RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Influence of radiation effect on extractability of *iso*butyl-BTP/ionic liquid system: quantitative analysis and identification of radiolytic products†

Weijin Yuan,[a,‡] Yinyong Ao,[b,‡] Long Zhao,[a*] Maolin Zhai,[b*] Jing Peng,[b] Jiuqiang Li,[b] and Yuezhou Wei [a]

Approaches were established for accessing the influence of radiation effect on extractability of 2,6-di(5,6-di*iso*Butyl-1,2,4-triazin-3-yl)pyridine (*iso*butyl-BTP) /1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([C_2mim][NTf_2]) extraction system. The substituted compounds formed between *iso*butyl-BTP and radicals of [C_2mim][NTf_2], especially imidazolium cation radicals, were responsible for keeping partial extraction ability for Dy^{3+} even at 500 kGy.

The long-term radiotoxicity of the spent nuclear fuel (SNF) still remains at a high-level due to the existence of minor actinides (MA(III), mainly Am and Cm), even if 99.5% of uranium and plutonium are removed by the PUREX process.[1-4] The MA(III) can be transmuted by neutron bombardment into shorter-lived nuclides or stable nuclides.[5] However, the lanthanides (Ln(III)), which is co-produced with MA(III) in the nuclear fission process, will sharply minimize the efficiency of transmutation due to its higher neutron capture section than the MA(III).[6] It becomes an essential to realize MA(III)-Ln(III) partitioning before any transmutation strategy is implemented. In recent years, room-temperature ionic liquids (RTILs) have received increasing attentions due to their unique properties and are considered as promising solvents in SNF reprocessing and recycling.[7-10] In an extraction process involving SNF, radiation stability of extraction systems should be assessed carefully before their practical application, because the separation of radioactive elements would be performed under the existence of α, β, and γ emitters.[11, 12] Therefore, studies on the radiation effect of RTILs extraction system are of great importance in the assessment of application feasibility in SNF reprocessing and recycling. The radiation effect on pure RTILs under γ-irradiation has been widely studied.[13-18] Yuan *et al.*[19] noted that less than 1% underwent radiolysis when 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ionic liquid ([C_4mim][NTf_2]) were exposed to a dose of 550 kGy. Recently, the main radiolytic products of anion of [C_4mim][NTf_2] have been definitely identified.[18] However, all of these studies mainly focused on the radiation stability of RTILs themselves, since it was extremely difficult to investigate the RTIL-based extraction systems under irradiation due to a challenge on clearly separating extractant, ionic liquid and their radiolytic products. Hence, there is an urgent need to find new methods that could effectively provide a quantitative analysis and identify the radiolytic products of RTIL-based extraction systems.

Herein, an extraction system that consisted of *iso*butyl-BTP (> 95%) as extractant and [C_2mim][NTf_2] (with a purity > 99%, Lanzhou Greenchem ILs, LICP, CAS, China) as diluents was designed. The irradiation of solid *iso*butyl-BTP, [C_2mim][NTf_2], *iso*butyl-BTP/[C_2mim][NTf_2], and *iso*butyl-BTP/1-octanol was carried out in air (298 ± 4 K) using a ^{60}Co source with an average dose rate of *ca*. 240 $Gy\cdot min^{-1}$ (Institute of Applied Chemistry of Peking University). Dy^{3+} is chosen for assessing the extractability and the radiation stability of *iso*butyl-BTP/[C_2mim][NTf_2] system based on previous work[20-22]. The extraction experiments were shown in ESI (Experiment part). The concentration of *iso*butyl-BTP in [C_2mim][NTf_2] after irradiation was quantified by Ultra-performance liquid chromatography/quadrupole time-of-flight mass spectrometry (UPLC/Q-TOF-MS), and the radiolytic products of *iso*butyl-BTP/[C_2mim][NTf_2] were identified by matrix assisted laser desorption ionization/Fourier transform mass spectrometry (MALDI-FTMS) (see Experiment part in ESI).

The extraction kinetics and the extraction capacity reflect the basic properties of the extraction system, so the extraction of Dy^{3+} by *iso*butyl-BTP/[C_2mim][NTf_2] is carried out at different concentrations of Dy^{3+} ([Dy^{3+}]). As seen in Fig.S1, the extraction equilibrium arrives within 5 min when the initial [Dy^{3+}] is 2 mM, and the equilibrium time slightly extends with increasing [Dy^{3+}]. The *iso*butyl-BTP/[C_2mim][NTf_2] is saturated when the initial [Dy^{3+}] is 8 mM as extraction efficiency of Dy^{3+} (E_{Dy}) decreases to 82.9% at equilibrium. In order to directly reveal the change of extraction capability of *iso*butyl-BTP, the initial [Dy^{3+}] was chosen to be 8 mM in following experiments, and the γ-radiation effect on Dy^{3+} extraction by irradiated *iso*butyl-BTP solid, irradiated *iso*butyl-BTP/[C_2mim][NTf_2] and irradiated *iso*butyl-BTP/1-octanol system at different doses was evaluated simultaneously.

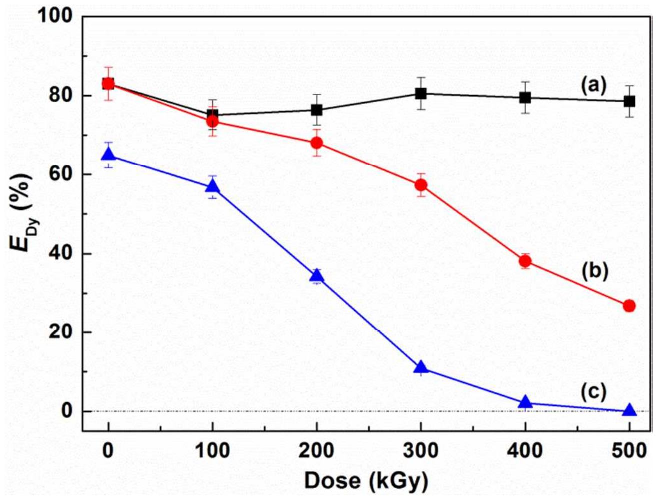

Fig. 1 Influence of dose on Dy^{3+} extraction by *iso*butyl-BTP extraction system: (a) irradiated *iso*butyl-BTP at different doses in combination with unirradiated $[C_2mim][NTf_2]$; *iso*butyl-BTP dissolved in $[C_2mim][NTf_2]$ (b) and *iso*butyl-BTP dissolved in 1-octanol (c) were irradiated at different doses.

The extraction experiments of Dy^{3+} using irradiated isobutyl-BTP in combination with unirradiated $[C_2mim][NTf_2]$ were carried out. As indicated in Fig. 1a, the extraction ability of solid isobutyl-BTP irradiated at different doses changed slightly compared with that of unirradiated sample, which indicated that solid *iso*butyl-BTP was changed slightly after irradiation even at 500 kGy (detail data in Table S1). ^1H NMR and Micro-FTIR were employed to analyse the chemical structure of *iso*butyl-BTP before and after irradiation. According to ^1H NMR spectra (Fig.S2) and Micro-FTIR (Fig.S3) of irradiated *iso*butyl-BTP, no obvious change was found even at 500 kGy, indicating that the chemical structure of *iso*butyl-BTP unchanged at 500 kGy. All the chemical shifts in ^1H NMR spectra were assigned to appropriate H atoms,[23] and all main peaks in FTIR spectra were assigned to appropriate groups[24]. Then *iso*butyl-BTP was dissolved in the $[C_2mim][NTf_2]$, and the *iso*butyl-BTP/$[C_2mim][NTf_2]$ solution was irradiated at different doses. An abnormal increase of Dy^{3+} partitioning in irradiated ionic liquid was observed due to the precipitation between Dy^{3+} and radiolytic products (F^- and SO_3^{2-}) of ionic liquid[22, 25], which could be removed simply by washing irradiated sample with water. In order to study the influence of radiolytic products of *iso*butyl-BTP in $[C_2mim][NTf_2]$ on Dy^{3+} partitioning, the irradiated *iso*butyl-BTP/$[C_2mim][NTf_2]$ samples were washed 3 times with deionized water before extraction. Whereafter, the irradiated *iso*butyl-BTP/$[C_2mim][NTf_2]$ solution was used to extract Dy^{3+} from aqueous solution and results were shown in Fig. 1b. The extraction results showed that the E_{Dy} decreased with increasing dose (detail data in Table S1). Xu *et. al* found that the Cs^+ partitioning in bis(2-propyloxy)calix[4]crown-6 (BPC6)/RTILs after irradiation decreased obviously, which indicated the damage of chemical structure of BPC6 was mainly responsible for Cs^+ partitioning.[26] *iso*butyl-BTP could be damaged by active species under irradiation, thus Dy^{3+} did not associate with the N-donor heteropolycyclic functional groups of *iso*butyl-BTP effectively, which lead to the decrease of Dy^{3+} partitioning in *iso*butyl-BTP/$[C_2mim][NTf_2]$. For comparison purpose, the extraction ability of *iso*butyl-BTP dissolved in 1-octanol under radiation was also studied. The concentration of isobutyl-BTP in 1-octanol was chosen at 100 mM, because the 20 mM *iso*butyl-BTP/1-octanol solution had not extraction ability for Dy^{3+}. Compared with E_{Dy} of isobutyl-BTP/$[C_2mim][NTf_2]$, the E_{Dy} of isobutyl-BTP/1-octanol decreased dramatically with the increasing dose, and isobutyl-BTP/1-octanol has no extraction capacity at 500 kGy (Fig. 1c, detail data in Table S1), which indicated that the N-donor heteropolycyclic functional groups of *iso*butyl-BTP were damaged seriously by active species of 1-octanol more than that by active species of $[C_2mim][NTf_2]$ under irradiation.

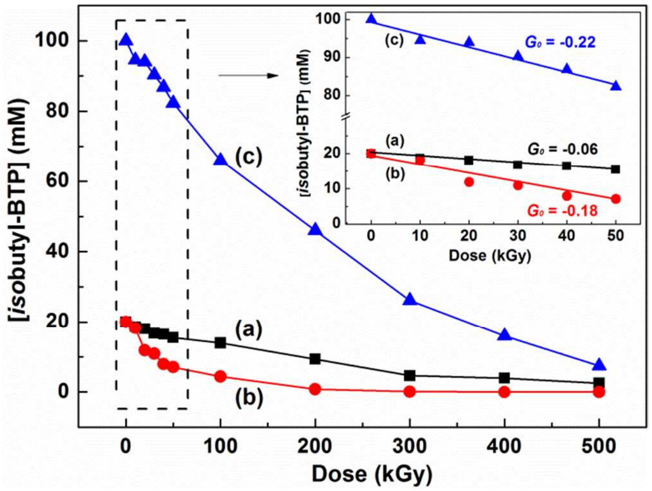

Fig. 2 The concentration of *iso*butyl-BTP dissolved in $[C_2mim][NTf_2]$ (20 mM (a)), and in 1-octanol (20 mM (b) and 100 mM (c)).

Table 1 The radiolytic yields (G_0) of *iso*butyl-BTP in $[C_2mim][NTf_2]$ and 1-octanol.

Diluent	[*iso*butyl-BTP] (mM)	G_0 ($\mu mol \cdot J^{-1}$)	R^2
$[C_2mim][NTf_2]$	20.0	-0.06	0.970
1-octanol	20.0	-0.18	0.918
1-octanol	100.0	-0.22	0.965

The concentration of *iso*butyl-BTP in $[C_2mim][NTf_2]$ after irradiation was quantified by UPLC/Q-TOF-MS for the first time (see Fig.2 and Fig.S4). As shown in Fig 2, the concentration of *iso*butyl-BTP in 1-octanol deceased more rapidly than that of *iso*butyl-BTP in $[C_2mim][NTf_2]$. The radiolytic yields of *iso*butyl-BTP dissolved in $[C_2mim][NTf_2]$ and 1-octanol have been evaluated and shown in Fig. 2 (Table 1), which indicated that the radiation stability of *iso*butyl-BTP in $[C_2mim][NTf_2]$ is better than that in 1-octanol. Meanwhile, the decrement of the *iso*butyl-BTP concentration under irradiation led to the decrease of Dy^{3+} partitioning. The *iso*butyl-BTP/1-octanol system almost lost extraction ability for Dy^{3+} at 400 kGy (E_{Dy} = 2.1%). However, the concentration of isobutyl-BTP in $[C_2mim][NTf_2]$ after irradiation was not in accordance with the decrement of Dy^{3+} partitioning. For instance, about 87.3% of isobutyl-BTP in $[C_2mim][NTf_2]$ have degraded (Fig.S6), but the E_{Dy} still keeps nearly 26.8% at 500 kGy. These results indicated that the radiolytic products were still reserved partial extraction ability of *iso*butyl-BTP and the N-donor heteropolycyclic functional groups of BTPs did not break down entirely during irradiation in $[C_2mim][NTf_2]$.

The identification of radiolytic products of *iso*butyl-BTP/[C_2mim][NTf_2] is of great significant in understanding the radiolysis of *iso*butyl-BTP/[C_2mim][NTf_2] and explaining the reasons for the decrease of Dy^{3+} partitioning in organic phase. MALDI-FTMS was employed to study the chemical structure of radiolytic products in *iso*butyl-BTP/[C_2mim][NTf_2] system after irradiation. Fig. 3 shows the MALDI–FTMS spectra of the *iso*butyl-BTP/[C_2mim][NTf_2] before and after irradiation at 500 kGy. As shown in Fig. 3(a), the peak at m/z = 462.335 is assigned to (*iso*butyl-BTP+H)$^+$ (theoretical m/z is 462.334), and the peaks at m/z = 502.097 and at m/z = 572.413 are assigned to association of cations in clusters ([C_2mim]$_2$[NTf_2])$^+$ and (*iso*butyl-BTP+[C_2mim])$^+$, respectively.

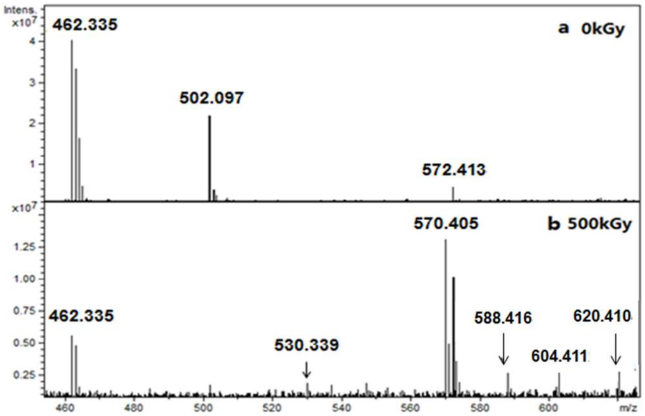

Fig. 3 MALDI-FTMS spectra of *iso*butyl-BTP/[C_2mim][NTf_2] before and after irradiation at 500 kGy.

As illustrated in Fig. 3(b), a new peak at m/z = 530.339 was observed. CF_3 radical generated from RTILs based on [NTf_2] anion under γ-irradiation was reported in previous work.[15, 16] The product at m/z = 530.339 was suggested to the substitution product between *iso*butyl-BTP and CF_3 radical (P1, theoretical m/z is 530.321). A few of the products containing hydroxyl group at m/z = 588.416 (P3, *iso*butyl-BTP(OH)+[C_2mim])$^+$, 604.411 (P4, *iso*butyl-BTP(OH)$_2$+[C_2mim])$^+$ and 620.410 (P5, *iso*butyl-BTP(OH)$_3$+[C_2mim])$^+$ are observed (Table 2). These hydroxyl products were supposed to be formed between isobutyl-BTP and hydroxyl radical due to the radiolysis of water in ionic liquids.[27, 28] Moreover, the peak at m/z = 570.405 with relative high signal intensity is corresponded to product (*iso*butyl-BTP-[C_2mim])$^+$ (Table2, P2, theoretical m/z is 570.403). Berthon *et al.*[15] have illustrated the existence of cation radical formed after the homolytic dissociation of the H-C_2 bond of the imidazolium ring during γ-irradiation. It can be concluded that the radiolytic product (*iso*butyl-BTP-[C_2mim])$^+$ is formed due to the recombination between *iso*butyl-BTP and [C_2mim] cation radical. The radiolytic products which are lighter than the initial m/z of molecular *iso*butyl-BTP are scarcely observed which indicated that the *iso*butyl-BTP/[C_2mim][NTf_2] system exhibits substituted products. Special crown ether [29] and carbamoylmethylphosphine oxide [30] based on the covalent attachment of imidazolium cations were synthesized and utilized for the biphasic extraction of metal ions from aqueous solutions. These special extractants still possess extraction ability for metal ions when crown ether or carbamoylmethylphosphine oxide is substituted by imidazolium cations. We proposed that the radiation stability of *iso*butyl-BTP was changed by imidazolium cations, because a bigger conjugated compound (P2) was formed during irradiation and reduced the radiolysis speed of *iso*butyl-BTP. Finally, UPLC/Q-TOF-MS gave a quantitative analysis of the concentration of *iso*butyl-BTP in [C_2mim][NTf_2], and the chemical structure of the substituted radiolytic products of *iso*butyl-BTP/[C_2mim][NTf_2] were identified effectively by MALDI-FTMS.

Table 2 The proposed chemical structures of radiolytic products of *iso*butyl-BTP/[C_2mim][NTf_2] extraction system.

Num	Experimental m/z	Chemical structure	Theoretical m/z
P1	530.339		530.321
P2	570.405		570.403
P3	588.416		588.413
P4	604.411		604.408
P5	620.410		620.403

In conclusion, UPLC/Q-TOF-MS and MALDI-FTMS were employed to give a quantitative analysis of the concentration of *iso*butyl-BTP in [C_2mim][NTf_2] and identify the chemical structure of the substituted radiolytic products of *iso*butyl-BTP/[C_2mim][NTf_2] for the first time, respectively. Compared with *iso*butyl-BTP in 1-octanol, the radiation stability of isobutyl-BTP in [C_2mim][NTf_2] is better than that in 1-octanol. Since 1-octanol can easily produce active free radicals under γ-irradiation,[27] these active species have led to serious subsequent radiolysis of *iso*butyl-BTP due to the reaction between *iso*butyl-BTP and free radical. However, [C_2mim][NTf_2] provides more protective environment than 1-octanol, because a bigger conjugated system was formed between *iso*butyl-BTP and imidazolium cations. This conjugated compound (P2) possessed partial extraction ability for Dy^{3+} due to the existence of N-donor heteropolycyclic functional groups, which led to the higher extraction ratio than that of 1-octanol system. The work for improving the radiation ability of *iso*butyl-BTP/ionic liquid extraction system is still under way.

Acknowledgement

One of the authors (Dr. Long Zhao) acknowledges the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning for supporting on this study. This work is also financially supported by the National Natural Science Foundation of China (91126014 and 11475112) and the Ph.D. Programs Foundation of Ministry of Education of China (20130073120051).We thank Dr. Lei Feng (Instrumental Analysis Center of SJTU) for assistance on UPLC/Q-TOF-MS measurement.

Notes and references

[a] Nuclear Chemical Engineering Laboratory, School of Nuclear Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China.

[b] Beijing National Laboratory for Molecular Sciences, Radiochemistry and Radiation Chemistry Key Laboratory for Fundamental Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

* Corresponding authors: Tel/Fax: +86-21-34207654; E-mail: ryuuchou@sjtu.edu.cn, mlzhai@pku.edu.cn.

‡ These authors contributed equally.

Electronic Supplementary Information (ESI) available.[Experiment part; E_{Dy} and D_{Dy} of isobutyl-BTP extraction system; Dependence of E_{Dy} in isobutyl-BTP/[C$_2$mim][NTf$_2$] system on oscillation time; ^{1}H NMR spectra of isobutyl-BTP before and after irradiation at 500 kGy; Micro-FTIR spectra of unirradiated and irradiated [C$_2$mim][NTf$_2$]; UPLC/Q-TOF-MS spectra of isobutyl-BTP/[C$_2$mim][NTf$_2$] (20 mM) before and after irradiation; UPLC/Q-TOF-MS spectra of isobutyl-BTP/1-octanol (20 mM) before and after irradiation; Radiolysis rate of isobutyl-BTP in [C$_2$mim][NTf$_2$] and 1-octanol at different doses.] See DOI: 10.1039/c000000x/

1. X. Sun, H. Luo and S. Dai, *Chem Rev*, 2011, **112**, 2100-2128.
2. P. J. Panak and A. Geist, *Chem Rev*, 2013, **113**, 1199-1236.
3. A. Rout, E. R. Souza and K. Binnemans, *Rsc Adv*, 2014, **4**, 11899-11906.
4. A. Sengupta, P. K. Mohapatra, M. Iqbal, W. Verboom, J. Huskens and S. V. Godbole, *Rsc Adv*, 2012, **2**, 7492-7500.
5. S. A. Ansari, P. Pathak, P. K. Mohapatra and V. K. Manchanda, *Chem Rev*, 2012, **112**, 1751-1772.
6. V. r. Hubscher-Bruder, J. Haddaoui, S. Bouhroum and F. o. Arnaud-Neu, *Inorganic chemistry*, 2010, **49**, 1363-1371.
7. K. Binnemans, *Chem Rev*, 2007, **107**, 2592-2614.
8. M. L. Dietz, S. Jakab, K. Yamato and R. A. Bartsch, *Green Chem*, 2008, **10**, 174-176.
9. A. Rout, S. Wellens and K. Binnemans, *Rsc Adv*, 2014, **4**, 5753-5758.
10. M. Sypula, A. Ouadi, C. Gaillard and I. Billard, *Rsc Adv*, 2013, **3**, 10736-10744.
11. D. Allen, G. Baston, A. E. Bradley, T. Gorman, A. Haile, I. Hamblett, J. E. Hatter, M. J. F. Healey, B. Hodgson, R. Lewin, K. V. Lovell, B. Newton, W. R. Pitner, D. W. Rooney, D. Sanders, K. R. Seddon, H. E. Sims and R. C. Thied, *Green Chem.*, 2002, **4**, 152-158.
12. S. E. Howett, J. M. Joseph, J. J. Noel and J. C. Wren, *J. Colloid Interface Sci.*, 2011, **361**, 338-350.
13. I. A. Shkrob, T. W. Marin, S. D. Chemerisov, J. L. Hatcher and J. F. Wishart, *The Journal of Physical Chemistry B*, 2011, **115**, 3889-3902.
14. I. A. Shkrob, T. W. Marin, S. D. Chemerisov and J. F. Wishart, *The Journal of Physical Chemistry B*, 2011, **115**, 3872-3888.
15. L. Berthon, S. Nikitenko, I. Bisel, C. Berthon, M. Faucon, B. Saucerotte, N. Zorz and P. Moisy, *Dalton Trans*, 2006, 2526-2534.
16. É. Bossé, L. Berthon, N. Zorz, J. Monget, C. Berthon, I. Bisel, S. Legand and P. Moisy, *Dalton Trans*, 2008, 924-931.
17. G. Le Rouzo, C. Lamouroux, V. Dauvois, A. Dannoux, S. Legand, D. Durand, P. Moisy and G. Moutiers, *Dalton Trans*, 2009, 6175-6184.
18. Y. Y. Ao, J. Peng, L. Y. Yuan, Z. P. Cui, C. Li, J. Q. Li and M. L. Zhai, *Dalton Trans.*, 2013, **42**, 4299-4305.
19. L. Y. Yuan, J. Peng, L. Xu, M. L. Zhai, J. Q. Li and G. S. Wei, *J. Phys. Chem. B*, 2009, **113**, 8948-8952.
20. R. J. Ellis, T. L. Anderson, M. R. Antonio, A. Braatz and M. Nilsson, *The Journal of Physical Chemistry B*, 2013, **117**, 5916-5924.
21. M. H. Mallah, F. Shemirani and M. G. Maragheh, *Environmental science & technology*, 2009, **43**, 1947-1951.
22. Y. Y. Ao, H. Y. Zhou, W. J. Yuan, S. J. Wang, J. Peng, M. L. Zhai, J. Y. Wang, Z. Q. Zhao, L. Zhao and Y. Z. Wei, *Dalton Trans.*, 2014, **43**, 5580-5585.
23. Z. K. Yu, F. L. Zeng, X. J. Sun, H. X. Deng, J. H. Dong, J. Z. Chen, H. M. Wang and C. X. Pei, *J. Organomet. Chem.*, 2007, **692**, 2306-2313.
24. D. Mercier, N. Leconte, C. Methivier, F. Suzenet, G. Guillaumet, A. Wuillaume and C. M. Pradier, *Phys. Chem. Chem. Phys.*, 2010, **12**, 6099-6106.
25. H. Y. Zhou, Y. Y. Ao, J. Yuan, J. Peng, J. Q. Li and M. L. Zhai, *Rsc Adv*, 2014, **4**, 45612-45618.
26. C. Xu, L. Y. Yuan, X. H. Shen and M. L. Zhai, *Dalton Trans.*, 2010, **39**, 3897-3902.
27. A. Fermvik, L. Berthon, C. Ekberg, S. Englund, T. Retegan and N. Zorz, *Dalton Trans.*, 2009, 6421-6430.
28. A. Fermvik, E. Aneheim, B. Gruner, Z. Hajkova, M. Kvicalova and C. Ekberg, *Radiochim. Acta*, 2012, **100**, 273-282.
29. H. M. Luo, S. Dai, P. V. Bonnesen and A. C. Buchanan, *J. Alloys Compd.*, 2006, **418**, 195-199.
30. P. K. Mohapatra, P. Kandwal, M. Iqbal, J. Huskens, M. S. Murali and W. Verboom, *Dalton Trans*, 2013, **42**, 4343-4347.