Designing a Redox Noninnocent Phenalenyl-Based Copper(II) Complex: An Autotandem Catalyst for the Selective Oxidation of Polycyclic Aromatic Hydrocarbons (PAHs)

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ABSTRACT: A square-planar [CuII] complex 1, based on the redox-active phenalenyl unit LH₂ = 9,9′-(ethane-1,2-diylbis(azanediyl))bis(1H-phenalen-1-one), is prepared and structurally characterized by single-crystal X-ray diffraction analysis. Complex 1 crystallizes at room temperature with the P1 space group. The molecular structure of 1 reveals the presence of intriguing C–H···Cu intermolecular anagostic interactions of the order ∼2.7715 Å. Utilizing the presence of anagostic interactions and the free nonbonding molecular orbitals (NBMOs) of the closed-shell phenalenyl unit in 1, the oxidation reactions of some industrially important polycyclic aromatic hydrocarbons (PAHs) in the presence of the [CuII] complex under very mild conditions have been reported. The direct conversion of anthracene-9-carbaldehyde to 9,10-anthraquinone in one step concludes that the catalyst shows dual activity in the chemical transformations. This also includes the first report of a “single-step” catalytic transformation of pyrene-1-carbaldehyde to the synthetically difficult pyren-4-ol, a precursor for the synthesis of several novel fluorescent probes for cell imaging.

INTRODUCTION

The realization of the redox noninnocent ligands by Jørgensen¹ and the discovery of their application as versatile tools to regulate the chemical transformations have uncovered many new catalytic reactions in the past few decades.²,³ Their prominent role in the elementary bond activation steps in a catalytic cycle and the synergistic cooperation between the metal and ligand facilitate the chemical process.⁴ The redox noninnocent ligand acts as an electron reservoir, which helps in delocalization of excess electronic charge, preventing metal ions from indulging in any unfavorable oxidation state during the catalytic reaction.⁵,⁶ Therefore, these ligands ease the electronic discrepancies on metal ions and help transition-metal catalysts mimic the characteristics of the noble metal catalyst.⁷ There has been continuous chemical advancements in these delocalized redox-active systems for the construction of new transition-metal complexes that can be employed as a catalyst.

Phenalenyl (PLY) is one such thermodynamically stable redox-active system that can exist in three redox states, i.e., a closed-shell cation, an open-shell radical, and a closed-shell anion.⁹ These amphoteric characteristics observed in PLY are due to the presence of energetically accessible low-lying nonbonding molecular orbitals (NBMOs), which can readily accept electrons and transform to a singly occupied molecular orbital (SOMO) without any compromises in the pi-electron delocalization energy.¹⁰ Therefore, electronic conversions from the closed shell to open shell and vice versa happen considerably, without affecting the stability of the proceeding species.¹¹ This behavior of redox noninnocent PLY is distinctive from other noninnocent ligands, where the latter generally use their antibonding orbitals to participate in the reaction mechanism.

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Table 1. Comparative Study for the Synthesis of PAHs

| type of reaction       | no. | reactionants | product yield (%) | reaction time/condition | reference no. |
|------------------------|-----|--------------|-------------------|-------------------------|---------------|
| single-step reaction   | 1   | naphthalene  | 39                | [Ru]/PTC, H2O2, 1 h, 40 °C | ref 25        |
|                        | 2   | naphthalene  | 13                | Pd(II)-SP resin, H2O2, AcOH, 50 °C, 8 h | ref 26        |
|                        | 3   | naphthalene  | 94                | Cu catalyst (5 mol %), H2O2, MeCN, 65 °C, 18 h | this work    |
|                        | 4   | anthracene   | 74                | HNO3/O3, MeOH, 95 °C, 2 h | ref 27–30     |
|                        | 5   | anthracene   | 80                | CrO3 in acetic acid, 90 °C | ref 27–30     |
|                        | 6   | anthracene   | 44                | BW3,Fe, H2O2, MeCN, 24 h | ref 31        |
|                        | 7   | anthracene   | 86                | Cu catalyst (5 mol %), H2O2, MeCN, 65 °C, 16 h | this work    |
|                        | 8   | 9-anthraldehyde| 97            | NBS, sq. DMF, 80 °C, 4 h | ref 32        |
|                        | 9   | 9-anthraldehyde| 82            | AuNCD, O2, 530 nm LED, MeCN, 3 h | ref 33        |
| multiple-step reaction | 10  | 9-anthraldehyde| 84            | Cu catalyst (5 mol %), H2O2, MeCN, 65 °C, 30 h | this work    |
|                        | 11  | pyrene       | five steps overall 73 | | ref 34        |
|                        | 12  | pyrene-1-carbaldehyde | single step 90 | | ref 54        |

Scheme 1. Synthesis of the [CuIIL] Complex, 1

Exploring the redox noninnocent behavior of the closed-shell cationic PLY species, Mukherjee and co-workers reported the phenalenyl-based organozinc compound [N(Cy),N(Cy)-PLY-ZnMe], (N(Cy),N(Cy)-PLY = 9-N-cyclohexyl-1-N′-cyclohexylphenalene) as a catalyst for the ring-opening polymerization reactions of cyclic esters and intramolecular hydroamination reactions.12,13 Bellan and co-workers have reported the PLY-based transition-metal catalyst [CoIII(OPN)2] (OPN = deprotonated 9-oxyphenalenone) for the catalytic chain transfer (CCT) polymerization of vinyl acetate.14 Vijaykumar and co-workers have shown that the ligand-based "electron reservoir" in the PLY–nickel(II) complex can assist in catalytic anti-Markovnikov’s hydroxylation reactions.5 In the recent past, redox participation of the PLY-based ligand LH3, (9,9′-(ethane-1,2-diyldibis(azanediyl))bis(1H-phenalen-1-one)), resulted in the development of an iron-based catalyst [FeII(L)Cl]15 and a chemoselective manganese-based catalyst [MnIII(L)Cl].16 In fact, the [MnIII(L)Cl] complex is the first catalyst reported in the literature to facilitate a controlled catalytic transformation of chemically inert primary amines into amines as well as nitriles by a slight modification of the reaction conditions. These pieces of evidence from the literature further emphasize the use of the phenalenyl-based ligand as a "redox storage motif" in designing new catalysts.

On the other hand, oxidation of polycyclic aromatic hydrocarbons (PAHs) is one of the important areas belonging to the biochemistry, astrochemistry, and chemical industries.17 Similarly, extended conjugation present in pyrene shows wide applications pertaining to the photophysical and electronic properties, which makes the pyrene nucleus a valuable component in materials, supramolecular, and biological chemistry.18 The oxidation of PAHs such as naphthalene, anthracene, and substituted anthracene provides a route for their detoxification, whereas oxidized products such as quinone are commonly used in organic synthesis and medicinal chemistry.19–24 There are a few reports in the literature toward this end, such as oxidation of naphthalene to naphthoquinone by [Ru]/PTC in a H2O2 medium or the Pd(II)-SP resin using H2O2 and AcOH conditions (see Table 1).25,26 Oxidation of anthracene to 9,10-anthaquinone using a strong acid like HNO3/O2 or CrO3 in acetic acid at 90 °C17–20 metal-catalysis by BW3,Fe;31 or, alternatively, oxidation of anthraldehyde to 9,10-anthaquinone using N-bromosuccinimide (NBS) in aqueous N,N-dimethylformamide at 75–80 °C or using gold nanocrystalline diamonds (AuNCD), O2, and a 530 nm light-emitting diode (LED) (see Table 1).32,33 These conversions suffer from several drawbacks such as hazardous reaction conditions, high temperatures, tedious purification process, and moderate yields. Furthermore, the rigid structure of pyrene restrains its synthetic developments by limiting the range of methods and direct substitution reaction. Despite several stepwise methods outlined in the literature,34 no direct method was found to be utilized to functionalize pyrene derivatives concisely. Considering the latest reports on PAH catalysis, where the transition-metal catalyzed pathways have emerged as environmentally friendly and economically affordable synthetic tools35 for the oxidation of PAHs, herein, we report the oxidation of naphthalene, anthracene, anthracene-9-carbaldehyde, and pyrene-1-carbaldehyde in a single step using a novel copper(II) catalyst [CuIIL], designed using a PLY-based synthon LH3, 9,9′-(ethane-1,2-diyldibis(azanediyl))bis(1H-phenalen-1-one). To our delight, this is the first report where a "single-step" selective oxidation of 1-pyrrenecarboxaldehyde to pyren-4-ol (a precursor for the synthesis of several novel fluorescent probes) has been confirmed in the presence of a benign oxidant (H2O2) and in the absence of any acid cocatalyst.
RESULTS AND DISCUSSION

Synthetic Aspects. The [CuII] complex 1 was synthesized by reacting equivalent moles of Cu(OAc)₂·H₂O and 9,9’-(ethane-1,2-diylbis(azanediyl))bis(1H-phenalen-1-one), LH₂, in methanol under reflux conditions for 24 h (Scheme 1). The formation of 1 was confirmed by the single-crystal X-ray diffraction technique. The complex 1 was also further characterized with a set of analytical techniques such as elemental analysis, HRMS, FT-IR, and UV–vis spectroscopy. The FT-IR spectrum of 1 shows two major diagnostic bands, whereas the sharp characteristic band for the ν(C==N) vibrational stretch appeared at 1631 cm⁻¹ and the ν(C–O) stretching band was observed at 1270 cm⁻¹ (see the SI, Figure S1). The UV–vis spectra of the [CuII] complex consists of one peak in the visible region (458 nm) and two distinct peaks in the ultraviolet region (289, 365 nm) (see the SI, Figure S2). The thermal stability of 1 was determined by the single-crystal X-ray diffraction technique for 24 h (Scheme 1).

Molecular Structure of 1. The molecular structure of 1 was determined by the single-crystal X-ray diffraction technique (Figure 1). The crystal structure refinement parameters of complex 1 are listed in Table S1 (Supporting Information). Complex 1 crystallizes in the P1 space group with two molecules per unit cell. The molecular structure of 1 showed that the CuII ion is symmetrically coordinated with two N-atoms and two O-atoms of the bis-phenalenone ligand (N1, N2, O1, and O2 as the coordinating sites) adopting a square-planar geometry. The Cu–N and Cu–O bond lengths observed in 1 (Cu1–N1, 1.9275(40) Å; Cu1–N2, 1.9269(35) Å and Cu1–O1, 1.9096(34) Å; Cu1–O2, 1.9011(38) Å) are comparable to those of the Cu–N and Cu–O bond lengths [Cu1–N1, 1.999(2) Å; Cu1–N2, 1.987(2) Å and Cu1–O1, 1.937(2) Å; Cu1–O2, 1.936(2) Å] reported in the CuII salen complex. The O–Cu–N bond angles in 1 [O2–Cu1–N2, 92.638(157)°; O1–Cu1–N1, 92.774(156)°] are also comparable to the bond angles found in the CuII salen complex [O2–Cu1–N2, 90.98(9)°; O1–Cu1–N1, 91.27(8)°].

A closer inspection of the molecular structure of 1 reveals the presence of intriguing C–H···Cu intermolecular anagostic interactions, [Cu1–H15A, 2.7715(14) Å; Cu1–H15A–C15, 134.551(305)°] between the hydrogen atom of the ethylene moiety of one molecule with the copper site of another molecule. Literature-reported M–H bond distance and bond angle parameters for the anagostic interactions lie in the range of 2.3–2.9 Å and C–H···M 130–170°, respectively. In general, sterically enforced anagostic interactions are observed in the square-planar transition-metal d⁸ complexes.

Contrary to that, Colombo and co-workers reported the intramolecular anagostic interaction [C–H···Cu, 2.60 Å] for the copper d⁹ complex. In another report, Singh and co-workers observed compelling intermolecular C–H···Cu, 2.79 Å anagostic interactions in the case of square-planar ferrocenyl-based Cu(II) dithiocarbamate. Complex 1 is one of the rare examples consisting of the intermolecular anagostic C–H···Cu interaction. The presence of these anagostic interactions restricts the change of geometry and improves the structural stability. Along with stability, they are also known to play an extensive role in catalytic transformations involving C–H activation. Together with the idea of the presence of an anagostic interaction along with the availability of free NBMO of the closed-shell phenalenyl unit in 1, the oxidation reactions of some of the PAHs in the presence of the [CuII] complex were successfully studied.

Catalytic Activity. Oxidation of PAHs is a challenging but very important process related to their derivatization and detoxification. Moreover, the oxidized products of PAHs such as anthraquinone derivatives are important for the synthesis of industrial-scale hydrogen peroxide, naphthoquinones as dye reagents, and pyrenequinones as photosensitizers in photodynamic therapy. Most of the methods reported in the literature for conversion of PAHs to quinones are achieved through powerful oxidants and harsh reaction conditions. Therefore, we initiated our study for the catalytic oxidation of PAHs in the presence of a novel [CuII] complex 1 derived from nontoxic transition metal and ligand based on an interesting redox-active PLY backbone, which has shown unusual chemistries and a broad spectrum of catalytic properties. We started a typical catalytic process with anthracene 2 in the presence of H₂O₂ (10 equiv) as a source of oxygen and [CuII] complex (10 mol %) at 23 °C in acetonitrile. To our delight, the reaction underwent smoothly to afford the oxidized product 9,10-anthraquinone 2a as a pale-yellow solid in a modest conversion (65% yield) when carried...
out for three days (see entry 1; Table 2). Further, to improve the yield and optimize the reaction condition, screening of catalyst loading, temperature, time, and oxidant equivalent was performed, and the results obtained are shown in Table 2.

Surprisingly, when the reaction was carried out at elevated temperature \(\sim 65^\circ C\) with 10 mol % cat. 1 and 10 equiv of H\(_2\)O\(_2\), the reaction was completed in just 17 h instead of three days with 72% yield (see entry 2; Table 2). Notably, the results obtained by changing the amount of H\(_2\)O\(_2\) (5/20 equiv) and keeping the amount of cat. 1 (5 mol %) and temperature 65 \(^\circ\)C constant do not improve the yield (see Table 2, entries 3 and 4, 60 and 49% yields, respectively). Interestingly, the reaction with 10 equiv of H\(_2\)O\(_2\) and 5 mol % Cu catalyst in CH\(_3\)CN at 65 \(^\circ\)C furnished the required product with the highest yield of 86% in just 16 h (see entry 5; Table 2). Further optimization of reaction conditions by changing the loading of catalyst mol %, temperature, and solvent (CH\(_2\)Cl\(_2\)) did not improve the yield (see entries 6 and 7; Table 2). Moreover, in the absence of the \([Cu^{II}L]\) catalyst, only a trace amount of product was formed, which confirms the role of the catalyst in the reaction (see entry 8, Table 2).

With the optimized reaction condition in hand, we next focused on checking the generality of the reaction. Hence, the protocol was further applied for the oxidation of naphthalene 3 to naphthoquinone 3a, where the reaction went through a similar process that furnished the desired product in 94% yield (see Scheme 2). The resulting compound 3a was easily separated using flash silica gel column chromatography, and its structure was confirmed by its spectroscopic data (\(^1\)H and \(^13\)C NMR).

Inspired by the results obtained, we turned our attention toward the development of an innovative substrate scope, where oxidation of the anthracene derivative such as anthracene-9-carbaldehyde 4 was planned. Thus, anthracene-9-carbaldehyde 4 was treated with H\(_2\)O\(_2\) in acetonitrile, in the presence of 1 (5 mol %) at 65 \(^\circ\)C for 30 h. The reaction progress was continuously monitored, and to our surprise, the product isolated here in 84% yield was the same as that obtained by the oxidation of anthracene, i.e., 9,10-anthraquinone 2a (see Scheme 3). Such a single-step direct chemical conversion of anthracene-9-carbaldehyde to 9,10-anthraquinone enlightens the idea of autotandem catalysis. It is worth noting that catalyst 1 shows two mechanistically distinct reactions in the one-pot sequence, where the first is detachment of the formyl group, followed by oxidation of the resulting anthracene intermediate into the product 9,10-anthraquinone 2a. The conceptual term “auto-tandem catalysis” has been used to define a similar process of two or more chemical transformations that occur under identical conditions, where the subsequent transformation takes place at the product functionalities synthesized in the former transformation. A similar kind of observation was noted through the oxidation of anthracene-9-carbaldehyde 4, which extends the scope for novel Cu catalysts toward numerous designs and the development in organic synthesis.

Plausible Mechanism for [Cu\(^{II}\)L] Catalyzed Oxidation of Anthracene to 9,10-Anthraquinone. In the proposed mechanism (see Scheme 4), anthracene 2 reacts with the activated intermediate \([L-Cu^{III}-O]_2\) to give intermediate G. Subsequently, the hydroxyl radical or the \([L-Cu^{III}-O]_2\) radical abstracts the hydrogen from G and generates intermediate H. In the next step, the activated intermediate A attacks the 10th position of anthracene intermediate H and generates intermediate I, followed by hydrogen abstraction to give the desired product 9,10-anthraquinone (see Scheme 4).

Encouraged by this surprising result, we became interested in examining an auto-tandem catalysis on the photochemically interesting pyrene derivate, pyrene-1-carbaldehyde 5. Possessing an exceptionally long fluorescence lifetime, pyrene is well known for its photophysical and electronic properties that make it widely applicable in organic electronics such as field-effect transistors, OLEDs, supramolecular photosensors, etc.

To our delight, the reaction of pyrene-1-carbaldehyde 5 under optimized conditions resulted in the formation of pyrene-4-ol 5a as a yellow solid with 90% yield (see Scheme 3).
pyrene-1-carbaldehyde to Pyrene-1-ol in the Presence of Complex 1

![Scheme 6](image)

Notably, pyrene-1-ol is a metabolite of pyrene and is known as one of the most commonly used exposure biomarkers of PAHs. Moreover, pyrene-1-ol is much more expensive (100 mg = $200) than pyrene (100 mg = $1) but could be easily made in a single step using the protocol disclosed here. Structures of the synthesized pyrene-1-ol were confirmed unambiguously from their spectroscopic analysis (¹H NMR, ¹³C NMR, and HRMS), which was in good agreement with the reported literature data.³⁴,⁵¹,⁵²

**Plausible Mechanism for [Cu⁹L] Catalyzed Auto-tandem Catalytic Transformation of Pyrene-1-carbaldehyde to Pyrene-4-ol**

In conclusion, we have synthesized a square-planar [Cu⁹L] complex based on the redox-active phenalenyl unit LH₂, 9,9'-[(ethane-1,2-diylbis(azanediyl))bis(1H-phenalen-1-one)]. Complex 1 is structurally characterized using the single-crystal XRD technique. The crystal structure of 1 reveals the presence of a rare C–H···Cu intermolecular anagostic interaction. Complex 1 is found to be an effective catalyst for the selective oxidation of industrially important PAHs such as naphthalene, anthracene, pyrene, and their derivatives. Notably, the dual activity of the catalyst 1 was reported for the direct conversion of anthracene-9-carbaldehyde to 9,10-anthraquinone in one step. Using the concept of auto-tandem catalysis, we report the

**CONCLUSIONS**

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application of a novel catalyst [CuIIL] in a single-step conversion of pyrene-1-carbaldehyde to pyrene-4-ol, which is an important starting material for the synthesis of the novel fluorescent probe 4-acrylatepyrene (PYAC). It is worth mentioning that the reaction proceeded in a single step (in contrast to the earlier five constructive steps) with a mild condition that led to 90% yield. The developed catalyst and protocol are robust and could be applied in synthesizing various oxidized PAHs in a one-pot manner. The effort toward the construction of such bioactive PAHs and their applications is ongoing and will be disclosed in due course.

### EXPERIMENTAL SECTION

**General Materials and Instrumentation.** The ligand 9,9’-(ethane-1,2-diylbis(azanediyl))bis(1H-phenalen-1-one) (LH2) was synthesized following a literature method.61 All other chemicals and reagents used for the synthesis and the catalytic reactions were procured from commercial sources and used as such without any further purification. Single-crystal X-ray diffraction data were recorded at a Bruker Smart Apex Single Crystal-XRD at 298 K. FT-IR measurements of 1 were measured on a BrukerVertex, 70V PMA50 instrument as KBr discs, and UV–vis absorption spectra were obtained with a Cary 4000 UV–vis spectrophotometer in CHCl3 solution. Elemental analysis was carried out on a Thermo Finnigan FLASH EA 112 series. The HRMS data were collected using a 6545 LC/Q-TOF HRMS. Thermogravimetry analysis (TGA) was carried out using the Perkin Elmer instrument STA6000. 1H and 13C NMR spectra were recorded using a Bruker High Performance Digital FT-NMR, 500 MHz, using CDCl3 as a solvent and tetramethyl silane as a reference.

**Synthesis of [CuIIL] Complex 1.** To a hot solution of LH2 (80 mg, 0.24 mmol) in methanol (25 mL), Cu(OAc)2·H2O (48 mg, 0.24 mmol) dissolved in methanol (5 mL) was slowly added. The resultant mixture was left to reflux under a N2 atmosphere for 24 h. The brown precipitate obtained was collected by gravity filtration and subsequently washed with methanol to remove any unreacted ligand and metal salt. X-ray-quality dark-brown needle-shaped crystals of 1 were grown via the slow diffusion of hexane to the concentrated solution of 1 in the CHCl3/DCM (2:1) mixture. Yield: 90 mg (78%). UV–vis (CHCl3) λ/nm (ε in M⁻¹ cm⁻¹): 289(45865), 347(25584), 364(48945), 458(15924), 488(sh). FT-IR (KBr pellet) ν (cm⁻¹): 465(m), 688(m), 838(s), 1513(s), 1586(s), 1630(s), 3039(w). Elemental analysis: Anal. calcd for C28H18CuN2O2: C, 70.36; H, 3.80; N, 5.86. Found: C, 70.10; H, 3.362; N, 6.01. ESI-MS (positive, CH3CN) (M + H)+: 478.0734 m/z.

**General Procedure for Catalytic Transformations.** A mixture of PAHs/derivatives 2–5 (0.780 mmol, 1.0 equiv) was dissolved in 3 mL of acetonitrile and treated with hydrogen peroxide (7.802 mmol, 10 equiv) followed by the catalyst [CuIIL] complex 1 (5 mol %) in a 10 mL glass vial at room temperature. The reaction mixture was then stirred at 65 °C for 16–48 h until complete conversion of the starting material (monitored by TLC) and then cooled to room temperature. After the completion of reaction, the reaction mixture was diluted with water and ethyl acetate. The mixture of layers was separated, and the aqueous phase was extracted with ethyl

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**Scheme 7. Plausible Mechanism for the Auto-tandem Catalysis Initiated by the [CuIIL] Catalyst**

![Scheme 7](https://example.com/scheme7.png)
acetate (3 × 10 mL). The combined organic layer was dried over Na₂SO₄, the solvent was removed under reduced pressure, and the residue was purified through silica gel column chromatography (EtOAc:hexane).

**Synthesis of Compound 2a.** ¹H NMR (500 MHz, CDCl₃) δ 8.45–8.16 (m, 4H), 8.01–7.68 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 183.19, 134.14, 133.55, 127.26.

**Synthesis of Compound 3a.** ¹H NMR (500 MHz, CDCl₃) δ 8.09 (dd, J = 5.7, 3.3 Hz, 2H), 7.77 (dd, J = 5.8, 3.3 Hz, 2H), 6.98 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 185.19, 138.84, 134.09, 132.09, 126.58.

**Synthesis of Compound 5a.** ¹H NMR (500 MHz, DMSO) δ 9.26 (d, J = 9.4 Hz, 1H), 8.59 (d, J = 8.1 Hz, 1H), 8.20 (d, J = 7.6 Hz, 2H), 8.13 (dd, J = 13.8, 6.1 Hz, 3H), 8.06–7.97 (m, 2H), 7.56 (d, J = 6.8 Hz, 1H); ¹³C NMR (126 MHz, DMSO) δ 134.01, 130.95, 130.89, 130.27, 129.45, 129.06, 128.74, 127.28, 126.42, 126.25, 126.07, 125.27, 124.67, 124.64, 124.25, 124.10; ESI-MS (positive, CH₃CN) Chemical formula C₁₆H₁₀O; calcd [M + H]⁺: 219.0804 m/z; found: 219.0799 m/z; calcld [M – H₂O]⁺: 200.06 m/z; found: 200.0620 m/z.

**Synthesis of Compound 6a.** ¹H NMR (500 MHz, DMSO) δ 10.65 (s, 1H), 8.32 (d, J = 9.1 Hz, 1H), 8.13 (dd, J = 10.1, 8.2 Hz, 3H), 8.07–7.96 (m, 3H), 7.91 (d, J = 8.9 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H); ¹³C NMR (126 MHz, DMSO) δ 152.62, 131.83, 131.80, 127.88, 126.68, 125.69, 125.97, 125.89, 124.91, 124.38, 124.26, 124.07, 121.88, 119.34, 118.51, 113.69; ESI-MS (positive, CH₃CN) Chemical formula C₁₆H₁₀O₂; calcld [M + H]⁺: 219.0804 m/z; found: 219.0788 m/z; calcld [M + Na]: 241.0624 m/z; found: 241.0647 m/z.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c07051.

Details of the spectroscopic characterization, crystal data, and structural refinement parameters of the [Cu⁴L⁴] complex I; general methods used for the PAH oxidation; and ¹H and ¹³C NMR spectra of the products obtained (PDF).

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Notes

The authors declare no competing financial interest.

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