Carbazolophane Enhances the Efficiency of Thermally Activated Delayed Fluorescence in Carbene Coinage Metal Amides

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Carbazole coinage metal carbazolates are currently the most efficient organometallic TADF emitters. Herein we report on the photophysical influence of introducing a [2.2]paracyclophane moiety via a carbazolophane ligand instead of carbazolate, which greatly enhances the radiative rate constants by a factor of three to 1⋅3⋅10^6 s⁻¹ for triplet exciton emission.

Coinage metal carbene complexes in the oxidation state +1 have emerged as a versatile class of photoactive compounds within the last decade. 1-4 Unlike d⁶ and d⁸ metal complexes with relatively strict octahedral and square-planar structures, the d⁴⁰ electron configuration allows for ligand coordination in various geometries, which greatly influences the nature and properties of the excited states and thus provides a high degree of photophysical tunability. Consequently, coinage metal carbenes have found myriad applications in catalysis, OLEDs, and stimulus-responsive materials. 1, 3, 5-13 Linearly coordinated systems featuring a donor-M-acceptor (D-M-A) structure often display thermally activated delayed fluorescence (TADF), bypassing the spin-forbidden phosphorescence from the T₁ state by endothermic reverse intersystem-crossing (rISC) and subsequent S₁→S₀ emission. 7-9, 14-20 With this alternative luminescence mechanism relevant for efficient triplet exciton harvesting in device technologies, radiative rate constants k_{TADF} of 10⁵-10⁶ s⁻¹ can be achieved that are competitive or even higher than obtained with traditional 4d/5d metal complexes that provide spin-orbit coupling (SOC) for phosphorescence. 2, 21-23 In this regard, coinage metal carbazolates (CMCz) have gained particular attention due to their exceptional luminescence efficiency, 7-9, 14-20 and high-level DFT and transient absorption studies have clarified the details of the TADF mechanism. 19, 24-28 Typically, their lowest energy excited states are of 1/3LLCT character, of which the energy gap depends on the relative orientation of the carbene and Cz ligands. In a co-planar arrangement, these states are energetically well separated, but the 1LLCT state bears significant oscillator strength for efficient radiative S₁→S₀ decay. Ligand rotation or M-N(Cz) bond bending, however, decouples the electron and hole in the 1/3LLCT states, and they become nearly isoenergetic, leading to strong spin-vibronic coupling and very facile (r)ISC processes S₁↔S₁.

This dynamic TADF mechanism is generally very similar to that found in many efficient organic emitters. 29, 30 However, organometallic complexes can enhance the operative SOC either by coupling of S₁ and T₁ by energetically close-lying metal-to-ligand charge-transfer (MLCT) states and by the heavy atom effect, both scenarios further accelerating the (r)ISC and thus the overall efficiency of TADF. Consequently, very high k_{TADF} of up to 1⋅2⋅10⁶ s⁻¹ have been achieved for some selected examples of Ag and Au complexes. 8, 16, 20 It should be noted that k_{TADF} of up to 1⋅10⁶ s⁻¹ have also been reported for a few organic TADF emitters by, e.g., designing through-space 1/3CT states that feature very small ΔE(S₁-T₁) or by introduction of intermediate triplet states fostering rISC. 25, 31 However, one has to bear in mind that this comes at the price of reducing the oscillator strength of the S₁→S₀ transition, which implies a natural limit of k_{TADF} for this particular approach. In order to find structural design principles for efficient emitters, we were curious whether k_{TADF} in linear CMCz as established TADF systems could be enhanced by reducing ΔE(S₁-T₁) to assist the rISC without sacrificing the oscillator strength of the emitting S₁ state. A suitable moiety for this purpose appears

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to be indolo[2,2]paracyclophane (carbazolophane, Czp) as a derivative of Cz, which has been reported to be a very potent donor moiety in organic TADF systems.\(^{32,33}\) Also, Czp provides greater steric encumbrance that would still allow for ligand rotation to some degree to decrease \(\Delta E(1^1\text{LLCT})\), but should avoid 90° conformations, which are associated with an absence of oscillator strength for fluorescence and hence slow \(k_{\text{TADF}}\), and consequently increase the probability of the vertical transition. Treatment of [MCl(cAAC)\(^{31}\)] (\(M = \text{Cu, Ag, Au}\); cAAC = cyclic (alkyl)(amino)carbene) with HCl and in the presence of KHMDS provides facile access to 1-3, of which yellow-to-green single crystals suitable for X-ray diffraction studies were obtained in good yields of 41-54% either from THF/n-pentane mixture (1) or cooling of saturated toluene solutions to -40 °C (2 and 3) (Scheme 1). The introduction of the paracyclophane motif as a steric modification of Cz has only negligible influence on the ground state structures. The Czp complexes 1-3 exhibit a nearly linear coordination environment with N–M–C\(^{12}\)arbene angles of \(~175^\circ\), and the cAAC\(^{31}\) and Czp ligands adopt a co-planar arrangement. The M–C\(^{12}\)arbene and M–N bond lengths increase in the order 1 (Cu) < 3 (Au) < 2 (Ag), resulting in N–C\(^{12}\)arbene distances of 3.7 Å (1), 4.1 Å (2) and 4.0 Å (3), which are also very close to those found for previously reported group 11 [M(Cz)(cAAC)] complexes.\(^8,9,18\)

UV/vis absorption spectra of 1-3 in 2-MeTHF show broad low energy MLCT/LLCT bands between 400-450 nm with low extinction coefficients of \(\varepsilon = 1,500-7,500 M^{-1} cm^{-1}\), that increase in the order Ag (2) < Cu (1) < Au (3), which is supported by TD-DFT calculations (Figure 1, and Supporting Information). Negative solvatochromism with shifts of up to ca. 4,500 cm\(^{-1}\) between nonpolar n-pentane and polar acetonitrile is observed for the S\(_0\)→S\(_1\) transitions, which suggests that the ground state in 1-3 is much more polar than the 1^1\text{LLCT} excited state (Figures S13-S15).\(^{34}\)

The more structured band between 330-400 nm exhibits higher extinction coefficients of 7,100 (1), 4,800 (2) and 11,500 (3) M\(^{-1}\) cm\(^{-1}\) and originates from a 1^1\text{LC}(Czp) transition with MLCT admixture. We note that the offset of the 1^1\text{LLCT} band and the absorption maximum of the 1^1\text{LC} transition of 1 are bathochromically shifted in comparison to [Cu(Cz)(cAAC)\(^{31}\)] (\(\lambda_{\text{offset,max}} = 450\) and 390 nm vs 425 and 370 nm) due to the paracyclophane motif of the Czp ligand.\(^9\) At higher energies in the UV, intense (\(\varepsilon \geq 20,000 M^{-1} cm^{-1}\)) \(\pi\wedge\pi^*\) transitions of the arenic moieties are observed.

All compounds show intense photoluminescence with lifetimes of a few hundred nanoseconds in solution at room temperature (Table 1 and Figure 2). Minor positive solvatochromism is displayed in the shifts of \(\lambda_{\text{max}}(\text{em})\), although the excited CT state is less polar than the ground state (see above, Figures S16-S18). This effect appears to arise from small solvent-dependent differences in the structural reorganization upon photoexcitation because the onsets of the emission are solvent independent.

Table 1. Luminescence properties of 1-3 in various solvents at room temperature.

<table>
<thead>
<tr>
<th>Medium</th>
<th>(\lambda_{\text{max}}/\text{nm})</th>
<th>(\phi_{\text{em}})</th>
<th>(\tau_{\text{em}}/\text{ns})</th>
<th>(k_{\text{PL}}/\text{s}^{-1})</th>
<th>(k_{\text{deq}}/\text{s}^{-1})</th>
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<tbody>
<tr>
<td>1 n-pentane</td>
<td>530</td>
<td>0.52</td>
<td>1190</td>
<td>4.4×10(^4)</td>
<td>4.0×10(^5)</td>
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<td>toluene</td>
<td>539</td>
<td>0.80</td>
<td>728</td>
<td>1.1×10(^5)</td>
<td>2.8×10(^5)</td>
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<tr>
<td>Et(_2)O</td>
<td>546</td>
<td>0.85</td>
<td>856</td>
<td>9.9×10(^4)</td>
<td>1.8×10(^5)</td>
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<tr>
<td>2-MeTHF</td>
<td>552</td>
<td>0.50</td>
<td>534</td>
<td>9.4×10(^4)</td>
<td>9.4×10(^4)</td>
</tr>
<tr>
<td>MeCN</td>
<td>553</td>
<td>0.29</td>
<td>293</td>
<td>9.9×10(^4)</td>
<td>2.4×10(^5)</td>
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<tr>
<td>2 n-pentane</td>
<td>553</td>
<td>0.36</td>
<td>110</td>
<td>3.3×10(^5)</td>
<td>5.8×10(^5)</td>
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<tr>
<td>toluene</td>
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<td>0.25</td>
<td>183</td>
<td>1.4×10(^5)</td>
<td>4.1×10(^5)</td>
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<tr>
<td>Et(_2)O</td>
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<td>0.11</td>
<td>118</td>
<td>9.3×10(^4)</td>
<td>7.5×10(^5)</td>
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<tr>
<td>2-MeTHF</td>
<td>575</td>
<td>0.06</td>
<td>146</td>
<td>4.1×10(^5)</td>
<td>6.4×10(^5)</td>
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<tr>
<td>MeCN</td>
<td>584</td>
<td>&lt;0.01</td>
<td>104</td>
<td>≤9.6×10(^5)</td>
<td>≥9.5×10(^6)</td>
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<td>3 n-pentane</td>
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<td>0.54</td>
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<td>2.7×10(^5)</td>
<td>2.3×10(^5)</td>
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<tr>
<td>toluene</td>
<td>550</td>
<td>0.42</td>
<td>149</td>
<td>2.8×10(^5)</td>
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<td>Et(_2)O</td>
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<td>0.25</td>
<td>397</td>
<td>6.3×10(^5)</td>
<td>1.9×10(^6)</td>
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<tr>
<td>2-MeTHF</td>
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<td>1.1×10(^6)</td>
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<td>1.1×10(^6)</td>
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</table>

*For multieponential decays, the amplitude averaged lifetimes are given (see also Supporting Information). \(^{34}\) \(k_{\text{PL}} = \phi_{\text{em}}/\tau \cdot k_{\text{deq}} = (1-\phi_{\text{em}})/\tau\).
The emission energies in the green to orange region of the electromagnetic spectrum are shifted bathochromically along the series Cu > Au > Ag.

Complex 1 is the most efficient emitter with the highest photoluminescence quantum yields $\Phi_{\text{PL}}$, reaching values of up to 0.85 in Et$_2$O, and concomitant high $k_{\text{nr}}$ of 0.9-1.1·10$^6$ s$^{-1}$ (Table 1). Interestingly, $k_1$ is reduced to 4.4·10$^5$ s$^{-1}$ in n-pentane. The comparison of 1 with previously reported [Cu(Cz)(cAAC)$_2$] ($k_1 = 3·10^5$ s$^{-1}$) in 2-MeTHF is very insightful and shows that the Cz moiety enhances $k_1$ by a factor of 3.$^5$ The $\Phi_{\text{PL}}$ are significantly reduced for the silver and gold congeners 2 and 3, which is a result of enhanced non-radiative decay in comparison to 1 and not due to reduced $k_1$ (Table 1). Actually, the $k_1$ of 2 and 3 are very high in nonpolar toluene and n-pentane with values of up to 3.3·10$^6$ s$^{-1}$(2) and 2.8·10$^6$ s$^{-1}$ (3), and are found to be among the highest values ever reported for organometallic triplet exciton emitters.$^2.4.7.9.11.13-16.18-20.23.35$

Such high $k_1$ in D-A compounds are typically the result of an efficient TADF process. Further indication that the excited state decays to the ground state from the $S_1$ state is provided by the high $k_{\text{nr}}$, excluding non-radiative decay from T1 as that process would be much slower due to its spin-forbidden nature.

Indeed, time-resolved VT measurements of 1-3 in polar 2-MeTHF show an increase of the radiative lifetimes by several orders of magnitude into the millisecond domain at 77 K, typical for a change of the emission mechanism from TADF to phosphorescence (Figure 2). The temperature-dependent spectral evolution reveals a thermal equilibrium between the $^{1/3}$LLCT states because the emission band remains broad until the glass transition temperature of the solvent, with very small estimated energy gaps of $\Delta E(1/3)$LLCT $= 130$ cm$^{-1}$ (16 meV) (1), 280 cm$^{-1}$ (35 meV) (2) and 210 (26 meV) (3). However, a vibrational progression and hypochromic emission shift are observed in the frozen glassy matrix at 77 K, originating from the $^{3}$LLCT state energetically above the $^{1}$LC state. Noteworthy, the $^{3}$LC(Cz) state is lower in energy by 2,000 cm$^{-1}$ (0.25 eV) than the $^{3}$LC(Cz) in related coinage metal complexes ($\lambda_{\text{em}} = 420$ nm) and exhibits a much greater spectral overlap with the $^{1/3}$LLCT states. In addition, we estimate small energy gaps of $\Delta E(1/3)$LLCT $= 1050$ cm$^{-1}$ (130 meV) (1), 1,540 cm$^{-1}$ (190 meV) (2) and 1430 cm$^{-1}$ (180 meV) (3) from the emission onsets, which indicates strong vibrational coupling of these states to facilitate efficient rISC for TADF.

In conclusion, exchanging the carbazolate ligand for carbazolophane in coinage metal carbene complexes shifts the steady state equilibrium between the excited states involved in the TADF process towards the $^{1}$LLCT state by reducing $\Delta E(1/3)$LLCT and opening another rISC channel via the $^{3}$LC(Cz) state. In addition, the steric demand of the [2.2]paracyclophane moiety apparently avoids dihedral angles between the ligands close to 90° with little oscillator strength for the transition $S_1\rightarrow S_0$. Consequently, very high $k_{\text{ADF}}$ in nonpolar solvents of 1-3:3·10$^6$ s$^{-1}$ are obtained, which are greatly increased compared to the analogous Cz complexes. Further studies on the excited state dynamics are currently underway.

**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**

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