Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Dehydrobenzoannulene-based three dimensional graphdiyne for photocatalytic hydrogen generation using Pt nanoparticles as co-catalyst and triethanolamine as sacrificial electron donor

Han Shen, Weixiang Zhou, Feng He, Yanan Gu, Yongjun Li and Yuliang Li*

1 Experiment Section

1.1 Materials

All reactions are performed under argon unless otherwise stated. Most of the chemical reagents were purchased commercially and used without further purification unless otherwise stated. Column chromatography was performed on silica gel (size 200-300 mesh).

1.2 Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 or Bruker AVANCE III 500WB instrument, at a constant temperature of 25 ℃. Chemical shifts are reported in parts per million from low to high field and referenced to TMS. Matrix-assisted laser desorption/ionization Fourier transform ion cyclotron resonance (MALDI-FT-ICR-MS) mass spectrometry were performed on a Bruker Solarix 9.4T FT-ICR-MS mass spectrometer. EI mass spectrometric measurements were performed on a SHIMADZU GCMS-QP2010 pulse Spectrometer. Infrared spectroscopy was measured on a Bruker TENSOR-27 spectrometer. Analytical size exclusion chromatography (SEC) was performed on SDV PSS GPC columns using DCB as eluent at a temperature of 303 K. Absorbance was determined on a UV S-3702 detector (SOMA) at a fixed wavelength of 270 nm. The samples were referenced with respect to standard polystyrene (PS). Raman spectra were recorded using an NT-MDT NTEGRA Spectra system, with excitation from an Ar laser at 473 nm. Solution UV–vis absorption spectra were recorded at room temperature on a Jasco V-570 spectrophoto-meter. Solution fluorescence emission spectra were recorded at room temperature on a Jasco FP-6000 spectrophotometer. Fluorescence quantum yield and lifetime was measured on a Techcomp FLS980 spectrophotometer. XPS was performed using an ESCALab250Xi apparatus using the GDYNR transferred onto a glass slide. DSC was performed on Discovery DSC2500. For the characterization of X-ray diffractometer (XRD), the PDBA was transferred onto a glass slide. The sample was characterized by XRD (Rigaku Dmax200, Cu Kα). The scanning rate was 2 °/min, and the 2θ range was from 2 ° to 80 °. The morphologies of the as-prepared samples were examined using field emission scanning electron microscopy (FESEM, Hitachi S-8020), TEM (HT7700, JEM-2100F) and AFM (Bruker Multimode 8).

Photocurrent measurements: The photocurrent measurements were performed using an electrochemical workstation (CHI660E) with a standard three- electrode photoelectrochemical cell, where the indium tin oxide (ITO) coated with PDBA sample, platinum wire and Ag/AgCl act as the working, auxiliary, and reference electrode, respectively. The electrodes were immersed in a sodium sulfate electrolyte solution (0.2 M, pH = 6.8), which was purged with N_2 for 30 min before the test. The working electrodes were prepared as follows: First, ITO glasses were washed sequentially with acetone and ethanol in an ultrasonic bath for 20 min. Next, 2 mg of PDBA was dispersed in a mixed solution of ethanol (0.75 mL), deionized water (0.25 mL) and Nafion (5 μL) with ultrasonic treatment for 2 h. Then the solution was ground to obtain slurry and uniformly coated onto the 1 cm × 2 cm ITO. The coated ITO was dried at room temperature for 6 h. The photocurrent was measured at various bias voltages (vs. Ag/AgCl) with a 300 W Xe lamp by intermittent irradiation. The EIS spectra were recorded by applying a 10 mV AC signal in the frequency range from 100K to 0.01Hz at a DC bias of 0.3V vs. RHE (i.e. − 0.3V vs. Ag/AgCl). Current density was calculated using the exposed geometric surface area of 1.0 cm^2 of the photoelectrode

($J_{\text{photocurrent density}} = J_{\text{measured photocurrent}}/S_{\text{exposed geometric surface area}}$)

The applied potential vs. Ag/AgCl is converted to RHE potential using the following equation:

$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^0_{Ag/AgCl} (E^0_{Ag/AgCl} = 0.199V)$

Photocatalytic H_2 generation reactions were performed in a 100-mL closed Pyrex reactor with a quartz window under the visible light irradiation. In a typical photocatalytic reaction, 20 mg of a certain PDBA sample was ultrasonically dispersed in 20 mL aqueous solution of triethanolamine (TEOA, 15 vol. %). Pt (0.5 wt %) was in-situ photodeposited on the PDBA surface as co-catalyst to boost H_2 generation. The suspension was purged with argon for 30 min to remove the residual air within the reactor prior to reaction. The reaction temperature was maintained at 25 ℃

through circulating a flow of water. The photocatalytic reaction was illuminated by a 300 W Xe lamp with a 420 nm cutoff filter under vigorous stirring. The gas products were analyzed periodically using an Inficon 3,000 micro GC gas analyzer.

1.3 Calculation conditions

Density functional theory (DFT) calculations were carried out by using Vienna ab-initio simulation package (VASP) [S1-4]. The generalized gradient approximation of Perdew–Burke–Ernzerhof was used for exchange correlation functional during the DFT calculations [S5]. The plane wave energy cutoffs were set as 400 eV. The first Brillouin zone was sampled in the Monkhorst−Pack grid and the 3×3×1 k-points grids were used for the structure optimization and the energy calculations [S6]. The dispersion corrections DFT-D3 was employed to describe the vdw interaction in this work. Besides, the spin polarization was considered in all calculation. Band gap and DOS calculations were performed with $DMol^3$ program [S7],[S8] with the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional, in which the semi-empirical Grimme scheme[S9] for the dispersion correction was included.

The Gibbs free-energy change (ΔG_{ads}) of H intermediate is obtained by calculating the adsorption energy of H, in which $1/2H_2$ (g) is used as reference. Besides, the corrections to entropy, zero point energy, and solvation energy are added to the DFT adsorption energy calculations according to the method developed by Nørskov et al. [S10]. Thus, the free energy change of H on the catalyst is defined as follows:

$$\Delta G_{ads} = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S + \Delta G_S$$

where ΔE_{ads} is the adsorption energy of the atomic H on the catalyst, ΔE_{ZPE} is the difference in zero point energy between the adsorbed hydrogen and hydrogen in the gas phase. ΔS is the entropy change of H atom from the absorbed state to the gas phase state. ΔG_S is the solvation energy for reaction intermediate and is set to – 0.22 eV according to previous report [S11]. Since the H atom is binding on the catalyst surface, the entropy of the adsorbed hydrogen can be negligible. Therefore, the ΔS can be estimated by $-1/2 \times S_0$, in which S_0 is the standard entropy of H_2 with gas phase at pressure of 1 bar and pH = 0 at 300 K. In summary, the Gibbs free-energy change (ΔG_{ads}) of H can be described as

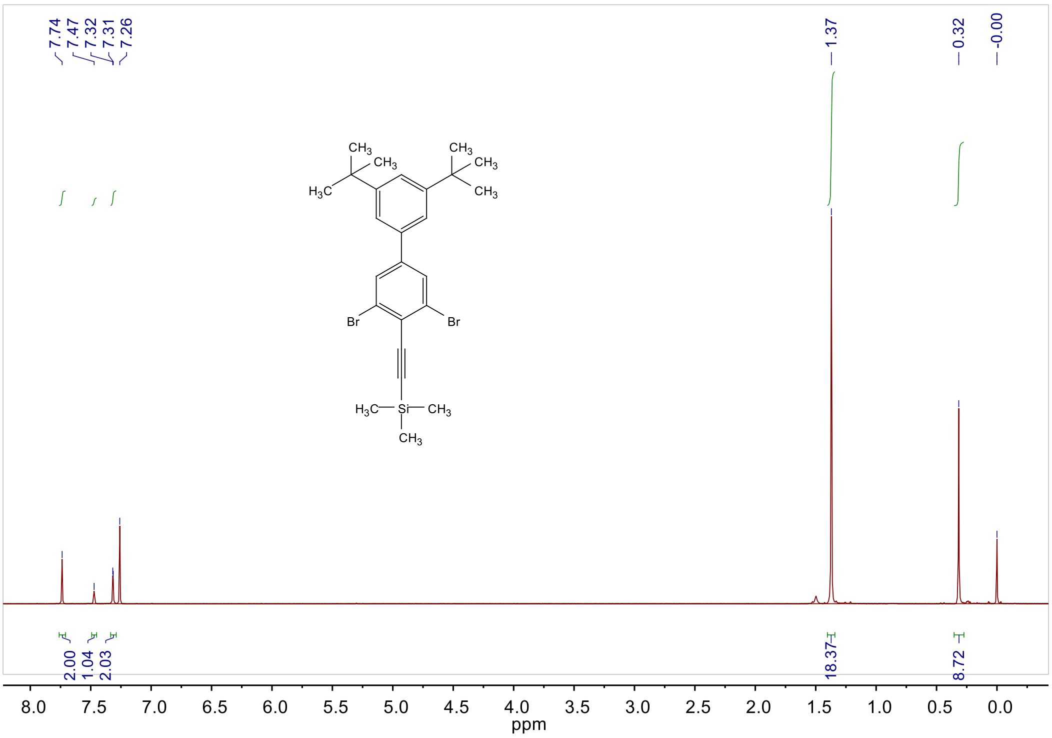
$$\Delta G_{ads} = \Delta E_{ads} + \Delta E_{ZPE} + +\Delta G_{S} + 0.0615eV$$

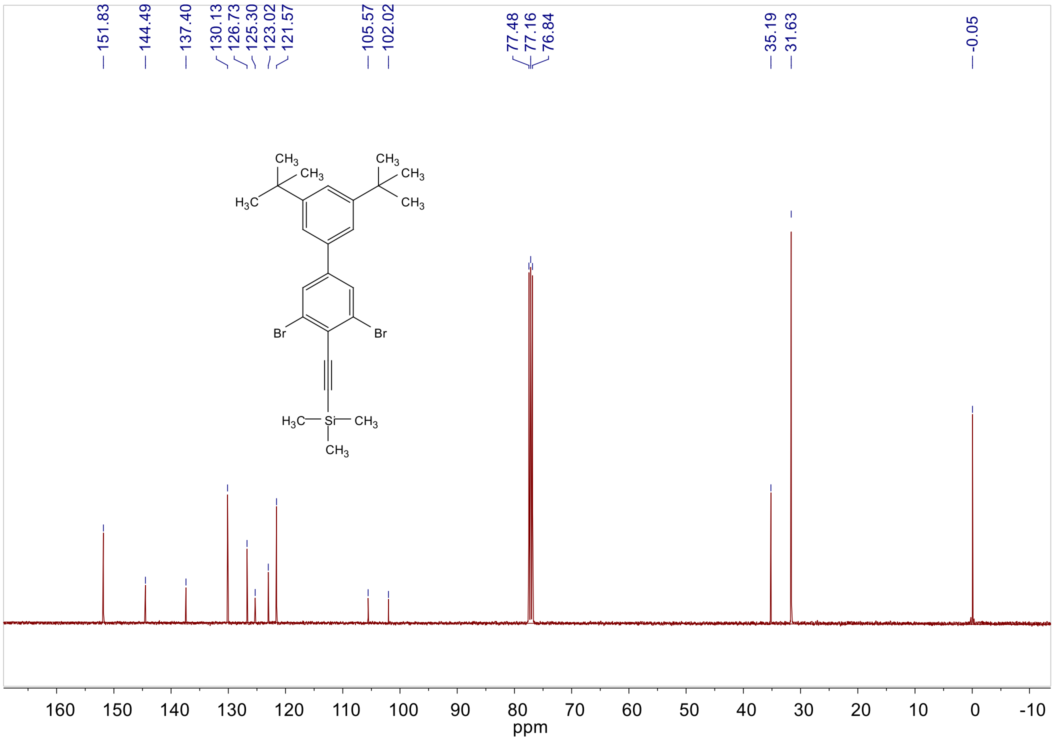
ZPE values could be derived after frequency calculation by [S12]:

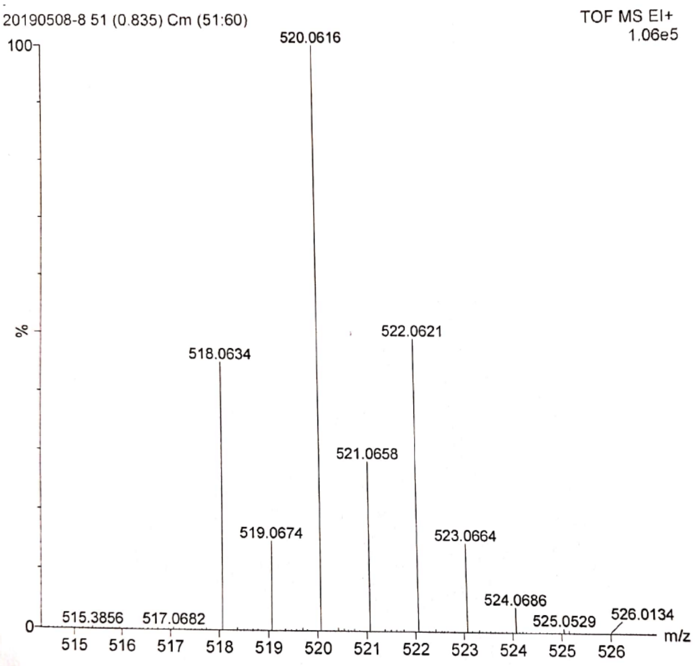
$$ZPE = \frac{1}{2}\sum hv_i$$

1.4 Synthesis

((3,5-dibromo-3',5'-di-tert-butyl-[1,1'-biphenyl]-4-yl)ethynyl)trimethylsilane 2: [$PdCl_2$ $(PPh3)_2$] (40 mg) and CuI (20 mg) were added under an argon flow at room temperature to a stirred solution of 3,5-dibromo-3',5'-di-tert-butyl-4-iodo-1,1'-biphenyl **1**(2.73 g, 5 mmol) and TMS acetylene (308 mg, 3.67 mmol) in THF/TEA (3:1 v/v). The reaction mixture was then sealed stirred for at 70 ℃ 20 h, and the mixture was washed with saturated NH_4Cl and water and then dried over anhydrous Na_2SO_4, then the solvent was removed by evaporation under reduced pressure. The mixture was purified by silica gel chromatography to obtain compound **2** (2.07 g, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.47 (s, 1H), 7.32 (d, *J* = 1.5 Hz, 2H), 1.37 (s, 18H), 0.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.83, 144.49, 137.40, 130.13, 126.73, 125.30, 123.02, 121.57, 105.57, 102.02, 35.19, 31.63, -0.05. HiRes-TOF MS (positive): m/z=518.0634, calcd for $C_{25}H_{32}Br_2Si$: m/z=518.0640.







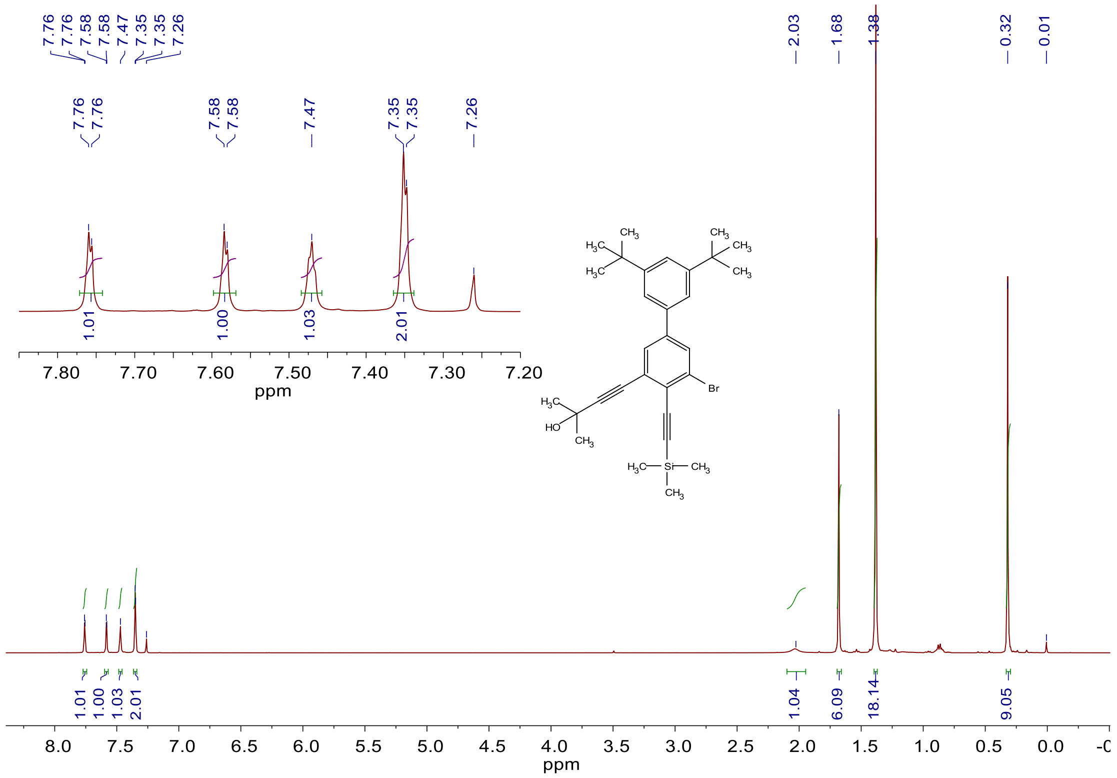
Elemental Composition Report

Multiple Mass Analysis: 3 mass(es) processed
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
228 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)

Minimum:	30.00				-1.5		
Maximum:	100.00		200.0	100.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
518.0634	45.03	518.0640	-0.6	-1.2	10.0	1	C25 H32 Si 79Br2
520.0616	100.00	520.0620	-0.4	-0.7	10.0	1	C25 H32 Si 79Br 81Br
522.0621	49.30	522.0599	2.2	4.2	10.0	1	C25 H32 Si 81Br2

4-(5-bromo-3',5'-di-tert-butyl-4-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-3-yl)-2-methylbut-3-yn-2-ol 3: [PdCl$_2$ (PPh3)$_2$] (40 mg) and CuI (20 mg) were added under an argon flow at room temperature to a stirred solution of ((3,5-dibromo-3',5'-di-tert-butyl-[1,1'-biphenyl]-4-yl)ethynyl)trimethylsilane **2** (2.07 g, 4 mmol) and 2-methylbut-3-yn-2-ol (308 mg, 3.67 mmol) in THF/TEA (3:1 v/v). The reaction mixture was then stirred for 20 h under reflux conditions, and the mixture was washed with saturated NH$_4$Cl and water and then dried over anhydrous Na$_2$SO$_4$, then the solvent was removed by evaporation under reduced pressure. The mixture was purified by silica gel chromatography to obtain 4-(5-bromo-3',5'-di-tert-butyl-4-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-3-yl)-2-methylbut- 3-yn-2-ol **3** (1.57 g, yield 75%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.47 (s, 1H), 7.35 (d, *J* = 1.6 Hz, 2H), 2.03(s, 1H), 1.68 (s, 6H), 1.38 (s, 18H), 0.32 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 151.71, 143.22, 137.81, 131.01, 129.38, 127.30, 126.44, 125.81, 122.77, 121.51, 104.24, 101.90, 98.45, 80.89, 65.89, 35.17, 31.64, 31.57, 0.09. HiRes-TOF MS (positive): m/z=545.1848, calcd for $C_{30}H_{39}BrNaOSi$ (M+Na): m/z=545.1846.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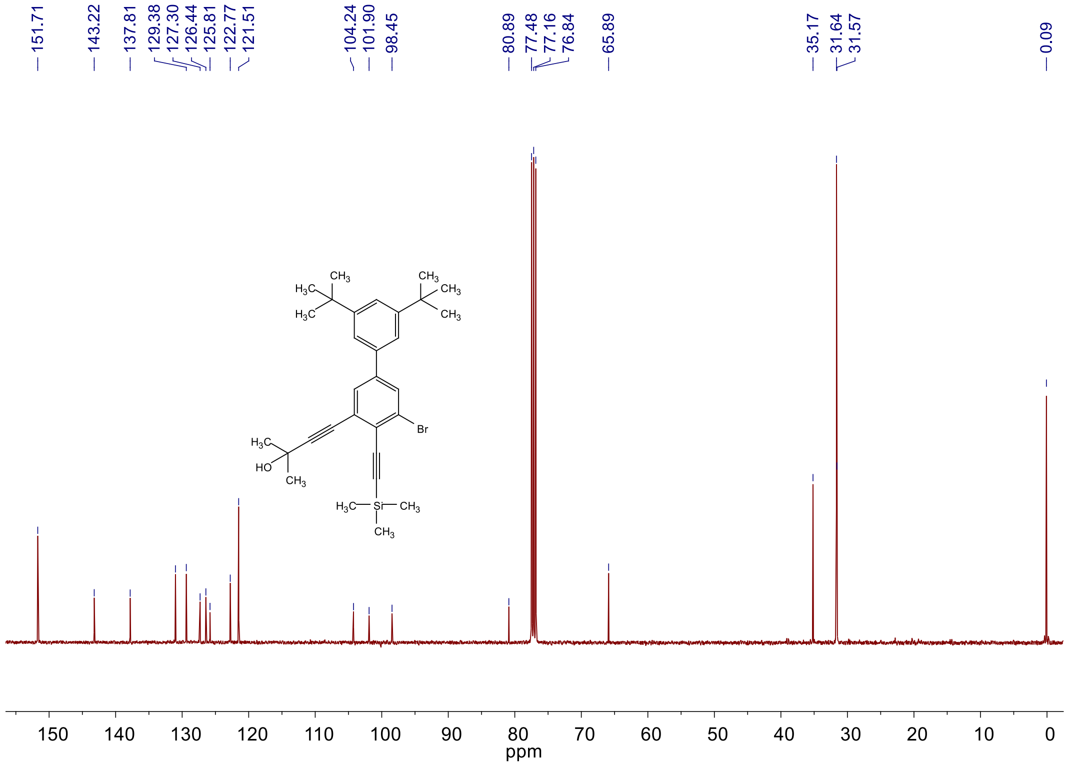
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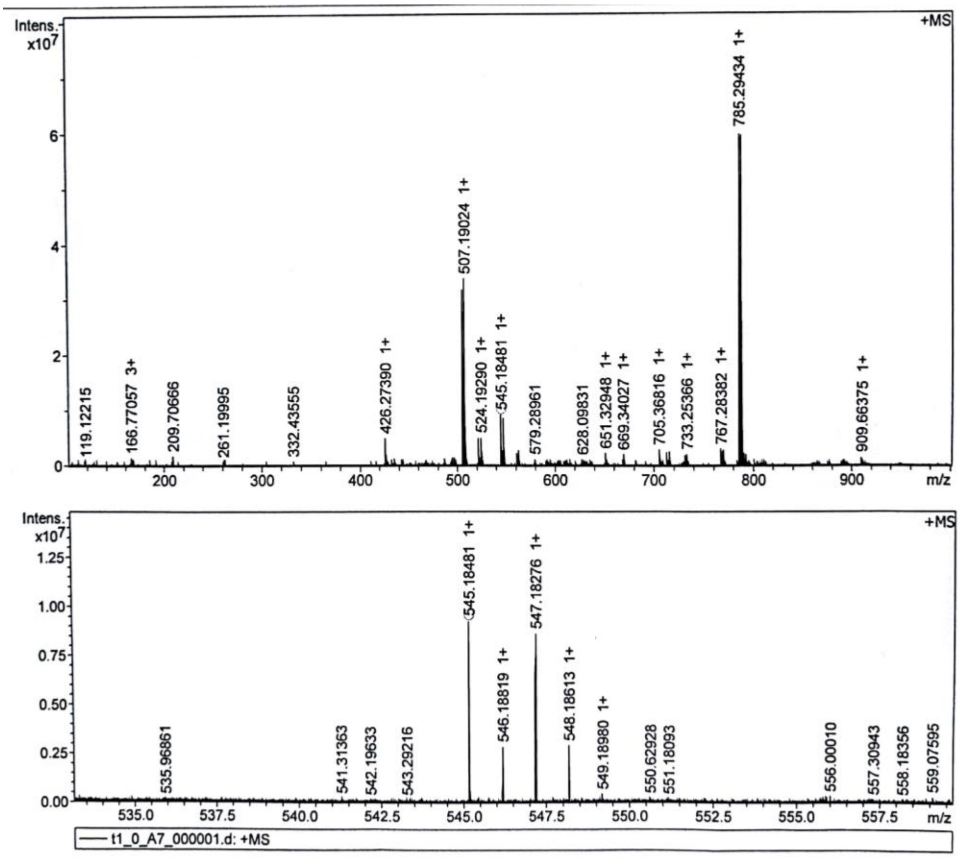

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
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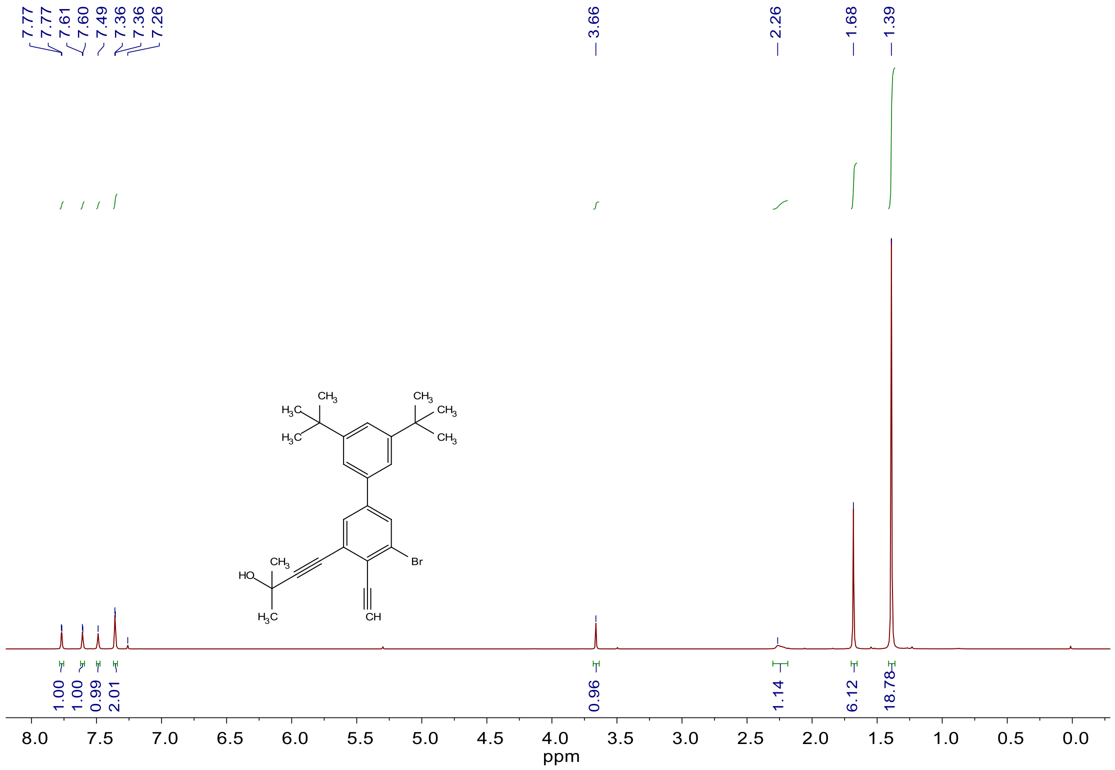
4-(5-bromo-3',5'-di-tert-butyl-4-ethynyl-[1,1'-biphenyl]-3-yl)-2-methylbut-3-yn-2-ol 4: Ground K_2CO_3 (690 mg, 5 mmol) was added to 4-(5-bromo-3',5'-di-tert-butyl-4-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-3-yl)-2-methylbut- 3-yn-2-ol **3** (1.31 g, 2.5 mmol) in MeOH/THF (1/1, 100 mL) , the reaction mixture was stirred at room temperature for 2 hours. Water (30 ml) was added to the reaction mixture. The resultant suspension was extracted with dichloromethane (3×50 mL). The combined organic layers were washed with water and then dried over anhydrous $NaSO_4$. The solvent was removed and the crude product was purified by column chromatography (silica gel, CH_2Cl_2) to obtain the desired compound 4-(5-bromo-3',5'-di-tert-butyl-4-ethynyl-[1,1'-biphenyl]-3-yl)-2-methylbut-3-yn-2-ol **4** (1.1 g, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 1.5 Hz, 1H), 7.61 (d, *J* = 1.5 Hz, 1H), 7.49 (s, 1H), 7.36 (d, *J* = 1.5 Hz, 2H), 3.66 (s, 1H), 2.06 (s, 1H), 1.68 (s, 6H), 1.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.72, 143.80, 137.78, 131.08, 129.44, 128.02, 126.14, 124.91, 122.83, 121.55, 98.81, 86.01, 80.99, 80.60, 65.88, 35.16, 31.62, 31.46. HiRes-TOF MS (positive): m/z=433.1527, calcd for $C_{27}H_{30}Br$ (M-OH): m/z=433.1525.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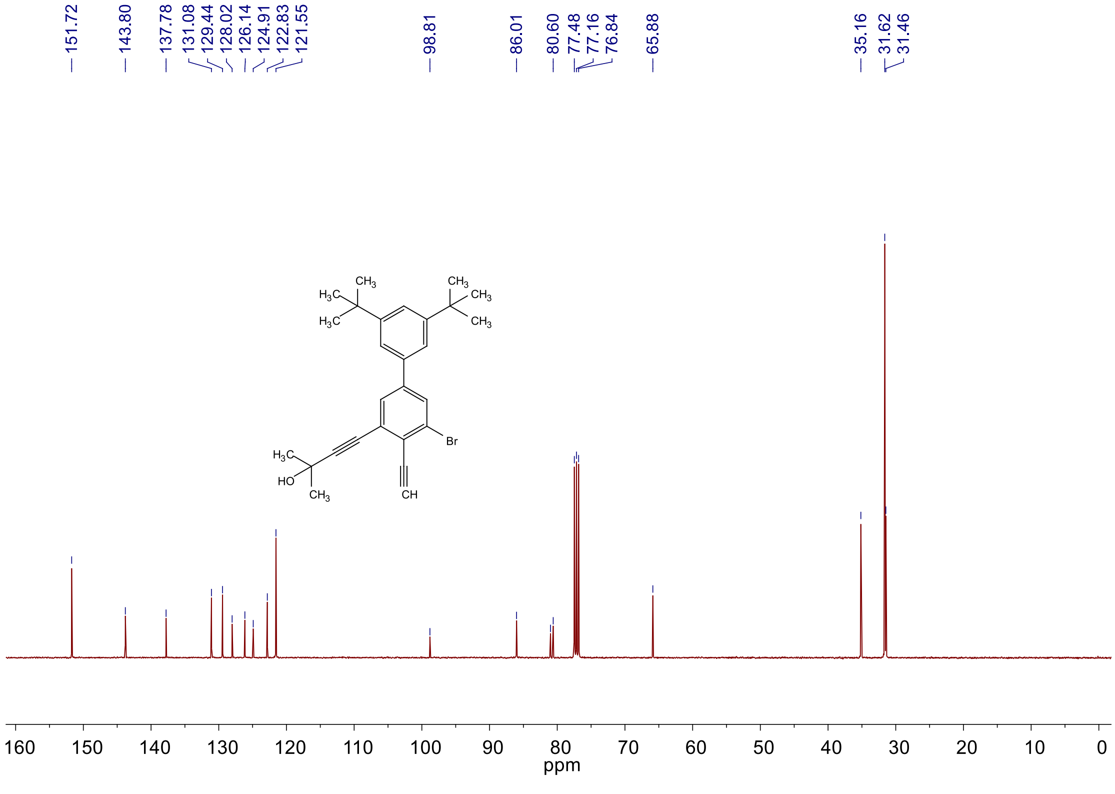
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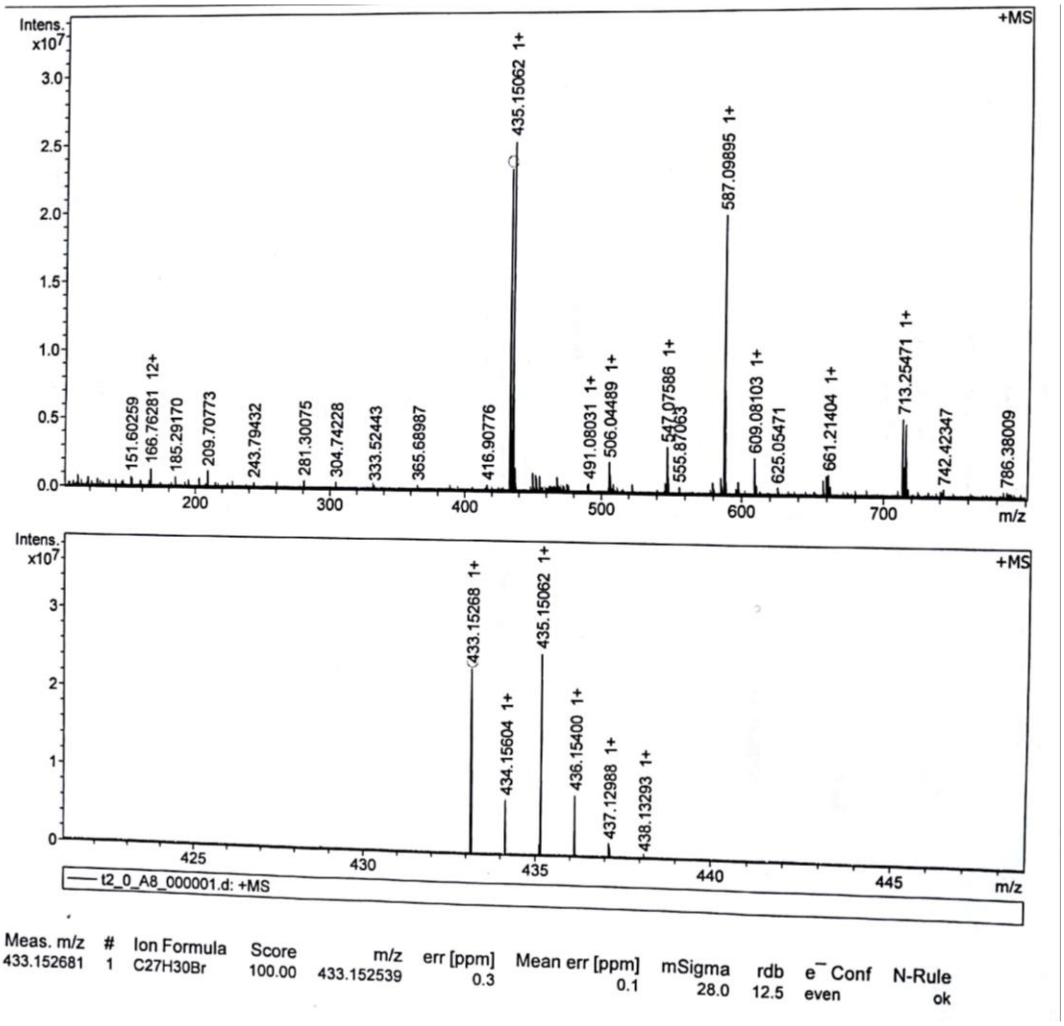

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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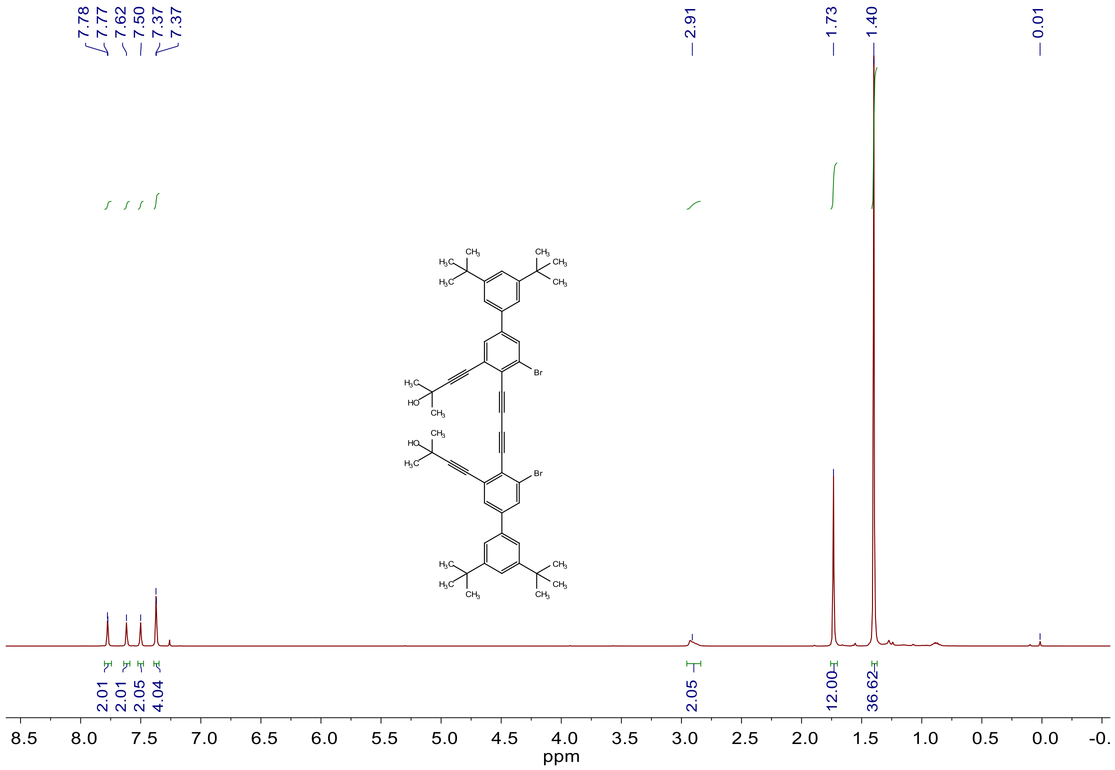
4,4'-(buta-1,3-diyne-1,4-diylbis(5-bromo-3',5'-di-tert-butyl-[1,1'-biphenyl]-4,3-diyl))bis(2-methylbut-3-yn-2-ol) 5:

To a dichloromethane (100 mL) solution of compound **4** (0.9 g, 2.0 mmol) and N,N,N',N'-tetramethyl-ethane-1,2-diamine (TMEDA) (2 mL) placed in round bottom flask was added CuCl (98 mg, 1 mmol) equipped with a magnetic stirring bar. The reaction mixture was stirred for 12 h at room temperature and quenched with 1.0 M HCl (aq). The aqueous layer was separated and extracted with 100 mL of diethyl ether. The combined ethereal layer was washed with brine and dried over Mg$_2$SO$_4$, concentration of the solution in vacuo gave a brown residue that was purified by column chromatography (dichloromethane/methanol = 100/1) to afford compound **5** (808 mg, 90%) as a while solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 1.4 Hz, 2H), 7.62 (s, 2H), 7.50 (s, 2H), 7.37 (d, *J* = 1.4 Hz, 4H), 2.91 (s,2H), 1.73 (s, 12H), 1.40 (s, 36H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 151.79, 144.23, 137.72, 131.06, 129.28, 129.19, 126.20, 124.97, 123.00, 121.57, 99.91, 82.03, 81.83, 80.32, 65.96, 35.18, 31.63, 31.45. HiRes-TOF MS (positive): m/z=898.2986, 864.2882, calcd for $C_{54}H_{60}Br_2O_2$ (M): m/z=898.2955, $C_{54}H_{58}Br_2$ (M-2OH): m/z=864.2905.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2.05
12.00
36.62
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7.5
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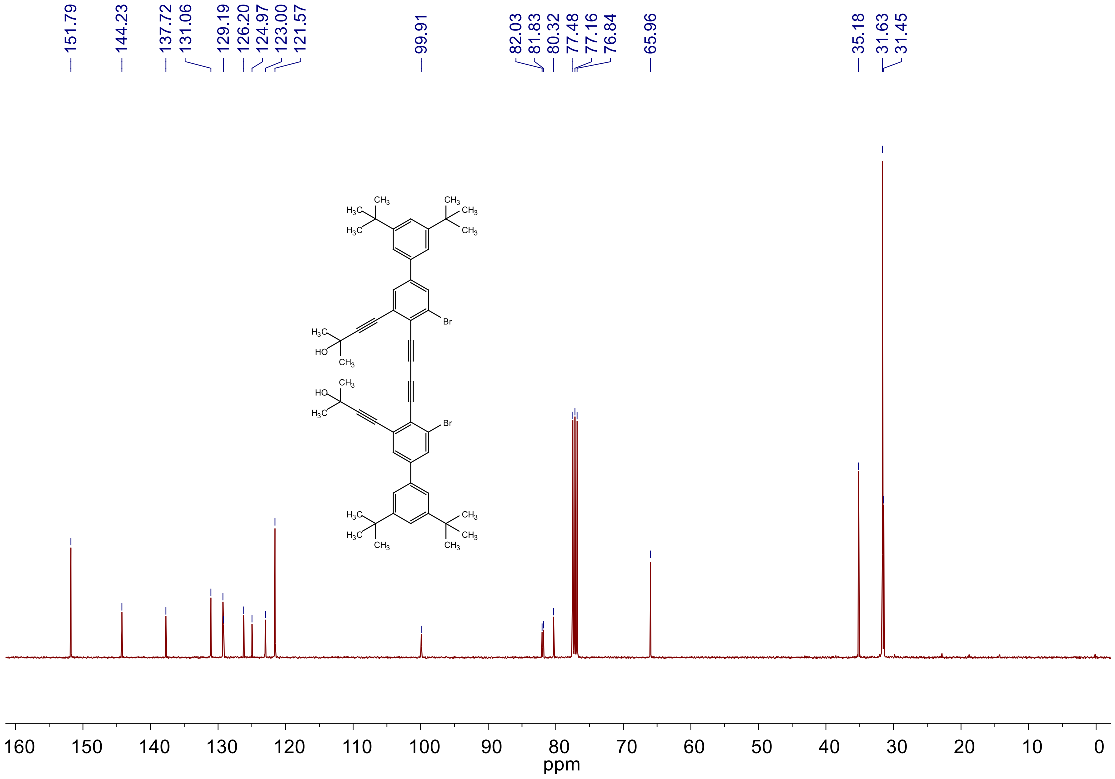
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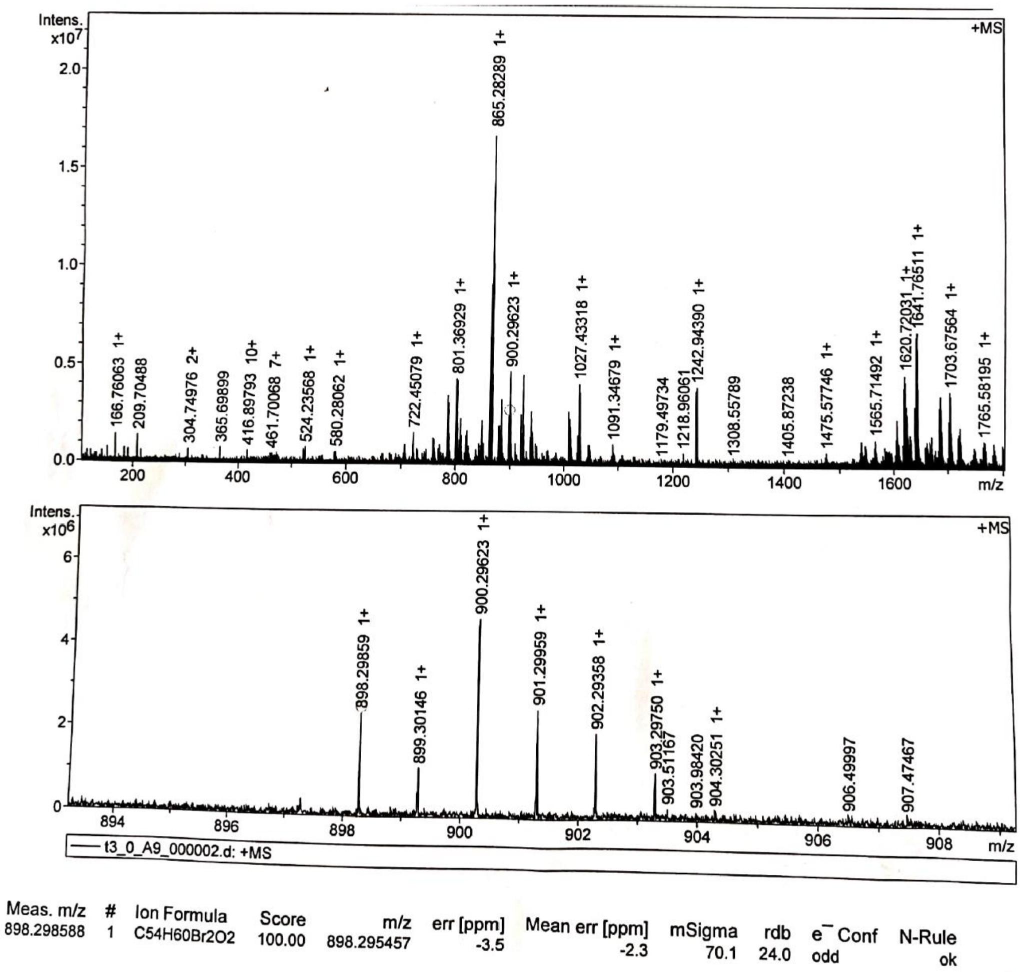

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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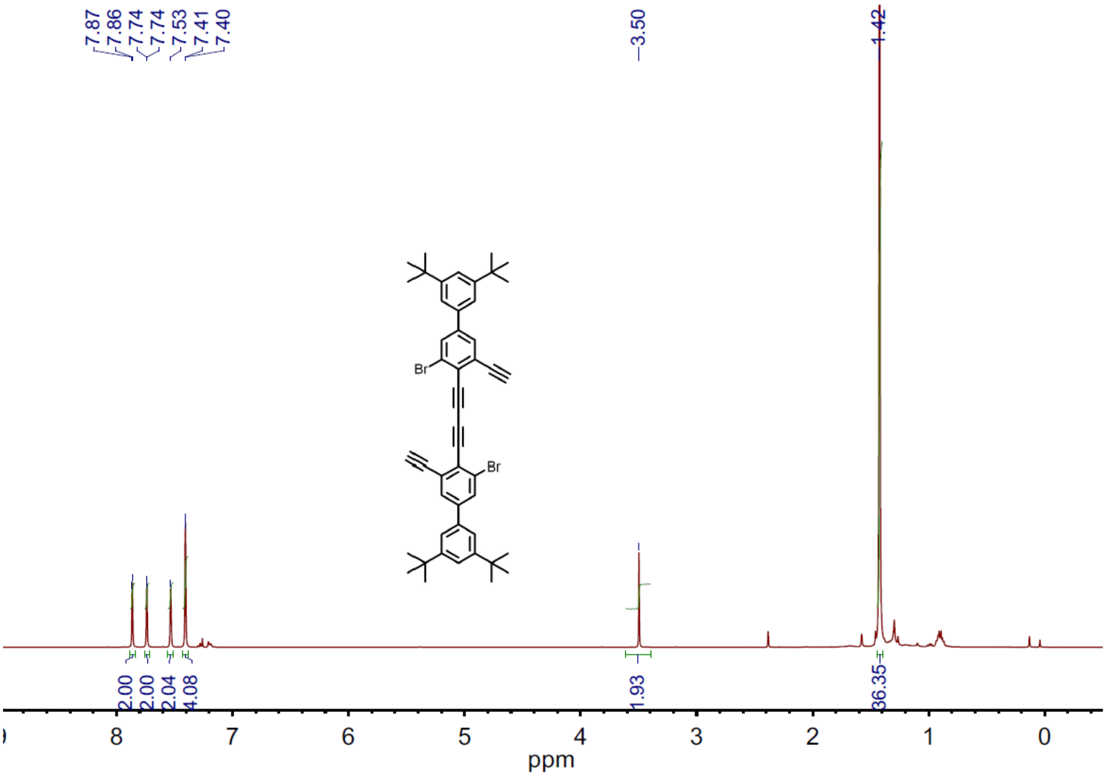
1,4-bis(3-bromo-3',5'-di-tert-butyl-5-ethynyl-[1,1'-biphenyl]-4-yl)buta-1,3-diyne 6:

Ground KOH (100 mg, 1.6 mmol) was added to compound **5** (718 mg, 0.8 mmol) in toluene which had already been heated to 120°C. The reaction mixture was stirred for 15 minutes. After cooling down to room temperature, water (30 ml) was added to the reaction mixture. The resultant suspension was extracted with dichloromethane (3×50 mL). The combined organic layers were washed with water and then dried over anhydrous $NaSO_4$. The solvent was removed and the crude product was purified by column chromatography (silica gel, petroleum ether) to obtain the desired compound 1,3 -diethinyl-2,4,6-triphenyl-benzol **6** (569 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.3 Hz, 2H), 7.74 (d, *J* = 1.3 Hz, 2H), 7.53 (s, 2H), 7.41 (d, *J* = 1.4 Hz, 4H), 3.50 (s, 2H), 1.42 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.85, 144.18, 137.60, 131.72, 130.43, 128.02, 127.02, 125.14, 123.06, 121.58, 82.80, 82.35, 81.37, 81.35, 35.18, 31.64. HiRes-TOF MS (positive): m/z=782.2138, calcd for $C_{48}H_{48}Br_2$: m/z=782.2117.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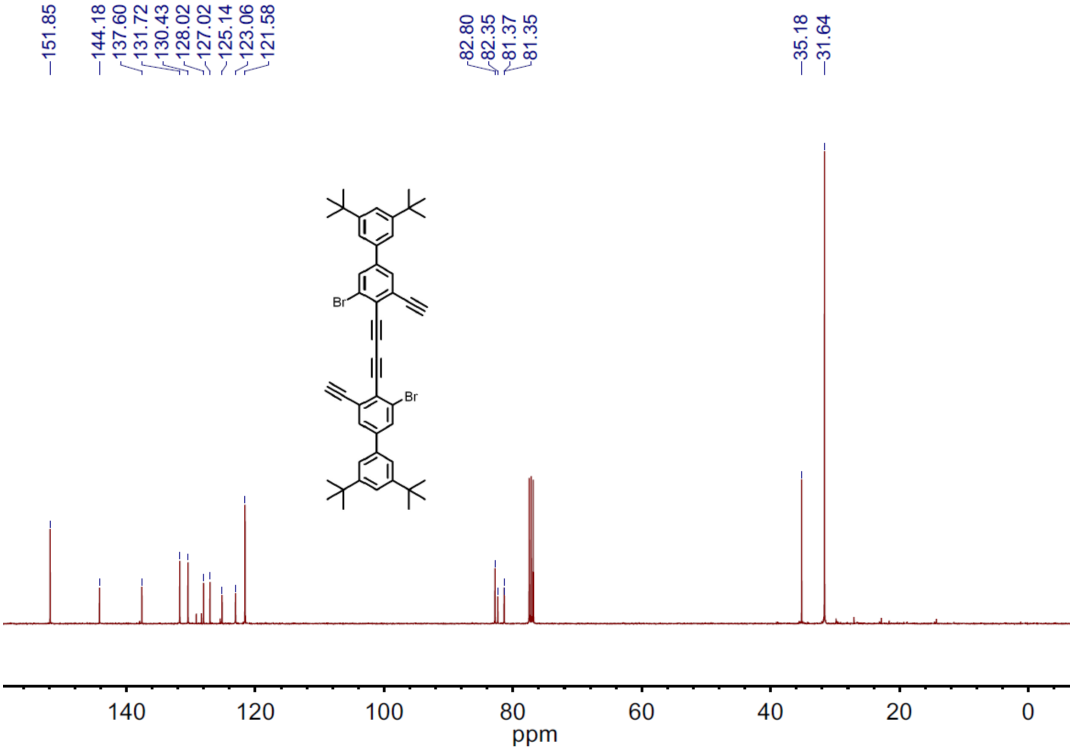
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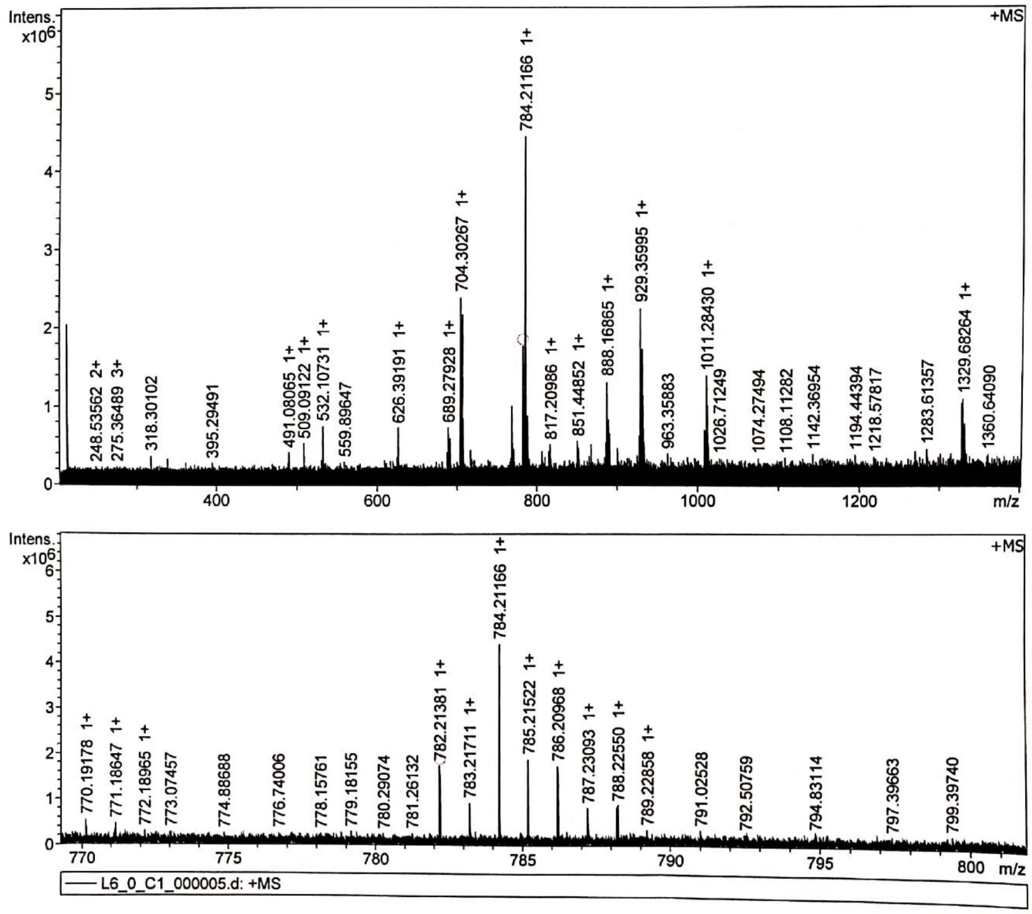
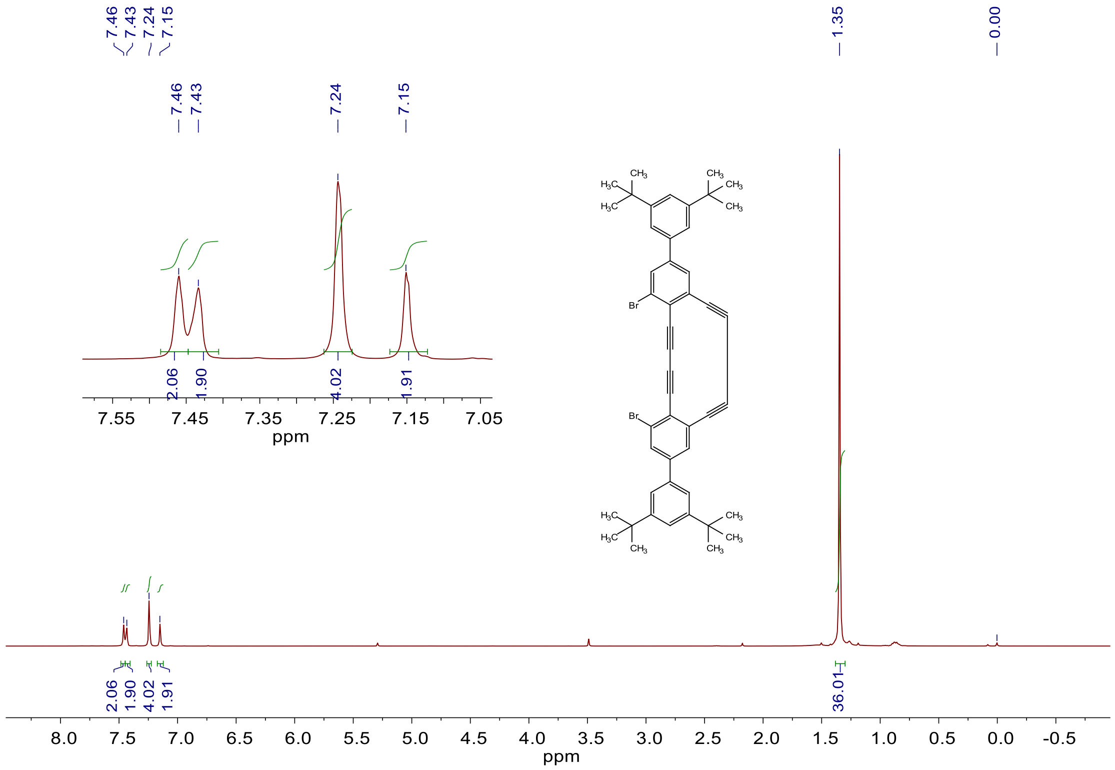


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
782.213815	1	C48H48Br2	100.00	782.211727	2.7	-1.8	87.8	24.0	odd	ok

DBA7: To an acetone-pyridine (100/10, 100 mL) solution of compound **6** (391 mg, 0.5 mmol) and N,N,N',N'-tetramethyl-ethane-1,2-diamine (TMEDA) (2 mL) placed in round bottom flask was added $Cu(OAc)_2$ (18 mg, 0.1 mmol), CuCl (9.8 mg, 0.1 mmol) equipped with a magnetic stirring bar. The reaction mixture was stirred for 36 h at 50 ℃ and quenched with saturated NH_4Cl (aq). The aqueous layer was separated and extracted with 100 mL of CH_2Cl_2. The combined CH_2Cl_2 layer was washed with brine and dried over Mg_2SO_4, concentration of the solution in vacuo gave a brown residue that was purified by column chromatography (dichloromethane/hexane = 1/1) to afford compound **7** (195 mg, 50%) as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (s, 2H), 7.43 (s, 2H), 7.24 (s, 4H), 7.15 (s, 2H), 1.35 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.79, 144.77, 137.26, 132.40, 131.97, 131.22, 126.46, 123.21, 122.66, 121.16, 92.23, 88.26, 84.72, 35.14, 31.59. HiRes-TOF MS (positive): m/z=780.1961 calcd for $C_{48}H_{46}Br_2$: m/z=780.1961.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7.35
7.25
7.15
7.05
ppm
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7.0
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4.5
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3.5
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ppm
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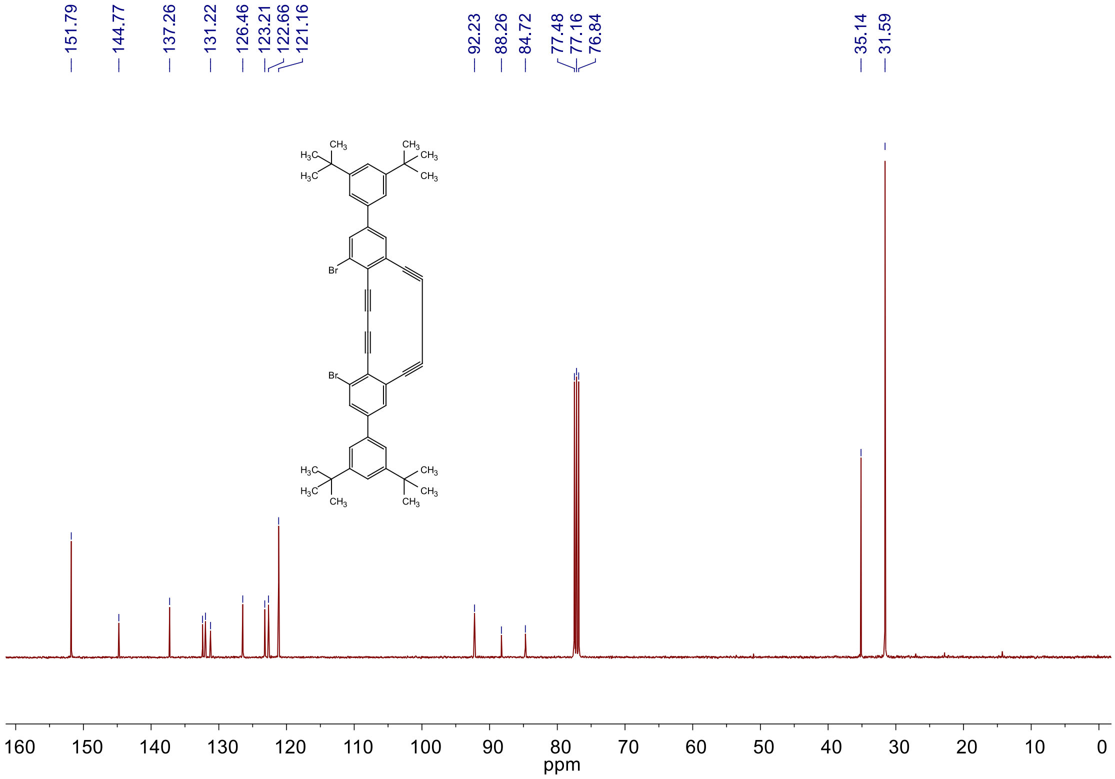
CH_3
Br
Br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35.14
31.59
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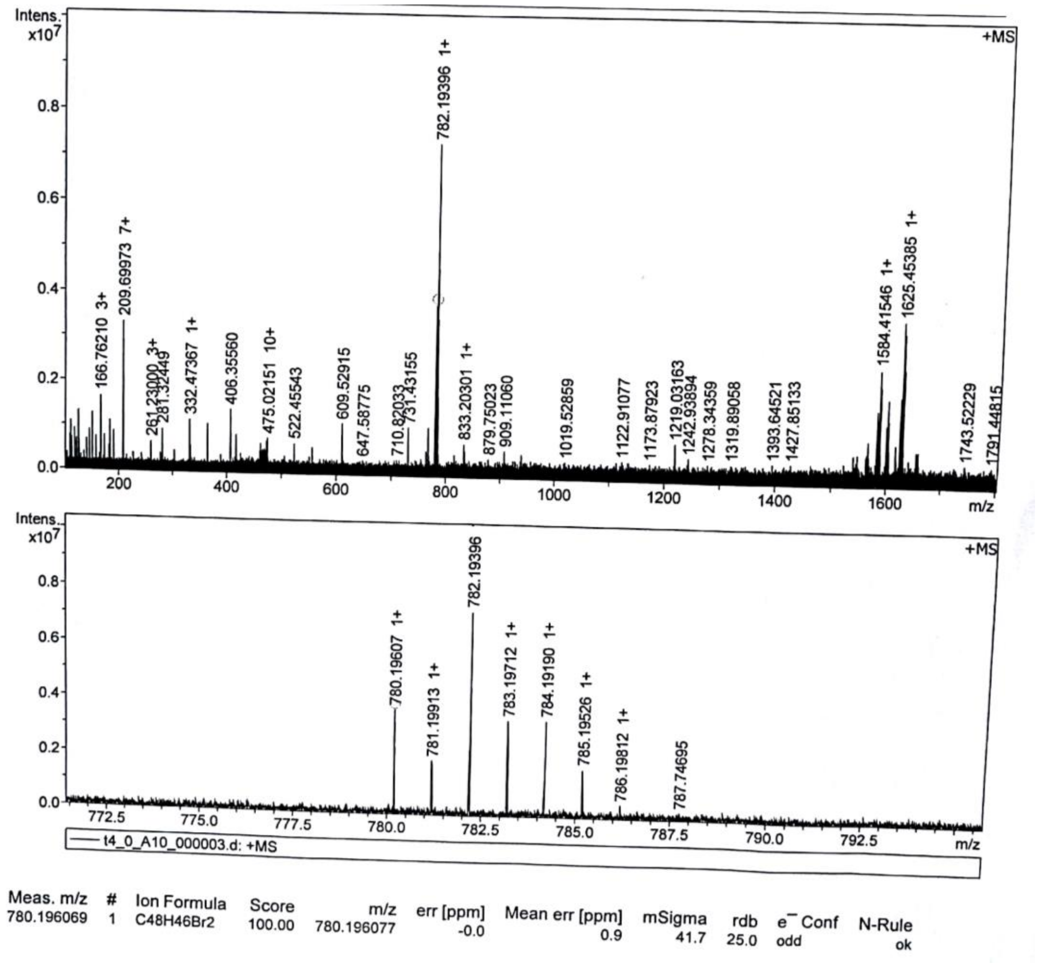
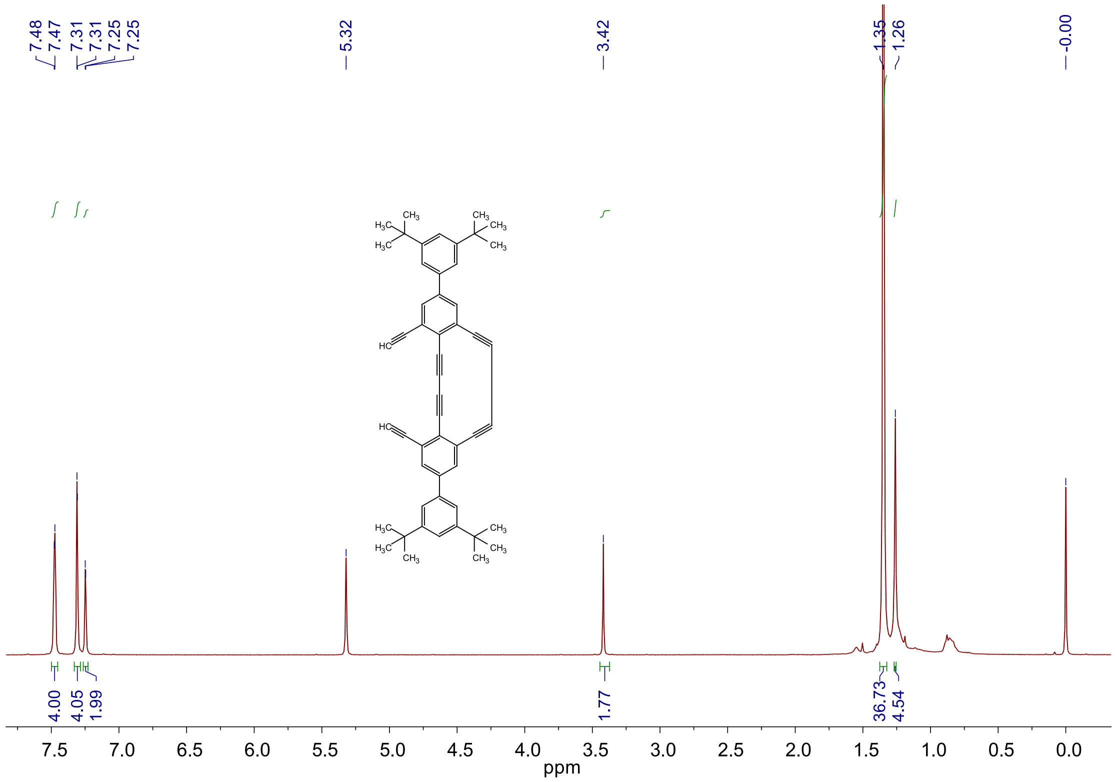


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
780.196069	1	C48H46Br2	100.00	780.196077	-0.0	0.9	41.7	25.0	odd	ok

DBA 8: [PdCl$_2$ (PPh3)$_2$] (20 mg) and CuI (10 mg) were added under an argon flow at room temperature to a stirred solution of compound **7** (156 mg, 0.2 mmol) and ethynyltrimethylsilane (98 mg, 1 mmol) in THF/TEA (3:1 v/v). The reaction mixture was then stirred for 20 h under reflux conditions, and the mixture was washed with saturated NH$_4$Cl and water and then dried over anhydrous Na$_2$SO$_4$, then the solvent was removed by evaporation under reduced pressure. The mixture was passed through a short silica gel column (dichloromethane/hexane = 1/1), the obtained sample was deprotected by K$_2$CO$_3$ in THF/Methanol solution, purification by silica gel chromatography (dichloromethane/hexane = 1/1) to obtain compound **8** (101 mg, yield 75% in two steps). ^{1}H NMR (400 MHz, Methylene Chloride-*d*$_2$) δ 7.50 – 7.45 (m, 4H), 7.31 (d, *J* = 1.4 Hz, 4H), 7.25 (d, *J* = 1.4 Hz, 2H), 3.42 (s, 2H), 1.35 (s, 36H), 1.26 (s, 6H). ^{13}C NMR (101 MHz, CD$_2$Cl2) δ 152.31, 144.20, 137.92, 132.45, 132.25, 131.67, 128.36, 123.60, 123.48, 121.60, 92.63, 92.38, 88.11, 84.55, 82.55, 81.31, 54.54, 54.27, 54.00, 53.73, 53.46, 35.48, 31.74, 30.26, 0.15. HiRes-TOF MS (positive): m/z=672.3754, calcd for C$_{52}$H$_{48}$: m/z=672.3751.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1.99
1.77
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4.54
7.5
7.0
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ppm
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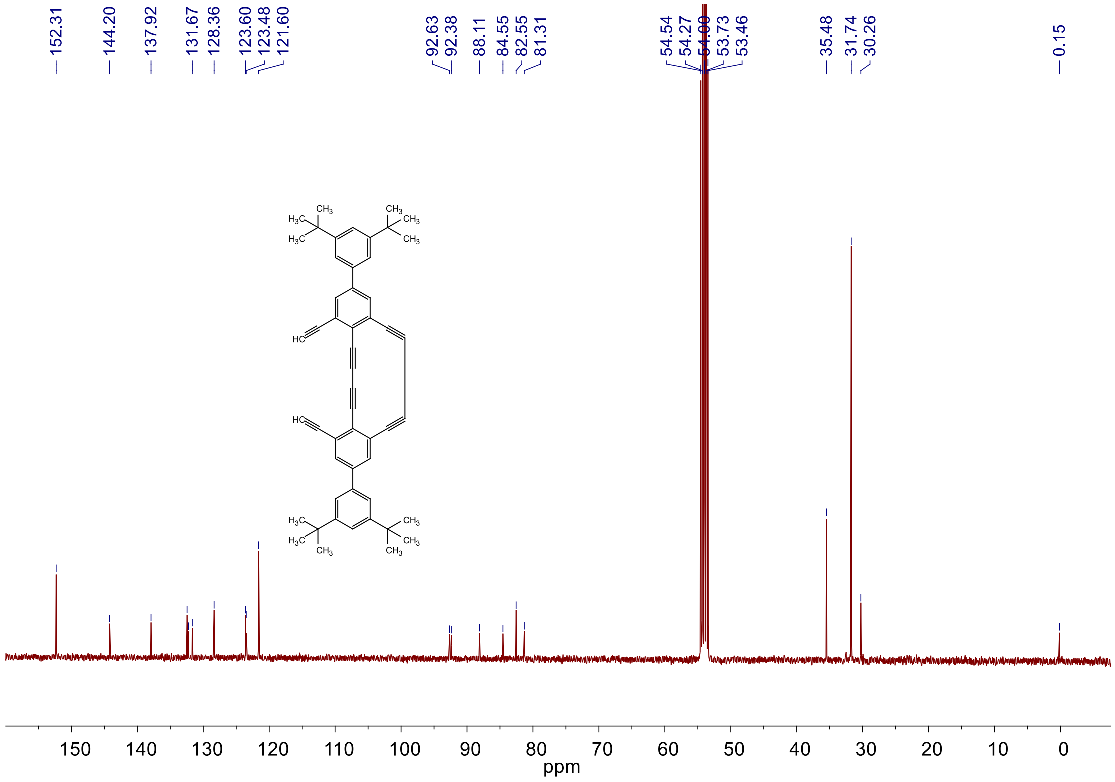
CH$_3$
HC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35.48
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150
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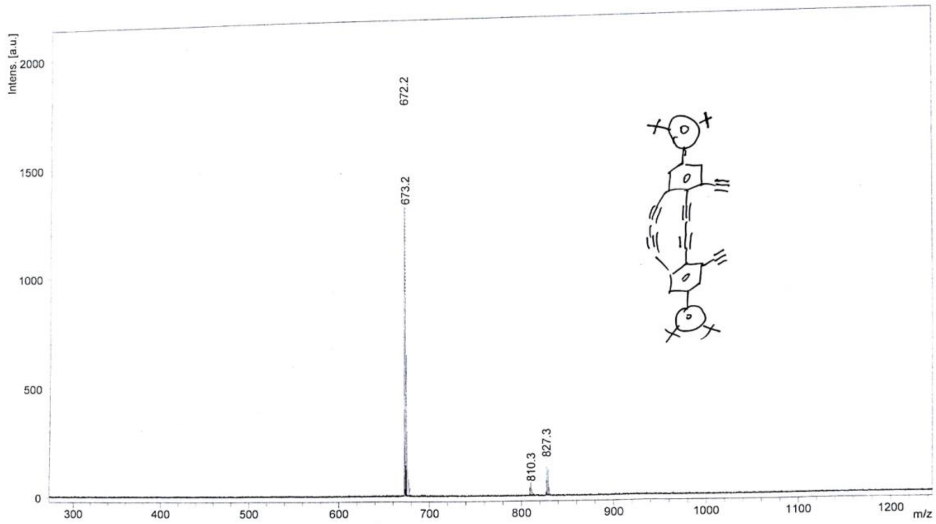
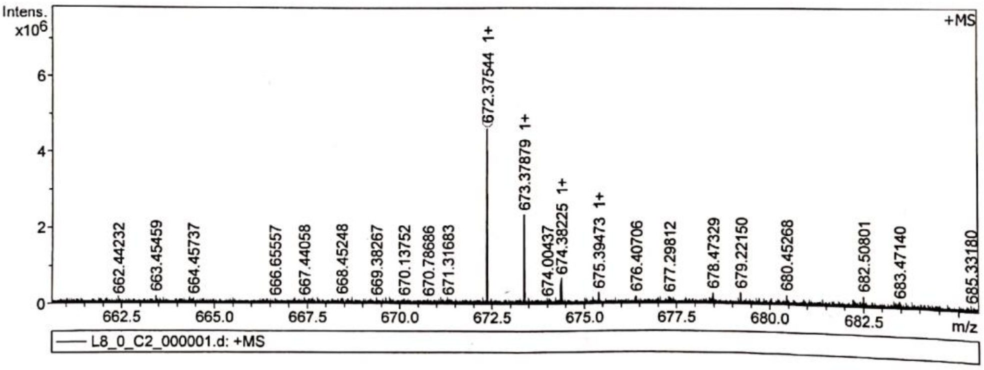
ppm
H$_3$C
CH$_3$
HC

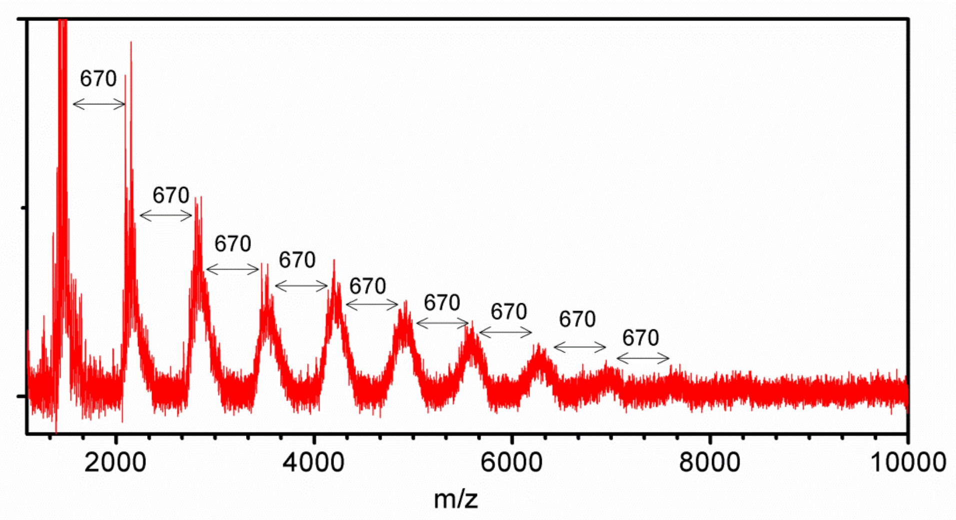




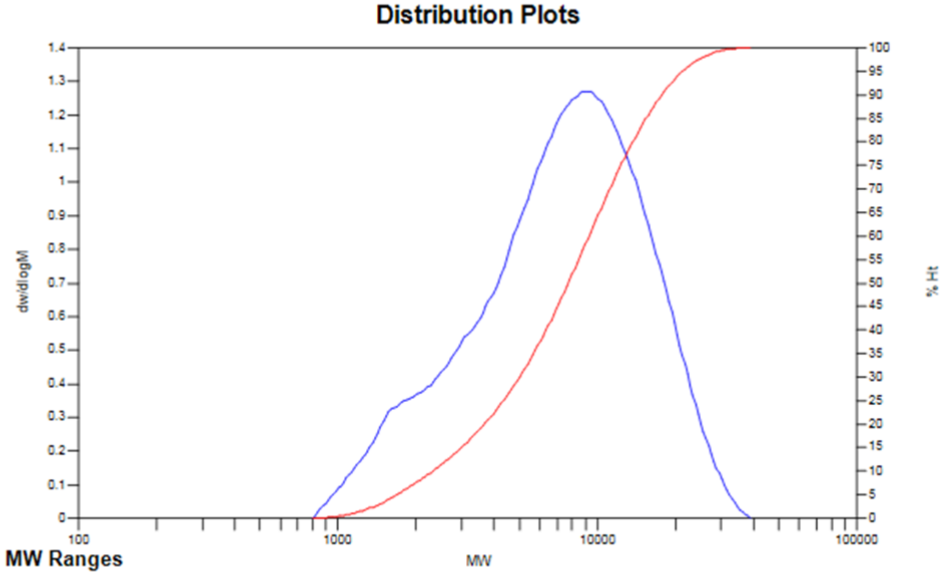
leas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
72.375440	1	C52H48	100.00	672.375053	-0.6	-0.6	28.7	29.0	odd	ok

Synthesis of **PDBA**:

To a dichloromethane (100 mL) solution of compound **8** (101 mg, 0.15 mmol) and N,N,N',N'-tetramethyl-ethane-1,2-diamine (TMEDA) (2 mL) placed in round bottom flask was added CuCl (2 mg, 0.02 mmol) equipped with a magnetic stirring bar. The reaction mixture was stirred for 24 h at room temperature. Pale yellow precipitate was collected and washed with methanol containing 10% $NH_3.H_2O$, methanol. The solid was then dried under vacuum (63 mg, 62% yield). The Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (MS) results of **PDBA** showed a regular pattern of signals reaching m/z = ~7400 with an interval of ~670, which was in agreement with the molecular weight of one repeating unit. The SEC analysis against polystyrene (PS) standard of **PDBA** showed weight-average molecular weight of 8.9±2 kg/mol and PDI of 1.75, which was ~13 units. MS results confirmed the formation of oligomers composed of **DBA 8**, the low degree of polymerization determined might be ascribed to the low solubility of the sample as indicated by the appearance of precipitate in the solution sample.



MALDI-TOF mass spectrum of PDBA



2 X-Ray Diffraction Data Analysis

A suitable crystal of $C_{97}H_{93}Br_4Cl_3$ was selected and mounted on a **XtaLAB Synergy R, HyPix** diffractometer. The crystal was kept at 169.99(10) K during data collection. Using Olex2 [13], the structure was solved with the ShelXT [14] structure solution program using Intrinsic Phasing and refined with the ShelXL [15] refinement package using Least Squares minimisation. Accession codes: The X-ray crystallographic coordinates for structure reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1916920. These data can be obtained free of charge from CCDC via http://www.ccdc.cam.ac.uk/data_request/cif.

Crystal structure determination of 7

Crystal Data for $C_{97}H_{93}Br_4Cl_3$ (M =1684.70 g/mol): triclinic, space group P-1 (no. 2), a = 12.72990(10) Å, b =18.8178(2) Å, c =19.8528(2) Å, α =69.7840(10) °, β =76.9750(10) °, γ = 0.2810(10) °, V =4169.07(8) Å^3, Z = 2, T =169.99(10) K, μ(CuKα) = 3.584 mm^{-1}, $Dcalc$ =

1.342 g/cm^3, 51723 reflections measured (4.78° ≤ 2θ ≤ 151.26°), 16627 unique (R_{int} = 0.0258, R_{sigma} = 0.0233) which were used in all calculations. The final R_1 was 0.0428 (I > 2σ(I)) and wR_2 was 0.1169 (all data).

Table S1 Crystal data and structure refinement for **7**

Identification code	**7**
Empirical formula	$C_{97}H_{93}Br_4Cl_3$
Formula weight	1684.7
Temperature/K	169.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.72990(10)
b/Å	18.8178(2)
c/Å	19.8528(2)
α/°	69.7840(10)
β/°	76.9750(10)
γ/°	70.2810(10)
Volume/Å^3	4169.07(8)
Z	2
ρ_{calc}g/cm^3	1.342
μ/mm^{-1}	3.584
F(000)	1732
Crystal size/mm^3	0.311 × 0.287 × 0.231
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/ °	4.78 to 151.26
Index ranges	$-15 \le h \le 15$, $-23 \le k \le 23$, $-24 \le l \le 24$
Reflections collected	51723
Independent reflections	16627 [R_{int} = 0.0258, R_{sigma} = 0.0233]
Data/restraints/parameters	16627/24/1023
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.1127
Final R indexes [all data]	R_1 = 0.0478, wR_2 = 0.1169
Largest diff. peak/hole / e Å^{-3}	1.49/-1.38

3 Characterization of **PDBA**

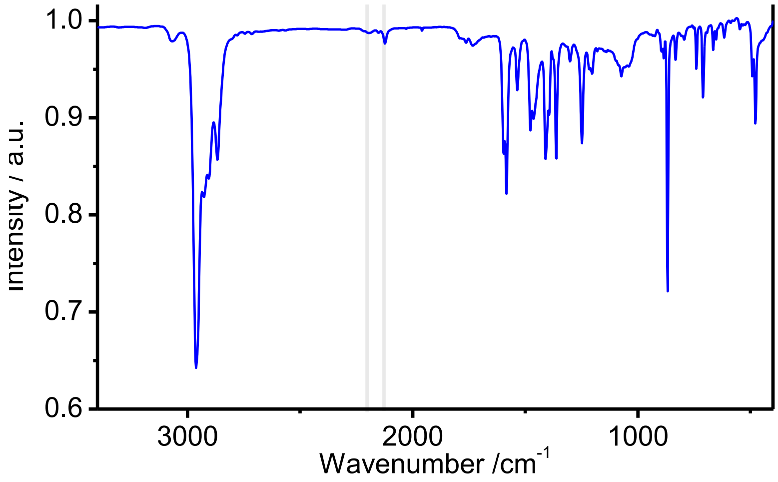


Figure S1. FTIR spectra of PDBA, the disappearance of the terminal alkyne C-H stretch and the C≡C stretch confirmed the formation of PDBA.

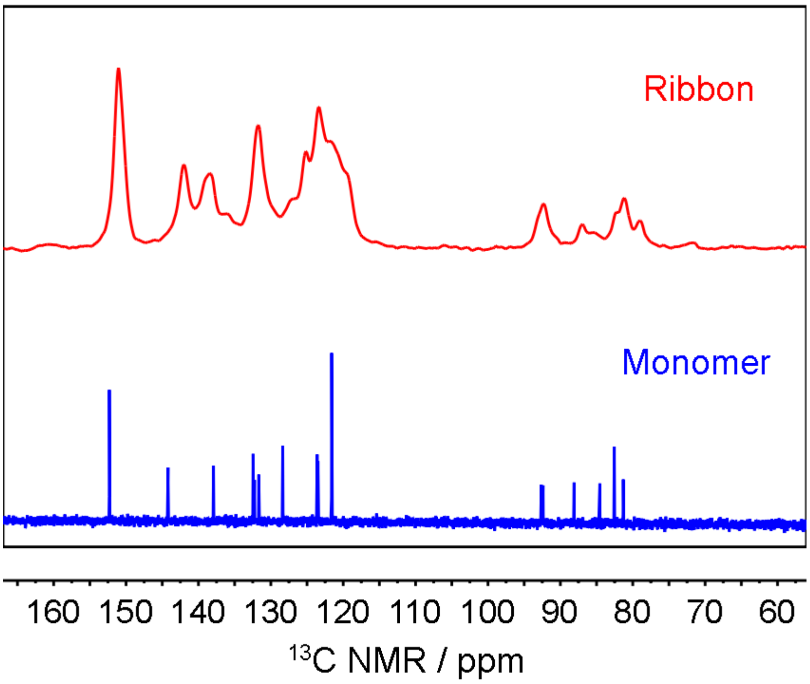


Figure S2. solid state ^{13}C NMR spectrum of **PDBA** and ^{13}C NMR spectrum of **7** in d-chloroform.

Table S2. X-ray Diffraction Data of Oriented **PDBA**.

d_{obs}/Å^{a}	D_{cal}/Å^{b}	*hkl*
24.6066	24.5342	100
19.0896	18.6517	001
12.2724	12.2671	200
9.4006	9.3259	002
8.6367	8.7173	102
8.145	8.1781	300
6.6062	6.6211	221
6.3773	6.3924	311
6.1793	6.1488	302
5.953	6.0267	103
5.7584	5.693	113
5.5908	5.6285	320
5.3544	5.3538	410
5.177	5.164	213
4.8973	4.9068	500
4.8057	4.8189	322
4.6101	4.5899	313
4.5455	4.5772	331
4.4582	4.4291	114
4.3313	4.3424	502
3.9949	3.9942	601
3.895	3.8946	224
3.6993	3.702	432
3.5687	3.569	205
3.5477	3.5412	440
3.4154	3.4164	603
3.2675	3.2711	315
3.1446	3.1413	540

[a] Spacings observed in X-ray diffraction patterns of **PDBA** fibers. [b] Spacings calculated and indexed on the basis of hexagonal unit cells (P6/mmm) with parameters *a*= 28.33 Å.

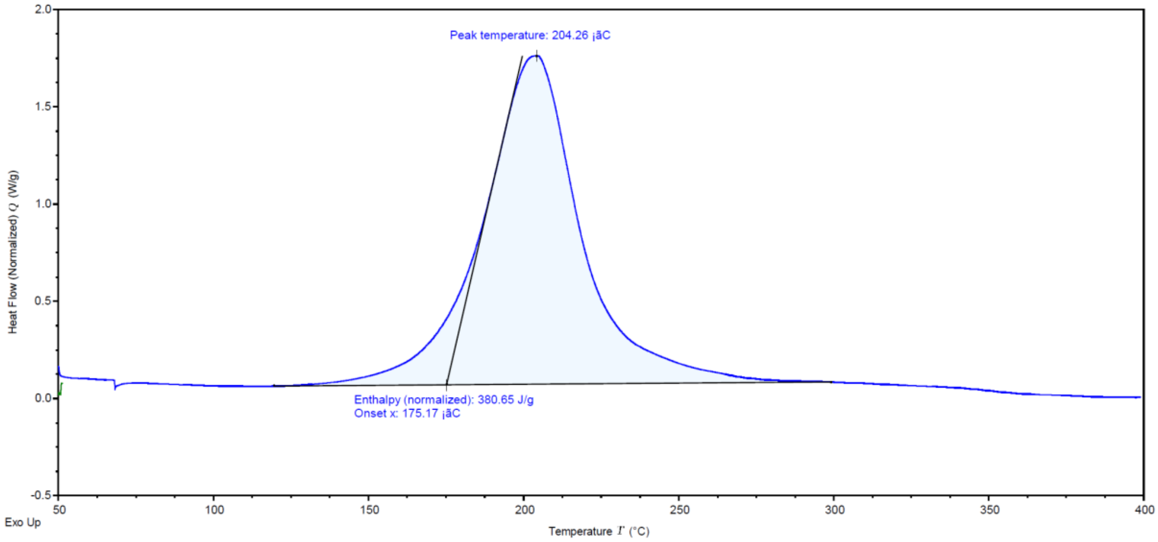


Figure S3. DSC curve showed an endothermic peak at 204.3 ^{o}C with a Δ*H* of 380.65 Jg^{-1}

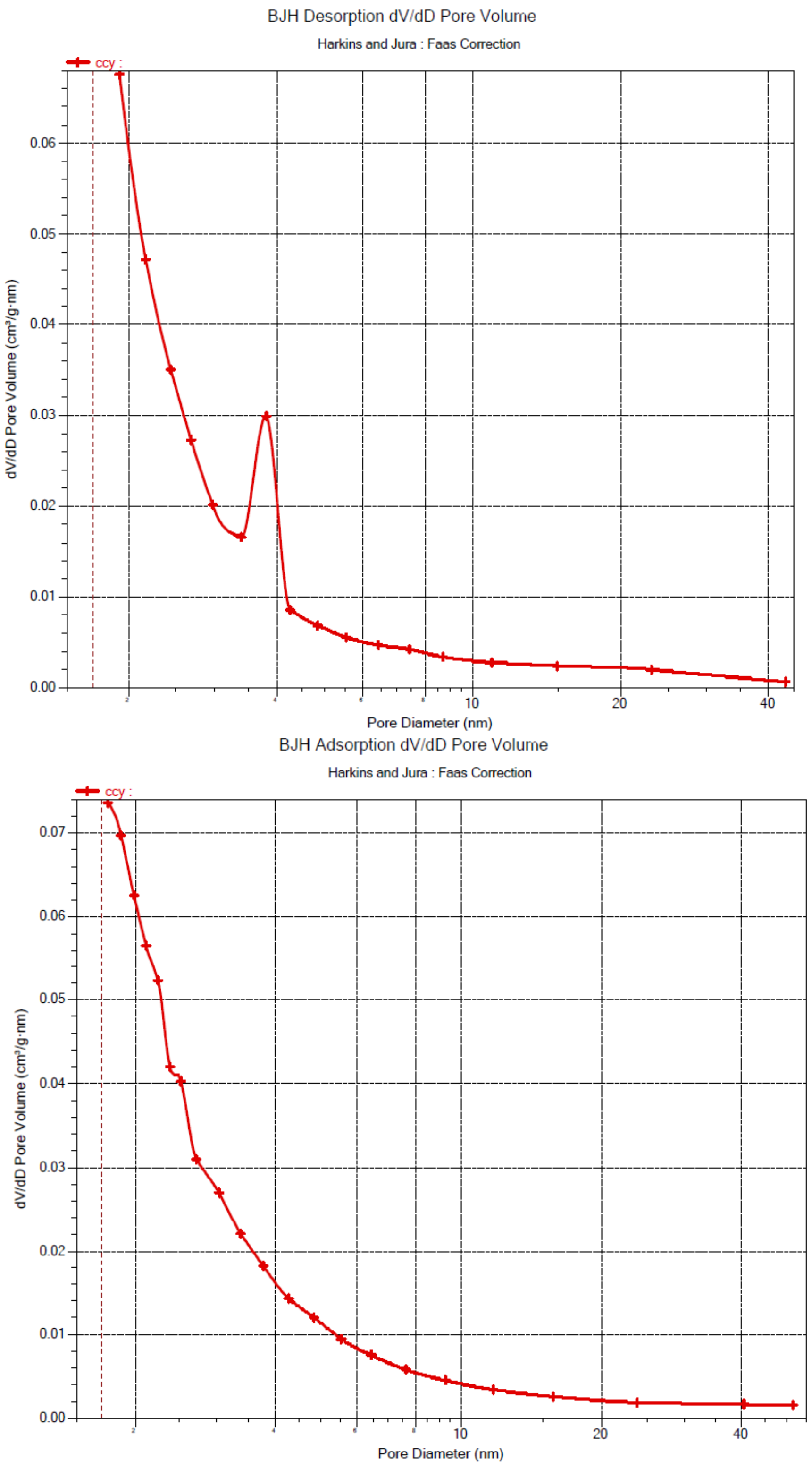


Figure S4. Pore size distribution based on Barrett-Joyner-Halenda (BHJ) adsorption mode.

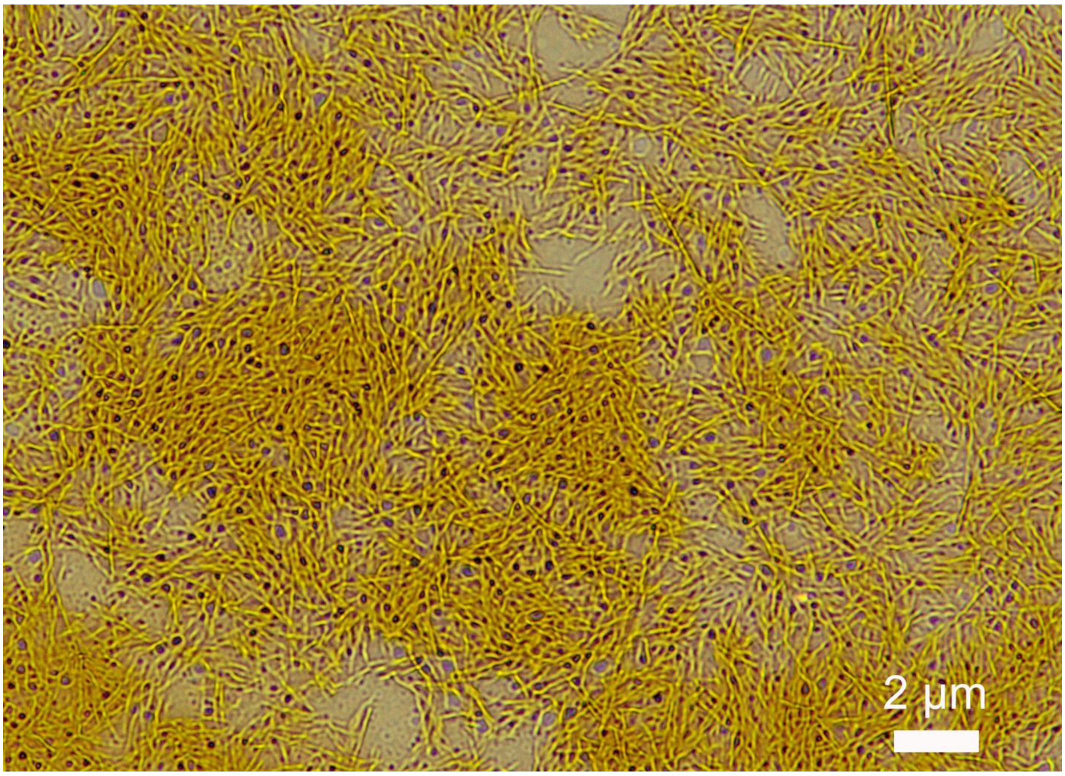


Figure S5. Optical microscopy of **PDBA** fibers transferred to a quartz substrate.

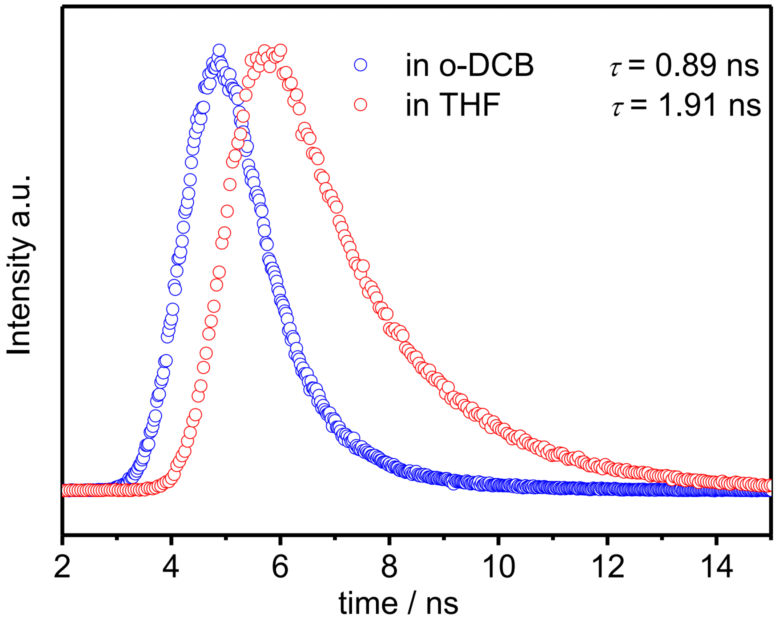


Figure S6. Fluorescence lifetime of **PDBA.**

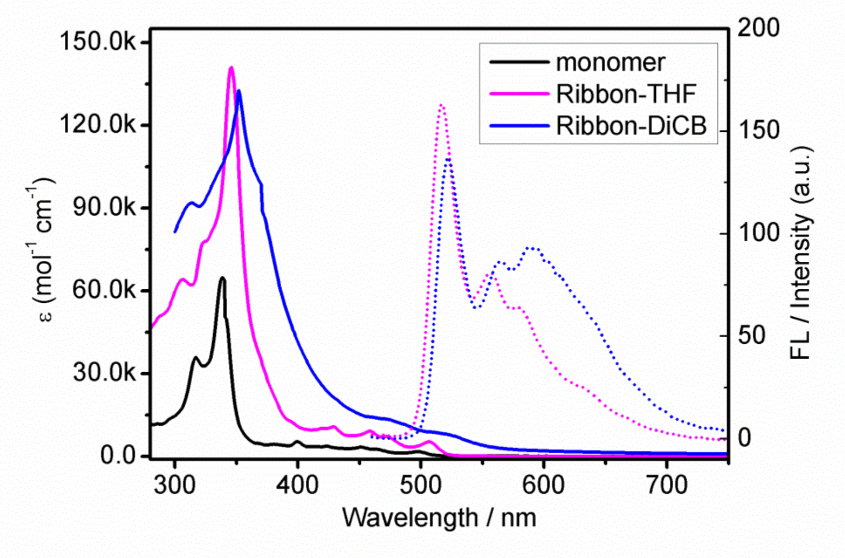
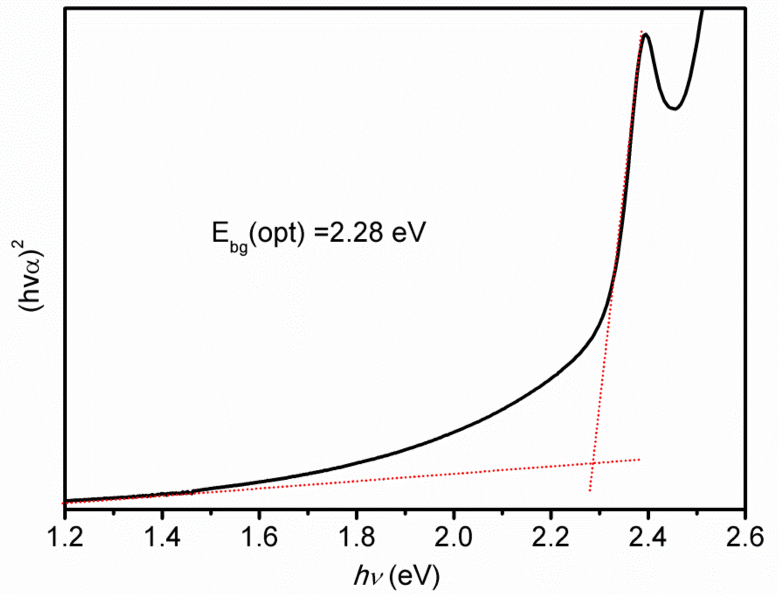


Figure S7. UV-vis spectra of PDBA in THF and dichlorobenzene.



Figue S8. The Tauc plot of PDBA for the determination of the optical band gap (E_{bg}).

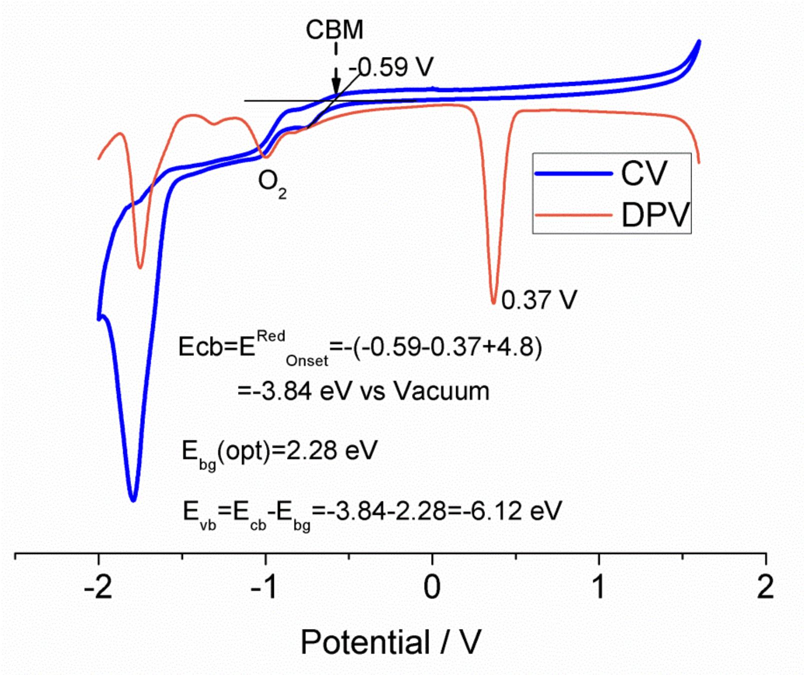


Figure 9. Combined the optical band gap with the reduction potential obtained from cyclic voltammetry, the energy level of valence band (E_{vb}) and conduction band (E_{cb}) of **PDBA** was determined to be -6.12 and -3.84 eV.

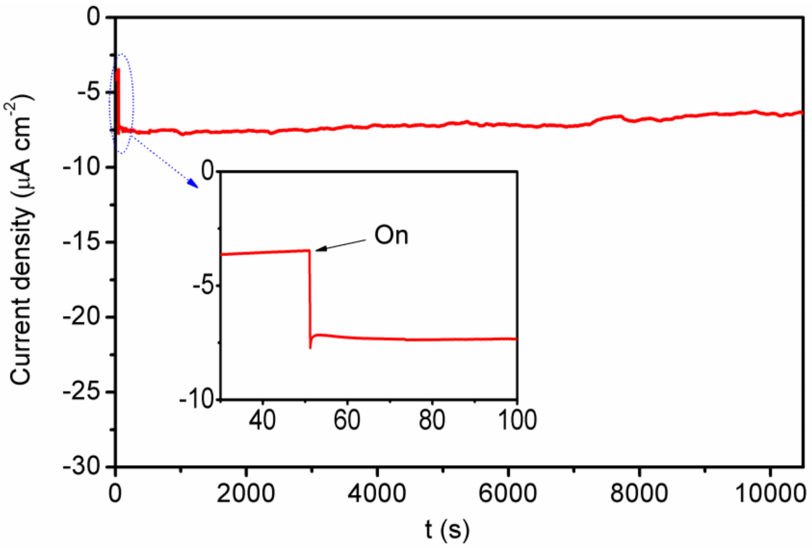


Figure S10. Current density vs. time of the **PDBA** electrode under illumination for 11000s. Inset: magnification of 30–100s, where light irradiation started at 50s.

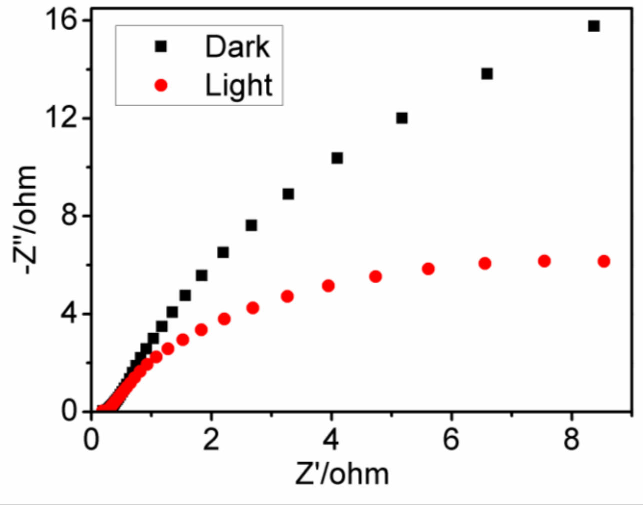


Figure S11. EIS (recorded at 0.30 V vs. RHE) of **PDBA** under light or in the dark: after long time irradiation.

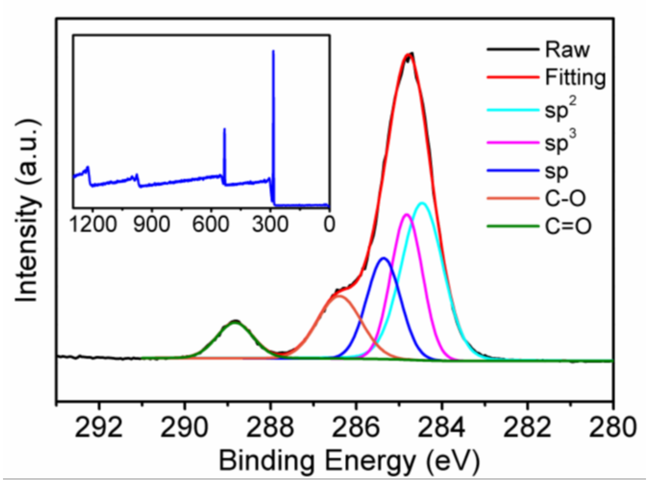


Figure S12. The XPS after photoelectrochemical experiments,which showed some increasing of C-O and C=O signals, indicating the oxidation of the nanofibers after longtime irradiation without protection.

4 Reference:

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