Electronic Supporting Information

High proton conducting fluorinated sulfonated poly(arylene ether sulfone)s copolymers with side chain grafting

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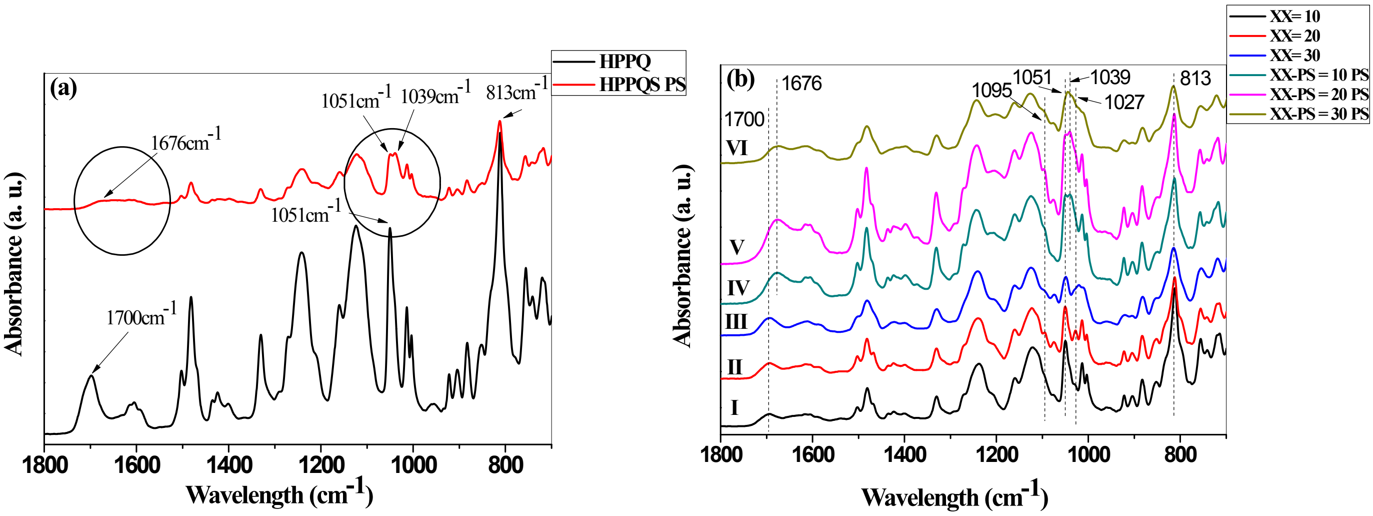
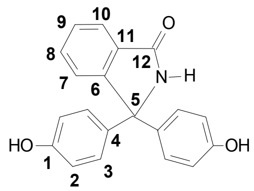


Figure S1. FT-IR spectra a) of homopolymer PTAQ and its post sulfonated form HPPQS PS, b) of HPPQS-XX and HPPQS-XX PS copolymers with different degree of sulfonation.

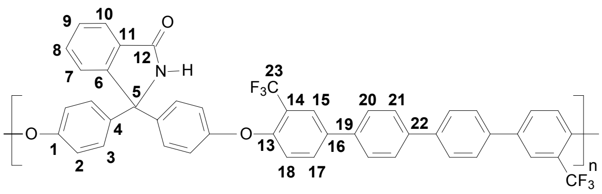
3,3'-Bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (HPP)



^{1}H NMR (DMSO-d_6, 30°C): 9.47 (s, 1H, NH), 9.42 (s, 2H, OH), 7.67 (d, 1H, 10), 7.58 (t, 1H, 8), 7.52 (d, 1H, 7), 7.47 (t, 1H, 9), 7.03 (d, 4H, 3), 6.69 ppm (d, 4H, 2).

^{13}C NMR (DMSO-d_6, 60°C): 168.28 (12), 156.62 (1), 150.97 (6), 133.80 (4), 131.80 (8), 131.11(11), 128.17 (3), 128.07 (9), 124.66 (7), 123.11 (10), 114.93 (2), 69.45 ppm (5).

HPPQ



^{1}H NMR (DMSO-d$_6$, 90°C): 9.44 (NH), 8.01 (15), 7.96 (17), 7.82 (21), 7.80 (20), 7.75 (10), 7.66 (7,8), 7.55 (9), 7.40 (3), 7.16 (18), 7.09 ppm (2).

^{13}C NMR (DMSO-d$_6$, 60°C): 168.1 (12), 155.2 (1), 153.6 (13), 149.7 (6), 138.9 (4), 138.7 (22), 137.1 (19), 135.0 (16), 132.1 (17), 132.0 (8), 131.0 (11), 128.7 (3), 128.4 (9), 127.1 (20), 127.0 (21), 124.8 (15; q, $^{3}J_{CF}$ = 4.5 Hz), 124.5 (7), 123.2 (10), 123.1 (23; q, $^{1}J_{CF}$ = 273 Hz), 120.4 (14; q, $^{2}J_{CF}$ = 31 Hz), 120.1 (18), 118.5 (2), 69.2 ppm (5).

^{19}F NMR (DMSO-d$_6$, 90°C): -60.1 ppm (23).

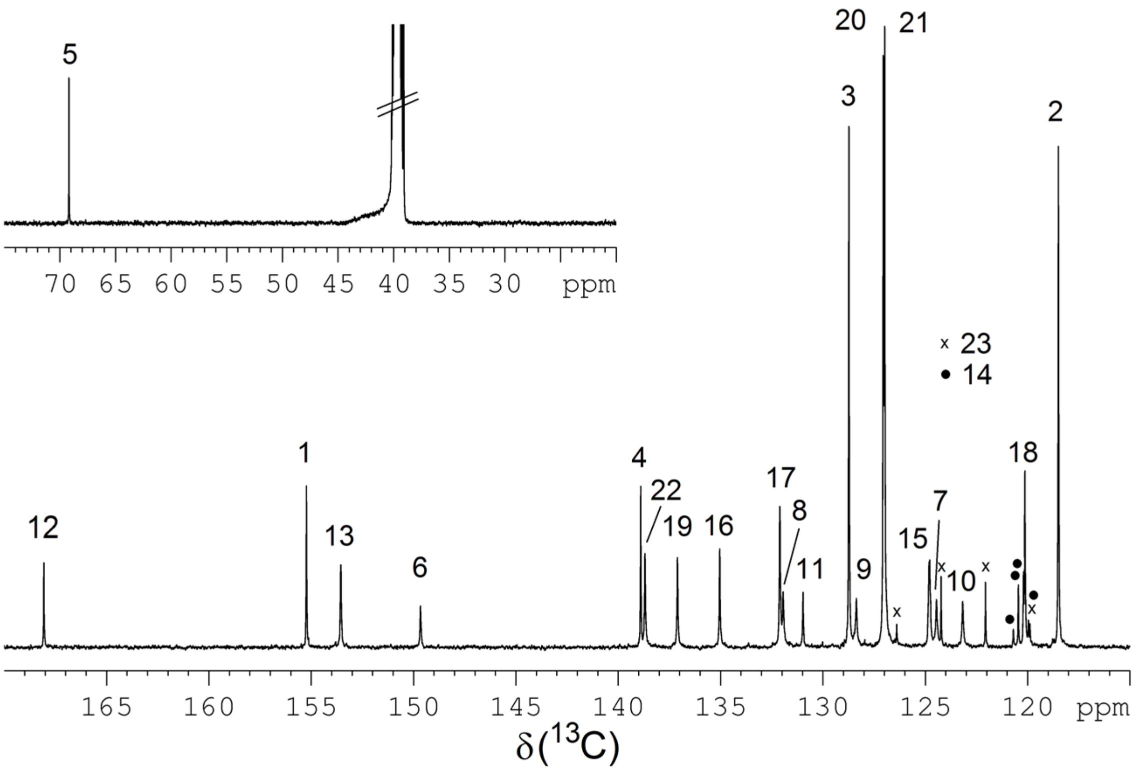
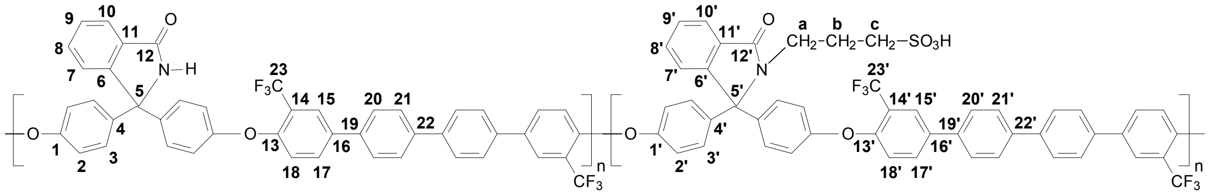


Figure S2. ^{13}C NMR spectrum of **HPPQ** (60°C, DMSO-d$_6$).

The ^{1}H NMR spectrum is depicted in the main part: Figure 1a.

HPPQSH PS (partially alkylated)



^{1}H NMR (DMSO-d_6, 90°C): 9.45 (NH), 8.02 (15), 8.00 (15’), 7.99 (17’), 7.96 (17), 7.84 (21), 7.82 (20), 7.79 (10’), 7.75 (10), 7.67 (7,8), 7.61 (8’), 7.56 (9), 7.53 (9’), 7.50 (7’), 7.40 (3), 7.31 (3’), 7.29 (18’), 7.17 (18), 7.14 (2’), 7.10 (2), 3.55 (a), 2.27 (c), 1.38 ppm (b).

^{13}C NMR (DMSO-d_6, 60°C): 168.1 (12), 166.8 (12’), 155.6 (1’), 155.3 (1), 153.8 (13’), 153.6 (13), 150.2 (6’), 149.7 (6), 138.9 (4), 138.7 (22,22’), 137.2 (19’), 137.1 (19), 136.4 (4’), 135.1 (16), 134.9 (16’), 132.5 (17’), 132.3 (8’), 132.2 (17), 132.0 (8), 131.0 (11), 130.3 (11’), 129.6 (3’), 128.8 (3), 128.4 (9,9’), 127.1 (20,20’), 127.0 (21,21’), 124.8 (15), 124.6 (7,15’), 123.6 (7’), 123.2 (10), 123.1 (23; q, $^1J_{CF}$ = 273 Hz), 122.8 (10’), 120.4 (18’), 120.2 (18), 120.0 (14,14’), 119.3 (2’), 118.5 (2), 69.2 (5), 68.9 (5’), 49.3 (c), 40.5 (a), 23.7 ppm (b).

^{19}F NMR (DMSO-d_6, 90°C): -60.1 ppm (23).

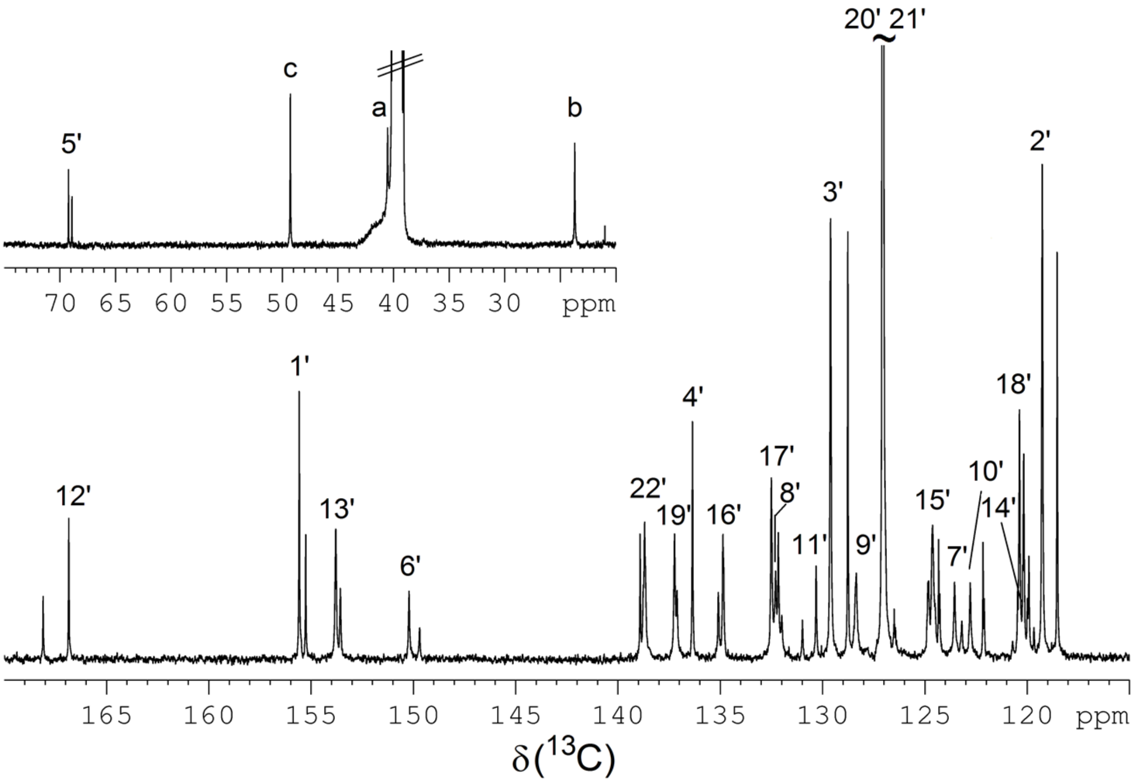
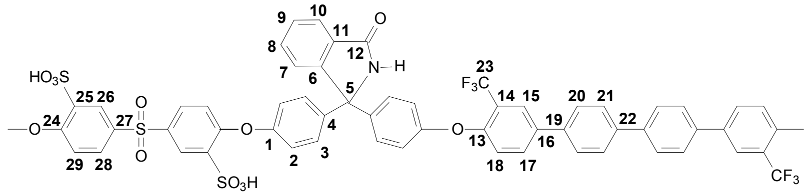


Figure S3. ^{13}C NMR spectrum of **HPPQSH PS** (60°C, DMSO-d_6). Only the new signals resulting from partial alkylation are labelled.

The ^{1}H NMR spectrum is depicted in the main part: Figure 1b.

HPPQSH-XX

The ^{1}H NMR spectra of **HPPQSH-10**, **-20**, and **-30** are given in the main part: Figures 2a-c.
The ^{13}C NMR spectrum is given in the main part: Figure 3.



The formula depicts a structural fragment with atom numbering.

The 3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (HPP) unit can be bonded to 4,4′-bis(3′-trifluoromethyl benzyl) biphenyl (QB) and to 3,3′-disodiumsulfonyl-diphenylsulfone (SDSP) units resulting in two different dyads – QB-HPP (*) and SDSP-HPP (#) – and three different HPP-centred triads: QB-HPP-QP (**I**), QP-HPP-SDSP (**II**), and SDSP-HPP-SDSP (**III**).

^{1}H NMR (DMSO-d_6, 90°C): 9.45 (NH^{I}), 9.41 (NH^{II}), 9.38 (NH^{III}), 8.34 (26), 8.02 (15), 7.97 (17), 7.85-7.78 (20,21,28), 7.75 (10), 7.66 (7,8), 7.54 (9), 7.39 (3^{*}), 7.31 ($3^{\#}$), 7.17 (18), 7.09 (2^{*}), 7.01 ($2^{\#}$), 6.94 ppm (29).

^{13}C NMR (DMSO-d_6, 60°C): 168.2 (12), 157.8 (24), 155.35 (1^{*}), 155.2 ($1^{\#}$), 153.6 (13), 149.9 (6^{III}), 149.8 (6^{II}), 149.7 (6^{I}), 139.7-139.3 (25), 139.2-138.5 (4), 138.7 (22), 137.2 (19), 135.1 (16), 134.4 (27), 132.2 (17), 132.0 (8), 131.0 (11), 129.5 (28), 128.8 (3^{*}), 128.5 ($3^{\#}$), 128.5-128.0 (9,26), 127.1 (20), 127.0 (21), 124.9 (15), 124.6 (7), 123.2 (10), 123.1 (23; q, $^{1}J_{CF}$ = 273 Hz), 120.4 (14; q, $^{2}J_{CF}$ = 31 Hz), 120.2 (18), 119.6 ($2^{\#}$), 119.5 (29), 118.6 (2^{*}), 69.3 ppm (5).

^{19}F NMR (DMSO-d_6, 90°C): -60.1 ppm (23).

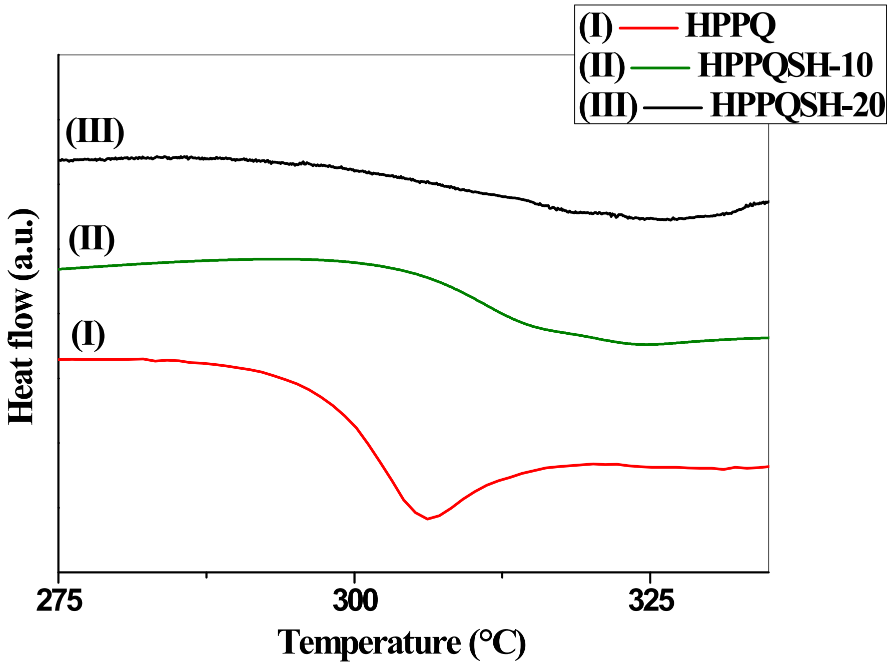


Figure S4. DSC plot of the HPPQSH-XX membranes.

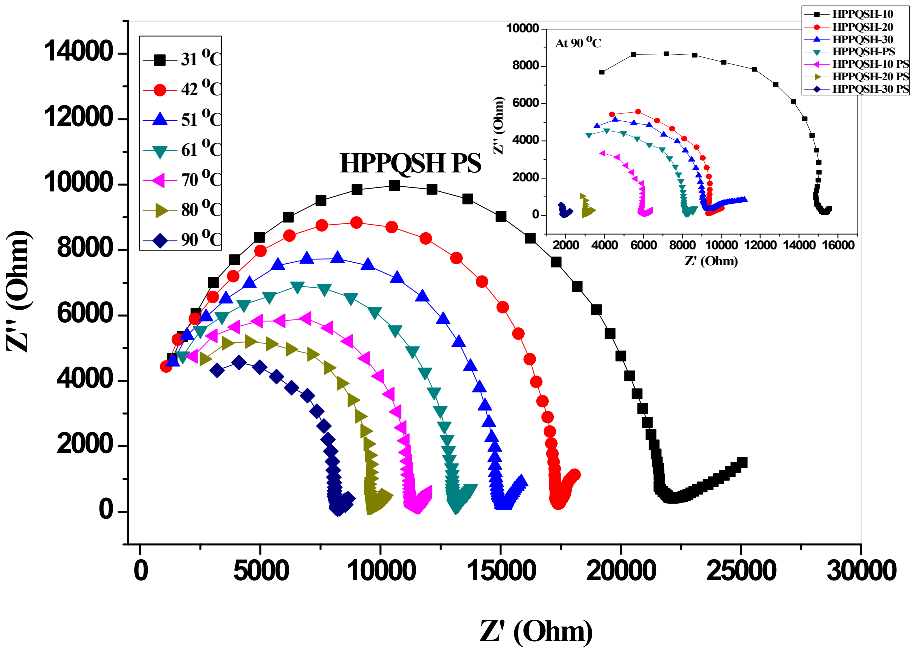


Figure S5. Complex impedance spectra of HPPQSH-PS membrane at different temperature and all copolymer membranes at fixed temperature.