Electronic Supplementary Information

Spherosilicate oligomer with eight stable silanol groups as a building unit of hybrid materials

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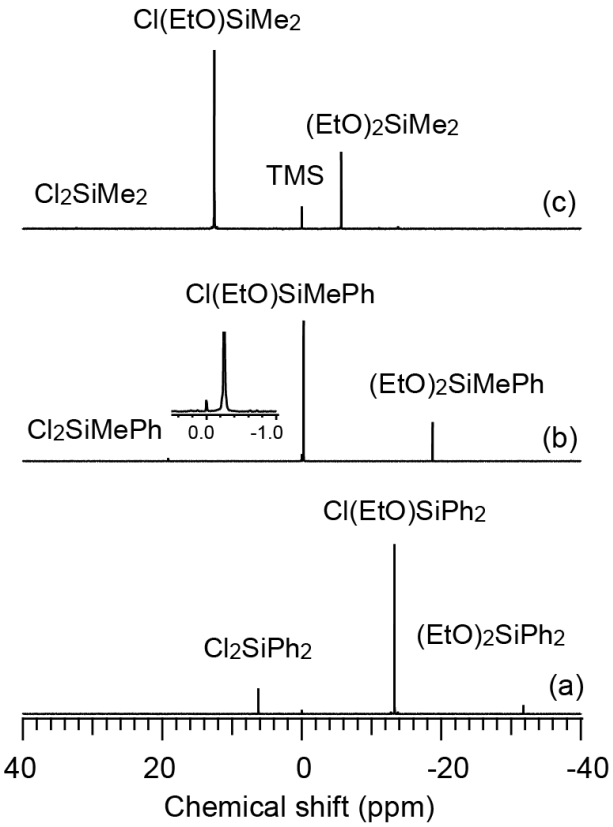

Fig. S1 ^{29}Si NMR spectra of silylation agents a) $Cl(EtO)SiPh_2$, b) Cl(EtO)SiMePh, and c) $Cl(EtO)SiMe_2$ (in $CDCl_3$).

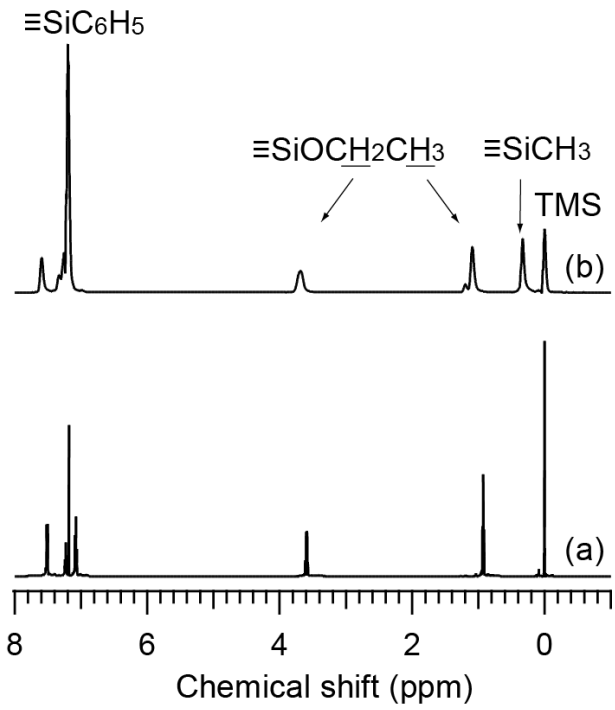

Fig. S2 ^{1}H NMR spectra of a) **PP(OEt)-D4R** and b) **MP(OEt)-D4R** (in $CDCl_3$).

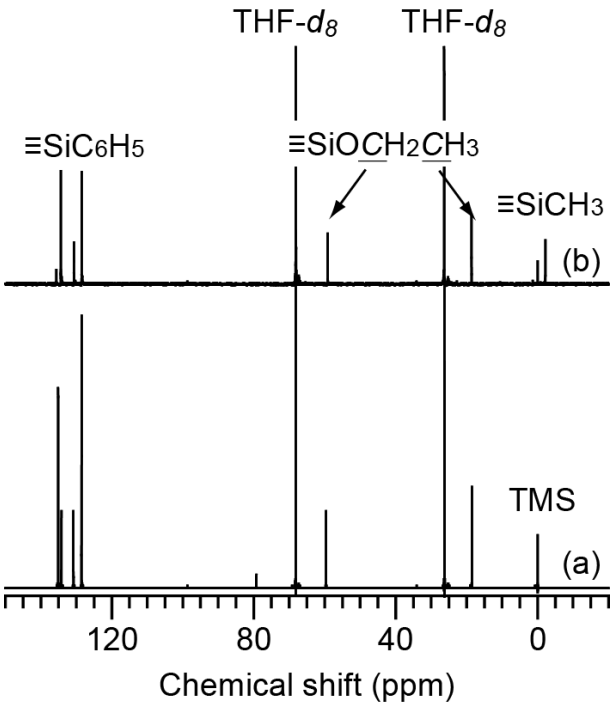

Fig. S3 ^{13}C NMR spectra of a) **PP(OEt)-D4R** and b) **MP(OEt)-D4R** (in THF-*d8*).

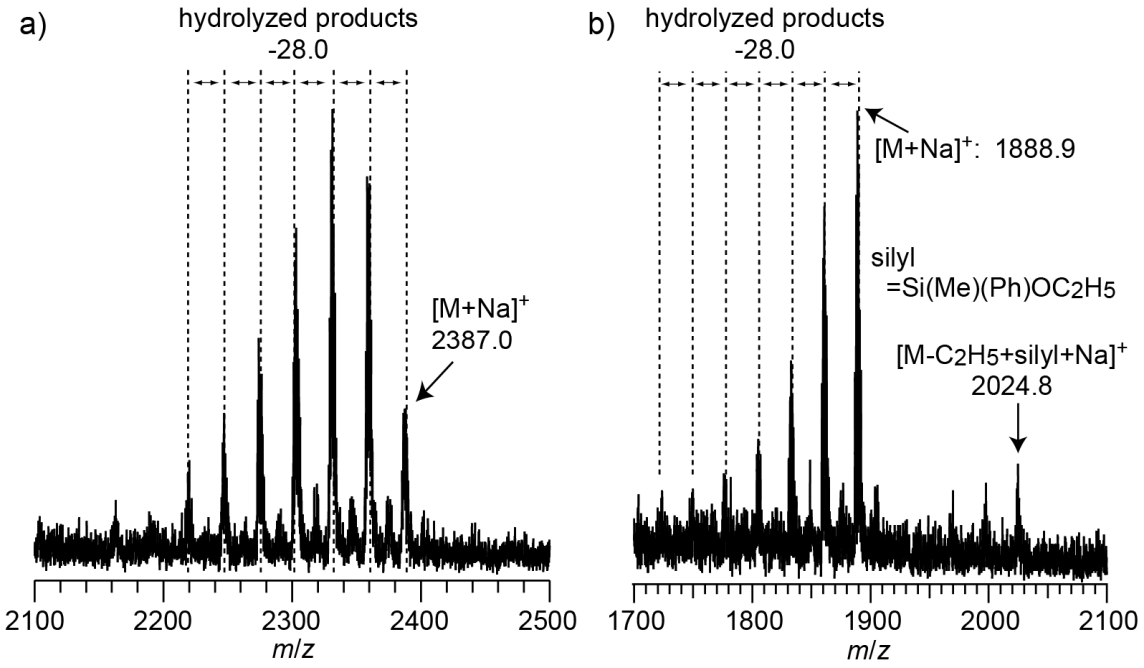

Fig. S4 MALDI-TOF mass spectra of a) **PP(OEt)-D4R** and b) **MP(OEt)-D4R**.

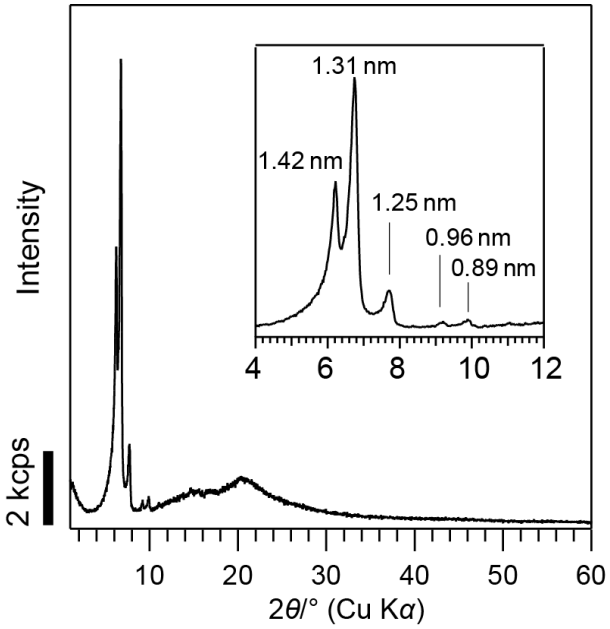

Fig. S5 XRD pattern of a cast film of **PP(OEt)-D4R** on a glass substrate.

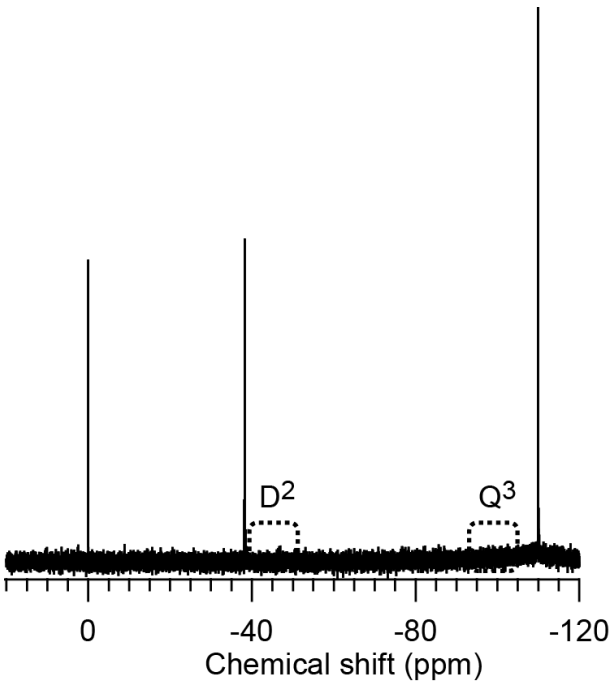

Fig. S6 ^{29}Si NMR spectrum of **PP(OH)-D4R** (in THF-*d8*) (overall view of Fig. 3).

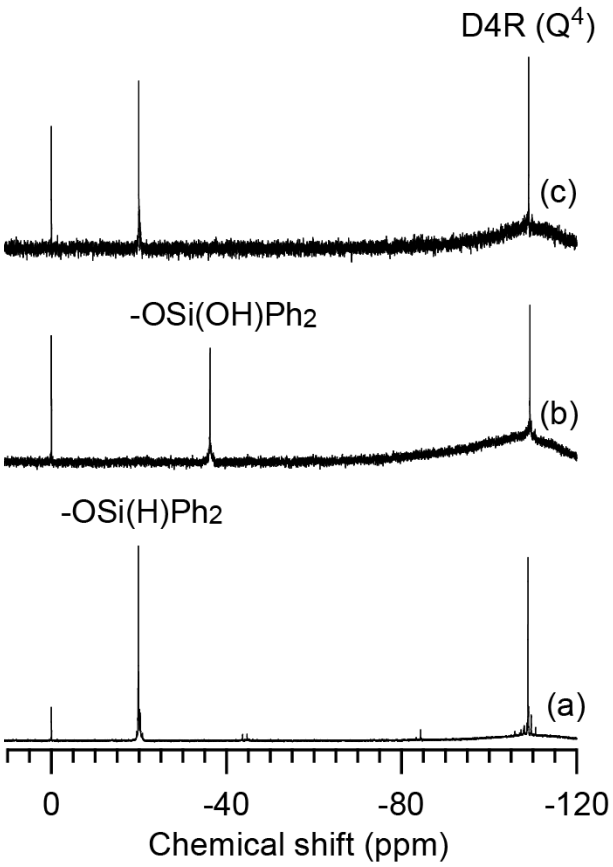

Fig. S7 ^{29}Si NMR spectra of a) **PP(H)-D4R**, b) oxidized product by $Pd(OH)_2/C$, and c) oxidized product by Pd/C (in $CDCl_3$).

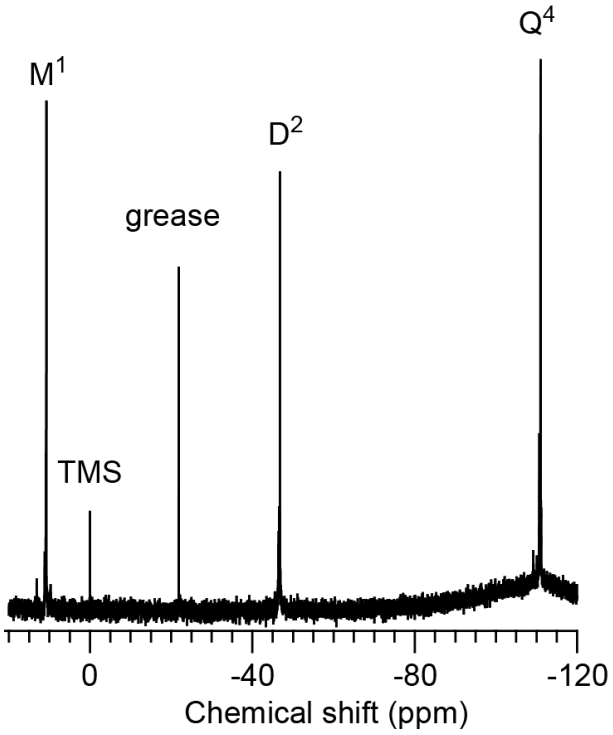

Fig. S8 ^{29}Si NMR spectrum of trimethylsilylated **PP(OH)-D4R** (in $CDCl_3$).

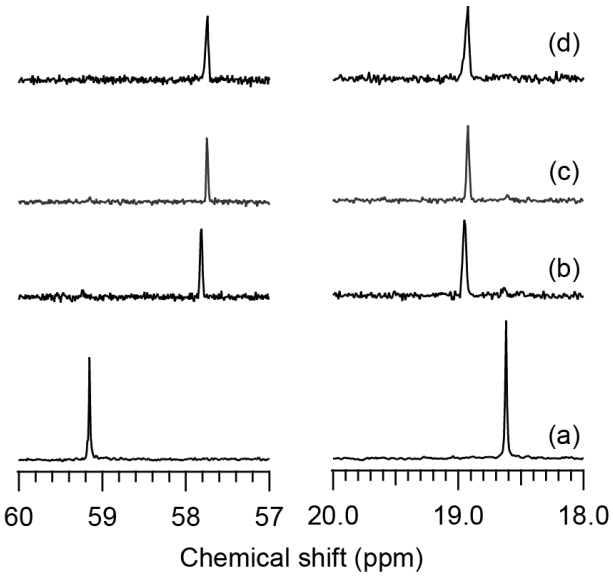

Fig. S9 ^{13}C NMR spectra of a) **MP(OEt)-D4R**, hydrolysis of **MP(OEt)-D4R** after b) 1 h, c) 3 h, and d) 1 d (in THF-*d8*).

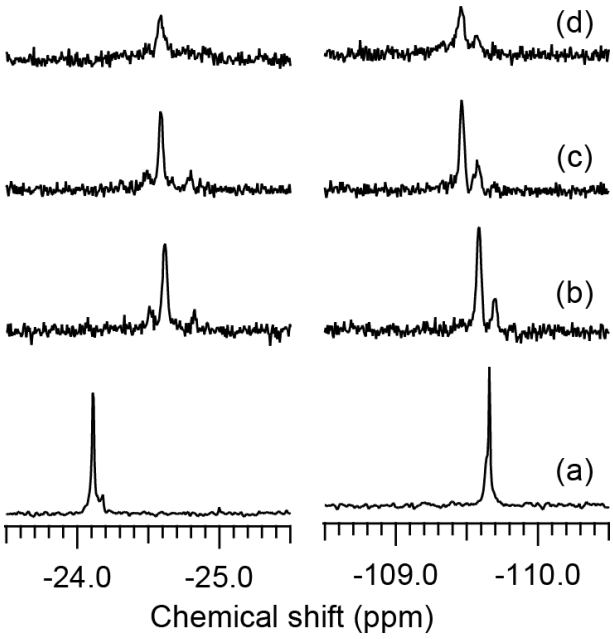

Fig. S10 ^{29}Si NMR spectra of a) **MP(OEt)-D4R**, hydrolysis of **MP(OEt)-D4R** after b) 1 h, c) 3 h, and d) 1 d (in THF-*d8*).

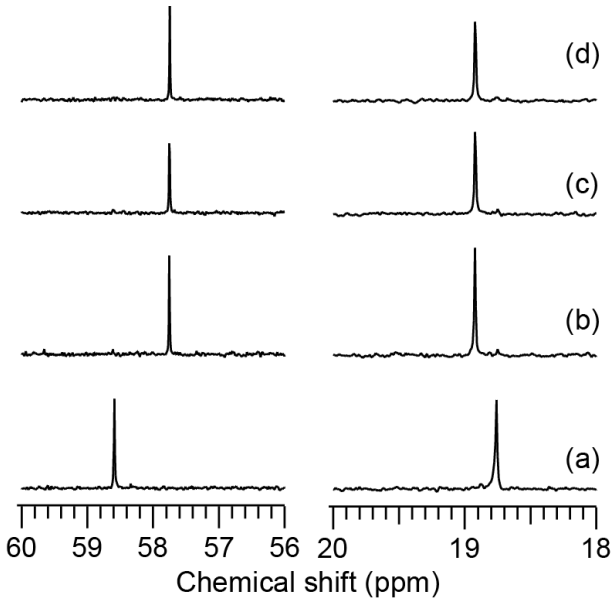

Fig. S11 ^{13}C NMR spectra of a) **MM(OEt)-D4R**, hydrolysis of **MM(OEt)-D4R** after b) 0.5 h, c) 1 h, and d) 3 h (in THF-*d8*).

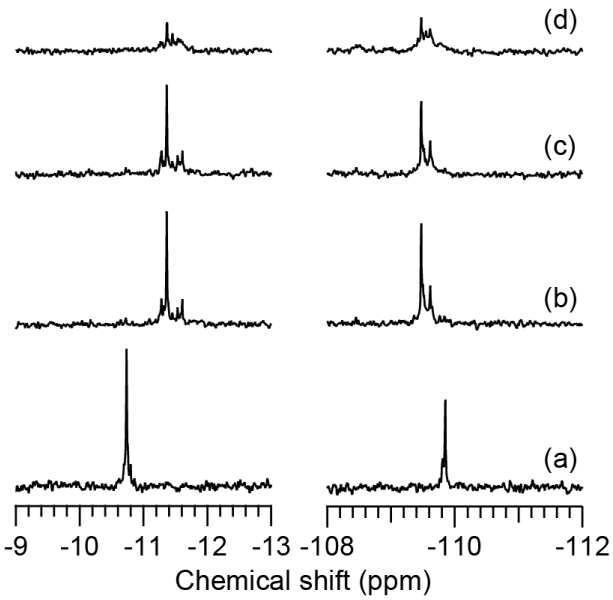

Fig. S12 ^{29}Si NMR spectra of a) **MM(OEt)-D4R**, hydrolysis of **MM(OEt)-D4R** after b)0.5 h, c)1 h, and d)3 h (in THF-*d8*).

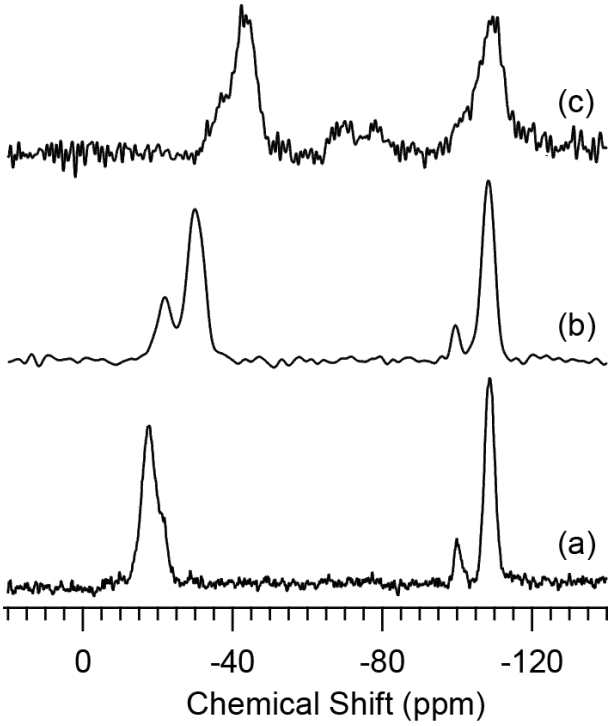

Fig. S13 ^{29}Si MAS NMR spectra of a) **MM-D4R-G**, b) **MP-D4R-G**, and c) **PP(OH)-D4R** heat-treated at 180 ºC for 8 d (reprinted from Fig. 7d).

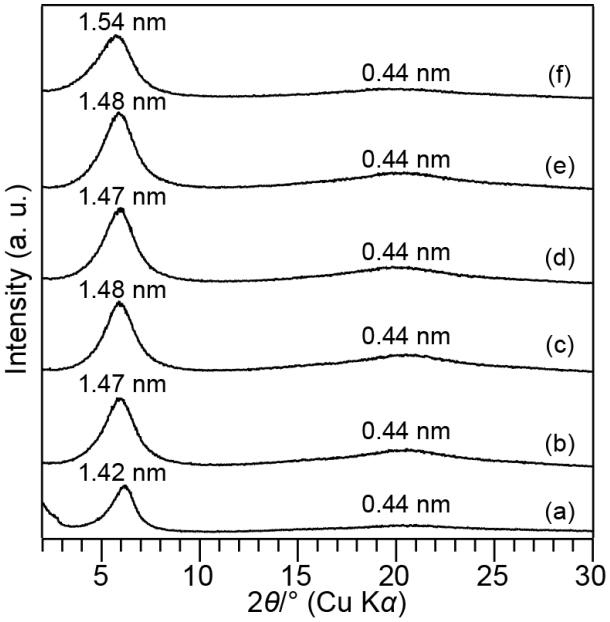

Fig. S14 XRD patterns of a) **PP(OH)-D4R** and heat-treated samples b) 120 ºC, 4 d, c) 120 ºC, 8 d, d) 180 ºC, 4 d, e) 180 ºC, 8 d, and f) 300 ºC, 2 d.

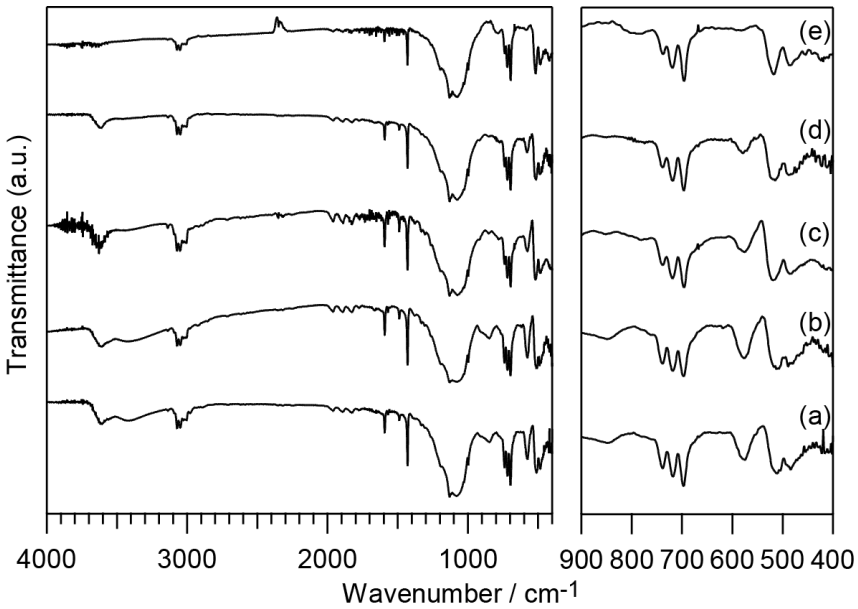

Fig. S15 IR spectra of heat-treated samples a) 120 ºC, 4 d, b) 120 ºC, 8 d, c) 180 ºC, 4 d, d) 180 ºC, 8 d, and e) 300 ºC, 2 d.

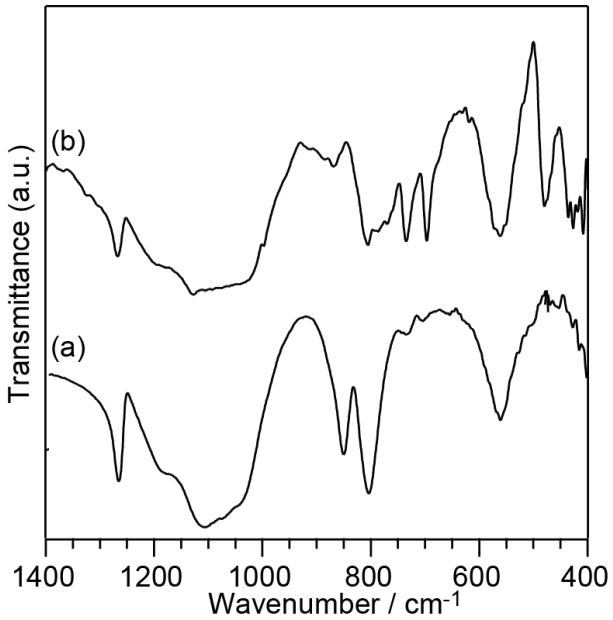

Fig. S16 IR spectra of a) **MM-D4R-G** and b) **MP-D4R-G**.

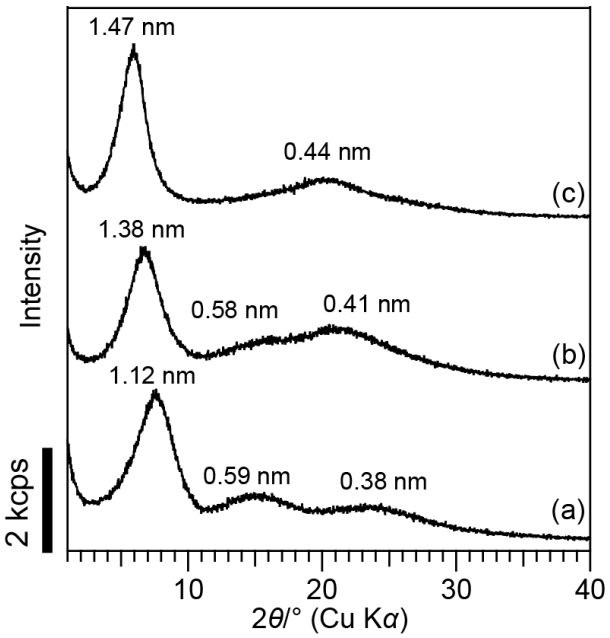

Fig. S17 XRD patterns of a) **MM-D4R-G**, b) **MP-D4R-G**, and c) heat-treated **PP(OH)-D4R** at 180 ºC for 8 d (reprinted from Fig. S14e, ESI†).

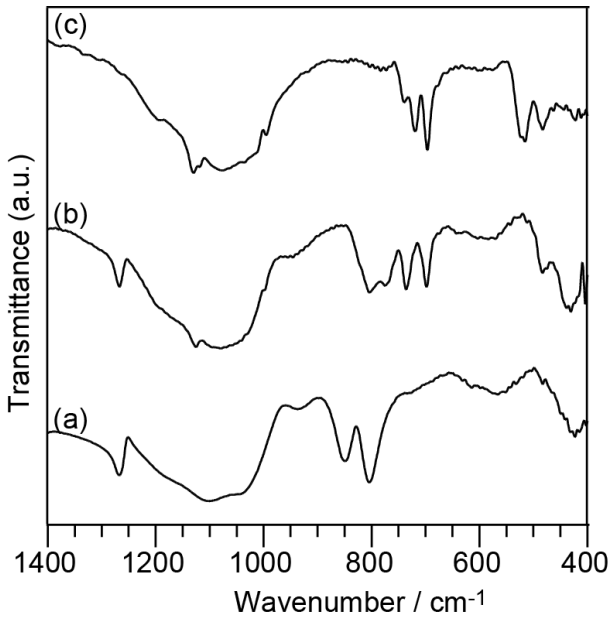

Fig. S18 FT-IR spectra of a) **MM-G**, b) **MP-G**, and c) **PP-G-heat**.

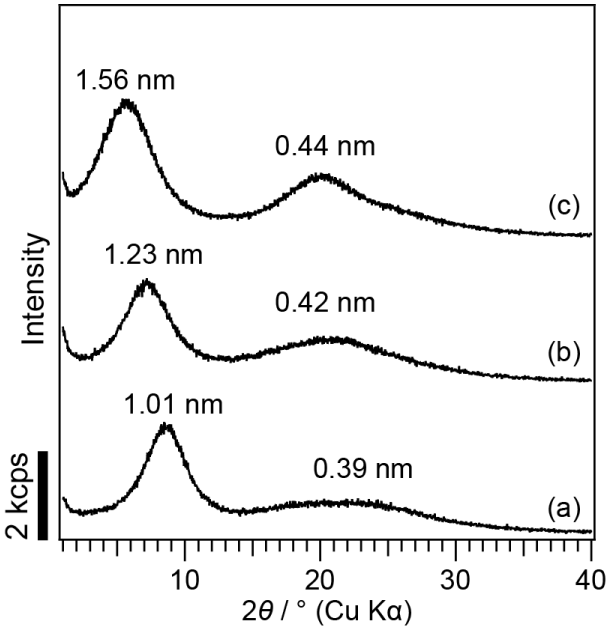

Fig. S19 XRD patterns of a) **MM-G**, b) **MP-G**, and c) **PP-G-heat**.

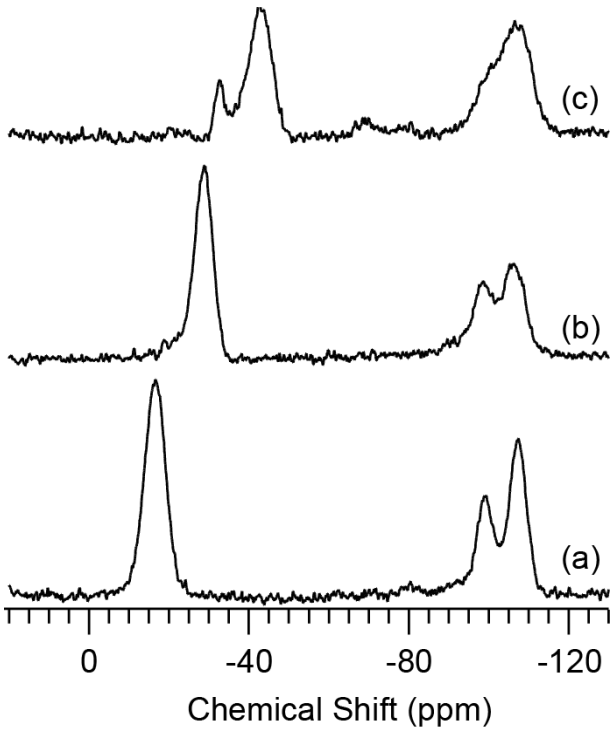

Fig. S20 Solid-state ^{29}Si NMR spectra of a) **MM-G**, b) **MP-G**, and c) **PP-G-heat**.