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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201901796

Link to VoR: http://dx.doi.org/10.1002/cssc.201901796



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Metal-Free Photochemical Degradation of Lignin-Derived Aryl Ethers and Lignin by Autologous Radicals via Ionic Liquids Induction

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Abstract: Degradation of lignin into aromatic products is very meaningful, but harsh conditions and metal-based catalysts are commonly needed to cleave the inert bonds. We herein demonstrate an efficient self-initiated radical photochemical degradation for ligninderived aryl ethers via ionic liquids (ILs) induction. The C-C/C-O bonds could be efficiently cleaved through free radicals-mediated reaction in the binary ILs system of [PMim][NTf₂] and the brønsted acid [PrSO₃HMim][OTf] at ambient conditions. [PMim][NTf₂] initiates the reaction by promoting the cleavage of C_{B} -H bond, and [PrSO₃HMim][OTf] catalyzes the subsequent C-O-C bond fragmentation. Furthermore, alkyl, hydroxyl and peroxy radicals were detected, which suggested the degradation was based on a photochemical free radical process. Additionally, alkali lignin could also be degraded in the ILs system. This work sheds light on the sustainable biomass utilization by self-initiated radical photochemical strategy under metal-free and mild condition.

Introduction

Lignin is a unique and abundant natural biopolymer, representing 15 – 30% by weight and 40% by energy of lignocellulosic biomass^[1]. It has a rich aromatic structure primarily derived from methoxylated hydroxycinnamyl alcohol building blocks and therefore can serve as a potentially valuable source of renewable fuels and aromatic compounds^[2]. However, until now the large amount of lignin is chemically under-exploited and only less than 5% of lignin is basically used as low-grade fuels or concrete additives^[3]. The heterogeneous and highly cross-linked recalcitrant structure impedes the upgradation of lignin to value-added fine chemicals^[4]. Meanwhile, lignin-derived compounds containing β -aryl ether bond, the most abundant linkage of native lignin^[5], are often adopted to study lignin conversion process^[4b, 6]. The existing strategies, including hydrogenolysis, catalytic cracking and oxidation^[7], have been

School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences Beijing 100190 (P. R. China) developed to effectively exploit the aromaticity of lignin and lignin-derived compounds. However, these processes still suffer from harsh and energy-intensive conditions issues, in which high gas pressure and elevated temperature are required to break the inert bonds in lignin, for example, the bond dissociation energy of C-O and C-C linkages are 293 kJ/mol and 314-494 kJ/mol respectively^[3a], resulting in high energy consumption^[8]. Consequently, developing effective elegant approaches to degradation of lignin under mild conditions are highly desired.

For the objective of mild lignin valorization, photocatalytic degradation, which has some attractive advantages such as the milder conditions, the avoidance of strong oxidants or reducing agents and the efficient reaction sequences minimizing side reactions^[9], has been considered as a superior alternative to conventional strategies^[10]. Among all the photocatalysts, semiconductor, like titanium dioxide (TiO₂), remains the most widely used^[11]. The photocatalysis with TiO₂ to carry out lignin degradation is based on free radicals production process, that is, when the light irradiates TiO₂, the energy of which is equal to or higher than TiO₂ energy band (3.2 eV for anatase phase), an electron is excited and leaves behind a hole, subsequently yielding 'OH or 'O₂' radical to oxidize target lignin linkages^[12]. Unfortunately, as demonstrated in previous researches, the band gap of conventional TiO₂ is large and recombination of electron-hole pairs is fast, limiting its photocatalytic efficiency^[9c]. In order to improve these constraints, a variety of metal-based catalysts, such as secondary semiconductors^[13] and noble metal nanoparticles^[14], are introduced to TiO₂ by facilitating electron transfer and decreasing the recombination rate^[15]. Nevertheless, metals in doped photocatalysts suffer from leaching issues, and as such, the photocatalysis efficiency degradation and the generation of harmful metal waste remain grand challenges, limiting the application of metal-based photocatalysts. A key step to address this issue is to develop metal-free photochemical routes, like the development of metal-free catalysts based on polymeric carbon nitride^[10b], which could yield free radicals to oxidize target organic species by producing electrons and holes after photons illumination. Obviously, the generation of free radicals, primarily contributing to the cleavage of lignin linkages, is the pivotal step for photochemical degradation method. Interestingly, lignin could generate free radicals from itself after exposing to UV irradiation and atmospheric oxygen^[16]. However, the process is very slow at ambient temperature. The finding stimulated us to develop an effective metal-free route to induce and accelerate free radical generation from lignin, which is also meaningful for photochemical process.

Recently, the use of ionic liquids (ILs) provides a promising alternative to meet these requirements. IL, an important type of high-efficient designable media having attractive properties such as high chemical stability and high solubility of

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substrates^[17], have shown great practical application in lignin upgradation acting not only as ideal solvent^[18] but also as catalyst for bond cleavage^[19]. In particular, the designable ILs has been exploited to promote free radicals generation and demonstrate considerable potential for metal-free lignin degradation. For example, the ILs containing anion [NTf₂]⁻ with strong electronegativity could contribute to the delocalization of electron pairs, which facilitate the formation of ·OOH and thereby promoted lignin transformation, producing desired products in encouraging yields^[20]. Hence, the application of this type of ILs in lignin photochemical degradation is promising, which remains great potential for accelerating lignin degradation by facilitating formation of free radicals under ambient conditions.

On the basis of the information and the experimental design above, we propose the metal-free photochemical strategy for the effective degradation of lignin-derived aryl ethers by autologous radicals via ionic liquids (ILs) induction. In our proposed process, the binary ILs system, namely [PMim][NTf₂] and the brønsted acid [PrSO₃HMim][OTf], is highly efficient for C-C/C-O bonds cleavage of lignin-derived aryl ethers to obtain desired aromatic products with more than 90% yields in the homogeneous system. The alkyl, hydroxyl and peroxy free radicals are detected, confirming that the process is based on a free radical reaction mechanism. In the experiment, the results show that [PMim][NTf₂] initiates the reaction by promoting the cleavage of C_B-H bond, and [PrSO₃HMim][OTf] catalyzes the subsequent C-O-C bond fragmentation. Meanwhile, the ILs could dissolve lignin to provide a homogeneous reaction system, which significantly accelerate the transmission of free radicals and therefore facilitate the subsequent degradation. In a word, this research is considered to propose a metal-free photochemical route for transforming lignin into renewable aromatics under ambient conditions.

Results and Discussion

Influence of ionic liquids on the photochemical degradation of 2-phenoxyacetophenone (1). The β -O-4 linkage has been reported to constitute 45% to 60% of native lignin linkages. Therefore, β -O-4 lignin dimmer, 2-phenoxyacetophenone (1), was selected for benzylic photochemical degradation. Here, we report the application of binary ILs system for the homogeneous photochemical degradation of 1 under atmospheric oxygen, room temperature and metal-free conditions. The ionic structure of ILs have been reported to be influential for the lignin degradation process^[20]. Hence, several families of neutral ILs with various anions ([NTf₂], [BF₄], [PF₆], [OTf]) and cations ([CPMim]⁺, [PMim]⁺, [BMim]⁺, [EMim]⁺, [AMim]⁺) were used to investigate their effects on the process (shown in Table 1, entries 1-6). The structures of these ILs were shown in Fig S1. With [PMim][NTf₂], the degradation of **1** achieves 87.1±2.7% conversion for 120 min, affording benzoic acid and phenol with vields up to 78.3±1.4% and 55.5±1.8%, respectively (Table 1, entry 1). The anions of ILs significantly influenced the photochemical degradation process. The presence of ILs with [NTf₂] is beneficial for the reaction, which facilitates degradation of **1** and formation of products through C-C/C-O bonds cleavage. (Table 1, entries 2 to 3). While the results without $[NTf_2]^-$, like [AMim][OTf], exerted obvious decrease on boosting the reaction and gave less than 15% yields of products under comparable conditions (Table 1, entries 4 to 6), suggesting that the bonds cleavage is likely $[NTf_2]^-$ assisted for the strong electronegativity as reported for disruption of lignin-derived compounds^[20]. However, the reaction in the absence of BAIL gives only a low yield of aromatic products (Table 1, entry 7), we hypothesize that the low yields could be due to the fact that the hydrogen attached to the carbon linking to two nitrogens (NCHN) was acidic^[8].

To validate the hypothesis, an evaluation of the brønsted acids was conducted (Table 1, entries 8-11). All the BAILs contain the same cation, with a SO₃H group covalently linked through a propyl chain to the imidazolium cation (Figure S1). Classic mineral acid phosphoric acid (H₃PO₄), the commonly used acid in lignin degradation, was used as a reference. The presence of BAILs is beneficial for the photochemical degradation. The benzoic acid and phenol yields reached up to 78.3±1.4% and 55.5±1.8% with minor catalytic amounts of [PrHSO₃Mim][OTf] (3 wt%). While other BAILs, like [PrHSO₃Mim][H₂PO₄], gave a much lower products yields. In order to draw a correlation between catalytic activity and the acids strength, the acid strength of all BAILs and H₃PO₄ were measured. The Hammett acidity functions (H_0) of the BAILs and H₃PO₄ were spectrophotometrically determined (Figure S2) and further calculated by UV/Vis spectroscopy (Table S1). The value of H_0 demonstrates that the acid strength of BAILs decrease as [PrSO₃HMim][OTf] [PrSO₃HMim][BF₄] follows: > $[PrSO_3HMim][Cl] > [PrSO_3HMim][H_2PO_4]$. In general, the catalytic activity is closely related to acid strength of BAILs^[21]. With BAILs in system, high acid strength is beneficial for the reaction, the conversion of 1 displayed a significantly increasing

Table 1.	Photocatalytic	degradation of	of 1 in various	ILs system ^a .

	O ILs, U Room ten	V, air	COOH +	ОН
	1		penzoic acid	pnenoi
Entry	ILs system	Conv.	Yield	(%)
Endy	.20 0)010111	(%)	Benzoic acid	Phenol
1	[PMim][NTf ₂]	87.1±2.7	78.3±1.4	55.5±1.8
2	[BMim][NTf ₂]	82.6±2.2	70.6±1.8	49.6±2.0
3	[EMim][NTf ₂]	85.1±1.8	73.9±2.5	42.6±1.7
4	[AMim][OTf]	56.9±2.7	12.9±1.4	5.1±1.1
5	[CPMim][BF ₄]	72.1±1.8	5.0±1.6	6.8±0.7
6	[BMim][PF ₆]	29.9±2.6	13.1±2.5	6.6±2.1
7 [*]	[PMim][NTf ₂]	32.3±3.4	17.5±1.3	2.0±0.8
8†	[PrHSO ₃ Mim][BF ₄]	76.6±1.4	42.4±2.6	22.2±2.7
9†	[PrHSO₃Mim][CI]	58.7±1.6	30.5±1.1	7.3±0.5
10 [†]	[PrHSO ₃ Mim][H ₂ PO ₄]	50.8±1.9	29.6±3.3	9.5±1.1
11 [†]	H ₃ PO ₄	43.7±1.7	28.0±2.2	14.7±3.0

^aConditions: **1** (10 mg), 500 mg of IL, [PrHSO₃Mim][OTf] 3% (weight, 0.028 mmol), H_2O 1% (weight), atmospheric air, room temperature, 120 min, UV irradiation.

 * 1 (10 mg), 500 mg of [PMim][NTf_2], H_2O 1% (weight), atmospheric air, room temperature, 120 min, UV irradiation. † 1 (10 mg), 500 mg of [PMim][NTf_2], BAILs/ H_3PO_4 (0.028 mmol), H_2O 1% (weight), atmospheric air, room temperature, 120 min, UV irradiation.

trend with the decrease of H_{0} , and [PrSO₃HMim][OTf] led to the highest yield. Meanwhile, H₃PO₄ gave low conversion and yields of products, probably relevant to the relatively low acid strength (Table S1).

Influence experimental conditions of on the photochemical degradation of 1. Light irradiation is indispensable for the degradation, as no conversion of 1 occur under dark conditions (Table S2, entry 1). The degradation under UV light irradiation gave the best performance. Besides, poor product yields were detected under argon atmosphere with a pronouncedly decreased conversion (8.5±2.7%), confirming the necessity of atmospheric oxygen, and the removal of active oxygen suppressed the C-C/C-O bond cleavage of 1 (Table S2, entry 4). In addition, amount of [PrSO₃HMim][OTf] also have great effects on the reaction activity (Figure 1a). A 3 wt% addition of [PrSO₃HMim][OTf] gave the highest product yields, beyond which a slightly decreasing trend was observed. The decline in yields could be attributed to the side reactions that were accelerated by large amount of [PrSO₃HMim][OTf]^[22]. Water is also beneficial for the reaction as an increasing trend of products vields was obtained with growing addition of water. Figure 1b. However, slight decrease in conversion was exerted with water addition beyond 3 wt%, which might be attributed to the diluted system^[20].

As illustrated in Table S3, elevated temperature significantly accelerates the reaction. The reaction time that was needed to achieve around 98.0% conversion at high temperature was much shorter in comparison to that at low temperature. At room



Figure 1. Effects of [PrHSO₃Mim][OTf] and water amount on the photocatalyic degradation. Conditions: 1 (10mg), 500 mg of [PMim][NTf₂], atmospheric air, room temperature, 120 min, UV irradiation, (a) H_2O 1% (weight), varying weight ratio of [PrSO₃HMim][OTf], (b) [PrHSO₃Mim][OTf] 3% (weight), varying weight ratio of H_2O .

temperature (the system automatically heats up to 45 °C), the reaction took 150 min to achieve conversion of 98.4±1.0%. However, when raising temperature to 100 °C, only 15 minutes were needed to afford **1** conversion with up to 97.7±2.2%, revealing that the photochemical degradation was sensitive to high temperature. Nevertheless, excessive temperature also exerted a slight decline in products yields, probably because of the repolymerization at high temperature^[8].

Reaction kinetics. In order to have more insights into the reaction dynamics, we monitored the reaction at different temperature as a function of time (Figure 2). The time-on-course process conducted at room temperature was measured (Figure 2a). Under UV light irradiation, 1 was converted with the formation of benzoic acid and phenol. $98.4\pm1.0\%$ of 1 conversion was achieved after 150 min of illumination, and yields of benzoic acid and phenol reached $93.3\pm4.7\%$ and $68.8\pm3.1\%$, respectively. A slightly decline trend of product yields was observed beyond 150 min, which might be caused by esterification or further oxidation^[20]. The experiments at other temperatures were also monitored to obtain the kinetic parameters (Figure 2b, c, d). The photochemical degradation



Figure 2. Time-on-course process at different temperatures and kinetics on the photochemical degradation of 1. (a) at room temperature (automatically heating up to 45 °C); (b) at 60 °C; (c) at 80 °C; (d) at 100 °C; (e) Kinetics on the photochemical degradation of 1 at room temperature to 100 °C. Reaction conditions: 1 (10 mg), [PMim][NTf₂] 500 mg, [PrHSO₃Mim][OTf] 3% (weight), H₂O 3% (weight), atmospheric air, UV irradiation.

conformed to the first-order reaction law from room temperature to 100 °C with an apparent activation energy (E_a) of 48.1 ± 5.4 kJ/mol (Figure 2e).

Stability and recyclability of the ILs. Subsequently, the photostability of [PMim][NTf₂] was also tested. Figure S3 showed the comparison of ¹H and ¹³C NMR for IL before and after UV-light irradiation. The [PMim][NTf₂] irradiated by UV-light for 150 min showed almost the same NMR spectra as that of fresh IL, indicating that no significant decomposition of the IL occured during UV irradiation. The ¹³C NMR spectra of the IL after UV irradiation present signals of strength assigned to the [NTf₂] unit, a quartet peak around 125 ppm, which show almost the same level as the IL before irradiation. This phenomenon indicates that almost no [NTf₂] is lost during the irradiation. Meanwhile, we examined the recyclability of [PMim][NTf₂] in the photochemical degradation. As shown in Figure 3, [PMim][NTf₂] could be reused at least 5 times without notable loss of efficiency, confirming the good stability of the IL in the reaction.



Figure 3. The reuse of $[PMim][NTf_2]$ at room temperature for 150 min. Other conditions were the same as those of Figure 2 (a).

Mechanism of the photochemical degradation. Our previous work showed that the binary ILs system, [PMim][NTf₂] and [PrHSO₃Mim][OTf], exhibited high performance for the reaction. Density functional theory (DFT) calculations indicated that the interaction of 1 with [NTf₂]⁻ could lower the bond dissociation energy of C_β-H₂ bond (Figure S4). Therefore, the presence of ionic liquid [PMim][NTf₂] could be favorable for cleavage of the C_β-H₂ bond, and then promote the formation of alkyl radical. Meanwhile, the imidazolium based BAIL, [PrHSO₃Mim][OTf], could provide H⁺ as well as facilitate the cleavage of C-O-C bonds by interacting with lignin moieties via protonated 'O'^[8], consistent with the experimental results that very low yields of products were obtained without BAIL.

Meanwhile, the experimental results showed that ultraviolet light irradiation and air had an important role in promoting **1** photochemical degradation. Actually, *Hon et al.*^[16] has reported a lignin photochemical degradation process based on a photochemical free-radical-mediated mechanism (exposed to UV light and atmospheric oxygen). Free radicals, such as alkyl radical and peroxy radical, were generated when lignin was irradiated with UV-light in the atmosphere, which could further lead to chain scission in lignin structure. Therefore, we deduce that the photochemical degradation of **1** is a free radical reaction related to alkyl radical (·R) and peroxy radical (·OOR).

To validate the hypothesis, we used electron spin resonance (ESR) to identify radicals generated in the reaction. The ESR spectrum of 1-ILs reaction system, which was irradiated with UV-light irradiation (or in dark) and trapped with 50 mM DMPO, was shown in Figure 4. As expected, two typical radicals, $\cdot R$ and $\cdot OOR$ free radicals, could be labeled through determining the hyperfine splitting constants (*A* factors). The spin adduct ($A_N = 1.39 \text{ mT}$, $A_\beta^H = 1.04 \text{ mT}$) could be reasonably assigned to the peroxy radical adduct^[23], which were labeled as radical *b* (Scheme 1). The spectrum also showed *A* factors of $A_N = 1.61$ -1.68 mT and $A_\beta^H = 2.14$ -2.15 mT, which could be assigned to the formation of $\cdot R^{[24]}$, labeled as radical *a*. Furthermore, it was interesting to notice the appearance of the *A* factors typical for hydroxyl radical ($A_N = 1.45 \text{ mT}$, $A_\beta^H = 1.33$ -1.37 mT)^[25], which was labeled as radical *c*. Negligible ESR signals were observed

under dark conditions.



Figure 4. ESR spectrum of 1-ILs reaction system at room temperature with UV-light irradiation or in dark.

On the basis of the above described experimental results, combined with experimental phenomena, we envisioned the mechanism shown in Scheme 1. It had been reported that the ether parts in polymer were selectively attacked and form radicals during photodegraded process^[26]. Firstly, assisted by anion $[NTf_2]^{-}$, **1** generated alkyl radical *a* on the β -C atom linking to ether bond with UV-light irradiation. Then free radical a reacted with atmospheric oxygen to form the peroxy radical b. Radical b subsequently abstracted protons from H₂O to generate hydroperoxides d and hydroxyl radical c, which further reacted with 1 to produce H_2O and radical *a*. The hydroperoxides *d*, attacked by H⁺, BAIL and water, was further transformed to benzoic acid and phenol. No formic acid was detected in the products which might be converted to CO2 during the UV irradiation^[20]. The conjecture was proved by the FT-IR spectrum of the reaction system conducted for 80 minutes, which showed the peak appearing at 2323 cm⁻² for CO₂ (Figure S5). The FT-IR spectrum of the reaction without adding 1 was also detected as a reference (Figure S5). Furthermore, Figure S6 showed the ESR detections of pure [PMim][NTf₂] or pure [PrHSO₃Mim][OTf] with UV-light irradiation, no free radical signal was observed. The result reveals that ionic liquid [PMim][NTf₂] and [PrHSO3Mim][OTf] cannot generate free radicals but promote the reaction.



Scheme 1. Possible free radical mechanism for photochemical degradation of 1.

Photodegradation of other lignin-derived aryl ethers and alkali lignin. To investigate the generality of the photochemical system, we set out to delve the degradation of another β -O-4 lignin-derived aryl ether, 2-(2-methoxyphenoxy)-1-(4methoxyphenyl) ethanone (2), and the results are shown in Table 2. As could be concluded from Table 2, the IL based system was also verified to be effective for photochemical degradation of 2, with anisic acid, guaiacol and p-acetanisole as main products. As expected, the conversion of 2 in the IL system showed an obvious trend towards higher value with prolonged irradiation time, which increases to nearly 99.0% after 120 min. Meanwhile, the reaction for 120 min gives the yields of anisic acid up to 72.8±1.6%.

Table 2. Photocatalytic degradation of 2^b.

o I	2	ILs, UV, air Room tempera	ture of anisic acid	+ HO + guaiacol	+ p-acetanisole
	Time			Yield (%)	
Entry	(min)	Conv. (%)	Anisic acid	Guaiacol	P-acetanisole
1	30	11 3+2 8	35 1+1 0	21.0+1.3	56+14

1	30	44.3±2.8	35.1±1.9	21.0±1.3	5.6±1.4
2	60	76.2±1.6	56.3±1.7	36.9±1.7	21.0±1.6
3	90	91.5±2.3	72.2±3.2	25.8±1.1	21.2±1.2
4	120	98.9±0.5	72.8±1.6	24.0±2.1	20.1±1.3
5	150	99.0±0.2	68.1±1.5	22.8±2.3	18.7±2.5

^bConditions: reactant (10 mg), 500 mg of [PMim][NTf₂], [PrHSO₃Mim][OTf] 3% (weight, 0.028 mmol), H₂O 3% (weight), atmospheric air, room temperature, UV irradiation.

In the subsequent experiments we turned our attention towards the photochemical degradation of 2-phenoxy-1-phenylethanol (3), as shown in Figure S7. From the GC-MS analysis, 3 first converted to ketone (1), and then underwent similar cleavage of C-C/C-O to 1. Further, attention was paid to the photochemical degradation of α -O-4 types of lignin-derived aryl ethers, benzyl phenyl ether (4) and 4–(benzyloxy)phenol (5), as shown in Figure S8. From the results, aromatic aldehydes originating from oxidative processes were detected, indicating

the implementation prospect of the photochemical system to C-O bond cleavage in lignin $\alpha\text{-}O\text{-}4$ linkages.

Subsequently, attention was paid to the photochemical degradation of alkali lignin. 2D (HSQC) NMR was employed to analyze the change in lignin interunit linkages (Figure 5) and functional groups in the MTBE soluble oily products (Figure S9). As shown in Figure 5, the signals observed at the characteristic regions of $\delta_{\rm C}/\delta_{\rm H}$ 100-140/6-8 and 50-90/2-6 ppm correspond to the aromatic and aliphatic lignin substructures^[8, 27]. In the aliphatic regions, the signals at $\delta_{\rm C}/\delta_{\rm H}$ 72.0/4.8, 63.8/3.2 and 71.5/3.8-4.2 ppm correspond to A_{α} , B_{ν} and C_{β} respectively in the lignin sample. Nonetheless, these signals were absent in the degraded lignin, manifesting that lignin undergoes degradation during the photochemical process. Additionally, in the aromatic regions, the cross-signals observed at $\delta_{\rm C}/\delta_{\rm H}$ 111.2/74, 115.4-115.7/6.6-6.9 ppm linked to G_2 , G_5 and G_6 , and the signals at $\delta_{\!C}\!/\,\delta_{\!H}$ 104.1/6.6 ppm linked to $S_{2/6}$ in lignin. While in the degraded lignin sample, the absence of signals for G₂ again confirms that lignin is degraded. Meanwhile, in oily products, the signal for aryl methoxy groups were also observed by the cross-signal at $\delta_{\rm C}/\delta_{\rm H}$ 56.3/3.7 ppm, which were in accordance with the products containing -OCH₃ group identified by GC-MS (Figure S10). However, due to the complex structure of alkali lignin, the selectivity for products still remains a challenge using this method.



Figure 5. HSQC NMR spectra (ppm) of lignin and degraded lignin samples. The photochemical degradation of alkali lignin (100 mg) was conducted at the same conditions as those of entry 5, table 2.

Conclusions

In summary, we report an efficient self-initiated radical photochemical strategy for degradation of lignin-derived aryl ethers via ionic liquids induction under metal-free condition. The C-C/C-O bonds could be effectively cleaved through free radicals-mediated reaction with high yields of products. The IL $[PMim][NTf_2]$ could promote the cleavage of the C_B-H bond, and the BAIL [PrSO₃HMim][OTf] catalyzes the subsequent C-O-C bond fragmentation. The mechanism is based on a free radicalmediated process, involving in the alkyl, hydroxyl and peroxy free radicals. In addition, alkali lignin could also be degraded using this strategy. Our strategy rendered the photochemical cleavage of C-C/C-O bonds effective under ambient conditions while obviating the need for participation of metal. Moreover, the self-initiated radical strategy opens an avenue for the metal-free photochemical degradation of other polymer containing ether linkages.

Experimental Section

Reagents and Materials. Methyl tertiary butyl ether (>99%), pnitroaniline(>99%) are purchased from Shanghai Aladdin Reagent Co. Ltd. Acetonitrile (>99.9%), phosphoric acid (H₃PO₄, 85% aqueous solution), phenol (99%), benzoic acid (99%), sodium acetate (>99%) were obtained from XiLong Scientific Co., Ltd. Acetic acid (>99%) are provided by Beijing Chemical Works. 2-phenoxyacetophenone was provided by Shanghai SHUYA Pharmaceutical Technology Co., Ltd. 2 -(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone was purchased from Bidepharm technology Co., Ltd. 2-phenoxy-1-phenylethanol (97%) was provided by Ark Pharm, Inc. benzyl phenyl ether (97%) was purchased from Alfa Aesar Reagent Co., Ltd. 4-(benzyloxy)phenol (98%) was provided from Aladdin Reagent Co., Ltd. Benzaldehyde (99%), benzyl alcohol (99%), hydroquinone (99%), 4-methoxyacetophenone (99%), anisic acid (99%) and guaiacol (99%) were purchased from Innochem Technology Co., Ltd. The ILs 1-propenyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl) [PMim][NTf₂], imide 1-butyl-3methylimidazolium bis((trifluoromethyl)sulfonyl) imide [BMim][NTf2], 1propylronitrile-3-methylimidazolium tetrafluoroborate [CPMim][BF₄], 1-Allyl-3-methylimidazolium trifluoromethanesulfonate [AMim]OTf, 1-butyl-3-methylimidazolium hexafluorophosphate [BMim][PF₆], 1-propylsulfonic-3-methylimidazolium chloride [PrSO₃HMim]Cl, 1-propylsulfonic-3methylimidazolium dihydrogen phosphate [PrSO₃HMim][H₂PO₄], 1propylsulfonic-3-methylimidazolium trifluoromethanesulfonate [PrSO₃HMim][OTf] and 1-propylsulfonic-3-methylimidazolium tetrafluoroborate [PrSO3HMim][BF4] were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The ILs were vacuum dried at 70 °C for 24 h before used. Alkali lignin was provided by Green Value SA.

Helium (>99%) was provided by Beijing Beiwen Special Gases Factory.

Light source. A Xenotest apparatus AULTT CEL-HXUV300 was used to simulate UV and visible light. The ultraviolet reflector UVREF was used to obtain UV, the cut-off filter UVIRCUT400 was used to simulate visible light. The samples were positioned in irradiation area of the lamp and irradiated in air.

Photochemical Reaction. The typical procedure of photochemical degradation experiments is as follows. A certain amount of ionic liquids, brønsted acidic ionic liquids, water, lignin-derived aryl ethers or alkali lignin were added into a quartz reaction vial and stirred. The reactor was exposed to the required gas (Ar or air) and placed under light illumination with a stirring of 1000 rpm. The radiation energy of light generated was 100 mW/cm². The autogenous temperature was measured by thermal

couple. After a suitable time, the reactants were allowed to stop by cooling to room temperature. The products were extracted by methyl tertiary butyl ether (MTBE) from the reaction mixture. All the experiments were carried out for three times.

The recycling experiments were performed as follows. The resulting mixture after products extraction was washed by 5 mL of water for three times, which was then dried at 70 $^{\circ}$ C for 24 h. Then the recycled IL was used in the subsequent reactions.

Analytical methods

Quantification by Ultra-high performance (1) liquid chromatography (UPLC). UPLC was applied to quantify the reactants and products in the reaction. UPLC spectra of the samples were detected on Waters UPLC-QTOF equipped with a UV detector (at 225 nm) and a C18+ column (2.1×100 mm). Column temperature was maintained at 298 K and the separation was conducted by gradient elution with a flow rate of 0.2 mL/min. Acetonitrile (CH₃CN) and 0.01 mol/L sodium acetate (NaOAc) solution, pH 5.4-5.8 adjusted by acetic acid, were used as the mobile phase. The gradient program was as follows: 1-2 min (CH₃CN:NaOAc(0.01mol/L) = 5:95), 2-4min (CH₃CN:NaOAc(0.01mol/L)= 20:80), 4-6min (CH₃CN:NaOAc(0.01mol/L)=30:70), 6-15min (CH₃CN:NaOAc(0.01mol/L)=50:50), 15-19min (CH₃CN:NaOAc(0.01mol/L)=95:5).

The conversion of lignin-derived aryl ethers and yields of products were calculated as follows:

Conversion (%) = $(C_0 - C_{\text{lignin}}) \times 100 / C_0$	(1)	
Yield (%) = $C_{\text{products}} \times 100 / C_0$	(2)	

Where C_0 represents the initial concentration of lignin-derived aryl ethers; C_{lignin} represents the concentration of lignin-derived aryl ethers at sampling time; and $C_{products}$ represents the concentration of the products, respectively.

(2) Gas chromatography – mass spectrometry (GC-MS). Qualitative analysis was proceeded by gas chromatography mass spectrometry (GC-MS). The GC-MS analyses were performed on a SHIMADZU GCMS-QP2020 instrument equipped with an Rtx-5MS capillary column (30m*0.25mm), with helium as carrier gas. An injection volume of 1 μ L was used with an injection temperature of 290 °C. The initial temperature of GC oven was 35 °C, then raised to 280 °C with a rate of 10 °C/min, where it was held for 10 minutes. The total run time was 34.5 minutes.

(3) NMR measurements. The ¹H spectra were recorded on Bruker Avance III HD 600 operating at 600 MHz. ¹³C NMR spectra were recorded on the same instrument at an operating frequency of 150 MHz. the spectra were detected at room temperature. The heteronuclear single quantum coherence (HSQC) NMR spectra were recorded on the same instrument. For each test, approximately 50 mg lignin sample or 20 mg oily products were dissolved in 0.5 mL of DMSO-*d*₆ in an NMR tube, respectively. The spectra were measured under the following acquisition parameters: spectral width of 11 ppm in F2 (¹H) with 1024 data points and 190 ppm in F1 (¹³C) with 512 data points; 64 scans and 1 s interscan delay. Bruker's Topspin 3.5 pl4 software was used for volume integration of contours in HSQC spectra.

(4) Electron spin resonance (ESR). ESR was performed on a JEOL JES-FA 200 ESR spectrometer at 298 K. The typical spectrometer parameters included: microwave frequency, 9.051 GHz; microwave power, 0.998 mW; center field, 3234 G; sweep width, 10 mT; sweep time, 1 min; time constant, 100 ms; modulation frequency 100 kHz; modulation amplitude, 1000.

The sample with 50 mM DMPO was shaken for several minutes. Then a certain amount of the mixtures were taken out and the ESR spectra were recorded in dark and under UV-light irradiation respectively at room temperature.

(5) FTIR characterization. FTIR spectra of the liquid samples were detected on a Nicolet 380 spectrometer at a 4-cm⁻¹ resolution. A total of 32 scans were collected for the samples.

(6) Theoretical calculations. DFT calculations were performed using Gaussian 03 program. The B3LYP/6-311+G(d,p) method has been used for structure optimizations. Frequency calculations were performed at the same level to verify the optimized structures to be ground states without imaginary frequencies (NImag = 0).

Acknowledgements

This research was financially supported by National Basic Research Program of China (973 Program, 2015CB251401), National Natural Science Foundation of China (No. 21878292, No. 21890762 No. 21878314, No. 21606240), K. C. Wong Education Foundation (No.GJTD-2018-04) and the Strategic Priority Research Program of Chinese Academy of Science (No. XDA21060300).

Keywords: metal-free • photochemical • ionic liquids • lignin • autologous radicals

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10.1002/cssc.201901796

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FULL PAPER

UV-light on lignin: an efficient selfinitiated radical photocatalytic strategy for degradation of lignin-derived aryl ethers and lignin via ionic liquids induction is developed.

In the homogeneous system, the C-C/C-O bonds could be efficiently cleaved through free radicalsmediated reaction and afford aromatic products in high yields at metal-free conditions.



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Metal-Free Photochemical Degradation of Lignin-Derived Aryl Ethers and Lignin by Autologous Radicals via Ionic Liquids Induction