Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

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 **Information for Authors**.

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** 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

www.rsc.org/chemcomm

Journal Name

COMMUNICATION

Tackling Poison and Leach: Catalysis by Dangling Thiol-Palladium Functions within a Porous Metal-Organic Solid

Bo Gui,[†a] Ka-Kit Yee,[†b] Yan-Lung Wong,[b] Shek-Man Yiu,[b] Matthias Zeller,[c] Cheng Wang,*[a] and Zhengta Xu*[b]

Self-standing thiol (-SH) groups within a Zr(IV)-based metal-organic framework (MOF) anchor Pd(II) atoms for catalytic applications: the spatial constraint prevents the thiol groups from sealing off/poisoning the Pd(II) center, while the strong Pd-S bond precludes Pd leaching, enabling multiple cycles of heterogeneous catalysis to be executed.

In traditional solution chemistry, the steric effect is commonly exerted via bulky substituents, as is often practiced by coordinating bulky ligands around metal centers. Such bulky ligands block off the coordination sphere, kinetically stabilize the coordinatively unsaturated metal centers, and often give rise to remarkable reactivities such as C-H bond and N_2 activation.[1] Here we depart from the dynamic, free-flowing solution regime, and set out instead to explore the steric effect in the context of organized open frameworks in the solid state (e.g., MOF systems[2]). For this, we envision, within a porous solid state network, a dangling, relatively isolated donor site that is without immediate neighboring donors; the incoming metal guest would perforce be bonded to at most one donor from the host net (the other donors being too far away). The metal center thus affixed to the dangling, isolated donor, would take on a distinct unsaturated character in its coordination sphere, with open sites[3] to accommodate substrates, and to effect catalytic processes not feasible under solution conditions. We here demonstrate that the dangling effect converts thiols from catalyst poisons into effective anchors for palladium atoms, resulting in highly recyclable heterogeneous catalysis for carbon-carbon bond formation reactions (the Suzuki–Miyaura reaction, SMR). Such a study thus complements the ongoing advances in MOF catalysis,[4] where intentions to exploit reactivity arising from the dangling, isolated character of the donors are less distinct.

The thiol donor is well suited for highlighting the dangling effect, as thiols in the solution phase are known to be incompatible with many transition metal catalysts (especially the heavy members of Pd and Pt). For example, thiol groups readily poison the Pd catalyst for the widely used SMRs for C-C bond formation between aryl groups.[5] Such poisoning can be ascribed to the strong and intractable thiol-Pd interactions that effectively seal off the coordination sphere
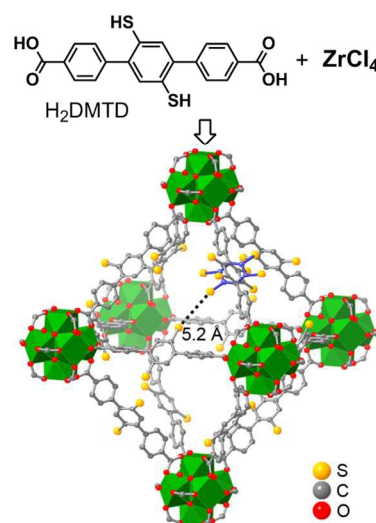

Fig. 1 Synthetic scheme for the ZrDMTD network. The network is simplified as an octahedral cage taken from the single crystal structure. The dotted line indicates a shortest intermolecular distance of 5.24 Å between sulfur atoms. Disorder of the central benzene ring is shown in only one linker; Zr coordination polyhedra displayed in green.

and suppress the bonding lability that is crucial for the catalytic process. Specifically, in a solution environment where the thiol groups can freely approach the metal center, palladium(II) dithiolate species—e.g., $Pd(SR)_2$—readily form as a thermodynamic trap from which reactivation into the catalytic cycle often entails elaborately designed ligands (e.g., the Josiphos ligands[6]).

By contrast, such poisoning from the thiol donors could be prevented in the setting of a rigid framework where the thiol groups are spaced too far apart to fully bond around the Pd center—the sulfur atoms therefore would not block off the catalytic steps as in

the solution case. Moreover, the use of the dangling, isolated thiol groups to anchor Pd atoms effectively turns the intractable Pd-S bond on its head, as its very strength would help to suppress Pd leaching, and to create more durable heterogeneous catalysts.

In general, leaching remains a central problem in heterogeneous catalysis. Instead of being truly "heterogeneous", many supported Pd catalysts for C-C coupling (e.g., SMR and Heck) reactions actually opearate through leached soluble Pd species.[7] To verify the heterogeneous nature, more rigorous procedures like the three-phase test are needed.[7e, 7f, 8] For example, with the three phases consisting of the catalyst solid, the solution phase, and a separate solid phase anchoring a test reagent (e.g., an aryl bromide for SMR), a truly heterogeneous catalyst, without leaching, should not cause significant reaction of the test reagent anchored on the separate solid phase.

Our choice of the framework system in which to install the dangling thiol groups is facilitated by recent discoveries of robust frameworks based on carboxylate linkers and chemically very hard Al(III),[9] Cr(III)[10] and Zr(IV)[11] ions. For example, hard ions generally prefer to bond with the carboxyl group (e.g., over the soft thiol), and free-standing thiol functions can be appended to the crystalline host net, as demonstrated in an earlier Eu(III) system back in 2009,[12] and in the recent Zr(IV) networks (e.g., from terephthalate-based linkers).[13,14] To explore the dangling effect, we here use the elongated building block of DMTD (DM: dimercapto; TD: terphenyldicarboxyl; Fig. 1), in order to make for larger pore opening, and to facilitate the diffusion of substrates. The longer molecule of DMTD, with the thiol groups being positioned at its central ring, also serve to further space apart the thiol groups, so as to accentuate their dangling, solitary character.

Reaction of H_2DMTD and $ZrCl_4$ (see SI) yielded single crystals of the framework ZrDMTD [composition: $Zr_6O_4(OH)_4(DMTD)_6$; see SI for more details, e.g., Fig. S1-3 for the TGA plot, Raman and IR spectra], which features the UiO-68 topology, with DMTD being the linear strut and $Zr_6O_4(OH)_4$ clusters the 12-connected nodes (Fig. 1).[15] The free-standing thiol group in the crystal structure is disordered over four sets of symmetry-related positions, from which the shortest S···S distance across the DMTD linkers is found to be 5.24 Å (Fig. 1). Such far-apart S atoms are not disposed to be simultaneously bonded with the same metal center, e.g., a typical Pd-S bond is of 2.20 Å, which would dictate the other Pd-S distance to be longer than 3.00 Å. In other words, only one S atom from the host grid could fully bond with each individual Pd center, thus leaving open its coordination sphere.

The ZrDMTD crystals can be safely stored in organic solvents (e.g., EtOH, $CHCl_3$ and DMF) for months, with no degradation of crystallinity (e.g., as checked by powder X-ray diffraction, PXRD). However, when the crystals are taken out of the solvent, the PXRD pattern starts to degrade within minutes, resulting in two broad peaks at the lower-angle region (Fig. 2, pattern c). The degraded structural order is also reflected in the gas sorption properties. Unlike most other Zr-based MOF solids, the desolvated ZrDMTD sample exhibits no significant N_2 sorption at 77 K. Nevertheless, at 273 K, CO_2 sorption does take place (pressure range: from 8×10^{-3} to 780 mmHg) with reproducible isotherms (Fig. S4) indicating a BET surface area of 1361 m^2/g. Such different sorption behaviors toward N_2 and CO_2 are often seen in porous polymers, wherein the pores blocked at 77 K become more accessible (e.g., to CO_2 gas) at higher temperatures due to stronger thermal motions.[16] As for the desolvated solid of ZrDMTD, the PXRD and BET studies together point to a largely disordered network with restricted access to the

pore region. Unless otherwise mentioned, the ZrDMTD crystals used in the following studies were continuously covered by solvents.

Upon contact with an acetonitrile solution of $Pd(CH_3CN)_2Cl_2$, the ZrDMTD crystals turned from light yellow to red (Fig. S5), with the resultant Pd-loaded sample (ZrDMTD-Pd) exhibiting a distinct Raman peak around 386 cm^{-1} (Fig. S2) that corresponds to the Pd-S stretch. The Pd uptake is quantified by ICP elemental analysis, which indicated a Zr/Pd ratio of 1:0.70 (corresponding to a 2.9:1 S/Pd ratio). The strong and sharp PXRD peaks (Fig. 2, pattern d) of the ZrDMTD-Pd sample also indicated retention of the structural integrity of the host net.

The catalytic activity of the ZrDMTD-Pd crystals was examined under especially convenient conditions for the SMR: by simply heating the reactants and the crystals (Pd/substrate molar ratio: about 1%) and in ethanol--without the commonly required phosphine
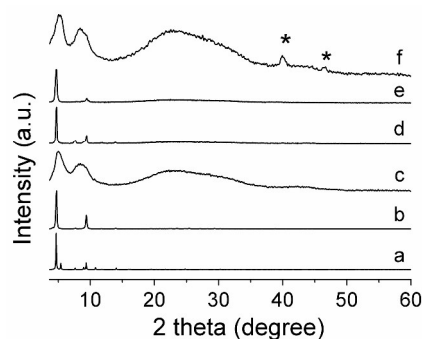

Fig. 2 PXRD patterns: (a) calculated from the single-crystal structure of ZrDMTD; (b) as-made ZrDMTD; (c) as-made ZrDMTD placed in air for 10 mins; (d) ZrDMTD-Pd; (e) the sample of (d) after 8 cycles of catalytic reaction; and (f) the sample of (e) after being placed in air for 2 days. Patterns a, b, d and e were taken with crystals covered by a thin layer of DMF to prevent solvent loss.

ligands, and without the need to exclude air. Even without stirring, the reactions proceed smoothly for iodide substrates, generally completing within several hours, with yields of the isolated products--in spite of the small reaction scale—being above 80% (Tables 1 and S1). For bromobenzene and the activated derivatives (e.g., by –F or –CN), similar yields can also be achieved, with somewhat longer reaction times (e.g., 12 hrs). Aryl bromides with electron-donating groups, are, however, less reactive under similar conditions (e.g., Table S1, entries 9 and 10). Higher efficiencies, however, can be achieved by magnetic stirring—e.g., within one hour, an iodo substrate generally registers a conversion rate over 90% as indicated by solution NMR (see Fig. S8 for details).

During the catalytic reaction, the red crystals of ZrDMTD-Pd turned black, suggesting the formation of Pd(0) species. XPS study on the Pd $3d_{5/2}$ state is also revealing. Before catalysis, the (red) ZrDMTD-Pd sample exhibits one single peak at 337.7 eV, associated with Pd(II) species. After catalysis, the blackened sample exhibits two peaks: one remaining at 337.7 eV, and the other being a new, strong peak at the lower energy of 335.4 eV, which is consistent with the lower binding energy of Pd(0) species (Fig. S6). On the other hand, the regular octahedral shape of the crystals was maintained (see Fig. S7 for SEM images), and the structural integrity of the crystalline host net was confirmed by powder X-ray diffraction, which reveals the same sharp peaks as the as-made sample (Fig. 2, pattern e). Notably, no peaks corresponding to elemental Pd were observed in the PXRD pattern, indicating that the

individual Pd(0) atoms are likely to remain well dispersed on within the host framework--i.e., the Pd atoms do not aggregate to form sizable, diffracting nanoparticles.

Table. 1 Efficiencies of selected Suzuki-Miyaura reactions catalyzed by ZrDMTD-Pd crystals and control experiments[a]
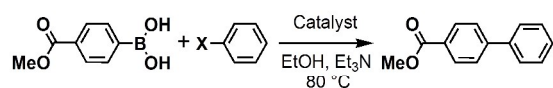
Entry	X	Catalyst	Time (hr)	Isolated Yield (%)	TON[e]
1	I	None	5	ND[f]	0
2	I	ZrDMTD-Pd cycle 1	5	86.0	126
3	I	ZrDMTD-Pd cycle 2[b]	5	83.1	122
4	I	ZrDMTD-Pd cycle 3[b]	5	82.0	120
5	I	ZrDMTD-Pd cycles 4-8[b]	5	84.3[d]	124[d]
6	I	H$_2$DMTD/PdCl$_2$[c]	5	8.6	13
7	I	Degraded ZrDMTD-Pd-d[g]	5	32.4	47
8	Br	ZrDMTD-Pd	12	85.6	125
9	Br	H$_2$DMTD/PdCl$_2$[c]	12	ND[f]	0

[a] Additional test reactions and the procedures included in SI. [b] See SI for the cycling procedure. [c] With a molar ratio of 1:0.70 between H$_2$DMTD and PdCl$_2$(CH$_3$CN)$_2$. [d] Average value of five runs. [e] TON defined as the molar ratio between product and Pd. [f] Not detected from TLC monitoring. [g] Degraded by exposing ZrDMTD-Pd to air (PXRD pattern shown in Fig. 2f).

Aggregation of the Pd(0) species, however, does occur when, after the catalytic cycle, the black ZrDMTD-Pd crystals were placed in air (i.e., without the covering solvent). Like the above-mentioned ZrDMTD crystals, the PXRD peaks from the host net broaden significantly. Simultaneously, new, broad peaks at higher angles appeared (pattern f of Fig. 2), which can be ascribed to crystalline Pd particles (i.e., 2θ 39.96∘ and 46.58∘, corresponding to the 111 and 200 diffractions from the Pd lattice). The degraded ZrDMTD-Pd solid (with the Pd atoms aggregated to form particles) shows largely subdued catalytic activity: for example, even for an iodo substrate (entry 7, Table 1), the isolated yield was found to be only 32% (TON: 47), less than half the yield obtained from the crystalline ZrDMTD-Pd catalyst. The subdued catalytic activity can be ascribed, in part, to the reduced accessibility of the Pd atoms after they pile up to form the nanoparticles.

Back to the crystalline ZrDMTD-Pd (containing more dispersed Pd species): the recyclability of this solid catalyst is highlighted in the constant yields and TONs observed in the 8 cycles tested: no trend of catalytic activity loss was observed, and the crystallinity of the host framework remained intact (as seen in PXRD pattern e, Fig. 2). To further keep track of the Pd species, the supernatant was subjected to ICP-OES analysis (see SI) and this registered no Pd presence; correspondingly, the Pd content in the crystals after the 8 catalytic cycles remained unchanged (see SI for details). Also, the isolated supernatant exhibits no catalytic activity under similar reaction conditions (as shown by the NMR data in Fig. S9); and a hot filtration test revealed no further reaction in the filtrate (Fig. S10).

Moreover, even when a large amount of the unmetallated ZrDMTD crystals (i.e., containing free thiols groups in the pores)are added to the reaction (i.e., as a form of poison test), no significant impairment on the ZrDMTD-Pd catalyst was observed, e.g., with the iodo substrate all consumed within 1.5 hrs (Fig. S11). Altogether, the leaching of Pd species was found to be negligible. Future deployment of the ZrDMTD-Pd solid in a continuous flow setup would serve to boost its overall turnover numbers, and highlight its operational advantages as a heterogeneous catalyst.

As a comparative study to highlight the catalytic activity arising from the spatial confinement effect imposed by the porous framework (in the form of the dangling –SH groups), the free ligand of H$_2$DMTD was used in conjunction with PdCl$_2$(CH$_3$CN)$_2$ (similar reaction conditions, with a similar ligand/Pd ratio as in the ZrDMTD-Pd solid, see SI for details) for the SMR. Very little catalytic activity was observed with the free ligand H$_2$DMTD: for the iodo substrate (Table 1, entry 6), the yield is below 10%, while bromobenzene remains unreacted even after being heated for 12 hrs (Table 1, entry 9).

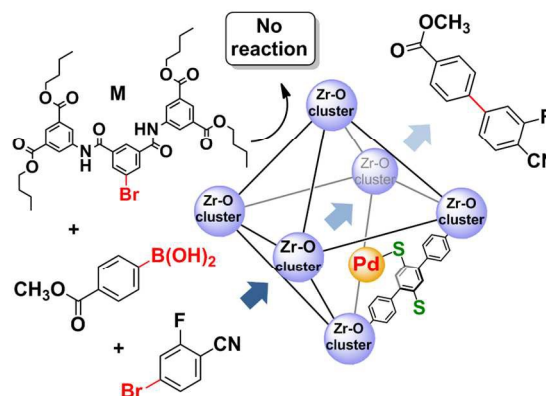To further illustrate that the catalytic Pd species are operating

Fig. 3 A schematic of the ZrDMTD-Pd-catalyzed coupling reaction between a boronic acid and 4-bromo-2-fluorobenzonitrile (bfbn) in the presence of the bulky substrate **M**; the lack of reaction of **M** indicates the heterogeneous nature of the solid catalyst of ZrDMTD-Pd (shown as an octahedral cage).

within the pores of the host net, we prepared molecule **M** (Fig. 3) as a bulky substrate of the SMR. In contrast with the above mentioned, smaller substrates which readily enter into the pores of ZrDMTD (pore opening: ~9 Å), molecule **M**, with a cross-section above 12 Å, is too bulky to penetrate the host net. In the setting of the three-phase test (mentioned above) for verifying the heterogeneous nature of the catalytic process, molecule **M** can therefore be used to serve the purpose of the third phase (the other two being the liquid solution and the MOF catalyst). In our test, molecule **M** and the small substrate 4-bromo-2-fluorobenzonitrile (bfbn) were added together to a reaction mixture containing the boronic acid reactant, the ZrDMTD-Pd catalyst solid and the solvents of EtOH/Et$_3$N. While the small bfbn molecule readily reacted to give the expected product, no reaction of **M** was observed (e.g., as monitored by TLC; see Fig. S12). Moreover, the more reactive iodo version of **M** also exhibited no reaction in a similar test (Fig. S13). Such observations strongly support the heterogeneous nature of the ZrDMTD-Pd catalyst.

To sum up, the catalytic activity observed of the ZrDMTD-Pd crystals, in contrast with the negative controls of the free ligand H$_2$DMTD/Pd(II) system and the bulky molecule **M**, highlights the dangling effect imposed by the porous host net, which turns the normally poisonous thiol groups into effective ligands as well as

robust anchors that preclude metal leaching from the solid catalyst. Besides advancing durable, truly heterogeneous catalyses, the dangling effect as embodied by the thiol-laced ZrDMTD solid opens up a versatile approach to imposing steric and electronic effects, so as to uncover novel reactivities within MOFs and other porous media (e.g., porous organic frameworks[17] and cages).

Notes and references

* Corresponding author

† These authors contributed equally to this work.

^{a} Key Laboratory of Biomedical Polymers (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China. E-mail: chengwang@whu.edu.cn

^{b} Department of Biology and Chemistry, City University of Hong Kong 83 Tat Chee Avenue, Kowloon, Hong Kong, China. E-mail: zhengtao@cityu.edu.hk.

^{c} Department of Chemistry, Youngstown State University, One University Plaza, Youngstown, OH 44555, USA

Electronic Supplementary Information (ESI) available: [Experimental procedures; network synthesis and activation; SEM photographs; elemental analysis, CO_2 sorption, TGA, IR/Raman, and PXRD data]. See DOI: 10.1039/c000000x/

1. a) C. C. Cummins, S. M. Baxter and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1988, **110**, 8731; b) M. M. Rodriguez, E. Bill, W. W. Brennessel and P. L. Holland, *Science* 2011, **334**, 780; c) J. A. Pool, E. Lobkovsky and P. J. Chirik, *Nature*, 2004, **427**, 527.
2. a) W.-Y. Gao, M. Chrzanowski and S. Ma, *Chem. Soc. Rev.*, 2014, **43**, 5841; b) C. Wang, D. Liu and W. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 13222; c) O. Shekhah, J. Liu, R. A. Fischer and C. Wöll, *Chem. Soc. Rev.*, 2011, **40**, 1081; d) D. Zhao, D. J. Timmons, D. Yuan and H.-C. Zhou, *Acc. Chem. Res.*, 2011, **44**, 123; e) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191; f) S. Kitagawa and R. Matsuda, *Coord. Chem. Rev.*, 2007, **251**, 2490; g) Z. Xu, *Coord. Chem. Rev.*, 2006, **250**, 2745; h) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273; i) O. M. Yaghi, G. M. Li and H. L. Li, *Nature*, 1995, **378**, 703; j) G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature* 1995, **374**, 792; k) L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325; l) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 5962.
3. a) M. Dincă and J. R. Long, *Angew. Chem., Int. Ed.*, 2008, **47**, 6766; b) S. Ma and H.-C. Zhou, *J. Am. Chem. Soc.*, 2006, **128**, 11734; c) S. Ma, D. Yuan, J.-S. Chang and H.-C. Zhou, *Inorg. Chem.*, 2009, **48**, 5398; d) M. Tonigold, Y. Lu, A. Mavrandonakis, A. Puls, R. Staudt, J. Moellmer, J. Sauer and D. Volkmer, *Chem. - Eur. J.*, 2011, **17**, 8671; e) B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115; f) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; g) B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559; h) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S.-i. Noro and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2684.
4. a) H. Fei, J. Shin, Y. S. Meng, M. Adelhardt, J. Sutter, K. Meyer and S. M. Cohen, *J. Am. Chem. Soc.*, 2014, **136**, 4965; b) J. Gascon, A. Corma, F. Kapteijn and F. X. Llabres i Xamena, *ACS Catal.*, 2014, **4**, 361; c) J. M. Falkowski, T. Sawano, T. Zhang, G. Tsun, Y. Chen, J. V. Lockard and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 5213; d) K. Manna, T. Zhang, M. Carboni, C. W. Abney and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 13182; e) M. A. Gotthardt, A. Beilmann, R. Schoch, J. Engelke and W. Kleist, *RSC Adv.*, 2013, **3**, 10676; f) D. T. Genna, A. G. Wong-Foy, A. J. Matzger and M. S. Sanford, *J. Am. Chem. Soc.*, 2013, **135**, 10586; g) V. Lykourinou, Y. Chen, X.-S. Wang, L. Meng, T. Hoang, L.-J. Ming, R. L. Musselman and S. Ma, *J. Am. Chem. Soc.*, 2011, **133**, 10382; h) P. Kaur, J. T. Hupp and S. T. Nguyen, *ACS Catal.*, 2011, **1**, 819; i) X. Gu, Z.-H. Lu, H.-L. Jiang, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 11822; j) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248.
5. a) T. Itoh and T. Mase, *J. Org. Chem.*, 2006, **71**, 2203; b) B. Zeysing, C. Gosch and A. Terfort, *Org. Lett.*, 2000, **2**, 1843.
6. E. Alvaro and J. F. Hartwig, *J. Am. Chem. Soc.*, 2009, **131**, 7858.
7. a) K. Koehler, W. Kleist and S. S. Proeckl, *Inorg. Chem.*, 2007, **46**, 1876; b) S. P. Andrews, A. F. Stepan, H. Tanaka, S. V. Ley and M. D. Smith, *Adv. Synth. Catal.*, 2005, **347**, 647; c) A. F. Schmidt and A. A. Kurokhtina, *Kinet. Catal.*, 2012, **53**, 714; d) J. M. Richardson and C. W. Jones, *J. Catal.*, 2007, **251**, 80; e) M. Weck and C. W. Jones, *Inorg. Chem.*, 2007, **46**, 1865; f) N. T. S. Phan, M. Van Der Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609.
8. a) J. D. Webb, S. MacQuarrie, K. McEleney and C. M. Crudden, *J. Catal.*, 2007, **252**, 97; b) I. W. Davies, L. Matty, D. L. Hughes and P. J. Reider, *J. Am. Chem. Soc.*, 2001, **123**, 10139; c) J. Rebek and F. Gavina, *J. Am. Chem. Soc.*, 1974, **96**, 7112.
9. a) T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey and N. Stock, *Inorg. Chem.*, 2009, **48**, 3057; b) T. Ahnfeldt, N. Guillou, D. Gunzelmann, I. Margiolaki, T. Loiseau, G. Férey, J. Senker and N. Stock, *Angew. Chem., Int. Ed.*, 2009, **48**, 5163; c) H. Reinsch, B. Marszalek, J. Wack, J. Senker, B. Gil and N. Stock, *Chem. Commun.*, 2012, **48**, 9486; d) H. Reinsch, M. Feyand, T. Ahnfeldt and N. Stock, *Dalton Trans.*, 2012, **41**, 4164.
10. a) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science* 2005, **309**, 2040; b) L. Hamon, C. Serre, T. Devic, T. Loiseau, F. Millange, G. Férey and G. De Weireld, *J. Am. Chem. Soc.*, 2009, **131**, 8775; c) C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Loueer and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519.
11. a) C. G. Silva, I. Luz, F. X. Llabrés i Xamena, A. Corma and H. García, *Chem.--Eur. J.*, 2010, **16**, 11133; b) M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632; c) A. Schaate, P. Roy, T. Preusse, S. J. Lohmeier, A. Godt and P. Behrens, *Chem.--Eur. J.*, 2011, **17**, 9320; d) W. Morris, C. J. Doonan and O. M. Yaghi, *Inorg. Chem.*, 2011, **50**, 6853; e) C. Wang, Z. Xie, K. E. de Krafft and W. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 13445; f) H.-L. Jiang, D. Feng, T.-F. Liu, J.-R. Li and H.-C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 14690; g) V. Guillerm, F. Ragon, M. Dan-Hardi, T. Devic, M. Vishnuvarthan, B. Campo, A. Vimont, G. Clet, Q. Yang, G. Maurin, G. Férey, A. Vittadini, S. Gross and C. Serre, *Angew. Chem., Int. Ed.*, 2012, **51**, 9188; h) C. Wang, J.-L. Wang and W. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 19895; i) M. Kim and S. M. Cohen, *CrystEngComm*, 2012, **14**, 4096; j) W. Morris, B. Volosskiy, S. Demir, F. Gandara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart and O. M. Yaghi, *Inorg. Chem.*, 2012, **51**, 6443; k) D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2012, **51**, 10307; l) V. Bon, V. Senkovskyy, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 8407.
12. J. He, C. Yang, Z. Xu, M. Zeller, A. D. Hunter and J. Lin, *J. Solid State Chem.*, 2009, **182**, 1821.
13. a) K.-K. Yee, N. Reimer, J. Liu, S.-Y. Cheng, S.-M. Yiu, J. Weber, N. Stock and Z. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 7795; b) S. Pullen, H. Fei, A. Orthaber, S. M. Cohen and S. Ott, *J. Am. Chem. Soc.*, 2013, **135**, 16997.
14. This paper was first submitted to JACS on Nov. 3, 2014. Afterwards we noted the following: *J. Am. Chem. Soc.*, 2015, **137**, 2191.
15. Crystal data for ZrDMTD: $C_{120}H_{76}O_{36}S_{12}Zr_6$, M_r = 3025.84, space group $Fm\overline{3}m$ with a = 32.7165(1) Å, V = 35018.7(3) Å^3, Z = 4, ρ_{calcd} = 0.574 gcm^{-3}, μ = 2.321 cm^{-1}, $2\theta_{max}$ = 143.02°, GOF = 1.300. A total of 25744 reflections were collected and 1751 are unique (R_{int} = 0.0302). R_1 (wR_2) = 0.0767 (0.2378) for 69 parameters and 1751 reflections [$I > 2\sigma(I)$]. CCDC 1035107 contains the crystallographic data.
16. a) J. Liu, K.-K. Yee, K. K.-W. Lo, K. Y. Zhang, W.-P. To, C.-M. Che and Z. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 2818; b) J. Jeromenok and J. Weber, *Langmuir*, 2013, **29**, 12982.
17. B. Li, Y. Zhang, D. Ma, Z. Shi and S. Ma, *Nat. Commun.*, 2014, **5**, 5537.