Stimulus-triggered Anion-Cation-Exciplex Formation in Copper(I)-Complexes as new Mechanism for Mechanochromic Phosphorescence


Dedicated to Professor Peter Jutzi on the occasion of his 80th birthday.

The investigation of the mechanisms of mechanochromic luminescence is of fundamental importance for the development of materials for photonic sensors, data storage or luminescence switches. The structural origin for this phenomenon in phosphorescent molecular systems is rarely known and thus the formulation of structure-property relationships remains challenging. For d^{10} coinage metal compounds, changes of M-M interactions have been proposed as the main mechanism. Herein, we describe a new mechanism, which is mechanically induced reversible cation-anion exciplex formation based on Cu-F interactions, that leads to highly efficient mechanochromic phosphorescence and for Cu complexes unusual large emission shift from UV-blue to yellow. The low-energy luminescence is thermo- and vaporesponsive, allowing for the generation of white light as well as for recovering the original UV-blue emission.

Dynamic functional materials, which change their photophysical properties in response to an external stimulus, have great potential as sensors, luminescence switches, for data storage and safety applications.[11] The stimulus-responsive functionality is often a result of changing the short- or long-range order that is formed due to intermolecular π-interactions or hydrogen bonding.[12, 2] Based on this, some design criteria have been proposed for fluorescent π-conjugated materials, which change their emission properties under the influence of a mechanical force (mechanochromic / piezochromic fluorocenes).[15-23] and some conceptual applications for the detection of strain and stress, in displays and as fluorescent switches have been demonstrated.[13, 4]

The development and application of mechanochromic phosphorescent (MRP) metal complexes is less advanced, although their properties, e.g. longer emission lifetimes, larger energy gaps between absorption and emission, as well as larger spectral changes after the stimulus compared to fluorescent (MRF) systems,[3c, 3d] are of great interest for innovative photonic applications.[14, 2a, 3c, 3d] The less often observed MRP phenomenon is mostly due to the formation or interruption of intra- or intermolecular metal-metal interactions, which are difficult to predict and thus serve only as a very limited design motif.

However, some very impressive examples of efficient MRP have been realised, e.g. in Pt[8] complexes, which can switch between 3MLCT, 3IL and 3MMLCT states by induced (des)aggregation and change their emission colour/intensity.[10, 5] Metallophilic interactions are of particular importance for the structures and photophysical properties of d^{10} metal complexes.[26, 6] Consequently, MRP phenomena have been reported in gold(I) compounds by mechanically induced formation of Au-Au contacts upon single-crystal-to-single-crystal transformation.[7] Cuprophilic interactions have been identified as origin for MRP behaviour in copper(I) clusters, of which the structure and properties can only be controlled to a limited extend.[8]

We demonstrate herein, that mechanically triggered exciplex formation between coordinatively unsaturated metal complexes and their counterions can serve as a new design strategy for the development of MRP materials and thus provides an attractive alternative to the limited scope of target-oriented formation of variable metal-metal interactions for MRP.

The dicopper(I) (1[8]-3) and monocopper(I) (4[10]) compounds have been prepared according to Scheme 1 and characterized by multinuclear NMR spectroscopy, elemental analysis and HR-ESI mass spectrometry (see ESI). Single crystals suitable for X-ray diffraction studies have been isolated by diffusion of Et2O in saturated solutions of 1-3 in CH3CN (ESI). The molecular structures thus obtained show no intermolecular metallophilic interactions and the intramolecular Cu-Cu distances of 6.419(4) (1), 6.224(9) (2) and 3.073(3) Å are beyond the sum of the Vander-Waals-radii of 2.8 Å. In addition, no Cu-F contacts can be observed in the ground state because the shortest distances are 4.625(2) (1), 4.114(5) (2) and 3.504(2) Å (3).
The propylene-bridged dicopper(I) complex [Cu₂(Bulm)-(CH₃)₂Bulm]PF₆ (1) shows UV-blue luminescence (λₑₓ(max) = 393 nm) with a long lifetime of τ = 660 μs and a quantum yield of η = 0.04 in single crystals as well as in powder samples, of which the single-crystalline composition has been confirmed by PXRD (Fig. 1 and Table S2, ES1). The emission properties are very similar to those of [Cu(Bulm)₂]PF₆ (4) (Fig. S16), and therefore we assign the blue phosphorescence of 1 to originate from the [Cu(NHC)₂] fragment. Our DFT/TD-DFT studies suggest that the small radiative rate constants are due to only small π-n* contributions in the emissive T₁ state, which is of 3MLCT character, and to large energy gaps to S₅ states with significant oscillator strength, reducing their coupling with T₁ (Figs. S7, S8 and Table S3).

Grinding of crystalline 1 leads to an unusually large bathochromic shift of the UV-blue emission by ca. 0.9 eV (7300 cm⁻¹) to yellow (λₑₓ(max) = 550 nm) and a ten-fold increase in efficiency (η = 0.51) combined with a decrease of the lifetime to only 37 μs (Fig. 1). The mechanical stimulus apparently gives rise to a great increase of the radiative rate constant k. The resulting yellow emitting phase is mainly amorphous, but chemically intact according to our ¹H-NMR-spectroscopic studies (Figs. S22, S26), and stable towards oxygen, moisture and heating to 250 °C. In addition, it shows a pronounced vapochromic luminescence in the presence of vapours of CH₃CN, CH₂Cl₂ or THF, regenerating the blue emitting phase (Figs. 1 and S18). The latter effect can also be observed upon addition of solvent drops. The overall process is reversible without any signs of degradation, so that recurrent grinding gives again yellow emission. Ground 1 exhibits also distinct thermochromic luminescence (TCL) as another fascinating facet (Figs. 1 and S9/10). Thus, the yellow emission can be turned into cyan at 177 K (λₑₓ = 265 nm) or cold white light at 127 K (λₑₓ = 280 nm), while at 77 K the blue emission is observed.

The MRP phenomenon of 1 must be the result of a dynamic process in the excited state, as IR and Raman spectroscopic measurements suggest identical ground state structures for both phases without metal-metal or metal-anion bonds (Figs. S55, S56), and temperature-dependent luminescence studies indicate an energy barrier between the yellow and blue emission. We exclude intermolecular interactions between the metal complexes in the solid state as the origin of the yellow emission, because crystalline as well as ground 1 dissolved in CH₂CN or doped in PMMA films (1%) also show intense emission at 550 nm with lifetimes of 14-20 μs, which switches to blue emission at 77 K (Figs. 1 and S1, S2, S5). Also, no aggregation-induced phenomena upon changing the concentration of 1 can be observed.

In order to exclude the formation of metalophilic interactions in the excited state as the cause for the MRP behaviour, we compared 1 with [Cu₂(Bulm)(CH₃)₂Bulm]PF₆ (3), which does not exhibit mechanochromic luminescence but features a short Cu-Cu distance of only 3.073 Å, giving rise to additional 3CC (cluster-centered) emission at 470 nm besides the 3MLCT phosphorescence (Fig. S15). The 3CC emission of 3 increases in intensity at 77 K and is strongly hypsochromically shifted compared to the yellow emission of 1, which decreases in intensity upon lowering the temperature. Since 1 partially decomposes in solution upon pulsed laser excitation (λₑₓ = 266 nm) in transient absorption measurements, and thus no definite conclusions are available from such experiments, we analysed the ground state and light-induced EPR spectra of 1 and 3.

Whereas the solid state EPR spectrum of 3 shows a distinct structure that has been successfully simulated using the available X-ray diffraction data under the assumption of dipolar interactions of electrons localised at two copper nucleus (see ESI), the spectra of 1 in its single crystalline solid state and in the ground phase are very broad and nearly identical (Fig. 2). This implies that the mechanical stimulus does not lead to the formation of short Cu-Cu contacts in 1, which could form 3CC states. We note that pure organic triplet states with small dipolar couplings D < 0.033 cm⁻¹ (MHz-GHz) can be investigated with transient EPR spectroscopy. However, for 1 and 3 no EPR signals upon laser excitation at 20 K or at room temperature have been detected, indicating that their emitting states have significant 3MLCT contributions and expected zero-field-splitting of at least 5 cm⁻¹ (150 GHz), which is in line with our DFT/TDDFT studies and assignments of state characters.

We postulate that the origin of the MRP behavior of 1 is an anion-controlled distortion of the linear [Cu(NHC)₂]-fragment. In the crystalline solid state only the blue emission is observed due to large Cu-PF₆ distances, but the mechanical stimulus leads to a decrease of the cation-anion distances and allows for the formation of Cu-F interactions in the excited state. This distortion
to a trigonal coordination geometry is hindered at low temperatures, so that the linear 3MLCT state is dominant. The yellow emission of 1 in PMMA films at room temperature is thus a consequence of tight ion-pairing in CH2Cl2 solution, from which the films have been prepared, leading to short cation-anion distances upon evaporation of the solvent. The much more intense yellow emission in PMMA at 77 K compared to the solid state at 77 K is due to a more flexible environment and thus more easily accessible distortion in the excited state. 1H-19F HOESY NMR spectra confirm the picture of tight ion-pairing in solution (Fig. S27), which consequently is also responsible for the yellow emission in CH3CN because on the timescale of the excited state lifetime (several ms), diffusion of the anion from the NHC to the Cu ion under formation of Cu-F interactions should be very fast (ps-ps). Exciplex formation with the solvent has to be excluded as the mechanochromic luminescence studies in the solid state always show regeneration of the blue emission when solvents have been added. Due to the stronger ion-pairing of the BF2-analogue 2, which generally exhibits the same emission behaviour in single crystals and upon grinding as 1 (see Fig. S11, Table S2) but does not regenerate the blue emission after addition of solvents, the partial formation of Cu-F interactions in its yellow emitting phase can even be observed in the ground state in the solid state 19F(1H) NMR spectrum (Fig. 3).

In line with the conception of an anion-controlled dynamic excited state behaviour, grinding of 1 or 2 with various salts leads to drastic changes of their luminescence properties in the solid state (Figs. 3 and S14, Table S2). Grinding with NaBPh4 gives highly efficient green emission, presumably due to the formation of Cu2L4-BPh4 interactions or partial intercalation of the bigger anion, which may result in longer Cu-F bonds (vide infra). NMR spectroscopic investigations of these ground samples still confirm the structural integrity of the dicopper(I) dications (Figs. S38-39). When employing Li[Al(OC(CF3)3)4], the weakly coordinating anion first leads to interruption of the Cu-F interactions and consequently to very efficient blue emission (φ = 0.18, τ = 323 μs) of the linear [Cu(NHC)2] fragment. Further intense grinding yields yellow luminescence, of which the higher radiative rate constant (φ = 0.17, τ = 31 μs) again points to the renewed formation of Cu-F interactions between the dicaticonic copper complex and the CF3 groups of the aluminato in the T1 state. In CH3CN solution, all samples give yellow luminescence (vide supra).

The MRP phenomenon via cation-anion exciplex formation is not observed for 3 and 4 because of steric protection of the metal centres by the NHC ligands. An analysis of the buried volume %Vbur reveals a coverage of the spherical volume of 85.6 (4) and 76.9 % (3) by the ligands (Fig. 4)39. In contrast, a value of only 70.3 % is found for the dication in 1 and 2 in combination with a coordination pocket for anion coordination in the SW quadrant with partial coverage of only 54.8 % (Table S5). This is further supported by our DFT studies of the model compound [Cu(iBuMeIm)2]BF4 (5-DFT), which experiences a geometrical distortion in the T1 state only because of the sterically less demanding ligands compared to 4 (Fig. 4). The T-shape structure is a result of a short Cu-F contact of only 2.09 Å (S3 = 2.61/2.76 Å) between the copper ion and the BF2 anion trans to one of the NHC ligands, thereby stabilizing the triplet state energetically compared to the linear T1 geometry. The geometry optimized T1 states of 1 and 2 exhibit very similar distortions of the coordination geometry of the Cu4 centre via generation of short Cu-F contacts, of which the specific distance has a large influence on the energy difference T1-S0 (vide supra) (Figs. S62 and S63).

![Figure 2](image_url)

**Figure 2.** Solid state EPR spectra of 3 (Cu-Cu distance: 3.073(3) Å) and 1 (Cu-Cu distance: 6.419(4) Å) at 20 K.
The luminescence properties of d10 coinage metal complexes in particular are very sensitive to distortions of the coordination geometry by solvent or anion coordination in the ground state as well as in the excited state.\cite{12, 13}

We note that mechanically induced counterion exciplex formation has been reported before as a very rare mode of action for mechanochromic luminescence (MRF) in organics.\cite{14} However, we illustrate for the first time, with the example of linear coordinated copper(I) NHC complexes with varying steric protection of the metal centre, that stimulus-triggered exciplex formation between a complex cation and the anion can give rise to highly efficient mechano-responsive phosphorescence (MRP) materials and provides an attractive alternative to distortions of modes of actions based on M-M interactions. The Cu-F interactions between the dinuclear [Cu2(NHC)3]2+ complexes with PF6− or BF4− in the triplet excited state are only possible upon grinding due to changes of the cation-anion distances, allowing for significant distortion of the emitting state. The mechanochromic luminescence is unusually efficient for Cu2 compounds, with interesting thermo- and vaporesponsive properties. Our current efforts are devoted to the investigation of other combinations of coordinatively unsaturated metal fragments and anions for MRP as well as their application in polymeric materials.

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Keywords: copper • phosphorescence • mechanochromic luminescence • NHC • exciplex formation


Figure 4. Left: buried volume %Vbur of the cations in 4, 3 and 1/2. Right: DFT-(D3BJ-PBE0/def2-TZVP/ZORA)-optimized T1 state with a frozen Cu-F distance of 2.606 Å and calculated distortion upon mechanically enabled exciplex formation of the model compound 4-DFT with non-frozen Cu-F distance.

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Grind 'n' Glow: Highly efficient mechanochromic, vapochromic and thermochromic phosphorescence is observed in ionic dicopper(I) complexes due to stimulus-triggered exciplex formation. Grinding leads to changes of the cation-anion distances and to the formation of Cu-F interactions in the triplet excited state.