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**Title** Ordered mesoporous materials from metal nanoparticle-block copolymer self-assembly

**One-sentence summary** Self-assembly of a block copolymer and platinum nanoparticle mixture produces lamellar and inverse hexagonal hybrids of which the latter can be converted to ordered mesoporous platinum-carbon nanocomposites and ordered platinum mesostructures.

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**Abstract** The synthesis of ordered mesoporous metal composites and ordered mesoporous metals is a significant challenge because metals have high surface energies. We present results from the self-assembly of block copolymers with ligand-stabilized platinum nanoparticles, leading to lamellar (CCM-Pt-4) and inverse hexagonal (CCM-Pt-6) hybrid mesostructures with high nanoparticle loadings. Pyrolysis of the CCM-Pt-6 hybrid produces an ordered mesoporous platinum-carbon nanocomposite with open and large ( $\geq 10\text{nm}$ ) pores. Removal of the carbon leads to ordered porous platinum mesostructures. The platinum-carbon nanocomposite has the highest electrical conductivity yet measured for ordered mesoporous materials fabricated from block copolymer self-assembly.

Despite considerable progress in the field of porous solids, major challenges remain in the synthesis of ordered mesoporous materials with high metal content from the co-assembly of macromolecular surfactants and inorganic species. Controlling the structure of metals at the mesoscale (2 to 50 nm) is crucial for the development of improved fuel cell electrodes and may also assist in the miniaturization of optical and electronic materials for data transmission, storage, and computation (1, 2). Previously, metal ions have been absorbed into and reduced within a pre-assembled block copolymer scaffold (3) and ligand stabilized nanoparticles have been co-assembled with block copolymers (4). More recently, polymer-coated nanoparticles behaving like surfactants have been isolated at the interface of block copolymer domains, leading to a bicontinuous morphology at higher loadings (5). Despite this progress, the conversion of metal-polymer hybrids into mesoporous materials with ordered and large ( $\geq 10$  nm) pores has not been accomplished, in part due to the low volume fraction of metals in most hybrids and the widespread use of gold, which has a high diffusion coefficient and therefore retains its mesostructure only at low temperatures (6-8). While a protective organic layer can be added to metal nanoparticles to prevent uncontrolled aggregation, even a thin organic layer represents a considerable volume of the overall material—for example, a 1 nm diameter metal nanoparticle with a relatively thin 1 nm organic shell is just 4% metal by volume. As a result, the typical metal content in most block copolymer-metal nanoparticle hybrids is only a few volume percent and the prospects for converting the hybrid into an ordered mesoporous material—where the metal would have a volume fraction between 60% and 75% for an inverse hexagonal structure—is poor. Notably, mesoporous metals have been synthesized at a smaller length scale, with 2 to 4 nm pores,

through the co-assembly of metal ions with small molecule surfactants followed by reduction (9-12). The small pore size, however, limits the flow of liquids through the material, which is essential for many applications (13, 14). Metals have also been deposited onto (15) or into (16) thin films of block copolymers to create metal wires, but the surface-dependent nature of the metal deposition most likely limits these processes to 2-dimensional materials.

Here, we demonstrate a route to mesostructured platinum nanoparticle-block copolymer hybrids with exceptionally high nanoparticle loadings and tunable phase separated morphologies with feature sizes above 10 nm. Metal-rich nanoparticles with a thin organic shell made from ionic liquid ligands, combined with nanoparticle loadings as high as 79 vol.% in the hydrophilic domains of the hybrid, ensure that mesostructure order is retained upon conversion to mesoporous metal-carbon composites. The carbon can be removed from the nanocomposites to produce ordered platinum mesostructures with ordered and large ( $\geq 10$  nm), uniform pores.

We use a strategy in which ligand-stabilized platinum nanoparticles (Fig. 1 A, B) co-assemble with block copolymers (Fig. 1 C) during the evaporation of organic solvents. This leads to the formation of metal-rich mesostructured nanoparticle-block copolymer hybrids (Fig. 1 D). Hybrids are pyrolyzed by heating under an inert atmosphere, leaving behind ordered mesoporous platinum-carbon composites (Fig. 1 E). Finally, the carbon is removed through use of an argon-oxygen plasma or acid etch to produce ordered porous platinum mesostructures (Fig. 1 F). The success of this strategy depends upon the synthesis of mesostructured hybrids with high metal volume fractions in one domain of the block copolymer, which is possible after meeting the following criteria.

First, the nanoparticles should exhibit high solubility in organic solvents. When nanoparticles have low solubility, some fraction of the particles macroscopically precipitate during solvent evaporation and thus do not mix with the block copolymer. We recently reported a ligand for metal nanoparticles based on a thiol-containing ionic liquid (17) that imparted liquid-like behavior to the nanoparticles, even in the absence of a solvent. This suggests that using certain ionic liquids as nanoparticle ligands provides a route to high solubility.

Second, the ligand-stabilized nanoparticles should have at least a modest metal volume fraction. While metal nanoparticles with high solubility have been reported (17, 18), the metal volume fraction was between 0.6 and 3% (17). Higher metal volume fractions are needed to prevent structural collapse upon removal of the organic components. Conventional short ligands can increase the metal volume fraction but usually result in insufficient solubility.

Third, the nanoparticles should be highly soluble in just one block of the block copolymer (2, 19). Mixing should thus be driven by a negative  $\chi$  interaction parameter between that block and the nanoparticles, which can be achieved through ionic interactions, hydrogen bonding, and dipole-dipole interactions, among many possible routes.

Fourth, in order to promote mixing, the diameter of the nanoparticles should be below a critical limit relative to the size of the block with which they mix, approximately the root-mean-square (RMS) end-to-end distance (equivalent to  $6^{1/2}$  times the radius of gyration for an ideal chain) of the relevant block of the copolymer (20). Although the

precise cut off may vary depending on enthalpic considerations and nanoparticle concentration, this provides a guideline for nanoparticle size.

We designed ligand-stabilized platinum nanoparticles (Fig. 1A, B) and a block copolymer (Fig. 1C) that met these four criteria. Two poly(isoprene-*block*-dimethylaminoethyl methacrylate), PI-*b*-PDMAEMA block copolymers (a, b) were synthesized by anionic polymerization (21) and had a polydispersity of 1.05 (a) / 1.04 (b) and molecular weights of 31.1 (a) / 27.8 (b) kg/mol, of which 33 (a) / 15 (b) wt.% was PDMAEMA. After examining a series of possible ligands for the platinum nanoparticles, we selected *N,N*-di-2-propoxyethyl-*N*-3-mercaptopropyl-*N*-methylammonium chloride (Fig. 1A). The synthesis of this ligand as well as the ligand-stabilized platinum nanoparticles are described in the Supporting Online Material. Transmission electron microscopy (TEM) revealed that the nanoparticles had a metal core diameter of  $1.8 \pm 0.5$  nm (Fig. 2 A) and a model of the ligand suggested a maximum radial extension of 1.4 nm (Fig. 1 B). Nuclear magnetic resonance (NMR) confirmed the chemical structure of the ligand on the nanoparticles and thermogravimetric analysis (TGA) revealed a metal content of 56.9% by weight, or 7.5% by volume (see Supporting Online Material). The nanoparticles exhibited hydrophilic properties: they were highly soluble in methanol, modestly soluble in water and acetone, poorly soluble in chloroform, and insoluble in tetrahydrofuran and ether. We selected a solvent combination of chloroform and methanol (9:1 w/w) in which both the block copolymer and nanoparticles exhibited high solubility. The nanoparticles were nearly insoluble in the absence of methanol and the polymer precipitated in solutions with more than 20% methanol.

The as-synthesized nanoparticles were too hydrophilic to form macroscopically homogeneous hybrids with PI-*b*-PDMAEMA when films were cast from a chloroform:methanol 9:1 (w/w) solution. Surprisingly, we found that the particles became less hydrophilic upon ageing (see below). In particular, boiling the particles five hours in water decreased their hydrophilicity to the extent that they became more soluble in solvents of moderate or low polarity, such as tetrahydrofuran and chloroform. After ageing, the nanoparticles were centrifuged to remove the organic byproducts of the ageing process. The metal content in the aged nanoparticles was typically 65.4% by mass or 10.4% by volume. The platinum particle size remained unchanged at 1.8 nm, as measured by TEM, and the platinum domain size increased from 1.2 nm to 1.4 nm, as determined by peak-width analysis of powder x-ray diffraction (PXRD, Fig. 3B). NMR of the aged nanoparticles showed a spectrum nearly identical to the as-synthesized particles (Supporting Online Material). On average, a single aged nanoparticle has 65 ligands, a decrease from 93 in the as-synthesized nanoparticle (see Supporting Online Material for calculations). The loss of ligands upon heating has been previously documented for 2-D gold surfaces (22) and gold nanoparticles (23). Interactions among polymer, ligands, metal surface, and solvents are complex and the relative contribution of each to nanoparticle solubility is therefore difficult to determine precisely. We speculate, however, that the significant decrease in the number of charges per particle (as inferred from the loss of ligands) is responsible for the nanoparticles' diminished hydrophilicity. Furthermore, loss of ligand may enhance polymer-nanoparticle interactions as the PDMAEMA's amine may chemisorb onto the more exposed platinum surface (24) thereby preventing the macrophase separation of nanoparticles from block copolymer.

Finally, loss of ligand from the nanoparticles increases the volume fraction of platinum in the nanoparticles by 39%, improving the ability of the mesostructure to survive pyrolysis.

A macroscopically homogeneous solution of aged nanoparticles and block copolymer (a) was prepared by combining 98 mg of nanoparticles, 28 mg of block copolymer, 1040 mg of chloroform, and 110 mg of methanol. The hydrophilic volume fraction (the volume fraction of PDMAEMA and nanoparticles, see Supporting Online Material for calculations) was 65%, which was anticipated to yield a hybrid with an inverse hexagonal mesostructure (CCM-Pt-6). The solution contents were transferred to an aluminum dish with a 1 cm diameter and heated at 50 °C beneath a hemispherical dish that was designed to slow solvent evaporation. Because chloroform's vapor pressure is higher than that of methanol and because the solvent composition needed to be maintained near 9:1 chloroform:methanol, a 20 mL vial containing 4 g of chloroform was placed beneath the hemispherical dish, thereby slowing the evaporation of chloroform from the nanoparticle-block copolymer solution.

After an hour of heating at 50 °C, nearly all solvent had evaporated. The sample was a homogeneous, shiny black solid and was weak and brittle (Fig. 2 B). Analysis of the sample by TEM (Fig. 2 C) revealed that a mesostructure had formed. The order could be improved, however, by annealing CCM-Pt-6 at 130 °C for 2 days under vacuum, as confirmed by small angle x-ray scattering (SAXS) (Fig. 3A) and TEM (Fig. 2 D). Comparison of representative SAXS patterns showed an increased intensity at higher order reflections for the annealed sample, consistent with a hexagonal lattice (see tic marks in Fig. 3A). This structural assignment was corroborated by TEM. The representative TEM image in Fig. 2D revealed an inverse hexagonal mesostructure with

grain sizes on the order of a few microns. Examining the mesostructure at higher magnification (Fig. 2 E) revealed that individual platinum nanoparticles composed the walls of the CCM-Pt-6 mesostructure with 3 to 5 nanoparticles spanning the thickness of the wall. Comparison of TGA profiles before and after annealing indicates a mass loss of 15% that arises from loss of ligand (see Supporting Online Material). Annealing the sample also caused the diameter of the Pt nanoparticles to increase to  $2.3 \pm 0.3$  nm, as measured by TEM (Fig. 2 E). The annealing process thus improves hybrid order *and* decomposes the ligands to the extent that the particles merge and grow. Interestingly, the average grain size of the mesostructure did not increase significantly with longer annealing times, suggesting that ligand decomposition and nanoparticle growth is accompanied by a loss in nanoparticle mobility.

Besides inverse hexagonal mesostructures (CCM-Pt-6), samples with lamellar morphology (CCM-Pt-4) were produced. Using PI-*b*-PDMAEMA copolymers (a) or (b), hybrids were cast from solution with a hydrophilic volume fraction of 56%. Similar to the CCM-Pt-6 hybrid, annealing at 130 °C led to a well-developed mesostructure as confirmed by SAXS and corroborated by TEM (Fig. 2 F, 3 A). These results suggest that similar to oxide structures, metal nanoparticle-block copolymer hybrid morphologies can be tailored by simply adjusting nanoparticle volume fraction (25).

We used a rapid pyrolysis process (26, 27) to convert the inverse hexagonal hybrid CCM-Pt-6 to an ordered mesoporous platinum-carbon composite. We heated the sample at 10 °C per minute under nitrogen or argon to at least 410 °C, followed by immediate cooling. Under these conditions, the  $sp^2$ -hybridized carbons of the PI block decompose into an amorphous carbon-rich material with slight graphitic character (Fig. 4

A) (27). As determined by TGA (Supporting Online Material), the pyrolysis led to a mass loss of 28%. Heating the material to temperatures as high as 550 °C did not result in further mass loss. The pyrolysis was accompanied by a decrease in the (1 0) d-spacing from 30.0 nm to 23.7 nm, as revealed by analysis of the SAXS patterns (Fig. 3 A). Characterization of the resulting material by TEM (Fig. 2 G) indicated that the inverse hexagonal structure was preserved. At the same time, the platinum interface had roughened, due to the growth of the nanoparticles to  $3.3 \pm 0.9$  nm in diameter. A roughened interface upon pyrolysis is consistent with the loss of higher order peaks observed in the SAXS profile. Examination of the structure by HRTEM revealed lattice fringes throughout the Pt walls (Fig. 2 H) showing that the walls were composed of crystalline platinum. Analysis by PXRD and application of the Scherrer equation indicated that the platinum nanocrystals domain size was  $4.1 \pm 0.4$  nm (Fig. 3 B), representing a significant increase from the aged nanoparticles. Together, SAXS, PXRD, and TEM analyses provide a consistent picture of a metal-carbon composite that is macroscopically homogeneous and uniformly mesostructured.

The carbon plays an important role in maintaining open, uniform pores of CCM-Pt-6 during pyrolysis (27). If the hybrid is heated in air instead of an inert atmosphere, the carbon is removed (a mass loss of 38% occurs) and the mesostructure is lost. This suggests that the platinum nanoparticles experience reduced mobility and aggregation within the carbonaceous matrix. In contrast, in the absence of carbon the nanoparticles sinter in an uncontrolled fashion. The grainy texture in the TEM images after sintering is indicative of carbon with a low graphite content (Fig. 2 G, H for TEM and Fig. 1E for illustration), which is confirmed by Raman spectroscopy (Fig. 4 A). Graphitic carbon has

signature D and G bands around  $1350\text{ cm}^{-1}$  and  $1550\text{ cm}^{-1}$ , respectively (28). The weak Raman signature of the carbon in the hybrid is likely due to the relatively low temperature ( $410\text{ }^{\circ}\text{C}$ ) reached during pyrolysis. Finally, nitrogen physisorption indicates that the mesopores are open (Fig. 3 C) and that 26% of the sample's volume (micropores and mesopores) is open space, as expected for an inverse hexagonal nanocomposite that has pores lined with carbon. The BET surface area of CCM-Pt-6 is  $18\text{ m}^2/\text{g}$ .

For many applications, such as fuel cells, it is desirable for the metal surface to be completely exposed. We thus sought a route to remove the carbon from the CCM-Pt-6 nanocomposite. While heating the pyrolyzed sample in air to  $500\text{ }^{\circ}\text{C}$  removed the carbon, it also caused the mesostructure to collapse. Instead, we were able to remove the carbon from microtomed thin films ( $\sim 50\text{ nm}$  thickness) of the CCM-Pt-6 nanocomposite using an argon-oxygen plasma. The mesoporous platinum was structurally similar to the platinum-carbon nanocomposite, as determined by TEM (Fig. 2 I). Close inspection of the pores in TEM images revealed that the grainy texture indicative of the carbon had disappeared. Furthermore, Raman spectra showed the absence of the D and G bands, suggesting that the carbon material had been successfully removed (Fig. 4 A).

Alternatively, for thicker films (10 to 100 microns thick) a sulfuric acid:nitric acid 3:1 (v/v) etch at  $70\text{ }^{\circ}\text{C}$  (29) successfully removed most carbon. Electrochemical data from acid etched samples indeed confirm that the metal surface is exposed showing current densities nearly identical to that of bulk platinum (Fig. 4D). Energy dispersive spectroscopy (EDS) on the CCM-Pt-6 metal-carbon nanocomposites (Fig. 4 B) showed a composition of 74 wt.% platinum, 18 wt.% carbon, 7 wt.% oxygen, and 1 wt.% sulfur. In contrast, after the plasma treatment, EDS revealed that over 98 wt.% of the sample was

platinum, with only trace contributions from carbon and oxygen (Fig. 4 C). Carbon removal was further confirmed by TGA. Pyrolyzed samples retained 80% of the original mass when heated to 550 °C in air, whereas carbon-etched samples retained 97% of the original mass. TEM confirmed that the samples were still mesostructured and that the grainy texture indicative of carbon had disappeared.

Because of easier accessibility of large quantities, we only measured the electrical conductivity of CCM-Pt-6 platinum-carbon nanocomposites. We chose 2-point measurements, which slightly underestimates the true conductivity, because the pyrolyzed platinum-carbon composites were too fragile for a 4-point measurement, even when pressed as a pellet. The nanoparticle-polymer hybrid had a conductivity of 2.5 mS/cm, which increased to 400 S/cm upon pyrolysis. Despite the presence of carbon, to the best of our knowledge, this already represents the highest electrical conductivity yet measured for ordered mesoporous materials derived from block copolymers.

Since polymer-nanoparticle interactions are largely mediated via the nanoparticle ligands, it may be possible to extend the present approach to other metals for which similarly sized ligand-stabilized nanoparticles can be synthesized. Thus, it may be possible to prepare ordered mesoporous metals of other elements, disordered alloys, or even ordered intermetallics. Furthermore, this discovery also creates a potential pathway to a new class of ordered mesoporous metals made from nanoparticles of distinct compositions. Such nano-heterogeneous, mesoporous metals may have a range of exceptional electrical, optical, and catalytic properties.

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### **Supporting Online Material**

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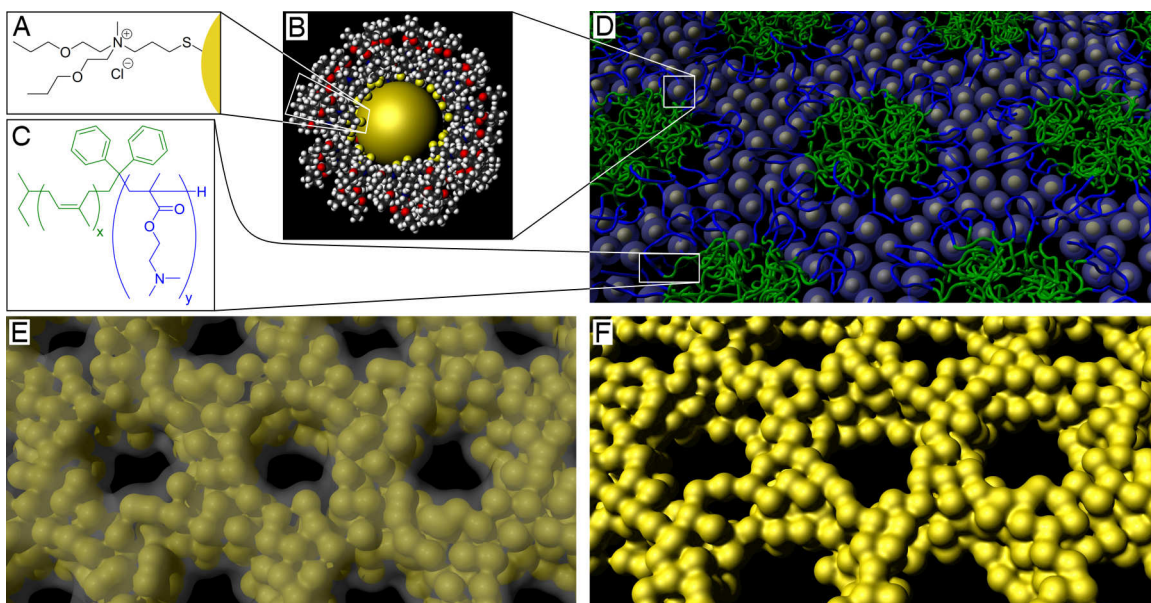
Materials and Methods

Supporting text

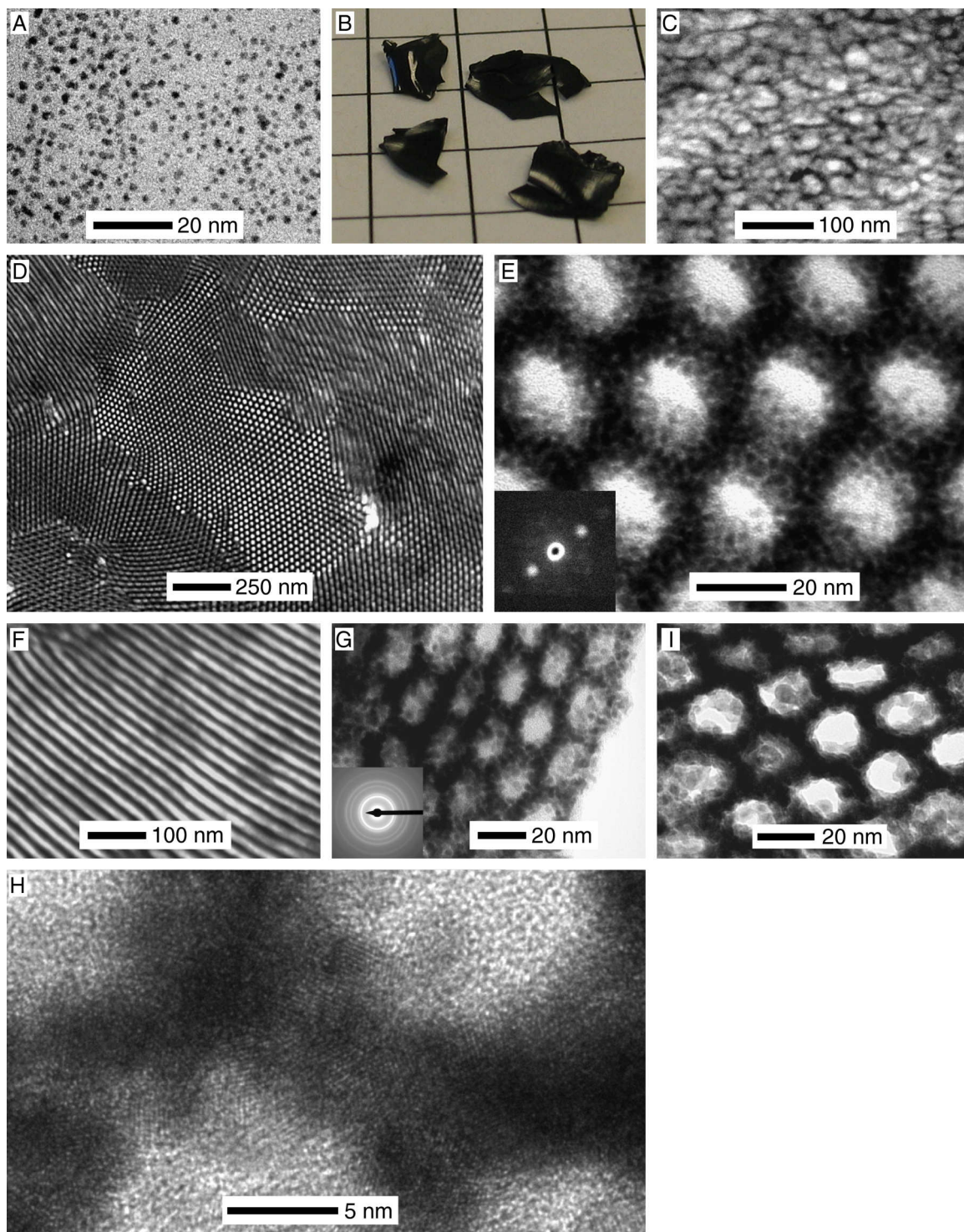
Supporting figures

Supporting tables

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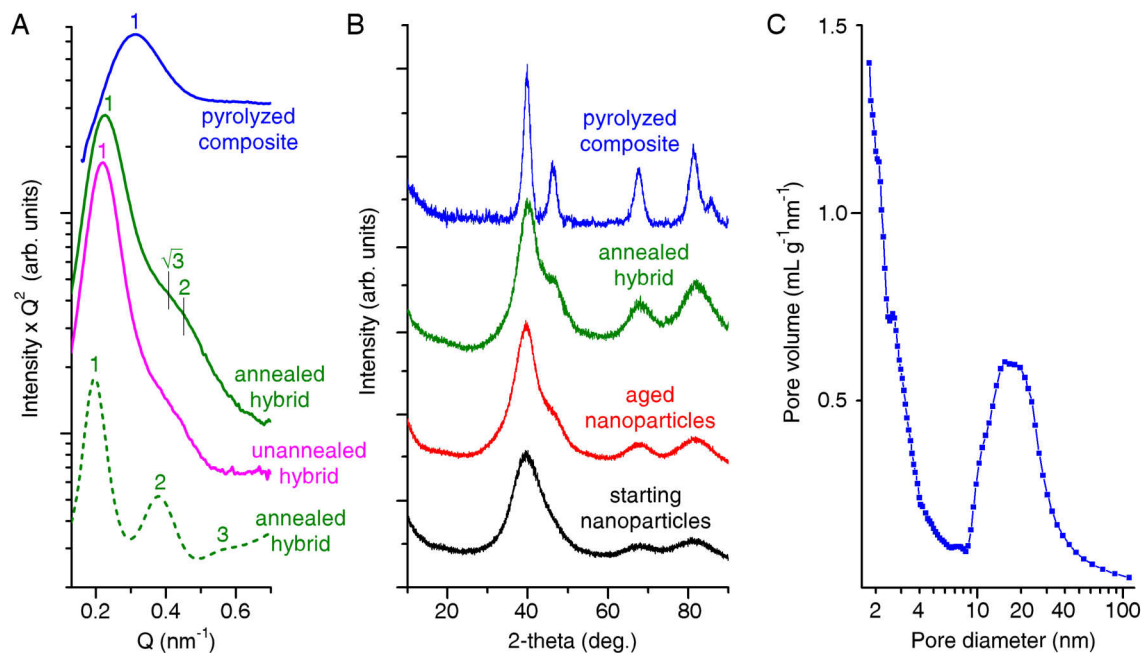


**Fig. 1.** Illustration of CCM-Pt-6 produced after each stage of the synthesis. **(A)** Chemical structure of *N,N*-di-2-propoxyethyl-*N*-3-mercaptopropyl-*N*-methylammonium chloride, the ligand used to produce moderately hydrophilic platinum nanoparticles with high solubility. **(B)** A true-scale model of a nanoparticle with a 1.8 nm diameter metal core and 1.4 nm ligand shell in which part of the metal surface is artificially exposed for illustrative purposes. The model has the same areal density of ligands as the aged nanoparticles, with about 65 ligands per nanoparticle. **(C)** Chemical structure of poly(isoprene-*block*-dimethylaminoethyl methacrylate), PI-*b*-PDMAEMA; PI is green and PDMAEMA is blue. **(D)** Self-assembly of platinum nanoparticles with block copolymer followed by annealing affords a hybrid with a regularly ordered structure, such as the inverse hexagonal morphology. **(E)** Pyrolysis of the hybrid under inert atmosphere produces a mesoporous platinum-carbon composite. **(F)** An argon-oxygen plasma treatment or acid etch of the platinum-carbon produces ordered mesoporous platinum. Figures 1D-F are illustrations that attempt to convey the approximate mesostructure geometry and are based on experimental data.

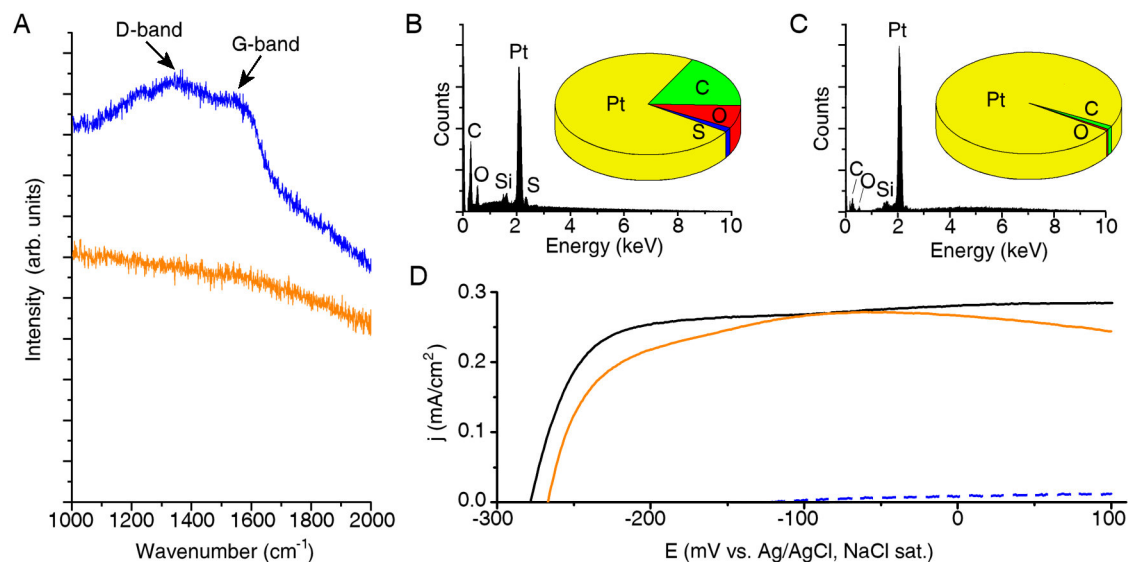


**Fig. 2.** Bright field transmission electron microscopy (TEM) images (A), (C)-(I) and photograph (B) of materials produced after each stage of the synthesis. (A) Ligand-capped platinum nanoparticles. (B) Pieces of unannealed CCM-Pt-6 inverse hexagonal

hybrid film. The grid paper had 5 mm markings. **(C)** Unannealed inverse hexagonal hybrid. **(D)** An annealed inverse hexagonal hybrid. **(E)** Examination of the hybrid from **(D)** at higher magnification resolved individual Pt nanoparticles, seen as dark spots in the bright field image. Inset: a typical electron diffraction (UHV-STEM) from a single platinum nanoparticle, demonstrating its crystallinity. **(F)** An annealed CCM-Pt-4 lamellar hybrid. **(G)** Pyrolysis of an annealed inverse hexagonal hybrid yields a mesoporous platinum-carbon composite. Inset: selected area electron diffraction, showing platinum's expected face-centered cubic (fcc) scattering profile. **(H)** HRTEM of the pyrolyzed sample resolved the platinum's lattice fringes. **(I)** Removal of carbon with an argon-oxygen plasma yielded mesoporous inverse hexagonal platinum.



**Fig. 3.** X-ray and physisorption measurements of materials produced after each stage of the synthesis. **(A)** Small angle x-ray scattering (SAXS) profiles of mesostructured materials. Solid curves correspond to data consistent with an inverse hexagonal mesostructure (CCM-Pt-6) and the dashed curve corresponds to data consistent with a lamellar mesostructure (CCM-Pt-4). For hybrids with the suggested inverse hexagonal hybrid morphology, the (1 0) reflections of the unannealed, annealed, and pyrolyzed samples correspond to d-spacings of 30.3, 30.0, and 23.7 nm, respectively. The first order reflection of the lamellar sample corresponds to 33.1 nm. Tic marks indicate positions of expected reflections. **(B)** Powder x-ray diffraction (PXRD) of samples at various stages of the synthesis. The platinum domain size increases after each stage of processing, from 1.2 nm (starting nanoparticles) to 1.4 nm (aged nanoparticles) to 1.5 nm (annealed hybrid) to 4.1 nm (pyrolyzed composite), as determined by Scherrer analysis. **(C)** BJH pore size distribution as derived from a nitrogen physisorption adsorption isotherm reveals a peak mesopore diameter of 17 nm.



**Fig. 4.** (A) Raman spectra of pyrolyzed CCM-Pt-6 (top) and argon-oxygen plasma-treated CCM-Pt-6 (bottom). (B) Energy dispersive spectroscopy (EDS) of pyrolyzed CCM-Pt-6. Pie chart displays elemental weight fractions. Sample is on a Si substrate and the primary energy is 10 keV. Pt = 74 wt.%, C = 18 wt.%, O = 7 wt.%, S = 1 wt.%. (C) Energy dispersive spectroscopy of acid-treated CCM-Pt-6. Pt = 98 wt.%, C = 1 wt.%, O = 0.5 wt.%. (D) Polarization curves of the  $\text{H}_2$  oxidation reaction in  $\text{H}_2$ -saturated 0.1 M  $\text{H}_2\text{SO}_4$  solution (2000 rpm, 10 mV/s). Blue, dashed = mesoporous Pt-carbon nanocomposite, orange = mesoporous Pt, black = planar Pt electrode.

## Supporting Online Material

### Materials and Equipment

**Block copolymer synthesis.** Isoprene (Aldrich, 99%), cyclohexane (J. T. Baker, 99%), THF (J. T. Baker, 99%) and 1,1-diphenylethylene (97%, Aldrich) were distilled from n-butyl lithium (Sigma-Aldrich, 1.6 M in hexanes) before use. DMAEMA (Aldrich, 98%) was distilled from CaH<sub>2</sub> (Aldrich, 90-95%). Methanolic HCl (Supelco, 3 N) was freeze-pump-thawed three times prior to use. Lithium chloride (Aldrich, 99.99%) was evacuated on a vacuum line overnight prior to usage. Sec-butyl lithium (Aldrich, 1.4 M in cyclohexane) was used as received.

**Ligand and nanoparticle synthesis.** 2-allyloxyethanol (Aldrich, 98%) was distilled from CaH<sub>2</sub> (Aldrich, 90-95%) under nitrogen and freeze-pump-thawed once prior to use. 1,3-dibromopropane (Sigma-Aldrich, 99%) was distilled from potassium carbonate (Sigma-Aldrich, 98%) before use. Pyridine (Aldrich, anhydrous 99.8%), phosphorus tribromide (Aldrich, 99%), 33 wt.% methylamine in ethanol (Aldrich), sodium carbonate (Sigma-Aldrich, 98%), methanol (J. T. Baker, anhydrous, for reaction to make **3** and the nanoparticle synthesis), methanol (Aldrich, anhydrous, 99.8%, for reaction to make **5**), sodium hydrosulfide hydrate (Aldrich), concentrated HCl (Sigma-Aldrich), sodium hydroxide (Sigma-Aldrich, 97%), chloroform (J. T. Baker, 99%), magnesium sulfate (Sigma-Aldrich, anhydrous, 99%), deuterated chloroform (Aldrich, 99.8 atom% D), deuterated water (Aldrich, 99.8 atom% D), platinum (IV) chloride (Aldrich, 99.9%), sodium borohydride (Sigma-Aldrich, 99%), and ether (J. T. Baker, anhydrous) were used as received.

**Hybrid synthesis.** Methanol (J. T. Baker, anhydrous), and chloroform (J. T. Baker) were used as received. Fisherbrand aluminum weighing dishes (Fisher, 08-732-100, 1-1/16 fl. oz. capacity) were formed into aluminum dishes with a 1 cm diameter by bending the aluminum dish around a cylindrical object with a 1 cm diameter. The walls of the dish were typically bent at a  $\sim 45^\circ$  with respect to the bottom of the dish.

**NMR, EM, x-ray and physics methods.** Standard Schlenk line techniques were used for the synthesis of the ligand. NMR spectra were acquired on a Mercury 300 at 300 MHz ( $^1\text{H}$ ) and 75 MHz ( $^{13}\text{C}$ ). Films were cast beneath a hemispherical dish made from the bottom half of a 1-L flask. Heating was controlled using a IKA RET control visc IKAMAG digital hotplate. Samples were prepared for TEM by sectioning at 60 nm with a Leica Ultracut UCT at  $-50^\circ\text{C}$ . The samples were collected on a water/DMSO eutectic solution and transferred to 300 mesh copper grids (no carbon film was used). Most TEM was performed on a Tecnai T12 at 120 kV and high resolution energy filtered (zero loss) TEM was performed on a Tecnai F20 with a Gatan Tridium Spectrometer at 200 kV. Single particle electron diffraction (convergent beam electron diffraction, CBED) was performed on a VG HB501UX UHV-STEM at 100 keV with a 0.2 nm probe. PXRD was performed on a Scintag XDS 2000, with a scan rate of  $0.1^\circ/\text{minute}$ , and the full width at half maximum determined using curve fitting within Jade. Every platinum reflection was used in the Scherrer analysis. Energy dispersive spectroscopy (EDS) was performed on a LEO 1550 FE-SEM at 10 kV. TGA was performed using a TA Instruments Q500 instrument equipped with an autosampler. SAXS experiments were performed on a Rigaku RU-H3R copper rotating anode ( $\lambda = 1.54 \text{ \AA}$ ) for CCM-Pt-6 and on the G1 station at the Cornell High Energy Synchrotron Source (CHESS) for CCM-Pt-4.

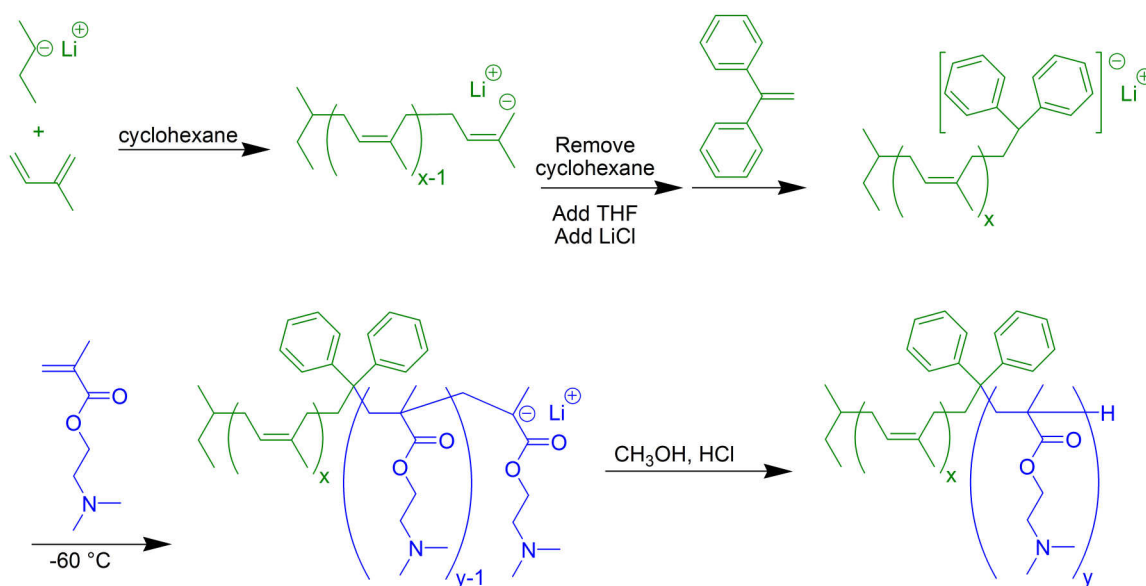
The Rigaku RU-H3R setup was operated at 40 kV and 50 mA. X-rays were monochromated with a Ni filter and focused using orthogonal Franks mirrors. SAXS patterns were collected with a homebuilt  $1\text{ K} \times 1\text{ K}$  pixel CCD detector. The SAXS data obtained at CHESS were collected with a CCD 2-D detector operating at X-ray energy of  $1.223\text{ \AA}$ . Nalgene Oakridge Teflon centrifuge tubes were employed for purifying nanoparticles. Centrifugation was performed using an Eppendorf 5810. Physisorption was performed on a Micromeritics ASAP 2020 using nitrogen as the physisorption gas. Raman spectroscopy was performed on a confocal Raman microscope using a Nd:YAG laser at 532 nm.

Statistics about the nanoparticle core diameters were taken from measurement of over 100 particles using intensity profiles drawn in Gatan DigitalMicrograph. The nanoparticle platinum (core) diameter was  $1.83 \pm 0.5\text{ nm}$  for both as-synthesized and aged particles.

**Electrochemistry methods.** We first added one small flake of the mesoporous platinum-carbon nanocomposite or mesoporous platinum onto a glassy carbon electrode. Next we added  $5\text{ }\mu\text{L}$  of a Nafion solution (5 wt.% solution in alcohol and water) and the liquids were evaporated at room temperature in air. The real surface area of the catalyst was estimated using a conventional procedure based on the coulometry of  $\text{H}_{\text{upd}}$  (taking  $210\text{ }\mu\text{C cm}^{-2}$  for a monolayer). A three-electrode cell equipped with the working electrode, a platinum coil counter electrode, and a sodium chloride saturated Ag/AgCl reference electrode was used for all electrochemical measurements.

## Block copolymer synthesis

Scheme S1 outlines crucial steps of the polymer synthesis. The synthesis of poly(isoprene-*block*-dimethylaminoethyl methacrylate) (PI-*b*-PDMAEMA) has been previously reported (1, 2). The PI-*b*-PDMAEMA block copolymers were synthesized by anionic polymerization under anhydrous and air-free conditions using a glovebox and Schlenk line techniques.



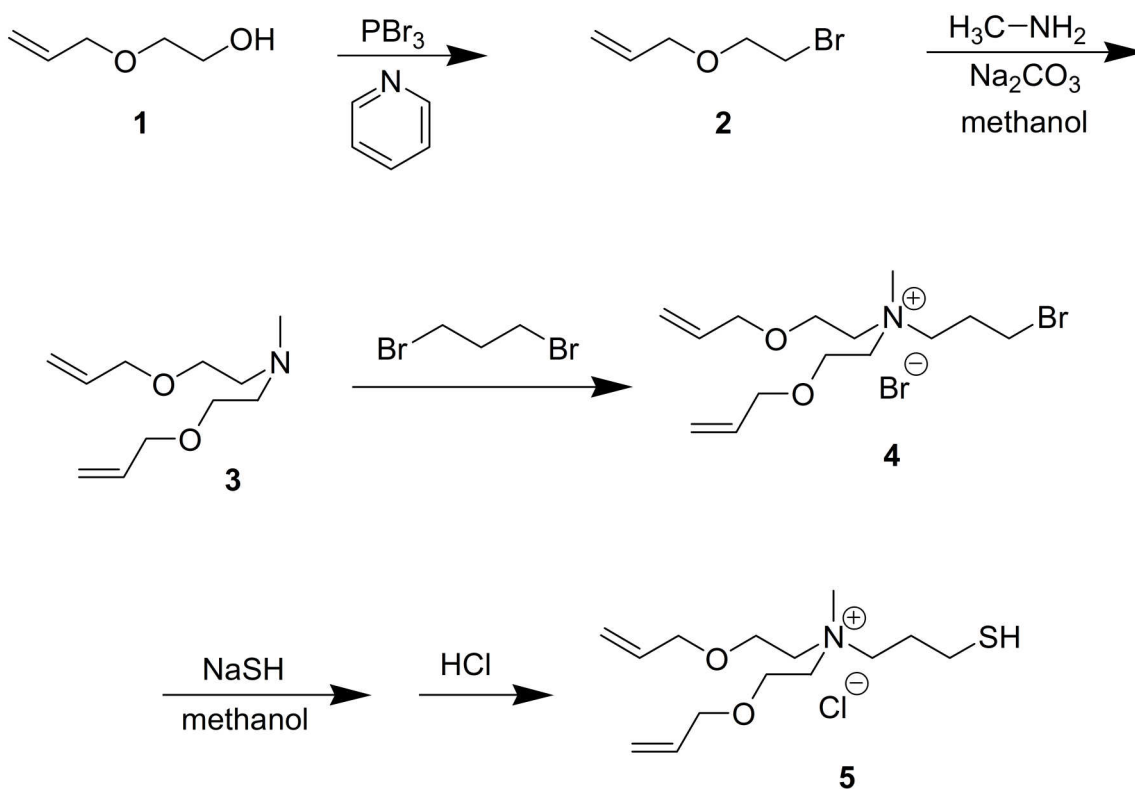
**Scheme S1.** Synthesis of PI-*b*-PDMAEMA.

Sec-butyl lithium was used to initiate isoprene in cyclohexane. After 8 hours of polymerization, cyclohexane was removed on a vacuum line and anhydrous THF and LiCl were subsequently added to the PI in a glovebox. A small amount of the PI was removed via syringe, terminated with methanolic HCl, and subjected to GPC to determine the PI MW. The polyisoprene was end-capped with a 5-fold excess of diphenylethylene and stirred for 30 min. The polymer solution was cooled to -60 °C before the addition of DMAEMA. The polymerization was allowed to proceed for

several hours before the reaction was terminated with methanolic HCl. To purify the polymer, it was precipitated in cold methanol and dried on a vacuum line for several days. The polymers were characterized by GPC to give the final polydispersity and NMR was used to determine PDMAEMA weight fraction. The polymer (a) used to make a lamellar and inverse hexagonal mesostructure had a polydispersity of 1.05 and a molecular weight of 31.1 kg/mol of which 33 wt.% PDMAEMA. A second polymer (b) used to make a lamellar mesostructure had a polydispersity of 1.04 and a molecular weight of 27.8 kg/mol of which 15 wt.% was PDMAEMA.

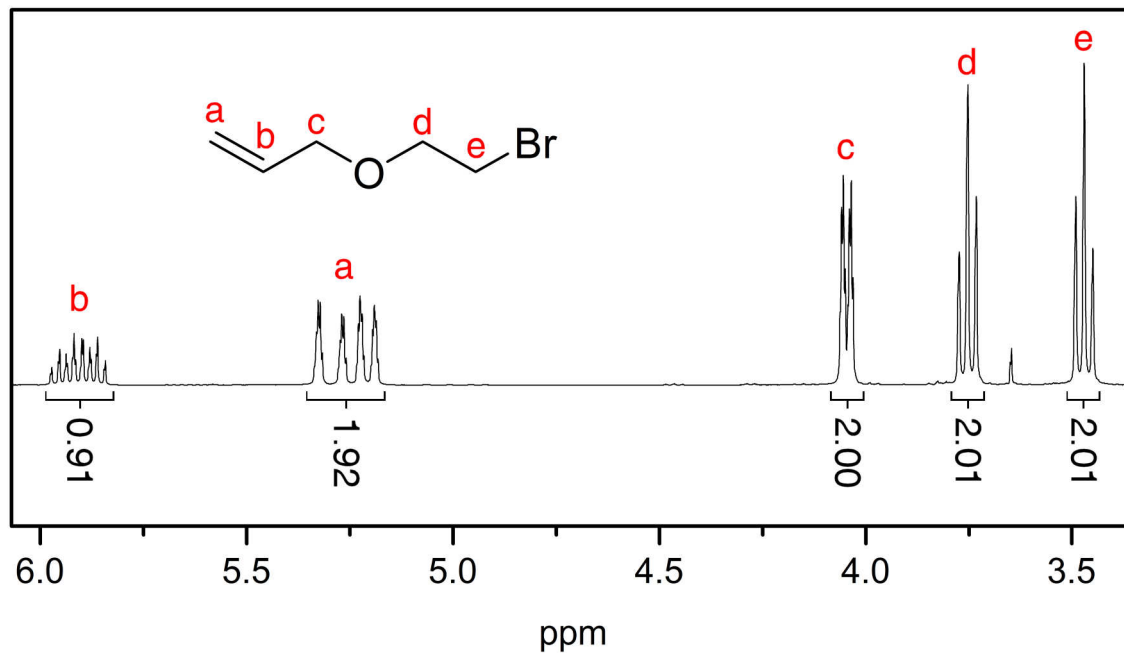
### Ligand synthesis

The ligand synthesis is depicted in Scheme S2.

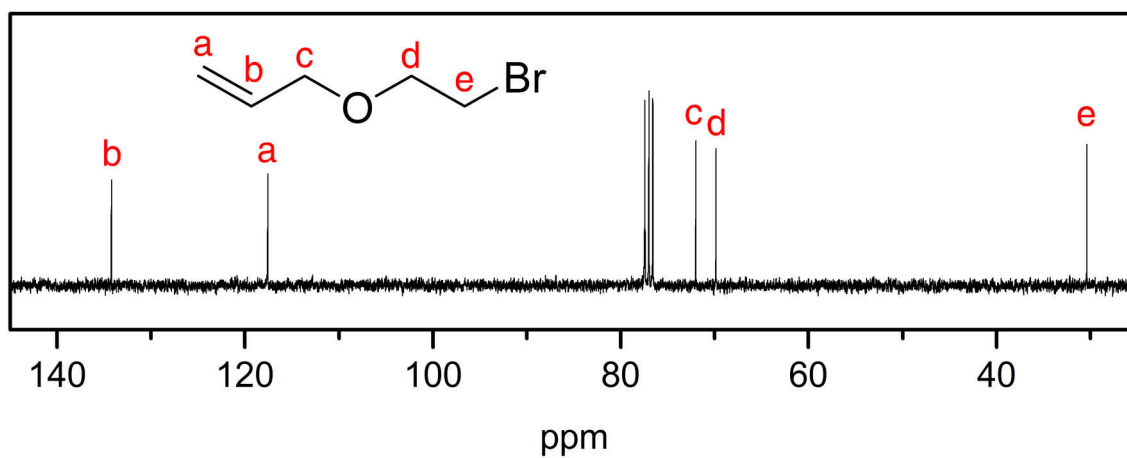


**Scheme S2.** Synthesis of *N,N*-di-2-allyloxyethyl-*N*-3-mercaptopropyl-*N*-methylammonium chloride, **5**.

**Allyloxyethylbromide (2).** *Warning: 2-allyloxyethanol and its derivatives may possibly be absorbed through skin, especially as vapor and may possibly exhibit toxicity (see Int. Arch. Occup. Environ. Health, 70, 232-236 (1997)). Care should be taken to handle these compounds in a fume hood.* In a glovebox, 200 g of PBr<sub>3</sub> (0.739 mol) was added to a 1 L round bottom flask containing a large stirbar. Separately, 54 g of anhydrous pyridine (0.683 mol) and 209 g of anhydrous 2-allyloxyethanol, **1**, (2.05 mol) were mixed in a beaker and transferred to a large pressure-equalizing addition funnel. The flask with PBr<sub>3</sub> and the addition funnel were removed from the glovebox, quickly assembled, and maintained beneath an atmosphere of nitrogen. The flask with PBr<sub>3</sub> was cooled in an ice bath with salt to -10 °C. The contents of the addition funnel were delivered to the PBr<sub>3</sub> over the course of 4 hours. Part way through the addition, a white precipitate accumulated in the flask, making stirring difficult. From this point on, the flask was manually swirled every 10 minutes or so to maintain good mixing. After the addition, the reaction was allowed to come to room temperature overnight. The product was distilled out of this mixture under dynamic vacuum, at approximately 0.05 mbar and between 25 and 28 °C. The distillate typically consisted of a mixture of **1** and **2**. A second distillation was used to separate the two; the boiling point of **2** is slightly higher than that of **1**. The reaction afforded 89 g of **2** (0.54 mol), a 26% yield. <sup>1</sup>H and <sup>13</sup>C NMR spectra are shown in Figures S1 and S2.



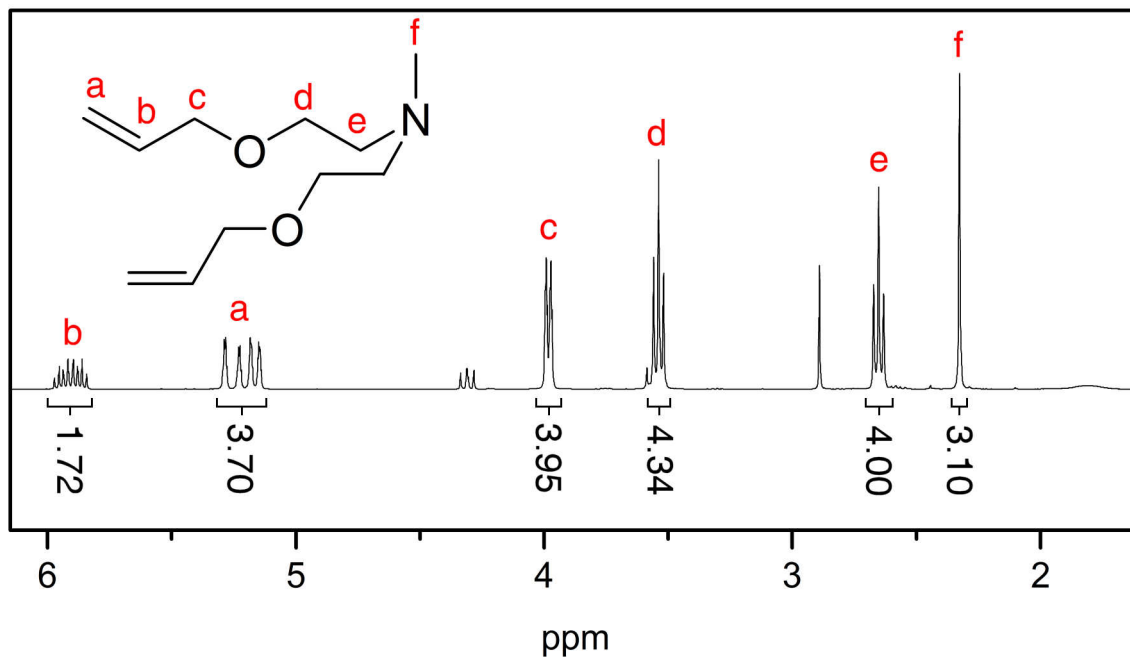
**Figure S1.**  $^1\text{H}$  NMR of **2**. ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  5.91 (**b**, m, 1H), 5.25 (**a**, m, 2H), 4.04 (**c**, m, 2H), 3.75 (**d**, t, 2H,  $J = 6.21$  Hz), 3.47 (**e**, t, 2H,  $J = 6.13$  Hz).



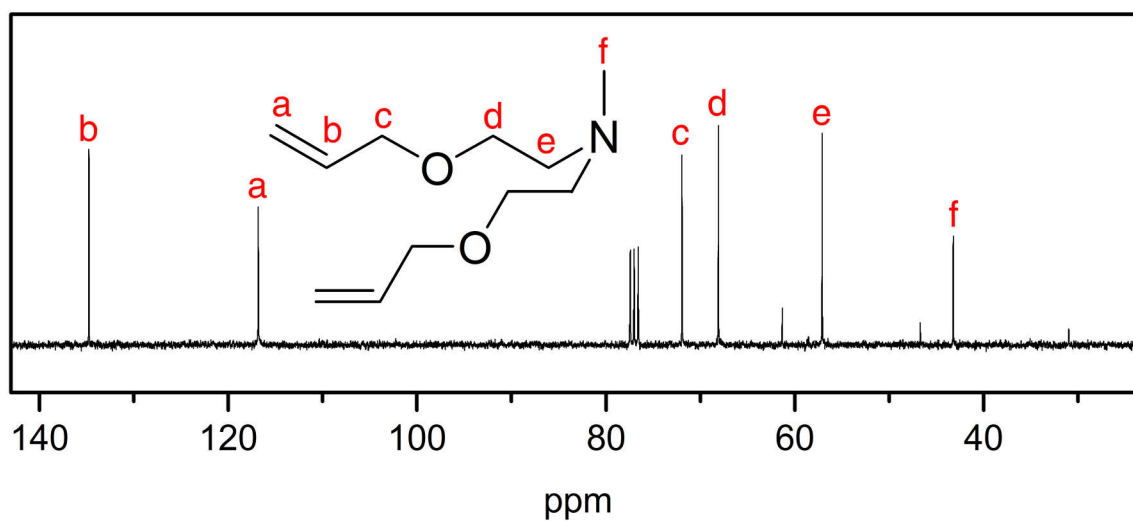
**Figure S2.**  $^{13}\text{C}$  NMR of **2**. ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  134.2 (**b**), 117.6 (**a**), 72.0 (**c**), 69.9 (**d**), 30.4 (**e**).

*N,N*-di-(2-(allyloxy)ethyl)-*N*-methylamine (**3**). To a 1-L flask with a stirbar, we added 89 g of **2** (0.54 mol), 440 g of methanol, 25.4 g of 33 wt.% methylamine in ethanol

(0.270 mol), and 57.2 g of  $\text{Na}_2\text{CO}_3$  (0.54 mol). The flask was equipped with a reflux condenser and heated at 36 °C in an oil bath under flowing nitrogen. After one day the temperature was increased to 58 °C. After one day at the elevated temperature the flask was removed from heat. The methanol was removed via rotary evaporation. The slurry was dumped into filter paper and washed with chloroform. The amine was extracted into an aqueous HCl solution from the chloroform solution, followed by extraction into chloroform by lowering the pH to between 12 and 14 with NaOH. The chloroform was dried over  $\text{MgSO}_4$  for 5 minutes, filtered through Whatman filter paper, and the chloroform was rotary evaporated. The amine was distilled under dynamic vacuum at 51 °C and 0.1 mbar. Often, the amine was fractionally distilled a second time to improve purity. The product was a colorless, transparent liquid. Approximately 8.50 g of **3** (0.0427 mol) was isolated from the reaction, a yield of 8%. The low yield is due to the preferential formation of the *N,N,N*-tri-(2-(allyloxy)ethyl)-*N*-methylammonium bromide.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are shown in Figures S3 and S4.



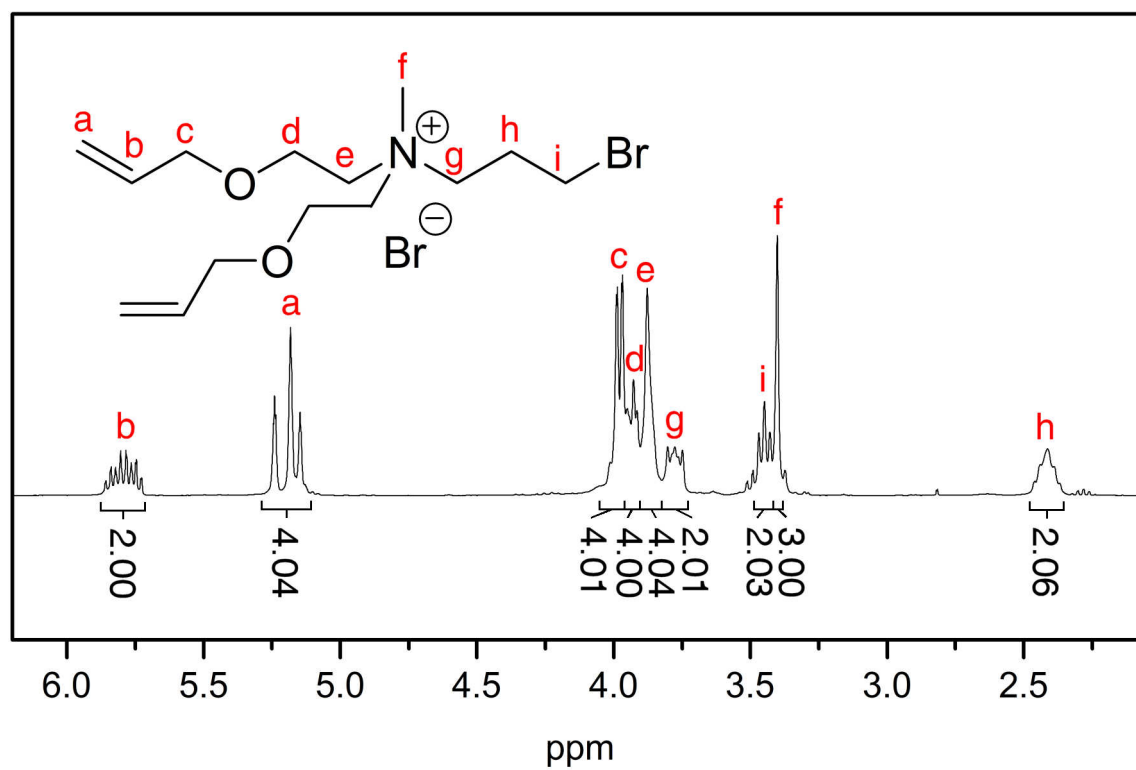
**Figure S3.**  $^1\text{H}$  NMR of **3**. ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  5.90 (**b**, m, 2H), 5.20 (**a**, m, 4H), 3.98 (**c**, m, 4H), 3.54 (**d**, t, 4H,  $J = 5.99$  Hz), 2.65 (**e**, t, 4H,  $J = 5.99$  Hz), 2.33 (**f**, s, 3H). The unlabeled peaks are from unknown contaminants.



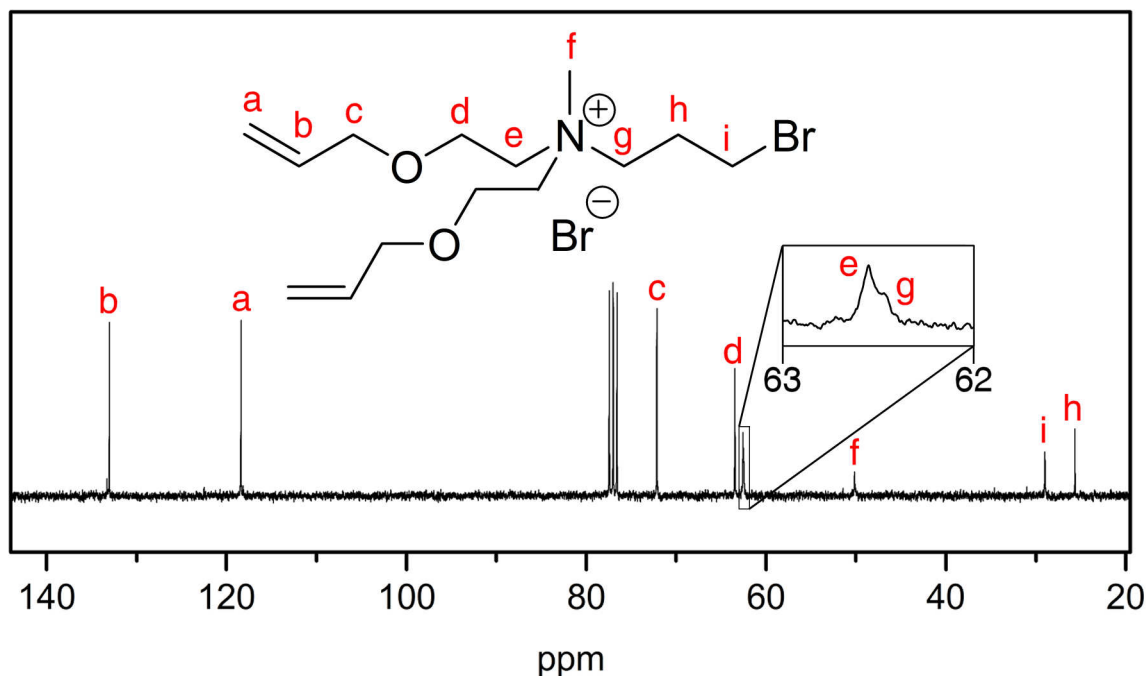
**Figure S4.**  $^{13}\text{C}$  NMR of **3**. ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  134.7 (**b**), 116.8 (**a**), 71.9 (**c**), 68.1 (**d**), 57.1 (**e**), 43.2 (**f**).

***N*-3-bromopropyl-*N,N*-di-(2-(allyloxy)ethyl)-*N*-methylammonium bromide**

(4). We began by weighing a 250 mL flask with stirbar. To this flask we added 8.50 g of **3** (0.0427 mol) and 274.74 g of 1,3-dibromopropane (1.361 mol). The reaction was heated in an oil bath at 50 °C for 16 hours. The excess 1,3-dibromopropane was removed from the reaction via distillation under vacuum. During the distillation, the flask was immersed in an oil bath at 50 °C; heating for prolonged periods at higher temperatures could decompose the product. The 1,3-dibromopropane could be re-used. The flask was connected directly to the vacuum line and evacuated overnight to remove the residual 1,3-dibromopropane. Finally, the flask was brought immediately into a glovebox to prevent the absorption of water. The contents of the flask, **4**, weighed 16.44 g (0.0410 mol), nominally a yield of 96%. The starting material **3** is not entirely pure (see Figures S3, S4), so the actual yield of this reaction is probably close to 100%. <sup>1</sup>H and <sup>13</sup>C NMR spectra are shown in Figures S5 and S6.



**Figure S5.** <sup>1</sup>H NMR of **4**. (CDCl<sub>3</sub>, 300 MHz) δ 5.79 (**b**, m, 2H), 5.18 (**a**, m, 4H), 3.98 (**c**, m, 4H), 3.93 (**d**, t, 4H), 3.88 (**e**, t, 4H), 3.78 (**g**, t (restricted rotation), 2H), 3.45 (**i**, t, 2H, J = 5.85 Hz), 3.40 (**f**, s, 3H), 2.41 (**h**, p, 2H, J = 6.91 Hz).



**Figure S6.**  $^{13}\text{C}$  NMR of **4**. ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  133.0 (**b**), 118.4 (**a**), 72.5 (**c**), 63.5 (**d**), 62.6 (**e**), 62.5 (**g**), 50.2 (**f**), 29.0 (**i**), 25.6 (**h**).

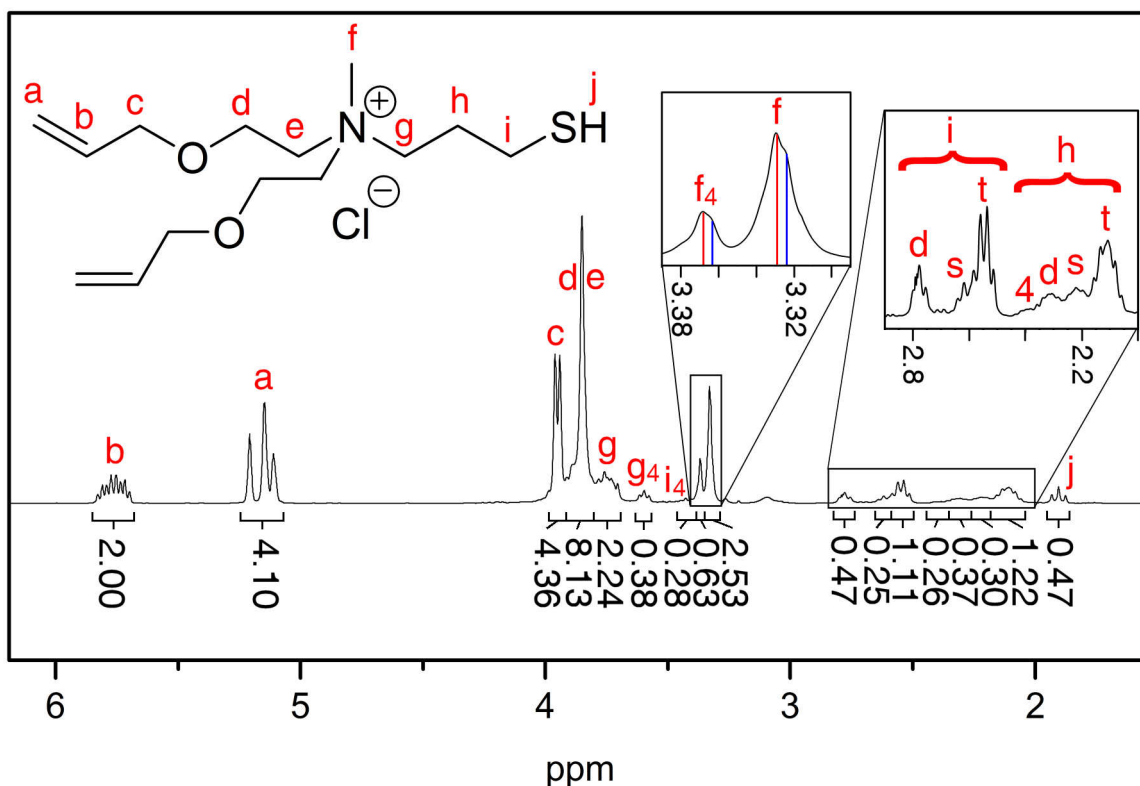
***N,N*-di-(2-(allyloxy)ethyl)-*N*-3-mercaptopropyl-*N*-methylammonium chloride**

(**5**). To the same flask with 16.44 g of **4** (0.0410 mol) we added 2.490 g of sodium hydrosulfate hydrate in a glovebox (water content varies from bottle to bottle and slowly decreases upon storage in an anhydrous environment; water content is typically less than 35 wt.% and may get as low as a few percent upon lengthy storage). We added 55 g of dry, degassed methanol to solvate the reagents, and assembled the flask with a reflux condenser under flowing nitrogen outside the glovebox. The reaction was heated at 65 °C for 8 hours. The reaction was cooled to room temperature and concentrated HCl was added (in air) until the pH stabilized at <2. Usually at least several mL of concentrated HCl were needed. During the addition NaCl precipitated from solution. The solution was then stirred for at least an hour in a well ventilated fume hood so that any excess

NaSH would react with the HCl and be removed as gaseous H<sub>2</sub>S (Caution! H<sub>2</sub>S is a toxic gas which can deaden one's sense of smell and can be fatal at modest concentrations!)

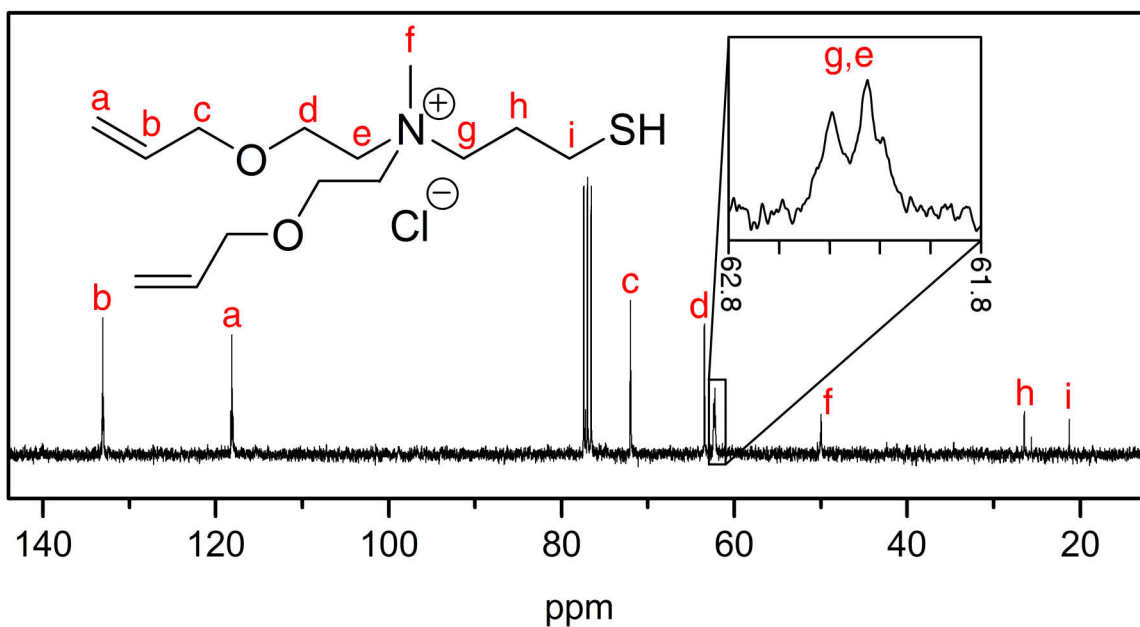
The solution was then rotary evaporated to remove the methanol. The flask with product mixture **5** was attached to a vacuum line for several hours to remove water and HCl. The product mixture was dissolved in chloroform and filtered through Whatman filter paper to remove remaining NaCl or NaBr. The chloroform was rotary evaporated and the product attached to a vacuum line overnight to remove residual solvent and water. The product mixture **5** is initially a viscous, yellow-orange liquid. Upon sitting for several weeks, the product begins to solidify. As determined by NMR, there is no detectible change upon sitting. The reaction afforded 12.23 g of the product mixture, a yield of 96% assuming exclusive production of **5**. The product was immediately brought into the glovebox to prevent absorption of water. As determined by NMR, the product mixture contains the thiol, disulfide and sulfide of **5** and a small amount of residual **4**. The relative proportions of each vary from synthesis to synthesis and a typical product distribution is shown in Figures S7 and S8. The variation in the product distribution is related to variations in the ratio of **4** and NaSH that are initially combined. An excess of NaSH promotes sulfide formation because NaSH deprotonates thiol **5** to form a thiolate which can nucleophilically substitute for the bromide of **4**. An excess of NaSH probably promotes disulfide formation via deprotonation of the thiol followed by oxidation, possibly by adventitious oxygen. Across five syntheses, thiol content varied between 13% and 45%, sulfide varied between 10 and 18%, disulfide varied between 19 and 43%, and **4** content varied between 20% and 26%. Importantly, variation in the product distribution did not seem to influence the synthesis of the nanoparticles. No further

purification was performed.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a typical product mixture are shown in Figures S7 and S8.



**Figure S7.**  $^1\text{H}$  NMR of product mixture **5**. Letters without subscripts (a through j) correspond to **5** as shown in the figure. Letters d, s, and t indicate the disulfide, sulfide, and thiol, respectively, for protons i and h. Letters with a subscript ( $f_4$ ,  $g_4$ ,  $h_4$ , and  $i_4$ ) label peaks from residual **4**. Red and blue lines highlight the fact that peaks f and  $f_4$  are the superposition of two smaller peaks. This arises from the presence of both the chloride salt (as drawn in the figure) and the bromide salt (not shown). Red lines correspond to molecules with a chloride anion and blue lines correspond to molecules with a bromide anion. The chloride salt predominates, so this form is what will be drawn throughout this manuscript. (CDCl<sub>3</sub>, 300 MHz) **Thiol 5**:  $\delta$  5.76 (**b**, m, 2H), 5.15 (**a**, m, 4H), 3.95 (**c**, m,

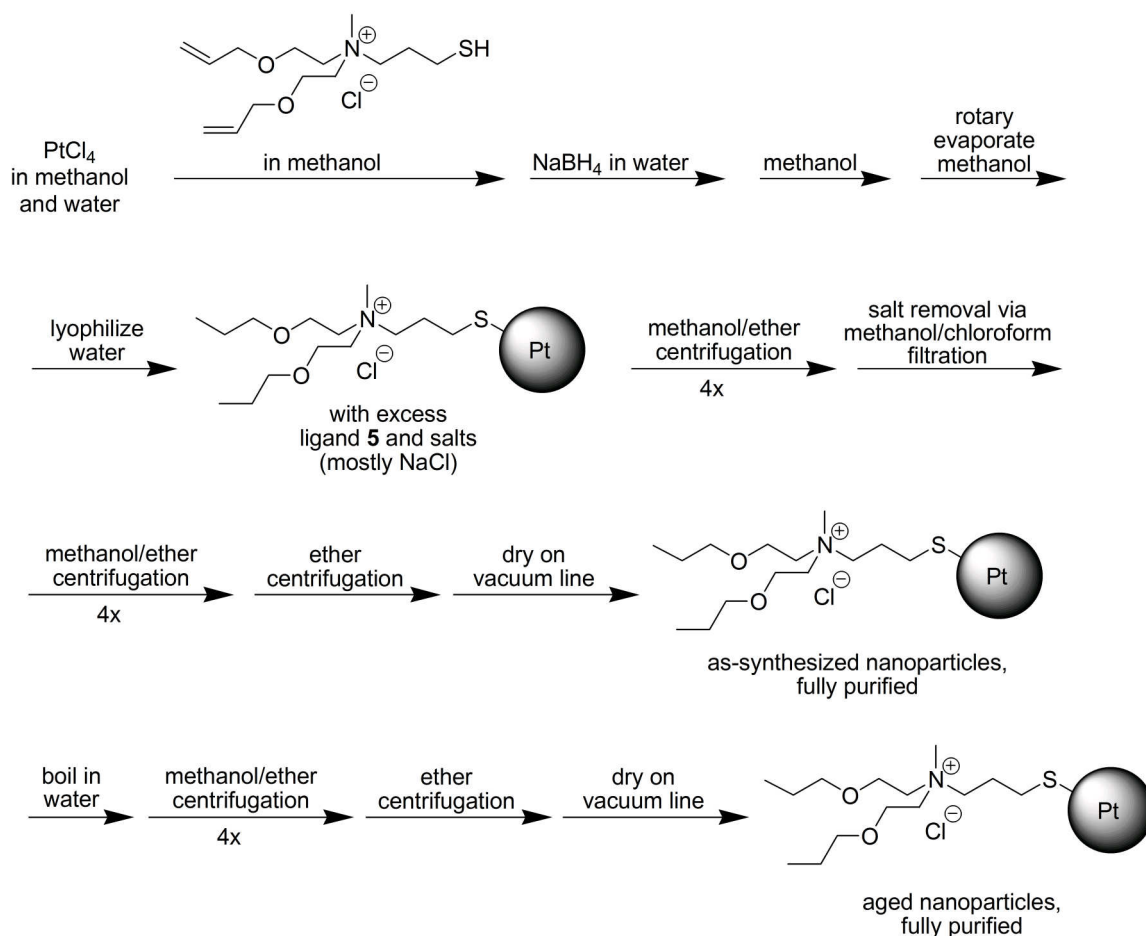
4H), 3.85 (**d**, **e**, t, 8H), 3.75 (**g**, t, 2H), 3.329 (**f**, **chloride**, s, 3H), 3.324 (**f**, **bromide**, s, 3H), 2.55 (**i**, q, 2H,  $J = 7.3$  Hz), 2.11 (**h**, p, 2H,  $J = 7.5$  Hz), 1.90 (**j**, t, 1H,  $J = 8.5$  Hz).



**Figure S8.** <sup>13</sup>C NMR of **5**. (CDCl<sub>3</sub>, 75 MHz) δ 133.1 (**b**), 118.1 (**a**), 72.0 (**c**), 63.5 (**d**), 62.4, 62.3 (**g**, **e**), 50.0 (**f**), 26.5 (**h**), 21.2 (**i**).

### Nanoparticle synthesis

The stages of nanoparticle synthesis, purification, and ageing are depicted in Scheme S3.



**Scheme S3.** Nanoparticle synthesis, purification, and ageing.

We performed the nanoparticle synthesis on a variety of scales, using between 1.0 g of  $\text{PtCl}_4$  and 2.0 g of  $\text{PtCl}_4$  and scaling the other reagents proportionally. Because of the precise timing required in the synthesis, batches made with more than 2.0 g of  $\text{PtCl}_4$  were less reproducible, largely because of the challenge in transferring large quantities of reagents in the short times required. Indeed, following the timing described below is essential to obtain Pt nanoparticles with a 1.83 nm diameter and variations from this process tended to give low yields or smaller particles (as small as 1.0 nm).

Three solutions were prepared immediately prior to the nanoparticle synthesis. The first solution was prepared in a one-neck 1-L round bottom flask with a large joint (at least 24/40) and a large stirbar. To this flask we added 2.000 g of  $\text{PtCl}_4$  (5.937 mmol), 100.0 g of water, and 100.0 g of methanol. The second solution was prepared in a 125 mL Erlenmeyer flask. To this flask we added 1.50 g of **5** and 30.0 g of methanol. The third solution was prepared in a 125 mL Erlenmeyer flask by combining 2.272 g of  $\text{NaBH}_4$  and 45.0 g of water.

Over a period of about 2 to 3 seconds, the second solution (**5**) was poured into the first solution ( $\text{PtCl}_4$ ), while stirring rapidly. About 1 to 2 seconds later, the third solution ( $\text{NaBH}_4$ ) was added to the first two solutions over a period of less than 5 seconds. About 10 minutes later, 200 mL of methanol was added to the solution. The solution was stirred for 10 more minutes before the stirbar was removed and the methanol rotary evaporated.

Careful timing in the above steps arises from the tendency of  $\text{Pt}^{4+}$  to form an insoluble complex with **5** within 3 to 5 seconds. If too much time proceeds between the addition of **5** and  $\text{NaBH}_4$ , large chunks of precipitate form that renders the  $\text{Pt}^{4+}$  inaccessible to  $\text{NaBH}_4$ . When this happens, the yield of nanoparticles is low. It should also be noted that rapid addition of the  $\text{NaBH}_4$  solution is made difficult by the rapid production of hydrogen bubbles. Thus using a large flask with a large opening is crucial. Despite careful addition of **5** and  $\text{NaBH}_4$ , a small amount of precipitate usually does form. Accordingly, adding methanol 10 minutes after the reduction solvates the precipitate and completes the reduction. Adding the methanol sooner than this is detrimental because changing the water:methanol ratio yields smaller nanoparticles.

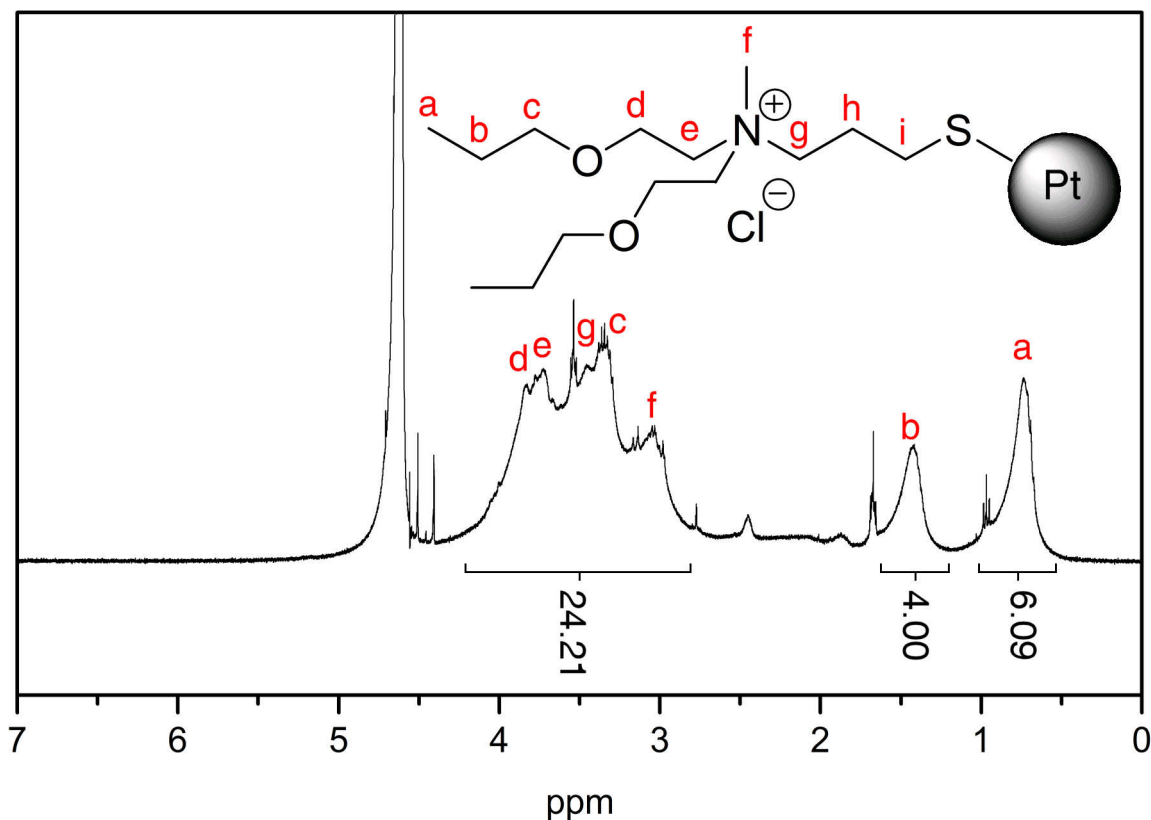
After removal of methanol via rotary evaporation, the water is lyophilized (freeze dried) by cooling the solution and attaching the flask to a vacuum line. If the solution is above about 5 °C, a foam forms that makes further removal of water difficult. The water does not need to be completely frozen during the evacuation and typically we placed a bath of luke-warm water beneath the flask to expedite water removal after about ten minutes.

The black solid is transferred by spatula to 50 mL centrifuge tubes (Nalgene Oakridge PTFE tubes). Residual nanoparticles are transferred by dissolution in a small volume of methanol. For a synthesis on the scale described above (2.0 g of PtCl<sub>4</sub>), distributing the solid into four 50 mL centrifuge tubes is necessary to allow for efficient centrifugation. To each of the centrifuge tubes, approximately 4 mL of methanol is added and the tubes are shaken for several minutes to dissolve most of the solid. Ether is added to the fill mark. The tubes are centrifuged at 10,000 rpm for 2 minutes. The faintly colored (dark) supernatant is decanted. The centrifugation with methanol and ether is repeated three more times.

To remove NaCl, the solid is dissolved in a solution of 3 g of methanol and 97 g of CHCl<sub>3</sub>. The solution is poured through Whatman filter paper. The remaining solid in the filter is washed four more times with 50 mL of 3 wt.% methanol and 97 wt.% CHCl<sub>3</sub>. The solvent is rotary evaporated from the nanoparticles. The nanoparticles are centrifuged four more times in methanol/ether as before and one last time in ether. The black solid is broken into a fine powder using a mortar and pestle (Caution! Dry nanoparticles should always be handled in a fume hood to prevent inhalation.) Finally,



heated oil bath, the flask was removed and allowed to cool naturally to room temperature. Following this, the water was lyophilized and the resulting black solid was centrifuged four times in methanol/ether and once in ether as described above. The solid was pulverized in a mortar and pestle and dried on a vacuum line for several hours. A  $^1\text{H}$  NMR spectrum is shown in Figure S10. The NMR shows that there are a very small number of impurities (integration of the impurities accounts for 1.8% of the total integrated area in the spectrum) and the fact that these appear as sharp peaks indicate that they are not directly associated with the nanoparticle. Thus NMR suggests that ageing the particles causes minimal changes in the composition of the organic material that is bound to the nanoparticles (although TGA measurements, shown later, demonstrate that there are fewer ligands per particle). Nevertheless, liquid-phase  $^1\text{H}$  NMR does a poor job of identifying organic material immediately adjacent to the surface (3) so we cannot rule out the possibility that there are relatively short organic (or inorganic) species bound to the nanoparticle surface.



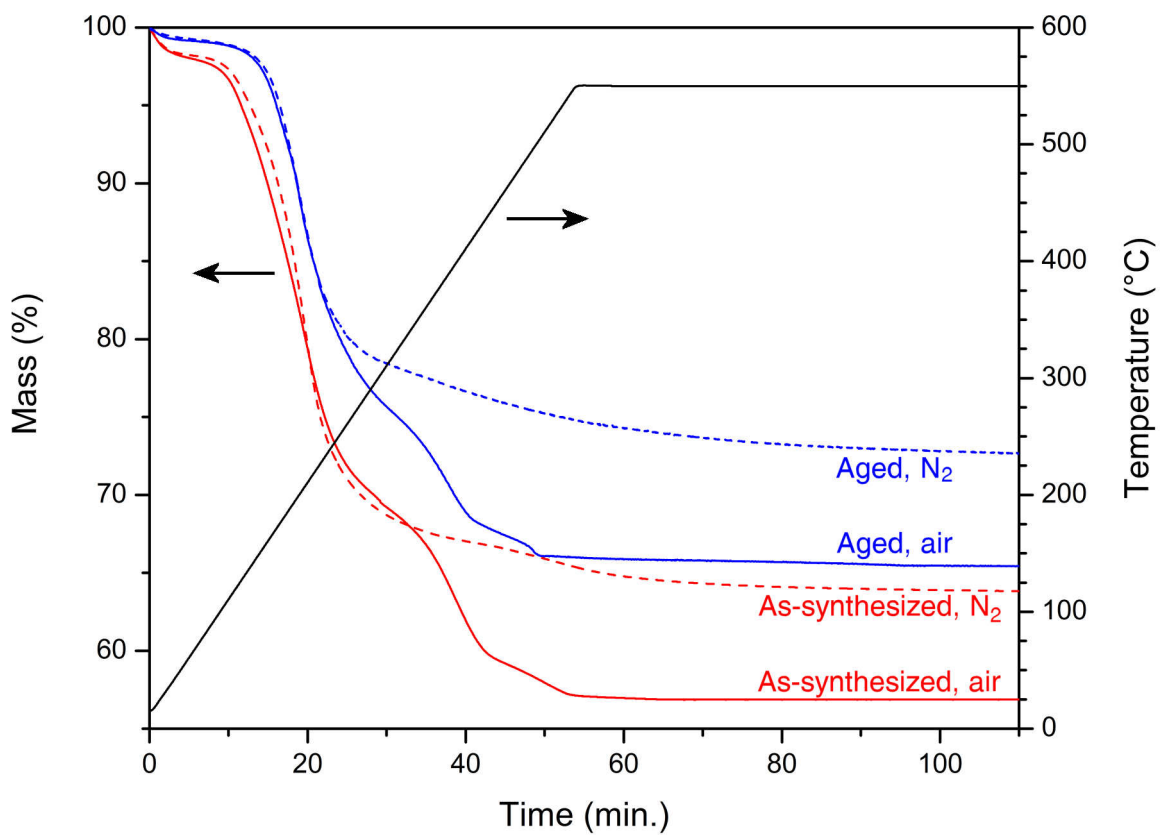
**Figure S10.**  $^1\text{H}$  NMR of aged Pt nanoparticles. Peak assignments for **c** through **g** are tentative. ( $\text{D}_2\text{O}$ , 300 MHz)  $\delta$  3.87 (**d**, 4H), 3.74 (**e**, 4H), 3.49 (**g**, 2H), 3.38 (**c**, 4H), 3.08 (**f**, 3H), 1.46 (**b**, 4H), 0.78 (**a**, 4H).

## TGA

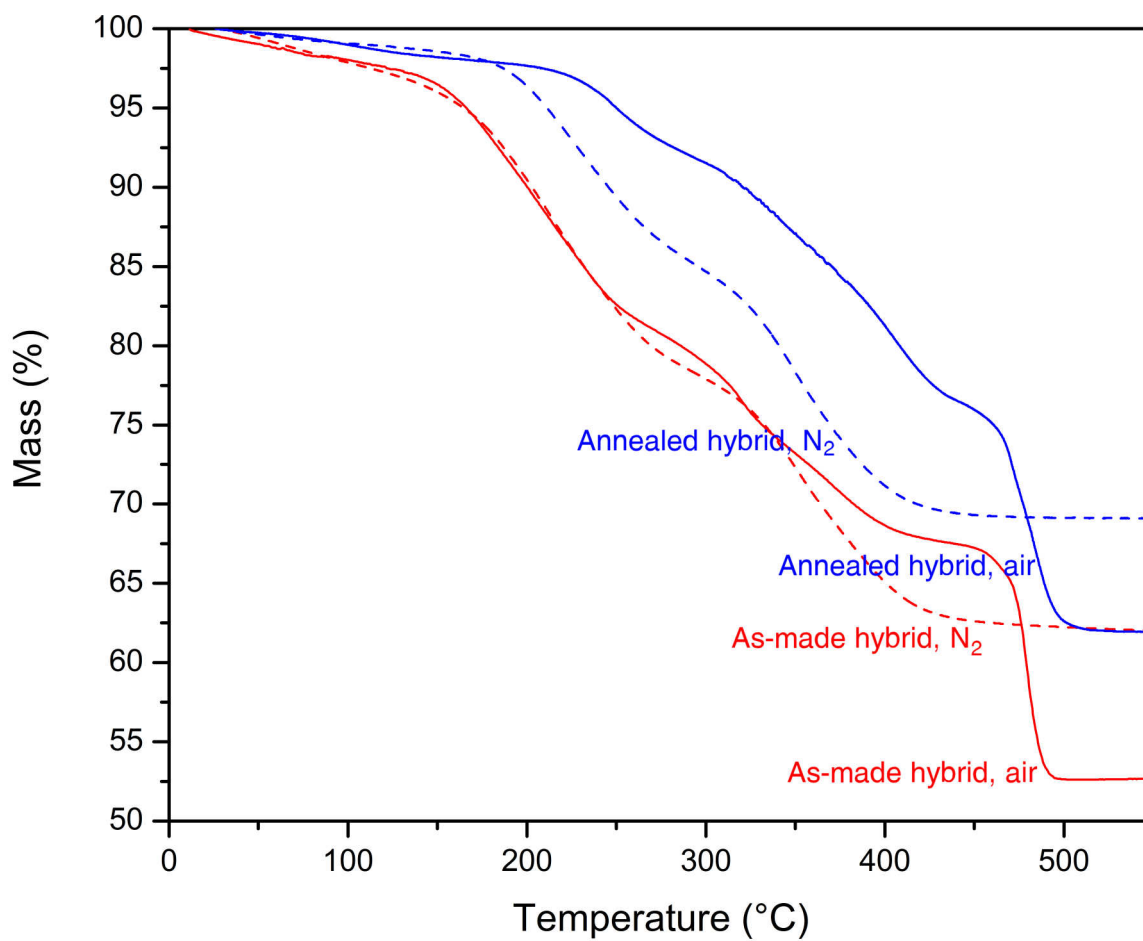
TGA was performed in air and nitrogen on as-synthesized and aged nanoparticles (Figure S11), on as-synthesized and annealed CCM-Pt-6 hybrids (Figure S12), and on the CCM-Pt-6 pyrolyzed and acid-treated films (Figure S13). We assumed that only platinum metal remains after performing TGA in air. We believe this is a good assumption because the resulting material is shiny and silvery like bulk Pt. Thus, we conclude that the aging process leads to a loss of ligand from the nanoparticle. Comparison of aged particles heated in air with those heated in nitrogen show that 18 wt.% of the ligand

remains after pyrolysis. Also noteworthy is the fact that most of the mass loss occurs between 150 °C and 250 °C when heating under nitrogen. In contrast, pyrolysis of the PI-*b*-PDMAEMA block copolymer by itself (data not shown) occurs mostly between 320 °C and 420 °C. Thus, two clearly defined mass loss steps are observed in the CCM-Pt-6 nanoparticle-block copolymer hybrids when heated under nitrogen (Figure S12). When heated in air, the mass loss is greater and the difference in mass loss reflects the approximate mass of carbonaceous material that remains in the pyrolyzed samples. In Figure S12, it is also evident that the annealed hybrids have less organic material than the as-made hybrids. Presumably during the annealing process (2 days at 130 °C under vacuum) the ligands partially decompose and volatilize. Indeed, comparison of the as-made and annealed hybrids show that the differences in mass loss occur primarily at temperatures below 275 °C, which we assign to ligand decomposition (as noted above).

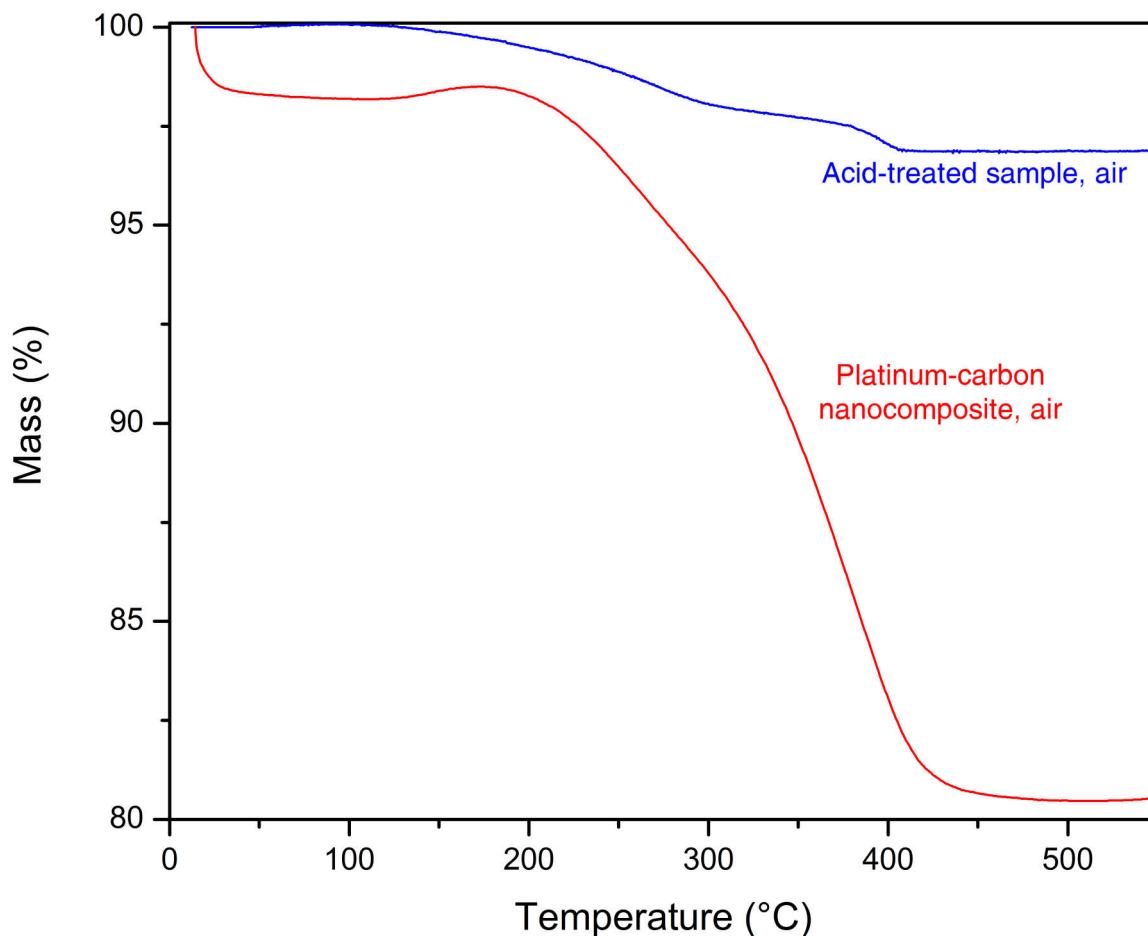
The CCM-Pt-6 platinum-carbon nanocomposite apparently absorbs a significant quantity of water or other volatile species from the atmosphere; these species rapidly evaporate during in TGA (Figure S13). There is a small increase in mass at 200 °C which may arise from the partial oxidation of the carbonaceous matrix. TGA suggests that the acid treatment removes nearly all combustible and volatile compounds from the platinum-carbon nanocomposite, consistent with EDS (Figure 4 C). The absence of a significant mass loss at temperatures below 150 °C (as occurs with the platinum-carbon nanocomposite) suggests that the carbonaceous matrix is where the adsorbed water and other volatile species primarily reside.



**Figure S11.** TGA traces of platinum nanoparticles. For all runs, the nanoparticles were heated at 10 °C/min. to 550 °C under flowing N<sub>2</sub> or air and held at 550 °C for one hour (black line).



**Figure S12.** TGA of CCM-Pt-6 hybrids, before and after annealing. For all runs, the hybrids were heated at 10 °C/min. to 550 °C.



**Figure S13.** TGA of CCM-Pt-6 platinum-carbon nanocomposite and acid-treated sample. Both samples were heated in air at 10 °C/min. to 550 °C.

### Calculations

To calculate the platinum and organic volume fraction in the nanoparticles, we assumed that the platinum nanoparticles were spherical and that the platinum core had the density of bulk platinum (21.09 g/cm<sup>3</sup>). We assumed the mass loss observed when performing TGA in air corresponded to the total mass of ligand and that only platinum remained after combustion. We also assumed that the composition of the ligand on the nanoparticle was the same as ligand **5** prior to the nanoparticle synthesis (see Figure S7),

which consisted of a mixture of chloride salt (313.9 g/mol, ~60%) and bromide salt (358.4 g/mol, ~40%) and thus has an averaged molecular weight of 331.7 g/mol.

A spherical platinum nanoparticle (metal core diameter of 1.83 nm) has a volume of  $3.21 \text{ nm}^3$ . This volume of metal weighs 67.7 zg ( $z = \text{zepto} = 10^{-21}$ ) and contains 209 platinum atoms. The as-synthesized platinum nanoparticles had a mass loss in TGA of 43.1%. From this we calculate that the mass of ligands attached to each nanoparticle is 51.3 zg, which suggests that approximately 93 ligands are attached to each nanoparticle, on average.

$$\text{mass of Pt} = \frac{4}{3} \cdot \pi \cdot \left( \frac{1.83 \text{ nm}}{2} \right)^3 \cdot \left( \frac{1 \text{ cm}^3}{10^{21} \text{ nm}^3} \right) \cdot \frac{21.09 \text{ g}}{\text{cm}^3} = 67.7 \cdot 10^{-21} \text{ g} = 67.7 \text{ zg} \quad [1]$$

$$\# \text{ of Pt atoms} = \frac{67.7 \cdot 10^{-21} \text{ g}}{195 \text{ g/mol}} \cdot \frac{6.022 \cdot 10^{23} \text{ atoms}}{\text{mol}} = 209 \text{ atoms} \quad [2]$$

$$\# \text{ of ligands per particle} = \frac{\left( \frac{67.7 \cdot 10^{-21} \text{ g}}{1 - 0.431} \right) - 67.7 \cdot 10^{-21} \text{ g}}{331.7 \text{ g/mol}} \cdot \frac{6.022 \cdot 10^{23} \text{ ligands}}{\text{mol}} = 93 \text{ ligands} \quad [3]$$

A similar calculation for the aged nanoparticles shows that there are 65 ligands per nanoparticle.

The calculation of platinum or ligand volume fraction in the nanoparticles can be performed in several ways. Perhaps the simplest method depends on finding the molar volume of the ligand, which can be done via bulk density measurements or computational approaches. We used both approaches and found both gave very similar results.

Optimizing the molecular structure using a variety of packages (MM2, Mopac) and

calculation of the atomic volume yielded approximately  $0.440 \text{ nm}^3$  for the bromide salt of **5** and  $0.430 \text{ nm}^3$  for the chloride salt of **5**. Conversion to a bulk density yields  $1.3 \text{ g/cm}^3$ , which is identical to our measured bulk density. Using this density, the TGA data can be used to calculate platinum and ligand volume fractions. Thus we calculate that the platinum volume fraction is 7.5% and 10.4% in the as-synthesized and aged particles, respectively.

$$\text{molar volume} = \left( \frac{0.440 \text{ nm}^3}{\text{ligand}} \cdot 0.4 + \frac{0.430 \text{ nm}^3}{\text{ligand}} \cdot 0.6 \right) \cdot \frac{\text{cm}^3}{10^{21} \text{ nm}^3} \cdot \frac{6.022 \cdot 10^{23} \text{ ligands}}{\text{mol}} = \frac{261 \text{ cm}^3}{\text{mol}} \quad [4]$$

$$\text{ligand density} = \frac{331.7 \text{ g/mol}}{261 \text{ cm}^3/\text{g}} = 1.3 \text{ g/cm}^3 \quad [5]$$

$$\text{platinum volume fraction} = \frac{\frac{56.9 \text{ wt.}\%}{21.09 \text{ g/cm}^3}}{\frac{43.1 \text{ wt.}\%}{1.3 \text{ g/cm}^3} + \frac{56.9 \text{ wt.}\%}{21.09 \text{ g/cm}^3}} = 7.5 \text{ vol.}\% \quad [6]$$

To calculate the volume fraction of the hydrophilic and hydrophobic components in the CCM-Pt-4 and CCM-Pt-6 hybrids, we converted the weights of the PI, PDMAEMA, and nanoparticles into volume fractions. We assumed that the PI and PDMAEMA in the hybrid had densities similar to their bulk values, i.e.,  $0.91 \text{ g/cm}^3$  and  $1.15 \text{ g/cm}^3$ , respectively. Table S1 outlines the quantities and volumes for the CCM-Pt-6 inverse hexagonal hybrid and Table S2 displays those of the CCM-Pt-4 lamellar hybrid. Lamellar hybrids were made from both PI-*b*-PDMAEMA block copolymers described in the polymer synthesis section, above. It is certainly noteworthy that hybrids self-

assemble into an ordered structure during annealing and that the annealing process also leads to loss of ligand. This decreases the hydrophilic volume fraction and is accounted for in the second set of columns of the tables. To determine the mass loss during annealing (15%), we assumed that both samples (as-synthesized and annealed) consisted solely of platinum following heat-treatment in air (Figure S11). Thus we were able to equate the masses of the two samples at the end of the TGA run and back-calculate their relative starting masses (prior to the TGA analysis). The as-synthesized hybrid retained 52.6% of its original mass and the annealed hybrid retained 62.0%. Compared to the starting mass of the annealed hybrid (100%), the as-synthesized hybrid had a mass of  $100\% \cdot 62.0\% / 52.6\% = 118\%$ . With respect to the as-synthesized hybrid, the annealed hybrid lost  $100\% - (100\% / 118\%) = 15\%$  during annealing.

**Table S1.** Volume fraction calculations for CCM-Pt-6. The mass of PI-*b*-PDMAEMA is 27.6 mg, of which 33 wt.% is PDMAEMA. The mass of the aged platinum nanoparticles is 97.5 mg, of which 65 wt.% is Pt.

	As-made				Annealed			
	Density	Mass (mg)	Volume (mL)	Volume %	Density	Mass (mg)	Volume (mL)	Volume %
PI	0.91	18.4	20.2	35.5	0.91	18.4	20.2	47.6
PDMAEMA	1.15	9.1	7.9	13.8	1.15	9.1	7.9	18.6
Pt	21.09	63.8	3.0	5.3	21.09	63.8	3.0	7.1
Ligand	1.3	33.7	25.9	45.4	1.3	14.7	11.3	26.7
Hydrophilic	2.89	106.6	36.8	64.5	3.94	87.6	22.3	52.4

**Table S2.** Volume fraction calculations for CCM-Pt-4. The mass of PI-*b*-PDMAEMA is 33.7 mg, of which 33 wt.% is PDMAEMA. The mass of the aged platinum nanoparticles is 73.2 mg, of which 65 wt.% is Pt.

	As-made				Annealed			
	Density	Mass (mg)	Volume (mL)	Volume %	Density	Mass (mg)	Volume (mL)	Volume %
PI	0.91	22.6	24.8	44.1	0.91	22.6	24.8	56.7
PDMAEMA	1.15	11.1	9.7	17.2	1.15	11.1	9.7	22.1
Pt	21.09	47.9	2.3	4.0	21.09	47.9	2.3	5.2
Ligand	1.3	25.3	19.5	34.6	1.3	9.1	7.0	16.0
Hydrophilic	2.69	84.3	31.4	55.9	3.60	68.1	18.9	43.3

## References

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