Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information for:

Palladium Metal Nanoparticle Size Control through Ion Paired Structures of $[PdCl_4]^{2-}$ with Protonated PDMAEMA

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Contents:

1. Materials

2-Dimethylaminoethylmethacrylate monomer (DMAEMA) 98% was purchased from Sigma-Aldrich. Potassium tetrachloropalladate(II) was purchased from Strem chemicals Inc. Hydrochloric acid (1N), potassium chloride and potassium hydroxide were obtained from Fisher Scientific Inc. and N,N-dimethylformamide, HPLC grade 99.7% was purchased from Alfa Aesar. Deuterated solvents including $CDCl_3$ (99.8%) and D_2O (99.9%) were purchased from Cambridge Isotope Laboratory Inc. All other chemicals and solvents purchased from Sigma-Aldrich and used without further purification.

2. Characterization and methods

^1H NMR spectra were obtained using Bruker 500MHz spectrometers with $CDCl_3$ as solvent and internal standard. All other ^1H NMR studies performed in 1:10 v/v D_2O/H_2O mixtures. Uv-visible spectra of all samples were recorded on a Shimadzu UV-1800 spectrophotometer using 1 cm quartz cells. Measurements of pH were performed by using a Fisher scientific XL 15 pH meter equipped with a thermo scientific Orien micro electrode. GPC measurements were carried out on a Shimadzu LC-20AV liquid chromatography system equipped with PolarGel-M 300 × 7.5 mm column and SPD-20AV UV/vis detector. In order to determine the molecular weight distributions of the polymer, small aliquots of the sample were dissolved in DMF and filtered through a 0.45μm PTFE filter before injection. DMF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C and calibration was based on polystyrene standards. DLS and zeta potential of the samples were measured by using a Zetasizer Nano ZS (Malvern Instruments, Westborough, MA) and the mean diameter of the particles as well as zeta potential were obtained from the instrument's DTS software. For size analysis 1mL of each sample was poured into 1 cm polystyrene cuvettes and all the measurements were performed after 2

minutes of equilibration time at 25 °C. The reported hydrodynamic diameter of each sample results from averaging 15 data points by the instrument DTS software. Zeta potential measurements were performed by using disposable capillary cells (DTS1061). Each sample was poured into to the cell slowly until the level of the solution reached the electrodes of the cell. All measurements were performed after 2 minutes of equilibration time at 25°C. The size of the particles was evaluated by a JEOL JEM-1400 TEM operating at an accelerating voltage of 120 kV. All samples diluted with DI water to 50 μg/mL (relative to K_2PdCl_4 concentration) to reduce aggregation during sample drying process. One drop of each solution was deposited on formvar side of ultra thin carbon type-A 400 mesh copper grid (Ted Pella Inc., Redding, CA) and the droplet was then blotted and allowed to evaporate under ambient conditions over night. Statistical analysis and histograms were obtained by using Origin lab 7.5 software or a minimum of 100 particle counts.

3. Experimental

3.1. Synthesis of Poly(2-(Dimethylamino)ethyl methacrylate) PDMAEMA

Methyl 4-Cyano-4(dodecylsulfanylthiocarbonyl)sulfanyl pentanoate (RAFT 2.2) was synthesized via the reported method [S1] on a reduced scale. RAFT 2.2 was used as the charge transfer agent in the synthesis of homopolymers of PDMAEMA. DMAEMA was passed through a neutral alumina column to remove the inhibitor and AIBN was recrystallized from methanol. A 0.5mL sample of RAFT2.2 (10^{-1}M) and AIBN (2×10^{-2}M) solutions were prepared in acetone and mixed with 8.5 mL of purified monomer (DMAEMA). The reaction mixtures were prepared in vacuum adapted bulbs in a RAFT2.2: initiatior : monomer ratio of 1:0.2:1000. Degassing of the solution was performed by three freeze-pump-thaw cycles on a high vacuum line. The reactions were carried out in 60°C oil bath for 12 hours. After 12 hours the polymerization was quenched by immersion of the

reaction vessel in cold water and the solvent removed under vacuum. The viscous polymer was then dissolved in a small amount of acetone and precipitated in hexane. After collecting the polymer via vacuum filtration, the product was dried on the high vacuum line for 48 hours and characterized by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy **(Figure S1 and S2)**. The number average molecular weight (M_n) of the polymer measured at 37,000 and PDI=1.32.

3.2. ^{1}H NMR study of PDMAEMA protonation in water as a function of pH

5 mL of PDAMEMA aqueous solution (5.72×10^{-5} M; M_n = 37 kDa, *Mw/Mn* = 1.32) , pH=7.9, was titrated by adding small aliquots of HCl (0.1N) to the pH=7.6 and the resulting solution stirred for 5 minutes. 0.5 mL of the solution removed for ^{1}H NMR measurement and the remaining solution titrated dropwise by adding HCl (0.1N) to the pH=6.6. After 5 minutes stirring another 0.5 mL aliquot removed from the solution for ^{1}H NMR measurement. Following the same procedure samples by pH values of 5.9, 5.7, 3.8 and 1.9 prepared for ^{1}H NMR studies. Another portion of PDMAEMA solution (pH=7.9) were titrated similarly with KOH (0.1N) and two samples with pH values of 8.6 and 10.2 prepared for ^{1}H NMR studies. The ^{1}H NMR peaks for the dimethyl amine groups of atactic PDMAEMA in different pH values were obtained and the plot of degree of protonation (α) for PDMAEMA derived for the pH range from 1.9 to 10.2 **(Figure S3 and S4)**.

0.125 mL K_2PdCl_4 (0.04M) in KCl (0.1M) was added to 2.6 mL of partially protonated PDMAEMA at pH= 6.3 and the mixture stirred for 20 minutes. The final pH measured at 5.8. A sample of 0.5 mL of colloidal solution was removed for ^{1}H NMR analysis. The chemical shift of dimethyl amine groups for atactic

PDMAEMA broadened and shifted to 2.64 ppm compared to the polymer solution at pH=7.9 (δ: 2.22 ppm) and partially protonated polymer at pH=6.3, confirming formation of cross linked colloidal particles [S2] (δ: 2.40 ppm) **(Figure S5)**. All ^{1}H NMR measurements performed in 1:10 (v/v) D_2O/H_2O mixture upon addition of 50 μL D_2O into 0.5mL of each sample.

3.3. Study of the effect of pH on the size and stability of the colloidal particles

25.0 mL of PDMAEMA aqueous solution (5.72×10^{-5}M) mixed with 1.0 mL of HCl (0.1N) and stirred at ambient temperature for 20 minutes. Subsequently 1.25 mL of K_2PdCl_4 (0.04M) in KCl (0.1M) added to the mixture and the resulting cloudy solution stirred for another 20 minutes and the pH of the colloid stock solution measured at 5.8 (5). The stock solution was divided into 10 (2.5 mL) aliquots to replicate the previous conditions for pH studies. pH of the acidic solutions (1 to 4) adjusted at by adding 50, 75, 100 and 150 μL of HCl (1N) and the pH measured after 5 minutes stirring as 4.6, 4.4, 3.8 and 2.7 respectively. pH of the basic solutions (6 to 10) adjusted at by adding 20, 100, 200, 300 and 500 μL of KOH (1N) and the pH measured after 5 minutes stirring as 6.2, 6.6, 7.4, 9.4 and 11.1 respectively. DLS and zeta potential measurement of the solutions were performed one day after making samples. The results of these experiments are summarized in **Figures S6** and **S7** and **Table S1**.

3.4. UV-Visible study of K_2PdCl_4 and $(H^+)_nPDMAEMA/[PdCl_4]^{2-}$ colloidal solution titration

0.125 mL K_2PdCl_4 (0.04M) in KCl (0.1M) diluted with 2.6 mL of DI water at pH=5.5 and the electronic spectra recorded. pH of this solution changed slightly by adding small aliquots (~μL) of HCl and KOH (0.1N) in the range of 3.3 to 6.1 and no significant change observed in electronic spectra. For a comparative study colloidal solution of $(H^+)_nPDMAEMA/[PdCl_4]^{2-}$ (1.8×10^{-3} M relative to K_2PdCl_4), prepared following the procedure described in section (3) and the electronic spectra recorded at pH=5.8. Titration of colloidal suspension in to the acidic region, from 6.1 to 3.3, performed by addition of small aliquots (~μL's) of HCl (0.1N) to the colloidal solution and the electronic spectra at each specific pH value recorded after 5 minutes stirring **(Figure S8)** . Back titration of the acidic solution from pH=1.9 to 6.1 performed by adding small amounts KOH (0.1N) and similarly the spectra recorded after 5 minutes stirring **(Figure S9)**. Electronic spectra of all samples recorded after diluting 50 μL of each solution with 3.0 mL DI water.

3.5. Synthesis palladium nanoparticles through ion paired structures of $[PdCl_4]^{-2}$ and protonated PDMAEMA

2.5 mL of PDMAEMA aqueous solution (5.72×10^{-5} M; M_n = 37 kDa, *Mw/Mn* = 1.32), pH=7.9, mixed with 0.1 mL of HCl (0.1M), pH=1.1, and stirred for 20 minutes (pH=6.1). Then 0.125 ml K_2PdCl_4 (0.04M) in KCl (0.1M) added to the mixture and stirred for another 20 minutes at room temperature. The pH of the resulting $(H^+)_nPDMAEMA/[PdCl_4]^{2-}$ colloidal suspension **(Figure S10)** was measured at 5.8. For synthesis of palladium nanoparticles, 0.1 mL of reducing agent aqueous solution (0.1M) added to the colloidal solution containing

PDMAEMA with reducing capability [S3]. The mixture stirred vigorously at room temperature and the reduction followed by UV-Visible spectroscopy for 48 hours. **(figure S11)**. Addition of 0.1 ml citric acid (0.1M), pH=2.3, and complete reduction of the particles resulted in formation of ~5 nm palladium nanoparticles. Addition of citric acid/sodium citrate (1:1) mixture (0.1M), pH=4.2, and sodium citrate (0.1M), pH=7.1 at the same concentration and reaction conditions resulted in formation of ~2.5 nm and ~1.4 nm palladium nanoparticles. The resulting palladium nano particles were stable in solution and no precipitation observed over 3 months. Resulting nanoparticle solutions then characterized by TEM and DLS without further purification **(Figures S12-16)**.

4. Supporting Figures and tables

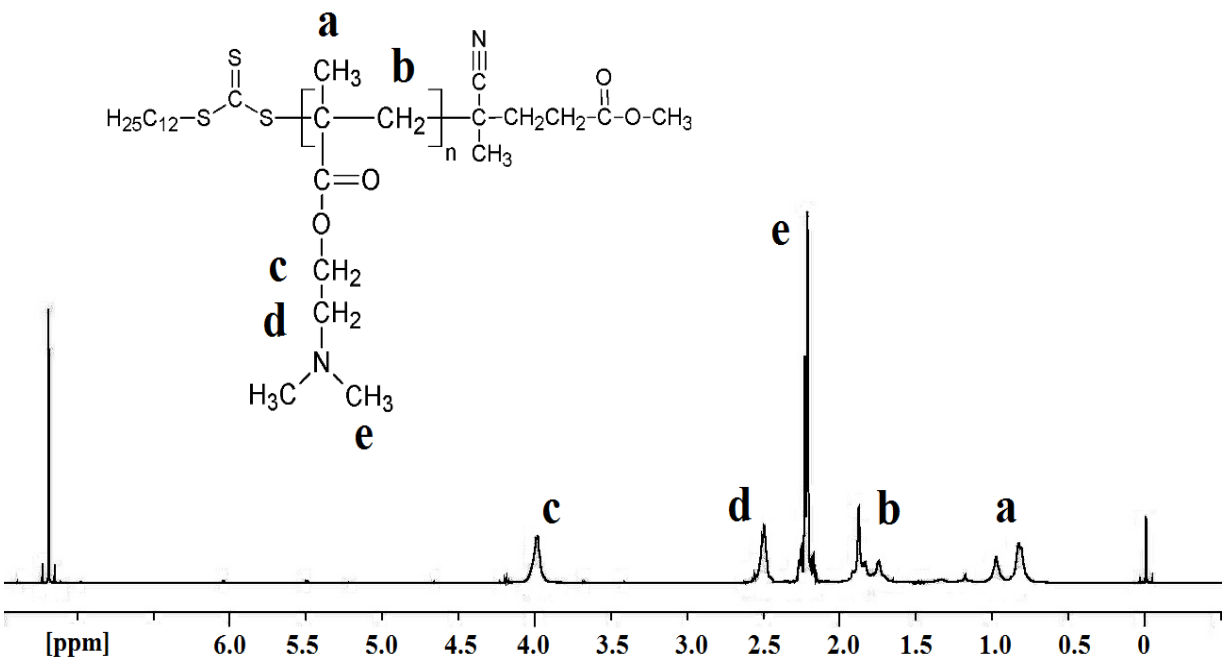

Figure S1. ^{1}H NMR spectra of PDMAEMA in $CDCl_3$ synthesized via RAFT polymerization.

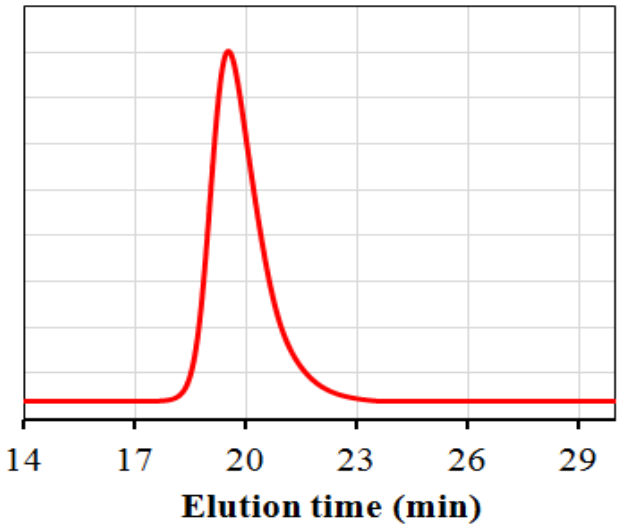

Figure S2. GPC trace for PDMAEMA homopolymer (M_n = 37 kDa, *Mw/Mn* = 1.32) in DMF as eluent.

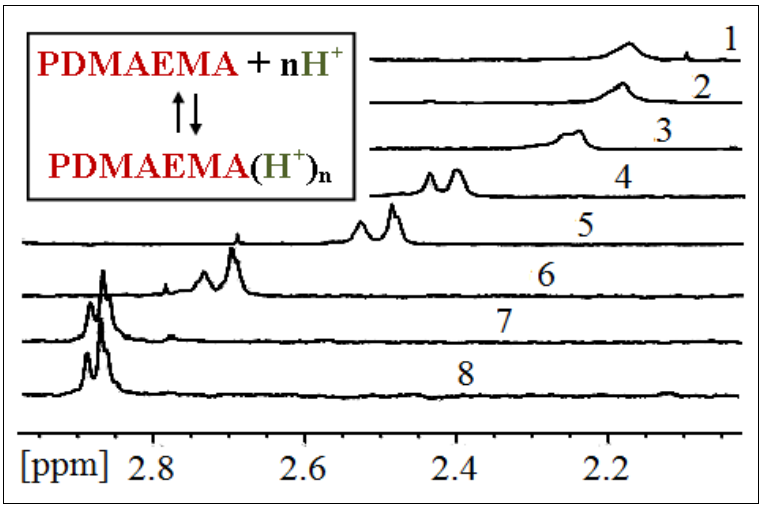

Figure S3. ^{1}HNMR chemical shifts for tertiary amine methyl hydrogens ($(CH_3)_2N$-) of PDMAEMA (5.72×10^{-5} M; M_n = 37 kDa, *Mw/Mn* = 1.32) at a series of pH values, (1) 10.2, (2) 8.6, (3) 7.6, (4) 6.6, (5) 5.9, (6) 5.7, (7) 3.8, (8) 1.9 (1:10 v/v D_2O/H_2O).

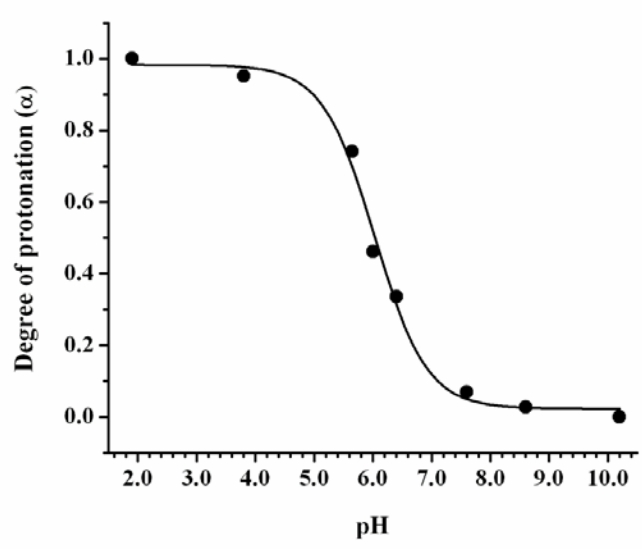

Figure S4. Plot of the degree of protonation (α) of PDMAEMA aqueous solution (5.72×10^{-5} M; M_n = 37 kDa, *Mw/Mn* = 1.32) versus pH. ^{1}HNMR chemical shifts for atactic tertiary amine groups at different pH values: pH=10.2 at 2.18 ppm; pH=8.6 at 2.20 ppm; pH=7.6 at 2.27 ppm; pH=6.6 at 2.44 ppm; pH=5.9 at 2.52 ppm; pH=5.7 at 2.73 ppm; pH=3.8 at 2.88 ppm and pH=1.9 at 2.91 ppm.

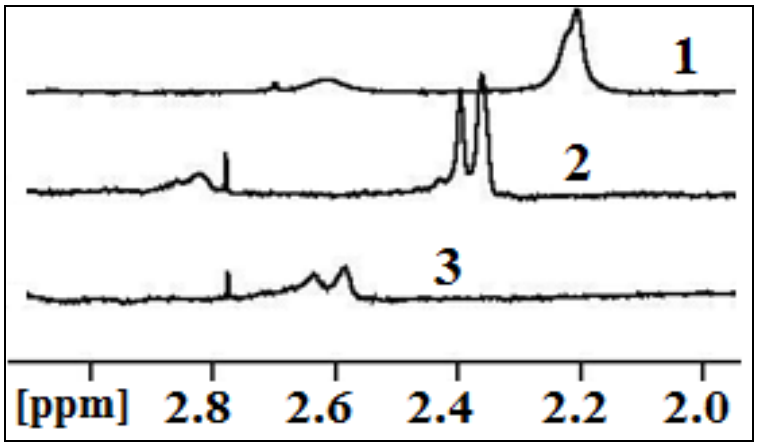

Figure S5. ^{1}H NMR chemical shifts for tertiary amine methyl hydrogens of (1) PDMAEMA at pH= 7.9, δ: 2.22 ppm, (2) PDMAEMA$(H^{+})_{n}$ at pH=6.3, δ: 2.40 ppm and (3) $(H^{+})_{n}$PDMAEMA/$[PdCl_4]^{2-}$ at pH=5.8, δ: 2.64 ppm .

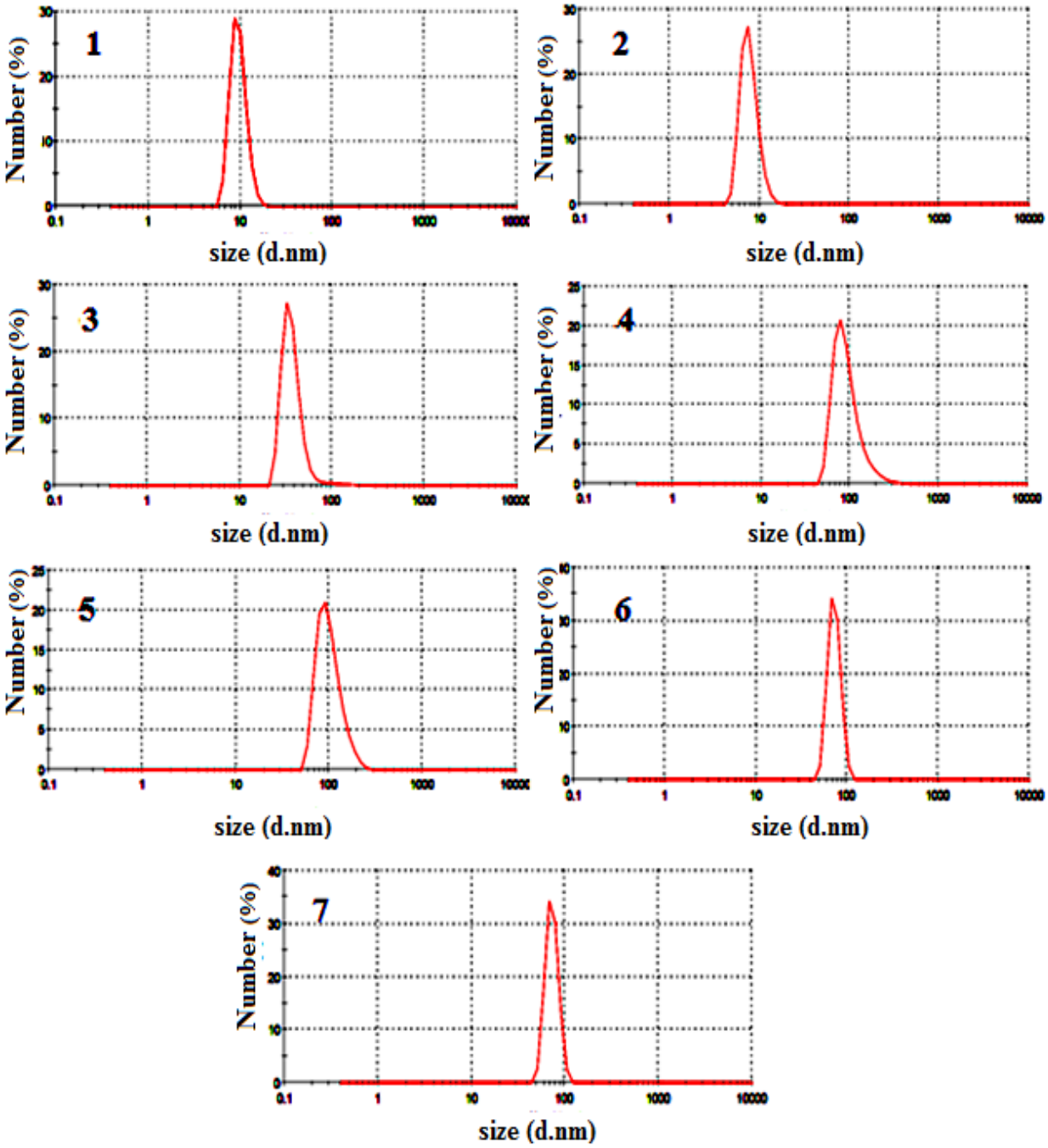

Figure S6. The effect of pH on the size of $(H^+)_n$PDMAEMA/$[PdCl_4]^{2-}$ colloidal particles measured by dynamic light scattering (DLS): (1) pH=2.79, size: 9.1 nm , (2) pH=3.89, size: 7.7 nm, (3) pH=4.46, size: 38.9 nm, (4) pH=4.76, size: 96.3 nm, (5) pH= 5.76, size: 108.2 nm, (6) pH=6.26, size: 102.5 nm, (7) pH=6.63, size 73.2 nm.

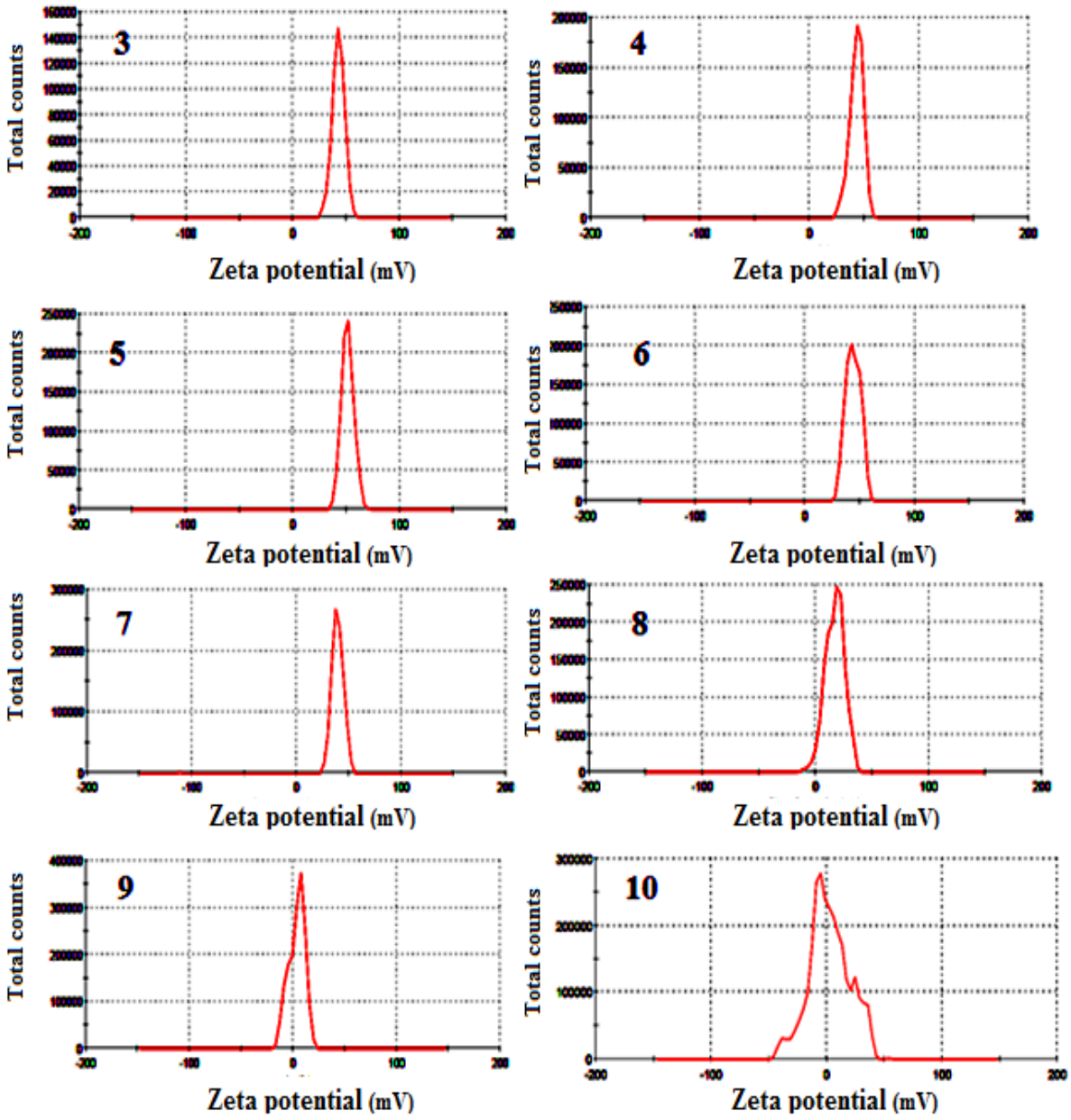

Figure S7. The effect of pH on stability of $(H^+)_nPDMAEMA/[PdCl_4]^{2-}$ colloidal dispersions evaluated by measuring zeta potential value (ζ): (3) pH=4.46, ζ= +42.6 mV, (4) pH=4.67, ζ= +42.7 mV, (5) pH= 5.76, ζ= +50.1 mV (6) pH=6.26, ζ= +43.6 mV, (7) pH=6.63, ζ= +38.9 mV, (8) pH=7.44, ζ= +16.8 mV, (9) pH=9.45, ζ= +3.4 mV, (10) pH=11.12, ζ= +2.3 mV.

Table S1. Summary of the data for the effect of pH on stability and the size of $(H^+)_n$PDMAEMA/$[PdCl_4]^{2-}$ colloidal particles.

#	Solution	pH	Size (d.nm)	ζ (mV)	Result
1	Colloid particles+150 µL HCl	**2.79**	**9.1**	**-**	Disassembled colloid
2	Colloid particles+100 µL HCl	**3.89**	**7.7**	**-**	Disassembled colloid
3	Colloid particles+75 µL HCl	**4.46**	**38.9**	**+42.6**	Colloid about disassembly
4	Colloid particles + 50 µL HCl	**4.67**	**96.3**	**+42.7**	Stable colloid
5	Colloid particles	**5.76**	**108.2**	**+50.1**	Stable colloid
6	Colloid particles+20 µL KOH	**6.26**	**102.5**	**+43.6**	Stable colloid
7	Colloid particles+100 µL KOH	**6.63**	**73.2**	**+38.9**	Colloid about precipitation
8	Colloid particles+200 µL KOH	**7.44**	**-**	**+16.8**	Precipitation
9	Colloid particles+300 µL KOH	**9.45**	**-**	**+3.4**	Precipitation
10	Colloid particles+500 µL KOH	**11.12**	**-**	**+2.3**	Precipitation

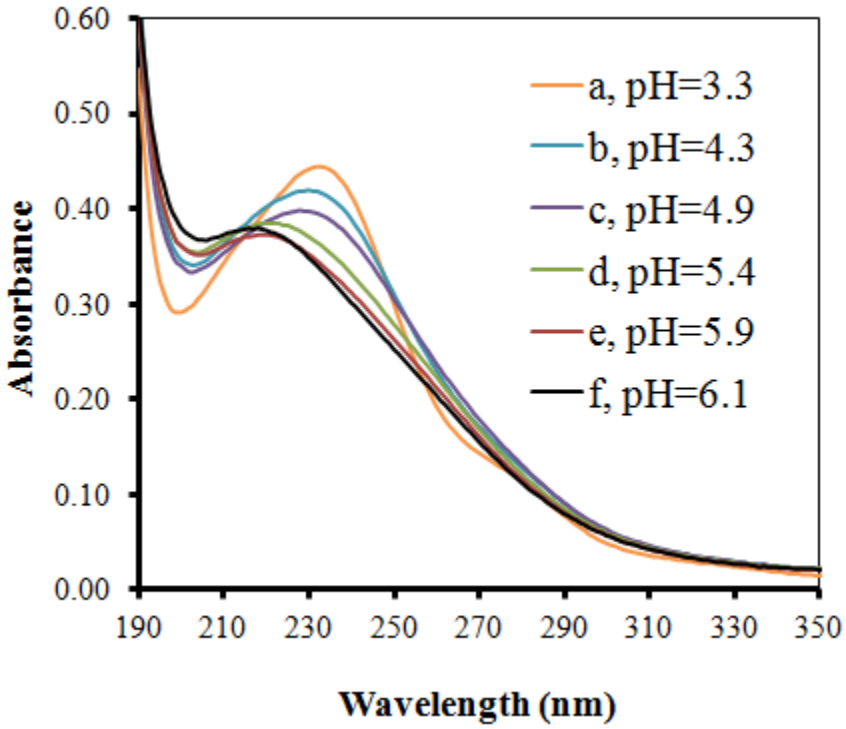

Figure S8. Uv-visible study of $(H^+)_n$PDMAEMA/$[PdCl_4]^{2-}$ colloidal solution titration with HCl (0.1N) in the pH range of 3.3 to 6.1: (a) pH=3.3, λ_{max} (233.0 nm, 0.44), (b) pH=4.3, λ_{max} (231.0 nm, 0.42), (c) pH=4.9, λ_{max} (230.0 nm, 0.39), (d) pH=5.4, λ_{max} (221.0 nm, 0.38), (e) pH=5.9, λ_{max} (218.0 nm, 0.37), (f) pH=6.1, λ_{max} (217.0 nm, 0.38).

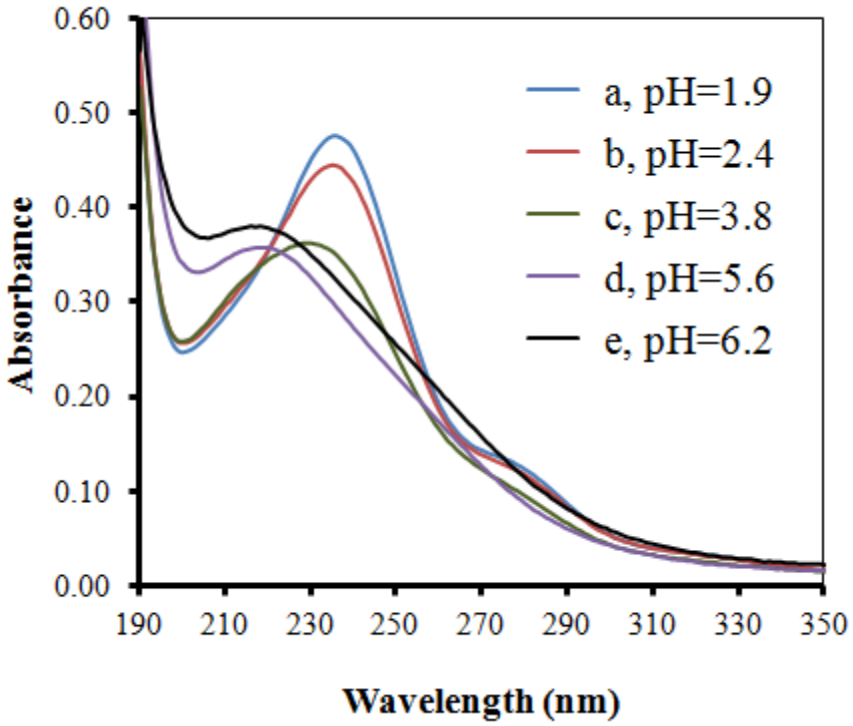

Figure S9. Uv-visible study of acidified $(H^+)_n$PDMAEMA/$[PdCl_4]^{2-}$ colloidal solution back titration with KOH (0.1N) in the pH range of 1.9 to 6.2: (a) pH=1.9, λ_{max} (235.0 nm, 0.47), (b) pH=2.4, λ_{max} (233.0 nm, 0.44), (c) pH=3.8, λ_{max} (232.0 nm, 0.36), (d) pH=5.6, λ_{max} (219.0 nm, 0.35), (e) pH=6.1, λ_{max} (217.0 nm, 0.37).

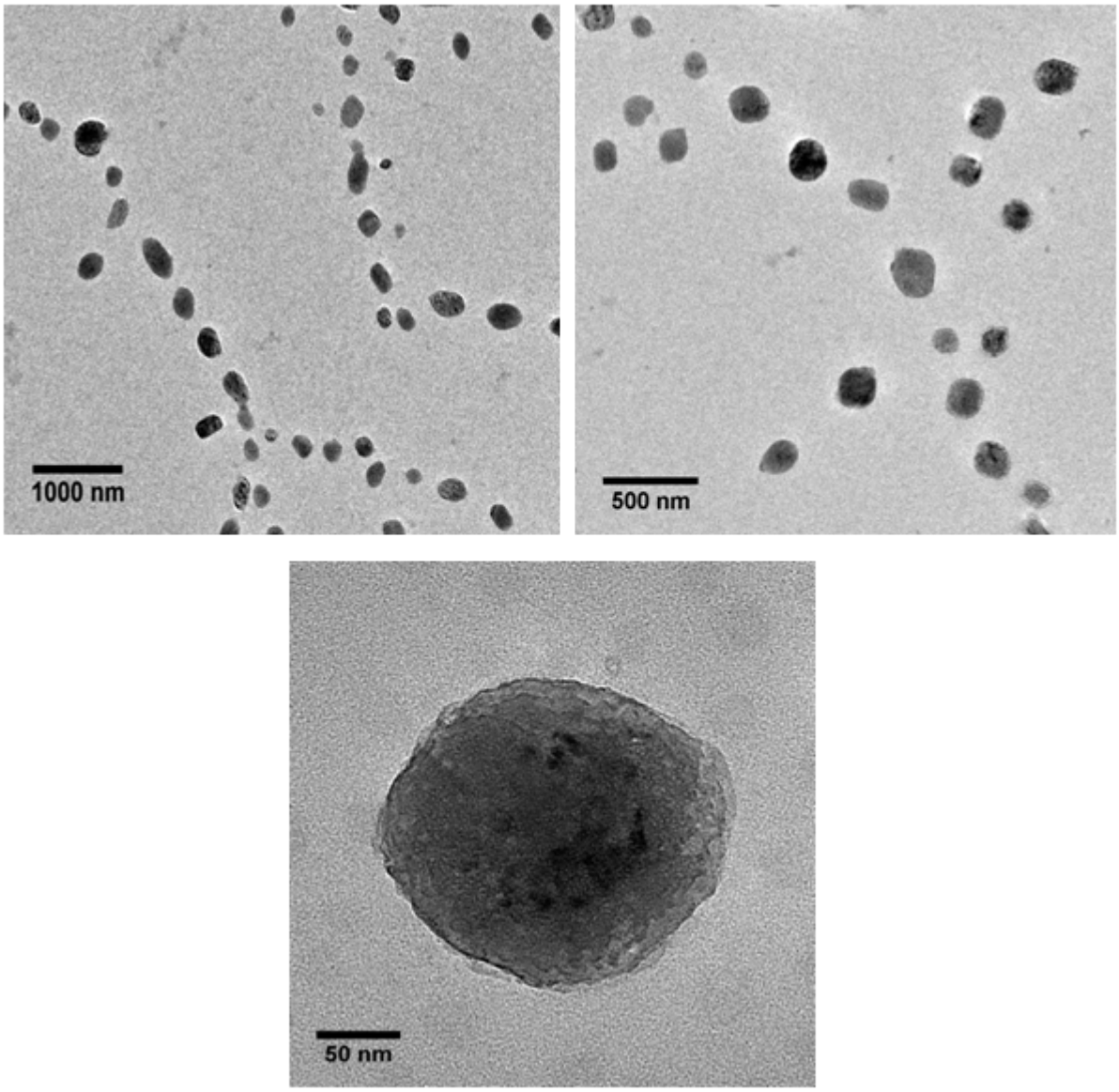

Figure S10. TEM images of $(H^+)_n$PDMAEMA/$[PdCl_4]^{2-}$ colloidal particles resulted from mixing K_2PdCl_4 solution and partially protonated PDMAEMA (5.72×10^{-5} M; M_n = 37 kDa, *PDI* = 1.32)

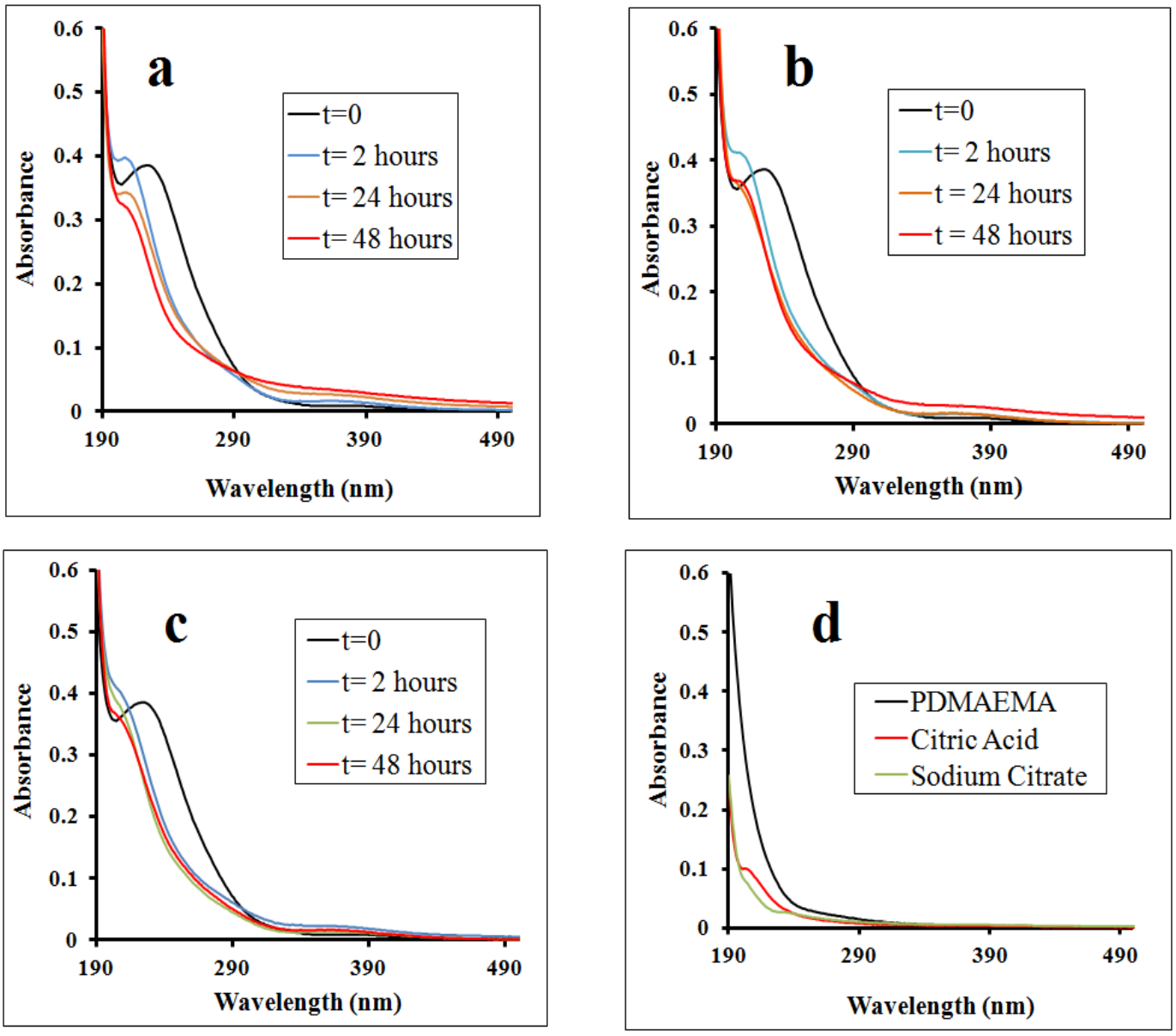

Figure S11. Electronic spectra changes for reduction of Pd^{2+} ions in the presence of PDMAEMA$(H^+)_n$ (5.72×10^{-5} M; M_n = 37 kDa, *PDI* = 1.32) for 48 hours: (a) with 0.1 mL citric acid (0.1M) at pH=3.3, (b) with 0.1mL citric acid/sodium citrate (0.1M) at pH= 4.5, (c) with 0.1 mL sodium citrate (0.1M) at pH=6.3 and (d) Uv-visible spectra of PDMAEMA (5.72×10^{-5} M), citric acid (0.1M) and sodium citrate (0.1M) aqueous solutions.

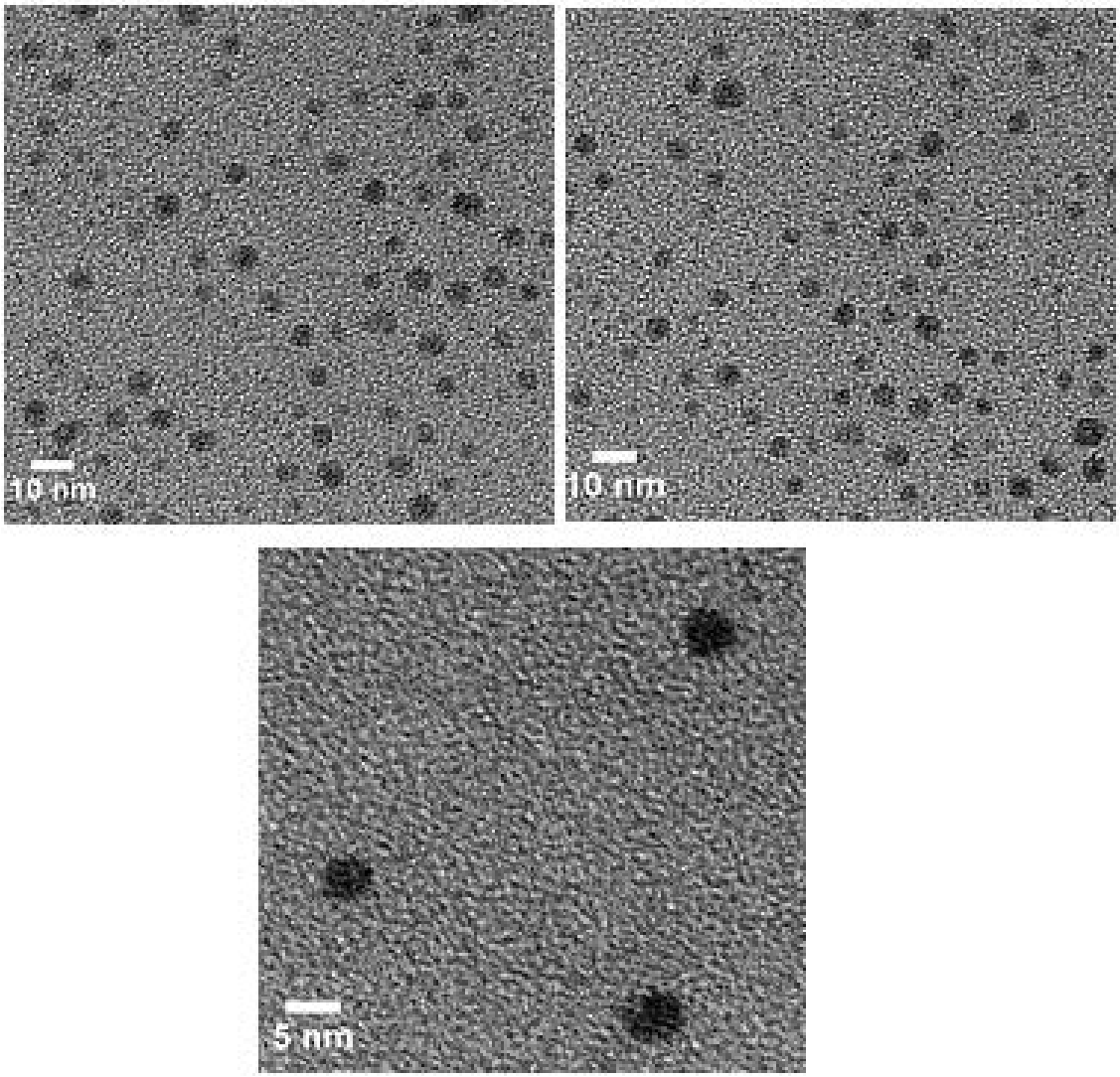

Figure S12. TEM images of palladium nanoparticles, 4.98 ± 0.63 nm, formed at pH= 3.3 reduced by citric acid (0.1M) in the presence of PDMAEMA$(H^+)_n$ (5.72×10^{-5} M; M_n = 37 kDa, *PDI* = 1.32).

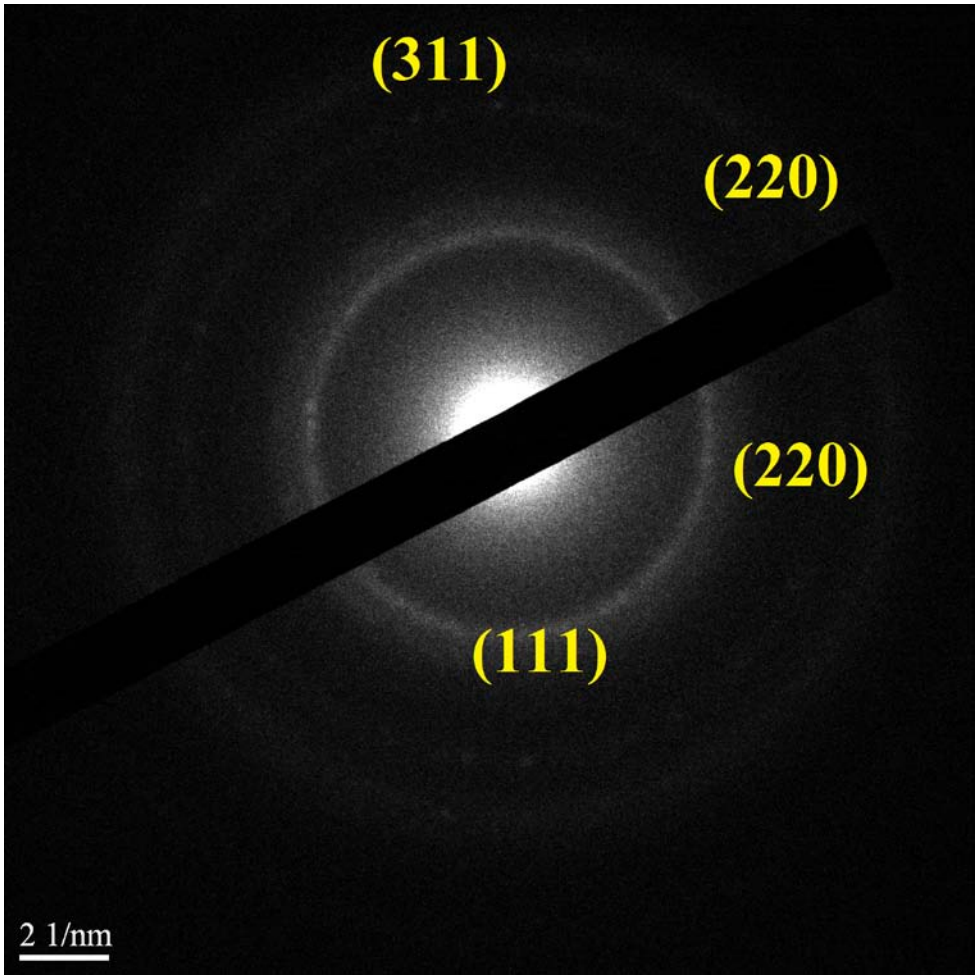

Figure S13. Typical electron diffraction pattern of palladium nanoparticles, 4.98 ± 0.63 nm, formed at pH= 3.3 shown four diffused rings, which were assigned to (111), (200), (220) and (311) reflections of fcc palladium.

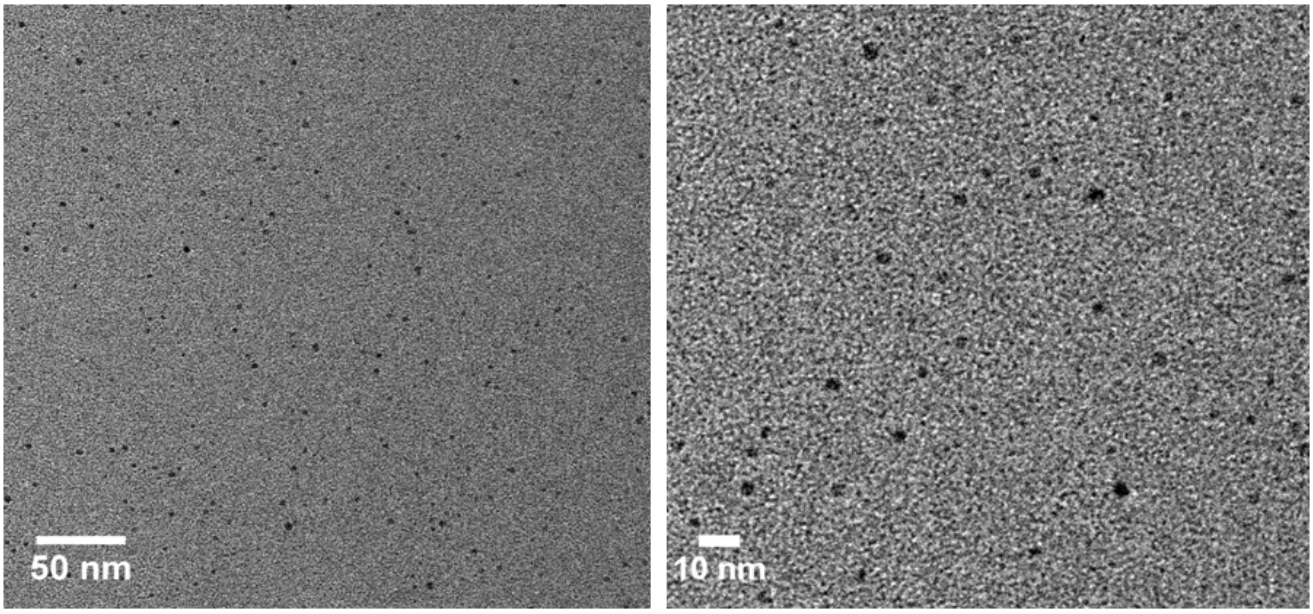

Figure S14. TEM images of palladium nanoparticles, 2.53 ± 0.44 nm, formed at pH= 4.5 reduced by citric acid/sodium citrate (0.1M) in the presence of PDMAEMA$(H^+)_n$ (5.72×10^{-5} M; M_n = 37 kDa, *PDI* = 1.32).

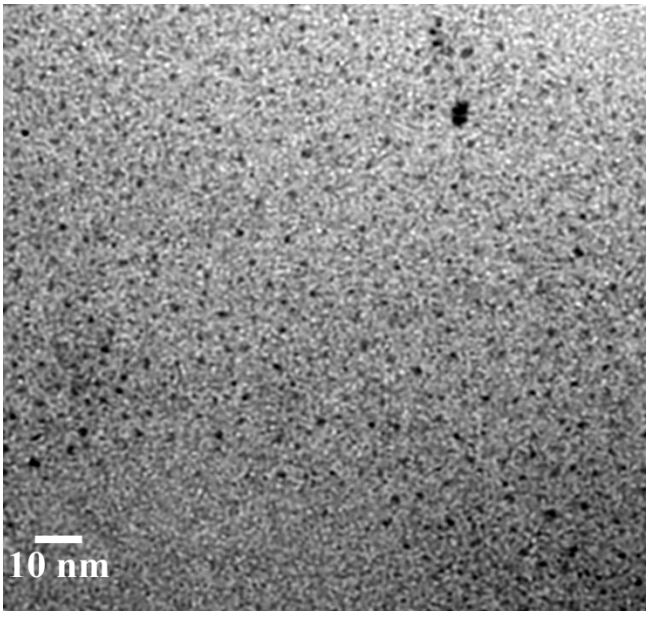

Figure S15. TEM image of palladium nanoparticles, 1.39 ± 0.15 nm, formed at pH= 6.3 reduced by sodium citrate (0.1M) in the presence of PDMAEMA$(H^+)_n$ (5.72×10^{-5} M; M_n = 37 kDa, *PDI* = 1.32)

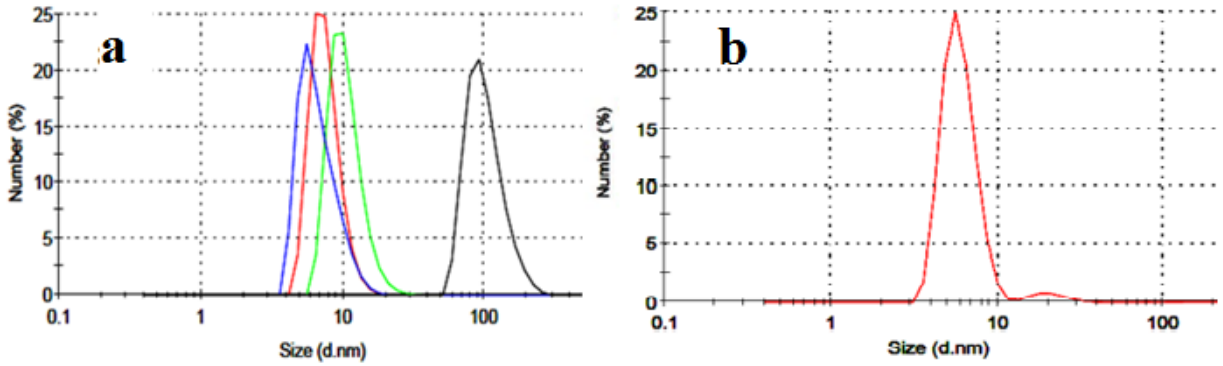

Figure S16. hydrodynamic diameter of the particles in solution measures by DLS (a) before and after reduction: (Black) $(H^+)_n$PDMAEMA/$[PdCl_4]^{2-}$ colloidal solution before adding reducing agent, Size= 108.2 nm, (Green) Solution of Palladium nanoparticles, 1.39 ± 0.15 nm, 48 hours after adding reducing agent at pH= 6.3, Size= 10.0 nm (Blue) Solution of Palladium nanoparticles, 2.53 ± 0.44 nm, 48 hours after adding reducing agent at pH= 4.5, Size= 6.8 nm, (Red) Solution of Palladium nanoparticles, 4.98 ± 0.63 nm, 48 hours after adding reducing agent at pH= 3.3, Size= 7.0 nm. (b) Hydrodynamic diameter of PDMAEMA aqueous solution was measured at 6.5 nm by DLS at pH=7.0, the same plots obtained for titration of PDMAEMA with HCl (0.1N) in the range of 2-8. (Not Shown).

5. References:

(S1) W. B. Farnham and W. Farnham, Synthesis of bis(alkylsulfanylthiocarbonyl) disulfides useful for preparing trithiocarbonate RAFT agents involves reacting thiol, sequentially with sodium or potassium t-butoxide, carbon disulfide and iodine in a solvent mixture. WO2005113493-A1, 11 May 2005.

(S2) T. K. Bronich, P. A. Keifer, L. S. Shlyakhtenko and A. V. Kabanov, *J. Am. Chem. Soc.* 2005, **127**, 8236.

(S3) H. Sun, Z. Gao, L. Yang, L. Gao and X. Lv, *Colloid Polym. Sci.* 2010, **288**, 1713; H. Sun, Z. Gao, L. Gao and K. Hou, *J. Macromol. Sci., Part A, Pure & Appl. Chem.* 2011, **48**, 291; C. Feng, L. Gu, D. Yang, J. Hu, G. Lu and X. Huang, *Polymer* 2009, **50**, 3990; L. Longenberg and G. Mills, *J. Phys. Chem.* 1995, **99**, 475.