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# A metal-organic framework constructed by a flexible tripodal ligand and tetranuclear copper cluster for sensing small molecules†

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**A new porous metal-organic framework (MOF)  $\{[\text{Cu}_4(\text{OH})_2(\text{tci})_2(\text{bpy})_2]\cdot 11\text{H}_2\text{O}\}$  (1) based on a tetranuclear copper cluster with intracluster antiferromagnetic interactions was synthesized. Quartz crystal microbalance (QCM) sensor studies reveal sensitive and selective sensing for small molecules.**

Metal-organic frameworks (MOFs) constructed from metal ions or metal clusters as nodes and multitopic organic ligands as linkers have received considerable attention not only because of their aesthetic appeal,<sup>1</sup> but also because of their potential applications in sensor, gas storage, separation and drug delivery.<sup>2</sup> These functions of MOFs mainly depend on the pore size and shape, pore surface characteristics such as hydrophilicity/hydrophobicity and chirality.<sup>3</sup> However, how to control synthesis of MOFs with expected structures and properties is still a formidable challenge for chemists. It is well known that a better strategy is using functional organic ligands to introduce guest-accessible sites on the pore surface.<sup>4</sup> The tripodal ligand, tri(2-carboxyethyl)-isocyanurate ( $\text{H}_3\text{tci}$ ) as a highly flexible polycarboxylate ligand has three freely rotatable  $-\text{CH}_2\text{CH}_2\text{COOH}$  arms and three secondary functional groups ( $-\text{C}=\text{O}$ ), which make it a good candidate for constructing diverse MOFs with oxygen-rich channels,<sup>5</sup> these MOFs could be the potential sensors for sensing small solvent molecules by H-bond interactions. For sensing materials, pore-surface functionalization and sensitive signal transduction when contacting to an analyte are very important. Quartz crystal microbalance (QCM) as a sensor device is one of mass sensitive device and could act as a suitable platform for detection of the sorption/desorption behaviour of porous materials toward an analyte vapour, its excellent selectivity and sensitivity to an analyte vapour are highly dependent on the chemical natures and physical properties of the materials.<sup>6</sup>

Herein, we selected the flexible  $\text{H}_3\text{tci}$  as a main ligand to synthesize new MOF, in order to increase the stability of the skeleton, the auxiliary rigid 4,4'-bipyridine (bpy) ligand was introduced into the synthesis process. A new 3D MOF  $\{[\text{Cu}_4(\text{OH})_2(\text{tci})_2(\text{bpy})_2]\cdot 11\text{H}_2\text{O}\}$  (1) with O-rich channels was obtained. To the best of our knowledge, this is an example of

having the largest pore volume of MOF based on tci ligand, which reveals highly sensitive sensing for small molecules.

An acetone solution (6 mL) containing  $\text{Cu}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (0.2 mmol) was layered upon an aqueous solution (4 mL) containing  $\text{H}_3\text{tci}$  (0.1 mmol), 4,4'-bipy (0.1 mL) and triethylamine (60  $\mu\text{L}$ ) in test tube, blue block crystals of **1** were collected in two weeks. Thermogravimetry analysis of **1** reveals all guest water molecules are released under 120 °C, with a mass loss of approximately 12.58 % (cal. 13.36 %), and no further loss up to 250 °C, then the framework gradually collapses with increasing temperature (Fig. S11). The X-ray powder diffraction (PXRD) pattern of as-synthesized matched the simulated pattern well, indicating the polycrystalline sample is pure phase, in addition, the PXRD patterns of acetone-activated samples and dehydrated samples obtained by heating at 100 °C in vacuo indicate that the framework can maintain good crystallinity (Fig. S8).

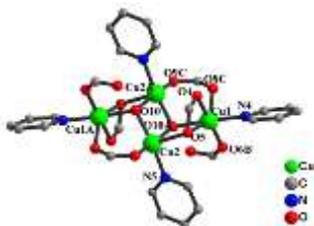
Single-crystal X-ray structural analysis reveals that **1** crystallizes in the monoclinic space group  $C2/c$ . The asymmetric unit consists of two  $\text{Cu}^{2+}$  ions, one tci ligand, one  $\mu_3\text{-OH}$ , two half-bpy ligands and some free water molecules. As shown in Fig. 1, in the tetranuclear copper cluster motif, two crystallographically independent  $\text{Cu}^{2+}$  centers that exhibit two different coordination geometry are connected by two  $\mu_3\text{-OH}$  and four carboxylate groups from four tci ligands to form a quasi-butterfly tetranuclear copper cluster with  $\text{Cu1-O5-Cu2}$ ,  $\text{Cu1-O10A-Cu2A}$  and  $\text{Cu2-O10-Cu2A}$  bond angle of 80°, 106° and 99°, respectively,  $\text{Cu1}\cdots\text{Cu2}$  and  $\text{Cu2}\cdots\text{Cu2A}$  distance of 3.321 Å and 3.013 Å, respectively. Cu1 is six-coordinated by four carboxylate oxygen atoms from three individual tci ligands, one  $\mu_3\text{-OH}$  group and one N atom from one bpy ligand with  $\text{Cu-O/N}$  bond lengths in the normal range of 1.959 - 2.202 Å except a weak coordination of  $\text{Cu1-O5}$  with bond length of 2.717 Å. Cu2 locates in a trigonal-bipyramidal coordination geometry from two carboxylate oxygen atoms from two distinct tci ligands, two  $\mu_3\text{-OH}$  groups and one N from one bpy ligand. The tci ligand exhibits the *cis-cis-trans* chair-conformation, three carboxyl groups of the ligand are deprotonated and adopt a pentadentate coordination mode in which one carboxylate group shows a  $\mu_1\text{-}\eta^1$  fashion, another one adopts *syn-syn*- $\mu_2\text{-}\eta^1\text{:}\eta^1$  mode, the third carboxylate group takes  $\mu_2\text{-}\eta^1\text{:}\eta^2$  mode (Fig. S1). Three flexible arms of the tci ligand bridge three tetranuclear copper clusters along three different directions, while each copper cluster connects six tci ligands, which finally results in a 3D structure (Fig. S2, left), then the 3D framework is further reinforced by the coordinated bpy ligands (Fig. S3, right). The resultant 3D framework contains two types of channel with different sizes along the *c*-axis (Fig. 2a). The smaller channels are occupied by the centrosymmetric ( $\text{H}_2\text{O}$ ),

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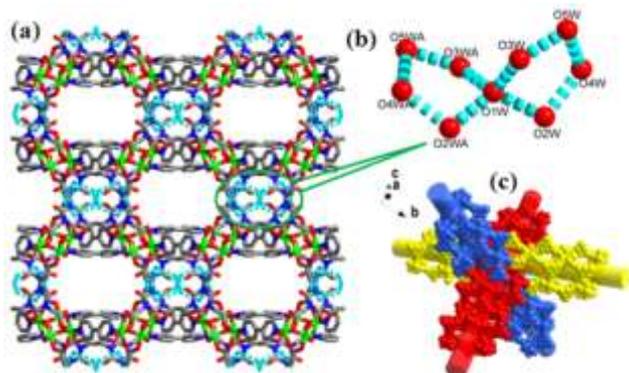
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† Electronic Supplementary Information (ESI) available: Experimental details, crystallographic data, hydrogen bond parameters for water cluster, and additional structural figures. FT-IR spectra, PXRD patterns, thermogravimetry analysis data, field-dependent magnetizations,  $\text{N}_2$  adsorption and desorption isotherms, the electrode structure of QCM. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x.

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**Fig. 1** Coordination environment of Cu<sup>2+</sup> centers in a teteannuclear copper unit.

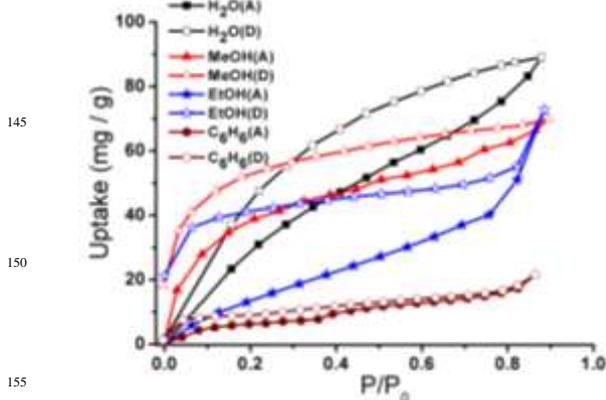


**Fig. 2** (a) Perspective view of 3D framework of **1** along the *c* axis, (b) nine nuclear water cluster and (c) schematic view of 3D interweaving channels.

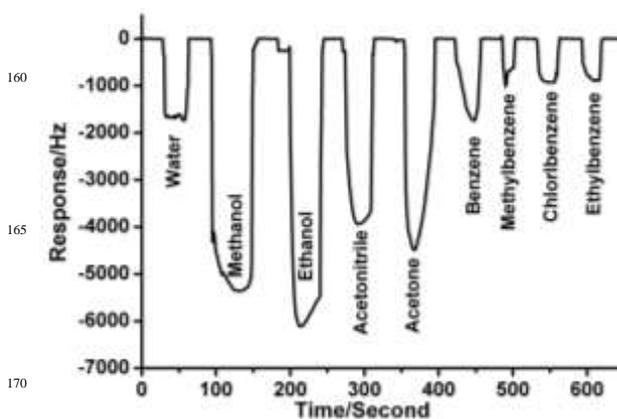
clusters which contain two pentamer water rings. In the (H<sub>2</sub>O)<sub>9</sub> cluster, O1W, O2W, O3W, O4W and O5W are hydrogen-bonded to their equivalents derived by a crystallographic inversion center to form a (H<sub>2</sub>O)<sub>9</sub> water cluster (Fig. 2b). In addition, some disordered water molecules locate in the bigger channels. The size of small channels and big channels is 3.36×10.58 Å and 11.21×12.45 Å (measured between opposite atoms), respectively. It should be noted that this framework contains three-dimensional interweaving channels which lead to shrinkage of the void space (Fig. 2c). After removing all of the guest water molecules from the channels, the total accessible volume is 55.1 % per unit cell volume calculated by PLATON.<sup>7</sup>

Taking into account of the O-rich ligands and bpy ligands in the walls of the channels, compound **1** could easily adsorb polar solvent molecules and aromatic molecules. Water, methanol, ethanol and benzene vapour sorption isotherms for compound **1** were measured at 298 K. As shown in Figure 3, compound **1** shows obvious hydrophilic affinity to the polar molecules, the adsorbed amount of water, methanol and ethanol gradually increases with increasing pressure, and the maximum uptake is 89 mg/g (7.3 H<sub>2</sub>O molecules per formula unit) for H<sub>2</sub>O, 70 mg/g (3.2 methanol molecules per formula unit) for methanol and 73 mg/g (2.4 ethanol molecules per formula unit) for ethanol at *P/P*<sub>0</sub> = 0.9, respectively. All of these adsorption behaviours fit to a type II isotherm, indicating unrestricted monolayer-multilayer adsorption. In the desorption process, the isotherm profile shows a hysteresis loop for water, non-closing hysteresis for methanol and ethanol, respectively, which can be attributed to the H<sub>4</sub> type hysteresis corresponding to narrow slit-like pores.<sup>8</sup> By contrast, at *P/P*<sub>0</sub> = 0.9, compound **1** shows a maximum uptake of 21 mg/g (0.4 benzene molecules per formula unit) for benzene vapour, the

value is much lower than that for polar small molecules, and the benzene adsorption maybe result from π-π interactions between host and guest. In fact, the small channel in **1** is hydrophilic because many carbonyl oxygen atoms of the tci expose on the pore surface, while the big channel is polar and non-polar coexistence resulted from carbonyl oxygen atoms of the tci and bpy ligands on the pore surface (Fig. 2a). The significantly different sorption capacities between polar small molecules and benzene vapour could be attributed to the fact that strong H-bond interactions formed between polar small molecule and pore surface, and the size exclusion caused by relatively small interweaving channels and larger size of benzene molecule.



**Fig. 3** The adsorption (A) and desorption (D) isotherms of water, methanol, ethanol and benzene at 298 K for **1**.



**Fig. 4** Frequency response curves of compound **1** based QCM sensor to a variety of solvent vapours at air condition (298K, 65% RH).

In order to further investigate the hydrophilic property of the pores and possible potential sensing applications, **1**-based QCM sensor was used to evaluate the response to several polar small molecules and aromatic molecules. When QCM sample sensor is exposed to an analyte vapour, the resonant frequency decreases proportionately with an increase of mass on the QCM electrode according to the Sauerbrey equation.<sup>9</sup> As shown in Figure 4, **1**-based QCM sensor was exposed to a variety of solvent vapours displaying a higher response value of 5300 Hz for methanol, 6100 Hz for ethanol, 3900 Hz for acetone, 4400 Hz for acetonitrile and 1600 Hz for water in air condition (298K, 65 % relative humidity), while for non-polarity aromatic molecules of benzene, methylbenzene, ethylbenzene and chlorobenzene, the frequency

response value is much lower, respectively. These results indicate compound **1** as potential sensor has high response and good selectivity to polar small molecules. Here, in order to evaluate the adsorption capacity of a variety of solvent vapours for compound **1**, we assume that the relative quantity of adsorbed water molecule is 1, then methanol is 1.71, ethanol is 1.36, acetone is 0.98, acetonitrile is 0.79, benzene, methylbenzene, ethylbenzene and chlorobenzene are 0.23, 0.09, 0.08 and 0.07 (Fig. S6). The frequency shift value and adsorption capacity for water are relative lower than those for methanol and ethanol, which may be due to the influence of air humidity.

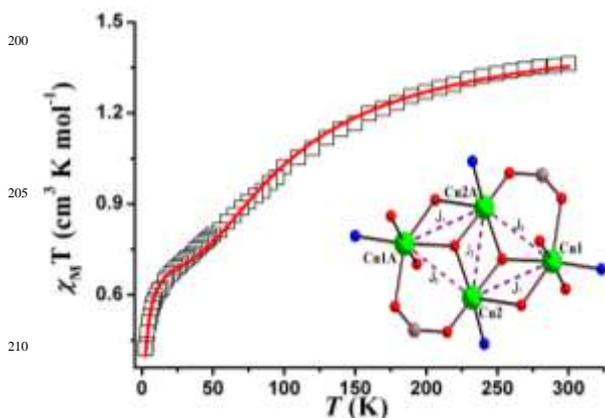


Fig. 5 Plots of  $\chi_M T$  vs.  $T$  for **1** under applied field of 2 kOe. The solid lines represent the theoretical fitting.

Magnetic susceptibilities of **1** were measured under fields of 2 kOe in the temperature range of 2–300 K (Fig. 5). The observed  $\chi_M T$  value at room temperature is  $1.36 \text{ cm}^3 \text{ K mol}^{-1}$ , which is a little less than the theoretical values of  $1.5 \text{ cm}^3 \text{ K mol}^{-1}$  for four uncoupled  $\text{Cu}^{2+}$  ions. Upon cooling, the  $\chi_M T$  value gradually decreases and reaches a value of  $0.65 \text{ cm}^3 \text{ K mol}^{-1}$  at 16 K, and then rapidly decreases to  $0.42 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K, which indicates strong  $\text{Cu}^{2+}\cdots\text{Cu}^{2+}$  antiferromagnetic interactions in **1**. The data above 100 K fit well with the Curie-Weiss law to give  $C = 1.45 \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = -28.61 \text{ K}$ . The negative Weiss constant indicates antiferromagnetic interactions between copper (II) centers in **1**. In order to further study the interactions between the copper centers, the  $\chi_M T$ - $T$  data was fitted to the theoretical expression for quasi-butterfly  $\text{Cu}_4$  model ( $J_1, J_2, J_3$ ),<sup>10</sup> to give  $J_1 = 3.83 \text{ cm}^{-1}$ ,  $J_2 = -67.60 \text{ cm}^{-1}$ ,  $J_3 = -1.18 \text{ cm}^{-1}$ , and  $g = 2.22$ . The positive  $J_1$  value indicates weak ferromagnetic interaction between Cu1 and Cu2 as well as Cu1A and Cu2A, resulting from small bond angle of  $80^\circ$  for Cu1-O<sub>carboxylate</sub>-Cu2, the large  $J_2$  is negative value, indicating strong antiferromagnetic interaction for Cu2-Cu2A mediated via two OH, while  $J_3$  is also negative value, illustrating the couplings between Cu1 and Cu2A as well as Cu1A and Cu2 are also antiferromagnetic.<sup>11</sup> Due to the dominant antiferromagnetic interactions in  $\text{Cu}_4$  cluster, the overall antiferromagnetic coupling is exhibited in compound **1**.

In conclusion, we have designed and synthesized a new porous MOF based on a flexible tripodal ligand and tetranuclear copper cluster with intracluster dominant antiferromagnetic interactions. This MOF has the largest void space for tci ligand and shows hydrophilic affinity to the polar small molecules by H-bond interactions. **1**-based QCM sensor studies reveal high sensitivity

and good selectivity toward methanol, ethanol, acetone and acetonitrile vapours in atmospheric condition, which indicates **1** could be the potential sensor for detection of polar solvent vapours in air.

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## Notes and references

§Crystal data for **1**:  $\text{C}_{44}\text{H}_{64}\text{N}_{10}\text{O}_{31}\text{Cu}_4$ ,  $M = 1483.21$ , monoclinic, space group  $C2/c$ ,  $a = 22.877(3) \text{ \AA}$ ,  $b = 23.111(3) \text{ \AA}$ ,  $c = 18.364(2) \text{ \AA}$ ,  $\beta = 105.399(2)^\circ$ ,  $V = 9361(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 296 \text{ K}$ ,  $R_1 (I > 2\sigma) = 0.0828$  and  $wR_2$  (all data) = 0.3120 for 29263 reflections collected, 6485 observed reflections ( $I > 2\sigma(I)$ ) of 10755 ( $R_{\text{int}} = 0.0663$ ) unique reflections and 399 parameters, GOF = 1.069. CCDC reference number: 1042356.

- (a) M. Li, D. Li, M. O'Keefe and O. M. Yaghi, *Chem. Rev.*, 2014, **114**, 1343; (b) H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673; (c) N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933.
- (a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (b) M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, **112**, 782; (c) S. Chaemchuen, N. A. Kabir, K. Zhou and F. Verpoort, *Chem. Soc. Rev.*, 2013, **42**, 9304; (d) A. Dhakshinamoorthy and H. Garcia, *Chem. Soc. Rev.*, 2012, **41**, 5262; (e) R. Yun, Z. Lu, Y. Pan, X. You and J. Bai, *Angew. Chem. Int. Ed.*, 2013, **52**, 11282; (f) J. Heine and K. Muller-Buschbaum, *Chem. Soc. Rev.*, 2013, **42**, 9232; (g) D. Liu, K. Lu, C. Poon and W. Lin, *Inorg. Chem.* 2014, **53**, 1916.
- (a) L. Pan, B. Parker, X.-Y. Huang, D. H. Olson, J.-Y. Lee and J. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4180; (b) Q. Han, C. He, M. Zhao, B. Qi, J. Niu and C. Duan, *J. Am. Chem. Soc.* 2013, **135**, 10186; (c) S. J. Lee and W. Lin, *Acc. Chem. Res.*, 2008, **41**, 521; (d) Z. Lu, H. Xing, R. Sun, J. Bai, B. Zheng and Y. Li, *Cryst. Growth Des.*, 2012, **12**, 1081.
- (a) O. Ohmori, M. Kawano and M. Fujita, *J. Am. Chem. Soc.*, 2004, **126**, 16292; (b) S. K. Ghosh, S. Bureekaew and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2008, **47**, 3403; (c) Z.-Z. Lu, R. Z., Y.-Zhi. Li, Zi.-J. Guo and H.-G. Z., *J. Am. Chem. Soc.*, 2011, **133**, 4172; (d) Z. J. Lin, J. Lu, M. Hong and R. Cao, *Chem. Soc. Rev.*, 2014, **43**, 5867; (e) L. Du, Z. Lu, K. Zheng, J. Wang, X. Zheng, Y. Pan, X. You and J. Bai, *J. Am. Chem. Soc.*, 2013, **135**, 562.
- (a) S. K. Ghosh, J. P. Zhang and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2007, **46**, 7965; (b) S. K. Ghosh, W. Kaneko, D. Kiriya, M. Ohba and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2008, **47**, 8843; (c) P. Cui, J. Wu, X. Zhao, D. Sun, L. Zhang, J. Guo and D. Sun, *Cryst. Growth Des.*, 2011, **11**, 5182; (d) Z.-B. Han, Guo.-X. Zhang, M.-H. Zeng, D.-Q. Yuan, Q.-R. Fang, J.-R. Li, J. Ribas and H.-C. Zhou, *Inorg. Chem.*, 2010, **49**, 769; (e) H. Li, B. Zhao, R. Ding, Y. Jia, H. Hou and Y. Fan, *Cryst. Growth Des.*, 2012, **12**, 4170; (f) Q. Zhu, C. Shen, C. Tan, T. Sheng, S. Hua and X. Wu, *Dalton Trans.*, 2012, **41**, 9604; (g) Z.-B. Han, M.-Y. Zhang, D.-Q. Yuan, S. Fu, G.-X. Zhang and X.-F. Wang, *CrystEngComm*, 2011, **13**, 6945.
- (a) Y. Fu and H. O. Finklea, *Anal. Chem.*, 2003, **75**, 5387; (b) M. M. Ayad, G. El-Hefnawey and N. L. Torad, *J. Hazard. Mater.*, 2009, **168**, 85; (c) Q. Zheng, Y. Zhu, J. Xu, Z. Cheng, H. Li and X. Li, *J. Mater. Chem.*, 2012, **22**, 2263.
- PLATON: A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- (a) T. F. Liu, J. Lu, X. Lin and R. Cao, *Chem. Commun.*, 2010, **46**, 8439; (b) D. Tanaka, A. Henke, K. Albrecht, M. Moeller, K. Nakagawa, S. Kitagawa and J. Groll, *Nat. Chem.*, 2010, **2**, 410.
- (a) L. Kong, J. Wang, T. Luo, F. Meng, X. Chen, M. Li and J. Liu, *Analyst*, 2010, **135**, 368; (b) X.-L. Hu, F.-H. Liu, H.-N. Wang, C. Qin, C.-Y. Sun, Z.-M. Su and F.-C. Liu, *J. Mater. Chem. A*, 2014, **2**, 14827.
- (a) Y. F. Song, C. Massera, O. Roubeau, P. Gamez, A. M. M. Lanfredi and J. Reedijk, *Inorg. Chem.*, 2004, **43**, 6842; (b) F. Yu and B. Li, *CrystEngComm*, 2011, **13**, 7025.

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- 11 (a) Y.-L. Bai, V. Tangoulis, R.-B. Huang, L.-S. Zheng and J. Tao, *Chem. Eur. J.*, 2009, **15**, 2377; (b) Y.-F. Zeng, F.-C. Liu, J.-P. Zhao, S. Cai and X.-H. Bu, J. Ribas, *Chem. Commun.*, 2006, 2227.

315 *Graphical Abstract*

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