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Quadruple Click. A Facile Pathway leading to Tetrakis(4-(1,2,3-triazolyl)methyl)-ethylenediamine as a New Class of Extracting Agent for Soft Metal Ions

Wataru Watanabe,[a] Tetsuya Maekawa,[a] Yuji Miyazaki,[a] Tatsuya Kida,[a] Kenji Takeshita,[b] Atsunori Mori,*[a]

Dedication ((optional))

Abstract:
Tetrakis(triazolylmethyl)ethylenediamine, which is a class of TPEN (tetrakis(2-pyridylmethyl)ethylenediamine) analogue, is synthesized by quadruple click (quad click) reaction of tetrapropargylated ethylenediamine and four equivalents of alkyl azide. The obtained compound efficiently extracted a soft metal cadmium(II) ion by solvent extraction. It is also found that NIPA (*N*-isopropylacryl amide) gel using the triazole ethylenediamine as a cross linker exhibits temperature-dependent change of extraction performance of cadmium(II) ion.

Keywords: quadruple click • azide • alkyne • TPEN • soft metal ion

Introduction

Multidentate chelating agents that capture a variety of metal ions have attracted much attention in environmental analyses, recovery of resources, catalysis, etc.[1] Thus, design of the molecular structure of chelating agents, which induce high-performance and/or metal-specific binding, is highly intriguing in organic synthesis. TPEN, which is composed of four 2-pyridylmethyl groups on 1,2-ethylenediamine, has been recognized as a multidentate ligand with six nitrogen donors for coordination of soft metal ions.[2] We have been interested in the use of TPEN derivatives as an extracting agent for soft metals such as Cd^{2+} or a minor actinide Am^{3+} and, indeed, several TPENs that bear hydrophobic substituents efficiently extracted the metal ions.[3,4] However, a major drawback of such modified TPENs is preparative difficulties involving multi-step synthetic pathways to construct the TPEN structure. On the other hand, click chemistry, which is the reaction of alkyne with azide forming triazole, has recently been extensively studied and employed for a wide range of fields, bioorganic chemistry and materials science.[5] The click reaction is a facile method to connect different functionalities into a single molecule with the stable triazole ring. We envisaged that a quadruple click reaction of an ethylenediamine derivative bearing alkyne moiety and four equivalents of alkyl azide can lead to the TPEN analogue bearing four triazole rings[6] as a surrogate of the pyridine ring and if the obtained compound similarly extracts metal ions, it would also be a new class of effective extracting agent for soft metal ions. We herein describe synthesis of tetrakis(triazolylmethyl)ethylenediamine derivatives via the quadruple click reaction of alkynes and azides and extraction behaviors of cadmium ions with the obtained TPEN analogue.

Abstract in Japanese:
四重クリック反応を利用することにより，簡便にエチレンジアミンの窒素原子上に４つのトリアゾール環が置換した化合物を得ることができる。この化合物はCd(II)などのソフト金属を効率よく吸着する。

Results and Discussion

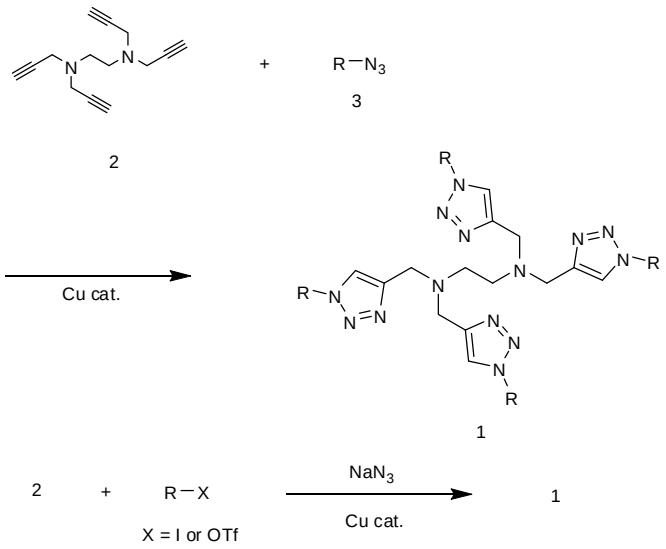
Synthesis of the ethylenediamine derivative bearing four triazole moiety **1** was carried out by the reaction of *N*,*N*,*N*',*N*'-tetrakis(2-propyn-1-yl-methyl)-ethane-1,2-diamine **2** and the corresponding azide **3a-3e** by the click reaction in the presence of a copper catalyst. Although such click chemistry was employed for the synthesis of sugar derivatives,[6] the reaction with hydrophobic azide derivatives has not been examined so far to the best of our knowledge. Indeed, the reaction was found to be unsuccessful when the reaction conditions for the use of sugar azide was employed for

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the reaction to **1** and octyl azide (**3a**). However, the reaction proceeded smoothly with ethanol as a solvent in the presence of 20 mol% of CuI to afford 84% of **1a**. Reactions with 1-dodecyl (**3b**) and 1-butyl (**3c**) azides similarly proceeded to afford the corresponding products **1b** and **1c** in 70% and 81% yields, respectively. The reaction with aryl azide **3d** and fluoroalkyl substituent azide **3e** were also examined in a similar manner to afford the corresponding product **1d** and **1e** in 35% and 27% yields, respectively, although the yields were slightly lower (Scheme 1, Table 1). It was found to be possible to afford **1a** by the one-pot reaction with 1-iodooctane (**3f**), tetraalkyne **2**, and sodium azide in 75% yield.[7] The related tetrakis triazole derivative bearing other fluoroalkyl substituents was obtained by the one-pot reaction of triflate **3g**, **2**, and sodium azide to afford **1f** in 52% yield.



Scheme 1. Synthesis of triazole ethylenediamine derivatives **1**

Table 1. Synthesis of triazole ethylenediamine derivatives **1**

3[a]	R	RN_3	RX	Product (%yield)[b]	
3a	$CH_3(CH_2)_7$	N_3		**1a**	84
3b	$CH_3(CH_2)_{11}$	N_3		**1b**	70
3c	$CH_3(CH_2)_3$	N_3		**1c**	81
3d	$CH_3(C_6H_4)$	N_3		**1d**	31
3e	$H(CF_2)_4CH_2$	N_3		**1e**	27
3f[c]	$CH_3(CH_2)_7$		I	**1a**	75
3g[c]	$H(CF_2)_2CH_2$		OTf	**1f**	52

[a] Unless noted, the reaction of was **2** (1.0 eq) and **3** (4.4-5.6 eq) carried out with CuI as a catalyst. [b] Isolated yield. [c] The reaction was performed with **2** (1.0 eq), **3** (4.8 eq), and sodium azide (4.8 eq) with CuI as a catalyst in methanol.

Worthy of note is the formation of tetratriazole derivatives in a single-step reaction of tetraalkyne **2** and four equivalents of azide by contrast that the related pyridyl methyl analogs (TPEN) have been synthesized in a multi-step reactions starting from the corresponding pyridine oxides. The one-pot preparation with alkyl halides and triflates in the presence of sodium azide is also a facile synthetic protocol particularly for those of low molecular weight avoiding isolation of explosive organic azide.

The obtained triazole ethylenediamine derivatives **1** were subjected to the extraction of cadmium(II) ions with $Cd(NO_3)_2$ aqueous solution, whose pH value and ionic strength were controlled by the addition of HNO_3 and NH_4NO_3, respectively. The cadmium ion of the aqueous phase was extracted into the organic phase, in which 1 mM of **1** was dissolved in chloroform. The extracted amount of the cadmium ion was estimated by measurement of the concentration of remaining Cd^{2+} in the aqueous phase by ICP-AES analysis. Table 2 summarizes the results.

Table 2. Solvent extraction of Cd^{2+} ion by **1a-1f**[a]

pH	*E* (%)[b]					
	1a	**1b**	**1c**	**1d**	**1e**	**1f**
5	47	46	45	31	26	26
3	41	41	45	19	31	31
1	36	30	23	16	27	35

[a] Extraction was performed with 1 mM of **1** and $Cd(NO_3)_2$ solutions by shaking the mixture at room temperature. [b] %*E*xtraction of Cd^{2+} ion value was estimated by ICP-AES analysis.

A series of triazole ethylenediamine derivatives **1** extracted cadmium ions in pH 1 to 5. The extracted amount was found to be 16-47%. The extraction performance of **1** was relatively inferior to that of TPEN derivatives, which extracted cadmium ion efficiently in the pH regions of ca. 2-5, however, the extraction performance of TPEN generally decreased as the pH of the aqueous phase became acidic. Subsequently, most of TEPN derivatives hardly extracted Cd^{2+} in an aqueous solution of ca. pH=1. By contrast, it was found that decrease of the %extraction value was not significantly remarkable at highly pH=1in **1a**, **1b**, and **1f**.

We then examined the effect of additive for the purpose of improving the extraction performance of Cd^{2+}. Extraction was carried out with **1c** (R= $CH_3(CH_2)_3$) using 2-bromoctanoic acid (**4**) that can be a counter ion of cadmium replaced by NO_3^- as an additive. Figure 1 summarizes the results of extraction at pH=3 by changing the concentration of **4** from 10 mM to 100 mM. The extraction performance was found to improve as the concentration of **4** increased. When the extraction was carried out with 100 mM of **4** ($CHCl_3$/**4**=30:1), 77% of the cadmium ion was extracted by **1c**. (45% extraction without **4** at pH=3).

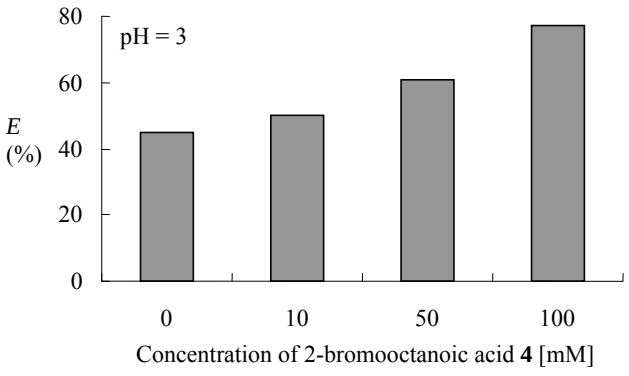


Figure 1. Solvent extraction of Cd^{2+} ion by **1c** at pH 3 with various concentration of 2-bromooctanoic acid **4**

Table 3 summarizes the results of the extraction of cadmium ion with several triazole ethylenediamine **1** in 30:1 of $CHCl_3$ and **4**. In

the pH range of 1-3, extraction performance was found to improve by the addition of 2-bromoctanoic acid **4**. The effect of additive was remarkable in **1c** bearing butyl substituent comparing **1a** (R= $CH_3(CH_2)_7$) and **1b** (R= $CH_3(CH_2)_{11}$)

We then examined the extraction of europium (III) ion with triazole ethylenediamine derivatives **1a-1c**. Extraction was carried out in a similar manner to the case of cadmium ion under pH range of ca. 1-3. The extracted amount was also estimated by IPC-AES analyses of the aqueous phase. As summarized in Table 4, **1a-1c** was found to hardly extract the Eu^{3+} ion. The results suggest that **1** selectively extracts cadmium and the separation factor of Cd/Eu is remarkably high. Since the extraction behaviors of cadmium was shown to be similar to that of minor actinides (MA) such as americium Am^{3+} and curium Cm^{3+}, these results suggest that triazole ethylenediamine derivatives **1** are also potentially effective for the separation of minor actinides and lanthanides, which is an indispensable process for the separation of high-level atomic waste of nuclear power generation.

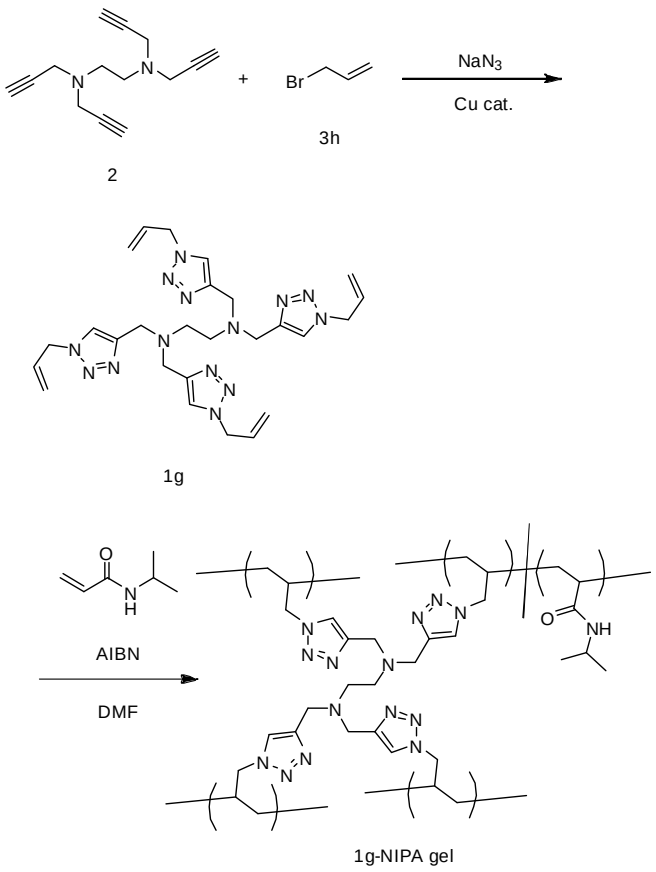
Table 3. Solvent extraction of Cd^{2+} and Eu^{3+} ions by **1a-1c**[a]

pH	*E* (%)[b]	Cd^{2+} Eu^{3+}	
	1a	**1b**	**1c**
3	71	69	77
	0	0.4	0
2	44	41	55
	0	0	0
1	33	24	49
	0	3.7	2.4

[a] Extraction of Cd^{2+} or Eu^{3+} ion was performed with 1 mM of **1** and 100 mM of 2-bromoctanoic acid (**4**) in chloroform and 1 mM aqueous solutions of $Cd(NO_3)_2$ or $Eu(NO_3)_2$ by shaking the mixture at room temperature. [b] %*E*xtraction of Cd^{2+} (upper) and Eu^{3+} (lower) values were estimated by ICP-AES analysis.

The extraction performance of soft metal ions with triazole ethylenediamine derivatives **1** was then applied to the extraction with polymer gel. Since polymer gels, in which TPEN derivatives are incorporated as cross linker, are shown to extract soft metal ions,[3b,c,e] it is intriguing to apply the related gel with **1** for the extraction. In particular, the polymer gel prepared by *N*-isopropyl acrylamide (NIPA) as a monomer was revealed to exhibit temperature-dependent change of extraction performance. Accordingly, the poly NIPA gel composed of **1** as cross linker would also be of much interest.

Synthesis of **1g** (R: $CH_2CH{=}CH_2$) was carried out in a similar manner to the case of other triazole ethylenediamine derivatives. The obtained **1g** was then subjected to radical polymerization of NIPA in the presence of AIBN as an initiator. When polymerization was carried out 1:40 of **1g** and NIPA with 3.4 mol% of AIBN, the corresponding polymer gel was obtained as shown in Scheme 2.[8] The gel was found to swell at 0 ºC (below LCST of poly-NIPA) while shrinking was observed at 40 ºC, respectively.[3b-d,4j,9] **1g**-NIPA gel was insoluble in any organic solvents as well as in water, thereby spectroscopic characterization of **1g**-NIPA gel was impossible for the understanding of chemical structure in detail. Then, the polymer gel was subjected to the extraction of cadmium ion from aqueous solution of $Cd(NO_3)_2$ under pH of 2 and 5 at the swollen (0 ºC) and shrinking (40 ºC) states.



Scheme 2. Synthesis of triazole ethylenediamine derivative **1g** and **1g**-NIPA gel

Figure 2 represents the extraction performance of cadmium ion. The result showed that temperature-dependent change was observed in the extraction with Cd^{2+} ion. In both pH of 2 and 5, superior extraction was observed with the swollen gel at 0 ºC, while little extraction at 40 ºC. Although the performance of the polymer gel was relatively inferior to that of TPEN-NIPA gel, similar temperature-dependent extraction change was observed.

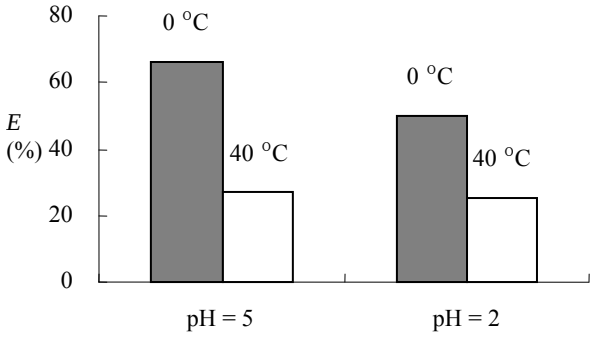


Figure 2. Temperature-dependent extraction of Cd^{2+} ion by **1g**-NIPA gel at pH 5 and 2.

Conclusion

In summary, we have shown that quadruple click is a facile synthetic pathway of triazole ethylenediamine derivatives **1**, which have been shown to extract a soft metal ion Cd^{2+} efficiently. The performance was found to improve when 2-bromoctanoic acid (**4**) was employed as an additive although. It was also found that

polymer gels composed of **1g** and NIPA exhibited temperature-dependent change of extraction performance.

Experimental Section

Quadruple click with *N,N,N',N'*-tetrakis(2-propyn-1-yl)ethylen-1,2-diamine (2) and alkylazide (3c): To 20 mL Schlenk tube were added 1-azidobutane (**3c**: 425 mg, 4.29 mmol), *N,N,N',N'*-tetrakis(2-propyn-1-yl)ethylen-1,2-diamine (**2**: 190 mg, 0.89 mmol), and ethanol (3 mL). CuI (34 mg, 0.18 mmol) was then added and the mixture was allowed to stir at room temperature for 5 min. The resulting solution was poured into aqueous ammonia and the product was extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid, which was recrystallized from hexanes to afford 0.44 g (81%) of *N,N,N',N'*-tetrakis(3-butyltriazole-2-yl-methyl)ethylen-1,2-diamine (**1c**) as a colorless solid. IR (ATR) 2955, 2917, 2850, 1467, 1053 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.68 (s, 4H), 4.25 (t, *J* = 7.4 Hz, 8H), 3.65 (s, 8H), 2.65 (s, 4H), 1.20-1.28 (m, 8H), 0.83 (t, *J* = 7.4 Hz, 12H) ; ^{13}C NMR ($CDCl_3$, 75 MHz) d 13.30, 19.57, 32.09, 47.74, 49.85, 50.78, 123.40, 143.70 ; HRMS (ESI+, M+H) found 609.4578, calcd for $C_{30}H_{53}N_{14}$ 609.4571.

Extraction of cadmium ion with 1a: Organic phases were prepared by dissolving 1 mM *N,N,N',N'*-tetrakis(3-butyltriazole-2-ylmethyl)ethylene-1,2-diamine in chloroform or nitrobenzene. Aqueous phases were prepared by dissolving 1 mM $Cd(NO_3)_2$. HNO_3 was used to control the pH from 1 to 5, and ionic strength was controlled as 0.1 by NH_4NO_3. A mixture of the equal volumes (1.8 mL) of the organic and aqueous solutions in a vial was shaken at room temperature for 5 min. These mixtures were then centrifuged and the concentration of Cd(II) in the aqueous phase was measured with ICP-AES. The distribution ratio [$D = [Cd]_{org}/[Cd]_{aq} \times 100$] and %extraction [$E = 100D/(D+V_{aq}/V_{org})$] of Cd(II) was calculated. $[Cd]_{org}$; $[Cd]_{aq}$: Concentration of cadmium ion in organic and aqueous phase, respectively.

Synthesis of NIPA gel with 1g: To a 20 mL screw-capped test tube were added *N*-isopropylacrylamide (181 mg, 1.6 mmol) and triazole ethylenediamine derivative **1g** (21.8 mg, 0.04 mmol). The mixture was dissolved in 0.15 mL of DMF and AIBN (3.4 mol%) was added in one portion to the solution. The resulting mixture was heated at 60 ºC for 18 h. Then, the mixture was cooled to room temperature and washed with water repeatedly. Water was removed under reduced pressure at 50 ºC to leave a colorless solid. Since the obtained **1g**-NIPA gel was found to be insoluble in any organic solvents and in water, attempted characterization of the polymer gel was unsuccessful.

Extraction of cadmium(II) ion with 1g-NIPA gel: A 1 mM of aqueous $Cd(NO_3)_2$ solution was prepared. The pH value of the solution was controlled to 2 and 5 by the addition of 1 M of aq NH_4NO_3 and 1 M of HNO_3. **1g**-NIPA gel (2.5 mol% of **1g** contents), whose concentration of the **1g** moiety was controlled to be 1.5 μmol, was added to 0.75 mL of the aqueous solution. Vigorous stirring of the mixture was continued for 60 min at 0 °C or 40 °C. An aliquot of the supernatant (0.2 mL) was taken and the solution was diluted by distilled water to 4.0 mL, which was subjected to ICP-AES analysis. The percent extraction value was calculated as $\%E = 100D/(D+1)$, {$D = ([Cd]_{ini}-[Cd])/[Cd]$ }; $[Cd]_{ini}$: concentration of Cd^{2+} in water before extraction; [Cd]: concentration of Cd^{2+} in water after extraction.

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[8] Since the obtained gel was hardly soluble in any solvents, it has been difficult to characterize the properties of **1g**-gel.

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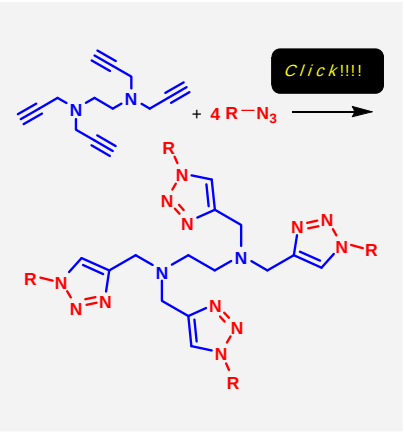
Entry for the Table of Contents (Please choose one layout only)

Layout 1:

Catch Phrase

*Wataru Watanabe, Tetsuya Maekawa, Yuji Miyazaki, Tatsuya Kida, Kenji, Takeshita, Atsunori Mori** ……...…… Page – Page

Quadruple Click. A Facile Pathway leading to Tetrakis(4-(1,2,3-triazolyl)methyl)-ethylenediamine as a New Class of Extracting Agent for Soft Metal Ions



Quadruple Click with tetraalkynyl ethlenediamine and four equivalents of azide gives tetrakis triazolyl ethlenediamine. The obtained molecule extracts cadmium(II), a class of soft metal ion, efficiently whereas europium(III) of slightly less softness ion is hardly extracted. The poly(*N*-isopropylacrylamide) (NIPA) gel composed of tetrakis triazolyl ethlenediamine moiety as a cross linker shows temperature-dependent change of extraction performance.