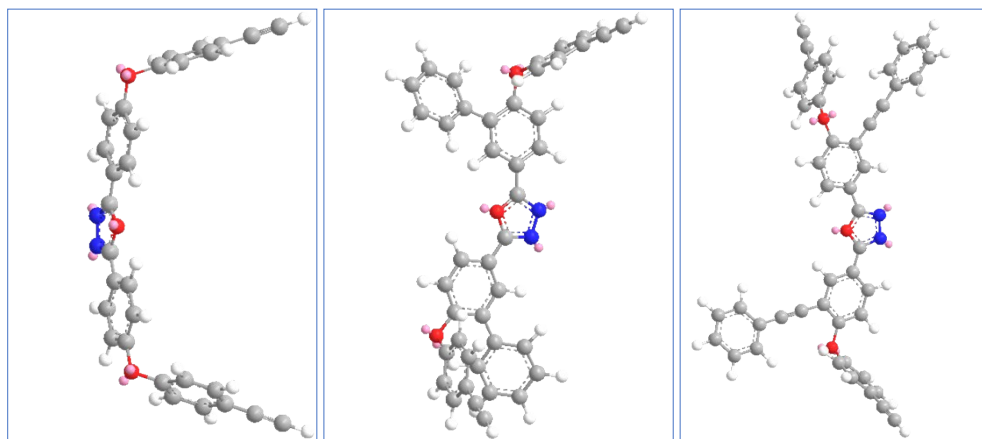


Figure S2 The 3D structures of diynes BEPOD, BEPOD-2P and BEPOD-2E, respectively