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Spectroscopic Characterization and Mechanistic Studies on Visible Light Photoredox Carbon-Carbon Bond Formation by Bis(Arylimino)Acenaphthene Copper Photosensitizers

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ABSTRACT: Currently, the most popular molecular photosensitizers used for synthetic organic chemistry and energy applications are still the noble metal-based ruthenium and iridium complexes that usually require expensive metal and ligand precursors. In contrast, bis(arylimino)acenaphthene (Ar-BIAN) are established redox non-innocent π -accepting ligands that are easily assembled in one condensation step from affordable and commercially available precursors. Herein, we have developed a series of Ar-BIAN Cu^I complexes as visible light harvesting photosensitizers. Notably, one of these panchromatic, homoleptic Ar-BIAN Cu^I complexes exhibits a *radiative* recombination lifetime that is longer than diffusion control, as observed by time-correlated single photon counting spectroscopy. The Ar-BIAN Cu^I facilitates visible-light promoted atom transfer radical addition reactions *via* carbon-carbon bond formation with CBr₃ radicals in good yields of up to 75%. Steady-state and transient absorption spectroscopic measurements, together with spectroelectrochemical experiments and intermediate isolation studies, were performed to obtain insights into this photoredox catalysis and provide guidelines for the general deployment of Ar-BIAN Cu^I photosensitizers in synthetic organic chemistry and renewable energy applications.

KEYWORDS: copper photosensitizer, bis(arylimino)acenaphthene, transient absorption spectroscopy, time-correlated single photon counting, visible-light photoredox catalysis, carbon-carbon bond formation

1. INTRODUCTION

The storage of solar energy in the form of chemical bonds, also known as artificial photosynthesis or the production of solar fuels,¹ is an increasingly attractive and complementary approach to photovoltaics for sustainable energy production. Furthermore, (visible) light is progressively being adopted as an alternative, eco-friendly energy source to drive photoredox catalysis in a renaissance for the application of organic radical chemistry in synthetic methodology under mild reaction conditions.² One of the critical components in sophisticated artificial photosynthetic units, photoredox reactions, and even photovoltaics such as dye-sensitized solar cells³ is the light harvester, which is necessary for the conversion of photon energy into chemical potential. Effective solar energy harvesters should ideally be panchromatic and absorb even some of the near infrared (NIR) wavelengths without compromising too much on the anodic and cathodic chemical potentials that can be derived. Moreover, to serve as a photosensitizer that can power the multi-electron catalytic processes in artificial photosynthesis, the excited state lifetimes must be sufficiently long to ensure that charge injection or transfer occurs before unproductive recombination processes. In this respect, molecules comprising precious metals like ruthenium (Ru), iridium (Ir), and platinum (Pt),⁴ or synthetically laborious ligands such as porphyrins, phthalocyanines, and corroles⁵ have remained the

mainstay of photosensitizers most commonly employed. However, the prohibitive high costs and toxicity of heavy metal-based chromophores have added impetus to the development of more sustainable and affordable alternatives, including organic or copper (Cu) dyes.⁶

Our team has recently been involved in assembling various components of an artificial photosynthetic construct, such as the multi-electron (photo)catalysts and the light harvesters, with exclusive use of only earth-abundant elements.⁷ Cu^I chromophores with suitable π -acceptor ligands have been likened to Ru^{II} polypyridyl complexes, since both classes of compounds can absorb visible light by metal-to-ligand (MLCT) charge transfer transitions, while minimizing non-radiative losses through energetically accessible dark states in other spin manifolds.⁸ Ligand systems that have been explored for supporting Cu^I chromophores include oligopyridines,^{8b} halides,⁹ phosphanes,^{8c} *N*-heterocyclic carbenes (NHCs),¹⁰ and bis(arylimino)acenaphthene (Ar-BIAN).^{7b}

However, unlike the Ru^{II} complexes, there are several current challenges to developing effective Cu^I photosensitizers that have amply long lifetimes for photochemistry. Since Cu^I has a d¹⁰ electronic configuration, the complexes typically have up to only four coordination sites, with the most common geometry being distorted tetrahedral, although some trigonal planar and linear complexes exist.¹¹ When the Cu^I complexes absorb

light *via* MLCT, the electron is usually promoted from an almost doubly or triply degenerate antibonding orbital to the ligand, which results in a pseudo Jahn-Teller distortion.^{8b} Consequently, the excited state lifetimes of Cu^I chromophores with small ligands such as halides or simple unhindered pyridines will be very short, since the distortion will provide many non-radiative relaxation pathways for the excited state to return to the ground state.^{8b} Some of the most successful examples possess bulky pyridine cores with branched hydrocarbon chains on the periphery,^{8b, 12} which can avert the structural reorganizations that are expected of the transient Cu^I to Cu^{II} excitations.¹³ However, these ligands will then require expensive precursors and consist of demanding synthetic routes with palladium-catalyzed coupling reactions, which negate the benefits from utilizing Cu instead of Ru or Ir. Another approach was to use bulky, strongly σ -donating ligands including phosphanes and NHCs, but the larger ligand fields resulted in Cu^I complexes that do not absorb beyond the blue to green region of the visible spectrum.^{8c, 10}

On the contrary, Ar-BIAN ligands are recognized as versatile, redox non-innocent π -acceptors¹⁴ that are easily assembled by condensation reactions between affordable, commercial anilines and acenaphthenequinone.¹⁵ A number of metal complexes supported by Ar-BIAN ligands have been reported recently,¹⁶ including several from our team.^{7b, 7f, 17} Previous attempts to develop Ar-BIAN Cu^I photosensitizers revealed that these ligands possessed low-lying, non-emissive triplet excited states, which would facilitate undesired thermal relaxation to the ground state.¹⁸ To understand the photophysical behavior of the Ar-BIAN Cu^I dyes, we have re-designed and prepared a series of new Ar-BIAN Cu^I complexes, and conducted electrochemical and transient absorption spectroscopic measurements on them. The complexes contain only earth-abundant elements, and noble metals have been excluded even during the synthetic process. Gratifyingly, a new homoleptic Ar-BIAN Cu^I chromophore that exhibits *radiative* recombination lifetimes longer than diffusion control is observed for the first time, and has been employed in photocatalytic carbon-carbon bond formation reactions as a proof of concept.

Herein, we explain our experimental findings on the Cu^I photosensitizers, provide examples of their application in photoredox atom transfer radical addition (ATRA),¹⁹ and present detailed spectroscopic and mechanistic studies to probe elementary steps of the catalysis. Critically, we can use the insights from this study to improve the photocatalyst design for future applications in other photoredox organic transformations such as atom transfer radical polymerization (ATRP), which is an established method for the production of polymeric materials of well-defined compositions.²⁰ In addition, ATRA reactions have also been instrumental for the highly enantioselective addition of CX₄ reagents to olefins, which can be another potentially impactful application for the Cu^I photosensitizers presented here.^{19a}

2. RESULTS AND DISCUSSION

The synthetic steps for the substituted Ar-BIAN ligands and detailed characterization data are described in the supporting information (SI). Briefly, the protocol reported by Gasperini and co-workers¹⁵ was adapted for the synthesis of Ar^{NHOH}-BIAN^{Br} (**1**), while Ar^{Br,OMe}-BIAN (**2**) and Ar^{OMe}-BIAN^{Br} (**3**) were synthesized via a TiCl₄-promoted condensation^{7b, 21} to give moderate yields. Subsequently, treatment of suspensions of [(CH₃CN)₄Cu^I]PF₆ in *N,N*-dimethylformamide (DMF) or

dichloromethane (DCM), with solutions of the corresponding Ar-BIAN in the same solvent under N₂ gave rise to the respective Ar-BIAN Cu^I complexes: [(Ar^{NHOH}-BIAN^{Br})₂Cu^I]PF₆ (**4**), [(Ar^{Br,OMe}-BIAN)₂Cu^I]PF₆ (**5**), and [(Ar^{OMe}-BIAN^{Br})₂Cu^I]PF₆ (**6**) (Scheme 1).

Scheme 1. Synthesis of the Ar-BIAN ligands and Cu^I Complexes. Inset: ORTEP from single crystal X-ray diffraction experiment of **4. The PF₆[−] counter-anion and the hydrogen atoms have been omitted for clarity.**

Crystals of **4** suitable for single crystal X-ray diffraction were obtained by recrystallization from DMF layered below a solution of diethyl ether (Et₂O) and 1,2-dimethoxyethane (DME). However, the crystal contained disordered solvent molecules in the unit cell, resulting in C-C bond distances that may not be very accurate. Nevertheless, the Oak Ridge thermal-ellipsoid plot (ORTEP) of **4** in Scheme 1 exhibits the expected distorted tetrahedral geometry around Cu^I, which is consistent with other tetrahedral Ar-BIAN Cu^I complexes.^{16b, 16c, 22}

To determine the feasibility of complexes **4-6** in redox catalysis, we performed cyclic voltammetry (CV) experiments on them. Electrochemical measurements were performed for all the compounds **1-6** (Figures S12-S14, Table S11). Notably, a quasi-reversible redox wave was observed for **6** at E_{1/2} = +0.29 V (Figure 1a) and is assigned to the Cu^{II/I} couple. During a cathodic scan, a similarly quasi-reversible reduction wave was detected at E_{1/2} = −0.99 V, as depicted in Figure 1b. Application of more negative potentials to **6** led to irreversible reductions. In addition, very similar redox waves were observed for **5** (Figure S14) since both complexes have similar structures except for the position of the bromide atoms. Due to the poor solubilities of **1** and **4** in DCM, the CV experiments were conducted in DMF instead. Hence, cathodically shifted redox potentials were observed for **4**. Nevertheless, the reversibility of the redox waves in **5** and **6** suggest that the regeneration of the complexes after photocatalytic activity should be plausible, which prompted us to explore if they could be applied as photoredox catalysts.

Figure 1. Cyclic voltammograms for **6** in DCM solutions at different scan rates: under (a) an anodic and (b) a cathodic scan. The pink arrows indicate the scan directions, with vertical dashed lines representing the initial potentials for each scan.

Next, UV-visible-NIR spectroscopy was employed to study the absorption characteristics of the Ar-BIAN ligands **1-3** (Figure S18) and the complexes **4-6** (Figure 2a), in order to explore their utilization as photocatalysts. Complexes **4-6** displayed panchromatic properties since their optical absorptions extend into the NIR region up to about 1000 nm. To evaluate if the structure of the Cu complex changed when dissolved in a coordinating solvent such as DMF, the Cu K-edge X-ray absorption near-edge structure (XANES) spectra were obtained under ambient temperature for **6** at the XAFCA beam-line of the Singapore Synchrotron Light Source.²³ The XANES spectra displayed almost identical profiles in both the solid state and after dissolution in DMF (Figure S20), implying that the oxidation state and coordination environment of Cu remained unchanged even when **6** was dissolved.

Figure 2. (a) Electronic absorption spectra of **4** in DMF, and **5** and **6** in DCM; (b) steady state emission spectra of **6** in DCM, with the excitation wavelengths labelled in different colors.

Like most previously documented homoleptic Cu^I Ar-BIAN complexes,^{16b, 16c, 18a} no steady-state emission signal was detected for **4** and **5**. On the contrary, the steady-state luminescence spectra of **6** contained emission signals as illustrated in Figure 2b. Upon excitation between 430 to 460 nm, **6** displayed an emission band at 510 nm, and a weaker broad shoulder around 615 nm. The emission at 510 nm is likely attributed to a ligand-centered emission since **3** shows a similar signal (Figure S21b) with comparable lifetimes (*vide infra*). This is further corroborated by previous reports of Ar-BIAN metal complexes with similar weak luminescence attributed to intraligand fluorescence.^{17b, 18b} On the other hand, the broad band at 615 nm arises from luminescence via the MLCT excited state, which has been corroborated by the transient absorption and emission spectra obtained after 580 nm photoexcitation (Figure S24). Since the ligand **3** does not absorb at 580 nm and Cu^I is a d^{10} system, the absorption maximum at 580 nm in **6** is likely due to MLCT. The absorption by **6** beyond the emission shoulder at 615 nm is probably due to

non-emissive low-lying states localized at the electron-withdrawing naphthyl part of the Ar-BIAN ligand.^{16c} The longer-lived emission signal for **6** could arise from the presence of the electron-withdrawing and heavy atom, Br, on the acenaphthene ring. The Br localizes the photoexcited negative charges on the acenaphthene motif, thus improving spatial separation of the LUMO from the HOMO on Cu, while the heavy atom facilitates intersystem crossing, both of which lead to longer-lived radiative excited states.

Despite these favorable modifications, ligand **3** and complex **6** have emission quantum yields, ϕ_r , of only 1.2×10^{-3} and 2.6×10^{-4} respectively, with [Ru(bpy)₃](PF₆)₂ (bpy = tris(bipyridine)) in DCM ($\phi_r = 0.029$) used as a reference.²⁴ The excitation wavelength used for all the samples was 460 nm, while the integrated area was from 480 – 800 nm. Therefore, the emission quantum yield measured for **6** is the total emission feature consisting of both the emission at 510 nm and the weak shoulder at 615 nm. The low quantum yield of **6** is consistent with the fact that only a small fraction of the MLCT transitions are emissive, while there are lower energy non-emissive states in the NIR region. Although **4** also has a Br atom at the same position on the ligand as **6**, quenching due to exciplex formation with DMF might have rendered it non-photoluminescent.²⁵ A strongly binding, polar solvent such as DMF was required for **4** due to its poor solubility in non-coordinating solvents such as DCM.

Considering the favorable photoluminescent property of **6**, we decided to ascertain the excited state lifetime of the Cu^I complexes using nanosecond time-resolved optical spectroscopy to evaluate their suitability for photoredox catalysis. For the transient absorption and emission spectroscopy (TAS and TES respectively) experiments, the samples were irradiated with UV or visible light pulses of 5 – 8 ns durations. They were then probed by an electronically synchronized broadband xenon lamp beam before and after the pulses, and the intensity of the transmitted light was detected. In all the TAS data in this manuscript, the logarithm of the ratio (ΔA) of the transmitted light intensity from the probe beam *after* laser excitation to the transmitted intensity *before* laser excitation are presented. The change in optical density (ΔOD) of the transient photoexcited state relative to the ground state thus indicates increased absorption (positive ΔA) or reduced absorption/emission (negative ΔA). The time evolution of the transient absorption signals of **6** are presented in Figure 3, while those of **4** and **5** are in Figures S21a and S22. Compound **6** was excited with 460 nm laser pulses to obtain the excited state absorption and emission difference spectra after increasing time intervals as labelled by the different colors in Figure 3.

Figure 3. Nanosecond transient (a) absorption and (b) emission spectra of **6** in DCM, at increasing delay times of 20 (red), 40 (blue), 60 (green), and 80 (orange) ns after the 460 nm pulse.

An absorbance (ΔA) bleach centered at ~ 550 nm was observed (Figure 3a), indicating a ground state bleach of **6** superimposed on the excited state emission, as confirmed by the TES obtained between 20 to 80 ns (Figure 3b). The latter concurs with the steady-state emission spectra. Since the lifetimes of **6** were in the same order of magnitude as the time-resolution of our TAS experiments, time-correlated single photon counting (TCSPC) measurements with higher resolution down to 100 ps were conducted on **6** in DCM at 510 nm with 466 nm irradiation (Figure 4a). The photoluminescence decay of **6** can be fitted with a bi-exponential decay function with a faster component (3.6 ± 0.1 ns) that can be attributed to relaxation of the MLCT excited state of Cu^{I} . A slower component (11 ± 0.3 ns) is similar to the luminescence lifetime of the ligand, **3** (9.9 ± 0.4 ns, Figure S25). To determine only the lifetime of the MLCT state, a longer excitation wavelength of 562 nm where **3** did not absorb was used to photoexcite **6**. From the time-resolved photoluminescence at 620 nm, we obtained a single exponential decay fit with a lifetime of 2.0 ± 0.1 ns (Figure 4b), which is similar to the faster decay component observed in Figure 4a. Compared to the ultrafast optical spectroscopic studies previously reported, when some *heteroleptic* Ar-BIAN complexes were excited at higher energies, the transient optical spectrum was mainly dominated by a triplet ligand-centered relaxation.¹⁸ Therefore, the photoluminescence decay of **6** consists of two contributions. The observation of more than one emission constituent is not uncommon. As described by Casadonte *et al.*, in a rigid matrix, two emission signals were observed from a triplet intraligand (^3IL) and a triplet charge transfer (^3CT) excited state.²⁶

Figure 4. Photoluminescence decay of **6** in DCM. (a) The sample was excited at 466 nm and the photoluminescence was recorded at 510 nm. The red line represents the bi-exponential fit for the decay signal. (b) The sample was excited at 562 nm and the photoluminescence was recorded at 620 nm. The red line represents the single exponential fit for the decay signal.

Although the excited state lifetime of **6** (~ 4 ns) is shorter than those of the prototypical ruthenium-based photosensitizers such as $\text{Ru}(\text{bpy})_3^{2+}$ (488 ns in DCM),²⁴ it is still one of the longest-lived *panchromatic chromophores* among first-row transition metal complexes. For example, the excited state lifetime of the longest-lived iron-based photosensitizer is 100 ps,²⁷ while the rest are on the order of tens of picoseconds or shorter.²⁸ The excited state lifetime of **6** is short compared to the state-of-the-art Cu^{I} -based photosensitizers,²⁹ an example being $[\text{Cu}(\text{dsbtmp})_2]^+$ (dsbtmp = 2,9-di(sec-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline), which has an excited state lifetime ranging from 1.2 to 2.8 μs .^{29a} However, $[\text{Cu}(\text{dsbtmp})_2]^+$ is not panchromatic and absorbs only up to 520 nm, and also has a more costly, multi-step ligand synthetic route.^{29a}

Visible-light assisted ATRA reaction. With a photoexcited lifetime in the nanosecond regime, the unimolecular recombination rate of **6** is now longer-lived than diffusion-controlled reactions, giving us the opportunity to apply it in electron transfer processes such as photoredox catalysis. As a proof-of-concept, the ability of **6** to photocatalyze carbon-carbon bond formation *via* ATRA³⁰ between styrenes and tetrabromomethane (**9**) was investigated. Table 1 summarizes the ATRA reaction carried out using visible light.

Table 1. ATRA Reaction Photocatalyzed by **6**^a

Alkene	Product	% conv. ^b	Yield (%) ^c
1		100	74
2 ^d		30	<3
3 ^e		18	<1
4 ^f		100	7
5 ^g		100	55
6 ^h		68	28
7		100	75
8 ^g		100	55
9		53	44
10 ⁱ		100	75
11 ^g		100	30
12		100	44 ^j
13		100	32 ^{j, k}

^a Conditions: Alkene (1 eq.), CBr_4 (1 eq.), **6** (0.60 mol%) in DCM (1.0 mL), irradiation with two white LEDs (48 W each) for 24 h. ^b The % conversion of styrene was monitored by ^1H NMR spectroscopy. ^c The ^1H NMR yields were calculated by comparing against 1,1,2,2-tetrachloroethane as the internal standard. ^d Dark reaction. ^e No catalyst. ^f $[(\text{CH}_3\text{CN})_4\text{Cu}]\text{PF}_6$, no Ar-BIAN ligand. ^g Ar-BIAN ligand (0.6 mol%) only as the catalyst. ^h Irradiation by one LED upon installation of a longpass filter to cut off wavelengths below 490 nm. ⁱ Reaction time: 48 h. ^j The desired ATRA product was not isolated due to hydrolysis upon purification. ^k The NMR spectra of both the crude reaction mixture and the hydrolyzed product have been presented as Figures S35-37.

Upon irradiation with two white light LEDs and a low catalyst loading (0.60 mol%), the reaction proceeded with moderate NMR yields (32-75%), calculated by comparison with an internal standard in the NMR. Notably, we could conduct the photocatalytic reaction even when light of shorter wavelengths (≤ 490 nm) was cut off (entry 6), highlighting an advantage over longer-lived Cu photosensitizers such as $[\text{Cu}(\text{dsbtmp})_2]^+$. The control experiments (entries 2-4) showed minimal product

formation. Although irradiation with the Ar-BIAN ligand alone led to some products, the yields and selectivities were poorer (entries 5, 8, and 11), especially for the slower substrate. Electron-donating methyl (entry 12) and electron-withdrawing chloro and cyano (entries 7 and 10) were all tolerated. In addition, fused rings such as naphthalene (entry 13) were also compatible for this reaction.

Evaluating the Reaction Pathway of the Photocatalyzed ATRA Reaction. The products obtained agree with those from previously reported Cu^{I} -photocatalyzed ATRA reactions and other photoredox catalytic reactions where a radical (ion) is often proposed as the key intermediate.^{19c, 19d, 31} As shown in Scheme 2, we propose that there are two possible reaction pathways. In the closed photoredox catalytic cycle, the photoexcited Cu^{I} complex transfers an electron to **9** to generate a CBr_3 radical (**10**), which adds to the styrene. The resulting intermediate (**11**) is then oxidized by the Cu^{II} species (**8**) to regenerate **6**, while intermediate **12** combines with Br^- to form the desired product (**13**). On the other hand, as shown by the pathway indicated by the blue arrows in Scheme 2, another plausible mechanism involves radical chain propagation, whereby **11** reacts with CBr_4 to generate **13**, while regenerating **11**.

In order to distinguish between the closed photoredox catalytic cycle (red arrows) and the chain propagation cycle (blue arrows) in Scheme 2, we conducted a series of experiments to evaluate if **6** was behaving as a radical initiator.

Scheme 2. Proposed Mechanism of the Cu^{I} -Photocatalyzed ATRA of CBr_4 and Styrenes

Firstly, the progress of the reaction was monitored in alternating periods of irradiation and darkness. We observed that **13** was formed only when the reaction mixture was under irradiation as shown in Figure 5. To confirm whether this trend was due to a rapidly terminating chain process or the absence of chain propagation, quantum yield measurements were performed. The reaction quantum yield (ϕ) was calibrated against

Figure 5. A “light-on light-off” experiment on the ATRA reaction.

the photodecomposition of potassium ferrioxalate as the chemical actinometer. The overall quantum yield for the formation of **13** was found to be $\phi = 3$, indicating that for every photon absorbed by **6**, three equivalents of **13** were produced. Yoon and coworkers demonstrated that a reaction with ϕ greater than one would be consistent with a radical chain propagation.³² Therefore, we propose that **6** may be undergoing a short chain propagation cycle, more consistent with the pathway illustrated by the blue arrows in Scheme 2.

To detect radical intermediates during the catalytic cycle, the stable radical (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) was employed as a radical trap. We observed inhibition of the ATRA reaction since none of desired product was detected in the ^1H NMR spectrum (Figure S41). A side reaction leading to the formation of benzaldehyde (green circles) was observed instead of the trapped intermediate. To obtain further insights into the proposed mechanism, UV-visible spectra of the different components (**6**, styrene, and CBr_4) were collected at 1 h intervals (Figure 6). The UV-visible spectra of the reaction mixture containing only **6**, and both **6** and styrene showed minimal decreases in the absorbance at 580 nm, as illustrated in Figure S42. However, in the absence of styrene, the λ_{max} at 580 nm decreased rapidly (Figure 6a), suggesting that **6** quickly depleted, due to the lack of **11** to reduce **8** back to **6**. Therefore, after irradiating for 3 h, the MLCT band of **6** at 580 nm diminished, which was then followed by the formation of a new species at λ_{max} of 470 nm, preventing the completion of the catalytic cycle. In contrast, when styrene was present, the absorption band at 580 nm persisted (with modest reduction due to photobleaching) even after 5 h of irradiation (Figure 6b), which indicated the regeneration of **6** during the catalytic cycle via the reduction of the Cu^{II} in **8**.

We then attempted to identify **8** formed during the photoredox reaction by carrying out spectroelectrochemical measurements on **6**.³³ The UV-visible spectra obtained in Figure 6c shows the changes in the absorption bands of **6** upon its oxidation when a potential of more than 0.50 V (versus Fc^+/Fc) was applied. This potential was chosen since the CV experiments indicated that **6** had a one-electron oxidation wave at 0.29 V (Table S11). The absorption band at 580 nm was diminished whereas the band at 434 nm grew slightly after **6** was oxidized electrochemically (black to orange, Figure 5c). Remarkably, the final spectrum after one-electron oxidation (orange line, Figure 6c) appears to be very similar to the intermediate from the reaction between **6** and CBr_4 after 3 h (grey dashed line, Figure 6c,

Figure 6. UV-visible spectra of the reaction mixture containing (a) only **6** and CBr_4 , and (b) **6**, styrene, and CBr_4 at 1 h intervals. UV-visible spectra of **6** obtained by spectroelectrochemical measurements (c) when an oxidative potential is applied at more than 0.50 V versus Fc^+/Fc with the time points at 0 (black), 5 (red), 10 (green), 15 (blue), and 20 (orange) min; and (d) when a reductive potential of -0.20 V versus Fc^+/Fc is applied on the orange sample in (c) with the time points at 0 (orange), 3 (green), 6 (red), and 9 (black) min. In both (c) and (d), the intermediate from the reaction between **6** and CBr_4 after 3 h (grey dashed line) has been reproduced and normalized from (a).

reproduced from Figure 6a). When a reductive potential at -0.20 V was applied, the characteristic absorption at 580 nm was recovered, while the band at 434 nm decreased slightly to regenerate the original UV-visible spectrum of **6** (Figure 6d). Therefore, we postulate that **8** in the photoredox catalytic cycle could be the one-electron oxidized intermediate obtained during the spectroelectrochemical experiments.

Attempts were made to isolate and identify **8** by irradiating a mixture of **6** and a stoichiometric equivalent of CBr_4 . Brown precipitate was collected, but single crystals could not be obtained after multiple recrystallization attempts. Therefore, the UV-visible spectrum of the brown precipitate was obtained and compared to the chemically oxidized **6**, which was formed by mixing tris(2,4-dibromophenyl)aminium hexafluoroantimonate ('Magic Green') with **6** to obtain a Cu^{II} product (**14**). However, as illustrated in Figure 7, the UV-visible spectra of **8** and **14** are patently distinct. Complex **14** consists of an octahedral Cu^{II} center with acetonitrile (ACN) molecules bound in the axial positions. A fully refined structure of **14** was not obtained due to the presence of disorder in the location of the Br atoms and also disordered molecules. ACN was necessary for the recrystallization of **14** due to its poor solubility in less polar solvents.

Figure 7. (a) ORTEP from the single crystal X-ray diffraction experiment of **14**. The structure of **14** has not been fully refined due to severe disorder in the position of the Br atoms. A model with equal occupancy of the Br as Br1 and Br1a provided adequate refinement, but the disordered solvent molecules could not be refined any further. The two counter-anions and the hydrogen atoms have been omitted for clarity. (b) UV-visible spectra comparison between **8**, **14** after stirring with two equivalents of LiBr, and **14**.

As anticipated for octahedral and distorted octahedral Cu^{II} complexes with ACN bound,³⁴ the higher symmetry and orbitally forbidden nature of the d-d transitions of **14** result in weak visible absorption bands. On the other hand, the optical absorption bands of **8** are dramatically red-shifted with intensity even in the NIR region up to around 1000 nm. Therefore, we anticipate that **8** is unlikely to have a distorted octahedral geometry similar to **14**, but may have a lower symmetry or could have at least one Br^- bound. This has been supported by Olshin and co-workers, who reported that Cu^{II} complexes in ACN, with increasing equivalents of added Br^- , demonstrated a marked red shift in their d-d absorption bands and a decrease in coordination number from six.³⁴ To further corroborate this proposed identity of **8**, we added 2.0 equivalents of LiBr to **14**. The steady-state absorption spectrum is displayed in black in Figure 7b. Gratifyingly, this product now shows red-shifted absorption bands in the NIR region, intermediate between **8** and **14**, although it is still not coincident with **8**. Thus, we propose that **8** may be a Cu^{II} complex with CBr_3 or Br^- coordinated, with a lower square pyramidal or trigonal bipyramidal symmetry. Additional in situ X-ray absorption spectroscopic experiments with photolysis will be necessary, which is beyond the scope of this report.

3. CONCLUSION

In conclusion, we have developed and characterized several panchromatic Ar-BIAN Cu^{I} complexes, one of which displays *radiative* recombination rates that are longer-lived than diffusion control. Notably, we demonstrated that this luminescent Ar-BIAN Cu^{I} complex is capable of photocatalytically facilitating ATRA carbon-carbon bond formation reactions under ambient conditions. Our insights into the reaction pathway of the photocatalytic cycle indicate that exciplex formation by coordination of photogenerated radicals may be occurring. Consequently, in addition to the introduction of electron-withdrawing heavy atoms on the acenaphthene motif to increase the photoexcited lifetimes, more steric protection of the Cu^{I} center will be necessary in future generations of Ar-BIAN Cu^{I} complexes for them to become generally exploitable in solar energy harvesting and synthetic organic chemistry applications.

4. EXPERIMENTAL SECTION

Instrumental Details

The ^1H and ^{13}C spectra were recorded at room temperature on a Bruker AVANCE 400 MHz spectrometer. The ^1H and ^{13}C chemical shifts (δ reported in ppm) are referenced to the residual solvent signal(s). Elemental analyses were performed with an Elementar vario MICRO cube analyzer. High-resolution mass spectra (HR-MS) were obtained with a Q-TOF Premier LC HR mass spectrometer.

UV-visible spectroscopic measurements were performed using a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer. Photoluminescence decay profiles were recorded on a time-correlated single-photon counting (TCSPC) spectrofluorimeter (Fluorocube, Horiba Jobin Yvon) with a time resolution of 100 ps. The samples were excited at 466 nm using a pulsed diode laser (NanoLED-466 L, Horiba Jobin Yvon) and the photoluminescence decay signals were recorded at 510 nm. The transient absorption and emission measurements were performed using an Edinburgh Instruments model LP920 transient absorption spectrometer equipped with a pulsed Xe probe lamp in conjunction with a Nd:YAG laser (Continuum model Surelite II-10) as the excitation source. The laser pulse width is 5–8 ns and the repetition rate is 10 Hz. During transient absorption measurements, the pulses are synchronized with the LP920 system at a frequency of 1 Hz. The pulse energy used was between 6–23 mJ/pulse.

Electrochemical measurements

Cyclic voltammetry (CV) experiments were conducted using a Biologic SP-300 potentiostat with 1.0 mM solutions of each sample and 0.10 M of tetrabutylammonium hexafluorophosphate (TBAH) as the electrolyte. The measurements of **1** and **4** were conducted in DMF while the measurements of **2**, **3**, **5**, and **6** were conducted in DCM, each at a scan rate of 100 mV s⁻¹ in a glovebox. A standard three-electrode electrochemical cell was used with a glassy carbon working electrode (3 mm in diameter from BAS), a Pt wire as the counter electrode, and another Pt wire as the pseudoreference electrode. The potentials were calibrated by addition of ferrocene as an internal reference (0 V) after the CV measurements on the compound have been conducted to avoid obscuring signals from our samples. The data are reported relative to the ferrocenium/ferrocene redox couple (Fc^+/Fc). Before each experiment, the working electrode (glassy carbon) was polished using a polishing pad infused with a 0.05 μm alumina suspension, followed by sonication in DI water for 10 min, washed with methanol and acetone, before drying in air.

Spectroelectrochemical experiments

The spectroelectrochemical cell was assembled by fitting a customized three-electrode setup (Latech Scientific Supply Pte. Ltd. and Tianjin AIDA Hengsheng Science-Techonology Development Co., Ltd.) into a 1 mm-path length customized cuvette (Starna Scientific Ltd.). The spectroelectrochemical cell was connected to a Bio-Logic SP-300 potentiostat. The experiments were carried out at RT. The concentration of **6** used was 0.50 mM with 0.10 M of TBAH as the electrolyte in DCM. The three electrodes used consisted of a Pt mesh working electrode, a Pt wire as the counter electrode immersed in a Chloropore jacket containing a solution of *p*-benzoquinone (0.010 M) and TBAH (0.10 M), and another Pt wire as a pseudoreference electrode in a Chloropore jacket containing a solu-

tion of TBAH (0.10 M). The data are reported relative to the ferrocenium/ferrocene redox couple (Fc^+/Fc).

Emission quantum yield measurements

Radiative quantum yields, ϕ_r , were measured in DCM solutions. Each sample was prepared in a glovebox under a N_2 atmosphere. The ϕ_r values were obtained by comparing the photoluminescence intensities to $\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ and calculated using the following expression:

$$\phi_r = \phi_{\text{ref}} \frac{I}{A} \frac{A_{\text{ref}}}{I_{\text{ref}}}$$

where ϕ_{ref} is the known quantum yield of the reference compound. The photosensitizer $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ dissolved in DCM ($\phi_r = 0.029$) was used as the reference; I is the integrated fluorescence intensity and A is the absorbance at the excitation wavelength of the sample (no subscripts) and the reference compound (subscript *ref*).

Time-correlated single photon counting (TCSPC)

The errors corresponding to the fits of the transient signal lifetimes were determined via the principle of error propagation by calculating the root-mean-square deviation from the sum of squares of the uncertainties in each measured value. For each time-resolved measurement, the associated uncertainties included the spectrofluorimeter time-resolution, mass of samples, and volumes of samples. Hence, the error of the transient signal lifetime, $\delta\tau$, was calculated according to the following equation:

$$\delta\tau = \tau \sqrt{\left(\frac{\delta\tau_a}{\tau_a}\right)^2 + \left(\frac{\delta m_k}{m_k}\right)^2 + \left(\frac{\delta V_n}{V_n}\right)^2}$$

where τ = transient signal lifetime; $\delta\tau_a$ = uncertainty of the spectrofluorimeter time-resolution; δm_k = uncertainty of the mass of the dissolved **6**; δV_n = uncertainty of the n^{th} volume measurement, where n represents the n different volume measurements including stock solution and sample preparations.

General procedure for ATRA reaction catalyzed by **6**

A solution of alkene (0.13 mmol), CBr_4 (0.13 mmol), and **6** (0.60 mol%) in DCM (1.0 mL) was degassed using two freeze-pump-thaw cycles, refilled with N_2 , and irradiated with two white LEDs for 24 h. The reaction mixture was concentrated in vacuo. The ^1H NMR yields were calculated using the following formula: yield (%) = 100% $\cdot$ [$v(\text{product}) / v(\text{standard})$] $\cdot n$, where $v(\text{product}) / v(\text{standard})$ is the integral ratio of the corresponding ^1H NMR peaks and n is the ratio of the standard to starting material (in mol). Some of these organic compounds have been previously reported and we have verified the identity of our products by comparing our spectroscopic data with those from the references.

Reaction quantum yield measurements³²

The photon flux of the light source used for the reaction was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared and 2.0 mL of the solution was added to a cuvette and irradiated for 5 min. After irradiation, 0.35 mL of a 1,10-phenanthroline solution was added. After the solution was allowed to rest for 1 h, the absorbance of the solution at 510 nm was recorded. The absorbance at 510 nm of another sample that was kept in the dark was also recorded. The following expression was used for calculation:

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \varepsilon}$$

where V is the total volume (0.00235 L) of the solution, ΔA is the difference in absorbance of the irradiated and non-irradiated solutions at 510 nm, l is the pathlength (1 cm), and ε is the molar extinction coefficient at 510 nm ($1.11 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).^{32, 35} The photon flux can be obtained from the following equation:

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\phi \times t \times f}$$

where ϕ is the quantum yield of the ferrioxalate actinometer (1.01), t is the time of irradiation (300 s), and f is the fraction of light absorbed at $\lambda = 436 \text{ nm}$ (0.998). The photon flux was calculated (average of three experiments) to be $3.78 \times 10^{-10} \text{ einstein s}^{-1}$.

Radical trapping experiment

To detect any radical intermediates during the catalytic reaction, the stable radical (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) was employed as a radical trap. A solution of styrene (0.13 mmol), CBr_4 (0.13 mmol), **6** (0.60 mol%), and TEMPO (0.65 mmol) in DCM (1.0 mL) was degassed using two freeze-pump-thaw cycles, refilled with N_2 , and irradiated with two white LEDs for 24 h. The reaction mixture was concentrated *in vacuo* and analyzed by ^1H NMR spectroscopy to obtain the yields.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

Detailed synthetic procedures of the ligands, Cu^{I} complexes, and the ATRA products, their thorough characterization data, and essential crystallographic data. (PDF)

X-ray crystallographic data for **4** and **14** are deposited under CCDC 1848314 and 1866188 respectively. (CIF)

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Notes

The authors declare no competing financial interest.

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