

Electronic Supplementary Information (ESI)

High catalytic activity of palladium nanoparticle clusters supported on the spherical polymer network

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Experimental section

Transmission electron microscope (TEM) images were obtained by using JEM-1200EX (JEOL, Japan) instrument at an accelerating voltage of 120 kV. The samples (2-5 μl) were applied on formvar coated copper grids, and then dried at room temperature. A high-resolution microscope Merlin Carl Zeiss combined with the ASB (Angle Selective Backscattering) and the SE InLens (Secondary Electrons Energy selective Backscattering) detectors was equipped for energy dispersive X-ray spectroscopy (EDX) analysis with AZTEC X-MAX energy-dispersion spectrometer from Oxford Instruments. A Zetasizer Nano instrument (Malvern, UK) equipped with a 4 mW He:Ne solid-state laser operating at 633 nm was used for the DLS experimental measurements. Malvern dispersion technology software 5.0 was used for the analysis of particle size. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 25 UV/Vis spectrometer. The NMR experiments were carried out with an Avance-600 (Bruker, Germany) spectrometer equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of about 56 $\text{G}\cdot\text{cm}^{-1}$. The content of palladium in solutions was determined by EDX-800HS2 (Shimadzu) X-ray fluorescence (XRF) spectrometer operating at 50 W with Rh radiation source (collimator: 10 mm; atmosphere: air; current: 100 μA ; filter: Zr; line: $\text{PdK}\alpha$; Energy: 21.12 keV; range of integration: 20.92-21.32 keV).

Sodium tetrachloropalladate (II) (Na_2PdCl_4 , 36 % Pd), sodium borohydride (NaBH_4 , 99 %), *p*-nitrophenol (99 %) and ascorbic acid (99 %) were purchased from Acros Organics

and used as received without further purification. *p*(MVCA-co-St) was synthesized as described in.¹ Regenerated cellulose tubular dialysis membranes (MWCO: Nominal: 1000) were acquired from Cellu•Sep. All the solutions were prepared with deionized water treated in a Millipore water purification system (Millipore Corp.).

Synthesis of Pdn-*p*(MVCA-co-St). Metal nanoclusters were synthesized using methods described in.² An aqueous solution of *p*(MVCA-co-St) (4 mg/ml, 0.5 ml) was mixed with 0.75 ml of 1.33 - 5.33 mM Na₂PdCl₄. After 1 minute 0.75 ml of 26.67 mM ascorbic acid was added. The mixture was kept at room temperature for 24 hours. The control of the reduction of [PdCl₄]²⁻ was performed by the disappearance of an absorption band at 410 nm in the UV/Vis spectra. The final colloidal solution was dialyzed (2 ml versus 3×800 ml water). Palladium concentration is determined by XRD analysis. C(Pd in Pd4-*p*(MVCA-co-St)) = 1.899±0.010 mM. The solutions of Pdn-*p*(MVCA-co-St) were diluted for the catalysis, so that the concentration of palladium was 0.2 mM.

Isolation of Pd⁰ from Pd4-*p*(MVCA-co-St). 2 ml of Pd4-*p*(MVCA-co-St) (2 mM of Pd⁰) was centrifuged (15000 rpm for 60 min). A solvent was gently removed and 1 ml of water was added to a black solid. Dispersion was sonicated for 10 minutes and centrifuged for 20 minutes. A procedure of sonication/centrifugation was repeated three times and a final black solid was dried on the air. UV spectrum of free Pd NPs is shown on Fig. S1B.

Reduction of *p*-nitrophenol by Pdn-*p*(MVCA-co-St). In a quartz cuvette (*l* = 0.5 cm), an aqueous dispersion of Pdn-*p*(MVCA-co-St) (0.2 mM of Pd, 16 μl) was added to the 1.6 ml of an aqueous solution containing 0.1 mM of *p*-nitrophenol and 5 mM NaBH₄. The reduction reactions were monitored by a temporary change in absorption at 400 nm in the UV/Vis spectra at 20 °C.

Reduction of *p*-nitrophenol by free Pd NPs was carried out in similar manner by adding 15 μl of 0.5 mM Pd NPs solution instead of Pdn-*p*(MVCA-co-St).

Suzuki-Miyaura coupling reaction. To an aqueous dispersion (10 ml) containing 7.5 mM iodobenzene, 7.5 mM phenylboronic acid and 22.5 mM K₂CO₃, a colloidal solution of 2 mM Pd in Pd4-*p*(MVCA-co-St) (187.5 μl for 0.5 mol% catalyst or 375 μl for 1 mol% catalyst) was added. The volume of the mixture was adjusted to 15 ml. The mixture was stirred at room temperature for 40 hours. The product was extracted with hexane. The hexane solution was washed with water, dried with MgSO₄ and the solvent was evaporated. The yield of biphenyl was determined by NMR spectra.

Table S1. Concentration of reagents in synthesis of Pd n -p(MVCA-co-St).

Cluster	C(<i>p</i> (MVCA-co-St)) (mg/ml)	C(Na ₂ PdCl ₄) (mM)	C(ascorbic acid) (mM)	Ratio MVCA : [PdCl ₄] ²⁻
Pd1- <i>p</i> (MVCA-co-St)		0.5		1:1
Pd2- <i>p</i> (MVCA-co-St)	1	1	10	1:2
Pd3- <i>p</i> (MVCA-co-St)		1.5		1:3
Pd4- <i>p</i> (MVCA-co-St)		2		1:4

Table S2. Size and hydrodynamic diameter of Pd n -*p*(MVCA-co-St) and *p*(MVCA-co-St) determined by TEM and DLS.

	Size estimated by TEM (nm)	Hydrodynamic size (nm)	DLS	Polydispersity index, DLS
Pd1- <i>p</i> (MVCA-co-St)	30	40±1 (92%); 220±50 (8%)		0.25
Pd2- <i>p</i> (MVCA-co-St)	40	60±3		0.10
Pd3- <i>p</i> (MVCA-co-St)	50	80±3		0.10
Pd4- <i>p</i> (MVCA-co-St)	75	100±3 (90%); 820±150 (10%)		0.20
<i>p</i> (MVCA-co-St)	110	140±5		0.27

Table S3. Amount and concentration of Pd in Pd n -*p*(MVCA-co-St), $n = 1-4$ used in the catalytic reduction of *p*-nitrophenol in water at 20 °C.

	N (nmole)	m (µg)	C (µg/ml)	C (mM)
Pd in Pd n - <i>p</i> (MVCA-co-St)	3.2	0.34	0.21	0.002

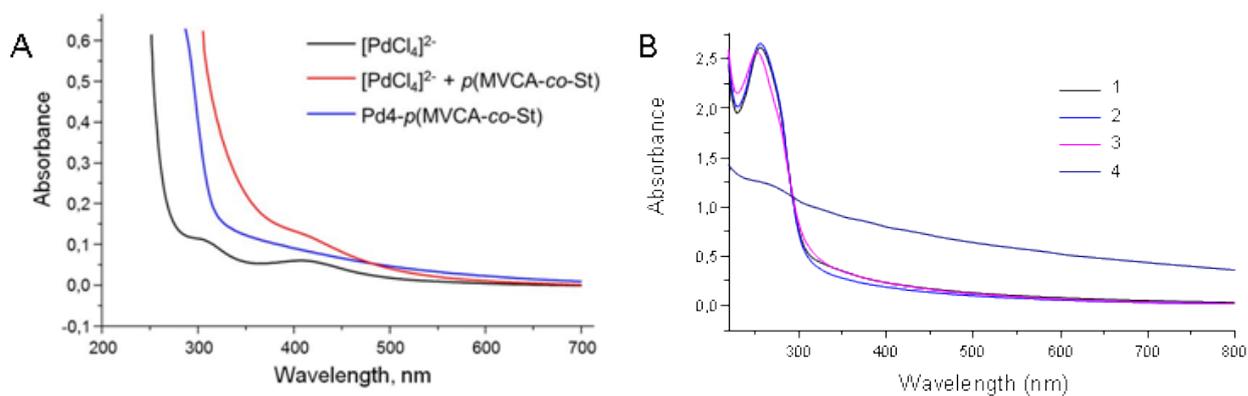


Fig. S1. UV spectra of (A) $\text{Na}_2[\text{PdCl}_4]$ (0.2 mM); a mixture $\text{Na}_2[\text{PdCl}_4]$ (0.2 mM)+ $p(\text{MVCA-co-St})$ (0.1 mg/ml); and $\text{Pd4-}p(\text{MVCA-co-St})$ ($C(\text{Pd}) = 0.06$ mM); (B) $\text{Pd4-}p(\text{MVCA-co-St})$ (0.2 mM) before (1) and after (2) dialysis; after the storage at room temperature for three weeks (3); 0.2 mM Pd NPs isolated from $\text{Pd4-}p(\text{MVCA-co-St})$ by centrifugation (4); (H_2O , 20 °C, $l = 0.5$ cm).

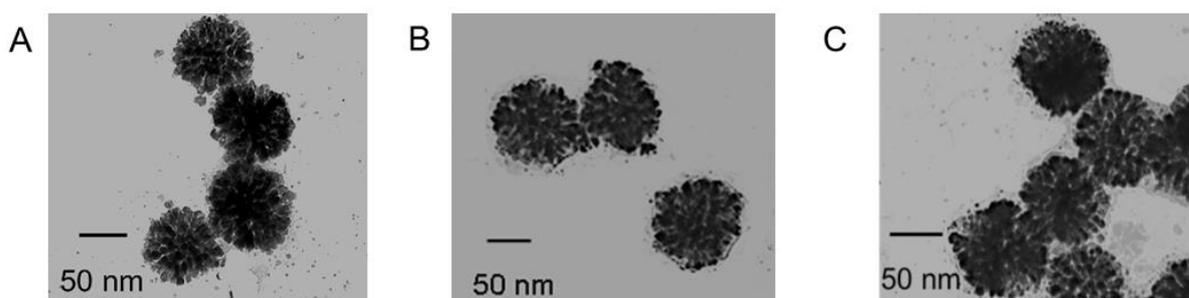


Fig. S2. TEM images of $\text{Pd4-}p(\text{MVCA-co-St})$ before (A) and after dialysis (B), and after the storage at room temperature for three weeks (3).

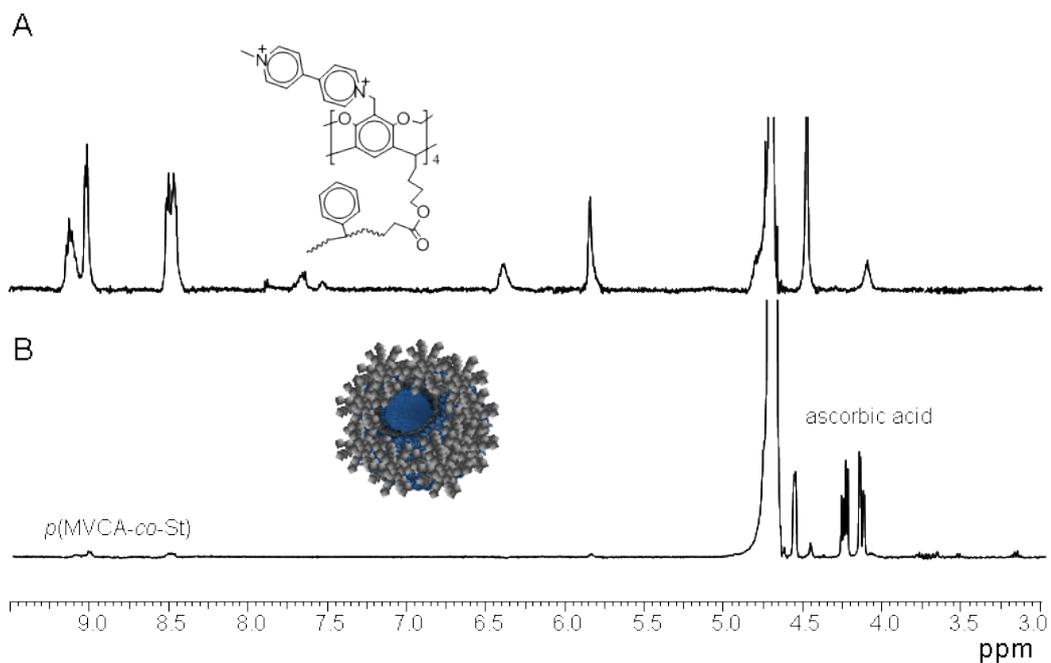


Fig. S3. ¹H NMR spectra of *p*(MVCA-co-St) (A), and Pd₂-*p*(MVCA-co-St) (B), (600 MHz, D₂O, 303K)

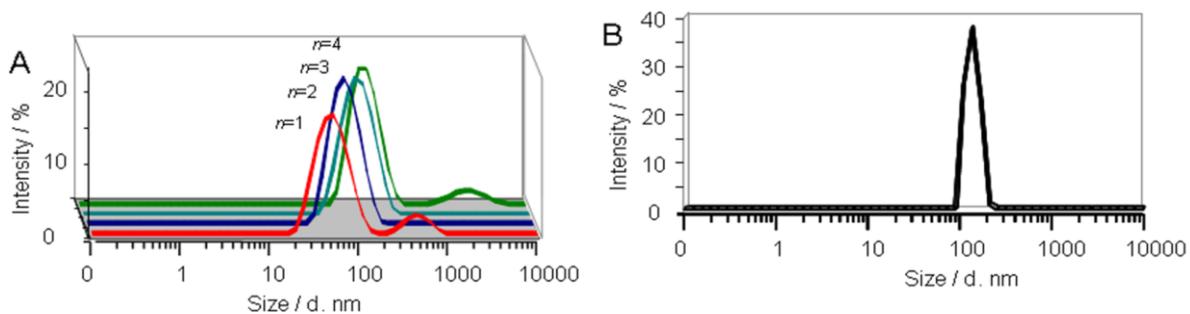


Fig. S4. Particle size distribution of (A) Pdn-*p*(MVCA-co-St), *n* = 1 – 4; and (B) *p*(MVCA-co-St); C = 1 mg/ml, 25 °C, H₂O.

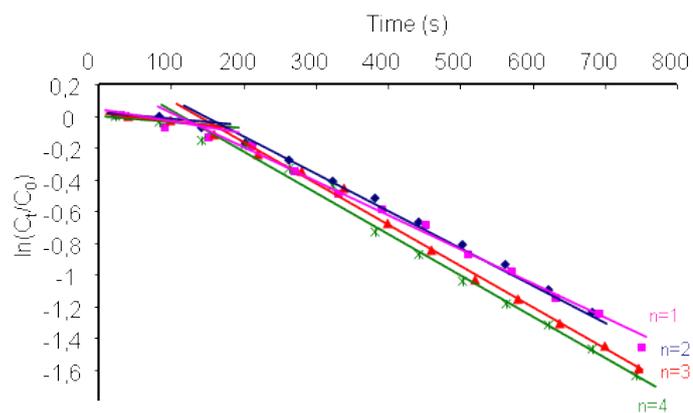


Fig. S5. Plots of $\ln(C_t/C_0)$ versus time of the reduction reaction of *p*-nitrophenol (0.1 mM) with NaBH_4 (5 mM) catalysed by Pd_n -*p*(MVCA-*co*-St) (3.2 nanomole), H_2O , 20 °C.

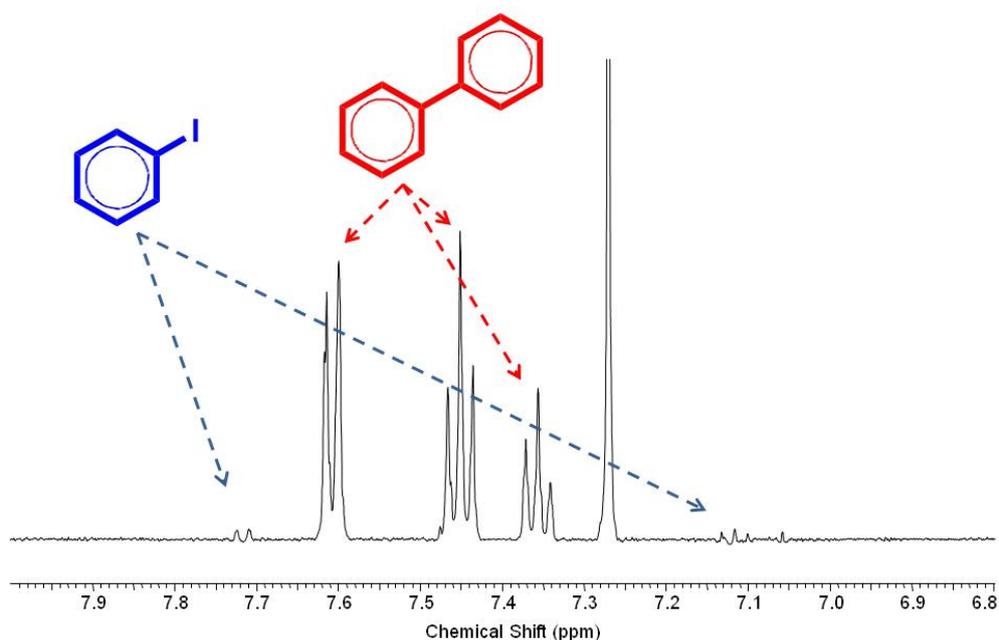


Fig. S6. ^1H NMR spectrum of the Suzuki-Miyaura coupling reaction of iodobenzene (5 mM) with phenylboronic acid (5 mM) catalyzed by 1 mol % Pd_4 -*p*(MVCA-*co*-St) (15 mM K_2CO_3 , H_2O , r.t., 40 h).

1. E. D. Sultanova, E. G. Krasnova, S. V. Kharlamov, G. R. Nasybullina, V. V. Yanilkin, I. R. Nizameev, M. K. Kadirov, R. K. Mukhitova, L. Y. Zakharova, A. Y. Ziganshina and A. I. Konovalov, *ChemPlusChem.*, 2015, **80**, 217 – 222.
2. A. Mohanty, N. Garg and R. Jin, *Angew. Chem. Int. Ed.*, 2010, **49**, 4962 –4966.