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Highly Emissive Cyclometalated Rhenium Metallacycles: Structure−Luminescence Relationship

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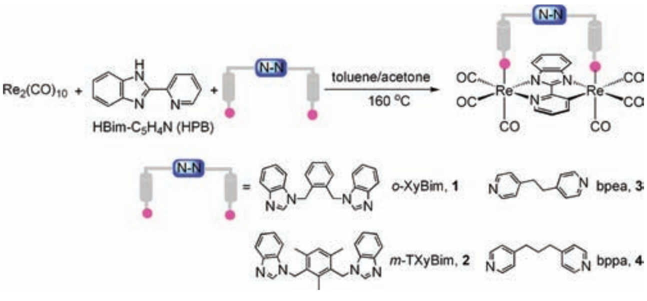
We report on a series of new self-assembled cyclometalated dirhenium(I) metallacyclic complexes via an unprecedented rhenium-mediated C−H bond activation and the relationship between their structures and luminescence properties.

Cyclometalated metallacycles,[1] a special class of metallacyclic complexes in which a ligand undergoes intramolecular (or, more rarely, intermolecular) metalation[2] as a result of C−H bond activation, have been attracting great interest because of their potential applications in organic synthesis, catalysis, photonics, and the design of new materials with unique properties.[3] Several families of cyclometalated ruthenium(II), osmium(II), and iridium(III) complexes, in which cyclometalating ligands have a beneficial effect on luminescence yields, have been reported.[4,5] Although a number of cyclometalated organometallic compounds containing nd^6 or nd^8 metal ions are known, only a few reports have appeared regarding rhenium(I) carbene complexes that contain cyclometalated ligands with carbon as the σ-donor atom.[6] Herein we report on a series of new rhenium(I) metallacycles synthesized via an unprecedented C−H-activated process. Also, the fundamental importance for their structures versus luminescence properties is unveiled.

Scheme 1. Self-Assembly of the Luminescent C−H Bond-Activated Metallacycles **1**−**4**



When Bim-C_5H_3N is incorporated as a new dianionic cyclometalating ligand and N−N as a flexible exobidentate ligand (Scheme 1), a facile one-pot synthesis[7] of dinuclear rhenium(I)-cyclometalated complexes [$\{Re(CO)_3\}_2$(μ-Bim-C_5H_3N)(μ-N−N)] (**1**−**4**) via an orthogonal bonding approach was achieved. These represent the first self-assembled cyclometalated dirhenium(I) metallacyclic complexes via rhenium-mediated C−H bond activation. Moreover, these C−H bond-activated metallacycles display highly intense phosphorescence that is red-shifted with respect to the corresponding

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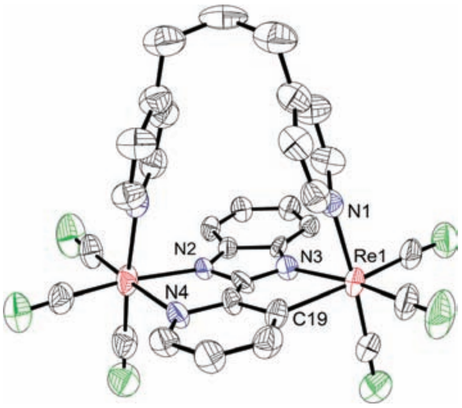

Figure 1. ORTEP plot (50% probability) of the cyclometalated rhenium(I) complex **4**. Hydrogen atoms and the disordered moieties of the Bim-C_5H_3N ligand and the disordered central methylene group of the bppa ligand are omitted for clarity.

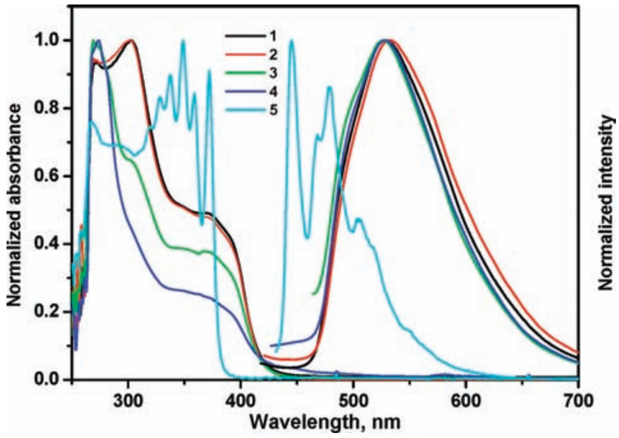

Figure 2. Absorption and emission spectra of **1**−**5** in DMF at room temperature.

non-C−H bond-activated analogue, [{$Re(CO)_3$}$_2$(μ-BiBzIm)-(μ-N−N)] [**5**, where BiBzIm = bis(benzoimidazolate)].

The synthetic protocol incorporated $Re_2(CO)_{10}$, flexible (N−N), and rigid (Bim-C_5H_3N, PB) building blocks with a 1:1:1 stoichiometric ratio in toluene/acetone (6:1, v/v) at 160 °C to afford complexes **1**−**4** (45−80%). Key steps involve C−H bond activation of the HPB ligand and the use of μ-N−N as a building block, permitting the preparation of unique dirhenium(I)-cyclometalated complexes.

Single-crystal X-ray diffraction analyses show that **1**−**4** all possess similar dirhenium molecular structures [Figure 1 for **1** and Figures S1−S3 in the Supporting Information (SI) for **2**−**4**], in which the flexible exobidentate ligand (μ-N−N) serves as a clip that binds two asymmetric octahedrally coordinated rhenium centers with C_3N_3 and C_4N_2 donors. The rhenium(I) centers are organized in pairs by a dianionic cyclometalating Bim-C_5H_3N ligand with CN_3 tetradentate doubly chelating sites. This unique configuration requires deprotonation of the benzimidazole N−H hydrogen and C−H bond activation on the C3 position of the 2-pyridyl moiety (in HPB; see Scheme 1). HPB has not yet been evaluated as a cyclometalating ligand so far.

UV−vis absorption spectra of **1**−**4** in dimethylformamide (DMF) at 298 K show similar spectral features. The intense absorption band at short wavelength (<~305 nm) with a molar extinction coefficient of $> 10^4\ M^{-1}\ cm^{-1}$ (Figure 2 and

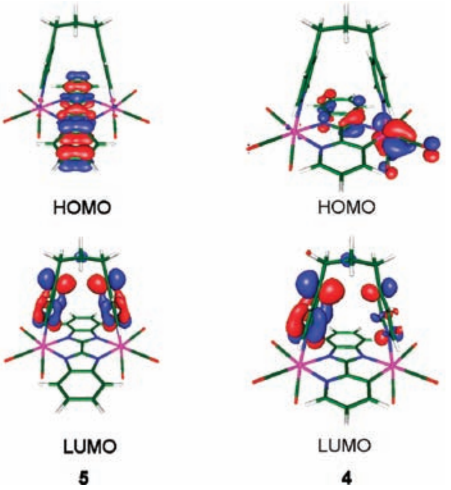

Figure 3. Frontier orbitals that involve in the lowest-lying transitions for **4** and **5**.

Table 1) is assigned to $\pi-\pi^*$ and intraligand charge-transfer transitions of Bim-C_5H_3N and μ-N−N because of their spectral similarity with respect to that of the free ligands.

The lower-lying transitions in the range of 360−400 nm, which show structureless, relatively weak absorptivity ($\varepsilon \sim 10^3-10^4\ M^{-1}\ cm^{-1}$), are attributed to a spin-allowed metal-to-ligand charge transfer (MLCT; $Re^I \rightarrow$ Bim-C_5H_3N) mixed with a certain extent of ligand-to-ligand charge transfer (LLCT; from Bim to a N−N bridging chromophore). This assignment is based on the time-dependent density functional theory (TDDFT) approach (B3LYP/SDD/6-31G** under an effective core potential; see the SI), the results of which indicate that the lowest-lying state involves a highest occupied molecular orbital (HOMO) → lowest unoccupied molecular (LUMO) transition (>90%), in which HOMO is attributed to a π-bonding interaction between dπ Re^I and the C−H bond-activated part of the cyclometalating ligand, while LUMO mainly consists of a delocalized π^* orbital on both of the N−N ligands (Figure 3).[8]

For all complexes **1**−**4**, an intense room temperature luminescence (Φ_{em} between 0.4 and 0.5; Table 1) with a peak wavelength in the range of 523−527 nm was resolved. The observed lifetimes (τ_{obs}) were measured to be 4−8 μs for **1**−**4** in degassed DMF. Taking the radiative decay time constant, $\tau_r = \tau_{obs}/\Phi_{em}$; τ_r is then deduced to be 10−20 μs for **1**−**4**. The long radiative lifetime, together with significant quenching of both the luminescence intensity and lifetime by O_2 (vide infra), ensures the emission originating from the triplet manifold, i.e., the phosphorescence. The lowest excited state of **1**−**4** in the triplet manifold can be best described as an admixture of ^{3}MLCT plus Bim (in PB) → N−N ^{3}LLCT.[6d,9] Further quantitative analysis indicates that the contribution of ^{3}MLCT is appreciable, being ~30% for complex **4** (see Table S2 in the SI). The spectral feature of **2** in butylnitrile at 77 K (Figure S4 in the SI) showed a certain vibronic progression, and the full width at half-maximum is relatively narrower than that in room temperature. The latter is mainly attributed to the lower thermal population at highly vibrational

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[8] Gaussian *03* (Revision E.01): Frisch, M. J.; , et al. (see Supporting Information); Gaussian, Inc.: Wallinford CT, 2008.

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Table 1. Photophysical Data for Complexes **1−5**

compd	λ_{abs} [nm] (ε)[a]	λ_{em} [nm][a]	τ_{obs} [μs][a]	Φ_{em}[a,b]	Φ_{Δ}[c]	$k_{q,SV}$[d]	$k_q(^1O_2)$[e]
1	269 (1.4), 302 (1.0), 370 (0.6)	527	4.76	0.48	0.40	6.79	2.22
2	267 (1.8), 301 (1.2), 369 (0.7)	527	4.13	0.45	0.41	6.72	1.61
3	272 (1.1), 304 (1.3), 371 (0.4)	524	8.17	0.47	0.55	6.99	2.19
4	273 (1.2), 301 (1.3), 367 (0.6)	523	5.76	0.45	0.55	6.19	1.40
5	267 (3.4), 289 (3.2), 319 (3.6), 328 (4.0), 337 (4.3), 349 (4.7), 359 (3.9), 372 (4.1)	445, 467 (sh) 480, 504, 518 (sh), 549 (sh)	0.18	0.01	*f*	*f*	*f*

[a] Data were recorded in a degassed DMF solution (via three freeze−pump−thaw cycles) at room temperature; $\varepsilon = 10^4$ M^{-1} cm^{-1}. [b] $Ru(bpy)_3^{2+}$ in deaerated CH_3CN, $\Phi_{em} = 0.062$. [c] With respect to perinaphthenone, which has a $^1O_2$ quantum yield (Φ_{Δ}) of 1.0 in DMF at 355 nm. [d] 10^9 M^{-1} s^{-1}. [e] 10^6 M^{-1} s^{-1}. [f] No effect.

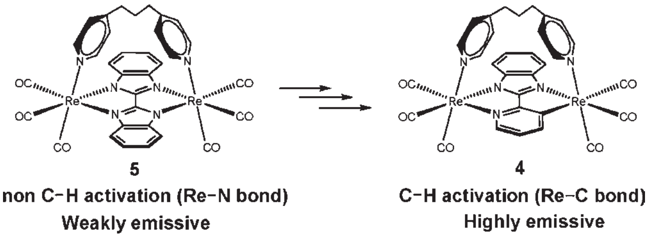
states. The former may imply certain clues for the existence of LLCT character, supporting the above assignment.

With the aim of exploring the structural effects on the photophysical properties of **1−4**, a non-C−H bond-activated dirhenium analogue, **5**, was also synthesized using a BiBzIm dianion instead of a dianionic cyclometalating PB ligand (Figure S5 in the SI). Complex **5** has a molecular structure similar to that of **4** except for the anionic BiBzIm ligand serving as an N_4 bischelator to bridge two *fac*-Re(CO)$_3$ cores. Each rhenium center exhibits a six-coordinated octahedral ReC_3N_3 geometry. In stark contrast, compound **5** showed a relatively weak ($\Phi_{em} = 0.01$), blue-shifted emission maximized at 480 nm (Figure 2), for which a lifetime was measured to be $\tau_{obs} = 183$ ns.[10] The radiative lifetime is then calculated to be 18.3 μs. As depicted in Figure 3, the computational results indicate that phosphorescence of **5** is dominated by a ligand π^*(μ-N−N) to BiBzIm delocalized π transition, while the contribution from ^{3}MLCT is estimated to be as small as 3.7% (see Table S2 in the SI). The result is also consistent with phosphorescence of **5**, revealing a dominant $\pi-\pi^*$ vibronic progressive feature (see Figure 2).

In theory, MLCT involves a Re^I d_π orbital and should greatly enhance the spin−orbit coupling, resulting in a short radiative lifetime relative to the pure $\pi-\pi^*$ transition.[11] It is thus surprising that **1−4**, possessing much greater ^{3}MLCT contributions (> 30% for, e.g., **4** vide supra), render similar magnitudes of radiative lifetime (10−20 μs) with respect to **5**. Careful analyses of frontier orbitals indicate that the distance (r) between chromophores involved in the lowest-lying transition may be responsible for this abnormity. For example, complex **4** mainly involves the transition from cyclometalated Re^I d_π to the N−N chromophore that attaches to the other Re^I ion (see Figure 3), such that the distance for the corresponding transition is relatively long (~4.0 Å). Because the spin−orbit coupling is also inversely proportional to the distance (r) to the 6 power (according to a qualitative approach for a hydrogen-like atom),[12] the spin−orbit coupling matrix is accordingly decreased, resulting in an increase of the radiative lifetime for **1−4**, despite their large MLCT percentage contribution.

The above structure−transition relationship between **1−4** and **5** is of great fundamental interest and may lie in a virtual increase in the σ-donor strength when proceeding from N (in **5**) to C$^-$ (in **1−4**). This consequently enriches the electron density at the rhenium(I) center, resulting in an increase of the MLCT character for **1−4**. The increase of the σ-donor strength may also destabilize the metal center $d_\pi-d_{\sigma^*}$ transition and thus avoid the crossing between the T_1 and $d_\pi-d_{\sigma^*}$ potential energy surfaces. In comparison to **1−4**, the relatively weaker σ-donor strength (N) for **5** should oppositely reduce the MLCT character of the lowest-lying transition as well as decrease the $d_\pi-d_{\sigma^*}$ gap. The combination of these two factors should increase the nonradiative decay rate, giving a short observed lifetime and, hence, a low emission yield (Scheme 2).

Scheme 2. C−H Activation toward the Design of Highly Emissive Compound **4**



In view of potential applications, the C−H bond-activated complexes **1−4** are found to behave as very efficient singlet oxygen ($^1O_2$) photosensitizers. The $^1O_2$ production yield was obtained by studying the $^1O_2$ chemical quenching[12] in the presence of 1,4-diazabicyclo[2.2.2]octane and 2,2,6,6-tetramethylpiperidine (TEMP) upon irradiation of **1−4** in aerated solvents, in which dramatic bleaching of the 2,2,6,6-tetramethylpiperidinooxyl radical (TEMPO) intensity was observed (Figure S8 in the SI).[13] Additional support for $^1O_2$ was obtained by an enhancement of the TEMPO signal in deuterated DMF under identical conditions, namely, an isotope effect in enhancing the $^1O_2$ lifetime.[14] Pertinent O_2 quenching data as well as yield $^1O_2$ production are listed in Table 1.

In summary, the syntheses of the first dinuclear rhenium(I)-cyclometalated complexes, **1−4**, via an effective one-pot assembly strategy are reported. The C−H bond-activated metallacycles are considerably more emissive than their non-C−H bond-activated analogue. This, in combination with the fundamentals of the structure−luminescence relationship, may pave a new route toward the design of highly luminescent rhenium(I)-based metallacyclic materials.

Supporting Information Available: Crystallographic data in CIF format, synthesis and characterization, and emission measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Complex **5** shows blue-shifted emission peak with no effect in Φ_{em} and τ_{em} (in *ns*) by dioxygen.

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