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# Synthesis and Metal-Complexation Ability of Cross-Linking Materials Containing Noria-Templated Cavities with Pendant Carboxylic Acid Groups

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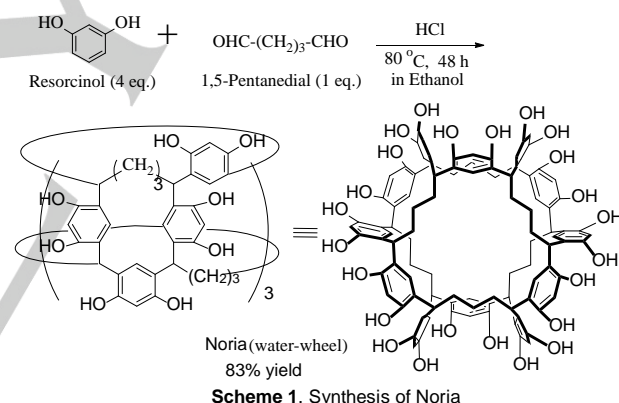
**Abstract:** We synthesized noria-containing cross-linking materials, Cross(Noria-MA-co-DM[*n*]<sub>*m*</sub>), by radical polymerization of a noria derivative with pendant methacryloyl groups (noria-MA) and  $\alpha$ ,  $\omega$ -alkanedimethacrylamides (DM[*n*], *n* = 3, 6, 12) at feed ratios of noria-MA/DM[*n*] = 1/2.4, 1/12, and 1/24 (*m* = 2.4, 12, and 24). Alkaline hydrolysis reaction of Cross(Noria-MA-co-DM[*n*]<sub>*m*</sub>) removed the noria moieties to give corresponding cross-linking materials, Cross-COOH-DM[*n*]<sub>*m*</sub>, containing noria-templated fixed cavities with pendant carboxylic acid groups. Among the noria-containing cross-linking materials, Cross(Noria-MA-co-DM[6]<sub>24</sub>) showed the greatest extent of removal of noria upon hydrolysis. Nitrogen and carbon dioxide absorption studies indicated that Cross(Noria-MA-co-DM[6]<sub>24</sub>) contains fixed cavities, whereas Cross-COOH-DM[6]<sub>24</sub> does not in the solid (unswollen) state. Examination of the inclusion-complex-forming ability of the synthesized cross-linking materials using aqueous solutions of metal ions revealed that Cross-COOH-DM[6]<sub>24</sub> has the greatest absorption capacity. These results indicate that Cross-COOH-DM[6]<sub>24</sub> indeed contains noria-templated cavities that can accommodate metal ions in aqueous solution.

## Introduction

Crown ethers are well-known macrocycles that form complexes with alkali metal salts, ammonium salts, and many transition metal and lanthanide salts <sup>[1-3]</sup>. However, although crown ethers can accommodate a variety of guest compounds, their selectivity is often poor due to their molecular flexibility. In contrast, cryptands <sup>[4-6]</sup> and spherands <sup>[7-9]</sup>, which have three-dimensional cyclic structures, show greater selectivity. Calixarenes containing cone-shape structures with fixed cavities also show complex-forming abilities with metal ions and some organic compounds <sup>[10]</sup>. Furthermore, cavitands and carserands, which contain intramolecular bridge-units in calixarene-type structures, provide extended cavities, which can accommodate various metal ions and some gases, such as oxygen and carbon disulfide. <sup>[11-12]</sup> In addition, cyclodextrins, which are natural macrocycles containing 1,4-glucose units, <sup>[13]</sup> have a hydrophilic

exterior and a hydrophobic interior, and form complexes selectively with organic compounds in water <sup>[14]</sup>. Polyrotaxanes <sup>[15-17]</sup> and nanotubes <sup>[18]</sup> also have the ability to form complexes with organic compounds.

On the other hand, we synthesized a ladder-type cyclic oligomer, which we called noria (water-wheel in Latin), by means of one-pot reaction using resorcinol and 1,5-pentanedial in high yield. <sup>[19]</sup> Single-crystal X-ray analysis confirmed that noria has 24 hydroxyl groups, 6 cavities in the side, and a large hydrophobic central hole, i.e., a water-wheel-like structure (Scheme 1). A noria derivative (noria-COOEt) containing carboxylic ester moieties could form a complex with Rb<sup>+</sup> ion, which was apparently enclosed in the central hole in the molecule. Other noria derivatives <sup>[20-27]</sup> and noria-like macrocycle compounds <sup>[28-31]</sup> have since been synthesized and their applications have been investigated.



In the present work, we used the noria structure to design and synthesize a new class of cross-linking materials containing noria-templated fixed cavities with pendant carboxylic acid groups, anticipating that they would show distinctive complexation abilities with metal ions. The cross-linking materials were synthesized by radical polymerization of a noria derivative having pendant methacryloyl groups with dimethacrylamides as cross-linkers, followed by aqueous alkaline hydrolysis reaction to remove the noria structures, yielding the corresponding cross-linking materials with noria-templated cavities containing pendant carboxylic acid groups. The adsorption properties of these cross-linking materials for gases (nitrogen and carbon dioxide) in the solid state and the inclusion complex-forming abilities with metal salts in aqueous solution were examined.

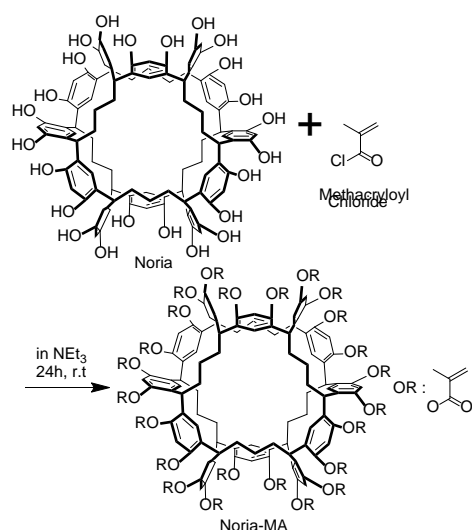
## Results and Discussion

### Synthesis of noria derivative (Noria-MA) with pendant methacryloyl groups

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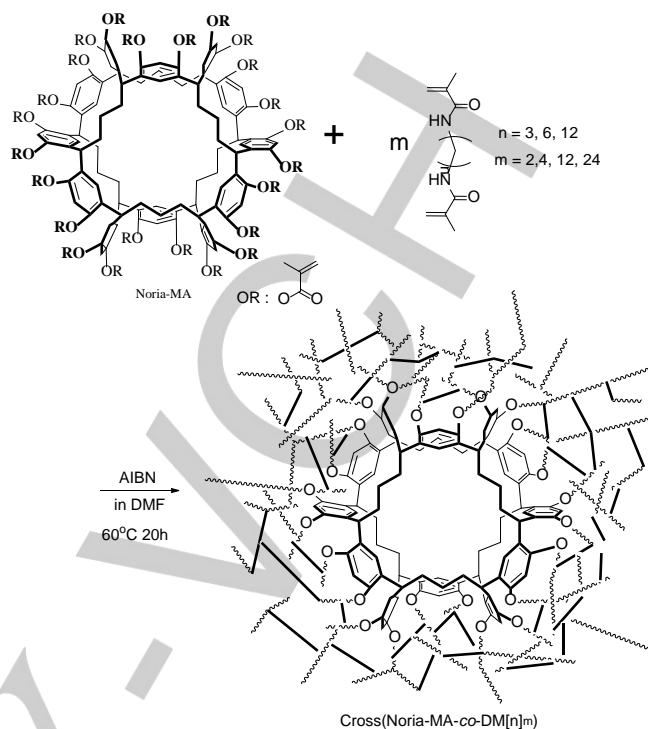
Reaction of noria and methacryloyl chloride was carried out in  $\text{NEt}_3$  as a solvent to give the corresponding noria derivative with pendant methacryloyl groups (noria-MA). The structure was confirmed by  $^1\text{H}$  NMR and IR spectroscopy. The  $^1\text{H}$  NMR spectrum showed peaks at 5.55 ~ 6.18 ppm assignable to methacryloyl groups. The IR spectrum also showed a peak at  $1739\text{ cm}^{-1}$  assignable to stretching vibration of carbonyl groups. No peaks assignable to hydroxyl groups were seen in the  $^1\text{H}$  NMR and IR spectra. These results indicate that all the hydroxyl groups of noria were converted to methacryloyl groups, i.e., noria-MA was obtained in 20 % yield as shown in Scheme 2.



Scheme 2. Synthesis of Noria-MA.

### Radical copolymerization of noria-MA and $\alpha,\omega$ -alkanedimethacrylamides (DM[n]) [Synthesis of Cross(Noria-MA-co-DM[n]<sub>m</sub>)]

We examined the synthesis of cross-linking materials by radical copolymerization of noria-MA and  $\alpha,\omega$ -alkanedimethacrylamides (DM[n],  $n = 3, 6, 12$ ) (Scheme 3). In the case of 1,6-bis(methacrylamido)hexane (DM[6]), Cross(Noria-MA-co-DM[6]<sub>m</sub>) was obtained in quantitative yield at feed ratios of noria-MA / DM[6] = 1 / 2.4, 1 / 12, and 1 / 24 ( $m = 2.4, 12, \text{ and } 24$ ) (Runs 4 ~ 6 in Table 1). Cross(Noria-MA-co-DM[3]<sub>m</sub>) and Cross(Noria-MA-co-DM[12]<sub>m</sub>) were similarly obtained by radical polymerization of noria-MA with DM[3] and DM[12], respectively. The conditions and results are summarized in Table 1.



Scheme 3. Radical polymerization of noria-MA and dimethacrylamides (DM[n]) ( $n = 3, 6, \text{ and } 12$ ).

Table 1. Radical copolymerization of noria-MA and DM[n] ( $n = 3, 6, 12$ )<sup>[a]</sup>

Run	Feed Ratios Noria-MA/DM[n]	Cross(Noria-MA-co-DM[n] <sub>m</sub> )	Yield (%)	$T_d$ <sup>[b]</sup> (°C)
1	Noria-MA/DM[3] = 1.0/2.4	$n = 3, m = 2.4$	>99	282.1
2	Noria-MA/DM[3] = 1.0/12	$n = 3, m = 12$	>99	280.1
3	Noria-MA/DM[3] = 1.0/24	$n = 3, m = 24$	>99	282.1
4	Noria-MA/DM[6] = 1.0/2.4	$n = 6, m = 2.4$	>99	277.5
5	Noria-MA/DM[6] = 1.0/12	$n = 6, m = 12$	>99	277.8
6	Noria-MA/DM[6] = 1.0/24	$n = 6, m = 24$	>99	277.2
7	Noria-MA/DM[12] = 1.0/2.4	$n = 12, m = 2.4$	>99	324.5
8	Noria-MA/DM[12] = 1.0/12	$n = 12, m = 12$	>99	324.3
9	Noria-MA/DM[12] = 1.0/24	$n = 12, m = 24$	>99	325.1

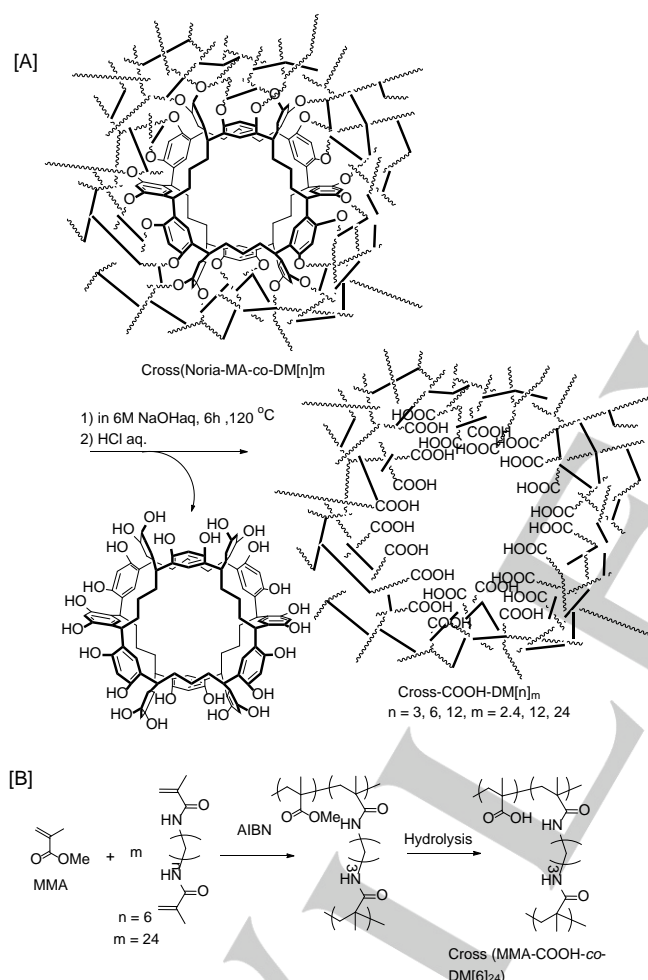
[a] Conditions; AIBN(3 mol%) in DMF at 60 °C for 20 h. [b] Determined by TGA.

Glass transition temperature ( $T_g$ ) and thermal decomposition temperature ( $T_d$ ) were determined by means of DSC and TGA, respectively. No  $T_g$  was observed in the range between 25 and 250 °C, and  $T_d$  values were in the range between 277.5 and

325.1 °C. The thermal stability of Cross(Noria-MA-co-DM[ $n$ ] <sub>$m$</sub> ) was consistent with the structures of the cross-linkers DM[ $n$ ]. The order of  $T_d$  was Cross(Noria-MA-co-DM[12] <sub>$m$</sub> ) > Cross(Noria-MA-co-DM[3] <sub>$m$</sub> ) > Cross(Noria-MA-co-DM[6] <sub>$m$</sub> ).

#### Hydrolysis of Cross(Noria-MA-co-DM[ $n$ ] <sub>$m$</sub> ) [Synthesis of Cross-COOH-DM[ $n$ ] <sub>$m$</sub> ] ( $n = 3, 6, 12, m = 2.4, 12, 24$ )

Hydrolysis reaction was performed in aqueous alkaline solution to remove noria from Cross(Noria-MA-co-DM[ $n$ ] <sub>$m$</sub> ) ( $n = 3, 6, 12, m = 2.4, 12, 24$ ) with the aim of obtaining insoluble cross-linking materials with noria-templated fixed holes, as shown in Scheme 4[A], as new functional materials for host-guest chemistry.

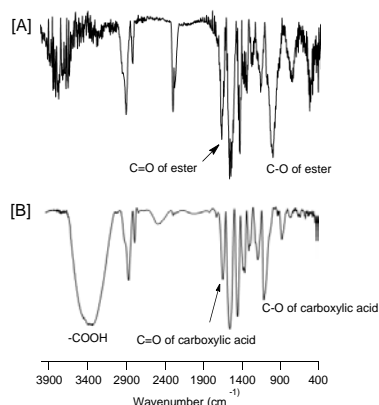


**Scheme 4.** Hydrolysis reaction of Cross(Noria-MA-co-DM[ $n$ ] <sub>$m$</sub> ) (Synthesis of Cross-COOH-DM[ $n$ ] <sub>$m$</sub> ) [A]. Synthesis of Cross(MMA-COOH-co-DM[6]<sub>24</sub>).

A suspension of Cross(Noria-MA-co-DM[6]<sub>24</sub>) in 6 M NaOH aq. was stirred at 120 °C. After 6 h, the insoluble part was collected by filtration, and washed with large amounts of 1 N HCl aq. and water. Figure 1 illustrates the IR spectra of the cross-linking materials before and after the hydrolysis reaction. Peaks at 1741

and 1126  $\text{cm}^{-1}$  assignable to C=O and C-O of ester moieties are seen in Figure 1[A]. After hydrolysis, new peaks at 1718 and 1182  $\text{cm}^{-1}$  appeared, as shown in Figure 1[B]; these are assignable to carboxylic acid groups. Furthermore, a broad peak at about 3400  $\text{cm}^{-1}$ , assignable to -OH groups, is also seen. These results show that hydrolysis proceeded to give a corresponding cross-linking product, Cross-COOH-DM[6]<sub>24</sub>, containing carboxylic acid groups due to removal of noria from Cross(Noria-MA-co-DM[6]<sub>24</sub>). The ratio of removal of noria was also investigated. After collection of Cross-COOH-DM[6]<sub>24</sub> by filtration following the hydrolysis, conc. HCl aq. was added to the filtrate (to pH = 2.0) to precipitate the solid. This was confirmed to be noria by  $^1\text{H}$  NMR. Thus, the ratio of hydrolysis (RH) could be calculated from the amount of precipitated noria. In the case of Cross-COOH-DM[6]<sub>24</sub>, the values of RH and yield were calculated to be 52 % and 50 %, respectively (Run 6 in Table 2). When Cross(Noria-MA-co-DM[6]<sub>12</sub>) was hydrolyzed, the corresponding Cross-COOH-DM[6]<sub>12</sub> with RH = 12% was obtained in 18% yield (Run 5 in Table 2). In the case of Cross(Noria-MA-co-DM[6]<sub>2.4</sub>), the suspension in 12 M NaOH aq. became homogeneous, i.e., all hydrolysis products were soluble, and the corresponding Cross-COOH-DM[6]<sub>2.4</sub> was not obtained (Run 4 in Table 2). This means that the feed ratio of 2.4 eq. of DM[6] as a cross-linker is too small for the present purpose. Furthermore, in the cases of Cross(Noria-MA-co-DM[3] <sub>$m$</sub> ) ( $m = 2.4, 12, \text{ and } 24$ ), only Cross-COOH-DM[3]<sub>24</sub> with RH = 36% was obtained in 60 % yield, and Cross-COOH-DM[3]<sub>2.4</sub> and Cross-COOH-DM[3]<sub>12</sub> were not obtained (Runs 1 ~ 3 in Table 2). When the hydrolysis of Cross(Noria-MA-co-DM[24] <sub>$m$</sub> ) ( $m = 2.4, 12, \text{ and } 24$ ) was similarly examined, the corresponding cross-linking products Cross-COOH-DM[24] <sub>$m$</sub>  ( $m = 12 \text{ and } 24$ ) were obtained in 64 and 96 % yields. However, their values of RH were 9 and 1% , respectively (Runs 7 ~ 9 in Table 2). These results indicate that hydrolysis of Cross(Noria-MA-co-DM[24] <sub>$m$</sub> ) hardly proceeded, presumably because DM[12] has longer methylene chains that might enhance its hydrophobicity. Thus, hydrolysis reaction of Cross(Noria-MA-co-DM[ $n$ ] <sub>$m$</sub> ) depends upon the length of the methylene unit and the amount of DM[ $n$ ] <sub>$m$</sub>  cross-linker in the feed.

Notably, Cross-COOH-DM[3]<sub>24</sub> (RH = 36), Cross-COOH-DM[6]<sub>12</sub> (RH = 12), Cross-COOH-DM[6]<sub>24</sub> (RH = 52), and Cross-COOH-DM[12]<sub>12</sub> (RH = 9) all showed high thermal stability, which was little different from that of the products before hydrolysis (Runs 3, 5, 6, and 8 in Table 2). Among them, Cross-COOH-DM[6]<sub>24</sub> might be expected to show higher inclusion complex-forming ability with metal ions, because the value of RH (52%, run 5 in Table 2) is higher than those of other cross-linking product, i.e., Cross-COOH-DM[6]<sub>24</sub> might contain many noria-templated cavities.



**Figure 1.** IR spectra of Cross(Noria-MA-co-DM[6]<sub>24</sub>) [A] and Cross-COOH-DM[6]<sub>24</sub> [B].

**Table 2.** Hydrolysis reaction of Cross(Noria-MA-co-DM[n]<sub>m</sub>)

Run	Cross(Noria-co-DM[n] <sub>m</sub> )	RH <sup>[a]</sup> (%)	Cross-COOH-DM[n] <sub>m</sub> (%)	T <sub>d</sub> <sup>[b]</sup> (°C)
1	n = 3, m = 2.4	- [b]	- [b]	- [b]
2	n = 3, m = 12	- [b]	- [b]	- [b]
3	n = 3, m = 24	36	60	278.8
4	n = 6, m = 2.4	- [b]	- [b]	- [b]
5	n = 6, m = 12	12	18	277.2
6	n = 6, m = 24	52	50	275.1
7	n = 12, m = 2.4	- [b]	- [b]	- [b]
8	n = 12, m = 12	9	64	323.1
9	n = 12, m = 24	>1	96	- [b]

[a] RH = ratio of removal of noria from Cross(Noria-MA-co-DM[n]<sub>m</sub>) [b] Determined by TGA.

### Complexation ability of Cross(Noria-MA-co-DM[n]<sub>m</sub>) and Cross-COOH-DM[n]<sub>m</sub> with metal ions in aqueous solution

The complex-forming abilities of Cross(Noria-MA-co-DM[n]<sub>m</sub>) and Cross-COOH-DM[n]<sub>m</sub> (Scheme 4 [A]) with alkali metal ions such as Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> were examined by means of liquid-gel extraction studies using the picrate salts of these metals in water. The results are summarized in Table 3.

**Table 3.** Alkali metal extraction rate of synthesized cross-linking materials<sup>a]</sup>

Run	Cross-linking materials	Alkali metal extraction rate (%)			
		Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
1	Cross(Noria-MA-co-DM[3] <sub>24</sub> )	20	6	18	12
2	Cross(Noria-MA-co-DM[6] <sub>24</sub> )	1>	1>	6	5
3	Cross(Noria-MA-co-DM[12] <sub>24</sub> )	3	11	11	7
4	Cross-COOH-DM[3] <sub>24</sub> (RH = 36)	56	65	41	74
5	Cross-COOH-DM[6] <sub>24</sub> (RH = 52)	92	94	94	95
6	Cross-COOH-DM[12] <sub>24</sub> (RH = >1)	1>	18	15	13
7	Cross(MMA-COOH-co-DM[6] <sub>24</sub> )	1>	1>	1>	1>

[a] Percentage cation extraction from an aqueous neutral alkali metal ion solution ( $2.5 \times 10^{-4}$  mol dm<sup>-3</sup>) in the presence of host cross-linking materials at 25 °C.

Cross(Noria-MA-co-DM[12]<sub>24</sub>) and Cross-COOH-DM[12]<sub>24</sub> showed almost the same inclusion complex-forming abilities in the range between 1> and 18 % (Runs 3 and 6 in Table 3), presumably because the hydrolysis reaction of Cross(Noria-MA-co-DM[12]<sub>24</sub>) did not proceed well, as discussed above. However, Cross-COOH-DM[3]<sub>24</sub> and Cross-COOH-DM[6]<sub>24</sub> showed higher inclusion complex-forming abilities compared to Cross(Noria-MA-co-DM[3]<sub>24</sub>) and Cross(Noria-MA-co-DM[6]<sub>24</sub>) (Runs 1, 2, 4, and 5 in Table 3). For comparison, a cross-linking polymer was synthesized by radical polymerization of methylmethacrylate (MMA) and DM[6], followed by hydrolysis reaction to give Cross(MMA-COOH-co-DM[6]) with pendant carboxylic acid groups (Scheme 4 [B]). However, Cross(MMA-COOH-co-DM[6]) showed no apparent complex-forming ability with any metal ions examined (Run 7 in Table 3). The remarkable extraction rate of Cross-COOH-DM[6]<sub>24</sub> suggests that the substantial removal ratio of noria from Cross(Noria-MA-co-DM[6]<sub>24</sub>) left many fixed holes that can accommodate metal ions, i.e., noria-templated fixed cavities containing carboxylic acid groups within the cross-linking material. Next, to examine the practical utility of the cross-linking materials, we examined their adsorption properties using a dilute aqueous solution of Cs<sup>+</sup> (100 ppm). The adsorption percentage and adsorption amount are summarized in Table 4. In the case of Cross(Noria-MA-co-DM[6]<sub>24</sub>), 5.3 % of Cs<sup>+</sup> was adsorbed, corresponding to 0.12 mmol(+)/g-cross-linking material. The adsorption percentage and adsorption amount of Cross-COOH-DM[6]<sub>24</sub> were 2.6 % and 0.059 mmol(+)/g-cross-linking material, respectively. Thus, Cross(Noria-MA-co-DM[6]<sub>24</sub>) and Cross-COOH-DM[6]<sub>24</sub> have an adsorption capacity for Cs<sup>+</sup>, again supporting the conclusion that Cross-COOH-DM[6]<sub>24</sub> contains noria-templated cavities lined with carboxylic acid groups, as shown in Scheme 4[A].

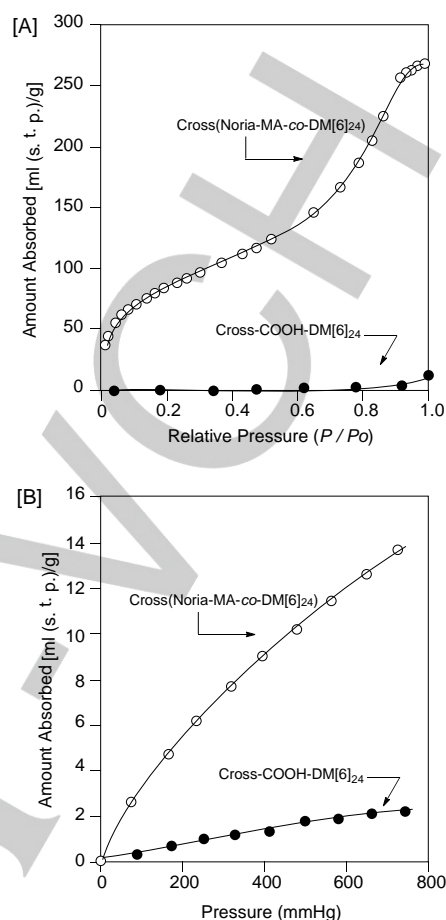
**Table 4.** Adsorption of Cs<sup>+</sup> by Cross(Noria-MA-co-DM[6]<sub>24</sub>) and Cross-COOH-DM[6]<sub>24</sub>

Run	Cross-linking material	Adsorption of Cs <sup>+</sup> (%)	Adsorption amount of Cs <sup>+</sup> (mmol(+)/g) <sup>a)</sup>
1	Cross(Noria-MA-co-DM[6] <sub>24</sub> )	5.3	0.12
2	Cross-COOH-DM[6] <sub>24</sub> (RH = 52)	2.6	0.059

[a] cross-linking material s; 0.01 g, 30 ml of aqueous solution at R.T. (100 ppm).

### Nitrogen and carbon dioxide adsorption properties of Cross(Noria-MA-co-DM[6]<sub>24</sub>) and Cross-COOH-DM[6]<sub>24</sub> in the solid state

It was reported that noria and noria derivatives adsorb carbon dioxide selectively, due to their central fixed holes<sup>[32]</sup>. Therefore, we examined the adsorption properties of Cross(Noria-MA-co-DM[6]<sub>24</sub>) and Cross-COOH-DM[6]<sub>24</sub> by measuring the nitrogen and carbon dioxide adsorption isotherms in the solid state. Figure 2 [A] illustrates the nitrogen adsorption at 77K. A rapid increase of adsorbed amount on Cross(Noria-MA-co-DM[6]<sub>24</sub>) in the low relative pressure range was observed, suggesting that the cross-linking material might have a microporous structure. Figure 2 [B] shows the results for carbon dioxide at 298K. These results were used to calculate the specific surface areas of the cross-linking materials, as summarized in Table 5. The estimated surface areas of Cross(Noria-MA-co-DM[6]<sub>24</sub>) are 292.7 m<sup>2</sup>/g (BET, N<sub>2</sub> at 77K) and 264.8 m<sup>2</sup>/g (DP, CO<sub>2</sub> at 298K), respectively. On the other hand, the corresponding values of Cross-COOH-DM[6]<sub>24</sub> were very small: 1.4 m<sup>2</sup>/g (BET, N<sub>2</sub> at 77K) and 65.6 m<sup>2</sup>/g (DP, CO<sub>2</sub> at 298K). These results indicate that many fixed holes exist in Cross(Noria-MA-co-DM[6]<sub>24</sub>), but not in Cross-COOH-DM[6]<sub>24</sub> in the solid state, i.e., hydrolysis reaction of Cross(Noria-MA-co-DM[6]<sub>24</sub>) removed the noria moieties to give the corresponding Cross-COOH-DM[6]<sub>24</sub> containing many carboxylic acid groups, as shown in Scheme 3. The Cross-COOH-DM[6]<sub>24</sub> swells in aqueous solution to generate cavities containing carboxylic acid groups, exhibiting high complexation ability with certain metal ions.

**Figure 2.** Nitrogen adsorption isotherms at 77K [A] and carbon dioxide adsorption isotherms at 298K [B] for Cross(Noria-MA-co-DM[6]<sub>24</sub>) and Cross-COOH-DM[6]<sub>24</sub>.**Table 5.** Estimated surface areas of Cross(Noria-MA-co-DM[6]<sub>24</sub>) and Cross-COOH-DM[6]<sub>24</sub>

Run	Cross-linking material	Specific surface area [m <sup>2</sup> /g]	
		BET(N <sub>2</sub> 77K)	DP(CO <sub>2</sub> 298K)
1	Cross(Noria-MA-co-DM[6] <sub>24</sub> )	292.7	264.8
2	Cross-COOH-DM[6] <sub>24</sub> (RH = 52)	1.4	65.6

### Conclusions

We examined the synthesis and properties of cross-linking materials containing noria moieties and noria-templated fixed cavities with pendant carboxylic acid groups. The radical polymerization of noria derivative noria-MA with pendant methacryloyl groups was performed with certain  $\alpha$ ,  $\omega$ -alkanedimethacrylamides (DM[n], n = 3, 6, 12) in the feeds ratios of noria-MA/DM[n] = 1/2.4, 1/12, and 1/24 (m = 2.4, 12, and 24), yielding corresponding cross-linking materials Cross(Noria-MA-

co-DM[n]<sub>m</sub>), quantitatively. After hydrolysis reaction of Cross(Noria-MA-co-DM[n]<sub>m</sub>), the cross-linking products Cross-COOH-DM[n]<sub>m</sub> were obtained by the removal of noria. The inclusion complex abilities was examined using Cross(Noria-MA-co-DM[n]<sub>m</sub>) and Cross-COOH-DM[n]<sub>m</sub> in the aqueous some metal salts solution, and it was found that Cross-COOH-DM[6]<sub>24</sub> has higher absorption abilities with some metals due to higher ratio of hydrolysis (RH = 52%), which have noria-templated cavities containing carboxylic acid groups. In the similar way for the synthesis of Cross-COOH-DM[n]<sub>m</sub>, the another cross-linking materials containing noria-templated cavities with pendant alcohol or amino groups can be synthesized. Their properties will be reported in the next paper in near future.

## Supporting Information Summary

Experimental section and <sup>1</sup>H NMR spectrum of noria-MA (Figure S1) were described.

## Acknowledgements

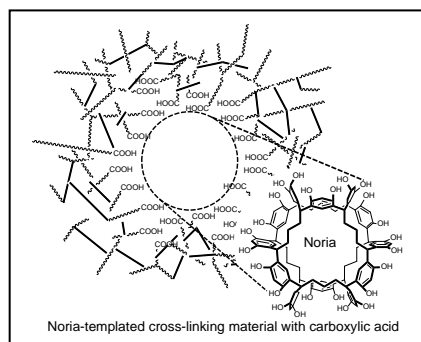
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**Keywords:** cavity • cross-linking • metal-complexation • noria • synthesis

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The synthesis and properties of cross-linking materials containing noria-templated fixed cavities with pendant carboxylic acid groups were examined. Examination of the inclusion-complex-forming ability of the synthesized cross-linking materials using aqueous solutions of metal ions revealed that the synthesized cross-linking materials have the great absorption capacities. These results indicate that they indeed contains noria-templated cavities with pendant carboxylic acids groups that can accommodate metal ions in aqueous solution.