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Introduction

Efficient utilization of sustainable lignin resources, owing to its functionalized aromatic rich feature, is currently of tremendous interest due to the dwindling fossil-based feedstocks and the ever-increasing requirement of aromatics.^{1,2} Structurally, plenty of C–C and C–O bonds are present in lignin to form various interunit linkages, such as the β -O-4, β -1, β - β or 5–5 types, *via* radical coupling of phenylpropanoid units.^{3–5} Cleaving the C–C/C–O bonds is a pivotal issue with a view to transforming lignin into high value-added aromatics.^{6–10} Yet,

Metal-free and mild photo-thermal synergism in ionic liquids for lignin $C_{\alpha}-C_{\beta}$ bond cleavage to provide aldehydes[†]

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Direct cleavage of the C–C bond in lignin linkages is a promising route to afford value-added aromatics, which, however, usually involves metal-based catalysts and harsh conditions. Here, a photo-thermal strategy is reported to deconstruct the $C_{\alpha}-C_{\beta}$ bond in lignin β -O-4 and β -1 interlinkages in the ionic liquid [BMim][NTf₂]. It was found that the synergism of UV light and heating could trigger the Norrish type I reaction by inducing the cleavage of the $C_{\alpha}-C_{\beta}$ bond and afford aromatic aldehydes through a free radical route in modest yields. Meanwhile, [BMim][NTf₂] could interact with lignin moieties and stabilize the intermediates, which significantly contribute to the $C_{\alpha}-OH$ protonation and accelerate lignin interunit linkage breakage. In this unique route, the $C_{\alpha}-C_{\beta}$ bond could be cleaved at 50 °C under UV light irradiation without the presence of a metal. Further comparison with photochemical or thermochemical alone strategies demonstrates that the photo-thermal route offers a significant improvement in the $C_{\alpha}-C_{\beta}$ bond cleavage reactivity. Alkali lignin could also be degraded into aromatic monomers in [BMim][NTf₂] using the protocol. Given the necessity of biomass upgradation, this work may provide a green and unique technology to boost the inert C–C bond cleavage upon photo-thermal synergism under metal-free and mild conditions that may underpin future advances in photo-thermal transformation and renewable energy production.

the homolytic bond dissociation enthalpy of C–C bonds (69–123 kcal mol⁻¹) is theoretically higher than that of C–O bonds (52–80 kcal mol⁻¹) and additional C–C bonds are generated during some delignification processes,¹¹ which makes the disruption of the C–C bonds, especially the β -O-4 linkages due to its abundance (percentage: 45–60%),¹² draw high levels of attention for native lignin upgradation.

Commonly, the C_{α} - C_{β} bond in lignin β -O-4 linkages is more prone to cleavage after the oxidation of C_{α} -OH into the C_{α} =O group.¹³ Based on the above finding, a two-step β -O-4 fragment methodology has been widely explored involving the following two main pathways: (1) the oxidation of the C_{α} -OH group to C_{α} =O in β -O-4-alcohols and (2) the downstream degradation of β -O-4-ketones bearing active C_{β} -H and C_{α} - C_{β} bonds.^{8,14-19} To further simplify the operation, direct C_{α} - C_{β} bond fragmentation in β-O-4-alcohols in one pot has been extensively investigated and it produced encouraging results.^{20,21} Nevertheless, strong oxidants and high temperature/pressure are commonly exploited in these existing strategies, demonstrating the difficulty in directly cleaving the inert C_{α} - C_{β} bond. Hence, exploiting greener technologies for C_{α} - C_{β} bond cleavage under mild conditions is a great necessity but is still challenging. Meanwhile, the cleavage of the C_{α} - C_{β} bond in other linkages

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like $\beta\text{-1}$ type (percentage: 1–15%)^{11} should also be taken into account.

In this respect, the photochemical process emerges as a promising alternative for chemoselective cleavage of lignin aliphatic linkages.^{22,23} Particularly, upon the excitation of a photocatalyst by light irradiation, cleavage of the C-C bond in lignin could be achieved by its direct homolytic cleavage through a free radical route.¹¹ Encouraging results could be achieved, while the photochemical methods face limited photon efficiency issues. Fortunately, studies on photothermal strategies, which couple thermal and photonic stimuli to drive chemical transformations, have proven that they have higher efficiency and lower energy consumption due to the formed photo-thermal synergism.^{24,25} In this process, the thermal effect could promote effective collisions among reactant molecules and render them in excited states, and then the energy for the excited molecules to overcome the activation barrier could be easily obtained by light irradiation, indicating that the formed photo-thermal synergism in a reaction could contribute to lowering of the energy barrier and promotion of active-site generation.^{26,27} Considerable reduction in apparent activation energy and operating temperature has been reported in a photo-thermal regime due to the photo-thermal synergism.²⁸ Whereas, metal-based catalysts are commonly used in the photo-thermal route to gain photo and thermal energy for excitation, triggering the subsequent active species generation like free radicals and chemical bond transition, which may lead to the depletion of limited metal resources and environmental issues. Interestingly, lignin is a good light absorber and could absorb UV light energy to yield active species due to the chromophores in its structure, which is a relatively timeconsuming process in air.²⁹⁻³¹ In this case, the combination of thermal and photonic stimuli may offer a potential green pathway, in which the photo-thermal synergism excites lignin substrates to yield free radicals upon the absorption of photons and thermal energy by lignin rather than metal-based catalysts, and then lower the activation barrier to induce the homolytic cleavage of the inert C-C bond cleavage even at relatively low temperature with energy saving and high efficiency.

As reported in previous studies, ionic liquids (ILs) could also accelerate the inert chemical bond cleavage in lignin β -O-4-ketones by the thermal or photo alone strategy, in which the interactions between ILs and lignin linkages could lower the chemical bond energy and activate them, and thus induce the formation of active substances like free radicals and the subsequent chemical bond scission.^{29,32-34} Hence, in a more powerful photo-thermal strategy, the use of IL may further accelerate lignin interunit linkage breakage, including β-O-4alcohols and β -1 linkages, by interacting with lignin. Additionally, due to the nature of ILs, the ions in ILs could coordinate with the reaction intermediates and stabilize them,³⁵ which could contribute to reduction of the activation barrier and promotion of the chemical bond disruption. In consequence, considering all the abovementioned advantages of ILs and their other attractive features like high stability, designability and negligible vapor pressure,36 we foresaw an



Scheme 1 Photo-thermal $C_{\alpha} – C_{\beta}$ bond cleavage of lignin linkages in this work.

opportunity to accelerate lignin interunit linkage breakage by the judicious implementation of the activation of ILs, which, with the assistance of photo-thermal synergism, may realize one-pot metal-free lignin C–C bond cleavage in a green, simple but effective approach.

On the basis of the above consideration, we herein reported a metal-free photo-thermal chemical strategy for the C_{α} - C_{β} bond cleavage of lignin under mild conditions in the ionic liquid ([BMim][NTf₂]) system in one pot. Using lignin model compounds, we confirmed a significant improvement of the synergistic effect of UV light and heating on the cleavage of the C_{α} - C_{β} bond in β -O-4 and β -1 linkages by testing thermal/photo alone and photo-thermal technologies. Meanwhile, the promotion effect of [BMim][NTf₂] on the chemical bond cleavage was verified by DFT calculations, where the interactions of IL ions with lignin model compounds and the intermediates were investigated and analyzed in depth. A free radical mediated mechanism of the C_{α} - C_{β} bond cleavage upon the initiation of ILs and the Norrish type I reaction triggered by photo-thermal synergism were revisited and clarified based on the free radical scavenging experiment, tracking the product distribution with time, chemical calculations and so on. Furthermore, native lignin conversion under photochemical, thermochemical and photo-thermal conditions was also tested to verify the synergism of UV light and heating. The structural variation of native lignin during the degradation process was carefully investigated. Owing to the photo-thermal synergism and the promotion of ILs, the photo-thermal chemical strategy shows a high activity in the one-pot conversion of lignin by the cleavage of inert chemical bonds (Scheme 1). Additionally, this report will also be of considerable interest to explore photothermal chemical routes for biomass upgradation, in which the cleavage of C-C bonds is a key issue.

Results and discussion

Photo-thermal degradation of β -O-4 lignin model compounds

2-Phenoxy-1-phenylethanol (1), a common β -O-4 lignin model compound, was initially studied to explore the photo-thermal technology for the C_{α} - C_{β} bond cleavage. It was found that in the IL system, compound 1 was degraded into benzaldehyde,

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phenylacetaldehyde and phenol as the main products under photo-thermal conditions (Table 1). As benzaldehyde is the dominant product derived from the C_{α} - C_{β} bond cleavage of 1, we evaluate the efficiency of the photo-thermal reaction for the C_{α} -C₆ bond cleavage by the yield of benzaldehyde. The photothermal reaction activity is highly dependent on the composition of ILs. The absence of anion [NTf₂]⁻ resulted in low conversion of 1 (Table 1, entries 1 and 2) as well as low yield of mononuclear aromatic products. Upon changing anion of ILs with $[NTf_2]^-$, not only the conversion of compound 1 significantly increased but also the product benzaldehyde was detected. Apparently, ILs with anion $[NTf_2]^-$ favor the conversion of compound 1 under the photo-thermal conditions and lead to the cleavage of the C_{α} - C_{β} bond. The influence of cation was also investigated by varying the cation structures, while the anion was maintained with $[NTf_2]^-$ (Table 1, entries 3–7). Different cation structures could result in different reaction efficiencies, although the difference in efficiency was not as obvious as that of anions. The cation [BMim]⁺ exerted the highest efficiency among all the cations used, which allowed 95.1% conversion and 18.0%, 14.0% and 50.4% yields of benzaldehyde, phenylacetaldehyde and phenol (Table 1, entry 3). From the above results, we can deduce that the IL composed of the $[BMim]^+$ cations and $[NTf_2]^-$ anions provided a promising reaction system for the C_{α} - C_{β} bond cleavage of compound 1 in a green and mild approach.

Varying the species of the Brønsted acid also has great influence on the reaction activity. As shown in Fig. 1a, several Brønsted acids referred to as inorganic acid, organic acid and the Brønsted acid ionic liquids were used to explore their effects on the photo-thermal reaction. On the whole, low acid strength led to low reaction efficiency. For example, [PrHSO₃Mim][H₂PO₄] is with the lowest acid strength among all the Brønsted acid ionic liquids used,²⁹ exerted the lowest efficiency by affording 11.8% conversion and lower than 5% product yields. Upon increasing the acid strength of the Brønsted acid, higher conversion and product yields were obtained. When H₂SO₄ was applied as the acid catalyst, nearly complete conversion of **1** was achieved with 20.1% yield of



Fig. 1 Influence of the Brønsted acid species and H₂SO₄ amount under the following conditions: **1** 5 mg, [BMim][NTf₂] 250 mg, temperature 60 °C, UV light (100 mW cm⁻²), reaction time 20 min, air atmosphere, *c* [H⁺] (0.2 mmol mL⁻¹) (a); varying amounts of H₂SO₄ (b).

benzaldehyde, which is the highest among all the Brønsted acids used. Hence, H_2SO_4 was used for the following reactions. Increasing the H_2SO_4 amount also benefitted the generation of benzaldehyde. As shown in Fig. 1b, almost complete conversion was achieved in all cases with H_2SO_4 , while the product

Table 1	Influence of IL's structure of	on the photo-the	rmal degradation of 2
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/	1	\checkmark	IL, AIF	\checkmark	\checkmark		\checkmark

Entry	IL	Conv. (%)	Phenol (%)	Benzaldehyde (%)	Phenylacetaldehyde (%)
1	[BMim][OAc]	35.6	n.d.	n.d.	n.d.
2	[BMim][SCN]	<1	n.d.	n.d.	n.d.
3	BMim NTf2	95.1	50.4	18.0	14.0
4	[EMim][NTf ₂]	96.5	43.3	16.1	13.0
5	[BzMim][NTf ₂]	98.1	49.6	15.9	11.0
6	CPMim NTf2	98.6	22.8	7.9	7.0
7	[HOEtMim][NTf ₂]	99.8	27.4	4.6	5.5

n.d. = not detected. Reaction conditions: 1 5 mg, IL 250 mg, [PrHSO₃Mim][OTf] 8 wt%, temperature 60 °C, UV light (100 mW cm⁻²), reaction time 20 min, atmosphere.

distribution was sensitive to the Brønsted acid amount added. The results show that the generation of benzaldehyde increased with H_2SO_4 addition and afforded 20.4% yield under the conditions of 1 wt% H_2SO_4 . While the benzaldehyde yield exhibits a decreasing trend with H_2SO_4 over 1 wt%, which might be related to the occurrence of side reactions due to excess acid. In sharp comparison, the photo-thermal reaction without the Brønsted acid shows no conversion of compound 1, which means that the reaction occurs only in the presence of the Brønsted acid, implying the important effect of H^+ .

The deconstructive strategy for the C_{α} - C_{β} bonds in model 1 may be dependent on UV-light irradiation and heat. For a better understanding of the degradation process, we also considered diverse illumination with various temperatures to further explore the contributions of UV light irradiation and heat on the chemical bond cleavage of compound 1. As shown in Fig. 2a, the production of benzaldehyde increases with an increase in light intensity from 0 to 100 mW cm⁻², the yield of benzaldehyde reached 21.1% when the light intensity was 100 mW cm⁻² at 50 °C. For comparison, in the case of dark (0 mW cm^{-2}) , no benzaldehyde was detected at various temperatures ranging from 10 to 60 °C, implying that UV light irradiation is crucial for the C_{α} - C_{β} bond cleavage of 1 to afford benzaldehyde. We then increased the temperature to as high as 220 °C and when the reaction proceeded in the dark (Table S1[†]), no benzaldehyde was detected, further confirming the important effect of UV light irradiation on the C_{α} - C_{β} bond



Fig. 2 Production of benzaldehyde (a) and phenylacetaldehyde (b) under the following conditions: 1 5 mg, [BMim][NTf₂] 250 mg, H₂SO₄ 1 wt%, temperature 10–60 °C, UV light (power density: 0–100 mW cm⁻²), reaction time 20 min, air atmosphere; benzaldehyde and phenylacetaldehyde production under continuous illumination without heating and at 50 °C with without UV light irradiation (power density: 100 mW cm⁻²) (c).

cleavage. In addition, the product distribution was also observed at low temperature (10 °C) with UV light irradiation of various light intensities (50 mW cm^{-2} and 100 mW cm^{-2}), these conditions afforded no benzaldehyde, meaning that heat also has a non-negligible influence on the C_{α} - C_{β} bond cleavage of 1. Increasing the temperature contributed to the generation of benzaldehyde, this afforded the highest yield of benzaldehyde at 50 °C. However, continuously increasing the temperature above 50 °C leads to a decline in the benzaldehyde yield, which might be due to the side-reaction like product repolymerization at higher temperature.37 Given the above experiment results, we can conclude that both UV light and heat are crucial for the C_{α} - C_{β} bond cleavage of 1 to afford benzaldehyde in the photo-thermal degradation, which indicates a synergism between these two factors. As phenylacetaldehyde is the product obtained from the C_{β} -O bond cleavage of compound 1, the generation of which was also analysed at various temperatures with UV light or in the dark, as shown in Fig. 2b. Interestingly, similar yields of phenylacetaldehyde $(\sim 50\%)$ were obtained at different temperatures (10 to 60 °C) when there was no UV light irradiation. In comparison, the synergism of UV light and heat lead to a significant decline in phenylacetaldehyde generation. More details of degradation of 1undert UV light/heating alone conditions are presented in Fig. S1.† Given the fact that no phenylacetaldehyde was obtained without H₂SO₄ (Fig. 1b), it could be concluded that the H^+ is mainly responsible for the C_{β} -O bond cleavage, while the C_{α} - C_{β} bond cleavage of compound 1 is primarily dependent on the synergism of UV light and heat.

To ensure the critical role of the synergism of UV light and heat, photo-, thermo- and photo-thermo degradation were conducted and the results were compared, as shown in Fig. 2c. For the production of benzaldehyde, continuous UV light irradiation without heating afforded no benzaldehyde after 5-35 minutes of the reaction. We further tested the reaction at 50 °C without and with UV-light irradiation by conducting the degradation in the dark for a few minutes and then continuing it under UV light for 20 minutes. In the first stage of the reaction in the dark (off), benzaldehyde was not detected in all cases. When UV light illuminated the reaction system (on) in the subsequent stage, the yield of benzaldehyde showed a significant increase from 0% to around 20%. That is, it is the synergism of UV light and heat that is responsible for the C_{α} - C_{β} bond cleavage to produce benzaldehyde, and the lightenhancement process is reproducible. The generation of phenylacetaldehyde was also observed, as shown in Fig. 2c, which presented an obvious contrary trend in comparison to benzaldehyde. A large amount of phenylacetaldehyde was generated under only heating (50 °C, 0 mW cm⁻²) or receiving UV light irradiation (5 °C, 100 mW cm⁻²), respectively. Once the reaction was conducted under the combined effect of light and heat at the same time (50 °C, 100 mW cm⁻²), the output of the phenylacetaldehyde, which was generated in the first stage (dark) is significantly reduced, and a certain amount of benzaldehyde is produced. These results indicate that the conversion of phenylacetaldehyde occurs under the synergism of



Fig. 3 Reuse of [BMim][NTf₂] under the following conditions: 1 5 mg, [BMim][NTf₂] 1000 mg, H_2SO_4 1 wt%, temperature 50 °C, UV light (100 mW cm⁻²), reaction time 20 min, air atmosphere.



light and heat, which might be relevant to the generation of benzaldehyde.

The cyclability of the ionic liquid system was investigated as shown in Fig. 3. The results demonstrate that the ionic liquid maintains high activity for the degradation of compound **1** after being circulated 5 times. In addition, we performed and compared the ¹H and ¹³C NMR spectra of the original [BMim][NTf₂] and that after five cycles, which presented almost the same signals for the IL, as shown in Fig. S2.† The above results indicated the stability of [BMim][NTf₂] under UV light and heat conditions.

Another β -O-4 lignin model compound, 2-(2-methoxyphenoxy)-1-phenylethanol (2), was also employed to evaluate the efficiency of the photo-thermal method for the C_{α} - C_{β} bond cleavage in [BMim][NTf₂]. As shown in Scheme 2, under UV light and heating conditions for only 10 min (other conditions were similar to those presented in Fig. 3), 97.6% of compound 2 could be converted and afford benzaldehyde with a yield of 13.1%, which is derived from the C_{α} - C_{β} bond cleavage of compound 2. This phenomenon further demonstrates the applicability of the photo-thermal method in [BMim][NTf₂] to fragment lignin β -O-4 linkages by disrupting the C_{α} - C_{β} bond through a green and mild pathway.

Mechanism

It is very interesting to investigate the reaction pathway for the photo-thermal degradation of compound **1** to products. As aforementioned, the reaction led to the C_{α} - C_{β} bond and C_{α} -O bond cleavage. The reaction profile for the C_{α} -O bond cleavage in the lignin β -O-4 model compound involving hydrolysis in

the presence of the Brønsted acid is well known,^{38,39} including the formation of an intermediate with the enol ether structure catalyzed by H^+ , which is then hydrolyzed to fragment the C_{α} -O bond. The cleavage of the C_{α} - C_{β} bond is closely related to the synergism of light and heat as discussed above. As many photochemical reactions in previous research studies were involved in the free radical mechanism, we envisioned that the generation of benzaldehyde from compound 1 proceeds through a free radical mechanism. To verify this conjecture, we added the radical scavenger 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO) (1.4 wt%) to the reaction system and analyzed the product distribution. As shown in Table S1,[†] only phenylacetaldehyde was detected in the products after 20 min of reaction, and no benzaldehyde was generated. This phenomenon indicated that the formation of benzaldehyde is based on a free radical process.

Further, electron paramagnetic resonance (EPR) was performed to detect and identify the free radicals generated in the photo-thermal reaction. The spectra of the 1/[BMim][NTf₂]/ H₂SO₄(1 wt%) system was recorded with 200 mM DMPO at 50 °C under 20 mW cm⁻² UV light irradiation with time (by using the Xenotest apparatus equipped with an X-band EPR spectrometer) or in the dark are shown in Fig. 4. It was evident that free radicals were generated during the photo-thermal reaction of 1. Through determining the hyperfine splitting constants (A factors), two typical radicals could be labelled. The spin adduct ($A_{\rm N}$ = 1.33–1.39 mT, $A_{\beta}^{\rm H}$ = 0.97 mT) could be assigned to the generation of 'OOR.⁴⁰ Meanwhile, the appearance of the *A* factors of $A_{\rm N}$ = 1.43 mT and $A_{\rm H}^{\ \beta}$ = 2.14 mT could be reasonably assigned to the 'R.⁴¹ In contrast, no signals for free radicals were observed when the reaction system was kept in the dark, indicating that the formation of free radicals was triggered by UV light irradiation. Furthermore, the radical signal intensity varied with time, which was the strongest at the beginning of the reaction, and then gradually decreased with respect to the depletion of the reactant. For comparison, the EPR detection of [BMim][NTf₂] was conducted under the same photo-thermal conditions, while almost no signal



Fig. 4 EPR spectra of 1-ILs photo-thermal system at various times.

appeared, as shown in Fig. S3,[†] indicating that no free radical was generated from [BMim][NTf₂] under UV light irradiation.

To get more insight into the reaction mechanism, we tracked the photo-thermal reaction with time at 50 °C under UV-light irradiation with 100 mW cm⁻² light intensity, as shown in Fig. 5. In the initial stage of the reaction, phenylacetaldehyde was firstly generated while the output of benzaldehyde was low. As the reaction proceeded, the yield of phenylacetaldehyde decreased significantly, accompanied by the generation of a certain amount of benzaldehyde. Continuously increasing the reaction time over 20 minutes led to the decrease of all products, which might be relevant to the sidereaction under the photo-thermal conditions. Meanwhile, the photo-thermal degradation of 1 under N2 and O2 was also conducted to investigate the effect of the atmosphere on the reaction, as shown in Table S2.† 18.0% yield of benzaldehyde was afforded under an O₂ atmosphere, which, however, showed a significant decline under a N2 atmosphere, indicating the necessity of O2 for the generation of benzaldehyde from the C_{α} - C_{β} bond cleavage of **1**.

Given the above experimental results, we speculated that it was phenylacetaldehyde that might be converted to benzaldehyde under the synergism of UV light and heat. In order to prove this speculation, phenylacetaldehyde was used as the substrate to perform the photo-thermal reaction while the other conditions were maintained the same, as shown in Fig. S4.† In this case, benzaldehyde was observed, supporting the above-indicated conversion of phenylacetaldehyde to benzaldehyde, which might be related to the well-known Norrish Type I reaction for the oxidation of an aldehyde involving the formation of free radicals.⁴²

Meanwhile, the IL [BMim][NTf₂] could also significantly trigger the chemical bond cleavage of **1** according to the experimental result of IL's structure evaluation. Hence, we studied the interaction between [BMim][NTf₂] and **1** by DFT calculations and was anticipated to accelerate the β -O-4 bond cleavage of **1**. The interaction structures of **1** with cation [BMim]⁺, anion [NTf₂]⁻ and ionic liquid [BMim][NTf₂] were analyzed and calculated. There are possible positions in which



Fig. 5 Study of product distribution with time under the following conditions: 1 5 mg, [BMim][NTf₂] 250 mg, H₂SO₄ 1 wt%, temperature 50 °C, UV light (100 mW cm⁻²), air atmosphere.

ions locate around 1. Different initial configurations were optimized, and the conformers with the lowest energy were obtained, as shown in Fig. 6. The NPA (natural population analysis) charge distributions by NBO calculations of the 'O' atom in the -OH group of 1 structures are depicted in Table 2. For the same 'O' atom of 1, the NPA charge values and bond lengths exhibited the same increasing trends. Obviously, the charge values change from -0.732 to -0.742 for 1 with [NTf₂]⁻, to -0.769 for 1 with $[BMim]^+$ and to -0.755 for 1 with [BMim][NTf₂], indicating that the electrons are concentrated for the 'O' atom. The increased electron density around the 'O' atom is favorable for the protonation of the -OH group in the presence of H⁺. Meanwhile, the interaction between 1 and [BMim][NTf₂] also leads to changes in the bond lengths. The C_{α} -O bond length becomes longer increasing from 1.426 Å to 1.433 Å for the interaction of **1** with $[NTf_2]^-$, to 1.449 Å for that with [BMim]⁺ and to 1.445 Å for that with [BMim][NTf₂]. Noteworthily, it seems that cation [BMim]⁺ led to greater changes in charge and bond lengths by interacting with 1, while the cation could directly interact with the -OH group and cause steric hindrance, preventing the H⁺ from attacking the -OH group. Therefore, it is the anion $[NTf_2]^-$ which plays a major role in the protonation of the -OH group in 1. The combined effect of cation $[BMim]^+$ and anion $[NTf_2]^-$ makes the charge density of the 'O' atom in the -OH group greater and the C_{α} –O bond length longer.

Furthermore, the formation of the carbocation intermediate is commonly involved during dehydration, which exhibits the highest energy along the reaction pathway.⁴³ Hence, the stability of the carbocation intermediate in [BMim][NTf₂] is of great importance for the hydrolysis of β -O-4-alcohol **1**. Based on the above consideration, the interactions of IL with the carbocation intermediate that might form during hydrolysis of **1**



Fig. 6Optimized structures of $[BMim][NTf_2]$ (a), 1 (b), 1 with $[NTf_2]^-$ (c),1 with $[BMim]^+$ (d), and 1 with $[BMim][NTf_2]$ (e) by B3LYP/6-311 + G(d,p).

 Table 2
 NPA charge distributions and the changes of bond length (Å) for different structures

Structure	1	1 with [NTf ₂] ⁻	1 with $[BMim]^+$	1 with [BMim][NTf ₂]
NPA charge of O Bond length of C–O	-0.732 1.426	-0.742 1.433	-0.769 1.449	-0.755 1.445
bond (Å)				

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were also selected to conduct geometry optimizations and energy calculations. There is no stable structure for the carbocation interacting with cation [BMim]⁺, because both of them are with a positive charge. The possible positions in which anion [NTf₂]⁻ and [BMim][NTf₂] were located around the carbocation intermediate were analyzed and the conformers with the lowest energy were obtained and are shown in Fig. 7. As expected, the interaction of the carbocation intermediate with anion [NTf₂]⁻/[BMim][NTf₂] could cause significant changes in the interaction energies which is 60.2 kcal mol⁻¹ for the carbocation with $[NTf_2]^-$, and 17.3 kcal mol⁻¹ for $[BMim][NTf_2]$. Apparently, the results indicated the strong interaction of the carbocation with the ionic liquids (especially the anion $[NTf_2]^{-}$, demonstrating that the carbocation becomes more stable in the IL [BMim][NTf₂], which, as a consequence, is beneficial for the hydrolysis of **1** and the subsequent β -O-4 bond cleavage.

Hence, taking into account all the aforementioned results, we proposed a photo-thermal driven Norrish Type I reaction mechanism for the C_{α} - C_{β} bond cleavage of compound 1 in tandem with the hydrolysis accelerated by [BMim][NTf₂], as shown in Scheme 3. Upon the interaction of [BMim][NTf₂] with 1, the C_{α} hydroxyl group was initially protonated by the H⁺ from the Brønsted acid and continued to dehydrate to harvest the benzyl cation intermediate (a), which was stabilized in [BMim][NTf₂]. Then, **a** underwent deprotonation and converted to the enol ether substructure (**b**), which was hydrolyzed under the attack of H₂O to produce phenol and phenylacetaldehyde. Afterward, phenylacetaldehyde underwent the Norrish Type I reaction upon heating and under UV light irradiation, affording a benzyl radical and 'COH radical.^{42,44} Subsequently, O₂ attacked the benzyl radical to yield a peroxy



Fig. 7 Optimized structures of the carbocation intermediate (a) and its interaction with $[NTf_2]^-$ (b) and with $[BMim][NTf_2]$ (c) by B3LYP/6-311 + G(d,p), and the corresponding changes of interaction energy (E).



Scheme 3 Possible mechanism of photo-thermal degradation of 1.

radical which then transformed to benzaldehyde and carbonic oxide after hydrogen abstraction by the latter.

To verify the formation of carbonic oxide, FT-IR analysis of the reaction system with and without **1** was conducted as shown in Fig. S5.† Compared to the spectrum without **1**, a new peak at 2017 cm⁻² typically for CO appeared in the system with **1**, indicating the generation of CO during the photo-thermal reaction.

Photo-thermal degradation of β-1 lignin model compounds

To further explore the application of the photo-thermal system for the $C_{\alpha}\text{-}C_{\beta}$ bond cleavage of lignin moieties, the lignin model compound with the β -1 linkage, bibenzyl (3), was tested for the cleavage of the C_{α} - C_{β} bond under photo-thermal conditions (Table 3). Corresponding aromatics, benzaldehyde and phenol, were formed as the dominant products during the reaction through the C_{α} - C_{β} bond fragment of 3, the yields of which gradually increased with the progress of the reaction, along with an increase in the conversion. While no products were detected only under heating (50 °C, 0 mW cm⁻²) or UV light irradiation (5 °C, 100 mW cm⁻²), further signifying the effect of non-negligible photo-thermal synergism on the C_{α} - C_{β} bond cleavage. Additionally, by comparing the constituents of the substrate and the products, we noticed that additional oxygen atoms appeared in the products, confirming the participation of oxygen in the degradation of 3. Although the modest yields of products were obtained, these cases still indicate that the photo-thermal system could lead to the degradation of lignin β-1 linkages and produced aromatic aldehydes and phenols from the inert C_{α} - C_{β} bond cleavage through a green and mild pathway.

Photo-thermal degradation of alkali lignin

To get a better understanding of the photo-thermal degradation of alkali lignin in ionic liquids, GC-MS analysis was performed to evaluate the reaction at the structural level. As listed in Table 4, a broad variety of monomers and dimers could be

Table 3 Photo-thermal degradation of compound 3

$(1, 2)^{\alpha} (1, 2)^{\alpha$					
Time (min)	Conv. (%)	Benzaldehyde (%)	Phenol (%)		
20	<1	n.d.	n.d.		
20	<1	n.d.	n.d.		
10	<1	n.d.	n.d.		
20	7.6	10.0	15.8		
30	32.2	13.5	20.7		
40	38.4	9.4	22.3		
50	51.7	7.6	23.9		
	α β 3 3 Time (min) 20 20 10 20 30 40 50	$\begin{array}{c c} & & & \\ & & \\ \hline \hline & & \\ \hline & & \\ \hline & & \\ \hline & & \\ \hline \hline & & \\ \hline & & \\ \hline \hline \\ \hline & & \\ \hline \hline \\ \hline \\$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		

n.d. = not detected. ^{*a*} UV light (100 mW cm⁻²) at 5 °C. ^{*b*} In the dark at 50 °C. Reaction conditions: 3 5 mg, $[BMim][NTf_2]$ 250 mg, H_2SO_4 1 wt%, temperature 50 °C, UV light (100 mW cm⁻²), reaction time 20 min, atmosphere.

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Table 4 Percentages of liquid extracts obtained from the photo-thermal degradation of alkali lignin

^{*a*} UV light (100 mW cm⁻²) at 5 °C. ^{*b*} In the dark at 50 °C. Reaction conditions: alkali lignin 100 mg, [BMim][NTf₂] 1000 mg, H₂SO₄ 1 wt%, temperature 50 °C, UV light (100 mW cm⁻²), reaction time 40 min, atmosphere. ^{*c*} Selectivity in photo-thermal oil products.

separated and identified as the degradation products after the alkali lignin is treated under UV light irradiation and heating conditions in [BMim][NTf₂]. The observation of carbonyl functionality on the C_{α} of the products is a sign of C_{α} - C_{β} cleavage, suggesting lignin side-chain oxidation through the photothermal degradation method. The H, G and S type products, as well as other benzene-based aromatics, which are derived from the lignin corresponding internal structure were also detected in the extracted liquid oil, further demonstrating the chemical bond cleavage among alkali lignin subunits. In sharp comparison, when we conducted the degradation by just applying UV light irradiation (5 °C, 100 mW cm⁻²) or heating (50 °C, in the dark), only a small amount of aromatics were obtained. The phenomenon signified that the acquisition of most products in lignin photo-thermal degradation is dependent on the synergism of UV light and heat, which could cause the C-C or C-O bond cleavage in lignin interunit linkages and release aromatic products through a green and mild pathway.

The output of all monomers and dimers detected by GC-MS accounts for 8.22 wt% of the total oily product through Table 4, demonstrating that there are more products present in the oil which could not be identified yet. For a more detailed understanding of the oil composition, ESI analysis was conducted. As shown in Fig. S6,† not only the signals in the range of m/z = 0-400 related to the products with low molecular weights were detected, but also those in the m/z = 400-1200 range appeared as anticipated, implying that the oil products contain an abundance of compounds with higher molecular weights like trimers and tetramers.

The chemical structure comparison of original and regenerated lignin was performed by FT-IR analysis, which also veri-

Fig. 8 FT-IR spectra of alkali lignin and residue lignin. Reaction conditions were the same as those in Table 4.

fied the photo-thermal degradation process of alkali lignin as presented in Fig. 8. It could be concluded from the spectra that both original and regenerated samples bear the characteristic absorption peaks of lignin. The absorption bands at 1612, 1515, 1463 and 1426 cm⁻¹ demonstrate similar core aromatic structures³⁴ (Table S3†). While the differences between the two FT-IR spectra indicate that the chemical structure changes after photo-thermal treatment exerted on alkali lignin in the [BMim][NTf₂] system. The signal observed at 1031 cm⁻¹ is attributed to the vibration between C–H and C–O in the plane of the G unit,⁴⁵ which almost disappeared in the spectrum of the regenerated lignin, thus indicating a decrease of G unit during the photo-thermal degradation. Meanwhile, the signal at 1123 cm⁻¹ corresponds to the aromatic C–H in-plane defor-

Fig. 9 HSQC NMR spectra [ppm] of alkali lignin and residue lignin. Reaction conditions were the same as those of Table 4.

mation of syringyl type,⁴⁶ while the intensity of the signal is lower for the regenerated lignin compared to the spectrum of the original one, suggesting the removal of part of the S unit from alkali lignin under photo-thermal conditions in this work. Additionally, the peak at 1155 cm⁻¹ represents the C–O stretching in ester groups, which is not observed in the spectrum of the regenerated lignin and revealed the cleavage of the C–O bond upon photo-thermal degradation of alkali lignin.⁴⁵ The differences mentioned above revealed that alkali lignin underwent chemical structure changes upon photo-thermal treatment, which might be involved in the fragmentation of lignin interunit linkages under UV light irradiation and heating, thus yielding various types of aromatics, as those displayed in Table 4.

HSQC analysis was also conducted to obtain structural information of lignin samples in detail, according to which the efficiency of the photo-thermal method in [BMim][NTf₂] to degrade lignin was further evaluated. As shown in Fig. 9, the signals appearing in $\delta_{\rm C}/\delta_{\rm H}$ 50–95/2.5–6 ppm and $\delta_{\rm C}/\delta_{\rm H}$ 100-130/6-7.25 ppm are related to lignin aliphatic and aromatic regions, respectively.²¹ All lignin samples showed strong signals of aryl methoxy groups at $\delta_{\rm C}/\delta_{\rm H}$ 56.3/3.8 ppm. While many differences could be observed between the spectra of original and regenerated lignin, revealing the changes in the lignin structure before and after photo-thermal degradation. The HSQC spectrum of original lignin contained the cross signals which corresponded to C_{α} -H_{α} in A (δ_C/δ_H 72.3/4.9 ppm) and B (δ_C/δ_H 87.8/5.5 ppm), and C_b-H_b in A (δ_C/δ_H 86.5/ 4.2 ppm) and B (δ_C/δ_H 54.7/3.6 ppm), and C_y-H_y in A (δ_C/δ_H 60.5/3.6 ppm), B ($\delta_{\rm C}/\delta_{\rm H}$ 62.1/3.8 ppm) and C ($\delta_{\rm C}/\delta_{\rm H}$ 70.3/ 3.5 ppm). In contrast, these signals almost disappeared in the

regenerated lignin sample, implying that these linkages, including the β -O-4, β -5 and β - β bonds, diminished after degradation of lignin by the photo-thermal method in [BMim][NTf₂]. Meanwhile, the signals belonging to the H lignin unit of C_{2,6}-H_{2,6} at $\delta_{\rm C}/\delta_{\rm H}$ 128.5/7.0 ppm and C_{3,5}-H_{3,5} at $\delta_{\rm C}/\delta_{\rm H}$ 116.1/6.8 ppm, and G lignin unit of C₂–H₂ at $\delta_{\rm C}/\delta_{\rm H}$ 110.1/ 7.2 ppm and $C_{5,6}$ -H_{5,6} at δ_C/δ_H 115.1/6.7 ppm along with the S lignin unit for C_{2,6}-H_{2,6} at $\delta_{\rm C}/\delta_{\rm H}$ 105.4/6.5 ppm appeared in the spectrum of original lignin, whereas most signals mentioned above depleted and only the peak for C5,6-H5,6 in the G unit was observed in regenerated lignin, indicating the removal of H, S or G units from lignin after photo-thermal treatment. The sharp contrast in the HSQC spectra between the original and regenerated lignin samples further elucidated that the synergism between UV light and heat contributes to lignin degradation by fragmenting lignin interunit linkages.

Conclusions

In summary, we have demonstrated that the synergism of UV light and heating can trigger the degradation of lignin, especially the C_{α} - C_{β} bond cleavage in lignin β -O-4 and β -1 interlinkages in the ionic liquid [BMim][NTf₂] under metal-free and mild conditions. Compared to the photo or thermal alone route, the photo-thermal strategy has plenty of promising features, such as environmental compatibility, energy saving and easy operation. Although switching from photo/thermal route to the photo-thermal strategy is a non-traditional approach, much attention has been paid to photo-thermal reactions to pursue superior performance. As pre-

sented in this work, the degradation of lignin model compounds and alkali lignin can take place in the ionic liquid [BMim][NTf₂] by the photo-thermal synergism to aid the cleavage of inert chemical bonds like the C-C bond under mild conditions (50 °C, atmosphere) without any metal-based catalysts present, but the product yield is rather low. Further improvements such as learning how to minimize side reactions and how to suppress the recondensation of products are needed to realize more effective and greener biomass valorization. Our results do point out that photo-thermal methods have a unique synergism of light and heat for inducing inert chemical bond cleavage, providing a green technology for disrupting this kind of inert bond under mild conditions and thus demonstrating their potential to be applied as powerful technologies for upgradation of macromolecular compounds. Moreover, the unique characteristics of photo-thermal technologies will also open a new avenue for investigating ecofriendly and energy saving approaches for practical macromolecular substance conversion.

Experimental

Photo-thermal degradation of lignin model compounds and alkali lignin

A certain amount of reactants (lignin model compounds/alkali lignin, ionic liquids, the Brønsted acid) were mixed in a quartz reaction vial under stirring at 1000 rpm, which was exposed to UV light irradiation/or kept in the dark at a desired temperature in the atmosphere/N₂/O₂. After the reaction ended, the reactants were cooled to room temperature and mixed with 3×2 mL methyl tertiary butyl ether (MTBE) to extract the products.

Calculation of conversion and product yield

Conversion (%) =
$$(m_0 - m_{\text{Lignin}}) \times 100/m_0$$
 (1)

Yield
$$(\%) = m_{\text{products}} \times 100/m_0$$
 (2)

where m_0 represents the initial mass of lignin model compounds/or alkali lignin used for the degradation, m_{Lignin} represents the mass of lignin model compounds/or alkali lignin at sampling time, and m_{products} is the mass of the obtained products.

Reuse of [BMim][NTf₂] in experiments

After the products were extracted by MTBE, the remaining reaction mixture was washed 3 times with 5 mL of water and dried in a vacuum at 70 $^{\circ}$ C for 24 h for next use.

Regeneration of alkali lignin

After the extraction of products by MTBE, the remaining reaction mixture was mixed with 50 mL of ethanol/water solution (volume ratio of 1:1) and centrifuged. The above steps were repeated twice to obtain the alkali lignin residue, which was subsequently dried in a vacuum at 70 °C for 24 h for further characterization.

Conflicts of interest

There are no conflicts to declare.

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