Supplementary Information

Influence of Functional Groups on Ethylene Polymerization Performance of Silsesquioxane-Supported Phillips-Type Catalyst

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A. NMR spectra of modified POSS (1a-1d)

\[(\text{tBu})_7\text{Si}_7\text{O}_{9}(\text{OH})_2(\text{OSiMe}_3)\] (1a)

**Figure S1.1.** $^1$H NMR spectrum of 1a in benzene-$d_6$ at r.t. (400 MHz).

**Figure S1.2.** $^{13}$C{$^1$H} NMR spectrum of 1a in benzene-$d_6$ at r.t. (100 MHz).
Figure S1.3. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of 1a in benzene-$d_6$ at r.t. (79 MHz).

$^{1}\text{H}$ NMR spectrum of 1b in benzene-$d_6$ at r.t. (400 MHz).
Figure S2.2. $^{13}$C{$^1$H} NMR spectrum of 1b in benzene-$d_6$ at r.t. (100 MHz).

Figure S2.3. $^{29}$Si{$^1$H} NMR spectrum of 1b in benzene-$d_6$ at r.t. (79 MHz).
Figure S3.1. $^1$H NMR spectrum of 1c in benzene-$d_6$ at r.t. (400 MHz).
Figure S3.2. $^{13}$C{\textsuperscript{1}H} NMR spectrum of 1c in benzene-$d_6$ at r.t. (100 MHz).

Figure S3.3. $^{29}$Si{\textsuperscript{1}H} NMR spectrum of 1c in benzene-$d_6$ at r.t. (79 MHz).

$^{1\text{Bu}}$Si$_3$O$_3$(OH)$_2$[OSiMe$_2$C$_6$H$_4$(PPh$_2$)$_2$] (1d)
**Figure S4.1.** $^1$H NMR spectrum of 1d in benzene-$d_6$ at r.t. (400 MHz).

**Figure S4.2.** $^{13}$C($^1$H) NMR spectrum of 1d in benzene-$d_6$ at r.t. (100 MHz).

**Figure S4.3.** $^{29}$Si($^1$H) NMR spectrum of 1d in benzene-$d_6$ at r.t. (79 MHz).
Figure S4.4. $^{31}$P-$^1$H NMR spectrum of 1d in benzene-$d_6$ at r.t. (162 MHz).
B. NMR spectra of POSS supported chromium catalysts (2a-2d)

\[ \text{[(i}{^\text{Bu}}\text{)}_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{]}\text{CrCH(SiMe}_3\text{)}_2 \] (2a)

Figure S5.1. $^{29}\text{Si}$\{\text{H}\} NMR spectrum of 2a in benzene-$d_6$ at r.t. (79 MHz).

\[ \text{[(i}{^\text{Bu}}\text{)}_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_2\text{Ph})\text{]}\text{CrCH(SiMe}_3\text{)}_2 \] (2b)

Figure S6. $^{29}\text{Si}$\{\text{H}\} NMR spectrum of 2b in benzene-$d_6$ at r.t. (79 MHz).
Figure S7. $^{29}$Si{$^1$H} NMR spectrum of 2c in benzene-$d_6$ at r.t. (79 MHz).

Figure S8.1. $^{29}$Si{$^1$H} NMR spectrum of 2d in benzene-$d_6$ at r.t. (79 MHz).
Figure S8.2. $^{31}$P NMR spectrum of 2d in benzene-$d_6$ at r.t. (162 MHz).
C. UV/vis spectra measurement

**Figure S9.** UV/vis (DRS) spectra of a) POSS-supported catalysts (2a-2d) and b) SiO$_2$-supported catalysts (SiO$_2$-b-d).
D. Assignment and analytical method in NMR for polyethylene

Figure S10 reports typical $^{13}$C–$^1$H and $^1$H NMR spectra of the obtained PE (entries 3 and 5 in Table 1). The chemical shift was referenced to methyl carbon (1.98 ppm) and methyl proton (0.09 ppm) of hexamethyldisiloxane (HMDS) in $^{13}$C–$^1$H and $^1$H NMR, respectively. The peak assignments have been done based on Refs. [1] and [2]. The fractions of methyl branches and the saturated ends were determined from $^{13}$C–$^1$H NMR based on the following equations.

Eq. (1) \[
\text{Fraction of methyl branch (/1000C)} = \frac{I_{B1}}{I_{totalC}} \times 1000
\]

Eq. (2) \[
\text{Fraction of saturated end (/1000C)} = \frac{I_{S}}{I_{totalC}} \times 1000
\]

Eq. (3) \[
I_{B1} = (I_{1B1} + I_{brB1} + I_{aB1})/4
\]

Eq. (4) \[
I_{S} = (I_{1S} + I_{2S} + I_{3S})/3
\]

Eq. (5) \[
I_{totalC} = I_{Main~chain}
\]
The fraction of the vinyl ends were determined from $^1$H NMR based on the following equations.

Eq. (6) \[ \text{Fraction of vinyl end (1000C)} = \frac{I_{Vi}}{I_{total}} \times 1000 \]

Eq. (7) \[ I_{Vi} = \frac{(I_{1V} + I_{2V})}{3} \]

Eq. (8) \[ I_{total} = \frac{I_{Main chain}}{2} \]

Figure S10.2. $^1$H NMR spectra of typical PE (400 MHz).
References
