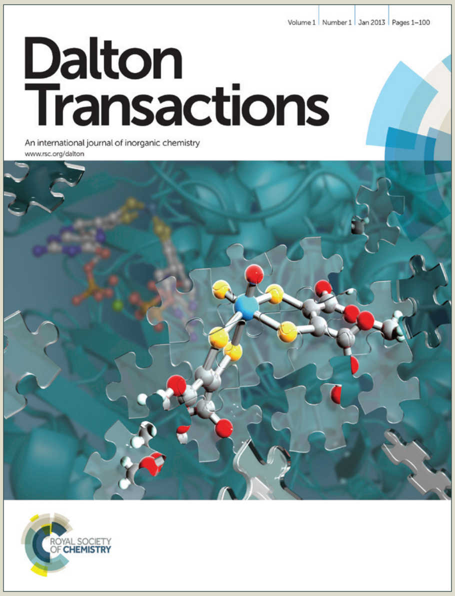
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Pillar[5]arene-based diglycolamides for highly efficient separation of americium(III) and europium(III)

Lei Wu, Yuyu Fang, Yiming Jia, Yuanyou Yang, Jiali Liao, Ning Liu, Xinshi Yang, Wen Feng*, Jialin Ming and Lihua Yuan*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Pillar[5]arenes, as a new intriguing class of calixarene analogues, were functionalized with ten diglycolamide (DGA) arms on both sides(rims) of the pillar framework and evaluated for their extraction behaviour towards Am(III) and Eu(III). These novel extractants exhibit excellent separation and extraction efficiency, suggesting its significant potential for nuclear waste remediation. Laser induced fluorescence experiments disclosed strong complexation of the trivalent metal ions with the pillararene-DGA ligands.

Pillararenes, which were firstly report by T. Ogoshi *et al*,[1] are being the focus of considerable research activity because of their interesting conformation and host-guest properties. These macrocycles are made up of hydroquinone units linked by methylene (–CH_2–) bridges at the 2 and 5 positions with pillar-shaped conformation. They can be considered as analogues of well-known calixarenes, but still differ in structures, particularly in their pillar conformation. Most of the studies are concerned with exploration of the interaction of the pillararene cavity and neutral molecules or organic cations, such as viologen and pyridinium derivatives, amino acid, imidazolium cations, ammonium salts, and alkyl chain derivatives.[2] A rapid surge in pillararene chemistry in recent years calls for the attention to the application of pillarene-derivatized compounds. In fact, pillar[n]arenes have been used to construct (pseudo)rotaxanes,[3] mechanically interlocked structure,[4] artificial transmembrane channels,[5] supramolecular polymers,[6] liquid crystals[7], amphiphiles and supramolecular amphiphiles[8] since their discovery. Inspired by the similarity in structural units of calixarenes serving as a platform for metal complexation, we envisioned that pillararenes could be exploited as a useful framework for preorganizing chelating groups for separation of metal ions by solvent extraction. However, no reports so far involved transition metal ions binding with pillar[n]arene derivatives and solvent based extraction.[9] Particularly, exploration of separation of actinides/lanthanides with pillararene-based extractants is still unknown to the best of our knowledge except for our recent work. Very lately, we have reported for the first time pillar[5]arene-based phosphine oxide extractants and demonstrated their pronounced selectivity for the thorium(IV) and uranyl(IV) cations in extraction from acidic media.[10] Only a moderate efficiency was observed in differentiating Eu(III) and Am(III) in the presence of a synergist (Br_6-COSAN). Given the need to handle large amounts of high-level nuclear wastes[11] by the well-known 'Partitioning & Transmutation' strategy,[12] search for more efficient extractants to separate Am(III) and Eu(III) still represents a current research focus towards solving the most challenging issue.

Diglycolamides (DGAs) as multidentate extractants have been recognized as one of the most efficient extractants for the extraction of actinides from acidic waste solutions.[13] Appending DGA species to calixarene[14] and trialkylphenyl[15] platforms, led to efficient metal ion binding and extraction due to preorganization effect. Therefore, it is intriguing to see if DGA ligands anchored on a pillararene framework could bring positive effect of preorganization of ligands on the extraction efficiency in separation of Am(III) and Eu(III).

In this communication, we report on the extraction of trivalent Am(III) and Eu(III) cations with three novel pillar[5]arenes substituted by ten diglycolamide groups (P5DGAs) (Fig. 1). These compounds were synthesized for the first time (†ESI). Pillar[5]arenes, the smallest member of pillar[n]arene family, are chosen because they are readily available by the conventional organic synthesis under Friedel-Crafts conditions.[16] For comparison purpose, TiPrDGA has been employed for the extraction (Fig. 1). Laser induced fluorescence spectral behaviour of their Eu^{3+} complexes is also reported. The solvent extraction studies were performed using 1.0 mM P5DGAs and 10 mM TiPrDGA in 1-octanol at different HNO_3 acidity. The extraction results for Am^{3+} and Eu^{3+} were obtained with the three P5DGA extractants along with comparative data of the distribution ratio

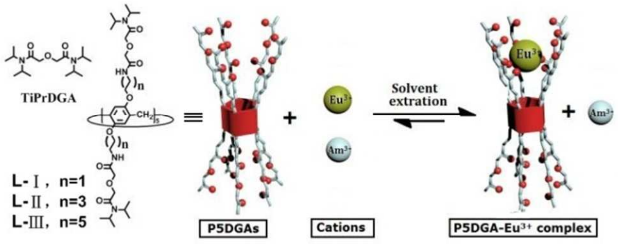


Fig.1 The structures of ligands **L-I**, **L-II**, **L-III** and the schematic solvent extraction process.

Table 1 Distribution value of Am(III) and Eu(III) from 0.1-4.0 M HNO_3 aqueous into 1-octanol containing 1 mM P5DGA or 10 mM TiPrDGA at 25 ± 1.0 °C.

Ligand	$[HNO_3]$ M	D_{Am}	D_{Eu}	$SF_{Eu/Am}$
L-I	0.1	< 0.001	0.68	> 680
	1	3.09	25.7	8.31
	2	3.70	7.75	2.09
	3	1.30	5.62	4.32
	4	1.34	6.91	5.16
L-II	0.1	0.70	6.80	9.71
	1	19.5	127	6.49
	2	10.0	35.3	3.52
	3	5.48	19.0	3.46
	4	3.45	8.80	2.55
L-III	0.1	0.37	4.50	12.2
	1	28.7	106	3.71
	2	18.0	64.2	3.56
	3	8.33	39.5	4.75
	4	5.60	20.5	3.66
TiPrDGA	0.1	< 0.001	< 0.001	—
	1	0.01	0.52	52.0
	2	0.10	0.71	7.10
	3	< 0.001	0.62	> 620
	4	< 0.001	0.49	> 490

(D) values for TiPrDGA and separation factors (SF) (Table 1). Interestingly, unusual high distribution ratio values were obtained with Am^{3+} and Eu^{3+} for all P5DGA in 1-octanol at 1.0 M HNO_3. In particularly, the exceptionally high D values for Eu^{3+} were maintained at acidity up to 4.0 M. The D values for ligands P5DGA are 10-1000 times larger than that of TiPrDGA at comparable conditions, which can be attributed to the advantages of the preorganization of chelating groups on the pillararene platform. For all the newly synthesized ligands P5DGA, both D_{Eu} and D_{Am} remarkably increase with increasing the HNO_3 concentration from 0.1 to 1.0 M, while the D-values usually show a maximum for $c(HNO_3) = 1.0$ M. This increase can be explained by the assumption that the nitrate anion is co-extracted together with Eu^{3+} and Am^{3+}.[17] On the contrary, and quite surprisingly, the D_M values decrease with increasing HNO_3 concentration from 1.0 M to 4.0 M, indicating that the competing effect of the H^+ ion started to interfere in the extraction at higher acidity.[18] For all the P5DGA extractants, Eu^{3+} was extracted to a greater extent than Am^{3+}, which agrees with the observation for other DGA extractants.[19] Furthermore, highly efficient separation of Eu^{3+} from Am^{3+} was realized at 0.1 M acidity as demonstrated by the separation factors (D_{Eu}/D_{Am}) of 9.71 and 12.16 for **L-II** and **L-III**, respectively. Even at 1.0 M HNO_3, the separation factor (8.31) for **L-I** was still better than that reported with TODGA(~6.17) with 1-octanol as the diluent.[18a] When feed acidity is raised to over 1.0 M, the $SF_{Eu/Am}$ values for all the extractants varied between 2.09 and 5.16, which is still separable for Eu^{3+} versus Am^{3+} but not efficient. To achieve better separation efficiency, the multiple extraction experiments[20] were carried out at 3.0 M (Table 2). It is intriguing that **L-I** showed excellent separation efficiency (10.5) for Eu^{3+} over Am^{3+} just with a second extraction.

Table 2 Multiple extraction of Am(III) and Eu(III) by P5DGA; ligand: 1 mM in 1-octanol with 3.0 M HNO_3; temperature: 25 ± 1.0 °C.

Ligand	Extraction no.	Total D_{Am}	Total D_{Eu}	$SF_{Eu/Am}$
L-I	2	5.61	58.9	10.5
	3	15.7	580	38.0
L-II	2	77.0	167	2.18
	3	80.5	210	2.61
L-III	2	95.0	322	3.39
	3	109	1660	15.2

The initial SF of 4.32 was further enhanced to 38.0 after the third extraction. Of particular notice is the exceptionally high distribution ratio for Eu^{3+} (1660) and Am^{3+} (109) in the case of the ligand **L-III**, resulting in a high SF value of 15.2. However, the ligand **L-II** failed to show good separation towards Eu^{3+} and Am^{3+} despite the large distribution ratio. These results from high acidity (3 M HNO_3) indicate that two or three successive extractions using P5DGAs(**L-I**/**L-III**) are enough for efficient separation of Eu^{3+} and Am^{3+}, suggesting its potential use in separation of Eu^{3+} and Am^{3+} for nuclear waste remediation.

To examine the number of ligands present in the extracted species, the slope analysis was performed. Plots of log D_{Eu} *versus* log C_L were found to be linear with slopes close to 1 (Fig. 2), suggesting the stoichiometry of the complex as 1:1 for all three extractants. This result is similar to the analogous studies with a both-side diglycolamide-functionalized calix[4]arene where a slope of ~ 1 was revealed.[21] The binding of metal ions in solvents with a ligand containing multiple chelating groups is a complicated process.[22] It could be assumed that one metal ion may bind to DGA groups tethered to one side of the pillararene molecule, while the other side is left uncoordinated or protonated at oxygen atoms as observed in the oxygen-containing ligand.[23] The nature of the coordination in the extracted species was explored by time-resolved laser fluorescence spectroscopy (TRLFS) technique using 4.0×10^{-6} M Eu^{3+} solution in 1×10^{-3} M HNO_3 diluted with ethanol/water (5:1). With the Eu^{3+} aquo complex (containing 4.0×10^{-6} M Eu^{3+}) in the absence of P5DGA, the emission spectrum only showed a very low intensity.

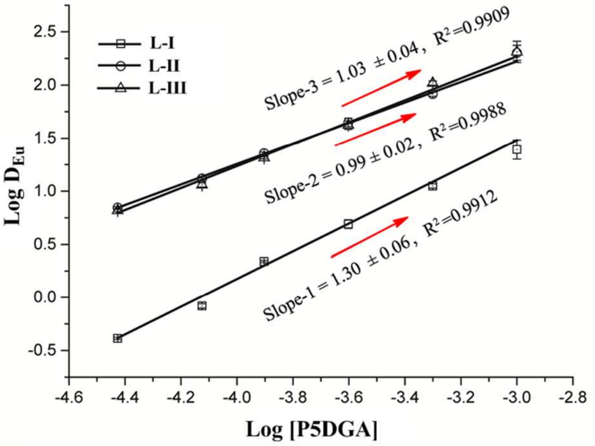


Fig. 2 Plots of Log D versus Log C_L for the extraction of europium(III) by P5DGA from 1 M HNO_3 aqueous solution into 1-octanol at 25 ± 1.0 °C.

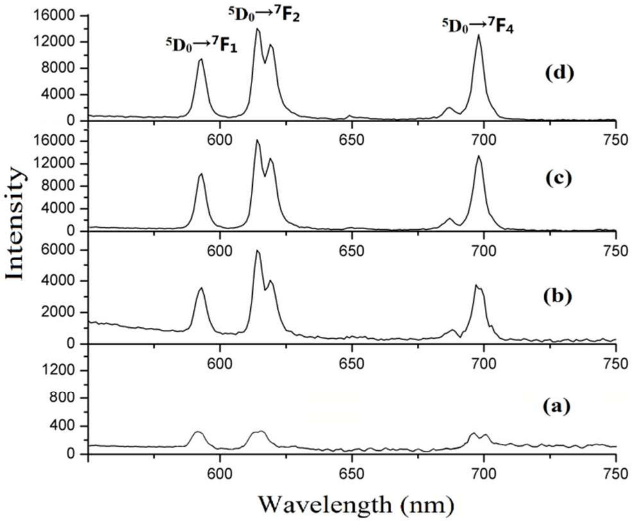


Fig.3 Emission spectra of the Eu^{3+}-solvent and Eu^{3+}-P5DGA complexes in solvent obtained by time-resolved fluorescence spectroscopy. (a) Eu^{3+} in the mixture solvent of EtOH/H_2O (5/1, v/v); (b) Eu^{3+}-**L-I**; (c) Eu^{3+}-**L-II**; (d) Eu^{3+}-**L-III**. The concentration of the Eu^{3+}-solvent and Eu^{3+}-P5DGA complexes is 4.0×10^{-6} M.

However, the characteristic emission at 617 nm ($^5D_0 \rightarrow {}^7F_2$ hypersensitive transition, electric dipole), 592 nm ($^5D_0 \rightarrow {}^7F_1$ transition, magnetic dipole), and at 690 nm ($^5D_0 \rightarrow {}^7F_4$ transition, electric dipole, sensitive to Eu^{3+} environment)[24] increased significantly (e.g., ca.50 times at 617 nm) in the presence of P5DGA (Fig. 3). In addition, the asymmetry factor of the Eu^{3+}-P5DGA complexes, defined as I_{617}/I_{592}, were calculated, and the symmetry of these complexes was found to increase in the order Eu^{3+}-**L-I** > Eu^{3+}-**L-II** > Eu^{3+}-**L-III**, suggesting a change of the environment within the Eu^{3+}-P5DGA extracted complexes (†ESI). At the same time, remarkable splitting of the peak at 617 nm with a significant change of intensity was also observed, indicating a strong interaction of the metal ion with DGA moieties on the pillararene. Similar results were reported for a calix[4]arene-based DGA ligands as well as the T-DGA-RTIL system.[25] The luminescence decay profiles of Eu^{3+}-P5DGA point to the presence of a single complexed species with 1:1 stoichiometry for all three extractants.

It is known that the lifetime of the complexing extractants could provide the information about the number of the inner-sphere water molecules. The number of the water molecules (N_{H_2O}) and the lifetime of $^5D_0$ emitting level (τ) follow the empirical relation:[26]

$$N_{H_2O} = (1.06/\tau) - 0.19 \qquad (1)$$

It was reported that the lifetime of the hydrated Eu^{3+} in the 0.001 M HNO_3 solution is 144 μs, which corresponds to about nine water molecules in its primary co-ordination sphere.[27] In the presence of the ligands, water molecules are replaced by the donor atoms attached to the ligands via metal cation-dipole interaction. The competitive complexation process by extractants can be signalled by an increase of the emission lifetime. Therefore, it is anticipated that the number of water molecules should be considerably reduced upon addition of the extractants with increased lifetime of the complexing species. Indeed, the lifetime data obtained from the decay curves of Eu^{3+}-P5DGA complexes by exponential decay fitting (†ESI) offered a prolonged lifetime of 1.507 and 1.506 ms for **L-II** and **L-III**, respectively, pointing to the number of inner-sphere water molecules being close to zero. This result suggests that in presence of the multiple functionalized ligands, the inner-sphere water molecules were completely replaced by the donor atoms of P5DGA. However, in the case of **L-I**, the life time was found to be 0.807 ms, pointing to the presence of about one inner-sphere water molecule in the extracted complex. This explains the relatively lower D_{Am} and D_{Eu} values of **L-I** at various feed acidities (Table 1) compared to those of **L-II** and **L-III**. These results confirmed the complexes formation and the strong interaction of P5DGA with Eu^{3+}.

In conclusion, preorganizing DGA moieties on the pillar[5]arene platform endows these novel diglycolamide-based pillararene extractants with highly efficient extraction and separation abilities towards partitioning of Eu(III) and Am(III) at feed acidities. The flexibility of spacer length of the pillararene-DGA ligands was found to implicate a significant effect upon the extraction abilities at highly acidic solution (3 M HNO_3). Of practical importance is the efficient separation of Eu(III) and Am(III) using multiple extraction. TRLFS studies and slope analysis results disclosed the stoichiometry of the extracted species in 1:1 without inner-sphere water molecules for **L-II** and **L-III**, but with one water molecule for **L-I**. As a new class of extractants with a framework of pillar conformation that is quite different from the calixarene extractants, pillararene-based diglycolamides as presented here may hold potential for the efficient separation of Eu(III) and Am(III) from radioactive liquid nuclear waste.

The authors acknowledge NSAF (11076018), Sichuan Province Science and Technology Support Programme (2011FZ0048), the Doctoral Program of the Ministry of Education of China (20130181110023), the National Science Foundation for Fostering Talents in Basic Research of the National Natural Science Foundation of China (J1210004 and J1103315), and Analytical & Testing Center of College of Chemistry for HRESI-MS for funding this work.

Notes and references

College of Chemistry, Key Laboratory for Radiation Physics and Technology of Ministry of Education, Institute of Nuclear Science and Technology, Sichuan University, Chengdu 610064, China. Fax: +86-28-85418755; Tel: +86-28-85412890; E-mail: lhyuan@scu.edu.cn; wfeng9510@scu.edu.cn.

† Electronic Supplementary Information (ESI) available: characterization details. See DOI: 10.1039/b000000x/.

1 T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakmoto, *J. Am. Chem. Soc.,* 2008, **130**, 5022-5023.

2 (a) P. J. Cragg, K. Sharma, Chem. Soc. Rev., 2012, **41**, 597-607; (b) M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.*, 2012, **45**, 1294-1308; (c) T. Ogoshi, T.-A. Yamagishi, *Eur. J. Org. Chem.*, 2013, **31**, 2961-2975; (d) X. Shu, J. Fan, J. Li, X. Wang, W. Chen, X. Jia and C. Li, *Org. Biomol. Chem.*, 2012, **10**, 3393-3397; (e) N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668-5671; (f) G. Yu, C. Han, Z. Zhang, J. Chen, X. Yan, B. Zheng, S. Liu and F. Huang, *J.*

Am. Chem. Soc., 2012, **134**, 8711-8717; (g) K. Wang, C. Y. Wang, Y. Wang, H. Li, C. Y. Bao, J. Y. Liu, S. X. Zhang and Y. W. Yang, *Chem. Commun*., 2013, **49**, 10528-10530; (h) Y. Chen, D. Cao, L. Wang, M. He, L. Zhou, D. Schollmeyer and H. Meier, *Chem. Eur. J,* 2013, **19**, 7064-7070; (i) C. L, J. Ma, L. Zhao, Y. Zhang, Y. Yu, X. Shu, J. Li and X. Jia, *Chem. Commun.,* 2013, **49**, 1924-1926;

3 (a) X. Chi, M. Xue, Y. Yao and F. Huang, *Org. Lett.,* 2013, **15**, 4722-4725; (b) X.-B. Hu, L. Chen, W. Si, Y. Yu and J. -L. Hou, *Chem. Commun.*, 2011, **47**, 4694-4696.

4 T. Ogoshi, T. Akutsu, D. Yamafuji, T. Aoki and T.-a. Yamagishi, *Angew. Chem. Int. Ed*., 2013, **52**, 8111-8115.

5 (a) W. Si, L. Chen, X.-B. Hu, G. Tang, Z. Chen, J. -L. Hou and Z. -T. Li, *Angew. Chem., Int. Ed*., 2011, **50**, 12564-12568; (b) X. -B. Hu, Z. Chen, G. Tang, J. -L. Hou and Z. -T. Li, *J. Am. Chem. Soc.,* 2012, **134**, 8384-8387.

6 Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem., Int. Ed*., 2011, **123**, 1397-1401.

7 M. Holler, N. Allenbach, J. Sonetand and J. F. Nierengarten, *Chem. Commun*., 2012, **48**, 2576-2578.

8 (a) G. Yu, M. Xue, Z. Zhang, J. Li, C. Han and F. Huang, *J. Am. Chem. Soc.,* 2012, **134**, 13248-13251; (b) Yao, M. Xue, J. Chen, M. Zhang and F. Huang, *J. Am. Chem. Soc.,* 2012, **134**, 15712–15715; (c) G. Yu, X. Zhou, Z. Zhang, C. Han, Z. Mao, C. Gao and F. Huang, *J. Am. Chem. Soc.*, 2012, **134**, 19489-19497; (d) G. Yu, Y. Ma, C. Han, Y. Yao, G. Tang, Z. Mao, C. Gao and F. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 10310-10313; (e) Y. Yao, M. Xue, Z. Zhang, M. Zhang. Y. Wang and F. Huang, *Chem. Sci.*, 2013, **4**, 3667-3672.

9 M.-m. Tian, D. -X. Chen, Y. -L. Sun, Y. -W. Yang and Q. Jia, *RSC Adv.,* 2013, **3**, 22111-22119.

10 Y. Fang, L. Wu, J. Liao, L. Chen, Y. Yang, N. Liu, L. He, S. Zou, W. Feng and L. Yuan, *RSC. Adv.,* 2013, **3**, 12376-12383.

11 (a) M. J. Hudson, L. M. Harwood, D. M. Laventine and F. W. Lewis, *Inorg. Chem.,* 2013, **52**, 3414-3428; (b) P. J. Panak and A. Geist, *Chem. Rev*. 2013, **113**, 1199-1236;(c) H. H. Dam, D. N. Reinhoudt and W. Verboom, *Chem. Soc. Rev.,* 2007, **36**, 367-377; (d) J. -H. Lan, W.-Q. Shi, L. -Y. Yuan, J. Li and Z. -F. Chai, *Inorg. Chem*., 2011, **50**, 9230-9237; (e) Y. Wei, A. Zhang, M. Kumagai, M. Watanabe and N. Hayashi, *J. Nucl. Sci. Technol.,* 2004, **41**, 315-322; (f) A. Zhang, Y. Wei, H. Hoshi and M. Kumagai, *Solvent Extr. Ion Exch.*, 2005, **23**, 231-247; (g) Y. Zhu, J. Chen and R. Jiao, *Solvent Extr. Ion Exch.,* 1996, **14**, 61-68.

12 M. Salvatores, *Nucl. Eng. Des.*, 2005, **235**, 805.

13 S. A. Ansari, P. N. Pathak, P. K. Mohapatra and V. K. Manchanda, *Chem. Rev.,* 2012, **112**, 1751-1772.

14 M. Iqbal, P. K. Mohapatra, S. A. Ansari, J. Huskens and W. Verboom, *Tetrahedron*, 2012, **68**, 7840-7847.

15 D. Janczewski, D. N. Reinhoudt, W. Verboom, C. Hill, C. Allignol, M. -T. Duchesne, *New J. Chem.,*2008, **32**, 490-495.

16 M. Holler, N. Allenbach, J. Sonet and J. F. Nierengarten, *Chem. Commun*., 2012, **48**, 2576-2578.

17 F. Sansone, M. Fontanella, A. Casnati, R. Ungaro, V. Böhmer, M. Saadioui, K. Liger and J. -F. Dozal, *Tetrahedron*, 2006, **62**, 6749-6753.

18 (a) Y. Wang and W. D. Horrocks, *Inorg. Chim. Acta*, 1997, **263**, 309-314; (b)L. He, Q. Jiang, Y. Jia, Y. Fang, S. Zou, Y. Yang, J. Liao, N. Liu, W. Feng, S. Luo, Y. Yang, L. Yang and L. Yuan, *J. Chem. Technol. Biotechol.,* 2013, **88**, 1930-1936; (c) H. Chu, L. He, Q. Jiang, Y. Fang, Y. Jia, X. Yuan, S. Zou, X. Li, W. Feng, Y. Yang, N. Liu, S. Luo, Y. Yang, L. Yang and L. Yuan, *J. Hazard. Mater.,* 2014, **264**, 211-218.

19 (a) Y. Sasaki, Y. Sugo, S. Suzuki and S. Tachimori, *Solvent Extr. Ion Exch.*, 2001, **19**, 91-103; (b) S. Panja, P. K. Mohapatra, S. C. Tripathi, G. D. Dhekane, P. M. Gandhi and P. Janardan, *Sep. Sci. Technol.,* 2013, **48**, 2179-2187; (c) P. K. Mohapatra, A. Sengupta, M. Iqbal, J. Huskens and W. Verboom, *Chem. Eur. J.,* 2013, **19**, 3230-3238. (c) G. Modolo, G. Asp, C. Schreinemachers and V. Vijgen, *Solvent Extr. Ion Exch.*, 2007, **25**, 703-721.

20 T. J. Bell and Y. Ikeda, *Dalton Trans*., 2012, **41**, 4303-4305.

21 P. K. Mohapatra, A. Senqupta, M. Iqbal, J. Huskens, S. V. Godbole and W. Verboom, *Dolton trans.,* 2013, **42,** 8558-8562.

22 H. H. Dam, D. N. Reinhoudt and W. Verboom, *New J. Chem*., 2007, **31**, 1620-1632.

23 W. J. Wang, J. Lin, A. Wang, P. Zheng, M. Wang and B. Wang, *Inorg. Chim. Acta,* 1988, **149**, 151-158.

24 P. K. Mohapatra, A. Sengupta, M. Iqbal, J. Huskens and W. Verboom, *Inorg. Chem*., 2013, **52**, 2533-2541.

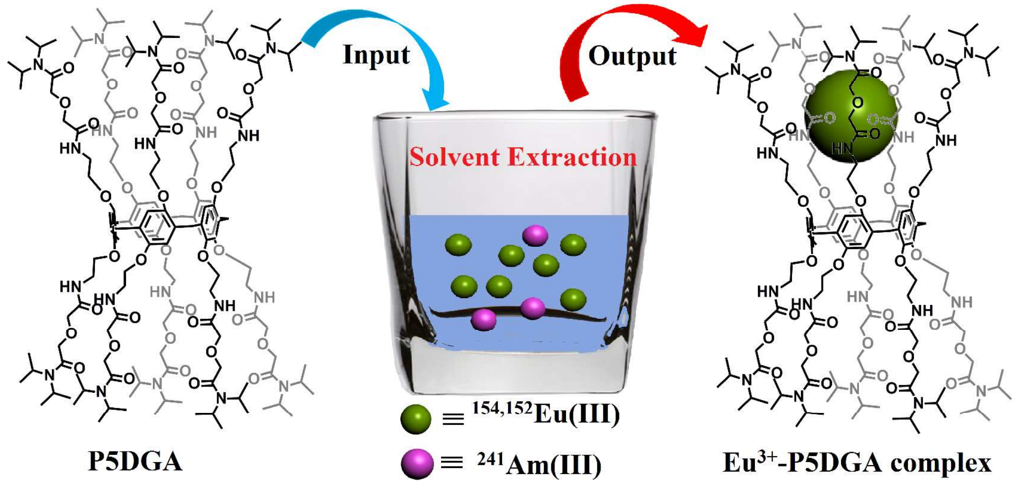
25 A. Sengupta, P. K. Mohapatra, M. Iqbal, W. Verboom, J. Huskens and S. V. Godbole, *RSC Adv.,* 2012, **2**, 7492-7500.

26 (a) G. R. Choppin and D. R. Peterman, *Coord. Chem. Rev*., 1998, **174**, 283; (b) P. Zhang and T. Kimura, *Solvent Extr. Ion Exch.,* 2006, **24**, 149-163.

27 D. R. Raut, P. K. Mohapatra, S. A. Ansari, S. V. Godbole, M. Iqbal,D. Manna, T. K. Ghanty, J. Huskens and W. verboom, *RSC Adv.*, 2013, **3,** 9296-9303.

Pillar[5]arene-based diglycolamides for highly efficient separation of americium(III) and europium(III)

Lei Wu, Yuyu Fang, Yiming Jia, Yuanyou Yang, Jiali Liao, Ning Liu, Xinshi Yang, Wen Feng,* Jialin Ming and Lihua Yuan*



Pillar[5]arenes were functionalized with ten diglycolamide (DGA) arms on both sides of the pillar framework and were found to exhibit excellent separation and extraction efficiency towards Am(III) and Eu(III) at highly acidity, suggesting its potential use for nuclear waste remediation.