RSC Advances

Graphical Abstract

We have displayed an easy approach to obtain the hydrophilic modified MSPNPs (M-MSPNPs) by simply coating monodispersed hydrophobic magnetite (Fe_3O_4) superparamagnetic nanoparticles (MSPNPs) with functional amphiphilic oligomers. And the resulting M-MSPNPs with abundant chelation groups on the surface, which could bond with Hg^{2+}, exhibit excellent ability in fast, efficient and selective removal of Hg^{2+} from water samples by low-field magnetic separation.

ARTICLE TYPE

Water-soluble Fe₃O₄ superparamagnetic nanocomposites for the removal of low concentration mercury(II) ions from water

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Functional amphiphilic oligomers were synthesized and could be easily used to coat monodisperse hydrophobic magnetite Fe₃O₄ superparamagnetic nanoparticles (MSPNPs) with 13-nm diameter. And the resulting hydrophilic modified
10 **MSPNPs (M-MSPNPs) with abundant groups on the surface, which could bond with Hg²⁺, exhibit excellent ability in fast, efficient and selective removal of Hg²⁺ from water samples by low-field magnetic separation.**

Nowadays, mercury contamination is a global crisis. Owing to
15 the widely ranged usage of mercury in gold-mining, electrical device production, chlor-alkali plants, and chemical synthesis, as well as its inadvertent release during the combustion of fossil fuels, especially coal,[1-4] pollution is now widespread. The presence of Hg in groundwater and oceans could give rise to
20 health problems, as it is well known that mercury is remarkably toxic[5-9] and tend to bioaccumulate in aquatic food chains. Accordingly, reducing the amount of mercury ion in the wastewater is of great concern. The permitted discharge limit of wastewater for total mercury is 50.0 μg/L.[10] Since mercury is
25 very toxic to organisms even in trace levels, [11] the drinking water criterion for mercury established by USEPA is 2.0 μg/L.[12] Compared with treatment of water samples with high and environmentally unrealistic mercury concentrations, it is more practical and formidable to reduce the low mercury concentration
30 (about 50.0 μg/L) below the safety limit for drinking water.

Conventional methods for the removal of mercury from wastewater include adsorption, biosorption, ion exchange, membrane filtration, chelate precipitation, precipitation/adsorption, and photoreduction.[13-19] Generally, in
35 most of these methods, centrifugation or filtration of the sample is needed to isolate contaminants after treatment. [20-22] In contrast, magnetic materials can be readily and rapidly isolated from sample solutions by the application of an external magnetic field. Consequently, magnetic iron oxide nanoparticles (MIONPs) have
40 shown widespread applications as solid phase adsorbent for removal of different types of pollutants such as dyes and heavy metals. [23-24]

The size of magnetic materials is a highly significant factor that directly impacts the adsorptive efficacy. Such like nanoscale
45 magnetite (Fe₃O₄) superparamagnetic nanoparticles (MSPNPs), with smaller size, have greater available sorptive areas. Moreover, they can be reused quite easily by avoiding recovery problem of bigger size NPs after magnetic capture. Consequently,

they show great superiorities, in comparison with conventional
50 magnetic iron oxide nanoparticles. [25] On the other hand, if nanoparticles are too small, magnetic separations require very large critical field strengths to overcome opposing forces, such as Brownian motion, viscous drag, and sedimentation.[26] This treatment assumes very large applied fields and the latest designs
55 for extremely high-gradient separators, which made magnetic separations prohibitively expensive in many settings.[27] For magnetic separation in massive water treatment, we should use NPs as large as possible that still show superparamagnetic properties. Colvin reported that 12-nm-diameter
60 superparamagnetic nanocrystals were suitable as adsorbant materials by low-field magnetic separation, and they used them to reduce the mass of waste associated with arsenic removal from water by orders of magnitude.[22] To the best of our knowledge, no example of MSPNPs has been exploited for removal of Hg²⁺
65 from water.

As efficient sorbents, the Fe₃O₄ particles not only facilitate a fast separation under a moderate magnetic field/ field gradient, but also to show higher uptake capacity for metal ions by surface functionalization. Although there are reports on efficient non-
70 functionalized magnetite particles for metal ions uptake from water, these particles tend to aggregate and decrease available sorptive areas.[28] Therefore, an increasing interest is focused on their chemical functionalization aiming to improve the capture efficiency of metal pollutants. Limited water-dispersion of
75 magnetite particles modified by small molecules or complicated modification procedure hammered the application in water treatment. [24, 29-30]
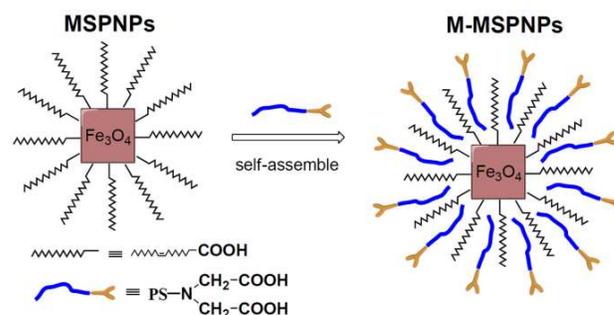
Scheme 1 Illustration for the preparation of M-MSPNPs based on
80 oligomer PS(COOH)₂ and MSPNPs

Herein we report the development of functional polymer

combined with MSPNPs as a new class of functional nanocomposites. Compared to previous reports on magnetic nanoparticle based separations, these modified MSPNPs (M-MSPNPs) have some advantages: 1) A facile procedure has been

5   developed for obtaining well dispersed hydrophilic superparamagnetic nanoparticles by simple self-assemble of amphiphilic functional polymer and hydrophobic 13-nm-sized MSPNPs(**Scheme 1)**. 2) Owing to their small size and well dispersion, M-MSPNPs have great suface area all covered with

10   functional groups of. And these functional groups could interact with Hg^{2+} fast, effectively, and selectively. 3) Also due to their appropriate size, they have more potential for low-field magnetic separation.

    Magnetite nanoparticles were firstly synthesized by thermal

15   decomposition of iron-oleate complex following published procedures.[28,31] The nanoparticles were capped with a hydrophobic layer composed of oleic acid and oleylamine, such that they were soluble in organic non-polar solvents (such as hexane, toluene and chloroform), as shown in **Fig. 1(A)**. For

20   these nanoparticles to be useful for water treatment applications, they have to be rendered water-soluble. Very recently, we succeeded in the synthesis of an oligomer comprising of — $N(CH_2COOH)_2$ as hydrophilic part and polystyrene as hydrophobic part via the reversible-addition–fragmentation

25   chain-transfer (RAFT) polymerization technique (**Scheme S1**).[32] Using the hydrophobic interaction between oligomer and capped layer of magnetite, we coated the oligomer on the surface of the pre-synthesized hydrophobic magnetite nanoparticles. The resulting modified NPs with hydrophilic carboxylic acid groups

30   on the surface can well disperse in the water, as shown in **Fig. 1(B)**. In addition, M-MSPNPs were further investigated by FTIR, XRD and VSM. As expected, Fourier infrared spectrum of M-MSPNPs (**Fig. S1**) shows the characteristic peaks of Fe-O stretches at 570-640 cm^{-1} and peaks of benzene rings in oligomers

35   at 1400-1600 cm^{-1}. The XRD pattern of M-MSPNPs (**Fig. S2**) agrees well with Fe_3O_4 reported previously. [31]The hysteresis loops for MSPNPs and M-MSPNPs were similar (**Fig. S3**) and consistent with surfactant-stablized magnetite nanoparticles reported in the literature. [31] As such, modification appeared to

40   have no significant effect on the magnetic properties of the magnetite.
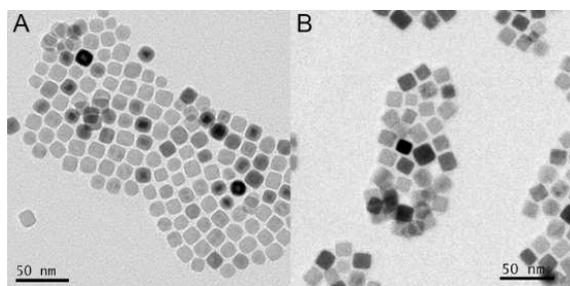
Fig. 1 TEM image of (A) MSPNPs dispersed in hexane and (B) M-MSPNPs dispersed in water

45   In order to study the effect of modification of MSPNPs by polymer on Hg^{2+} removal from water samples, 20 mL solutions with different mercury concentrations ranging from 5 to 100 μg/L were adsorbed by fixed amount (8 mg) of MSPNPs and polymer modified MSPNPs (M-MSPNPs). As shown in **Fig. 2**A, the

50   modification of MSPNPs strongly improved the adsorption ability of the adsorbent. Except mentioned in the following part of this paper, parameters are: amount of M-MSPNPs = 8mg, shaking time = 10 min, shaking speed = 350 rpm and pH = 7.

    The pH value of the solution is an important parameter for the

55   adsorption experiments. Because the current limit for pH value range is 6~9 for discharged water from industrial sectors,[11] the initial concentration of 50 μg/L was selected. The effect of pH on the adsorption of Hg^{2+} (20 mL, 50 μg/L) by 8 mg PMMNPs was investigated in this range. The result is shown in **Fig. 2**B, which

60   indicate that the removal of Hg^{2+} remains constant when pH value ranging from 6 to 9. Since the pH value did not change significantly the removal effect of Hg^{2+}, the pH of working solutions was adjusted to 7 for further works in this paper.
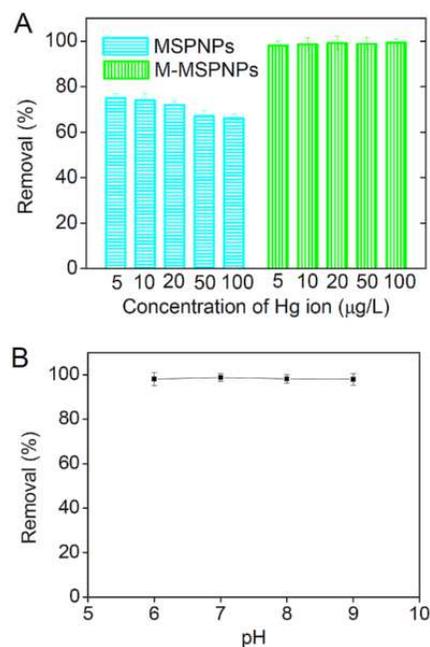
65   **Fig. 2** (A) Removal efficiency for different concentrations of Hg^{2+} using modified and nonmodified MSPNPs with PS(COOH)$_2$. (B) Effect of pH on the adsorption of Hg^{2+} (time = 10 min, temperature = 20 ◦C).

    To further determine the amount of polymer required for effective removal of Hg^{2+}, different amount of the polymer (2~30

70   mg) for modification of MSPNPs with fixed amount (3 mg) and its effect for the removal of Hg^{2+} from 20 mL solutions of mercury ion (50 μg/L) were investigated. From **Fig. 3**A, it can be seen that, the optimized amount of polymer for coating of 3 mg MSPNPs is 5 mg. Further increase in the amount of polymer has

75   a negligible effect on the sorption amount of Hg^{2+}.

    To completely remove Hg^{2+} from water samples, different amount of M-MSPNPs were investigated from 2 up to 20 mg. Results are shown in **Fig. 3B**. The optimum amount of the adsorbent required for quantitative removal of Hg^{2+} (50 μg/L)

80   from 20 mL solution was 8mg. Higher amounts of M-MSPNPs did not improve removal efficiency further.

    Because rapid adsorption is of great importance in water treatment, the investigation of adsorption equilibration time was performed. The optimum adsorptive time required for

85   quantitative removal of Hg^{2+} (50 μg/L) from 20 mL solutions, was obtained by testing the effect of different adsorbent time

ranging from 2 to 60 min. The amount of Hg^{2+} adsorbed is increased sharply with time in the first 2 min, and then slowed down approaching equilibrium in approximately 10 min. As shown in **Fig. 4**A, the adsorbent time of 10 min with a shaking
5 speed of 350 rpm is enough for complete removal of Hg^{2+} from 20 mL solution (50 µg/L). Prolonged contact time did not improve removal efficiency any further.
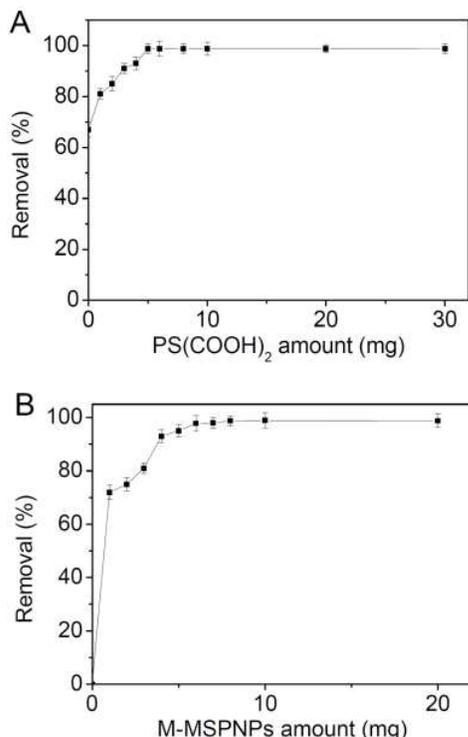
Fig. 3 (A) The effect of PS(COOH)₂ amount for modification of MSPNPs
10 (3 mg) for quantitative removal of Hg^{2+} from 20 mL solutions of Hg^{2+} (50µg/L) at optimized pH value and contact time. (B) The effect of different amounts (2–20 mg) of pretreated modified M-MSPNPs for quantitative removal of Hg^{2+} from 20 mL solutions of mercury ion (50µg/L) at optimized pH value and contact time.

15   An accurate mathematical description of the equilibrium data between the concentration of the sorbate in the liquid and the amount in the solid phase is essential for a consistent prediction of the sorption parameters and for quantitative comparison of the sorption capacity of different sorbents. This mathematical
20 function, called isotherm, is a basic requirement for designing any sorption system.[33]

The adsorption isotherm of Hg^{2+} is shown in **Fig. 4B**. In order to further investigate the mechanism of Hg^{2+} removal by M-MSPNPs, the isotherm data are correlated with Freundlich and
25 Langmuir model, respectively. The parameters of the isotherm models obtained from the corresponding fittings are presented in Table 1.

By comparison, it is shown that Langmuir model fitted slightly better than the Freundlich model. It should be mentioned that R_L
30 value ($R_L=1/(1+K_fC_0)$) indicates the type of isotherm. R_L values between 0 and 1 suggest favorable adsorption. [34] R_L values of Hg^{2+} presented in Table 2 are between 0 and 1 for all initial concentrations, indicating favorable adsorption. This means the adsorption of Hg^{2+} onto M-MSPNPs can be considered to be a
35 monolayer adsorption process. This may be due to the formation

of a monolayer strong complex between the coated polymer on the surface of M-MSPNPs and Hg^{2+} which covers the surface of M-MSPNPs and no more complex molecules can form on the first layer.
40
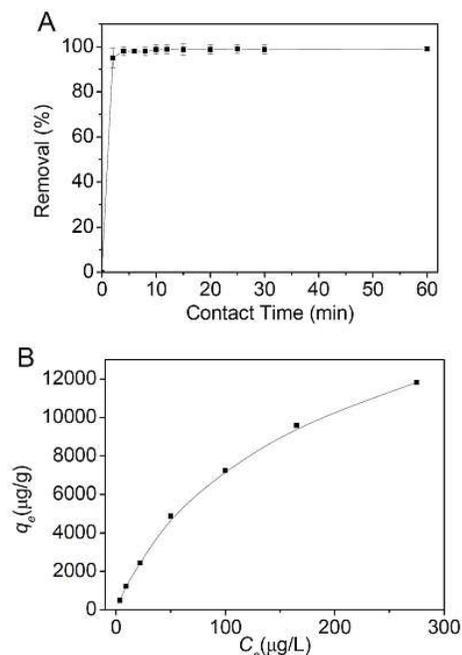
Fig. 4 (A) The effect of contact times between M-MSPNPs and Hg^{2+} solutions for quantitative removal of the analyte. (B) Adsorption isotherm of Hg^{2+} on M-MSPNPs at 298K. The adsorption isotherms for Hg^{2+} on M-
45 MSPNPs were obtained for concentrations ranging from 200 to 5000 µg/L, while keeping all other parameters constant. These parameters are: amount of M-MSPNPs = 8mg, shaking time = 10 min, shaking speed = 350 rpm and pH = 7.

Table 1 Fitted isotherm models for the adsorption of Hg^{2+} on M-MSPNPs

Model	Linearized equation	Parameters	R^2
Freundlich	$\ln(q_e) = \ln(K_f) + 1/n\ \ln(C_e)$	$K_f = 36.6$ n = 1.3663	0.9865
Langmuir	$C_e/q_e = 1/(Kq_m) + C_e/q_m$	$q_m = 16.9$ $K=8.15$	0.9953

50

Table 2 R_L values for adsorption of Hg^{2+} on M-MSPNPs

Hg^{2+} initial concentration, mg/L	R_L
0.2	0.380
0.5	0.197
1	0.109
2	0.058
3	0.0393
4	0.0298
5	0.0239

Because in real water samples, mercury ions are often found coexisted with other ions, it is indispensable to investigate the
55 effect of other ions on the Hg^{2+} removal. It is well known that in the presence of chloride ions, Hg^{2+} forms chloro-complexes of Hg^{2+} and consequently some adsorbents become useless in saline waters.[35]

The effect of salinity concentration (adjusted by NaCl) on the
60 adsorption and removal of Hg^{2+} (20 mL, 50 µg/L) was

investigated. The removal of Hg^{2+} remained almost constant within the concentration range of 0.01 – 1.00 mol/L of NaCl in the test solution. This implied that the complex formation between polymer ligand on the M-MSPNPs and Hg^{2+} in the test
5 solution was not affected significantly even by high NaCl concentration under the examined conditions. It could be contributed that chloro-complexes of Hg^{2+} are less stable than the complexes formed between mercury and the polymer ligand on the surface of M-MSPNPs.

10 Because of low concentration of Hg^{2+} in natural waters relatively to the concentration of other competitive ions, it is very important to investigate the adsorbent capacity to remove Hg^{2+} in the presence of competitive ions. This competitive effect was investigated by removal of Hg^{2+} in real and model wastewater
15 samples using M-MSPNPs, As real wastewater sample, Jinji Lake water collected from Suzhou, in Jiangsu Province, China, were spiked with Hg^{2+} and the final concentrations were 5, 10, 20, 50 μg/L. As model wastewater sample, tap water collected from the lab, added with 50 mg/L of usual ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-,
20 NO_3^-, SO_4^{2-}), were spiked with Hg^{2+} and the final concentrations were 5, 10, 20, 50 μg/L. And the influence of coexisting ions on the adsorption efficiency of Hg^{2+} is shown in **Table 3**, which indicated that whether real or model water samples with the Hg^{2+} concentration under the current limit value for Hg^{2+} discharged
25 from industrial sectors, after treated with M-MSPNPs, could meet the drinking water criterion for mercury.

Table 3 Effect of the initial Hg^{2+} concentrations on the adsorption rate and the residual concentration

Initial concentration (μg/L)	River sample		Model sample	
	Adsorption rate (%)	Residual concentration(μg/L)	Adsorption rate (%)	Residual concentration(μg/L)
5	97.0	0.15	98.0	0.1
10	97.9	0.21	98.0	0.2
20	95.8	0.84	97.5	0.5
50	96.8	1.6	97.8	1.1

To deal with mercury contamination, new materials are
30 required to selectively remove Hg^{2+} because it is bioaccumulative and highly toxic. [36] To investigate whether the adsorbent could bind selectively with mercury in the presence of other heavy metals, M-MSPNPs were mixed with mercury and up to 100-fold molar excess of lead, zinc, or cadmium ions. In all these cases,
35 mercury binding was specific. As shown in **Fig. 5**A-C, only mercury was bound in notable amounts, and the extent of Hg^{2+} binding was unaffected by the competing heavy metals.

Using a strong complexing agent, 2-mercaptoethanol, could effectively remove the bound Hg^{2+} after treatment. The
40 regenerated adsorbents were fully functional even after three repeating cycles, as shown in **Fig. 6**. In each cycle, the removal percent was higher than 98%, which means the original 50 μg/L Hg^{2+} added was reduced to < 1 μg/L, a concentration below the required drinking water limit of 2 μg/L.

45 The loading capacity of adsorbent was determined under optimized conditions by batch method. The adsorbent was added to a 20 mL solution containing 5 mg/mL of Hg^{2+} and shaked for 1 h. Removal percent and adsorbed amount of Hg^{2+} was determined by cold vapor atomic absorption measurement of the sample
50 solution before and after removing process. The loading capacity was determined to be 36.495 mg/g.

Compared with other adsorbents in removing low

concentration of Hg^{2+} (50 μg/L) from water samples, M-MSPNPs can relatively fast, efficiently deal with the contamination (Table
55 4). Considering their size, they have more potential for low-field magnetic separation.
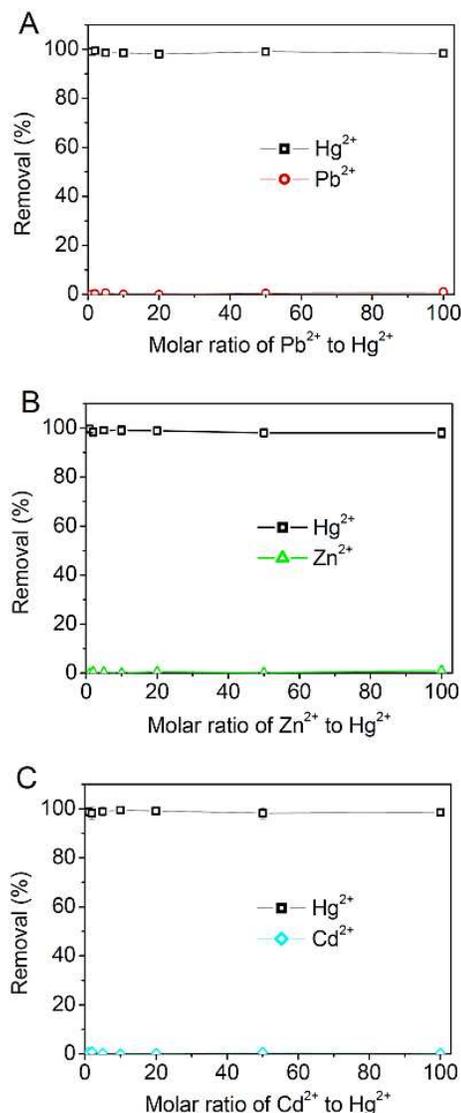
Fig. 5 Selectivity of M-MSPNPs. Binding of Hg^{2+} by M-MSPNPs in the
60 presence of competing heavy metal ions Pb^{2+} (A), Zn^{2+} (B), or Cd^{2+} (C)
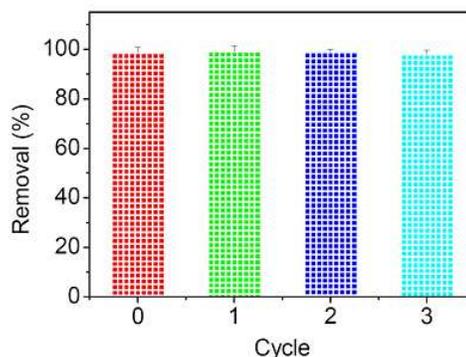
Fig. 6 Recycling of M-MSPNPs

Table 4 Comparison of the removal capacity of the proposed method for low concentration of Hg^{2+} (50 μg/L) with some of the reported methods in literature.

Adsorbent type	Contact time (min)	Removal efficiency(%)	Ref.
Walnut shell activated carbon	30	>99	37
Silica coated magnetite	1200	74	38
magnetite coated with siliceous hybrid shells	<480	>99	24
Dithiocarbamate grafted on magnetite particles	<1440	>99	30
Lemna minor powder	40	87.2	39
magnetite modified with 2-mercaptobenzothiazole (40-50nm)	4	>99	29
M-MSPNPs	10	>99	This work

Conclusions

In conclusion, an easy method has been developed for obtaining monodisperse water-soluble magnetite superparamagnetic nanocomposites by simply coating hydrophobic magnetite superparamagnetic nanoparticles with functional amphiphilic oligomers. The resultant M-MSPNPs with abundant groups on the surface, could interact with Hg^{2+} quickly, selectively, and then efficiently remove low concentration of Hg^{2+} from water samples. Owing to theie size suitable for low-field magnetic separation, the nanocomposites have great potential in water treatment application.

Acknowledgment

Notes and references

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† Electronic Supplementary Information (ESI) available: detail experimental procedures. See DOI: 10.1039/b000000x/

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