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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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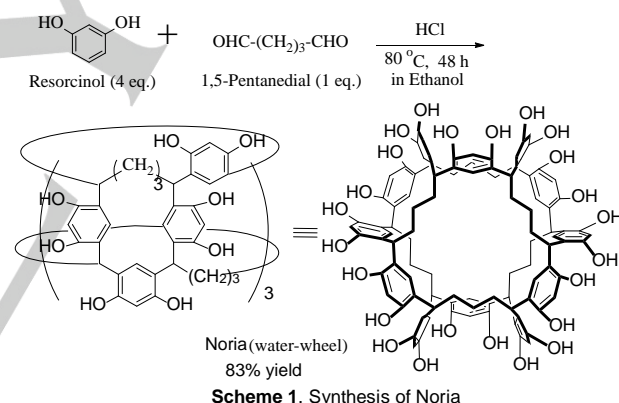
Abstract: We synthesized noria-containing cross-linking materials, Cross(Noria-MA-co-DM[n]_m), by radical polymerization of a noria derivative with pendant methacryloyl groups (noria-MA) and α , ω -alkanedimethacrylamides (DM[n], n = 3, 6, 12) at feed ratios of noria-MA/DM[n] = 1/2.4, 1/12, and 1/24 (m = 2.4, 12, and 24). Alkaline hydrolysis reaction of Cross(Noria-MA-co-DM[n]_m) removed the noria moieties to give corresponding cross-linking materials, Cross-COOH-DM[n]_m, containing noria-templated fixed cavities with pendant carboxylic acid groups. Among the noria-containing cross-linking materials, Cross(Noria-MA-co-DM[6]₂₄) showed the greatest extent of removal of noria upon hydrolysis. Nitrogen and carbon dioxide absorption studies indicated that Cross(Noria-MA-co-DM[6]₂₄) contains fixed cavities, whereas Cross-COOH-DM[6]₂₄ 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]₂₄ has the greatest absorption capacity. These results indicate that Cross-COOH-DM[6]₂₄ 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 ^[1-3]. However, although crown ethers can accommodate a variety of guest compounds, their selectivity is often poor due to their molecular flexibility. In contrast, cryptands ^[4-6] and spherands ^[7-9], 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 ^[10]. 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. ^[11-12] In addition, cyclodextrins, which are natural macrocycles containing 1,4-glucose units, ^[13] have a hydrophilic

exterior and a hydrophobic interior, and form complexes selectively with organic compounds in water ^[14]. Polyrotaxanes ^[15-17] and nanotubes ^[18] 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. ^[19] 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⁺ ion, which was apparently enclosed in the central hole in the molecule. Other noria derivatives ^[20-27] and noria-like macrocycle compounds ^[28-31] 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.

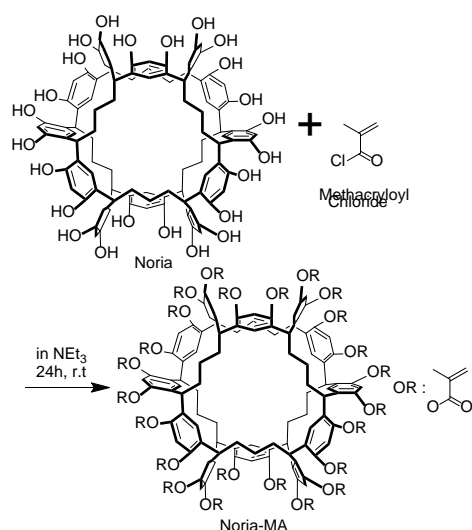
Results and Discussion

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

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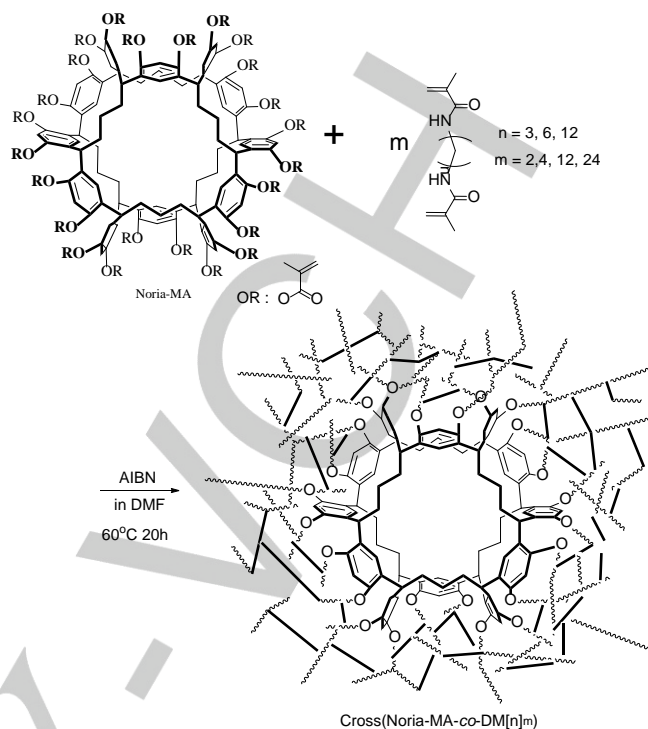
Reaction of noria and methacryloyl chloride was carried out in NEt_3 as a solvent to give the corresponding noria derivative with pendant methacryloyl groups (noria-MA). The structure was confirmed by ^1H NMR and IR spectroscopy. The ^1H NMR spectrum showed peaks at 5.55 ~ 6.18 ppm assignable to methacryloyl groups. The IR spectrum also showed a peak at 1739 cm^{-1} assignable to stretching vibration of carbonyl groups. No peaks assignable to hydroxyl groups were seen in the ^1H 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 α,ω -alkanedimethacrylamides (DM[n]) [Synthesis of Cross(Noria-MA-co-DM[n]_m)]

We examined the synthesis of cross-linking materials by radical copolymerization of noria-MA and α,ω -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]_m) was obtained in quantitative yield at feed ratios of noria-MA / DM[6] = 1 / 2.4, 1 / 12, and 1 / 24 ($m = 2.4, 12,$ and 24) (Runs 4 ~ 6 in Table 1). Cross(Noria-MA-co-DM[3]_m) and Cross(Noria-MA-co-DM[12]_m) 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]) ($n = 3, 6,$ and 12).

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

Run	Feed Ratios Noria-MA/DM[n]	Cross(Noria-MA-co-DM[n] _m)	Yield (%)	T_d ^[b] (°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

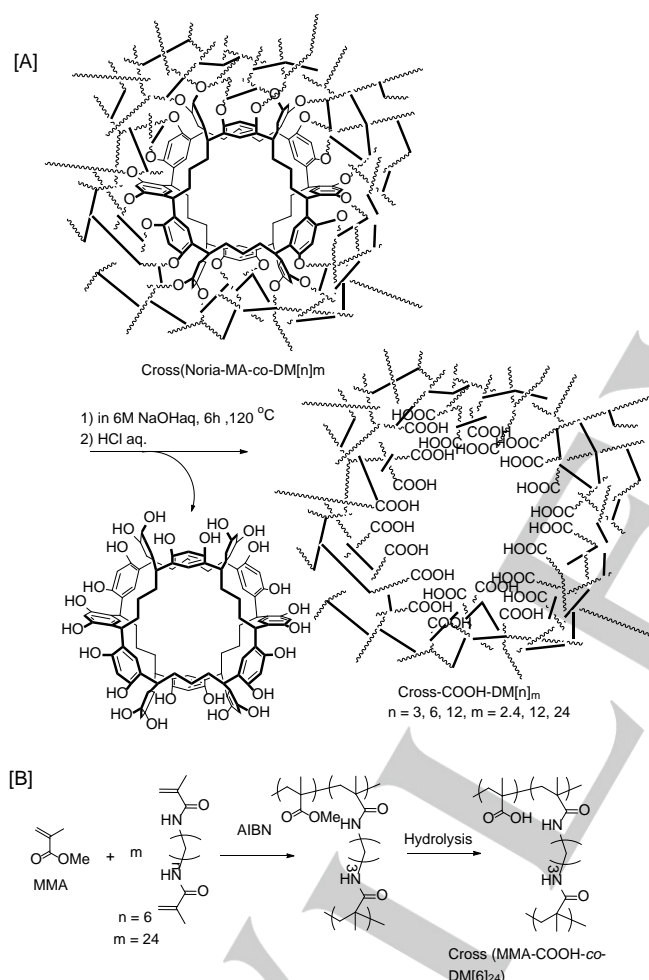
[a] Conditions; AIBN(3 mol%) in DMF at 60 °C for 20 h. [b] Determined by TGA.

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] _{m}) was consistent with the structures of the cross-linkers DM[n]. The order of T_d was Cross(Noria-MA-co-DM[12] _{m}) > Cross(Noria-MA-co-DM[3] _{m}) > Cross(Noria-MA-co-DM[6] _{m}).

Hydrolysis of Cross(Noria-MA-co-DM[n] _{m}) [Synthesis of Cross-COOH-DM[n] _{m}] ($n = 3, 6, 12, m = 2.4, 12, 24$)

Hydrolysis reaction was performed in aqueous alkaline solution to remove noria from Cross(Noria-MA-co-DM[n] _{m}) ($n = 3, 6, 12, m = 2.4, 12, 24$) 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] _{m}) (Synthesis of Cross-COOH-DM[n] _{m}) [A]. Synthesis of Cross(MMA-COOH-co-DM[6]₂₄).

A suspension of Cross(Noria-MA-co-DM[6]₂₄) 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 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 cm^{-1} appeared, as shown in Figure 1[B]; these are assignable to carboxylic acid groups. Furthermore, a broad peak at about 3400 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]₂₄, containing carboxylic acid groups due to removal of noria from Cross(Noria-MA-co-DM[6]₂₄). The ratio of removal of noria was also investigated. After collection of Cross-COOH-DM[6]₂₄ 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 ^1H NMR. Thus, the ratio of hydrolysis (RH) could be calculated from the amount of precipitated noria. In the case of Cross-COOH-DM[6]₂₄, 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]₁₂) was hydrolyzed, the corresponding Cross-COOH-DM[6]₁₂ with RH = 12% was obtained in 18% yield (Run 5 in Table 2). In the case of Cross(Noria-MA-co-DM[6]_{2.4}), the suspension in 12 M NaOH aq. became homogeneous, i.e., all hydrolysis products were soluble, and the corresponding Cross-COOH-DM[6]_{2.4} 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] _{m}) ($m = 2.4, 12, \text{ and } 24$), only Cross-COOH-DM[3]₂₄ with RH = 36% was obtained in 60 % yield, and Cross-COOH-DM[3]_{2.4} and Cross-COOH-DM[3]₁₂ were not obtained (Runs 1 ~ 3 in Table 2). When the hydrolysis of Cross(Noria-MA-co-DM[24] _{m}) ($m = 2.4, 12, \text{ and } 24$) was similarly examined, the corresponding cross-linking products Cross-COOH-DM[24] _{m} ($m = 12 \text{ and } 24$) 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] _{m}) 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] _{m}) depends upon the length of the methylene unit and the amount of DM[n] _{m} cross-linker in the feed.

Notably, Cross-COOH-DM[3]₂₄ (RH = 36), Cross-COOH-DM[6]₁₂ (RH = 12), Cross-COOH-DM[6]₂₄ (RH = 52), and Cross-COOH-DM[12]₁₂ (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]₂₄ 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]₂₄ might contain many noria-templated cavities.

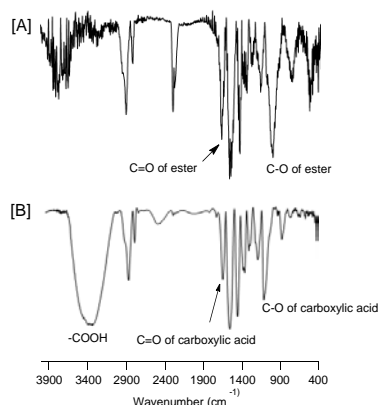


Figure 1. IR spectra of Cross(Noria-MA-co-DM[6]₂₄) [A] and Cross-COOH-DM[6]₂₄ [B].

Table 2. Hydrolysis reaction of Cross(Noria-MA-co-DM[n]_m)

Run	Cross(Noria-co-DM[n] _m)	RH ^[a] (%)	Cross-COOH-DM[n] _m (%)	T _d ^[b] (°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]_m) [b] Determined by TGA.

Complexation ability of Cross(Noria-MA-co-DM[n]_m) and Cross-COOH-DM[n]_m with metal ions in aqueous solution

The complex-forming abilities of Cross(Noria-MA-co-DM[n]_m) and Cross-COOH-DM[n]_m (Scheme 4 [A]) with alkali metal ions such as Na⁺, K⁺, Rb⁺, and Cs⁺ 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^{a]}

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

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

Cross(Noria-MA-co-DM[12]₂₄) and Cross-COOH-DM[12]₂₄ 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]₂₄) did not proceed well, as discussed above. However, Cross-COOH-DM[3]₂₄ and Cross-COOH-DM[6]₂₄ showed higher inclusion complex-forming abilities compared to Cross(Noria-MA-co-DM[3]₂₄) and Cross(Noria-MA-co-DM[6]₂₄) (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]₂₄ suggests that the substantial removal ratio of noria from Cross(Noria-MA-co-DM[6]₂₄) 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⁺ (100 ppm). The adsorption percentage and adsorption amount are summarized in Table 4. In the case of Cross(Noria-MA-co-DM[6]₂₄), 5.3 % of Cs⁺ was adsorbed, corresponding to 0.12 mmol(+)/g-cross-linking material. The adsorption percentage and adsorption amount of Cross-COOH-DM[6]₂₄ were 2.6 % and 0.059 mmol(+)/g-cross-linking material, respectively. Thus, Cross(Noria-MA-co-DM[6]₂₄) and Cross-COOH-DM[6]₂₄ have an adsorption capacity for Cs⁺, again supporting the conclusion that Cross-COOH-DM[6]₂₄ contains noria-templated cavities lined with carboxylic acid groups, as shown in Scheme 4[A].

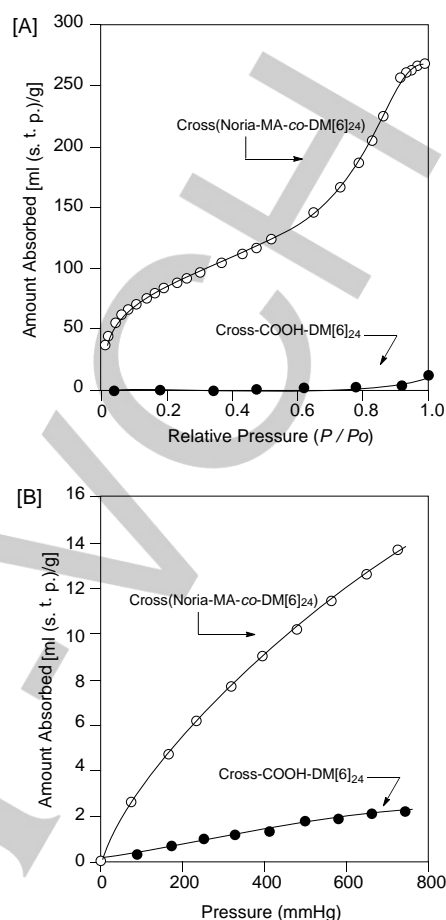
Table 4. Adsorption of Cs⁺ by Cross(Noria-MA-co-DM[6]₂₄) and Cross-COOH-DM[6]₂₄

Run	Cross-linking material	Adsorption of Cs ⁺ (%)	Adsorption amount of Cs ⁺ (mmol(+)/g) ^{a)}
1	Cross(Noria-MA-co-DM[6] ₂₄)	5.3	0.12
2	Cross-COOH-DM[6] ₂₄ (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]₂₄) and Cross-COOH-DM[6]₂₄ in the solid state

It was reported that noria and noria derivatives adsorb carbon dioxide selectively, due to their central fixed holes^[32]. Therefore, we examined the adsorption properties of Cross(Noria-MA-co-DM[6]₂₄) and Cross-COOH-DM[6]₂₄ 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]₂₄) 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]₂₄) are 292.7 m²/g (BET, N₂ at 77K) and 264.8 m²/g (DP, CO₂ at 298K), respectively. On the other hand, the corresponding values of Cross-COOH-DM[6]₂₄ were very small: 1.4 m²/g (BET, N₂ at 77K) and 65.6 m²/g (DP, CO₂ at 298K). These results indicate that many fixed holes exist in Cross(Noria-MA-co-DM[6]₂₄), but not in Cross-COOH-DM[6]₂₄ in the solid state, i.e., hydrolysis reaction of Cross(Noria-MA-co-DM[6]₂₄) removed the noria moieties to give the corresponding Cross-COOH-DM[6]₂₄ containing many carboxylic acid groups, as shown in Scheme 3. The Cross-COOH-DM[6]₂₄ 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]₂₄) and Cross-COOH-DM[6]₂₄.**Table 5.** Estimated surface areas of Cross(Noria-MA-co-DM[6]₂₄) and Cross-COOH-DM[6]₂₄

Run	Cross-linking material	Specific surface area [m ² /g]	
		BET(N ₂ 77K)	DP(CO ₂ 298K)
1	Cross(Noria-MA-co-DM[6] ₂₄)	292.7	264.8
2	Cross-COOH-DM[6] ₂₄ (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 α , ω -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]_m), quantitatively. After hydrolysis reaction of Cross(Noria-MA-co-DM[n]_m), the cross-linking products Cross-COOH-DM[n]_m were obtained by the removal of noria. The inclusion complex abilities was examined using Cross(Noria-MA-co-DM[n]_m) and Cross-COOH-DM[n]_m in the aqueous some metal salts solution, and it was found that Cross-COOH-DM[6]₂₄ 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]_m, 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 ¹H NMR spectrum of noria-MA (Figure S1) were described.

Acknowledgements

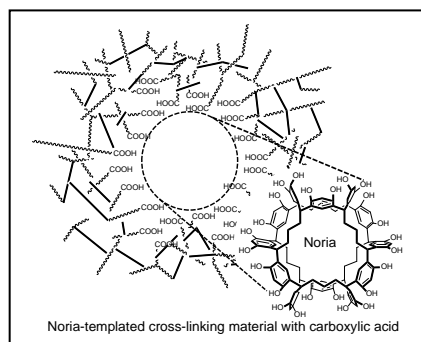
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Keywords: cavity • cross-linking • metal-complexation • noria • synthesis

- [1] C. J. Pederson, *J. Am. Chem. Soc.*, **1967**, *89*, 7017 - 7036.
- [2] C. J. Pederson, *Angew Chem Int Ed.* **1988**, *27*, 1021 - 1027; *Angew. Chem.* **1988**, *100*, 1053 - 1059.
- [3] C. J. Pederson, *Org. Syn.* **1988**, *50*, 395 - 400.
- [4] For example; J. M. Lehn, J. P. Sauvage, *J. Am. Chem. Soc.*, **1975**, *97*, 6700 - 6707.
- [5] For example; B. Dietrich, J. M. Lehn, J. P. Sauvage, *J. Chem. Soc., Chem. Commun.* **1973**, *1*, 15 - 16.
- [6] For example; J. M. Lehn, E. Sonveaux, A. K. Willard, *J. Am. Chem. Soc.*, **1987**, *100*, 4914 - 4916.
- [7] For example; E. Graf, J. M. Lehn, *J. Am. Chem. Soc.*, **1975**, *97*, 5022 - 5024.
- [8] For example; E. Graf E, J. M. Lehn, *J. Am. Chem. Soc.*, **1976**, *98*, 6403 - 6405.
- [9] For example; D. J. Cram, T. Kaneda, *J. Am. Chem. Soc.*, **1979**, *101*, 6752 - 6754.
- [10] C. D. Gutsche, *Calixarenes* Royal Society of Chemistry: Cambridge **1989**.
- [11] D. J. Cram, K. D. Stewart, I. Goldberg, K. N. Trublood, *J. Am. Chem. Soc.*, **1985**, *107*, 2574 - 2575.
- [12] W. Xu, J. P. Rouke, J. J. Vittal, R. J. Puddephatt, *J. Chem Soc., Chem. Commun.*, **1993**, *2*, 145 - 147.
- [13] J. Szejtli, *J. Chem Rev.* **1998**, *98*, 1743 - 1753.
- [14] K. A. Connors, *Chem Rev.* **1997**, *97*, 1325 - 1357.
- [15] For example; Y. Inoue, M. Miyauchi, H. Nakajima, Y. Takashima, H. Yamaguchi, A. Harada, *J. Am. Chem Soc.*, **2006**, *128*, 8994 - 8995.
- [16] For example; A. Harada, J. Li, M. Kamachi, *J. Am. Chem Soc.*, **1994**, *116*, 3192 - 3196.
- [17] For example; A. Harada, J. Li, M. Kamachi, *Nature* **1992**, *356*, 325 - 327.
- [18] A. Harada, J. Li, M. Kamachi, *Nature* **1993**, *364*, 516 - 518.
- [19] H. Kudo, R. Hayashi, K. Mitani, T. Yokozawa, N. C. Kasuga, T. Nishikubo, *Angew. Chem. Int. Ed.* **2006**, *45*, 7948 - 7952; *Angew. Chem.* **2006**, *118*, 8116 - 8120.
- [20] H. Kudo, D. Watanabe, T. Nishikubo, K. Maruyama, D. Shimizu, T. Kai, T. Shimokawa, C. K. Ober, *J. Mater. Chem.* **2008**, *18*, 3588 - 3592.
- [21] X. André, J. K. Lee, A. DeSilva, C.K. Ober, H.B. Cao, H. Deng, H. Kudo, D. Watanabe, and T. Nishikubo, *SPIE* **2007**, 6519 - 65194B.
- [22] T. Nishikubo, H. Kudo, Y. Suyama, H. Oizumi, and T. Itani, *J. Photopolym. Sci. Technol.*, **2009**, *22*, 3 - 76.
- [23] H. Kudo, Y. Suyama, H. Oizumi, T. Itani, T. Nishikubo, *J. Mater. Chem.* **2010**, *20*, 4445 - 4450.
- [24] N. Niina, H. Kudo, H. Oizumi, T. Itani, T. Nishikubo, *Thin Solid Films* **2013**, *534*, 459 - 464.
- [25] H. Kudo, M. Jinguji, T. Nishikubo, H. Oizumi, T. Itani, *J. Photopolym. Sci. Technol.* **2010**, *23*, 657 - 664.
- [26] H. Seki, Y. Kato, H. Kudo, H. Oizumi, T. Itani, T. Nishikubo, *Jpn. J. Appl. Phys.* **2010**, *49*, 06GF06/1 - 6.
- [27] H. Yamamoto, H. Kudo, T. Kozawa, *Microelectron. Eng.* **2015**, *133*, 16 - 22.
- [28] H. Seki, S. Kuwabara, H. Kudo, T. Nishikubo, *Chem. Lett.* **2012**, *41*, 699 - 701.
- [29] H. Seki, S. Kuwabara, H. Kudo, T. Nishikubo, *Chem. Lett.* **2011**, *40*, 464 - 466.
- [30] N. Nobumitsu, H. Kudo, T. Nishikubo, *Chem. Lett.* **2009**, *38*, 1198 - 1199.
- [31] H. Kudo, K. Shigematsu, K. Mitani, T. Nishikubo, N. C. Kasuga, H. Uekusa, Y. Ohashi, *Macromolecules*, **2008**, *41*, 2030 - 2036.
- [32] J. Tian, P. Thallapally, S. J. Dalgarno, P. B. McGrail, J. L. Atwood, *Angew. Chem. Int. Ed.* **2009**, *48*, 5492 - 5495; *Angew. Chem.* **2009**, *121*, 5600 - 5603.

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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.