Showcasing research from Laboratoire SPCMIB, Université de Toulouse 3, France, with collaboration from Institut für Funktionelle Materialien und Katalyse (Universität Wien, Austria), Laboratoire de Chimie de Coordination du CNRS (Toulouse, France), Narcotic Research Department, National Center for Social and Criminological Research (Giza, Egypt), Laboratoire SOFTMAT (Université de Toulouse 3, France) and IMU and UCSI University, (Kuala Lumpur, Malaysia).

1,2,3-Triazol-5-ylidene- vs. 1,2,3-triazole-based tricarbonylrhenium(I) complexes: influence of a mesoionic carbene ligand on the electronic and biological properties.

Three tricarbonylrhenium complexes incorporating a mesoionic carbene ligand were synthesized and compared with their 1,2,3-triazole-based analogues. This thorough study encompasses theoretical calculations, crystallography, electrochemistry, spectroscopy and microbiology. It appeared that one of the 1,2,3-triazole-based complexes displayed astounding photoluminescence efficiency and proved to be an excellent candidate for applications linked to aggregation-induced emission (AIE), while one of the triazolylidene-based complexes showed attractive antibacterial activity. This study highlights the potential of these new molecules for applications in the fields of photoluminescent and therapeutic materials.

Acknowledgements: Many thanks to Ms. Cécily Noaillac for the background photo.
1,2,3-Triazol-5-ylidene- vs. 1,2,3-triazole-based tricarbonylrhenium(i) complexes: influence of a mesoionic carbone ligand on the electronic and biological properties†

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The tricarbonylrhenium complexes that incorporate a mesoionic carbene ligand represent an emerging and promising class of molecules, the solid-state optical properties of which have rarely been investigated. The aim of this comprehensive study is to compare three of these complexes with their 1,2,3-triazole-based analogues. The Hirshfeld surface analysis of the crystallographic data revealed that the triazolylidene derivatives are more prone to π–π interactions than their 1,2,3-triazole-based counterparts. The FT-IR and electrochemical data indicated a stronger electron donor effect from the organic ligand to the rhenium atom for triazolylidene derivatives, which was confirmed by DFT calculations. All compounds were phosphorescent in solution, where the 1,2,3-triazole-based complexes showed unusually strong dependence on dissolved oxygen. All compounds also emitted in the solid state, some of them exhibited marked solid-state luminescence enhancement (SLE) effect. The 1,2,3-triazole based complex Re-Phe even displayed astounding photoluminescence efficiency with quantum yield up to 0.69, and proved to be an excellent candidate for applications linked to aggregation-induced emission (AIE). Interestingly, one triazolylidene-based complex (Re-T-BOP) showed attractive antibacterial activity. This study highlights the potential of these new molecules for applications in the fields of photoluminescent and therapeutic materials, and provides the first bases for the design of efficient molecules in these research areas.

Introduction

Over the past few years, 1,2,3-triazol-5-ylidenes have developed as a burgeoning subclass of mesoionic carbene ligands.1–3 Their modular synthesis and impressive sigma electron-donating properties have made them excellent ligands for transition metals. Many of the resulting Ir(III),4 Au(III),5 Ru(II) and Os(II)6 complexes exhibit very attractive physicochemical and biological properties. Curiously, rhenium(i) complexes are completely under-represented in these studies. An exception is the pioneering work of Sarkar and co-workers. By comparing seven tricarbonylrhenium(i) complexes, this group has established through detailed FTIR spectroscopy and electrochemical investigations that triazolylidene are indeed stronger electron donors than pyridine and triazoles,7 and that these phosphorescent complexes are excellent electrocatalysts for the reduction of CO2 to CO.8 If considering a broader perspective, the tricarbonylrhenium(i) N-heterocyclic carbenes (NHC) complexes have proven to be particularly valuable.9,10 Many of them are very efficient electrocatalysts and
The 2-pyridyl-1,2,3-triazole ligands were obtained via condensation of an azide derivative with 2-ethynylpyridine via a copper(1) catalyzed alkyne cycloaddition using classical click reaction conditions. Specifically, 2-(1-phenyl-1H-1,2,3-
triazol-4-yl)pyridine L-Phe was prepared following a described one-pot procedure, in which azidobenzene was generated in situ from iodobenzene. The o-tolyl derivative L-Tol was obtained in 77.5% yield starting from commercially available azido-2-methylbenzene. The benzoazole derivative L-BOP was prepared as previously described. Subsequent reaction of the ligands L-Phe, L-PBO and L-Tol in refluxing methanol in the presence of [Re(CO)5Cl] afforded respectively the previously described tricarbonylrhenium complexes Re-Phe50 and Re-BOP,59 as well as the new complex Re-Tol in 86% yield (Scheme 1).

Concerning the methylated triazolylidene precursors, the triazolium salt L-T-Phe was selectively synthesized from L-Phe with good efficiency, using a 3-step described procedure that involves the protection of the pyridine nitrogen as an N-oxide, followed by a methylation using Meerwein’s salt, and subsequent N-O bond cleavage in the presence of Mo(CO)6. Following a similar procedure, the triazolium salt L-T-Tol was obtained in 82.2% yield. However, this protocol failed when applied to the phenylbenzoazole pyridyl-1,2,3-triazole ligand L-T-BOP, as the methylation step only afforded an unusable mixture of compounds. Thus, direct methylation of the ligand in the presence of methyl trifluoromethane sulphonate (MeOTf) was performed, leading to a mixture of the expected product L-T-BOP in 25% yield, along with the undesired product N-MP-BOP resulting from the methylation of the pyridine nitrogen, which occurred in 43% yield (Scheme 2). The syntheses of the tricarbonylrhenium complexes from the triazolium salts7 were finally accomplished in the presence of an excess of NEt3 in refluxing toluene for more than two days, leading to Re-T-Phe, Re-T-Tol and Re-T-BOP in good yields (76%, 65.9% and 69%, respectively).

The new compounds were characterized by 1H and 13C NMR spectroscopy (Fig. S1–S8†), mass spectrometry (Fig. S9–S12†), single crystal X-ray diffraction analysis (vide infra) and FT-IR spectroscopy (Table S1 and Fig. S13, 14†). It is noteworthy that the IR stretching bands of all complexes were split when using the attenuated total reflectance (ATR) technique on microcrystalline powders, which is not the case in solution. This effect, already noticed by us for closely related complexes, was attributed to crystallinity.41,43 According to Sarkar’s group, the average of the νC=O values measured in solution accurately reflects the electron density on the metal center.7 In the present case, these values were found to be very close for the compounds of the same series, showing the weak effect of substitution. In contrast, they were significantly lower for the triazolylidene-based complexes (νC=O ~ 1939 cm⁻¹) than for their triazole-based counterparts (νC=O ~ 1951 cm⁻¹), indicating that the introduction of the mesoionic carbene leads to an increase in the overall donor capacity of the organic ligand, in good agreement with the literature.7 The purity of the complexes was checked by elemental analysis.

Scheme 1  Synthesis of tricarbonylrhenium(I) complexes Re-Phe, Re-Tol, Re-T-Phe and Re-T-Tol. Conditions and reagents: (a) R = Me: CuSO4·5H2O, Na ascorbate, THF/H2O; (b) i) m-chloro-perbenzoic acid (m-CPBA), CH2Cl2, reflux, 30 min; ii) MeOBF4, CH2Cl2, RT, 4 days; (iii) Mo(CO)6, EtOH, reflux, 1 h; (c) [Re(CO)5Cl], MeOH, 65 °C, 16 h; (d) [Re(CO)5Cl], excess of NEt3, toluene, 110 °C, 2.5 days.

Scheme 2  Synthesis of tricarbonylrhenium(I) complexes Re-BOP and Re-T-BOP. Conditions and reagents: (a) [Re(CO)5Cl], MeOH, 65 °C, 16 h; (b) reflux, MeOTf, CH2Cl2, 16 h; (c) [Re(CO)5Cl], NEt3 toluene, 110 °C, 2 days.
Crystal structures

X-Ray-quality crystals of Re-Phe, Re-T-Phe, Re-Tol and Re-T-Tol were grown from CH3CN, CH3Cl/pentane, CH2Cl2 and CH2Cl2/CH3CN, respectively. Selected crystallographic data are collected in Tables S2–4.†

The coordination sphere of all complexes exhibits a quasi-octahedral geometry, as confirmed by the calculation of the distortion parameters (Table S5†). In every case, the rhenium atom is coordinated to three carbonyl groups in a fac configuration, one chlorine atom and the nitrogen atom of the pyridyl ring. It is also coordinated to the triazolylidene C(4) atom for the Re-T-Phe and Re-T-Tol complexes, and to one of the triazole nitrogen atoms for Re-Phe and Re-Tol. Distances and angles of the coordination sphere are quite close for the various compounds, and the pyridyl-triazolylidene and pyridyl-triazole moieties are almost planar. In contrast, significant differences appear when considering the molecular geometry. The most striking indicator is probably the dihedral angle α between the phenyl ring and the triazolylidene or triazole moiety. For instance, Re-T-Phe is a moderately twisted structure, whose α value is 42.8°. The α angle widens till 78.6° for Re-T-Tol due to steric hindrance of the methyl group borne by the phenyl with the triazolylidene ring, on the one hand, and the carbonyl ligand, on the other hand (Fig. 2). Triazole-based complexes, where the phenyl ring is far from the coordination sphere, are comparatively less twisted. Complex Re-Phe exhibits an angle of 34.6°, which increases to 54.2° for Re-Tol. It is instructive to compare the effect of the benzoxazole substituent. The X-ray structure of Re-T-BOP could not be obtained, but DFT calculations (vide infra) indicated that the angle in dichloromethane (DCM) solution should be around 55° (Fig. S31†). In contrast, in the triazole-based series, the presence of benzoxazole leads to planarization of the whole electron conjugated system for Re-BOP (α = 9°).39 Some substituents therefore play a very different role on the molecular geometry in both series.

For all complexes, two enantiomers, which differ by the position of the organic ligand with respect to the chlorine atom, coexist in the crystal cell in identical proportions. The intermolecular arrangement varies from one complex to another (Fig. 3), as described in detail in the ESI (Tables S6–8 and Fig. S15–25†). Briefly, the molecules of the triazolylidene derivatives are displayed in two separate planes, at an angle of ~40° for Re-T-Phe, and close to perpendicular for Re-T-Tol. The crystal structures are stabilized by C–H⋯O and C–H⋯Cl interactions (Table S6†). Specifically, intermolecular hydrogen bonds between the CH group of the phenyl ring and the oxygen atom of the equatorial carbonyl group induce the neighboring molecules of Re-T-Phe to assemble into an infinite one-dimensional chain, which expands along the e axis (Fig. S15†). For Re-T-Tol, the same type of chain results from interactions between the CH group of the pyridine ring and the chloride ligand of an adjacent molecule (Fig. S17†). Additionally, for both compounds, the packing arrangement promotes intermolecular C–H⋯π and π⋯π stacking interactions (Tables S7 and 8†), because the phenyl group of one molecule partly overlaps the pyridyl ring of a neighboring one (Cp–Cp < 3.68 Å) (Fig. 3, S16 and S18†).

Considering the triazole-based complexes Re-Phe and Re-Tol, the pyta moieties are situated on rather close planes, with their long axis oriented along four distinct directions. The

![Fig. 2 Asymmetric units of complexes Re-T-Phe, Re-T-Tol, Re-Phe and Re-Tol, with the dihedral angle α indicated in blue ink. Hydrogen atoms are not represented for the sake of clarity. Displacement ellipsoids are drawn at 30% probability.](image-url)
neighboring molecules of Re-Tol interact with each other via C–H⋯Cl hydrogen bonds between the triazole and pyridine rings, and form a one-dimensional infinite chain along the c axis (Fig. S22†). Numerous C–H⋯O contacts induce the formation of a two-dimensional network in the ab plane (Fig. S23†). Re-Tol is further stabilized by π⋯π interactions between the pyridyl ring of one molecule and the triazole ring of a neighboring one (Cp–Cp = 3.78 Å) (Fig. S24†). Regarding Re-Phe, intermolecular C–H⋯O hydrogen bonds between one hydrogen atom of the pyridyl ring and one carbonyl oxygen atom connect the neighboring molecules, which form a one-dimensional infinite zig-zag chain along the b axis (Fig. S19†). The presence of three basic nitrogen atoms within a five-membered 1,2,3-triazole ring makes the C–H bond highly acidic, strongly enhancing its involvement in hydrogen bonding with chloride acceptors. The bifurcated hydrogen bond between the chloride ligand, on the one hand, and the C–H groups of the 1,2,3-triazole ring and pyridine ring of neighboring molecules, on the other hand, contributes to the formation of a two-dimensional network in the ac plane (Fig. S20†). Crystals of Re-Phe are further stabilized by C–H⋯π interactions (Fig. S21 and Table S7†), but they differ from those of the other analogues by the total absence of π⋯π interactions.

The Hirshfeld surface (HS) analysis was performed to visualize and quantify the intermolecular interactions in the crystal lattice of the four complexes. In the example given in Fig. 4a, HS were mapped over \( d_{norm} \) for Re-Phe and Re-T-Phe. The red spots mainly correspond to C–H⋯O and C–H⋯Cl short interatomic contacts. The white zones refer to intermolecular distances close to the sum of the van der Waals radii of the atoms considered; they indicate H⋯H interactions. The blue areas illustrate the domains where neighboring atoms are too far away to interact with each other. The comparison of the four molecules shows that the distribution of short contacts is indeed different, but the number and type of H-mediated interactions remain relatively close (Fig. S26†). In contrast, the overall molecular shape is very different. Re-Phe is the most angular molecule and the least able to offer flat surfaces where π⋯π stacking can take place. The shape index of the Hirshfeld surface (Fig. 4b) is a tool to visualize π⋯π stacking interactions by the presence of adjacent red and blue triangles. Blue triangles represent the convex region, which is formed due to the carbon atoms present in the molecule inside the surface, while red triangles represent concave regions due to the carbon atoms of the π-stacked molecule above it. Such adjacent triangles were not observed for Re-Phe, which confirms the absence of π⋯π stacking interactions, while this...
pattern can be found at least twice for the other complexes. The relative contributions of the various interactions to the total HS are shown in the 2D fingerprint plots given in Fig. S27–30.† The reciprocal C–O⋯H/H⋯O−C interactions give two sharp symmetrical spikes, with a contribution to the HS reaching 27.8% for Re-T-Phe. The C⋯H/H⋯C interactions, which correspond to C–H⋯π interactions, appear as two symmetrical broad wings and contribute up to 23.4% for Re-Phe. The H⋯H interactions appear in the middle of the scattered points, with an overall contribution varying between 15.1% and 23.5% (for Re-Phe and Re-T-Tol, respectively). The C–H⋯Cl interactions also generate two sharp spikes, and they contribute for ~10%. Other interactions (N⋯H, C⋯N, C⋯O, O⋯O, C⋯C) have minor contributions. For the sake of comparison, the relative contributions of the various interactions to the HS are collected in Fig. 4c. Generally, triazole-based complexes show slightly more C⋯H interactions, and less C–H⋯Cl and O⋯H interactions, than their triazolylidene-based counterparts. Noticeably, π⋯π stacking interactions (C⋯C/C⋯C) are only 2.5% for Re-Phe, and between 4.2% and 5.8% for the other three complexes.

**Electronic properties**

Computational studies were made using the time-dependent density functional theory (TD-DFT) method considering the complexes in vacuum and in dichloromethane continuum (Tables S9–30 and Fig. S31–41†). Only the latter ones will be commented. The tolyl derivatives Re-T-Tol and Re-Tol were considered assuming that their properties are very close to those of the unsubstituted analogues. Complex Re-T-BOP was also studied to understand the influence of the BOP fragment; the results were compared to those previously acquired for Re-BOP.† For the three new complexes, the calculated bond lengths and angles were in excellent agreement with the experimental data (Tables S9–11†). It is also the case for the FT-IR spectra (Fig. S41†). Regarding the composition of the frontier molecular orbitals (Tables S13–18, S25 and Fig. 5, S32–38†), the three highest occupied molecular orbitals (HOMO, HOMO−1 and HOMO−2) are localized on the rhenium atom and carbonyl ligands, and on the chloride atom for the first two, as is commonly the case for tricarbonylrhenium(i) complexes. For Re-T-Tol and Re-Tol, the LUMO, L+1 and L+2 are centered on the pyta and pytz moieties, respectively. Some differences appear for lower and higher orbitals. For example, if considering the orbitals centered on the organic ligand, the H–4 and H–5 orbitals of Re-T-Tol are concentrated on the phenyl ring, while electrons are more evenly distributed between the pyta moiety and the phenyl ring for the H–3, H–4 and H–5 orbitals of Re-Tol. Regarding Re-T-BOP, an important contribution of the PBO moiety is noticed for orbitals H–2, H–5 and H–6, as well as for L+1 and L+5 (H–2, H–4 and H–5, as well as L+1, L+2, L+3 and L+5 for Re-BOP†).

For all compounds, the lowest energy transitions correspond to a shift of the electronic density from the coordination sphere to the organic ligand (Tables S19–24 and S26†). They are therefore of metal-to-ligand charge transfer (MLCT), halogen-to-ligand charge transfer (XLCT) and ligand-to-ligand charge transfer (LLCT) type. At low energy, the significantly active transitions are H–1 → LUMO, expected at 366.2, 344.5, 364.8 and 347.4 nm for Re-T-Tol, Re-Tol, Re-T-BOP and Re-BOP, respectively. Higher-energy transitions are of various natures. Re-T-Tol is characterized by a strong MLCT transition around 244.9 nm, while Re-Tol exhibits a strong ILCT band around 236.7 nm. The transitions with the highest oscillator factor have intraligand charge transfer (ILCT) character for Re-T-BOP and Re-BOP.

Calculations allow to highlight differences in the electronic system of the two series of complexes in the ground state. For instance, according to the natural population analysis (NPA) (Table S29†) that indicates the charge transferred between the donor and acceptor moieties, the charge on the rhenium atoms is ~−1.0 (e) in complexes Re-Tol and Re-BOP, vs. ~−1.2 (e) in complexes Re-T-Tol and Re-T-BOP. The pyridyl nitrogen atom donates as much as 0.40 (e) to the Re atom in the first series of complexes, and 0.38 (e) in the second series. In triazole-based complexes, the triazole nitrogen atom also donates ~0.19 (e), while the C(4) atom of the triazolylidene-based complexes is enriched with a charge of ~−0.12 (e). Consequently, there is better electron density delocalization from the organic ligand to the metal center for triazolylidene-based complexes. In every complex, the positively-charged carbon atom of the carbonyl ligands is found to accept as much as ~0.76 (e) from the Re atom, while the chlorine atom Cl(1) gives it ~0.47 (e).

The HOMO–LUMO gap, which reflects the chemical reactivity or stability of the molecules, was smaller for the triazolylidene-based complexes than for their triazole-based counterparts (~4.12 eV for Re-T-Tol and Re-T-BOP vs. 4.43 eV for Re-Tol and 4.38 eV for Re-BOP†) due to the increase of the HOMO energy level in the first case. The examination of the frontier molecular orbital descriptors (Table S30†), i.e. ionization potential, electron affinity, hardness, electronegativity, chemical potential, softness and electrophilicity index, allows to conclude that the triazolylidene-based complexes Re-T-Tol and Re-T-BOP are less kinetically stable and more chemically reactive than their triazole-based counterparts Re-Tol and Re-BOP.

**Electrochemical properties**

The electrochemical behavior of the new complexes Re-Tol, Re-T-Tol and Re-T-BOP was studied by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSVW) measurements in DCM at room temperature. The results are summarized in Tables 1 and S31,† and Fig. 6, and selected curves are given in Fig. S42–50†. The new compound Re-Tol exhibited electrochemical characteristics close to those of Re-BOP.† Thus, the first one-electron oxidation process at 1.48 V was mainly assigned to the Re(i) oxidation, while the first reduction process around −1.60 V was ligand centered on the pyta moiety. These data also indicate that the pyridyl-1,2,3-triazole ligand is not very sensitive to the nature of its phenyl substituent. However, it is noteworthy that the first reduction process
presented more reversibility at high scan rate for the Re-Tol compound than for Re-BOP (see below).

The two new triazolylidene-based complexes Re-T-Tol and Re-T-BOP displayed distinct electrochemical properties. Indeed, in CV at 0.2 V s$^{-1}$, two irreversible processes were detected at around 1.26 V in oxidation, and −1.52 V in reduction. These potential values clearly differed from those observed for our previously studied pyridyl-1,2,3-triazole- and pyridyl-1,2,4-triazole-based Re complexes.\textsuperscript{39–41,44} The first one-electron oxidation process occurred now at lower anodic potential (around −200 mV) when compared with those of their pyridyl-1,2,3-triazole-based counterparts. This is due to the increased electron density on the rhenium center, which is supported by theoretical calculations. These results also suggest that the triazolylidene ligands are likely better electron donors than the corresponding pyridyl-1,2,3-triazole ligands. The Re-T-BOP complex also presented a second reduction process around −1.9 V that was attributed to the reduction of the PBO moiety, thus confirming that the latter is not involved in the complexation process.\textsuperscript{39}

Regarding now the literature data, the value of the first oxidation potential of the Re-T-Tol and Re-T-BOP complexes was

<table>
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<tr>
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<th>Re-T-Tol</th>
<th>Re-Tol</th>
<th>Re-T-BOP</th>
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<tr>
<td>LUMO+2</td>
<td>(-1.16 eV)</td>
<td>(-1.37 eV)</td>
<td>(-1.63 eV)</td>
</tr>
<tr>
<td>LUMO+1</td>
<td>(-1.63 eV)</td>
<td>(-1.60 eV)</td>
<td>(-2.03 eV)</td>
</tr>
<tr>
<td>LUMO</td>
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<td>(-2.21 eV)</td>
<td>(-2.31 eV)</td>
</tr>
<tr>
<td>HOMO</td>
<td>(-6.41 eV)</td>
<td>(-6.64 eV)</td>
<td>(-6.42 eV)</td>
</tr>
<tr>
<td>HOMO-1</td>
<td>(-6.56 eV)</td>
<td>(-6.74 eV)</td>
<td>(-6.58 eV)</td>
</tr>
<tr>
<td>HOMO-2</td>
<td>(-6.91 eV)</td>
<td>(-7.19 eV)</td>
<td>(-6.86 eV)</td>
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Fig. 5 Isodensity plots (isovalue = 0.03 e bohr$^{-3}$) and energy levels of the first frontier molecular orbitals, for complexes Re-T-Tol, Re-Tol and Re-T-BOP in DCM, according to DFT calculations at the PBE1PBE/LANL2DZ level of theory.
Table 1. Selected electrochemical data of complexes Re-Tol, Re-BOP, Re-T-Tol, and Re-T-BOP, [10-3 M]. Values determined by OSWV on a Pt working electrode in CH2Cl2 + 0.1 M [nBu4N][BF4] at room temperature. a,b Ferrocene was used as internal reference.

<table>
<thead>
<tr>
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<th>Oxidation</th>
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<tr>
<td></td>
<td>E1</td>
<td>E2</td>
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<tr>
<td>Re-Tol</td>
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</tr>
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<td>Re-BOP</td>
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<td>Re-T-Tol</td>
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</tr>
<tr>
<td>Re-T-BOP</td>
<td>1.62</td>
<td>1.27</td>
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a OSWVs were obtained using a sweep width of 20 mV, a frequency of 20 Hz, and a step potential of 5 mV. b Potential values in volts vs. SCE (Fc+/Fc is observed at 0.55 V ± 0.01 V vs. SCE). c Data from ref. 39.

Fig. 6 Cyclic voltammograms of the first oxidation and reduction processes of complexes Re-Tol (red dotted line), Re-T-Tol (red line), and Re-T-BOP (green line) on a Pt working electrode in CH2Cl2 + 0.1 M [nBu4N][BF4] at room temperature and at a scan rate of 0.2 V s⁻¹ toward cathodic potentials.

Fig. 7 UV-vis absorption spectra (a) and normalized emission spectra (b) of complexes Re-T-Phe (blue solid line), Re-T-Tol (red solid line), Re-T-BOP (green solid line), Re-Phe (blue dotted line), Re-Tol (red dotted line), and Re-BOP (green dotted line) in undegassed DCM. Concentrations ∼3.3 × 10⁻⁵ M for absorption, 1.2 × 10⁻⁵ M for emission. Excitation in the low-energy absorption band.

Close to that of the mesoionic carbene complexes synthesized by Suntrup et al.: 0.74–0.78 V range vs. Fc+/FcH. This value is not very sensitive to the nature of the R group grafted on the triazole ring, and the comparison with 1,2,3-triazole-based complexes shows that it correlates well with the overall donor strength of the corresponding organic ligands. The first reduction potential can be used as an approximation to gauge the π-acceptor capacity of our ligands, the triazolylidene ligand being a better π acceptor than the 1,2,3-triazole ligand. The first reduction potentials of the rhenium complexes reported in Table 1 maintain the same π acceptor character than their respective ligands.

The experimental data of Table 1 were also in good agreement with the TD-DFT calculations. In particular, the latter predict that (i) for Re-Tol and Re-BOP, the HOMO are Re-centered and very close in energy; (ii) for Re-T-Tol and Re-T-BOP, the (Re centered) HOMO and (triazolylidene-centered) LUMO present respectively the same energy level; (iii) the calculated HOMO–LUMO energy gap value $E_{calc}$ for the first series of compounds is superior to that of the second one (around 0.3 eV) as observed experimentally.

Considering further the Re-BOP and Re-T-BOP complexes, a different electrochemical behavior regarding the first reduction process was noted in CV when increasing the scan rate. This one became more reversible only for Re-T-BOP. This property is probably related to the different nature of the two compounds. Indeed, for Re-BOP, the LUMO and LUMO+1 energy levels only differ by 0.07 eV. Consequently, the first reduction potential detected at −1.60 V may originate from the contribution of both the LUMO and LUMO+1 energy levels involving respectively the π*(pyta) and π*(pyta) + π*(PBO) orbitals. In contrast, for Re-T-BOP, the energy difference between these levels is greater (0.28 eV) and allows an easier electrochemical assignment of this reduction process exclusively resulting from its π*(pytrz) orbital. This is reminiscent of the electrochemical first reduction behavior of Re-[1,2,4]-BOP, which presents a LUMO-LUMO+1 energy difference of 0.4 eV and a LUMO of exclusively π*(pyta) nature.39 In the latter case, the first reduction process becomes quasi-reversible at 1 V s⁻¹. Concerning the Re-Tol and Re-T-Tol complexes, the LUMO-LUMO+1 energy difference is at least of 0.6 eV, and their...
LUMO is respectively of pure $\pi^\ast$(pyta) or $\pi^\ast$(pytrz) nature, suggesting that some reversibility can occur at high scan rate in CV for each compound, which is actually observed.

Finally, the values of the electrochemical HOMO–LUMO gap ($E_{\text{LUMO}}$) found for Re-Tol and the triazolylidene-based complexes, i.e. 3.0 and 2.7 eV, respectively, also fit very well with the calculated $E_{\text{calc}}$ gap values 3.0 and 2.8 eV, highlighting good correlations with the theoretical study (Table S31†).

**UV-visible absorption and emission properties**

Whatever the complex, no photochemical instability that could interfere with the measurements was detected during the spectroscopic study. The dilute DCM solutions of all complexes were almost colorless in daylight. The absorption spectra were in very good agreement with the calculated ones (Fig. S41†). All of them (Fig. 7a and Table 2) showed an intense high-energy band, attributed to a combination of ILCT and MLCT transitions, as well as a low-energy band of moderate intensity with MLCT character, almost not visible for Re-BOP. The absorption maxima of the triazolylidene-based complexes were slightly red-shifted with respect to triazole-based complexes. The absorptivity values of the high-energy band were markedly increased for both BOP derivatives, due to the extension of the conjugated electron system.

Regarding the emission properties in DCM solutions, the complexes can clearly be divided into two groups. When illuminated by UV light (365 nm), the triazolylidene-based complexes emitted very weak orange-red light, while triazole-based complexes emitted green light. All emission spectra showed a single unresolved band, peaking between around 616 nm for triazolylidene complexes and 546 nm for triazole-based complexes. For Re-T-Tol, Re-T-BOP and Re-Tol, the experimental emission maxima were close to those calculated by DFT and TD-DFT (Table S27†). Since calculations consider the involvement of the lowest $^3$MLCT state, the comparison of the experimental and theoretical values confirms that emission is indeed phosphorescence in every case. For triazolylidene-based complexes in aerated solutions, the quantum yields were quite low, around $1 \times 10^{-2}$. The emission decays (Fig. S51†) were monoexponential for Re-T-Phe and Re-T-Tol, with lifetimes below 50 nanoseconds. For Re-T-BOP, a second lifetime at 217 ns with contribution around 29% could arise from the presence of conformers in solution. For the triazole-based complexes, the quantum yields were 1.5 fold higher, and the lifetimes were longer, between 145 and 192 ns, than for their triazolylidene-based analogues. Considering the whole set of compounds, the radiative rate constants were slightly higher, and the non-radiative rate constants were markedly higher for triazolylidene-based complexes. This suggests that these complexes are intrinsically a little more emissive than their triazole-based counterparts, but this trend is compensated by the promotion of thermal de-excitation pathways, as can be expected from the energy gap law.53

It is striking to see that the three triazolylidene derivatives, on the one hand, and the three 1,2,3-triazole derivatives, on the other hand, show great similarity in their emission properties.

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**Table 2** Spectroscopic data of all complexes in DCM. Maximum absorption wavelength ($\lambda_{\text{abs}}$), molar extinction coefficient ($\epsilon$), maximum wavelength of emission ($\lambda_{\text{em}}$), emission quantum yield ($\phi$), lifetime ($\tau$) with relative amplitude ($f$) and chi square ($\chi^2$) values, mean lifetime ($\langle\tau\rangle$), radiative ($k_r$) and non-radiative ($k_{\text{nr}}$) deactivation constants. Concentrations: $\sim 3 \times 10^{-5}$ M for absorption, $\sim 1.0 \times 10^{-5}$ M to $3.5 \times 10^{-5}$ M for emission. Emission characteristics in the solid state (pristine powders): Photoluminescence maximum wavelength ($\lambda_{\text{PL}}$), emission quantum yield ($\phi_{\text{PL}}$), lifetime ($\tau_{\text{PL}}$) and mean lifetime ($\langle\tau_{\text{PL}}\rangle$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\epsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\phi$</th>
<th>$\langle\tau\rangle$ (ns)</th>
<th>$\langle\tau\rangle$ (ns)</th>
<th>$\langle\tau\rangle$ (ns)</th>
<th>$k_r$ (s$^{-1}$)</th>
<th>$k_{\text{nr}}$ (s$^{-1}$)</th>
<th>$\lambda_{\text{PL}}$ (nm)</th>
<th>$\phi_{\text{PL}}$</th>
<th>$\tau_{\text{PL}}$ (ns)</th>
<th>$\langle\tau_{\text{PL}}\rangle$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re-T-Phe</td>
<td>240 20 700</td>
<td>616 9.7 $\times$ 10$^{-3}$</td>
<td>616 1.1 $\times$ 10$^{-2}$</td>
<td>48</td>
<td>48</td>
<td>2.9 $\times$ 10$^5$</td>
<td>2.1 $\times$ 10$^5$</td>
<td>537 0.16</td>
<td>537 0.16</td>
<td>64 0.03</td>
<td>711 0.96</td>
<td>1.07</td>
<td>543</td>
</tr>
<tr>
<td>Re-T-Tol</td>
<td>240 16 700</td>
<td>616 1.1 $\times$ 10$^{-2}$</td>
<td>240 16 700</td>
<td>616 1.1 $\times$ 10$^{-2}$</td>
<td>48</td>
<td>48</td>
<td>2.9 $\times$ 10$^5$</td>
<td>2.1 $\times$ 10$^5$</td>
<td>537 0.16</td>
<td>537 0.16</td>
<td>64 0.03</td>
<td>711 0.96</td>
<td>1.07</td>
</tr>
<tr>
<td>Re-T-BOP</td>
<td>238 21 200</td>
<td>616 1.2 $\times$ 10$^{-2}$</td>
<td>238 21 200</td>
<td>616 1.2 $\times$ 10$^{-2}$</td>
<td>89</td>
<td>89</td>
<td>1.3 $\times$ 10$^5$</td>
<td>1.1 $\times$ 10$^5$</td>
<td>537 0.16</td>
<td>537 0.16</td>
<td>64 0.03</td>
<td>711 0.96</td>
<td>1.07</td>
</tr>
<tr>
<td>Re-Phe</td>
<td>242 20 600</td>
<td>154</td>
<td>1.7 $\times$ 10$^{-2}$</td>
<td>154</td>
<td>1.7 $\times$ 10$^{-2}$</td>
<td>1.1 $\times$ 10$^5$</td>
<td>6.3 $\times$ 10$^5$</td>
<td>510 0.69</td>
<td>510 0.69</td>
<td>32 (&lt;0.01)</td>
<td>1164 (0.99)</td>
<td>1.28</td>
<td>1154</td>
</tr>
<tr>
<td>Re-Tol</td>
<td>240 19 100</td>
<td>454</td>
<td>1.6 $\times$ 10$^{-2}$</td>
<td>240 19 100</td>
<td>454</td>
<td>1.6 $\times$ 10$^{-2}$</td>
<td>1.1 $\times$ 10$^5$</td>
<td>6.7 $\times$ 10$^5$</td>
<td>528 0.07</td>
<td>528 0.07</td>
<td>107 (0.14)</td>
<td>921 (0.84)</td>
<td>1.53</td>
</tr>
<tr>
<td>Re-BOP</td>
<td>240 16 900</td>
<td>192</td>
<td>1.5 $\times$ 10$^{-2}$</td>
<td>240 16 900</td>
<td>192</td>
<td>1.5 $\times$ 10$^{-2}$</td>
<td>1.1 $\times$ 10$^5$</td>
<td>6.7 $\times$ 10$^5$</td>
<td>528 0.07</td>
<td>528 0.07</td>
<td>107 (0.14)</td>
<td>921 (0.84)</td>
<td>1.53</td>
</tr>
</tbody>
</table>

*a* Pristine powders, except for Re-Tol (ground powder). b Decays are triexponential, the full data are given in the ESI (Fig. S32†). c When not specified, data are from ref. 39. d This work.
properties in solution. This is explained by the fact that, within the same series of compounds, the first excited triplet state is almost the same for each derivative because the electron density is centered on the rhenium coordination sphere and does not involve the organic substituents borne by the pytrz or pyta moiety (Fig. S39).

The effect of dissolved oxygen on the emission efficiency was investigated. Bubbling the complex solutions with argon for 4 min multiplies the emission intensity by 1.6, 2.9 and 1.3 for Re-T-Phe, Re-T-Tol and Re-T-BOP, respectively, like for the previously studied 1,2,4-triazole-based complexes. The short emission lifetimes of triazolylidene derivatives may explain the low sensitivity to oxygen quenching. In contrast, the emission was dramatically enhanced by 8.3, 12.1 and 13.4 for Re-Phe, Re-Tol and Re-BOP in the same conditions, so that the quantum yield changes by one order of magnitude. The longer lifetimes are one of the factors contributing to this effect, making the 1,2,3-triazole derivatives the most oxygen-sensitive compounds among all rhenium(i) complexes examined to date in the group.

All compounds were emissive in the solid state. Unlike solutions, where the spectra were identical by class of compounds, dramatic differences appeared between all compounds. The PL spectra covered a large range of wavelengths (Fig. 8a), with very different intensities (Fig. 8b). The microcrystalline pristine powders of the triazolylidene-based complexes emitted yellow to orange-yellow light, with moderate to low quantum yields (between 0.16 for Re-T-Phe to 0.04 for Re-T-BOP) (Table 2). Triazole-based complexes emitted green light. The emission of Re-Phe was exceptionally strong, with quantum yield around 0.69. These superior solid-state PL properties can be explained jointly by the absence of π–π stacking in the crystal network and by the prevention of quenching by dissolved oxygen, to which the compound is very sensitive when in solution. Again, the BOP derivative was the weakest luminoaphore of the series. Curiously, pristine Re-T-Tol was virtually not emissive, but emission was induced by grinding the powder with a pestle in a mortar, which generally leads to partial amorphization of the sample, suggesting that the crystal packing mode is detrimental to light emission. The influence of mechanical stimulus was investigated by grinding the pristine powders of the other five complexes, but no significant differences were observed, ruling out any mechanoresponsive luminescence behavior for these compounds.

All decays were found to be multiexponential (Fig. S32†). The preponderant contribution was associated to lifetimes between 414 and 1164 ns. Minor contributions with lifetimes of many tens of nanoseconds can be attributed to molecules experiencing a different environment. Very weak contributions associated to lifetimes in the nanosecond range are probably due to fluorescent impurities. The mean lifetimes were much longer than for the corresponding complexes in solution, as currently observed in the team for Re(i) complexes in the solid-state.

It was interesting to see if our molecules can be used as AIE-gens in aqueous medium, knowing that the formation of aggregates in this medium is not always compatible with good light emission. The AIE behavior was investigated using Re-T-Phe and Re-Phe that exhibit the best solid-sate emission properties in their respective series of complexes. The complexes were dissolved in acetonitrile, where they are very stable chemically and photochemically (no change in the UV-vis spectra was detected for 3 h upon irradiation with a 385 nm emitting diode). By increasing the water proportion in acetonitrile solutions of Re-T-Phe, the weak orange-red emission centered at 512 nm progressively became a strong green-yellow emission with maximum at 536 nm, and then the emission intensity decreased again (Fig. 9a and b). Under the same conditions, the green-yellow emission of Re-Phe at 544 nm was shifted to 508 nm with dramatic increase of intensity for water content (\(f_w\)) above 70% (Fig. 9c and d). The intensity of the PL signal at the maximum wavelength of the most intense band was multiplied by 33 and 72, respectively. It is noteworthy that
these emission maxima are similar to those of the solid compounds. In fact, these spectroscopic changes were accompanied by the appearance of small particles. The examination under the fluorescence microscope showed for Re-T-Phe the presence of rare, strongly-emissive rod-like microcrystals, which were about 200–150 µm × 5 µm (Fig. 9e). Suspensions of Re-Phe contained a large number of particles visible to the naked eye, which turned out to be agglomerates of very thin microfibers measuring 10–20 µm long (Fig. 9f).

The AIE effect was therefore clear in both cases, but the superior emission properties of Re-Phe (Fig. 9g) make this compound the best candidate for AIE-related applications.

Antibacterial properties

Finally, the antibacterial activities of the complexes were tested. One Gram-positive strain, i.e. Staphylococcus aureus (S. aureus), and three Gram-negative strains, Pseudomonas aeruginosa (P. aeruginosa), Acinetobacter baumannii (A. baumannii) and Escherichia coli (E. coli), were selected as common causative agents of the most dangerous nosocomial infections. Both antibiotic susceptible (S) and multidrug-resistant (R) strains were used. The three triazolylidene complexes and their 1,2,3-triazole-based counterparts were studied, together with Re-[1,2,4]Phe and Re-[1,2,4]-BOP for the sake of comparison. Given their low solubility in water, the complexes were previously dissolved in DMSO, before introduction and dilution into aqueous medium. The final concentration of complexes in each well ranged from 0.125 to 128 µM, and the highest concentration of DMSO was below 1.25%. The bacteria suspended in their culture medium were then put in contact with the complexes and incubated for 18 h in the dark. The minimum inhibitory concentration (MIC), i.e. the lowest concentration of a compound at which bacterial growth is completely inhibited, was measured. Results are collected in Table 3. Remarkably, antibacterial activity was observed only against S. aureus, whatever the strain is susceptible or resistant to conventional antibiotics. Among the active complexes, the triazolylidene-based derivative Re-T-BOP exhibited the stronger antibacterial activity, with a MIC value around 4 µM. This complex is the most lipophilic of all, but probably not enough to explain the difference in antibacterial activity. A connection between the antibacterial activity of all complexes and common drug likeness parameters (i.e. topological polar surface area (TPSA), lipophilicity (miLogP) and molecular weight (MW)) was sought. These parameters are typically determined for eukaryotic cells, but can be used to some extent for bacteria. In particular, the lipophilicity may facilitate drug penetration and cellular uptakes through interaction with bacterial membranes.

TPSA has been associated with bioavailability, and it is suggested that compounds with a TPSA greater than 140 tend to be poor at permeating cell membranes. In the present case, if considering the whole set of data, no obvious correlation was found with the drug likeness parameters considered. The presence of the benzoxazole substituent in Re-T-BOP certainly brings a benefit, because this fragment is considered to be one of the most relevant biologically-active heterocycles, often incorporated in ligands to target a variety of receptors and enzymes in medicinal chemistry studies. However, the presence of benzoxazole in Re-BOP and Re-[1,2,4]-BOP is not sufficient to endow these compounds with an antibacterial activity. Besides, it is noteworthy that the presence of the methyl group in Re-Tol and Re-T-Tol modifies the antibacterial activity in comparison with their analogues Re-Phe and Re-T-Phe. Therefore, the activity could be related to the nature of the coordination sphere, and more precisely to the molecular geometry in space or flexibility. The examination of new complexes substituted by a methyl group in the meta and para positions could be instructive. It would allow validat-
The antibiotic-susceptible strain of S. aureus, particularly dioporins, which make internalization of active compounds particularly difficult. Indeed, these bacteria have an additional outer membrane, as well as an abundance of efflux pumps and highly selective porins, which make internalization of active compounds particularly difficult.

Finally, a photochemical effect was investigated. Our complexes are not prone to photodecarbonylation. However, the presence of rhenium as a heavy atom induces fast population of the first excited triplet state, and the photogeneration of singlet oxygen could take place via energy transfer. In the present case, irradiation of the samples in the near UV does not lead to different results in most of the cases. Exceptions are Re-BOP and Re-T-Tol that show enhanced activity towards the antibiotic-susceptible strain of S. aureus (Table S32†).

Conclusions

In this comprehensive study, the properties of three new triazolylidene-based complexes were compared with those of their 1,2,3-triazole-based analogues, for which very little information was available. From an electronic point of view, the superior electron-donating properties of the mesoionic carbene ligand resulted in an increase in the charge density on the rhenium atom. The crystallographic data showed that small structural variations strongly influence the molecular conformation and intermolecular interactions in the solid state, and the Hirshfeld surface analysis allowed the latter to be finely quantified. The compounds of the two series were emissive in solution and in the solid state. Complex Re-Phe showed exceptional emission efficiency in the form of powder, and was a remarkable AIE-gen in aqueous medium. Although less efficient, our triazolylidene-based complexes proved to be photochemically stable, unlike the Re(NHC) complexes reported in the literature, and are therefore well suited for light-related applications. Until now, only 1,2,4-triazole-based complexes had shown attractive spectroscopic properties in the solid state. This work shows that some triazolylidene- and 1,2,3-triazole-based complexes must be considered for potential applications in the fields of photoluminescent materials and AIE-gens. However, the mecha-noresponsive emission behavior remains the prerogative of the 1,2,4-triazole-based series. It would be instructive to extend the solid-state emission study to other rhenium(i) complexes incorporating various mesoionic and N-heterocyclic carbenes.

Finally, one triazolylidene-based complex (Re-T-BOP) showed clear superiority over all other compounds as regards the antibacterial properties. It would be instructive to test the cytotoxicity of this molecule on eukaryotic cells to see if it could be used in therapy. A thorough examination of the mechanism of action would facilitate the further development of more effective molecules. This result confirms that triazolylidene-based Re(i) complexes must be considered as potential candidates in the highly demanding field of therapeutic chemistry.

Experimental section

General methods

All purchased chemicals were of the highest purity commercially available and used without further purification. Unless otherwise noted, all experiments were carried out under a...
nirgen atmosphere. All reactions were monitored by TLC on silica gel Alugram® Xtra Sil G/UV254. Column chromato-
graphy was performed on Machery–Nagel silica gel. NMR
spectra were recorded with a Bruker Avance 300 instrument.
Chemical shifts are given in ppm and are referenced by using
the residual signals of the solvent as internal standard. Signals
are described as follow: s, singlet; d, doublet; t, triplet; m, multi-
ple. HRMS data were recorded on a Xero G2 QTOF (Waters)
instrument. Infrared spectra were obtained on a Nexus
tiplet. HRMS data were recorded on a Xero G2 QTOF (Waters)
are described as follow: s, singlet; d, doublet; t, triplet; m, mul-
tiple. HRMS data were recorded on a Xero G2 QTOF (Waters)
instrument. Infrared spectra were obtained on a Nexus
Thermonicolet apparatus with DTGS as the detector. The
microanalyses were made in the ‘Service d’analyse’ of LCC
using a PerkinElmer 2400 series II analyzer.

Synthesis

The syntheses of ligand L-T-Phe,51 and complexes Re-Phe30
and Re-BOP1910 have been previously described.

Tricarbonylrhenium(i) complex [Re(CO)3(L-T-Tol)Cl],
(Re-T-Tol)

To a suspension of the ligand L-T-Phe (101 mg, 0.31 mmol)
and [Re(CO)5Cl] (113 mg, 0.31 mmol) in toluene (15 mL) was
added excess of Et3N (0.8 mL). The reaction mixture was
refluxed for 60 h. After cooling to room temperature, the
solvent was removed under reduced pressure. Silicone gel
column chromatography (CH2Cl2/acetone 9 : 1 v/v) afforded
pure complex Re-T-Tol (127 mg, 76%) as a yellow solid.

1H NMR (300 MHz, DMSO-d6) δ (ppm): 9.08 (dt, J = 5.5, 1.2
Hz, 1H), 8.34–8.22 (m, 2H), 7.97–7.87 (m, 2H), 7.81–7.67 (m,
3H), 7.64 (td, J = 5.7, 3.1 Hz, 1H), 4.68 (s, 3H). 13C NMR
(75 MHz, DMSO-d6) δ (ppm): 198.5, 198.4, 190.1, 180.9, 155.2,
149.6, 149.1, 139.9, 138.2, 130.6, 129.8, 126.3, 124.9, 124.2,
39.8. HRMS (ESI) m/z 558.0479 ([M + Na]+ calcd for
C18H14N4O3NaCl185Re: 557.0197), m/z 519.0609 ([M − Cl]−
calcd for C18H14N4O185Re: 519.0595). IR (ATR) νc=o: 2019, 1917,
1888, 1868 cm−1. Anal. calcd (%) for C18H14N4O3ClRe: C 38.74,
H 2.08, N 9.79.

3-Methyl-1-(2-phenylbenzo[d]oxazol-6-yl)-4-(pyridin-2-yl)-1H-
1,2,3-triazol-3-ium trifluoromethanesulfonate (L-T-BOP)

To a solution of triazole L-BOP (79 mg, 0.233 mmol) in anhy-
drous CH2Cl2 (5 mL) was added MeOff (31 μL, 0.283 mmol).
The reaction mixture was refluxed overnight. The solvent was
removed in vacuo and the crude product was purified by silicone
column chromatography (CH2Cl2/MeOH 9 : 1 v/v) to give
the expected triazolium triflate L-T-BOP as a beige solid
(30 mg, 25%) along with the N-methylpyridinium triflate
derivative N-MP-BOP as a beige powder (51 mg, 43%).

For L-T-BOP,1H NMR (300 MHz, DMSO-d6) δ (ppm): 10.24
(s, 1H), 8.92 (d, J = 4.7 Hz, 1H), 8.64 (d, J = 2.1 Hz, 1H),
8.33–8.20 (m, 4H), 8.18–8.09 (m, 2H), 7.78–7.64 (m, 4H),
4.73 (s, 3H). 13C NMR (75 MHz, DMSO-d6) δ (ppm): 165.3,
150.3, 150.2, 144.0, 143.0, 139.5, 132.9, 132.1, 127.9,
128.6, 127.8, 126.1, 124.6, 121.3, 118.8, 105.5, 41.3. HRMS
(DCI-CH4) m/z 354.1364 ([M]+ calcd for C21H16N5O:
354.1355).

3-Methyl-4-(pyridin-2-yl)-1-(o-tolyl)-1H-1,2,3-triazol-3-ium
tetrafluoroborate (L-T-Tol)

A mixture of triazole L-Tol (394 mg, 1.77 mmol) and m-CBPA
(70%, 823 mg, 3.34 mmol) in CHCl3 (25 mL) was refluxed
for 30 min. After cooling to room temperature, aqueous Na2S2O3
solution (0.5 M) was added and the aqueous layer was
extracted with CHCl3. The combined organic layers were
washed with aqueous NaOH (1 M) and concentrated in vacuo.
The obtained pyridine N-oxide was dissolved in anhydrous
CH2Cl2 (10 mL) and Me3OBF2 (1.12 mg, 7.6 mmol) was added.
The reaction mixture was stirred at room temperature for 4
days. The solvent was evaporated to dryness and the residue
dissolved in EtOH (50 mL). Mo(CO)5 (501 mg, 1.9 mmol) was
added and the reaction mixture was refluxed for 1 h. The
solvent was removed under reduced pressure. Silicone gel
column chromatography (CH2Cl2/MeOH 9 : 1 v/v) afforded
pure compound L-T-Tol (464 mg, 82.2%) as a solid.

1H NMR (300 MHz, DMSO-d6) δ (ppm): 9.81 (s, 1H), 9.19–9.08
(m, 1H), 8.76–8.63 (m, 2H), 8.58 (t, J = 1.3 Hz, 1H), 8.27 (dd, J =
7.6, 2.0 Hz, 2H), 8.20–8.10 (m, 3H), 7.78–7.59 (m, 3H), 4.60 (s,
3H). 13C NMR (75 MHz, DMSO-d6) δ (ppm): 164.4, 150.4,
147.5, 145.1, 144.3, 139.2, 133.1, 132.6, 129.5, 128.0,
127.6, 127.4, 126.6, 125.9, 120.9, 118.2, 104.4, 48.2. HRMS
(ESI) m/z 354.1355 ([M − OTf]+ calcd for C21H16N5O:
354.1356).

Tricarbonylrhenium(i) complex [Re(CO)3(L-T-Tol)Cl],
(Re-T-Tol)

To a suspension of the ligand L-T-Tol (89 mg, 0.263 mmol)
and [Re(CO)5Cl] (96 mg, 0.265 mmol) in toluene (15 mL) was
added excess of Et3N (0.8 mL). The reaction mixture was
refluxed for 60 h. After cooling to room temperature, the
solvent was removed under reduced pressure. Silicone gel
column chromatography (CH2Cl2/acetone 9 : 1 v/v) afforded
pure complex Re-T-Tol (96 mg, 65.9%) as a yellow solid.

1H NMR (300 MHz, DMSO-d6) δ (ppm): 9.04 (d, J = 5.5 Hz,
1H), 8.68–8.15 (m, 2H), 7.88–7.17 (m, 4H), 4.67 (s, 3H), 2.22 (s,
3H). 13C NMR (75 MHz, DMSO-d6) δ (ppm): 198.9, 197.5, 190.0,
155.3, 149.3, 149.2, 139.8, 137.7, 134.4, 131.2, 131.0, 127.1,
127.1, 126.2, 122.4, 39.1, 17.0. HRMS (ESI) m/z 577.0197
([M + Na]+ calcd for C18H14N4O3NaCl185Re: 577.0182), m/z 519.0609
([M − Cl]− calcd for C18H14N4O185Re: 519.0595). IR (ATR)
νc=o: 2019, 1917, 1888, 1868 cm−1. Anal. calcd (%) for
C18H14N4O3ClRe: C 37.89, H 2.54, N 10.08; found: C 37.84, H
2.08, N 9.79.
Tricarbonylrhenium(i) complex [Re(CO)₅(L-T-BOP)], (Re-T-BOP)

To a suspension of the ligand L-T-BOP (32 mg, 0.0636 mmol) and [Re(CO)₅Cl] (24 mg, 0.0663 mmol) in toluene (6 mL) was added an excess of Et₃N (0.22 mL). The reaction mixture was refluxed for 48 h. After cooling to room temperature, the solvent was removed under reduced pressure. Silica gel column chromatography (CH₂Cl₂/MeOH 9.5:0.5 v/v) afforded pure compound (29, 69%) as a yellow solid.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm) = 9.10 (d, J = 5.4 Hz, 1H), 8.41 (d, J = 2.0 Hz, 1H), 8.34–8.25 (m, 4H), 8.15 (d, J = 8.5 Hz, 1H), 7.98 (dd, J = 8.5, 2.1 Hz, 1H), 7.68 (q, J = 6.0, 4.8 Hz, 4H), 4.72 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) = 198.5, 198.4, 190.0, 181.6, 164.7, 155.2, 149.8, 149.6, 149.0, 143.0, 140.0, 135.3, 132.7, 129.5, 127.7, 126.4, 125.8, 122.2, 120.6, 108.8, 39.3. HRMS (ESI) m/z 680.0265 ([M + Na]⁺ calcd for C₂₄H₁₅N₅O₄NaCl: 680.0240), ν = 237.1138 ([M + H]⁺ calcd for C₂₄H₁₅N₅O₄: 560.0498, [M + NH₄]⁺ calcd for [C₂₄H₁₅N₅O₄ClRe]: 560.0499). IR (ATR) ν(CO) = 2077, 1852, 1844 cm⁻¹.

5.4 Hz, 1H), 8.32 (s, 1H), 8.28 (dt, J = 0.9 Hz, 1H), 8.35 (s, 1H), 8.28 (dt, J = 8.25 (m, 4H), 8.15 (d, J = 2.0 Hz, 1H), 7.91 (m, 5H), 7.36 (m, 2H), 4.72 (s, 3H), 2.23 (s, 3H). ¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 9.10 (d, J = 5.4 Hz, 1H), 8.41 (d, J = 2.0 Hz, 1H), 8.34–8.25 (m, 4H), 8.15 (d, J = 8.5 Hz, 1H), 7.98 (dd, J = 8.5, 2.1 Hz, 1H), 7.68 (q, J = 6.0, 4.8 Hz, 4H), 4.72 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) = 198.5, 198.4, 190.0, 181.6, 164.7, 155.2, 149.8, 149.6, 149.0, 143.0, 140.0, 135.3, 132.7, 129.5, 127.7, 126.4, 125.8, 122.2, 120.6, 108.8, 39.3. HRMS (ESI) m/z 680.0265 ([M + Na]⁺ calcd for C₂₄H₁₅N₅O₄NaCl: 680.0240), ν = 237.1138 ([M + H]⁺ calcd for C₂₄H₁₅N₅O₄: 560.0498, [M + NH₄]⁺ calcd for [C₂₄H₁₅N₅O₄ClRe]: 560.0499). IR (ATR) ν(CO) = 2077, 1852, 1844 cm⁻¹.

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Tricarbonylrhenium(i) complex [Re(CO)₅(L-T-BOP)], (Re-T-BOP)

To a suspension of the ligand L-T-BOP (32 mg, 0.0636 mmol) and [Re(CO)₅Cl] (24 mg, 0.0663 mmol) in toluene (6 mL) was added an excess of Et₃N (0.22 mL). The reaction mixture was refluxed for 48 h. After cooling to room temperature, the solvent was removed under reduced pressure. Silica gel column chromatography (CH₂Cl₂/MeOH 9.5:0.5 v/v) afforded pure compound (29, 69%) as a yellow solid.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm) = 9.10 (d, J = 5.4 Hz, 1H), 8.41 (d, J = 2.0 Hz, 1H), 8.34–8.25 (m, 4H), 8.15 (d, J = 8.5 Hz, 1H), 7.98 (dd, J = 8.5, 2.1 Hz, 1H), 7.68 (q, J = 6.0, 4.8 Hz, 4H), 4.72 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) = 198.5, 198.4, 190.0, 181.6, 164.7, 155.2, 149.8, 149.6, 149.0, 143.0, 140.0, 135.3, 132.7, 129.5, 127.7, 126.4, 125.8, 122.2, 120.6, 108.8, 39.3. HRMS (ESI) m/z 680.0265 ([M + Na]⁺ calcd for C₂₄H₁₅N₅O₄NaCl: 680.0240), ν = 237.1138 ([M + H]⁺ calcd for C₂₄H₁₅N₅O₄: 560.0498, [M + NH₄]⁺ calcd for [C₂₄H₁₅N₅O₄ClRe]: 560.0499). IR (ATR) ν(CO) = 2077, 1852, 1844 cm⁻¹.
After stirring for 3 h in the dark, the samples were sonicated for 5 min before optical measurement.

Solid state spectra were recorded on a HORIBA FluoroLog 3-2iHR320 spectrofluorometer and were corrected. The absolute photoluminescence quantum yield values (φ\textsubscript{PL}) were determined using the Xenius SAFAS spectrofluorometer provided with an integrating sphere, by a method based on the one developed by De Mello et al.,\textsuperscript{75} as described elsewhere.\textsuperscript{41} The error was estimated to be about 20%.

Emission decay curves were recorded using the time-correlated single photon counting method (TCSPC) on the Horiba FluoroLog 3-2iHR320 spectrofluorometer equipped with a Nanoled-370 (λ\textsubscript{exc} = 371 nm). Emitted photons were detected at 90° by means of a Hamamatsu R928 photomultiplier. Emission was recorded near the maximum with a bandpass of 4 nm. The instrumental response was recorded directly before each decay curve, using the scattering of the sample at 371 nm. All analyses were recorded using the Datastation v2.7 software from Horiba. The decay curves were analyzed with reconvolution and global non-linear least-squares minimization method using DAS6 v6.8 software. The absorbance of solutions at λ\textsubscript{exc} was lower than 0.1. Solid state samples were deposited on a quartz holder.

Fluorescence microscopy was performed with a Leitz Laborlux D fluorescence microscope equipped with an Andor Luca camera (λ\textsubscript{em} ~ 450–490 nm, λ\textsubscript{em} > 500 nm).

### Computational details

The GAUSSIAN16 program package\textsuperscript{76} was employed for all calculations (the geometry optimization, the ground-state and excited-state electronic structures, and optical spectra) with the aid of the ChemCraft visualization program.\textsuperscript{77} The ground state (S\textsubscript{0}), the first excited state (S\textsubscript{1}) and the lowest triplet state (T\textsubscript{1}) geometries of Re-Tol, Re-T-Tol and Re-T-BOP, were fully optimized with the restricted and unrestricted density functional theory (R-DFT and U-DFT) methods using the Perdew–Burke–Ernzerhof PBE1PBE functional with no symmetry constraints.\textsuperscript{78} In all calculations, the “double-ζ” quality basis set LANL2DZ with Hay and Wadt’s relative effective core potential ECP (outer-core [[5s25p\textsuperscript{2}]] electrons and [5d\textsuperscript{6}] valence electrons)\textsuperscript{79,80} was employed for the Re atom. The 6-311+G** basis set for H, C, N and O atoms was used.\textsuperscript{81} The solvent effect (dichloromethane, ε = 8.93) was simulated using the Self-Consistent Reaction Field (SCRF) under the Conductor Polarizable Continuum Model (CPCM).\textsuperscript{82–84} The vibrational frequencies calculations were performed using the optimized structural parameters of the complexes, to confirm that each optimized structure represents a local minimum on the potential energy surface and all eigenvalues are non-negative. To obtain a good agreement with the experimental vibrational frequencies in solid state, the theoretically calculated vibrational frequencies were scaled with a scaling factor of 0.9485. The optimized Cartesian coordinates of Re-Tol, Re-T-Tol and Re-T-BOP are included in the ESI part (see Tables S33–471). On the basis of the optimized ground and excited state geometries, the absorption and emission properties were calculated by the time dependent density functional theory (TD-DFT) method at the PBE1PBE/LANL2DZ/6-31+G** level. These methods have already shown good agreement with experimental studies for different rhenium(II) complexes.\textsuperscript{85}

### Electrochemistry

The electrochemical properties of the complexes were determined by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) in DCM. The solutions used during the electrochemical studies were typically 1 × 10\textsuperscript{−3} M in complex, and 0.1 M in supporting electrolyte. The supporting electrolyte [nBu\textsubscript{4}N][BF\textsubscript{4}] (Fluka, 99% electrochemical grade) was used as received and simply degassed under Ar. DCM was dried using an MB SPS-800 solvent purification system just prior to use. The measurements were carried out with an Autolab PGSTAT100 potentiostat controlled by GPES 4.09 software. Experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/Ar line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a Pt wire of ca. 1 cm\textsuperscript{2} apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). Under these experimental conditions, Fe\textsuperscript{3+}/Fe\textsuperscript{2+} is observed at +0.55 ± 0.01 V vs. SCE. OSWVs were obtained using an amplitude of 20 mV, a frequency of 20 Hz, and a step potential of 5 mV.

### Microbiology

The bacteria strains were obtained from the American Type Culture Collection (ATCC). Susceptible strains include Acinetobacter baumannii ATCC 19606, Escherichia coli ATCC 25922, Pseudomonas aeruginosa ATCC 27853 and Staphylococcus aureus ATCC 35923 whereas resistant strains include A. baumannii ATCC BAA-1797, E. coli ATCC BAA-196, P. aeruginosa ATCC BAA-2108 and S. aureus ATCC 43300.

The minimum inhibitory concentration (MIC) of synthesized compounds against all eight bacteria were determined using the broth microdilution method adapted from Standard Operating Procedures (SOP) drafted by Monash University Facility for Anti-Infective Drug Development and Innovation (FADDI) and Clinical and Laboratory Standards Institute (CLSI) guidelines.\textsuperscript{86} Gentamicin and ampicillin were used as controls. Stock solutions of all compounds were prepared at a concentration of 1.024 × 10\textsuperscript{−3} M by dissolving the solid powders in dimethyl sulfoxide (DMSO). Two-fold serial dilution was carried out using cation-adjusted Mueller Hinton Broth (CAMHB) to obtain a final concentration ranging from 0.125 to 128 μM in the wells of 96 wells U-bottomed plate. The highest concentration of DMSO in the well was maintained at no more than 1.25%. Bacteria suspension was prepared following 0.5 McFarland standard. For quantification of the bacteria, absorbance was taken using Tecan microplate reader at a wavelength of 625 nm, and the optical density (OD\textsubscript{625}) values were adjusted to 0.07–0.08. Briefly, bacteria colonies were aseptically

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taken and resuspended into 1 mL of sterile normal saline (0.9% NaCl) to make bacteria suspension before checking for absorbance. Then, 200 µL of the optical density-adjusted bacteria suspension was added to 19.8 mL of 0.9% NaCl. Lastly, 100 µL of this bacteria suspension was added to each well containing 100 µL of the compounds and plates were incubated for 18 hours at 37 °C. To study the photodynamic therapy activities of the complexes, plates were incubated for 15 minutes after addition of compounds and irradiated for 10 minutes using LED light (365 nm) at a light density of 1.57 mW before incubation overnight. The light intensity was measured with a calibrated power meter through adjustment of distance between the LED light source and the 96-well plates. All assays were performed as at least duplicated experiments. Results were observed visually and tabulated after addition of resazurin.

Author contributions
Corinne Vanucci-Bacqué: investigation, writing (original draft); Mariusz Wolff: investigation, writing (original draft); Béatrice Delavaux-Nicot: investigation, writing (original draft); Abanoub Mosaad Abdallah: investigation; Sonia Mallet-Ladeira: investigation, writing (editing); Charles-Louis Serpentini: investigation; Florence Bedos-Belval: investigation, writing (editing), funding acquisition; Kar Wai Fong: investigation; Xiao Ying Ng: investigation; May Lee Low: investigation, writing (original draft), project administration, funding acquisition; Suzanne Fery-Forgues: investigation, methodology, writing (original draft).

Conflicts of interest
There are no conflicts to declare.

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