

TITLE

Renewably Sourced Amino Acid/Lignin Based Solid-State-Emitters

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SUMMARY (145 words)

The development of sustainable solid-state emitters remains challenging due to reliance on toxic metals, complex synthetic procedures, and non-renewable starting materials. This study demonstrates the development of solid-state emitters based on lignin, a renewable paper industry byproduct, and the amino acid histidine or its methyl ester through simple anti-solvent crystallization under mild conditions. Prepared materials exhibited excited-state proton transfer (ESPT)-induced fluorescence, with optimal performance achieved at 0.43-0.62 mole-% phenolic hydroxyl content. Notably, the lignin/histidine methyl ester emitter displayed room temperature afterglow phosphorescence with lifetimes up to 359 ms without requiring heavy atoms for intersystem crossing. Using pXRD and UV/Vis data, we postulate that the histidine methyl ester host matrix provides sufficient framework rigidity and H-aggregation, thereby enabling efficient intersystem crossing and triplet excited state stabilization. This work offers a sustainable strategy for tunable and renewably sourced solid-state photoluminescent materials for a variety of different applications.

INTRODUCTION

Photoluminescent materials are prevalent in a range of technology that impacts on modern human lifestyles, for instance solid-state emitters in display technology. The organic light-emitting diode market size was estimated to be approximately USD 25 billion annually in 2023 with projections of growth up to over 590 billion by 2036.^{1,2} Solid-state emitters are not only the crucial component in lighting and displays,^{3,4} but they also enable other optical-responsive functions across a diverse range of fields, from biomedical diagnostics^{5,6} to passive cooling technologies in modern architecture.⁷

Over the last few decades, significant progress has been made in designing and fabricating solid-state emitters, primarily using synthetic organic and inorganic frameworks,^{5,8} often involving various precious or toxic metals and usually fabricated in multi-step synthesis protocols.⁹ For example, Pt(II) complexes with diazine ligands can exhibit photoluminescence quantum yields in the ranges of 55–86% in solid films.¹⁰ However, their synthesis typically involves multi-step procedures using a range of hazardous reagents, such as potassium tetra chloroplatinate,¹¹ aniline,¹² and dibromomethoxypyridine¹³ during the preparation of cyclo-metalated ligands for coordination to the platinum center. Gold nanocluster-based solid fluorescent materials have also been reported, with photoluminescence quantum yields reaching 16%–40% when co-doped with silver.¹⁴ These systems often require toxic thiol ligands (e.g. benzenedithiol¹⁵ and phenylethanethiol¹⁶) to protect the co-doped gold-nanoclusters and stabilize emission. Cadmium chalcogenide quantum dots (e.g., CdS/Ag₂S core-shell structures) can achieve quantum efficiencies of around 24%,¹⁷ and lanthanides such as some Cerium(III) complex can achieve nearly 100% photoluminescence quantum yield.^{18,19} However, these materials can pose significant health risks due to the toxicity and bioaccumulation potential of heavy metals. The production processes of current solid-state emitters often still involve complex and/or energy-intensive steps. For instance, the synthesis of quantum dot-type photoluminescent materials typically requires high-temperature calcination, often reported in the range of 200–800°C.²⁰ These starting materials, reagents and synthesis strategies raise significant concerns regarding toxicity, waste generation, and more broadly, their sustainability.²¹

To produce materials in a way that reduces the burden on the environment and human health, chemists and engineers are focused on developing functional materials in more sustainable ways, i.e. moving away from the reliance on finite resources, such as fossil-based materials and

scarce metals, whilst reducing the use of harmful chemicals and large amounts of solvents.²² Guided by the principles of Green Chemistry,²³ innovative new materials and synthetic approaches can accelerate the development of the next generation of sustainable and environmentally benign solid-state emitters and ensure their production is also aligned with green chemistry principles.²⁴ One of the principles of green chemistry is to move away from finite feedstocks to renewable ones where possible. Lignin, as one part of lignocellulosic biomass, is the most abundant renewable aromatic biopolymer in the world²³ yet also an underutilized resource,²² as only 2% of lignin is currently used to create materials while the remainder is either burnt for energy or disposed of in landfills.^{25,26} Recent studies have demonstrated lignin utilization in the preparation of luminescence materials.^{25,26} However, the majority of reported photophysical properties and applications are in the solution phase, not in the solid-state where, importantly, many of the real-world applications lie.^{27,28}

Lignin contains a variety of phenolic structures, such as the guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) units and many others (**Figure 1**).²⁹ Phenolic structures enable macromolecular lignin to exhibit photoacid behavior and perform excited-state proton transfer (ESPT), a photophysical process that is commonly observed in phenolic compounds.³⁰⁻³² Upon photoexcitation, the electronic distribution in the excited state compound is altered, causing a significant drop in the acid dissociation constant in the excited state (pK_a^*) versus the acid dissociation constant in the ground state (pK_a), thus facilitating deprotonation at the phenolic hydroxyl sites.³³ For example, the pK_a of pure phenol in the ground state is *ca.* ~10 yet upon excitation at 250 nm (UV region), a pK_a^* of ~3 is observed, meaning the excited state is ~7 orders of magnitude more acidic.³¹ This dramatic drop in pK_a drives the equilibrium shift from excited phenol (Ph-OH^*) to excited phenolate (Ph-O^-)*, thereby releasing a proton (H^+). In

photoluminescent materials, these released protons are usually captured by a nearby proton acceptor such as a base. When the excited, deprotonated Ph-O^{-*} relaxes back to its ground state, its emission wavelength is usually a longer wavelength and of lower energy than the initially absorbed wavelength, causing the so-called red shift in fluorescence spectra.^{32,34} Due to the presence of phenolic groups and the various conjugated systems within lignin, it has the potential to act as a solid state photoluminescent material with various photophysical properties still to be explored.

In addition to ESPT-induced fluorescence, phosphorescence is another possible photophysical feature of photoluminescent materials. Phosphorescence occurs when some excited electrons undergo intersystem crossing (ISC) from a singlet excited state to a triplet excited state, a process often facilitated by heavy atoms or metals.³⁵ Due to the spin-forbidden nature of this transition, the electrons in the triplet excited state take longer to relax back to the ground state. This delayed return to the ground state results in the emission of light over an extended period (so called “afterglow”) even after the excitation source is removed, which is characteristic of phosphorescence.^{35,36}

Additionally, developing solid-state emitters with afterglow room-temperature phosphorescence (RTP) characteristics is particularly challenging: Often, at room temperature, the thermal energy present is sufficient to promote molecular motions such as vibrational relaxation and internal conversion that destabilize a potential triplet excited state and thereby shorten the lifetime of triplet excitons.¹⁹ To achieve persistent phosphorescence at room temperature, strategies to stabilize the triplet excited state include designing rigid molecular frameworks or incorporating protective matrices that suppress molecular motions and enhance the longevity of the triplet excited state.^{37,38} To date, few studies have reported lignin-derived solid-state emitters

that demonstrate RTP features and these usually employ synthetic polymer matrices, including acrylate- and lactide based networks,³⁹⁻⁴¹ and often require crosslinking agents (e.g., hexamethylene diisocyanate, urethane dimethacrylate)^{42,43}, radical formation accelerators (e.g., tetramethylethylenediamine, TMEDA),⁴⁰ and hazardous catalysts or solvents (e.g. dibutyltin dilaurate);⁴² all of which can pose environmental and health concerns (see **Table S4** for details). Here, imidazole-derived compounds such as 4-methylimidazole were used, as these are common bases in ESPT-induced photoluminescence studies due to their pK_a values being close to neutral pH, which prevents ESPT-responsive groups from deprotonation in their ground state.⁴⁴⁻⁴⁷

Herein, we report a technically simple protocol for synthesizing solid-state emitter materials from commercially available alkali lignin (AL) and the non-problematic amino acid histidine (His) or its methyl ester (His-ME), which share structural features with 4-methylimidazole (4-MI; **Figure 1**). Due to its common use in ESPT materials, 4-MI was also explored as host material,⁴⁸ however, we explicitly note that there remain concerns regarding its toxicity.⁴⁹ Here, the solid imidazole-based matrices perform several essential functions: 1) They act as proton acceptors during the ESPT process and enhance emission; 2) they serve as host structures for lignin, preventing excessive π - π interactions between lignin molecules that would lead to fluorescence quenching;^{50,51} and 3) they provide a framework that confines lignin, which is a crucial aspect for room temperature phosphorescence (RTP).

In this study, we synthesized three distinct mixture series of imidazole-derived compounds (4-MI, His, His-ME) with the ethyl-acetate refined fraction lignin (RL) of commercial AL at varying amounts to explore the effects of lignin-to-imidazole ratios on photoluminescence performance. Synthesized materials (called matrix material/RL-number) were characterized using steady-state fluorescence spectroscopy and time-resolved photoluminescence lifetime decay

kinetics to illustrate the photophysical features. The role of phenolic moieties in lignin was demonstrated by silylation. Notably, the His-ME/lignin emitter materials exhibited significant afterglow RTP characteristics. This work not only leverages green chemistry by utilizing renewable feedstocks such as lignin and amino acid derivatives but also advances the understanding of fundamental photo-physics, particularly in the realm of environmentally benign solid-state photoluminescent materials.

RESULTS & DISCUSSION

In the following, refined lignin (RL) as described above, and the general term ‘lignin’ will be used interchangeably.

1. Design and synthesis of imidazole-derived compounds/lignin solid-state emitters

1.1 4-methylimidazole/lignin (4-MI/RL)

One of the key challenges in 4-MI/RL solid-state emitter synthesis was determining the optimal balance of reactant ratio. While increasing the lignin content could potentially enhance the fluorescence intensity by promoting interactions between lignin hydroxyl groups and imidazole groups, excessive lignin may result in quenching effects due to extensive intra-lignin interactions.

To balance these factors, we initially synthesized the emitter with the mass ratio of 4-MI-to-RL at 0.62:100 (**Table 1, Entry 1**). This ratio falls within the typical lower ranges of guest-host solid emitters design suggested in literature,⁵²⁻⁵⁴ and ensures an effective “dilution” of RL within the matrix to exhibit fluorescent properties. Akali lignin was fractionated to RL using an established extraction technique with ethyl acetate to yield the fraction with the highest phenolic content.⁵⁵⁻⁵⁷ ³¹P NMR using established methods revealed that RL consists of approx. 57% (m/m)

phenolic motifs (**Figure S2, Table S2**).⁵⁸ To explore the effects of increasing lignin content in the materials, a series of 4-MI/RL emitters with gradually increasing 4-MI-to-RL ratios ranging from 100:0.62 to 100:6.1 were synthesized (**Table 1, Entry 1-6**).

1.2 Histidine/lignin (His/RL) & histidine methyl ester/lignin (His-ME/RL)

One challenge in synthesizing the His/RL and His-ME/RL emitters was finding a common solvent that could dissolve both starting materials. To overcome this challenge, we applied an alternative synthesis protocol based on those employed in previous studies, utilizing the hydrophobic domains in histidine-derivatives to entrap hydrophobic molecules and form solid crystals during the antisolvent crystallization process.^{59,60} We also ensured that the molar ratios of the 3 tested imidazole-derivatives were similar across the tested materials. To ensure repeatability, RL generated from a new container of commercial AL (RLrep) from the same supplier was used for repeat experiments of the “-2” samples of all matrix materials: Results indicate similar RL integration into the matrix, as well as similar photophysical properties (see **Table S5** for statistical analysis, and **Figures S1-2, S5-6, Tables S2**).

The experimental results showed that with increasing RL starting material, relatively less RL material was integrated into the final material matrix, levelling off at ratios of approximately 100:1.2 (His/RL) and 100:1.3 (His-ME/RL), respectively (**Table 1, Entries 12, 19**). These results are consistent with findings from a previous study entrapping histidine in hydrophobic molecules.⁵⁹ The limited entrapment is likely due to the bulky structure of lignin, which reduces its ability to fit inside the relatively confined spaces of the hydrophobic domains in histidine-based matrices. Interestingly, the level-off value reported above varies between His and His-ME, with slightly higher amounts of RL integrated into His-ME over His. This difference could be a result

of the relatively lower polarity of His-ME over His, which might render it more compatible with lignin. The reduced polarity of His-ME may facilitate a better interaction with lignin, allowing more efficient integration into the matrix despite its bulkiness.

2. Photo-physical properties

2.1 Fluorescent properties of prepared materials

All prepared materials demonstrated significant fluorescent properties upon photoexcitation (**Table 1, Figure 2a**). All three material series exhibited a maximum for fluorescence intensity for the samples labeled “-2”, with mole-% of Ph-OH in the ESPT system of 0.43-0.62 (**Table 1, Entries 2, 9, 16**), which seems to be the optimal range for fluorescent behavior. Specifically, 4-MI/RL-2 exhibited the highest fluorescence intensity of 9.90×10^6 at 459 nm; His-ME/RL-2 exhibited a maximum fluorescence intensity of 8.90×10^6 at 447 nm (83.8% signal strength vs. 4-MI/RL-2); and His/RL-2 exhibited a maximum fluorescence intensity of 7.49×10^6 at 447 nm (67.1% signal strength vs. 4-MI/RL-2) and an additional shoulder at 522nm (**Figure 2a**). The red-shifted fluorescence demonstrated by these three materials aligns with typical ESPT emission characteristics of phenolic photoacid compounds.^{33,34} The host matrix ensures adequate spacing for the excited lignin molecules, preventing lignin aggregation-induced quenching.^{50,51} Additionally, the host matrix can act as proton acceptor in the process to enhance ESPT dynamics, resulting in the observed fluorescence.^{52,61} Control experiments of the pure starting materials showed only weak intrinsic fluorescence at least one order of magnitude lower than the prepared materials: RL with a peak maximum at 422 nm, 4-MI with a peak maximum at 439 nm, and negligible emission signals for pure His and His-ME (**Figure 2a, inset**), confirming that synergistic

interactions between lignin and the imidazole-based solid matrices are the cause for the observed fluorescence.

2.2 Comparison of photophysical performance with reported lignin-based RTP emitters

To provide a benchmark of the photophysical performance of the developed materials, their performance including their fluorescence quantum yields (Φ_{Fluo}), phosphorescence quantum efficiencies (Φ_{Phos}) and room temperature phosphorescence (RTP) lifetimes were compared to previously reported lignin-based solid-state emitter systems: The best-performing emitter for each matrix material (His-ME, His, 4-MI) are summarized in Table 2 and contrasted with other existing studies utilizing lignin to prepare fluorescent or phosphorescent materials (see **Table S3** for Φ_{Fluo} , Φ_{Phos} , and RTP lifetime data for all materials presented in this study). Materials reported in this study (**Table 2, Entries 7-10**) exhibited superior Φ_{Fluo} and Φ_{Phos} results compared to those studies that did also report such values (**Table 2, Entries 1-2**). While reported RTP lifetimes are in the same order of magnitude, only one study reported higher RTP lifetimes than materials developed in this study (**Table 2, Entry 4**), highlighting the promising photophysical efficiency of the presented materials. Notably, all but one study reported in Table 2 utilized polymeric materials as host materials. These typically require a more complex synthetic approach than the “simple” anti-solvent crystallization employed in this study (see **Table S4** for synthetic details, and Section 4 *Sustainability considerations* below).

2.3 Influence of free phenolic hydroxyl groups

To further test the hypothesis that phenolic hydroxyl units within lignin play the important role of photoacid in the observed ESPT dynamic behavior with imidazole derivatives, we blocked

46-51% of the free -OH groups within lignin by silylation (“Si-RL” samples) while keeping the mass ratio of the imidazole derivative to RL or Si-RL similar (Compare **Table 1, Entries 2&7, 9&14, 16&21**). The resulting fluorescence intensities were decreased by 58% to 4.14×10^6 for 4-MI/Si-RL-2 (vs. 4-MI/RL-2), 55% to 3.35×10^6 for His/Si-RL-2 (vs. His/RL-2), and 70% to 2.65×10^6 for His-ME/Si-RL-2 (vs. His-ME/RL-2; see **Table 1** and **Figure 2b**). As the silylation of the free phenolic-OH groups is a simple and direct method to reduce the ESPT process and thereby reduce the observed fluorescence,³² these results support the hypothesis that ESPT-induced fluorescence is dependent on the number of free phenolic-OH groups within lignin that are available for deprotonation followed by proton transfer to the matrix.

2.4 Influence of imidazole derivatives-to-lignin ratios

The influence of the relative amount of free Ph-OH groups within the ESPT materials, expressed in mole-%, to the observed fluorescence intensities is visualized in **Figure 3**: As outlined in *Section 2.2*, while there is an initial increase in fluorescence intensity all samples exhibit a maximum for sample “-2”, and decreasing fluorescence intensity beyond. In the area of observed decreasing intensity, increased fluorescence quenching likely occurred due to inner filter effects, where excess lignin can absorb excitation photons, and re-absorption of fluorescence by other lignin molecules can also occur.^{62,63} These processes reduce the observed fluorescence intensities. These results demonstrate that quenching effects dominate and outweigh the benefits of additional phenolic hydroxyl groups beyond a certain lignin content, but this effect is dependent on the host matrix material and is less pronounced for 4-MI compared to His or His-ME.

One possible factor for the observed differences between 4-MI, His, and His-ME as host matrix material (**Figure 3**) could be a higher degree of lignin aggregation found in His/RL and

His-ME/RL emitters. Such lignin aggregation could reduce the effective interfacial area available for the ESPT process between lignin and the imidazole-derivative matrices. Additionally, lignin aggregation could promote non-radiative energy dissipation mechanisms such as increased vibrational/rotational coupling or non-radiative internal energy transfer, further contributing to fluorescence quenching.⁶⁴⁻⁶⁶

We propose two hypotheses for lignin aggregate formation: (A) The solvent systems for His and His-ME, i.e., water and methanol-water respectively, are known to act as anti-solvents for lignin,^{67,68} potentially leading to lignin aggregation during the preparation of His or His-ME/RL emitters. (B) Higher lignin loads in the emitter (**Table 1 & Figure 3**) could increase the chance for lignin aggregation within the final materials due to preferential inter-lignin interactions over interactions with the host matrix material, which is likely more relevant at higher RL content (resulting in higher mol-% Ph-OH in the ESPT system). To test these hypotheses, confocal laser scanning microscopy (CLSM) and time-resolved fluorescence lifetime decay measurements were carried out.

2.4.1 Confocal Laser Scanning Microscopy (CLSM)

CLSM provided microscopic evidence of lignin aggregation through the appearance of dark spots, which indicate a reduction of fluorescence intensity. To highlight the effects of lignin content on aggregation, the emitters with the highest and lowest lignin content (“-10” and “-1” samples, respectively) were investigated by CLSM: For samples with the highest lignin load (“-10” samples), more frequent and larger dark (non-fluorescent) areas exist compared to their counterparts with lowest lignin content (**Figure 4**, left hand side vs. right hand side, respectively), suggesting lignin aggregation. A comparison of CLSM images of the emitters with lowest lignin

content (“-1 samples), no significant dark spots were observed in the 4-MI/RL-1 emitter (**Figure 4a**); in contrast, macroscopic dark spots (ranging from 0.5 μm to 20 μm) were observed in the His/RL-1 and His-ME/RL-1 emitters (**Figure 4b**), suggesting higher lignin aggregation in these two latter samples.

Combining these results, we postulated two hypotheses: It seems more likely for His/RL and His-ME/RL samples that hypothesis A (antisolvent effects) is relevant at low lignin load because an increase in lignin content in the “-2” samples did not result in increased aggregation as evidenced by higher fluorescence intensity. Hypothesis B (excess lignin) is more relevant at high lignin load samples as evidenced by the inverse correlation with fluorescence intensity in this part of the curve (**Figure 4**). While these results generally also hold true for 4-MI/RL materials, the less steep slope of 4-MI/RL samples with higher mol-% Ph-OH suggests that less lignin aggregation occurred in these samples, possibly due to the different solvent system used in the co-crystallization process: Ethyl acetate was used for both 4-MI and RL, thereby no anti-solvent effects were present in this system. Of note, ethyl acetate could not be used for the His and His-ME samples as neither were sufficiently soluble in ethyl acetate, thereby requiring the use of a multi-solvent system.

2.4.2 Fluorescence lifetime decay measurements

Time-resolved fluorescence lifetime decay measurements were carried out to provide further insights into the dynamic processes occurring after photoexcitation. Fluorescence lifetimes were measured at the wavelength of the fluorescence peak maxima for each emitter, which are attributed to the relaxation of the excited, deprotonated phenolic species (Ph-O^*), and indicate how long Ph-O^* stays in the excited state before returning to the ground state. Longer

fluorescence lifetimes indicate a more efficient stabilization of the Ph-O* in excited state and fewer non-radiative decay pathways.⁶⁹ The amplitude reflects the contribution of each excited component to the total decay time, with higher percentages of a component indicating a more significant role in the overall observed fluorescence lifetime.^{69,70}

Results from the fluorescence lifetime decay (τ_F) showed maximum fluorescence lifetimes for all “-1” samples, specifically 4-MI/RL-1 ($\tau_{F1} = 4.81$ ns, $A_{F1} = 100\%$; **Fig. 5ai & aii**), His-ME/RL-1 ($\tau_{F1} = 4.56$ ns, $A_{F1} = 94.2\%$, $\tau_{F2} = 0.96$ ns, $A_{F2} = 5.8\%$, ; **Fig. 5bi & bii**), and His/RL-1 ($\tau_{F1} = 4.02$ ns, $A_{F1} = 86.2\%$, $\tau_{F2} = 0.93$ ns, $A_{F2} = 13.8\%$; **Fig. 5ci & cii**).

For all of the series, a general trend toward reduced lifetimes (τ_{F1}) and related components thereof (A_{F1}) with increasing lignin yield (and resulting higher lignin aggregation, see Section 2.3.1) was observed (**Figure 5**, left and right side, respectively). The component with longer emission lifetime (A_{F1}) is attributed to Ph-O* embedded in a matrix with lower lignin aggregation leading to less non-radiative interactions (leading to slower decay), while the component with shorter emission lifetime (A_{F2}) is attributed to Ph-O* embedded in a matrix with a higher lignin aggregation leading to more non-radiative interactions. Notably, His-ME/RL-10 and His/RL-10 exhibited a significantly smaller proportion of components A_{F1}/A_{F2} with shorter lifetimes (both τ_{F1} and τ_{F2}) compared to 4-MI/RL-10 (see **Figure 5** and **Figure S3**). Overall, the 4-MI/RL emitter series showed a relatively higher amplitude ratio of the long-lived component (A_{F1}), as well as longer fluorescence lifetimes (both τ_{F1} and τ_{F2}), compared to the His-ME/RL and His/RL emitters. These results suggest that in the 4-MI/RL emitters, a lower degree of non-radiative decay occurs with an increasing lignin load, which also correlates to the finding of lower lignin aggregation as observed by CLSM.

Taken together, the results of the time-resolved fluorescence lifetime decay measurements and in combination with results from CLSM indicate that lignin aggregation is a significant factor contributing to the reduction in the fluorescence intensities besides the previously mentioned inner filter and re-absorption effects with increasing lignin content. Moreover, lignin aggregation is more severe in the His/RL and His-ME/RL emitter series with increasing lignin content leading to greater non-radiative decay compared to the 4-MI/RL emitters series, resulting in the steeper decline in fluorescence intensity with increasing RL content. (**Figure 4**).

2.5 Influence of imidazole-derived matrices on fluorescence peak maxima

In addition to differences in fluorescence intensities, the variation in the fluorescence peak maximum wavelengths among the emitters is of significant interest. The peak wavelength largely depends on the extent of free Ph-O^{-*} formation and stabilization within the ESPT systems.⁷¹ In the studied systems, the formation and stabilization of Ph-O^{-*} in the emitters can be attributed to three key factors: (A) the basicity of the solid matrices, (B) the stability of Ph-O^{-*} in the excited state, and (C) the microenvironments provided to Ph-O^{-*} by the solid matrices.³²

(A) 4-MI is more basic ($pK_a \approx 7.51$) than His-ME and His ($pK_a \approx 6$ for both). The higher basicity of 4-MI promotes the equilibrium shift toward the formation of Ph-O^{-*} from the excited phenolic species (Ph-OH*) during the ESPT process.^{30,33,69} (B) The Ph-O^{-*} of 4-MI/RL emitters exhibit greater stability in the excited state, with less non-radiative decay, likely due to a lower degree of lignin aggregation, as outlined above. The combination of higher basicity and greater stability of Ph-O^{-*} in the excited state leads to a higher number of free and stabilized Ph-O^{-*} species generated via the EPST process in the 4-MI/RL emitters as compared to His/RL and His-ME/RL emitters, resulting in the most red-shifted (longer) fluorescence peak maximum

wavelengths among the three series. Generally, the red-shifted fluorescence peak maximum wavelengths in ESPT-type fluorophores indicate a higher population of more stable free Ph-O* species in the excited state.⁷¹

Although His/RL and His-ME/RL share similar basicity and indistinguishable levels of lignin aggregation observed via CLSM, His-ME/RL emitters displayed by a more red-shifted fluorescence peak maximum wavelength than His/RL emitters. This difference is (C) likely due to the distinctly different microenvironments offered by the respective solid matrices due to the distinct differences in their structures: A carboxylate group ($-\text{COO}^-$) in histidine vs. an ester group ($-\text{COOCH}_3$) in histidine methyl ester. In the His/RL emitter system, the $-\text{COO}^-$ group can form more robust hydrogen bonding networks with Ph-OH present in lignin, as compared to the $-\text{COOCH}_3$ group in His-ME/RL.^{72,73} These stronger hydrogen bonding networks in His/RL hinder the dissociation of Ph-OH* to form the important Ph-O* during the ESPT process,⁷⁴⁻⁷⁶ resulting in the observed most blue-shifted (shortest) fluorescence peak maximum wavelength for His/RL.

3. Phosphorescence properties of the His-ME/RL emitters

3.1 Observed phosphorescence of His-ME/RL

While analyzing the His-ME/RL emitters for fluorescence, their phosphorescent properties became apparent, i.e., a prolonged decay lifetime ($\tau_P > 1$ second) resulting in an afterglow room temperature (RT) phosphorescence (see image in **Figure 6a**). To further elucidate the emission characteristics, normalized fluorescence and phosphorescence spectra of His-ME/RL-1 were collected, indicating a distinct phosphorescence emission peak at 504 nm (**Figure 6b**). When probing the observed shoulder at 522 nm (also see Figure 2) in the His-ME/RL-1 system, a prolonged decay lifetime of $\tau_{P1} = 359.38$ ms with an amplitude $A_{P1} = 69.7\%$ was observed, clearly

indicating afterglow RT phosphorescence. Similar afterglow RT phosphorescence in the millisecond range was found for the whole series of His-ME/RL materials, albeit with decreasing lifetimes τ_1 with increasing lignin load (**Figure 6c-e**). Reported phosphorescence lifetimes of His-ME/RL emitters ranging from 194-359 ms were found to be similar and in some cases higher than for most reported lignin-based solid-state emitters, which ranged from 24-431 ms (see **Tables 2 & S3-4**) These findings raise the question why this phenomenon was uniquely observed in the His-ME/RL emitter systems but not the 4-MI/RL or His/RL systems. The answer may lie in three key factors, discussed in detail in the following sections: (3.2) differences in framework rigidity due to molecular packing and crystallinity of the matrix; (3.3) differences in hydrogen-bonding networks arising from molecular structure; and (3.4) the modulation of the singlet–triplet energy gap via keto–enol tautomerization triggered by ESPT based on results of density functional theory (DFT) calculations.

3.2 Differences in framework rigidity

A rigid framework is crucial for exhibiting phosphorescence in solid-state emitters, as it restricts molecular motion and thereby minimizes non-radiative decay pathways and extends the lifetime of the triplet excited states following ISC.^{38,77,78} The changes of the framework rigidity after lignin addition (during the synthesis) were evaluated by comparing powder X-ray diffraction (pXRD) patterns of the solid emitters to those of their respective, pure matrices.⁷⁹ In pXRD, higher reflection peak intensity and sharper reflection peaks indicate a more ordered and rigid crystalline structure.

The pXRD results show declining reflection peak intensities, reflection peak broadening, and a greater reflection peak shift to lower 2θ angles with increasing lignin load for 4-MI/RL

(**Figure 7a**), suggesting an increasing loss of crystallinity with increasing lignin load. In contrast, both His-ME/RL and His/RL (**Figure 7b and c**, respectively) exhibited only a small decrease in the reflection peak intensities, less diffuse reflection peaks, and no significant reflection peak shift toward lower 2θ angles with increasing lignin load, suggesting that these materials retained their rigid crystalline structure upon lignin addition. The contrasting changes in pXRD patterns with increasing lignin load between 4-MI/RL, and His/RL or His-ME/RL emitters can be attributed to differences in intermolecular interactions that affect crystal rigidity. In 4-MI/RL, fewer hydrogen bonds (**Figure 8a**, purple dashed lines) result in less structural rigidity. In contrast, His/RL and His-ME/RL (**Figure 8b and c**, respectively) exhibit a more extensive network of hydrogen bonds due to the carboxylate and ester moieties, which are not present in 4-MI. These extensive hydrogen-bonding networks create a more rigid framework that can enhance triplet excited state lifetimes by restricting molecular motion and reducing non-radiative decay pathways, thereby facilitating phosphorescence.⁸⁰

Interestingly, although both His-ME/RL and His/RL emitters possess rigid molecular frameworks, RTP was observed only in the His-ME/RL emitter series. This distinction can be plausibly attributed to differences in their hydrogen-bonding networks, which critically influence phosphorescence behavior.

3.3 Differences in hydrogen bonding network between His/RL and His-ME/RL

Recent studies have highlighted the “double-edged sword” nature of hydrogen bonding in aromatic systems and the effects on phosphorescence properties: On one hand, intermolecular hydrogen bonds restrict molecular motion and suppress nonradiative decay, thereby promoting phosphorescence; on the other hand, overly strong or directional hydrogen bonds may increase

molecular vibrations and reorganization energy, leading to enhanced nonradiative energy dissipation and phosphorescence quenching.⁸¹ Thus, precise tuning of hydrogen bond strength and orientation is essential for achieving efficient RTP.

The contrasting RTP outcomes between His/RL and His-ME/RL align with the outlined hydrogen-bond “double-edged sword” concept. In His, the COO^- group readily forms strong electrostatic interactions with neighboring NH_3^+ groups on adjacent His molecules, resulting in a highly directional and rigid hydrogen-bonding network.⁸² This structural rigidity may constrain molecular conformations in a way that disfavors close face-to-face π - π interactions among aromatic moieties—interactions known to stabilize triplet excitons.⁸³ Furthermore, previous studies have suggested that when host materials form excessively strong intermolecular hydrogen bonds, they may exclude interactions with guest emitters, thus failing to sufficiently restrict the molecular motions of the guest and diminishing RTP efficiency.⁸⁴

In contrast, in the His-ME molecule, the COO^- group is esterified (COOR), where the carbonyl oxygen (C=O) serves as the primary hydrogen bond acceptor. The adjacent alkoxy oxygen (O-R) is only a weak acceptor due to resonance delocalization. As a result, the hydrogen-bonding network in the His-ME/RL matrix is less rigid and less directionally constrained compared to that in His/RL, yet still provides sufficient structural support to restrict molecular motion and reduce nonradiative decay, while maintaining the flexibility needed for favorable π - π stacking. This balance appears to be beneficial for promoting RTP.

To further probe the structural distinctions between the two systems, UV-vis absorption spectroscopy was employed. In His-ME/RL samples, an additional absorption band emerged at ~ 272 nm, which is blue-shifted relative to the characteristic lignin band at ~ 284 nm (**Figure S4a**). This feature intensified with increasing concentrations of integrated AL, suggesting enhanced

aggregation in the His-ME/RL system. By contrast, no such blue-shifted features were observed in the spectra of His/RL or 4-MI/RL samples (**Figures S4b** and **S4c**, respectively), regardless of lignin content.

3.4 Density function theory (DFT) computation study on the RTP mechanism

To gain deeper insights into the photo-physical process of the observed RTP of the His-ME/RL system, DFT calculations were conducted to explore the electronic interactions between the aromatic units of lignin and the imidazole group of His-ME. Here, a representative G-type monomer of lignin was selected as a model compound for lignin to model the local interactions within the His-ME/RL matrix.

The proposed photophysical pathway, incorporating both excited-state proton transfer (ESPT) and intersystem crossing (ISC), is depicted in the energy diagram for the model interaction between His-ME and G-lignin in Figure 9a. In the ground state, the system exists in the enol form ($S_0(\text{Ph-OH})$). Upon photoexcitation ($h\nu$), the singlet excited state of $S_1(\text{Ph-OH}^*)$ undergoes proton transfer, yielding a lower-energy tautomeric form $S_1(\text{Ph-O}^*)$. The calculations indicate a strong tendency for proton transfer from the excited Ph-OH group of lignin to the imidazole moiety of His-ME, consistent with previous studies on the photoacidity of vanillin derivatives with a reported excited-state pK_a drop of approximately 3.4.⁸⁵ This ESPT process leads to the formation of a charge-separated ion pair that facilitates subsequent photophysical transitions. The energy gap between $S_1(\text{Ph-O}^*) \rightarrow T_1(\text{Ph-O}^*)$ states of this ion pair was calculated as -0.6 kJ/mol. In contrast, for the G-type lignin monomer alone (no His-ME; **Figure 9b**), the corresponding $S_1(\text{Ph-OH}^*) \rightarrow T_1(\text{Ph-OH}^*)$ energy gap was substantially larger (-104.9 kJ/mol). Even the nearest triplet state, $T_3(\text{Ph-OH}^*)$, lies 23.1 kJ/mol below $S_1(\text{Ph-OH}^*)$. ISC is more likely to occur when the energy gap between the singlet excited state (S_1) and the relevant triplet state (T_n) is small, as this facilitates

population of the triplet manifold and enhances phosphorescence.⁴² Therefore, the presented results for G-lignin alone vs. in the presence of His-ME suggest that His-ME facilitates ISC by reducing the S_1 – T_1 energy gap, in part due to the stabilization of the $S_1(\text{Ph-O}^*)$ state through keto–enol tautomerization (**Figure 9c**).

Taken together, these findings indicate that His-ME plays a dual role in the His-ME/RL system: As outlined above, (1) it provides structural rigidity that suppresses nonradiative decay pathways; and (2) it acts as an effective proton acceptor, triggering ESPT that activates the lignin chromophore and promotes ISC by reducing the $S_1 \rightarrow T_1$ gap. The resulting charge-separated excited state stabilizes the triplet level and contributes to the observed RTP emission.

4. Sustainability considerations

Both lignin and histidine are bio-derived molecules: Lignin is an abundant “waste” material from the paper pulping industry that is mostly burned for caloric value.⁸⁶ The amino acid histidine is commonly found in protein-rich food waste and can be produced microbially, and its methyl ester can be produced via a mild, one-step methylation process. In contrast, 4-methylimidazole is derived from petroleum feedstocks and requires multiple chemical steps to produce.⁸⁷ Comparing the inherent safety of these molecules, lignin as an important component in lignocellulosic biomass is generally considered to be safe, although its production process and physico-chemical characteristics have an influence on properties such as fire and explosion hazard.⁸⁸ That said, the proportion of lignin in the prepared materials is low (~1%). Histidine and its methyl ester, the latter easily converted back to histidine in the body, is an essential amino acid required in the human body and thus unproblematic.⁸⁹ On the other hand, 4-methylimidazole is classified as “possibly carcinogenic to humans” by the International Agency for Research on Cancer (IARC), and also

has various other GHS Hazard statements including “acutely toxic”, “corrosive”, “irritant”, and “health hazard”.⁹⁰ Finally, the preparation of His/RL and His-ME/RL emitters involves a simple anti-solvent crystallization process using the rather unproblematic solvents water, acetone, and methanol,⁹¹ at room temperature conditions.

Taken together, the presented fluorescent and phosphorescent emitters based on lignin and histidine were prepared using mild conditions and non-problematic solvents, contain biobased materials that do not rely on fossil resources that contribute to climate change, and have an excellent safety profile.

CONCLUSION

In this study, we developed novel and sustainable solid-state emitters using the renewable feedstocks lignin and histidine (or its methyl ester) as matrix material. Materials composed of the 4-methylimidazole, commonly employed in photoluminescent materials, and refined lignin were prepared for comparison purposes. One drawback remains the somewhat low yield of refined lignin using ethyl acetate extraction, but further studies on using a larger proportion of RL obtained by other extraction methods, or the direct use of alkali lignin, is warranted in the future. Co-crystallization was then used to prepare series of varying lignin content materials in the respective matrices. Synthesize materials demonstrated ESPT-induced photoluminescent properties and notably, the histidine methyl ester/lignin solid-state emitters also showed significant afterglow room temperature phosphorescence (RTP). By optimizing lignin-to- matrix ratios and examining the role of phenolic hydroxyl groups, we highlighted the influence of available free phenolic hydroxy groups, lignin aggregation, and molecular interactions on the emitters’ fluorescence and phosphorescence performance.

This work advances the development of environmentally benign solid-state photoluminescent materials and opens new possibilities for lignin-derived emitters in applications such as lighting, sensing, and other optical technologies. By adhering to green chemistry principles, this research establishes a foundation for developing sustainable and highly functional materials with reduced environmental impact, contributing to the broader goals of a circular economy and renewable resource utilization.

METHODS

Lignin Fractionation

Alkali lignin (AL) was purchased from Sigma-Aldrich (Prod. No. 370959; St. Louis, MO) and, according to the supplier, was obtained after Kraft pulping of pinewood. AL was fractionated as follows: 2g AL were stirred in 20 mL of ethyl acetate (HPLC grade; Sigma-Aldrich) at room temperature for 6 h. Then, the insoluble residue was filtered while the soluble lignin was isolated by solvent evaporation under reduced pressure using a rotary evaporator. The isolated yield of RL was 15.6 % (312 mg), and that of RLrep was 16.2% (324 mg).

Synthesis of 4-methyl imidazole/lignin (4-MI/RL) solid state emitters

4-MI/RL solid state emitter materials were synthesized by co-crystallization of RL with 4-MI at varying ratios (**Table 1**). The general procedure for their synthesis was as follows: For example, for 4-MI/RL-1, 166.5 mg of 4-MI and 1 mg of RL were dissolved in 5 mL of ethyl acetate. The solution was sonicated for 10 minutes and the solvent was evaporated. The resulting oily liquid was stored in a refrigerator (4°C) overnight to enhance crystallization. The mass of the obtained product was 167.53 mg.

528

529 *Synthesis of histidine/lignin (His/RL) solid state emitters*

530 His/RL samples were synthesized by anti-solvent crystallization of RL with histidine at
531 varying ratios (Table 1). The general procedure for their synthesis was as follows: For example,
532 for His/RL-1, 314.9 mg of L-histidine (His) was dissolved in 10 mL of DI water. Then, 1 mg RL
533 dissolved in 10 mL of acetone was added using a syringe pump at a flow rate of 15 μ L/min over
534 the course of 11 hours. The resulting material was stored in a refrigerator (4°C) overnight to
535 enhance antisolvent crystallization. Then, the crystals were filtered and washed with acetone and
536 dried under vacuum. The mass of the obtained product was 291.70 mg. In addition, the acetone
537 wash solution was evaporated, and the resulting solid was re-dissolved in 3 mL acetonitrile to
538 determine residual RL amounts using UV-vis spectroscopy. In the case of His/RL-1, the residual
539 RL mass was 0.18 mg.

540

541 *Synthesis of histidine methyl ester/lignin (His-ME/RL) solid state emitters*

542 His-ME/RL samples were synthesized by anti-solvent crystallization of RL with histidine
543 methyl ester at varying ratios (**Table 1**) using a similar procedure as for His/RL, but the starting
544 material His-ME $\cdot$ 2HCl was first neutralized with an equivalent molar amount of NaOH in 5mL
545 MilliQ water prior to integration with RL. The general procedure for their synthesis was as follows:
546 For example, for the synthesis of His-ME/RL-1, 343.5 mg of the neutralized His-ME was dissolved
547 in 10 mL of HPLC-grade methanol/ MilliQ water mixed solution (v/v = 1:1). Then, 1 mg RL
548 dissolved in 10 mL of acetone was added using a syringe pump at a flow rate of 15 μ L/min over
549 the course of 11 hours. The resulting material was stored in a refrigerator (4°C) overnight to
550 enhance antisolvent crystallization. Then, the crystals were filtered and washed with acetone and

dried under vacuum. The mass of the obtained product was 314.3 mg, and the mass of residual RL remaining in solution was 0.05 mg.

Synthesis of 4-MI/His/His-ME / Si-AL solid state emitters

Solid-state emitters with silylated RL (Si-RL) instead of RL were prepared as described in each of the 3 above sections, using freshly prepared Si-RL instead of RL. To prepare Si-RL, 0.2 g of RL was dissolved in 2 mL THF in a 10mL round bottom flask pre-flushed with nitrogen. Then, 1 mL of pyridine and 0.82 mL of BSTFA were added and heated to 50 °C for 1 h. (NOTE. The exact ratio of silylation reagents was determined with respect to the total amount of lignin hydroxyl groups in RL as determined by phosphorylation of RL followed by ³¹P NMR spectroscopy; see Supplemental Information). After 1h, deionized water was added to quench the reaction and precipitate the product, which was then filtered and washed with deionized water. The washed product was resubstituted in 25 mL THF and dried over anhydrous NaSO₄. The solid product was obtained after solvent evaporation in vacuo and stored under nitrogen until analysis. Si-AL yield was ca. 68.3% (136.6 mg).

DFT Calculations

All DFT calculations were carried out using Gaussian 09, version B.01.⁹² The structures of the ground state of the model fragment were optimized using Density Functional Theory (DFT) with the B3LYP functional^{93,94} and 6-31+G(d,p) basis set.⁹⁵ The first singlet excited state (S₁) and various triplet excited states with energy close to S₁ were calculated by time-dependent density functional theory (TD-DFT). Vibrational analysis was done after optimization to ensure that the structures were located at the minima of potential energy surfaces. The effects of the surrounding

environment to the model fragment were taken into account by the polarized continuum model with integral equation formalism (IEF-PCM).⁹⁶ See **Tables S6-S14** for details.

Instrumental characterization

Further details regarding the instrumental characterization methods can be found in the Supplemental Methods.

RESOURCE AVAILABILITY

Lead contact

Reasonable requests for further information and resources should be directed to Paul T. Anastas (paul.anastas@yale.edu).

Materials availability

Compounds synthesized in this project are available upon reasonable request from the lead contact and may require a completed materials transfer agreement.

Data and code availability

All data are available upon reasonable request.

SUPPLEMENTAL INFORMATION

Please see the Supplemental Information for relevant UV Spectra and the relationship between concentration and UV-vis absorbance at 284 nm for RL, Si-RL, and RLrep (**Figure S1**), for time-

resolved photoluminescence spectra of His-ME/RL emitters (**Figure S5**), and a comparison of photoluminescence spectra (**Figure S6**).

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AUTHOR CONTRIBUTIONS

Ho-Yin Tse: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Visualization; **Hanno C. Erythropel:** Methodology, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration; **Andreas Backhaus:** Investigation, Formal Analysis, Writing - Review & Editing; **Darren S. Lee:** Formal analysis, Writing - Review & Editing; **Shun Cheung Cheng:** Investigation, Formal analysis, Writing - Review & Editing; **Chi Shun Yeung:** Investigation, Formal analysis, Writing - Review & Editing; **David Lee Phillips:** Writing - Review & Editing, Supervision; **Julie B. Zimmerman:** Writing - Review & Editing, Supervision, Funding acquisition; **Paul T. Anastas:** Conceptualization, Methodology, Writing - Review & Editing, Supervision, Funding acquisition.

DECLARATION OF INTERESTS

The authors declare no conflicting interests.

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FIGURE TITLES

Figure 1: Structures of starting materials. (Left) Partial structure of lignin highlighting 3 phenolic structures: Syringyl (S) units, guaiacyl (G) units, and *p*-hydroxyphenyl (H) units. (Right) Host matrix materials used in this study: 4-methylimidazole (4-MI), histidine (His), and histidine methyl ester (His-ME).

Figure 2: Fluorescence intensities ($\lambda_{\text{excitation}} = 370\text{nm}$) of **(a)** the prepared 4-MI/RL (black line), His/RL (blue line), and His-ME/RL (red line) and **(inset)** fluorescence spectra of the respective starting materials; **(b)** comparison of the fluorescence intensities ($\lambda_{\text{excitation}} = 370\text{nm}$) between materials prepared with RL (solid lines) and Si-RL (dashed lines).

Figure 3: Fluorescence intensities ($\lambda_{\text{excitation}} = 370\text{ nm}$) vs mole-% of Ph-OH in EPST system. Symbols represent measured data points, and shaded areas represent the standard deviation of the means.

Figure 4: Confocal fluorescence images of (ai) 4-MI/RL-10; (aii) 4-MI/RL-1; (bi) His/RL-10; (bii) His/RL-1; (ci) His-ME/RL-1 & (cii) His-ME/RL-1. White bar scale represents 50 μm .

Figure 5: Fluorescence lifetimes (τ_{F1} and τ_{F2}) and corresponding amplitudes (A_{F1} and A_{F2}) for the excited components of **(ai, aii)** 4-MI/RL emitters ($\lambda_{\text{excitation}} = 405\text{nm}$; $\lambda_{\text{Probing}} = 459\text{nm}$); **(bi, bii)** His-ME/RL emitters ($\lambda_{\text{excitation}} = 405\text{nm}$; $\lambda_{\text{Probing}} = 447\text{nm}$); and **(ci, cii)** His/RL emitters ($\lambda_{\text{excitation}} = 405\text{nm}$; $\lambda_{\text{Probing}} = 429\text{nm}$).

Figure 6: Phosphorescence data for the His-ME/RL series: **(a)** Photographs of His-ME/RL emitters under daylight (top left), under 365nm UV light on (left, 2nd from top), and a time-series after UV off with seconds indicated (0.0 – 1.21) showing phosphorescence decay. Numbers (#) correspond to the samples name (His-ME/RL-#). **(b)** Normalized fluorescence spectrum (red line) and phosphorescence spectrum (green line) of His-ME/RL-1. **(c)** Time-resolved phosphorescence decay lifetime data and fitting results for His-ME/RL emitters ($\lambda_{\text{excitation}} = 405\text{nm}$; $\lambda_{\text{probing}} = 522\text{nm}$) **(d)** Phosphorescence lifetimes (τ_{P1} and τ_{P2}) and **(e)** corresponding amplitudes (A_{P1} and A_{P2}) for the excited components of His-ME/RL emitters ($\lambda_{\text{excitation}} = 405\text{nm}$; $\lambda_{\text{probing}} = 522\text{nm}$).

Figure 7: pXRD spectra of **(a)** 4-MI/RL, **(b)** His-ME/RL, and **(c)** His/RL emitters with increasing lignin load from no lignin (black lines), “-2” samples (red lines), “-6” samples (blue lines), and “-10” samples (green lines, highest lignin load); see Table 1 for details.

Figure 8: Schematic overview of possible molecular interactions in the three types of emitters **(a)** 4-MI/RL, **(b)** His-ME/RL, and **(c)** His-ME/RL. The following molecular interactions are highlighted: Excited state proton transfer (orange dashed line), hydrogen bonding (grey dashed line), π - π stacking (purple dotted line), and electrostatic interactions (teal line).

Figure 9. Density functional theory (DFT) level calculations of the proposed photophysical pathway. **(a)** His-ME/G-lignin demonstrating the low energy barrier for intersystem crossing (ISC) from $S_1(\text{Ph-O}^*) \rightarrow T_1(\text{Ph-O}^*)$ ($\Delta = -0.60 \text{ kJ/mol}$), following the excited-state proton transfer (ESPT) transition from $S_1(\text{Ph-OH}^*) \rightarrow S_1(\text{Ph-O}^*)$, leading to the observed room temperature phosphorescence (RTP) behavior; **(b)** pure G-lignin demonstrating that ISC from $S_1(\text{Ph-OH}^*) \rightarrow$

T₁(Ph-OH*) or T₃(Ph-OH*) is unlikely due to the large energy gaps ($\Delta S_1 \rightarrow T_1 = -104.90$ kJ/mol; $\Delta S_1 \rightarrow T_1 = -23.05$ kJ/mol). Crossed arrows suggest that ISC is unlikely to happen. (c) Optimized molecular geometry for the interaction of His-ME and G-lignin demonstrating the Enol-Keto transformation between relevant parts of the molecules in the box with purple dashed lines.

TABLES AND TABLE TITLES

Table 1: Prepared Materials, mean mass ratio of RL to imidazole-derivative (For His and His-ME: additional column for mass ratio in final product as not all RL was incorporated), calculated mol-% of Ph-OH groups in RL or Si-RL in emitters, mean maximum fluorescence intensity, and wavelength fluorescence peak maximum. All experiments n=3. See Table S1 for details.

Abbreviations: Max. fluo. - Maximum fluorescence; m - Mass; λ_{fluo} – Wavelength of fluorescence; RL - Refined lignin; Si-RL - Silylated refined lignin; 4-MI - 4-Methylimidazol; His - Histidine; His-ME - Histidine methyl ester.

Entry	Sample	m ratio in final product	Mole% Ph-OH in ESPT system	Max. fluo. intensity (div. by 10 ⁶)	λ_{fluo} intensity maximum
1	4-MI/RL-1	100 : 0.62	0.31	8.51	459 nm
2	4-MI/RL-2	100 : 1.26	0.62	9.90	
3	4-MI/RL-4	100 : 2.46	1.20	8.12	
4	4-MI/RL-6	100 : 3.62	1.76	7.22	
5	4-MI/RL-8	100 : 4.88	2.36	5.82	
6	4-MI/RL-10	100 : 6.10	2.93	4.30	
7	4-MI/Si-RL-2	100 : 1.24	0.32	4.14	460 nm

Entry	Sample	m ratio of reactants	m ratio in final product	Mole% Ph-OH in ESPT system	Max. fluo. intensity (div. by 10 ⁶)	λ_{fluo} intensity maximum
8	His/RL-1	100 : 0.32	100 : 0.28	0.24	6.97	429 nm
9	His/RL-2	100 : 0.66	100 : 0.50	0.43	7.49	
10	His/RL-4	100 : 1.29	100 : 0.78	0.66	4.97	
11	His/RL-6	100 : 1.96	100 : 1.01	0.86	3.54	
12	His/RL-8	100 : 2.57	100 : 1.20	1.02	1.90	
13	His/RL-10	100 : 3.18	100 : 1.22	1.03	1.20	
14	His/Si-RL-2	100 : 0.66	100 : 0.44	0.21	3.35	429 nm
15	His-ME/RL-1	100 : 0.32	100 : 0.31	0.30	7.66	447 nm
16	His-ME/RL-2	100 : 0.59	100 : 0.57	0.52	8.90	
17	His-ME/RL-4	100 : 1.16	100 : 0.82	0.75	5.72	
18	His-ME/RL-6	100 : 1.76	100 : 1.07	0.98	4.66	
19	His-ME/RL-8	100 : 2.33	100 : 1.30	1.19	2.99	
20	His-ME/RL-10	100 : 2.92	100 : 1.36	1.26	1.88	
21	His-ME/Si-RL-2	100 : 0.59	100 : 0.52	0.28	2.65	447 nm

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Table 2: Fluorescence quantum yield (Φ_{Fluo}), phosphorescence quantum efficiency (Φ_{Phos}) and room temperature phosphorescence (RTP) lifetime comparison between reported (see columns Material and Reference) and best-performing lignin-based emitters in this study. UPY: (1-(6-isocyanatohexyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea).⁴²

Entry	Material	Φ_{Fluo} (%)	Φ_{Phos} (%)	RTP lifetime (ms)	Ref.
1	Alkali lignin within polylactic acid	5.10	2.95	221.1	41
2	Crosslinked methacrylated lignosulfonate and gelatin methylacrylamide	1.36	-	110.0	40
3	Lignosulfonate within poly(acrylic acid)	-	-	275.2	39
4	Basswood treated with NaOH and H ₂ O ₂	-	-	431.0	97
5	Alkali lignin or Na lignosulfonate within 2-Hydroxyethyl acrylate and urethane dimethacrylate	-	-	202.9	43
6	Lignosulfonate within in UPY-based polymer	-	-	24.2	42
7	His-ME/RL-1	23.79	6.43	359.4	This study
8	His-ME/RL-2	27.33	6.07	331.0	
9	His/RL-2	25.41	-	-	
10	4-MI/RL-2	35.42	-	-	