Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Preparation of a new class of phosphonated hydrocarbon polymers based on polysulfone

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^{31}P NMR spectra:

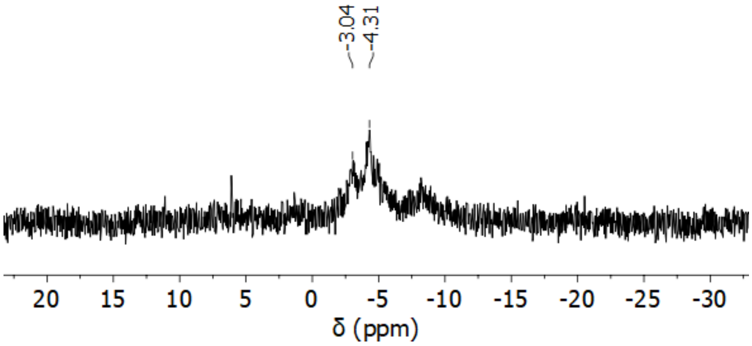

Figure S1 - ^{31}P NMR spectrum of p-PSUb, measured in DMSO-d_6 at room temperature.

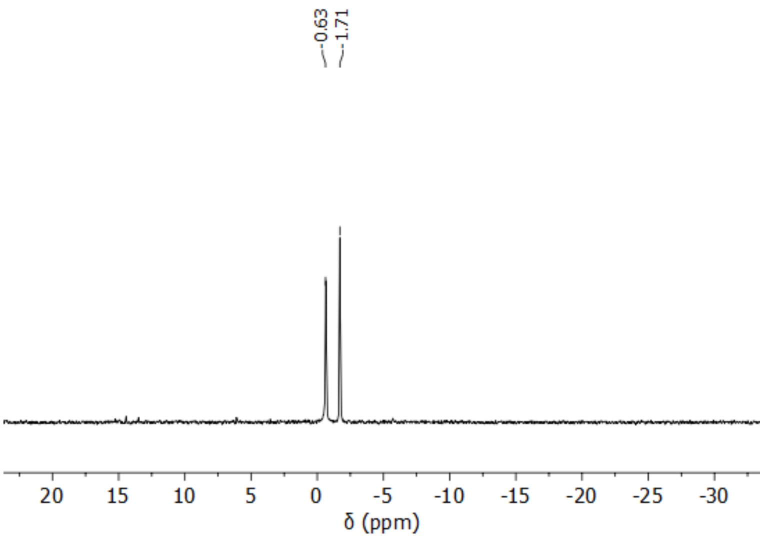

Figure S2 - ^{31}P NMR spectrum of p-PSUs, measured in DMSO-d_6 at room temperature.

IR-measurements

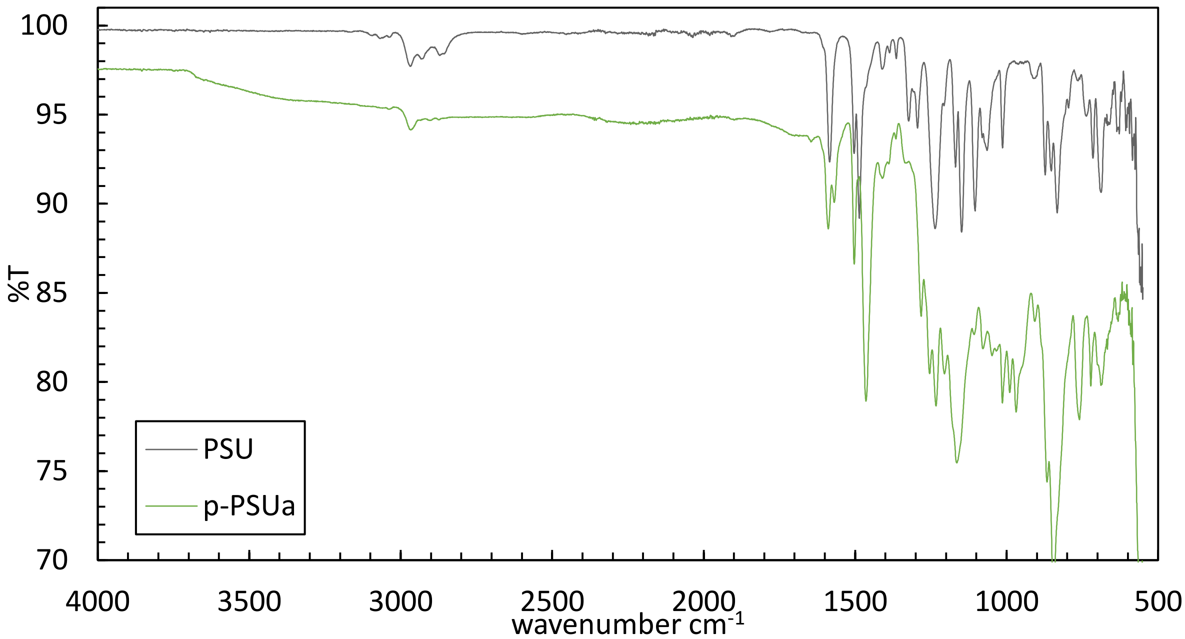

Figure S3 - FTIR-spectra of PSU and PSUa in comparison.

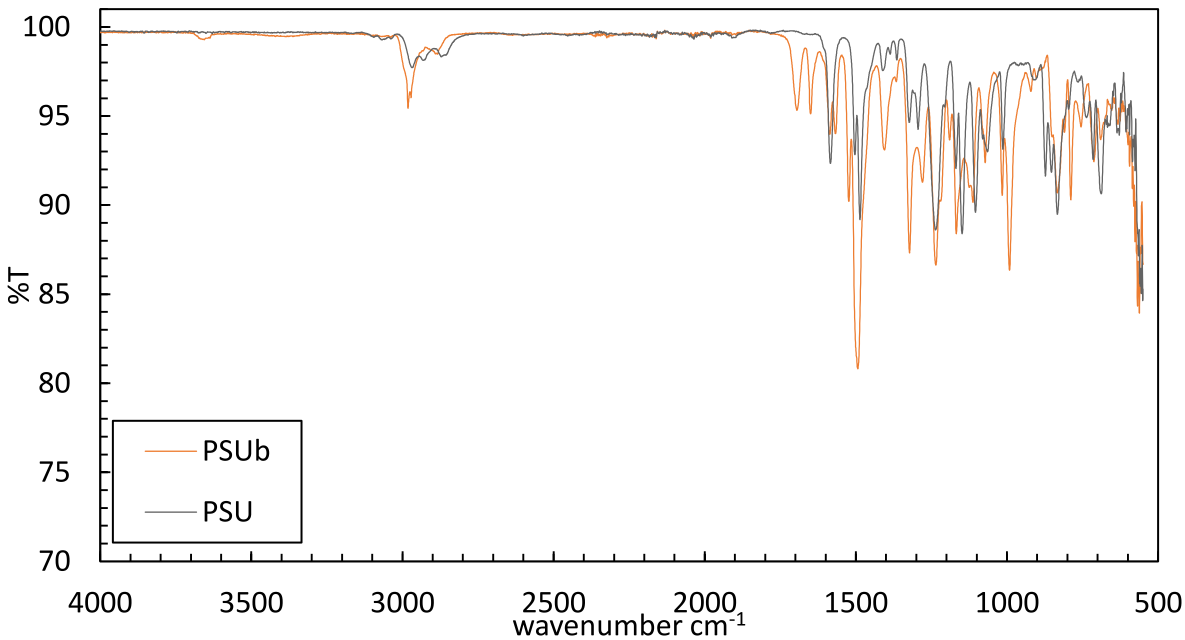

Figure S4 - FTIR-spectra of PSU and PSUb in comparison.

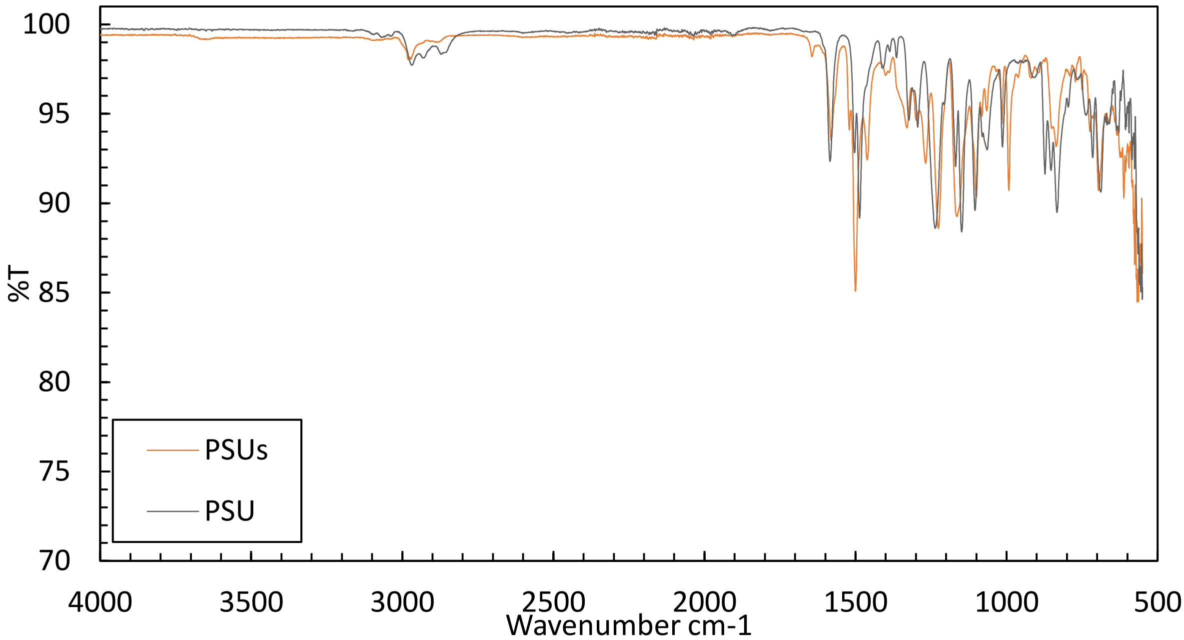

Figure S5 - FTIR-spectra of PSU and PSUs in comparison.

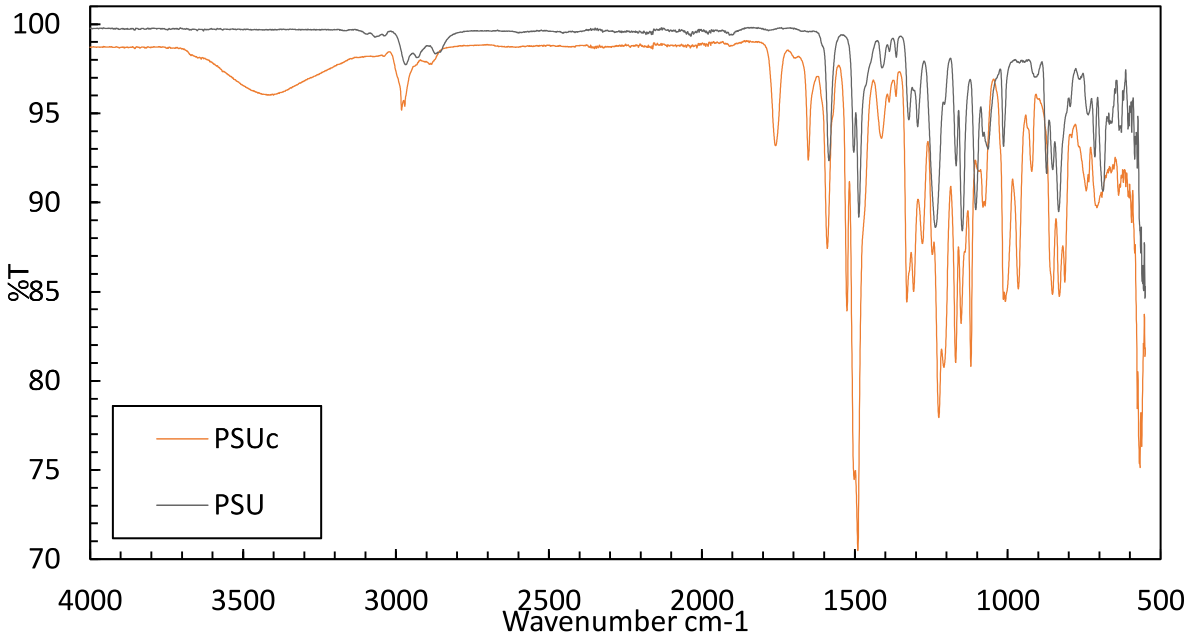

Figure S6 - FTIR-spectra of PSU and PSUc in comparison.

GPC measurements

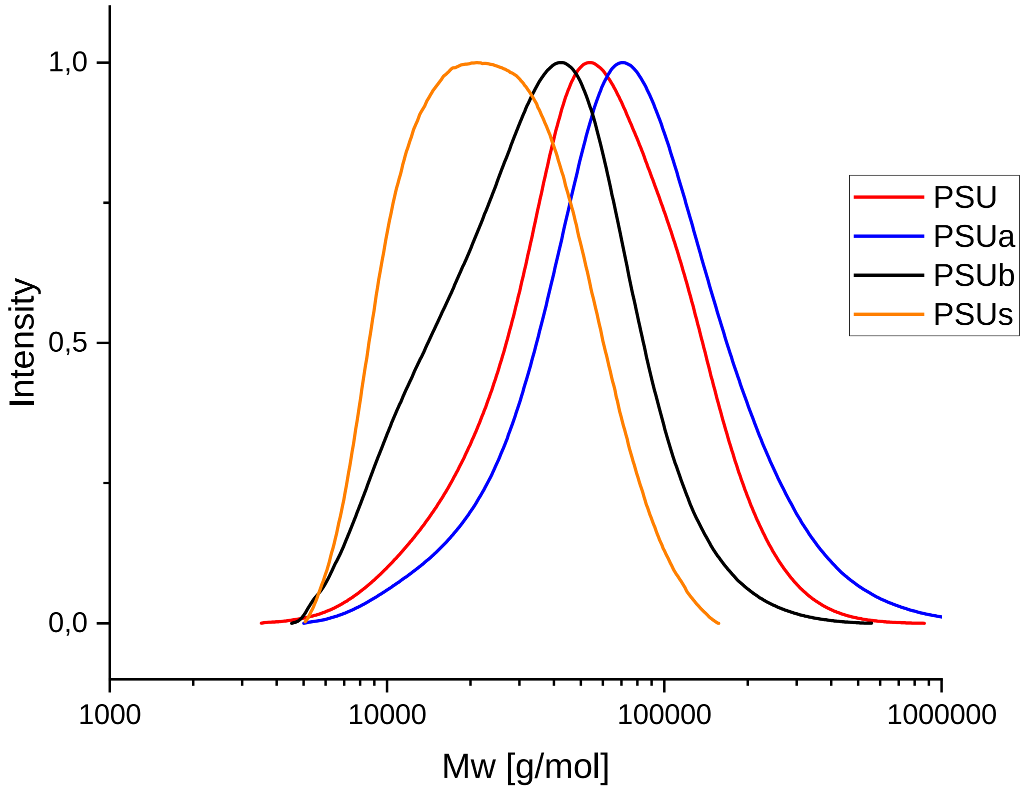

Figure S7 – GPC curves of virgin PSU and the three soluble modified PSUs (PSUa, PSUb, PSUs).

DSC measurements

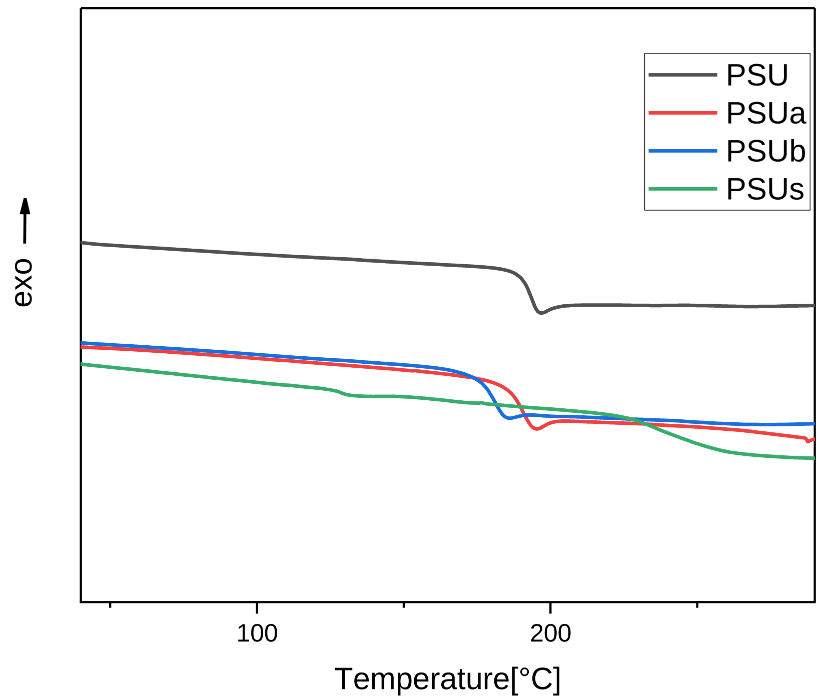

Figure S8 – DSC curves (2nd heating cycle) of PSU, PSUa, PSUb and PSUs.

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of p-PSUa/TerPhos

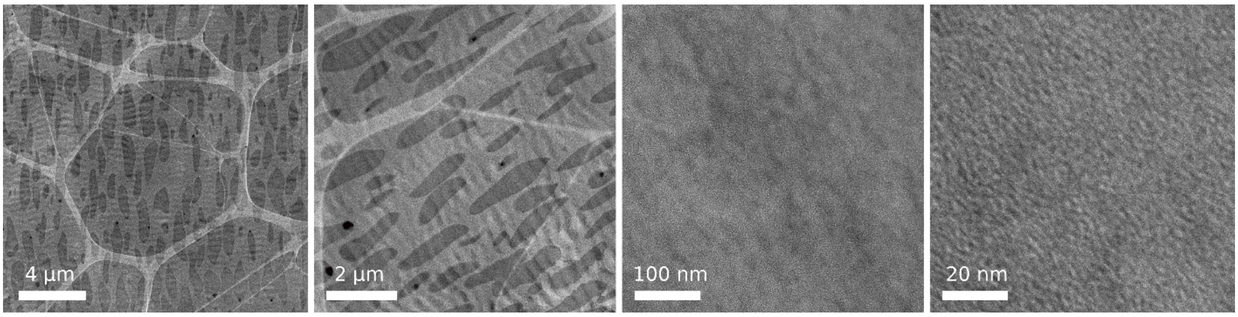

Figure S9 – Exemplary HAADF-STEM images of the Pb stained blend membrane p-PSUa/TerPhos with 2048 x 20048 pixels at different magnifications.

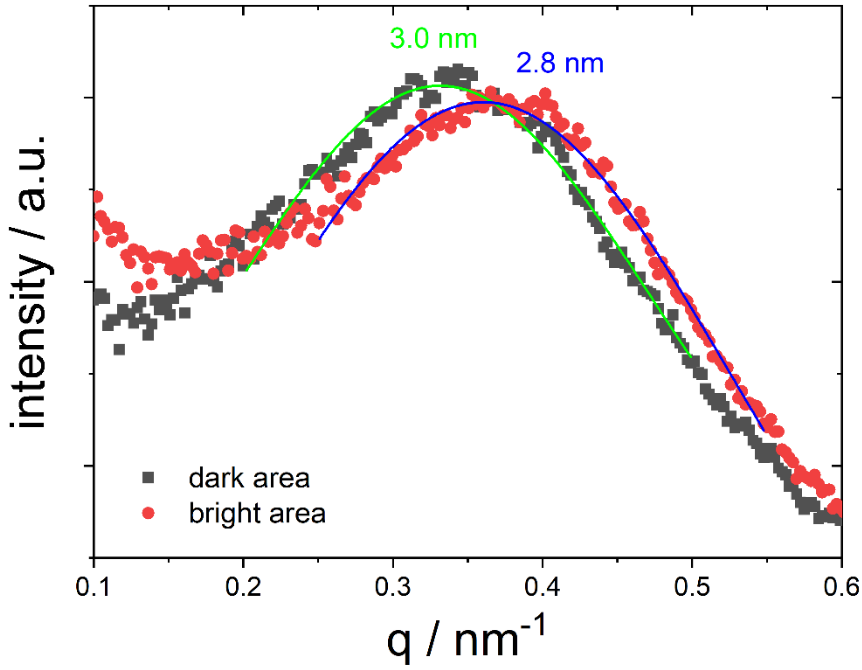

Figure S10 – Structure size distribution within the blend membrane p-PSUa/TerPhos as obtained from diffractograms of the HAADF-STEM images.

The micostructure of the blend membrane containing p-PSUa and TerPhos was investigated by STEM. In Figure S9, images of the membrane are shown in different resolutions. Furthermore, the structure size distribution was determined (Figure S10). For the dark area, a size distribution of 3.0 ± 2.3 nm and for the bright area of 2.8 ± 2.1 nm was calculated. The images and the size distribution show an amorphous homogeneous structure. Similar behavior is expected for the other blend membranes produced in this work.

Comparison of membrane conductivity to similar studies

To compare several membrane types to each other, we focused on PSU-based or similar materials. Furthermore, we limited the comparison to membranes characterized by the same measuring cell under similar conditions to show comparable values.

Table S1: Comparison of membrane conductivity to similar works.

Membrane	Polymer/membrane type	Composition	IEC in mmol g^{-1}	σ in mS cm^{-1}
1	Pentafluorophenyl side-chain modified PSU	p-PSUa/Ter-Phos(c)	3.19	76
2	Pentafluorophenyl side-chain modified PSU	p-PSUb/Ter-Phos(c)	1.98	154
3	Pentafluorophenyl side-chain modified PSU	p-PSUs/Ter-Phos(c)	1.47	46
4	Polyphenylene copolymer	Ter-Phos(a)	2.04	29
5[1]	Pentafluorophenyl side-chain modified PSU	s-PSUa(a)	1.15	100
6[1]	Pentafluorophenyl side-chain modified PSU	s-PSUs(a)	1.09	52
7[1]	Pentafluorophenyl side-chain modified PSU	s-PSUb/OPBI(b)	0.8	55
8[2]	Polypentafluorostyrene-block-copolymers	POS-b-PWN-60(a)	1.22	33
9[2]	Polypentafluorostyrene	PVDF-PWN-75(d)	1.25	21
10[2]	PFSA	N211(a)	0.91	55
11[3]	Modified Polypentafluorostyrene	PWN70-C10(a)	2.08	79
12[3]	Modified Polypentafluorostyrene	PWN70-C12(a)	3.25	74
13[3]	Modified Polypentafluorostyrene	PWN70-C14(a)	2.16	57
14[3]	Modified Polypentafluorostyrene	PWN70-C16(a)	1.50	59
15[3]	Modified Polypentafluorostyrene	PWN70-C18(a)	1.52	55
16[3]	Polypentafluorostyrene	PWN66(a)	2.24	104
17[3]	PFSA	N212(a)	0.81	47

(a)Pure membrane, (b)acid-base blend membrane, (c)acid-acid blend membrane

Lists of NMR data - chemical shifts

PSU:

^{1}H NMR (THF-d8, 500 MHz): δ 7.88-7.87 (4H), δ 7.31-7.28 (4H), δ 7.02-6.95 (8H), δ 1.68 (6H).

PSUa:

^{1}H NMR (THF-d8, 500 MHz): δ 7.46-7.44 (2H), δ 7.27-7.25 (6H), δ 6.98 (4H), δ 6.91 (2H), δ 1.72 (6H).

^{19}F NMR (THF-d8, 500 MHz): δ -73.6 (3F), δ -136.5 (2F), δ – 151.0 (1F), δ – 159.5 (2F).

PSUb:

^{1}H NMR (THF-d8, 500 MHz): δ 7.88-7.86 (2H), δ 7.35 (4H), δ 7.17 (4H), δ 7.06-7.04 (4H), 1.29 (6H).

^{19}F NMR (THF-d8, 500 MHz): δ -139.2 (2F), δ -149.7 (1F), δ -163.3 (2F).

PSUc:

^{1}H NMR (THF-d8, 500 MHz): δ 8.10-8.08 (2H), 7.23-7.21 (4H) 7.15 (4H), 6.89-6.91 (4H), 1.67 (6H).

^{19}F NMR (THF-d8, 500 MHz): δ -135.2 (1F), δ -137.4 (1F), δ -146.0 (0.5F), δ -150.4 (0.5F), -159.0 (2F).

PSUs:

^{1}H NMR (THF-d8, 500 MHz): δ 7.86-7.76 (2H), δ 7.29 (6H), δ 7.09 (6H), δ 1.61 (6H).

^{19}F NMR (THF-d8, 500 MHz): δ -137.7 (2F), δ -147.5 (1F), δ -161.8 (F).

p-PSUa:

^{1}H NMR (DMSO-d6, 500 MHz): δ 7.83 (1H), δ 7.66 (1H), δ 7.24 (4H), δ 6.97 (8H), δ 1.61 (6H).

^{19}F NMR (DMSO-d6, 500 MHz): δ -133.6 (2F), δ -136.7 (2F).

^{31}P NMR (DMSO-d6, 500 MHz): δ -2.9 (2P).

p-PSUb:

^{1}H NMR (DMSO-d6, 500 MHz): δ 7.72 (2H), δ 7.46 (2H), δ 7.18 (6H), δ 6.95 (4H), δ 1.56 (6H).

^{19}F NMR (DMSO-d6, 500 MHz): δ -133.1 (2F), δ -140.2 (2F).

^{31}P NMR (DMSO-d6, 500 MHz): δ -4.3 (2P).

p-PSUs:

^{19}F NMR (DMSO-d6, 500 MHz): δ -133.0 (2F), δ -139.5 (2F).

^{31}P NMR (DMSO-d6, 500 MHz): δ 0.6 (1P), -1.7 (1P).

Synthesis strategy for Ter-Phos

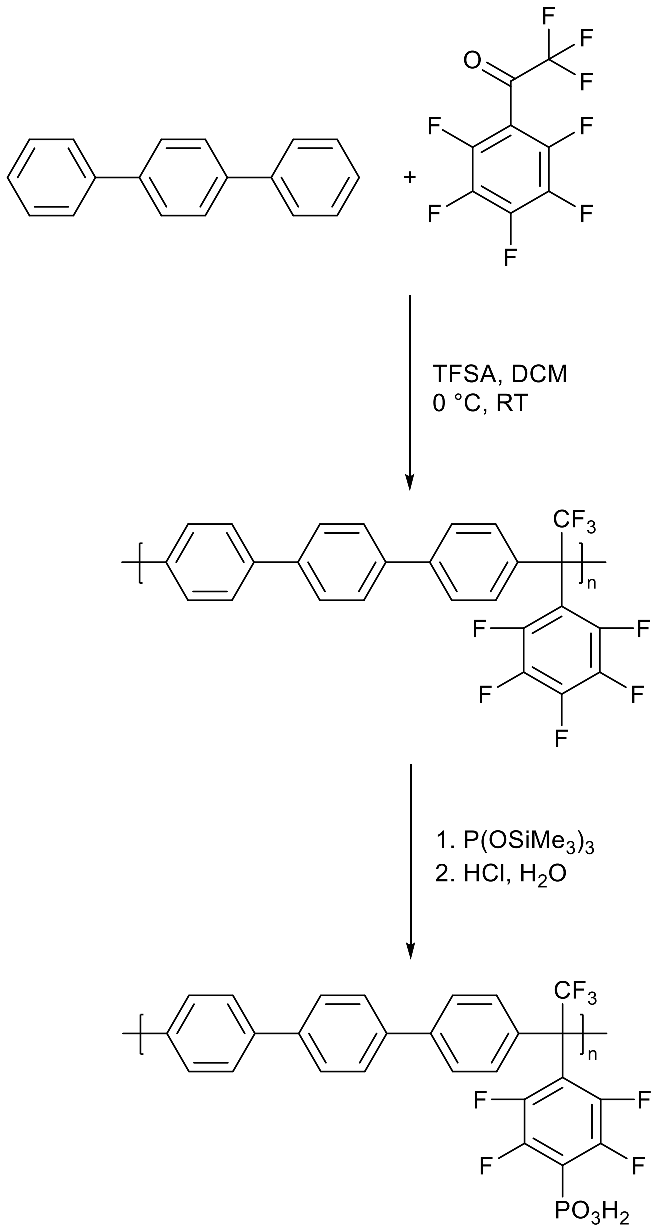

Figure S11 – Synthesis route to obtain Ter-Phos.

References

[1] P. Martschin, V. Atanasov, S. Thiele, J. Kerres, *ACS Polym. Au* **2024**.

[2] S. Auffarth, M. Wagner, A. Krieger, B. Fritsch, L. Hager, A. Hutzler, T. Böhm, S. Thiele, J. Kerres, *ACS Materials Lett.* **2023**, *5*, 2039.

[3] T. Stigler, M. Wagner, S. Thiele, J. Kerres, *Macromolecules* **2024**, *57*, 364.

[4] K. Ninomiya, N. Shida, T. Nishikawa, T. Ishihara, H. Nishiyama, I. Tomita, S. Inagi, *ACS Macro Lett.* **2020**, *9*, 284.