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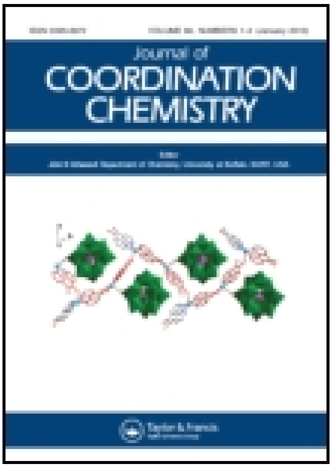

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Accepted author version posted online: 17 Sep 2014.Published online: 07 Oct 2014.

To cite this article: Bin Wang, Ya-Bo Xie, Hui Yang, Ming Li & Jian-Rong Li (2014) A fluorescent 3-D metal-organic framework with unusual tetranuclear zinc secondary building units, Journal of Coordination Chemistry, 67:21, 3484-3491, DOI: 10.1080/00958972.2014.965698

To link to this article: http://dx.doi.org/10.1080/00958972.2014.965698

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Journal of Coordination Chemistry, 2014
Vol. 67, No. 21, 3484–3491, http://dx.doi.org/10.1080/00958972.2014.965698

A fluorescent 3-D metal-organic framework with unusual tetranuclear zinc secondary building units

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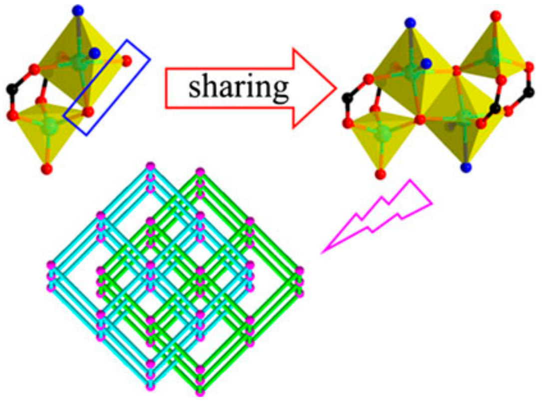
(*Received 25 January 2014; accepted 15 July 2014*)



A 3-D metal-organic framework (MOF) $\{Zn_4(\mu_3\text{-}OH)_2(bdc)_3(pad)_2\}\cdot 2H_2O$ (**1**, H_2bdc = 1,4-benzenedicarboxylic acid, pad = 1,10-phenanthroline-5,6-dione) with unusual $Zn_4(\mu_3\text{-}OH)_2(COO)_6(N_2)_2$ secondary building units (SBUs) has been hydrothermally synthesized and characterized by single crystal X-ray diffraction, powder X-ray diffraction, thermogravimetric analysis, elemental analysis, and infrared spectroscopy. The tetranuclear Zn_4 SBU was formed through two dinuclear Zn_2 clusters by sharing two μ_3-OH bridges. Considering this Zn_4 SBU as a six-connected node, the overall framework of **1** has a *pcu* topology. This tetranuclear Zn_4 SBU can be used as a node in construction of MOFs.

Keywords: Metal-organic framework; Zn_4 SBUs; Crystal structure; *pcu* Topology

1. Introduction

Construction of metal-organic frameworks (MOFs) has attracted attention due to fascinating architectures and intriguing topologies [1] as well as potential applications in gas storage and separation [2], sensing [3], and heterogeneous catalysis [4]. These extended networks

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are comprised of metal ions or polynuclear units linked by organic ligand bridges and assembled principally through strong coordination bonds.

Usually, in the design and construction of MOFs, one of the powerful and effective synthetic ways is to replace a vertex in a network by a clustered metal-ligands entity as a secondary building unit (SBU) [1b]. For instance, because zinc(II) can adopt different coordination modes, various polynuclear units were observed when assembling with di- or multi-carboxylate and/or N-donor ligands such as the dinuclear paddlewheel $[Zn_2(camph)_2(py)_2]$ (H_2camph = (1R,3S)-(+)-camphoric acid, py = pyridine) [5], the trinuclear $[Zn_3(4,4'\text{-adb})_3(bib)_2]$ (4,4′-adb = azobenzene-4,4′-dicarboxylic acid, bib = 1,4-bis(2-methyl-imidazol-1-yl)butane) [6], the tetranuclear $[Zn_4O(bdc)_6]$ (H_2bdc = terephthalic acid) [7], the pentanuclear $[Zn_5(\mu_3\text{-}O)_2(bpdc)_4(dmf)_2(EtOH)_2]$ [8], (bpdc = 4,4′-biphenyldicarboxylate, dmf = *N,N*-dimethylformamide), the hexanuclear $[Zn_6(ndc)_5(OH)_2(dmf)_2]$ (ndc = 1,4-naphthalenedicarboxylate) [9], the heptametallic $[Zn_7O_2(pda)_5(H_2O)_2]$ (H_2pda = p-phenylenediacrylic acid) [10], and the octanuclear $[Zn_8(\mu_3\text{-}OH)_4(oba)_6(bbi)(H_2O)_2]$ (H_2oba = 4,4′-oxybis(benzoate), bbi = 1,1-(1,4-butanediyl)bis(imidazole)) [11]. These results showed that various MOFs can be obtained by use of different clusters.

Considering that SBUs act as nodes in a MOF and organic ligands act as edges, the complicated structure can be simplified and identified by three-letter topology symbol such as *pcu*, *dia*, *nbo,* and *ncb*. In an ideal primitive cubic *pcu* net (Schläfli symbol, $4^{12}\cdot 6^3$), there is one kind of vertex and one kind of edge, and one vertex connects with six adjacent vertices through edges. Single metal ions or metal clusters of Cu_2, Zn_4 or Ln_4 incorporating different linear organic ligands have been used to construct various octahedral *pcu* nets.

Herein, a MOF with a twofold interpenetrated *pcu* topological structure was assembled by 1,4-benzenedicarboxylic acid (H_2bdc) with Zn ion by employing 1,10-phenanthroline-5,6-dione(pad). An unusual tetranuclear SBU $Zn_4(\mu_3\text{-}OH)_2(COO)_6(N_2)_2$ was found in the structure. Generally, in the construction of mixed linker MOFs, linear ligands are more promising because they tend to form MOFs with regular pores. In our case, however, angular N-donor ligand pad was used, and it is coordinated with the Zn2 center, preventing further coordination of bdc ligands with Zn centers, being important in the formation of dinuclear SBUs. Two adjacent dinuclear SBUs are combined to form tetranuclear SBUs by sharing two μ_3-OH. To the best of our knowledge, this kind of SBU is rare, and the tetranuclear Zn_4 SBU presented here has never been reported. This tetranuclear Zn_4 SBU can be used as a node in the construction of MOFs.

2. Experimental

2.1. *Materials and instrumentation*

All general reagents and solvents (AR grade) were commercially available and used as received. Elemental analysis (EA) were performed by Atlantic Microlab, Inc. FT-IR data were recorded on an IRAffinity-1 instrument. Thermogravimetric analysis (TGA) data were obtained on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 10 °C min^{-1} under N_2. Powder X-ray diffraction patterns (PXRD) were recorded on a BRUKER D8-Focus Bragg–Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$) at room temperature. Simulation of the PXRD spectrum was carried out by single-crystal data and diffraction-crystal module of the *Mercury* program.

Fluorescence spectra were obtained in the solid state on a Perkin-Elmer LS-50b luminescence spectrometer.

2.2. *Preparation of {$Zn_4(\mu_3\text{-}OH)_2(bdc)_3(pad)_2$}·$2H_2O$ (1)*

The mixture of $ZnCl_2 \cdot 2H_2O$ (0.5 mM, 0.085 g), H_2bdc (0.5 mM, 0.083 g), pad (0.2 mM, 0.042 g), and 10 mL H_2O was sealed in a 20 mL vial and heated to 160 °C for 2 days. The reaction mixture was cooled to room temperature and washed by ethanol, giving dark-yellow block crystals (66% yield). EA for **1**, $C_{48}H_{30}N_4O_{20}Zn_4$ (1244.24): Calcd C, 46.34; H, 2.43; N, 4.50. Found. C, 46.57; H, 2.23; N, 4.21. FTIR (KBr pellets): 3100(w), 1590(s), 1500(m), 1450(s), 1360(s), 810(m), 754(m), 696(m).

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction data were collected on a Bruker-AXS APEX-II CCD X-ray diffractometer equipped with a low temperature device and a fine-focus sealed-tube X-ray source (graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, ω-scans with a 0.5° step). Suitable single crystals were directly picked from the mother liquor, attached to a glass loop and transferred to a designed cold stream of liquid nitrogen (110K) for data collections. Raw data collection and reduction were done using APEX2 software [12a]. Absorption corrections were applied using SADABS [12b]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the SHELXTL software package [12c]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogens of ligands were calculated in ideal positions with isotropic displacement parameters. The relevant

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{24}H_{15}Zn_2N_2O_{10}$
Formula weight	622.12
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	13.8660(16)
b (Å)	18.942(2)
c (Å)	19.033(2)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	4998.9(10)
Z	8
Calculated density (mg m^{-3})	1.653
Independent reflections ($I > 2\sigma(I)$)	4393
F (000)	2504
θ range for data collection	2.15–24.68
Limiting indices	$-10 \le h \le 16$ $-22 \le k \le 21$ $-22 \le l \le 21$
Goodness-of-fit on F^2	1.022
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	$R_1 = 0.0378$, $wR_2 = 0.0834$
R_1[a], wR_2[b] (all data)	$R_1 = 0.0772$, $wR_2 = 0.1032$
Largest diff. peak and hole (e Å^{-3})	1.049 and −0.471

[a] $R_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$.

[b] $wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Zn(1)–O(6)^{i}	1.913(03)	Zn(1)–O(1)	1.962(03)
Zn(1)–O(7)	1.957(03)	Zn(1)–O(3)	1.967(03)
Zn(2)–O(4)	2.075(03)	Zn(2)–N(1)	2.167(04)
Zn(2)–O(2)	2.096(03)	Zn(2)–N(2)	2.187(04)
Zn(2)–O(7)	2.098(03)		
O(6)^{i}–Zn(1)–O(7)	120.40(15)	O(7)–Zn(1)–O(3)	108.31(14)
O(6)^{i}–Zn(1)–O(1)	99.79(15)	O(1)–Zn(1)–O(3)	103.23(14)
O(7)–Zn(1)–O(1)	110.68(14)	O(6)^{i}–Zn(1)–Zn(2)	159.17(12)
O(6)^{i}–Zn(1)–O(3)	112.82(15)	O(7)–Zn(1)–Zn(2)	40.48(09)
O(4)–Zn(2)–O2)	91.87(14)	O(4)–Zn(2)–N(1)	94.09(14)
O(4)–Zn(2)–O(7)	92.46(13)	O(2)–Zn(2)–N(1)	88.13(14)
O2)–Zn(2)–O(7)	95.29(13)	O(7)–Zn(2)–N(1)	172.51(14)
O(4)–Zn(2)–N(2)	86.52(14)	O(2)–Zn(2)–N(2)	162.79(14)

Note: Symmetry transformations used to generate equivalent atoms: (i) x, $-y + 3/2$, $z + 1/2$.

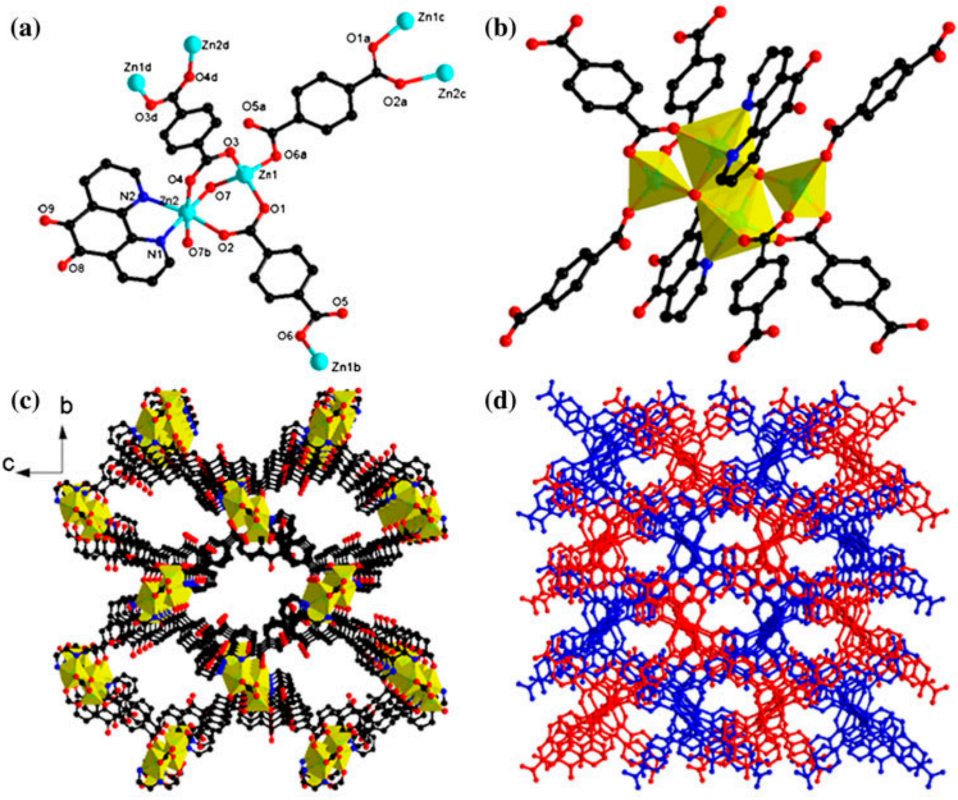

Figure 1. The structural presentation of **1** (all hydrogens are omitted for clearly): (a) The coordination environment of Zn^{2+}, bdc^{2-} and pad ligands (symmetry codes: a: x, $1.5 - y$, $0.5 + z$; b: $2 - x$, $2 - y$ $1 - z$; c: x, $1.5 - y$, $-0.5 + z$; d: $1 - x$, $2 - y$, $1 - z$); (b) The 6-connected tetrameric $Zn_4(\mu_3\text{-OH})_2(COO^-)_6(N)_2$ SBU; (c) View of the single open framework in **1** along the *a axis*, showing large elliptical channels; and (d) View of the 3-D framework of **1** along the *a axis*, showing twofold interpenetration of the network.

crystallographic data are presented in table 1, while selected bond lengths and angles are summarized in table 2.

3. Results and discussion

3.1. *Crystal structure of 1*

Compound **1** was hydrothermally synthesized by employing $ZnCl_2\cdot 2H_2O$, H_2bdc, and pad in H_2O at 160 °C for 2 days. Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the centrosymmetric orthorhombic space group *Pbca* and possesses an extended 3-D framework (figure 1). There are two types of coordination environments around zinc. One zinc (Zn_1) adopts distorted tetrahedral geometry by coordinating to three oxygens (O1, O3, O6a) from three carboxylates of three *bdc* ligands and O7 from the μ_3-OH [figure 1(a)]. The Zn1–O bond distances are 1.957–1.967(3) Å. Another zinc (Zn_2) adopts distorted octahedral geometry coordinated by O4 and O2 from two carboxylates of two bdc ligands, O7 and O7b from μ_3-OH and N1 and N2 atoms from one pad. The Zn2–N bond distances are 2.167(4) (Zn2–N1) and 2.187(4) (Zn2–N2) Å and the Zn2–O bond distances are 2.075–2.098(3) Å. These values are comparable to reported zinc complexes [13].

Bdc can be classified into two kinds of coordination modes. One adopts μ_3-bridge (O1, O2, O6) with O5 left uncoordinated, another adopts μ_4-bridge model by its four carboxylate oxygens (O3, O4, O3d and O4d). The pad adopts chelating coordination with Zn2.

An unprecedented tetranuclear $Zn_4(\mu_3\text{-}OH)_2(COO)_6(N_2)_2$ SBU was observed in **1** [figure 1(b)]. Zn_1 and Zn_2 are bridged by three carboxylates, two nitrogens, and one μ_3-OH to form a dinuclear $Zn_2(\mu_3\text{-}OH)(COO)_3(N_2)$ SBU [figure 1(a)]. Next, two such dinuclear SBUs combine to form a tetranuclear $Zn_4(\mu_3\text{-}OH)_2(COO)_6(N_2)_2$ SBU by sharing two μ_3-OH [figure 1(b)]. Finally, the tetranuclear SBUs are further connected by bdc to form a 3-D framework with interesting ellipse nanotube channels along the *a* axis, which shows large dimension about 9.5 × 16.1 $Å^2$ (the distance between the atoms) [figure 1(c)]. Furthermore, two such frameworks are mutually interpenetrated [figure 1(d)].

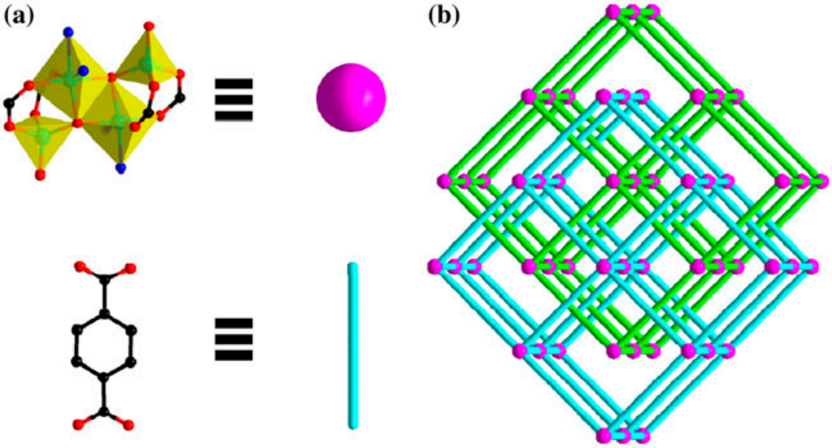

Figure 2. (a) The defined 6-connected nodes and linear connector; (b) Topological representation of two interpenetrating *pcu* nets of **1**.

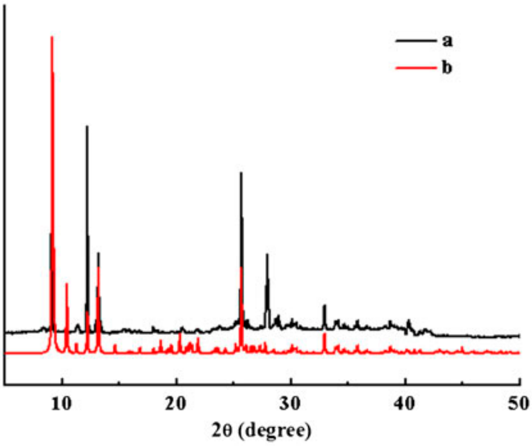

Figure 3. The PXRD patterns of **1**: (a, black) experimental; (b, red) simulated (see http://dx.doi.org/10.1080/00958972.2014.965698 for color version).

To simplify the structure, the tetranuclear $Zn_4(\mu_3\text{-}OH)_2(COO)_6(N_2)_2$ SBU can be considered as a six-connected node and the bdc ligands can be treated as the linker [figure 2(a)]. In this way, the 3-D framework of **1** can be simplified as a twofold interpenetrated *pcu* net [figure 2(b)] [14–16].

3.2. *PXRD analysis*

The phase purity of as-synthesized samples of **1** has been characterized by PXRD (figure 3). The experimental PXRD patterns correspond well with the pattern simulated from the single-crystal data, indicating the pure phase of **1**. The difference in reflection intensities between the simulated and experimental patterns may be due to variation in preferred orientation of the powder samples during collection of the experimental PXRD data.

3.3. *Thermal analysis*

TGA (figure 4) in N_2 atmosphere with a heating rate of 10 °C min^{-1} was performed on polycrystalline sample to determine thermal stability from 25 to 600 °C. TGA on the as-synthesized sample of **1** indicated that the host framework was stable to *ca.* 270 °C. After that temperature, the framework decomposed.

3.4. *Photoluminescence properties*

Previous studies have shown that metal–organic coordination polymers, especially zinc and cadmium carboxylate compounds, exhibit photoluminescence properties [17]. The emission spectrum of **1** was measured in the solid state at room temperature. It exhibits intense emission at 385 nm upon photo excitation at 382 nm [figure 5(a)]. In comparison, free H_2bdc also shows emission peak at 385 nm upon excitation at 382 nm, but free pad shows different photoluminescent phenomena upon excitation at 444 nm [figure 5(b) and (c)]. The emission of **1** is assigned tentatively to intra H_2bdc ligand charge transfer [18].

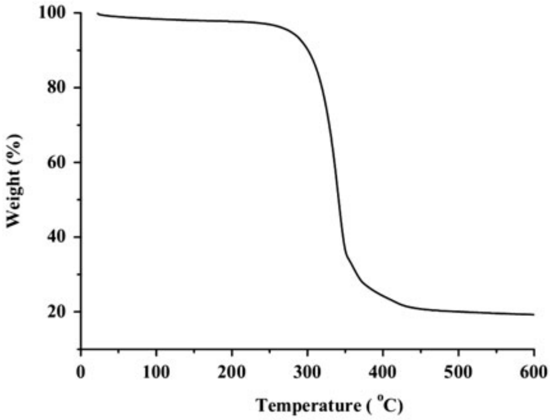

Figure 4. The TGA curve of **1**.

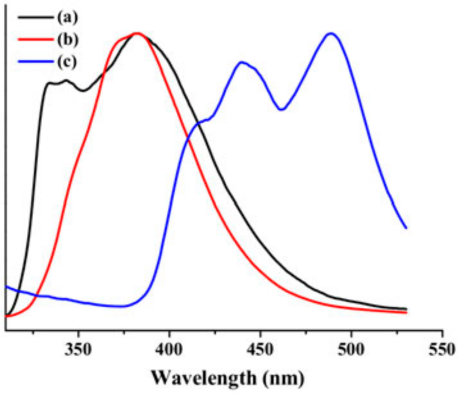

Figure 5. The solid-state emission spectra of **1** (a, black), free H_2bdc (b, red) and free pad (c, blue) ligand at room temperature (see http://dx.doi.org/10.1080/00958972.2014.965698 for color version).

4. Conclusion

We presented a two-fold interpenetrated MOF with a six-connected *pcu* topology based on $Zn_4(\mu_3\text{-OH})_2(COO)_6(N_2)_2$ building blocks. Each of such tetranuclear SBU can be considered as the unity of two adjacent dinuclear $Zn_2(\mu_3\text{-OH})_2(COO)_3(N_2)$ units by sharing two μ_3-OH entities. Zn_4 SBUs play important roles in the construction of MOFs, for example, Zn_4O SBU was used to construct well-known MOF-5. So far, numerous Zn_4 SBUs were used to construct MOFs with charming structure or remarkable properties [19, 20]. Our work expands the scope of Zn_4 SBUs and this new tetranuclear SBU can be considered as a promising node in construction of new MOFs. In addition to an interesting topology, the compound also exhibited good photoluminescence.

Supplementary material

CCDC 981,309 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

Funding

We thank the financial support of this work from Natural Science Foundation of China [grant number 21271015], [grant number 21322601] and Beijing Municipal Natural Science Foundation [grant number 2132013].

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