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# Impregnation of metal ions in porphyrin-based imine gels to modulate guest uptake and to assemble a catalytic microfluidic reactor<sup>+</sup>

Lihua Zeng, Peisen Liao, Haoliang Liu, Liping Liu, Ziwei Liang, Jianyong Zhang, \* Liuping Chen and Cheng-Yong Su

A series of (metallo)porphyrin imine gels have been synthesized based on imine chemistry. The resulting aerogels have sponge-like porous networked structures consisting of interconnected nanoparticles with hierarchical porosity. The aerogels have high specific surface areas (up to 719 m<sup>2</sup> g<sup>-1</sup>) and large pore volumes (up to 2.60 cm<sup>3</sup> g<sup>-1</sup>). The effect of metal ions on the uptake of gases in these aerogels was investigated. The impregnation of various metal ions (Pd(II), Ni(II), Mn(III), Fe(III) and Sn(IV)) enhances the uptake capacity of various gases (e.g., CO<sub>2</sub>) despite their higher densities. Among the metal ions, Pd(II) is the best to increase the adsorption capacity and the isosteric heat of CO<sub>2</sub> adsorption. Pd-tapp-**A4** aerogel exhibits CO<sub>2</sub> volumetric uptake (1.62 mmol g<sup>-1</sup>, 7.13 wt% at 298 K, 1 bar) with high isosteric heat of adsorption (40.0 kJ mol<sup>-1</sup>). The gels also show potential applications in catalysis arising from their unique hierarchical porosity and the availability of metal centers. In combination with microfluidic technology, a catalytic gel capillary reactor has been assembled with the Pd-tapp-**A4** gel supported on the inner surface of a functionalized capillary.

# Introduction

Aerogels are a class of porous materials with intriguing properties, such as low density, high specific surface area, large pore size distribution, etc. They receive much attention due to their tremendous potential applications in catalysis, absorbents, sensors and others.<sup>1</sup> Besides conventional aerogels like metal oxides, carbons and organic polymers, several new catalogues of aerogels have been developed recently including graphene,<sup>2</sup> chalcogenide,<sup>3</sup> metal-organic<sup>4</sup> and dynamic covalent aerogels.5-7 Recently we make our efforts to develop imines gels/aerogels based on dynamic covalent chemistry.<sup>5-7</sup> Imine gels are constructed from polycondensation of bridging amines and aldehydes,<sup>8</sup> affording an extraordinary feature to engender desired functional behaviour by choosing appropriate small molecular precursors. The availability of various building blocks makes it possible to construct highly tuneable aerogels with unique properties for diverse applications, for example, offering readily accessible active sites for mass transport and allow large guest molecules to access the active sites inside the gel/aerogel.

On the other hand, porphyrins are a kind of important

macrocyclic ligands with rich coordination chemistry. A number of metal ions can be readily incorporated into the porphyrin centre, and the resulting metalloporphyrins are known in light harvesting, natural and artificial catalysis and oxygen delivery. They are good building units with accessible coordinatively unsaturated metal centre, and have been used in the synthesis of microporous materials, including porous organic materials<sup>9-12</sup> and metal-organic frameworks (MOFs).<sup>13-16</sup> Porous materials with porphyrin building units are easily functionalized through built-in metal sites with various applications in gas storage/separation,<sup>10,11,14</sup> catalysis,<sup>11,12,15</sup> and light-harvesting.<sup>16</sup>

Herein we incorporate porphyrin functional units into imine gels to get a series of functional porphyrin imine gels by reacting 5,10,15,20-tetrakis(p-aminophenyl)porphyrin (tapp) and its metalated derivatives (M-tapp, M = Pd, Ni, MnCl, FeCl, di/multifunctional aldehydes (tetrakis-(4-SnCl<sub>2</sub>) with formylphenyl)methane, A4, 1,3,5-triformylbenzene, A3 and 1,4-diformylbenzene, A2) (Scheme 1). These hierarchically porous gels offer readily accessible (metallo)porphyrin active sites for mass transport. In addition the synthetic availability of these porphyrin-based aerogels affords an opportunity to finetune their structure and properties. The adsorption properties of the aerogels have been studied including CO<sub>2</sub>, H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> gases. To show their potential application in catalysis, the Pdtapp gel has been supported inside walls of a capillary to assemble a catalytic gel microfluidic reactor.

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Sun Yat-Sen University, Lehn Institute of Functional Materials, MOE Laboratory of Bioinorganic and Synthetic Chemistry, MOE Key Laboratory of Polymeric Composite and Functional Materials, Guangzhou 510275, China. Email: zhjyong@mail.sysu.edu.cn

<sup>+</sup> Electronic Supplementary Information (ESI) available: Experimental details, SEM and TEM images, UV-vis, MS, IR, EDX, XPS spectra, XRPD patterns, TGA, gas sorption and catalysis data. See DOI: 10.1039/x0xx00000x



Scheme 1 Molecular structures of building units for imine gels, H₂tapp, Pdtapp, Ni-tapp, Mn-tapp, Fe-tapp, Sn-tapp, A4, A3 and A2.

# **Results and discussion**

## Synthesis and gelation tests

In this study, a free-base porphyrin 5,10,15,20-tetrakis(paminophenyl)porphyrin (H<sub>2</sub>tapp) was chosen. It contains four amine groups and can act as a building unit with multiple functional ends for imine gels. H<sub>2</sub>tapp was synthesized via dipyrrolemethane condensation between and 4nitrobenzaldehyde followed by reduction of nitro groups according to the literature procedure.<sup>17</sup> The free-base porphyrin H<sub>2</sub>tapp was subsequently metallated with metal salts (PdCl<sub>2</sub>, NiCl<sub>2</sub>·6H<sub>2</sub>O, Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O and SnCl<sub>2</sub>·2H<sub>2</sub>O) to obtain the corresponding metalloporphyrins Mtapp (M = Pd, Ni, MnCl, FeCl and SnCl<sub>2</sub>) (Scheme S1, Fig. S1-S3).<sup>18</sup> Among the metalloporphyrins, M-tapp (M = MnCl, FeCl and SnCl<sub>2</sub>) were obtained by air oxidation of corresponding precursors during the synthesis. For metalloporphyrins 5,10,15,20-tetrakis(p-aminophenyl)porphyrinatopalladium (Pd-tapp) and 5,10,15,20-tetrakis(paminophenyl)porphyrinatonickel (Ni-tapp) with divalent metal ions (M = Pd(II) and Ni(II)), the axial positions of metal ions are left uncoordinated. For metalloporphyrins with trivalent and

tetravalent metal ions (M = Mn(III), Fe(III) and Sn(IV)), the axial positions are occupied by one chloride for 5,10,15,20-tetrakis(p-aminophenyl)porphyrinatomanganese chloride (Mn-tapp) and 5,10,15,20-tetrakis(p-aminophenyl)porphyrinatoiron chloride (Fe-tapp) or two chlorides for 5,10,15,20-tetrakis(p-aminophenyl)porphyrinatotin chloride (Sn-tapp).



Scheme 2 Synthesis of H<sub>2</sub>tapp-A4 gel from H<sub>2</sub>tapp and A4.





Fig. 1 a) Photographic images of H<sub>2</sub>tapp-A4 wet gel, b) SEM and c,d) TEM images of H<sub>2</sub>tapp-A4 aerogel (bars represent 500, 100 and 20 nm, respectively).

Rigid building blocks with at least two functional groups are necessary to create a porous structure for uptake of guest molecules.<sup>5</sup> H<sub>2</sub>tapp or M-tapp are rigid planar molecules containing four amino functional groups. Based on these considerations, various imine gels were successfully prepared by reacting H<sub>2</sub>tapp or M-tapp with rigid bridging aldehydes tetrakis-(4-formylphenyl)methane (A4), 1,3,5-triformylbenzene (A3) or 1,4-diformylbenzene (A2) in a 1:1 molar ratio of  $-NH_2$  and -CHO reactive groups in DMSO in the presence of a catalytic amount of acetic acid (Scheme 2). Heating the precursor solution at 80 °C accelerated the gelation to result in opaque deep coloured gels (Fig. 1,2,54) within 0.5-8 h (Table S1). Heating for a longer time caused the gels to turn more

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firmly, and the gels are thermally irreversible. As representatives the gels formed with the porphyrin precursor concentration 0.030 mol  $L^{-1}$  were selected for subsequent investigation<sup>5</sup> in order to focus on the effect of impregnated metal ions. The aerogels were produced by subcritical CO<sub>2</sub>(I) drying of the corresponding wet gels to minimize changing of the original gel structure. The shrinkage percentage of the aerogels was 80-90% and the density of the aerogels was about 0.12 g cm<sup>-3</sup>.

## Characterization

SEM and TEM investigations show that the imine aerogels have sponge-like porous networked structures consisting of interconnected nanoparticles for the aerogels of H<sub>2</sub>tapp-A2, H<sub>2</sub>tapp-A3, H<sub>2</sub>tapp-A4, Mn-tapp-A4, Fe-tapp-A4, Ni-tapp-A4, Pd-tapp-A4 and Sn-tapp-A4 (Fig. 1,2,S5-S10). The particle sizes range around 20~50 nm. TEM reveals that macro- and mesopores are distributed in the gel network. All the aerogels and wet gels are amorphous, as revealed by the broad powder X-ray diffraction patterns (Fig. S11).



Fig. 2 a) Photographic images of Pd-tapp-A4 wet gel, b) SEM and b,c) TEM images of Pd-tapp-A4 aerogel (bars represent 500, 100 and 20 nm, respectively).

The chemical composition of the aerogels has been characterized by FT-IR. All the aerogels display a characteristic Ar–C=N– stretching band at around 1600-1650 cm<sup>-1</sup> (Fig. S12), confirming formation of imine bonds via condensation of aldehyde and amine groups. A broad band at around 3400 cm<sup>-1</sup> is due to the N-H stretching of unreacted amine functional groups for both the wet gels and aerogels. C=O stretching bands of unreacted aldehyde functional groups were also detected at around 1665-1700 cm<sup>-1</sup> for the aerogels. It suggests that the condensation of aldehyde and amine groups is incomplete in the aerogels. <sup>13</sup>C cross polarization magic angle spinning (CP/MAS) NMR of the aerogels showed a peak at around 160 ppm and confirmed the formation of imine bonds (Fig. S13-S16).<sup>19</sup> Elemental composition analysis of the

aerogels by energy dispersive X-ray spectroscopy (EDX) (Fig. S17) and ICP-AES (Table S2) revealed the presence of corresponding metal atoms, Ni, Pd, Mn, Fe, Sn, and the corresponding Cl<sup>-</sup> counterions. The fitting of X-ray photoelectron spectroscopy (XPS) curves of metal elements confirms the  $3d_{3/2}$  and  $3d_{5/2}$  state of divalent Pd(II) (binding energies 344.0 and 338.7 eV) and the  $2p_{1/2}$  and  $2p_{3/2}$  state of divalent Ni(II) (binding energy 873.2 and 855.8 eV) for Pd-tapp-A4 and Ni-tapp-A4, respectively (Fig. S18). The XPS analyses also confirm the presence of trivalent Mn(III), Fe(III) and tetravalent Sn(IV) for Mn-tapp-A4, Fe-tapp-A4 and Sn-tapp-A4, respectively.

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The aerogels were stable in neutral and alkaline solutions (e.g., 3 mol L<sup>-1</sup> NaOH) evidenced by SEM (Fig. S19), however, they were disrupted in acidic solution (e.g., 3 mol L<sup>-1</sup> HCl) arising from the dynamic nature of imine bonding. The thermostability of the aerogels was studied by thermogravimetric analysis (TGA) (Fig. S20). The aerogels H<sub>2</sub>tapp-A2, H<sub>2</sub>tapp-A3, H<sub>2</sub>tapp-A4, Mn-tapp-A4, Fe-tapp-A4, Ni-tapp-A4, Pd-tapp-A4 and Sn-tapp-A4 have a high thermal stability with significant decomposition only observed at temperatures > 300 °C.

#### **Porosity analysis**

Nitrogen physisorption was performed at 77 K to characterize the porosity of the porphyrin-based imine aerogels. H<sub>2</sub>tapp-A4, H<sub>2</sub>tapp-A3 and H<sub>2</sub>tapp-A2 aerogels with different aldehyde precursors are compared first. The nitrogen isotherm for H<sub>2</sub>tapp-A4 aerogel display a combination of Type I and Type IV characteristics according to IUPAC classification. The isotherms of H<sub>2</sub>tapp-A4 aerogel exhibit a steep rise of uptake within the region P < 0.001 MPa, indicative of the presence of substantial micropores. The isotherms are accompanied by a remarkable hysteresis in the desorption isotherm showing a range of mesopores are present. Meanwhile, H<sub>2</sub>tapp-A2 and H<sub>2</sub>tapp-A3 aerogels showed type II adsorption branch with a steep rise at P > 0.09 MPa (Fig. 3a). Brunauer-Emmett-Teller (BET) surface area and total volume analysis derived from the adsorption data reveal that the H<sub>2</sub>tapp-A4 aerogel with free-base porphyrin moieties has the highest BET surface area of 719 m<sup>2</sup>  $g^{-1}$  and pore volume of 2.60 cm<sup>3</sup>  $g^{-1}$ . All the aerogels have analogical non-local density functional theory (NL-DFT) and Horvath-Kawazoe (HK) pore size distributions with a wide range of mesopores up to ca. 50 nm (Fig. 3b,c,S21). Therefore, precursors with tetrahedral structure, A4, prefer to create a more porous structure.<sup>20</sup> It may efficiently prevent the aggregation of porphyrin moieties through formation of a three-dimensional network and is used as a precursor for further investigation of metalloporphyrin-based imine gels.

The effect of impregnated metal ions on the porosity properties of the aerogels was investigated (Table 1). All the nitrogen isotherms of Mn-tapp-A4, Fe-tapp-A4, Ni-tapp-A4, Pd-tapp-A4 and Sn-tapp-A4 aerogels display a combination of Type I and Type IV characteristics according to IUPAC classification (Fig. 4a). The BET specific surface areas of Pd-tapp-A4 and Ni-tapp-A4 are 618 and 695 m<sup>2</sup> g<sup>-1</sup>, slightly lower than that of H<sub>2</sub>tapp-A4. However, Mn-tapp-A4, Fe-tapp-A4 and Sn-tapp-A4 have significantly lower BET specific surface areas

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(358~384 m<sup>2</sup> g<sup>-1</sup>). Ni-tapp-**A4** and Pd-tapp-**A4** aerogels also have high pore volumes, 2.380 and 1.909 cm<sup>3</sup> g<sup>-1</sup>, respectively. NL-DFT pore size distributions show that these aerogels have a wide range of mesopores up to ca. 50 nm, while HK micropore sizes are centred at around 0.6 nm (Fig. 4b,c,S21). In addition, all the tap aerogels display similar NL-DFT pore size profiles with maxima for the same pore sizes at around 6, 17 and 29 nm, showing that they have similar textures.<sup>21</sup>





Because surface area is reported as an area per given mass, Pd-tapp-A4, Ni-tapp-A4, Mn-tapp-A4, Fe-tapp-A4 and Sn-tapp-A4 are each composed of heavier metalloporphyrins and therefore are expected to provide lower surface areas. When the surfaces of the aerogels are converted to an area per mmol porphyrin units, the difference is minimal for H<sub>2</sub>tapp-A4 (744 m<sup>2</sup> mmol<sup>-1</sup>), Pd-tapp-A4 (705 m<sup>2</sup> mmol<sup>-1</sup>) and Ni-tapp-A4  $(759 \text{ m}^2 \text{ mmol}^{-1})$ . This indicates that the surface area differences arise from variation in the density of the building unit for H<sub>2</sub>tapp-A4, Pd-tapp-A4 and Ni-tapp-A4. In contrast, the surface areas are significantly lower for Mn-tapp-A4 (402  $m^{2} \text{ mmol}^{-1}$ ), Fe-tapp-A4 (405  $m^{2} \text{ mmol}^{-1}$ ) and Sn-tapp-A4 (470 m<sup>2</sup> mmol<sup>-1</sup>) with the axial chlorides. The axial chloride ligands in porous network are not effective porogens and result in lower pore size and BET surface area.<sup>22</sup> Pore blockage or partial occupation of the metal sites by the axial chlorides, solvent molecules or unreacted ligands may be responsible for the lower surface areas. Simultaneously aggregation of porphyrin moieties may also affect the porosity.<sup>23</sup> These results suggest that impregnation of divalent metal ions in the porphyrin-based imine aerogels does not change the porosity significantly, while impregnation of trivalent or tetravalent metal ions lowers the surface area of the aerogels.





#### Gas sorption

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High BET surface areas and pore volumes make the present aerogels potential candidates in gas adsorption. The present aerogels also provide a platform to observe the effect of exposed metal species on gas sorption (e.g.,  $CO_2$ , <sup>24</sup>  $H_2^{25}$  and hydrocarbons<sup>26</sup>) in aerogels. CO<sub>2</sub> adsorption isotherms indicate that  $H_2$ tapp-A4 has an uptake capacity of 1.05 mmol g<sup>-1</sup> (4.62 wt%) at 298 K, 1 bar and 1.79 mmol  $g^{-1}$  (7.88 wt%) at 273 K, 1 bar (Fig. 5). Mn-tapp-A4, Fe-tapp-A4, Sn-tapp-A4 and Ni-tapp-A4 have similar capacities (0.99~1.09 mmol  $g^{-1}$  at 298 K; 1.87~2.08 mmol g<sup>-1</sup> at 273 K) (Fig. S22-S25), while Pd-tapp-A4 exhibits significantly higher CO2 volumetric uptake at 1 bar (1.62 mmol g<sup>-1</sup>, 7.13 wt% at 298 K; 2.39 mmol g<sup>-1</sup>, 10.5 wt% at 273 K) despite its higher density (Fig. 5, Table 1). The isosteric enthalpies of  $CO_2$  adsorption ( $Q_{st}$ ) were calculated by the Clausius-Clapeyron equation from CO<sub>2</sub> isotherms collected at 273 and 298 K (Table 1). The Q<sub>st</sub> at zero coverage was 32.9 kJ mol<sup>-1</sup> for H<sub>2</sub>tapp-**A4** aerogel. After incorporation of metal ions, the initial affinity turns higher (36.8~37.7 kJ mol<sup>-1</sup>) for Ni-tapp-A4, Mn-tapp-A4, Fe-tapp-A4 and Sn-tapp-A4. Pd-tapp-A4 aerogel has the highest isosteric heat of adsorption (40.0 kJ  $mol^{-1}$ ). The  $Q_{st}$  at zero coverage is higher than those of some imine-based (porphyrin) covalent organic frameworks (18~21 kJ mol<sup>-1</sup>)<sup>27</sup> and those of imine-based amorphous networks  $(31^{-35} \text{ kJ mol}^{-1})$ .<sup>28</sup> These high  $Q_{st}$  values may be primarily attributed to the electrostatic field provided by the impregnated metal ions together with the strong interaction of CO<sub>2</sub> with imine and residue amine groups. Adsorption selectivity of  $CO_2$  over  $N_2$  was estimated using the ideal adsorbed solution theory (IAST).<sup>29</sup> At 298 K IAST selectivities with bulk phase equilibrium partial pressure of 85 kPa N<sub>2</sub> and 15 kPa CO<sub>2</sub> were 24.4 and 34.1 for H<sub>2</sub>tapp-A4 and Pd-tapp-A4, respectively (Fig. S26).



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Fig. 5 a) CO<sub>2</sub> adsorption-desorption isotherms of H<sub>2</sub>tapp-A4 and Pd-tapp-A4 aerogels at 273 and 298 K, b) isosteric heats of adsorption ( $Q_{st}$ ) as a function of gas loading, estimated from low pressure isotherms at 273 and 298 K by applying the virial equation.

Aerogel	S <sub>BET</sub> <sup>a</sup> /m <sup>2</sup> g <sup>-1</sup>	$V_t^b$ /cm <sup>3</sup> g <sup>-1</sup>	$V_{\rm micro}^{c}$ /cm <sup>3</sup> g <sup>-1</sup>	$V_{\text{meso}}^{d}$ /cm <sup>3</sup> g <sup>-1</sup>	$\rm CO_2$ uptake at 1.0 bar /wt% (mmol g $^{-1})$		$Q_{st}^{e}$ /kJ mol <sup>-1</sup>
					@273 K	@298 K	
H <sub>2</sub> tapp- <b>A2</b>	213	0.98	0.048	0.957			
H₂tapp- <b>A3</b>	267	1.49	0.067	1.454			
H₂tapp- <b>A4</b>	719(744)	2.60	0.140	2.481	7.88 (1.79)	4.62 (1.05)	32.9
Pd-tapp- <b>A4</b>	618(705)	1.91	0.114	1.796	10.52 (2.39)	7.13 (1.62)	40.0
Ni-tapp- <b>A4</b>	695(759)	2.38	0.152	2.220	8.27 (1.88)	4.44 (1.01)	37.5
Mn-tapp- <b>A4</b>	358(402)	2.33	0.083	2.274	8.36 (1.90)	4.80 (1.09)	36.8
Fe-tapp- <b>A4</b>	360(405)	1.60	0.056	1.565	8.22 (1.87)	4.36 (0.99)	37.6
Sn-tapp- <b>A4</b>	384(470)	1.50	0.116	1.382	9.15 (2.08)	4.40 (1.00)	37.7

 Table 1 Porosity properties and CO2 adsorption performance of various imine aerogels.

<sup>*a*</sup> S<sub>BET</sub> is the BET specific surface area in the units of m<sup>2</sup> g<sup>-1</sup> and m<sup>2</sup> mmol(porphyrin)<sup>-1</sup>; <sup>*b*</sup>V<sub>t</sub> is the total specific pore volume; <sup>*c*</sup> V<sub>micro</sub> is the specific micropore volume calculated using the SF method; <sup>*c*</sup> V<sub>meso</sub> is the specific mesopore volume calculated using the BJH method; <sup>*c*</sup> Q<sub>st</sub> is the isosteric enthalpy of CO<sub>2</sub> adsorption at zero coverage.

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**Fig. 6** a)  $H_2$  adsorption-desorption isotherms of Pd-tapp-**A4** and  $H_2$ tapp-**A4** aerogels at 77 and 87 K, b) isosteric heats of adsorption ( $Q_{st}$ ) as a function of gas loading.

Encouraged by the improved CO<sub>2</sub> adsorption, Pd-tapp-A4 was subjected for further  $H_2$  and  $C_2H_4$  adsorption study with H<sub>2</sub>tapp-A4 as reference (Fig. 6). H<sub>2</sub> adsorption experiments reveal that Pd-tapp-A4 and H2tapp-A4 adsorbs H2 gas up to 1.26 and 0.94 wt% respectively at 77 K and 1 bar, and 0.84 and 0.60 wt% at 87 K and 1 bar (Fig. 6). Pd-tapp-A4 aerogel again exhibits higher H<sub>2</sub> volumetric uptake despite its higher density, which may be attributed to the incorporation of accessible Pd(II) sites. The  $Q_{st}$  of H<sub>2</sub> adsorption was estimated by fitting the  $H_2$  isotherms at 77 and 87 K to the virial equation. The initial  $Q_{st}$  of Pd-tapp-A4 is 7.75 kJ mol<sup>-1</sup>, while that of H<sub>2</sub>tapp-A4 is 7.32 kJ mol<sup>-1</sup>. This probably indicates that the impregnated Pd<sup>2+</sup> ions exert effects on the interaction energy between H<sub>2</sub> and the aerogel at low loadings.<sup>30</sup> Pd-tapp-A4 and  $H_2$ tapp-A4 have similar and decreased  $Q_{st}$  at high  $H_2$  loadings. This is consistent with their imine polymer nature.

Pd-tapp-**A4** and H<sub>2</sub>tapp-**A4** were also subjected for C<sub>2</sub>H<sub>4</sub> adsorption (Fig. 7). Pd-tapp-**A4** uptakes more C<sub>2</sub>H<sub>4</sub> (2.18%) at 298 K, 1 bar than H<sub>2</sub>tapp-**A4** (1.78 wt%). The initial  $Q_{st}$  of Pd-tapp-**A4** is 32.2 kJ mol<sup>-1</sup>, while that of H<sub>2</sub>tapp-**A4** is 31.2 kJ mol<sup>-1</sup>. The impregnation of Pd(II) metal ions probably enhances the isosteric heat of C<sub>2</sub>H<sub>4</sub> adsorption at low loading.<sup>30</sup> The Pd(II) metal centres are more capable of accepting  $\pi$  electron density and/or donating electron density into the empty  $\pi^*$ 

orbital of olefin, thus showing stronger interaction between  $C_2H_4$  guest molecules and the host network.



Fig. 7 a)  $C_2H_4$  adsorption-desorption isotherms of Pd-tapp-A4 and  $H_2$ tapp-A4 aerogels at 273 and 298 K, b) isosteric heats of adsorption ( $Q_{st}$ ) as a function of gas loading.



Fig. 8 a) Vapor sorption isotherms of methanol, benzene, cyclohexane and hexane for H<sub>2</sub>tapp-A4 aerogel at 298 K (Filled shapes represent adsorption and open shapes represent desorption).

**Organic vapour sorption.** To further study the adsorption properties, MeOH, benzene, cyclohexane and hexane vapour sorption was carried out for H<sub>2</sub>tapp-**A4** at 298 K (Fig. 8). MeOH sorption isotherm is type II and show maximum uptake of 181 cm<sup>3</sup> g<sup>-1</sup>, corresponding to 26 wt%. Benzene sorption isotherm is also type II and show maximum uptake of 174 cm<sup>3</sup> g<sup>-1</sup> (61

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wt%). The sorption capacity for benzene is remarkably higher than those for saturated hydrocarbons cyclohexane (51 cm<sup>3</sup> g<sup>-1</sup>, 19 wt%) and hexane (30 cm<sup>3</sup> g<sup>-1</sup>, 12 wt%). Both the desorption branches of MeOH and benzene do not trace the adsorption ones, leaving large hysteresis loops. Such behaviours may arise from favourable  $\pi$ - $\pi$  (H-bonding) interactions between guest benzene (MeOH) molecules and the aromatic (imine) framework. It may also be attributed to the unique features of the hierarchical imine aerogels.

## Catalytic gel microfluidic reactor

The hierarchically porous nature and the availability of metal centres of the present metalloporphyrin imine gels prompted us to investigate their catalytic activity. As a representative, Pd-tapp-**A4** gel was chosen and immobilized within the channels of a microfluidic flow reactor because a combination of gel catalysts and microfluidic techniques may significantly enhance the catalytic system.



Fig. 9 Schematic representation of setup of the catalytic gel microfluidic reactor using a capillary, and SEM images of a cross-section of the capillary (ID 0.53 mm) coated with Pd-tapp-A4 gel with about 2 μm thickness (bars represent 10.0 and 2.0 μm from left to right).

Pd-tapp-**A4** gel was introduced into a fused-silica capillary reactor via in situ gelation. First the surface of the inner wall of the capillaries was modified with amine groups in order to anchor the Pd-tapp-**A4** gel via imine bonding. Pd-tapp and **A4** precursors in the presence of AcOH catalyst reacted inside the capillary upon heating to form the Pd-tapp-**A4** gel. Following our previously reported strategy,<sup>6</sup> a gel layer with ca. 2 µm (evidenced by SEM) was successfully coated onto the capillary (Fig. 9).



Scheme 3 Suzuki-Miyaura cross-coupling of 4-bromoanisole and phenylboronic acid catalyzed by Pd-tapp-A4 gel in a capillary reactor.

The catalytic activity of the Pd-tapp gel microfluidic system was investigated in Suzuki-Miyaura cross-coupling<sup>31</sup> of 4-bromoanisole and phenylboronic acid as a model reaction (Scheme 3). Pd-tapp-**A4** gel was used as catalyst in DMF-H<sub>2</sub>O

(v:v = 1:1). DMSO solvent in the gel was exchanged to DMF prior to catalysis. The reaction system was assembled as shown in Fig. 9. Specifically a homogeneous DMF-H<sub>2</sub>O solution of 4-bromoanisole (0.05 mol  $L^{-1}$ ), benzeneboronic acid (0.075 mol  $L^{-1}$ ) and CsF (0.12 mol  $L^{-1}$ ) was introduced using a syringe pump and entered the capillary reactor. A capillary of 1000 mm long with 0.53 mm in diameter coated with 2 µm catalytic gel layer was used for the reactor. The reaction mixture was allowed to pass the capillary during a period of 30 min at 100 °C. The cross-coupling biaryl product was afforded in 85% yield for an aliquot of 50  $\mu$ L substrate solution. In addition, the present gel microfluidic reactor shows advantage in catalyst recovery and ready separation from the products. The reactor could be readily reused for the next run after flushing with DMF-H<sub>2</sub>O (1 mL  $\times$  3). No significant loss of reactivity was observed over at least five runs (Table S3).

The catalytic performance of the capillary reactor was compared to control experiments under batch conditions. Over a range of different Pd-tapp-A4 gel catalyst loading (0.5-10 mol%), optimal catalyst performance was found to be 1.0 mol% (Fig. S27). 34% yield was obtained after 30 min at 100 °C. After 2.0 h, 87% yield was achieved. However, further increasing of the gel catalyst amount did not improve the performance. The catalytic performance of the capillary reactor was also compared with that of Pd-tapp homogeneous precursor. Under homogeneous conditions (1.0% Pd-tapp), the cross-coupling biaryl product was obtained in only 15% yield after 30 min and 70% after 2.0 h (Fig. S27). In comparison, similar yields were achieved in much shorter reaction time under the gel-capillary flow reaction conditions (85% yield after 30 min). The faster reaction in the capillary reactor than those of the homogeneous and heterogeneous reactions should be contributed to the combination of gel catalysts with microfluidic technology.<sup>32</sup> Much larger surface area is exposed and the regents interact with a much larger proportion of the catalytic gel in the capillary reactor. Furthermore the rigid gel matrix with hierarchical porosity further improves mass transfer.

## Conclusions

In summary, a series of (metallo)porphyrin imine aerogels have been synthesized. The aerogels have sponge-like porous consisting of networked structures interconnected nanoparticles with hierarchical porosity. The aerogels have high specific surface areas (up to 719 m<sup>2</sup> g<sup>-1</sup>) and large pore volumes (up to 2.60  $\text{cm}^3 \text{g}^{-1}$ ). The effect of metal ions on the uptake of gases was investigated for these aerogels. The incorporation of divalent metal ions (Pd(II), Ni(II)) in the porphyrin-based imine aerogels does not change the porosity significantly, while impregnation of trivalent or tetravalent metal ions (Mn(III), Fe(III) and Sn(IV)) lowers the surface area of the aerogels. After incorporation of metal ions (Ni(II), Mn(III), Fe(III) and Sn(IV)), the initial affinity turns higher, while their CO<sub>2</sub> adsorption capacities does not change notably. Among the investigated metal ions, Pd(II) is the best to increase the CO<sub>2</sub> adsorption.Pd-tapp-A4 aerogel exhibits CO<sub>2</sub>

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volumetric uptake (1.62 mmol g<sup>-1</sup>, 7.13 wt% at 298 K, 1 bar; 2.39 mmol g<sup>-1</sup>, 10.5 wt% at 273 K) with high isosteric heat of adsorption (40.0 kJ mol<sup>-1</sup>). Pd-tapp-**A4** aerogel also shows improved adsorption capacities for H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. Vapour sorption shows that H<sub>2</sub>tapp-**A4** aerogel show good adsorption ability for both aromatic benzene and polar methanol at saturated vapour pressure and room temperature.

The present hierarchically porous gels are prepared under relatively mild synthesis conditions. It is thus possible to obtain some materials (e.g., free-base porphyrin porous materials) that are difficult to synthesize under other synthesis conditions (e.g., at higher temperature and/or in the presence of metal ions).<sup>33</sup> The unique hierarchical porosity of gels offers better diffusion channels for guest molecules than the related microporous materials (e.g., MOFs), which enhances mass transfer. Pd-tapp-A4 gel catalyst and microfluidic technique have been successfully combined in the catalytic gel microfluidic reactor. In the microfluidic reactor, a layer of Pdtapp-A4 gel is coated onto a functionalized capillary. In the gel capillary reactor similar yields were achieved in much shorter reaction time in Suzuki-Miyaura cross-coupling of 4bromoanisole and phenylboronic acid compared to the batch processes. These materials thus show potential applications not only in gas storage, but also in supported catalysis. The present strategy may help develop new metal-decorated polymeric materials.<sup>34</sup>

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A series of (metallo)porphyrin imine gels show tuneable gas adsorption and potential to assemble a catalytic gel capillary reactor.