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Supplemental Information

Not all nitrogen atoms are equal: Contribution of peripheral versus internal amines to the observed reactivity and capture properties of melamine dendrons on SBA-15

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Contents

S1. Experimental

S1.1 Chemicals

Tetraethoxysilane (TEOS, Alfa Aesar, 99.9%), Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5800, BASF), and hydrochloric acid (HCl, BDH, 3.0 N) were used in the SBA-15 synthesis. 3-Aminopropyldimethylethoxysilane (Gelest) was used in the aminosilane grafting step. Cyanuric chloride (CC, Alfa Aesar, 98%), diisopropylethylamine (DIPEA, Pfaltz & Baner, 98%, Hunig's base), piperazine (Alfa Aesar, 99%), piperidine (MilliporeSigma, 99.9%), and 2-Chloro-4,6-dimethoxy-1,3,5-triazine (Sigam-Aldrich, 97%)) were used in the dendrimer synthesis. Potassium tetrachloropalladate (II) (K_2PdCl_4, Strem Chemicals, 99%), sodium borohydride ($NaBH_4$, granular, Aldrich-Sigma, 99.99% trace metals) and hydrochloric acid (HCl, BDH, 1.0 N) were used in the Palladium sequestration experiments. Nitrobenzaldehyde (Sigam-Aldrich, 98%) and nitromethane (Sigam-Aldrich, > 96%) were used in the Nitroaldol reaction. Methanol (ACS grade) was obtained from BDH. Deuterated chloroform ($CDCl_3$, Cambridge Isotope, 99.8%) was used as the solvent for the ^1H NMR measurements. All chemicals above were used as received. Tetrahydrofuran (THF, EMD, ACS solvent grade), dichloromethane (DCM) (BDH, ACS solvent grade), and toluene (BDH, ACS solvent grade) were dried using an MBraun solvent system prior to use.

S1.2 Synthesis

S1.2.1 SBA-15 Synthesis.

4.0 g of Pluronic P123 were dissolved in 80 mL of 3.0 M HCl and 65 mL of deionized water by stirring for 5 h at room temperature until the solution is clear without any solid surfactant visible. After that, 8.5 g of TEOS were added to that solution and stirred for 24 h at 35 °C in a water bath. The mixture was placed into an oven at 80 °C for 24 h under static conditions. After completion of the reactions, the OMS solid products were filtered, washed with deionized water, and air-dried overnight. The solid products were calcined to remove the organic molecule used in synthesis. The calcination procedure was as follows: the air-dried samples were heated from room temperature to 100 °C at a rate of 1 °C/min; held at 100 °C for 2 h; increased from 100 to 550 °C at a rate of 1 °C/min; and then held at 550 °C for 8 h.

S1.2.2 Amine-Functionalization of OMS

Amine-functionalized MCM-41 and SBA-15 were prepared via standard post-synthetic grafting. As an example, 94 µL aliquot of 3-aminopropyldimethylethoxysilane was added to 1 g of calcined OMS in 50 mL of anhydrous toluene under argon. This mixture was stirred for 24 h in a closed container at room temperature. The product was purified by filtration with 100 mL of toluene and 50 mL of methanol, and air-dried overnight. Unless stated otherwise all amine grafting experiments were performed with a target loading of 0.5 mmol/g.

S1.2.3. Synthesis of OMS-Dendron Materials

Dendrons were synthesized via growth from the amine handle on amine-functionalized SBA-15 per prior work. A 0.3 M cyanuric chloride (CC) solution was prepared by adding 1.25 g of CC (7 mmol) and 2.5 mL of N,N-Diisopropylethylamine (DIPEA) (14 mmol) to 25 mL of tetrahydrofuran (THF). Then a 0.4 M diamine solution was prepared by adding 0.86 g of piperazine (PIP, 10 mmol) or 1 mL of piperidine (capped dendron, 10 mmol) to 25 mL of THF. 1 g of silane-functionalized OMS was placed in a Schlenk flask and then was heated at approximately 80 ºC under vacuum for two hours. The prepared CC solution was then added to the flask and stirred for approximately 24 h at room temperature under argon. After the reaction, the sample was filtrated, rinsed with 50 mL portions of dichloromethane, THF, and methanol sequentially, and then air-dried. The sample was then transferred back into a Schlenk flask with 25 mL of the diamine solution, and stirred for 24 h at room temperature under argon. The material was filtered and rinsed as described previously. The same procedure was followed to increase the dendron generation. In the diamine step, piperazine was used all the time for PIP dendron synthesis. However, piperidine was only used in the last step for CAP dendron synthesis, while piperazine was used in the initial one or few steps.

S1.3 Material characterization

The Thermal gravimetric analyses (TGA) were performed using a TA Instruments Q500 over a temperature range of 25–600 °C using air as a carrier gas and a temperature ramping rate of 1 °C/min. Ultraviolet–visible spectroscopy (UV-vis) spectroscopy measurements were performed using an Evolution 300 instrument. Liquid UV-Vis absorbance spectra were obtained using quartz cuvettes (Starna) in the same instrument at 25 ºC. Scanning Transmission Electron Microscopy (STEM) measurements were performed using a FEI TECNAI G^2 F30 FEG TEM. The samples were dispersed in methanol with sonication for 30 seconds and deposited on carbon-coated Cu grids (200 mesh, Electron Microscopy Science) until solvent was evaporated.

S1.4 Catalysis

The nitroaldol (Henry) reaction was performed as follows (Scheme 2). 100 mg of the catalyst were added into an Schlenk flask and dried under vacuum for 12 h. After cooling down to room temperature, nitrobenzaldehyde (0.38 g, 2.5 mmol) and nitromethane (1.35 mL, 25 mmol) were introduced into the reaction tube. The mixture was then transferred into a 20 mL amber vial in an oil bath and kept at 40 °C under stirring. At different intervals, 100 µL of the reaction mixture was transferred into a small centrifuge tube. After adding 1 mL of deuterated chloroform, the solid catalyst was removed from the solution using a centrifuge.

The liquid was analyzed by ^{1}H NMR using a Varian Inova 500 MHz spectrometer at 25 °C. Conversion and selectivity were calculated by integrating the peaks for 1-(4-nitrophenyl)-2-nitroethanol peak (δ 5.58-5.64 ppm, ^{1}H) and 1-nitro-4-(2-nitrovinyl)benzene (δ 7.72-7.75 ppm, ^{1}H) products with respect to that of nitrobenzaldehyde (δ 9.9-10.1 ppm, 1H).

S1.5 CO_2 uptake experiment

The pure CO_2 uptake experiments were performed using a TA Instruments Q500. The CO_2 uptake was recorded in flowing N_2 gas at 110 °C for 1 h and then CO_2 gas for 12 h after cooling to 25 °C under a N_2 flow. The gas flow rate in all cases is 90 mL/min. The CO_2 amount adsorbed on each sample was estimated by the weight difference of the weight after flowing CO_2 for 12 hours and the weight before flowing CO_2.

S1.6 Pd metal binding experiment

A standard K_2PdCl_4 solution (10 mL of 1.3 mM standard solution for PIP samples, and 10 mL of 1.7 mM standard solution for CAP samples) and a significant period of exposure (12 h) were used for the same amount (10 mg) of different samples. The filtrate obtained after metal complexation was collected and the UV-vis spectra for both PIP and CAP samples were shown in Figure S4. It's noteworthy that the samples in the centrifuge tube need to be washed at least twice to extract the excess K_2PdCl_4 solution adsorbed inside the OMS pores. The blank spectrum is the standard solution used and the pH was adjusted to 3 for each sample. The feature at 307 nm was used to determine the amount of Pd^{2+} in solution.

The 1 wt.% Pd/G2-CAP and 1 wt.% Pd/G2-PIP were prepared by dispending 1 g sample in 200 mL water, then 10 mL of 9.40 mM K_2PdCl_4 solution and several drops of 1 N HCl solution were added to adjust pH=3. After the mixture was stirred for 4 hours, about 10 mL of 1 M $NaBH_4$ solution were added and stirred for another 2 hours. Then the mixture was filtered, washed with 200 mL D.I. water and dried under vacuum overnight.

2. Characterizations of dendrimers

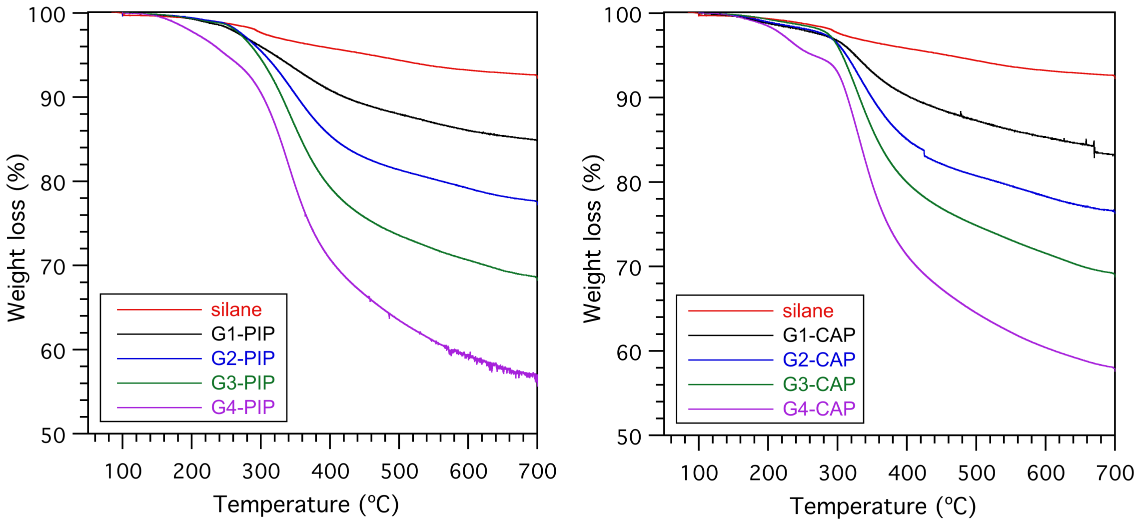

Figure S1. TGA raw curves of (left) PIP and (right) CAP dendrimers

Table S1. TGA table with explanation of calculations

	Fragment	TGA	Weight fraction of		Mass	mmol of			
Sample	**MW (g/mol)**	**Weight loss%**	**Ligand**	**Silica**	**Ligand /g-silica**	**Ideal ligand/g-silica**	**Total N/g-silica**	**Diamine N/g-silica**	**Capping N/g-silica**
Silane	89.07	6.53	0.065	0.935	0.070				
G1-PIP	336.42	13.43	0.134	0.866	0.155	0.485	3.881	1.940	1.940
G2-PIP	831.03	20.03	0.200	0.800	0.250	0.301	6.631	3.617	2.411
G3-PIP	1820.25	28.24	0.282	0.718	0.394	0.216	10.810	6.054	3.459
G1-CAP	334.42	14.14	0.141	0.859	0.165	0.492	2.955	0.985	0.985
G2-CAP	827.03	20.86	0.209	0.791	0.264	0.319	5.737	2.550	1.275
G3-CAP	1812.25	27.33	0.273	0.727	0.376	0.208	10.376	4.150	1.660

The MW information of dendron fragment is from ChemDraw. In above data, the weight loss is the weight fraction of ligand. The weight fraction of silica amount in each sample equals to (1-weight loss%). Then the ligand mass per gram silica can be calculated as (weight fraction of ligand/weight fraction of silica). From it, the ideal ligand mole can be estimated by dividing MW value. Once the ideal ligand mole value is known, then total Nitrogen mole, diamine Nitrogen mole, and capping Nitrogen mole can be estimated according to the Nitrogen numbers in each dendron.

Table S2. Textural properties of PIP and CAP dendrimers

Sample	**$S_{(\alpha\text{-}s)}$**	**v_{meso} (cm^3/g)**	**d_p (BJH) (nm)**
SBA-15	755	0.85	6.13
G1-PIP	482	0.41	5.59
G2-PIP	368	0.31	4.60
G3-PIP	280	0.22	4.34
G1-CAP	500	0.55	5.97
G2-CAP	332	0.36	4.62
G3-CAP	322	0.31	4.36

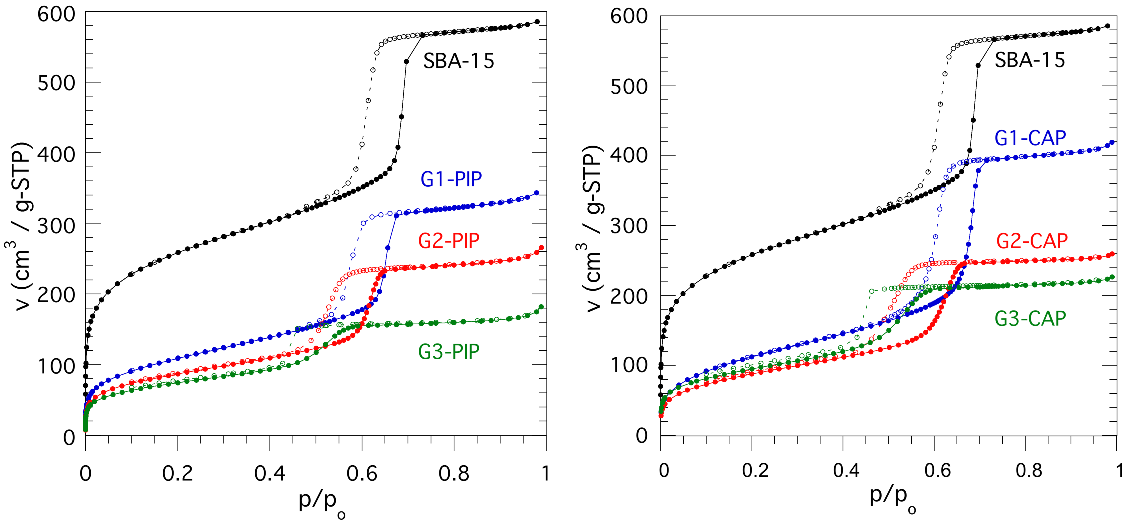

Figure S2. N_2 adsorption data of PIP (left) and CAP (right) dendrimers

3. Figures for Nitroaldol reaction

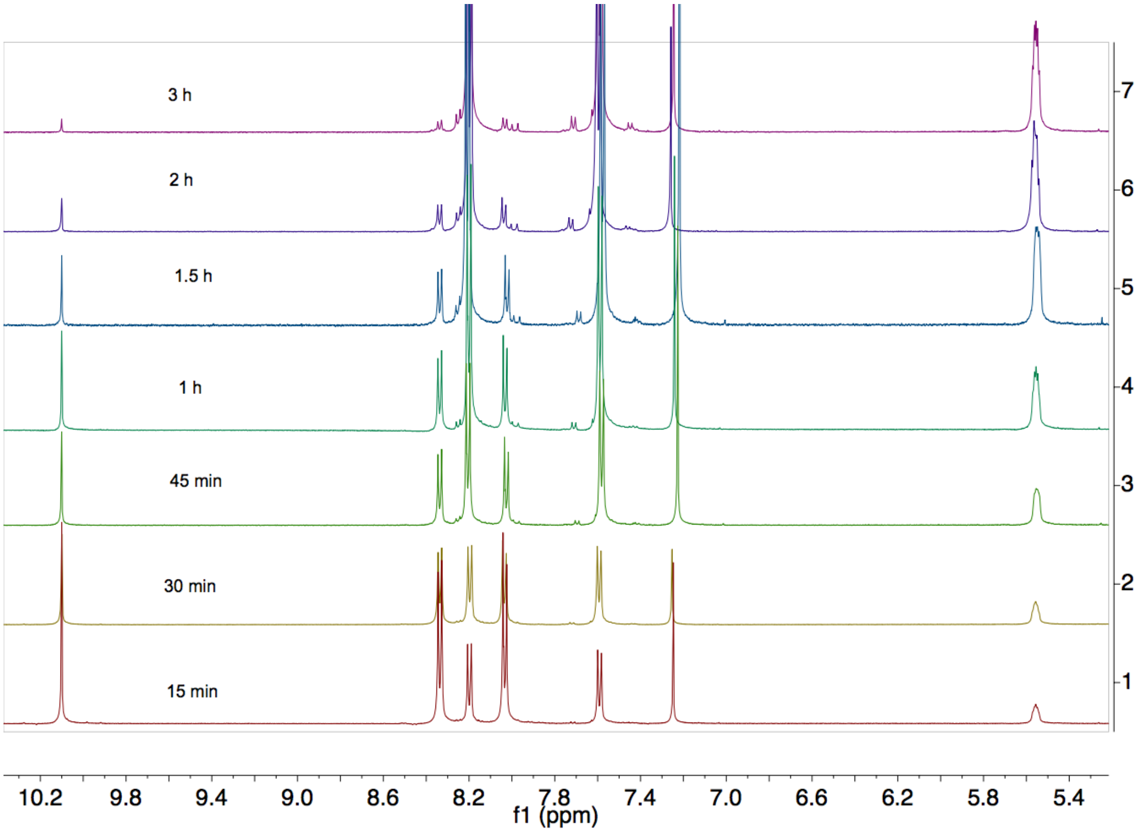

Figure S3. ^{1}H NMR spectra of Henry reaction for G2-PIP (representative spectrum)

Table S3. Nitroaldol (Henry) reaction data

Nitrobenzaldehyde conversion (%)								Alcohol selectivity (%)
Dendrimer	**Time (h)**							
	0.25	**0.5**	**0.75**	**1**	**1.5**	**2**	**3**	
G1-PIP	31	45.3	55.8	63.3	76	83	92.9	80
G2-PIP	32.6	52.1	71.2	81.5	92.1	95.1	98.1	96
G3-PIP	23.1	35.5	44.8	56.2	71.1	78.4	88.2	97
G1-CAP	13.6	22.1	28.8	35.5	48	57.2	69	96
G2-CAP	8.7	13.7	18.2	24.2	32.2	37.9	50.8	96
G3-CAP	6.3	9	12.9	15.7	22.8	25.5	37.1	97
G0.5 (treat w/wo water)	0	0	0	0	0	0	0	0

*The alcohol selectivity for all samples is almost a constant in the reactions.

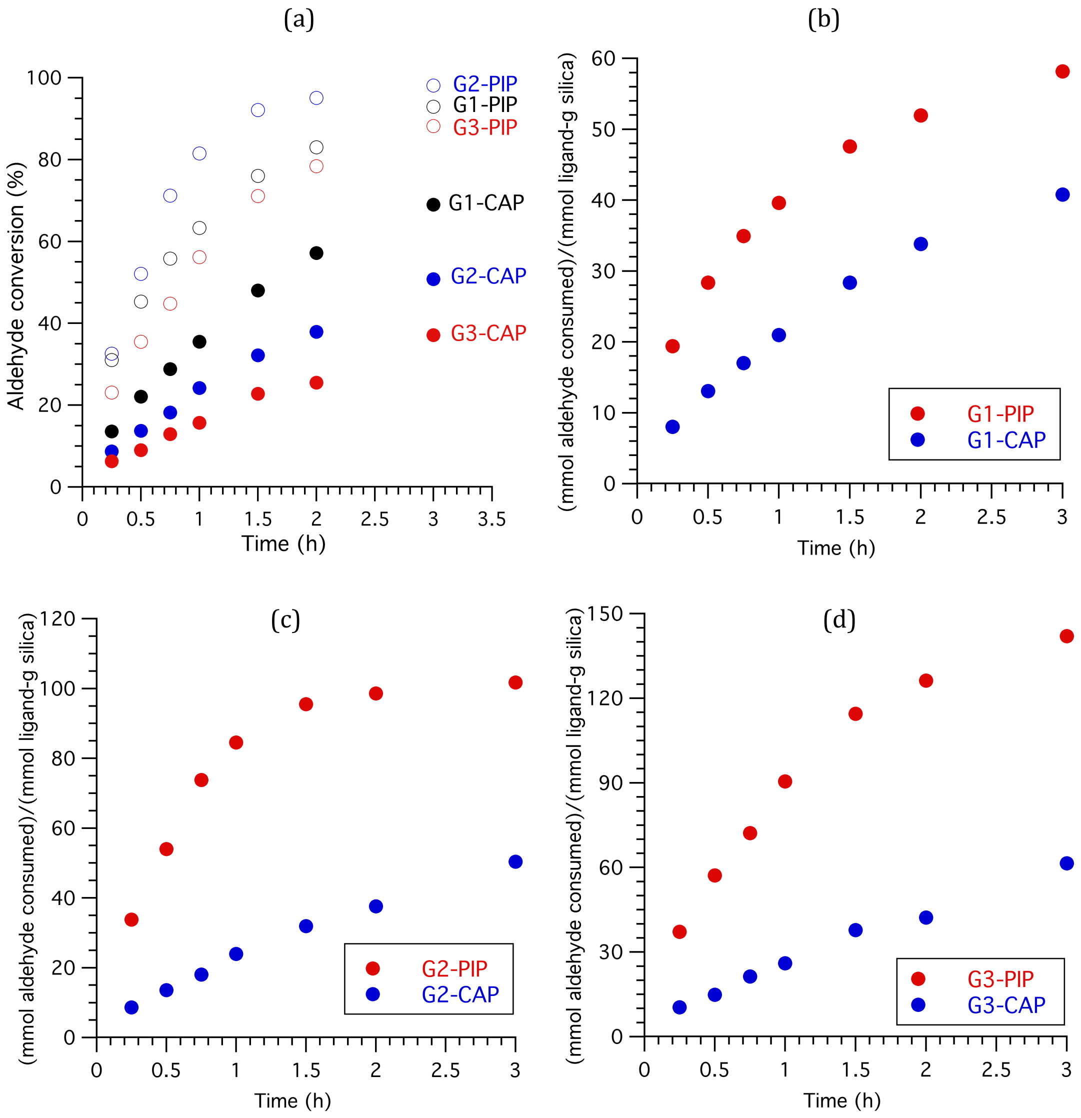

Figure S4. Nitroaldol reaction plots of (a) aldehyde conversion, and aldehyde consumed per ligand per gram silica for (b) G1, (c) G2 and (d) G3 samples.

4. Figures for Pd sequestration

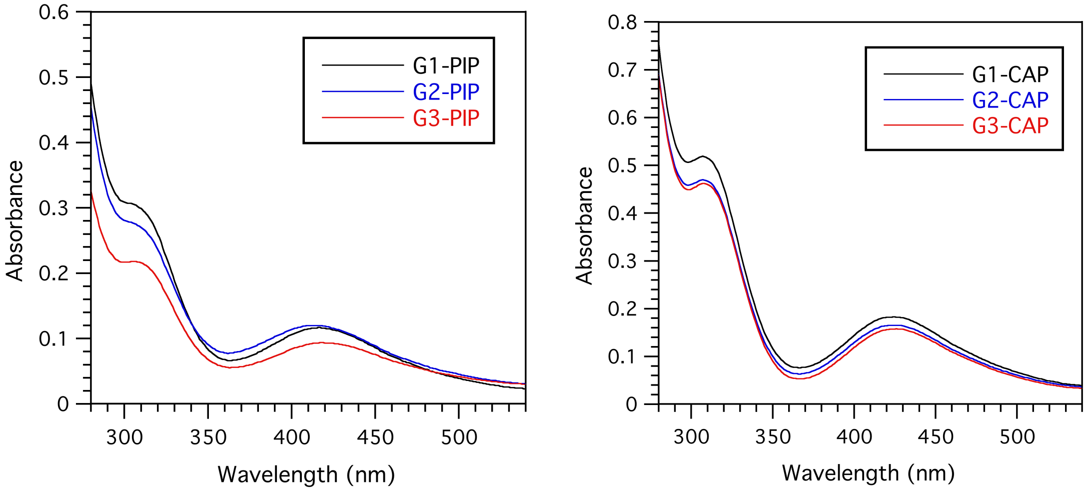

Figure S5. UV-Vis spectra of Pd sequestration experiment of (left) PIP and (right) CAP

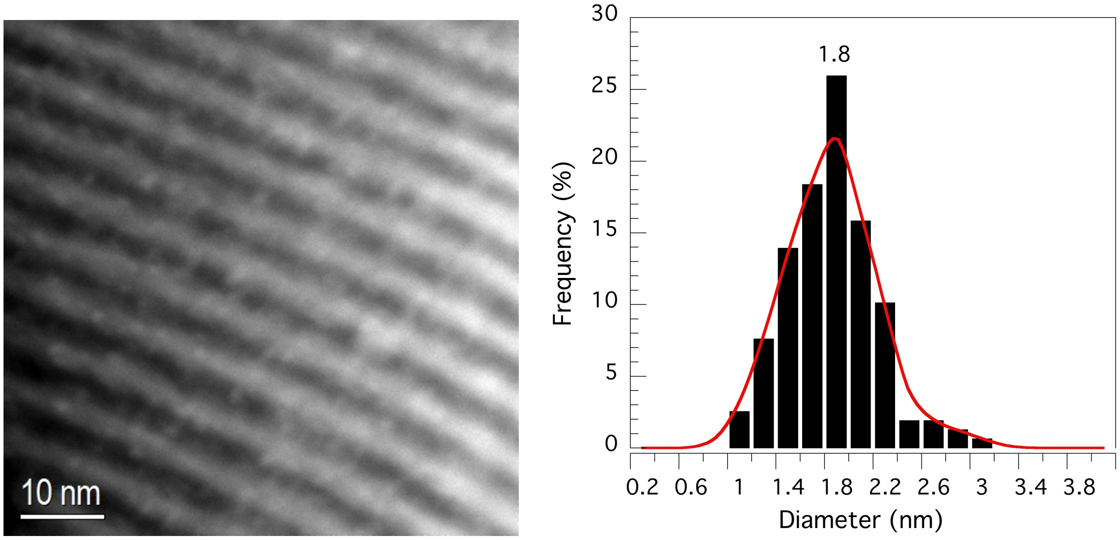

Figure S6. (a) TEM image and (b) histogram image of 1%Pd/G2-PIP.

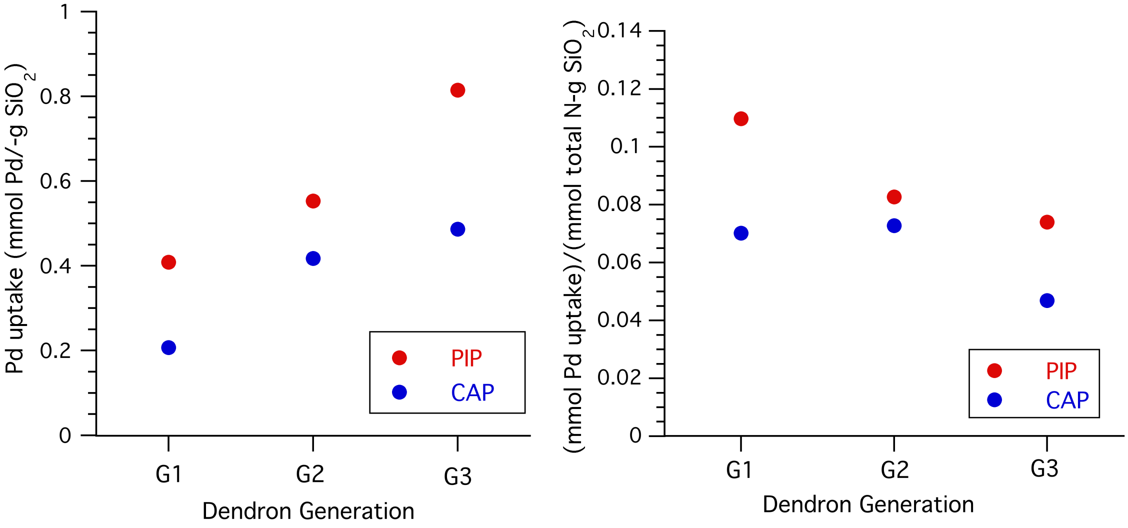

Figure S7. Pd uptake (left) and normalized Pd uptake on basis of (right) total N per gram silica

5. Figures for CO_2 capture

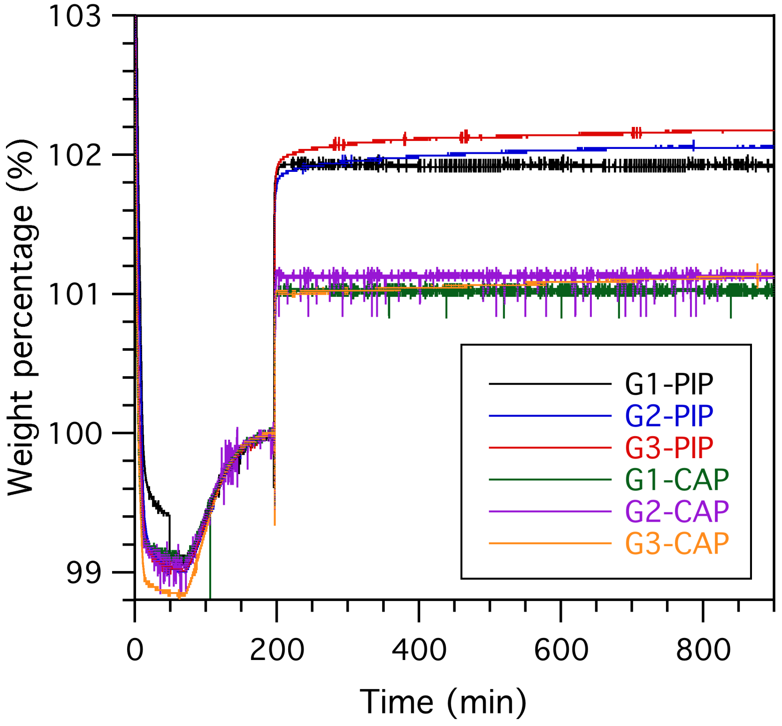

Figure S8. TGA-CO_2 raw curves of PIP and CAP (G1-G3)

Table S4. CO_2 capture data of all samples

Sample ID	**Dry CO_2 weight gain %**	**mmol CO_2 adsorbed /g solid**	**g silica percentage per 1 g solid***	**mmol CO_2 adsorbed /g silica**
G1-PIP	1.93%	0.4384	0.8657	0.5064
G2-PIP	2.05%	0.4653	0.7997	0.5818
G3-PIP	2.16%	0.4903	0.7176	0.6832
G1-CAP	1.02%	0.2317	0.8586	0.2699
G2-CAP	1.11%	0.2534	0.7914	0.3201
G3-CAP	0.98%	0.2235	0.7267	0.3075
SBA-15	2.70%	0.6125	1.0000	0.6125
G-0.5 treated with water	1.37%	0.3113	0.8931	0.3486

*This data is from TGA measurements (Table S1)

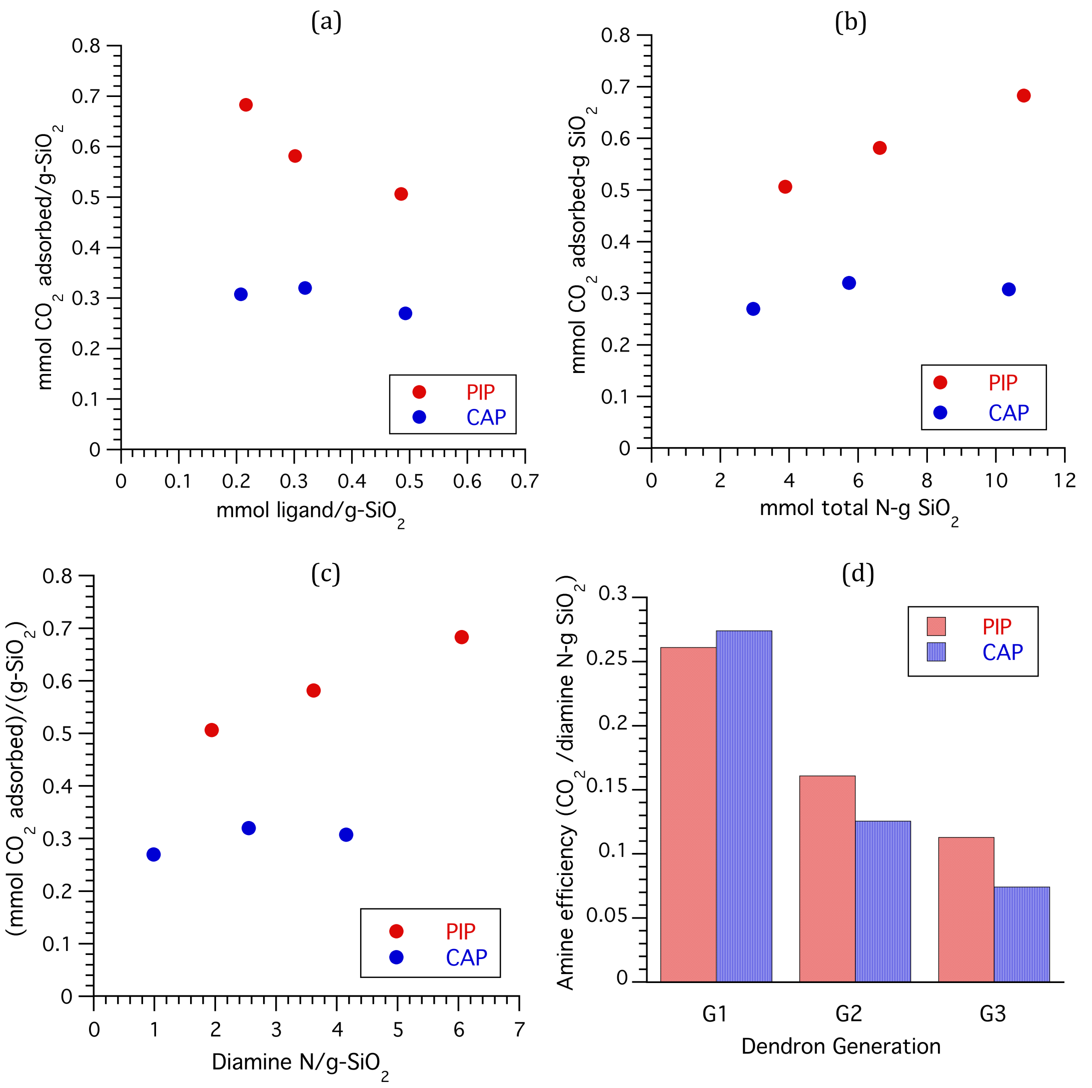

Figure S9. CO_2 uptake on basis of (a) ligand, (b) total N per gram silica, (c) diamine N per gram silica, and (d) amine efficiency on a basis of diamine N per gram silica.