Pergamon

Tetrahedron Letters 43 (2002) 9385–9389

TETRAHEDRON LETTERS

Strongly basic macrocyclic triamines, 1,5,9-triazacyclododecanes for solvent extraction of gold(I) cyanide

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Received 13 September 2002; accepted 11 October 2002

Abstract—Solvent extraction of gold(I) dicyanide anion from alkaline gold(I) cyanide solution using unusually basic amine extractants was conducted. 1,5,9-Triazacyclododecane (**4**) is known as an unusually basic macrocyclic amine having $pK_a = 12.3$–12.7, and is thus a good candidate as a basic amine extractant. Three lipophilic derivatives of **4** expected to stay in the organic phase during gold solvent extraction were synthesized. *N*-Dodecyl-1,5,9-triazacyclododecane (**3**) was prepared from 1,5,9-triazacyclododecane-2,4-dione (**1**) by N-alkylation with *n*-dodecyl iodide and then reduction with BH_3-THF. *N*,*N*′-Didodecyl-1,5,9-triazacyclododecane (**5**) and *N*,*N*′,*N*″-tridodecyl-1,5,9-triazacyclododecane (**6**) were efficiently synthesized by selective di-alkylation of **4** with *n*-dodecyl iodide, and by reductive alkylation of **4** with *n*-dodecanal, respectively. The extractants **3** and **6** showed $pH_{50} = 10.5$, which is the minimum value required for practical application.

Amines are an important class of extractants in solvent metal extraction technology, and have been used industrially for the recovery of uranium and copper.[1,2]

Development of extractants for gold dicyanide anion, $Au(CN)_2^-$ is an active area of research.[3] Of particular significance are the extraction of gold from dilute, alkaline cyanide solutions and the possible use of solvent extraction for gold recovery in cyanidation processes.[3] Solvent extraction and enriching processes are performed in two stages: extraction of gold from dilute, alkaline cyanide leach solutions into a hydrocarbon medium containing a lipophilic extractant, and then stripping the gold into a more basic solution, from which the pure metal can be obtained by electrowinning.

The pH of a typical alkaline gold cyanide leach solution is about 10.5. Since the pK_a of HCN is 9.21,[4] below pH 10 toxic HCN is evolved. Thus, the lipophilic amine extractant must be protonated in the hydrocarbon extraction medium at $pH \geq 10.5$ to form an ion-pair with $Au(CN)_2^-$, which is extracted to the organic phase.

The basicity of the lipophilic amine is a critical factor for application in gold extraction and stripping processes. Practical amine extractants for $Au(CN)_2^-$ have not been reported with sufficiently high basicity required in hydrocarbon extraction media.

1,5,9-Triazacyclododecane (**4**) is known to be an unusually basic azacrown compound which has $pK_{a3} = 12.3$–12.7, $pK_{a2} = 7.3$–8.0 and $pK_{a1} = 2.4$–3.3.[5,6] The strong basicity is attributable stabilization of a proton in the monocation by hydrogen bonding with nitrogen atoms in the fashion of a macrocyclic complex. To keep the protonated amine in the organic phase, lipophilic dodecyl groups are attached to nitrogen atoms of **4**. Syntheses of the alkylated amines are shown in Scheme 1.

Many synthetic methods for azacrowns are known.[7] Representative methods for preparation of **4** are Weisman synthesis via a tricyclic orthoamide intermediate, the Parker approach involving condensation of a malonate ester and bis(3-aminopropyl)amine, and Richman-Atkins cyclization of a bis-*p*-toluenesulfonamide salt with a bis-tosylate.[8] For efficient and selective mono-alkylation on one of three identical nitrogens of **1**, the Parker synthesis is most practical. Condensation of bis(3-aminopropyl)amine with diethyl malonate in the presence of a catalytic amount of sodium methoxide in ethanol increased the yield of **1** to 22%, compared to 14% without sodium methoxide, as reported by Parker et al.[8a]

Keywords: 1,5,9-triazacyclododecane; amine extractant; solvent extraction; gold cyanide; gold leach solution; pH_{50}.

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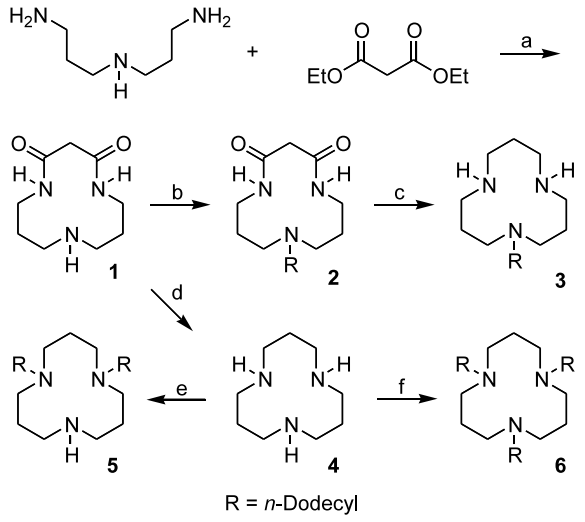
0040-4039/02/$ - see front matter
PII: S0040-4039(02)02322-5



Scheme 1. *Reagents and conditions*: (a) MeONa, EtOH, reflux, 7 d, 22%; (b) *n*-dodecyl iodide, DMA, rt, overnight, 60%; (c) BH_3·THF, reflux, 24 h, 95%; (d) BH_3·THF, reflux, 24 h, 99%; (e) *n*-dodecyl iodide, $NaHCO_3$, DMA, 80°C, overnight, 88%; (f) *n*-dodecanal, $NaCNBH_3$, H_2O/CH_3CN, pH = 4–5, rt, overnight, 90%.

Acyclic by-products initially formed by intermolecular oligomerization may be in equilibrium with the starting materials in the presence of sodium methoxide in hot ethanol. Heating the reaction mixture under reflux for a prolonged period (7 days) gave **1** in 22% yield after column chromatography.[9] Alkylation of **1** with *n*-dodecyl iodide in DMA gave **2** in 60% yield after crystallization from MeOH–CH_2Cl_2.[10] Reduction of **2** with BH_3·THF gave **3** in 95% yield.[11] Azacrown **4**, prepared by reduction of **1** using BH_3·THF[8a] was treated with excess *n*-dodecyl iodide in DMA in the presence of $NaHCO_3$ to give *N*,*N*′-didodecyl azacrown **5** in 80% yield as the trihydrochloride salt after treatment with HCl gas in THF.[12] This selective alkylation of two of the three equivalent nitrogens of **4** can be attributed to the characteristic of its strong basicity. Under the reaction conditions, product **5** is monoprotonated, apparently reducing the nucleophilicity of the remaining secondary amine nitrogen. Reductive amination of **4** with *n*-dodecanal gave **6** in 90% yield.[13] The NMR spectra of **3** and **6**·3HCl demonstrated the expected molecular symmetry. However, ^1H and ^{13}C NMR spectra of **5**·3HCl in DMSO-d_6 did not show the C_{2v} symmetry expected from its structure even at 130°C, suggesting the presence of cis and trans stereoisomeric salts.

The equilibrium distributions of $Au(CN)_2^-$ were determined after mixing the organic extractant phase consisting of a toluene solution of the lipophilc amine with the alkaline cyanide aqueous phase (pH 3–13). The pH of the aqueous phase was adjusted, and continuously monitored by means a glass pH electrode. After equilibrium of the phases was established, samples of the aqueous solution were taken. An equal amount of the organic phase was also removed to maintain a fixed phase ratio, keeping a 1:1 organic to aqueous volume ratio.[14]

The pH_{50} value is the pH at which 50% of the desired metal has been extracted from the aqueous solution by a particular amine. A higher value of pH_{50} is indicative of an increase in base strengh of the amine. A pH_{50} value greater than or equal to 10.5 is desired for practical application in gold cyanide extraction.[3] The percentage of gold extracted as a function of pH is shown in Fig. 1 for azacrown extractants, **3**, **5**, and **6** as well as for *n*-dodecylamine, di-*n*-dodecylamine, and tri-*n*-dodecylamine.

Primary, secondary and tertiary aliphatic amines have been examined for the extraction of $Au(CN)_2^-$ from alkaline gold cyanide solution. The pH_{50} value of these amines were reported to be below 8.[3] It is generally known that the basicities of alkylamines in polar solvents increase in the order: secondary>primary>tertiary amine, due to opposing inductive and solvation effects.[15] The pH_{50} values for gold extraction with amines increased as the amine concentration was increased, but varying the gold concentration or organic solvent type did not significantly change the pH_{50} value.[3a] The pH_{50} values for 50 mM solutions of commercial lipophilic primary, secondary and tertiary amines in xylene were reported as 6.6, 7.2 and 5.7, respectively,[3b] which is parallel to the order of amine basicity.

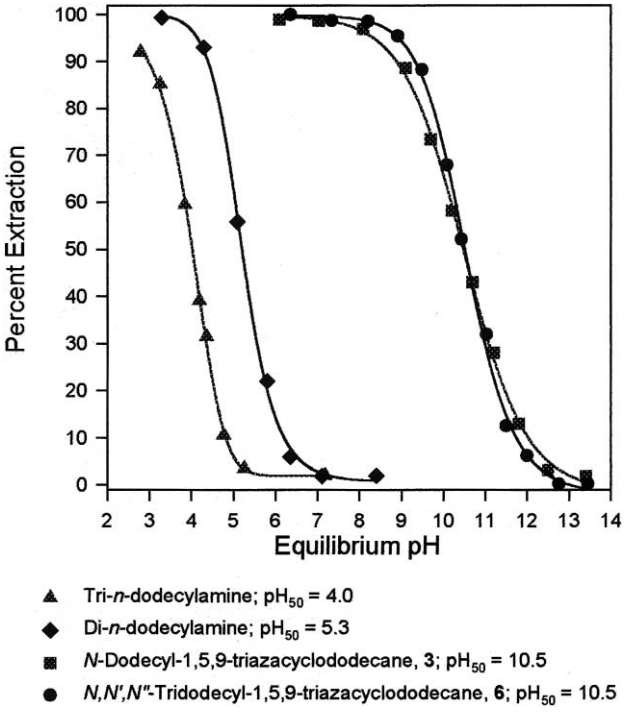


Figure 1. Percent extraction of $Au(CN)_2^-$ from alkaline gold cyanide solution as a function of pH for amine extractants in toluene. Aqueous phase: 0.05 mM $KAu(CN)_2$ in 125 ppm cyanide solution (10 ppm Au); Organic phase: 5 mM amine extractant in toluene.

Table 1. The pH_{50} values of amine extractants for gold solvent extraction under the given extraction conditions

Extraction condition[a]	Amine extractants				
	Di[b]	Tri[c]	**6**	**3**	**5**
1 mM amine/10 ppm Au	–	–	9.6	9.8	>13
5 mM amine/10 ppm Au	5.2	4.0	10.5	10.5	>13
5 mM amine/100 ppm Au	5.8	4.2			
50 mM amine/100 ppm Au	6.9	5.4			

[a] The extraction was conducted in two phases; toluene containing amine/alkaline gold cyanide solution at rt.
[b] Di-*n*-dodecylamine.
[c] Tri-*n*-dodecylamine.

In the current study, the pH_{50} values of solutions of 5 mM di-*n*-dodecylamine and tri-*n*-dodecylamine in toluene were measured as 5.2 and 4.0, respectively, as shown in Table 1. Increasing gold concentration by a factor of ten did not affect the pH_{50} amine basicity, but ten-fold increase of amine concentration enhanced the pH_{50} values over one pH unit. Under these extraction conditions, *n*-dodecylamine did not extract $Au(CN)_2^-$ anion from gold cyanide solution. It is apparent that *n*-dodecylamine stays in the acidic aqueous phase at the expected pH_{50} value. The extraction of gold with simple alkylamine extractants is limited to acidic solutions. Thus, polar modifiers such as tributyl phosphate or dibutyl butyl phosphonate have been added to the organic phase enhance the pH_{50} values up to 4 pH uints.[3]

However, under the same extraction conditions, the amine extractants **3** and **6** based on the highly basic 1,5,9-triazacyclododecane skeleton markedly shifted the position of the percent extraction/pH curves to pH_{50} values of 10.5. Dialkylated analog **5** completely extracted gold over the entire pH range tested, pH 5 to 13, and did not show the usual sigmoid extraction/pH curve. Dilution of the amine concentration to 1 mM in toluene slightly reduced the pH_{50} values to 9.6 and 9.8 for **3** and **6**, respectively. However, 1 mM solutions of any of the alkyamines were not able to extract gold from 10 ppm gold cyanide solution. The results are presented in Table 1.

It is not clear why dialkyl derivative **5** behaves as a more basic amine under these extraction conditions than the monoalkyl (**3**) and trialkyl (**6**) analogs. The major factors affecting alkylamine basicity are the inductive and solvation effects.[15] If these effects determine the basicities of its derivatives, **3** bearing two secondary amines and one tertiary amine should be most basic than **5** and **6,** which have one secondary amine and none of secondary amine, respectively. However, for azacrown **4** and its derivatives, basicity is influenced by specific hydrogen bonding interactions between the nitrogens and the proton held in the cavity of the macro ring. Extractant **5** may be too basic to be applicable for gold solvent extraction because the stripping process using basic hydroxide might be not efficient. However, compounds **3** and **6** are novel extractants, from which gold can be stripped at high pH.

In conclusion, the unusually basic lipophilic amine extractants, **3**, **5** and **6**, based on 1,5,9-triazacyclododecane (**4**) were synthesized and examined for solvent extraction of gold from alkaline gold cyanide solution. The pH_{50} values for **3** and **6** were measured to be 10.5. These amines are the first efficient amine extractants that can be used for solvent extraction of gold without modifiers. We plan to further examine the applicability of polyamines in this new structural class for extraction of gold from alkaline gold cyanide leach solutions.

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-2001-015-200110211). We also thank Dr. Maurice C. Fuerstenau, professor of Metallurgy, University of Nevada, Reno, for helpful information and advice concerning this project.

References

1. (a) Coleman, C. F.; Brown, K. B.; Moore, J. G.; Crouse, D. J. *Ind. Eng. Chem.* **1958**, *50*, 1756; (b) Moore, F. L. *Anal. Chem.* **1960**, *32*, 1075; (c) Itzkovitch, I. J.; Rickelton, W. A. Can. CA 157278, 1983; *Chem. Abstr.* **1984**, *100*, 160090.
2. (a) Virnig, M. J.; Mackenzie, J. M. US Patent 466166; *Chem. Abstr.* **1997**, *126*, 110207; (b) Power, K. L. *Solvent Extr., Proc. Int. Solvent Extr. Conf.* **1971**, *2*, 1409; *Chem. Abstr.* **1975**, *83*, 182483.
3. (a) Miller, J. D.; Mooiman, M. B. *Sep. Sci. Technol.* **1984**, *19*, 895; (b) Mooiman, M. B.; Miller, J. D. *Miner. Metall. Process* **1984**, *1*, 153; (c) Mooiman, M. B.; Miller, J. D. *Hydrometallurgy* **1986**, *16*, 245; (d) Miller, J. D.; Wan, R. Y.; Mooiman, M. B.; Sibrell, P. L. *Sep. Sci. Technol.* **1987**, *22*, 487; (e) Riveros, P. A. *Hydrometallurgy* **1990**, *24*, 135; (f) Kordosky, G. A.; Sierakoski, J. M.; Virnig, M. J.; Mattison, P. L. *Hydrometallurgy* **1992**, *30*, 291; (g) Sastre, A. M.; Madi, A.; Alguacil, F. J. *Hydrometallurgy* **2000**, *54*, 171.
4. Perrin, D. D. *Ionisation Constants of Inorganic Acids and Bases in Aqueous Solution*; 2nd Edn; Pergamon Press: Oxford, 1982.
5. (a) Bell, T. W.; Choi, H.-J.; Harte, W. *J. Am. Chem. Soc.* **1986**, *108*, 7427; (b) Choi, H.-J. Ph.D. Dissertation, State University of New York, Stony Brook, 1989.

6. (a) Reido, T. J.; Kaden, T. A. *Chimia* **1977**, *31*, 220; (b) Zompa, L. J. *Inorg. Chem.* **1978**, *17*, 2531; (c) Briellmann, M.; Kaderli, S.; Meyer, C. J.; Zuberbuhler, A. D. *Helv. Chim. Acta* **1987**, *70*, 680; (d) Geraldes, C. F. G. C.; Sherry, A. D.; Marques, M. P. M.; Alpoim, M. C.; Cortes, S. *J. Chem. Soc., Perkin Trans. 1* **1991**, 137.
7. Parker, D. In *Macrocycle Synthesis A Practical Approach*; Parker, D., Ed.; Oxford University Press: Oxford, 1996; pp. 1–23.
8. (a) Helps, I. M.; Parker, D.; Jankowski, K. J.; Chapman, J.; Nicholson, P. E. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2079; (b) Hoye, R. C.; Richman, J. E.; Dantas, G. A.; Lightbourne, M. F.; Shinneman, L. S. *J. Org. Chem.* **2001**, *66*, 2722; (c) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268; (d) Atkins, T. J.; Richman, J. E.; Oettle, W. F. *Org. Syn.* **1978**, *58*, 86; (e) Alder, R. W.; Mowlam, R. W.; Vachon, D. J.; Weisman, G. R. J. Chem. Soc. *Chem. Commun.* **1992**, 507.
9. 1,5,9-Triazacyclododecane-2,4-dione, **1**: A mixture of diethyl malonate (8.03 g, 50 mmol), bis(3-aminopropyl)amine (6.56 g, 50 mmol), sodium methoxide (270 mg, 5 mmol) and abs ethanol (600 mL) was heated at reflux for 7 days under nitrogen. The solvent was removed under reduced pressure. The oily residue was purified by a column chromatography on silica gel using $MeOH/CH_2Cl_2/NH_4OH$ (75:20:5) to afford the product (2.2 g, 22%) as a white solid, which can be crystallized from MeOH-CH_2Cl_2 to give plate-like crystals: mp 153-154°C (lit. 152–154°C[8a]).
10. 9-Dodecyl-1,5,9-triazacyclododecane-2,4-dione**, 2**: A mixture of **1** (1.00 g, 5.02 mmol), *n*-dodecyl iodide (4.50 g, 15.2 mmol) and DMA (50 mL) was stirred at room temperature overnight. The solvent was removed by vacumm distillation at 80°C. The residue was washed with hexane on a filter paper to remove excess dodecyl iodide. The solid was dissolved in CH_2Cl_2 and washed with a Na_2CO_3 solution. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was crystallized from MeOH–CH_2Cl_2 to give needle shaped crystals (1.11 g, 60%): mp 134–135°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (br s, 2 H), 3.40 (q, $J=5.5$ Hz, 4 H), 3.18 (s, 2 H), 2.53 (t, $J=5.5$ Hz, 4 H), 2.38 (t, $J=7.8$ Hz, 2 H), 1.75 (quin., $J=5.5$ Hz, 4 H), 1.46 (quin., $J=7.8$ Hz, 2 H), 1.26 (m, 18 H), 0.88 (t, $J=6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 53.7, 53.3, 46.4, 40.0, 31.9, 29.67, 29.65, 29.62, 29.4, 27.6, 26.0, 24.6, 22.7, 14.1; MS (EI, relative intensity) m/z 369 (M+2, 2), 368 (M+1, 8), 367 (M^+, 15), 213 (47), 212 (100), 210 (31).
11. 9-Dodecyl-1,5,9-triazacyclododecane, **3**: To a solution of **2** (300 mg, 0.82 mmol) in THF (15 mL) under nitrogen was added a solution of BH_3·THF (1 M, 6 mL) dropwise by a syringe. The mixture was heated at reflux for 24 h. After cooling to room temperature in an ice bath was slowly added methanol (5 mL), and then HCl solution (1 M, 0.5 mL). The mixture was stirred for 10 min, and concentrated under reduced pressure. To the residue was added HCl solution (6 M, 15 mL). The mixture was heated at reflux for 3 h. After cooling to room temperature, the mixture was basicified to pH 13 with concd NaOH solution, and extracted with CH_2Cl_2 (3×15 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give oily product **3** (265 mg, 95%). The product was dissolved in THF (15 mL), and bubbled with HCl gas. The precipitate was collected by decanting off THF, washed with hexane, and dried under high vacuum to afford **3**·3HCl salt (336 mg, 92%) as slightly yellow solid: For **3**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (br t, $J=5.5$ Hz, 2 H), 2.95 (t, $J=5.3$ Hz, 4 H), 2.83 (t, $J=5.3$ Hz, 4 H), 2.59 (t, $J=5.7$ Hz, 4 H), 2.44 (t, $J=7.7$ Hz, 2 H), 1.95 (quin., $J=5.3$ Hz, 2 H), 1.82 (quin., $J=5.5$ Hz, 4 H), 1.43 (quin., $J=7.7$ Hz, 2 H), 1.27 (m, 18 H), 0.88 (t, $J=6.7$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 51.0, 49.8, 47.4, 32.1, 29.88, 29.83, 29.80, 29.51, 27.8, 26.7, 24.6, 24.3, 24.0, 22.9, 14.3; MS (EI, relative intensity) m/z 340 (M+1, 16), 339 (M^+, 50), 171 (20), 170 (100).
12. 1,5-Didodecyl-1,5,9-triazacyclododecane, **5**: A mixture of **4** (171 mg, 1 mmol), *n*-dodecyl iodide (2.96 g, 10 mmol), $NaHCO_3$ (0.84 g, 10 mmol) and DMA (20 mL) was heated at 80°C overnight. The solvent was removed by vacumm distillation at 80°C. The residue was basicified with concd NaOH solution (15 mL), and extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was loaded on a silica gel column, and washed with hexane to elute out excess *n*-dodecyl iodide. The product was eluted using $MeOH/CH_2Cl_2/NH_4OH$ (79:20:1) to afford the oily product **5** (447 mg, 88%). The dried oily product was dissolved in THF, and filtered. The filtrate (20 mL) was bubbled with HCl gas. The precipitate was collected by decanting off the solvent, washed with hexane, and dried under high vacuum to afford **5**·3HCl salt (494 mg, 80%) as slightly yellow soild: For **5**·3HCl, ^{1}H NMR (400 MHz, DMSO-d_6, 130°C) δ 3.33 (br t, $J=7.8$ Hz, 2 H), 3.11 (br t, $J=8.2$ Hz, 2 H), 2.42 (br t, $J=5.0$ Hz, 2 H), 2.33 (br t, $J=7.0$ Hz, 4 H), 1.72 (m, 2 H), 1.67 (m, 2 H), 1.58 (m, 2 H), 1.42 (br quin., $J=6.8$ Hz, 2 H), 1.38–1.20 (m, 44 H), 0.89 (t, $J=6.8$Hz, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6, 80°C) δ 57.3, 54.9, 52.6, 50.3, 48.0, 31.0, 28.83, 28.74, 28.65, 28.62, 28.48, 28.40, 28.06, 26.9, 25.9, 25.5, 23.1, 21.8, 20.7, 19.2, 13.6 MS (EI, relative intensity) m/z 508 (M+1, 12), 507 (M^+, 30), 214 (8), 213 (74), 212 (100), 211 (20), 210 (77).
13. 1,5,9-Tridodecyl-1,5,9-triazacyclododecane, **6**: A mixture of 1,5,9-triazacyclododecane (100 mg, 0.58 mmol), *n*-dodecanal (1.76 g, 9.5 mmol), $NaCNBH_3$ (160 mg, 2.54 mmol), acetonitrile (10 mL) and water (3 mL) was acidified to pH 4–5 with diluted HCl solution. The mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure. The residue was basicified with concd NaOH solution (3 M, 10 mL), and extracted with CH_2Cl_2 (3×15 mL). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The oily residue was distilled under high vacuum to remove excess dodecanal. The residue was loaded on a silica gel column, and washed with CH_2Cl_2 to elute out excess *n*-dodecanal. The product was eluted using $MeOH/CH_2Cl_2/NH_4OH$ (79:20:1) to afford the oily product **6** (380 mg, 96%). The oily product was dissolved in THF (10 mL), and filtered. The filtrate was bubbled with HCl gas. The precipitate was collected by filteration, washed with hexane, and dried under high vacuum to afford **6**·3HCl salt (410 mg, 90%) as slightly yellow soild: ^{1}H NMR of **6**·3HCl salt

(400 MHz, DMSO-d_6 at 130°C) δ 2.93 (br s, 12 H), 2.74 (br t, $J=7.0$ Hz, 6 H), 1.93 (br s, 6 H), 1.62 (br t, $J=7.0$ Hz, 6 H), 1.34–1.25 (m, 54 H), 0.90 (t, $J=6.8$ Hz, 9 H); ^{13}C NMR (100 MHz, DMSO-d_6, 80°C) δ 53.8, 48.1, 31.3, 29.03, 29.00, 28.92, 28.72, 26.5, 23.9, 22.1, 14.0; MS (EI, relative intensity) m/z 676.7 (M+1, 2), 675.7 (M^+, 5), 674.7 (M–1, 4), 507.5 (42), 506.5 (100).

14. General procedure for solvent extraction of gold: Alkaline gold cyanide solution, 10 ppm Au in 125 ppm cyanide was prepared by adding AuCN (11.32 mg, 0.05 mmol) and KCN (312.8 mg) in a 1 L volumetric flask, and by filling with water. 5 mM Extractant solution was prepared by dissolving amine extractant (0.25 mmol) in toluene (50 mL). Equal volume of mixture, the alkaline gold cyanide solution (50 mL) and the extractant solution (50 mL) in a beaker was vigorously stirred using a magnetic stirrer for 5–10 min. The pH of the aqueous phase was adjusted by small additions of concd 1 M H_2SO_4 and 1 M (3 M or pellet) KOH, and was continuously monitored by a pH electrode. After stirring, the mixture was kept for 15 to 30 min to be separated, and samples, 2 mL of the aqueous phase were removed. An equal amount of the organic phase was also removed to maintain a fixed phase ratio, thus the organic to aqueous phase ratio was kept as 1:1. The aqueous phase samples were measured by an atomic absorption spectrometer, Chem. Tech. Analytical-2000, to detemine gold concentration in range of 0–10 ppm Au, which was caliberated prior to measure.
15. Trotman-Dickenson, A. F. *J. Chem. Soc.* **1949**, 1293–1297.