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ARTICLE TYPE

Dual Colorimetric Sensing of Mercury and Iodide ions by Steroidal 1,2,3-Triazole-Stabilized Silver Nanoparticles

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Bile acid-based 1,2,3-triazole ligands have been synthesized, which show excellent ability to stabilize silver nanoparticles. These AgNPs have been found to exhibit highly selective dual colorimetric sensing of Hg^{2+} and I^- ions.

Metal nanoparticles have extraordinary size and shape-dependent optical properties and have been the subject of intense research during the past decade.[1] Recently, metal-nanoparticle-based sensing of metal ions and anions have received considerable attention, since they show a greater enhancement in ion-binding affinity and provide fast colorimetric detection of ions even at low concentration. Most of the nanoparticle-based ion-sensing studies have been focussed on the detection of ions using gold-nanoparticles.[2] Recently, silver nanoparticles have also attracted increasing interest for their applications in metal ion as well as anion sensing.[3]

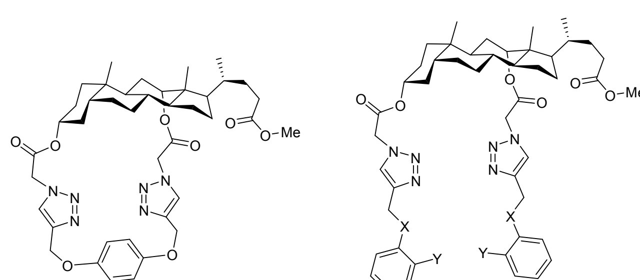
Mercury is one of the most toxic elements and environmental pollutants, which is continuously released to the environment from coal burning plants, oceanic and volcanic emission, chemical industries and gold mining. Elementary mercury vapours are eventually oxidized to Hg^{2+} and accumulated in the environment. A fraction of this Hg^{2+} is converted to methyl mercury by bacteria living in aqueous sediments. Methyl mercury is known as a potent neurotoxin. Although considerable attention has been devoted to the development of highly sensitive chemosensors based on fluorophores and chromophores[4] for the detection of Hg^{2+} ion, recently, metal nanoparticle-based sensors have received much attention because they can provide visual sensing even at low concentration.

Anion recognition has attracted increasing attention in recent years because of their biological, chemical and environmental relavance.[5] Among anions, iodide is one of the key elements that influence neurological and thyroid activities. Thus, there is a considerable interest in the development of systems capable of selectively recognizing iodide over other anions.[6]

The importance of click chemistry in the design of receptors for the recognition of anions and metal ions has now been well-established.[7] Recently, there has been considerable interest in the application of click chemistry in the functionalization of nanoparticles and their ion-sensing properties. Consequently, a variety of triazole-fuctionalized gold and silver nanoparticles have been developed which show selective metal ion sensing ability for Pb^{2+}, Cd^{2+}, Co^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+}ions.[8] However, in all these cases, there is no direct involvement of the triazole units in the stabilization of nanoparticles. Astruc and co-workers have recently used a PEGylated 1,2,3-triazole ligand to stabilize gold nanoparticles which recognize Hg^{2+} ion.[9]

Recently, the design of receptors that are capable of recognizing both a cation and an anion has emerged as a topic of great interest because a single probe can be utilized for the sensing of both the ions, which may be useful for biological and environmental analysis.[10] However, to the best of our knowledge, there is no example where a triazole-stabilized nanoparticle-based sensor is used for the dual sensing of cations and anions.

Earlier, we reported the remarkable ability of bile acid-based triazole-linked polymers for the stabilization of silver nanoparticles, which showed highly selective iodide-sensing property.[11] This inspired us to investigate the potential of other simple bile acid-based triazole ligands in terms of their nanoparticle-stabilizing properties and ion-sensing. Therefore, we synthesized a number of triazole ligands **1**−**4** based on steroidal framework (Fig. 1) and studied their behaviour towards the stabilization of silver nanoparticles and their further ion-sensing ability. We found that these steroidal triazole-stabilized nanoparticles show dual sensing ability for Hg^{2+} ion as well as I^- ion.



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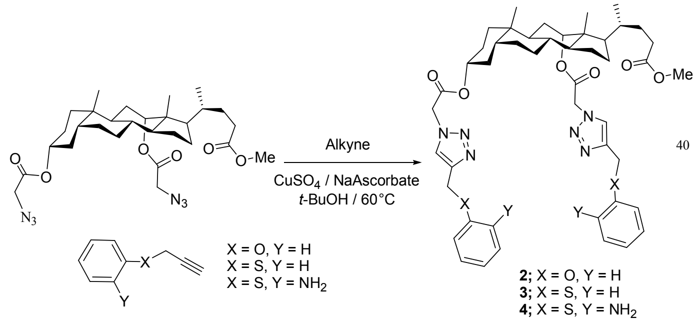
2; X = O, Y = H
3; X = S, Y = H
4; X = S, Y = NH_2

Fig. 1 Ligands **1–4**

The synthesis of ligand **1** has been reported earlier.[7b] The 1,3-dipolar cycloaddition reactions of methyl 3α,12α-bis(azidoacetyl)-deoxycholate[7b] with appropriate alkyne derivatives in presence of $CuSO_4$ (10 mol %) and sodium ascorbate (20 mol %) in *t*-BuOH/H_2O (1:1) at 60 °C led to the formation of the ligands **2–4** (Scheme 1).



Scheme 1. Synthesis of ligands **2–4**

These triazole ligands were used to synthesize silver nanoparticles. The AgNPs were synthesized by reduction of $AgNO_3$ by sun light in presence of 1,2,3-triazole-based compounds **1**−**4**. Stoichiometric amount of $AgNO_3$ *vs.* 1,2,3-triazole rings were added to the solution of ligands in $CHCl_3$/MeOH (1:1) and this solution was exposed to sun light for 15-20 min. The colour of the solution turned dark yellow that indicate the formation of silver nanoparticles. The presence of 1,2,3-Triazole-based compounds is essential for the synthesis of nanoparticles and without them nanoparticles are not formed even on exposure to sun light for longer time. The UV-vis spectrum showed a band around 420 nm (Fig. S1 in SI) for the triazole-stabilized AgNPs. The transmission electron microscopy (HRTEM) data confirmed the formation of silver nanoparticles of 2−10 nm size (Figs. 2 and S2, S3 in SI).

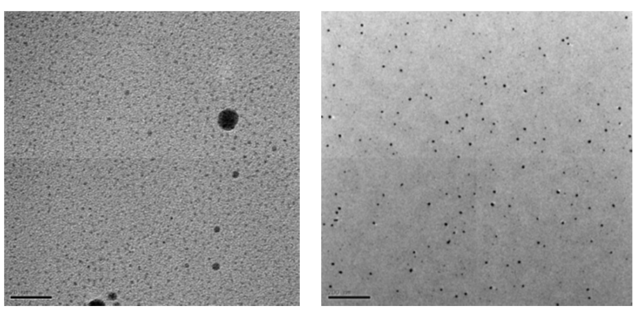


Fig. 2 HRTEM image of AgNPs stabilized with ligands **1** and **3**, respectively (scale bar 20 nm and 200 nm)

The colorimetric sensing properties of 1,2,3-triazole-stabilized silver nanoparticles towards metal ions such as Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Mg^{2+} (as perchlorates) and anions such as HSO_4^-, $H_2PO_4^-$, OAc^-, F^-, Cl^-, Br^- and I^- (as tetrabutylammonium salts) were studied by monitoring the changes in the colour after addition of ions to the solution of 1,2,3-triazole-stabilized AgNPs. The addition of Hg^{2+} ion to the solution containing AgNPs stabilized with ligands **1-4**, resulted colourless solution within a minute due to Hg^{2+}-induced aggregation of AgNPs (Figs. 3, 4, S4 and S5). The HRTEM data also confirmed the Hg^{2+}-induced aggregation of silver nanoparticles (Figs. 5 and S6). The aggregation behaviour may be explained in terms of the formation of Ag-Hg amalgam through the partial transfer of electron density from Ag to Hg^{2+} ion.[12]

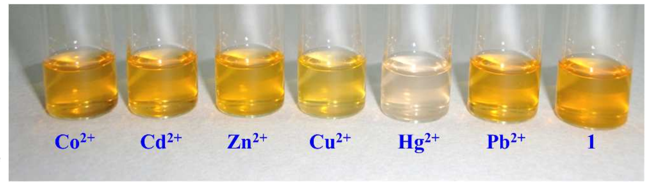


Fig. 3 A photograph of the solutions of AgNPs stabilized with ligand **1** after addition of different metal ions. Ion concentration of Co^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+} is 1 mM; [Hg^{2+}] = 100 µM.

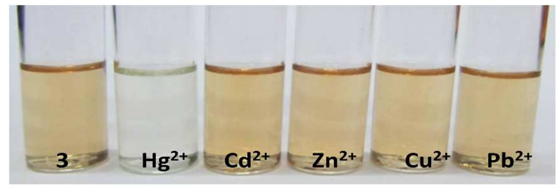


Fig. 4 A photograph of the solutions of AgNPs stabilized with ligand **3** after addition of different metal ions. Ion concentration of Cd^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+} is 1mM; [Hg^{2+}] = 600 µM.

All of these AgNPs showed high selectivity for the sensing of Hg^{2+} ion. The minimum concentration of mercury ion detectable by colour change was evaluated by addition of different amount of Hg^{2+} ion to the solution of 1,2,3-triazole stabilized AgNPs. Among all, the silver nanoparticles stabilized with ligand **1** showed the highest sensitivity for Hg^{2+} ion at the level of 100 µM.

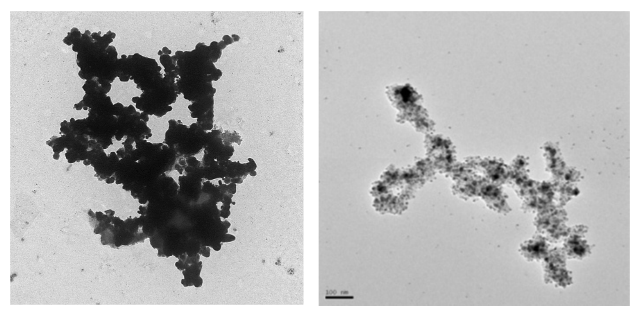


Fig. 5 HRTEM image of AgNPs stabilized with ligand **1** and **3** respectively after addition of Hg^{2+} (scale bar 500 nm and 100 nm)

We also studied the anion-sensing properties of silver nanoparticles stabilized with these ligands (Figs. 6, 7, S7 and S8). Addition of iodide ions to the solutions of **1**-**4**.AgNPs resulted in disappearance of the colour of the solution. However, addition of $H_2PO_4^-$, HSO_4^-, OAc^-, Br^-, Cl^- and F^- ions (2 mM) failed to induce any detectable colour change. The HRTEM analysis of the solution of NPs after addition of I^- ions indicated the aggregation of nanoparticles (Figs. 8 and S9). This may be due to the iodine adsorption on the nanoparicles surface which lowers the surface potential and increases the van der Waals attraction between iodine-coated nanoparticles leading to their aggregation.[13] The minimum detectable concentration of iodide ions was evaluated by addition of different amounts of iodide salt to the solution of **1**−**4**.AgNPs. The AgNPs stabilized with ligand **3** showed the highest selectivity for iodide ion at the level of 200 µM.

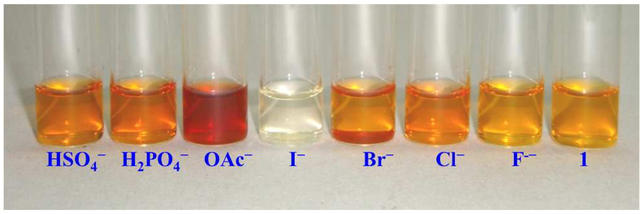


Fig. 6 A photograph of the solutions of AgNPs stabilized with ligand **1** after addition of different anions. Ion concentration of HSO_4^-, $H_2PO_4^-$, OAc^-, Br^-, Cl^- and F^- is 2 mM; [I^-] = 813 μM.

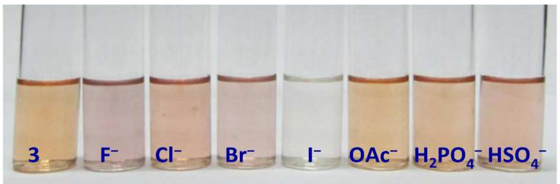


Fig. 7 A photograph of the solutions of AgNPs stabilized with ligand **3** after addition of different anions. Ion concentration of F^-, Cl^-, Br^-, OAc^-, $H_2PO_4^-$ and HSO_4^- is 2 mM; [I^-] = 200 μM.

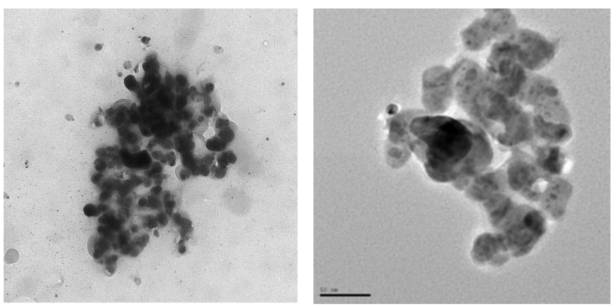


Fig. 8 HRTEM image of AgNPs stabilized with ligands **1** and **3**, respectively after addition of I^- (scale bar 100 nm and 50 nm)

The aggregation of **1−4** stabilized AgNPs after addition of Hg^{2+} and I^- was studied using UV-Vis spectroscopy. The UV-vis spectra showed the complete disappearance of the absorption band at 420 nm (Figs. S10 and S11). On the other hand, the addition of other transition metal ions had no effect on the absorption spectra of AgNPs. Further, the energy dispersive X-ray spectra (EDX) of AgNPs (**3**,**4**) after addition of Hg^{2+} and I^- were recorded using transmission electron microscope. These spectra (Figs. S12−S15) showed the presence of silver as well as mercury (when Hg^{2+} was added) and silver as well as iodine (when I^- was added). Thus the aggregation of AgNPs in presence of Hg^{2+} and I^- is due to the formation of Ag-Hg amalgam or absorption of iodide ion on NPs surface.

In summary, we have synthesized various steroidal 1,2,3-triazole ligands which were found to be excellent capping agents for the stabilization of silver nanoparticles. These triazole-stabilized silver nanoparticles show dual colorimetric sensing for mercury as well as iodide ions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, HRTEM images and characterization data for ligands **2-4**. See DOI: 10.1039/b000000x/

1 (*a*) M.-C. Daniel and D. Astruc, *Chem. Rev*., 2004, **104**, 293; (*b*) U. Drechsler, B, Erdogan and V. M. Rotello, *Chem. Eur. J.*, 2004, **10**, 5570; (*c*) C. J. Murphy, A. M. Gole, S. E, Hunyadi, J. W. Stone, P. N. Sisco, A. Alkilany, B. E. Kinard and P. Hankins, *Chem. Commun.*, 2008, 544; (*d*) Z. Wang and L. Ma, *Coor. Chem. Rev*., 2009, **253**, 1607; (*e*) H. Jansa and Q. Huo, *Chem. Soc. Rev*., 2012, **41**, 2849; (*f*) Y. Lu and W. Chen, *Chem. Soc. Rev*., 2012, **41**, 3594; (*g*) N. Li, P. Zhao and D. Astruc, *Angew. Chem*., *Int. Ed*., 2014, **53**, 1756.

2 (*a*) G. Patel, A. Kumar, U. Pal and S. Menon, *Chem. Commun.*, 2009, 1849; (*b*) J. R. Kalluri, T. Arbneshi, S. A. Khan, A. Neely, P. Candice, B. Varisli, M. Washington, S. McAfee, B. Robinson, S. Banerjee, A. K. Singh, D. Senapati and P. C. Ray, *Angew. Chem*., *Int. Ed*., 2009, **48**, 9668; (*c*) S. Kim, J. W. Park, D. Kim, D. Kim, I.-H. Lee and S. Jon, *Angew. Chem*., *Int. Ed*., 2009, **48**, 4138; (*d*) C.-Y. Lin, C. J. Yu, Y.-H. Lin and W.-L. Tseng, *Anal. Chem*., 2010, **82**, 6830; (*e*) J. Zhang, X. Xu, C. Yang, F. Yang and X. Yang, *Anal. Chem*., 2011, **83**, 3911; (*f*) C.-Y. Liu and W.-L. Tseng, *Chem. Commun*., 2011, **47**, 2550; (*g*) T. Senapati, D. Senapati, A. K. Singh, Z. Fan, R. Kanchanapally and P. C. Ray, *Chem. Commun*., 2011, **47**, 10326; (*h*) K. Saha, S. S. Agasti, C. Kim, X. Li and V. M. Rotello, *Chem. Rev*., 2012, **112**, 2739; (*i*) D. Vilela, M. C. González and A. Escarpa, *Anal Chim Acta,* 2012, **751**, 24; (*j*) J. Du, L. Jiang, Q. Shao, X. Liu, R. S. Marks, J. Ma and X. Chen, *Small*, 2013, 1467; (*k*) S. Kim, M, S. Eom, S. K. Kim, S. H. Seo and M. S. Han, *Chem. Commun*., 2013, **49**, 152.

3 (*a*) C. Han, L. Zhang and H. Li, *Chem. Commun*., 2009, 3545; (*b*) T. K. Misra and C.-Y. Liu, *J. Nanopart. Res*., 2009, **11**, 1053; (*c*) G.-Y. Lan, C.-C. Huang and H.-T. Chang, *Chem. Commun*., 2010, **46**, 1257; (*d*) S. Liu, F. Lu and J.-J. Zhu, *Chem. Commun*., 2011, **47**, 2661; (*e*) F. Qu, N. B. Li and H. Q. Luo, *Anal. Chem*., 2012, **84**, 10373; (*f*) A. K. Singh, R. Kanchanapally, Z. Fan, D. Senapati and P. C. Ray, *Chem. Commun*., 2012, **48**, 9047; (*g*) L. Deng, X. Ouyang, J. Jin, C. Ma, Y. Jiang, J. Zheng, J. Li, Y. Li, W. Tan and R. Yang, *Anal. Chem*., 2013, **85**, 8594; (*h*) H. K. Sung, S. Y. Oh, C. Park and Y. Kim, *Langmuir*, 2013, **29**, 8978; (*i*) H. Zhang, L. Ye, X. Wang, F. Li and J. Wang, *Chem. Commun*., 2014, **50**, 2565.

4 (*a*) E. M. Nolan and S. J. Lippard, *Chem. Rev*., 2008, **108**, 3443; (*b*) H. N. Kim, M. H. Lee, H. J. Kim and J. S. Kim, *Chem. Soc. Rev*., 2008, **37**, 1465; (*c*) D. T. Quang and J. S. Kim, *Chem. Rev*., 2010, **110***,* 6280; (*d*) G. Aragay, J. Pons and A. Merkoçi, *Chem. Rev*., 2011, **111**, 3433; (*e*) H. N. Kim, W. X. Ren, J. S. Kim and J. Yoon, *Chem. Soc. Rev*., 2012, **41**, 3210.

5 (*a*) J. L. Sessler, P. A. Gale and W. S. Cho, *Anion Receptor Chemistry*; The Royal Society of Chemistry: Cambridge, U. K., 2006; (*b*) P. R. Brotherhood and A. P. Davis, *Chem. Soc. Rev*, 2010, **39**, 3633; (*c*) Y. Hua and A. H. Flood, *Chem. Soc. Rev*., 2010, **39**, 1262; (*d*) M. E. Moragues, R. Martíınez-Máñez and F. Sancenón, *Chem. Soc. Rev*., 2011, **40**, 2593; (*e*) M. Wenzel, J. R. Hiscock and P. A. Gale, *Chem. Soc. Rev*., 2012, **41**, 480; (*f*) L. E. Santos-Figueroa, M. E. Moragues, E. Climent, A. Agostini, R. Martíınez-Máñez and F. Sancenón, *Chem. Soc. Rev*., 2013, **42**, 3489; (*g*) P. A. Gale, N. Busschaert, C. J. E. Haynes, L. E. Karagiannidis and I. L. Kirby, *Chem. Soc. Rev*., 2014, **43**, 205.

6 (*a*) H. A. Ho and M. Leclerc, *J. Am. Chem. Soc*., 2003, **125**, 4412; (*b*) M. Vetrichelvan, R. Nagarajan and S. Valiyaveettil, *Macromolecules*, 2006, **39**, 8303; (*c*) J. Zhang, X. Xu, C. Yang, F. Yang and X. Yang, *Anal. Chem*., 2011, **83**, 3911; (*d*) E. Jung, S. Kim, Y. Kim, S. H. Seo, S. S. Lee, M. S. Han and S. Lee, *Angew. Chem*., *Int. Ed*., 2011, **50**, 4386; (*e*) S.-C. Wei, P.-H. Hsu, Y.-F. Lee, Y.-W. Lin and C.-C. Huang, *ACS Appl. Mater. Interfaces,* 2012, **4**, 2652; (*f*) G.-Li. Wang, X.-Y. Zhu, Y.-M. Dong, H.-J. Jiao, X.-M. Wua and Z.-J. Li, *Talanta,* 2013, **107**, 146; (*g*) L. Chen, W. Lu, X. Wang and L. Chen, *Sens. Actuators B*: *Chem.,* 2013, **182**. 482.

7 (*a*) C. Ornelas, J. R. Aranzaes, E. Cloutet, S. Alves and D. Astruc, *Angew. Chem*., *Int. Ed*., 2007, **46**, 872; (*b*) A. Kumar and P. S. Pandey, *Org. Lett*., 2008, **10**, 165; (*c*) A. Kumar and P. S. Pandey, *Tetrahedron Lett*., 2009, **50**, 5842; (*d*) H. Struthers, T. L. Mindt and R. Schibli, *Dalton Trans*., 2010, **39**, 675; (*e*) Y. H. Lau, P. J.

Rutledge, M. Watkinson and M. H. Todd, *Chem. Soc. Rev.*, 2011, **40**, 2848; (*f*) R. K. Chhatra, A. Kumar and P. S. Pandey, *J. Org. Chem.*, 2011, **76**, 9086; (*g*) B. Schulze and U. S. Schubert, *Chem. Soc. Rev.*, 2014, **43**, 2522.

8 (*a*) H. Li, Y. Yao, C. Han and J. Zhan, *Chem. Commun.,* 2009, 4812; (*b*) H. Li, Q. Zheng and C. Han, *Analyst*, 2010, **135**, 1360; (*c*) Y. Yao, D. Tian and H. Li, *ACS Appl. Mater. Interfaces*, 2010, **2**, 684; (*d*) Y. Yao, Z. Sun, Z. Zou and H. Li, *Nanotechnology*, 2011, **22**, 435502; (*e*) J. Zhan, L. Wen, F. Miao, D. Tian, X. Zhu, H. Li, *New J. Chem*., 2012, **36**, 656; (*f*) Y.-C. Chen, I.-L. Lee, Y.-M. Sung and S.-P. Wu, *Sens. Actuators B: Chem*, 2013, **188**, 354; (*g*) Y.-C. Chen, I.-L. Lee, Y.-M. Sung and S.-P. Wu, *Talanta*, 2013, **117**, 70; (*h*) I.-L. Lee, Y.-M. Sung and S.-P. Wu, *RSC Advances*, 2014, **4**, 25251.

9 P. Zhao, Na Li, L. Salmon, Na Liu, J. Ruiz, D. Astruc, *Chem. Commun.* 2013, **49**, 3218.

10 (*a*) J. Y. Lee, S. K. Kim, J. H. Jung, J. S. Kim, *J. Org. Chem.* 2005, **70**, 1463; (*b*) H. J. Jung, N. Singh, D. Y. Lee, D. O. Jang, *Tetrahedron Lett*., 2010, **51**, 3962; (*c*) X. He and V. W.-W. Yam, *Org. Lett.,* 2011, **13**, 2172; (*d*) C. Bhaumik, S. Das, D. Maity and S. Baitalik, *Dalton Trans.*, 2011, **40**, 11795; (*e*) M. Alfonso, A. Tárraga, and P. Molina, *Org. Lett.,* 2011, **13**, 6432; (*f*) C. Bhaumik, D. Maity, S. Das, and S. Baitalik, *RSC Advances*, 2012, **2**, 2581; (*g*) V. K. Bhardwaj, P. Saluja, G. Hundal, M. S. Hundal, N. Singh and D. O. Jang, *Tetrahedron*, 2013, **69**, 1606; (*h*) G. J. Park, Y. J. Na, H. Y. Jo, S. A. Lee, A. R. Kim, I. Noh and C. Kim, *New J. Chem.,* 2014, **38**, 2587; (*i*) S. Das, S. Karmakar, S. Mardanya and S. Baitalik, *Dalton Trans*., 2014, **43**, 3767.

11 A. Kumar, R. K. Chhatra and P. S. Pandey, *Org. Lett.,* 2010, **12**, 24.

12 B. Adhikari and A. Banerjee, *Chem. Mater*., 2010, **22**, 4364.

13 W. Chang, S. Dong and E. Wang, *Angew. Chem., Int. Ed*., 2003, **42,** 449.

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