Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Journal Name RSCPublishing

COMMUNICATION

Cleavage of C-N Bonds in carbon fiber/epoxy resin composites‡

Cite this: DOI: 10.1039/x0xx00000x

Tiansheng Deng[a+], Ying Liu[a+], Xiaojing Cui[b], Yongxing Yang[a], Shiyu Jia[a], Yingxiong Wang[a], Chunxiang Lu[a], Debao Li[b], Rong Cai[a] and Xianglin Hou[a]*

Received 00th January 2012,
Accepted 00th January 2012

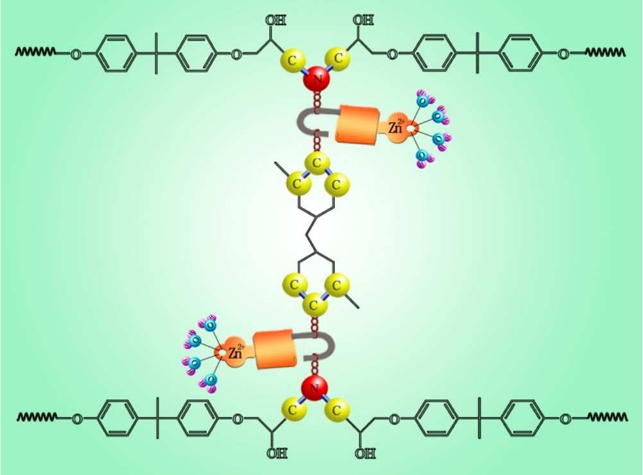
DOI: 10.1039/x0xx00000x

www.rsc.org/

The incompletely coordinated zinc ions in water enable the cleavage of R2C (secondary carbon)-N bonds without breaking C-O (aromatic ether) and C-C bonds in carbon fiber/epoxy resin composites. This selective cleavage of C-N bonds favors the recovery of valuable carbon fibre and basic carbon unit of epoxy resin from their composites waste.

For synthesized organic materials and natural resources, the selective cleavage of specific C-heteroatom bond is of fundamental interest and an essential process in a number of industrial applications, including the synthesis of fuels from biomass or lignite resources,[1] denitrogenation of fossil feedstock,[2] synthesis of amines,[3] and the recovery of valuable units from end-of-life polymeric materials.[4]

A typical example is epoxy resin/carbon fibre composites (CF/EP), which has been extensively used in aeronautical, automotive and sports industries.[5] The degradation of EP to recover CFs from appreciable amount of CF/EP composites wastes is desirable in view of the expensiveness of CFs and environmental protection. The cleavage of chemical bonds in EP by current chemical strategies is unselective, which inevitably introduces a complex distribution of products, causes a severe damage in the strength of CFs, and produces small toxic molecules.[6-11] EP is typically bisphenol-A diglycidyl ether epoxy resin (DGEBA) cured with 4,4-methylene dimethyl cyclohexylamine by C-N bonds, while the basic unit of DGEBA has a two-benzene-ring structure linking by a C-C bond (See Scheme 1, Figure S1 in ESI). Therefore, the selective cleavage of C-N bonds would facilitate not only the decomposition of EP to recycle CFs, but also the preservation of valuable carbon skeleton of EP.



Scheme. 1 The selective cleavage of C-N bonds in CF/EP composites by incompletely coordinated zinc ions in water.

The selective break of C-N bond is notoriously difficult, and massive of reports focus on the cleavage of both single C-N bond in aniline and allylamine, and one C-N bond of C=N double bond[12]. The studies that involve the cleavage of secondary carbon-nitrogen bond is however scarce. More importantly, most examples of C-N bond cleavage are accomplished by metal supported catalysts, or organic metal complexes in which C-N bond is held in close to the metal center.[13] It is impossible for large-sized metal complexes and solid catalysts to diffuse into thermoset EP to interact with its C-N bonds. Hence, Small-sized Lewis acid centres are required to coordinate with N atom of C-N bonds in EP. We noticed that zinc chloride ($ZnCl_2$) is much more soluble in water than other metal chloride counterparts ($MgCl_2$, $CaCl_2$, $FeCl_3$, $CuCl_2$), and its concentration can reach more than 80 wt% with a H_2O/Zn ratio near 3:1, which is less than 6:1 for a complete coordination of Zn with H_2O. The existence of incompletely coordination of zinc ions (IC Zn^{2+} ions) in concentrated $ZnCl_2$ solution has been clarified by our previous research.[14] It is therefore likely that IC Zn^{2+} ions could coordinate with N atoms to cleave C-N bond in EP. Moreover, IC Zn^{2+} ions are readily to enter EP matrix and favors its degradation in view of the small size of H_2O ligands.

Table 1 The catalytic decomposition of EP[a].

Entry	Catalyst	Concen. wt%	H_2O/metal mol/mol	Temp. °C	Dr %[b]
1	$ZnCl_2$	10	68.0	220	Swollen
2	$ZnCl_2$	50	7.6	220	96.5
3	$ZnCl_2$	60	5.0	220	97.3
4	HCl[c]	-	-	220	Swollen
5	$ZnBr_2$	72	4.9	220	85.2
6	$Zn(NO_3)_2$	60	7.0	220	100[d]
7	$ZnCl_2$	60	5.0	210	95.1
8	$ZnCl_2$	60	5.0	200	71.4
9	$ZnCl_2$	60	5.0	190	25.4
10	$ZnCl_2$	60	5.0	170	Swollen
11	$MgCl_2$	40	8.8	220	Swollen
12	$CaCl_2$	42	8.5	220	Swollen
13	$FeCl_3$	45	11.0	220	Swollen
14	$CuCl_2$	42	10.4	220	Swollen
15[e]	$ZnCl_2$	60	5.0	200	Swollen
16[e]	$ZnCl_2$	60	5.0	250	100

[a] Reaction condition in each run: 30ml of metal chloride or HCl aqueous solution, EP (10×10×3 mm^3), 9 h. [b] $Dr = (W_1 - W_2)/W_1$, W_1 and W_2 represent the mass of EP before and after decomposition, respectively. [c] The pH value of HCl solution is 1.9. [d] EP and CF/EP composites were completely decomposed. [e] The curing agent for EP is triethylene tetramine.

More importantly, it is essential for a green and sustainable process if the catalyst recovery is low-cost and convenient. Particularly, the recycling process for homogeneous metal catalysts would be highly problematic and often costly if the metal concentrations are low in the waste streams or the waste stream is monophasic mixture. These challenges would be alleviated in this work because that no water is produced during the degradation process and the concentrations of Zn are high after the reaction. Meanwhile, CFs and the basic organic carbon unit of EP are insoluble in water. Hence, we report using concentrated $ZnCl_2$ aqueous solution to cleave selectively C-N bond in EP to recycle both CFs and basic unit of EP from their composites (See Scheme 1).

Table 2 Atomic ratios of the original EP, the swollen EP and the decomposed products of EP.

Sample	C	H	O	N	Zn
Original EP[a]	1.00	1.45	0.17	0.03	-
Swollen EP[b] [c] [d]	1.00	1.63	0.25	0.03	0.02
Decomposed EP[e]	1.00	1.47	0.16	0.03	0.0003
Decomposed EP[f]	1.00	1.47	0.16	0.03	-

[a] EP (0.01-0.087 mm^3); [b] EP after degradation in 60 wt% $ZnCl_2$ at 220 °C for 1 h; [c] $\Delta n_H/\Delta n_O$ =(1.63-1.45)/(0.25-0.17), which represents the molar ratio of increased amount of H and O in the swollen EP; [d] $\Delta n_{H2O}/\Delta n_{Zn}$ represents the molar ratio of entered H_2O to Zn^{2+} in the swollen EP, a value of 4.5 can be obtained when the$\Delta n_{H2O}/\Delta n_{Zn}$ ratio was calculated on the basis of$\Delta \mathrm{n}_{H2O}/\Delta \mathrm{n}_{Zn}$ (0.18/0.02=9, 9/2=4.5), while a value of 4 can be obtained on the basis of$\Delta n_{H2O}/\Delta n_{Zn}$ (0.08/0.02=4), and an approximately average value of 4.3 can be obtained ((4.5+4)/2=4.3); the solid decomposed products of EP after degradation in 60 wt% $ZnCl_2$ at 220 °C for 9 h [e] without any treatment and [f] with a pretreatment process (detailed in ESI) before ICP analysis.

10 wt% aqueous $ZnCl_2$ solution was inactive for EP degradation (Entries 1, Table 1). In contrast, EP was swollen and decomposed in concentrated $ZnCl_2$ solutions (Entry 2-3, Table 1), and the solid decomposed products of EP was observed to be above the $ZnCl_2$ aqueous solution. The Zn^{2+} ions in 10 wt% $ZnCl_2$ solution are completely coordinated with H_2O and thereby unable to decompose EP. In contrast, IC Zn^{2+} ions in concentrated solutions can catalyze the decomposition of EP. It is possible that H^+ ions existed in concentrated solutions show catalytic effect on EP degradation. The

diluted hydrochloric acid with an identical pH value to 60 wt% $ZnCl_2$ solution was used, and EP was only swollen in it (Entry 4, Table 1). This evidenced that instead of H^+ ions, IC Zn^{2+} ions were active centres for EP degradation. The coordination state of Zn^{2+} ions that entered the EP matrix was further studied. More H and O atoms existed in swollen EP compared with original EP, and the molar ratio of increased amount of H and O ($\Delta n_H/\Delta n_O$) is 2.3 (Table 2). This apparently implied that H_2O entered EP matrix during the swelling. The molar ratio of entered H_2O to Zn^{2+} in the swollen EP ($\Delta n_{H2O}/\Delta n_{Zn}$) was 4.3:1 (Table 2). This suggested that the incompletely coordinated nature of Zn^{2+} ions retained after entering the EP matrix. A trace amount of Zn ions were detected on the solid decomposed products of EP. These Zn ions cannot be eliminated by washing with water, indicating the existence of the interaction of Zn ions with N atom in the solid decomposed products of EP.

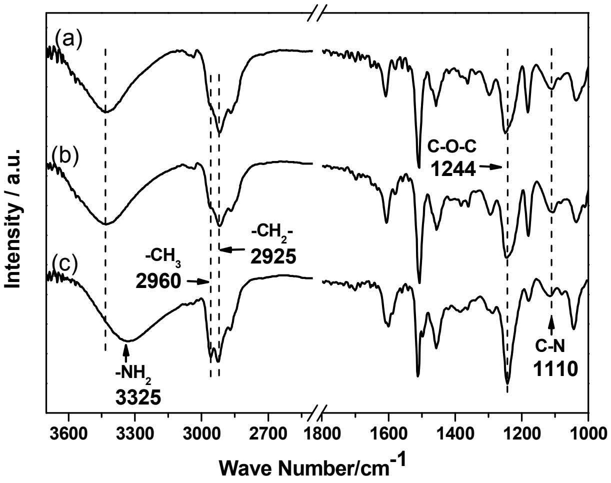


Fig. 1 IR spectra of (a) original EP, and EP after decomposition in 60 wt% $ZnCl_2$ solution at 220 °C for (b) 1 h (the swollen EP) and (c) 9 h (the decomposed EP).

Besides, the effect of anions on EP degradation was investigated. The observation of EP degradation in 72 wt% $ZnBr_2$ solution further proved the above result, that is, IC Zn^{2+} ions in concentrated solutions were capable of catalyzing EP degradation (Entry 5, Table 1). A complete decomposition of EP occurred in $Zn(NO_3)_2$ solution (Entry 6, Table 1). However, CFs of CF/EP composites also decomposed entirely in this solution. This likely resulted from the strong oxidation of NO_3^-. Degradation of EP was also tested in several saturated or near saturated metal chloride aqueous solutions (Entries 11-14, Table 1). No EP decomposition occurred, as H_2O in these solutions was too abundant to create incompletely coordinated metal ions.

The catalytic cleavage of chemical bonds in EP by IC Zn^{2+} ions was studied by IR. The likeness in the IR spectra of original and swollen EPs revealed that no chemical reactions occurred during swelling of EP (Figure 1). For the decomposed EP, the remarkable reduce in peak intensity for C-N bond at 1110 cm^{-1} suggested the cleavage of C-N bond during the decomposition (Figure 1). A shift for peaks at 3084-3682 cm^{-1} to low wave numbers implied that substantial N-H bonds existed in the decomposed EP, which also proved the cleavage of C-N bonds in EP. A clear decline in the ratio of peak intensity of $-CH_2-$ (2925 cm^{-1}) to $-CH_3$ (2960 cm^{-1}) showed a loss in $-CH_2-$ groups for EP. As $-CH_2-$ groups come from the carbon rings of 4, 4-methylene dimethyl cyclohexylamine, that is, the curing agent of EP, it inferred the elimination of part of the curing agent part from EP by the cleavage of C-N bonds. The elimination of the curing agent part led no decrease in the nitrogen content in the decomposed EP (Table 2). Hence, only the R2C-N bond in EP, that is, the secondary carbon-N bond, was cleaved by IC Zn^{2+} ions. The curing agent part was not detected in the solid decomposed products of EP. Hence, it may dissolved in the $ZnCl_2$ solution. The $ZnCl_2$ solution after the degradation was analyzed by GC-MS and NMR. However, the curing agent part was not observed. It is hence likely that the curing agent part may be transformed in the $ZnCl_2$ solution. In order to elucidate the chemistry of C-N bond cleavage in EP, triethylamine and N, N-dimethyl isopropyl amine that has primary carbon-nitrogen bond and secondary carbon-nitrogen bond respectively, were selected as model molecules, and their transformations in 60 wt% $ZnCl_2$ solution were investigated. N, N-dimethyl isopropyl amine was much more active than triethylamine, and the cleavage of C-N bond in N, N-dimethyl isopropyl amine led to the formation of isopropanol (Table S1 in ESI). This result suggested that the cleavage of secondary carbon-nitrogen bond resulted in the formation of C-OH bond. We inferred that the end groups of the curing agent part are hydroxyl groups. The degradation products of EP is illustrated in Figure S2 in ESI based on the above characterization results.

The degradation of EP cured with triethylene tetramine was also performed in the 60 wt% $ZnCl_2$ solution. EP cured with triethylene tetramine is stable in the 60 wt% $ZnCl_2$ aqueous solution at 200 ^oC for 10 h, and it only changed colour (into black), whereas it decomposed completely within 6 h when the temperature was increased to 250 ^oC (Table 1, entries 15-16). This result indicated the capability of $ZnCl_2/H_2O$ to cleave the H_3C(primary carbon)-N bond and the effectiveness of $ZnCl_2/H_2O$ towards the EPs with the curing agents belong to the class of aliphatic amines.

The peak intensity of aromatic ethers at 1244 cm^{-1} (C-O-C) remained, indicating the reservation of C-O-C bond in aromatic ethers in EP after degradation. The above results suggested that IC Zn^{2+} ions enabled the cleavage of C-N bond without breaking C-O bond of aromatic ethers in EP.

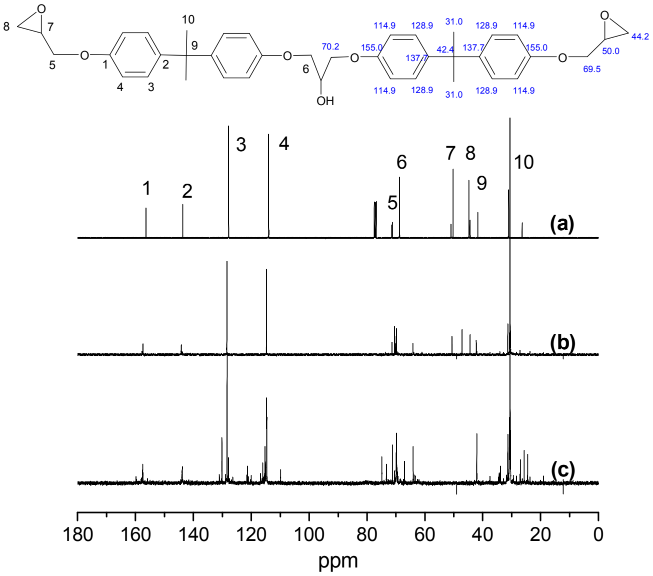


Fig. 2 The ^{13}C-NMR of (a) fresh DGEBA, and after degradation in the 60 wt% zinc chloride aqueous solution for (b) 3h and (c) 9h.

The solid decomposed products of EP that floated on the $ZnCl_2$ aqueous solution were collected and analyzed by NMR and GC (Figure S3 and Figure S4 in ESI). The average molecular weight of these decomposed products was 1183, which was close to that of dimer of DGEBA in EP (Figure S3a in ESI). As shown in NMR spectra, no chemical shifts were observed in the signals 1 to 4 and 9 to 10 after degradation for 3 hours and 9 hours. This implied the preservation of carbon framework of bisphenol A in DGEBA (Figure 2, and Figure S5 in ESI). Therefore, the selective cleavage of C-N bonds without breaking C-C bond in EP facilitated the preservation of basic carbon unit of EP.

Furthermore, IC Zn^{2+} ions were applied to catalyze the decomposition of EP in CF/EP composites. The degradation of EP in CF/EP composites was much faster than EP, for more pores exist among the layers of CF/EP composites. These pores enlarged the contact area of EP with IC Zn^{2+} ions (Figure S6 in ESI). CFs were below $ZnCl_2$ solution after the degradation; while the curing agent part of EP was dissolved in $ZnCl_2$ solution and the solid decomposed products of EP floated on $ZnCl_2$ solution. The structure properties of recycled CFs were characterized by Raman spectroscopy, SEM and XPS. In Raman spectra, the integrated intensity ratio of G to D band (I_G /I_D), which presents the degree of graphitization, of the recovered CFs matched well with virgin CFs (Figure S7 in ESI). This result showed that the graphite crystal structure of CFs preserved after the recycling. SEM results demonstrated that the recovered CFs were as clean and smooth as virgin CFs (Figure S8 in ESI). The tensile strengths of all recovered CFs maintained more than 90% of original one (Figure S9 in ESI). Especially, the tensile strength of CFs after degradation in 50 wt% $ZnCl_2$ solution at 200 °C decreased only 2.1% compared to virgin CFs. It is noticed that the tensile strength of CFs declined with increasing $ZnCl_2$ concentration. It likely results from damage of the sizing on the surface of CFs in concentrated $ZnCl_2$ concentration. A sizing improves the tensile strength of CFs. It usually has C-O groups. The excess incompletely coordinated Zn ions in concentrated $ZnCl_2$ solution may cleave these C-O groups. This would cause damage in the sizing and consequently a decrease in the tensile strength of carbon fibre. This assumption was verified by the XPS results. As indicated by XPS results, the surface oxygen content of recycled CFs was similar to those of virgin CF without sizing (Figure S10, Table S3a and Table 3b in ESI).

The solid decomposed EP that floated on the $ZnCl_2$ solution was recycled with a yield of more than 90 wt% (Detailed in Experimental section in ESI). As indicated by IR, the recycled EP has abundant N-H bonds. It was hence used as the curing agent for preparing new EP. The new EP had a comparable strength to virgin EP when the content of the recycled EP in the whole curing agent was no more than 10 wt% (Table S4 in ESI). Besides, 60 wt% $ZnCl_2$ aqueous solution exhibited excellent availability of reusing. It showed high activity after recycling for six times without treatments (Figure S11 in ESI). The Zn content in the solution after the recycling process was analyzed by ICP (Table S5 in ESI). IC Zn ions could enter the matrix of EP, but they cannot enter into the body of CFs. Hence, the possible Zn loss occurs only during the separation of solid decomposed products of epoxy resin from the solution. The total amount of the lost Zn in these solid decomposed products, as indicated by ICP analysis, were trace, in comparison with the total amount of Zn in the solution. Therefore, the Zn amount in the recycled solution was almost identical to that of the fresh solution. This result indicated that the process developed in this work is green and sustainable, and shows potential as a general application protocol for recycling most carbon fibre reinforced epoxy resin composites waste.

Conclusions

We report a green and effective method to cleave C-N bond in carbon fibre/epoxy resin (CF/EP) composites using concentrated $ZnCl_2$ aqueous solutions. The incompletely coordinated Zn^{2+} ions can selectively cleave -R_2CH-N bond, namely the secondary carbon-nitrogen bond, without breaking the –RCH_2-N bond (the primary carbon-nitrogen bond), C-C bond and C-O bond from aromatic ether group in EP. This selective cleavage of C-N bonds favors the recovery of expensive CFs and valuable basic carbon unit of EP from CF/EP composites wastes without the emission of small toxic gases. Besides its effectiveness, the concentrated $ZnCl_2$ solution owns superior capability of reusing.

Notes and references

[a] Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, PR China.

[b] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, PR China.

[+] Authors contributed equally.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

‡ We thank Scientific and technological project of Shanxi Province (20130322005-01) for funding.

1 D. Tilman, J. Hill, C. Lehman, *Science*, 2006, ***314***, 1598-1600; G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.*, 2006, ***106***, 4044-4098; A. Corma, S. Iborra, A. Velty, *Chem. Rev.*, 2007, ***107***, 2411-2502; H. B. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science*, 2007, ***316***, 1597-1600; A. Rahimi, A. Ulbrich, J. J. Coon, S. S. Stahl, *Nature*, 2014, accepted, doi:10.1038/nature13867; R. M. Fakoussa, M. Hofrichter, *Appl. Microbiol. Biotechnol.*, 1999, ***52***, 25-40;

2 S. D. Gary, D. P. Smith, M. A. Bruck, D. E. Wigley, *J. Am. Chem. Soc.*, 1992, ***114***, 5462-5463; S. D. Gary, K. J. Weller, M. A. Bruck, P. M. Briggs, D. E. Wigley, *J. Am. Chem. Soc.*, 1995, ***117***, 10678-10693; T. S. Kleckley, J. L. Bennett, P. T. Wolczanski, E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1997, ***119***, 247-248.

3 S. I. Murahashi, N. Yoshimura, T. Tsumiyama, T. Kojima, *J. Am. Chem. Soc.*, 1983, ***105***, 5002-5011; H. Inui, S. Murata, *J. Am. Chem. Soc.*, 2005, ***127***, 2628-2636;

4 S. Enthaler, and A. Trautner, *ChenSusChem*, 2013, **6**, 1334-1336.

5 R. Steward, J. Reinf, *Plast Compos.*, 2009, ***53***, 16-21; *Plast Compos.* 2011, ***55***, 26-31; A Jacob, J. Reinf, *Plast Compos.*, 2006, ***50***, 22-24.

6 N. Rose, M. Bras, R. Delobel, B. Costes, *Polym. Degrad. Stabil.*, 1993, ***42***, 307-216; J. R. Kennerley, R. M. Kelly, N. J. Fenwick, S. J. Pickering, C. D. Rudd, *Compos. Pt. A-Appl. Sci. Manuf.*, 1998, ***29***, 839-845; H. L. H. Yip, S. J. Pickering, C. D. Rudd, *Plast. Rubber Compos.*, 2002, ***31***, 278-282; S. J. Pickering, R. M. Kelly, J. R. Kennerley, C. D. Rudd, N. J. Fenwick, *Compos. Sci. Technol.*, 2000, ***60***, 509-523.

7 E. Asmatutu, J. Twomey, M. Overcash, *J. Compos Mater.*, 2013, ***0***, 1-16.

8 S. J. Pickering in *Wiley Encyclopedia of Composites*, ***Vol. 1*** (Eds.: L. Nicolais, A. Borzacchiello, S. M. Lee), John Wiley & Sons, New Jersey, 2012, pp. 1-17.

9 M. Goto, *J. Supercrit. Fluids.*, 2009, ***47***, 500-507; S. G. Kazarian, *Polym. Sci. Ser. C*, 2000, ***42***, 78-101; Y. Liu, J. Liu, Z. Jiang, T. Tang, *Polym. Degrad. Stabil.*, 2012, ***97***, 214-220; R. Piñero-Hernanz, J. García-Serna, C. Dodds, J. Hyde, M. Poliakoff, M. J. Cocero, S. Kingman, S. Pickering, E. Lester, *J. Supercrit. Fluids.*,

2008, ***46***, 83-92; H. Yan, C. Lu, D. Jing, X. Hou, *Polym.Degrad. Stabil.*, 2013, ***98***, 2571-2582.

10 W. Dang, M. Kubouchi, S. Yamamoto, H. Sembokuya, K. Tsuda, *Polymer.*, 2002, ***43***, 2953-2958; W. Dang, M. Kubouchi, H. Sembokuya, K. Tsuda, *Polymer.*, 2005, ***46***, 1905-1912.

11 P. Xu, J. Li, J. Ding, *Compos. Sci. Technol.*, 2013, ***82***, 54-59; J. Li, P. Xu, Y. Zhu, J. Ding, L. Xue, Y. Wang, *Green Chem.*, 2012, ***14***, 3260-3263.

12 S．Gupta, S. Pal, A. K. Barik , S. Roy, A. Hazra, T. N. Mandal,R. J. Butcher, S. K. Kar, *Polyhedron,* 2009, ***28***, 711–720; R. Bloch, *Chem. Rev.,* 1998, ***98***, 1407-1438; W. L. Man, J. Xie, Y. Pan, W. W. Y. Lam, H. K. Kwong, K. W. Ip, S. M. Yiu, K. C. Lau, T. C. Lau, *J. Am. Chem. Soc.,* 2013, ***135***, 5533−5536; T. Koreeda, T. Kochi, F. Kakiuchi, *J. Am Chem. Soc.,* 2009, ***131***, 7238–7239; X. Zhao, D. Liu, H. Guo, Y. Liu, W. Zhang, *J. Am. Chem. Soc*., *2011*, ***133***, 19354–19357; K. Ishimaru, T. Kojima, *J. Org. Chem.* 2000, ***65***, 8395-8398; V. Mahalingam, N. Chitrapriya, F. R. Fronczek, K. Natarajan, *Polyhedron,* 2010, ***29***, 3363–3371; H. Hamaki, N. Takeda, N. Tokitoh, *Organometallics,* 2006, ***25***, 2457-2464; M. K. Zhu, J. F. Zhao, T. P. Loh, *Org. Lett.,* 2011, ***13***, 6308-6311; K. Hiraki, T. Matsunaga，*Organometallics,* 1994, ***13***, 1878-1885.

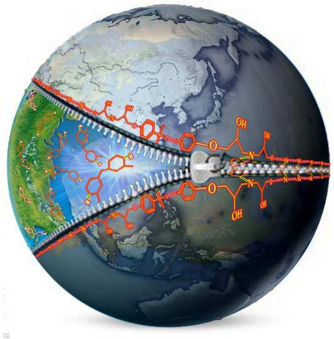
13 S. D. Gray, K. J. Weller, M. A. Bruck, P. M. Briggs, D. E. Wigley, *J. Am. Chem. Soc.*, 1995, ***117***, 10678-10693; Y. Lei, A. D. Wroleski, J. E. Golden, D. R. Powell, J. Aubé, *J. Am. Chem. Soc.*, 2005, ***127***, 4552-4553; T. Koreeda, T. Kochi, F. Kakiuchi, *J. Am. Chem. Soc.*, 2009, ***131***, 7238-7239; K. J. Weller, S. D. Gray, P. M. Briggs, D. E. Wigley, *Organometallics*, 1995, ***14***, 5588-5597; M. Tayebani, K. Feghali, S. Gambarotta, C. Bensimon, *Organometallics*, 1997, ***16***, 5084-5088; F. Basuli, U. J. Kilgore, D. Brown, J. C. Huffman, D. J. Mindiola, *Organometallics*, 2004, ***23***, 6166-6175; A. Arunachalampillai, P. Crewdson, I. Korobkov, S. Gambarotta, *Organometallics*, 2006, ***25***, 3856-3866; M. Yashiro, T. Mori, M. Sekiguchi, S. Yoshikawa, S. Shiraishi, *J. Chem. Soc., Chem. Commun.*, 1992, 1167-1168; M. C. Rodriguez, F. Lambert, I. Morgenstern-Badarau, *Inorg. Chem.*, 1997, ***36***, 3525-3531; C. J. Hu, R. M. Chin, T. D. Nguyen, K. T. Nguyen, P. S. Wagenknecht, *Inorg. Chem.*, 2003, ***42***, 7602-7607.

14 T. S. Deng, X. J. Cui, Y. Q. Qi, Y. X. Wang, X. L. Hou, Y. L. Zhu, *Chem. Commun.*, 2012, ***48***, 5494-5496.

Graphical abstract for

Cleavage of C-N Bonds in carbon fiber/epoxy resin composites[‡]

Tiansheng Deng[a+], Ying Liu[a+], Xiaojing Cui[b], Yongxing Yang[a], Shiyu Jia[a],
Yingxiong Wang[a], Chunxiang Lu[a], Debao Li[b], Rong Cai[a] and Xianglin Hou[a*]



$ZnCl_2$ enables the effective recovery of carbon fiber and epoxy resin from composites waste by cleaving C-N bonds.