Electronic Supplementary Information (ESI)

Super long-term highly active and selective hydroformylation in a room temperature-solidifiable guanidinium salt with a polyether tag

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General experimental details and materials

All reagents were obtained commercially and were used as received, except as noted. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents and reagents used were rigorously deoxygenated prior to use. The hydroformylation reactions were performed in a home-made 60 ml stainless steel autoclave. The conversions and selectivity were determined by GC using an OV-101 capillary column. GC/MS data were recorded on a HP5890-HP5989A apparatus with a DB-5 capillary column. NMR spectra were recorded on Bruker 500MB instrument. Mass spectra (MS) were obtained by electrospray technique using a Q-Tof Ultima Global mass spectrometry. ICP-AES data were measured on an IRIS Istrepid II XSP apparatus. Differential scanning calorimetry (DSC) measurements of the ionic liquids were performed on a Mettler Toledo DSC1 instrument. The decomposition temperatures of the ionic liquids were measured with a Mettler Toledo TGA/DSC1 instrument.

General procedure for Rh-catalyzed biphasic hydroformylation of C_8~C_{14} alkenes in [Me(EO)$_{16}$TMG]OMs and for catalyst recycling

A 60-mL autoclave was charged with $RhCl_3 \cdot 3H_2O$ (1.0 mg, 3.88×10^{-3} mmol), 10 equivalents of TPPTS (3.88×10^{-2} mmol) and 1.0 g [Me(EO)$_{16}$TMG]OMs under an argon atmosphere. The catalyst precursor solution was stirred at 85°C for 24h under 5.0 MPa of syngas (CO/H_2=1:1). Subsequently, C_8~C_{14} alkenes (3.88 mmol) were added via a syringe. The reactor was pressurized with syngas to 5.0 MPa, followed by heating the reaction system to 85°C while stirring. After 5 h, the stirring was stopped and the autoclave was rapidly cooled on ice. Upon releasing the gases, the upper phase was removed by extraction with 3mL of *n*-heptane under atmospheric conditions for GC analysis and the new substrate was added to the IL for next catalyst recycling.

Synthesis and characterization of $Me(OCH_2CH_2)_{16}OMs$

The $Me(OCH_2CH_2)_{16}OMs$ was prepared following the reported procedure.[1, 2] **^{1}H NMR** (500.0 MHz, D_2O): δ=3.71 (m, 62H, $(OCH_2CH_2)_n$), 3.38 (s, 3H, OCH_3), 3.24 (s, 3H,-SO_3CH_3); **^{13}C NMR** (125.7MHz, $CDCl_3$): δ=71.86, 70.49, 69.25, 68.95, 58.96, 37.66.

Synthesis and characterization of $Me(OCH_2CH_2)_{22}OMs$

The $Me(OCH_2CH_2)_{22}OMs$ was prepared following the reported procedure.[1, 2] **^{1}H NMR** (500.0 MHz, D_2O): δ=3.69 (m, 86H, $(OCH_2CH_2)_n$), 3.37 (s, 3H, OCH_3), 3.20 (s, 3H,-SO_3CH_3); **^{13}C NMR** (125.7MHz, $CDCl_3$): δ=71.92, 70.56, 69.21, 68.99, 58.96, 37.71.

Synthesis and characterization of $Me(OCH_2CH_2)_{42}OMs$

The $Me(OCH_2CH_2)_{42}OMs$ was prepared following the reported procedure.[1, 2] **^{1}H NMR** (500.0 MHz, D_2O): δ=3.68 (m, 172H, $(O\mathit{CH_2CH_2})_n$), 3.36 (s, 3H, $O\mathit{CH_3}$), 3.22 (s, 3H,-$SO_3\mathit{CH_3}$); **^{13}C NMR** (125.7MHz, $CDCl_3$): δ=71.78, 70.42, 69.17, 68.87, 58.89, 37.58.

Synthesis and characterization of $[Me(EO)_{16}TMG]OMs$

The $Me(OCH_2CH_2)_{16}OMs$ reacted with 5 equivalents of N, N, N', N'-tetramethylguanidine (TMG) in THF (tetrahydrofuran) for 24h at reflux temperature under a nitrogen atmosphere. Then, THF and the excess of TMG were evaporated under reduced pressure, followed by extracting residual TMG with *n*-heptane to give an orange viscous liquid in quantitative yield. The orange viscous liquid slowly solidified at 20°C. **^{1}H NMR** (500.0 MHz, D_2O): δ=3.71 (m, 66H, $(O\mathit{CH_2CH_2})_n$), 3.39 (s, 3H, $O\mathit{CH_3}$), 2.97 (s, 12H, 4×$\mathit{CH_3}$), 2.80 (s, 3H, $\mathit{CH_3}SO_3^-$); **^{13}C NMR** (125.7MHz, $CDCl_3$): δ=162.90, 71.84, 70.47, 69.68, 58.95, 44.80, 39.86, 39.40; **MS** (Q-Tof MS, ES+): m/z=526.5 ($[Me(EO)_9TMG]^+$), 570.5 ($[Me(EO)_{10}TMG]^+$), 614.5 ($[Me(EO)_{11}TMG]^+$), 658.6 ($[Me(EO)_{12}TMG]^+$), 702.6 ($[Me(EO)_{13}TMG]^+$), 746.6 ($[Me(EO)_{14}TMG]^+$), 790.7 ($[Me(EO)_{15}TMG]^+$), 834.7 ($[Me(EO)_{16}TMG]^+$), 878.8 ($[Me(EO)_{17}TMG]^+$), 922.8 ($[Me(EO)_{18}TMG]^+$), 966.9 ($[Me(EO)_{19}TMG]^+$), 1010.9 ($[Me(EO)_{20}TMG]^+$), 1054.9 ($[Me(EO)_{21}TMG]^+$); The glass-transition temperature (T_g) and the thermal decomposition temperature (T_d) are 23.8°C and 341.8°C, respectively.

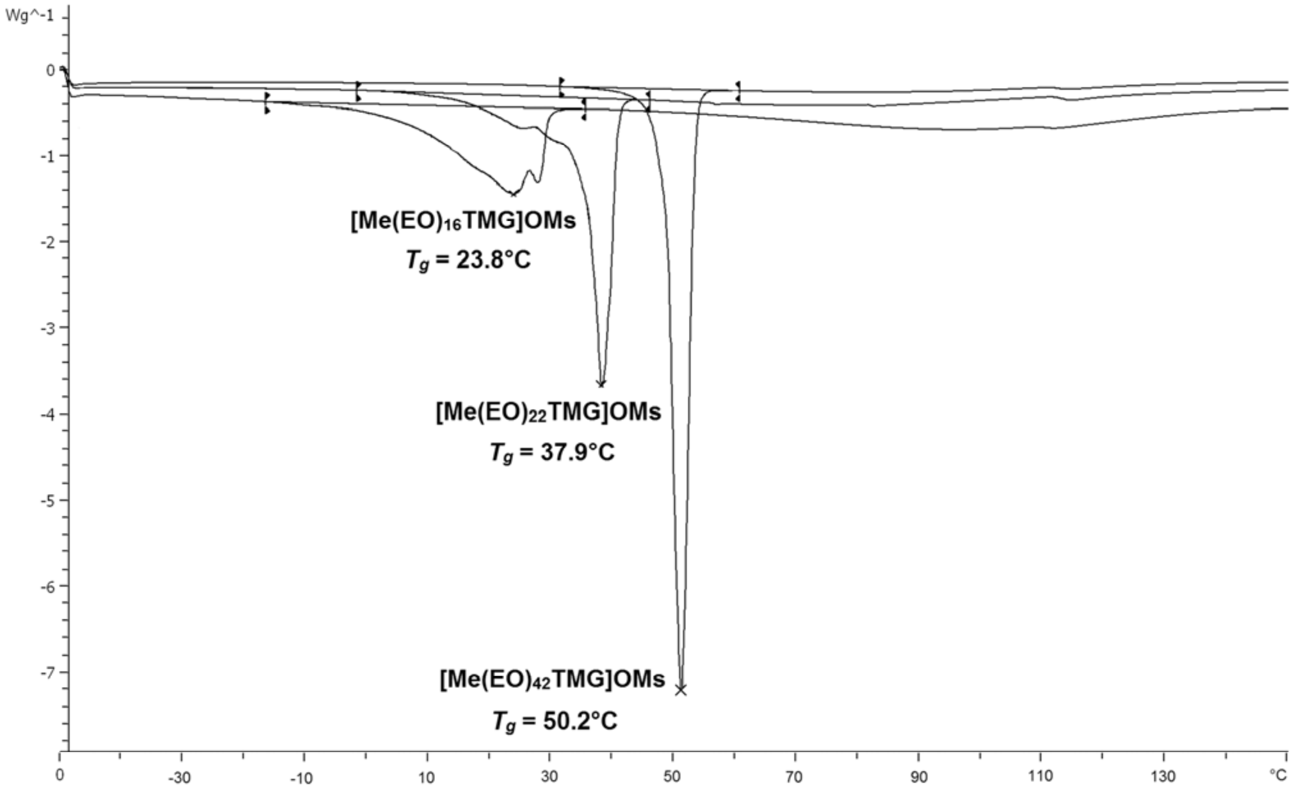
Synthesis and characterization of $[Me(EO)_{22}TMG]OMs$

The synthesis was performed as described for $[Me(EO)_{16}TMG]OMs$. **^{1}H NMR** (500.0 MHz, D_2O): δ=3.68 (m, 86H, $(O\mathit{CH_2CH_2})_n$), 3.37 (s, 3H, $O\mathit{CH_3}$), 2.96 (s, 12H, 4×$\mathit{CH_3}$), 2.79 (s, 3H, $\mathit{CH_3}SO_3^-$); **^{13}C NMR** (125.7MHz, $CDCl_3$): δ= 162.96, 71.85, 70.48, 69.71, 58.88, 44.77, 39.89, 39.38; **MS** (Q-Tof MS, ES+): m/z=702.3 ($[Me(EO)_{13}TMG]^+$), 746.3 ($[Me(EO)_{14}TMG]^+$), 790.4 ($[Me(EO)_{15}TMG]^+$), 834.4 ($[Me(EO)_{16}TMG]^+$), 878.4 ($[Me(EO)_{17}TMG]^+$), 922.4 ($[Me(EO)_{18}TMG]^+$), 966.4 ($[Me(EO)_{19}TMG]^+$), 1010.5 ($[Me(EO)_{20}TMG]^+$), 1054.6 ($[Me(EO)_{21}TMG]^+$), 1098.7 ($[Me(EO)_{22}TMG]^+$), 1142.7 ($[Me(EO)_{23}TMG]^+$), 1186.7 ($[Me(EO)_{24}TMG]^+$), 1230.7 ($[Me(EO)_{25}TMG]^+$), 1274.7 ($[Me(EO)_{26}TMG]^+$), 1318.8 ($[Me(EO)_{27}TMG]^+$), 1362.8 ($[Me(EO)_{28}TMG]^+$), 1406.8 ($[Me(EO)_{29}TMG]^+$); The glass-transition temperature (T_g) and the thermal decomposition temperature (T_d) are 37.9°C and 342.3°C, respectively.

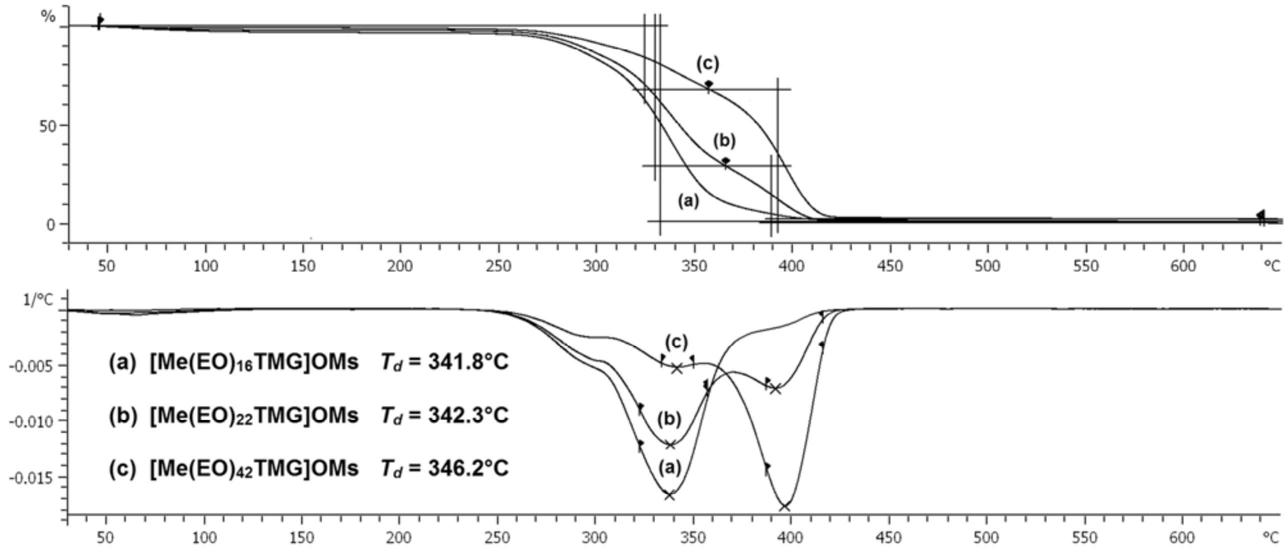
Synthesis and characterization of $[Me(EO)_{42}TMG]OMs$

The synthesis was performed as described for $[Me(EO)_{16}TMG]OMs$. **^{1}H NMR** (500.0 MHz, D_2O): δ=3.68 (m, 170H, $(O\mathit{CH_2CH_2})_n$), 3.36 (s, 3H, $O\mathit{CH_3}$), 2.95 (s, 12H, 4×$\mathit{CH_3}$), 2.78 (s, 3H, $\mathit{CH_3}SO_3^-$); **^{13}C NMR** (125.7MHz, $CDCl_3$): δ= 162.85, 71.80, 70.43, 69.67, 58.92, 44.73, 39.77, 39.36; **MS** (Q-Tof MS, ES+): m/z=1714.7 ($[Me(EO)_{36}TMG]^+$), 1758.7 ($[Me(EO)_{37}TMG]^+$), 1802.7 ($[Me(EO)_{38}TMG]^+$), 1846.7 ($[Me(EO)_{39}TMG]^+$), 1890.8 ($[Me(EO)_{40}TMG]^+$), 1934.8 ($[Me(EO)_{41}TMG]^+$), 1978.8 ($[Me(EO)_{42}TMG]^+$), 2022.8 ($[Me(EO)_{43}TMG]^+$), 2066.9 ($[Me(EO)_{44}TMG]^+$), 2110.9 ($[Me(EO)_{45}TMG]^+$), 2154.9 ($[Me(EO)_{46}TMG]^+$), 2198.9 ($[Me(EO)_{47}TMG]^+$); The glass-transition temperature (T_g) and the thermal decomposition temperature (T_d) are 50.2°C and 346.2°C, respectively.

DSC spectrum of [Me(EO)$_n$TMG]OMs (n=16, 22, 42)



TGA analysis of [Me(EO)$_n$TMG]OMs (n=16, 22, 42)



Data of recycling experiments of Rh-TPPTS catalyst

Table 1 Recycling and reuse of Rh-TPPTS catalyst for biphasic hydroformylation of 1-octene in $[Me(EO)_{16}TMG]OMs$ [a]

Cycle	Conv.[b] (%)	S_{ald}[c] (%)	n/i[d]	Rh[e] leaching (%)	P[e] leaching (%)
1	35.9	97.2	2.3	0.06	0.16
2	82.0	98.4	2.4	—	—
3	98.0	98.3	2.0	—	—
4	98.5	96.8	2.2	—	—
5	98.3	98.2	2.3	—	—
6	98.8	96.5	2.1	—	—
7	98.4	97.9	2.3	0.07	0.11
8	98.3	98.1	2.3	—	—
9	98.9	96.2	2.1	—	—
10	98.6	95.4	2.1	—	—
11	98.8	95.1	2.2	—	—
12	98.7	97.8	2.2	—	—
13	98.8	95.7	2.2	—	—
14	98.7	96.4	2.1	—	—
15	99.1	91.0	2.3	—	—
16	98.5	98.1	2.2	0.04	0.13
17	98.8	96.2	2.3	—	—
18	98.9	96.4	2.3	—	—
19	99.1	93.9	2.3	—	—
20	98.5	96.4	2.3	—	—
21	98.8	95.7	2.2	—	—
22	98.8	96.9	2.3	—	—
23	98.8	96.6	2.3	—	—
24	98.4	92.5	2.1	—	—
25	98.7	79.2	2.2	—	—
26	98.1	89.4	2.2	—	—
27	97.9	91.3	2.3	—	—
28	96.6	90.6	2.3	—	—
29	96.9	91.5	2.3	—	—
30	98.2	85.1	2.2	—	—
31	97.7	88.7	2.3	—	—
32	95.2	89.0	2.3	—	—
33	83.9	88.0	2.3	—	—
34	92.8	87.5	2.3	—	—
35	85.3	86.7	2.1	—	—

[a] $p(H_2/CO=1:1)$=5.0MPa, T=85°C, t=5h, $RhCl_3\cdot 3H_2O$ 1.0mg, TPPTS/Rh=10, alkenes/Rh=1000, 1g of $[Me(EO)_{16}TMG]$ OMs, the experimental results were obtained after 24 h of preformation of active catalyst. [b] Percent of converted alkenes. [c] Selectivity for normal aldehyde and 2-methyl aldehyde (combined). [d] Ratio of normal aldehyde to 2-methyl aldehyde. [e] Percentage of leached Rh or P in the total Rh or P charged, determined by ICP-AES analysis.

References

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