Energy, Environmental, and Catalysis Applications

A Facile and Scalable Route to the Preparation of Catalytic Membranes With In-situ Synthesized Supramolecular Dendrimer Particle Hosts for Pt(0) Nanoparticles Using a Low Generation PAMAM Dendrimer (G1-NH₂) as PrecursorMadhusudhana Rao Kotte, Alex Kuvarega, Siddulu Naidu
Talapaneni, Manki Cho, Ali Coskun, and Mamadou DialloACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.8b11351 • Publication Date (Web): 10 Sep 2018Downloaded from <http://pubs.acs.org> on September 11, 2018**Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

A Facile and Scalable Route to the Preparation of Catalytic Membranes With In-situ Synthesized Supramolecular Dendrimer Particle Hosts for Pt(0) Nanoparticles Using a Low Generation PAMAM Dendrimer (G1-NH₂) as Precursor

Madhusudhana Rao Kotte¹⁺, Alex T. Kuvarega²⁺, Siddulu N. Talapaneni¹, Manki Cho¹,
Ali Coskun^{1‡} and Mamadou S. Diallo^{1,3*}

Revised Manuscript
Submitted to *ACS Applied Materials & Interfaces*

September 7, 2018

¹Graduate School of EEWS (Energy, Environment, Water and Sustainability)
Korea Advanced Institute of Science and Technology (KAIST)
291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

²Nanotechnology and Water Sustainability Research Unit
College of Science, Engineering and Technology, University of South Africa (UNISA)
UNISA Science Campus, Florida, 1709, Johannesburg, Republic of South Africa

³Division of Chemistry and Chemical Engineering
California Institute of Technology
1200 East California Boulevard, Pasadena, CA 91125, USA

⁺Authors with equal contributions

[‡]Present address: Department of Chemistry, University of Fribourg
Av. de l'Europe, CH-1700 Fribourg, Switzerland

*Corresponding Author: Mamadou S. Diallo
E-mail: diallo@caltech.edu and mdiallokaist1@gmail.com

ABSTRACT

Since the first reports of Cu dendrimer encapsulated nanoparticles (DENs) published in 1998, the dendrimer-templating method has become the best and most versatile method for preparing ultrafine metallic and bimetallic nanoparticles (1-3 nm) with well-defined compositions, high catalytic activity and tunable selectivity. However, DENs have remained for the most part model systems with limited prospects for scale up and integration into high performance and reusable catalytic modules and systems for industrial-scale applications. Here, we describe a facile and scalable route to the preparation of catalytic polyvinylidene fluoride (PVDF) membranes with in-situ synthesized supramolecular dendrimer particles (SDPs) that can serve as hosts and containers for Pt(0) nanoparticles (2-3 nm). These new catalytic membranes were prepared using a reactive encapsulation process similar to that utilized to prepare Pt DENs by addition of a reducing agent (sodium borohydride) to aqueous complexes of Pt(II) + G4-OH/G6-OH polyamidoamine (PAMAM) dendrimers. However, the SDPs (2.4 μm average diameter) of our new mixed matrix PVDF-PAMAM membranes were synthesized in the dope dispersion without purification prior to film casting using (i) a low-generation PAMAM dendrimer (G1-NH₂) as particle precursor and (ii) epichlorohydrin, an inexpensive functional reagent as crosslinker. In addition, the membrane PAMAM particles contain secondary amine groups (~1.9 meq per gram of dry membrane), which are more basic and thus have higher Pt binding affinity than the tertiary amine groups of the G4-OH and G6-OH PAMAM dendrimers. Proof-of-concept experiments show that our new PVDF-PAMAM-G1-Pt membranes can serve as highly active and reusable catalysts for the hydrogenation of alkenes and alkynes to the corresponding alkanes using (i) H₂ at room temperature and a pressure of 1 bar and (ii) low catalyst loadings of ~1.4-1.6 mg of Pt. Using cyclohexene as model substrate, we observed near quantitative conversion to cyclohexane (~98%). The regeneration studies showed that our new Pt/membrane catalysts are stable and can be reused for five consecutive reaction cycles for a total duration of 120 hr including 60 hr of heating at 100°C under vacuum for substrate, product and solvent removal with no detectable loss of cyclohexene hydrogenation activity. The overall results of our study point to a promising, versatile and scalable path for the integration of catalytic membranes with in-situ synthesized SDP hosts for Pt(0) nanoparticles into high throughput modules and systems for heterogeneous catalytic hydrogenations, an important class of reactions that are widely utilized in industry to produce pharmaceuticals, agrochemicals and specialty chemicals.

Keywords: catalytic membranes; supramolecular polymer chemistry; mixed matrix membranes, dendrimer encapsulated nanoparticles; heterogeneous catalysis; hydrogenation

INTRODUCTION

Dendritic macromolecules, which include dendrimers, dendrigraft polymers, and hyperbranched polymers, are among the most versatile classes of building blocks for multifunctional nanomaterials.¹⁻³ Dendrimers are highly branched 3-D macromolecules with controlled composition and architecture consisting of three components: a *core*, *interior branch cells* and *terminal branch cells*. Poly(amidoamine) [PAMAM] dendrimers were the first family of dendrimers to be commercialized.³⁻⁴ They possess functional amine and amide groups arranged in regular “branched upon branched” patterns, which are displayed in geometrically progressive numbers as a function of generation level. Since the first reports of dendrimer encapsulated Cu nanoparticles published in 1998 by Crooks and co-workers⁵ and Balogh and Tomalia⁶, significant research efforts have been devoted to the utilization of dendrimers as templates for the synthesis of metallic nanoparticles with well-defined sizes, structures and compositions.⁷⁻²⁹ These new materials, commonly referred as dendrimer-encapsulated nanoparticles (DENs), can be efficiently prepared by reactive encapsulation, a two-step process involving the complexation of precursor metal ions in the interior of a dendrimer in an aqueous or non-aqueous solution followed by addition of a reducing agent.¹⁶ During the last two decades, many research groups have reported the successful use of higher generation PAMAM dendrimers (G4-OH and G6-OH) with ethylene diamine (EDA) core and terminal hydroxyl groups to prepare a variety of DENs including Cu, Ag, Au, Pd, Pt, PdPt, PdAu, PdCu, PtCu, PtAu and RuO₂ DENs.⁵⁻²¹ Other dendritic macromolecules that have been utilized to synthesize DENs include poly(propylene imine), triazole and phenylazomethine dendrimers.²²⁻²⁴ By combining transmission electron microscopy (TEM), x-ray photon electron spectroscopy (XPS), x-ray absorption spectroscopy (e.g. EXAFS), high energy x-ray scattering (e.g. XRD-PDF) and high resolution NMR spectroscopy (e.g. COSY, HMBC and HSQC), Crooks and co-workers¹⁵⁻¹⁶ and others^{13-14, 22-24} have established the formation of metallic nanoparticles or clusters of 1-3 nm in size that are encapsulated within the interior of DENs. In addition to these characterization studies, it has also been shown that DENs can serve as efficient catalytic materials for various homogenous, heterogeneous and electrochemical reactions including 1) hydrogenation¹⁶, 2) carbon-carbon coupling reactions¹⁶, 3) hydrolysis¹⁸, 4) oxygen reduction reactions (ORR)²⁵ and (iv) hydrogen evolution reactions (HER)²⁶. DENs have also been utilized as building blocks for novel sensors and analytical assays.²⁷⁻²⁹ Peng et al.³⁰ have reviewed the synthesis and catalytic applications of

bimetallic DENs. More recently, Somorjai and co-workers³¹ have described the preparation of heterogeneous catalysts by immobilizing Pt, Rh, and Pd DENs onto SBA-15 mesoporous silica supports. They showed for the first time that DEN-based catalysts could be utilized to carry out high temperature reactions in a gas flow reactor. The authors reported that their Pt DEN-based catalysts showed very high activity for the hydrogenation of methylcyclopentane at 200-225 °C with high turnover frequency (TOF) up to 334 h⁻¹ and selectivity up to 99.6%.

Although significant advances have been made on the synthesis, characterization and applications of DENs during the last two decades⁵⁻³¹, the availability of facile, efficient and scalable routes for processing metallic and bimetallic DENs into high throughput catalytic media, membranes and electrodes has remained elusive. To date, higher generation dendrimers have been utilized in the preparation of metallic and bimetallic DENs (1-3 nm) with well defined compositions, high catalytic activity and tunable selectivity.⁵⁻³¹ However, high generation dendrimers (e.g. G4-OH and G6-OH PAMAM) are expensive and thus are not affordable as functional materials for non-biomedical applications due to the multiple steps required for their synthesis and purification⁴. Because of this, DENs have remained for the most part model systems for fundamental investigations with limited prospects for scale up and utilization in sustainability and industrial applications including (i) ORR and HER in polymer electrolyte membrane (PEM) fuel cells²⁵⁻²⁶ and (ii) catalytic hydrogenations for the production of pharmaceuticals, agrochemicals and specialty chemicals³¹⁻³³. Here, we describe a facile and scalable route to the preparation of catalytic polyvinylidene fluoride (PVDF) membranes with in-situ synthesized PAMAM supramolecular dendrimer particles (SDPs) that can serve as hosts and containers for Pt(0) nanoparticles (2-3 nm). These new catalytic membranes were prepared using a reactive encapsulation process similar to that utilized to prepare metallic DENs by addition of a reducing agent (e.g. sodium borohydride) to aqueous solutions of Pt(II) laden G4-OH/G6-OH PAMAM dendrimers¹³⁻¹⁶. However, the SDPs (2.4 μm average diameter) of these new Pt catalytic membranes were synthesized in the dope dispersion without purification prior to film casting using (i) a low-generation PAMAM (G1-NH₂) with EDA core and terminal primary amine groups as dendrimer particle precursor and (ii) epichlorohydrin (ECH) as crosslinker (Figure 1). Our proof-of-concept experiments show that the new PVDF-PAMAM-G1-Pt membranes can serve as highly active and reusable catalysts for the hydrogenation of alkenes

and alkynes to the corresponding alkanes at room temperature and using H₂ at a pressure of 1 bar.

RESULTS AND DISCUSSION

Preparation and characterization of a chelating PVDF membrane with in-situ synthesized G1-NH₂ PAMAM supramolecular dendrimer particles. Membranes have become the critical components of a broad range of sustainable chemistry, engineering and materials (*SusChEM*) applications including (i) energy generation (e.g. PEM fuel cells), (ii) energy storage (e.g. battery separators), (iii) water reuse and desalination (e.g. reverse osmosis and nanofiltration) and (iv) gas separations (e.g. natural gas purification)³⁴⁻³⁵. The convergence between nanotechnology and membrane science is enabling the development of a new generation of multifunctional membranes with embedded nanomaterials including metal oxide nanoparticles³⁶, metallic and bimetallic nanoparticles³⁷⁻³⁸, metal-organic frameworks³⁹, carbon nanotubes⁴⁰ and graphene⁴¹. Such membranes are being designed to carry out multiple functions (e.g. retention, adsorption and catalysis) with improved properties and performance including higher permselectivity and flux, greater mechanical strength and lower fouling propensity. DENs exhibit many features that make them particularly attractive as building blocks for the preparation of catalytic membranes and membrane-electrode assemblies for sustainability related applications including green chemistry^{20,30} and energy generation and storage^{19, 25-26}. To advance the integration of DENs into catalytic membrane modules for *SusChEM* related applications, we first prepared a chelating PVDF membrane with in-situ synthesized PAMAM SDPs (Figure 1). This mixed matrix PVDF-PAMAM membrane was prepared using the integrated in-situ particle synthesis and phase inversion casting process (Figure 1A) developed by Diallo and co-workers⁴²⁻⁴⁵. PVDF, G1-NH₂ PAMAM and ECH were selected as (i) matrix precursor, (ii) dendrimer particle precursor and (iii) crosslinker, respectively, for the preparation of our chelating membrane substrate (Figure 1A). This selection was motivated by several considerations. First, PVDF has been widely used as base polymer and binder in the preparation of catalytic membranes^{38,46} and lithium-ion battery electrodes⁴⁷, respectively. Second, PVDF membranes/films can be prepared by phase inversion casting using thermally induced phase separation (TIPS) and/or non-solvent induced phase separation (NIPS) with various solvents including N-methyl-2-pyrrolidone (NMP),

dimethylformamide (DMF) and triethyl phosphate (TEP).⁴²⁻⁴⁵ Third, technical grade G1-NH₂ PAMAM is available from a commercial source⁴⁸ at a price that is ~10X lower than those of the higher generation PAMAM dendrimers (G4-OH and G6-OH) that were utilized to prepare Pt(0) DENs in previous investigations^{13-15, 25-26, 29,31}. Finally, Kotte et al.⁴⁵ have shown that the primary amine groups of a G1-NH₂ PAMAM can react with the epoxy and chloro groups of ECH (an inexpensive functional reagent) in a PVDF dope membrane casting dispersion to generate crosslinked SDPs (Scheme 1) with a high density of ligands (i.e, secondary amines, tertiary amines and amide groups) that can serve as supramolecular hosts and containers for Cu(II) ions.

Scheme 1: In-situ synthesis of supramolecular dendrimer particles in a PVDF casting solution using a G1-NH₂ PAMAM as precursor and epichlorohydrin (ECH) as crosslinker.

A PVDF-PAMAM membrane with *in situ* synthesized G1-NH₂ PAMAM SDPs was prepared in this study. The Supporting Information (SI) provides a description of the membrane preparation and characterization procedures. SI Table S1 lists the composition and relevant physicochemical properties of the G1-NH₂ PAMAM dendrimer that was utilized as particle precursor in the preparation of the PVDF-PAMAM-G1 membrane. A combined TIPS and NIPS casting process with TEP as solvent was utilized to prepare the PVDF-PAMAM-G1 membrane⁴⁵. SI Table S2 lists the composition of the membrane casting dispersion. The morphology, surface composition and physicochemical properties (surface layer pore size, wettability and surface charge) of the PVDF-PAMAM-G1 membrane were characterized using (i) field emission scanning electron microscopy (FESEM), (ii) attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy, (iii) x-ray photoelectron spectroscopy (XPS) and (iv) contact angle and zeta potential measurements, respectively. Membrane thermal stability was evaluated using differential scanning calorimetry (DSC) and thermal gravimetry analysis (TGA). To guide the

analysis of the FT-IR/XPS spectra and DSC/TGA curves, a control PVDF membrane (15 wt%) was prepared (SI Table S2). The sizes of the SDPs of the PVDF-PAMAM-G1 membrane were estimated using FESEM with ImageJ analysis and validated using dynamic light scattering (DLS) measurements of a dispersion that was prepared by dissolving the membrane in TEP, a good solvent for PVDF. Table 1 summarizes the results of the membrane characterization studies. The SEM micrographs (Figures 1B and 1C) and Table 1 indicate that the PVDF-PAMAM-G1 membrane is asymmetric with a dry thickness of 151 μm and a neutral and hydrophilic surface layer of 8 μm in thickness. The N_2 adsorption and desorption measurements (SI Figure S1) yield average pore diameters of ~22-28 nm for the membrane surface layer. As shown in Figure 1B, the matrix of the PVDF-PAMAM-G1 membrane consists predominantly of a network of interpenetrating PAMAM SDPs and PVDF spherulites. This sponge-like microstructure is characteristic of a membrane with strong mechanical integrity³². The SEM micrographs confirm that the PAMAM SDPs are uniformly distributed through the cross section of the membrane; they are present in both the membrane matrix and surface layer (Figures 1B and 1C).

Table 1 indicates that the membrane has a high loading of PAMAM SDPs (~48 wt%). SEM analysis using the Image J software indicates that the diameters of the membrane PAMAM SDPs range from 0.7 μm to 3.3 μm with an average diameter of 2.4 μm (SI Table S3). The DLS measurements (SI Figure S2) confirm that the sizes of the PAMAM SDP particles in the TEP dispersion (~1.4 to 2.3 μm) are comparable to the FESEM particle size estimates. Figure 2 summarizes the results of the DSC and TGA measurements. Figure 2A indicates that the melting temperatures (T_m) of both the PVDF-PAMAM-G1 and pristine PVDF membranes are equal to 166 °C. These values are comparable to the manufacturer's listed T_m of 170 °C for the sample of Kynar 761 PVDF resin⁴⁹ that we used to cast our membranes. In contrast, the second DSC cooling scan (Figure 2B) indicates that the crystallization temperature of the PVDF-PAMAM-G1 membrane (138 °C) is higher by 8 °C than that of the pristine PVDF membrane (130 °C). It is worth mentioning that in previous studies⁵⁰, the blending of PVDF (60 wt %) with poly(methyl methacrylate) (PMMA) [40 wt%] was shown to inhibit the crystallization of PVDF leading to both a decrease of the fraction of its crystalline phase (from 44.3 % to 33.6 %) and melting temperature from 170.5 °C for to 161.6 °C. However in our case, the DSC measurements

(Figures 2A and 2B) suggest that the embedded PAMAM particles of the PVDF-PAMAM-G1 membrane do not suppress the crystallization of its PVDF matrix or shift its melting point to a lower temperature value. These observations are consistent with the SEM images showing that our mixed matrix membrane consists of a network of interpenetrating PAMAM SDPs and PVDF spherulites (Figure 1B). The TGA measurements confirm that the PVDF-PAMAM-G1 membrane is thermally stable up to 165 °C before the onset of melting. Figures 2C and 2D show negligible loss of mass for the PVDF-PAMAM-G1 membrane (i.e. < 4 wt% due to dehydration) when heated up to 218 °C in nitrogen (N₂). Table 2 indicates that the embedded PAMAM particles of the PVDF-PAMAM-G1 membrane contain a diversity of Pt-complexing ligands including secondary and tertiary amines (Scheme 1). In contrast, tertiary amines are the main Pt-complexing ligands of the G4-OH and G6-OH PAMAM dendrimers that were employed to prepare DENs in previous investigations.⁶⁻²¹ The FT-IR and XPS spectra (SI Figures S3 and S4) corroborate the presence of PAMAM particles at the surface of the membrane. Collectively taken together, the contact angle and zeta potential measurements (Table 1) and XPS spectra (SI Figure S4) suggest that the ECH-crosslinked PAMAM SDPs expose their OH groups (Scheme 1) as they become incorporated within the matrix and surface layer of the PVDF-PAMAM-G1 membrane (Figures 1B and 1C).

Pt(IV) uptake by PVDF-PAMAM membranes with in-situ synthesized G1-NH₂ PAMAM supramolecular dendrimer particles. The first step in the preparation of our new catalytic membranes is to load and encapsulate Pt ions into a PVDF-PAMAM chelating membrane substrate. For this purpose, we selected hydrogen hexachloroplatinate(IV) hexahydrate (H₂PtCl₆·6H₂O) as source of Pt(IV) ions. For the metal ion loading experiments, each membrane was cast onto a polyethylene terephthalate (PET) microporous support to enable metal ion loading by pumping and recirculating a 10 mg/L solution of Pt(IV) in deionized water (DIW) through the membrane at a pressure of 2 bar. Because the pristine PVDF membrane has a very low water flux with no Pt(IV) complexation ability, no control experiment of metal ion loading was conducted. Following Kotte et al.⁴⁵, the Pt(IV) loading experiments were performed on a custom-built cross-flow ultrafiltration (UF) system (SI Figure S5). To eliminate potential metal ion sorption onto the components of the UF system, its filtration cell, pump head, reservoir and tubing were built using Teflon and polyvinyl chloride⁴⁵. Based on the results of our previous

investigations of Cu(II) uptake by a PVDF-PAMAM membrane that was prepared using a G1-NH₂ PAMAM dendrimer as particle precursor⁴⁵, we also kept the flow rate through the UF system at ~1.7 L/min with a crossflow velocity of ~37.2 cm/s. These flow conditions were selected to benchmark the kinetics of Pt(IV) extraction from solution against that of Cu(II) loading onto a PVDF-PAMAM-G1 membrane with similar properties.⁴⁵ The SI describes the methods and procedures used in the Pt(IV) loading experiments. Figure 3A indicates that the amount of Pt(VI) bound to the membrane gradually increases as a function of time without exhausting the available loading capacity (~55 mg/mL of dry membrane) after 3 hours of filtration. In contrast, Kotte et al.⁴⁵ reported that the amount of Cu(II) bound onto a similar membrane reached the available loading capacity (~55 mg/mL of membrane) in less than 5 minutes of filtration. For all tested solution pH values, approximately 65-69% of Pt(IV) was extracted from solution by the PVDF-PAMAM-G1 membrane after 3 hours of filtration (Table 2). We fitted the Pt(IV) extraction data to a first order kinetic model (Eq.1):

$$\left(\frac{C_{\text{Pt(IV)}}^t}{C_{\text{Pt(IV)}}^0} \right) = \exp(-k_{\text{ext}}^f t) \quad \text{Eq. 1}$$

where $C_{\text{Pt(IV)}}^0$ is the initial concentration of Pt(IV) in the membrane feed, $C_{\text{Pt(IV)}}^t$ is the concentration of Pt(IV) in the membrane feed at time t and k_{ext}^f is the rate of Pt(IV) extraction from the feed. We used the kinetic model to estimate $T_{\text{ext}}^{\text{f99}}$ (Eq.2), the time required to extract 99% of Pt(IV) in the membrane feed solution:

$$T_{\text{ext}}^{\text{f99}} = \frac{\ln(10/0.1)}{k_{\text{ext}}^f} \quad \text{Eq. 2}$$

To estimate $T_{\text{ext}}^{\text{f99}}$, we assumed that the PVDF-PAMAM-G1 membrane can bind all the amount of Pt(IV) available in the feed solution (20 mg) without reaching saturation. This assumption is supported by the results of our previous investigations of Cu(II) uptake by a similar membrane⁴⁵.

Figures 3B, 3C and 3D highlight the kinetic model fits. Table 2 summarizes the results of the kinetic analysis. In contrast to previous studies reporting a slow binding of Pt(II) and Pt(IV) to G4-OH and G6-OH PAMAM dendrimers with up to 3 days for complete complexation^{13-15, 51-52},

the estimated $T_{\text{ext}}^{\text{f99}}$ values suggest that the PVDF-PAMAM-G1 membrane can extract 99% of the Pt(IV) ions in the feed water in 9-12 hr of filtration depending on solution pH (Table 2). Surprisingly, the estimated rate constants of Pt(IV) extraction (0.41-0.52 hr^{-1}) by the membrane are ~3X times larger than the rate constant of PtCl_4^{2-} hydrolysis (0.14 hr^{-1}) in aqueous solutions of K_2PtCl_4 .⁵² The hydrolysis of PtCl_4^{2-} is considered as the rate limiting step for the complexation of Pt(II) with the tertiary amine groups of G4-OH and G6-OH PAMAM dendrimers.^{15, 51-52} At the present time, it is not completely clear as to why the kinetics of Pt(IV) extraction by a PVDF-PAMAM-G1 membrane is significantly faster than that of Pt(II) complexation with the tertiary amine groups of G4-OH and G6-OH PAMAM dendrimers. However, this faster kinetics can be attributed for the most part to a synergistic combination of three effects: 1) enhanced Pt(IV) binding affinity due to the membrane high content of amines and amide ligands, 2) the documented ability of Pt(IV) to form stronger complexes with the amine/amide groups of G4-OH PAMAM dendrimers than Pt(II)¹³ and 3) enhanced mass transfer for Pt(IV) extraction from aqueous solutions by cross flow filtration. Table 1 indicates that the PVDF-PAMAM-G1 membrane is a porous UF membrane with a high content of amine and amide ligands (~6.2 meq per gram of dry membrane) including secondary amines (~1.9 meq per gram of dry membrane), which are more basic and thus have higher Pt(IV) binding affinity than the tertiary amine and amide groups of a G4-OH PAMAM. Regarding the relative strengths of the binding affinity of Pt ions to amine and amide groups, Alexeev et al.¹³ used X-ray absorption near edge structure (XANES) spectroscopy to carry out a comparative study of Pt(IV) and Pt(II) complexation in deionized water and aqueous solutions of a G4-OH PAMAM dendrimer. By comparing the relative sizes of the “white lines” (i.e. observed band structures for the Pt L_3 edge) of the XANES spectra, the authors were able to establish that Pt(IV) ions form stronger complexes with the amine/amide groups of a G4-OH PAMAM via ligand-to-metal charge transfer.¹³ Based on the above observations, we hypothesize that the combination of (i) membrane porosity and high content of secondary/tertiary amine and amide ligands, (ii) Pt(IV) higher binding affinity for nitrogen ligands and (iii) enhanced mass transfer from the cross filtration process accelerate the kinetics of Pt(IV) extraction from solution by the PVDF-PAMAM-G1 membrane compared to that of Pt(II) complexation with the tertiary amine groups of the G4-OH and G6-OH PAMAM dendrimers. The overall results of the metal ion extraction experiments and kinetic modeling studies (Figure3 and Table 2) show that cross-flow UF (SI

Figure S5) provides a efficient means for controlling the amount of precursor Pt(IV) ions that can be loaded onto a PVDF-PAMAM-G1 membrane. For a feed solution with a specified volume and metal ion concentration [i.e. a 2-L solution of Pt(IV) in DIW (10mg/L) in this study], the amount of Pt(IV) loaded onto the chelating PVDF-PAMAM-G1 membrane depends on filtration time and solution pH (Figure 3A). In the remainder of this study, we will exploit this key finding to control the amounts of Pt(0) that will be loaded onto PVDF-PAMAM-G1 membranes for our proof-of-concept catalytic experiments.

Preparation and characterization of PVDF-PAMAM-G1 membranes with in-situ synthesized Pt(0) nanoparticles. For the proof-of-concept experiments on the preparation and characterization of a Pt(0) loaded catalytic membrane, we selected a PVDF-PAMAM-G1 membrane (24 cm²) that was cast onto a microporous PET support (Figure 4A). First, we pumped and recirculated a 2-L solution of Pt(IV) ions (10 mg/L in DIW and pH 7) thorough the membrane by cross flow filtration at 2 bar for 3 hours (Figure 4B) to achieve a metal ion loading of 0.525 mg per cm² of membrane, which yields a total Pt(IV) loading of 13 mg. Following metal ion loading, the Pt(IV) loaded membrane was immersed in a sealed polypropylene (PP) centrifuge tube filled with a 50 mL solution (100 mg/L) of sodium borohydride (NaBH₄) in DIW under continuous mixing for 1 hour. After completion of the reactive encapsulation process, the Pt loaded membrane (Figure 4C) was washed with DIW and characterized by SEM, XPS, FT-Raman spectroscopy and TEM. A key objective of our proof-concept experiments was to compare and benchmark our reactive encapsulation film preparation methodology with the dendrimer templating approach that has been utilized in previous studies to prepare Pt DENs¹²⁻¹⁵. Knecht et al.¹⁵ published one of the most comprehensive articles on the preparation of Pt nanoparticles by dendrimer templating. The authors used a three-step process to synthesize their Pt DENS. First, they mixed aliquots of an aqueous solution of a G6-OH PAMAM dendrimer with 55, 147, or 240 equivalents of a 100 mM K₂PtCl₄ aqueous solutions for 3 days under constant stirring to ensure complete complexation of the Pt(II) ions with the dendrimer tertiary amine/amide groups¹⁵. Following this, the authors mixed the aqueous solutions of Pt(II) laden G6-OH PAMAM solutions (10 μM) with at least a 10-fold molar excess of NaBH₄ for 24 hours in a sealed reaction vessel. Finally, the reduced metal + dendrimer slurries were freeze dried to prepare powders of Pt DENs¹⁵. By combining UV-vis spectroscopy, XPS, TEM, EXAFS and

high energy XRD-PDF, Knecht et al.¹⁵ found that only a fraction of their Pt²⁺/dendrimer precursors are reduced to Pt(0) DENs.

Figures 4A, 4B and 4C illustrate our facile and efficient route to the preparation of a PVDF-PAMAM-G1 membrane with *in-situ* synthesized Pt(0) nanoparticles. It is noteworthy that our integrated Pt(IV) membrane loading and reactive encapsulation process takes a total of 4 hr to complete compared to 96 hr (4 days) for the direct preparation of Pt(0) DENs using aqueous of G6-OH PAMAM dendrimer + NaBH₄ without galvanic exchange¹⁵⁻¹⁶. Not surprisingly, the color of the PVDF-PAMAM-G1 membrane changes from gray (Figure 4A) to faint yellow (Figure 4B) and dark black (Figure 4C), respectively, following Pt(IV) loading and reduction with NaBH₄. Pellechia et al.⁵¹ have observed similar color changes (i.e. faint yellow to dark black) during their NMR and AFM investigations of Pt(II) complexation and Pt(0) DEN preparation using aqueous solutions of G4-OH PAMAM. Figure 4D shows a SEM micrograph of the Pt(0) loaded PVDF-PAMAM-G1 membrane using FESEM with a backscattering (BSE) detector. As expected, the BSE detector enhances the contrast of the metal loaded membrane and shows the Pt(0) loaded PAMAM SDPs as “bright spots” that are present in the membrane matrix and surface layer (Figure 4D). The TEM micrograph (Figure 4E) provides further supporting evidence for the presence of Pt(0) loaded PAMAM SDPs in the membrane. For the TEM characterization, a small piece of a Pt(0) loaded membrane was dissolved by sonication (30 mins) in a 2 mL solution of triethyl phosphate (TEP), which is the solvent that was utilized to dissolve PVDF during our membrane casting experiments (Figure 1A). To eliminate or minimize the amount of PVDF in the dispersion of Pt(0) loaded PAMAM particles, a drop of the dispersion was added to 2 mL of ethanol. The resulting solution was sonicated for 5 mins and dried on a copper grid prior to the TEM imaging experiments (Figure 4E). Figures 5A and 5B and SI Table S4 summarize the results of the XPS studies. The binding energies and peak splits (SI Table S4A) were taken from the NIST database.⁵³ The XPS compositions (SI Table 4B) are expressed in both atomic % percent and weight %.⁵⁴ In contrast to the partial reduction of Pt(II) reported by Knecht et al.¹⁵ when they reacted aqueous solutions of Pt(II) + G6-OH PAMAM dendrimers with 10-fold molar excess of NaBH₄ for 24 hours in a sealed reaction vessel, the XPS spectra (Figure 5B and SI Table 4B) indicate a complete reduction of the membrane loaded Pt(IV) ions to Pt(0) following 1 hr of chemical reaction in a sealed PP centrifuge tube containing

50 mL of a 100 mg/L solution of NaBH_4 in DIW. Both the shifts of the Pt-4f peak binding energies along with the values of the Pt-4f_{5/2} and Pt-4f_{7/2} peak splits (SI Table 4A) are consistent with a complete reduction of the Pt(IV) ions that were loaded in the PVDF-PAMAM-G1 membrane. The estimated XPS surface compositions (SI Table 4B) and FT-Raman spectra (Figure 5C) provide additional supporting evidence for the complete reduction of the Pt(IV) loaded membrane. Collectively taken together, Figure 5C and SI Table 4B provide strong evidence that the loaded Pt(IV) ions are coordinated to both N and Cl^- ligands at the surface of the PVDF-PAMAM-G1 membrane. This observation is consistent with the EXAFS investigations by Alexeev et al.¹³ These authors have established that approximately 2 Cl^- ligands remain in the first coordination shell of Pt(IV) following the complexation of PtCl_6^{2-} with the N ligands (e.g. tertiary amines and amides) of a G4-OH PAMAM dendrimer in aqueous solutions. In contrast, no Cl was detected in the XPS spectra following the reduction of the Pt(IV) loaded membrane (SI Table 4B). Similarly, the drops in the intensities of the Pt-Cl and N-Pt-N Raman bands to background levels (Figure 5C) following reactive encapsulation provide additional evidence for the absence of unreduced Pt ions at the surface of the Pt(0) loaded PVDF-PAMAM-G1 membrane. Here again, we attribute this observation to a synergistic combination of two effects: 1) the membrane high density of amine/amide groups, which have higher binding affinity for Pt(IV) than Pt(II) and 2) the membrane form factor as a porous and open film with immobilized amine/amide ligands that transfer electron density to the bound Pt(IV) ions. We speculate this transfer of electron density from the amine/amide groups of the membrane PAMAM SDPs to the bound Pt(IV) ions will facilitate their complete reduction to Pt(0) when the Pt(IV) loaded membrane is immersed in a 50 mL aqueous solution of NaBH_4 (100 mg/L) in DIW under continuous mixing for 1 hour. However, more in-depth investigations will be required to validate this hypothesis.

We utilized a high resolution TEM micrograph (Figure 4E) to estimate the size range of Pt(0) nanoparticles that are embedded inside a PAMAM supramolecular dendrimer particle of a PVDF-PAMAM-G1 membrane. As shown in Figure 5E, the membrane Pt(0) domains consist predominantly of 2-3 nm nanoparticles and thus are comparable in sizes to those obtained when using the dendrimer templating approach^{13-15, 25-26}. We also detected the presence of a small fraction of Pt(0) aggregates (5-10 nm) in the high resolution TEM micrographs (Figure 4E).

Knecht et al.¹⁵ have also detected the presence of Pt(0) agglomerates in their TEM characterization of Pt DENs. For their TEM experiments, Knecht et al.¹⁵ also dried several drops of a Pt DEN solution onto a Cu grid coated with an ultrathin carbon film¹⁵. The authors speculated that the presence of the Pt(0) agglomerates could be related to artifacts from their TEM sample preparation procedures. In our case, we also speculate the agglomeration of Pt(0) clusters (Figure 5E) could be an artifact of our TEM sample preparation protocol. However, more-in-depth characterization (e.g. synchrotron based in-situ XRD-PDF measurements, x-ray microtomography, Pt L3-edge EXAFS and N K-edge NEXAFS) would be required to determine the size, structure and ligand field environment of Pt(0) nanoparticles that are embedded within the in-situ synthesized PAMAM SDPs (Figure 4E) of PVDF-PAMAM-G1 membranes.

Hydrogenation of alkenes and alkynes using PVDF-PAMAM-G1 membrane catalysts with in-situ synthesized Pt(0) nanoparticles. To evaluate the catalytic properties of Pt(0) loaded PVDF-PAMAM-G1 membranes, we investigated the hydrogenation of representative alkenes and alkynes.⁵⁵⁻⁵⁶ For the first set of catalytic experiments, we prepared a membrane coupon with a surface area of 24-cm². The membrane was cast onto a microporous PET support with a loading 0.067 mg of Pt(0) per cm² to achieve a total catalyst loading of 1.62 mg. Because Pt DENs have been utilized to prepare efficient cathodes and anodes for PEM fuel cells²⁵⁻²⁶ with significantly lower catalyst loadings than commercial Pt supported carbon catalysts, we selected our membrane catalyst loading for the hydrogenation experiments based on the 2020 US Department of Energy (DOE) total target loading of 0.125 mg of Pt per cm² of electrode materials (anode and cathode) for commercial PEM fuel cells.⁵⁷⁻⁵⁸ First, we investigated the hydrogenation of cyclohexene. In these experiments, we utilized a 50-mL glass-lined stainless reactor with a magnetic stirrer and pressure control system. The reactor was charged with 4 mL of a 2 mM solution of cyclohexane in methanol and 100 mg of a Pt/membrane coupon that was cut into five small pieces. The reaction was carried out at room temperature and constant stirring (400 rpm) under 1 bar of H₂ for 12 hours. After the completion of the reaction, hydrogen was slowly released and the reactor was purged with N₂ gas. The reaction mixture was then filtered off and concentrated under reduced pressure using a rotary evaporator followed by ¹H NMR and gravimetric analyses to determine the conversion and product yield. The SI describes the methods and procedures used in the hydrogenation experiments. Table 3 summarizes the results

of the catalytic experiments. As shown by the ^1H NMR spectra (SI Figure S6), we observed near quantitative conversion (~98%) of cyclohexene into cyclohexane, thus demonstrating the high catalytic activity of the Pt/membrane coupons. Figure 6 shows that the Pt/membrane coupons can be reused for five consecutive reaction cycles without losing their activity as hydrogenation catalysts for the conversion of cyclohexene to cyclohexane. These results are consistent with the TGA/DTG data (Figures 2C and 2D) and indicate that our new Pt/membrane catalysts are thermally stable up to the onset of PVDF melting (Figure 2A). More to the point, our new PVDF-PAMAM-Pt membrane catalysts can be reused for a total duration of 120 h including 60 h of heating at 100°C under vacuum for product and solvent recovery with no detectable loss of cyclohexene hydrogenation activity.

To gain further insight into the catalytic activity of our new Pt/membranes, we evaluated the hydrogenation of five additional compounds as listed in Table 3 including cyclooctene (Entry 2), 1-hexyne (Entry 5), 1-hexene (Entry 8), 1, 5 hexadiene (Entry 10) and 3-hexene (Entry 13). These compounds were selected to benchmark the catalytic activity of our new Pt/membrane catalysts based on the results of a published study of hydrogenation using two Pt-based catalysts⁵⁶: 1) a nanocatalyst (Pt@ZIF-8) and a platinum on carbon (Pt/C) catalyst. The Pt@ZIF-8 nanocatalyst was prepared by loading nanocrystals (150 nm) of a zeolitic imidazolate framework (ZIF-8) with polyvinylpyrrolidone (PVP) coated Pt nanoparticles (2.7 nm) as described by Stephenson et al⁵⁶. The Pt/C catalyst was supplied by Sigma-Aldrich.⁵⁶ Both catalysts were loaded with 0.1 mmol of Pt. This yields a mass loading of 19.5 mg Pt for each catalyst. For the benchmark catalytic experiments, we prepared a new batch of Pt membrane coupons with PET supports and platinum loadings of 0.059 mg of Pt(0) per cm² to achieve a total catalyst loading of 1.43 mg. These experiments were carried out without catalyst recycling and reuse. Thus, in each case, the reactor was charged with 4 mL of a 2 mM solution of the target compound in methanol and 100 mg of a Pt/membrane coupon that was cut into five small pieces. For cyclooctene and the alkykenes/alkynes with terminal unsaturations, Table 3 and the ^1H NMR spectra (SI Figures S6-S10) show near quantitative conversion (95-98%) to the corresponding cyclic and linear alkanes after 12 h of reaction, respectively. In contrast, no conversion and very low conversion (7.6%) of cyclooctene to cyclooctane were observed for the Pt@ZIF-8 (Table 3; Entry 3) and Pt/C catalyst (Table 3; Entry 4), respectively, after 24 h under similar reaction conditions⁵⁶ even though the Pt loadings (19.5 mg) of both catalysts were about ~10X times

higher than that of our Pt/membrane catalyst (1.43 mg). Table 3 also indicates that the extents of conversion of 1-hexyne (98%; Entry 5) and 1-hexene (96%; Entry 8) by the Pt-membrane catalyst are about 2X times higher than those of Pt@ZIF-8, which are both equal to 40% (Entry 6 and Entry 9). It is worth mentioning that for the Pt@ZIF-8 catalyst, the hydrogenation of 1-hexyne and 1-hexene generate mixtures of products, i.e. 80% of 1-hexene and 20% of hexane for 1-hexyne and 85% of 1-hexene and 15% of hexane for 1-hexene, respectively⁵⁰. Although the Pt/C catalyst exhibits a high conversion (90%) for 1-hexyne (Table 3; Entry 7), it also generates a mixture of products; i.e. 1-hexyne (30%) and n-hexane (70%). Conversely, only n-hexane is generated during the hydrogenation of 1-hexyne and 1-hexene by the Pt/membrane catalysts as shown by the corresponding ¹H NMR spectra (SI Figures S8 and S9).

Interestingly, no conversions of 3-hexene were observed after 24 h of reaction for both the Pt/membrane catalyst [(Table 3; Entry 13) and SI Figure S11] and the Pt@ZIF-8 nanocatalyst (Table 3; Entry 14)⁵⁶. In contrast, the Pt/C catalyst achieved a high conversion of 1-hexyne (80%) [Table 3; Entry 15] and produced a mixture with a high content of n-hexane (85%)⁵⁰. At the present time, it is not clear as to why the Pt/membrane and Pt@ZIF-8 are unable to catalyze the hydrogenation of 3-hexene to n-hexane. The overall results of the proof-of-concept experiments suggest that PVDF-PAMAM-G1 membranes with in-situ synthesized Pt(0) nanoparticles are promising functional materials for the fabrication of catalytic flow modules⁵⁹ with high activity and throughput for heterogeneous catalytic hydrogenation reactions, which are among the most important reactions in the pharmaceutical and specialty chemical industry³²⁻³³. Because the sizes of the Pt nanoparticles in our new catalytic membranes and Pt@ZIF-8 nanocatalyst⁵⁶ are comparable (i.e. 2-3 nm), we attribute the higher hydrogenation activity of a Pt(0) loaded PVDF-PAMAM membrane to a synergistic combination of two effects: 1) a high concentration of Pt(0) nanoparticles at the surface and inside the matrix of a porous membrane that facilitates the transport and access of small molecules (reactants) to the Pt(0) loaded PAMAM SDPs (Figure 4E) and 2) an interfacial electronic effect induced by the secondary/tertiary amine groups of the membrane PAMAM SDPs that enhances the catalytic activity of the embedded Pt(0) nanoparticles. Recent articles by Zheng and co-workers⁶⁰⁻⁶¹ provide indirect support for our hypothesis. The authors showed that the hydrogenation of nitrobenzene by a Pt nanowire catalyst could be tuned to produce N-hydroxyaniline with 100% selectivity by attaching ethylene diamine (EDA) ligands at the surface of the catalyst.⁶⁰⁻⁶¹ They

1
2
3 attributed this selectivity enhancement to electron donation from EDA ligands that makes the
4 surface of the Pt nanowires “*highly electron rich*”.⁶⁰⁻⁶¹ Table 1 indicates that our PVDF-
5 PAMAM-G1 membrane substrate has a high content of secondary and tertiary amine groups; i.e.
6 ~3.3 meq per gram of dry membrane. We speculate that these ligands will donate electrons to the
7 Pt(0) nanoparticles that are embedded in the membrane PAMAM SDPs (Figure 4E) thereby
8 enhancing their hydrogenation catalytic activity. However, more-in-depth investigations will be
9 required to validate this hypothesis.
10
11
12
13
14
15
16

17 CONCLUSIONS

18 Since the first reports of Cu dendrimer encapsulated nanoparticles (DENs) published two
19 decades ago, the dendrimer-templating method has become the best and most versatile method
20 for preparing ultrafine metallic and bimetallic nanoparticles (1-3 nm in sizes) with well-defined
21 compositions, high catalytic activity and tunable selectivity. However, DENs have remained for
22 the most part model systems for fundamental investigations with limited prospects for scale up
23 and integration into high performance and reusable catalytic modules and systems for industrial-
24 scale chemical manufacturing and energy generation/storage related applications. The emerging
25 view from our work is that the convergence between dendrimer nanotechnology, supramolecular
26 polymer chemistry and membrane technology provides a viable, versatile and scalable path for
27 the integration of catalytic DENs into high throughput and compact membrane modules and
28 systems for sustainability and industrial applications. By combining in-situ particle synthesis in a
29 polymer dispersion without purification, phase inversion casting (e.g. NIPS and TIPS) and metal
30 ion loading by ultrafiltration followed by chemical reduction using sodium borohydride, we have
31 demonstrated a facile and highly efficient route to the preparation of a new family of catalytic
32 polymer membranes with in-situ synthesized PAMAM supramolecular dendrimer particles that
33 can serve as hosts and containers for Pt(0) nanoparticles (2-3 nm) using (i) a low generation and
34 affordable dendrimer (G1-NH₂ PAMAM) as particle precursor, (ii) a commercially available
35 polymer (PVDF) as membrane matrix and (iii) an inexpensive and widely utilized crosslinker
36 (Epichlorohydrin). Because phase inversion casting is the most efficient and cost effective
37 process for industrial manufacturing of membranes (e.g. 1000 to 100,000 m²) for large-scale
38 applications (e.g. water purification and gas separations), our new membrane preparation
39 methodology is scalable and thus could be optimized to produce a new generation of Pt-loaded
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

membrane modules with high catalytic activity and throughput including (i) plate and frame modules for integration into membrane-electrode assemblies for PEM fuel cells and (ii) spiral-wound modules for integration into catalytic hydrogenation reactor systems for the production of pharmaceuticals, agrochemicals and specialty chemicals. Finally, we would like to mention that our integrated in-situ particle synthesis and solvent film casting process opens up new opportunities to leverage the diverse and rich chemistry of synthetically accessible and affordable low-generation dendrimers through the preparation of new families of membranes/films with in-situ synthesized supramolecular dendrimer particles. In addition to their potential applications in industrial scale catalysis and energy generation/storage, such new materials could provide efficient platforms for carrying out fundamental investigations of the supramolecular chemistry and reactivity of macroligand fields with embedded transition metal ions, metal oxide nanoparticles and metallic, bi-metallic and tri-metallic nanoparticles, etc. Such studies would advance the discovery and development of the next generation of catalysts and electrocatalysts with high activity and tunable selectivity for sustainability related applications including 1) room-temperature catalytic water purification, 2) next generation PEM fuel cells, 3) room temperature and low pressure CO₂ hydrogenation to methanol, 4) high efficiency and scalable cathodes for CO₂ electrochemical reduction and 5) catalytic membrane modules for chemical manufacturing and process intensification.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information (SI) is available free of charge on the ACS Publications website. The SI includes (i) materials and methods, (ii) membrane preparation and characterization procedures, (iii) methods and procedures for the Pt(IV) loading studies and (iv) methods and procedures for the preparation, characterization and evaluation of Pt(0) loaded catalytic membranes along with other supporting data including tables (SI Tables S1-S4 and figures (SI Figures S1-S11).

Acknowledgements

This research was carried out at the Korea Advanced Institute of Science and Technology (KAIST) and at the California Institute of Technology (Caltech). Funding for KAIST was provided by the National Research Foundation of Korea (NRF) [MEST grant No.

2012M1A2A2026588] and the EEWS Center (NT080607C0209721). Funding for Caltech was provided by the National Science Foundation (NSF) [CBET EAGER Award 0948485]. ATK thanks the University of South Africa for financial support.

Author contributions

MSD conceived the research project and designed the study. MRK and AK contributed equally to this manuscript. MRK prepared and characterized the chelating PVDF membrane substrates with in-situ synthesized G1-NH₂ PAMAM supramolecular dendrimer particles. AK and MC carried out the Pt(IV) membrane loading studies. AK prepared and characterized the Pt(0) loaded PVDF-PAMAM-G1 membranes. AC designed and supervised the catalytic studies. SNT performed the catalytic experiments. MSD drafted the manuscript with contributions from all authors.

Additional information

Corresponding author email: diallo@caltech.edu and mdiallokaist1@gmail.com

Notes

The authors declare no competing financial interests.

REFERENCES

1. Astruc, D.; Boisselier, E. and Ornelas, C. Dendrimers Designed for Functions: From Physical, Photophysical and Supramolecular Properties to Applications in Sensing, Catalysis, Molecular Electronics, Photonics and Nanomedicine. *Chem. Rev* **2010**, 110, 1857-1959.
2. Caminade A. M.; Turrin C. O.; Laurent R.; Ouali A. and Delavaux-Nicot B. *Dendrimers: Towards Catalytic, Material and Biomedical Uses* John Wiley & Sons: 2011.
3. Tomalia, D. A. and Diallo, M. S. Dendrimers: Synthetic Science to Controlled Organic Nanostructures and a Window to a New Systematic Framework for Unifying Nanoscience. In *Handbook of Nanoscience, Engineering and Technology*. (Eds; Goddard, W. A. III.; Brenner, D. W.; Lyshevski, S. E. and Iafate, G. J.), CRC Press: Boca Raton. 3rd Edition, Chapter 16: 413-467: 2012).
4. Esfand, R. and Tomalia, D. A. Laboratory Synthesis of Poly(amidoamine) (PAMAM) Dendrimers. In *Dendrimers and Other Dendritic Polymers* (Eds: J. Fréchet, J. M. J. and Tomalia, D. A), John Wiley & Sons, Ltd, Chichester: UK, Chapter 25: 587-604 (2001).
5. Zhao, M., Sun, L. & Crooks, R. M. Preparation of Cu Nanoclusters within Dendrimer Templates, *J. Am. Chem. Soc* **1998**, 120, 4877-4878.

6. Balogh, L. and Tomalia, D. A. Poly(amidoamine) Dendrimer-Templated Nanocomposites. 1. Synthesis of Zero Valent Copper Nanoclusters. *J. Am. Chem. Soc* **1998**, 120, 7355-7366.
7. Zhao, M. and Crooks, R. M. Homogeneous Hydrogenation Catalysis Using Monodisperse, Dendrimer-Encapsulated Pd and Pt Nanoparticles. *Angew. Chem. Int. Ed* **1999**, 38, 364-366.
8. Zhao, M. and Crooks, R. M. Dendrimer-Encapsulated Pt Nanoparticles: Synthesis, Characterization, and Applications to Catalysis. *Adv. Mater* **1999**, 11, 217-220.
9. Balogh, L.; Valuzzi, R.; Laverdure, K. S.; Gido, S. P., Hagnauer, G. L. and Tomalia, D. A. Formation of Silver and Gold Dendrimer Nanocomposites. *J. Nanopart. Res* **1999**, 1, 353-368.
10. Gröhn, F.; Bauer, B. J.; Akpalu, Y. A.; Jackson, C. L. and Amis, E. J. Dendrimer Templates for the Formation of Gold Nanoclusters. *Macromolecules* **2000**, 33, 6042–6050.
11. Niu, Y. H., Yeung, L. K. & Crooks, R. M. Size-Selective Hydrogenation of Olefins by Dendrimer-Encapsulated Palladium Nanoparticles. *J. Am. Chem. Soc.* **2001**, 123, 6840-6846.
12. Scott, R. W. J.; Datye, A. K. and Crooks, R. M. Bimetallic Palladium-Platinum Dendrimer-Encapsulated Catalysts. *J. Am. Chem. Soc* **2003**, 125, 3708-3709.
13. Alexeev, O. S.; Siani, A.; Lafaye, G.; Williams, C. T.; Ploehn, H. J. and Amiridis, M. D. EXAFS Characterization of dendrimer-Pt Nanocomposites Used for the Preparation of Pt/g-Al₂O₃ Catalysts. *J. Phys. Chem. B* **2006**, 110, 24903-24914.
14. Huang, W.; Kuhn, J. N.; Tsung, C-K.; Zhang, Y.; Habas, S. E.; Yang, P. and Somorjai, G. A. Dendrimer Templated Synthesis of One Nanometer Rh and Pt Particles Supported on Mesoporous Silica: Catalytic Activity for Ethylene and Pyrrole Hydrogenation. *Nano Lett* **2008**, 8, 2027-2034.
15. Knecht, M. R.; Weir, M. G.; Myers, V. S.; Pyrz, W. D.; Ye, H.; Petkov, V.; Buttrey, D. J.; Frenkel, A. I. and Crooks, R. M. Synthesis and Characterization of Pt Dendrimer-Encapsulated Nanoparticles: Effect of the Template on Nanoparticle Formation. *Chem. Mater* **2008**, 20, 5218-5228.
16. Myers, S. V., Weir, M. G., Carino, E. V., Yancey, D. F., Pande, S. & Crooks, R. M. Dendrimer-Encapsulated Nanoparticles: New Synthetic and Characterization Methods and Catalytic Applications. *Chem. Sci* **2011**, 2, 1632-1646.
17. Welborn, M.; Tang, W.; Ryu, J.; Petkov, V. and Henkelman, G. A Combined Density Functional and x-ray Diffraction Study of Pt Nanoparticle Structure. *J. Chem. Phys* **2011**, 135, 014503.
18. Aranishi, K.; Zhu, Q-L.; and Xu, Q. Dendrimer-Encapsulated Cobalt Nanoparticles as High performance Catalysts for the Hydrolysis of Ammonia Borane. *ChemCatChem* **2014**, 6, 1-6.
19. Bhattacharya, P.; Nasybulin, E. N.; Engelhard, M. H.; Kovarik, L.; Bowden, M. E.; Li, X. S.; Gaspar, D. J.; Xu, W. and Zhang, J-G. Dendrimer-Encapsulated Ruthenium Oxide Nanoparticles as Catalysts in Lithium-Oxygen Batteries. *Adv. Funct. Mater* **2014**, 24, 7510-7519.
20. Ricciardi, R.; Huskens, J.; Holtkamp, M.; Karst, Uwe and Verboom, W. Dendrimer-Encapsulated Palladium Nanoparticles for Continuous-flow Suzuki–Miyaura Cross-Coupling Reactions. *ChemCatChem* **2015**, 7, 936-942

21. Luo, L.; Duan, Z.; Li, H.; Kim, J.; Henkelman, G. and Crooks, R. M. Tunability of the Adsorbate Binding on Bimetallic Alloy Nanoparticles for the Optimization of Catalytic Hydrogenation. *J. Am. Chem. Soc* **2017**, 139, 5538-5546.
22. Ornelas, J.; Aranzaes, R.; Salmon, L. and Astruc, D. "Click" Dendrimers: Synthesis, Redox Sensing of Pd(OAc)₂, and Remarkable Catalytic Hydrogenation Activity of Precise Pd Nanoparticles Stabilized by 1,2,3-Triazole-Containing Dendrimers. *Chem-Eur. J* **2008**, 14, 50-64.
23. Yamamoto, K.; Imaoka, T.; Chun, W. J.; Enoki, O.; Katoh, H.; Takenaga, M. and Sonori, A. Size-Specific Catalytic Activity of Platinum Clusters Enhances Oxygen Reduction Reactions. *Nat. Chem* **2009**, 1, 397-402.
24. Liu, X.; Gregurec, D.; Irigoyen, J.; Martinez, A.; Moya, S.; Ciganda, R.; Hermange, P.; Ruiz, J. and Astruc, D. Precise Localization of Metal Nanoparticles in Dendrimer Nanosnakes or Inner Periphery and Consequences in Catalysis. *Nat. Commun* **2016**, 7, 131512.
25. Kottakkat, T.; Sahu, A. K.; Bhat, S. D.; Sethuraman, P. and Parthasarathi, S. Catalytic Activity of Dendrimer Encapsulated Pt Nanoparticles Anchored onto Carbon Towards Oxygen reduction Reaction in Polymer Electrolyte Fuel Cells. *Appl. Catal. B* **2011**, 110, 178-185.
26. Devadas, B. and Imae, T. Hydrogen Evolution Reaction Efficiency by Low Loading of Platinum Nanoparticles Protected by Dendrimers on Carbon Materials. *Electrochem. Commun* **2016**, 72, 135-139.
27. Rahman, Md. A.; Noh, H-B. and Shim, Y-B. Direct Electrochemistry of Laccase Immobilized on Au Nanoparticles Encapsulated Dendrimer Bonded Conducting Polymer: Application for a Catechin Sensor. *Anal. Chem* **2008**, 80, 8020-8027.
28. Kim, Y. and Kim, J. Modification of Indium Tin Oxide with Dendrimer-Encapsulated Nanoparticles To Provide Enhanced Stable Electrochemiluminescence of Ru(bpy)₃²⁺/Tripropylamine While Preserving Optical Transparency of Indium Tin Oxide for Sensitive Electrochemiluminescence-Based Analyses. *Anal. Chem* **2014**, 86, 1654-1660.
29. Lim, H.; Ju, Y. and Kim, J. Tailoring Catalytic Activity of Pt Nanoparticles Encapsulated Inside Dendrimers by Tuning Nanoparticle Sizes with Subnanometer Accuracy for Sensitive Chemiluminescence-Based Analyses. *Anal. Chem* **2016**, 88, 4751-4758.
30. Peng, X.; Pan, Q. and Rempel, G. L. Bimetallic Dendrimer Encapsulated Nanoparticles as Catalysts: a Review of the Research Advances. *Chem. Soc. Rev* **2008**, 37, 1619-1628.
31. Deraedt, C.; Melaet, G.; Ralston, W. T.; Ye, R. and Somorjai, G. A. Platinum and Other Transition Metal Nanoclusters (Pd, Rh) Stabilized by PAMAM Dendrimer as excellent Heterogeneous Catalysts: Application to the Methylcyclopentane (MCP) Hydrogenative Isomerization. *Nano Lett* **2017**, 17, 1853-1862.
32. Zhang, W.; Li, G.; Li, Wang, L.; and Xiangwen, X. Catalytic Hydrogenation by Noble-Metal Nanocrystals With well-Defined Facets: a Review. *Catal. Sci. Technol* **2015**, 5, 2532-2553.
33. Karunananda, M. K and Mankad, N. P. Cooperative Strategies for Catalytic Hydrogenation of Unsaturated Hydrocarbons. *ACS. Catal* **2017**, 7, 6110-6119.
34. Park, H. B; Kamcev, J.; Robeson, L. M.; Elimelech, M. and Freeman, B. D. Maximizing the Right Stuff: The Trade-off Between Membrane Permeability and Selectivity. *Science* **2017**, 356, eaab0530. DOI; 10.1126/science.aab0530.

35. Koros, W. J. and Zhang, C. Materials for Next-Generation Molecularly Selective Synthetic Membranes. *Nat. Mater* **2017**, 16, 289-297.
36. Yan, L.; Li, Y.S.; Xiang, C.B.; and Xianda, S. Effect of Nanosized Al₂O₃ Particle Addition on PVDF Ultrafiltration Membrane Performance. *J. Membr. Sci* **2006**, 276, 162-167.
37. Taurozzi, J.S.; Arul, H.; Bosak, V.Z.; Burban, A.F.; Voice, T.C.; Bruening, M.L. and Tarabara, V.V. Effect of Filler Incorporation Route on the Properties of Polysulfone Silver Nanocomposite Membranes of Different porosities, *J. Membr. Sci* **2008**, 325, 58-68.
38. Xu, J. and Bhattacharyya, D.B. Fe/Pd nanoparticle immobilization in microfiltration membrane pores: Synthesis, Characterization and Application in the Dechlorination of Polychlorinated Biphenyls. *Ind. Eng. Chem. Res* **2007**, 46, 2348-2359.
39. Bae, T.H.; Lee, J.S.; Qiu, W.L.; Koros, W.J.; Jones, C.W. and Nair, S.A. High Performance Gas Separation Membrane Containing Submicrometer Sized Metal Organic Framework Crystals. *Angew. Chem. Int. Ed* **2010**, 49, 9863-9866.
40. Kim, S.; Chen, L.; Johnson, J .K. and Marand, E. Polysulfone and Functionalized Carbon Nanotube Mixed Matrix Membranes for Gas Separation: Theory and Experiment. *J. Membr. Sci* **2007**, 294, 147-158.
41. Bano, S.; Mahmood, A.; Kim, S.J. and Lee, K.H. Graphene Oxide Modified Polyamide Nanofiltration Membrane with Improved Flux and Antifouling Properties. *J. Mater. Chem. A* **2015**, 3, 2065-2071.
42. Kotte, M. R.; Cho, M., and Diallo, M. S. A facile Route to the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes With *In-situ* Generated Polyethyleneimine Particles. *J. Memb. Sci* **2014**, 450, 93-102.
43. Kotte, M. R.; Hwang, T.; Han, J-I. and Diallo, M. S. A One-pot Method for the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes With *In Situ* Synthesized and PEGylated Polyethyleneimine Particles. *J. Memb. Sci* **2015**, 474, 277-287.
44. Hwang, T.; Kotte, M. R.; Han, J-I.; Oh, Y-K. and Diallo, M. S. Microalgae Recovery by Ultrafiltration Using Novel Fouling-Resistant PVDF Membranes With *In Situ* PEGylated Polyethyleneimine Particles. *Water Res* **2015**, 73, 181-192.
45. Kotte, M. R.; Kuvarega, A.; Cho, M.; Mamba, B. B and Diallo, M. S. Mixed Matrix PVDF Membranes With *In-situ* Synthesized PAMAM Dendrimer-like Particles: A New Class of sorbents for Cu(II) Recovery from Aqueous Solutions by Ultrafiltration. *Environ. Sci. Technol* **2015**, 49, 9431-9442.
46. Hernández, S.; Lei, S.; Rong, W.; Ormsbee, L.; Bhattacharyya, D. Functionalization of Flat Sheet and Hollow Fiber Microfiltration Membranes for Water Applications. *ACS Sustainable Chem. Eng* **2016**, 4, 907-918.
47. Spreafico, M. A.; Cojocaru, P.; Magagnin, L.; Triulzi, F.; Apostolo, M. PVDF Latex as a Binder for Positive Electrodes in Lithium-Ion Batteries. *Ind. Eng. Chem. Res* **2014**, 53, 9094-9100.
48. Dendritech. Technical Grade PAMAM Dendrimers. Available online at <http://www.dendritech.com/pricing.html>. Accessed on June 25, 2018.
49. Arkema. Kynar Fluoropolymers: Performance Characteristics & Data. Available online at <https://www.extremematerials-arkema.com/en/product-families/kynar-pvdf-family/>. Accessed on June 25, 2018.

50. Freire, E.; Bianchi, O.; Madalena, M.; Martins, J. N.; Monteiro, E.E.C. and Forte, M. M. C. Non-isothermal Crystallization of PVDF/PMMA Blends Processed in Low and High Shear Mixers. *J. Non-Cryst. Solids* **2012**, 358, 2674-2681.
51. Pellechia, P. J.; Gao, J.; Gu, Y.; Ploehn, H. J. and Murphy, C. J. Platinum Ion Uptake by Dendrimers: an NMR and AFM Study. *Inorg. Chem* **2004**, 43, 1421-1428.-1
52. Yamamoto, D.; Watanabe, S. and Miyahara, M. T. Modeling Pt²⁺ Coordination Process within Poly(amidoamine) Dendrimers for Synthesis of Dendrimer-Encapsulated Pt Nanoparticles. *Ind. Eng. Chem. Res* **2011**, 50, 7332-7337.
53. NIST X-ray Photoelectron Spectroscopy Database. NIST Standard Reference Database 20, Version 4.1. Available online at <https://srdata.nist.gov/xps/Default.aspx>. Accessed on June 26, 2018.
54. X-ray Photoelectron Spectroscopy (XPS) Reference Pages. Converting from Atomic Percent to Weight Percent and Vice Versa. Available online at <http://www.xpsfitting.com/2009/11/converting-from-atomic-percent-to.html>. Accessed on June 26, 2018.
55. Guang, L.; Li, S.; Guo, Zh.; Farha, O. K.; Hauser, B.; Qi, X.; Wang, Y.; Wang, X.; Han, S.; Liu, X.; DuChene, J. S.; Zhang, H.; Zhang, Q.; Chen, X.; Ma, J.; Loo, S.Y.J.; Wei, W. D.; Yang, Y.; Hupp, J. T. and Huo, F. Imparting Functionality to a Metal-Organic Framework Material by Controlled Nanoparticle Encapsulation. *Nat. Chem* **2012**, 4, 310-316.
56. Casey J. Stephenson, C. J.; Hupp, J. T. and Farha, O. K. Pt@ZIF-8 Composite for the Regioselective Hydrogenation of Terminal Unsaturations in 1,3-Dienes and Alkynes. *Inorg. Chem. Front* **2015**, 448-452.
57. Cooper, C.D; Burk, J. J.; Taylor, C. P. and Burrato, S. K. Ultra-low Pt Loading Catalyst Layers Prepared by Pulse Electrochemical Deposition for PEM Fuel Cells. *J. Appl. Electrochem* **2017**, 47, 699-709.
58. US Department of Energy (DOE). Multi-Year Research, Development, and Demonstration Plan 3.4 Fuel Cells, 2016. Available online at https://www.energy.gov/sites/prod/files/2016/10/f33/fcto_myrrdd_fuel_cells.pdf. Accessed on June, 25, 2018.
59. Ricciardi, R.; Huskens, J.; Holtkamp, M.; Karst, U and Verboom, W. Dendrimer-Encapsulated Palladium Nanoparticles for Continuous-Flow Suzuki-Miyaura Cross-Coupling Reactions. *ChemCatChem* **2015**, 7, 936-942.
60. Chen, G.; Chaofa X.; Huang, X.; Ye, J.; Gu, L.; Li, G.; Tang, Z.; Wu, B.; Yang, H.; Zhao, Z.; Zhou, Z.; Fu, G. and Zheng, N. Interfacial Electronic Effects Control the Reaction Selectivity of Platinum Catalysts. *Nat. Mat.* **2016**, 564-569.
61. Liu, P.; Qin, R.; Fu, G. and Zheng, N. Surface Coordination Chemistry of Metal Nanomaterials. *J. Am. Chem. Soc* **2017**, 139, 2122-2131.

Table 1. Estimated Composition and Physicochemical Properties of the PVDF-PAMAM-G1 Chelating Membrane Substrate. Figure 1A highlights the preparation of the membrane. For the characterization experiments, the PVDF-PAMAM-G1 membrane was prepared without a PET support. The SI describes the membrane preparation and characterization procedures.

Membrane Composition and Properties	PVDF-PAMAM-G1
A. Composition	
Mass fraction of PVDF (%)	52.29
Mass fraction of PAMAM supramolecular dendrimer particles (%)	47.71
^a Primary amine content (meq per gram of dry membrane)	0
^a Secondary amine (N) content (meq per gram of dry membrane)	1.91
^a Tertiary amine (N) content (meq per gram of dry membrane)	1.43
^a Amide (N) content (meq per gram of dry membrane)	2.86
Total nitrogen (N) ligand content (meq per gram of dry membrane)	6.20
B. Properties	
Thickness of membrane surface layer (μm)	7.58
Thickness of dry membrane (μm)	151.5
Contact angle (Degree)	59.0
Zeta potential at pH 7.0 (mV)	0.46
Surface-layer average pore diameter from BET measurements (nm)	
Adsorption	28.03
Desorption	22.48
^b Estimations of PAMAM particle diameters by FESEM (μm)	
Minimum	0.82
Maximum	3.34
Average	2.29
^b Estimations of PAMAM particle diameters by DLS (μm)	
Minimum	1.8
Maximum	3.12
Average	2.44

^aEstimated assuming that all primary amine groups were consumed during the *in-situ* crosslinking of the supramolecular dendrimer clusters (Figure 1A) via a reaction between the epoxy and chloro groups of epichlorohydrin molecules and the primary amino groups of the G1-NH₂ PAMAM dendrimer macromolecules in the dope solution⁴⁵ (Scheme 1).

^bEstimated diameters of the membrane PAMAM particles using (i) FESEM micrographs with Image J software and (ii) dynamic light scattering (DLS) following the dissolution of a PVDF-PAMAM-G1 membrane in a solution of triethyl phosphate, a good solvent for PVDF⁴⁵.

Table 2. Pt(IV) Extraction from Solution and Membrane Loading: Summary of Results.

The data were compiled from Figure 3. For the metal loading studies, the PVDF-PAMAM-G1 membrane was cast onto a PET support. The composition of the membrane is listed in Table 1. For the metal loading experiments, a 2-L solution of Pt(IV) [10 mg/L] in DIW at constant pH (7, 9 and 3) was pumped and recirculated through each membrane for 3 hours at room temperature using a pressure of 2 bar.

Solution pH	^a Membrane Loading (mg/mL after 3 hours)	Metal Extraction from Solution (% Extraction after 3 hours)	^b Metal Extraction Rate Constant (hr ⁻¹)	^c Estimated Time (T ^{f99} _{ext}) Required for Extraction of 99% of Pt(IV) from Solution (hr)
7.0	35.0	67.0	0.46	10
9.0	34.0	65.0	0.41	11
3.0	38.0	69.0	0.52	9

^aBased on the total amount of metal ion in solution (20 mg), the maximum amount of Pt(VI) that can be loaded onto a chelating PVDF-PAMAM-G1 membrane is equal to ~55.0 mg of metal ion per mL of membrane.

^bEstimated by fitting the Pt(IV) extraction to a first model (Eq.1) [See Figures 3B-3D].

^cCalculated using Eq. 2.

Table 3. Hydrogenation of Alkenes and Alkynes Using Pt(0) Loaded PVDF-PAMAM-G1 Membranes: Summary of Results. For the catalytic experiments, the membranes were cast onto PET supports. These experiments were carried out at room temperature using H₂ at pressure of 1 bar. The ¹H NMR spectra of the substrates and products are provided in the SI.

Entry	Catalyst	Substrate	Time (hr)	Conversion (%)	Target Product	Product Distribution
1	^a Pt/membrane		12	98		^a Cyclohexane (100%)
2	^b Pt/membrane		12	95		^b Cyclooctane (100%)
3	^c Pt@ZIF-8		24	0		^c No conversion
4	^d Pt/C		24	7.6		^d Cyclooctane (100%)
5	^b Pt/membrane		12	98		^b n-Hexane (100%)
6	^c Pt@ZIF-8		24	40		^c n-Hexyne (80%) ^c n-Hexane (20%)
7	^d Pt/C		24	90		^d 1-Hexyne (30%) ^d n-Hexane (70%)
8	^b Pt/membrane		12	96		^b n-Hexane (100%)
9	^c Pt@ZIF-8		24	40		^c n 1-hexene (85%) ^c n n-hexane (15%)
10	^b Pt/membrane		12	95		^b n-Hexane (100%)
11	^c Pt@ZIF-8		24	60		^c 3-Hexene (95%)
12	^d Pt/C		24	100		^d 3-Hexene (20%) ^d n-Hexane (80%)
13	^b Pt/membrane		24	0		^b No conversion
14	^c Pt@ZIF-8		24	0		^b No conversion
15	^d Pt/C		24	80		n-Hexane (85%)

^aPt/membrane catalyst with a Pt loading of 1.62 mg (This Study). The catalyst was regenerated and reused for five consecutive reaction cycles (Figure 6).

^bPt/membrane catalyst with a Pt loading of 1.43 mg (This Study).

^cPt@ZIF-8 catalyst with a Pt loading of 0.1 mmol (19.5 mg).⁵⁶

^dCommercial carbon supported catalyst (Pt/C) with a Pt loading of 0.1 mmol (19.5 mg).⁵⁶

Figure 1. Preparation of a chelating PVDF-PAMAM-G1 membrane with in-situ synthesized supramolecular dendrimer particles (SDPs). Panel A): The PVDF-PAMAM-G1 membrane was prepared using a 4-step process: STEP-1: preparation of a homogeneous PVDF solution in triethyl phosphate (TEP) by mixing at 80 °C; STEP-2): addition of a solution of a G1-NH₂ PAMAM in TEP into the PVDF+TEP solution followed by high-shear mixing to produce a homogeneous dispersion; STEP-3: addition of solution of epichlorohydrin (ECH) in TEP in the dispersion to initiate the crosslinking reactions (Scheme 1) following by 3 hours of curing at 80 °C.; STEP-4: preparation of a mixed matrix flat sheet membrane with in-situ synthesized PAMAM SDPs by phase inversion casting using a combined TIPS and NIPS process.⁴⁵ Panel B): a cross section FESEM micrograph showing the distribution of in-situ synthesized SDPs and membrane microstructure. Panel C): a FESEM micrograph of the membrane surface.

Figure 2. DSC and TGA curves for the PVDF-PAMAM-G1 and pristine PVDF membranes. The DSC and TGA studies were carried out using 5 mg samples of unsupported PVDF-PAMAM-GI and pristine PVDF membranes. Each membrane sample was first annealed by heating from 25°C to 200°C followed by cooling to 25°C to erase its thermal history. All the measurements were carried out in nitrogen (N_2) at a constant heating/cooling rate of $10^{\circ}\text{C}/\text{min}$. Panels A and B show the traces of the second heating and cooling DSC scans following the initial heating and cooling scans. Panels C and D show the TGA curve (loss of mass as a function of temperature) and differential thermogravimetric (DTG) curve.

Figure 3. Pt(IV) extraction and loading from solution by a PVDF-PAMAM-G1 membrane. Panel A shows the amount of Pt(IV) loaded into the membranes as a function of filtration time and solution pH. Panels B, C and D show the Pt(IV) extraction kinetic model fits. For the metal loading experiments, the membranes were cast onto PET supports. The composition of a PVDF-PAMAM-G1 membrane is listed in Table 1. For each metal ion loading experiment, a 2-L solution of Pt(IV) [10 mg/L] in DIW at constant pH (3, 7 and 9) was pumped and recirculated through the membrane at room temperature using a pressure of 2 bar. We used a first order kinetic model (Eq. 1) to fit the Pt(IV) extraction data. Table 2 summarizes the results of the Pt(IV) extraction experiments and kinetic modeling.

Figure 4. Preparation and characterization of a PVDF-PAMAM-G1 membrane with *in-situ* synthesized Pt(0) nanoparticles. Panel A): The pristine membrane was cast onto a PET support. Panel B): For the metal ion loading experiment, a 2-L solution of Pt(IV) [10 mg/L] in DIW at constant pH 7 was pumped through the pristine membrane at 2 bar for 3 hr. Panel C): The Pt(IV) loaded membrane was immersed in a sealed centrifuge containing a 50 mL solution of NaBH₄ (100 mg/L) in DIW under continuous mixing for 1 hour. Panel D): a SEM micrograph of the Pt(0) loaded PVDF-PAMAM-G1 membrane using FESEM with a BSE detector. For the SEM imaging studies, the membrane was prepared without PET support. We used a batch process to load the membrane with Pt(IV) ions following by chemical reduction with NaBH₄ as described in the SI. Panel E): a TEM micrograph of a Pt(0) loaded G1-NH₂ PAMAM supramolecular dendrimer particle. For the TEM imaging studies, a small piece of a Pt(0) loaded PVDF-PAMAM-G1 membrane was dissolved in 2 mL of triethyl phosphate (a good solvent for PVDF) by sonication for about 30 mins. A drop of the resulting suspension was added to 2 mL of ethanol and sonicated for 5 mins. The sample was dried on a copper grid and mounted on the TEM instrument for imaging.

Figure 5. Characterization of Pt loaded PVDF-PAMAM-G1 membranes by FT-Raman spectroscopy, XPS and TEM. Panels A, B and C show the XPS and FT-Raman spectra of the Pt(IV) and Pt(0) loaded membranes, respectively. For the XPS and FT-Raman characterization, the membranes were cast onto PET supports. Panel D shows a high resolution TEM micrograph of the Pt(0) loaded PAMAM supramolecular dendrimer particle from Figure 4E. Panel E): ImageJ analysis was used to estimate the size distribution of Pt(0) nanoparticles from the high resolution TEM micrograph of the Pt loaded PAMAM particle (Figure 4E).

27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Figure 6. Pt(0) loaded PVDF-PAMAM-G1 membrane coupons as reusable catalysts for the hydrogenation of cyclohexene. The membrane catalyst was cast onto a PET support with a total Pt(0) loading of 1.62 mg and cut into five small coupons. Each hydrogenation reaction was carried out for 12 h at room temperature using H₂ at a pressure of 1 bar. For the reuse experiments, the pieces of membrane catalyst were dried at 100°C under vacuum for 12 hr to remove the substrate, product and solvent prior to each reaction cycle. The SI gives a detailed description of the methods and procedures used in the catalytic experiments.

TOC Graphic