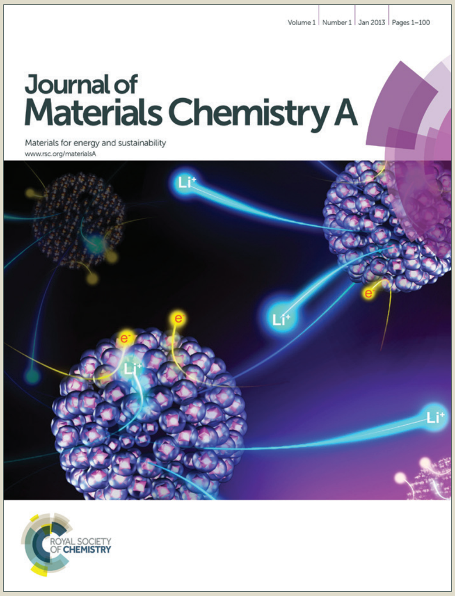
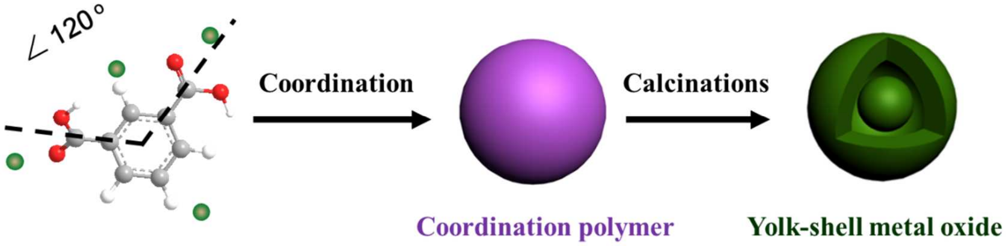
Journal of
Materials Chemistry A



ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/materialsA

Unitary and multinary metal-carboxylic acid coordination polymers (CP) were prepared by utilization of the geometric angle of carboxylic groups in organic linkers. Further calcination of these CP would generate unitary and multinary metal oxides with the yolk-shell structure.



Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

# Organic Linker Geometry Controlled Synthesis of Coordination Polymer Spheres and Their Thermal Transformation to Yolk-Shell Metal Oxides

Min Wang, Feng Wang,* Jiping Ma and Jie Xu*

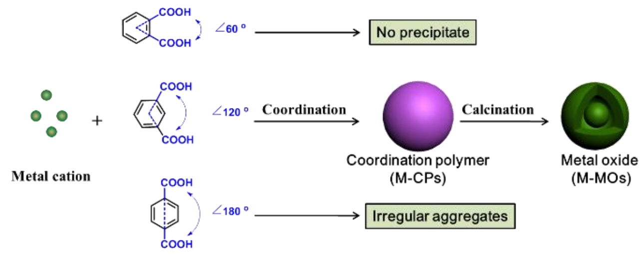
Precise control over size, morphology and composition of coordination polymers (CPs) is challenging but important for extending these hybrid materials to many more applications. Herein, we report a protocol of preparing unitary and multinary metal-carboxylic acid coordination polymers without additive. We found the CPs morphology was controlled by the geometric angle (∠) of carboxylic groups in organic linkers. At the ∠120 º, the mono-dispersed and uniform spherical CPs were obtained with the central distribution size ranging from nanoscale to microscale, adjusted by the precursor concentration and reaction time. We also obtained a series of spherical metal-CPs including transition and rare earth metal (Mg, Ni, Zn, In, Y, Sm, Eu, Gd, Er, Ho, Yb and Lu) and homogeneously distributed multinary metal-CP. Moreover, the calcination of these CPs generated unitary and multinary metal oxides with the yolk-shell structure. In addition, metal-CPs contain the coordinatively unsaturated metal sites, confirmed by probe molecule adsorption-IR spectroscopy, and could catalyze the cyanosilylation of carbonyl substrates at 25 ºC. Sixteen examples were tested with good to excellent yields over Eu-CPs.

## Introduction

Spherical materials have been of continuous research interests in material science, physics, chemistry and biology because of their unique properties shown in areas of photonics, catalysis, drug delivery and biosensors.[1,2] Considerable attention has been paid to novel synthetic strategies for mono-dispersed colloidal spheres. Organic polymers,[3] carbon[4-6] and inorganic materials[7-10] with spherical morphology have been well obtained with narrow size distribution. Coordination polymers (CPs) constitute another important class of organic-inorganic hybrid materials formed by the coordination of metal ions with organic linkers. They have shown a number of promising applications due to the diverse structure and functionalities.[11-30] Recent interests have been diverted to nano-CPs with defined morphology and size.[31, 32] Different with the organic or inorganic materials, the control of infinite growth of metal ions and linkers in a self-assembly environment to the desired morphology and size is sophisticated and time-consuming. Up to now, CPs with cube,[33] polyhedron,[34] rod,[35] plate[36] and fiber[37] morphologies have been reported. However, the convenient control of size and morphology requires more efforts.

Most of the CP inherently tend to grow into the multifaceted crystals with large particle size (larger than 1 µm). Some transform after being contacted with solvents or exposed to ambient environment.[38,39] Mirkin and coworkers have proposed a strategy based on coordination polymerization and generated spherical CPs precipitations by adding diethyl ether or pentane.[38a-d] These CPs were instable and could be dissolved in excess pyridine. The spheres could change into rods in methanol.[38c] Zeng *et al*. has prepared spherical CPs *via* anti-solvent effects and the *in situ* oxidation of diethylene glycol to provide carboxylic groups.[38e] The CPs started to decompose from 200 ºC. Moreover, the use of additives and unusual linkers would complicate the synthesis procedure. Therefore, a general strategy of preparing well-defined stable spherical CP with controllable size and chemically tailorable composition is desirable.

We herein report the synthesis of spherical CP without additive. The CP morphology was controlled by the geometric angle of carboxylic linkers (Scheme 1). Spherical CP were formed at the angle of 120º. The size of CP was tuned from nanoscale to microscale by adjusting the precursor’s concentration or solvothermal time. Moreover, a wide scope of CP, including unitary metal-CP, such as Mg, Ni, Zn, In, Y, Sm, Eu, Gd, Er, Ho, Yb and Lu, and multinary metals-CP were prepared. Metal oxides with yolk-shell structure were obtained by calcining their corresponding CP. Catalytic cyanosilylation of carbonyl substrates to silylated cyanohydrins were employed as model reaction. The coordinatively unsaturated metal sites confirmed by the probe adsorption Fourier transform infrared (FT-IR) function as catalytically active sites.



**Scheme 1** Organic linker geometry controlled synthesis and transformation to yolk-shell metal oxides.

## Experimental

### Materials

Reagents and solvents were purchased from commercial sources and used without further purification. The organic linkers 1,4-benzenedicarboxylic acid (L1), 4,4'-biphenyldicarboxylic acid (L2), *trans*-2-butenedioic acid (L3), 1,4-naphthalenedicarboxylic acid (L4), 1,3-benzene-dicarboxylic acid (L5), 5-nitro-1,3-benzenedicarboxylic acid (L6), 5-bromo-1,3-benzenedicarboxylic acid (L7) and 3,5-pyridinedicarboxylic acid (L8) were used and designated in the parenthesis.

### Preparation of M-CPs and M-MOs

In a typical synthesis of unitary M-CPs, the mixture of 0.05 mmol organic acid and 0.05 mmol M(NO$_3$)$_X$ dissolved in 20 mL N,N-dimethylmethanamide (DMF) was put in pressure bottle and then placed in an oil-bath thermally stabilized at 160 °C to trigger fast precipitation. The precipitates were recovered by centrifugation, washed with CH3CN (3 mL × 20 times), and then dried under vacuum. The concentration of the precursors (2.5-15 mM), reaction time (10-360 min) and solvothermal temperature (140-160 °C) were adjusted accordingly to tune the particle size. The multinary metal-CPs were prepared by the above-mentioned procedures using L5 as organic linker. The M-MOs were prepared by calcination of the M-CPs at 600 °C in air (30 mL min$^{-1}$) for 3 h in a horizon furnace.

### Catalytic cyanosilylation of carbonyl substrates

A 20 mL glass tube was charged with 5 mg catalyst, 0.25 mmol carbonyl substrates, 0.5 mmol trimethylsilyl cyanide and 1.5 mL dichloromethane. The mixture was magnetically stirred at room temperature (25 °C) for the desired time under Ar atmosphere. The products were analyzed by gas chromatography−mass spectrometry (GC−MS) using an Agilent 7890A/5975C instrument equipped with an HP-5 MS column (30 m in length, 0.25 mm in internal diameter). p-Xylene was used as internal standard for quantification. In the recycle experiment, the catalyst was washed with ethanol and dried before use. In a filtration test, the 2-h reaction mixture was quickly filtered through a Teflon-membrane filter to the second tube placed at the same temperature. The filtrate was further stirred for 5 h before sampling and analysis.

### Characterizations

The X-ray powder diffraction (XRD) patterns were obtained using a Rigaku D/Max 2500/PC powder diffractometer with Cu Kα radiation (λ = 0.15418 nm). Fourier transform infrared (FT-IR) spectra were collected on a Bruker Tensor 27 FT-IR spectrometer in KBr media. Fluorescence measurements were performed on a VARIAN CARY Eclipse fluorescence spectrophotometer. The thermogravimetric analysis (TGA) were carried out on a NETZSCH STA 409 PC instrument. Samples were heated at a heating rate of 10 °C min–1 from 100 °C to 800 °C in an air flow of 30 mL min–1. Sample morphologies were observed by transmission electron microscopy (TEM, JEOL JEM-2000EX) and field-emission scanning electron microscopy (FE-SEM, FEI Quanta 200F). Chemical mapping was conducted on FE-SEM (JSM-7800F).

## Results and discussion

### Synthesis of Eu-CPs

Our initial exploration of CPs synthesis started with several carboxylic acids as linkers and Eu$^{3+}$ as metal node. When the linkers and Eu(NO$_3$)$_3$ were dissolved in DMF and heated at 160 °C, the mixture gradually turned milky. A white colloid solution was formed in 30 min. TEM and SEM observations revealed the morphology of the resulting CPs depended on the geometry of the linkers. The coordination sites with the angle of ∠120° favor the formation of spherical CPs. When L1-L4 with linear coordination sites (∠180°) were used as linkers, micro-flake or rod-like aggregates were obtained (Fig. 1a-d). No spherical CPs were formed when 1, 2-benzenedicarboxylic acid and cis-2-butenedioic acid (∠60°) were used. Instead, they generated small aggregates with Eu$^{3+}$. Sub-microscale spheres were formed with the angle of ∠120° in several linkers (L5-L8, Fig. 1e-h). The kinked geometry and rigid structure of the linkers (L5-L8) make it hard crystallize but with amorphous structure, confirmed by XRD characterizations (Fig. S1). This amorphous structure facilitates the formation of spherical morphology, which is similar to the known methods involving of complex additives and linkers to make amorphous structure to obtain spherical morphology.[38] As for linkers with linear coordination sites, they are easy to crystalize, thus with multifaceted morphology instead of spheres. Furthermore, with L5 as linker, the size of the CPs could be adjusted from nanoscale to microscale by controlling the precursors' concentration. With the concentration of the precursors increasing from 2.5 mM to 15 mM, the diameter of the CPs spheres increased from 100 nm to 700 nm (Fig. 2a-f). Moreover, the particle size was tuned by solvothermal time. Along the reaction proceeded, the particle size gradually increased until the precursors were depleted. For example, at 15 mM of L5, the spherical CPs size increased from ca. 500 nm to 1 μm with reaction time increasing from 10 min to 30 min (Fig. 2d, e, g and Fig. S2).

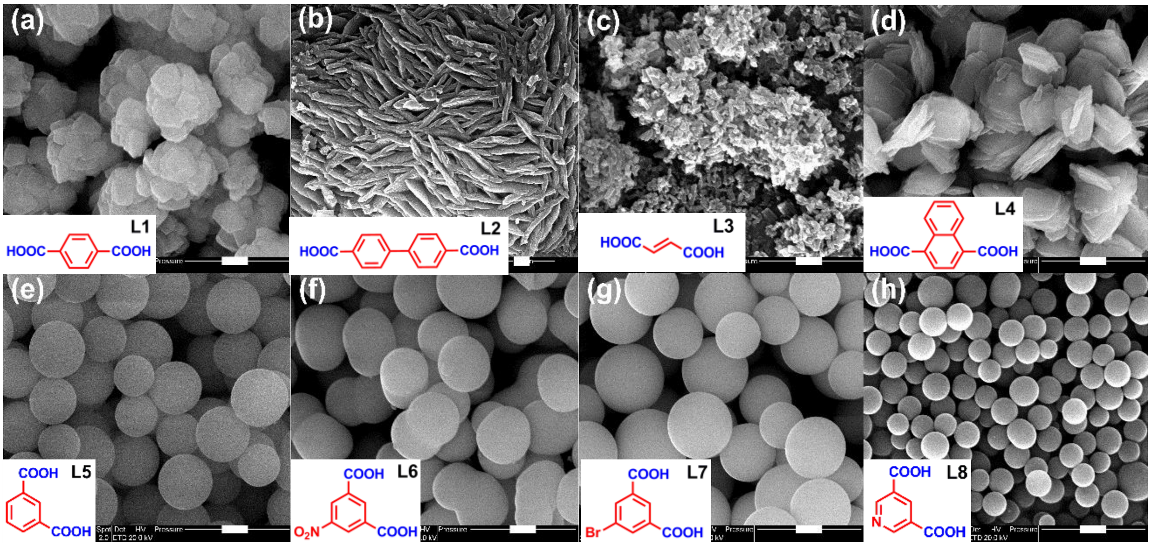


**Fig. 1**. SEM images of Eu-CPs prepared with different organic linkers. Preparation conditions: 5 mM precursors, 160 °C, 30 min. The insert images show the structure of the organic linkers. All scale bars: 500 nm.

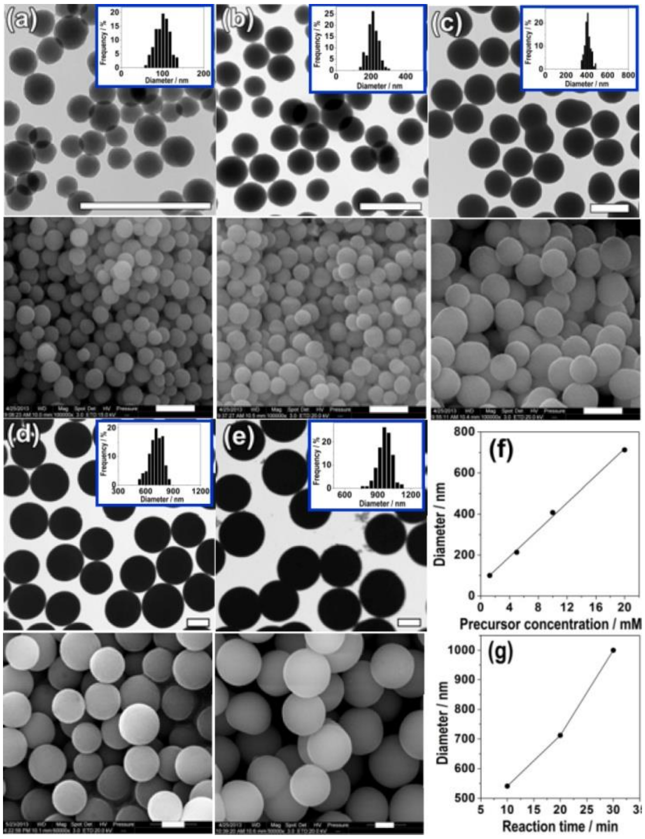


**Fig. 2**. TEM and SEM images and size-distribution diagrams of the CPs prepared at different concentration for 20 min (a) 2.5 mM, (b) 5 mM, (c) 10 mM and (d) 15 mM. (e) 15 mM, 30 min. (f) The correlations between the precursor concentration and the resulting diameter. (g) The diameter changed with reaction time. All scale bars: 500 nm.

We then studied the coordination state and stability of the Eu-CPs. FT-IR analysis showed the carboxylate groups coordinate to Eu trivalent cation, as evidenced by a 36 cm$^{-1}$ shift in C=O stretching frequency from 1694 cm$^{-1}$ for free L5 molecule to 1658 cm$^{-1}$ for Eu-CPs (Fig. S3). The wavenumber separation between asymmetrical and symmetric bands (1658-1398 cm$^{-1}$) is 260 cm$^{-1}$. This indicates the monodentate interaction between the carboxylate groups and Eu trivalent cation.[40] Change in precursor concentrations had no effect on the IR spectra, indicating their similar coordination state. As characterized by TGA, Eu-CPs were thermally stable up to 420 ℃ in air (Fig. S4), which was higher than other spherical CPs (200 °C).[38e] TGA revealed the Eu-CP did not contain much guest molecules after washing and vacuum drying, as evidenced by no substantial weight loss until 420 ℃. Based on the elemental analysis and TGA result, the molar ratio of L5 to Eu was obtained as 1.2.

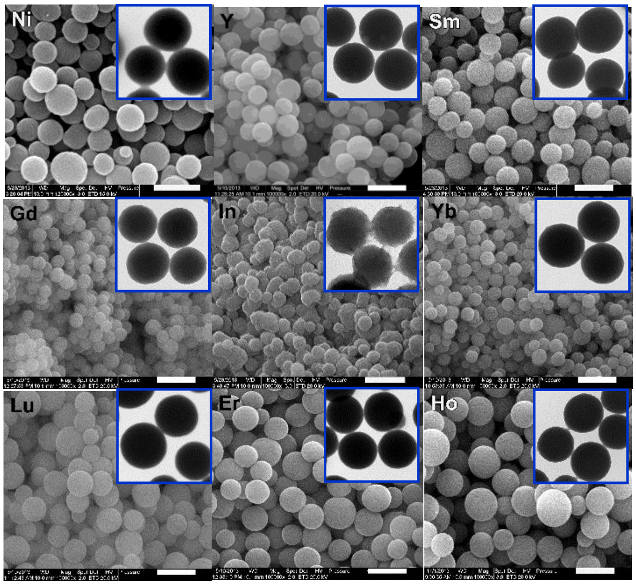


**Fig. 3.** SEM and TEM images of the M-CPs prepared with several metal cations. All scale bars: 500 nm.

Next we synthesized CP with transition metal and rare earth metal trivalent and divalent cation (Mg, Ni, Zn, In, Y, Sm, Gd, Er, Ho, Yb and Lu) using L5 linker. They had well-defined spherical morphology with narrow size distribution in nanoscale and microscale (Table S1, Fig. 3, S5 and S6).

### Synthesis of multinary complex CPs

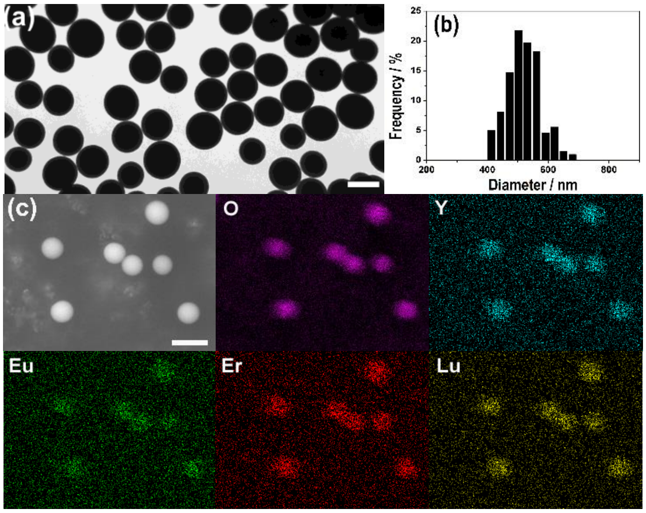


**Fig. 4.** TEM (a), size distribution (b) and Chemical mapping (c) of the quaternary YEuErLu-CPs. Scale bar: 500 nm.

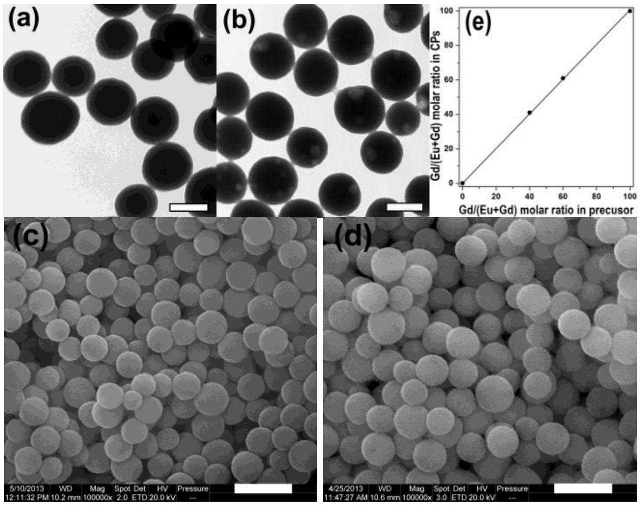


**Fig. 5** TEM and SEM images of EuGd-CPs with different molar ratio of Gd:Eu. (a,c) 4:6 and (b, d) 6:4. (e) The linear ship of Gd in CPs and in precusors. Scale bar: 500 nm.

Multinary colloidal CP spheres combining two or more kinds of metals are expected to provide unique properties.[41] In this study, we conveniently synthesized tailor-made multinary CPs by mixing multiple metal ions and L5 linker. Four metal salts, Y, Eu, Er and Lu, were used in the study. TEM images (Fig. 4) indicated the formation of uniform spherical morphology and narrow size distribution centering at 520 nm. An EDS analysis further revealed the presence of Y, Eu, Er and Lu (Fig. S7). Chemical mappings showed the four elements formed homogeneous phase. The molar ratio of each metal element in the final sphere products was tuned by the preset ratio of metal precursors. For example, in binary EuGd-CPs, EDS results showed the molar ratio of Gd in CPs could be adjusted by the amount of Gd in precursors (Fig. 5). As a result, the Gd concentration in EuGd-CPs had a linear relationship with the added Gd.

### Synthesis of yolk-shell metal oxides

Unitary or multinary metal oxide spheres were obtained by the calcination of CPs. The metal oxide retained the similar spherical morphology of CPs. The rough surface and holes was due to the decomposition of organic linkers and the shrinkage of framework (Fig. 6 and S8). TEM indicated yolk-shell structures were formed for most of metal oxides. Increase of the accelerate voltage of SEM to 10 kilovolt, electron could penetrate the shell and the yolk-shell structure became visible (Fig. 6b). The yolk-shell materials have wide applications.[42-60] Some applications require multinary yolk-shell metal oxide. However, these kinds of metal oxides are difficult to be synthesized by general ways because of the easy phase segregation to mixed oxides other than solid solution.[61] In this study, the materials were obtained by first preparing homogeneous multinary metal coordination structure and then thermally removing linkers. For the multinary metal oxide spheres, the distribution of each element was homogeneous as indicated by chemical mappings (Fig. 6d).

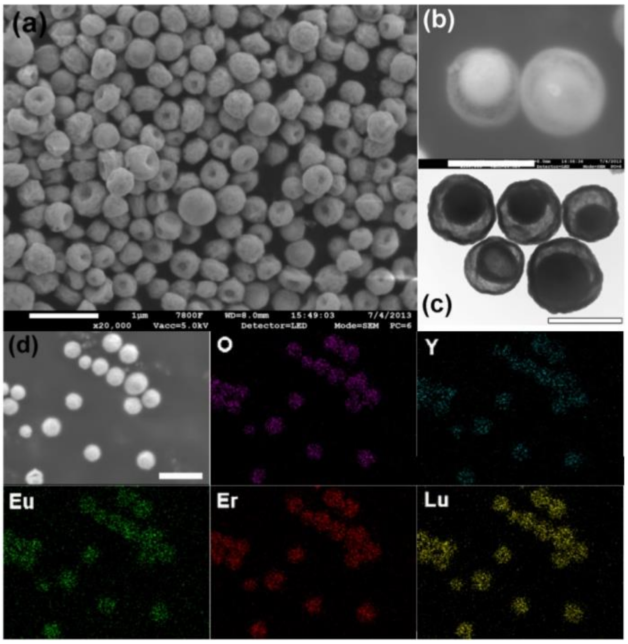


**Fig. 6** SEM images of YEuErLu-MOs with 5 kV (a) and 10 kV (b). (c) TEM image. (d) Chemical mapping. The scale bar in (a) and (d) is 1000 nm and in (b) and (c) is 500 nm.

The crystalline phase of multinary oxides could be tuned by metal molar ratio. For example, in the XRD patterns of binary SmYb-MOs (Cubic, space group: I a-3), with increasing the molar ratio of Yb to Sm, the 2θ degree of the (222) diffraction increases from 28.75° to 29.64° (Fig. S9). This indicates the homogeneous replacement of Sm by Yb in the crystalline lattice.

The increase of 2θ value infers the shrinkage of the lattice because the diameter of $Yb^{3+}$ (8.58 Å) is smaller than $Sm^{3+}$ (9.64 Å). No phase separation is observed.

### Catalysis of Eu-CPs

We studied the catalytic performance of Eu-CPs. Many known CP materials rely on post grafting or immobilization to build catalytic sites.[62] Direct use of CP framework nodes as catalytic sites are very limited, as exampled by Long and others.[63] A recent calculation by Keiji Morokuma et al. suggested the flexible coordination environment (large coordination number, such as 6-12) might exist for lanthanide trivalent cations.[64] This leads to the unique bonding character, quite different from that of transition metals, and thus may generate the coordinatively unsaturated sites, creating the open metal sites for catalysis. This calculation is confirmed in this study by using n-octanal as probe molecule. When *n*-octanal was adsorbed on Eu-CPs, the carbonyl stretching frequency red-shifted from 1726 $cm^{-1}$ to 1709 $cm^{-1}$ accompanied by the disappearance of typical C–H vibration (2820 $cm^{-1}$ and 2714 $cm^{-1}$) of aldehyde group (Fig. 7). This may infer the C=O bond is weakened due to bonding to the unsaturated Eu sites.

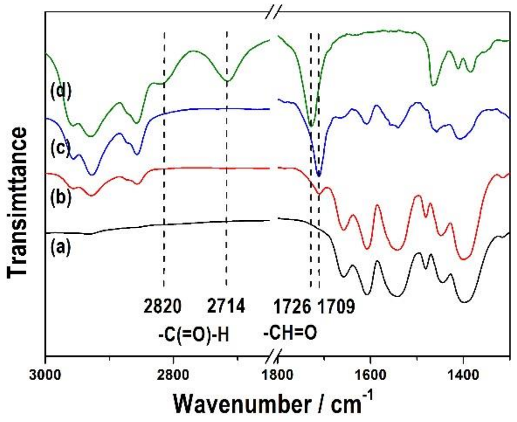
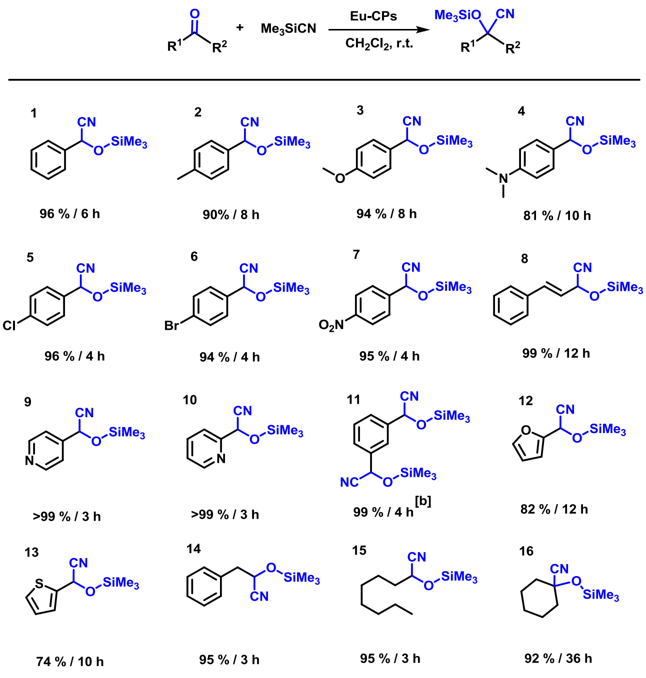


**Fig. 7** FT-IR spectra of carbonyl group interaction with open Eu sites of Eu-CPs. (a) Eu-CPs; (b) *n*-octanal adsorbed on the Eu-CPs flake; (c) using (a) as backgroud and (d) *n*-octanal.

We then tested the activity of the Eu-CPs in the cyanosilylation of benzaldehyde (Figure S10), which is one of the most efficient methods for the synthesis of silylated cyanohydrins. This reaction is almost inactive without catalyst. The catalytic activities of Eu-CPs increase with decreasing the size of Eu-CPs particle. The highest activity with 96% yield at 6 h was achieved over the Eu-CPs with a diameter of 100 nm. When the size increased to 400 nm, the reaction slowed down with 80% yield at 6 h. The microscale Eu-CPs with diameter of 1000 nm showed the lowest activity with 20 % yield at 7 h. The results may be due to the difference in surface area, *i.e.*, the smaller Eu-CPs with more accessible outer surface, easier for the substrate/product diffusion to-and-from the active sites.

The stability and reusability of the Eu-CP was tested. Eu-CP were stable under reaction conditions and could be reused at least three times without obvious loss of activity (Fig. S11). The removal of Eu-CPs by filtration after 2 h completely stopped the reaction, affording only 41% yield upon further 5 h reaction (Fig. S10). Because Eu ion has fluorescence, this property can be used to check the leaching of Eu ion after reaction. No fluorescence in the filtrate was observed, indicating the concentration of Eu ion in the filtrate was below the detection limits (Fig. S12). All the above results indicate the catalyst was heterogeneous in nature.

**Table 1** The cyanosilylation of carbonyl substrates by Eu-CPs with diameter of 100 nm.[a]



[a] Reaction conditions: 5 mg catalyst, 0.25 mmol substrates, 0.5 mmol $Me_3SiCN$, 1.5 mL $CH_2Cl_2$, room temperature, under Ar. Results were showed as yield/reaction time. [b] 1 mmol $Me_3SiCN$.

A wide range of carbonyl substrates was converted to the corresponding silylated cyanohydrins with good to excellent yields with the nanosized Eu-CPs at r.t. (25 °C) (Table 1). Substituted benzaldehydes with electron-withdrawing groups were more reactive than those containing electron-donating groups (Table 1, entries 1-7). The decrease of electron density of the carbon atom in carbonyl groups by electron-withdrawing groups facilitates the nucleophilic reaction. The olefin C=C double bond is not affected in the case of cinnamaldehyde (Table 1, entry 8). Pyridinecarboxaldehyde was converted to silylated cyanohydrin with 99% yield (Table 1, entries 9 and 10). Isophthalaldehyde with two aldehyde groups gave 99% yield in 4 h (Table 1, entry 11). Reactions with heterocyclic compounds, such as furfural and 2-thenaldehyde, gave 82% conversion at 12 h and 74% conversion at 10 h, respectively (Table 1, entries 12 and 13). Aliphatic aldehydes were more reactive than aromatic aldehydes. Yields of 95% were achieved at 3 h for both *n*-octanal and phenylacetaldehyde (Table 1, entries 14 and 15). Ketones, like cyclohexanone, were smoothly converted with high conversions at extended reaction time (Table 1, entry 16).

## Conclusions

We have shown the geometry of carboxylic acid groups in organic linker determines the morphology of final CP material. Spherical unitary and multinary CP were obtained at the geometric angle of 120°. In addition, the yolk-shell metal oxides were prepared by further calcination of the corresponding CP precursor. The crystalline phase of multinary oxides was homogenous. We believe the present strategy may open a new avenue of controlling the CP morphology and preparing the yolk-shell metal oxides. The conclusions section should come at the end of article, before the acknowledgements.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (21303183, 21273231, 21233008), and Hundred Person Project of the Chinese Academy of Sciences.

## Notes and references

a Dalian National Laboratory for Clean Energy, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 (China).

Electronic Supplementary Information (ESI) available: Materials preparation parameters and characterizations by FT-IR, XRD, TGA, fluorescence spectrometry, and electron microscopy and photos. GC-MS spectra of reactions. See DOI: 10.1039/b000000x/B.

1. F. Li, D. P. Josephson, A. Stein, *Angew. Chem. Int. Ed.* 2011, ***50***, 360.
2. U. Jeong, Y. L. Wang, M. Ibisate, Y. N. Xia, *Adv. Funct. Mater.* 2005, ***15***, 1907.
3. Z. C. Sun, F. Bai, H. M. Wu, S. K. Schmitt, D. M. Boye, H. Y. Fan, *J. Am. Chem. Soc.* 2009, ***131***, 13594.
4. J. Liu, S. Z. Qiao, H. Liu, J. Chen, A. Orpe, D. Y. Zhao, G. Q. Lu, *Angew. Chem. Int. Ed.* 2011, ***50***, 5947.
5. Y. Fang, D. Gu, Y. Zou, Z. X. Wu, F. Y. Li, R. C. Che, Y. H. Deng, B. Tu, D. Y. Zhao, *Angew. Chem. Int. Ed.* 2010, ***49***, 7987.
6. X. M. Sun, Y. D. Li, *Angew. Chem. Int. Ed.* 2004, ***43***, 597.
7. C. Urata, H. Yamada, R. Wakabayashi, Y. Aoyama, S. Hirosawa, S. Arai, S. Takeoka, Y. Yamauchi, K. Kuroda, *J. Am. Chem. Soc.* 2011, ***133***, 8102.
8. Y. S. Lin, N. Abadeer, K. R. Hurley, C. L. Haynes, *J. Am. Chem. Soc.* 2011, ***133***, 20444.
9. V. Polshettiwar, D. Cha, X. X. Zhang, J. M. Basset, *Angew. Chem. Int. Ed.* 2010, *49*, 9652.
10. M. Wang, C. Chen, J. P. Ma, J. Xu, *J. Mater. Chem.* 2011, ***21***, 6962.
11. Z. Wang, G. Chen, K. L. Ding, *Chem. Rev.* 2009, ***109***, 322.
12. M. S. Wang, S. P. Guo, Y. Li, L. Z. Cai, J. P. Zou, G. Xu, W. W. Zhou, F. K. Zheng, G. C. Guo, *J. Am. Chem. Soc.* 2009, ***131***, 13572.
13. N. Stock, S. Biswas, *Chem. Rev.* 2012, ***112***, 933.
14. A. Dhakshinamoorthy, H. Garcia, *Chem. Soc. Rev.* 2012, ***41***, 5262.
15. Y. Cui, Y. Yue, G. Qian, B. Chen, *Chem. Rev.* 2012, ***112***, 1126.
16. L. J. Murray, M. Dincă, J. R. Long, *Chem. Soc. Rev.* 2009, *38*, 1294.
17. C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp, R. Q. Snurr, *Nat. Chem.* 2012, ***4***, 83.
18. D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Ed.* 2009, *48*, 7502.
19. A. U. Czaja, N. Trukhan, U. Müller, *Chem. Soc. Rev.* 2009, ***38***, 1284.
20. J. Canivet, S. Aguado, Y. Schuurman, D. Farrusseng, *J. Am. Chem. Soc.* 2013, ***135***, 4195.
21. J. M. Roberts, B. M. Fini, A. A. Sarjeant, O. K. Farha, J. T. Hupp, K. A. Scheidt, *J. Am. Chem. Soc.* 2012, ***134***, 3334.
22. C. Wang, J. L. Wang, W. B. Lin, *J. Am. Chem. Soc.* 2012, ***134***, 19895.
23. H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* 2013, ***341***, 974.
24. A. Carné, C. Carbonell, I. Imaz, D. Maspoch, *Chem. Soc. Rev.* 2011, ***40***, 291.
25. A. M. Spokoyny, D. Kim, A. Sumrein, C. A. Mirkin, *Chem. Soc. Rev.* 2009, ***38***, 1218.
26. K. Sumida, D. Stuck, L. Mino, J. D. Chai, E. D. Bloch, O. Zavorotynska, L. J. Murray, M. Dinca, S. Chavan, S. Bordiga, M. Head-Gordon, J. R. Long, *J. Am. Chem. Soc.* 2013, ***135***, 1083.
27. X. T. Rao, T. Song, J. K. Gao, Y. J. Cui, Y. Yang, C. D. Wu, B. L. Chen, G. D. Qian, *J. Am. Chem. Soc.* 2013, ***135***, 15559.
28. D. W. Feng, W. C. Chung, Z. W. Wei, Z. Y. Gu, H. L. Jiang, Y. P. Chen, D. J. Darensbourg, H. C. Zhou, *J. Am. Chem. Soc.* 2013, ***135***, 17105.
29. C. Y. Sun, X. L. Wang, X. Zhang, C. Qin, P. Li, Z. M. Su, D. X. Zhu, G. G. Shan, K. Z. Shao, H. Wu, J. Li, *Nat. Commun.* 2013, ***4***, 2717.
30. H. Chevreau, T. Devic, F. Salles, G. Maurin, N. Stock, C. Serre, *Angew. Chem. Int. Ed.* 2013, ***52***, 5056.
31. Y. S. Bae, C. Y. Lee, K. C. Kim, O. K. Farha, P. Nickias, J. T. Hupp, S. T. Nguyen, R. Q. Snurr, *Angew. Chem. Int. Ed.* 2012, ***51***, 1857.
32. N. Planas, A. L. Dzubak, R. Poloni, L. C. Lin, A. McManus, T. M. McDonald, J. B. Neaton, J. R. Long, B. Smit, L. Gagliardi, *J. Am. Chem. Soc.* 2013, ***135***, 7402.
33. (a) M. Pang, A. J. Cairns, Y. Liu, Y. Belmabkhout, H. C. Zeng, M. Eddaoudi, *J. Am. Chem. Soc.* 2012, ***134***, 13176. (b) Y. Furukawa, T. Ishiwata, K. Sugikawa, K. Kokado, K. Sada, *Angew. Chem. Int. Ed.* 2012, ***51***, 10566. (c) Y. Pan, D. Heryadi, F. Zhou, L. Zhao, G. Lestari, H. Su, Z. Lai, *CrystEngComm* 2011, ***13***, 6937. (d) M. L. Pang, A. J. Cairns, Y. L. Liu, Y. Belmabkhout, H. C. Zeng, M. Eddaoudi, *J. Am. Chem. Soc.* 2013, ***135***, 10234. (e) Z. Ni, R. I. Masel, *J. Am. Chem. Soc.* 2006, ***128***, 12394.
34. (a) H. L. Guo, Y. Z. Zhu, S. Wang, S. Q. Su, L. Zhou, H. J. Zhang, *Chem. Mater.* 2012, ***24***, 444; (b) L. H. Wee, M. R. Lohe, N. Janssens, S. Kaskel, J. A. Martens, *J. Mater. Chem.* 2012, *22*, 13742; (c) A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke, P. Behrens, *Chem. Eur. J.* 2011, ***17***, 6643; (d) A. Umemura, S. P. Diring, S. Furukawa, H. Uehara, T. Tsuruoka, S. Kitagawa, *J. Am. Chem. Soc.* 2011, ***133***, 15506; (e) J. Cravillon, R. Nayuk, S. Springer, A. Feldhoff, K. Huber, M. Wiebcke, *Chem. Mater.* 2011, ***23***, 2130; (f) B. Seoane, J. M. Zamaro, C. Tellez, J. Coronas, *CrystEngComm* 2012, ***14***, 3103; (g) M. Sindoro, A. Y. Jee, S. Granick, *Chem. Commun.* 2013, ***49***, 9576.
35. (a) M. H. Pham, T. Vuong, A. T. Vu, T. O. Do, *Langmuir* 2011, ***27***, 15261; (b) W. Cho, S. Park, M. Oh, *Chem. Commun.* 2011, ***47***, 4138; (c) K. M. L. Taylor, W. J. Rieter, W. Lin, *J. Am. Chem. Soc.* 2008, ***130***, 14358; (d) K. M. L. Taylor, A. Jin, W. Lin, *Angew. Chem. Int. Ed.* 2008, ***47***, 7722; (e) T. Chalati, P. Horcajada, R. Gref, P. Couvreur, C. Serre, *J. Mater. Chem.* 2011, ***21***, 2220; (f) W. Cho, H. J. Lee, M. Oh, *J. Am. Chem. Soc.* 2008, ***130***, 16943; (g) W. J. Rieter, K. M. L. Taylor, H. An, W. Lin, W. Lin, *J. Am. Chem. Soc.* 2006, ***128***, 9024.
36. (a) H. Xu, X. T. Rao, J. K. Gao, J. C. Yu, Z. Q. Wang, Z. S. Dou, Y. J. Cui, Y. Yang, B. L. Chen, G. D. Qian, *Chem. Commun.* 2012, ***48***,

7377; (b) X. J. Zhang, M. A. Ballem, Z. J. Hu, P. Bergman, K. Uvdal, *Angew. Chem. Int. Ed.* 2011, ***50***, 5729; (c) X. J. Zhang, M. A. Ballem, M. Ahren, A. Suska, P. Bergman, K. Uvdal, *J. Am. Chem. Soc.* 2010, ***132***, 10391; (d) I. Boldog, A. B. Gaspar, V. Martinez, P. Pardo-Ibanez, V. Ksenofontov, A. Bhattacharjee, P. Gutlich, J. A. Real, *Angew. Chem. Int. Ed.* 2008, ***47***, 6433; (e) K. E. Dekrafft, Z. G. Xie, G. H. Cao, S. Tran, L. Q. Ma, O. Z. Zhou, W. B. Lin, *Angew. Chem. Int. Ed.* 2009, ***48***, 9901.

37. (a) S. Y. Zhang, S. J. Yang, J. B. Lan, Y. R. Tang, Y. Xue, J. S. You, *J. Am. Chem. Soc.* 2009, ***131***, 1689; (b) J. Puigmarti-Luis, M. Rubio-Martinez, U. Hartfelder, I. Imaz, D. Maspoch, P. S. Dittrich, *J. Am. Chem. Soc.* 2011, ***133***, 4216; (c) I. Imaz, M. Rubio-Martinez, W. J. Saletra, D. B. Amabilino, D. Maspoch, *J. Am. Chem. Soc.* 2009, ***131***, 18222.
38. Carboxylate based spherical CPs. (a) M. Oh, C. A. Mirkin, *Nature* 2005, ***438***, 651; (b) I. Imaz, D. Maspoch, M. Oh, C. A. Mirkin, *Angew. Chem. Int. Ed*. 2006, ***45***, 5492; (c) Y. M. Jeon, J. Heo, C. A. Mirkin, *J. Am. Chem. Soc.* 2007, ***129***, 7480; (d) Y. M. Jeon, G. S. Armatas, J. Heo, M. G. Kanatzidis, C. A. Mirkin, *Adv. Mater*. 2008, ***20***, 2105; (e) C. C. Li, H. C. Zeng, *J. Am. Chem. Soc*. 2012, ***134***, 19084.
39. Nitrogen containing linker based spherical CPs. (a) G. D. Liang, J. T. Xu, X. S. Wang, *J. Am. Chem. Soc.* 2009, ***131***, 5378; (b) X. Sun, S. Dong, E. Wang, *J. Am. Chem. Soc.* 2005, ***127***, 13102; (c) C. Rodriguez-Blanco, J. M. Perez-Falcon, J. Campo, D. Ruiz-Molina, *Angew. Chem. Int. Ed.* 2008, ***47***, 1857; (d) N. R. Champness, *Angew. Chem. Int. Ed.* 2009, ***48***, 2274; (e) I. Imaz, J. Hernando, D. Ruiz-Molina, D. Maspoch, *Angew. Chem. Int. Ed*. 2009, ***48***, 2325.
40. M. Taguchi, S. Takami, T. Naka, T. Adschiri, *Cryst. Growth Des*. 2009, ***9***, 5297.
41. L. J. Zhou, Z. J. Gu, X. X. Liu, W. Y. Yin, G. Tian, L. Yan, S. Jin, W. L. Ren, G. M. Xing, W. Li, X. L. Chang, Z. B. Hu, Y. L. Zhao, *J. Mater. Chem.* 2012, ***22***, 966.
42. J. Liu, S. Z. Qiao, J. S. Chen, X. W. Lou, X. R. Xing, G. Q. Lu, *Chem. Commun.* 2011, *47*, 12578.
43. A. Guerrero-Martinez, J. Perez-Juste, L. M. Liz-Marzan, *Adv. Mater*. 2010, ***22***, 1182.
44. W. Li, J. P. Yang, Z. X. Wu, J. X. Wang, B. Li, S. S. Feng, Y. H. Deng, F. Zhang, D. Y. Zhao, *J. Am. Chem. Soc*. 2012, ***134***, 11864.
45. X. J. Wu, D. S. Xu, *Adv. Mater.* 2010, ***22***, 1516.
46. P. M. Arnal, M. Comotti, F. Schuth, *Angew. Chem. Int. Ed.* 2006, ***45***, 8224.
47. X. L. Liang, J. Li, J. B. Joo, A. Gutierrez, A. Tillekaratne, I. Lee, Y. D. Yin, F. Zaera, *Angew. Chem. Int. Ed*. 2012, ***51***, 8034.
48. S. Wu, J. Dzubiella, J. Kaiser, M. Drechsler, X. H. Guo, M. Ballauff, Y. Lu, *Angew. Chem. Int. Ed.* 2012, ***51***, 2229.
49. W. Li, Y. H. Deng, Z. X. Wu, X. F. Qian, J. P. Yang, Y. Wang, D. Gu, F. Zhang, B. Tu, D. Y. Zhao, *J. Am. Chem. Soc.* 2011, ***133***, 15830.
50. R. Liu, S. M. Mahurin, C. Li, R. R. Unocic, J. C. Idrobo, H. J. Gao, S. J. Pennycook, S. Dai, *Angew. Chem. Int. Ed.* 2011, ***50***, 6799.
51. I. Lee, J. B. Joo, Y. D. Yin, F. Zaera, *Angew. Chem. Int. Ed.* 2011, ***50***, 10208.
52. J. Liu, S. Z. Qiao, S. B. Hartono, G. Q. Lu, *Angew. Chem. Int. Ed*. 2010, ***49***, 4981.
53. X. J. Wu, D. S. Xu, *J. Am. Chem. Soc.* 2009, ***131***, 2774.
54. J. Lee, J. C. Park, H. Song, *Adv. Mater.* 2008, ***20***, 1523.
55. Z. F. Bian, J. Zhu, J. G. Wang, S. X. Xiao, C. Nuckolls, H. X. Li, *J. Am. Chem. Soc.* 2012, ***134***, 2325.
56. C. H. Kuo, Y. Tang, L. Y. Chou, B. T. Sneed, C. N. Brodsky, Z. P. Zhao, C. K. Tsung, *J. Am. Chem. Soc.* 2012, ***134***, 14345.
57. Y. J. Hong, M. Y. Son, Y. C. Kang, *Adv. Mater*. 2013, ***25***, 2279.
58. J. Liu, H. Xia, D. F. Xue, L. Lu, *J. Am. Chem. Soc.* 2009, ***131***, 12086.
59. M. Wang, J. P. Ma, C. Chen, F. Lu, Z. T. Du, J. Y. Cai, J. Xu, *Chem. Commun.* 2012, ***48***, 10404.
60. S. Shi, M. Wang, C. Chen, J. Gao, H. Ma, J. P. Ma, J. Xu, *Chem. Commun.* 2013, ***49***, 9591.
61. R. Si, Y. W. Zhang, L. M. Wang, S. J. Li, B. X. Lin, W. S. Chu, Z. Y. Wu, C. H. Yan, *J. Phys. Chem. C* 2007, ***111***, 787.
62. (a) D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Ed.* 2009, *48*, 7502; (b) A. Dhakshinamoorthy, H. Garcia, *Chem. Soc. Rev.* 2012, ***41***, 5262; (c) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* 2009, ***38***, 1450; (d) T. H. Park, A. J. Hickman, K. Koh, S. Martin, A. G. Wong-Foy, M. S. Sanford, A. J. Matzger, *J. Am. Chem. Soc.* 2011, ***133***, 20138; (e) M. H. Alkordi, Y. L. Liu, R. W. Larsen, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc*. 2008, ***130***, 12639; (f) N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dybtsev, V. P. Fedin, O. A. Kholdeeva, *J. Catal.* 2008, ***257***, 315; (g) A. G. Hu, H. L. Ngo, W. B. Lin, *J. Am. Chem. Soc.* 2003, ***125***, 11490; (h) C. D. Wu, A. Hu, L. Zhang, W. B. Lin, *J. Am. Chem. Soc*. 2005, ***127***, 8940; (i) L. Alaerts, E. Seguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs, D. E. De Vos, *Chem. Eur. J.* 2006, *12*, 7353; (k) Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Ferey, *Angew. Chem. Int. Ed.*, 2008, ***47***, 4144.
63. (a) S. Horike, M. Dinca, K. Tamaki, J. R. Long, *J. Am. Chem. Soc.* 2008, ***130***, 5854; (b) R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong, Q. Xu, *J. Am. Chem. Soc.* 2007, ***129***, 8402; (c) R. Saha, B. Joarder, A. S. Roy, S. M. Islam, S. Kumar, *Chem. Eur. J.* 2013, ***19***, 16607; (d) A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Adv. Synth. Catal.* 2010, ***352***, 3022.
64. M. Hatanaka, K. Morokuma, *J. Am. Chem. Soc*. 2009, ***135***, 13972.