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Copper(I) photosensitisers for antimicrobial photodynamic therapy: from solution studies to silica-immobilised composite materials

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Antimicrobial photodynamic therapy (aPDT) is an emerging approach to treat localised drug-resistant infections by generating reactive oxygen species with spatial and temporal control. Herein, we report the systematic assessment of six heteroleptic Cu(I) diimine-diphosphine photosensitisers of the type [Cu(N^N)(P^P)]$^+$ and their transition from solution studies to silica-immobilised composite materials (Cu(I)@SiO_2). Targeted ligand variations (steric bulk, polarity and π-extension) within a comparable coordination framework result in markedly different absorption and emission characteristics across the series. Antibacterial screening against representative Gram-positive (methicillin-resistant *Staphylococcus aureus*, MRSA) and Gram-negative (*Escherichia coli*) strains revealed no measurable activity against *E. coli* up to 100 μM, neither in the dark nor under irradiation. However, several complexes showed pronounced activity against MRSA with enhanced potency upon 405 nm irradiation. **Cubiipo** displayed the strongest light-dependent response (minimum inhibitory concentration, MIC_{light} = 6.25 μM, phototoxicity index >16), while **Cuphen** and **Cuneo** exhibited measurable dark activity in the low-micromolar range. Immobilisation on silica using an established adsorption protocol afforded Cu(I)@SiO_2 composite materials that retained light-enhanced antibacterial activity against MRSA (*e.g.* **Cubiipo@SiO_2** MIC_{light} = 0.62–1.23 mg mL^{-1}), albeit with reduced dark/light differences compared to the molecular complexes. These results demonstrate that small ligand modifications can cause strongly differentiated aPDT-relevant behaviour and that silica-immobilised Cu(I) photosensitisers offer a promising option for light-mediated surface disinfection/sanitation applications.

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Introduction

In the search for new treatment modalities against drug-resistant bacterial infections, antimicrobial photodynamic therapy (aPDT) has emerged as an attractive approach.[1–6] The use of light to trigger the generation of reactive oxygen species (ROS) with high spatiotemporal control enables localised, on-demand treatment.[7] Although this largely restricts aPDT to accessible infections, it offers several advantages over conventional antibiotics. In particular, the local generation of highly reactive species that damage multiple classes of biomolecules makes it difficult to build up resistance.[8] Indeed, no clinically relevant bacterial resistance to aPDT therapy has been reported to date.[9] Furthermore, for the treatment of localised infections both the photosensitiser (PS) and light can be applied locally, thereby reducing systemic exposure and potential side effects. Similar to the field of anticancer PDT, transition-metal-based photosensitisers have attracted increasing interest for aPDT.[10] While ruthenium(II)[11–15] and iridium(III)[16–18] complexes have been widely used, there is growing interest in more abundant first-row transition metals as PS candidates.[19–21] Recent progress in this area has been summarised by Gourdon *et al.*[22] and Rees *et al.*[23]

Recent studies have broadened the range of metal-based PDT and aPDT beyond molecular photosensitisers alone. In particular, silica-based platforms and metal-complex-functionalised nanomaterials have been explored as strategies to

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improve handling, local delivery, and biological performance of photosensitisers. Examples include photosensitiser-loaded or -functionalised mesoporous silica nanoparticles as well as Ru(II)-polypyridine-functionalised silica materials.[24–27] In parallel, photoactive first-row or related transition-metal systems, including Mn-, Cu-, Ni-, Zn- and Pd-based compounds, have been investigated for medicinal PDT and antimicrobial photodynamic applications.[28–32]

Copper(I) complexes have been explored for their biological activity in several studies, including clinical studies in humans for the treatment of amyotrophic lateral sclerosis.[33–35] In addition, a few classes of copper complexes with promising light-mediated activity have been described.[36–40] However, systematic investigations of Cu(I) complexes as photosensitisers for aPDT remain comparatively scarce.[41]

A notable benchmark was reported by Appleby *et al.*, who studied a heteroleptic diimine-diphosphine Cu(I) complex ($[Cu(neo)(xant)]^+$, with neo = 2,9-dimethyl-1,10-phenanthroline, xant = xantphos) and its immobilisation on silica.[41] Under 405 nm light irradiation, the silica-bound Cu(I) complex showed antibacterial activity against Gram-positive methicillin-resistant *Staphylococcus aureus* (MRSA) and Gram-negative *Escherichia coli* (*E. coli*) bacteria.[41] Against MRSA, the silica-bound complex exhibited low dark toxicity, while irradiation led to rapid and pronounced killing, reaching a 6-$\log_{10}$ reduction in colony forming units (CFU) after 2 h. The authors identified 5 mg mL^{-1} silica composite particles (corresponding to 11 μM of Cu complex per milligram of silica) as an optimal concentration.[41] A longer irradiation time was needed to kill *E. coli*, but even at higher PS loadings only modest CFU reductions were observed.[41] This trend is commonly attributed to the additional outer membrane of Gram-negative bacteria, which can hinder uptake and/or limit oxidative stress in the periplasm and cytosol.[42]

Based on the urgent need for novel antimicrobial strategies and the potential of aPDT to treat localised drug-resistant bacterial infections, we report a systematic assessment of six heteroleptic Cu(I) complexes and their silica-immobilised analogues for potential applications in aPDT (Fig. 1). The selected complexes share a common $[Cu(N^N)(P^P)]^+$ design, enabling a targeted variation of the diimine and/or diphosphine environment while maintaining a comparable coordination framework. Our workflow combines (i) photophysical characterisation relevant to aPDT (including singlet oxygen ($^1O_2$) generation in solution), (ii) antibacterial testing against representative Gram-positive and Gram-negative strains under defined light and dark conditions, and (iii) conversion into a heterogeneous format by immobilising the photosensitisers on silica ($Cu(I)@SiO_2$) to probe whether photodynamic activity can be retained (Fig. 1).

Together, these data provide a consistent framework for evaluating copper-based aPDT systems and for identifying practical parameters that guide future design and testing.



Fig. 1 Schematic workflow of the present study, which deals with the investigation of heteroleptic Cu(I) complexes for aPDT. Because light-triggered activity is multifactorial, antibacterial performance cannot be predicted using a single photophysical descriptor.

Results and discussion

Although a broad range of coordination environments around Cu(I) has been reported, including two-coordinate linear structures[43,44] and three-coordinate trigonal structures,[45,46] maintaining coordination and redox stability in polar or aqueous media can be challenging for low-coordinate Cu(I) complexes due to their open coordination sphere and increased electrophilicity.[47] In contrast, four-coordinate, pseudo-tetrahedral Cu(I) complexes are well established as robust solution-phase photosensitisers, particularly when kinetic stabilisation is achieved using chelating (bidentate) ligands.[48–51] A comprehensive overview of photoactive Cu(I) complexes has been provided by Moucheron and Evano.[47]

Besides the well-known homoleptic bis-diimine complexes of the general formula $[Cu(N^N)_2]^+$,[51,52] heteroleptic diimine-diphosphine complexes $[Cu(N^N)(P^P)]^+$ have emerged as a particularly attractive platform.[48,53,54] They often pair enhanced excited-state performance (*e.g.* stronger emission and longer excited-state lifetimes) with a modular ligand design.[48,49,55]

For the present study, six structurally related but strategically diversified heteroleptic diimine-diphosphine complexes of the type $[Cu(N^N)(P^P)]^+$ were selected (Fig. 2). Five complexes share the same xantphos diphosphine, while the phenanthroline-based diimine is varied to tune steric demand, polarity and π-extension. This library enables a comparative evaluation of the impact of targeted ligand modifications on photophysical parameters relevant to aPDT and subsequent antibacterial screening.

Within the xantphos series, both **Cubcp** and **Cuneo** feature 2,9-substitution at the phenanthroline core (Fig. 2), which is commonly used to suppress excited-state flattening, resulting in enhanced emission and prolonged excited-state lifetimes compared to the unsubstituted **Cuphen**.[50,56,57] **Cubcp** further carries 4,7-diphenyl substituents, which extend the π-system and can act as an additional "antenna", enhancing light absorption relative to **Cuneo**.[49,58] **CuPOP** is closely related to **Cubcp**, but bears a different P^P ligand (bis[(2-diphenylphosphino)phenyl]ether), which is more flexible.[53,59] This modification provides a second design parameter while keeping the diimine scaffold comparable.

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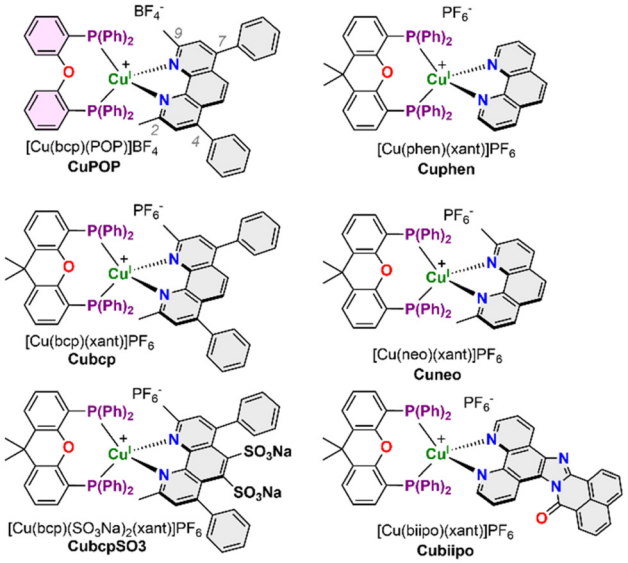


Fig. 2 Overview of the investigated Cu(I) complexes and their abbreviations. With phen = 1,10-phenanthroline, neo = neocuproine, bcp = bathocuproine, bcpSO3 = bathocuproine-5,6-disulfonate disodium salt, biipo = 16*H*-benzo-[4′,5′]-isoquinolino-[2′,1′:1,2]-imidazo-[4,5-*f*]-[1,10]-phenanthrolin-16-one, POP = bis[(2-diphenylphosphino)phenyl] ether, xant = xantphos.

To address further effects relevant to biological assays, **CubcpSO$_3$** introduces sulfonate groups at the periphery to increase polarity and solubility in aqueous media.[60,61] In parallel, **Cubiipo** incorporates a larger π-extended diimine ligand,[62,63] which is expected to affect solubility/aggregation behaviour and may also alter the local environment of ROS generation. Importantly, these structural variations were chosen to probe multiple factors beyond intrinsic photophysical properties, as antibacterial performance in aPDT is typically multifactorial and can also depend on solubility, aggregation, and interactions with biological media.

Synthesis of the copper complexes

In general, the heteroleptic $[Cu(N^N)(P^P)]^+$ complexes are commonly prepared *via* a one-pot, two-step procedure.[57,64] First, the P^P ligand coordinates to a $[Cu(MeCN)_4]^+$ precursor (MeCN = acetonitrile) yielding $[Cu(P^P)(MeCN)_2]^+$. In the second step, the final heteroleptic complex is obtained by slow, dropwise addition of the N^N ligand, typically at reduced temperature, to minimise ligand scrambling and the formation of homoleptic by-products.[59,65] With only minor variations, all six Cu(I) complexes were prepared in this manner, as reported previously.[60,62–66] The identity of the complexes used in this study was confirmed by ^{1}H NMR spectroscopy and HRMS, and the obtained data were consistent with the previously reported analytical data (see SI section 2 and Fig. S2–S7).[60,62–66]

Photophysical properties of the copper complexes in solution

Although all six selected Cu(I) photosensitisers share the same heteroleptic diimine-diphosphine architecture, they exhibit a wide range of absorption and excited-state properties (Table 1 and Fig. 3). Overall, the series spans short- to microsecond excited-state lifetimes and markedly different light-harvesting efficiencies, providing a suitable photophysical window for subsequent $^1O_2$ generation and aPDT screening. In deaerated acetonitrile, the parent **Cuphen** shows no distinct emission.[63] In contrast, **Cuneo** is only weakly emissive ($\lambda_{em,max} \approx 564$ nm, $\Phi_{em} \approx 0.86\%$), while the benchmark **Cubcp** features significant emission ($\lambda_{em,max} \approx 578$ nm, $\Phi_{em} \approx 1.35\%$) with a microsecond-scale emission lifetime of 0.31 μs.[65,66] Introducing ionic sulfonate groups to give **CubcpSO3**, which increases polarity, retains a similar absorption onset, but leads to a higher Φ_{em} under inert conditions ($\Phi_{em} \approx 6\%$) together with a longer τ_{em} (≈1.9 μs, in methanol).[60]

Table 1 Summary of the main photophysical properties of the investigated heteroleptic Cu(I) complexes in acetonitrile under inert conditions at room temperature

Complex	$\lambda_{abs,MLCT}$/nm ($\varepsilon/10^3$ M^{-1} cm^{-1})	$\lambda_{em,max}$/nm	ϕ_{em}	τ_{em}/ns	Ref.
CuPOP	384 (6)	590	0.027	990	67
Cubcp	387 (5.2)	578	0.0135	310	66
CubcpSO3[a]	390 (3.0)[b]	585	0.06	1891	60
Cuphen	380 (3)	504	—[c]	<10	62
Cuneo	378 (3)	564	0.0086	204	65
Cubiipo	406 (16.3)	556	—[c]	9.7[d]	62

[a] In methanol. [b] Extinction coefficients were determined within this study. [c] Below detection limit. [d] An additional long-lived dark state ($\tau \approx$ 2.6 μs) was reported.

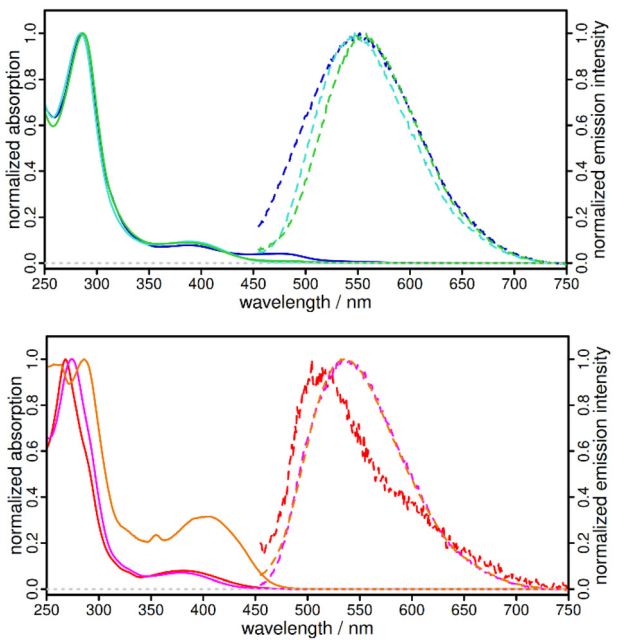


Fig. 3 Normalised absorption (solid line) and emission (dashed line) spectra of the Cu(I) complexes in acetonitrile. Top panel: **CuPOP** (blue), **Cubcp** (cyan) and **CubcpSO3** (green). Bottom panel: **Cuphen** (red), **Cuneo** (magenta), **Cubiipo** (orange). All emission spectra were recorded upon excitation at 400 nm.

Within the series, targeted steric shielding (*e.g.* 2,9-substitution) and π-extension act as additional design handles to tune light harvesting and excited-state behaviour. For example, in inert acetonitrile the π-extended **Cubiipo** displays a much higher extinction coefficient ($\lambda_{abs,MLCT} \approx 406$ nm, $\varepsilon \approx 16.3 \times 10^3$ M^{-1} cm^{-1}) compared to Cubcp ($\lambda_{abs,MLCT} \approx 387$ nm, $\varepsilon \approx 5.2 \times 10^3$ M^{-1} cm^{-1}), highlighting enhanced visible-light absorption within the series.[62] At the same time, **Cubiipo** is only very weakly emissive ($\lambda_{em,max} \approx 556$ nm), while a longer-lived dark state ($\tau \approx 2.6$ μs) has been reported.[62,63] Finally, the POP-based analogue **CuPOP** provides a useful comparison where the diimine is kept similar, while the diphosphine backbone is changed. This results in $\lambda_{em,max} \approx 590$ nm, $\Phi_{em} \approx 2.7\%$, and $\tau_{em} \approx 0.99$ μs, highlighting that the P^P ligand offers an additional option to tune the excited-state properties.

Collectively, the data demonstrate that the selected Cu(I) photosensitisers cover a broad range of the photophysical window in terms of absorption strength, emission efficiency and excited-state lifetimes, making them well suited for subsequent biological studies.

$^1O_2$ generation of the copper complexes in solution

For aPDT, singlet oxygen ($^1O_2$) is a key cytotoxic ROS and is commonly used as an operational readout for excited-state triplet sensitisation by molecular photosensitisers.[1,7,68] Accordingly, we quantified $^1O_2$ formation *via* its characteristic near-infrared phosphorescence at ≈1275 nm (ref. 69 and 70) in aerated deuterated acetonitrile (CD_3CN), which can enhance $^1O_2$ detection due to its longer lifetime.[71]

Under 400 nm excitation, all six Cu(I) complexes photosensitise singlet oxygen and give singlet oxygen quantum yields (ϕ^1O_2) spanning from 0.011 to 0.376 (Fig. 4 and Table 2). **CuPOP**, **Cubcp**, **CubcpSO3** and **Cuneo** exhibit the highest ϕ^1O_2 values of 0.333, 0.360, 0.376 and 0.306, respectively. **Cubiipo** delivers a moderate ϕ^1O_2 of 0.195. In contrast, the parent compound **Cuphen** shows the weakest NIR emission with a very low ϕ^1O_2 of 0.011. These results confirm that all complexes generate singlet oxygen in solution and that the ligand variation tunes the oxygen-sensitising efficiency.

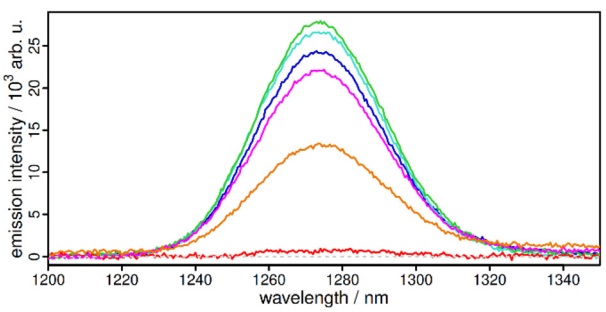


Fig. 4 Singlet oxygen emission generated by the heteroleptic Cu(I) complexes **CuPOP** (blue), **Cubcp** (cyan), **CubcpSO3** (green), **Cuphen** (red), **Cuneo** (magenta) and **Cubiipo** (orange) in aerated deuterated acetonitrile solution excited at 400 nm. Dashed grey line represents the baseline.

Table 2 Singlet oxygen quantum yields ϕ^1O_2 of the Cu(I) complexes in aerated deuterated acetonitrile, excited at 400 nm, and observed rate constants k_{obs} for the DPF photooxidation in aerated acetonitrile

Complex	ϕ^1O_2 [a]	$k_{obs}/10^{-3}$ min^{-1} [b]
CuPOP	0.333	0.9
Cubcp	0.360	1.1
CubcpSO3	0.376	3.2
Cuphen	0.011	0.2
Cuneo	0.306	0.6
Cubiipo	0.195	10.9

[a] Relative to phenalenone ($\phi^1O_2 = 1$ in CD_3CN).[72] [b] For calculation, see SI section 1 and eqn (S2), (S3).

To complement the direct NIR method, we also benchmarked $^1O_2$-mediated photooxidation of 2,5-diphenylfuran (DPF) to *cis*-1,2-dibenzoylethylene (DBE) in aerated acetonitrile (Fig. S11–S13).[66,68] Because this transformation proceeds *via* at least one transient peroxidised intermediate,[66,68] DPF decay and DBE growth were analysed using a mechanistic pre-equilibrium model, from which an observed rate constant k_{obs} was derived (SI, eqn (S2) and (S3)). The resulting k_{obs} values (Table 2) track the NIR-derived ϕ^1O_2 only weakly across the series, consistent with the broadband irradiation conditions (λ > 400 nm) and the multi-step reaction kinetics. Notably, **Cubiipo** shows the highest k_{obs} despite only moderate ϕ^1O_2, which can be rationalised by its substantially stronger absorption above 400 nm. Overall, the DPF photooxidation provides a complementary and indirect proof for $^1O_2$ generation under broadband irradiation (λ > 400 nm) and demonstrates the ability of these Cu(I) complexes to produce $^1O_2$, which is relevant for the subsequent antibacterial experiments.

Immobilisation of the copper complexes on silica

To convert the Cu(I) photosensitisers into a heterogeneous format for aPDT studies, all complexes were immobilised on silica using a well-established adsorption protocol reported for related Cu(I) systems.[41] In a typical preparation, 250 mg of silica (silica gel 60 M, particle size 0.04–0.063 mm) were suspended in acetonitrile (10 mL) and treated with 5 mg of the respective Cu(I) complex (see SI, section 1 for further details). Under argon, the suspension was gently stirred for 24 h in a rotary evaporator without a magnetic stir bar to prevent mechanical silica abrasion. The solid was then collected and washed repeatedly with acetonitrile until the supernatant was colourless, and finally dried under high vacuum for 7 h to afford the Cu(I)-loaded silica material (Cu(I)@SiO_2). Representative Cu(I)@silica samples were analysed using ICP-OES, which revealed a comparable Cu loading of 0.26–0.58 mg Cu per g silica (0.026–0.058 wt% Cu, Table S1).

Photophysical properties of the immobilised copper complexes

Upon immobilisation on silica (Cu(I)@SiO_2), the MLCT absorption maxima remain essentially the same as in solution (Fig. S8), with only the SO_3-substituted complex **CubcpSO3**

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Table 3 Comparison of the MLCT absorption and the emission properties of the Cu(I) complexes in acetonitrile solution and immobilised on SiO_2

	In solution		On SiO_2	
Complex	λ_{abs}/nm	λ_{em}/nm	λ_{abs}/nm	λ_{em}/nm
CuPOP	384	590	385	≈550
Cubcp	387	578	387	≈550
CubcpSO3	390	585	401	≈550
Cuphen	380	504	375	(Very weak)
Cuneo	378	564	376	(Very weak)
Cubiipo	406	556	410	≈510

exhibiting a ≈10 nm redshift (Table 3). This indicates that the Cu(I) chromophores largely preserve their MLCT absorption characteristics upon adsorption, consistent with the retained broad MLCT bands typically observed for immobilised Cu(I) photosensitisers.[60] Emission bands on SiO_2 are markedly broadened (Fig. S9), and the inherently weak luminescence of the phen- and neo-based complexes **Cuphen** and **Cuneo** renders their signals indistinguishable from the bare support. Such broadening and signal loss are consistent with heterogeneous local environments and additional non-radiative deactivation pathways in the solid state.[73] Overall, immobilisation largely preserves the MLCT absorption positions while substantially altering the emission signatures.

Biological properties of the copper complexes in solution

Next, the antibacterial properties of the Cu(I) photosensitisers against two representative bacterial strains, namely MRSA (Gram-positive)[74] and *E. coli* (Gram-negative) were evaluated. Briefly, bacteria were grown as an overnight culture, re-diluted the next morning and grown until mid-log phase before addition to plates together with the serially diluted copper complexes. To assess light-dependent activity, the 96-well plates containing freshly added compound were irradiated using an Atlas Photonics LUMOS BIO irradiator, followed by overnight incubation.[74] Bacterial growth was quantified by optical density measurement utilizing a plate reader.[74]

Initially, three excitation windows (600, 505 and 405 nm) were screened. No measurable light-enhanced antibacterial effect was observed at 600 and 505 nm, which is in accordance with the absorption behaviour of these complexes (Table 1 and Fig. 3). Therefore, 405 nm irradiation was used for all subsequent experiments. An irradiation time of 10 min was found to be a practical compromise between light dose and assay throughput. No significant antibacterial activity was observed against the Gram-negative *E. coli* up to the highest tested concentration (100 μM) under either dark or light conditions (Table 4). This behaviour is consistent with the well-known increased tolerance of Gram-negative bacteria towards many photosensitisers,[41,75] which is commonly attributed to their additional outer membrane barrier.[40,76]

In contrast, a different activity profile was observed for the Gram-positive MRSA. Under dark conditions, **Cuphen** and **Cuneo** showed significant growth inhibition in the low micromolar range (6.25 μM), whereas **CubcpSO3** displayed only moderate activity and **Cubcp**, **Cubiipo** and **CuPOP** were inactive up to 100 μM (Table 4). Upon 405 nm irradiation, all complexes except **Cubcp** exhibited enhanced activity, yielding low-micromolar MIC values for **CubcpSO3**, **Cubiipo**, **Cuphen** and **Cuneo**. **Cubiipo** showed the most pronounced light response with a phototoxicity index (PTI = MIC_{dark}/MIC_{light}) > 16.

To exclude contributions from potentially uncoordinated ligands, key ligands used in complex synthesis were tested under identical conditions (see Table S3). No significant antibacterial activity was observed for these ligands up to 100 μM, supporting that the antibacterial effects observed for the Cu(I) complexes arise from the coordination compounds rather than from the ligands.

To evaluate potential off-target effects, the cytotoxicity of the Cu(I) complexes against human embryonic kidney cells (HEK293T) and haemolysis in human red blood cells was assessed.[77] Only **CubcpSO3** showed detectable haemolysis within the tested range, causing 10% haemolysis (HC_{10}) at 78.8 ± 12.0 μM, whereas all other compounds displayed HC_{10} values >200 μM (Table 4). In contrast, all complexes exhibited measurable cytotoxicity towards HEK293T cells, with **Cuphen**, **Cuneo** and **CuPOP** showing CC_{50} values in the low micromolar range (≈1–4 μM), whereas **Cubcp**, **CubcpSO3** and **Cubiipo** displayed higher CC_{50} values (≥11 μM, Table 4).

As the molecular complexes did not exhibit sufficient selectivity towards bacteria over human cells, we therefore immobilised the Cu(I) photosensitisers on silica to explore a

Table 4 Minimum inhibitory concentrations (MICs, μM) of the Cu(I) photosensitisers against MRSA and *E. coli* under dark conditions and after 405 nm irradiation (10 min, 250 mW per LED). The phototoxicity index (PTI = MIC_{dark}/MIC_{light}) describes the light-driven activity enhancement. CC_{50}: concentration at which 50% of HEK293T cells are not viable (mean ± standard deviation). HC_{10}: concentration at which 10% haemolysis is observed in human red blood cells

	MIC (MRSA)/μM			MIC (*E. coli*)/μM			
Complex	Dark	Light	PTI	Dark	Light	CC_{50}/μM	HC_{10}/μM
CuPOP	>100	25	>4	>100	>100	4.1 ± 0.5	>200
Cubcp	>100	>100	1	>100	>100	11.4 ± 4.2	>200
CubcpSO3	25–50	6.25	4–8	>100	>100	18.3 ± 1.3	78.8 ± 12.0
Cuphen	6.25	3.125	2	>100	>100	1.0 ± 0.4	>200
Cuneo	6.25	3.125	2	>100	>100	1.1 ± 0.2	>200
Cubiipo	>100	6.25	>16	>100	>100	11.1 ± 5.1	>200

heterogeneous format for light-mediated surface disinfection/sanitation, inspired by Appleby *et al.*[41]

Biological properties of copper complexes on silica

The biological activity of the silica-immobilised Cu(I) complexes (Cu(I)@SiO_2) was evaluated in a dose-dependent manner analogous to the assays conducted for the molecular complexes (Table 5). Consistent with the behaviour of the free compounds, no antibacterial activity was detected against *E. coli* up to the highest tested particle concentration, neither in the dark nor upon irradiation.

Encouragingly, measurable antibacterial activity was observed against MRSA, and most composite materials showed enhanced growth inhibition upon 405 nm irradiation (Table 5), indicating a retained light response in the heterogeneous format. **Cubiipo@SiO_2** exhibited the most pronounced light-driven enhancement, in line with the trends observed for the corresponding molecular complex. Overall, the data demonstrate that immobilisation on silica preserves antibacterial photoactivity across the series, although the magnitude of the dark/light separation (phototoxicity index) is generally reduced in the particle format.

The stability of **Cubiipo@SiO_2** was interrogated in two separate ways. First, a stock suspension of the material in DMSO (123 mg mL^{-1}) was irradiated for 20 min with 405 nm light before the biological assays were repeated. The MIC of the composite material was found to remain unchanged under these conditions, suggesting that no significant photodegradation of **Cubiipo@SiO_2** occurs under these conditions. In a second experiment, we pre-incubated **Cubiipo@SiO_2** in Mueller-Hinton (MH) growth medium for 24 h at room temperature. Then bacterial cultures were diluted and added and the MIC was determined the next day. No change in MIC was observed compared to the original experiment, suggesting that the silica-immobilised complex remains largely intact under the applied biological testing conditions (Table S2).

ICP-OES analysis revealed comparable copper loadings across the immobilised materials of 0.26–0.58 mg Cu per g SiO_2 (0.026–0.058 wt% Cu; Table S1), indicating that differences in antibacterial performance are not dominated by major variations in Cu loading. Accordingly, MIC values for the composite materials are discussed on a particle-mass basis (mg mL^{-1}). The increased activity seen upon light irradiation mirrors the effect observed for the molecular complexes, suggesting that the Cu(I) photosensitisers largely retain their photoresponse upon immobilisation. Nevertheless, the phototoxicity index (MIC_{dark}/MIC_{light}) was reduced to ≈2–8. Taken together, the observation of light-enhanced antibacterial activity for Cu(I)@SiO_2 materials supports their potential as heterogeneous photosensitisers for local disinfection and surface sanitation applications, where recovery and re-use of the photoactive material are desirable.

Table 5 Cu(I) complexes immobilised on SiO_2 and their activity against methicillin-resistant *Staphylococcus aureus* (MRSA). Minimum inhibitory concentration (MIC) values (mg mL^{-1}) of Cu(I)@SiO_2 composite materials against MRSA under dark conditions and after 405 nm irradiation (10 min, 250 mW per LED)

	MRSA [mg mL^{-1}]		
Immobilised complex	Dark	Light	PTI
CuPOP@SiO_2	>4.92	2.46	>2
Cubcp@SiO_2	2.46–4.92	1.23–2.46	1–4
CubcpSO3@SiO_2	4.92	0.62–1.23	4–8
Cuphen@SiO_2	0.31–0.62	0.62–1.23	0.25–1
Cuneo@SiO_2	0.62–1.23	0.62–1.23	1–2
Cubiipo@SiO_2	2.46–4.92	0.62–1.23	2–8

Conclusions

In this work, we performed a comparative study of six heteroleptic Cu(I) diimine-diphosphine photosensitisers and transferred them from solution into silica-immobilised composite materials to probe their suitability for antimicrobial photodynamic therapy. Even within the closely related [Cu(N^N)(P^P)]$^+$ design, targeted ligand modifications (in terms of steric bulk, polarity and π-extension) resulted in markedly altered absorption/emission behaviour and, crucially, in strongly different antibacterial activities.

From the biological screening, two conclusions are particularly instructive. First, the set displays a clear bacterial strain dependence: none of the Cu(I) compounds showed measurable activity against *E. coli* under the applied conditions, whereas several complexes exhibited pronounced activity against MRSA, which was enhanced upon 405 nm light irradiation. This underlines that, for such Cu(I)-based aPDT systems, Gram-status and the associated barriers remain a decisive factor for efficacy and should be considered early when selecting target applications and assay conditions. Second, the data indicate that antibacterial performance is multifactorial and cannot be rationalised by a single photophysical property (*e.g.* excited-state lifetime) alone. The observed differences across the series emphasise the importance of evaluating not only intrinsic excited-state properties, but also factors such as solubility, polarity and biological interactions when developing new Cu(I) photosensitisers.

A key practical outcome is that immobilisation on silica preserves light-enhanced antibacterial activity in the heterogeneous format. Additional control experiments further indicate that the composite materials are stable to both photodegradation and under biological testing conditions. Although the dark/light differences generally decrease compared to the molecular complexes, the retention of photoactivity demonstrates that Cu(I) photosensitisers can be implemented as recoverable composite materials. This provides a realistic direction for Cu(I)-based aPDT where re-use and handling in aqueous media are desirable, for example in local disinfection or surface sanitation scenarios.

Overall, this study establishes a coherent workflow that links molecular Cu(I) photosensitiser design, solution photophysics and particle immobilisation with antibacterial activity.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article are included in the supplementary information (SI). Supplementary information: detailed experimental procedures, characterisation *via* ^{1}H-NMR and HRMS spectra as well as additional photophysical characterisation (solution and silica-immobilised samples, including $^{1}O_2$ data), and full biological assay methods and results (MIC screening, cytotoxicity and haemolysis), along with supporting tables and figures. See DOI: https://doi.org/10.1039/d6dt00707d.

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