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COMMUNICATION

Visible Light-Enabled Selective Depolymerization of Oxidized Lignin by an Organic Photocatalyst

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The development of economic, environmental-friendly and energy-saving process for selective depolymerization of lignin is an outstanding challenge. Herein, a novel and efficient visible-light-induced photocatalytic process for the selective depolymerization of lignin model compounds and organosolv lignin was first developed by using perylene diimide (PDI) as a metal-free organocatalyst. Interestingly, it can completely decompose the oxidized lignin models to phenolic and ketone fragmentation molecules with very high selectivity at room temperature under visible light illumination. Furthermore, the use of home-made photocatalytic continuous-flow reactor efficiently shortened the reaction time within an hour. Ever for organosolv lignin, nearly 86% mass ratio of lignin was degraded to low-molecular-mass monoaromatics or diaromatics products. We founded that the superior performances were realized by single-electron transfer (SET) from the photoexcited strongly reducing PDI^{•-} anion to the ketone groups of the β -O-4 linkage in the lignin.

The increasing global population and the growing environmental pressure stimulate our society to utilize the renewable resources by the efficient and sustainable technologies.^[1] A promising starting material for conversion to fuels and chemicals is lignocellulose due to nonedible and carbon-neutral properties.^[2] Until now, significant achievements have been made for the fractionation of lignocellulose to three major components of cellulose, hemicellulose, and lignin.^[3] Accordingly, these constituents are expected to be fully valorized to acquire maximum economic and environmental benefits. In this context, lignin is believed as the valuable resource since it is the sole renewable carbon source with aromatic structure.^[4] Thus, it would be very interesting to selectively depolymerize lignin to value-added aromatic compounds, which one stone with two birds strategy can realize pollutant control and resource utilization as well as energy saving.^[5] However, the utilization of lignin is extremely

challenging owing to the rigid, highly cross-linked and complicated structure. To date, different approaches including thermal pyrolysis, chemical or biological catalytic process have been investigated in recent years. But, in these cases, the requirement of harsh conditions or the use of expensive catalysts remains a critical issue, which inevitably hinders future practical application.^[6]

Inspired by the production of lignin by photosynthesis in nature, photocatalysis presents a powerful tool to address these challenges because of its natural abundance, non-pollution and mild reaction condition.^[7] In the initial exploration, photocatalytic lignin depolymerization was carried out in the ultraviolet region by using TiO₂ as the photocatalyst. The obvious drawback is that lignin itself adsorbs ultraviolet light, resulting in the unavoidable side reactions with low selectivity. Moreover, the use of ultraviolet light requires the special equipment with high energy consumption.^[3] Accordingly, visible-light-driven photocatalytic depolymerization of lignin provides an opportunity to overcome these drawbacks.^[8] Several different catalysts including Iridium or Vanadium compound and quantum dots were successfully used for C-O bond or C-C bond cleavage of lignin. However, despite their excellent catalytic performances, these metal-based photosensitizers are expensive and toxic, which bring the potential environmental risks. Furthermore, metal-free heterogenous catalyst such as conjugated porous polymer and mesoporous graphitic carbon nitride can selectively depolymerize lignin models. Nevertheless, they were often only used to degrade lignin models and none of them have been explored for the depolymerization of real lignin.^[9] It was maybe due to brown colour and large molecular size of real lignin, which reduced the light adsorption efficiency and the active species accessibility of solid photocatalysts.

Recently, organic visible light photocatalysts (OPCs) receive much attention owing to their distinct properties such as commercial availability, low toxicity and structural tunability.^[10] Until now, a variety of OPCs has been developed and used in a wide range of photocatalytic transformations including dehalogenation, carbon-carbon cross coupling, C-H functionalization and polymerization.^[11] But, to the best of our knowledge, the utilization of OPCs for the depolymerization of

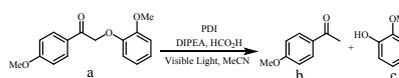
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real lignin has not yet been reported until now. Herein, we demonstrated for the first time that perylene diimide (PDI) can act as an efficient metal-free photocatalyst for the depolymerization of oxidized lignin models and real organosolv lignin at room temperature under visible light illumination. Moreover, interestingly, with the aid of home-made photocatalytic continuous-flow reactor, our PDI catalyzed system can further obtain higher catalytic efficiency with the decreased amounts of the catalyst and the additives in a very short time. Also, we found that this unique catalytic performance was attributed to efficient irradiation of the reaction mixture, decreased mass transfer limitation as well as the strong photoexcited reducing PDI^{-•} anion.

Table 1. Degradation rate of (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) by using different amounts of PDI or different organic photocatalysts.^[a]



Entry	PC (mol%)	DIPEA (equiv.)	HCO ₂ H (equiv.)	Conversion (%)	Yield of b (%)	Yield of c (%)
1	5.0	9.0	9.0	>99	99	99
2	2.5	9.0	9.0	99	99	99
3	1.25	9.0	9.0	93	83	85
4	--	9.0	9.0	trace	trace	trace
5	2.5	--	--	trace	trace	trace
6*	2.5	9.0	9.0	trace	trace	trace
7 ^[b]	2.5	9.0	9.0	84	0.03	75
8 ^[c]	2.5	9.0	9.0	20	18	10

[a] Reaction conditions: model molecule (0.50 mmol), MeCN (5.0 mL), Xenon lamp (>420 nm), 25°C, N₂, 10 h. * no light; [b] 4CzIPN photocatalyst; [c] Acr⁺-Mes photocatalyst.

The most common target in the depolymerization of lignin is the β-O-4 linkage, which constitutes 45-60% of native linkages.^[12] Accordingly, we firstly chosen (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) as the oxidized β-O-4 model molecule to explore the catalytic performance of organocatalyst PDI. As shown in Table S1, by using 5.0 mol% PDI as the photocatalyst, 6.0 equiv. DIPEA as organic base, 6.0 equiv. HCOOH as hydrogen source and 5.0 ml CH₃CN as the solvent, no depolymerization reaction occurred in the dark. Interestingly, under visible light, the concentration of model molecule gradually decreased with 57% depolymerization rate after 10 h irradiation. Furthermore, we care-fully optimized the reaction parameters. Gratifyingly, the oxidized β-O-4 lignin model can be completely degraded (Table 1, S1-2). Moreover, we used HPLC system to analyze the depolymerization products and only two products of 4'-methoxyacetophenone and guaiacol were observed (Figure S1a). Also, the control experiments showed that, in the absence of PDI, no depolymerization reaction of model molecule was happened. Noted that the undesired oxidation and fragmentation of the guaiacol was not observed, and the β-hydroxy phenyl ketones did not undergo retro-aldol or elimination reactions, which confirmed this mild reaction conditions deliver the highly selective and atom-economical process. In addition, UV-Vis spectra showed that the model molecule displayed one strong absorption peak centered at 273 nm. But, PDI catalyst has one

most intense band at 521 nm with a second shorted wavelength at 486 nm and a shoulder peak around at 455 nm, indicating that it is the only visible light absorbing species in the reaction system (Figure S1b).^[13] Therefore, we can safely conclude that both PDI photocatalyst and visible-light illumination were indispensable for this selective depolymerization process. Furthermore, we investigated the depolymerization performances use 4CzIPN or acridinium salts instead of PDI. As shown in Table 1, entry 7-8, the organic photocatalysts of 4CzIPN and acridinium salts provided 84% and 20% conversion, respectively. The inferior catalytic performances of 4CzIPN and acridinium salts were probably attributed to the low reduction potential (-1.21 eV and -0.57 eV), respectively. Also, when 4CzIPN was used as a photocatalyst, the product of ketone was further reacted with acetonitrile to α, β-unsaturated nitrile under base condition^[14]

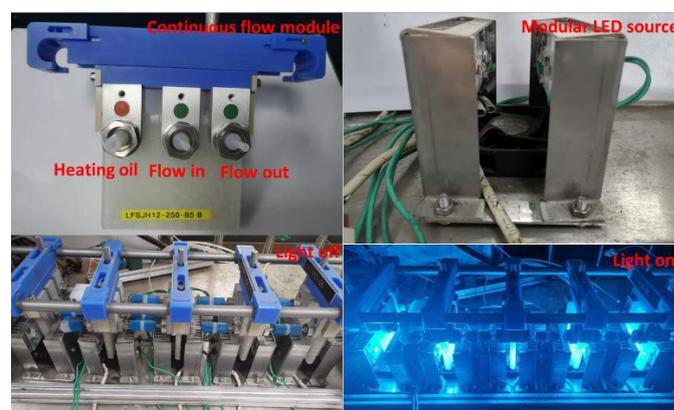
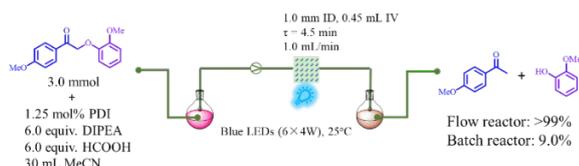


Figure 1. Photograph of the photocatalytic continuous-flow set-up.

Based on the findings outlined above, we focused the obvious drawback of the tediously long depolymerization time in our PDI catalyzed system. This was probably due to the major limitation of photocatalytic reactions in batch with inefficient irradiation of the reaction mixture, resulting in low catalytic efficiency and difficult scale-up.^[15] Then, we translated our PDI catalyzed batch reactor into a continuous micro-flow system equipped with a Corning Advanced Flow Micro-reactor, a blue light-emitting diodes light source and a high pressure peristaltic micro-pump (Figure 1). 2.5 mol% PDI, 3.0 mmol oxidized β-O-4 lignin model and the additives (9.0 equiv. DIPEA and HCOOH) were pumped and mixed in the reactor under the evolution of nitrogen gas. The change of flow rates found that too fast flow rate led to the reduced catalytic efficiency due to the short contact time between the reactant and PDI photocatalyst while too slow flow rate also gave the inferior performances owing to the possibly existed mass transfer resistance (Table S3). With the optimal flow rate, we further explored the amount of PDI and the additives of HCOOH and DIPEA (Table S4-5). Interestingly, only using 1.25 mol% PDI, 6.0 equiv. DIPEA and HCOOH can deliver very high depolymerization rate (99%) for oxidized β-O-4 lignin model in the residence time of 55 minutes (Scheme 1). As comparison, in the batch reactor, the photocatalytic depolymerization rate was very low with 9.0% under the same reaction conditions (Figure S2). The significant increase in depolymerization efficiency could be attributed to the continuous-flow reactor, the key feature of our microreactor is the small size (1.0 mm internal diameter). It can

ensure the fast mixing of the reactant, the additives and the photocatalyst, therefore increasing the homogeneity of the catalytic system.^[16]



Scheme 1. PDI photocatalytic depolymerization of oxidized β -O-4 model molecule in continuous-flow reactor.

Table 2. Different model molecule depolymerization performances of organocatalyst PDI in photocatalytic continuous-flow and batch reactor.^[a]

Sample	Continuous-flow reactor ^[b]				Batch reactor ^[c]			
	Time (min)	Conv. (%)	Yield of b (%)	Yield of c (%)	Time (h)	Conv. (%)	Yield of b (%)	Yield of c (%)
	55	99	98	97	8.0	99	92	94
	70	99	96	96	9.0	99	95	95
	55	99	99	96	8.0	99	93	90
	55	99	99	99	8.0	99	95	93

[a]Reaction conditions: [b]model molecule (3.0 mmol), 1.0 mL/min, PDI (1.25 mol%), HCOOH (6.0 equiv.), DIPEA (6.0 equiv.), MeCN (30 mL), Blue LEDs; [c]model molecule (0.50 mmol), PDI (2.50 mol%), MeCN (5.0 mL), HCOOH (9.0 equiv.), DIPEA (9.0 equiv.), Xenon lamp (>420 nm); 25°C, N₂.

Different functional groups were mainly contained in the aromatic units of native lignin, which may affect the depolymerization performances.^[17] Especially, different numbers of methoxy groups are extensively existed in the various positions of β -O-4 units.^[18] We further investigated the performances of our PDI catalyzed photocatalytic continuous-flow system in the depolymerization of oxidized model compounds with *p*-hydroxyphenyl (H)-, guaiacyl (G)- or syringyl (S)-type lignin β -O-4 units. As shown in Table 2, methoxy-substituted non-phenolic model can be almost degraded after 55 minutes under the same reaction conditions. The similar results were also found in the compounds with guaiacyl and syringyl units. Only for *p*-Hydroxyphenyl unit, the complete depolymerization was obtained for 70 minutes, which was maybe attributed to the absence of electron-withdrawing methoxy groups in the benzene ring. Noted that no matter where the methoxy groups were located, all the oxidized β -O-4 model compounds were degraded to the corresponding phenol and ketone fragmentation molecules. Furthermore, the catalytic result by using 2.50 mol% PDI in the batch reactor was

added in Table 2. It was found that even with the higher catalyst amount, the depolymerization reaction in the batch reactor needed a much longer reaction time.

These promising results provided the basis for evaluating the depolymerization of authentic lignin. We selected birch as the lignin source since it is a representative hard wood. 2D HSQC NMR spectrum showed that the major lignin sidechain units including β -O-4, β -5 and β - β linkages in the extracted lignin were well resolved in the fingerprint region (Figure 2a).^[8] Then, the extracted lignin was oxidized by the previously reported DDQ/tBuONO/O₂ procedure.^[19] 50 mg oxidized lignin was subjected to visible light photocatalytic depolymerization reaction with 10 mg PDI, 780 μ l DIPEA and 340 μ l HCOOH. After solvent evaporation, the residue was extracted with ethyl acetate. A soluble fraction, corresponding to 86 wt% of the original lignin, was obtained (Figure 2b). The soluble fraction, containing the majority of the lignin derived mass, was analyzed by GC-MS to identify the depolymerization products. As shown in Figure 2c, the original lignin was converted to low-molecular-mass aromatics including mono-aromatic and diaromatic compounds, such as 4-hydroxy-3-methoxybenzoic acid (rt: 7.28 min) and 4-hydroxy-3,5-dimethoxybenzaldehyde (rt: 7.88 min).

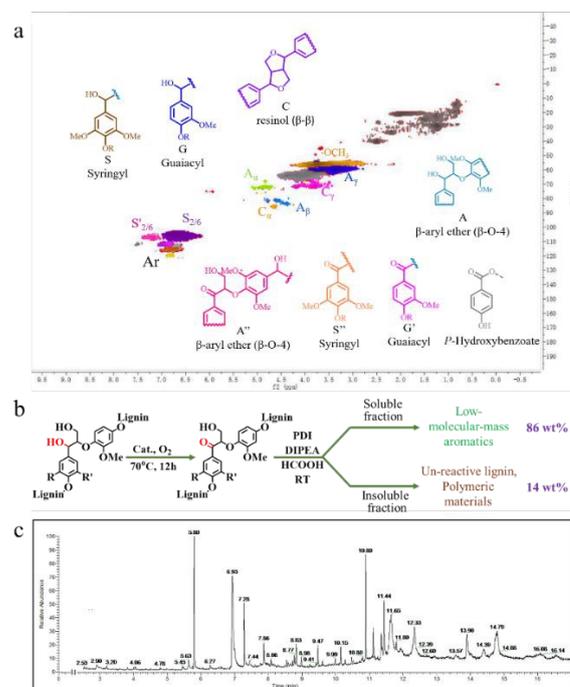
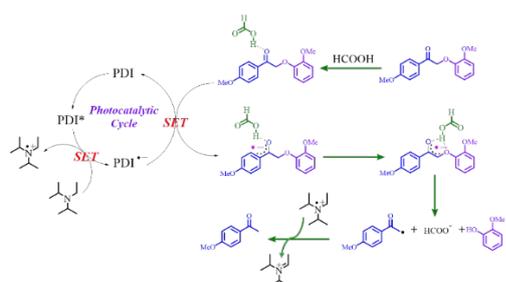


Figure 2. 2D HSQC NMR spectra (in CDCl₃) of extracted lignin (a), Scheme of PDI photocatalytic depolymerization of authentic lignin (b), GC-MS spectra of the depolymerization products (c).

To gain insight into PDI-catalyzed reaction mechanism, the trapping experiments were firstly performed by using (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) as the model. As shown in Figure S3, AgNO₃, Na₂S/Na₂SO₃ and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) acted as the scavenger of electron, hole and free radical, respectively. The photocatalytic activity decreased dramatically with the addition of AgNO₃ or TEMPO. But, after adding Na₂S/Na₂SO₃, no reduction of catalytic efficiency was observed, confirming electron and free radical played a dominant role. UV-Vis and

fluorescence spectral experiment was tested to analyze the interactions between PDI and different additives. Figure S4 showed that the peak intensity and wavelength of PDI photocatalyst didn't display the obvious changes after adding DIPEA, HCOOH and the model molecule, confirming that the absorption of visible light was mainly from PDI molecules. Moreover, in the fluorescence spectra, neither HCO₂H nor the lignin model was shown to significantly reduce the photoluminescence intensity of PDI, even with a large amount of the reactant. However, DIPEA can gradually decrease the photoluminescence intensity of PDI with the increasing addition amount, indicating that the excited state of PDI (PDI*) was quenched by DIPEA. Since it was not quenched by the lignin model, a reductive quenching mechanism was probably occurred in which the excited state PDI* is generated via visible light absorption and then is quenched by DIPEA to produce the catalytic active species PDI^{•-} anion. Next, we used the isotope experiment by using deuterium formic acid and deuterium acetonitrile instead of HCOOH additive and CH₃CN solvent to explore the proton source for the activation of the carbonyl moiety in the lignin. The NMR results revealed that the deuterium substitution reaction was only found in the depolymerization products by using deuterium formic acid, indicating that it merely serves as a proton source and the reaction solvent CH₃CN didn't supply the proton in our system (Figure S6-S7). Thus, the photocatalytic mechanism was proposed, as shown in Scheme 2. In our PDI/DIPEA/HCOOH catalytic system, PDI was a photocatalyst, DIPEA provided the electron and HCOOH was a proton source. After visible light illumination, the generated photoexcited *PDI oxidized DIPEA to create the strongly reducing PDI^{•-} anion ($E_{1/2red} = -2.14$ V). single-electron transfer (SET) from the PDI^{•-} anion to the lignin/formic acid complex produced the intermediate product and meanwhile this process regenerated the ground state PDI. The intermediate product underwent the selective C-O bond cleavage to give the desired phenol fragmentation product through protonation reaction by HCOOH and the other ketone radical product. Meanwhile, the radical product went through a hydrogen atom transfer process with the oxidized DIPEA to afford the ketone product.^[19]



Scheme 2. Plausible mechanism of PDI photocatalytic depolymerization lignin.

In summary, we have demonstrated the first use of organic molecule perylene diimide as a catalyst for visible-light-induced selective depolymerization of oxidized lignin model by breaking β -O-4 ketone bonds. Using a home-made continuous-flow reactor can further shorten reaction time and decrease the amount of catalyst and stoichiometric additives. Importantly, it also showed the excellent capability for the depolymerization of real lignin to the low mass weight monoaromatic or diaromatic

compounds. The superior catalytic performances could be attributed to efficient irradiation of the reaction mixture, decreased mass transfer limitation as well as the strong photoexcited reducing PDI^{•-} anion. This novel method implies the potential of metal-free organophotocatalyst in the effective transformation of renewable resources since it is cheap, commercial availability and low toxicity.

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Conflicts of interest

There are no conflicts to declare.

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A novel and efficient strategy to selective depolymerization of lignin model compounds and organosolv lignin via the visible-light-induced photocatalytic continuous-flow reactor was first developed by using perylene diimide (PDI) as a metal-free organocatalyst. Furthermore, it showed the excellent capability for the depolymerization of real lignin to monoaromatic or diaromatic compounds.

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