**QUEEN'S
UNIVERSITY
BELFAST**

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

Hupp, B., Nitsch, J., Schmitt, T., Bertermann, R., Edkins, K., Florian, H., Fischer, I., Auth, M., Sperlich, A., & Steffen, A. (2018). Stimulus-triggered Anion-Cation-Exciplex Formation in Copper(I)-Complexes as new Mechanism for Mechanochromic Phosphorescence. *Angewandte Chemie International Edition*.
<https://doi.org/10.1002/anie.201807768>

Published in:
Angewandte Chemie International Edition

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

Publisher rights

© 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. This work is made available online in accordance with the publisher's policies. Please refer to any applicable terms of use of the publisher.

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Accepted Article

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

Authors: Benjamin Hupp, Jörn Nitsch, Tanja Schmitt, Rüdiger Bertermann, Katharina Edkins, Florian Hirsch, Ingo Fischer, Michael Auth, Andreas Sperlich, and Andreas Steffen

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201807768
Angew. Chem. 10.1002/ange.201807768

Link to VoR: <http://dx.doi.org/10.1002/anie.201807768>
<http://dx.doi.org/10.1002/ange.201807768>

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

Benjamin Hupp,^[a] Jörn Nitsch,^[a] Tanja Schmitt,^[a] Rüdiger Bertermann,^[a] Katharina Edkins,^[a] Florian Hirsch,^[b] Ingo Fischer,^[b] Michael Auth,^[c] Andreas Sperlich,^[c] and Andreas Steffen^{*,[a]}

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^{I} 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.^[1] 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.^[1d-f, 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 fluorescence),^[1e, 1f, 2-3] and some conceptual applications for the detection of strain and stress, in displays and as fluorescent switches have been demonstrated.^[19-j, 4]

The development and application of mechano-responsive 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.^[1e, 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^{II} complexes, which can switch between $^3\text{MLCT}$, ^3IL and $^3\text{MMLCT}$ states by induced (des)aggregation and change their emission colour/intensity.^[11, 5] Metallophilic interactions are of particular importance for the structures and photophysical properties of d^{10} metal compounds.^[2b, 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**–**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 Et_2O in saturated solutions of **1**–**3** in CH_3CN (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) (**3**) Å are beyond the sum of the Van der 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) (**3**) Å.

Scheme 1. Synthesis of copper(I) NHC complexes **1**–**4** and molecular structure of **1** determined by single crystal X-ray diffraction (see also ESI).

[a] B. Hupp, Dr. J. Nitsch, T. Schmitt, Dr. R. Bertermann, Dr. K. Edkins, Priv.-Doz. Dr. A. Steffen

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg
E-mail: andreas.steffen@uni-wuerzburg.de

[b] F. Hirsch, Prof. Dr. I. Fischer

Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg

[c] M. Auth, Dr. A. Sperlich

Physikalisches Institut, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg

Supporting information for this article is given via a link at the end of the document.

The propylene-bridged dicopper(I) complex $[\text{Cu}_2\{\text{fBulm}(\text{CH}_2)_3\text{fBulm}\}_2](\text{PF}_6)_2$ (**1**) shows UV-blue luminescence ($\lambda_{\text{em}}(\text{max}) = 393$ nm) with a long lifetime of $\tau \approx 660$ μs and a quantum yield of $\phi = 0.04$ 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, ESI). The emission properties are very similar to those of $[\text{Cu}(\text{fBu}_2\text{Im})_2]\text{PF}_6$ (**4**) (Fig. S16), and therefore we assign the blue phosphorescence of **1** to originate from the $\{\text{Cu}(\text{NHC})_2\}$ fragment. Our DFT/TD-DFT studies suggest that the small radiative rate constants are due to only small $\pi\text{-}\pi^*$ contributions in the emissive T_1 state, which is of $^3\text{MLCT}$ character, and to large energy gaps to S_n states with significant oscillator strength, reducing their coupling with T_1 (Figs. S57, S58 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 ($\lambda_{\text{em}}(\text{max}) = 550$ nm) and a ten-fold increase in efficiency ($\phi = 0.51$) 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_r . 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 CH_3CN , CH_2Cl_2 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 ($\lambda_{\text{ex}} = 265$ nm) or cold white light at 127 K ($\lambda_{\text{ex}} = 280$ 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, be-

cause crystalline as well as ground **1** dissolved in CH_3CN 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 metallophilic interactions in the excited state as the cause for the MRP behaviour,^[6a, 7a, 7b, 8a, 8b, 11] we compared **1** with $[\text{Cu}_2\{\text{fBulm}(\text{CH}_2)_3\text{fBulm}\}_2](\text{PF}_6)_2$ (**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 $^3\text{MLCT}$ 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 ($\lambda_{\text{ex}} = 266$ 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 $D < 0.033\text{ cm}^{-1}$ (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 $^3\text{MLCT}$ contributions and expected zero-field-splitting of at least 5 cm^{-1} (150 GHz), which is in line with our DFT/TD-DFT 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 $\{\text{Cu}(\text{NHC})_2\}$ -fragment. In the crystalline solid state only the blue emission is observed due to large Cu- PF_6 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

Figure 1. Left: emission spectra of single crystals of **1** (blue), upon grinding (orange) and influence of MeCN vapours on the ground sample (blue, dashed). Middle: reversible mechanochromic luminescence of **1** by regeneration of the blue emission with solvent vapours. Right: thermochromic luminescence of the ground sample.

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.

to a trigonal coordination geometry is hindered at low temperatures, so that the linear $^3\text{MLCT}$ state is dominant. The yellow emission of **1** in PMMA films at room temperature is thus a consequence of tight ion-pairing in CH_2Cl_2 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 - ^{19}F HOESY NMR spectra confirm the picture of tight ion-pairing in solution (Fig. S27), which consequently is also responsible for the yellow emission in CH_3CN because on the timescale of the excited state lifetime (several ms), diffusion of the anion from the NHC to the Cu^{I} ion under formation of Cu-F interactions should be very fast (ps-ns). Exciplex formation with the solvent has to be excluded,^[12] 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 BF_4^- 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 $^{19}\text{F}\{^1\text{H}\}$ 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 NaBPh_4 gives highly efficient green emission, presumably due to the formation of $(\text{Cu}_2\text{L}_4)^+-\text{BPh}_4^-$ 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 $\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$, the weakly coordinating anion first leads to interruption of the Cu-F interactions and consequently to very efficient blue emission ($\phi = 0.18$, $\tau = 323 \mu\text{s}$) of the linear $\{\text{Cu}(\text{NHC})_2\}$ fragment. Further intense grinding yields yellow luminescence, of which the higher radiative rate constant ($\phi = 0.17$, $\tau = 31 \mu\text{s}$) again points to the

renewed formation of Cu-F interactions between the dicationic copper complex and the CF_3 groups of the aluminate in the T_1 state. In CH_3CN 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 $\%V_{\text{bur}}$ reveals a coverage of the spherical volume of 85.6 (**4**) and 76.9 % (**3**) by the ligands (Fig. 4).^[13] 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 $[\text{Cu}(\text{tBuMelm})_2]\text{BF}_4$ (**5-DFT**), which experiences a geometrical distortion in the T_1 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 ($S_0 = 2.61/2.76$ Å) between the copper ion and the BF_4^- anion *trans* to one of the NHC ligands, thereby stabilizing the triplet state energetically compared to the linear T_1 geometry. The geometry optimized T_1 states of **1** and **2** exhibit very similar distortions of the coordination geometry of the Cu^{I} centre via generation of short Cu-F contacts, of which the specific distance has a large influence on the energy difference T_1-S_0 (vide supra) (Figs. S62 and S63).

Figure 3. Top: $^{19}\text{F}\{^1\text{H}\}$ solid state and ^1H - ^{19}F HOESY NMR spectrum in D_3 -MeCN of **2**. Bottom: a) ground **2**, b) NaBPh_4 ground with a), c) $\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ ground with a), d) intense ground c).

Figure 4. Left: buried volume %V_{bur} 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 **5-DFT** with non-frozen Cu-F distance.

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.^[1d, 2b, 12, 14] We note that mechanically induced counterion exciplex formation has been reported before as a very rare mode of action for mechanochromic fluorescence (MRF) in organics.^[3e] 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 modes of actions based on M-M interactions. The Cu-F interactions between the dicationic [Cu₂(NHC)₂]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 Cu^I compounds, with interesting thermo- and vapo-responsive 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.

Acknowledgements

We thank the DFG (STE1834/4-1 and /5-1, and GRK 2112) for financial support and Prof. Dr. I. Krossing (Freiburg) for a sample of Li[Al(OC(CF₃)₃)₄].

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

- [1] a) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759; b) C. E. Olson, M. J. R. Previte, J. T. Fourkas, *Nat. Mater.* **2002**, *1*, 225; c) H. Sun, S. Liu, W. Lin, K. Y. Zhang, W. Lv, X. Huang, F. Huo, H. Yang, G. Jenkins, Q. Zhao, W. Huang, *Nat. Commun.* **2014**, *5*, 4601/1; d) O. S. Wenger, *Chem. Rev.* **2013**, *113*, 3686; e) A. J. McConnell, C. S. Wood, P. P. Neelakandan, J. R. Nitschke, *Chem. Rev.* **2015**, *115*, 7729; f) J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2015**, *115*, 11718; g) D. R. T. Roberts, S. J. Holder, *J. Mater. Chem.* **2011**, *21*, 8256; h) Y. Sagara, T. Komatsu, T.

- Ueno, K. Hanaoka, T. Kato, T. Nagano, *J. Am. Chem. Soc.* **2014**, *136*, 4273; i) D. Genovese, A. Aliprandi, E. A. Prasetyanto, M. Mauro, M. Hirtz, H. Fuchs, Y. Fujita, H. Uji-I, S. Lebedkin, M. Kappes, L. De Cola, *Adv. Funct. Mater.* **2016**, *26*, 5271; j) R. Goestl, R. P. Sijbesma, *Chem. Sci.* **2016**, *7*, 370; k) S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem., Int. Ed.* **2015**, *54*, 11572; l) A. Aliprandi, D. Genovese, M. Mauro, L. D. Cola, *Chem. Lett.* **2015**, 1152; m) S. Theis, A. Iturmendi, C. Gorsche, M. Orthofer, M. Lunzer, S. Baudis, A. Ovsianikov, R. Liska, U. Monkowius, I. Teasdale, *Angew. Chem., Int. Ed.* **2017**, *56*, 15857.
- [2] a) Y. Sagara, S. Yamane, M. Mitani, C. Weder, T. Kato, *Adv. Mater.* **2016**, *28*, 1073; b) V. W. W. Yam, V. K. M. Au, S. Y. L. Leung, *Chem. Rev.* **2015**, *115*, 7589.
- [3] a) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, J. Xu, *Chem. Soc. Rev.* **2012**, *41*, 3878; b) F. Ciardelli, G. Ruggeri, A. Pucci, *Chem. Soc. Rev.* **2013**, *42*, 857; c) X. Zhang, Z. Chi, Y. Zhang, S. Liu, J. Xu, *J. Mater. Chem. C* **2013**, *1*, 3376; d) P. Xue, J. Ding, P. Wang, R. Lu, *J. Mater. Chem. C* **2016**, *4*, 6688; e) G. Li, F. Song, D. Wu, J. Lan, X. Liu, J. Wu, S. Yang, D. Xiao, J. You, *Adv. Funct. Mater.* **2014**, *24*, 747.
- [4] a) Y. Ren, W. H. Kan, V. Thangadurai, T. Baumgartner, *Angew. Chem., Int. Ed.* **2012**, *51*, 3964; b) A. Kishimura, T. Yamashita, K. Yamaguchi, T. Aida, *Nat. Mater.* **2005**, *4*, 546; c) S. Zeng, D. Zhang, W. Huang, Z. Wang, S. G. Freire, X. Yu, A. T. Smith, E. Y. Huang, H. Nguon, L. Sun, *Nat. Commun.* **2016**, *7*, 11802.
- [5] a) A. Han, P. Du, Z. Sun, H. Wu, H. Jia, R. Zhang, Z. Liang, R. Cao, R. Eisenberg, *Inorg. Chem.* **2014**, *53*, 3338; b) V. N. Kozhevnikov, B. Donnio, D. W. Bruce, *Angew. Chem., Int. Ed.* **2008**, *47*, 6286; c) M. Krikorian, S. Liu, T. M. Swager, *J. Am. Chem. Soc.* **2014**, *136*, 2952; d) X. Zhang, J.-Y. Wang, J. Ni, L.-Y. Zhang, Z.-N. Chen, *Inorg. Chem.* **2012**, *51*, 5569; e) X.-P. Zhang, J.-F. Mei, J.-C. Lai, C.-H. Li, X.-Z. You, *J. Mater. Chem. C* **2015**, *3*, 2350.
- [6] a) C.-M. Che, Z. Mao, V. M. Miskowski, M.-C. Tse, C.-K. Chan, K.-K. Cheung, D. L. Phillips, K.-H. Leung, *Angew. Chem., Int. Ed.* **2000**, *39*, 4084; b) P. Woidy, A. J. Karttunen, M. Widenmeyer, R. Niewa, F. Kraus, *Chem. Eur. J.* **2015**, *21*, 3290; c) J. Nitsch, F. Lacemon, A. Lorbach, A. Eichhorn, F. Cisnetti, A. Steffen, *Chem. Commun.* **2016**, *52*, 2932; d) R. Molteni, R. Bertermann, K. Edkins, A. Steffen, *Chem. Commun.* **2016**, *52*, 5019; e) M. Hailmann, N. Wolf, R. Renner, T. C. Schafer, B. Hupp, A. Steffen, M. Finze, *Angew. Chem., Int. Ed.* **2016**, *55*, 10507; f) I. O. Koshevoy, Y. C. Chang, A. J. Karttunen, J. R. Shakhova, J. Janis, M. Haukka, T. Pakkanen, P. T. Chou, *Chem. Eur. J.* **2013**, *19*, 5104; g) A. Belyaev, T. Eskelinen, T. M. Dau, Y. Y. Ershova, S. P. Tunik, A. S. Melnikov, P. Hirva, I. O. Koshevoy, *Chem. Eur. J.* **2018**, *24*, 1404; h) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931.
- [7] a) Y.-A. Lee, R. Eisenberg, *J. Am. Chem. Soc.* **2003**, *125*, 7778; b) H. Ito, T. Saito, N. Oshima, N. Kitamura, S. Ishizaka, Y. Hinatsu, M. Wakeshima, M. Kato, K. Tsuge, M. Sawamura, *J. Am. Chem. Soc.*

- 2008**, 130, 10044; c) J. Schneider, Y.-A. Lee, J. Pérez, W. W. Brennessel, C. Flaschenriem, R. Eisenberg, *Inorg. Chem.* **2008**, 47, 957.
- [8] a) S. Perruchas, X. F. Le Goff, S. Maron, I. Maurin, F. Guillen, A. Garcia, T. Gacoin, J.-P. Boilot, *J. Am. Chem. Soc.* **2010**, 132, 10967; b) Q. Benito, X. F. Le Goff, S. Maron, A. Fargues, A. Garcia, C. Martineau, F. Taulelle, S. Kahlal, T. Gacoin, J.-P. Boilot, S. Perruchas, *J. Am. Chem. Soc.* **2014**, 136, 11311; c) M. S. Deshmukh, A. Yadav, R. Pant, R. Boomishankar, *Inorg. Chem.* **2015**, 54, 1337; d) Q. Xiao, J. Zheng, M. Li, S.-Z. Zhan, J.-H. Wang, D. Li, *Inorg. Chem.* **2014**, 53, 11604.
- [9] E. Kuhnle, I. V. Shishkov, F. Rominger, T. Oeser, P. Hofmann, *Organometallics* **2012**, 31, 8000.
- [10] S. Diez-Gonzalez, E. D. Stevens, N. M. Scott, J. L. Petersen, S. P. Nolan, *Chem. Eur. J.* **2008**, 14, 158.
- [11] H. Ito, M. Muromoto, S. Kurenuma, S. Ishizaka, N. Kitamura, H. Sato, T. Seki, **2013**, 4, 2009.
- [12] C. E. Strasser, V. J. Catalano, *J. Am. Chem. Soc.* **2010**, 132, 10009.
- [13] a) P. Albert, R. Francesco, M. Ronaldo, D. Reto, C. Luigi, *Chem. Eur. J.* **2010**, 16, 14348; b) A. Poater, F. Ragone, S. Giudice, C. Costabile, R. Dorta, S. P. Nolan, L. Cavallo, *Organometallics* **2008**, 27, 2679.
- [14] a) D. T. Walters, R. B. Aghakhanpour, X. B. Powers, K. B. Ghiassi, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2018**, 140, 7533; b) K. Chen, M. M. Nenzel, T. M. Brown, V. J. Catalano, *Inorg. Chem.* **2015**, 54, 6900; c) K. Chen, C. E. Strasser, J. C. Schmitt, J. Shearer, V. J. Catalano, *Inorg. Chem.* **2012**, 51, 1207; d) W.-F. Fu, K.-C. Chan, V. M. Miskowski, C.-M. Che, *Angew. Chem. Int. Ed.* **1999**, 38, 2783; e) C. Hemmert, R. Poteau, F. J.-B. dit Dominique, P. Ceroni, G. Bergamini, H. Gornitzka, *Eur. J. Inorg. Chem.* **2012**, 3892; f) A. A. Penney, V. V. Sizov, E. V. Grachova, D. V. Krupenya, V. V. Gurzhiy, G. L. Starova, S. P. Tunik, *Inorg. Chem.* **2016**, 55, 4720; g) M. El Sayed Moussa, S. Evariste, H.-L. Wong, L. Le Bras, C. Roiland, L. Le Polles, B. Le Guennic, K. Costuas, V. W.-W. Yam, C. Lescop, *Chem. Commun.* **2016**, 52, 11370.

COMMUNICATION

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.

B. Hupp, J. Nitsch, T. Schmitt, R. Bertermann, K. Edkins, F. Hirsch, I. Fischer, M. Auth, A. Sperlich, A. Steffen*

Page No. – Page No.

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