

New Emitters for OLEDs: The Coordination- and Photo-Chemistry of Mononuclear Neutral Copper(I) Complexes

L. Bergmann,^{1,2} J. Friedrichs,² G. J. Hedley,³ M. Nieger,⁴ T. Baumann,² I. D. W. Samuel,³ S. Bräse¹

¹Institute of Organic Chemistry, Karlsruhe Institute of Technology, Germany; ²CYNORA GmbH, Bruchsal, Germany; ³Organic Semiconductor Centre, SUPA, University of St Andrews, UK;

⁴Laboratory of Inorganic Chemistry, University of Helsinki, Finland.

1. Introduction

19% of the world's electricity consumption is used for lighting. In this respect, the relevance of efficient lighting and a resource saving production is tremendous. Organic light emitting diodes (OLEDs) present an attractive technology for large-area and energy saving lighting and furthermore find application in displays for mobile phones, tablets and the automotive sector due to their high efficiency.

However, emitting materials based on iridium are nowadays used for the generation of light from energy, which exhibit a low natural abundance and cannot be recycled from the displays. Herein, a series of luminescent copper(I) complexes as cost-efficient and environmentally friendly alternative to iridium compounds is presented. Due to their high emission quantum yields and the tuning of their emission color by ligand variation, they show a high potential for OLED applications.

2. Development of a Novel Class of Luminescent Copper(I) Complexes

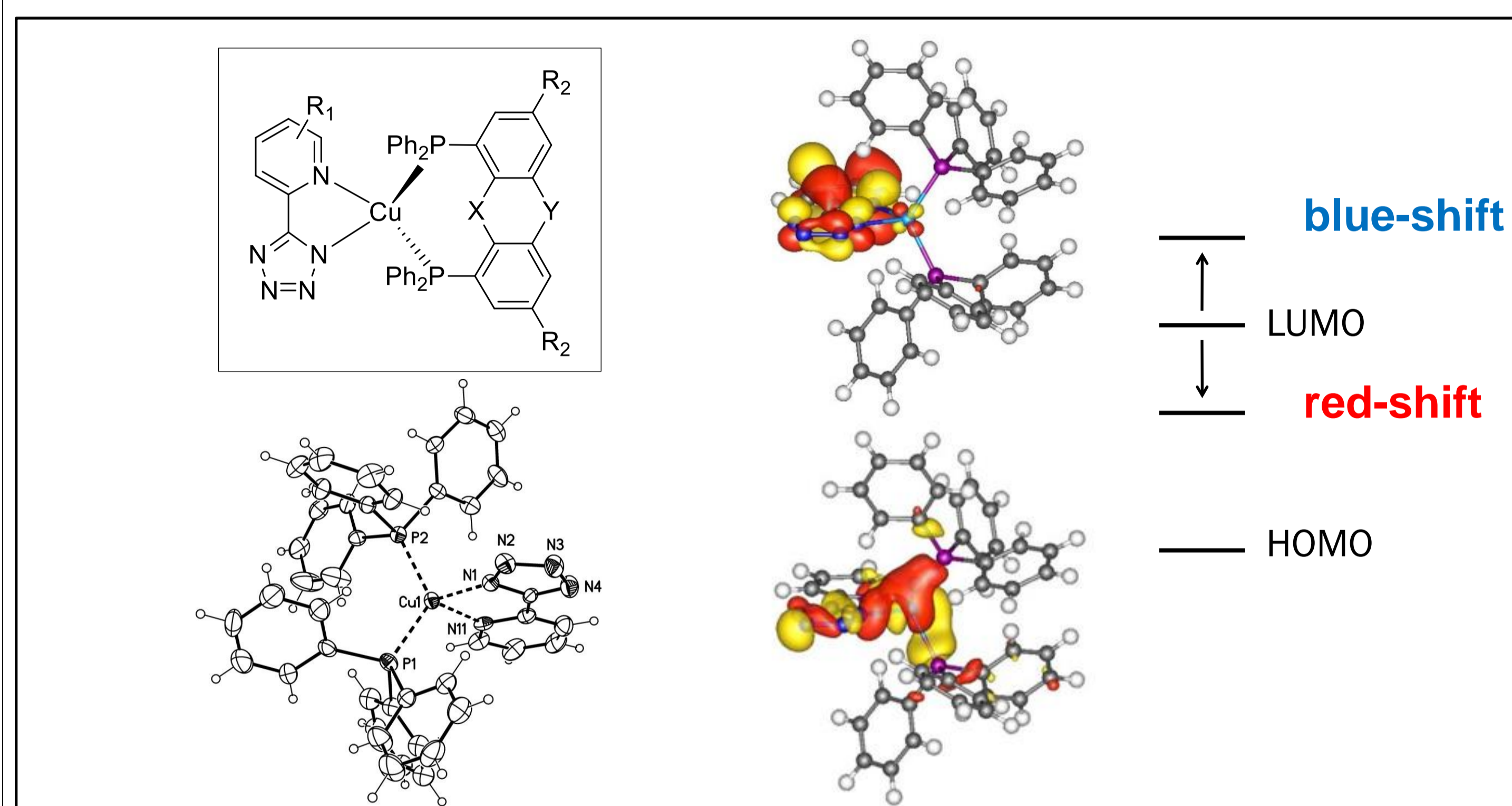


Figure 1. A series of neutral, mononuclear copper(I) complexes based on tetrazolate and different phosphine ligands was developed and their photophysical properties studied. DFT calculations support the material design to tune the emission color. [6]

3. Spectroscopic Studies on the Photophysical Properties

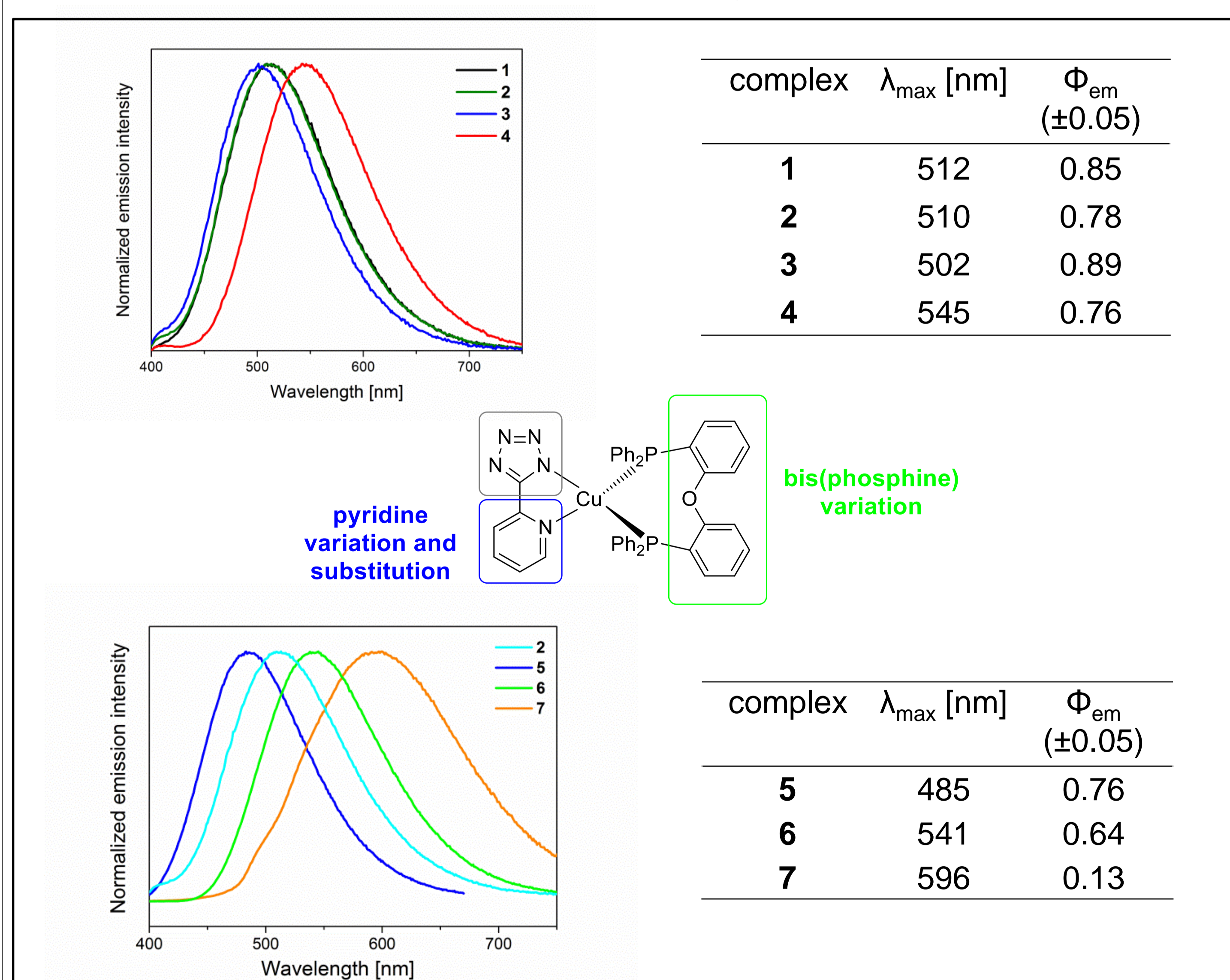


Figure 2. By comprehensive (time-resolved) spectroscopic measurements, a deeper knowledge on the structure-property relations was achieved. The emission color could be modulated from 485–600 nm at high photoluminescence efficiencies by ligand variation.

4. Mechanism of Thermally Activated Delayed Fluorescence and ISC Determination

The herein presented copper(I) compounds are characterized by thermally-activated delayed fluorescence (TADF), which opens up a new way for blue emitters while enabling high internal efficiencies at the same time. After intersystem crossing, the excitons are back-transferred from the triplet reservoir to the excited singlet state and finally deactivate by delayed fluorescence due to a small energy gap ΔE between T_1 and S_1 (below 0.2 eV).

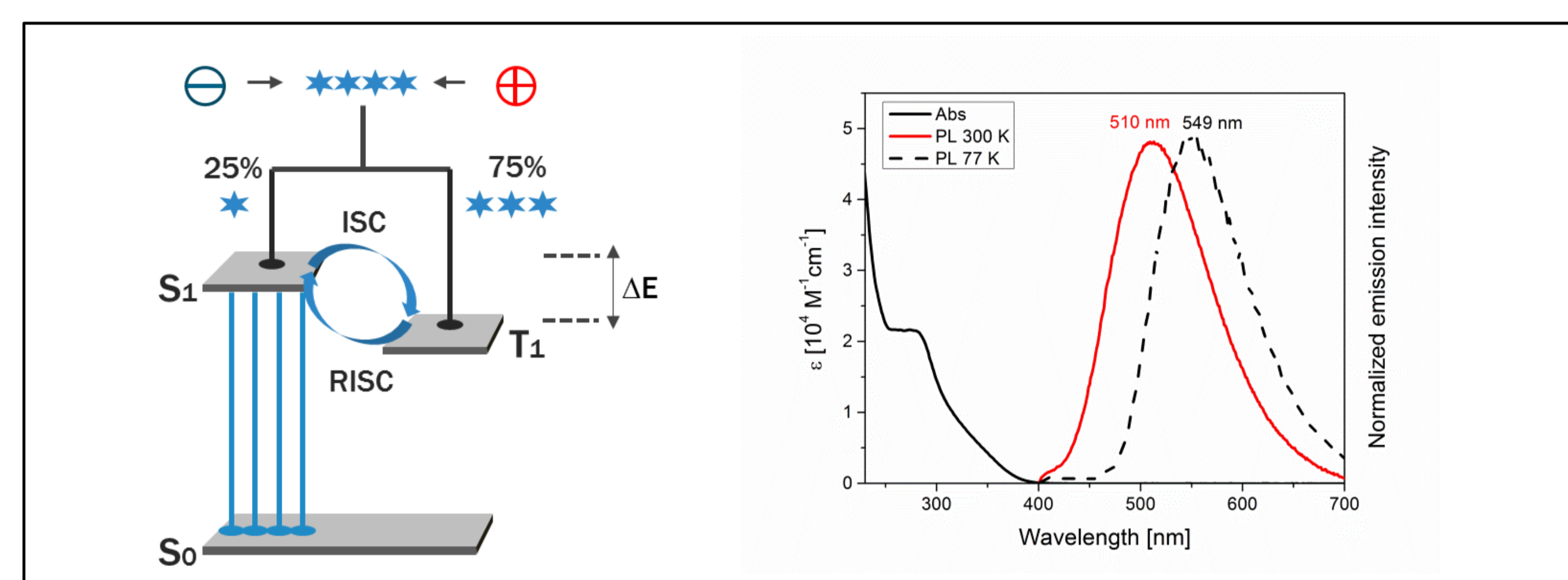


Figure 3. The thermally activated delayed fluorescence of complex 2 is indicated by a red-shift of the emission color and a significant increase of the decay times from RT to 77 K.

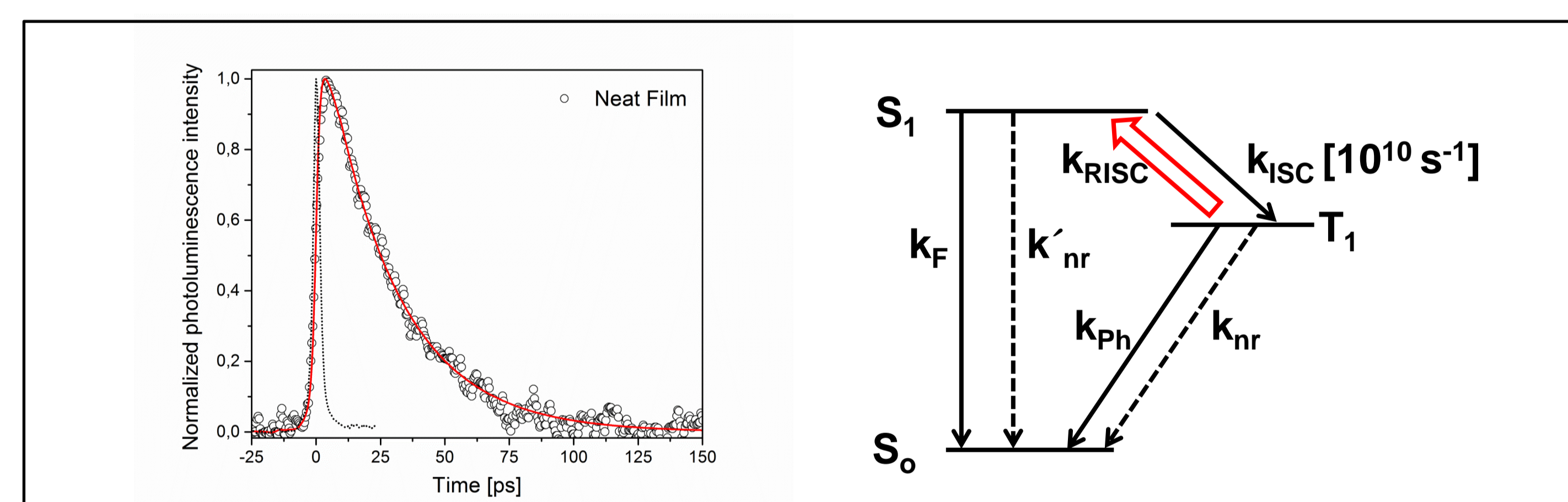


Figure 4. The picosecond luminescence decay dynamics of complex 2 in the solid state indicates intersystem crossing (ISC) in the order of 10^{10} s^{-1} . Thus, the TADF mechanism could be determined by time-resolved spectroscopic measurements in the micro-, nano- and picosecond time regime. [1]

5. Conclusion

Novel and resource efficient emitting materials were developed as basis for the efficient generation of light for display and lighting applications:

The emission efficiencies and colors of neutral, mononuclear copper(I) complexes were tuned by systematic ligand design. In comprehensive spectroscopic measurements, combined with DFT calculation and cyclovoltammetric investigations, the structure-property relationships were studied, and the TADF mechanism could be determined by time-resolved spectroscopy measurements in the micro-, nano- and picosecond time regime. Furthermore, picosecond time-resolved emission spectroscopy was established as a new method to determine intersystem crossing rates in highly luminescent copper(I) complexes.

Publications

- [1] L. Bergmann, D. M. Zink, S. Bräse, T. Baumann, D. Volz, *Top. Curr. Chem.* **2016**, 374, 1–39.
 [2] L. Bergmann, G. J. Hedley, T. Baumann, S. Bräse, I. D. W. Samuel, *Sci. Adv.* **2016**, 2, e1500889.
 [3] L. Bergmann, M. Nieger, J. Friedrichs, T. Baumann, S. Bräse, in preparation, **2016**. [4] D. M. Zink, L. Bergmann, D. Ambrosek, M. Wallesch, D. Volz, M. Mydlak, *Transl. Mater. Res.* **2014**, 1, 015003.
 [5] D. Volz, L. Bergmann, D. M. Zink, T. Baumann, S. Bräse, *SPIE Newsroom* **2013**, Doi: 10.1117/2.1201308.005080. [6] L. Bergmann, J. Friedrichs, M. Mydlak, T. Baumann, M. Nieger, S. Bräse, *Chem. Commun.* **2013**, 49, 6501–6503.

Acknowledgements

