

# ChemComm

Accepted Manuscript



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.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

## COMMUNICATION

## A copper(I)/copper(II)-salen coordination polymer as a bimetallic catalyst for three-component strecker reactions and degradation of organic dyes

Yun-Long Hou, Raymond Wai-Yin Sun, Xiao-Ping Zhou, Jun-Hao Wang and Dan Li\*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A copper(I)/copper(II)-salen coordination polymer prepared by solvothermal reactions shows prominent bimetallic catalytic activities towards three-component strecker reactions and photodegradation of organic dyes under visible-light illumination.

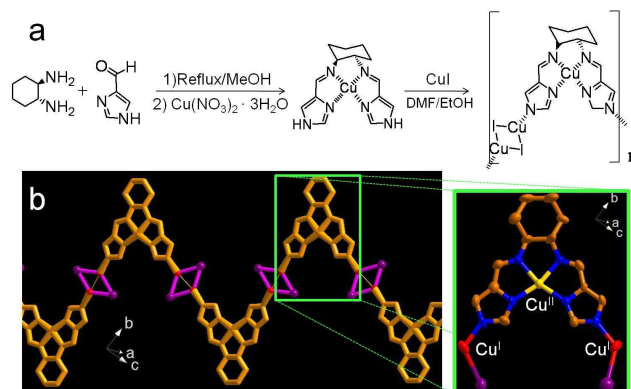
Inspired by the fact that several multi-functional enzymes contain multiple metal-based catalytic units,<sup>1</sup> worldwide efforts have been made to employ different materials as novel classes of bi-/multi-metallic<sup>2</sup> and multi-functional catalysts.<sup>3</sup> Metal-organic frameworks (MOFs), a subcategory of coordination polymers (CPs) having structural flexibility to bear more than one catalytic units resulting from the huge variations of metal nodes and organic linkers,<sup>4</sup> have recently been demonstrated to achieve bifunctional catalytic activities.<sup>5</sup> For instances, some site-isolated Lewis acid-Brønsted base MOFs have been employed in aldol-condensations,<sup>5a</sup> Knoevenagel reactions<sup>5b</sup> and one-pot tandem reactions,<sup>5c-e</sup> with coordinatively unsaturated metal sites (CUSs)<sup>4b,6</sup> and organic ligands served as acidic and basic catalytic sites, respectively. Moreover, various MOFs/CPs are insoluble and stable in common organic solvents or aqueous solutions. These intrinsic properties thus render MOFs/CPs to be potentially used as green heterogeneous catalysts which could readily be reused. Nevertheless, preparation of bimetallic MOFs/CPs via integration of one type of CUSs with another type of metal-based catalytic moiety remains a formidable challenge.<sup>7</sup> Limited examples include a bimetallic heterogeneous catalyst palladium(II)-copper(II) MOF which could be synthesized via post-synthetic modification (PSM)<sup>8</sup> with potent catalytic activity in a multi-component reaction.<sup>7a</sup> The reported PSM approach in preparing MOFs, however is sometimes limited by its sophisticated modification steps, as well as their chemical and physical instabilities of the intermediates/products.<sup>8</sup>

Metalloligands have been widely employed as linkers for the

Department of Chemistry and Research Institute for Biomedical and Advanced Materials, Shantou University, Guangdong 515063, P. R. China.

E-mail: dli@stu.edu.cn; Tel: +86-754-86502741

†Electronic supplementary information (ESI) available: Synthesis and characterizations of **1**, experiment details for catalysis and dye degradation reactions, and other physical measurements. For ESI and crystallographic data in CIF (CCDC 966731) see DOI: 10.1039/b000000x/.



**Fig. 1** (a) Schematic drawing of solvothermal synthesis of **1** from  $\text{Cu}^{\text{II}}(\text{SalImCy})$  and  $\text{Cu}^{\text{I}}$ . (b) A representative zigzag chain and the asymmetric unit of **1** viewed along the *a*-axis.

preparation of MOFs/CPs,<sup>9</sup> since these ligands could feature in straightforward immobilization of CUSs under solvothermal synthesis.<sup>6,9c-e</sup> A notable example of metalloligands is metallosalen, and the reported metallosalen-based MOF catalysts usually contain single CUS.<sup>4b,10</sup> With the ease in structural modification, metallosalens indeed could be readily tuned to display a wide range of catalytic activity towards a number of organic transformations.

In literature, several  $\text{Cu}_2\text{I}_2$  clusters have shown prominent catalytic activity in a multi-component reaction.<sup>11</sup> Moreover, various copper(I)-based CPs including these copper(I) clusters which may have potential to be used as effective heterogeneous catalysts have been structurally characterized and reviewed by others<sup>12</sup> and us.<sup>13</sup> As a continuous effort in exploring the catalytic applications of different kinds of polymeric materials,<sup>3</sup> we aim to design a novel bimetallic CP which could present multi-functional catalytic activities by combining catalytic active units copper(I) and metallosalens. In this work, we develop a straightforward solvothermal approach for the preparation of a bimetallic CP,  $\{[\text{Cu}^{\text{II}}(\text{SalImCy})][\text{Cu}^{\text{I}}\text{I}_2\cdot\text{DMF}]\}_n$  (**1**, wherein  $\text{SalImCy} = N,N'$ -bis-[(imidazol-4-yl)methylene]cyclohexane-1,2-diamine), Fig. 1a), which contains copper(II)-salen-based catalysts  $\text{Cu}^{\text{II}}(\text{SalImCy})$  and copper(I) iodide clusters. Its bimetallic catalytic activities toward three-component coupling reactions and visible-light driven degradation of organic dyes have been examined.

The copper(II)-salen ligand  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$  was prepared by a one-pot reaction of situ-formed SalHImCy with

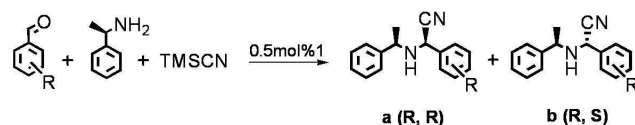
$\text{Cu}^{\text{II}}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in a molar ratio of 1:1 (see Electronic Supporting Information, ESI†). This ligand exhibits good solubility (>10 mg/mL) in dimethylformamide (DMF),  $\text{CH}_3\text{CN}$  and  $\text{C}_2\text{H}_5\text{OH}$  and is stable in air at 298 K, which in turn could be used as a precursor for subsequent solvothermal reactions.

CP **1** in the form of red cuboid-like crystals was obtained by a solvothermal reaction of  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$  with  $\text{Cu}^{\text{I}}$  in a molar ratio of 1:2 in a DMF/ $\text{C}_2\text{H}_5\text{OH}$  mixture (v/v, 2:1) for 24 h (Fig. 1a). It has been formulated and characterized on the basis of elemental analysis, IR, thermogravimetric and single-crystal X-ray diffraction analyses. The experimental details are given in ESI† (Table S1 & Fig. S1). CP **1** can be readily prepared by either one of the four different forms of the 1,2-cyclohexanediamine (i.e., 1S, 2S (+)-1,2-cyclohexanediamine); while all of them render **1** to form crystal lattices in the triclinic centro-symmetric *P*-1 space group (Table S1, ESI†). The phase purity of the bulk sample has been established by comparing its observed and simulated powder X-ray diffraction (PXRD) patterns (Fig. S2, ESI†). CP **1** is found to be highly stable in air as well as in solvent including  $\text{H}_2\text{O}$ , DMF,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{CN}$  at 298 K.

Single-crystal X-ray diffraction analysis reveals that prominent structural features of **1** include the square-planar 4-coordinate  $\text{Cu}^{\text{II}}$  in the metallosalen units (Fig. 1b, yellow) and the 3-coordinate  $\text{Cu}^{\text{I}}$  in the rhomboid  $\text{Cu}_2\text{I}_2$  clusters (Fig. 1b, purple). The  $\text{Cu}^{\text{II}}$  ion which embraces CUS is chelated by two imines [ $\text{Cu}^{\text{II}}-\text{N}_{\text{imine}}$ , 1.9571(12)–1.9613(14) Å] and two imidazols [ $\text{Cu}^{\text{II}}-\text{N}_{\text{imidazol}}$ , 1.9630(13)–1.9631(13) Å] (Fig. 1b). The copper(II)-salen linker, with an angle of 112.5° between two deprotonated imidazol N atoms, is bridged by two  $\text{Cu}_2\text{I}_2$  nodes to form a zigzag chain along the *a*-axis. Along the *b*-axis, 1D zigzag chains stack with each other to form tubular channels which could be used to trap DMF molecules (Fig. S3, ESI†).

Given that various metallosalens and  $\text{Cu}^{\text{I}}$  have demonstrated potent catalytic activities on three-component strecker reactions,<sup>11,14</sup> we first examined the catalytic activity of **1** on this reaction using aldehyde, trimethylsilyl cyanide and asymmetric amine as substrates. For instance, the reaction was carried out by mixing benzaldehyde, (*R*)-(+)-1-phenylethylamine and trimethylsilyl cyanide (TMSCN) in the presence of **1** at 0.5 mol% in  $\text{CD}_3\text{CN}$  at 283 K for 1 h. Two  $\alpha$ -aminonitriles (*R,R*)-(+)- $\alpha$ -phenyl- $\alpha$ -[(1-phenylethyl)amino]-acetonitrile and (*R,S*)-(+)- $\alpha$ -phenyl- $\alpha$ -[(1-phenylethyl)amino]-acetonitrile are the reaction products and were found in the mixture with a 99% yield as determined by <sup>1</sup>H-NMR spectrometry (Table 1, entry 1). The turnover frequency (TOF) of **1** was found to be 198 h<sup>-1</sup>. Apart from benzaldehyde, four other aromatic aldehydes have also been employed as substrates in the **1**-catalyzed strecker reaction. Similarly to that of **1**, up to 99% conversion yields can be obtained by using aromatic aldehydes substituted with a 4-methyl (entry 2) or 4-*tert*-butyl (entry 3) group. Increasing the bulkiness such as using 3,5-di-*tert*-butyl (entry 4) or 4-phenyl (entry 5) substitution may result in slightly changing the percentage yields of  $\alpha$ -aminonitriles from 99% to 93% and 86%, respectively. The effect on the change of reaction temperature from 283 K to 273 K (Table S2, ESI†) and 298 K (Table S3, ESI†) has also been examined. We found that these temperature changes did not significantly affect the catalytic activities of **1** in the strecker

**Table 1** Asymmetric three-component strecker reaction catalyzed by **1**<sup>a</sup>



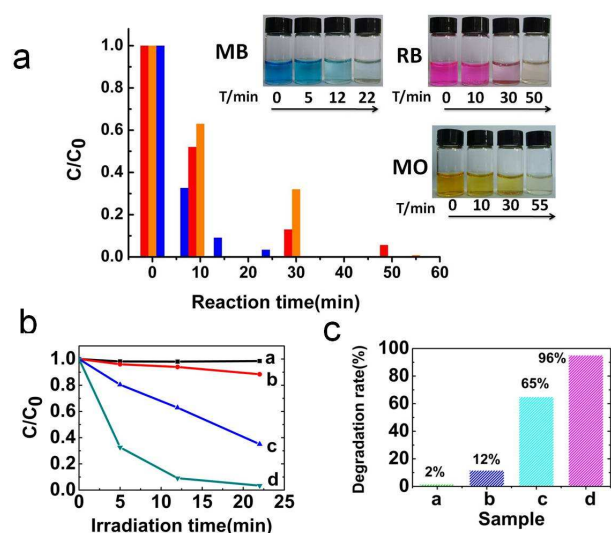
Entry	substrate (R)	t (h) <sup>b</sup>	Yield (%) <sup>c</sup>	a:b <sup>d</sup>	TOF (h <sup>-1</sup> ) <sup>e</sup>
1	H	1	99	67:33	198
2	4-methyl	2	99	68:32	99
3	4- <i>tert</i> -butyl	2	99	70:30	99
4	3,5-di- <i>tert</i> -butyl	2	93	71:29	92
5	4-phenyl	3	86	67:33	60
6	H	1	99 <sup>f</sup>	67:33	198
7	H	1	95 <sup>g</sup>	66:34	191

<sup>a</sup>Aromatic aldehydes (1 mmol), (*R*)-(+)-1-phenylethylamine (1 mmol), TMSCN (1.5 mmol) and  $\text{CD}_3\text{CN}$  (2 mL), **1** (0.5 mol%), sealed in a screw-cap vial were stirred at 283 K. <sup>b</sup>Reaction time t, hour. <sup>c</sup>% yields were determined by GC. <sup>d</sup>Diastereoselectivity were determined by H-NMR. <sup>e</sup>TOF = turnover frequency (moles of reactants converted per moles of active sites unit time), h<sup>-1</sup>. <sup>f</sup>The second cycle. <sup>g</sup>The third cycle.

reaction in terms of percentage yield (86–99%) and diastereoselectivity (2–2.4) (Fig. S4, ESI†). Since changes in temperature as well as the size of the aldehyde substrate did not render a significant impact on the catalytic activity of **1** in terms of percentage yields and diastereoselectivity, we reckon that the catalytically active metal centers on the solid exterior surface may be highly accessible, as evidenced by reported efficient salen-based 1D CP catalysts.<sup>15</sup>

For comparison, the catalytic activities of two reference compounds  $\text{Cu}^{\text{I}}$  and  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$  have also been examined under similar experimental conditions. Both of them were found to display a much lower catalytic activity than **1**, in terms of the amount employed (10 mol% for  $\text{Cu}^{\text{I}}$ , 0.5 mol% for  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$ ) and reaction time required (3 h), as well as the percentage yields obtained (82% for  $\text{Cu}^{\text{I}}$  and 87% for  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$ ) for the  $\alpha$ -aminonitrile products (Table S4, ESI†). The superior catalytic activity of **1** indicates that there is a cooperative catalytic event achieved by two different active catalytic sites (i.e.,  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$ ) of **1**. In this reaction, the  $\text{Cu}^{\text{I}}$ -Im moieties of **1** may function as Brønsted bases to activate the cyanides, while  $\text{Cu}^{\text{II}}$  ions act as Lewis acids to activate the imine enol intermediates in the strecker reaction.<sup>7a,16</sup> Furthermore, the inductively-coupled-plasma spectroscopic analysis demonstrates the heterogeneity of **1** with less than 0.02% of copper content in the reaction mixture.<sup>9b,17</sup> A recycling test with three consecutive runs shows that **1** can be re-used without a significant loss of catalytic activity (the yields can reach from 95 to 99%, see Table 1, entries 6 and 7). Solid residues of **1**, which were isolated from the reaction mixture via centrifugation, displayed the same PXRD pattern as that of the pristine solid of **1** (Fig. S2, ESI†). These results support that **1** has adequate stability and recoverability to be used as an efficient bimetallic heterogeneous catalyst for the three-component reactions.

To further elucidate the bimetallic catalytic nature of **1** which contains two kinds of metal-based catalytic sites, catalytic degradation experiments of various organic dyes in the presence or absence of visible light have been carried out. The **1**-catalyzed



**Fig.2** Photocatalytic degradation of organic dyes catalyzed by **1** upon visible-light illumination. (a) Photographs of different dye solutions and concentration in term of absorbance changes of dyes as a function of time [blue pillar: methylene blue (MB); red pillar: rhodamine (RhB); orange pillar: methyl orange (MO)]. (b) Time-dependent concentration changes and (c) % degradation rates of MB over different conditions [**1**/ visible-light illumination]: a [-/-]; b [-/+]; c [+/-]; d [+/+].

(photo-)degradation of methylene blue (MB) aqueous solution (12 mg/L) has first been examined by means of UV-vis spectrophotometry (Fig. S5, ESI<sup>†</sup>). In the absence of visible-light illumination, 65% of MB had been decomposed in the solution (Fig. 2b, 2c). We reckon that the Cu<sup>II</sup> ions in **1** is crucial in decomposing MB, since various studies have shown that Cu<sup>II</sup> could play major catalytic role in various oxidation reactions.<sup>18</sup> It should be noted that up to 96% of MB could be decomposed when the reaction was performed under visible-light illumination (Fig. 2b, 2c). We reckon that the enhanced degradation of MB is due to the cooperative decomposition achieved by photoactive Cu(I) moieties in **1**.<sup>19</sup> Apart from MB, the photodegradation of other organic dyes including rhodamine B (RhB) and methyl orange (MO) by **1** have also been examined. Similar high photocatalytic efficiencies (>95%) were observed in both cases after a ~50-min light illumination (Fig. 2a and Fig. S6–S9, ESI<sup>†</sup>). Furthermore, the stability and recoverability of **1** have also been examined. After repeating the photocatalytic degradation of MB three times, the solid residues left in the reaction mixture retained similar PXRD pattern as that of the pristine solid of **1**. As expected, these residues also displayed similar photocatalytic efficiency as that of **1** (Fig. S10–S11, ESI<sup>†</sup>).

In summary, this work has described a feasible approach in preparing a copper(I)/copper(II)-salen coordination polymer (**1**) having high bimetallic catalytic activity through the incorporation of two different metal-based catalytic moieties into a single framework. The CP **1** could be used as an efficient heterogeneous multifunctional catalyst for the synthesis of  $\alpha$ -aminonitriles via asymmetric three-component strecker reaction. Meanwhile, **1** has also been demonstrated to display promising visible-light-driven bimetallic catalytic activity in degrading various organic dyes. This work paves the way to the solvothermal synthesis of efficient heterogeneous multifunctional materials which could catalyze transformations through a bimetallic pathway.

We acknowledge the National Basic Research Program of China (973 Programs, 2012CB821706 & 2013CB834803), the National Natural Science Foundation for Distinguished Young Scholars of China (20825102), the National Natural Science Foundation of China (91222202, 21171114, 21101103) and Shantou University.

## Notes and references

- L. Que, Jr and W. B. Tolman, *Nature*, 2008, **455**, 333.
- (a) D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem. Soc. Rev.*, 2012, **41**, 8075; (b) M. Delferro and T. J. Marks, *Chem. Rev.*, 2011, **111**, 2450.
- M. J. Climent, A. Corma and S. Iborra, *Chem. Rev.*, 2011, **111**, 1072.
- (a) T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, 2013, **113**, 734; (b) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.
- (a) F. Vermoortele, R. Ameloot, A. Vimont, C. Serrec and D. D. Vos, *Chem. Commun.*, 2011, **47**, 1521; (b) P. Wu, J. Wang, Y. Li, C. He, Z. Xie and C. Duan, *Adv. Funct. Mater.*, 2011, **21**, 2788; (c) B. Li, Y. Zhang, D. Ma, L. Li, G. Li, G. Li, Z. Shi and S. Feng, *Chem. Commun.*, 2012, **48**, 6151; (d) J. Park, J.-R. Li, Y.-P. Chen, J. Yu, A. Yakovenko, Z. U Wang, L.-B. Sun, P. B. Balbuena and H.-C. Zhou, *Chem. Commun.*, 2012, **48**, 9995; (e) R. Srirambalaji, S. Hong, R. Natarajan, M. Yoon, R. Hota, Y. Kim, Y. H. Ko and K. Kim, *Chem. Commun.*, 2012, **48**, 11650.
- (a) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (b) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670.
- (a) A. Arnanz, M. Pintado-Sierra, A. Corma, M. Iglesias and F. Sánchez, *Adv. Synth. Catal.*, 2012, **354**, 1347; (b) Y. Pan, B. Yuan, Y. Li and D. He, *Chem. Commun.*, 2010, **46**, 2280; (c) F. G. Cirujano, F. X. Llabrés i Xamena and A. Corma, *Dalton Trans.*, 2012, **41**, 4249.
- S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970.
- (a) M. E. Kosal, J.-H. Chou, S. R. Wilson and K. S. Suslick, *Nat. Mater.*, 2002, **1**, 118; (b) A. Hu, H. L. Ngo and W. Lin, *Angew. Chem., Int. Ed.*, 2003, **42**, 6000; (c) S. Kitagawa, S.-i. Noro and T. Nakamura, *Chem. Commun.*, 2006, 701; (d) W.-X. Ni, M. Li, X.-P. Zhou, Z. Li, X.-C. Huang and D. Li, *Chem. Commun.*, 2007, 3479; (e) W.-X. Ni, M. Li, S.-Z. Zhan, J.-Z. Hou and D. Li, *Inorg. Chem.*, 2009, **48**, 1433.
- (a) S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp and T. E. Albrecht-Schmitt, *Chem. Commun.*, 2006, 2563; (b) F. Song, C. Wang, J. M. Falkowski, L. Ma and W. Lin, *J. Am. Chem. Soc.*, 2010, **132**, 15390.
- (a) M. Meldal and C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2952; (b) T. Yang, H. Cui, C. Zhang, L. Zhang and C.-Y. Su, *ChemCatChem*, 2013, **5**, 3131.
- Y. Kang, F. Wang, J. Zhang and X. Bu, *J. Am. Chem. Soc.*, 2012, **134**, 17881.
- (a) R. Peng, M. Li and D. Li, *Coord. Chem. Rev.*, 2010, **254**, 1; (b) S.-Z. Zhan, M. Li, X.-P. Zhou, J.-H. Wang, J.-R. Yang and D. Li, *Chem. Commun.*, 2011, **47**, 12441.
- (a) H. Gröger, *Chem. Rev.*, 2003, **103**, 2795; (b) M. Shibasaki and M. Kanai, *Chem. Rev.*, 2008, **108**, 2853; (c) S. J. Zuend, M. P. Coughlin, M. P. Lalonde and E. N. Jacobsen, *Nature*, 2009, **461**, 968.
- (a) Y. Huang, T. Liu, J. Lin, J. Lü, Z. Lin and R. Cao, *Inorg. Chem.*, 2011, **50**, 2191; (b) A. Bhunia, M. A. Gotthardt, M. Yadav, M. T. Gamer, A. Eichöfer, W. Kleist and P. W. Roesky, *Chem.–Eur. J.*, 2013, **19**, 1986.
- (a) T. Blasco, M. Boronat, P. Concepción, A. Corma, D. Law and J. A. Vidal-Moya, *Angew. Chem. Int. Ed.*, 2007, **46**, 3938; (b) S. Handa, V. Gnanadesikan, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc.*, 2010, **132**, 4925.
- A. Hu, H. L. Ngo and W. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 11490.
- (a) J. Ackermann, F. Meyer, E. Kaifer and H. Pritzkow, *Chem.–Eur. J.*, 2002, **8**, 247; (b) S. Afzal, W. A. Daoud and S. J. Langford, *Appl. Mater. Interfaces*, 2013, **5**, 4753.
- T. Wen, D.-X. Zhang, J. Liu, R. Lin and J. Zhang, *Chem. Commun.*, 2013, **49**, 5660.



TOC

