ABSTRACT

Massive release of greenhouse carbon dioxide from anthropogenic activities has imposed a grave threat to our global warming and environments, leading to an earnest demand for novel technologies to mitigate carbon dioxide emission including the capture and sequestration. Whilst the sequestration technologies have been well developed, the capture technologies require a lot more research works as none of the existing technologies fulfills the target performance criteria. By virtue of exceptionally high active surface area, remarkably large void volume, structural and chemical tunability and potential scalability to industrial scale, porous coordination polymers and metal organic frameworks have surfaced with a great new hope for unprecedented carbon dioxide capture performance. In order to achieve the target performance criteria, high adsorption capacity and selectivity are required. Several strategies have been proposed including the installing of desired functionalities on the organic linkers, the generation of coordinative unsaturated or open metal sites to the frameworks and the introduction of framework flexibility without disrupting framework hydrothermal stability.

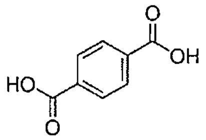
Here, new coordination polymers/metal organic frameworks have been designed and synthesized by putting two major strategies into practice, including the generation of coordinative unsaturated or open metal sites using lanthanide nodes and the introduction of framework flexibility through the use of mixed rigid and flexible dicarboxylates. Through the attempts to synthesize the porous coordination polymers for carbon dioxide capture application, the recently emerging ratiometric-photoluminescent properties of the yielded coordination polymers has been revealed leading to an extension of the project to include the ratiometric photoluminescent temperature sensing. The inherent multifunctional nature of lanthanide coordination polymers/metal organic frameworks has therefore been acknowledged.

Through the employment of benzene-1,4-dicarboxylate (BDC^{2-}), 2-nitro-benzene-1,4-dicarboxylate (NO_2-BDC^{2-}), phthalic acid (H_2phth), adipic acid (H_2ad) and pyridine-2,6-

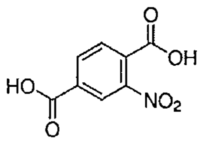
dicarboxylic acid (H_2pdc),[*] eleven series of lanthanide coordination polymers have been synthesized, including

- $[La_2(NO_2\text{-}BDC)_3(H_2O)_4]$,
- $[Ln(L)_{0.5}(NO_2\text{-}BDC)(H_2O)]\cdot 3H_2O$ (Ln=Eu, Tb, Dy, Ho; L=BDC^{2-}, $BDC^{2-}/NO_2\text{-}BDC^{2-}$),
- $[Tm(NO_2\text{-}BDC)_{1.5}(H_2O)]\cdot H_2O$,
- $[Ln_2(BDC)_3(DMF)_2(H_2O)_2]_n$ (Ln = Gd, Eu, Tb),
- $[Ln_xGd_{2-x}(BDC)_3(DMF)_2(H_2O)_2]_n$ (Ln = Eu, Tb),
- $[Ln(pdc)(H_2O)_4]_3\cdot 3Cl$ (Ln = Pr, Nd, Sm, Eu, Gd),
- $[Ln(pdc)(Hpdc)(H_2O)_2]\cdot 3H_2O$ (Ln = Pr, Nd, Sm),
- $[Ln(pdc)(H_2O)_4]_3\cdot 3Cl$ (Ln = Sm, Eu),
- $[Nd_2(ad)(phth)_2(H_2O)_4]$,
- $[Ln(ad)_{0.5}(phth)(H_2O)_2]$ (Ln = Eu, Gd, Tb, Dy, Er, Tm, Eu/Tb), and
- $[Ln(bdc)_{0.5}(phth)(H_2O)_2]$ (Ln = Eu, Tb, Ho, Er, Tm, Gd, Eu/Tb).

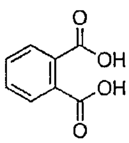
Among these complexes, $[Ln(L)_{0.5}(NO_2\text{-}BDC)(H_2O)]\cdot 3H_2O$ (Ln=Eu, Tb, Dy, Ho; L=BDC^{2-}, $BDC^{2-}/NO_2\text{-}BDC^{2-}$) are microporous in nature and show excellent selectivity toward carbon dioxide through the open metal site mechanism. The other dense framework complexes exhibit outstanding ratiometric photoluminescent temperature sensing performance.



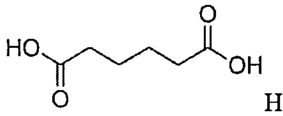
H_2BDC



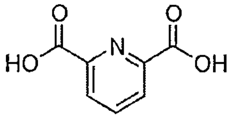
$NO_2\text{-}H_2$BDC



H_2phth



H_2ad



H_2pydc