Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Stable and recyclable Au_{25} clusters for the reduction of 4-nitrophenol.

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Experimental

Materials: Tetraoctylammonium bromide (TOAB, 98%, Aldrich), Sodium borohydride ($NaBH_4$, 98%, EMD), Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4.3H_2O$, 99.9% on metal basis, Aldrich), 1-Dodecanethiol ($C_{12}H_{25}SH$, ≥ 98%, Aldrich), Phenylethanethiol (C_8H_9SH, 99%, Acros Organics), 1-Hexanethiol ($C_6H_{13}SH$, 97%, Alfa Aesar), 4-Nitrophenol ($C_6H_5NO_3$, 99%, Alfa Aesar). High purity THF and Acetonitrile were purchased from Fischer Scientific and 100% ethanol was purchased from Commercial Alcohols. 18MΩ cm Milli-Q (Millipore, Bedford, MA) was used throughout.

Synthesis of Au_{25} MPCs: Alkanethiolate Au_{25} (hexanethiolate Au_{25} and dodecanethiolate Au_{25}) and phenylethanethiolate Au_{25} MPCs were prepared by modifying the literature procedure.[1] A typical synthesis is as follows: 50 mL solution of THF with 500 mg of $HAuCl_4.3H_2O$ was mixed with 1.2 equiv. of TOAB and resulting solution was stirred for 10 min. After that, the stirring rate was decreased to 60 rpm and 5 eq of alkanethiol (hexanethiol, dodecanethiol) or phenylethanethiol was added dropwise and the solution was left under slow stirring until it became transparent. After getting a transparent solution, the stirring rate was increased to 1100 rpm and a solution of 10 eq of $NaBH_4$ in 10 mL ice cold water was added all at once and the final solution was left under high stirring for 4 days. After the reaction was over, the solvent was evaporated using a rotary evaporator and the reaction residue was sequentially washed with copious amounts of 75/25, 85/15 and 90/10 mixtures of ethanol/water. After washing, alkanethiolate Au_{25} MPCs were extracted with THF and phenylethanethiolate Au_{25} MPCs were extracted with acetonitrile.

Synthesis of $Au_{\sim 180}(SC_6H_{13})_{\sim 100}$ MPCs: A 25 ml solution of THF with 200 mg of $HAuCl_4.3H_2O$ was mixed with 1.2 equiv. of TOAB and solution was stirred for 10 min. After stirring, 3 equiv. of hexanethiol was added and the solution was stirred until it became clear. To this clear solution, 10 equiv. of $NaBH_4$ in 5 ml ice cold water was added and the resulting solution was stirred for 2 hours. After the completion of the reaction, the solvent was evaporated and the residue was sequentially washed with the copious amount of water, ethanol and acetonitrile. The number of Au atoms and the number of ligands in the formula were calculated using a combination of TEM and TGA.[2]

Reduction catalysis: The reduction of 4-nitophenol was studied using UV-Vis spectroscopy. The entire reaction was done under N_2 atmosphere. In a typical catalytic reaction, 7.0 mg of nitrophenol was dissolved in 25/5 mL mixture of THF/water. To this solution, Au MPCs (4.87×10^{-4} mM in Au) were added (alkanethiolate MPCs or phenylethanethiolate MPCs) and the solution was stirred under N_2 atmosphere. After stirring, 30 equiv. of $NaBH_4$ in ice cold water was added. Immediately after the addition of $NaBH_4$, UV-Vis spectra were recorded. The rate constant of the reduction process was determined by measuring the change in the absorbance of the initially observed peak at 400 nm for 4-nitrophenolate as a function of time. Control experiments were carried out at the same conditions without MPCs and no nitrophenol reduction was observed. Very short induction times (< 2 min) were observed due to the remnant oxygen and kinetic data were plotted after removing the induction time.

Treatment of Au MPCs with $NaBH_4$: Stability of Au_{25} MPCs and larger hexanethiolate Au MPCs towards $NaBH_4$ was studied with UV-Vis spectroscopy. In a typical procedure; to a solution of Au_{25} MPCs or larger hexanethiolate Au MPCs, 37500 equiv. of $NaBH_4$ was added

and immediately after the addition of $NaBH_4$, UV-Vis spectra were recorded over the period of 30 minutes.

Characterization: Absorption spectra were recorded on a Varian Cary 50 Bio UV-Vis spectrometer with an optical path length of 1 cm. A transmission electron micrograph before catalysis was obtained with a Philips 410 microscope operating at 100 kV and a micrograph after catalysis was obtained with a Philips CM10 Microscope operating at 60 kV. Mass spectral analysis was done on an Applied Biosystems 4800 MALDI-TOF/TOF instrument (Frederic, MD, USA) operating in linear positive ion mode using DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix.[2] A mixture of insulin and ubiquitin was used as an external standard.[2]

Figure S1: UV-Vis spectra of a) phenylethanethiolate Au_{25}, b) dodecanethiolate Au_{25} and c) hexanethiolate Au_{25} MPCs.

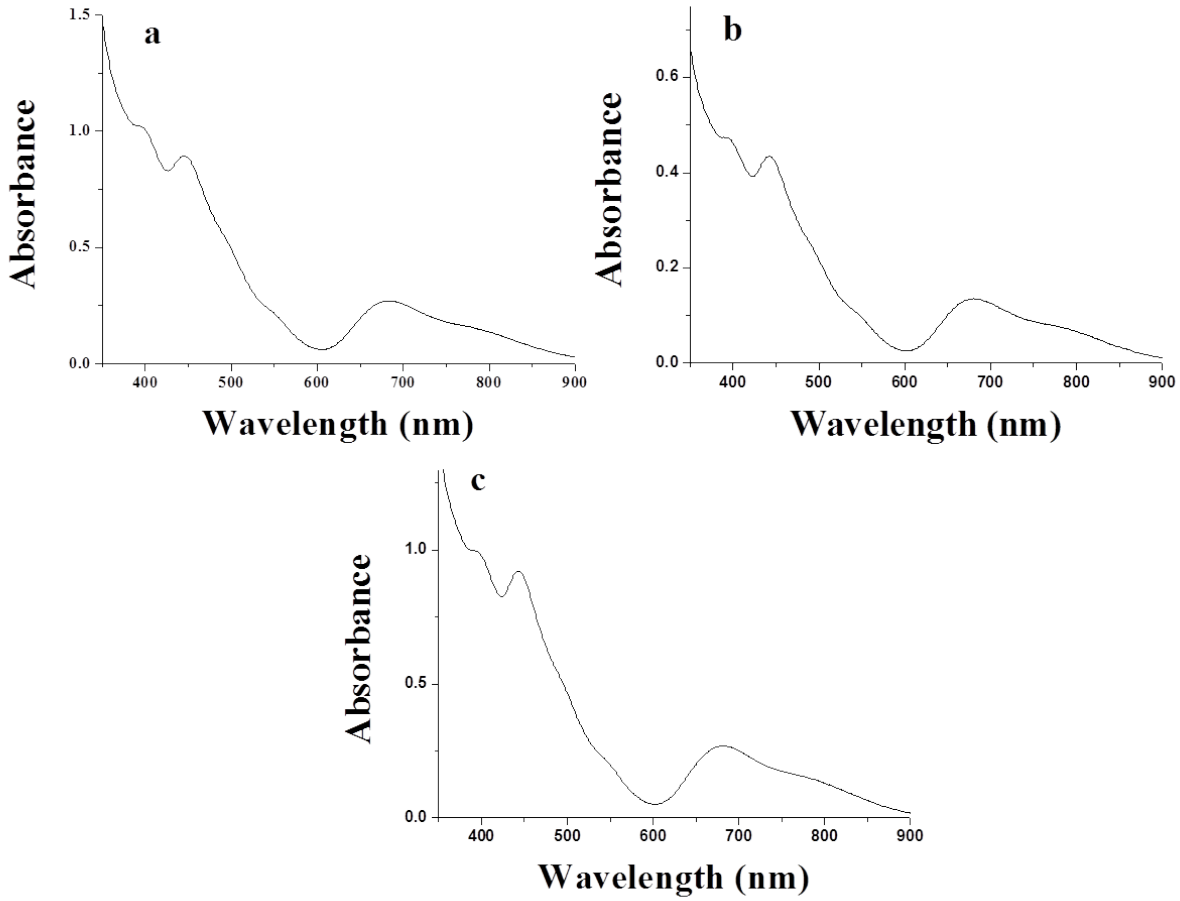


Figure S2: MALDI/TOF spectra of a) phenylethanethiolate Au_{25}, b) dodecanethiolate Au_{25} and c) hexanethiolate Au_{25} MPCs

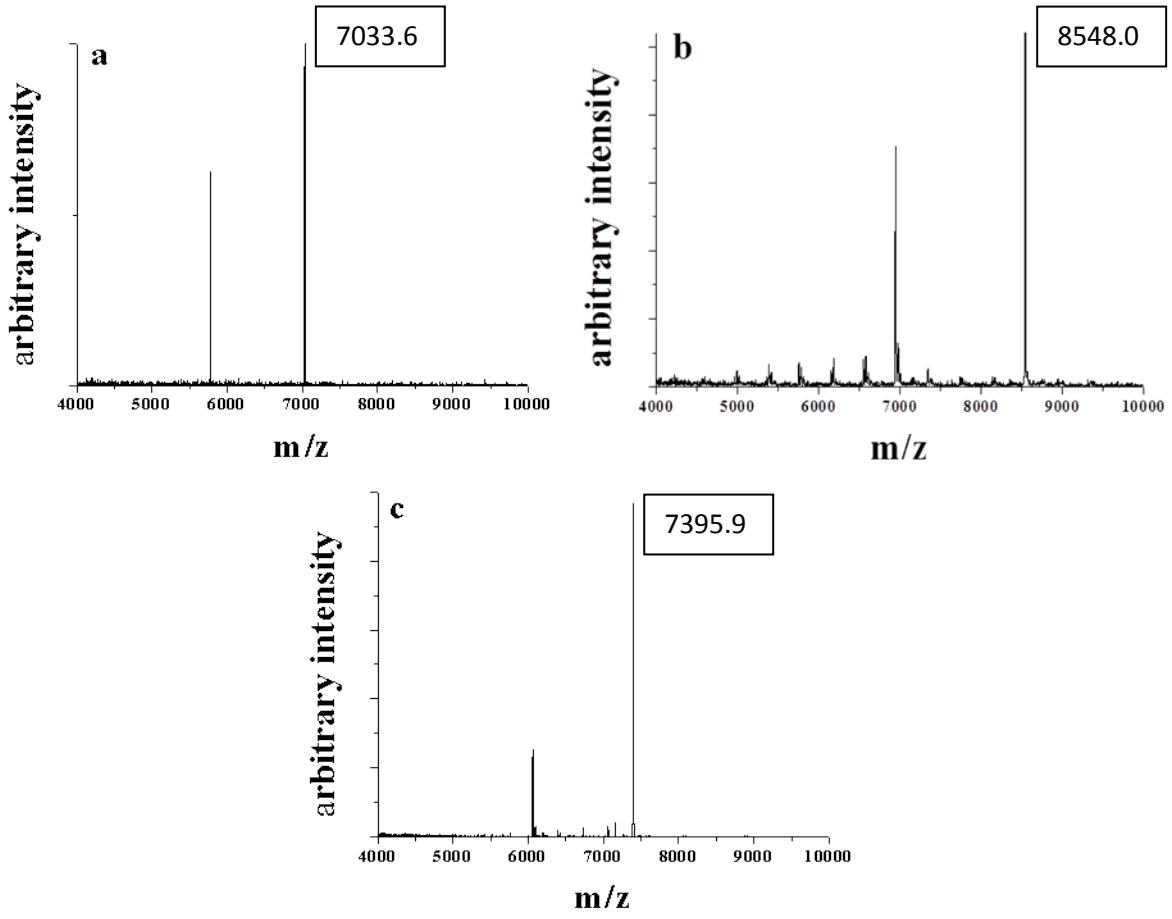


Table 1: Experimental and theoretical masses of Au_{25} MPCs

Catalyst	**Theoretical mass (m/z)**	**Experimental mass (m/z)**	**Error (Da)**
$Au_{25}(SC_6H_{13})_{18}$	7034.4	7033.6	-0.8
$Au_{25}(SC_8H_9)_{18}$	7394.1	7395.9	1.8
$Au_{25}(SC_{12}H_{25})_{18}$	8549.2	8548.0	-1.2

Figure S3: Representative UV-Vis spectra of the reduction of 4-nitrophenolate to 4-aminophenol over dodecanethiolate Au_{25} MPCs. Conditions: BH_4^-: total Au: substrate: 37500:1:105.

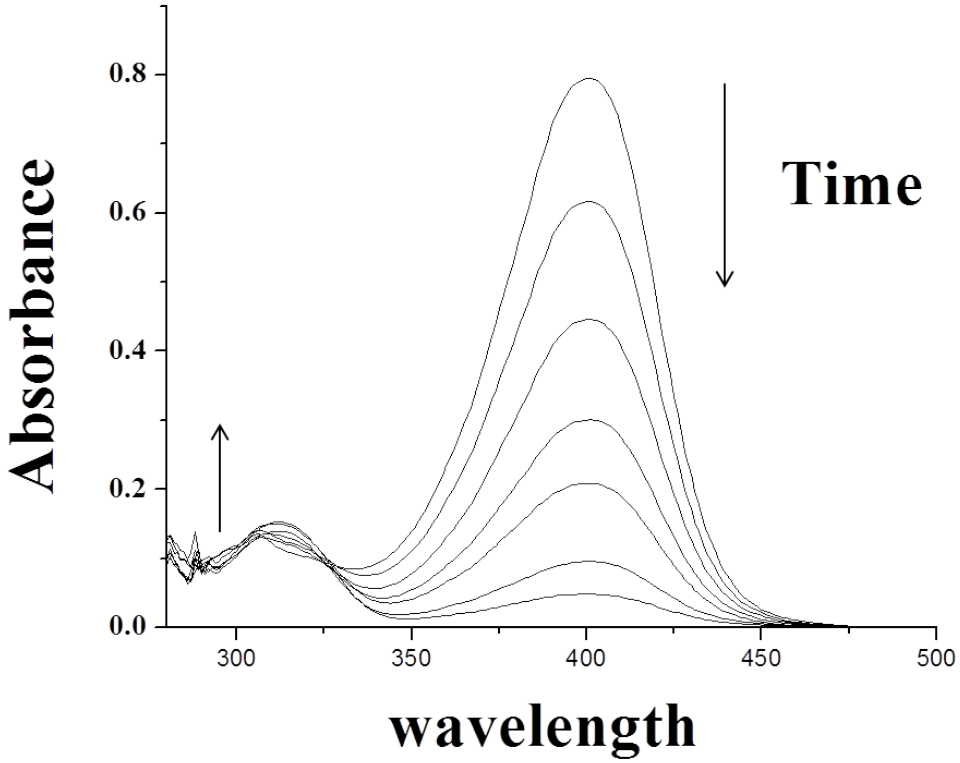
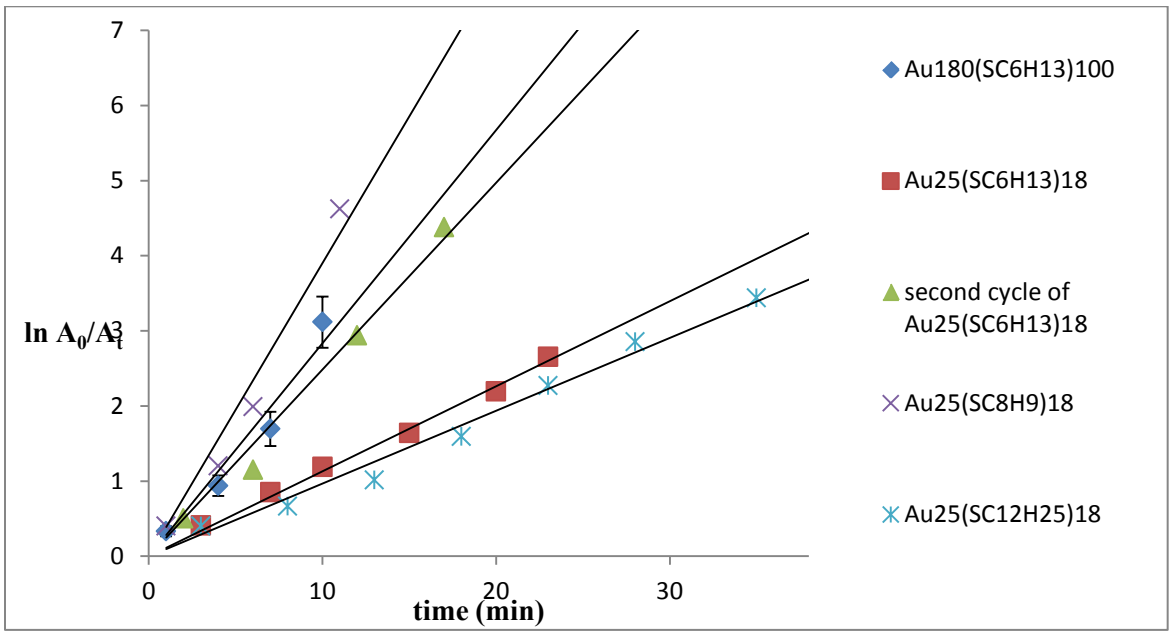


Figure S4: Kinetic pseudo-first order rate plots of the nitrophenolate absorption peak at 400 nm vs. time during reduction reactions using various Au MPCs.



Fitting parameters:

Catalyst	R^2 value	slope
$Au_{1\sim180}(SC_6H_{13})_{\sim100}$	.959	.30±.03
$Au_{25}(SC_8H_9)_{18}$	.964	.51±.10
Second cycle of $Au_{25}(SC_8H_9)_{18}$	.996	.49±.05
$Au_{25}(SC_6H_{13})_{18}$	.994	.12±.01
Second cycle of $Au_{25}(SC_6H_{13})_{18}$	.994	.25±.03
$Au_{25}(SC_{12}H_{25})_{18}$	.983	.08±.03

Pseudo-first order rate equation:

$$ln\frac{A_0}{A_t} = kt$$

A_0 – initial absorbance

A_t – absorbance at time t (min).

K – pseudo-first order rate constant

t – time (min)

Figure S5: UV-Vis spectra showing the effect of the addition of 37500 equiv. of $NaBH_4$ to a) hexanethiolate Au_{25} MPCs, b) phenylethanethiolate Au_{25} MPCs, c) dodecanethiolate Au_{25} and d) larger hexanethiolate Au MPCs.

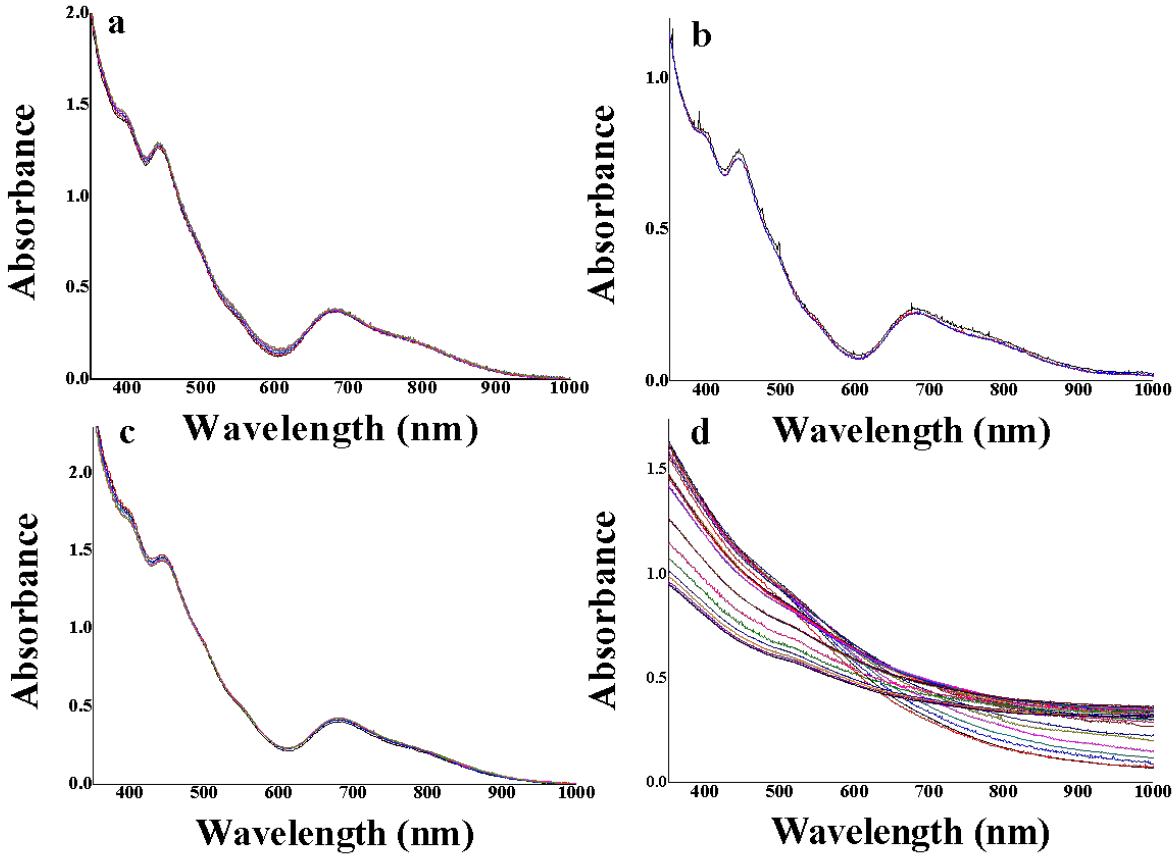
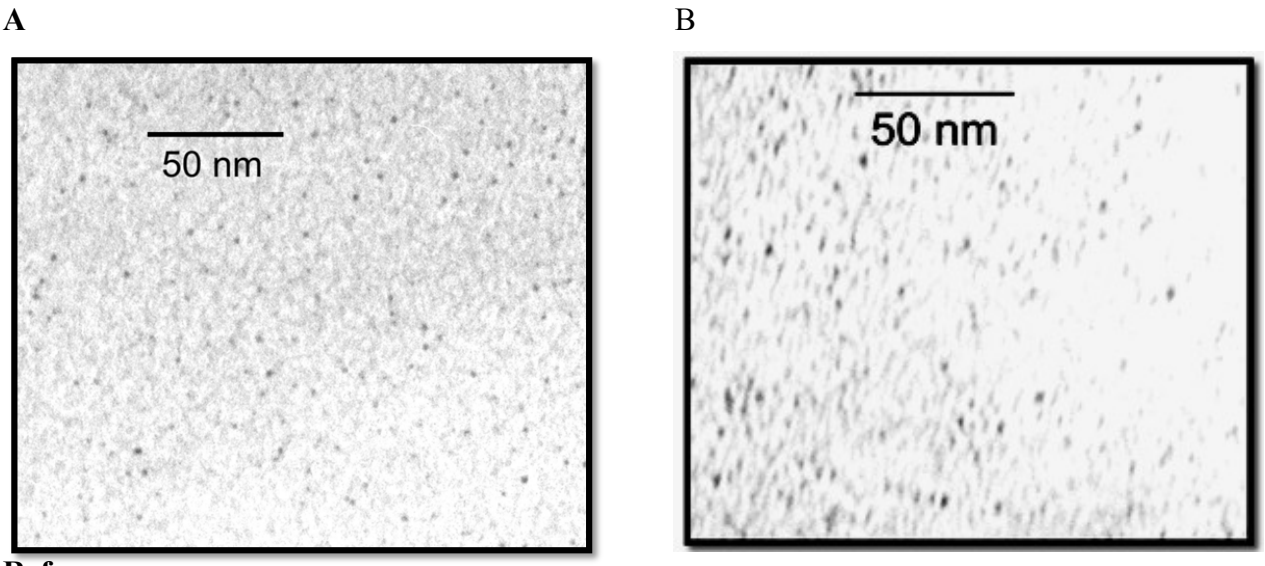


Figure S6: TEM images of hexanethiolate Au_{25} MPCs a) before catalysis and b) after catalysis.



References:

1. M. Zhu, E. Lanni, N. Garg, M. E. Bier and R. Jin, *J. Am. Chem. Soc.*, 2008, **130**, 1138.
2. W. B. Hou, M. Dasog and R. W. J. Scott, *Langmuir*, 2009, **25**, 12954.
3. A. Dass, A. Stevenson, G. R. Dubay, J. B. Tracy and R. W. Murray, *J. Am. Chem. Soc.*, 2008, **130**, 5940.