Supplementary Material (ESI) for Chemical Communications

Supplementary Information for

A polymer support with controllable solubility in mutually immiscible solvents

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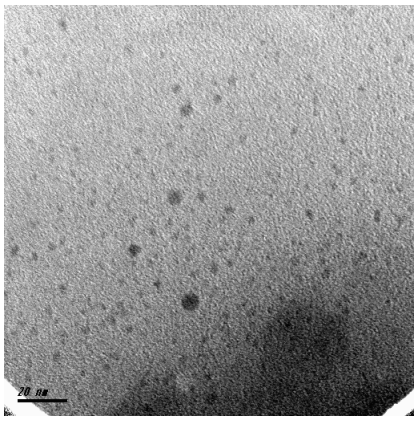
Synthetic procedures

Solvents and chemicals were of reagent grade and were used as received, apart from the monomers for microgel synthesis, which were freshly distilled to free them from inhibitors prior to use. UV-visible spectra were recorded on a Perkin Elmer Λ5 spectrophotometer. TEM analyses were carried out at CIGS – University of Modena, Italy. TEM grids were loaded with a drop of a dichloromethane solution of the various microgel samples followed by solvent evaporation in air. Average metal nanocluster sizes and size distributions were estimated from the measured size of at least 100 particles from different fields on the same grid.

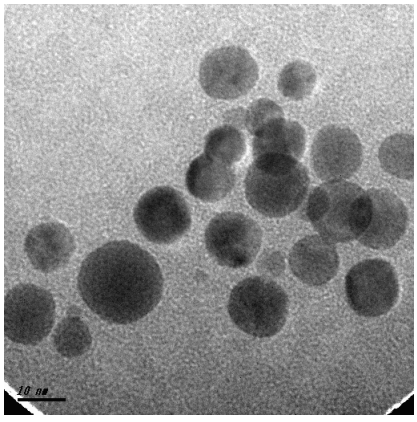
Microgel preparation. *N,N*-dimethylacrylamide (1.168g, 11.78mmol), dimethylaminoethyl methacrylate (2.264g, 14.40mmol) and ethylene dimethacrylate (0.587g,2.96 mmol) were mixed in a round-bottomed flask. The resulting mixture was diluted with 46g cyclopentanone. 0.15g (3% w/w with respect to the monomer mixture) azobis(isobutyronitrile) (AIBN) were then added. The resulting solution was degassed, put under nitrogen and placed for 48 hours in a thermostated oven preheated at 80°C. The polymerisation solution was concentrated to about half of the original volume and subsequently poured in the fivefold volume of petroleum ether under efficient stirring. The microgel separated as a sticky oil which was redissolved in 20 mL dichloromethane and precipitated again from petroleum ether to yield a whitish powder which was filtered off and dried under vacuum to constant weight.

Preparation of MPdEtOH. 1g microgel was dissolved in 80 mL dichloromethane under an inert atmosphere. 50 mg $Pd(OAc)_2$ (0.25 eq. with respect to the available amino groups) were then added, and the resulting solution was stirred at room temperature for 24 hours. Subsequently, the solution was brought to reflux and 6 mL ethanol were added. The solution was maintained at reflux with efficient stirring for 12 hours. The solution was concentrated to about half of the original volume and the nanocluster-containing microgel was subsequently precipitated as a grey powder by pouring the solution in the fivefold volume of petroleum ether under efficient stirring.



TEM micrograph of sample **MPdEtOH**

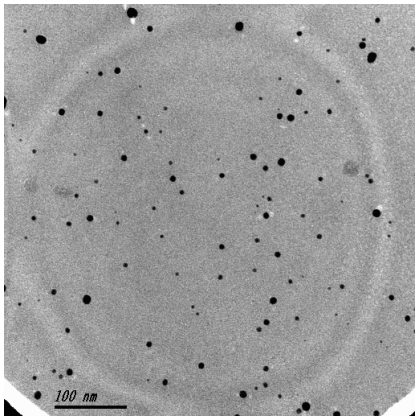
Preparation of MAuEtOH. 1g microgel was dissolved in 80 mL ethanol under an inert atmosphere. 68 mg $AuCl_3$ (0.25 eq. with respect to the available amino groups) were then added, and the resulting solution was stirred at room temperature for 24 hours, upon which the solution turned from yellow to dark red. The solution was concentrated to about 30 mL and the nanocluster-containing microgel was subsequently precipitated by pouring the solution in the fivefold volume of petroleum ether under efficient stirring. The microgel separated as an oil which was redissolved in the minimum amount of dichloromethane and precipitated again from petroleum ether to yield a dark red powder which was filtered off and dried under vacuum to constant weight.



TEM micrograph of sample **MPdEtOH**

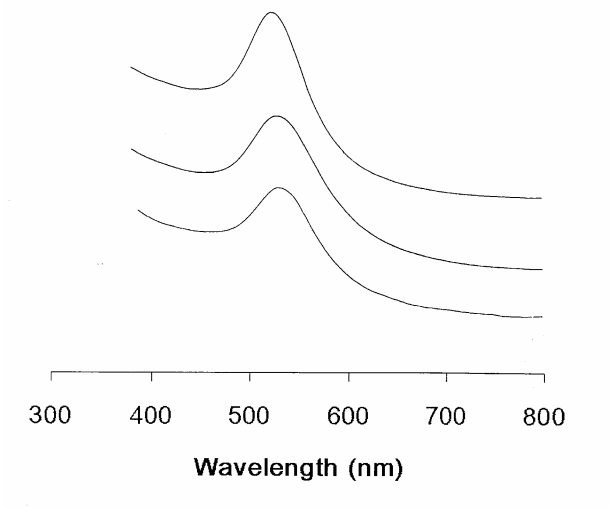
Preparation of MAuH_2O. 1g microgel was dissolved in 80 mL water under an inert atmosphere. 68 mg $AuCl_3$ (0.25 eq. with respect to the available amino groups) were then added, and the resulting solution was stirred at room temperature for 24 hours, upon which the solution turned from yellow to dark red. The solution was concentrated to about 20 mL, diluted to 80 mL with

ethanol and subsequently concentrated again to remove residual water by azeotropic distillation. This procedure was repeated twice, after which the microgel-stabilised nanoclusters were isolated as outlined above for the sample prepared in ethanol.



TEM micrograph of sample **MAuH$_2$O**

UV-visible spectra



UV-visible spectra of sample **MAuEtOH** in different solvents (5 mg microgel-protected nanoclusters in 4 mL). From top to bottom: water (neutral pH), dichloromethane (after extraction from water), 0.08M perfluorooctanoic acid in perfluoro(methylcyclohexane) (after extraction from dichloromethane).