ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Facile, one-pot, *in aqua* synthesis of catalytically competent gold nanoparticles using pyrogallol[4]arene as the sole reagent

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Experimental Section

Materials and reagents

All experiments were carried out using ultrapure Millipore water purified to a resistivity of 18.2 MΩ cm. Acetaldehyde (402788, ≥95.0%), butyraldehyde (538191, ≥99.0%, dry), valeraldehyde (110623, ≥97%), hexanal (W255718, ≥97.0%), octanal (05608, ≥99.0%), hydrochloric acid (258148, 37.0%), gold(III) chloride (520918, ≥99.9%), 4-nitrophenol (241326, ≥99%), and sodium borohydride (480886, 99.99%) were all purchased from Sigma-Aldrich (St. Louis, MO). Methanol (A452SK, HPLC Grade) and ethyl acetate (E195SK, HPLC Grade) were purchased from Fisher Scientific (King of Prussia, PA). Pyrogallol (22779, 99.90%) was purchased from CHEM-IMPEX INT'L INC. (Wood Dale, IL).

Characterization techniques

UV–vis spectra were measured in 1 cm path length disposable poly(methyl methacrylate) (PMMA) cuvettes using a Cary 50 Bio UV–vis spectrophotometer. Transmission electron microscopy (TEM) was conducted on carbon-coated copper grids (Ted Pella, Inc. 01814-F, support films, carbon type-B, 400 mesh copper grid) using an FEI Tecnai (F20) microscope operating at a 200 keV accelerating electron voltage. At least 300 particles were analyzed for each sample using ImageJ to generate particle size histograms.

Synthesis of pyrogallol[4]arenes

1.00 g (8 mmol) of pyrogallol was mixed with 0.55 g (8 mmol) of 2,3-dihyroxyfuran and 10 mL of methanol (MeOH) in a 100 mL round-bottom flask and refluxed at 60 °C for 5 min to obtain a clear solution. 5 drops of concentrated HCl was then added to the clear reaction mixture and the solution was left to reflux at the same temperature for 24 h, forming solid product. Upon cooling, the crude solid product was vacuum filtered and washed twice with 5 mL of cold methanol followed by vacuum drying of the solid product for 12 h to obtain a net yield of 60% (0.92 g). PgC_3, PgC_5, and PgC_7 were also synthesized following the same procedure taking equimolar quantities of pyrogallol and butyraldehyde, valeraldehyde, or heptanal in methanol with the reflux being carried out at a higher temperature of 110 °C.

Synthesis of gold nanoparticles

In a typical synthesis, 100 µL each of 50 mM aqueous PgC_R solution and X M aqueous NaOH solution (where X is dependent upon the desired molar ratio of PgC_R:NaOH) were added to 19.70 mL of water in a falcon tube and vortex mixed (Thermo Scientific Vortex Maxi Mix II) for 10 s followed by the addition of 100 µL of 0.5 M aqueous $HAuCl_4$ solution (the aqueous dispersion of PgC_3 was sonicated for 45 min before pipetting to obtain a homogenous milky dispersion). The reaction mixture was quickly homogenized by vortex mixing to obtain a pink or red AuNP solution. UV–vis spectra were collected for these solutions in 1 cm path length disposable poly(methyl methacrylate) (PMMA) cuvettes using a Cary 50 Bio UV–vis spectrophotometer. Similarly, AuNP synthesis using PgC_3OH as the reducing/stabilizing agent was carried out supplementing sodium methoxide (CH_3ONa) and pyridine for NaOH using a base:PgC_3OH ratio of 10:1.

Purification of AuNPs

The unreacted PgC_R and other reduced organic products in the AuNPs solutions were removed by passing the AuNP solutions through a NAP-5 column. After equilibrating the column with 10 mL of ultrapure Millipore water, about 7 mL of AuNP solution was passed through the column and collected in a vial for TEM imaging and catalytic studies.

4-NP reduction catalysis

The sodium borohydride-assisted reduction of 4-nitrophenol (4-NP) was used as a model reaction to study the catalytic activity of the PgC_R-AuNPs which had aged for 5 d. As reported in a previous study,[1] 2.10 mL of 0.20 mM aqueous 4-NP and 0.90 mL of freshly prepared 100 mM aqueous $NaBH_4$ were mixed in a 4 mL PMMA cuvette (1 cm path length) to obtain a yellow solution of 4-nitrophenolate. The catalyzed reaction was triggered by the addition of 84 µL of 0.25 mM PgC_R-AuNP solution (that is, the [Au] is 0.25 mM), making a final solution containing 5 mol% Au relative to 4-NP. The cuvette with the final solution was mixed through gentle inversion and the progress of the reaction was monitored spectrophotometrically at a fixed wavelength of 400 nm (λ_{max} for the 4-nitrophenolate ion). The apparent rate constants were calculated from the linear correlation of $\ln(A_0/A_t)$ *versus* time. To recycle the catalyst, a completed reduction was spiked with 90 µL of 1.0 M $NaBH_4$ and 84 µL of 5.0 mM 4-NP and thoroughly mixed with gentle inversion to restart the reaction. This was performed five consecutive times using the same sample and corresponding aliquot of catalyst.

Table S1. The pH values of the NaOH:PgC_R reaction mixtures before and after addition of $HAuCl_4$ solution.

PgC_R	**NaOH:PgC_R**	**pH**	
		Before $HAuCl_4$ addition	**After $HAuCl_4$ addition**
PgC_3	0:1	5.59	3.18
PgC_3	1:1	8.76	3.31
PgC_3	2:1	9.40	3.44
PgC_3	10:1	9.97	7.44
PgC_3	20:1	10.83	10.15
PgC_3OH	0:1	4.39	3.20
PgC_3OH	1:1	4.44	3.28
PgC_3OH	2:1	5.46	3.41
PgC_3OH	10:1	10.03	7.43
PgC_3OH	20:1	10.36	10.30
PgC_5	0:1	5.56	3.28
PgC_5	1:1	7.02	3.28
PgC_5	2:1	7.38	3.45
PgC_5	10:1	9.97	8.02
PgC_5	20:1	10.92	10.57
PgC_7	10:1	10.63	9.28
PgC_7	20:1	10.96	9.77

Table S2. Absorption maxima, full width @ 75% peak maximum (FW@0.75 max) and extinction values of AuNPs obtained in aged PgC$_R$ using different NaOH:PgC$_R$ molar ratios.

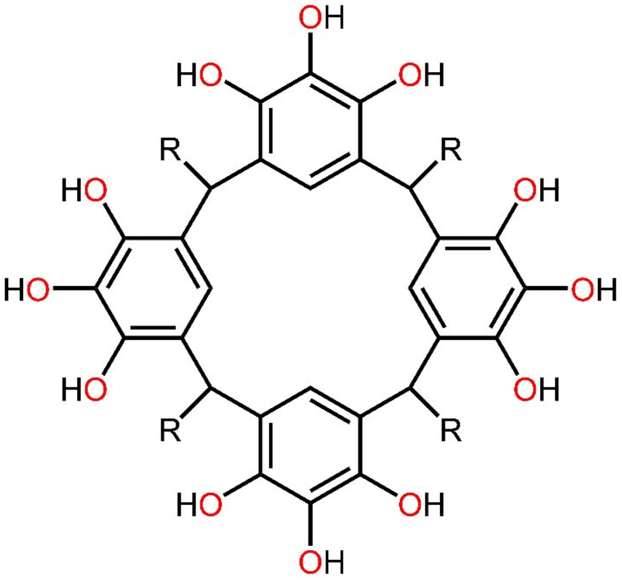
NaOH:PgC$_R$	**PgC$_R$**	**LSPR$_{max}$ (FW@0.75 max), nm; extinction**				
		fresh	**5 d**	**10 d**	**20 d**	**30 d**
0:1	PgC$_3$	539 (61); 0.88	540 (58); 0.91	537 (52); 0.94	537 (53); 0.96	536 (52); 0.65
	PgC$_3$OH	535 (59); 1.10	535 (58); 0.94	535 (58); 1.02	536 (59); 1.07	536 (59); 0.77
	PgC$_5$	536 (a); 0.46	537 (a); 0.43	535 (73); 0.46	534 (65); 0.56	532 (57); 0.64
1:1	PgC$_3$	534 (93); 0.85	530 (83); 0.90	530 (80); 0.90	531 (69); 0.88	531 (69); 0.88
	PgC$_3$OH	522 (65); 0.88	523 (65); 0.88	522 (66); 0.87	523 (67); 0.89	523 (67); 0.89
	PgC$_5$	544 (a); 0.56	539 (a); 0.53	537 (84); 0.54	536 (71); 0.63	533 (65); 0.69
2:1	PgC$_3$	527 (87); 0.99	527 (82); 0.97	528 (77); 0.93	529 (76); 0.92	529 (76); 0.93
	PgC$_3$OH	523 (57); 0.95	523 (56); 0.95	523 (57); 0.95	524 (58); 0.95	524 (58); 0.95
	PgC$_5$	543 (a); 0.67	537 (a); 0.63	535 (84); 0.63	533 (85); 0.63	533 (85); 0.64
10:1	PgC$_3$	525 (72); 0.89	523 (70); 0.89	522 (72); 0.91	520 (70); 0.87	520 (69); 0.88
	PgC$_3$OH	521 (71); 0.88	521 (70); 0.87	520 (70); 0.87	520 (69); 0.87	520 (68); 0.87
	PgC$_5$	547 (90); 1.13	547 (87); 1.10	547 (86); 1.08	548 (86); 1.08	547 (85); 1.08
	PgC$_7$	539 (98); 0.48	538 (93); 0.56	532 (77); 0.73	532 (74); 0.74	532 (74); 0.73
20:1	PgC$_3$	522 (91); 0.85	522 (88); 0.84	523 (86); 0.84	523 (87); 0.86	523 (86); 0.86
	PgC$_3$OH	520 (73); 0.93	519 (78); 0.88	519 (77); 0.88	519 (74); 0.88	519 (72); 0.88
	PgC$_5$	538 (75); 1.08	537 (74); 1.08	537 (73); 1.08	538 (72); 1.10	539 (72); 1.10
	PgC$_7$	531 (79); 0.53	530 (78); 0.53	530 (77); 0.52	531 (67); 0.54	530 (67); 0.53

[a] No discernable full width at 0.75 max.

Table S3. Spectroscopically-determined plasmonic values and catalytic rate for 4-NP reduction for PgC_3OH-AuNPs synthesized in the presence of various bases.

Base:PgC_3OH (molar ratio)	**Base**	**$LSPR_{max}$ (FW@0.75 max), nm; extinction**		**4-NP reduction k_{app} (s^{-1})**
		First batch	**Second batch**	
10:1	$NaOCH_3$	519 (80); 2.92	520 (79); 2.93	1.48 (±0.02) × 10^{-2}
10:1	NaOH	520 (71); 2.70	520 (70); 2.92	1.15 (±0.03) × 10^{-2}
10:1	Pyridine	538 ([a]); 1.23	539 ([a]); 1.24	Unstable[b]

[a] No discernable full width at 0.75 max. [b] Aggregate formation precludes the use of these AuNPs for catalysis.



PgC_3
R = $-CH_2-CH_2-CH_3$

PgC_3OH
R = $-CH_2-CH_2-CH_2-OH$

PgC_5
R = $-CH_2-CH_2-CH_2-CH_2-CH_3$

PgC_7
R = $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

Fig. S1 Chemical structure of the *C*-alkyl pyrogallol[4]arenes studied in this work.

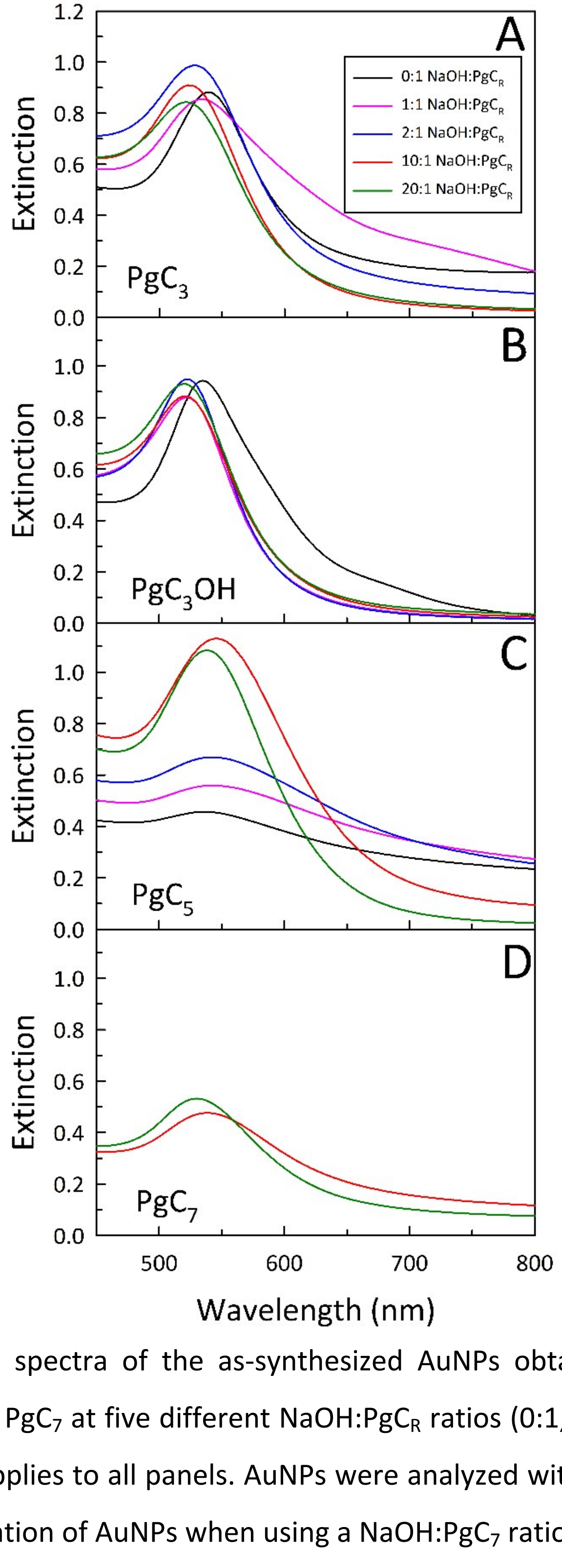


Fig. S2 UV–vis extinction spectra of the as-synthesized AuNPs obtained using (A) PgC$_3$, (B) PgC$_3$OH, (C) PgC$_5$, and (D) PgC$_7$ at five different NaOH:PgC$_R$ ratios (0:1, 1:1, 2:1, 10:1, and 20:1). The legend in panel (A) applies to all panels. AuNPs were analyzed within 3 h of synthesis. PgC$_7$ did not result in the formation of AuNPs when using a NaOH:PgC$_7$ ratio below 10:1.

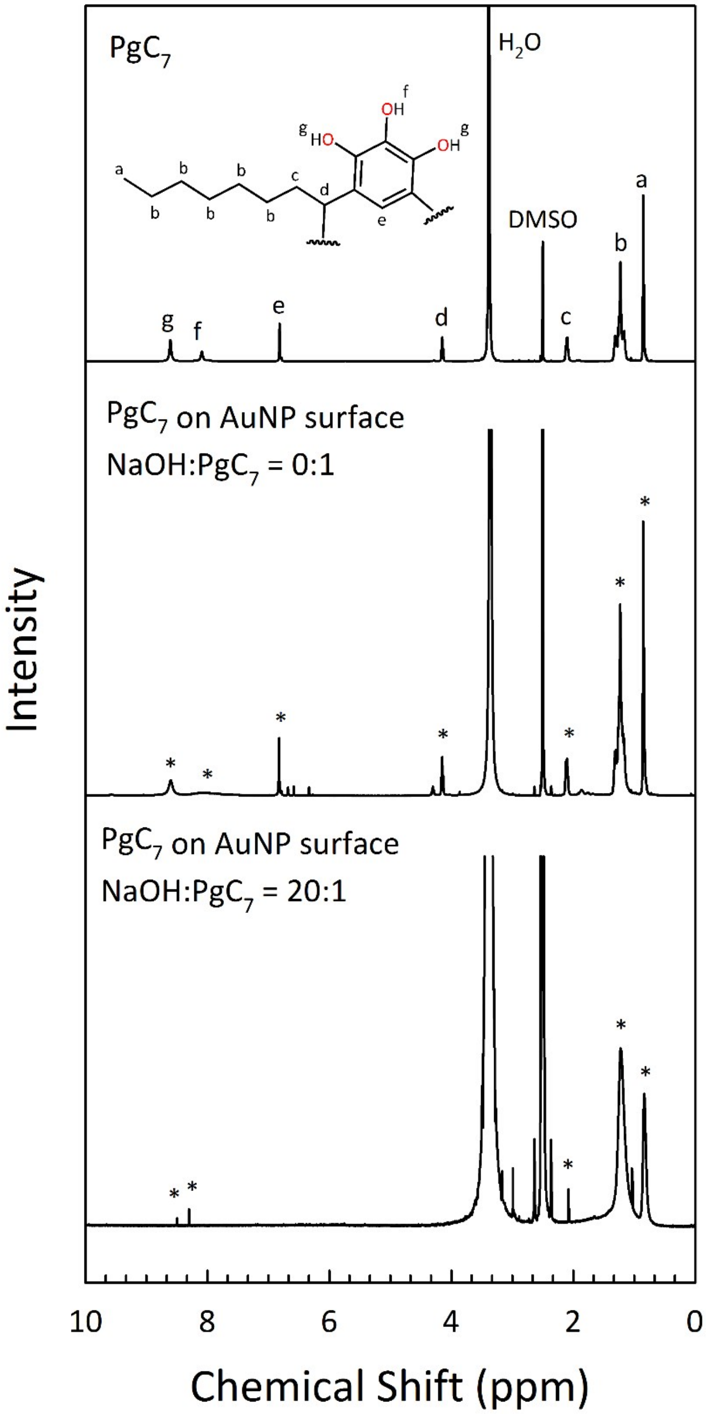


Fig. S3 ^{1}H-NMR spectroscopic analysis of PgC_7 (A) pristine, (B) when used to produce AuNPs absent NaOH, and (C) when used in conjunction with NaOH to produce AuNPs. Notably, in (C) the phenolic hydrogens are absent and peaks “d” and “e” are pushed downfield beyond 8 ppm, indicating the formation of phenoxide.

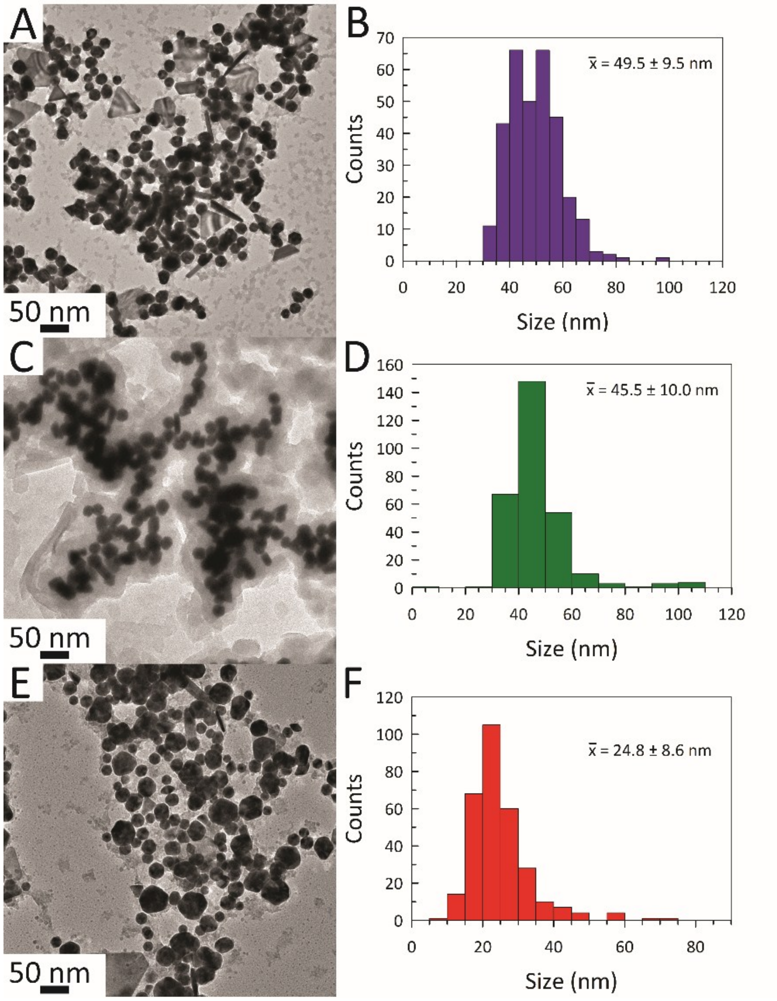


Fig. S4 Representative TEM micrographs (A, C, E) of AuNPs obtained in PgC_3, PgC_3OH, and PgC_5, respectively, in absence of NaOH solution, alongside their respective particle size distribution histograms (B, D, F). PgC_7 did not result in the formation of AuNPs in absence of NaOH solution.

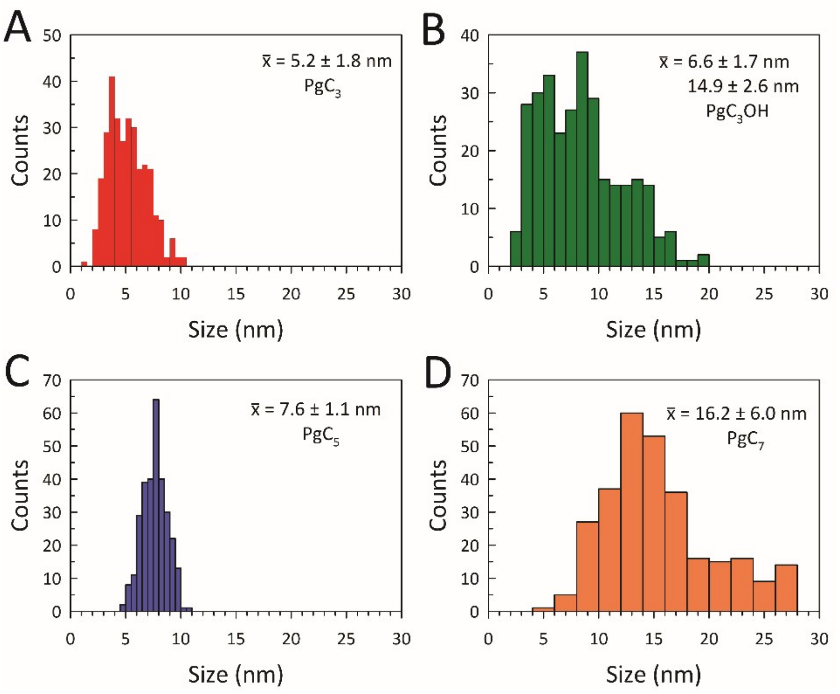


Fig. S5 Histograms showing AuNPs sizes (~300 AuNPs counted in each case) for (A) PgC_3, (B) PgC_3OH, (C) PgC_5, and (D) PgC_7 (representative TEM images can be found in Fig. 2) for a NaOH to PgC_R ratio of 10:1.

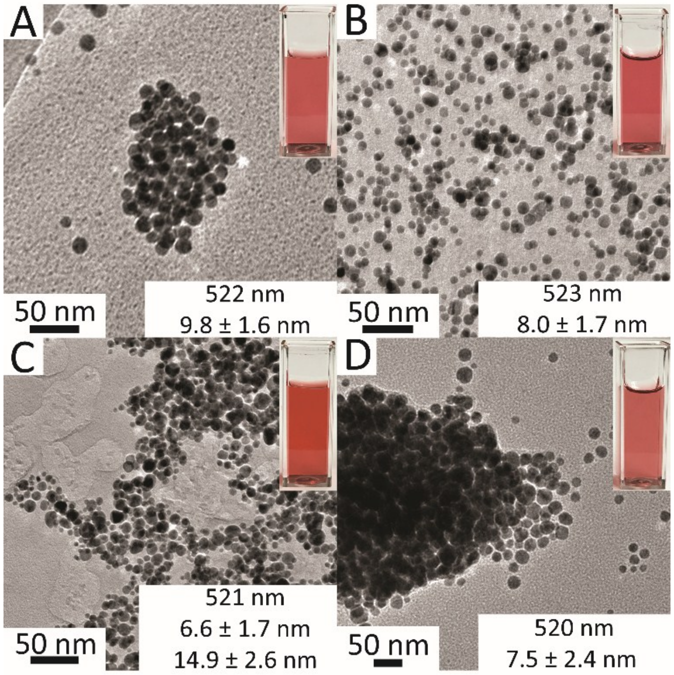


Fig. S6 TEM micrographs of PgC_3OH-AuNPs synthesized in a solution containing a NaOH:PgC_R molar ratio of (A) 1:1, (B) 2:1, (C) 10:1, and (D) 20:1. The inset in each panel shows photographs, λ_{max}, and average AuNP sizes of the respective solutions.

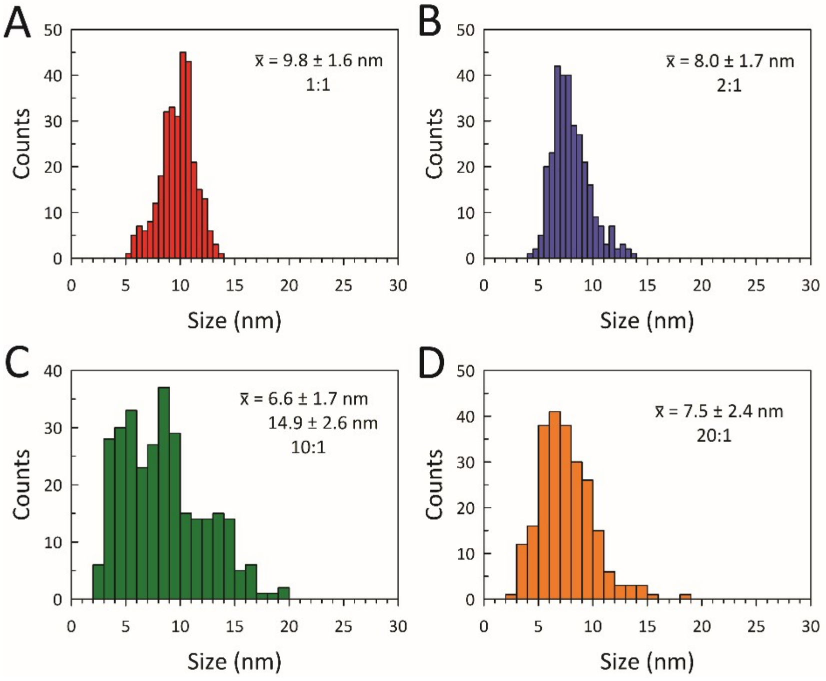


Fig. S7 Histograms of PgC_3OH-AuNPs synthesized in a solution containing a NaOH:PgC_R molar ratio of (A) 1:1, (B) 2:1, (C) 10:1, and (D) 20:1.

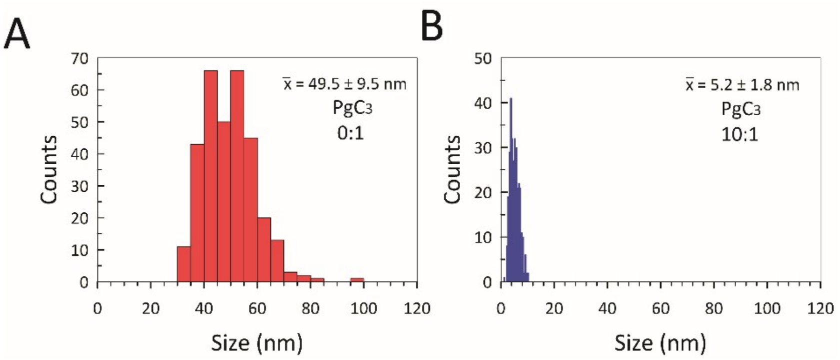


Fig. S8 Histograms for PgC_3-AuNPs (A) without addition of NaOH and (B) with a NaOH:PgC_3 molar ratio of 10:1.

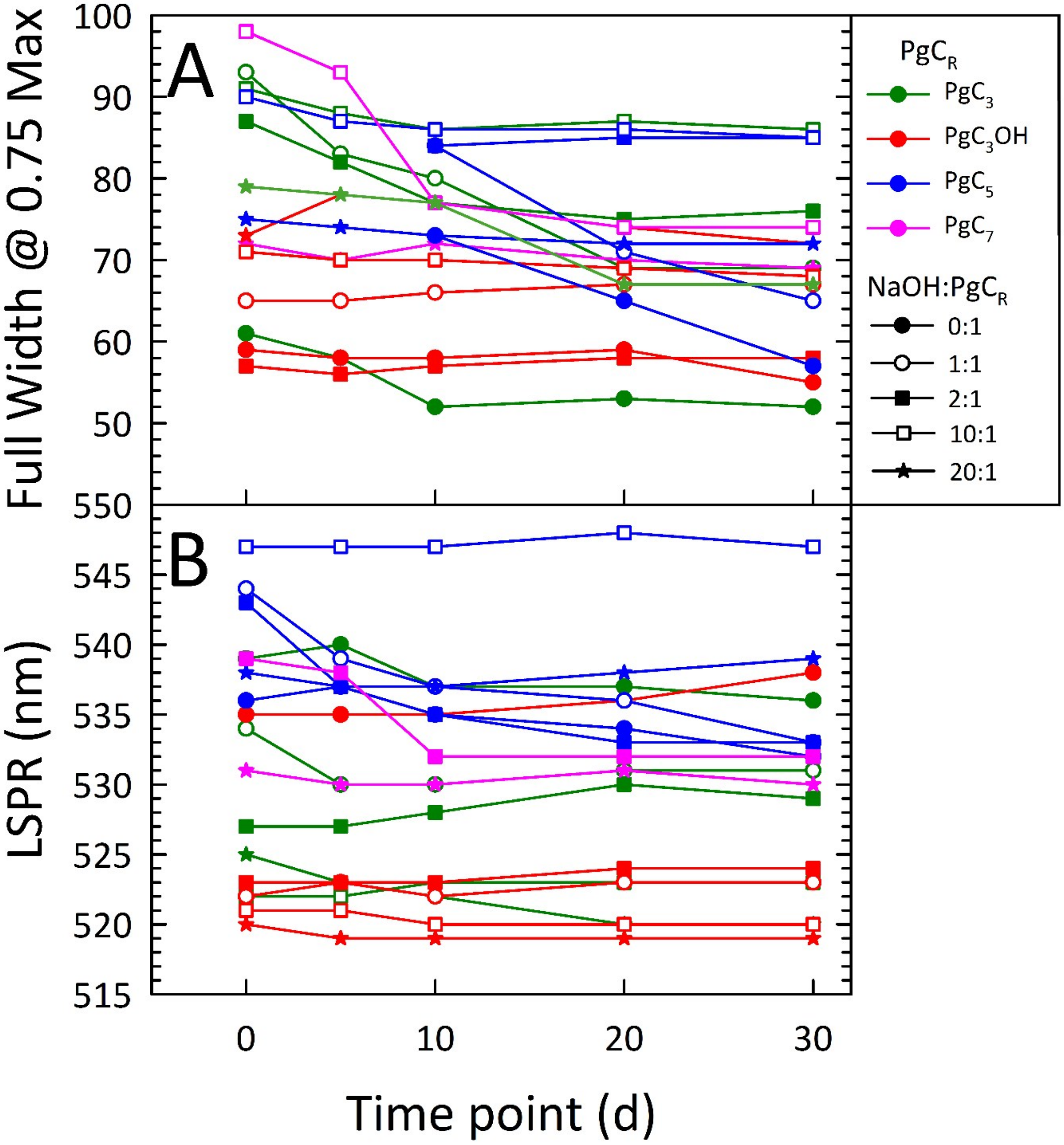


Fig. S9 (A) Full width at 75% peak maximum (FW@0.75 max) and (B) localized surface plasmon resonance (LSPR) band maxima values extracted from the normalized spectra of the AuNPs obtained using PgC_3, PgC_3OH, PgC_5, and PgC_7 at five different NaOH:PgC_R ratios (0:1, 1:1, 2:1, 10:1, and 20:1) plotted against time. The legends in panel (A) applies to all panels. The LSPR and FW@0.75 max values for AuNPs obtained at higher NaOH:PgC_R ratios remain relatively constant over the monitored aging period. These values for AuNPs obtained using PgC_3, PgC_5, and PgC_7 for a lower NaOH to PgC_R ratio allude to morphological changes over time, particularly within the initial 10 d following synthesis.

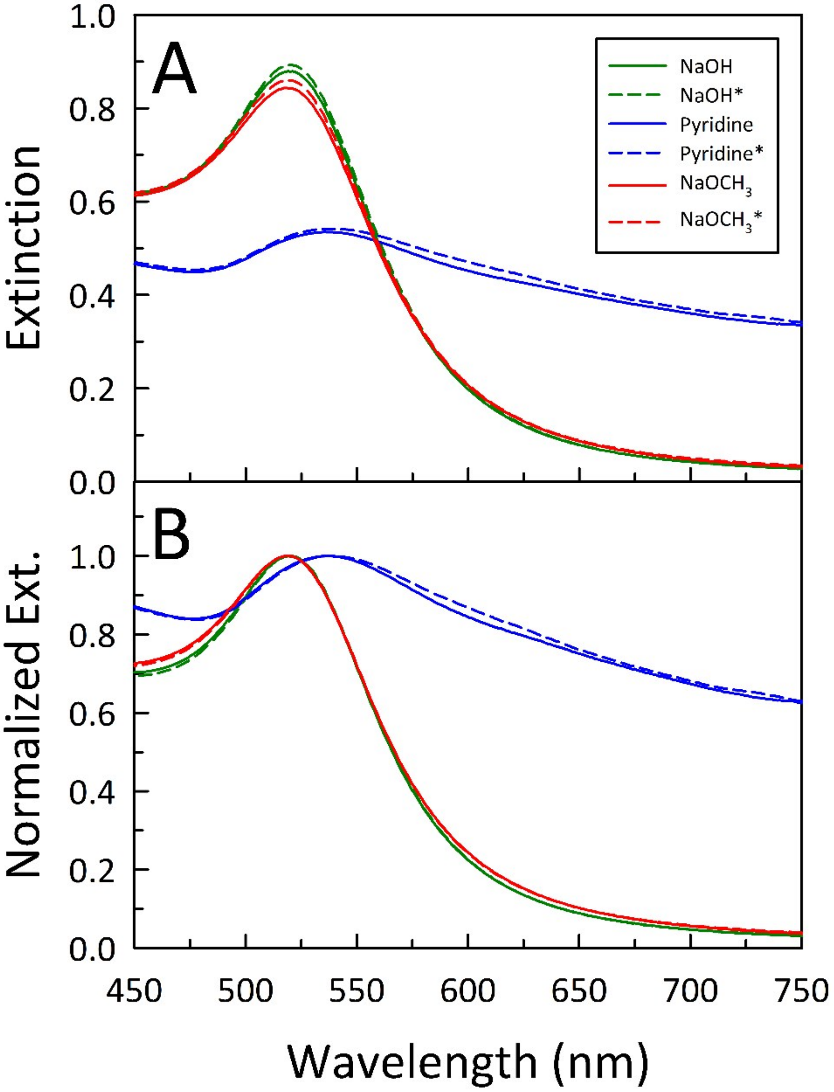


Fig. S10 (A) UV–vis extinction spectra and (B) the corresponding normalized spectra for the as-synthesized AuNPs obtained using PgC_3OH in the presence of three different bases. The legend in (A) applies to both panels. A base:PgC_3OH ratio of 10:1 was used in all cases. The AuNPs obtained in strong bases NaOH and CH_3ONa appear stable with red solution coloration and show similar spectral properties while those obtained in pyridine resulted in a dark blue solution with aggregates present within 24 h of synthesis. The experiment was repeated to evaluate reproducibility, with the second data set denoted by a *.

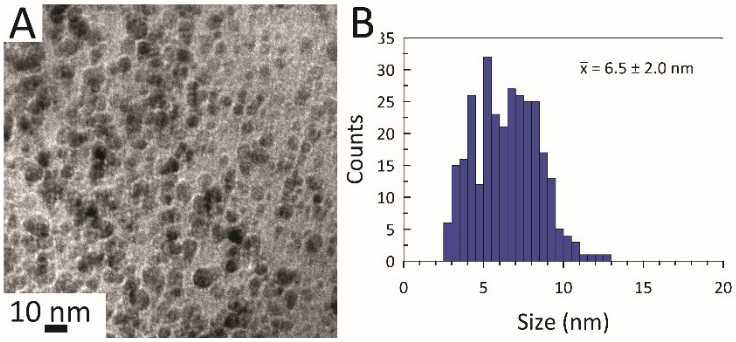


Fig. S11 (A) TEM micrograph and (B) particle size distribution histogram of representative PgC_3OH-AuNPs obtained in a solution of CH_3ONa solution for a CH_3ONa:PgC_3OH ratio of 10:1.

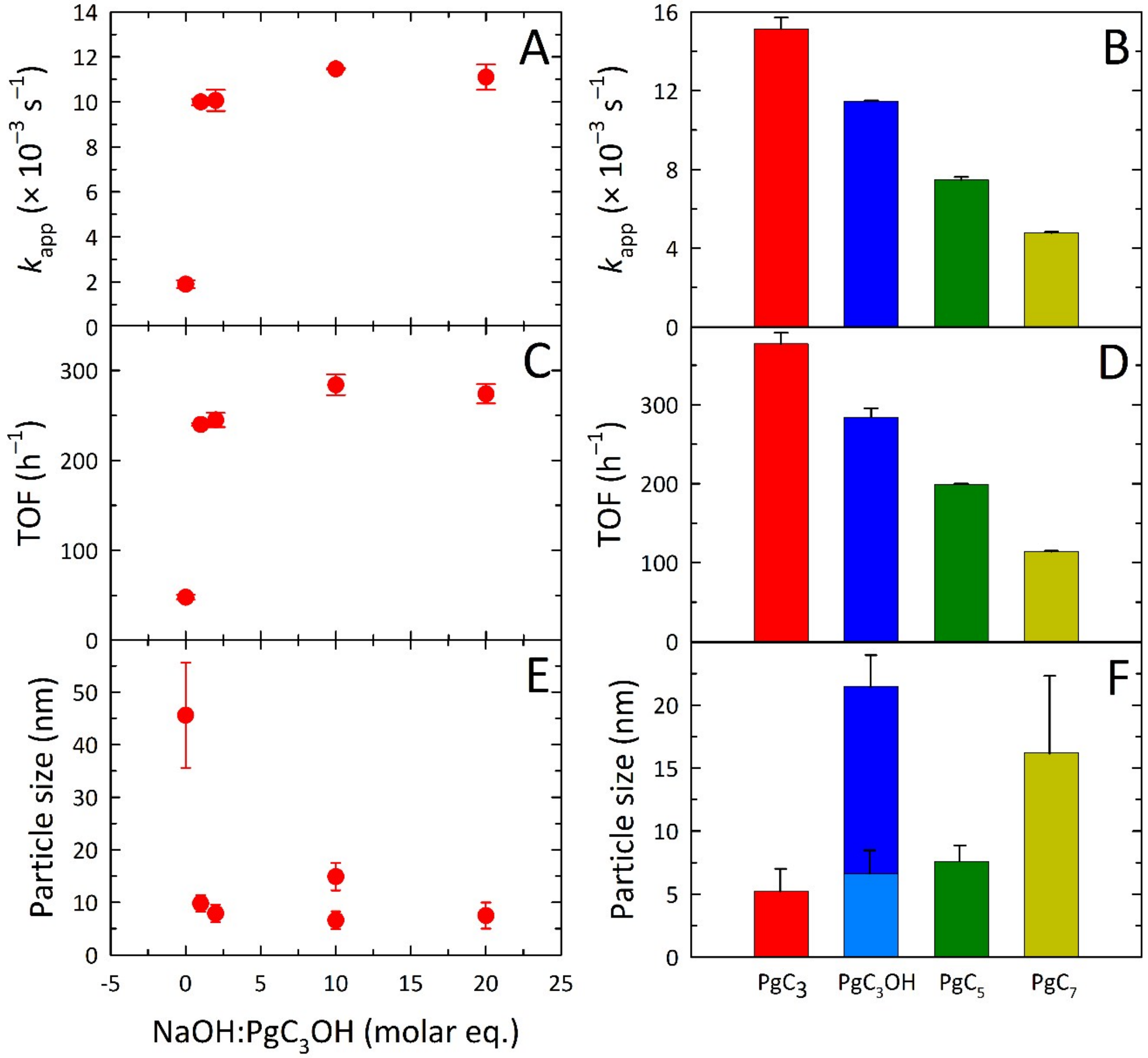


Fig. S12 (A) Apparent rate constant (k_{app}) for 4-NP reduction, (C) turnover frequency (TOF) for 4-NP reduction, and (E) average particle sizes for PgC_3OH-AuNPs synthesized at five different NaOH:PgC_3OH molar ratios (0:1, 1:1, 2:1, 10:1 and 20:1). Similarly, (B) k_{app}, (D) TOF, and (F) average particle sizes of PgC_R-AuNPs synthesized using a NaOH:PgC_R molar ratio of 10:1. Note that using PgC_3OH as a reducing/stabilizing agent resulted in a bimodal AuNP distribution in panels E and F.

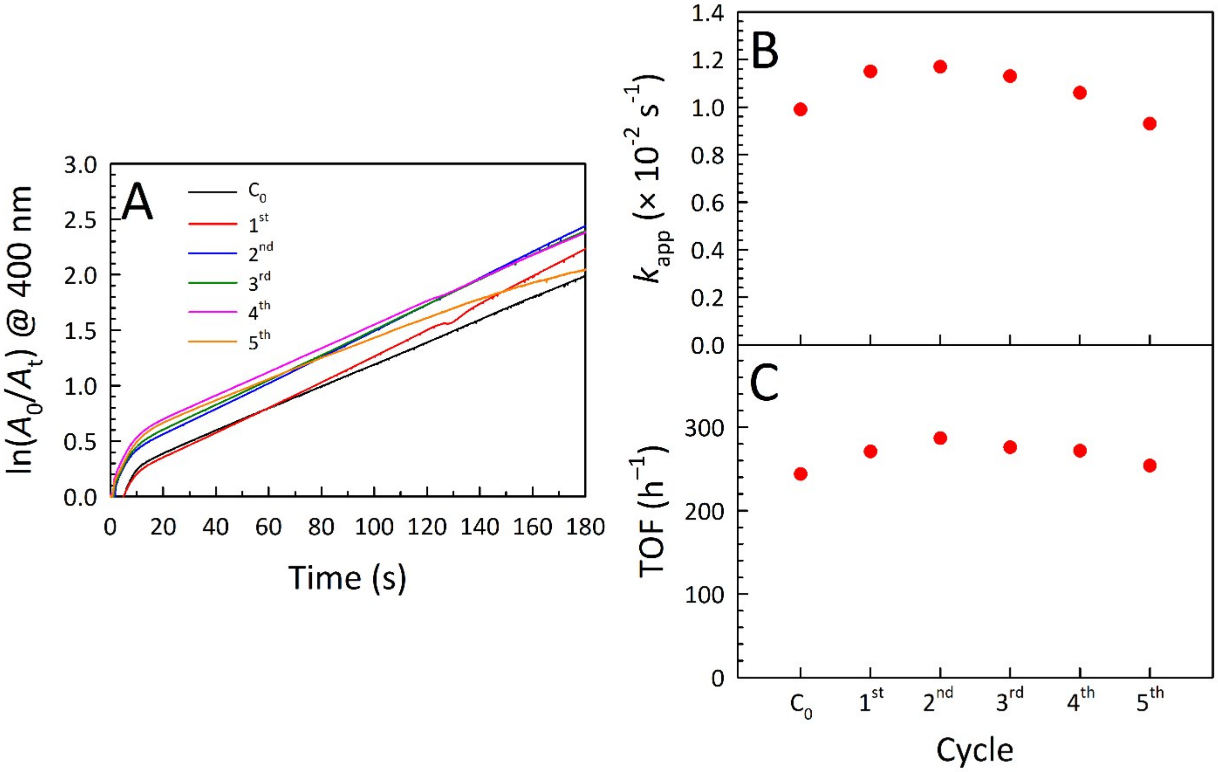


Fig. S13 (A) Pseudo-first-order rate plots for 4-NP reduction using recycled 20:1 molar ratio NaOH:PgC_3OH AuNPs as catalyst. Recycling was performed by spiking the initial reduction cycle (C_0) solution with additional $NaBH_4$ and 4-NP as specified above. Consecutive reduction cycles (1^{st} – 5^{th}) show little change in the rate plot and the corresponding (B) k_{app} and (C) TOF values, indicating good recyclability.

References

1. N. E. Larm, J. B. Essner, K. Pokpas, J. A. Canon, N. Jahed, E. I. Iwuoha and G. A. Baker, *J. Phys. Chem. C*, 2018, **122**, 5105-5118.