Check for updates

View Article Online
View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Lou and D. Shantz, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC08157J.

Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm
Chemical Communications
www.rsc.org/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION
Marilyn M. Olmstead, Alan L. Balch, Josep M. Poblet, Luis Echegoyen et al.
Reactivity differences of $Sc_3N@C_{2n}$ (2n = 68 and 80). Synthesis of the first methanofullerene derivatives of $Sc_3N@D_{5h}$-C_{80}

175 YEARS

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

View Article Online
DOI: 10.1039/C7CC08157J

Chemical Communications

COMMUNICATION

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

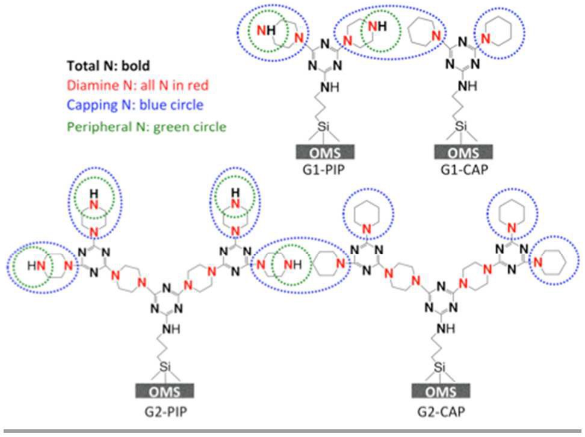
www.rsc.org/

Y. Lou,[a] and D. F. Shantz[a,*]

The role of different nitrogen atoms in melamine dendrons tethered to SBA-15 is elucidated. For the Nitroaldol (Henry) reaction both nitrogen atoms of the capping group particpate in the reaction. For metal binding, uptake correlates with the diamine content indicating interior amines are accessible. Carbon dioxide uptake properties are dictated by the presence of the peripheral amines with little interior contribution. The results show that different nitrogen atoms contribute to different processes including catalysis, metal sequestration, and gas separations.

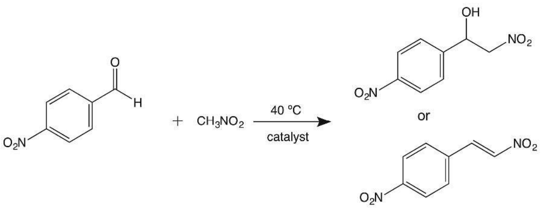
Organic-inorganic hybrid materials are a scientifically interesting and technologically relevant class of materials that have found use in areas ranging from biomaterials and drug delivery to environmental remediation and solar energy applications.[1-5] As the community pushes to ever more complex materials, a key to advancing the field will be the ability to understand the function of various structural centers.

Organosilane chemistry has been used extensively to functionalize silica to give a variety of hybrid materials, which can be further modified to develop more complicated hybrids.[6-8] As an example, many labs have investigated complex polyamine brushes on silica supports for carbon dioxide capture.[9-12] Going forward the ability to understand how various amine groups, i.e. primary versus secondary, contribute to the mechanism of carbon dioxide capture, and how the organic architecture can be tuned will be key.[13, 14]



Scheme 1. Molecular structure of Gx-PIP and Gx-CAP (x is dendron generation) and terms for various types of nitrogen.

Here we study the different amine groups in the melamine dendrons our lab has reported previously.[15-17] As shown in scheme 1 there are multiple types of nitrogen atoms: those in the aromatic ring of the triazine moiety, tertiary and secondary amines associated with the diamine spacers, and the amine of the silane. In this paper, we demonstrate how the different types of amines in the dendron participate in catalysis, metal sequestration, and gas separations. We couple this with a model dendron which employs piperazine as the diamine spacer, but where the dendron is terminated with piperidine, resulting in a dendron that is structurally identical except that it does not contain any nitrogen on the external surface of the dendron, i.e. there are no peripheral amines. As can be seen in Scheme 1, the difference between the PIP and the CAP samples is the termination step. The CAP samples have no peripheral –NH– groups, and half as many nitrogen atoms in their capping groups. Thermogravimetric analysis (TGA) and porosimetry of the materials (Figure S1 and Tables S1, S2, ESI) show that piperidine capping has negligible differences on the



Scheme 2. Nitroaldol (Henry) reaction.

---

[a] Department of Chemical and Biomolecular Engineering, Tulane University, 6823 St. Charles Avenue, New Orleans, LA 70118, United States. Email: dshantz@tulane.edu

Electronic Supplementary Information (ESI) available: Materials and Methods. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7CC08157J

material properties, i.e. these samples have very similar ligand loadings and the only difference is the presence or absence of the external –NH– group.

The Nitroaldol reaction was first explored as a material probe. Figure 1 shows the results of the Nitroaldol reaction over the G1-G3 PIP and CAP samples (raw ^{1}H NMR data and conversion plots are given in Figure S3 and Figure S4, ESI). The data has been analysed in numerous ways, including plots of nitrobenzaldehyde conversion versus time as well as various normalized nitrobenzaldehyde consumption rates versus time. In all cases the selectivity to the nitroalcohol is very high (>95%) except G1 PIP (80%).

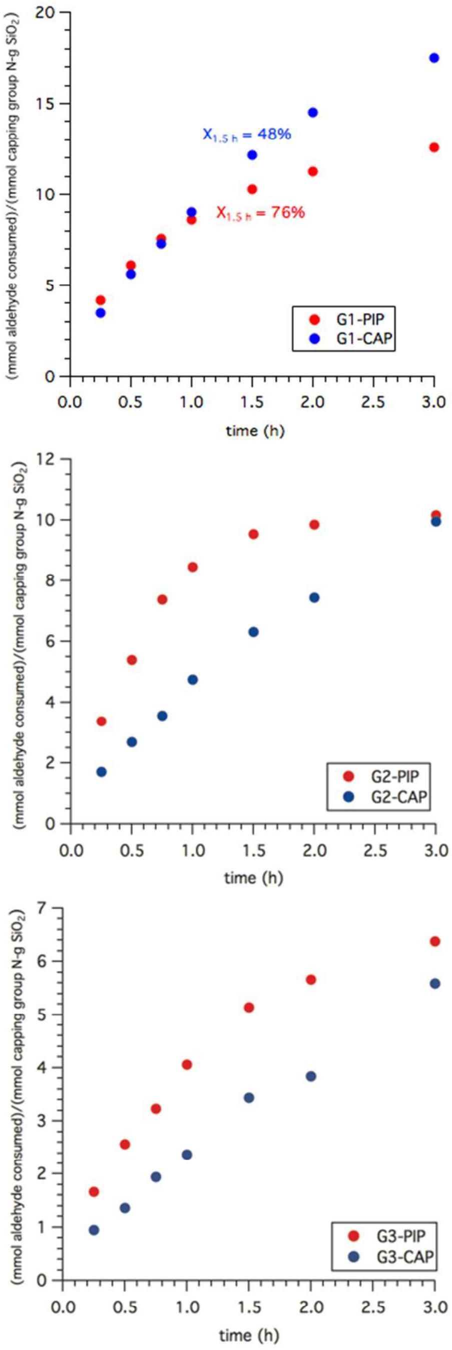


Figure 1. Henry reaction comparison results of dendrimer with and without capping for (top to bottom), G1, G2, and G3. Aldehyde consumption rate is normalized by nitrogen in the capping group.

Figure 1 shows the most interesting normalization, where the consumption rate is normalized by the amount of nitrogen in the capping group of the dendrimer, i.e. the last diamine used to terminate the dendron. For the G1 case on a capping group nitrogen basis the PIP and CAP samples have the same reaction rate. This result indicates that for the G1 sample, not only the external secondary amine in the piperazine but also the interior tertiary amine of the peripheral PIP and CAP groups contribute to the observed reactivity. If only the peripheral nitrogen was responsible for the observed reactivity the CAP samples would display little or no reactivity. That the PIP samples fall off relative to the CAP samples at times after 1.5 h is due to the high conversion for the PIP samples at that point (>80%). In contrast, the initial rates for the G2 and G3 samples are not the same, as the G2 and G3 PIP materials are more active on any normalization basis. A simple explanation for this is that as the dendrons grow larger and there is more mass transfer resistance, the contribution of the peripheral –NH– group to the observed rate increases. More plots including conversion versus time on stream are given in the supporting information (Figure S4, ESI). One last point worth noting is that a control sample was prepared where the cyanuric chloride was hydrolysed, i.e. G-0.5 was made. This sample shows no reactivity, indicating the triazine group does not contribute to the observed reactivity.

Palladium metal binding was used to probe how the different nitrogen atoms participate in metal chelation (Figure 2). As expected, with increasing dendron generation more metal is captured. However, on a total nitrogen basis the metal uptake goes down with increasing dendron generation. Possible explanations for this observation include that for larger dendrons as the available void space in the pores decreases that there is a decrease in metal uptake. Also, given that not all amines are likely participating in metal chelation, the normalization on a total nitrogen basis is not the most meaningful one. Consistent with this, the most interesting observation is that on a unit diamine nitrogen basis the two materials PIP and CAP bind the same amount of metal, which is shown in Figure 2 (middle). This and the fact that the G1-CAP binds half as much Pd as G1-PIP leads to the conclusion that both nitrogen atoms in the diamine bind metal but a smaller fraction is accessible as one goes to larger generation dendrons. This last observation is consistent with the rate of decrease of metal uptake in Figure 2 (middle) being similar. Finally, Figure 2 (bottom) where one normalizes by the capping groups further indicates that the diamine nitrogen is the key factor for binding Pd. The metal capture is the same at G1, but different at G2 and G3, perhaps due to more surface peripheral amines in PIP interacting with the surface silanols groups as the dendrons get larger and span the pores. The results in Figure 2 show Pd^{+2} can penetrate into the dendron. This is in contrast to what is observed for the Henry reaction.

View Article Online
DOI: 10.1039/C7CC08157J

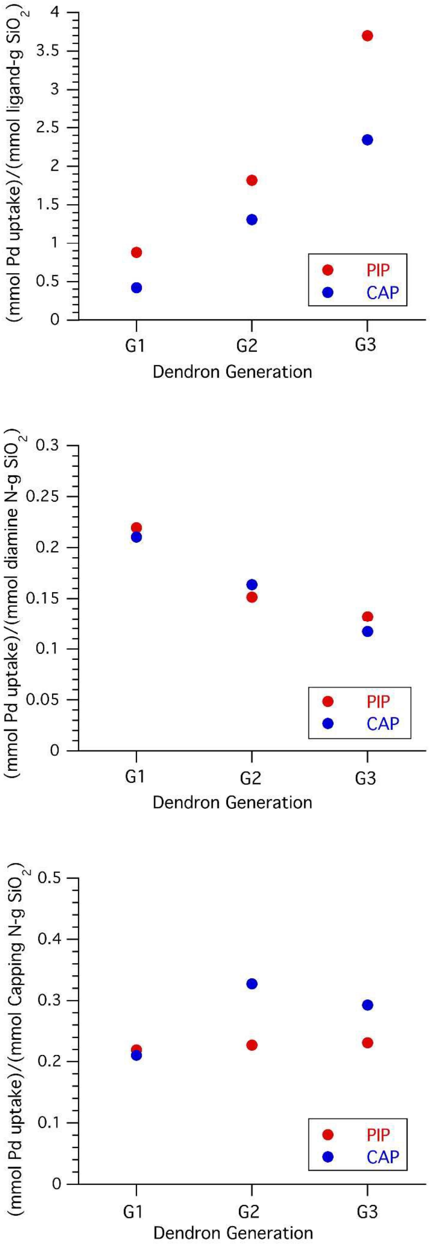


Figure 2. Pd uptake results of dendrimer with and without capping (top) per ligand, (middle) per diamine N, (bottom) per capping group N.

These findings provide insights into the size of probes that can access the dendron interior.

Interestingly, these two very similar dendrons clearly bind the palladium differently. As evidence of this, 1 wt% Pd was loaded in the G2-CAP sample, following with reduction to Pd^0. STEM images of this material and the Pd particle size histogram are shown in Figure 3. The Pd particles are distributed uniformly in the sample with an average particle size of 2.8 nm. In our previous report,[18] 1 wt% Pd/G2-PIP was successfully prepared with an average size of 1.8 nm (Figure S6, ESI). From the direct comparison of those two samples, the only difference in the parent materials is the terminating group on the dendron. The conclusion from this is that the absence of the nitrogen atoms on the periphery leads to larger nanoparticles. This result shows that by changing the dendron microstructure it is possible to manipulate nanoparticle size.

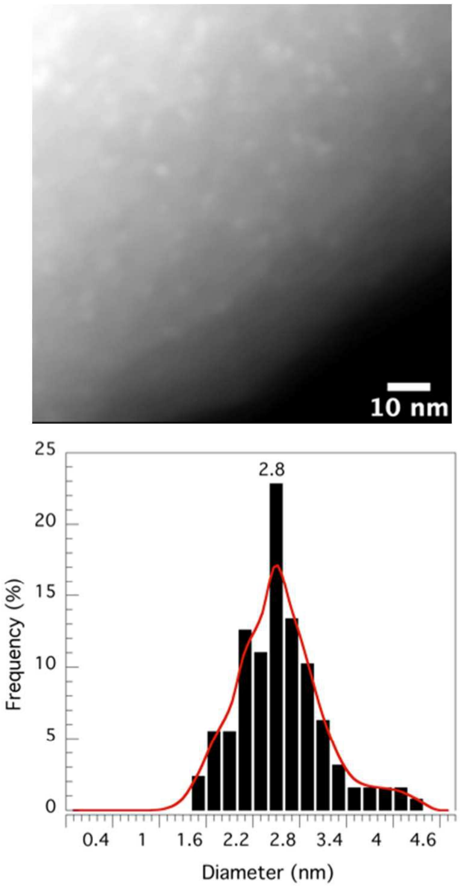


Figure 3. (a) TEM image and (b) histogram image of 1%Pd/G2-CAP.

Figure 4 shows the carbon dioxide uptake from a gas stream of pure carbon dioxide on a unit silica basis (top). The two most significant observations are that the carbon dioxide uptake only marginally increases (~15%) with each increasing generation, and that by contrast capping with piperidine versus piperazine leads to much larger differences in the amount of CO_2 adsorbed at a given generation. The CO_2 uptake of CAP samples is approximately half of the uptake of PIP samples, consistent with a decrease of a factor of two in the number of capping amine groups. To further test our hypothesis that the CO_2 uptake is mostly due to the peripheral amines, the CO_2 uptake was plotted versus the number of capping amines for each sample, as shown in Figure 4 (middle). It shows a linear relationship between CO_2 uptake and number of amine capping groups. This finding is consistent with our hypothesis that the capping amine groups largely determine carbon dioxide uptake, and that the tertiary interior amines are much less important for carbon dioxide capture. This is consistent with prior literature that indicates tertiary amines

View Article Online
DOI: 10.1039/C7CC08157J

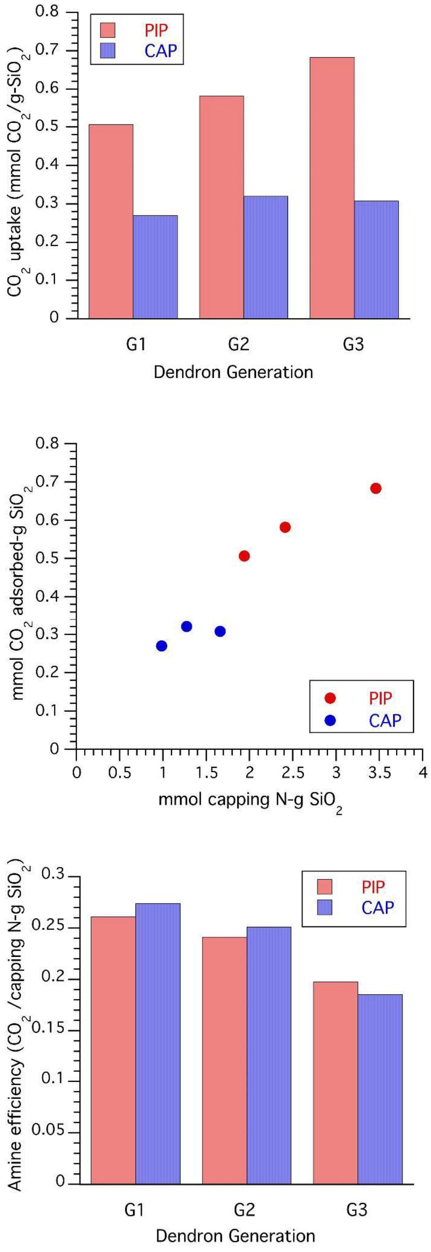


Figure 4. CO_2 uptake results for G1 to G3 (top), CO_2 uptake plotted as a function of mmol of Nitrogen in the capping group (middle), and amine efficiencies on a capping N basis (bottom).

should only contribute minimally for CO_2 capture in dry conditions. The amine efficiency on a capping nitrogen basis is also shown in Figure 4 (bottom). In the case the efficiencies are very similar for the PIP and CAP samples, as expected based on the above.

Conclusions

The current work, through using well-controlled model dendrons and a variety of probe molecule binding tools, shows the role of the different nitrogen groups in melamine dendrons. The Nitroaldol reaction findings indicate that the amine sites in the capping group of the dendron contribute most to the reactivity, whereas for palladium binding all the non-aromatic amines contribute. Finally, for carbon dioxide capture the peripheral amine groups are the major contributor to the uptake properties. These types of molecular insights are key to developing next-generation complex hybrid materials for a range of emerging applications.

Acknowledgement

Y. L. acknowledges partial financial support from Schlumberger via a Schlumberger Scholarship. D. F. S. acknowledges partial financial support from Entergy and Tulane University.

Conflicts of interest

There are no conflicts to declare.

References

1. F. Hoffmann, M. Cornelius, J. Morell and M. Froba, *Angew Chem Int Ed Engl*, 2006, **45**, 3216-3251.
2. A. P. Wight and M. E. Davis, *Chemical Reviews*, 2002, **102**, 3589-3613.
3. V. Dufaud and M. E. Davis, *Journal of the American Chemical Society*, 2003, **125**, 9403-9413.
4. M. Vallet-Regí, F. Balas and D. Arcos, *Angewandte Chemie International Edition*, 2007, **46**, 7548-7558.
5. C. Sanchez, B. Julian, P. Belleville and M. Popall, *Journal of Materials Chemistry*, 2005, **15**, 3559-3592.
6. N. Hiyoshi, K. Yogo and T. Yashima, *Microporous and Mesoporous Materials*, 2005, **84**, 357-365.
7. Y. G. Ko, S. S. Shin and U. S. Choi, *Journal of Colloid and Interface Science*, 2011, **361**, 594-602.
8. X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923-926.
9. N. A. Brunelli, S. A. Didas, K. Venkatasubbaiah and C. W. Jones, *Journal of the American Chemical Society*, 2012, **134**, 13950-13953.
10. Y. Kuwahara, D.-Y. Kang, J. R. Copeland, P. Bollini, C. Sievers, T. Kamegawa, H. Yamashita and C. W. Jones, *Chemistry-a European Journal*, 2012, **18**, 16649-16664.
11. A. Goeppert, M. Czaun, R. B. May, G. K. S. Prakash, G. A. Olah and S. R. Narayanan, *Journal of the American Chemical Society*, 2011, **133**, 20164-20167.
12. E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas and C. W. Jones, *Chemical Reviews*, 2016, **116**, 11840-11876.
13. A. Mehdi, C. Reye and R. Corriu, *Chemical Society Reviews*, 2011, **40**, 563-574.
14. E. L. Margelefsky, R. K. Zeidan and M. E. Davis, *Chemical Society Reviews*, 2008, **37**, 1118-1126.
15. J. Han, Y. Lou, X. Cai, B. C. Gibb and D. F. Shantz, *The Journal of Physical Chemistry C*, 2017, DOI: 10.1021/acs.jpcc.7b05602.
16. S. Yoo, J. D. Lunn, S. Gonzalez, J. A. Ristich, E. E. Simanek and D. F. Shantz, *Chemistry of Materials*, 2006, **18**, 2935-2942.
17. E. J. Acosta, C. S. Carr, E. E. Simanek and D. F. Shantz, *Adv. Mater.*, 2004, **16**, 985-989.
18. Y. Lou and D. F. Shantz, *Journal of Materials Chemistry A*, 2017, **5**, 14070-14078.

View Article Online
DOI: 10.1039/C7CC08157J

View Article Online
DOI: 10.1039/C7CC08157J

6x3mm (300 x 300 DPI)