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AIE-active tetraphenylethene functionalized metal-organic framework for selective detection of nitroaromatic explosives and organic photocatalysis[†]

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AlE-active luminogen tetraphenylethene (TPE) was incorporated into UiO-isoreticular zirconium metal-organic framework via the strategy of mixed dicarboxylate struts, which shows a strong bluegreen emission and selective sensing of nitroaromatic explosives 2,4,6-trinitrophenol (TNP) and 2,4-dinitrophenol (DNP) through fluorescence quenching. Moreover, the luminescent MOF exhibits efficient photocatalytic activities for aerobic crossdehydrogenative coupling reactions mediated by visible light. AlE-active luminogen tetraphenylethene (TPE) was incorporated into UiO-isoreticular zirconium metal-organic framework via the strategy of mixed dicarboxylate struts, which shows a strong bluegreen emission and selective sensing of nitroaromatic explosives 2,4,6-trinitrophenol (TNP) and 2,4-dinitrophenol (DNP) through fluorescence quenching. Moreover, the luminescent MOF exhibits efficient photocatalytic activities for aerobic crossdehydrogenative coupling reactions mediated by visible light.

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Metal-organic frameworks (MOFs) are composed of multidentate organic linkers and inorganic metal nodes, representing a novel class of porous crystalline materials.¹ Due to their well-ordered structures, high porosity and adjustable organic ligands/metal clusters, MOFs have demonstrated the great promise for diverse applications,²⁻⁷ such as gas storage,² separation,³ light harvesting,⁴ heterogeneous catalysis⁵ and biomedical related area.⁶ Recently, a kind of fascinating luminescent MOFs has been developed for achieving the purpose of light-emitting, detection/sensing and even photocatalysis, through the introduction of various photoactive components including rare-earth metal ions, fluorescent ligands or encapsulated dye species.⁸

It seems that rigidifying fluorescent linkers within MOFs is much more appealing, which usually reduces their nonradiative decay rate and results in increased quantum efficiencies. However, many conventional luminophores suffer from the reduced emission in the condensed phase due to the aggregation-caused quenching (ACQ) effect.⁹ In contrast, some molecules featuring aggregation-induced emission (AIE) characteristics, such as tetraphenylethylene (TPE), exhibit highly enhanced emission in the aggregate state.⁹ Thus, it can be expected that the introduction of AIE-functional cores into reported the first example of TPE-based luminescent MOF by using a newly designed tetrakis(4-carboxyphenyl)ethylene ligand, which shows the potential utility toward sensing of small organic molecules.^{10a} Subsequently, Zhou and his coworkers have utilized an extended TPE-based carboxylate linker to react with ZrCl₄ in the presence of variable competing acid, giving rise to two robust and highly fluorescent Zr-MOFs with different topologies.^{10e,10f} More interestingly, one of the two MOFs, PCN-128, exhibited a unique piezofluorochromic behavior under the pressures.^{10f} Also, pyridyl-decorated TPEbased ligand was employed by Li's group to construct luminescent MOF for highly effective and selective detection of mycotoxins.^{10g} These reported pioneering examples have revealed the charm of MOFs integrating with AIE, however, this fantastic research field is still in its infancy stage. Thereby, much more

charm of MOFs integrating with AIE, however, this fantastic research field is still in its infancy stage. Thereby, much more effort should be devoted into such active area for developing multifunctional luminescent MOFs, as well as further exploring their other applications apart from the chemical sensing. This may largely depend on the development of novel ligands with AIE properties.¹¹



Herein, we designed and synthesized an AIE-active TPEconjugated terphenyldicarboxylate linker, denoted as H₂-etpdc; then, a UiO-isoreticular zirconium MOF was successfully constructed by the solvothermal reaction of $ZrCl_4$ with the mixture of struts H₂-etpdc and H₂-mtpdc via the mix-andmatch approach¹² (Scheme 1). The new TPE-functionalized Zr-

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MOF, denoted as UiO-68-mtpdc/etpdc, exhibits a strong bluegreen emission, which can be used to selectively detect nitroaromatic explosives 2,4,6-trinitrophenol (TNP) and 2,4dinitrophenol (DNP) via fluorescence quenching. Moreover, the MOF can work as a highly active photocatalyst for visible light promoted aerobic cross-dehydrogenative coupling (CDC) reactions. To our knowledge, this is the first study of AIE-core functionalized MOF in the application of organic photocatalysis.

The new ligand H2-etpdc was conveniently obtained via several typical organic reaction steps as described in Scheme S1 (for details, see ESI). Initially, we found that the direct solvothermal reaction of ZrCl₄ and H₂-etpdc in N,N'dimethylformamide (DMF) failed to give the desirable crystalline UiO MOF, presumably due to the steric bulk of TPE moiety of organic linker. Thus, a combination of H₂-etpdc and H₂-mtpdc in 1:1 molar ratio was treated by ZrCl₄ in DMF at 100 ^oC to produce UiO-68 derivative MOF UiO-68-mtpdc/etpdc¹³ (for detail, see ESI). Such a mixed-strut approach can allow for accommodation of the relatively sterically demanding TPE motif within the parent framework, while maintain the porosity and open pores of framework to facilitate substrate diffusion for achieving efficient catalysis. Powder X-ray diffraction (PXRD) of UiO-68-mtpdc/etpdc revealed its highly crystalline nature and isostructure with the parent framework UiO-68 (Fig. S1 and S2 in ESI). Additionally, nitrogen sorption investigation at 77 K exhibited a typical type I isotherm with BET surface area of 960 $m^2 g^{-1}$ (Fig. S5 in ESI), confirming the high porosity of UiO-68-mtpdc/etpdc.



Fig. 1 (a) Emission spectra of MOF UiO-68-mtpdc/etpdc dispersed in CH₃OH (0.02 mg/mL) upon incremental addition of TNP. Inset: corresponding Stern-Volmer plot of the quenching fluorescence intensity as a function of TNP concentration. (b) Percentage of fluorescence quenching obtained for different nitroaromatic compounds (100 μ M). Excited at 370 nm.

As expected, the TPE-integrated MOF UiO-68-mtpdc/etpdc shows a strong blue-green emission centered at 490 nm with a quantum yield (Φ) of 48% in the solid state (Fig. S6 and S7 in ESI). In comparison, its linker precursor H₂-etpdc exhibits the emission maxima at 518 nm with Φ value of 32%. The blue shift and quantum yield enhancement of UiO-68-mtpdc/etpdc should be attributed to the immobilization of H₂-etpdc linker in rigid framework, which was also observed in other reported TPE-core based MOFs,^{9,10} such as PCN-94.^{10e} Furthermore, both H₂-etpdc and UiO-68-mtpdc/etpdc exhibit a similar biexponential fluorescence decays comprised of one short τ_1 and a longer τ_2 (Table S1 in ESI), which can be attributed to monomer and excimer fluorescence lifetimes, respectively.^{10a}

The highly photoluminescent (PL) efficiency makes UiO-68mtpdc/etpdc serve as a promising luminescent-based sensory

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material. Thus, we investigated its chemo-sensing behaviors by using 2,4,6-trinitrophenol (TNP) as an explosive 490713 found that the dispersion of MOF UiO-68-mtpdc/etpdc in CH₃OH also exhibits a strong emission centered at 490 nm, which can be quickly and dramatically quenched by incremental addition of TNP into the suspension (Fig. 1a). When the concentration of TNP is as low as 40 ppm, the initial PL intensity is quenched over 50%, indicating that UiO-68mtpdc/etpdc is highly sensitive towards TNP. And the Stern-Volmer quenching constant (k_{sv}) was estimated to be 2.8 × 10⁴ M⁻¹ for TNP, which is comparable with other reported MOFbased sensors.¹⁴ Besides, we found that 2,4-dinitrophenol (2,4-DNP) and p-nitrophenol (p-NP) can also efficiently quench the emission of UiO-68-mtpdc/etpdc with k_{sv} values of 2.3 × 10⁴ M⁻ 1 and 7.2 \times 10 3 M $^{-1}$ (Fig. S11 and S12 in ESI), respectively. And the fluorescence quenching degrees in the presence of nitrophenol species with the same concentration of 100 µM, are 92%, 76% and 42% for TNP, DNP and p-NP, respectively. In contrast, the quenching degree by other nitrobenzene compounds, such as 2,4,6-trinitrotoluene (TNT), 2,4dinitrotoluene (DNT), 1,3-dinitrobenzene (DNB), 0nitrotoluene (o-NT), m-nitrotoluene (m-NT), p-nitrotoluene (p-NT), nitrobenzene (NB), are much lower under otherwise identical condition (Fig. 2b and Fig. S13 in ESI). These results indicate that UiO-68-mtpdc/etpdc offers a selective sensing of nitrophenols, such as TNP and DNP, among the above nitroaromatics. Such high selectivity of the MOF towards nitrophenols over other nitroaromatics, could be attributed to electrostatic and/or hydrogen-bonding interactions the between the acidic hydroxyl group of nitrophenols and Lewis basic N-donor sites of imidazole in etpdc ligand (Fig. 2),^{14,15} which was also confirmed by density functional theory (DFT) calculations at the B3LYP/3-21G level (Fig. S14 in ESI).¹⁶ The strong interactions would facilitate the electron and energy transfer process from the electron-rich TPE moiety to electrondeficient nitrophenols, thus, leading to the highly effective and selective quenching response.



Fig. 2 Schematic representation of electrostatic and hydrogen-bonding interactions between TNP and etpdc-linker in MOF UiO-68-mtpdc/etpdc.

Subsequently, in order to further explore applications of AIE-integrated MOFs, UiO-68-mtpdc/etpdc was tentatively used as photocatalyst to promote aerobic CDC reactions, which involve the direct formation of C-C bond via two C-H bonds under oxidative conditions.¹⁷ The initial study was performed by a typical model cross-coupling reaction of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**) with indole (**2a**) at

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ambient temperature (Scheme 2).¹⁸ When the reaction mixture in the presence of a catalytic amount of UiO-68-mtpdc/etpdc was irradiated by blue LEDs (λ_{max} = 450 nm) for several hours, to our delight, the desired product **3a** can be readily obtained (Table S2 in ESI). And a yield of ~93% was obtained after optimization of irradiation time and amount of MOF. Control experiments revealed that each element of the CDC reaction, including photocatalyst, light and oxygen, is indispensable for the efficient progress of the aerobic coupling reaction. Moreover, no catalytic activity was observed when using MOF UiO-68-mtpdc as photocatalyst that only contains the ligand H₂-mtpdc.^{12d} This confirms that AIE-active TPE moiety in MOF UiO-68-mtpdc/etpdc works as an active photocatalytic center for driving the reaction.



The heterogeneous nature of UiO-68-mtpdc/etpdc catalysis was confirmed by filtration reaction and results of recycle catalysis. The MOF photocatalyst was removed from the reaction system after 5 h, which was followed by another 8 h of irradiation. Almost no more production of 3a was observed, indicating no leaching of active catalyst species into solution as well as the heterogeneity of MOF UiO-68-mtpdc/etpdc during photocatalysis. Meanwhile, the reusability of UiO-68mtpdc/etpdc as a heterogeneous catalyst for the coupling reaction was investigated, which can be readily recovered from the reaction mixture by centrifugation. And the catalyst can be at least reused five times without loss of activity (Fig. S15 in ESI). In addition, PXRD pattern of UiO-68-mtpdc/etpdc after five cycles revealed no deterioration of crystallinity (Fig. S16 in ESI), mainly due to the robust Zr-based UiO framework.¹⁹



Fig. 3 EPR measurements of a solution in CH₃OH of UiO-68-mtpdc/etpdc without **1a** (a) and with **1a** (b) in the presence of TEMP upon the irradiation of blue LEDs for 60 s; a solution in CH₃OH of UiO-68-mtpdc/etpdc without **1a** (c) and with **1a** (d) in the presence of DMPO upon the irradiation of blue LEDs for 60 s. In air atmosphere.

We have found that almost no photoproduct was detected when the reaction was conducted in $N_{\rm 2}$ atmosphere (Table S2

in ESI), indicating the important role of molecular oxygen for the aerobic CDC reaction. Thus, electron¹⁰³paramagnetic resonance (EPR) experiments were performed to determine the active species of oxygen in the photocatalysed process, in which 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6tetramethyl-1-piperidine (TEMP) were employed to capture superoxide radical anion $O_2^{\bullet-}$ and singlet oxygen 1O_2 , respectively. As shown in Fig. 3, no signal was observed upon irradiation of the mixture containing TEMP and UiO-68mtpdc/etpdc in the absence or presence of 1a, indicating no ¹O₂ formation in the process. There was also no signal when DMPO was added into CH₃OH solution of UiO-68-mtpdc/etpdc. Whereas the signal of $O_2^{\bullet-}$ captured by using DMPO as a radical scavenger was clearly detected in the presence of 1a. This revealed that there is an effective single electron transfer (SET) from 1a to excited TPE-integrated MOF UiO-68mtpdc/etpdc (PC*) upon irradiation, along with the formation of radical cation **1a**⁺⁺ and radical anion PC⁺⁻ (Scheme 3). The generated PC^{•-} subsequently reacts with oxygen to produce $O_2^{\bullet-}$, which abstracts a proton from $1a^{\bullet+}$ to afford intermediate 1a[•]. Furthermore, the radical 1a[•] was oxidized to the imine cation 1a⁺ that was attacked by nucleophile to afford the product.

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Scheme 3 Proposed mechanism for the photocatalytic aerobic CDC reaction by MOF UiO-68-mtpdc/etpdc (photocatalyst, PC).

Considering the highly catalytic activity and recyclability of MOF UiO-68-mtpdc/etpdc based photocatalyst, along with well understanding of the reaction mechanism, we further examined the scope of the coupling reaction photocatalyszed by the MOF. As shown in Table S3 and Table S4 (in ESI), most of the CDC reaction between a variety of substituted tetrahydroisoquinoline derivatives with different nucleophilic indoles and nitroalkanes gave good-to-excellent yields.

In summary, we have designed and synthesized an AIEactive TPE-conjugated terphenyldicarboxylate strut, which was successfully incorporated into the robust UiO-68-based framework through a mix-and-match strategy using the mixed dicarboxylate struts. Due to the restricted intramolecular rotation of AIE-characteristic TPE unit in rigid framework, the MOF shows a strong blue-green emission, which can further be used for the selective and sensitive detection of nitrophenol type explosives via a luminescence quenching. Moreover, the TPE-based MOF have demonstrated a highly catalytic activity for visible light-driven aerobic CDC reactions between tertiary amines and different carbon nucleophiles. To the best of our knowledge, this is the first demonstration of MOF integrated AIE-core for organic photocatalysis. Furthermore, it can be expected that more MOFs incorporated AIE-luminogens would be developed for various applications in the near future.

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Notes and references

- (a) H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444; (b) H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673-674; (c) H.-C. Zhou and S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5415-5418; (d) C. Wang, D. Liu and W. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 13222-13234; (e) Y. Cui, B. Li, H. He, W. Zhou, B. Chen and G. Qian, *Acc. Chem. Res.*, 2016, **49**, 483-493.
- (a) Y. He, W. Zhou, G. Qian and B. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5657-5678; (b) J. Sculley, D. Yuan and H.-C. Zhou, *Energy Environ. Sci.*, 2011, **4**, 2721-2735; (c) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724-781.
- 3 (a) S. Qiu, M. Xue and G. Zhu, *Chem. Soc. Rev.*, 2014, 43, 6116-6140; (b) Z. Y. Yeo, S.-P. Chai, P. W. Zhu and A. R. Mohamed, *RSC Adv.*, 2014, 4, 54322-54334; (c) Q. Yang, D. Liu, C. Zhong and J.-R. Li, *Chem. Rev.*, 2013, 113, 8261-8323; (d) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, 112, 869-932; (e) P.-Z. Li, X.-J. Wang, S. Y. Tan, C. Y. Ang, H. Chen, J. Liu, R. Zou and Y. Zhao, *Angew. Chem. Int. Ed.*, 2015, 54, 12748-12752.
- 4 (a) J.-L. Wang, C. Wang and W. Lin, ACS Catal., 2012, 2, 2630-2640; (b) M. C. So, G. P. Wiederrecht, J. E. Mondloch, J. T. Hupp and O. K. Farha, Chem. Commun., 2015, 51, 3501-3510; (c) H.-Q. Peng, L.-Y. Niu, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung and Q.-Z. Yang, Chem. Rev., 2015, 115, 7502-7542.
- 5 (a) A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov and F. Verpoort, *Chem. Soc. Rev.*, 2015, **44**, 6804-6849; (b) S. Ou and C.-D. Wu, *Inorg. Chem. Front.*, 2014, **1**, 721-734; (c) P.-Z. Li, X.-J. Wang, J. Liu, J. S. Lim, R. Zou and Y. Zhao, *J. Am. Chem. Soc.*, 2016, **138**, 2142-2145.
- 6 (a) C. He, D. Liu and W. Lin, *Chem. Rev.*, 2015, **115**, 11079-11108; (b) J. Park, Q. Jiang, D. Feng, L. Mao and H.-C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 3518-3525.
- 7 (a) W. Xia, A. Mahmood, R. Zou and Q. Xu, *Energy Environ. Sci.*, 2015, **8**, 1837-1866; (b) J. Jiang and O. M. Yaghi, *Chem. Rev.*, 2015, **115**, 6966-6997; (c) B. Li, M. Chrzanowski, Y. Zhang and S. Ma, *Coord. Chem. Rev.*, 2016, **307**, 106-129.
- 8 (a) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126-1162; (b) Y. Cui, B. Chen and G. Qian, *Coord. Chem. Rev.*, 2014, **273**, 76-86; (c) J. Rocha, L. D. Carlos, F. A. Almeida Paz and D. Ananias, *Chem. Soc. Rev.*, 2011, **40**, 926-940; (d) J. Heine and K. Muller-Buschbaum, *Chem. Soc. Rev.*, 2013, **42**, 9232-9242; (e) T. Zhang and W. Lin, *Chem. Soc. Rev.*, 2014, **43**, 5982-5993.
- 9 (a) J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, 2015, **115**, 11718-11940; (b) J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang and B. Z. Tang, *Adv. Mater.*, 2014, **26**, 5429-5479; (c) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332-4353; (d) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361-5388.
- 10 (a) N. B. Shustova, B. D. McCarthy and M. Dinca, J. Am. Chem. Soc., 2011, 133, 20126-20129; (b) N. B. Shustova, T.-C. Ong,

Journal Name

A. F. Cozzolino, V. K. Michaelis, R. G. Griffin and M. Dinca, J. Am. Chem. Soc., 2012, **134**, 15061-15070; (c) No Recention A. F. Cozzolino and M. Dinca, J. Am. Chem. Soc., 2012, **134**, 19596-19599; (d) N. B. Shustova, A. F. Cozzolino, S. Reineke, M. Baldo and M. Dinca, J. Am. Chem. Soc., 2013, **135**, 13326-13329; (e) Z. Wei, Z.-Y. Gu, R. K. Arvapally, Y.-P. Chen, R. N. McDougald, Jr., J. F. Ivy, A. A. Yakovenko, D. Feng, M. A. Omary and H.-C. Zhou, J. Am. Chem. Soc., 2014, **136**, 8269-8276; (f) Q. Zhang, J. Su, D. Feng, Z. Wei, X. Zou and H.-C. Zhou, J. Am. Chem. Soc., 2015, **137**, 10064-10067; (g) Z. Hu, W. P. Lustig, J. Zhang, C. Zheng, H. Wang, S. J. Teat, Q. Gong, N. D. Rudd and J. Li, J. Am. Chem. Soc., 2015, **137**, 16209-16215; (h) Z. Hu, G. Huang, W. P. Lustig, F. Wang, H. Wang, S. J. Teat, D. Banerjee, D. Zhang and J. Li, Chem. Commun., 2015, **51**, 3045-3048.

- (a) W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle Iii, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561-5593; (b) F. A. Almeida Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tome, J. A. S. Cavaleiro and J. Rocha, *Chem. Soc. Rev.*, 2012, **41**, 1088-1110; (c) D. Zhao, D. J. Timmons, D. Yuan and H.-C. Zhou, *Acc. Chem. Res.*, 2011, **44**, 123-133.
- 12 (a) C. Wang, Z. Xie, K. E. deKrafft and W. Lin, J. Am. Chem. Soc., 2011, 133, 13445-13454; (b) P. W. Siu, Z. J. Brown, O. K. Farha, J. T. Hupp and K. A. Scheidt, Chem. Commun., 2013, 49, 10920-10922; (c) C. M. McGuirk, M. J. Katz, C. L. Stern, A. A. Sarjeant, J. T. Hupp, O. K. Farha and C. A. Mirkin, J. Am. Chem. Soc., 2015, 137, 919-925; (d) W.-Q. Zhang, Q.-Y. Li, Q. Zhang, Y. Lu, H. Lu, W. Wang, X. Zhao and X.-J. Wang, Inorg. Chem., 2016, 55, 1005-1007.
- 13 The molar ratio of H_2 -etpdc and H_2 -mtpdc in MOF UiO-68mtpdc/etpdc was determined to be 1:1.2 by ¹H NMR of digested MOF with DMSO- d_6 /HF. The slightly higher content of mtpdc linker in MOF should be ascribed to the steric bulk of TPE moiety of etpdc linker.
- 14 (a) Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, 43, 5815-5840; (b) D. Banerjee, Z. Hu and J. Li, *Dalton Trans.*, 2014, 43, 10668-10685; (c) X. Sun, Y. Wang and Y. Lei, *Chem. Soc. Rev.*, 2015, 44, 8019-8061; (d) S. S. Nagarkar, A. V. Desai and S. K. Ghosh, *CrystEngComm*, 2016, 18, 2994-3007.
- 15 (a) S. Dalapati, S. Jin, J. Gao, Y. Xu, A. Nagai and D. Jiang, J. Am. Chem. Soc., 2013, 135, 17310-17313; (b) B. Joarder, A. V. Desai, P. Samanta, S. Mukherjee and S. K. Ghosh, Chem. Eur. J., 2015, 21, 965-969; (c) S. S. Nagarkar, A. V. Desai and S. K. Ghosh, Chem. Commun., 2014, 50, 8915-8918; (d) Y. Peng, A.-J. Zhang, M. Dong and Y.-W. Wang, Chem. Commun., 2011, 47, 4505-4507.
- 16 (a) E. Torres and G. A. DiLabio, J. Phys. Chem. Lett., 2012, 3, 1738-1744; (b) M. Zheng, Y. Liu, C. Wang, S. Liu and W. Lin, Chem. Sci., 2012, 3, 2623-2627; (c) M. Carboni, C. W. Abney, S. Liu and W. Lin, Chem. Sci., 2013, 4, 2396-2402.
- (a) S. A. Girard, T. Knauber and C.-J. Li, Angew. Chem. Int. Ed., 2014, 53, 74-100; (b) C.-J. Li, Acc. Chem. Res., 2009, 42, 335-344; (c) C. S. Yeung and V. M. Dong, Chem. Rev., 2011, 111, 1215-1292.
- (a) C.-J. Wu, J.-J. Zhong, Q.-Y. Meng, T. Lei, X.-W. Gao, C.-H. Tung and L.-Z. Wu, *Org. Lett.*, 2015, **17**, 884-887; (b) Q.-Y. Meng, J.-J. Zhong, Q. Liu, X.-W. Gao, H.-H. Zhang, T. Lei, Z.-J. Li, K. Feng, B. Chen, C.-H. Tung and L.-Z. Wu, *J. Am. Chem. Soc.*, 2013; (c) J.-J. Zhong, Q.-Y. Meng, G.-X. Wang, Q. Liu, B. Chen, K. Feng, C.-H. Tung and L.-Z. Wu, *Chem. Eur. J.*, 2013, **19**, 6443-6450.
- (a) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti,
 S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850-13851;
 (b) Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J.-R. Li and H.-C. Zhou, *Chem. Soc. Rev.*, 2016, **45**, 2327-2367.