Supporting Information

Hydrophobicity / Hydrophilicity Tunable Hyperbranched Polystyrenes As Novel Supports for Transition Metal Nanoparticles

Keisuke Kojima,[a*] *Katsumi Chikama,*[a] *Makoto Ishikawa,*[a] *Akihiro Tanaka,*[a] *Takashi Nishikata,*[b]
Hironori Tsutsumi, [b] *Kazunobu Igawa,*[b] *and Hideo Nagashima*[b]*

[a]*Nissan Chemical Industries Ltd.,* [b]*Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*
nagasima@cm.kyushu-u.ac.jp

Contents

1. General Methods

All reactions were carried out under a nitrogen or argon atmosphere. ^{1}H and ^{13}C NMR spectra were measured on JEOL GSX-270 (270 MHz) and ECA-600 (600 MHz) spectrometers. Chemical shifts (δ values) were given in ppm relative to the solvent signal (7.26 ppm for $CDCl_3$). Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (δ= 77.1). TEM (Hitachi, H-8000, V=200 kV), ICP-MS (Shimadzu ICPM-8500) and HRMS (JEOL JMS-700) analysis were performed at the Analytical Center in Institute for Materials Chemistry and Engineering, Kyushu University or Nissan Chemical Industry. IR spectra were measured on JASCO FT/IR-550 and 4200 spectrometers. Analytical thin-layer chromatography (TLC) was performed on glass plates and aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F254, layer thickness 0.25 and 0.2 mm, respectively). Visualization was accomplished by UV light (254 nm). SEC (Size Exclusion Chromatography) was carried out on a Shodex KF-804L column connected with a KF-803L column by means of THF as eluent. The separation of the samples was monitored by using UV (254 nm), RI, and MALS detectors. Mw(calib) was calibrated by commercially available polystyrene standards. TEM analyses were performed on a Hitachi-H-8000 apparatus by using an acceleration voltage of 200 kV. Samples were prepared by applying a drop of the THF solution (0.01~0.05 wt%) to a carbon-mesh grid, followed by drying the sample. A linear analogue of HPS-DC, $[CH_2CH(C_6H_4)CH_2DC\text{-}p]_n$, was synthesized from p-chloromethylstyrene by radical polymerization followed by replacement of its chlorine atoms by $NaSCSNEt_2$.

2. Preparation of polymers.

Photochemical polymerization of HPS-DC. Photopolymerization of p-(N,N-diethyldithiocarbamylmethyl)styrene ($p\text{-}CH_2{=}CHC_6H_4CH_2DC$) was performed according to the procedure reported by Ishizu and coworkers.[ref. 2 in the text] In a 50 mL flask was placed HPS-DC (6 g) dissolved in xylene (4 g), and the solution was irradiated by 100 W high pressure Hg lamp for 7 h at room temperature. Insoluble materials formed were filtered off, and the solution was poured into 300 mL of methanol. The polymer product was dissolved in xylene (20 g) again, and then the solution was poured into methanol (600 g). The precipitates were separated by filtration. The purified polymer as white powder was dried under vacuum to give HPS（2.4 g, 40% yield）. $M_{w\mathrm{GPC}}$=15,000, $M_{w\mathrm{Mals}}$=31,000, degree of branching= M_{wMals}/ M_{wGPC} = 2.1.

Thermal polymerization of HPS-DC. In a two-necked round bottom flask (100 mL), p-(N,N-diethyldithiocarbamylmethyl)styrene was dissolved in xylene (4 g). The solution was stirred for 3 h at 140 °C under a nitrogen atmosphere. The reaction mixture cooled to room temperature was diluted by Xylene (20 g). The solution was poured into methanol (300 g) to precipitate the polymer product, which was isolated by filtration. The white powder was dissolved in xylene (20 g) again, and then the solution was poured into methanol (600 g). The precipitates were separated by filtration. The purified polymer as white powder was dried under vacuum to give $(\text{HPS-DC})_\Delta$（3.6g）. $M_{w\mathrm{GPC}}$=40,000, $M_{w\mathrm{Mals}}$=78,000, M_n=18,000, *d*egree of branching= $M_{w\mathrm{GPC}}/ M_{w\mathrm{Mals}}$=1.96.

Thermal polymerization using Disulfiram(DCDC) as a chain transfer reagent. In a two-necked round bottom flask (100 mL), p-(N,N-diethyldithiocarbamylmethyl)styrene（6 g) and DC-DC [0.06 g, 1 mol% of p-(N,N-diethyldithiocarbamylmethyl)styrene)] were dissolved in xylene (4 g). The solution was stirred for 3 h at 140 °C under a nitrogen atmosphere. The reaction mixture cooled to room temperature was diluted by xylene (20 g). The solution was poured into methanol (300 g) to precipitate the polymer product, which was isolated by filtration. The white powder was dissolved in xylene (20 g) again, and then the solution was poured into methanol (600 g). The precipitates were separated by filtration. The purified polymer as white powder was dried under vaccum to give the product, (HPS-DC)$_{\Delta\mathrm{DCDC}}$ (3.6g). M_w(calib) =21,000, M_w(mals) =42,000, M_n=9,400, M_w(mals)/ M_w(calib)=2.0.

Large scale production of (HPS-DC)$_{\Delta\mathrm{DCDC}}$. In a 5 L flask, p-(N,N-diethyldithiocarbamylmethyl)styrene（595 g) and DC-DC (11.9 g, 2 mol% of p-(N,N-diethyldithiocarbamylmethyl)styrene) were dissolved in xylene (255 g). The solution was stirred for 12 h at 120 °C under a nitrogen atmosphere. The reaction mixture cooled to room temperature was diluted by cyclohexanone (4.5 kg). The solution was poured into methanol (25 kg) to precipitate white powder, which was isolated by filtration. The white powder was dried under vaccum to give the product, (HPS-DC)$_{\Delta\mathrm{DCDC}}$ (476 g). M_w(calib) =20,000, M_w(mals) =39,000, M_w(calib)/ M_w(mals)=1.95.

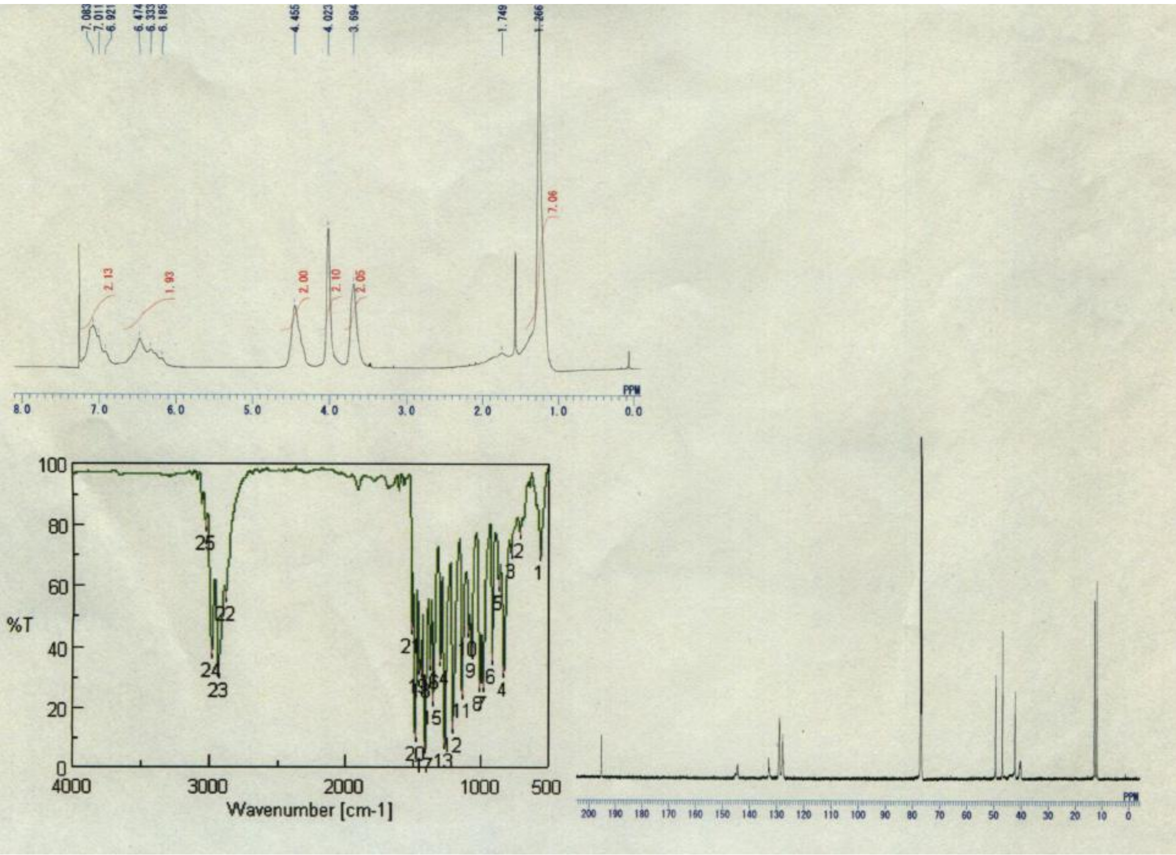
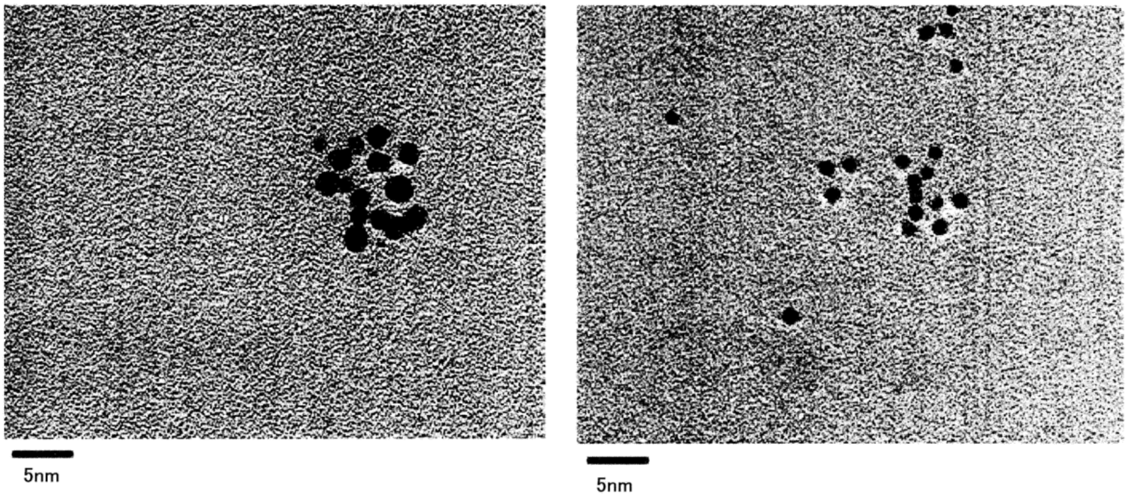
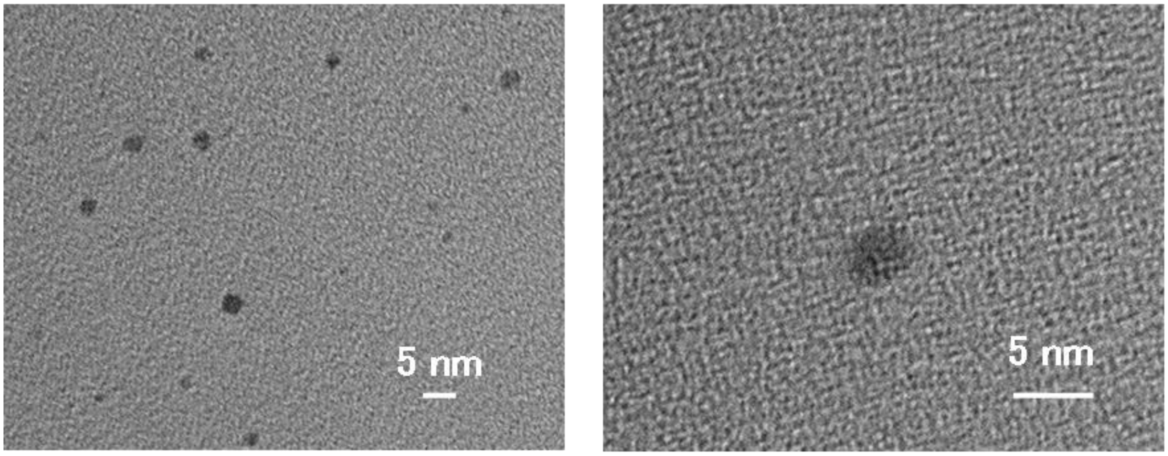


Fig. S-1a. ^{1}H, ^{13}C, and IR spectra of (HPS-DC)$_{\Delta\mathrm{DCDC}}$.



(HPS-DC)$_{h\nu}$ (HPS-DC)$_{\Delta}$



(HPS-DC)$_{\Delta}$ (HPS-DC)$_{\Delta}$

Fig. S-2. TEM image of (HPS-DC)$_{h\nu}$ (upper left) and (HPS-DC)$_{\Delta}$ (right and lower).

Characterization of polymers by SEC. In the size exclusion chromatography (SEC), a sample is separated according to its hydrodynamic volume; big molecules come out first, and then the smaller ones elute. Since HBPs are compact due to their globular structures, they elute slower than the corresponding linear polymer having similar molecular weight [M_w(mals)]. In other words, it is reasonable that M_w(calib) of HBP according to the calibration curb made by linear polystyrene standards is much smaller than M_w(mals). In Table S-1 are shown comparison of SEC data among (HPS-DC)$_{h\nu}$, (HPS-DC)$_{\Delta}$, and (HPS-DC)$_{\Delta DCDC}$. Photo-assisted polymerization gave (HPS-DC)$_{h\nu}$ of Mw(mals)=31,000 with somewhat broader molecular weight distribution. Thermal polymerization gave relatively large molecular weight polymer. Addition of DC-DC induced chain transfer reactions to give (HPS-DC)$_{\Delta DCDC}$ of Mw(mals)=42,000 with somewhat broader molecular weight distribution.* For getting evidence that (HPS-DC)$_{\Delta DCDC}$ is different from the corresponding linear analogue, we carefully synthesized the linear PS-DC with the same Mw(mals) of 42,000 according to the procedure shown in the next section. The data clearly indicate that property of (HPS-DC)$_{h\nu}$, and (HPS-DC)$_{\Delta DCDC}$ is roughly similar, but different from the linear analogue.

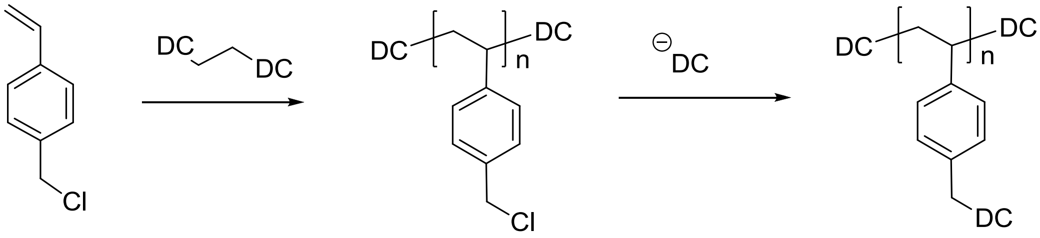
* We used DC-DC as the chain-transfer reagent to adjust the molecular weight of the polymer. The present polymerization proceeds in living fashion. The polymer having DC end groups is a dormant species, which is in equilibrium with the growing radical species. In the presence of DC-DC, regeneration of the dormant species from the radical species is more favorable than the propagation. This slow down the propagation to give (HPS-DC)$_{\Delta DCDC}$ of which M_w(mals) is close to that of (HPS-DC)$_{h\nu}$.

Table S-1. SEC data of HPS-DC.

HPS-DC[b]	M_w(calib) [b]	M_w / M_n	M_w (mals) [c]	M_w(mals) / M_w(calib)
(HPS-DC)$_{h\nu}$	15,000	4.0	31,000	2.1
(HPS-DC)$_{\Delta}$	40,000	2.4	78,000	2.0
(HPS-DC)$_{\Delta DCDC}$	21,000	2.4	42,000	2.0
Linear PS-DC	35,000	2.2	42,000	1.2

[a] Preparative methods are described in the supporting information. [b] Calibrated by polystyrene standards. [c] Determined by GPC-MALS.

Preparation of linear homologue (linear PS-DC) for SEC analysis. Polymerization of p-chloromethylstyrene (20 g) was carried out in toluene (20 g) in the presence of $DCCH_2CH_2DC$ (0.24 g) irradiated by 100W High pressure Hg lamp for 5 h at room temperature. The desired linear polymer was obtained (2.8 g). The polymer (2.0 g) was treated with $NaSC(S)NEt_2$ (4. 0 g) in NMP (48 g) at 40^{o}C for 18 h. Removal of NMP is followed by extraction of the residue by toluene. The extracts were washed with water, and the organic layer was separated and concentrated. Precipitation from MeOH / toluene gave the linear polymer, $(CH_2CHC_6H_4CH_2DC\text{-}p)_n$ (3.2 g). M_w(calib) =35,000, M_w(mals) =42,000, M_w(mals)/ M_w(calib)=1.2.



3. Preparation of HPS-Cl

Laboratory scale synthesis: In a 300 mL flask, (HPS-DC)$_{\Delta DCDC}$ (15 g containing 57 mmol of DC groups) was dissolved in $CHCl_3$ (150 g). In a two necked 500 mL flask, SO_2Cl_2 (27 g, 200 mmol, 3.6 eq. to the DC group in the above HPS-DC) was dissolved in $CHCl_3$ (50 g). To the SO_2Cl_2 solution precooled at -5 ~ 5^{o}C, the HPS-DC solution was added dropwise over 60 min, during which the temperature of the reaction mixture was kept at -5 ~ 5 ^{o}C. Addition of the reaction mixture to isopropanol (1.2 kg) resulted in the polymer precipitation. The crude polymer was redissolved in $CHCl_3$ (100 g), and isopropanol (500 g). The resulting polymer was separated by filtration, and dried under vacuum. HPS-Cl was obtained as a white powder (8.5 g, 99%). GPC analysis showed M_w and M_w / M_n of the formed HPS-Cl to be 14,000 and 2.9, respectively. ^{1}H NMR (395.8 MHz, $CDCl_3$) δ1.16-1.51 and 1.60-185 (broad bump, polystyrene methylene and methine) , 4.50 (br, CH_2Cl), 6.24-6.66 and 6.89-7.23 (br, polystyrene phenyl). ^{13}C NMR (150.9 MHz, $CDCl_3$) 39.7, 39.7-45.8, 45.8 (CH_2Cl), 127.9, 134.4, 144.9. Comparison in ^1H NMR spectra between HPS-DC and HPS-Cl clearly showed that three signals due to the DC group (NCH_2CH_3) dissapeard and a broad signal due to the CH_2Cl moiety was observed (Fig. S-3), indicating all of the DC groups were converted to the Cl moieties. Elemental analysis for HPS-Cl (C 60.7, H 5.8, N 0.2, Cl 20, S 3.4)

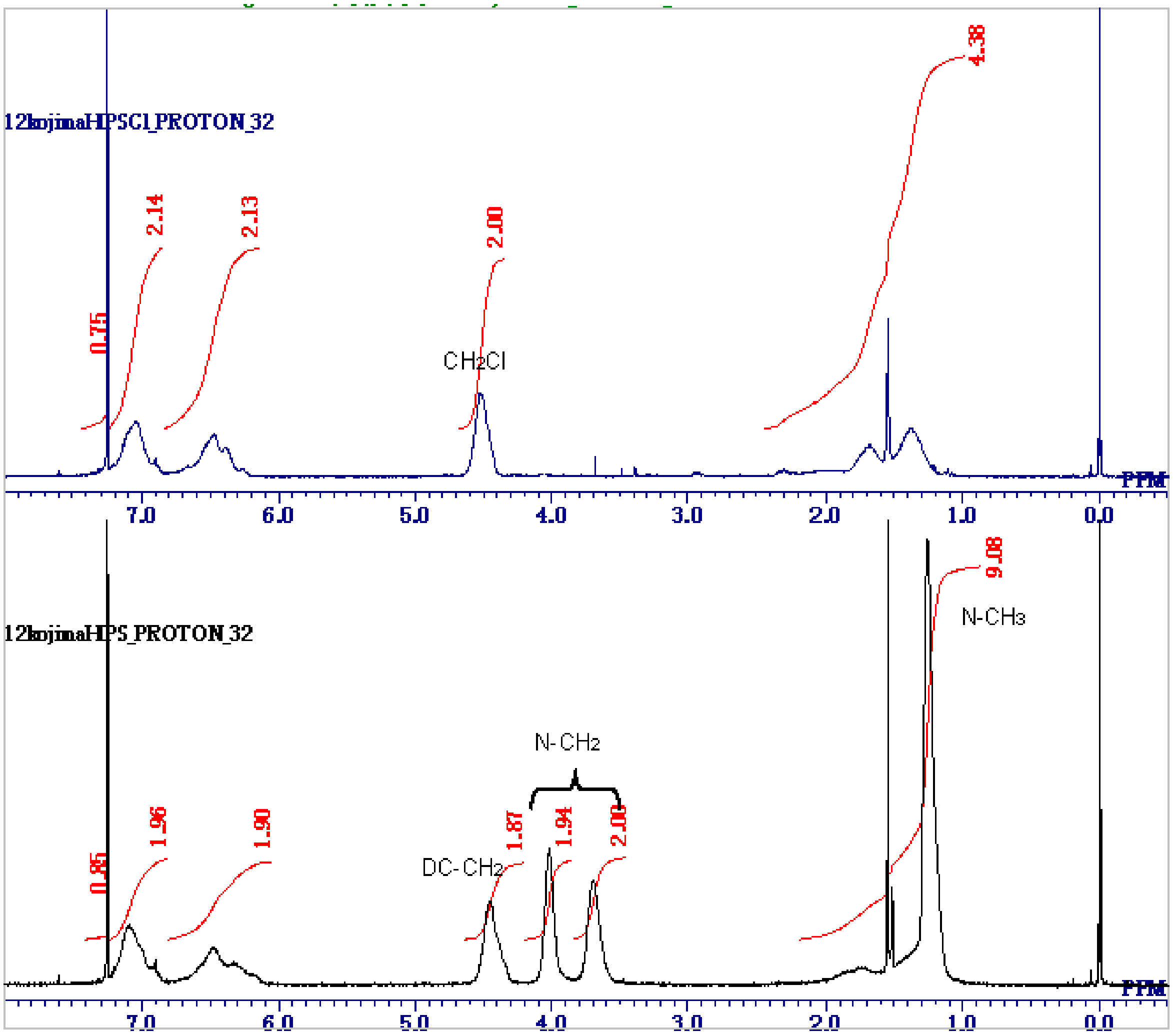


Fig. S-3. ^1H spectra of HPS-Cl (upper) and HPS-DC (lower).

Batch scale synthesis: In a 20 L flask, HPS-DC（0.7 kg）was dissolved in $CHCl_3$ (7 kg). In a 10L flask, SO_2Cl_2 (1.28 kg) was dissolved in $CHCl_3$ (2.35 kg). To the SO_2Cl_2 solution precooled at -5-0°C, the HPS-DC solution was added over 1.5h, during which the temperature of the reaction mixture was kept at around -5 °C. After stirring the mixture for 6 h at around -5 °C, addition of the reaction mixture to isopropanol (46.7 kg) resulted in the polymer precipitation. The resulting polymer was separated by filtration. After washing with isopropanol (5.25 kg), the polymer was dried under vacuum. HPS-Cl was obtained as a white powder (399 g).

4. Preparation of HPS-$NR_3^+Cl^-$

Preparation of HPS-$NR_3^+Cl^-$ was generally performed by treatment of HPS-Cl with NR_3 in $CHCl_3$ under reflux for 48 h. Solubility of HPS-$NR_3^+Cl^-$ is dependent on the R group; the polymer is soluble to water but insoluble in toluene and hexane, when R = Et, Bu, and $(C_2H_4O)_2Me$. In contrast, HPS-$NR_3^+Cl^-$, where R = n-octyl or n-dodecyl, is soluble in hydrocarbons but insoluble in water. Typical examples to synthesize liposoluble and water-soluble HPS-$NR_3^+Cl^-$ are described below. As deduced from a model image shown in Fig. S-14, HPS compounds contain plenty of functional groups of which steric circumstances are different. In HPS-Cl, the CH_2Cl groups close to the surface are likely more reactive towards the reaction with NR_3 than those close to the core. HPS-Cl contains CHCl groups, which should be less reactive than CH_2Cl moieties. It is likely that HPS-$NR_3^+Cl^-$ have many ammonium groups on the surface but contain some unreacted CH_2Cl and CHCl moieties in its inner structure. As shown below, the conversion of the CH_2Cl group to the $CH_2NR_3^+$ moiety can be roughly estimated from ^{13}C NMR spectra ; the $CH_2NR_3^+$ / CH_2Cl ratio was dependent on the R group and reaction conditions, but careful optimization raised the ratio from 7 / 3 to 9 / 1.

Preparation of HPS-$N(C_{12}H_{25})_3^+Cl^-$. In a typical example, a solution of tridodecylamine (10.1 g, 20 mmol) dissolved in isopropanol (7.5 g) was added to a solution of HPC-Cl (3.04 g corresponding to 20 mmol of the chloride) in $CHCl_3$ (30 g) under a nitrogen atmosphere. The solution was heated under reflux for 48 h. The solvents were removed (evaporator), and the residue was dried under vacuum at 50°C for 2 h. The crude ammonium salt obtained as yellow solids was dissolved in $CHCl_3$ (100 g). The solution was poured into hexane (500 g) to precipitate pale yellow powder, which was isolated by filtration. The crude HPS-$N(C_{12}H_{25})_3^+Cl$ was dried under vacuum at 50°C to give the product (11.16 g). In ^{13}C NMR spectrum of the HPS-$NR_3^+Cl^-$ product, a signal at δ 46 due to the CH_2-Cl in HPS-Cl was visible. From the integral ratio compared with the other ^{13}C signals due to HPS-$(C_{12}H_{25})_3$, 71% of the chloride in HPS-Cl was converted to HPS-$N(C_{12}H_{25})_3^+Cl^-$. The obtained polymer is soluble in common organic solvents such as hexane, toluene, MeOH, EtOH, THF, acetone, DMF, MeCN, CH_2Cl_2, and $CHCl_3$, but insoluble in water. ^1H NMR (395.8 MHz, $CDCl_3$) δ0.88 (br), 1.26 (br), 1.79 (br), 3.21 (br), 4.48 (br), 6.50 (br), 7.14 (br). ^{13}C NMR (150.9 MHz, $CDCl_3$) 14.4, 22.9, 26.7, 29.6, 29.9, 32.10, 58.6, 128.1, 129.0, 132.7, 135.6. As shown in Fig. S-4, ^1H NMR signals due to the remaining CH_2Cl and the formed $CH_2N(CH_2C_{11}H_{23})_3$ were visible as broad bump around 4.5 and 3.2 ppm, respectively, from which estimation of the Cl / ammoniuim salt conversion was difficult. ^{13}C resonance at δ46 due to the unreacted $\mathit{C}H_2Cl$ moieties could be compared with δ14 ppm of $N(C_{11}H_{22}\boldsymbol{Me})_3$; this suggests 82% conversion of the chloride to the ammonium salts. Elemental analysis: C:77.4, H:12.7, N:2.1, Cl:5.7

Preparation of HPS-$N[(C_2H_4O)_2Me]_3^+Cl^-$. In a typical example, a solution of tris[2-(2-methoxyethoxy)ethyl]amine (6.47 g, 20 mmol) dissolved in isopropanol (7.5 g) was added to a solution of HPC-Cl (3.04 g corresponding to 20 mmol of the chloride) in $CHCl_3$ (30 g) under a nitrogen atmosphere. The solution was heated under reflux for 48 h. The solvents were removed (evaporator), and the residue was dried under vacuum at 50°C for 2 h. The crude ammonium salt obtained as yellow solids was dissolved in $CHCl_3$ (100 g). The solution was poured into hexane (500 g) to separate pale yellow oil at the bottom of the flask. The supernatant was removed by decantation. The crude HPS-$N[(C_2H_4O)_2Me]_3^+Cl$ was dried under vacuum at 50°C to give the product as yellow powder (8.6 g). ^{13}C NMR data indicated that 69% of the chloride in HPS-Cl was converted to HPS-$N[(C_2H_4O)_2Me]_3{}^+Cl$. The obtained polymer is soluble in water and polar organic solvents such as MeOH, EtOH, THF, acetone, DMF, MeCN, CH_2Cl_2, and $CHCl_3$, but insoluble to hexane.^{1}H NMR (395.8 MHz, $CDCl_3$) δ3.26 (br), 3.50 (br), 3.60 (br), 3.65 (br), 4.04 (br), 5.06 (br), 6.55 (br), 7.44 (br). ^{13}C NMR (150.9 MHz, $CDCl_3$) 54.9, 59.1, 59.2, 60.5, 65.6, 71.1, 72.6, 72.7, 126.9, 129.3, 134.8, 149.0. As shown in Fig. S-5a, the ^{1}H signal due to the remaining CH_2Cl was visible, but estimation of the Cl / ammoniuim salt conversion was difficult. ^{13}C resonance at δ46 due to the unreacted $\mathit{C}H_2Cl$ moieties could be compared with singals due to the $\mathit{C}H_2N(\mathit{C}H_2CH_2O)_2\mathit{Me}$ moieties; this suggests 69% conversion of the chloride to the ammonium salts. Elemental analysis: C:57.0, H:9.0, N:2.5, Cl:10.3

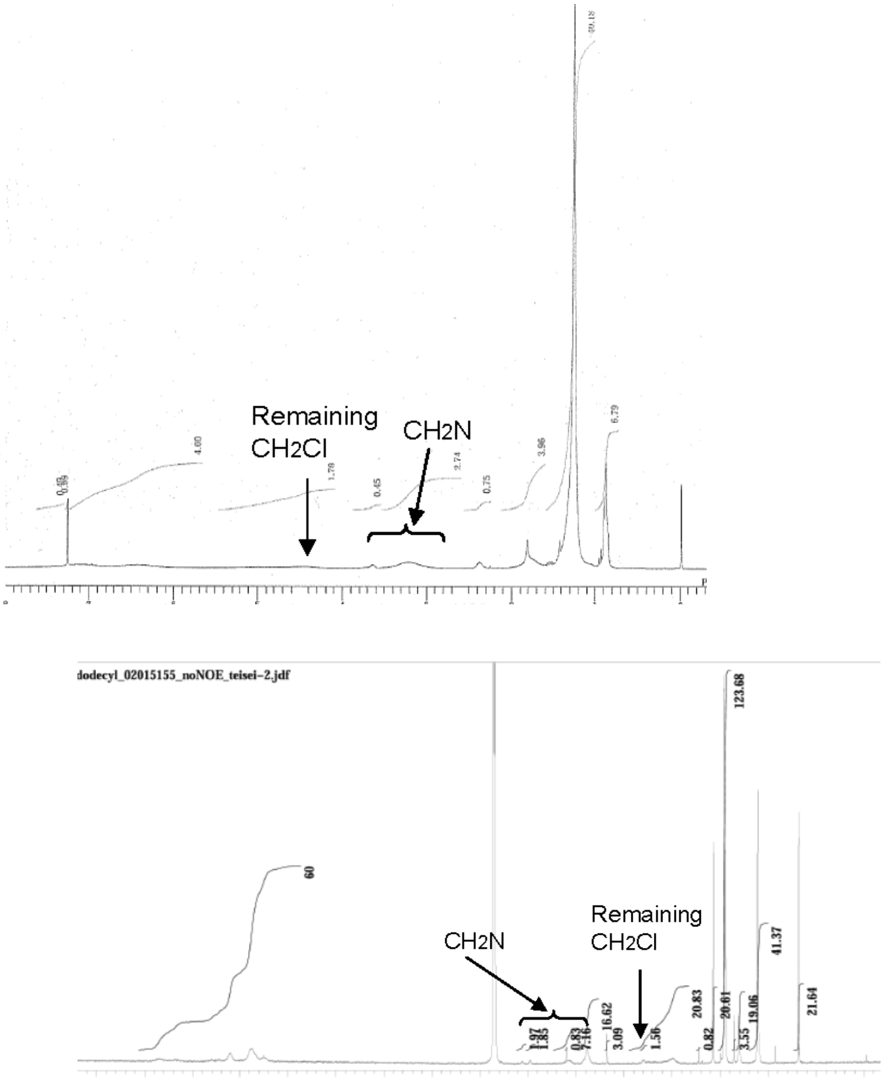


Fig. S-4. ^{1}H and ^{13}C spectra of HPS-$N(C_{12}H_{25})_3{}^+Cl^-$.

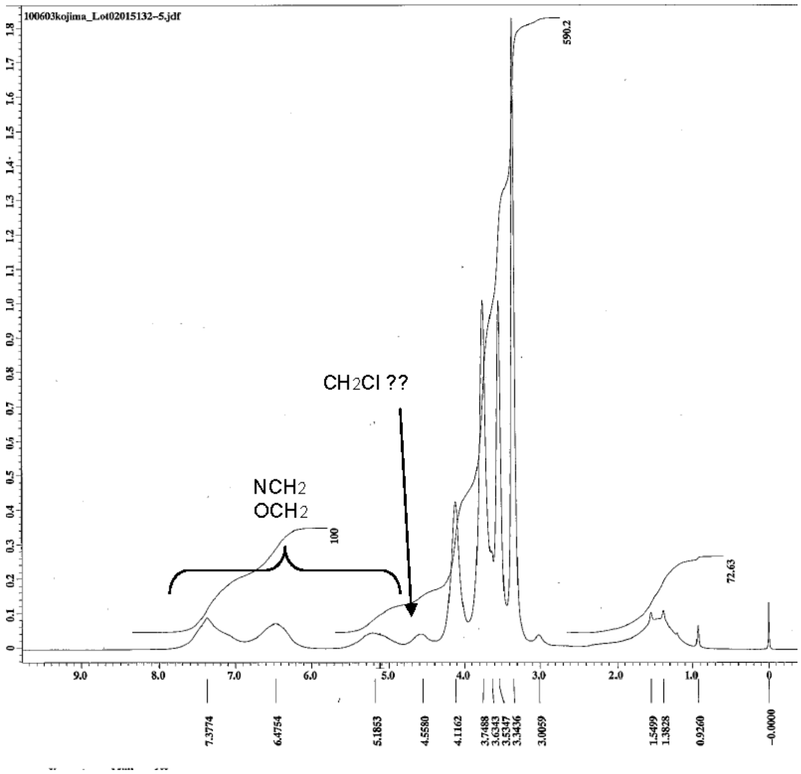


Fig. S-5. ^{1}H NMR spectrum of HPS-N[$(C_2H_4O)_2Me]_3^+Cl^-$.

5. Preparation of Pt@HPS-$NR_3^+Cl^-$

Preparation of Pt@HPS-N($C_{12}H_{25})_3^+Cl^-$. In a two-necked round bottom flask (300 mL), HPS-N($C_{12}H_{25})_3^+Cl^-$ (4 g) and $Pt(DBA)_2$ (2.86 g) were dissolved in $CHCl_3$ (100 g). EtOH (25 g) was added to the solution. The mixture was stirred for 6 h at 50 °C under nitrogen atmosphere. Removal of the solvent was performed *in vacuo* for 2 h at 50 °C. The black solid residue was dissolved in $CHCl_3$ (50 g), and the solution was poured into hexane (200 g) to precipitate black powder. After filtration, the solid materials were dried up at 50°C *in vacuo* to give Pt@HPS-N($C_{12}H_{25})_3^+Cl^-$.(4.8 g. [Pt]=21wt% by TG analysis and ICP MS). Elemental analysis: C:43.5, H:6.1, N:1.1, Cl:8.2, Pt:41.1

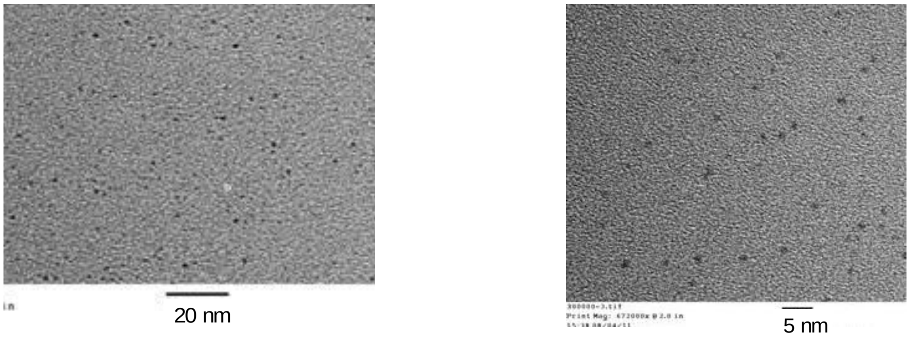


Fig. S-6. TEM analysis of the product: Average particle size =1.69 nm.

Preparation of Pt@ HPS-N[(C_2H_4O)$_2$Me]$_3^+$Cl$^-$: In a two-necked round bottom flask (300 mL), HPS-N($C_2H_4OC_2H_4OMe$)$_3$Cl (4 g) and Pt(DBA)$_2$ (2.86 g) were dissolved in $CHCl_3$ (100 g). EtOH (25 g) was added to the solution, and the mixture was stirred for 6 h at 50 °C under nitrogen atmosphere. The solvent was removed *in vacuo* for 2 h at 50 °C. A black solid residue was dissolved in $CHCl_3$ (50g), and the solution was poured into hexane (200g) to precipitate black powder. After decantation of a solvent and the residue was dried up at 50 °C *in vacuo*, the powder was obtained. (4.6g. [Pt]=16wt% by TG analysis and ICP MS), Elemental analysis: C:45.3, H:5.8, N:1.6, Cl:8.9, Pt:23.9

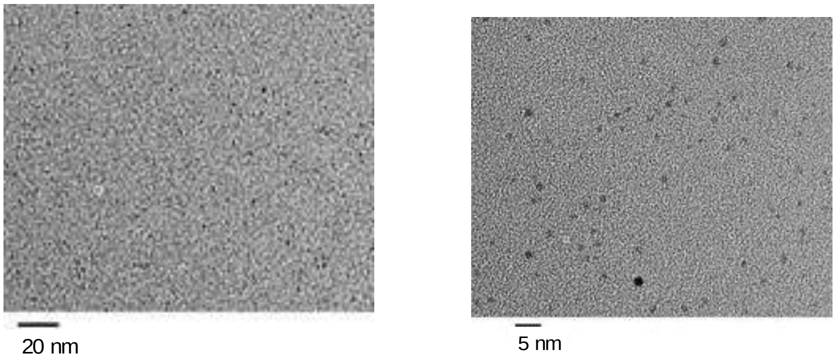
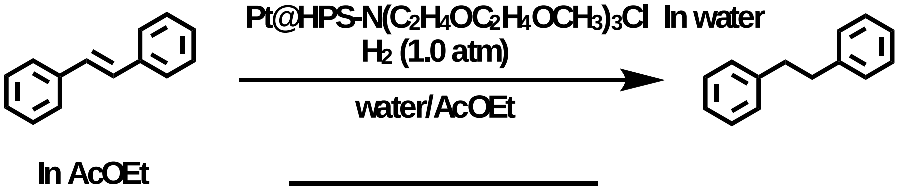


Fig. S-7. TEM analysis of the product: Average particle size =1.89 nm.

6. Typical procedures for biphasic hydrogenation.

A. Reduction of stilbene with recycling the catalyst recycle.



Cycle	Yield(%)
1	99
2	99
3	99
4	99
5	99

The biphasic system was prepared by stilbene (180 mg, 1 mmol) dissolved in AcOEt (2 mL) and Pt@HPS-N($C_2H_4OC_2H_4OMe$)$_3$Cl (13 mg, 21wt%, S/C=71) dissolved in water (2 mL). The resulting mixture was stirred under hydrogen atmosphere (1 atm) for 10 h. The organic phase was separated by decantation, and the solvent was removed *in vacuo*. The residue was purified by silica gel chromatography to afford dibenzyl in 99% yield. The spectrum of the product was matched with the data previously reported. (Ratheesh Kumar, Venugopal K.; Gopidas, Karical R. *Tetrahedron Lett.*, **2011**, *52*, 3102 - 3105) The aqueous phase containing the catalyst was used for another run of hydrogenation reaction according to the procedure described above. Five repeated experiments showed no catalyst deactivation, affording stilbene quantitatively. TEM analysis of before and after five repeated experiments of hydrogenation revealed little change of the particle size.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88(s, 4H), 7.08-7.18(m, 6H) , 7.20-7.27(m, 4H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 38.0, 126.0, 128.3, 128.4, 141.8

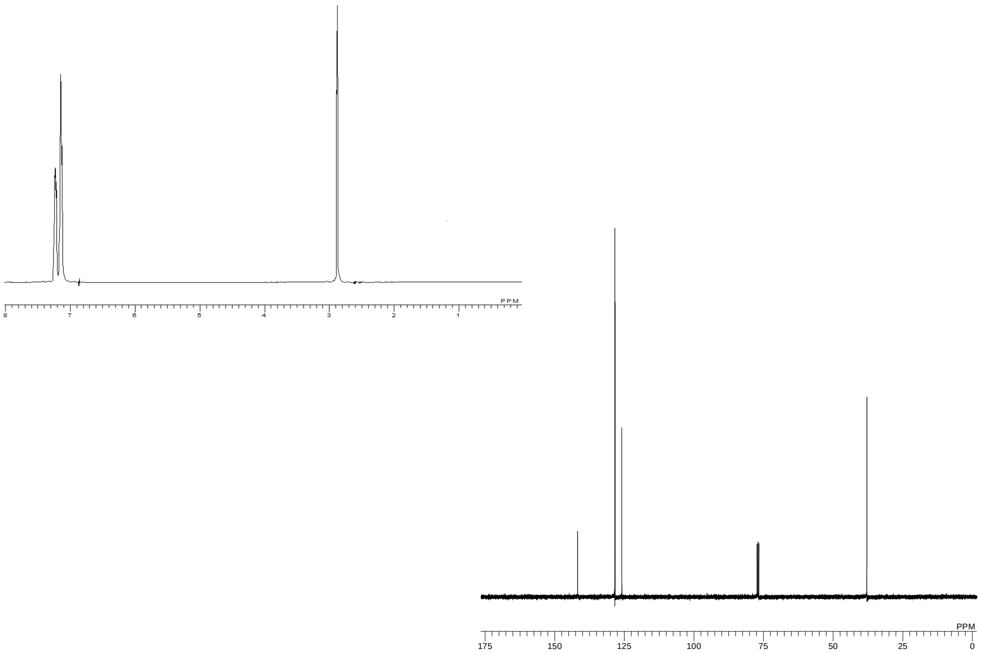


Fig. S-8. ^{1}H and ^{13}C spectra of stilbene.

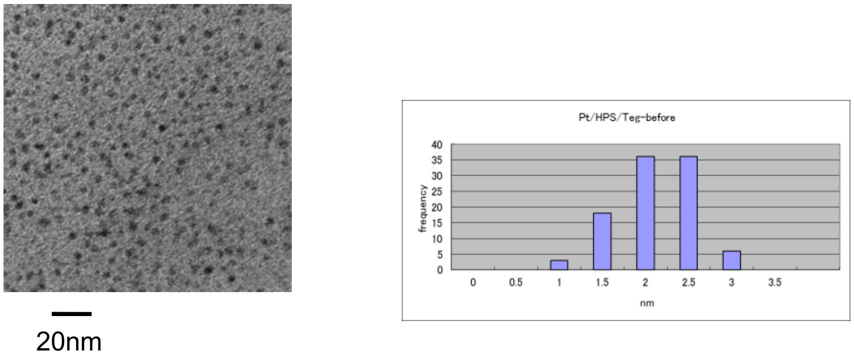


Fig. S-9. TEM image of Pt@ HPS-N$[(C_2H_4O)_2Me]_3{}^{+}Cl^{-}$ before hydrogenation. Average particle size =1.89 nm

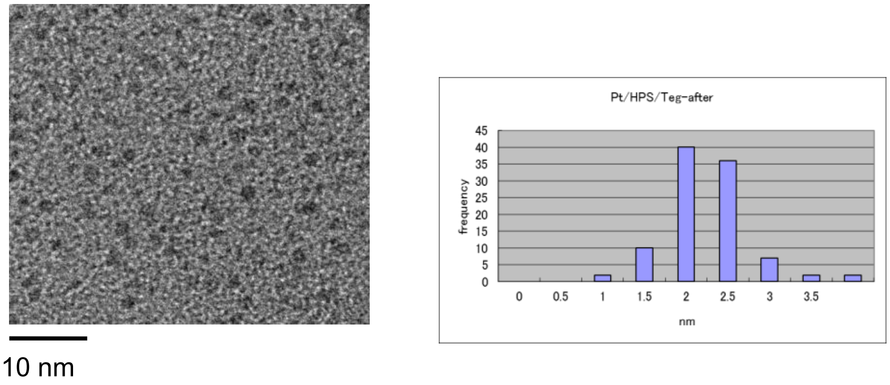
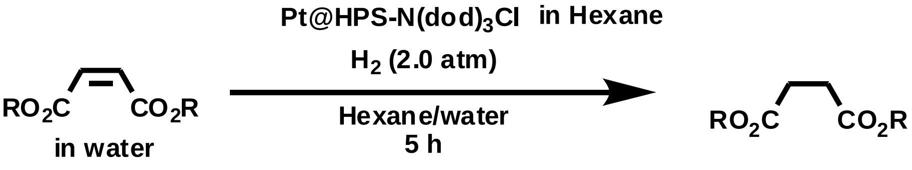


Fig. S-10. TEM image of Pt@ HPS-N[$(C_2H_4O)_2Me]_3^+Cl^-$ after five runs of hydrogenation: Average particle size =2.01 nm.

B. Reduction of a maleic ester, $Me(OC_2H_4)_2OCOCH=CHCO_2(C_2H_4O)_2Me$ with recycling the catalyst.



Cycle	Yield (%)
1	99
2	99
3	99
4	99
5	99

The biphasic system was prepared by the ester shown above (232 mg, 1 mmol) dissolved in water (2 mL) and Pt@ HPS-N$(C_{12}H_{25})_3^+Cl^-$ (13 mg, 16wt%, S/C=100) in hexane (2 mL). Since the reaction under 1 atm of H_2 was slow, we carried out the reaction under 2 atm of H_2. The resulting mixture was stirred under H_2 pressure (2 atm) in a pressure bottle for 5 h., The hexane phase containing the catalyst was removed by decantation. The aqueous phase was extracted with AcOEt and purified by silica gel chromatography to give the corresponding succitante in >99% yield. The hexane phase containing the catalyst was used for another run of hydrogenation according to the procedure described above.

^{1}H NMR (395.8 MHz, $CDCl_3$)
2.65(s, 4H), 3.37(s, 6H), 3.53(t, J = 4.8 Hz, 4H), 3.63(t, J = 4.8 Hz, 4H), 3.68(t, J = 4.8 Hz, 4H), 4.24(t, J = 4.8 Hz, 4H)
^{13}C NMR (150.9 MHz, $CDCl_3$)
29.1, 59.0, 63.8, 69.1, 70.5, 71.9, 172.2

HRMS (FAB): calcd for $C_{14}H_{27}O_8$, 323.1706; found, 323.1704.

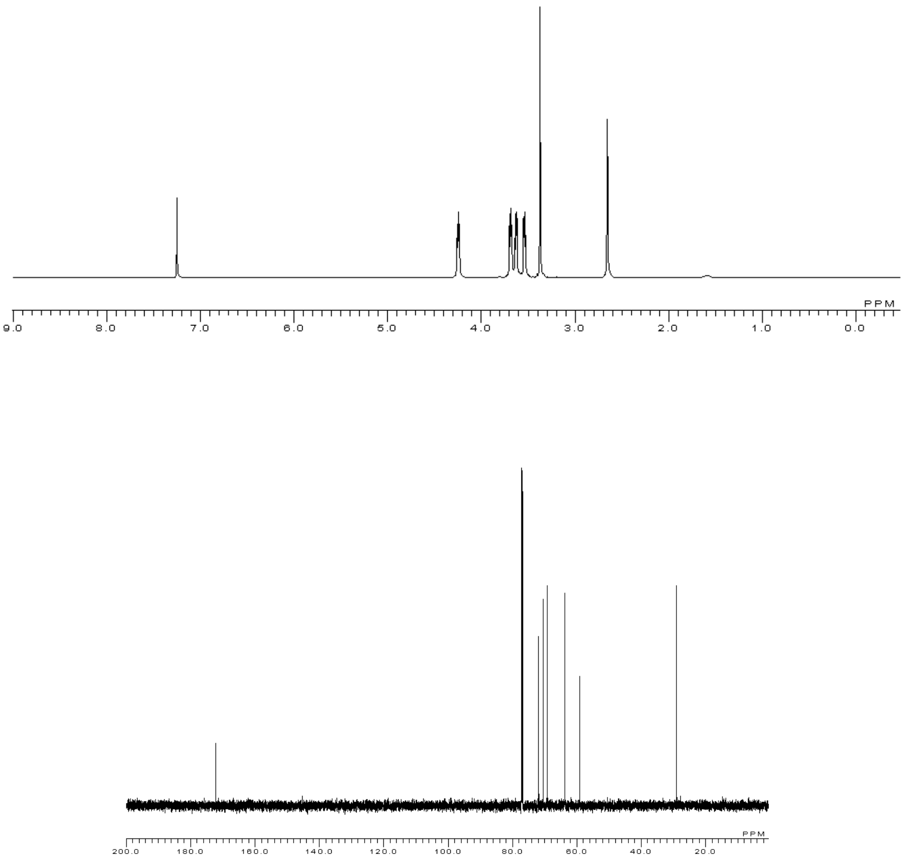
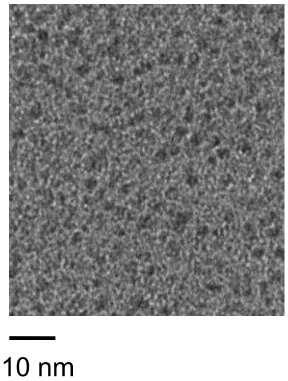


Fig. S-11. ^{1}H and ^{13}C spectra of stilbene.



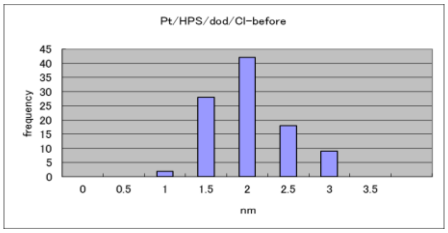


Fig. S-12. TEM image of Pt@ HPS-N($C_{12}H_{25}$)$_3^+$Cl$^-$ before hydrogenation. Average particle size =1.69 nm.

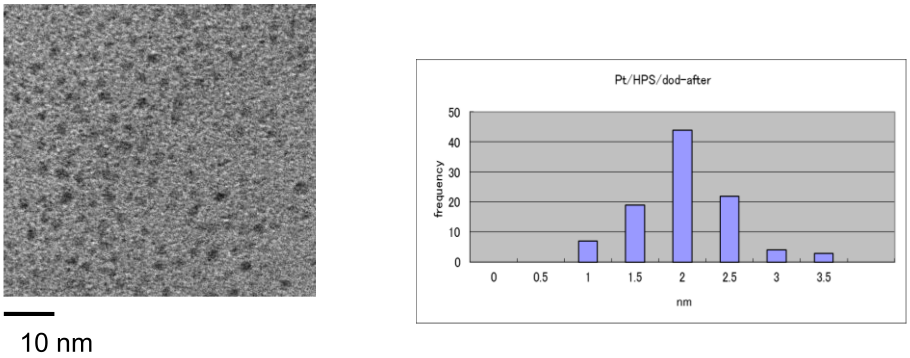
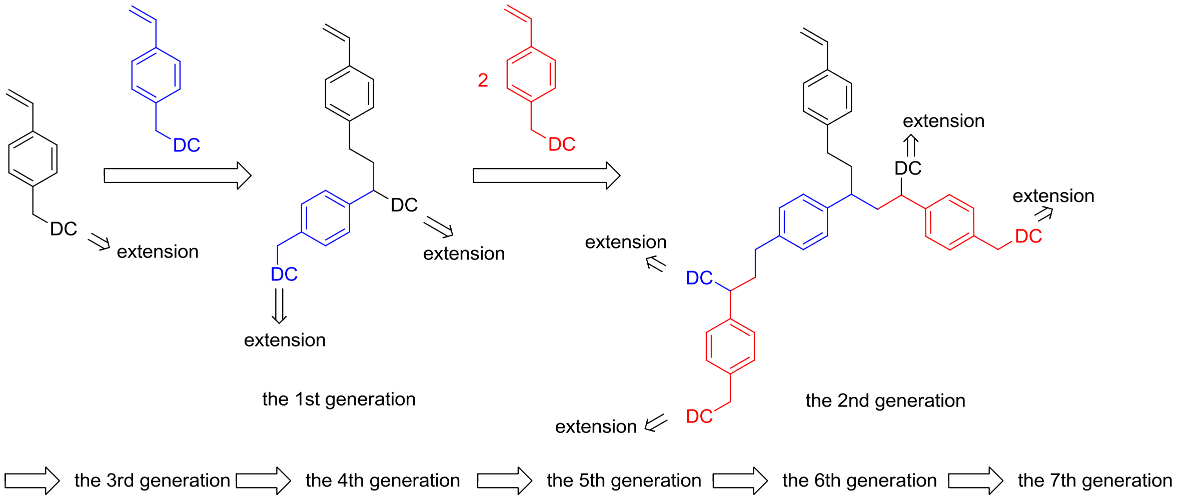


Fig. S-13. TEM image of Pt@ HPS-N($C_{12}H_{25}$)$_3^+$Cl$^-$ after five runs of hydrogenation. Average particle size =1.75 nm.

7. Molecular mechanics calculations of HPS-DC.

The initial structures were prepared according to the scheme below (Scheme S1). The DC group of $CH_2{=}CHC_6H_4CH_2DC$ reacts with another molecule of $CH_2{=}CHC_6H_4CH_2DC$ to form the 1st generation of the HPS-DC. Two DC groups in the 1st generation HPS-DC reacts with another two molecules of $CH_2{=}CHC_6H_4CH_2DC$ to give the 2nd generation of HPS-DC. In similar fashion, initial structures of 3rd, 4th, 5th, 6th, and 7th generation of HPS-DC were prepared. The initial structures were optimized by Chem. 3D program by using MMFFS as the parameter. The optimized structures of 5th and 7th generation of HPS-DC are depicted in Fig. S14, of which molecular size are 5.6 and 7.0 nm, respectively.



Scheme S1. Preparation of model structures of HPS-DC.

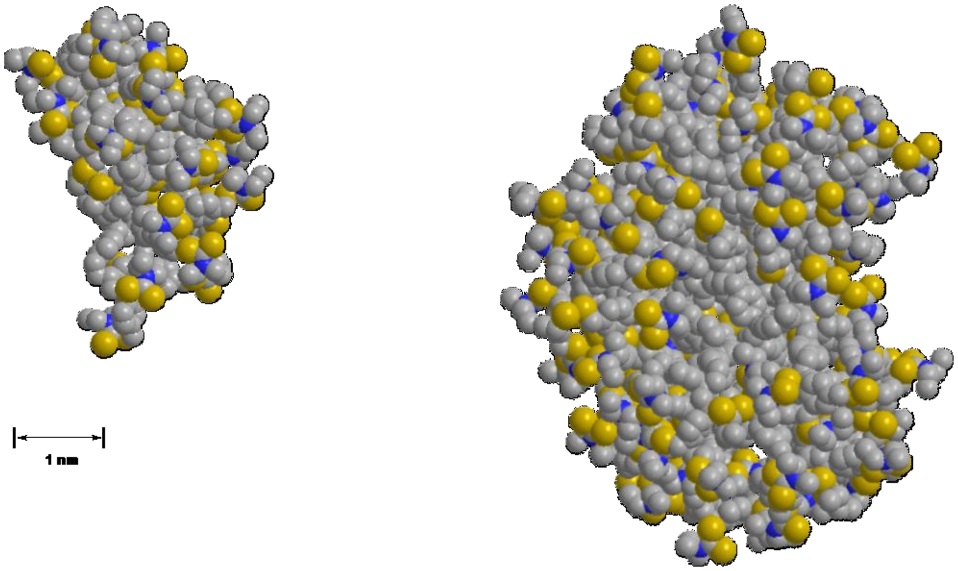


Fig. S-14. Model images for the 5th (left) and 7th generation of HPS-DC.

8. ICP analysis to check the metal leaching in experiments of the biphasic catalysis.

I. Biphasic hydrogenation of stilbene by Pt@HPS-$N^+(C_2H_4OC_2H_4OMe)_3Cl^-$(21wt%).

The hydrogenation was performed by a procedure described above using 2 mL of an aqueous solution of Pt@HPS-$N^+(C_2H_4OC_2H_4OMe)_3Cl^-$ and 2 mL of stilbene dissolved in 2 mL of AcOEt at room temperature under a hydrogen atmosphere (1 atm). After the reaction, standing the mixture for a while resulted in half-way phase separation. We first examined to separate whole volume of the organic phase by a pipet; however, it was impossible to get the solution without contamination of the aqueous catalyst phase. The improved procedure is following; 2 mL of AcOEt was added to the reaction mixture, and stirred vigorously. Then, the mixture was allowed to stand for 1 h to make sure the complete phase separation. A half amount of the organic phase (2 mL) was transferred to a flask by a whole-pipet, and the solvent was removed under vacuum. The residue was treated with 0.1 N HNO_3 aq. (5 mL) at 70°C for 12 h. The resulting solution was diluted with 0.1 N HNO_3 till the weight of the solution reached 15 g (Solution A). Dilution of the solution A by 0.1 N HNO_3 double and four times gave solution B and solution C, respectively. The minimum detectable Pt content by ICP-MS was 3 ppb. The results showed the Pt content to be below 3 ppb (Sample A; 2.8 ppb, Sample B; 2.7 ppb, Sample C; 2.7 ppb). This means that the amount of Pt leached from the aqueous solution of Pt@HPS-$N^+(C_2H_4OC_2H_4OMe)_3Cl$ into the organic phase (just after the reaction, before the addition of 2 mL of AcOEt) was lower than 3.6 X 10^{-7} mg. Since the charged amount of Pt was 2.1 mg, we concluded that the leaching of Pt was negligible.

II. Biphasic hydrogenation of stilbene by Pt@HPS-$N(C_{12}H_{25})_3{}^+Cl^-$ (16 wt%).

The hydrogenation was performed by a procedure described above using 2 mL of a hexane solution of Pt@HPS-$N(C_{12}H_{25})_3{}^+Cl^-$ and 2 mL of the fumarate dissolved in 2 mL of water at room temperature under H_2 (2 atm). After the reaction, standing the mixture for a while resulted in half-way phase separation. The hexane solution containing the catalyst was removed by a pipet as careful as possible, and the aqueous phase was diluted double. Since the surface of this solution may be contaminated by a trace amount of the catalyst, 2 mL of the aqueous phase was separated by a whole pipet carefully from the bottom part of the flask. Dilution of the sample by 0.1 N HNO_3 gave sample D (15 times dilution), sample E (30 times dilution), and F (60 timed dilution). The Pt content of these samples determined by ICP-MS analysis showed 12.0, 6.0, and 2.5 ppb, respectively. The former two are above the detection limit of the ICP-MS, suggesting the amount of leached Pt in the aqueous phase after the reaction to be 3.6 X 10^{-7} mg. Since the charged amount of Pt was 2.1 mg, we concluded that the leaching of Pt was negligible.