

Highly durable spirobifluorene-based aromatic anion conducting polymer for a solid ionomer of alkaline fuel cells and water electrolysis cells

Shoji Miyanishi^{†,‡}, Takeo Yamaguchi^{*†,‡}

[†]Laboratory for Chemistry and Life Science Institute of Innovative Research, Tokyo Institute of Technology,
R1-17, 4259, Midori-ku, Yokohama, Kanagawa, 226-8503, Japan

[‡]Core Research for Evolutionary Science and Technology, Japan Science and Technology Agency, (JST-
CREST)

Corresponding author: yamag@res.titech.ac.jp

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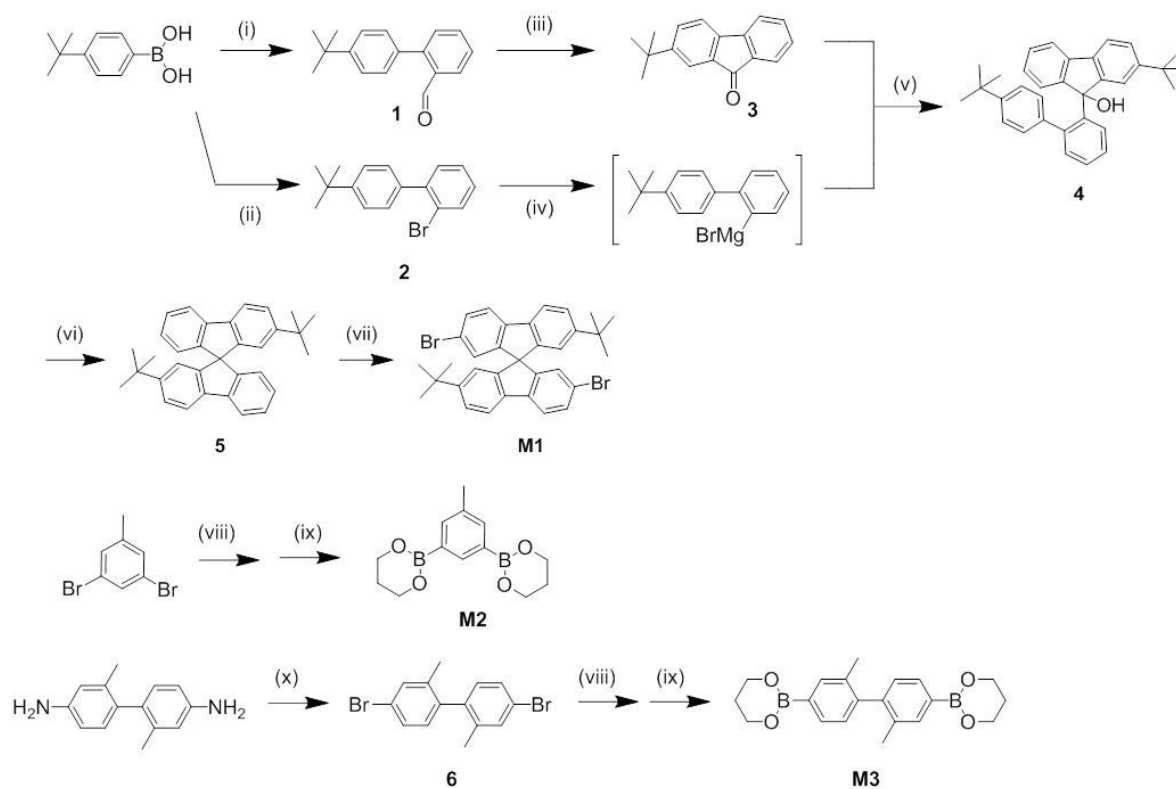
Experimental

$^1\text{H-NMR}$ spectra were recorded on a Bruker Biospin Advance III system (400 MHz). GPC was performed on a high-performance liquid chromatography L-7100 system (Hitachi Corp.) equipped with a UV detector and Asahipak GF-7MHQ columns ($\times 2$) using CHCl_3 as the eluent at $40\text{ }^\circ\text{C}$. The molecular weights were calculated against polystyrene standards. Water adsorption of the membrane was recorded on a MSB-AD-V-FC system (BEL Japan Inc.). The membrane was pretreated under vacuum at $70\text{ }^\circ\text{C}$ for 90 min.

Ion exchange capacity (IEC) of polymer samples were measured by titration using an automatic titrator COM-1700 (Hiranuma Corp., Japan). Typically, a polymer sample (30 mg) was soaked in 1 M NaOH aq. for 24 h to exchange the anion. After removing the solid polymer by filtration, the Br^- anion-containing solution was neutralized with HNO_3 aq. and titrated with 0.01 M AgNO_3 aq.

In-plane anion conductivity (HCO_3^- and OH^-) was measured using the AC impedance method with a Solartron 1260 impedance/gain phase analyzer in the frequency range of 1 to 10^6 Hz and at a signal amplitude of 10–100 mV. The measurement conditions were controlled by a SH-221 benchtop-type temperature and humidity chamber (Espec Corp., Japan). For OH^- conductivity measurements, the polymer membranes (HCO_3^-) were soaked in 1 M NaOH aq. for 24 h to exchange HCO_3^- to OH^- anions and subsequently soaked in pure water for 2 h to remove residual NaOH. The membrane resistance was measured in water. Benzyl trimethyl ammonium modified polyether sulfone AEM (IEC=2.2 meq g^{-1}) and benzyl trimethyl ammonium modified polyphenylene oxide AEM (IEC=2.3 meq g^{-1}) were synthesized by following the reference [1,2]

Scheme S1. Synthetic scheme of the monomers^a

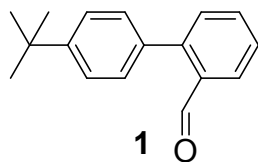


^a Reagent and conditions: (i) 2-bromobenzaldehyde, Na₂CO₃, Pd(PPh₃)₄, 1,2-dimethoxyethane/H₂O, reflux (ii) 1-bromo-2-iodobenzene, Na₂CO₃, Pd(PPh₃)₄, 1,2-dimethoxyethane/H₂O, reflux (iii) tert-butyl hydroperoxide, ferrocene, acetonitrile, 90 °C (iv) Mg, I₂, anhydrous tetrahydrofuran (THF), reflux (v) THF, rt (vi) CH₃COOH, *conc* HCl, 80 °C (vii) Br₂, FeCl₃, CHCl₃, rt (viii) tetrahydroxydiborane, CH₃OH, 10 °C, 254nm UV irradiation (ix) 1,3-propanediol, diethylether, rt (x) CH₃CN/CH₃COOH, H₂SO₄ aq., NaNO₂ aq. and then CuBr, *conc* HBr, 35 °C

Synthesis

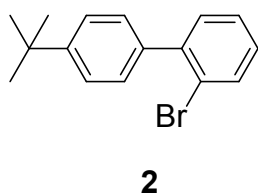
All reagents were used as received from the provider unless otherwise stated.

M1-M3 were synthesized by similar procedure of the literatures [3-5]



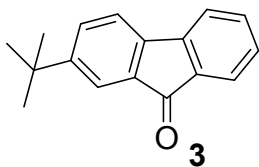
4-tertbutylphenyl boronic acid (11.6 g, 65 mmol), 2-bromobenzaldehyde (9.25 g, 50 mmol), tetrakis(triphenylphosphine)palladium (0) (1733 mg, 1.5 mmol), sodium carbonate (15.9 g, 150 mmol) were dissolved into dimethoxyethane (65 mL)/H₂O (30 mL). After nitrogen was bubbled into the solution for 10 min, the solution was refluxed under nitrogen for 24 h. After removing the solvent by evaporator, the residue was extracted with dichloromethane and washed with water. The solvent was removed by evaporator and the residue was purified by column chromatography (Eluent:hexane:chloroform=4:1) to afford **1**(9.77 g) in 82% yield.

¹H-NMR (CDCl₃): δ 10.01 (1H, s), δ 8.02 (1H, d), δ 7.63 (1H, t), δ 7.50- 7.43 (4H, m), δ 7.32 (2H, d), δ 1.39 (9H, s)



4-tertbutylphenyl boronic acid (9.8 g, 55 mmol), 2-iodobromobenzene (14.1 g, 50 mmol), tetrakis(triphenylphosphine)palladium (0) (1733 mg, 1.5 mmol), sodium carbonate (15.9 g, 150 mmol) and aliquat-336 (1 g) were dissolved into Toluene (70 mL)/ H₂O (30 mL). After nitrogen was bubbled into the solution for 10 min, the solution was refluxed under nitrogen for 24 h. Organic layer was washed with water several times and the solvent was removed by evaporator. The residue was purified by column chromatography (Eluent:hexane) to afford **2** (10.4 g, 36 mmol) in 72% yield.

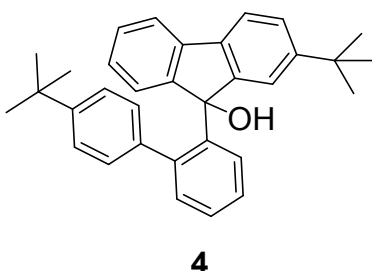
¹H-NMR (CDCl₃): δ 7.67 (1H, d), δ 7.44 (2H, m), δ 7.34 (4H, m), δ 7.18 (1H, m), δ 1.38 (9H, s)



1 (7.15 g, 30 mmol) and catalytic amount of ferrocene (186 mg, 1 mmol) were dissolved into acetonitrile (10 mL). 5.5M tert-butyl hydroperoxide solution in decane (6 mL, 33 mmol) was added into the mixture and reacted for 12 h at 90 °C. Then, another tert-butyl hydroperoxide solution in decane (6 mL, 33 mmol) was added again and stirred further for 12h.

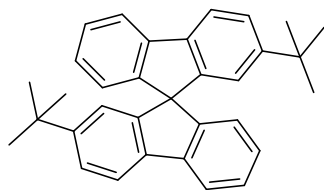
The solvent was removed by evaporator and column chromatography (hexane:chloroform=3:1) of the residue afforded crude product, which is further purified by recrystallization in hexane to afford analytically pure compound **3** (4.86 g) in 68% yield. [3]

¹H-NMR (CDCl₃): δ 7.71 (1H, s), δ 7.62 (1H, d), δ 7.51-7.41 (4H, m), δ 7.24 (1H, t), δ 1.34 (9H, s)



2 (5.78 g, 20 mmol), Mg (5.34 g, 22 mmol) and I₂ (100 mg) were dissolved in anhydrous THF (20 mL) and refluxed under nitrogen for 6 h. The resulting grignard solution was cooled to room temperature and **3** (4.77 g, 20 mmol) in THF (10 mL) was added. After stirring for 2h, the reaction was quenched with small portion of water. The solvent was removed by evaporator and column chromatography of the residue (chloroform:hexane=1:1) afforded compound **4** (4.77 g, 17 mmol) in 85 % yield. [2]

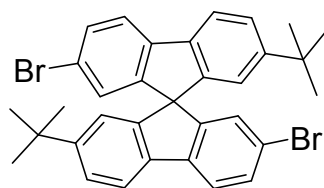
¹H-NMR (CDCl₃): δ 8.47 (1H, d), δ 7.53 (1H, t), δ 7.32 (1H, t), δ 7.22-7.11 (6H, m), δ 7.01 (1H, d), δ 6.95 (1H, d), δ 6.58 (2H, d), δ 6.00 (1H, br), δ 5.83 (1H, br), δ 2.24 (1H, s), δ 1.31 (9H, s), δ 1.22 (9H, s)



5

4 (6.70 g, 15mmol) was dissolved into acetic acid (20 mL) at 80 °C. 10M HCl solution (2 mL) was added and stirred for 1h. The white precipitated was collected by filtration and washed with water several times to afford **5** (6.17 g) in 97% yield. [4]

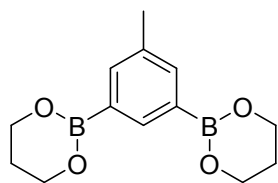
¹H-NMR (CDCl₃): δ 7.80 (2H, d), δ 7.77 (2H, d), δ 7.42 (2H, d), δ 7.32 (2H, t), δ 7.04 (2H, t), δ 6.73 (2H, s), δ 6.66 (2H, d), δ 1.16 (18H, s)



M1

5 (6.0 g, 14 mmol) and FeCl₃(III) (162 mg, 1 mmol) were dissolved into chloroform (100 mL). Br₂ (6.39 g, 40 mmol) was added in the mixture and stirred for 4 h at room temperature. Saturated Na₂S₂O₃ solution was added in the mixture and stirred until red color fades out. The organic layer was washed with water several times and the solvent was removed by evaporator. Column chromatography of the residue afforded compound **M1** (7.63 g) in 93% yield.

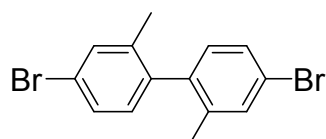
¹H-NMR (CDCl₃): δ 7.73 (2H, d), δ 7.66 (2H, d), δ 7.45 (4H, t), δ 6.77 (2H, s), δ 6.69 (2H, s), δ 1.17 (18H, s)



M2

3,5-dibromotoluene (2.5 g, 10 mmol), tetrahydroxydiborane (2.7 g, 30 mmol) was dissolved into methanol (80 mL). The solution was stirred under UV-irradiation (254 nm) at 25 °C for 6 h [5]. Additional tetrahydroxydiborane (2.7 g, 30mmol) was added in the mixture again and reacted under the same condition for 6 hr. The reaction mixture was dried in vacuo to remove the solvent and dispersed into 1 M HCl aqueous (100 mL). The resulting mixture was washed with water and collected by filter. The resulting solid was dried in vacuo to remove water. The dried solid and 1,3-propane diol was stirred for 12 h at 25 °C in diethyl ether (100 mL). The solvent was removed by rotary evaporator and column chromatography on silica gel (chloroform:hexane=4:1) afforded **M2** (1.01 g, 3.7 mmol) in 37% yield.

¹H-NMR 400MHz (CDCl₃): δ 8.00 (1H, s), δ 7.64 (2H, s), δ 4.15 (8H, t), δ 2.34 (3H, s), δ 2.04 (4H, m)



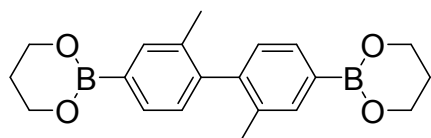
6

4,4'-dibromo-2,2'-dimethylbiphenyl (**6**)

10.6 g (50 mmol) of *m*-tolidine was dissolved into 85 g of acetonitrile and 75 g of acetic acid and added with 112 g of 30 wt% sulfuric acid. The mixture was warmed to 70 °C for 0.5 h and cooled to 0 °C. 18 g of 40 wt% aqueous sodium nitrite was added in the mixture to form a diazonium salt. CuBr in HBr solution (17.3 g CuBr in 100 g of 48% HBr) was then added dropwise within 0.5 h. The solution was then mixed at 35 °C for 2 h. 100 g water was added to the mixture. The organic phase was extracted with toluene (3 × 100 g) and then washed with water twice. After removing the solvent by evaporator, short column chromatography of the residue on silica gel (Eluent: hexane) afforded

brown solid. The solid was further purified by recrystallization in ethanol to obtain 12.2 g of the product as a light yellow solid in 72% yield.

$^1\text{H-NMR}$ (CDCl_3): δ 7.43 (2H, s), δ 7.35 (2H, d), δ 6.93 (4H, d), δ 2.02 (6H, s)

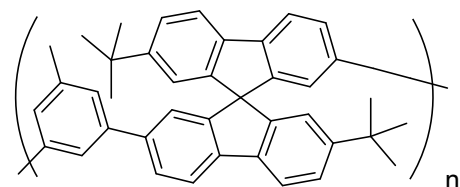


M3

6 (3.4 g, 10 mmol) and tetrahydroxydiborane (2.7 g, 30 mmol) was dissolved into hot methanol (80 mL). The solution was stirred under UV-irradiation (254 nm) at 25 °C for 6 h. Additional tetrahydroxydiborane (2.7g, 30 mmol) was added in the mixture again and reacted under the same condition for 6 hr. The reaction mixture was dried in vacuo to remove the solvent and dispersed into 1 M HCl aqueous (100 mL). The resulting mixture was washed with water and collected by filter. The resulting solid was dried in vacuo to remove water. The dried solid and 1,3-propane diol was stirred for 12 h at 25 °C in diethyl ether (100 mL). The solvent was removed by rotary evaporator and column chromatography (chloroform:hexane=3:1) on silica gel afforded compound **M3** (2.4 g, 6.9 mmol) in 69% yield.

$^1\text{H-NMR}$ 400MHz (CDCl_3): δ 7.67 (2H, s), δ 7.61 (2H, d), δ 7.08 (2H, d), δ 4.18 (8H, t), δ 2.07 (4H, m), δ 2.03 (6H, s)

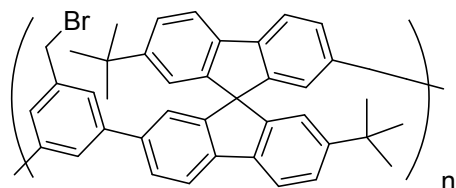
PSBFP-Me



M1 (1 mmol) and **M2** (1 mmol) were dissolved in toluene (8 mL). sodium carbonate (6 mmol) in water (4 mL), Aliquat-336 (50 mg), and [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.02 mmol) were then added. Nitrogen was bubbled into the mixture for 15 min and the solution was

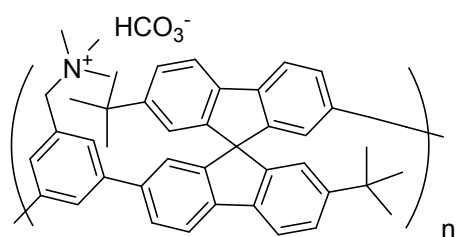
heated to 100 °C. After 60 h under nitrogen, the solution was reprecipitated in methanol. The solid was filtered and dissolved into chloroform. The solution was washed with 1 M HCl aq. twice to remove the catalyst and then concentrated. The residue was reprecipitated in acetone, hexane, and, finally, methanol. The resulting solid was dried to afford PSBFP-Me (338 mg) in 66% yield.

PSBFP-Br



PSBFP-Me (200 mg) was dissolved in chlorobenzene (20 mL). Then, *N*-bromosuccinimide (178 mg) and 2,2'-Azobis(isobutyronitrile) (2 mg) were added. The resulting solution was stirred at 110 ° C for 3 h under nitrogen. The solution was concentrated on a rotary evaporator, and the residue was reprecipitated into methanol twice. The solid was collected by filtration and dried in vacuum to afford PSBFP-Br (183 mg) in 79% yield.

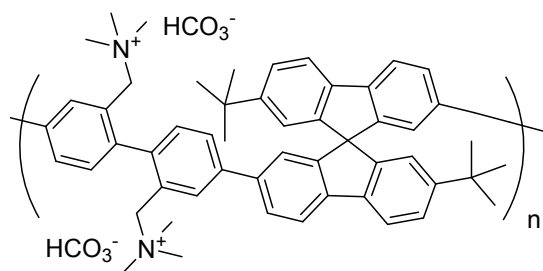
PSBFP-TMA



PSBFP-Br (150 mg) was dissolved in THF (15 mL). Then, 30 wt% trimethylamine aq. (1 mL) was added. The solution was stirred for 3 h at room temperature and concentrated on a rotary evaporator. The residue was immersed into 1 M NaOH aq. (100 mL) and stirred for 24 h. The solid was collected by filtration and washed with water.

The resulting solid was dried at 40 °C in vacuum to afford PSBFP-TMA (HCO₃ form, 141 mg) in 88% yield.

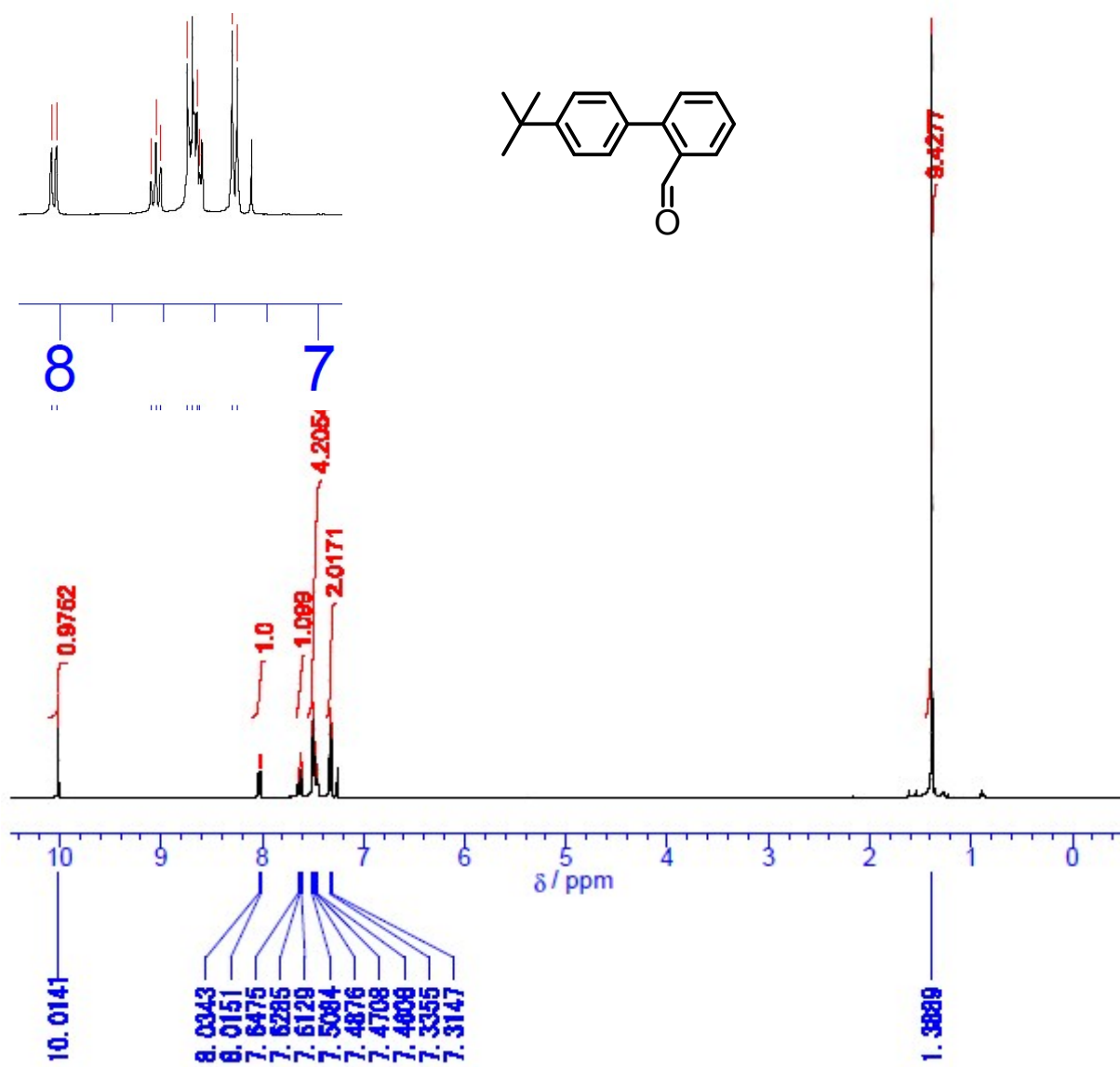
PSBFBP-TMA

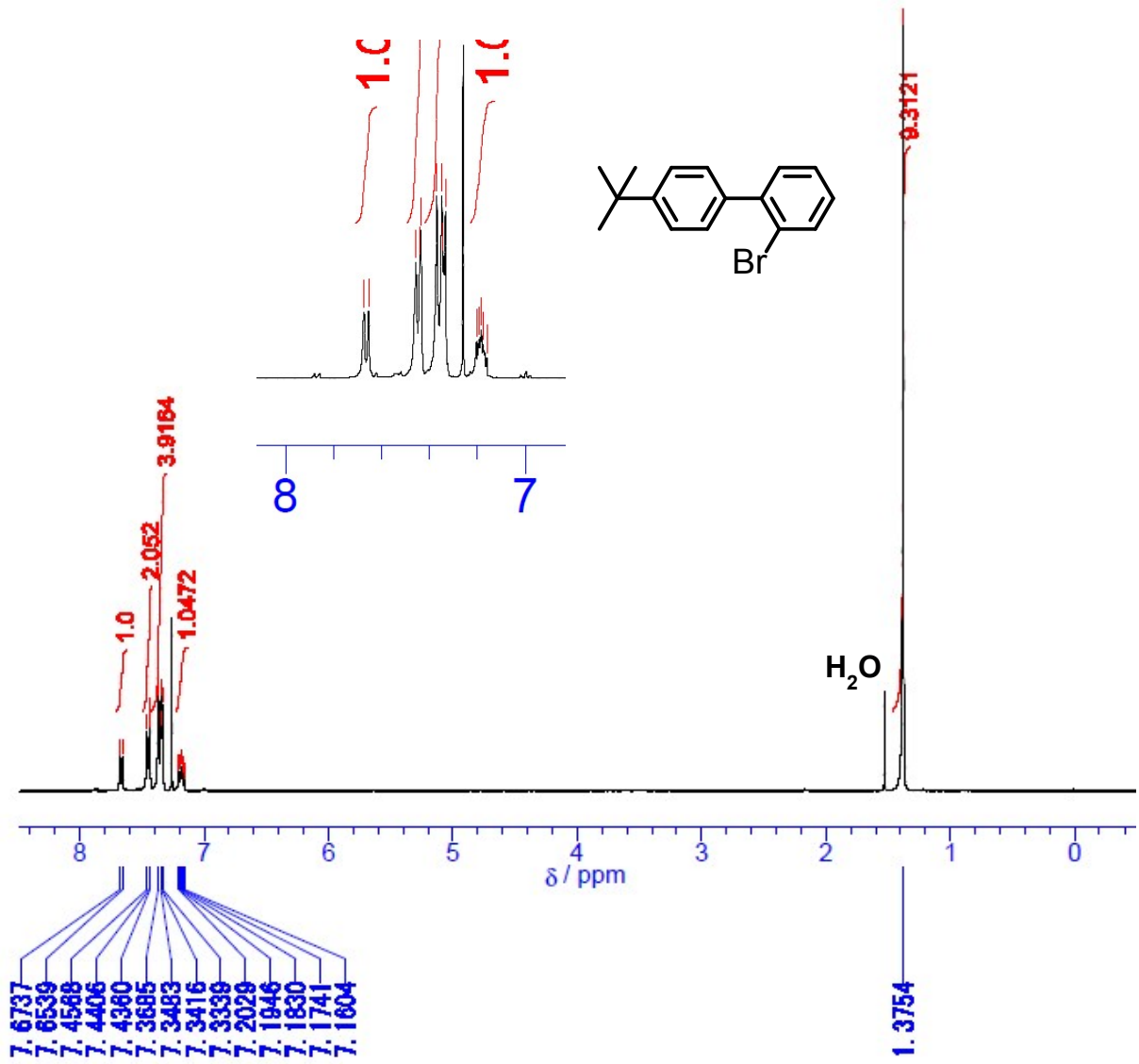


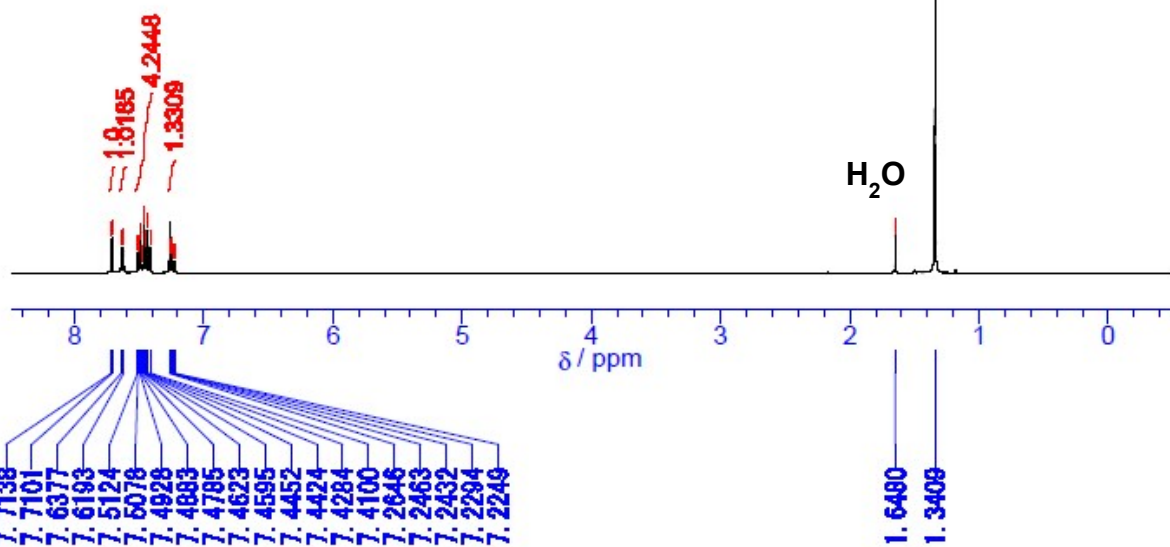
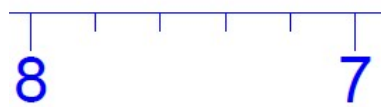
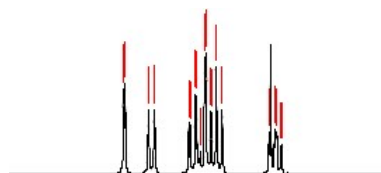
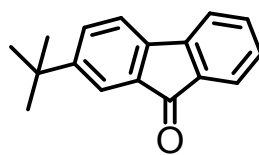
PSBFBP-TMA was synthesized by similar procedure of PSBFP-TMA.

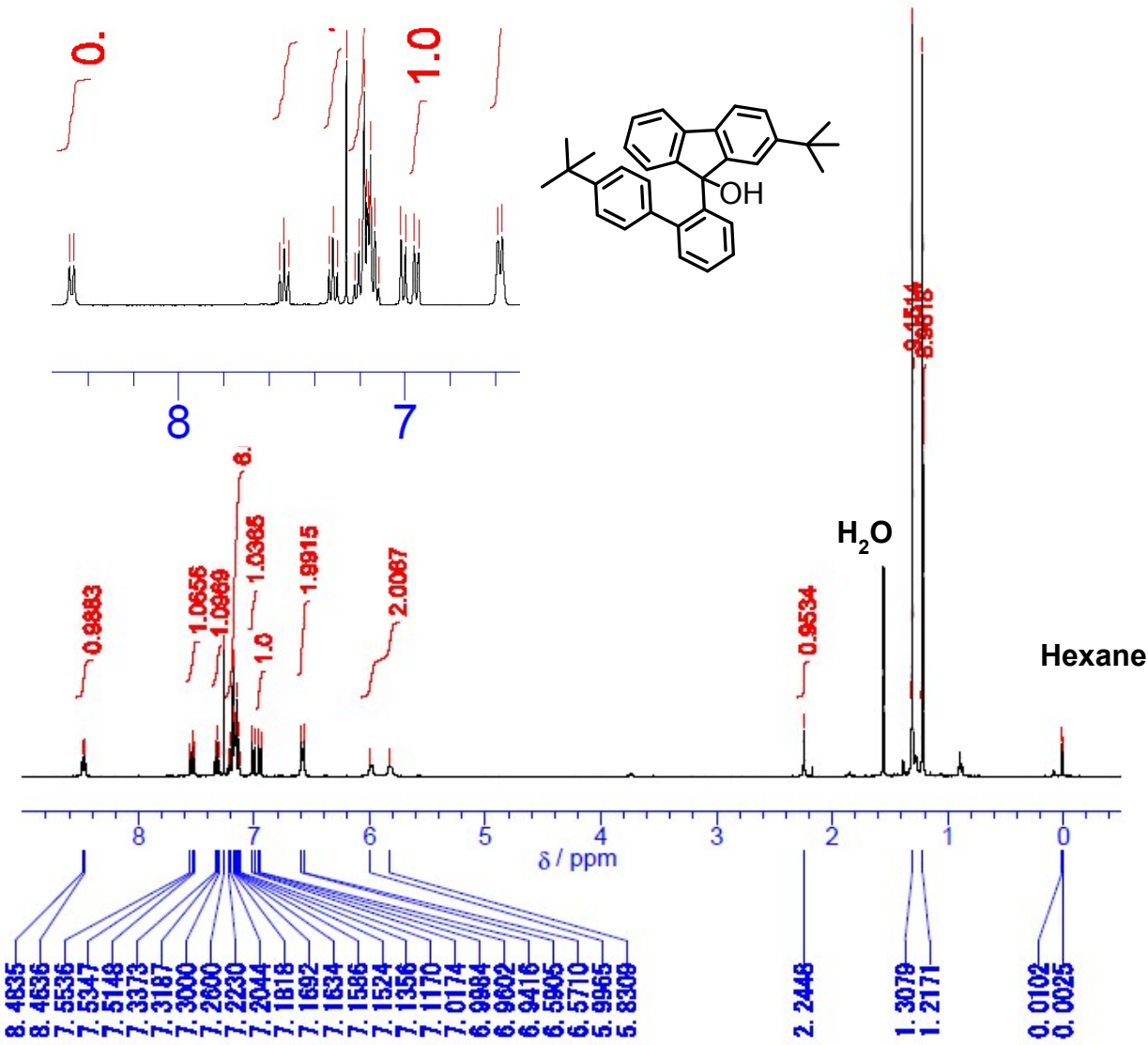
Typically, Suzuki-coupling of **M1** (1 mmol) and **M3** (1 mmol) afforded PSBFBP-Me (351 mg) in 58% yield. Then, PSBFBP-Me (200 mg) and *N*-bromosuccinimide (360 mg) were reacted at 110 °C in chlorobenzene to afford PSBFBP-Br (211 g) in 84% yield. PSBFBP-Br (200 mg) was quaternized with trimethyl amine aq. in THF-methanol mixing solvent to afford PSBFBP-TMA (191 mg) in 86% yield.

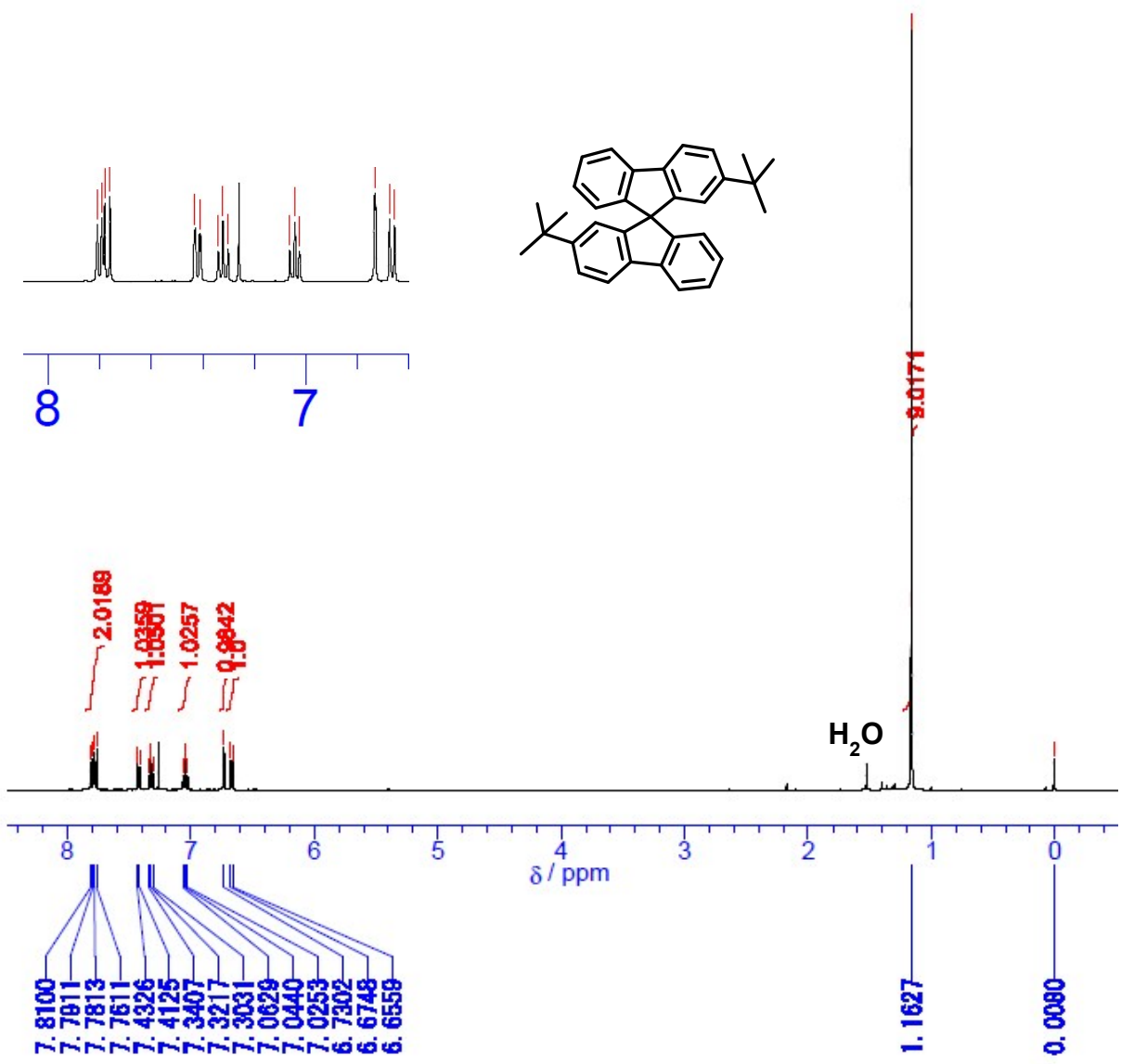
Figure S1. ¹H-NMR spectra of synthetic intermediate of PSBFP-TMA and PSBFBP-TMA

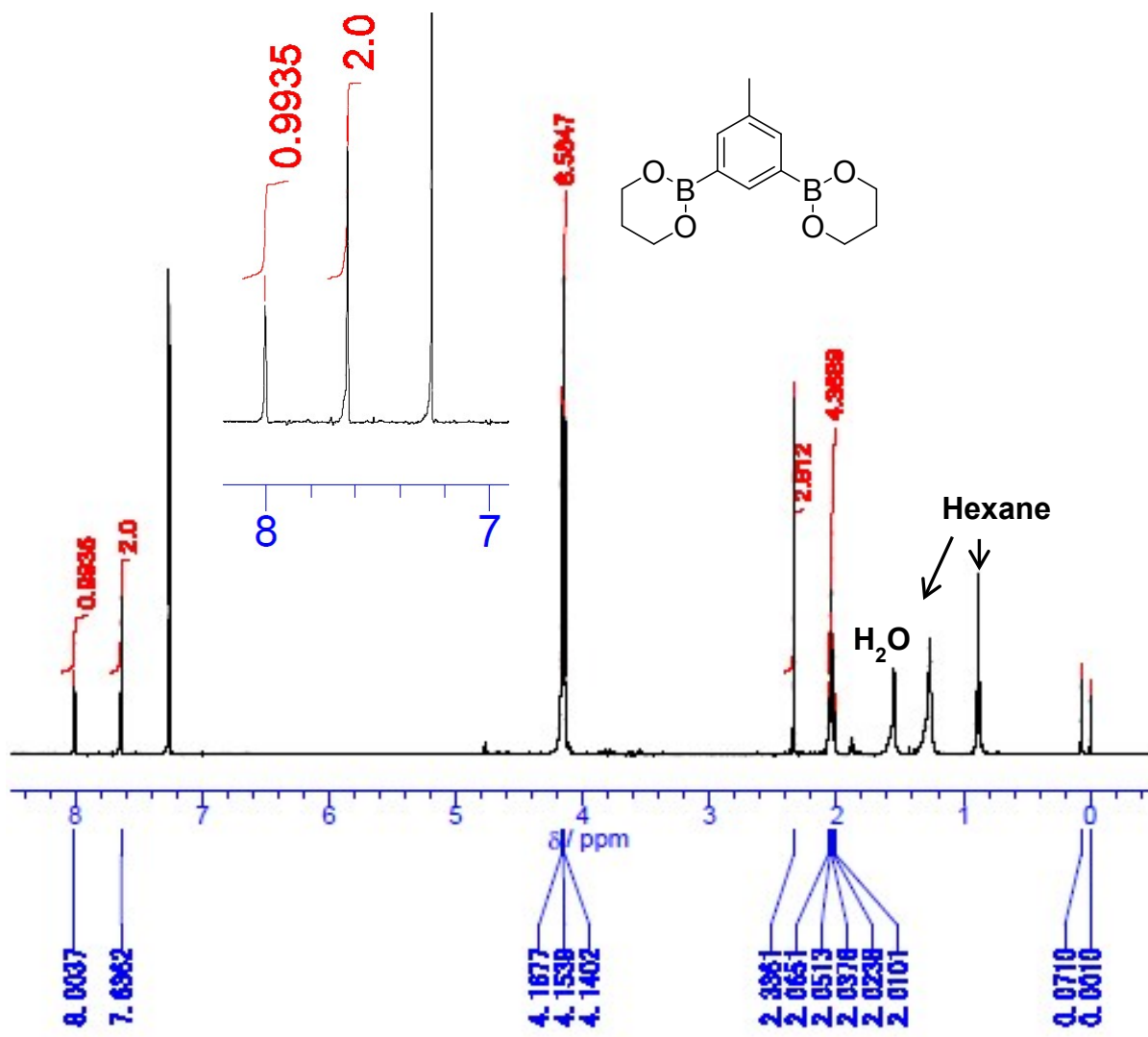


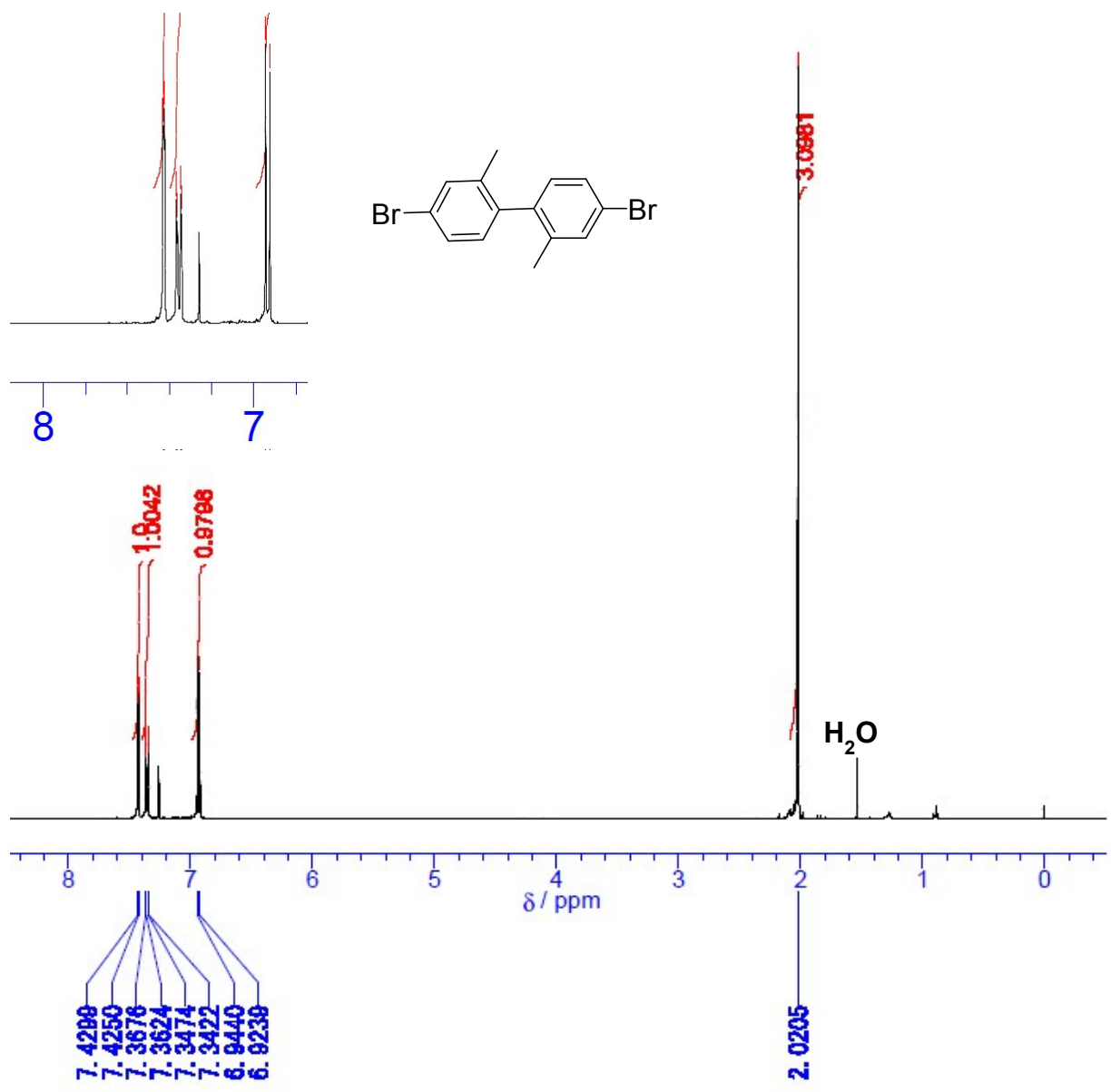












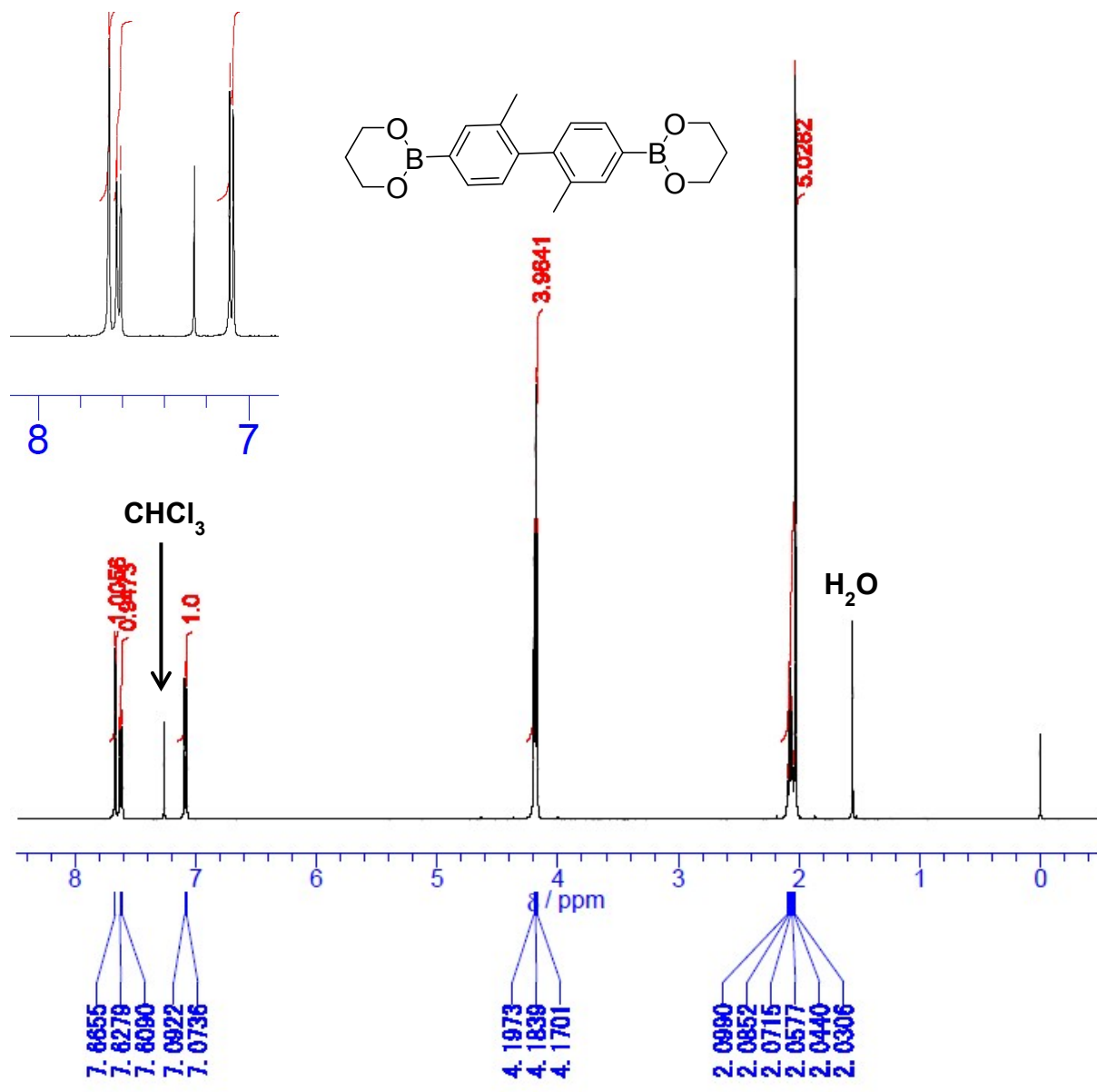
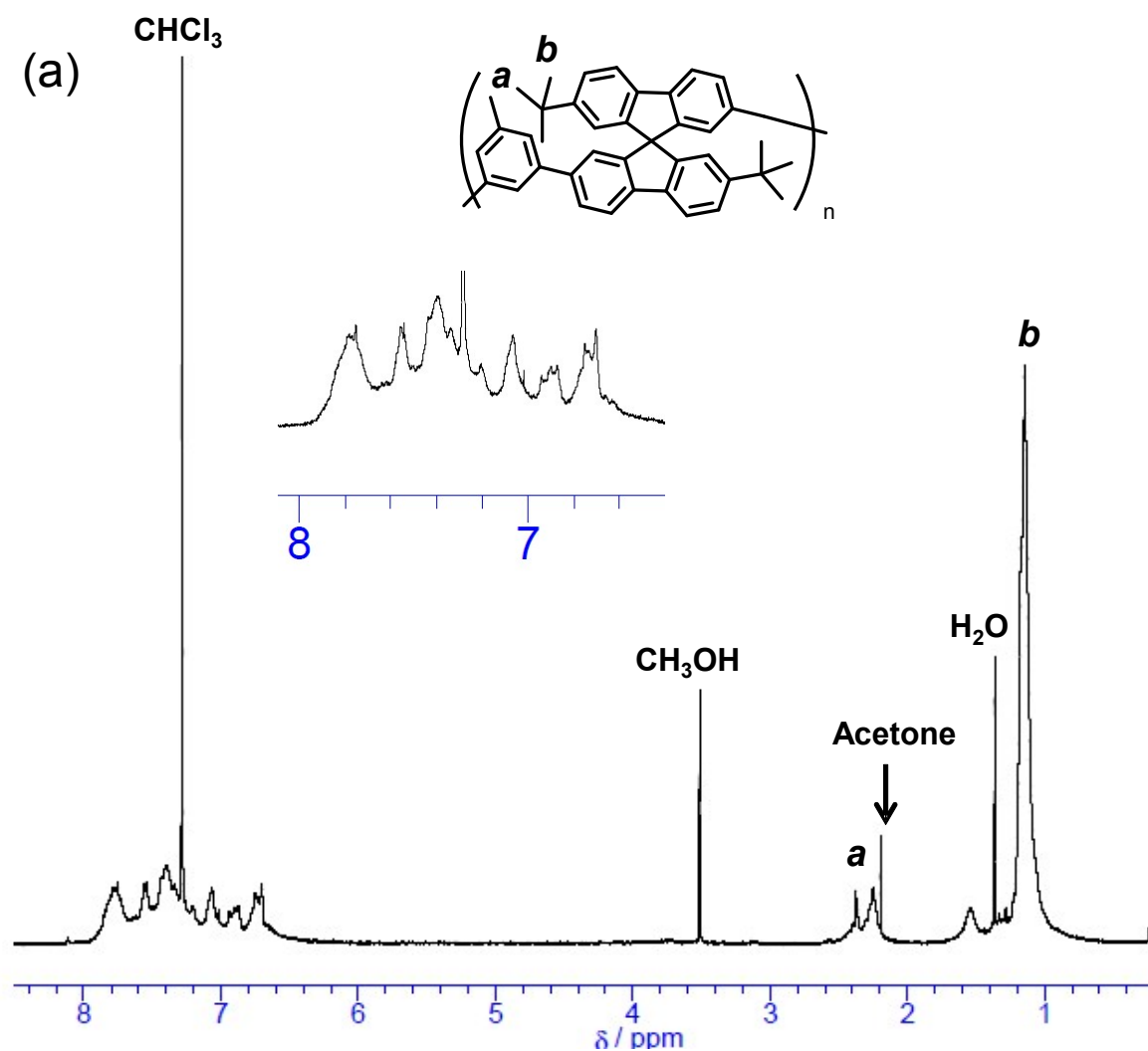
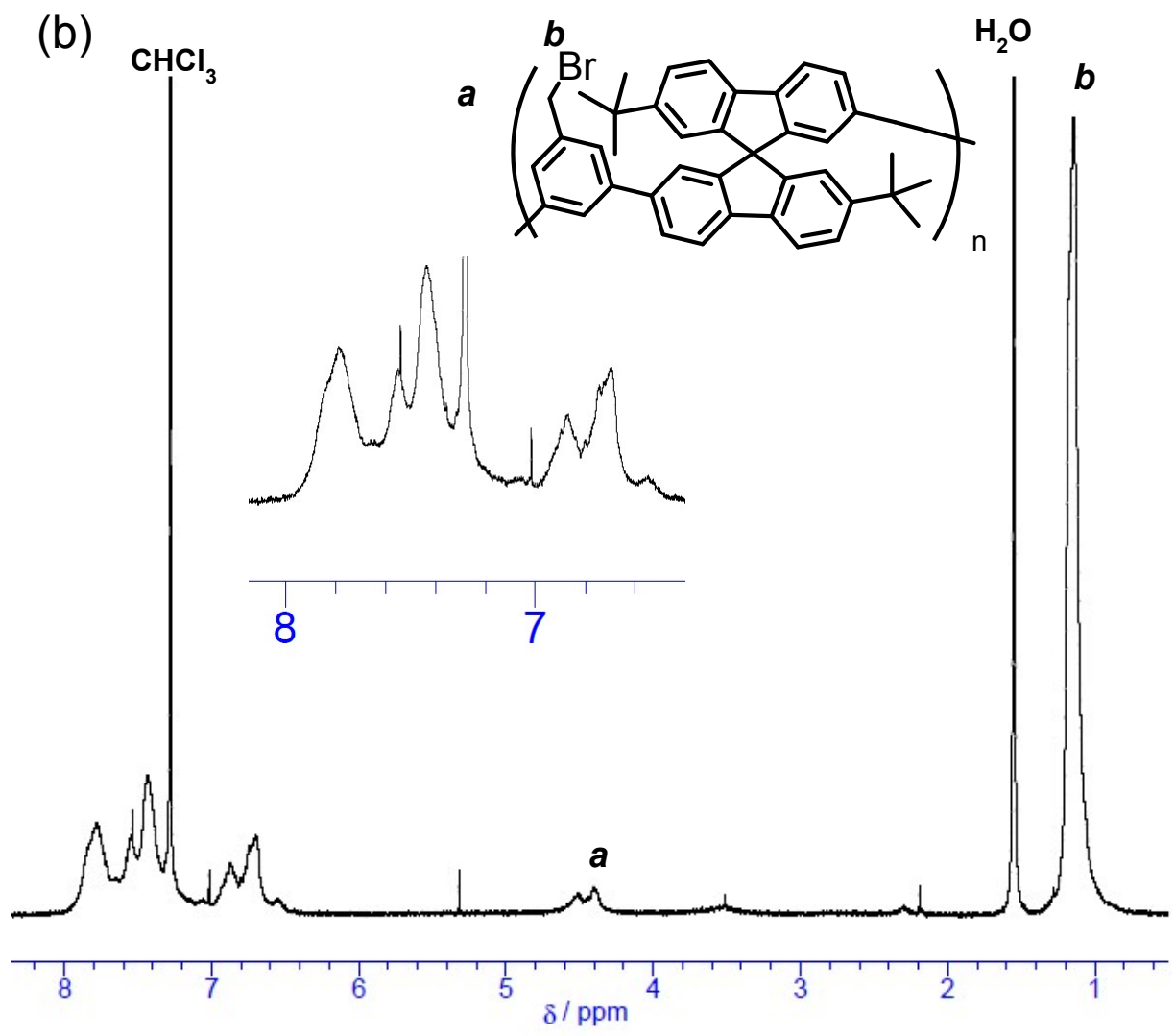
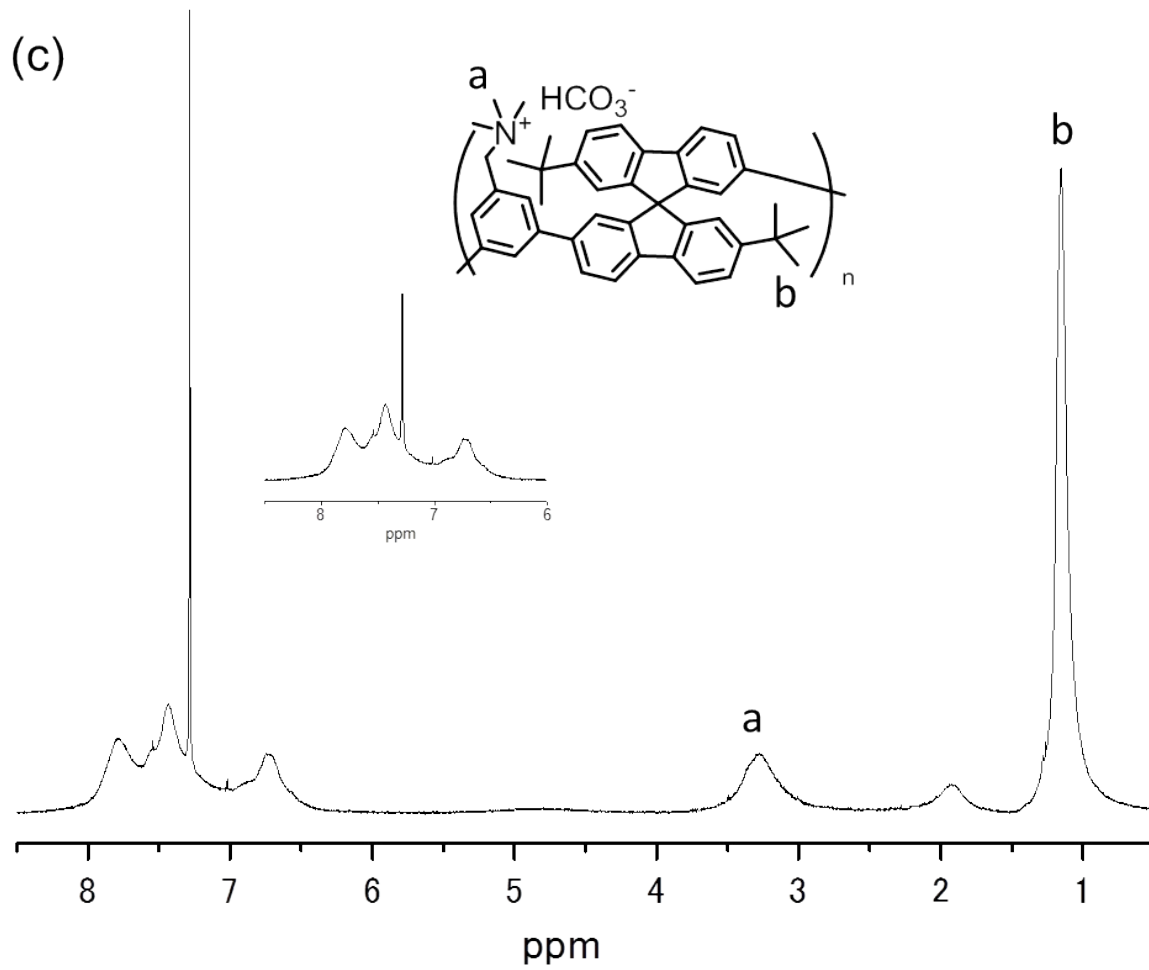


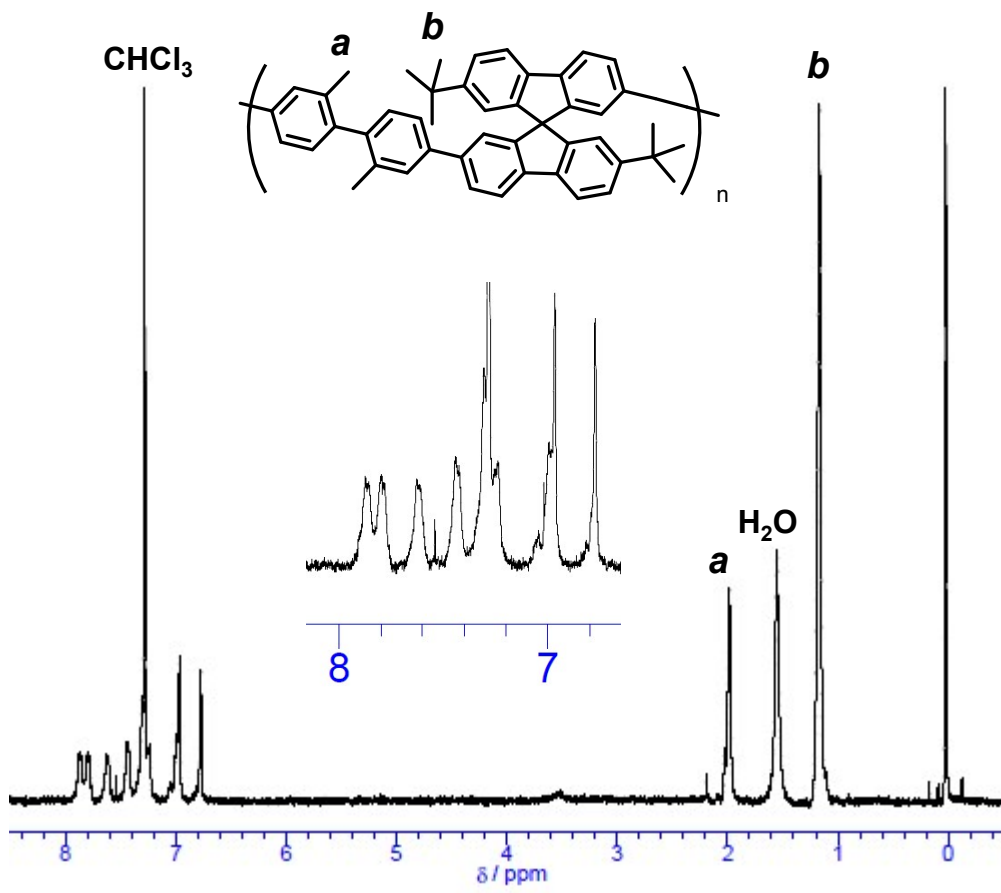
Figure S2 ^1H -NMR spectra of (a) PSBFP-Me, (b) PSBFP-Br, (c) PSBFP-TMA (d) PSBFBP-Me and (e)PSBFBP-Br in CDCl_3 and (f) PSBFBP-TMA in CD_3OD







(d)



(f)

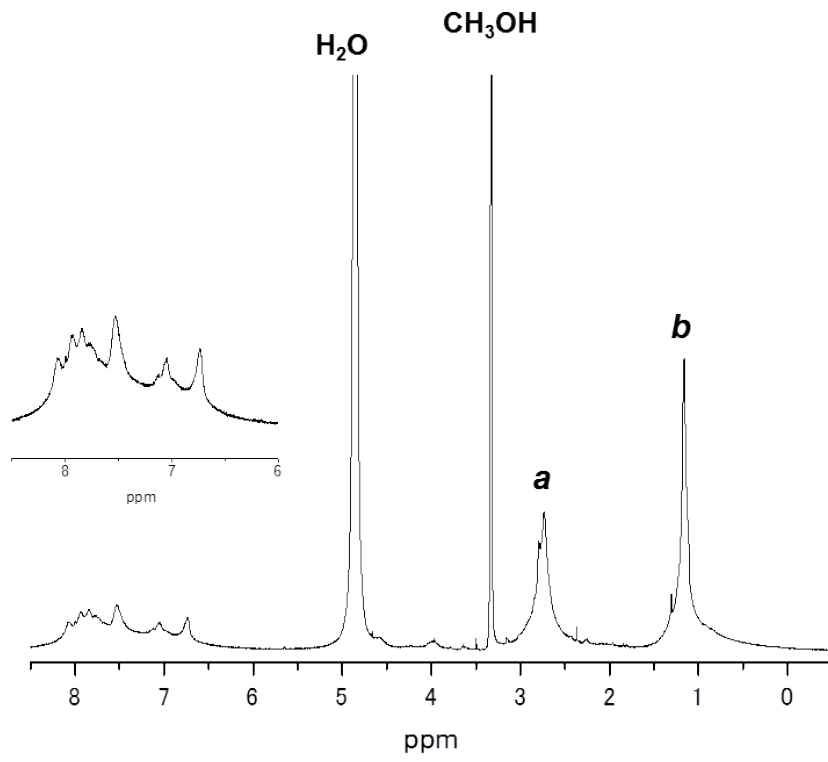
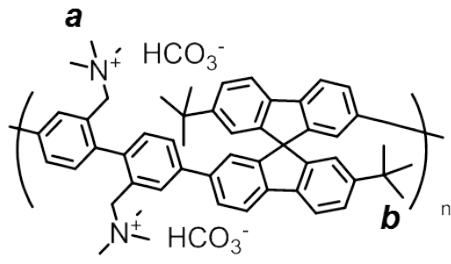


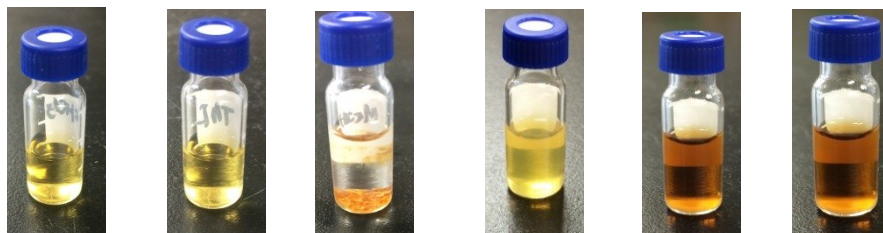
Table S1. Solubility of the synthesized polymers^a

AEM	CHCl ₃	THF	MeOH	EtOH	1-propanol	DMF	DMSO	H ₂ O
PSBFP-TMA (HCO ₃ ⁻)	++	++	--	--	--	+	+	--
PSBFBP-TMA (HCO ₃ ⁻)	-	--	++	+	+	+	++	--

^a ++: highly soluble (>50mg/mL), +: soluble (>10mg/mL), -: partially soluble and --: insoluble

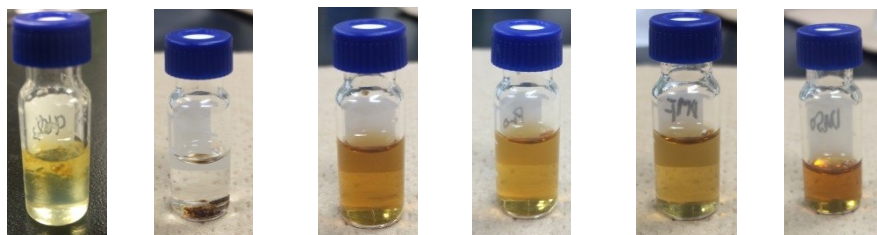
Figure S3. Appearance of (a) PSBFP-TMA (HCO_3^-) solution and (b) PSBFBP-TMA (HCO_3^-) solution in various solvents (10mg/mL)

PSBFP-TMA (HCO_3^-)



CHCl_3 THF MeOH THF-*n*-PrOH (1:3) DMF DMSO

PSBFBP-TMA (HCO_3^-)



CHCl_3 THF MeOH *n*-PrOH DMF DMSO

Figure S4. Arrhenius plot of PSBFBP-TMA (HCO_3^-) and PSBFBP-TMA (HCO_3^-) bicarbonate conductivity

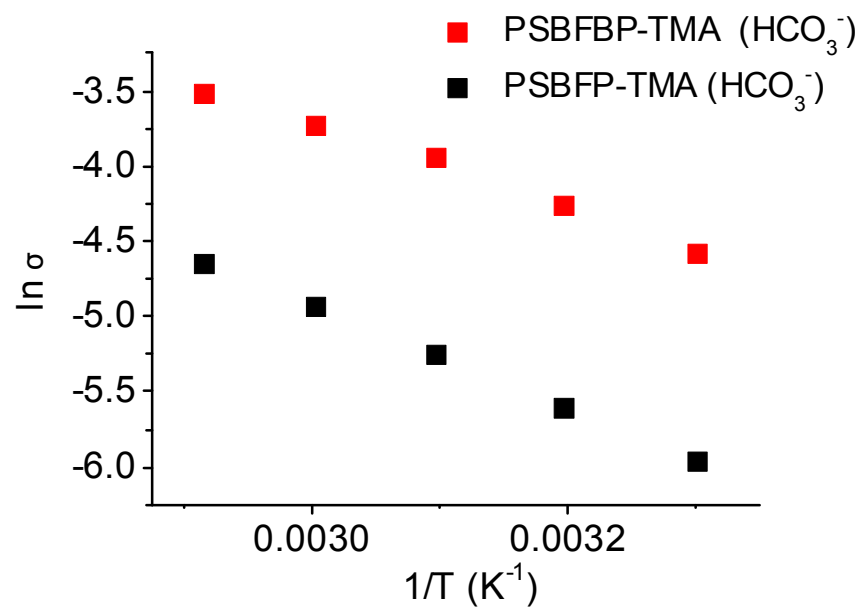
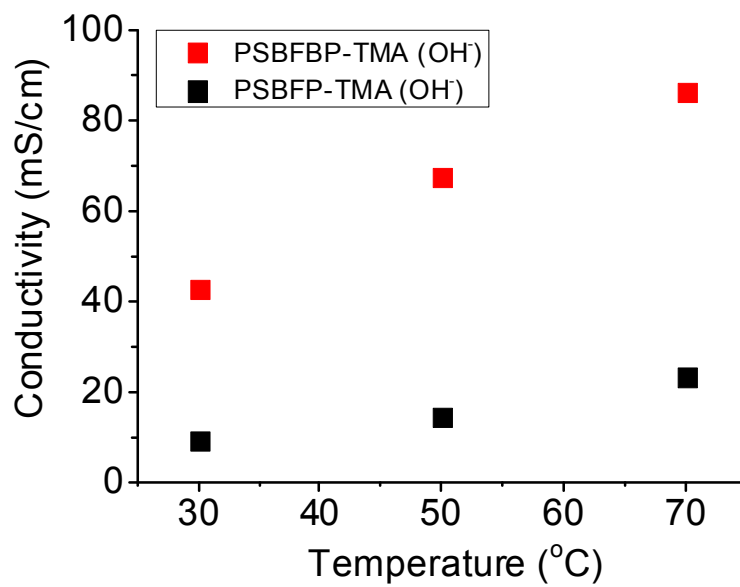


Figure S5. OH⁻ conductivity as a function of temperature for PSBFBP-TMA (OH⁻) and PSBFBP-TMA (OH⁻) in water



Reference

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